

# Self-assembly of $M_4L_4$ Tetrahedral Cages Incorporating Pendant P=S and P=Se Functionalised Ligands

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## Supporting Information

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## General Methods

All moisture sensitive reactions were performed under nitrogen with dried solvent using oven-dried glassware. Dry Toluene was distilled over Na with benzophenone and triethylamine was dried over 4 Å molecular sieves prior to use. All uncharacterised chemicals were obtained from commercial suppliers and used as received.

NMR spectra were collected at 298 K on a Bruker Avance III 400 (400 MHz for  $^1\text{H}$ , 101 MHz for  $^{13}\text{C}$ , 162 MHz for  $^{31}\text{P}$ , and 76 MHz for  $^{77}\text{Se}$ ), Bruker Avance 600 (600 MHz for  $^1\text{H}$ , 151 MHz for  $^{13}\text{C}$ ), and Bruker Ascend 700 (700 MHz for  $^1\text{H}$ , 176 MHz for  $^{13}\text{C}$ ) spectrometers. Chemical shifts ( $\delta$ ) are reported in ppm and coupling constants ( $J$ ) are measured Hz.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  chemical shifts are reported relative to the relevant residual solvent, whereas  $^{31}\text{P}\{^1\text{H}\}$  and  $^{77}\text{Se}$  chemical shifts are reported relative to the external references ( $\delta = 0.00$  ppm)  $\text{H}_3\text{PO}_4$  and  $\text{Me}_2\text{Se}$ , respectively.

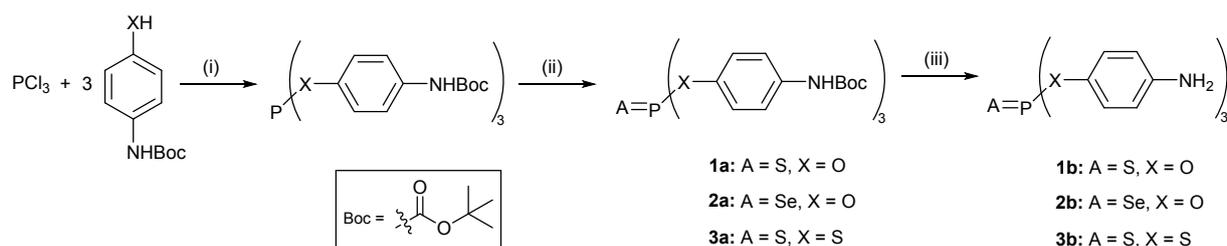
Diffusion NMR data was collected on a Bruker Avance 600 at 298 K fitted with a 5 mm CP TCI probe and z-gradient coil of  $5.35 \times 10^{-4}$  T  $\text{cm}^{-1}$  maximum field strength. The convection compensated pulse program, *dstepbpgp3s*, was used to mitigate the low viscosity of  $d_3$ -acetonitrile. The gradient pulse length and diffusion time were determined individually for each sample by calibrating the parameters required for 95% signal attenuation at 95% gradient strength. All experiments were conducted by increasing the gradient strength from 2 - 90% in 16 equal steps. Diffusion data was processed by Dynamics Centre and the DOSYToolbox<sup>1</sup>. Errors were estimated from the standard error of the regression model and compared with the diffusion coefficient range as indicated by the HR-DOSY plot. Hydrodynamic radii were calculated by the Stokes-Einstein equation using reported viscosity values for acetonitrile.<sup>2</sup>

Small molecule HR-ESI MS was performed on a Waters LCT Premier OA-TOF mass spectrometer. Mass spectra for the assembled cages were acquired using a Thermo Orbitrap Elite fitted with a hybrid ion trap-orbitrap mass spectrometer under conditions adapted from Yang *et al.*<sup>3</sup> Samples were injected straight, without dilution, at approximately 0.7 mM, and into the ion source at a flow rate of 15  $\mu\text{L}/\text{min}$  with a capillary temperature of 50°C. The ions were generated *via* ESI with a constant applied voltage of 5 kV in order to minimise fragmentation. Analyses including isotope matching and error estimation were performed using Thermo Xcalibur.

Small molecule single-crystal X-ray diffraction data was obtained using an Oxford Diffraction SuperNova diffractometer at 150 K. The data was collected and reduced with CrysAlisPro.<sup>4</sup>

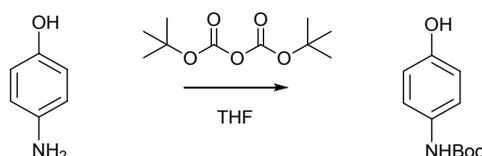
Diffraction data of the assembled cages was recorded on the MX-1 beamline at the Australian Synchrotron. The data was collected using BluIce<sup>5</sup> and reduced with XDS.<sup>6</sup> All structures were solved within Olex2<sup>7</sup> by ShelXT<sup>8</sup> with refinement by ShelXL.<sup>9</sup> Additional graphics were generated using the program Mercury.

## Experimental



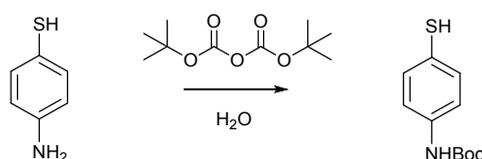
**Scheme S1** The general synthesis of the thio- and selenophosphate pro-ligands. Conditions: (i)  $\text{NEt}_3$ , toluene (ii)  $\text{S}_8$  or Se, reflux (iii) TFA, DCM.

### N-Boc-4-aminophenol



Adapted from Sleath.<sup>10</sup> *Di*-*t*-butyl dicarbonate (4.19 g, 19.2 mmol) was dissolved in THF (50 mL) and 4-aminophenol (2.0 g, 18.3 mmol) was added in small portions over 5 min. The mixture was stirred for 30 h before the solvent was evaporated to dryness. The residue was extracted into ethyl acetate and washed with brine ( $3 \times 40$  mL) and dried over magnesium sulfate. The solvent was then removed under reduced pressure to obtain the product as a white crystalline solid. Yield 89% (3.41 g, 16.3 mmol).  $^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO)  $\delta$  9.02 (s, 1H), 8.96 (s, 1H), 7.20 (d,  $J = 8.4$  Hz, 2H), 6.63 (d,  $J = 8.4$  Hz, 2H), 1.44 (s, 9H).  $^{13}\text{C}$  NMR (101 MHz,  $d_6$ -DMSO)  $\delta$  153.0 (C=O), 152.5 (C), 131.0 (C), 120.0 (CH), 115.0 (CH), 78.4 (C), 28.2 ( $\text{CH}_3$ ). ESI-MS(+ve ion): Found:  $m/z = 232.2$ . Calcd for  $[\text{C}_{11}\text{H}_{15}\text{NO}_2\text{S} + \text{Na}]^+ 232.2$   $[\text{M} + \text{Na}]^+$ .

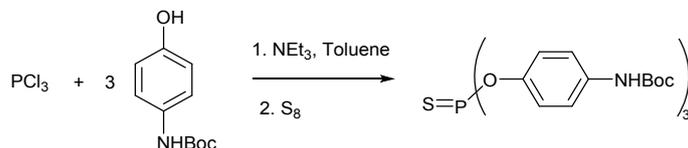
### N-Boc-4-aminothiophenol



Adapted from Das.<sup>11</sup> To 4-aminothiophenol (1.17 g, 9.4 mmol) suspended in water (9 mL) was added *di*-*t*-butyl dicarbonate (2.26 g, 10.4 mmol). The mixture was heated to  $38^\circ\text{C}$  and stirred for 1 h, after which it was cooled to r.t. resulting in the formation of a yellow precipitate. The crude product was washed with warm water ( $4 \times 15$  mL), then dried under high vacuum to yield a pale yellow solid.

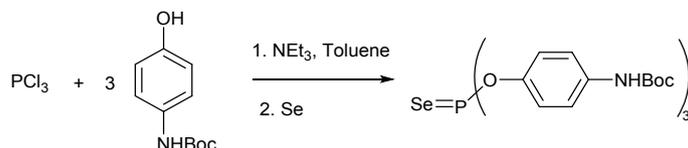
Yield 47% (0.99 g, 4.4 mmol).  $^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO)  $\delta$  9.30 (s, 1H), 7.34 (d,  $J = 8.6$  Hz, 2H), 7.17 (d,  $J = 8.6$  Hz, 2H), 5.12 (s, 1H), 1.46 (s, 9H).  $^{13}\text{C}$  NMR (101 MHz,  $d_6$ -DMSO)  $\delta$  152.6 (C=O), 137.2 (C), 129.5 (CH), 123.5 (C), 118.7 (CH), 79.0 (C), 28.1 (CH<sub>3</sub>). HR-ESI(+ve ion): Found:  $m/z = 248.0718$ . Calcd for  $[\text{C}_{11}\text{H}_{15}\text{NO}_2\text{S} + \text{Na}]^+ 248.0721$   $[\text{M} + \text{Na}]^+$ .

### Tris(*N*-Boc-4-aminophenyl)thiophosphate [1a]:



Under nitrogen, *N*-Boc-4-aminophenol (500 mg, 2.39 mmol) was dissolved in dry toluene (20 mL) and cooled to 0°C. Triethylamine (0.333 mL, 2.39 mmol) was added dropwise and the white suspension stirred for 10 min before slowly adding a solution of  $\text{PCl}_3$  (0.70 mL, 0.80 mmol) in toluene (5 mL) over 10 min, after which the reaction was allowed to warm to r.t. and stirred for 24 hours. The resulting white suspension was frozen with liquid nitrogen and elemental sulfur (38.3 mg, 0.150 mmol) was added. The flask was evacuated and backfilled with nitrogen ( $\times 4$ ), and once returned to r.t., was heated to reflux for 30 hours. Afterwards, the reaction was filtered through a pad of Celite, washing with additional toluene ( $2 \times 20$  mL) and the solvent removed under reduced pressure to yield the title compound as a colourless powder. Yield 72% (395 mg, 0.574 mmol).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 (d,  $J = 6.8$  Hz, 6H), 7.12 (d,  $J = 6.8$  Hz, 6H), 6.45 (s, 3H), 1.51 (s, 27H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  152.8 ( $3 \times \text{C}=\text{O}$ ), 146.1 ( $3 \times \text{C}$ ), 136.2 ( $3 \times \text{C}$ ), 121.8 ( $6 \times \text{CH}$ ), 119.8 ( $6 \times \text{CH}$ ), 80.9 ( $3 \times \text{C}$ ), 27.5 ( $9 \times \text{CH}_3$ ).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  54.6 (s). IR: 2978 (N-H), 2945, 1706 (C=O), 1474, 1396, 1171, 1035, 807, 462  $\text{cm}^{-1}$ . HR-ESI(+ve ion): Found:  $m/z = 710.2277$ . Calc'd for  $[\text{C}_{33}\text{H}_{42}\text{N}_3\text{O}_9\text{PS} + \text{H}]^+ 710.2272$   $[\text{M} + \text{H}]^+$ .

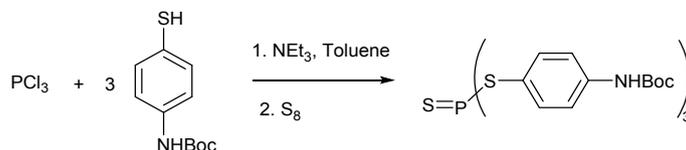
### Tris(*N*-Boc-4-aminophenyl)selenophosphate [2a]:



Under nitrogen, *N*-Boc-4-aminophenol (500 mg, 2.39 mmol) was dissolved in dry toluene (20 mL) and cooled to 0°C. Triethylamine (0.333 mL, 2.39 mmol) was added dropwise and the white suspension stirred for 10 min before slowly adding a solution of  $\text{PCl}_3$  (0.70 mL, 0.80 mmol) in toluene (5 mL) over 10 min, after which the reaction was allowed to warm to r.t. and stirred for 24 hours.

The resulting white suspension was frozen with liquid nitrogen and elemental selenium (94.3 mg, 1.20 mmol) was added. The flask was evacuated and backfilled with nitrogen ( $\times 4$ ), and once returned to r.t., was heated to reflux for 30 hours. Afterwards, the reaction was filtered through a pad of Celite, washing with additional toluene ( $2 \times 20$  mL) and the solvent removed under reduced pressure to yield the title compound as a colourless powder. Yield 87% (513 mg, 0.698 mmol).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (d,  $J = 8.8$  Hz, 6H), 7.14 (d,  $J = 8.8$  Hz, 6H), 6.46 (s, 3H), 1.51 (s, 27H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  152.8 ( $3 \times \text{C}=\text{O}$ ), 146.0 ( $3 \times \text{C}$ ), 136.3 ( $3 \times \text{C}$ ), 122.1 ( $6 \times \text{CH}$ ), 119.7 ( $6 \times \text{CH}$ ), 80.9 ( $3 \times \text{C}$ ), 28.5 ( $9 \times \text{CH}_3$ ).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  60.3 (s).  $^{77}\text{Se}$  NMR (76 MHz,  $\text{CDCl}_3$ )  $\delta$  -296.7 (d,  $^1J_{\text{PSe}} = 1022.5$  Hz). IR: 2980 (N-H), 1698 (C=O), 1505, 1150, 926, 829, 772, 513  $\text{cm}^{-1}$ . HR-ESI(+ve ion): Found:  $m/z = 774.1459$ . Calc'd for  $[\text{C}_{33}\text{H}_{42}\text{N}_3\text{O}_9\text{PSe} + \text{K}]^+ 774.1461$   $[\text{M} + \text{K}]^+$ .

### **Tris(*N*-Boc-4-aminophenyl)tetrathiophosphate [3a]:**

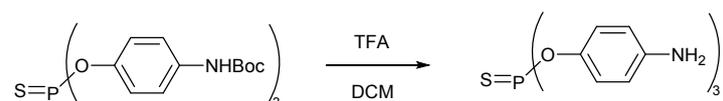


Under dry nitrogen, *N*-Boc-4-aminothiophenol (500 mg, 2.2 mmol) was dissolved in dry toluene (20 mL) and cooled to  $0^\circ\text{C}$ . Triethylamine (0.31 mL, 2.2 mmol) was then added and the mixture stirred for 10 min, before slowly adding a solution of  $\text{PCl}_3$  (0.064 mL, 0.74 mmol) in toluene (5 mL) over 10 min. The reaction was allowed to warm to r.t. and stirred for 24 h before being frozen with liquid nitrogen. Elemental sulfur (30 mg, 0.11 mmol) was added and the flask evacuated and refilled with nitrogen ( $\times 4$ ). After allowing to warm to r.t., the mixture was heated to reflux for 18 h, then filtered through a pad of Celite, washing with toluene ( $2 \times 20$  mL). The solvent was removed under reduced pressure and the crude product purified by flash chromatography (pet. spirits : ethyl acetate, 4:1) affording the title compound as a pale yellow powder. Yield 68% (368 mg, 0.500 mmol).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (d,  $J = 6.7$  Hz, 6H), 7.39 (d,  $J = 6.7$  Hz, 6H), 6.56 (s, 3H), 1.52 (s, 27H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.4 ( $3 \times \text{C}=\text{O}$ ), 140.6 ( $3 \times \text{C}$ ), 137.7 ( $3 \times \text{C}$ ), 121.6 ( $6 \times \text{CH}$ ), 118.7 ( $6 \times \text{CH}$ ), 81.2 ( $3 \times \text{C}$ ), 28.5 ( $9 \times \text{CH}_3$ ).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  94.6 (s). IR: 3319 (N-H), 2976, 1699 (C=O), 1585, 1508, 1228, 1149, 827, 508  $\text{cm}^{-1}$ . HR-ESI(+ve ion): Found:  $m/z = 758.1591$ . Calc'd for  $[\text{C}_{33}\text{H}_{42}\text{N}_3\text{O}_6\text{PS}_4 + \text{Na}]^+ 758.1586$   $[\text{M} + \text{Na}]^+$ .

### General Boc Deprotection Procedure:

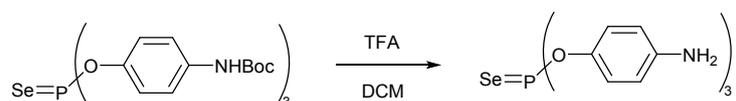
To a solution of DCM : TFA (4:1, v:v) was added the Boc-protected substrate. The mixture was stirred for 4 hours and thereafter the DCM was removed under reduced pressure. The resulting residue was extracted into ethyl acetate (25 mL) and washed with saturated sodium bicarbonate solution (2 × 25 mL) and brine (25 mL). The organic phase was then dried over sodium sulfate before evaporating to dryness to obtain the freebase product.

### Tris(4-aminophenyl)thiophosphate [1b]:



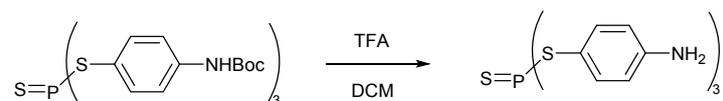
Obtained as an orange residue by the general Boc deprotection procedure. Yield 88% (88.7 mg, 0.229 mmol). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN) δ 6.94 (d, J = 8.7 Hz, 6H), 6.62 (d, J = 8.7 Hz, 6H), 4.15 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (176 MHz, CD<sub>3</sub>CN) δ 146.9 (3 × C), 142.9 (3 × C), 122.6 (6 × CH), 115.9 (6 × CH). <sup>31</sup>P NMR (162 MHz, CD<sub>3</sub>CN) δ 57.6 (s). IR: 3234, 3077, 2900, 1584, 1239, 949, 804, 618 cm<sup>-1</sup>. HR-ESI(+ve ion): Found: m/z = 388.0884. Calc'd for [C<sub>18</sub>H<sub>18</sub>N<sub>3</sub>O<sub>3</sub>PS + H]<sup>+</sup> 388.0885 [M + H]<sup>+</sup>.

### Tris(4-aminophenyl)selenophosphate [2b]:



Obtained as an orange residue by the general Boc deprotection procedure. Yield 83% (51.8 mg, 0.12 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.01 (d, J = 8.6 Hz, 6H), 6.63 (d, J = 8.6 Hz, 6H), 3.61 (bs, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 144.2 (3 × C), 143.2 (3 × C), 122.3 (6 × CH), 115.9 (6 × CH). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 62.3 (s). <sup>77</sup>Se NMR (76 MHz, CDCl<sub>3</sub>) δ -302.1 (d, <sup>1</sup>J<sub>PSe</sub> = 1009.2 Hz). IR: 3448, 3322, 2980, 1620, 1501, 1175, 933, 824, 489 cm<sup>-1</sup>. HR-ESI(+ve ion): Found: m/z = 436.0330. Calc'd for [C<sub>18</sub>H<sub>18</sub>N<sub>3</sub>O<sub>3</sub>PSe + H]<sup>+</sup> 436.0329 [M + H]<sup>+</sup>.

### Tris(4-aminophenyl)tetrathiophosphate [3b]:



Obtained as an orange residue by the general Boc deprotection procedure. Yield 78% (28.1 mg, 0.06 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.33 (d, J = 8.5 Hz, 6H), 6.64 (d, J = 8.5 Hz, 6H), 3.87 (br s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 148.2 (3 × C), 138.0 (6 × CH), 115.8 (3 × C), 115.2 (6 × CH). <sup>31</sup>P NMR

(162 MHz, CDCl<sub>3</sub>)  $\delta$  98.1 (s). IR 3372, 3239, 2952, 1677, 1442, 1098, 944, 728, 504 cm<sup>-1</sup>. HR-ESI(+ve ion): Found: m/z = 436.0188. Calc'd for [C<sub>18</sub>H<sub>19</sub>N<sub>3</sub>PS<sub>4</sub>]<sup>+</sup> 436.0194 [M + H]<sup>+</sup>.

**General Procedure for Self-Assembly of Fe<sub>4</sub>L<sub>4</sub>+ Cages [1c, 2c, 3c]:**

To a vial containing the phosphate pro-ligand (0.02 mmol, 4 equiv.) was added Fe[BF<sub>4</sub>]<sub>2</sub> (0.02 mmol, 4 equiv.) and MeCN (10 mL). The mixture was stirred for 10 min before 2-formylpyridine (0.06 mmol, 12 equiv.) was added, following which the reaction was stirred for 24 h. The assembly was then filtered and the filtrate used as-is for subsequent crystallisations.

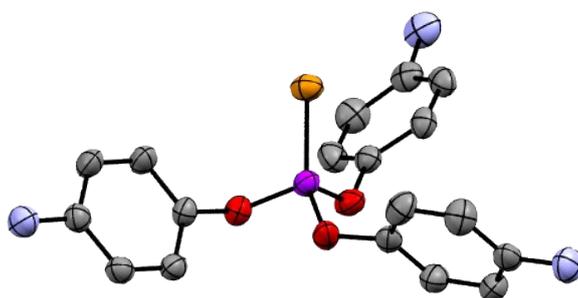
**General Procedure for Self-Assembly of Co<sub>4</sub>L<sub>4</sub> Cages [1d, 2d, 3d]:**

To a vial containing the phosphate pro-ligand (0.02 mmol, 4 equiv.) was added Co[BF<sub>4</sub>]<sub>2</sub>, (0.02 mmol, 4 equiv.) and MeCN (10 mL). The mixture was stirred for 10 min before 2-formylpyridine (0.06 mmol, 12 equiv.) was added, following which the reaction was stirred for 24 h. The assembly was then filtered and the filtrate used as-is for subsequent crystallisations.

