Electronic Supplementary Information

Synthesis, characterization, and reactivity of a side-on manganese(III)-peroxo complex bearing a pentadentate aminopyridine ligand

Junyi Du,[ab] Daqian Xu,[a] Chunxi Zhang,*[c] Chungu Xia,[a] Yong Wang*[a] and Wei Sun*[a]

[a] State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China.
Email: wsun@licp.cas.cn, wangyong@licp.cas.cn
[b] University of Chinese Academy of Sciences, Beijing 100039, China.
[c] Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, China.
E-mail: chunxizhang@iccas.ac.cn

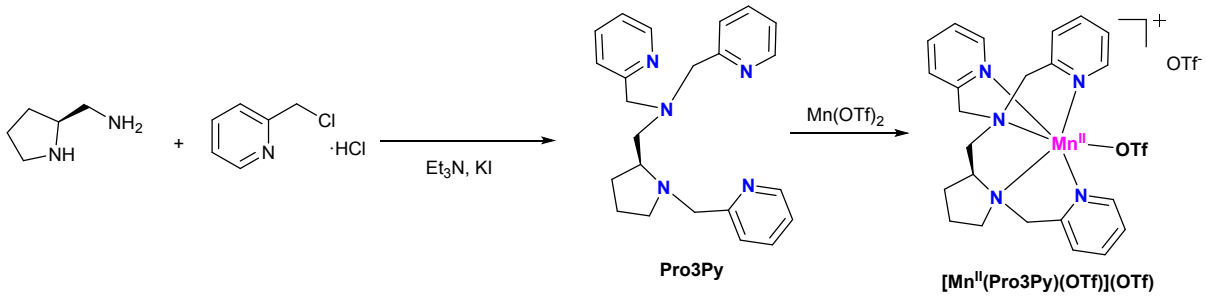
Contents

1. General Remarks
2. Preparation and Characterization of Ligand Pro3Py and the corresponding [Mn^{II}(Pro3Py)(OTf)](OTf)
3. In Situ Preparation of Peroxomanganese(III) Complex, [$Mn^{III}(O_2)$(Pro3Py)](OTf)
4. Kinetic data for decay of 1 upon addition of 2-PPA
5. UV-vis spectral changes of upon addition of SCN^-
6. Density functional theoretical (DFT) calculations

1. General Remarks

UV-vis spectra were recorded on an Agilent 8454 spectrophotometer equipped with a variable-temperature liquid-nitrogen cryostat (UNISOKU Scientific Instruments). HRMS was determined on a Bruker micrOTOF-Q^{II} mass spectrometer using an electrospray ionization (ESI) source. X-ray crystallographic data were collected on a Bruker SMART CCD1000 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III HD 400MHz spectrometer. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. EPR spectra were recorded on a Bruker E500 spectrometer equipped with an Oxford ESR900 liquid helium cryostat and ITC-503 temperature controller. A dual mode resonance cavity (DM203) was used for liquid-helium temperature measurements. EPR conditions: microwave frequency, 9.38 GHz for parallelmode spectra; modulation amplitude, 9.22 G; modulation frequency, 100 kHz; temperature, 5 K; microwave power, 10 mW. GC-MS was measured on an Agilent 7890A/5975C spectrometer. Column chromatography was generally performed on silica gel (200-300 mesh) and TLC inspections were on silica gel GF_{254} plates. All chemicals and solvents were used as received from commercial suppliers unless noted otherwise. THF was dried over sodium benzophenone ketyl anion radical and freshly distilled prior to use. (*S*)-(+)-2-(Aminomethyl)pyrrolidine was prepared by a previously reported reductive procedure from L-prolinamide and $LiAlH_4$.[1]

2 Preparation and Characterization of Ligand Pro3Py and the corresponding [Mn^{II}(Pro3Py)(OTf)](OTf)



A solution of (*S*)-(+)-2-(aminomethyl)pyrrolidine (1.91 g, 19 mmol), KI (0.95g, 5.7 mmol), Et_3N (13.52 g, 133 mmol) and 2-(chloromethyl)pyridine hydrochloride (9.38 g, 57 mmol) in CH_3CN (40 ml) was stirred for 12 h at ambient temperature, afterwards the solvent was evaporated under reduced pressure. The residue was dissolved in saturated aqueous $NaHCO_3$ solution (15 ml) and extracted with ethyl acetate (15 ml×3). The organic layer was separated and dried with Na_2SO_4. The solvent was evaporated and the residue was purified over silica gel column chromatography eluting with ethyl acetate/ petroleum ether to give 3.52 g (ligand Pro3Py, 30% yield) of pure product as a colourless oil.

Pro3Py: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 – 8.46 (m, 3H), 7.66 – 7.57 (m, 3H), 7.54 (d, J = 7.6 Hz, 2H), 7.32 (d, J = 8.0 Hz, 1H), 7.18 – 7.09 (m, 3H), 4.28 (d, J = 13.6 Hz, 1H), 3.90 – 3.78 (m, 4H), 3.45 (d, J = 14.0 Hz, 1H), 2.97 – 2.88 (m, 1H), 2.85 – 2.72 (m, 2H), 2.54 (q, J = 7.6 Hz, 1H), 2.21 (q, J = 8.4 Hz, 1H), 2.06 – 1.95 (m, 1H), 1.71 – 1.56 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 159.7, 148.9, 136.2, 123.0, 129.1, 121.9, 121.7, 62.3, 61.4, 61.2, 59.2, 54.8, 30.1, 22.6.

HRMS calcd. for $C_{23}H_{28}N_5$ $[M+H]^+$: 374.2339, found: 374.2335.

