

## Electronic Supporting Information

for

# Transition Metal Complexes of Cyclam with Two 2,2,2-Trifluoroethylphosphinate Pendant Arms as Probes for $^{19}\text{F}$ Magnetic Resonance Imaging

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## <sup>19</sup>F NMR spectra of M(II)–H<sub>2</sub>L complexes

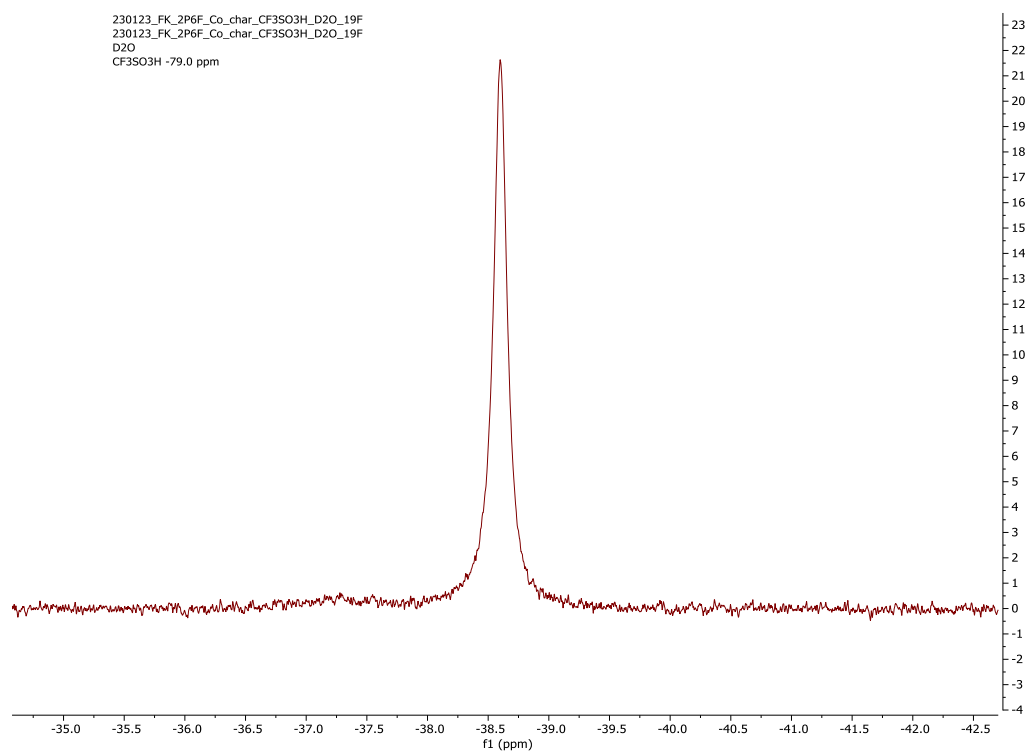


Figure S1. <sup>19</sup>F NMR spectrum of *cis*-[Co(L)] (H<sub>2</sub>O, pH 8.0, 565 MHz).

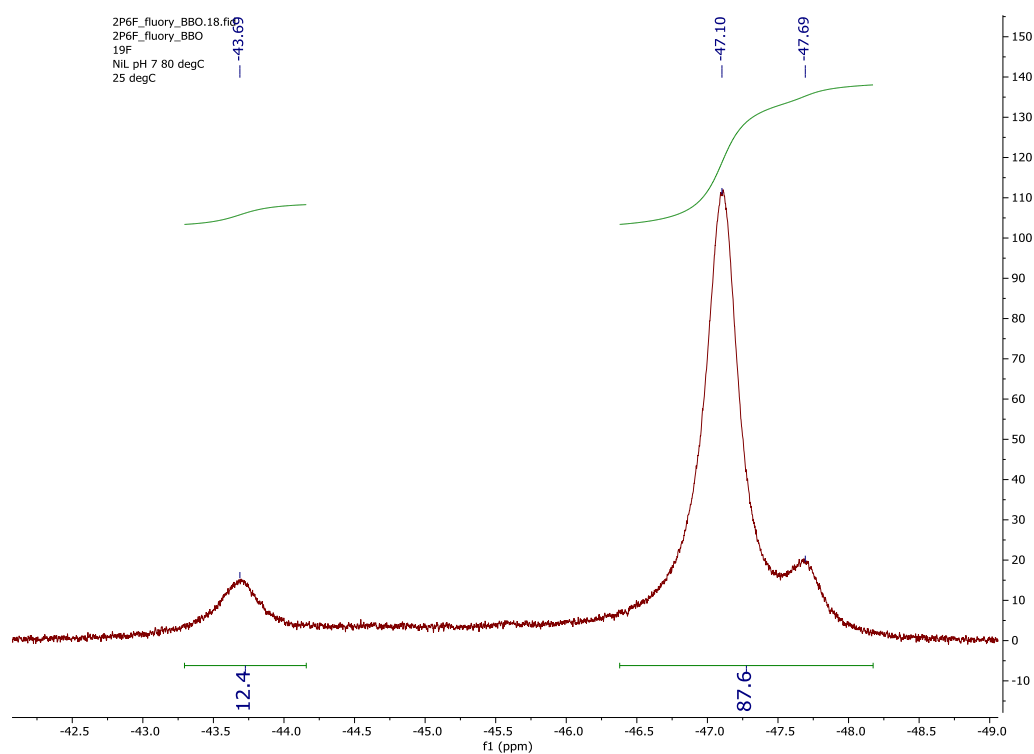
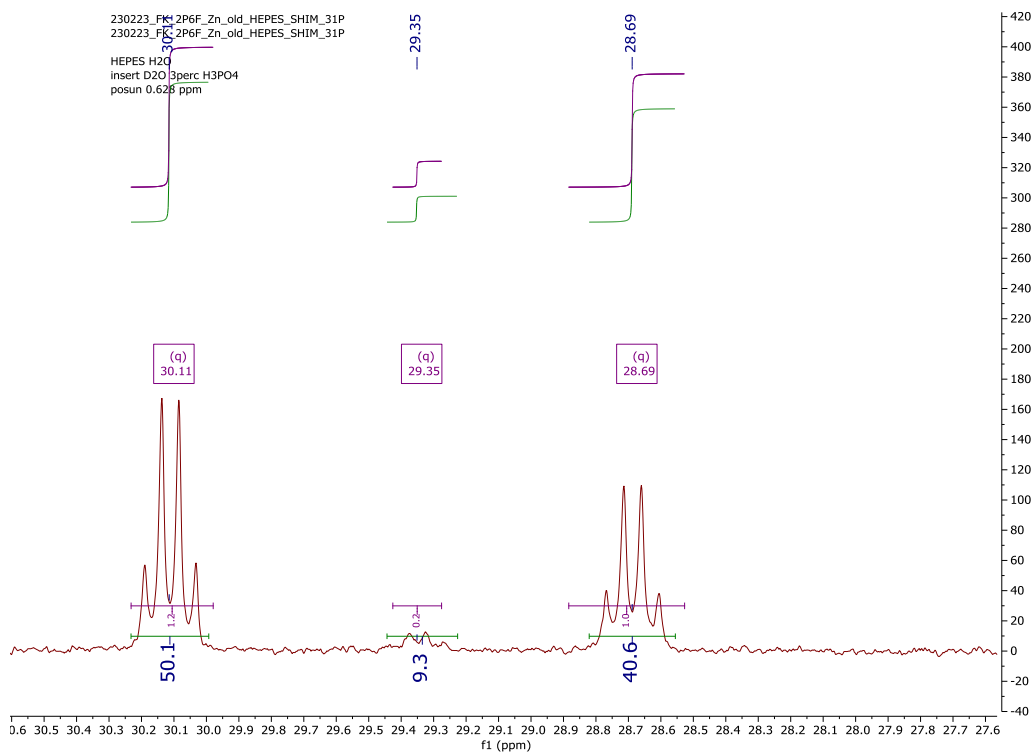
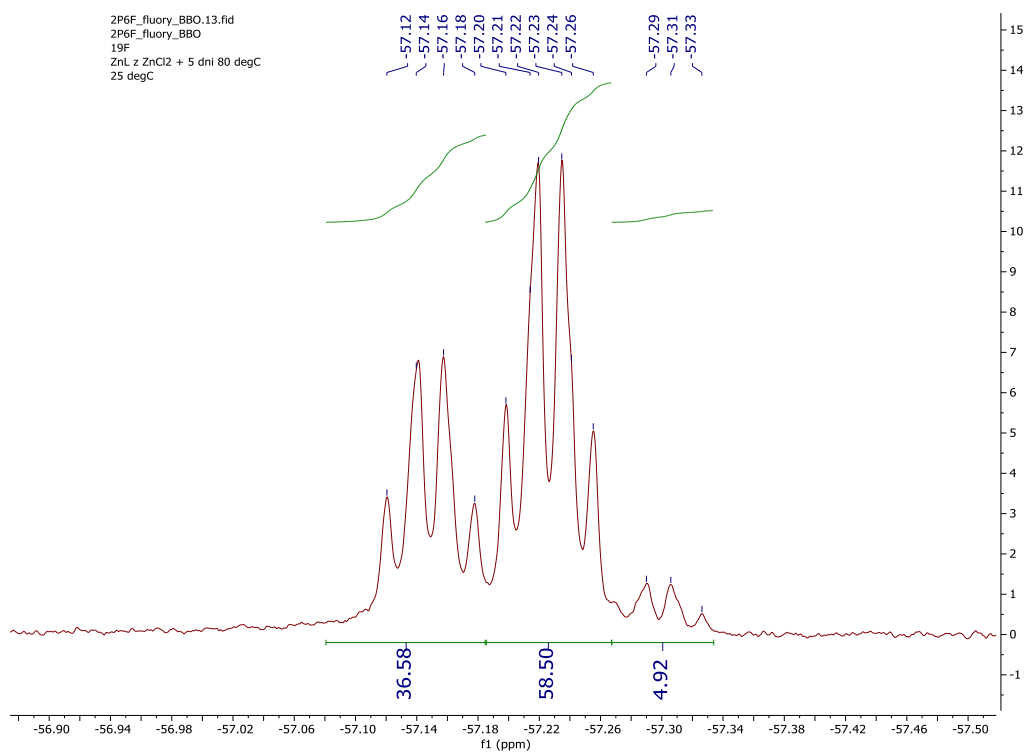


Figure S2. <sup>19</sup>F NMR spectrum of *cis*-[Ni(L)] (H<sub>2</sub>O, pH 7.4, 565 MHz).



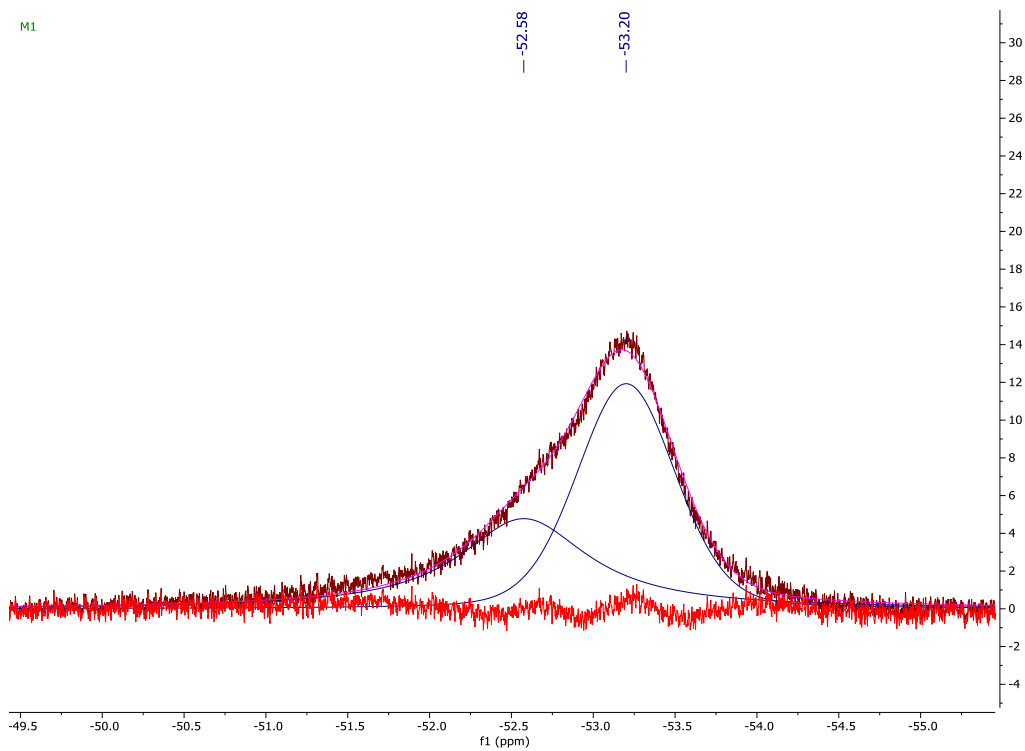


Figure S5.  $^{19}\text{F}$  NMR spectrum of *pc*-[Cu(L)] ( $\text{H}_2\text{O}$ , pH 4.0, 565 MHz).

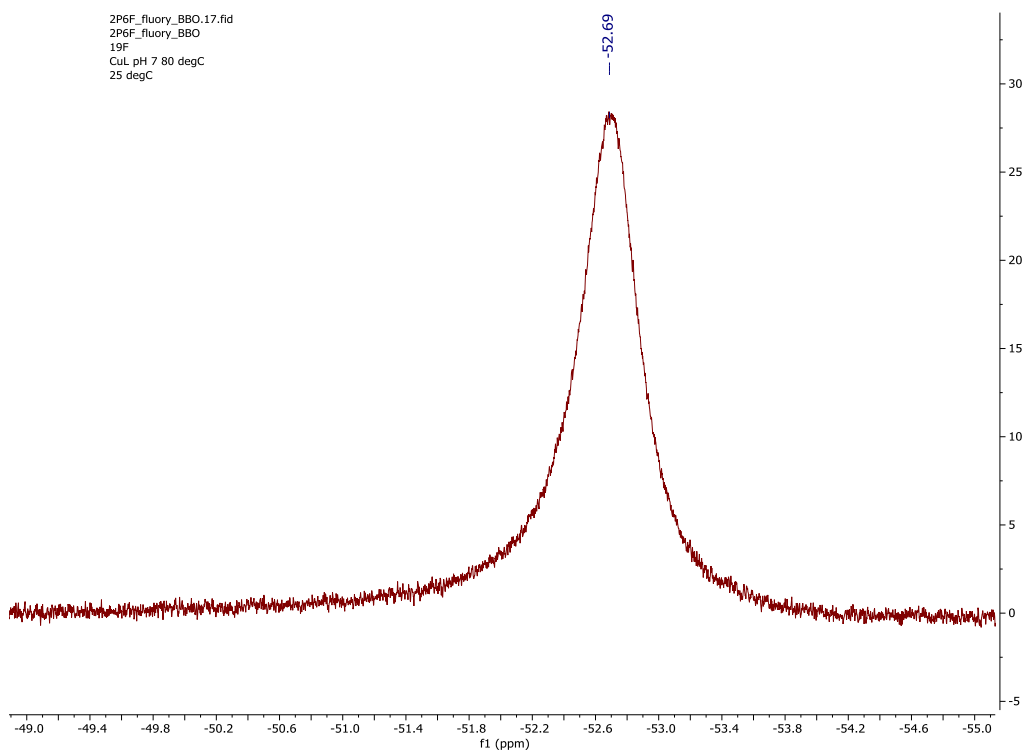


Figure S6.  $^{19}\text{F}$  NMR spectrum of *trans*-[Cu(L)] ( $\text{H}_2\text{O}$ , pH 7.4, 565 MHz).

