

Supporting Information

A side-on Mn(III)-peroxo supported by a non-heme pentadentate N3Py2 ligand: Synthesis, characterization and reactivity studies

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Magnetic moment calculation and determination of number of unpaired electrons in complex 1 and 1a: Evans' method of ¹H-NMR was performed to determine the number of unpaired electrons (spin state) in complex **1** and **1a** at room temperature^{S1-S3}. A WILMAD® coaxial insert (with a sealed capillary) tube containing the only CD₃CN solvent (with 1.0% TMS) was inserted into the normal NMR tubes containing the complex **1** (3.0 mM, with 0.1% TMS) or **1a** (2.0 mM, with 0.1% TMS). We have calculated the chemical shift value of the TMS peak in the presence of the complex **1** or **1a** with respect to that of the TMS peak in the outer NMR tube. The magnetic moment was calculated using the given equation,

$$\mu_{eff} = 0.0618(\Delta\nu T / 2fM)^{1/2}$$

Complex 1.

$$\mu_{eff} = 0.0618 * (76 * 298 / 2 * 400 * 0.003)^{1/2}$$

$$\mu_{eff} = 5.97 \text{ BM}$$

Complex 1a.

$$\mu_{eff} = 0.0618 * (12 * 298 / 2 * 400 * 0.002)^{1/2}$$

$$\mu_{eff} = 2.91 \text{ BM}$$

Where f = oscillator frequency (400 MHz) of the superconducting spectrometer, T = absolute temperature, M = molar concentration of the complex **1** or **1a**, and ν = difference in frequency (Hz) between the two TMS signals^{S3}. The calculated magnetic moment of complexes **1** and **1a** were determined to be 5.97 BM and 2.91 BM respectively in CD₃CN at RT, suggesting 5 unpaired electrons in Mn²⁺ centre of complex **1** and 2 unpaired electrons in Mn³⁺ centre of complex **1a**.

