Electronic Supplementary Information (ESI) for:

Selective separation of trivalent *f*-ions using 1,10-phenanthroline-2,9-dicarboxamide ligands in ionic liquids

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Supplementary sections.

Section S1. Materials and synthetic methods.

Solvents.

All reagents were obtained from Aldrich in their purest form and used without further purification. 1-alkyl-3-methylimidazolium bis[(trifluoromethyl)-sulfonyl]amide ([$C_n$mim][NTf_2]) ionic liquids (n=4, 6, and 8), were synthesized using modified procedures from [1, 2].

Extractants: synthetic strategy and analytical detail.

The synthesis of extractants **1** to **4** followed Scheme S1. Phenanthroline dicarboxamide ligands were prepared from phenanthroline dicarboxylic acid **7** obtained by oxidation of neocuproine **5** [3, 4]. Ligands **1** and **2** were obtained by converting the dicarboxylic acid **7** into diacyl chloride that was reacted with *N,N*-dioctylamine and *N*-octylamine, respectively. Compounds **8** and **9** were obtained by peptide conjugation of **7** with *N*-(3-aminopropyl)-imidazole using carbonyldiimidazole (CDI) as a coupling reagent. Imidazole moieties were quarternized in presence of 1-butylbromide to yield **10** and **11**. Finally, the bromide metathesis was performed using $LiNTf_2$ to obtain **3** and **4**. Below we give the synthetic procedures, ^{1}H and ^{13}C nuclear magnetic resonance spectra (see Figs. S6 to S13 and Figs. S14 to S21, respectively) and high resolution mass spectra (HRMS) or electrospray ionization mass spectra (ESI/MS) for these compounds.

^{1}H and ^{13}C NMR spectra were recorded using a Varian Mercury 300 MHz or a Varian VNMRS 500 MHz spectrometers. The chemical shifts at 25 °C (given in parts per million) were referenced to the residual protonated solvent. The mass peaks for protonated molecules were determined using DART (direct analysis in real time) for neutral compounds (as protonated molecules) or ESI/MS for charged species. All mass spectrometry analyses were conducted at the Mass Spectrometry Center located in the Department of Chemistry at the University of Tennessee. The DART analyses were performed using a JEOL AccuTOF-D time-of-flight mass spectrometer with a DART ionization source from JEOL USA, Inc. (Peabody, MA). The

ESI/MS analyses were performed using a QSTAR Elite quadrupole time-of-flight (QTOF) mass spectrometer with an electrospray ionization source from AB Sciex (Concord, Ontario, Canada).

2,9-bis*(N,N*-dioctylaminocarbonyl)-1,10-phenanthroline (1)

Phenanthroline dicarboxylic acid (429 mg, 1.6 mmol) was refluxed in thionyl chloride (10 mL) for 6 h. $SOCl_2$ was removed under vacuum. The crude diacyl chloride was dissolved in dichloromethane. A solution of *N,N*-diisopropylethylamine (DIPEA, 0.58 mL, 3.5 mmol) and di-*N,N*-octylamine (1.06 mL, 3.5 mmol) in dichloromethane (75 mL) was added dropwise at 0°C. The mixture was refluxed for 6 h. After cooling, the organic layer was separated and washed with 1 M HCl (2X 30 mL) and water (6X 10 mL), dried over $MgSO_4$, and reduced in vacuum. The yellow residue was purified by silica gel flash chromatography (hexanes/ethyl acetate, 100:0 to 70:30 v/v) to yield the title compound as a white powder. Yield: 670 mg (59%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.73 (t, 6H, ^3J = 7.1 Hz), 0.89 (t, 6H, ^3J = 7.1 Hz), 0.93-1.10 (m, 20H), 1.24-1.46 (m, 20H), 1.63 (p, 4H, ^3J = 7.2 Hz), 1.76 (p, 4H, ^3J = 7.2 Hz), 3.56 (t, 4H, ^3J = 7.6 Hz), 3.75 (t, 4H, ^3J = 7.6 Hz), 7.83 (s, 2H), 8.01 (d, 2H, ^3J = 8.3 Hz), 8.31 (d, 2H, ^3J = 8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 14.1, 22.5, 22.7, 26.7, 27.3, 27.8, 29.0, 29.1, 29.3, 29.5, 31.6, 31.9, 47.0, 49.1, 123.4, 127.1, 128.8, 136.7, 144.2, 154.7, 168.3
HRMS: *m/z*: 715.5899. [M + H$^+$]. $C_{46}H_{75}N_4O_2^+$ requires 715.5890.

2,9-bis*(N*-octylaminocarbonyl)-1,10-phenanthroline (2)

Phenanthroline dicarboxylic acid **7** (429 mg, 1.6 mmol) was refluxed in thionyl chloride (10 mL) for 6 h. $SOCl_2$ was removed under vacuum. The crude diacyl chloride was dissolved in CH_2Cl_2. A solution of DIPEA (0.58 mL, 3.5 mmol) and *N*-octylamine (0.58 mL, 3.5 mmol) was added dropwise at 0 °C. After cooling, the organic layer was washed with 1 M HCl (2X 30 mL) and with water (6X 10 mL), dried over $MgSO_4$ and reduced in vacuum. The residue was purified by silica gel flash chromatography (95:5 v/v CH_2Cl_2/MeOH) to yield the title compound as a pale yellow powder. Yield: 361 mg (46%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.84 (t, 6H, ^3J = 7.0 Hz), 1.17-1.38 (m, 20H), 1.38-1.63 (m, 4H) 3.19-3.44 (m, 4H), 7.92 (s, 2H), 8.44 (d, 2H, ^3J = 8.3 Hz), 8.61 (d, 2H, ^3J = 8.3 Hz), 8.65-8.73 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 22.6, 27.1, 29.2, 29.3, 29.8, 31.8, 39.7, 127.7, 127.7, 130.5, 137.9, 144.1, 150.1, 164.0; HRMS: *m/z*: 491.3389 [M + H$^+$]. $C_{30}H_{43}N_4O_2^+$ requires 491.3386.

2,9-bis(*N*-(1-(3-butylimidazolium))propylaminocarbonyl)-1,10-phenanthroline di[bis(trifluoromethylsulfonyl)imide)] (3)

To a solution of **10** (1.62 g, 2.14 mmol) in acetonitrile (20 mL) was added dropwise a solution of lithium bis(trifluoromethane sulfonyl)imide ($LiNTf_2$, 3.07 g, 10.7 mmol) in acetonitrile (15 mL). The mixture was stirred at room temperature for 2 days. The solvent was removed in vacuum and the residue was washed with water, diethyl ether, and dichloromethane. The highly viscous oil was dried in vacuum for 5 h. Yield: 2.10 g (85%)

^{1}H NMR (300 MHz, DMSO-d_6): δ 0.88 (t, 6H, 3J = 7.3 Hz), 1.18-130 (m, 4H), 1.69-1.79 (m, 4H), 2.19-2.30 (m,4H), 3.53 (q, 4H, ^3J = 6.5 Hz), 4.14 (t, 4H, ^3J = 7.2 Hz), 4.33 (t, 4H, ^3J =6.8 Hz), 7.80 (s, 2H), 7.87 (s, 2H), 8.49 (d, 2H, ^3J = 8.3 Hz), 8.77 (d, 2H, ^3J = 8.77 Hz), 9.24 (s, 2H), 9.53 (s, 2H, ^3J = 6.1 Hz); ^{13}C NMR (126 MHz, DMSO-d_6): δ 13.6, 19.2, 30.4, 31.7, 36.5, 47.5, 49.1, 118.6, 121.2, 122.3, 128.4, 130.8, 136.6, 136.7, 139.4, 141.1, 150.0, 164.8; HRMS: ESI$^+$ *m/z*: 298.1797. $C_{34}H_{44}N_8O_2^{2+}$ requires 298.1794; ESI$^-$ *m/z*: 279.9174. NTf_2^- requires 279.9173.

2,9-bis(*N*-(1-(3-butyl-2-methyl-imidazolium))propylaminocarbonyl)-1,10-phenanthroline di[bis(trifluoromethylsulfonyl)imide)] (4)

To a solution of **11** (255 mg, 0.325 mmol) in acetonitrile (10 mL) was added dropwise a solution of $LiNTf_2$ (467 mg, 1.62 mmol) in acetonitrile (3 mL). Further synthesis proceeded as explained above for **3**. Yield: 340 mg (88%).

^{1}H NMR (300 MHz, DMSO-d_6): δ 0.74 – 0.89 (m, 6H), 1.10-1.24 (m, 4H), 1.55 (m, 4H), 2.64 (s, 6H), 3.52 (m, 4H), 3.98 (t, 4H, ^3J = 7.5 Hz), 4.26 (t, 4H, ^3J = 7.5 Hz), 7.64 (d, 2H, ^3J = 2.1 Hz), 7.79 (d, 2H, ^3J = 2.1 Hz),8.19 (s, 2H), 8.44 (d, 2H, ^3J = 8.3 Hz), 8.74 (d, 2H, ^3J = 8.3 Hz), 9.46 (t, 2H, ^3J =6.1 Hz); ^{13}C NMR (126 MHz, DMSO-d_6): δ 9.7, 13.7, 19.3, 29.3, 31.4, 36.8, 46.2, 47.7, 116.1, 118.6, 121.2, 121.6, 121.7, 128.4, 130.8, 138.7, 144.3, 150.0, 167.7; HRMS: ESI$^+$ *m/z*: 312.1955. $C_{36}H_{48}N_8O_2^{2+}$ requires 312.1950; ESI$^-$ *m/z*: 279.9172. NTf_2^- requires 279.9173.

2,9-bis(*N*-(1-imidazolyl)propylaminocarbonyl)-1,10-phenanthroline (8)

A solution of 1,10-phenanthroline-2,9-dicarboxylic acid **7** (1.8 g, 6.71 mmol) in *N,N*-dimethylformamide (DMF, 35 mL) was heated to 45°C. CDI (3.41 g, 21.0 mmol) was added in several portions. The mixture was heated at 45°C for 2 h. After cooling to 20 °C, *N*-(3-aminopropyl)-imidazole (1.72 mL, 14.4 mmol) was added dropwise. The mixture was stirred at room temperature for 4 days. Water was added and DMF was removed in vacuum. A solution of Na_2CO_3 (1 M, 100 mL) was added to the residue. After standing overnight at 5°C, the yellow precipitate was filtered, washed with water and diethyl ether. Yield: 1.90 g (59%).

