Electronic Supplementary Information

Anion Coordination Selective [Mn_3] and [Mn_4] Assemblies: Synthesis, Structural Diversity, Magnetic Properties and Catechol Oxidase Activity

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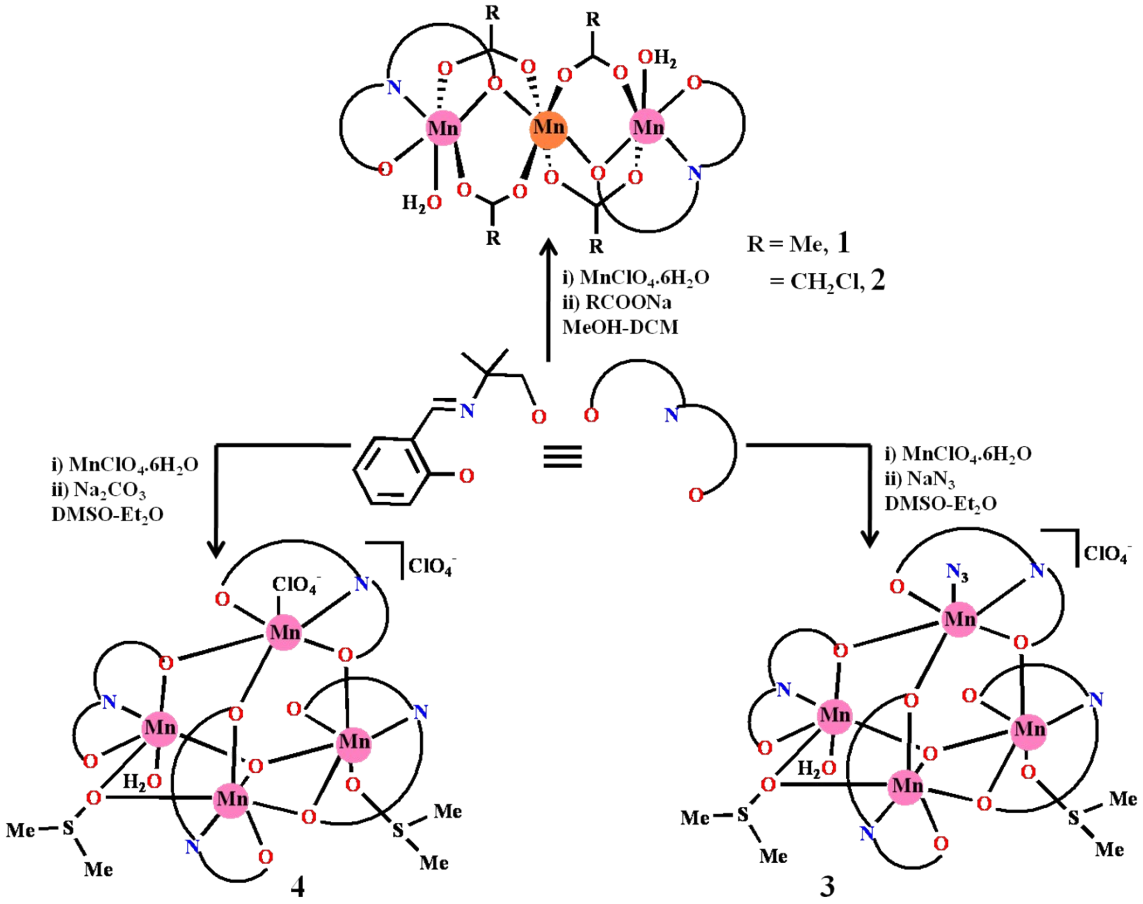
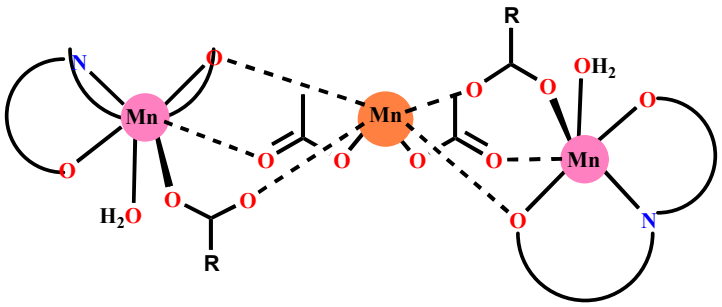
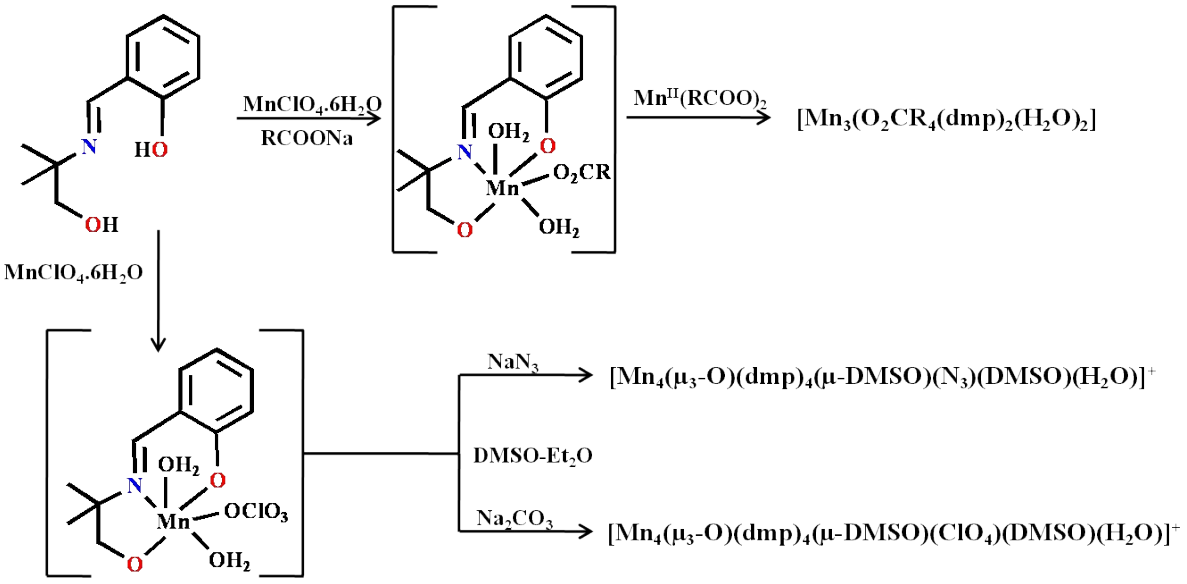


