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Supporting Information

The catalytic activities and magnetic behaviours of a μ_3-chlorido and a $\mu_{1,1,1}$-azido bridged rare defective dicubane tetranuclear Mn(II) complexes

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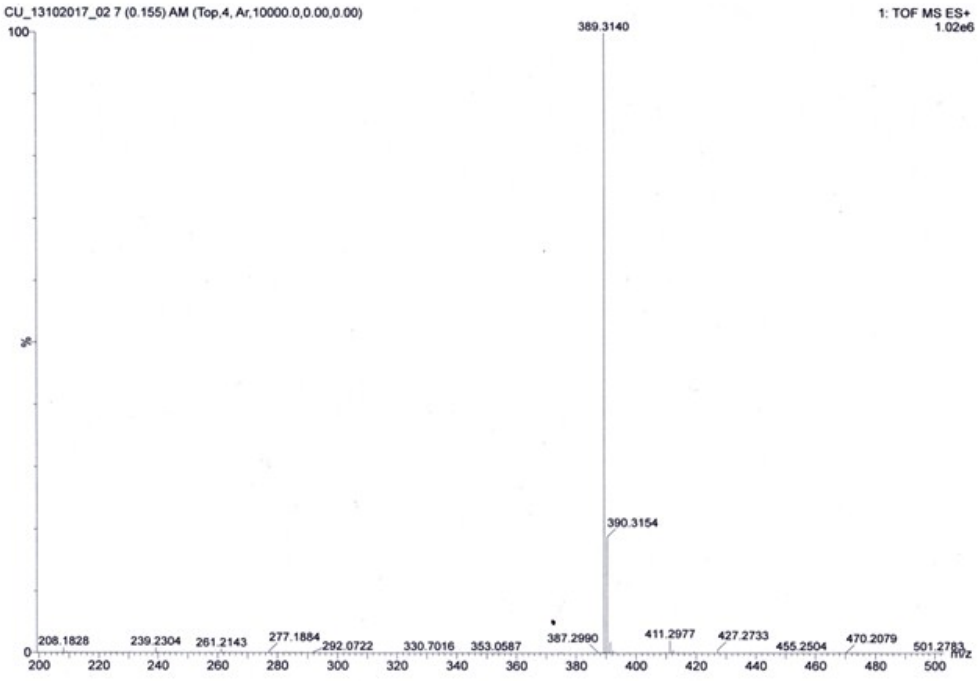

Fig. S1. Mass spectrum of ligand H_2L in CH_3OH solvent.

