Supporting information

Water free metathesis reaction: a route to ionic liquids

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Experimental

We worked at the melting point of the halide salts. All the ionic liquids were synthesised following this experimental procedure: 1-butyl-3-methylImidazolium chloride heated gently at 70°C. Then the salt of lithium or sodium of each anion were added under argon and stirred for 24h. The resultant product was dissolved in THF or CH_2Cl_2 (based on the nature of the anion) and stirred for 20 min to precipitate the resulting salt which was filtered off (0.2µm filter). The resulting filtrate was placed in the fridge (-5°C) for one night for complete precipitation of the salt, in case of salt precipitation another filtration was performed and the resulting filtrate evaporated to dryness.

RK: N-butyl-N-metylpyrrolidinium chloride and tetrabutylphosponium bromide melts at 120°C. THF used for dicyanamide anion while CH_2Cl_2 was used for the other anions.

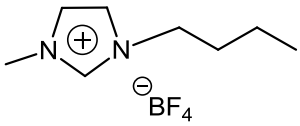
The possible presence of residual Cl^- was examined via inspection of the appreciate mass regions of the respective mass spectra. In case of ionic liquids based on: $(C_1C_4Im)^+$ the chloride peak appears at m/z=313, $(C_1C_6Im)^+$ at m/z=369, $(C_1C_8Im)^+$ at m/z=425, $(P_{14})^+$ at m/z= 319 and $(P_{4444})^+$ at m/z= 553.5.

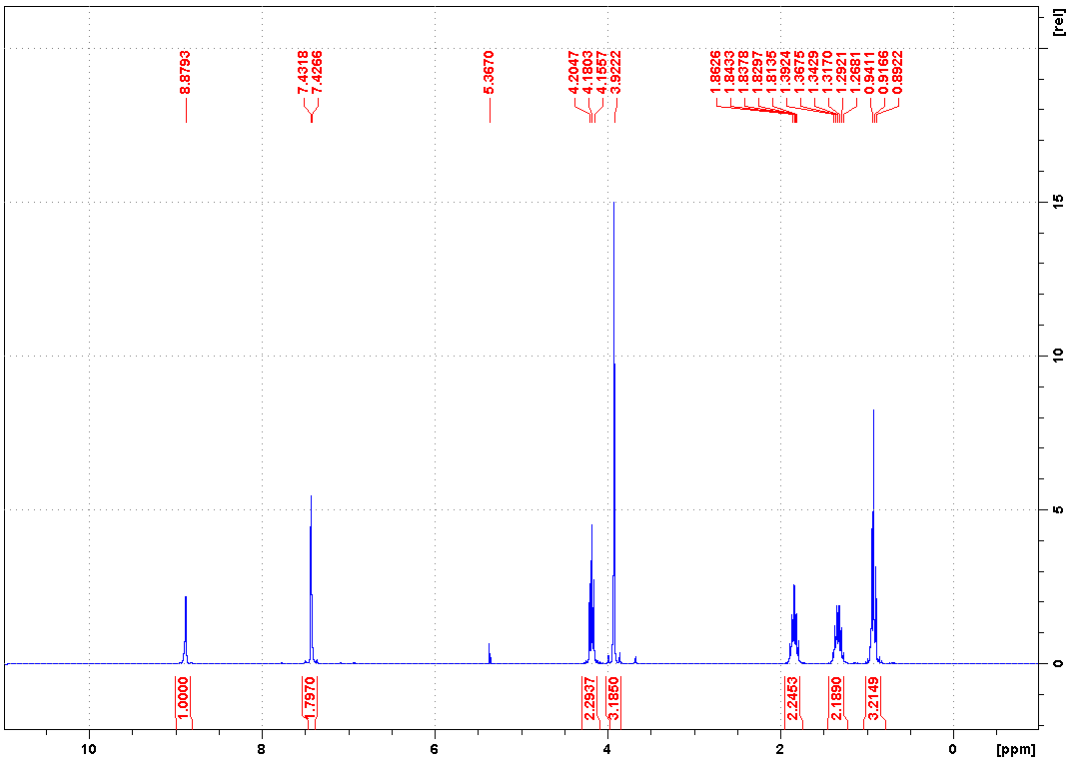
NMR spectroscopy and ESI-MS analysis

NMR spectra were recorded on BRUKER AVANCE 300 spectrometer (^1H: 300.1 MHz, ^{13}C: 75.4, ^{11}B: 96.2 MHz, ^{19}F:282.2 MHz and ^{31}P 121.4 MHz). Deuterated solvents (CD_2Cl_2, D_2O and d6-DMSO) were used as internal standards. The chemical shift are noted in parts per million (ppm), the coupling constant in Hz.

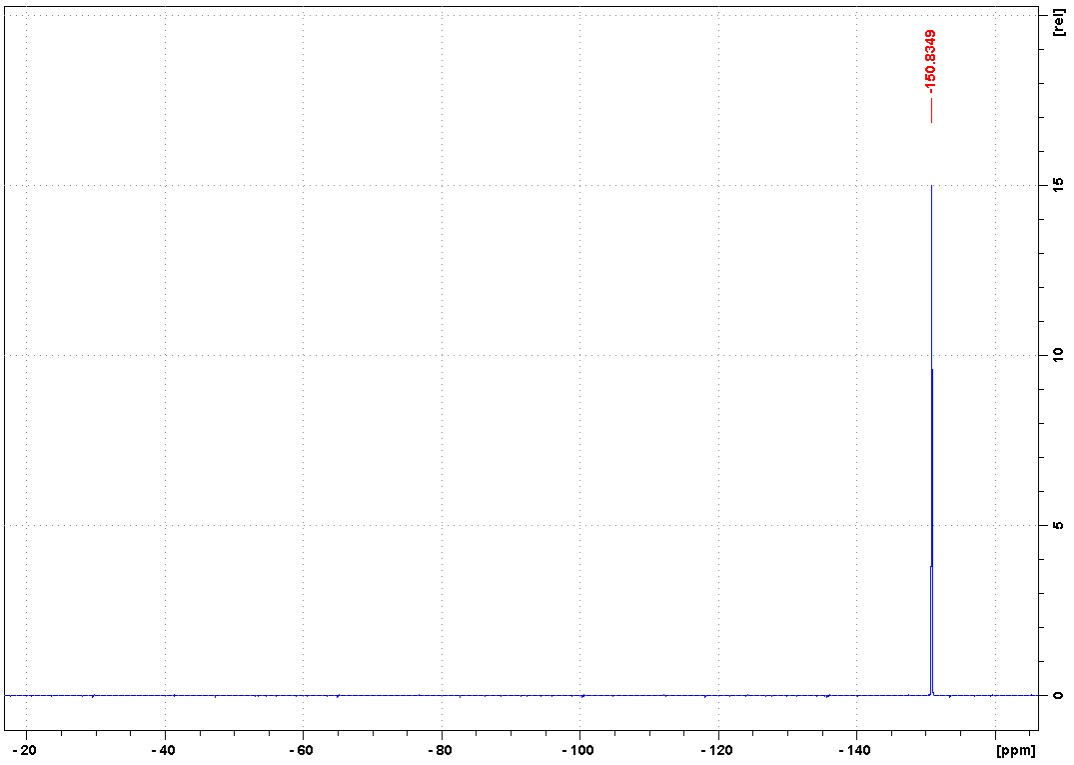
The high resolution mass spectra were recorded in a positive and negative ion mode on a hybrid quadrupole time-of-flight mass spectrometer (MicroTOFQ-II, Bruker Daltonics, Bremen) with an Electrospray Ionization (ESI) ion source. The gas flow of spray gas is 0.6bar and the capillary voltage is +/-4.5kV. The solutions are infused at 180µL/h. The mass range of the analysis is 50-1000m/z and the calibration was done with sodium formate.

