A facile route to functionalised, protic and chiral ionic liquids based on the triaminocyclopropenium cation

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Supplmentary material

General procedures

All reagents and solvents were obtained from commercial sources. Liquid reagents and solvents were typically distilled under a dinitrogen atmosphere prior to use.

All operations were performed using standard Schlenk techniques with a dinitrogen atmosphere in order to reduce exposure to water.

^{1}H- and ^{13}C{^{1}H}-NMR spectra were collected on a Varian Unity-300 operating at 300 and 75 MHz respectively, or on a Varian INOVA-500 operating at 500 and 126 MHz respectively, in $CDCl_3$, referenced to residual solvent peaks.

DSC was performed on a Perkin Elmer Q100. Samples of mass 5-20 mg were sealed in a vented aluminium pan and placed in the furnace with a 50 mL/min nitrogen stream; the temperature was raised at 10 °C/min.

Viscosities were measured on a Brookfield-Wells cone-and-plate viscometer operating at 0.005 – 0.2 s^{-1} rotation speed range.

TGA data were collected on dried samples using a TA Instruments SDT Q600 at 10 °C/min after further drying at 100 °C for one hour in the instrument.

Electrospray mass spectrometry was carried out on a Micromass LCT, with samples dissolved in acetonitrile.

Water contents were determined by Karl Fischer titration using a Metrohm 831 KF coulometer.

Chloride contents were determined using a AutolabEco Chemie, with associated GPES software, under a dinitrogen atmosphere. The electrodes were either a glassy carbon (3 mm diameter) or platinum (1 mm diameter) working electrode, a platinum wire counter electrode and a silver reference electrode.

Microanalysis was performed by the Campbell Microanalytical Laboratory, Department of Chemistry, University of Otago, Dunedin, New Zealand.

Bis(diethylamino)cyclopropenone, $(Et_2N)_2C_3O$

KOH (300 g) was dissolved into water (4 L). Tris(diethylamino)cyclopropenium chloride (42 g, 0.15 mol) was added to the solution, and heated to 70 °C for 18 h. Organic compounds were extracted from aqueous solution using CH_2Cl_2 (3 x 250 mL). CH_2Cl_2 removed *in vacuo* and neutralized using a small amount of HCl. Ethanol (25 mL) added to allow filtering to remove an insoluble impurity, followed by removal of the ethanol *in vacuo*. Addition of acetone (75 mL) precipitated KCl, which was filtered off. Acetone was removed *in vacuo*, yielding a dark orange liquid (22 g, 77%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.21 (q, $^3J_{HH}$ = 7.2 Hz, 8H, NCH_2CH_3), 1.20 (t, $^3J_{HH}$ = 7.2 Hz, 12H, NCH_2CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 133.74 (CO), 119.32 (C_2), 46.01 (NCH_2CH_3), 14.18 (NCH_2CH_3).

General preparation of methylsulfate triaminocyclopropenium salts from cyclopropenone

Triaminocyclopropenium methylsulfate salts were prepared from the respective diaminocyclopropenone. The cyclopropenone was dried, typically by using an *iso*-propanol or ethanol azetrope. Dimethylsulfate was added while under a dry, inert atmosphere, and the solution was then stirred for approximately 1 h. An excess of a primary or secondary amine was then added, and the mixture was stirred for a further 1 h. Excess amine was removed by washing with diethylether or petroleum ether and ammonium salts were removed by water-chloroform extractions.

(1) Bis(diethylamino)dimethylaminocyclopropenium methylsulfate, $[C_3(NEt_2)_2(NMe_2)]MeSO_4$

Cyclopropenone $(Et_2N)_2C_3O$ (8.91 g, 45.5 mmol), Me_2SO_4 (8.60 g, 68.2 mmol) and $HNMe_2$ (6.80 g, 150 mmol) were reacted as described in the general synthetic procedure and gave a yellow liquid (5.72 g, 37.6%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.68 (s, 3H, $MeSO_4$), 3.40 (q, $^3J_{HH}$ = 7.3 Hz, 8H, NCH_2CH_3), 3.17 (s, 6H, NCH_3), 1.27 (t, $^3J_{HH}$ = 7.2 Hz, 12H, NCH_2CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 117.83 (C_1), 116.31 (C_2), 54.02 (CH_3SO_4), 47.28 (NCH_2CH_3), 42.07 (CH_3), 14.07 (NCH_2CH_3).

(2) Bis(diethylamino)dimethylaminocyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NEt_2)_2(NMe_2)]NTf_2$

$[C_3(NEt_2)_2(NMe_2)]MeSO_4$ (2.74 g, 8.18 mmol) was stirred with $LiNTf_2$ (8.0 g, 28.0 mmol) in H_2O (200 mL). The product was extracted with Et_2O (200 mL), washed with H_2O (3 x 200 mL) and dried in vacuo to yield a pale yellow liquid (2.63 g, 63.7%). ES-MS$^+$: m/z 224.21 (100%, M$^+$). ^{1}H and ^{13}C NMR as for $[C_3(NEt_2)_2(NMe_2)]MeSO_4$ with an alternative peak in the ^{13}C NMR due to NTf_2^- replacing $MeSO_4^-$.

(3) Bis(diethylamino)dimethylaminocyclopropenium dicyanoamide, $[C_3(NEt_2)_2(NMe_2)]DCA$

$[C_3(NEt_2)_2(NMe_2)]MeSO_4$ (4.34 g, 13.0 mmol) was stirred with NaDCA (5.60 g, 62.9 mmol) in H_2O (100 mL). The product was extracted with chloroform (100 mL), washed with H_2O (3 x 100 mL) and dried in vacuo to yield a pale yellow liquid (3.24 g, 86.0%). ^{1}H and ^{13}C NMR as for $[C_3(NEt_2)_2(NMe_2)]MeSO_4$ with an alternative peak due to DCA replacing $MeSO_4$. MS$^+$ as for $[C_3(NEt_2)_2(NMe_2)]TFSA$.

(4) Tris(diethylamino)cyclopropenium dicyanoamide, $[C_3(NEt_2)_3]DCA$

$[C_3(NEt_2)_3]Cl$ (8.30 g, 28.3 mmol) was stirred with NaDCA (9.50 g, 107 mmol) in H_2O (100 mL). The product was extracted with chloroform (150 mL), washed with H_2O (3 x 100 mL) and dried *in vacuo* to yield an orange liquid (7.88 g, 85.8%). ^{1}H, ^{13}C NMR and MS$^+$ as for $[C_3(NEt_2)_3]Cl$.

(5) Bis(diethylamino)dibutylaminocyclopropenium methylsulfate, $[C_3(NEt_2)_2(NBu_2)]MeSO_4$

Cyclopropenone $(Et_2N)_2C_3O$ (6.23 g, 31.8 mmol), Me_2SO_4 (4.40 g, 34.9 mmol) and $HNBu_2$ (4.91 g, 38.0 mmol) were reacted as described in the general synthetic procedure and gave a dark orange liquid (6.31 g, 47.4%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.69 (s, 3H, $MeSO_4$), 3.40 (q, $^3J_{HH}$ = 7.1 Hz, 8H, $\mathrm{NC}H_2\mathrm{CH}_3$), 3.28 (t, $^3J_{HH}$ = 7.91 Hz, 4H, $\mathrm{NC}H_2\mathrm{CH}_2$), 1.60 (m, 4H, $\mathrm{NCH_2C}H_2$), 1.19–39 (m, 16H, $\mathrm{NCH_2CH_2C}H_2$ and $\mathrm{NCH_2C}H_3$), 0.93 (t, $^3J_{HH}$ = 7.33 Hz, 6H, $\mathrm{CH_2CH_2C}H_3$). ^{13}C NMR (126 MHz, $CDCl_3$): δ 116.76 (C_1), 116.64 (C_2), 54.35 ($C\mathrm{H_3SO_4}$), 53.17 ($\mathrm{N}C\mathrm{H_2CH_2}$), 47.35 ($\mathrm{N}C\mathrm{H_2CH_3}$), 31.28 ($\mathrm{NCH_2}C\mathrm{H_2}$), 20.10 ($\mathrm{NCH_2CH_2}C\mathrm{H_2}$), 14.54 ($\mathrm{NCH_2}C\mathrm{H_3}$), 14.00 ($\mathrm{CH_2CH_2}C\mathrm{H_3}$).

