Supporting Information

Synthesis of Mn_3O_4 nanozymes from structurally characterized phenoxazinone synthase models based on manganese(III) Schiff base complexes

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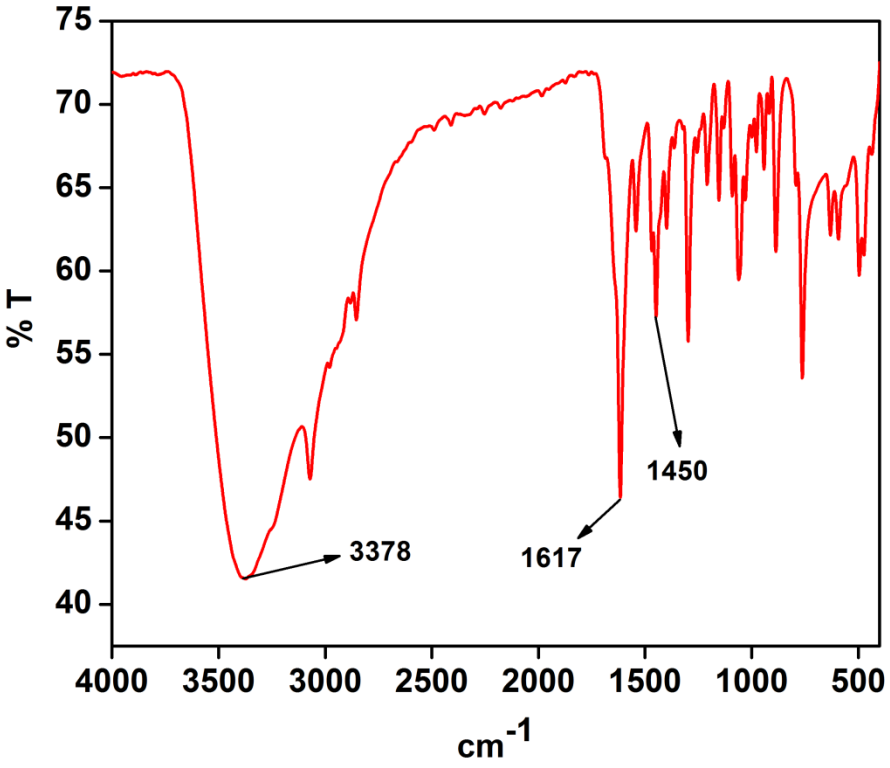


Fig. S1 FTIR spectrum of Complex **1.**

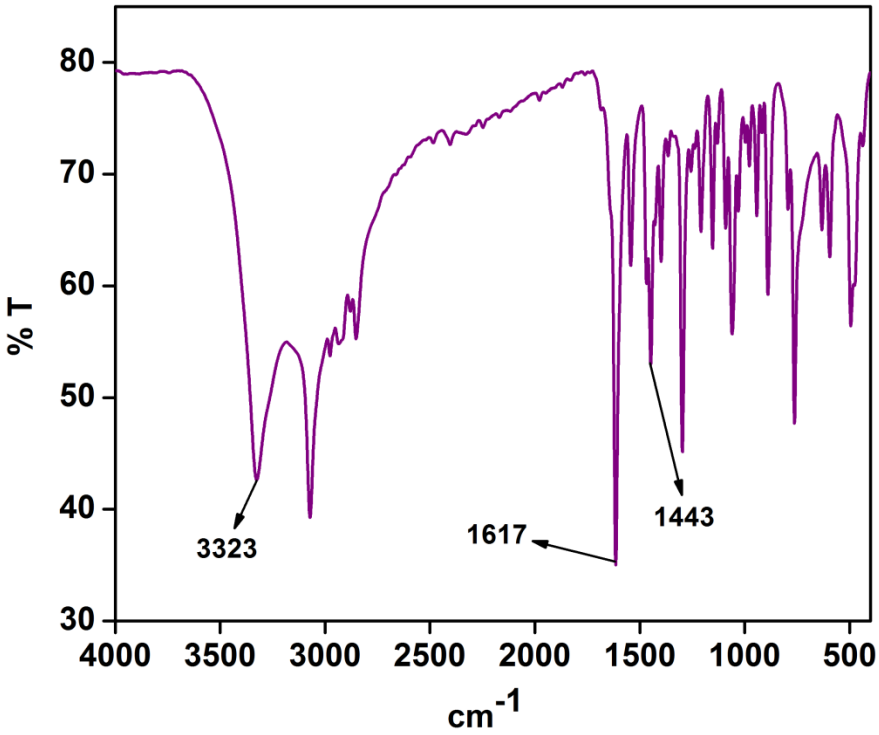


Fig. S2 FTIR spectrum of Complex **2.**

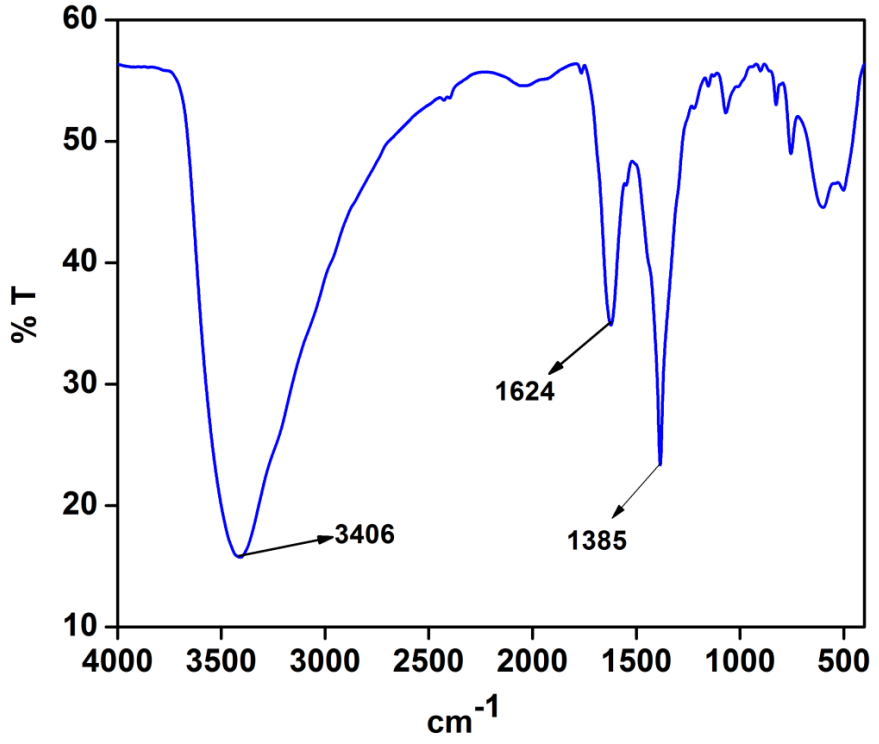


Fig. S3 FTIR spectrum of Complex **3**

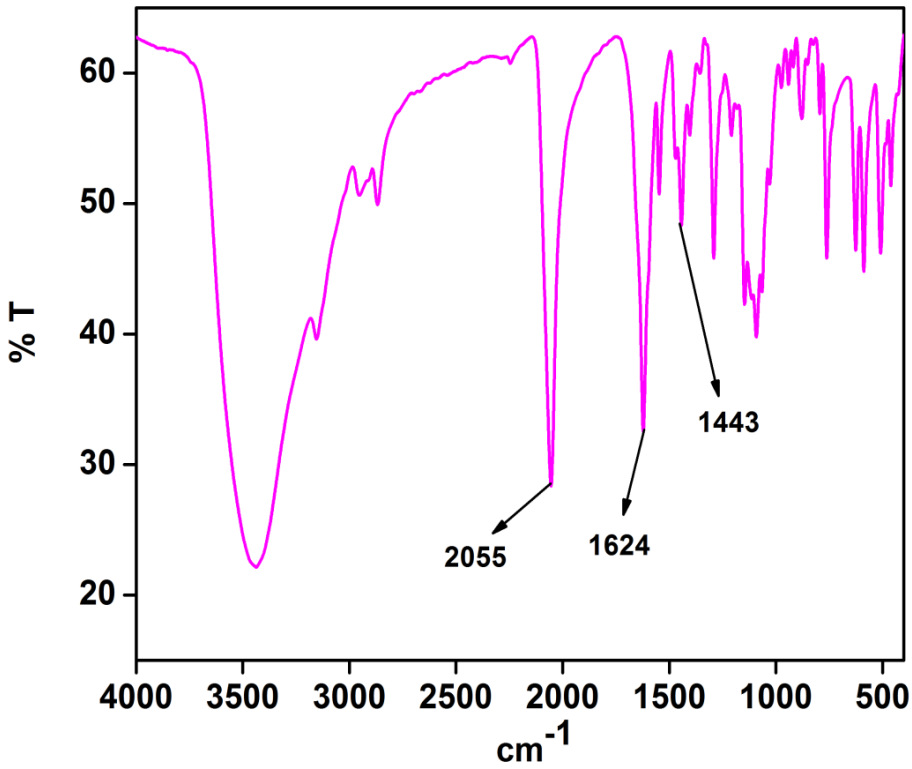


Fig. S4 FTIR spectrum of Complex **4.**

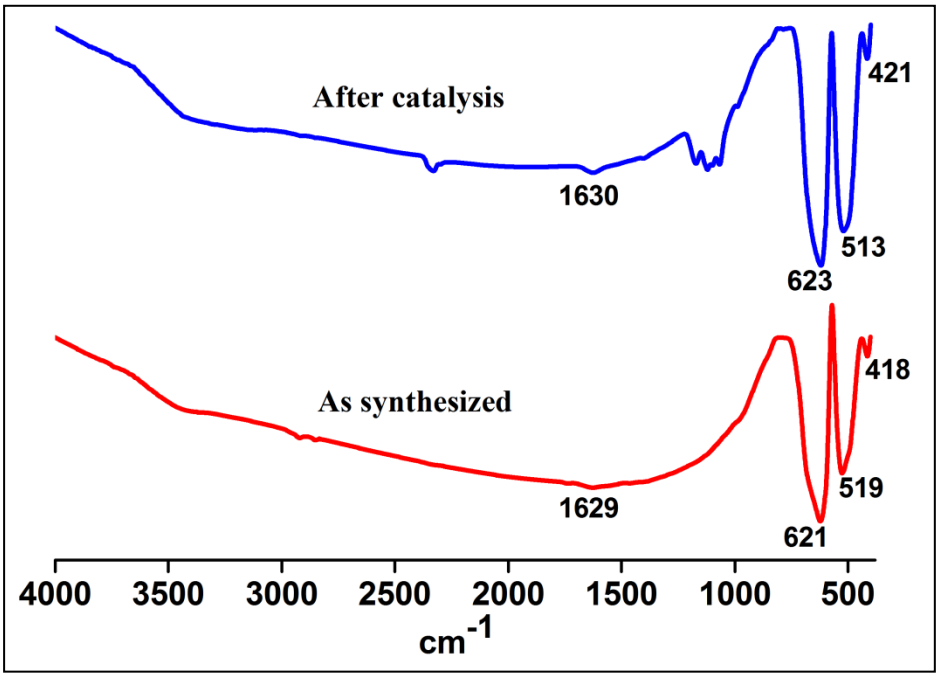


Fig. S5 FTIR spectrum of as synthesized, and after catalysis of cube shaped (Nc) Mn_3O_4 NPs.

