Beyond Transition Block Metals: Exploring the Reactivity of Phosphines PTA and it's oxide [PTA(O)] towards Gallium(III)

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SUPPORTING INFORMATION

Table of Contents

1. FT-IR spectra of compounds 1 – 4

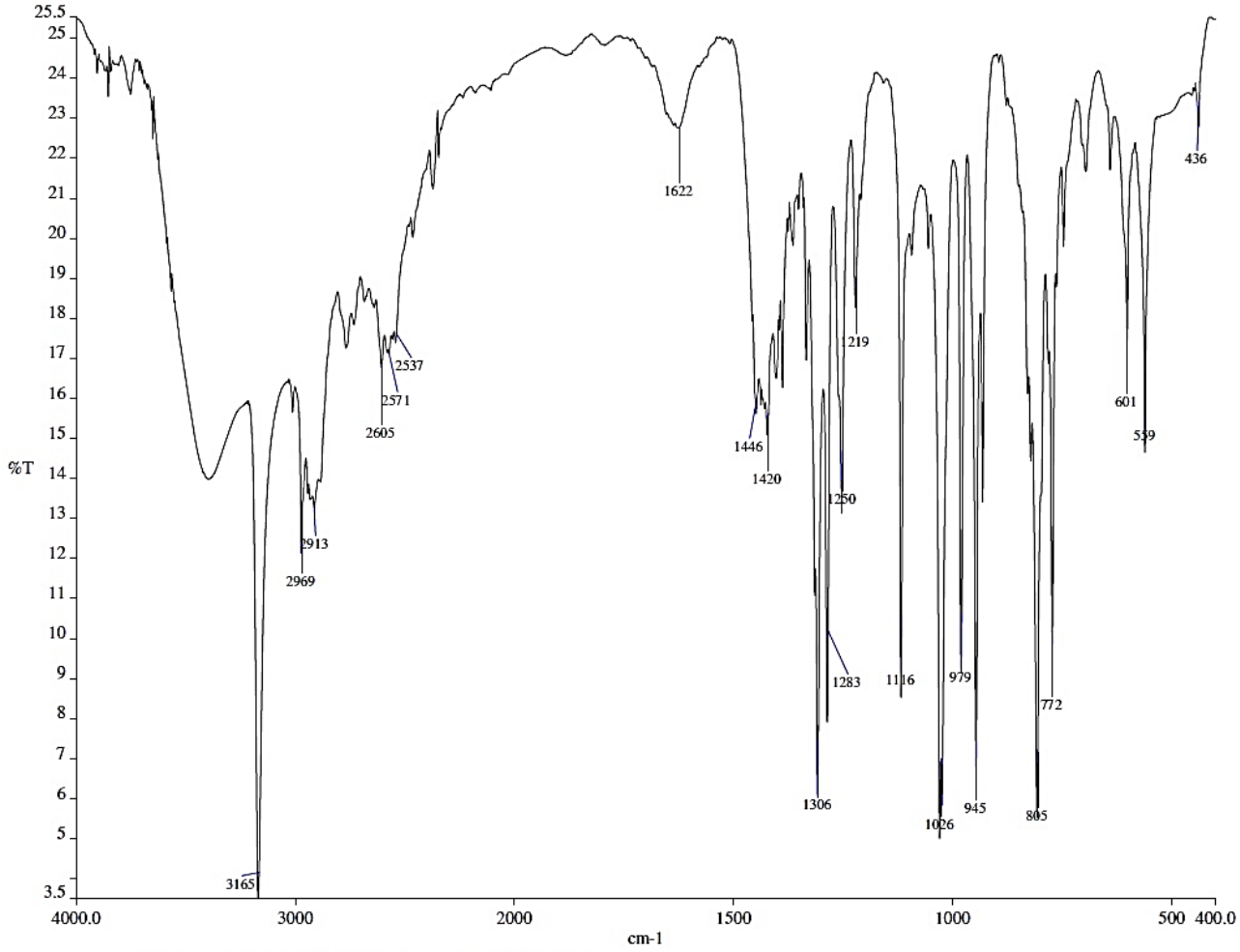


Figure S1. FT-IR spectrum of compound [PTA-H]•[$GaCl_4$] (**1**) in KBr (range 400-4000 cm^{-1}).

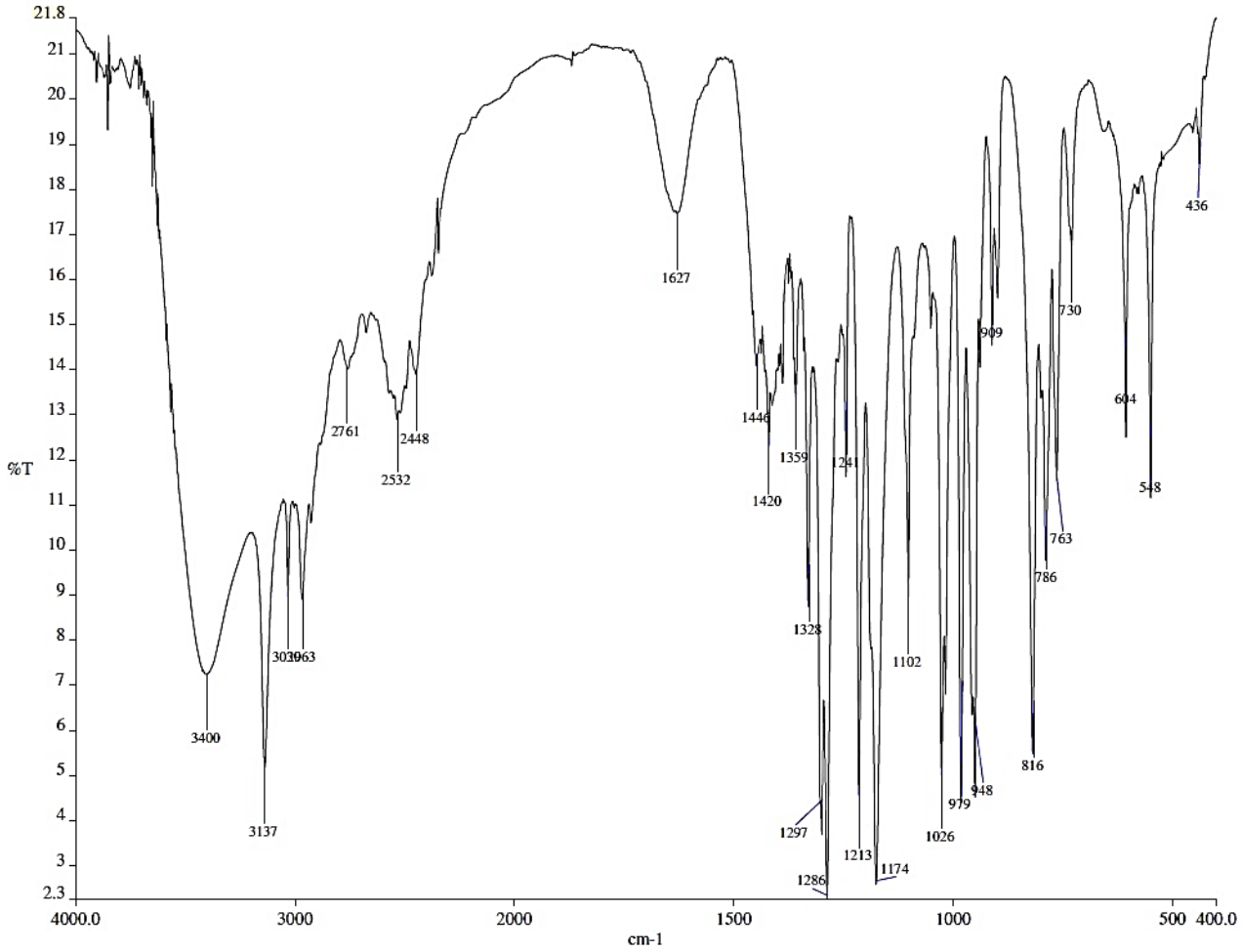


Figure S2. FT-IR spectrum of compound [PTA(O)-H]•[$GaCl_4$] (**2**) in KBr (range 400-4000 cm^{-1}).

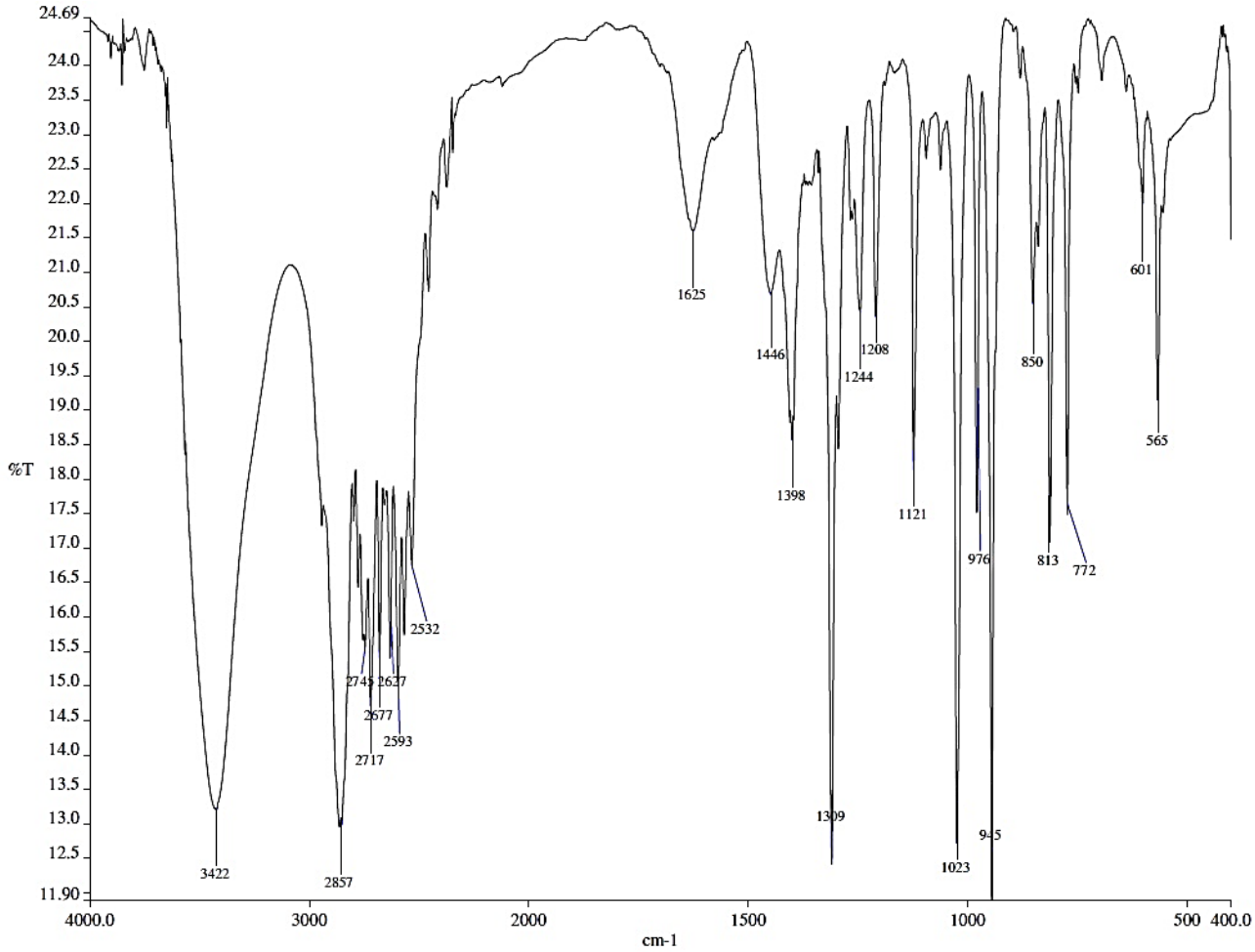


Figure S3. FT-IR spectrum of compound [PTA-H]•[I] (**3**) in KBr (range 400-4000 cm^{-1}).

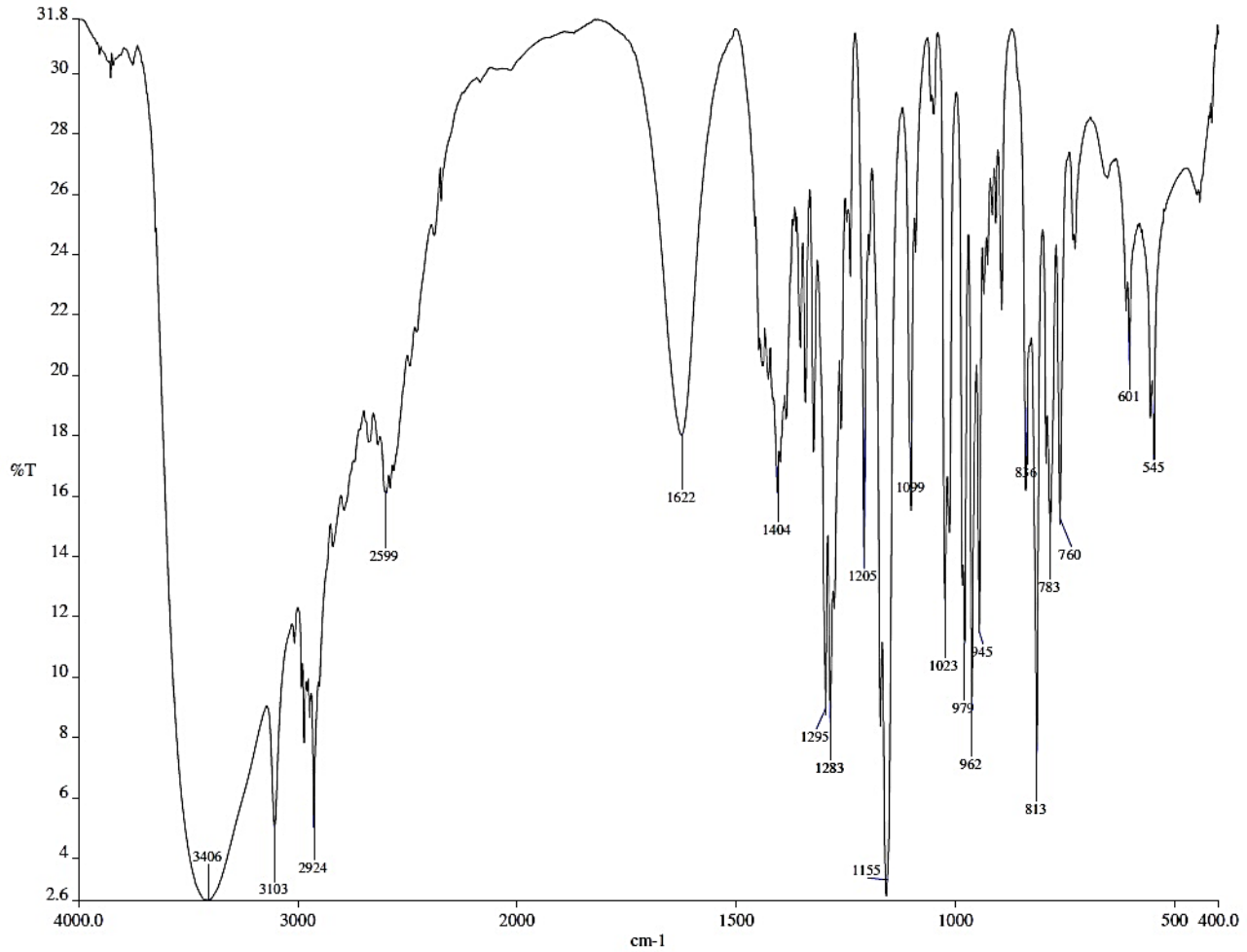


Figure S4. FT-IR spectrum of compound [PTA(O)-H]•[I] (**4**) in KBr (range 400-4000 cm^{-1}).