(6) Bis(diethylamino)dibutylaminocyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NEt_2)_2(NBu_2)]NTf_2$

$[C_3(NEt_2)_2(NBu_2)]MeSO_4$ (7.35 g, 17.5 mmol) was stirred with $LiNTf_2$ (10.0 g, 34.8 mmol) in H_2O (150 mL). The product was extracted with chloroform (150 mL), washed with H_2O (3 x 150 mL) and dried *in vacuo* to yield a dark orange liquid (6.71 g, 65.2%). ^{1}H and ^{13}C NMR as for $[C_3(NEt_2)_2(NBu_2)]MeSO_4$ with an additional peak in the ^{13}C NMR due to NTf_2^-.

(7) Bis(diethylamino)dibutylaminocyclopropenium dicyanoamide, $[C_3(NEt_2)_2(NBu_2)]DCA$

$[C_3(NEt_2)_2(NBu_2)]MeSO_4$ (6.31 g, 15.0 mmol) was stirred with NaDCA (4.00 g, 44.9 mmol) in H_2O (150 mL). The product was extracted with chloroform (150 mL), washed with H_2O (3 x 150 mL) and dried *in vacuo* to yield a dark orange liquid (5.05 g, 90.0%). ^{1}H and ^{13}C NMR as for $[C_3(NEt_2)_2(NBu_2)]MeSO_4$ with an additional peak in the ^{13}C NMR due to DCA.

(8) Bis(diethylamino)dihexylaminocyclopropenium methylsulfate, $[C_3(NEt_2)_2(NHex_2)]MeSO_4$

Cyclopropenone $(Et_2N)_2C_3O$ (5.53 g, 28.2 mmol), Me_2SO_4 (5.33 g, 42.3 mmol) and $HNHex_2$ (9.03 g, 48.7 mmol) were reacted as described in the general synthetic procedure and gave an orange liquid (10.9 g, 81.1%). ^1H NMR (300 MHz, $CDCl_3$): δ 3.69 (s, 3H, $MeSO_4$), 3.41 (q, $^3J_{HH}$ = 7.3 Hz, 8H, $\mathrm{NC}\mathit{H}_2\mathrm{CH}_3$), 3.27 (t, $^3J_{HH}$ = 8.5 Hz, 4H, $\mathrm{NC}\mathit{H}_2\mathrm{C}_5\mathrm{H}_{11}$), 1.60 (m, 4H, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{C_4H_9}$), 1.19–35 (m, 24H, $\mathrm{N(CH_2)_2(C}\mathit{H}_2\mathrm{)_3CH_3}$ and $\mathrm{NCH_2C}\mathit{H}_3$), 0.86 (t, $^3J_{HH}$ = 6.5 Hz, 6H, $\mathrm{N(C_5H_{10})C}\mathit{H}_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 116.45 (C_1), 116.38 (C_2), 54.26 (CH_3SO_4), 53.17 ($\mathrm{N}\mathit{C}\mathrm{H_2C_5H_{11}}$), 47.10 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_3}$), 31.39 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_2C_4H_9}$), 29.02 ($\mathrm{NC_2H_4}\mathit{C}\mathrm{H_2C_3H_7}$), 26.25 ($\mathrm{NC_3H_6}\mathit{C}\mathrm{H_2C_2H_5}$), 22.47 ($\mathrm{NC_4H_8}\mathit{C}\mathrm{H_2CH_3}$), 14.29 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_3}$), 13.91 ($\mathrm{NC_5H_{10}}\mathit{C}\mathrm{H_3}$).

(9) Bis(diethylamino)dihexylaminocyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NEt_2)_2(NHex_2)]NTf_2$

$[C_3(NEt_2)_2(NHex_2)]I$ samples contaminated with $(Et_2N)_2C_3O$, prepared by treatment of $(Et_2N)_2C_3O$ with excess EtI followed by removal of EtI by washing with diethylether, addition of $HNHex_2$, and further washing with diethylether, were combined and a large excess of $LiNTf_2$ (20 g, 69.7 mmol) in H_2O (300 mL) was added. The product was extracted with chloroform (300 mL) and washed with H_2O (2 x 300 mL). $(Et_2N)_2C_3O$ was removed by washing with petroleum ether/diethylether mix (1:1, 3 x 100 mL) and the product was dried *in vacuo* to yield a dark brown liquid (4 g). ^1H and ^{13}C NMR as for $[C_3(NEt_2)_2(NHex_2)]MeSO_4$ with an alternative peak in the ^{13}C NMR due to NTf_2^- replacing $MeSO_4^-$.

(10) Bis(diethylamino)dihexylaminocyclopropenium dicyanoamide, $[C_3(NEt_2)_2(NHex_2)]DCA$

$[C_3(NEt_2)_2(NHex_2)]MeSO_4$ (10.9 g, 22.9 mmol) was stirred with NaDCA (7.50 g, 84.2 mmol) in H_2O (150 mL). The product was extracted with chloroform (150 mL), washed with H_2O (4 x 100 mL) and dried *in vacuo* to yield an orange liquid (8.86 g, 90%). ^1H and ^{13}C NMR as for $[C_3(NEt_2)_2(NHex_2)]MeSO_4$ with an alternative peak in the ^{13}C NMR due to DCA replacing $MeSO_4$.

(11) Bis(diethylamino)dihexylaminocyclopropenium iodide, $[C_3(NEt_2)_2(NHex_2)]I$

Dihexylamine (1.72 mL, 7 mmol) was added to a solution of $[C_3(NEt_2)_2(OEt)]I$ (2 g, 5.6 mmol) (prepared as described above for $[C_3(NEt_2)_2(NBu_2)]I$) in dichloromethane (10 mL) and stirred for 2 h. Dichloromethane was removed *in vacuo*. The product was washed several times with diethyl ether to remove unreacted amine. This gave a yellow liquid (2.5 g, 87%). ^1H and ^{13}C NMR as for $[C_3(NEt_2)_2(NHex_2)]MeSO_4$ with no peaks due to $MeSO_4$.

(12) Bis(diethylamino)dihexylaminocyclopropenium trifluoromethylsulfonate, $[C_3(NEt_2)_2(NHex_2)]OTf$

Dried bis(diethylamino)cyclopropenone (1.14 g, 6 mmol) was stirred with $MeCF_3SO_3$ (0.8 mL, 8 mmol) in dry dichloromethane for 2 h in an inert atmosphere. Solvent was removed *in vacuo.* The mixture was washed with dry diethyl ether several times to remove excess $MeCF_3SO_3$ and cyclopropenone. This gave an orange viscous oil of $[C_3(NEt_2)(OMe)]CF_3SO_3$ which was then stirred with Hex_2NH (1.23 mL, 5.2 mmol) for 2 h. The mixture was dissolved in chloroform:ethanol (2:1) (30 mL) and the product was washed with water (3x30 mL) to remove ammonium salts. Solvent was removed in vacuo to give a brown oil (1.6 g, 77%). ^1H, ^{13}C NMR and MS^+ as for $[C_3(NEt_2)_2NHex_2]MeSO_4$.

(13) Bis(diethylamino)diallylaminocyclopropenium methylsulfate, $[C_3(NEt_2)_2(N(CH_2CHCH_2)_2)]MeSO_4$

Cyclopropenone $(Et_2N)_2C_3O$ (7.54 g, 38.5 mmol), Me_2SO_4 (6.27 g, 49.7 mmol) and $HN(CH_2CHCH_2)_2$ (6.30 g, 64.8 mmol) were reacted as described in the general synthetic procedure and gave an orange liquid (7.44 g, 50%). ^1H NMR ($CDCl_3$, 500 MHz): δ 5.81 (m, 2H, $NCH_2C\mathit{H}{=}CH_2$), 5.28 (d, $^3J_{HH}$ = 10.5 Hz, 2H, $NCH_2CH{=}C\mathit{H}_2$), 5.25 (d, $^3J_{HH}$ = 17 Hz, 2H, $NCH_2CH{=}C\mathit{H}_2$), 3.92 (d, $^3J_{HH}$ = 5.5 Hz ,4H, $NC\mathit{H}_2CH{=}CH_2$), 3.68 (s, 3H, $C\mathit{H}_3SO_4$), 3.35 (q, $^3J_{HH}$ = 7 Hz, 8H, $NC\mathit{H}_2CH_3$), 1.23 (t, $^3J_{HH}$ = 7 Hz,12H, $NCH_2C\mathit{H}_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ 131.34 ($NCH_2\mathit{C}HCH_2$), 118.60 ($NCH_2CH\mathit{C}H_2$), 116.48 (ring C), 116.15 (ring C), 54.34 ($NCH_2CH\mathit{C}H_2$), 54.04 ($MeSO_4$), 46.95 ($N\mathit{C}H_2CH_3$), 13.97 $(NCH_2\mathit{C}H_3)_2$. ES-MS^+: m/z 276.245 (M^+, 100%).