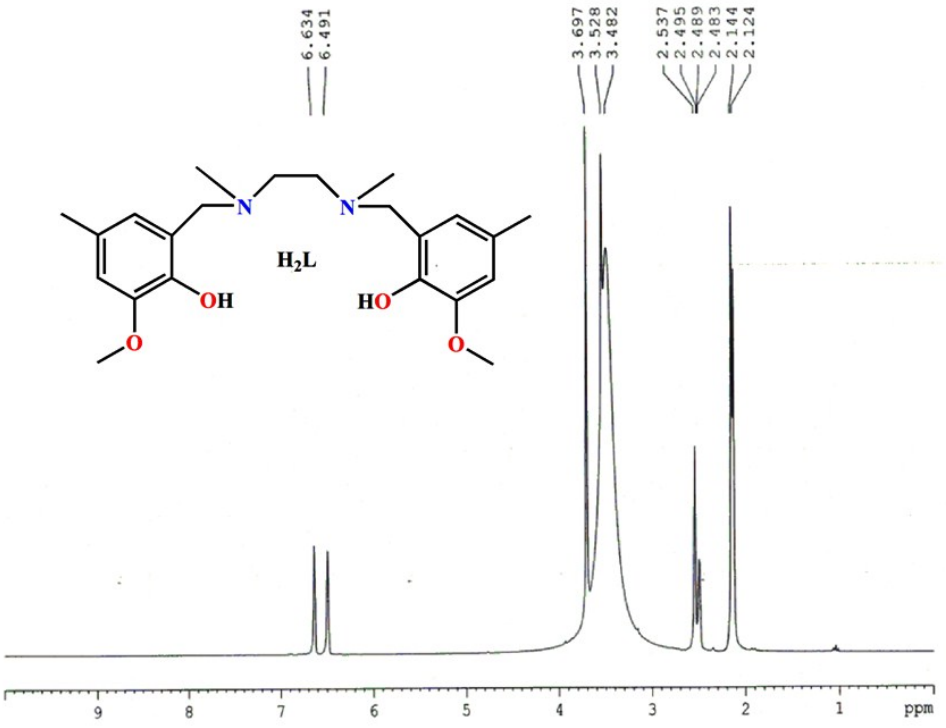

Fig. S2. ^{1}H NMR spectrum of ligand H_2L in DMSO-d_6

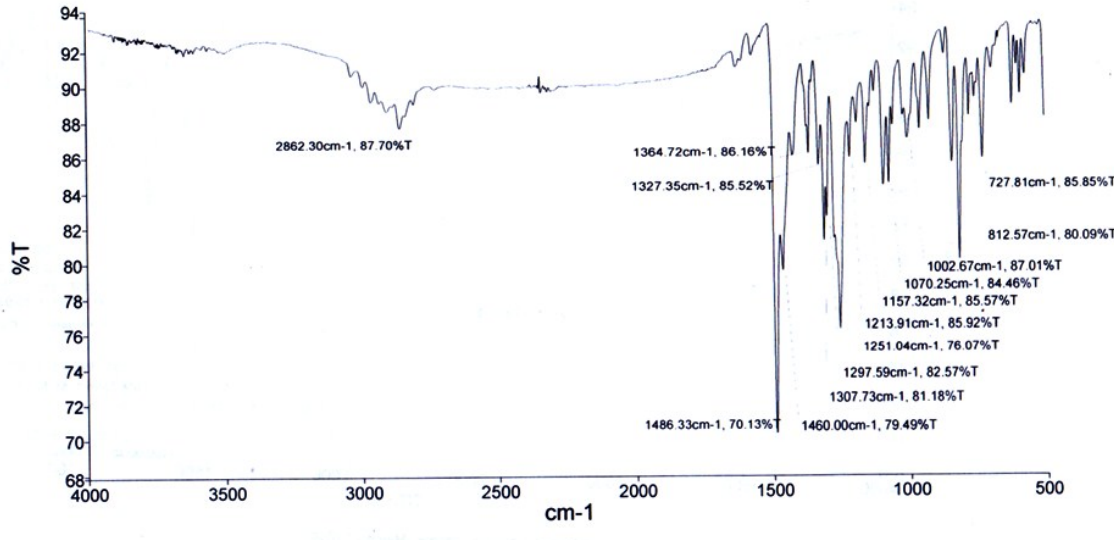

Fig. S3. Representative IR spectrum of complex **1.**

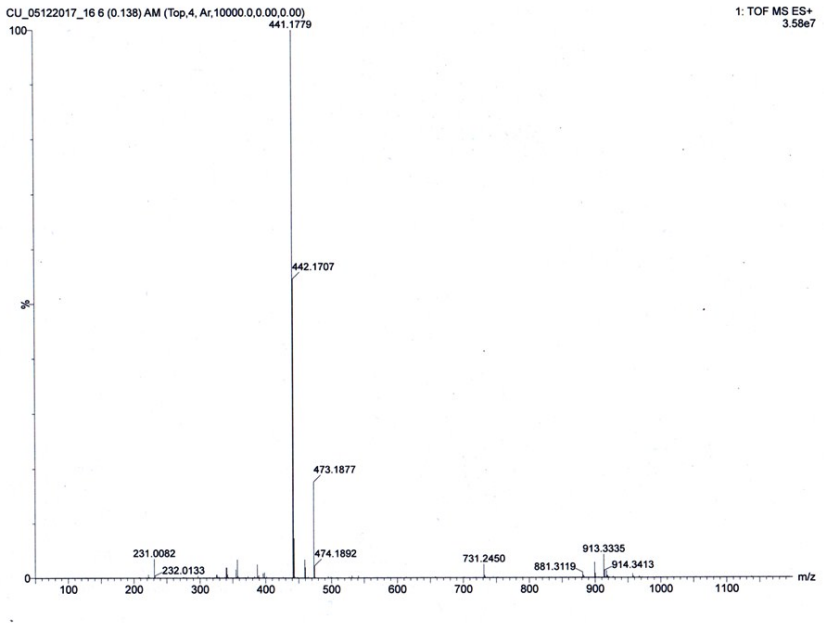

Fig. S4. Representative ESI mass spectrum of complex **1.**

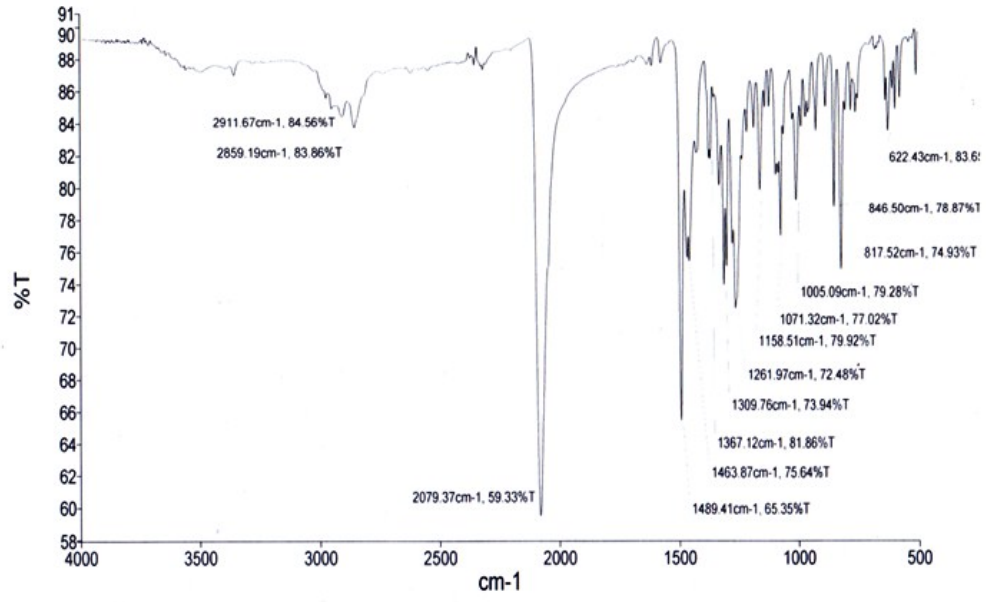

Fig. S5. Representative IR spectrum of complex **2.**

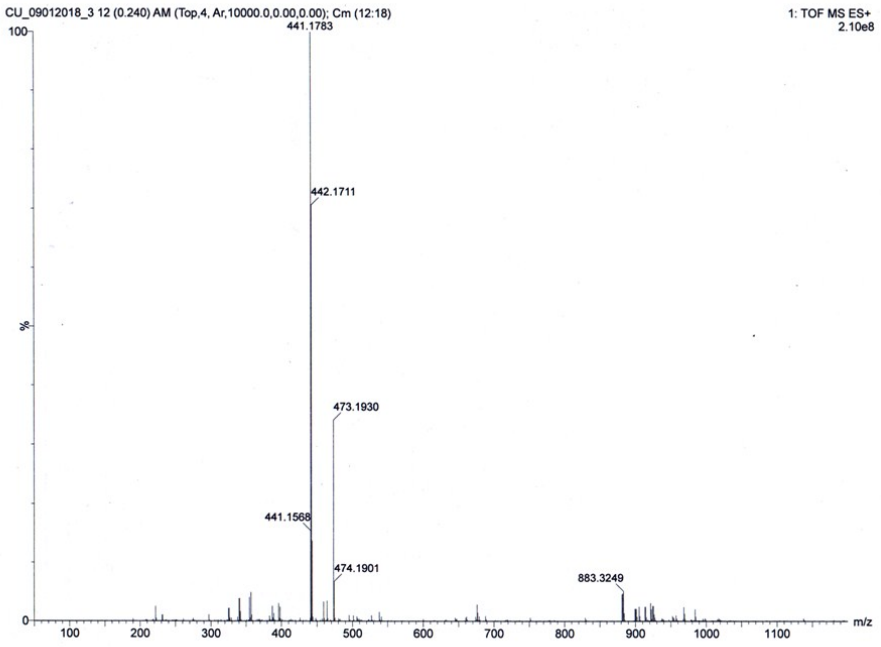

Fig. S6. Representative ESI mass spectrum of complex **2.**

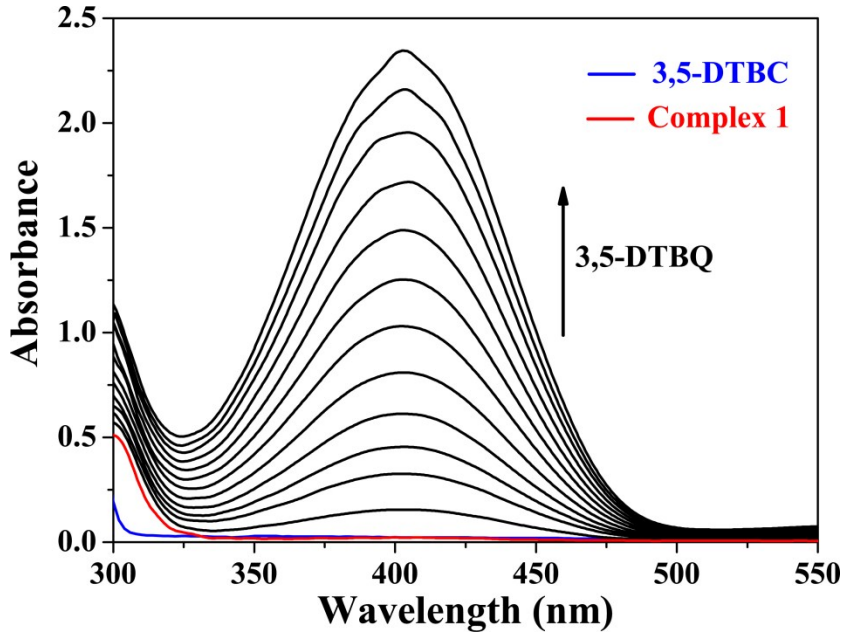

Fig. S7. Increase of absorption spectra after addition of 3,5-DTBC to a DCM/Methanol solution of complex **1**. These spectra were recorded at 5 min intervals.