2. NMR spectra of compounds 1 – 4

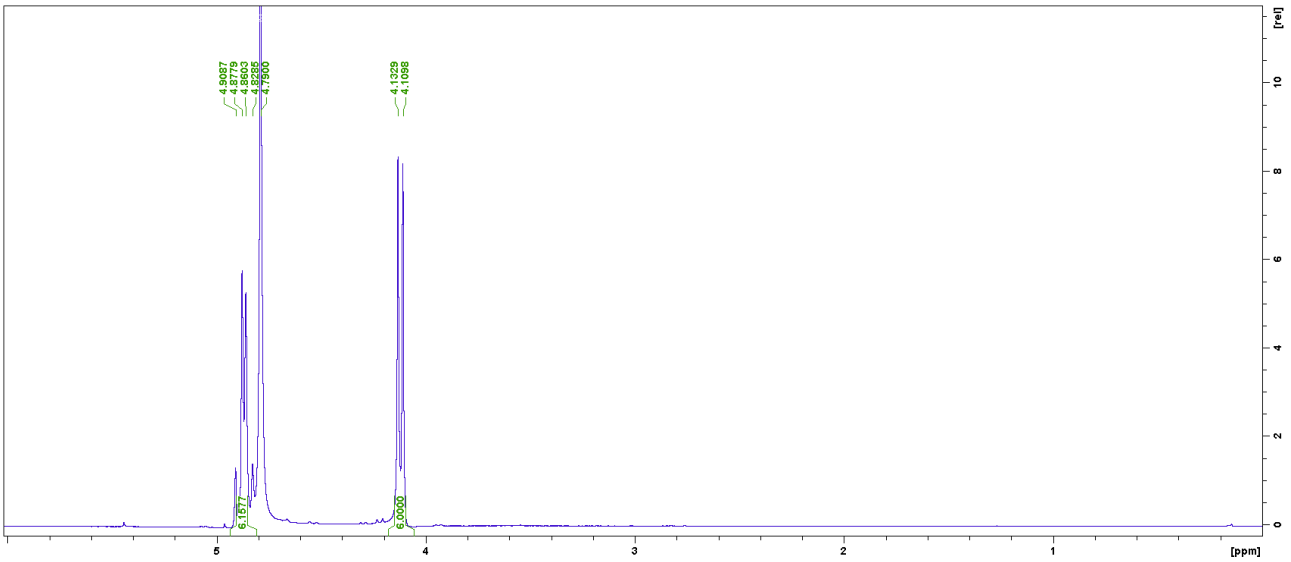


Figure S5. ^{1}H NMR of compound [PTA-H]•[$GaCl_4$] (**1**) in D_2O (400.13 MHz, recorded at 298K with a spectral width of 10 ppm, expanded in the region where signals were detected)

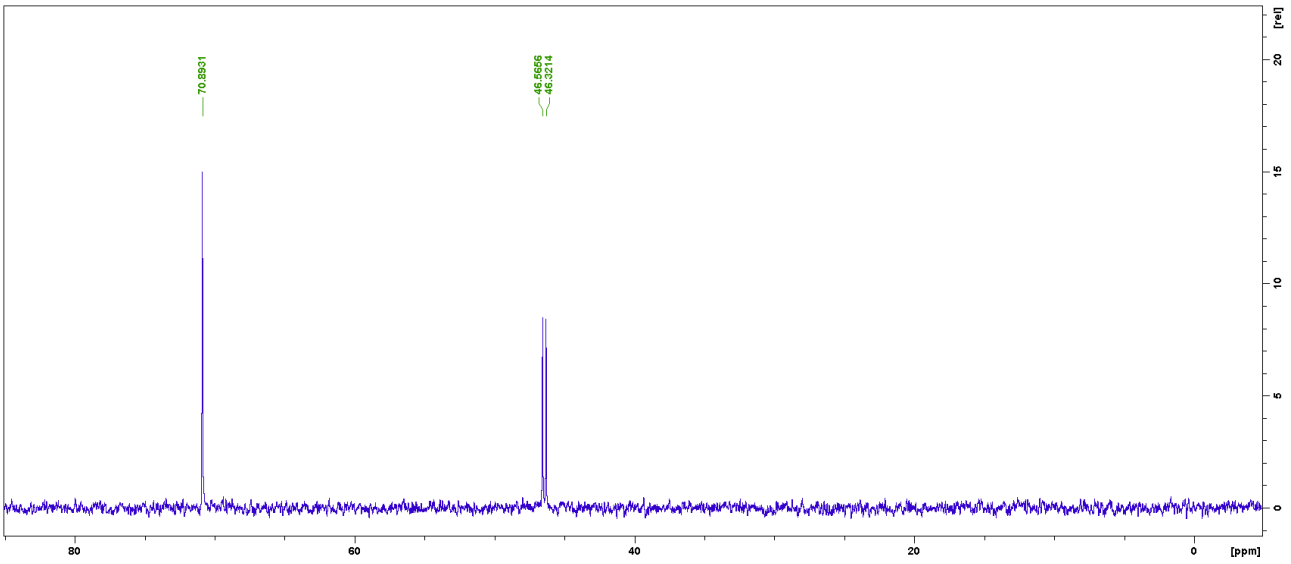


Figure S6. $^{13}C\{^{1}H\}$ NMR of compound [PTA-H]•[$GaCl_4$] (**1**) in D_2O (100.61 MHz, recorded at 298K with a spectral width of 130 ppm, expanded in the figure in the region where signals were detected)

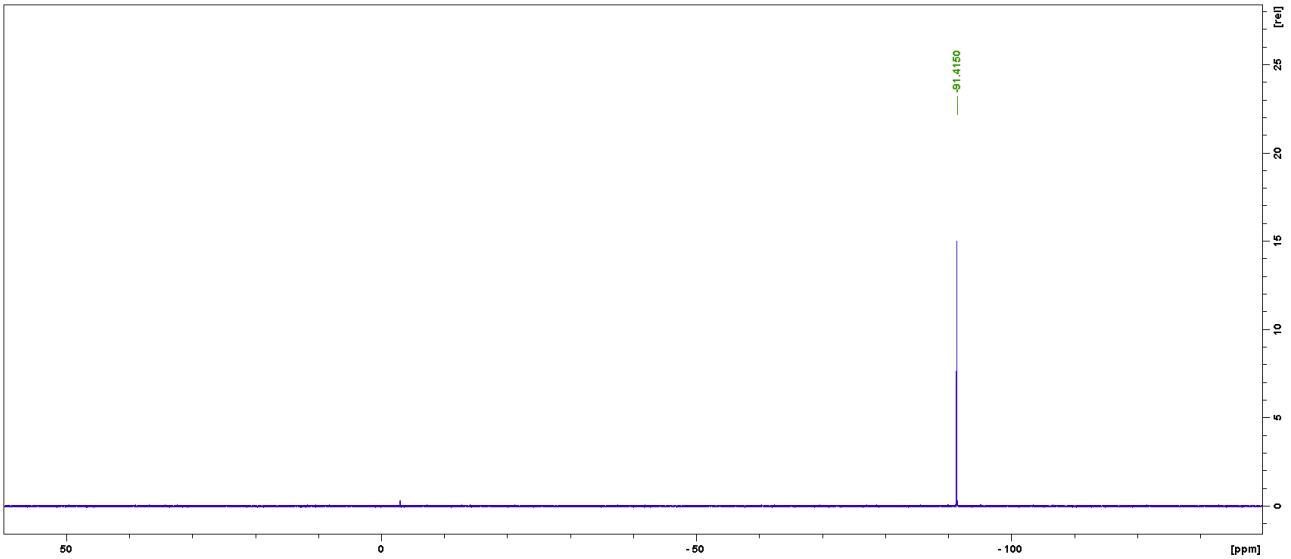


Figure S7. $^{31}P\{^{1}H\}$ NMR of compound [PTA-H]•[$GaCl_4$] (**1**) in D_2O (161.98 MHz, recorded at 298K with a spectral width of 200 ppm)

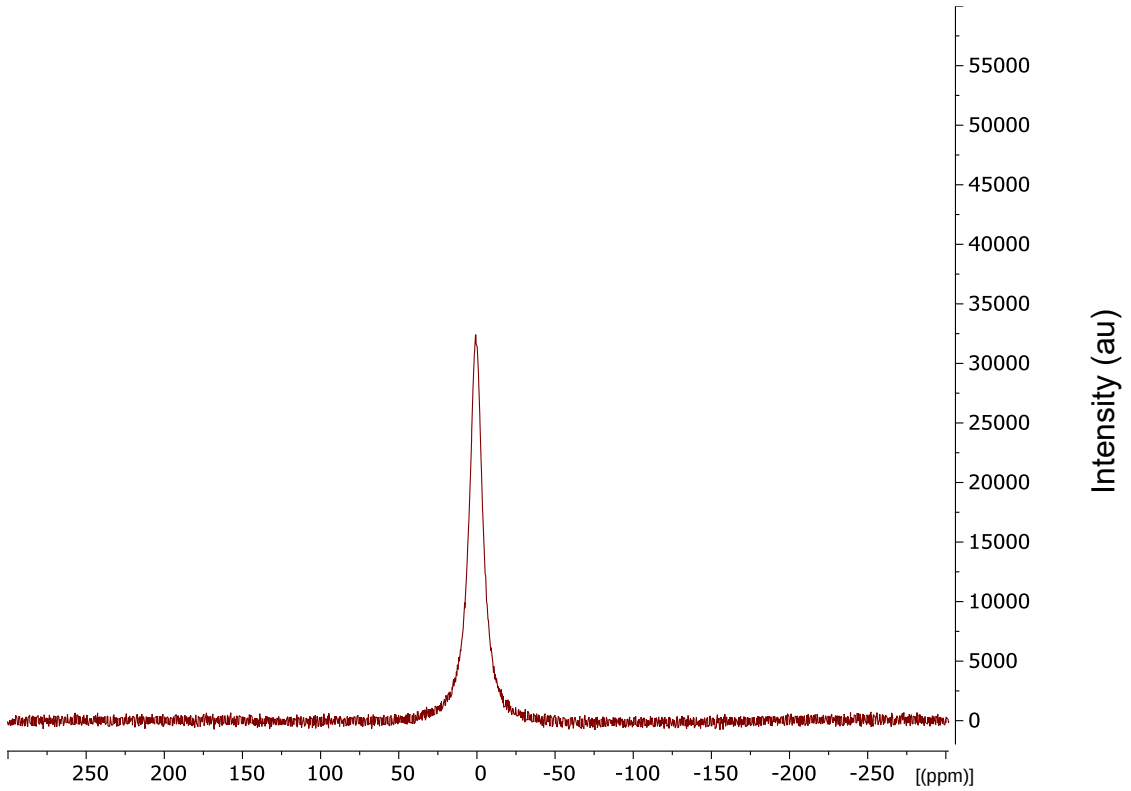


Figure S8. ^{71}Ga NMR spectrum of [PTA-H]•[$GaCl_4$] (**1**) in D_2O (recorded at 298K with a transmitter frequency offset of 0 ppm and a spectral width of 600 ppm, expanded in the figure in the region where signal was detected).

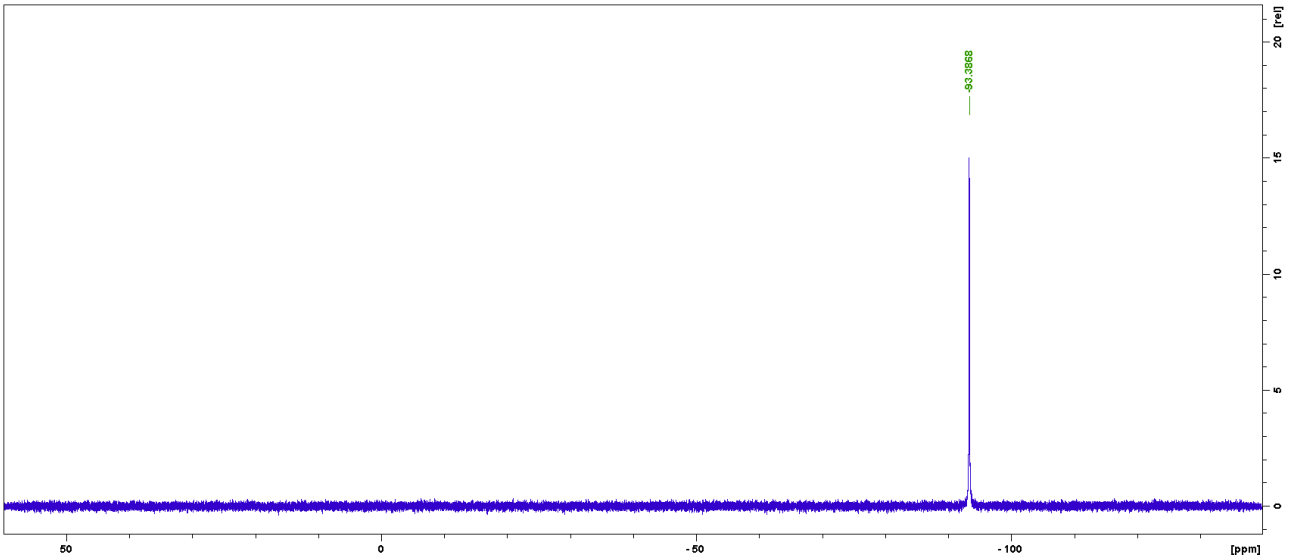


Figure S9. $^{31}P\{^{1}H\}$ NMR of DCM mother solution of [PTA-H]•[$GaCl_4$] (**1**) (161.98 MHz, recorded with a C_6D_6 insert at 298K, with a spectral width of 200 ppm).

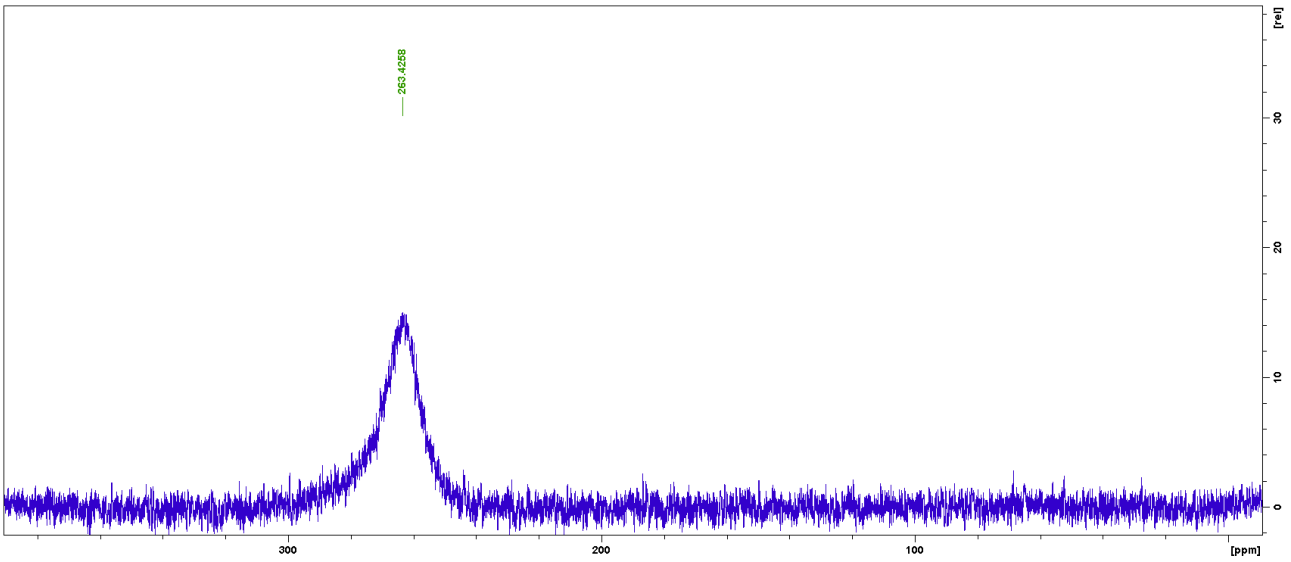


Figure S10. ^{71}Ga NMR spectrum of DCM mother solution of [PTA-H]•[$GaCl_4$] (**1**) (122.03 MHz, recorded with a C_6D_6 insert at 298K, with a spectral width of 400 ppm).