1-butyl-3-methylImidazolium tetrafluoroborate: $[C_1C_4Im][BF_4]$

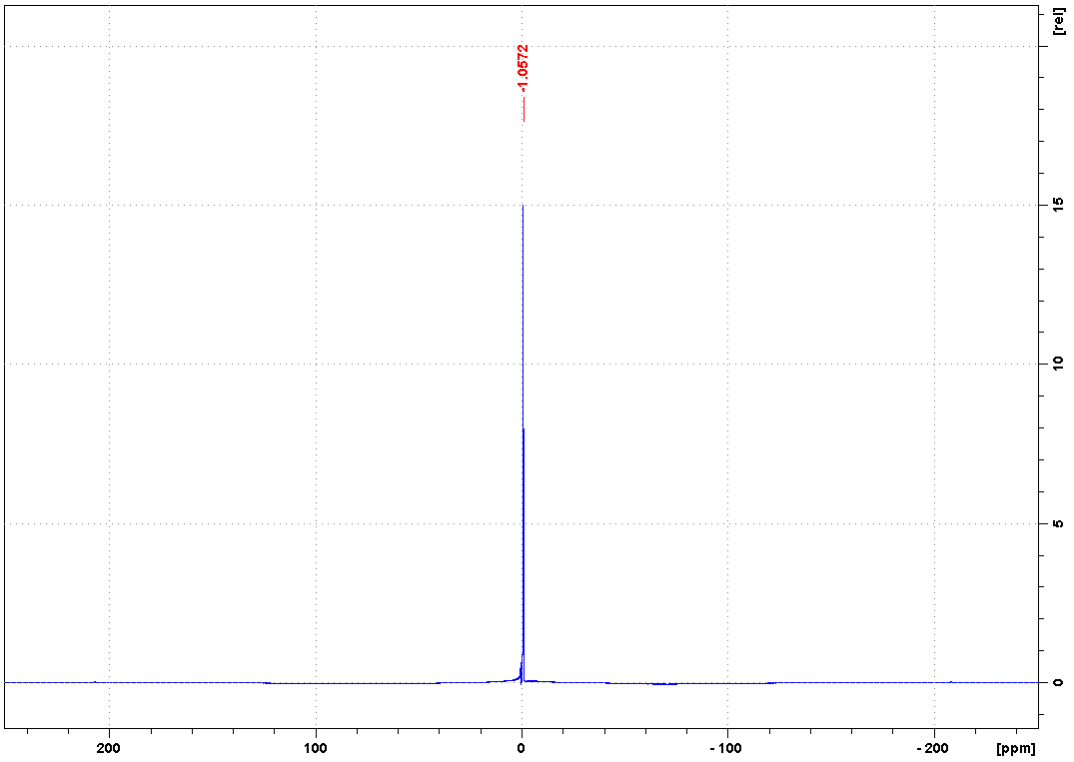




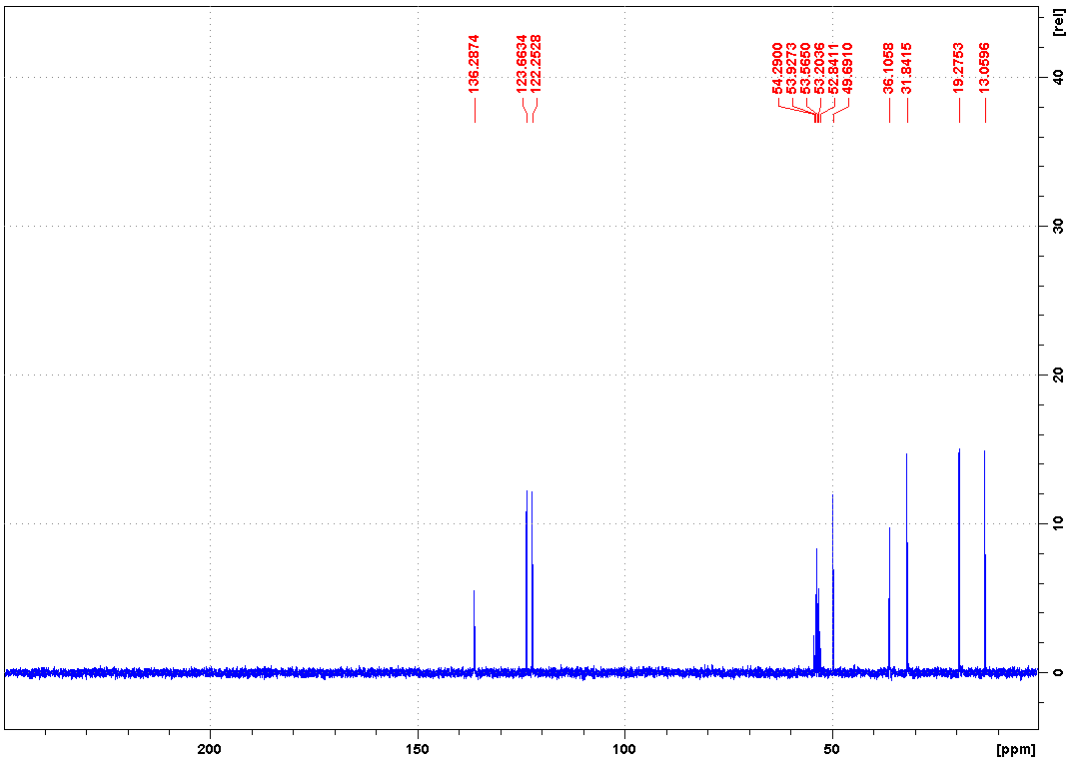
^{1}H NMR in CD_2Cl_2



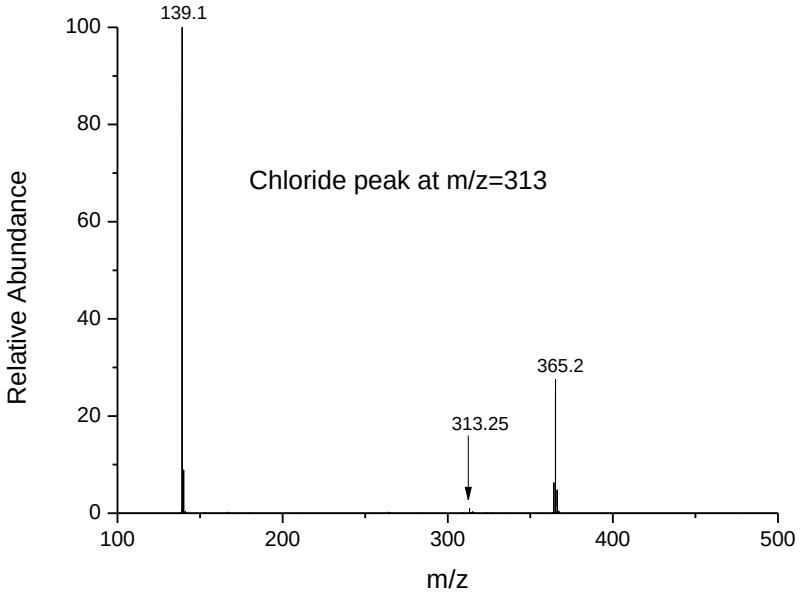
^{19}F NMR in CD_2Cl_2



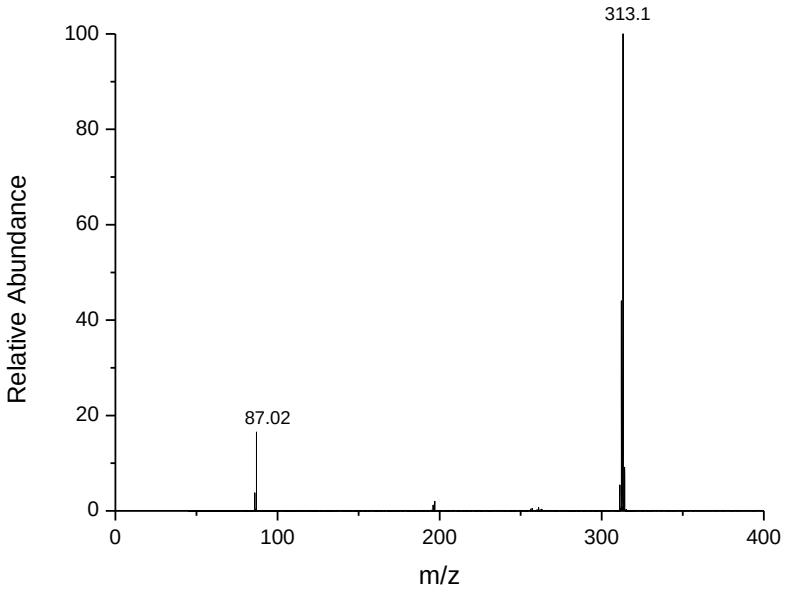
^{11}B NMR in CD_2Cl_2



^{13}C NMR in CD_2Cl_2



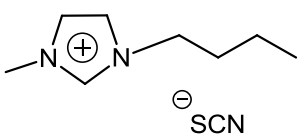
ESI$^+$ mass spectrum

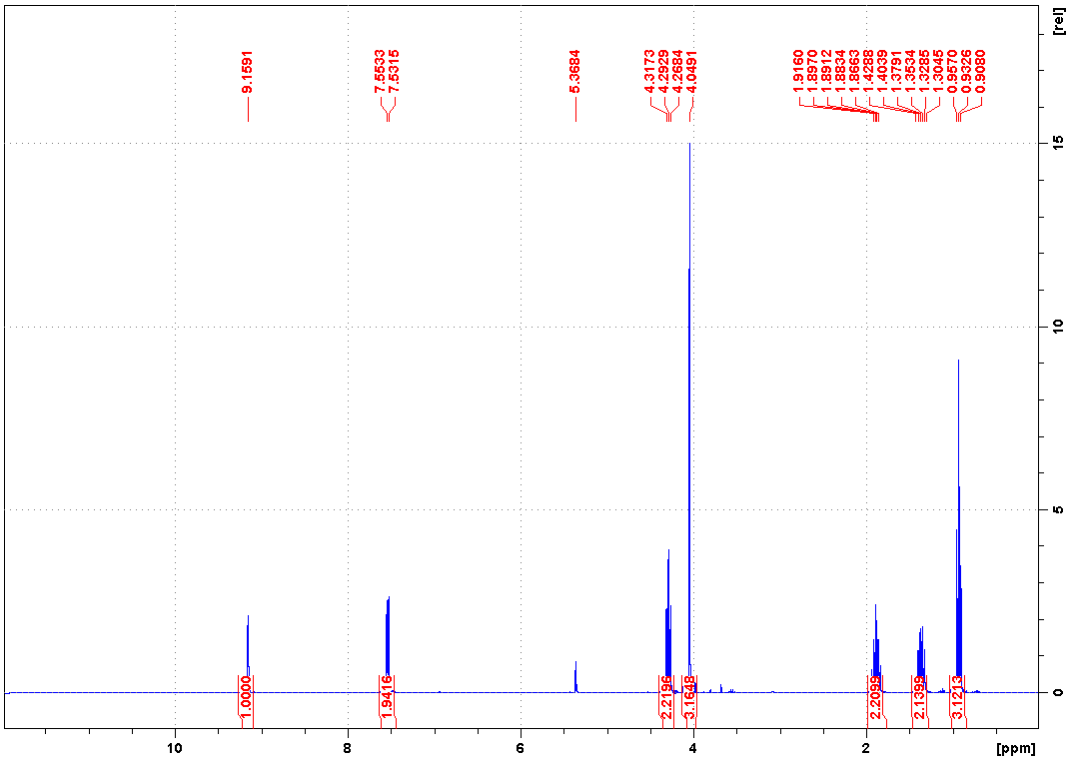


ESI$^-$ mass spectrum

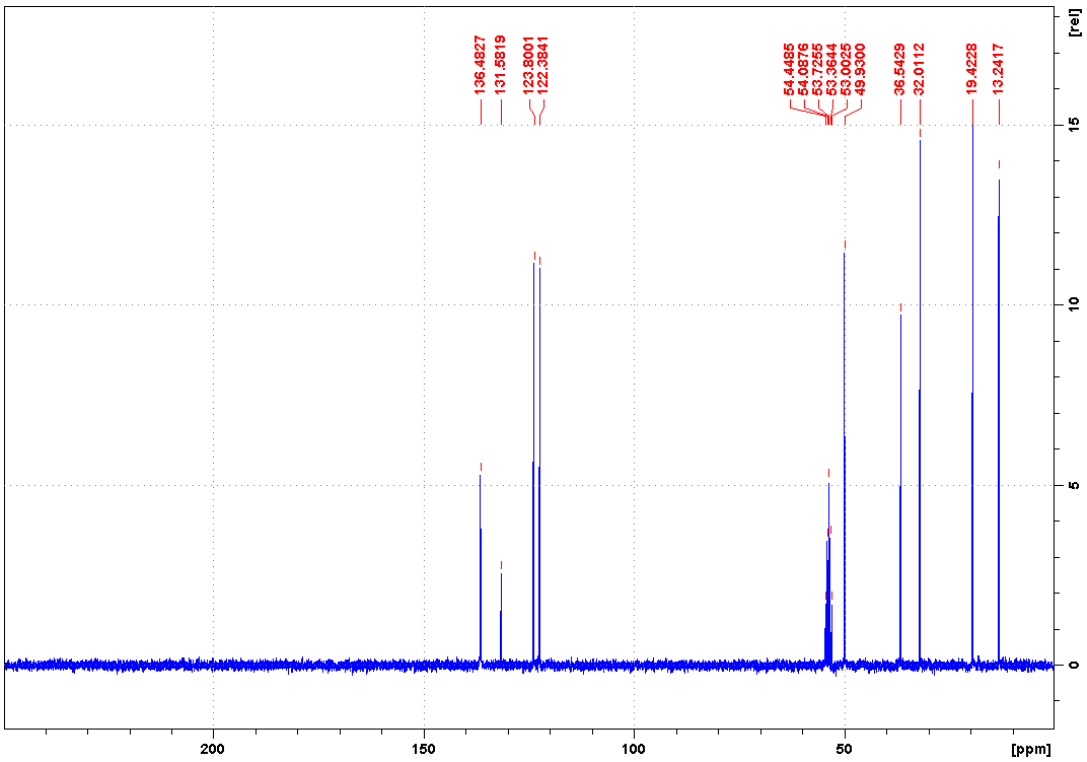
	Entire	Cation	Anion
Mass calculated	226.1	139.1	87.0

1-butyl-3-methylImidazolium thiocyanate : [C_1C_4Im][SCN]

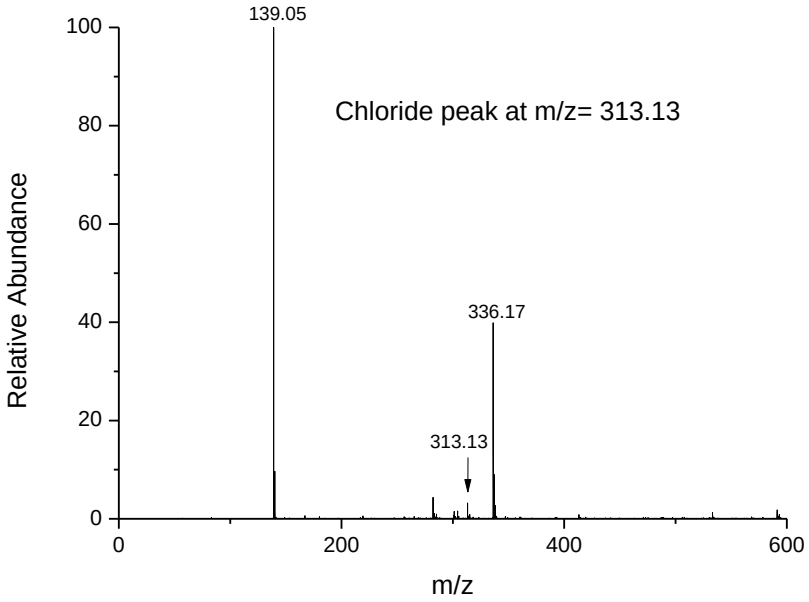




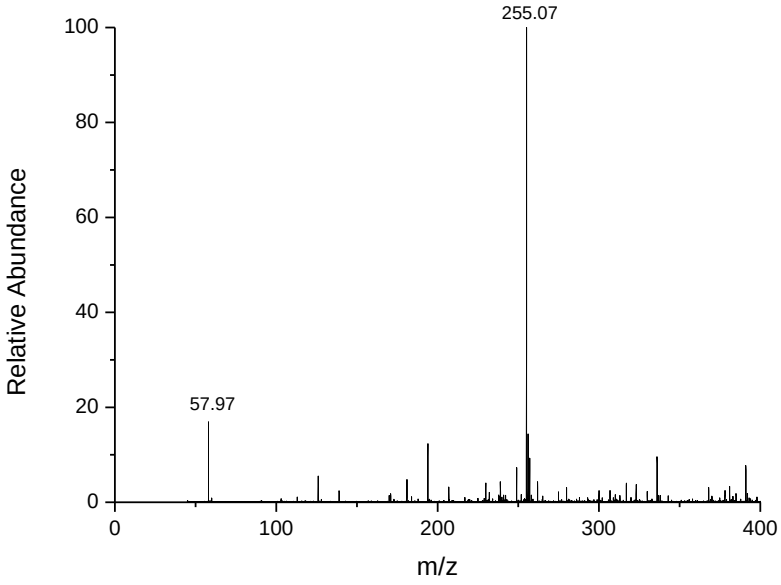
^{1}H NMR in CD_2Cl_2



^{13}C NMR in CD_2Cl_2



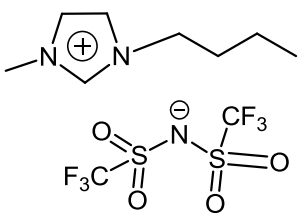
ESI$^+$ mass spectrum

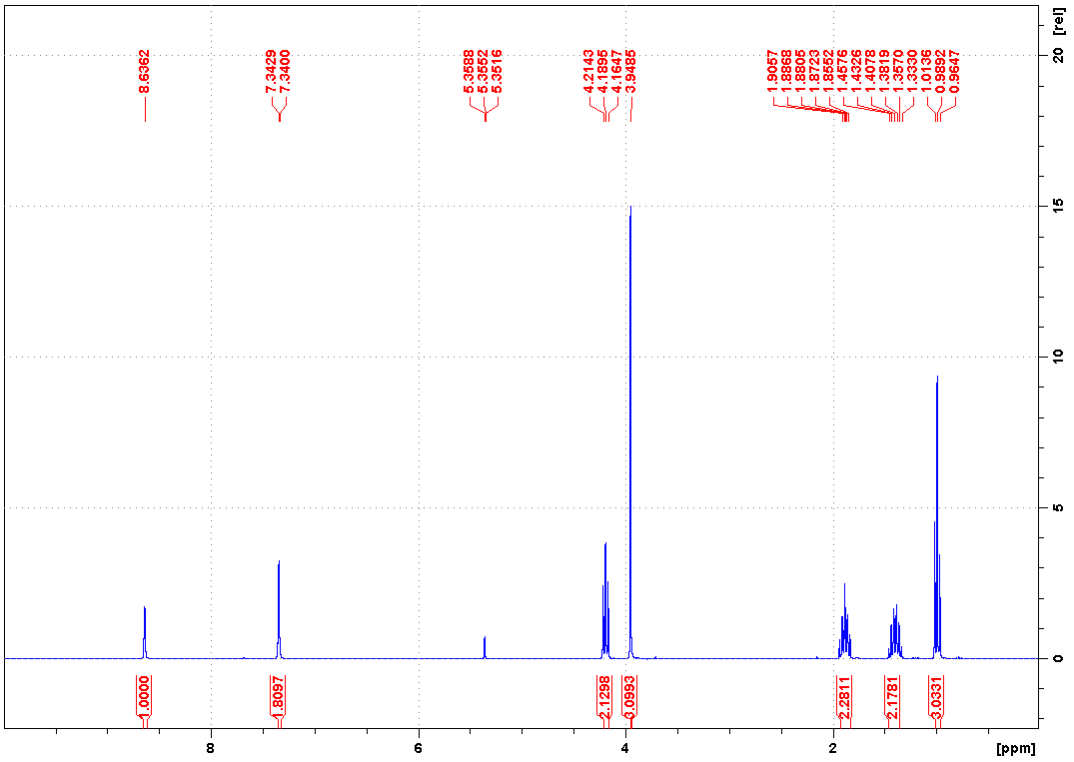


ESI$^-$ mass spectrum

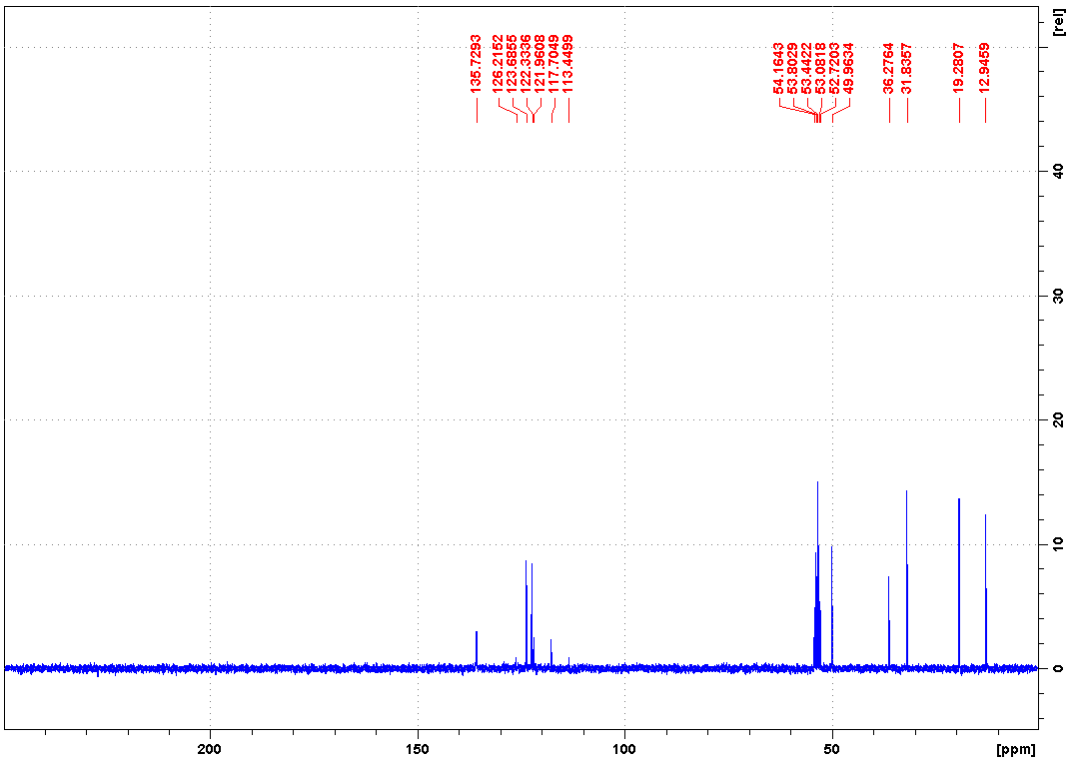
	Entire	Cation	Anion
Mass calculated	197.1	139.1	57.9

1-butyl-3-methylImidazolium bis(trifluoromethylsulfonyl)imide: [C_1C_4Im][NTf_2]

