

Supporting information

Halogen free 1,2,3- and 1,2,4-triazolide based ionic liquids: synthesis and properties

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Characterization

NMR spectra were recorded on Bruker 400 MHz spectrometer using residual signal of DMSO at 2.5 ppm as a reference for ¹H NMR spectra and at 39.52 ppm – for ¹³C NMR spectra. ¹H-¹³C gradient enhanced Heteronuclear Single Quantum Coherence (HSQC) spectra were acquired using one bond coupling constant value of 146 Hz. ¹H-¹³C gradient enhanced Heteronuclear Multiple Bond Correlation (HMBC) spectra were acquired using multiple bond coupling constant value of 8 Hz. NOESY spectra were acquired using NOE mixing time 200 ms. MestReNova v. 11.0.4-18998 software was used to process acquired FIDs.

High resolution mass (HR-MS) spectra were obtained using Waters Xevo-G2-XS (Q-TOF). Samples were prepared by dissolving the IL in methanol.

Fourier transform infrared (FT-IR) spectra were recorded on Thermo Scientific Nicolet iD5 spectrometer.

Thermo gravimetric analysis mass spectroscopy (TGA-MS). TGA-MS measurements were performed using a thermo microbalance TG 209 F1 Libra (Netzsch, Selb, Germany) with uncertainty of mass measurement 0.1 µg and the uncertainty of preset temperature 0.2 K. The thermo microbalance TG 209 F1 Libra was coupled with a Thermostat Mass spectrometer GSD 301 T3 (Pfeiffer Vacuum; Asslar/Germany). The ionization was by electron impact using an iridium filament as ion source; ionization energy was 75 eV, and ions were separated in a quadrupole mass filter. A platinum crucible was used for the measurement of 10±1 mg of samples in a helium flow of 10 mL·min⁻¹ and a purge flow of 10 mL·min⁻¹. Data were analyzed using Proteus (6.0.0) and Quadstar (7.03) software packages.

Differential scanning calorimetry (DSC) was performed using Netzsch DSC204 equipped with TASC 414/4 and CC200L controllers under flow of nitrogen at the heating rate 5 K·min⁻¹ and preset temperature uncertainty 0.2 K. The standard uncertainty of glass transition temperature measurement did not exceed 0.3 K.

Density (ρ) of the ILs was determined in a density oscillation tube (DMA 5000M, Anton Paar, Graz). The declared by the manufacturer accuracy of density measurement is 5·10⁻⁶ g·cm⁻³ and temperature 0.01 °C. The declared by the manufacturer uncertainty of density measurement is 10⁻⁶ g·cm⁻³ and temperature 0.001 °C. The measurements were performed at

25±0.01 °C. The viscosity-related errors are automatically corrected over the full viscosity range by measuring the damping effect of the viscous sample followed by a mathematical correction of the density value. The uncertainty of the measurements were checked repeating measurements three times. In all cases deviation did not exceed 0.001 g·cm⁻³. The relative standard uncertainty of water content determination leads to the relative standard uncertainty of 0.1% in density measurement.

Linear sweep voltammetry (LSV) was measured using BioLogic MPG2 potentiostat and a three electrode setup with a platinum wire counter electrode, a glassy carbon working electrode¹ (1.6 mm diameter) and a reference electrode for organic media (silver wire in 0.01 M silver nitrate and 0.1 M tetrabutylammonium phosphate solution in acetonitrile). Scan rate was 1 mV·s⁻¹. The potential of the reference electrode was compared to ferrocene measured under the same conditions with 0.1 M tetrabutylammonium phosphate auxiliary electrolyte. The measurements were performed at 25±1 °C.

Energy dispersive X-Ray (EDX) analysis was performed on JEOL JSM-7500F electron microscope equipped with two Oxford Instruments EDX detectors, located at opposite sides from the sample. The angle between the sample film surface and EDX detector axis was 28°. Electrons accelerating voltage was set to 6.0 keV. Aztec 3.3 software was used to process EDX data and to calculate elemental composition. A homemade specimen holder was manufactured to perform EDX analysis of the ILs. A commercial aluminum specimen holder of cylindrical shape (diameter 10 mm, height 5 mm) was taken for modification. A circular punctum (diameter 2 mm, depth 1 mm) was made in the center of the commercial specimen holder. An amount of IL, sufficient to fill the cavity (ca. 2-5 µL), was taken for analysis.

Water mass fraction (w) in ILs was determined by Karl Fischer titration which was carried out on a Metrohm 756 KF coulometer, which has a nominal detection limit 10 µg of water, equipped with a Metrohm 703 Ti Stand using Hydranal–Coulomat AD. The relative standard uncertainty of water content determination did not exceed 5.6% in all measurements.

Conductivity (κ) of the IL was determined by impedance spectroscopy between 20 kHz and 100 mHz at an amplitude of 10 mV. The measurements were performed at 25±1 °C. We used a two electrode Swagelok cell with two stainless steel electrodes and a BioLogic MPG2 potentiostat. Conductivity of the electrolyte was obtained from the Nyquist plot using the intercept with the real axis in the high frequency region after fitting with a Randles circuit model. Measurements were repeated three times to determine the standard deviation of conductivity values. The accuracy of conductivity measurement was tested using standard KCl solution and was 0.003 mS·cm⁻¹. The relative standard uncertainty of conductivity measurement did not exceed 15%. The relative standard uncertainty of water content determination leads to the relative standard uncertainty of 0.84% in conductivity measurement.

Dynamic (shear) viscosity (μ) of the IL was measured on an Anton Paar MCR 301 stress-controlled rheometer using a 12 mm diameter cone – plate geometry with a 1° cone angle and a 20 µm truncation. The torque sensor resolution of the specified device is 1 µN·m. Rotatory shear rate sweeps (500 – 3000 s⁻¹) were performed at 25±0.2 °C and stress response of the different IL was monitored. Temperature sweeps (25 - 80°C) were performed at 1000 s⁻¹ using a constant heating rate of 2 °C·min⁻¹. The relative standard uncertainty of dynamic

viscosity measurement did not exceed 5.3%. The relative standard uncertainty of water content determination causes the relative standard uncertainty of 0.3% in dynamic viscosity measurement.

The standard uncertainty of the measured parameters (w , T_g , μ , ρ , κ) is given below.

Ionic liquid	$w_w^{[a]}$	$T_g^{[b]} \text{ } ^\circ\text{C}$	$\mu^{[c]} \text{ cP}$	$\rho^{[d]} \text{ g}\cdot\text{cm}^{-3}$	$\kappa^{[e]} \text{ mS}\cdot\text{cm}^{-1}$
IL-1	$w_w = 0.00832 \pm 0.0002$	$T_g = -66.6 \pm 0.1$	$\mu = 87 \pm 1$	$\rho = 1.107 \pm 0.001$	$\kappa = 2.122 \pm 0.185$
IL-2	$w_w = 0.0144 \pm 0.0008$	$T_g = -39.0 \pm 0.3$	$\mu = 376 \pm 4$	$\rho = 1.325 \pm 0.001$	$\kappa = 1.180 \pm 0.008$
IL-3	$w_w = 0.0102 \pm 0.0004$	$T_g = -55.4 \pm 0.2$	$\mu = 414 \pm 5$	$\rho = 1.181 \pm 0.001$	$\kappa = 0.731 \pm 0.110$

[a] water mass fraction;

[b] glass transition temperature;

[c] dynamic viscosity;

[d] density;

[e] conductivity.

Experimental procedures

Chemicals

Diaminomaleonitrile (98%), silver nitrate ($\geq 99\%$), sodium nitrite ($\geq 97\%$), trifluoroacetic acid (99%), and iodomethane ($\geq 99\%$) were purchased from Sigma-Aldrich; 4H-1,2,4-triazol-4-amine (99%) and 3-aminotriazole-1,2,4 (96%) were purchased from Alfa Aesar; aminoguanidinium hydrocarbonate (98.5%) was purchased from Acros Organics; 1-butyl-2,3-dimethyl-1H-imidazol-3-ium chloride (99%) was purchased from Ionic Liquids Technologies. All chemicals were used as received without additional purification.

2H-1,2,3-triazole-4,5-dicarbonitrile was synthesized according to the procedure given in the literature.² To a stirred suspension of diaminomaleonitrile (15.63 g, 145 mmol) in HCl solution (148 mL, 1 mol·L⁻¹), a solution of HCl (50 mL, 37 wt. %) was added. The solution was cooled on the ice bath, and a solution of NaNO₂ (10.2 g, 148 mmol) in water (100 mL) was added dropwise so the temperature inside the reactor remained below +5 °C. The reaction mixture was maintained stirring in the ice bath for additional 30 min, ice bath was removed and the mixture was stirred at +25 °C for 1 hour. The precipitate was filtered off, and the aqueous solution was extracted with diethyl ether (4x50 mL). Extracts were combined, dried over anhydrous Na₂SO₄ and concentrated in vacuum affording a pale-yellow solid. Yield: 16.44 g, 95%. ¹H NMR (400 MHz, DMSO-d₆): δ 14.4 (s, 1H, NH). ¹³C NMR (400 MHz, DMSO-d₆): δ 110.79 (s, C), 123.83 (s, C).

Silver(I) 4,5-dicyano-1,2,3-triazol-2-ide. 2H-1,2,3-triazole-4,5-dicarbonitrile (2.6 g, 22 mmol) was dissolved in solution of NaOH (0.54 mol·L⁻¹, 40 mL). A solution of AgNO₃ (3.71 g, 22 mmol) was added dropwise. White solid was filtered off, washed with water and dried in vacuum affording white solid. Yield: 4.83 g, 99%.

1-Butyl-2,3-dimethyl-1H-imidazol-3-ium 4,5-dicyano-1,2,3-triazol-2-ide (IL1). To a stirred suspension of silver(I) 4,5-dicyano-1,2,3-triazol-2-ide (1.83 g, 8.1 mmol) in methanol (10 mL), a solution of 1-butyl-2,3-dimethyl-1H-imidazol-3-ium chloride (1.53 g, 8.1 mmol) in methanol (20 mL) was added. The reaction mixture was stirred at room temperature overnight. The precipitate was filtered off and washed with methanol. Methanol solution was flash chromatographed through silica gel. After methanol evaporation, the oily residue was dried in vacuum (0.1 mbar, 80°C). Yield: 2.06 g, 94%. ¹H NMR (400 MHz, DMSO-d₆): δ 0.893 (t, ³J_{H,H} = 7.5 Hz, 3H, CH₃), 1.273 (sex, ³J_{H,H} = 7.5 Hz, 2H, CH₂), 1.677 (quin, ³J_{H,H} = 7.5 Hz, 2H, CH₂), 2.575 (s, 3H, CH₃), 3.744 (s, 3H, CH₃), 4.097 (t, ³J_{H,H} = 7.5 Hz, 2H, CH₂), 7.605 (d, ³J_{H,H} = 2.0 Hz, 1H, CH), 7.635 (d, ³J_{H,H} = 2.0 Hz, 1H, CH). ¹³C NMR (400 MHz, DMSO-d₆): δ 9.15 (s, CH₃), 13.4 (s, CH₂), 18.9 (s, CH₂), 31.2 (s, CH₂), 34.7 (s, CH₃), 47.3 (s, CH₂), 113.9 (s), 120.9 (s), 121.0 (s), 122.3 (s), 144.2 (s). HR-MS: 153.1467 (cation) (Calculated 153.1386), 118.0166 (anion) (Calculated 118.0159). Elemental analysis. Calculated C 57.55, N 36.14, H 6.32 Found C 57.24, N 36.20, H 6.29, O 0.27.

1-Methyl-4-amino-4H-1,2,4-triazol-1-ium iodide was synthesized according to the literature procedure.³ To a solution of 4H-1,2,4-triazol-4-amine (2.93 g, 35 mmol) in *iso*-propanol (150 mL), iodomethane (14.86 g, 105 mmol) was added in one portion. The solution was stirred at room temperature for 6 days. An additional amount of iodomethane (2.84 g, 20 mmol) was added to the reaction mixture and stirring was continued for another 6 days. The precipitate was filtered off, washed with cold *iso*-propanol (3x5 mL) and diethyl ether (2x10 mL) and dried in vacuum affording white solid. Yield: 6.6 g, 84%. Elemental analysis calculated C 15.94, N 24.79, H 3.12 Found C 16.05, N 23.62, H 3.168. ¹H NMR (400 MHz, DMSO-d₆): δ 4.03 (s, 3H, CH₃), 6.93 (br.s., 2H, NH₂), 9.15 (s, 1H, CH), 10.11 (s, 1H, CH). ¹³C NMR (400 MHz, DMSO-d₆): δ 39.07 (s, CH₃), 142.86 (s, CH), 144.96 (s, CH).

1-Methyl-4-amino-4H-1,2,4-triazol-1-ium 4,5-dicyano-1,2,3-triazol-2-ide (IL2). To a stirred suspension of silver(I) 4,5-dicyano-1,2,3-triazol-2-ide (2.36 g, 10 mmol) in MeOH (15 mL), a solution of 4-amino-1-methyl-4H-1,2,4-triazol-1-ium iodide (2.36 g, 10 mmol) in MeOH (25 mL) was added in one portion. The reaction mixture was stirred at room temperature overnight. The precipitate was filtered off and washed with methanol. Methanol solution was flash chromatographed through silica gel. After methanol evaporation, the yellow oily residue was dried in vacuum (0.1 mbar, 80°C). Yield: 2.13 g, 94%. ¹H NMR (400 MHz, DMSO-d₆): δ 4.029 (s, 3H, CH₃), 6.963 (s, 2H, NH₂), 9.148 (s, 1H, CH), 10.079 (s, 1H, CH). ¹³C NMR (400 MHz, DMSO-d₆): δ 38.9 (s, CH₃), 113.9 (s, C), 121.0 (s, C), 143.0 (s, CH), 145.1 (s, CH). HR-MS: 99.0668 (cation) (Calculated 99.0665), 118.0156 (Calculated 118.0159) (anion). Elemental analysis. Calculated C 38.71, N 58.04, H 3.25 Found C 38.57, N 57.50, H 3.57, O 0.35.

3-Nitro-1H-1,2,4-triazole. 3-aminotriazole-1,2,4 (8.4 g, 100 mmol) was dissolved in HCl solution (18.2 mL, 37 wt. %).⁴ The resultant solution was carefully added dropwise to a solution of NaNO₂ (19.32 g, 280 mmol) in water (45 mL), stirred at room temperature. Evolution of brown gas was observed. Reaction mixture was stirred at room temperature for 1 hour, then heated at +50 °C for 30 min and cooled to room temperature. A solution of HCl was added to pH = 1, followed by addition of urea (3.5 g) solution in water (4 mL). The mixture was cooled in an ice bath. The precipitate was filtered, washed thoroughly with water and dried in vacuum affording a white solid. Yield: 8.04 g, 71%. ¹H NMR (400 MHz, DMSO-d₆): δ 8.84 (s, 1H, CH). ¹³C NMR (400 MHz, DMSO-d₆): δ 146.18 (s, CH), 163.09 (s, C).

Silver(I) 3-nitro-1,2,4-triazol-1-ide. 3-nitro-1H-1,2,4-triazole (1.0 g, 8.8 mmol) was dissolved in a solution of NaOH (342 mg, 8.6 mmol) in water (30 mL) followed by addition of AgNO₃ (1.49 g, 8.8 mmol) solution in water (20 mL). A pale yellow solid precipitated. It was filtered, washed thoroughly with water and dried in vacuum at +50 °C. Yield: 1.89 g, 100%.

1-Butyl-2,3-dimethyl-1H-imidazol-3-ium 3-nitro-1,2,4-triazol-1-ide (IL3). To a suspension of silver(I) 3-nitro-1,2,4-triazol-1-ide (1.91 g, 8.6 mmol) in MeOH (25 mL), a solution of 1-butyl-2,3-dimethyl-1H-imidazol-3-ium chloride (1.61 g, 8.5 mmol) in MeOH (10 mL) was added in one portion. The mixture was stirred at room temperature overnight. The precipitate was filtered off and washed with methanol. Methanol solution was flash chromatographed through silica gel. After methanol evaporation, the oily residue was dried in vacuum (0.1 mbar, 80°C) affording a yellow liquid. Yield: 2.08 g, 92%. ¹H NMR (400 MHz, DMSO-d₆): δ 0.891 (t, ³J_{H,H} = 7.5 Hz, 3H, CH₃), 1.268 (sex, ³J_{H,H} = 7.5 Hz, 2H, CH₂), 1.674 (quint, ³J_{H,H} = 7.5 Hz, 2H, CH₂), 2.579 (s, 3H, CH₃), 3.747 (s, 3H, CH₃), 4.101 (t, ³J_{H,H} = 7.5 Hz, 2H, CH₂), 7.630 (d, ³J_{H,H} = 2.0 Hz, 1H, CH), 7.657 (d, ³J_{H,H} = 2.0 Hz, 1H, CH), 7.727 (s, 1H, CH). ¹³C NMR (400 MHz, DMSO-d₆): δ 9.13 (s, CH₃), 13.4 (s, CH₃), 18.9 (s, CH₂), 31.2 (s, CH₂), 34.7 (s, CH₃), 47.3 (s, CH₂), 120.9 (s, CH), 122.3 (s, CH), 144.2 (s, C), 151.6 (s, CH). HR-MS: 153.1471 (cation) (Calculated 153.1386), 113.0090 (Calculated 113.0105) (anion). Elemental analysis. Calculated C 49.61, N 31.56, H 6.81, O 12.02 Found C 49.55, N 31.52, H 6.85, O 12.08.

Table S1. Elemental composition of ILs.

		C, ^a wt. %	H, ^a wt. %	N, ^a wt. %	O, ^b wt. %	Cl, ^b wt. %	Ag, ^b wt. %	w _w ^c	x _w ^d	Purity ^e
IL-1	Calc.	57.55	6.32	36.14	-	-	-			
	Found	57.24± 0.065	6.29± 0.026	36.20± 0.025	0.27± 0.03	0.00	0.00	0.00832	0.112	0.982
IL-2	Calc.	38.71	3.25	58.04	-	-	-			
	Found	38.57± 0.06	3.57± 0.002	57.50± 0.025	0.35± 0.07	0.00	0.00	0.0144	0.150	0.968
IL-3	Calc.	49.61	6.81	31.56	12.02	-	-			
	Found	49.55± 0.095	6.85± 0.072	31.52± 0.024	12.08 ±0.16	0.00	0.00	0.0102	0.133	0.982

^a C, H, N were determined by combustion elemental analysis as an average of two measurements;

^b O, Cl, Ag elements were determined by EDX;

^c water mass fraction determined by Karl-Fischer titration method;

^d water mole fraction;

^e determined combining ¹H NMR, EDX and water content data.