^{1}H NMR (300MHz, DMSO-d_6): δ 2.09 (p, 4H, ^3J = 7.0 Hz), 3.46 (q, 4H, ^3J = 6.7 Hz), 4.08 (t, 4H, ^3J = 6.8 Hz), 6.90 (s, 2H), 7.24 (s, 2H), 7.71 (s, 2H), 8.21 (s, 2H), 8.46 (d, 2H, ^3J = 8.3 Hz), 8.73 (d, 2H, ^3J = 8.3 Hz), 9.52 (t, 2H, ^3J = 8.3 Hz); ^{13}C NMR (75 MHz, DMSO-d_6): δ 31.0, 36.5, 43.9, 119.4, 121.1, 127.9, 128.4, 130.3, 137.4, 138.2, 143.7, 149.7, 164.1; HRMS: *m/z*: 483.2253 [M + H$^+$]. $C_{26}H_{27}N_8O_2^+$ requires 483.2257.

2,9-bis(*N*-(1-(2-methylimidazolyl)propylaminocarbonyl)-1,10-phenanthroline (9)

A solution of 1,10-phenanthroline-2,9-dicarboxylic acid **7** (0.714 g, 2.66 mmol) in DMF (15 mL) was heated to 45°C. The carbonyldiimidazole (CDI, 1.5 g, 8.33 mmol) was added in several portions. The mixture was heated at 45°C for 2 h. After cooling of this reaction mixture to 20 °C, *N*-(3-aminopropyl)-2-methyl-imidazole (0.98 mL, 7.18 mmol) was added dropwise. The mixture was stirred at room temperature for 4 days. Water was added (10 mL) and DMF was removed in vacuum. A solution of Na_2CO_3 (1 M, 75 mL) was added to the residue. After standing at 5°C

overnight, the yellow precipitate was filtered and washed with water and diethyl ether. Yield: 620 mg (46%)

^{1}H NMR (300 MHz, DMSO-d_6): δ 2.02 (p, 4H, ^3J = 7.0 Hz), 2.26 (s, 6H), 3.62 (m, 4H), 3.94 (t, 4H, ^3J = 7.0 Hz), 6.73 (s, 2H), 7.11 (s, 2H), 8.14 (s, 2H), 8.44 (d, 2H, ^3J =8.3 Hz), 8.70 (d, 2H, ^3J =8.3 Hz), 9.48 (d, 2H, ^3J = 6.2 Hz); ^{13}C NMR (75 MHz, DMSO-d_6): δ 13.0, 30.7, 37.0, 43.4, 120.1, 121.6, 126.6, 128.4, 130.7, 138.7, 144.1, 150.1, 164.5, 208.2; HRMS: *m/z*: 511.2561 [M + H^+]. $C_{28}H_{31}N_8O_2^+$ requires 511.2570.

2,9-bis(*N*-(1-(3-butylimidazolium)propylaminocarbonyl))-1,10-phenanthroline dibromide (10)

1-bromobutane (0.21 mL, 1.96 mmol) was added dropwise to a solution of **8** (390 mg, 0.81 mmol) in acetonitrile (20 mL) at 0°C. The mixture was stirred at 20 °C for 12 h and then at 85°C for 2 days. The solvent was removed in vacuum. The resulting yellow residue was washed with hexanes. The yellow powder was dried in vacuum. Yield: 543 mg (89%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.81 (t, 6H, ^3J = 7.2 Hz), 1.15-1.28 (m, 4H), 1.68-1.79 (m, 4H), 2.39-2.55 (m, 4H), 3.71-3.75 (m, 4H), 4.18 (t, 4H, ^3J = 7.2 Hz), 4.58 (t, 4H, ^3J = 6.5 Hz), 7.40 (s, 2H), 7.84 (d, 2H, ^3J = 10.3 Hz), 8.34 (d, 2H, ^3J = 8.2 Hz), 8.43(d, 2H, ^3J = 8.2 Hz), 9.84 (t, 2H, ^3J = 5.9Hz), 10.21 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.5, 19.5, 30.3, 32.0, 36.8, 48.2, 49.9, 122.0, 123.2, 127.9, 130.5, 136.8, 137.8, 144.6, 150.6, 165.6; ESI$^+$ *m/z*: 298.1794. $C_{34}H_{44}N_8O_2^{2+}$ requires 298.1794; ESI$^-$: *m/z*: 78.9182. Br^- requires 78.9183.

2,9-bis(*N*-(1-(3-butyl-2-methyl-imidazolium))propylaminocarbonyl)-1,10-phenanthroline dibromide (11)

1-bromobutane (0.084 mL, 0.784 mmol) was added dropwise to a solution of **9** (204 mg, 0.81 mmol) in acetonitrile (15 mL) at 0°C. The mixture was stirred at 20 °C for 12h then at 85°C for 2 days. The solvent was removed in vacuum. The resulting yellow residue was washed with hexanes. The yellow powder was dried in vacuum. Yield: 231 mg (90%).

^{1}H NMR (300 MHz, DMSO-d_6): δ 0.82 (t, 4H, ^3J = 7.3 Hz), 1.18 (m, 4H), 1.57 (p, 4H, ^3J = 7.3 Hz), 2.22 (t, 4H, ^3J = 6.4 Hz), 2.67 (s, 6H), 3.56 (d, 4H, ^3J = 6.4 Hz), 4.01 (t, 4H, ^3J = 7.4 Hz), 4.28 (m, 4H), 7.68 (d, 2H, ^3J = 2.1 Hz), 7.84 (d, 2H, ^3J = 2.1 Hz), 8.21 (s, 2H), 8.45 (d, 2H, ^3J = 8.4 Hz), 8.76 (d, 2H, ^3J = 8.4 Hz), 9.49 (t, 2H, ^3J = 6.1 Hz); ^{13}C NMR (126 MHz, DMSO-d_6): δ 10.0, 13.8, 19.3, 29.3, 31.4, 36.9, 46.2, 47.7, 121.6, 121.8, 128.4, 130.8, 138.7, 144.2, 144.3, 150.1, 164.7; ESI$^+$ *m/z*: 312.1961. $C_{36}H_{48}N_8O_2^{2+}$ requires 312.1950; ESI$^-$: *m/z*: 78.9177 Br^- requires 78.9183.

Section S2. Determination of distribution ratios.

Caution! ^{152,154}Eu and ^{241}Am are radioactive. All radiotracer experiments were carried out in radiochemical laboratories equipped for handling these isotopes.

The distribution ratio (D_M) for extraction of trivalent metal ions (M^{3+}) is defined by

$$D_M = \frac{(C_{aq,i} - C_{aq,f})}{(C_{aq,f})} \times \frac{Volume\ of\ aqueous\ phase}{Volume\ of\ IL\ phase} \qquad \text{(S1)}$$

In this equation, $C_{aq,i}$ and $C_{aq,f}$ represent the initial and final (equilibrium) concentrations of the metal ions in the aqueous phase, respectively. Although the value of D_M depends on the concentration of free extractant, the trends reflected in D_M should be the same as for the corresponding equilibrium constants for a given extractant concentration. A volume ratio is needed in the calculation of distribution ratios to account for the difference in volume between the two immiscible phases. In all of our experiments, the volume ratio was close to 1:1 v/v. Separation factors SF for the metal ions *M* and *M'* are defined from

$$SF_{M/M'} = D_M / D_{M'} \qquad \text{(S2)}$$

Eu/Am measurements.

The distribution ratios for extraction using radiotracer techniques were calculated by measuring the amount of radioactivity of both aqueous and organic phases at equilibrium. Counting efficiency (^{241}Am or ^{152,154}Eu gamma ray absorption in solid scintillators) is identical for both phases; hence, the distribution ratio is defined by the ratio of specific radioactivity *S* (Bq/mL) of element *M* in the IL vs. aqueous phases

$$D_M = \frac{C_{IL,f}}{C_{aq,f}} \propto \frac{S_{org,f}}{S_{aq,f}} \qquad \text{(S3)}$$

Europium-152/154 was obtained from Isotope Products (presently owned by Eckert & Ziegler) and americium-241was produced at Oak Ridge National Laboratory. An equal volume of both IL (containing 4 mM extractant) and aqueous phases, 0.4 mL of each were used, respectively. Each sample was individually spiked with a 10 µL solution containing 50 µCi/mL of each radiotracer respectively. The solutions were mixed using a rotating wheel set at 60 rpm for 3 h at 25±0.2 °C. After 3 h the samples were centrifuged at 3,000 rpm for 5 min at 25 °C to ensure the phases separated from each other. Then 100 µL aliquots were subsampled from each phase and placed into polypropylene tubes that were sealed with a cap. These tubes were then placed in a Canberra Gamma Analyst germanium spectrometer to determine the amounts of ^{241}Am and ^{152,154}Eu present in each sample. Prior to testing these samples, a quality assurance calibration was

performed. The organic and aqueous samples were counted for a period of 30 min to ensure an accurate measurement. Additional blank samples (no isotopes present in solution) were run to ensure no background subtraction was necessary. Once the data was collected the total counts for each isotope in the samples was normalized to give the average counts per minute.

Lanthanide series.

