Electronic Supplementary Information

Synthesis of New Acyclic Chelators H_4aPyta and H_6aPyha and their Complexes with Cu^{2+}, Ga^{3+}, Y^{3+}, and Bi^{3+}

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Content

1. NMR and mass spectra of compounds

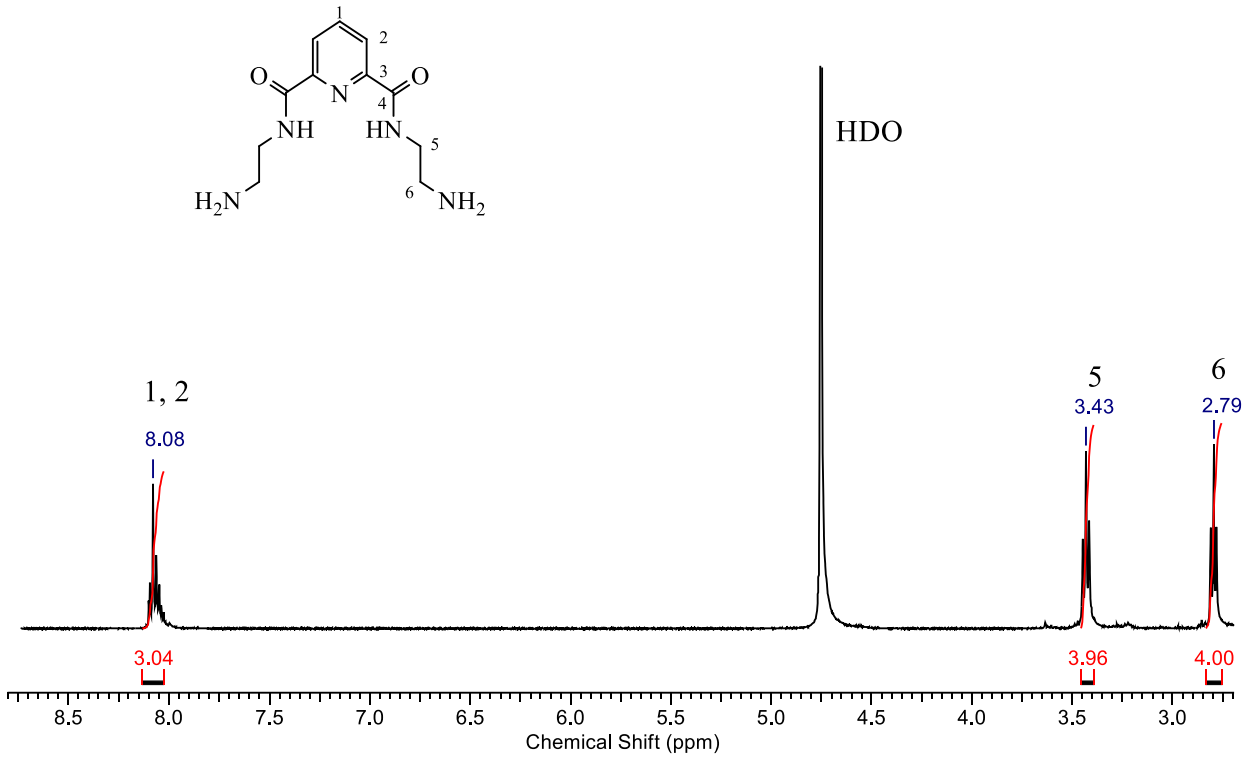


Figure S1. ^{1}H NMR spectrum of **2** in D_2O.

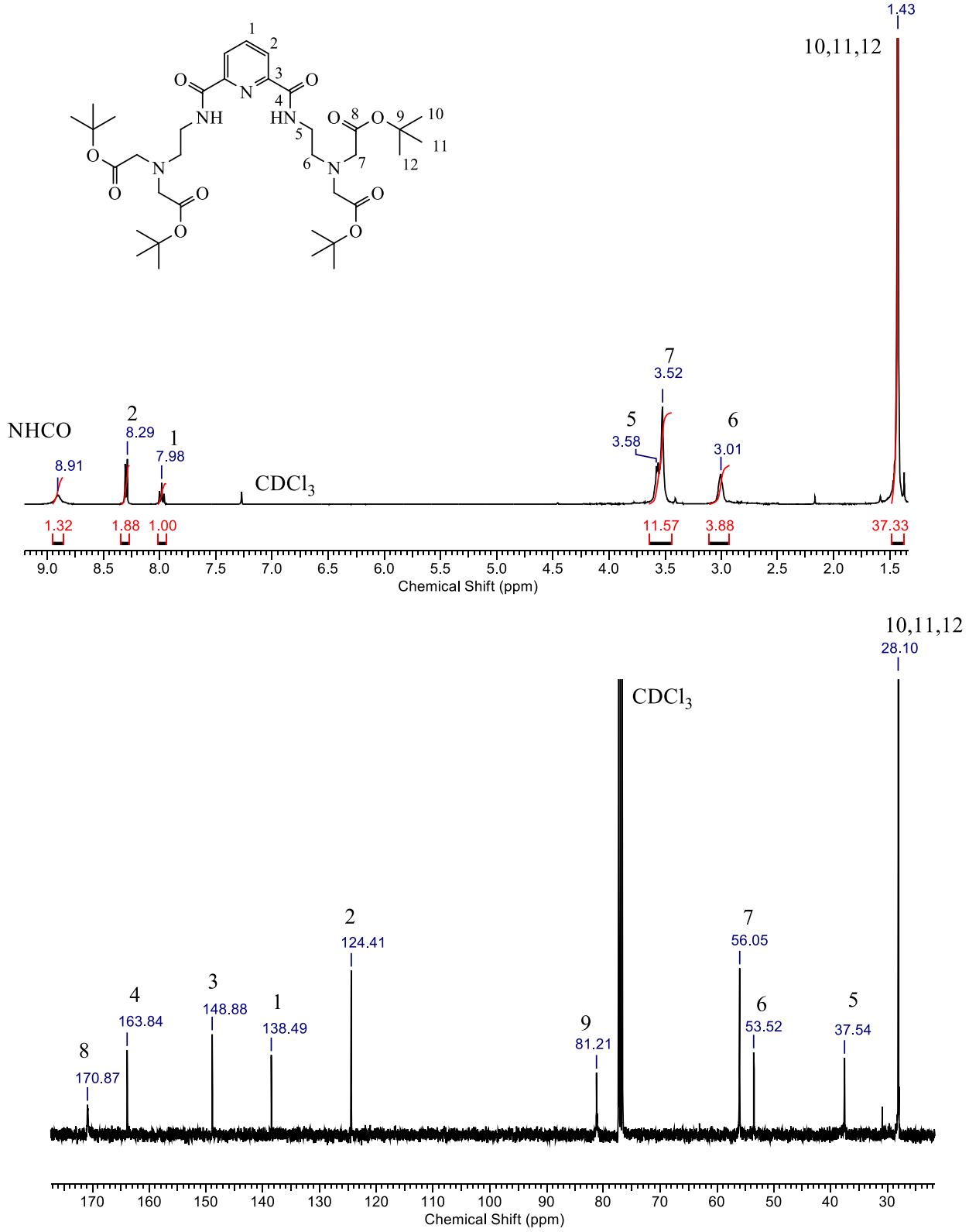


Figure S2. ^{1}H and ^{13}C NMR spectra of **3** in $CDCl_3$.

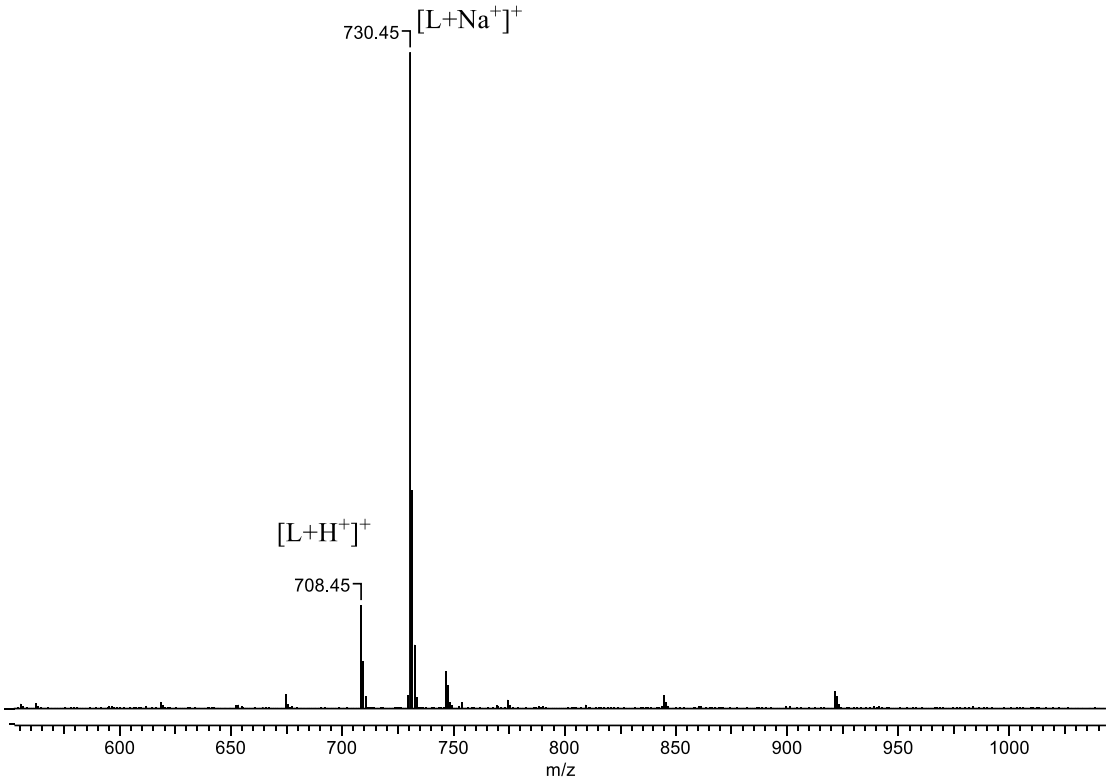


Figure S3. MS (ESI) spectrum of **3**.

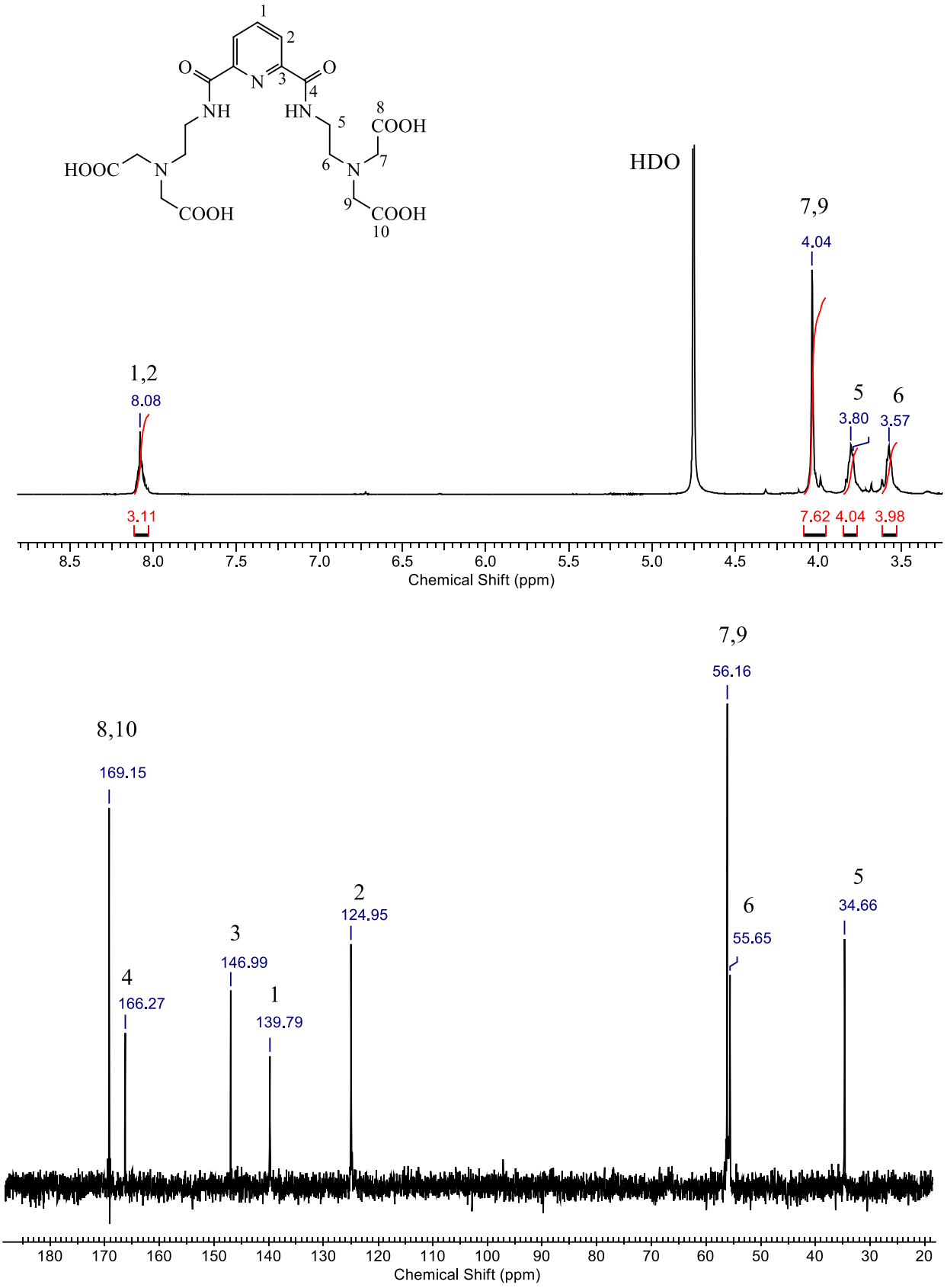


Figure S4. ^{1}H and ^{13}C NMR spectra of **H_4aPyta** in D_2O.

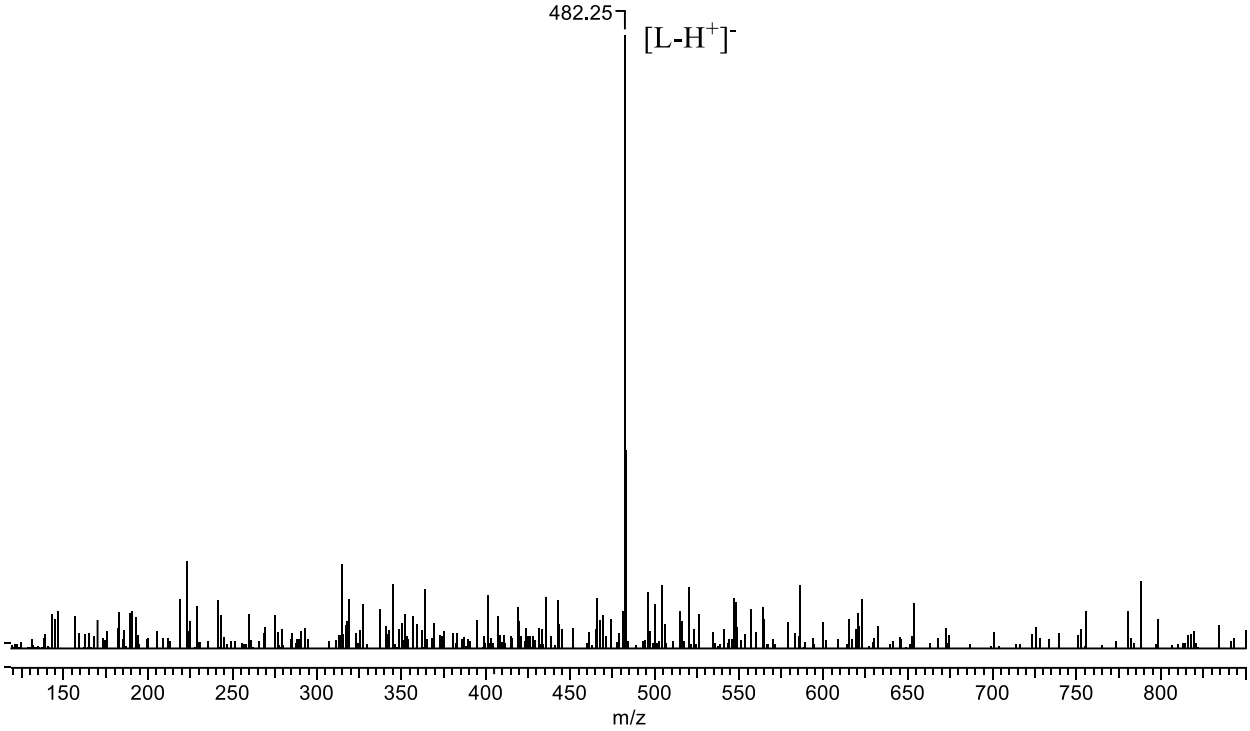


Figure S5. MS (ESI) spectrum of **H_4aPyta.**

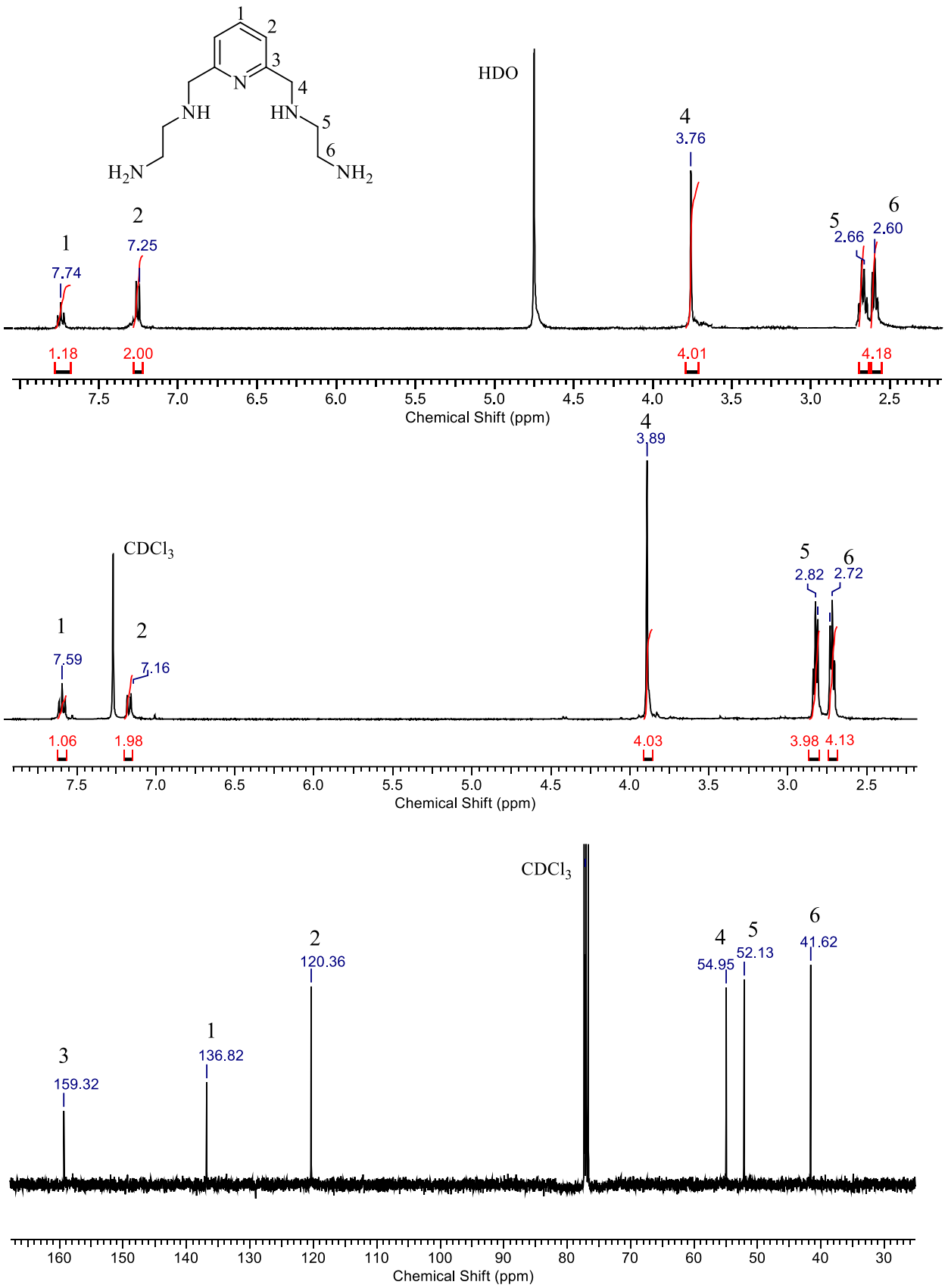


Figure S6. ^{1}H and ^{13}C NMR spectra of **5** in D_2O and $CDCl_3$.

