Electronic Supplementary Material (ESI) for Dalton Transactions.

A Pentadentate Member of the Picolinate Family for Mn(II) Complexation and an Amphiphilic Derivative

Rosa Pujales-Paradela,[a] Fabio Carniato,[b] Rocío Uzal-Varela,[a] Isabel Brandariz,[a] Emilia Iglesias,[a] Carlos Platas-Iglesias,[a] Mauro Botta[b] and David Esteban-Gómez*[a]*

Electronic Supplementary Information (ESI)

ESI Summary

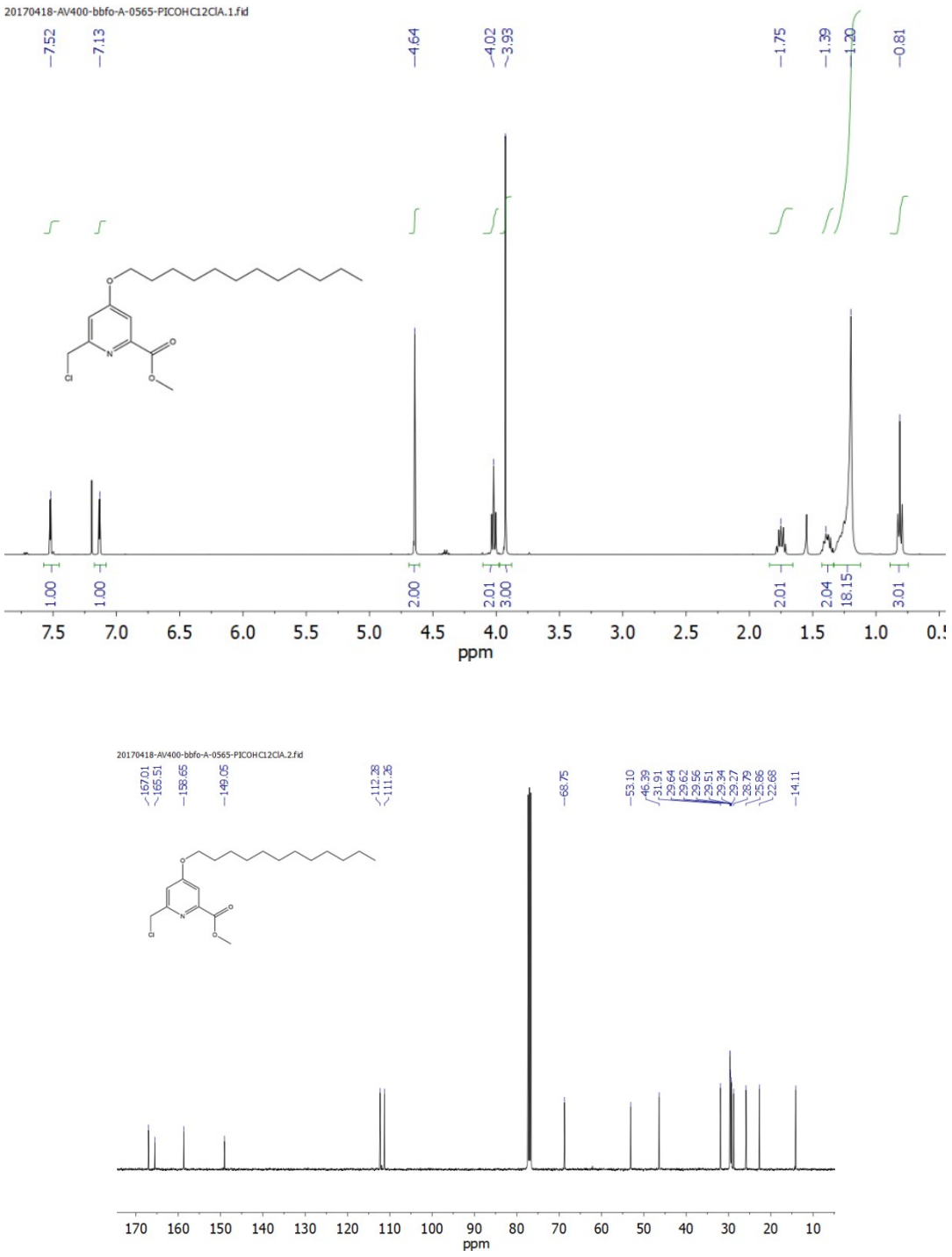

Figure S1. ^{1}H (300 MHz, 25 ^{o}C, top) and ^{13}C (75 MHz, 25 ^{o}C, bottom) NMR spectra of compound **3** recorded in $CDCl_3$ solution.