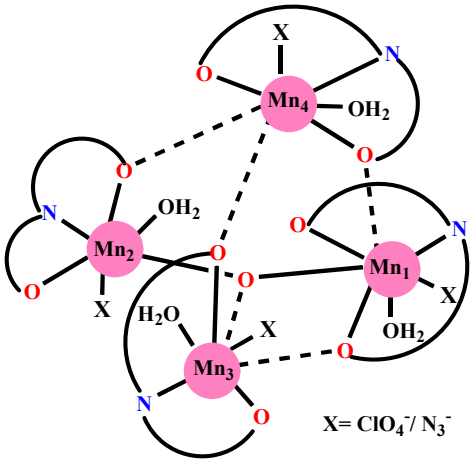
Scheme S1. Synthesis of complexes



Scheme S2. Formation of complexes **1** and **2** through aggregation



Scheme S3. Proposed reaction sequence for formation of the trimers and tetramers



Scheme S4. Formation of complexes **3** and **4**

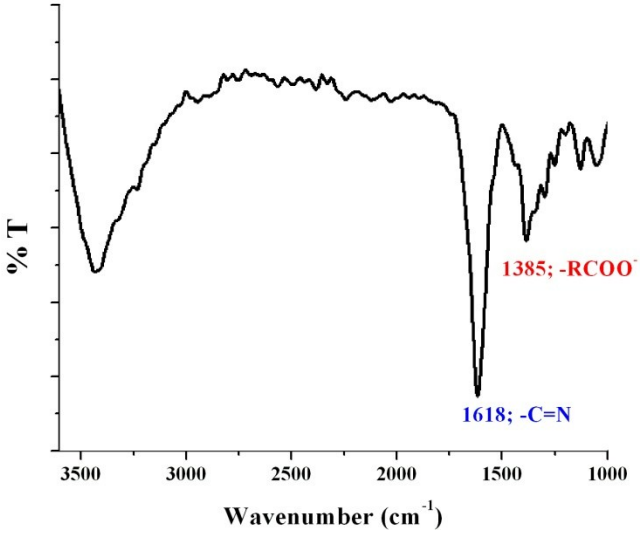


Fig. S1 FT-IR spectrum of complex **2**

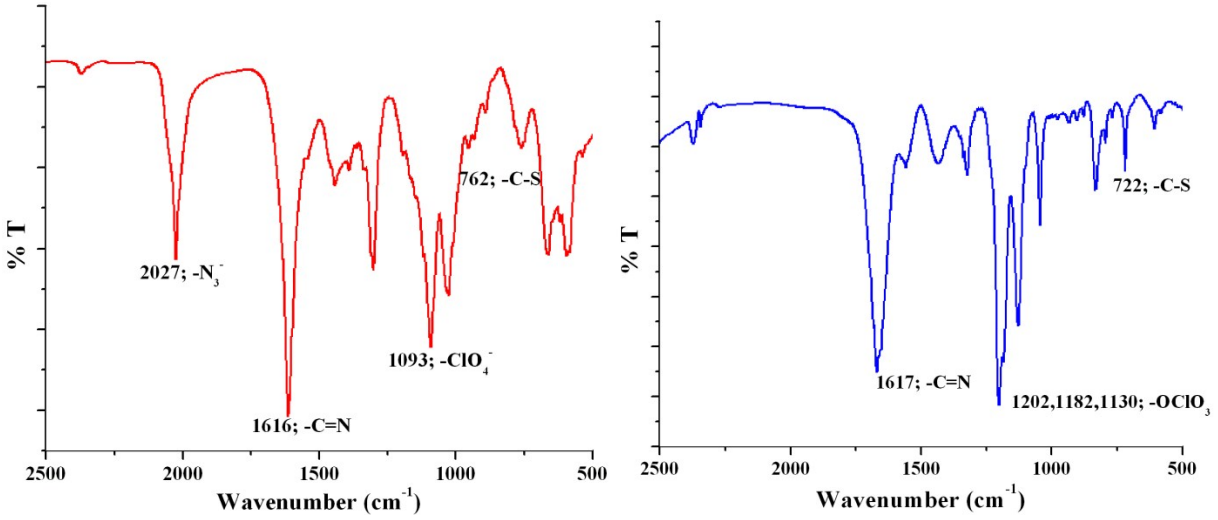