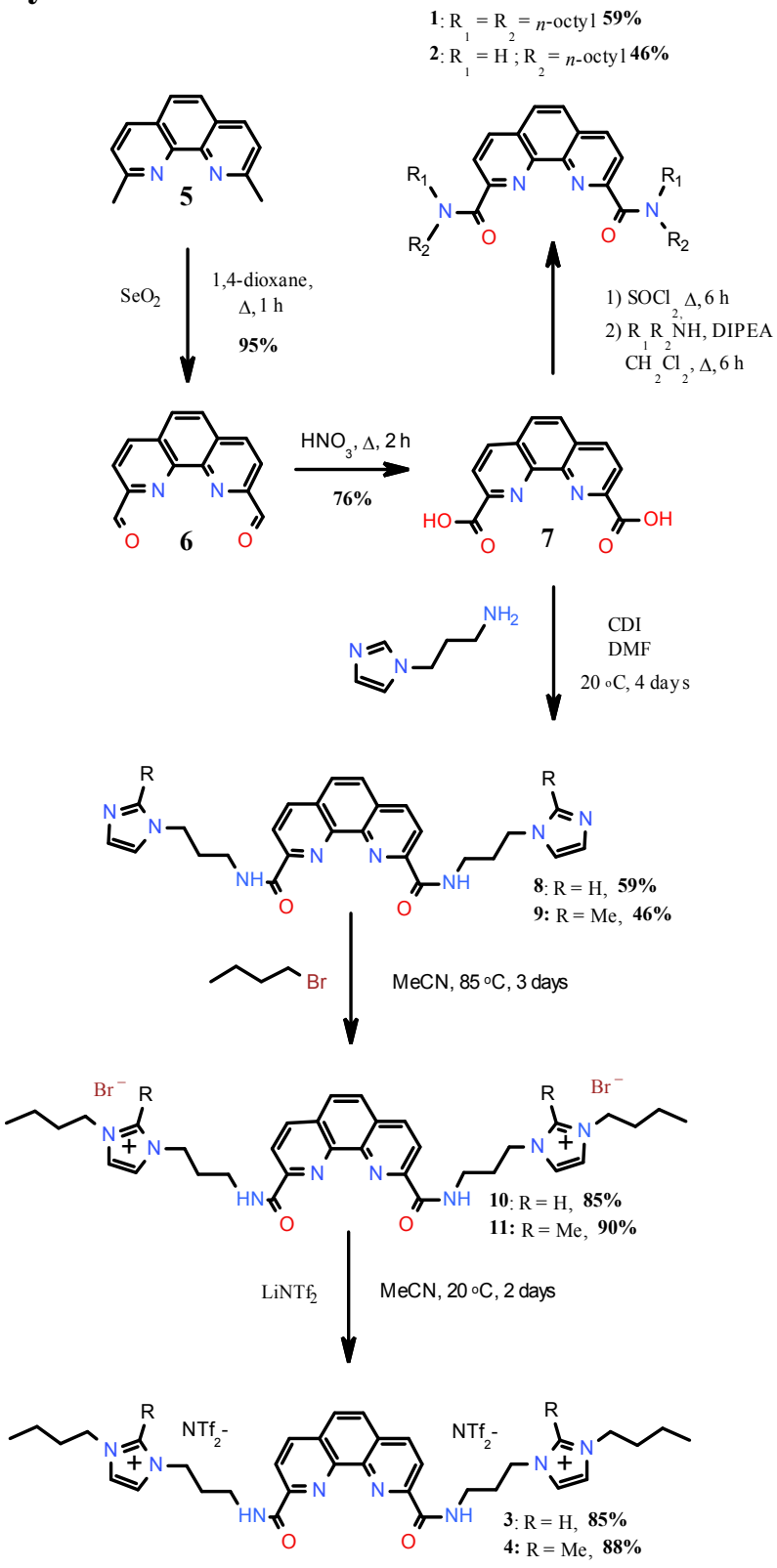
Extraction experiments were performed by contacting 0.5 mL of IL containing 4 mM of extractant **1** or **3** with 0.5 mL of aqueous phase (pH 3.25) containing ~35 μM of each lanthanide nitrate hydrate for elements given in Tables S2 and S3. The aqueous solutions were prepared in deionized water (with a specific resistance 18 MΩ-cm or greater). These solutions were mixed in a vibrating mixer for 3 h and then stirred for a day at 25 ^{o}C; this treatment was followed by centrifugation for 5 min at 3,000 rpm to separate the two phases. The upper (aqueous) phase was separated, and metal ion concentrations were determined using inductively coupled plasma - mass spectrometry (Thermo X-series ICP-MS). The values of D_{Ln} were obtained in triplicate with an uncertainty less than 5%, and the average values are given in this Communication.

Section S3. Computational approach.

The structures and energetics for Ln complexes in the gas phase were estimated using Sparkle/RM1 semiempirical method developed by Simas and co-workers [5, 6] from MOPAC2016 suit. [7, 8] The method typically gives ~ 50 pm accuracy in Ln-X distances for X=O, N, S and P atoms. [5] In this method, the lanthanide ion is replaced with a "sparkle": a ghost atom with +3 charge and a set of parameterized Gaussian orbitals centered on this ion. According to the method developers, "the principle behind the Sparkle Model was that the 4*f* electrons do not participate in the chemical bond because they are shielded from the coordination polyhedron by the more diffuse 5*s* and 5*p* closed shells, rendering the coordination bond essentially electrostatic." [5] Therefore, the covalent character of Ln-X bonds is entirely neglected in this model. All other bonds are treated at the RM1 (Recife Model 1) semiempirical level. [9]

In our calculations, no solvent was included, and the molecular symmetry was externally imposed. To calculate the energetics of nitrate addition, all degrees of freedom except for the Ln-N distance in the nitrate ligand were optimized. X-ray absorption spectra were calculated for the gas phase geometry optimized structures using program FEFF 8.2. [10, 11]

Supplementary schemes.



Scheme S1 Synthetic scheme for extractants **1** to **4**.

Supplementary tables.

Table S1 Distribution ratios (D_{Am} and D_{Eu}) and separation factors ($SF_{Am/Eu}$) for Am(III) and Eu(III) ions in nitric acid solutions. The extractant (**L**) concentration in [$C_n$mim] [NTf_2] was 4 mM (1:1 v/v extraction).

L	[$C_n$mim] [NTf_2] *n*	**0.1 M HNO_3**			**1.0 M HNO_3**		
		D_{Am}	D_{Eu}	$SF_{Am/Eu}$	D_{Am}	D_{Eu}	$SF_{Am/Eu}$
1	4	12.7	0.7	19.0	0.17	0.0065	26.2
	6	1.7	1.0	1.7	0.11	0.011	10.0
	8	0.95	0.1	9.5	0.053	0.0023	23.0
3	4	97	31	3.1	28	0.64	44.0
	6	16.4	6.1	2.7	5.9	0.12	48.9
	8	1.5	1.1	1.3	2.8	0.01	28.3
4	4	130	3.5	37.6	8.3	0.53	15.7
	6	2.1	0.2	8.7	2.7	0.053	50.9
	8	1.8	0.09	20.2	1.7	0.034	48.8

Table S2 Distribution ratios D_{Ln} for Ln(III) ions for extraction from aqueous solution (pH 3.25) using 4 mM **1** in different imidazolium ILs (*n* is the carbon number for the alkyl arm of the IL cation) and *n*-dodecane.

Ln	[$C_n$mim] [NTf_2]				*n*-dodecane
	2	4	6	8	
La	96	97	12	0.41	0.034
Ce	100	110	17	0.58	0.038
Pr	78	88	20	1.1	0.031
Nd	36	41	15	0.82	0.037
Sm	11	14	39	2.3	0.036
Eu	6.7	11	57	3.0	0.040
Gd	4.2	7.3	34	2.0	0.031
Tb	8.6	17	110	5.6	0.024
Dy	13	27	180	6.0	0.028
Ho	14	74	300	8.8	0.033
Er	90	160	520	15	0.031
Tm	180	310	1300	42	0.029
Yb	150	270	1600	85	0.045
Lu	190	220	2800	180	0.039

Table S3: Distribution ratios D_{Ln} for Ln(III) ions for extraction from aqueous solution (pH 3.25) using 4 mM **3** in different imidazolium ILs (*n* is the carbon number for the alkyl arm of the IL cation).

Ln	[$C_n$mim] [NTf_2]		
	2	4	6
x	10^3	1	10^3
La	14	1400	250
Ce	-	3400	-
Pr	30	2750	300
Nd	21	1600	170
Sm	13	490	130
Eu	5.2	200	42
Gd	1.8	70	23
Tb	1.0	42	6.8
Dy	0.32	23	83
Ho	0.30	30	73
Er	0.28	37	54
Tm	0.30	59	22
Yb	0.23	75	92
Lu	0.32	170	100

Supplementary figures.

