

**Supplemental Figures and Tables for:**

**Correlation Between Structural, Spectroscopic, and Reactivity  
Properties Within a Series of Structurally Analogous Metastable  
Manganese(III)-Alkylperoxo Complexes**

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**Supplemental Figures:**

**Figure S-1.** Quantitative UV/vis of  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}2}\text{N}_4(\text{QuinoEN}))(\text{OO}^t\text{Bu})](\text{BPh}_4)$  (**1a**) in  $\text{CH}_2\text{Cl}_2$  at 258 K. Extinction coefficient matches that obtained via in situ stoichiometric titrations, and is estimated based on a MW that includes the counterion + complex.

**Figure S-2.** Quantitative UV/vis of  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}2}\text{N}_4(\text{QuinoPN}))(\text{OO}^t\text{Bu})](\text{PF}_6)\bullet\text{pentane}$  (**2a**) in  $\text{CH}_2\text{Cl}_2$  at 258 K. Extinction coefficient matches that obtained via in situ stoichiometric titrations, and is estimated based on a MW that includes the counterion + complex, but not solvent of crystallization.

**Figure S-3.** Quantitative UV/vis of  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}2}\text{N}_4(6\text{-Me-DPEN}))(\text{OO}^t\text{Bu})](\text{BPh}_4)\bullet\text{Et}_2\text{O}$  (**3a**) in  $\text{CH}_2\text{Cl}_2$  at 258 K. Extinction coefficient matches that obtained via in situ stoichiometric titrations, and is estimated based on a MW that includes the counterion + complex, but not solvent of crystallization.

**Figure S-4.** Quantitative UV/vis of  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}2}\text{N}_4(6\text{-Me-DPPN}))(\text{OO}^t\text{Bu})(\text{BPh}_4)\bullet\text{Et}_2\text{O}$  (**4a**) in  $\text{CH}_2\text{Cl}_2$  at 258 K. Extinction coefficient matches that obtained via in situ stoichiometric titrations, and is estimated based on a MW that includes the counterion + complex, but not solvent of crystallization.

**Figure S-5.** Titration of 0-2.0 equiv of tBuOOH (in 0.4 equiv aliquots) to a  $\text{CH}_2\text{Cl}_2$  solution  $[\text{Mn}^{\text{II}}(\text{S}^{\text{Me}2}\text{N}_4(2\text{-QuinoPN}))](\text{PF}_6)$  (**2**; 2.1 mM), in the presence of 2 equiv of  $\text{Et}_3\text{N}$ , at -15 °C as monitored by visible absorption spectroscopy.

**Figure S-6.** Titration of 0-2.5 equiv of tBuOOH (in 0.3 equiv aliquots) to a  $\text{CH}_2\text{Cl}_2$  solution  $[\text{Mn}^{\text{II}}(\text{S}^{\text{Me}2}\text{N}_4(6\text{-Me-DPEN}))](\text{BPh}_4)$  (**3**; 1.1 mM), in the presence of 2 equiv of  $\text{Et}_3\text{N}$ , at -15 °C as monitored by visible absorption spectroscopy.

**Figure S-7.** ESI-MS of  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}2}\text{N}_4(\text{QuinoPN}))({}^{16}\text{O}{}^{16}\text{O}^t\text{Bu})](\text{PF}_6)\bullet\text{C}_5\text{H}_{12}$  (**2a**).

**Figure S-8.** ESI-MS of  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}2}\text{N}_4(\text{QuinoPN}))({}^{18}\text{O}{}^{18}\text{O}^t\text{Bu})](\text{PF}_6)\bullet\text{C}_5\text{H}_{12}$  (**2a**).

**Figure S-9.** ESI-MS of  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}2}\text{N}_4(6\text{-Me-DPEN}))({}^{16}\text{O}{}^{16}\text{O}^t\text{Bu})](\text{BPh}_4)$  (**3a**).

**Figure S-10.** ESI-MS of  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}2}\text{N}_4(6\text{-Me-DPEN}))({}^{18}\text{O}{}^{18}\text{O}^t\text{Bu})](\text{BPh}_4)$  (**3a**).

