Supplementary Information

Manganese(II) complexes of scorpiand-like azamacrocycles as MnSOD mimics.

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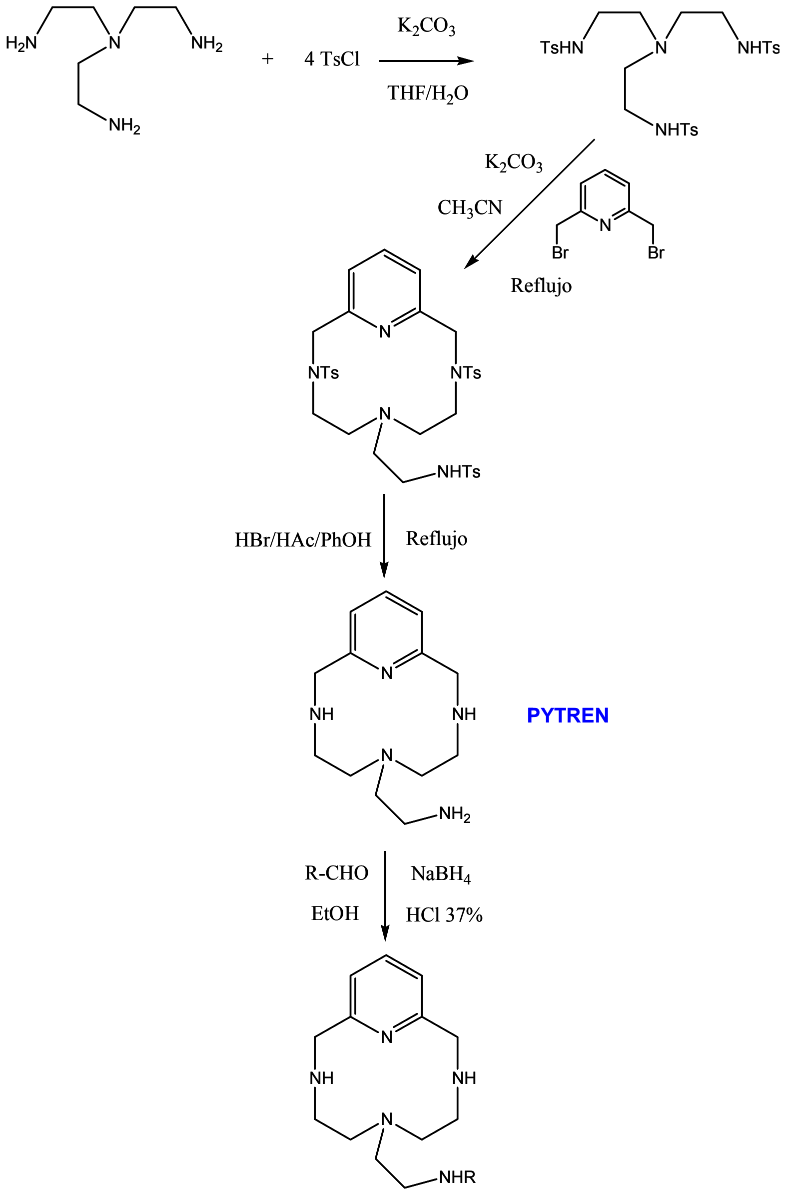
1.- Synthesis of 2 and 3.

The synthesis of ligands **2** and **3** was accomplished following a modification of the Richman-Atkins procedure by reaction of the pertosylated polyamine tren with 2,6-bis(bromomethyl)pyridine in 1:1 molar ratio using K_2CO_3 as a base in refluxing CH_3CN (Scheme 1). Detosylation is carried out with HBr/HAc, and the final product is obtained as the hydrobromide salt.[1] Compounds **2** and **3** was obtained by reacting **1** in its free amine form with 2 or 4-quinoline carbaldehyde in dry ethanol followed by in situ reaction with sodium borohydride and precipitation as a hydrochloride salt.



Scheme 1. General procedure of synthesis of the ligands.

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[1] B.Verdejo, A.Ferrer, S.Blasco, C.E.Castillo, J.González, J.Latorre, M.A.Máñez, M.García Basallote, C.Soriano,| and E.García-España, *Inorg. Chem.* 2007, **46,** 5707-5719

5-(2-(N-2-quinolil)etilamino)-2, 5, 8, - triaza [9] - 2, 6 –piridinofano (2).

$C_{23}H_{30}N_6 \cdot 4HCl$ (PM 536.367 g/mol). Yield: 60%. Anal calcd for $C_{23}H_{30}N_6 \cdot 4HCl \cdot 4H_2O$ C 45.40; H 6.95; N 13.81, found C 45.37; H 7.01; N 14.01. ^{1}H NMR (D_2O, 300.13 MHz): δ_H (ppm): 2.96 (t, J = 5Hz, 4H), 3.17-3.31 (m, 6H), 3.50-3.55 (m, 2H), 4.65 (s, 4H), 4.76 (s, 2H), 7.45 (d, J = 8Hz, 2H), 7.94-8.01 (m,2H), 8.13 (d, J = 8Hz, 1H),8.15 (t, J = 8Hz, 1H), 8.72 (d, J = 8Hz, 1H). ^{13}C NMR (75.47 MHz, D_2O): δ_C (ppm): 44.8, 46.2, 49.1, 49.8, 50.8, 51.2, 121.0, 122.2, 122.5, 129.4, 130.7, 135.7, 140.1, 147.3, 149.1.

5-(2-(N-4-quinolil)etilamino)-2, 5, 8, - triaza [9] - 2, 6 –piridinofano (3).