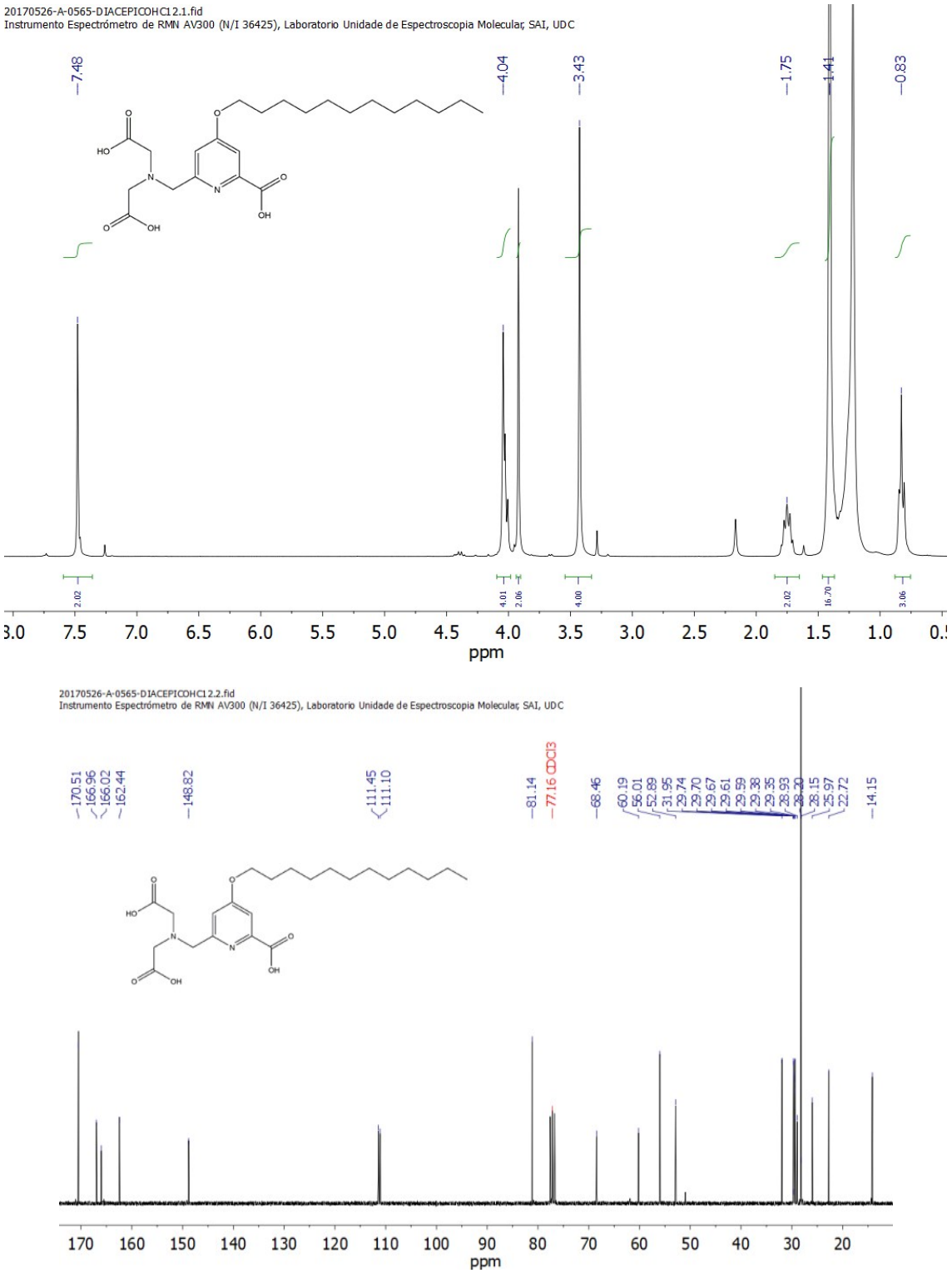

Figure S2. ^{1}H (300 MHz, 25 ^{o}C, top) and ^{13}C (75 MHz, 25 ^{o}C, bottom) NMR spectra of **H_3C_{12}OPAADA** recorded in $CDCl_3$ solution.