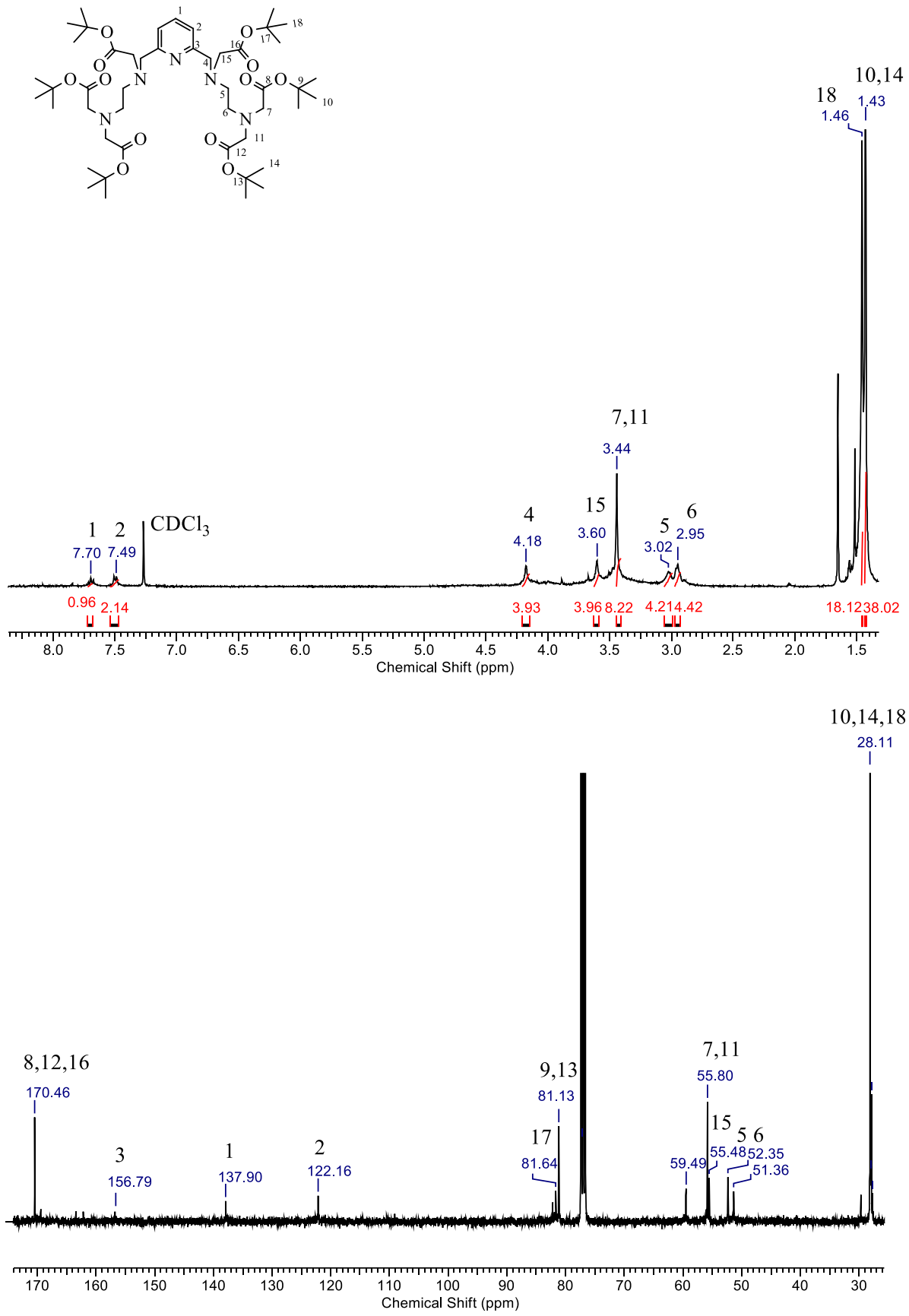


Figure S7. ^{1}H and ^{13}C NMR spectra of **6** in $CDCl_3$.

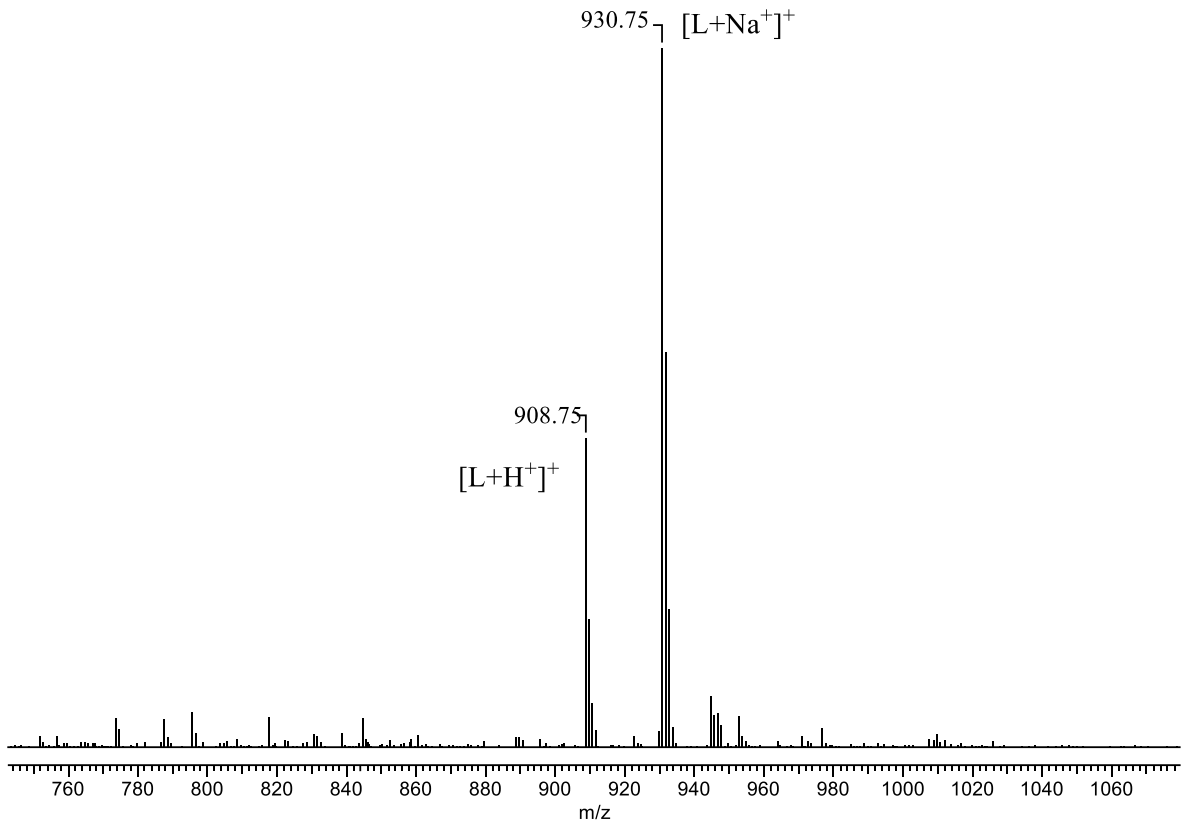


Figure S8. MS (ESI) spectrum of **6.**

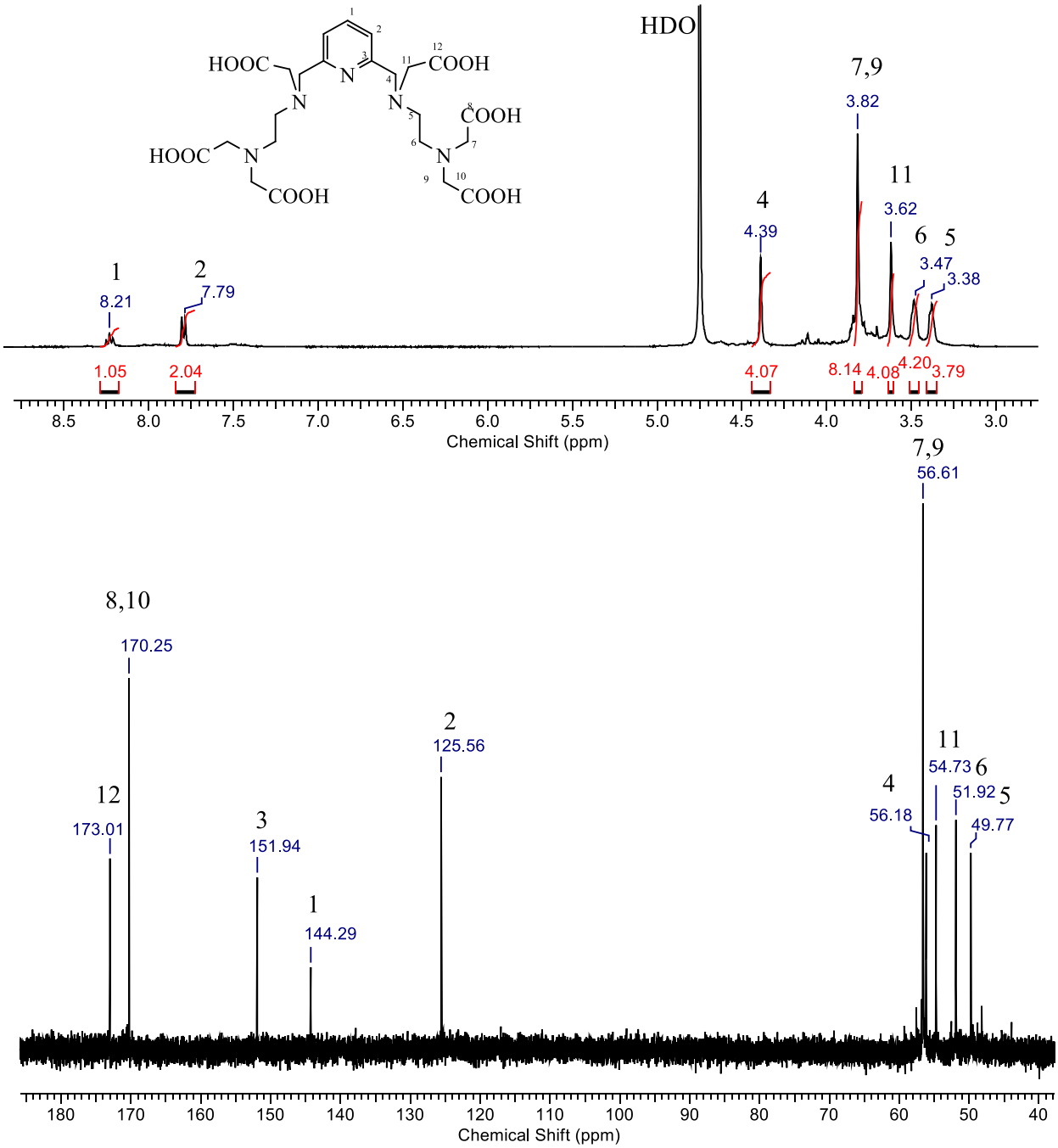


Figure S9. ^{1}H and ^{13}C NMR spectra of **H_6aPyha** in D_2O.

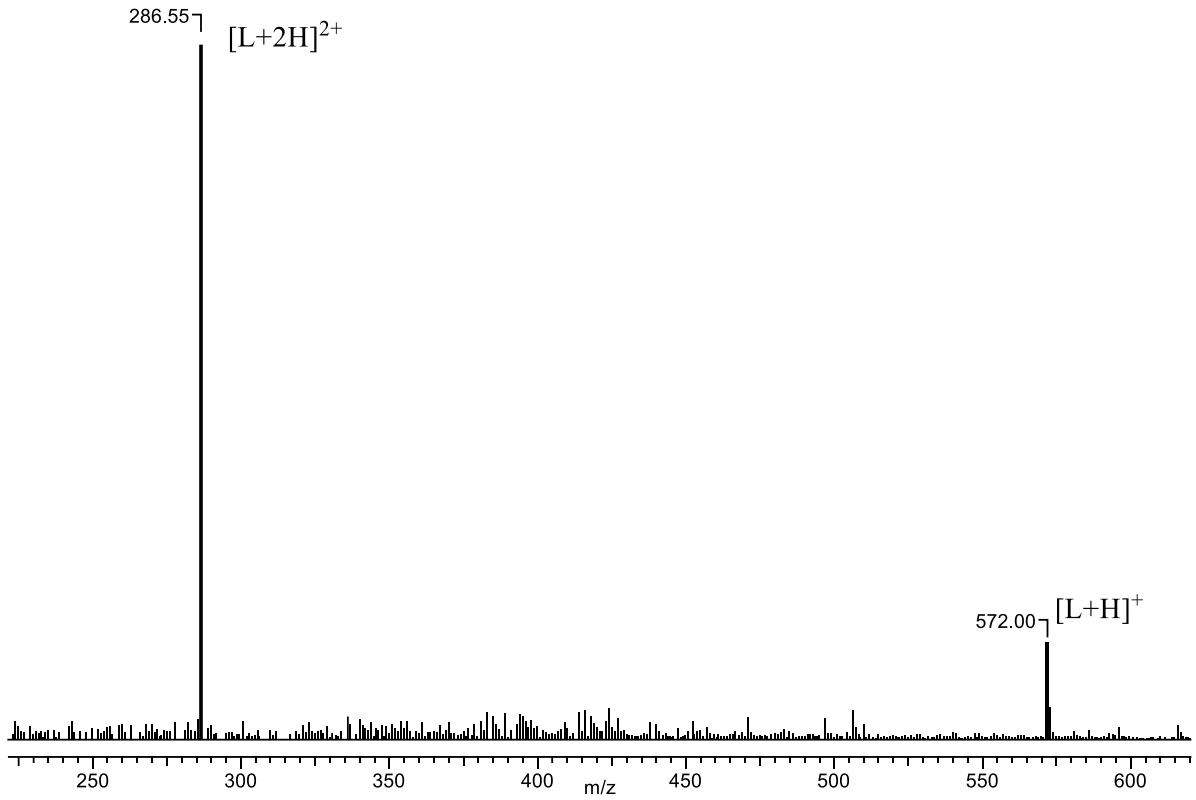


Figure S10. MS (ESI) spectrum of **H_6aPyha.**

2. Mass spectra of complexes

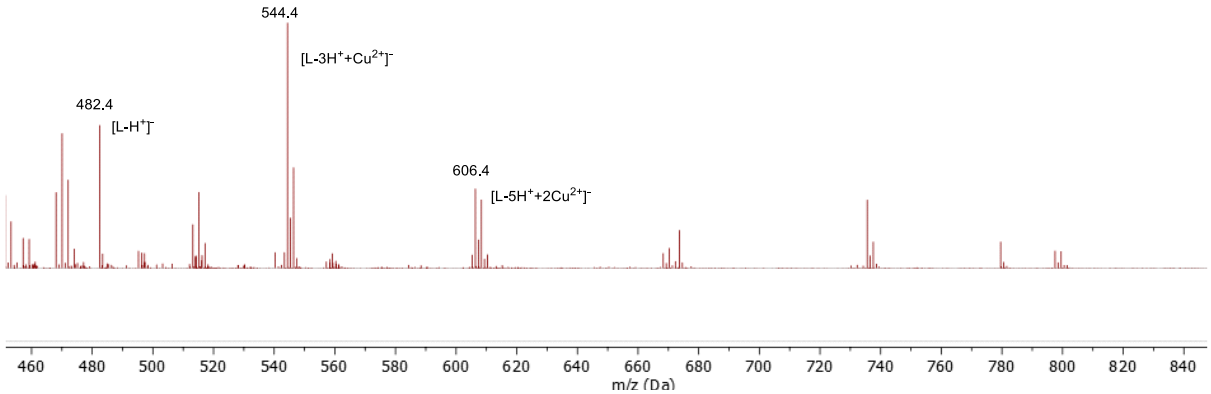


Fig. S11 MS (MALDI TOF) spectra of the ligand **H_4aPyta** in the presence of Cu^{2+}.