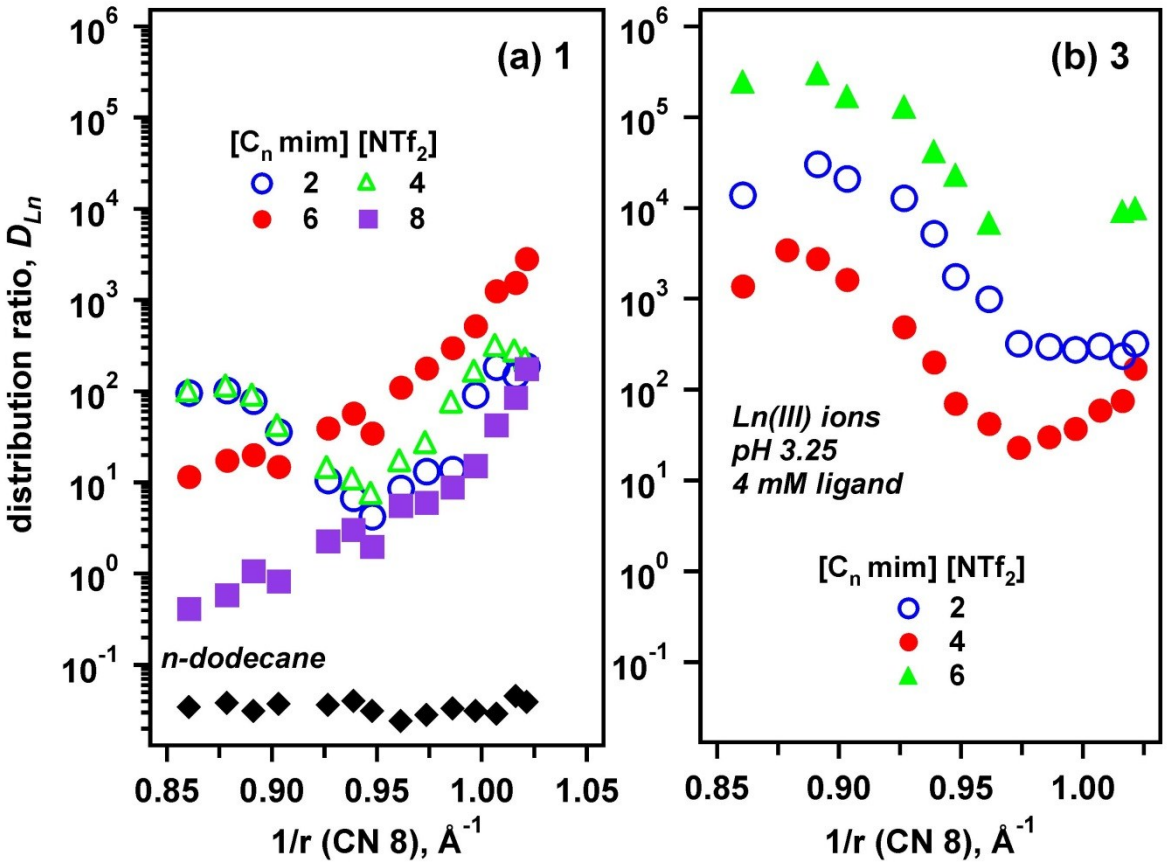


Fig. S1 Extraction of Ln(III) ions from 1 mM nitric acid using 4 mM **1** (a) or **3** (b) for different imidazolium ILs ([$C_n$mim] [NTf_2], n=2-8) and n-dodecane (in panel a). The distribution ratios D_{Ln} are plotted vs. 1/r, where r is the ionic radius for coordination number 8. In panel a, the complex dependencies observed for [C_2mim] [NTf_2] and [C_4mim] [NTf_2] are likely to arise due to interference of cation exchange, which is entirely suppressed for more hydrophobic cations.

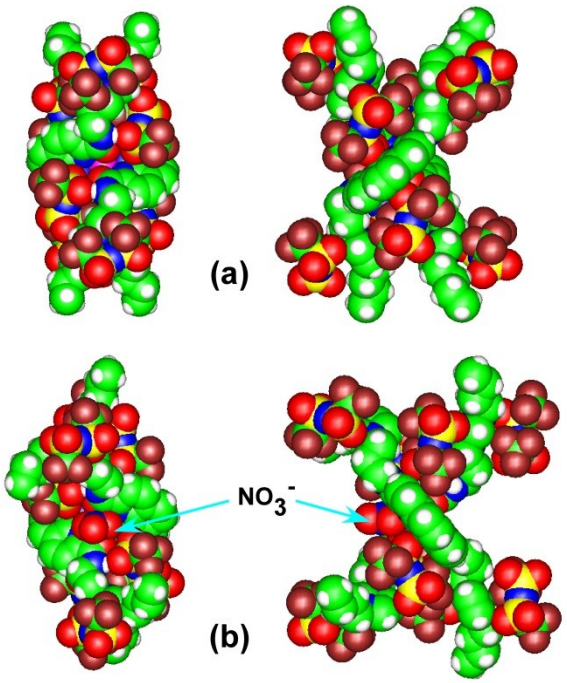


Fig. S2 Space filling renditions of optimized geometry axisymmetric $[Gd^{III}L_2(NO_3^-)_x](NTf_2^-)_8$ complexes for ligand **3**: (a) x=0 and (b) x=1 complexes. The arrows indicate the nitrate ligand. Top views and side views of these helical complexes are given side by side.

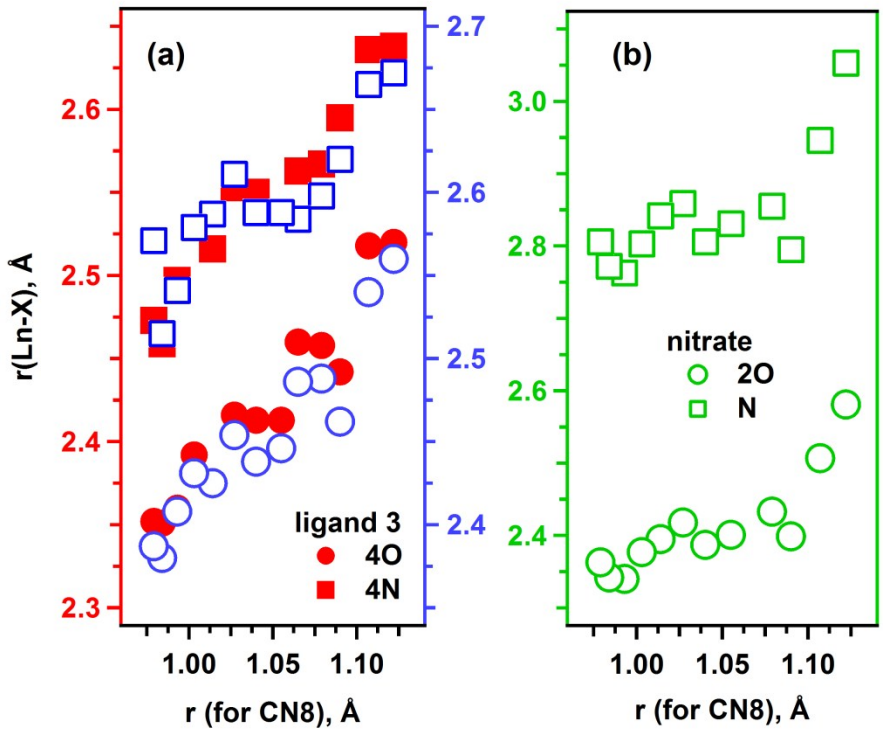


Fig. S3 Ionic radius dependences for Ln-X distances in optimized geometry $[Ln^{III}L_2(NO_3^-)_x](NTf_2^-)_8$ complexes for ligand **3** assuming x=0 (*filled symbols*) and x=1 (*open symbols*). Panel a is for O and N atoms in ligand **3**, panel b is for the nitrate ligand. X=O corresponds to the circles and X=N corresponds to the squares. The ionic radii (across the lanthanide period) are for the coordination number of eight. As the ionic radius increases for lighter lanthanide ions, the ligands move away from the metal ion, making it more accessible to nitrate addition.

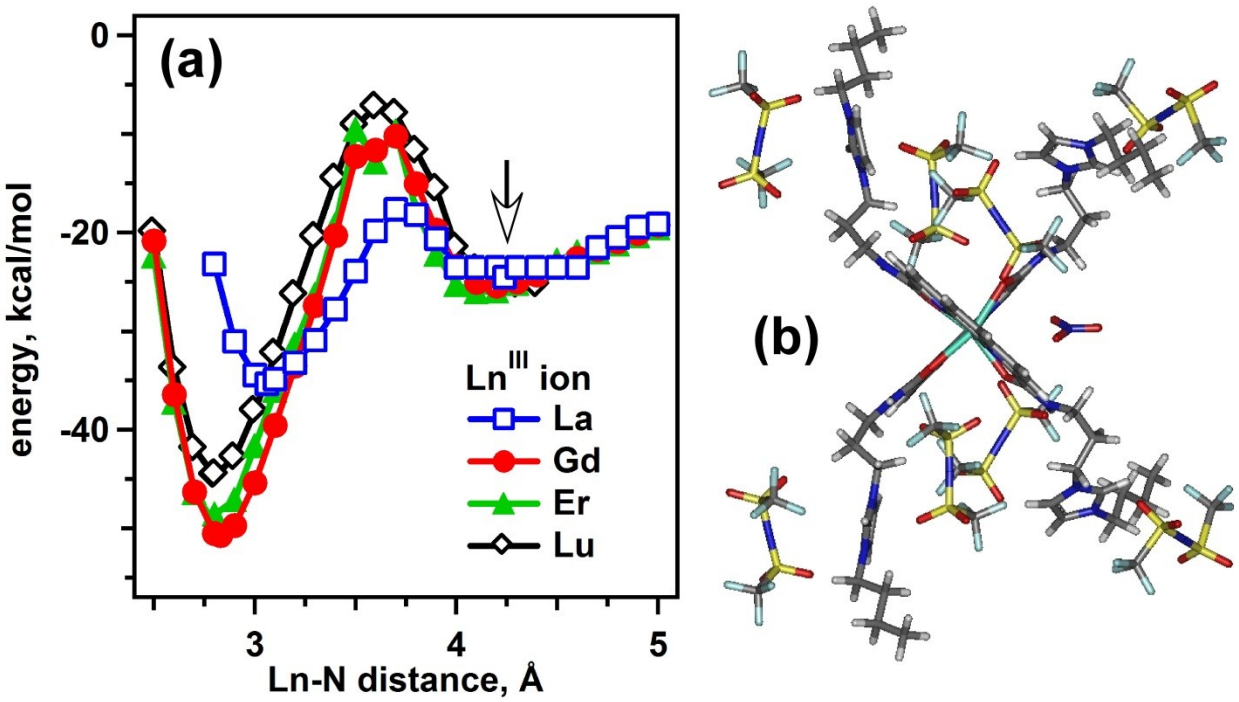


Fig. S4 (a) Energy profile for the axisymmetric $[Ln^{III}L_2(NO_3^-)](NTf_2^-)_8$ complex (for La, Gd, Er and Lu) as a function of Ln-N distance for the NO_3^- nitrogen (all other degrees of freedom optimized). The arrow indicates a local potential minimum for the nitrate anion in between the two imidazolium cations in this complex, as shown in panel b. As the ionic radius increases, the energy barrier to NO_3^- addition systematically decreases, and so does the enthalpy of this addition. Zero energy corresponds to the nitrate anion removed from the complex.

