Controlling water exchange rates in potential Mn^{2+}-based MRI agents derived from $NO2A^{2-}$

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Electronic Supplementary Information (ESI)

ESI Summary

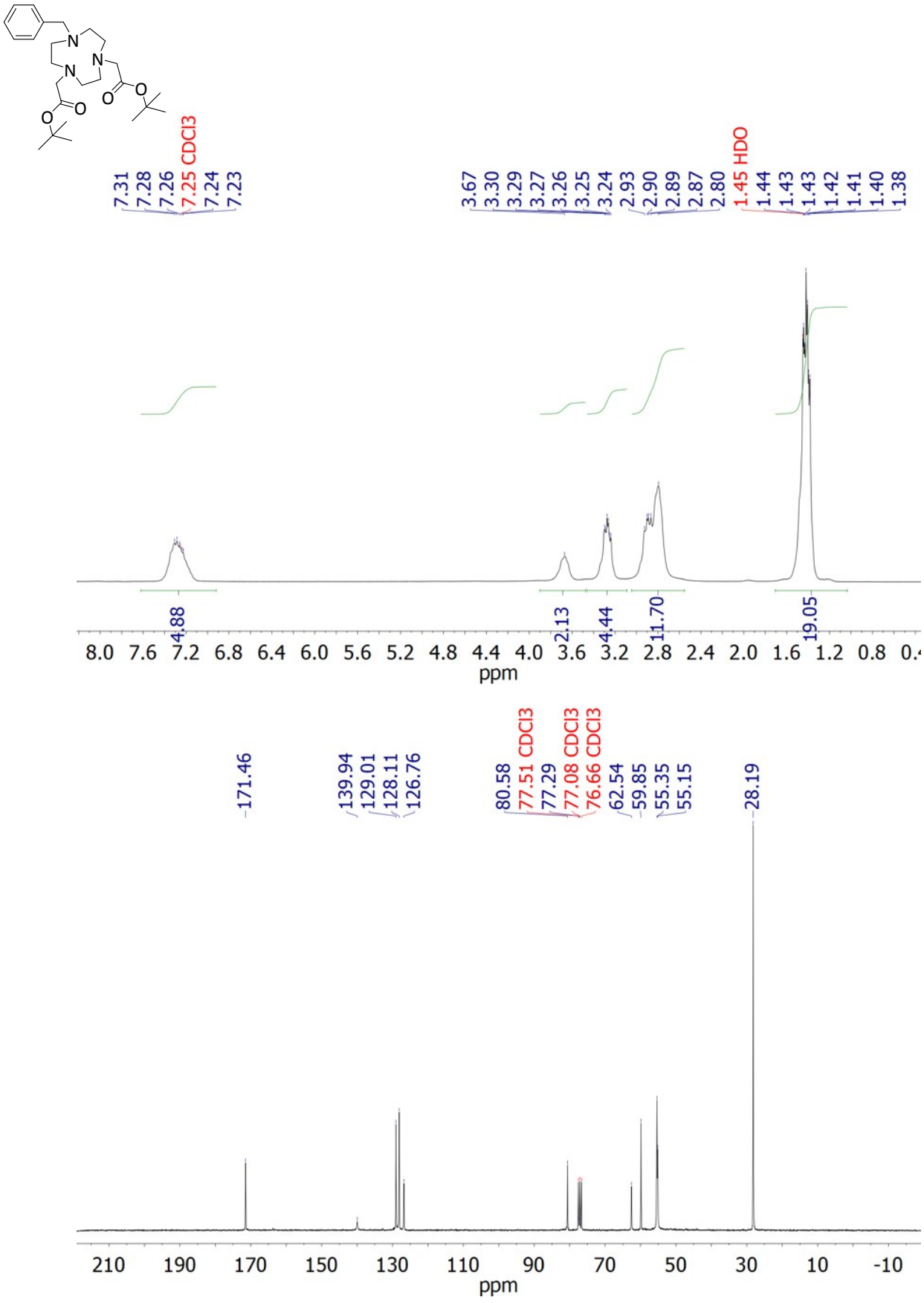

Figure S1. ^{1}H (300 MHz, 25 ^{o}C, top) and ^{13}C (75 MHz, 25 ^{o}C, bottom) NMR spectra of compound **2a** recorded in $CDCl_3$ solution.

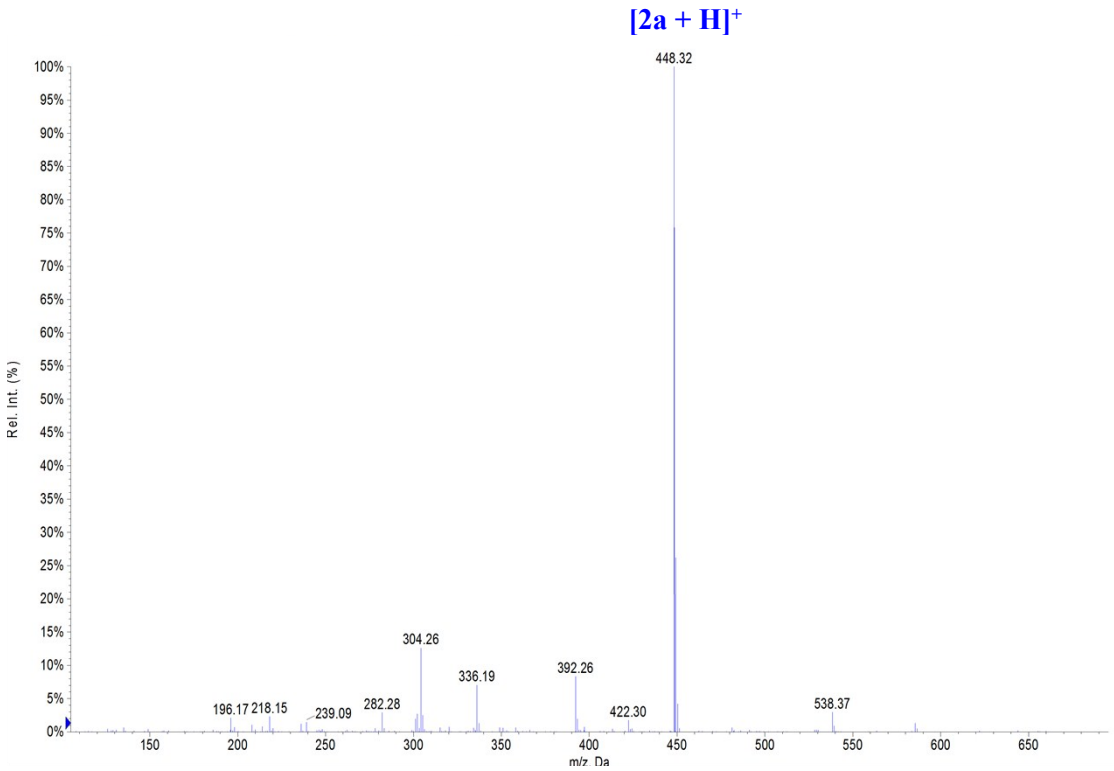

Figure S2. ESI-MS (positive detection) of intermediate **2a**.

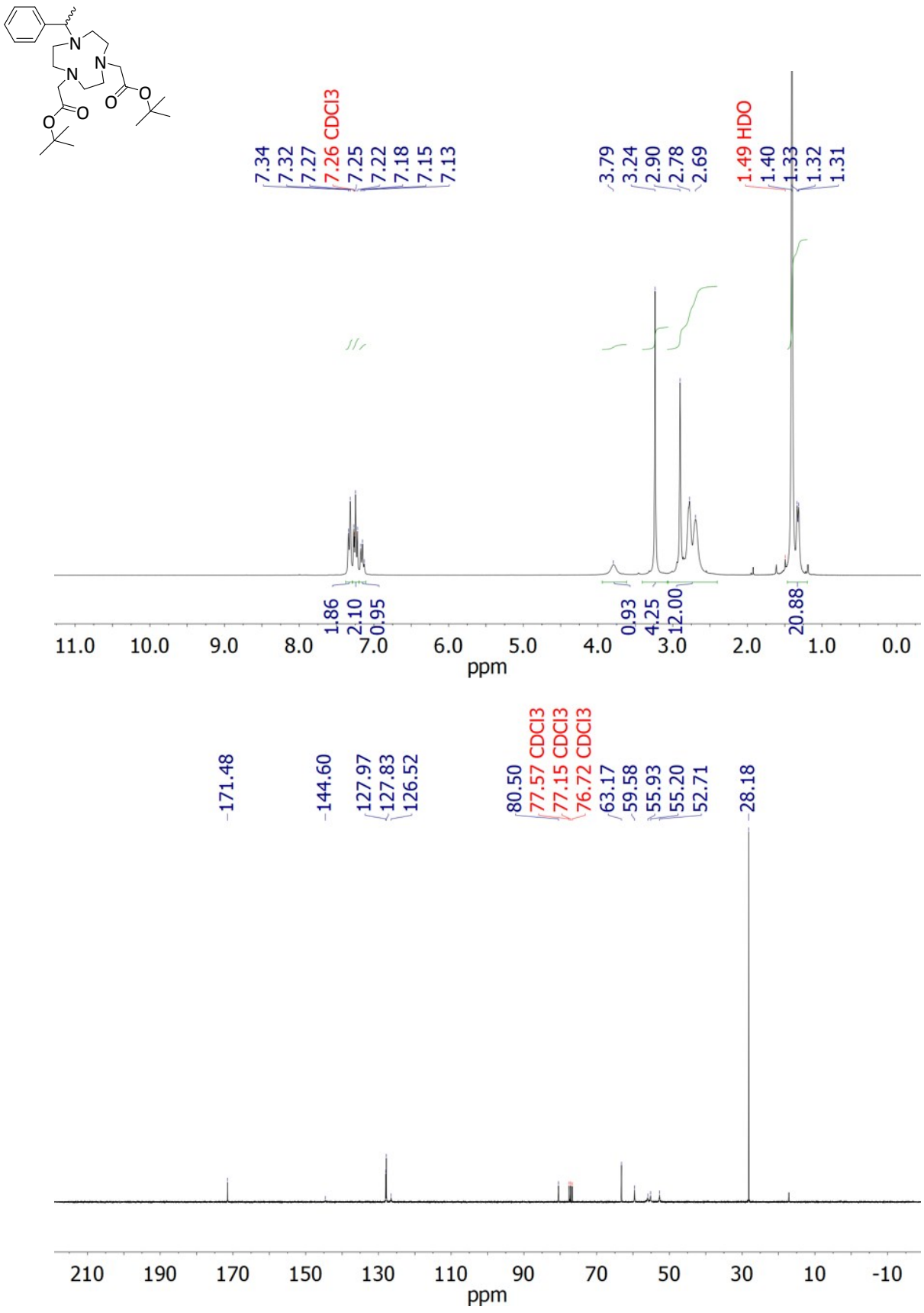

Figure S3. ^{1}H (300 MHz, 25 ^{o}C, top) and ^{13}C (75 MHz, 25 ^{o}C, bottom) NMR spectra of **2b** recorded in $CDCl_3$ solution.