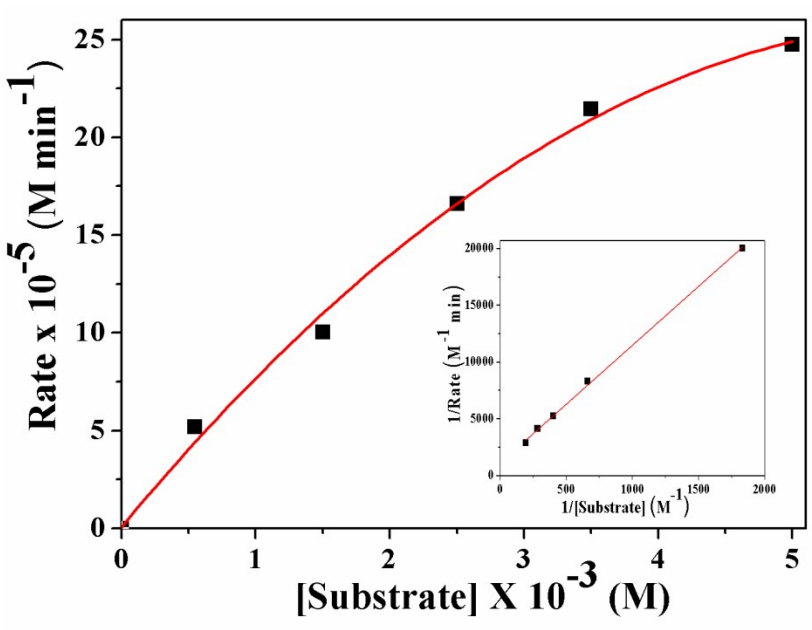

Fig. S8. Plot of the rate *vs*. substrate concentration for complex **1**. The inset shows the corresponding Lineweaver - Burk plot.

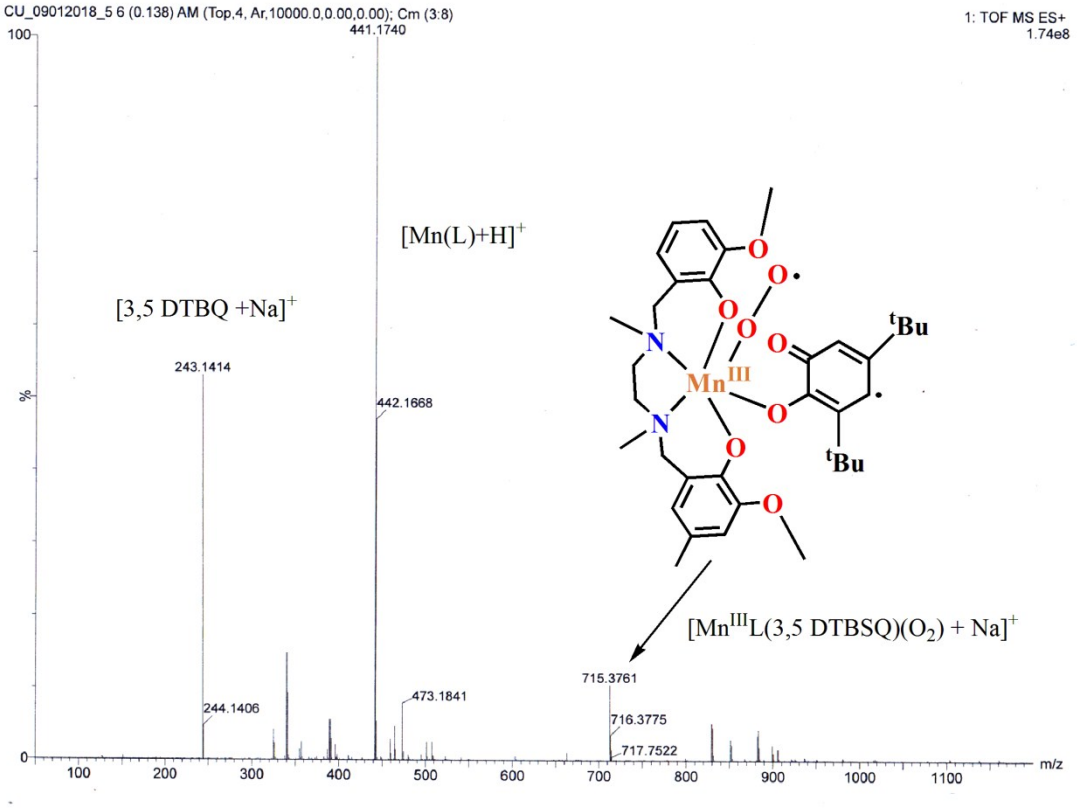

Fig. S9. Representative ESI mass spectrum of complex **2** after addition of 3,5-DTBC.

