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Supporting Information

# Novel quadruple-stranded heterometallic $Ln_2Na$ complexes hosting sodium ion inside the cryptand-like cavity

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**Synthesis of $H_2L$.** [1] Fine powders of 2,2,3,3,4,4-hexafluoropentanediamide (13.25 g, 56 mmol) and phosphorus pentachloride (23.18 g, 112 mmol) were combined in a 500-ml round-bottom flask equipped with a water-cooled condenser connected to a bubble counter. Tetrachloromethane (50 ml) was added to the flask and the resulting mixture was heated to 65 ℃ and stirred at this temperature until the hydrogen chloride evolution rate slowed down. Afterwards the temperature was increased to about 75 °C and the reaction was allowed to continue until hydrogen chloride evolution ceased. Then the mixture was cooled down to room temperature and the solvent was removed in vacuum. The resulting residue was dissolved in tetrahydrofuran (70 ml) and added dropwise to a stirred solution of triethylamine (62 ml, 445 mmol) in methanol (150 ml) cooled down to -5 °C. The temperature upon addition was kept in the range of 0 – 5 °C. The obtained solution was allowed to warm up to room temperature and left to stay overnight. Then the solvents were evaporated under vacuum. The obtained residue was dissolved in water (100 ml), whereupon the acetic acid was carefully added to the solution until its medium became weakly acidic. The white precipitate of the product formed was filtered, washed with water and dried in air (17.30 g, 68%). IR (KBr, $cm^{-1}$): 3095*w* (ν(N–H)), 1746*s* (ν(C=O)), 1478*m* (Amide-2), 1212*s* (ν(P=O)); $^1$H NMR (400 MHz, DMSO-d6, 25 °C): δ = 3.74 ppm (d, *J* = 11.6 Hz, 12H), 11.38 (d, NH, 2H).

**Table S1**. Crystal data and structure refinement of the synthesized complexes.

| Compounds | **2** | **3** | **4** |
|---|---|---|---|
| Formula weight | 2268.30 | 2186.43 | 2197.09 |
| Temperature (K) | 100 | 173 | 173 |
| Crystal system | tetragonal | triclinic | triclinic |
| Space group | $P42_12$ | *P* -1 | *P* -1 |

| | | | |
|---|---|---|---|
| a, (Å) | 17.8807(6) | 12.3617(9) | 12.1643(2) |
| b, (Å) | 17.8807(6) | 12.7385(9) | 12.6444(2) |
| c, (Å) | 16.2846(6) | 14.0359(12) | 14.1504(3) |
| α, (°) | 90 | 104.654(6) | 105.257(2) |
| β, (°) | 90 | 103.976(6) | 104.052(2) |
| γ, (°) | 90 | 109.378(5) | 109.3800(10) |
| Cell volume, ($Å^3$) | 5206.5(4) | 1884.6(3) | 1845.88(6) |
| Z | 2 | 1 | 1 |
| $D_{calc}$($g/cm^3$) | 1.446 | 1.927 | 1.976 |
| μ ($mm^{-1}$) | 1.223 | 1.448 | 13.769 |
| F (000) | 2252 | 1078 | 1084 |
| Reflections collected/unique | 4579/4061 | 8230/6755 | 7381/6805 |
| GoF | 1.078 | 1.020 | 1.062 |
| Final R indices [$I>2\sigma(I)$] | R1= 0.0496, $wR_2$ = 0.1405 | R1= 0.0405, $wR_2$ = 0.1010 | R1= 0.0508, $wR_2$ = 0.1491 |
| R indices (all data) | R1= 0.0565, $wR_2$ = 0.1336 | R1= 0.0528, $wR_2$ = 0.0962 | R1= 0.0538, $wR_2$ = 0.1459 |
| CCDC | 2062595 | 2082894 | 2082895 |

**Table S2.** Analysis of the $Ln^{3+}$ coordination geometry in the complexes **2**, **3** and **4** using SHAPE 2.1 software.