**Figure S-11.** ESI-MS of  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}2}\text{N}_4(6\text{-Me-DPPN}))({}^{16}\text{O}{}^{16}\text{O}^t\text{Bu})](\text{BPh}_4)\bullet\text{Et}_2\text{O}$  (**4a**).

**Figure S-12.** ESI-MS of  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}2}\text{N}_4(6\text{-Me-DPPN}))({}^{18}\text{O}{}^{18}\text{O}^t\text{Bu})](\text{BPh}_4)\bullet\text{Et}_2\text{O}$  (**4a**).

**Figure S-13.** FT-IR (nujol mull) of metastable  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}2}\text{N}_4(\text{QuinoPN}))({}^{16}\text{O}{}^{16}\text{O}^t\text{Bu})](\text{BPh}_4)$  (**2a**) versus metastable  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}2}\text{N}_4(\text{QuinoPN}))({}^{18}\text{O}{}^{18}\text{O}^t\text{Bu})](\text{BPh}_4)$  (**2a**).

**Figure S-14.** FT-IR (nujol mull) of metastable  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}^2}\text{N}_4(6\text{-Me-DPPN}))^{16}\text{O}^{16}\text{O}^{\text{tBu}}](\text{BPh}_4)$  (**4a**) versus metastable  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}^2}\text{N}_4(6\text{-Me-DPPN}))^{18}\text{O}^{18}\text{O}^{\text{tBu}}](\text{BPh}_4)$  (**4a**).

**Figure S-15.** Plot of  $\nu(\text{O}-\text{O})$  ( $\text{cm}^{-1}$ ) versus O(1)-O(2) bond length ( $\text{\AA}$ ) for **1a-4a**.

**Figure S-16.** Correlation between the highest energy electronic absorption bands associated with complexes **1a-4a** and the average  $\text{Mn}^{\bullet\bullet\bullet}\text{N}(3,4)$  distance.

**Figure S-17.** Plot of  $\text{Mn}(\text{III})\text{-O}(1)$  bond length ( $\text{\AA}$ ) versus  $\text{Mn}(\text{III})\text{-N}(3,4)_{\text{ave}}$  distance ( $\text{\AA}$ ) for **1a-4a**. Data for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}^2}\text{N}_4(6\text{-Me-DPEN}))(\text{OOCm})(\text{BPh}_4)$  (**3b**) is represented by the pink triangle and is not included in the linear fit correlation coefficient ( $R^2$ ).

**Figure S-18.** Plot of  $\text{Mn}(\text{III})\text{-O}(1)$  ( $\text{\AA}$ ) versus O(1)-O(2) bond length ( $\text{\AA}$ ) for **1a-4a**. Data for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}^2}\text{N}_4(6\text{-Me-DPEN}))(\text{OOCm})(\text{BPh}_4)$  (**3b**) is represented by the pink triangle and is not included in the linear fit correlation coefficient ( $R^2$ ).

**Figure S-19.** Plot of  $\text{Mn}(\text{III})\text{-O}(1)\text{-O}(2)\text{-R}$  dihedral angle (degrees) versus extinction coefficient of the high energy absorption band exhibited by **1a-4a**. Data for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}^2}\text{N}_4(6\text{-Me-DPEN}))(\text{OOCm})(\text{BPh}_4)$  (**3b**) is represented by the pink triangle and is not included in the linear fit correlation coefficient ( $R^2$ ).

**Figure S-20.** Plot of  $\text{Mn}(\text{III})\text{-O}(1)\text{-O}(2)$  bond angle (degrees) versus  $\text{Mn}(\text{III})\text{-O}(1)$  bond length ( $\text{\AA}$ ) for **1a-4a**.

**Figure S-21.** Plot of  $\text{Mn}(\text{III})\text{-O}(1)\text{-O}(2)$  bond angle (degrees) versus O(1)-O(2) bond length ( $\text{\AA}$ ) for **1a-4a**. Data for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}^2}\text{N}_4(6\text{-Me-DPEN}))(\text{OOCm})(\text{BPh}_4)$  (**3b**) is represented by the pink triangle and is not included in the linear fit correlation coefficient ( $R^2$ ).