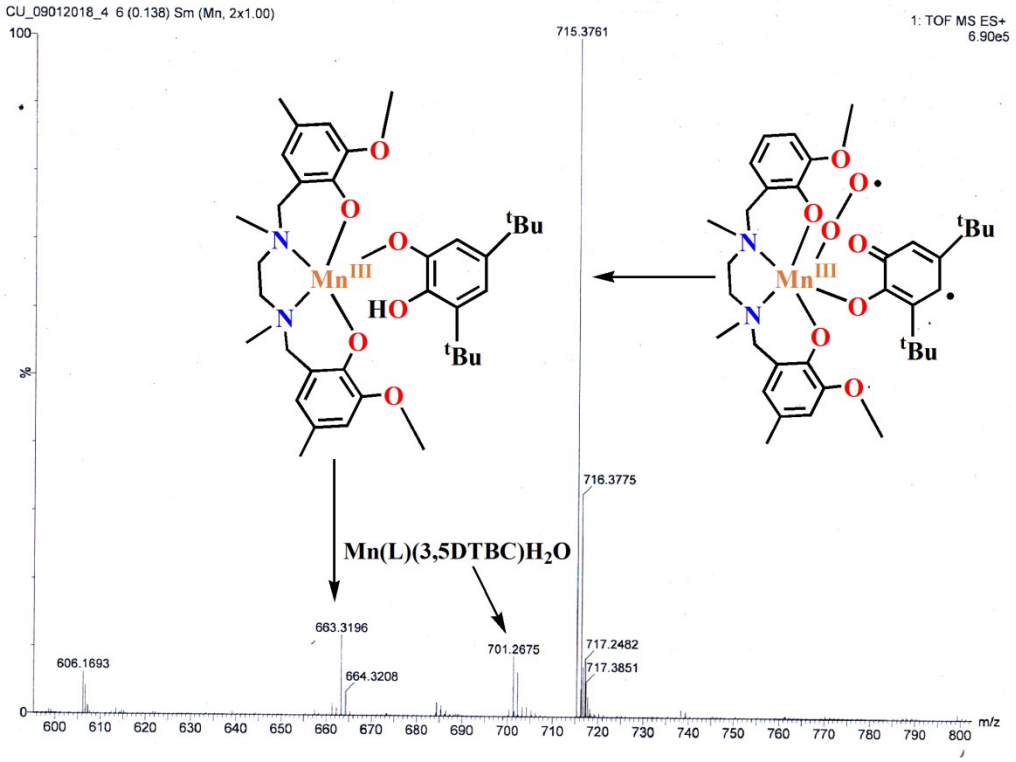

Fig. S10. Representative ESI mass spectrum of complex **2** after addition of 3,5-DTBC (Expanded from 600 to 800).

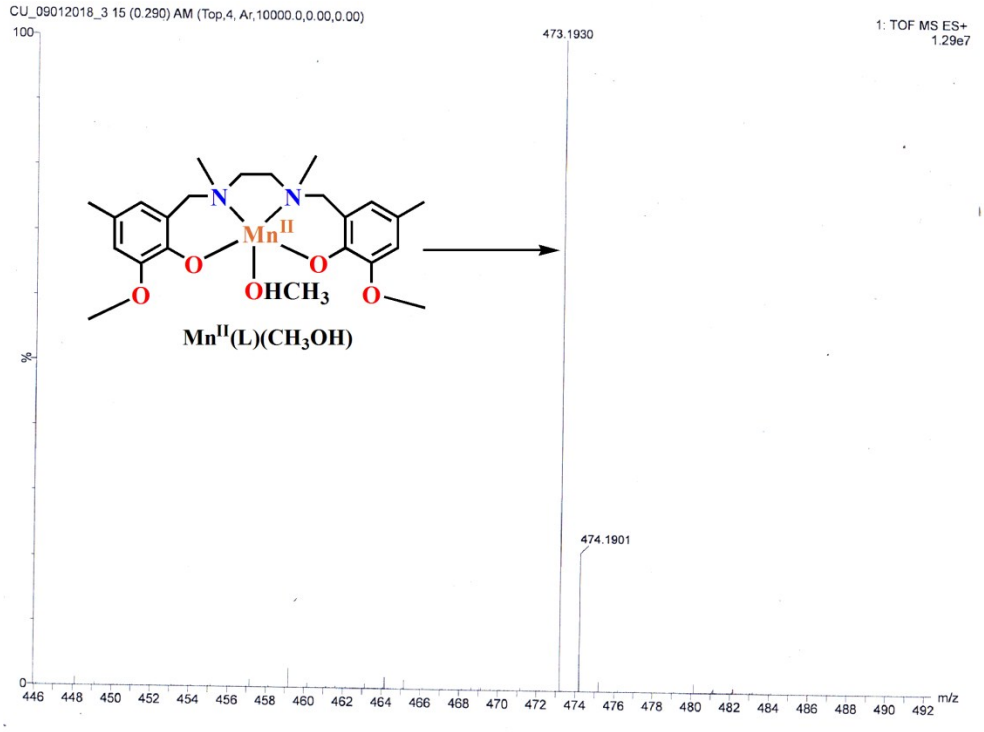

Fig. S11. Representative ESI mass spectrum of complex **2** after addition of 3,5-DTBC (Expanded from 446 to 492).

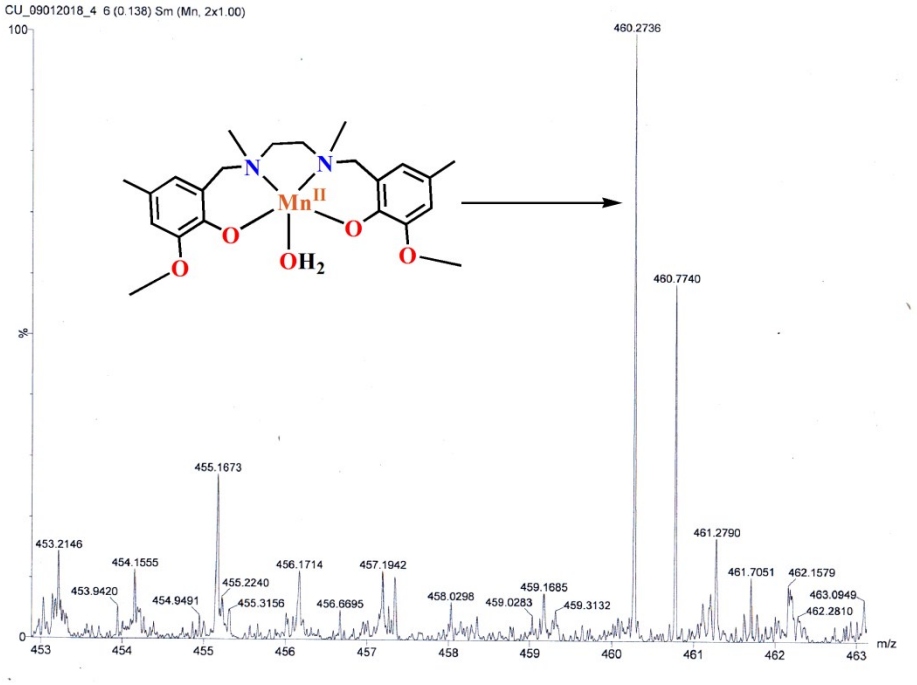

Fig. S12. Representative ESI mass spectrum of complex **2** after addition of 3,5-DTBC (Expanded from 453 to 463).

