Electronic Supplementary Material (ESI) for Dalton Transactions.

Developing the Family of Picolinate Ligands for Mn^{2+} Complexation

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Electronic Supplementary Information(ESI)

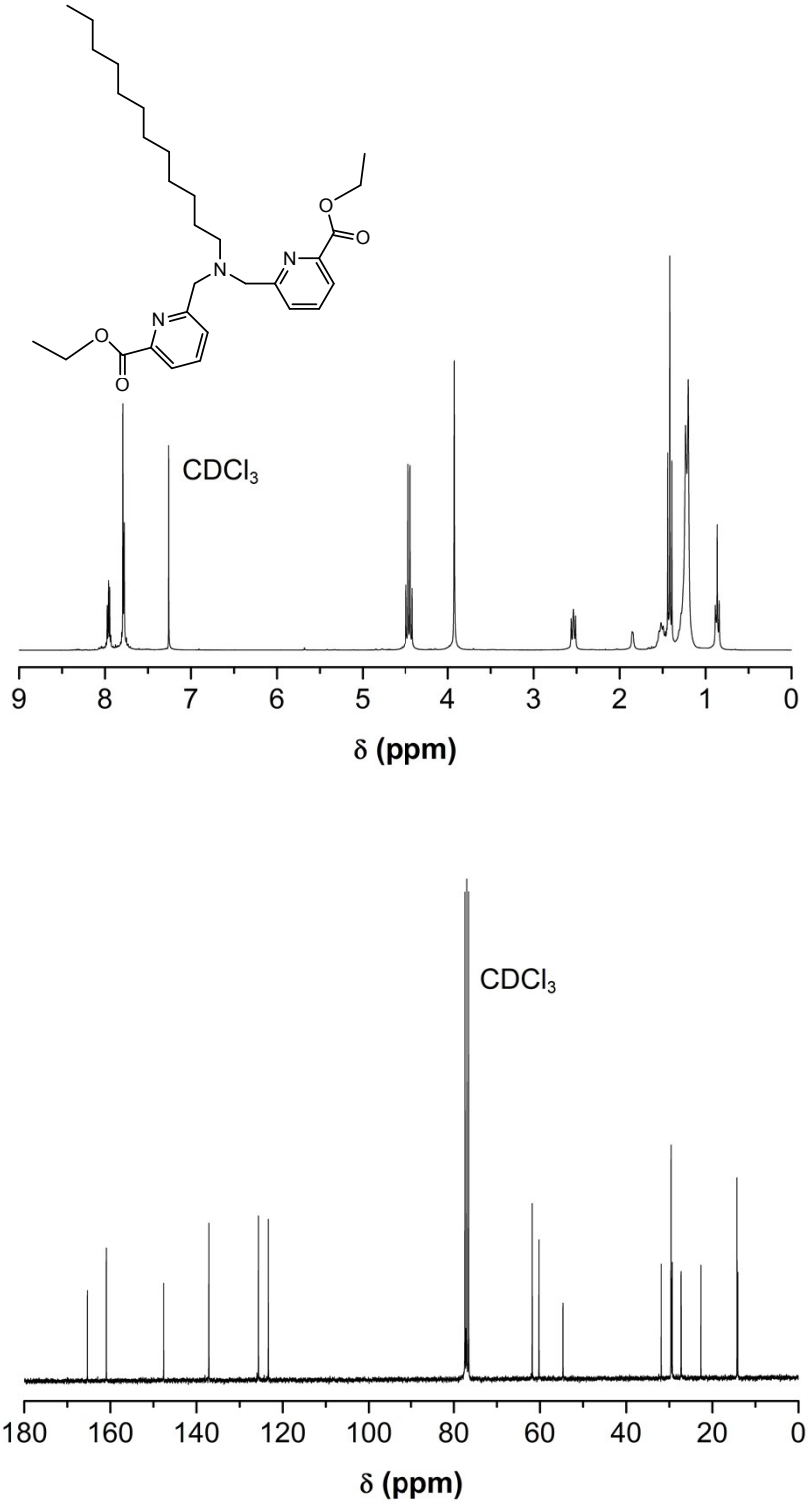

Figure S1. ^{1}H (300 MHz, 25 ^{o}C, top) and ^{13}C (75 MHz, 25 ^{o}C, bottom) NMR spectra of the **ethyl ester precursor** of **H_2DPADA** recorded in $CDCl_3$ solution.

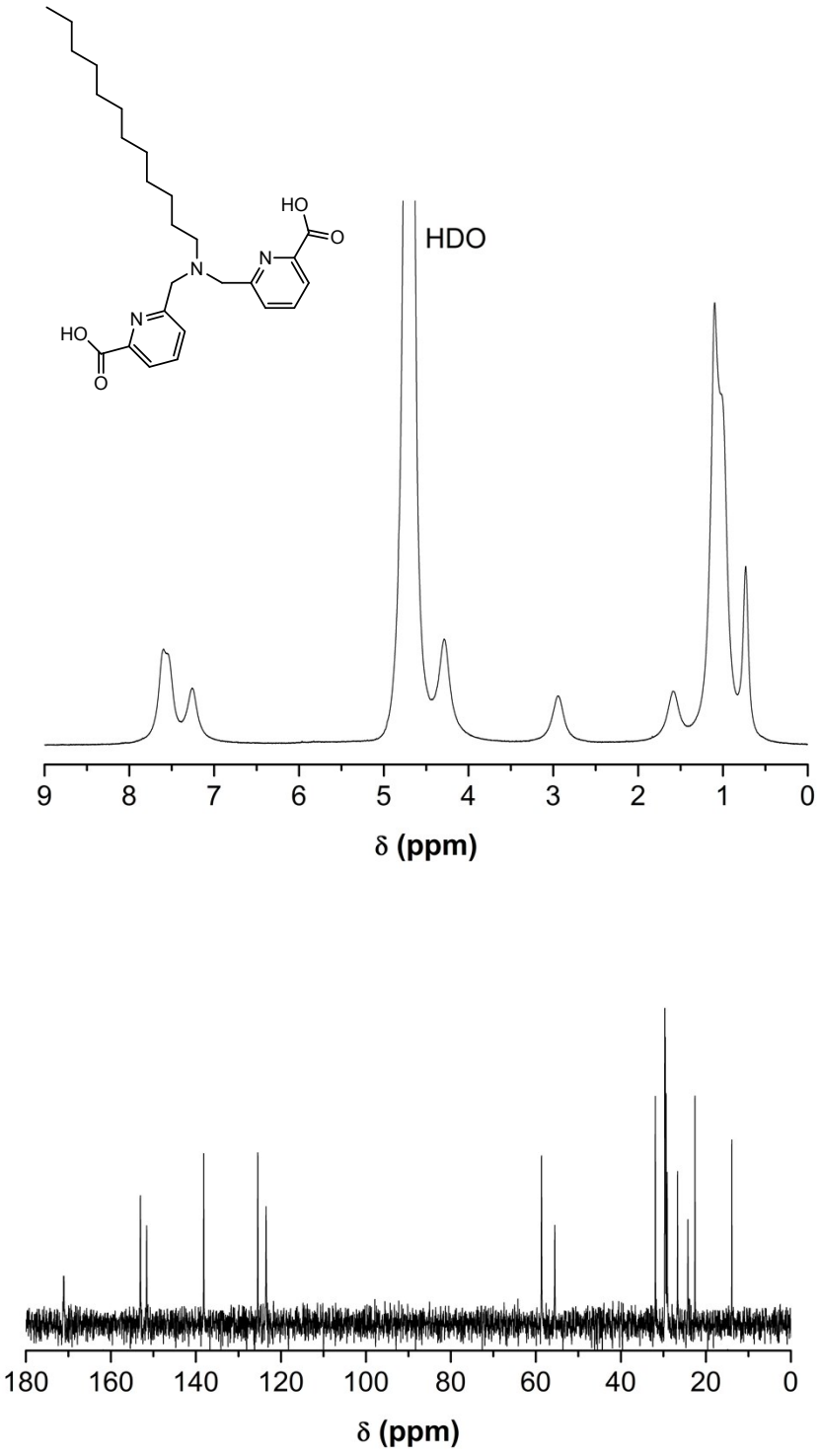

Figure S2. ^{1}H (500 MHz, 25 ^{o}C, pD 7.0, top) and ^{13}C (125.8 MHz, 25 ^{o}C, pD 7.0, bottom) NMR spectra of H_2DPADA recorded in D_2O solution.