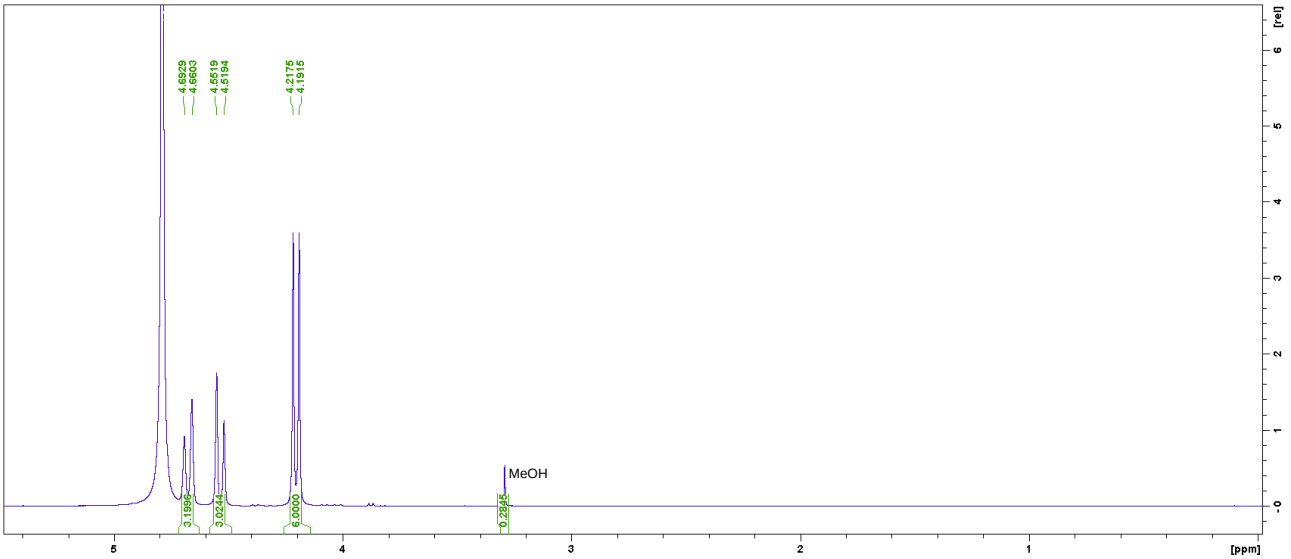


Figure S11. ^{1}H NMR of compound [PTA(O)-H]•[$GaCl_4$] (**2**) in D_2O (400.13 MHz, recorded at 298K with a spectral width of 12 ppm, expanded in the figure in the region where signals were detected)

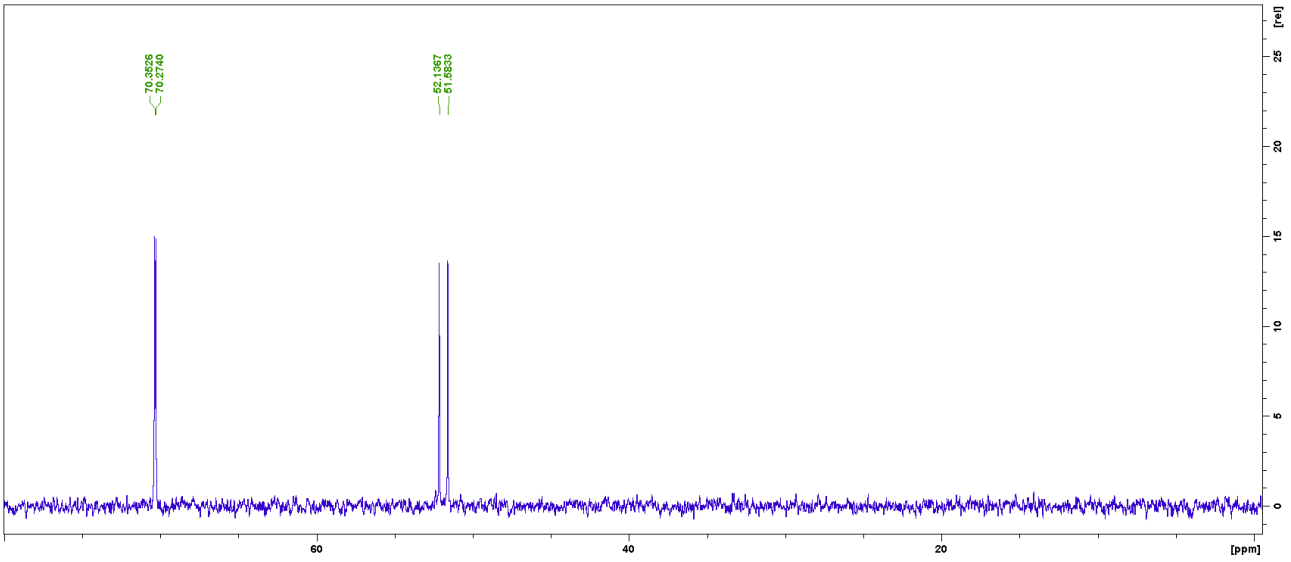


Figure S12. $^{13}C\{^{1}H\}$ NMR of compound [PTA(O)-H]•[$GaCl_4$] (**2**) in D_2O (100.61 MHz, recorded at 298K with a spectral width of 150 ppm, expanded in the figure in the region where signals were detected)

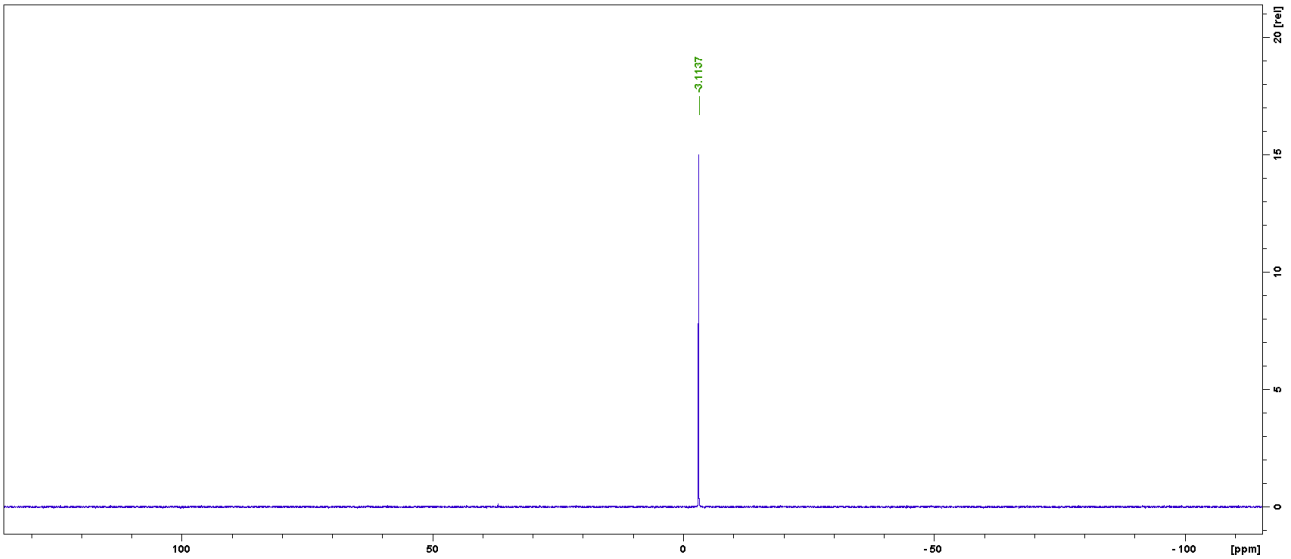


Figure S13. $^{31}P\{^{1}H\}$ NMR of compound [PTA(O)-H]•[$GaCl_4$] (**2**) in D_2O (161.98 MHz, recorded at 298K with a spectral width of 250 ppm)

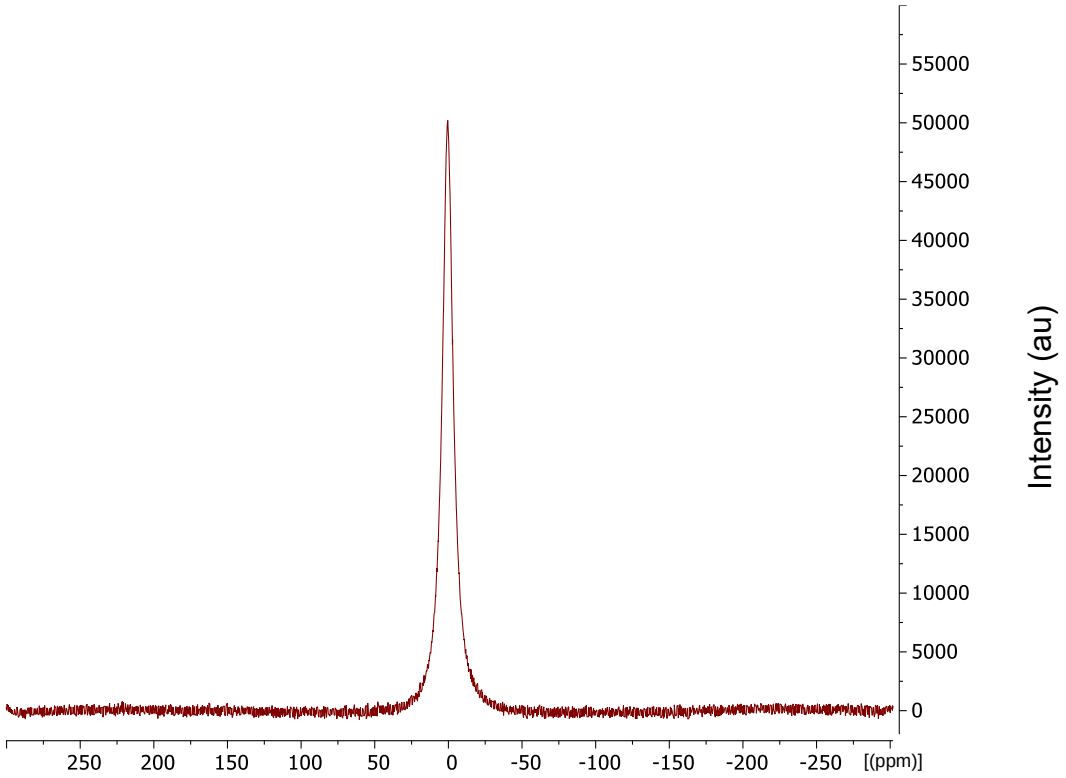


Figure S14. ^{71}Ga NMR spectrum of [PTA(O)-H]•[$GaCl_4$] (**2**) in D_2O (recorded at 298K with a transmitter frequency offset of 0 ppm and a spectral width of 600 ppm, expanded in the figure in the region where signals was detected).

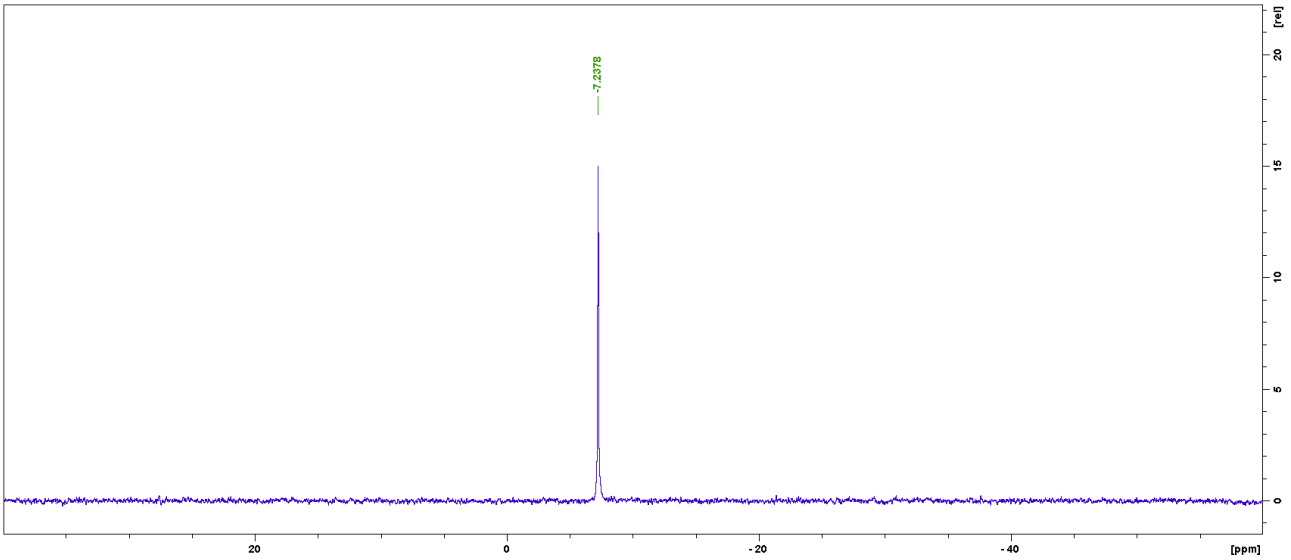


Figure S15. $^{31}P\{^{1}H\}$ NMR of DCM/MeOH mother solution of [PTA(O)-H]•[$GaCl_4$] (**2**) (161.98 MHz, recorded with a C_6D_6 insert at 298K with a spectral width of 100 ppm)

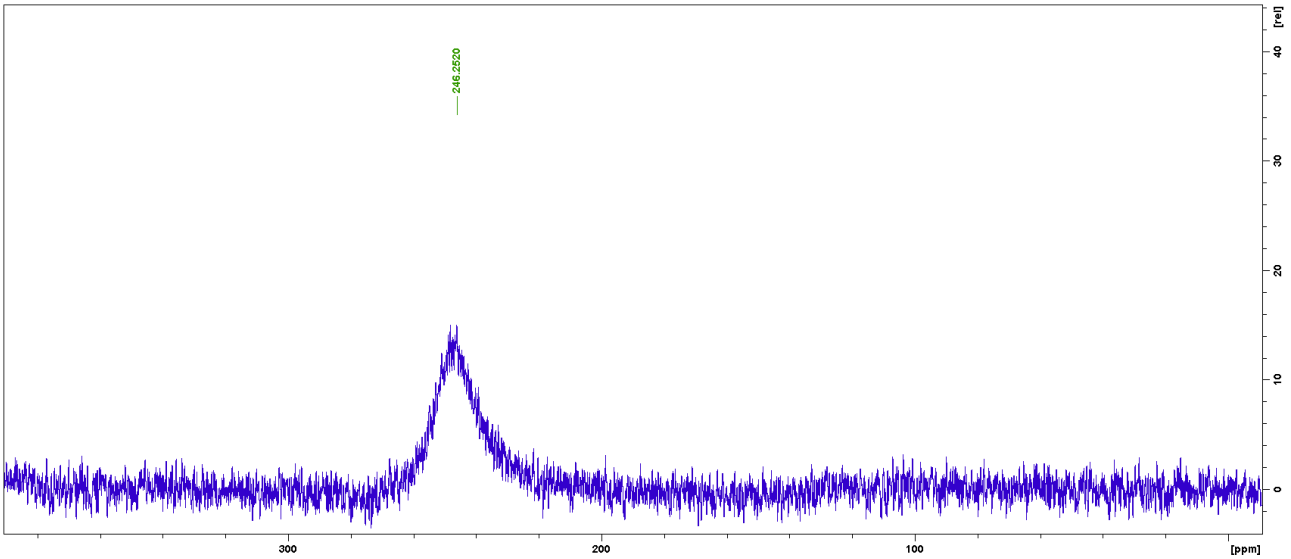


Figure S16. ^{71}Ga NMR spectrum of DCM/MeOH mother solution of [PTA(O)-H]•[$GaCl_4$] (**2**) (122.03 MHz, recorded with a C_6D_6 insert, at 298K, with a spectral width of 400 ppm).