[Mn(Pro3Py)(OTf)](OTf) complex was prepared from equimolar amounts of $Mn(OTf)_2$ and ligand Pro3Py in CH_3CN at room temperature. Crystals of the Mn(II) complex used for X-ray analysis and further study were

recrystallized from its concentrated solution of acetonitrile by layering with diethyl ether.
[Mn(Pro3Py)(OTf)](OTf): colourless crystal. HRMS calcd. for $C_{24}H_{27}F_3MnN_5O_3S$ $[M\text{-}OTf]^+$: 577.1167, found: 577.1141.

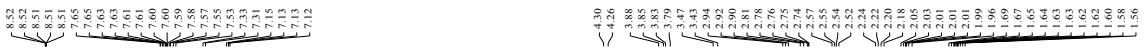
Table S1 Crystal data for $[Mn(Pro3Py)(OTf)]^+$

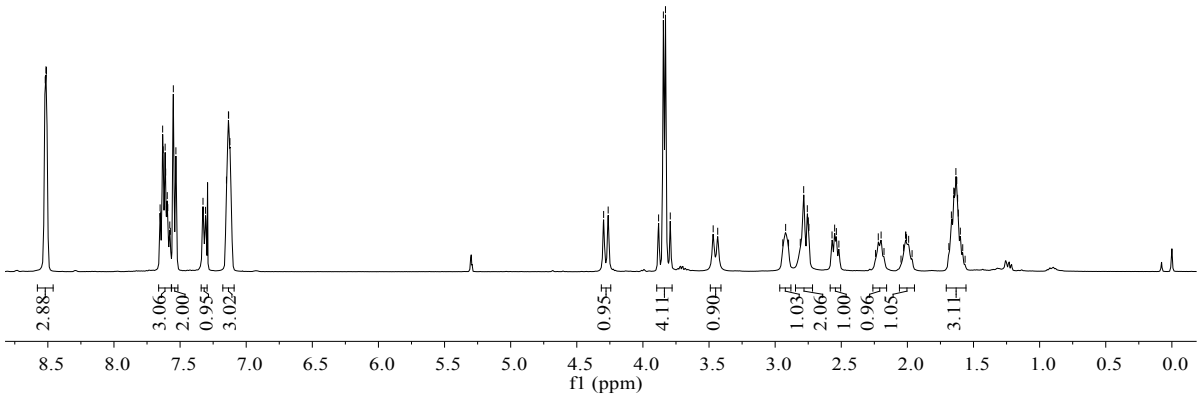
Formula sum	C25 H27 F6 Mn1 N5 O6 S2
Formula weight	726.58 g/mol
Crystal system	Orthorhombic
Space-group	P 21 21 21 (19)
Cell parameters	a=9.1669(16) Å, b=14.119(2) Å, c=24.261(4) Å
Cell ratio	a/b=0.6493, b/c=0.5820, c/a=2.6466
Cell volume	3140.04(88) $Å^3$
Z	4
Calculated density	1.53685 g/cm^3

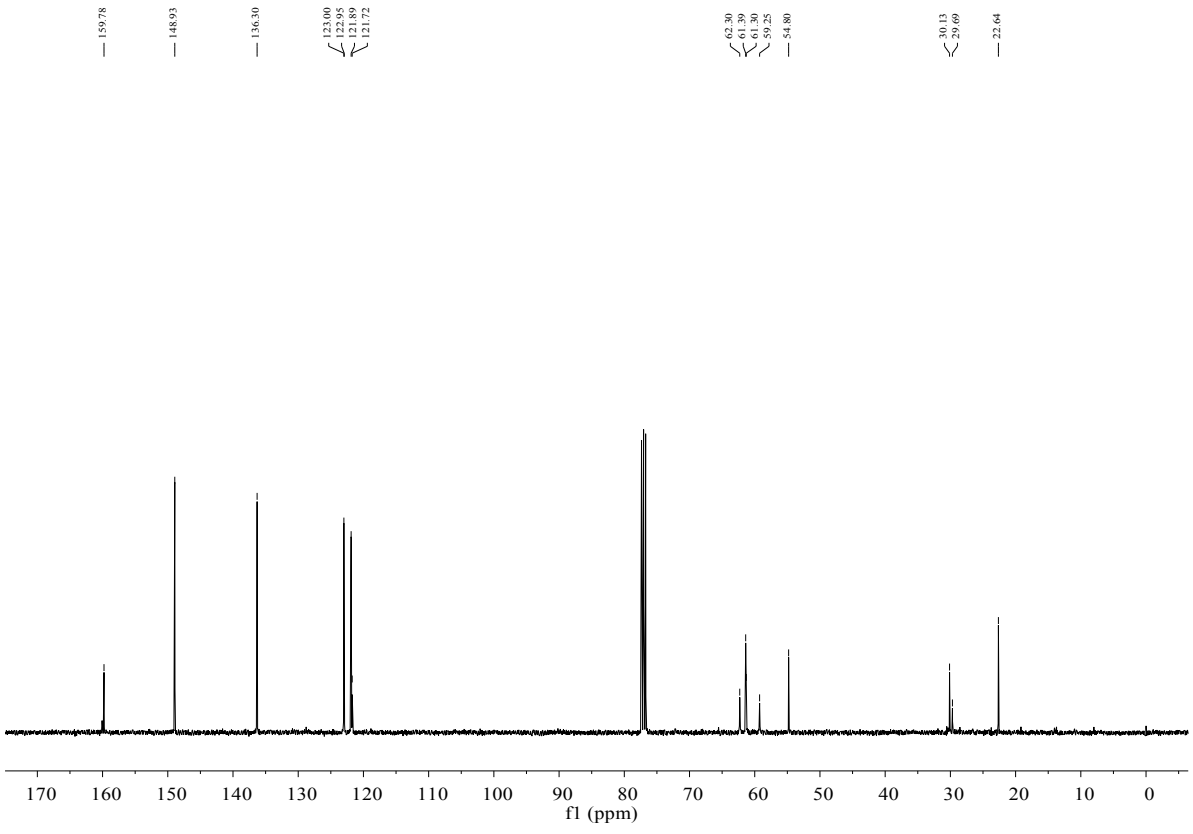
Table S2. Selected bond distances and angles of $[Mn(Pro3Py)(OTf)]^+$.