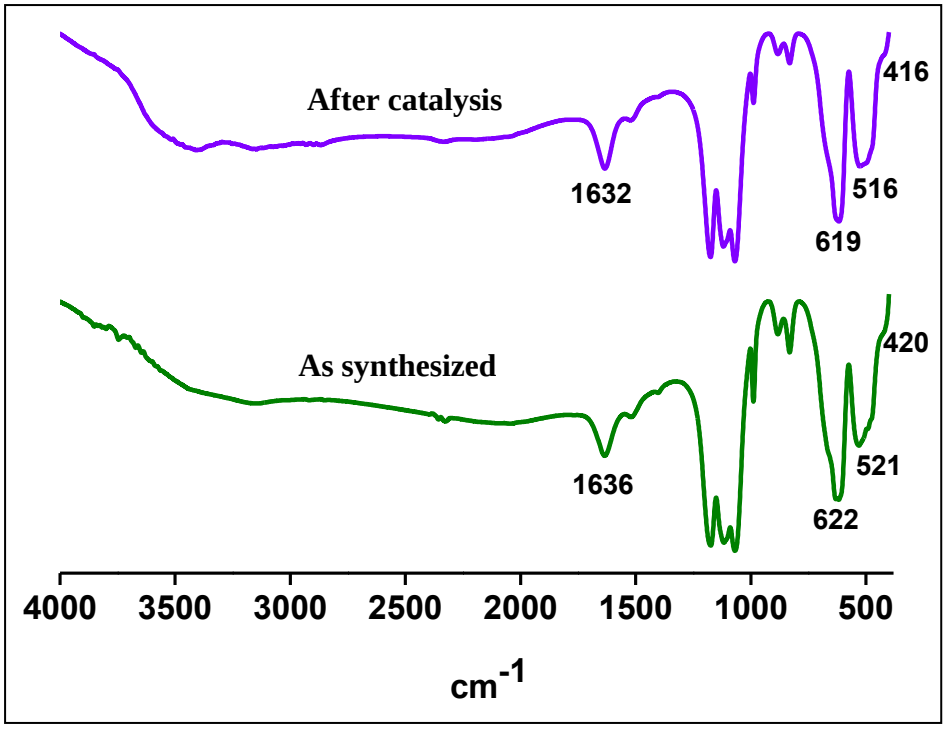
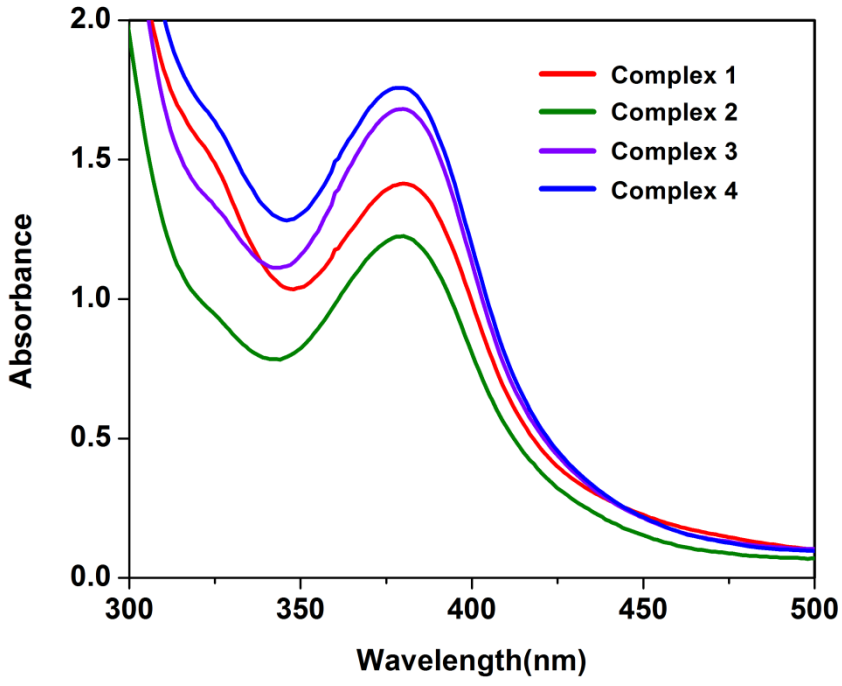
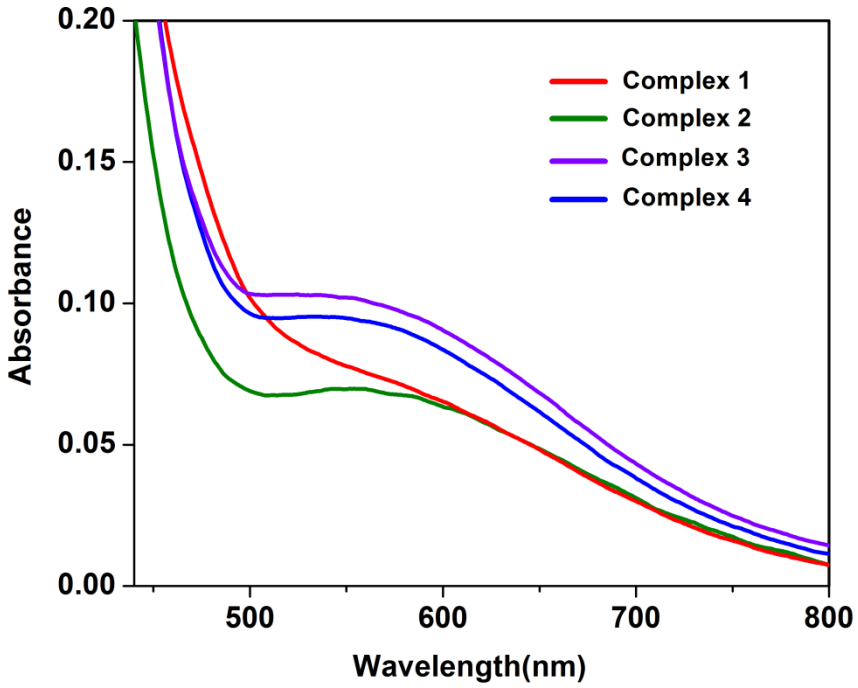


Fig. S6 FTIR spectrum of as synthesized, and after catalysis of needle (Nn) like Mn_3O_4 NPs.



(a)



(b)

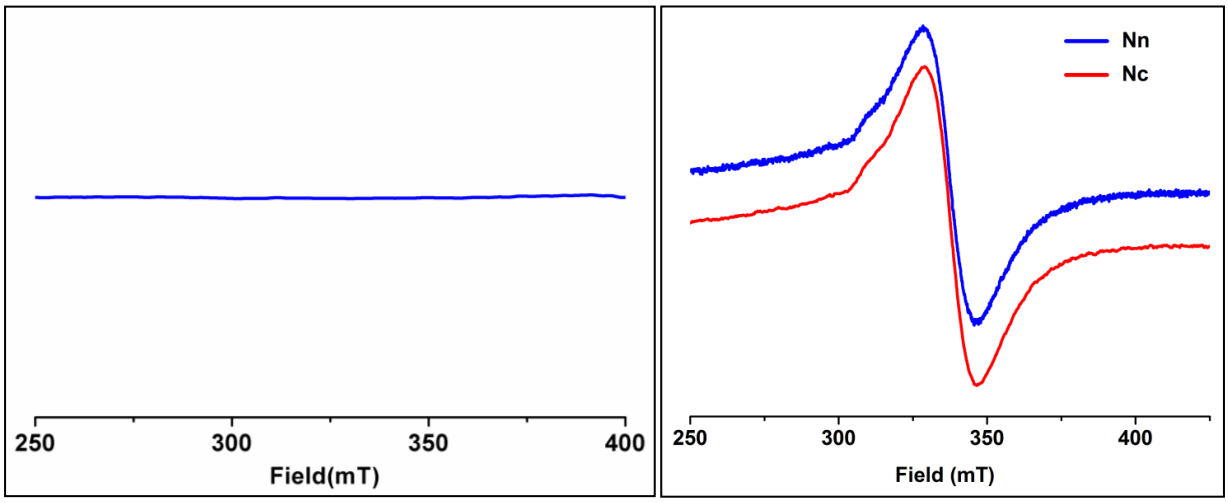
Fig. S7 (a) charge transfer, (b) d-d transition of complexes **1-4** in DMF medium

Table S1 Crystallographic data and details of refinement for complex **1**, **3** & **4**

	1	**3**	**4**
CCDC Number	1934500	1934498	1934499
Empirical formula	$C_{12}H_{20}ClMnN_2O_4$	$C_{12}H_{20}MnN_3O_7$	$C_{39}H_{49}Mn_3N_9O_{6.75}S_3$
Formula weight	346.69	373.25	1012.87
Crystal system	Orthorhombic	Orthorhombic	Triclinic
Space group	*P*bca	*P*bca	$P\bar{1}$
a/Å	18.4286(4)	18.4749(4)	14.004(2)
b/Å	7.7670(2)	8.1865(2)	14.366(2)
c/Å	20.6985(5)	21.1388(5)	14.520(3)
α/°	90	90	67.61(3)
β/°	90	90	61.177(17)
γ/°	90	90	78.511(19)

Volume/Å^3	2962.68(12)	3197.13(13)	2365.9(9)
Density	1.555	1.551	1.422
Z	8	8	2
F(000)	1440	1552	1046
μMoK$_\alpha$/mm^{-1} Mo Kα radiation	1.085 λ=0.71073Å	0.865 λ=0.71073Å	0.983 λ=0.71073Å
Temperature/K	296	293	295
R_{int}	0.0326	0.0375	0.1670
$\theta_{min/max/}$°	1.97/28.13	2.89 / 26.03	2.24 / 25.05
Reflections collected/ unique [$I>2\sigma(I)$][a]	3615/2911	3132/ 2538	8261/ 3159
GOF on F^2	1.043	1.025	0.983
$R_{indices}$[I>2σ(I)]	*R1* = 0.0281 *wR2* = 0.0672	*R1* = 0.0435 *wR2* = 0.1015	*R1* = 0.0987 *wR2* = 0.2290

[a] $R1 = \Sigma \big| |Fo| - |Fc| \big| / \Sigma |Fo|$, $wR2 = [\Sigma w (Fo^2 - Fc^2)^2 / \Sigma w (Fo^2)^2]^{½}$



(a) (b)

Fig. S8 (a) ERP spectra of complex **4**, (b) Solid state EPR spectra of the synthesized Mn_3O_4 NPs.

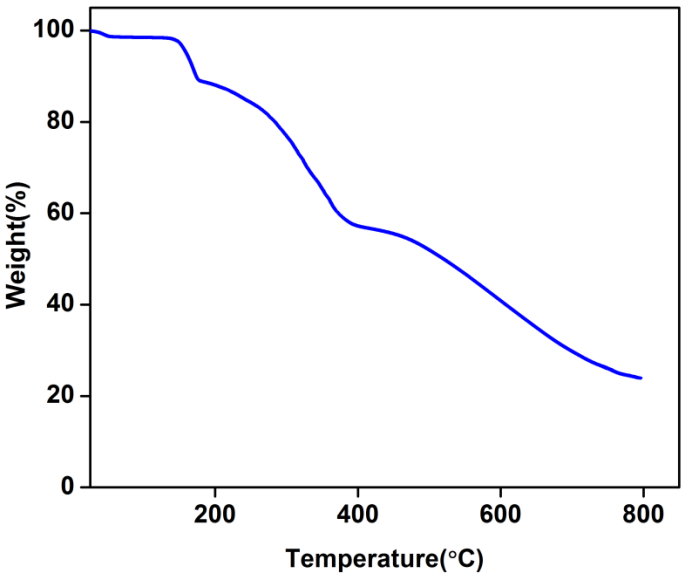


Fig. S9 TGA curve of Complex **1** collected under N2 atmosphere.

Calculated residual mass % of Mn_3O_4 = (228.8117/3*346.6892)*100%

= 21.99% (experimentally obtained 23.34%)

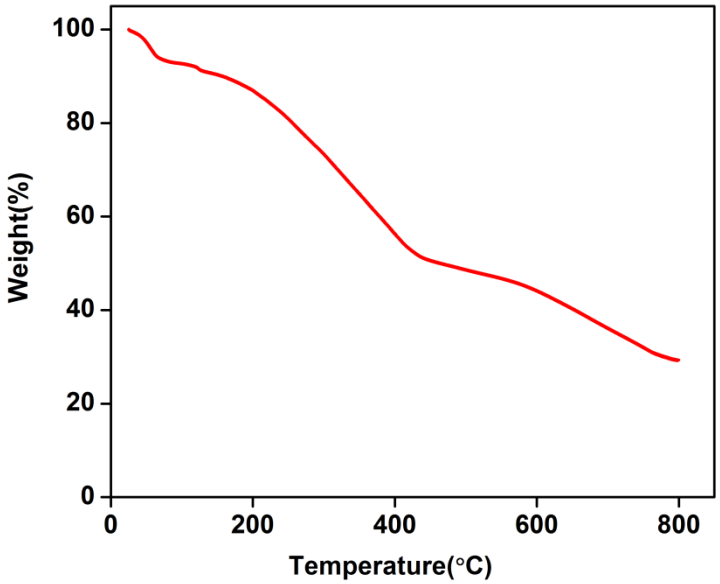


Fig. S10 TGA curve of Complex **1** collected under N2 atmosphere.

Calculated residual mass % of Mn_3O_4 = (228.8117/3*333.2881)*100%

= 22.87% (experimentally obtained 26.12%)