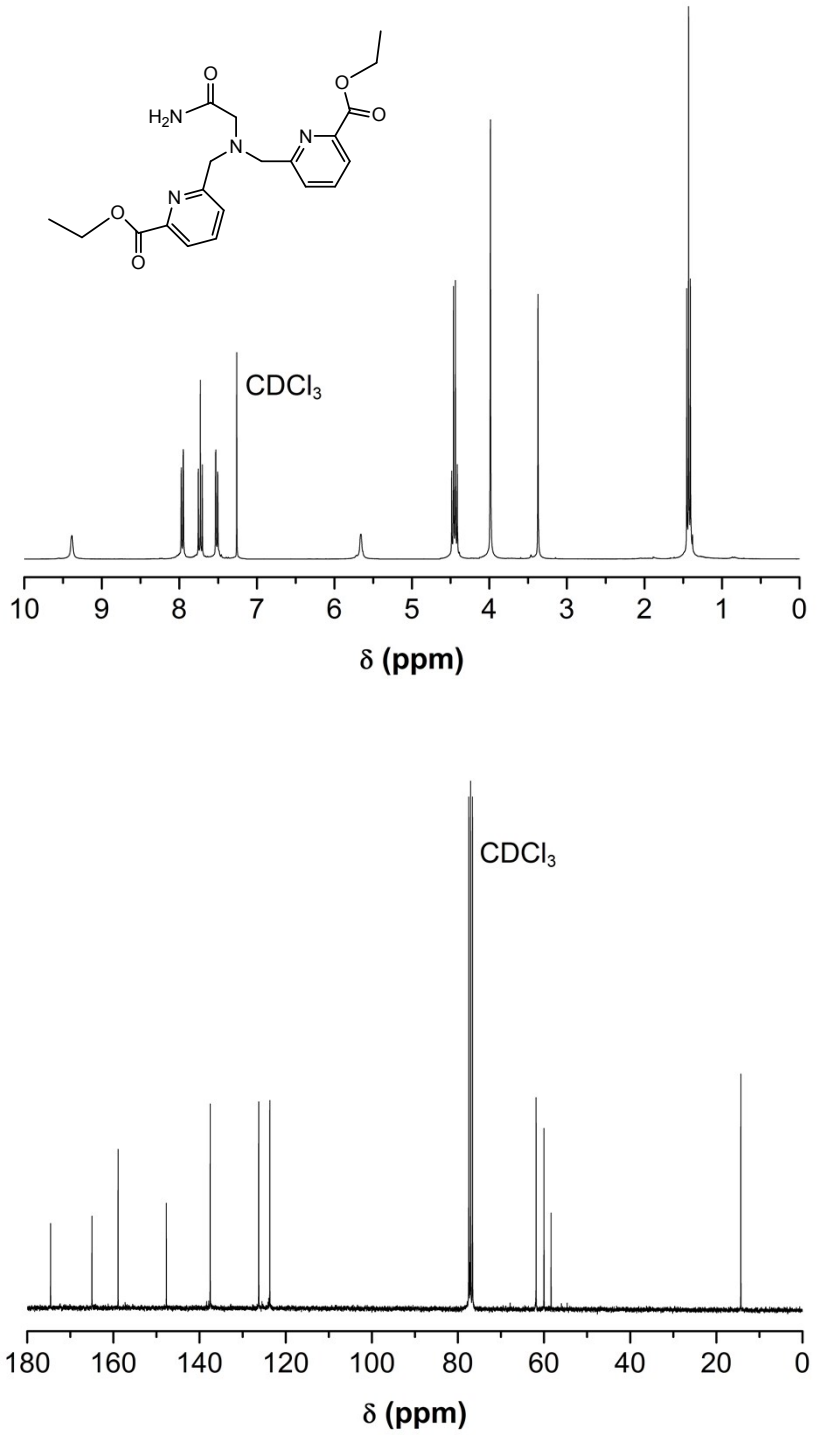

Figure S3. ^{1}H (300 MHz, 25 ^{o}C, top) and ^{13}C (75 MHz, 25 ^{o}C, bottom) NMR spectra of ethyl ester precursor of H_3DPAA recorded in $CDCl_3$ solution.

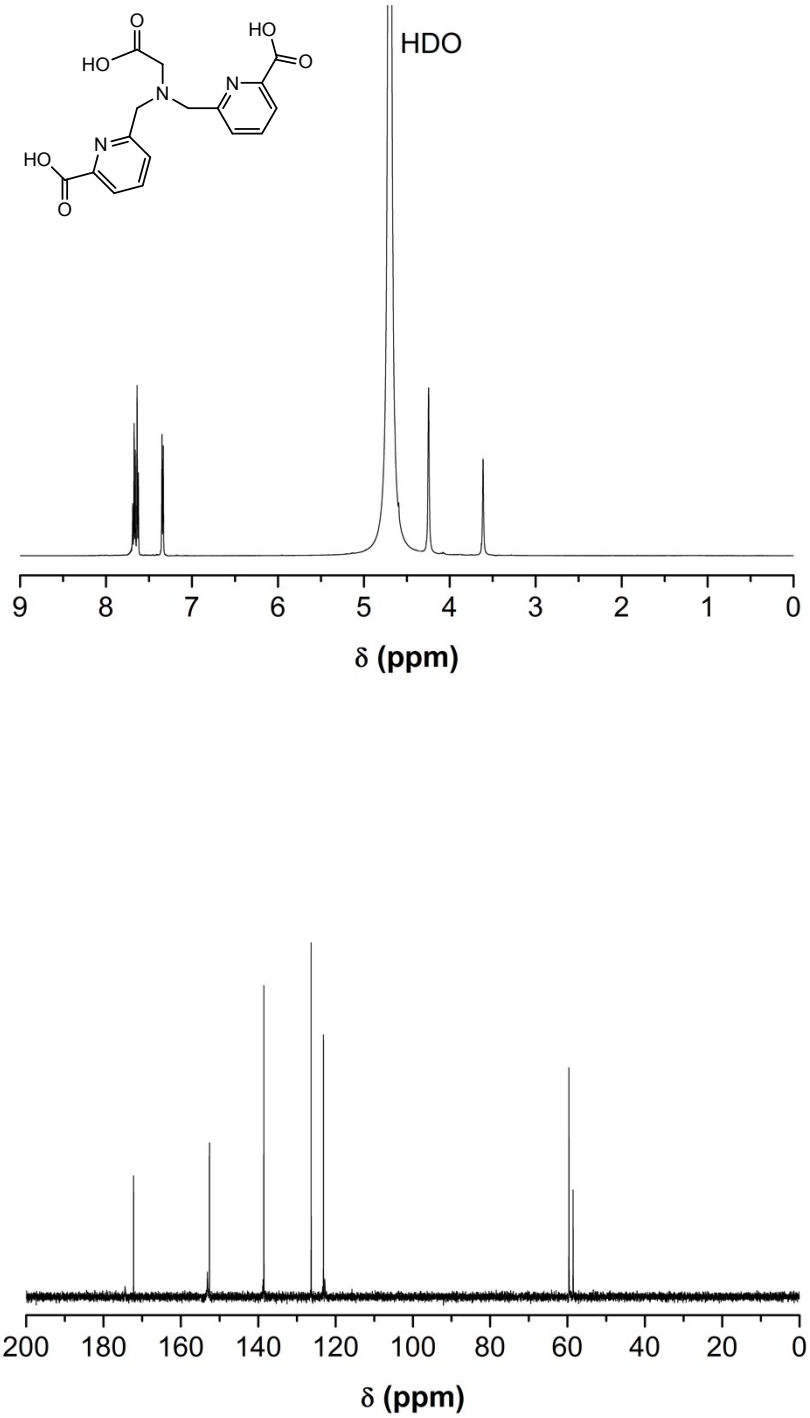

Figure S4. ^{1}H (500 MHz, 25 ^{o}C, pD 7.0, top) and ^{13}C (125.8 MHz, 25 ^{o}C, pD 7.0, bottom) NMR spectra of H_3DPAA recorded in D_2O solution.

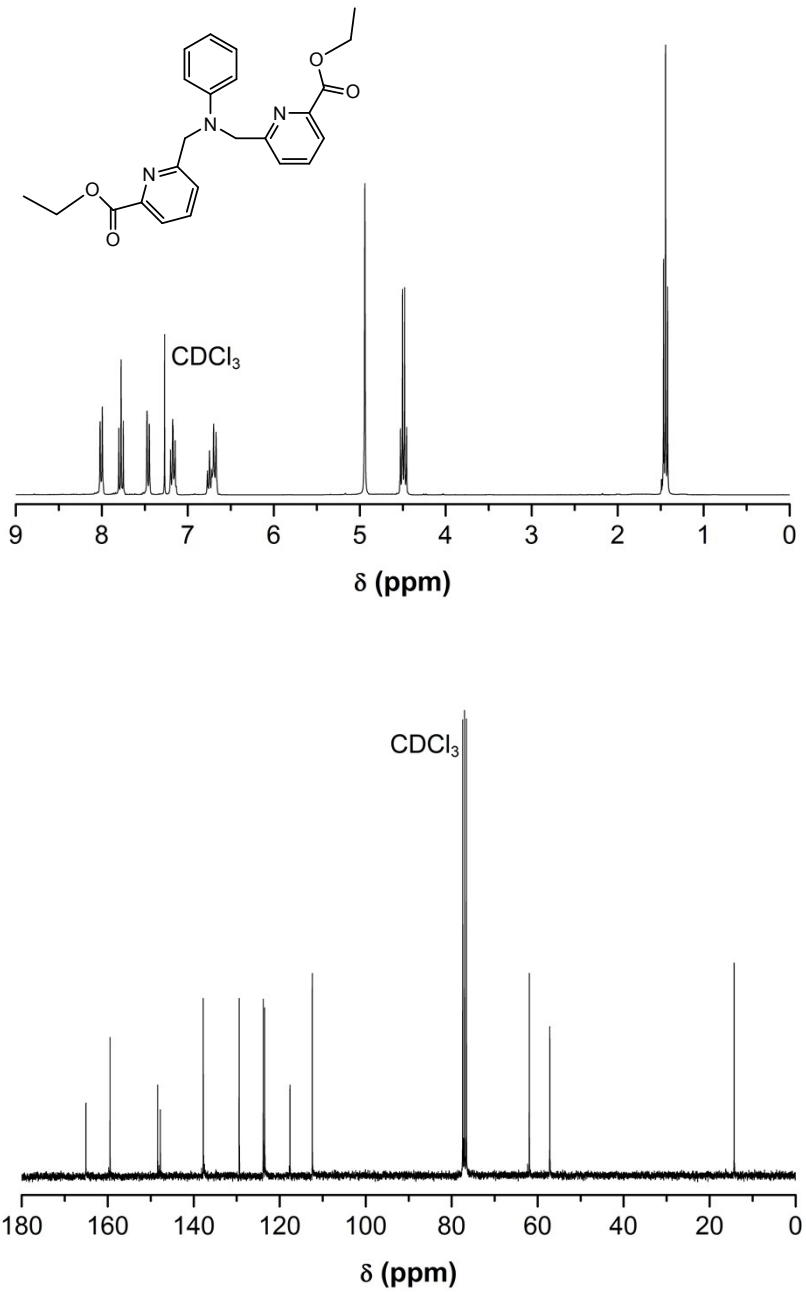

Figure S5. ^{1}H (300 MHz, 25 ^{o}C, top) and ^{13}C (75 MHz, 25 ^{o}C, bottom) NMR spectra of ethyl ester precursor of H_2DPAPhA recorded in $CDCl_3$ solution.