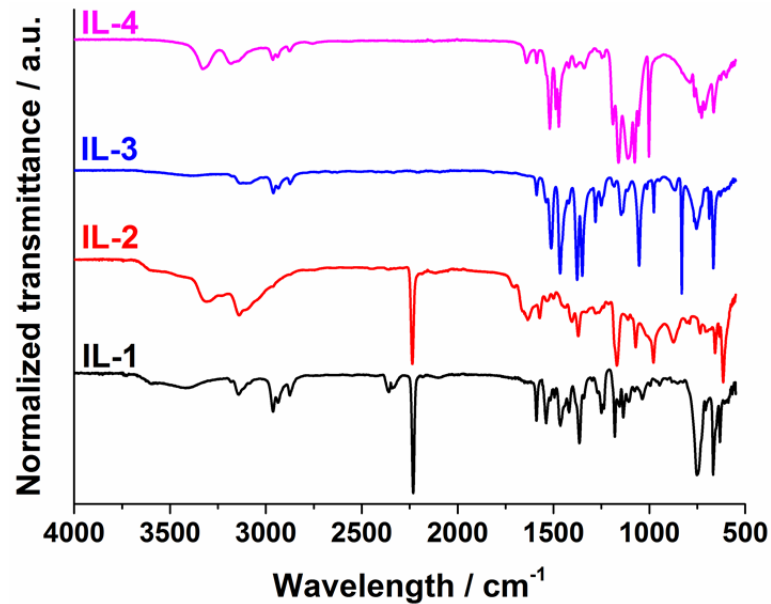


Figure S1 SX. FT-IR spectra of IL-X (X = 1, 2, 3, 4).

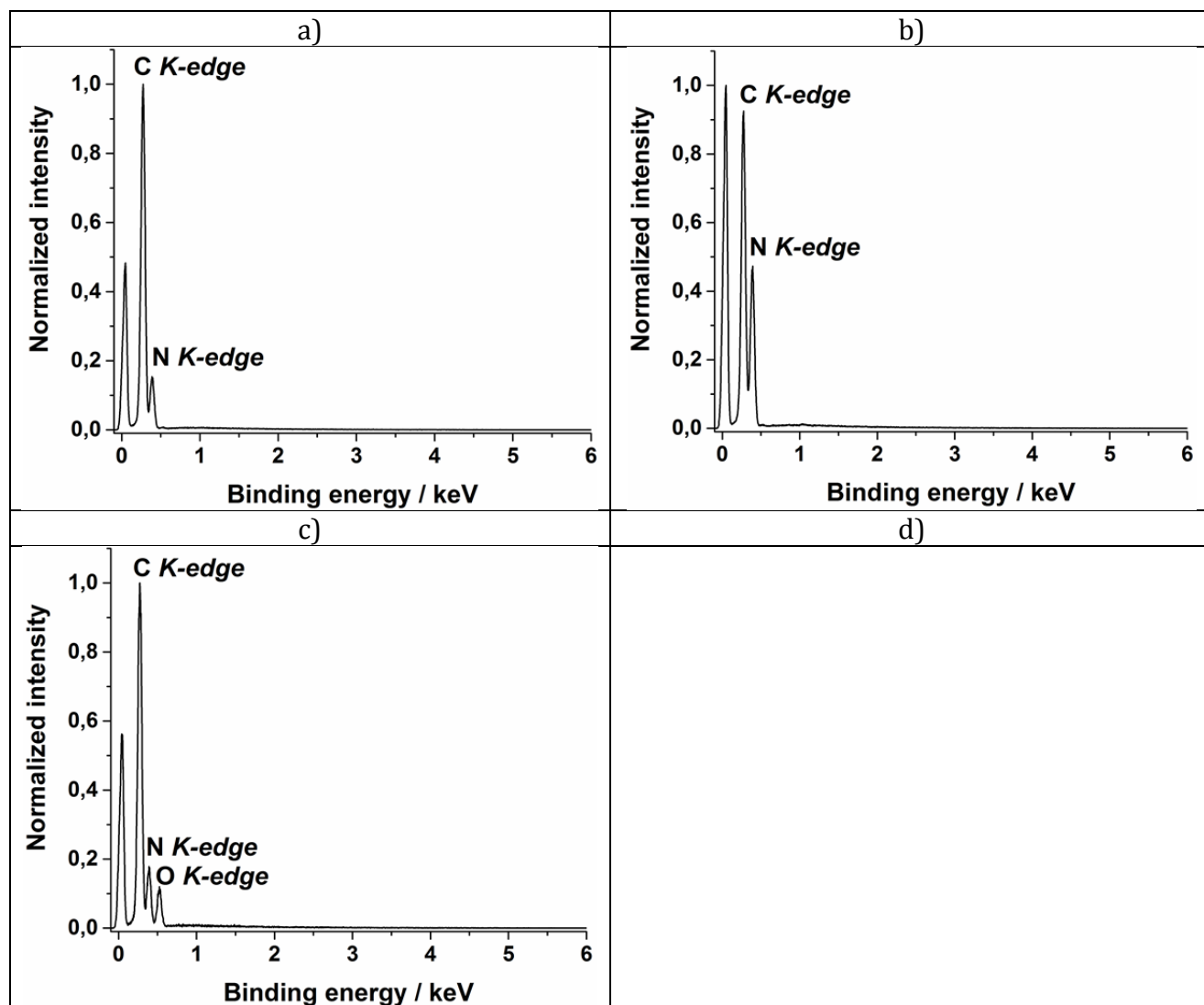


Figure S2. EDX spectra of IL-1 (a), IL-2 (b) and IL-3 (c).

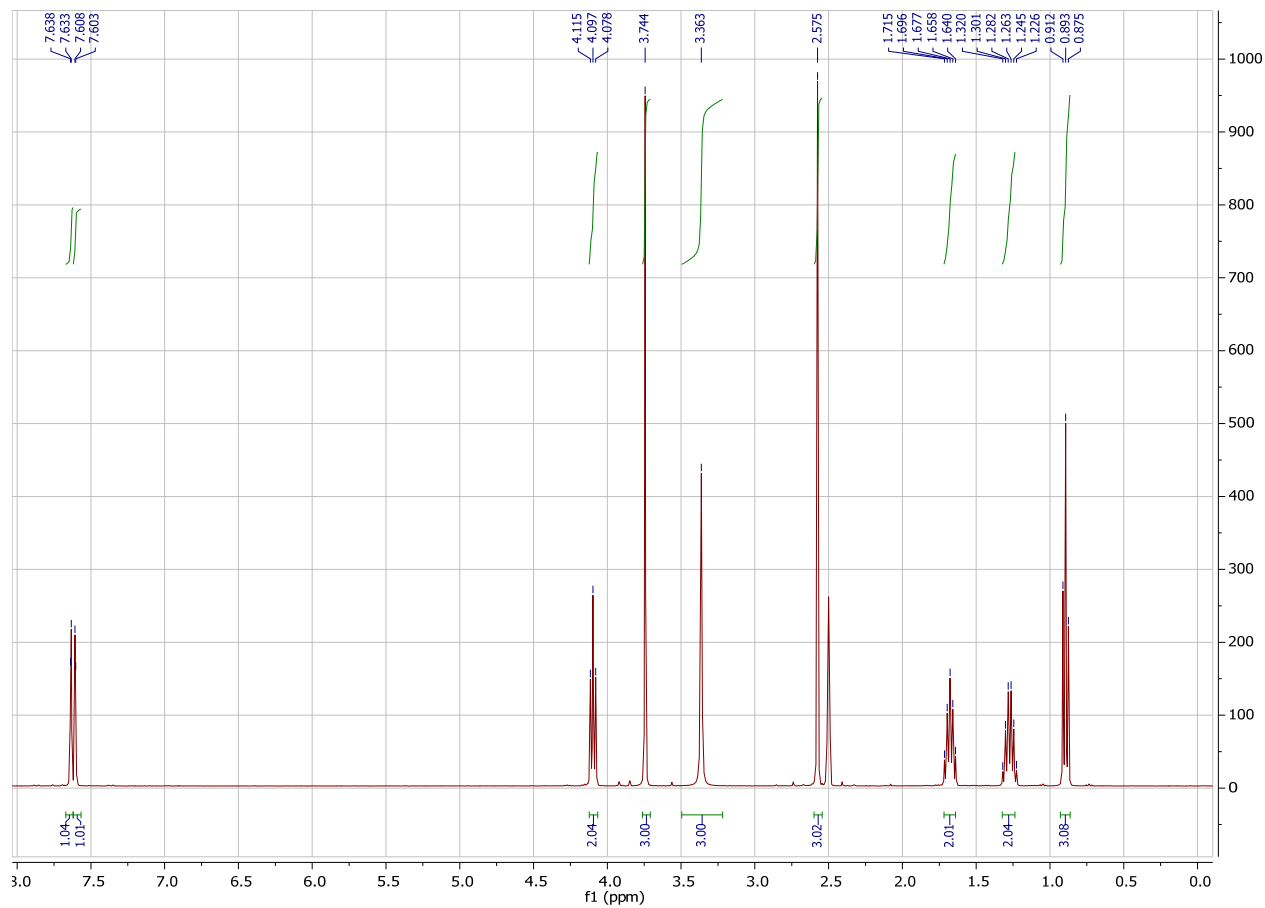


Figure S3. IL-1 ^1H NMR spectrum.

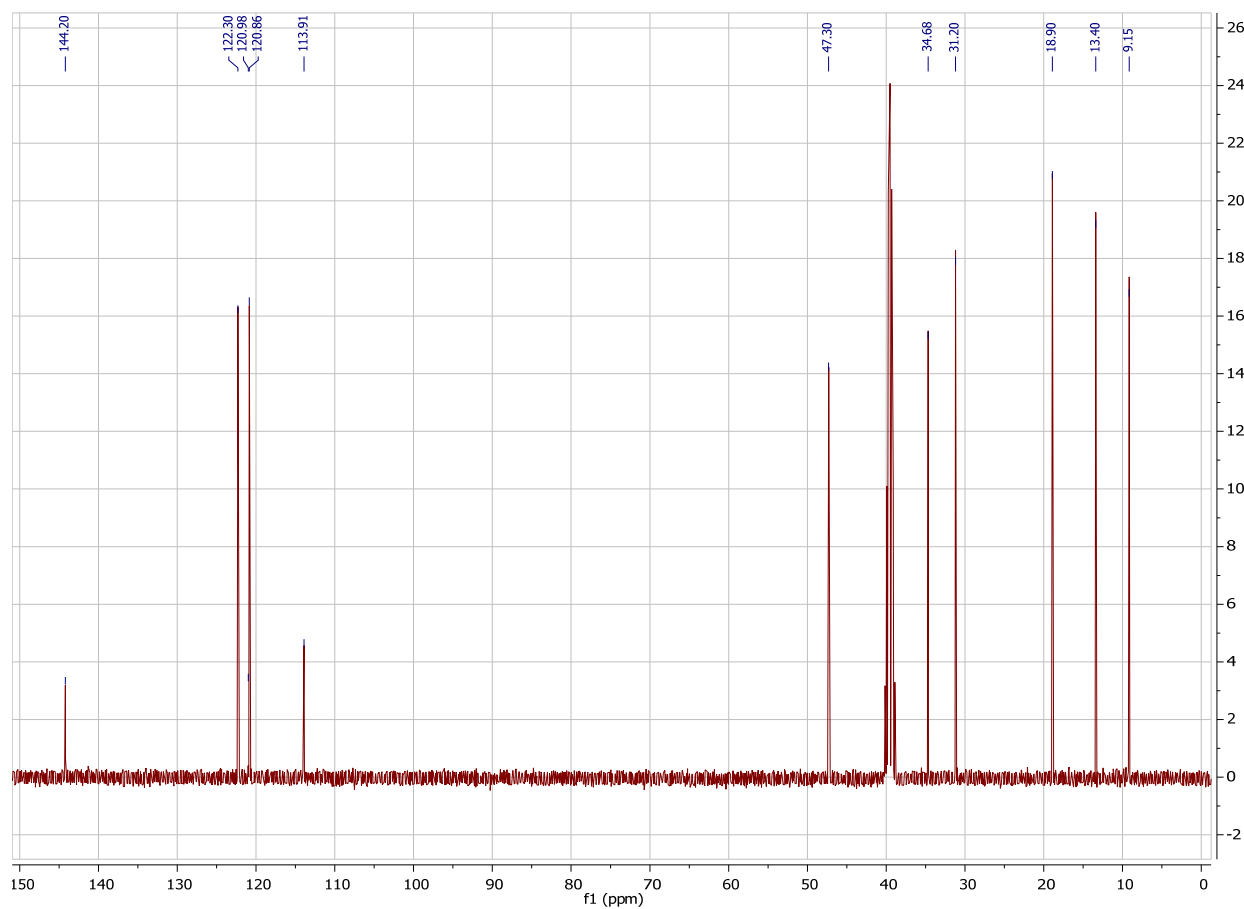


Figure S4. IL-1 ^{13}C NMR spectrum.



Figure S5. IL-1 COSY spectrum.

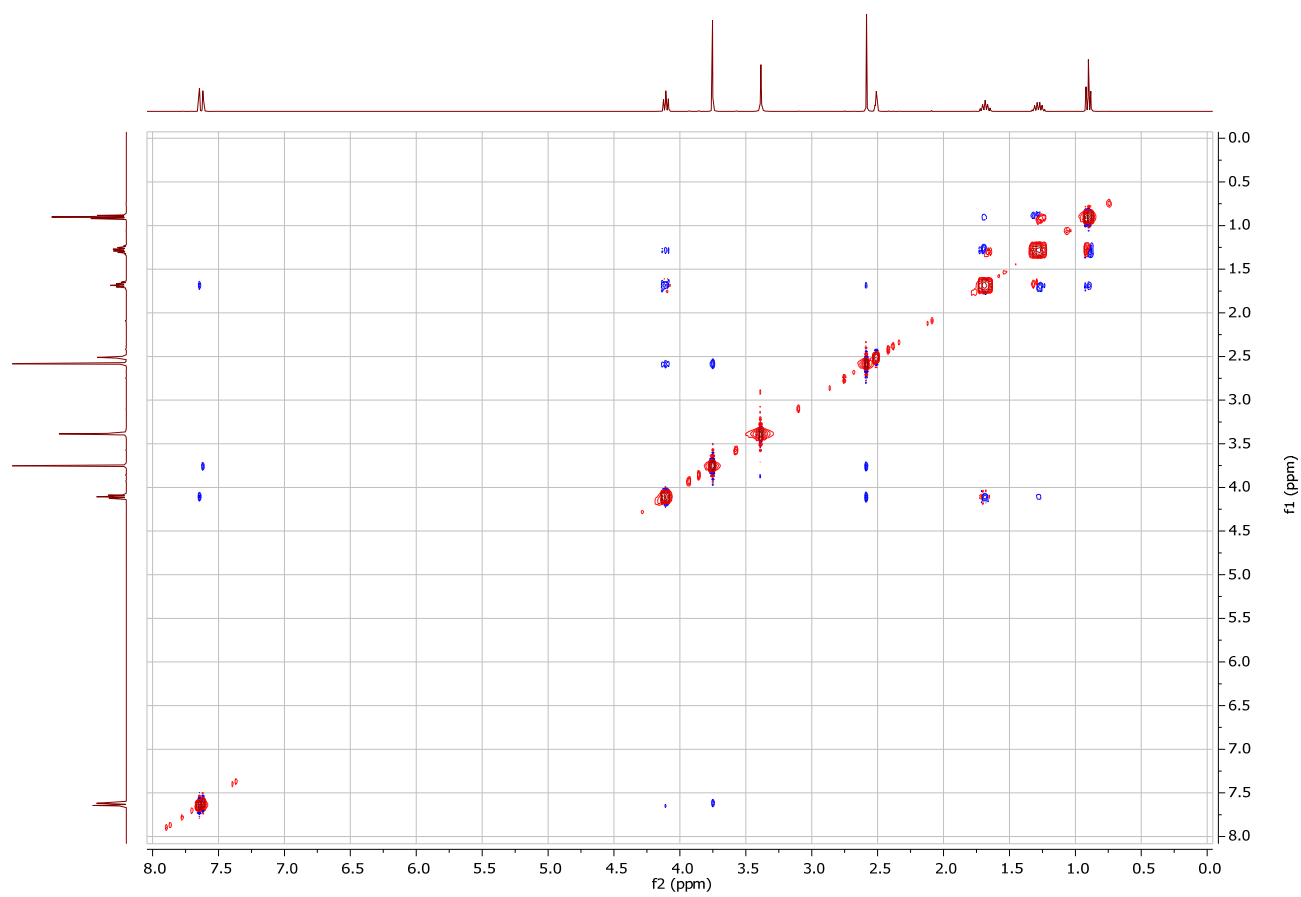


Figure S6. IL-1 NOESY spectrum.

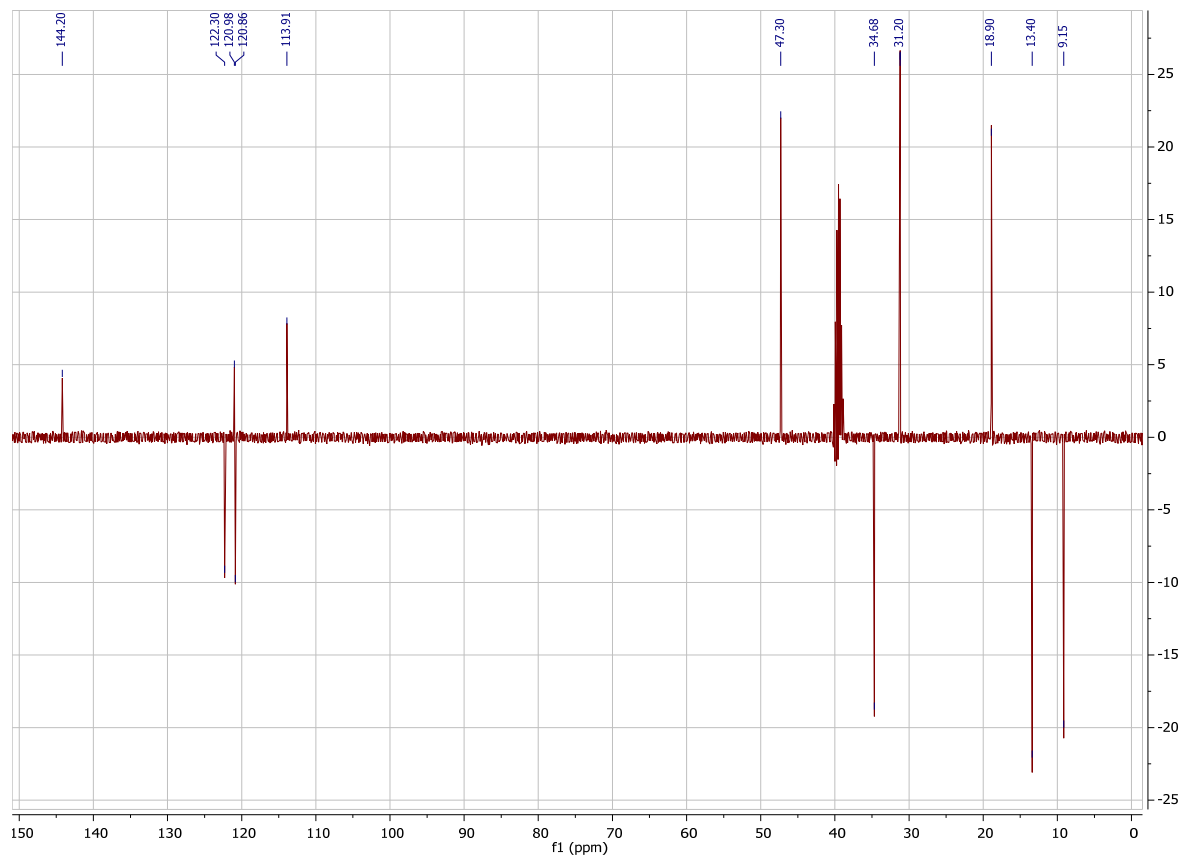
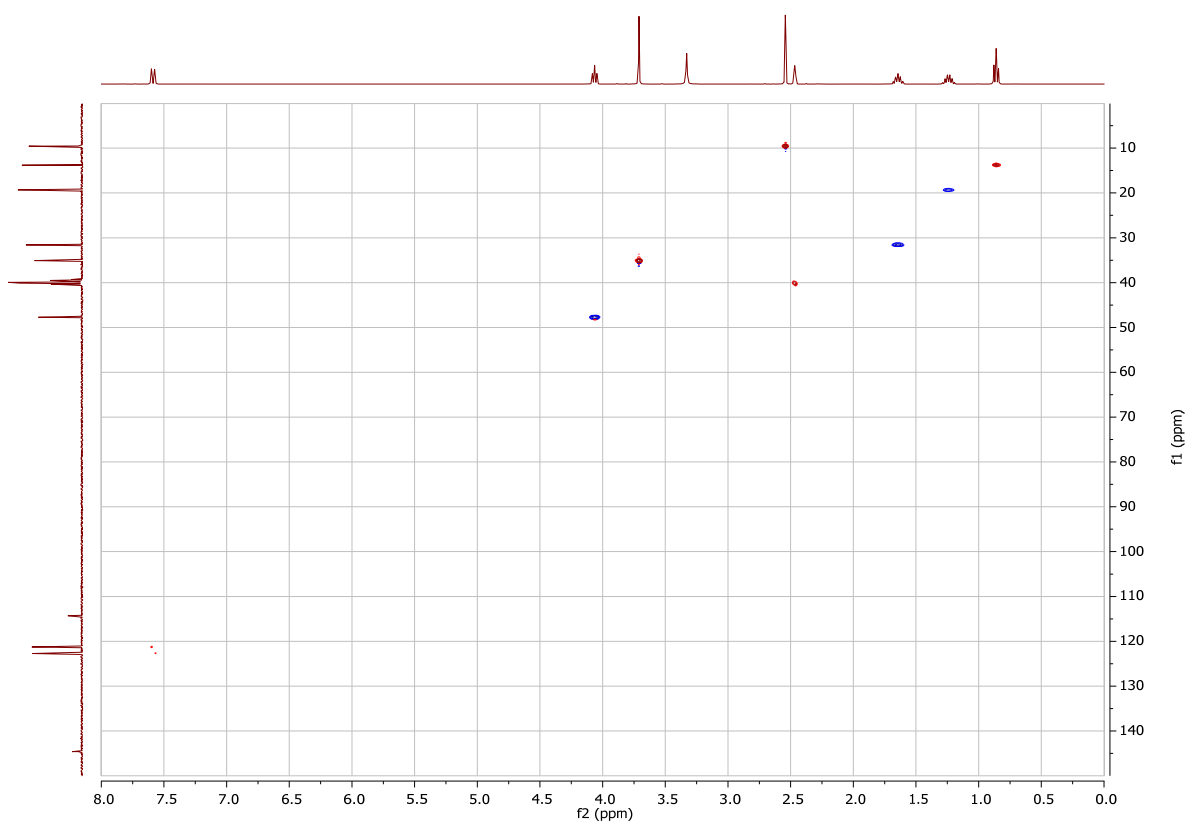