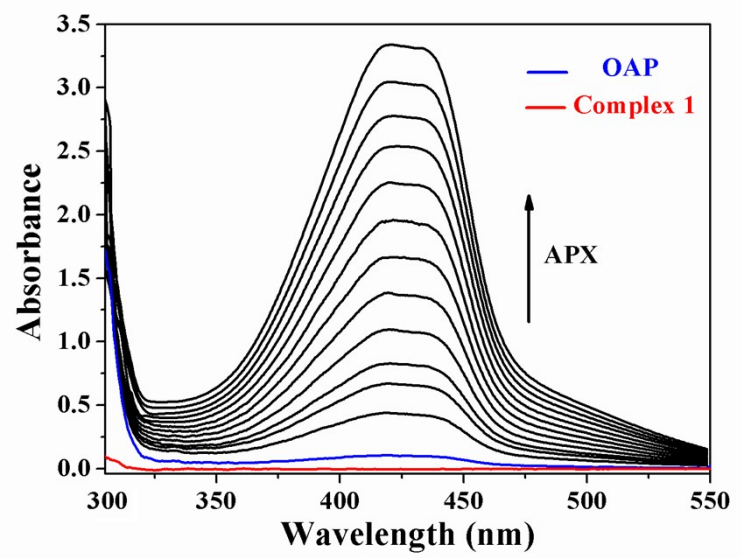

Fig. S13. Increase of the APX band at 432 nm after the addition of OAP to a DCM/methanol solution with complex **1**. The spectra were recorded at 5 min intervals.

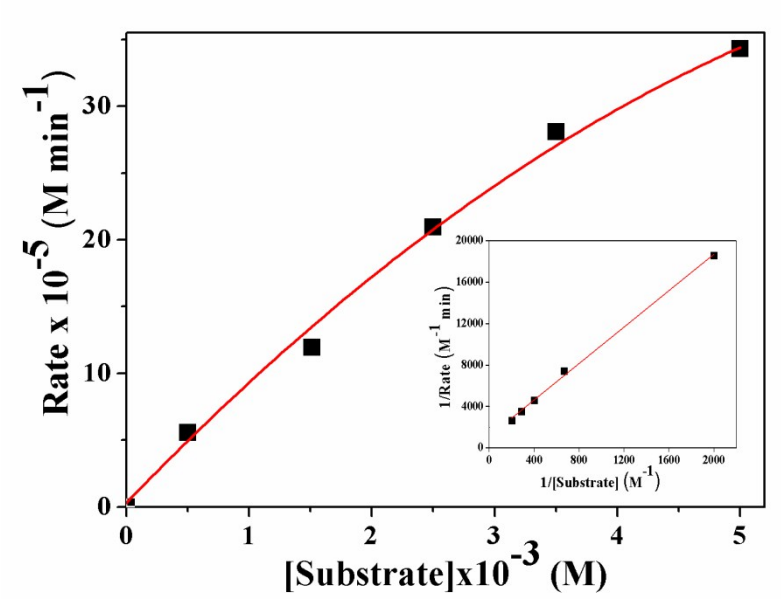

Fig.14. Plot of the rate *vs* substrate concentration for complex **1**. Inset shows the corresponding Lineweaver−Burk plot.

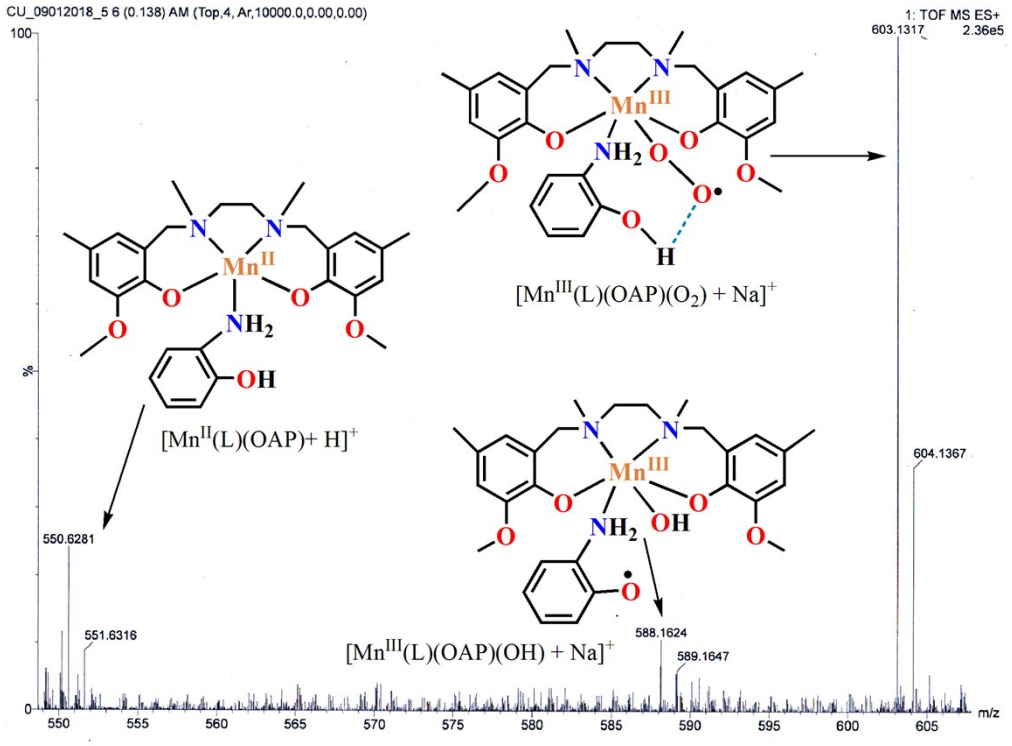

Fig. S15. Representative ESI mass spectrum of complex **2** in DCM/CH_3OH solvent after addition of OAP (Expanded from 550 to 606).

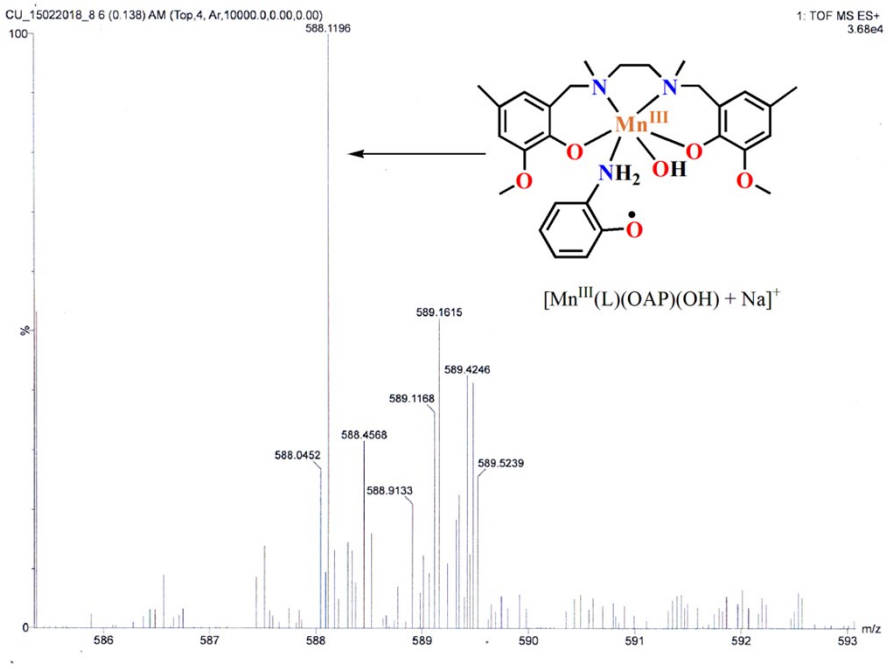

Fig. S16. Representative ESI mass spectrum of complex **2** in DCM/CH_3OH solvent after addition of OAP (Expanded from 585 to 593).