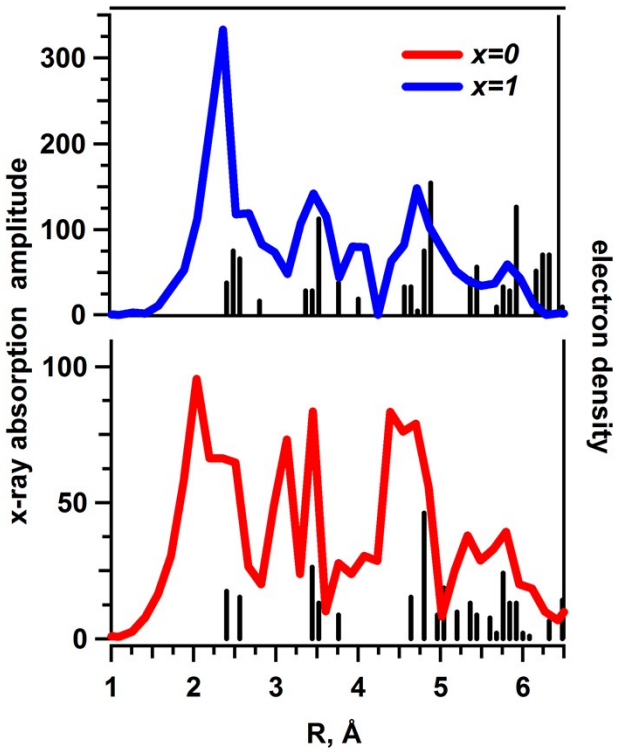


Fig. S5 Simulated *R*-space k^3-weighted EXAFS (extended X-ray absorption fine structure) patterns for $[Gd^{III}L_2(NO_3^-)_x](NTf_2^-)_8$ complexes for x=0 and x=1 (*see the legend in the plot*) juxtaposed onto the electron density distribution in these two complexes. The large amplitude in the first peak due to the presence of the bound nitrate ligand makes it easy to quantify the degree of nitrate involvement by means of X-ray absorption spectroscopy.

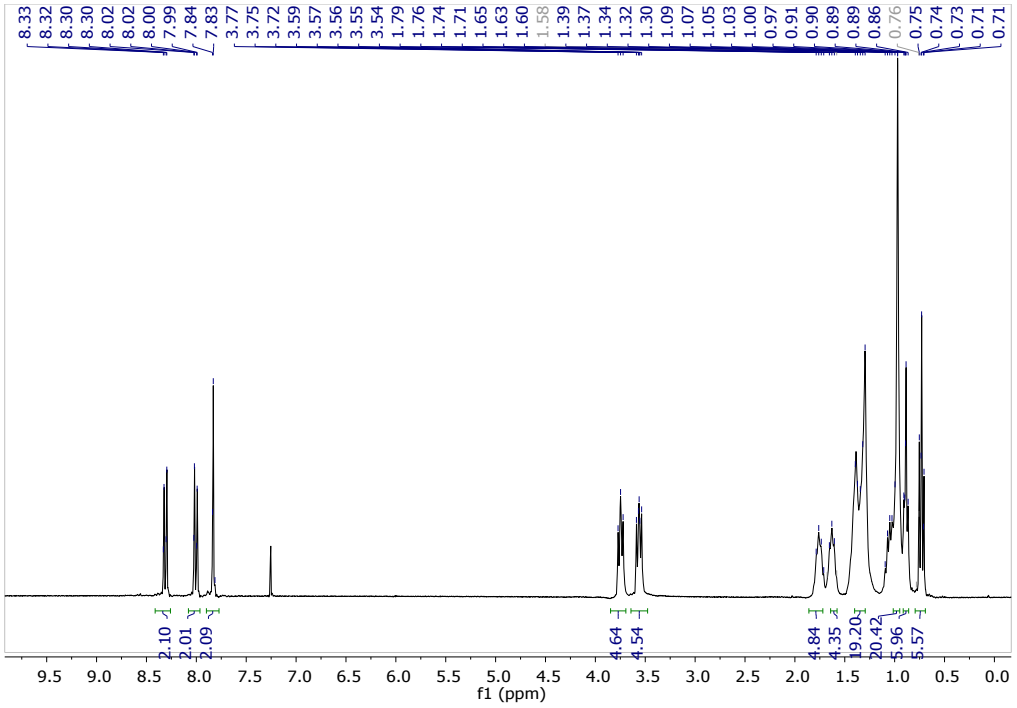


Figure S6 ^{1}H NMR of compound **1** in $CDCl_3$.

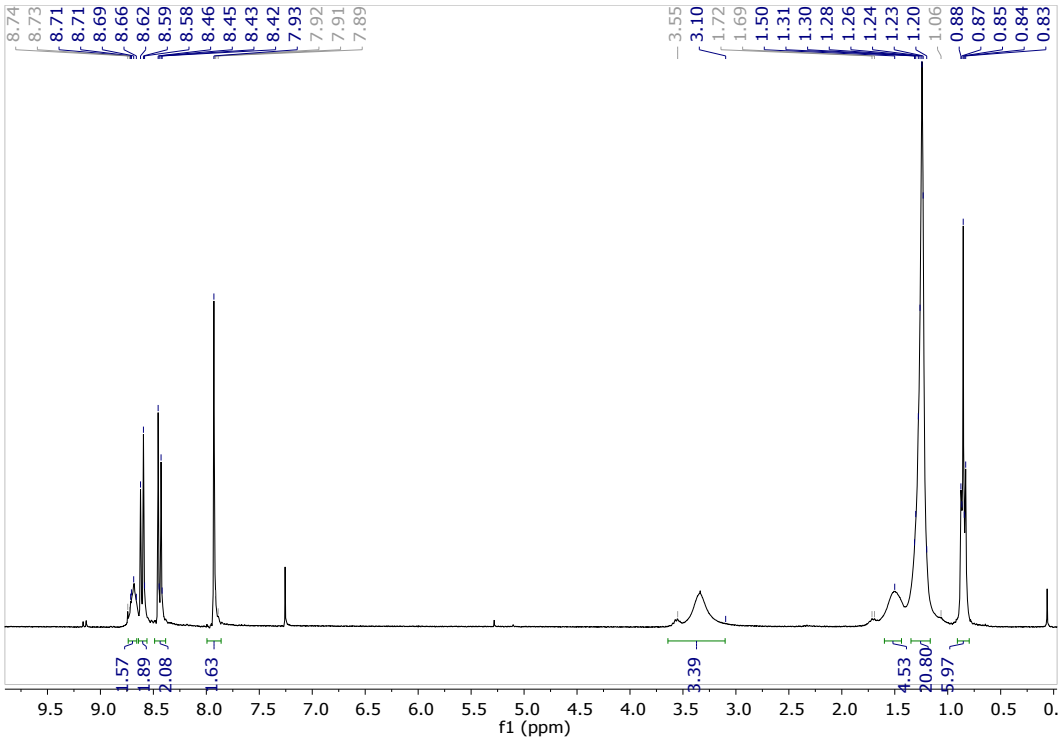


Figure S7 ^{1}H NMR of compound **1** in $CDCl_3$.

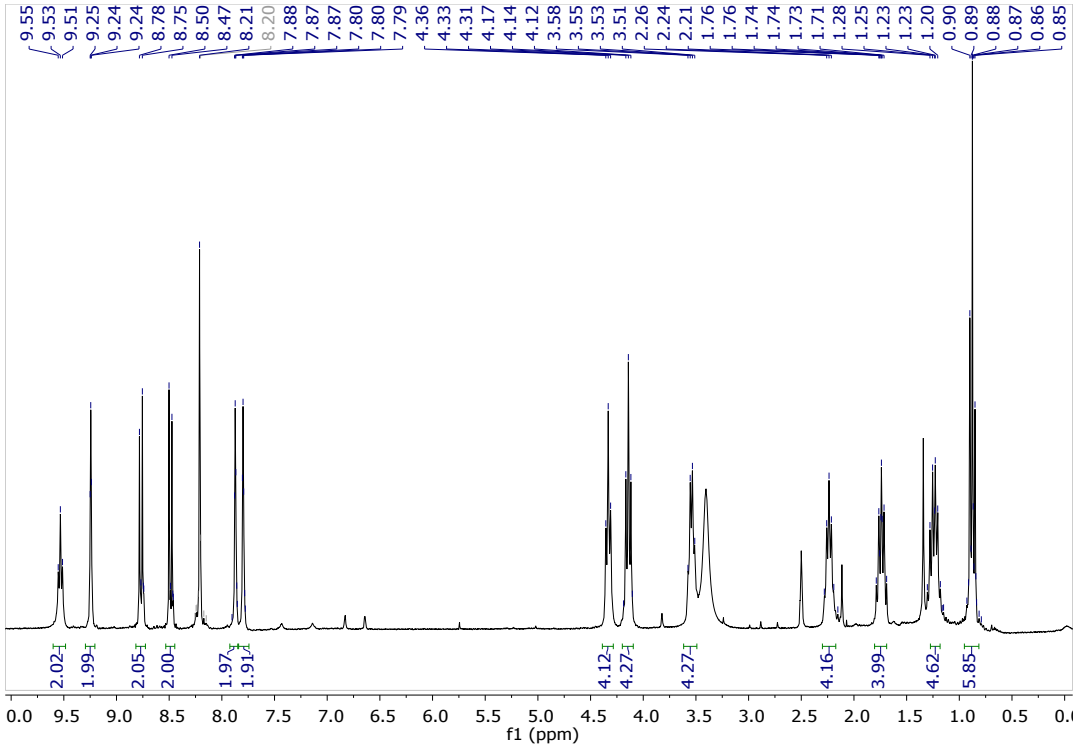


Figure S8 ^{1}H NMR of compound **3** in DMSO-d_6.