(14) Bis(diethylamino)diallylaminocyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NEt_2)_2(N(CH_2CHCH_2)_2)]NTf_2$

$[C_3(NEt_2)_2(N(CH_2CHCH_2)_2)]MeSO_4$ (7.44 g, 19.2 mmol) was stirred with $LiNTf_2$ (3 equivalents) in H_2O (100 mL). The product was extracted with chloroform (100 mL), washed with H_2O (3 x 100 mL) and dried *in vacuo* to yield an orange liquid (7.0 g, 84%). ^1H, ^{13}C NMR and MS^+ as for $[C_3(NEt_2)_2(N(CH_2CHCH_2)_2)]MeSO_4$ with an alternative peak in the ^{13}C NMR due to NTf_2^- replacing $MeSO_4^-$.

(15) Bis(diethylamino)diethanolaminocyclopropenium iodide, $[C_3(NEt_2)_2(N(CH_2CH_2OH)_2)]I$

Cyclopropenone $(Et_2N)_2C_3O$ (7.68 g, 39.2 mmol) was dried using ethanol azetropes (5 x 50 mL). Iodoethane (97.5 g, 625 mmol) was added and the solution was heated to reflux for 18 h. It was then cooled to ambient temperature and $HN(C_2H_4OH)_2$ (8.44 g, 80.3 mmol) was added and stirred at ambient temperature 48 h. Excess iodoethane was removed *in vacuo* and H_2O (100 mL) added. Cyclopropenone was extracted with dichloromethane (100 mL and 50 mL) and the combined extracts were washed with H_2O (2 x 100 mL). The H_2O washings were combined with the main product H_2O layer and were then extracted with dichloromethane (3 x 100 mL) to yield a yellow liquid (3.50 g, 21.7%). ^1H NMR (300 MHz, D_2O): δ 3.73 (t, $^3J_{HH}$ = 5.3 Hz, 4H, NCH_2CH_2OH), 3.47 (t, $^3J_{HH}$ = 5.3 Hz, 4H, NCH_2CH_2OH), 3.37 (q, $^3J_{HH}$ = 7.1 Hz, 8H, NCH_2CH_3), 1.17 (t, $^3J_{HH}$ = 7.1 Hz, 12H, NCH_2CH_3). ^{13}C NMR (75 MHz, D_2O, methanol added as reference): δ 117.89 (C_1), 117.26 (C_2), 59.46 (NCH_2CH_2OH), 54.38 (NCH_2CH_2OH), 47.20 (NCH_2CH_3), 13.98 (NCH_2CH_3). MS^+ as for $[C_3(NEt_2)_2(N(CH_2CH_2OH)_2)]MeSO_4$.

(16) Bis(diethylamino)diethanolaminocyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NEt_2)_2(N(CH_2CH_2OH)_2)]NTf_2$

$[C_3(NEt_2)_2(N(CH_2CH_2OH)_2)]I$ (3.50 g, 8.52 mmol) was stirred with $LiNTf_2$ (5.0 g, 17 mmol) in H_2O (150 mL). The product was extracted with chloroform (150 mL), washed with H_2O (4 x 150 mL) and dried *in vacuo* to yield a yellow liquid (3.5 g, 73%). ^1H and ^{13}C NMR as for $[C_3(NEt_2)_2(N(CH_2CH_2OH)_2)]I$ with an additional peak at 119.8 in the ^{13}C NMR spectrum due to NTf_2^-. MS^+ as for $[C_3(NEt_2)_2(N(CH_2CH_2OH)_2)]MeSO_4$.

(17) Bis(diethylamino)diethanolaminocyclopropenium dicyanoamide, $[C_3(NEt_2)_2(N(CH_2CH_2OH)_2)]DCA$

To $[C_3(NEt_2)_2(N(CH_2CH_2OH)_2)]MeSO_4$ (6.10 g, 16 mmol, prepared from $C_3(NEt_2)O$, Me_2SO_4 and $HN(CH_2CH_2OH)_2$ as described above) in water (50 mL) was added with NaDCA (4.2 g, 48 mmol) in water (50 mL). The product was extracted with CH_2Cl_2 (3 x 50 mL) and the solvent removed in vacuo. This material was then dissolved in water (50 mL) with a further 4.2 g of NaDCA and the product again extracted with CH_2Cl_2 (3 x 50 mL). Removal of solvent yielded a brown oil (4.70 g) of crude product. This was dissolved in water (100 mL), washed with diethyl ether (4 x 50 mL), and extracted with chloroform (4 x 50 mL). The sample was then put on a silica column and washed with CH_2Cl_2 and ethanol, the product was extracted with water. The solvent was then removed to give a yellow solid. This was then then extracted with CH_2Cl_2. Recrystallisation from CH_2Cl_2/diethyl ether yielded a white solid (150 mg, 2.7%). Clearly, this synthesis and pourification procedure could be optimied further. ^1H and ^{13}C NMR as for $[C_3(NEt_2)_2(N(CH_2CH_2OH)_2)]I$.

(18) Bis(diethylamino)butylmethylaminocyclopropenium methylsulfate, $[C_3(NEt_2)_2(NBuMe)]MeSO_4$

Cyclopropenone $(Et_2N)_2C_3O$ (6.41 g, 32.7 mmol), Me_2SO_4 (8.26 g, 65.5 mmol) and HNBuMe (7.14 g, 81.9 mmol) were reacted as described in the general synthetic procedure and gave an orange liquid (9.70 g, 78.6%).

Using an alternative route, to a stirred solution of $[C_3(NEt_2)_2(NHBu]MeSO_4$ (1.0 g, 2.8 mmol) in dry THF at –78 °C in an inert atmosphere was slowly added *n*-BuLi (1.89 mL, 3.03 mmol). The reaction was then stirred for 6 h and brought to room temperature. Me_2SO_4 (0.33 mL, 2.76 mmol) was added to this solution and stirred for 1 h. The solvent was removed *in vacuo*, the oil was washed with dry diethyl ether several times, the product was then dissolved in chloroform and filtered to remove $LiMeSO_4$. Removal of solvent *in vacuo* gave an orange oil (0.90 g, 87%).

^1H NMR (300 MHz, $CDCl_3$): δ 3.66 (s, 3H, $MeSO_4$), 3.39 (q, $^3J_{HH}$ = 7.3 Hz, 8H, NCH_2CH_3), 3.30 (t, $^3J_{HH}$ = 7.9 Hz, 2H, NCH_2CH_2), 3.13 (s, 3H, NCH_3), 1.59 (m, 2H, NCH_2CH_2), 1.19–38 (m, 14H, $NCH_2CH_2CH_2$ and NCH_2CH_3), 0.92 (t, $^3J_{HH}$ = 7.3 Hz, 3H, CH_2CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ 117.20 (C_1), 116.14 (C_2), 55.16 (NCH_2CH_2), 54.04 (CH_3SO_4), 47.18 (NCH_2CH_3), 39.53 (NCH_3), 30.01 (NCH_2CH_2), 19.72 ($NCH_2CH_2CH_2$), 14.14 (NCH_2CH_3), 13.68 ($CH_2CH_2CH_3$).

(19) Bis(diethylamino)butylmethylaminocyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NEt_2)_2(NBuMe)]NTf_2$

$[C_3(NEt_2)_2(NBuMe)]MeSO_4$ (3.90 g, 10.3 mmol) was stirred with $LiNTf_2$ (10 g, 34.8 mmol) in H_2O (100 mL). The product was extracted with chloroform (150 mL), washed with H_2O (3 x 100 mL) and dried *in vacuo* to yield an orange liquid (4.48 g, 79.3%). ^1H and ^{13}C NMR as for $[C_3(NEt_2)_2(NBuMe)]MeSO_4$ with an alternative peak in the ^{13}C NMR due to NTf_2^- replacing $MeSO_4^-$.