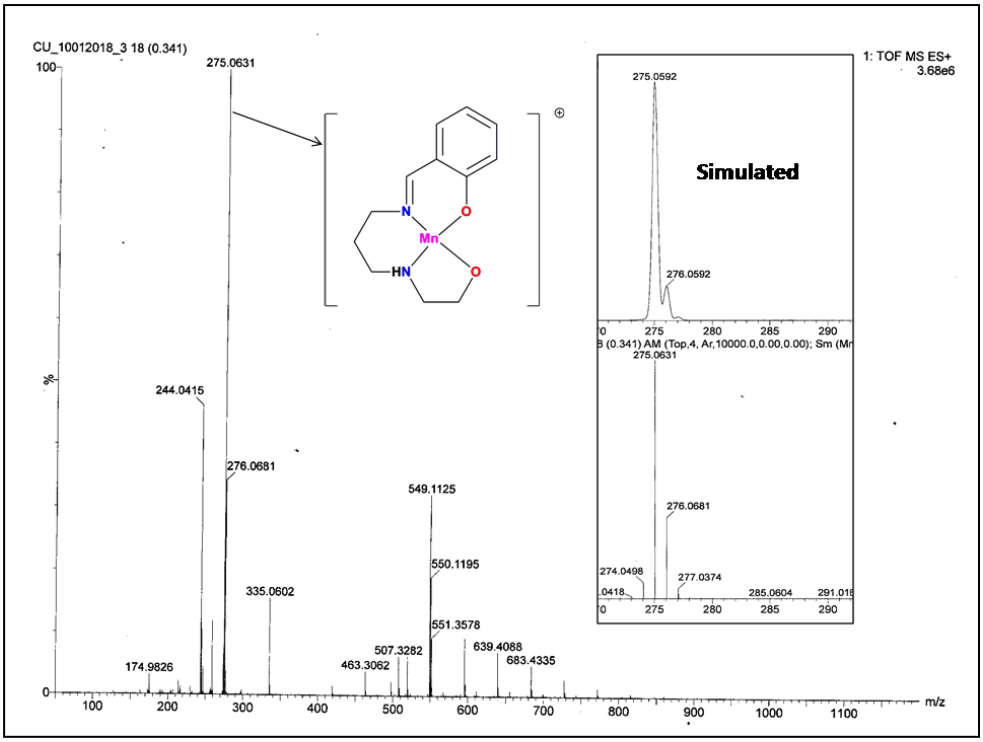


Fig. S11 ESI-MS spectrum of Complex **1.**

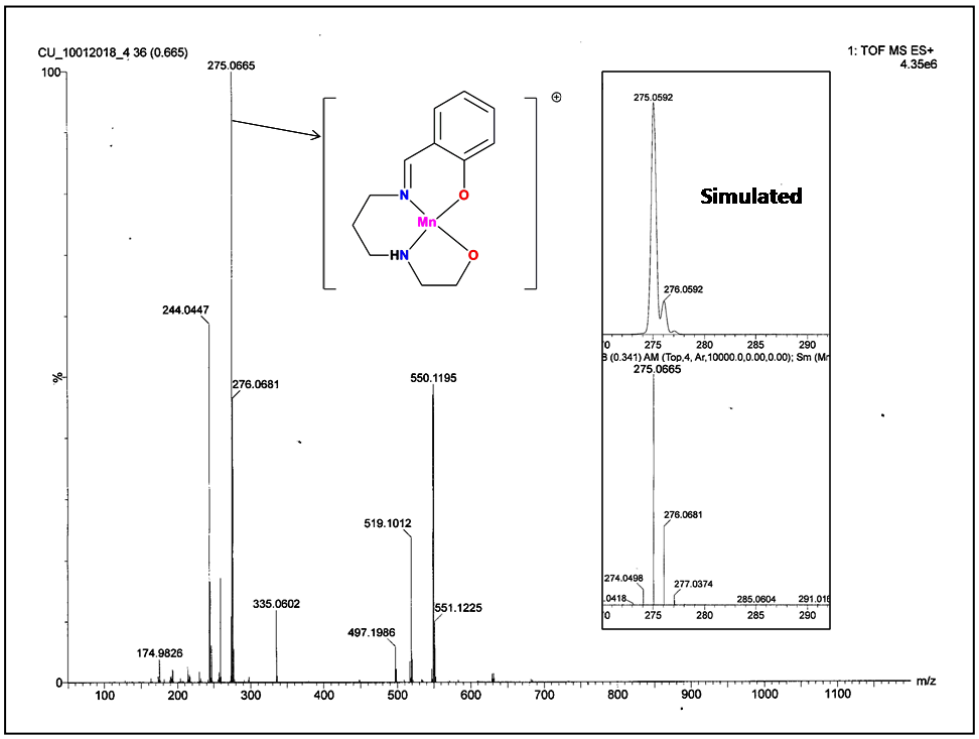


Fig. S12 ESI-MS spectrum of Complex **2.**

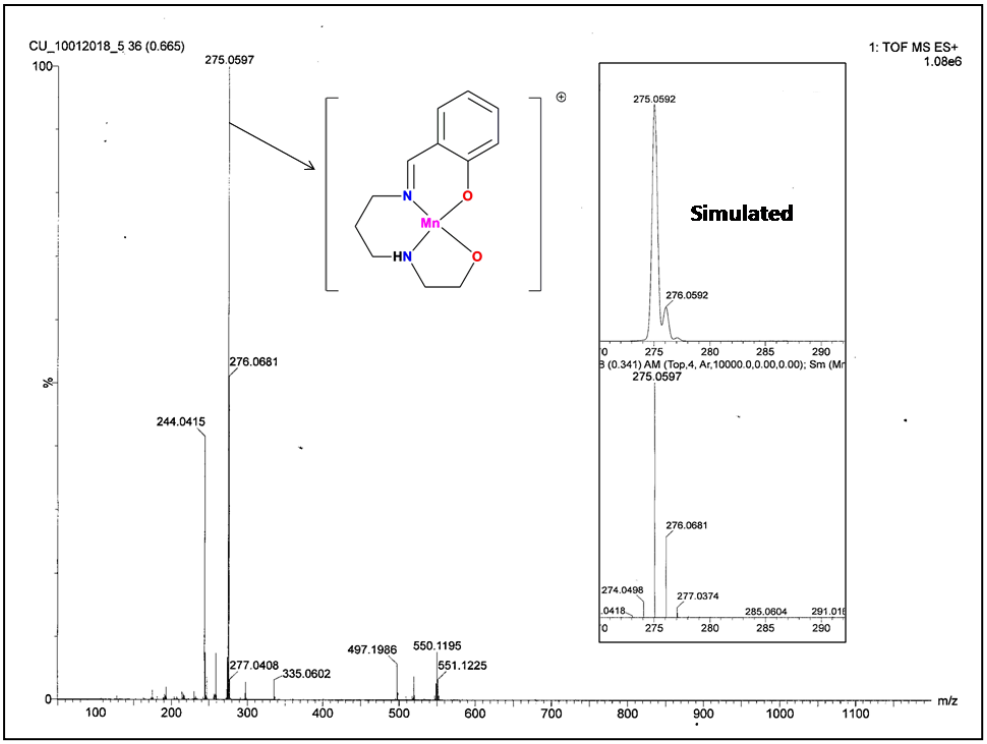


Fig. S13 ESI-MS spectrum of Complex **3.**

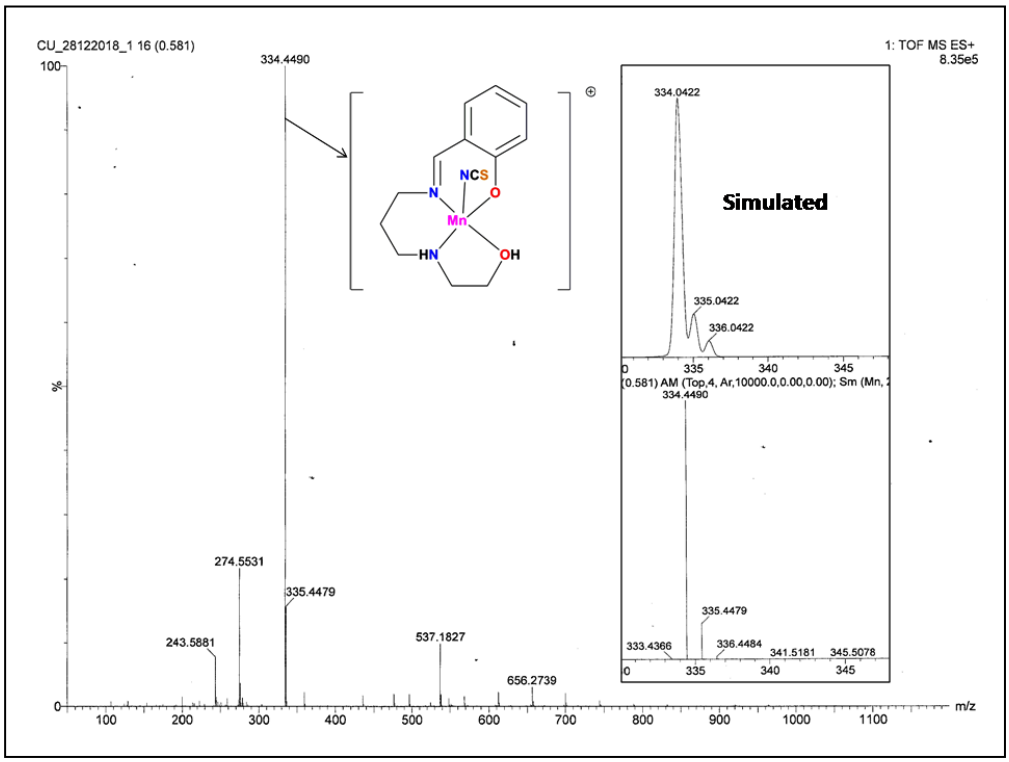


Fig. S14 ESI-MS spectrum of Complex **4.**

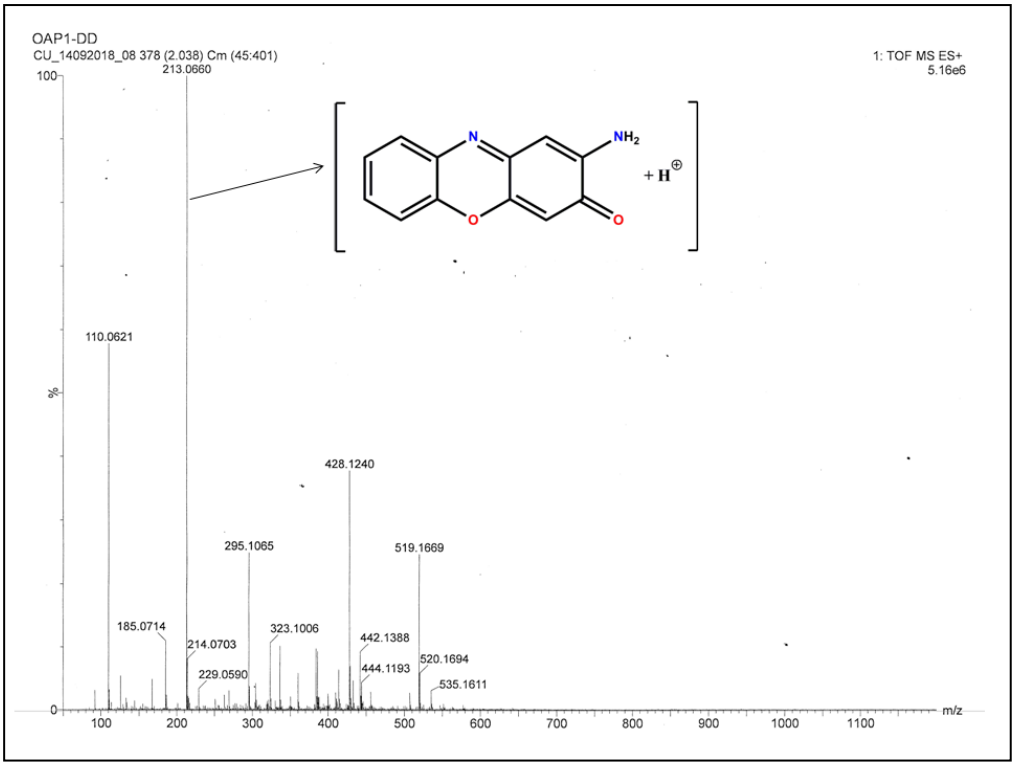


Fig. S15 ESI-MS spectrum of APX.

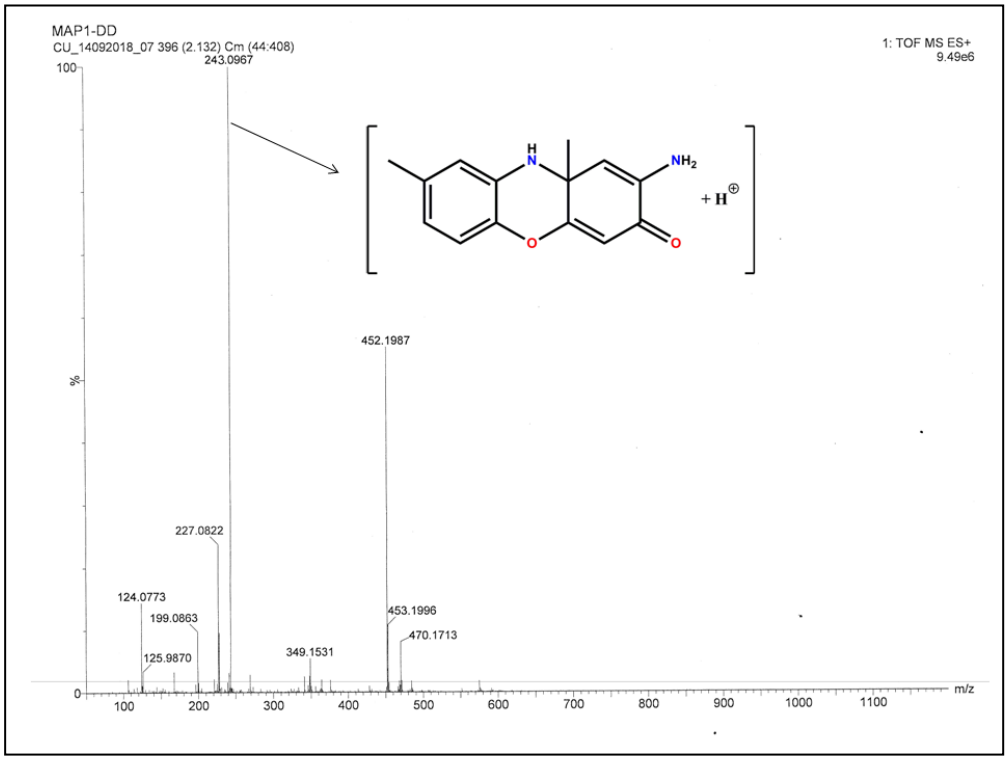


Fig. S16 ESI-MS spectrum of MPX.

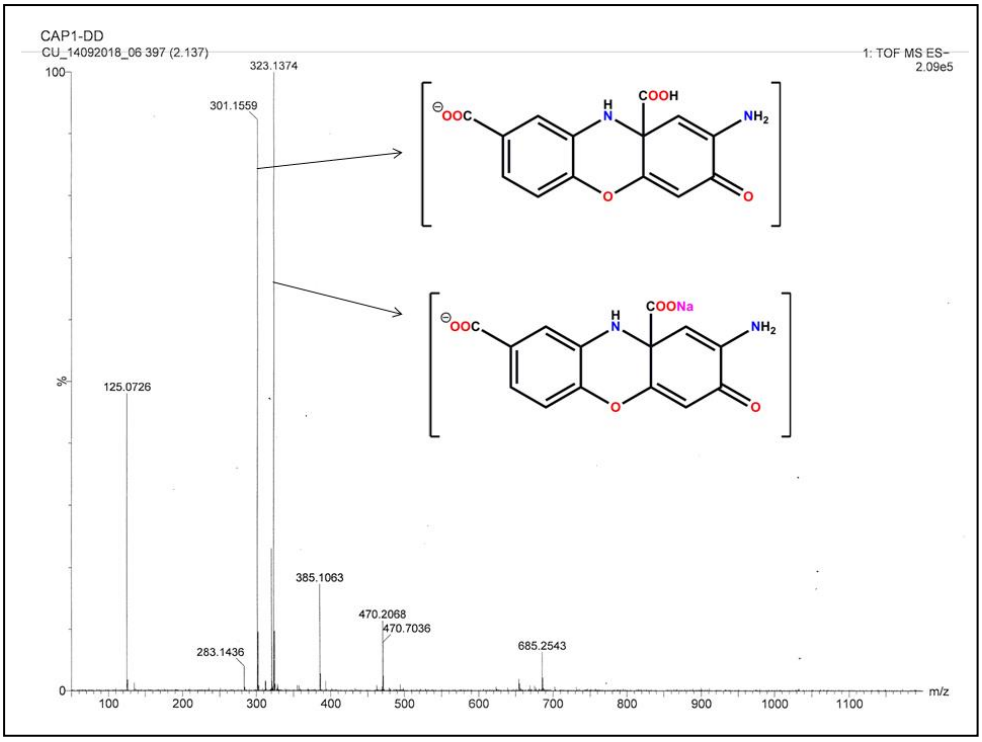


Fig. S17 ESI-MS spectrum of CPX.