## Crystallographic Data

### *Tris(4-aminophenyl)selenophosphate [2b]*

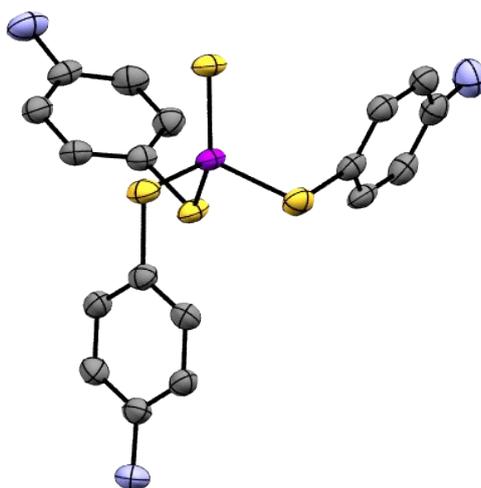
Crystal data:  $C_{18}H_{18}N_3O_3PSe$ ,  $M_r = 434.28$ ,  $T = 150(2)$  K, triclinic, space group  $P-1$  (No. 2),  $a = 9.8993(7)$ ,  $b = 10.0421(7)$ ,  $c = 10.7965(8)$  Å,  $\alpha = 77.237(6)^\circ$ ,  $\beta = 78.194(6)^\circ$ ,  $\gamma = 66.810(7)^\circ$ ,  $V = 953.87(13)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calcd}} = 1.512$  Mg m<sup>-3</sup>,  $\mu(\text{Cu } K\alpha) = 3.66$  mm<sup>-1</sup>, yellow plate,  $0.09 \times 0.07 \times 0.05$  mm, 9196 measured reflections with  $2\theta_{\text{max}} = 147.8^\circ$ , 3851 independent reflections, 3851 absorption-corrected data used in  $F^2$  refinement, 243 parameters, 0 restraints,  $R_1 = 0.039$ ,  $wR_2 = 0.109$  for 3563 reflections with  $I > 2\sigma(I)$ . CCDC 1938074.



**Figure S1** The molecular structure of *tris(4-aminophenyl)selenophosphate 2b*. Thermal ellipsoids at 50% probability. Hydrogen atoms omitted for clarity.

### *Tris(4-aminophenyl)tetrathiophosphate [3b]*

Crystal data:  $C_{18}H_{18}N_3PS_4$ ,  $M_r = 435.56$ ,  $T = 150(2)$  K, triclinic, space group  $P-1$  (No. 2),  $a = 9.7504(5)$ ,  $b = 10.5449(3)$ ,  $c = 19.9570(7)$  Å,  $\alpha = 91.015(3)^\circ$ ,  $\beta = 92.969(4)^\circ$ ,  $\gamma = 98.585(4)^\circ$ ,  $V = 2025.53(14)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calcd}} = 1.428$  Mg m<sup>-3</sup>,  $\mu(\text{Cu } K\alpha) = 5.12$  mm<sup>-1</sup>, yellow block,  $0.11 \times 0.06 \times 0.05$  mm, 27571 measured reflections with  $2\theta_{\text{max}} = 148.0^\circ$ , 8041 independent reflections, 8041 absorption-corrected data used in  $F^2$  refinement, 243 parameters, 0 restraints,  $R_1 = 0.089$ ,  $wR_2 = 0.257$  for 6441 reflections with  $I > 2\sigma(I)$ . CCDC 1938076.

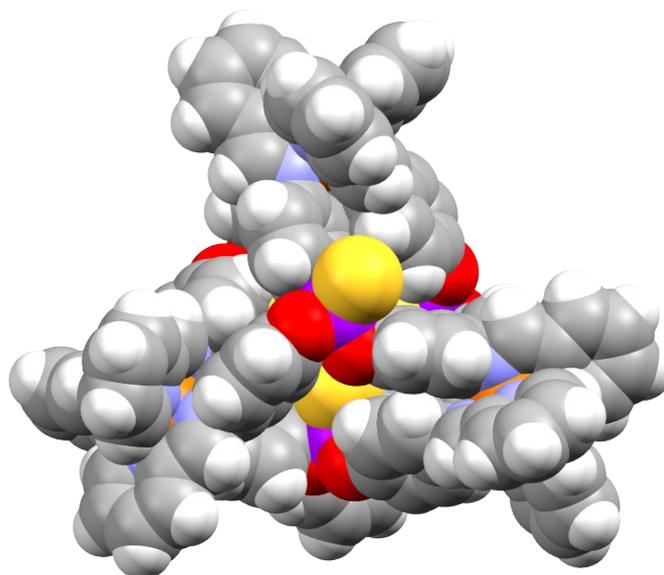


**Figure S2** The molecular structure of *tris*(4-aminophenyl)tetrathiophosphate **3b**. Thermal ellipsoids at 50% probability.

Hydrogen atoms omitted for clarity.

**Co<sub>4</sub>L<sub>4</sub> (L = *tris*(4-(((E)-pyridin-2-ylmethylene)amino)phenyl)thiophosphate) [1d]**

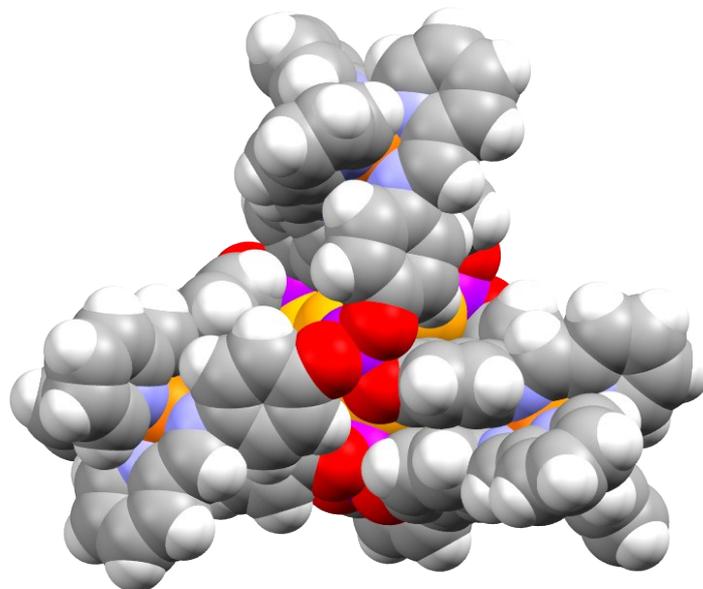
Crystal data: C<sub>144</sub>H<sub>108</sub>Co<sub>4</sub>N<sub>24</sub>O<sub>12</sub>P<sub>4</sub>S<sub>4</sub>·8(BF<sub>4</sub>), *M<sub>r</sub>* = 3548.86, T = 150(2) K, orthorhombic, space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, a = 22.900(5), b = 24.860(5), c = 38.800(8) Å, V = 22089(8) Å<sup>3</sup>, Z = 4, D<sub>calcd</sub> = 1.067 Mg m<sup>-3</sup>, μ(Mo *K*α) = 0.44 mm<sup>-1</sup>, yellow plate, 0.2 × 0.1 × 0.03 mm, 192192 measured reflections with 2θ<sub>max</sub> = 49.6°, 32756 independent reflections, 32756 absorption-corrected data used in F<sup>2</sup> refinement, 1739 parameters, 2224 restraints, R<sub>1</sub> = 0.101, wR<sub>2</sub> = 0.311 for 19966 reflections with *I* > 2σ(*I*). CCDC 1938073.



**Figure S3** Space-filling model of the thiophosphate-functionalised Co<sub>4</sub>L<sub>4</sub> cage **1d**.

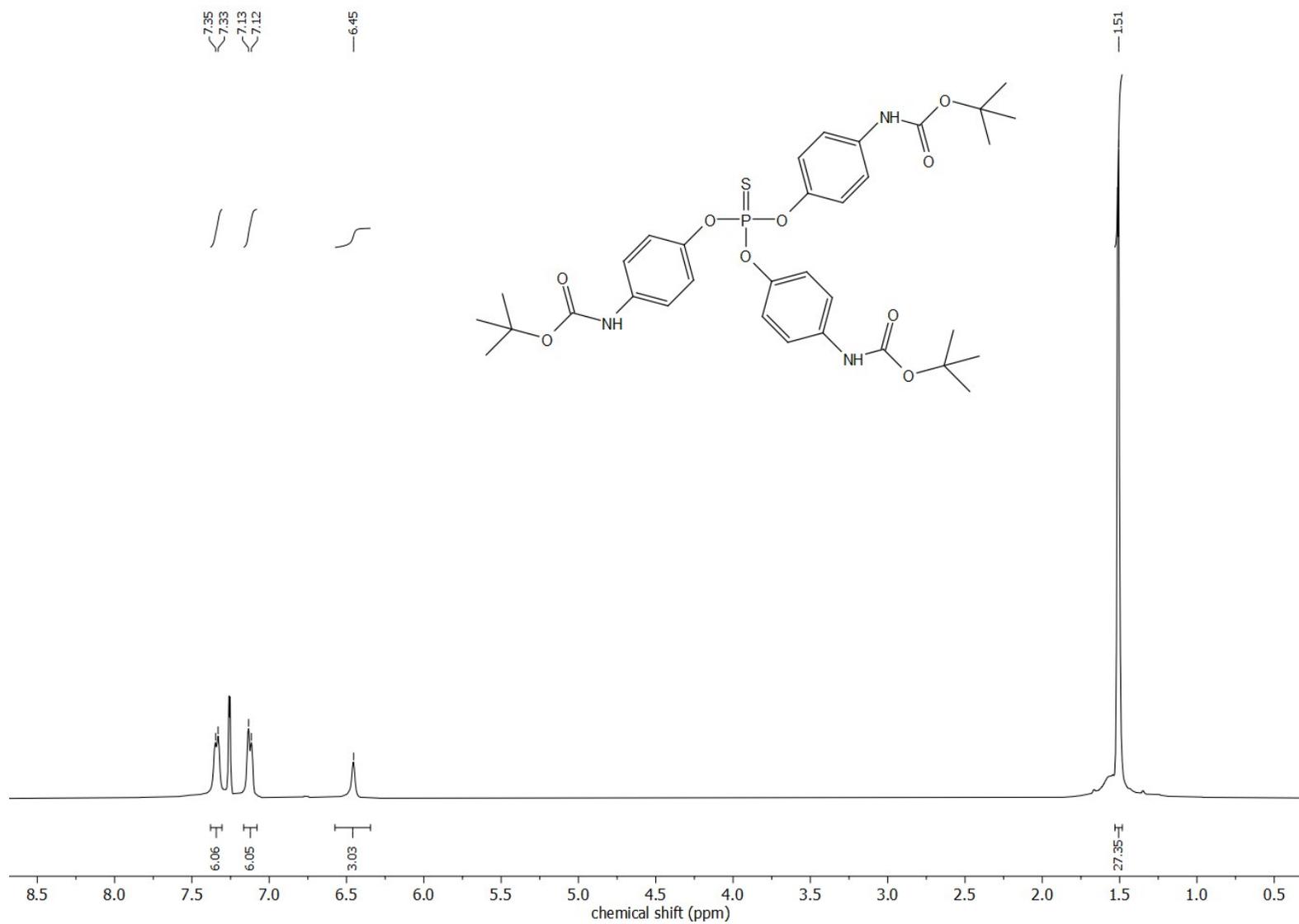
**Co<sub>4</sub>L<sub>4</sub> (L = *tris*(4-(((E)-pyridin-2-ylmethylene)amino)phenyl)selenophosphate) [2d]**

Crystal data: C<sub>144</sub>H<sub>108</sub>Co<sub>4</sub>N<sub>24</sub>O<sub>12</sub>P<sub>4</sub>Se<sub>4</sub>·8(BF<sub>4</sub>),  $M_r = 3736.46$ , T = 150(2) K, monoclinic, space group C2/c, a = 41.505(8), b = 12.145(2), c = 41.753(8) Å,  $\beta = 117.41(3)^\circ$ , V = 18683(8) Å<sup>3</sup>, Z = 4,  $D_{\text{calcd}} = 1.328$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 1.25$  mm<sup>-1</sup>, yellow block, 0.1 × 0.1 × 0.05 mm, 21615 measured reflections with  $2\theta_{\text{max}} = 40.8^\circ$ , 6739 independent reflections, 6739 absorption-corrected data used in F<sup>2</sup> refinement, 865 parameters, 970 restraints, R<sub>1</sub> = 0.095, wR<sub>2</sub> = 0.272 for 4599 reflections with  $I > 2\sigma(I)$ . CCDC 1938075.

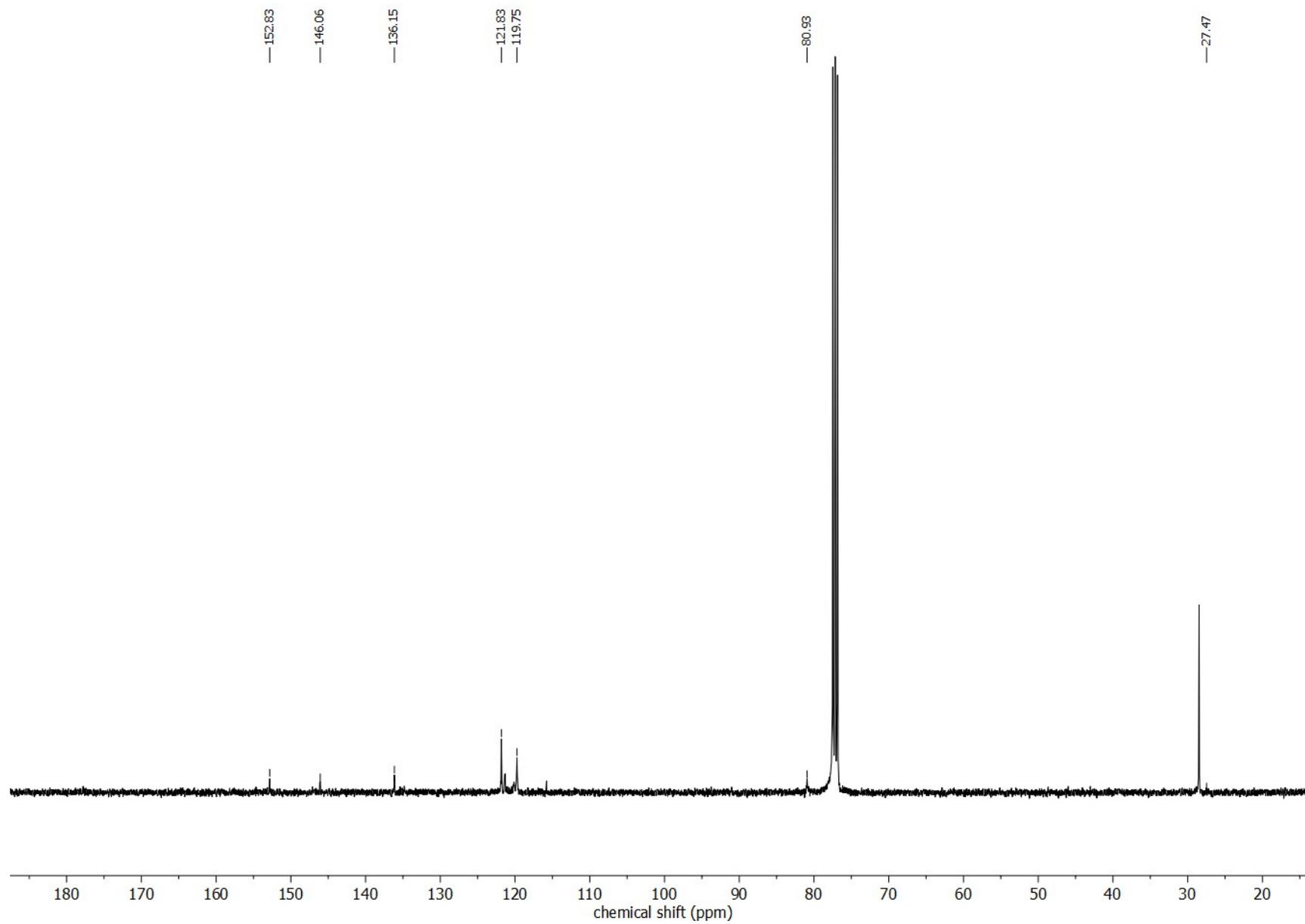


**Figure S4** Space-filling model of the selenophosphate-functionalised Co<sub>4</sub>L<sub>4</sub> cage **2d**.

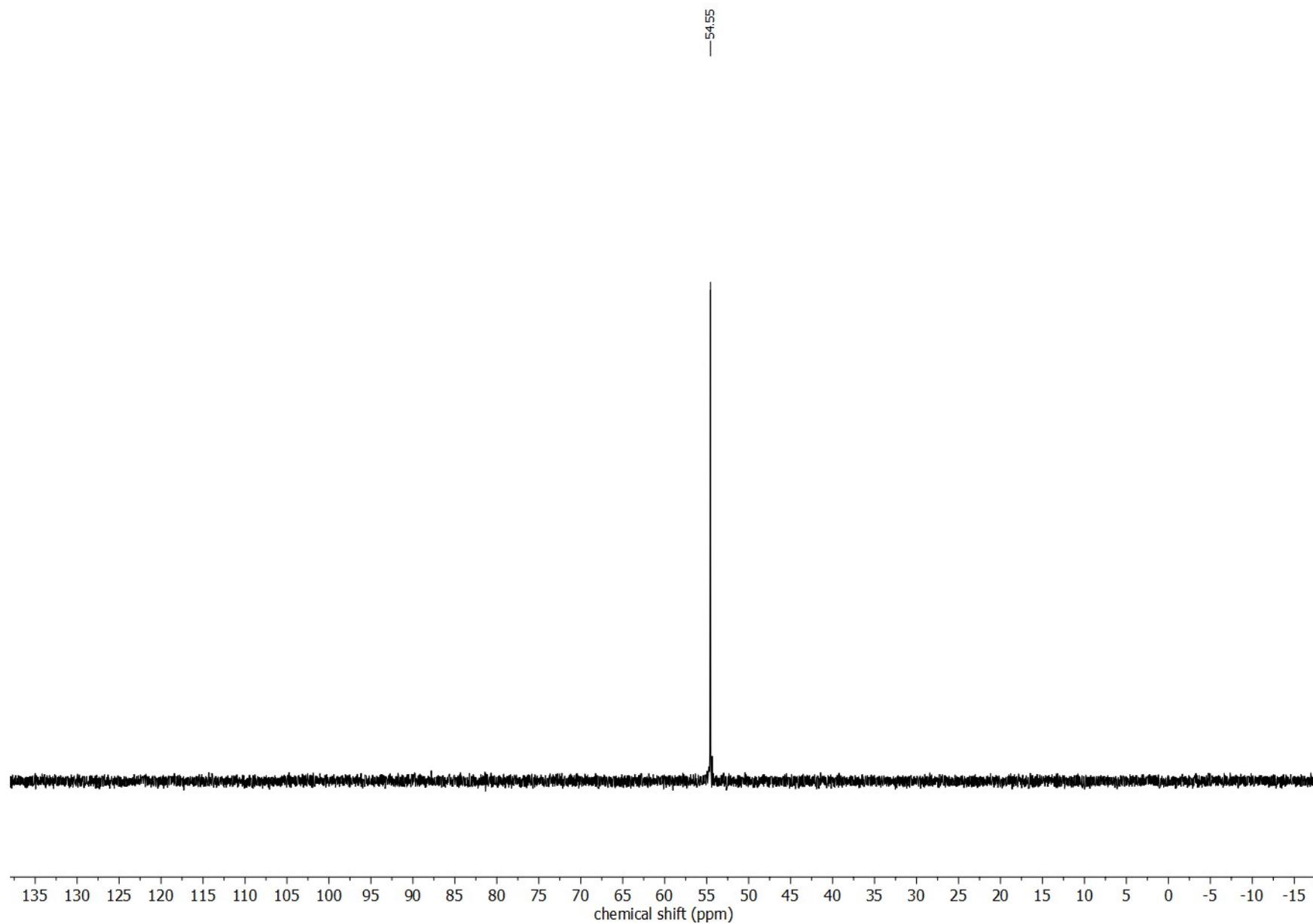
# NMR Spectra



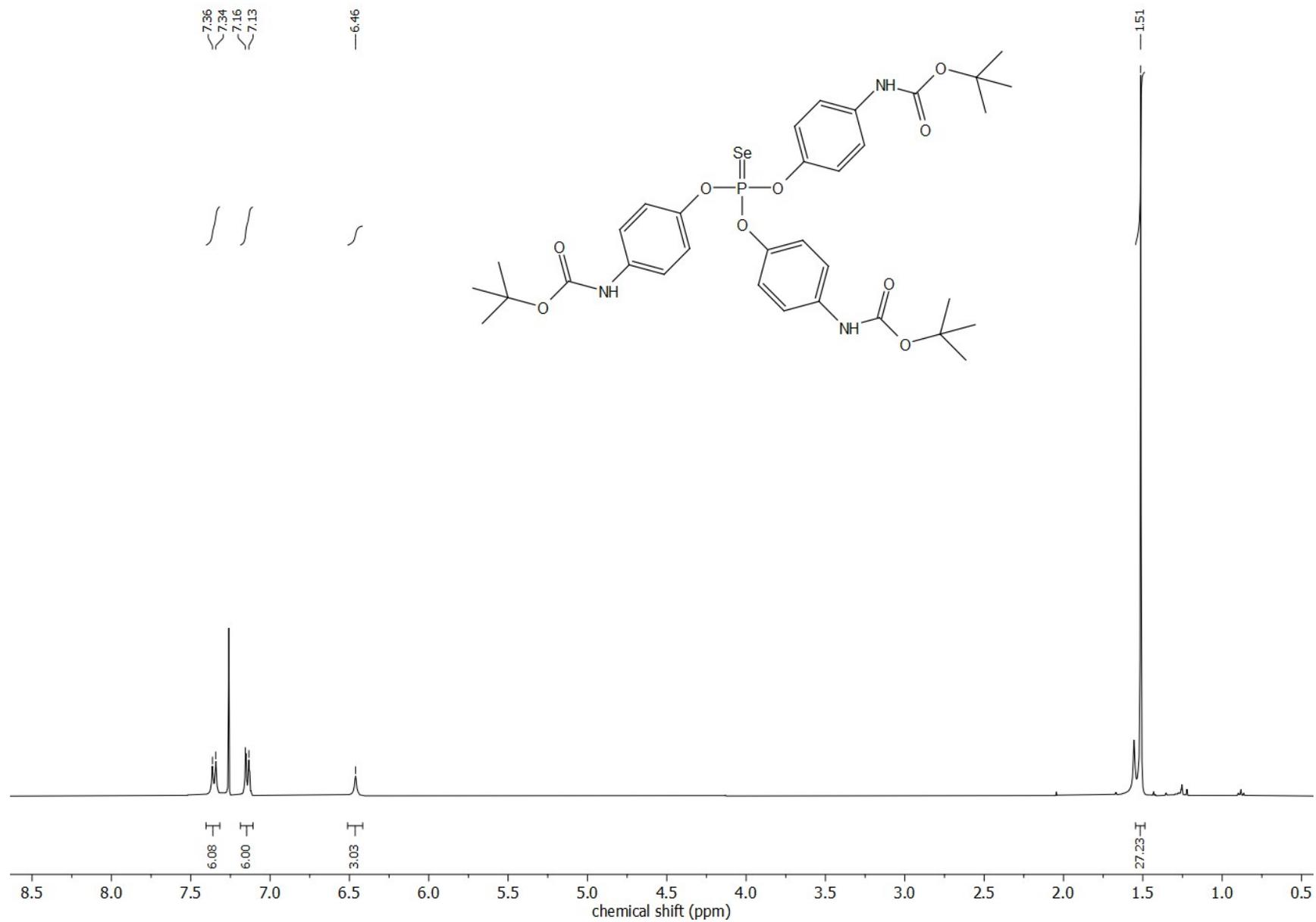
**Figure S5** The <sup>1</sup>H NMR (CDCl<sub>3</sub>) spectrum for the Boc-protected thiophosphate **1a**.