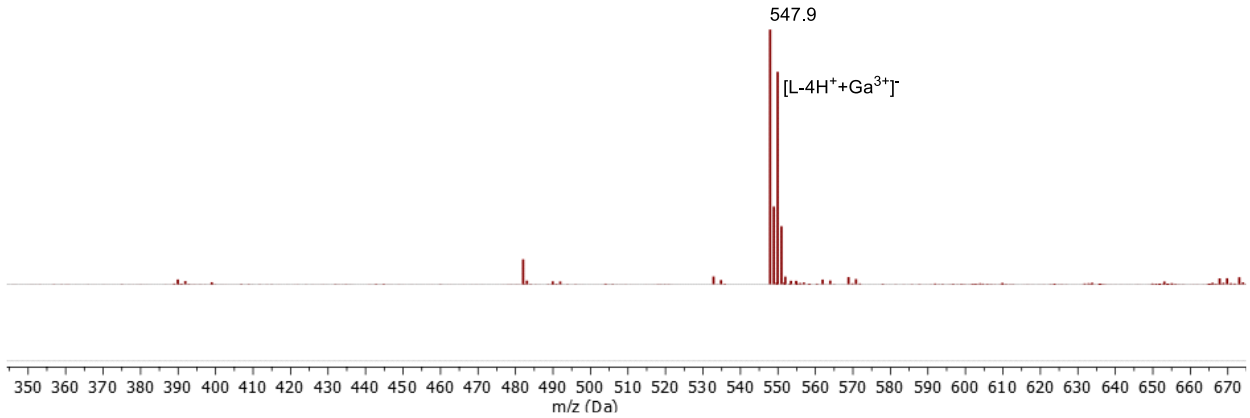


Fig. S12 MS (MALDI TOF) spectrum of the ligand **H_4aPyta** in the presence of Ga^{3+}.

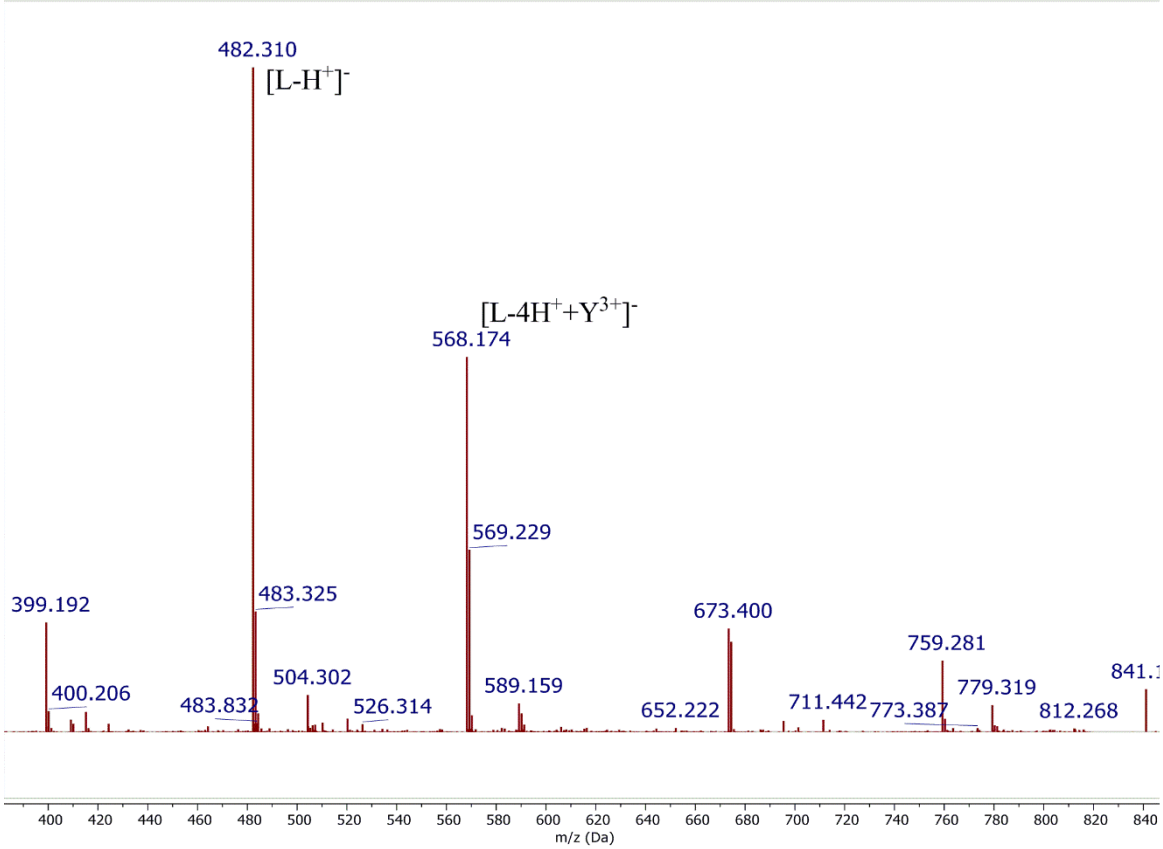


Figure S13. MS (MALDI TOF) spectrum of the ligand **H_4aPyta** in the presence of Y^{3+}.

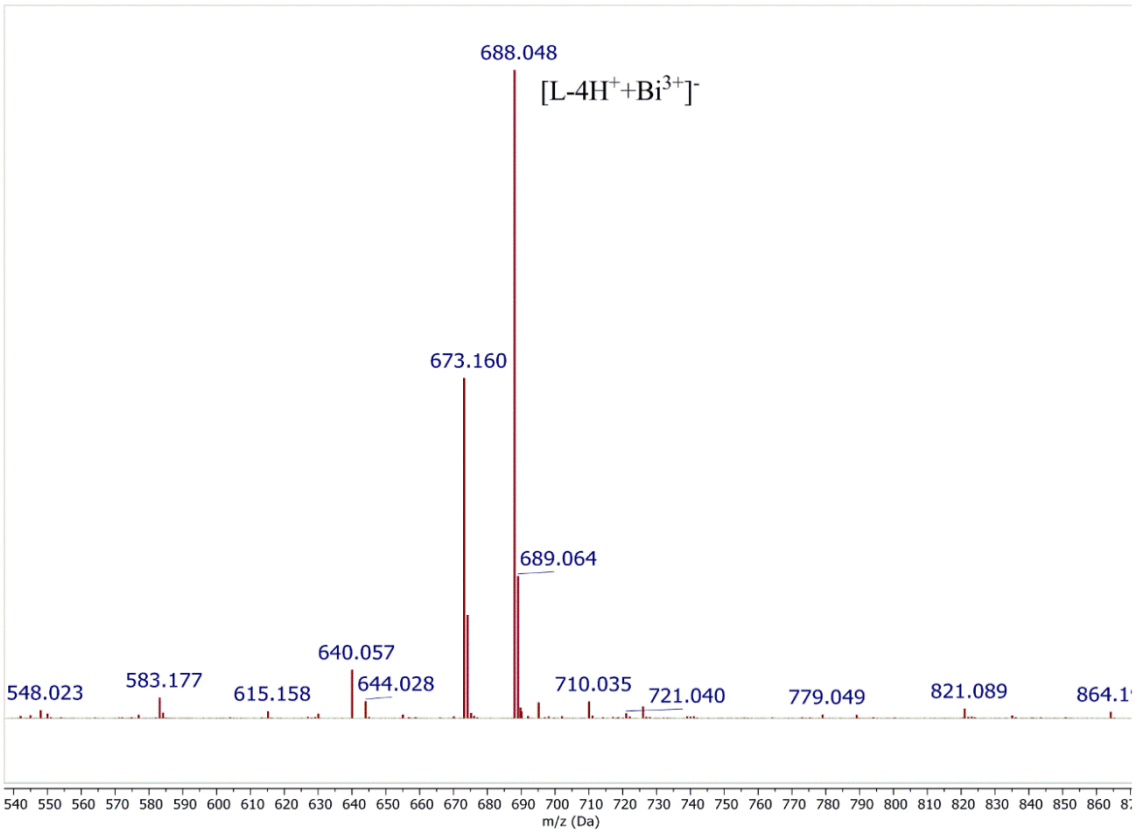


Figure S14. MS (MALDI TOF) spectrum of the ligand **H_4aPyta** in the presence of Bi^{3+}.

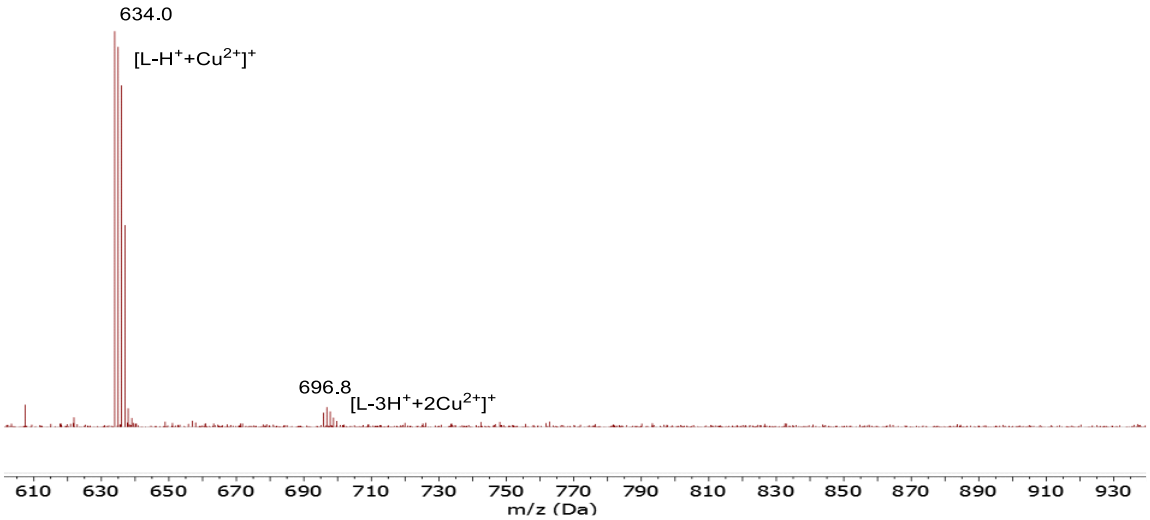


Fig. S15 MS (MALDI TOF) spectra of the ligand **H_6aPyha** in the presence of Cu^{2+}.

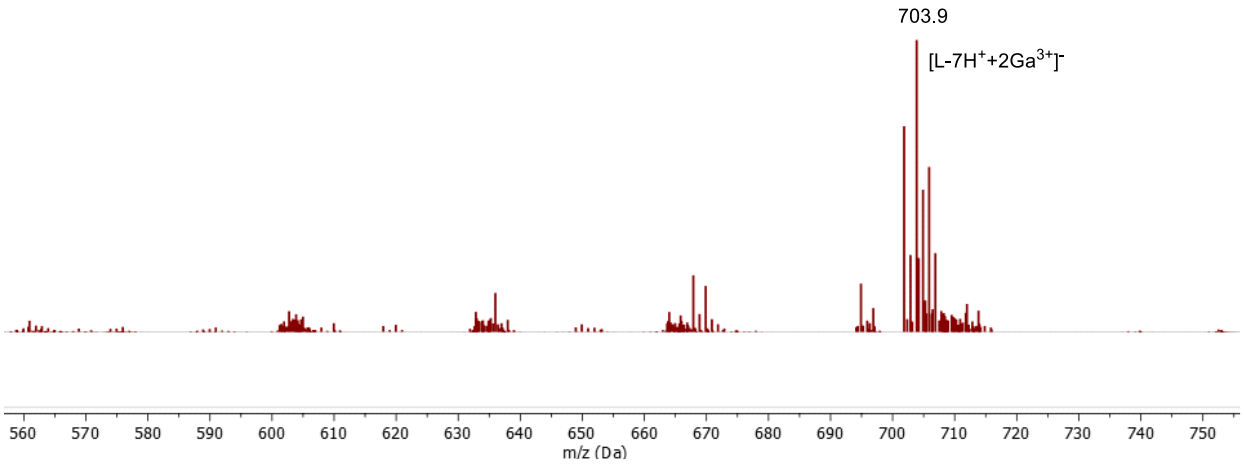


Fig. S16 MS (MALDI TOF) spectrum of the ligand **H_6aPyha** in the presence of Ga^{3+}.

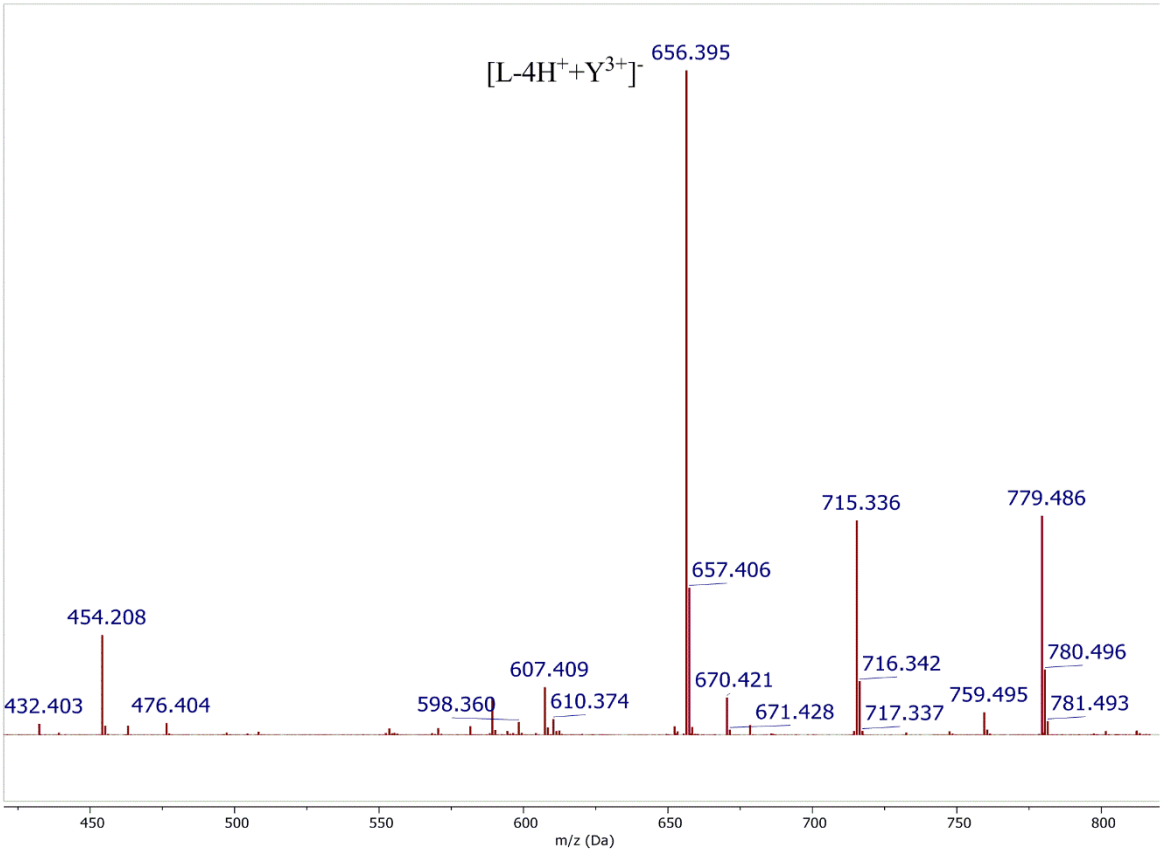


Figure S17. MS (MALDI TOF) spectrum of the ligand **H_6aPyha** in the presence of Y^{3+}.

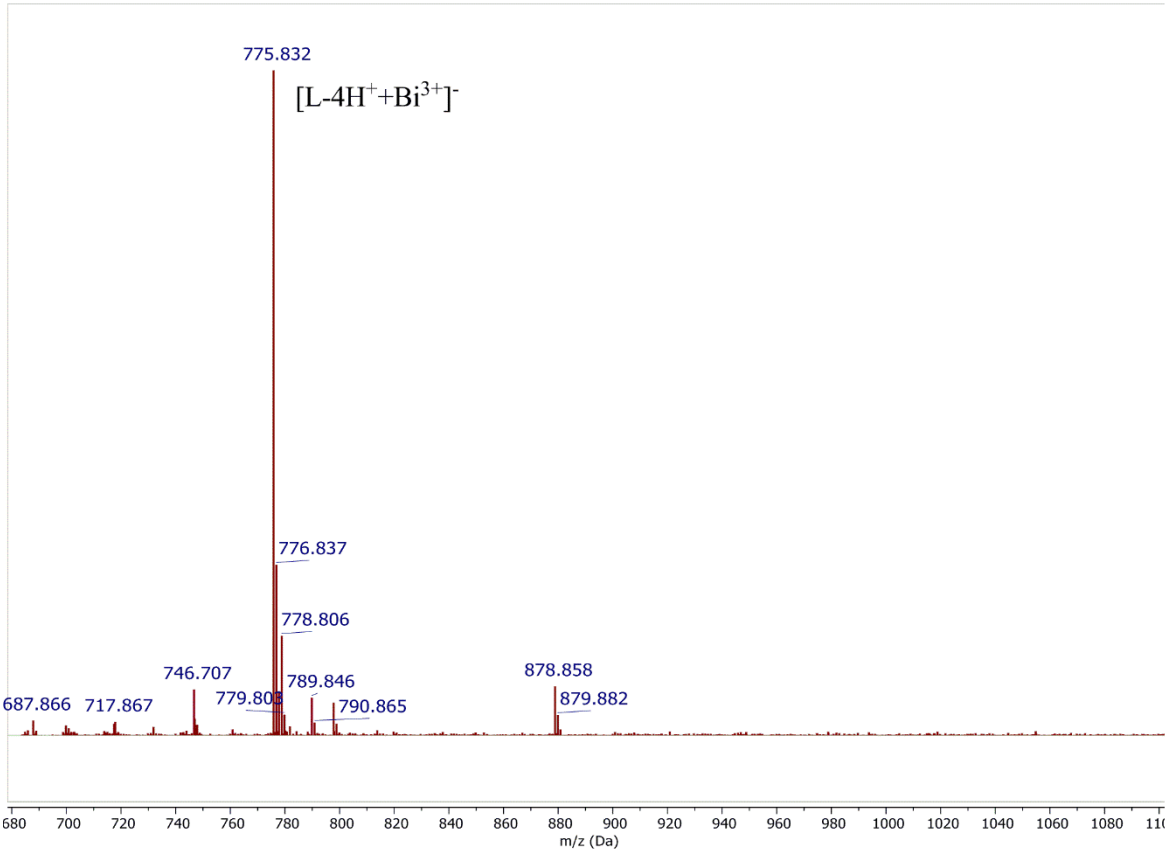


Figure S18. MS (MALDI TOF) spectrum of the ligand **H_6aPyha** in the presence of Bi^{3+}.