## Colour difference and re-arrangement of isomeric Cu(II)–H<sub>2</sub>L complexes

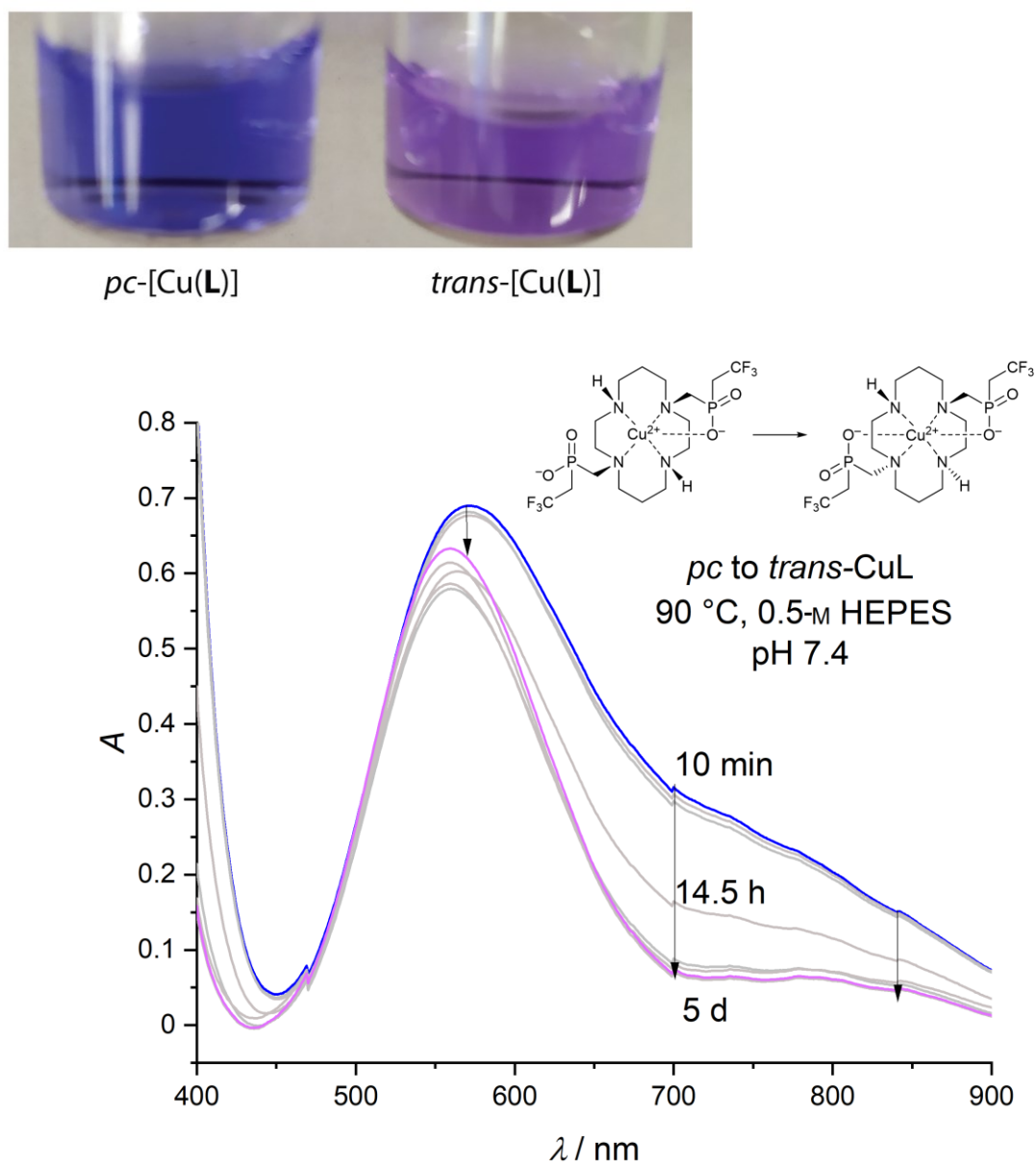


Figure S7. UV-Vis spectra showing rearrangement of *pc*-[Cu(L)] to *trans*-[Cu(L)] and colours of appropriate solutions.

### Details on refinement of crystal structures

In general, all non-hydrogen atoms were refined anisotropically. All hydrogen atoms were localized in electron density map; however, those bound to the carbon atoms were placed in theoretical positions using  $U_{\text{eq}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$  to keep a number of parameters low and only hydrogen atoms bound to heteroatoms (O, N) were fully refined.

In the structure of  $\text{H}_2\mathbf{3} \cdot 6\text{CF}_3\text{CO}_2\text{H} \cdot 2\text{H}_2\text{O}$ , the independent part is formed by one half of the formula unit due to crystallographic centrosymmetry. Whereas molecule of  $\text{H}_2\mathbf{3}$  was well-defined with small thermal factors, all trifluoroacetic acid molecules showed significantly higher thermal ellipsoids. Two of them were refined with disordered trifluoromethyl groups staggered in two positions, but still with high thermal factors. Disorder of trifluoroacetic acid molecules led to a relatively high *R*-factor.

The structure of  $\text{H}_2\mathbf{3} \cdot 6\text{H}_2\text{O}$  is also centrosymmetric leading to one half of the formula unit as crystallographically independent part. Two hydrogen atoms belonging to two water molecules of crystallization were modelled as disordered in two positions with half occupancy as result of hydrogen bond system. For one of hydrogen positions, DFIX was used as the atom comes too close to parent oxygen atom when fully refined.

The structures of  $\text{H}_2\mathbf{L} \cdot 4\text{AcOH}$  and  $(\text{H}_4\mathbf{L})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$  are also centrosymmetric. Positions of all atoms were well-defined.

In the crystal structure of  $\text{H}_2\mathbf{L} \cdot \text{LiCl} \cdot 6\text{H}_2\text{O}$ , two centrosymmetric halves of the ligand molecule are present in the independent part. One of them showed disorder in trifluoroethyl part, which was solved by splitting trifluoromethyl group into two positions.

In the crystal structure of  $pc\text{-}[\text{Cu}(\mathbf{3})] \cdot \text{Cu}(\text{AcO})_{1.8}(\text{tfa})_{0.2} \cdot 4\text{H}_2\text{O} \cdot 0.5\text{acetone}$ , the formula unit forms the structurally independent part. Two units are centrosymmetry-related forming a dimeric molecule through structural motive of copper(II) acetate dimer. However, in this central  $\{\text{Cu}(\text{OAc})_2\}_2$  dimer unit a number of maxims in electron density map with tetrahedral geometry around terminal carbon atoms of bridging acetate anions were found. It was best interpreted as superposition of acetate and trifluoroacetate anions in ratio 0.9:0.1.

In the crystal structure of  $cis\text{-}[\text{Co}(\mathbf{L})] \cdot \text{LiCl} \cdot 3\text{H}_2\text{O}$ , two formula units form the structurally independent part. Geometries of both complex units are very similar.

In the crystal structure of  $cis\text{-}[\text{Ni}(\mathbf{L})] \cdot 3.5\text{H}_2\text{O}$ , the formula unit forms the independent part and only one of water molecules of crystallization can be located with well-defined hydrogen bonds. Additional number of residual peaks in electron density map attributable to other water molecules were found in very close positions. However, the disorder cannot be reliably modelled, so the corresponding electron density was smoothed using Platon's SQUEEZE function.<sup>[1]</sup>

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[1] (a) A. L. Spek, *PLATON—A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 2019. (b) A. L. Spek, *Acta Crystallogr.*, 2009, **D65**, 148–155.

In the crystal structure of *pc*-[Cu(L)]·3H<sub>2</sub>O, the formula unit forms the independent part.

In the crystal structure of *trans*-[Cu(L)]·NH<sub>4</sub>(Cl<sub>0.54</sub>Br<sub>0.46</sub>), one half of the centrosymmetric formula unit forms the independent part. A high electron maximum present in this structure was best interpreted as superposition of chloride and bromide anions over the same position using EXYZ/EADP commands with refined ratio 0.54:0.46.

The crystal structure of *trans*-[Cu(L)]·(H<sub>3</sub>O)(ClO<sub>4</sub>)·H<sub>2</sub>O is centrosymmetric with two independent halves of the complex molecules.

In the structure of *cis*-[Zn(L)]·2H<sub>2</sub>O·0.5(C<sub>3</sub>H<sub>6</sub>O), one of water molecules of crystallization was refined disordered over two close positions sharing hydrogen atoms. Molecule of acetone is placed close to centre of symmetry which causes that only one half present in the independent unit.

All the data for the structures reported here have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-2262037–2262048 (for overview of experimental crystallographic data see Table S1).

Table S1. Experimental crystallographic data for the reported structures.

Compound	H <sub>2</sub> 3·6CF <sub>3</sub> CO <sub>2</sub> H·2H <sub>2</sub> O	H <sub>2</sub> 3·6H <sub>2</sub> O	H <sub>2</sub> L·4AcOH	(H <sub>4</sub> L)Cl <sub>2</sub> ·4H <sub>2</sub> O	H <sub>2</sub> L·LiCl·6H <sub>2</sub> O	<i>pc</i> -[Cu(3)]·Cu(AcO) <sub>1.8</sub> (tfa) <sub>0.2</sub> ·4H <sub>2</sub> O·0.5acetone
Formula	C <sub>42</sub> H <sub>54</sub> F <sub>24</sub> N <sub>4</sub> O <sub>18</sub> P <sub>2</sub>	C <sub>30</sub> H <sub>56</sub> F <sub>6</sub> N <sub>4</sub> O <sub>10</sub> P <sub>2</sub>	C <sub>24</sub> H <sub>48</sub> F <sub>6</sub> N <sub>4</sub> O <sub>12</sub> P <sub>2</sub>	C <sub>16</sub> H <sub>42</sub> Cl <sub>2</sub> F <sub>6</sub> N <sub>4</sub> O <sub>8</sub> P <sub>2</sub>	C <sub>16</sub> H <sub>44</sub> ClF <sub>6</sub> LiN <sub>4</sub> O <sub>10</sub> P <sub>2</sub>	C <sub>35.5</sub> H <sub>58.4</sub> Cu <sub>2</sub> F <sub>6.6</sub> N <sub>4</sub> O <sub>12.5</sub> P <sub>2</sub>
<i>M</i>	1420.83	808.72	760.60	665.37	670.88	1055.68
Crystal system	monoclinic	triclinic	monoclinic	triclinic	triclinic	tetragonal
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> -1	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> -1	<i>P</i> -1	<i>I</i> 4 <sub>1</sub> / <i>a</i>
<i>a</i> / Å	12.3608(4)	8.9086(3)	8.1091(3)	7.5425(4)	9.4863(6)	36.5804(9)
<i>b</i> / Å	11.3394(4)	10.8155(4)	19.7189(8)	9.9805(5)	11.7783(6)	36.5804(9)
<i>c</i> / Å	21.7985(8)	11.9920(4)	10.8818(5)	11.3345(5)	13.6581(8)	15.8953(5)
$\alpha$ / °	90	63.673(1)	90	71.9230(10)	99.947(2)	90
$\beta$ / °	90.019(2)	70.031(1)	90.755(2)	72.7220(10)	90.009(2)	90
$\gamma$ / °	90	76.398(1)	90	69.5340(10)	99.799(2)	90
<i>U</i> / Å <sup>3</sup>	3055.37(18)	968.51(6)	1739.88(12)	742.71(6)	1480.50(15)	21269.9(12)
<i>Z</i>	2	1	2	1	2	16
Unique refl.	6464	4447	4007	2900	8637	10478
Obsd. refl.	5214	3810	3515	2854	7835	8168
<i>R</i> ( <i>I</i> >2σ( <i>I</i> )), <i>R</i> '	0.0729; 0.0864	0.0339; 0.0415	0.0317; 0.0376	0.0261; 0.0264	0.0387; 0.0424	0.0514; 0.0720
<i>wR</i> ( <i>I</i> >2σ( <i>I</i> )), <i>wR</i> '	0.2061; 0.2216	0.0876; 0.0930	0.0804; 0.0842	0.0698; 0.0701	0.1043; 0.1077	0.1467; 0.1584
CCDC ref. no.	2262048	2262037	2262042	2262045	2262039	2262041



Table S1 – continuation. Experimental crystallographic data for the reported structures.

Compound	<i>cis</i> -[Co(L)]·LiCl·3H <sub>2</sub> O	<i>cis</i> -[Ni(L)]·3.5H <sub>2</sub> O	<i>pc</i> -[Cu(L)]·3H <sub>2</sub> O	<i>trans</i> -[Cu(L)] ·NH <sub>4</sub> (Cl <sub>0.54</sub> Br <sub>0.46</sub> )	<i>trans</i> -[Cu(L)] ·(H <sub>3</sub> O)(ClO <sub>4</sub> )·H <sub>2</sub> O	<i>cis</i> -[Zn(L)] ·2H <sub>2</sub> O·0.5(C <sub>3</sub> H <sub>6</sub> O)
Formula	C <sub>16</sub> H <sub>36</sub> ClCoF <sub>6</sub> LiN <sub>4</sub> O <sub>7</sub> P <sub>2</sub>	C <sub>16</sub> H <sub>37</sub> F <sub>6</sub> N <sub>4</sub> NiO <sub>7.5</sub> P <sub>2</sub>	C <sub>16</sub> H <sub>36</sub> CuF <sub>6</sub> N <sub>4</sub> O <sub>7</sub> P <sub>2</sub>	C <sub>16</sub> H <sub>34</sub> Br <sub>0.46</sub> Cl <sub>0.54</sub> CuF <sub>6</sub> N <sub>5</sub> O <sub>4</sub> P <sub>2</sub>	C <sub>16</sub> H <sub>35</sub> ClCuF <sub>6</sub> N <sub>4</sub> O <sub>10</sub> P <sub>2</sub>	C <sub>17.5</sub> H <sub>37</sub> F <sub>6</sub> N <sub>4</sub> O <sub>6.5</sub> P <sub>2</sub> Zn
<i>M</i>	673.75	640.14	635.97	655.86	718.41	648.82
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	triclinic	monoclinic
Space group	<i>P2</i> <sub>1</sub> / <i>n</i>	<i>P2</i> <sub>1</sub> / <i>n</i>	<i>P</i> -1	<i>C2</i> / <i>c</i>	<i>P</i> -1	<i>P2</i> <sub>1</sub> / <i>n</i>
<i>a</i> / Å	21.9609(12)	9.6825(3)	10.0011(4)	15.9852(6)	9.8024(3)	9.7340(2)
<i>b</i> / Å	10.4910(5)	13.4090(4)	10.5012(4)	12.6453(5)	10.5793(3)	13.3794(3)
<i>c</i> / Å	25.9042(14)	20.7058(5)	13.4258(5)	12.6956(4)	13.9063(4)	20.7034(4)
$\alpha$ / °	90	90	85.725(1)	90	86.5240(10)	90
$\beta$ / °	111.540(2)	92.318(1)	71.907(1)	102.1106(12)	83.3100(10)	93.6720(10)
$\gamma$ / °	90	90	76.141(1)	90	72.3210(10)	90
<i>U</i> / Å <sup>3</sup>	5551.3(5)	2686.09(13)	1301.29(9)	2509.15(16)	1364.17(7)	2690.77(10)
<i>Z</i>	8	4	2	4	2	4
Unique refl.	12767	6178	5984	2907	6257	6164
Obsd. refl.	12162	5545	5459	2734	5931	5843
<i>R</i> ( <i>I</i> >2 $\sigma$ ( <i>I</i> )), <i>R</i> '	0.0322; 0.0335	0.0239; 0.0272	0.0256; 0.0301	0.0250; 0.0275	0.0276; 0.0294	0.0253; 0.0268
<i>wR</i> ( <i>I</i> >2 $\sigma$ ( <i>I</i> )), <i>wR</i> '	0.0891; 0.0902	0.0598; 0.0611	0.0615; 0.0635	0.0636; 0.0648	0.0673; 0.0685	0.0643; 0.0651
CCDC ref. no.	2262044	2262040	2262047	2262043	2262038	2262046

## Crystal structures of the complexes

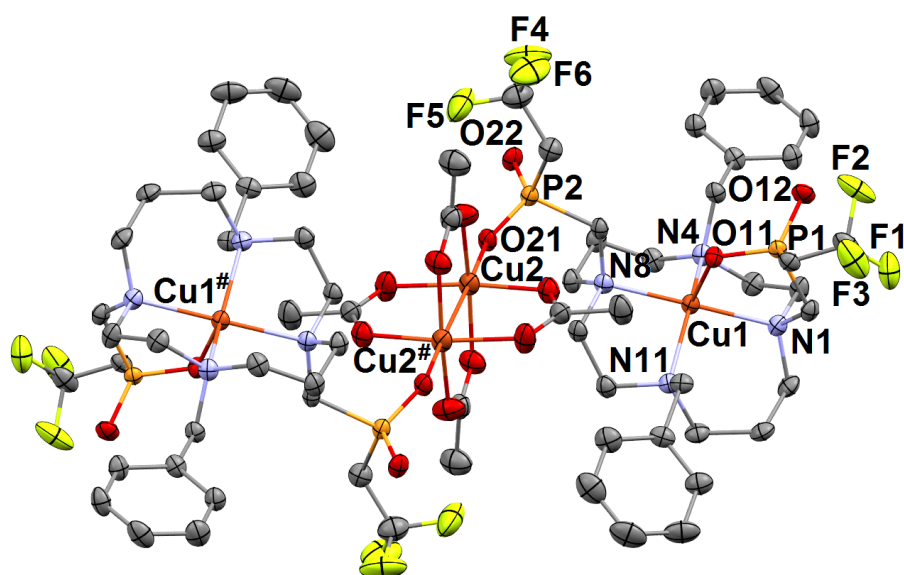


Figure S8. Molecular structure of  $\{pc\text{-[Cu(3)]}\cdot\text{Cu}(\text{AcO})_{1.8}(\text{tfa})_{0.2}\}_2$  dimer found in the crystal structure of  $pc\text{-[Cu(3)]}\cdot\text{Cu}(\text{AcO})_{1.8}(\text{tfa})_{0.2}\cdot 4\text{H}_2\text{O}\cdot 0.5\text{acetone}$ ; the copper(II)-acetate-like dimeric motif connecting two  $pc\text{-[Cu(3)]}$  units is noteworthy. Hydrogen and fluorine atoms of partly occupied trifluoroacetic acid from  $\text{Cu}(\text{AcO})_{1.8}(\text{tfa})_{0.2}$  fragment are omitted for clarity. Selected centrosymmetry-related atoms are labelled with #.