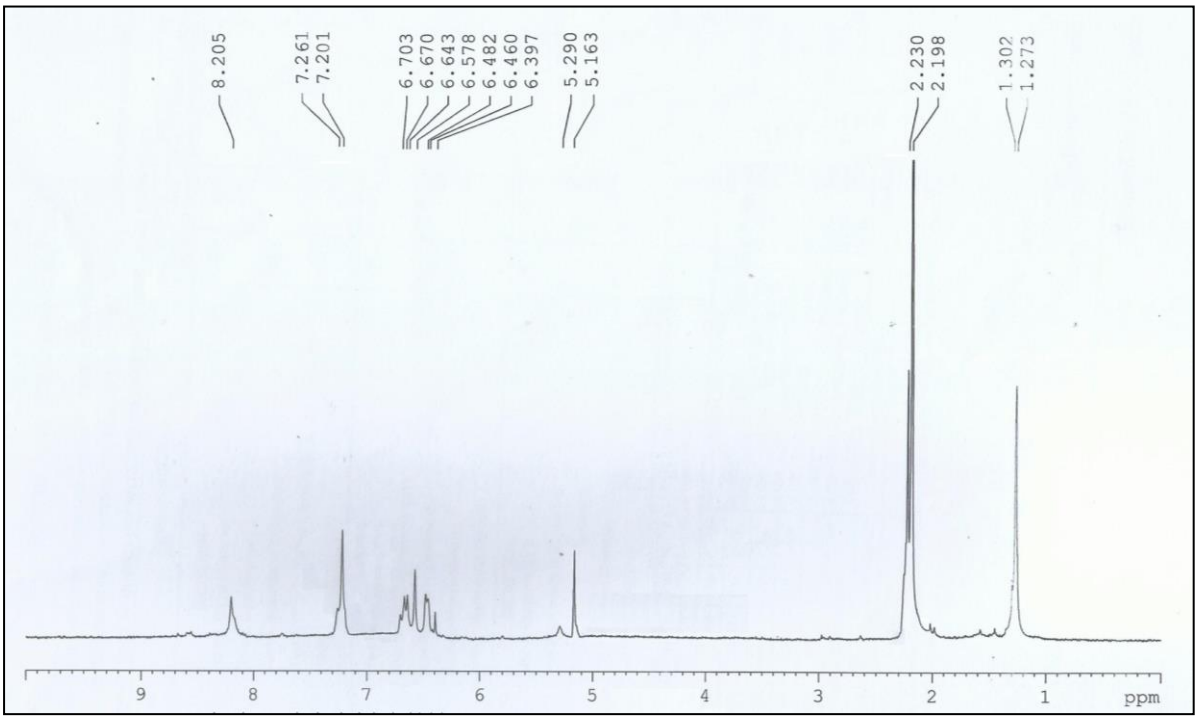


Fig. S18 ^{1}H NMR spectra of MPX in $CDCl_3$.

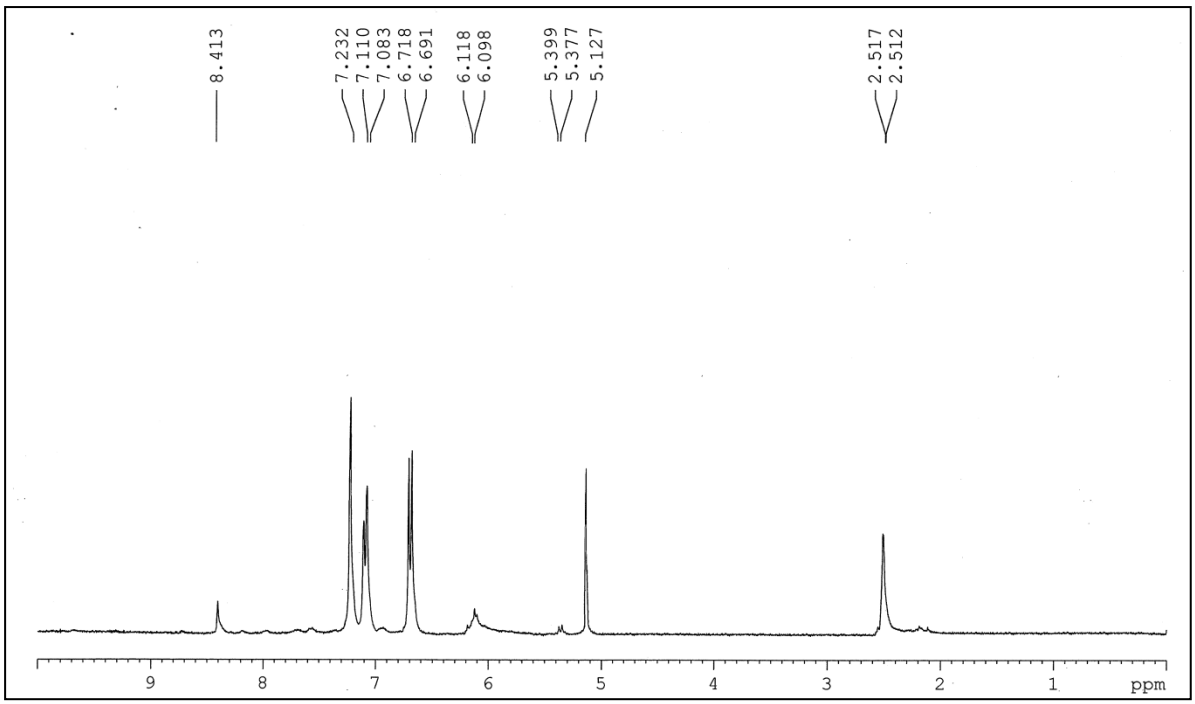


Fig. S19 ^{1}H NMR spectra of CPX in DMSO-d_6.

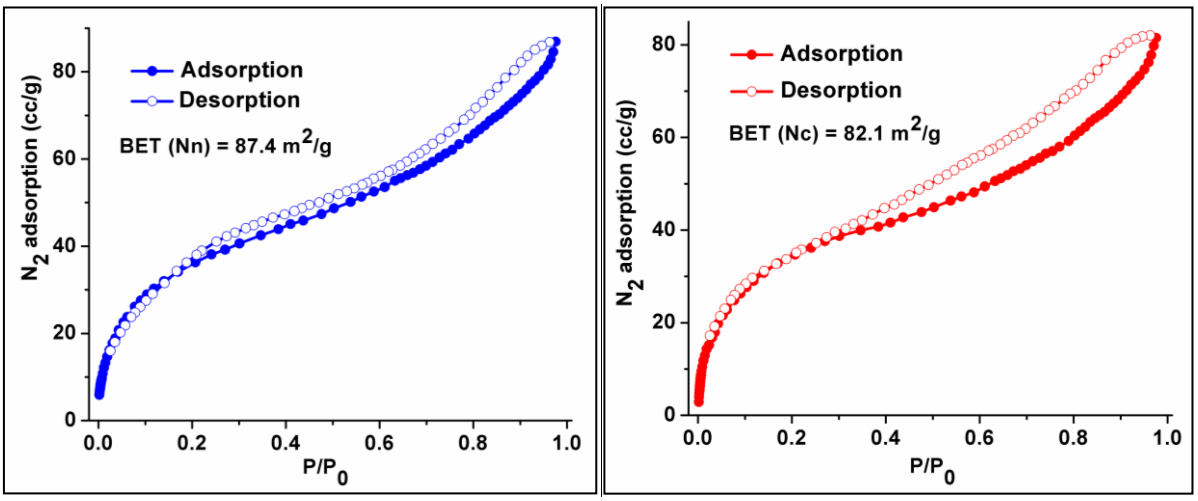
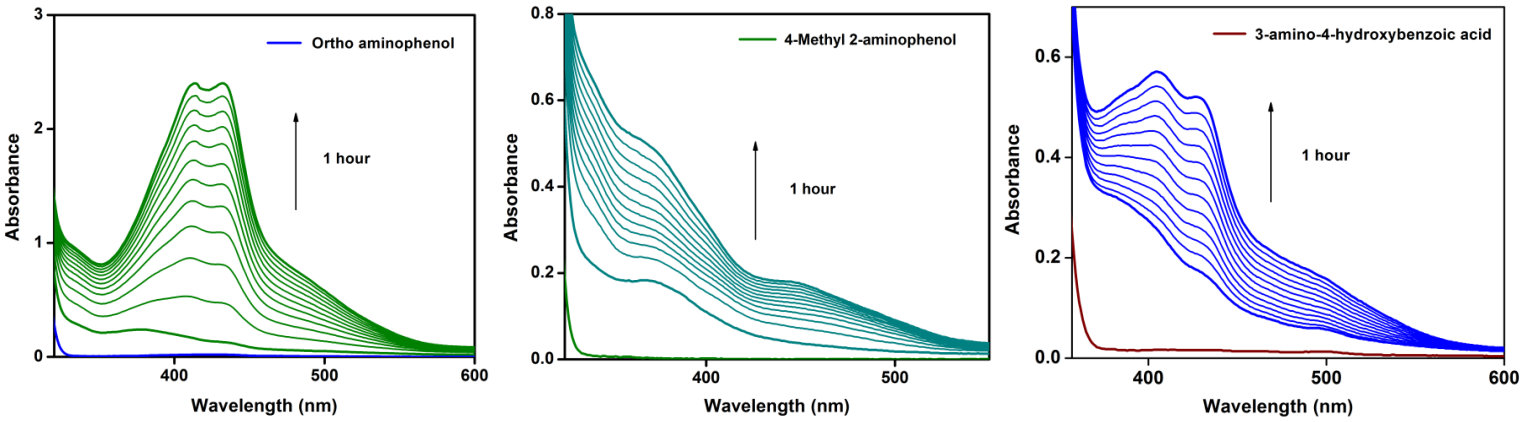
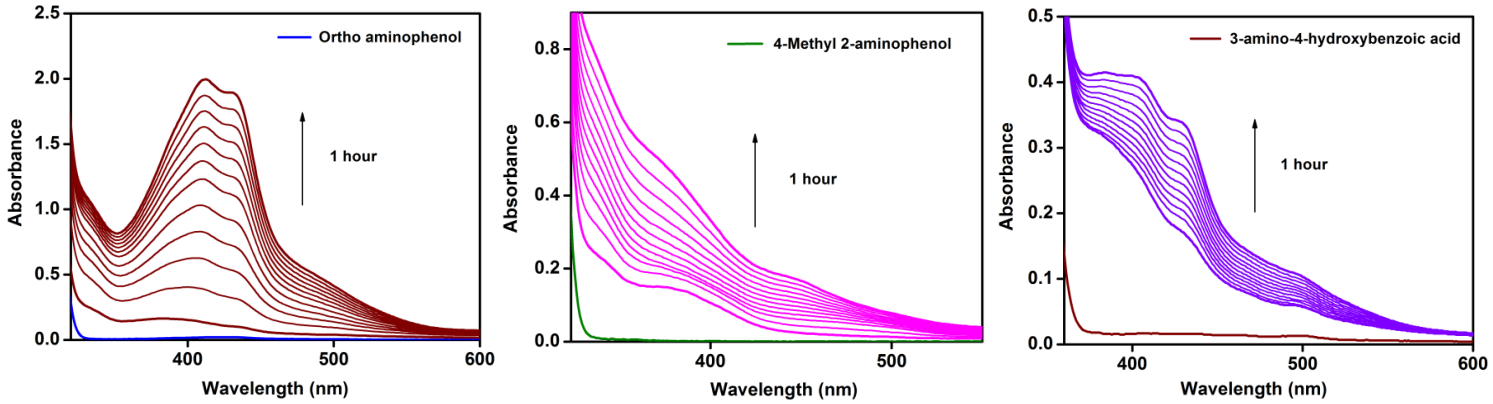


Fig. S20 BET surface area analysis of the synthesized nanoparticles Nn & Nc



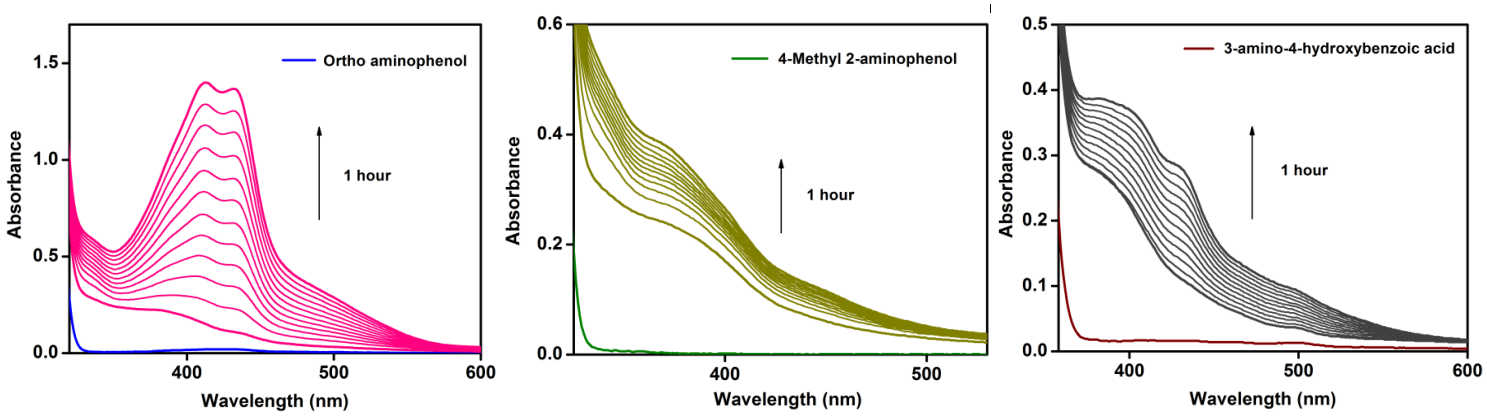
(a) (b) (c)

Fig. S21 Catalytic oxidation of (a) OAP, (b) MAP and (c) CAP by complex **1** in DMF at room temperature. The spectra were recorded at a 5 min interval.