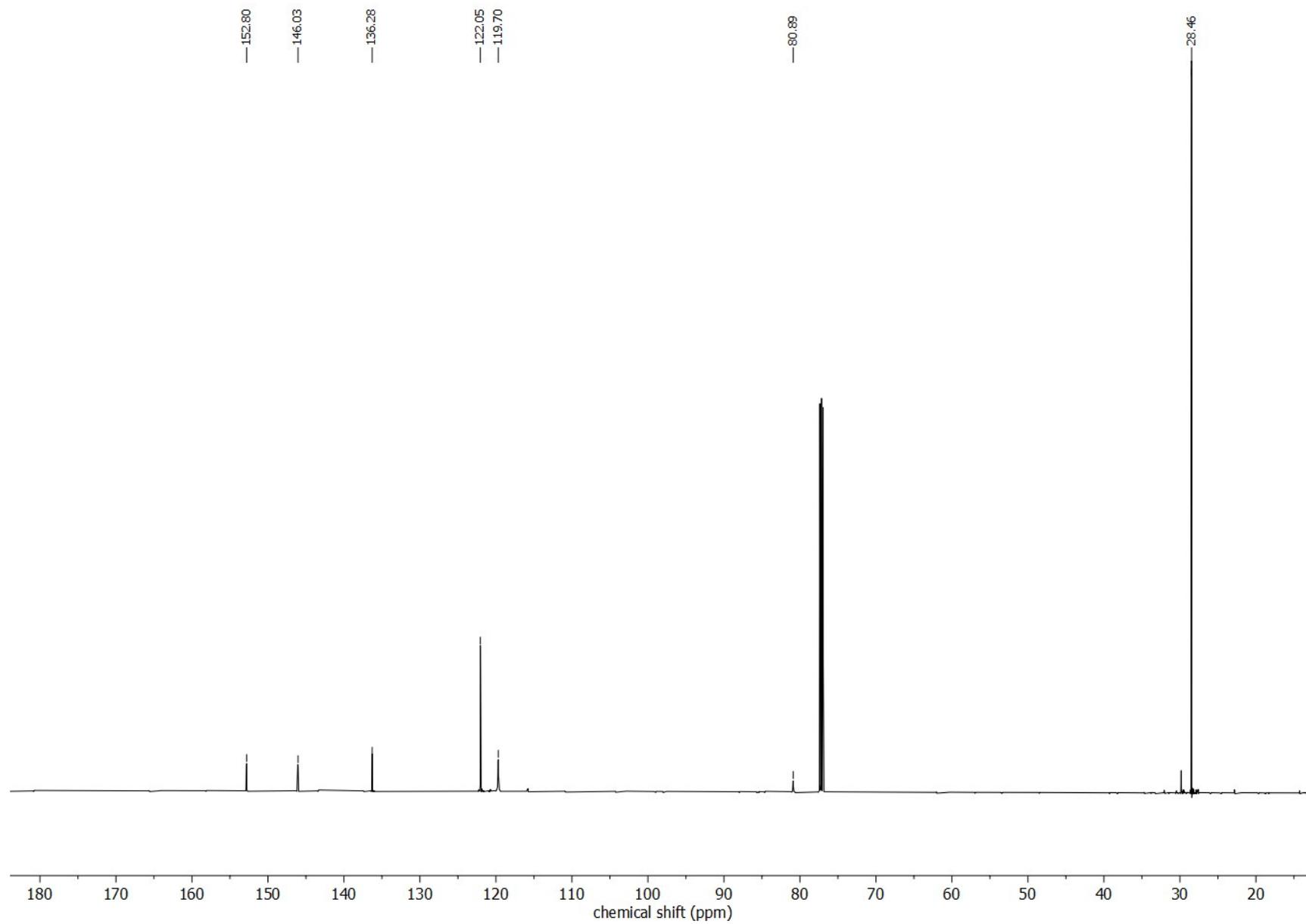
**Figure S6** The  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ) spectrum for the Boc-protected thiophosphate **1a**.



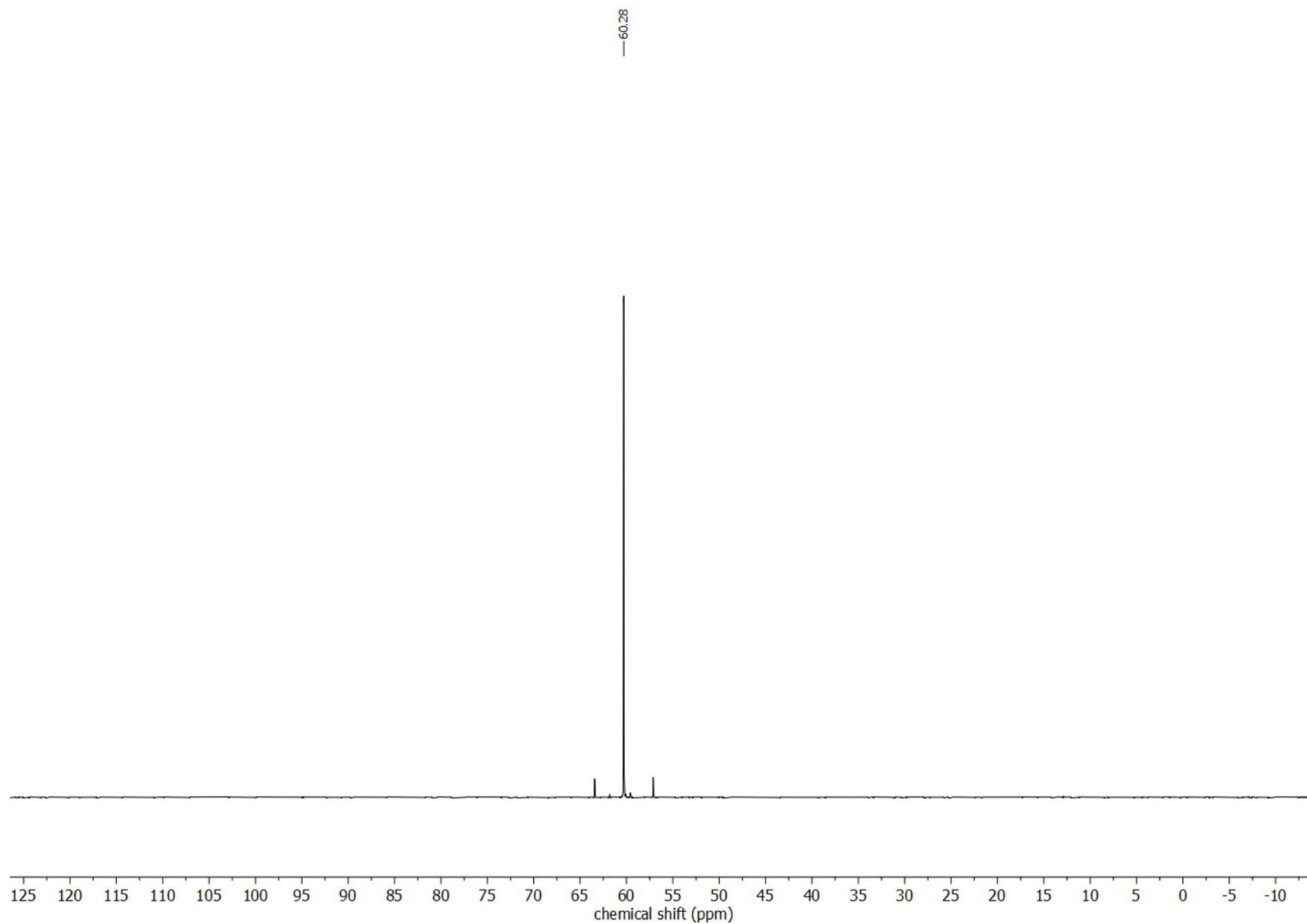
**Figure S7** The  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ) spectrum for the Boc-protected thiophosphate **1a**.



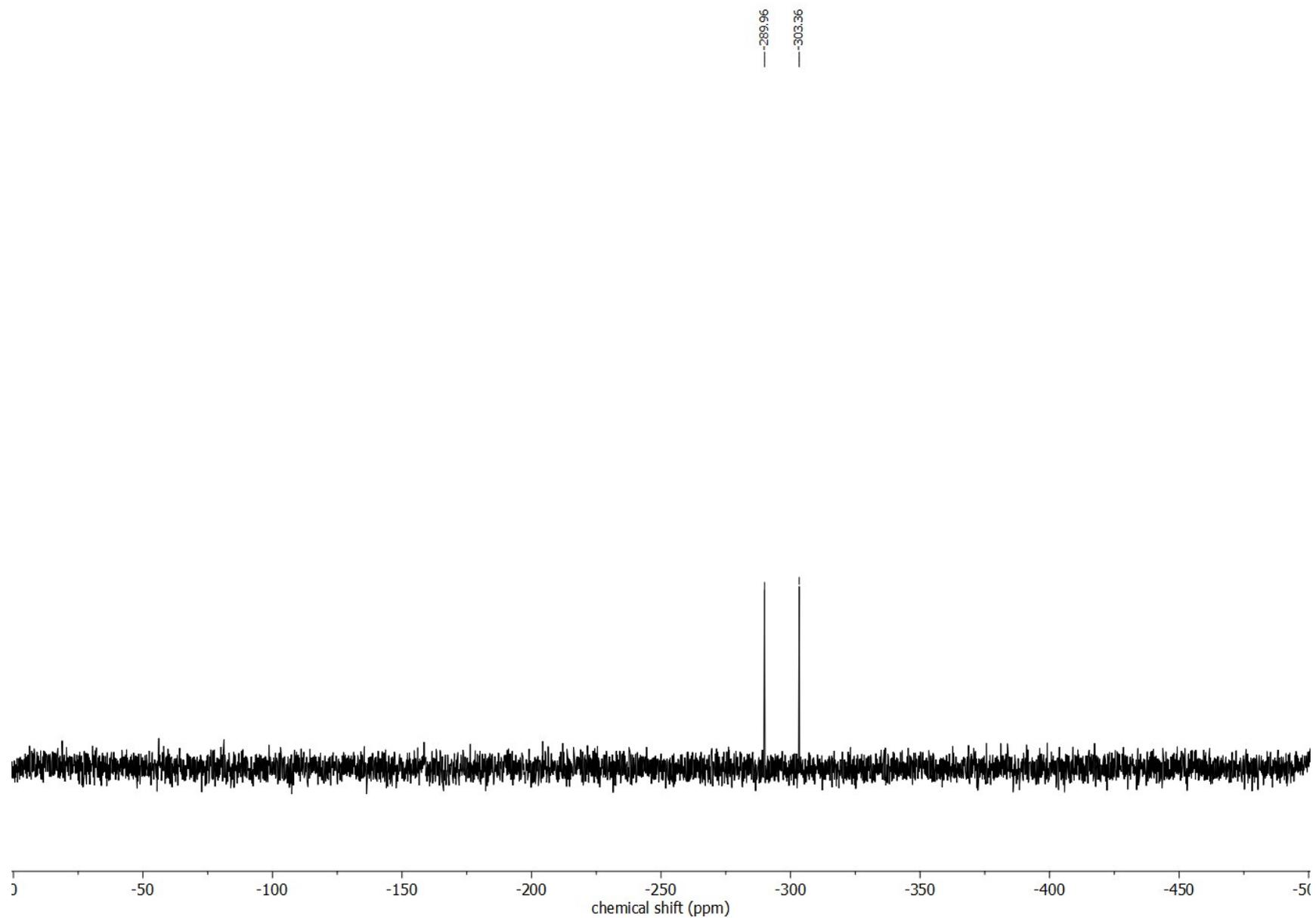
**Figure S8** The <sup>1</sup>H NMR (CDCl<sub>3</sub>) spectrum for the Boc-protected selenophosphate **2a**.



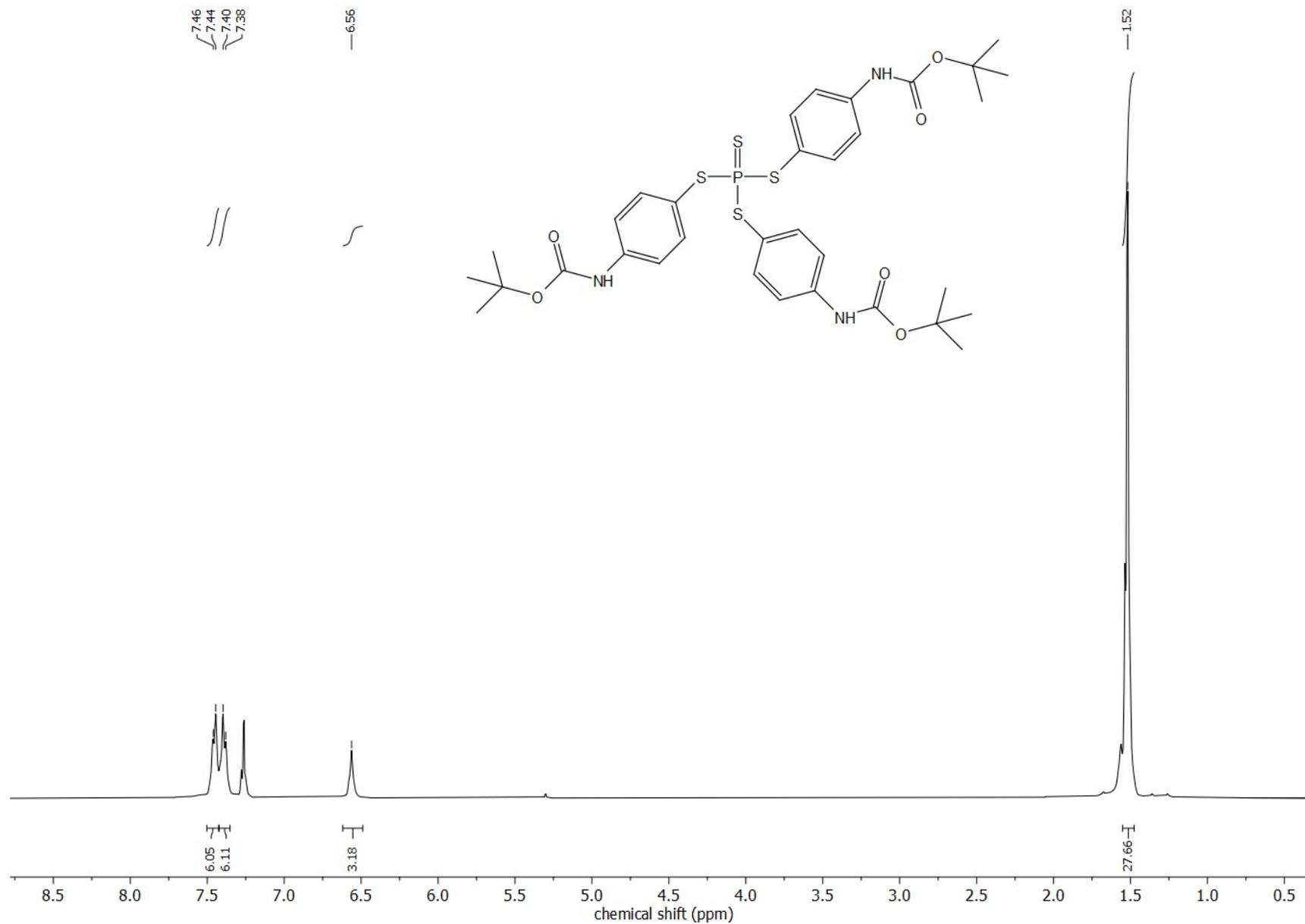
**Figure S9** The  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ) spectrum for the Boc-protected selenophosphate **2a**.



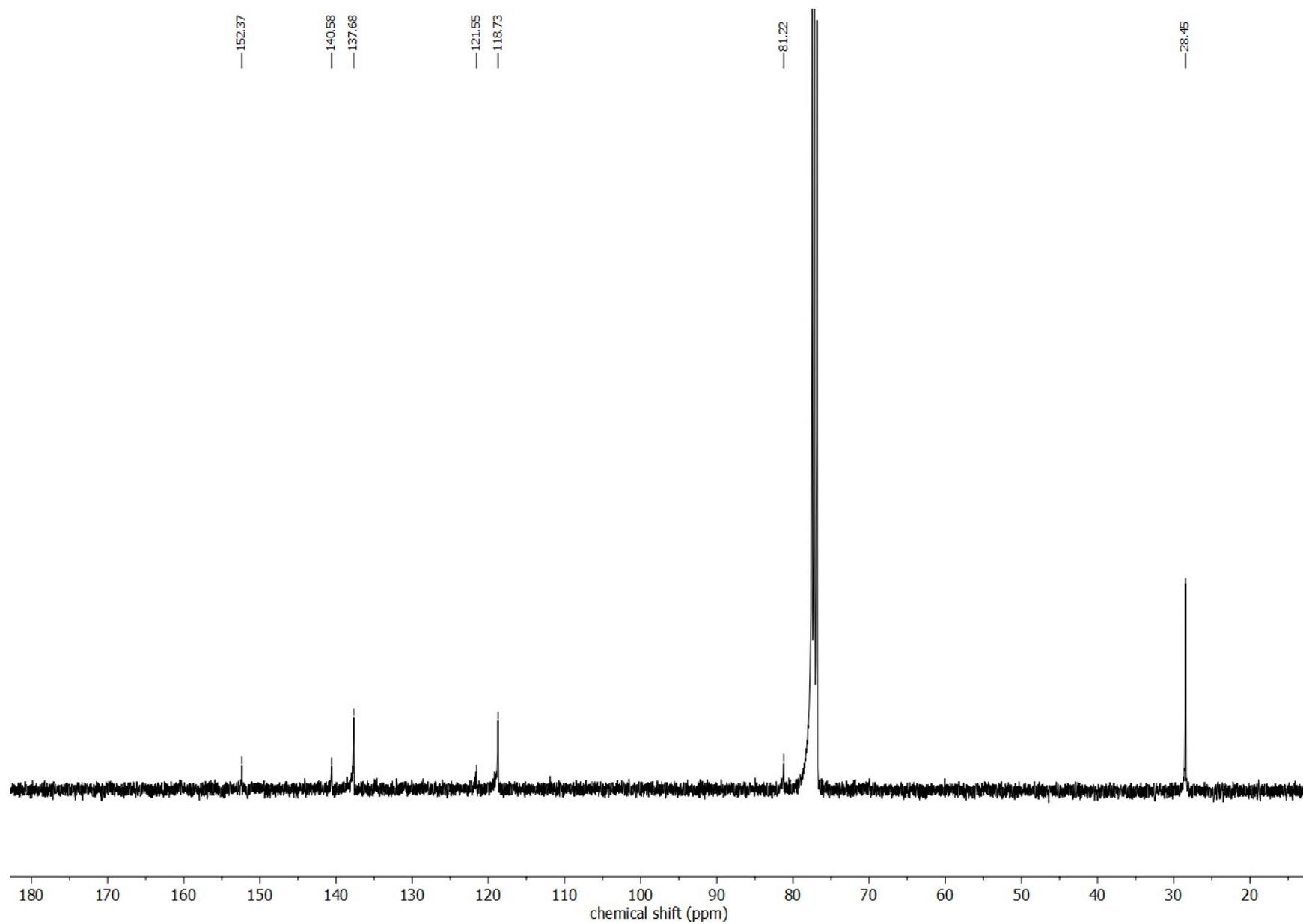
**Figure S10** The  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ) spectrum for the Boc-protected selenophosphate **2a**.