Fig. S2 FT-IR spectrum of complexes **3** (left) and **4** (right).

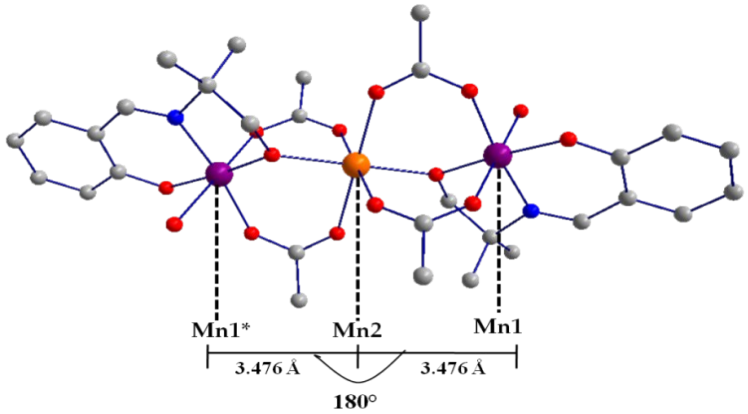


Fig. S3 Linear trinuclear units in complex **1**

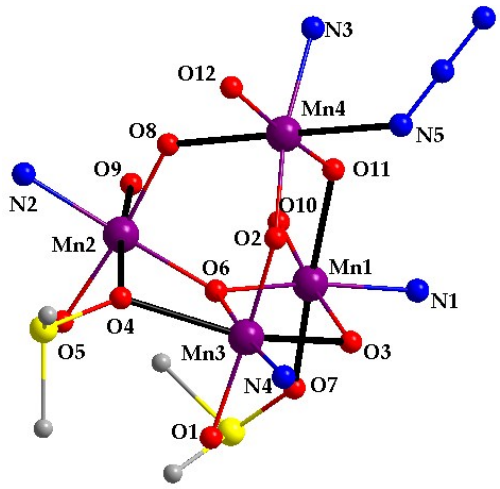


Fig. S4 Core structure of **3** with the O-Mn-O Jahn−Teller axis on the terminal atoms indicated as black bonds.

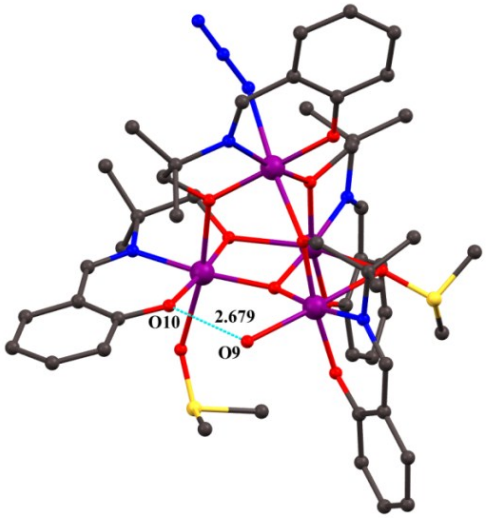


Fig. S5. Intramolecular H-bond present in complex **3**.