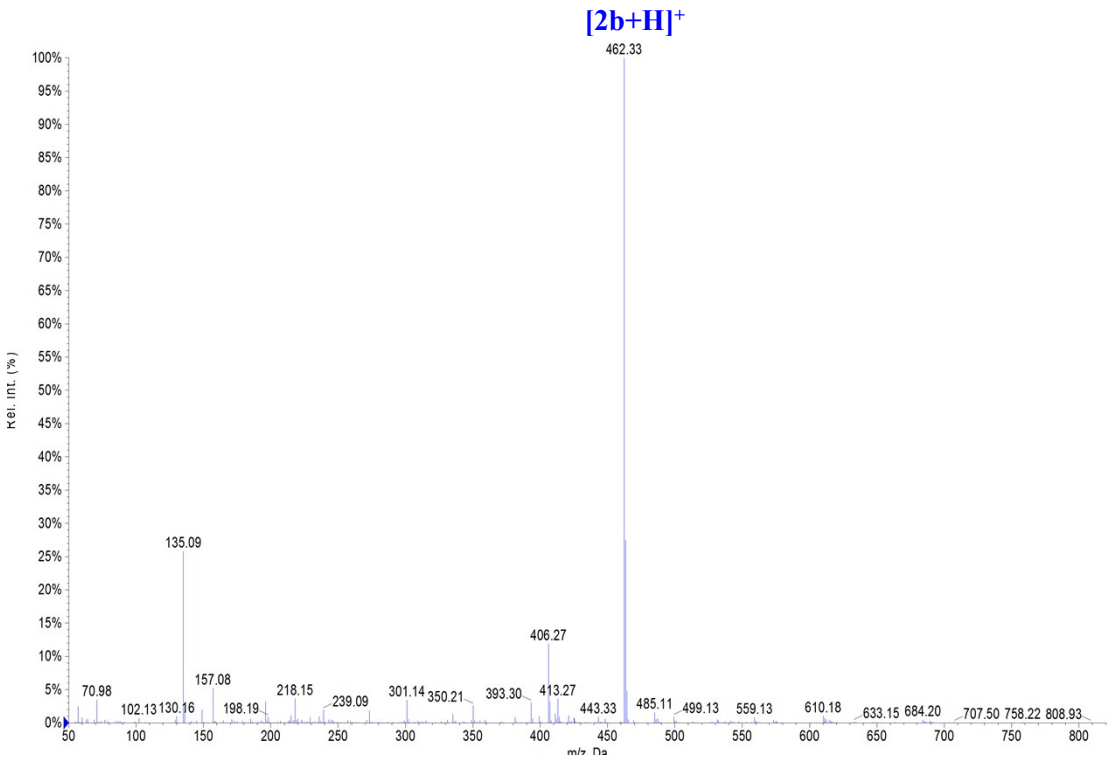

Figure S4. ESI-MS (positive detection) of intermediate **2b**.

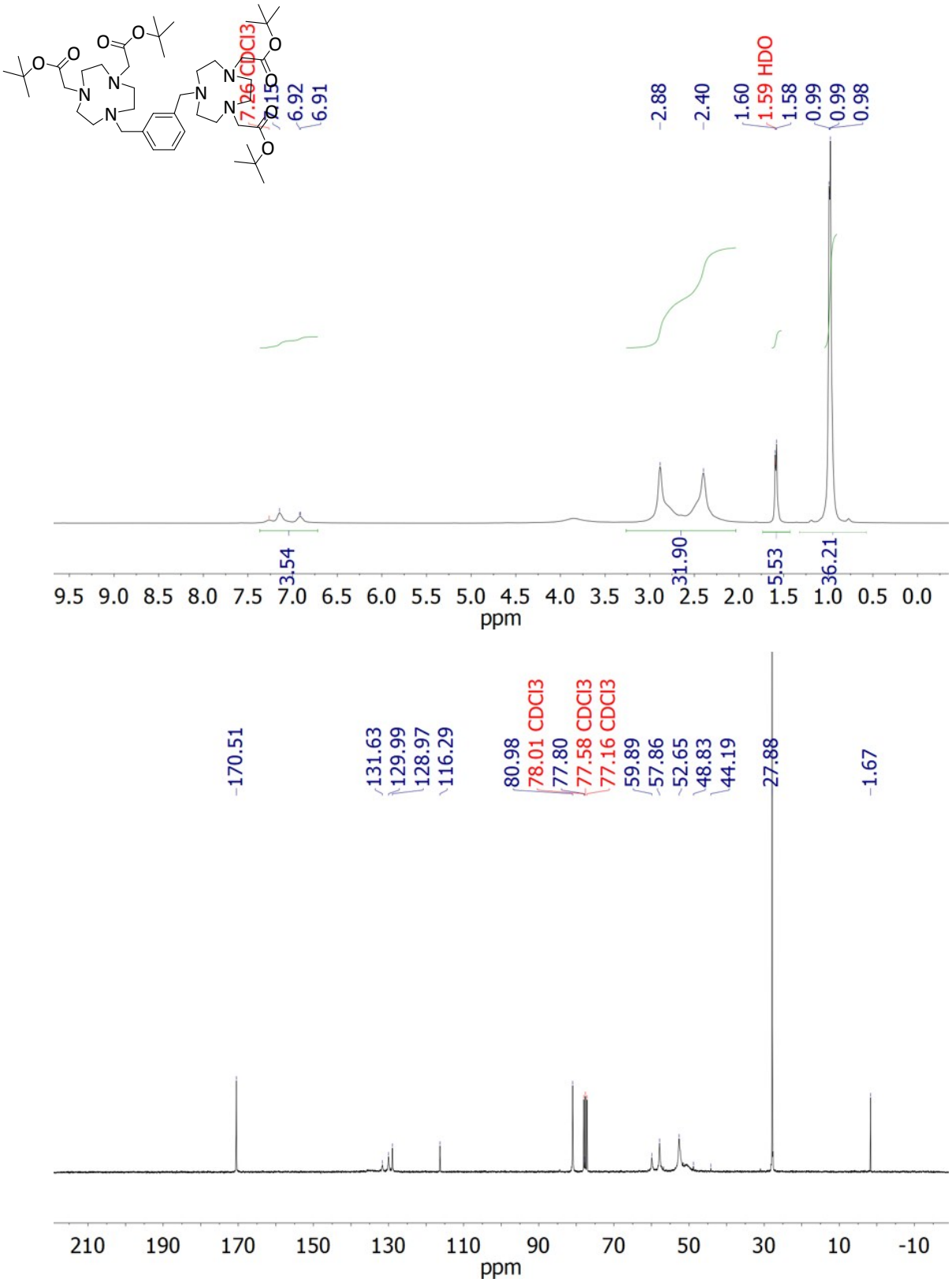

Figure S5. ^{1}H (300 MHz, 25 ^{o}C, top) and ^{13}C (75 MHz, 25 ^{o}C, bottom) NMR spectra of compound **2c** recorded in $CDCl_3$ solution.

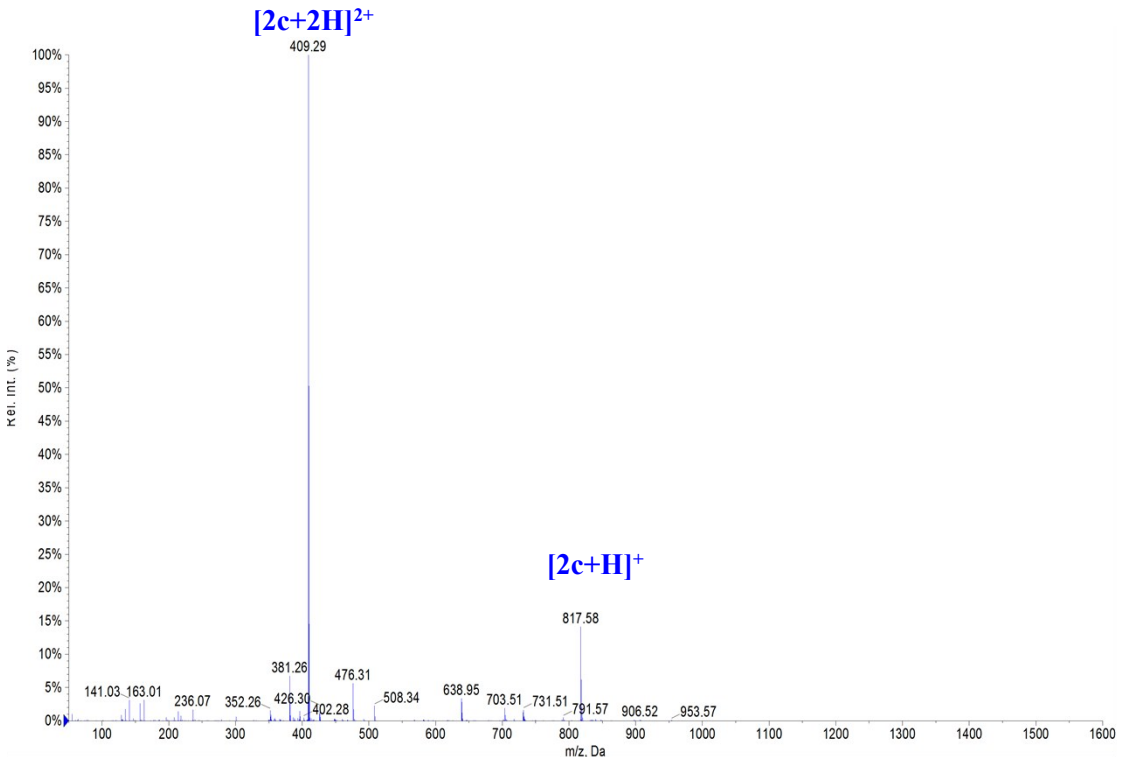

Figure S6. ESI-MS (positive detection) of intermediate **2c**.