(20) Bis(diethylamino)butylmethylaminocyclopropenium dicyanoamide, $[C_3(NEt_2)_2(NBuMe)]DCA$

$[C_3(NEt_2)_2(NBuMe)]MeSO_4$ (5.50 g, 14.6 mmol) was stirred with NaDCA (4.00 g, 44.9 mmol) in H_2O (100 mL). The product was extracted with chloroform (100 mL), washed with H_2O (3 x 100 mL) and dried *in vacuo* to yield an orange liquid (4.10 g, 84.6%). ^1H and ^{13}C NMR as for $[C_3(NEt_2)_2(NBuMe)]MeSO_4$ with an alternative peak in the ^{13}C NMR due to DCA replacing $MeSO_4$.

(21) Bis(diethylamino)hexylmethylaminocyclopropenium methylsulfate, $[C_3(NEt_2)_2(NHexMe)]MeSO_4$

Cyclopropenone $(Et_2N)_2C_3O$ (4.77 g, 24.3 mmol) and dimethylsulfate (3.68 g, 29.1 mmol) were mixed at ambient temperature for 30 min. Hexylmethylamine (3.45 g, 29.9 mmol) was added and the solution stirred at ambient temperature for 30 min. The product was washed with pentane (3 x 75 mL), to remove excess hexylmethylamine, and then with diethylether (3 x 75 mL), to remove residual bis(diethylamino)cyclopropenone. The product was then dissolved in $CHCl_3$ (100 mL) and washed with H_2O (3 x 100 mL). $CHCl_3$ was removed *in vacuo* to give an orange liquid (7.70 g, 78.2%). ^1H NMR (300 MHz, $CDCl_3$): δ 3.67 (s, 3H, $MeSO_4$), 3.40 (q, $^3J_{HH}$ = 7.2 Hz, NCH_2CH_3), 3.30 (t, $^3J_{HH}$ = 7.8 Hz,

$NCH_2(CH_2)_4CH_3$), 3.14 (s, NCH_3), 1.55–69 (m, $NCH_2CH_2(CH_2)_3CH_3$), 1.19–36 (m, NCH_2CH_3 and $N(CH_2)_2(CH_2)_3CH_3$), 0.85 (t, $^3J_{HH}$ = 6.9 Hz, $NCH_2(CH_2)_4CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 117.36 (C_1), 116.40 (C_2), 55.73 ($NCH_2C_5H_{11}$), 54.04 ($MeSO_4$), 47.39 (NCH_2CH_3), 39.66 (NCH_3), 31.63 ($NCH_2CH_2C_4H_9$), 28.21 ($N(C_2H_4)CH_2C_3H_7$), 26.45 ($NC_3H_6CH_2C_2H_5$), 22.72 ($NC_4H_8CH_2CH_3$), 14.25 (NCH_2CH_3), 14.16 ($NC_5H_{10}CH_3$).

(22) Bis(diethylamino)hexylmethylaminocyclopropenium bis(trifluoromethanesulfonyl)amide, [$C_3(NEt_2)_2$(NHexMe)]NTf_2

[$C_3(NEt_2)_2$(NHexMe)]$MeSO_4$ (3.10 g, 7.65 mmol) was stirred with $LiNTf_2$ (7.20 g, 25.08 mmol) in H_2O (150 mL). The product was extracted with chloroform (150 mL), washed with H_2O (3 x 150 mL) and dried *in vacuo* to yield a yellow liquid (3.60 g, 82.0%). Water content: 173.1 ppm. ^{1}H and ^{13}C NMR as for [$C_3(NEt_2)_2$(NHexMe)]$MeSO_4$ with an alternative peak in the ^{13}C NMR at 119.85 (q, $^1J_{CF}$ = 321.6 Hz, CF_3), due to NTf_2^- replacing $MeSO_4^-$.

(23) Bis(diethylamino)hexylmethylaminocyclopropenium dicyanoamide, [$C_3(NEt_2)_2$(NHexMe)]DCA

[$C_3(NEt_2)_2$(NHexMe)]$MeSO_4$ (4.60 g, 11.4 mmol) was stirred with NaDCA (3.40 g, 38.2 mmol) in H_2O (150 mL). The product was extracted with chloroform (150 mL), washed with H_2O (3 x 150 mL) and dried *in vacuo* to yield a yellow liquid (3.75 g, 91.6%). ^{1}H and ^{13}C NMR as for [$C_3(NEt_2)_2$(NHexMe)]$MeSO_4$ with an alternative peak in the ^{13}C NMR due to DCA replacing $MeSO_4$.

(24) Bis(diethylamino)butylaminocyclopropenium methylsulfate, [$C_3(NEt_2)_2$(NHBu)]$MeSO_4$

Cyclopropenone $(Et_2N)_2C_3O$ (9.00 g, 45.9 mmol), Me_2SO_4 (8.70 g, 69.0 mmol) and H_2N^nBu (4.37 g, 59.7 mmol) were reacted as described in the general synthetic procedure and gave an orange liquid (10.46 g, 62.7%). Before H_2NBu was added, the product was washed with dry diethyl ether (5 x 20 mL) to remove unreacted Me_2SO_4. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (br, 1H, NH), 3.67 (s, 3H, CH_3SO_4), 3.35 (q, $^3J_{HH}$ = 7.16 Hz, 2H, NCH_2CH_3), 3.20 (t, $^3J_{HH}$ = 6.83 Hz, 2H, NCH_2CH_2), 1.61 (m, 2H, NCH_2CH_2), 1.33 (m, 2H, $NCH_2CH_2CH_2$), 1.21 (t, $^3J_{HH}$ = 7.25 Hz, 3H, NCH_2CH_3), 0.87 (t, $^3J_{HH}$ = 7.25 Hz, 3H, $CH_2CH_2CH_3$). ^{13}C NMR (126 MHz, $CDCl_3$): δ 115.94 (equivalent C_3 atoms), 114.65 (br, unique C_3 atom), 53.92 (CH_3SO_4), 46.79 (NCH_2CH_2), 46.27 (NCH_2CH_3), 32.044 (NCH_2CH_2), 19.46 ($NCH_2CH_2CH_2$), 13.95 (NCH_2CH_3), 13.34 ($CH_2CH_2CH_3$).

(25) Bis(diethylamino)butylaminocyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NEt_2)_2(NHBu)]NTf_2$

$[C_3(NEt_2)_2(NHBu)]MeSO_4$ (3.40 g, 9.37 mmol) was stirred with $LiNTf_2$ (8.10 g, 28.2 mmol) in H_2O (150 mL). The product was extracted with chloroform (150 mL), washed with H_2O (2 x 100 mL) and dried *in vacuo* to yield an orange liquid (3.67 g, 73.7%). ^1H and ^{13}C NMR similar to $[C_3(NEt_2)_2(NHBu)]MeSO_4$ with some differences: ^1H NMR NH resonance at 6.22 ppm. ^{13}C NMR resonance for NTf_2^- at 119.79 ppm (q, $^1J_{CF}$ = 322 Hz, CF_3), C_3 ring resonances at 115.40 (equivalent C_3 atoms) and 115.37 (unique C_3 atom) ppm.

(26) Bis(diethylamino)butylaminocyclopropenium dicyanoamide, $[C_3(NEt_2)_2(NHBu)]DCA$

$[C_3(NEt_2)_2(NHBu)]MeSO_4$ (5.92 g, 16.3 mmol) was stirred with NaDCA (4.37 g, 49.1 mmol) in H_2O (150 mL). The product was extracted with chloroform (2 x 100 mL), washed with H_2O (4 x 100 mL) and dried *in vacuo* to yield an orange liquid (3.36 g, 64.8%). ^1H and ^{13}C NMR similar to $[C_3(NEt_2)_2(NHBu)]MeSO_4$ with some differences: ^1H NMR resonance for NH at 7.92 ppm. ^{13}C NMR resonance for DCA at 119.39 ppm, C_3 ring resonances at 115.54 (equivalent C_3 atoms) and 114.81 (slightly br, unique C_3 atom) ppm.