Table S1 Selected bond angles (°) for **1**·2H_2O and **2**·H_2O·MeOH

1·2H_2O			
O2-Mn1-O1	174.68(7)	N1-Mn1-O7	85.46(8)
O2-Mn1-O4	98.55(7)	O6-Mn1-O7	179.60(8)
O1-Mn1-O4	86.58(7)	O4-Mn1-O7	84.95(8)
O2-Mn1-N1	83.24(8)	O3-Mn2-O2	89.11(7)
O1-Mn1-N1	91.47(8)	O3*-Mn2-O2*	90.89(7)
O4-Mn1-N1	170.19(8)	O3-Mn2-O5*	87.55(8)

O2-Mn1-O6	91.32(7)	O1-Mn1-O7	90.69(9)
O1-Mn1-O6	89.60(8)	O3-Mn2-O5	92.45(8)
O4-Mn1-O6	95.34(8)	O2-Mn2-O5	88.71(7)
N1-Mn1-O6	94.26(8)	O2*-Mn2-O5*	91.29(7)
O2-Mn1-O7	88.36(9)		

2·H_2O·MeOH			
O2-Mn1-O1	173.82(18)	O2-Mn1-O7	88.98(19)
O1-Mn1-O4	86.33(18)	O4-Mn1-O7	85.4(2)
O2-Mn1-O4	99.71(17)	N1-Mn1-O7	91.5(2)
O1-Mn1-N1	90.6(2)	O6-Mn1-O7	170.06(18)
O2-Mn1-N1	83.26(19)	O2-Mn2-O3	91.34(15)
O4-Mn1-N1	175.67(19)	O2-Mn2-O3*	88.66(15)
O1-Mn1-O6	90.5(2)	O2-Mn2-O5	88.97(17)
O2-Mn1-O6	91.37(18)	O2-Mn2-O5*	91.03(17)
O4-Mn1-O6	84.8(2)	O3-Mn2-O5	87.3(2)
N1-Mn1-O6	98.4(2)	O3*-Mn2-O5*	92.7(2)
O1-Mn1-O7	90.2(2)		

Table S2 Bond-Valence Sums for the Mn Atoms of Complexes **1**−**4**

Complex	Atom	Mn^{II}	Mn^{III}
1	Mn1	3.25	<u>3.02</u>
	Mn2	<u>2.04</u>	1.86
2	Mn1	3.27	<u>3.02</u>
	Mn2	<u>2.07</u>	1.90
3	Mn1	3.10	<u>2.87</u>
	Mn2	3.05	<u>2.82</u>
	Mn3	3.01	<u>2.79</u>
	Mn4	3.05	<u>2.84</u>
4	Mn1	3.16	<u>2.92</u>
	Mn2	3.25	<u>3.01</u>
	Mn3	3.16	<u>2.95</u>
	Mn4	3.13	<u>2.91</u>

Table S3 Selected bond angles (°) for **3**·ClO_4·DMSO and **4**·ClO_4·DMSO

3·ClO4·DMSO			
O3-Mn1-O6	84.52(17)	O1-Mn3-O6	95.64(19)
O6-Mn1-O10	100.75(18)	O6-Mn3-O2	93.33(17)
O3-Mn1-N1	83.2(2)	O1-Mn3-N3	89.3(2)
O10-Mn1-N1	91.6(2)	O2-Mn3-N3	81.9(2)
O3-Mn1-O11	93.21(17)	O1-Mn3-O3	96.06(19)
O6-Mn1-O11	88.98(16)	O6-Mn3-O3	76.42(16)
O10-Mn1-O11	85.87(18)	O2-Mn3-O3	92.31(17)
N1-Mn1-O11	92.91(19)	N3-Mn3-O3	101.85(19)
O3-Mn1-O7	94.97(19)	O1-Mn3-O4	90.91(19)
O6-Mn1-O7	98.64(18)	O6-Mn3-O4	79.73(17)
O10-Mn1-O7	85.3(2)	O2-Mn3-O4	84.33(17)
N1-Mn1-O7	81.3(2)	N3-Mn3-O4	101.5(2)
O3-Mn1-O10	174.62(18)	O1-Mn3-O2	168.94(19)
O6-Mn1-N1	167.7(2)	O6-Mn3-N3	174.9(2)
O11-Mn1-O7	169.31(18)	O3-Mn3-O4	155.67(17)
O8-Mn2-O6	93.02(18)	O12-Mn4-O2	91.70(19)
O5-Mn2-O6	93.23(18)	O11-Mn4-O2	94.94(18)
O8-Mn2-N2	83.0(2)	O12-Mn4-N4	90.2(2)
O5-Mn2-N2	90.3(2)	O11-Mn4-N4	83.7(2)
O8-Mn2-O9	88.98(19)	O12-Mn4-O8	84.71(19)
O5-Mn2-O9	94.8(2)	O11-Mn4-O8	92.69(18)
O6-Mn2-O9	96.31(17)	O2-Mn4-O8	91.74(17)
N2-Mn2-O9	90.3(2)	N4-Mn4-O8	98.83(19)
O8-Mn2-O4	92.62(18)	O12-Mn4-N5	90.9(2)
O5-Mn2-O4	84.3(2)	O11-Mn4-N5	92.0(2)
O6-Mn2-O4	77.96(16)	O2-Mn4-N5	85.3(2)
N2-Mn2-O4	95.55(19)	N4-Mn4-N5	84.2(2)
O8-Mn2-O5	172.3(2)	O12-Mn4-O11	172.9(2)
O6-Mn2-N2	172.3(2)	O2-Mn4-N4	169.4(2)
O9-Mn2-O4	174.12(17)	O8-Mn4-N5	174.7(2)
Mn1-O6-Mn2	136.0(2)	Mn1-O3-Mn3	94.96(17)
Mn1-O6-Mn3	103.17(18)	Mn1-O11-Mn4	125.5(2)
Mn2-O6-Mn3	115.3(2)	Mn2-O8-Mn4	127.4(2)
Mn2-$O4_{DMSO}$-	85.83(15)	Mn3-O2-Mn4	130.4(2)