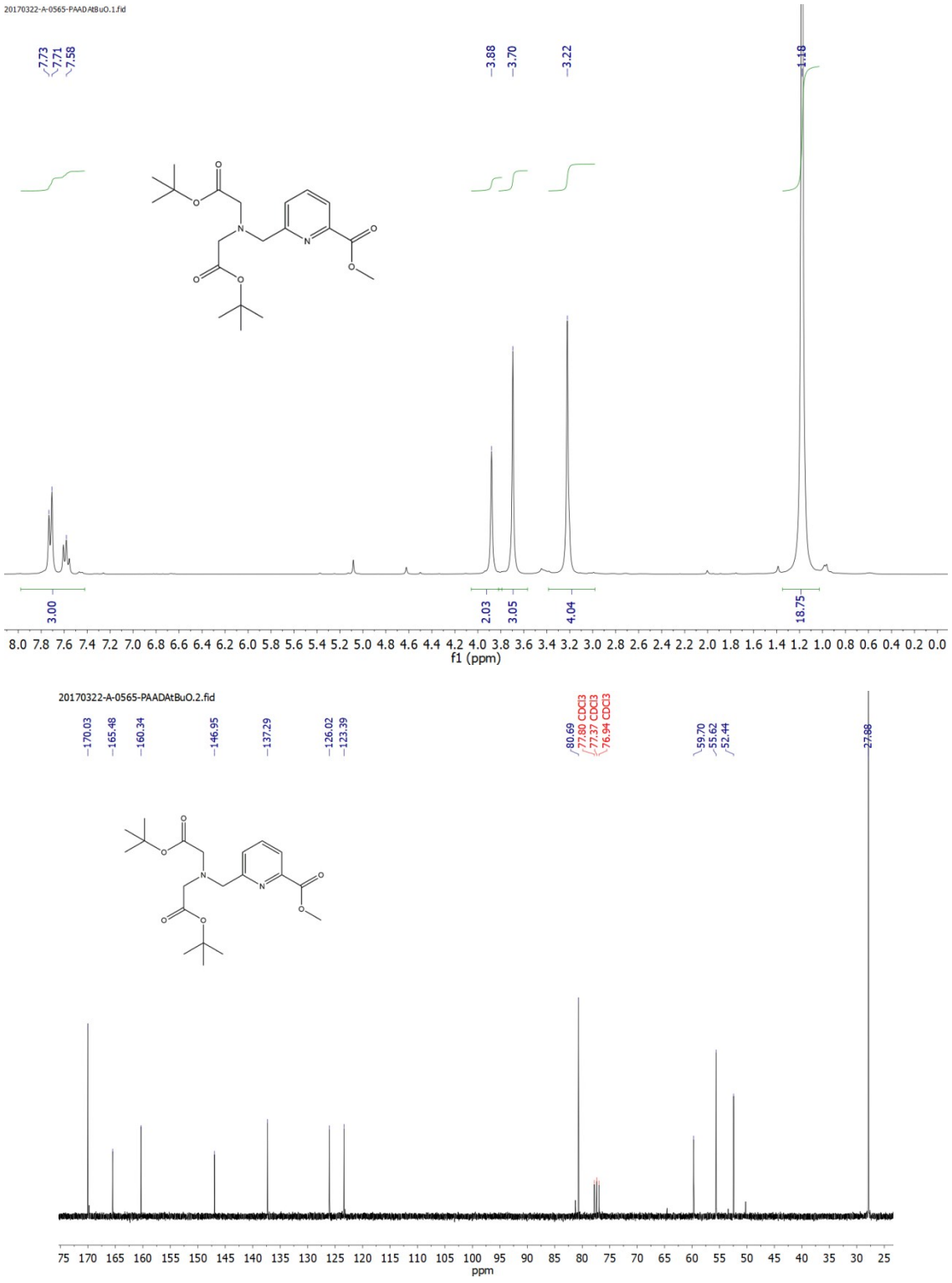

Figure S3. ^{1}H (300 MHz, 25 ^{o}C, top) and ^{13}C (75 MHz, 25 ^{o}C, bottom) NMR spectra of compound **6** recorded in $CDCl_3$ solution.