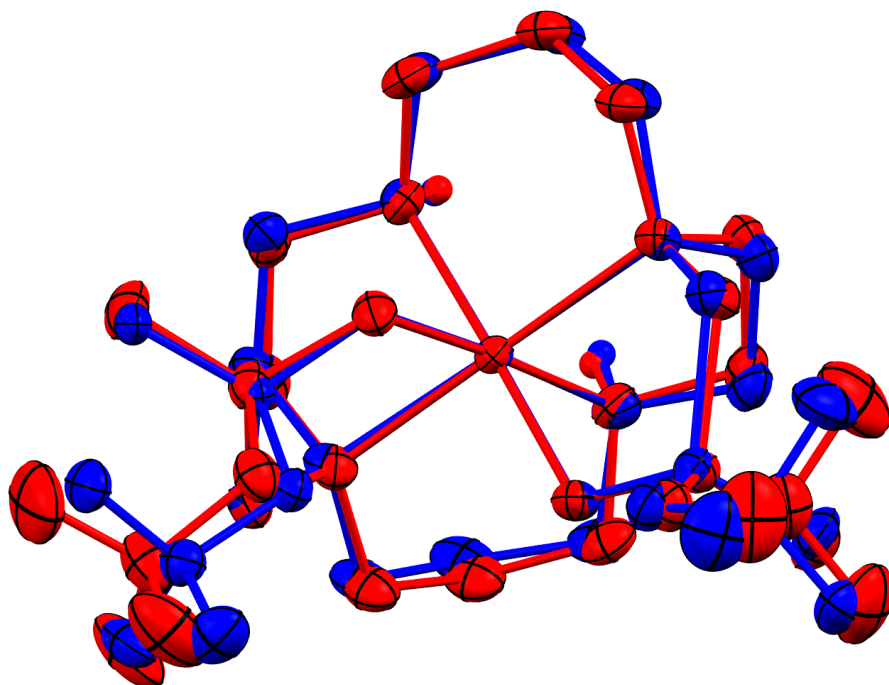


Figure S9. Overlay of two independent  $cis\text{-O,O}'\text{-[Co(L)]}$  molecules found in the crystal structure of  $cis\text{-O,O}'\text{-[Co(L)]}\cdot\text{LiCl}\cdot 3\text{H}_2\text{O}$ . Carbon-bound hydrogen atoms are omitted for clarity.

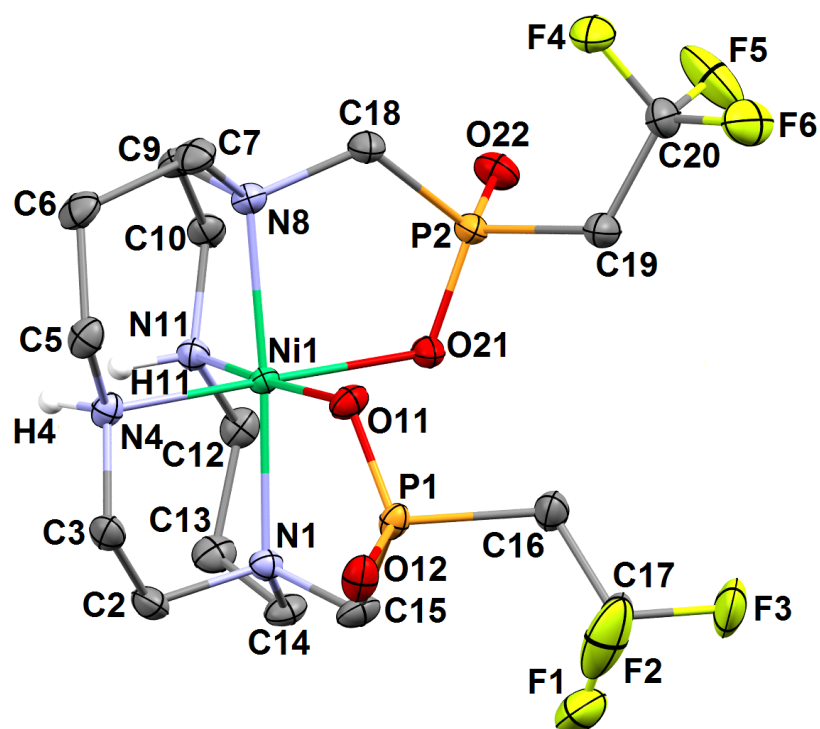


Figure S10. Molecular structure of *cis-O,O'*-[Ni(L)] found in the crystal structure of *cis-O,O'*-[Ni(L)]·3.5H<sub>2</sub>O. Carbon-bound hydrogen atoms are omitted for clarity.

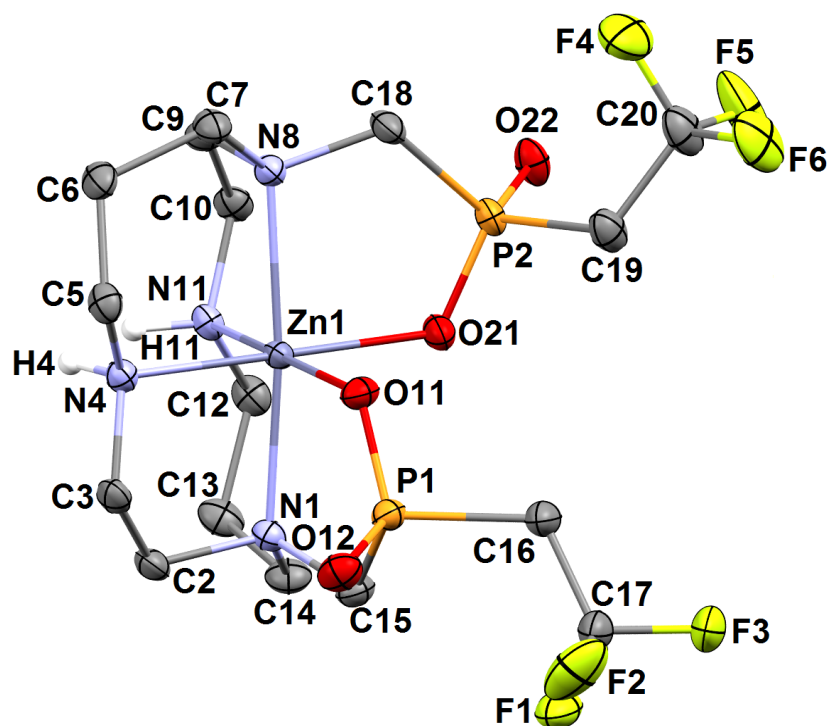


Figure S11. Molecular structure of *cis-O,O'*-[Zn(L)] found in the crystal structure of *cis-O,O'*-[Zn(L)]·2H<sub>2</sub>O·0.5acetone. Carbon-bound hydrogen atoms are omitted for clarity.

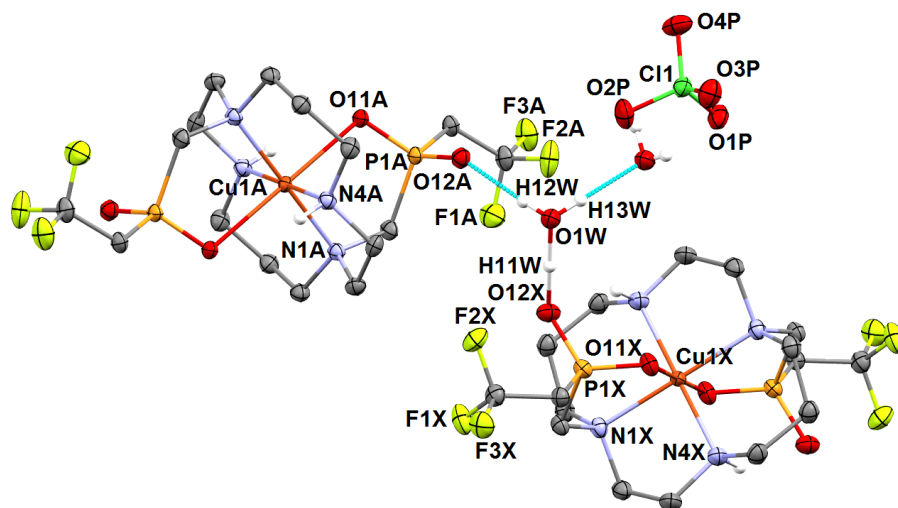


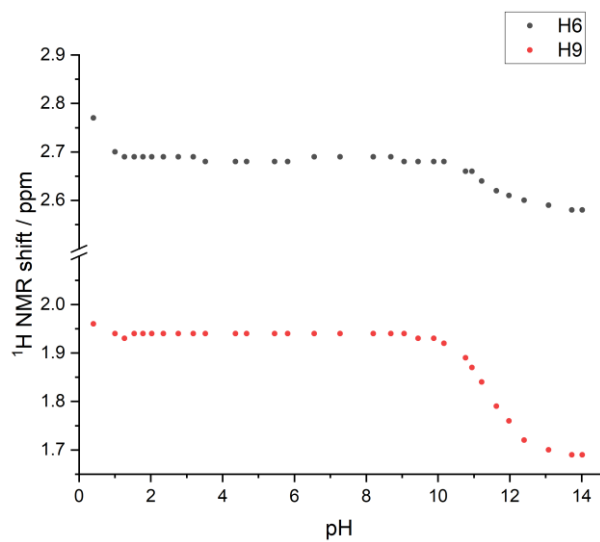
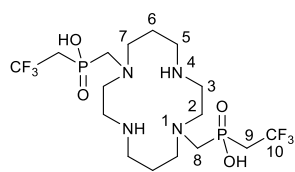
Figure S12. Structural motive found in the crystal structure of *trans-O,O'*-[Cu(L)]·(H<sub>3</sub>O)(ClO<sub>4</sub>)·H<sub>2</sub>O. Carbon-bound hydrogen atoms are omitted for clarity. Hydrogen bonds involving oxonium ion (oxygen O1W) are shown as turquoise dashed lines; the strongest hydrogen bond to O12X is shown as solid line [ $d(\text{O1W}\cdots\text{O12X}) = 2.44 \text{ \AA}$ ,  $\text{angle}(\text{O1W}-\text{H12}\cdots\text{O12X}) = 176^\circ$ ].

Table S2. Selected geometric parameters found in the crystal structures of studied complexes.

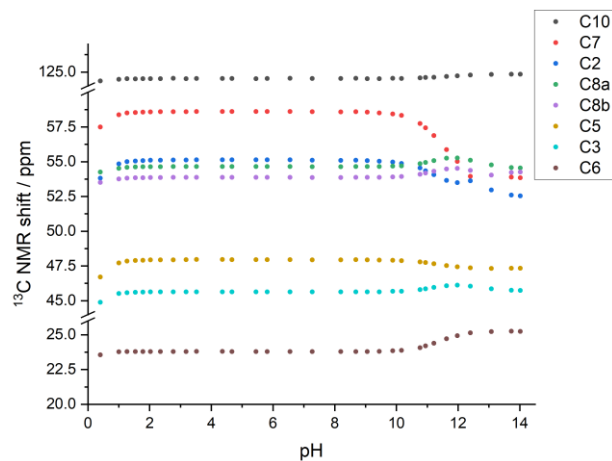
Parameter	<i>pc</i> -[Cu(3)]	<i>cis</i> -[Co(L)]		<i>cis</i> -[Ni(L)]	<i>pc</i> -[Cu(L)]	<i>trans</i> -[Cu(L)]	<i>trans</i> -[Cu(L)]		<i>cis</i> -[Zn(L)]
	·Cu(AcO) <sub>1.8</sub> (tfa) <sub>0.2</sub> ·4H <sub>2</sub> O·0.5acetone	·LiCl·3H <sub>2</sub> O	mol. 1	mol. 2	·3.5H <sub>2</sub> O	·3H <sub>2</sub> O	·NH <sub>4</sub> (Cl <sub>0.54</sub> Br <sub>0.46</sub> )	·(H <sub>3</sub> O)(ClO <sub>4</sub> )·H <sub>2</sub> O	·2H <sub>2</sub> O·0.5(C <sub>3</sub> H <sub>6</sub> O)
Distances (Å)									
M–N1	2.102(3)	2.182(2)	2.212(2)	2.154(1)	2.067(1)	2.069(1)	2.068(1)	2.099(1)	2.183(1)
M–N4	2.122(3)	2.115(2)	2.124(2)	2.104(1)	2.017(1)	2.006(1)	2.021(1)	2.024(2)	2.130(1)
M–N8	2.088(3)	2.174(2)	2.189(1)	2.129(1)	2.064(1)	2.069(1) <sup>#</sup>	2.068(1) <sup>#</sup>	2.099(1) <sup>#</sup>	2.217(1)
M–N11	2.119(3)	2.134(2)	2.121(2)	2.083(1)	2.022(1)	2.006(1) <sup>#</sup>	2.021(1) <sup>#</sup>	2.024(2) <sup>#</sup>	2.161(1)
M–O11	2.093(3)	2.094(1)	2.081(1)	2.071(1)	2.148(1)	2.433(1)	2.412(1)	2.372(1)	2.154(1)
M–O21	–	2.085(1)	2.109(1)	2.113(1)	–	2.433(1) <sup>#</sup>	2.412(1) <sup>#</sup>	2.372(1) <sup>#</sup>	2.080(1)
M··F1	5.884(3)	5.570(1)	5.702(1)	5.620(1)	5.813(1)	5.813(1)	5.809(1)	5.904(1)	5.637(1)
M··F2	6.284(3)	6.266(1)	6.205(1)	6.240(1)	6.338(1)	6.414(1)	6.370(1)	6.377(1)	6.362(1)
M··F3	6.768(3)	6.484(2)	6.413(1)	6.415(1)	6.701(1)	6.908(1)	6.973(1)	6.993(1)	6.502(1)
M··F4	7.170(3)	5.815(2)	5.868(2)	5.596(1)	5.075(1)	5.813(1) <sup>§</sup>	5.809(1) <sup>§</sup>	5.904(1) <sup>§</sup>	5.668(1)
M··F5	7.647(3)	6.330(1)	6.322(1)	6.319(1)	6.590(1)	6.414(1) <sup>§</sup>	6.370(1) <sup>§</sup>	6.377(1) <sup>§</sup>	6.261(1)
M··F6	7.747(3)	6.634(1)	6.658(1)	6.478(1)	6.966(1)	6.908(1) <sup>§</sup>	6.973(1) <sup>§</sup>	6.993(1) <sup>§</sup>	6.439(1)
Angles (°)									
N1–M–N4	85.24(12)	84.04(6)	82.84(6)	84.27(4)	87.29(5)	86.32(5)	86.44(6)	86.29(6)	84.35(5)
N1–M–N8	179.60(12)	174.71(6)	175.99(6)	175.83(4)	177.50(5)	180 <sup>#</sup>	180 <sup>#</sup>	180 <sup>#</sup>	173.67(4)
N1–M–N11	93.67(12)	92.53(6)	94.28(6)	92.77(4)	93.24(5)	93.68(5) <sup>#</sup>	93.56(6) <sup>#</sup>	93.71(6) <sup>#</sup>	91.92(5)
N1–M–O11	87.24(11)	86.27(5)	85.15(5)	88.37(4)	85.46(5)	86.25(5)	85.49(5)	85.34(5)	86.14(4)
N1–M–O21	–	96.19(5)	97.62(5)	95.83(4)	–	93.75(5) <sup>#</sup>	94.51(5) <sup>#</sup>	94.66(5) <sup>#</sup>	97.08(4)
N4–M–N8	94.73(12)	93.38(6)	94.52(6)	92.48(4)	93.81(5)	93.68(5) <sup>#</sup>	93.56(6) <sup>#</sup>	93.71(6) <sup>#</sup>	92.06(4)
N4–M–N11	149.30(12)	94.47(6)	97.11(6)	96.54(4)	146.28(5)	180 <sup>#</sup>	180 <sup>#</sup>	180 <sup>#</sup>	96.40(5)
N4–M–O11	110.70(11)	87.87(6)	86.71(5)	88.71(4)	109.00(5)	93.75(5)	95.14(5)	90.11(6)	87.33(4)
N4–M–O21	–	175.88(6)	174.20(5)	175.56(4)	–	86.25(5) <sup>#</sup>	84.86(5) <sup>#</sup>	89.89(6) <sup>#</sup>	174.31(4)
N8–M–N11	86.15(12)	83.05(6)	83.02(6)	84.99(4)	87.09(5)	86.32(5) <sup>#</sup>	86.44(6) <sup>#</sup>	86.29(6) <sup>#</sup>	83.28(5)
N8–M–O11	93.14(11)	98.27(5)	97.75(5)	94.18(4)	92.06(4)	93.75(5) <sup>#</sup>	94.51(5) <sup>#</sup>	94.66(5) <sup>#</sup>	98.93(4)
N8–M–O21	–	86.71(5)	85.31(5)	87.62(4)	–	86.25(5) <sup>#</sup>	85.49(5) <sup>#</sup>	85.34(5) <sup>#</sup>	86.99(4)
N11–M–O11	99.87(11)	177.25(6)	176.04(5)	174.71(4)	104.65(5)	86.25(5) <sup>#</sup>	84.86(5) <sup>#</sup>	89.89(6) <sup>#</sup>	175.61(4)
N11–M–O21	–	89.62(5)	88.62(6)	87.89(4)	–	93.75(5) <sup>#</sup>	95.14(5) <sup>#</sup>	90.11(6) <sup>#</sup>	89.06(4)
O11–M–O21	–	88.04(5)	87.56(5)	86.85(4)	–	180 <sup>#</sup>	180 <sup>#</sup>	180 <sup>#</sup>	87.28(4)