(a) (b) (c)

Fig. S22 Catalytic oxidation of (a) OAP, (b) MAP and (c) CAP by complex **2** in DMF at room temperature. The spectra were recorded at a 5 min interval.



(a) (b) (c)

Fig. S23 Catalytic oxidation of (a) OAP, (b) MAP and (c) CAP by complex **3** in DMF at room temperature. The spectra were recorded at a 5 min interval.

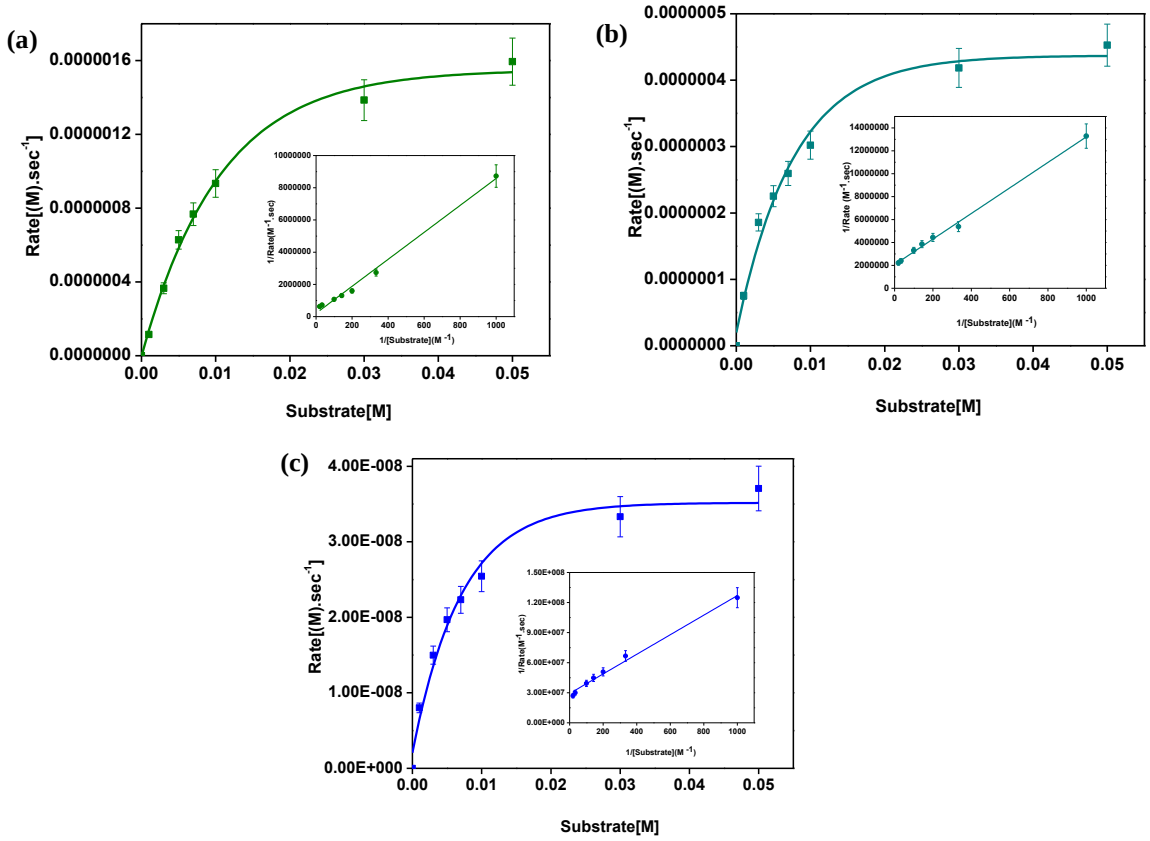


Fig. S24 Plot of rate vs substrate concentration (insets: Lineweaver–Burk plot) of (a) OAP, (b) MAP and (c) CAP for complex **1**.

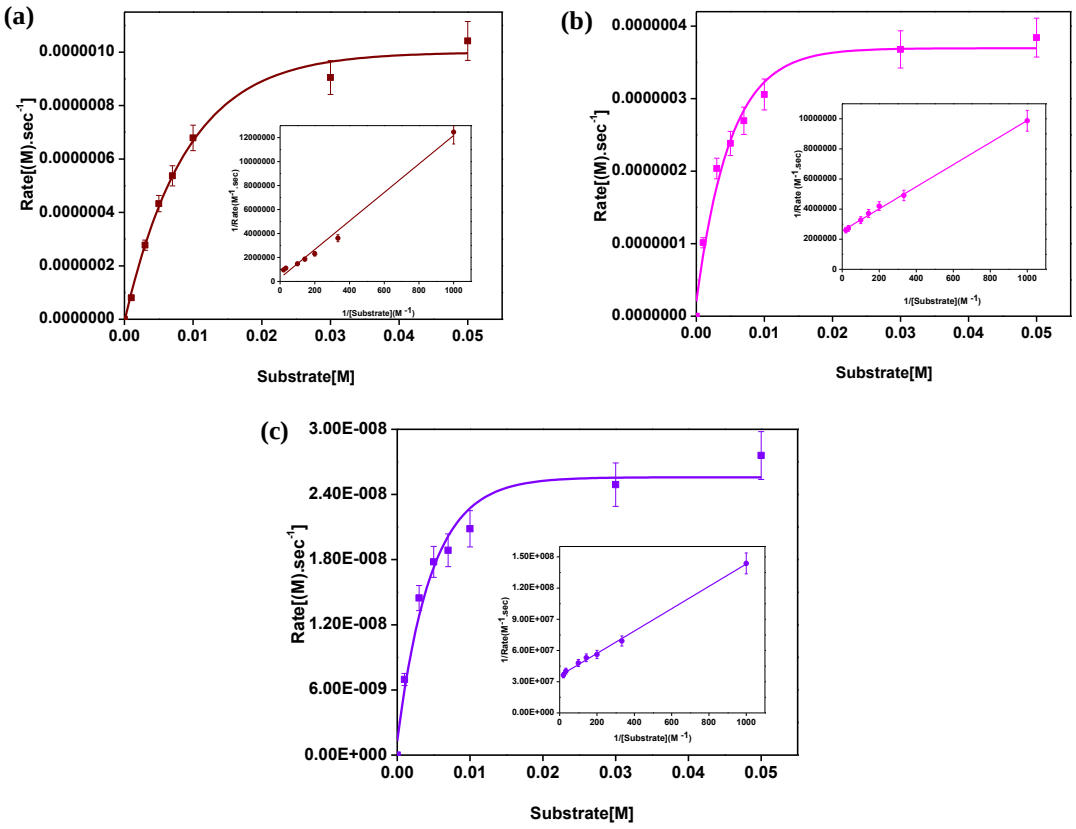


Fig. S25 Plot of rate vs substrate concentration (insets: Lineweaver–Burk plot) of (a) OAP, (b) MAP and (c) CAP for complex **2**.

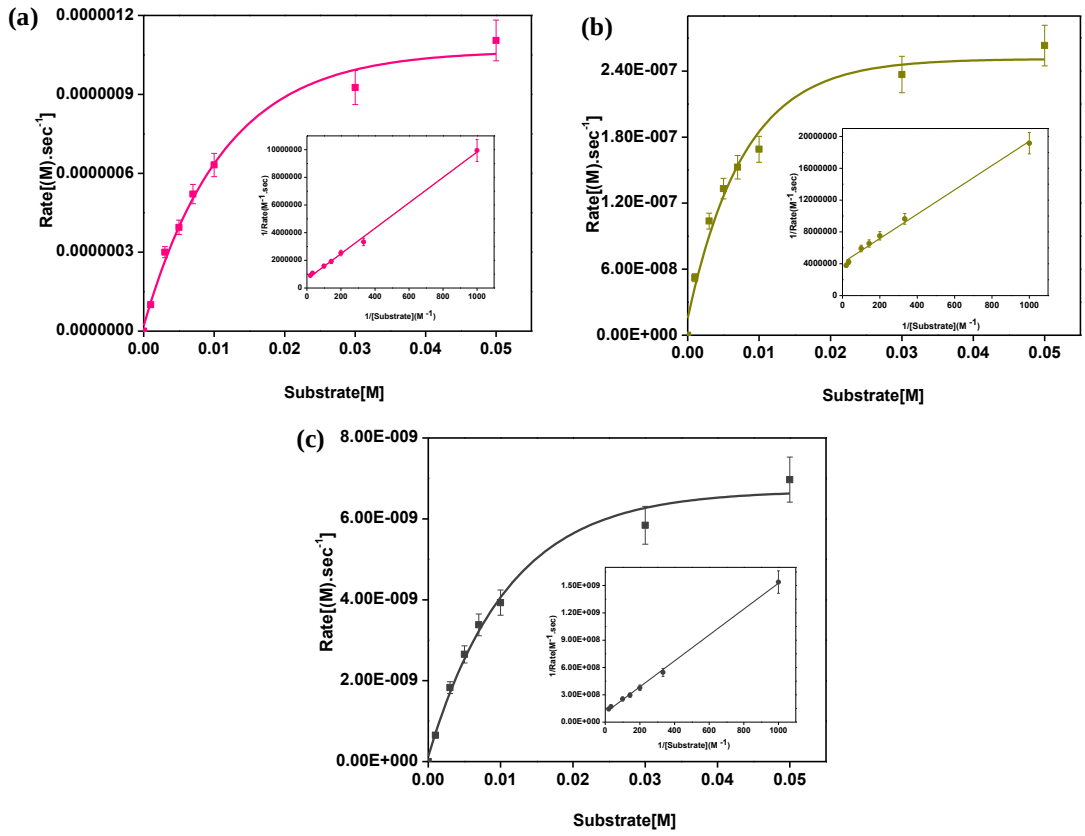


Fig. S26 Plot of rate vs substrate concentration (insets: Lineweaver–Burk plot) of (a) OAP, (b) MAP and (c) CAP for complex **3**.

Table S2 Bond distances (Å) and angles (°) for complexes **1** and **3.** DFT optimized data of complex **1** has also been reported.

Complex	**1**		**3**
	SCXRD	DFT	
Mn(1)-O(1)	1.8754(11)	1.935	1.8682(19)
Mn(1)-O(2)	1.8914(11)	2.012	1.8837(19)
Mn(1)-N(1)	2.0121(13)	2.051	2.009(2)
Mn(1)-N(2)	2.0573(14)	1.782	2.031(2)
Mn(1)-O(3)	2.2615(13)	2.070	2.298(2)
Mn(1)-O(4)	2.2405(13)	2.087	2.261(2)
O(1)-Mn(1)-O(2)	91.95(5)	88.30	92.39(9)
O(1)-Mn(1)-N(1)	90.81(5)	90.15	90.71(9)
O(2)-Mn(1)-N(1)	177.00(5)	175.21	176.43(9)
O(1)-Mn(1)-N(2)	175.90(6)	173.80	175.18(10)
O(2)-Mn(1)-N(2)	85.00(5)	85.63	83.97(9)
N(1)-Mn(1)-N(2)	92.18(6)	95.99	92.84(10)
O(1)-Mn(1)-O(4)	89.80(5)	85.18	91.19(9)
O(2)-Mn(1)-O(4)	93.63(5)	97.92	93.69(9)

N(1)-Mn(1)-O(4)	87.55(5)	86.47	88.03(9)
N(2)-Mn(1)-O(4)	93.13(6)	94.38	92.19(9)
O(1)-Mn(1)-O(3)	89.30(5)	85.55	90.56(9)
O(2)-Mn(1)-O(3)	92.57(5)	73.99	91.16(8)
N(1)-Mn(1)-O(3)	86.28(5)	101.37	87.03(9)
N(2)-Mn(1)-O(3)	88.09(5)	93.99	86.37(9)
O(4)-Mn(1)-O(3)	173.76(5)	167.87	174.78(8)

Table S3 Bond distances (Å) and angles (°) for complex **4.**

Mn(1)-O(2)	1.883(6)	Mn(2)-O(4)	1.876(6)	Mn(3)-O(6)	1.867(6)
Mn(1)-O(1)	1.883(6)	Mn(2)-O(3)	1.890(6)	Mn(3)-O(5)	1.889(6)
Mn(1)-N(1)	2.005(9)	Mn(2)-N(3)	1.990(8)	Mn(3)-N(6)	2.019(7)
Mn(1)-N(2)	2.024(8)	Mn(2)-N(4)	2.031(7)	Mn(3)-N(5)	2.023(8)
Mn(1)-N(7)	2.180(11)	Mn(2)-N(8)	2.135(9)	Mn(3)-N(9)	2.143(9)
Mn(1)-O(4)	2.675(6)	Mn(2)-O(6)	2.692(6)	Mn(3)-O(2')	2.847(6)