(27) Bis(diethylamino)butylaminocyclopropenium tetrafluoroborate, $[C_3(NEt_2)_2(NHBu)]BF_4$

Dried bis(diethylamino)cyclopropenone (1.03 g, 5 mmol) was stirred with $[Me_3O]BF_4$ (1.01 mL, 6.5 mmol) for 4 h in an inert atmosphere to give $[C_3(NEt_2)_2(OMe)]BF_4$ as a yellow oil (1.3 g, 83%). Butylamine (0.56 mL, 5.67 mmol) was then added and the mixture was stirred for 2 h. The product was washed several times with diethyl ether to remove unreacted amine. This yielded a yellow oil (1.2 g, 82%). ^1H and ^{13}C NMR spectra as for $[C_3(NEt_2)_2(NHBu)]MeSO_4$ but with NH peak at 6.81 ppm and no peaks due to $MeSO_4$.

(28) Bis(diethylamino)hexylaminocyclopropenium methylsulfate, $[C_3(NEt_2)_2(NHHex)]MeSO_4$

Dried cyclopropenone $(Et_2N)_2C_3O$ (4.61 g, 23.5 mmol) and dimethylsulfate (5.93 g, 47.0 mmol) were mixed at ambient temperature for 1 h. Hexylamine (15.32 g, 151 mmol) was added and the solution was stirred at ambient temperature for 3 h. The product was washed with a diethyl ether/petroleum ether mixture (3 x 75 mL, 1:1 ratio). The product was then dissolved in H_2O (50 mL), acidified with aqueous HCl, extracted with CH_2Cl_2 (50 mL) and washed with H_2O (3 x 75 mL). CH_2Cl_2 was removed *in vacuo*, and the product was then washed with diethyl ether (4 x 50 mL). Aqueous NaOH (200 mL, 0.38 mol/L) was added, and the product was washed with pet ether (4 x 100 mL) and diethyl ether (3 x 100 mL). The product was acidified with aqueous HCl and H_2O removed *in vacuo*. Addition of acetone caused precipitation of NaCl, which was filtered off. Removal of acetone *in vacuo* yielded a yellow liquid (2.64 g, 33.9%). ^1H NMR (500 MHz, $CDCl_3$): δ 9.04 (br. s, 1H, N*H*), 3.69 (s, $(CH_3)SO_4$), 3.39 (br. q, $^3J_{HH}$ = 7.0 Hz, NCH_2CH_3), 3.19

(q, $^3J_{HH}$ = 7.0 Hz, $NC\mathit{H_2}(CH_2)_4CH_3$), 1.65 (m, $NCH_2C\mathit{H_2}(CH_2)_3CH_3$), 1.18–35 (m, $NCH_2C\mathit{H_3}$ and $N(CH_2)_2(C\mathit{H_2})_3CH_3$), 0.82 (t, $^3J_{HH}$ = 6.8 Hz, $NCH_2(CH_2)_4C\mathit{H_3}$). ^{13}C NMR (125 MHz, $CDCl_3$): 116.93 (C_1 and C_2), 54.61 (CH_3SO_4), 47.64 ($N\mathit{C}H_2C_5H_{11}$), 46.82 ($N\mathit{C}H_2CH_3$), 31.65 ($NCH_2\mathit{C}H_2C_4H_9$), 30.67 ($N(C_2H_4)\mathit{C}H_2C_3H_7$), 26.69 ($NC_3H_6\mathit{C}H_2C_2H_5$), 22.74 ($NC_4H_8\mathit{C}H_2CH_3$), 14.53 ($NCH_2\mathit{C}H_3$), 14.123($NC_5H_{10}\mathit{C}H_3$). MS$^+$ as for $[C_3(NEt_2)_2(NHHex)]$TFSA.

(29) Bis(diethylamino)hexylaminocyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NEt_2)_2(NHHex)]NTf_2$

$[C_3(NEt_2)_2(NHHex)]MeSO_4$ (2.64 g, 7.97 mmol) was stirred with $LiNTf_2$ (6.9 g, 24.1 mmol) in H_2O (200 mL) for 30 min. The product was extracted with diethyl ether (200 mL). Additional $LiNTf_2$ (6.3 g, 22.0 mmol) and H_2O (200 mL) were added and the mixture stirred for 1.5 h. The organic layer was washed with H_2O (4 x 75 mL) and dried *in vacuo* to yield a yellow liquid (3.50 g, 78.4%). ^{1}H and ^{13}C NMR as for $[C_3(NEt_2)_2(NHHex)]MeSO_4$ with additional peaks in the ^{13}C NMR due to NTf_2^- and no peaks due to $MeSO_4^-$. ES-MS$^+$: m/z 280.3 (100%, M$^+$).

(30) Bis(diethylamino)aminocyclopropenium methylsulfate, $[C_3(NEt_2)_2(NH_2)]MeSO_4$

$NH_{3(g)}$ (excess) was passed through a rapidly stirred sample of $[C_3(NEt_2)_2(OMe)]MeSO_4$ (3 g, 9 mmol) for 2 h in an inert atmosphere. Excess NH_3 was removed *in vacuo* to give an orange viscous oil (2.86 g, 100%). ^{1}H NMR (500 MHz, D_2O): δ 3.60 (s, 3H, CH_3SO_4), 3.24 (q, $^3J_{HH}$ = 7.3 Hz , 8H, $NC\mathit{H_2}CH_3$), 1.08 (t, $^3J_{HH}$ = 7.3 Hz, 12H, $NCH_2C\mathit{H_3}$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18 (s, 2H, $N\mathit{H}$), 3.77 (s, 3H, CH_3SO_4), 3.39 (q, $^3J_{HH}$ = 7 Hz , 8H, $NC\mathit{H_2}CH_3$), 1.23 (t, $^3J_{HH}$ = 7 Hz, 12H, $NCH_2C\mathit{H_3}$). ^{13}C NMR (126 MHz, D_2O) δ 116.57 (equivalent ring C), 113.97 (unique ring C), 55.55 (CH_3SO_4), 46.42 ($N\mathit{C}H_2CH_3$), 13.80 ($NCH_2\mathit{C}H_3$). EI-MS: m/z 196.18 (M$^+$).

(31) Bis(diethylamino)aminocyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NEt_2)_2(NH_2)]NTf_2$

$[C_3(NEt_2)_2(NH_2)]MeSO_4$ (2.35 g, 8 mmol) was stirred with $LiNTf_2$ (6.58 g, 24 mmol) in water (10 mL) for 30 min. The product was extracted with chloroform (3 x 10 mL) to give a yellow oil (2.83 g, 78%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.83 (s, 2H, $N\mathit{H}$), 3.36 (q, $^3J_{HH}$ = 7 Hz , 8H, $NC\mathit{H_2}CH_3$), 1.25 (t, $^3J_{HH}$ = 7 Hz, 12H, $NCH_2C\mathit{H_3}$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 120.74 (q, $^1J_{CF}$ = 299 Hz, CF_3), 116.23 (equivalent ring C), 114.18 (unique ring C), 46.80 ($N\mathit{C}H_2CH_3$), 14.40 ($NCH_2\mathit{C}H_3$). EI-MS: m/z 196.18 (M$^+$).

(32) Tris(diallylamino)cyclopropenium chloride, $[C_3(N(CH_2CHCH_2)_2)_3]Cl$

C_3Cl_5H (6.67 g, 31.1 mmol) and $HN(CH_2CHCH_2)_2$ (23.6 g, 243 mmol) gave a yellow liquid (9.95 g, 88.9% yield) after separation from diallylammonium chloride by extraction of an aqueous solution with chloroform. ^{1}H NMR (500 MHz, CDCl$_3$): δ 5.58 (m, 6H, NCH$_2$C*H*CH$_2$), 5.04 (m, 12H, NCH$_2$CHCH_2), 3.76 (d, $^{3}J_{HH}$ = 5.14 Hz, 13H, NCH$_2$CHCH_2). ^{13}C NMR (126 MHz, CDCl$_3$): δ 130.81 (NCH$_2$*C*HCH$_2$), 118.39 (NCH$_2$CH*C*H$_2$), 116.36 (C$_3$), 54.03 (N*C*H$_2$CHCH$_2$). ES-MS$^+$: m/z 324 (100%, M$^+$).