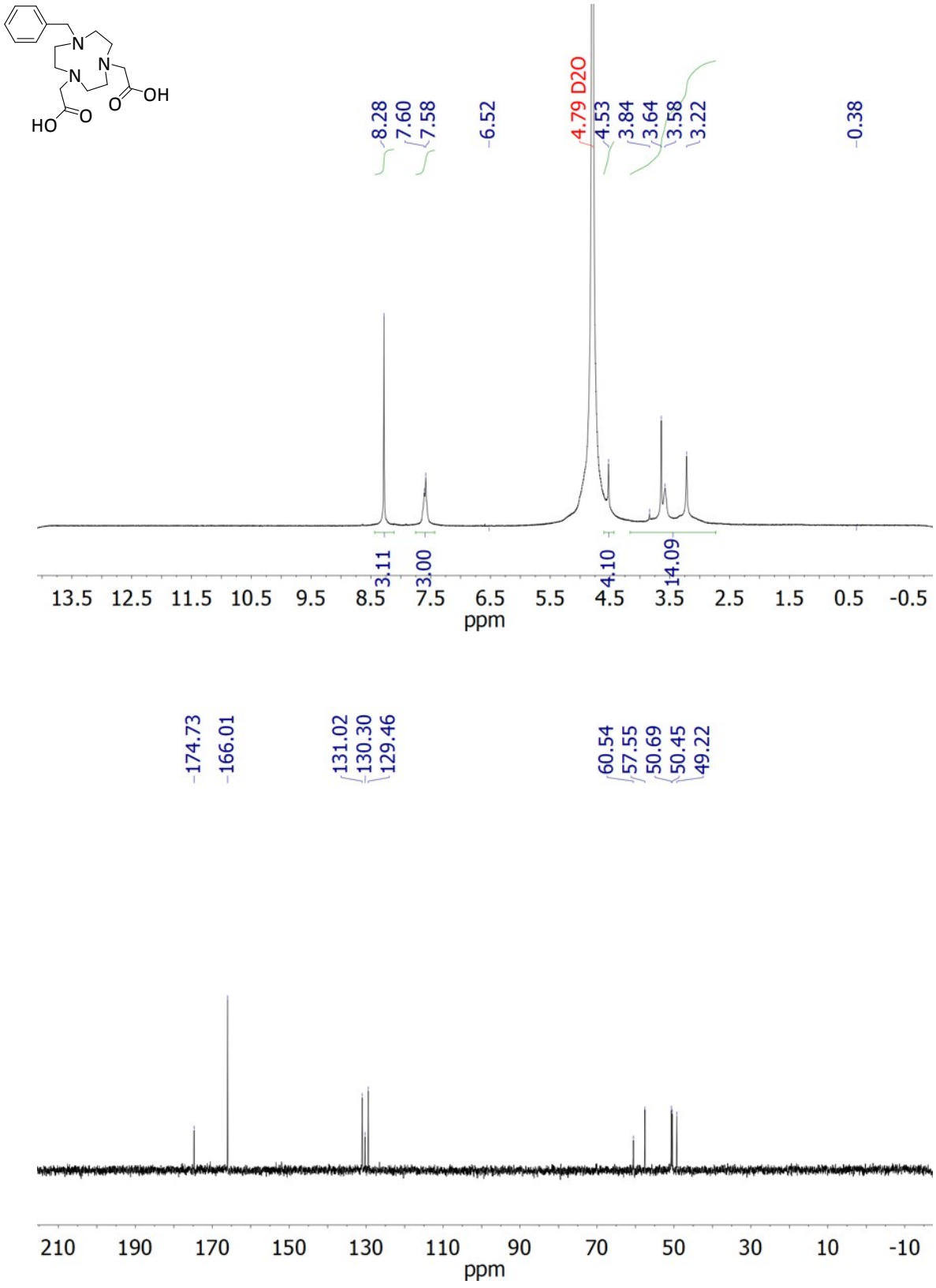

Figure S7. ^{1}H (300 MHz, 25 ^{o}C, top) and ^{13}C (75 MHz, 25 ^{o}C, bottom) NMR spectra of $H_2BzNO2A$ recorded in D_2O solution.

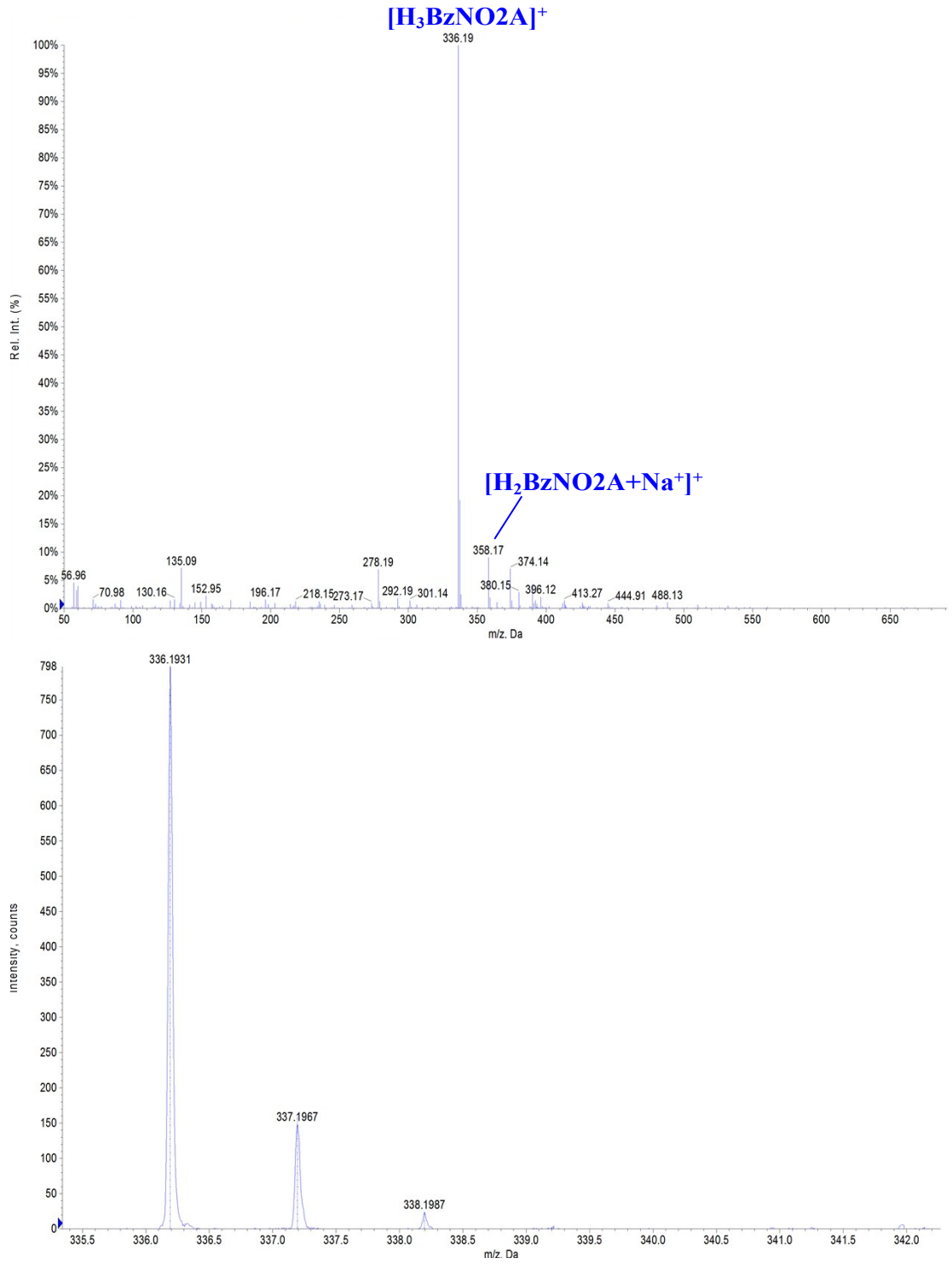

Figure S8. ESI-MS (positive detection) and high resolution mass spectra of ligand H_2BzNO2A.

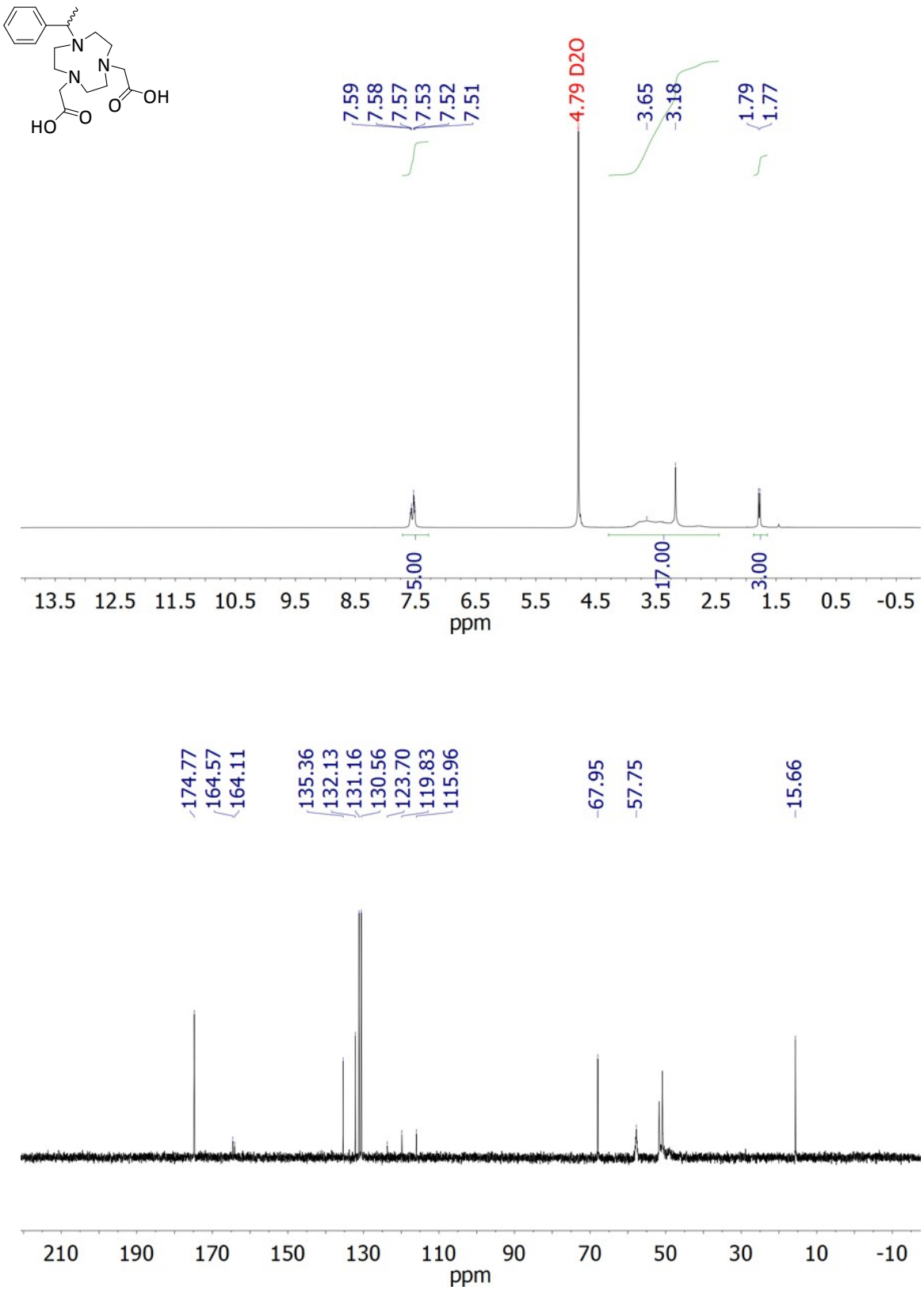

Figure S9. ^{1}H (300 MHz, 25 ^{o}C, top) and ^{13}C (75 MHz, 25 ^{o}C, bottom) NMR spectra of H_2MeBzNO2A recorded in D_2O solution.

