Electronic Supporting Information

A Mn(IV)-peroxo complex in the reactions with proton donors

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Table S1. X-ray crystallographic data of **2a**, **2b**, **3**, **4b**, **5** and **6**.

	2a·OC_4H_8	**2b**·C_6H_{14}	**3**	**4b**	**5**·$O(CH_2CH_3)_2$	**6**·OC_4H_8
Empirical formula	$C_{49}H_{59}MnO_2P_2S_3Si_3$	$C_{51}H_{64}MnOP_2S_3Si_3$	$C_{69}H_{71}MnNP_3S_4Si_3$	$C_{69}H_{71}MnNOP_3S_3Si_3$	$C_{68}H_{79}MnNO_2P_3S_3Si_3$	$C_{67}H_{74}ClMnNOP_3S_3Si_3$
Formula weight	977.29	990.35	1274.62	1258.57	1270.62	1273.02
T, K	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Orthorhombic
Space group	P2(1)/n	P2(1)/c	P2(1)/c	P2(1)/c	*P*-1	Pbca
a, Å	12.7101(5)	10.9507(4)	14.0964(2)	14.0431(7)	15.0558(6)	27.5405(4)
b, Å	26.1516(12)	19.2495(8)	27.5253(4)	27.6116(14)	15.3325(6)	17.3814(2)
c, Å	15.7091(7)	25.3023(11)	17.3067(2)	17.2199(9)	16.6334(6)	27.9799(3)
α, °	90	90	90	90	76.5443(8)	90
β, °	92.9222(11)	100.6307(11)	99.8295(6)	99.8492(12)	76.9538(9)	90
γ, °	90	90	90	90	65.6410(7)	90
V, $Å^3$	5214.7(4)	5242.1(4)	6616.55(15)	6578.6(6)	3365.2(2)	13393.8(3)
Z	4	4	4	4	2	8
ρ_{calcd}, Mg m^{-3}	1.245	1.255	1.280	1.271	1.254	1.263
μ, mm^{-1}	0.539	0.536	0.494	0.466	0.457	0.497
F (000)	2056	2092	2672	2640	1340	5344
Reflections collected	33242	40144	32273	42853	44024	40401
Independent reflections	11969	12045	11652	15105	15447	11785
R_{int}	0.0534	0.0643	0.0368	0.0493	0.0385	0.0591
Goodness-of-fit on F^2	1.152	1.049	1.115	1.025	1.042	1.029
R [$I > 2\sigma(I)$]	0.0639	0.0543	0.0531	0.0470	0.0492	0.0420
wR [$I > 2\sigma(I)$]	0.1312	0.1145	0.1581	0.1038	0.1155	0.0944

Table S2. Mulliken spin densities of intermediate **A**

	Mn	O1	O2H	^{TMS}PS3
^{2}[Mn^{IV}(OOH)(^{TMS}PS3)]	0.77	0.18	0.04	0.01
^{4}[Mn^{IV}(OOH)(^{TMS}PS3)]	2.83	0.07	0.01	0.09
^{6}[Mn^{IV}(OOH)(^{TMS}PS3)]	3.70	0.10	0.06	1.13

Table S3. Key geometric parameters, selective distances (Å) and angle (^{o}), of intermediate **A**

	Mn-O1	Mn-O2	Mn-S_{avg}	Mn-P	O1-O2	$\theta_{(Mn\text{-}O1\text{-}O2)}$
$^{2}[Mn^{IV}(OOH)(^{TMS}PS3)]$	1.808	2.803	2.163	2.245	1.427	117.05
$^{4}[Mn^{IV}(OOH)(^{TMS}PS3)]$	1.881	2.140	2.287	2.299	1.460	78.53
$^{6}[Mn^{IV}(OOH)(^{TMS}PS3)]$	1.856	2.636	2.374	2.333	1.456	104.78

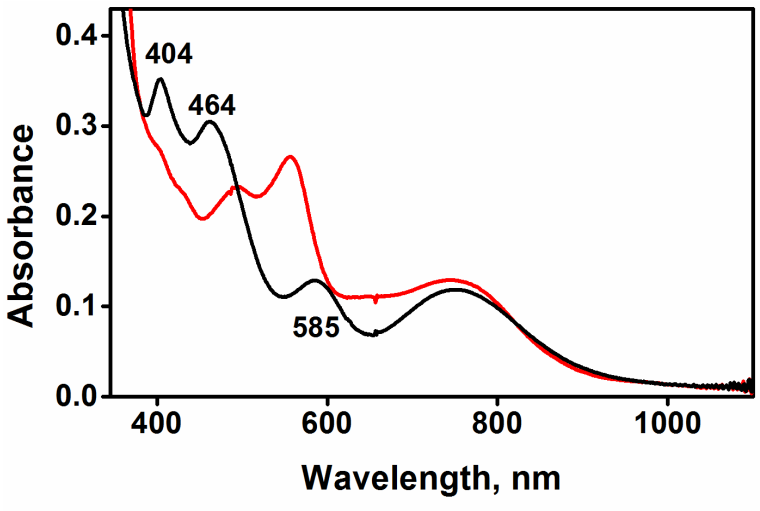

Fig. S1 UV-vis spectral changes for the formation of a putative intermediate $Mn^{III}(NCCH_3)(^{TMS}PS3)$ (black line) observed upon addition of $HClO_4$ (1 equiv.) to an acetonitrile solution of **1** (0.10 mM; red line) at −40 ^{o}C.