(33) Tris(diallylamino)cyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(N(CH_2CHCH_2)_2)_3]NTf_2$

$[C_3(N(CH_2CHCH_2)_2)_3]Cl$ from above (4.11 g, 11.4 mmol) was stirred with LiNTf$_2$ (7.00 g, 24.4 mmol) in H$_2$O (100 mL). The product was extracted with chloroform (2 x 100 mL), washed with H$_2$O (3 x 100 mL), and then dried *in vacuo* to yield a light yellow liquid (5.00 g, 72.4%). ^{1}H, ^{13}C NMR and MS$^+$ as for $[C_3(N(CH_2CHCH_2)_2)_3]Cl$ with an additional peak in the ^{13}C NMR due to NTf$_2^-$.

(34) Tris(diallylamino)cyclopropenium dicyanoamide, $[C_3(N(CH_2CHCH_2)_2)_3]DCA$

$[C_3(N(CH_2CHCH_2)_2)_3]Cl$ from above (5.19 g, 14.4 mmol) was stirred with NaDCA (2.84 g, 31.9 mmol) in H$_2$O (100 mL). The product was extracted with chloroform (2 x 100 mL), washed with H$_2$O (3 x 100 mL), and then dried *in vacuo* to yield a light yellow liquid (5.06 g, 89.9%). ^{1}H, ^{13}C NMR and MS$^+$ as for $[C_3(N(CH_2CHCH_2)_2)_3]Cl$ with an additional peak in the ^{13}C NMR due to DCA.

(35) Bis(diethylamino)-*S*-(1-carboxylethylamino)cyclopropenium methylsulfate, $[C_3(NEt_2)_2(NH((S)\text{-}CHMeCOOH))]MeSO_4$

Dried bis(diethylamino)cyclopropenone (21.13 g, 108 mmol) was stirred with Me$_2$SO$_4$ (13.3 mL, 140 mmol) for 30 minutes in an inert atmosphere. The mixture was washed with dry diethyl ether several times to remove excess Me$_2$SO$_4$ and cyclopropenone. This gave $[C_3(NEt_2)(OMe)]MeSO_4$ as an orange viscous oil (24.2 g, 70%).

$[C_3(NEt_2)_2(OMe)]MeSO_4$ (11.37 g, 35.31 mmol) was stirred with L-alanine (4.1 g, 46 mmol) and NEt$_3$ (17 mL, 106 mmol) in water (20 mL) overnight. Water was removed *in vacuo* and the product was dissolved in acetone (20 mL) and filtered to remove unreacted L-alanine. The solvent was removed in vacuo and NEt$_3$ was removed by washing with dry diethylether (5 x 50 mL) to give an orange oil (10.4 g, 75.7%). ^{1}H NMR (500MHz, CDCl$_3$): δ 8.36 (d, $^{3}J_{HH}$ = 7 Hz, 1H, NH), 5.65 (br, 1H, COOH), 4.01 (dq, $^{3}J_{HH}$ = 7 Hz, $^{3}J_{HH}$ = 7 Hz, 1H, CH), 3.71 (s, 3H, MeSO$_4$), 3.38 (q, $^{3}J_{HH}$ = 6.6 Hz, 8H, NCH_2CH$_3$), 1.58 (d, $^{3}J_{HH}$ = 7 Hz, 3H, Me), 1.24 (t, $^{3}J_{HH}$ = 6.6 Hz, 12H, NCH$_2$CH_3). ^{13}C NMR (CDCl$_3$, 126 MHz) δ 175.37 (COOH), 115.75 (unique ring C), 115.18 (equivalent ring C), 56.54 (*C*HMe), 54.74 (MeSO$_4$), 46.54 (N*C*H$_2$CH$_3$), 18.34 (CH*C*H$_3$), 14.22 (NCH$_2$*C*H$_3$). EI-MS: m/z 268.93 (M$^+$). $[\alpha]_{25}^{D}$ –29.1° (c 1.9, 1 M HCl(aq)), –9.5° (c 4.1, 1 M NaOH(aq)).

(36) Bis(diethylamino)-*S*-(1-carboxylethylamino)cyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NEt_2)_2(NH((S)\text{-}CHMeCOOH))]NTf_2$

$[C_3(NEt_2)_2(NH((S)\text{-}CHMeCOOH))]MeSO_4$ (2.1 g, 5 mmol) was stirred with $LiNTf_2$ (4.71 g, 16 mmol) in 10 mL of water. Extraction with chloroform (3 x 10 mL) yielded the product (2.57 g, 86%). ^1H and ^{13}C NMR spectra similar to $[C_3(NEt_2)_2(NH((S)\text{-}CHMeCOOH))]MeSO_4$ with no peaks due to $MeSO_4^-$ and additional peaks in the ^{13}C NMR due to NTf_2^-. ES-MS$^+$ as for $[C_3(NEt_2)_2(NH((S)\text{-}CHMeCOOH))]MeSO_4$.

(37) Bis(diethylamino)-*S*-(2-carboxypyrrolidino)cyclopropenium methylsulfate, $[C_3(NEt_2)_2(N(C_4H_7COOH))]MeSO_4$

$[C_3(NEt_2)_2(OMe)]MeSO_4$ (5.65 g, 18 mmol) was stirred with L-proline (2.62 g, 23 mmol) and NEt_3 (3.64 mL, 23 mmol) in water (20 mL) overnight. Water was removed *in vacuo* and the product was dissolved in acetone (20 mL) and filtered to remove unreacted L-proline. The mixture was dissolved in ice cold water and the product was extracted with chloroform:ethanol (2:1) (3 x 30 mL). The solvent was removed *in vacuo* to give an orange oil (5.53 g, 78%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 (br, 1H, COOH), 4.42 (dd, $^3J_{HH}$ = 3.6Hz, , $^3J_{HH}$ = 8Hz, 1H, CH), 3.72 (m, 1H, NCH_2), 3.68 (s, 3H, CH_3SO_4), 3.60 (ddd, $^3J_{HH}$ = 7.9Hz, 1H, NCH_2), 3.34 (m, 8H, NCH_2CH_3), 2.31 (m, 2H, $NCH_2CH_2CH_2$), 2.01 (m, 2H, NCH_2CH_2), 1.21 (t, $^3J_{HH}$ = 6.6 Hz, 12H, NCH_2CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.09 (COOH), 116.08 (equivalent ring C), 114.80 (unique ring C), 64.60 (NCH), 54.26 (CH_3SO_4), 51.89 (NCH_2), 46.77 (NCH_2CH_3), 31.13 ($NCHCH_2$), 24.32 ($NCH_2CH_2CH_2$), 13.94 (NCH_2CH_3). EI-MS: m/z 295.00 (M^+). $[\alpha]_{25}^{D}$ –58.3° (c 7.8, 1 M HCl(aq)), –84.8° (c 1.5, 1 M NaOH(aq)).

(38) Bis(diethylamino)-*S*-(2-carboxypyrrolidino)cyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NEt_2)_2(N(C_4H_7COOH))]NTf_2$

$[C_3(NEt_2)_2(N(C_4H_7COOH))]MeSO_4$ (2.1 g, 5 mmol) was stirred with $LiNTf_2$ (4.71 g, 16 mmol) in 10 mL of water. Extraction with chloroform (3 x 10 mL) yielded the product (2.57 g, 86%). ^1H and ^{13}C NMR similar to $[C_3(NEt_2)_2(N(C_4H_7COOH))]MeSO_4$ but with no peaks due to $MeSO_4^-$ and additional peaks in the ^{13}C NMR due to NTf_2^-. ES-MS$^+$ as for $[C_3(NEt_2)_2(N(C_4H_7COOH))]MeSO_4$.