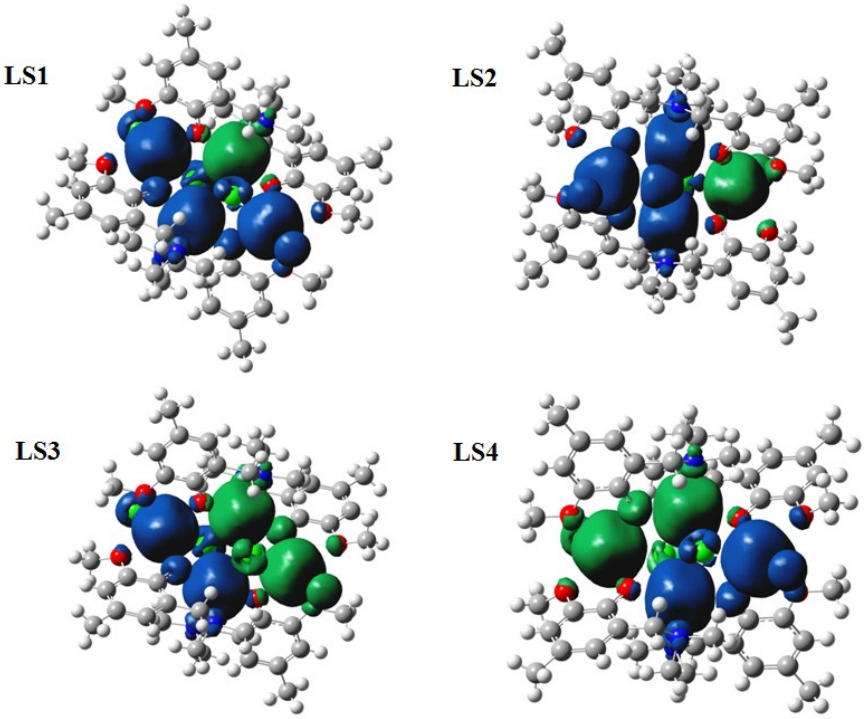

Fig. S17. The calculated spin density surfaces for lowspin state of complex **1** with surface cut off value 0.002 e/Å^3. Positive and negative spin densities are represented by blue and green surfaces respectively.

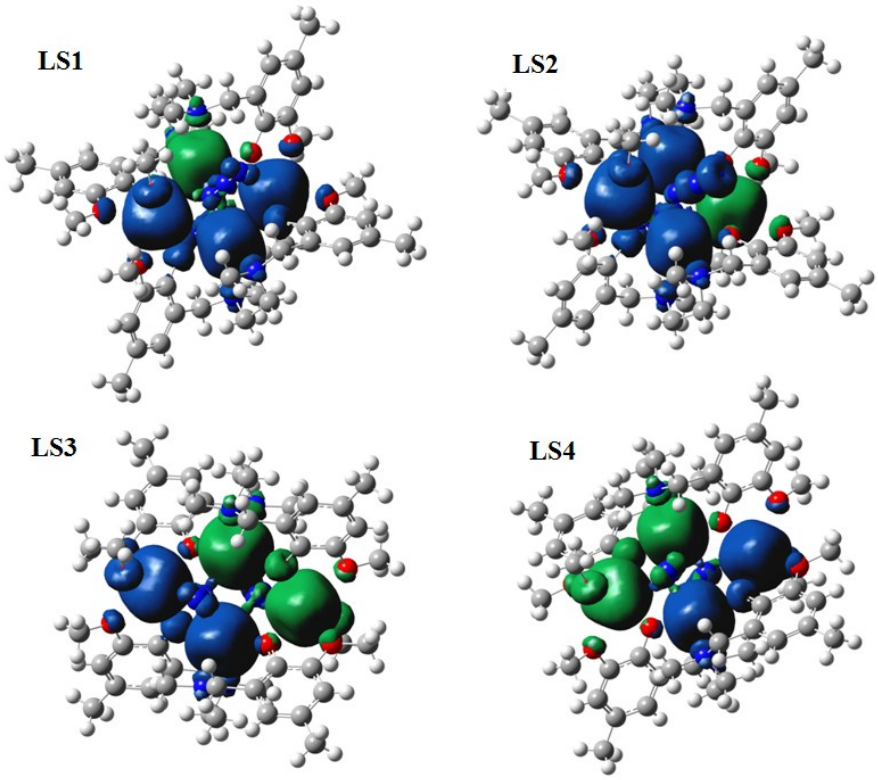

Fig. S18. The calculated spin density surfaces for lowspin state of complex **2** with surface cut off value 0.002 e/Å^3. Positive and negative spin densities are represented by blue and green surfaces respectively.

Table S1. Selected bond lengths and bond angles for complexes **1 -2**.

Bond Distances(Å)		
Parameters	**1** (X=Cl)	**2** (X=N)
Mn(1) O(1)	2.129(7)	2.128(2)
Mn(1) O(3)	2.135(8)	2.127(2)
Mn(1) X(1)	2.553(3)	2.297(2)
Mn(1) N(1)	2.264(8)	2.301(3)
Mn(1) N(2)	2.268(9)	2.279(2)
Mn(1) X(1)[a]	2.613(3)	2.333(3)
Mn(2) O(1)	2.104(7)	2.094(2)
Mn(2) O(2)	2.455(8)	2.397(3)
Mn(2) X(1)	2.618(3)	2.323(3)
Mn(2) X(2)	2.372(4)	2.077(5)
Mn(2) O(3)[a]	2.146(7)	2.117(2)
Mn(2) O(4)[a]	2.280(7)	2.287(2)
Bond Angles(deg)		
O(1) Mn(1) O(3)	168.5(3)	168.38(10)
O(1) Mn(1) N(1)	86.5(3)	84.70(10)

O(1) Mn(1) N(2)	101.1(3)	101.91(9)
O(1) Mn(1) X(1)	91.3(2)	94.55(9)
O(3) Mn(1) N(1)	103.7(3)	105.90(9)
O(3) Mn(1) N(2)	86.2(3)	85.16(9)
O(3) Mn(1) X(1)	83.0(2)	78.75(9)
N(1) Mn(1) N(2)	80.1(3)	78.65(11)
X(1) Mn(2) O(1)	79.8(2)	141.48(14)
X(1) Mn(2) O(2)	125.87(19)	87.12(16)
O(1) Mn(2) O(2)	95.3(3)	70.60(9)
O(1) Mn(2) O(3)[a]	95.3(3)	94.32(9)
O(2) Mn(2) O(4)[a]	81.6(3)	81.90(10)
Mn(1) O(1) Mn(2)	112.5(3)	107.60(11)
Mn(1) X(1) Mn(2)	85.75(9)	94.10(12)
Mn(1) X(1) Mn(1)[a]	86.88(10)	98.37(10)

[a] = 1-x,1-y,1-z (for **1**) and 5/3-x,4/3-y,4/3-z (for **2**).