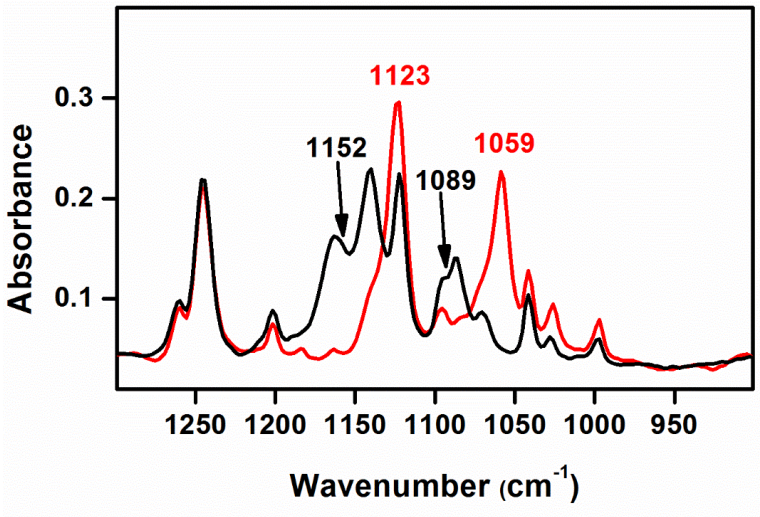

Fig. S2 FTIR spectra of ^{16}O-labeled **2a** (black line) and ^{18}O-labeled **2a** (red line). The peaks at 1152 cm^{-1} (averaged position of two peaks, 1163 and 1140) and 1089 cm^{-1} (averaged position of two peaks, 1093 and 1087) were shifted to the peaks at 1123 and 1059 cm^{-1} when ^{18}O-labeled **1** was used, respectively.

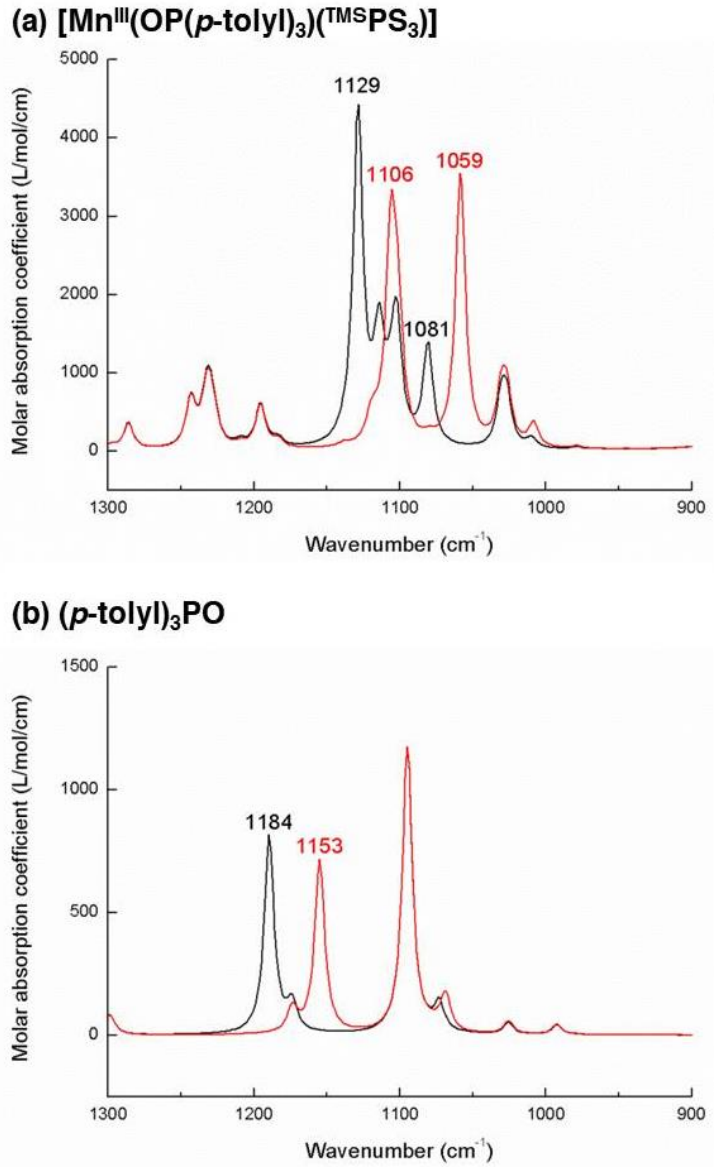

Fig. S3 DFT-calculated IR spectra of (a) $Mn^{III}(OP(p\text{-tolyl})_3)(^{TMS}PS3)$ (**2b**) and (b) pure tri-*p*-tolyl-phosphine oxide, [(*p*-tolyl)$_3$PO], with ^{16}O (black line) and ^{18}O (red line) isotopic incorporation.