3. NMR study of ligand protonation and complex formation

Table S1. ^{1}H NMR (400 MHz, 298 K) chemical shifts ($\Delta\delta$, ppm) of the ligand **H_4aPyta** at different pH values in D_2O. See Figure 2 for proton labeling.

H_4aPyta	**pH**			
	12	**8.7**	**7.3**	**2.2**
H_1	8.09	8.11 ($\Delta\delta$ = 0.02)	8.14 ($\Delta\delta$ = 0.05)	8.15 ($\Delta\delta$ = 0.06)
H_2	8.14	8.17 ($\Delta\delta$ = 0.03)	8.18 ($\Delta\delta$ = 0.04)	8.19 ($\Delta\delta$ = 0.05)
H_5	3.47	3.66 ($\Delta\delta$ = 0.19)	3.84 ($\Delta\delta$ = 0.37)	3.87 ($\Delta\delta$ = 0.40)
H_6	2.82	3.24 ($\Delta\delta$ = 0.42)	3.54 ($\Delta\delta$ = 0.74)	3.62 ($\Delta\delta$ = 0.80)
$H_{7,9}$	3.24	3.59 ($\Delta\delta$ = 0.35)	3.84 ($\Delta\delta$ = 0.60)	4.04 ($\Delta\delta$ = 0.80)

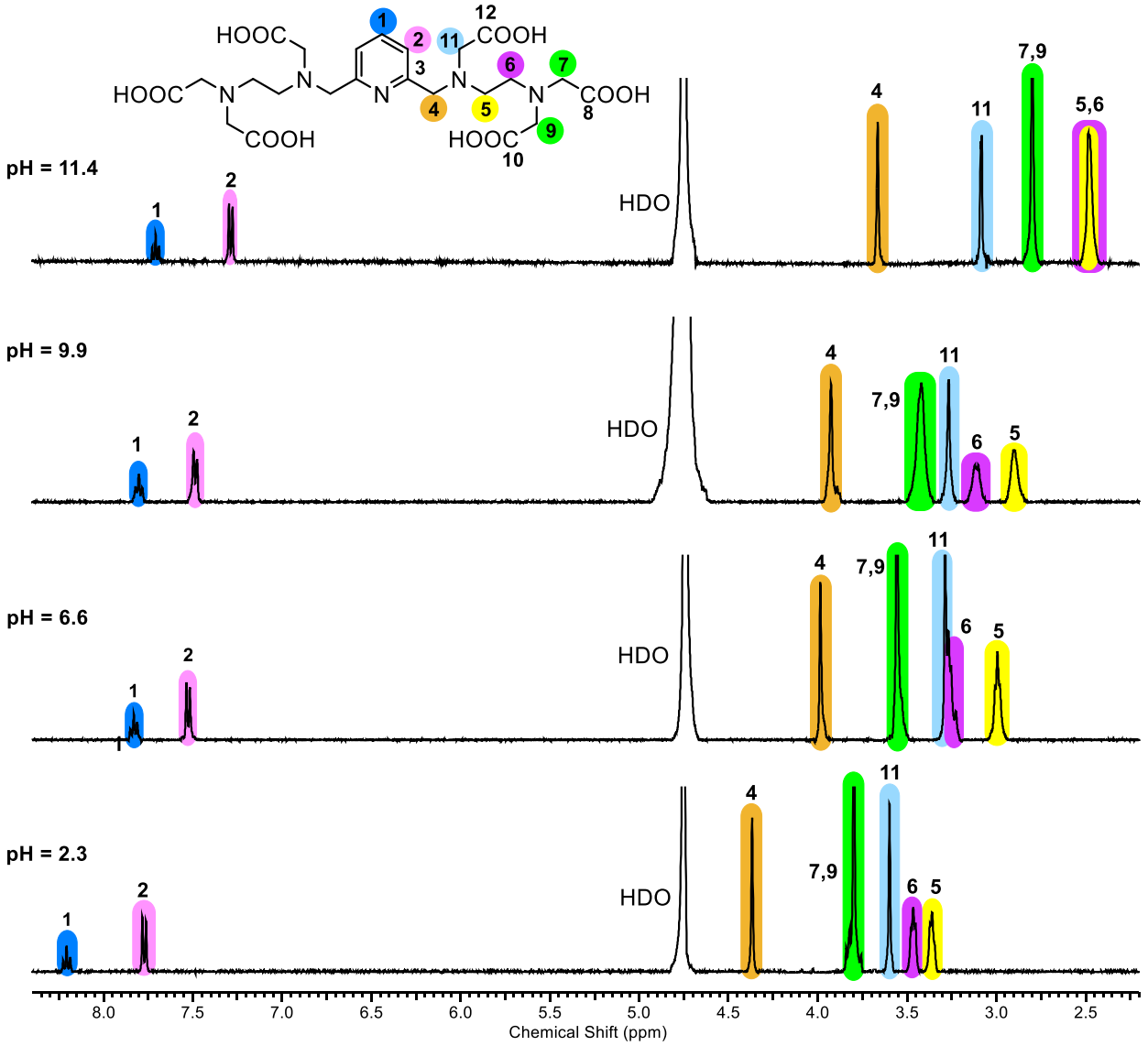


Figure S19. ^{1}H NMR spectra of the ligand **H_6aPyha** (C_L = 15 mM) at different pH values in D_2O.

Table S2. ^{1}H NMR (400 MHz, 298 K) chemical shifts (Δδ, ppm) of the ligand **H_6aPyha** at different pH values in D_2O. See Figure S19 for proton labeling.

H_6aPyha	**pH**			
	11.4	**9.9**	**6.6**	**2.3**
H_1	7.71	7.80 (Δδ = 0.09)	7.83 (Δδ = 0.12)	8.21 (Δδ = 0.50)
H_2	7.28	7.48 (Δδ = 0.20)	7.52 (Δδ = 0.24)	7.76 (Δδ = 0.48)
H_4	3.66	3.93 (Δδ = 0.27)	3.99 (Δδ = 0.33)	4.37 (Δδ = 0.71)
H_5	2.48	2.90 (Δδ = 0.42)	2.99 (Δδ = 0.51)	3.36 (Δδ = 0.88)
H_6	2.48	3.11 (Δδ = 0.63)	3.25 (Δδ = 0.77)	3.47 (Δδ = 0.99)
$H_{7,9}$	2.80	3.42 (Δδ = 0.62)	3.56 (Δδ = 0.76)	3.80 (Δδ = 1.00)
H_{11}	3.08	3.27 (Δδ = 0.19)	3.29 (Δδ = 0.21)	3.60 (Δδ = 0.52)

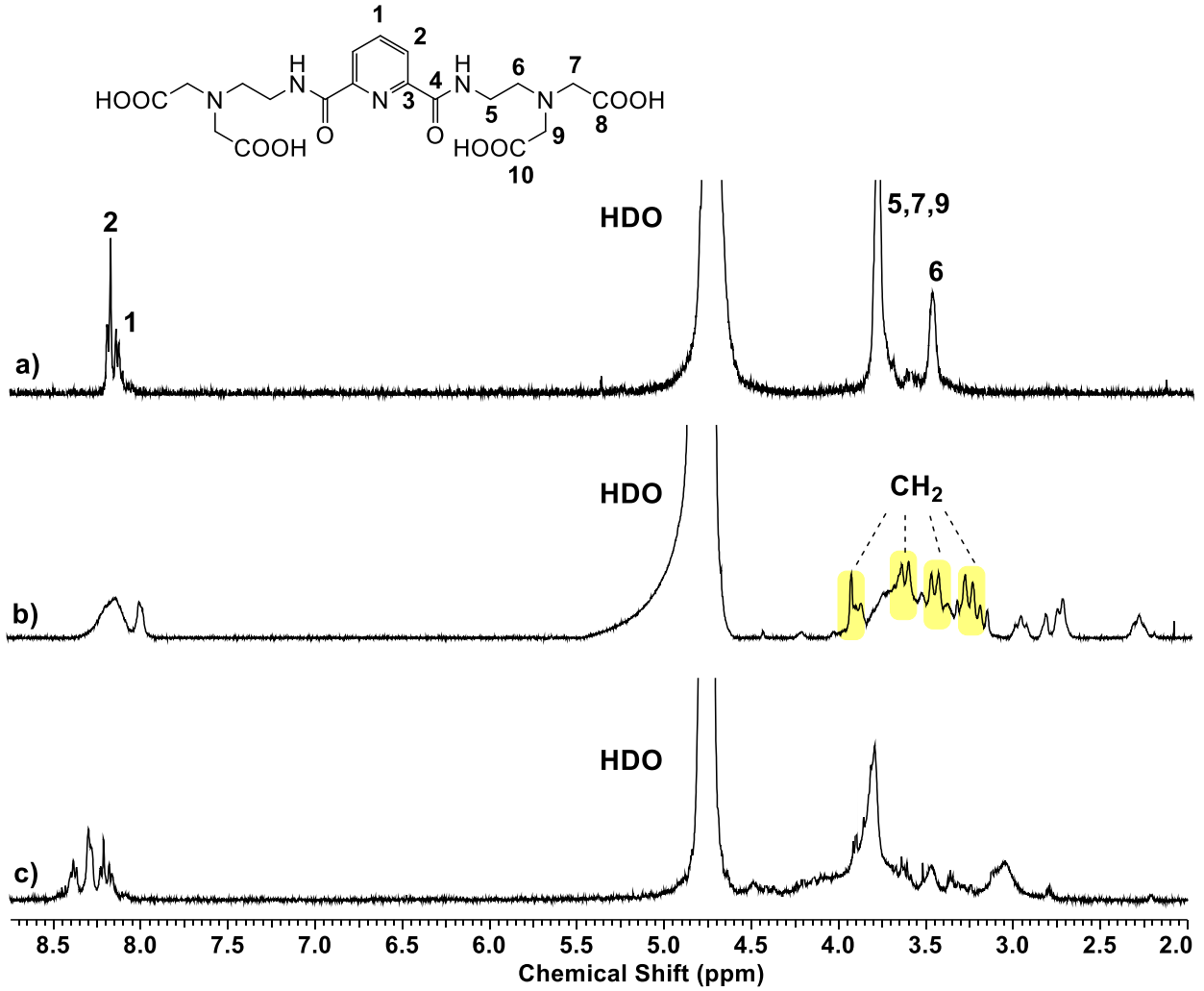


Figure S20. ^{1}H NMR spectra of: a) **H_4aPyta** (C_L = 10 mM, pH=7.1), b) **H_4aPyta** in the presence of Y^{3+} (pH=7.2), c) **H_4aPyta** in the presence of Bi^{3+} (pH=7.5) in D_2O.

4. HPLC of complexes

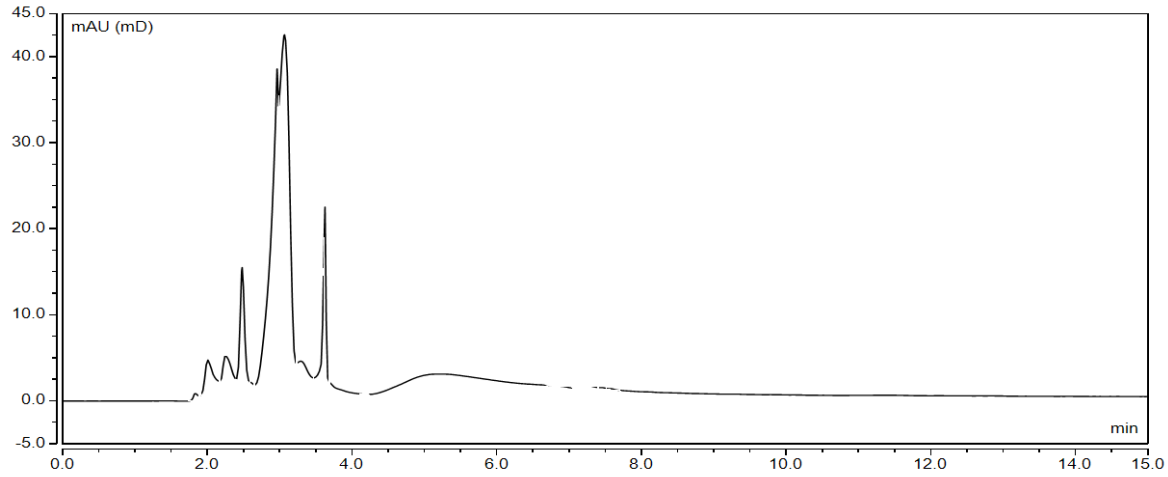


Figure S21. HPLC of **H_4aPyta** in the presence of Cu^{3+} (t_r=2.482, 3.067 min).

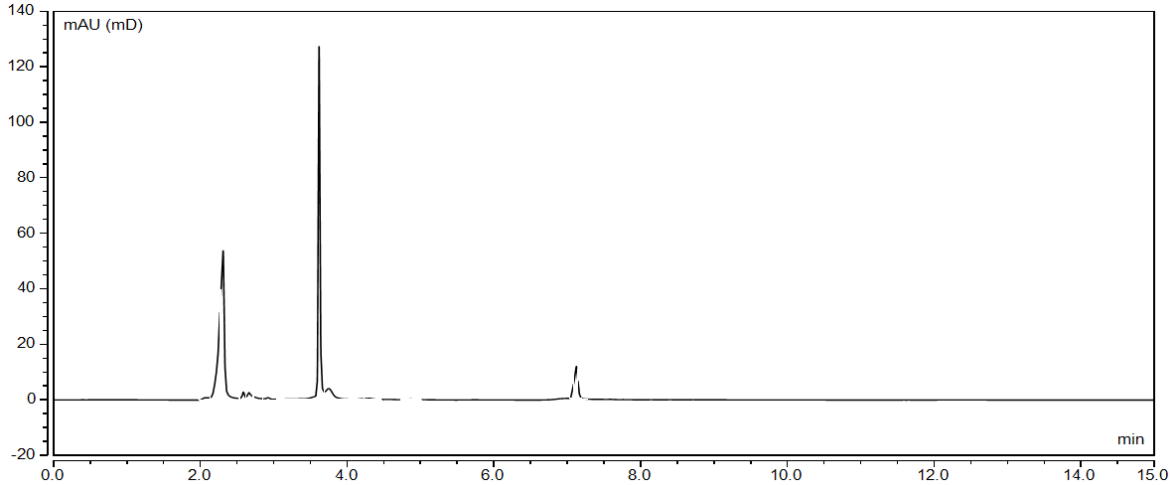


Figure S22. HPLC of **H_4aPyta** in the presence of Y^{3+} (t_r=2.310 min).

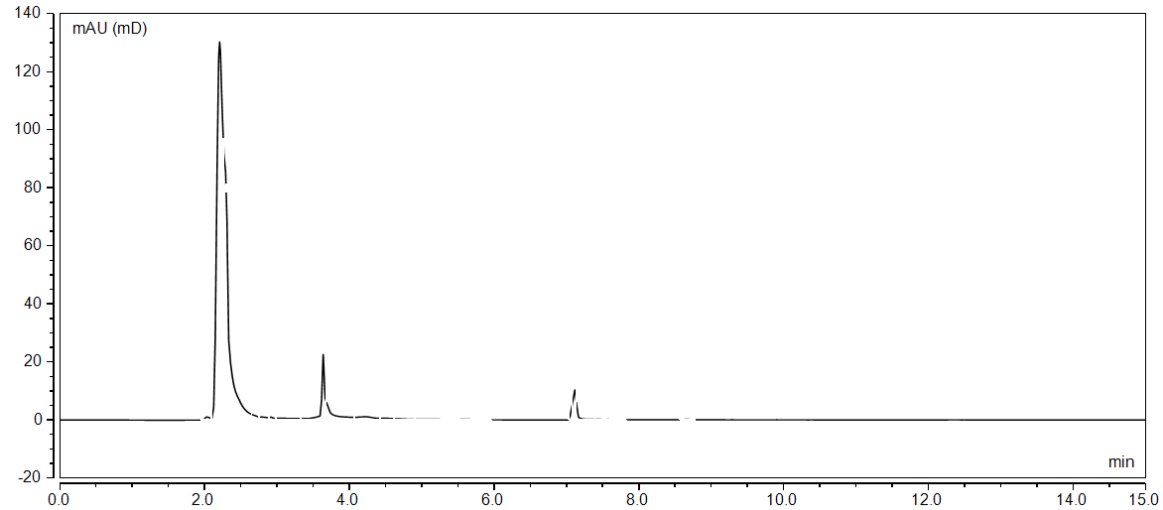


Figure S23. HPLC of **H_4aPyta** in the presence of Bi^{3+} (t_r=2.208 min).

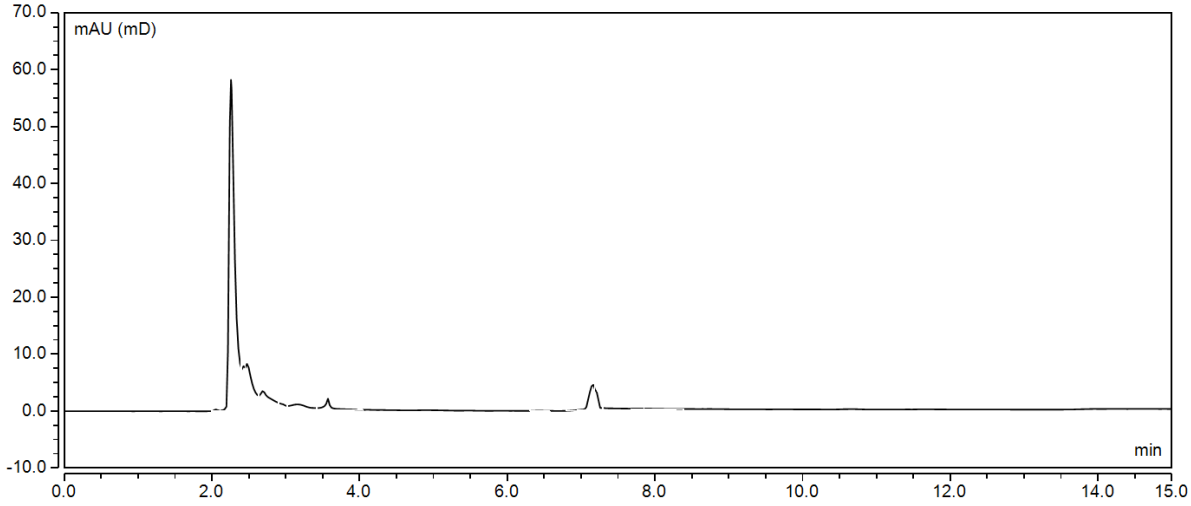


Figure S24. HPLC of **H_6aPyha** in the presence of Cu^{2+} (t_r=2.260 min).