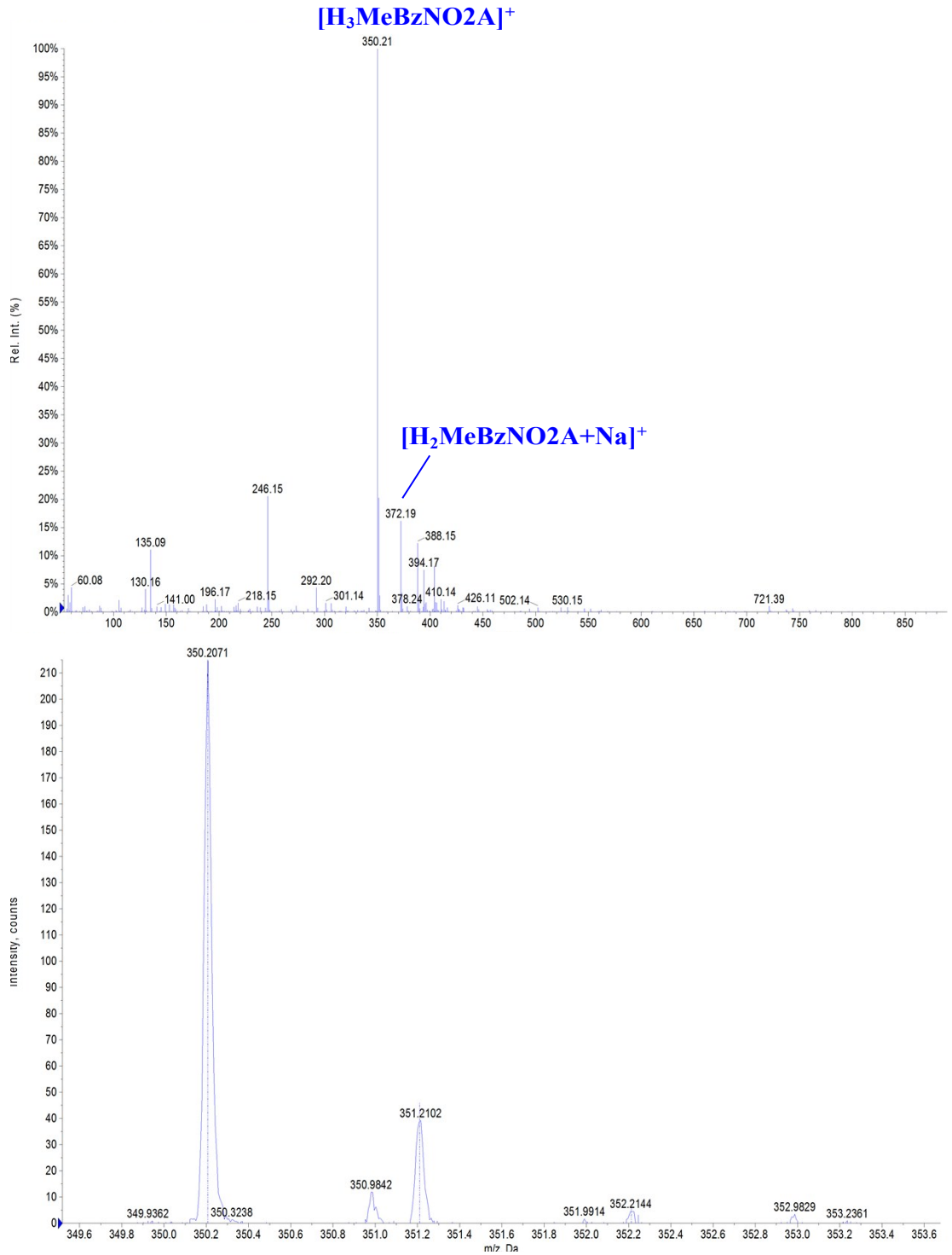

Figure S10. ESI-MS (positive detection) and high resolution mass spectra of ligand H_2MeBzNO2A.

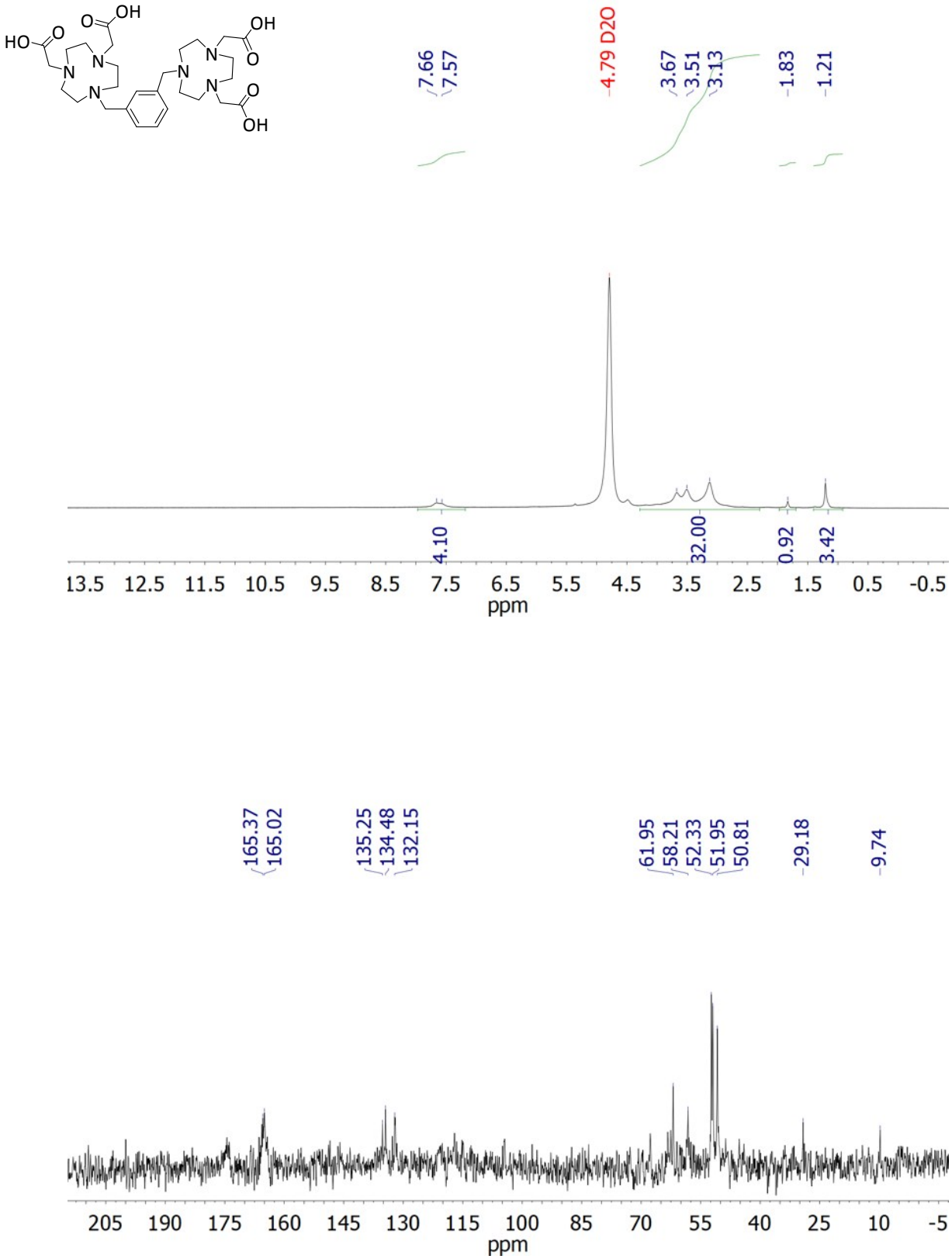

Figure S11. ^{1}H (300 MHz, 25 ^{o}C, top) and ^{13}C (75 MHz, 25 ^{o}C, bottom) NMR spectra of *m*Bz(H_2NO2A)$_2$ recorded in D_2O solution.