Bond	Distances(Å)	Angle	Value(°)
Mn-O1	2.102(4)	O1-Mn-N1	96.59(17)
Mn-N1	2.241(4)	O1-Mn-N2	87.26(16)
Mn-N2	2.242(4)	O1-Mn-N3	117.03(17)
Mn-N3	2.295(4)	O1-Mn-N4	93.65(17)
Mn-N4	2.286(4)	O1-Mn-N5	157.61(16)
Mn-N5	2.276(4)		

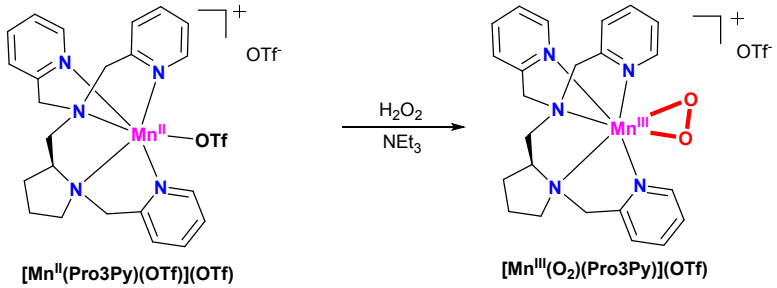
^{1}H and ^{13}C NMR data of ligand Pro3Py







3. In Situ Preparation of Peroxomanganese(III) Complexes.



[Mn^{II}(Pro3Py)(OTf)](OTf) **[$Mn^{III}(O_2)$(Pro3Py)](OTf)**

The blue [$Mn^{III}(O_2)$(Pro3Py)](OTf) intermediates was formed by treating an acetonitrile solution of [Mn^{II} (Pro3Py)(OTf)](OTf) complex with 20 equiv of H_2O_2 and 2 equiv of triethylamine in CH_3CN at 0 °C.

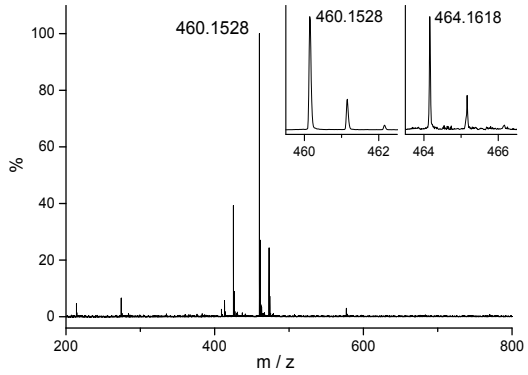


Fig. S1 ESI-MS spectrum of 1. Insets show the observed isotope distribution patterns for [Mn($^{16}O_2$)(Pro3Py)]$^+$ (left) and [Mn($^{18}O_2$)(Pro3Py)]+ (right).

