New route to carbonate-functionalized imidazolium and pyrrolidinium-based ionic liquids

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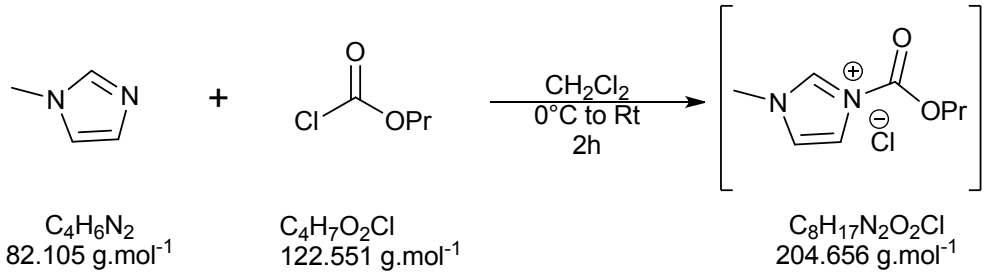
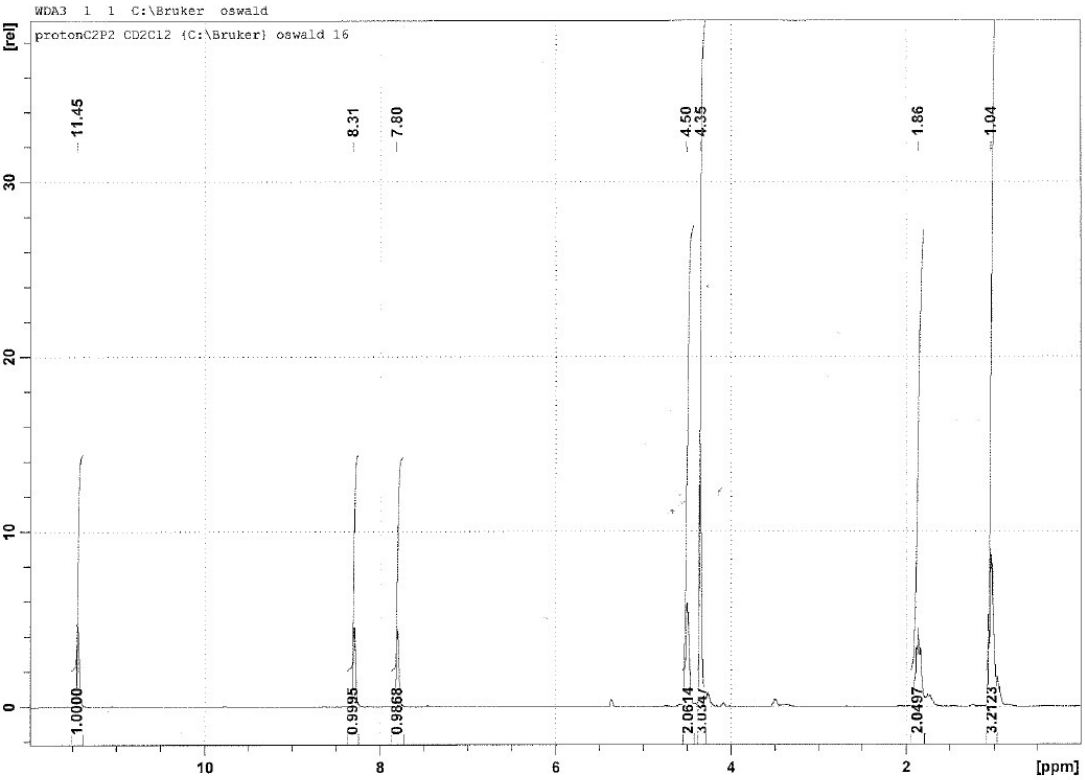
Synthesis and characterizations

Formation of 3-methyl-1-(propyloxycarbonyl)imidazolium chloride intermediate **(1)**



The reaction was carried out under inert gas atmosphere. A solution of Propyl chloroformate (1.317 g, 1.208 mL, 10.749 mmol) in anhydrous CH_2Cl_2 (2 mL) was added drop wise at 0°C to a solution of 1-Methylimidazole (0.802 g, 0.779 mL, 9.772 mmol) in dried CH_2Cl_2 (2 mL). The mixture was warmed to room temperature and stirred for 2 h. Thereafter, the solvent was smoothly removed under vacuum. A colourless precipitate was performed (2.000 g, 9.772 mmol, 100%). The obtained solid was used for synthesis of **4** and **5** without further purification.

Scheme 1: The white precipitate of compound **1** intermediate.



Scheme 2: Proton NMR of the compound **1** intermediate.

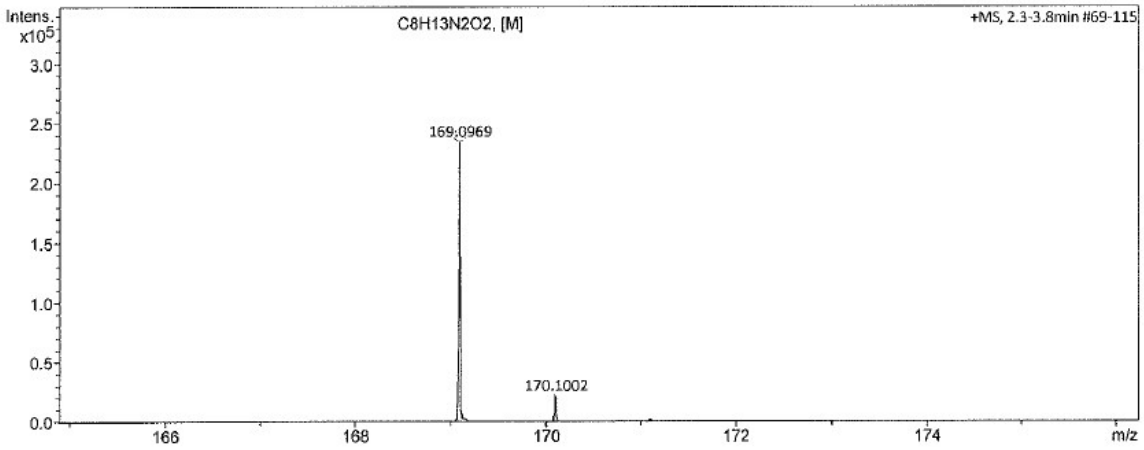
CENTRE COMMUN DE SPECTROMETRIE DE MASSE

Analysis Info

Analysis Name	QTOF170822_01_BM27.d		
Method	2016_03_17_Infusion_50-1000_pos.m	Acquisition Date	8/22/2017 8:08:10 AM
Comment		Instrument / Ser#	micrOTOF-Q 228888.10 231

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	3500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	400.0 Vpp	Set Divert Valve	Waste



Meas. m/z	Ion Formula	m/z	err [ppm]	mSigma
169.0969	C8H13N2O2	169.0972	1.6	1.4

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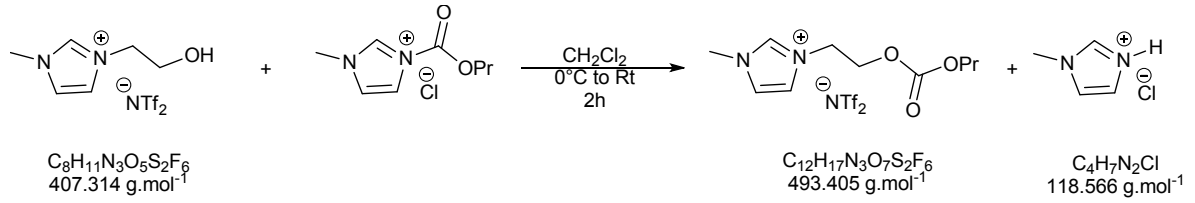
Scheme 3: ESI$^+$ of intermediate **1,** m/z=169 corresponding to the compound **1**.