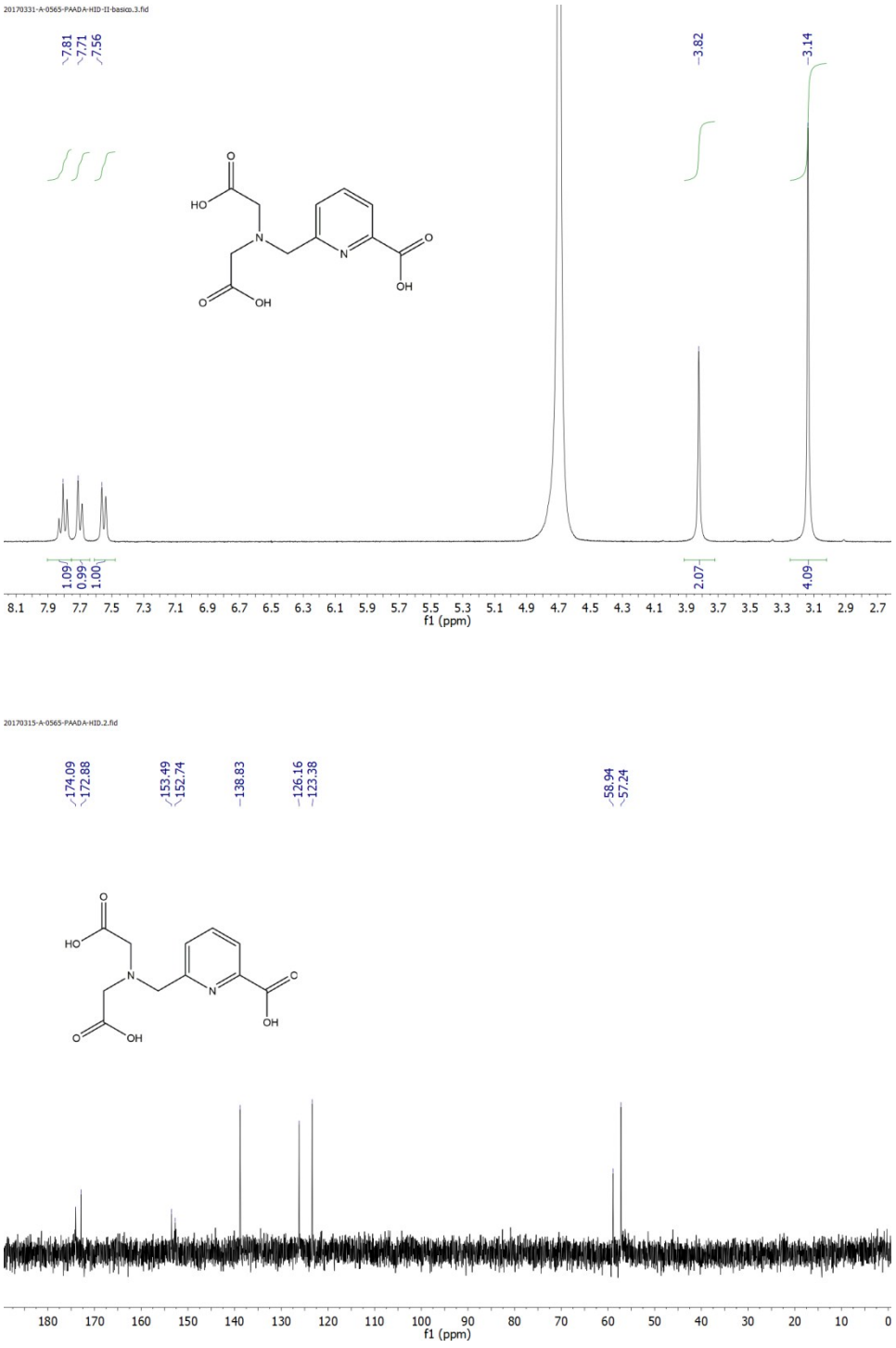

Figure S4. ^{1}H (300 MHz, 25 ^{o}C, top) and ^{13}C (75 MHz, 25 ^{o}C, bottom) NMR spectra of H_3PAADA recorded in D_2O solution.

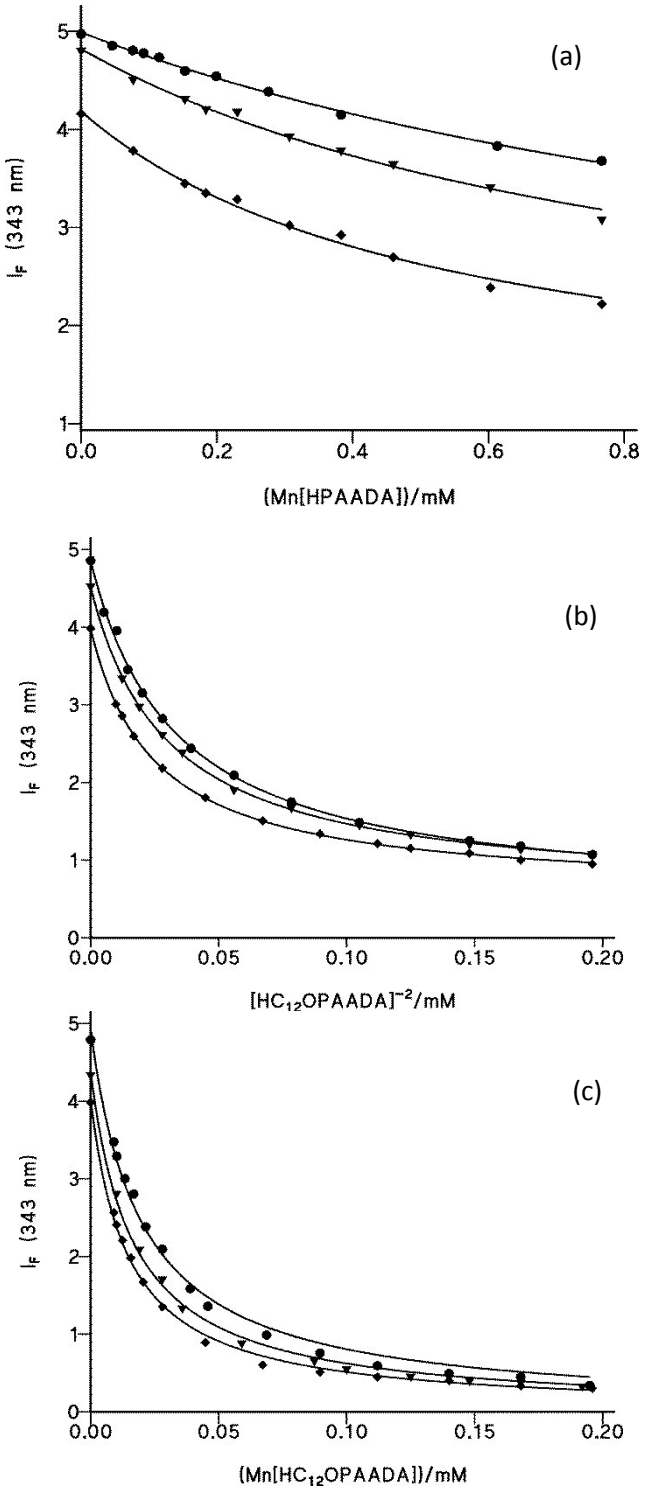

Figure S5. The fluorescence intensity, I_F, of BSA measured as a function of the ligand concentration at three temperatures: (●) 15, (②)25, and (✹)36 °C. Solid lines represent the fits of the experimental data of I_F-$[L]_o$ to eq. (7).