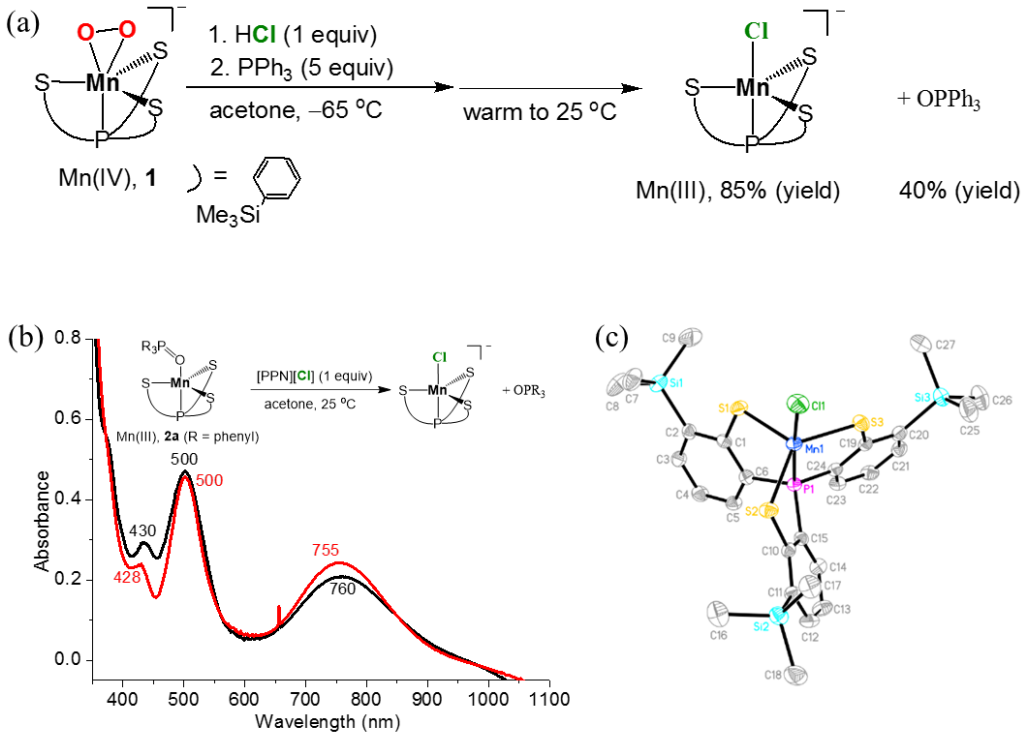

Fig. S4 (a) Schematic diagram showing the reaction of **1** with HCl (1 equiv.) in the presence of PPh_3 (5 equiv.) in acetone at –65 °C to produce **6** and $OPPh_3$. The isolation of $OPPh_3$ instead of the formation of **2a**, which is phosphine oxide bound Mn(III) complex, may be attributed to ligand displacement by chloride (Cl^-). (b) UV-vis spectral changes observed in the reaction of **2a** (black line) with [PPN][Cl] (1 equiv.) in acetone at 25 °C. Inset shows schematic diagram of the reaction of **2a** (black line) with [PPN][Cl] (1 equiv.) to form **6** and $OPPh_3$. (c) ORTEP diagram of $[Mn^{III}(^{TMS}PS3)(Cl)]^-$ moiety in **6** showing 50% probability ellipsoids (see Table S1 for X-ray Crystallographic Data). Hydrogen atoms and solvents in the crystal structures are omitted for clarity.

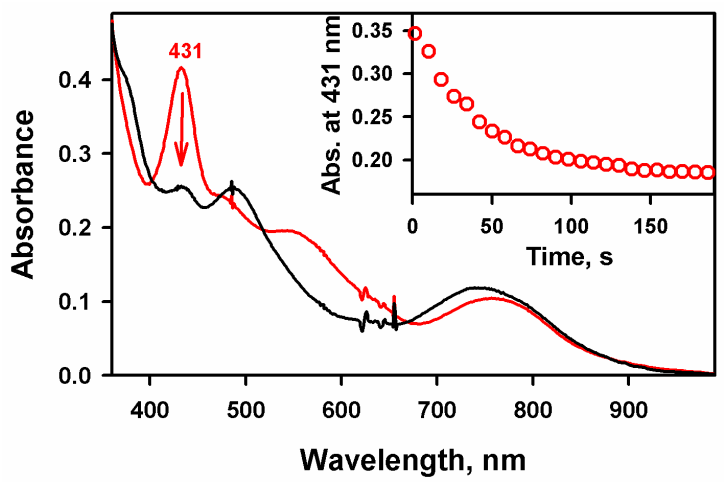

Fig. S5 UV-vis spectral changes observed in the reaction of intermediate **A** (0.10 mM, red line) with PPh_3 (5 mM, black line) in acetone at −65 °C. The inset shows the time trace monitored at 431 nm due to intermediate **A**.