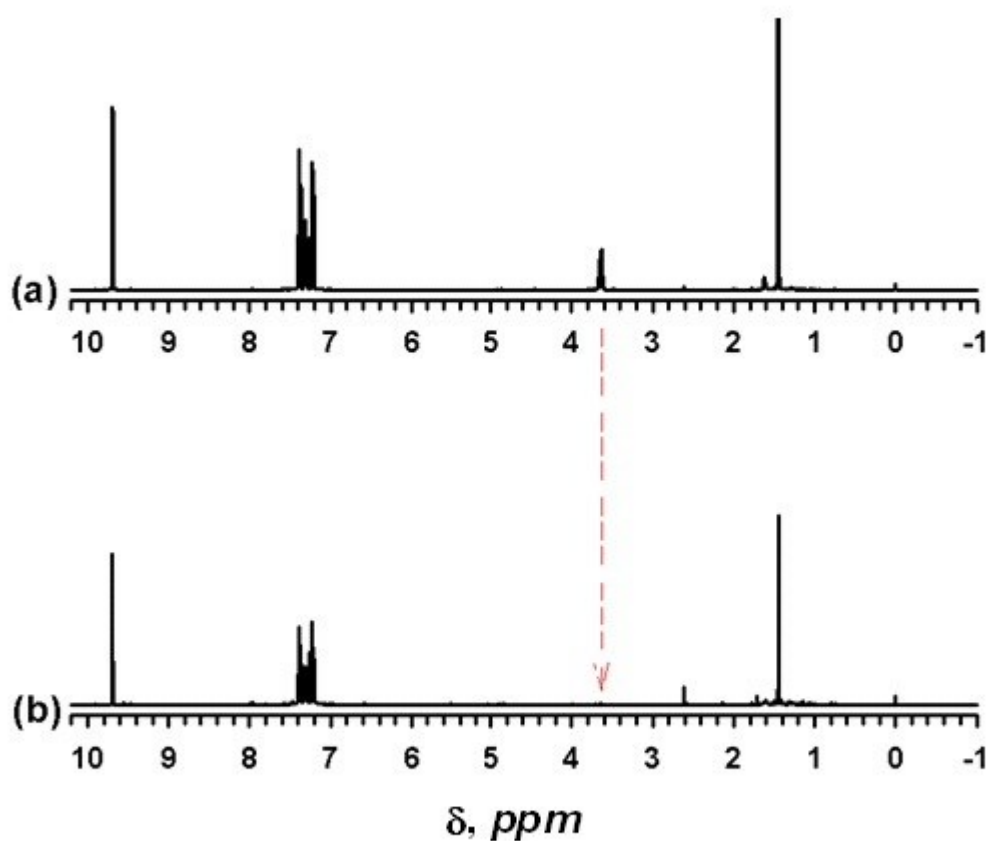


Figure S1. ^1H -NMR spectra of (a) 2-phenylpropionaldehyde, (b) deuterated 2-phenylpropionaldehyde recorded in an CDCl_3 at 298 K. The indicated arrow (red color) shows that the occurrence of the deuteration in the 2-phenylpropionaldehyde.

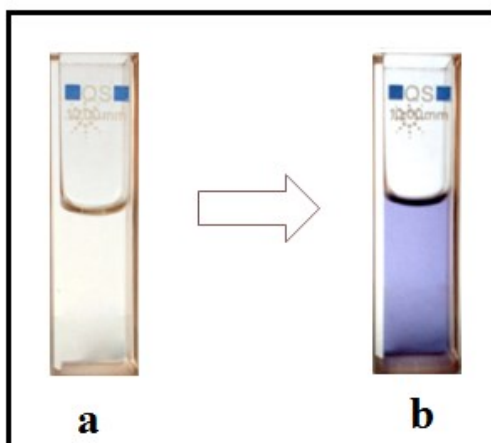


Fig. S2. Color changes observed a) before b) after the addition of 10 equiv of H_2O_2 in presence of 5 equiv TEA (triethylamine) to the solution of **1** in acetonitrile. The purple colour solution is species **1a**.