Figure S7. IL-1 ^{13}C APT spectrum.



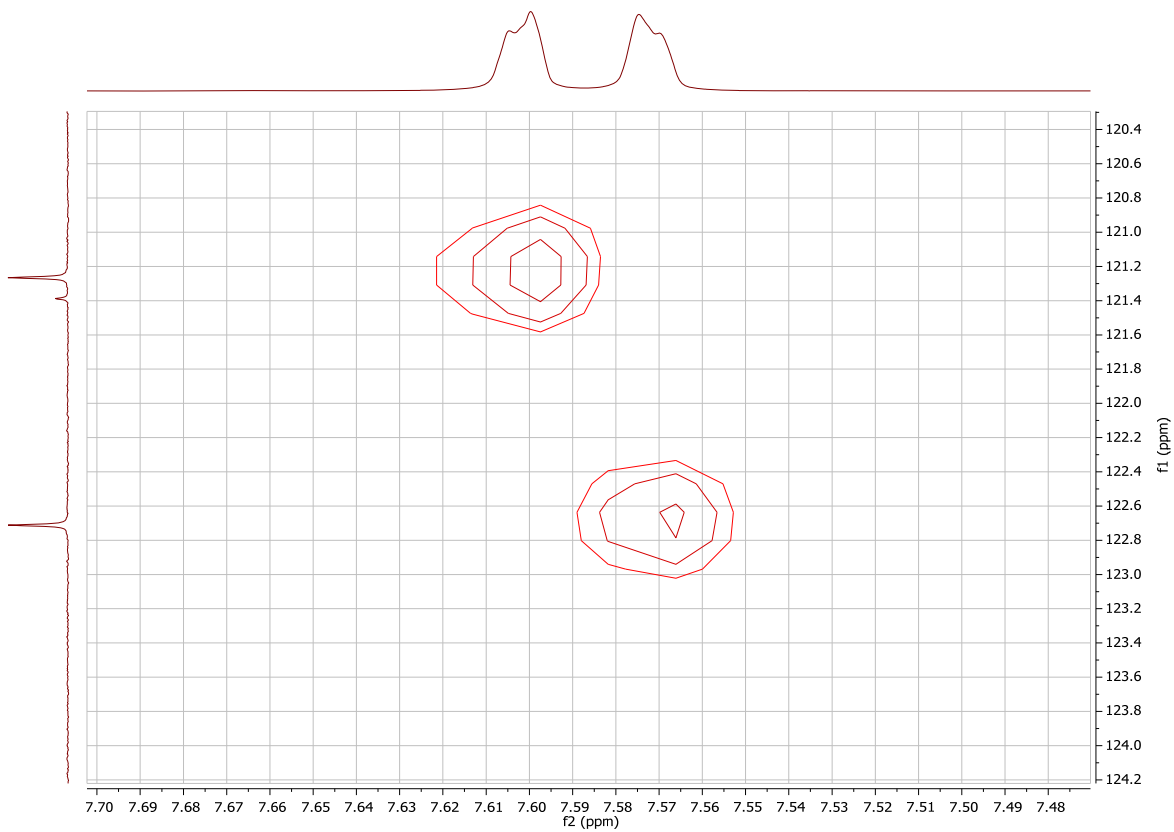


Figure S8. IL-1 HSQC spectra.

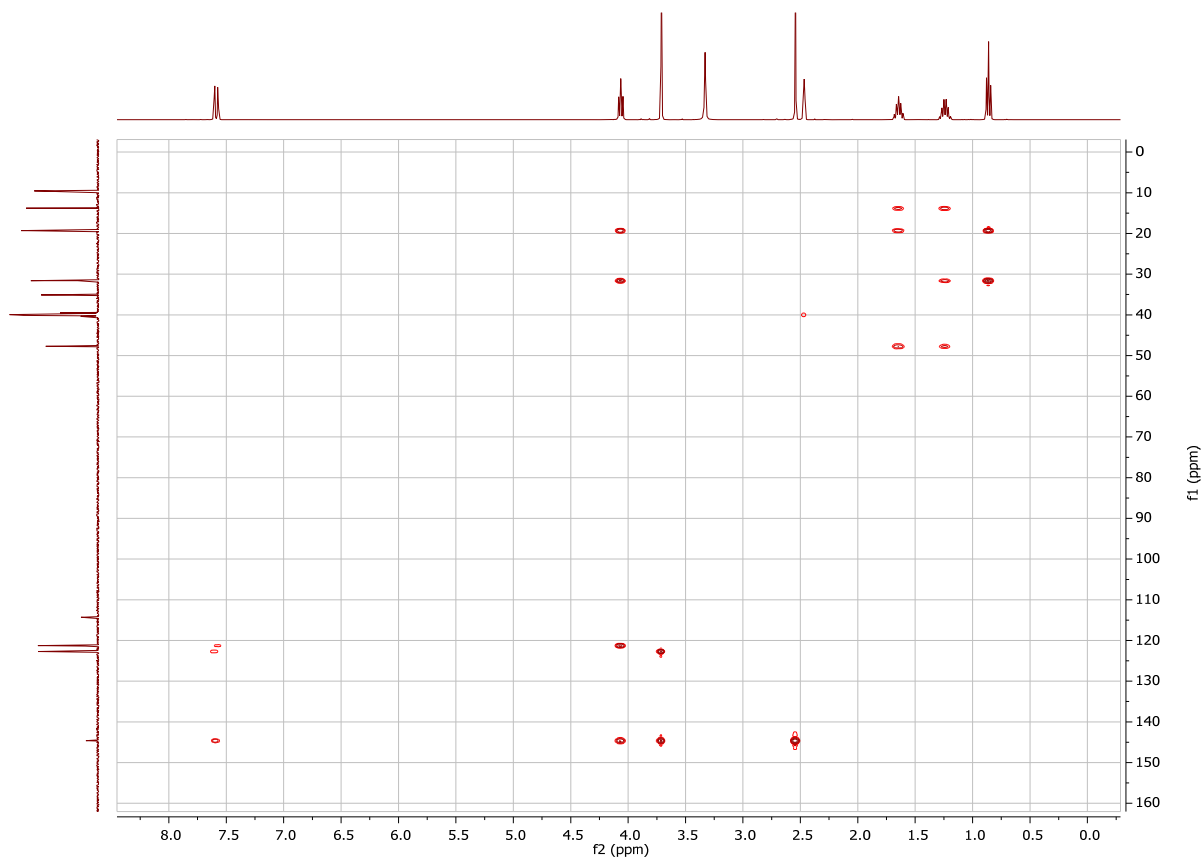


Figure S9. IL-1 HMBC spectra.

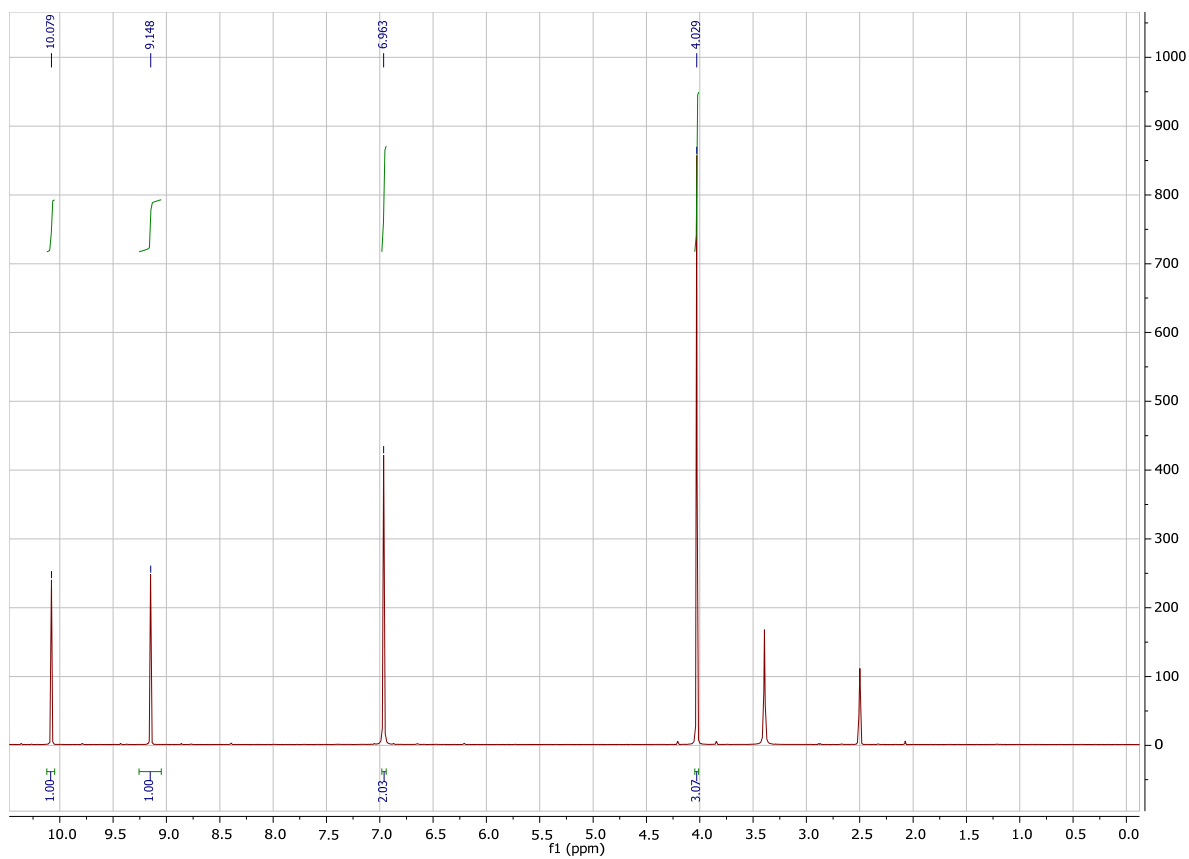


Figure S10. IL-2 ^1H NMR spectrum.

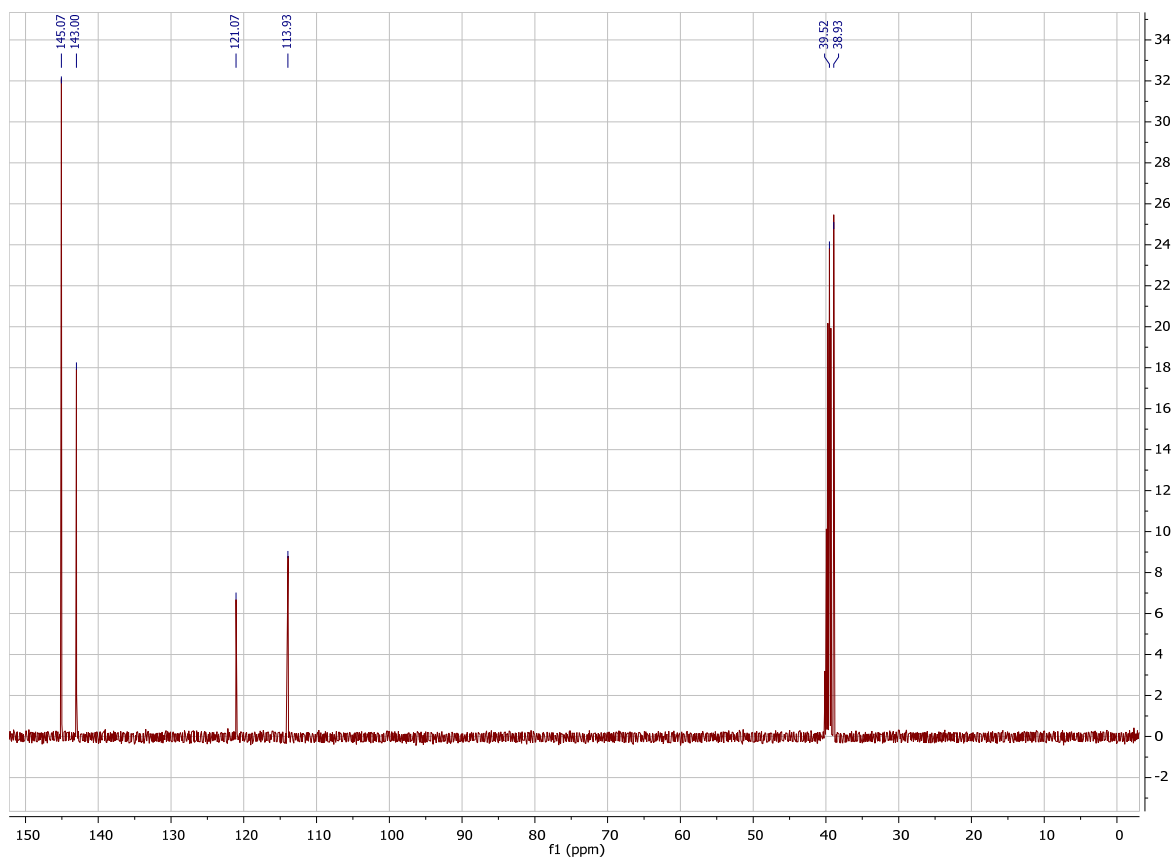


Figure S11. IL-2 ^{13}C NMR spectrum.

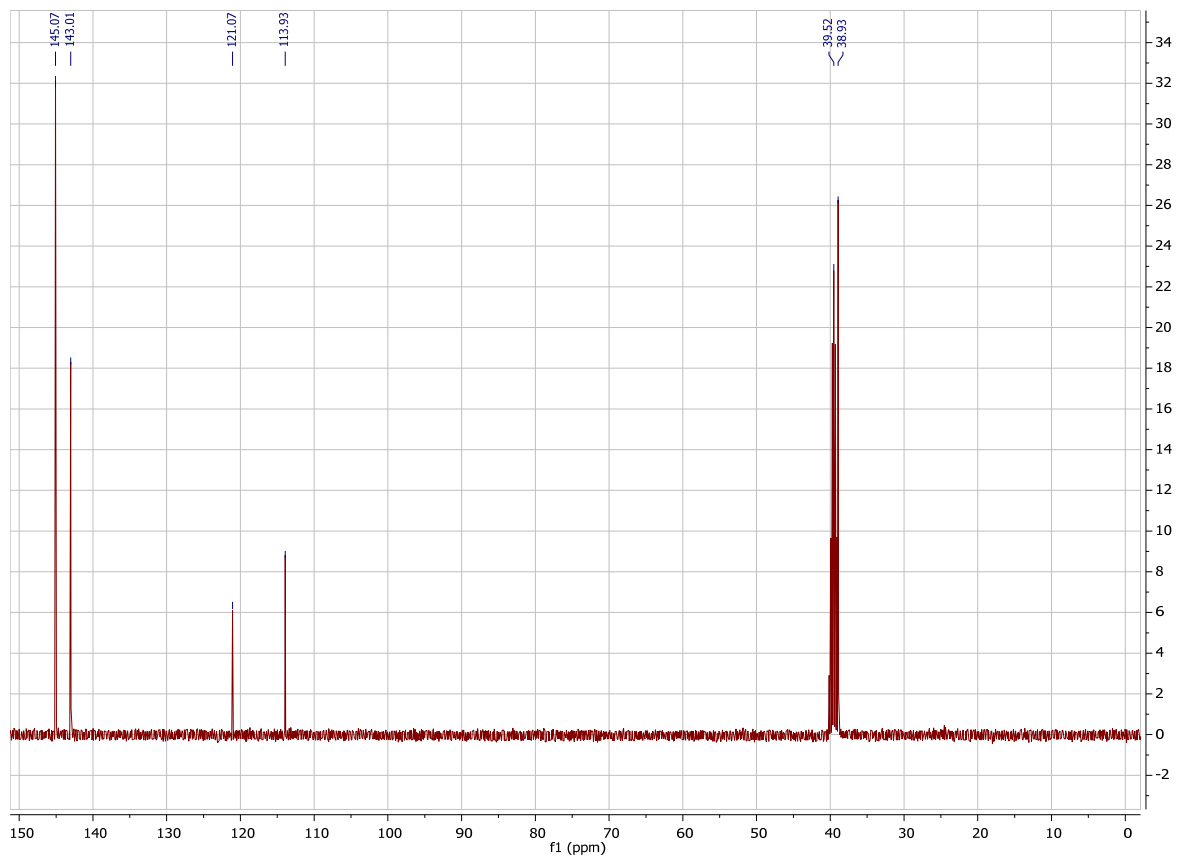


Figure S12. IL-2 ^{13}C APT spectrum.