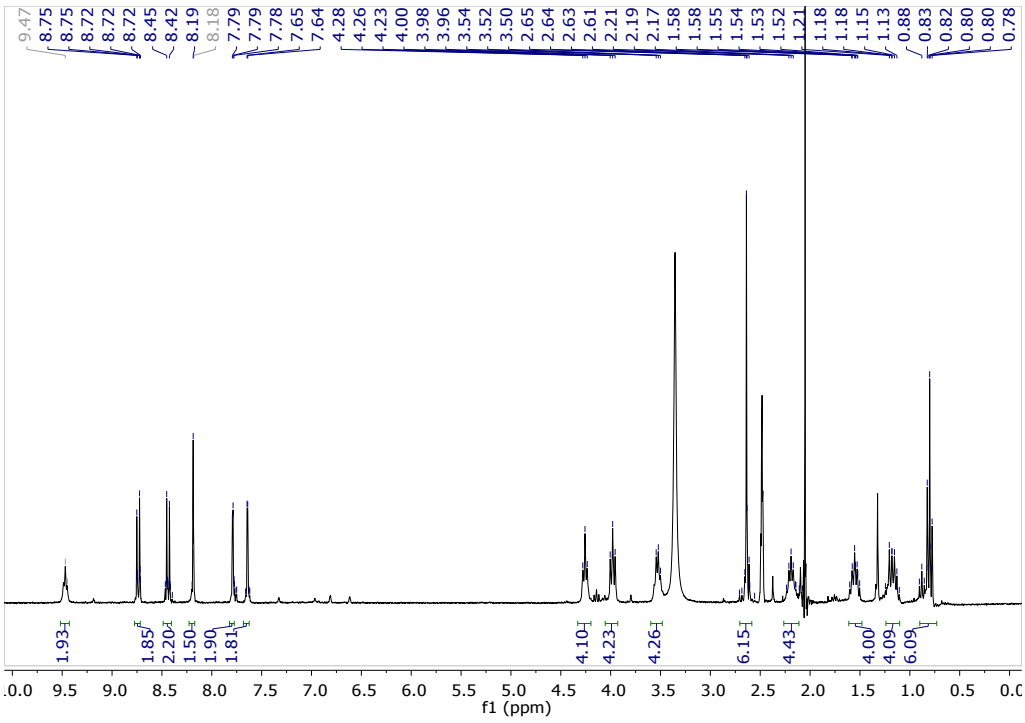


Figure S9 ^{1}H NMR of compound **4** in DMSO-d_6.

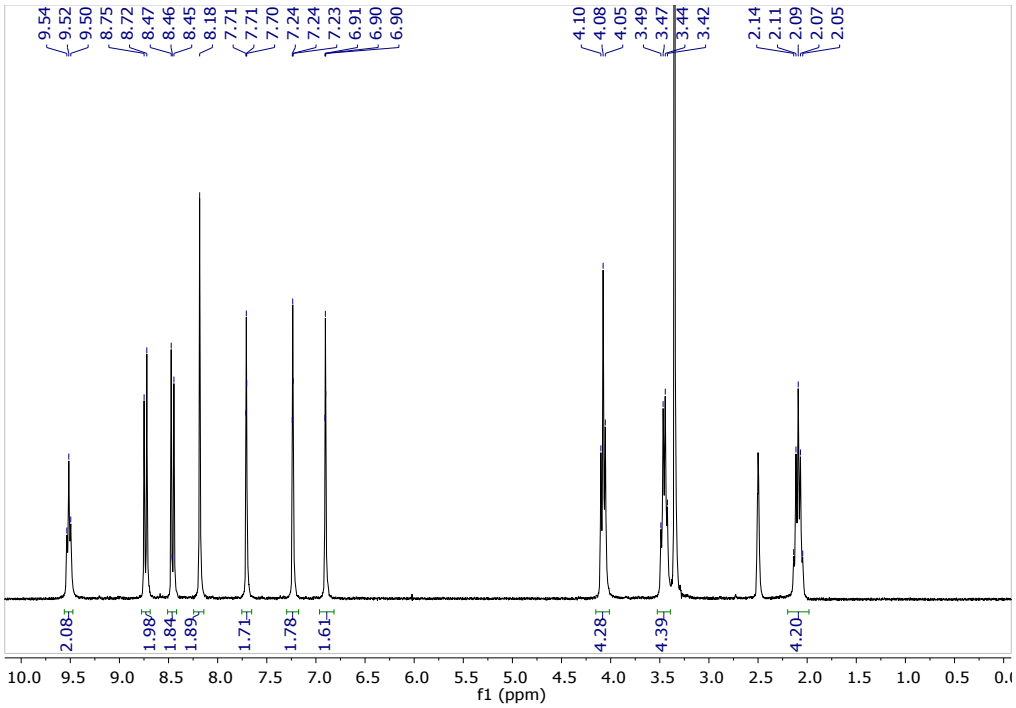


Figure S10 ^{1}H NMR of compound **8** in DMSO-d_6.

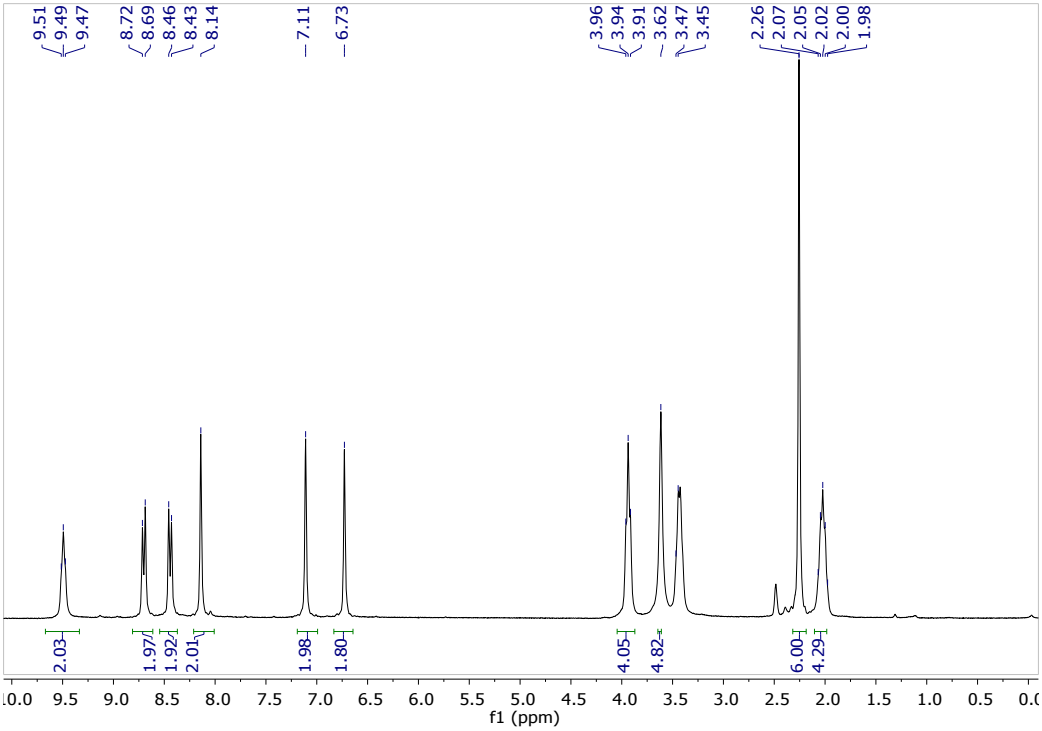


Figure S11 ^{1}H NMR of compound **9** in DMSO-d_6.

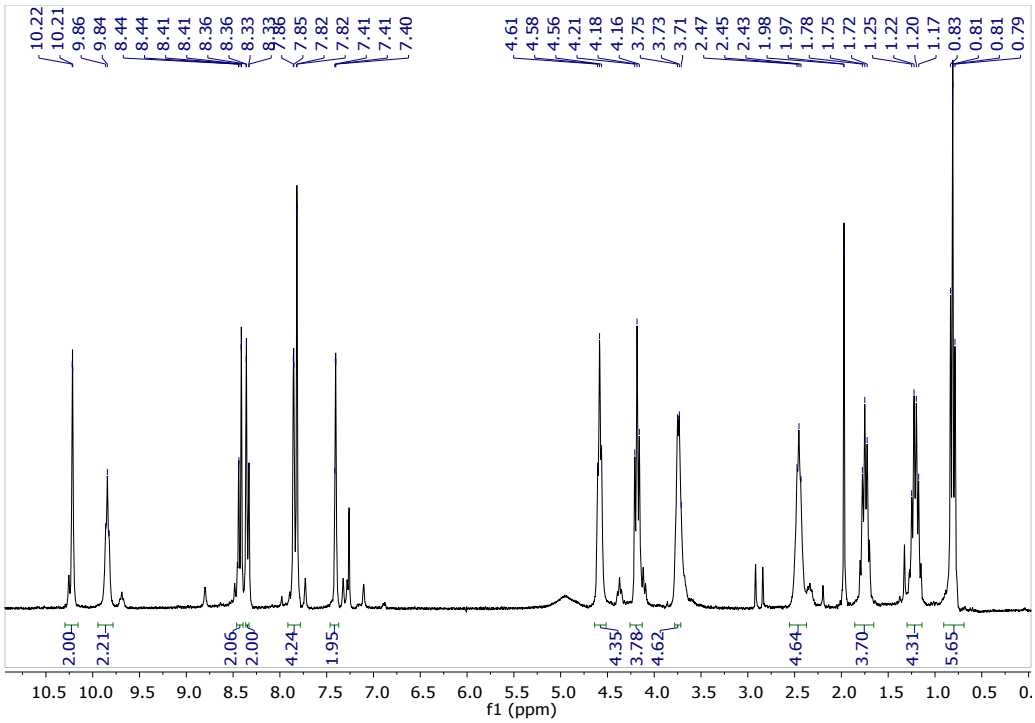


Figure S12 ^{1}H NMR of compound **10** in $CDCl_3$.

