Supporting Information

Semi-rigid (aminomethyl)piperidine-based pentadentate ligands for Mn(II) complexation

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1. Fitting of ^{1}H NMRD profiles and ^{17}O NMR relaxivity data

From the two contributions (inner sphere ($r_{1,IS}$) and outer-sphere ($r_{1,OS}$)) to the longitudinal proton relaxation rate (r_1) (eq. 1), the former one is considered for the fitting of ^{1}H NMRD profiles (1).

$$r_1 = r_{1,IS} + r_{1,OS} \tag{1}$$

According to the Solomon–Bloembergen theory, the $r_{1,IS}$ is dominated by the dipolar interaction (eqs. 2 and 3), where q is the number of water molecules directly coordinated to the Mn-ion, T_{1M} is their longitudinal relaxation time, τ_M is the water-exchange correlation time (2-4).

$$r_{1,IS} = \frac{q}{55556(T_{1M}+\tau_M)} \tag{2}$$

$$\frac{1}{T_{1M}} = \frac{2}{15}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\hbar^2 y_S^2 y_I^2}{r_{MnH}^6} S(S+1)\left(\frac{3\tau_{d1}}{1+\omega_I^2\tau_{d2}^2}\right) \tag{3}$$

Here, r_{MnH} is the distance between the proton of a bound H_2O molecule and Mn-ion (fixed at 3.0 Å), $\mu_0/4\pi$) is the magnetic permeability in vacuum, S is the electron spin (7/2), γ_I and γ_S are the gyromagnetic ratios, and ω_I and ω_S are the Larmor frequencies of the proton and electron, resp. T_{ie} (i = 1,2) represents electronic relaxation time that contributes to $\tau_{di}^{-1} = \tau_M^{-1} + \tau_R^{-1} + T_{ie}^{-1}$, expressed by eqs. 4 and 5 due to zero-field splitting (ZFS) (5).

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

$$\frac{1}{T_{2e}} = \Delta^2\tau_V\left(\frac{5.26}{1+0.372\omega_S^2\tau_V^2} + \frac{7.18}{1+1.24\omega_S^2\tau_V^2}\right) \tag{5}$$

Here, Δ^2 represents the mean-squared fluctuation of the ZFS, τ_v is the correlation time for the instantaneous distortion of the coordination polyhedron of Gd-ion. The outer-sphere contribution to the relaxivity ($r_{1,OS}$) is described by eqs. 6 and 7, where N_A is the Avogadro's number, a_{GdH} the distance of diffusing water molecule in the closest approach to Gd-ion (fixed at 4.0 Å), D_{GdH} is diffusion coefficient and $J_{os}(\omega_S, Tje)$ (j = 1, 2) are spin density functions (6).

$$r_{1,IS} = \left(\frac{32\pi}{405}\right)\left(\frac{\mu_0}{4\pi}\right)^2 y_I^2 y_S^2 \hbar^2 S(S+1)\frac{N_A}{a_{MnH}D_{MnH}}[3J_{OS}(\omega_I, T_{1e}) + 7J_{OS}(\omega_S, T_{1e})] \tag{6}$$

$$J_{OS}(\omega_I, T_{je}) = Re\left\{\frac{1+\frac{1}{4}\left[i\omega\tau_{MnH}+\left(\frac{\tau_{MnH}}{T_{je}}\right)\right]^{\frac{1}{2}}}{1+\left[i\omega\tau_{MnH}+\left(\frac{\tau_{MnH}}{T_{je}}\right)^{\frac{1}{4}}\right]+\frac{4}{9}\left[i\omega\tau_{MnH}+\left(\frac{\tau_{MnH}}{T_{je}}\right)\right]+\frac{1}{9}\left[i\omega\tau_{MnH}+\left(\frac{\tau_{MnH}}{T_{je}}\right)^{\frac{1}{2}}\right]}\right\} \tag{7}$$

All correlation times τ (X = R, M, V) exhibit an exponential dependence (eq. 8), where E_X are activation energies (fixed at E_V = 1 kJ mol^{-1}, E_R = 1 kJ mol^{-1}) and R is the gas constant, leading to a temperature dependent diffusion coefficient D (fixed at 2.24×10^{-5} cm^2 s^{-1} for 298.15K).

$$\tau_X^T = \tau_X^{298} exp\left[\frac{E_X}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right] \quad (8)$$

$$D_{MnH}^T = D_{MnH}^{298} exp\left[\frac{E_D}{R}\left(\frac{1}{298.15} - \frac{1}{T}\right)\right] \quad (9)$$

Mn-induced water ^{17}O longitudinal and transverse relaxation rates ($1/T_{1r}$ and$1/T_{2r}$) and angular frequencies ($\Delta_{\omega r}$) were calculated using eqs. 10 and 11 (7-8).

$$\frac{1}{T_{1r}} = \frac{1}{T_{1M}+\tau_M} \quad (10)$$

$$\frac{1}{T_{2r}} = \frac{1}{\tau_M}\frac{1}{T_{1M}+\tau_M} \quad (11)$$

2. Computational modeling

Table S1: Calculated bond distances for Mn complexes with AMPTA.