| | **2** (Nd1) | **2** (Nd2) | **3** (La1) | **4** (Nd1) |
|---|---|---|---|---|
| Octagon (D8h) | 25.210 | 25.050 | 26.949 | 25.226 |
| Heptagonal pyramid (C7v) | 24.672 | 24.671 | 22.738 | 24.439 |
| Hexagonal bipyramid (D6h) | 17.196 | 17.526 | 12.110 | 16.350 |
| Cube (Oh) | 9.614 | 9.975 | 5.895 | 9.426 |
| Square antiprism (D4d) | 0.168 | 0.202 | 1.869 | 0.321 |
| Triangular dodecahedron (D2d) | 2.658 | 2.786 | 2.889 | 2.623 |
| Johnson gyrobifastigium J26 (D2d) | 16.621 | 16.767 | 14.362 | 15.465 |
| Johnson elongated triangular bipyramid J14 (D3h) | 28.333 | 28.312 | 25.743 | 27.116 |
| Biaugmented trigonal prism J50 (C2v) | 2.880 | 2.855 | 4.399 | 2.878 |
| Biaugmented trigonal prism (C2v) | 1.978 | 1.843 | 3.666 | 1.922 |
| Snub diphenoid J84 (D2d) | 5.373 | 5.430 | 6.335 | 5.145 |
| Triakis tetrahedron (Td) | 10.476 | 10.833 | 6.624 | 10.202 |
| Elongated trigonal bipyramid (D3h) | 23.497 | 23.540 | 22.025 | 22.384 |

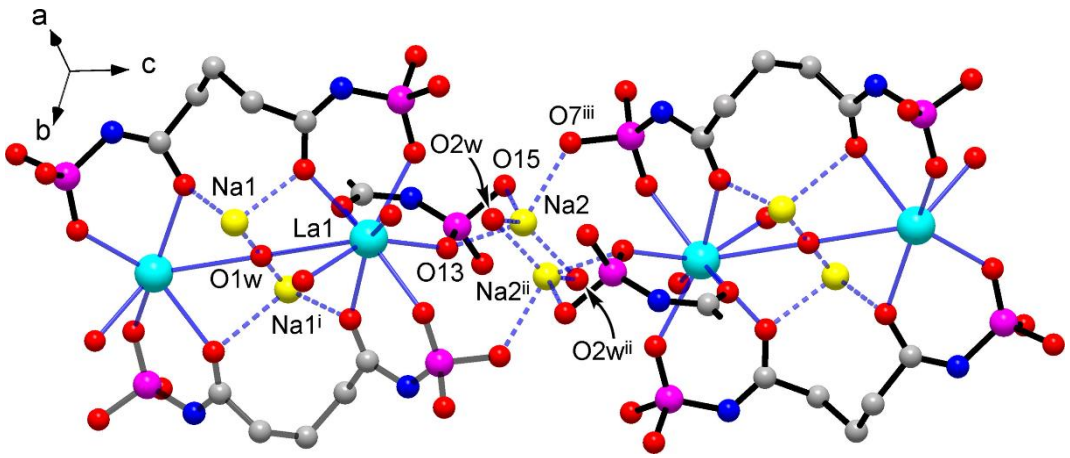



**Figure S1**. Connection of the anionic species $[NaLa_2L_4(H_2O)]^-$ and outer Na2 cations in the crystal structure of 3 resulting in 1D linear chains along c-axis direction in the crystal. Na2 is equally disordered across a center of inversion. Part of the organic ligands are omitted for clarity. Symmetry codes: (i) -*x*, -*y*, -*z*; (ii) -*x*, -*y*, -*z*+1; (iii) *x*, *y*, *z*+1.