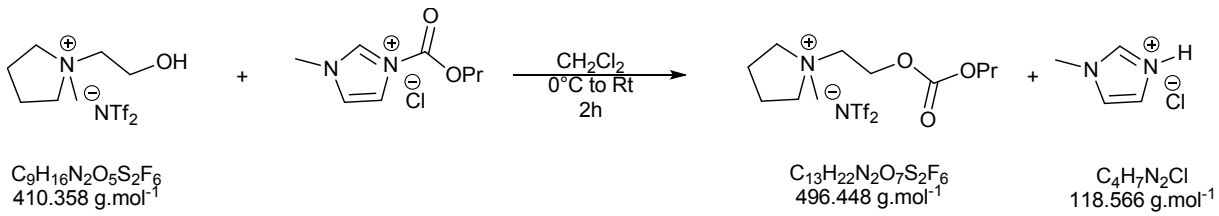
Formation of 1-[2-(propyloxycarbonyloxy)ethyl]-3-methylimidazolium bis(trifluoromethane)sulfonimide **(4)** : [$C_1C_2O(CO)OPrIm$][NTf_2]



Via syringe 1-[2-(Hydroxy)ethyl]-3-methylimidazolium bis(trifluoromethane)sulfonimide (3.619 g, 8.885 mmol) was added drop wise to freshly generated precipitate **1** (2.000 g, 9.772 mmol) at 0 °C. The resulting clear solution was warmed to 50 °C and stirred overnight. After cooling to room temperature, CH_2Cl_2 (9 mL) was added. The organic phase was washed with deionised water until no chloride was detected in the aqueous phase ($AgNO_3$ standard test). Evaporation of CH_2Cl_2 yielded a colourless viscous fluid (3.534 g, 7.164 mmol, 81 %).

^{1}H-NMR (CD_2Cl_2): δ (ppm): 8.76 (s, 1H, C2*H*); 7.33 (d, 2H, C4*H*, C5*H*); 4.48 (m, 4H, NCH_2CH_2O); 4.09 (t, 2H, $OCH_2CH_2CH_3$); 3.95 (s, 3H, NCH_3); 1.67 (st, 2H, $OCH_2CH_2CH_3$); 0.94 (t, 3H, $OCH_2CH_2CH_3$).
$^{13}C\{^1H\}$-NMR (CD_2Cl_2): δ (ppm): 155.0 (O(*C*O)O); 136.9 (*C*2H); 124.3 (*C*5H); 123.2 (*C*4H); 120.2 (CF_3); 70.4 ($OCH_2CH_2CH_3$); 65.6 (NCH_2CH_2O); 53.8 (NCH_2CH_2O); 36.2 (NCH_3); 21.9 ($OCH_2CH_2CH_3$); 9.6 ($OCH_2CH_2CH_3$).
Electrospray, MS (+ve): *m/z* 213 (100% - [$C_1C_2O(CO)OPrIm$]$^+$), MS (-ve): *m/z* 280 (100% - [NTf_2]$^-$).

Formation of *N*-methyl-*N*-[2-(propyloxycarbonyl)ethyl]pyrrolidinium bis(trifluoromethane)sulfonimide **(5)** : [$C_1C_2O(CO)OPrPy$][NTf_2]



Via syringe *N*-Methyl-*N*-[2-(Hydroxy)ethyl]-pyrrolidinium bis(trifluoromethane)sulfonimide (3.620 g, 8.822 mmol) was added drop wise to freshly generated precipitate **1** (2.000 g, 9.772 mmol) at 0 °C. The resulting clear solution was warmed to 50 °C and stirred overnight. After cooling to room temperature, CH_2Cl_2 (9 mL) was added. The organic phase was washed with deionised water until no chloride was detected in the aqueous phase ($AgNO_3$ standard test). Evaporation of

CH_2Cl_2 yielded slightly yellowish oil (3.478 g, 7.006 mmol, 79 %).

^{1}H-NMR (CD_2Cl_2): δ (ppm): 4.55 (m, 2H, NC*H*$_2$CH$_2$O); 4.13 (t, 2H, OC*H*$_2$CH$_2$CH$_3$); 3.72 (t, 2H, NCH$_2$C*H*$_2$O); 3.59 (m, 4H, C2*H*$_2$, C5*H*$_2$); 3.12 (s, 3H, NC*H*$_3$); 2.28 (m, 4H, C3*H*$_2$, C4*H*$_2$); 1.69 (st, 2H, OCH$_2$C*H*$_2$CH$_3$); 0.95 (t, 3H, OCH$_2$CH$_2$C*H*$_3$).
^{13}C{^{1}H}-NMR (CD_2Cl_2): δ (ppm): 154.7 (O(*C*O)O); 120.3 (*C*F$_3$); 70.5 (O*C*H$_2$CH$_2$CH$_3$); 65.6 (*C*2H$_2$, *C*5H$_2$); 62.7 (NCH$_2$*C*H$_2$O); 61.7 (N*C*H$_2$CH$_2$O); 48.6 (N*C*H$_3$); 21.9 (*C*3H$_2$, *C*4H$_2$); 21.3 (OCH$_2$*C*H$_2$CH$_3$); 9.7 (OCH$_2$CH$_2$*C*H$_3$).
Electrospray, MS (+ve): *m/z* 216 (100% - [C_1C_2O(CO)OPrPy]$^+$), MS (-ve): *m/z* 280 (100% - [NTf$_2$]$^-$).