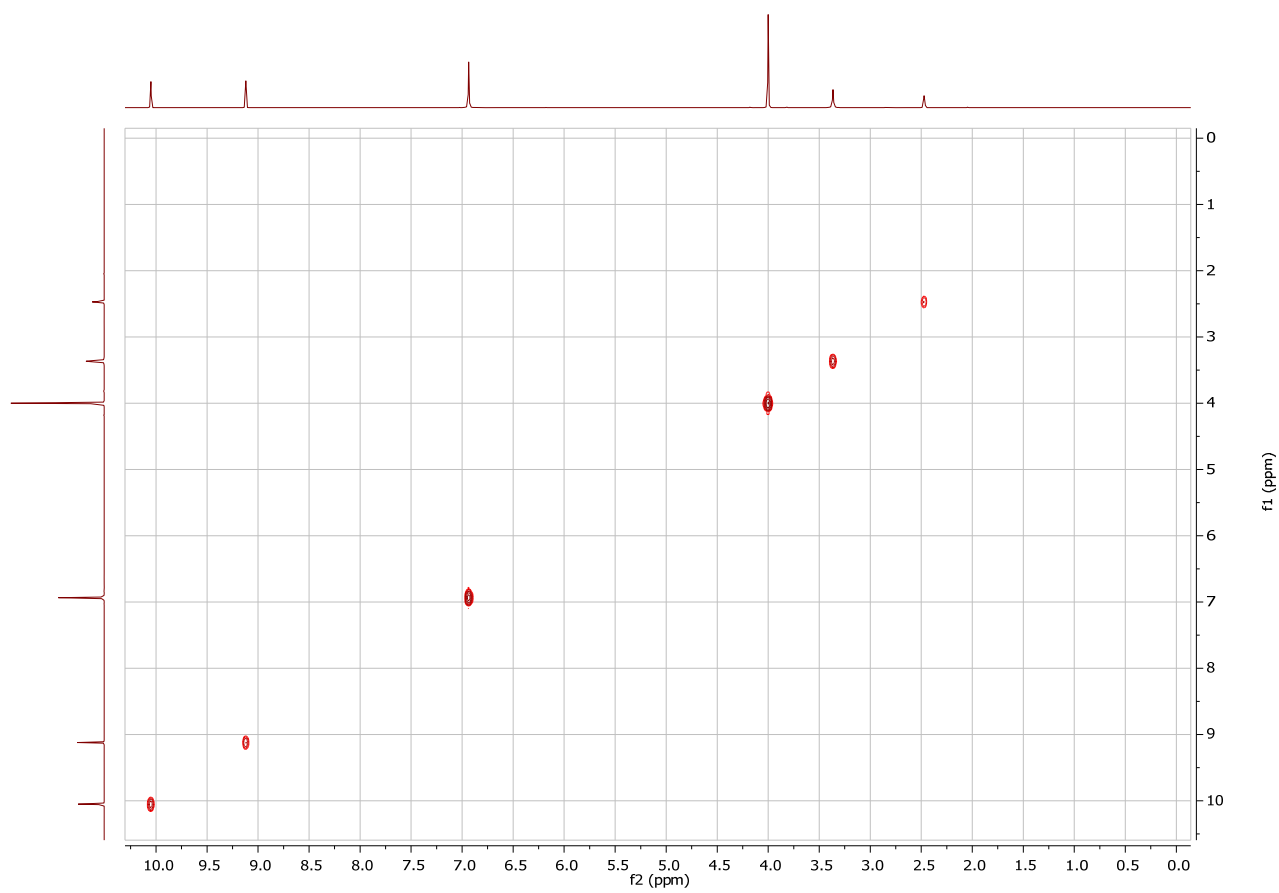


Figure S13. IL-2 COSY spectrum.

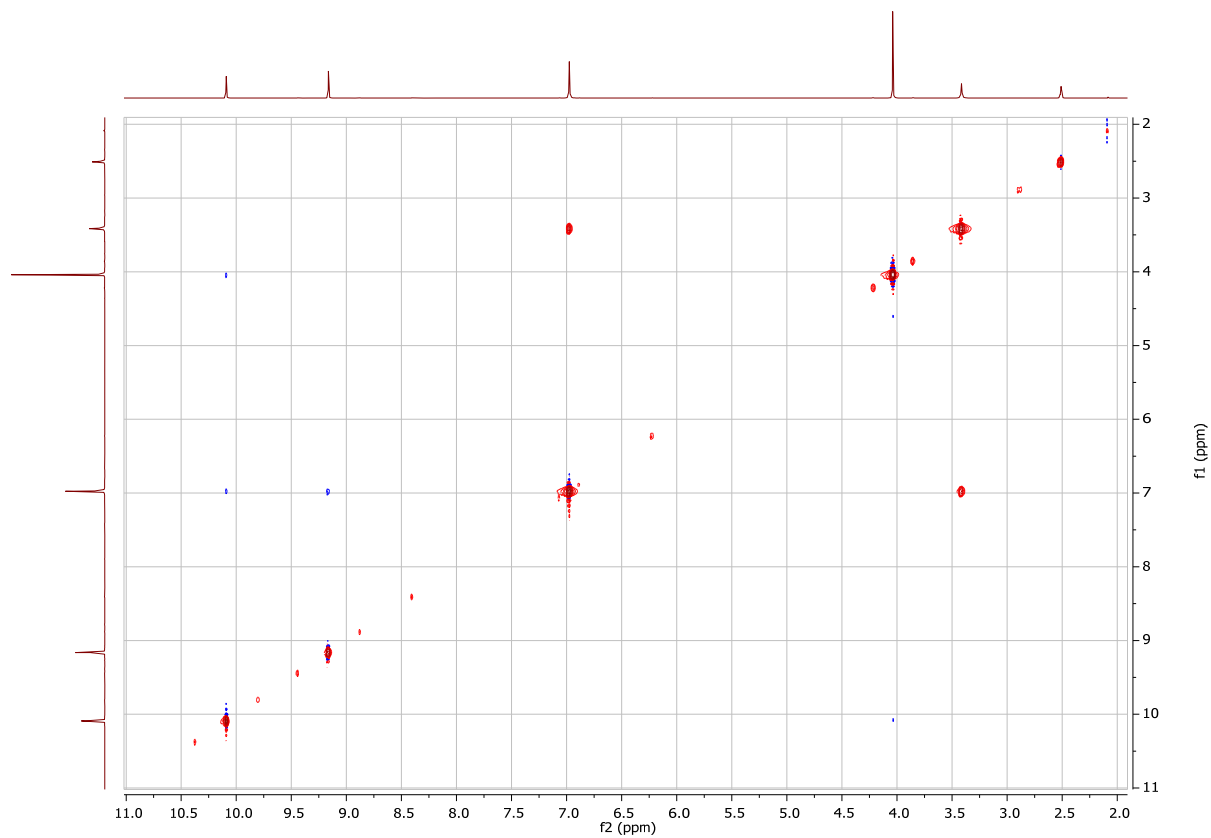


Figure S14. IL-2 NOESY spectrum.

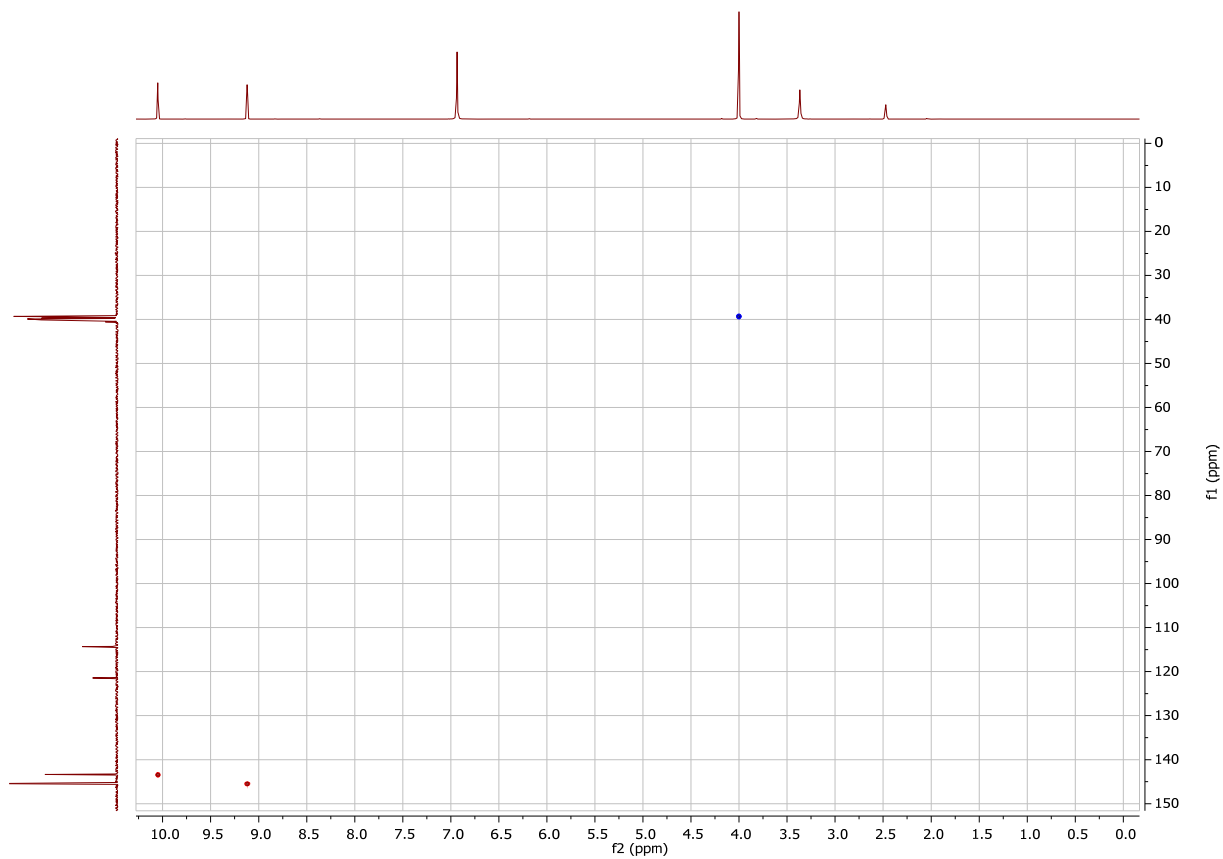


Figure S15. IL-2 HSQC spectrum.

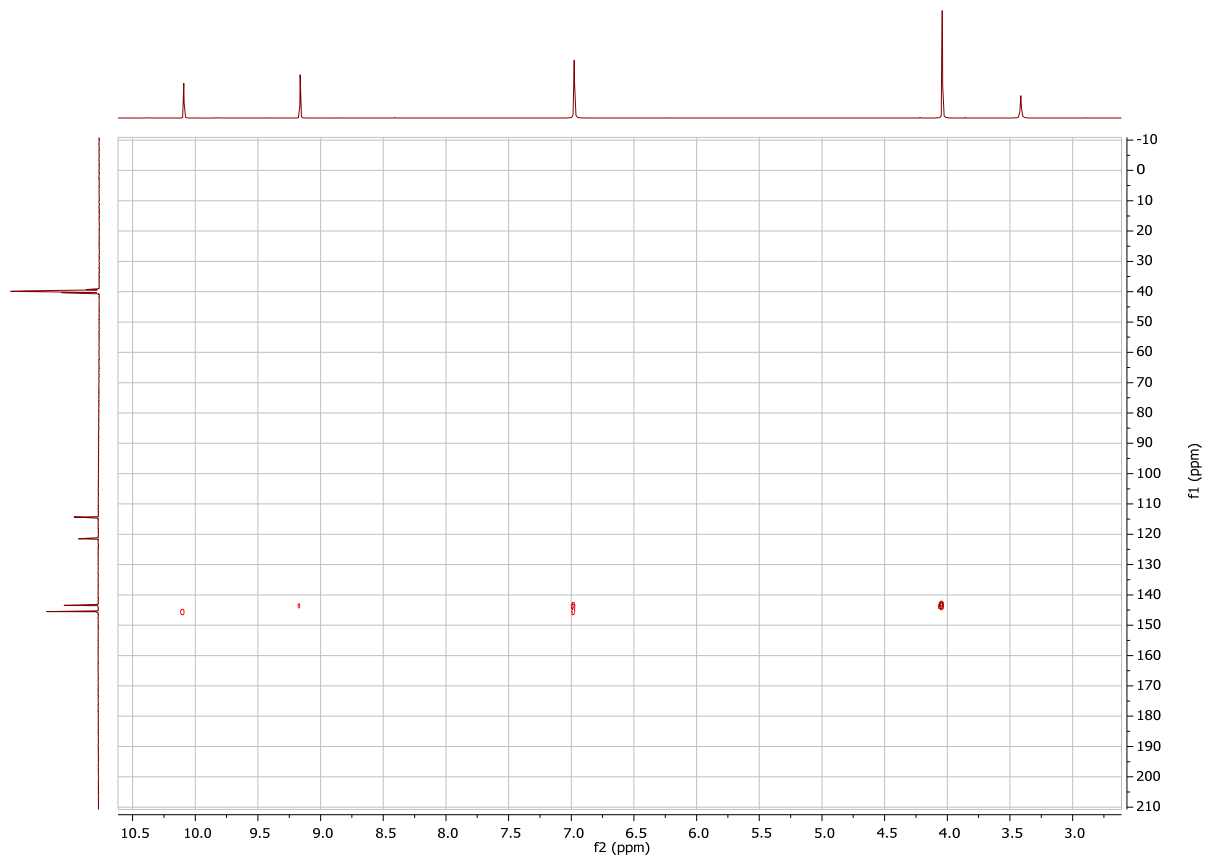


Figure S16. IL-2 HMBC spectrum.

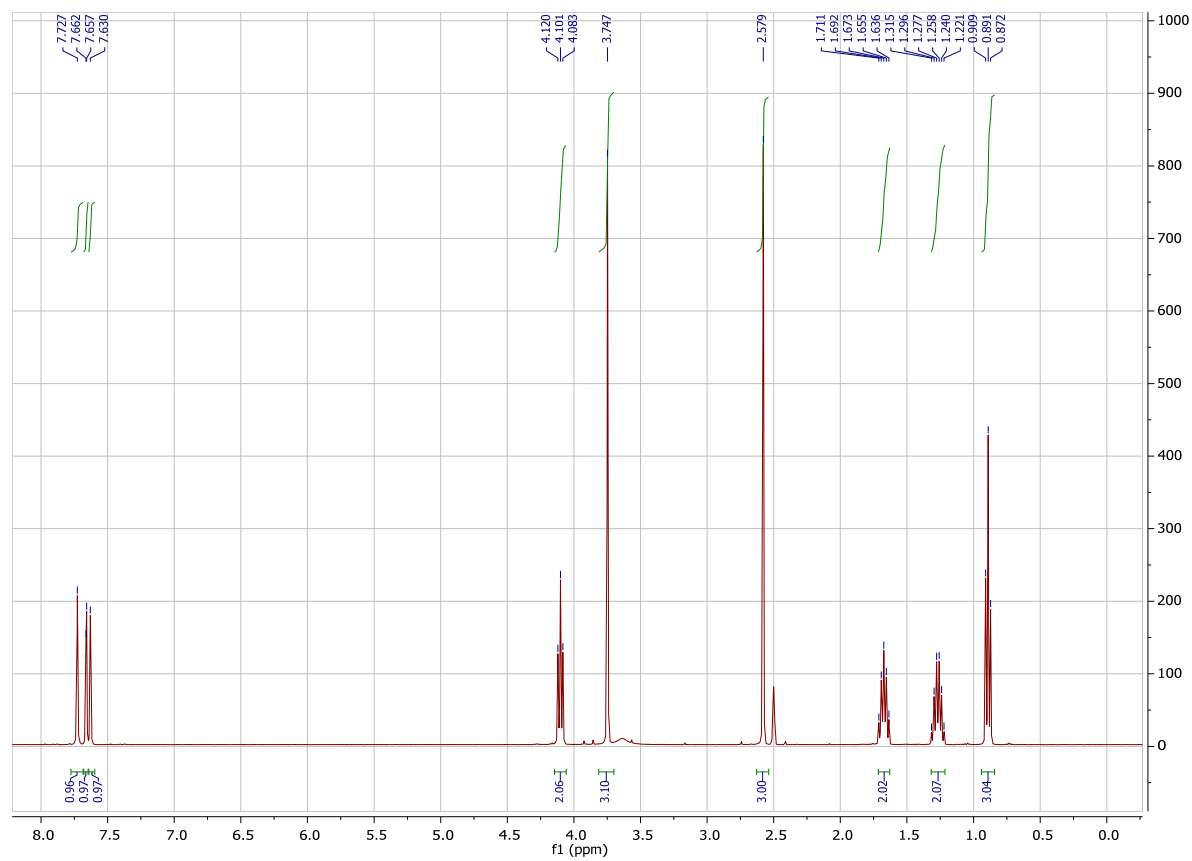


Figure S17. IL-3 ^1H NMR spectrum.

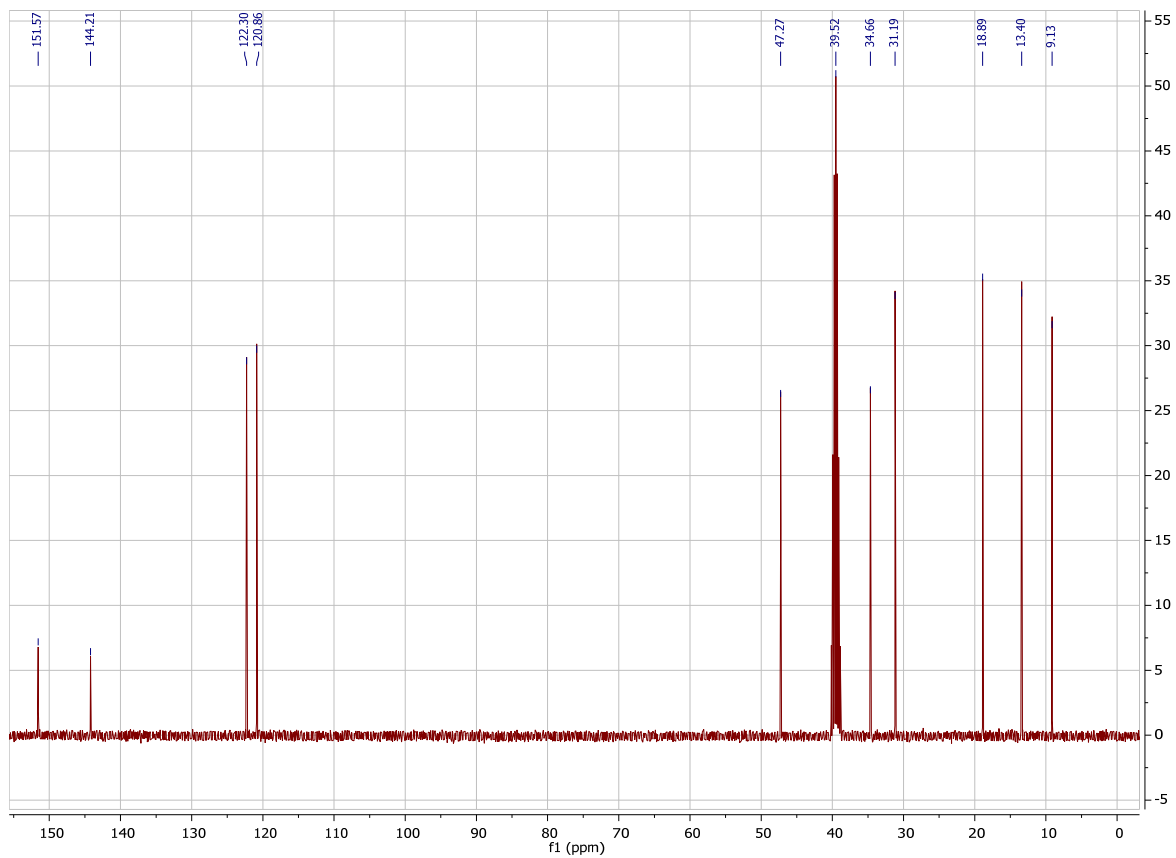


Figure S18. IL-3 ^{13}C NMR spectrum.