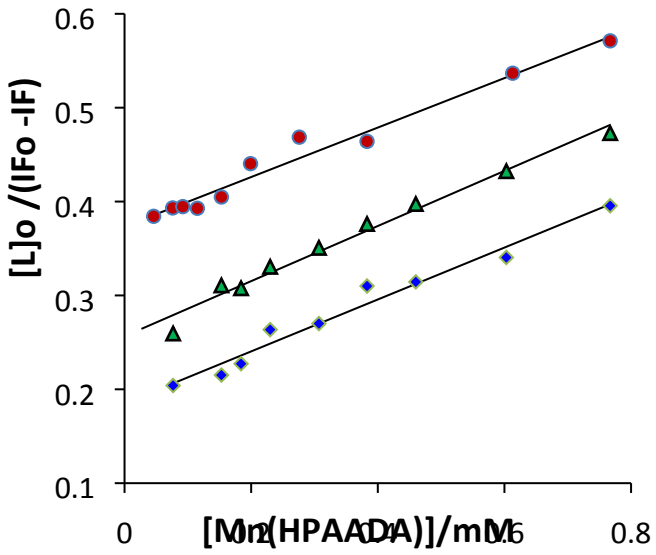

Figure S6. Benessi-Hildebrand plot for the experimental data of Figure S5 (a).

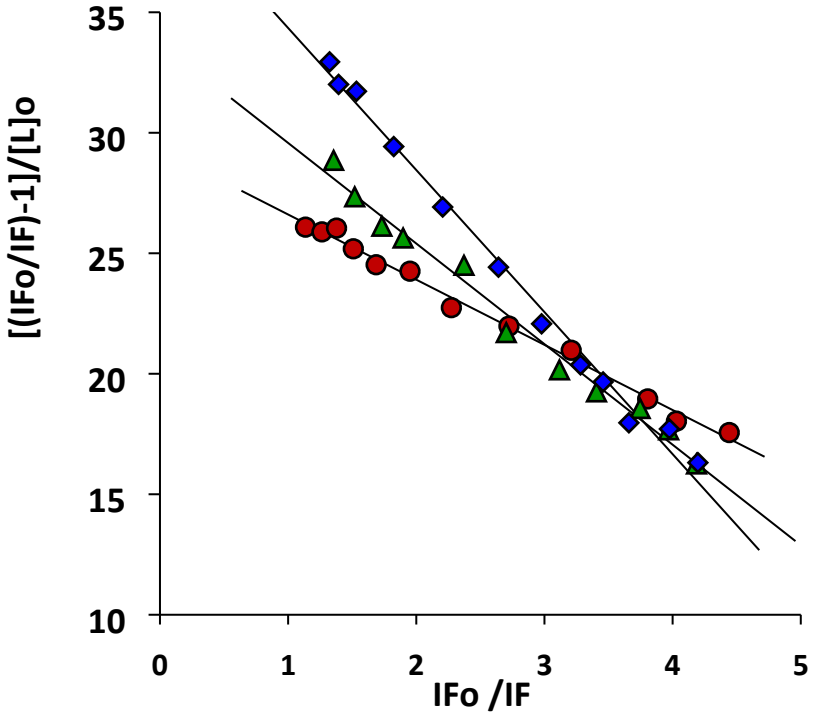

Figure S7. Scatchard plot for the case of BSA fluorescence quenching by the substrate $[HC_{12}OPAADA]^-$ using the experimental data of Figure S5(b).