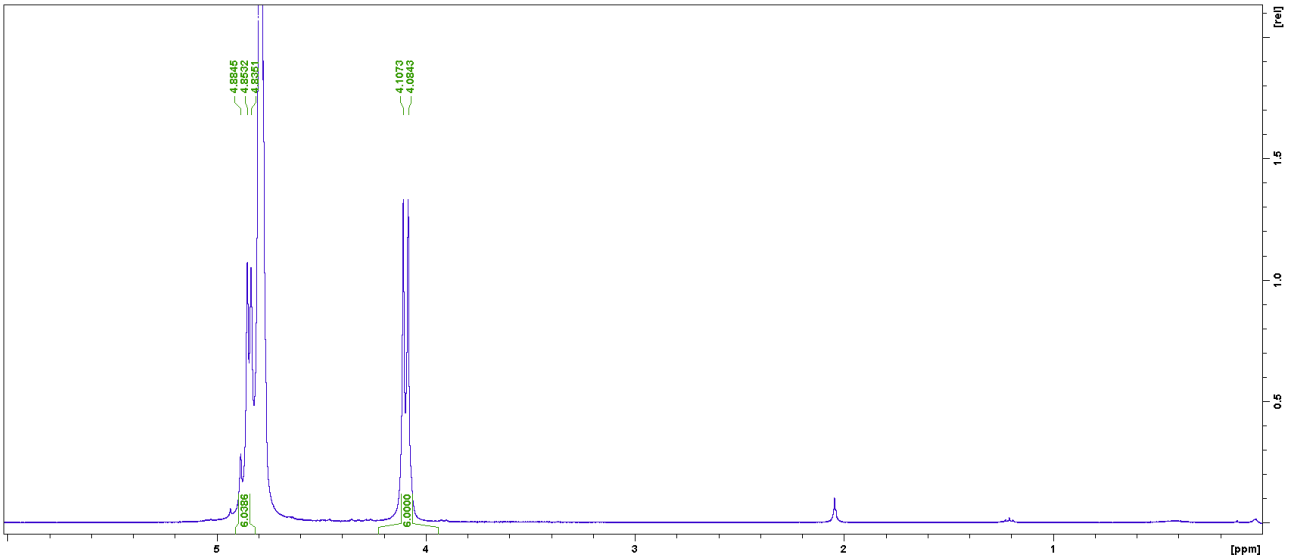


Figure S17. ^{1}H NMR of compound [PTA-H]•[I] (**3**) in D_2O (400.13 MHz, recorded at 298K with a spectral width of 12 ppm, expanded in the figure in the region where signals were detected)

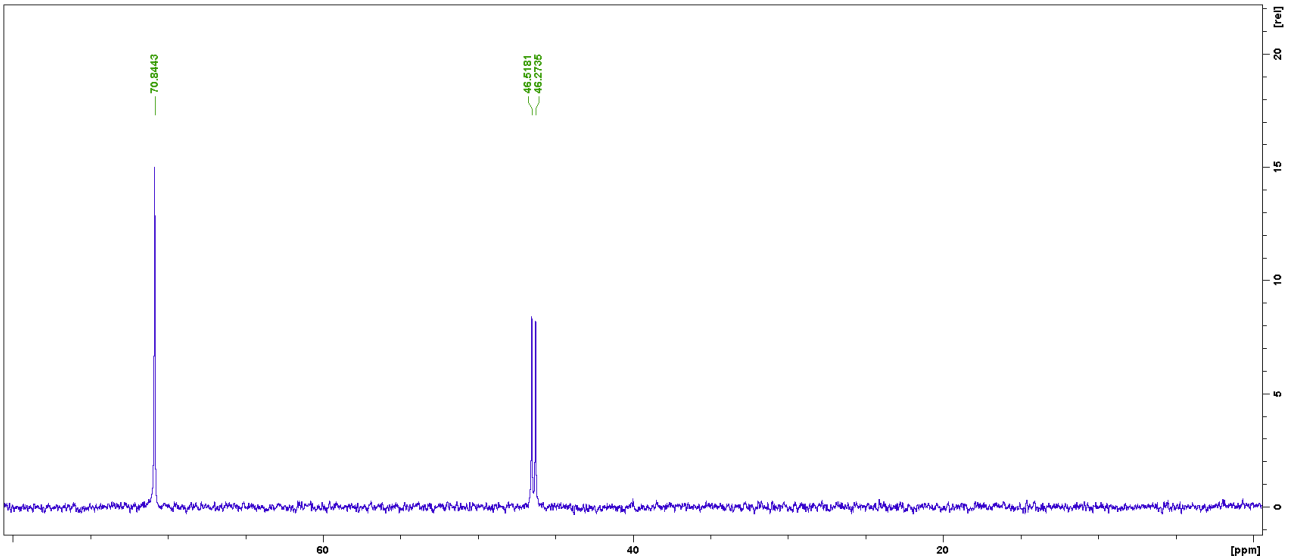


Figure S18. ^{13}C{^{1}H} NMR of compound [PTA-H]•[I] (**3**) in D_2O (100.61 MHz, recorded at 298K with a spectral width of 110 ppm, expanded in the figure in the region where signals were detected)

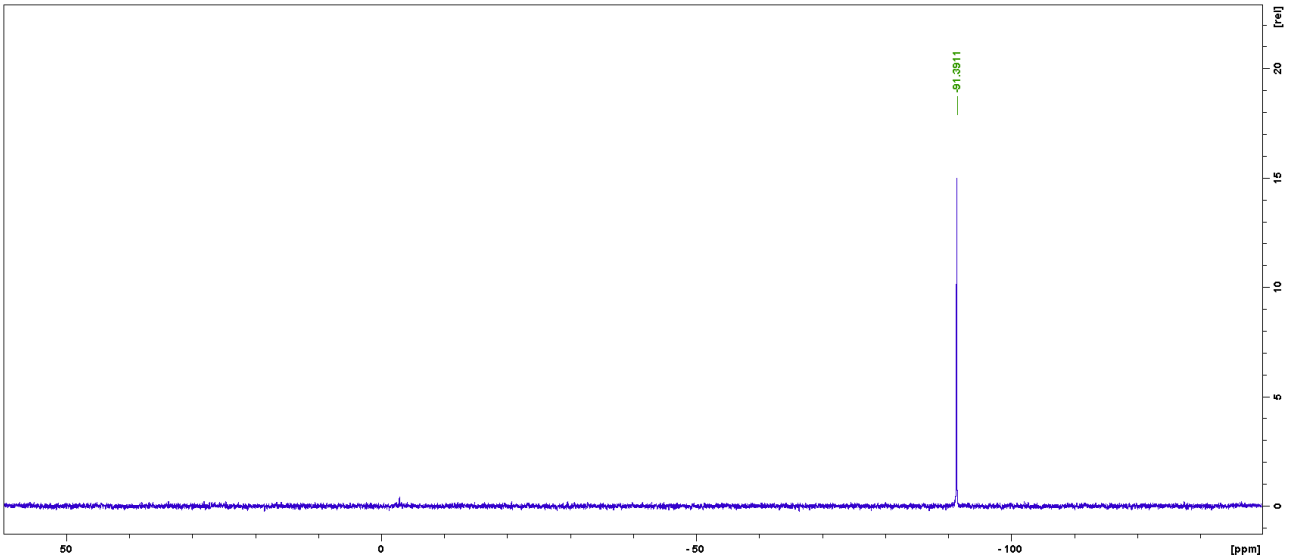


Figure S19. $^{31}P\{^{1}H\}$ NMR of compound [PTA-H]•[I] (**3**) in D_2O (161.98 MHz, recorded at 298K with a spectral width of 250 ppm)

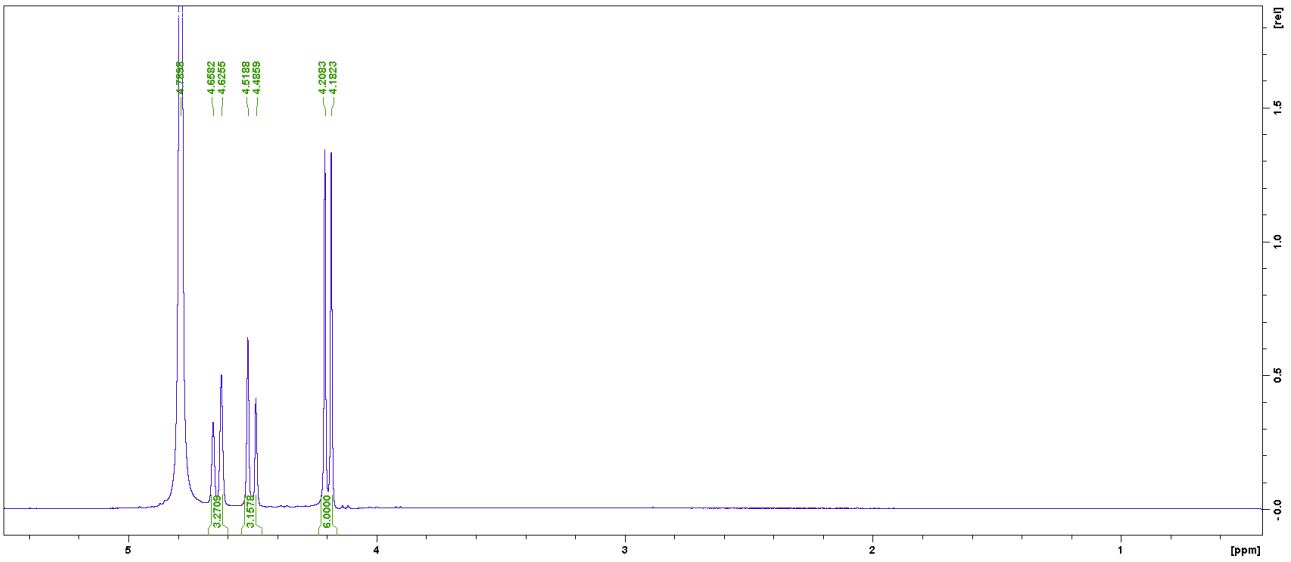


Figure S20. ^{1}H NMR of compound [PTA(O)-H]•[I] (**4**) in D_2O (400.13 MHz, recorded at 298K with a spectral width of 12 ppm, expanded in the figure in the region where signals were detected)

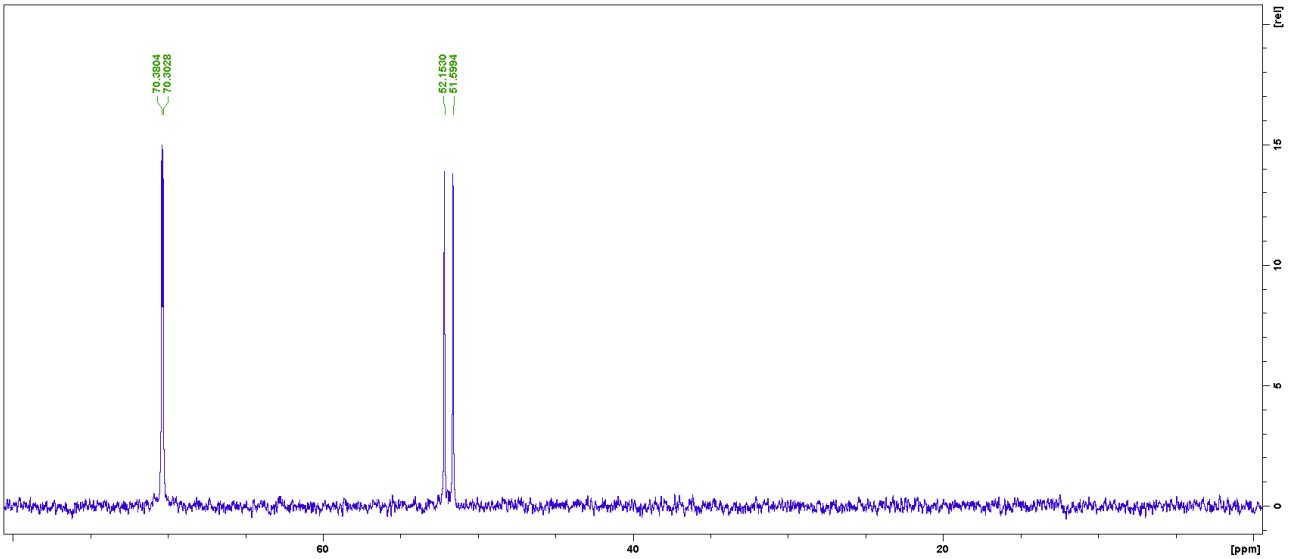


Figure S21. $^{13}C\{^{1}H\}$ NMR of compound [PTA(O)-H]•[I] (**4**) in D_2O (100.61 MHz, recorded at 298K with a spectral width of 110 ppm, expanded in the figure in the region where signals were detected)

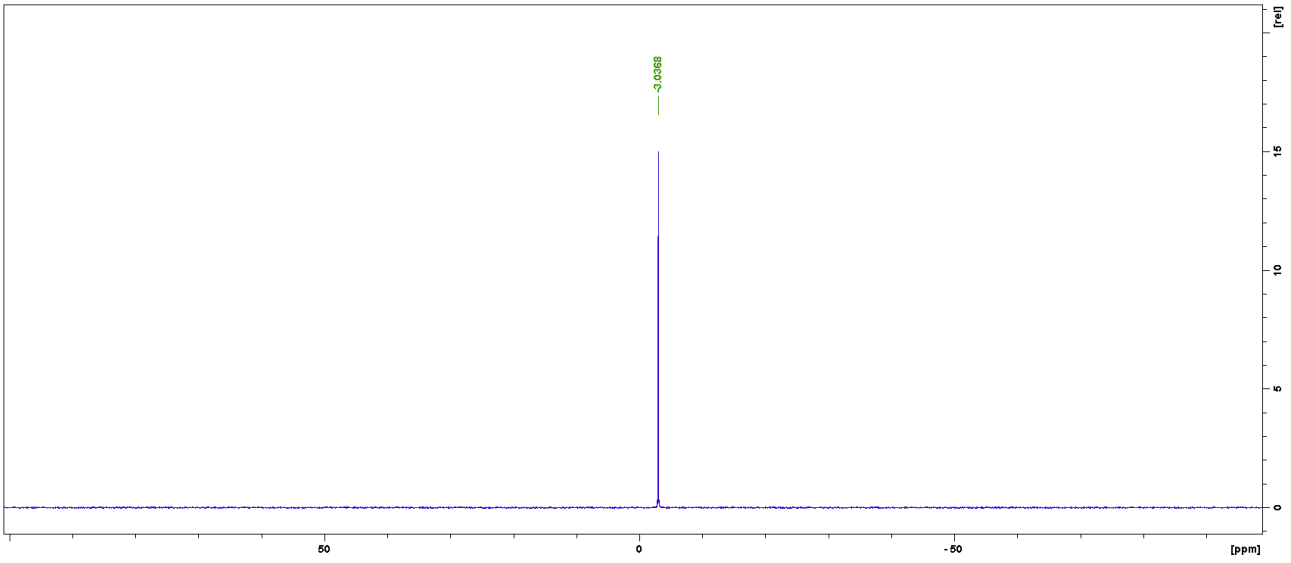


Figure S22. $^{31}P\{^{1}H\}$ NMR of compound [PTA(O)-H]•[I] (**4**) in D_2O (161.98 MHz, recorded at 298K with a spectral width of 200 ppm)

3. ^{1}H-DOSY experiments for compounds [PTA-H]•[$GaCl_4$] (1), [PTA(O)-H]•[$GaCl_4$] (2), PTA and [PTA(O)]: general information and spectra

The intensities of the phosphor-coupled doublet of the $[PTA\text{-}H]^+$ and $[PTA(O)\text{-}H]^+$ ions from the DOSY experiments were plotted against the gradient strength. To derive their diffusion constants (**D**) in deuterated water, the data were fit to equation 1.

$$\text{Eq 1)} \quad I = I_0 e^{-D^2\gamma^2\delta^2\left(\frac{\Delta-\delta}{3}\right)}$$

Where; **I** is the measured signal intensity, $\mathbf{I_0}$ is the initial signal intensity, **γ** is the gyromagnetic ratio of ^{1}H, **Δ** is the diffusions time and **δ** is the gradient pulse width.

To find the hydrodynamic radius (r_s) of each ion, equation 2 was used with a temperature (T) of 298K and a deuterated water viscosity (η) of 1.1 x 10^{-3} kg $m^{-1}s^{-1}$.[1]

$$\text{Eq 2)} \quad D = \frac{k_b T}{6\,\pi\,\eta\,r_s}$$

Where; k_b is the Boltzmann constant.

Using this equation, the hydrodynamic radii of $[PTA\text{-}H]^+$, $[PTA(O)\text{-}H]^+$, PTA and [PTA(O)] were found to be 3.36 Å, 3.52 Å, 3.92 Å and 3.72 Å, respectively.

[1] R. Evans, G. Dal Poggetto, M. Nilsson, G. A. Morris. *Anal. Chem.* **2018**, *90*, 6, 3987–3994.

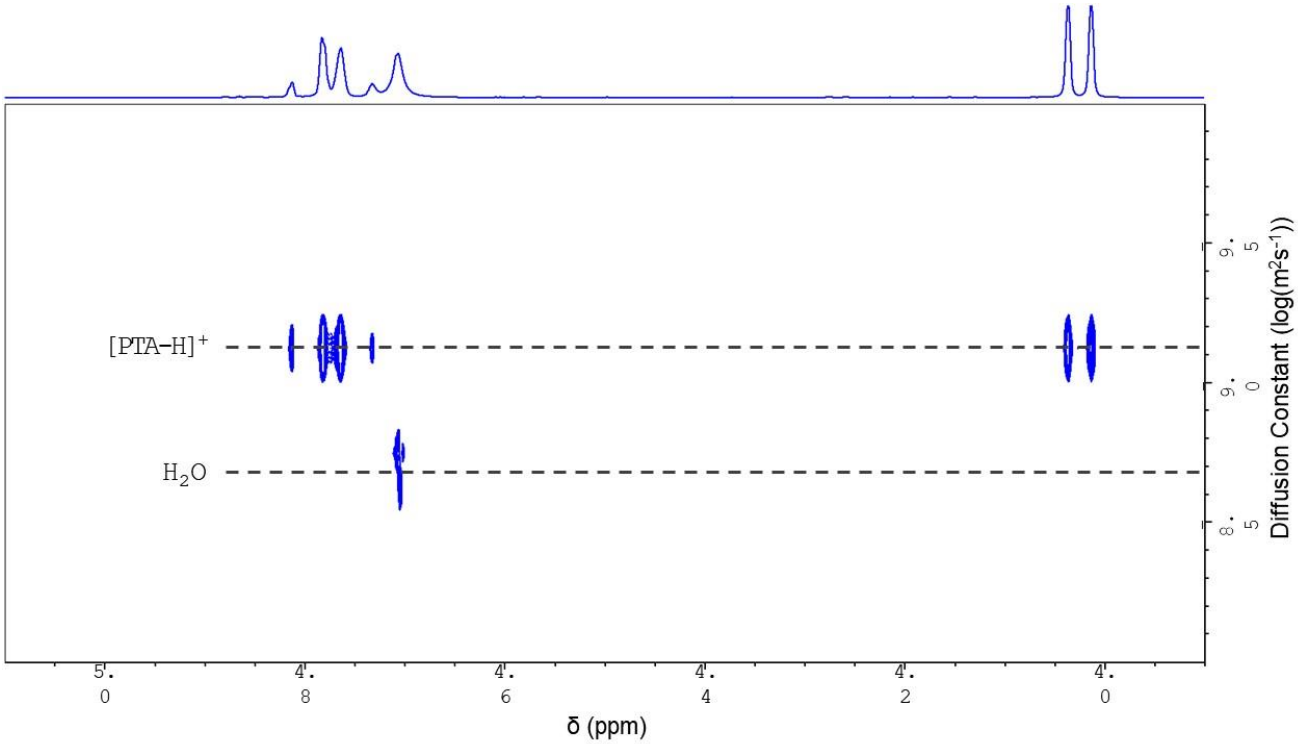


Figure S23. Two-dimensional ^{1}H-DOSY NMR projection of compound [PTA-H]•[$GaCl_4$] (**1**) in D_2O processed using TopSpin 3.6.5 (peaks for $[PTA\text{-}H]^+$ and H_2O appeared in the range -8.5 and -9.5 Log(m^2s^{-1})).