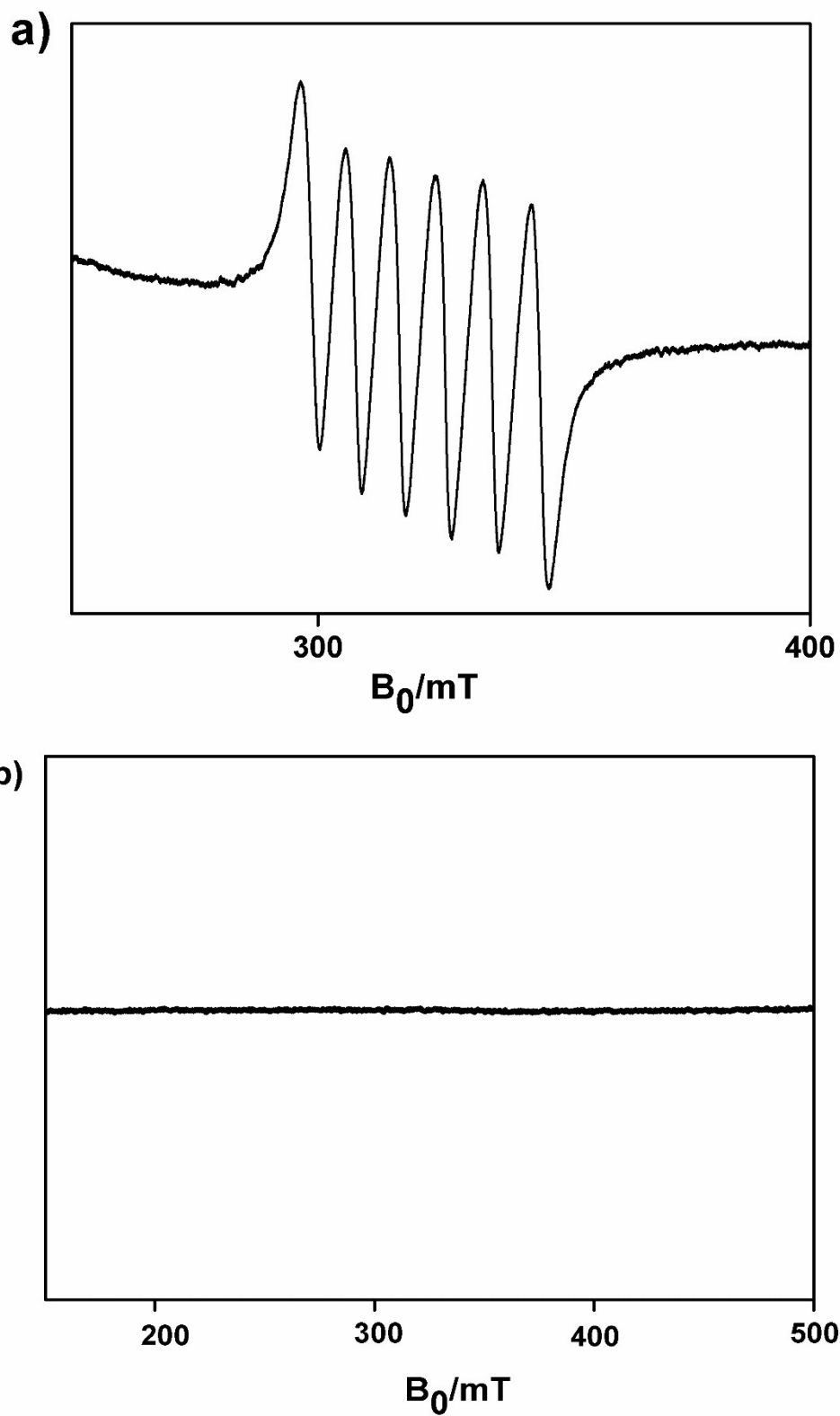
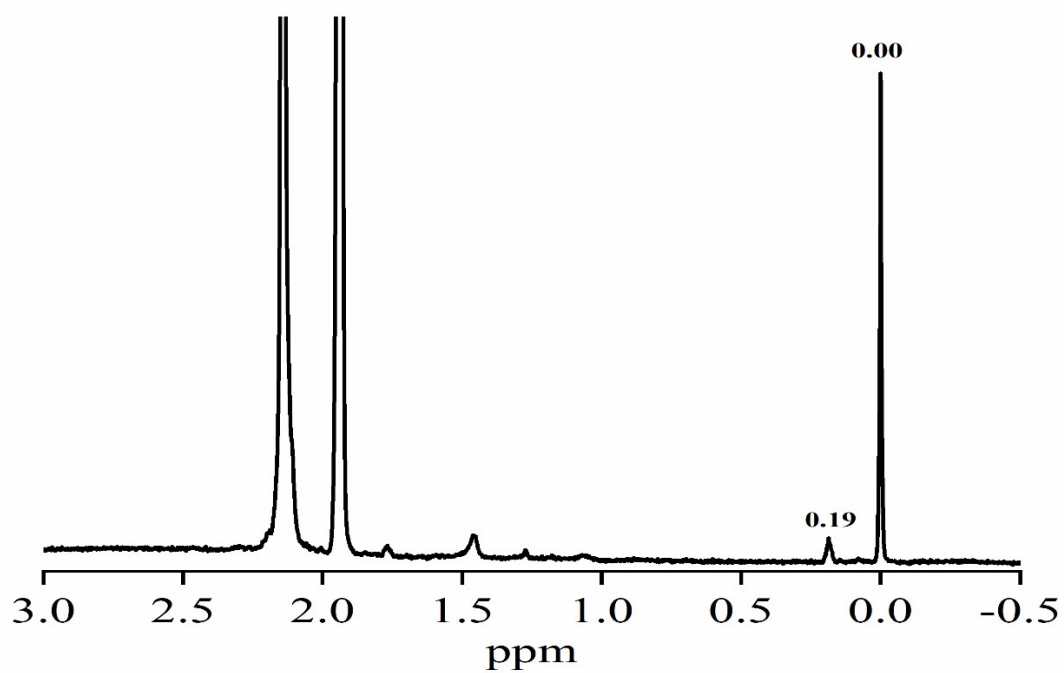