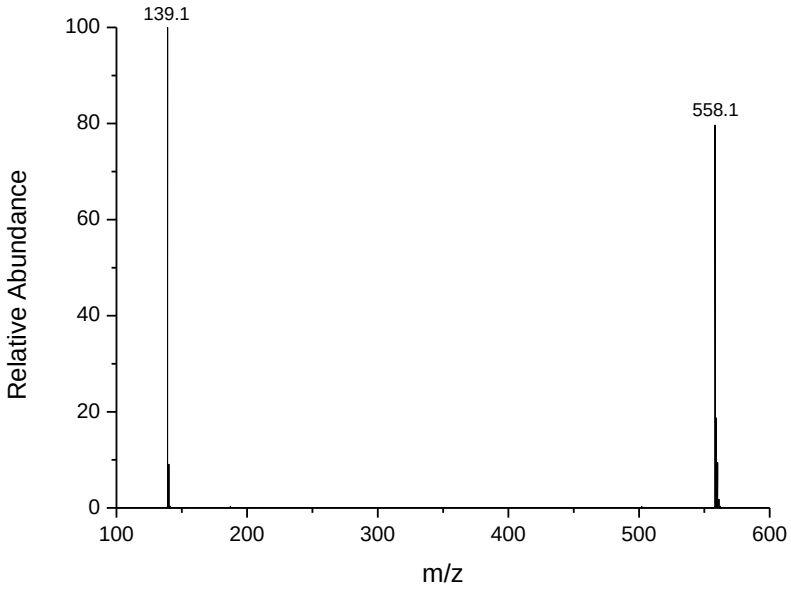




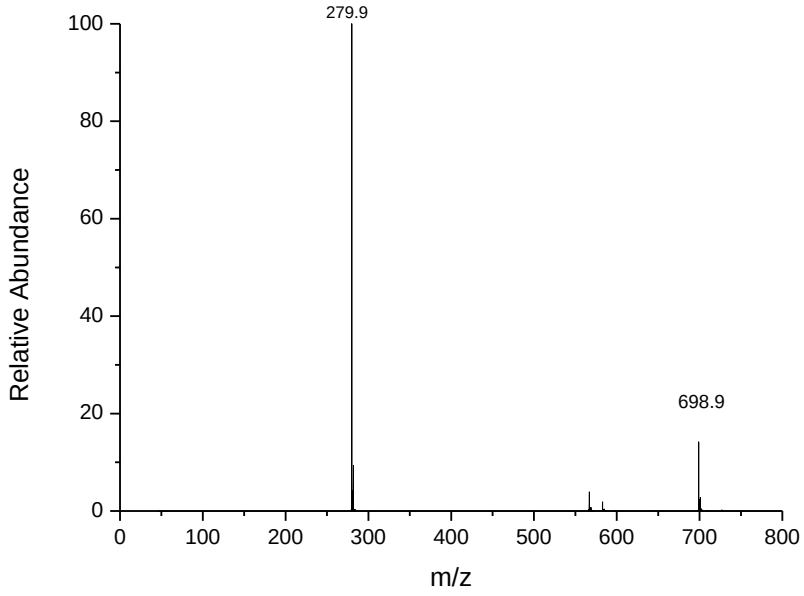
^{1}H NMR in CD_2Cl_2



^{13}C NMR in CD_2Cl_2



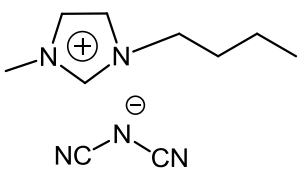
ESI$^+$ mass spectrum

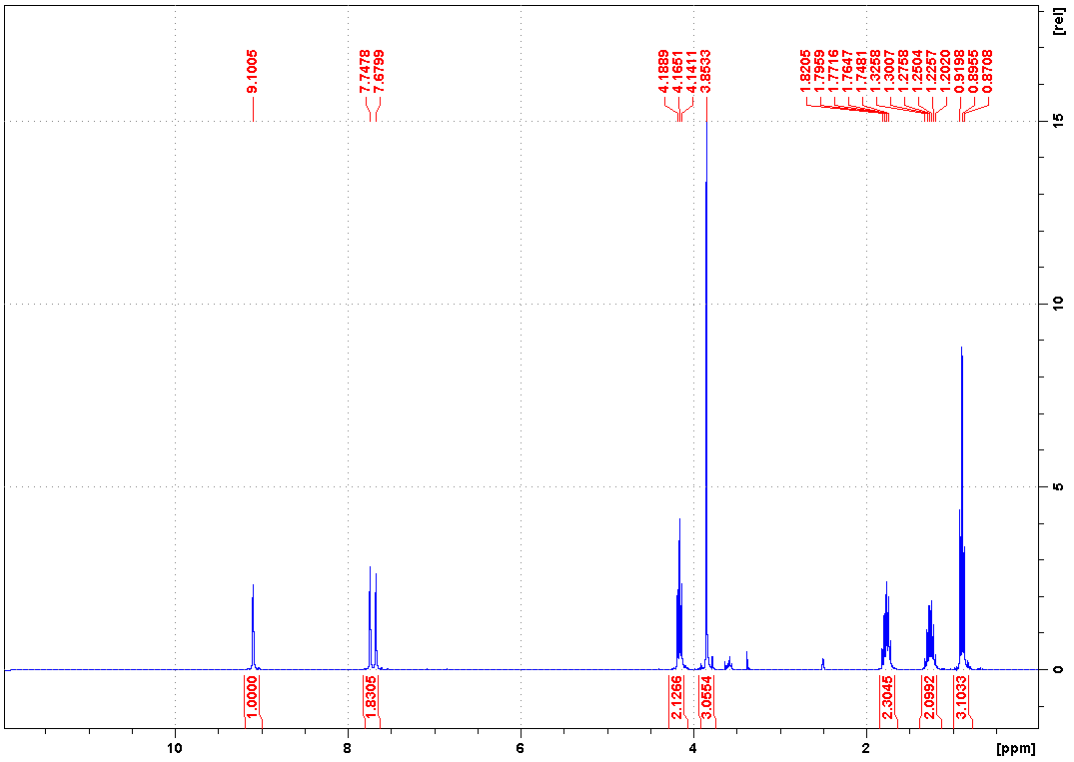


ESI$^-$ mass spectrum

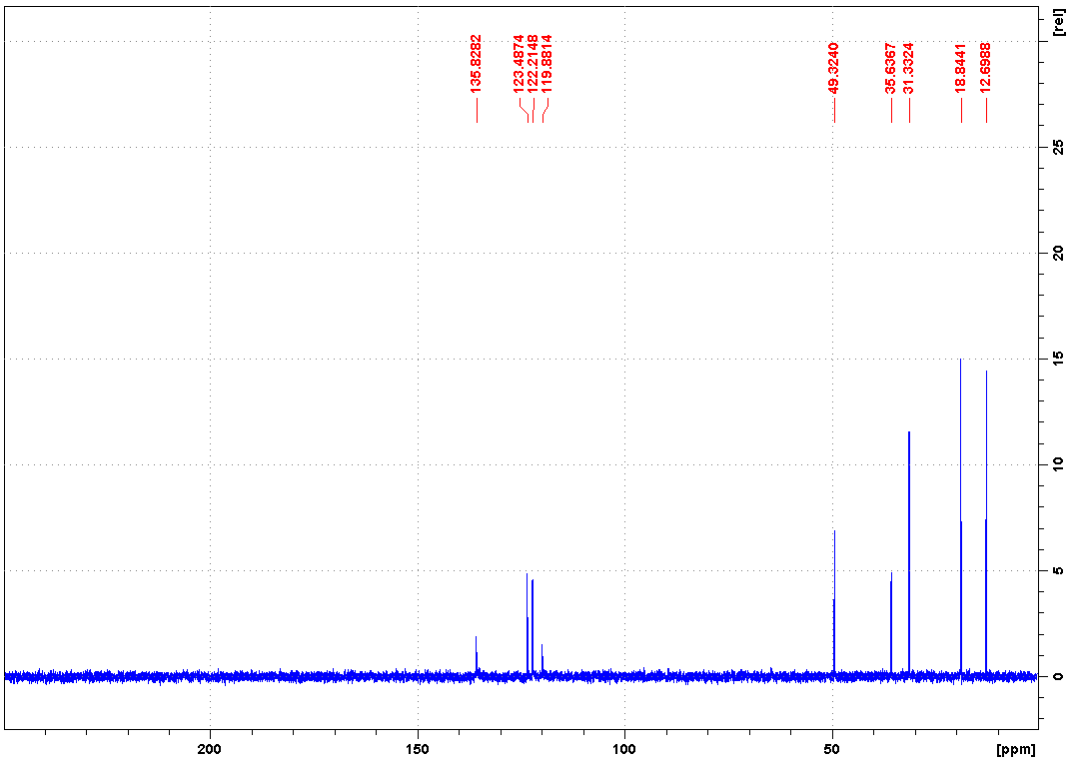
	Entire	Cation	Anion
Mass calculated	419.0	139.1	279.9

1-butyl-3-methylImidazolium dicyanamide: [C_1C_4Im][$N(CN)_2$]

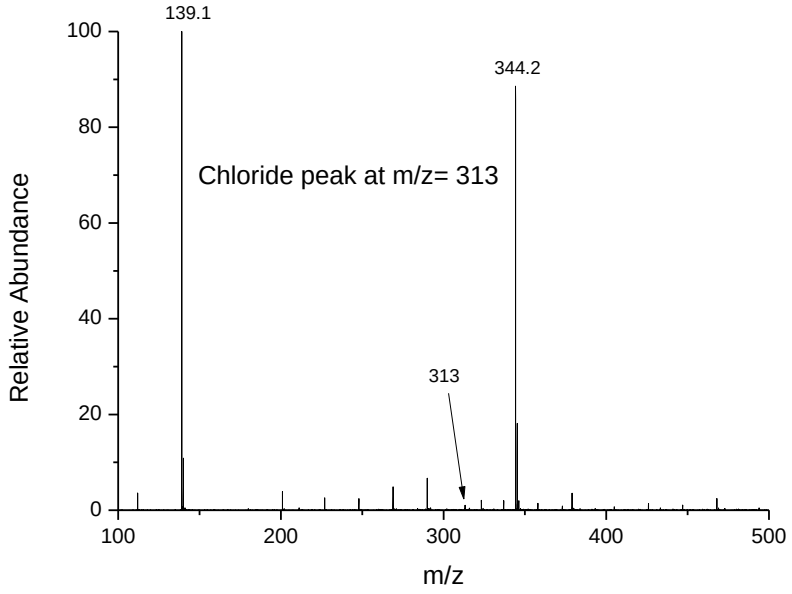




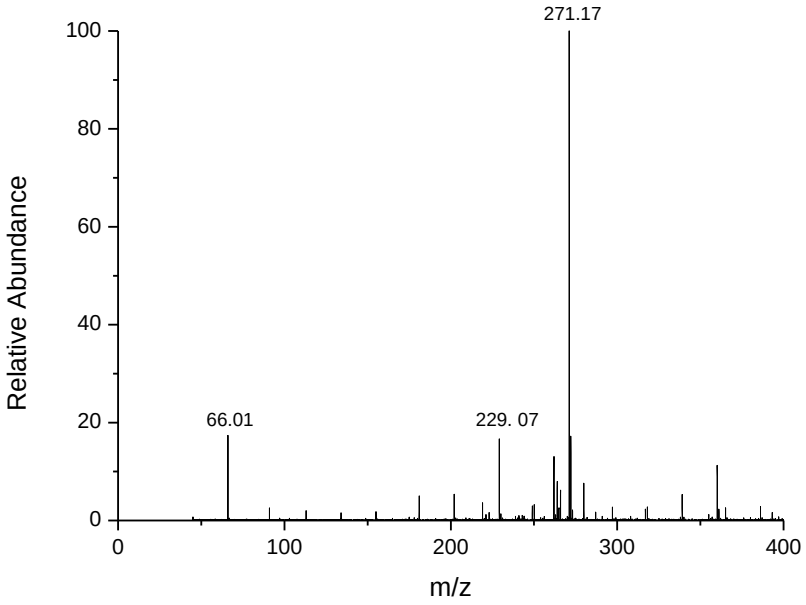
^{1}H NMR in d6-DMSO



^{13}C NMR in d6-DMSO



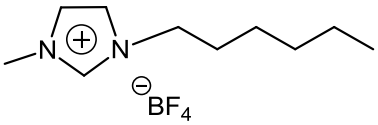
ESI$^-$ mass spectrum

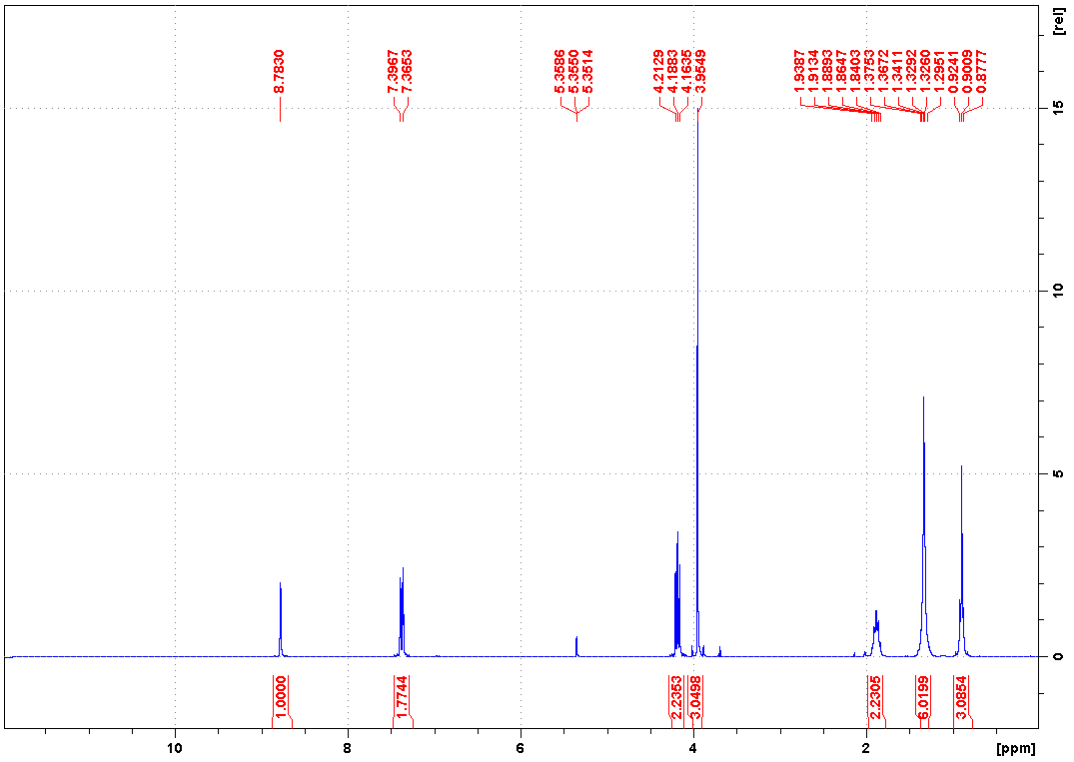


ESI$^-$ mass spectrum

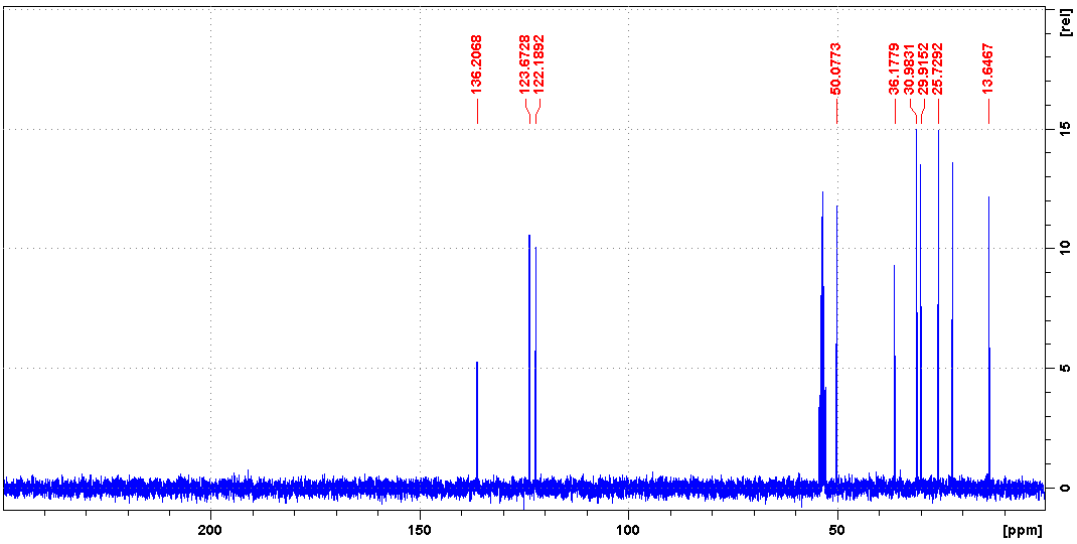
	Entire	Cation	Anion
Mass calculated	205.1	139.1	66.0

1-hexyl-3-methylimidazolium tetrafluoroborate: [C_1C_6Im][BF_4]