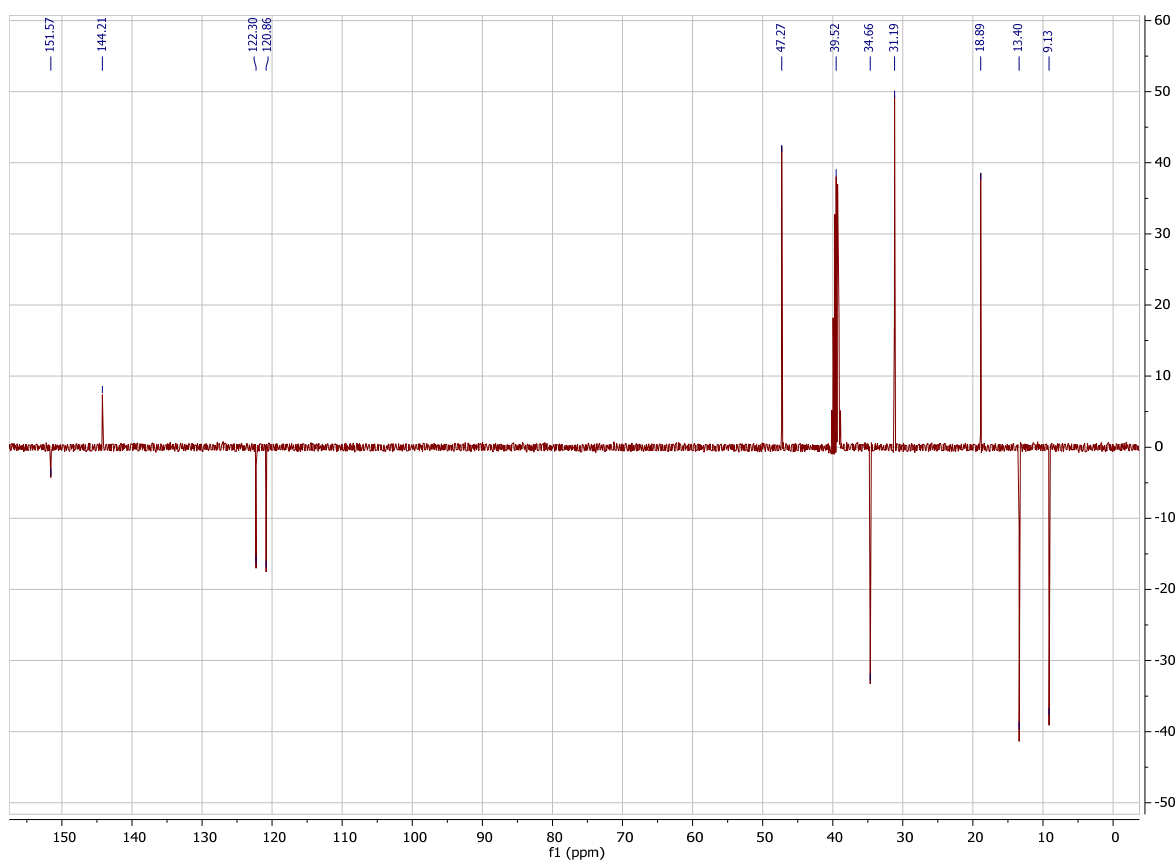


Figure S19. IL-3 ^{13}C APT NMR spectrum.

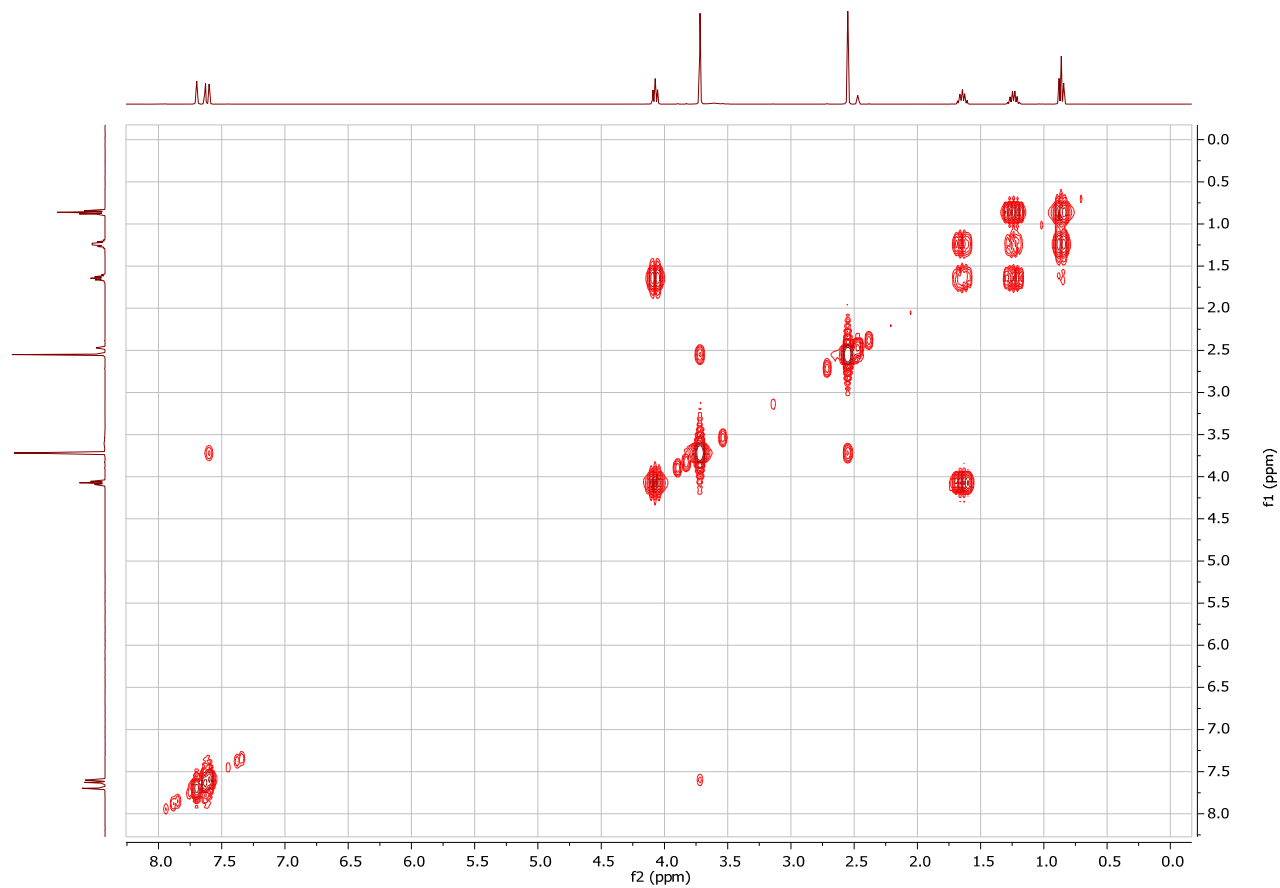


Figure S20. IL-3 COSY spectrum.

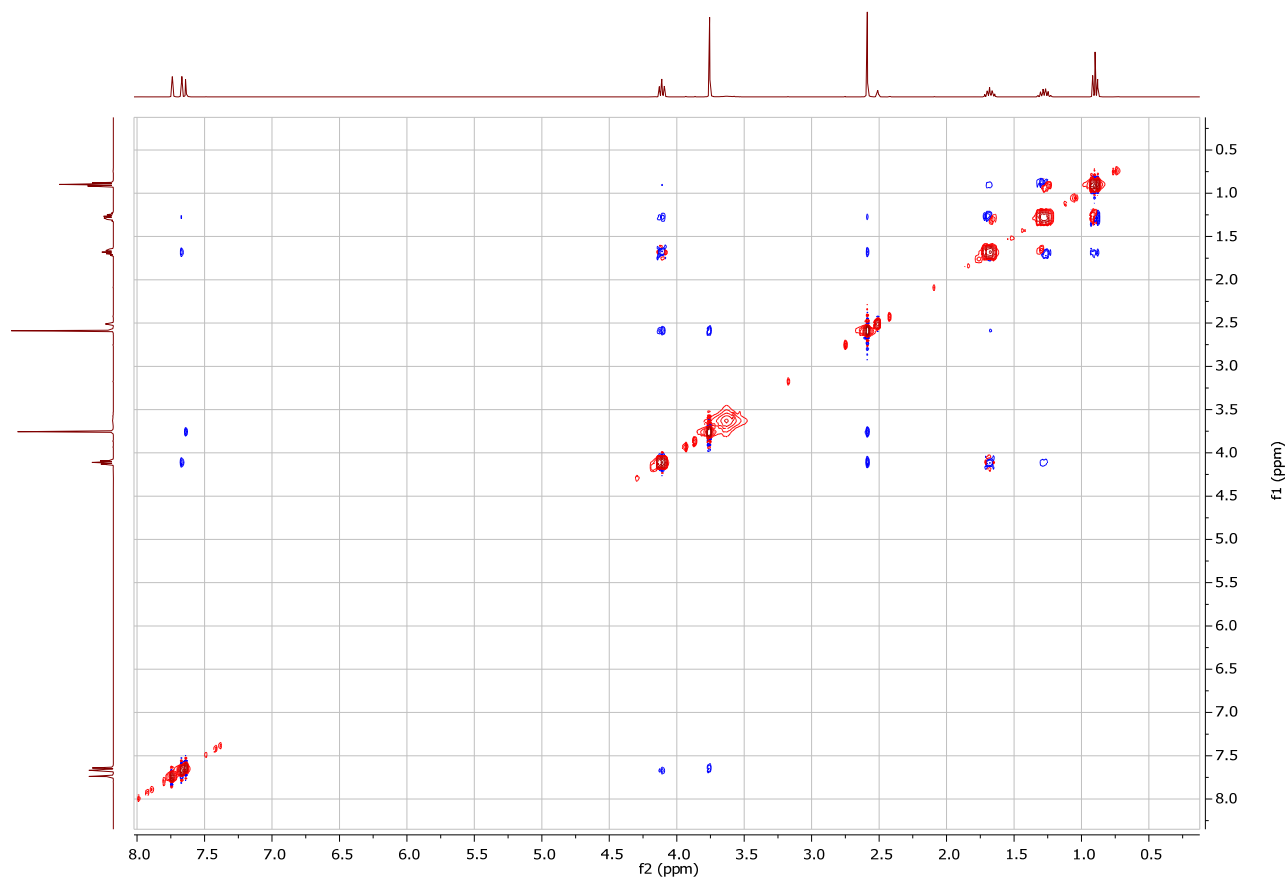


Figure S21. IL-3 NOESY spectrum.

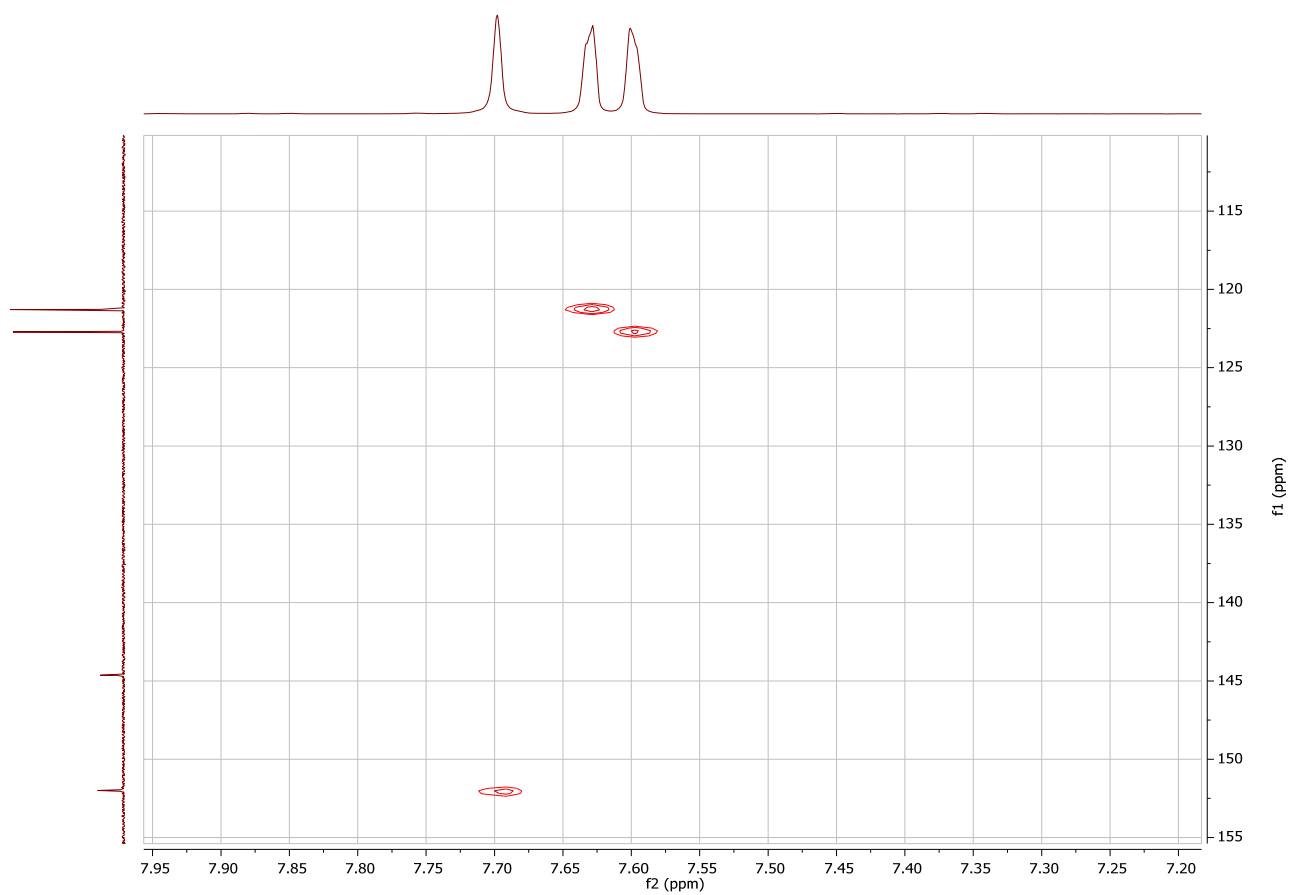
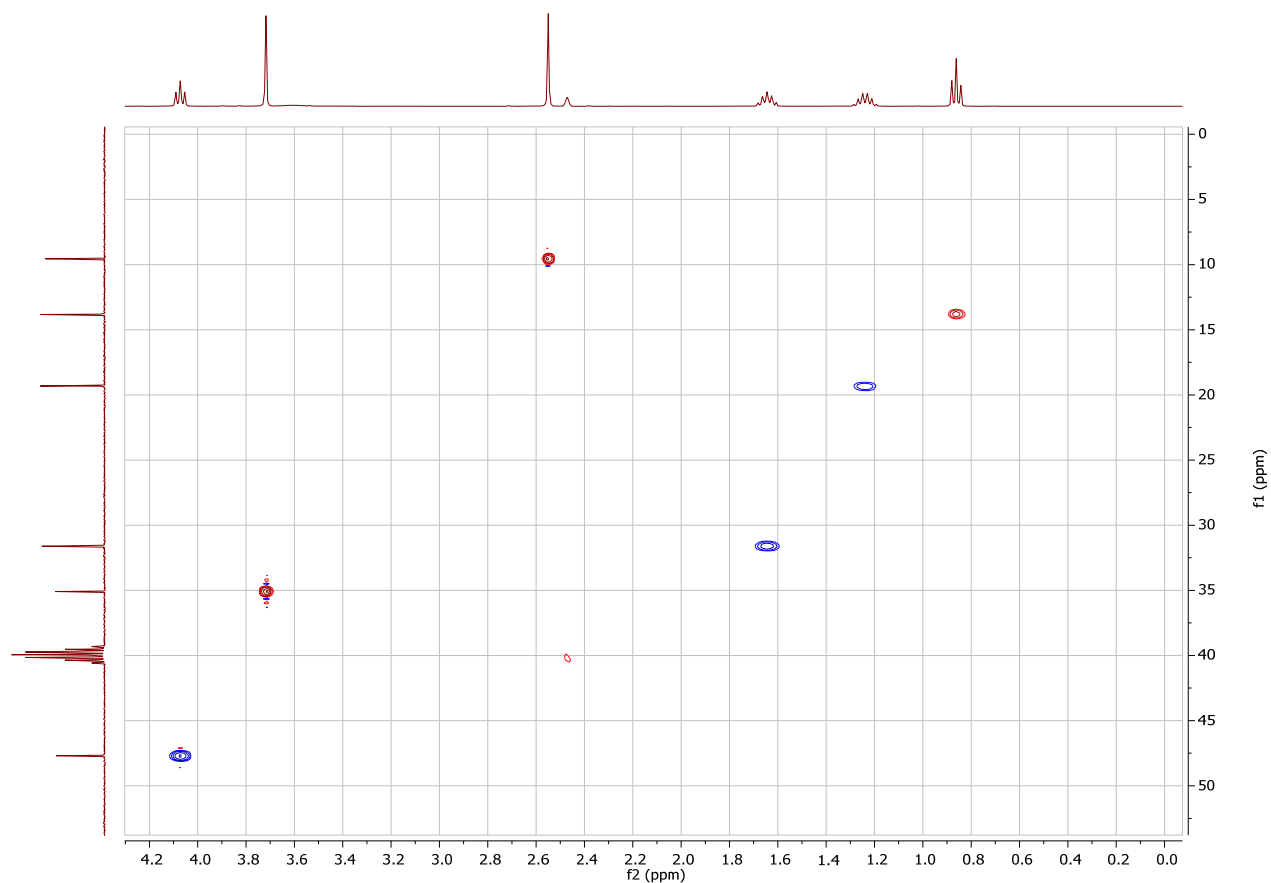


Figure S22. IL-3 HSQC spectrum.