$C_{23}H_{30}N_6 \cdot 4HCl$ (PM 536.367 g/mol) Yield: 48.6%. Anal calcd for $C_{23}H_{30}N_6 \cdot 4HCl \cdot 5H_2O$ C 44.09; H 6.39; N 13.41, found C 43.70; H 6.32; N 13.32. ^{1}H NMR (D_2O, 300.13 MHz): δ_H (ppm): 2.98 (t, J = 5Hz, 4H), 3.19-3.32 (m, 6H), 3.58-3.66 (m, 2H), 4.64 (s, 4H), 5.18 (s, 2H), 7.45 (d, J = 8Hz, 2H), 7.95 (t, *J* = 8Hz ,1H), 8.09(t, J = 8Hz, 1H), 8.19-8.25 (m,2H), 8.46 (d, *J* = 8 Hz, 1H), 9.21 (d, J = 6Hz, 1H). ^{13}C NMR (75.47 MHz, D_2O): δ_C (ppm): 46.2, 47.7, 49.8, 50.9, 51.2, 121.4, 121.8, 122.5, 124.64, 127.2, 135.9, 140.1, 144.3, 149.2.

2.- Protonation constants.

pH-Metric studies were carried out at 298.1 K in aqueous solution in 0.15 M $NaClO_4$ using the equipment previously described.[2] The data was analyzed by means of the HYPERQUAD set of programs to derive the ligand basicity constants and the Mn^{II} complexes formation constants.

Table S1.- Logarithms of protonation constants of ligands. Determined in 0.15 mol.dm^{-3} $NaClO_4$ at 298.1 ± 0.1 K.

Reaction[a]	PyTREN	PyTREN-2Q	PyTREN-4Q
$L+H \leftrightarrows HL$	10.19(6)[c]	10.03(1)[b]	9.93(1)
$HL+H \leftrightarrows H_2L$	9.19(3)	8.40(1)	8.31(1)
$H_2L+H \leftrightarrows H_3L$	7.94(4)	6.23(1)	5.94(1)
$H_3L+H \leftrightarrows H_4L$			2.82(1)
Log β	27.32(8)	24.66(2)	27.00(1)

[a] Charges omitted for clarity. [b] Values in parentheses are standard deviations in the last significant figure. [c] Values obtained of ref.[1]

3.- Molar fraction distribution of compounds 1,2and 3.

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[2] E. García-España, M. J. Ballester, F. Lloret, J.-M. Moratal, J. Faus and A. Bianchi, *J. Chem. Soc. Dalton Trans.*, **1988**, *1*, 101-104.

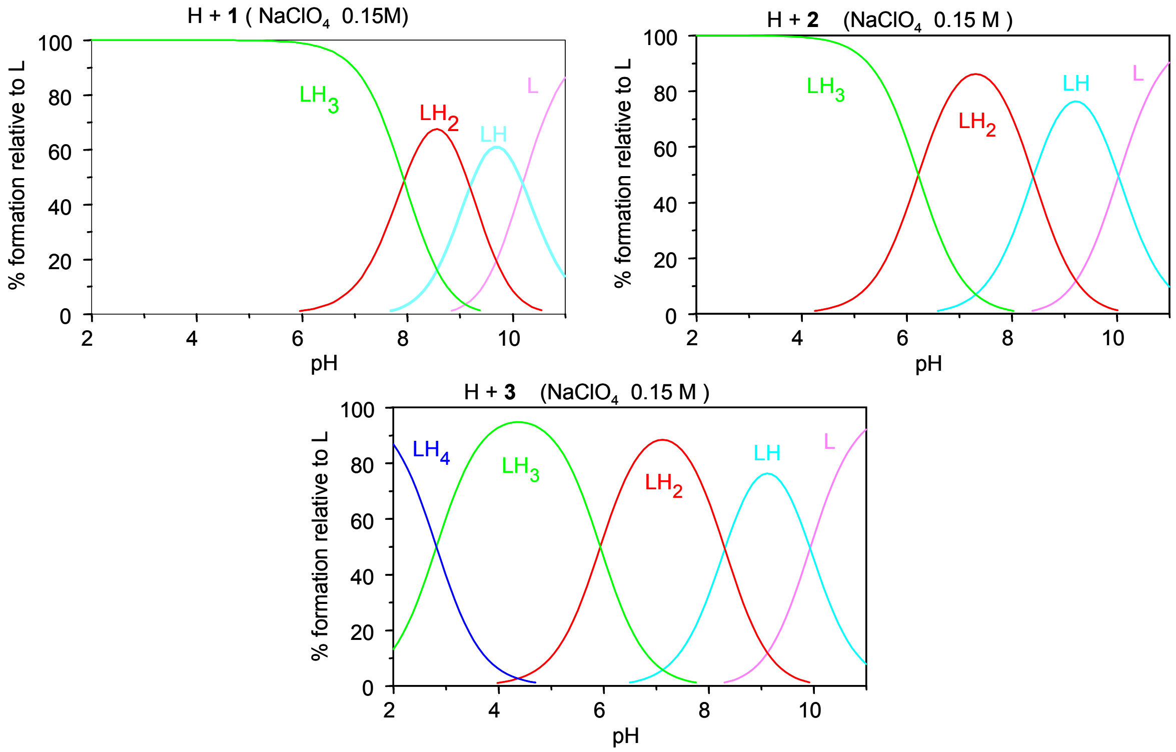
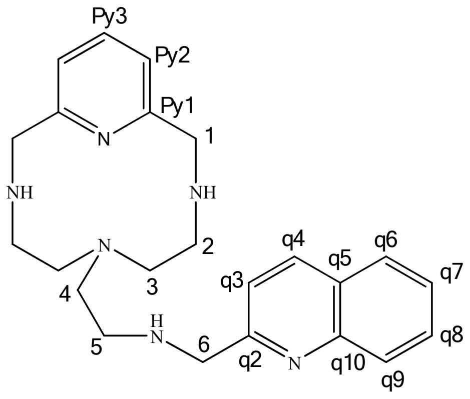