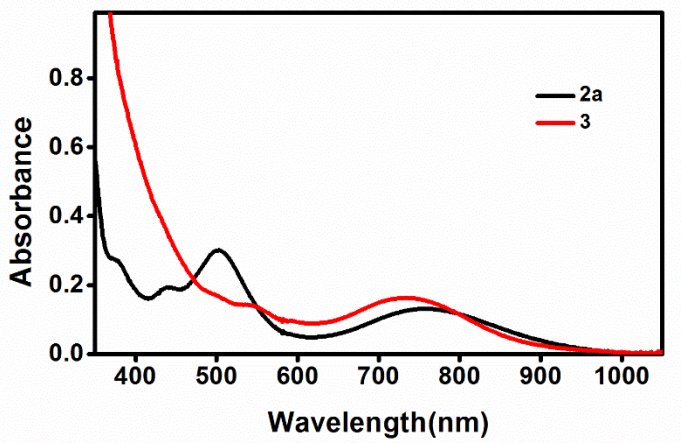

Fig. S6 UV-vis spectral changes for the formation of complex **3** (red line) observed in the reaction of **2a** (black line) with [PPN][PhS] (1 equiv.) in acetone at 25 ^{o}C.

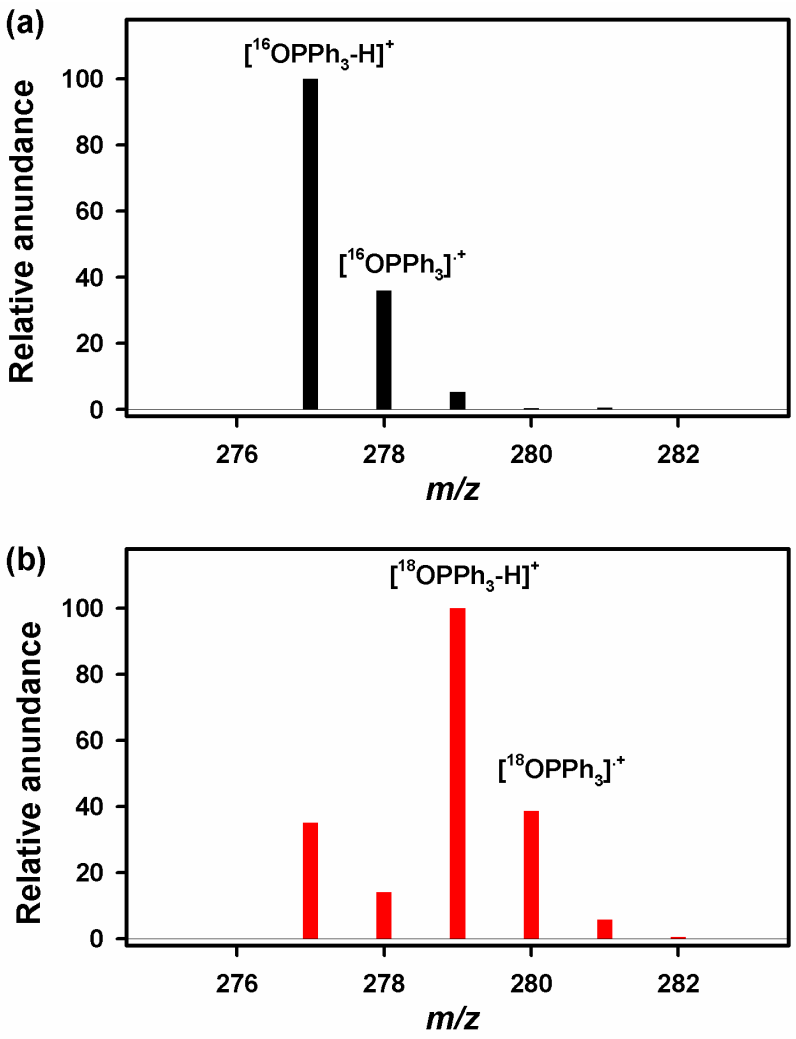

Fig. S7 GC-mass spectra of O=PPh$_3$ produced in the reaction (a) ^{16}O-labeled and (b) ^{18}O-labeled **1** with PhSH (3 equiv.) in the presence of PPh$_3$ in acetone at 25 ^{o}C. The ratio of isotopic incorporation (^{16}O/^{18}O) is about 30:70.