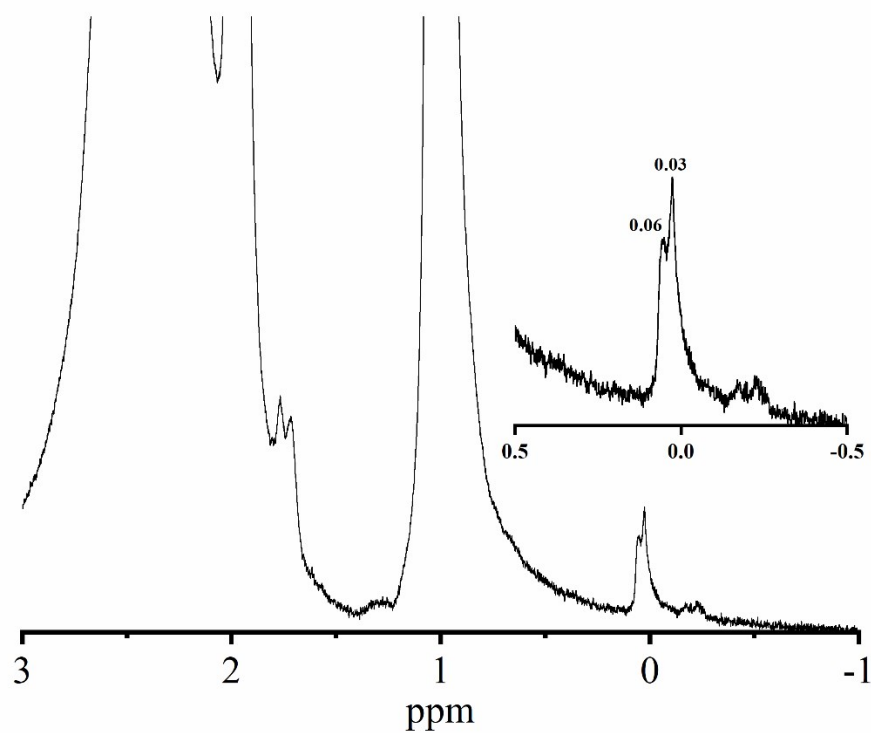