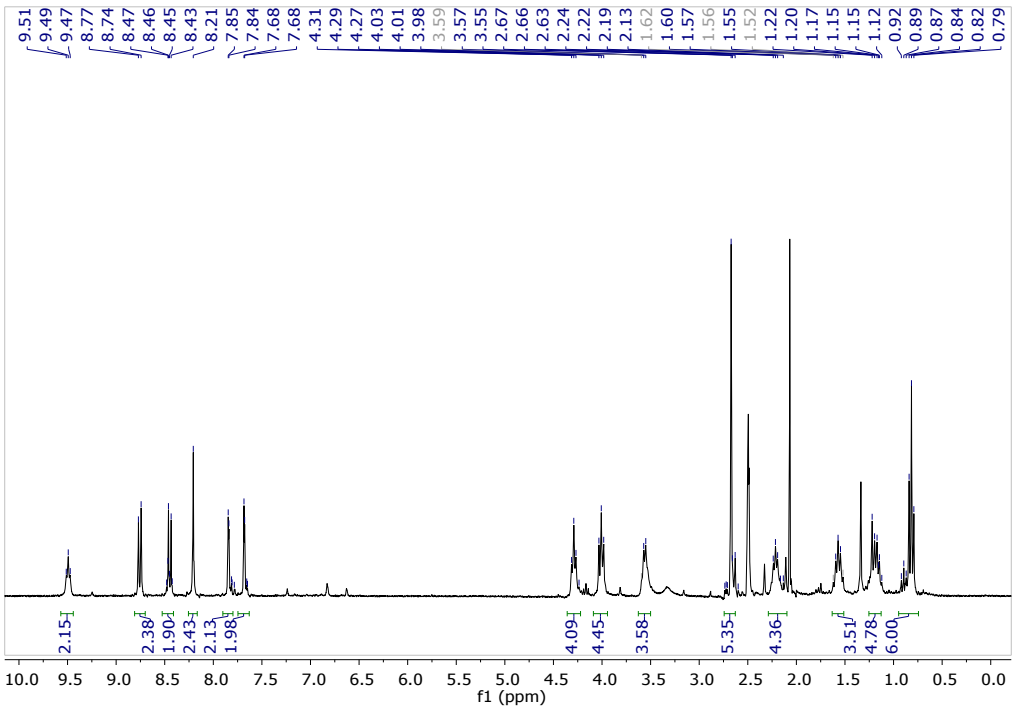


Figure S13 ^{1}H NMR of compound **11** in DMSO-d_6.

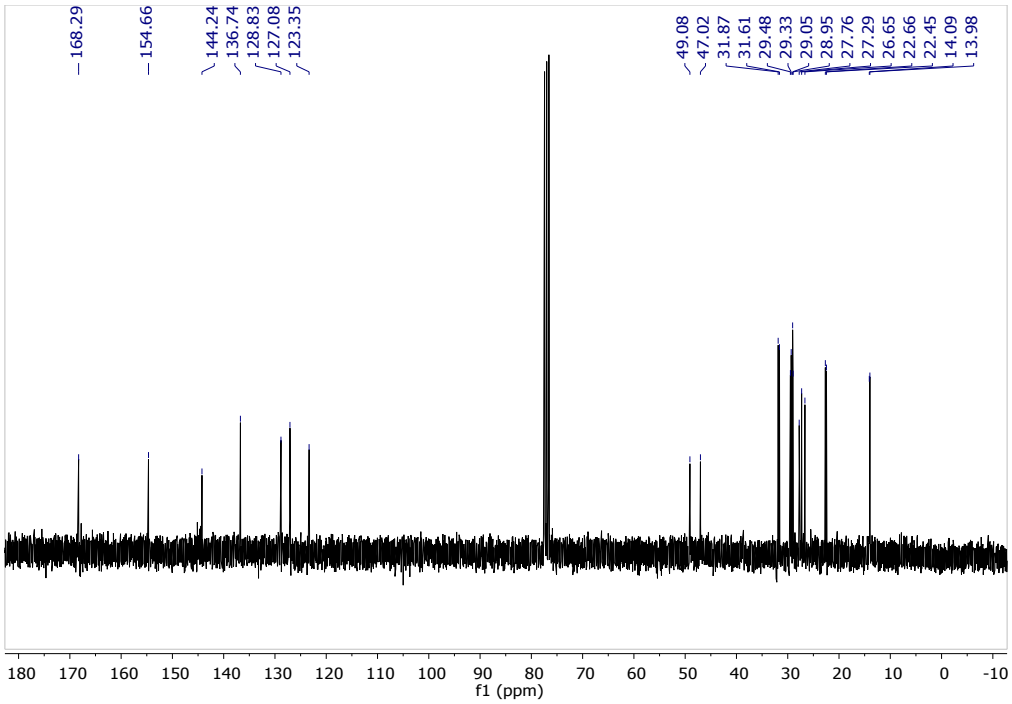


Figure S14 ^{13}C NMR of compound **1** in $CDCl_3$.

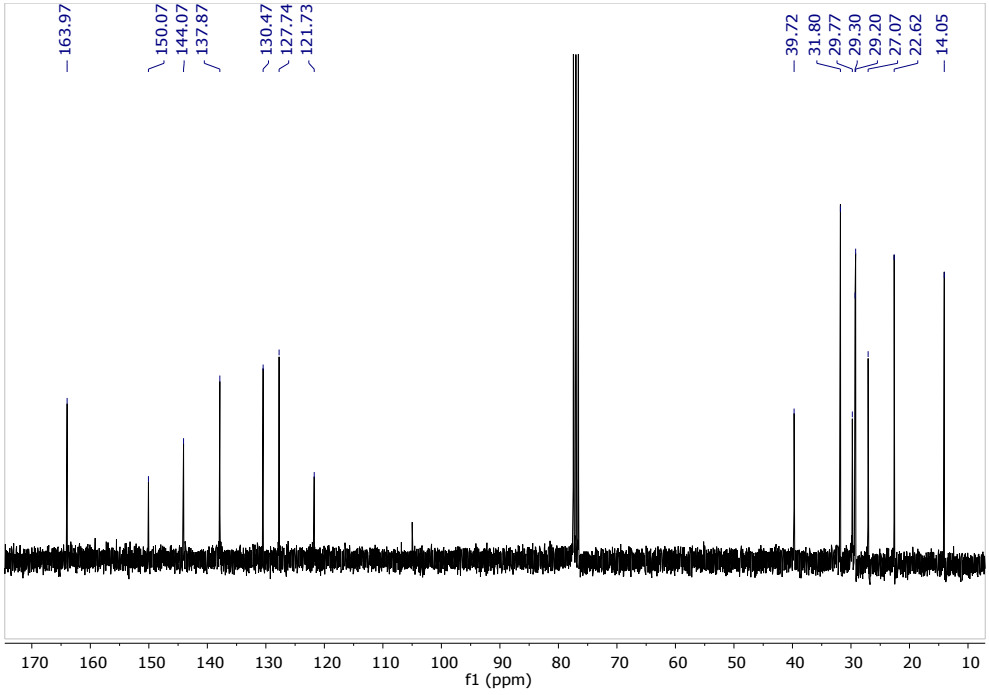


Figure S15 ^{13}C NMR of compound **2** in $CDCl_3$.

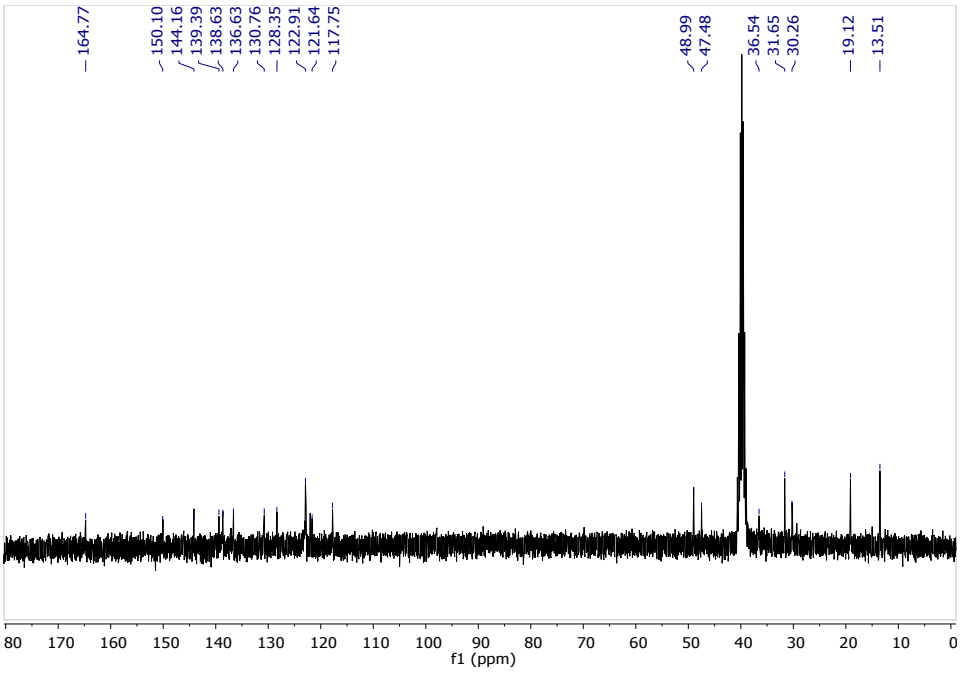


Figure S16 ^{13}C NMR of compound **3** in DMSO-d_6.

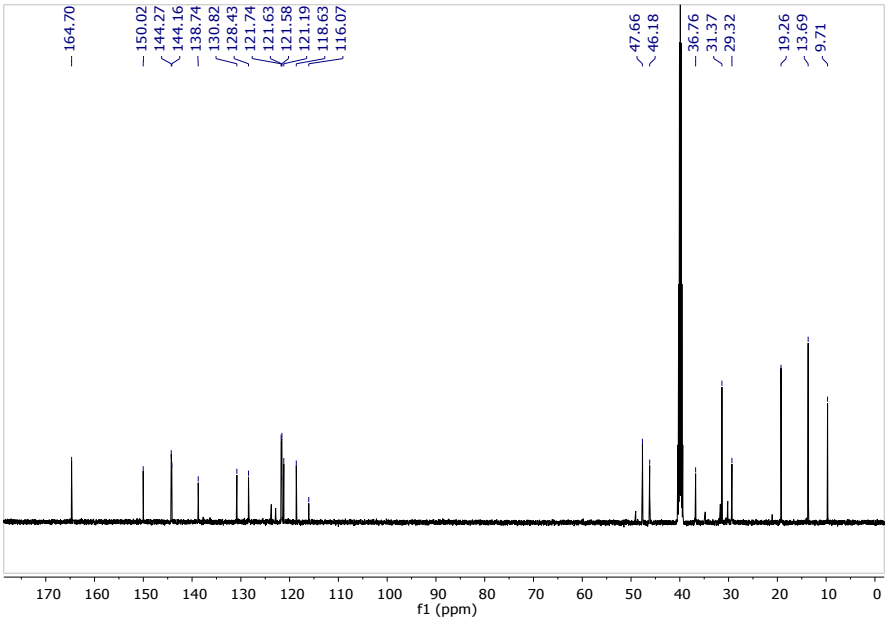


Figure S17 ^{13}C NMR of compound **4** in DMSO-d_6.