Mn((*S*)-AMPTA)	Distance (Å)	**Mn((*R*)-AMPTA)**
2.093	Mn-O_{water}	2.093
2.138	Mn-N2	2.137
2.074	Mn-N1	2.075
2.020	Mn-O	2.021
2.008	Mn-O1	2.008
2.054	Mn-O2	2.054

Table S2: Calculated bond distances for Mn complexes with AMPDA-HB.

Mn((*S*)-AMPDA-HB)	Distance (Å)	**Mn((*R*)-AMPDA-HB)**
2.103	Mn-O_{water}	2.103
2.145	Mn-N2	2.145
2.078	Mn-N1	2.078
2.042	Mn-O	2.042
2.000	Mn-O1	2.000
2.067	Mn-O2	2.067

3. NMR Spectra

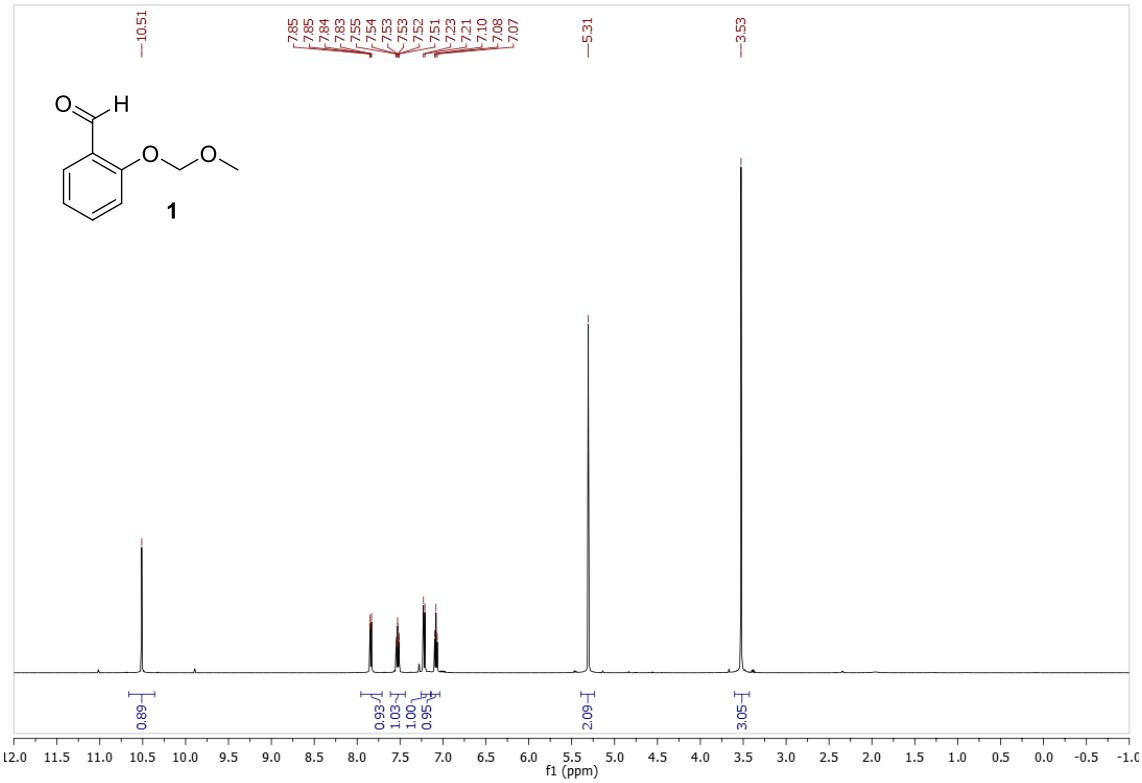

Figure S1. ^{1}H NMR spectrum in $CDCl_3$ of protected salicylaldehyde **1**.