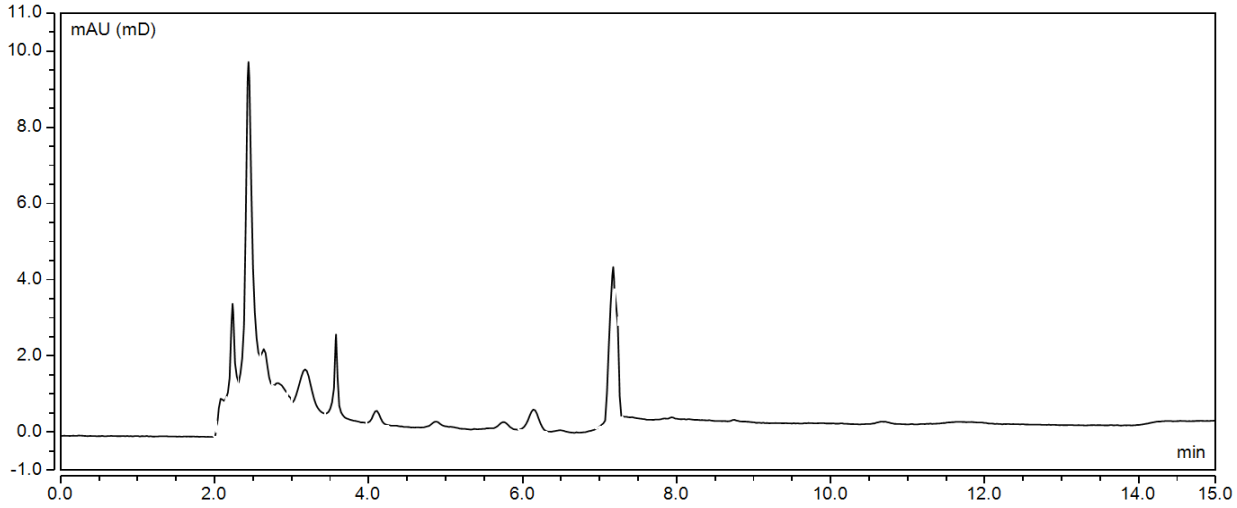


Figure S25. HPLC of **H_6aPyha** in the presence of Y^{3+} (t_r=2.440 min).

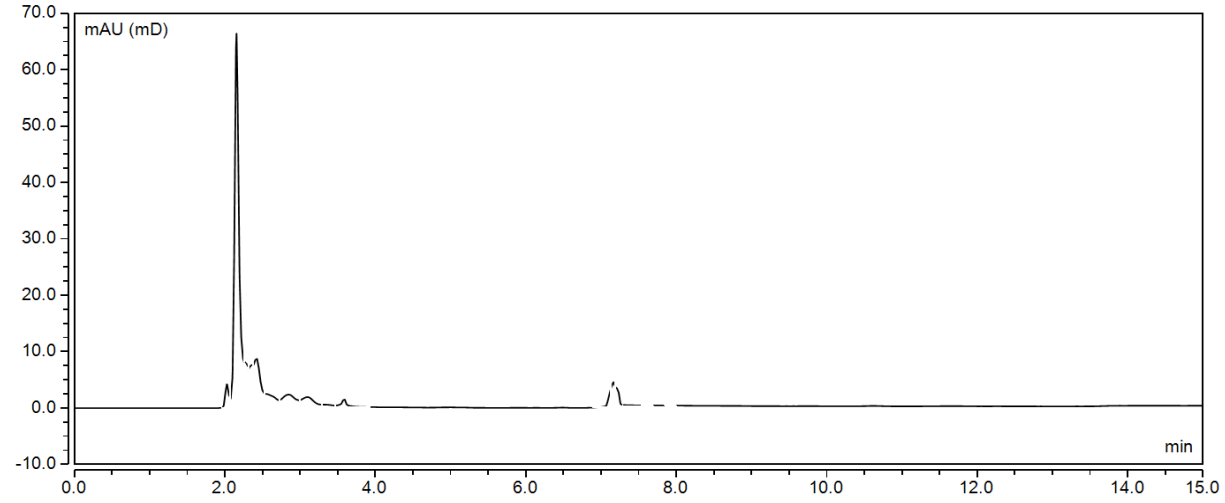


Figure S26. HPLC of **H_6aPyha** in the presence of Bi^{3+} (t_r=2.155 min).

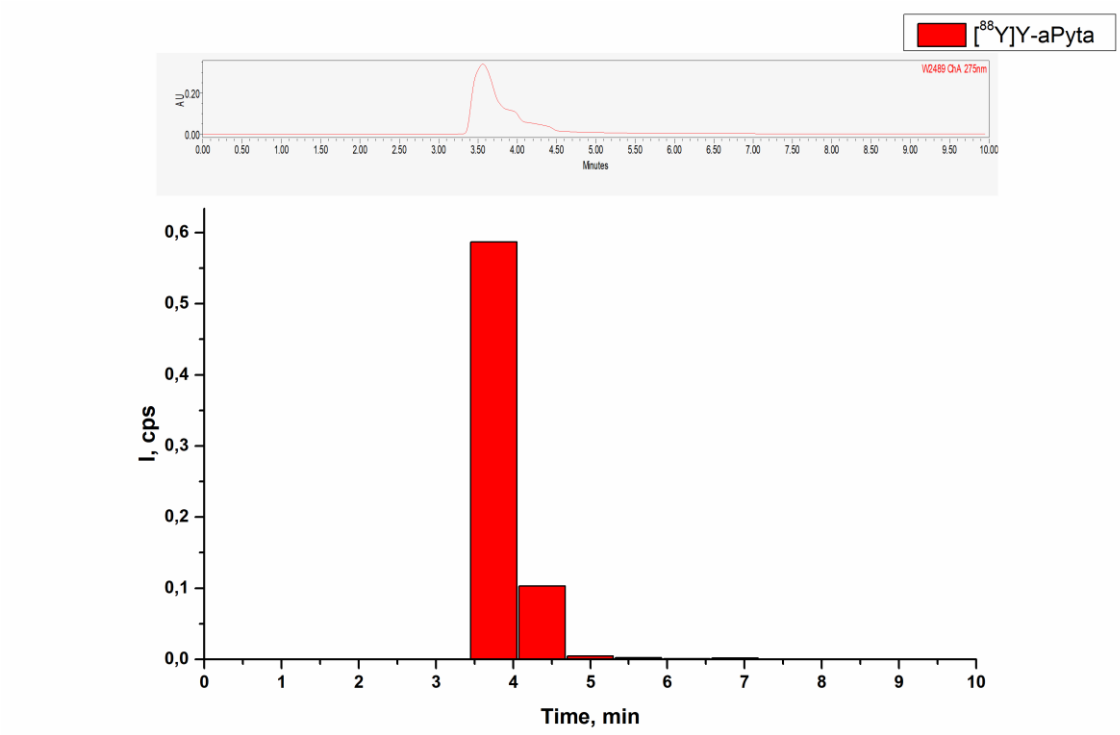


Figure S27. HPLC chromatogram obtained by UV-vis absorption detector and radioactivity measurements of **H_4aPyta** complexes with $[^{88}Y]Y^{3+}$.

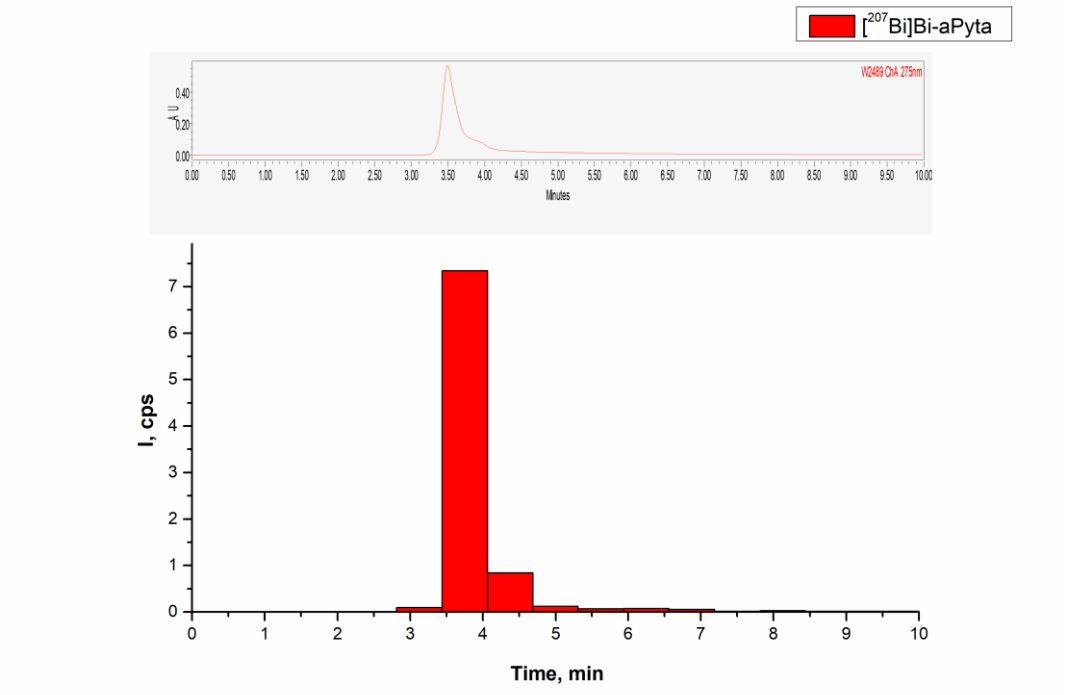


Figure S28. HPLC chromatogram obtained by UV-vis absorption detector and radioactivity measurements of **H_4aPyta** complexes with $[^{207}Bi]Bi^{3+}$.

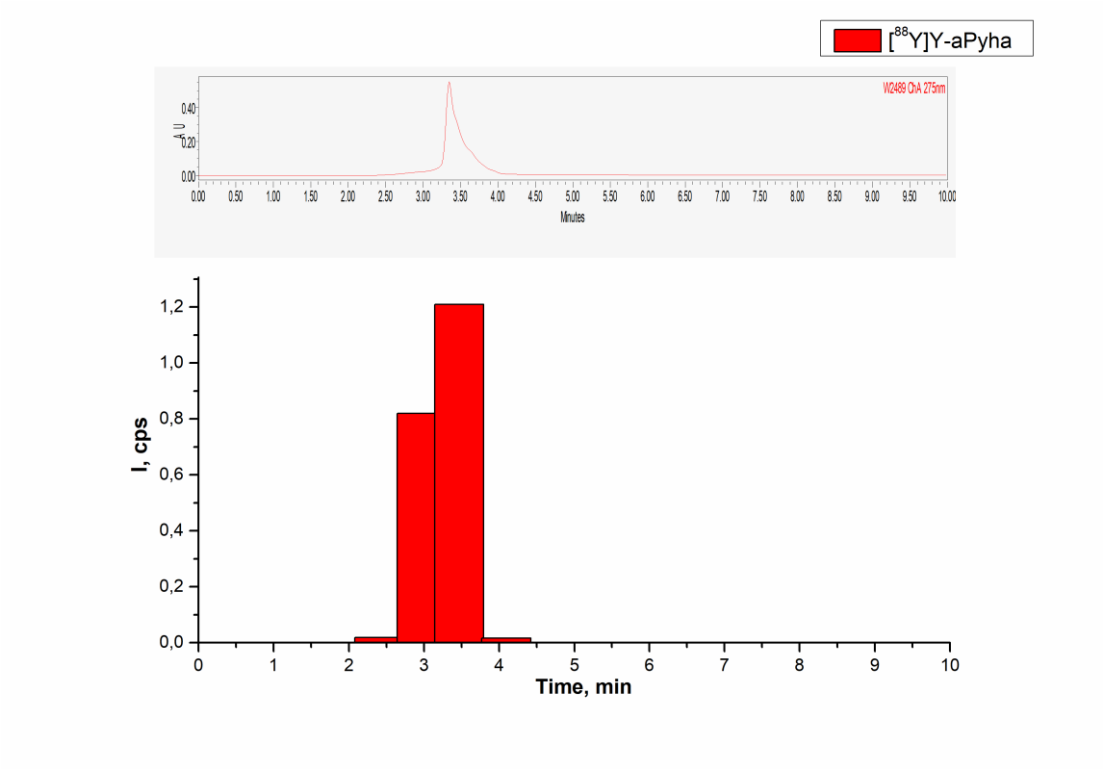


Figure S29. HPLC chromatograms obtained by UV-vis absorption detector and radioactivity measurements of **H_6aPyha** complexes with $[^{88}Y]Y^{3+}$.

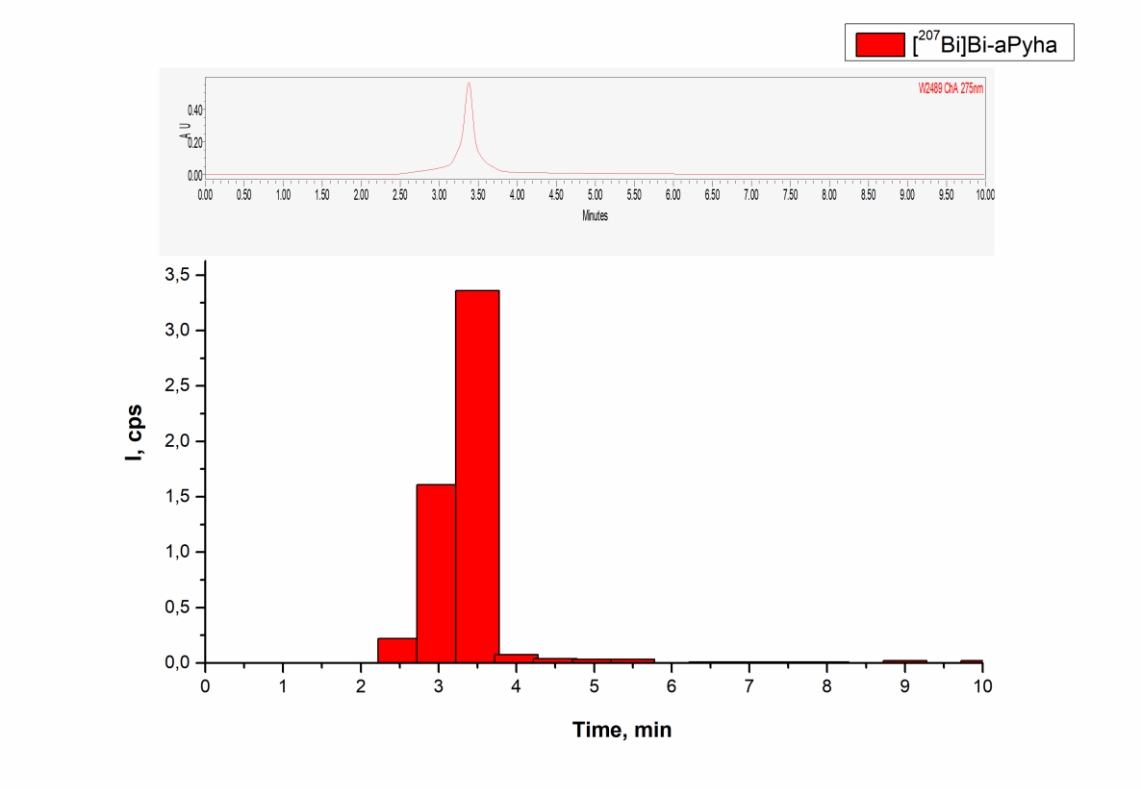


Figure S30. HPLC chromatograms obtained by UV-vis absorption detector and radioactivity measurements of **H_6aPyha** complexes with $[^{207}Bi]Bi^{3+}$.

5. DFT calculations

QTAIM analysis

We have performed a QTAIM analysis to investigate the Ga coordination in the **Ga-aPyta** complex. We may conclude the Ga ion is 6-coordinated with four oxygen and two nitrogen atoms (Table S3, Figure S31).

Table S3. The parameters of bond critical points (3,-1).

Bond	**ρ**	**$\nabla^2\rho$**	**dH**
Me-N	0.0381	0.0734	-0.0079
Me-N	0.0387	0.0716	-0.0079
Me-O	0.1000	0.4810	-0.0234
Me-O	0.1024	0.4951	-0.0251
Me-O	0.1000	0.4771	-0.0239
Me-O	0.0990	0.4732	-0.0230

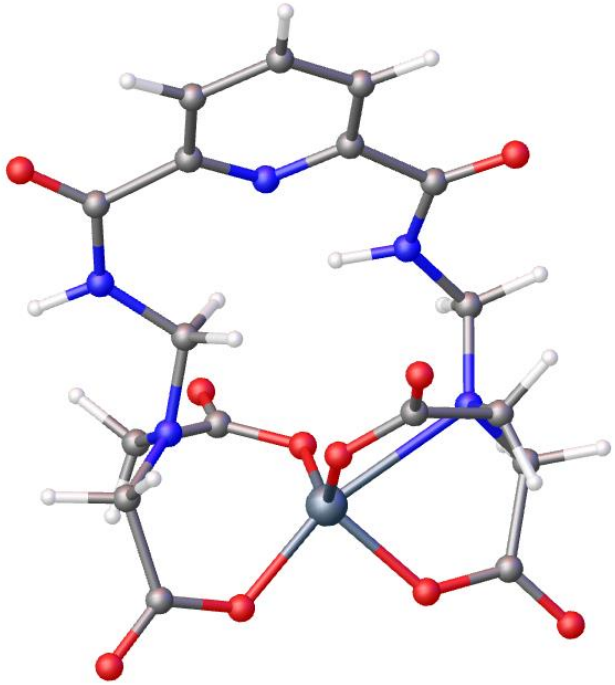


Figure S31. Geometries of complex **Ga-aPyta** calculated by the DFT method.