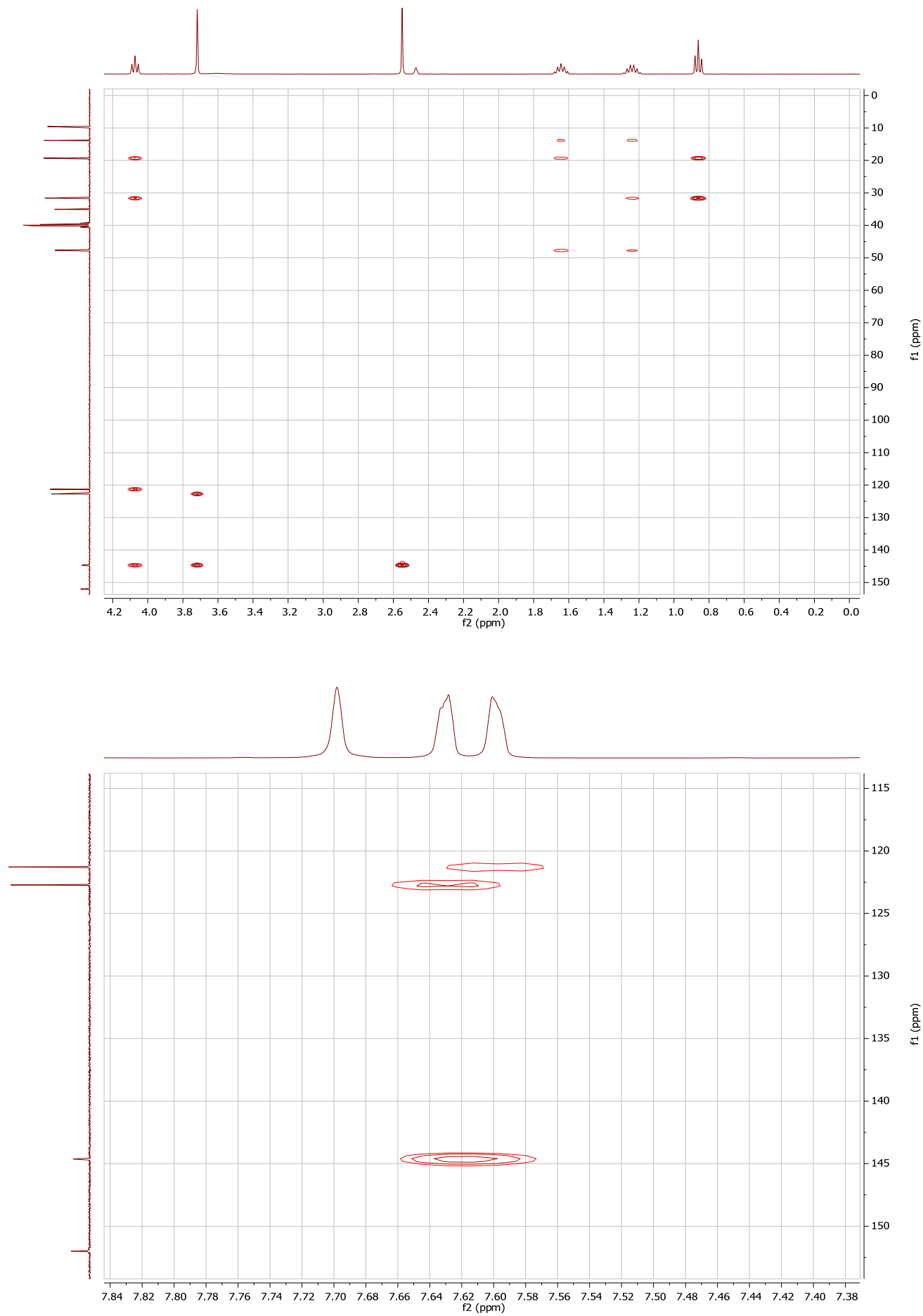
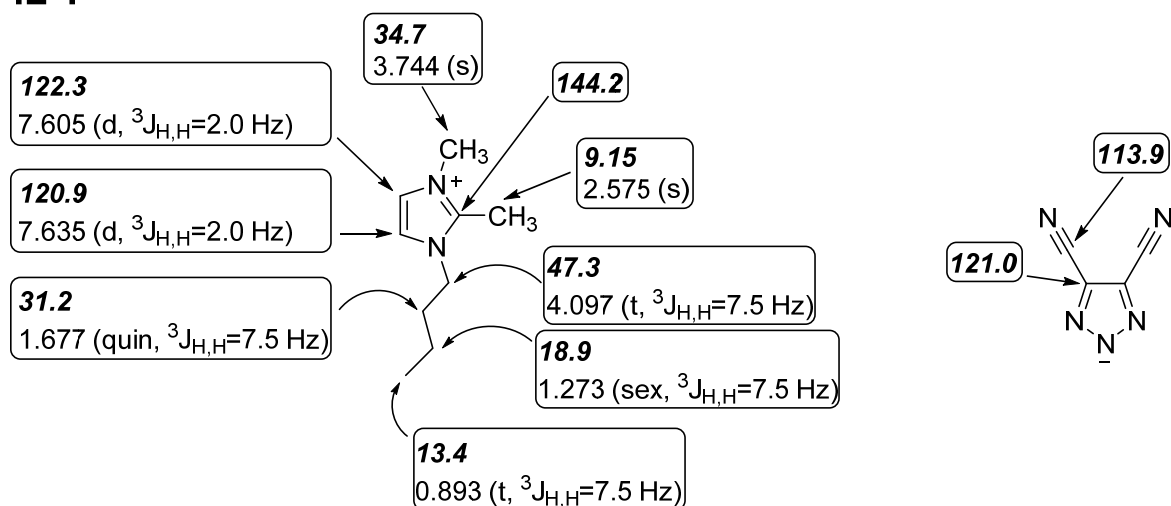
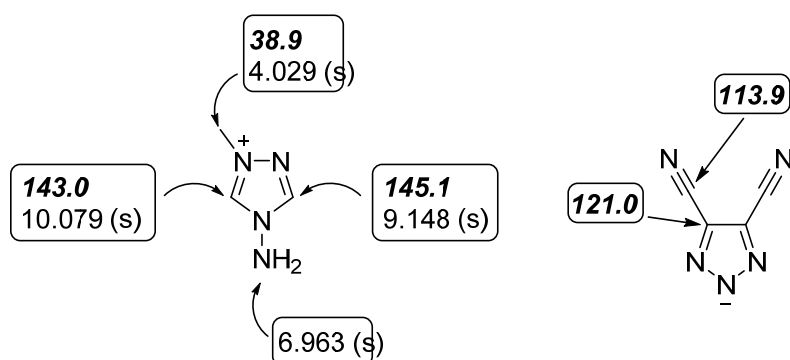


Figure S23. IL-3 HMBC spectrum.

IL-1



IL-2



IL-3

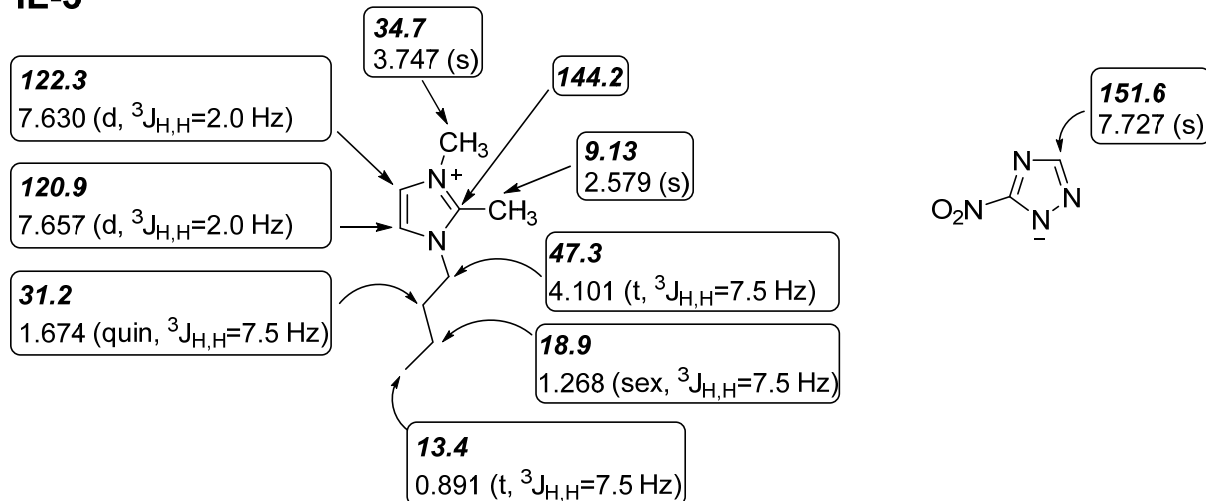


Figure S24. ILs NMR peaks assignment. Chemical shifts of carbon atoms are shown in bold italic; chemical shifts of the neighbor protons with observed multiplicity and coupling constants are depicted below.

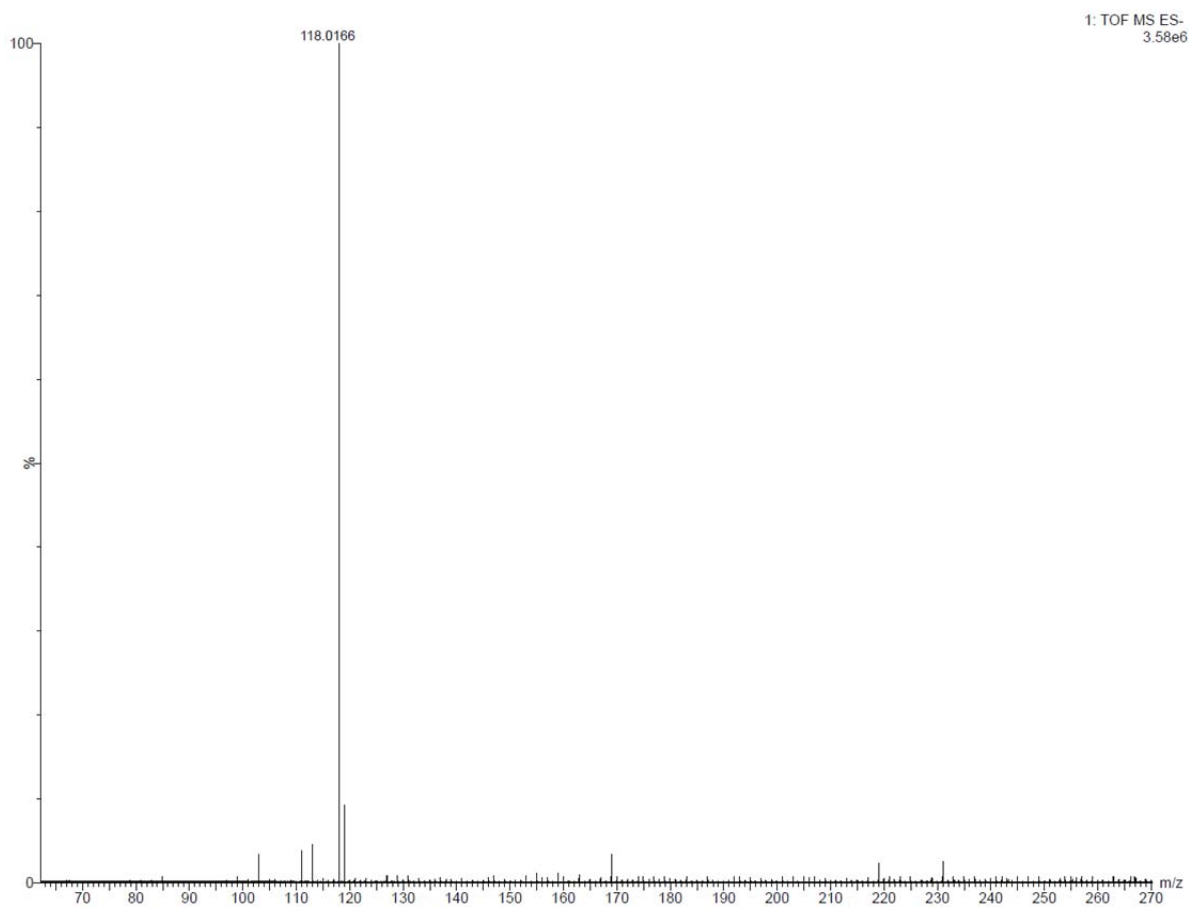
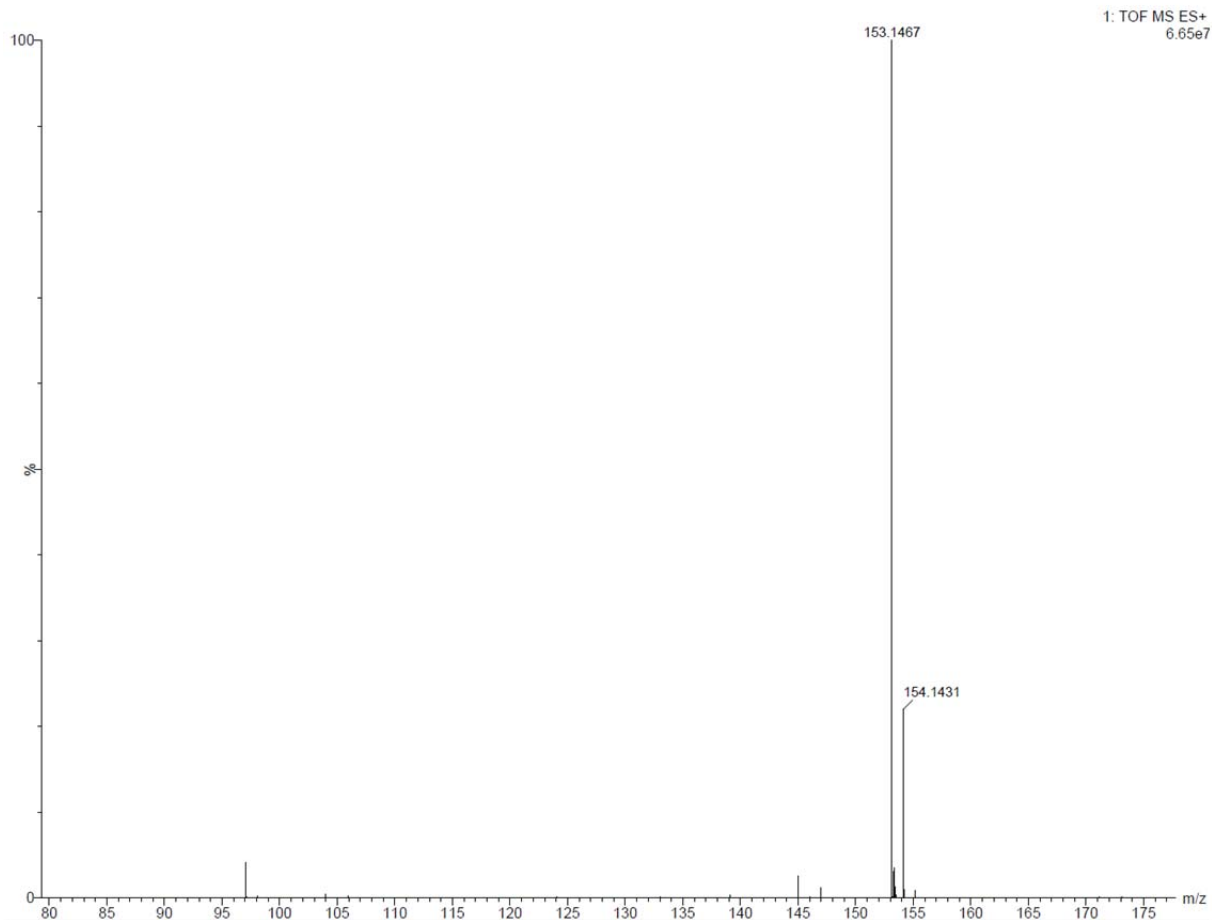


Figure S25. HR-MS spectra of IL-1: positive (top) and negative (bottom) ion mode.

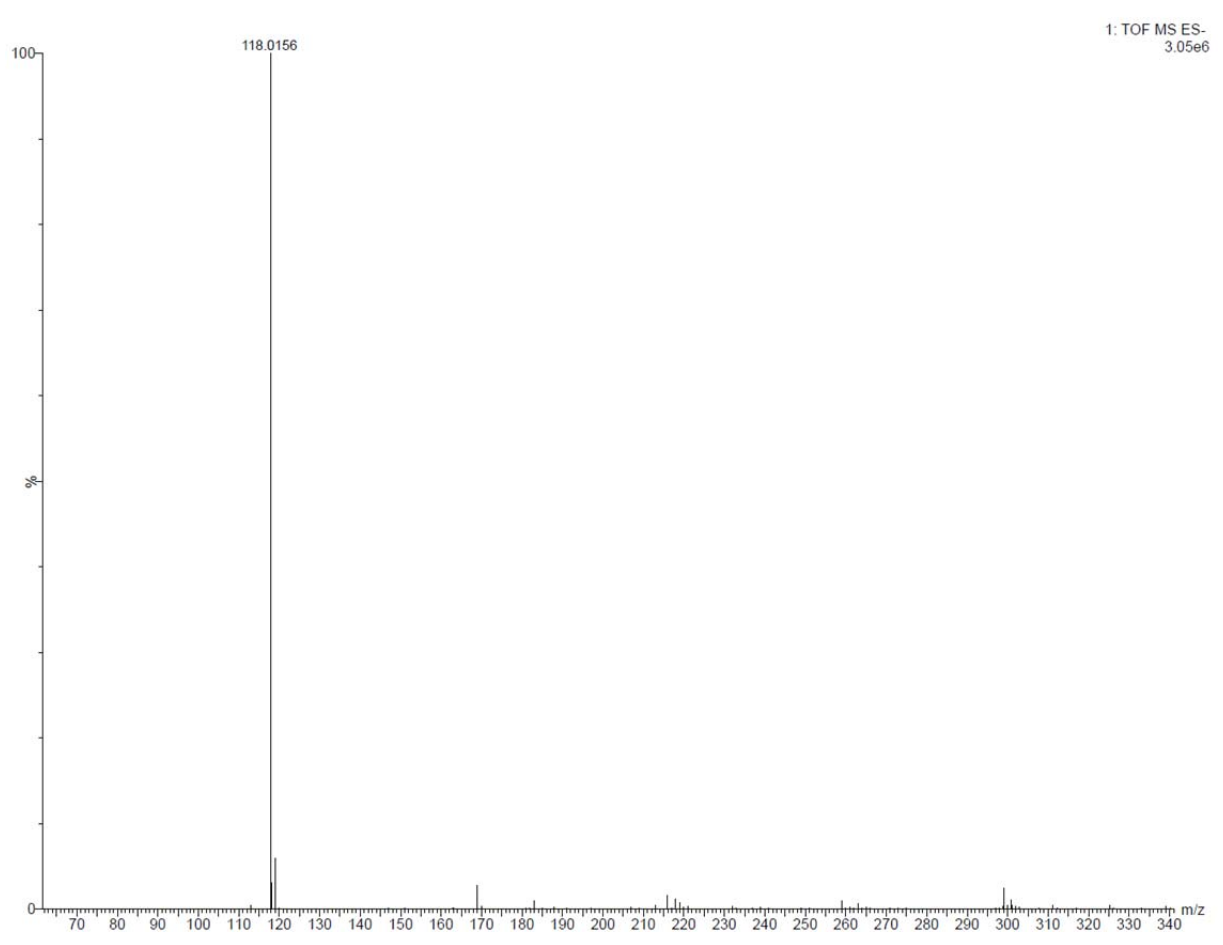
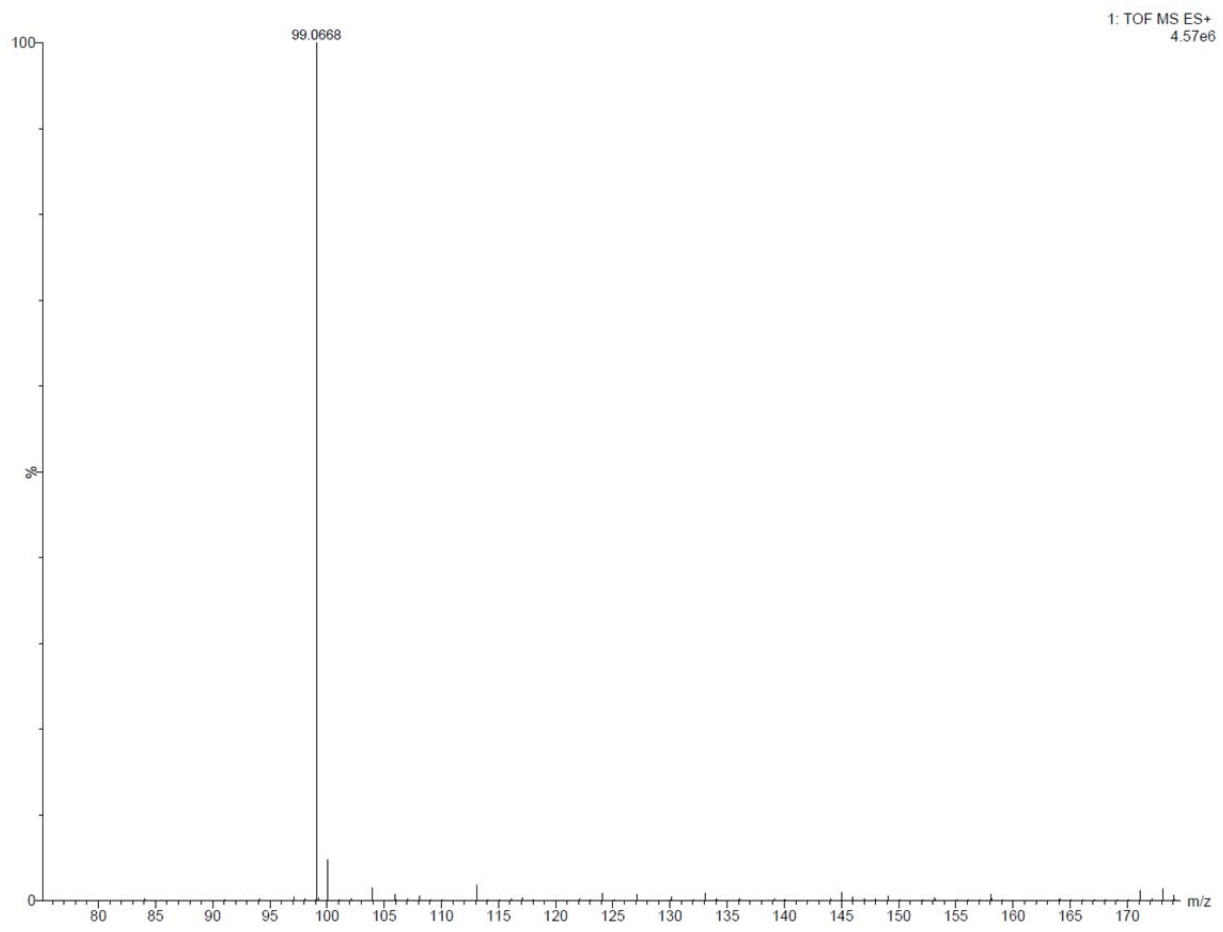