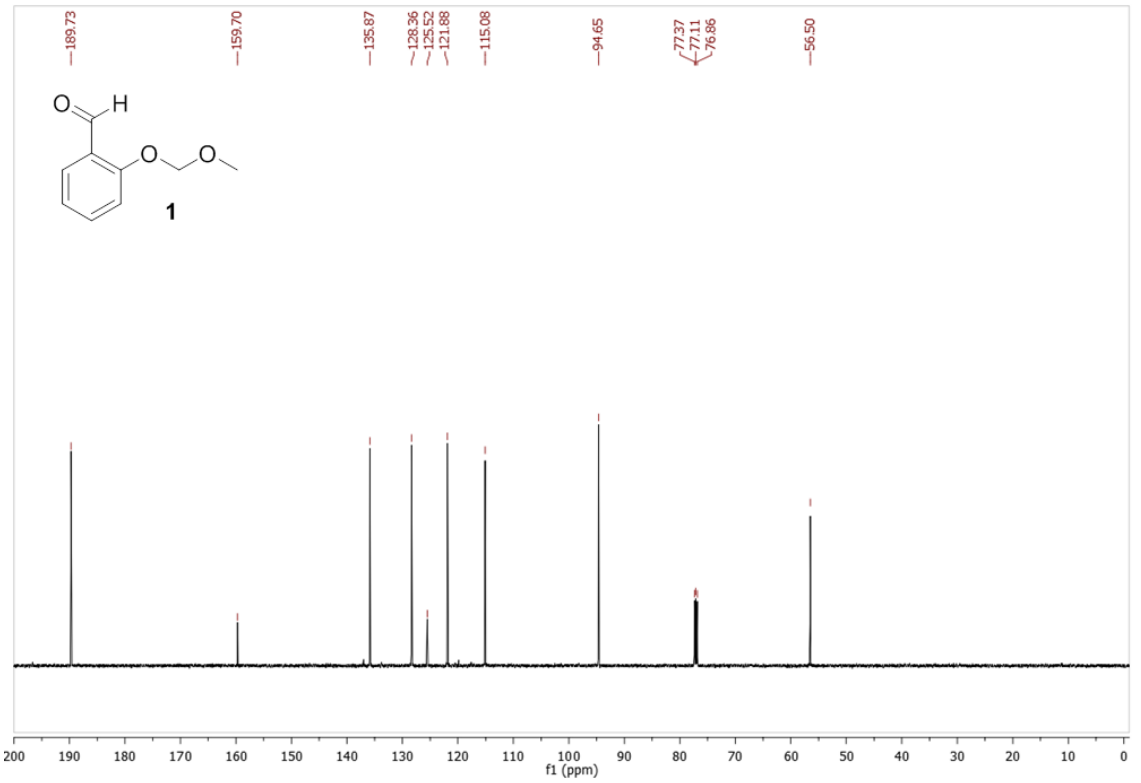

Figure S2. ^{13}C NMR spectrum in $CDCl_3$ of protected salicylaldehyde **1**.