Fig. S3. The X-band EPR spectrum of **1** (top) (Ref S24) and **1a** (bottom) in CH_3CN recorded at 77 K.



(a)



(b)

Fig. S4. Evans method ^1H NMR spectra of **1** (top) and **1a** (bottom) used to obtain the magnetic moments of **1** and **1a** respectively. Using Evans method magnetic moment (μ) for **1** is 5.97 BM while for **1a** it is 2.91 BM.

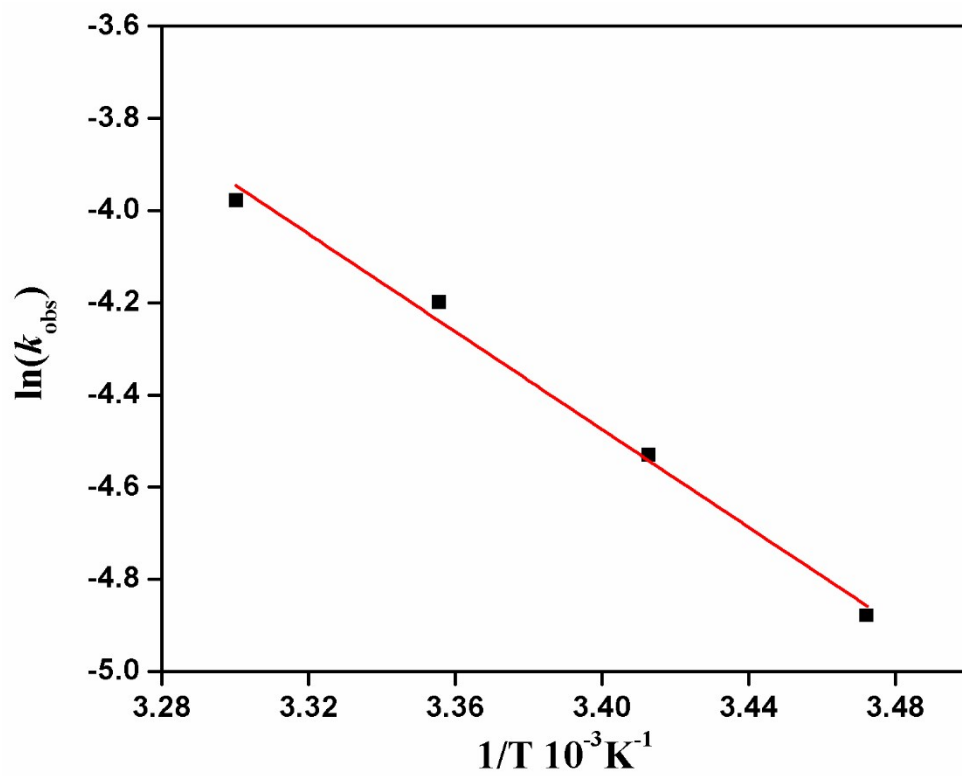


Fig. S5 Plot of first-order rate constants against $1/T$ to determine activation energy for the reaction of 1a (1mM) and 60 equiv of 2-PPA.