Mn3			
4·ClO_4·DMSO			
O3-Mn1-O6	84.7(2)	O1-Mn3-O6	95.1(2)
O6-Mn1-O10	101.4(2)	O6-Mn3-O2	93.6(2)
O3-Mn1-N1	82.5(2)	O1-Mn3-N3	89.5(3)
O10-Mn1-N1	91.4(2)	O2-Mn3-N3	82.0(2)
O3-Mn1-O11	92.8(2)	O1-Mn3-O3	96.5(2)
O6-Mn1-O11	87.61(19)	O6-Mn3-O3	77.0(2)
O10-Mn1-O11	87.0(2)	O2-Mn3-O3	92.0(2)
N1-Mn1-O11	91.1(2)	N3-Mn3-O3	101.5(2)
O3-Mn1-O7	94.4(2)	O1-Mn3-O4	90.1(2)
O6-Mn1-O7	100.6(2)	O6-Mn3-O4	80.0(2)
O10-Mn1-O7	85.1(2)	O2-Mn3-O4	84.9(2)
N1-Mn1-O7	82.3(2)	N3-Mn3-O4	101.2(2)
O3-Mn1-O10	174.0(2)	O1-Mn3-O2	169.0(2)
O6-Mn1-N1	167.0(2)	O6-Mn3-N3	175.3(2)
O11-Mn1-O7	169.6(2)	O3-Mn3-O4	156.5(2)
O8-Mn2-O6	92.7(2)	O12-Mn4-O2	91.0(2)
O5-Mn2-O6	93.7(2)	O11-Mn4-O2	92.7(2)
O8-Mn2-N2	82.5(2)	O12-Mn4-N4	90.9(3)
O5-Mn2-N2	90.8(3)	O11-Mn4-N4	83.8(2)
O8-Mn2-O9	90.0(2)	O12-Mn4-O8	89.4(2)
O5-Mn2-O9	92.5(3)	O11-Mn4-O8	96.1(2)
O6-Mn2-O9	95.9(2)	O2-Mn4-O8	97.4(2)
N2-Mn2-O9	89.6(2)	N4-Mn4-O8	100.5(2)
O8-Mn2-O4	92.1(2)	O12-Mn4-O13	82.1(1)
O5-Mn2-O4	86.1(2)	O11-Mn4-13	92.5(9)
O6-Mn2-O4	78.3(2)	O2-Mn4-13	80.6(1)
N2-Mn2-O4	96.4(2)	N4-Mn4-O13	81.8(7)
O8-Mn2-O5	172.9(2)	O12-Mn4-O11	173.0(2)
O6-Mn2-N2	172.7(3)	O2-Mn4-N4	162.0(2)
O9-Mn2-O4	173.9(2)	O8-Mn4-O13	171.2(3)
Mn1-O6-Mn2	136.6(3)	Mn1-O3-Mn3	94.5(2)
Mn1-O6-Mn3	102.8(2)	Mn1-O11-Mn4	124.8(2)
Mn2-O6-Mn3	115.9(3)	Mn2-O8-Mn4	126.2(3)
Mn2-$O4_{DMSO}$-	85.11(18)	Mn3-O2-Mn4	127.2(3)