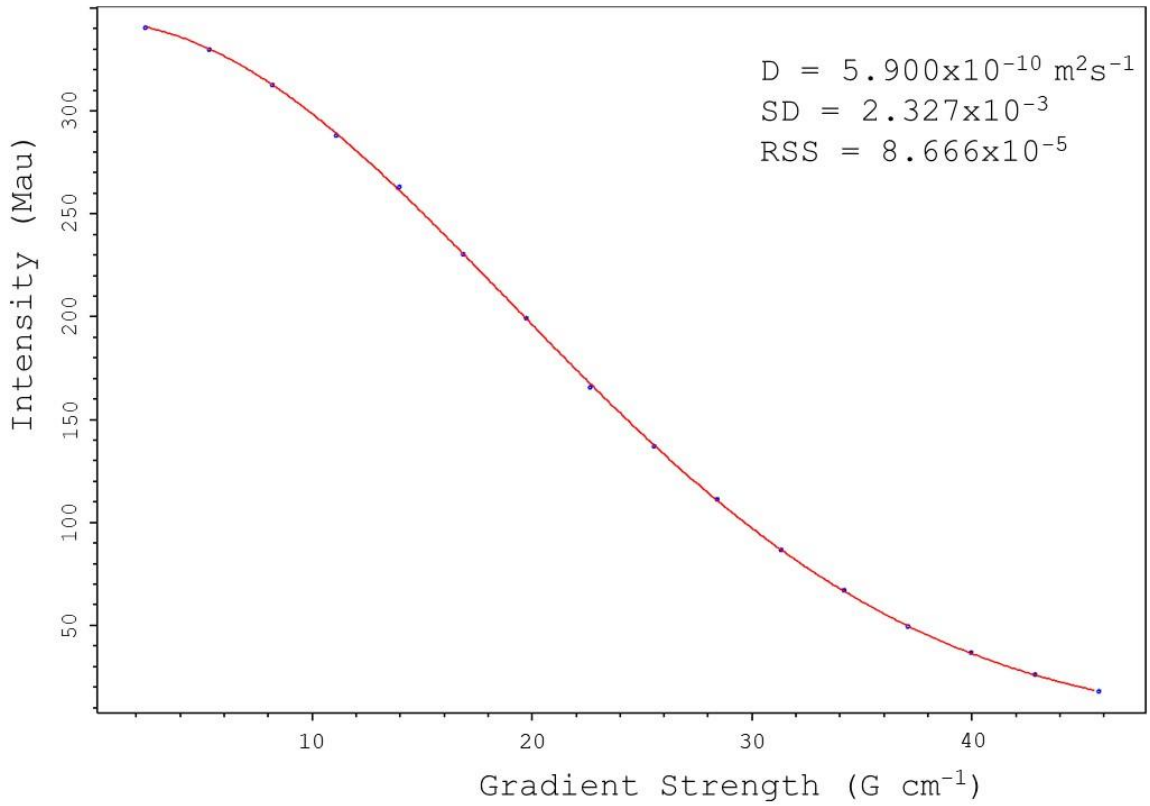


Figure S24. Plot of the intensity of the phosphor-coupled doublet of $[PTA\text{-}H]^+$ in [PTA-H]•[$GaCl_4$] (**1**) as a function of varied gradient strength over the 16 increments of the DOSY experiment. The datapoints were fit to equation 1 using the T1/T2 function in the dynamics module in TopSpin 3.6.5. (upper right: diffusion constant (D), alongside the standard deviation (SD) and the root sum of squares (RSS) for the fitting).

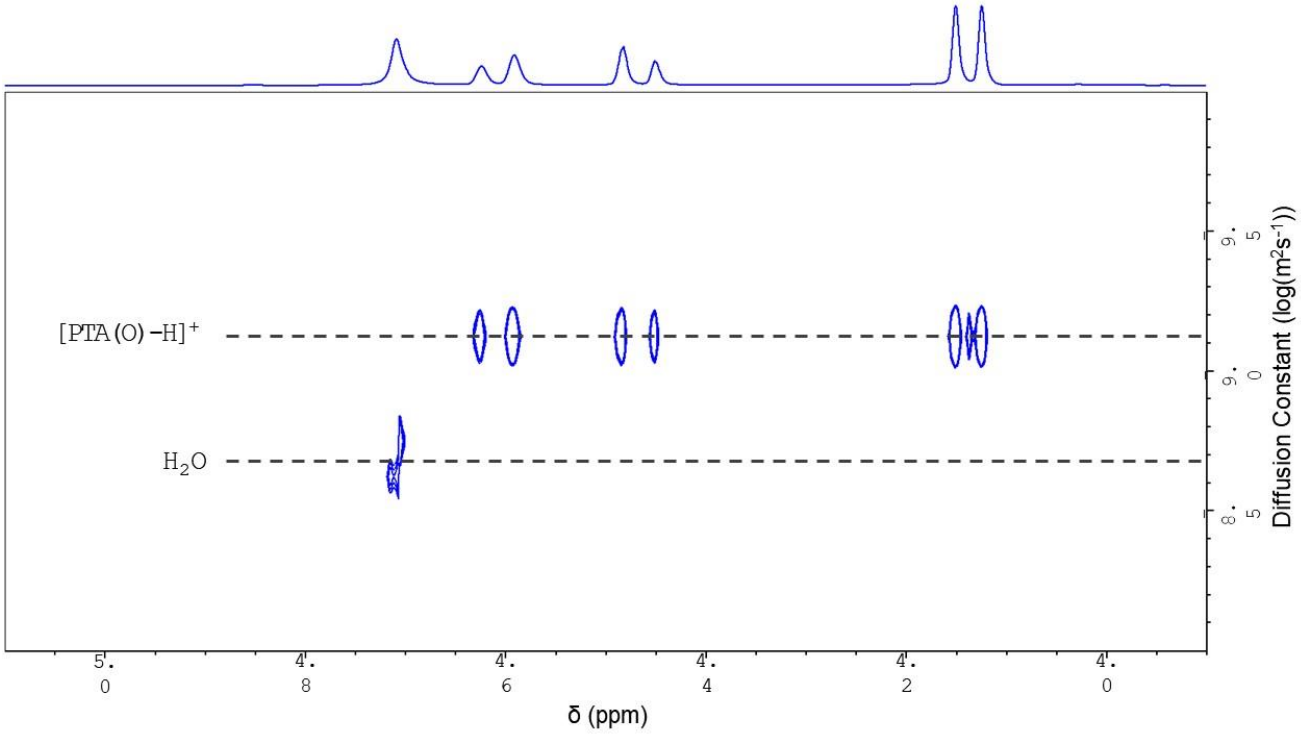


Figure S25. Two-dimensional ^{1}H-DOSY NMR projection of compound [PTA(O)-H]•[$GaCl_4$] (**2**) in D_2O processed using TopSpin 3.6.5 (peaks for $[PTA(O)\text{-}H]^+$ and H_2O appeared in the range -8.5 and -9.5 Log(m^2s^{-1})).

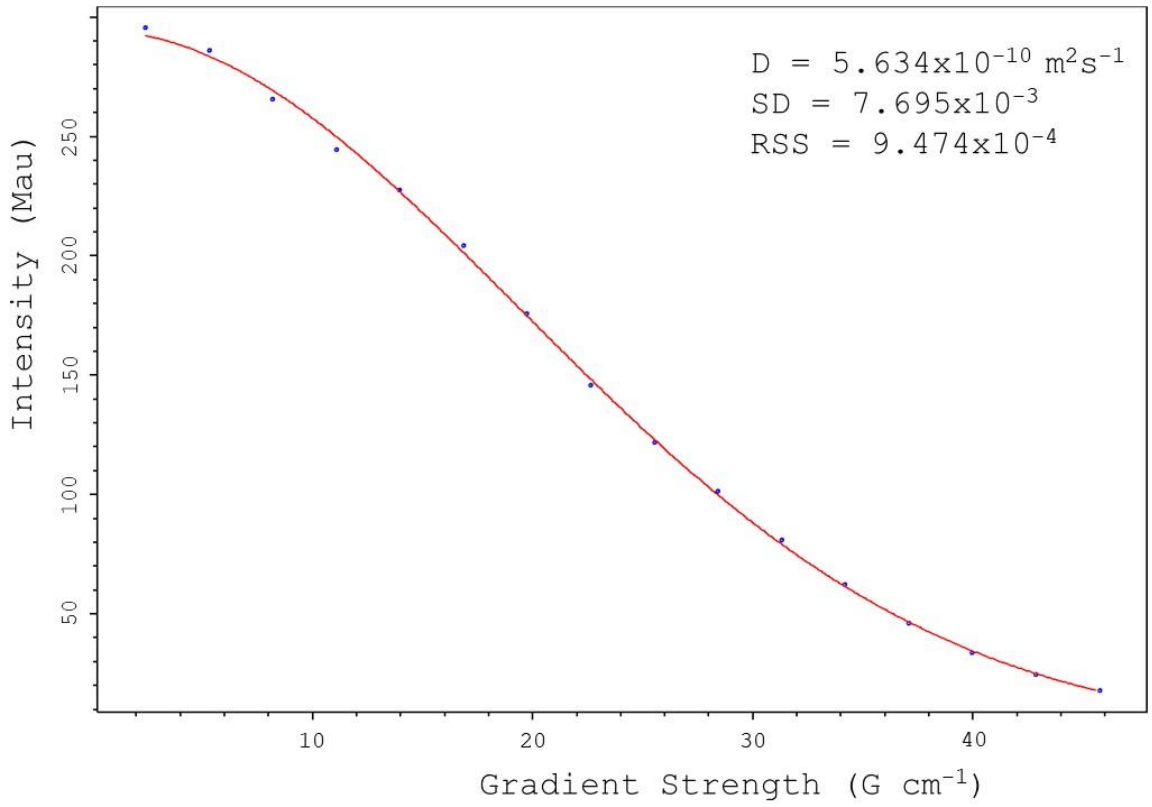


Figure S26. Plot of the intensity of the phosphor-coupled doublet of $[PTA(O)\text{-}H]^+$ in [PTA(O)-H]•[$GaCl_4$] (**2**) as a function of varied gradient strength over the 16 increments of the DOSY experiment. The datapoints were fit to equation 1 using the T1/T2 function in the dynamics module in TopSpin 3.6.5. (upper right: diffusion constant (D), alongside the standard deviation (SD) and the root sum of squares (RSS) for the fitting).

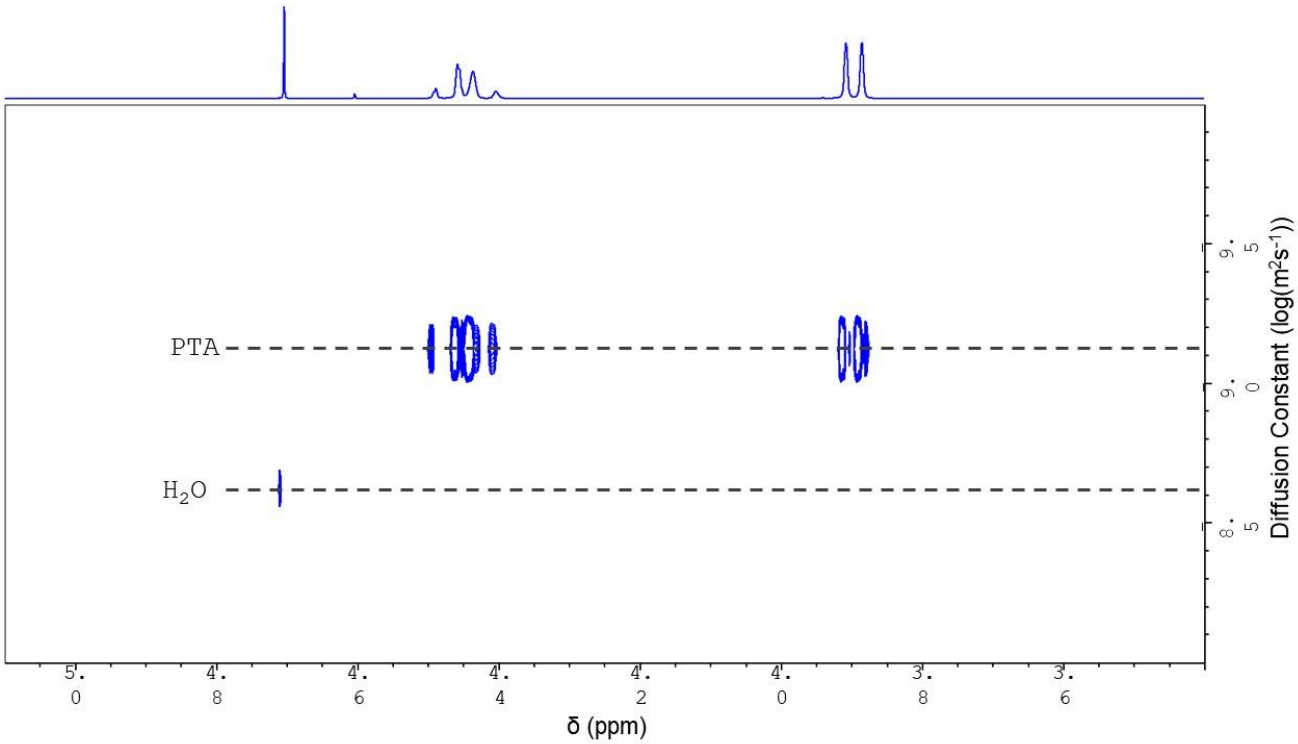


Figure S27. Two-dimensional ^{1}H-DOSY NMR projection of PTA (free ligand) in D_2O processed using TopSpin 3.6.5 (peaks for PTA and H_2O appeared in the range -8.5 and -9.5 Log(m^2s^{-1})).