Appendix A

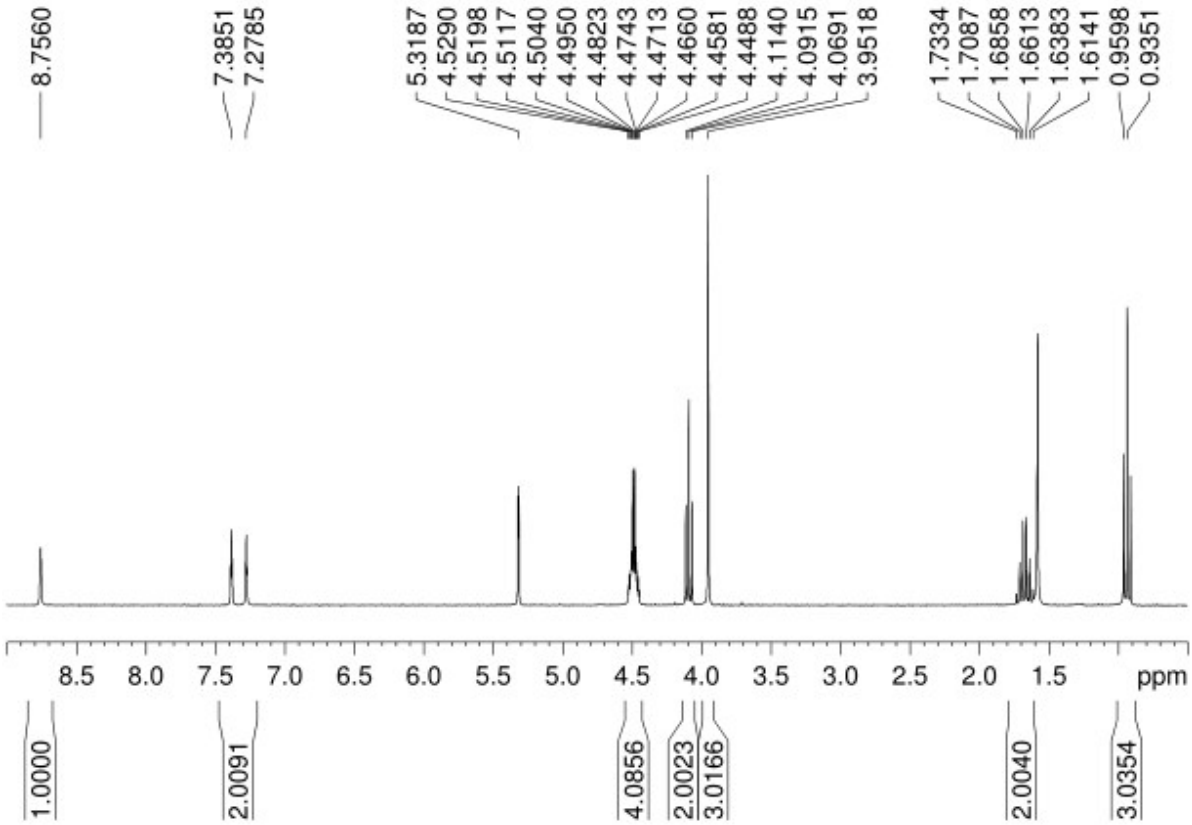


Fig A1 ^{1}H NMR spectra of ionic liquid **4**.

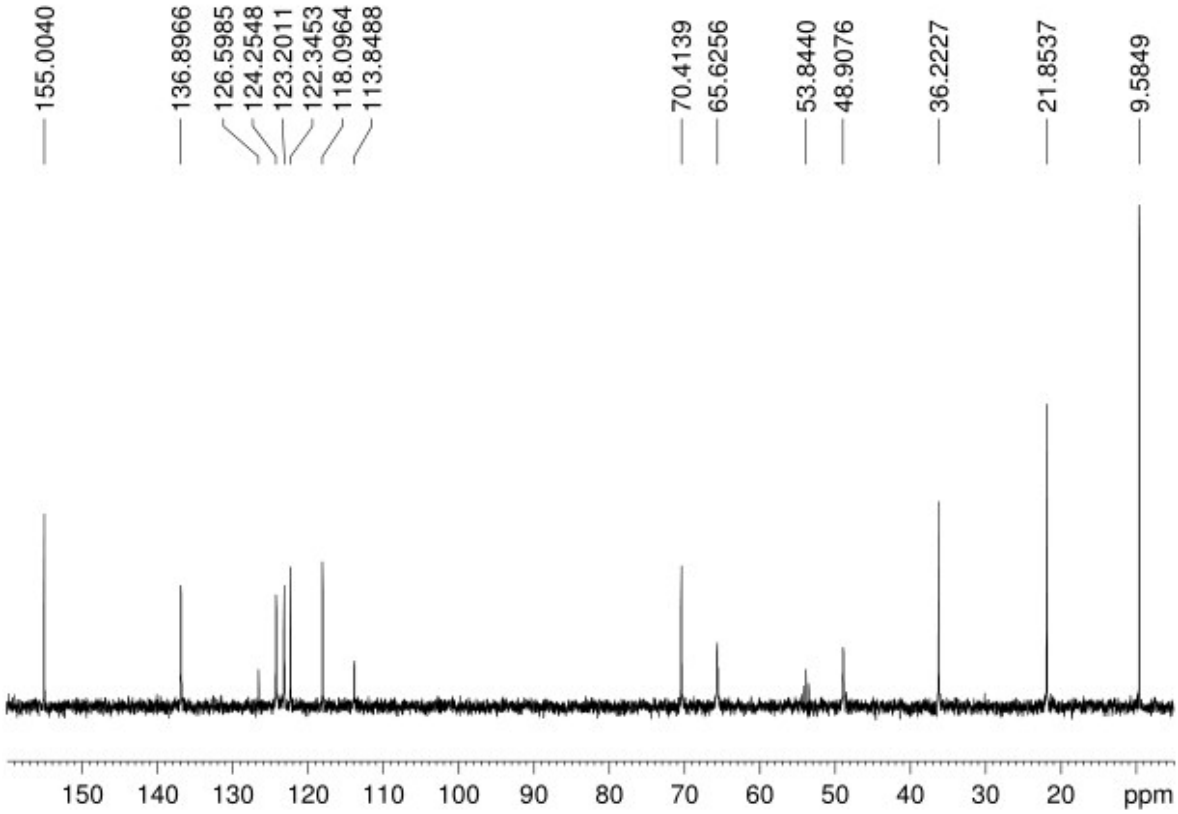


Fig A2 ^{13}C NMR spectra of ionic liquid **4**.

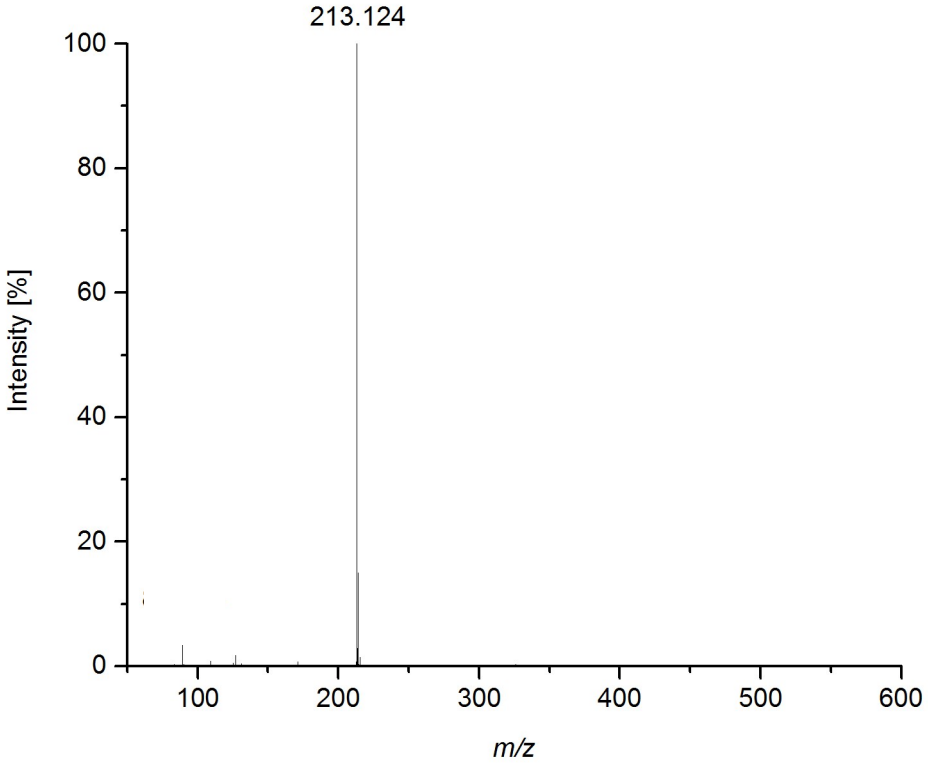


Fig A3 ESI$^+$ spectra of ionic liquid **4**. Chloride cluster $[C1(C_2O(CO)OC_3)Im]_2[Cl]$ peak at *m/z* = 461 is absent.