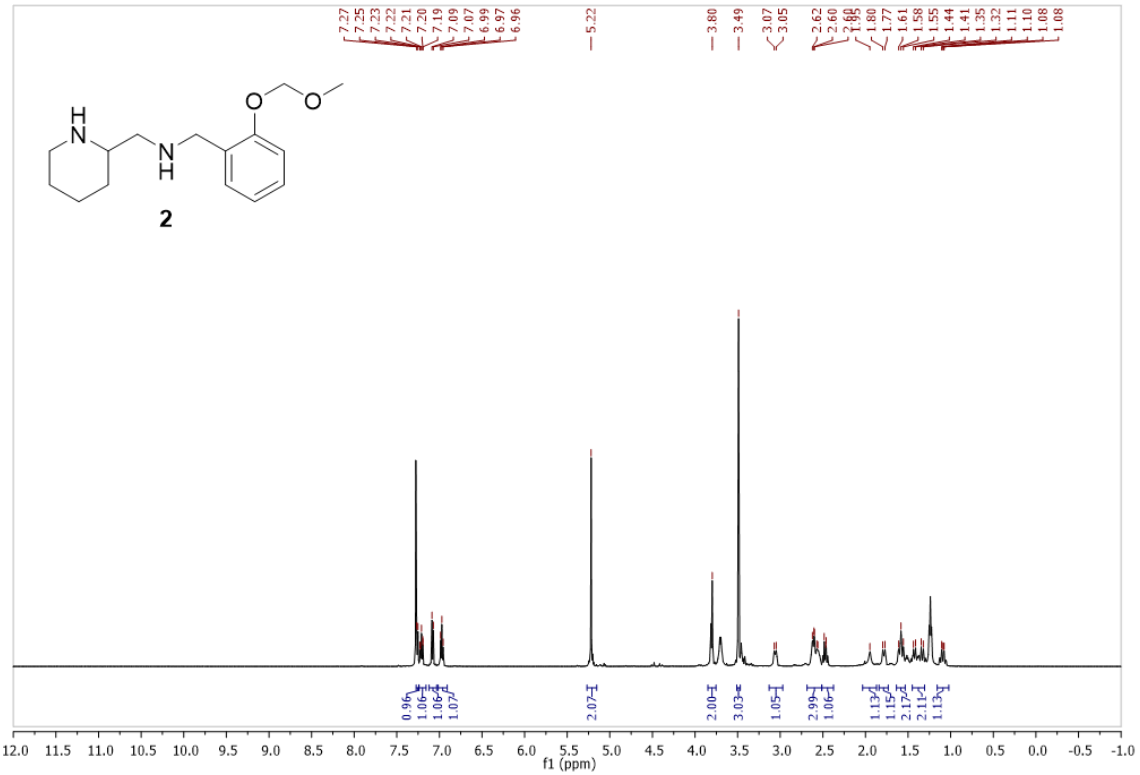

Figure S3. ^{1}H NMR spectrum in $CDCl_3$ of intermediate **2** (signals from residual EtOH at 3.67 and 1.22 ppm are also observable).

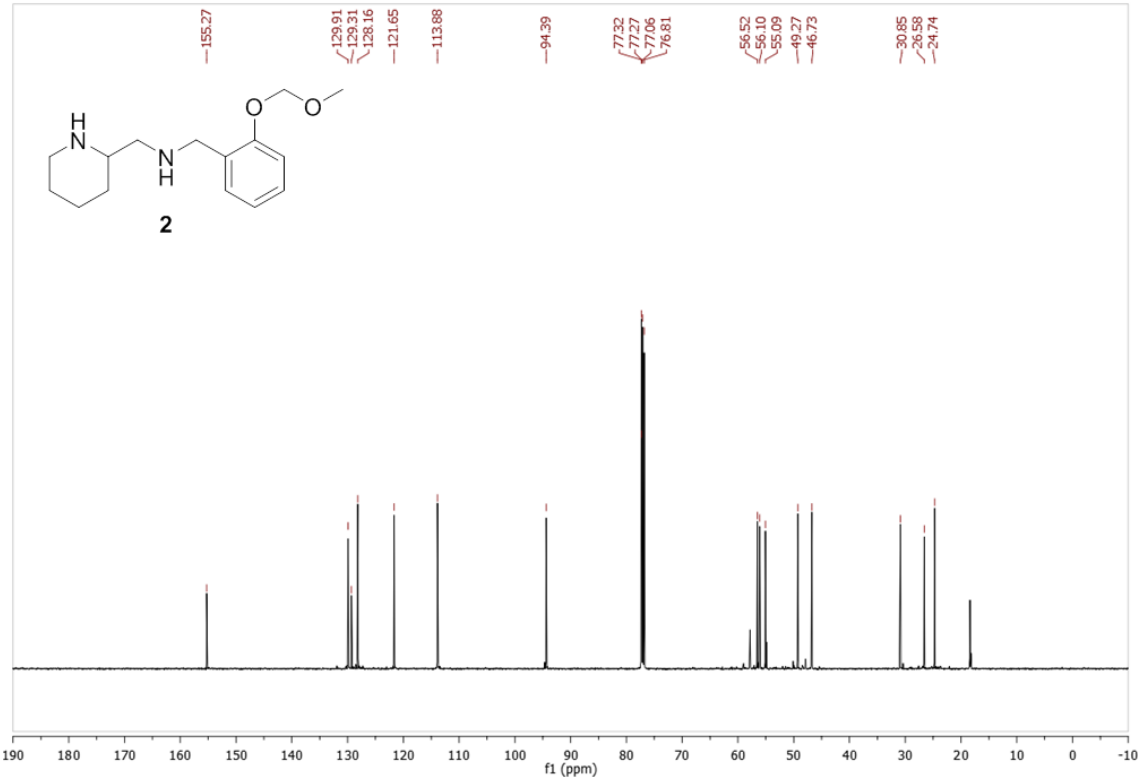

Figure S4. ^{13}C NMR spectrum in $CDCl_3$ of intermediate **2** (signals from residual EtOH at 18.4 and 57.8 ppm are also observable).