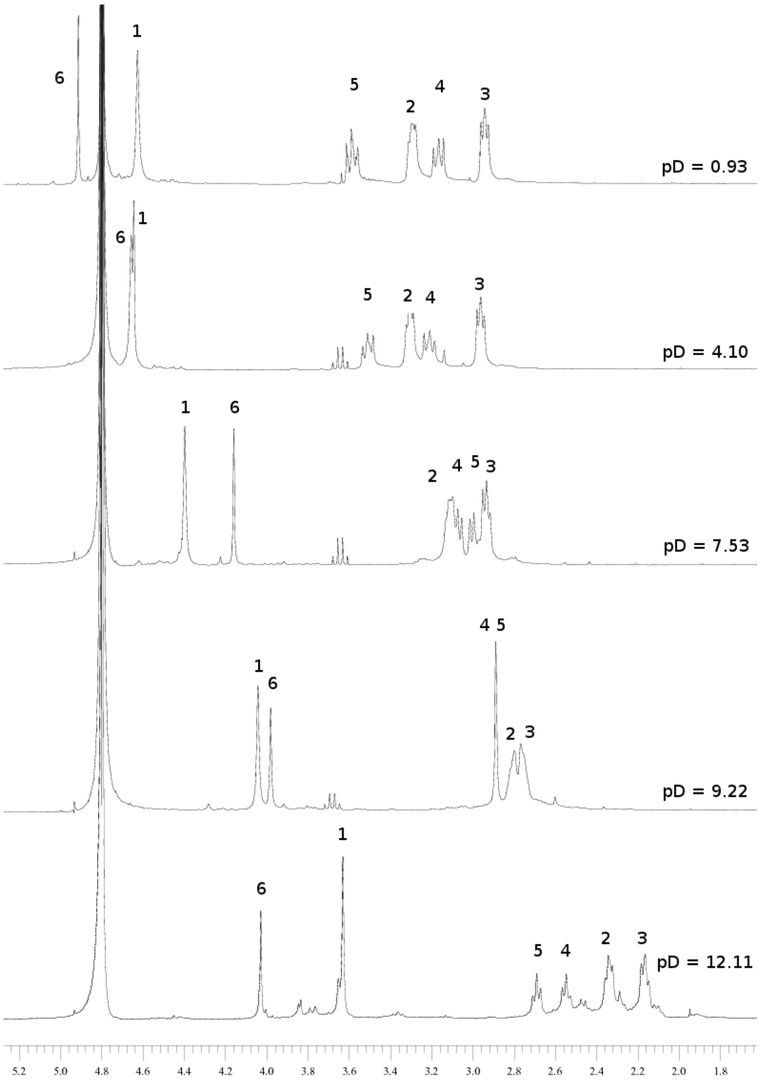
Figure S1.- Distribution diagrams for the protonation of compounds **1-3.**

4.- NMR variation.

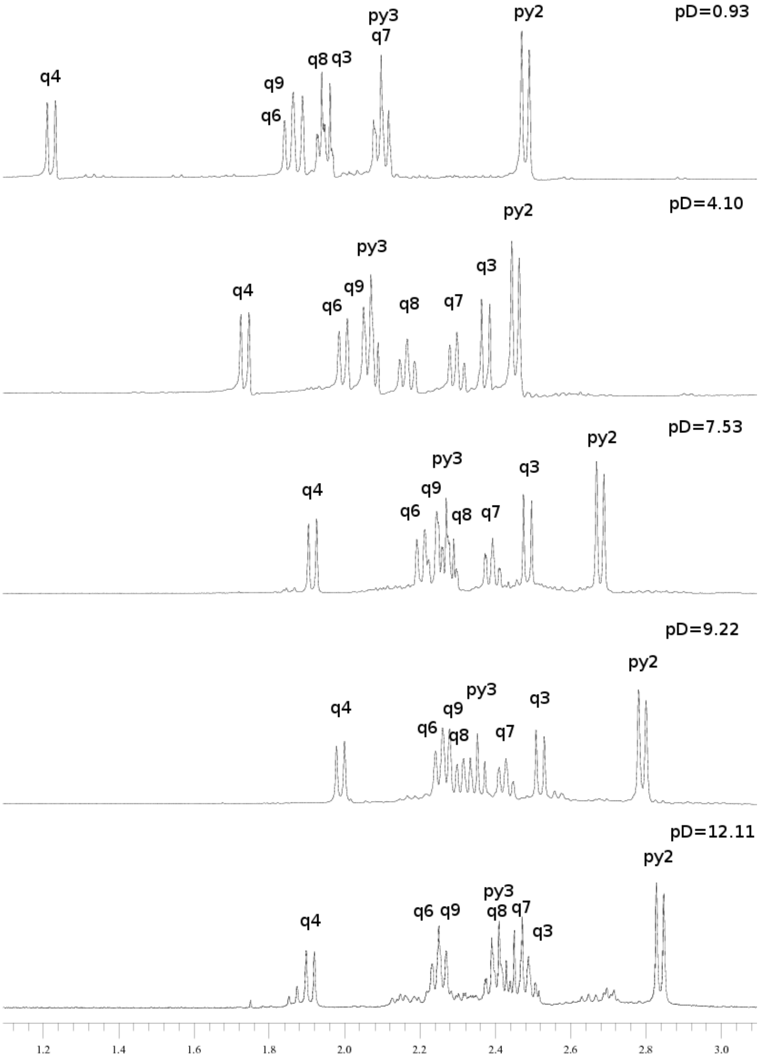


Protonation secuence of 2:

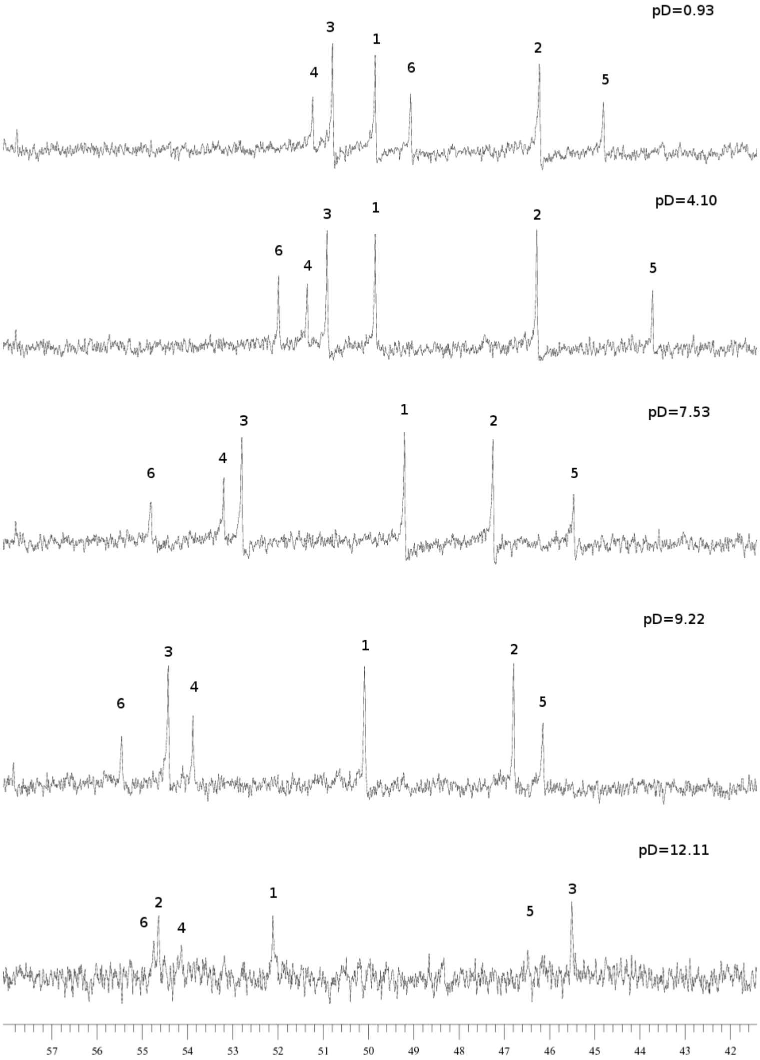
^{1}H NMR Spectra Aliphatic region



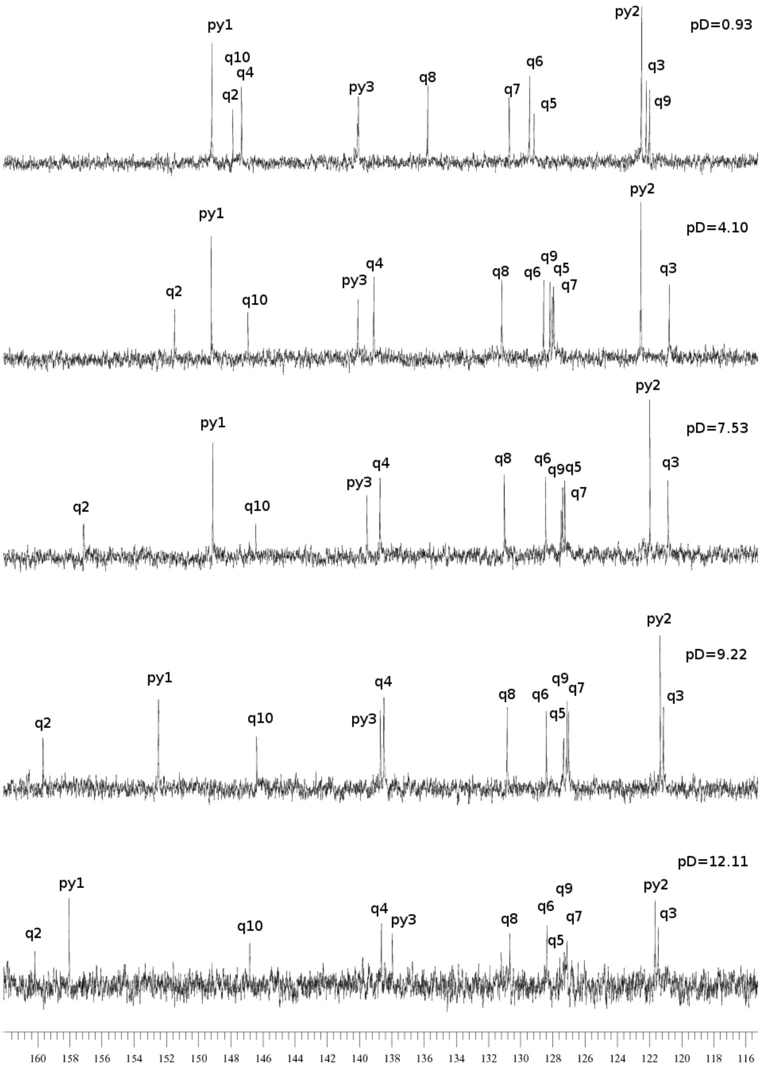
^{1}H NMR Spectra Aromatic region



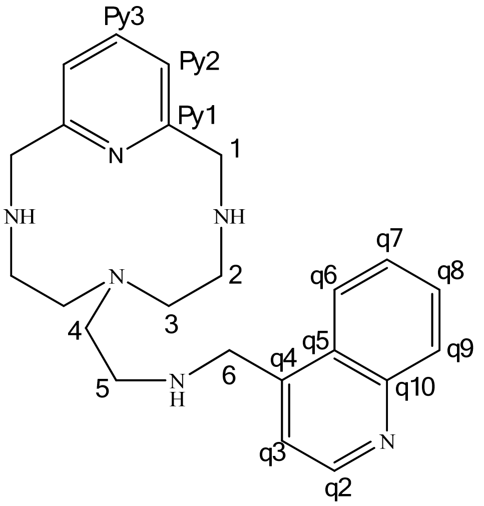