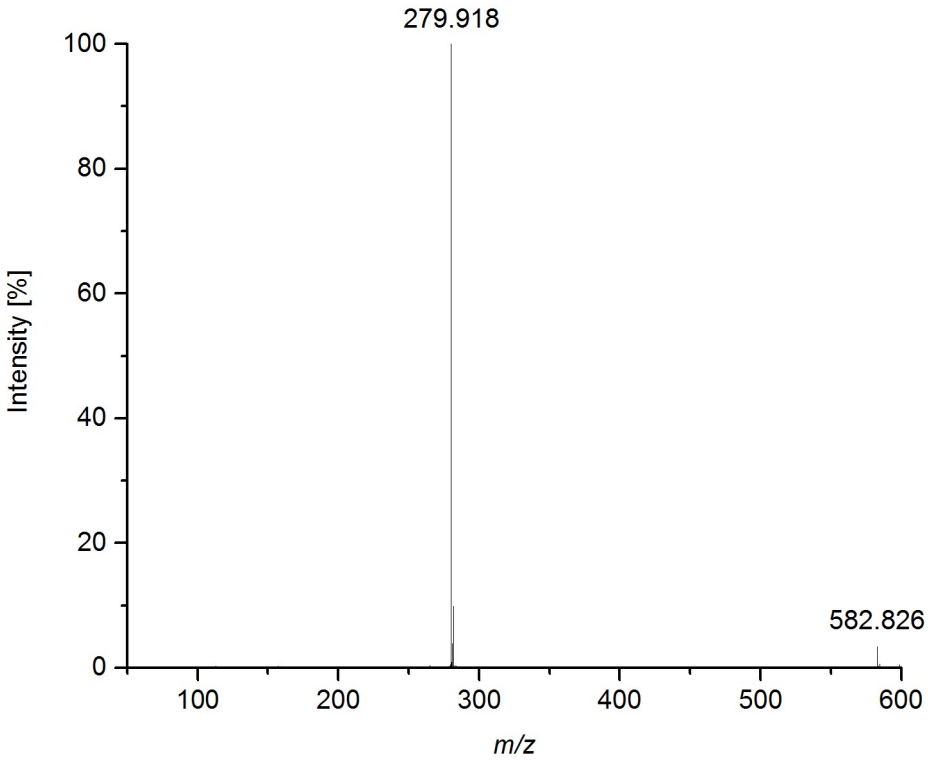


Fig A4 ESI$^-$ spectra of ionic liquid **4**.

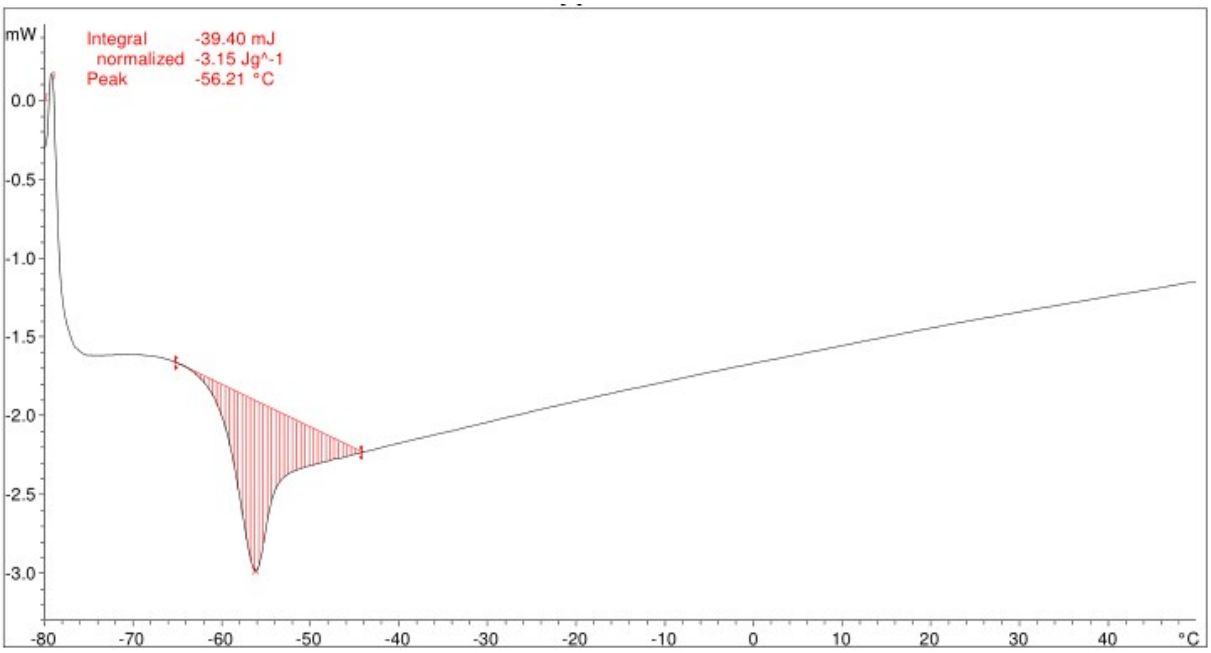


Fig A5 DSC spectra of ionic liquid **4**.