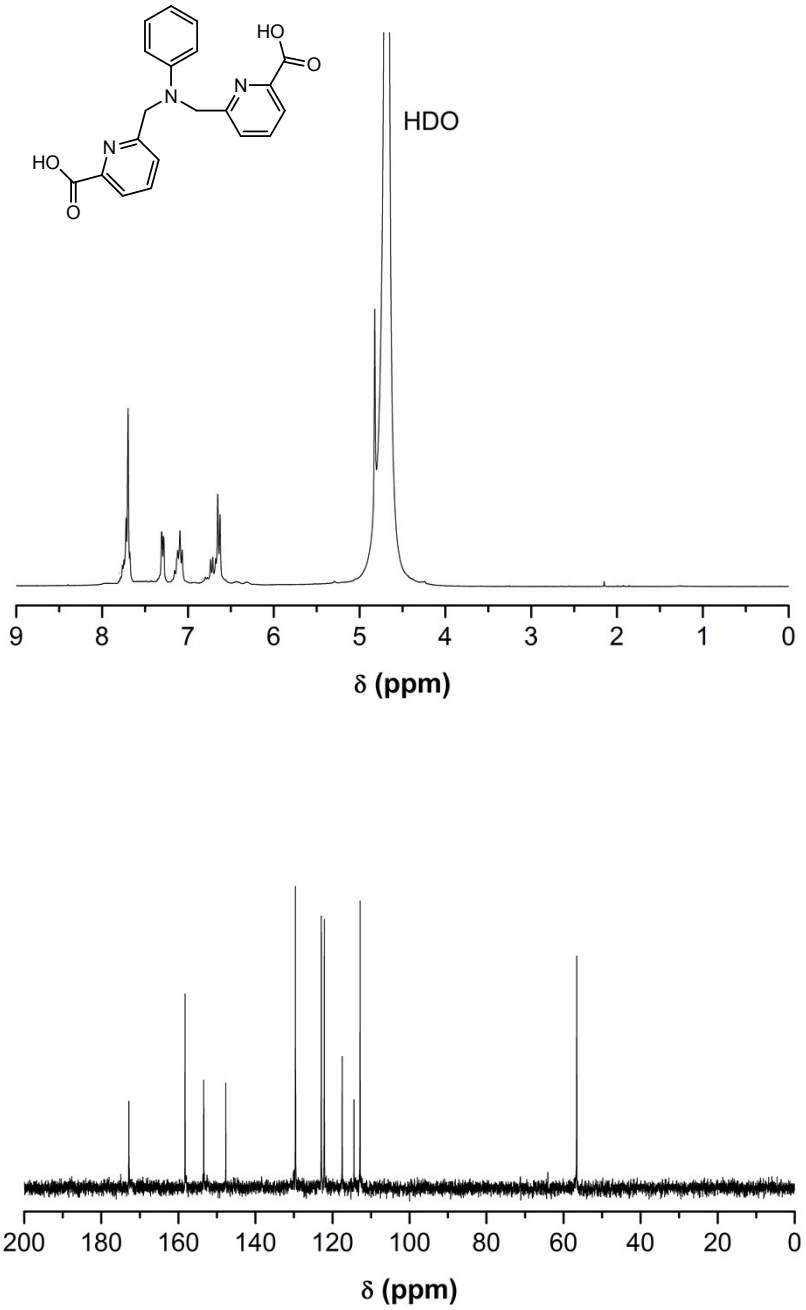

Figure S6. ^{1}H (300 MHz, 25 ^{o}C, pD 7.0, top) and ^{13}C (75 MHz, 25 ^{o}C, pD 7.0, bottom) NMR spectra of $H_2DPAPhA$ recorded in D_2O solution.

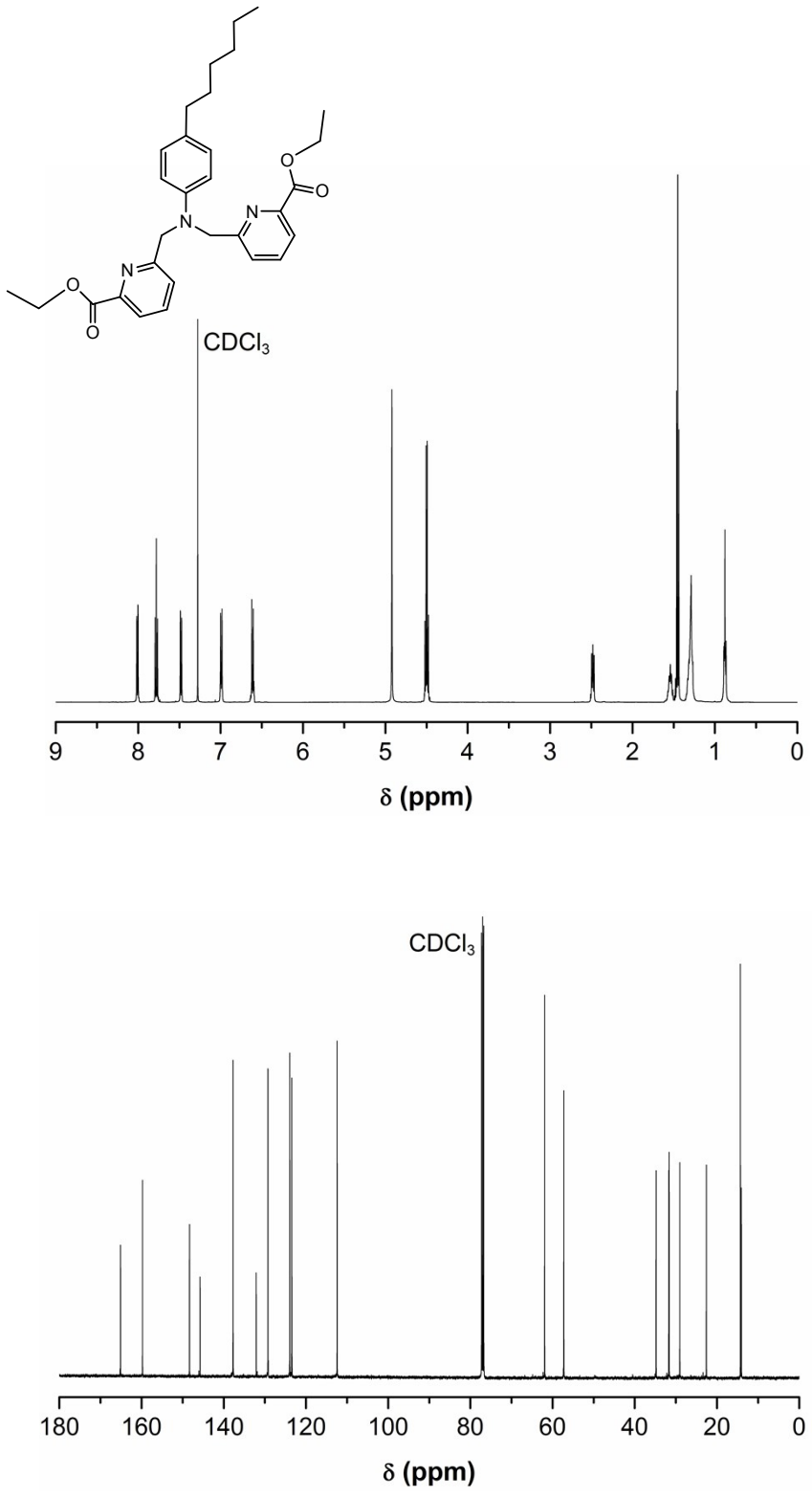

Figure S7. ^{1}H (500 MHz, 25 ^{o}C, top) and ^{13}C (125.8 MHz, 25 ^{o}C, bottom) NMR spectra of ethyl ester precursor of H_2DPAHPhA recorded in $CDCl_3$ solution.

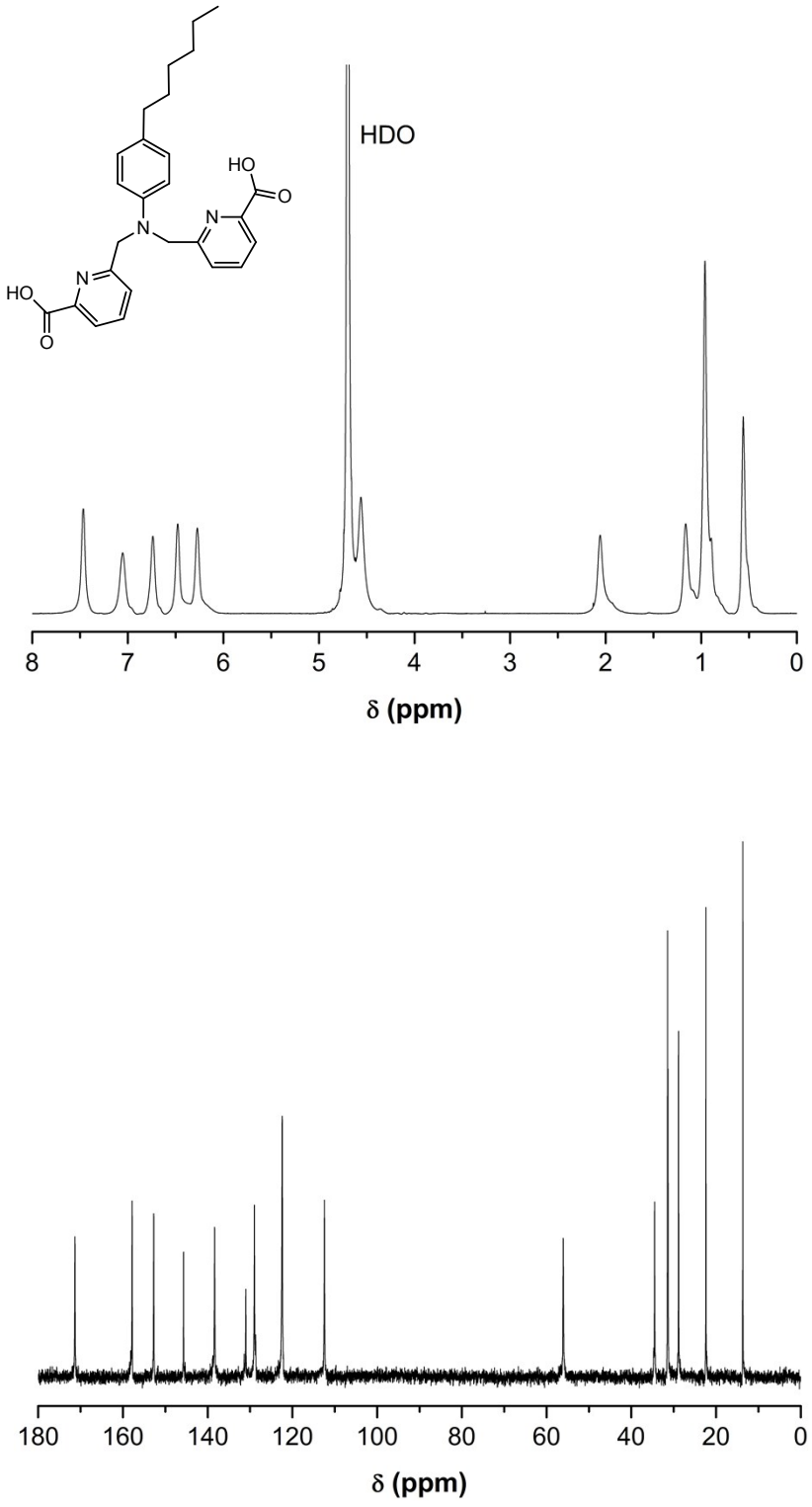

Figure S8. ^{1}H (500 MHz, 25 ^{o}C, pD 7.0, top) and ^{13}C (125.8 MHz, 25 ^{o}C, pD 7.0, bottom) NMR spectra of **H_2DPAHPhA** recorded in D_2O solution.