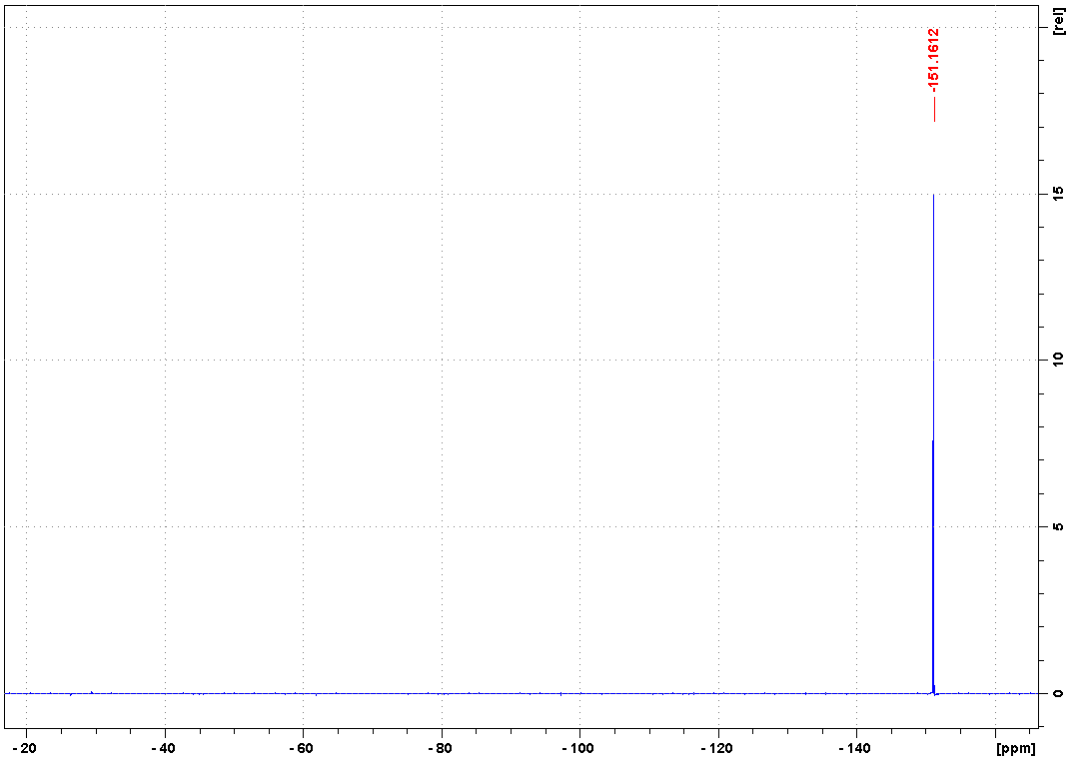




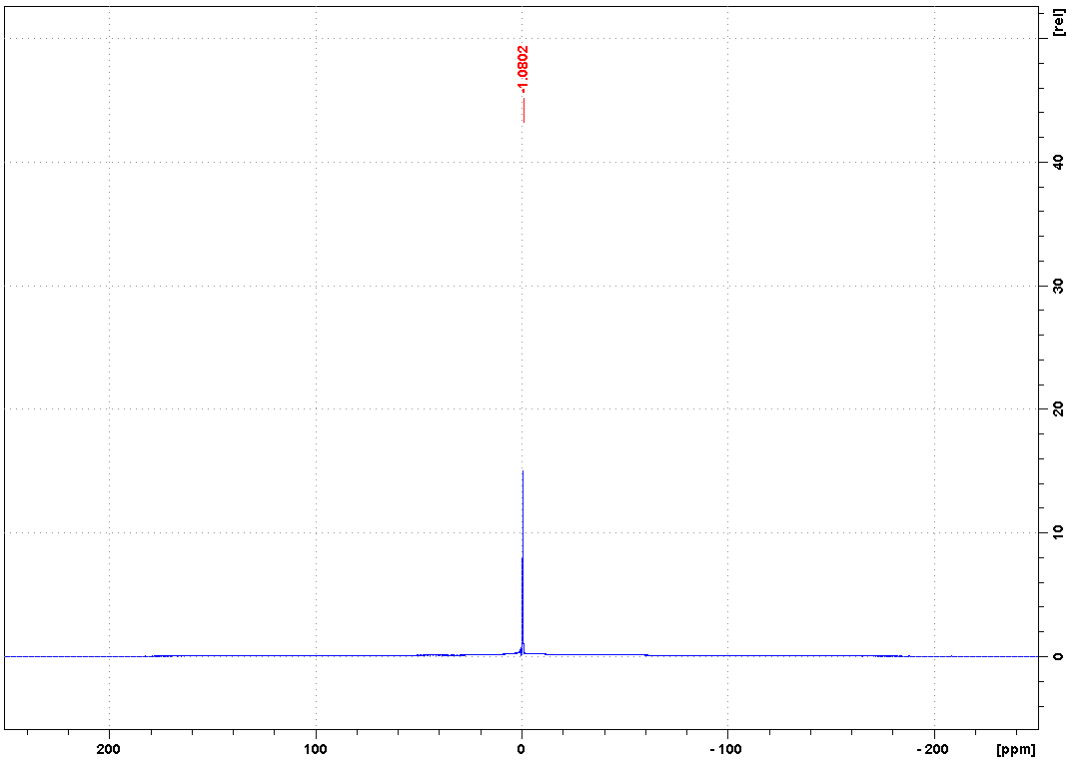
^{1}H NMR in CD_2Cl_2



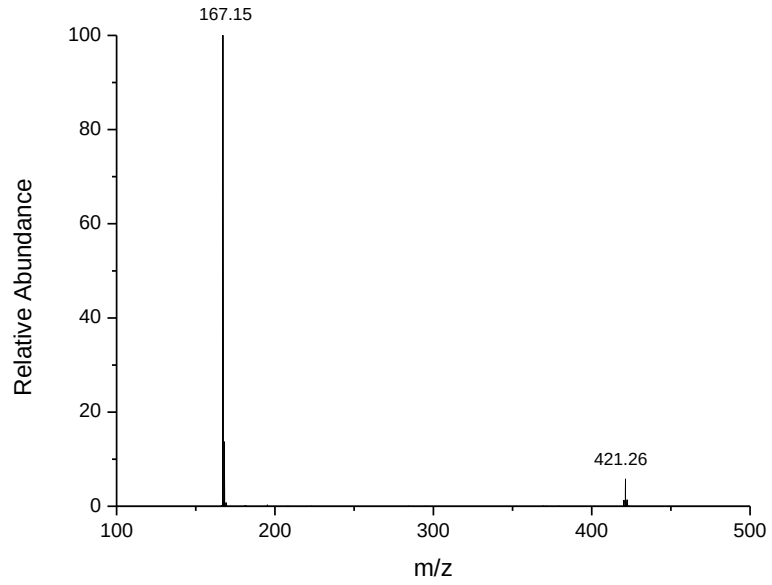
^{13}C NMR in CD_2Cl_2



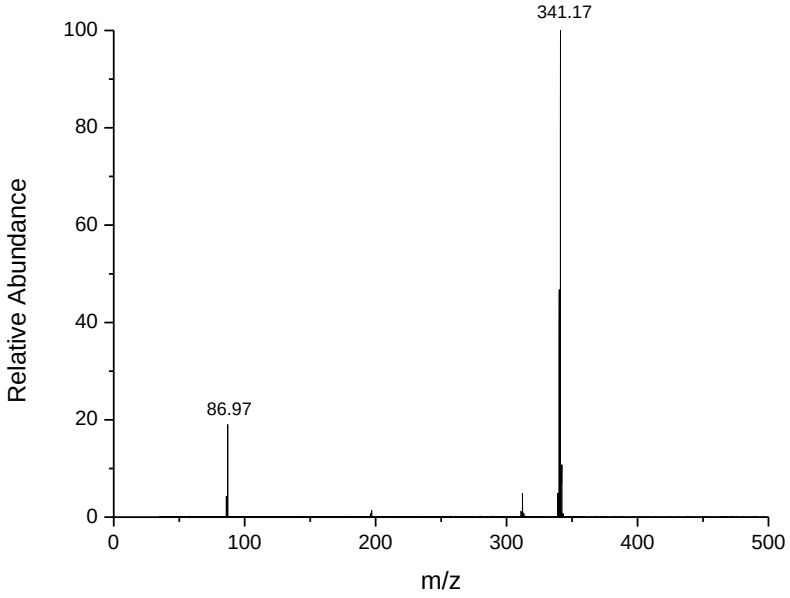
^{19}F NMR in CD_2Cl_2



^{11}B NMR in CD_2Cl_2



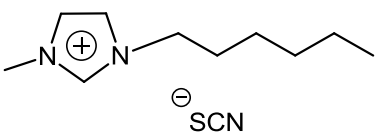
ESI$^+$ mass spectrum

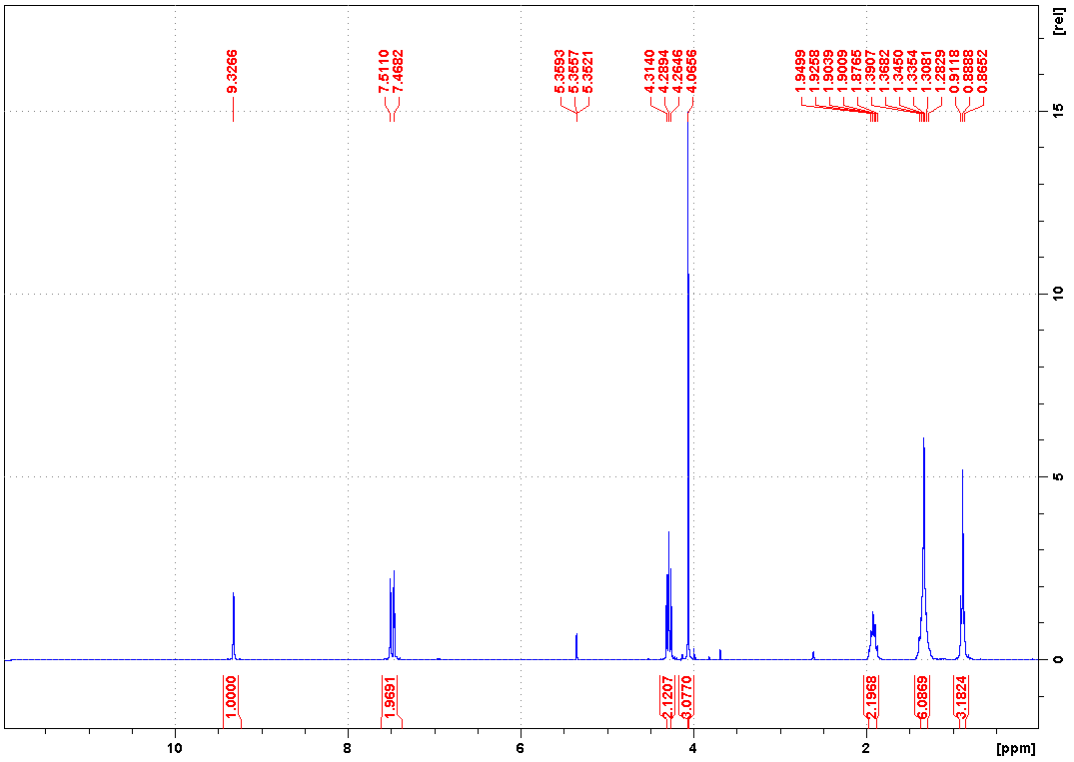


ESI$^-$ mass spectrum

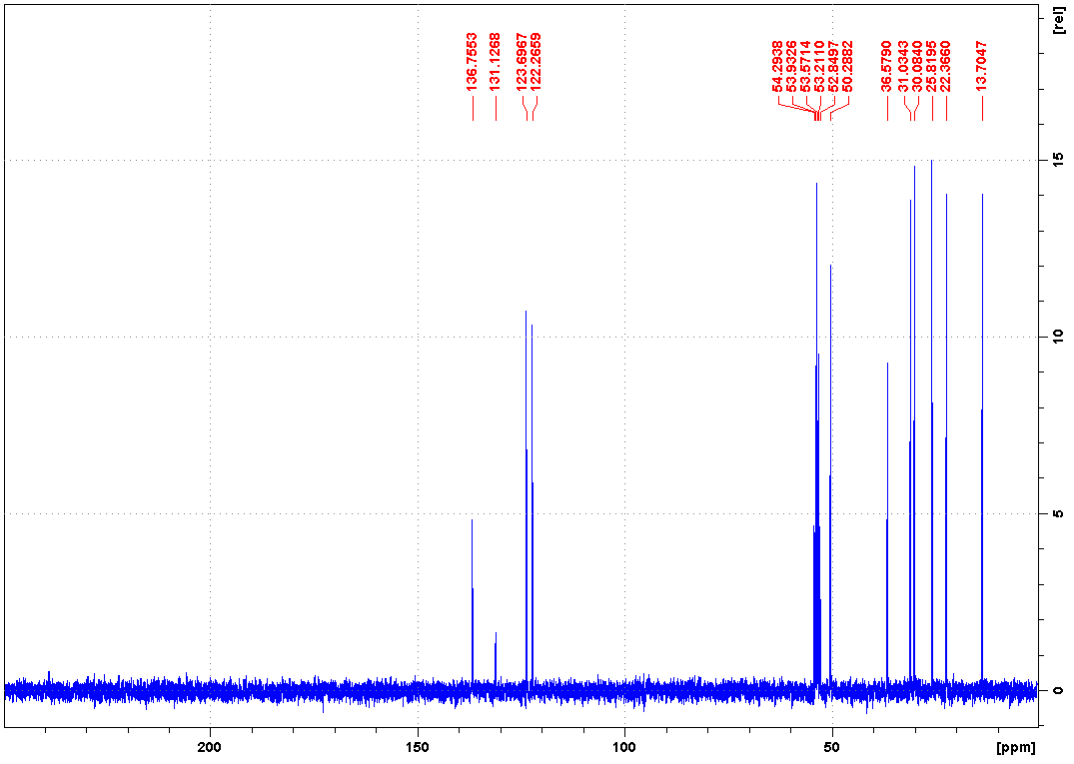
	Entire	Cation	Anion
Mass calculated	254.1	167.1	87

1-hexyl-3-methylimidazolium thiocyanate : [C_1C_6Im][SCN]

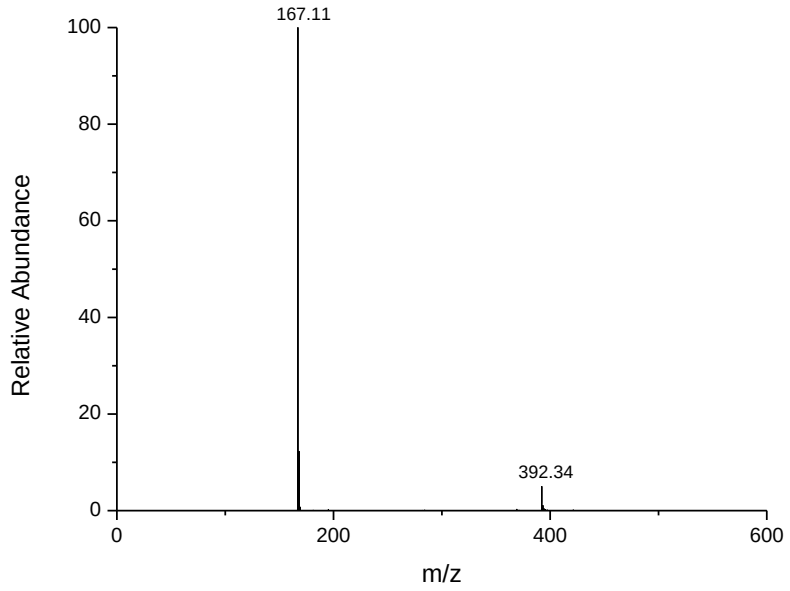




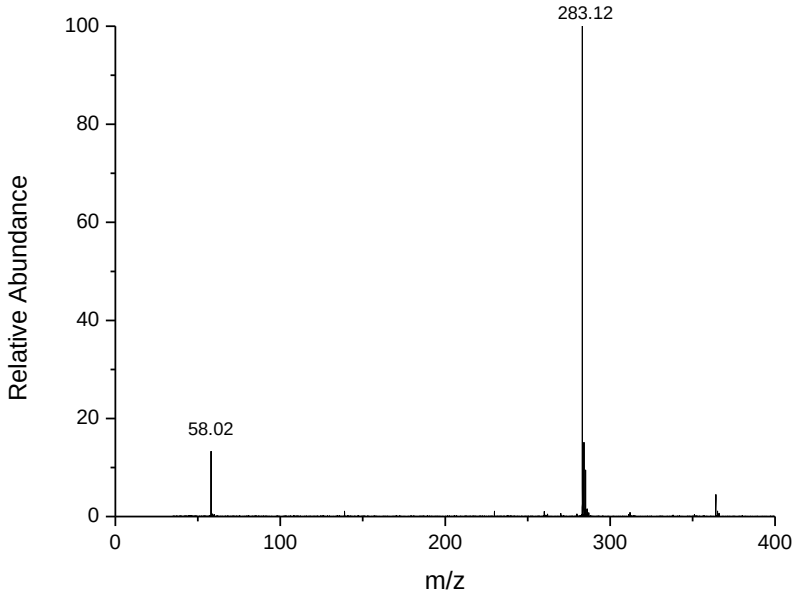
^{1}H NMR in CD_2Cl_2



^{13}C NMR in CD_2Cl_2



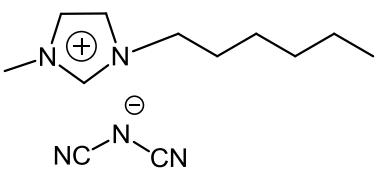
ESI$^+$ mass spectrum

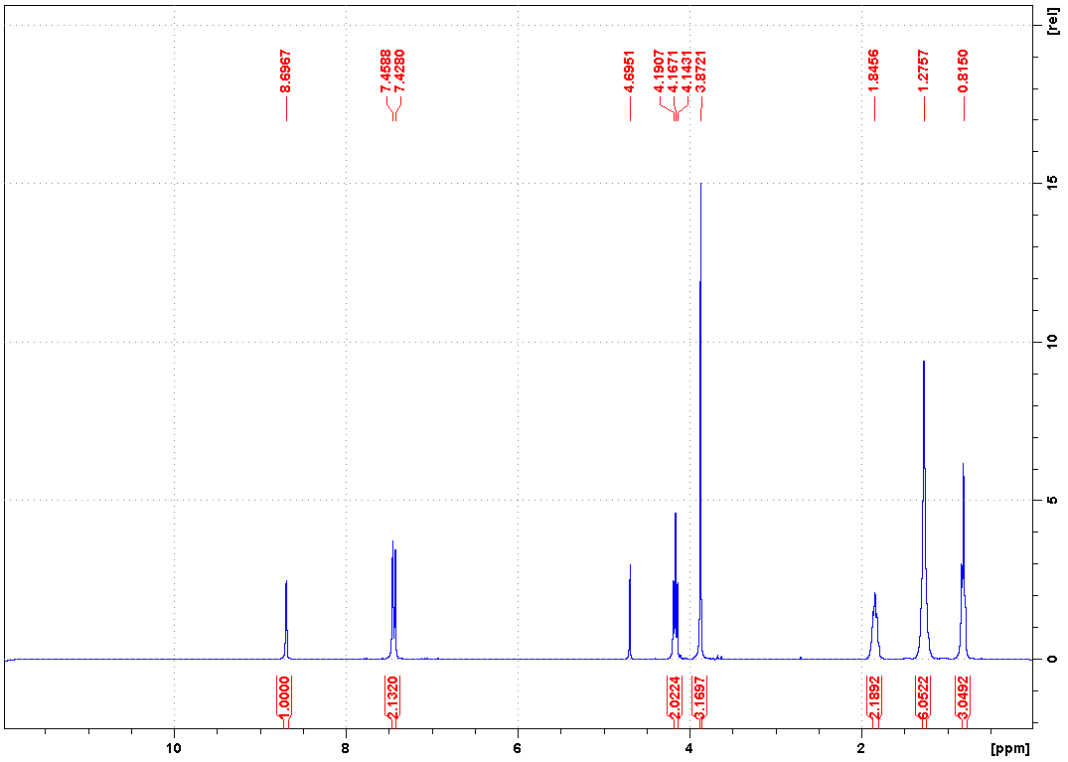


ESI$^-$ mass spectrum

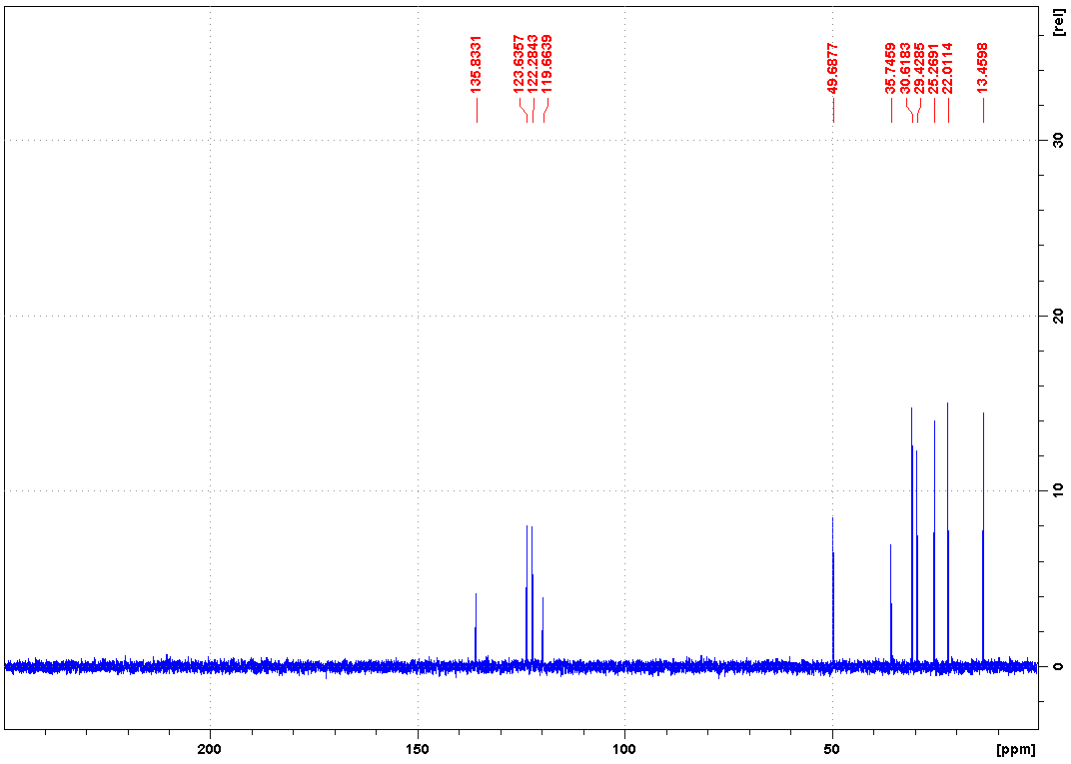
	Entire	Cation	Anion
Mass calculated	225.1	167.1	57.9

1-hexyl-3-methylimidazolium dicyanamide: [C_1C_6Im][N(CN)$_2$]