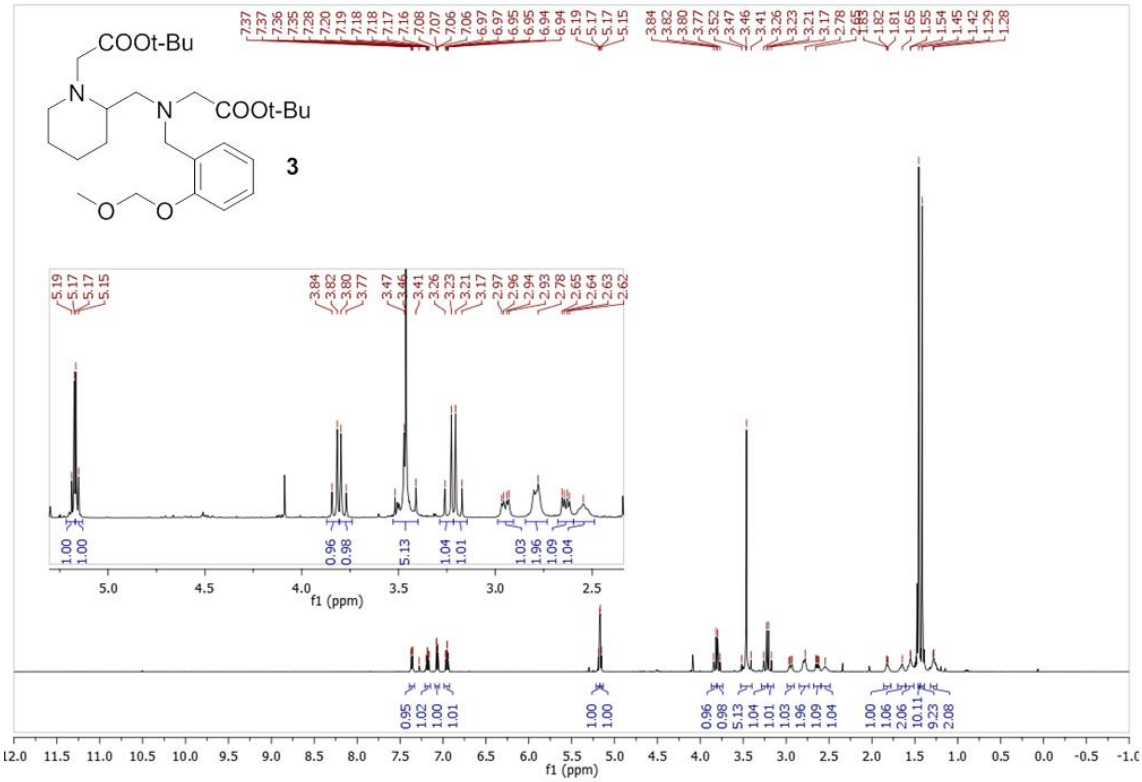

Figure S5. ^{1}H NMR spectrum in $CDCl_3$ of intermediate **3**.