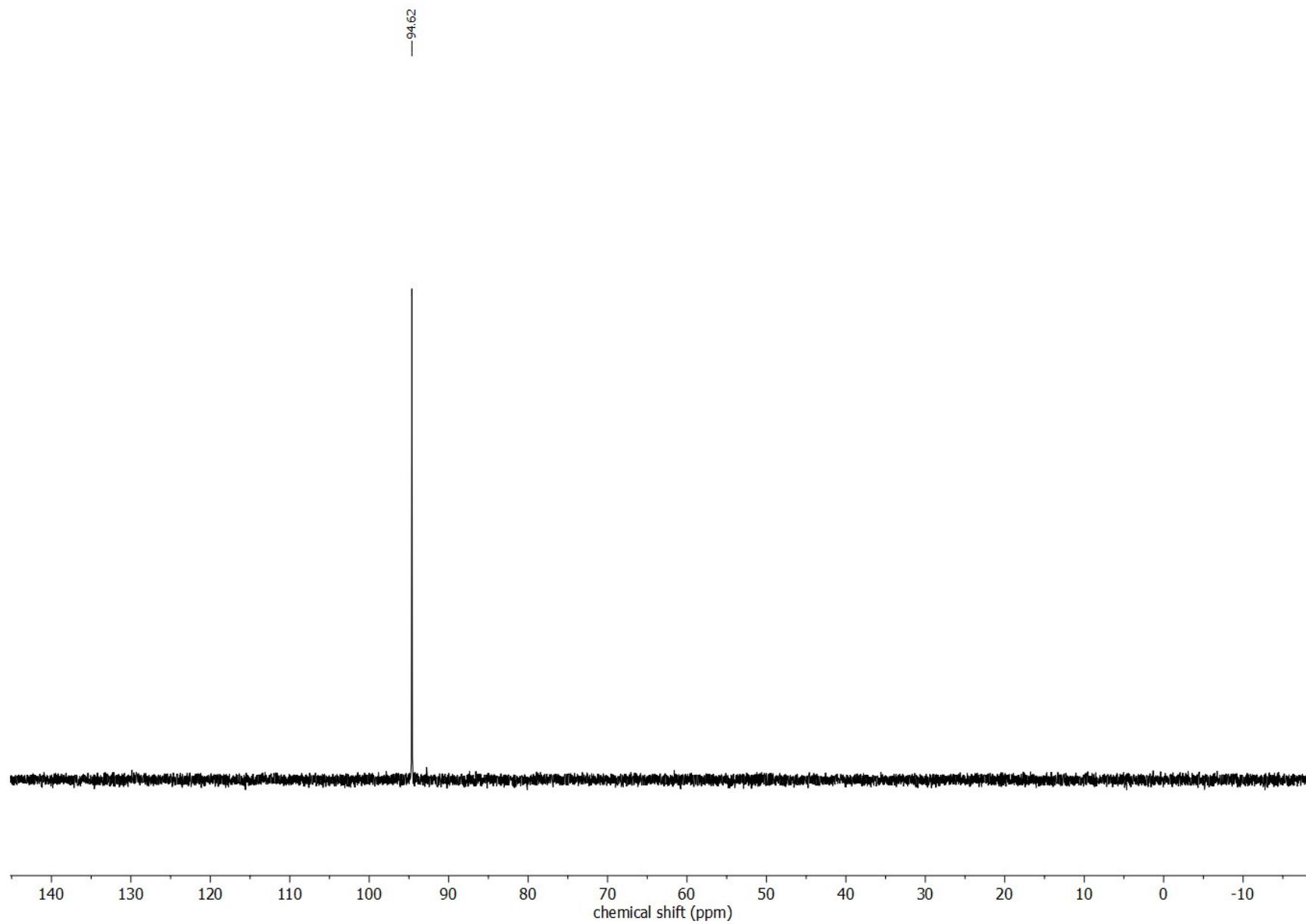
**Figure S11** The  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ ) spectrum for the Boc-protected selenophosphate **2a**.



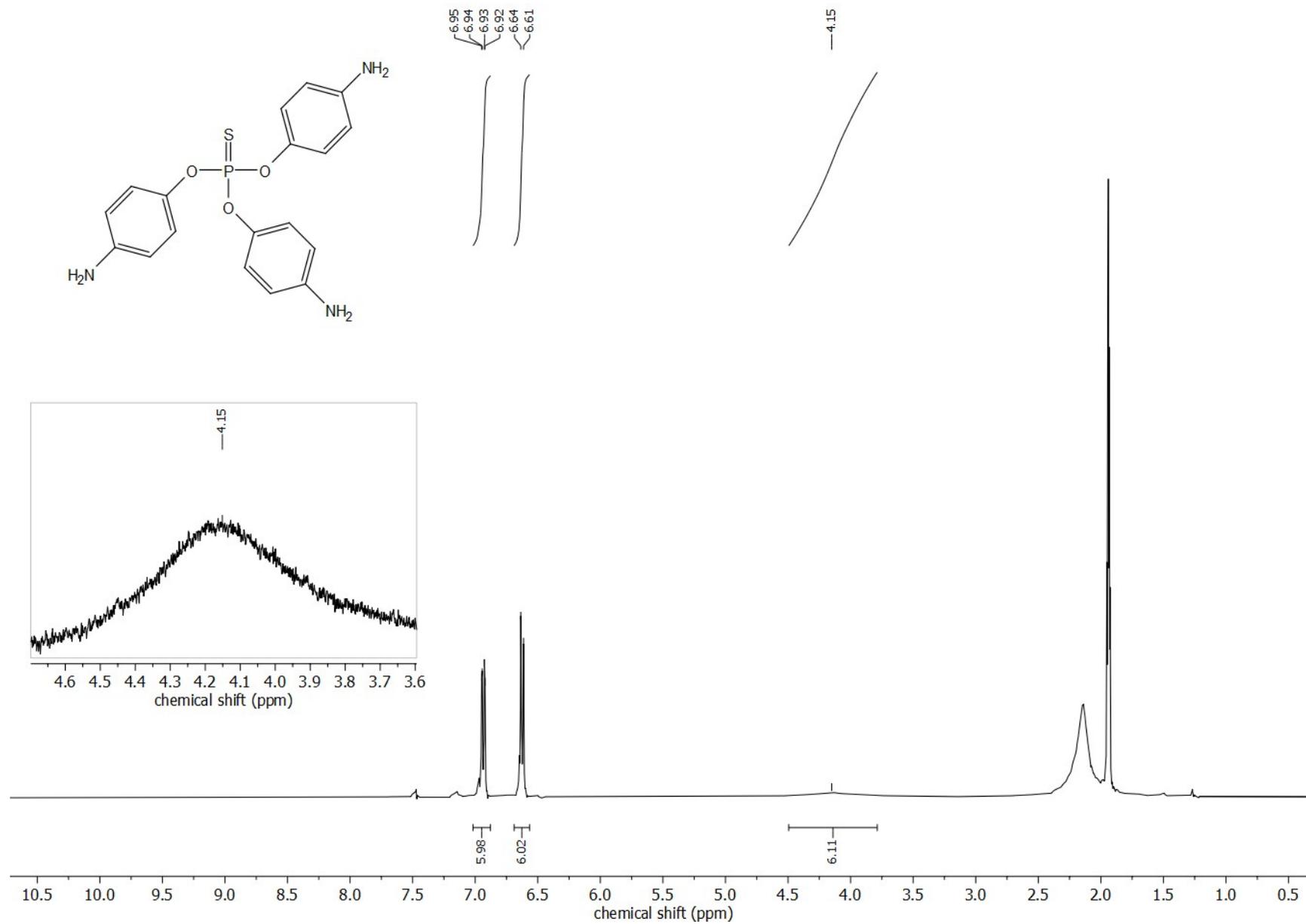
**Figure S12** The  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) spectrum for the Boc-protected tetrathiophosphate **3a**.



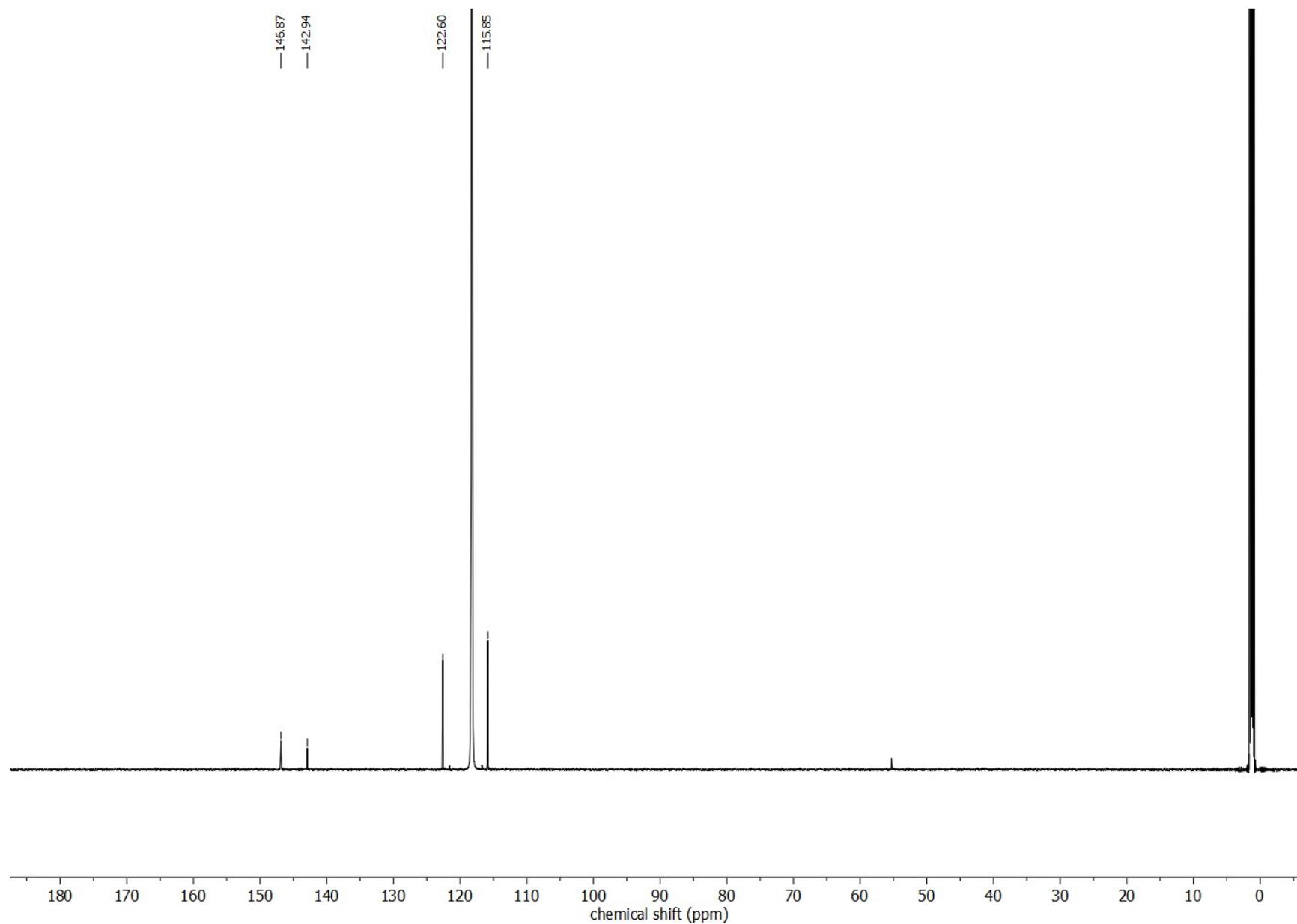
**Figure S13** The  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ) spectrum for the Boc-protected tetrathiophosphate **3a**.



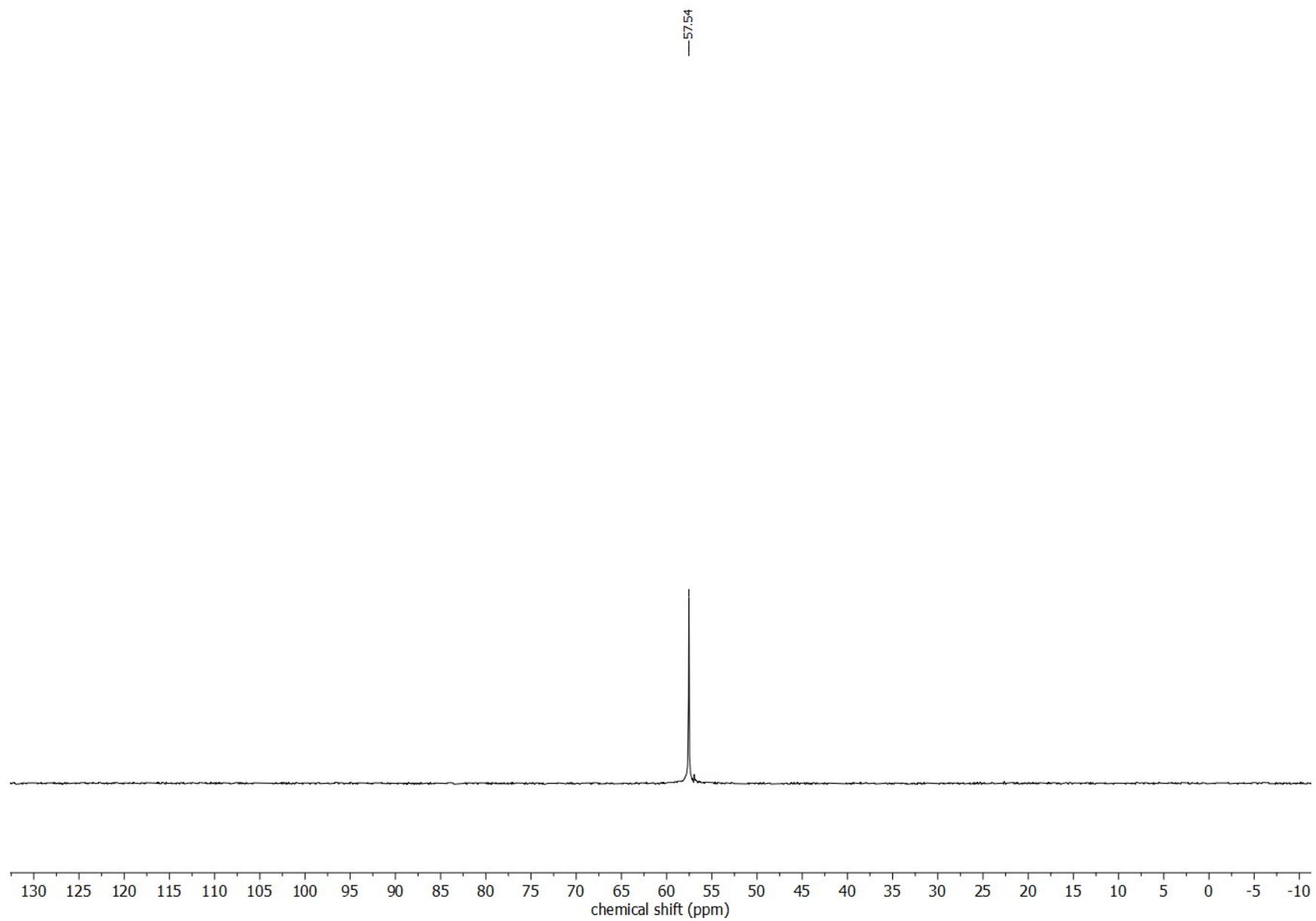
**Figure S14** The  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ) spectrum for the Boc-protected tetrathiophosphate **3a**.



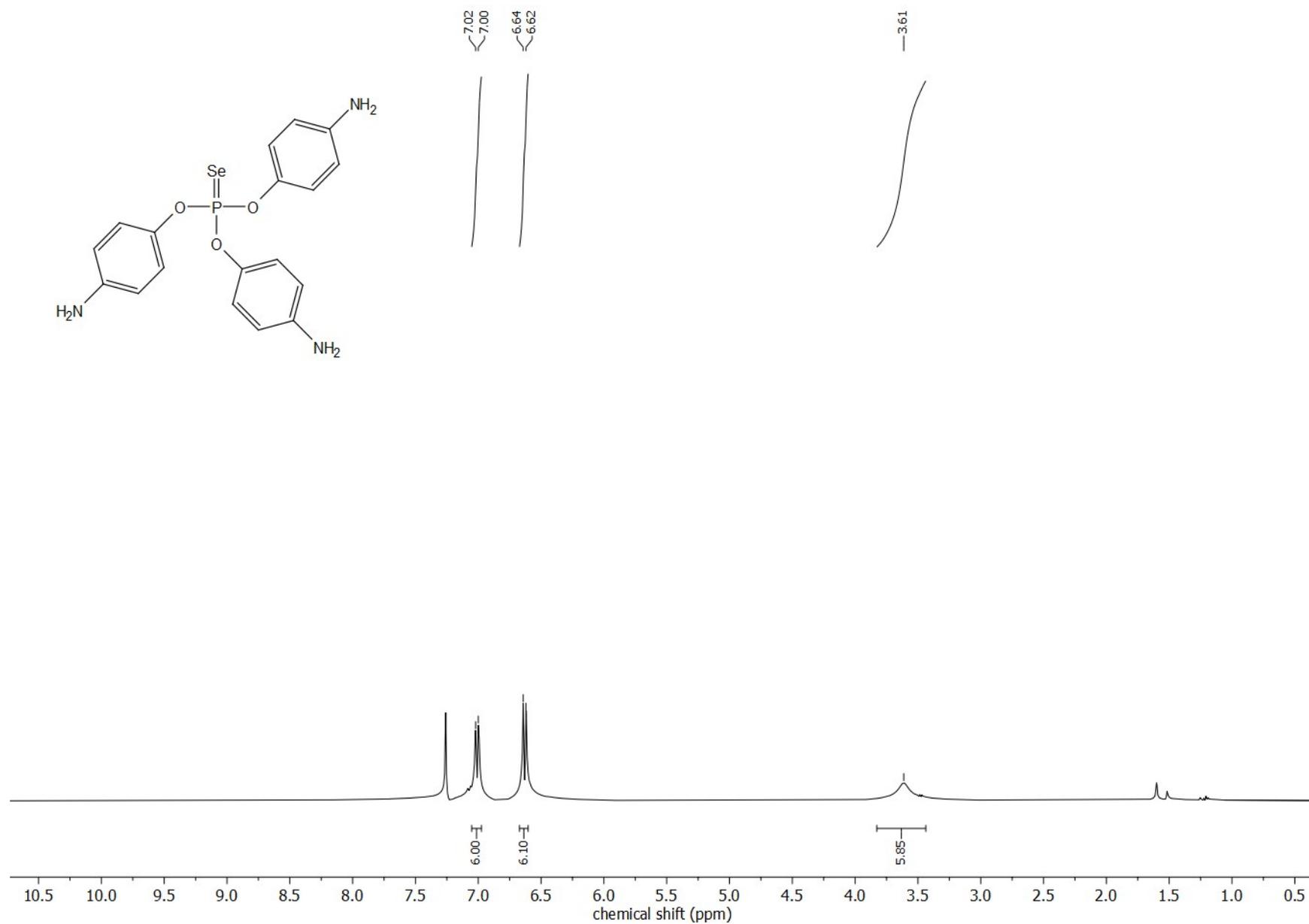
**Figure S15** The <sup>1</sup>H NMR (CD<sub>3</sub>CN) spectrum for the thiophosphate ligand **1b**, the amine resonance was found to be broadened by exchange (insert).



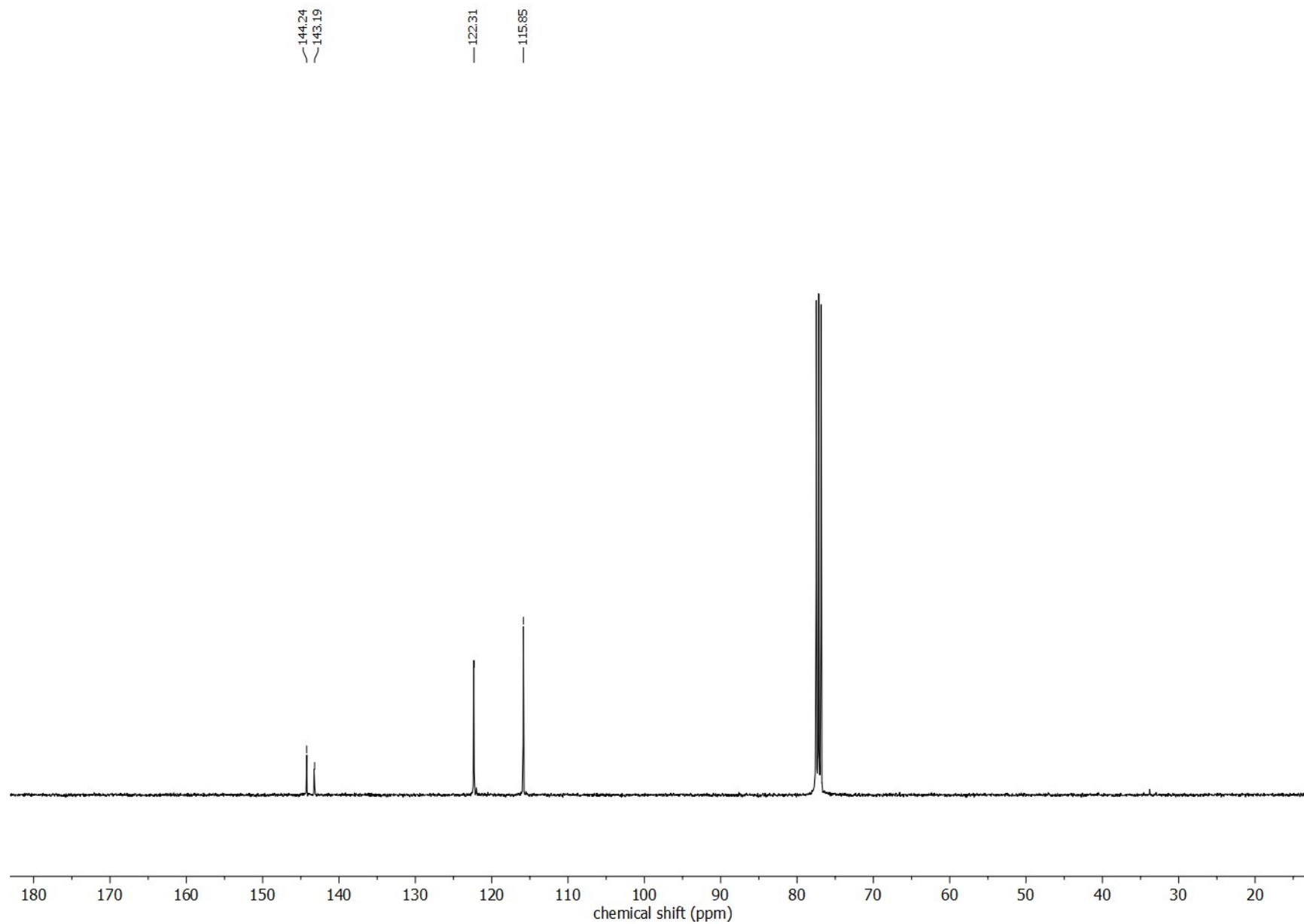
**Figure S16** The  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{CN}$ ) spectrum for the thiophosphate pro-ligand **1b**.