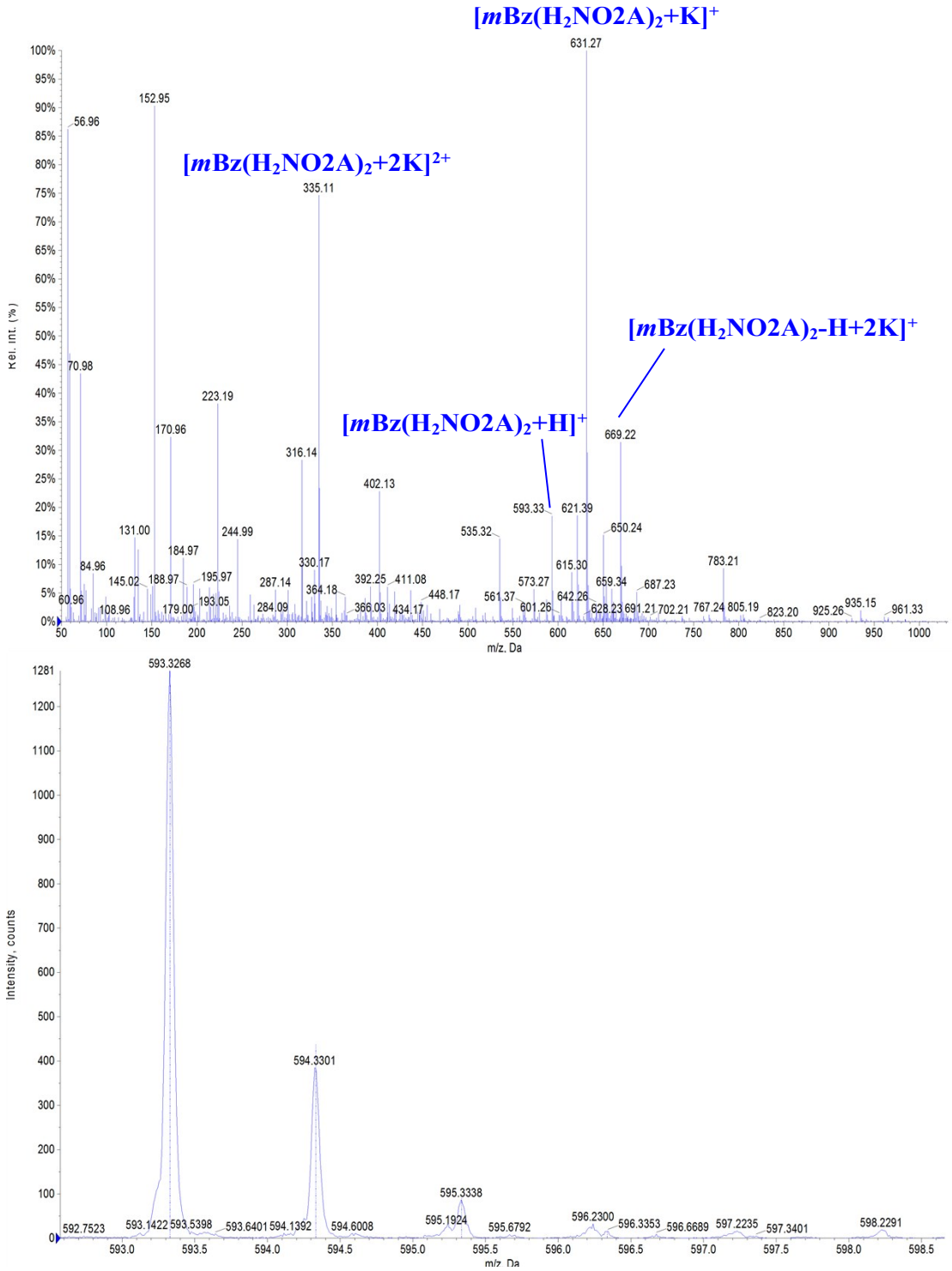

Figure S12. ESI-MS (positive detection) and high resolution mass spectra of ligand *m*Bz(H_2NO2A)$_2$.

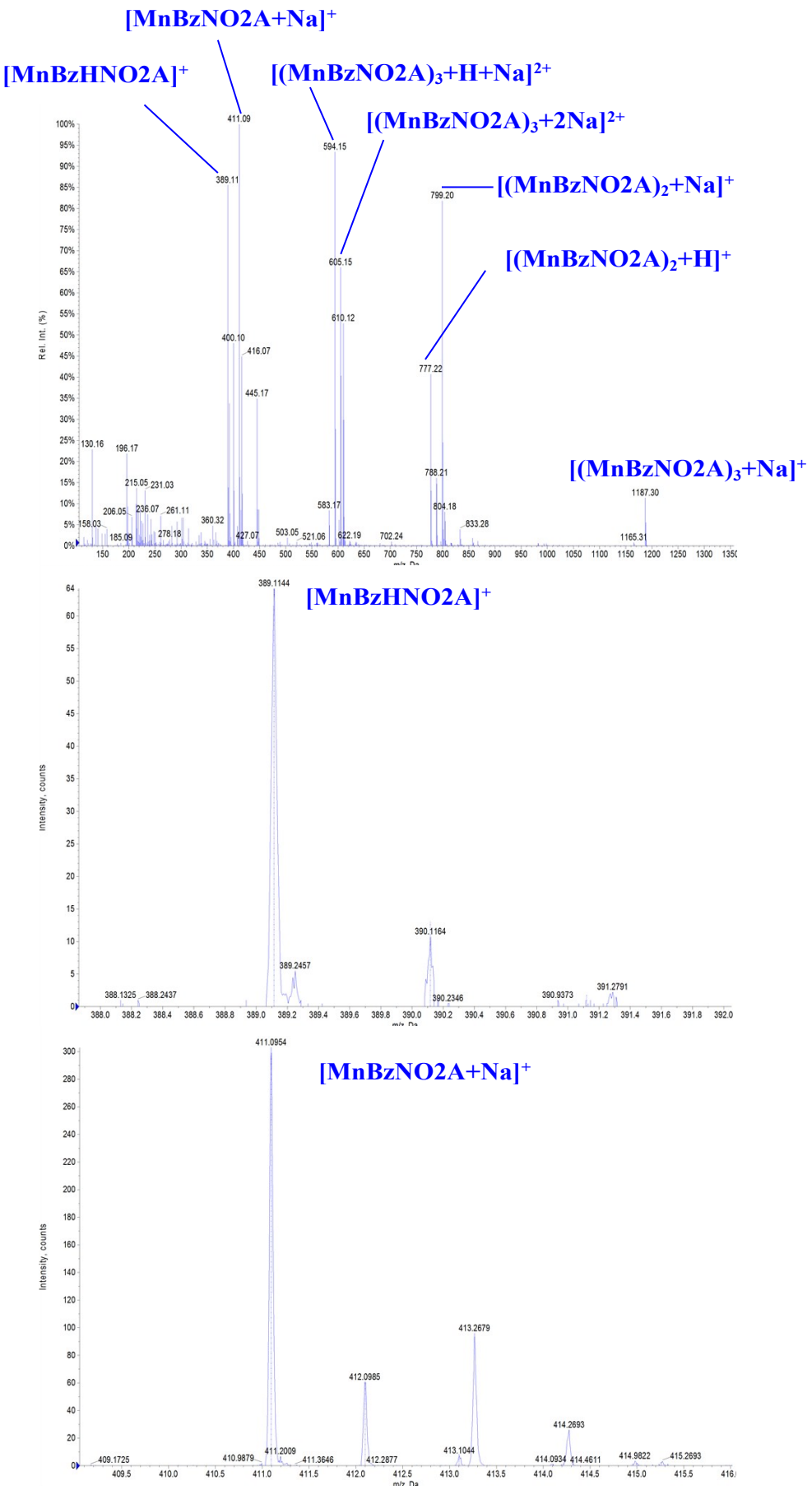

Figure S13. ESI-MS (positive detection) and high resolution mass spectra of the MnBzNO2A complex.

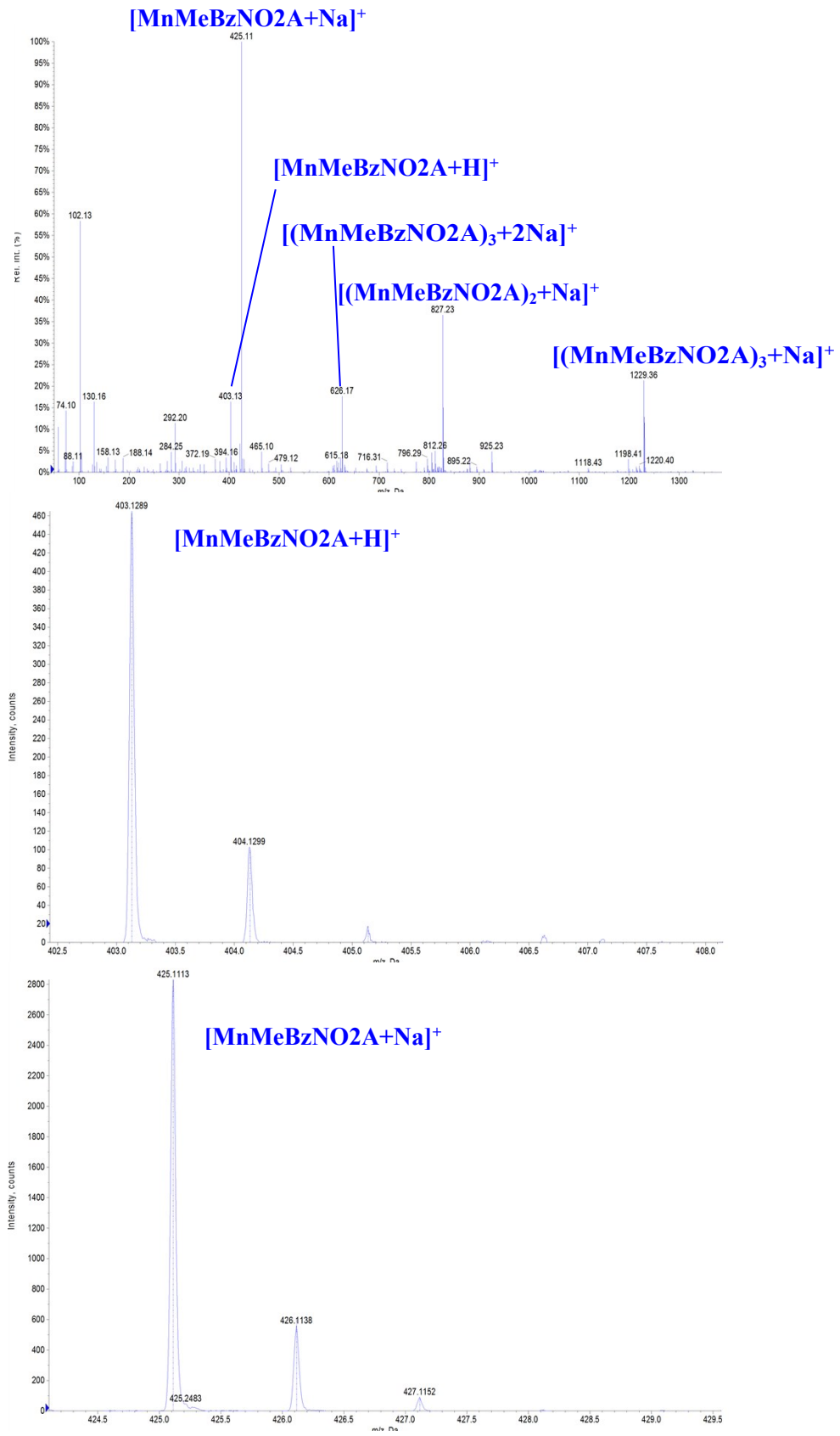

Figure S14. ESI-MS (positive detection) and high resolution mass spectra of the MnMeBzNO2A complex.