^{13}C NMR Spectra Aliphatic region



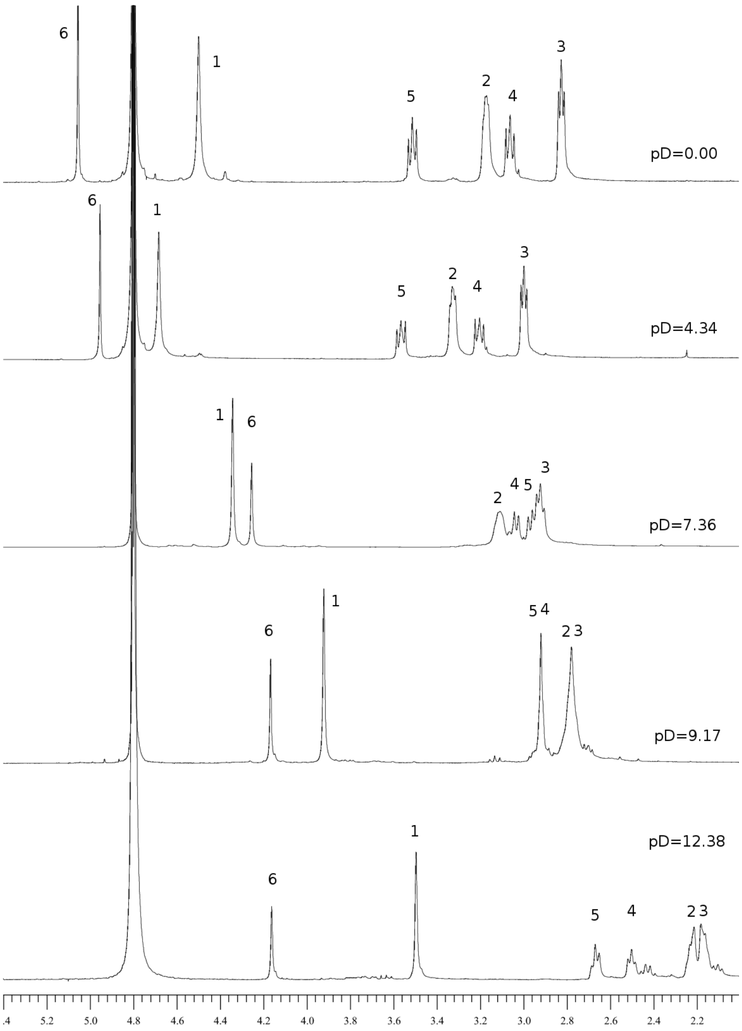
^{13}C NMR Spectra Aromatic region



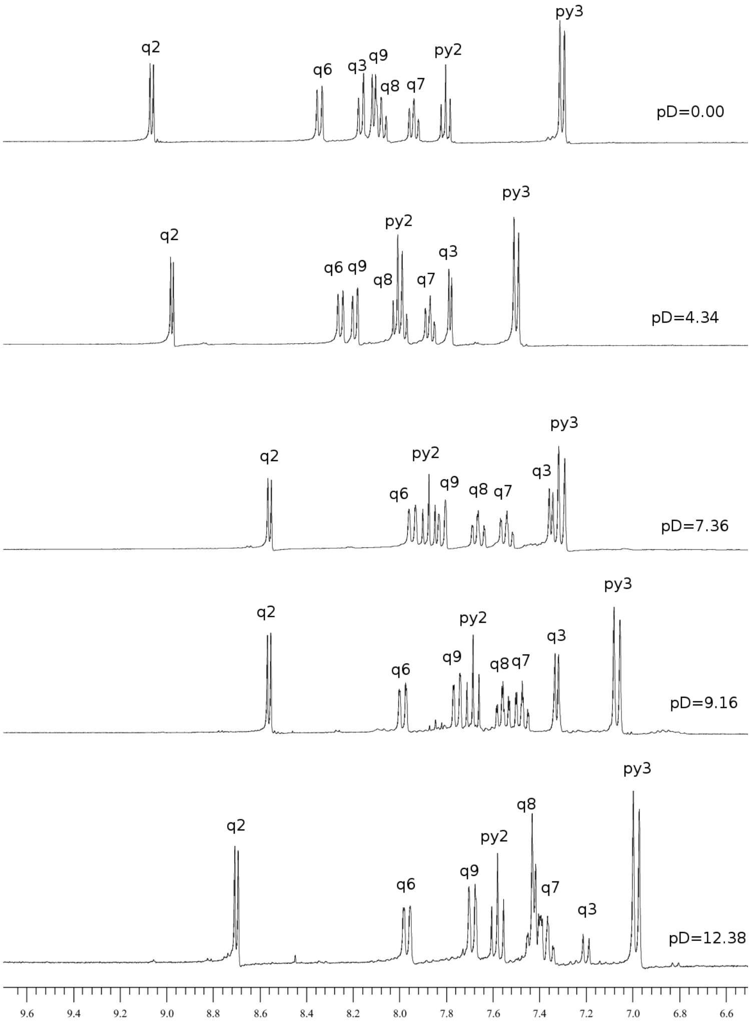
Protonation secuence of 3:



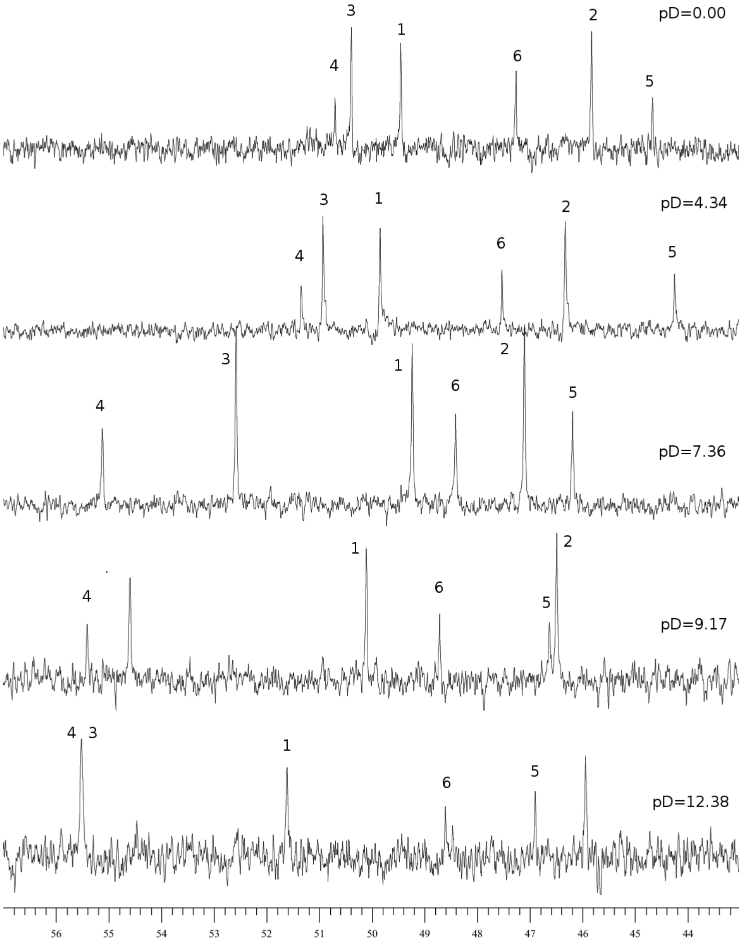
^{1}H NMR Spectra Aliphatic region



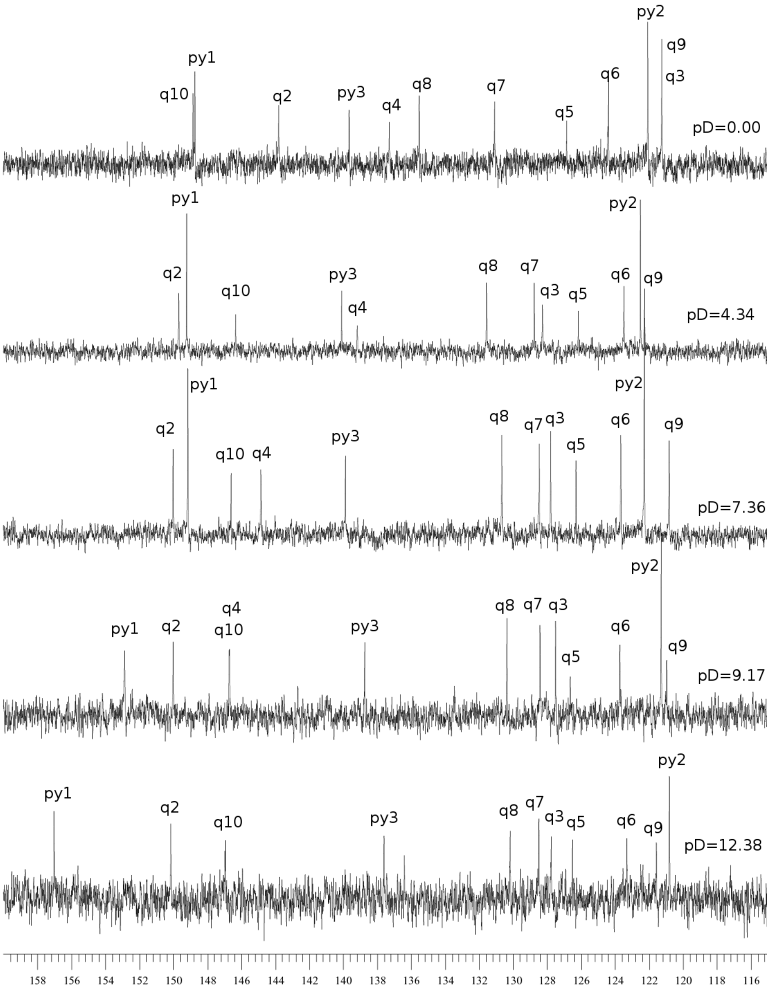
^{1} H NMR Spectra Aromatic region



^{13}C NMR Spectra Aliphatic region



^{13}C NMR Spectra Aromatic region



5.- Stabiliy constants.

Table S2.- Logarithms of stability constants of compounds 1, 2 and 3 with Mn(II). Determined in 0.15 mol.dm^{-3} $NaClO_4$ at 298.1 ± 0.1 K.

Reaction [a]	**PyTREN**	**PyTREN-2Q**	**PyTREN-4Q**
$Mn+L \leftrightarrows MnL$	11.43(5)[b]	11.08(1)	8.91(1)
$Mn+L+H \leftrightarrows HMnL$	17.32(6)	16.23(6)	
$Mn+L+H_2O \leftrightarrows MnL(OH)+H^+$	0.58(6)		-1.36(1)
$MnL+H \leftrightarrows HMnL$	5.88(2)	5.15(2)	
$MnL+OH \leftrightarrows MnL(OH)$	2.89(1)		3.45(1)

[a] Charges omitted for clarity. [b] Values in parentheses are standard deviations in the last significant figure.