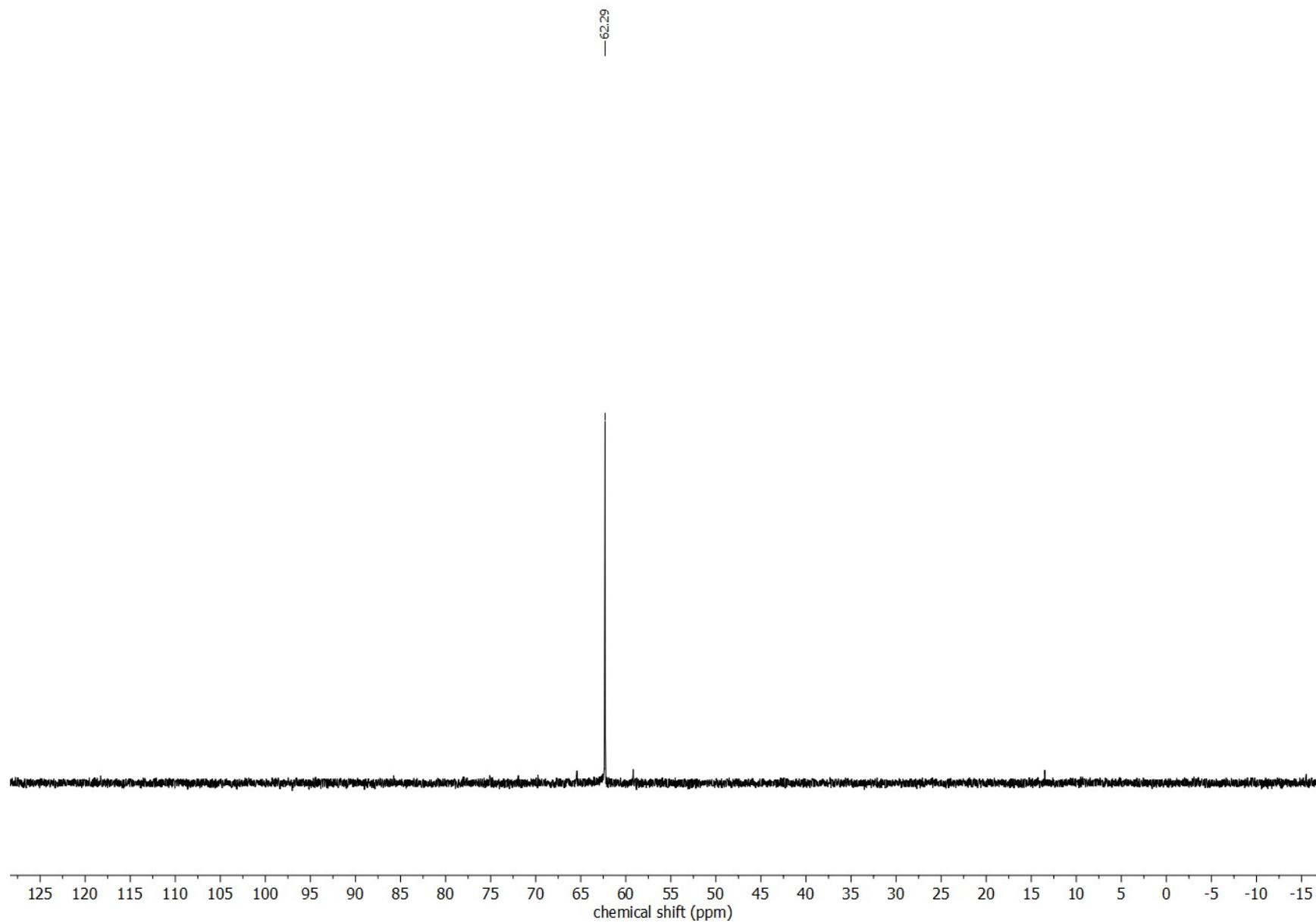
**Figure S17** The  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{CN}$ ) spectrum for the thiophosphate pro-ligand **1b**.



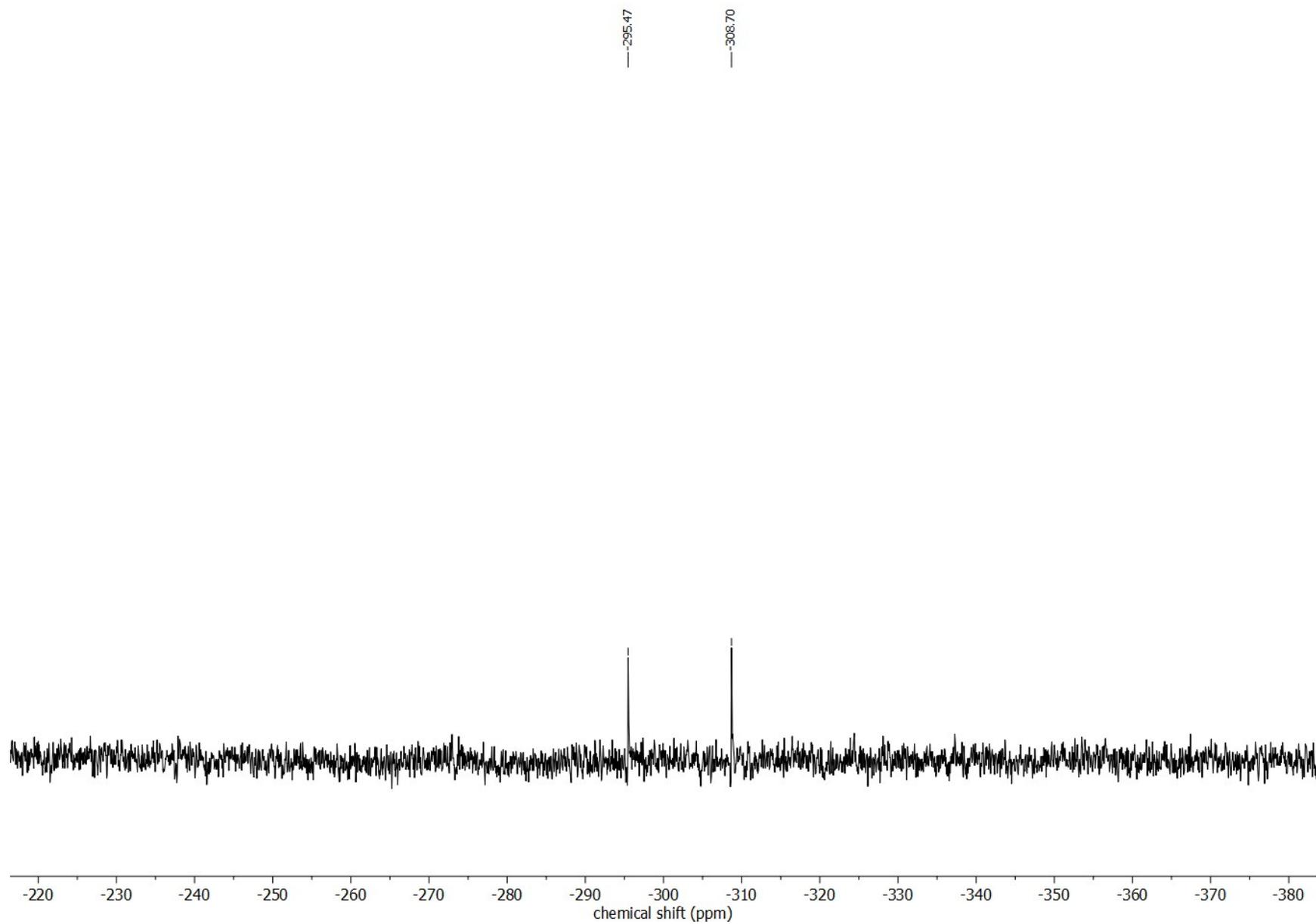
**Figure S18** The  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) spectrum for the selenophosphate pro-ligand **2b**.



**Figure S19** The  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ) spectrum for the selenophosphate pro-ligand **2b**.



**Figure S20** The  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ) spectrum for the selenophosphate pro-ligand **2b**.



**Figure S21** The  $^{77}\text{Se}$  NMR ( $\text{CDCl}_3$ ) spectrum for the selenophosphate pro-ligand **2b**.

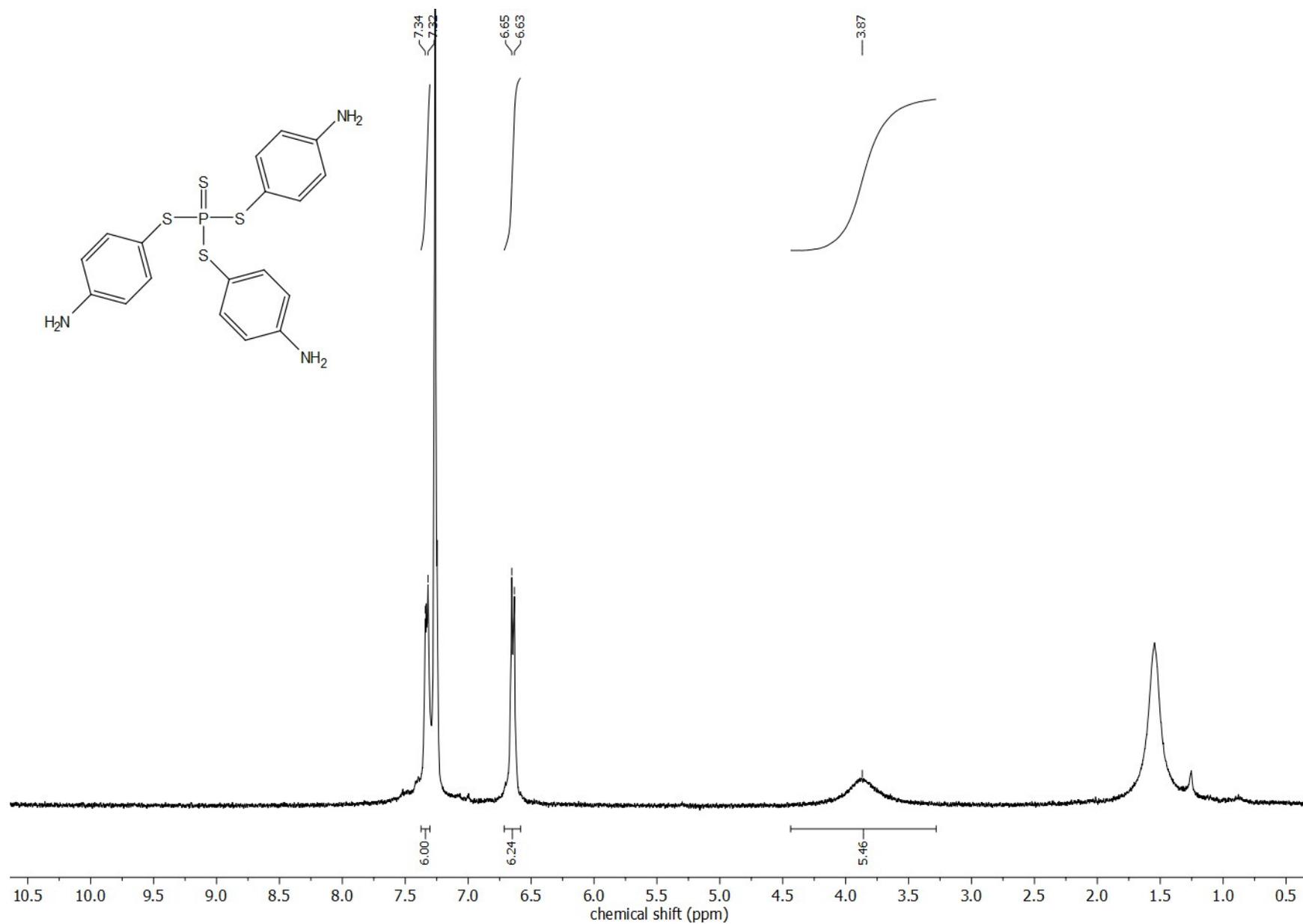
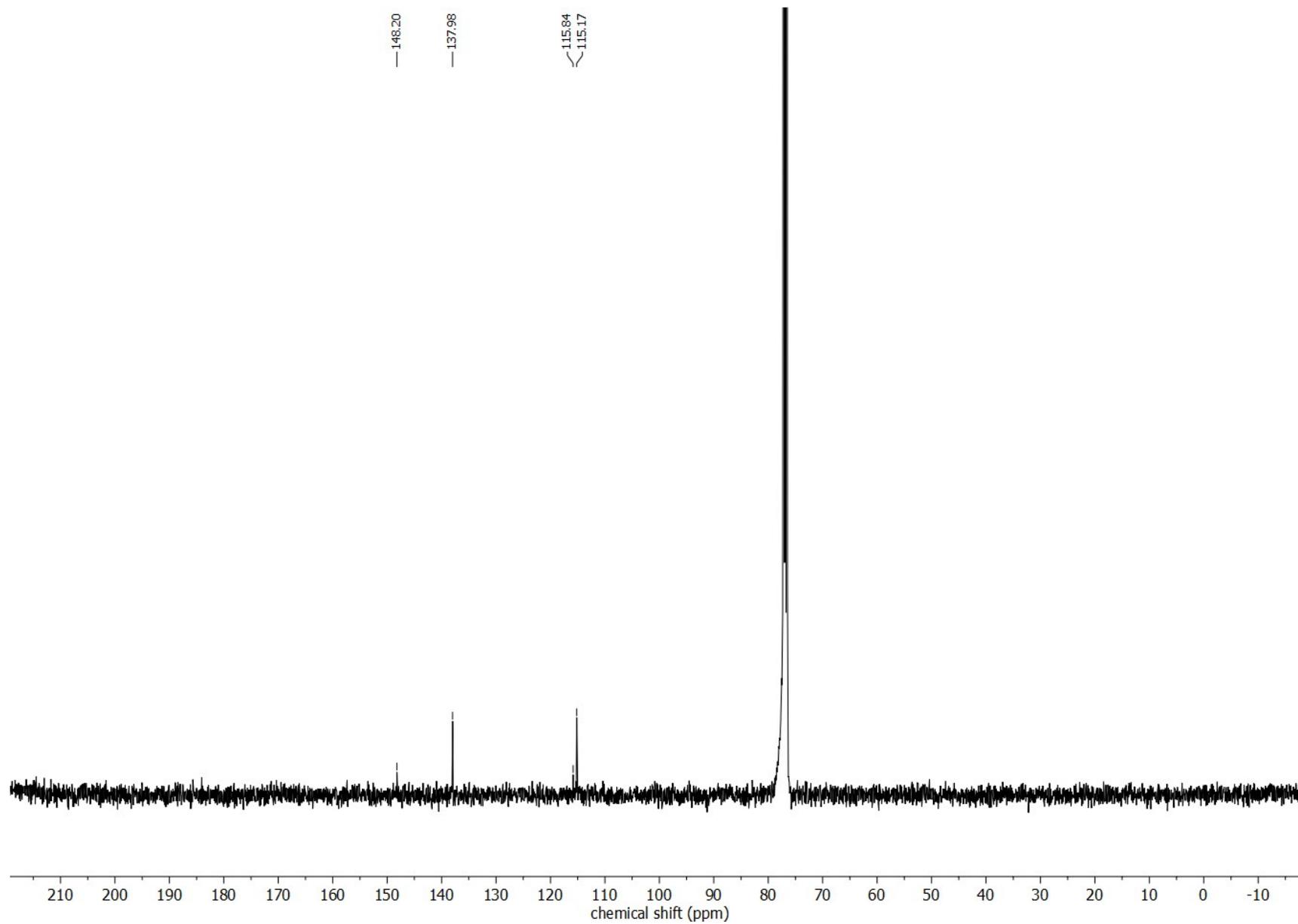
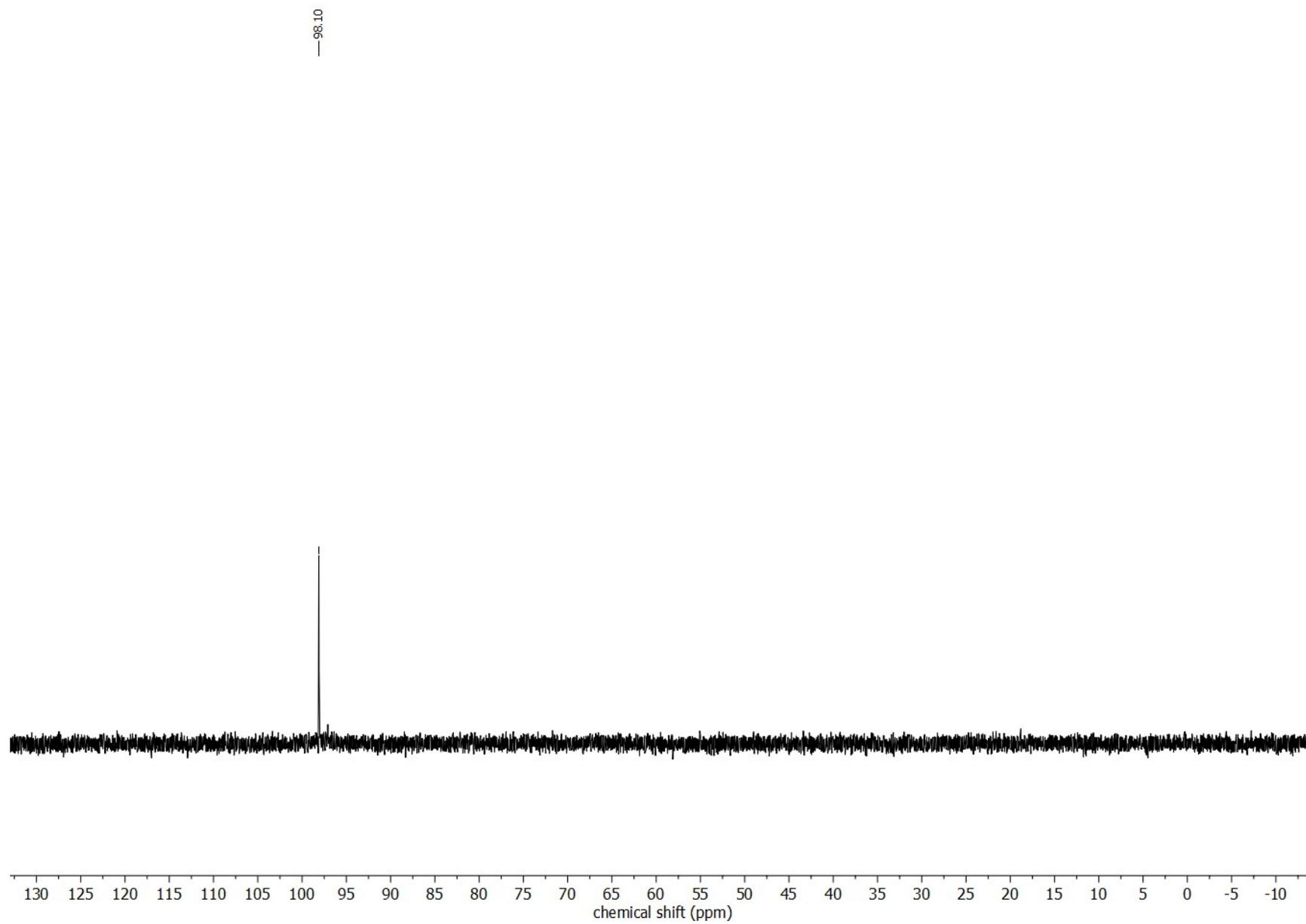


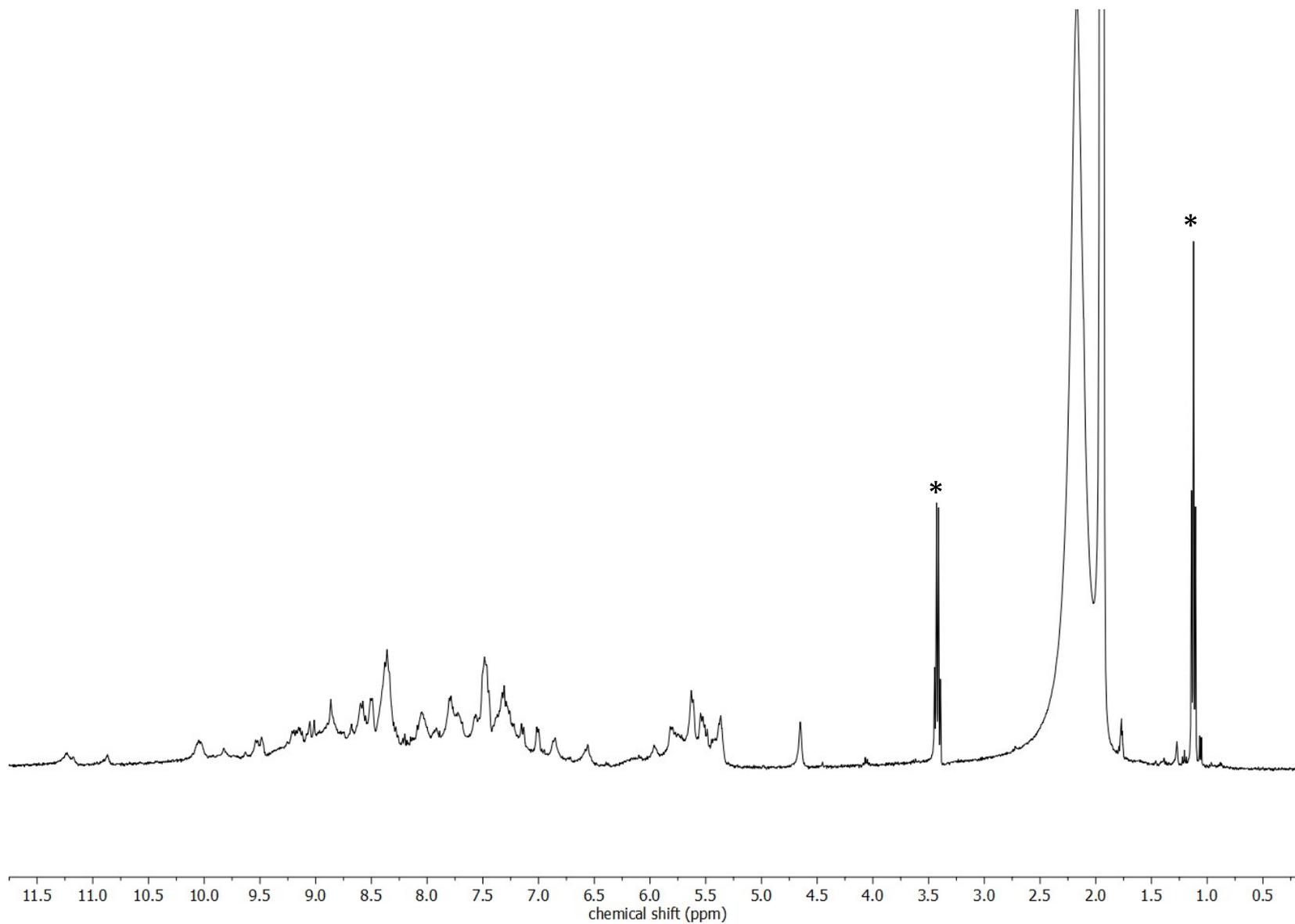
Figure S22 The  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) spectrum for the tetrathiophosphate pro-ligand **3b**.