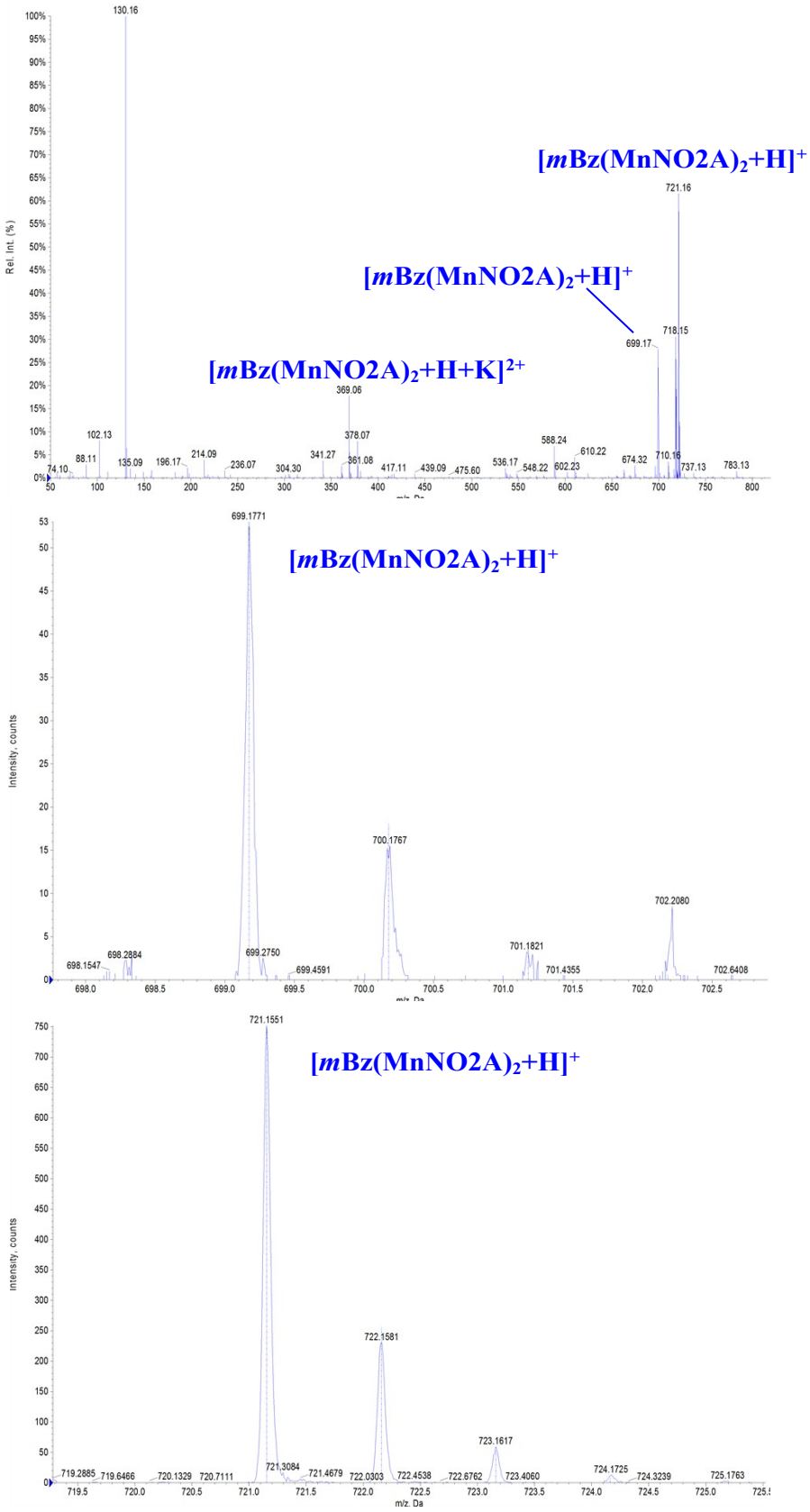

Figure S15. ESI-MS (positive detection) and high resolution mass spectra of the *m*Bz(MnNO2A)$_2$ complex.

Equations used for the analysis of ^{17}O NMR and NMRD data

The reduced relaxation rates, $1/T_{1r}$, $1/T_{2r}$ and reduced chemical shifts (Eqs. (1) – (2)) were obtained from the measured ^{17}O NMR transversal relaxation rates and angular frequencies of the paramagnetic solutions, $1/T_1$, $1/T_2$ and ω, and of the acidified water reference, $1/T_{1A}$, $1/T_{2A}$ and ω_A.

$$\frac{1}{T_{2r}} = \frac{1}{P_m}\left[\frac{1}{T_2} - \frac{1}{T_{2A}}\right] = \frac{1}{\tau_m}\frac{T_{2m}^{-2} + \tau_m^{-1}T_{2m}^{-1} + \Delta\omega_m^2}{\left(\tau_m^{-1} + T_{2m}^{-1}\right)^2 + \Delta\omega_m^2} + \frac{1}{T_{2OS}} \quad (1)$$

$$\Delta\omega_r = \frac{1}{P_m}(\omega - \omega_A) = \frac{\Delta\omega_m}{(1 + \tau_m T_{2m}^{-1})^2 + \tau_m^2\Delta\omega_m^2} + \Delta\omega_{os} \quad (2)$$

where $1/T_{2m}$ is the relaxation rate of the bound water and $\Delta\omega_m$ is the chemical shift difference between bound and bulk water, τ_m is the mean residence time of a water molecule in the inner coordination sphere ($\tau_m = 1/k_{ex}$) and P_m is the mole fraction of the bound water.[1,2]

The outer sphere contributions to the ^{17}O relaxation rates and chemical shifts were neglected in the present study. $\Delta\omega_m$ is determined by the hyperfine or scalar coupling constant, $A/\hbar$, which is expressed as in Equation (3).

$$\Delta\omega_m = \frac{g_L\mu_B S(S+1)B}{3k_B T}\frac{A}{\hbar} \quad (3)$$

where B represents the magnetic field strength, S is the electron spin (S = 5/2 for high-spin Mn^{2+} complexes) and g_L is the isotropic Landé g factor.[3]

The exchange rate is assumed to obey the Eyring equation (Eq. (4)):

$$\frac{1}{\tau_m} = k_{ex} = \frac{k_B T}{h}\exp\left\{\frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT}\right\} = \frac{k_{ex}^{298}T}{298.15}\exp\left\{\frac{\Delta H^{\ddagger}}{R}\left(\frac{1}{298.15} - \frac{1}{T}\right)\right\} \quad (4)$$

where $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ are the entropy and enthalpy of activation for the water exchange process, and k_{ex}^{298} is the exchange rate at 298.15 K.

In the transverse relaxation the scalar contribution, $1/T_{2sc}$, is the most important, as given by Eq. (5), with $1/\tau_{s1}$ being the sum of the exchange rate constant and the electron spin relaxation rate.

$$\frac{1}{T_{2m}} \cong \frac{1}{T_{2SC}} = \frac{S(S+1)}{3}\left(\frac{A}{\mathsf{h}}\right)^2 \tau_{S1} \tag{5}$$

$$\frac{1}{\tau_{S1}} = \frac{1}{\tau_m} + \frac{1}{T_{1e}} \tag{6}$$

The measured longitudinal proton relaxation rate ($R_1^{obs)}$ is the sum of the paramagnetic and diamagnetic contributions as given in Eq. (7), where r_{1p} is the proton relaxivity:

$$R_1^{obs} = R_1^d + R_1^p = R_1^d + r_{1p}[Mn(II)] \tag{7}$$

The relaxivity is the result of both inner- and outer-sphere contributions:

$$r_1 = r_{1is} + r_{1os} \tag{8}$$

The inner sphere term is given in Eq. (9), where q is the number of inner sphere water molecules.[4]

$$r_{1is} = \frac{1}{1000} \times \frac{q}{55.55} \times \frac{1}{T_{1m}^H + \tau_m} \tag{9}$$

The longitudinal relaxation rate of proton nuclei of a coordinated water molecule, $1/T_{1m}^{H}$, is given by Eq. (10):

$$\frac{1}{T_{1m}^H} = \frac{2}{15}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma_I^2 g^2 \mu_B^2}{r_{MnH}^6} S(S+1)\left[\frac{3\tau_{d1}}{1+\omega_I^2\tau_{d1}^2} + \frac{7\tau_{d2}}{1+\omega_S^2\tau_{d2}^2}\right] \tag{10}$$

where r_{MnH} is the effective distance between the electron charge and the ^{1}H nucleus, ω_I is the proton resonance frequency and ω_S is the Larmor frequency of the Mn^{2+} electron spin.

$$\frac{1}{\tau_{di}} = \frac{1}{\tau_m} + \frac{1}{\tau_R} + \frac{1}{T_{ie}} \qquad i = 1\ ,\ 2 \tag{11}$$

The longitudinal and transverse electronic relaxation rates, $1/T_{1e}$ and $1/T_{2e}$ are approximated by Eqs. (12)-(14),[5] where τ_V is the electronic correlation time for the modulation of the zero-field-splitting interaction, E_V the corresponding activation energy and Δ^2 is the mean square zero-field-splitting energy. We assumed a simple exponential dependence of τ_V versus $1/T$ as shown in Eq. (14).

$$\frac{1}{T_{1e}} = \frac{1}{25}\Delta^2\tau_V\{4S(S+1)-3\}\left(\frac{1}{1+\omega_s^2\tau_v^2}+\frac{4}{1+4\omega_s^2\tau_v^2}\right) \tag{12}$$

$$\frac{1}{T_{2e}} = \left(\left(0.02\times\left(4S^2+4S-3\right)\times\tau_V\times\Delta^2\times\left(\left(\frac{5}{1+{\omega_s}^2{\tau_V}^2}\right)\right)\right)+\left(\frac{2}{1+4{\omega_s}^2{\tau_V}^2}\right)+3\right) \tag{13}$$

$$\tau_v = \tau_v^{298}\exp\left\{\frac{E_v}{R}\left(\frac{1}{T}-\frac{1}{298.15}\right)\right\} \tag{14}$$

The outer-sphere contribution can be described by Eq. (15) where N_A is the Avogadro constant, and J_{os} is the associated spectral density function.[6,7]

$$r_{1os} = \frac{32N_A\pi}{405}\left(\frac{\mu_0}{4\pi}\right)^2\frac{\mathsf{h}^2\gamma_S^2\gamma_I^2}{a_{MnH}D_{MnH}}S(S+1)[3J_{os}(\omega_I;T_{1e})+7J_{os}(\omega_I;T_{2e})] \tag{15}$$

$$J^{OS}(\omega,T_{je}) = \mathrm{Re}\left[\frac{1+\frac{1}{4}\left(i\omega\tau_{MnH}+\frac{\tau_{MnH}}{T_{je}}\right)^{1/2}}{1+\left(i\omega\tau_{MnH}+\frac{\tau_{MnH}}{T_{je}}\right)^{1/2}+\frac{4}{9}\left(i\omega\tau_{MnH}+\frac{\tau_{MnH}}{T_{je}}\right)+\frac{1}{9}\left(i\omega\tau_{MnH}+\frac{\tau_{MnH}}{T_{je}}\right)^{3/2}}\right] \tag{16}$$

where $j = 1,2$, $\tau_{MnH} = \frac{{a_{MnH}}^2}{D_{MnH}}$.