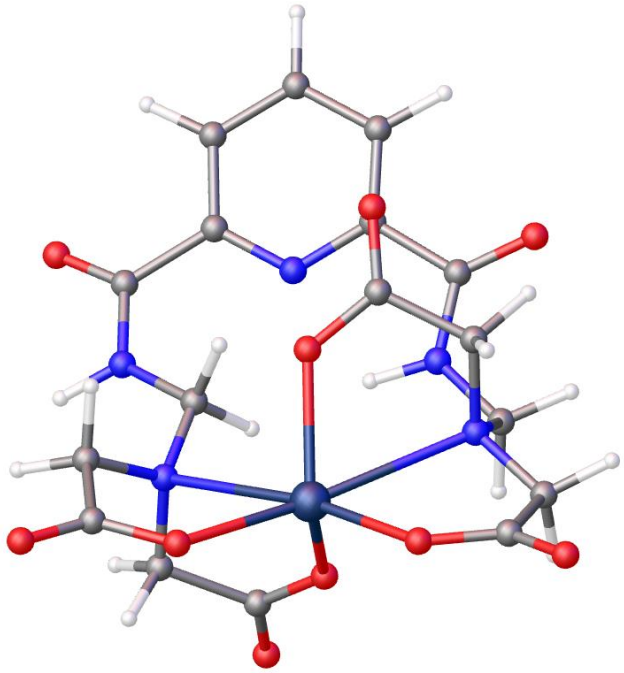


Figure S32. Geometries of complex **Y-aPyta** calculated by the DFT method.

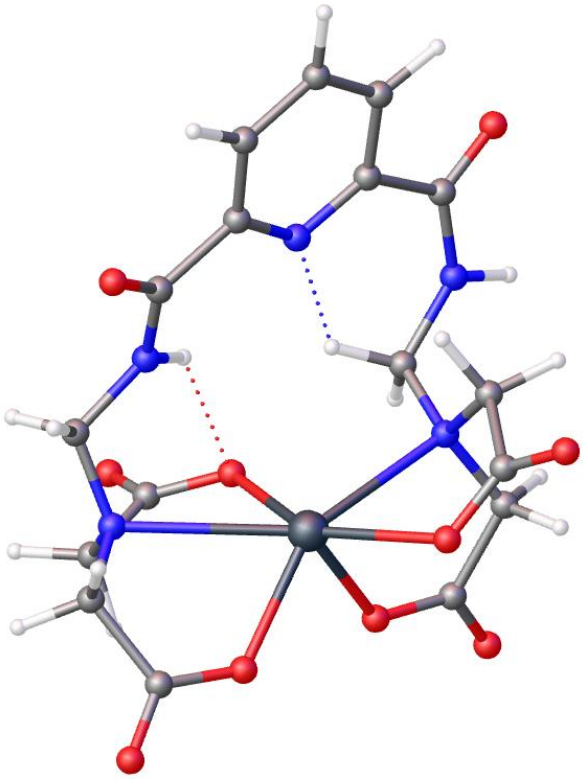


Figure S33. Geometries of complex **Bi-aPyta** calculated by the DFT method.

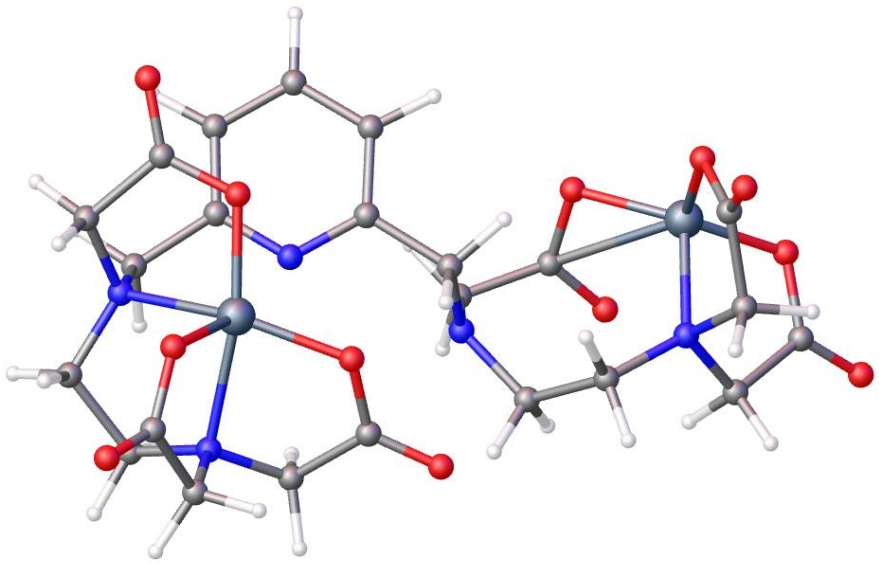


Figure S34. Geometries of complex **Ga_2-aPyha** calculated by the DFT method.

6. Radiolabeling

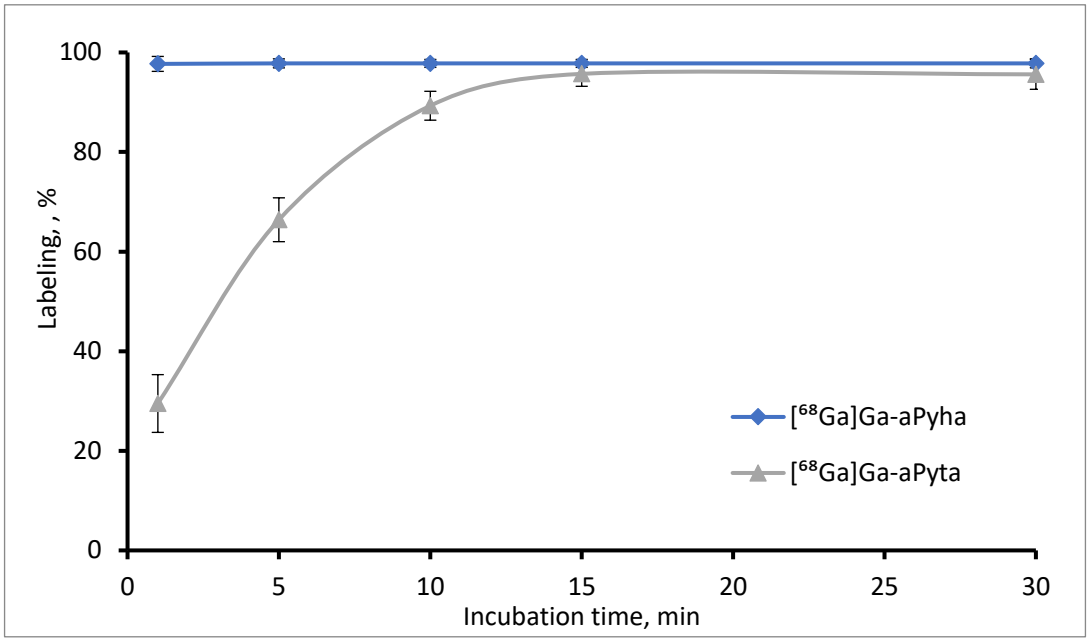


Figure S35. Time dependences of [^{68}Ga]Ga-**aPyta** and [^{68}Ga]Ga-**aPyha** formation (95°C, pH 5).

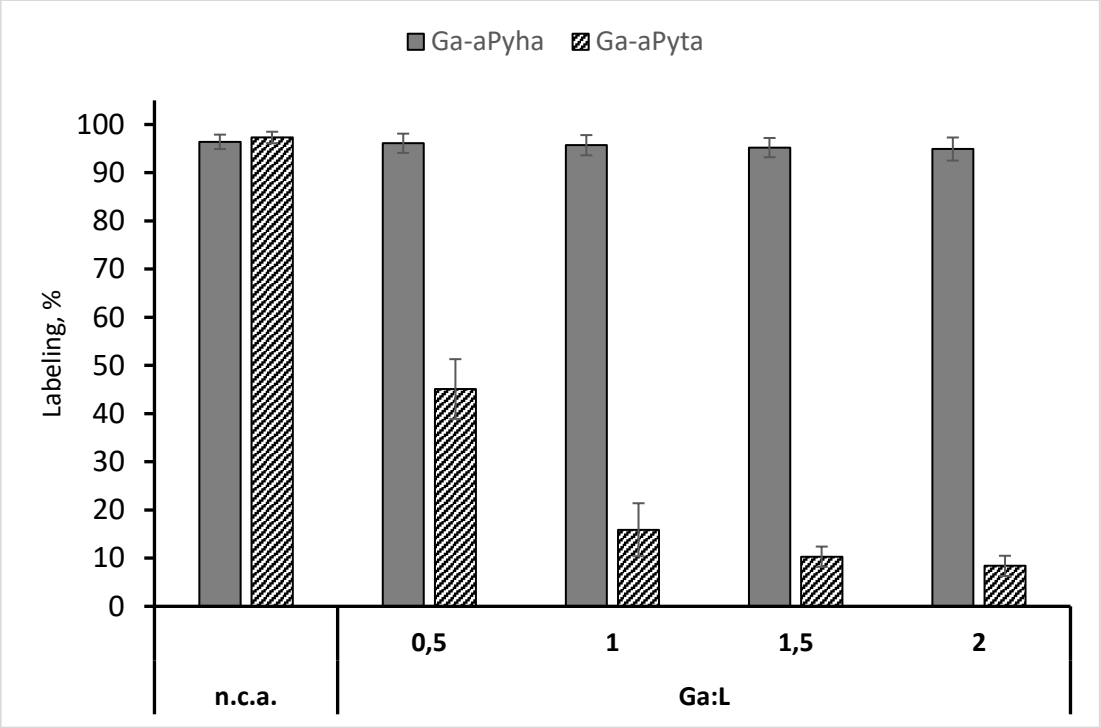


Figure S36. Influence of metal:ligand ratio on the yield of complexation reaction of **H_4aPyta** and **H_6aPyha** with ^{68}Ga (95°C, pH 5).

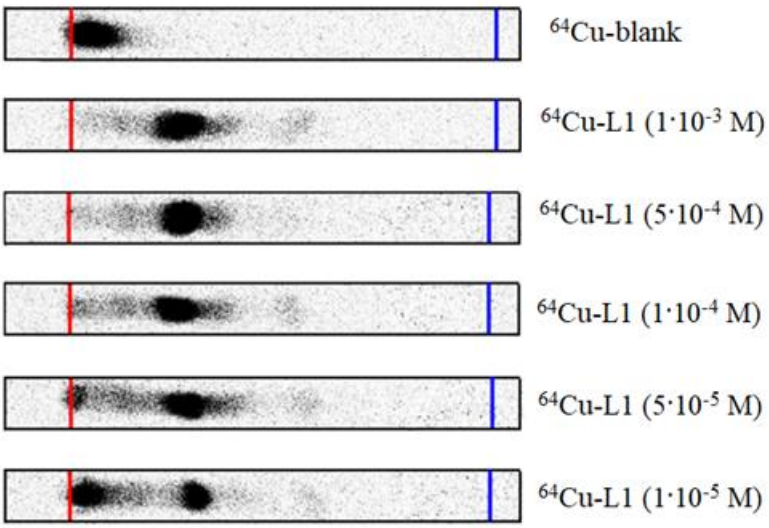


Figure S37. The image of TLC plates (Al-backed SiO_2 plates) after elution (20% NH_4Cl/MeOH =1/1) of ^{64}Cu complexes with **H_6aPyha**. Red – start line, blue – front line.

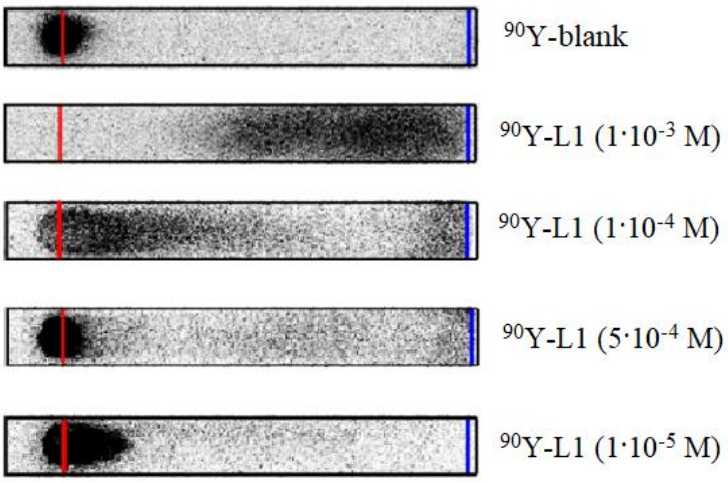


Figure S38. The image of "Whatman" sheets after elution (20% NH_4Cl/MeOH =3/7) of ^{90}Y complexes with **H_6aPyha**. Red – start line, blue – front line.

7. *In vitro* stability

Table S4. Stability of labelled **H_6aPyha** complex ^{207}Bi in the presence of serum proteins.

Incubation time	Intact [^{207}Bi]Bi-**aPyha** complex, %
0 min	92,87356
30 min	84,53159
1 h	86,99552
2 h	85,7997
3 h	83,10912
4 h	90,58296
6 h	89,98505
1 d	97,3262
2 d	103,908
3 d	83,21839
4 d	90,55258
8 d	98,75223

8. Potentiometry

Table S5. Stepwise protonation constants (LogK) of the **aPyta^{4-}** and **aPyha^{6-}**.

Reaction equations	LogK
$aPyta^{4-} + H^+ \leftrightarrow HaPyta^{3-}$	9.19
$HaPyta^{3-} + H^+ \leftrightarrow H_2aPyta^{2-}$	7.9
$H_2aPyta^{2-} + H^+ \leftrightarrow H_3aPyta^-$	3.04
$H_3aPyta^- + H^+ \leftrightarrow H_4aPyta$	2.22
$aPyha^{6-} + H^+ \leftrightarrow HaPyha^{5-}$	10.16
$HaPyha^{5-} + H^+ \leftrightarrow H_2aPyha^{4-}$	9.36
$H_2aPyha^{4-} + H^+ \leftrightarrow H_3aPyha^{3-}$	5.87
$H_3aPyha^{3-} + H^+ \leftrightarrow H_4aPyha^{2-}$	4.57
$H_4aPyha^{2-} + H^+ \leftrightarrow H_5aPyha^-$	3.22
$H_5aPyha^- + H^+ \leftrightarrow H_6aPyha$	1.88

Table S6. Hydrolysis constants of Cu^{2+}, Y^{3+}, Ga^{3+} and Bi^{3+} ions used to calculate the total binding constants of the **aPyta^{4-}** and **aPyha^{6-}** complexes with Cu^{2+}, Y^{3+}, Ga^{3+} and Bi^{3+} in the Hyperquad2003 program.

Reaction equations	M^{n+} =			
	Cu^{2+}	**Y^{3+}**	**Ga^{3+}**	**Bi^{3+}**
$M^{n+} + H_2O \leftrightarrow MOH^{(n-1)} + H^+$	-7.97[c]	-7.7[a]	-2.6[b]	-1.09[a]
$M^{n+} + 2H_2O \leftrightarrow M(OH)_2^{(n-2)} + 2H^+$	-16.23[c]	-16.4[a]	-5.9[b]	-4.0[a]
$M^{n+} + 3H_2O \leftrightarrow M(OH)_3^{(n-3)} + 3H^+$	-26.6[b]	-26.0[a]	-10.3[b]	-8.86[a]
$M^{n+} + 4H_2O \leftrightarrow M(OH)_4^{(n-4)} + 4H^+$	-39.7[b]	-36.5[a]	-16.6[b]	-21.8[a]
$2M^{n+} + H_2O \leftrightarrow M_2OH^{(2n-1)} + H^+$	-6.71[c]	-	-	-
$6M^{n+} + 12H_2O \leftrightarrow M_4(OH)_4^{(6n-12)} + 12H^+$	-	-	-	-1.0[b]
$2M^{n+} + 2H_2O \leftrightarrow M_2(OH)_2^{(2n-2)} + 2H^+$	-10.55[c]	-14.23[a]	-	-
$3M^{n+} + 4H_2O \leftrightarrow M_3(OH)_4^{(3n-4)} + 4H^+$	-20.95[c]	-	-	-
$3M^{n+} + 5H_2O \leftrightarrow M_2(OH)_6^{(3n-5)} + 5H^+$	-	-31.6[a]	-	-
$26M^{n+} + 65H_2O \leftrightarrow M_{26}(OH)_{65}^{(26n-65)} + 65H^+$	-	-	-139.1[b]	-

[a] Baes, C.F. and Mesmer, R.E. "*The Hydrolysis of Cations*", John Wiley & Sons, Inc., New York, 1976, P. 489.

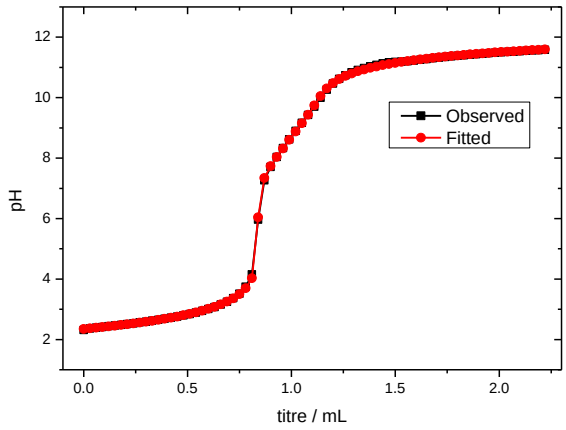
[b] Paul L. Brown and Christian Ekberg, "*Hydrolysis of Metal Ions*", Wiley-VCH, 2016, V.2, P.917.

[c] Natalia V. Plyasunova, Mingsheng Wang, Yu Zhang, Mamoun Muhammed, Critical evaluation of thermodynamics of complex formation of metal ions in aqueous solutions II. Hydrolysis and hydroxo-complexes of Cu^{2+} at 298.15 K, Hydrometallurgy, 1997, 45, 37-51.

Table S7. Stepwise binding constants of protonated **aPyta^{4-}** and **aPyha^{6-}** with Cu^{2+}, Y^{3+}, Ga^{3+} and Bi^{3+} ions.