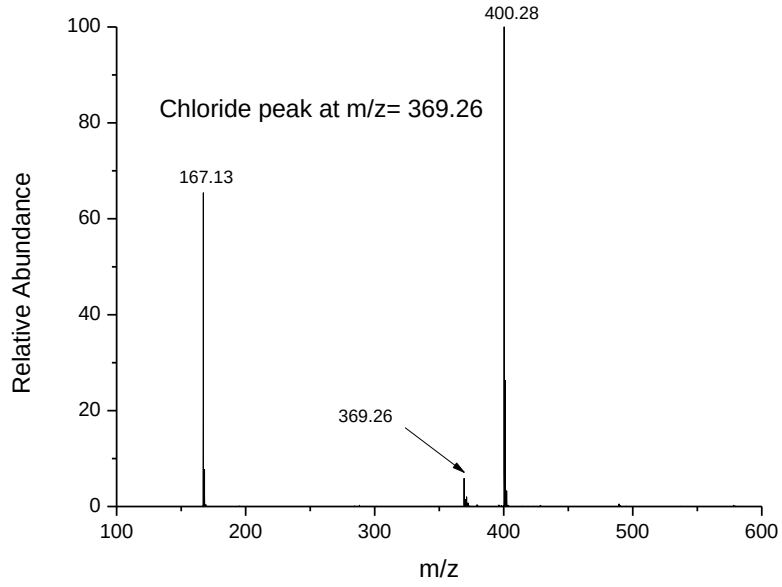




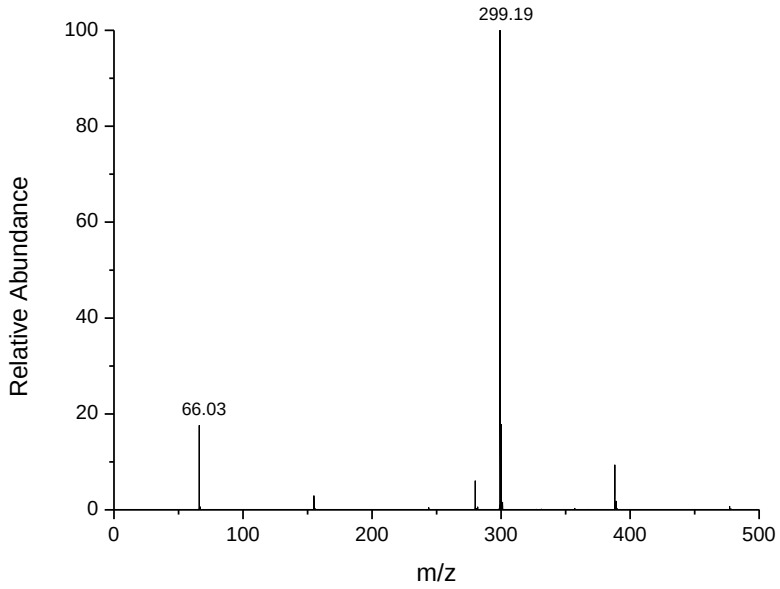
^{1}H NMR in D_2O



^{13}C NMR in D_2O



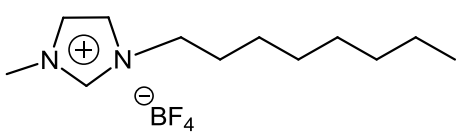
ESI$^+$ mass spectrum

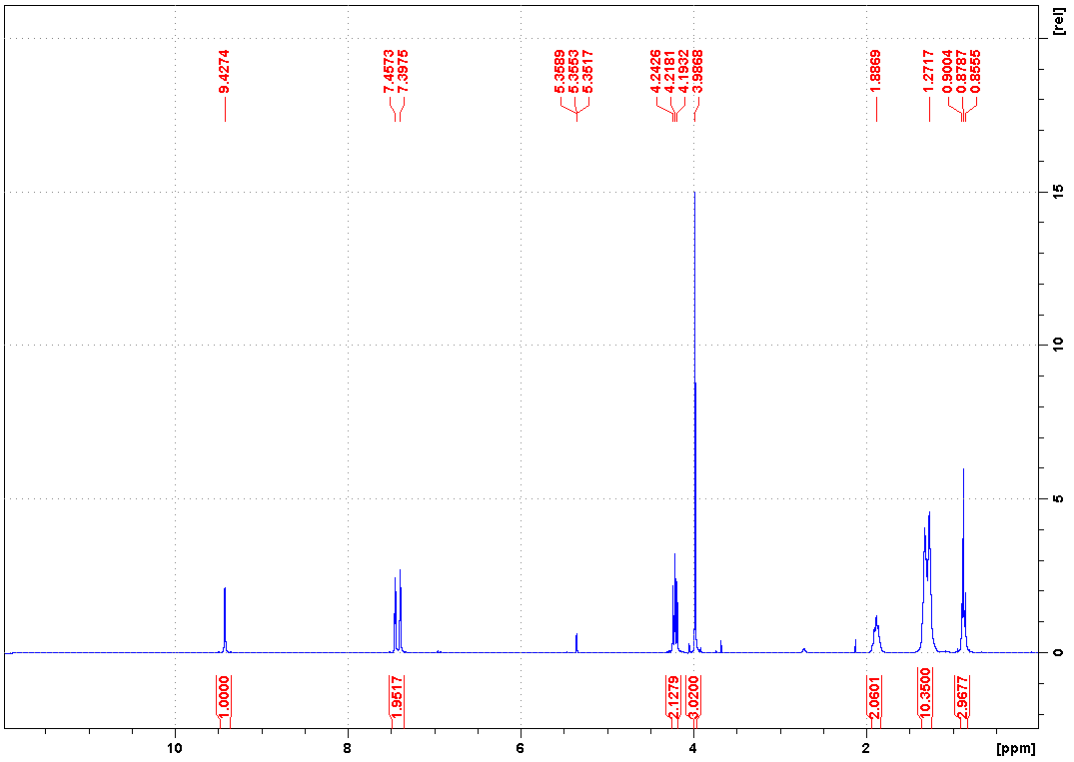


ESI$^-$ mass spectrum

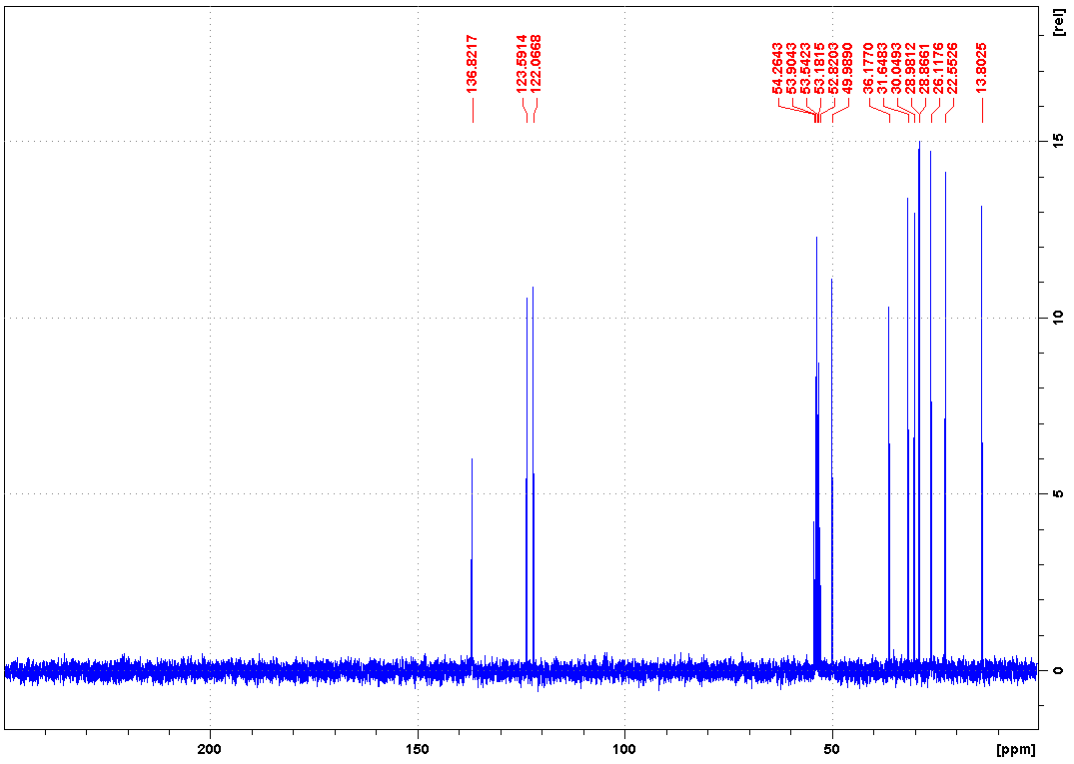
	Entire	Cation	Anion
Mass calculated	233.1	167.1	66.0

1-octyl-3-methylimidazolium tetrafluoroborate: [C_1C_8Im][BF_4]