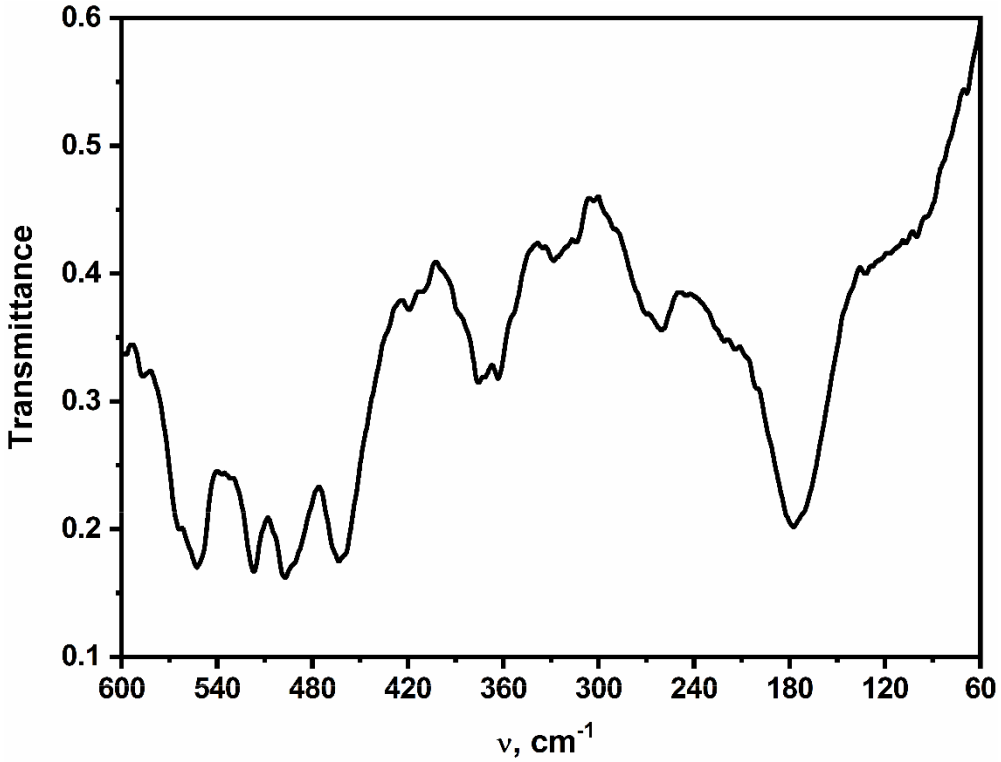



**Figure S2**. FTIR spectrum of the complex **2** in 60-600 $cm^{-1}$ region.

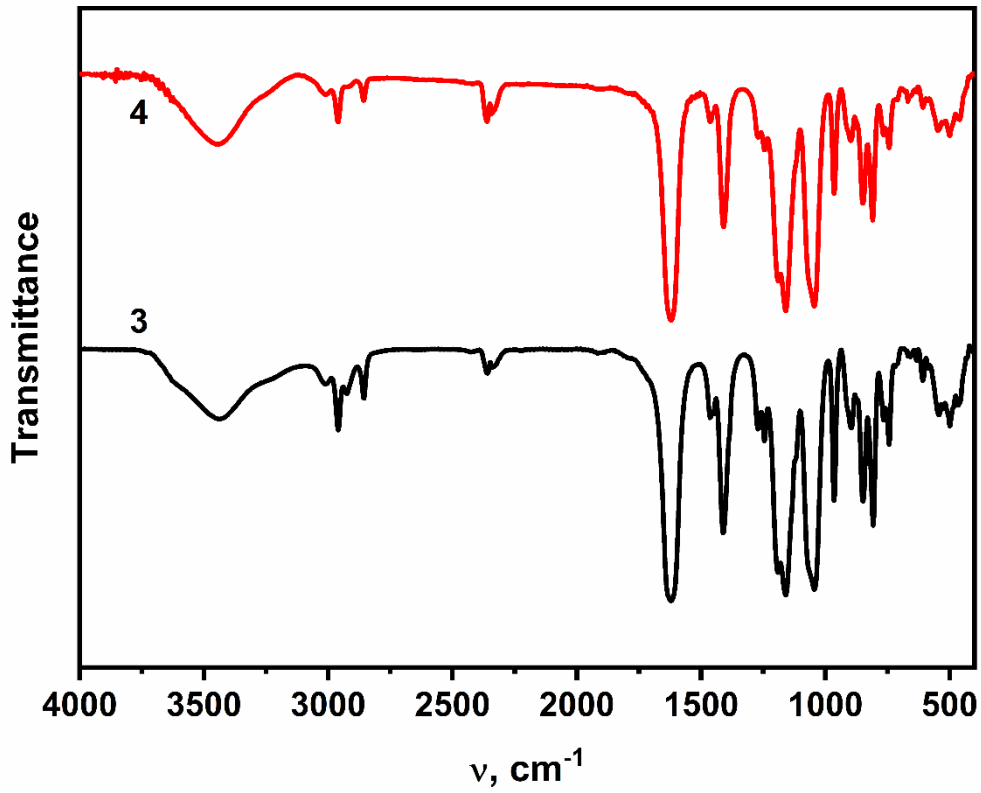
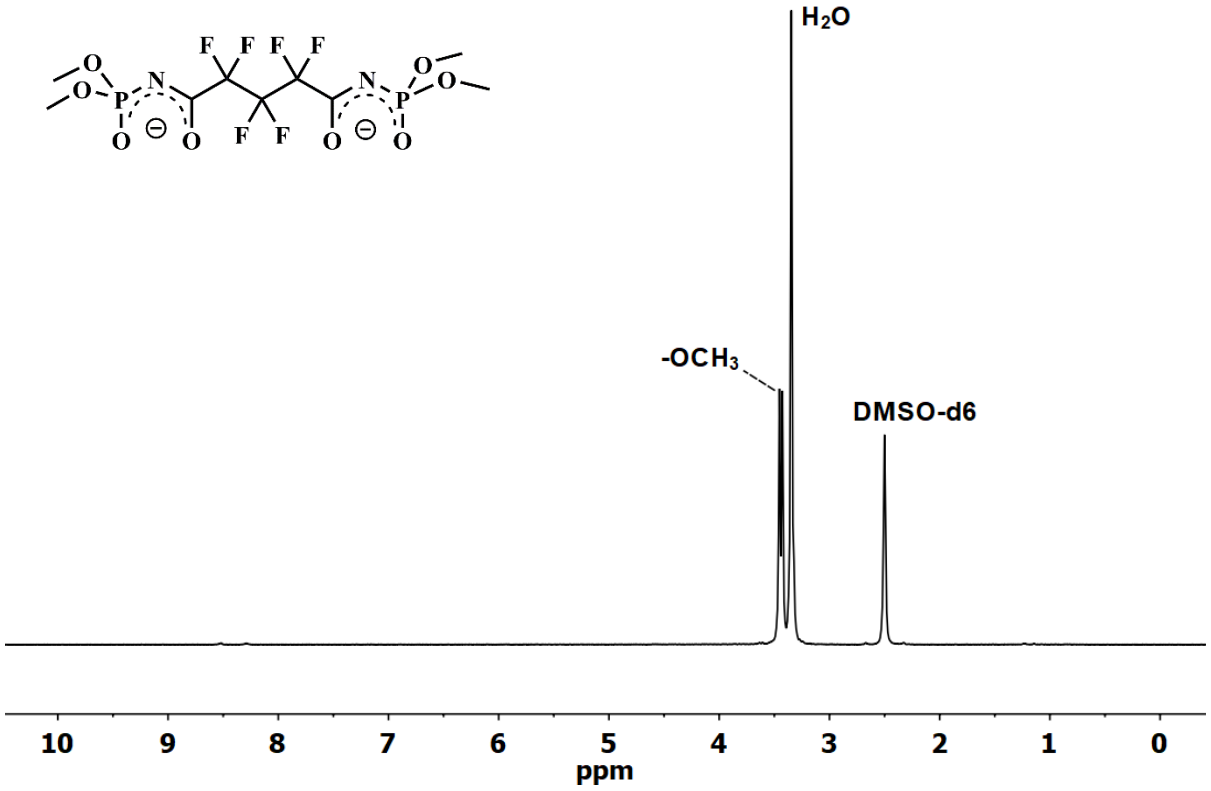