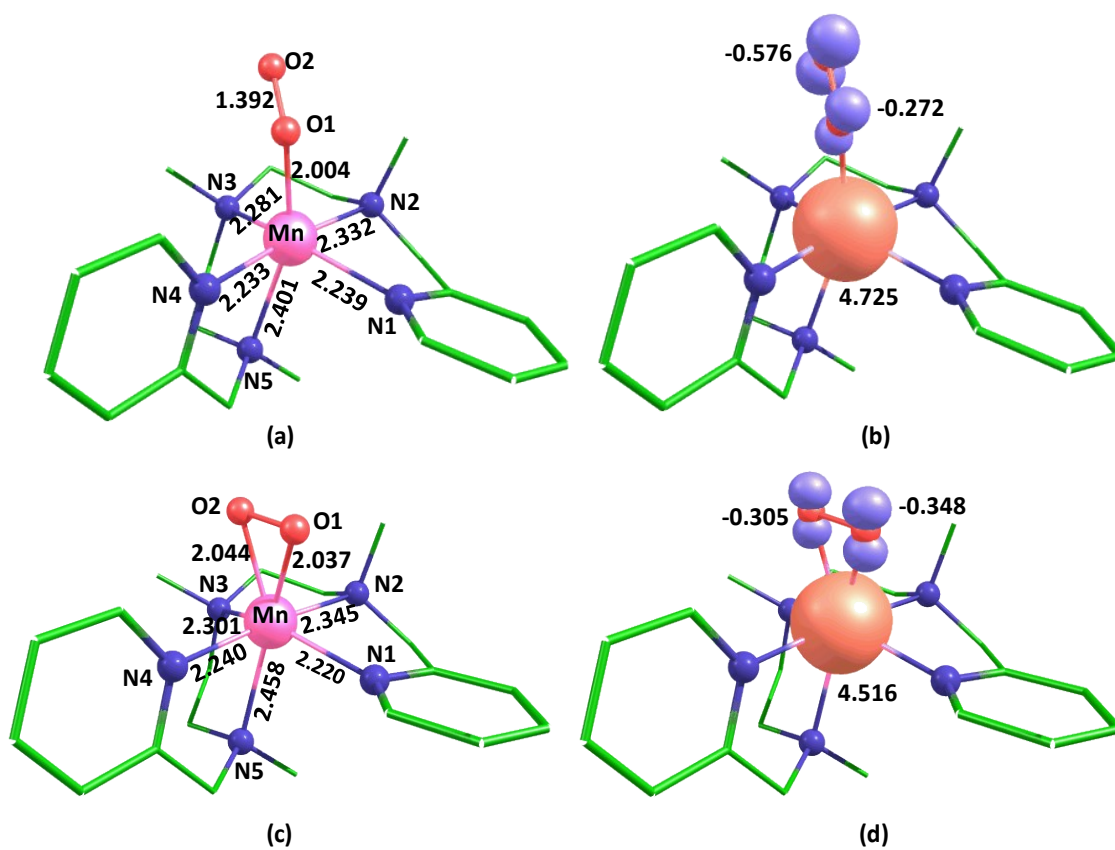


Fig. S6. B3LYP-D2 optimized structures and spin density plots of the ground state of end-on $[\text{Mn}(\text{N}_3\text{Py}_2)(\eta^1\text{-O}_2)]^+$ (a and b) and side-on $[\text{Mn}(\text{N}_3\text{Py}_2)(\eta^2\text{-O}_2)]^+$ (c and d) species.

Table S1: List of the Mn^{III}-peroxo prepared by a different synthetic approach along with their UV-Vis spectral features and thermal stability.

Sr. No.	Mn-Peroxo complex	UV-Vis features λ_{\max} nm (L mol ⁻¹ cm ⁻¹) (thermal stability or $t_{1/2}$)	Ref.
I	Reaction of Mn^{II} complex with H₂O₂		
1	[Mn ^{III} (O ₂)(Tp ^{<i>i</i>Pr₂}) pz ^{<i>i</i>Pr₂}] (brown isomer)	561 (50), (stable at RT for few h)	[S4]
2	[Mn ^{III} (O ₂)(Tp ^{<i>i</i>Pr₂}) pz ^{<i>i</i>Pr₂}] (blue isomer)	583 (60), (stable at RT for few h)	[S4]
3	[Mn ^{III} (O ₂)(Tp ^{<i>i</i>Pr₂})(Me-Im)]	381 (314), 478 (173)	[S5]
II	Reaction of Mn^{II} complex with H₂O₂ in presence of TEA		
a4	[Mn ^{III} (O ₂)(L ⁷ py ₂ ^H)] ⁺	445 (280), 590(120)(15min at 0°C)	[S6]
a5	[Mn ^{III} (O ₂)(L ⁷ py ₂ ^{6-Me})] ⁺	415 (280), 620 (80) (6 min at 0°C)	[S6]
a6	[Mn ^{III} (O ₂)(L ⁷ py ₂ ^{6-MeO})] ⁺	416 (250), 560(80) (~ seconds at 0°C)	[S6]
a7	[Mn ^{III} (O ₂)(L ⁷ py ₂ ^{5-Br})] ⁺	445 (220), 589 (90) (3 min at 0 °C)	[S6]
8	[Mn ^{III} (O ₂)(L ⁷ q ₂)] ⁺	415 (305), 606 (70) (4 min at 0°C)	[S7]
9	[Mn ^{III} (O ₂)(L ⁷ py ₂ ^{4-Me})] ⁺	445(260), 588(100) (6 min at 0°C)	[S7]
10	[Mn ^{III} (O ₂)(L ⁸ py ₂ ^H)] ⁺	465 (280), 599 (120) (12 min at 0°C)	[S7]
11	[Mn ^{III} (O ₂)(L ⁷ py ₂ ^{4-Cl})] ⁺	442 (262), 568(102) (10 min at 0°C)	[S8]
12	[Mn ^{III} (O ₂)(L ⁷ iso-q ₂)] ⁺	446 (291), 587 (112) (30 min at 0°C)	[S8]
13	[Mn ^{III} (O ₂)(14-TMC)] ⁺	453 (490), 630 (120) (5 h at 25 °C)	[S9]
b14	[Mn ^{III} (O ₂)(13-TMC)] ⁺	452 (390), 615 (190) (several days at 25 °C)	[S10,S11]
15	[Mn ^{III} (O ₂)(12-TMC)] ⁺	455 (250), 620 (200) (Stability ND)	[S12]
16	[Mn ^{III} (O ₂)(L2)] ⁺	440 (175), 597 (41) (4 min at 0°C)	[S13]
17	[Mn ^{III} (O ₂)(L3)] ⁺	434 (214) , 592 (42) (22 min at 0°C)	[S13]
18	[Mn ^{III} (O ₂)(L4)] ⁺	435 (149) , 558 (39) (6 min at 0°C)	[S13]
19	[Mn ^{III} (O ₂)(Pro3Py)] ⁺	580 (200) (2 h at 0°C)	[S14]
20	[Mn ^{III} (O ₂)(L ¹)] ⁺	605 (270) (60 min. at 15 °C)	[S15]
21	[Mn ^{III} (O ₂)(L ²)] ⁺	450 (160) (100 sec. at 15°C)	[S16]
22	[Mn ^{III} (O ₂)(Pro3Bzim)] ⁺	540 (140) (30 min at 20°C)	[S17]
III	Reaction of Mn^{II} complex with KO₂		
23	[Mn ^{III} (O ₂)(TPP)] ⁻	983 (50)	[S18]
24	[Mn ^{III} (O ₂)(Tp ^{Ph₂})(THF)]	379 (324), 436(73) (4.5 days stability)	[S19]
25	[Mn ^{III} (O ₂)(Me ₂ EBC)] ⁺	650 (530), 400 (185) (decays within 40 min at -60 °C)	[S20]
IV	Reaction of Mn^{II} complex with electrochemically generated O₂⁻		
a,c26	[Mn ^{III} (O ₂)(imL ₅ ²)] ⁺	542 (484)	[S21]