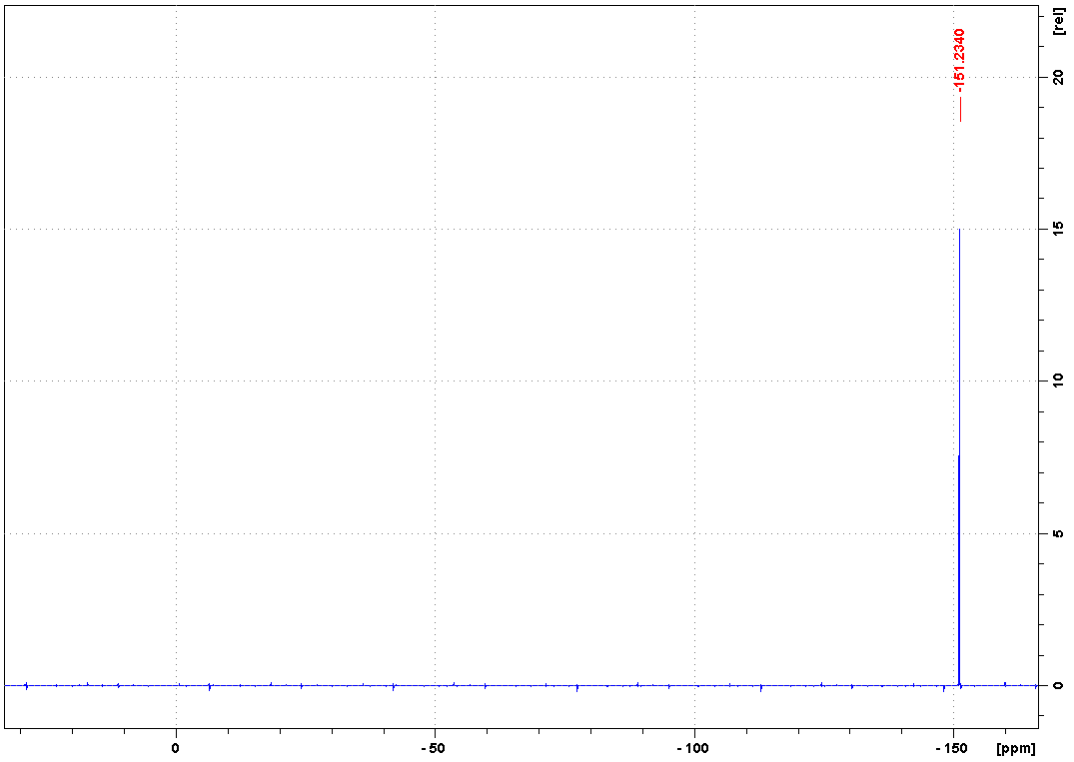




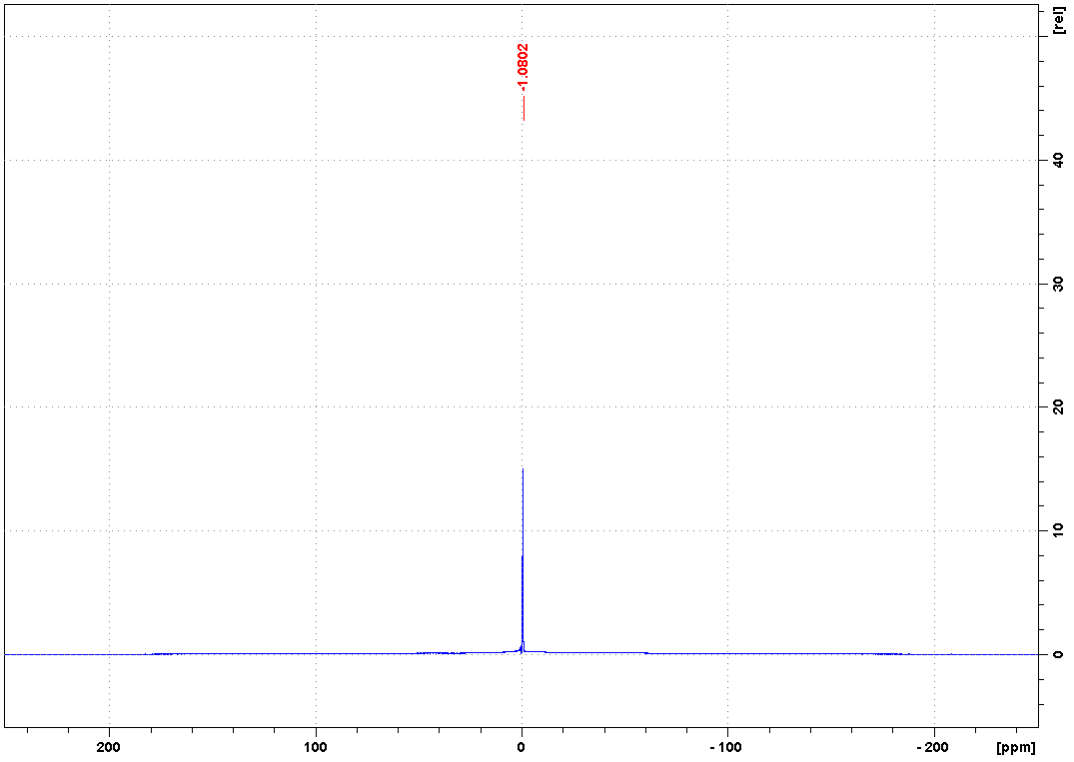
^{1}H NMR in CD_2Cl_2



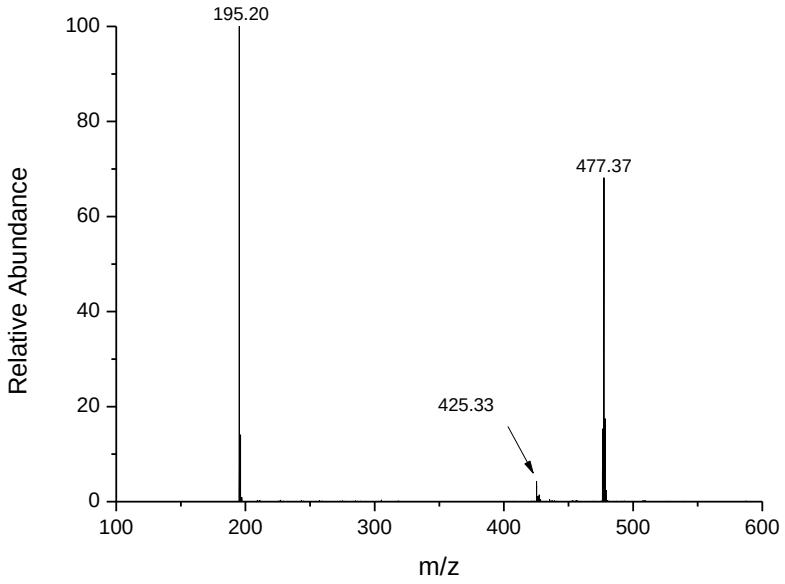
^{13}C NMR in CD_2Cl_2



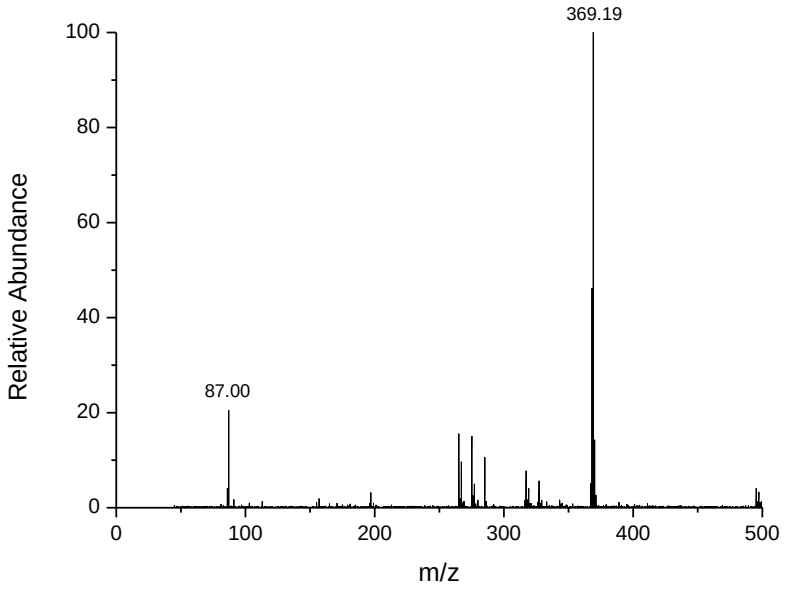
^{19}F NMR in CD_2Cl_2



^{11}B NMR in CD_2Cl_2



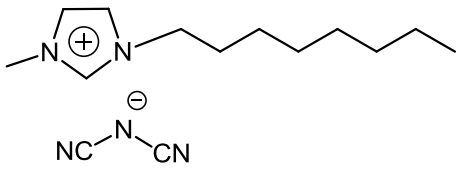
ESI$^+$ mass spectrum

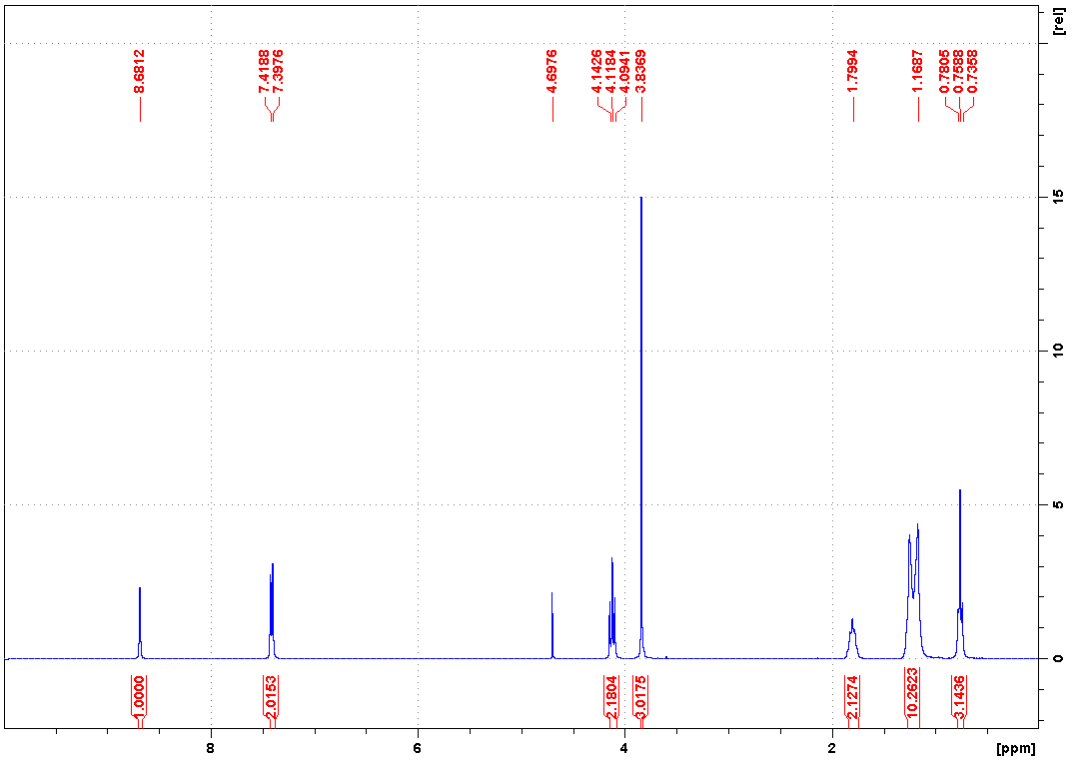


ESI$^-$ mass spectrum

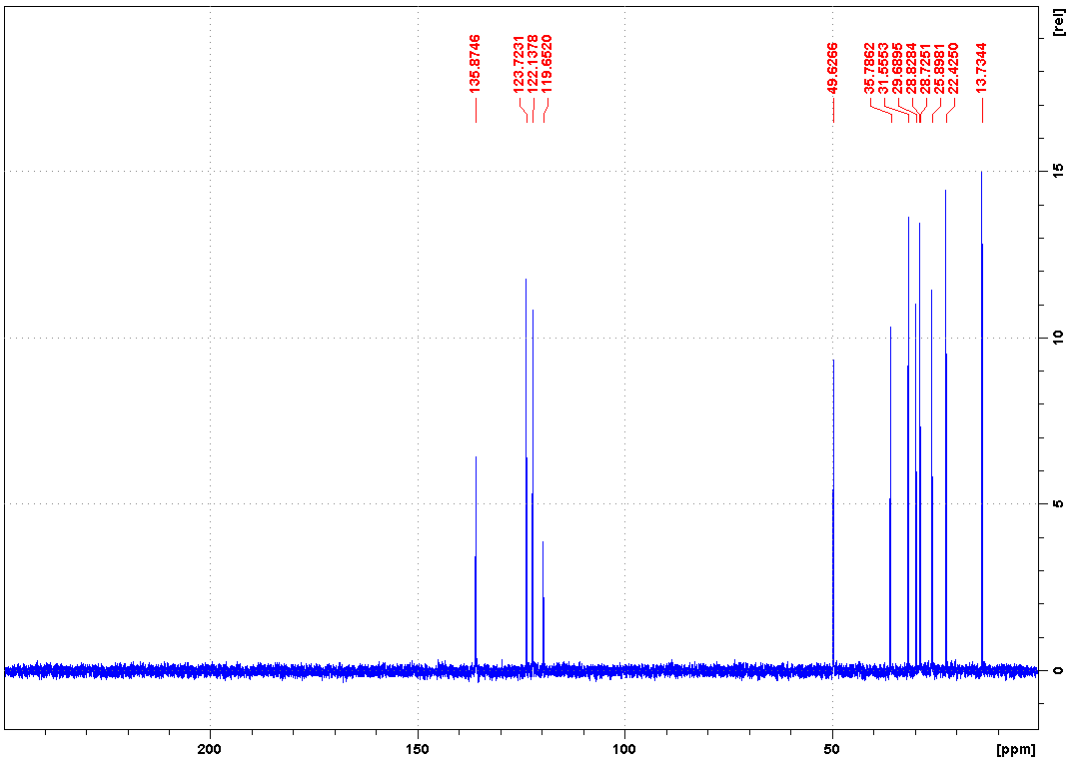
	Entire	Cation	Anion
Mass calculated	282.1	195.1	87.0

1-octyl-3-methylimidazolium dicyanamide: [C_1C_8Im][$N(CN)_2$]

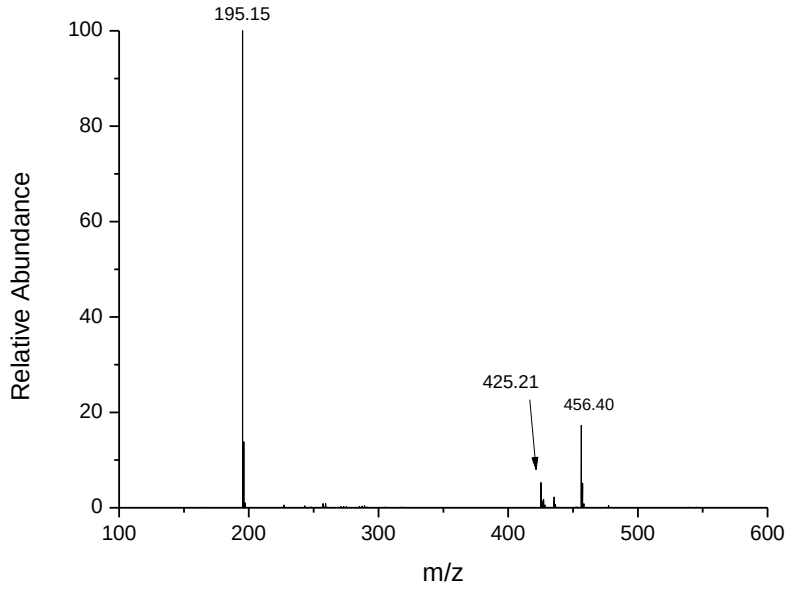




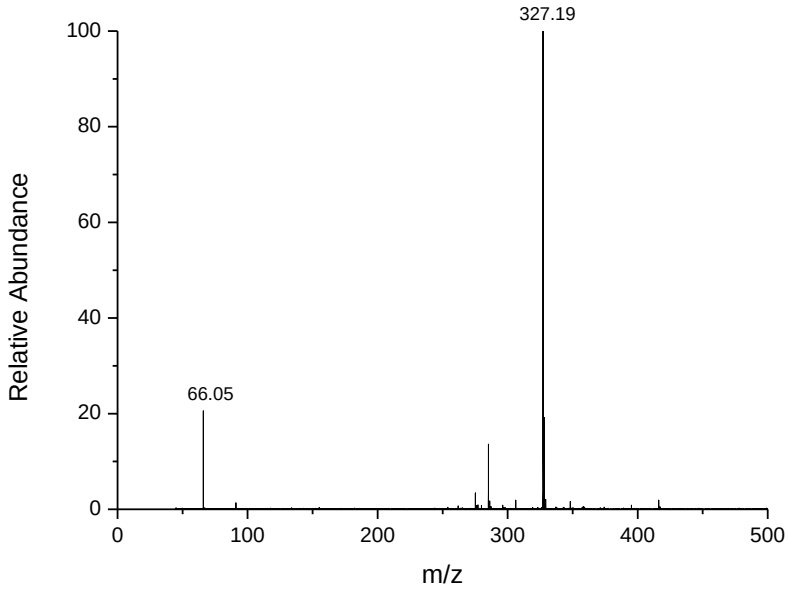
^{1}H NMR in D_2O



^{13}C NMR in D_2O



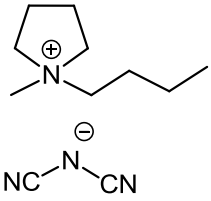
ESI$^+$ mass spectrum

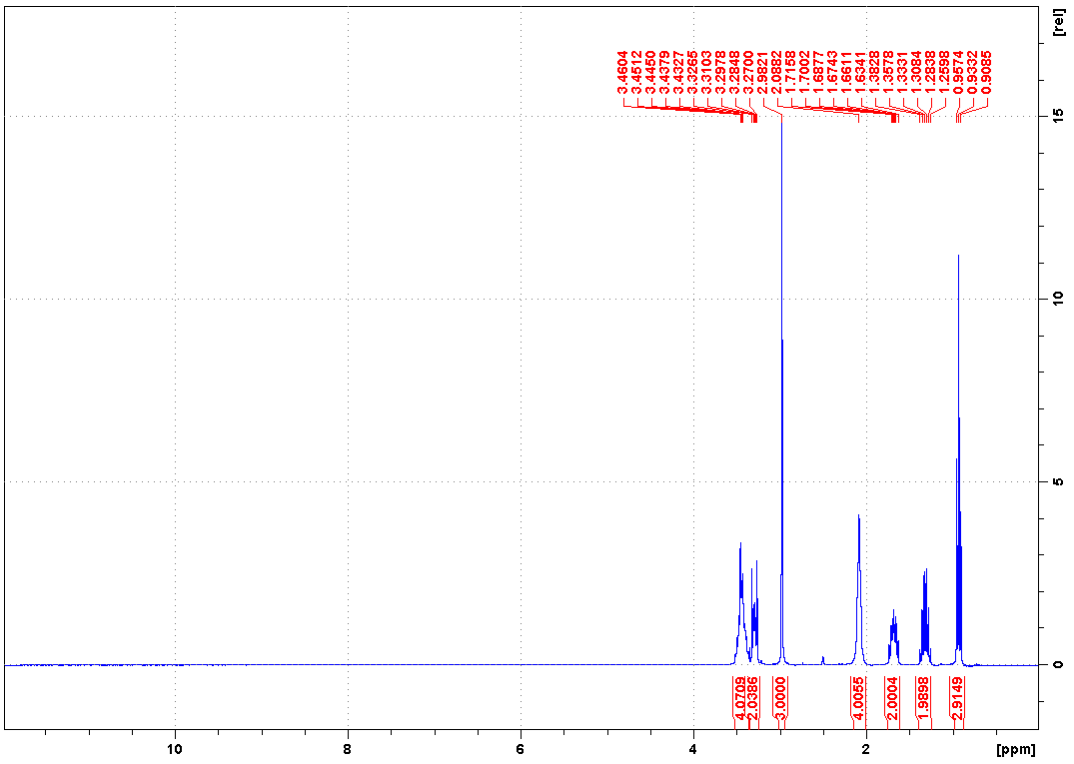


ESI$^-$ mass spectrum

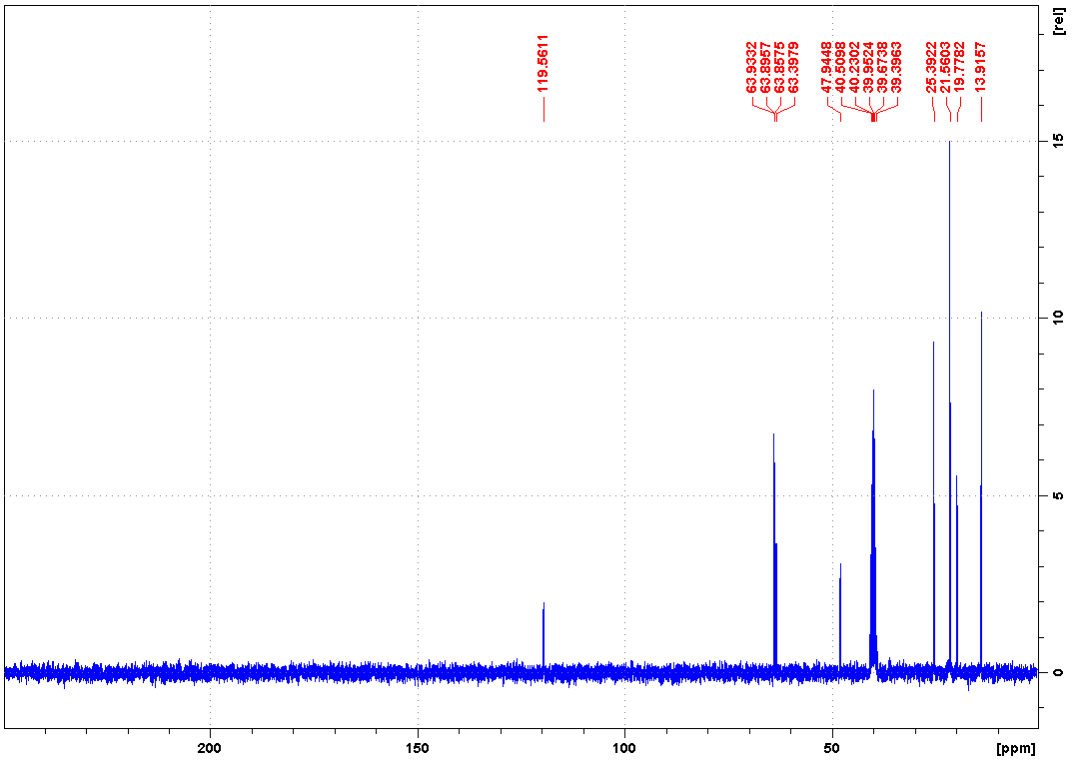
	Entire	Cation	Anion
Mass calculated	261.2	195.1	66.0