O(2)-Mn(1)-O(1)	91.8(3)	O(4)-Mn(2)-O(3)	92.1(3)	O(6)-Mn(3)-O(5)	91.6(3)
O(2)-Mn(1)-N(1)	176.2(3)	O(4)-Mn(2)-N(3)	173.7(3)	O(6)-Mn(3)-N(6)	86.0(3)
O(1)-Mn(1)-N(1)	90.5(3)	O(3)-Mn(2)-N(3)	90.3(3)	O(5)-Mn(3)-N(6)	160.7(3)
O(2)-Mn(1)-N(2)	85.5(3)	O(4)-Mn(2)-N(4)	85.6(3)	O(6)-Mn(3)-N(5)	172.5(3)
O(1)-Mn(1)-N(2)	164.2(3)	O(3)-Mn(2)-N(4)	165.1(3)	O(5)-Mn(3)-N(5)	89.5(3)
N(1)-Mn(1)-N(2)	91.5(3)	N(3)-Mn(2)-N(4)	90.6(3)	N(6)-Mn(3)-N(5)	90.6(3)
O(2)-Mn(1)-N(7)	95.2(3)	O(4)-Mn(2)-N(8)	95.9(3)	O(6)-Mn(3)-N(9)	99.1(3)
O(1)-Mn(1)-N(7)	100.3(3)	O(3)-Mn(2)-N(8)	100.5(3)	O(5)-Mn(3)-N(9)	101.0(3)
N(1)-Mn(1)-N(7)	87.5(3)	N(3)-Mn(2)-N(8)	89.3(3)	N(6)-Mn(3)-N(9)	98.2(3)
N(2)-Mn(1)-N(7)	95.4(3)	N(4)-Mn(2)-N(8)	94.3(3)	N(5)-Mn(3)-N(9)	88.0(3)
O(2)-Mn(1)-O(4)	86.6(2)	O(4)-Mn(2)-O(6)	88.3(2)	O(2')-Mn(3)-N(9)	167.4(3)
O(1)-Mn(1)-O(4)	87.1(2)	O(3)-Mn(2)-O(6)	88.9(2)	O(2')-Mn(3)-O(5)	89.1(2)
N(1)-Mn(1)-O(4)	90.4(3)	N(3)-Mn(2)-O(6)	85.9(3)	O(2')-Mn(3)-O(6)	88.0(2)
N(2)-Mn(1)-O(4)	77.2(3)	N(4)-Mn(2)-O(6)	76.3(2)	O(2')-Mn(3)-N(5)	84.6(3)
N(7)-Mn(1)-O(4)	172.2(3)	N(8)-Mn(2)-O(6)	169.4(3)	O(2')-Mn(3)-N(6)	71.8(3)

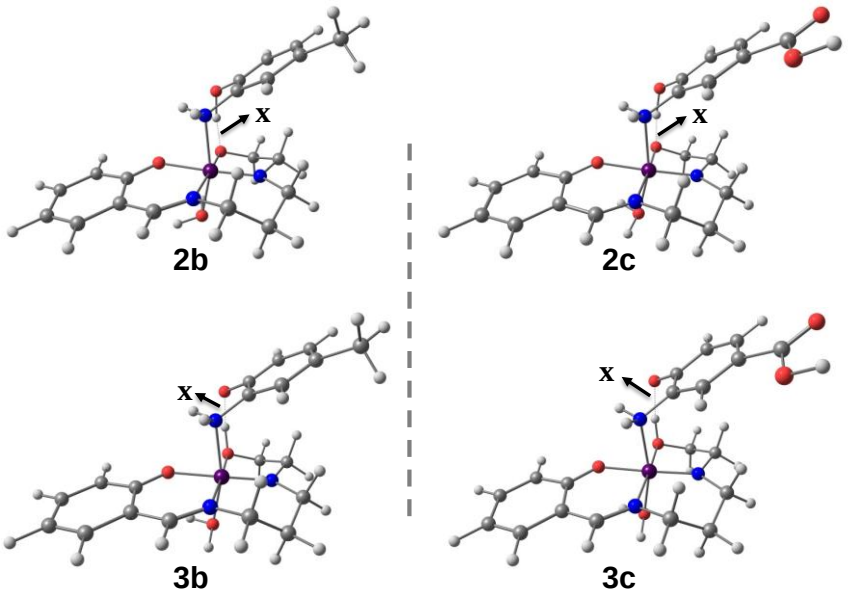
O2' atom at 1-x, 1-y, 2-z.

Table S4 Hydrogen bond parameters (Å/°) for complexes **1**, **3** and **4**.

Complex 1						
D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A	Symmetry code
N2-H2a	0.82(2)	2.52(2)	176.9(16)	3.3421(15)	Cl1	-
O3-H3a	0.83(2)	1.91(2)	169(2)	2.7267(17)	O2	1-x,-1/2+y,1/2-z
O3-H3b	0.82(2)	2.270(19)	172.2(18)	3.0869(13)	Cl1	-
O4-H4a	0.81(2)	2.36(2)	164(2)	3.1463(14)	Cl1	x,1+y,z
O4-H4b	0.81(2)	1.94(2)	176(2)	2.7536(18)	O2	1-x,1/2+y,1/2-z
Complex 3						

N2-H2a	0.98	2.53	107	2.969(4)	O3	-
N2-H2a	0.98	1.91	154	2.826(6)	O11	x,-1+y,z
N2-H2a	0.98	2.10	173	3.080(8)	O22 [a]	x,-1+y,z
O3-H3a	0.86(3)	1.88(3)	165(3)	2.716(3)	O2	1-x,-1/2+y,1/2-z
O3-H3b	0.82(3)	1.93(3)	162(3)	2.720(6)	O10	x,-1+y,z
O3-H3b	0.82(3)	2.14(3)	154(3)	2.898(9)	O22 [a]	x,-1+y,z
O4-H4a	0.84(3)	1.92(3)	173(3)	2.760(3)	O2	1-x,1/2+y,1/2-z
O4-H4b	0.83(3)	1.95(3)	158(3)	2.733(3)	O10	-
O4-H4b	0.83(3)	2.01(3)	163(4)	2.814(7)	O20 [a]	-
Complex 4						
N2-H2a	0.98	2.02	165	2.981(11)	O3	-
N2-H2a	0.98	2.38	119	2.978(13)	O4	-
N4-H4a	0.98	2.06	165	3.022(10)	O5	-
N4-H4a	0.98	2.37	119	2.965(10)	O6	-
N6-H6a	0.98	2.11	161	3.050(10)	O1	1-x,1-y,2-z
N6-H6a	0.98	2.28	123	2.930(12)	O2	1-x,1-y,2-z

[a] O20 and O22 in **3** represent disordered nitrate oxygen atoms.



Structure	O···H bond distance (x) in angstrom
2b	**1.380**
3b	**1.402**
2c	**1.337**
3c	**1.516**

Fig. S27 M06-2X/cc-PVTZ calculated structures of **2b**, **2c**, **3b** and **3c**.The O···H bond (x) distances are provided in Å.

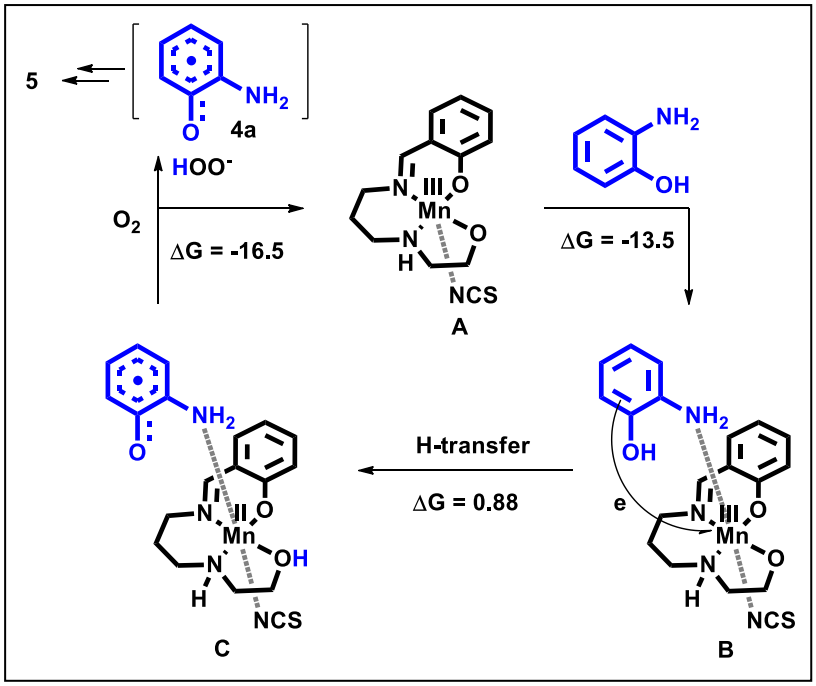


Fig. S28 Proposed mechanism of phenoxazinone synthase activity exhibited by complex **4**. M06-2X/cc-PVTZ calculated free energies are provided in kcal/mol at 25 °C.

XYZ coordinates for complex 1

1

Charge 0, Multiplicity 1

C	2.142167000	-0.718186000	0.091858000
C	3.260128000	-1.579473000	-0.064070000
C	4.543848000	-1.087499000	-0.189745000
C	4.795789000	0.294753000	-0.157497000
C	3.729456000	1.155184000	0.008567000
C	2.406642000	0.683699000	0.129979000
H	3.063511000	-2.647126000	-0.085479000
H	5.369638000	-1.782653000	-0.314124000
H	5.806024000	0.676437000	-0.253362000
H	3.898492000	2.229052000	0.051526000
O	0.953122000	-1.236631000	0.198860000
C	1.368548000	1.672876000	0.346948000
H	1.721749000	2.704363000	0.461929000
N	0.106964000	1.448467000	0.414277000
Mn	-0.773689000	-0.372464000	0.074682000
C	-0.787298000	2.582837000	0.617703000

H	-1.294834000	2.452482000	1.582439000
H	-0.213065000	3.516119000	0.658761000
C	-1.820014000	2.629578000	-0.507566000
H	-2.279816000	3.622859000	-0.532749000
H	-1.304135000	2.480918000	-1.463219000
C	-2.924768000	1.594840000	-0.335412000
H	-3.561510000	1.892533000	0.515509000
H	-3.577195000	1.598118000	-1.221657000
N	-2.434297000	0.252640000	-0.094962000
C	-3.491740000	-0.745313000	0.049619000
H	-3.753985000	-0.877594000	1.113874000
H	-4.406937000	-0.428039000	-0.468548000
C	-2.925435000	-2.045563000	-0.528097000
H	-3.554343000	-2.901079000	-0.234088000
H	-2.977464000	-1.969829000	-1.629959000
O	-1.606804000	-2.195636000	-0.097229000
O	-1.071134000	-1.048757000	2.008270000
H	-1.440068000	-1.833714000	1.468796000
O	-0.289754000	-0.086764000	-1.935308000
H	-0.344695000	-0.974927000	-2.329144000
H	0.649609000	0.160869000	-1.997140000
H	-1.834792000	-0.599037000	2.403906000

2a

Charge 0, Multiplicity 1

C	-2.748832387	-1.006570271	-0.104260618
C	-3.642842424	-2.100458492	0.033225981
C	-4.971348786	-2.002016707	-0.330735251
C	-5.489589529	-0.809836987	-0.863200808
C	-4.637613629	0.264731502	-1.023936810
C	-3.280118407	0.198485390	-0.651770155
H	-3.240679885	-3.021765608	0.443736290
H	-5.623297803	-2.861960428	-0.202981809
H	-6.532796858	-0.738579037	-1.149848715
H	-5.009758059	1.194413906	-1.449189468

O	-1.510194080	-1.147171607	0.275752677
C	-2.462971895	1.364071837	-0.929171748
H	-2.964004852	2.153111099	-1.502452216
N	-1.236758141	1.544657277	-0.593723644
Mn	-0.143248810	0.240855025	0.577418635
C	-0.584048167	2.762879926	-1.063327706
H	0.129828346	2.484978790	-1.852353209
H	-1.321545565	3.441004696	-1.509436827
C	0.168742454	3.452228545	0.065755565
H	0.456098929	4.455285079	-0.266360839
H	-0.500499017	3.569359812	0.926816909
C	1.429367547	2.709999773	0.484902576
H	2.138783096	2.677618888	-0.361096267
H	1.928667448	3.276487722	1.283165927
N	1.186330195	1.355185892	0.946182680
C	2.328290465	0.789761060	1.663403064
H	3.100399759	0.488695189	0.937603658
H	2.779776556	1.546077060	2.320753393
C	1.828367192	-0.403495536	2.478856738
H	2.662949565	-1.082669134	2.708346623
H	1.438552476	-0.030023930	3.439137758
O	0.808417733	-1.076220051	1.780508402
O	-1.250675502	0.535170711	2.319623600
H	-0.883599532	-0.280577186	2.720534104
H	-2.184140994	0.332966792	2.137178630
C	2.106429199	-0.727163096	-1.219297937
C	2.710607798	-1.764211330	-0.483750557
C	2.870344713	0.177299779	-1.945876821
C	4.101663970	-1.888766954	-0.539486680
C	4.259028054	0.051801690	-1.973336358
H	2.377221897	0.975576888	-2.496282016
C	4.869641448	-0.989606436	-1.276828500
H	4.564886154	-2.694987014	0.021308380
H	4.853959281	0.756762096	-2.544271513