<sup>#</sup> Centrosymmetry-related atoms (N8 = N1#, N11 = N4#, O21 = O11#). <sup>§</sup> Centrosymmetry-related atoms (F4 = F1\$, F5 = F2\$, F6 = F3\$).

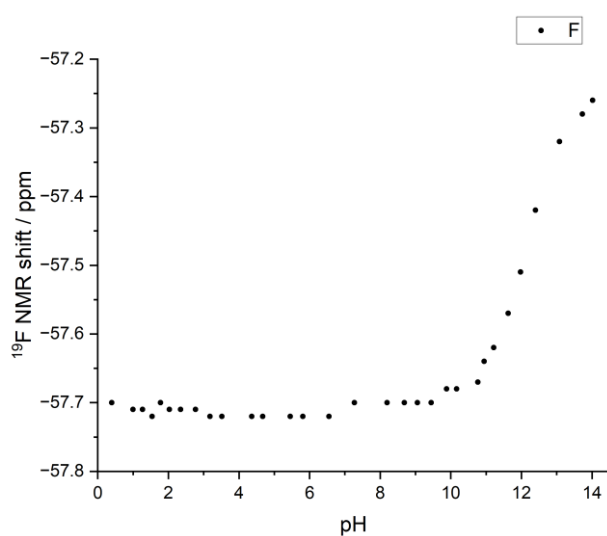
## NMR titration of H<sub>2</sub>L



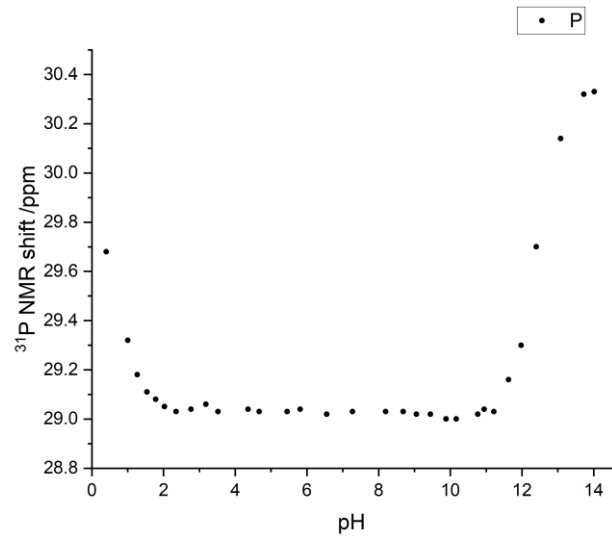
a



b



c



d

Figure S13. The pH dependence of NMR chemical shifts of H<sub>2</sub>L. a) <sup>1</sup>H, b) <sup>13</sup>C, c) <sup>19</sup>F, d) <sup>31</sup>P and an atom numbering scheme.

Distribution diagram of  $H_2L$

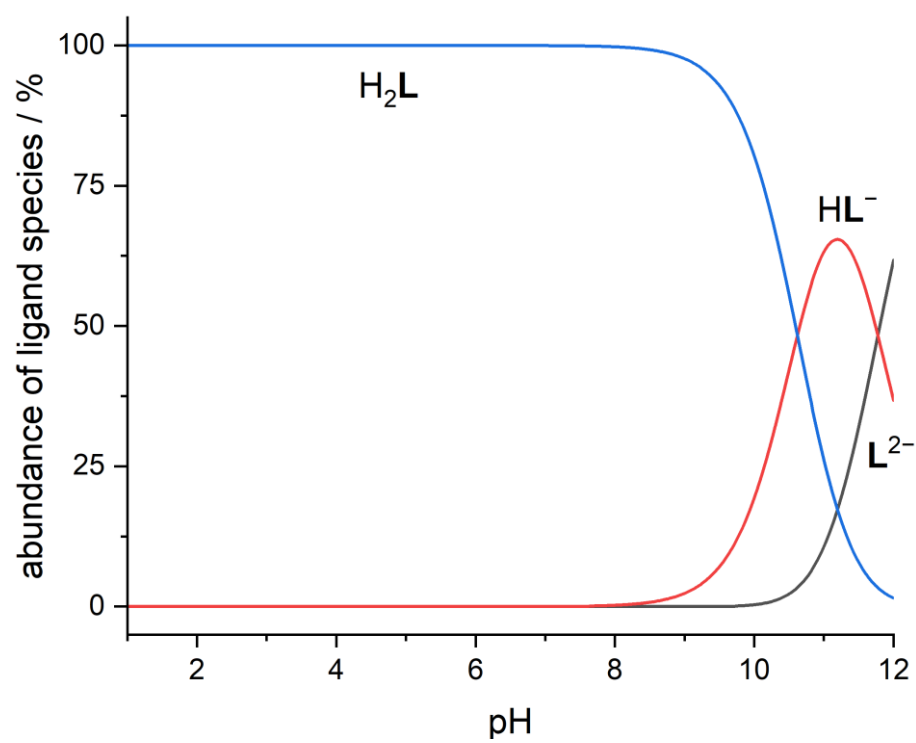
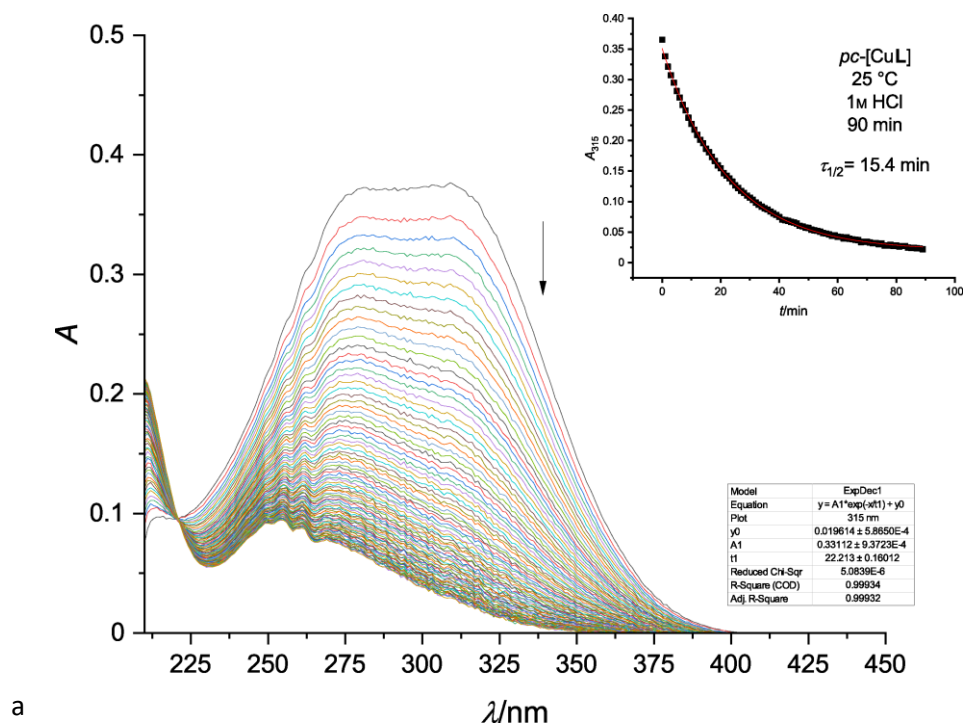
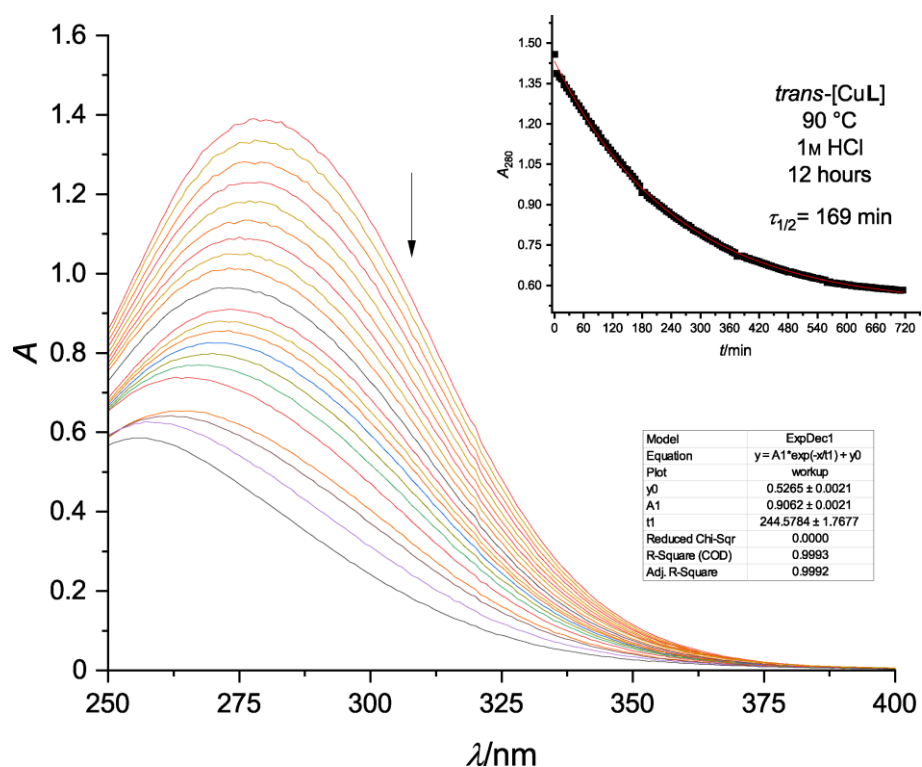


Figure S14. Distribution diagram of  $H_2L$ .

### Dissociation kinetics of the complexes



a



b

Figure S15. Examples of acid-assisted dissociation of Cu(II)–H<sub>2</sub>L complexes in 1-M HCl. a) Changes in UV spectrum and time trace of  $\rho c$ -[Cu(L)] dissociation followed at 315 nm and 25 °C. b) Changes in UV spectrum and time trace of  $trans$ -O,O'-[Cu(L)] dissociation followed at 280 nm and 90 °C.



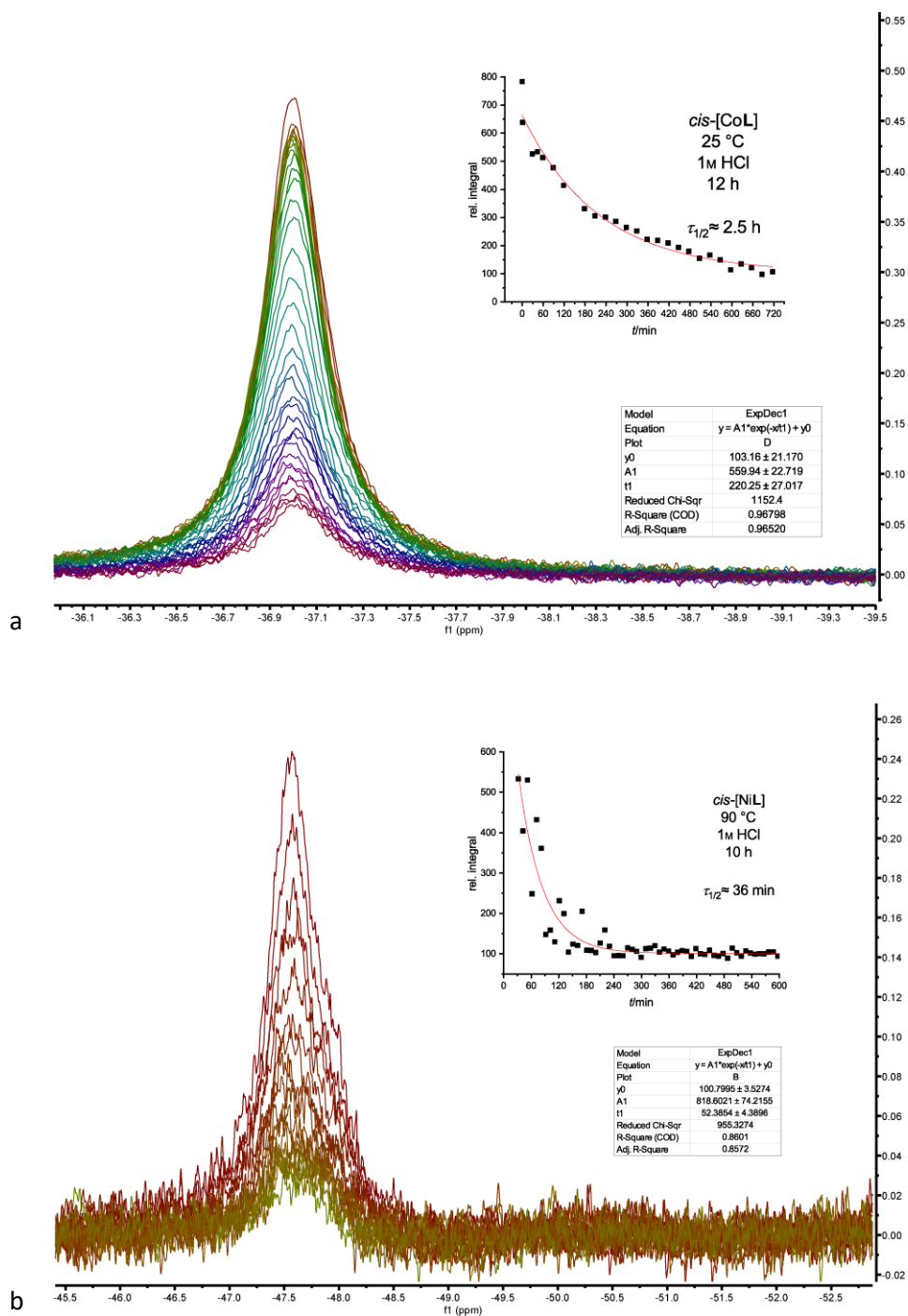


Figure S16. Examples of acid-assisted dissociation of *cis*-*O,O'*-[M(L)] (M = Co, Ni) in 1-M HCl. a) Changes in  $^{19}\text{F}$  NMR spectrum and time trace of integral intensity of *cis*-*O,O'*-[Co(L)] at 25 °C. b) Changes in  $^{19}\text{F}$  NMR spectrum and time trace of integral intensity of *cis*-*O,O'*-[Ni(L)] at 90 °C.