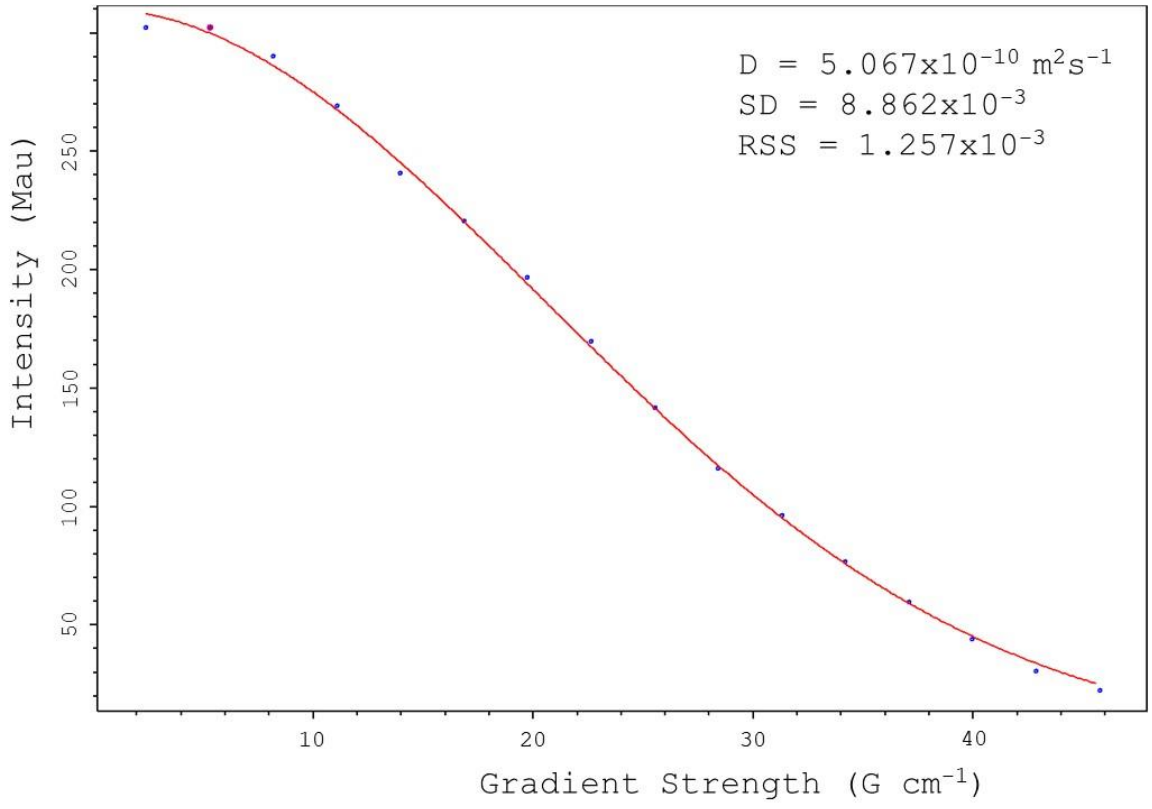


Figure S28. Plot of the intensity of the phosphor-coupled doublet of PTA (free ligand) as a function of varied gradient strength over the 16 increments of the DOSY experiment. The datapoints were fit to equation 1 using the T1/T2 function in the dynamics module in TopSpin 3.6.5. (upper right: diffusion constant (D), alongside the standard deviation (SD) and the root sum of squares (RSS) for the fitting).

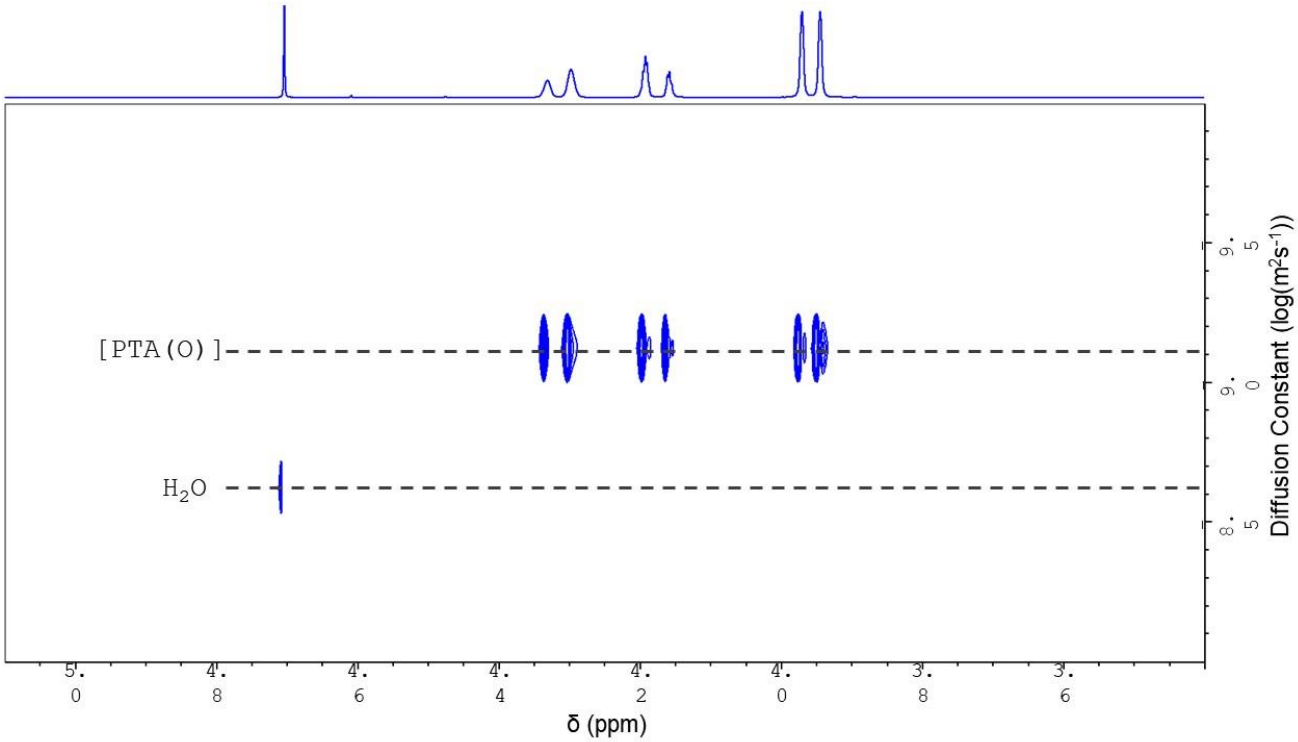


Figure S29. Two-dimensional ^{1}H-DOSY NMR projection of [PTA(O)] (free ligand) in D_2O processed using TopSpin 3.6.5 (peaks for PTA and H_2O appeared in the range -8.5 and -9.5 Log(m^2s^{-1})).

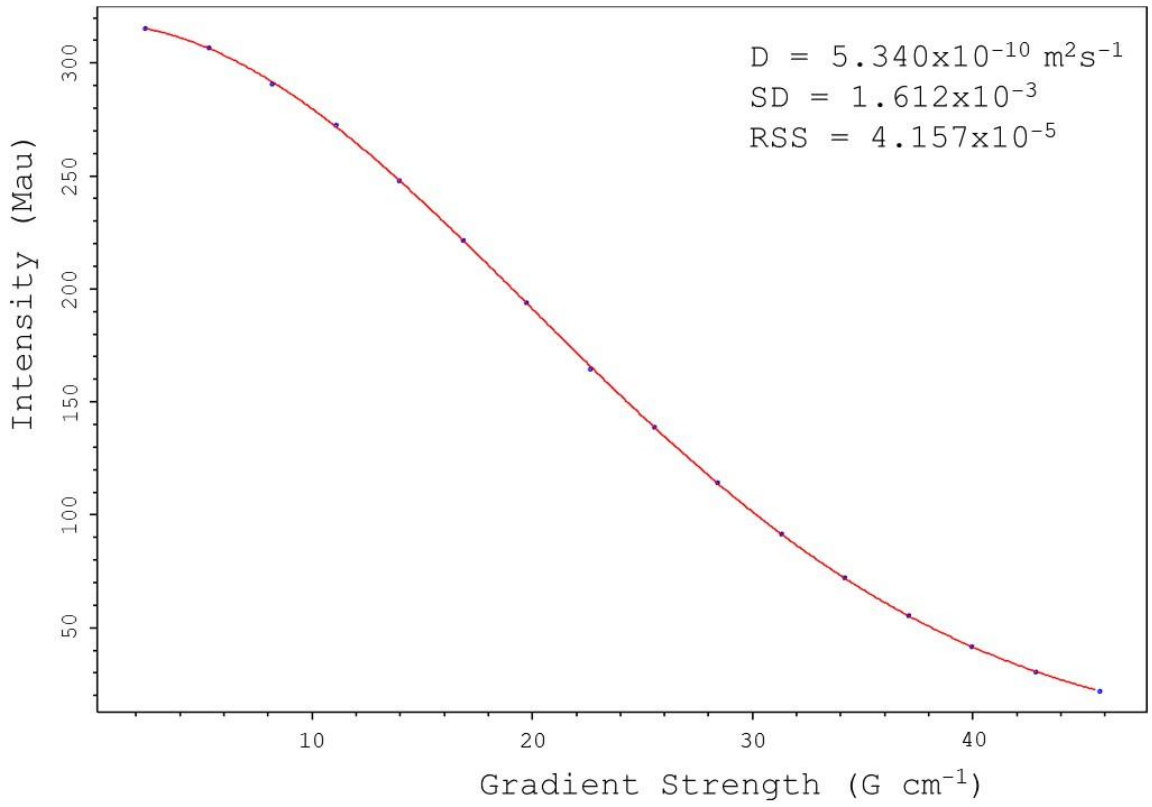


Figure S30. Plot of the intensity of the phosphor-coupled doublet of [PTA(O)] (free ligand) as a function of varied gradient strength over the 16 increments of the DOSY experiment. The datapoints were fit to equation 1 using the T1/T2 function in the dynamics module in TopSpin 3.6.5. (upper right: diffusion constant (D), alongside the standard deviation (SD) and the root sum of squares (RSS) for the fitting).

4. Inductively coupled plasma mass spectrometry (ICP-MS): general information and measurements for compounds 1 and 2.

All analytical chemicals were of trace analysis grade or equivalent. For the preparation and analysis of samples, deionized water (conductivity ≤ 0.5 μS), ultra-pure concentrated (65%) nitric acid and multi-elemental standards (for calibration of the ICP-MS spectrometer) were used; all volumetric flasks were polymethyl pentene (PMP), polypropylene (PP) Class A or equivalent quality polymer. Samples of compounds [PTA-H]•[$GaCl_4$] (**1**) and [PTA(O)-H]•[$GaCl_4$] (**2**) and all solutions prepared from them were stored at room temperature. All sample preparation steps and measurements were performed at the London Metallomics Facility (King's College London, KCL), under GMP settings. Preparation of the samples was performed as follows: dried samples of **1** (1.31 mg) and **2** (1.09 mg) were transferred into a Teflon dish, quenched with 2 mL of a 2% HNO_3 aqueous solution and were subjected to mineralization by microwave digestion (30 min). All samples were spiked with germanium to obtain a concentration of 10 ug Ge/L in all samples to act as an internal standard to correct for matrix differences and/or instrumental drift. All measurements were conducted on a Thermo Fisher iCAP TQ ICP-MS in Dynamic Reaction Cell mode (DRC) with oxygen gas. The introduction system to the instrument was a Cetac ASX-520 autosampler coupled to a meinhard glass nebulizer that was fitted to a quartz cyclonic spray chamber. The typical settings used for ICP-QMS measurements are presented in Table S1. Data reduction involved the normalization of raw intensities using internal standard measurements of ^{72}Ge and blank correcting this signal by removing the average analyte intensity of blank measurements. Finally, external standardization was applied using an eight-point calibration curve to convert the corrected intensities into concentration measurements (see Table S2). The calibration curve for both P and Ga revealed a good linearity over the whole range of concentrations (0.10-1000 μg/L), with determination coefficients ≥ 0.999. Three blank replicates, consisting of 2% HNO_3 in deionized water, were performed to calculate the limit of quantitation (LOQ).

Table S1. Typical settings used for ICP-QMS measurements.

Thermo Fisher iCAP TQ ICP-QMS	
RF Power	1500 W
Ar plasma gas flow	18 L min^{-1}
Ar auxiliary gas flow	1.2 L min^{-1}
Nebusliser gas flow	1.0 L min^{-1}
CRC operation mode	DRC (O_2)
Oxygen DRC gas flow	0.33 L min^{-1}
Method acquisition	
Scanning mode	Peak-hopping
Dwell time	100 ms amu^{-1}
Sweeps per reading	50
Readings per replicate	1
Replicates per reading	5
Sample uptake rate	~130 µL min^{-1}

Table S2. Results of content of [Ga] and [P] elements in **1** and **2** compounds determined via ICP-MS.

COMPOUND	**^{31}P (µg/L)**	**^{31}P (RSD)**	**^{71}Ga (µg/L)**	**^{71}Ga (RSD)**	**P (mg/L)**	**Ga (mg/L)**
1 (1.31 mg)	54444.22	3.57	115735.50	3.70	54.44	115.74
2 (1.09 mg)	41884.26	2.83	90654.54	3.11	41.88	90.65

5. Tests of stability in aqueous solution for compounds [PTA-H]•[$GaCl_4$] (1) and [PTA(O)-H]•[$GaCl_4$] (2)

To test the stability of compounds **1** and **2**, the solutions of each sample in D_2O were prepared on air, maintained at room temperature and monitored over time by ^{1}H and ^{71}Ga NMR spectroscopy using an Avance III HD spectrometer (operating at 400.13 and 122.03 MHz, respectively).

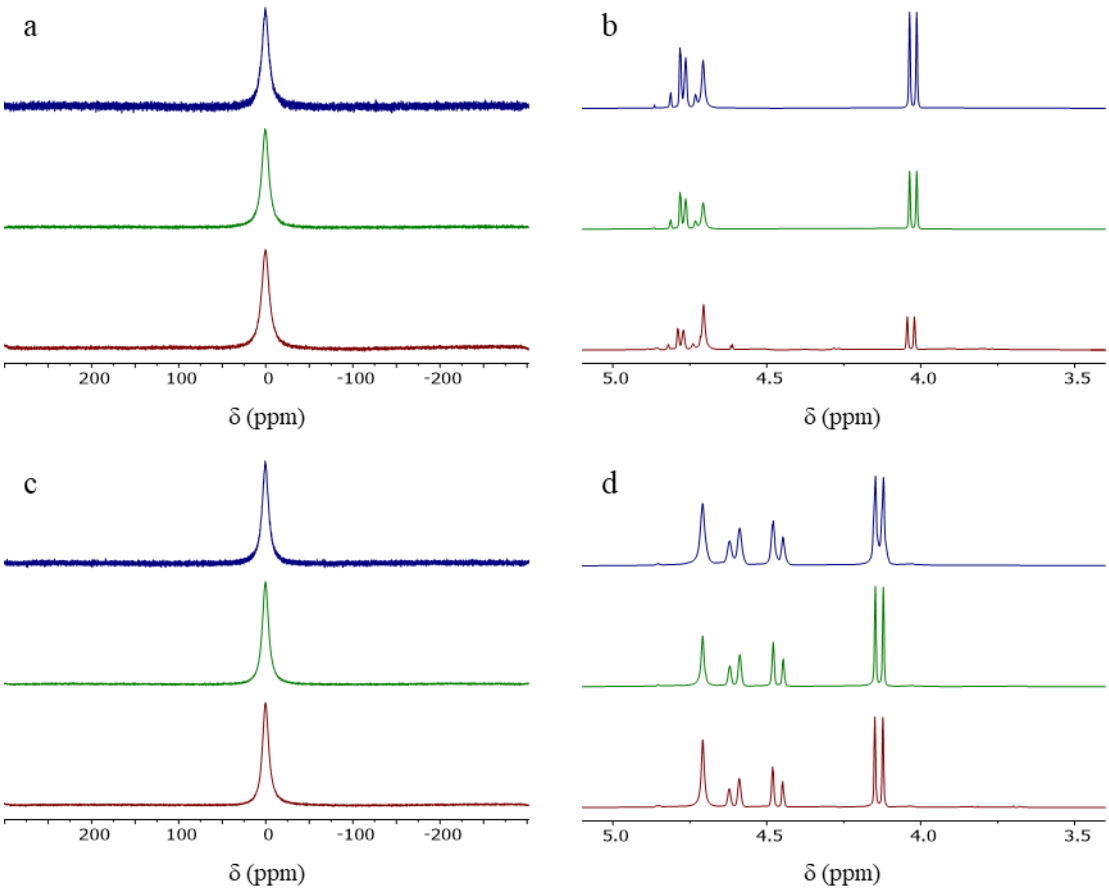


Figure S31. ^{71}Ga (a) and ^{1}H NMR spectra (b) of **1** and ^{71}Ga (c) and ^{1}H NMR spectra (d) of **2** in D_2O recorded at t= 0 (blue), one day later (green) and one month later (red). ^{71}Ga spectra were recorded with a transmitter offset frequency of 0.0 ppm and a spectral width of 600 ppm. To improve clarity, each stacked plot was normalised to the height of the largest peak. ^{1}H spectra were run with a transmitter frequency offset of 2.5 ppm and a spectral width of 7 ppm. Either ^{71}Ga and ^{1}H NMR spectral widths shown in the figure were expanded in the region where signals were detected.

6. CSD search

Mean P-C distance in PTA 1.843(17) on 3366 P-C bonds in 680 hits.

Mean C-N distance around not protonated nitrogen atom in monoprotonated PTA 1.461(9) (534 bonds in 54 hits).

Mean C-N distance around protonated nitrogen atom in monoprotonated PTA 1.55(2) (267 bonds in 54 hits).