(39) Bis(diethylamino)-*S*-(1-carboxy-2-methylpropylamino)cyclopropenium methylsulfate, $[C_3(NEt_2)_2(NH(C_4H_8COOH))]MeSO_4$

$[C_3(NEt_2)_2(OMe)]MeSO_4$ (15 g, 47 mmol) was stirred with L-valine (7.09 g, 61 mmol) and NEt_3 (9.67 mL, 61 mmol) in water (50 mL) overnight. Water was removed *in vacuo* and the product was dissolved in acetone (20 mL) and filtered to remove unreacted L-valine. The mixture was dissolved in ice cold water and the product was extracted with chloroform:ethanol (2:1) (3 x 30 mL). The solvent was removed *in vacuo* to give a yellow solid 10.00 g, 55%). ^{1}H NMR (400MHz, CDCl$_3$): δ 8.44 (br, 1H, N*H*), 3.67 (s, 3H, CH_3SO_4), 3.62 (d, $^3J_{HH}$ = 6.4Hz, 1H, C*H*), 3.38 (m, 8H, NC*H*$_2$CH$_3$), 2.23 (m, 1H, C*H*), 1.22 (t, $^3J_{HH}$ = 7.2 Hz, 12H, NCH$_2$C*H*$_3$), 1.03 (d, $^3J_{HH}$ = 6.8 Hz, 3H, C*H*$_3$), 0.98 (d, $^3J_{HH}$ = 6.8 Hz, 3H, C*H*$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ 174.25 (*C*OOH), 115.87 (equivalent ring C), 115.46 (unique ring C), 68.82 (*C*HNH), 54.27 (CH_3SO_4), 46.62 (N*C*H$_2$CH$_3$), 31.00 (*C*H(CH$_3$)$_2$), 19.28 (*C*H$_3$), 18.80 (*C*H$_3$), 14.27 (NCH$_2$*C*H$_3$). EI-MS: m/z 296.233 (M$^+$). $[\alpha]_{25}{}^{D}$ –3.2° (c 0.6, 1 M HCl(aq)), –1.7° (c 0.6, 1 M NaOH(aq)).

(40) Bis(diethylamino)-*S*-(1-carboxy-2-methylpropylamino)cyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NEt_2)_2(NH(C_4H_8COOH))]NTf_2$

$[C_3(NEt_2)_2(NH(C_4H_8COOH))]MeSO_4$ (2.1 g, 5 mmol) was stirred with LiNTf$_2$ (4.71 g, 16 mmol) in 10 mL of water. Extraction with chloroform (3 x 10 mL) yielded the product (2.57 g, 86%). ^{1}H and ^{13}C NMR spectra similar to $[C_3(NEt_2)_2(NH(C_4H_8COOH))]MeSO_4$ but with no peaks due to $MeSO_4^-$ and additional peaks in the ^{13}C NMR due to NTf_2^-. ES-MS$^+$ as for $[C_3(NEt_2)_2(NH(C_4H_8COOH))]MeSO_4$.

(41) Bis(diethylamino)-*S*-(1-carboxy-2-hydroxylpropylamino)cyclopropenium methylsulfate, $[C_3(NEt_2)_2(NH(C_3H_5OHCOOH))]MeSO_4$

$[C_3(NEt_2)_2(OMe)]MeSO_4$ (10 g, 31 mmol) was stirred with L-threonine (4.8 g, 40 mmol) and NEt$_3$ (6.45 mL, 40 mmol) in water (50 mL) overnight. Water was removed *in vacuo* and the product was dissolved in acetone (20 mL) and filtered to remove unreacted L-threonine. The mixture was dissolved in ice cold water and the product was extracted with chloroform:ethanol (2:1) (3 x 30 mL). The solvent was removed *in vacuo* to give a yellow solid (9.30 g, 76%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.04 (br, 1H, N*H*), 5.27 (br, 2H, O*H*+H$_2$O), 4.08 (m,1H, NC*H*), 3.69 (m, 1H, C*H*OH), 3.67 (s, 3H, CH_3SO_4), 3.37 (q, $^3J_{HH}$ = 7.16 Hz , 8H, NC*H*$_2$CH$_3$), 1.23 (d, $^3J_{HH}$ = 7.5 Hz, 3H, C*H*$_3$), 1.21 (t, $^3J_{HH}$ = 7.25 Hz, 12H, NCH$_2$C*H*$_3$).^{13}C NMR (126 MHz, CDCl$_3$) δ 173.37 (*C*OOH), 115.98 (equivalent ring C), 115.35 (unique ring C), 67.78 (*C*HCH$_3$), 67.20 (*C*HNH), 54.31 (CH_3SO_4), 46.49 (N*C*H$_2$CH$_3$), 19.42 (*C*H$_3$), 14.20 (NCH$_2$*C*H$_3$). EI-MS: m/z 298.87 (M$^+$). $[\alpha]_{25}{}^{D}$ –6.0° (c 3.0, 1 M HCl(aq)), –3.6° (c 4.1, 1 M NaOH(aq)).

(42) Bis(diethylamino)-*S*-(1-carboxy-2-hydroxylpropylamino))cyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NEt_2)_2(NH(C_3H_5OHCOOH))]NTf_2$

$[C_3(NEt_2)_2(NH(C_3H_6OCOOH))]MeSO_4$ (2.1 g, 5 mmol) was stirred with LiNTf$_2$ (4.71 g, 16 mmol) in 10 mL of water. Extraction with chloroform (3 x 10 mL) yielded the product (2.57 g, 86%). ^{1}H and ^{13}C NMR spectra similar to $[C_3(NEt_2)_2(NH(C_3H_6OCOOH))]MeSO_4$ but with no peaks due to $MeSO_4^-$ and additional peaks in the ^{13}C NMR due to NTf_2^-. MS$^+$ as for $[C_3(NEt_2)_2(NH(C_3H_6OCOOH))]MeSO_4$.

Aldol reactions of benzaldehyde with acetone

The reaction mixtures were stirred at room temperature for 25 h and then filtered to recover L-proline. Acetone was removed in vacuo. The pure aldol addition product was obtained as a yellow oil after flash silica gel column chromatography, eluting with n-hexane/ EtOAc (2:1).

Table 1a. Viscosity (cP) and water (ppm) and chloride (ppm) content data.

Compound	**20 °C**	**30 °C**	**40 °C**	**50 °C**	**60 °C**	**70 °C**	**80 °C**	**90 °C**	**H_2O**	**Cl**
(2) $[C_3(NEt_2)_2(NMe_2)]NTf_2$	83.6	52.4	35.2	24.7	17.9	13.4	10.3	8.15	141.7	62
(3) $[C_3(NEt_2)_2(NMe_2)]DCA$	58.4	37.1	25.4	17.9	13.2	10	7.94	6.41	1115	3554
(4) $[C_3(NEt_2)_3]DCA$	64.2	41.9	28.3	19.9	14.6	11.4	8.89	7.07	1040	960
(6) $[C_3(NEt_2)_2(NBu_2)]NTf_2$	126	76.4	49.9	32.7	23.1	17.2	13	9.91	56.9	83
(7) $[C_3(NEt_2)_2(NBu_2)]DCA$	105	63.3	40.8	27.4	19.4	14.2	11	8.56	623.9	263
(9) $[C_3(NEt_2)_2(NHex_2)]NTf_2$	182	108	67.8	44.2	30.2	21.7	15.8	12	76	–
(10) $[C_3(NEt_2)_2(NHex_2)]DCA$	131	76.8	48.4	32	22.2	16	12	9.25	894	519
(11) $[C_3(NEt_2)_2(NHex_2)]I$	–	–	547	238	123	75.1	36.4	24.9	1279	–
(12) $[C_3(NEt_2)_2(NHex_2)]OTf$	444	240	138	82.8	54.7	38.8	26.2	20.5	720	125
(14) $[C_3(NEt_2)_2(N(CH_2CHCH_2)_2)]NTf_2$	111	67.4	43.7	29.6	20.9	15.3	11.7	9.04	67	519
(16) $[C_3(NEt_2)_2(N(CH_2CH_2OH)_2)]NTf_2$	–	–	249	143	89.0	58.5	40.1	28.7		422
(19) $[C_3(NEt_2)_2(NBuMe)]NTf_2$	106	66.4	43.3	29.7	21.1	15.5	11.9	9.12	407	97
(20) $[C_3(NEt_2)_2(NBuMe)]DCA$	73.7	45.8	30.2	20.8	15.3	11.5	8.94	7.1	1040	202
(22) $[C_3(NEt_2)_2(NHexMe)]NTf_2$	102	62.8	41.4	28.3	20.3	15.2	11.6	9.07	82	103
(23) $[C_3(NEt_2)_2(NHexMe)]DCA$	86.2	52.8	34.4	23.4	17.0	12.7	9.78	7.71	604	619
(24) $[C_3(NEt_2)_2(NHBu)]MeSO_4$	344	188	106	67.4	45.0	31.7	22.7	16.8	365	1063
(25) $[C_3(NEt_2)_2(NHBu)]NTf_2$	176	96	54.5	36.5	25.5	18.4	13.8	10.8	72	1437
(26) $[C_3(NEt_2)_2(NHBu)]DCA$	251	126	75.6	47.0	31.6	23	17	12.9	492	2033
(27) $[C_3(NEt_2)_2(NHBu)]BF_4$	131	65.9	37.8	22.7	14.7	10.1	7.0	5.13	36	32
(29) $[C_3(NEt_2)_2(NHHex)]NTf_2$	171	103	61.3	40.8	27.9	20.4	15.2	11.4	145	426

Compound	**20 °C**	**30 °C**	**40 °C**	**50 °C**	**60 °C**	**70 °C**	**80 °C**	**90 °C**	**H_2O**	**Cl**
(33) $[C_3(N(CH_2CHCH_2)_2)_3]NTf_2$	126	72.6	45.5	30.8	21.1	15.3	11.4	8.64	150	231
(34) $[C_3(N(CH_2CHCH_2)_2)_3]DCA$	211	113	65.3	41.1	27.2	19.3	15.2	10.7	170	638

Table 1b. Viscosity (cP) and water (ppm) and chloride (ppm) content data.