**Figure S3**. IR spectra of the complexes **3** (black) and **4** (red).

**Table S3.** Some characteristic vibration bands of the synthesized compounds.

| **Compound** | **Vibration band, cm$^{-1}$** | | | |
|---|---|---|---|---|
| | ν(N–H) | ν(C=O) | Amide-2 | ν(P=O) |
| $H_2L$ [1] | 3095 | 1746 | 1478 | 1212 |
| $Na_2L$ | – | 1630 | 1406 | 1202 |
| **1** | – | 1621 | 1411 | 1159 |
| **2** | – | 1623 | 1410 | 1160 |
| **3** | – | 1622 | 1412 | 1160 |
| **4** | – | 1624 | 1411 | 1161 |

**a**)




**b**)

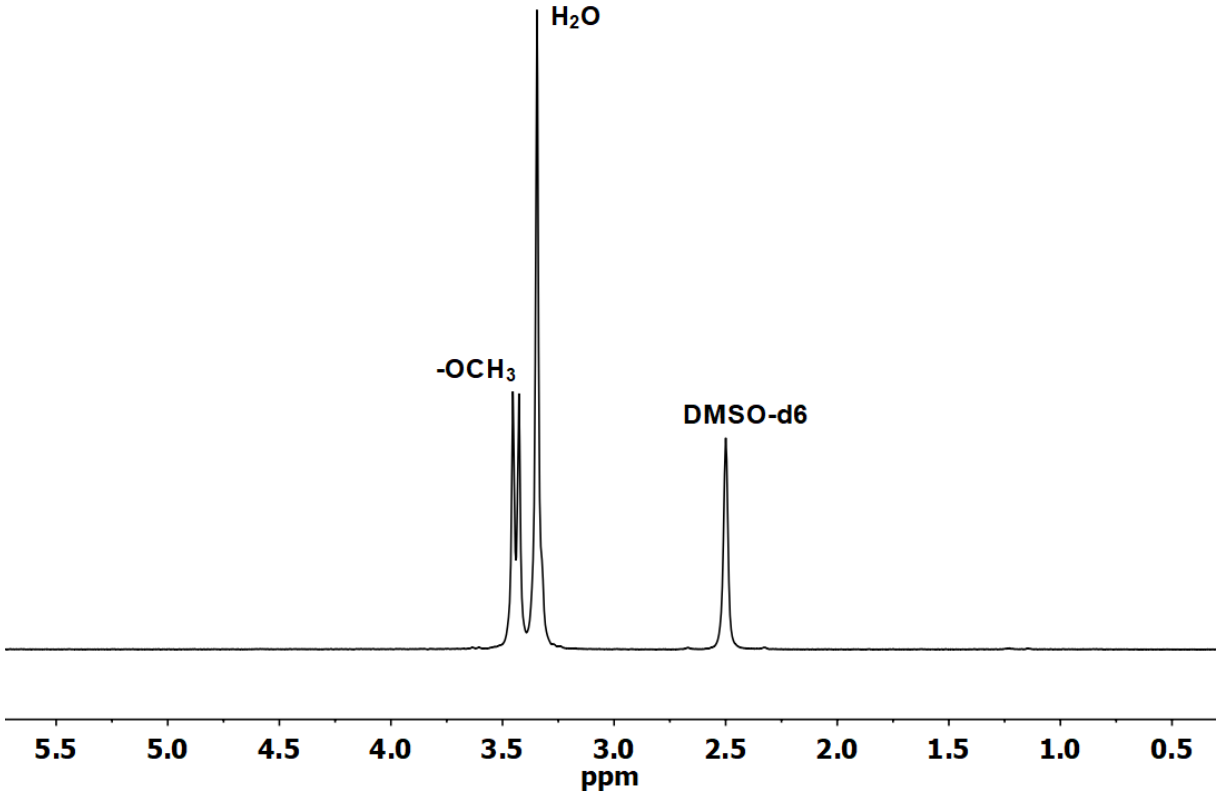



**Figure S4**. $^{1}$H NMR spectrum of $Na_2L$ in DMSO-d6 (**a**) and its expanded aliphatic region (**b**).

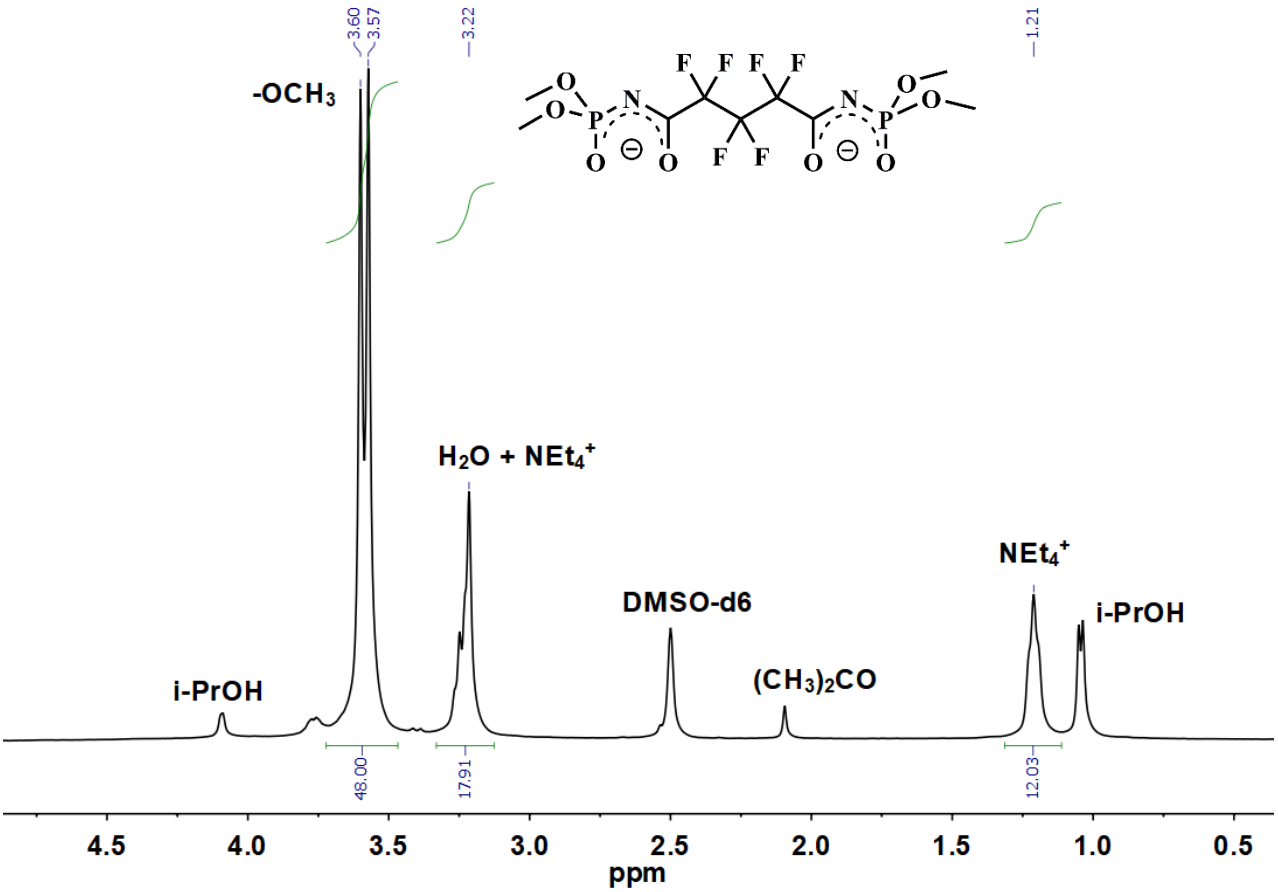