N-butyl-N-methylpyrrolidinium dicyanamide: $[P_{14}][N(CN)_2]$

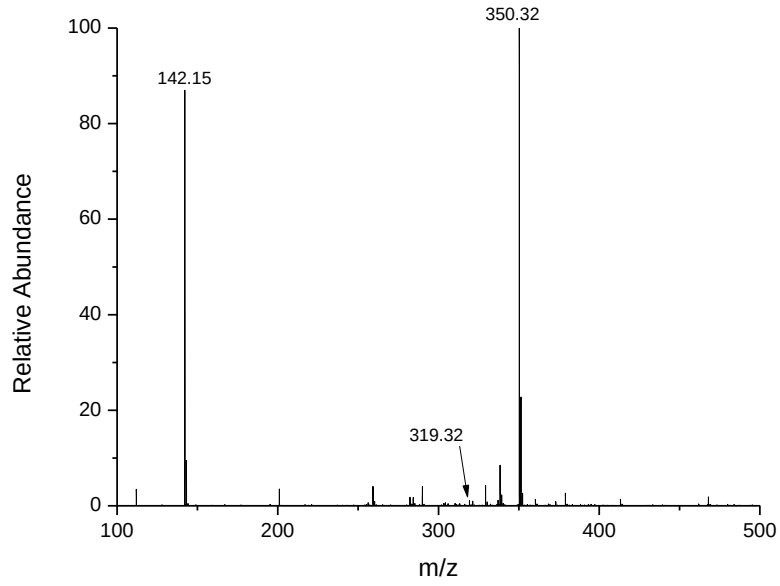




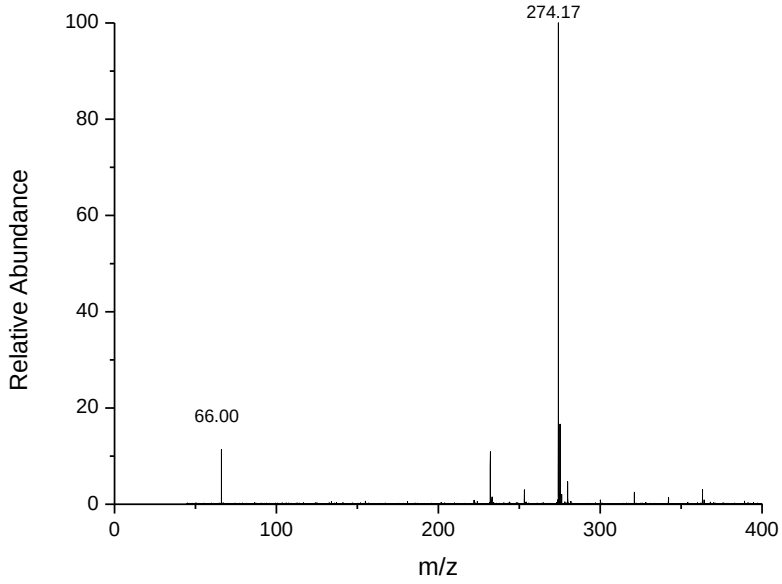
^{1}H NMR in d6-DMSO



^{13}C NMR in d6-DMSO



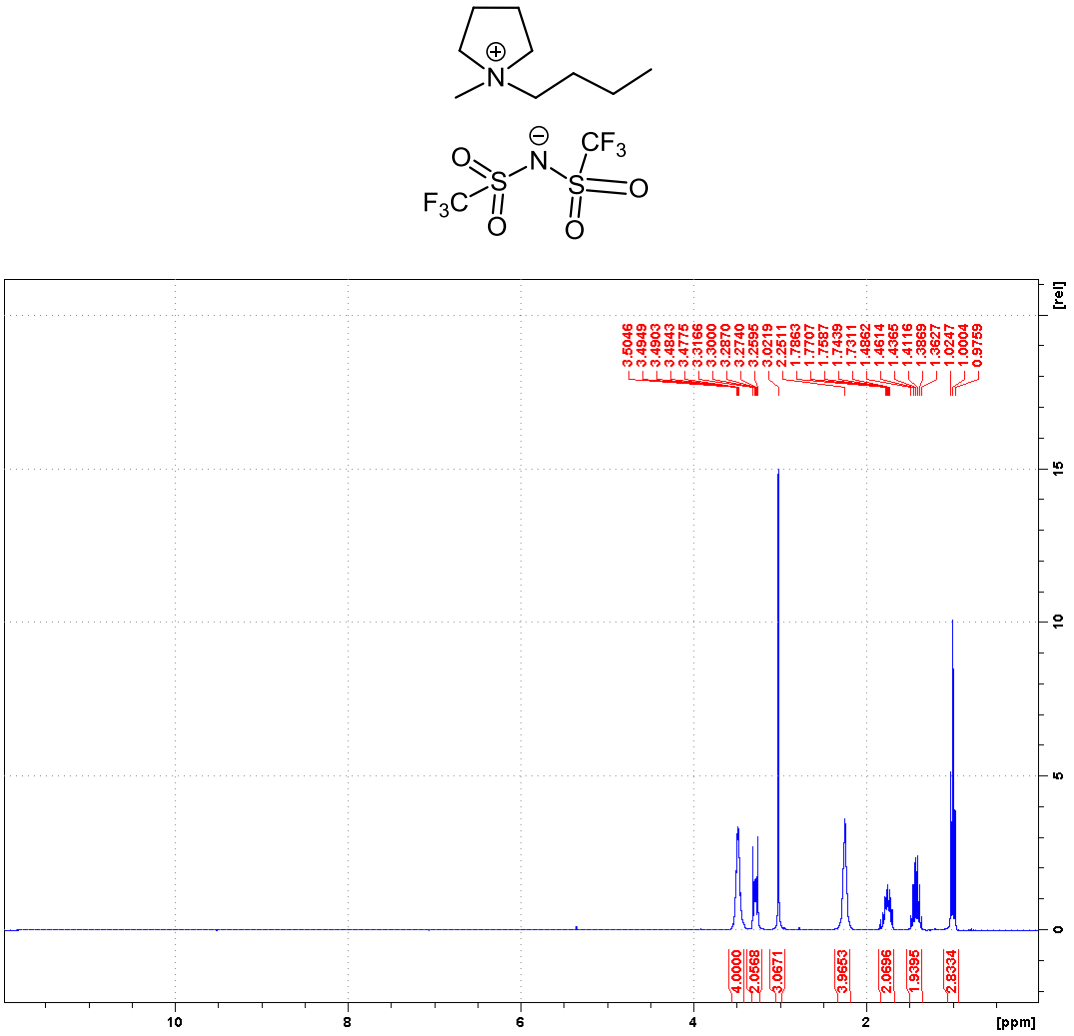
ESI$^+$ mass spectrum



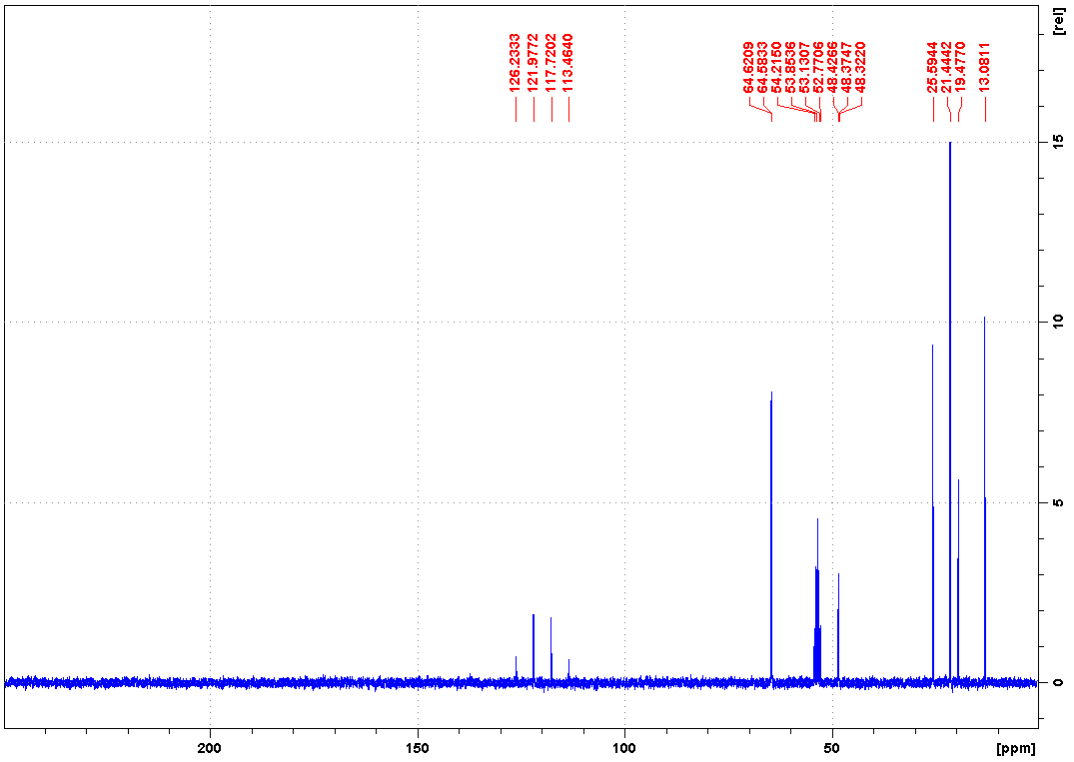
ESI$^-$ mass spectrum

	Entire	Cation	Anion
Mass calculated	208.1	142.1	66.0

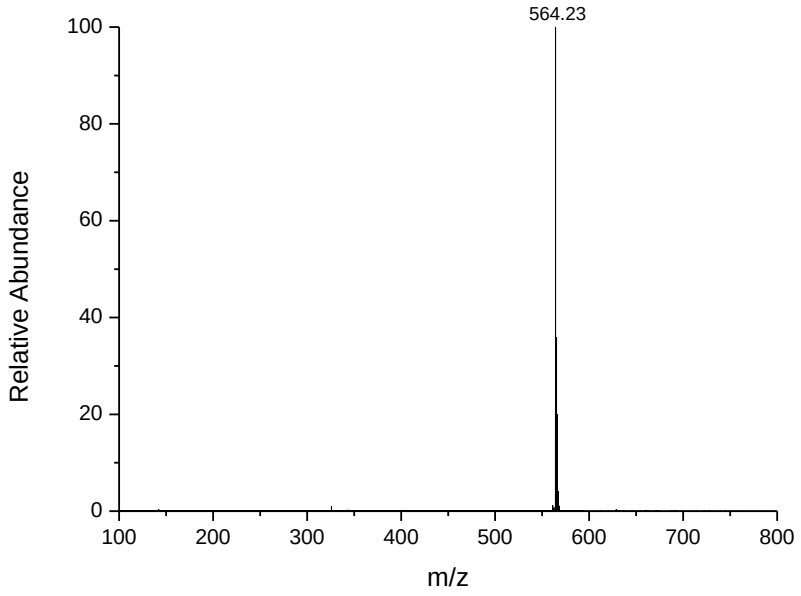
N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide: [P_{14}][NTf_2]



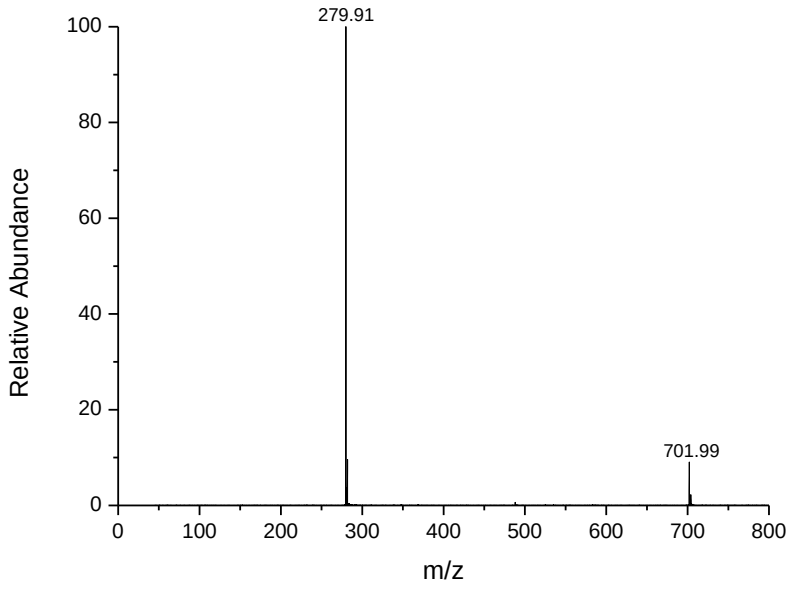
^{1}H NMR in CD_2Cl_2



^{13}C NMR in CD_2Cl_2



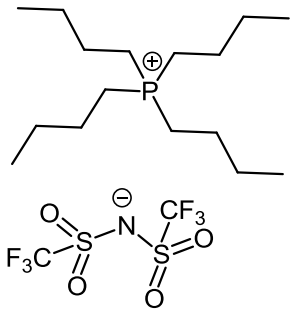
ESI^+ mass spectrum

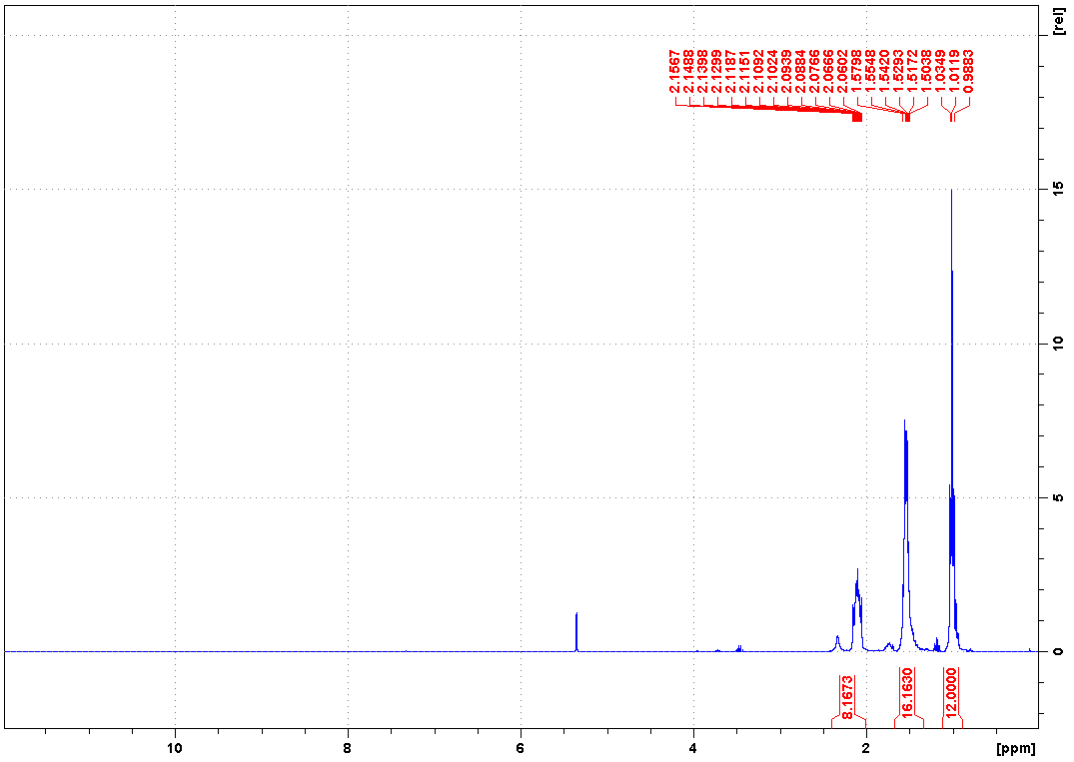


ESI$^-$ mass spectrum

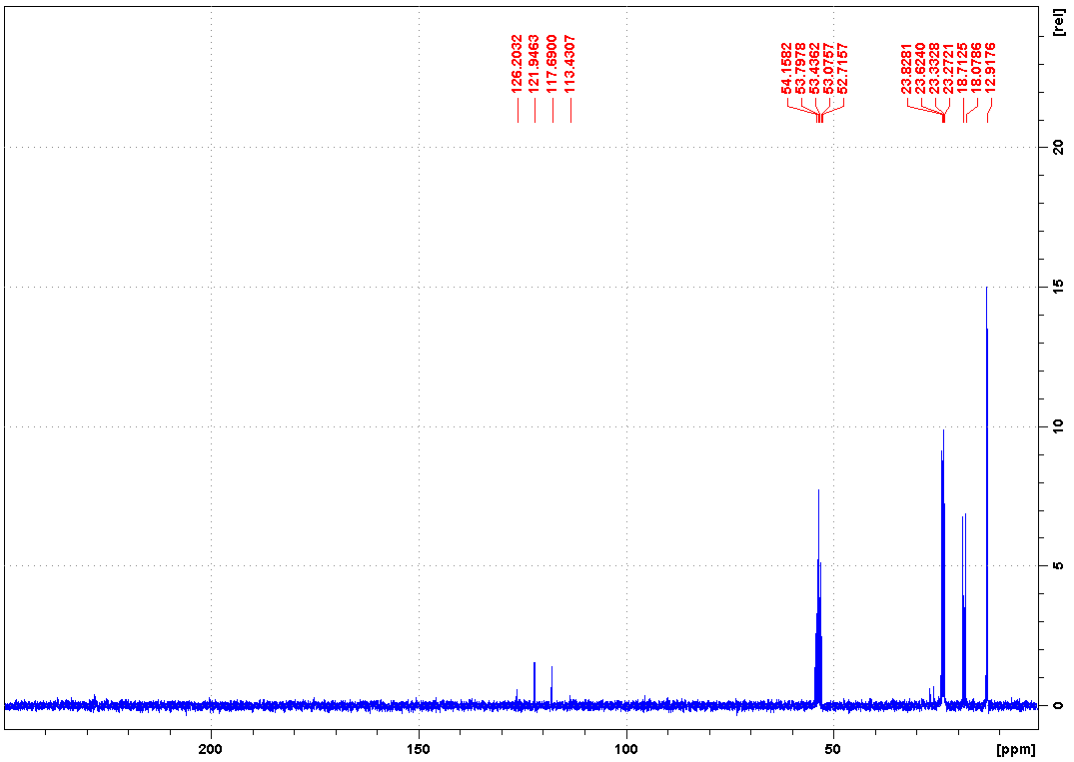
	Entire	Cation	Anion
Mass calculated	422.0	142.1	279.9

Tetrabutylphosphonium bis(trifluoromethylsulfonyl)imide: [P_{4444}][NTf_2]