^{a,c} 27	[Mn ^{III} (O ₂)(mL ₅ ²)] ⁺	585 (335)	[S21]
^{a,c} 28	[Mn ^{III} (O ₂)(N4py)] ⁺	617 (280)	[S21]
V	Reaction of Mn^{II} complex with dioxygen		
29	[Mn ^{III} (O ₂)(H ₂ bupa)] ⁻	660 (300), 490 (ND)	[S22]
^a 30	[Mn ^{III} (O ₂)(H ₂ bpa)]	590 (58), 460 (ND)	[S23]

Note: Mn(III)-peroxo species can also be prepared using a) KO₂; b) O₂ and c) H₂O₂ oxidants.

Table S2: Computed structural parameters for Mn(III) peroxo intermediate.

<i>end-on [Mn(N₃Py₂)(η¹-O₂)]⁺ (1a₁)</i>													
B3LYP-D2													
	Mn-O1	Mn-O2	O1-O2	Mn-N1	Mn-N2	Mn-N3	Mn-N4	Mn-N5	Mn-O1-O2	Mn-O2-O1	O1-Mn-N5	N1-Mn-N3	N2-Mn-N4
HS	2.004		1.392	2.239	2.332	2.281	2.233	2.401	122.6		157.3	146.7	172.5
IS	1.882		1.402	2.032	2.143	2.136	2.045	2.240	119.6		164.5	158.0	174.9
LS	1.746		1.412	2.043	2.123	2.120	2.098	2.264	128.9		156.7	157.4	172.2
B3LYP													
HS	2.040		1.391	2.281	2.357	2.323	2.271	2.475	121.3		153.4	142.2	173.2
IS	1.892		1.400	2.061	2.157	2.172	2.065	2.304	118.8		163.8	144.2	174.3
LS	1.913		1.385	2.063	2.150	2.163	2.081	2.292	123.5		160.0	151.5	172.5
<i>side-on [Mn(N₃Py₂)(η²-O₂)]⁺ (1a₂)</i>													
B3LYP-D2													
HS	2.037	2.044	1.443	2.220	2.345	2.301	2.240	2.458	69.5	69.0	154.0	141.9	174.9
IS	1.843	2.013	1.497	2.075	2.119	2.270	2.043	2.620	73.3	61.3	155.2	143.0	174.1
LS	1.946	1.942	1.470	2.038	2.161	2.158	2.039	2.231	67.6	67.9	150.9	151.3	176.2
B3LYP													
HS	2.068	2.063	1.439	2.259	2.376	2.338	2.275	2.540	69.4	69.8	154.6	142.2	175.9
IS	1.839	2.023	1.495	2.101	2.130	2.340	2.061	2.669	73.9	60.9	156.8	144.2	175.6
LS	1.946	1.939	1.471	2.060	2.176	2.181	2.051	2.275	67.5	68.0	151.1	151.5	175.3