**Figure S-22.** Plot of  $\text{Mn}(\text{III})\text{-S}(1)$  bond length ( $\text{\AA}$ ) versus O(1)-O(2) bond length ( $\text{\AA}$ ) for **1a-4a** showing that there is very little correlation between these two parameters.

**Figure S-23.** Electronic absorption spectra demonstrating the thermal decay of **3a** at 268 K in  $\text{CH}_2\text{Cl}_2$  with each scan representing 30 minute intervals. Rate constants were calculated from monitoring the time-dependent absorbance value changes at 594 nm.

**Figure S-24.** Eyring plot from the variable-temperature thermal decay kinetics data for **1a** in  $\text{CH}_2\text{Cl}_2$ .

**Figure S-25.** Eyring plot from the variable-temperature thermal decay kinetics data for **3a** in  $\text{CH}_2\text{Cl}_2$ .

**Figure S-26.** Eyring plot from the variable-temperature thermal decay kinetics data for **4a** in  $\text{CH}_2\text{Cl}_2$ .

**Figure S-27.** Electronic absorption spectra demonstrating the thermal decay of **3b** at 268 K in  $\text{CH}_2\text{Cl}_2$ . Rate constants were calculated from monitoring the time-dependent absorbance value changes at 590 nm.

**Figure S-28.** Eyring plot from the variable-temperature thermal decay kinetics data for **3b** in  $\text{CH}_2\text{Cl}_2$ .

**Figure S-29.** Isokinetic plot from the variable-temperature kinetics data for **1a-4a** and **3b**.

**Figure S-30.** Plot of activation parameter  $\Delta H^\ddagger$  versus IR stretching frequency  $\nu_{\text{O}-\text{O}}$  for **1a-4a**.

**Figure S-31.** Plot of activation enthalpy (kcal/mol) from the thermal decay kinetics versus Mn-O(2) bond length ( $\text{\AA}$ ) for **1a-4a** and **3b**.

**Figure S-32.** Plot of activation entropy (cal/mol•K) from the thermal decay kinetics versus Mn-O(2) bond length ( $\text{\AA}$ ). Data for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}^2}\text{N}_4(6\text{-Me-DPEN}))(\text{OOCm})(\text{BPh}_4)]$  (**3b**) is represented by the pink triangle in is not included in the linear fit correlation coefficient ( $R^2$ ).

**Figure S-33.** ESI-MS of 3-methyl-2-butanone-3-disulfide, which was obtained in high yield from the thermal decay of **1a-4a**.

**Figure S-34.**  $^1\text{H}$  NMR spectrum of 3-methyl-2-butanone-3-disulfide obtained in high yield from the thermal decay of **1a-4a**.

**Figure S-35.** Rate constant ( $k_{\text{obs}}$ ) versus  $\text{PEt}_3$  concentration plot for the decay of **1a** in the presence of  $\text{PEt}_3$  showing zero order dependence on substrate.

**Figure S-36.** Rate constant ( $k_{\text{obs}}$ ) versus cyclohexanecarboxaldehyde (CCA) concentration plot for the decay of **1a** in the presence of CCA showing zero order dependence on substrate.

**Figure S-37.** Rate constant ( $k_{\text{obs}}$ ) versus TEMPOH concentration plot for the decay of **1a** in the presence of TEMPOH showing zero order dependence on substrate.

**Figure S-38.** Rate constant ( $k_{\text{obs}}$ ) versus  $\text{PEt}_3$  concentration plot for the decay of **2a** in the presence of  $\text{PEt}_3$  showing zero order dependence on substrate.

**Figure S-39.** Rate constant ( $k_{\text{obs}}$ ) versus cyclohexanecarboxaldehyde (CCA) concentration plot for the decay of **2a** in the presence of CCA showing zero order dependence on substrate.

**Figure S-40.** Rate constant ( $k_{\text{obs}}$ ) versus TEMPOH concentration plot for the decay of **2a** in the presence of TEMPOH showing zero order dependence on substrate.

**Figure S-41.** Rate constant ( $k_{\text{obs}}$ ) versus PEt<sub>3</sub> concentration plot for the decay of **3a** in the presence of PEt<sub>3</sub> showing zero order dependence on substrate.