6.- Molar fraction distribution for 1,2 and 3 with Mn(II)

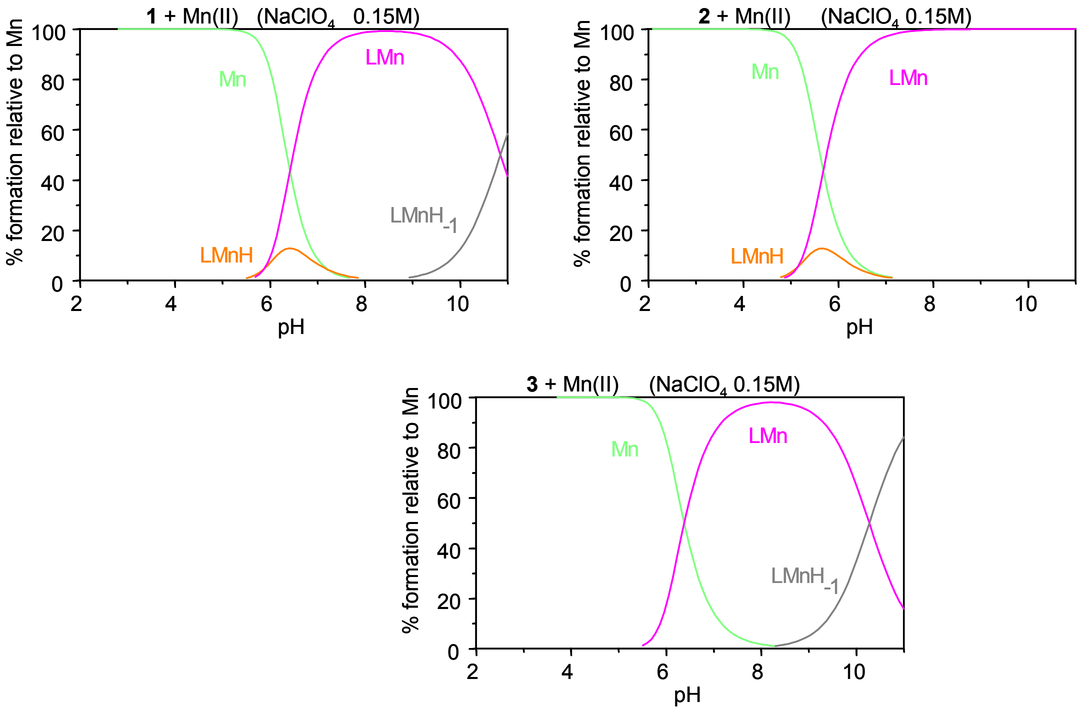


Figure S2.- Distribution diagrams for the systems Mn(II)-**1-3**

7.- Synthesis of 4 and 5.

Crystal preparation for X-ray diffraction

Slow evaporation of aqueous solutions containing either **2** or **3** along with $MgSO_4$ and $NaClO_4$ at pH value of c.a. 8 yielded crystals suitable for monocrystal X-ray diffraction.

X-ray diffraction experimental: One single crystal of **4** was measured in an Enraf-Nonius KappaCCD single-crystal diffractometer using MoKα radiation (λ=0.71073Å) at room temperature. 10151 reflections were collected. One single-crystal of **5** was measured in an Oxford Diffraction SuperNova single crystal diffractometer with MoKα radiation (λ=0.71073Å) . This crystal showed very low reflectivity; therefore it was measured at 120K. 5548 reflections were collected. In both cases the structure was solved with SHELXS-97 program and further refined with SHELXL-97[3] up to the final structure. Hydrogen atoms were placed in calculated positions. Final drawings of the structures were made with the Mercury program[4]

Anal. Calcd for $[C_{23}H_{30}N_6Mn](ClO_4)_2$ (**4**) C, 42.9, H, 4.7, N, 13.0 Found: C, 43.1, H, 5.0, N, 12.8.

Anal. Calcd for $[C_{23}H_{30}N_6Mn](ClO_4)_2(H_2O)$ (**5**) C, 41.7, H, 4.9, N, 12.7 Found: C, 42.0, H, 5.1, N, 12.5.

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[3] G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112-122.

[4] Mercury CSD 2.0 - New Features for the Visualization and Investigation of Crystal Structures C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Cryst.*, 2008, **41**, 466-470.

8.- Crystallographic data for crystals 4 and 5.

Table S3: Crystallographic data for crystals **4** and **5**.

	4	**5**
sum formula	$C_{23}H_{32}Cl_2MnN_6O_9$	$C_{23}H_{32}Cl_2MnN_6O_9$
size, mm	0.19 × 0.14 × 0.10	0.10 × 0.04 × 0.02
system	monoclinic	monoclinic
space group	$P\,2_1/c$	$P\,2_1$
a, Å	9.329(3)	8.7809(4)
b, Å	17.568(5)	15.2321(6)
c, Å	18.335(5)	10.2323(5)
β, deg.	105.680(16)	94.030(5)
V, $Å^3$	2893.1(15)	1365.2(1)
T, K.	293	120
Mr, g/mol	662.39	662.39
ρ, g/cm3	1.521	1.611
Z	4	2
μ, mm-1	0.701	0.743
F(000)	1372.0	686.0
R1(reflections)	0.1139(1365)	0.0746(2567)
wR2(reflections)	0.4127(4520)	0.1806(4042)
GooF	1.034	1.027
parameters	372	371

9.- Crystal 4.

Table S4a: Selected bond distances (Å) and angles (deg.) for crystal **4**

Mn(1)—N(1)	2.155(12)	N(1)—Mn(1)—N(5)	168.0(6)
Mn(1)—N(5)	2.220(17)	N(1)—Mn(1)—N(6)	114.9(4)
Mn(1)—N(6)	2.229(13)	N(5)—Mn(1)—N(6)	77.1(6)
Mn(1)—N(4)	2.303(12)	N(1)—Mn(1)—N(4)	74.5(5)
Mn(1)—N(3)	2.287(12)	N(5)—Mn(1)—N(4)	103.0(7)
Mn(1)—N(2)	2.335(12)	N(6)—Mn(1)—N(4)	111.7(5)
		N(1)—Mn(1)—N(3)	91.9(5)
		N(5)—Mn(1)—N(3)	76.1(6)
		N(6)—Mn(1)—N(3)	152.9(5)
		N(4)—Mn(1)—N(3)	78.0(5)
		N(1)—Mn(1)—N(2)	73.7(5)
		N(5)—Mn(1)—N(2)	103.1(7)
		N(6)—Mn(1)—N(2)	102.9(5)
		N(4)—Mn(1)—N(2)	140.3(5)
		N(3)—Mn(1)—N(2)	79.9(5)