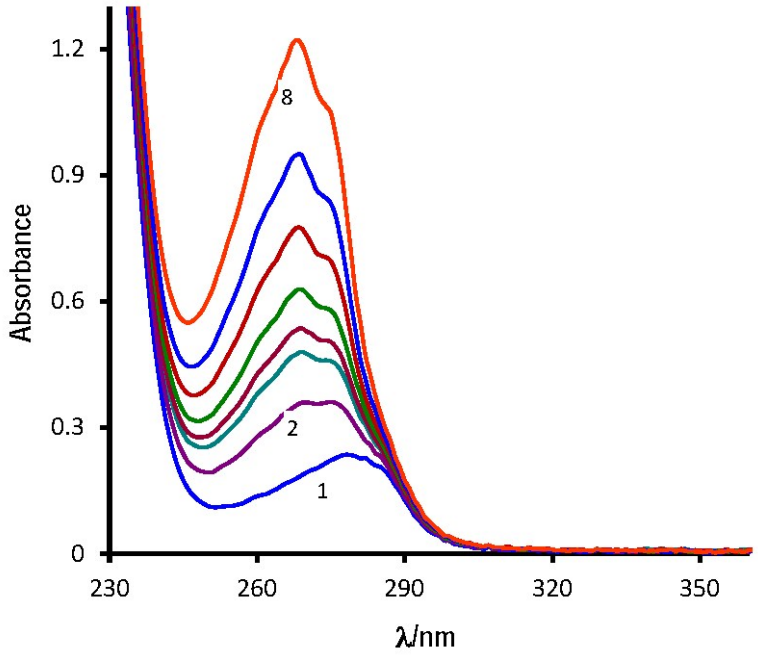

Figure S8. UV-vis absorption spectra of 5.2 μM BSA in 10 mM Tris-HCl buffer at pH 7.4 (1) as a function of increasing concentration of ligand, [$HPAADA^{2-}$] equal to: (1) no ligand; (2) 46 μM to (8) 0.276 mM.

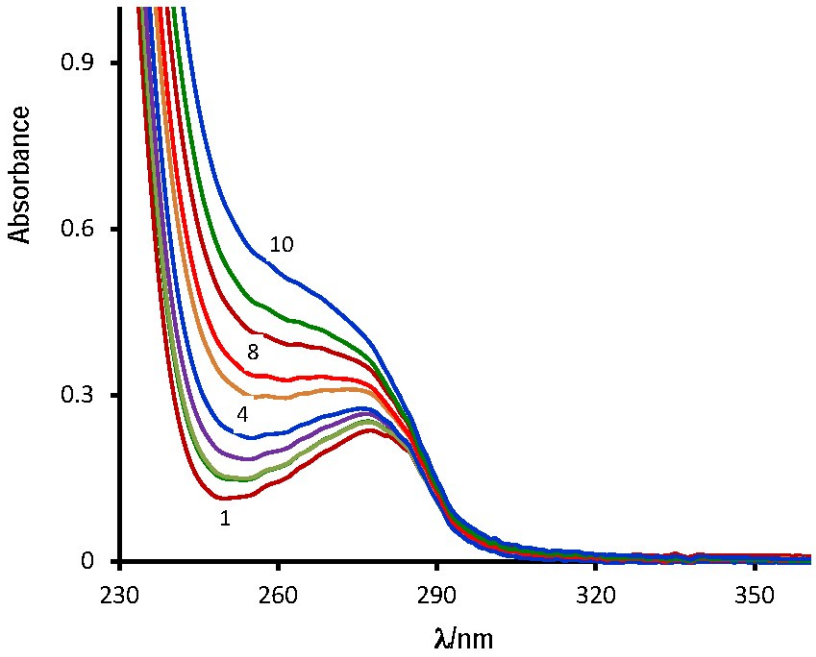

Figure S9. UV-vis absorption spectra of 5.2 μM BSA in 10 mM Tris-HCl buffer at pH 7.4 (1) as a function of increasing concentration of ligand $[HC_{12}OPAADA]^{2-}$ at: [1] 0; [4] 28; [8] 112, and [10] 168 μM. The absorbance values at 290 nm are: [1] 0.108; [4] 0.113; [8] 0.134, and [10] 0.145.

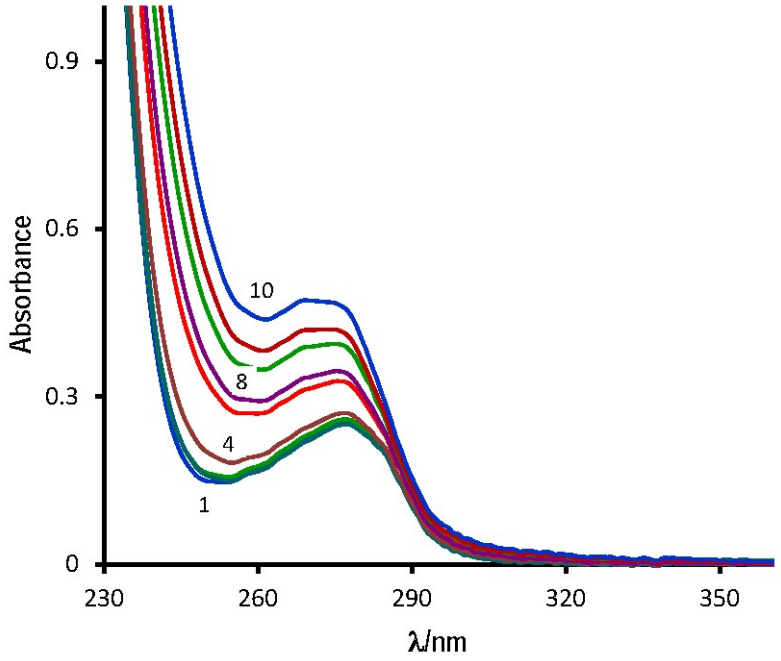

Figure S10. UV-vis absorption spectra of 5.2 μM BSA in 10 mM Tris-HCl buffer at pH 7.4 (1) as a function of increasing concentration of both ligand $[HC_{12}OPAADA]^{2-}$ and Mn^{+2} (Mn:L 1:1) at: [1] 0; [4] 28; [8] 112, and [10] 168 μM. The absorbance values at 290 nm are: [1] 0.108; [4] 0.111; [8] 0.140, and [10] 0.148.