Reaction equations	**logK**			
	Cu^{2+}	**Y^{3+}**	**Ga^{3+}**	**Bi^{3+}**
$aPyta^{4-} + M^{n+} \leftrightarrow MaPyta^{n-4}$	14.96	8.9	19.5	28.78
$HaPyta^{3-} + M^{n+} \leftrightarrow MHaPyta^{n-3}$	11.31	6.89	14.21	26.25
$H_2aPyta^{2-} + M^{n+} \leftrightarrow MH_2aPyta^{n-2}$		3.54		
$aPyha^{6-} + M^{n+} \leftrightarrow MaPyha^{n-6}$	-	15.05	27.38	-
$HaPyha^{5-} + M^{n+} \leftrightarrow MHaPyha^{n-5}$	18.21	13.23	-	
$H_2aPyha^{4-} + M^{n+} \leftrightarrow MH_2aPyha^{n-4}$	11.38	8.7	-	-
$H_3aPyha^{3-} + M^{n+} \leftrightarrow H_3MaPyha^{n-3}$		5.77	19.81	-

A



Refinement successful
Chi-squared = 12.53
Chi-squared should be less than 12.60 at the 95% confidence
level
sigma = 1.2596

				Value	relative std devn	log beta	standard deviation
Beta	1	1	refined	1.5450E+09	0.0886	9.1889	0.0385
Beta	2	1	refined	1.2409E+17	0.1054	17.0937	0.0458
Beta	3	1	refined	1.3393E+20	0.1317	20.1269	0.0572
Beta	4	1	refined	2.2191E+22	0.1322	22.3462	0.0574
Beta	-1	0	constant	1.6596E-14		-13.7800	

B

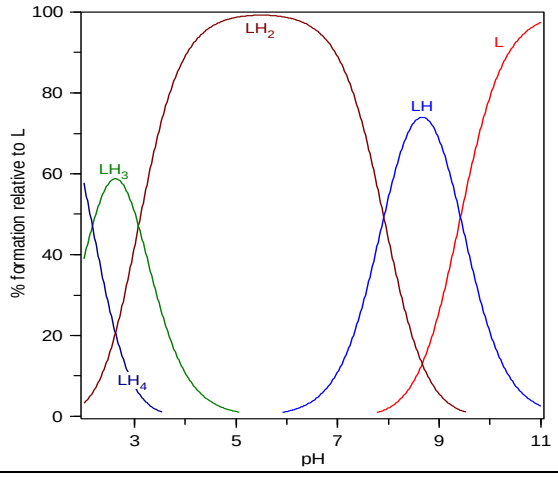
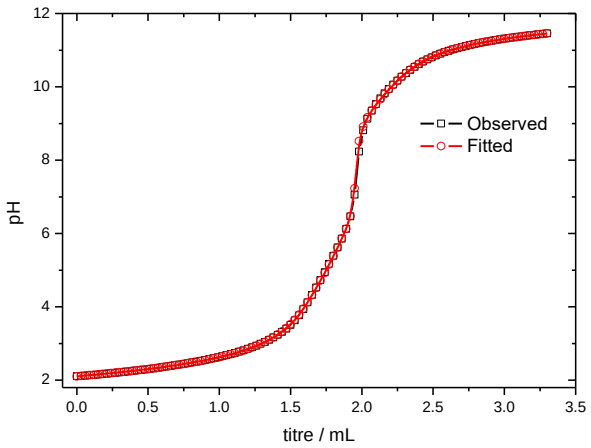


Figure S39. Potentiometric titration curves observed (black points) and fitted (red points) and statistical parameters obtained by the HYPERQUAD2003 program (A), and ligand **aPyta^{4-}** (1 mM) species distribution as a function of pH (B).

A



Refinement successful
Chi-squared = 11.88
Chi-squared should be less than 12.60 at the 95% confidence level
sigma = 0.4616

			Value	relative std devn	log beta	standard deviation
Beta	1	1 refined	1.4499E+10	0.0243	10.1614	0.0105
Beta	2	1 refined	3.3004E+19	0.0263	19.5186	0.0114
Beta	3	1 refined	2.4768E+25	0.0414	25.3939	0.0180
Beta	4	1 refined	9.1047E+29	0.0429	29.9593	0.0186
Beta	5	1 refined	1.5071E+33	0.0456	33.1781	0.0198
Beta	6	1 refined	1.1580E+35	0.0569	35.0637	0.0247
Beta	-1	0 constant	1.6596E-14		-13.7800	

B

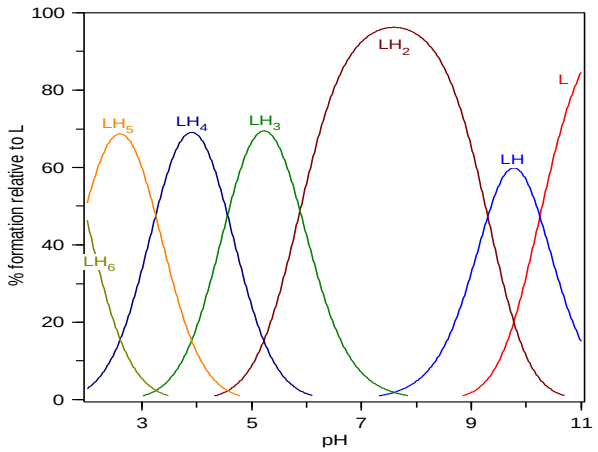
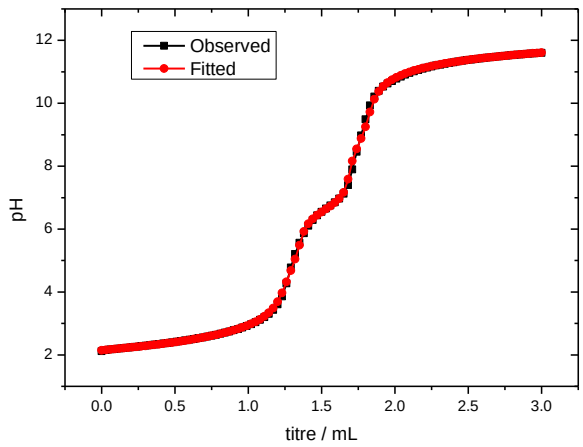


Figure S40. Potentiometric titration curves observed (black points) and fitted (red points) and statistical parameters obtained by the HYPERQUAD2003 program (A), and ligand **aPyha**$^{6-}$ (1 mM) species distribution as a function of pH (B).

A



Refinement successful
Chi-squared = 15.62
Chi-squared should be less than 12.60 at the 95% confidence level
sigma = 1.0541

					Value	relative std devn	log beta	standard deviation	
Beta	1	1	0	constant	1.5488E+09		9.1900		
Beta	2	1	0	constant	1.2303E+17		17.0900		
Beta	3	1	0	constant	1.3490E+20		20.1300		
Beta	4	1	0	constant	2.2387E+22		22.3500		
Beta	1	1	1	refined	1.2026E+16	0.1394	16.0801	0.0605	
Beta	2	1	1	refined	4.2487E+20	0.0951	20.6283	0.0413	
Beta	0	1	1	refined	8.0303E+08	0.3609	8.9047	0.1567	
Beta	-1	1	1	refined	7.2738E+02	0.1330	2.8618	0.0577	
Beta	-2	1	1	refined	1.4441E-06	0.1923	-5.8404	0.0835	
Beta	-1	0	1	constant	1.9953E-08		-7.7000		
Beta	-2	0	1	constant	3.9811E-17		-16.4000		
Beta	-3	0	1	constant	1.0000E-26		-26.0000		
Beta	-4	0	1	constant	3.1623E-37		-36.5000		
Beta	-2	0	2	constant	5.8884E-15		-14.2300		
Beta	-5	0	3	constant	2.5119E-32		-31.6000		
Beta	-1	0	0	constant	1.6596E-14		-13.7800		

B

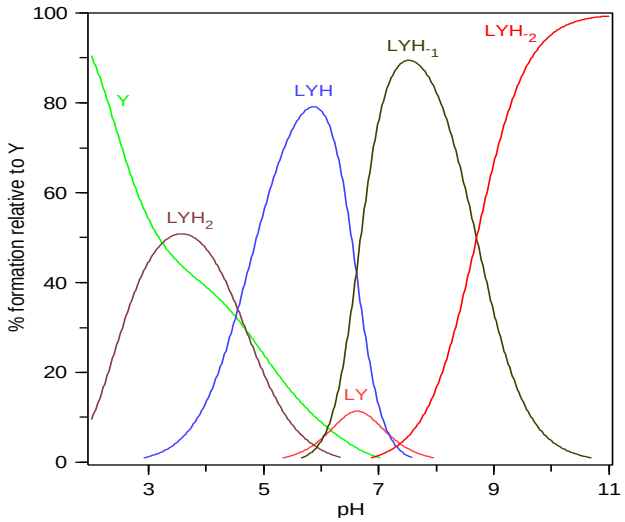
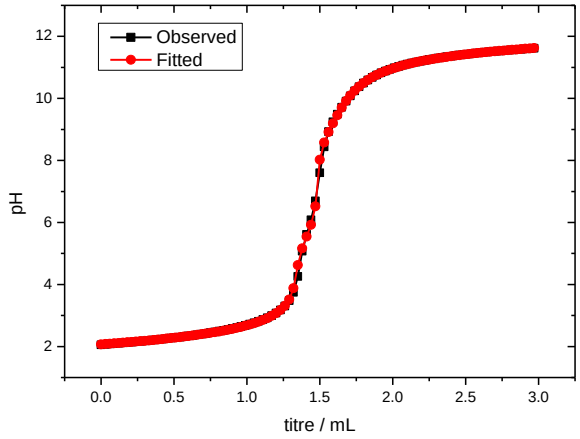


Figure S41. Potentiometric titration curves observed (black points) and fitted (red points) and statistical parameters obtained by the HYPERQUAD2003 program (A), and species distribution diagram in the system Y^{3+} (1 mM), **aPyta**$^{4-}$ (1 mM), KNO_3(0.1 M) as a function of pH (B).

A



Refinement successful
Chi-squared = 7.12
Chi-squared should be less than 12.60 at the 95% confidence level

sigma = 0.8999

					Value	relative std devn	log beta	standard deviation
Beta	1	1	0	constant	1.5488E+09		9.1900	
Beta	2	1	0	constant	1.2303E+17		17.0900	
Beta	3	1	0	constant	1.3490E+20		20.1300	
Beta	4	1	0	constant	2.2387E+22		22.3500	
Beta	0	1	1	refined	9.0958E+14	0.1538	14.9588	0.0668
Beta	1	1	1	refined	3.1950E+20	0.1174	20.5045	0.0510
Beta	-1	1	1	refined	9.9701E+05	0.1716	5.9987	0.0745
Beta	-2	1	1	refined	4.7215E-05	0.1698	-4.3259	0.0737
Beta	-1	0	1	constant	1.0715E-08		-7.9700	
Beta	-2	0	1	constant	5.8884E-17		-16.2300	
Beta	-3	0	1	constant	2.5119E-27		-26.6000	
Beta	-4	0	1	constant	1.9953E-40		-39.7000	
Beta	-2	0	2	constant	2.8184E-11		-10.5500	
Beta	-1	0	2	constant	1.9498E-07		-6.7100	
Beta	-4	0	3	constant	1.1220E-21		-20.9500	
Beta	-1	0	0	constant	1.6596E-14		-13.7800	

B

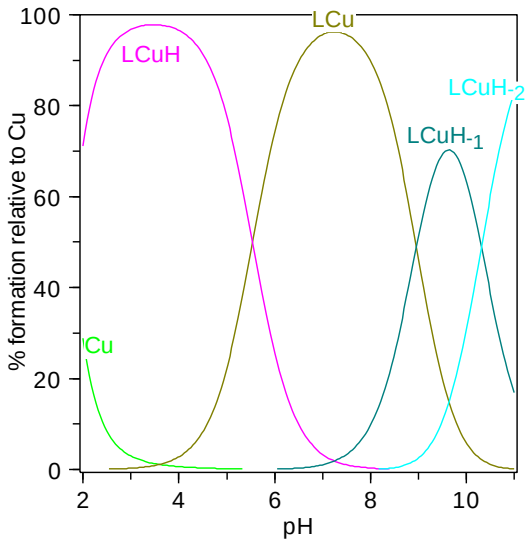
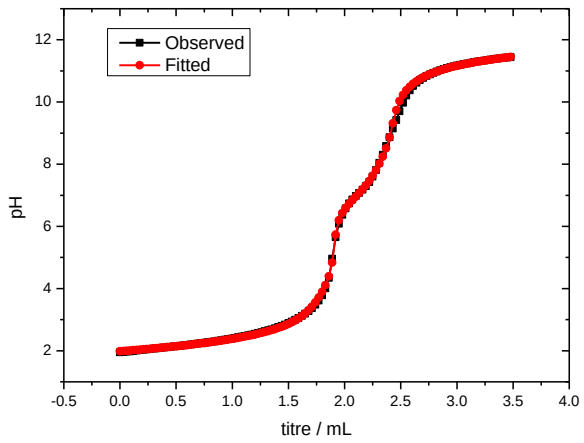


Figure S42. Potentiometric titration curves observed (black points) and fitted (red points) and statistical parameters obtained by the HYPERQUAD2003 program (A), and species distribution diagram in the system Cu^{2+} (1 mM), **aPyta**$^{4-}$ (1 mM), KNO_3(0.1 M) as a function of pH (B).

A



Refinement successful
Chi-squared = 10.25
Chi-squared should be less than 12.60 at the 95% confidence level

sigma = 1.0491

					Value	relative std devn	log beta	standard deviation
Beta	1	1	0	constant	1.5488E+09		9.1900	
Beta	2	1	0	constant	1.2303E+17		17.0900	
Beta	3	1	0	constant	1.3490E+20		20.1300	
Beta	4	1	0	constant	2.2387E+22		22.3500	
Beta	-1	0	1	constant	2.5119E-03		-2.6000	
Beta	-2	0	1	constant	1.2589E-06		-5.9000	
Beta	-3	0	1	constant	5.0119E-11		-10.3000	
Beta	-4	0	1	constant	2.5119E-17		-16.6000	
Beta	0	1	1	refined	3.1904E+19	0.3329	19.5038	0.1446
Beta	1	1	1	refined	2.5819E+23	0.3870	23.4119	0.1681
Beta	-3	1	1	refined	3.9340E-03	0.1539	-2.4052	0.0668
Beta	-1	1	1	refined	4.7798E+12	0.3649	12.6794	0.1585
Beta	-2	1	1	refined	5.0404E+05	0.3435	5.7025	0.1492
Beta	-1	0	0	constant	1.6596E-14		-13.7800	

B

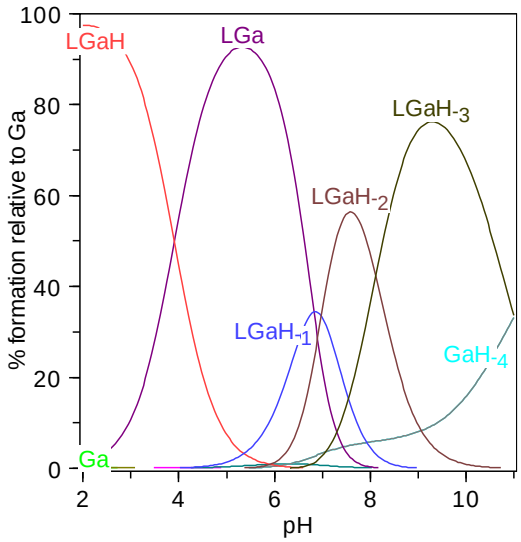
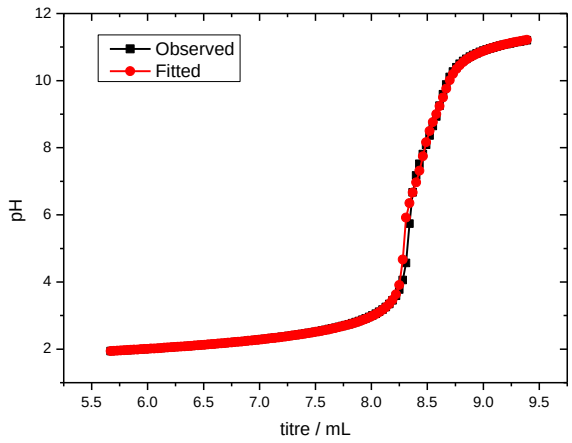


Figure S43. Potentiometric titration curves observed (black points) and fitted (red points) and statistical parameters obtained by the HYPERQUAD2003 program (A), and species distribution diagram in the system Ga^{3+} (1 mM), **aPyta**$^{4-}$ (1 mM), KNO_3(0.1 M) as a function of pH (B).

A



Refinement successful
Chi-squared = 21.11
Chi-squared should be less than 12.60 at the 95% confidence level

sigma = 1.0596

					Value	relative std devn	log beta	standard deviation
Beta	1	1	0	constant	1.5488E+09		9.1900	
Beta	2	1	0	constant	1.2303E+17		17.0900	
Beta	3	1	0	constant	1.3490E+20		20.1300	
Beta	4	1	0	constant	2.2387E+22		22.3500	
Beta	-1	0	1	constant	8.1283E-02		-1.0900	
Beta	-2	0	1	constant	1.0000E-04		-4.0000	
Beta	-3	0	1	constant	1.3804E-09		-8.8600	
Beta	-4	0	1	constant	1.5849E-22		-21.8000	
Beta	-12	0	6	constant	1.0000E-01		-1.0000	
Beta	0	1	1	refined	6.0817E+28	0.1203	28.7840	0.0523
Beta	1	1	1	refined	2.7565E+35	0.1959	35.4404	0.0851
Beta	-1	1	1	constant	6.7352E+19		19.8284	
Beta	-1	0	0	constant	1.6596E-14		-13.7800	

B

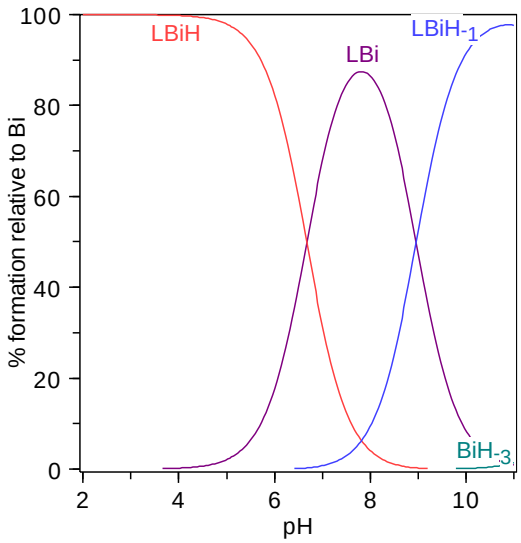
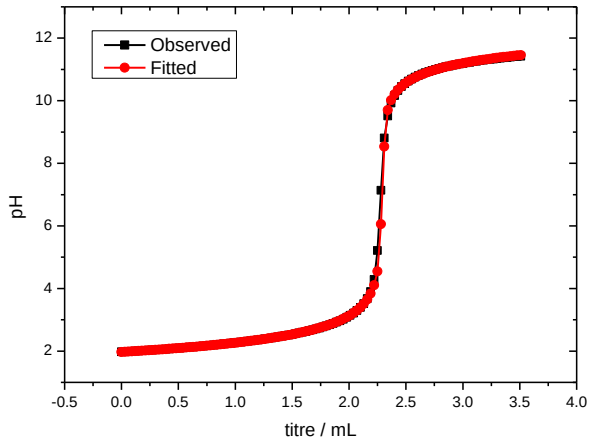


Figure S44. Potentiometric titration curves observed (black points) and fitted (red points) and statistical parameters obtained by the HYPERQUAD2003 program (A), and species distribution diagram in the system Bi^{3+} (1 mM), **aPyta^{4-}** (1 mM), KNO_3(0.1 M) as a function of pH (B).