4. Kinetic data for decay of 1 upon addition of 2-PPA

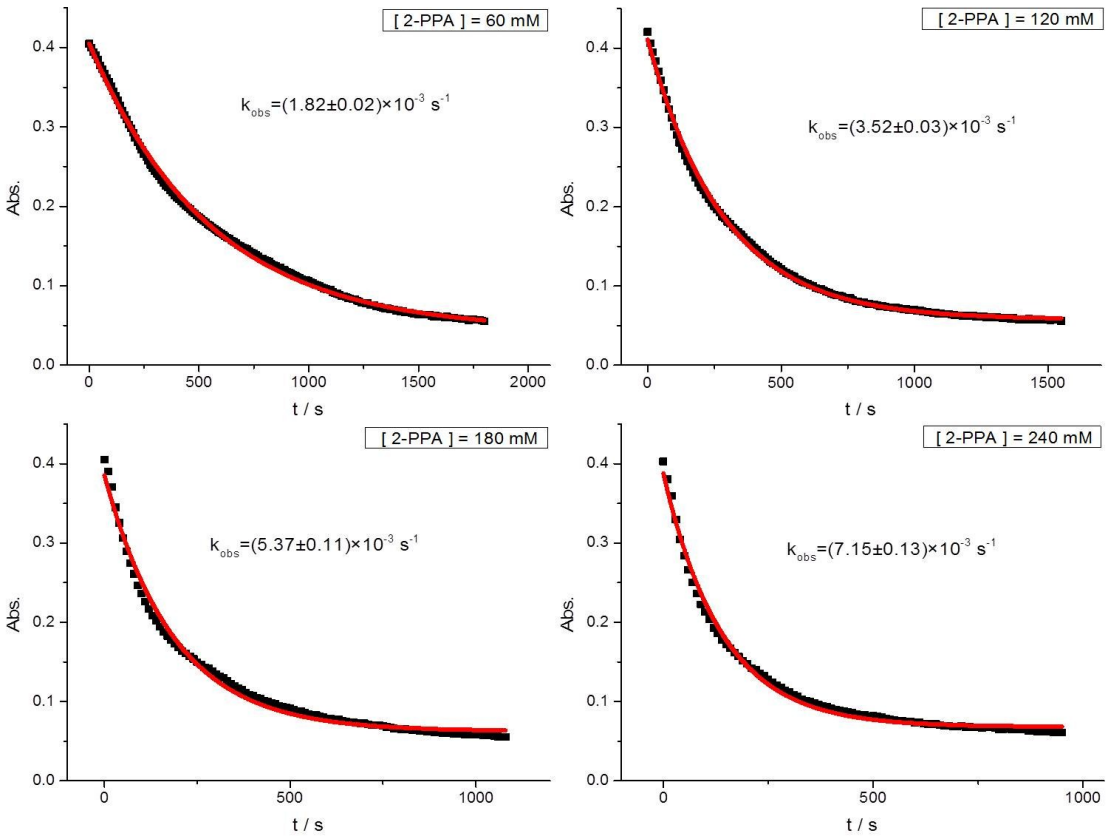


Fig. S2. k_{obs} measured upon addition of increasing 2-PPA concentrations via UV-VIS spectroscopy. The black squares represent the experimental data and the red curves represent the corresponding experimental fit data in each subgraph.

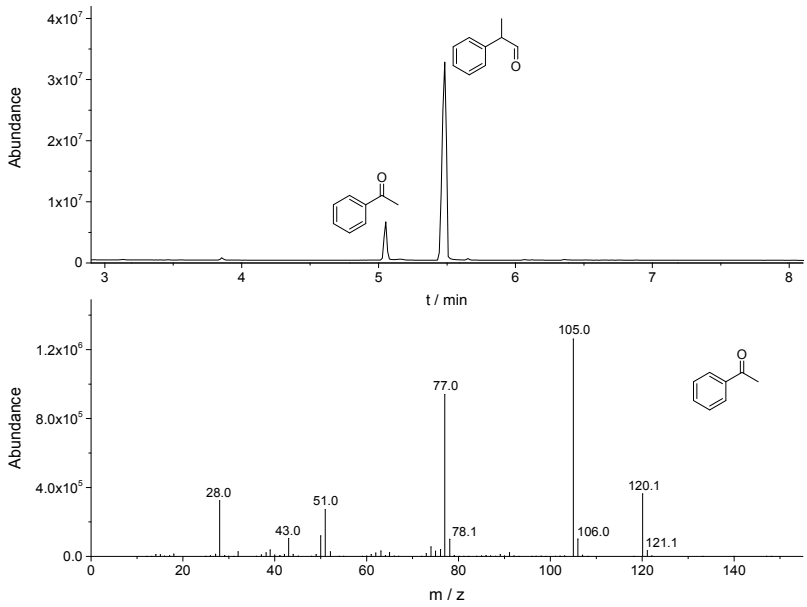


Fig. S3 GC-MS analysis of the product in the deformylation reaction of **1** with phenylpropionaldehyde **(**2-PPA).

5. UV-VIS spectral changes of upon addition of SCN^-

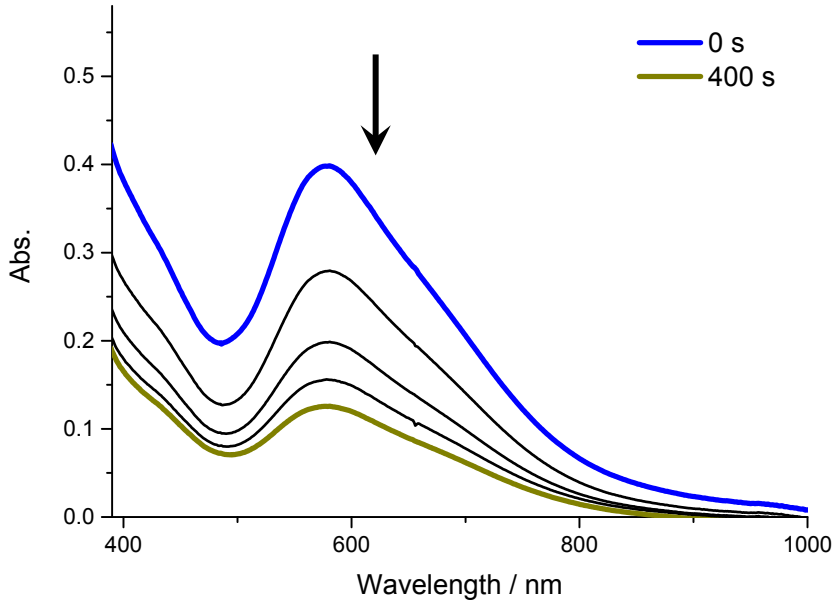


Fig.S4. UV-VIS spectral changes of **1** (2 mM) upon addition of 1.2 equiv.NaSCN at 0 °C.

References:

1. B. Wang, C. Miao, S. Wang, C. Xia and W. Sun, *Chem. Eur. J.*, 2012, **18**, 6750-6753.

6. Density Functional Theoretical (DFT) calculations.

The spin-unrestricted BP86 functional was employed with a hybrid basis set for geometry optimization: The TZVP basis set for Mn, O and N atoms, and SVP basis set for the resting H and C atoms. All optimizations were ascertained by vibrational frequency analysis to possess no imaginary frequency. Calculations were performed with solvation included using the self-consistent reaction field (SCRF) calculations, in the conductor-like polarizable continuum model (CPCM); the experimental solvent acetonitrile (ε = 35.688) was used. Single-point energy calculations in solvent were doned on the optimized structure at the UB3LYP/def2-TZVPP computational level. DFT calculations were performed with Gaussian 09 suite of quantum chemical packages. Only the data on the quintet ground state were presented in text. The energies presented in text are the sum of SCRF(at the UB3LYP/def2-TZVPP level) energies, ZPE(at the UBP86/TZVP(Mn,N,O)+SVP(H,C) level) energies and entropies (at the UBP86/TZVP(Mn,N,O)+SVP(H,C) level. Data were obtained according to Gibbs free energy expression $G = H - T\Delta S$).