Mn3			

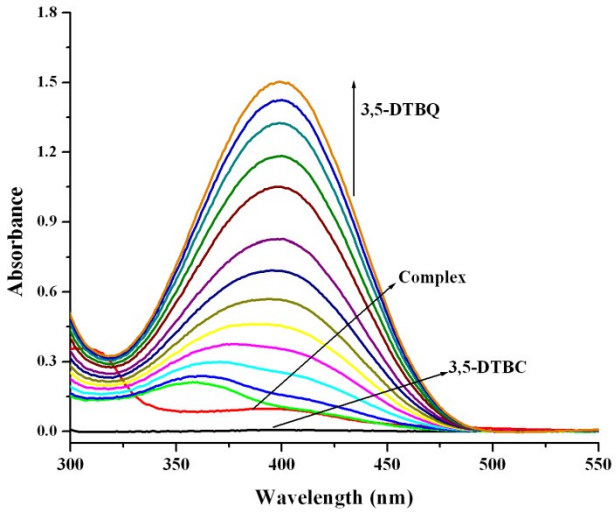
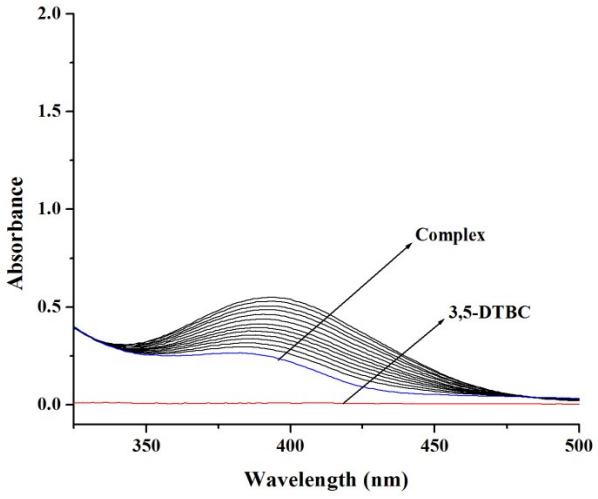


Fig. S6 Increase of absorption spectra after addition of 100 equiv of 3,5-DTBC to a solution containing complex **2** (1×10^{-6} M) in MeCN. The spectra were recorded after every 5 min up to 1 h in MeCN.

Complex 1



Complex 3

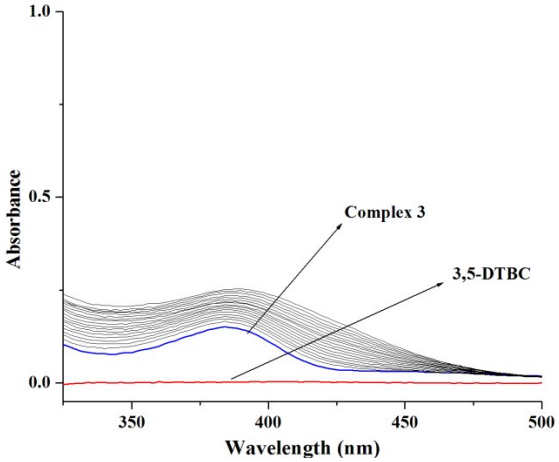


Fig. S7 Absorption spectra of complexes 1 (left) and 3 (right) (1× 10^{-6} M) with 100 equiv of 3,5-DTBC in MeOH. The spectra were recorded after every 15 min up to 3 h in MeOH.

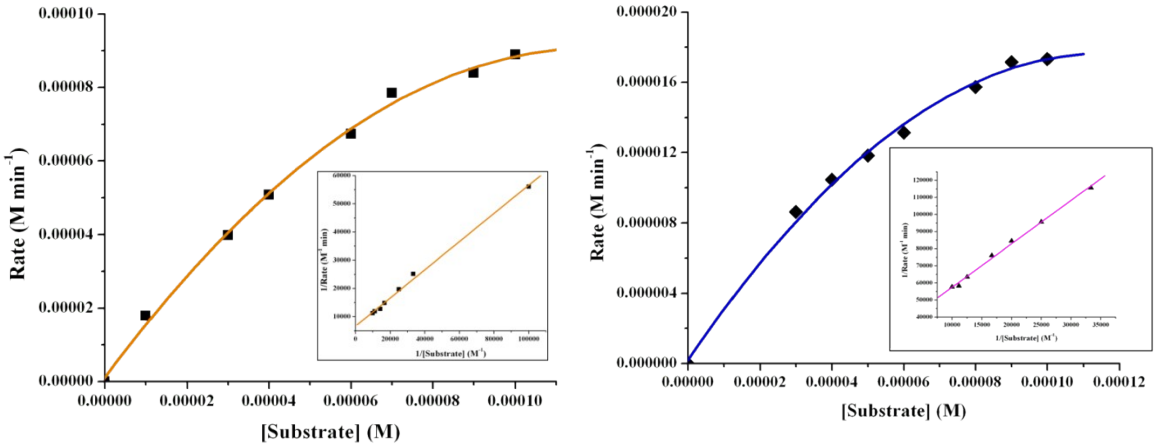


Fig. S8 Plot of initial rates vs substrate concentration for the oxidation reaction catalyzed by complexes **2** (left) and **4** (right). Inset shows the Lineweaver−Burk plot.