### Crystal structures of organic compounds

Re-crystallization of H<sub>2</sub>3 from 50% v/v aq. trifluoroacetic acid afforded single crystals of H<sub>2</sub>3·6CF<sub>3</sub>CO<sub>2</sub>H·2H<sub>2</sub>O suitable for X-ray diffraction analysis. Despite to presence of several strong acid molecules in the crystal structure, the azamacrocycle is only double-protonated (molecule is zwitterionic) and the protons are located on amino groups bearing benzyl protecting groups. The molecule possess crystallographic centre of symmetry and the macrocycle adopt common (3,4,3,4)-B conformation of diprotonated cyclams (Figure S17).<sup>[2,3]</sup>

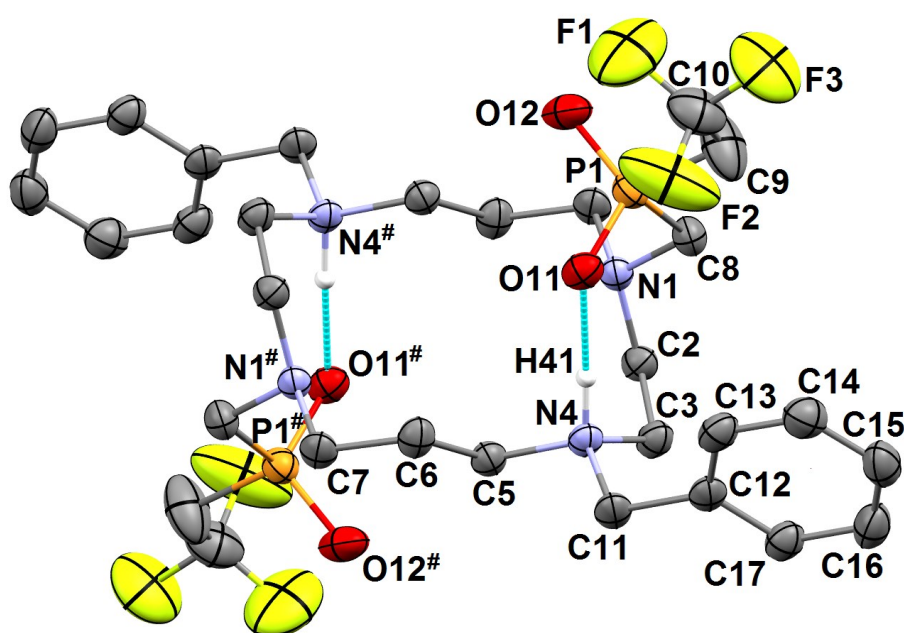


Figure S17. Molecular structure of H<sub>2</sub>3 found in the crystal structure of H<sub>2</sub>3·6CF<sub>3</sub>CO<sub>2</sub>H·2H<sub>2</sub>O. Carbon-bound hydrogen atoms are omitted for clarity. Intramolecular hydrogen bonds are shown as turquoise dashed lines. Selected centrosymmetry-related atoms are labelled with #.

The pendant arms are deprotonated and the molecular conformation is stabilized by strong intramolecular hydrogen bond between pendant oxygen atom O11 and protonated nitrogen N4 ( $d(\text{N4}\cdots\text{O11}) = 2.72 \text{ \AA}$ ), similarly as observed for related cyclam-1,8-bis(methylenephosphorus acid) derivatives.<sup>[4]</sup> Trifluoroacetic acid is presented in the neutral (*i.e.* protonated) form and its molecules are involved in a wide network of strong hydrogen bonds (Figure S18). Trifluoroacetic acid was

[2] M. Meyer, V. Dahaoui-Ginderey, C. Lecomte and R. Guillard, *Coord. Chem. Rev.*, 1998, **178–180**, 1313–1405.

[3] P. Hermann, J. Kotek and V. Kubíček, *Comprehensive Heterocyclic Chemistry*, Eds.: D. StC. Black, J. Cossy and C. V. Stevens, Elsevier 2022. Vol. 14, Chapter 14.11, 591–683.

[4] J. Kotek, P. Vojtišek, I. Císařová, P. Hermann, P. Jurečka, J. Rohovec, I. Lukeš, *Collect. Czech. Chem. Commun.*, 2000, **65**, 1289–1316.

removed by re-crystallization of  $\text{H}_2\mathbf{3}\cdot 6\text{CF}_3\text{CO}_2\text{H}\cdot 2\text{H}_2\text{O}$  from water and  $\text{H}_2\mathbf{3}\cdot 6\text{H}_2\text{O}$  was obtained. Slow cooling of saturated hot aq. solution afforded its crystals suitable for determination of crystal structure of the compound. The zwitterionic molecule of  $\text{H}_2\mathbf{3}$  is also centrosymmetric and has the same (3,4,3,4)-B macrocycle conformation<sup>[2,3]</sup> as found in the crystal structure discussed above (Figure S19); the molecular structures of  $\text{H}_2\mathbf{3}$  found in both crystal structures differs only slightly in spatial orientation of the trifluoroethyl side groups (Figure S20).

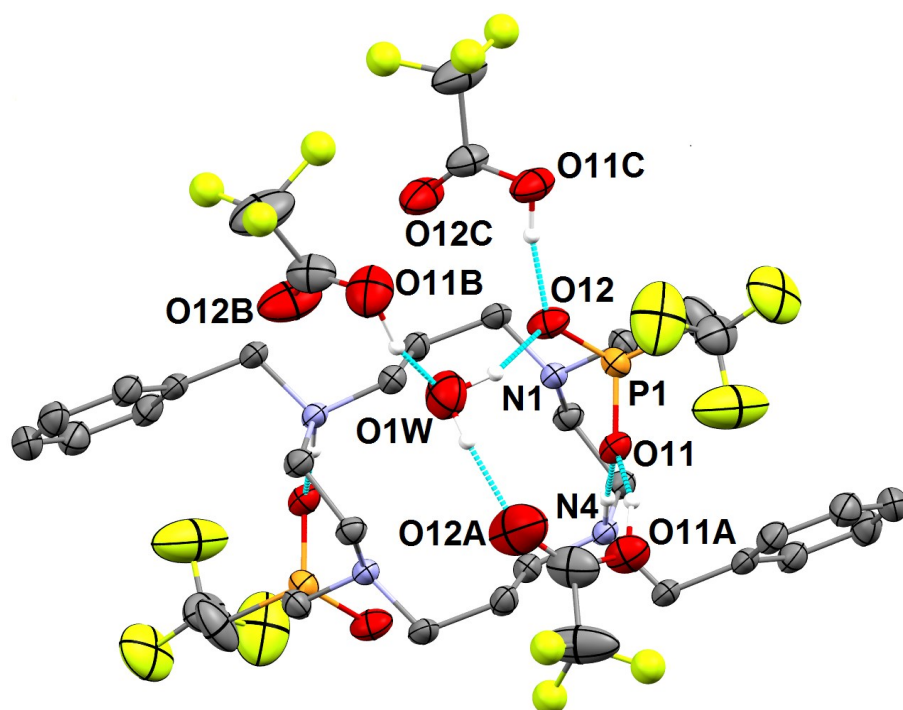


Figure S18. Selected part of the crystal structure of  $\text{H}_2\mathbf{3}\cdot 6\text{CF}_3\text{CO}_2\text{H}\cdot 2\text{H}_2\text{O}$ . Carbon-bound hydrogen atoms are omitted for clarity. Hydrogen bonds are shown as turquoise dashed lines. Fluorine atoms belonging to trifluoroacetic acid molecules are shown as small balls to keep clearness of the figure.

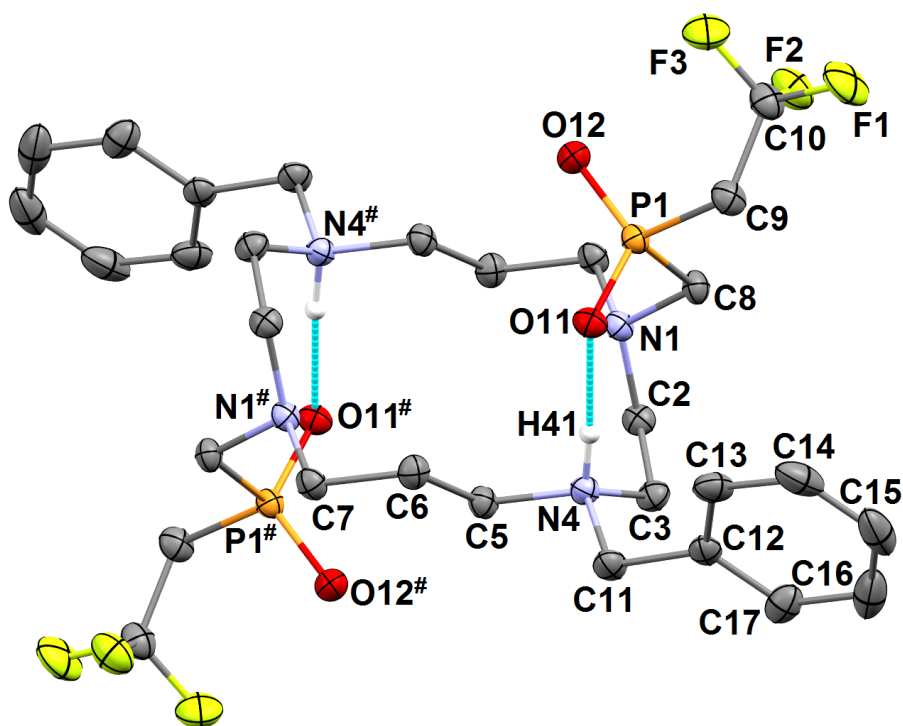


Figure S19. Molecular structure of  $H_2\mathbf{3}$  found in the crystal structure of  $H_2\mathbf{3}\cdot 6H_2O$ . Carbon-bound hydrogen atoms are omitted for clarity. Intramolecular hydrogen bonds are shown as turquoise dashed lines. Selected centrosymmetry-related atoms are labelled with #.

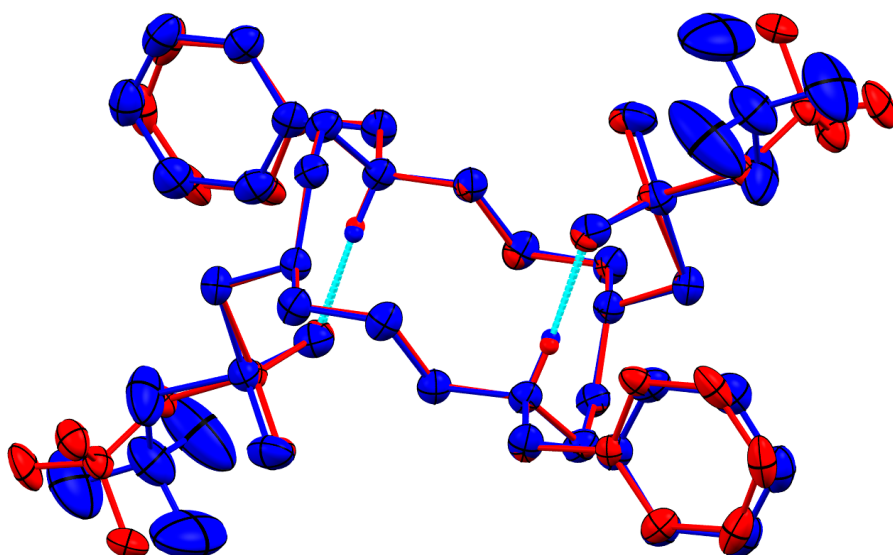


Figure S20. Overlay of the molecular structures of  $H_2\mathbf{3}$  found in the crystal structures of  $H_2\mathbf{3}\cdot 6CF_3CO_2H\cdot 2H_2O$  (blue) and  $H_2\mathbf{3}\cdot 6H_2O$  (red). Carbon-bound hydrogen atoms are omitted for clarity. Intramolecular hydrogen bonds are shown as turquoise dashed lines.

In the crystal structure of H<sub>2</sub>L·4AcOH, the ligand H<sub>2</sub>L is present in zwitterionic form and both molecules of the co-crystallized acetic acid are protonated and bound by a very strong hydrogen bonds to the phosphinate oxygen atoms ( $d(\text{O}[\text{AcOH}] \cdots \text{O11}/\text{O12}) = 2.58 \text{ \AA}$ , Figure S21).