Figure S26. HR-MS spectra of IL-2: positive (top) and negative (bottom) ion mode.

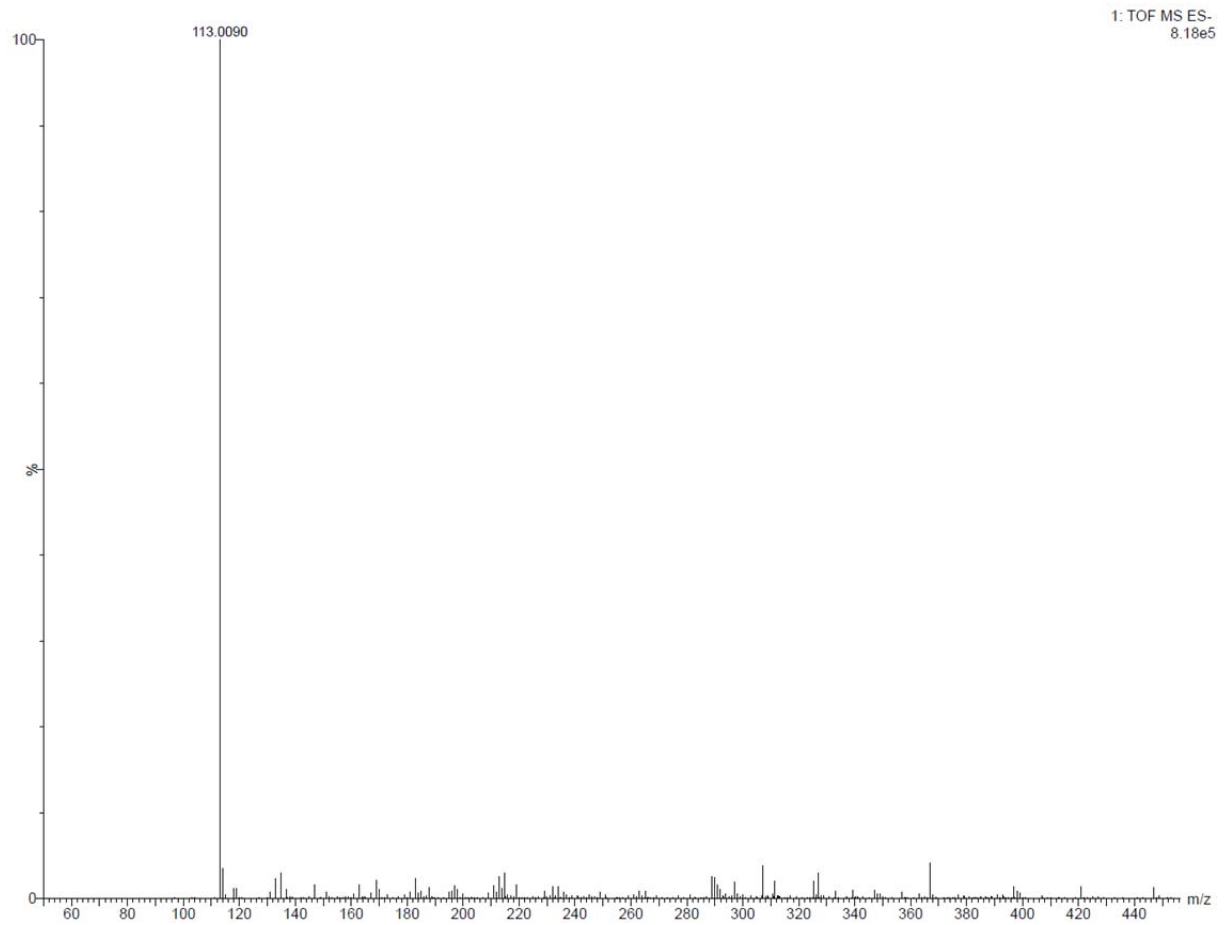
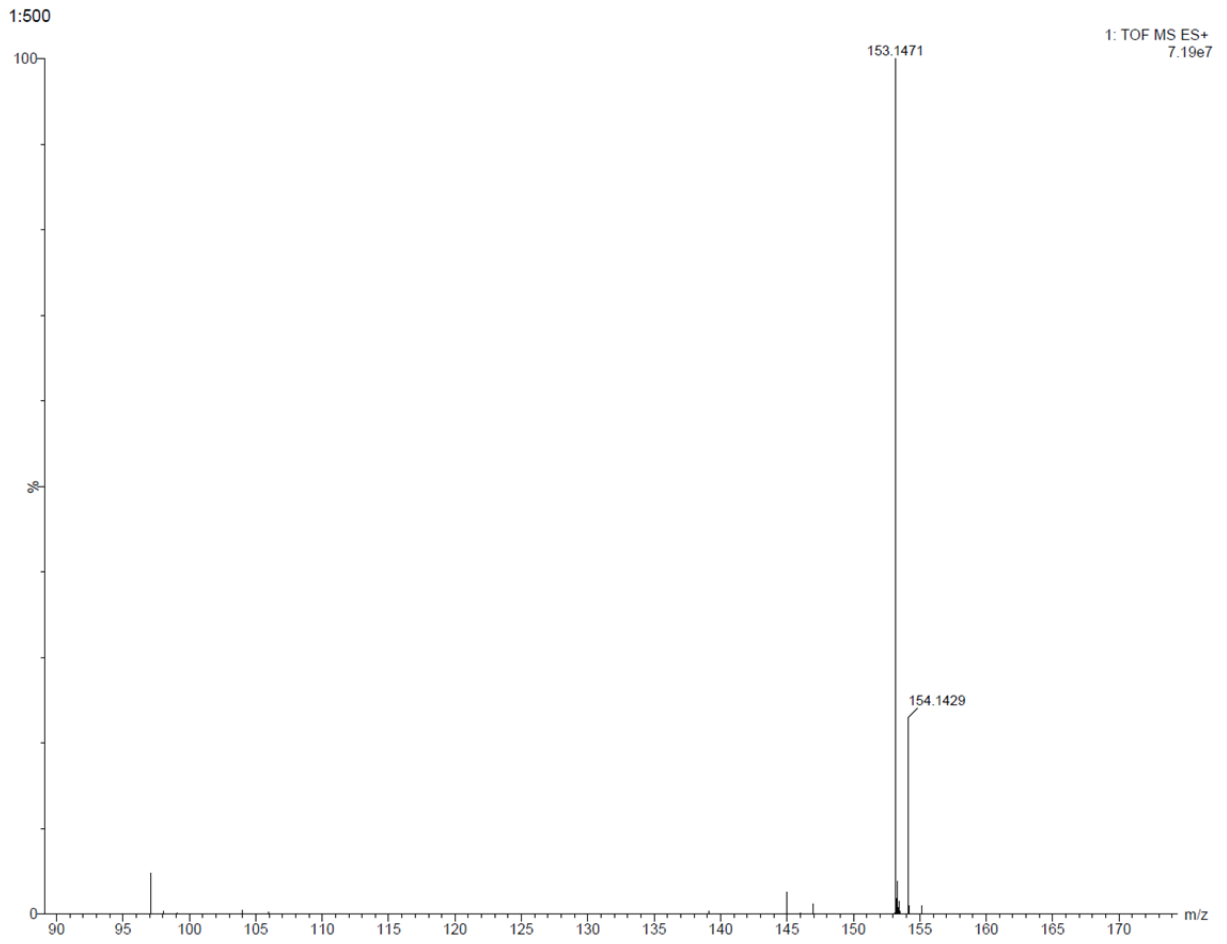


Figure S27. HR-MS spectra of IL-3: positive (top) and negative (bottom) ion mode.

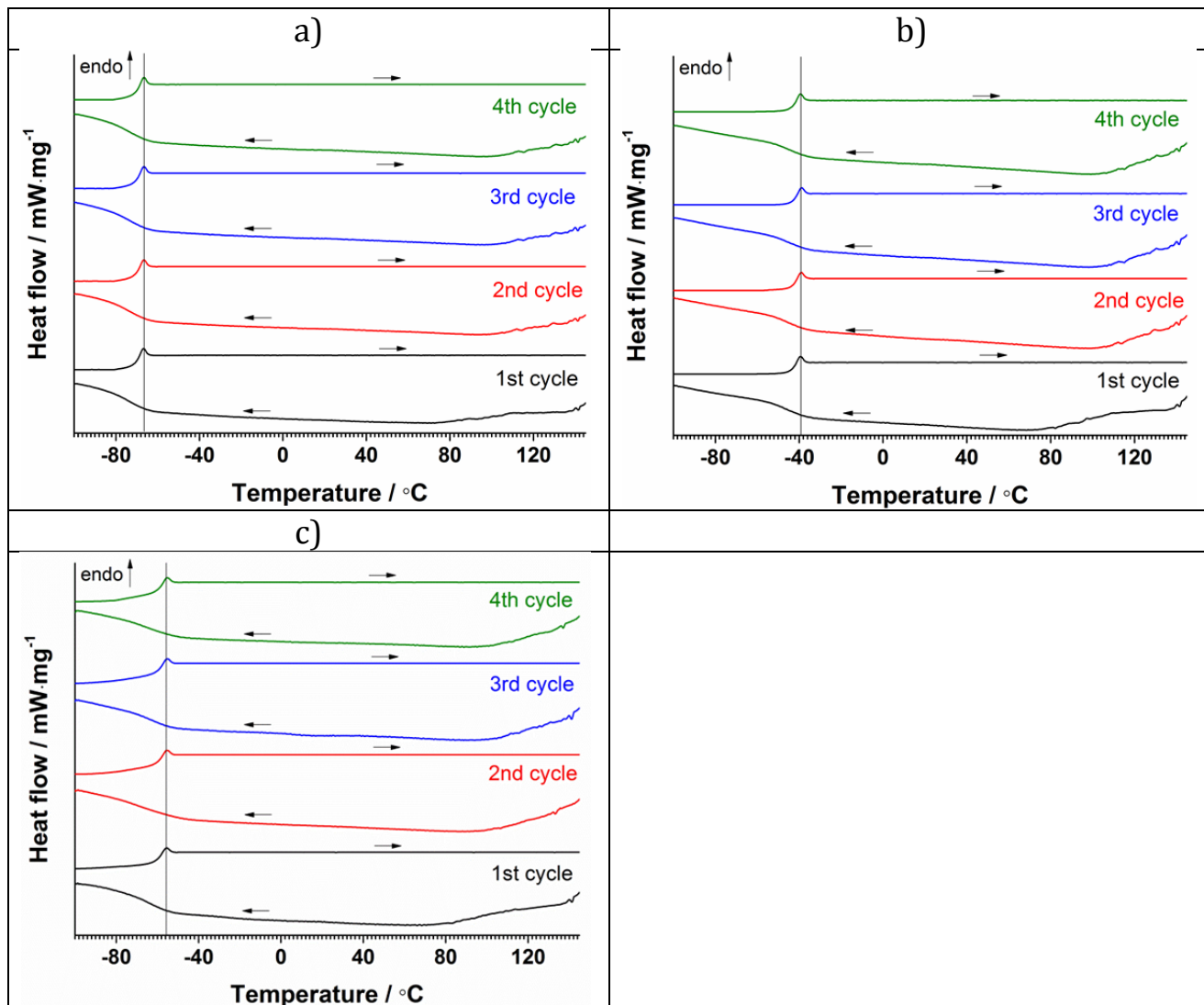


Figure S28. DSC curves recorded in the range of temperatures of -100...+140 $^{\circ}\text{C}$ of IL-1 (a), IL-2 (b) and IL-3 (c).

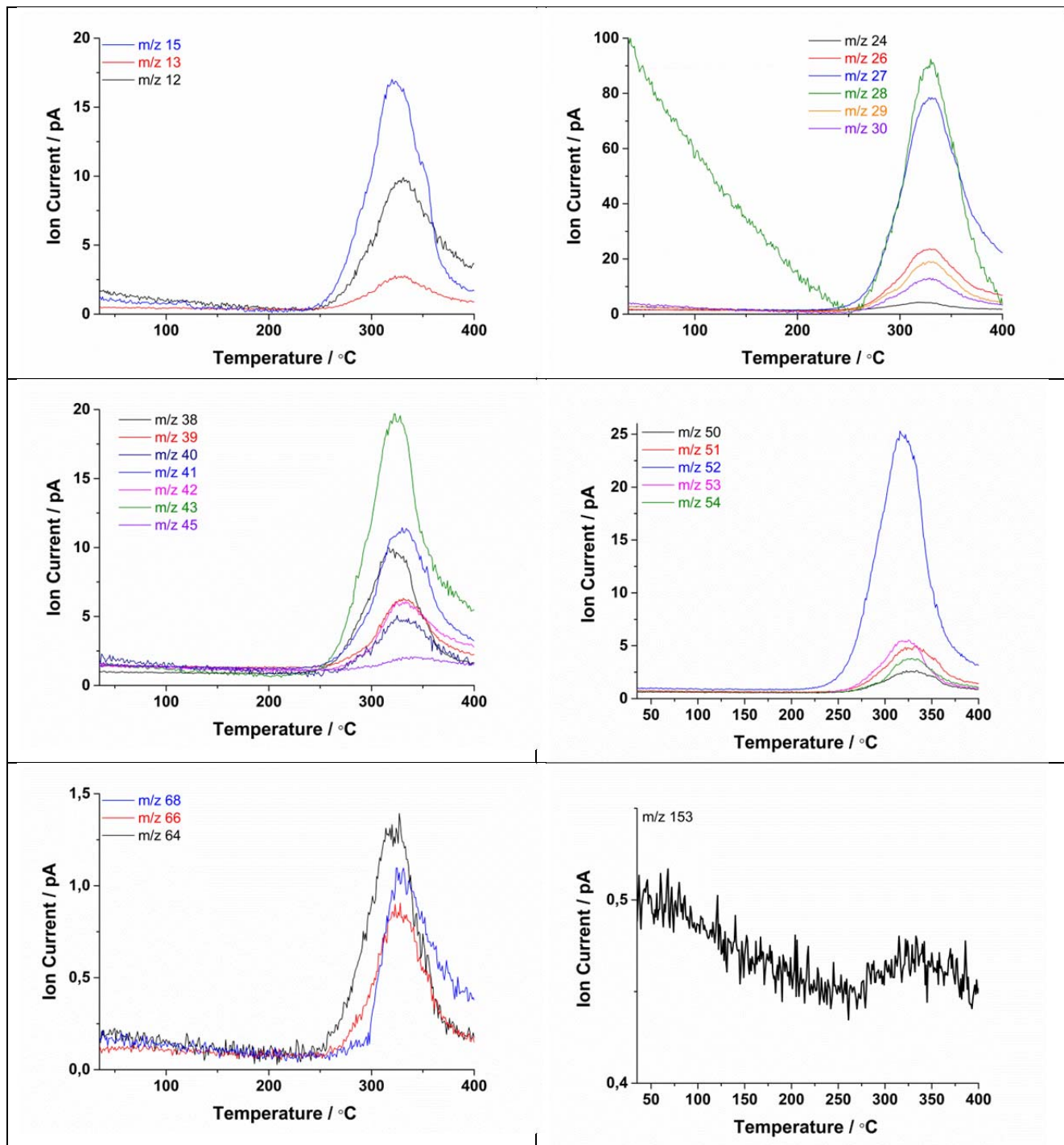


Figure S29. IL-1 TGA-MS ion current profiles.