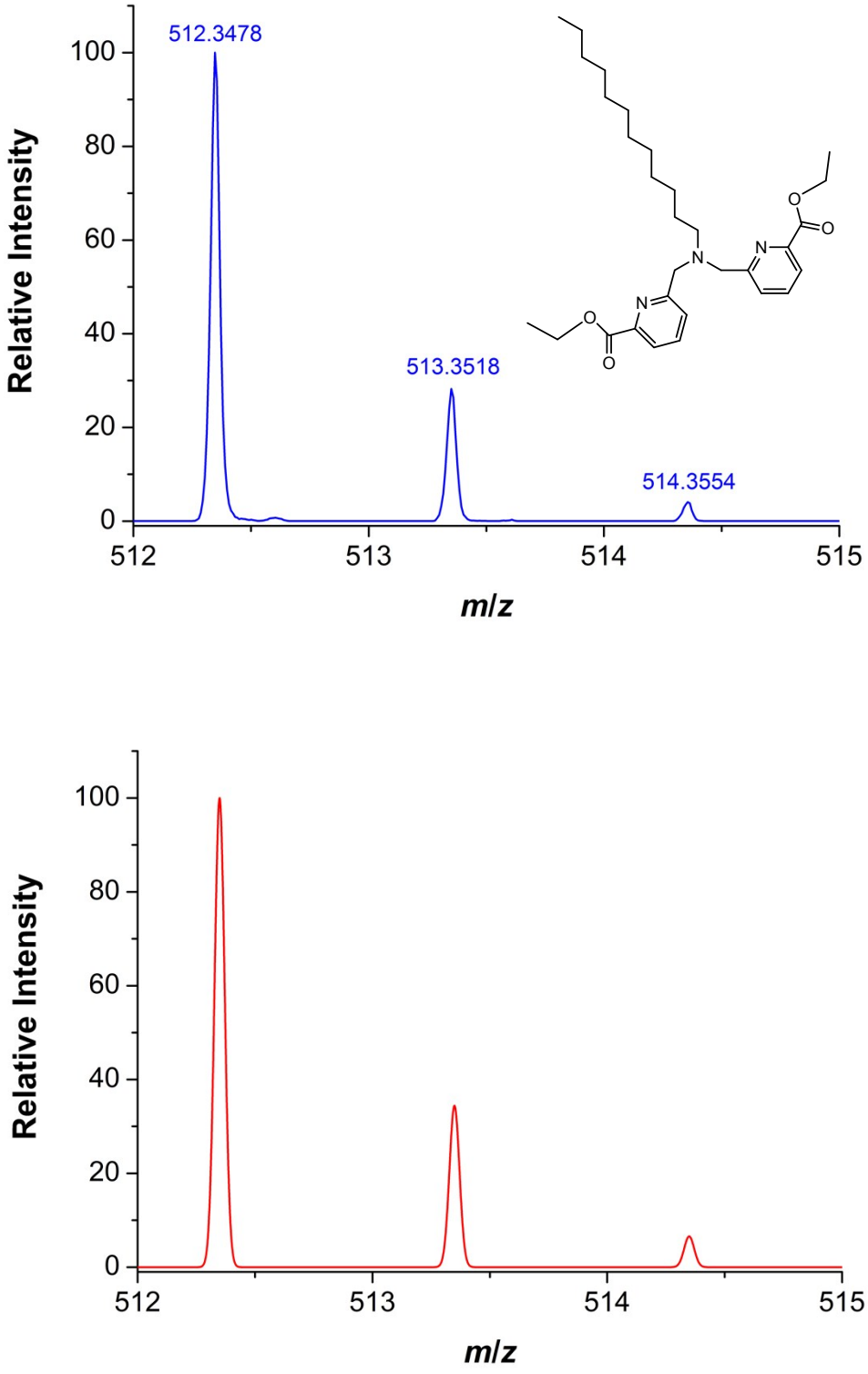

Figure S9. Observed (top) and theoretical (bottom) mass spectral isotopic distribution for the fragment $[DPA(OEt)_2DA+H]^+$ obtained in CH_3CN.

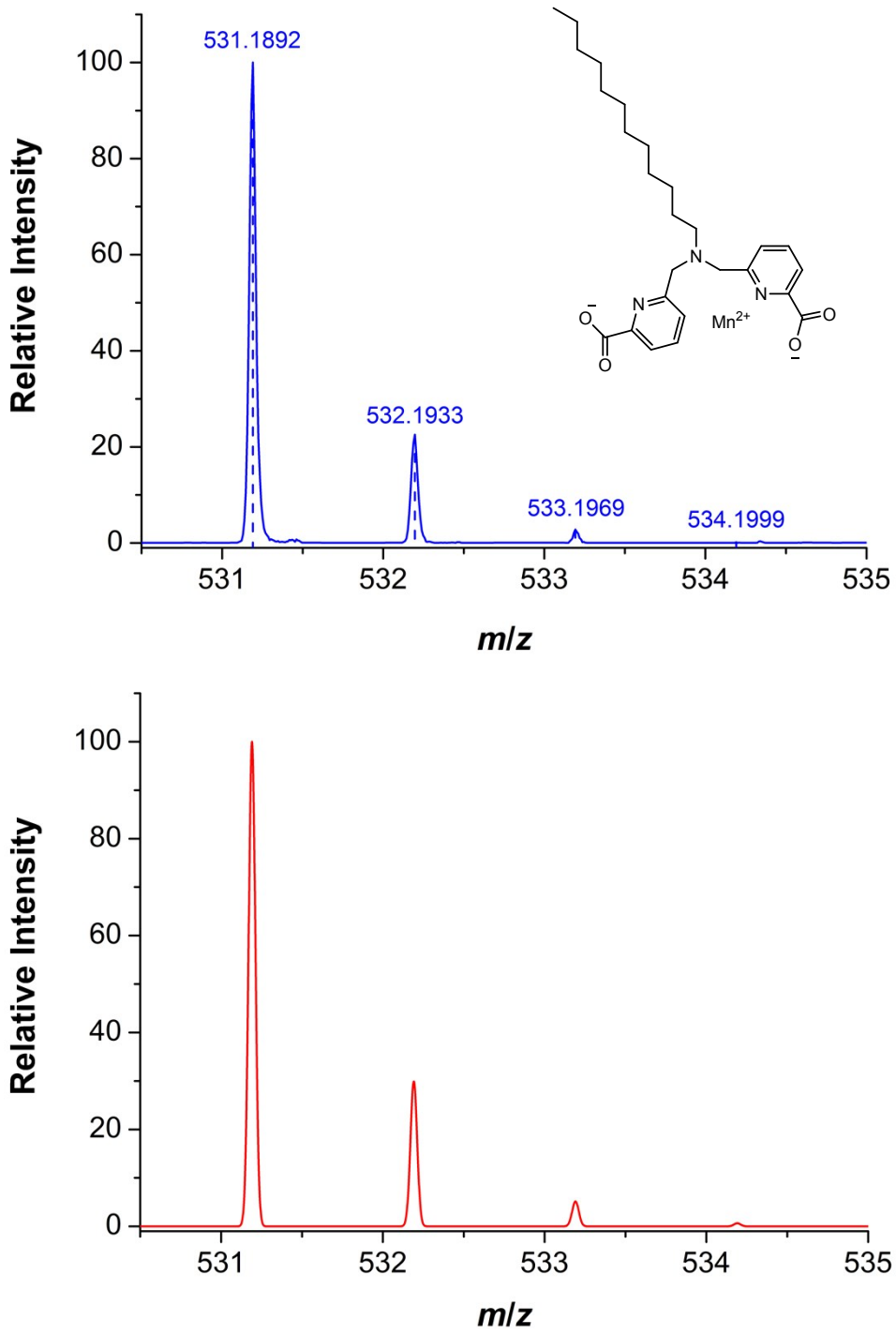

Figure S10. Observed (top) and theoretical (bottom) mass spectral isotopic distribution for the fragment $[Mn(DPADA+Na)]^+$ obtained from a solution of the complex in MeOH.