Table S2. Kinetic Parameters for the Oxidation of 3,5-DTBC Catalyzed by Complexes **1-2**.

Complexes	V_{max} (M min^{-1})	Std. error	K_M (M)	Std. error	k_{cat} (h^{-1})
1	9.85 x 10^{-4}	4.15 x 10^{-5}	98.95 x10^{-4}	2.12 x 10^{-5}	1492.4
2	9. 69x 10^{-4}	3.93 x 10^{-5}	92. 28x10^{-4}	2.53 x 10^{-5}	1431.2

Table S3. Catecholase activity data for some manganese complexes .

Complex	Solvent used	k_{cat} (h^{-1})	References
$[Mn^{II}_4L^1_2(\mu_3\text{-}Cl)_2Cl_2]$ (**1**)	DCM/CH_3OH	1492.4	This work
$[Mn^{II}_4L^1_2(\mu_{1,1,1}\text{-}N_3)_2(N_3)_2]$ (**2**)	DCM/CH_3OH	1431.2	This work
$Mn^{II}(HL^2)(H_2O)_2(CH_3CN)](ClO_4)_2$	DMF	48.8	29a
$[Mn^{II}(o\text{-}(NO_2)\ C_6H_4COO)_2(L^3)(H_2O)]_n$	CH_3CN	177	12d
$[Mn^{II}(L^4)_2(OH_2)_2]$	CH_3OH	598.0	29b
$[Mn^{II}(HL^5)(SCN)_2]$	CH_3OH	604.0	29c
$[Mn^{II}(HL^5)(N(CN)_2)$	CH_3OH	871.2	29c
$[Mn^{II}(HL^5)_2]\cdot 2ClO_4$	CH_3OH	1038.0	29c
$[Mn^{III}L^6Cl\cdot 4H_2O]$	CH_3CN	1790.0	30a

$[Mn^{III}L^{7}Cl{\cdot}4H_2O]$	CH_3OH	2470.0	30a
$[Mn^{III}L^{8}Cl{\cdot}4H_2O]$	CH_3CN	1080.0	30a
$[Mn^{III}L^{9}Cl{\cdot}4H_2O]$	CH_3OH	7200.0	30a
$[Mn^{III}(L^{10})(Cl)_2](ClO_4)$	CH_3OH	230.0	30b
$[Mn^{III}(HL^{11})(Cl)_2].CH_3OH$	CH_3OH	130.0	30b
$[Mn^{IV}(HL^{12})_2(N_3)_2](ClO_4)_2{\cdot}2H_2O$	CH_3CN	398.7	31
$[Mn^{IV}(L^{12})_2](ClO_4)_2{\cdot}0.88H_2O$	CH_3CN	136.0	31
$[Mn^{III}_2Mn^{II}(O_2CCH_2Cl)_4(L^{13})_2(H_2O)_2]{\cdot}H_2O{\cdot}CH_3OH$	CH_3CN	9011.0	32a
$[Mn^{III}_2\ Mn^{II}(O_2CMe)_4(L^{13})_2(H_2O)_2]{\cdot}2H_2O$	CH_3CN	8220.0	32a
$[\{Mn^{III}(L^{14})_2\}\{Mn^{II}(bpy)_2\}(ClO_4)(H_2O)_{0.5}]_{\infty,}$	CH_3OH	126.9	32b
$[Mn^{III}_2Mn^{II}_4O_2(L^{15})_2(C_6H_5CH_2COO)_{10}]_n$	CH_3CN	2547.0	15a
$[Mn^{III}_2Mn^{II}_4O_2(hmt)_4(OCOC_6H_5)_{10}]$	CH_3CN	2337.9	14c

[Where L^1 = *N,N*′-dimethyl-*N,N*′-bis(2-hydroxy-3-methoxy-5-methylbenzyl)ethylenediamine, L^2 = 1,3-Bis(6′-methyl-2-pyridylimino)isoindoline, L^3 = Pyrazine, L^4 = 3-methoxy-4-hydroxy-benzaldehyde, L^5 = 4-tert-butyl-2,6-bis-[(2-pyridin-2-yl-ethylimino)-methyl]-phenol, L^6 = N,N′-ethylenebis(3-formyl-5-methylsalicylaldimine), L^7 = N,N′-1-methylethylenebis(3-formyl-5-methylsalicylaldimine), L^8 = N,N′-1, 1-dimethylethylenebis(3-formyl-5-methylsalicylaldimine),L^9 = N,N′-cyclohexenebis(3-formyl-5-ethylsalicylaldimine), L^{10}= bis((1-methylimidazole-2-yl)methyl)((2-pyridyl)methyl)amine, L^{11} = ((1-methylimidazole-2-yl)methyl)((2-pyridyl)methyl)-(2-hydroxyphenyl)amine, L^{12} = 2-[(3-(dimethylamino)propylimino)methyl]-4-bromophenol, L^{13} = 2-[(2-Hydroxy-1,1-dimethyl-ethylimino)-methyl]-phenol, L^{14} = N-salicylidene-L-alanine and bpy = 2,2'-bipyridine, L^{15} = 3-(3,3-bis(hydroxymethyl)pent-1-enyl)-2-hydroxy-5-methylbenzaldehyde]

Table S4. Kinetic parameters for the oxidation of *o*-aminophenol catalyzed by **1-2**.

Complexes	V_{max} (M min^{-1})	Std. error	K_M (M)	Std. error	k_{cat} (h^{-1})
1	1.14×10^{-3}	4.33×10^{-4}	2.45×10^{-3}	2.31×10^{-4}	2265.5
2	1.02×10^{-3}	3.32×10^{-4}	2.21×10^{-3}	3.12×10^{-4}	2132.2

Table S5. Phenoxazinone synthase-like activity data for some manganese complexes.