**Figure S5**. $^{1}$H NMR spectrum of **1** in DMSO-d6.

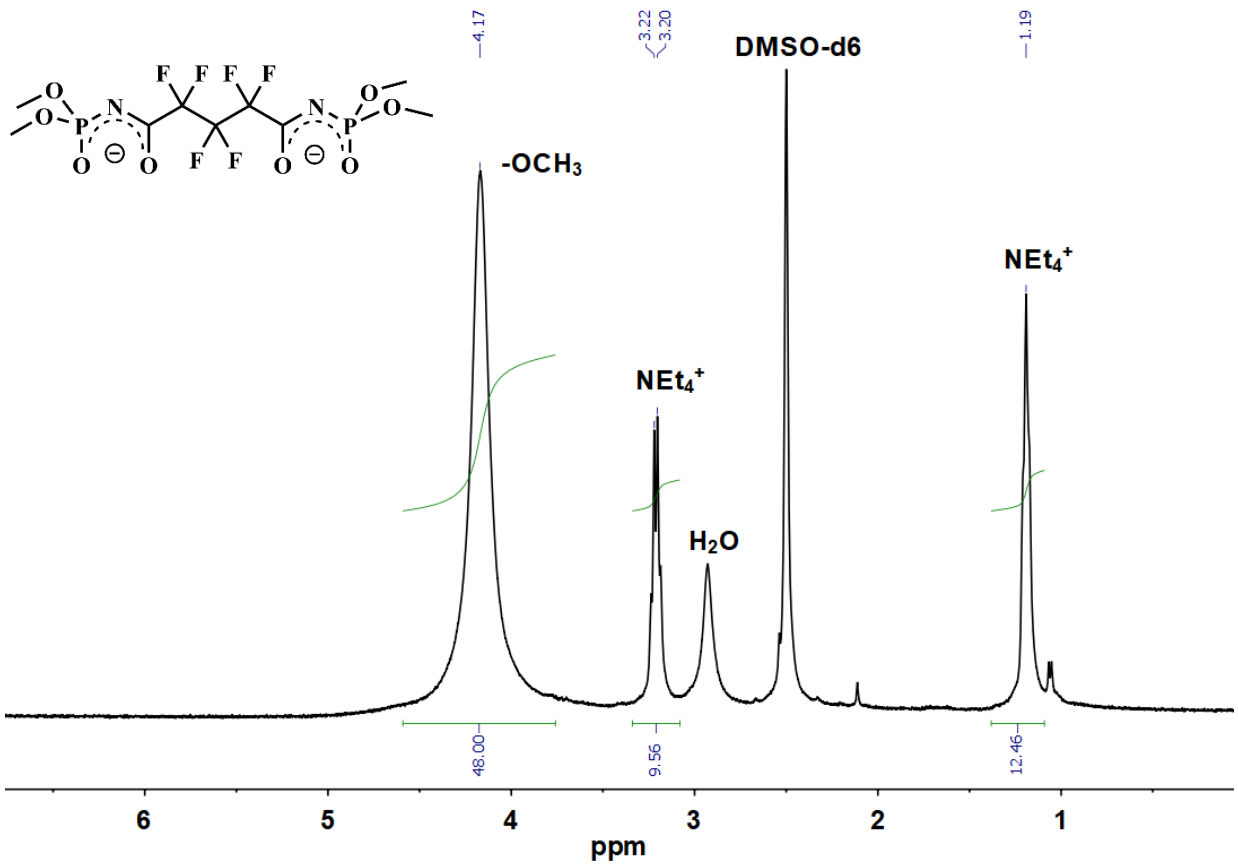


**Figure S6**. $^{1}$H NMR spectrum of **2** in DMSO-d6.

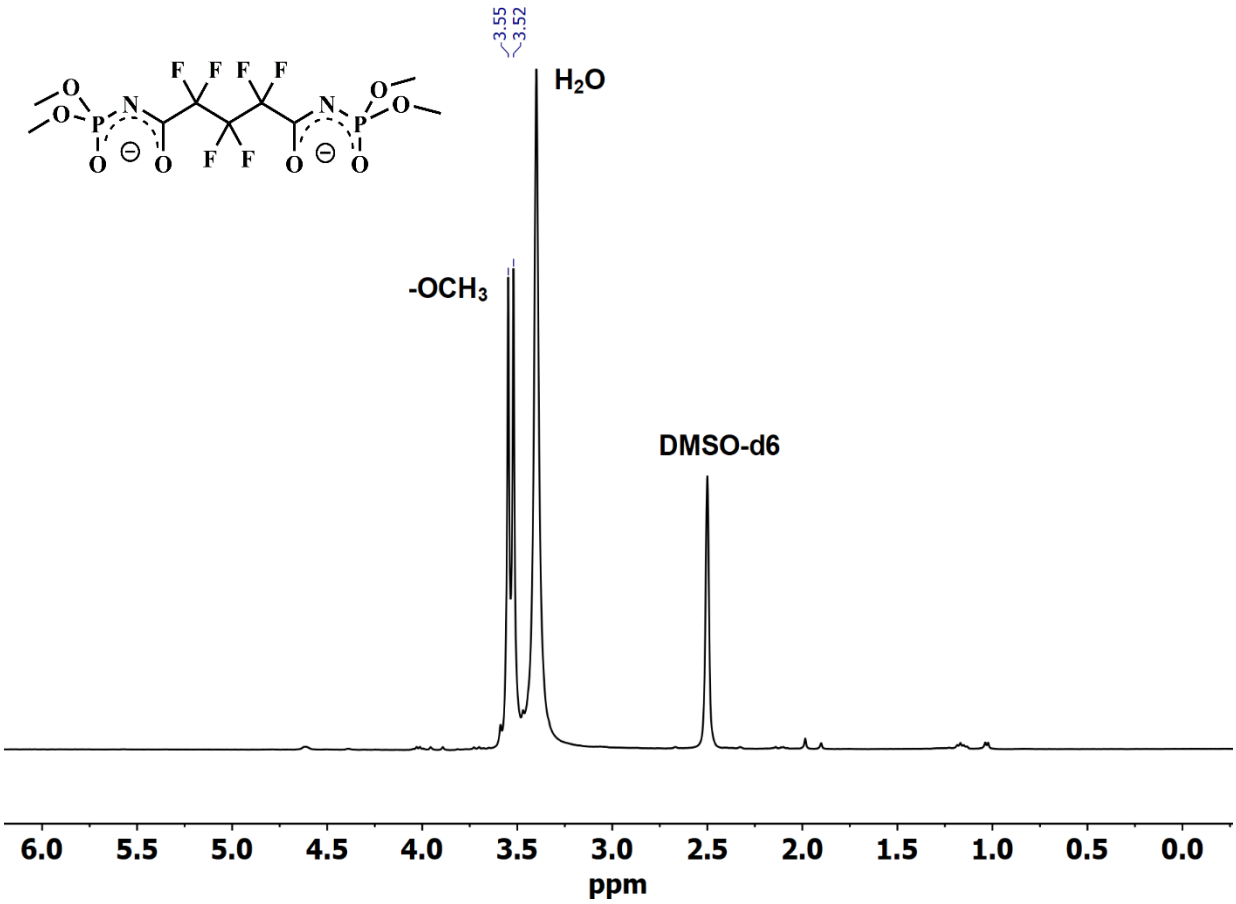



**Figure S7**. $^{1}$H NMR spectrum of **3** in DMSO-d6.

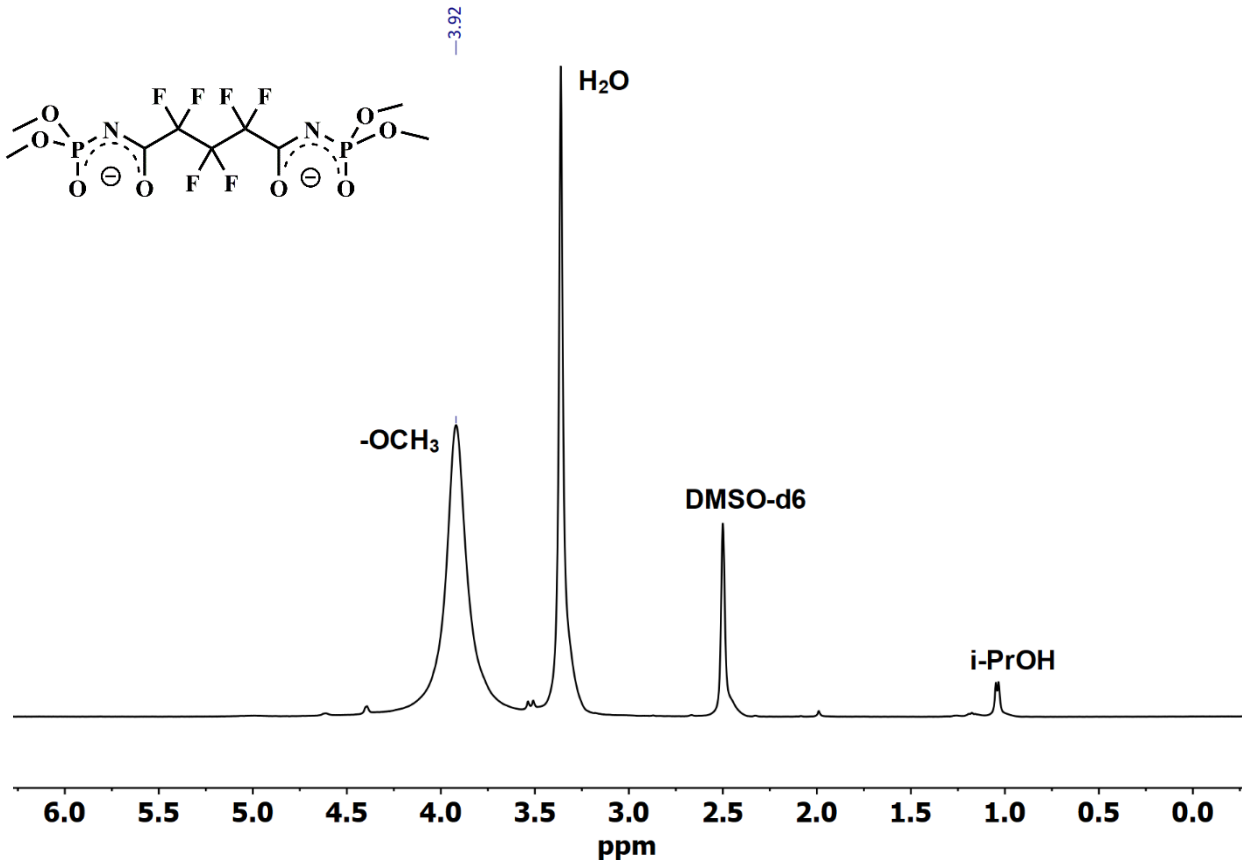



**Figure S8**. $^{1}$H NMR spectrum of **4** in DMSO-d6.

## References

(1) Trush, V. A.; Gubina, K. E.; Gumeniuk, Y. O.; Sliva, T. Y.; Konovalova, I. S. Tetramethyl N,N′-(2,2,3,3,4,4-Hexa-Fluoro-1,5-Dioxopentane-1,5-Diyl)Bis-(Phosphoramidate). *Acta Crystallogr. Sect. E Struct. Reports Online* **2012**, *68*, o1127. https://doi.org/10.1107/S1600536812011191.