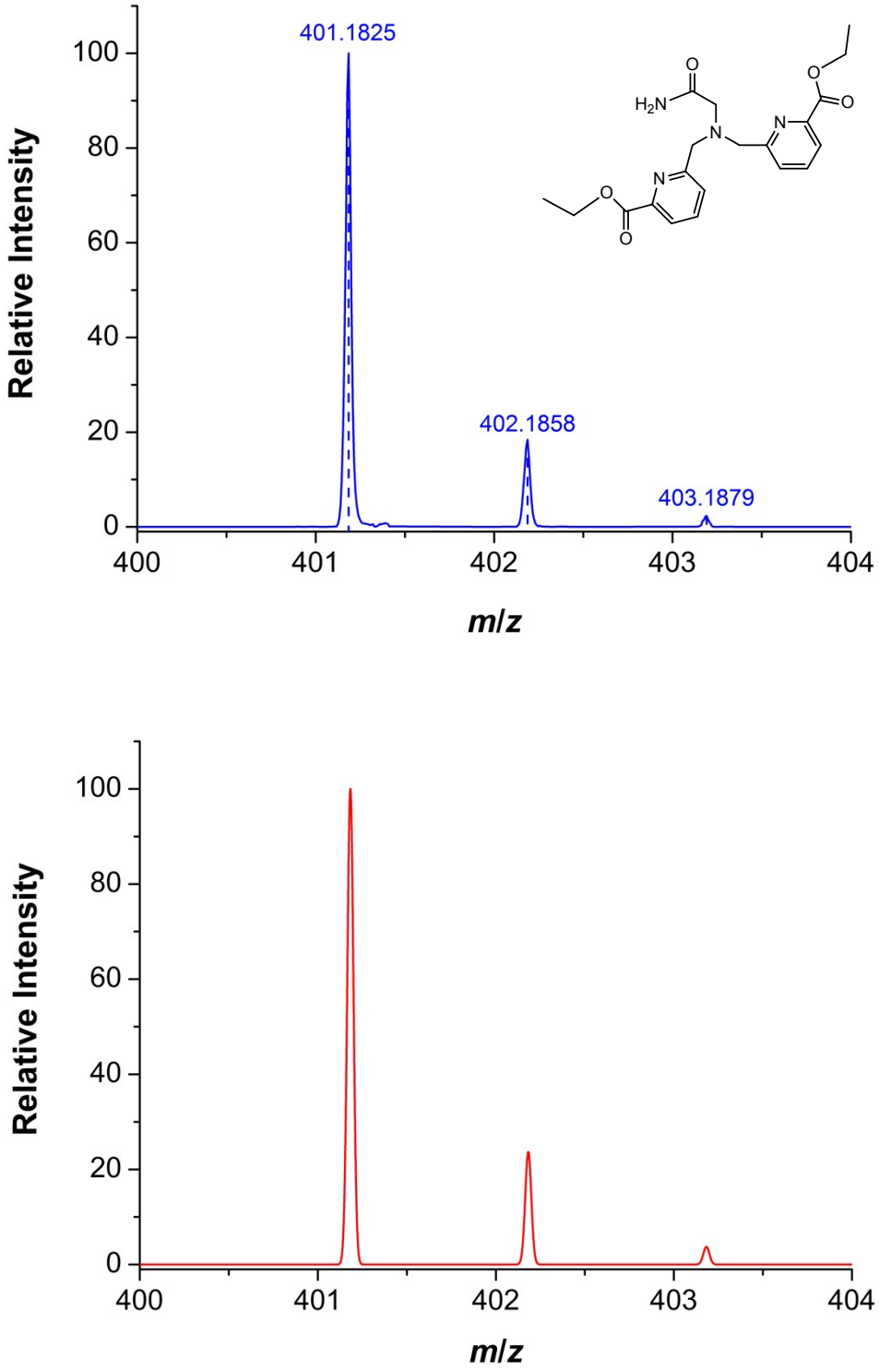

Figure S11. Observed (top) and theoretical (bottom) mass spectral isotopic distribution for the fragment $[DPA(OEt)_2A+H]^+$ obtained from a solution of this compound in CH_3CN.

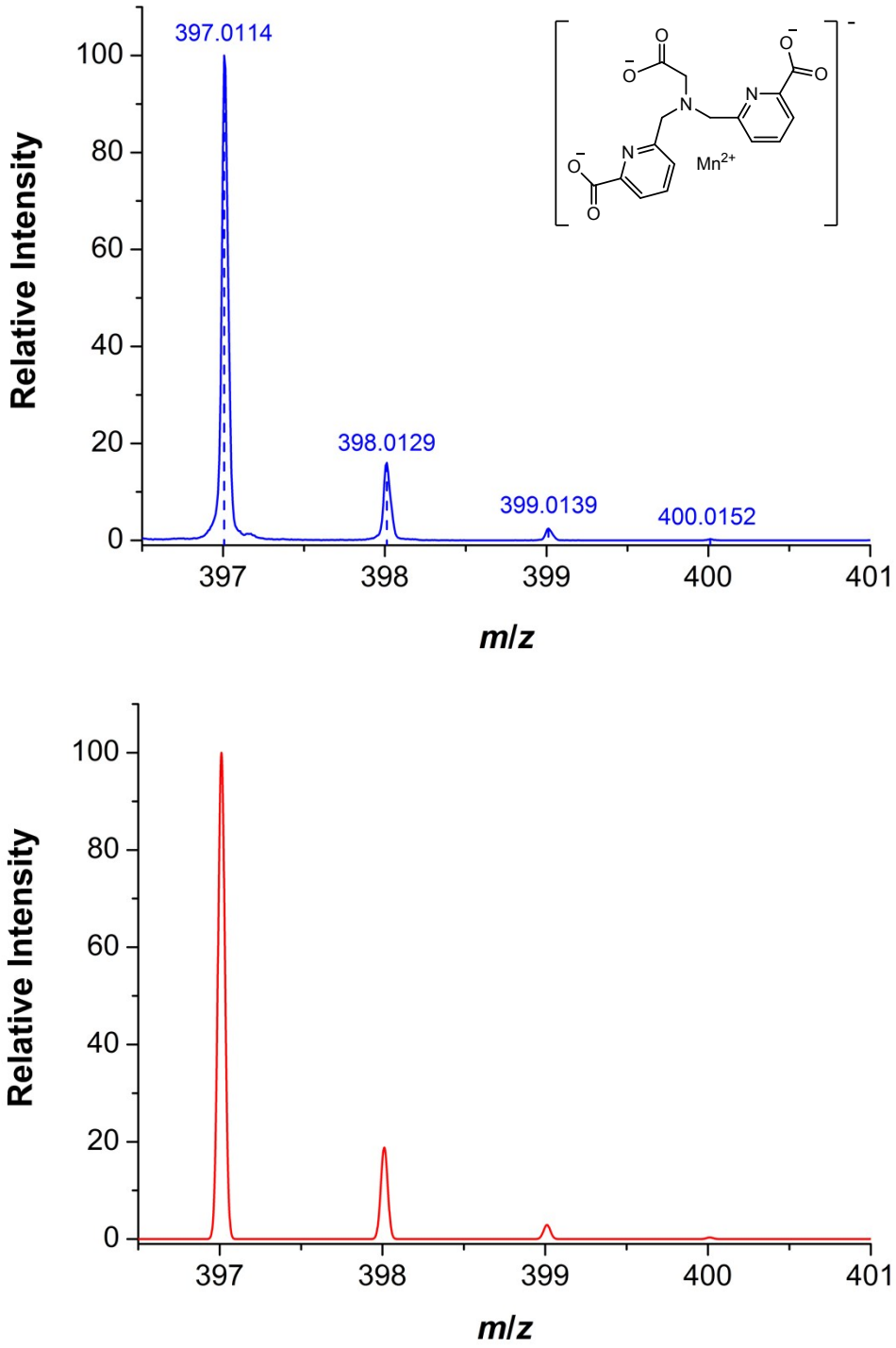

Figure S12. Observed (top) and theoretical (bottom) mass spectral isotopic distribution for the fragment $[Mn(DPAA)]^-$ obtained from a solution of this compound in MeOH.

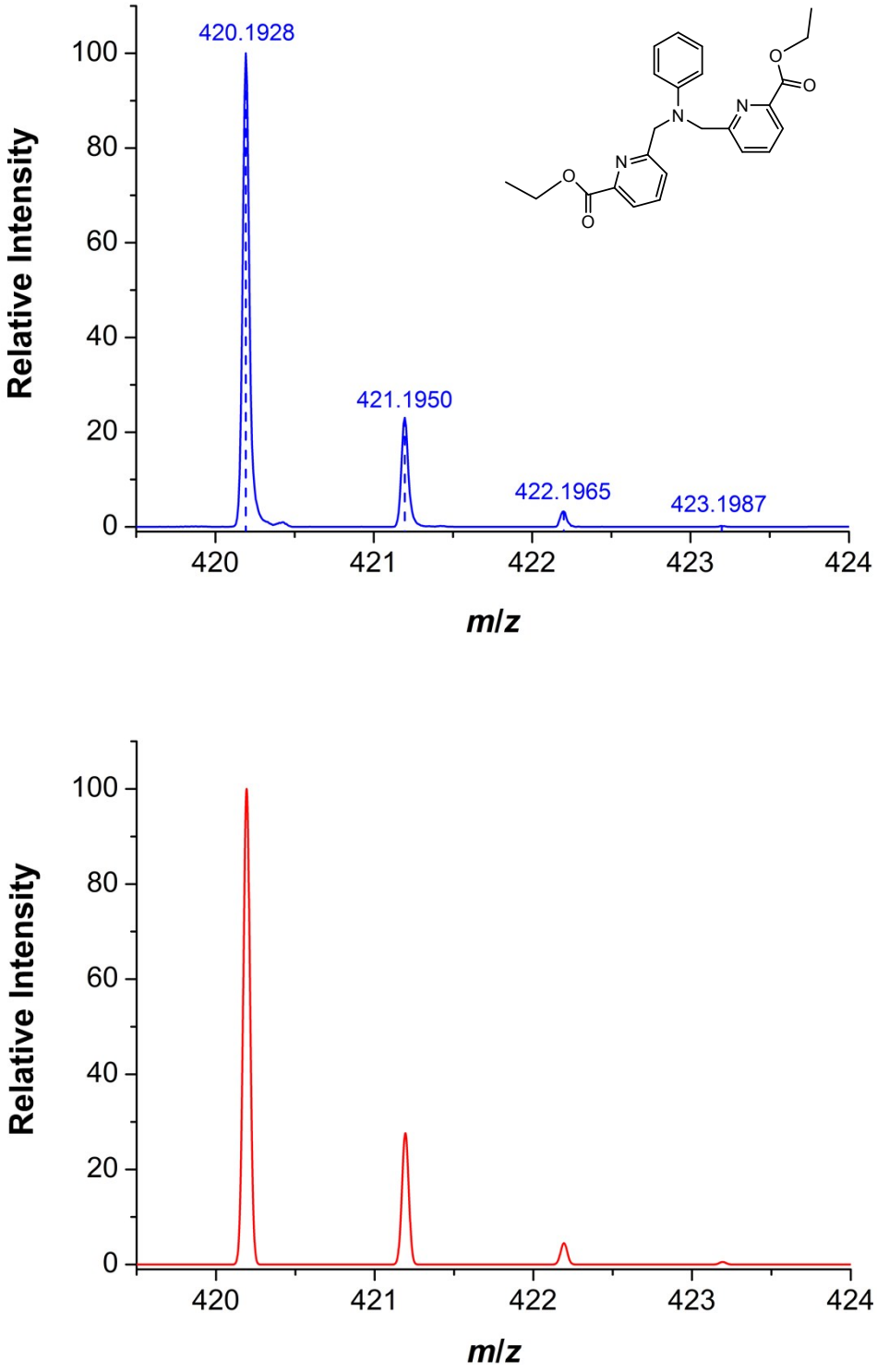

Figure S13. Observed (top) and theoretical (bottom) mass spectral isotopic distribution for the fragment $[DPA(OEt)_2PhA+H]^+$ obtained in CH_3CN.