Table S3 Various SCRF and free energies of the proposed reactive intermediates. Calculations were performed at the UB3LYP/def2-TZVPP//UBP86/Mn,N,O(TZVP)+H,C(SVP) level.

	SCRF/B2		SCRF/B2+ZPE/B1		SCRF/B2+ZPE/B1-$T\Delta S$	
1	-2468.319053	0.0	-2467.856477	0.0	-2467.933081	0.0
1-N1	-2468.306711	7.7	-2467.844142	7.1	-2467.922083	6.2
1-N2	-2468.298663	12.8	-2467.837087	12.6	-2467.915214	11.5
1-N3	-2468.303119	10.0	-2467.840803	10.0	-2467.919257	9.1

Table S4 Mulliken charges and spin densities of the proposed reactive intermediates. Calculations were performed at the UBP86/Mn,N,O(TZVP)+H,C(SVP) level.

	APT charge					Mulliken spin			
	Mn	O1	O2	C1		Mn	O1	O2	C1
1	0.72	0.74	-0.23	-0.24		3.89	0.13	-0.01	-0.01
1-N1	0.72	0.74	-0.24	-0.23		3.91	0.10	0.00	0.00
1-N2	0.60	0.82	-0.21	-0.20		3.83	0.11	0.03	0.03
1-N3	0.75	0.68	-0.22	-0.21		3.84	0.06	0.06	0.04

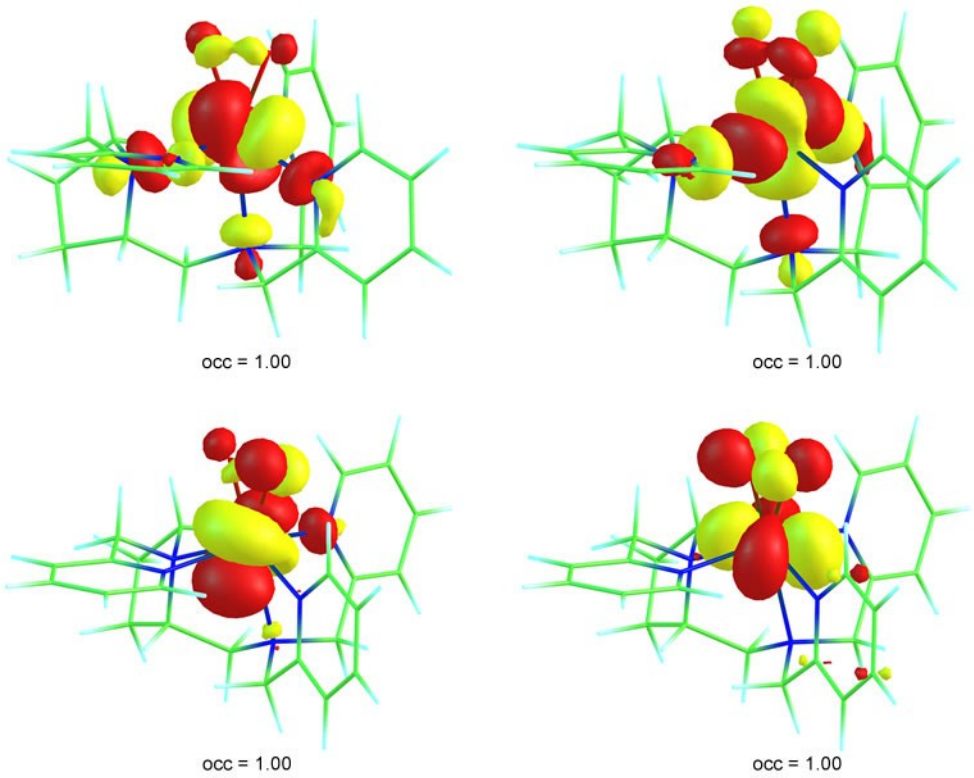


Fig. S5 Single-occupied natural orbitals of reactive intermediate **1** on the ground quintet spin state. Calculations were performed at the UBP86/Mn,N,O(TZVP)+H,C(SVP) level.

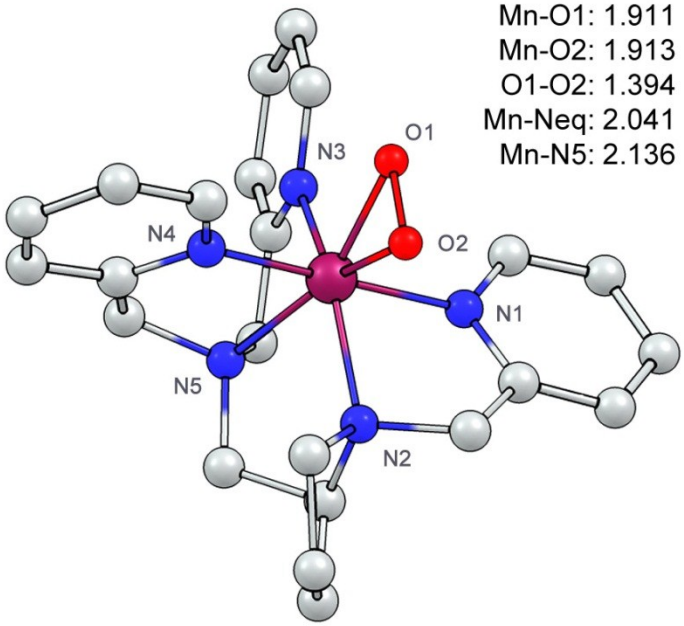


Fig. S6 Geometric information of reactive intermediate **1** on **the excited singlet spin state**. Calculations were performed at the UBP86/Mn,N,O(TZVP)+H,C(SVP) level. Bond lengths of the first-layer coordination are presented in Å units.