H	5.949498006	-1.099312817	-1.299897453
H	1.389887749	-1.994692893	0.948204666
H	0.259270393	-1.548158314	-1.086934303
H	0.295124268	-0.151702417	-1.965222483
N	0.679233396	-0.616449690	-1.142456109
O	1.950489659	-2.602760416	0.244999012

2b

Charge 0, Multiplicity 1

C	-2.981532261	-0.863540010	-0.366458420
C	-3.935456275	-1.908679894	-0.479925664
C	-5.214855519	-1.675856192	-0.944646478
C	-5.620542906	-0.388525640	-1.333697063
C	-4.707784120	0.643795983	-1.247551769
C	-3.398786405	0.439942619	-0.767033426
H	-3.619877189	-2.903378603	-0.179788500
H	-5.915813228	-2.503569845	-1.010477716
H	-6.624923442	-0.211957184	-1.701910763
H	-4.991456993	1.647592836	-1.556819358
O	-1.794425234	-1.135939820	0.096834145
C	-2.506671882	1.582780794	-0.780448070
H	-2.916267244	2.480815752	-1.258307826
N	-1.309318925	1.634830139	-0.318900202
Mn	-0.375380348	0.094575616	0.694053534
C	-0.560252125	2.868184611	-0.540443962
H	0.187874328	2.674089276	-1.322891792
H	-1.227482722	3.655628404	-0.911397213
C	0.153806955	3.317501605	0.726270374
H	0.520564360	4.338354370	0.576670378
H	-0.562728145	3.343254016	1.556164766
C	1.338006153	2.434771511	1.092209671
H	2.099278427	2.484314143	0.292655657
H	1.815619312	2.836905473	1.996589465
N	0.984191365	1.045916716	1.320150654
C	2.037133967	0.303551416	2.011360389

H	2.848986590	0.083065482	1.300431922
H	2.469637941	0.914656416	2.816101928
C	1.420593788	-0.976543166	2.578154203
H	2.201910237	-1.734584284	2.737630234
H	0.985163464	-0.747476094	3.564287648
O	0.419896855	-1.459467678	1.714551750
O	-1.580463526	0.178230602	2.395053054
H	-1.287393524	-0.715095209	2.672103273
H	-2.508127119	0.069503198	2.124969453
C	1.939192254	-0.693102073	-1.089756934
C	2.450952163	-1.865278893	-0.503316357
C	2.782297556	0.286683891	-1.592904484
C	3.835729647	-2.031921571	-0.484922685
C	4.171874149	0.128387397	-1.549751666
H	2.353130574	1.187577995	-2.029749828
C	4.681089774	-1.048778507	-0.999423732
H	4.237691627	-2.937505773	-0.040596891
H	5.757189172	-1.197144461	-0.961563217
H	1.026704936	-2.267416031	0.773911143
H	0.058256065	-1.436808308	-1.205187955
H	0.206776539	0.076802669	-1.849862901
N	0.515412290	-0.528504665	-1.089117688
O	1.608457532	-2.778799165	0.020995107
C	5.077330289	1.203239525	-2.096908771
H	4.939426169	1.329106450	-3.176240384
H	4.870078549	2.171392056	-1.628826623
H	6.127809571	0.959916946	-1.918454327

2c

Charge 0, Multiplicity 1

C	-3.328786839	-0.325196353	-0.843363011
C	-4.359102880	-1.020188118	-1.528642786
C	-5.511807036	-0.383821784	-1.943947441
C	-5.705390128	0.987736852	-1.708774192
C	-4.712953123	1.690774757	-1.056207097

C	-3.528802610	1.067122965	-0.612391959
H	-4.206235215	-2.079897839	-1.709538324
H	-6.278617150	-0.954179606	-2.460963668
H	-6.611100803	1.484036848	-2.038862260
H	-4.832534481	2.756573721	-0.873443034
O	-2.271190652	-0.983731510	-0.458905685
C	-2.535977189	1.916946172	0.013865502
H	-2.775908270	2.986743070	0.005280660
N	-1.423846111	1.551327027	0.545288050
Mn	-0.797895044	-0.414270643	0.712308032
C	-0.534201787	2.607793950	1.021130054
H	0.278322362	2.721195047	0.288812242
H	-1.070883828	3.563107583	1.066600667
C	0.067862220	2.261000815	2.374577069
H	0.553747478	3.155173838	2.778712910
H	-0.734083676	1.979753691	3.068523709
C	1.100374876	1.145385634	2.302075553
H	1.941297322	1.458576543	1.657047645
H	1.523918821	0.985397360	3.302938118
N	0.562786884	-0.108049527	1.806107351
C	1.389999934	-1.262663484	2.150739856
H	2.291305208	-1.264839990	1.515781133
H	1.731314497	-1.192903105	3.193183052
C	0.548201171	-2.518727069	1.933062265
H	1.199879249	-3.400352241	1.836138160
H	-0.088034985	-2.671847152	2.817818579
O	-0.257643173	-2.356323100	0.794823699
O	-2.216938871	-0.837757437	2.178543358
H	-2.714554402	-1.538066374	1.718164972
H	-2.839172998	-0.097253253	2.279382845
C	1.640491277	-0.443187004	-1.100672803
C	2.089040434	-1.783854919	-1.096259464
C	2.537452006	0.608867638	-1.073492672
C	3.470786262	-2.021242774	-1.129126134

C	3.913949453	0.351622936	-1.065957188
H	2.176768497	1.633760142	-1.075523125
C	4.372224889	-0.967535511	-1.110840414
H	3.810037034	-3.051757787	-1.144480741
H	5.441389949	-1.151857472	-1.117013796
H	0.500875791	-2.618670659	-0.274585841
H	-0.240478780	-0.950209190	-1.657479454
H	-0.012161552	0.675663566	-1.519924062
N	0.223788529	-0.225484013	-1.103301755
O	1.210524179	-2.783749619	-1.076669323
C	4.906989191	1.445070352	-1.019534055
O	6.110138226	1.291335895	-1.054565060
O	4.346181430	2.664646637	-0.924739359
H	5.072512130	3.313276654	-0.906281128

3a

Charge 0, Multiplicity 3

C	-2.785494316	-0.952391516	0.030123415
C	-3.710249021	-2.013576584	0.200916430
C	-4.992288859	-1.946200149	-0.308380159
C	-5.427363047	-0.818988049	-1.024739042
C	-4.542942761	0.223847268	-1.213353689
C	-3.230793267	0.186850370	-0.699528401
H	-3.371722164	-2.884299117	0.754370744
H	-5.671864103	-2.779376498	-0.151701359
H	-6.433820603	-0.771275311	-1.424944683
H	-4.851158875	1.103455746	-1.774173092
O	-1.591119569	-1.064735317	0.546747521
C	-2.379575149	1.319746363	-0.998420412
H	-2.829749939	2.071946422	-1.656505768
N	-1.173091238	1.514275095	-0.598605833
Mn	-0.136208107	0.241228095	0.639257230
C	-0.477422127	2.687115503	-1.122414579
H	0.230775786	2.345344260	-1.891066229
H	-1.190331833	3.364757662	-1.606784274

C	0.293176367	3.405167754	-0.024923719
H	0.609702151	4.383765186	-0.400026250
H	-0.370953781	3.582694550	0.830385997
C	1.531128861	2.644255321	0.424630875
H	2.239528390	2.558667780	-0.418288686
H	2.045263717	3.223387431	1.203935393
N	1.247863454	1.312753285	0.929101897
C	2.378250089	0.741415427	1.659105616
H	3.123478767	0.371447503	0.937613183
H	2.867605691	1.507857762	2.275196524
C	1.856120952	-0.384654709	2.543377203
H	2.663836996	-1.062817050	2.841605626
H	1.402129735	0.038067424	3.445278860
O	0.841236248	-1.100811976	1.853852369
O	-1.228061642	0.839615378	2.322512907
H	-1.817923350	0.070741473	2.428158912
H	-1.807758384	1.590832226	2.111621486
C	2.010398345	-0.814927143	-1.210381830
C	2.685718475	-1.824533832	-0.473643272
C	2.681474473	0.097268599	-2.008967979
C	4.087228544	-1.871766077	-0.624415395
C	4.072501012	0.035727402	-2.121753643
H	2.117382109	0.855910333	-2.548829846
C	4.764031957	-0.958027783	-1.429180747
H	4.627768816	-2.640147847	-0.078491274
H	4.600566459	0.746942683	-2.747934902
H	5.845760743	-1.020627864	-1.513060633
H	1.306565616	-1.817144930	1.219415944
H	0.252327588	-1.720473243	-0.850257132
H	0.108312529	-0.416563568	-1.861574652
N	0.583694148	-0.767880110	-1.029950909
O	2.005045717	-2.634794161	0.302201485

3b

Charge 0, Multiplicity 3

C	-3.004802302	-0.828840271	-0.312642681
C	-3.983633630	-1.846023720	-0.448775116
C	-5.219539266	-1.591131740	-1.009410365
C	-5.551791669	-0.308217701	-1.474809055
C	-4.612079769	0.696836477	-1.365139187
C	-3.344708195	0.469141561	-0.790473862
H	-3.723276307	-2.836972150	-0.089307128
H	-5.943330974	-2.397257077	-1.092131882
H	-6.522438742	-0.114466860	-1.917293841
H	-4.839544492	1.696499397	-1.729115237
O	-1.859673318	-1.124863082	0.241344514
C	-2.424924051	1.587872537	-0.770894833
H	-2.790470170	2.491546938	-1.272315677
N	-1.246612479	1.618333567	-0.257034090
Mn	-0.370838420	0.045722502	0.737636043
C	-0.463335428	2.835372447	-0.456048657
H	0.288108966	2.631522258	-1.232294531
H	-1.107003350	3.643428223	-0.823163786
C	0.248412734	3.248377298	0.823328361
H	0.639033917	4.263044509	0.695441036
H	-0.473481344	3.277554544	1.648973459
C	1.409427089	2.332413814	1.179710717
H	2.178513194	2.383224355	0.388202313
H	1.886033754	2.700284079	2.098773062
N	1.024015128	0.945302129	1.364666632
C	2.061223703	0.165686984	2.038001289
H	2.860963459	-0.068715782	1.317970444
H	2.513315173	0.748193658	2.852274897
C	1.424103291	-1.102257159	2.595732413
H	2.177973963	-1.875563453	2.782259455
H	0.916974742	-0.873392762	3.538617260
O	0.440677117	-1.582728934	1.690913402
O	-1.590119953	0.313544929	2.420785885
H	-2.190230766	-0.446901829	2.309850225

H	-2.146265133	1.104326772	2.317442860
C	1.888618785	-0.705374223	-1.114624561
C	2.444069155	-1.895265251	-0.574599178
C	2.671298395	0.321915454	-1.612360214
C	3.847844631	-1.986192719	-0.607752133
C	4.068808413	0.222858236	-1.614734103
H	2.192172318	1.216908702	-2.009792437
C	4.634189852	-0.950082187	-1.111397109
H	4.307398030	-2.886365554	-0.208596380
H	5.717110875	-1.055009569	-1.106258268
H	0.926028964	-2.177520458	0.946416576
H	0.066895413	-1.554753450	-1.123675608
H	0.078761154	-0.052039291	-1.821823386
N	0.455134239	-0.609205783	-1.054599985
O	1.654114416	-2.816185538	-0.067520371
C	4.915788350	1.349075483	-2.153224872
H	4.723961068	1.525850847	-3.217575477
H	4.711687331	2.289960040	-1.629544716
H	5.980488742	1.127410541	-2.038973916

3c

Charge 0, Multiplicity 3

C	-3.354225448	-0.428771687	-0.707036897
C	-4.399204991	-1.203478183	-1.269241686
C	-5.545355286	-0.616898432	-1.769122095
C	-5.714222096	0.777346033	-1.743591939
C	-4.705046686	1.554713762	-1.212077314
C	-3.526500689	0.984292967	-0.689252838
H	-4.265108830	-2.280778285	-1.287399345
H	-6.325611264	-1.246412980	-2.187911912
H	-6.615294532	1.232526839	-2.138818551
H	-4.806476206	2.637533711	-1.190699611
O	-2.301187593	-1.039297767	-0.231533568
C	-2.515356210	1.899553703	-0.202475387
H	-2.746641593	2.960522337	-0.351143501

N	-1.393143247	1.599286361	0.349910518
Mn	-0.779061625	-0.319909343	0.748146561
C	-0.487490782	2.702811429	0.661707574
H	0.310072997	2.712049276	-0.095350861
H	-1.019040862	3.658934704	0.590767660
C	0.137056907	2.533182604	2.038380180
H	0.633183862	3.468839948	2.315628841
H	-0.653370916	2.351351480	2.777218513
C	1.165883844	1.414395005	2.092114425
H	2.005445775	1.649189363	1.413276854
H	1.590758141	1.366180608	3.103957947
N	0.628962615	0.112032645	1.738943646
C	1.509160067	-0.981900557	2.145195136
H	2.350525434	-1.052524552	1.437917993
H	1.934710123	-0.787868193	3.138655570
C	0.696660790	-2.270272000	2.175053434
H	1.341058976	-3.154202798	2.130540102
H	0.102801147	-2.310910167	3.092095381
O	-0.226675720	-2.279598749	1.088955231
O	-2.119192954	-0.508390108	2.343131770
H	-2.804007582	-1.076421138	1.945202650
H	-2.557182379	0.337722508	2.536890019
C	1.587686796	-0.585992364	-1.120373013
C	2.017357555	-1.948419518	-1.037800195
C	2.472556883	0.467803801	-1.143027620
C	3.420850451	-2.160646583	-1.035394556
C	3.855486480	0.223209080	-1.099030766
H	2.105122131	1.489554050	-1.196360220
C	4.310839799	-1.101559174	-1.057784574
H	3.774832988	-3.186033338	-0.989444507
H	5.381536298	-1.280859243	-1.031683965
H	0.268896656	-2.596193855	0.244580433
H	-0.279990858	-1.198025541	-1.549329912
H	-0.104852238	0.444432158	-1.634436960