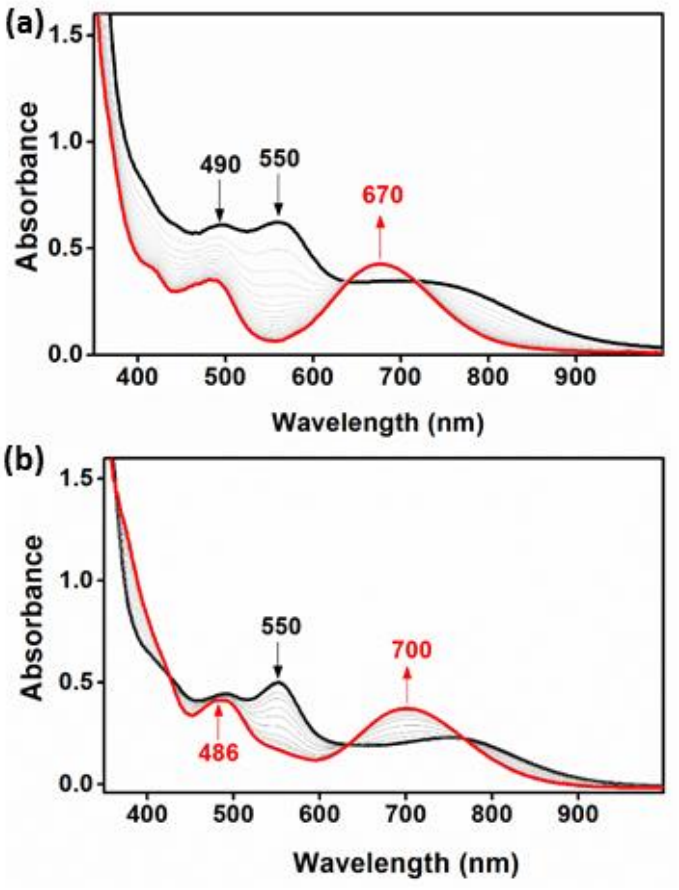

Fig. S8 (a) UV-vis spectral changes for the formation of **5** observed upon addition of MeOH (240 mM) to an acetone solution of **1** (0.24 mM) at 25 ^{o}C. The time interval for each measurement is 6 min. (b) UV-vis spectral changes for the formation of **4b** observed upon addition of PhOH (40 mM) to an acetone solution of **1** (0.18 mM) at 25 ^{o}C. The time interval for each measurement is 10 min.