Cartesian coordinates

Reaction intermediate **1**

Mn	0.069419000	0.036526000	0.215929000
N	1.396449000	-1.466905000	-0.663711000
N	1.310464000	1.905611000	-0.355498000
N	-1.991446000	0.911453000	-0.386850000
N	-1.497150000	-1.730608000	0.315361000
N	0.122594000	0.307136000	-2.287684000
C	1.233483000	-1.850166000	-1.956440000
C	1.996749000	-2.886876000	-2.519116000
C	2.951051000	-3.543929000	-1.725154000
C	2.325707000	-2.090242000	0.098071000
C	0.177452000	-1.092548000	-2.739933000
C	1.350477000	1.051215000	-2.638695000
C	1.670140000	2.147331000	-1.636766000
C	2.373065000	3.308943000	-2.005108000
C	2.736480000	4.227471000	-1.007374000
C	2.380981000	3.959383000	0.324843000
C	1.660551000	2.789500000	0.604995000
C	-1.093415000	1.029753000	-2.705384000
C	-2.326092000	0.720583000	-1.839416000
C	-3.474861000	1.723880000	-2.143344000
C	-3.330099000	2.834732000	-1.060510000
C	-2.120979000	2.394287000	-0.197790000
C	-2.964641000	0.207247000	0.491272000
C	-2.760966000	-1.291292000	0.517927000
C	-3.817353000	-2.170158000	0.821736000
C	-3.549012000	-3.540922000	0.951435000
C	-2.232087000	-3.991966000	0.765296000
C	-1.244673000	-3.050907000	0.444551000
C	3.122859000	-3.133704000	-0.392934000
H	1.846086000	-3.168440000	-3.572727000
H	3.560506000	-4.358499000	-2.146177000
H	2.413434000	-1.729629000	1.134814000
H	0.368101000	-1.188210000	-3.836709000
H	-0.813405000	-1.556473000	-2.543929000
H	1.306745000	1.465401000	-3.673830000
H	2.200305000	0.334963000	-2.628198000
H	2.637230000	3.484407000	-3.059726000
H	3.290020000	5.142900000	-1.268355000
H	2.649471000	4.648621000	1.139148000
H	1.329403000	2.528409000	1.623004000
H	-1.343026000	0.834269000	-3.776649000
H	-0.867109000	2.113037000	-2.632050000
H	-2.637687000	-0.333498000	-1.989410000
H	-3.394786000	2.120932000	-3.175935000
H	-4.462114000	1.225015000	-2.081367000
H	-4.251406000	2.912781000	-0.449479000
H	-3.161823000	3.837066000	-1.501304000
H	-1.182535000	2.866711000	-0.546996000
H	-2.214660000	2.624184000	0.880304000
H	-4.020327000	0.441464000	0.226526000
H	-2.789617000	0.582251000	1.522764000
H	-4.835815000	-1.777275000	0.965659000
H	-4.357208000	-4.247446000	1.196119000
H	-1.970180000	-5.055851000	0.863351000
H	-0.199762000	-3.361300000	0.288303000
H	3.866655000	-3.609089000	0.263325000
O	0.885224000	-0.143471000	1.884274000
O	-0.254379000	0.701783000	1.936161000

Reaction intermediate **1 in the excited singlet spin state**

Mn	-0.073490000	0.016849000	-0.152058000
N	1.312221000	-1.305555000	-0.716905000
N	1.128904000	1.613903000	-0.355841000
N	-1.947733000	0.988960000	-0.463923000
N	-1.361153000	-1.507226000	0.204671000
N	-0.035450000	0.195499000	-2.281058000
C	1.153057000	-1.861236000	-1.962955000
C	1.971536000	-2.892535000	-2.429858000
C	2.992698000	-3.394306000	-1.598096000
C	2.317093000	-1.773399000	0.076580000
C	0.045604000	-1.216038000	-2.755258000
C	1.212261000	0.943143000	-2.666213000
C	1.557852000	1.953875000	-1.605019000
C	2.336408000	3.092153000	-1.849447000
C	2.728647000	3.897161000	-0.763196000
C	2.325898000	3.519812000	0.526269000
C	1.526811000	2.379592000	0.695668000
C	-1.224762000	0.933467000	-2.796438000
C	-2.425705000	0.756045000	-1.879680000
C	-3.526016000	1.822876000	-2.141846000
C	-3.300548000	2.915838000	-1.052185000
C	-2.014393000	2.483135000	-0.316888000
C	-2.899555000	0.335135000	0.487239000
C	-2.645031000	-1.144558000	0.506335000
C	-3.630017000	-2.073648000	0.868494000
C	-3.293170000	-3.432054000	0.979751000