**Figure S-42.** Rate constant ( $k_{\text{obs}}$ ) versus cyclohexanecarboxaldehyde (CCA) concentration plot for the decay of **3a** in the presence of CCA showing zero order dependence on substrate.

**Figure S-43.** Rate constant ( $k_{\text{obs}}$ ) versus TEMPOH concentration plot for the decay of **3a** in the presence of TEMPOH showing zero order dependence on substrate.

**Figure S-44.** Rate constant ( $k_{\text{obs}}$ ) versus PEt<sub>3</sub> concentration plot for the decay of **3b** in the presence of PEt<sub>3</sub> showing zero order dependence on substrate.

**Figure S-45.** Rate constant ( $k_{\text{obs}}$ ) versus cyclohexanecarboxaldehyde (CCA) concentration plot for the decay of **3b** in the presence of CCA showing zero order dependence on substrate.

**Figure S-46.** Rate constant ( $k_{\text{obs}}$ ) versus TEMPOH concentration plot for the decay of **3b** in the presence of TEMPOH showing zero order dependence on substrate.

**Figure S-47.** Rate constant ( $k_{\text{obs}}$ ) versus PEt<sub>3</sub> concentration plot for the decay of **4a** in the presence of PEt<sub>3</sub> showing zero order dependence on substrate.

**Figure S-48.** Rate constant ( $k_{\text{obs}}$ ) versus cyclohexanecarboxaldehyde (CCA) concentration plot for the decay of **4a** in the presence of CCA showing zero order dependence on substrate.

**Figure S-49.** Rate constant ( $k_{\text{obs}}$ ) versus TEMPOH concentration plot for the decay of **4a** in the presence of TEMPOH showing zero order dependence on substrate.

**Supplemental Tables:**

**Table S-1.** DFT calculated geometric parameters for compounds 1a-4a. Table shows crystal structure bond distances and angles followed by geometry optimized structures without the Van der Waals correction (vdw10) and with the correction. The last two lines of each section show the difference between calculated structural parameters and the crystal structure.

**Table S-2.** Mulliken charge densities for Van der Waals corrected, geometry optimized compounds **1a-4a**.

**Table S-3.** Geometry optimized structural parameters and Mulliken charges derived from relaxed surface scans over the 1.1 to 1.6 O-O bond range for compound **3a** and **4a**.

**Table S-4.** Crystal data and structure refinement for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}^2}\text{N}_4(\text{QuinoPN}))(\text{OOtBu})](\text{PF}_6)\bullet\text{pentane}$  (**2a**).

**Table S-5.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}^2}\text{N}_4(\text{QuinoPN}))(\text{OOtBu})](\text{PF}_6)\bullet\text{pentane}$  (**2a**).  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

**Table S-6.** Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}^2}\text{N}_4(\text{QuinoPN}))(\text{OOtBu})](\text{PF}_6)\bullet\text{pentane}$  (**2a**).

**Table S-7.** Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}^2}\text{N}_4(\text{QuinoPN}))(\text{OOtBu})](\text{PF}_6)\bullet\text{pentane}$  (**2a**). The anisotropic displacement factor exponent takes the form:  $-2p^2[h^2a^*{}^2U^{11} + \dots + 2hka^*b^*U^{12}]$

**Table S-8.** Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}^2}\text{N}_4(\text{QuinoPN}))(\text{OOtBu})](\text{PF}_6)\bullet\text{pentane}$  (**2a**).

**Table S-9.** Crystal data and structure refinement for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}^2}\text{N}_4(6\text{-Me-DPEN}))(\text{OOtBu})](\text{BPh}_4)\bullet\text{Et}_2\text{O}$  (**3a**).

**Table S-10.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}^2}\text{N}_4(6\text{-Me-DPEN}))(\text{OOtBu})](\text{BPh}_4)\bullet\text{Et}_2\text{O}$  (**3a**).  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

**Table S-11.** Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}^2}\text{N}_4(6\text{-Me-DPEN}))(\text{OOtBu})](\text{BPh}_4)\bullet\text{Et}_2\text{O}$  (**3a**).

**Table S-12.** Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}^2}\text{N}_4(6\text{-Me-DPEN}))(\text{OOtBu})](\text{BPh}_4)\bullet\text{Et}_2\text{O}$  (**3a**).