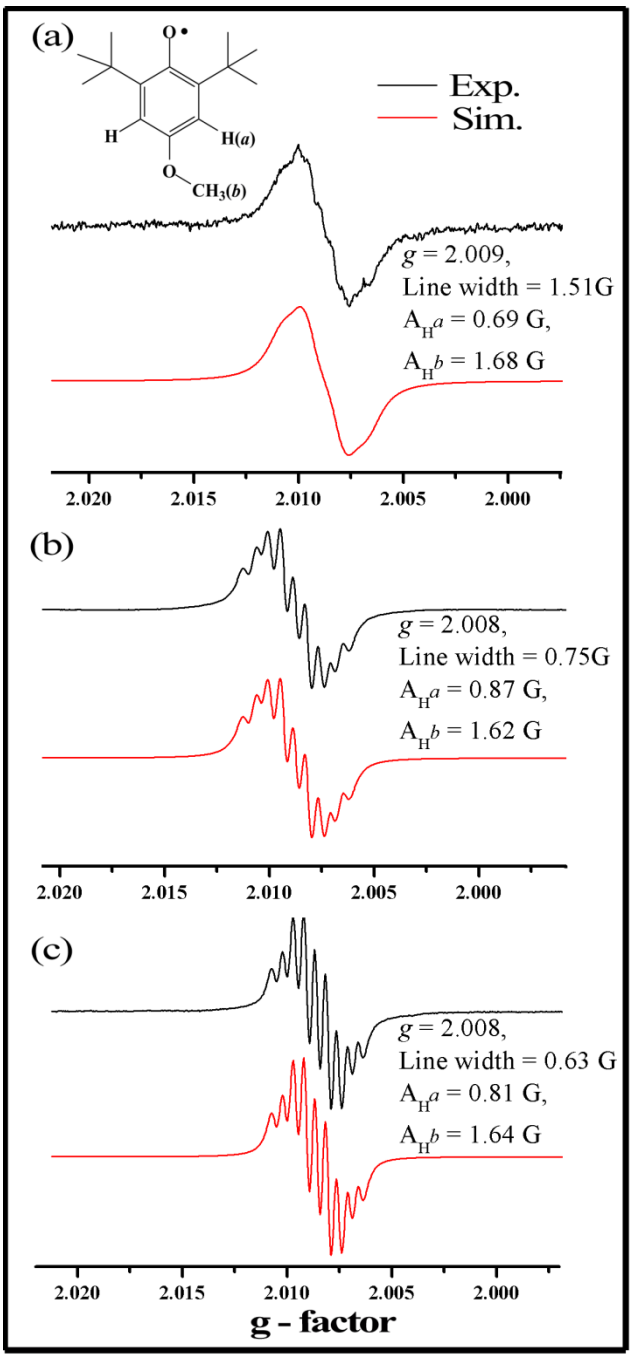

Fig. S9 The X-band spectra of 2,6-di-*tert*-butyl-4-methoxyphenoxyl radical recorded in (a) acetone (b) toluene and (c) methylene chloride (black lines) at 213 K and their simulation spectra (red lines). 2,6-di-*tert*-butyl-4-methoxyphenoxyl radical was generated by reacting **1** (0.12 mM) with 2,6-di-*tert*-butyl-4-methoxyphenol (*p*-OMe-2,6-DTBP; 30 mM) at 25 ºC. The best-fit EPR parameters are given above the simulated spectra [see references; (*a*) M. Lucarini, V. Mugnaini, G. F. Pedulli and M. Guerra, *J. Am. Chem. Soc.*, 2003, **125**, 8318-8329; (*b*) R. Amorati and G. F. Pedulli, *Org. Biomol. Chem.*, 2012, **10**, 814-818.] Experimental conditions: microwave frequency = 9.87 GHz, field modulation amplitude = 100 kHz, microwave power = 2.0 mW, modulation amplitude = 0.30 G, time constant = 40.96 ms.

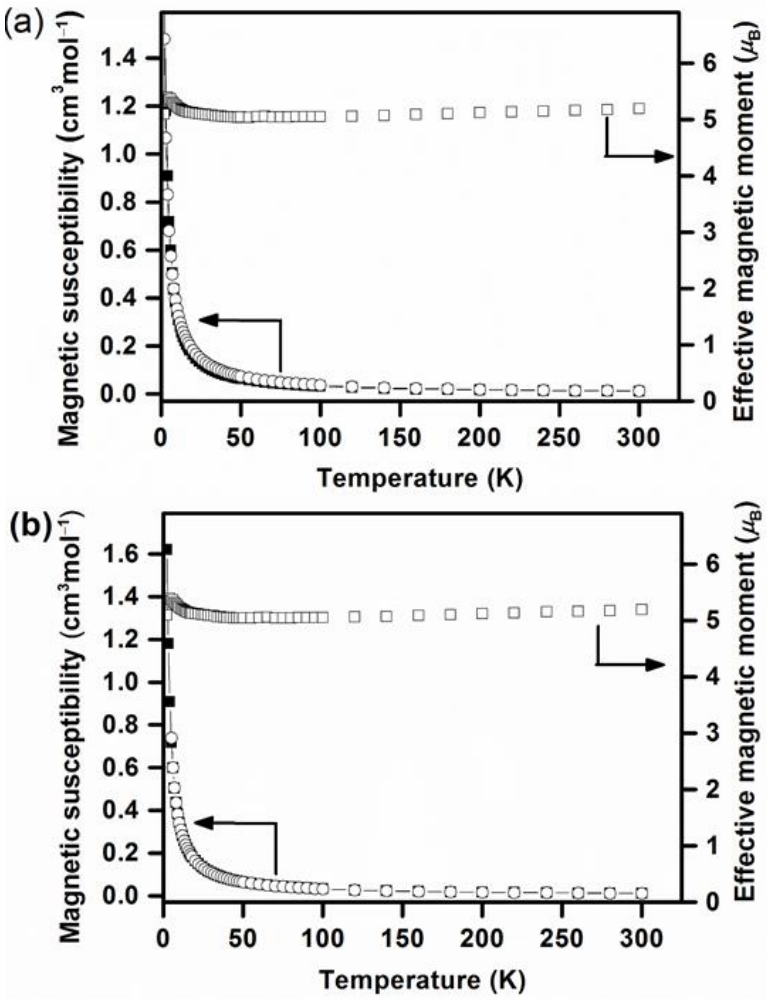

Fig. S10 Plots of magnetic susceptibility (open circles) and effective magnetic moment (open squares) *versus* temperature for the complexes (a) **3** and (b) **5**. The solid line is the best fit of the experimental data to the theoretical model described in the text.