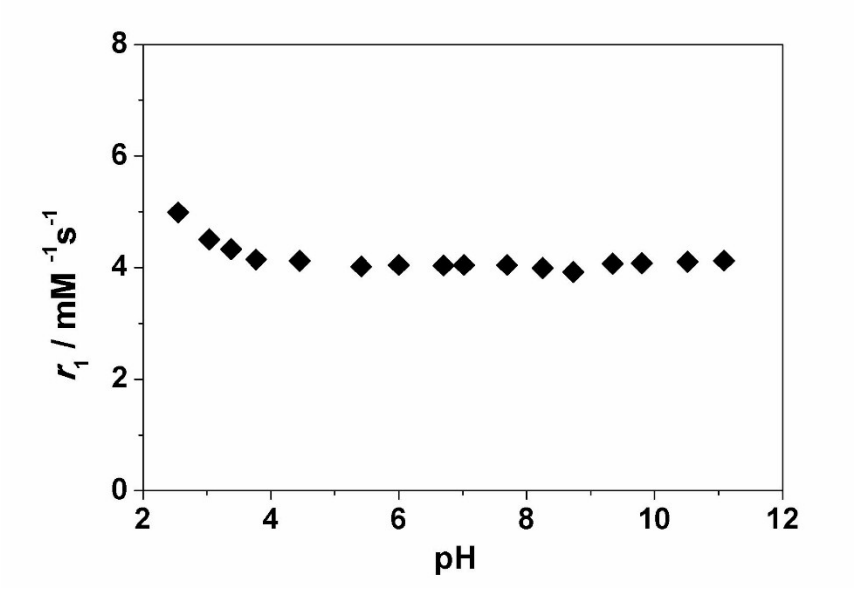

Figure S11. pH dependence of the proton relaxivity (r_1) for $[Mn(PAADA)]^-$ measured at 20 MHz and 298 K.

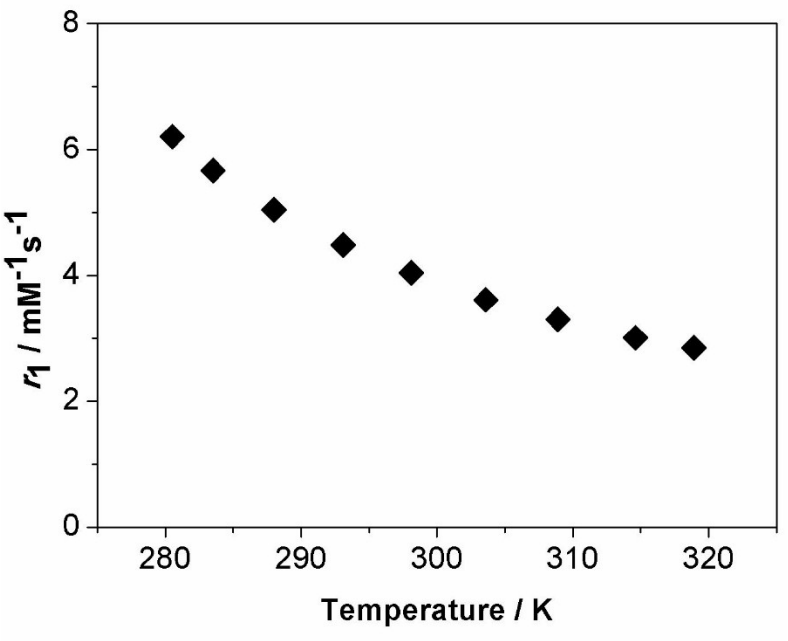

Figure S12. Temperature dependence of the proton relaxivity values at 20 MHz for $[Mn(PAADA)]^-$ (pH = 7.5).