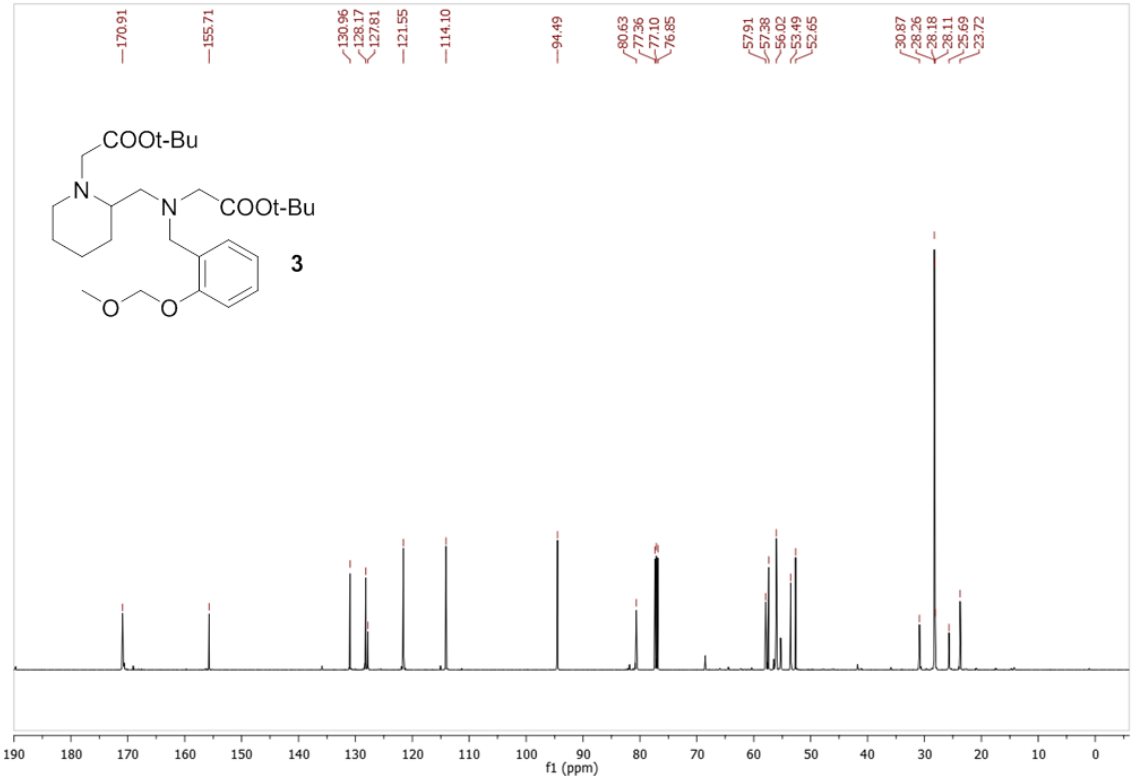

Figure S6. ^{13}C NMR spectrum in $CDCl_3$ of intermediate **3**.

4. HPLC-MS

Analytical HPLC gradient conditions for AMPDA-HB and (*R*)-AMPTA:
Solvent A = H_2O (TFA 0.1%); solvent B = ACN (TFA 0.1%); flow = 1 mL/min;