C	-1.964340000	-3.802744000	0.721864000	C	1.154479000	1.015231000	-2.785365000
C	-1.039908000	-2.822519000	0.344657000	C	1.636011000	2.199859000	-1.972310000
C	3.164717000	-2.810581000	-0.332948000	C	2.378960000	3.249730000	-2.536995000
H	1.811271000	-3.297869000	-3.440602000	C	2.875772000	4.264037000	-1.703251000
H	3.643709000	-4.212605000	-1.939667000	C	2.615454000	4.199427000	-0.324535000
H	2.417045000	-1.284195000	1.055312000	C	1.858509000	3.128542000	0.165835000
H	0.233421000	-1.277687000	-3.852120000	C	-1.269308000	1.226644000	-2.508711000
H	-0.929310000	-1.704187000	-2.545118000	C	-2.436458000	0.897892000	-1.568600000
H	1.102352000	1.402213000	-3.672496000	C	-3.583365000	1.946734000	-1.678101000
H	2.044594000	0.213611000	-2.737535000	C	-3.505095000	2.796523000	-0.379245000
H	2.646332000	3.334090000	-2.877594000	C	-2.182638000	2.364170000	0.278643000
H	3.344227000	4.794848000	-0.925394000	C	-2.823483000	0.032967000	0.741452000
H	2.622169000	4.103894000	1.410290000	C	-2.673218000	-1.465157000	0.529487000
H	1.152220000	2.048516000	1.673869000	C	-2.157983000	-2.284805000	1.555427000
H	-1.462439000	0.623526000	-3.838517000	C	-2.144622000	-3.677004000	1.370864000
H	-0.951226000	2.006875000	-2.834384000	C	-2.630533000	-4.205654000	0.165427000
H	-2.809866000	-0.281753000	-1.943727000	C	-3.103008000	-3.309856000	-0.809285000
H	-3.439051000	2.229001000	-3.170262000	C	2.436691000	-3.311107000	-0.070278000
H	-4.538284000	1.379524000	-2.070881000	H	1.143755000	-3.359356000	-3.244614000
H	-4.162185000	2.959876000	-0.356716000	H	2.654419000	-4.708509000	-1.732522000
H	-3.192529000	3.930159000	-1.483409000	H	2.005096000	-1.677699000	1.337670000
H	-1.113367000	2.912508000	-0.794556000	H	-0.069370000	-1.206698000	-3.631286000
H	-1.974320000	2.747840000	0.755921000	H	-1.224425000	-1.333456000	-2.271178000
H	-3.956687000	0.561565000	0.230740000	H	1.024409000	1.300058000	-3.856407000
H	-2.688620000	0.743901000	1.495540000	H	1.954038000	0.241897000	-2.758168000
H	-4.651488000	-1.723342000	1.082092000	H	2.568537000	3.264445000	-3.621307000
H	-4.046969000	-4.178670000	1.271143000	H	3.460785000	5.095393000	-2.126183000
H	-1.631656000	-4.847063000	0.815100000	H	2.990241000	4.967035000	0.368246000
H	0.006087000	-3.091414000	0.155737000	H	1.629778000	3.012355000	1.237534000
H	3.958370000	-3.149962000	0.349191000	H	-1.603903000	1.094045000	-3.566331000
O	0.662150000	-0.293776000	1.585076000	H	-0.982100000	2.294512000	-2.401829000
O	-0.415899000	0.589376000	1.641871000	H	-2.807187000	-0.127729000	-1.762506000
Reaction intermediate **1-N1**				H	-3.454003000	2.568850000	-2.587924000
Mn	0.181766000	0.562821000	0.216277000	H	-4.567641000	1.449450000	-1.777920000
N	1.029859000	-1.393853000	-0.473298000	H	-4.363275000	2.582114000	0.288638000
N	1.371833000	2.153708000	-0.641293000	H	-3.521754000	3.886681000	-0.574975000
N	-1.964086000	0.925182000	-0.128167000	H	-1.334156000	2.959071000	-0.121216000
N	-3.134667000	-1.975103000	-0.637975000	H	-2.159851000	2.449950000	1.382416000
N	-0.065460000	0.422774000	-2.209157000	H	-3.893106000	0.295321000	0.584666000
C	0.780415000	-1.841771000	-1.727856000	H	-2.556936000	0.271997000	1.787698000
C	1.353946000	-3.028394000	-2.215780000	H	-1.775458000	-1.833392000	2.482646000
C	2.192019000	-3.776177000	-1.372831000	H	-1.762405000	-4.339388000	2.163379000
C	1.839515000	-2.110776000	0.338153000	H	-2.650997000	-5.290399000	-0.019682000
C	-0.195480000	-1.010328000	-2.540274000	H	-3.492118000	-3.682520000	-1.773287000