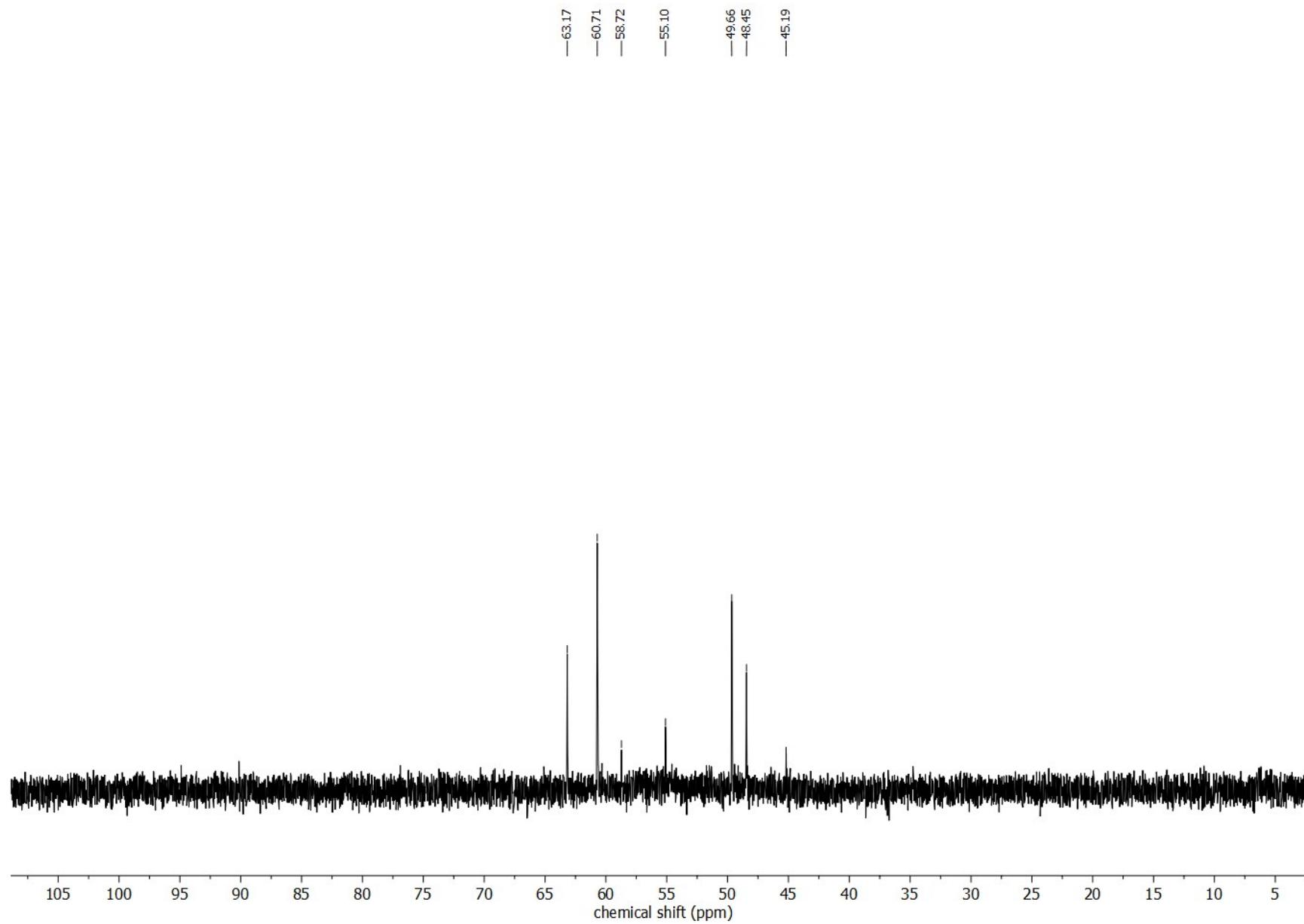
**Figure S23** The  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ) spectrum for the tetrathiophosphate pro-ligand **3b**.



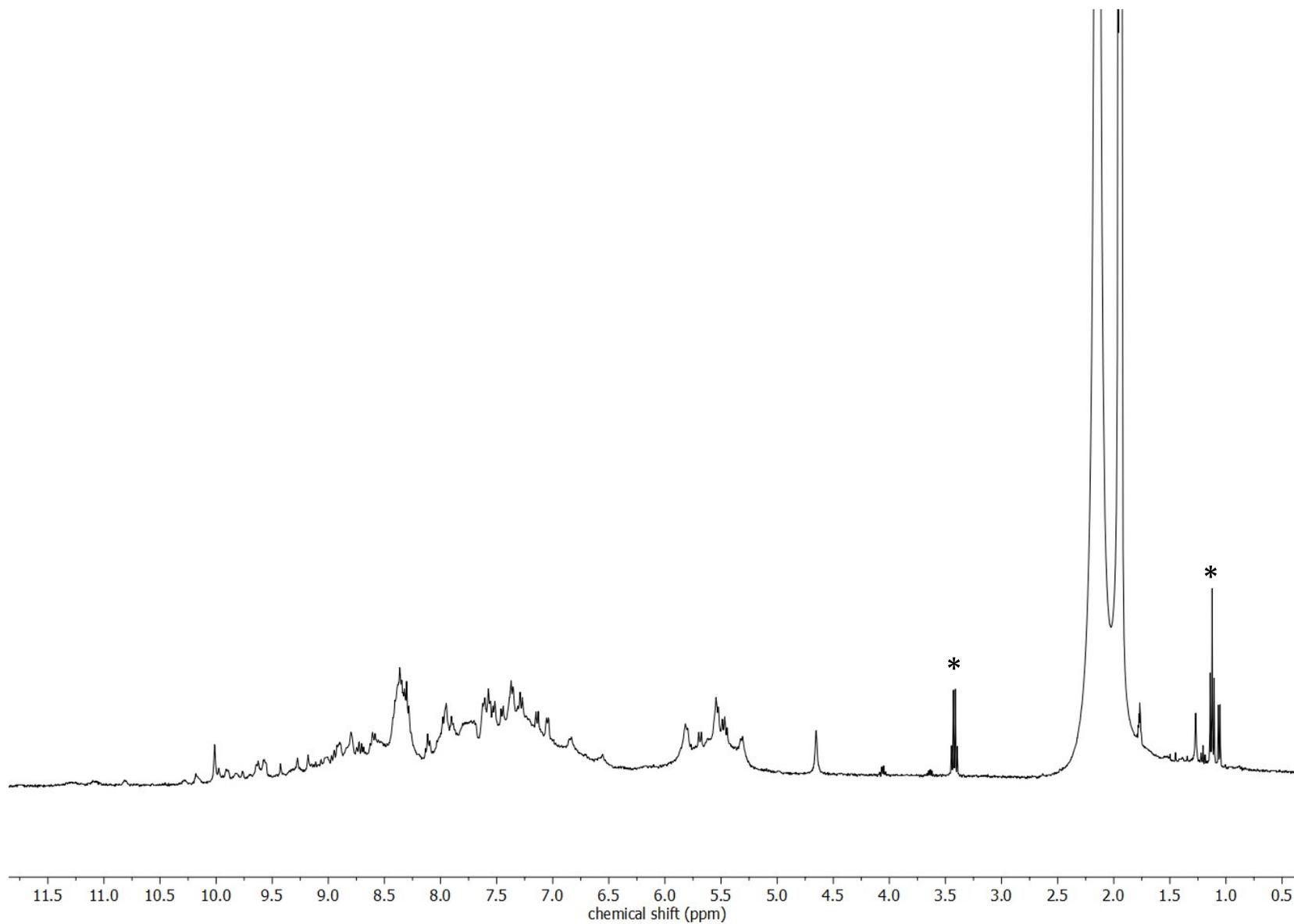
**Figure S24** The  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ) spectrum for the tetrathiophosphate pro-ligand **3b**.



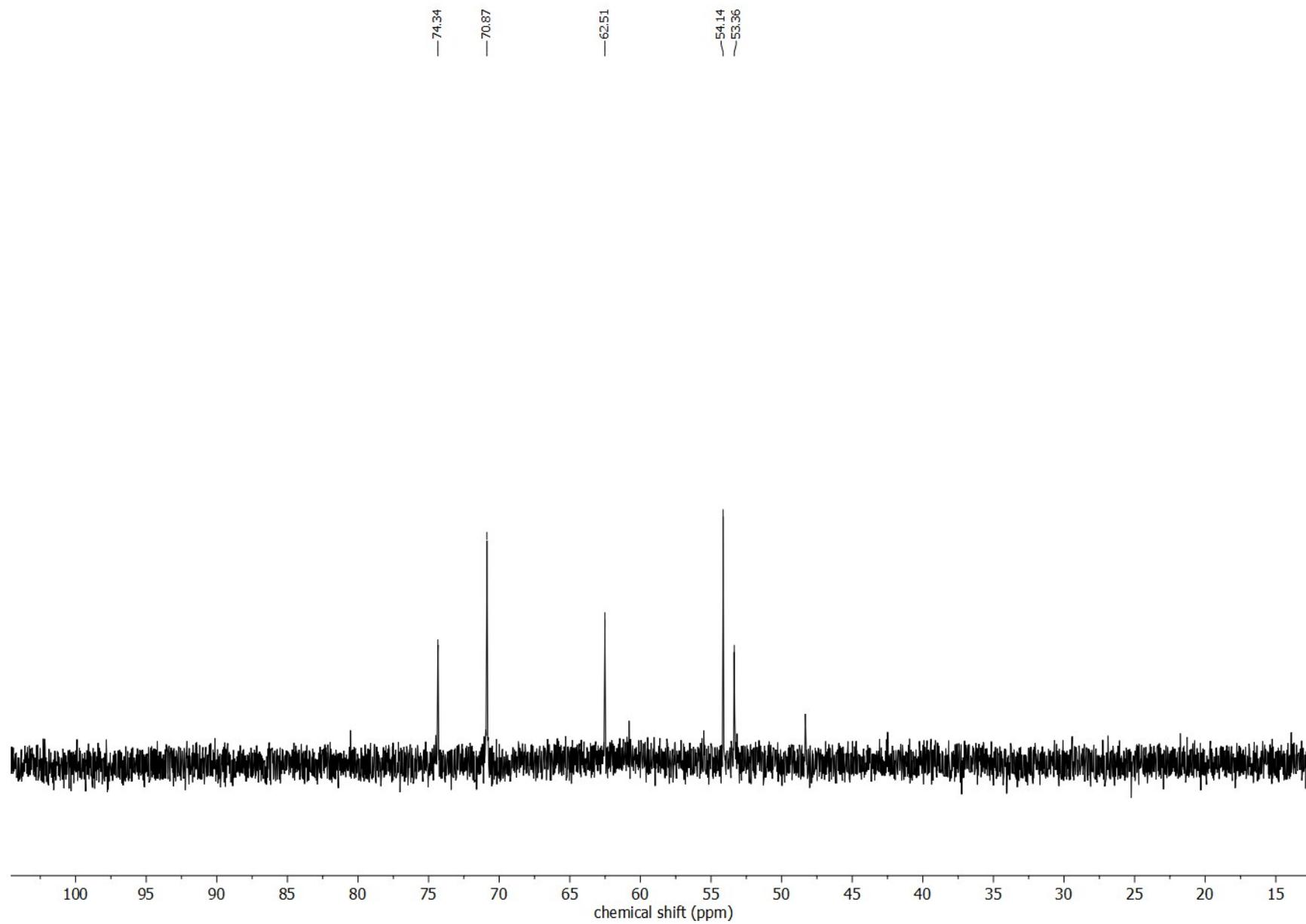
**Figure S25** The <sup>1</sup>H NMR (CD<sub>3</sub>CN) spectrum for the thiophosphate functionalised Fe<sub>4</sub>L<sub>4</sub> cage **1c**. The asterisk marked signals correspond to residual solvent from the self-assembly.



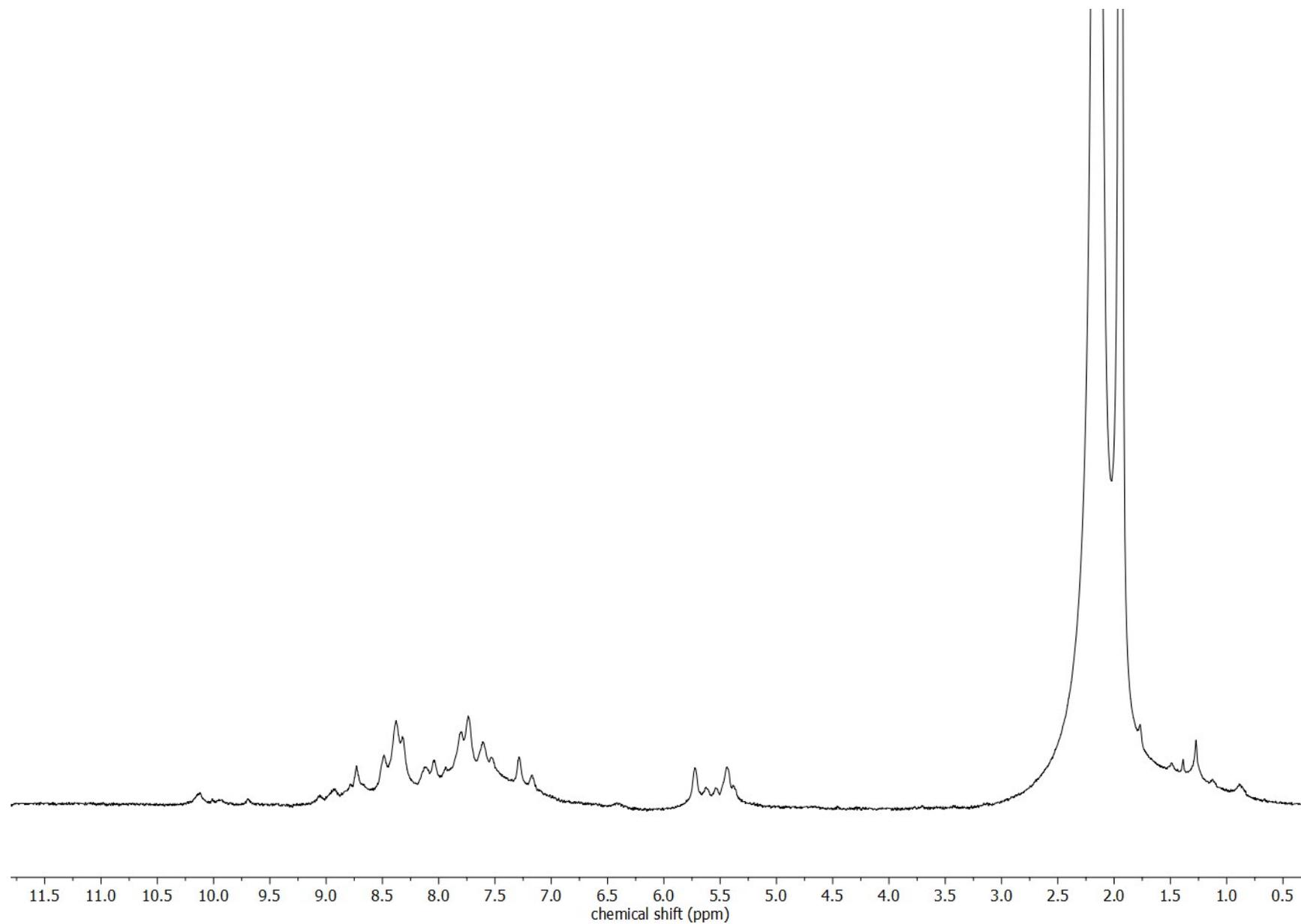
**Figure S26** The  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{CN}$ ) spectrum for the thiophosphate  $\text{Fe}_4\text{L}_4$  cage **1c**.



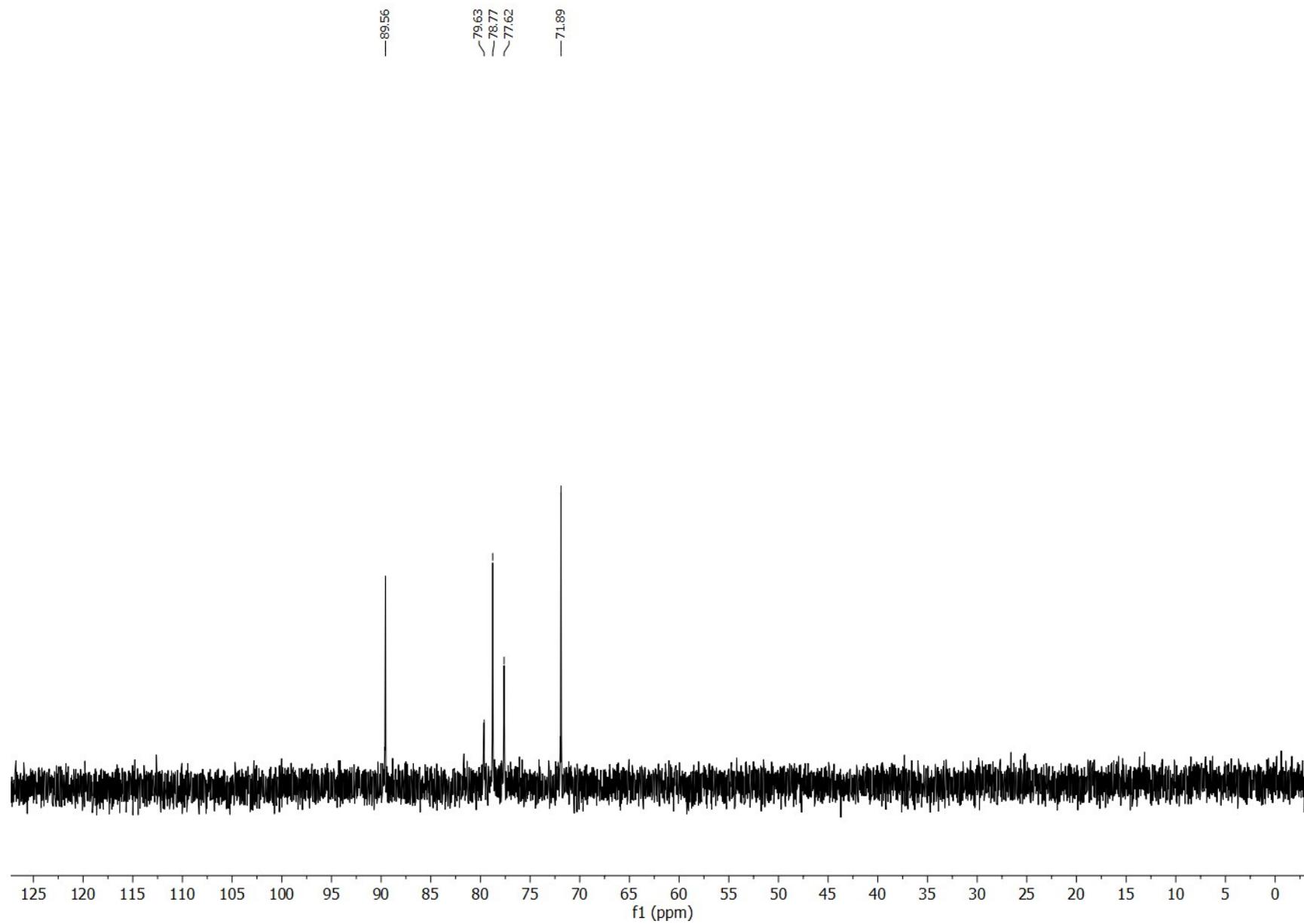
**Figure S27** The <sup>1</sup>H NMR (CD<sub>3</sub>CN) spectrum for the selenophosphate functionalised Fe<sub>4</sub>L<sub>4</sub> cage **2c**. The asterisk marked signals correspond to residual solvent from the self-assembly.