The diffusion coefficient for the relative diffusion of the complex and water protons away from the Mn^{2+} complex, D_{MnH}, is assumed to obey an exponential law versus the inverse of the temperature, with an activation energy E_{MnH}, as shown in Eq. (17). D_{MnH}^{298} is the diffusion coefficient at 298.15 K.

$$D_{MnH} = D_{MnH}^{298} \exp\left\{\frac{E_{MnH}}{R}\left(\frac{1}{298.15} - \frac{1}{T}\right)\right\} \quad (17)$$

Table S1. [Mn(MeNO2A)(H_2O)]·2H_2O, M06-2X/TZVP, aqueous solution (0 Imaginary Frequencies).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	-1.898472	-0.671549	0.720483
2	6	-2.659757	0.549295	1.054309
3	6	-2.269957	1.757395	0.200775
4	6	-0.228880	2.306797	1.450582
5	6	1.005695	1.471258	1.779444
6	7	0.751017	0.030666	1.617644
7	6	-0.246099	-0.500545	2.567757
8	6	-1.335372	-1.345145	1.899529
9	1	-2.516453	0.776085	2.110141
10	1	-3.732129	0.372866	0.927402
11	1	-2.619794	1.615916	-0.822736
12	1	-2.766351	2.650138	0.602840
13	1	-0.985849	2.188923	2.224568
14	1	0.053572	3.362955	1.465836
15	1	1.803924	1.737269	1.083060
16	1	1.346850	1.718172	2.792608
17	1	-0.699061	0.332376	3.103868
18	1	0.242821	-1.115157	3.329104
19	1	-0.904498	-2.285778	1.557026
20	1	-2.107687	-1.575286	2.644309
21	7	-0.810301	1.955113	0.134407
22	6	-2.654013	-1.564765	-0.157884
23	1	-2.149316	-2.534644	-0.182184
24	1	-3.680106	-1.722970	0.187097
25	6	1.972313	-0.770331	1.572747
26	1	2.273557	-1.136738	2.558987
27	1	2.789688	-0.151376	1.194983
28	6	-2.670796	-1.059283	-1.613546
29	8	-1.616671	-0.450881	-2.005669
30	8	-3.655868	-1.303776	-2.307297
31	8	1.872600	0.560644	-1.360612
32	6	1.895444	-1.956675	0.598603
33	8	0.921639	-1.996369	-0.211137
34	8	2.846654	-2.753927	0.611764
35	25	-0.059252	-0.121813	-0.607333
36	1	2.538572	-0.129932	-1.574862
37	1	2.317915	1.431228	-1.342009
38	6	-0.479781	2.970856	-0.874610
39	1	0.600535	3.113812	-0.901568
40	8	3.594841	-1.524323	-1.817778
41	8	3.049044	3.015703	-1.146599
42	1	3.198825	3.548660	-1.935132
43	1	3.856171	3.087304	-0.625513
44	1	3.486859	-2.145186	-1.073233
45	1	4.541661	-1.380373	-1.912415
46	1	-0.814074	2.627598	-1.854858
47	1	-0.960732	3.930141	-0.649339

E(UM062X) = -2276.2343733 Hartree
Zero-point correction = 0.394609
Thermal correction to Energy = 0.420651
Thermal correction to Enthalpy = 0.421595
Thermal correction to Gibbs Free Energy = 0.338967

Sum of electronic and zero-point Energies = -2275.839764
Sum of electronic and thermal Energies = -2275.813722
Sum of electronic and thermal Enthalpies = -2275.812778
Sum of electronic and thermal Free Energies = -2275.895406

Table S2. [Mn(BzNO2A)(H_2O)]·2H_2O, M06-2X/TZVP, aqueous solution (0 Imaginary Frequencies).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	-1.099756	2.060877	0.822512
2	6	0.274905	2.370484	1.263068
3	6	1.359128	1.659357	0.449478
4	6	1.144814	-0.503779	1.599533
5	6	-0.061741	-1.417468	1.801045
6	7	-1.333462	-0.708697	1.584578
7	6	-1.584414	0.362211	2.570056
8	6	-1.995018	1.689754	1.928111
9	1	0.372821	2.112905	2.316829
10	1	0.459143	3.447153	1.199341
11	1	1.400382	2.079795	-0.557455
12	1	2.326300	1.848058	0.929672
13	1	1.214241	0.221894	2.407951
14	1	2.050199	-1.109115	1.673950
15	1	-0.012893	-2.225563	1.067742
16	1	-0.004840	-1.866936	2.800342
17	1	-0.690057	0.500888	3.176326
18	1	-2.373413	0.061094	3.264981
19	1	-2.995599	1.591380	1.508640
20	1	-2.025693	2.463826	2.705468
21	7	1.101402	0.214024	0.304928
22	6	-1.649420	3.105875	-0.041499
23	1	-2.729239	2.954367	-0.123984
24	1	-1.477228	4.110807	0.354914
25	6	-2.476542	-1.606703	1.422511
26	1	-2.992457	-1.804440	2.367060
27	1	-2.124143	-2.567726	1.041343
28	6	-1.103183	3.015487	-1.478043
29	8	-0.848678	1.837577	-1.904195
30	8	-0.992493	4.051713	-2.130313
31	8	-0.997899	-1.824902	-1.421592
32	6	-3.501111	-1.120019	0.385265
33	8	-3.176420	-0.146395	-0.356786
34	8	-4.551934	-1.773844	0.287813
35	25	-1.059946	0.192444	-0.583891
36	1	-1.849293	-2.213946	-1.724354
37	1	-0.344314	-2.544177	-1.318940
38	6	1.973077	-0.414226	-0.722235
39	1	1.648373	-1.451594	-0.818341
40	1	1.764301	0.093012	-1.668189
41	8	-3.472439	-2.751444	-2.122980
42	8	0.906155	-3.734852	-0.914365
43	1	1.492855	-4.053664	-1.609338
44	1	0.650093	-4.515157	-0.410062
45	1	-4.075254	-2.489218	-1.401845
46	1	-3.631269	-3.687532	-2.280024

47	6	3.456745	-0.383927	-0.434153
48	6	4.086114	-1.495071	0.126373
49	6	4.224843	0.743150	-0.727902
50	6	5.445508	-1.472412	0.415773
51	1	3.507061	-2.390829	0.326297
52	6	5.583272	0.770377	-0.439722
53	1	3.758579	1.602432	-1.196531
54	6	6.195267	-0.336123	0.138961
55	1	5.918577	-2.343033	0.852444
56	1	7.254454	-0.316283	0.362772
57	1	6.165880	1.652454	-0.674247

E(UM062X) = -2507.2648342 Hartree
Zero-point correction = 0.476732
Thermal correction to Energy = 0.507283
Thermal correction to Enthalpy = 0.508227
Thermal correction to Gibbs Free Energy = 0.414728
Sum of electronic and zero-point Energies = -2506.788103
Sum of electronic and thermal Energies = -2506.757551
Sum of electronic and thermal Enthalpies = -2506.756607
Sum of electronic and thermal Free Energies = -2506.850106

Table S3. [Mn(MeBzNO2A)(H_2O)]·2H_2O, M06-2X/TZVP, aqueous solution (0 Imaginary Frequencies).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	-1.164424	2.056352	0.870603
2	6	0.215400	2.359812	1.299343
3	6	1.299930	1.652899	0.478918
4	6	1.084852	-0.496602	1.637158
5	6	-0.116717	-1.413890	1.841250
6	7	-1.391632	-0.709120	1.632737
7	6	-1.639833	0.358823	2.622422
8	6	-2.051193	1.687851	1.984462
9	1	0.319065	2.103137	2.352499
10	1	0.401473	3.436096	1.234622
11	1	1.336824	2.089763	-0.519169
12	1	2.261672	1.845645	0.967318
13	1	1.146780	0.237269	2.438048
14	1	1.990935	-1.098417	1.728107
15	1	-0.067854	-2.221118	1.106487
16	1	-0.053987	-1.864931	2.839549
17	1	-0.744334	0.495063	3.227447
18	1	-2.427603	0.055904	3.317802
19	1	-3.055640	1.593018	1.573377
20	1	-2.072076	2.462293	2.761661
21	7	1.055811	0.203558	0.328524
22	6	-1.719855	3.106598	0.016003
23	1	-2.802281	2.965274	-0.047095
24	1	-1.532010	4.109550	0.410156
25	6	-2.532415	-1.611109	1.477888
26	1	-3.036835	-1.817381	2.426753
27	1	-2.179677	-2.568101	1.086417
28	6	-1.202004	3.013139	-1.430478

29	8	-0.949999	1.835019	-1.856604
30	8	-1.110017	4.047690	-2.088522
31	8	-1.060802	-1.805064	-1.398972
32	6	-3.569397	-1.121696	0.454581
33	8	-3.249226	-0.150711	-0.293004
34	8	-4.623624	-1.771600	0.371358
35	25	-1.134924	0.197238	-0.531643
36	1	-1.915874	-2.210479	-1.669365
37	1	-0.398160	-2.517366	-1.298910
38	6	1.969500	-0.472650	-0.649102
39	1	1.684879	-1.525827	-0.589633
40	8	-3.536174	-2.782518	-2.025503
41	8	0.835517	-3.729179	-0.920217
42	1	1.416779	-4.037922	-1.624302
43	1	0.560370	-4.519943	-0.442992
44	1	-4.140822	-2.515557	-1.307997
45	1	-3.683227	-3.723202	-2.165743
46	6	1.731205	-0.015329	-2.084815
47	1	0.700017	-0.183107	-2.394798
48	1	1.963412	1.037654	-2.238206
49	1	2.376364	-0.597744	-2.743553
50	6	3.442768	-0.391814	-0.279712
51	6	4.080472	-1.506066	0.264309
52	6	4.195754	0.763258	-0.498032
53	6	5.427887	-1.465735	0.605184
54	1	3.516162	-2.421255	0.412487
55	6	5.540962	0.809393	-0.155718
56	1	3.737443	1.635855	-0.947457
57	6	6.160418	-0.304230	0.400692
58	1	5.903404	-2.342599	1.026504
59	1	6.107848	1.715240	-0.330990
60	1	7.209961	-0.268303	0.664594