7. Additional drawing of X-Ray Structures

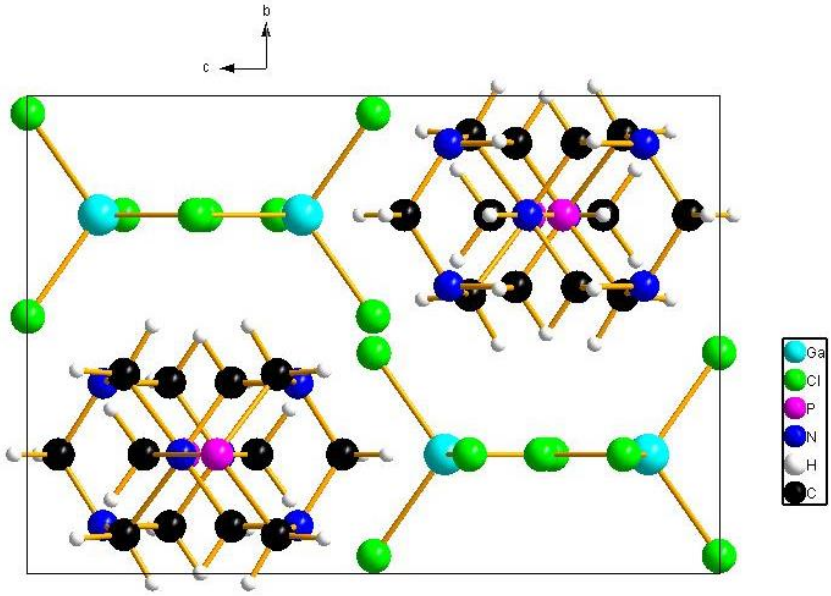


Figure S32. Packing diagram of [PTA-H]•[$GaCl_4$] (**1**) along *a* axis.

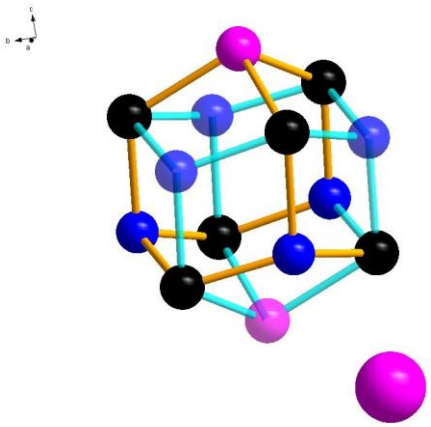
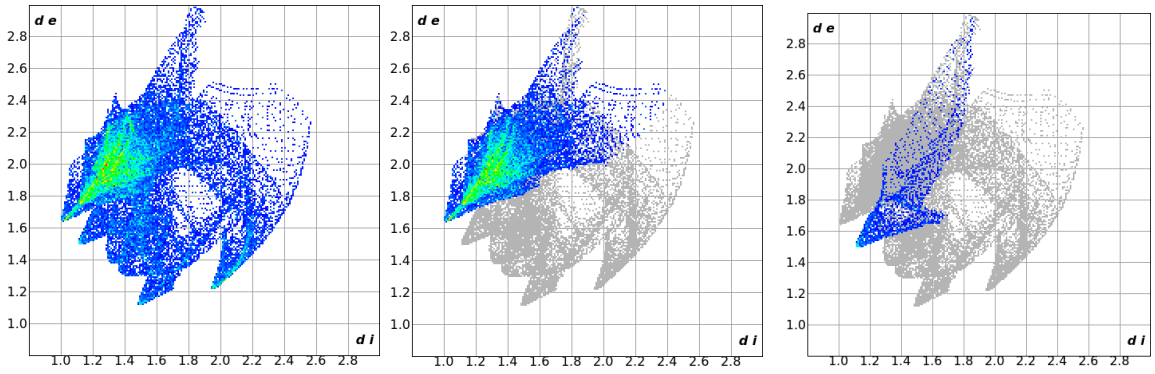


Figure S33. Molecular structure of [PTA-H]•[I] (**3**) showing the two disordered $[PTA\text{-}H]^+$ molecules in the same crystallographic site. Empirical formula: $C_6H_{13}IN_3P$; Formula weight: 285.06; Space group: Monoclinic; Space group *C2/m*; Cell dimension: 8.0895(6)Å, 9.0090(7) Å, 6.7561(6)Å, 98.987(3); Volume: 486.33(7) $Å^3$; Z=2;

8. Fingerprint plots for compounds [PTA-H]•[$GaCl_4$] (1), [PTA(O)-H]•[$GaCl_4$] (2) and [PTA(O)-H]•[I] (4)



(a) (b) (c)

Figure S34. (a) Fingerprint plot for [PTA-H]•[$GaCl_4$] (**1**), (b) with highlight of the $[PTA\text{-}H]^+$ with Cl atoms of neighbor anions and (c) with N atoms of neighbor cations.

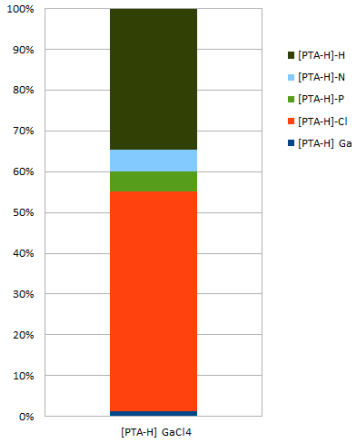


Figure S35. Percentage distribution of different interactions present in [PTA-H]•[$GaCl_4$] (**1**) as obtained from fingerprint plots.

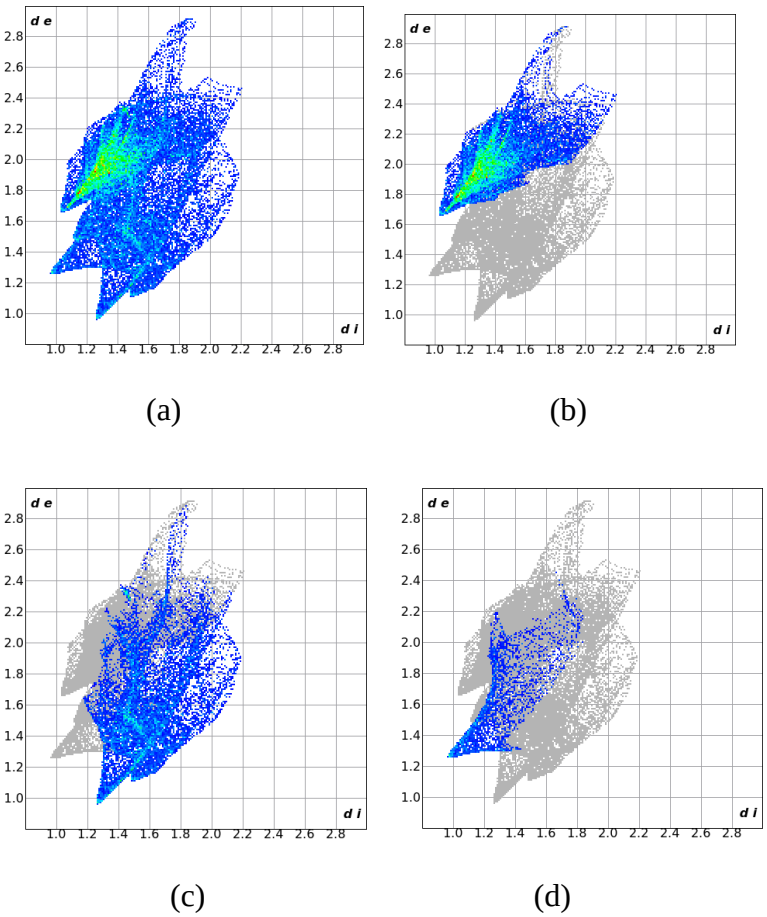


Figure S36. (a) Fingerprint plot for [PTA(O)-H]•[$GaCl_4$] (**2**), (b) with highlight of the $[PTA(O)-H]^+$ with Cl atoms of neighbor anions, (c) with H atoms of neighbor cations and (d) with O atoms of neighbor cations.

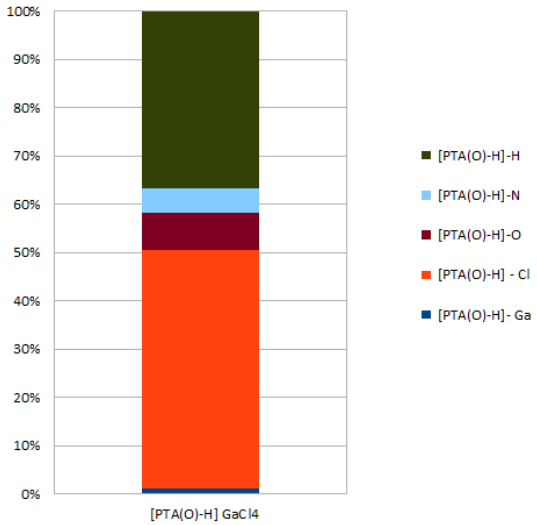


Figure S37. Percentage distribution of different interactions present in [PTA(O)-H]•[$GaCl_4$] (**2**), as obtained from fingerprint plots.

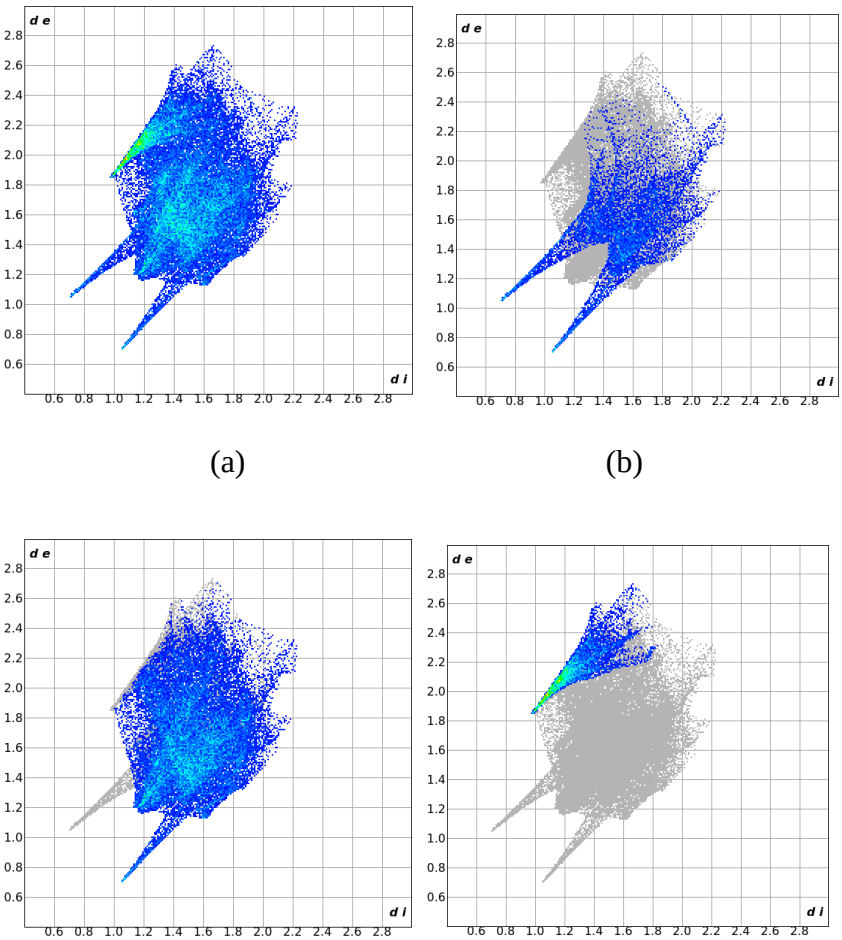


Figure S38. (a) Fingerprint plot for [PTA(O)-H]•[I] (**4**), (b) with highlight of the [PTA(O)-H]$^{+}$ with O atoms of neighbor cations, (c) with H atoms of neighbor cations and (d) with I atoms.

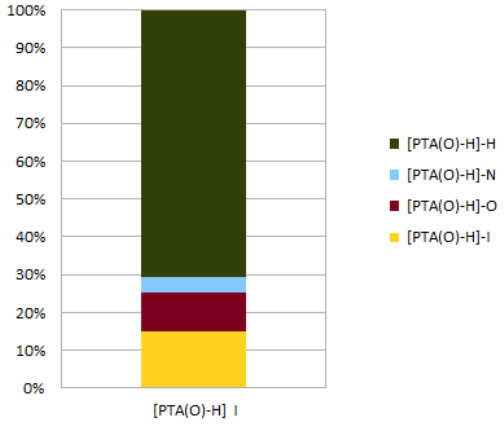


Figure S39. Percentage distribution of different interactions present in [PTA(O)-H]•[I] (**4**) as obtained from fingerprint plots.

9. DFT calculations and cartesian coordinates of optimized compounds

Table S3. Free energy values calculated by DFT for the formation of [(PTA)GaX_3] and [(PTA-H)GaX_3] coordination compounds (X= Br or I).

Ga-phosphine-halide adduct formation			Calculated free energy (kcal/mol)
PTA + $GaBr_3$	→	[(PTA)$GaBr_3$]	ΔG = – 15.4
(PTA-H) + $GaBr_3$	→	[(PTA-H)$GaBr_3$]	ΔG = + 2.0
PTA + GaI_3	→	[(PTA)GaI_3]	ΔG = – 13.4
(PTA-H) + GaI_3	→	[(PTA-H)GaI_3]	ΔG = + 3.5

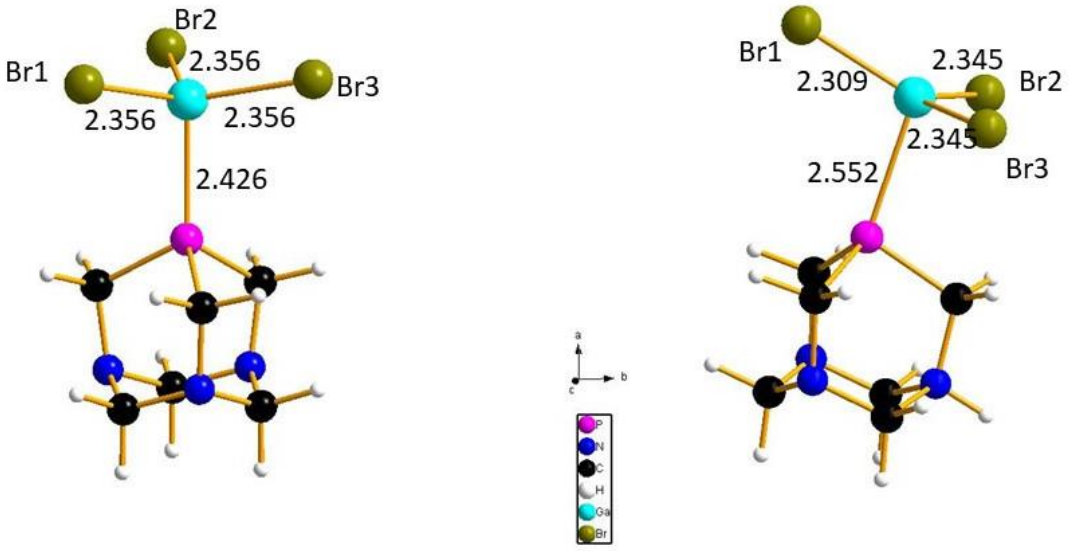


Figure S40. Optimized structures of [(PTA)$GaBr_3$] (left) and [(PTA-H)$GaBr_3$] (right) coordination complexes.

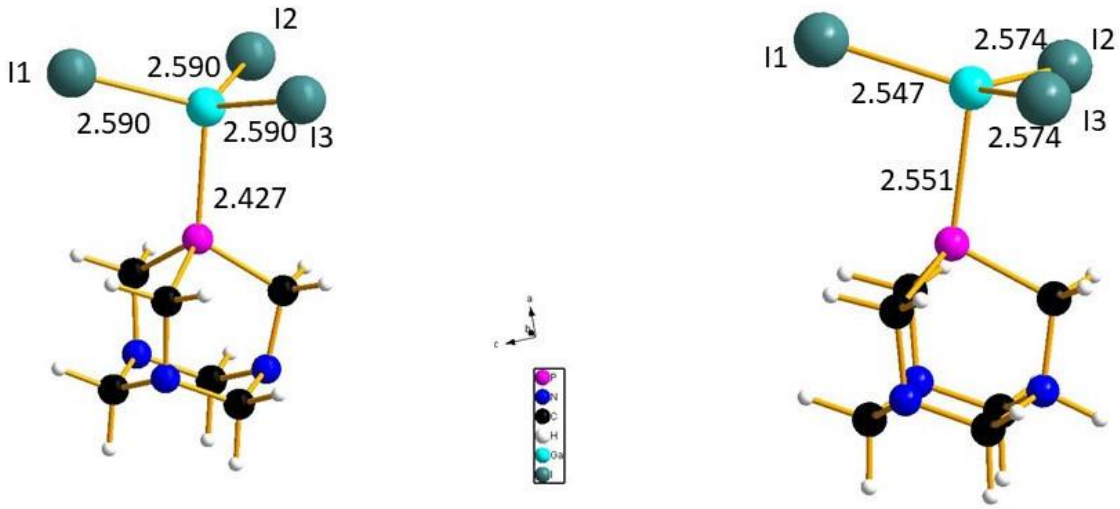


Figure S41. Optimized structures of [(PTA)GaI_3] (left) and [(PTA-H)GaI_3] (right) coordination complexes.