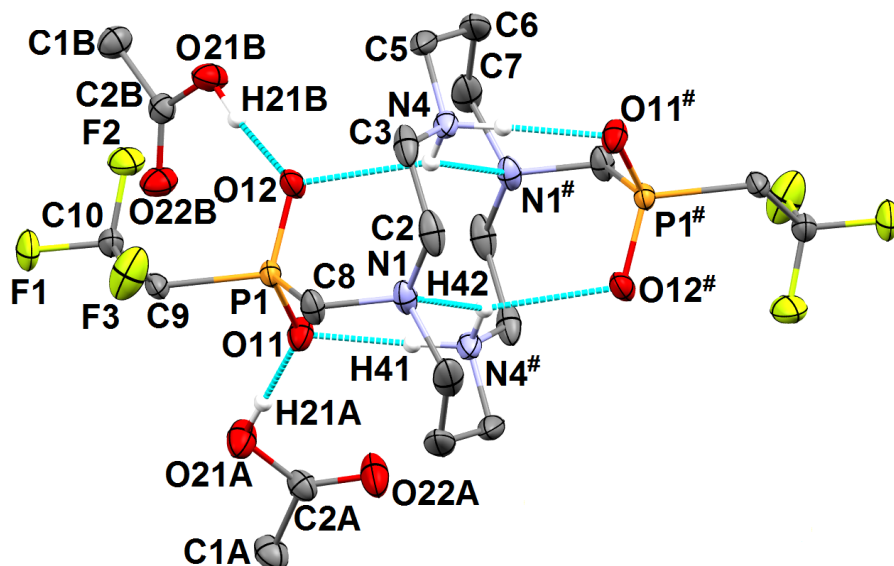
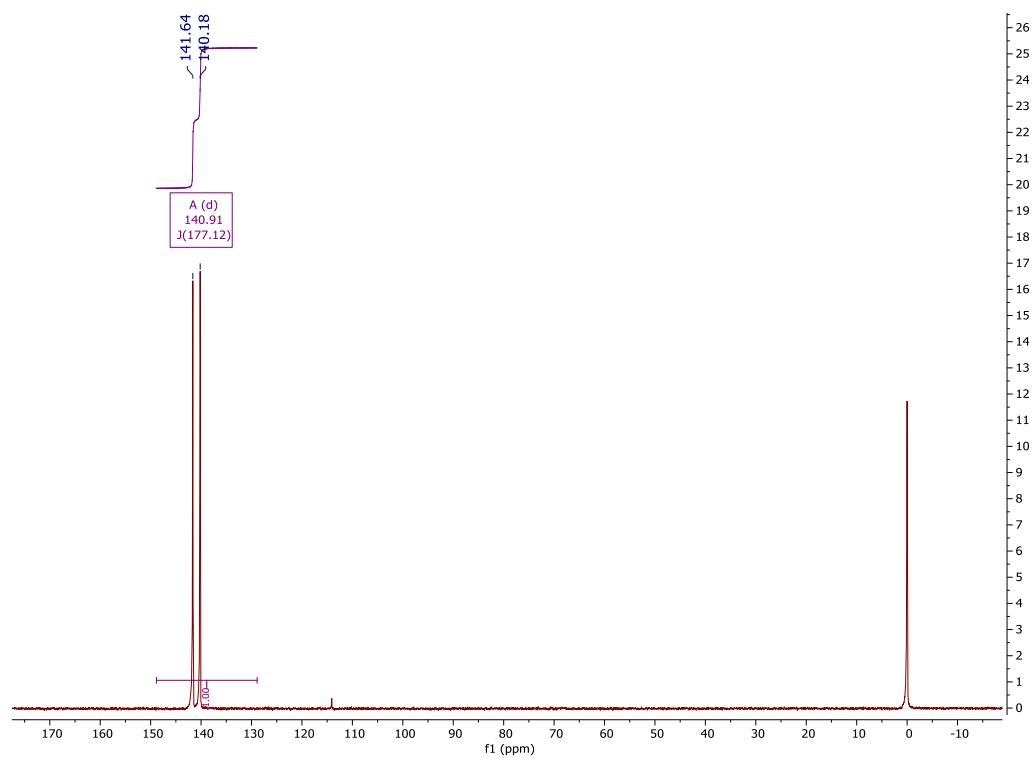


Figure S21. Selected part of the crystal structure of H<sub>2</sub>L·4AcOH. Carbon-bound hydrogen atoms are omitted for clarity. Hydrogen bonds are shown as turquoise dashed lines. Selected centrosymmetry-related atoms are labelled with #.

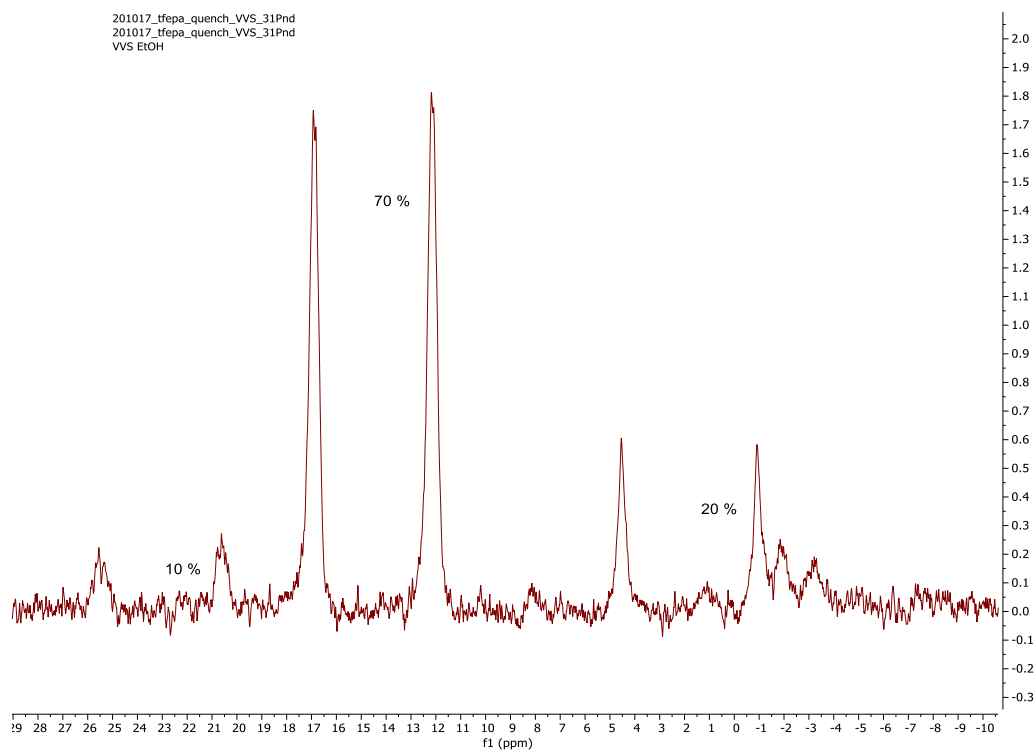
Attempts to structurally characterize the ligand in its deprotonated form by crystallization of H<sub>2</sub>L solution neutralised by LiOH to pH ca. 9 (a higher pH leads to a slow degradation of the ligand molecule) led to a formation of single crystals of H<sub>2</sub>L·LiCl·6H<sub>2</sub>O, pointing to a high basicity of the macrocycle secondary amino groups. Two centrosymmetric ligand molecules form the crystallographically independent unit. Both adopt the same molecular structure with “common” anangular conformation<sup>[2,3]</sup> stabilized by intramolecular strong hydrogen bond system similar to that found in the structure of H<sub>2</sub>L·4AcOH. One of oxygen atoms of each pendant arm of one of the ligand molecules is coordinated to lithium(I) counter ion, whose coordination sphere is filled by three water molecules forming almost regular tetrahedron (Figure S22).



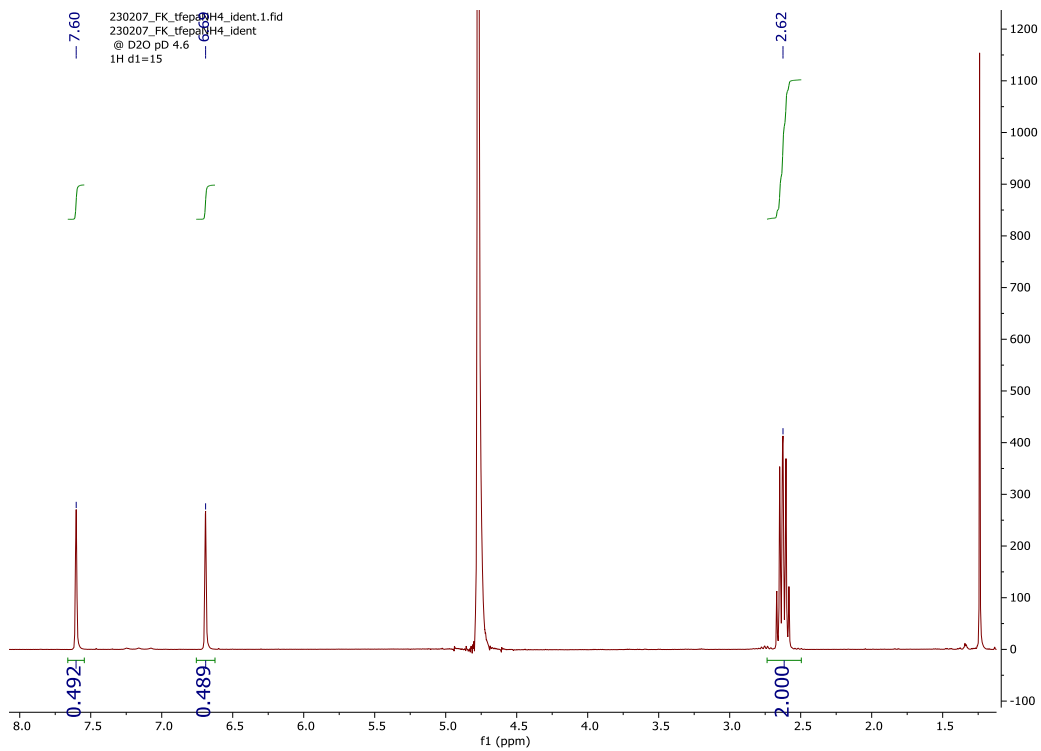
## Characterization NMR spectra of organic compounds



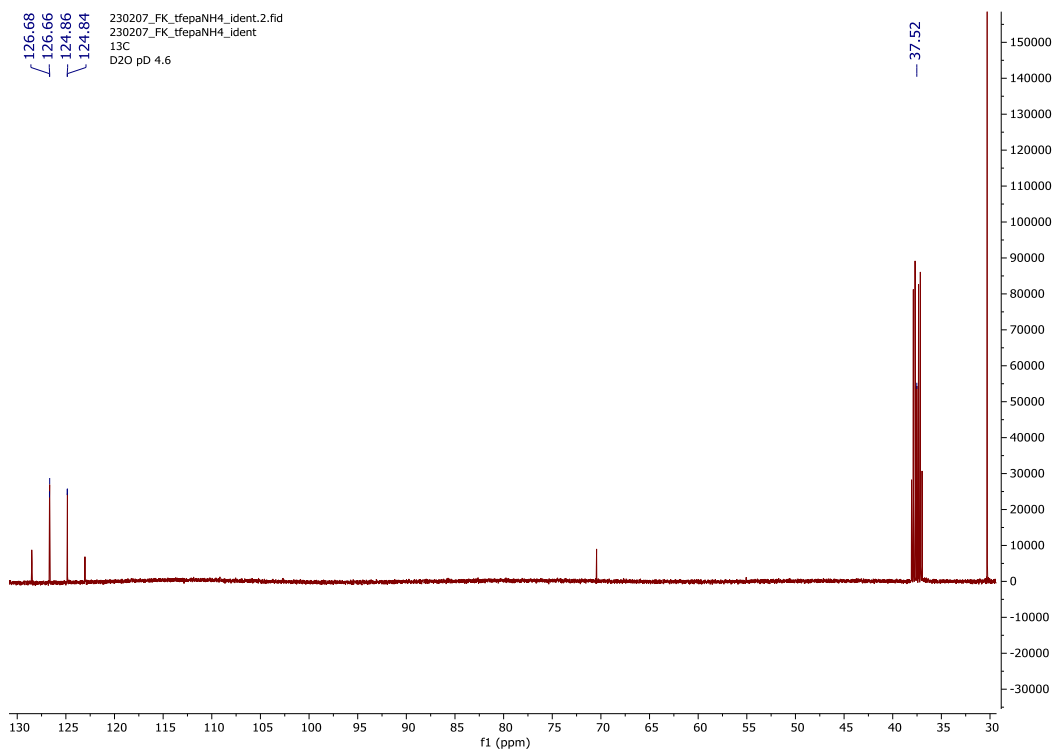
$^{31}\text{P}$  NMR spectrum of crude reaction mixture with generated  $\text{HP}(\text{OTMS})_2$ .



$^{31}\text{P}$  NMR spectrum of crude reaction mixture during preparation of 2,2,2-trifluoroethylphosphinic acid after hydrolysis/ethanololysis.

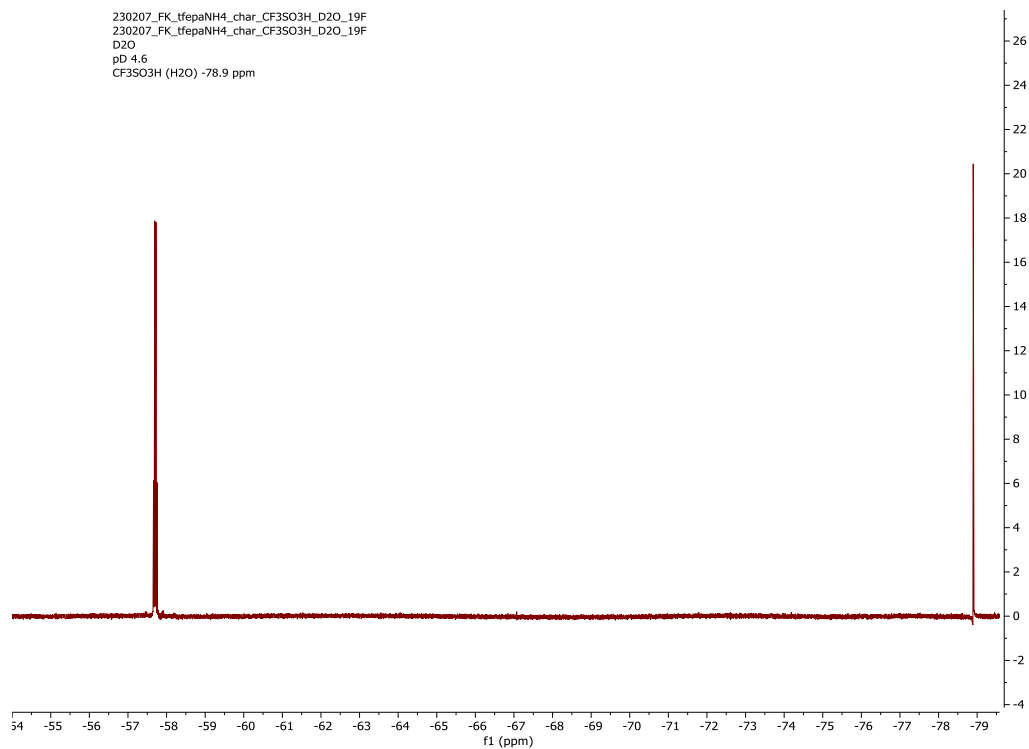


$^1\text{H}$  NMR spectrum of 2,2,2-trifluoroethylphosphonic acid ( $\text{D}_2\text{O}$ , pH = 4.6).

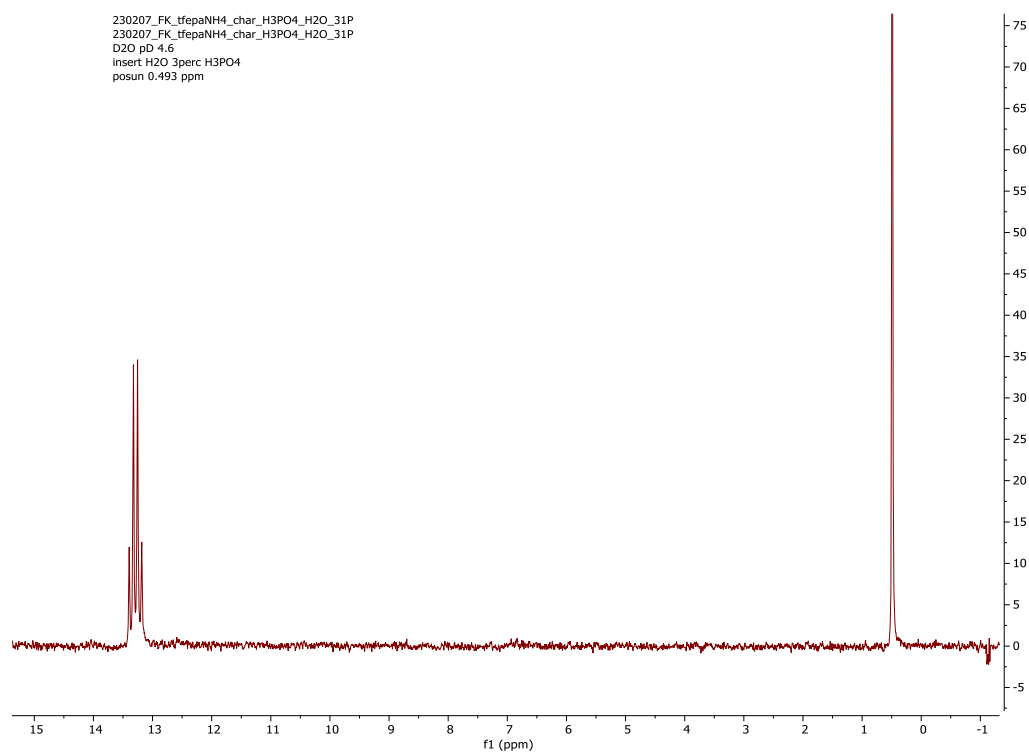


$^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 2,2,2-trifluoroethylphosphonic acid ( $\text{D}_2\text{O}$ , pH = 4.6).