Time (min)	Solvent A (%)	Solvent B (%)
0	99	1
2,00	99	1
16,00	0	100
19,00	0	100

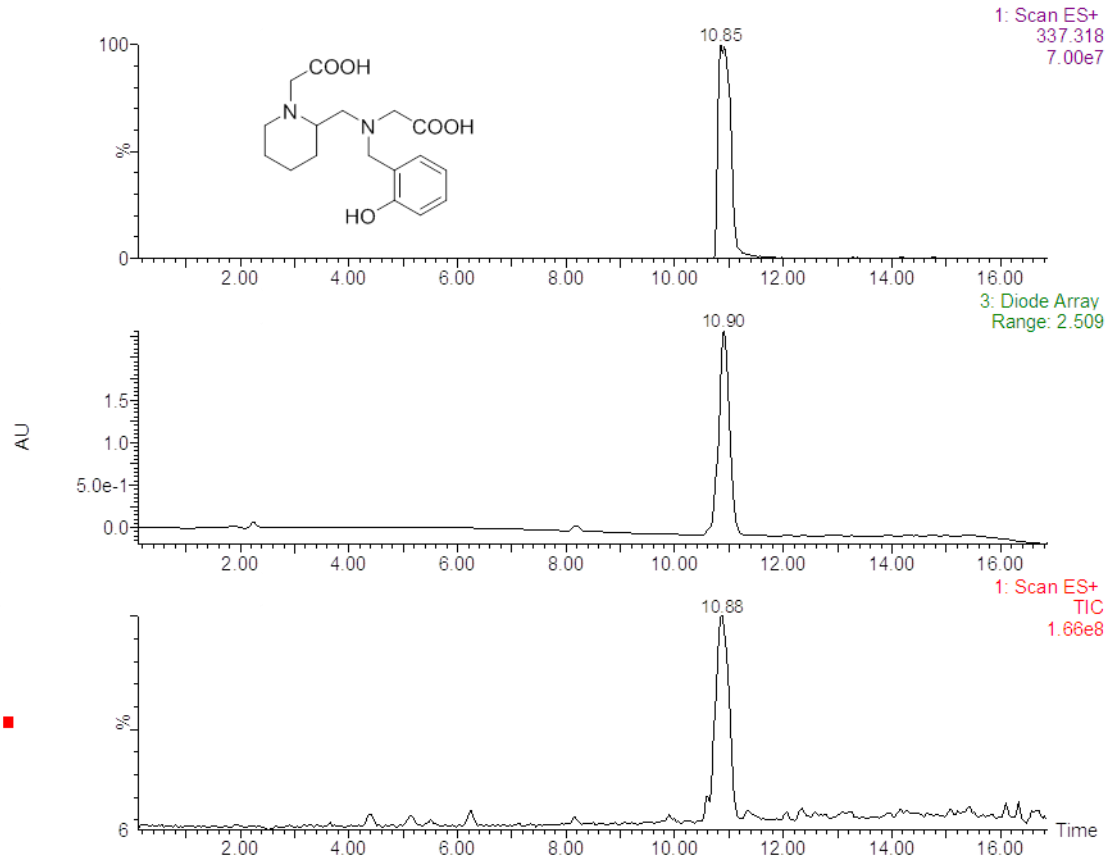

Figure S7. ESI$^+$ MS (*bottom*), UV (254 nm, *middle*) and specific ion (M+H$^+$, *top*) HPLC chromatograms of AMPDA-HB (t_R = 10.9 min) prepared according to the new method.

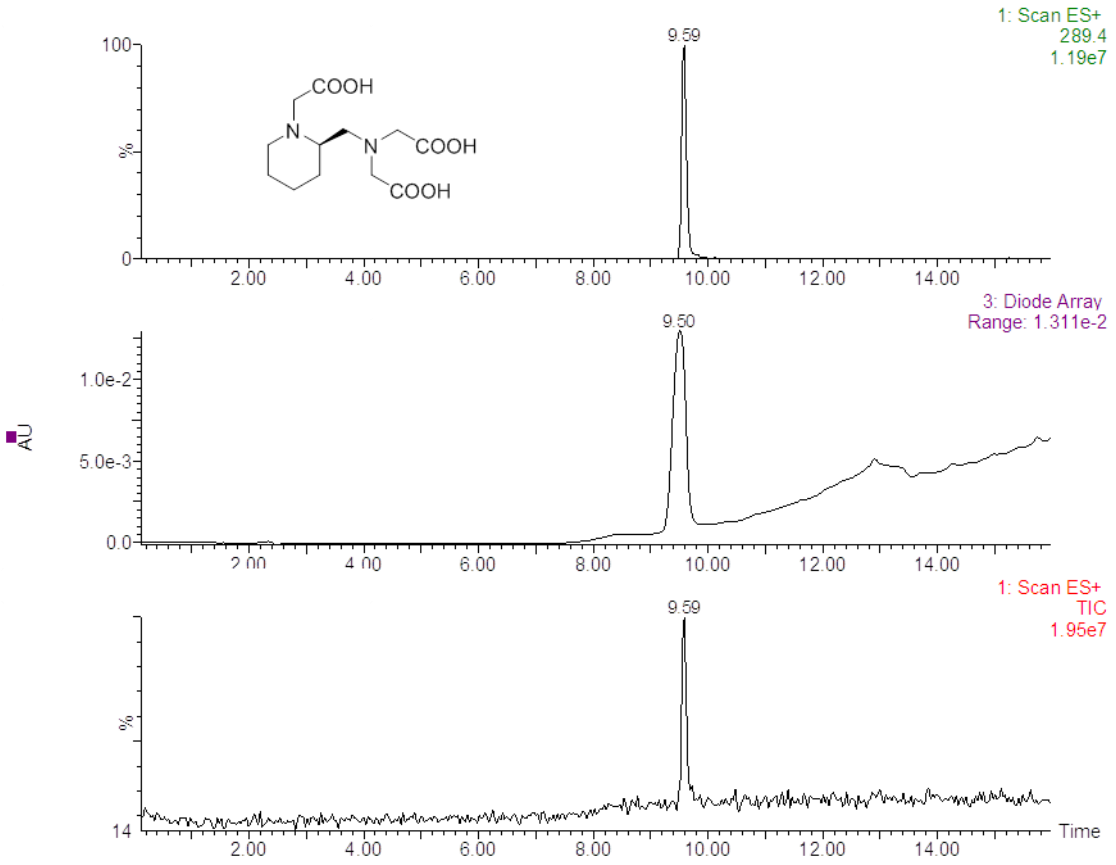

Figure S8. ESI$^+$ MS (*bottom*), UV (254 nm, *middle*) and specific ion (M+H$^+$, *top*) HPLC chromatograms of (*R*)-AMPTA (t_R = 9.5 min).