Cartesian Coordinates

$^{2}[Mn^{IV}(OOH)(^{TMS}PS3)]$

25	1.710907000	5.081944000	10.813167000	6	-1.225408000	7.283173000	13.757989000
16	3.339633000	4.496558000	12.116837000	1	-0.740152000	8.164400000	14.174803000
16	-0.285604000	4.327132000	11.146271000	6	-5.229026000	3.538988000	12.675317000
16	1.941951000	6.799061000	9.519318000	1	-5.795697000	2.683332000	12.283133000
15	1.222301000	6.579969000	12.412074000	1	-5.792735000	4.445919000	12.421068000
14	5.521986000	3.641254000	14.576138000	1	-5.208226000	3.442514000	13.768581000
14	-3.497037000	3.528678000	11.917718000	6	-3.673611000	3.680184000	10.045508000
14	2.423063000	9.760563000	7.914469000	1	-2.702390000	3.646890000	9.539053000
6	2.246702000	6.283683000	13.893117000	1	-4.166465000	4.622306000	9.772303000
6	3.242013000	5.304466000	13.700350000	1	-4.288268000	2.855183000	9.659484000
6	4.139351000	4.953412000	14.737933000	6	-2.656153000	1.909002000	12.394492000
6	3.972945000	5.620596000	15.964887000	1	-3.249189000	1.058421000	12.030999000
1	4.638162000	5.378155000	16.792889000	1	-2.570368000	1.817096000	13.485083000
6	2.978343000	6.578974000	16.172548000	1	-1.649788000	1.827141000	11.967941000
1	2.877547000	7.061597000	17.143596000	6	1.520056000	8.275547000	11.806321000
6	2.111604000	6.911928000	15.133050000	6	1.815282000	8.330344000	10.429563000
1	1.326524000	7.647590000	15.299385000	6	2.034608000	9.569029000	9.777460000
6	6.764626000	4.143949000	13.248394000	6	1.964391000	10.723455000	10.577897000
1	7.582740000	3.411659000	13.206906000	1	2.131705000	11.696744000	10.117952000
1	7.203138000	5.125248000	13.471637000	6	1.699197000	10.676374000	11.948533000
1	6.305483000	4.196781000	12.254748000	1	1.670206000	11.595202000	12.532510000
6	6.436082000	3.550180000	16.228515000	6	1.474206000	9.447180000	12.565399000
1	5.781517000	3.245012000	17.055240000	1	1.278224000	9.408490000	13.635836000
1	6.907043000	4.504240000	16.498657000	6	4.058595000	8.925263000	7.482980000
1	7.236718000	2.801575000	16.153080000	1	4.292852000	9.082470000	6.420992000
6	4.787725000	1.941716000	14.214641000	1	4.027089000	7.845558000	7.668371000
1	4.256228000	1.917837000	13.256481000	1	4.882058000	9.346637000	8.074256000
1	4.081084000	1.644490000	15.000457000	6	2.590119000	11.607337000	7.541711000
1	5.587037000	1.188492000	14.179496000	1	3.415018000	12.074851000	8.095050000
6	-0.531708000	6.430003000	12.897176000	1	1.670157000	12.163704000	7.763843000
6	-1.182983000	5.320380000	12.322054000	1	2.799975000	11.738748000	6.471310000
6	-2.532262000	5.019639000	12.629712000	6	1.009950000	9.080259000	6.866118000
6	-3.184206000	5.894176000	13.517744000	1	1.220151000	9.244761000	5.800272000
1	-4.223585000	5.702743000	13.782254000	1	0.065769000	9.587237000	7.104260000
6	-2.557250000	7.014074000	14.068795000	1	0.865344000	8.005224000	7.021968000
1	-3.107414000	7.676247000	14.735792000	8	2.151264000	4.012804000	9.422702000
				8	2.093771000	2.559757000	9.651112000

1	2.382949000	2.254519000	8.770890000

^{4}[Mn^{IV}(OOH)(^{TMS}PS3)]

25	1.595204000	4.682504000	10.928088000
16	3.655286000	4.885213000	11.983201000
16	-0.617198000	4.181837000	11.140176000
16	1.596060000	6.446217000	9.514487000
15	1.102659000	6.223648000	12.561180000
14	6.005745000	4.194560000	14.384577000
14	-3.943672000	3.853678000	11.686931000
14	2.387544000	9.365423000	8.003326000
6	2.104588000	5.861903000	14.027129000
6	3.336581000	5.252039000	13.698185000
6	4.286531000	4.964234000	14.705890000
6	3.916312000	5.272543000	16.029459000
1	4.616103000	5.052910000	16.835036000
6	2.681355000	5.832170000	16.362611000
1	2.432158000	6.030361000	17.403833000
6	1.767638000	6.134556000	15.353625000
1	0.797162000	6.563145000	15.598782000
6	7.038454000	5.328077000	13.286674000
1	8.037688000	4.897408000	13.134276000
1	7.165272000	6.314268000	13.751961000
1	6.578402000	5.475693000	12.302885000
6	6.888335000	4.010255000	16.045938000
1	6.349996000	3.346312000	16.734783000
1	7.041317000	4.974053000	16.548532000
1	7.880131000	3.569059000	15.876535000
6	5.848832000	2.474834000	13.620216000
1	5.420326000	2.516252000	12.612566000
1	5.215295000	1.823484000	14.236112000
1	6.840203000	2.006864000	13.546615000
6	-0.663887000	6.258723000	12.954126000
6	-1.417499000	5.269320000	12.284456000
6	-2.814487000	5.155951000	12.515254000
6	-3.385711000	6.075848000	13.411016000
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1	-6.112097000	5.072217000	12.121868000
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6	-3.996697000	4.106333000	9.818832000
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6	1.607816000	7.834176000	11.900527000
6	1.779140000	7.902281000	10.499173000
6	2.105631000	9.138423000	9.880648000
6	2.253670000	10.252895000	10.723164000
1	2.505574000	11.215581000	10.279762000
6	2.114469000	10.181496000	12.112385000
1	2.263821000	11.068091000	12.726438000
6	1.791339000	8.964047000	12.703279000
1	1.698150000	8.886820000	13.786329000
6	3.876154000	8.356565000	7.433598000
1	4.051709000	8.517710000	6.360997000
1	3.731382000	7.282918000	7.598244000
1	4.782366000	8.662136000	7.972633000
6	2.756012000	11.192685000	7.683657000
1	3.663212000	11.535685000	8.197910000
1	1.925332000	11.845188000	7.982772000
1	2.916545000	11.341350000	6.606963000
6	0.836341000	8.909441000	7.030265000
1	1.001422000	9.088517000	5.958811000
1	-0.017387000	9.523302000	7.345887000
1	0.560757000	7.856727000	7.159392000
8	2.183561000	3.533976000	9.558937000
8	2.006910000	2.598931000	10.666312000
1	2.917721000	2.555168000	11.039591000