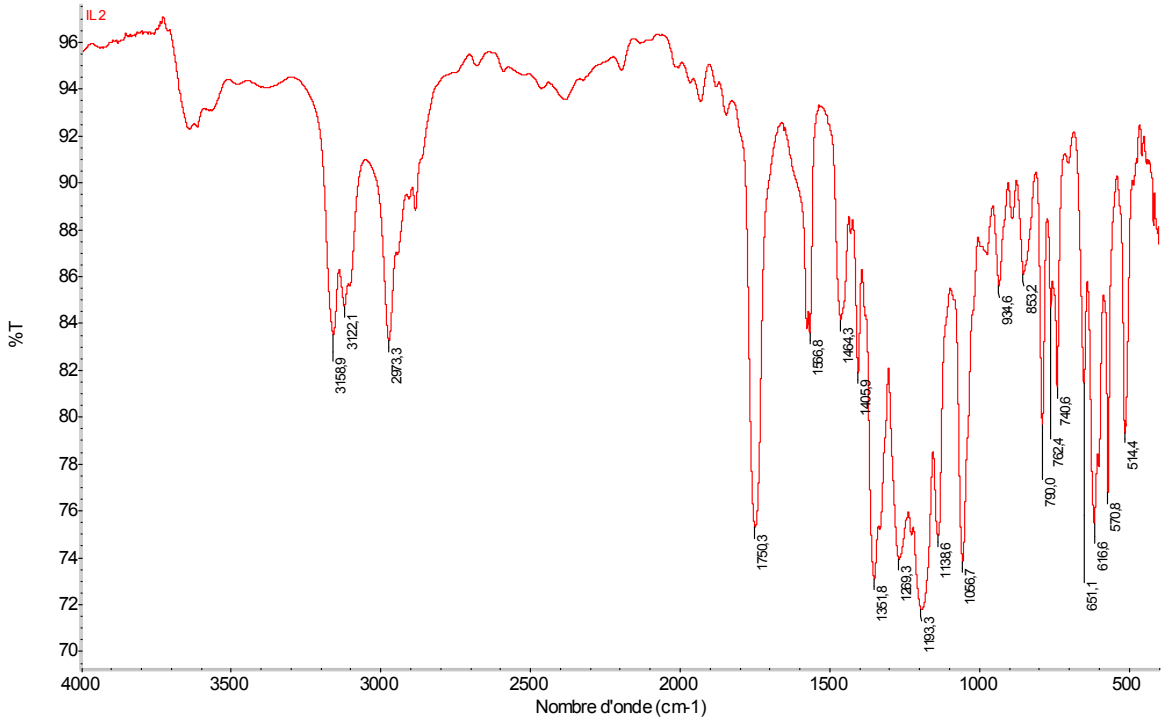
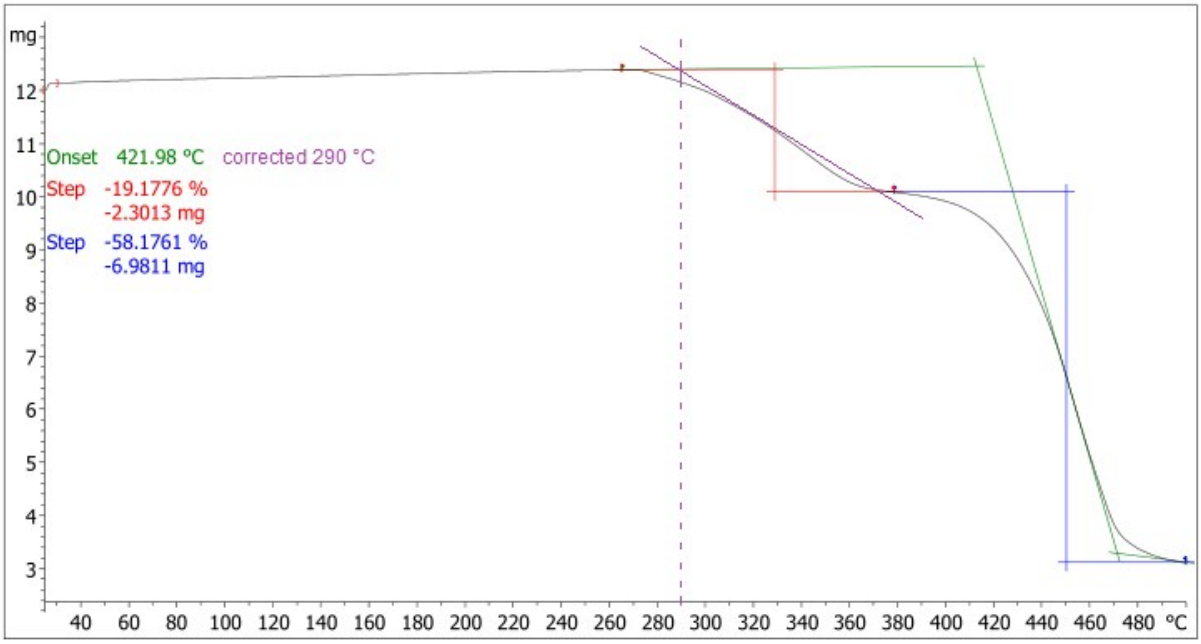
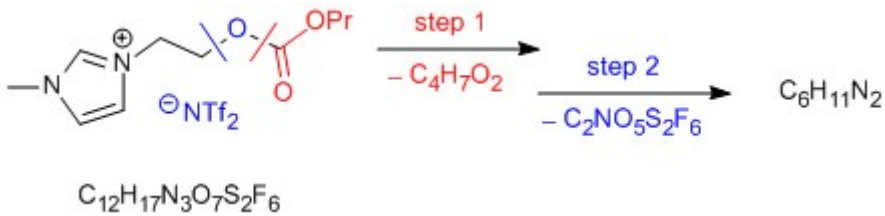


Fig A6 Infrared spectra of IL**4**.





$C_{12}H_{17}N_3O_7S_2F_6$ (**5**)	m_{lost} theoret.	m_{lost} found
Step 1: $C_4H_7O_2$	17.6 %	19.1 %
Step 2: $C_2NO_5S_2F_6$	60.0 %	58.1 %
$\sum m_{lost}$	77.6 %	77.2 %

Fig A7 Thermogram of **IL4** demonstrates onset point, corrected onset point and two steps of decomposition.