5. Equilibrium studies of the Mn(II) complexes

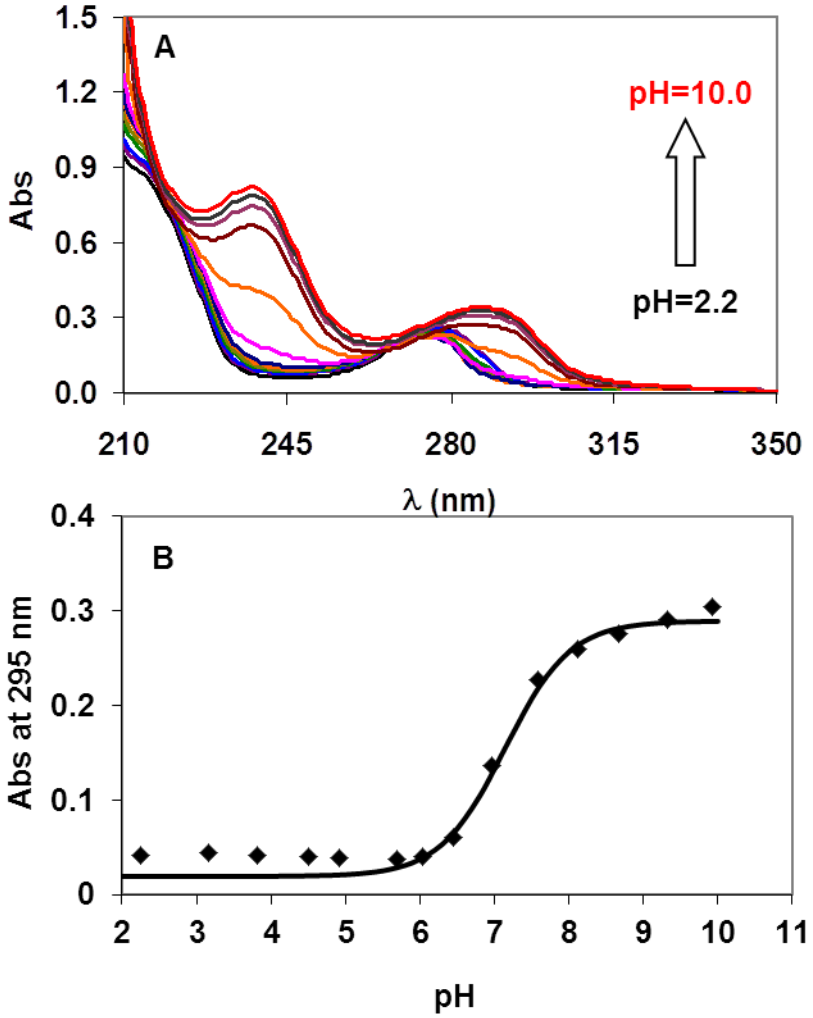

Figure S9. Absorption spectra (**A**) and absorbance values at 295 nm (**B**) of Mn^{2+}-AMPDA-HB system as a function of pH ([Mn^{2+}] = [AMPDA-HB] = 1.0×10^{-4} M, l = 1.0 cm, 0.15 M NaCl, 25 °C).

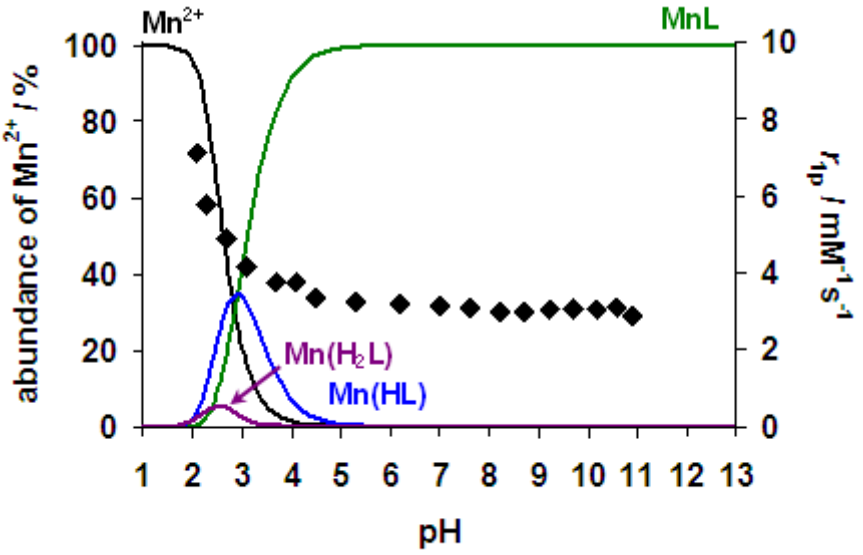

Figure S10. Species distribution and relaxivity values (◆) of Mn^{2+}-CDTA system as a function of pH ([Mn^{2+}] = [CDTA] = 1.0 mM, 20 MHz, 0.15 M NaCl, 25 ℃).