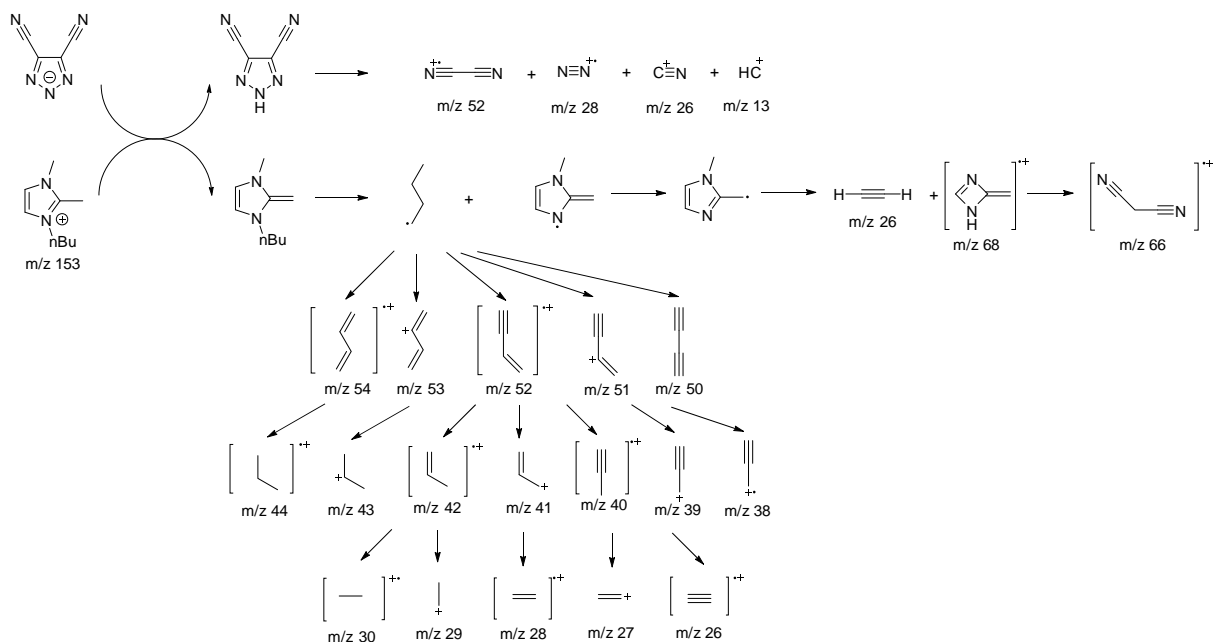


Figure S30. The proposed mechanism of IL-1 thermal decomposition. Masses of hypothetical products that were observed by MS are indicated below the structures.

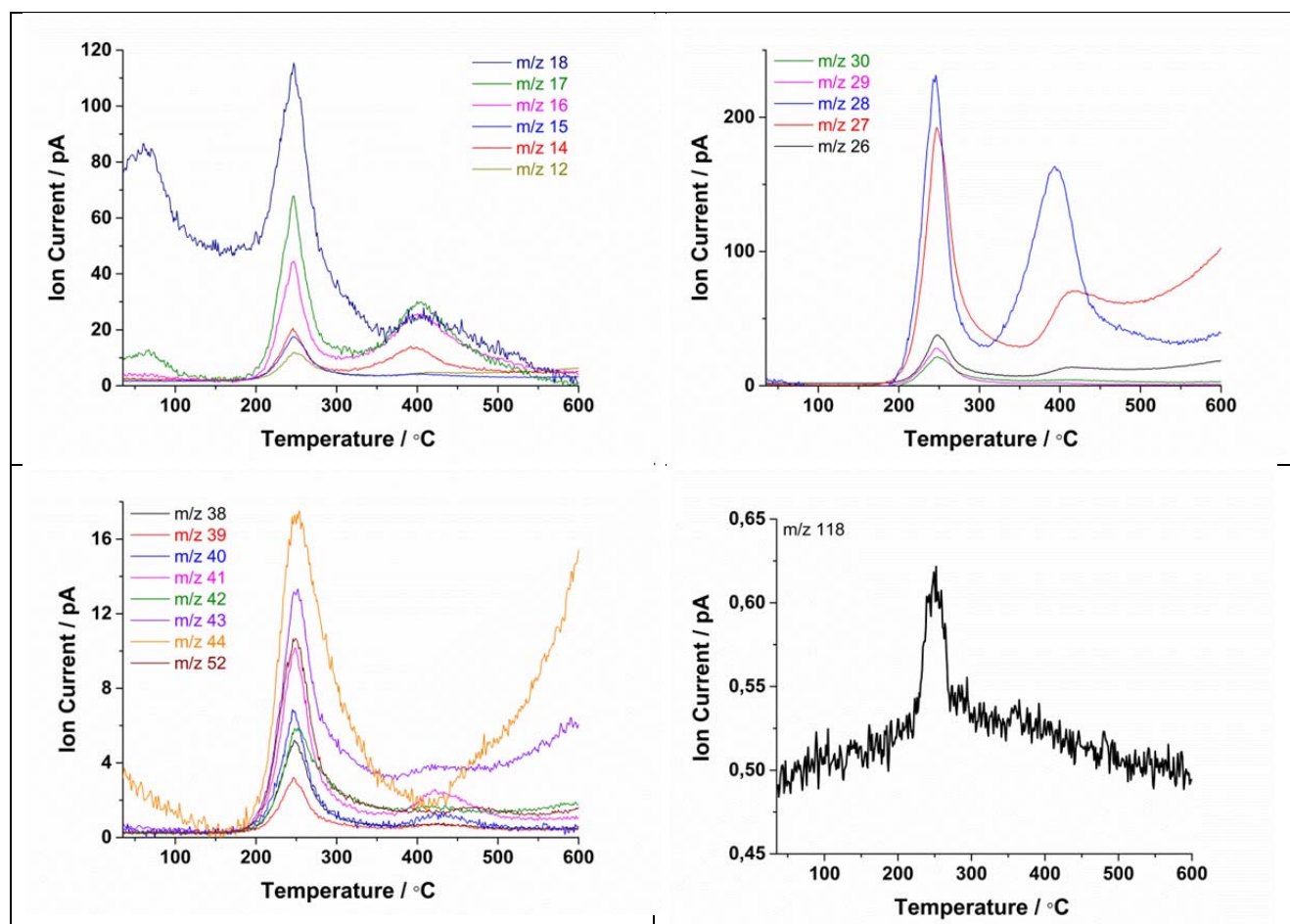


Figure S31. IL-2 TGA-MS ion current profiles.

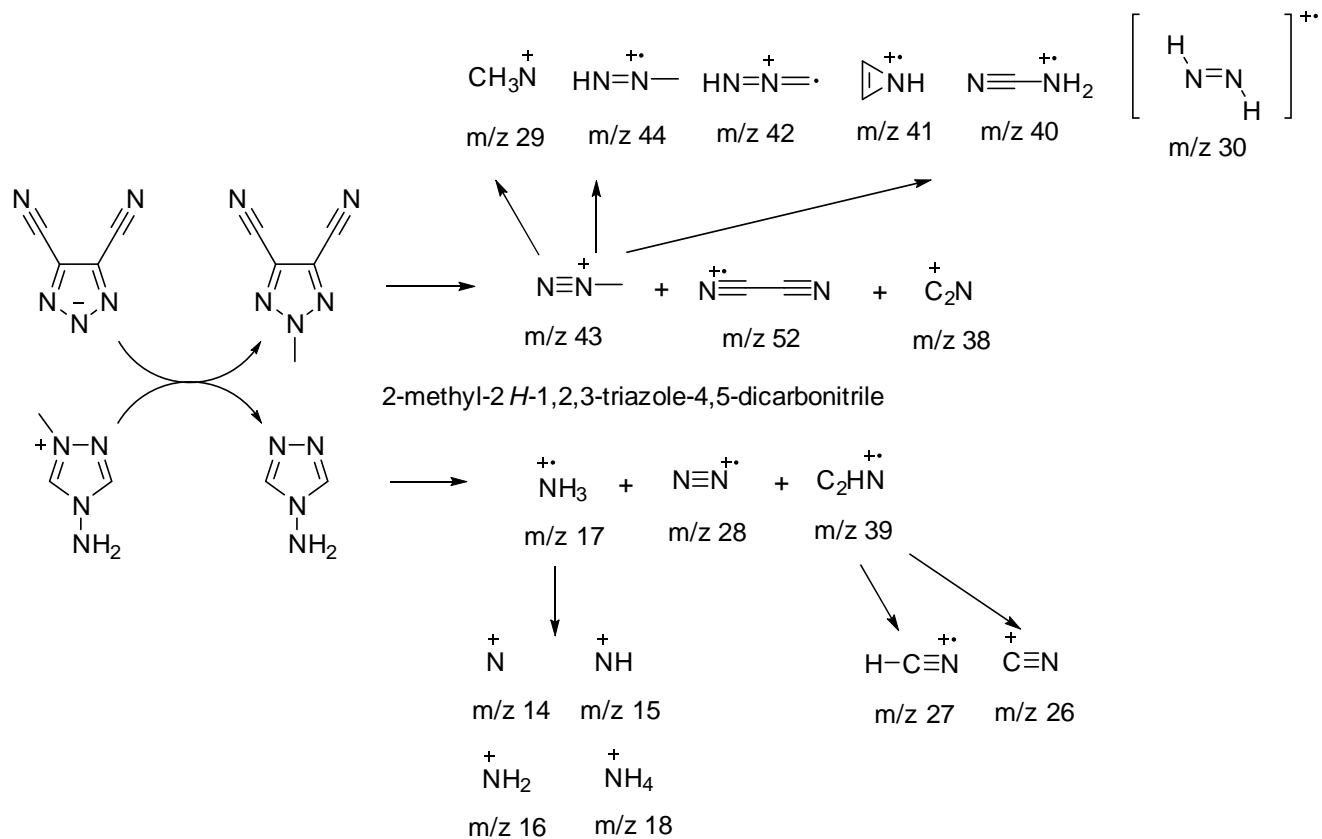
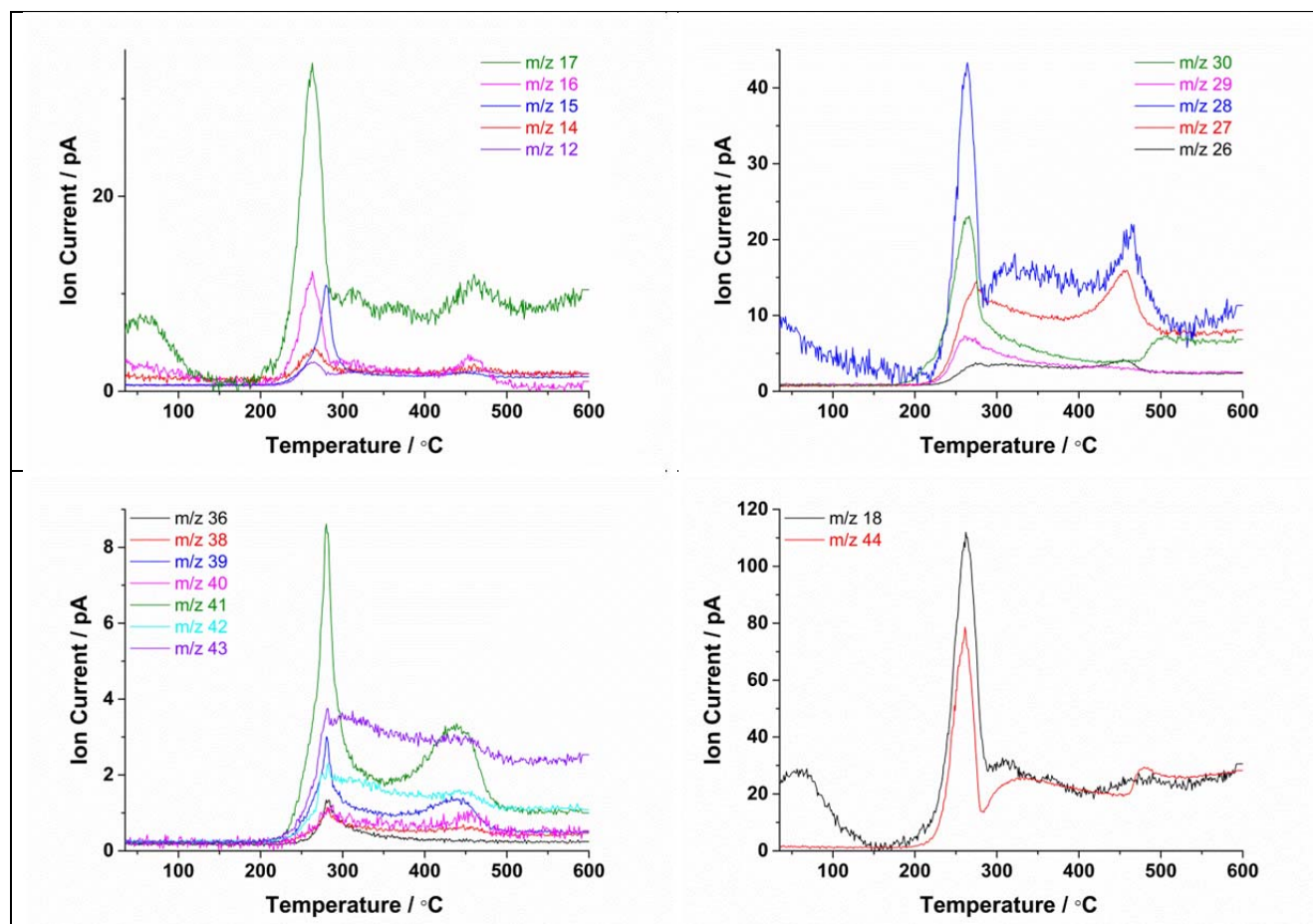


Figure S32. The proposed mechanism of IL-2 thermal decomposition. Masses of hypothetical products that were observed by MS are indicated below the structures.



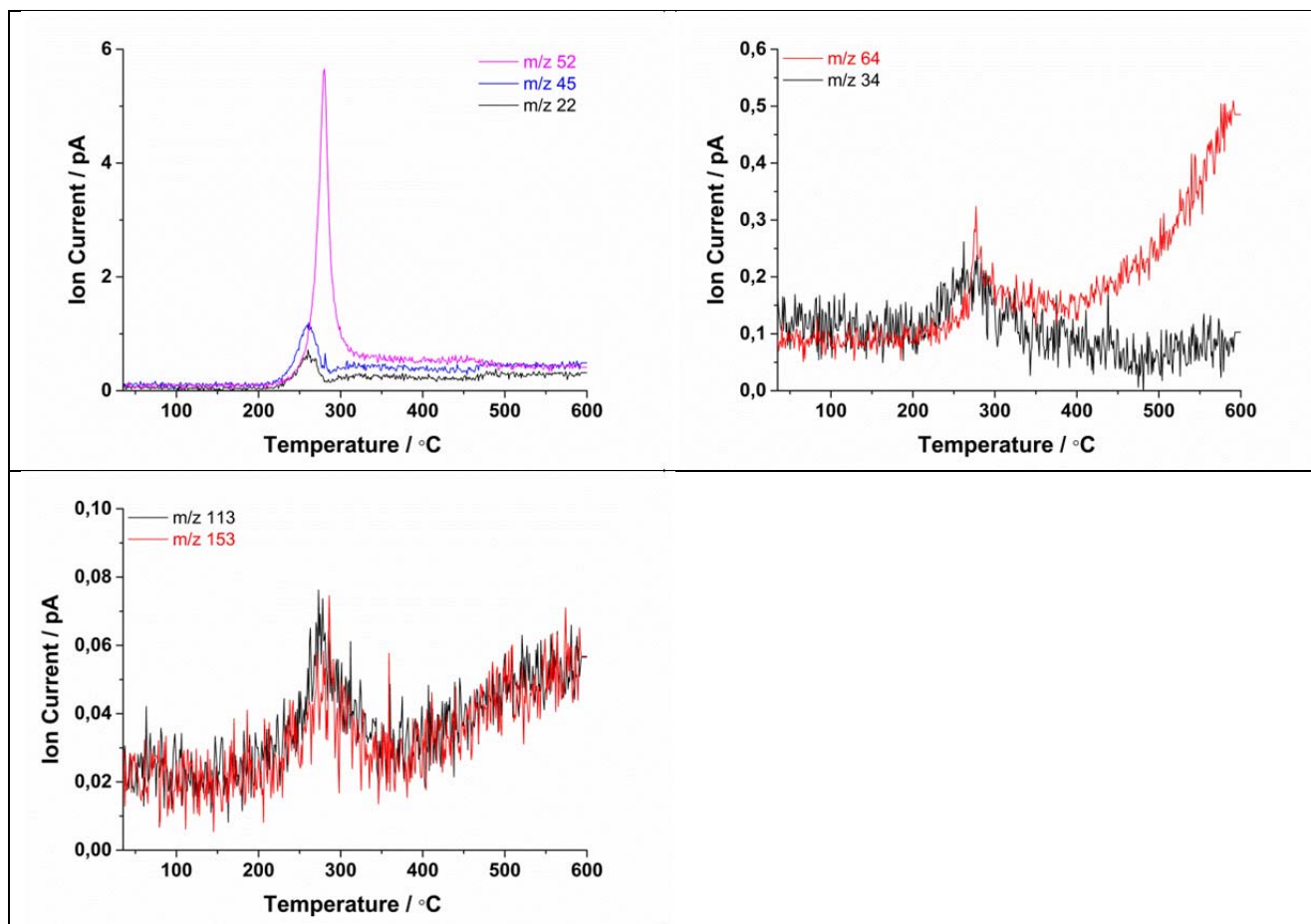


Figure S33. IL-3 TGA-MS ion current profiles.

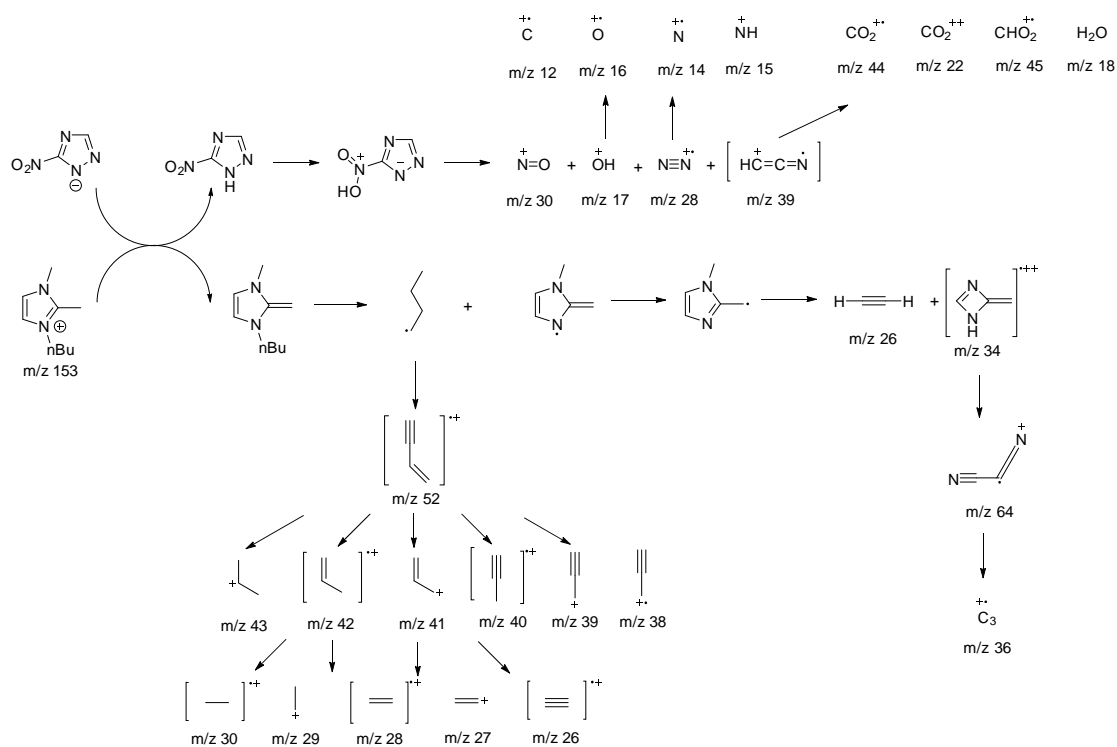


Figure S34. The proposed mechanism of IL-3 thermal decomposition. Masses of hypothetical products that were observed by MS are indicated below the structures.

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