Cartesian coordinates of optimized compounds

Structure: [(PTA)$GaCl_3$]

List	Sy	X	Y	Z
1	P	8.182895	2.068498	9.410750
2	N	5.546024	2.068465	8.599119
3	N	6.062474	3.302298	10.673158
4	C	6.900255	2.068571	8.036443
5	H	7.047397	2.951819	7.406761
6	C	7.495922	3.491840	10.428647
7	H	8.036724	3.548803	11.378683
8	H	7.666727	4.431811	9.894265
9	C	5.288830	3.266594	9.418734
10	H	5.511013	4.162132	8.830620
11	H	4.225258	3.277876	9.676820
12	C	5.790704	2.068255	11.432493
13	H	6.388009	2.068244	12.349254
14	H	4.731965	2.068111	11.709969
15	N	6.062774	0.834412	10.672962
16	H	7.047425	1.185427	7.406620
17	C	7.496214	0.645060	10.428696
18	H	8.036941	0.588316	11.378789
19	H	7.667254	-0.294918	9.894404
20	C	5.289182	0.870139	9.418519
21	H	5.511679	-0.025257	8.830311
22	H	4.225604	0.858508	9.676573
23	Ga	10.540971	2.068150	8.825784
24	Cl	11.532996	2.068156	10.793151
25	Cl	10.759333	3.928137	7.665147
26	Cl	10.758496	0.207654	7.665778

Sum of electronic and thermal Free Energies = -4044.892389

Structure: **[(PTA-H)$GaCl_3$]$^+$**

List	Sy	X	Y	Z
1	P	8.255600	2.068581	9.621578
2	N	5.665944	2.068423	8.560982
3	N	6.005499	3.287925	10.669565
4	C	7.116355	2.068555	8.133353
5	H	7.306561	2.955235	7.521713
6	C	7.459843	3.491438	10.555984
7	H	7.897399	3.559870	11.555841
8	H	7.672415	4.433829	10.042306
9	C	5.322715	3.331817	9.420764
10	H	5.604847	4.204245	8.827339
11	H	4.239237	3.306854	9.562528
12	C	5.653102	2.068249	11.417848
13	H	6.173310	2.068237	12.377004
14	H	4.576017	2.068141	11.608078
15	N	6.005720	0.848736	10.669406
16	H	7.306706	1.181938	7.521667
17	C	7.460091	0.645501	10.555823
18	H	7.897642	0.577043	11.555680
19	H	7.672860	-0.296785	10.042037
20	C	5.322926	0.804866	9.420626
21	H	5.605186	-0.067448	8.827095
22	H	4.239446	0.829656	9.562406
23	Ga	10.617829	2.068181	8.639738
24	Cl	11.939611	2.068355	10.345444
25	Cl	10.297926	3.917865	7.507160
26	Cl	10.297205	0.217878	7.508297
27	H	5.073664	2.068420	7.723074

Sum of electronic and thermal Free Energies = -4045.226342

Structure: $GaCl_3$

List	Sy	X	Y	Z
1	Ga	11.295878	2.068494	8.866983
2	Cl	11.572200	2.068070	10.993460
3	Cl	11.176657	3.925312	7.801023
4	Cl	11.138684	0.211525	7.806140

Sum of electronic and thermal Free Energies = -3303.577082

Structure: PTA

List	Sy	X	Y	Z
1	P	8.166901	2.068350	9.238069
2	N	5.385984	2.068350	8.633901
3	N	6.040225	3.303213	10.669997
4	C	6.717560	2.068350	8.007989
5	H	6.805866	2.948044	7.359140
6	C	7.459315	3.466761	10.314029
7	H	8.050347	3.538530	11.234860
8	H	7.585233	4.418290	9.783580
9	C	5.186529	3.261878	9.472187
10	H	5.368219	4.158308	8.869918
11	H	4.140763	3.274344	9.800255
12	C	5.819072	2.068350	11.440631
13	H	6.476884	2.068350	12.316086
14	H	4.780251	2.068350	11.790237
15	N	6.040225	0.833487	10.669997
16	H	6.805866	1.188656	7.359140
17	C	7.459315	0.669939	10.314029
18	H	8.050347	0.598170	11.234860
19	H	7.585233	-0.281590	9.783580
20	C	5.186529	0.874822	9.472187
21	H	5.368219	-0.021608	8.869918
22	H	4.140763	0.862356	9.800255

Sum of electronic and thermal Free Energies = -741.289873

Structure: [PTA-H]$^+$

List	Sy	X	Y	Z
1	P	8.281376	2.068631	9.394403
2	N	5.542248	2.068392	8.587083
3	N	6.058535	3.287980	10.656538
4	C	6.958255	2.068561	8.040119
5	H	7.068747	2.953429	7.406345
6	C	7.500461	3.470363	10.402231
7	H	8.020572	3.542266	11.362240
8	H	7.659341	4.423539	9.887250
9	C	5.272642	3.327957	9.472666
10	H	5.501632	4.200981	8.857112
11	H	4.204201	3.301506	9.704334
12	C	5.771000	2.068281	11.429191
13	H	6.372744	2.068298	12.339460
14	H	4.713783	2.068160	11.712165
15	N	6.058781	0.848713	10.656423
16	H	7.068927	1.183774	7.406263
17	C	7.500745	0.666646	10.402097
18	H	8.020870	0.594753	11.362099
19	H	7.659817	-0.286447	9.887023
20	C	5.272897	0.808690	9.472546
21	H	5.502062	-0.064230	8.856909
22	H	4.204451	0.834904	9.704218
23	H	4.879766	2.068362	7.804763

Sum of electronic and thermal Free Energies = -741.652745

Structure: PMe_3

List	Sy	X	Y	Z
1	P	6.741960	2.629722	5.537495
2	C	7.692366	2.634456	7.143604
3	C	7.643278	3.998645	4.644831
4	C	7.538300	1.154973	4.716214
5	H	7.385713	1.778224	7.753406
6	H	7.455368	3.543060	7.706852
7	H	8.777849	2.587512	6.990539
8	H	7.307123	4.040147	3.603515
9	H	8.732211	3.864554	4.658586
10	H	7.401261	4.960520	5.108691
11	H	7.198385	1.086086	3.677581
12	H	7.227141	0.237976	5.227311
13	H	8.634151	1.209373	4.725607

Sum of electronic and thermal Free Energies = -461.029867

Structure: [(PMe_3)$GaCl_3$]

List	Sy	X	Y	Z
1	Ga	4.512339	2.626502	5.382949
2	Cl	3.941844	1.082566	6.852028
3	Cl	4.014841	4.693913	5.970871
4	Cl	4.051294	2.124092	3.284695
5	P	6.931158	2.592930	5.447126
6	C	7.588951	2.984442	7.113437
7	C	7.674829	3.809942	4.294587
8	C	7.616656	0.955233	4.988222
9	H	7.205607	2.254594	7.831609
10	H	7.241113	3.976754	7.412972
11	H	8.683151	2.963343	7.119453
12	H	7.344850	3.588257	3.276077
13	H	8.767831	3.777780	4.339956
14	H	7.327639	4.812723	4.557789
15	H	7.285912	0.697586	3.978458
16	H	7.233616	0.199091	5.678812
17	H	8.710468	0.962499	5.023960

Sum of electronic and thermal Free Energies = -3764.638447

Structure: [(PTA-H)AuCl]$^+$

List	Sy	X	Y	Z
1	Au	-0.019462	-0.031645	-0.076583
2	P	0.001160	-0.037657	2.201386
3	Cl	-0.041040	-0.025569	-2.398003
4	N	1.447010	-0.073508	4.568194
5	N	-0.715803	-1.262823	4.584184
6	N	-0.664327	1.205059	4.590000
7	C	1.644616	-0.074177	3.113162
8	C	-0.837909	-1.439143	3.131603
9	C	-0.778455	1.393315	3.138182
10	C	0.742277	1.137617	5.024642
11	C	0.692275	-1.256289	5.018870
12	C	-1.355743	-0.016086	5.040127
13	H	2.202669	-0.967530	2.813240
14	H	2.239650	0.796393	2.817407
15	H	-1.895166	-1.476749	2.848339
16	H	-0.386213	-2.390894	2.832318
17	H	-1.833065	1.476937	2.854923
18	H	-0.286893	2.326614	2.843610
19	H	0.759266	1.146994	6.119227
20	H	1.274924	2.023251	4.664414
21	H	0.708758	-1.271553	6.113402
22	H	1.187427	-2.161721	4.654393
23	H	-1.360273	-0.018538	6.134878
24	H	-2.392960	0.006326	4.691555

Sum of electronic and thermal Free Energies = -1337.366403

Structure: [(PTA)AuCl]

List	Sy	X	Y	Z	
1	Au	0.028406	-0.031110	-0.074144	
2	P	-0.058610	-0.034736	2.181664	
3	Cl	0.142774	-0.027622	-2.355251	
4	N	1.465916	-0.066752	4.537241	
5	N	-0.691346	-1.247497	4.589483	
6	N	-0.648224	1.189379	4.594733	
7	C	1.617808	-0.066211	3.030591	
8	C	-0.851342	-1.441656	3.137429	
9	C	-0.801050	1.395271	3.143526	
10	C	0.704478	1.209352	5.035458	
11	C	0.659759	-1.317240	5.030002	
12	C	-1.340363	-0.018272	5.078052	
13	H	2.172580	-0.961605	2.736223	
14	H	2.203818	0.810317	2.740000	
15	H	-1.915848	-1.489131	2.890602	
16	H	-0.407531	-2.394531	2.832970	
17	H	-1.863155	1.481630	2.896898	
18	H	-0.323603	2.333068	2.843134	
19	H	0.766042	1.180632	6.126411	
20	H	1.251038	2.073402	4.651015	
21	H	0.722210	-1.295412	6.121073	
22	H	1.175425	-2.198435	4.641817	
23	H	-1.327981	-0.020813	6.171792	
24	H	-2.379062	0.000864	4.744469	
25	H	2.397737	-0.084182	4.967280	

Sum of electronic and thermal Free Energies = -1337.701678

Structure: AuCl

List	Sy	X	Y	Z
1	Au	-0.000101	-0.000566	-0.007836
2	Cl	-0.029410	-0.165533	-2.290013

Sum of electronic and thermal Free Energies = -596.006313

Structure: [(PTA)$GaBr_3$]

List	Sy	X	Y	Z
1	P	8.184112	2.067787	9.410456
2	N	5.548026	2.068461	8.598468
3	N	6.064604	3.301871	10.672740
4	C	6.902385	2.068550	8.035697
5	H	7.050153	2.952032	7.406512
6	C	7.498353	3.491021	10.428839
7	H	8.039190	3.546855	11.378884
8	H	7.669843	4.431003	9.894761
9	C	5.291417	3.266562	9.418107
10	H	5.514144	4.162074	8.830174
11	H	4.227775	3.278289	9.676054
12	C	5.792269	2.067889	11.431961
13	H	6.389245	2.067691	12.348939
14	H	4.733406	2.068145	11.709086
15	N	6.063936	0.833768	10.672611
16	H	7.049933	1.185444	7.405968
17	C	7.497667	0.644279	10.427939
18	H	8.038746	0.587291	11.377774
19	H	7.668850	-0.295231	9.892935
20	C	5.290896	0.870134	9.417863
21	H	5.513038	-0.025234	8.829462
22	H	4.227261	0.858897	9.675790
23	Ga	10.538060	2.066295	8.824677
24	Br	11.586802	2.068906	10.934710
25	Br	10.755483	4.056245	7.581913
26	Br	10.751567	0.071173	7.589213

Sum of electronic and thermal Free Energies= -10378.549655

Structure: $[(PTA\text{-}H)GaBr_3]^+$

List	Sy	X	Y	Z
1	P	8.254296	2.067473	9.601444
2	N	5.656605	2.068124	8.560322
3	N	6.011694	3.288033	10.666329
4	C	7.103434	2.067715	8.122129
5	H	7.291000	2.954590	7.509967
6	C	7.465805	3.490018	10.541661
7	H	7.910676	3.558421	11.538267
8	H	7.675439	4.431897	10.025952
9	C	5.320180	3.331707	9.422537
10	H	5.598321	4.203887	8.826895
11	H	4.237696	3.306908	9.571950
12	C	5.664263	2.068345	11.416890
13	H	6.191490	2.068242	12.372187
14	H	4.588515	2.068701	11.614746
15	N	6.010932	0.848346	10.666491
16	H	7.290541	1.180664	7.510075
17	C	7.464936	0.645490	10.541768
18	H	7.909787	0.576845	11.538363
19	H	7.673996	-0.296525	10.026071
20	C	5.319408	0.804891	9.422693
21	H	5.597047	-0.067563	8.827212
22	H	4.236941	0.830320	9.572114
23	Ga	10.627102	2.066155	8.660602
24	Br	11.979459	2.066638	10.532493
25	Br	10.317159	4.051627	7.451887
26	Br	10.315346	0.079497	7.454242
27	H	5.057679	2.068257	7.727133

Sum of electronic and thermal Free Energies = -10378.885441

Structure: $GaBr_3$

List	Sy	X	Y	Z
1	Ga	10.919105	2.062481	8.728915
2	Br	11.469815	2.066009	10.957160
3	Br	10.643832	4.051809	7.617537
4	Br	10.643137	0.074894	7.615333

Sum of electronic and thermal Free Energies = -9637.235923

Structure: $[(PTA\text{-}H)GaI_3]^+$

List	Sy	X	Y	Z
1	P	8.195107	1.956202	9.341875
2	N	5.523522	2.076878	8.627040
3	N	6.134730	3.315230	10.662736
4	C	6.863100	2.015529	8.017264
5	H	7.025843	2.882734	7.370300
6	C	7.612545	3.421000	10.358145
7	H	8.165837	3.462616	11.300989
8	H	7.794966	4.349810	9.809645
9	C	5.280332	3.278772	9.350035
10	H	5.548482	4.167249	8.774183
11	H	4.238604	3.340300	9.675214
12	C	5.808541	2.015242	11.474018
13	H	6.441260	2.031647	12.364128
14	H	4.756445	2.101572	11.757504
15	N	6.033301	0.857452	10.676895
16	H	6.939104	1.122844	7.390317
17	C	7.457245	0.594295	10.406363
18	H	8.014315	0.518277	11.344972
19	H	7.560301	-0.363104	9.888202
20	C	5.214183	0.896085	9.452558
21	H	5.390436	-0.009473	8.870024
22	H	4.157685	0.927573	9.734030
23	Ga	10.688129	2.139975	8.831297
24	I	11.455578	2.208002	11.287145
25	I	10.540321	4.398882	7.606430
26	I	11.037343	0.011137	7.477306
27	H	5.851408	4.130260	11.218046

Sum of electronic and thermal Free Energies = -2698.895781

Structure: [(PTA)GaI_3]

List	Sy	X	Y	Z
1	P	8.183076	2.069361	9.410967
2	N	5.546149	2.068725	8.599483
3	N	6.061796	3.301785	10.673533
4	C	6.899513	2.068992	8.035596
5	H	7.047054	2.952428	7.406425
6	C	7.494972	3.493176	10.430179
7	H	8.035859	3.549198	11.380126
8	H	7.665727	4.432851	9.895400
9	C	5.288572	3.266772	9.418945
10	H	5.511498	4.162253	8.831139
11	H	4.224886	3.278202	9.676551
12	C	5.790157	2.067616	11.432726
13	H	6.387775	2.067346	12.349212
14	H	4.731445	2.067199	11.710321
15	N	6.062569	0.834542	10.672489
16	H	7.047398	1.185425	7.406631
17	C	7.495764	0.644361	10.429158
18	H	8.036603	0.588134	11.379119
19	H	7.666924	-0.294911	9.893892
20	C	5.288981	0.870091	9.418201
21	H	5.512034	-0.024973	8.829834
22	H	4.225370	0.858199	9.676179
23	Ga	10.539276	2.068059	8.825867
24	I	11.696122	2.069594	11.143044
25	I	10.785622	4.255002	7.460819
26	I	10.783177	-0.122384	7.465753

Sum of electronic and thermal Free Energies = -2698.559737

Structure: GaI_3

List	Sy	X	Y	Z
1	Ga	10.948811	2.067460	8.724513
2	I	11.555432	2.069045	11.169916
3	I	10.648284	4.249995	7.502150
4	I	10.644524	-0.114461	7.502422

Sum of electronic and thermal Free Energies = -1957.248623