H	3.090290000	-3.862059000	0.622068000
O	-0.088302000	0.063609000	1.988354000
O	1.212097000	0.606196000	1.780710000

Reaction Intermediate **1-N2**

Mn	0.642578000	-0.336866000	0.509796000
N	1.646910000	-1.682862000	-0.762282000
N	1.415887000	1.677856000	0.094723000
N	-3.105157000	1.023235000	-0.798280000
N	-1.242645000	-1.490142000	0.542180000
N	0.072662000	0.306194000	-1.947600000
C	1.263011000	-1.873365000	-2.055460000
C	1.888828000	-2.837061000	-2.865317000
C	2.921922000	-3.624585000	-2.335202000
C	2.659453000	-2.433643000	-0.254102000
C	0.123004000	-1.024567000	-2.581217000
C	1.298110000	1.084675000	-2.257858000
C	1.604131000	2.102785000	-1.180786000
C	2.117464000	3.378075000	-1.465165000
C	2.460023000	4.230796000	-0.402501000
C	2.273343000	3.780911000	0.913909000
C	1.744193000	2.499541000	1.119548000
C	-1.105451000	1.101954000	-2.415327000
C	-2.537256000	0.590019000	-2.085693000
C	-3.579068000	1.194676000	-3.058452000
C	-3.971693000	2.551190000	-2.411182000
C	-3.527324000	2.427351000	-0.931083000
C	-2.441128000	0.649739000	0.430957000
C	-2.437215000	-0.853620000	0.622650000
C	-3.630662000	-1.559039000	0.864223000
C	-3.583452000	-2.946283000	1.058629000
C	-2.337944000	-3.595562000	1.002855000
C	-1.196686000	-2.829628000	0.742377000
C	3.317237000	-3.414607000	-1.003801000
H	1.564401000	-2.960322000	-3.909880000
H	3.419051000	-4.384334000	-2.957792000
H	2.931866000	-2.220489000	0.790852000
H	0.196513000	-0.958391000	-3.695121000
H	-0.832471000	-1.545903000	-2.357518000
H	1.229438000	1.577546000	-3.256164000
H	2.159785000	0.385392000	-2.312173000
H	2.249232000	3.694830000	-2.511214000
H	2.864361000	5.235176000	-0.602443000
H	2.527338000	4.411837000	1.778336000
H	1.563213000	2.084925000	2.124503000
H	-1.020595000	1.210133000	-3.525468000
H	-0.982149000	2.122610000	-1.994440000
H	-2.560253000	-0.520659000	-2.132204000
H	-3.199624000	1.299244000	-4.094381000
H	-4.455196000	0.518350000	-3.093730000
H	-5.059694000	2.736438000	-2.499686000
H	-3.462880000	3.403357000	-2.904914000
H	-2.696143000	3.143689000	-0.700801000
H	-4.340402000	2.638973000	-0.204671000
H	-2.995186000	1.116578000	1.273483000
H	-1.383516000	1.031823000	0.514917000
H	-4.581756000	-1.007431000	0.903597000
H	-4.504363000	-3.514310000	1.262567000
H	-2.246885000	-4.679846000	1.163720000
H	-0.197552000	-3.289352000	0.700429000
H	4.129883000	-3.996536000	-0.545076000
O	1.399960000	-1.052176000	2.077999000
O	0.523118000	0.033776000	2.321413000

Reaction intermediate **1-N3**

Mn	-0.218542000	0.461227000	0.309129000
N	1.872321000	-2.784403000	-3.093407000
N	1.002273000	2.275073000	-0.327341000
N	-2.181000000	1.123683000	-0.299450000
N	-1.588795000	-1.420790000	0.548644000
N	0.183304000	0.177212000	-1.872116000
C	1.394020000	-2.084196000	-2.040974000
C	1.962858000	-2.167731000	-0.752405000
C	3.071035000	-3.010154000	-0.557422000
C	2.921238000	-3.602095000	-2.888196000
C	0.173991000	-1.238692000	-2.379862000
C	1.448080000	0.863445000	-2.265214000
C	1.682682000	2.144838000	-1.488928000
C	2.620109000	3.105024000	-1.910386000
C	2.878810000	4.207749000	-1.081774000
C	2.194533000	4.319289000	0.141237000
C	1.261080000	3.330580000	0.476821000
C	-0.973010000	0.931550000	-2.470502000
C	-2.316279000	0.724146000	-1.758747000
C	-3.420067000	1.650353000	-2.354597000
C	-3.598958000	2.804032000	-1.325856000
C	-2.452210000	2.602441000	-0.316212000
C	-3.188672000	0.423442000	0.549664000

C	-2.873194000	-1.045393000	0.749940000
C	-3.857797000	-1.946164000	1.192952000
C	-3.489939000	-3.271597000	1.469446000
C	-2.151157000	-3.654157000	1.286995000
C	-1.238891000	-2.697843000	0.822384000
C	3.560393000	-3.749966000	-1.644644000
H	1.565338000	-1.580395000	0.092438000
H	3.540330000	-3.085977000	0.435955000
H	3.273724000	-4.161768000	-3.772264000
H	0.095085000	-1.238994000	-3.489528000
H	-0.742016000	-1.717921000	-1.975620000
H	1.472413000	1.050323000	-3.363697000
H	2.287713000	0.170062000	-2.046717000
H	3.148631000	2.980289000	-2.868254000
H	3.612824000	4.970256000	-1.385137000
H	2.378170000	5.159903000	0.826459000
H	0.696874000	3.356424000	1.422910000
H	-1.081386000	0.656494000	-3.544441000
H	-0.715355000	2.009705000	-2.441477000
H	-2.601245000	-0.345517000	-1.795054000
H	-3.112064000	2.027745000	-3.350966000
H	-4.364557000	1.094836000	-2.513778000
H	-4.585411000	2.739262000	-0.824190000
H	-3.550469000	3.805854000	-1.795405000
H	-1.527089000	3.111503000	-0.651228000
H	-2.670156000	2.954024000	0.710607000
H	-4.218078000	0.541472000	0.144289000
H	-3.172706000	0.919714000	1.544327000
H	-4.896414000	-1.607221000	1.330013000
H	-4.239309000	-3.995763000	1.824452000
H	-1.813439000	-4.679791000	1.496208000
H	-0.181645000	-2.956060000	0.658048000
H	4.423109000	-4.424787000	-1.537401000
O	0.999763000	0.007550000	1.639520000
O	-0.119585000	0.746087000	2.130579000