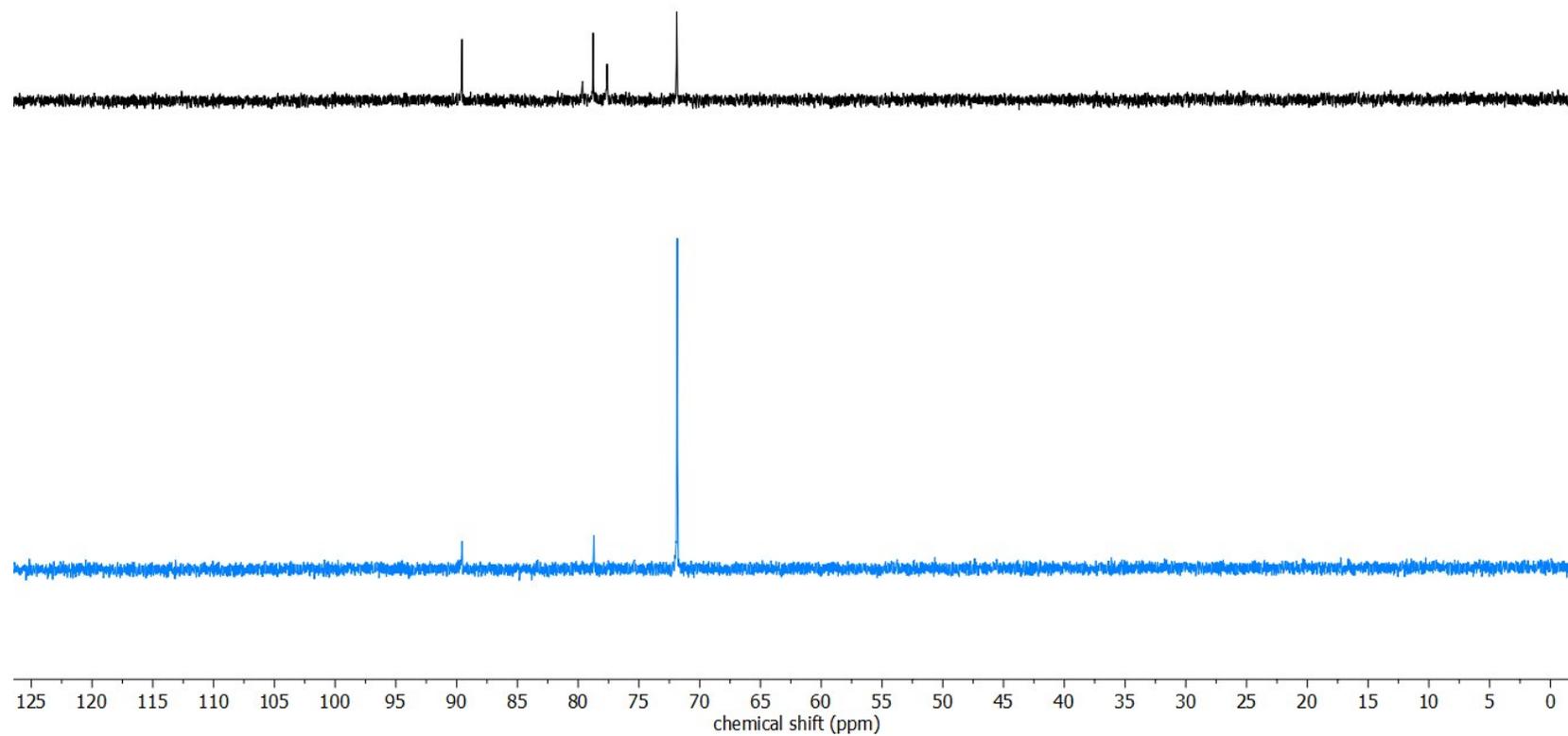
**Figure S28** The  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{CN}$ ) spectrum for the selenophosphate  $\text{Fe}_4\text{L}_4$  cage **2c**.



**Figure S29** The  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ) spectrum for the tetrathiophosphate  $\text{Fe}_4\text{L}_4$  cage **3c**.



**Figure S30** The  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{CN}$ ) spectrum for the tetrathiophosphate functionalised  $\text{Fe}_4\text{L}_4$  cage **3c**.



**Figure S31** The  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{CN}$ ) spectrum for the tetrathiophosphate assembly **3c** (above) and after mixing with  $[\text{Cu}(\text{NCMe})_4][\text{BF}_4]_2$  (8 equiv.) for 24 h at  $50^\circ\text{C}$ .

# Mass Spectra

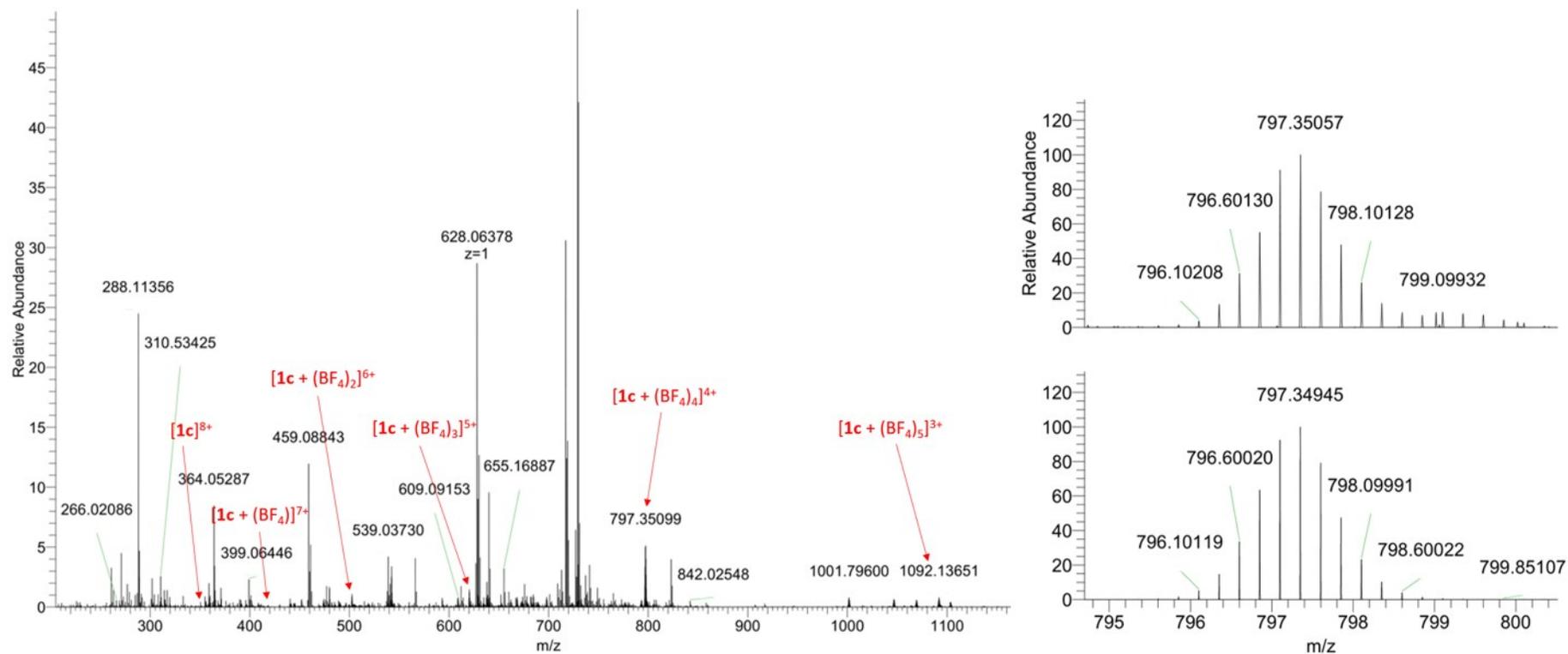
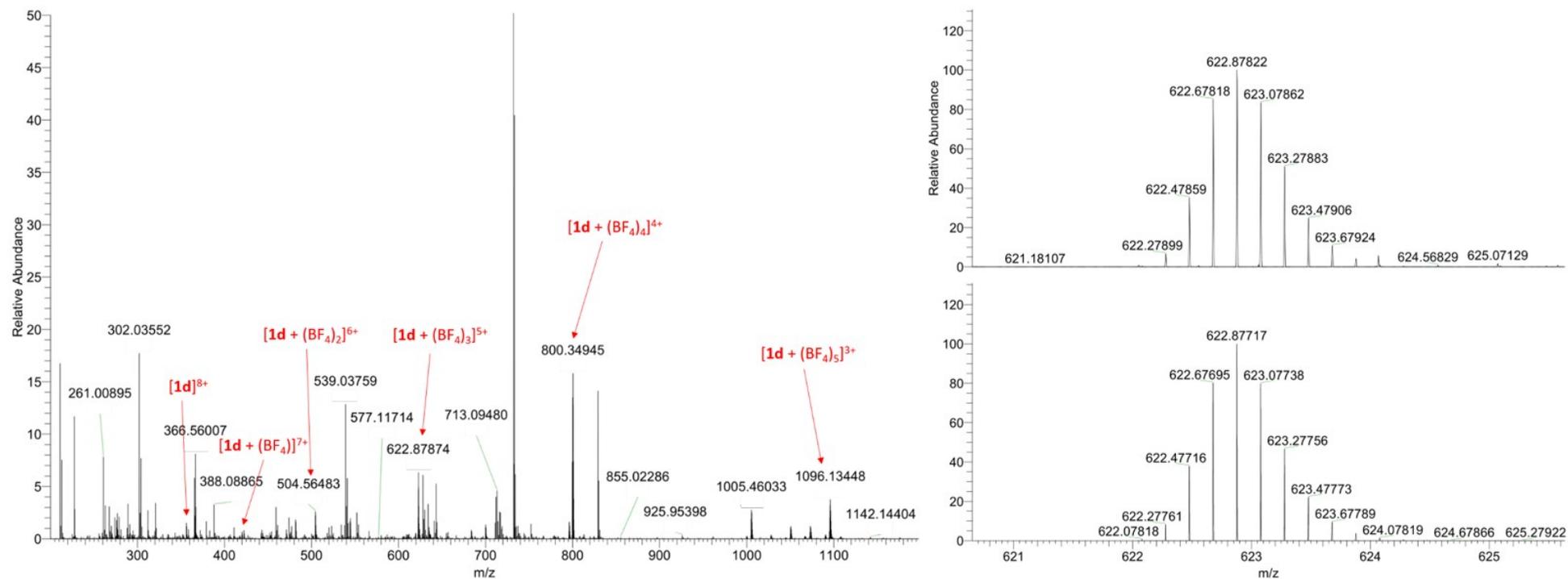
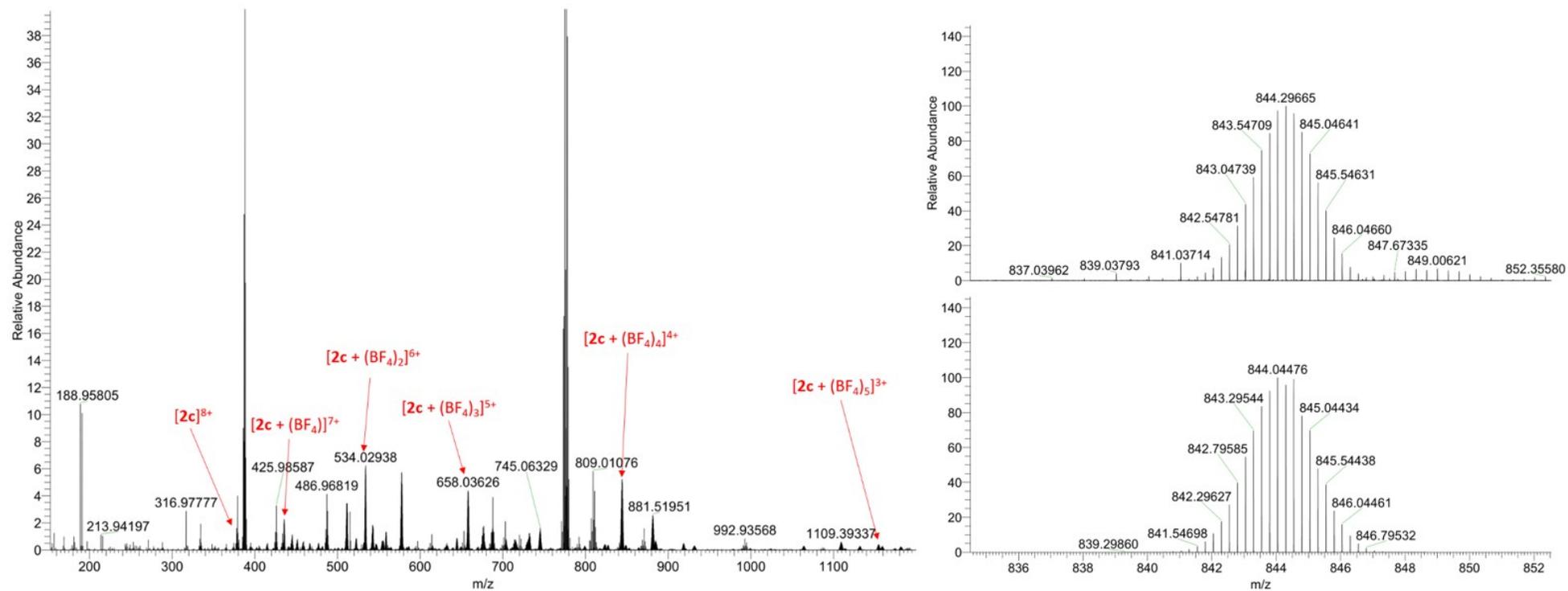


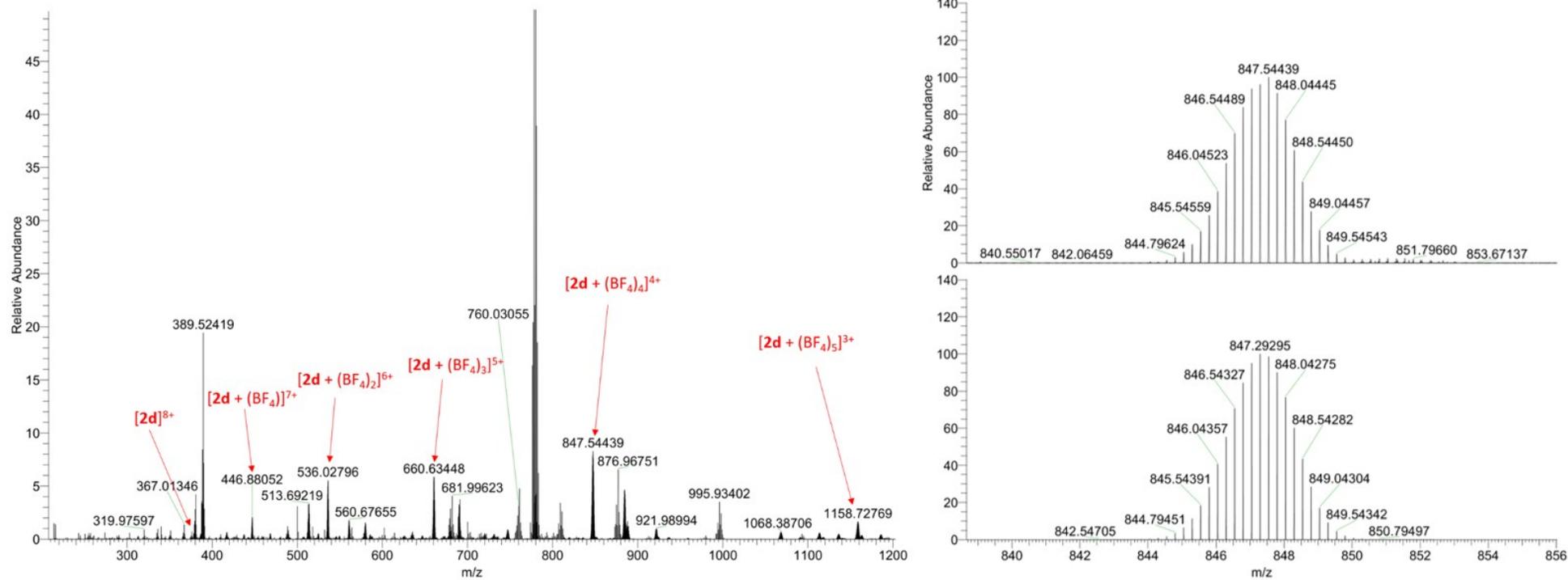
Figure S32 The mass spectrum of cage **1c** (left). The experimental (top right) and simulated (bottom right) isotopic distributions for  $[1c + (BF_4)_4]^{4+}$  are presented additionally.



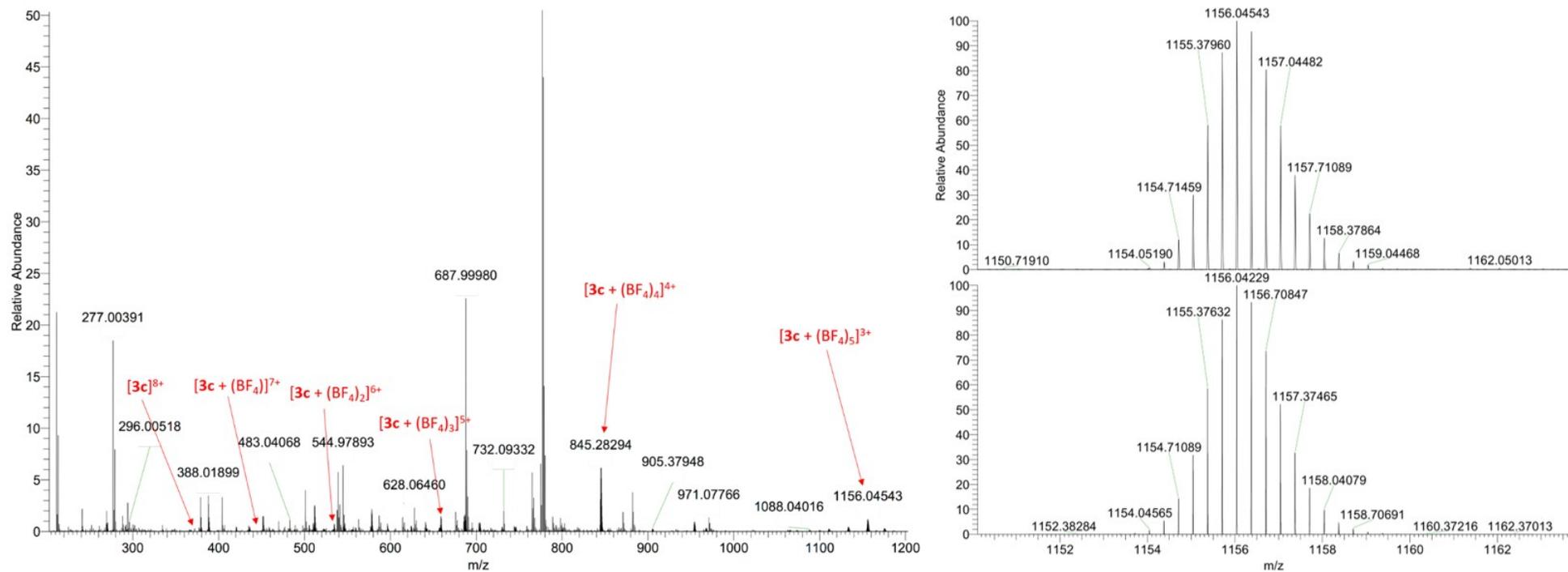
**Figure S33** The spectrum of cage **1d** (left). The experimental (top right) and simulated (bottom right) isotope distributions for  $[1d + (BF_4)_3]^{5+}$  are presented additionally.