Appendix B

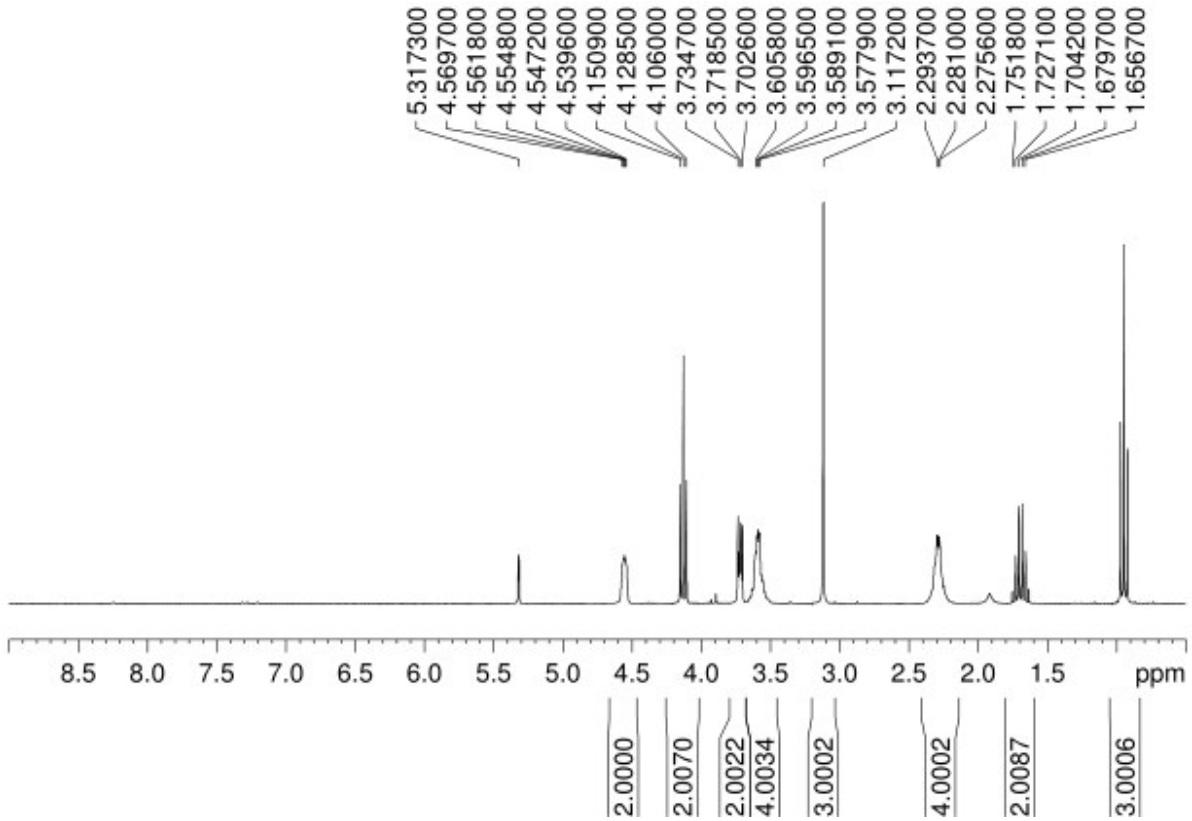


Fig B1. ^{1}H NMR spectra of **IL5**.

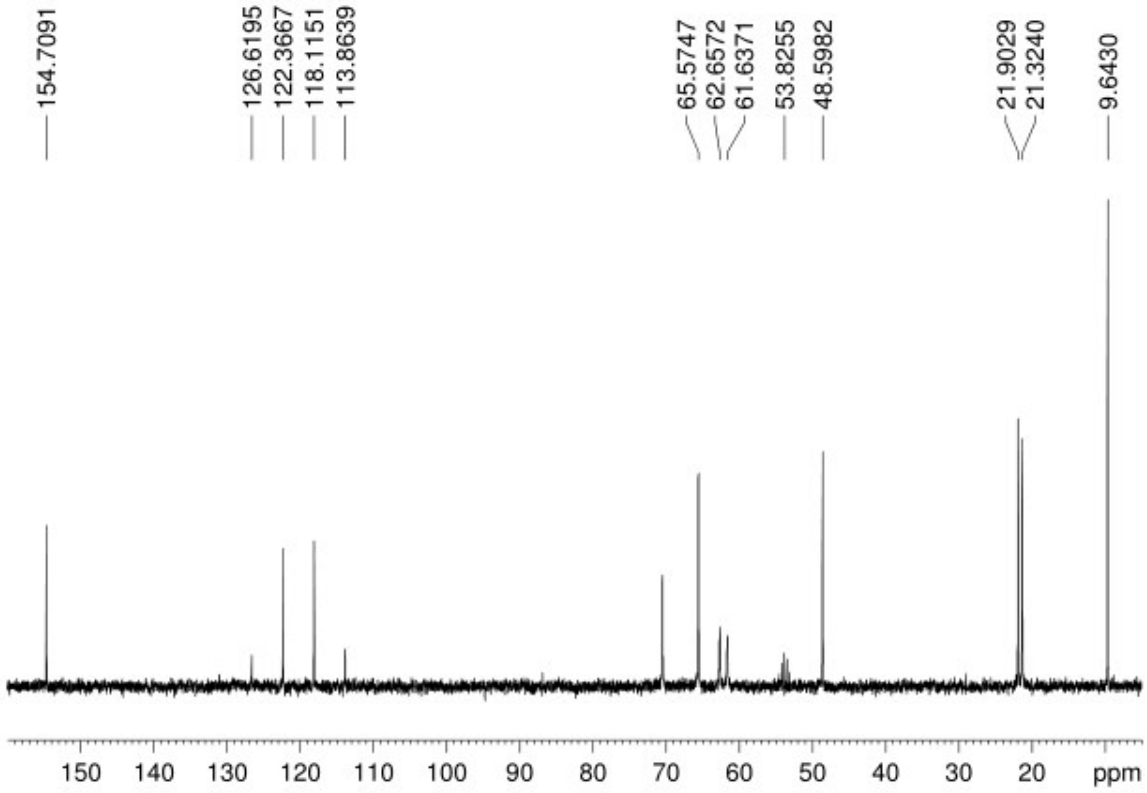


Fig B2. ^{13}C NMR spectra of **IL5**.

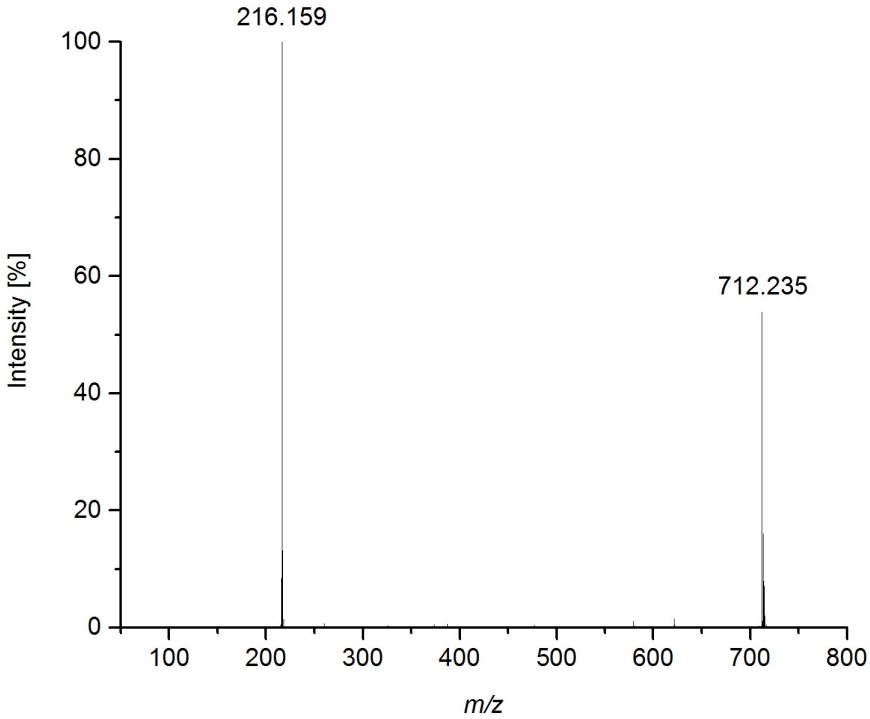


Fig B3. ESI^+ spectra of **IL5**. Chloride cluster $[C_1(C_2O(CO)OC_3)Py]_2[Cl]$ peak at *m/z* = 467 is absent.