^{6}[Mn^{IV}(OOH)(^{TMS}PS3)]

25	1.738536000	4.857810000	10.638574000
16	3.686117000	4.717599000	11.976116000
16	-0.324424000	3.956288000	11.426579000
16	1.437465000	6.823288000	9.348508000
15	1.222856000	6.399016000	12.311984000
14	5.743393000	3.896818000	14.562951000
14	-3.635524000	3.529690000	12.024550000
14	2.252036000	9.806277000	7.936833000
6	2.075084000	5.935953000	13.836587000
6	3.264594000	5.192565000	13.620782000
6	4.091231000	4.844375000	14.724100000
6	3.641537000	5.219911000	16.000005000
1	4.244173000	4.957310000	16.869077000
6	2.440770000	5.906796000	16.214457000
1	2.129364000	6.162487000	17.226093000
6	1.651840000	6.269036000	15.125701000
1	0.714148000	6.803662000	15.273920000
6	6.966542000	4.880344000	13.516817000
1	7.923741000	4.344865000	13.451953000
1	7.161914000	5.863142000	13.965384000
1	6.594189000	5.039922000	12.498708000
6	6.477270000	3.701499000	16.294846000
1	5.834278000	3.110079000	16.959580000
1	6.674260000	4.667366000	16.777999000
1	7.437686000	3.173769000	16.216759000
6	5.465503000	2.170044000	13.853787000
1	5.063451000	2.210469000	12.835310000
1	4.763406000	1.598298000	14.474406000
1	6.415526000	1.618809000	13.825485000
6	-0.561731000	6.429452000	12.596344000
6	-1.230949000	5.235227000	12.217275000
6	-2.627116000	5.096250000	12.460857000
6	-3.285246000	6.194785000	13.033521000
1	-4.355603000	6.126720000	13.225323000
6	-2.631936000	7.390050000	13.358659000
1	-3.190975000	8.219071000	13.790082000
6	-1.262161000	7.510041000	13.136827000
1	-0.740748000	8.435156000	13.380335000
6	-5.424572000	3.824751000	12.563507000
1	-6.016697000	2.928016000	12.334630000
1	-5.891014000	4.665404000	12.033489000
1	-5.514398000	4.007024000	13.642401000
6	-3.629070000	3.224143000	10.164011000
1	-2.623594000	3.001454000	9.789807000
1	-4.007303000	4.099806000	9.620610000
1	-4.279865000	2.372426000	9.922228000
6	-2.982342000	2.036470000	12.974103000
1	-3.604319000	1.156480000	12.759477000
1	-3.015588000	2.214317000	14.056941000
1	-1.948744000	1.798718000	12.699299000
6	1.780658000	8.035392000	11.785913000
6	1.822390000	8.198889000	10.375830000
6	2.175947000	9.457699000	9.816241000
6	2.513437000	10.479875000	10.716554000
1	2.802647000	11.453846000	10.322984000
6	2.514398000	10.303749000	12.105783000
1	2.796251000	11.126594000	12.761026000
6	2.148255000	9.073270000	12.645270000
1	2.150618000	8.917517000	13.723569000
6	3.548169000	8.716996000	7.106857000
1	3.627241000	8.974755000	6.041642000
1	3.297608000	7.652855000	7.182071000
1	4.535956000	8.865595000	7.562253000
6	2.766593000	11.611757000	7.705891000
1	3.759441000	11.822787000	8.124165000
1	2.050062000	12.312907000	8.153314000
1	2.812735000	11.835551000	6.631210000
6	0.552358000	9.580661000	7.150466000
1	0.596396000	9.847641000	6.085492000
1	-0.190666000	10.232148000	7.628713000
1	0.198809000	8.546597000	7.228809000
8	2.276146000	3.731594000	9.264363000
8	1.975318000	2.389898000	9.744285000
1	2.848104000	2.118222000	10.088308000