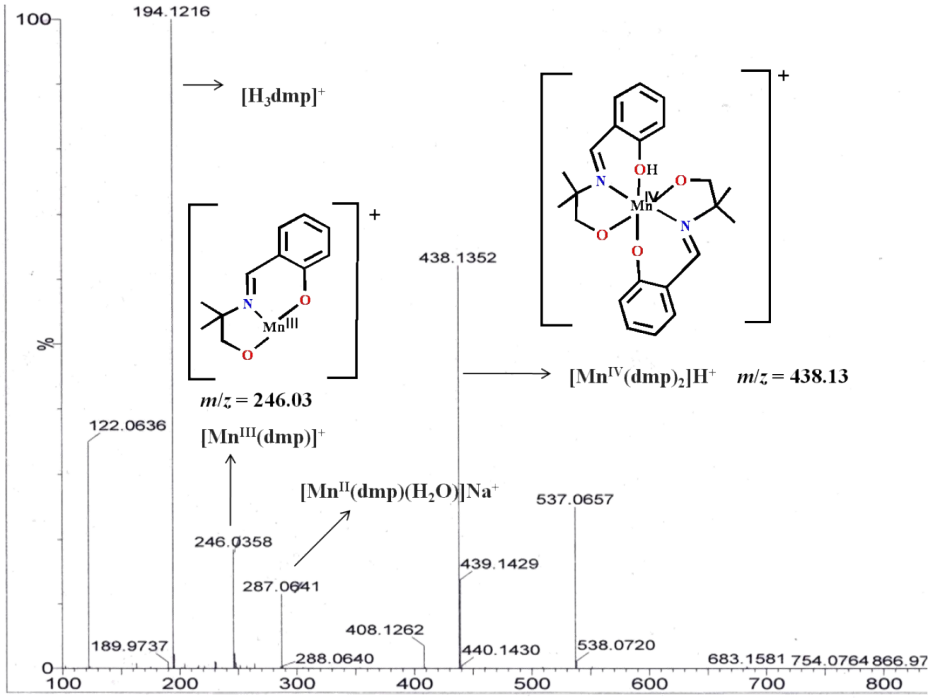


Fig. S9 Electrospray mass spectrum (ESI-MS positive) of complex **1** in acetonitrile.

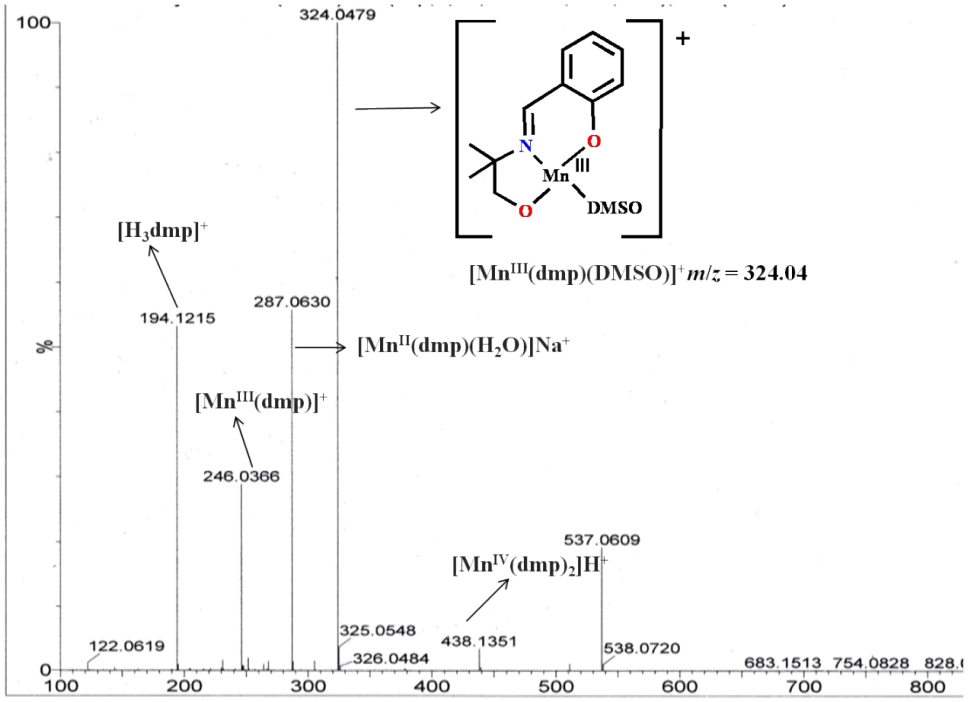


Fig. S10 Electrospray mass spectrum (ESI-MS positive) of complex **3** in acetonitrile.