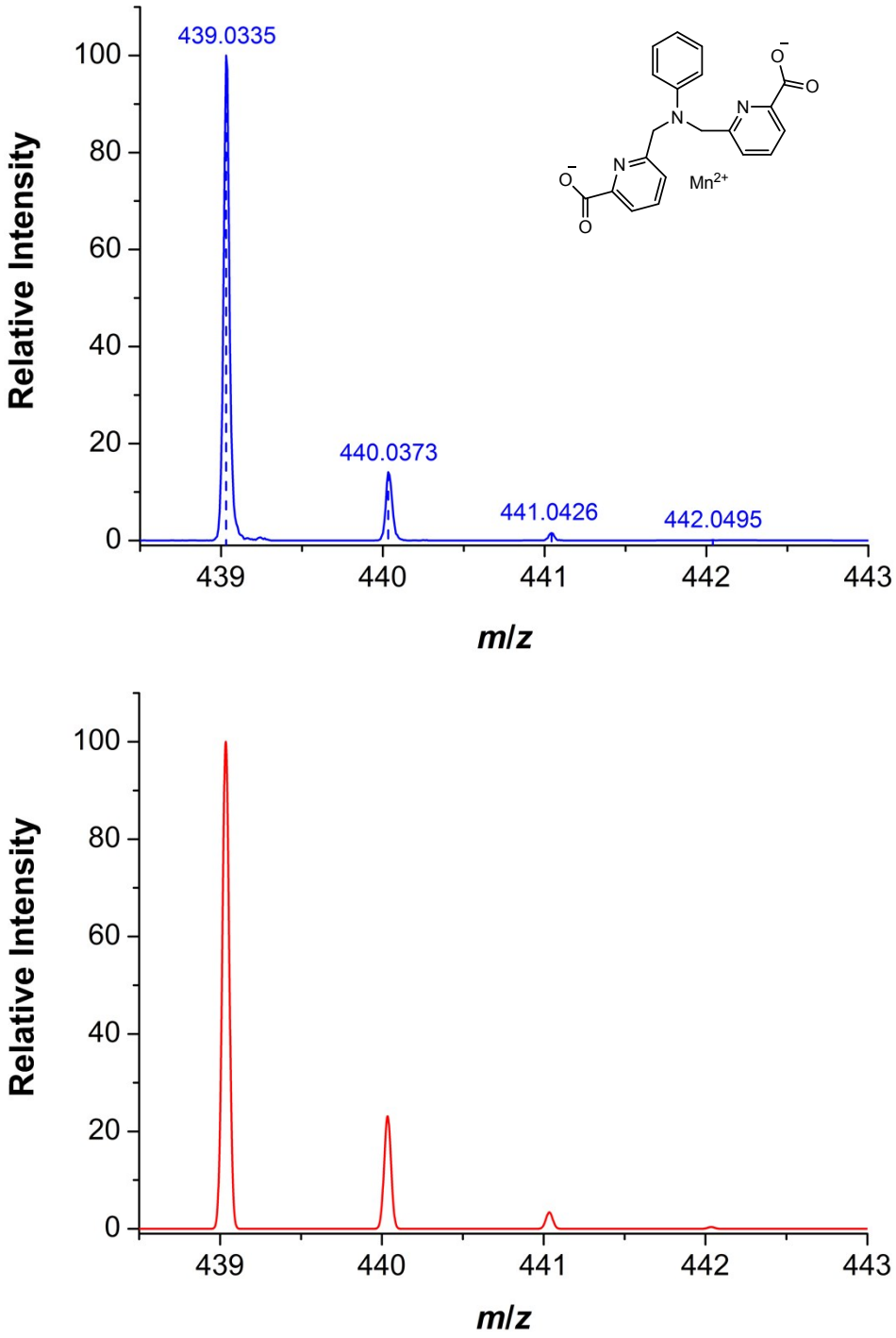

Figure S14. Observed (top) and theoretical (bottom) mass spectral isotopic distribution for the fragment $[Mn(DPAPhA+Na)]^+$ obtained from a solution of the complex in MeOH.

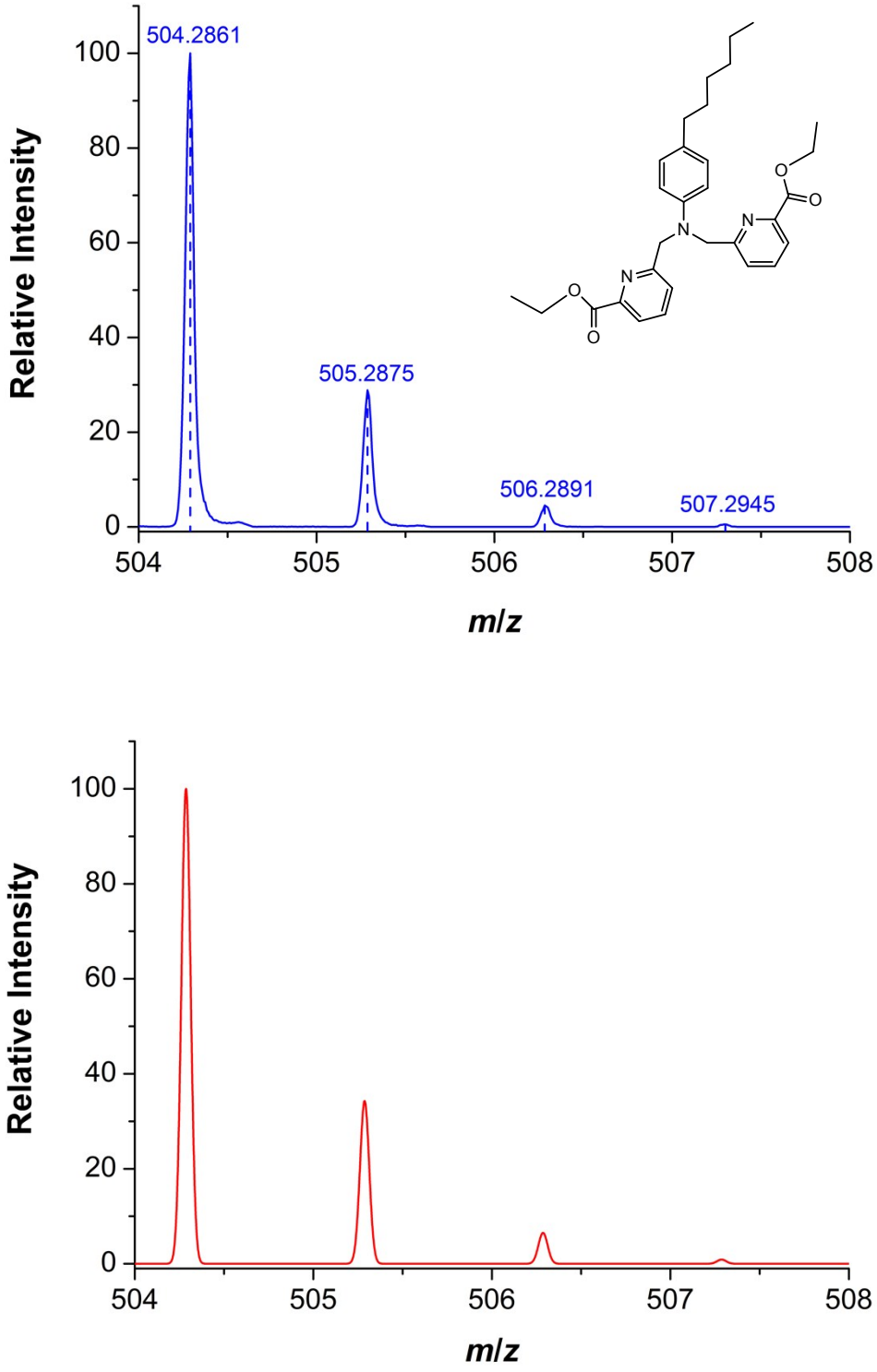

Figure S15. Observed (top) and theoretical (bottom) mass spectral isotopic distribution for the fragment $[DPA(OEt)_2HPhA+H]^+$ obtained in CH_3CN.