Note: HS=High spin, IS=Intermediate spin and LS=Low spin

Table S3: Computed Mulliken spin densities for Mn(III) peroxo intermediate.

<i>end-on [Mn(N₃Py₂)(η¹-O₂)]⁺ (1a₁)</i>			
B3LYP-D2			
Side-on	Mn	O1	O2
HS	4.726	-0.272	-0.576
IS	1.232	0.377	0.465
Ls	0.000	0.000	0.000
B3LYP			
HS	4.769	-0.288	-0.600
IS	1.207	0.3753	0.487
Ls	-1.046	0.602	0.361
<i>side-on [Mn(N₃Py₂)(η²-O₂)]⁺ (1a₂)</i>			
B3LYP-D2			
HS	4.516	-0.348	-0.305
IS	2.138	-0.035	-0.087
Ls	0.000	0.000	0.000
B3LYP			
HS	4.576	-0.371	-0.329
IS	2.157	-0.039	-0.096
Ls	0.000	0.000	0.000

Table S4: B3LYP-D2 computed potential energy surface (ΔG in kJ mol⁻¹) for Mn(III) peroxo intermediate.

B3LYP-D2	
<i>side-on [Mn(N₃Py₂)(η²-O₂)]⁺ (1a₂)</i>	
HS	0
IS	99.6
Ls	152.6
<i>end-on [Mn(N₃Py₂)(η¹-O₂)]⁺ (1a₁)</i>	
HS	14.6
IS	122.2
Ls	179.1
B3LYP	
<i>side-on [Mn(N₃Py₂)(η²-O₂)]⁺ (1a₂)</i>	
HS	0
IS	116.8
Ls	182.5
<i>end-on [Mn(N₃Py₂)(η¹-O₂)]⁺ (1a₁)</i>	
HS	10.7
IS	145.5
Ls	223.5

Kinetic data, thermodynamic parameters as well as product analysis data with standard deviation are also shown as below

1. Determination of second-order rate constant (k_2) for 2-PPA and 2-PPA-*d* with standard deviations (shown in bracket)

Reactivity of	k_2 second-order rate constant (from graph) M s^{-1}
2-PPA	$1.59 (0.23) \times 10^{-1} \text{ M s}^{-1}$
2-PPA- <i>d</i>	$9.3374 (0.47) \times 10^{-2} \text{ M s}^{-1}$

2. Calculation for Eyring plot to obtain ΔH and ΔS with PPA-*d* with standard deviations (shown in bracket)

$$\Delta H = 42 (\pm 2) \text{ kJ mol}^{-1}$$

$$\Delta S = -139 (\pm 4) \text{ J mol}^{-1}\text{K}^{-1}$$

$$E_a = 42 (\pm 1) \text{ kJ mol}^{-1}$$

3. Product analysis with a standard deviation (shown in bracket)

$$\% \text{ of acetophenone formed based on 1a} = 88 (\pm 2) \%$$

4. Product analysis with a standard deviation (shown in bracket)

$$\% \text{ of cyclohexene formed based on 1a} = 70 (\pm 2) \%$$

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