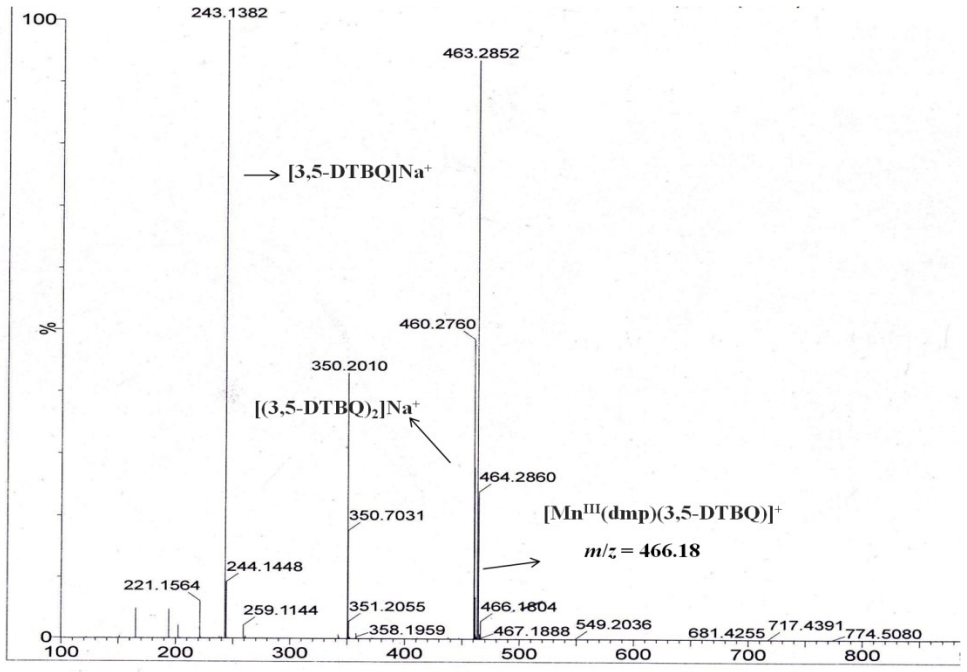


Fig. S11 Electrospray mass spectrum (ESI-MS positive) of a 1:100 **1**/3,5-DTBC mixture in

acetonitrile, recorded within 5 min of mixing.

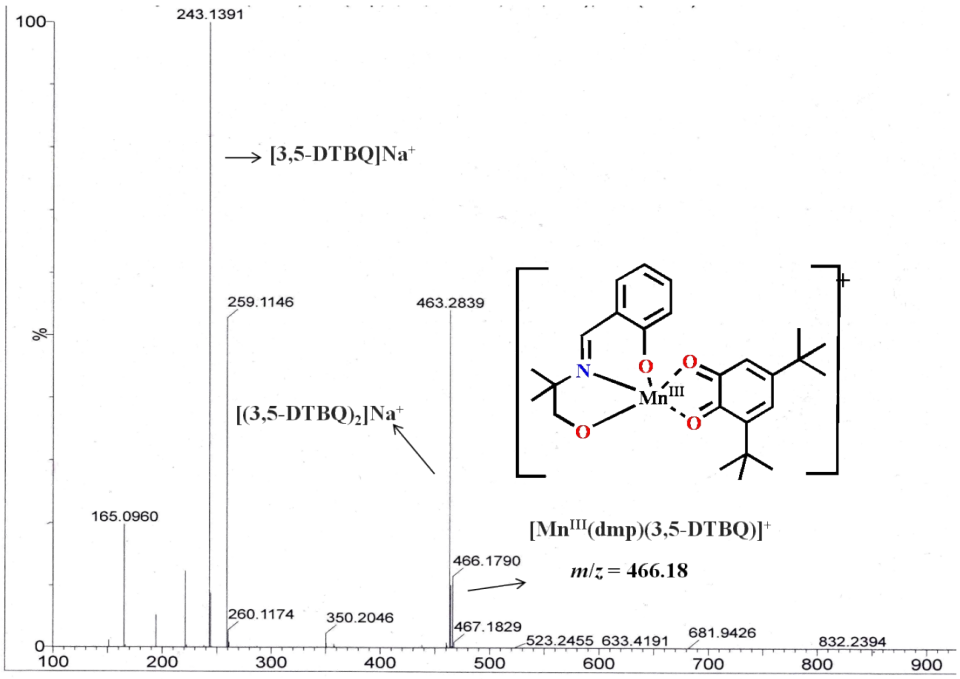


Fig. S12 Electrospray mass spectrum (ESI-MS positive) of a 1:100 **3**/3,5-DTBC mixture in acetonitrile, recorded within 5 min of mixing.