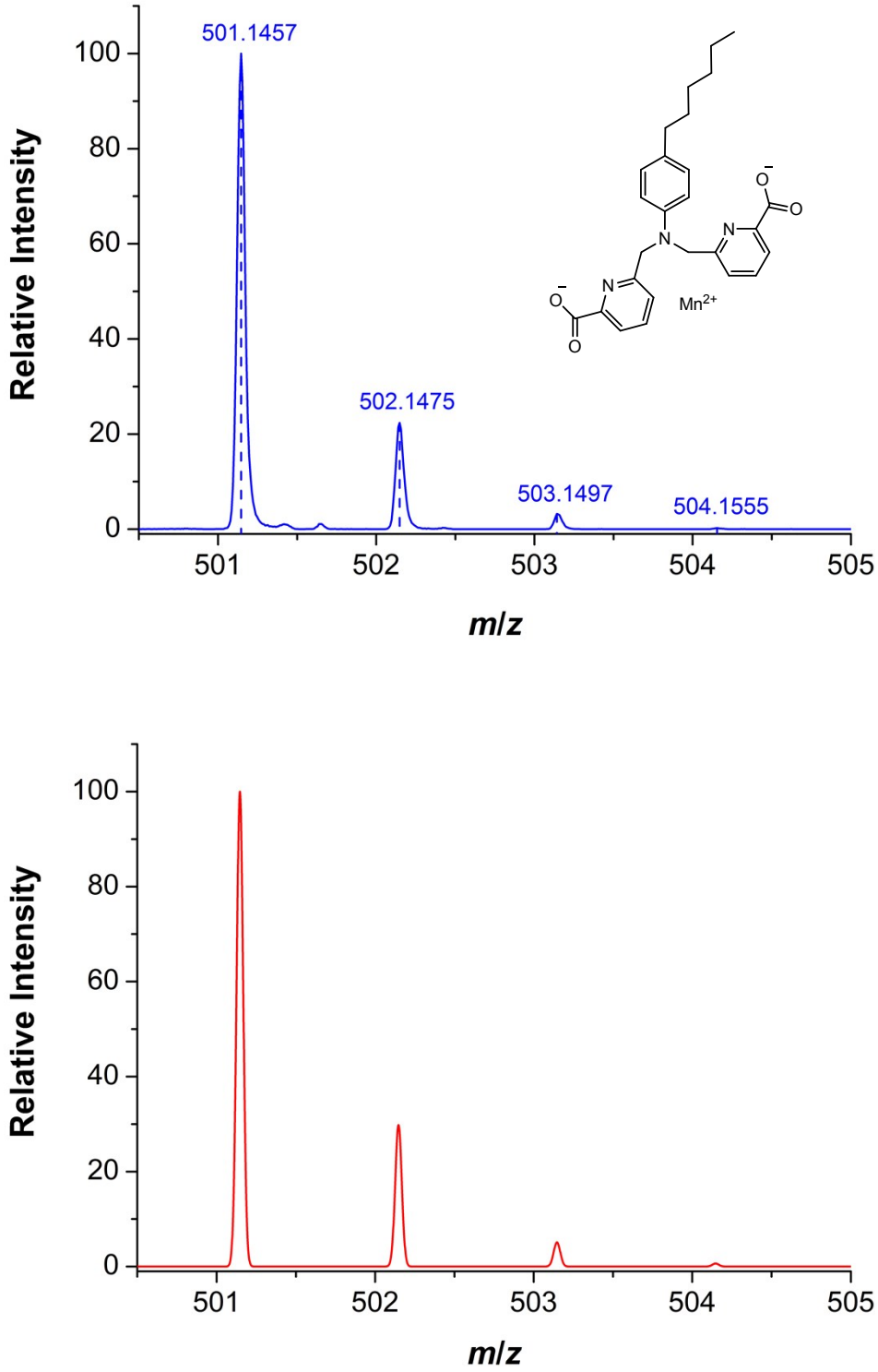

Figure S16. Observed (top) and theoretical (bottom) mass spectral isotopic distribution for the fragment $[Mn(DPAHPhA+H)]^+$ obtained from a solution of the complex in MeOH.

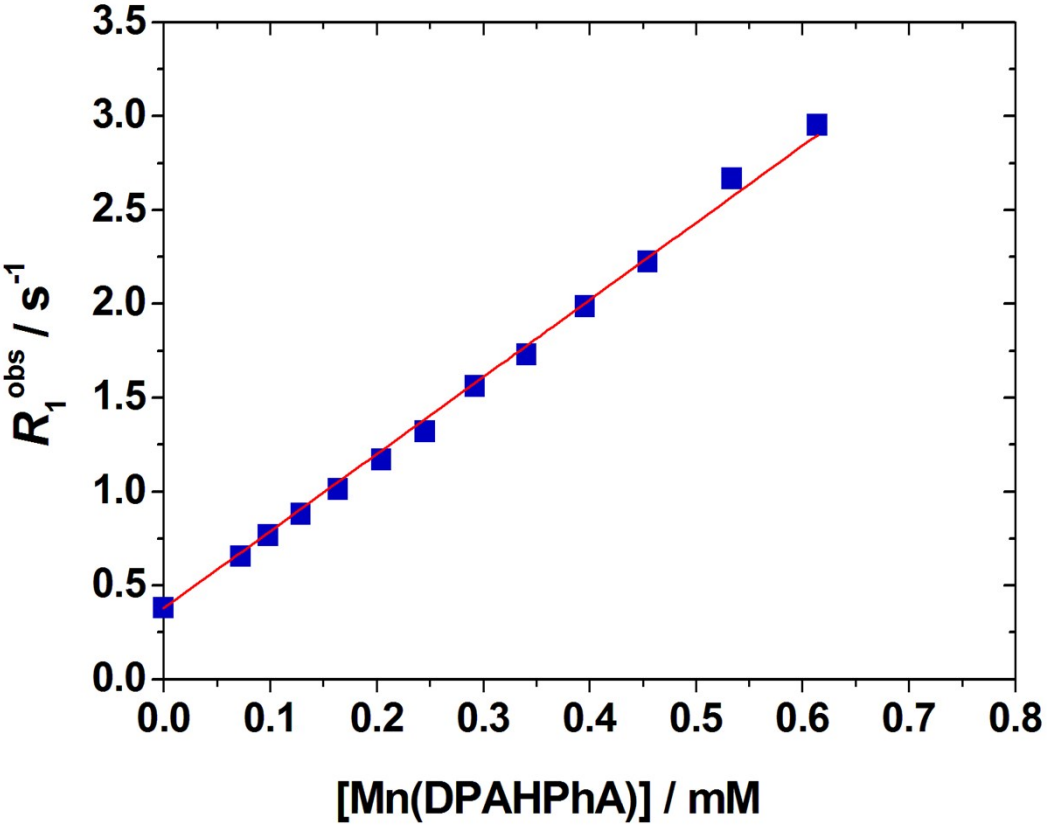

Figure S17. Paramagnetic relaxation enhancement of water proton nuclei (R_1^{obs}) as a function of [Mn(DPAHPhA)] concentration.

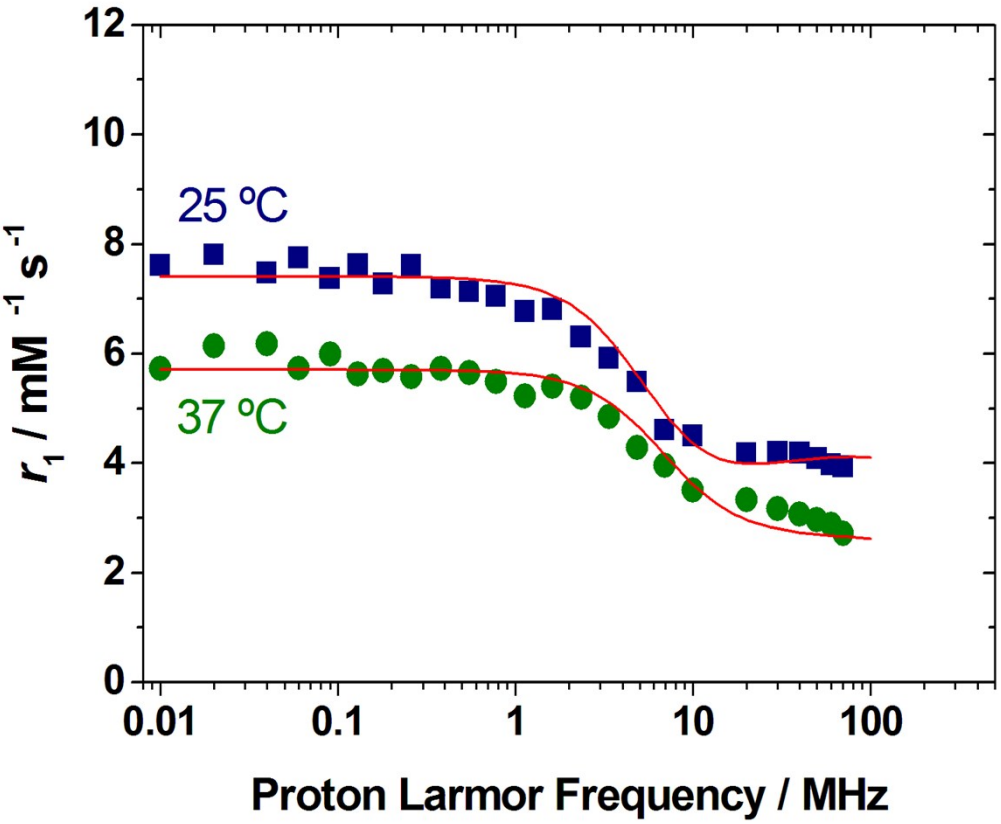

Figure S18. ^{1}H NMRD profiles recorded at different temperatures for [Mn(DPAHPhA)].

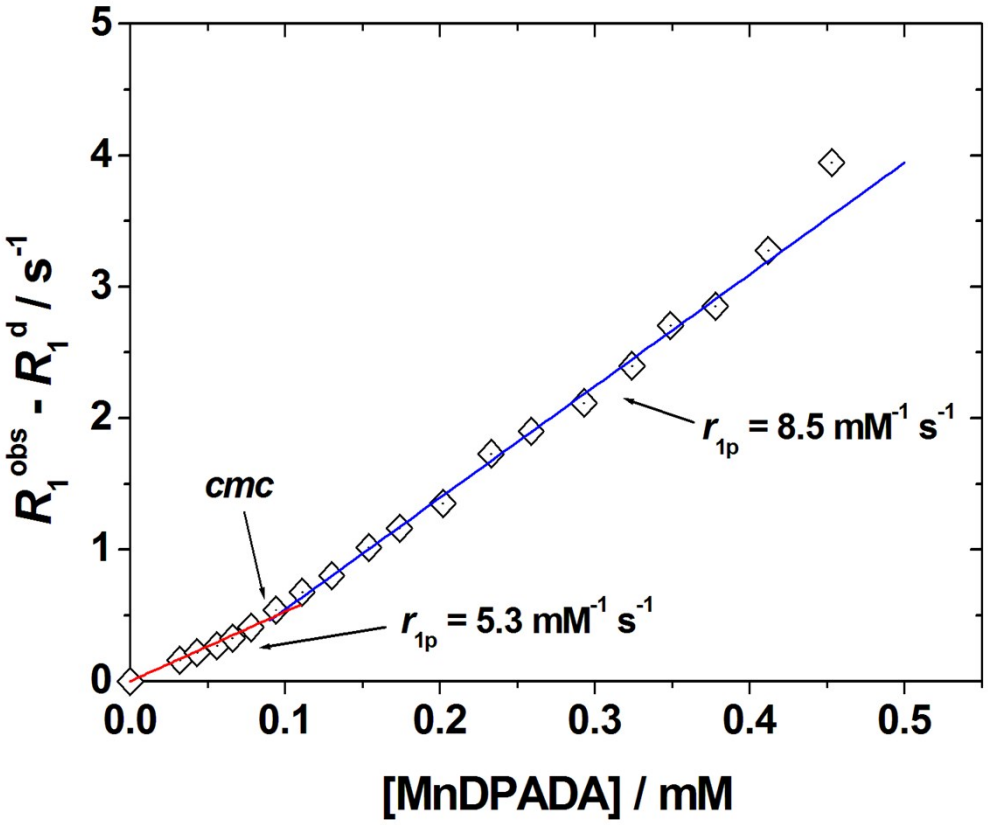

Figure S19. Paramagnetic relaxation enhancement of water proton nuclei (R_1^{obs}) as a function of [Mn(DPADA)] concentration.