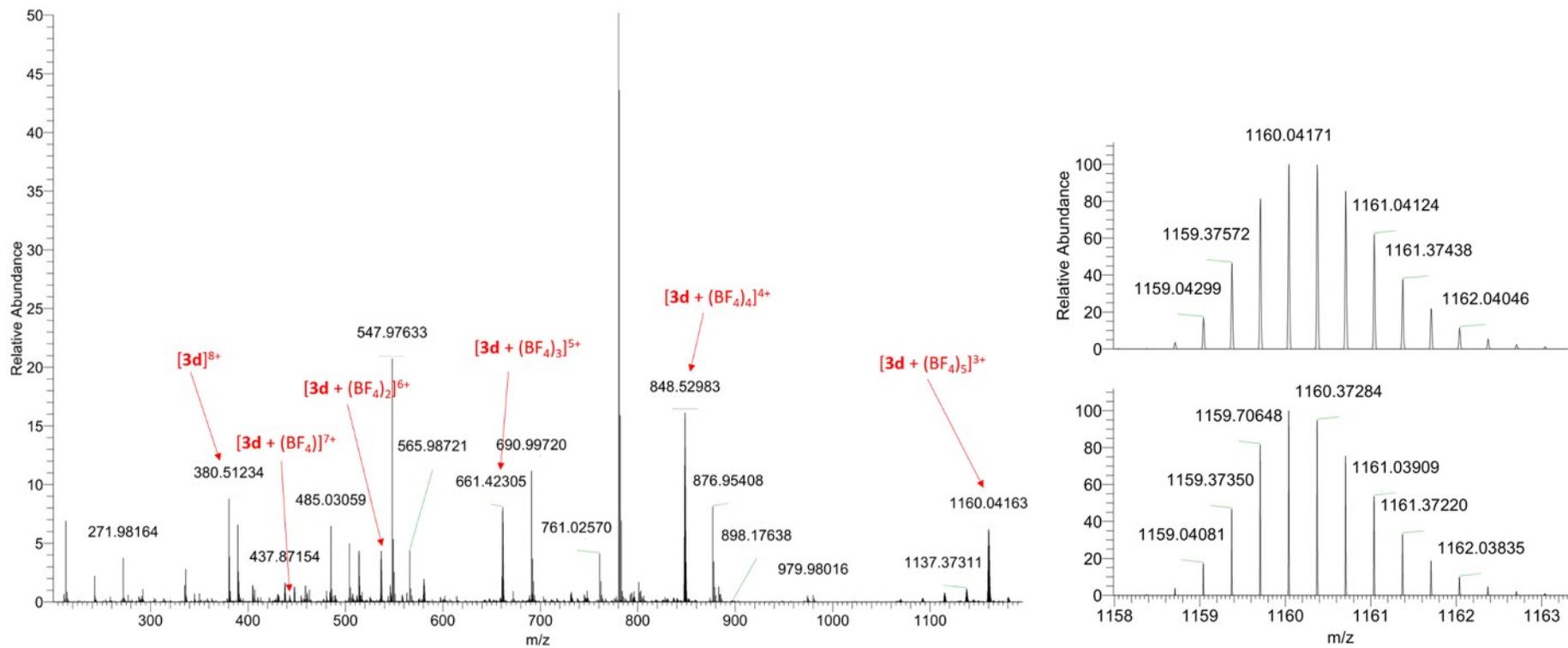
**Figure S34** The mass spectrum of cage **2c** (left). The experimental (top right) and simulated (bottom right) isotope distributions for  $[2c + (BF_4)_4]^{4+}$  are presented additionally.



**Figure S35** The mass spectrum of cage **2d** (left). The experimental (top right) and simulated (bottom right) isotope distributions for  $[2d + (BF_4)_4]^{4+}$  are presented additionally.

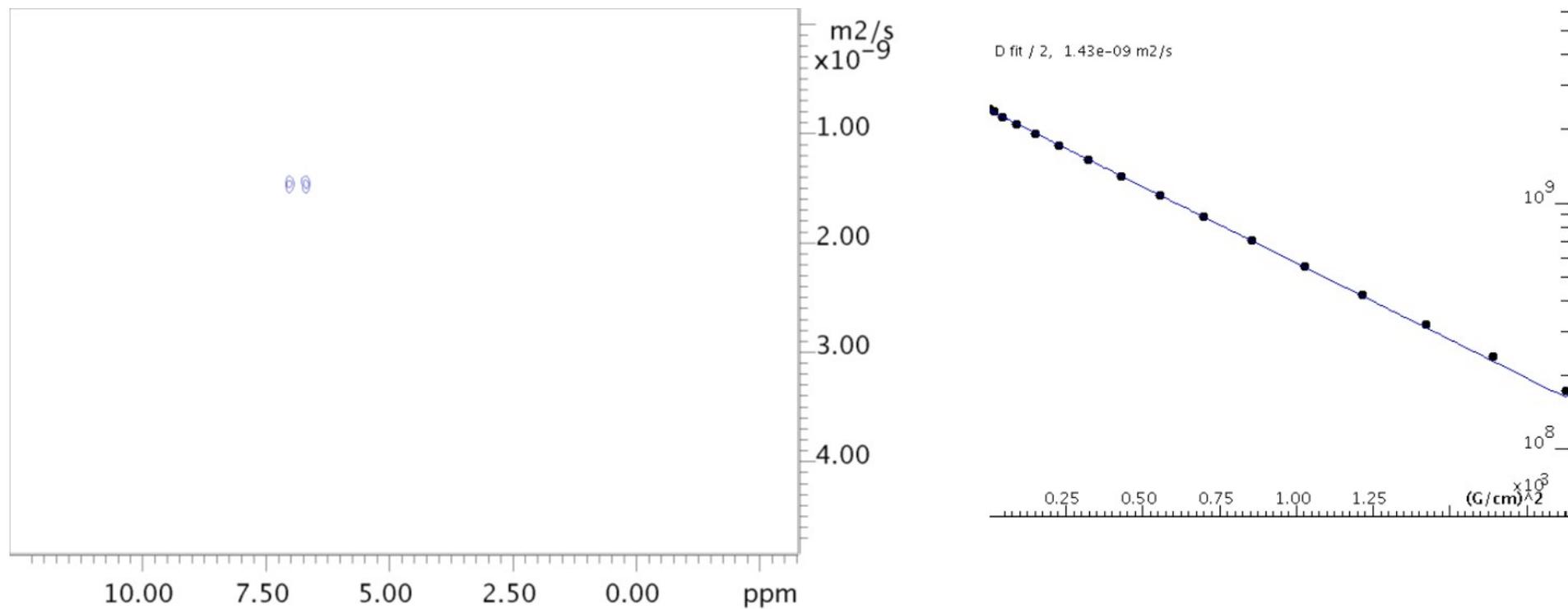


**Figure S36** The mass spectrum of cage **3c** (left). The experimental (top right) and simulated (bottom right) isotope distributions for  $[3c + (BF_4)_5]^{3+}$  are presented additionally.

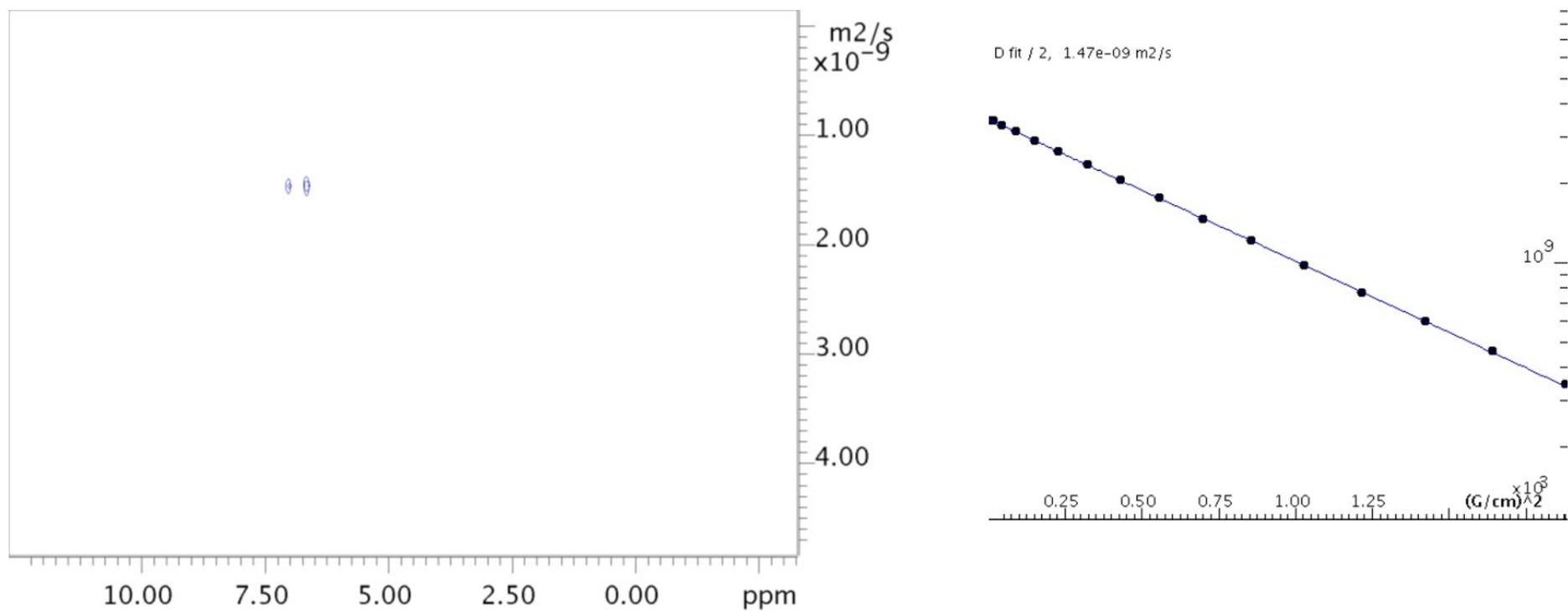


**Figure S37** The mass spectrum of cage **3d** (left) with the experimental (top right) and simulated (bottom right) isotope distributions for  $[3d + (BF_4)_5]^{3+}$  are presented additionally.

## Diffusion NMR Spectra



**Figure S38** The diffusion NMR plot (left) of the thiophosphate pro-ligand (**1b**) and the associated logarithmic fit (right).



**Figure S39** The diffusion NMR plot (left) of the selenophosphate pro-ligand (**2b**) and the associated logarithmic fit (right).

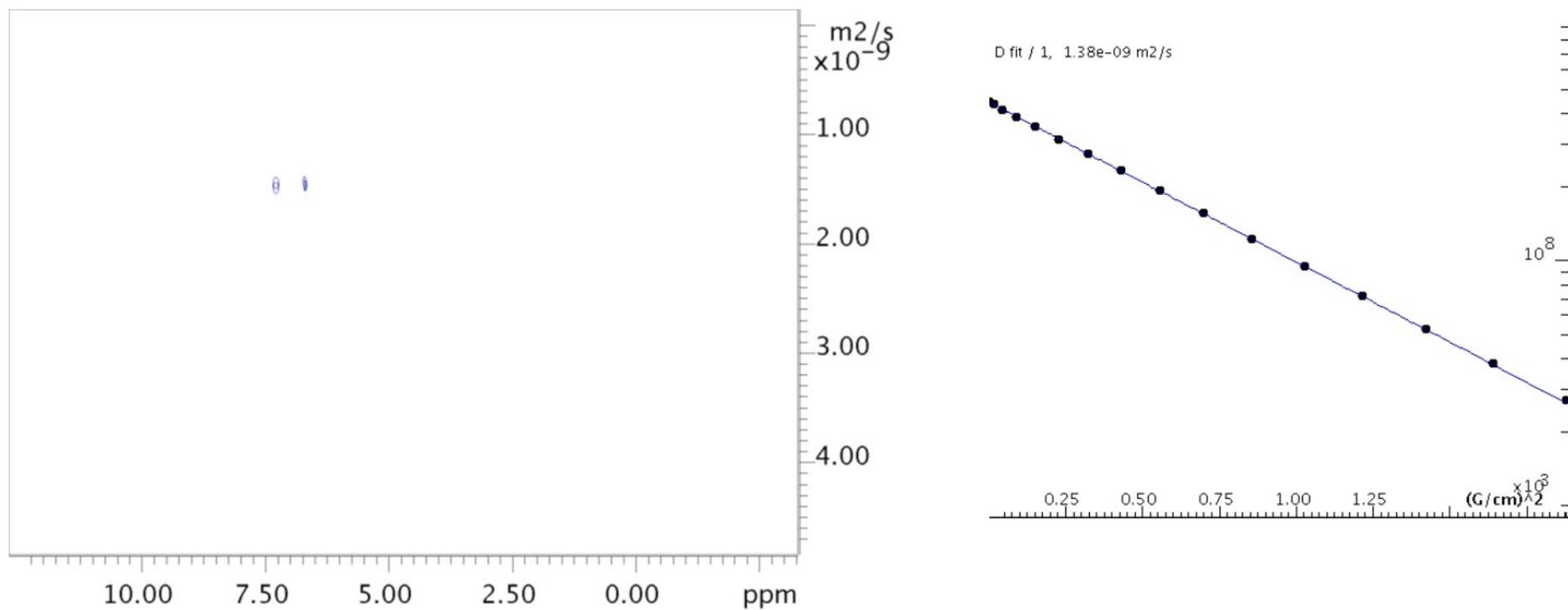
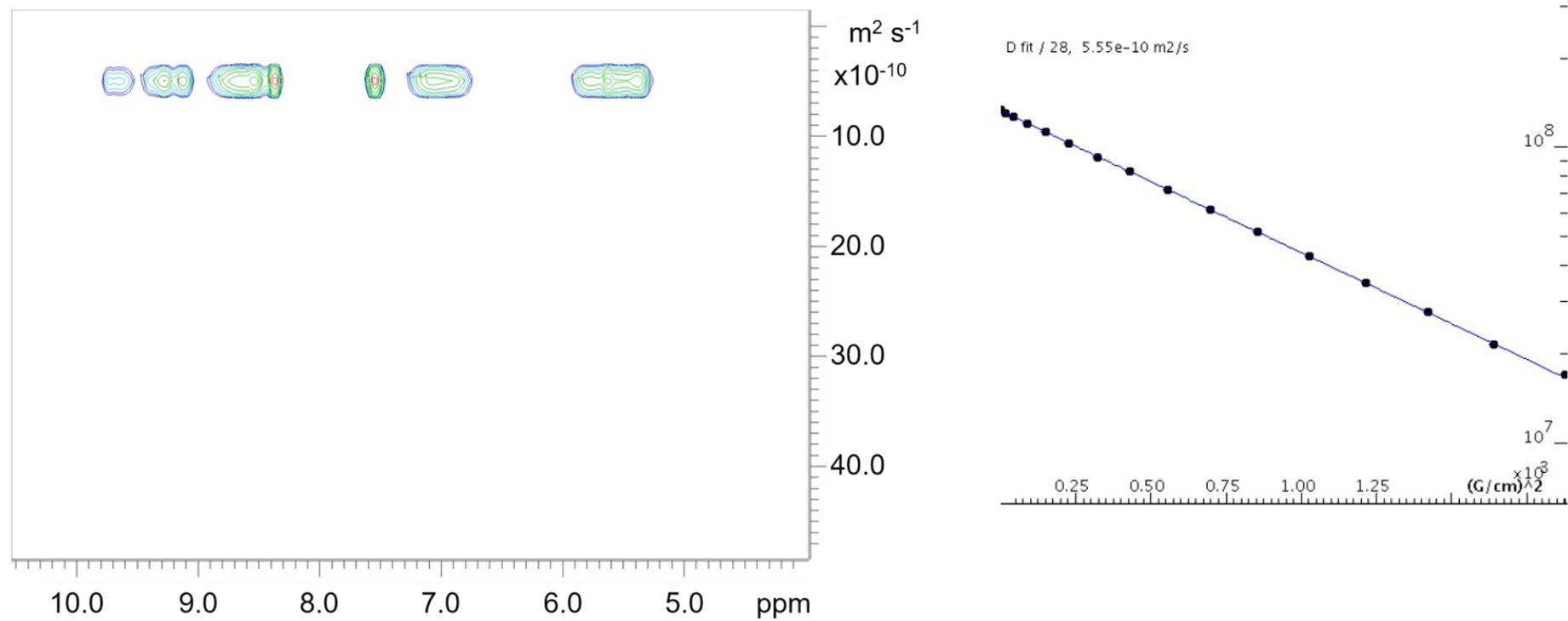
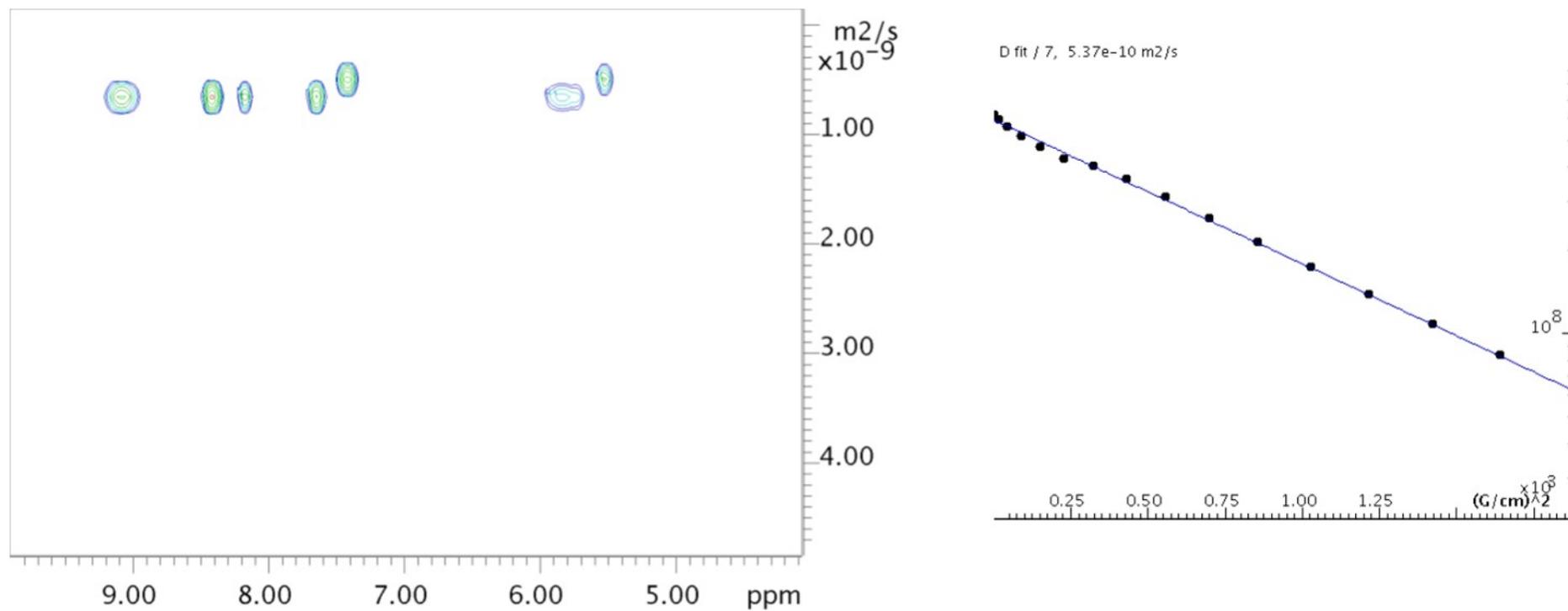


Figure S40 The diffusion NMR plot (left) of the tetrathiophosphate ligand (**3b**) and the associated logarithmic fit (right).



**Figure S41** The diffusion NMR plot (left) of cage **1c** and the associated logarithmic fit (right).



**Figure S42** The diffusion NMR plot (left) of cage **2c** and the associated logarithmic fit (right).

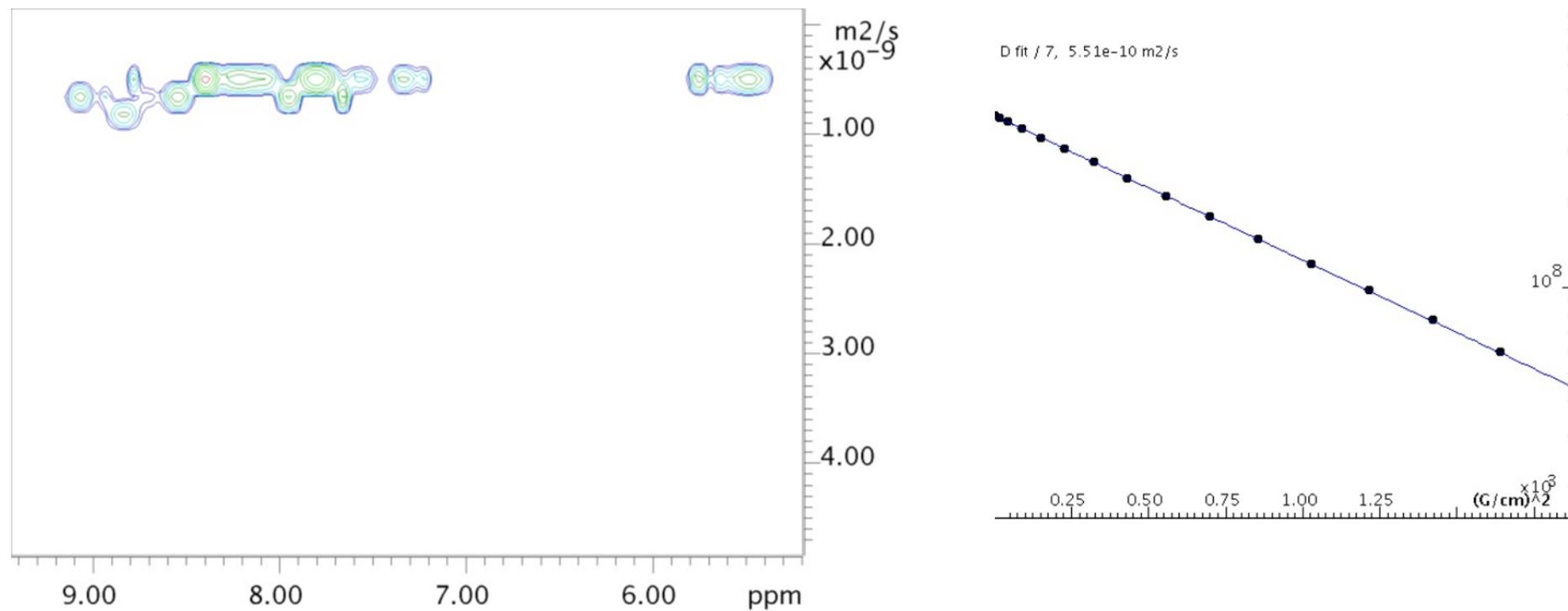


Figure S43 The diffusion NMR plot (left) of the cage **3c** and the associated logarithmic fit (right).

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- 2 G. Ritzoulis, N. Papadopoulos and D. Jannakoudakis, *J. Chem. Eng. Data*, 1986, **31**, 146–148.
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- 9 G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.*, 2015, **71**, 3–8.
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