Table S4b: Hydrogen-bond geometry for crystal **4** (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O(1)—H(1C)···O(23)[i]	0.92	2.23	2.91(3)	131.5
O(1)—H(1D)···O(12)[ii]	0.72	2.34	3.03(3)	160.5
N(2)—H(2)···O(11)[iii]	0.91	2.37	3.25(3)	161.8
N(4)—H(4)···O(21)	0.91	2.60	3.45(3)	157.8
N(5)—H(5)···O(13)[iii]	0.91	2.36	3.26(3)	168.9
Symmetry codes: (i) -*x*+*1*, *y*+*1/2*, -*z*+1/2; (ii) −*x*, *y*+1/2, −*z*+1/2; (iii) *x*, -*y*+*1/2*, *z*-*1/2*				

10.- Crystal 5.

Table S5a: Selected bond distances (Å) and angles (deg.) for crystal **5**

Mn(1)—O(1)	2.081(7)	O(1)—Mn(1)—N(1)	93.6(3)
Mn(1)—N(1)	2.220(8)	O(1)—Mn(1)—N(3)	169.7(3)
Mn(1)—N(3)	2.267(9)	N(1)—Mn(1)—N(3)	96.1(3)
Mn(1)—N(5)	2.285(8)	O(1)—Mn(1)—N(5)	90.9(3)
Mn(1)—N(4)	2.341(8)	N(1)—Mn(1)—N(5)	174.8(3)
Mn(1)—N(2)	2.319(8)	N(3)—Mn(1)—N(5)	79.6(3)
		O(1)—Mn(1)—N(4)	102.3(3)
		N(1)—Mn(1)—N(4)	72.5(3)
		N(3)—Mn(1)—N(4)	77.3(3)
		N(5)—Mn(1)—N(4)	109.2(3)
		O(1)—Mn(1)—N(2)	109.2(4)
		N(1)—Mn(1)—N(2)	73.0(3)
		N(3)—Mn(1)—N(2)	77.2(4)
		N(5)—Mn(1)—N(2)	103.0(3)
		N(4)—Mn(1)—N(2)	134.1(3)

Table S5b: Hydrogen-bond geometry for crystal **5** (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O(1)—H(1C)···O(24)^{i}	0.85	2.34	3.081(16)	148.2
O(1)—H(1D)···N(6)^{ii}	0.93	2.34	2.772(11)	112.4
N(2)—H(2)···O(13)^{i}	0.93	2.23	3.059(13)	148.1
N(4)—H(4)···O(11)^{iii}	0.93	2.57	3.390(17)	148.1
N(4)—H(4)···O(13)^{iii}	0.93	2.43	3.214(17)	142.5
N(5)—H(5)···O(14)^{iii}	0.93	2.40	3.221(11)	146.5
Symmetry codes: (i) -*x*+*1*, *y*-*1/2*, -*z*+1; (ii) *x*, *y*, *z*-1; (iii) -*x*, *y*-*1/2*, -*z*+*1*				

11.- Electrochemistry studies.

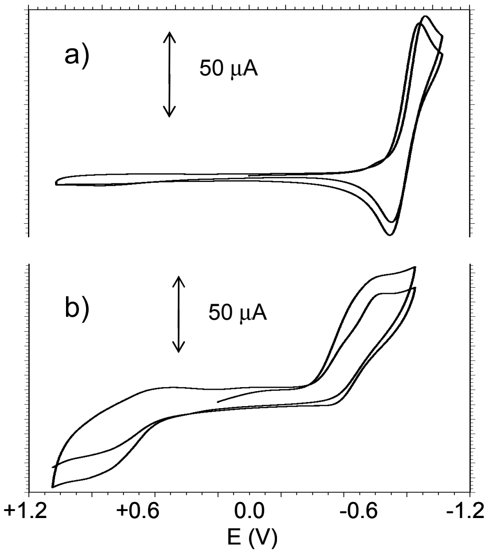

Figure S3.Cyclic voltammograms for a) unmodified and, b) **4**-modified glassy carbon electrodes immersed into O_2-saturated 0.10 M Et_4NClO_4/MeCN. Potential scan rate 50 mV/s.

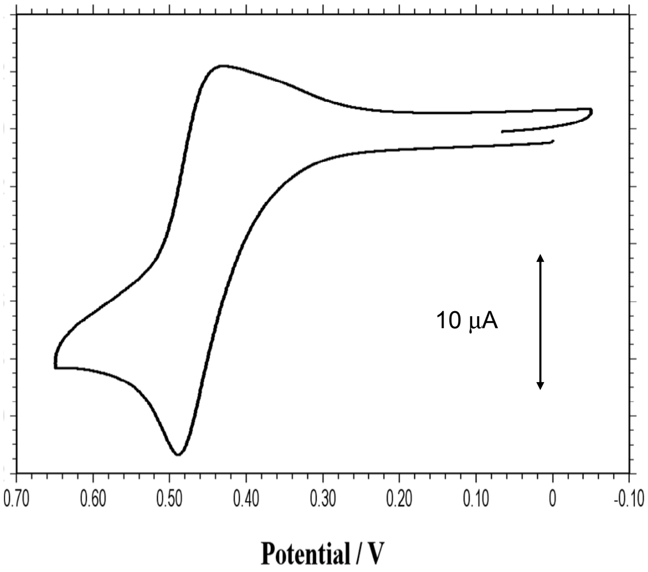

Figure S4. Cyclic voltammogram for a 1.0 mM solution of Mn-**2** in 0.15 M NaClO4 at pH 7.4. Potential scan rate 20 mV/s.