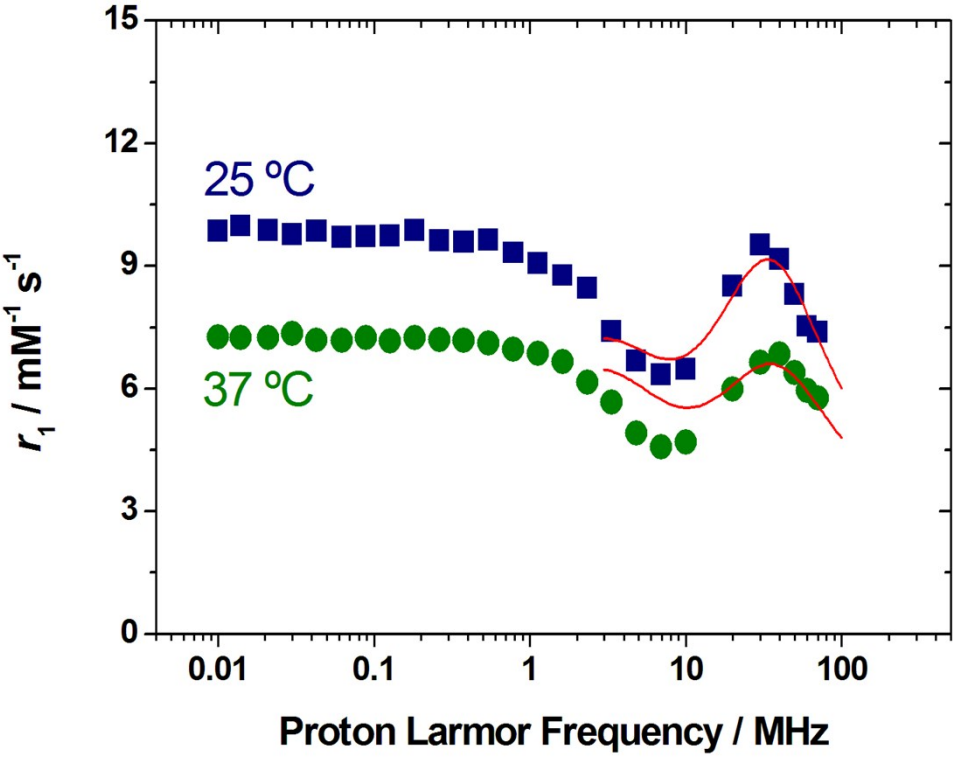

Figure S20. ^{1}H NMRD profiles recorded for [Mn(DPADA)] above the cmc.

Table S1. [Mn(DPAA)(H_2O)]$^{-}$·2H_2O, TPSSh/tzvp, aqueous solution (0 Imaginary Frequencies)

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	8	1.561826	1.930602	0.895871
2	8	-1.479745	2.046495	0.737358
3	8	3.605611	2.094378	1.832385
4	7	2.164681	-0.357324	-0.268744
5	7	-2.140233	-0.261626	-0.351088
6	8	-3.553170	2.351710	1.566774
7	6	-2.396779	-1.441632	-0.927529
8	6	2.405467	-1.498232	-0.925764
9	7	0.003023	-1.901950	-0.834953
10	6	2.759846	1.523873	1.128198
11	6	3.148270	0.235583	0.420528
12	6	-4.404525	-0.125146	0.399745
13	1	-5.157378	0.429105	0.944387
14	6	3.670765	-2.081313	-0.934786
15	1	3.839225	-3.005840	-1.473950
16	6	-2.702057	1.702053	0.941601
17	6	1.216629	-2.086802	-1.648100
18	1	1.074002	-1.549124	-2.590128
19	1	1.404308	-3.140570	-1.891301
20	6	4.436922	-0.287677	0.466381
21	1	5.199626	0.222573	1.039480
22	6	-3.111433	0.381749	0.309631
23	6	-1.222297	-2.078135	-1.630579
24	1	-1.432710	-3.135288	-1.838714
25	1	-1.074515	-1.573386	-2.589754
26	6	-3.665160	-2.015904	-0.882557
27	1	-3.845455	-2.973803	-1.355665
28	6	4.700241	-1.461845	-0.231713
29	1	5.692449	-1.897929	-0.219994
30	6	-4.683016	-1.342579	-0.212902
31	1	-5.677762	-1.769890	-0.160821
32	8	0.131742	1.486210	-1.975402
33	1	0.903259	2.099664	-1.956899
34	1	-0.629832	2.107909	-2.047225
35	6	0.006293	-2.765701	0.369611
36	1	-0.711373	-3.583827	0.258150
37	1	0.991649	-3.229674	0.470264
38	8	-1.680336	3.519710	-1.598611
39	1	-1.652600	3.190666	-0.670373
40	1	-2.617023	3.537430	-1.834000
41	8	1.927802	3.479487	-1.377853
42	1	1.841040	3.124197	-0.463618
43	1	2.877467	3.505390	-1.552766
44	6	-0.260005	-2.065229	1.721408
45	25	0.023384	0.453493	0.063735
46	8	-0.521521	-2.814885	2.679082
47	8	-0.141740	-0.794583	1.783397

E(RTPSSh) = -2613.8095041 Hartree
Zero-point correction = 0.341598 Hartree/particle
Sum of electronic and thermal Energies = -2613.437362 Hartree
Sum of electronic and thermal Enthalpies = -2613.436418 Hartree
Sum of electronic and thermal Free Energies = -2613.532353 Hartree

Table S2. [Mn(DPAPhA)$(H_2O)_2$]·4H_2O, TPSSh/tzvp, aqueous solution (0 Imaginary Frequencies)

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	8	-1.666092	-2.179747	0.738027
2	8	1.338354	-2.518973	0.509743
3	8	-3.500741	-1.877819	2.004311
4	7	-2.130123	0.107812	-0.541957
5	7	2.001953	-0.198412	-0.666663
6	8	3.188164	-2.389956	1.795023
7	6	2.349799	0.794510	-1.493790
8	6	-2.378627	1.121543	-1.378396
9	7	0.043641	1.763213	-1.327329
10	6	-2.767889	-1.597235	1.037506
11	6	-3.155582	-0.457876	0.123034
12	6	4.319186	-0.666109	-0.256700
13	1	5.054210	-1.257274	0.273093
14	6	-3.679521	1.568872	-1.617895
15	1	-3.849951	2.379836	-2.315874
16	6	2.477051	-2.036206	0.835259
17	6	-1.205416	1.742438	-2.105792
18	1	-1.020896	1.140466	-2.997456
19	1	-1.483244	2.748672	-2.440920
20	6	-4.470153	-0.040167	-0.029185
21	1	-5.252745	-0.517087	0.545656
22	6	2.967935	-0.912834	-0.057253
23	6	1.242930	1.581905	-2.161207
24	1	1.643253	2.544899	-2.498665
25	1	0.938968	1.026155	-3.050518
26	6	3.687849	1.071696	-1.779410
27	1	3.936032	1.870094	-2.468312
28	6	-4.736909	0.979293	-0.938036
29	1	-5.752527	1.318095	-1.104836
30	6	4.683407	0.332389	-1.154792
31	1	5.727790	0.538327	-1.357356
32	25	-0.099778	-0.854227	-0.123108
33	8	-0.279915	-1.775042	-2.168014
34	1	-1.076623	-2.358770	-2.171885
35	1	0.463124	-2.411997	-2.305646
36	8	1.548533	-3.781406	-1.982466
37	1	1.569400	-3.526250	-1.034142
38	1	2.468606	-3.756262	-2.276344
39	8	-2.193089	-3.646292	-1.629264
40	1	-2.109415	-3.349160	-0.699404
41	1	-3.137482	-3.603105	-1.828924
42	8	0.084724	-0.070371	1.963578
43	1	-0.455594	-0.556386	2.636874
44	1	0.973614	0.033454	2.380880
45	8	-1.429342	-1.437393	3.830653
46	8	2.527899	-0.065322	3.268151
47	1	3.159990	0.656761	3.156037
48	1	2.970597	-0.860300	2.903432
49	1	-1.775210	-0.887533	4.545953
50	1	-2.221769	-1.741950	3.334023
51	6	0.134055	2.786717	-0.340766
52	6	-1.017847	3.394159	0.186229
53	6	1.379007	3.217901	0.147093

54	6	-0.924033	4.371690	1.172596
55	1	-2.001895	3.112001	-0.159991
56	6	1.461686	4.196236	1.133487
57	1	2.299140	2.794613	-0.229836
58	6	0.313687	4.781956	1.659472
59	1	-1.836107	4.816819	1.555075
60	1	2.440996	4.502270	1.485091
61	1	0.382256	5.544287	2.426663

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Zero-point correction = 0.466321 Hartree/particle
Sum of electronic and thermal Energies = -2846.329197 Hartree
Sum of electronic and thermal Enthalpies = -2846.328252 Hartree
Sum of electronic and thermal Free Energies = -2846.442871 Hartree