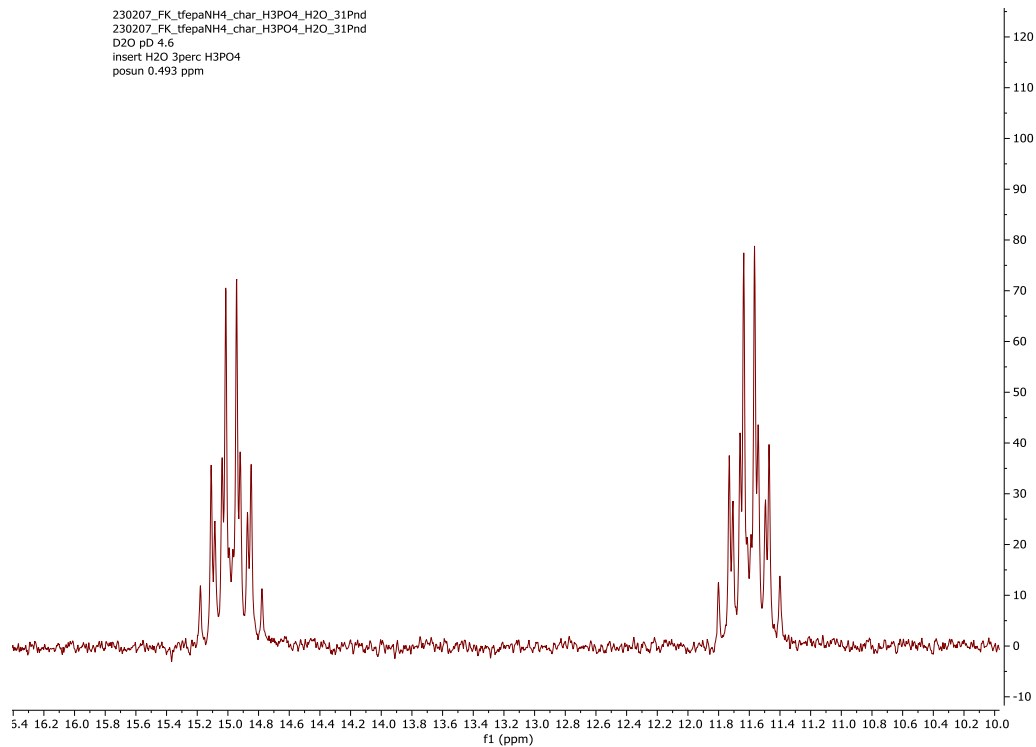




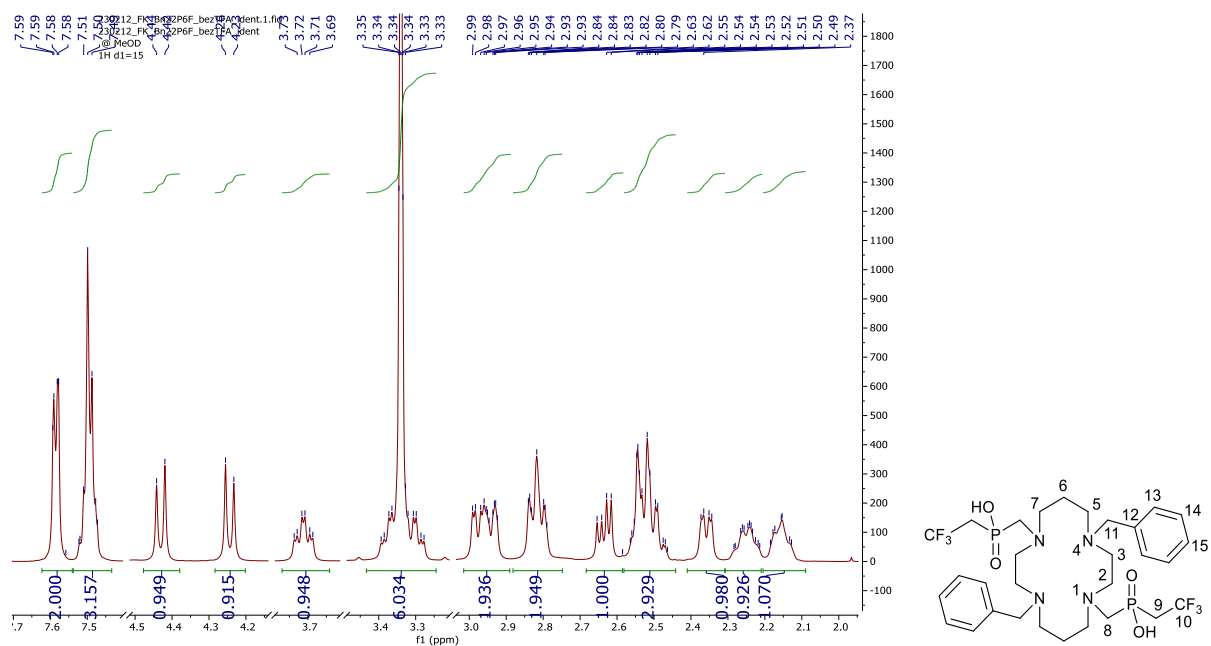
$^{19}\text{F}$  NMR spectrum of 2,2,2-trifluoroethylphosphinic acid ( $\text{D}_2\text{O}$ , pD = 4.6).



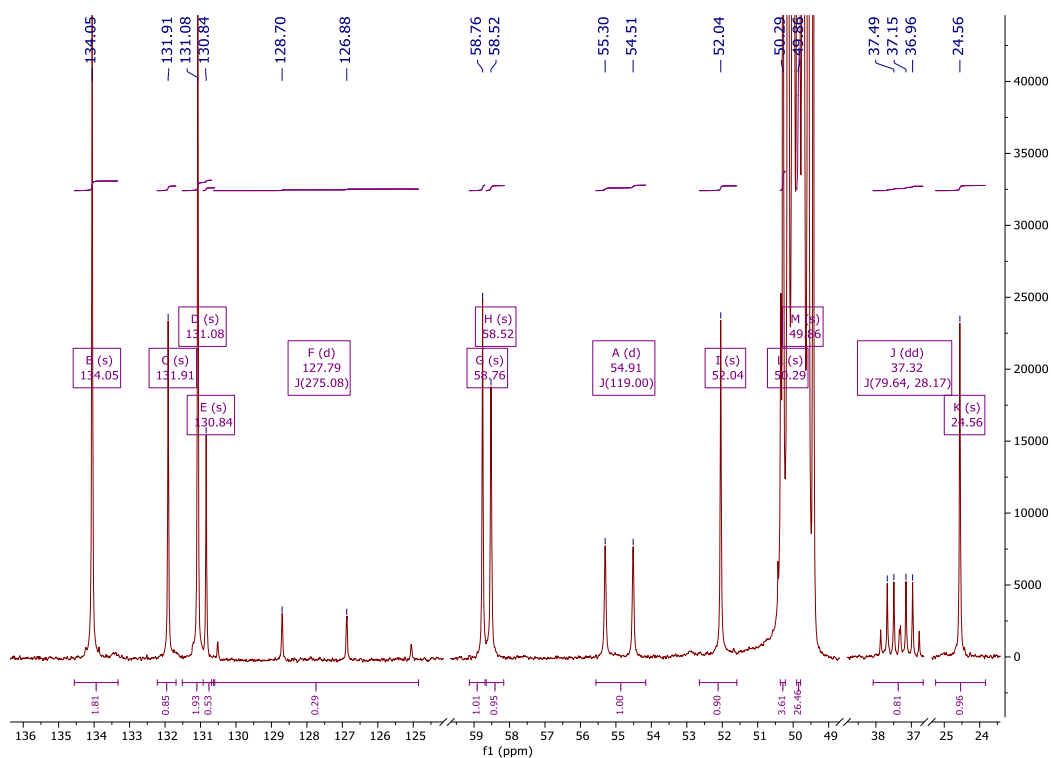
$^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of 2,2,2-trifluoroethylphosphinic acid ( $\text{D}_2\text{O}$ , pD = 4.6).



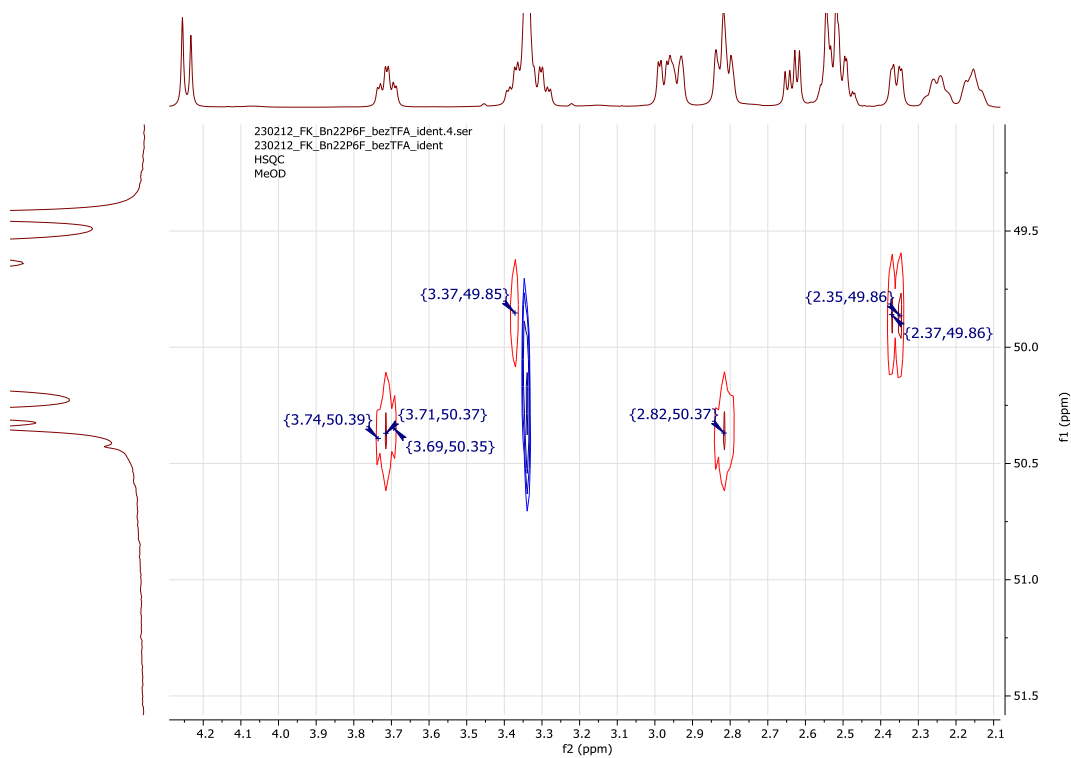
$^{31}\text{P}$  NMR spectrum of 2,2,2-trifluoroethylphosphonic acid ( $\text{D}_2\text{O}$ , pD = 4.6).



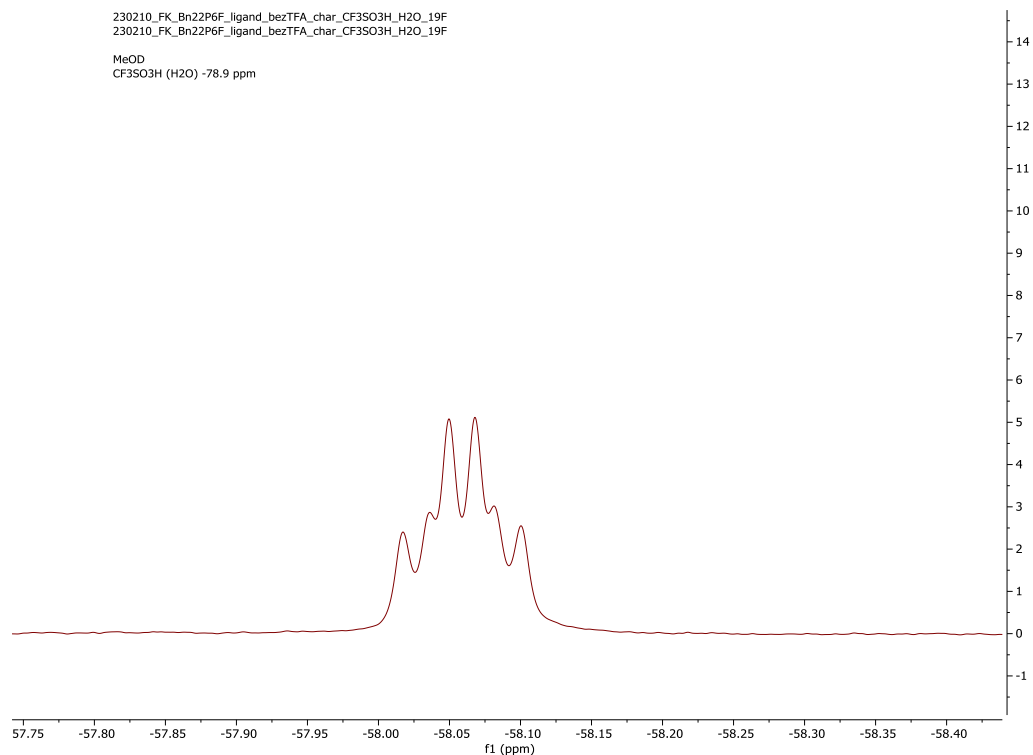
$^1\text{H}$  NMR spectrum of  $\text{H}_2\mathbf{3}\cdot 6\text{H}_2\text{O}$  ( $\text{MeOH}\text{-}d_4$ ) and an atom numbering scheme.



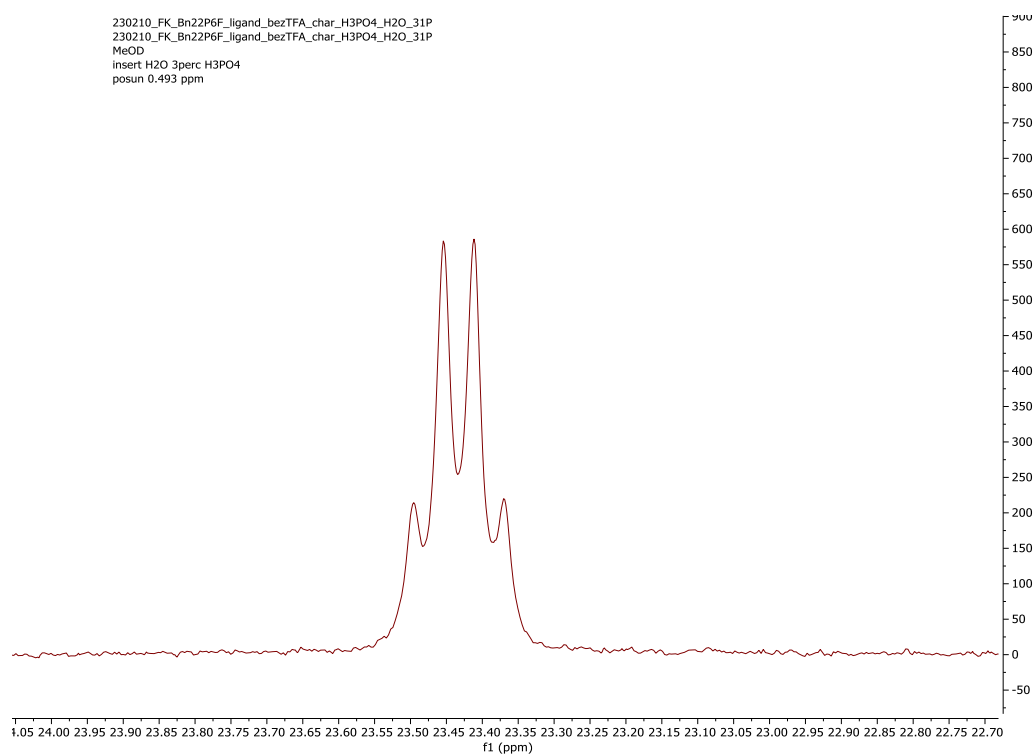
$^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $\mathbf{3}\cdot 6\text{H}_2\text{O}$  (MeOH- $d_4$ ).