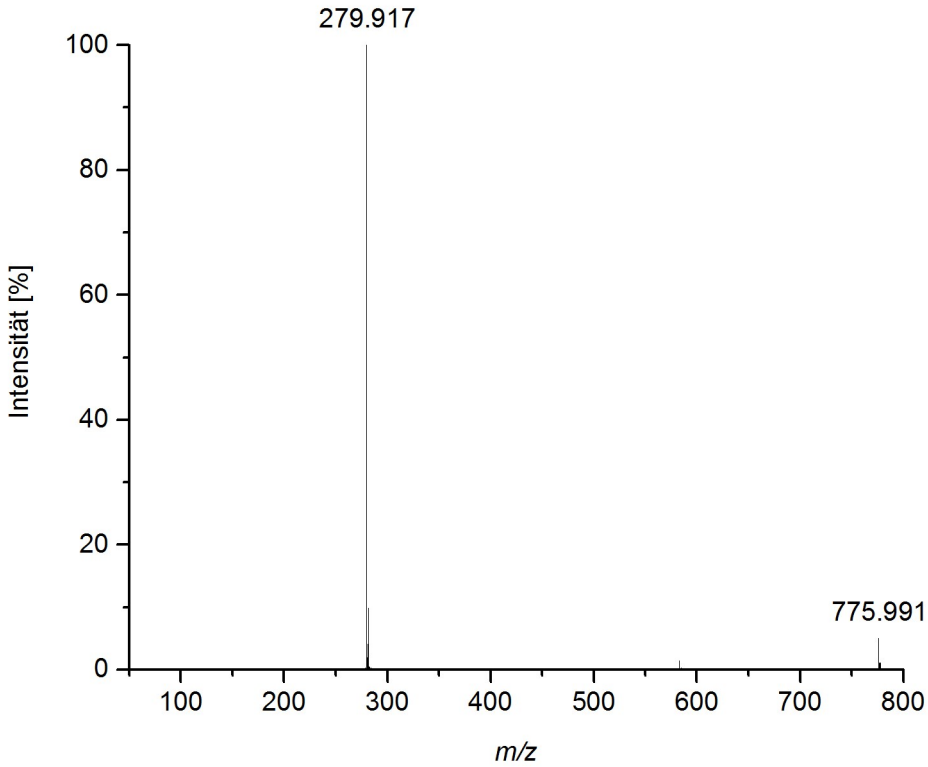


Fig B4 ESI$^-$ spectra of **IL5**.

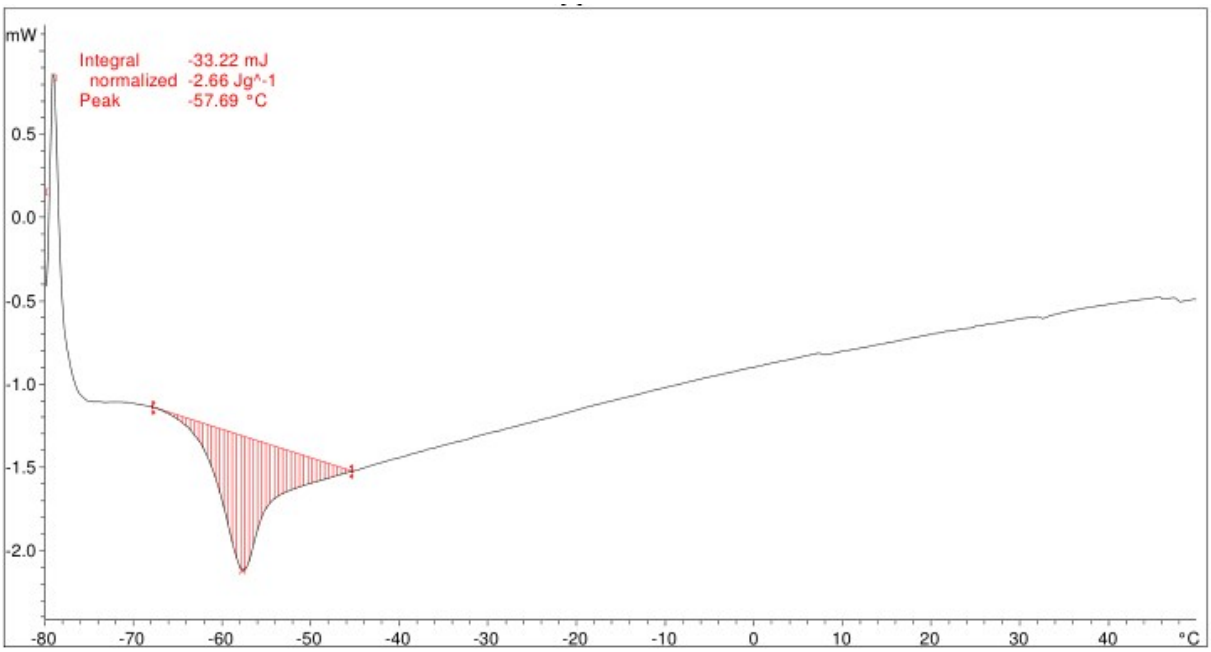


Fig B5 DSC spectra of **IL5**.