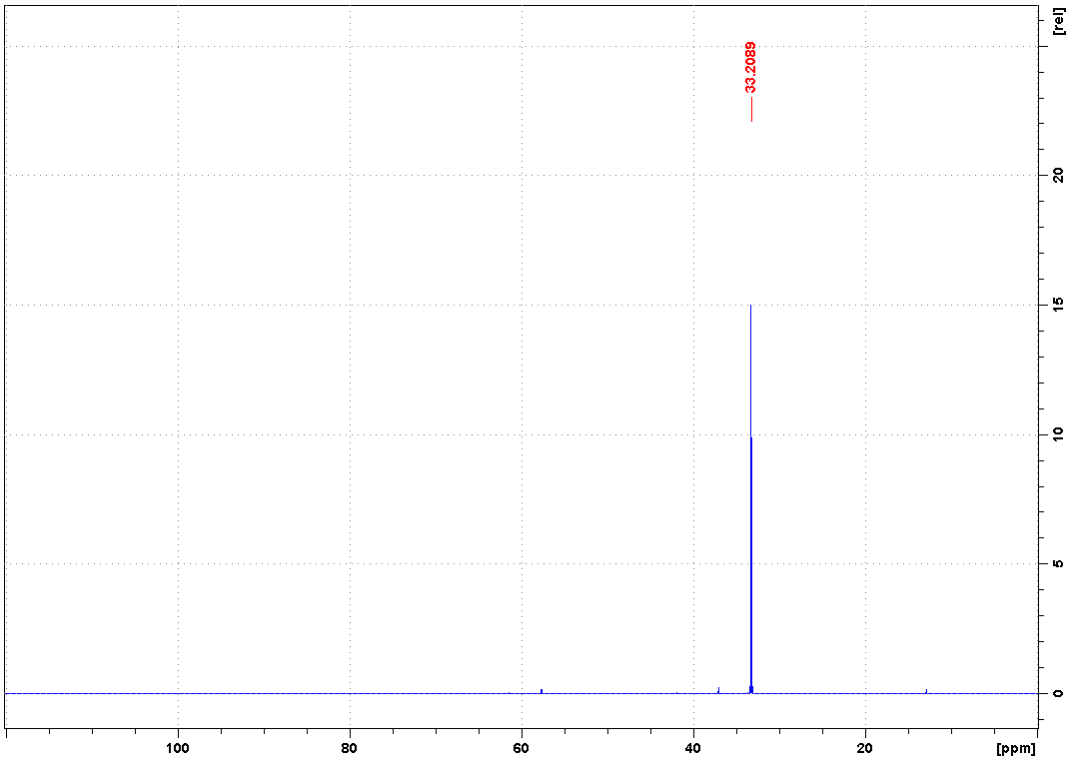




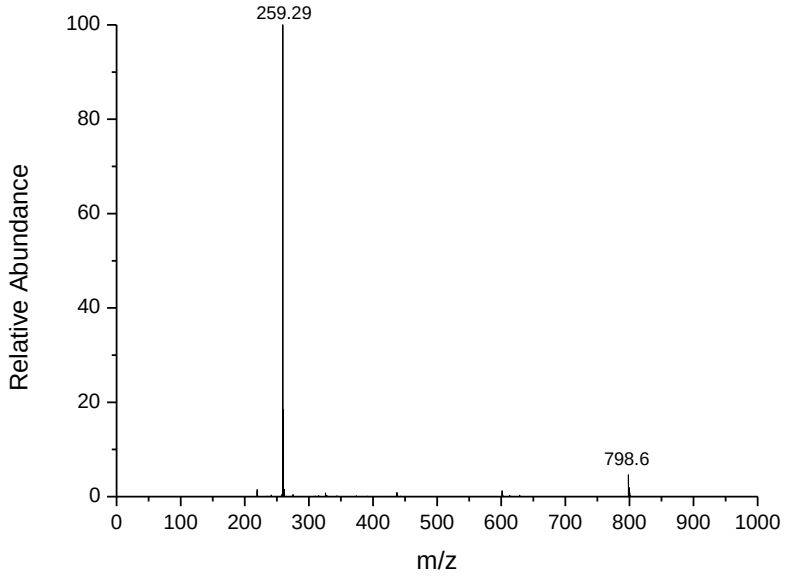
^{1}H NMR in CD_2Cl_2



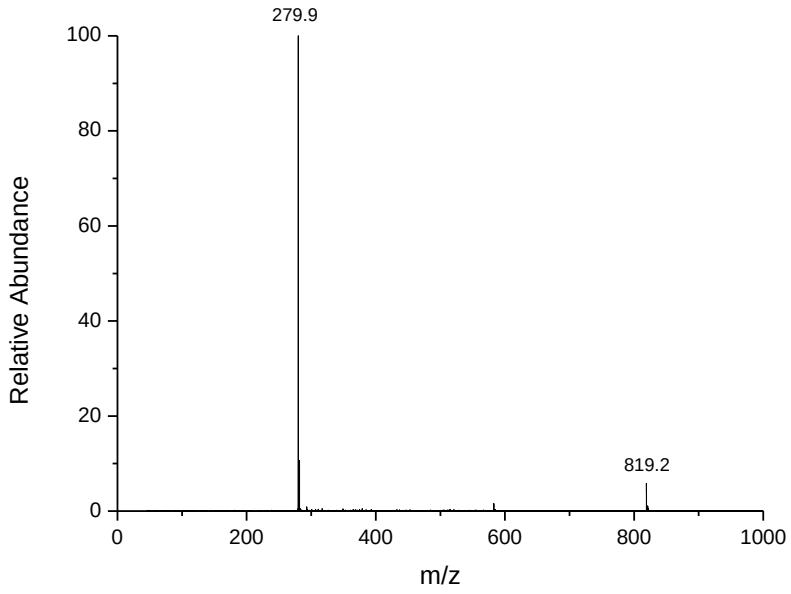
^{13}C NMR in CD_2Cl_2



^{31}P NMR in CD_2Cl_2



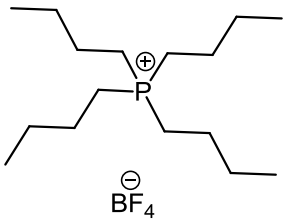
ESI^+ mass spectrum

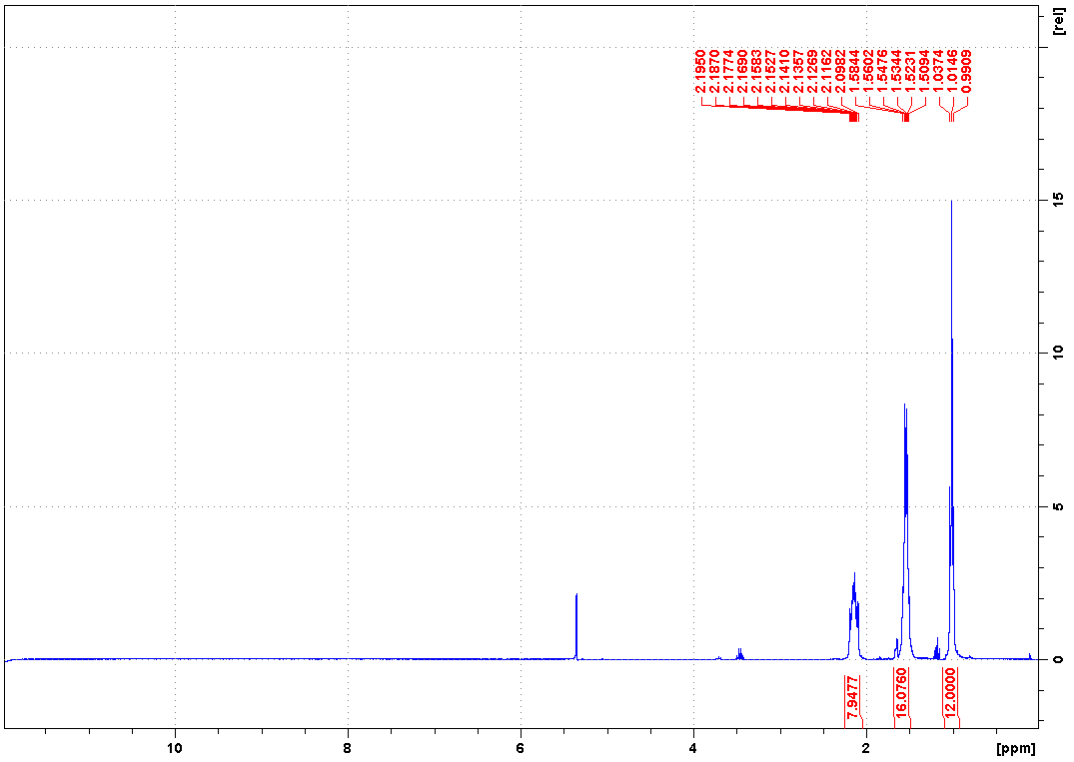


ESI$^-$ mass spectrum

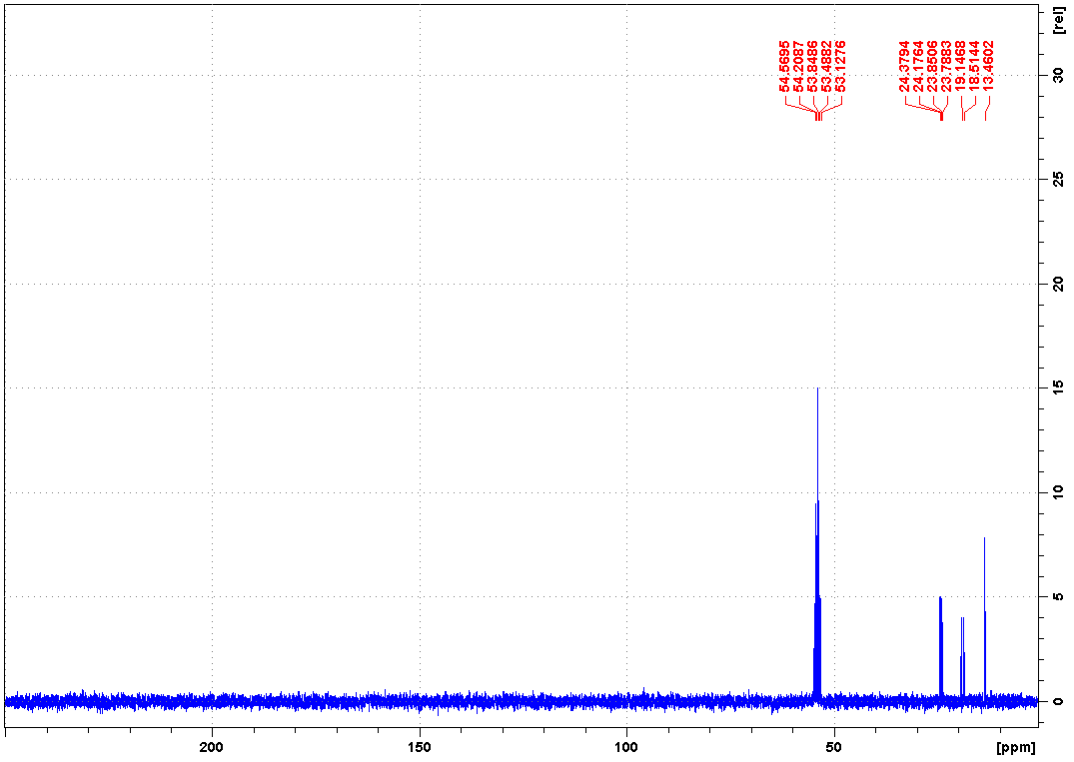
	Entire	Cation	Anion
Mass calculated	539.1	259.2	279.9

Tetrabutylphosphonium tetrafluoroborate: [P_{4444}][BF_4]

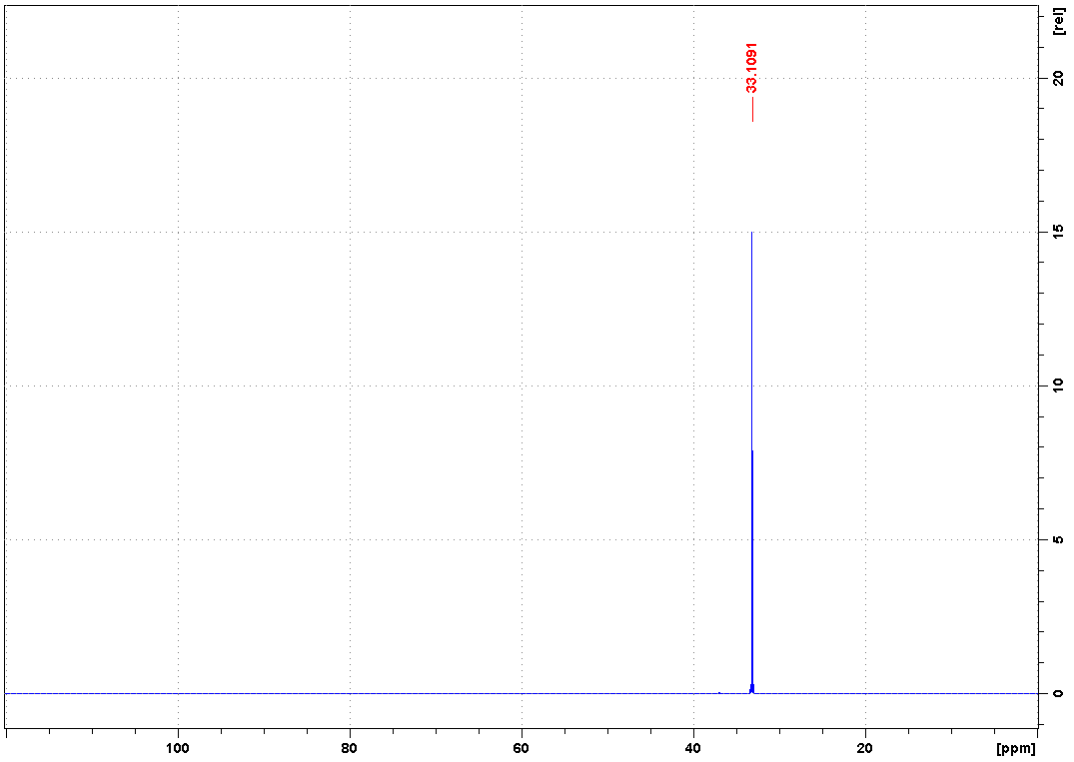




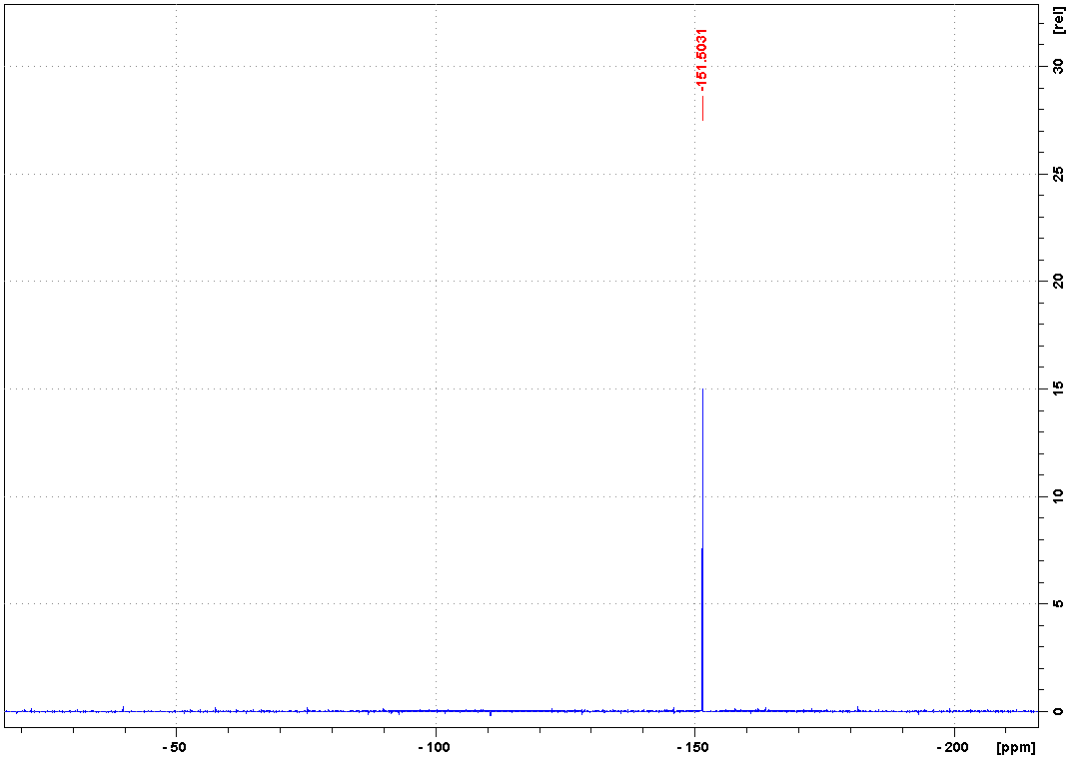
^{1}H NMR in CD_2Cl_2



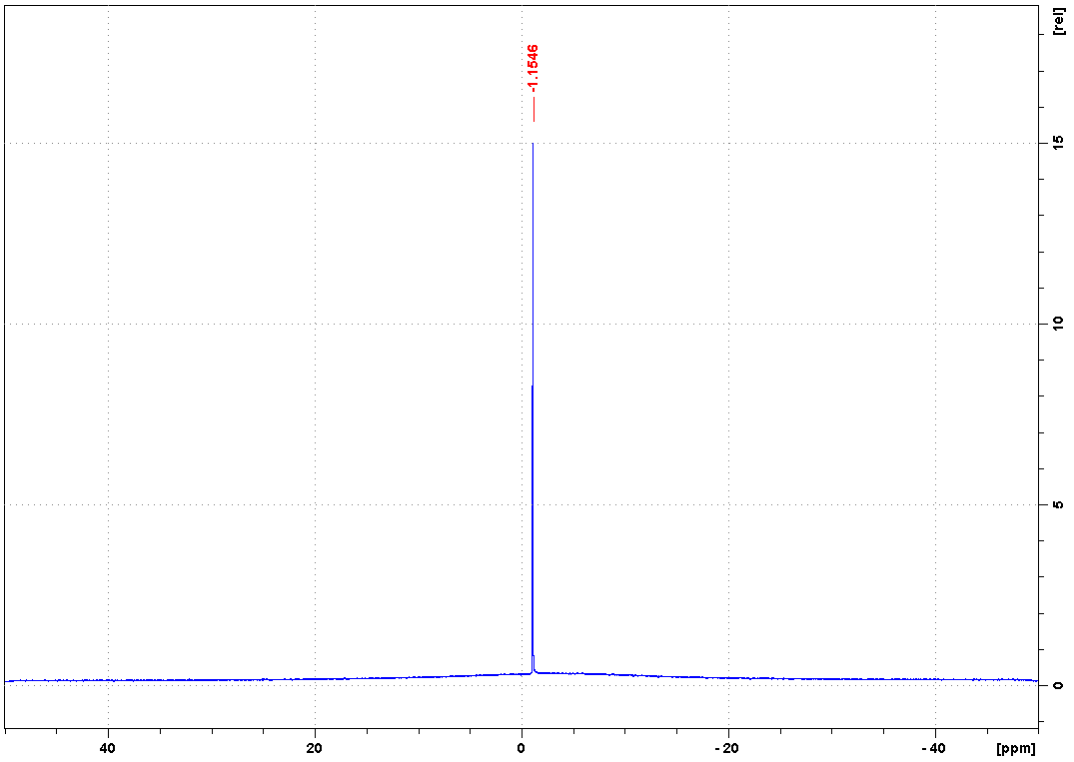
^{13}C NMR in CD_2Cl_2



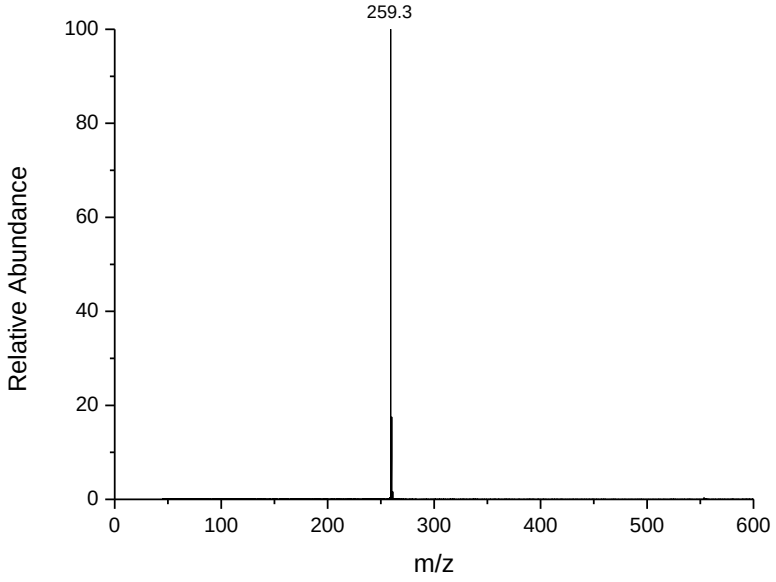
^{31}P NMR in CD_2Cl_2



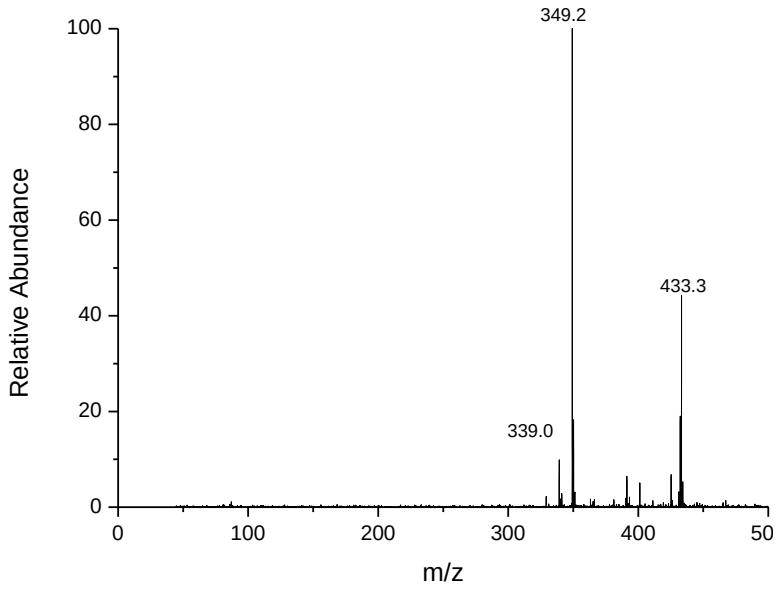
^{19}F NMR in CD_2Cl_2



^{11}B NMR in CD_2Cl_2



ESI^+ mass spectrum



ESI$^-$ mass spectrum

	Entire	Cation	Anion
Mass calculated	346.2	259.2	87.0