Compound	**60 °C**	**65 °C**	**70 °C**	**75 °C**	**80 °C**	**85 °C**	**90 °C**	**H_2O**	**Cl**
(35) (Ala) $[C_3(NEt_2)_2(NH((S)\text{-}CHMeCOOH))]MeSO_4$	–	1006	742	562	437	363	349	14400	2289
(36) (Ala) $[C_3(NEt_2)_2(NH((S)\text{-}CHMeCOOH))]NTf_2$	820	590	435	329	255	197	156	46	435
(37) (Pro) $[C_3(NEt_2)_2(N(C_4H_7COOH))]MeSO_4$	–	–	–	834	615	460	412	514	9706
(38) (Pro) $[C_3(NEt_2)_2(N(C_4H_7COOH))]NTf_2$	564	406	303	231	179	139		603	174
(39) (Val) $[C_3(NEt_2)_2(NH(C_4H_8COOH))]MeSO_4$	–	–	–	–	–	–	–	3070	41369
(40) (Val) $[C_3(NEt_2)_2(NH(C_4H_8COOH))]NTf_2$	–	–	–	–	–	–	–	188	186
(41) (Threo) $[C_3(NEt_2)_2(NH(C_3H_5OHCOOH))]MeSO_4$	–	–	–	–	–	–	–	2660	3229
(42) (Threo) $[C_3(NEt_2)_2(NH(C_3H_5OHCOOH))]NTf_2$	–	–	–	884	617	456	329	1152	38

Table 2. Microanalytical data (Calc./Exptl).

Compound	**C**	**H**	**N**	**Cl**	**F**	**S**
(2) $[C_3(NEt_2)_2(NMe_2)]NTf_2$	35.71 36.38	5.19 5.48	11.11 11.13			
(3) $[C_3(NEt_2)_2(NMe_2)]DCA.1H_2O$	58.41 58.91	9.15 8.90	27.25 26.66			
(4) $[C_3(NEt_2)_3]DCA$	64.12 63.99	9.49 9.77	26.39 26.59			
(6) $[C_3(NEt_2)_2(NBu_2)]NTf_2$	42.85 42.95	6.51 6.72	9.52 9.60		19.36 19.42	10.89 10.79
(7) $[C_3(NEt_2)_2(NBu_2)]DCA$	67.34 64.93	10.23 9.68	22.44 21.85			
(9) $[C_3(NEt_2)_2(NHex_2)]NTf_2$	46.57 47.35	7.19 7.58	8.69 8.78		17.68 14.87	
(10) $[C_3(NEt_2)_2(NHex_2)]DCA.0.85H_2O$	67.33 67.43	10.78 10.62	18.84 18.71			

Compound	**C**	**H**	**N**	**Cl**	**F**	**S**
(11) $[C_3(NEt_2)_2(NHex_2)]I.0.25H_2O$	55.69 55.62	9.44 9.53	8.47 8.52			
(12) $[C_3(NEt_2)_2(NHex_2)][CF_3SO_3]$	56.12 55.95	9.03 9.23	8.18 7.96			
(14) $[C_3(NEt_2)_2(N(CH_2CHCH_2)_2)]NTf_2$	41.00 41.03	5.43 5.47	10.07 10.04			
(16) $[C_3(NEt_2)_2(N(CH_2CH_2OH)_2)]NTf_2$	36.17 36.45	5.36 5.24	9.92 9.86			
(17) $[C_3(NEt_2)_2(N(CH_2CH_2OH)_2)]DCA$	58.26 58.19	8.63 8.84	23.98 24.09			
(19) $[C_3(NEt_2)_2(NBuMe)]NTf_2$	39.55 40.41	5.90 5.87	10.25 10.28		20.85 17.08	
(20) $[C_3(NEt_2)_2(NBuMe)]DCA.0.5H_2O$	63.31 63.08	9.74 9.86	24.61 24.78			
(22) $[C_3(NEt_2)_2(NHexMe)]NTf_2$	41.80 42.78	6.31 6.35	9.75 9.75		19.84 17.29	11.16 10.07
(23) $[C_3(NEt_2)_2(NHexMe)]DCA$	66.63 64.61	10.06 9.95	23.31 21.89			
(24) $[C_3(NEt_2)_2(NHBu)]MeSO_4$	52.87 52.27	9.15 9.25	11.56 11.49			
(25) $[C_3(NEt_2)_2(NHBu)]NTf_2$	64.12 63.91	9.50 9.93	26.40 25.96			
(26) $[C_3(NEt_2)_2(NHBu)]DCA$	64.12 63.91	9.50 9.93	25.96 25.96			
(27) $[C_3(NEt_2)_2(NHBu)]BF_4.0.25H_2O$	52.31 52.41	9.23 8.94	12.22 12.22			
(29) $[C_3(NEt_2)_2(NHHex)]NTf_2$	40.71 41.43	6.11 6.26	9.99 10.07			
(30) $[C_3(NEt_2)_2(NH_2)]MeSO_4.1.5H_2O$	43.10 42.78	8.43 8.29	12.56 12.84			
(31) $[C_3(NEt_2)_2(NH_2)]NTf_2$ With 4% cyclopropenone	34.51 34.15	4.87 4.94	11.86 11.89			
(32) $[C_3(N(CH_2CHCH_2)_2)_3]Cl.0.9H_2O$	67.22 67. 22	8.51 8.51	11.20 10.82	9.45 9.17		

Compound	**C**	**H**	**N**	**Cl**	**F**	**S**
(33) $[C_3(N(CH_2CHCH_2)_2)_3]NTf_2$	45.68 45.95	5.00 5.22	9.27 9.56			
(34) $[C_3(N(CH_2CHCH_2)_2)_3]DCA.0.5H_2O$	69.11 69.11	7.82 7.71	21.02 21.06			
(35) $[C_3(NEt_2)_2(NH((S)\text{-}CHMeCOOH))]MeSO_4$ (25% zwitterion)	51.33 51.70	8.13 8.34	12.23 11.82			
(36) $[C_3(NEt_2)_2(NH((S)\text{-}CHMeCOOH))]NTf_2$ (4% zwitterion)	36.15 36.14	4.96 5.31	10.43 10.40			
(37) $[C_3(NEt_2)_2(N(C_4H_7COOH))]MeSO_4$ (38% zwitterion + 3% water)	54.47 54.57	8.38 8.89	11.52 11.59			
(38) $[C_3(NEt_2)_2(N(C_4H_7COOH))]NTf_2$ (15% zwitterion + 3% water)	40.59 40.41	5.73 5.69	10.13 10.24			
(39) $[C_3(NEt_2)_2(NH(C_4H_8COOH))]MeSO_4$ (50% zwitterion, 1% water)	57.01 57.10	9.05 9.01	12.15 12.08			
(40) $[C_3(NEt_2)_2(NH(C_4H_8COOH))]NTf_2$ (19% zwitterion, 3% water)	41.49 41.38	6.27 6.46	10.27 10.56			
(41) $[C_3(NEt_2)_2(NH(C_3H_6OCOOH))]MeSO_4$ (55% zwitterion)	54.44 54.43	8.47 8.46	12.39 12.38			
(42) $[C_3(NEt_2)_2(NH(C_3H_6OCOOH))]NTf_2$ (8% zwitterion)	38.51 38.57	5.39 5.51	10.36 10.52			