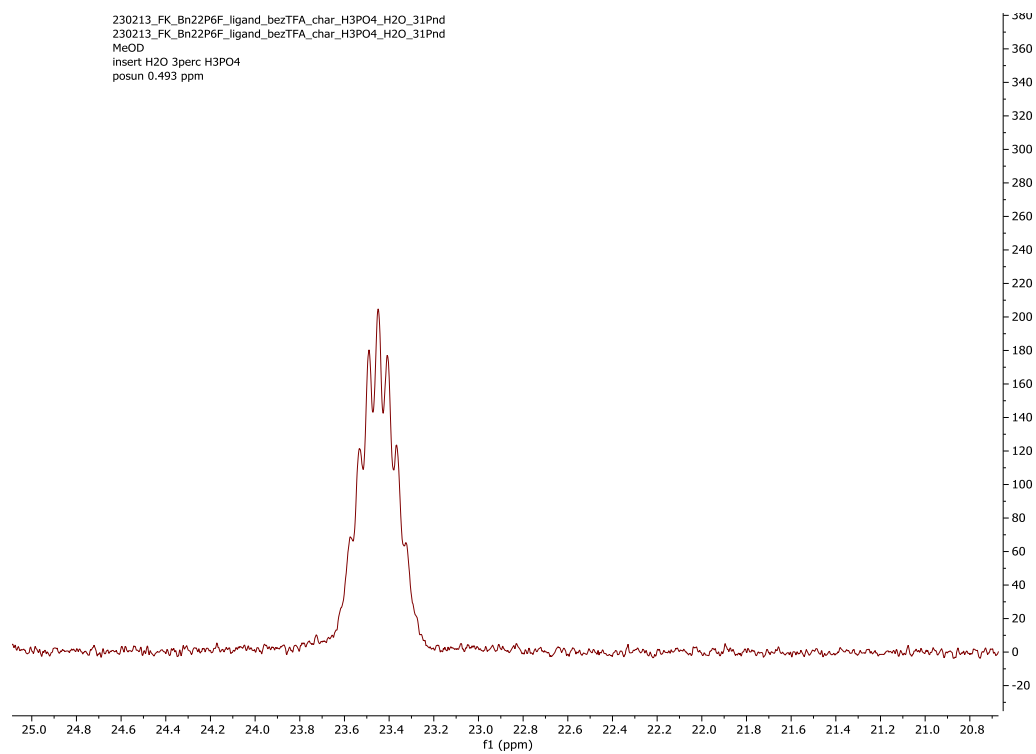
$^1\text{H}-^{13}\text{C}$  HSQC NMR spectrum of  $\mathbf{3}\cdot 6\text{H}_2\text{O}$  (MeOH- $d_4$ ).



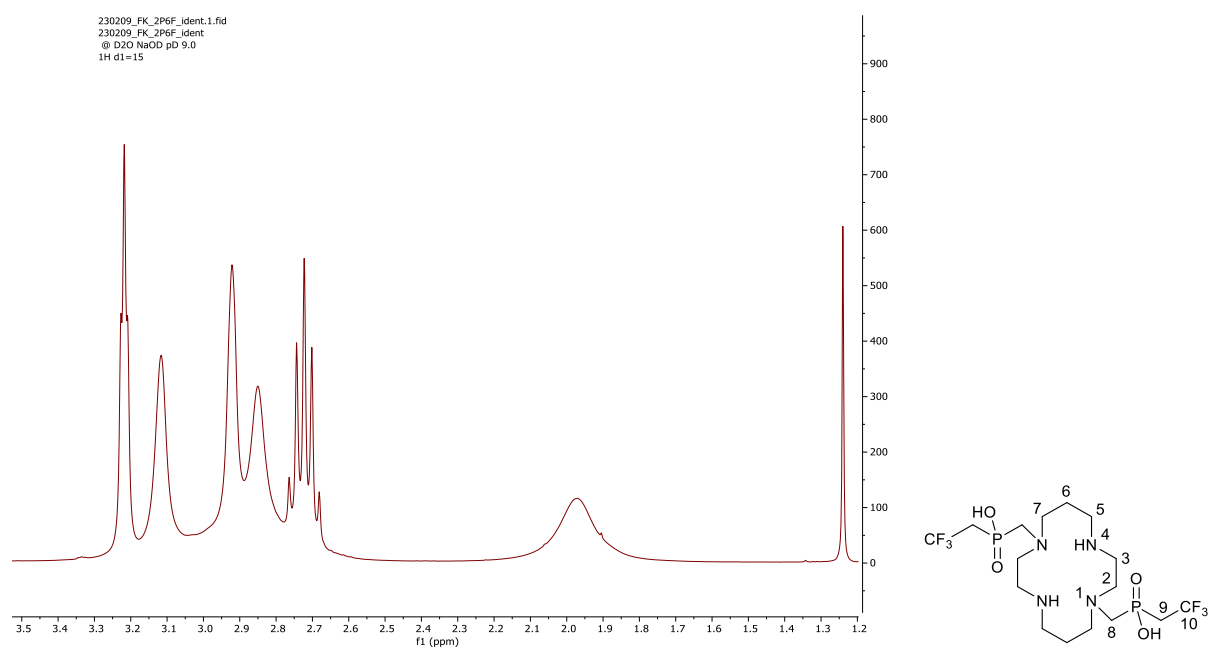
$^{19}\text{F}$  NMR spectrum of  $\mathbf{3}\cdot 6\text{H}_2\text{O}$  (MeOH- $d_4$ ).



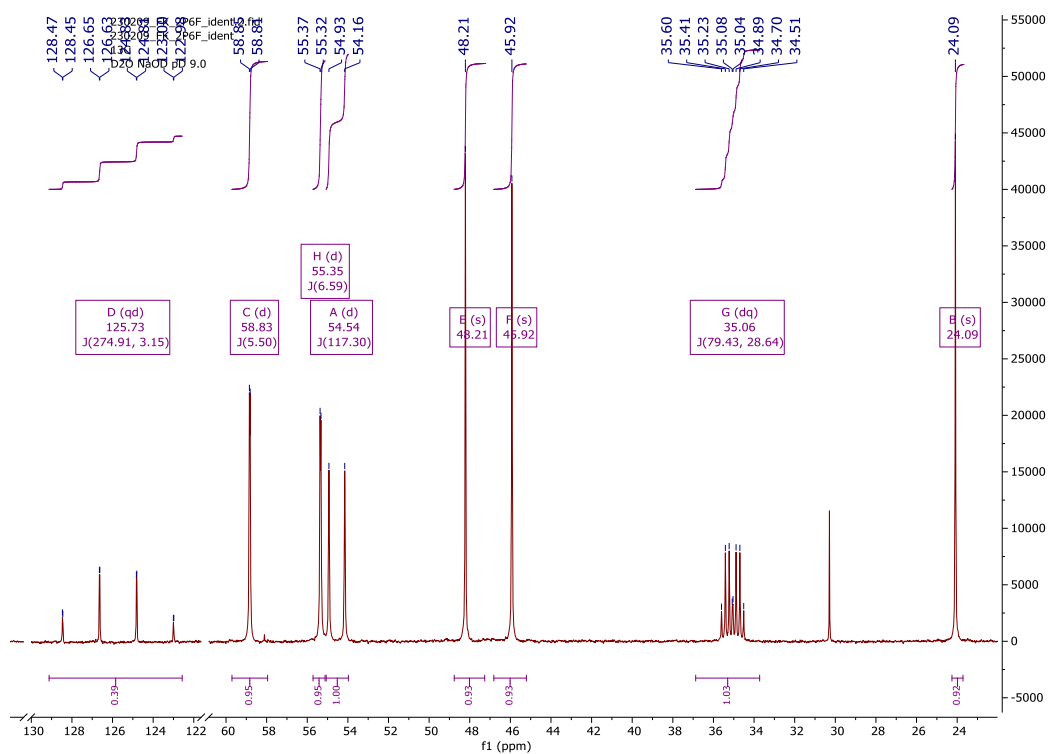
$^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $\mathbf{3}\cdot 6\text{H}_2\text{O}$  (MeOH- $d_4$ ).



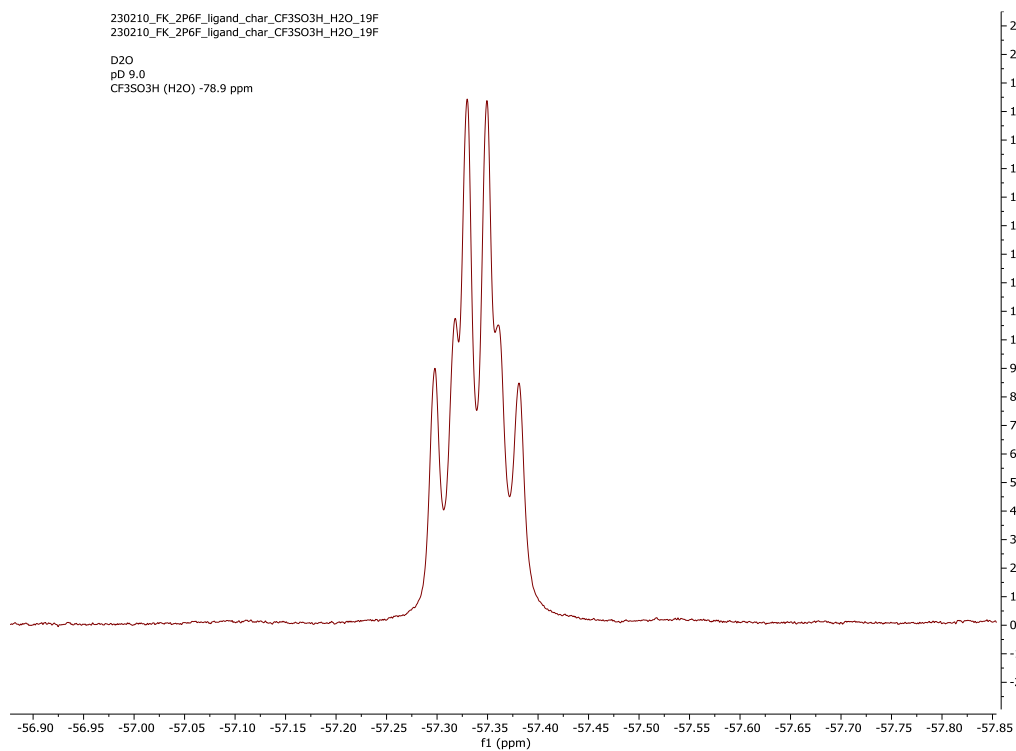
$^{31}\text{P}$  NMR spectrum of  $3 \cdot 6\text{H}_2\text{O}$  ( $\text{MeOH-d}_4$ ).



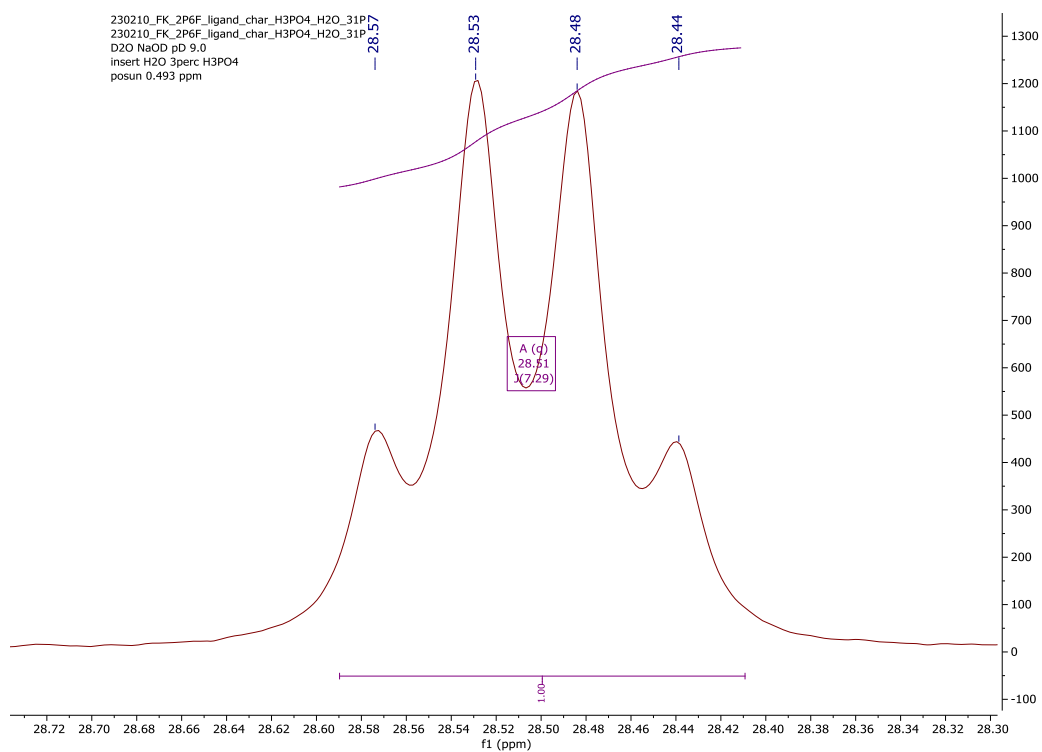
$^1\text{H}$  NMR spectrum of  $\text{H}_2\text{L}$  ( $\text{D}_2\text{O}$ , pD 9.0) and an atom numbering scheme.



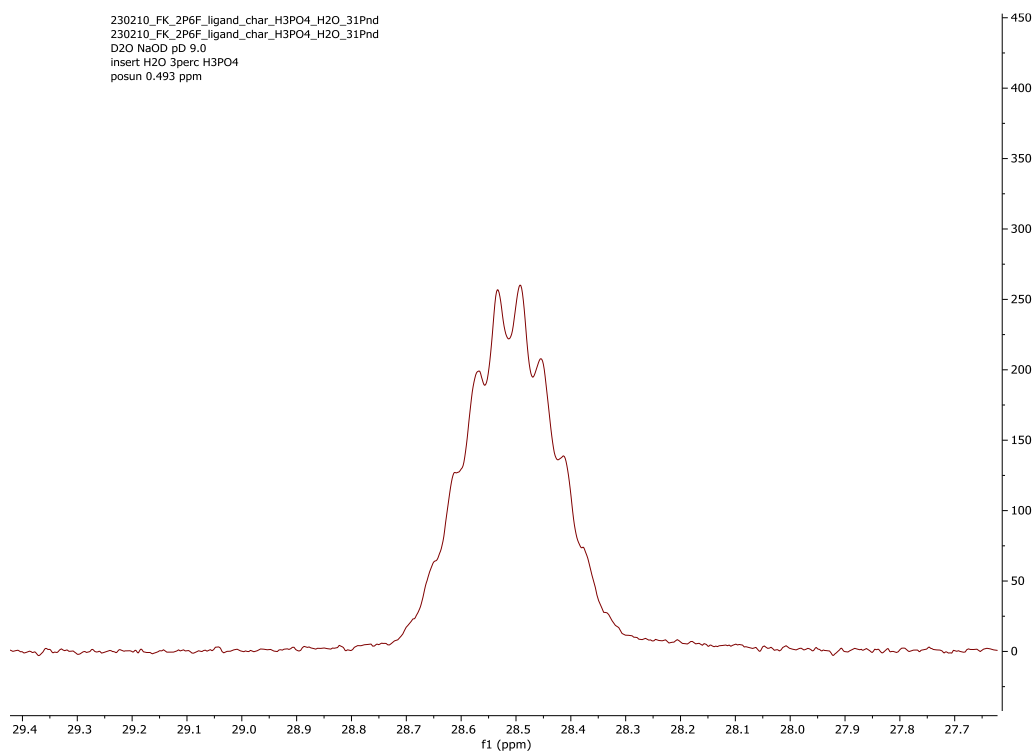
<sup>13</sup>C{<sup>1</sup>H} NMR spectrum of H<sub>2</sub>L (D<sub>2</sub>O, pD 9.0).



<sup>19</sup>F NMR spectrum of H<sub>2</sub>L (D<sub>2</sub>O, pD 9.0).



$^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $\text{H}_2\text{L}$  ( $\text{D}_2\text{O}$ , pD 9.0).



$^{31}\text{P}$  NMR spectrum of  $\text{H}_2\text{L}$  ( $\text{D}_2\text{O}$ , pD 9.0).