Complex	Solvent used	k_{cat} (h^{-1})	References
$[Mn^{II}_4L^1_2(\mu_3\text{-}Cl)_2Cl_2]$ (**1**)	DCM/CH_3OH	2265.5	This work
$[Mn^{II}_4L^1_2(\mu_{1,1,1}\text{-}N_3)_2(N_3)_2]$ (**2**)	DCM/CH_3OH	2132.2	This work
$[Mn^{II}(HL^2)(H_2O)_2(CH_3CN)](ClO_4)_2$	DMF	2.916	29a
$[Mn^{II}(L^3)Cl_2]$	CH_3OH	11.90	33a
$[Mn^{II}(L^4)Cl_2]$	CH_3OH	9.66	33a
$[Mn^{II}(L^5)Cl_2]$	CH_3OH	8.32	33a
$[Mn^{II}(L^6)Cl_2]$	CH_3OH	26.32	33a
$[Mn^{II}(L^7)_2(OH_2)_2]$	CH_3OH	315	33a
$[Mn^{II}(HL^8)_2]\cdot 2ClO_4$	CH_3OH	138.62	29c
$[Mn^{II}(HL^8)(N(CN)_2)$	CH_3OH	64.07	29c
$[Mn^{II}(HL^8)(SCN)_2]$	CH_3OH	14.2	29c
$[Mn^{III}(L^9)_2]ClO_4$	CH_3CN	60	33b
$[Mn^{III}(L^{10})(NCS)(H_2O)]$.DMSO	CH_3CN	308.13	33b
$[Mn^{III}(L^{11})Cl(H_2O)].H_2O$	CH_3OH	35.24	14b
$[Mn^{III}(HL^{12})_2(CH_3OH)_2][Mn^{III}(HL^{11})_2(N_3)_2]$	CH_3CN	215.58	33c
$[Mn^{IV}(L^{13})_2](ClO_4)_2\cdot 0.88H_2O$	CH_3CN	65.82	33d
$[Mn^{IV}(HL^{13})_2(N_3)_2](ClO4)_2\cdot 2H_2O$	CH_3CN	68.46	33d
$[Mn^{IV}(HL^{14})(L^{12})(NCS)]_n$	CH_3CN	280.4	33f
$[Mn^{IV}(HL^{15})_2(OH)Cl]$	CH_3CN	166.2	33f
$[\{Mn^{III}(L^{16})_2\}\{Mn^{II}(bpy)_2\}(ClO_4)(H_2O)_{0.5}]_\infty$	CH_3OH	738	32b

[Where L^1 = *N,N*′-dimethyl-*N,N*′-bis(2-hydroxy-3-methoxy-5-methylbenzyl)ethylenediamine, L^2 = 1,3-Bis(6′-methyl-2-pyridylimino)isoindoline, L^3 = 2-(tetrahydro-2-(pyridin-2-yl)pyrimidin-1(2H)-yl)-N-((pyridin-2-yl)methylene)ethanamine, L^4 = N-(methoxy(pyridin-2-yl)methyl)-2-(2-(pyridin-2-yl)imidazolidin-1-yl)ethanamine, L^5 = 2-(2-(6-methylpyridin-2-yl)imidazolidin-1-yl)-N-((6-methylpyridin-2-yl)methylene)ethanamine, L^6 = hexahydro-1-(2-(tetrahydro-2-(pyridin-2-yl)pyrimidin-1(2H)-yl)ethyl)-2-(pyridin-2-yl)pyrimidine, L^7 = 3-methoxy-4-hydroxy-benzaldehyde, L^8 = 4-tert-butyl-2,6-bis-[(2-pyridin-2-yl-ethylimino)-methyl]-phenol, L^9 = 3-(N,N-dimethylamino)propyliminomethyl-6-ethoxyphenol, L^{10} = N,N′-bis(3-ethoxysalicylidene)ethane-1,2-diamine, L^{11} = (E)-6,6′-((1E,1′E)-(ethane-1,2-diylbis(azanylylidene))bis(methanylylidene))bis(2-methoxy-4-((E)-p-tolyldiazenyl)phenol)], L^{12} = 1-(5-hydroxy-3-oxapentyliminomethyl)-3-ethoxyphenol, L^{13} = 2-[(3-(dimethylamino)propylimino)methyl]-4-bromophenol, L^{14} = 1-(5-hydroxy-3-oxapentyliminomethyl)-3-ethoxyphenol, L^{15} = 1-(5-hydroxy-3-oxapentyliminomethyl)-4-chlorophenol, L^{16} = N-salicylidene-L-alanine and bpy = 2,2'-bipyridine].

Table S6. Structural parameters and magnetic coupling constants for Mn^{II} complexes with a $[Mn_2(\mu\text{-}Cl)_2]$ unit.

Compound	Mn···Mn distance (Å)	∠Mn-Cl-Mn (°)	Mn –Cl distance (Å)	J (cm^{-1})	Ref.
Complex **1**	3.510	86.88	2.618, 2.553	-6.87	This work
VAVDIG	3.636	92.63	2.526,2.503	-0.36	39a
VAVDEC	3.752	94.33	2.592,2.524	-0.14	39a
QEMREF	3.786	95.72	2.537, 2.568	0.34	39b
WIJFUR	3.694	93.80	2.451, 2.606	0.47	39c
AZULOW	3.850	96.42	2.568, 2.595	0.55	39d
JAMMIU	3.740	93.53	2.558, 2.575	0.17	39e
COLDIQ	3.514	90.16	2.480, 2.482	-4.70	40a
COLDIQ10	3.515	90.18	2.480	-2.41	40b
MIKKIB	3.521	88.64	2.629, 2.406	-8.80	40c
OCUNEG	3.514	88.53	2.513, 2.521	-4.21	40d
YUZYOI	3.663	91.94, 91.39	2.553	0.23	40e

Table S7. Bond Angles (deg) and Lengths (Å) and Magnetic Parameters of all the Mn(II)-azide Compounds Containing Double $\mu1,1\text{-}N_3$ Bridges.

Compound	$Mn{-}N_{1,1}{-}Mn$ (deg)	$Mn{-}N_{1,1}$ (Å)	Mn···Mn (Å)	$J_{1,1}$ (cm^{-1})	Ref
Complex**2**	98.37	2.332, 2.297	3.418, 3.504	-0.64	This work
RALKAR	101.70, 102.58	2.236, 2.249	3.468, 3.509	0.77	45a
RALKEV	104.29	2.276, 2.204	3.537	2.04	45a
RALKIZ	103.58	2.222, 2.275	3.534	1.75	45a
HEMPIY	104.61	2.183, 2.272	3.525	1.20	45b
CUCDUZ	101.39	2.207, 2.262	3.458	1.65	45c
CUCHEN	99.60	2.214, 2.280	3.433	1.15	45c

CUQDAT	101.57, 100.40	2.204, 2.199, 2.233, 2.176	3.414, 3.386	0.40	45d
HOTDAV	102.18	2.203, 2.337	3.533	1.75	45e
VEVCUU	101.14, 99.75	2.225, 2.243, 2.268, 2.245	3.451	0.40	46a
WISWOK01	101.37	2.260, 2.229	3.472	0.69	46a
FIBJIK	102.99	2.208, 2.280	3.513	0.58	46b
VECDAJ	100.85, 102.33	2.225, 2.212, 2.192, 2.199	3.420	1.27	46b
ECAJAU	101.98, 101.98	2.218, 2.249	3.471	1.46	46c
RASHUP	102.71, 102.52	2.228, 2.231	3.480	0.64	46d