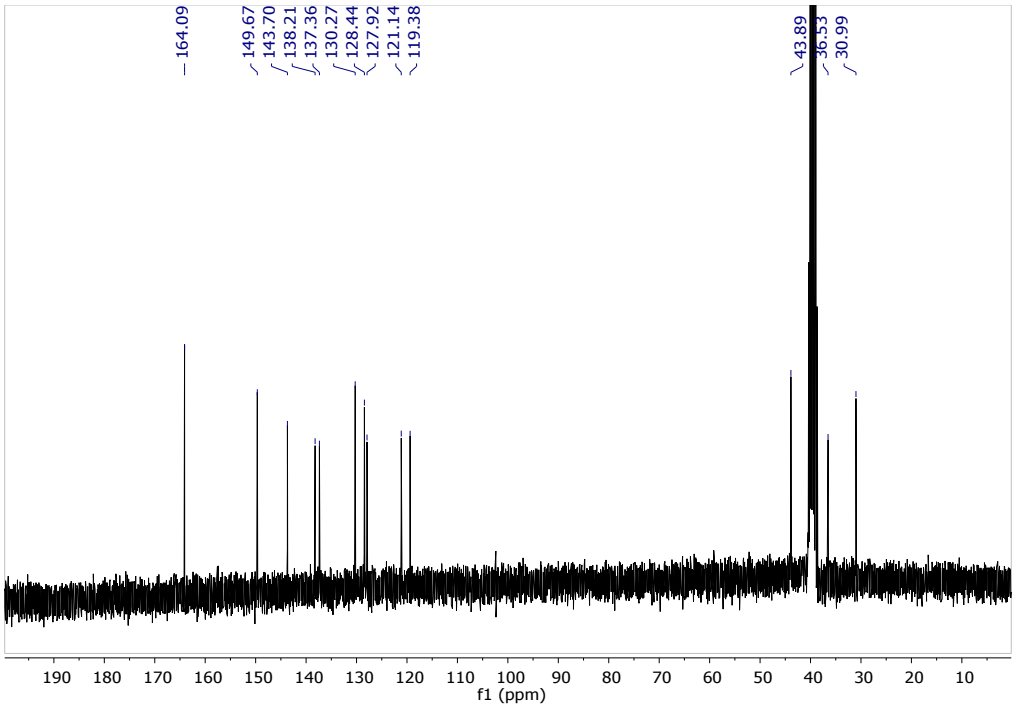


Figure S18 ^{13}C NMR of compound **8** in DMSO-d_6.

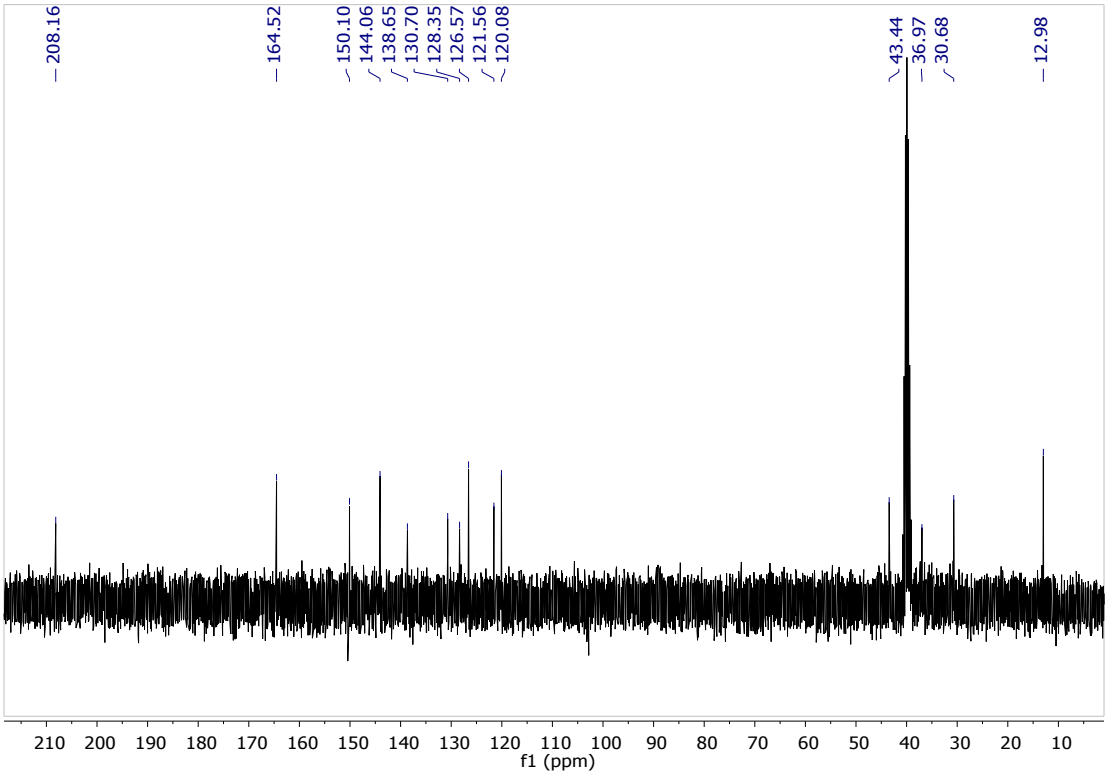


Figure S19 ^{13}C NMR of compound **9** in DMSO-d_6.

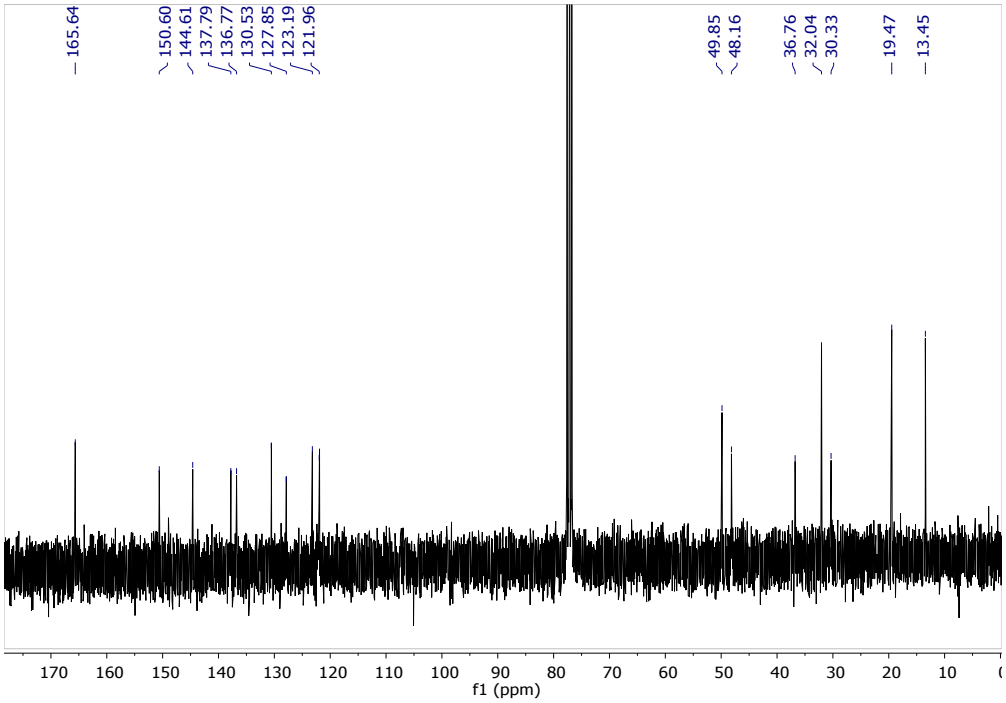


Figure S20 ^{13}C NMR of compound **10** in $CDCl_3$.

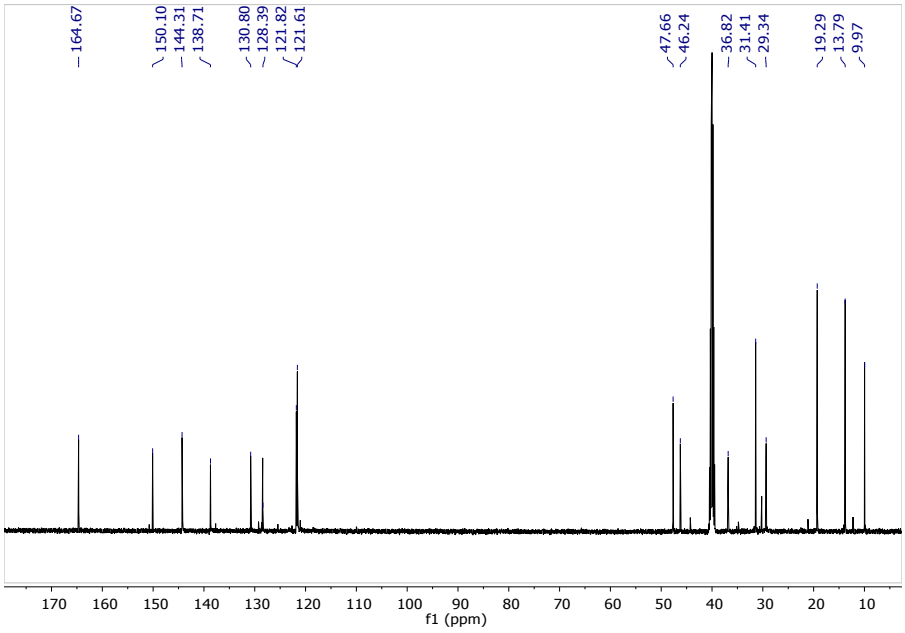


Figure S21 ^{13}C NMR of compound **11** in DMSO-d_6.

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