N	0.164743461	-0.387331287	-1.108754927
O	1.143916109	-2.898456725	-0.956004210
C	4.835724891	1.315251002	-1.086237376
O	6.044656246	1.178882025	-1.090263357
O	4.268777616	2.541456819	-1.057448017
H	4.997709222	3.186724444	-1.053236825

a

Charge 0, Multiplicity 1

C	1.850047000	-0.826887000	0.013029000
C	0.588885000	-1.423761000	0.012945000
C	-0.562517000	-0.642445000	-0.004406000
C	-0.440436000	0.756982000	-0.001735000
C	0.813876000	1.357770000	-0.021227000
C	1.958169000	0.561237000	-0.017705000
H	2.740759000	-1.446342000	0.026284000
H	0.490683000	-2.506367000	0.020577000
H	0.877215000	2.441309000	-0.021652000
H	2.936498000	1.031763000	-0.028798000
O	-1.562296000	1.523374000	0.027073000
H	-2.297123000	0.912416000	0.231430000
N	-1.895701000	-1.150932000	0.029562000
H	-2.312225000	-1.150377000	-0.900951000
H	-1.915675000	-2.110249000	0.364187000

b

Charge 0, Multiplicity 1

C	-1.590582000	0.058637000	0.002336000
C	-0.602947000	1.051659000	0.004436000
C	0.748585000	0.729053000	-0.007703000
C	1.131281000	-0.623294000	-0.001406000
C	0.166844000	-1.620865000	-0.022882000
C	-1.185298000	-1.275042000	-0.025095000
H	-0.892257000	2.101254000	0.008293000
H	0.482885000	-2.659362000	-0.019088000
H	-1.934900000	-2.062057000	-0.037240000

O	2.454086000	-0.944440000	0.032009000
H	2.923439000	-0.121817000	0.269727000
N	1.810064000	1.679570000	0.034535000
H	2.245823000	1.785588000	-0.880984000
H	1.472394000	2.596531000	0.313330000
C	-3.051065000	0.436935000	0.015506000
H	-3.301779000	1.024220000	0.905095000
H	-3.313130000	1.044045000	-0.857391000
H	-3.686510000	-0.452365000	0.009285000

c

Charge 0, Multiplicity 1

C	-0.920593000	-0.150287000	-0.004422000
C	-0.046871000	0.944326000	-0.007424000
C	1.324341000	0.741655000	-0.013427000
C	1.825398000	-0.575004000	0.003812000
C	0.960035000	-1.667812000	-0.016475000
C	-0.410419000	-1.450424000	-0.022525000
H	-0.439394000	1.956535000	-0.010435000
H	1.375619000	-2.669656000	-0.006639000
H	-1.102072000	-2.286188000	-0.029792000
O	3.158965000	-0.771654000	0.047949000
H	3.555418000	0.106584000	0.221080000
N	2.307788000	1.773943000	0.017315000
H	2.651763000	1.981630000	-0.919647000
H	1.927483000	2.637282000	0.395007000
C	-2.390176000	0.026049000	0.003495000
O	-3.195729000	-0.880754000	-0.015638000
O	-2.767324000	1.316615000	0.034521000
H	-3.740921000	1.331532000	0.036367000

4a

Charge 0, Multiplicity 2

C	-0.638263000	-0.629266000	-0.000001000
C	-0.499161000	0.837355000	-0.000133000
C	0.501957000	-1.460148000	-0.000205000

C	0.845406000	1.356871000	0.000164000
C	1.755981000	-0.893031000	-0.000074000
H	0.375433000	-2.538690000	-0.000593000
C	1.927487000	0.521004000	0.000184000
H	0.955917000	2.436730000	0.000293000
H	2.632061000	-1.533205000	-0.000245000
H	2.932991000	0.929969000	0.000399000
N	-1.895038000	-1.087537000	0.000049000
O	-1.528905000	1.549543000	-0.000235000
H	-2.641790000	-0.403115000	0.000710000
H	-2.118547000	-2.071989000	0.001370000

4b

Charge 0, Multiplicity 2

C	-0.791340000	-0.758732000	0.000053000
C	-1.236526000	0.644973000	-0.000330000
C	0.577353000	-1.077246000	0.000382000
C	-0.198445000	1.641941000	0.000261000
C	1.533218000	-0.077087000	0.000543000
H	0.879871000	-2.122025000	0.000293000
C	1.123263000	1.290073000	0.000636000
H	-0.511714000	2.681389000	0.000531000
H	1.890159000	2.060083000	0.001244000
N	-1.771993000	-1.670891000	-0.000281000
O	-2.462973000	0.901750000	-0.000640000
H	-2.725919000	-1.331884000	0.001003000
H	-1.593412000	-2.663973000	0.002717000
C	2.997886000	-0.425679000	-0.000643000
H	3.255903000	-1.034567000	0.871987000
H	3.260342000	-1.008101000	-0.890001000
H	3.620052000	0.471859000	0.013899000

4c

Charge 0, Multiplicity 2

C	1.361348000	0.780468000	-0.000081000
C	1.942325000	-0.579947000	0.000104000

C	-0.034225000	0.970232000	-0.000185000
C	1.004427000	-1.679533000	0.000124000
C	-0.866751000	-0.130027000	-0.000097000
H	-0.442346000	1.975391000	-0.000305000
C	-0.339206000	-1.458756000	0.000075000
H	1.419296000	-2.682007000	0.000197000
H	-1.043792000	-2.283727000	0.000095000
N	2.245158000	1.779998000	-0.000351000
O	3.179807000	-0.712064000	0.000280000
H	3.229079000	1.535790000	-0.000270000
H	1.972364000	2.752834000	-0.000252000
C	-2.342136000	0.018809000	-0.000049000
O	-3.121024000	-0.910381000	-0.000581000
O	-2.744639000	1.299469000	0.000650000
H	-3.718552000	1.298080000	0.000850000

XYZ coordinates for complex 4

A

Charge 0, Multiplicity 1

Mn	0.202263000	-0.607052000	-0.243133000
S	3.664727000	2.068496000	-1.855322000
O	-1.335808000	-0.335164000	-1.251777000
O	0.275757000	-2.361177000	-0.395448000
N	1.810064000	-1.092662000	1.108100000
H	1.315622000	-1.537652000	1.886687000
N	-0.298110000	0.767886000	1.080987000

N	1.493153000	0.424550000	-1.216368000
C	2.654700000	-0.037788000	1.674796000
H	3.135408000	0.501186000	0.852570000
H	3.445691000	-0.476653000	2.298963000
C	1.784528000	0.894166000	2.507014000
H	1.307559000	0.331614000	3.321736000
H	2.423906000	1.648950000	2.976285000
C	0.720205000	1.628715000	1.697353000
H	1.207476000	2.172227000	0.878047000
H	0.223296000	2.367288000	2.338330000
C	-1.544212000	1.098646000	1.248237000
H	-1.764023000	1.868509000	1.996086000
C	-2.665604000	0.610661000	0.510351000
C	-3.966005000	0.941309000	0.963337000
H	-4.065220000	1.468531000	1.909589000
C	-5.080915000	0.604703000	0.237572000
H	-6.072891000	0.849426000	0.599646000
C	-4.914648000	-0.050994000	-1.002168000
H	-5.791227000	-0.311429000	-1.588327000
C	-3.666647000	-0.358245000	-1.488989000
H	-3.528753000	-0.850116000	-2.445487000
C	-2.496459000	-0.050532000	-0.745400000
C	2.511996000	-2.154044000	0.372230000
H	3.293932000	-2.634157000	0.975621000
H	2.968089000	-1.692299000	-0.508765000
C	1.396256000	-3.117212000	-0.023046000
H	1.700765000	-3.763398000	-0.853831000
H	1.137868000	-3.765081000	0.829232000
C	2.402630000	1.119903000	-1.506977000

B

Charge 0, Multiplicity 1

Mn	0.106325000	-0.483178000	-0.590117000
S	-0.476674000	-5.010295000	0.233727000
O	1.865672000	-0.374224000	-1.233892000

O	-0.869722000	-0.001181000	-2.053232000
N	-1.904474000	-0.743438000	0.106759000
H	-2.225005000	0.219030000	0.246197000
N	0.784728000	-0.575991000	1.329283000
N	0.062753000	-2.453923000	-0.783038000
C	-2.210701000	-1.493201000	1.338518000
H	-1.996326000	-2.550461000	1.147706000
H	-3.282074000	-1.404902000	1.564060000
C	-1.375378000	-1.008608000	2.511419000
H	-1.500640000	0.072465000	2.655232000
H	-1.744610000	-1.498803000	3.418514000
C	0.100123000	-1.358889000	2.360599000
H	0.191665000	-2.417160000	2.080839000
H	0.616818000	-1.221308000	3.318646000
C	1.939725000	-0.086656000	1.638105000
H	2.263879000	-0.164694000	2.682517000
C	2.894942000	0.509602000	0.740494000
C	4.003561000	1.190149000	1.295385000
H	4.040949000	1.325854000	2.374175000
C	5.016269000	1.674298000	0.501542000
H	5.854285000	2.206331000	0.937035000
C	4.959246000	1.443586000	-0.888098000
H	5.762437000	1.807091000	-1.522605000
C	3.911687000	0.756085000	-1.458211000
H	3.869159000	0.559597000	-2.524075000
C	2.833505000	0.278967000	-0.668208000
C	-2.635333000	-1.314619000	-1.050004000
H	-3.697099000	-1.046025000	-0.992316000
H	-2.553493000	-2.400508000	-0.973373000
C	-1.974419000	-0.819652000	-2.356004000
H	-1.643943000	-1.679100000	-2.948840000
H	-2.684453000	-0.234938000	-2.954393000
C	-0.139949000	-3.540493000	-0.371957000
N	0.227154000	1.660742000	-0.390444000

C	-0.957013000	2.301485000	0.097924000
C	-1.985757000	2.613752000	-0.808191000
C	-1.117732000	2.549466000	1.458196000
C	-3.152914000	3.203568000	-0.319900000
C	-2.291662000	3.126940000	1.935238000
H	-0.308259000	2.292646000	2.138508000
C	-3.306479000	3.457239000	1.039585000
H	-3.930039000	3.449516000	-1.035960000
H	-2.406164000	3.322858000	2.995842000
H	-4.223966000	3.911011000	1.399751000
O	-1.843136000	2.399474000	-2.134334000
H	-1.380738000	1.521511000	-2.265624000
H	1.036860000	1.915190000	0.175961000
H	0.425445000	1.956576000	-1.349359000

C

Charge 0, Multiplicity 3

Mn	0.281178000	-0.343947000	-0.441329000
S	2.135465000	-4.568448000	-0.585899000
O	1.328176000	0.912258000	-1.206741000
O	-0.957905000	-0.236609000	-2.076441000
N	-1.313474000	-1.506071000	0.243287000
H	-2.014813000	-0.840484000	0.589950000
N	1.425759000	-0.438236000	1.243812000
N	1.075527000	-2.012069000	-0.976631000
C	-1.019020000	-2.467074000	1.325136000
H	-0.450069000	-3.295610000	0.889077000
H	-1.962883000	-2.876908000	1.706725000
C	-0.224159000	-1.839733000	2.467528000
H	-0.709716000	-0.913103000	2.801492000
H	-0.256204000	-2.533091000	3.314627000
C	1.248258000	-1.570920000	2.149534000
H	1.686928000	-2.458647000	1.675805000
H	1.799009000	-1.383769000	3.080023000
C	2.331286000	0.426571000	1.514525000

H	2.908839000	0.312416000	2.439544000
C	2.680027000	1.568379000	0.690559000
C	3.593220000	2.502083000	1.212219000
H	3.984692000	2.343598000	2.214419000
C	3.993870000	3.601958000	0.478024000
H	4.693872000	4.316429000	0.896172000
C	3.487614000	3.776309000	-0.816952000
H	3.794655000	4.635798000	-1.404811000
C	2.600600000	2.864341000	-1.360421000
H	2.203082000	2.979305000	-2.362989000
C	2.176162000	1.743696000	-0.622942000
C	-1.874856000	-2.170981000	-0.955582000
H	-2.828279000	-2.659256000	-0.716094000
H	-1.157909000	-2.934651000	-1.261833000
C	-2.060546000	-1.132652000	-2.056891000
H	-2.147454000	-1.638317000	-3.024088000
H	-2.981957000	-0.562080000	-1.886409000
C	1.545980000	-3.088605000	-0.833702000
N	-0.735581000	1.298188000	0.431900000
C	-2.169214000	1.362325000	0.573547000
C	-2.851378000	1.688964000	-0.632408000
C	-2.824276000	1.130385000	1.777056000
C	-4.259769000	1.773248000	-0.533506000
C	-4.215271000	1.205804000	1.830162000
H	-2.248731000	0.915154000	2.676864000
C	-4.916553000	1.532976000	0.666551000
H	-4.809204000	2.034746000	-1.432360000
H	-4.736931000	1.029505000	2.763989000
H	-6.000227000	1.603344000	0.699794000
O	-2.173011000	1.886017000	-1.723098000
H	-1.387860000	0.733988000	-2.038838000
H	-0.261384000	1.561679000	1.296031000
H	-0.509906000	1.995340000	-0.290433000