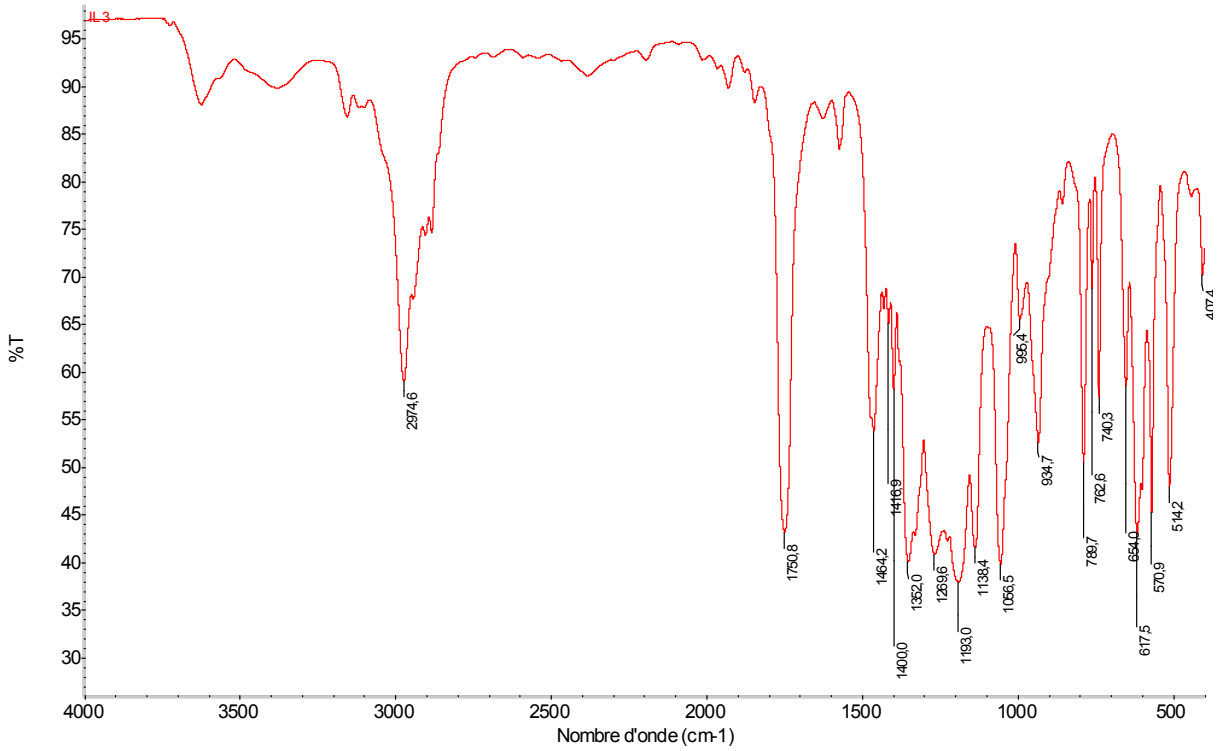
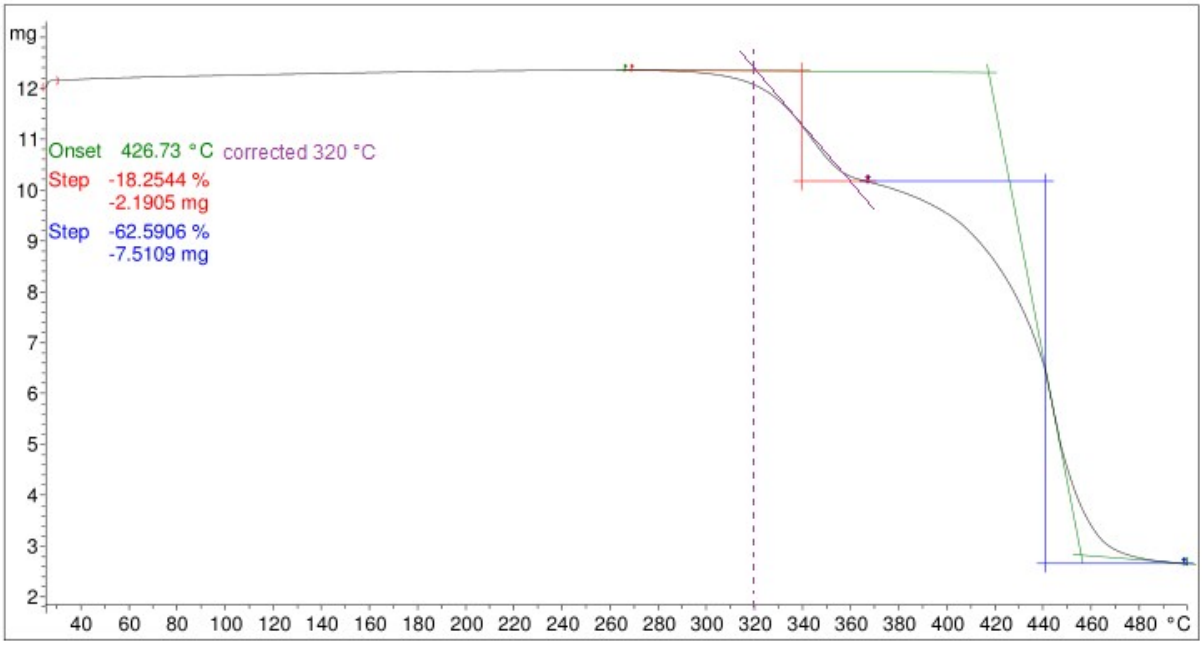
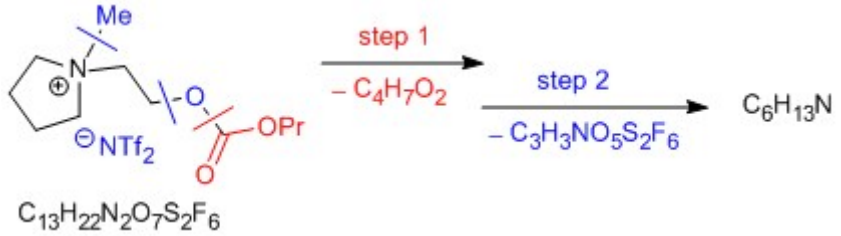


Fig B6 Infrared spectra of **IL5**.





$C_{13}H_{22}N_2O_7S_2F_6$ (**5**)	m_{lost} theoret.	m_{lost} found
Step 1: $C_4H_7O_2$	17.5 %	18.3 %
Step 2: $C_3H_3NO_5S_2F_6$	62.7 %	62.6 %
$\sum m_{lost}$	80.2 %	80.9 %

Fig B7 Thermogram of **IL5** demonstrates onset point, corrected onset point and two steps of decomposition.

Appendix C

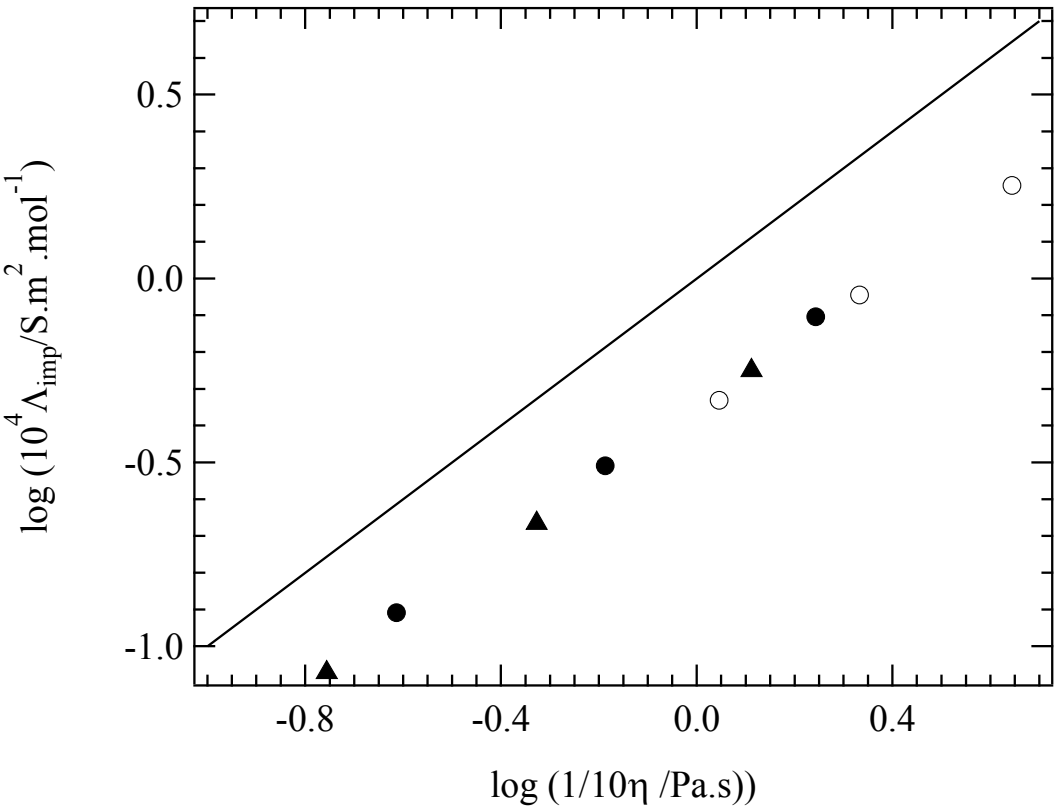


Fig C1 Walden plots of **IL4** (ꕥ), **IL5** (□) and $[C_8C_1ImNTf_2]$[1] (ꕥ) as a function of temperature from 298K to 333K. Black line, reference line (KCl, 0.01 M).

References

1. H. Tokuda, S. Tsuzuki, M. A. B. H. Susan, K. Hayamizu and M. Watanabe, *J. Phys. Chem. B*, 2006, **110**, 19593-19600.