Table S1. $[Mn(NTA)(H_2O)_2]^{-}\cdot 4H_2O$, M06-2X/Def2-TZVP, aqueous solution (0 Imaginary Frequencies).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	-2.071818	-0.168555	-0.244522
2	6	-2.810124	0.497967	0.823999
3	6	-2.374189	-1.592204	-0.341282
4	6	-1.149457	-2.467786	-0.643583
5	8	-0.017397	-2.005499	-0.271153
6	8	-1.334056	-3.563396	-1.166614
7	6	-1.331579	1.850969	-1.486674
8	6	-2.132040	0.538147	-1.516757
9	8	-0.489582	1.982254	-0.533093
10	8	-1.530087	2.667049	-2.382881
11	1	-3.847468	0.156692	0.885443
12	1	-2.828415	1.571938	0.626328
13	1	-2.742222	-1.936638	0.629086
14	1	-3.156710	-1.801936	-1.076118
15	1	-3.158183	0.752123	-1.835946
16	1	-1.669890	-0.087902	-2.286076
17	8	2.110719	-0.010019	1.390204
18	1	2.622651	0.820093	1.368007
19	8	1.327502	0.114610	-1.626011
20	1	1.922746	-0.654601	-1.714039
21	1	2.740042	-0.737094	1.228460
22	1	1.831751	0.947069	-1.688883
23	6	-2.134439	0.332077	2.196275
24	8	-0.879698	0.121444	2.191211
25	8	-2.841377	0.456285	3.198146
26	8	2.021990	2.768187	-1.319647
27	8	2.393743	-2.419402	-1.469232
28	1	1.085233	2.722455	-1.037909
29	1	2.532993	2.801003	-0.496439
30	1	3.031731	-2.447120	-0.740764
31	1	1.516043	-2.498986	-1.039188
32	8	3.952276	-2.082499	0.929028
33	8	3.431446	2.456831	1.191683
34	1	3.957180	-2.790534	1.583198
35	1	4.867133	-1.788204	0.851711
36	1	4.392820	2.430267	1.121563
37	1	3.236466	3.083499	1.898068
38	25	0.183839	0.071839	0.327606

E(UM062X) = -2348.4253432 Hartree
Zero-point correction = 0.284542
Thermal correction to Energy = 0.313633
Thermal correction to Enthalpy = 0.314577
Thermal correction to Gibbs Free Energy = 0.222716
Sum of electronic and zero-point Energies = -2348.140801
Sum of electronic and thermal Energies = -2348.111710
Sum of electronic and thermal Enthalpies = -2348.110766
Sum of electronic and thermal Free Energies = -2348.202628

Table S2. $[Mn(PAADA)(H_2O)_2]^{-}\cdot 4H_2O$, M06-2X/Def2-TZVP, aqueous solution (0 Imaginary Frequencies).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	8	-0.858200	2.074649	0.633369
2	7	-1.827685	-0.044040	-0.579101
3	8	-2.787060	3.180579	0.424322
4	6	-2.260713	-1.206965	-1.051625
5	7	-0.042326	-2.139212	-0.534010
6	6	-4.061163	0.759918	-0.442668
7	1	-4.727744	1.570526	-0.186708
8	6	-2.086863	2.179759	0.307386
9	6	1.204229	-2.527694	-1.180589
10	1	1.216880	-2.141328	-2.201082
11	1	1.333976	-3.614558	-1.245403
12	6	-2.695298	0.914241	-0.271158
13	6	-1.187015	-2.193186	-1.439996
14	1	-1.609015	-3.202264	-1.511121
15	1	-0.846643	-1.913182	-2.439391
16	6	-3.615895	-1.457911	-1.229113
17	1	-3.945943	-2.419868	-1.597919
18	6	-4.524786	-0.456110	-0.924279
19	1	-5.585813	-0.625902	-1.053622
20	8	1.264165	0.917840	-1.474354
21	1	2.234144	0.783351	-1.536904
22	1	1.101427	1.866852	-1.664457
23	6	-0.280805	-2.902697	0.695534
24	1	-0.863857	-3.805992	0.492689
25	1	0.685691	-3.216497	1.096790
26	8	0.966012	3.624749	-1.839149
27	1	0.939488	3.943354	-0.915662
28	1	0.145723	3.922747	-2.244825
29	8	4.025852	0.482817	-1.596280
30	1	4.310086	0.766786	-0.712698
31	1	4.052229	-0.488958	-1.528597
32	6	-0.947146	-2.122493	1.843204
33	25	0.318780	0.159105	0.381885
34	8	-1.691278	-2.755140	2.596410
35	8	-0.621982	-0.902113	1.974176
36	6	2.429733	-1.928293	-0.494776
37	8	2.223171	-1.105978	0.449474
38	8	3.542371	-2.242288	-0.939366
39	8	1.654392	1.453909	1.690022
40	1	1.541148	2.409095	1.546683
41	1	2.609419	1.263164	1.644673
42	8	0.795580	4.028927	0.890643
43	8	4.192891	0.460646	1.224241
44	1	4.846641	0.165281	1.864600
45	1	3.605911	-0.307824	1.005410
46	1	-0.007286	3.436706	0.884762
47	1	0.591148	4.813455	1.407832

E(UM062X) = -2595.5407108 Hartree
Zero-point correction = 0.354360
Thermal correction to Energy = 0.387126
Thermal correction to Enthalpy = 0.388070
Thermal correction to Gibbs Free Energy = 0.288586
Sum of electronic and zero-point Energies = -2595.186350
Sum of electronic and thermal Energies = -2595.153585
Sum of electronic and thermal Enthalpies = -2595.152641
Sum of electronic and thermal Free Energies = -2595.252124