E(UM062X) = -2546.5716587 Hartree
Zero-point correction = 0.505080
Thermal correction to Energy = 0.536918
Thermal correction to Enthalpy = 0.537862
Thermal correction to Gibbs Free Energy = 0.442106
Sum of electronic and zero-point Energies = -2546.066578
Sum of electronic and thermal Energies = -2546.034741
Sum of electronic and thermal Enthalpies = -2546.033796
Sum of electronic and thermal Free Energies = -2546.129553

Table S4. [Mn(MeNO2A)(H_2O)]·5H_2O, M06-2X/TZVP, aqueous solution (0 Imaginary Frequencies).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	0.344273	-2.016545	-0.812447
2	6	-0.036050	-2.910209	0.302440
3	6	-0.649143	-2.162381	1.488557
4	6	1.485839	-1.389825	2.423599
5	6	2.618309	-0.566705	1.813758
6	7	2.550935	-0.550482	0.342323
7	6	2.767128	-1.876351	-0.272618
8	6	1.707494	-2.250764	-1.313788
9	1	0.843586	-3.465906	0.624607
10	1	-0.755826	-3.658597	-0.042233
11	1	-1.640895	-1.788391	1.223850
12	1	-0.775018	-2.864585	2.322545
13	1	1.647943	-2.451867	2.247612
14	1	1.509142	-1.260158	3.508737
15	1	2.518897	0.467906	2.147125
16	1	3.578605	-0.952311	2.177080
17	1	2.796203	-2.628082	0.515113
18	1	3.746623	-1.914394	-0.757741
19	1	1.834161	-1.627360	-2.198330
20	1	1.858101	-3.296639	-1.608320
21	7	0.158022	-0.998407	1.894589
22	6	-0.671760	-2.006694	-1.865721
23	1	-0.263977	-1.493409	-2.740552
24	1	-0.982954	-3.012053	-2.162255
25	6	3.377068	0.495174	-0.260301
26	1	4.392270	0.155156	-0.485767
27	1	3.463634	1.327290	0.444139
28	6	-1.891695	-1.198064	-1.412348
29	8	-1.627099	-0.102800	-0.807845
30	8	-3.026837	-1.617138	-1.650063
31	8	0.775745	2.086150	0.939520
32	6	2.758041	1.112730	-1.524334
33	8	1.535221	0.870069	-1.756381
34	8	3.473333	1.883183	-2.180988
35	25	0.373131	0.213491	-0.074854
36	1	1.202071	2.777725	0.386624
37	1	0.009958	2.496003	1.409194
38	6	-0.574389	-0.181417	2.872414
39	1	0.033287	0.679540	3.150446
40	8	2.058479	3.873792	-0.709329
41	8	-1.463626	2.952259	2.155055
42	1	-2.188845	2.460472	1.711638
43	1	-1.701370	3.883614	2.108906
44	1	2.606457	3.420153	-1.374162
45	1	2.613783	4.561796	-0.328982
46	8	-5.220308	1.984494	-1.397978
47	1	-4.484863	2.264533	-0.837640
48	1	-5.384215	1.082843	-1.078820
49	8	-3.218079	1.480144	0.694970
50	1	-2.669167	0.937154	0.085313
51	1	-3.954077	0.885490	0.907333
52	8	-4.993447	-0.534626	-0.115612
53	1	-5.611370	-1.219650	0.156008

54	1	-4.318753	-0.969047	-0.687665
55	1	-0.816369	-0.756492	3.773607
56	1	-1.500000	0.182847	2.421938

E(UM062X) = -2505.5769148 Hartree
Zero-point correction = 0.471142
Thermal correction to Energy = 0.504600
Thermal correction to Enthalpy = 0.505544
Thermal correction to Gibbs Free Energy = 0.406021
Sum of electronic and zero-point Energies = -2505.105773
Sum of electronic and thermal Energies = -2505.072315
Sum of electronic and thermal Enthalpies = -2505.071371
Sum of electronic and thermal Free Energies = -2505.170893

Table S5. [Mn(MeNO2A)(H_2O)$_2$]·4H_2O, M06-2X/TZVP, aqueous solution (0 Imaginary Frequencies).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	0.030978	-2.057941	-0.871424
2	6	-0.260606	-3.018282	0.215692
3	6	-0.751541	-2.375663	1.517307
4	6	1.419087	-1.609806	2.314674
5	6	2.498138	-0.746094	1.673436
6	7	2.307549	-0.640937	0.218916
7	6	2.482216	-1.928742	-0.481497
8	6	1.359504	-2.253119	-1.469031
9	1	0.637221	-3.604554	0.411469
10	1	-1.017955	-3.736233	-0.113362
11	1	-1.778970	-2.038478	1.403747
12	1	-0.733709	-3.139086	2.307248
13	1	1.572287	-2.657543	2.059263
14	1	1.522024	-1.549153	3.401986
15	1	2.428374	0.263087	2.078338
16	1	3.484072	-1.156076	1.929176
17	1	2.563465	-2.723208	0.259295
18	1	3.428104	-1.936955	-1.031545
19	1	1.427997	-1.583432	-2.325012
20	1	1.496025	-3.281351	-1.828768
21	7	0.053475	-1.207284	1.909002
22	6	-1.036742	-2.018319	-1.867438
23	1	-0.677142	-1.486380	-2.752544
24	1	-1.362197	-3.013486	-2.189382
25	6	3.101036	0.429562	-0.377002
26	1	4.096428	0.095944	-0.689039
27	1	3.246792	1.220722	0.363030
28	6	-2.244689	-1.225946	-1.362231
29	8	-2.040366	-0.494363	-0.342868
30	8	-3.309489	-1.280797	-1.990275
31	8	0.797579	1.854975	1.280606
32	6	2.406944	1.104962	-1.567341
33	8	1.189693	0.829976	-1.766080
34	8	3.073366	1.939553	-2.204008
35	25	0.043240	0.183948	-0.034843
36	1	1.234665	2.573247	0.772573
37	1	0.027860	2.257788	1.729164
38	6	-0.614057	-0.470056	2.989563
39	1	0.009616	0.372320	3.288679
40	8	2.085343	3.754948	-0.261122
41	8	-1.672707	2.780515	2.069569
42	1	-2.436002	2.172043	1.928386
43	1	-1.940772	3.446511	2.709510
44	1	2.517107	3.363132	-1.041970
45	1	2.747180	4.313183	0.159316
46	8	-1.265881	2.111748	-0.649432
47	1	-1.440228	2.676262	0.118676
48	1	-2.143859	1.868131	-1.000053
49	8	-3.592569	1.058516	1.254044
50	1	-3.091237	0.408072	0.713870
51	1	-4.120464	1.504758	0.576324
52	8	-3.903909	1.406776	-1.534322
53	1	-4.340943	1.831068	-2.279137

54	1	-3.861213	0.448777	-1.741499
55	1	-0.794996	-1.109225	3.862423
56	1	-1.568757	-0.081199	2.629755

E(UM062X) = -2505.5809106 Hartree
Zero-point correction = 0.473123
Thermal correction to Energy = 0.505544
Thermal correction to Enthalpy = 0.506488
Thermal correction to Gibbs Free Energy = 0.412760
Sum of electronic and zero-point Energies = -2505.107788
Sum of electronic and thermal Energies = -2505.075366
Sum of electronic and thermal Enthalpies = -2505.074422
Sum of electronic and thermal Free Energies = -2505.168151

Table S6. [Mn(MeNO2A)(H_2O)$_2$]·4H_2O, M06-2X/TZVP, aqueous solution (1 Imaginary Frequency).

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	0.391628	-1.997165	-0.981805
2	6	0.232976	-3.048568	0.045623
3	6	-0.368739	-2.545804	1.360860
4	6	1.690952	-1.549693	2.240943
5	6	2.629496	-0.493569	1.666996
6	7	2.438133	-0.332876	0.216159
7	6	2.800770	-1.537635	-0.558114
8	6	1.737376	-1.961453	-1.575140
9	1	1.205012	-3.504923	0.231700
10	1	-0.406014	-3.851569	-0.333220
11	1	-1.425344	-2.315611	1.221825
12	1	-0.297738	-3.348771	2.106257
13	1	1.996717	-2.544997	1.922126
14	1	1.784257	-1.543394	3.330271
15	1	2.399201	0.469117	2.126505
16	1	3.665024	-0.755261	1.917493
17	1	2.997044	-2.354226	0.135080
18	1	3.737886	-1.372715	-1.097862
19	1	1.709344	-1.237067	-2.388270
20	1	2.023317	-2.934349	-1.994294
21	7	0.281905	-1.317480	1.849733
22	6	-0.676583	-2.030783	-1.979263
23	1	-0.371527	-1.439447	-2.846730
24	1	-0.902459	-3.042308	-2.330742
25	6	3.057784	0.881116	-0.309949
26	1	4.093217	0.724289	-0.627862
27	1	3.073249	1.641300	0.476527
28	6	-1.960606	-1.375286	-1.464438
29	8	-1.822245	-0.550526	-0.499634
30	8	-3.033123	-1.617155	-2.024102
31	8	0.371670	1.895996	1.297413
32	6	2.266415	1.518984	-1.461749
33	8	1.081265	1.111466	-1.651569
34	8	2.810335	2.453644	-2.068104
35	25	0.129874	0.137776	0.011474
36	1	0.677612	2.691551	0.807987
37	1	-0.471824	2.130973	1.741154
38	6	-0.476100	-0.747197	2.971336
39	1	0.012991	0.167493	3.306199
40	8	1.353168	4.014610	-0.165631
41	8	-2.142144	2.347023	2.219664
42	1	-2.767666	1.603974	2.040821
43	1	-2.432393	2.794522	3.020007
44	1	1.869218	3.737516	-0.943194
45	1	1.884537	4.680135	0.282884
46	8	-2.046983	2.413489	-0.680513
47	1	-2.194810	2.643378	0.246552
48	1	-2.766283	1.802669	-0.914071
49	8	-3.639991	0.325419	1.304763
50	1	-3.006496	-0.069369	0.665247
51	1	-4.339677	0.640807	0.713949
52	8	-4.352141	0.740223	-1.367319
53	1	-4.982756	1.021192	-2.036997

54	1	-4.007729	-0.133434	-1.652328
55	1	-0.537959	-1.449516	3.810887
56	1	-1.487375	-0.497878	2.644245

E(UM062X) =-2505.5785633 Hartree
Zero-point correction = 0.471389
Thermal correction to Energy = 0.503779
Thermal correction to Enthalpy = 0.504724
Thermal correction to Gibbs Free Energy = 0.410549
Sum of electronic and zero-point Energies = -2505.107175
Sum of electronic and thermal Energies = -2505.074784
Sum of electronic and thermal Enthalpies = -2505.073840
Sum of electronic and thermal Free Energies = -2505.168015

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