A



Refinement successful
Chi-squared = 8.59
Chi-squared should be less than 12.60 at the 95% confidence level
sigma = 0.1115

					Value	relative std devn	log beta	standard deviation	
Beta	1	1	0	constant	1.4454E+10		10.1600		
Beta	2	1	0	constant	3.3113E+19		19.5200		
Beta	3	1	0	constant	2.4547E+25		25.3900		
Beta	4	1	0	constant	9.1201E+29		29.9600		
Beta	5	1	0	constant	1.5136E+33		33.1800		
Beta	6	1	0	constant	1.1482E+35		35.0600		
Beta	1	1	1	refined	2.3384E+28	0.0254	28.3689	0.0110	
Beta	0	1	2	refined	1.5230E+28	0.0546	28.1827	0.0237	
Beta	-1	1	2	refined	8.8638E+16	0.1081	16.9476	0.0470	
Beta	2	1	1	refined	7.9571E+30	0.0331	30.9008	0.0144	
Beta	-1	0	1	constant	1.0715E-08		-7.9700		
Beta	-2	0	1	constant	5.8884E-17		-16.2300		
Beta	-3	0	1	constant	2.5119E-27		-26.6000		
Beta	-4	0	1	constant	1.9953E-40		-39.7000		
Beta	-2	0	2	constant	2.8184E-11		-10.5500		
Beta	-4	0	3	constant	1.1220E-21		-20.9500		
Beta	-1	0	2	constant	1.9953E-07		-6.7000		
Beta	-1	0	0	constant	1.6596E-14		-13.7800		

B

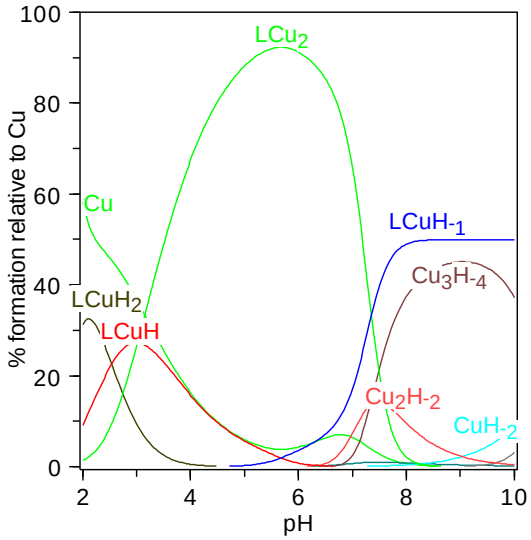
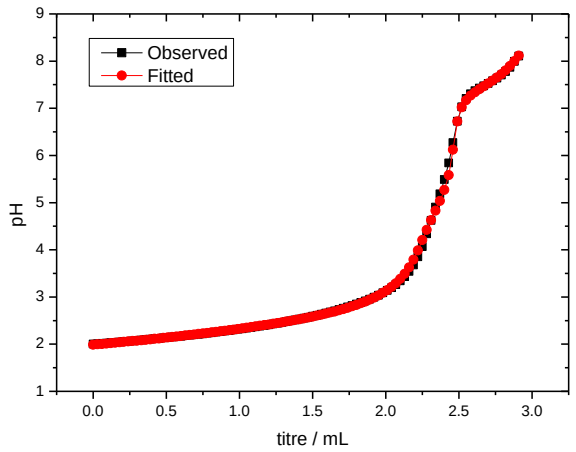


Figure S45. Potentiometric titration curves observed (black points) and fitted (red points) and statistical parameters obtained by the HYPERQUAD2003 program (A), and species distribution diagram in the system Cu^{2+} (2 mM), **aPyha**$^{6-}$ (1 mM), KNO_3(0.1 M) as a function of pH (B).

A



Refinement successful
Chi-squared = 9.20
Chi-squared should be less than 12.60 at the 95% confidence level

sigma = 0.9986

					Value	relative std devn	log beta	standard deviation	
Beta	1	1	0	constant	1.4454E+10		10.1600		
Beta	2	1	0	constant	3.3113E+19		19.5200		
Beta	3	1	0	constant	2.4547E+25		25.3900		
Beta	4	1	0	constant	9.1201E+29		29.9600		
Beta	5	1	0	constant	1.5136E+33		33.1800		
Beta	6	1	0	constant	1.1482E+35		35.0600		
Beta	0	1	1	refined	1.1216E+15	0.1099	15.0499	0.0477	
Beta	1	1	1	refined	2.4360E+23	0.0860	23.3867	0.0373	
Beta	2	1	1	refined	1.6723E+28	0.0335	28.2233	0.0146	
Beta	3	1	1	refined	1.4334E+31	0.0391	31.1564	0.0170	
Beta	-1	0	1	constant	1.9953E-08		-7.7000		
Beta	-2	0	1	constant	3.9811E-17		-16.4000		
Beta	-3	0	1	constant	1.0000E-26		-26.0000		
Beta	-4	0	1	constant	3.1623E-37		-36.5000		
Beta	-2	0	2	constant	5.8884E-15		-14.2300		
Beta	-5	0	3	constant	2.5119E-32		-31.6000		
Beta	-1	0	0	constant	1.6596E-14		-13.7800		

B

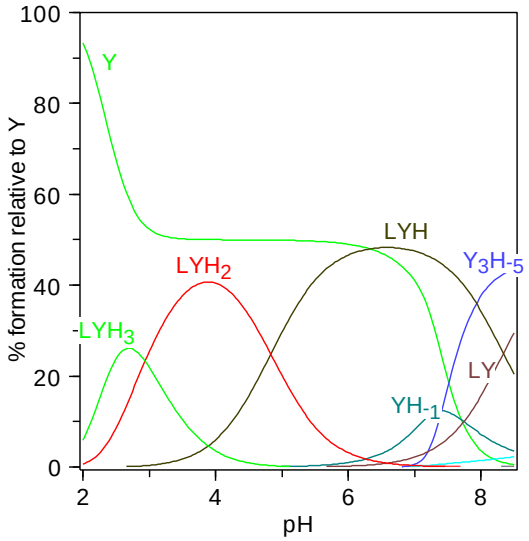
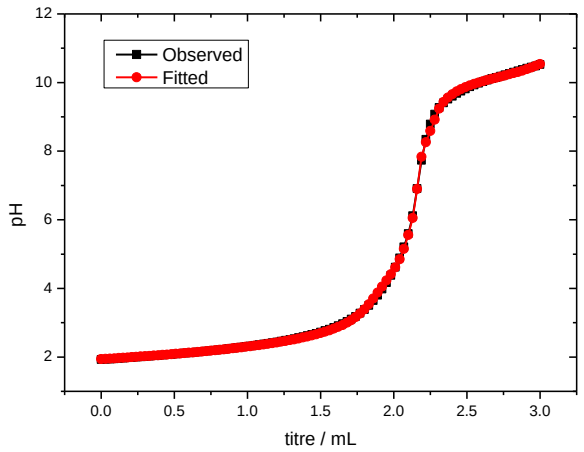


Figure S46. Potentiometric titration curves observed (black points) and fitted (red points) and statistical parameters obtained by the HYPERQUAD2003 program (A), and species distribution diagram in the system Y^{3+} (3.2 mM), **aPyha**$^{6-}$ (1.6 mM), KNO_3(0.1 M) as a function of pH (B).

A



Refinement successful
Chi-squared = 9.02
Chi-squared should be less than 12.60 at the 95% confidence level
sigma = 0.9032

					Value	relative std devn	log beta	standard deviation
Beta	1	1	0	constant	1.4454E+10		10.1600	
Beta	2	1	0	constant	3.3113E+19		19.5200	
Beta	3	1	0	constant	2.4547E+25		25.3900	
Beta	4	1	0	constant	9.1201E+29		29.9600	
Beta	5	1	0	constant	1.5136E+33		33.1800	
Beta	6	1	0	constant	1.1482E+35		35.0600	
Beta	-1	0	1	constant	2.5119E-03		-2.6000	
Beta	-2	0	1	constant	1.2589E-06		-5.9000	
Beta	-3	0	1	constant	5.0119E-11		-10.3000	
Beta	-4	0	1	constant	2.5119E-17		-16.6000	
Beta	-65	0	26	constant	7.9433-140		-139.1000	
Beta	0	1	1	refined	2.3827E+27	0.0627	27.3771	0.0272
Beta	0	1	2	refined	5.5636E+51	0.3892	51.7454	0.1690
Beta	3	1	1	refined	1.6155E+45	0.2561	45.2083	0.1112
Beta	-1	0	0	constant	1.6596E-14		-13.7800	

B

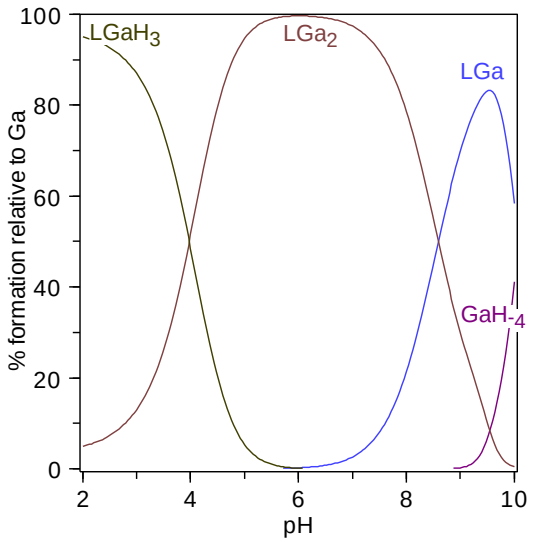
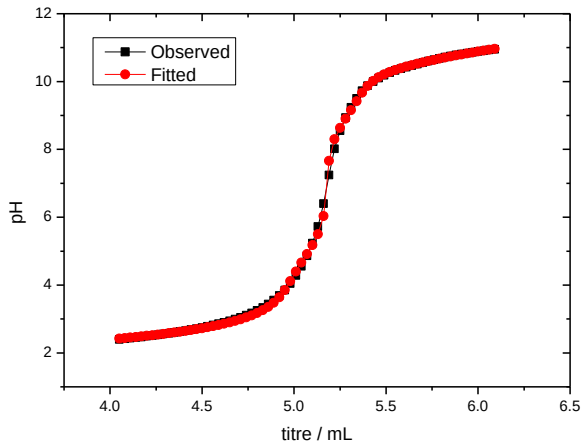


Figure S47. Potentiometric titration curves observed (black points) and fitted (red points) and statistical parameters obtained by the HYPERQUAD2003 program (A), and species distribution diagram in the system Ga^{3+} (1 mM), **aPyha**$^{6-}$ (1 mM), KNO_3(0.1 M) as a function of pH (B).

A



Refinement successful
Chi-squared = 7.17
Chi-squared should be less than 12.60 at the 95% confidence level
sigma = 0.8117

					Value	relative std devn	log beta	standard deviation
Beta	1	1	0	constant	1.4454E+10		10.1600	
Beta	2	1	0	constant	3.3113E+19		19.5200	
Beta	3	1	0	constant	2.4547E+25		25.3900	
Beta	4	1	0	constant	9.1201E+29		29.9600	
Beta	5	1	0	constant	1.5136E+33		33.1800	
Beta	6	1	0	constant	1.1482E+35		35.0600	
Beta	-1	0	1	constant	8.1283E-02		-1.0900	
Beta	-2	0	1	constant	1.0000E-04		-4.0000	
Beta	-3	0	1	constant	1.3804E-09		-8.8600	
Beta	-4	0	1	constant	1.5849E-22		-21.8000	
Beta	-12	0	6	constant	1.0000E-01		-1.0000	
Beta	0	1	1	refined	4.8725E+29	0.9028	29.6878	0.3921
Beta	2	1	1	refined	7.1775E+50	0.8623	50.8560	0.3745
Beta	3	1	1	refined	4.9693E+59	0.9077	59.6963	0.3942
Beta	4	1	1	refined	3.9223E+64	0.9319	64.5935	0.4047
Beta	-1	0	0	constant	1.6596E-14		-13.7800	

B

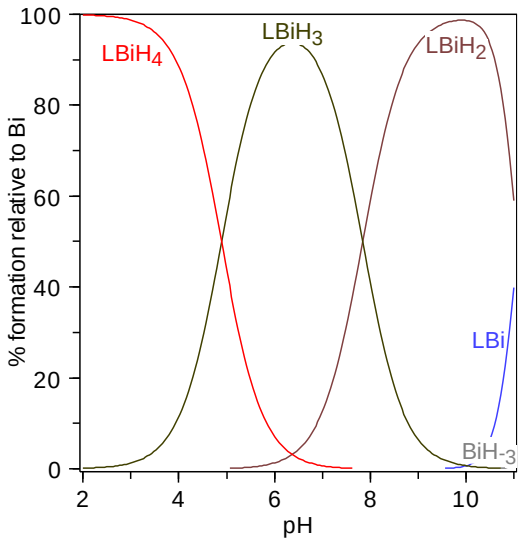


Figure S48. Potentiometric titration curves observed (black points) and fitted (red points) and statistical parameters obtained by the HYPERQUAD2003 program (A), and species distribution diagram in the system Bi^{3+} (0.9 mM), **aPyha**$^{6-}$ (1 mM), KNO_3(0.1 M) as a function of pH (B).

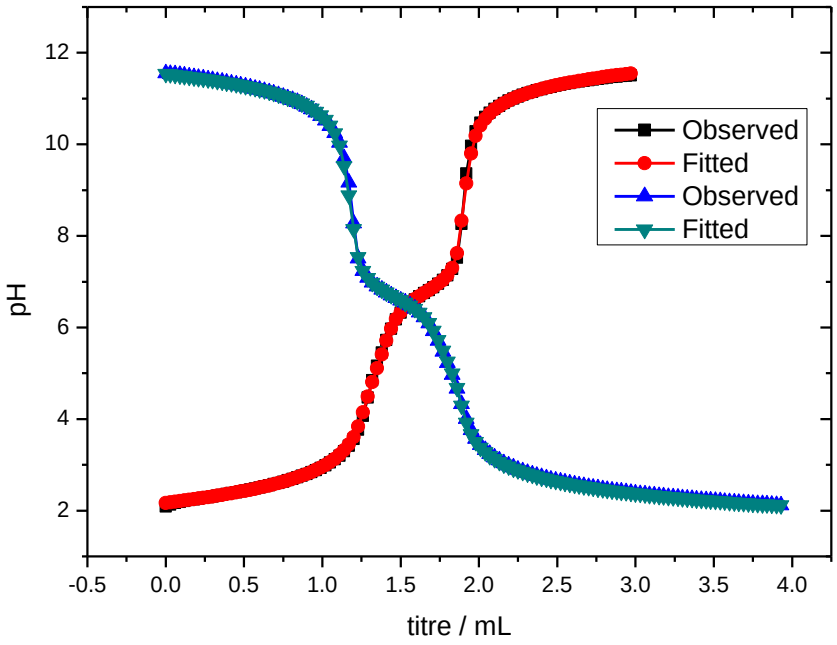


Figure S49. Potentiometric titration curves for direct titration observed (black points) and fitted (red points) and for back titration observed (blue points) and fitted (teal points) in the system Y^{3+} (1 mM), **aPyta**$^{4-}$ (1.3 mM), KNO_3(0.1 M).

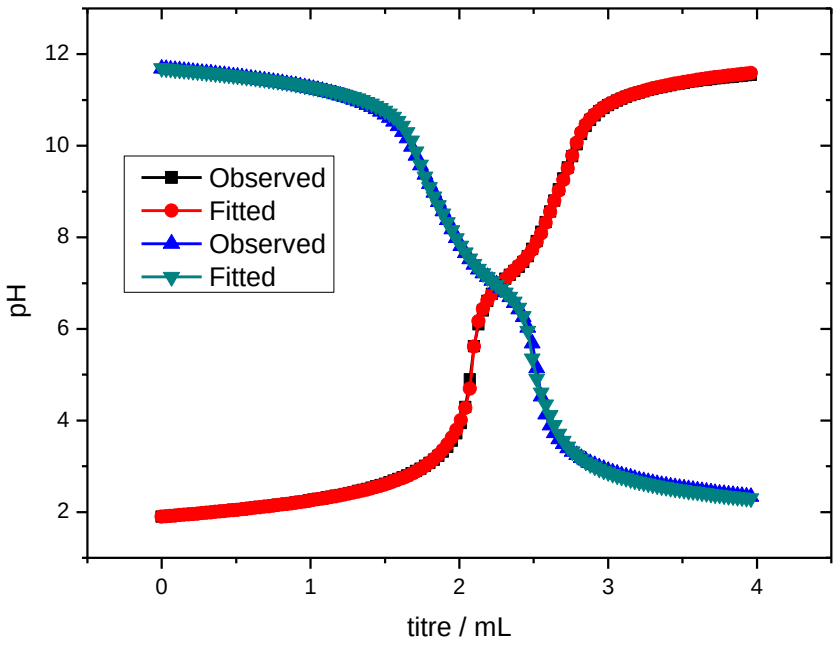


Figure S50. Potentiometric titration curves for direct titration observed (black points) and fitted (red points) and for back titration observed (blue points) and fitted (teal points) in the system Ga^{3+} (1 mM), **aPyta**$^{4-}$ (1.3 mM), KNO_3(0.1 M).