DPEN))(OOtBu])(BPh<sub>4</sub>)•Et<sub>2</sub>O (**3a**). The anisotropic displacement factor exponent takes the form: -2p<sup>2</sup>[ h<sup>2</sup>a\*<sup>2</sup>U<sup>11</sup> + ... + 2 h k a\* b\* U<sup>12</sup> ]

**Table S-13.** Hydrogen coordinates ( x 10<sup>4</sup>) and isotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for Mn<sup>III</sup>(S<sup>Me<sup>2</sup></sup>N<sub>4</sub>(6-Me-DPEN))(OOtBu])(BPh<sub>4</sub>)•Et<sub>2</sub>O (**3a**).

**Table S-14.** Crystal data and structure refinement for [Mn<sup>III</sup>(S<sup>Me<sup>2</sup></sup>N<sub>4</sub>(6-Me-DPEN))(OOCm](BPh<sub>4</sub>) (**3b**).

**Table S-15.** Atomic coordinates ( x 10<sup>4</sup>) and equivalent isotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for [Mn<sup>III</sup>(S<sup>Me<sup>2</sup></sup>N<sub>4</sub>(6-Me-DPEN))(OOCm](BPh<sub>4</sub>) (**3b**). U(eq) is defined as one third of the trace of the orthogonalized U<sup>ij</sup> tensor.

**Table S-16.** Bond lengths [Å] and angles [°] for [Mn<sup>III</sup>(S<sup>Me<sup>2</sup></sup>N<sub>4</sub>(6-Me-DPEN))(OOCm](BPh<sub>4</sub>) (**3b**).

**Table S-17.** Anisotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for [Mn<sup>III</sup>(S<sup>Me<sup>2</sup></sup>N<sub>4</sub>(6-Me-DPEN))(OOCm](BPh<sub>4</sub>) (**3b**). The anisotropic displacement factor exponent takes the form: -2p<sup>2</sup>[ h<sup>2</sup>a\*<sup>2</sup>U<sup>11</sup> + ... + 2 h k a\* b\* U<sup>12</sup> ]

**Table S-18.** Hydrogen coordinates ( x 10<sup>4</sup>) and isotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for [Mn<sup>III</sup>(S<sup>Me<sup>2</sup></sup>N<sub>4</sub>(6-Me-DPEN))(OOCm](BPh<sub>4</sub>) (**3b**).

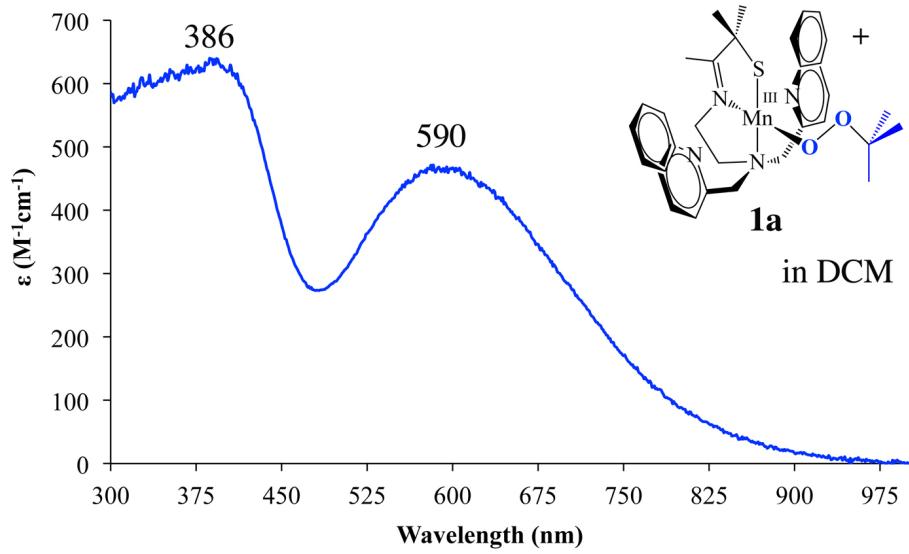
**Table S-19.** Crystal data and structure refinement for [Mn<sup>III</sup>(S<sup>Me<sup>2</sup></sup>N<sub>4</sub>(6-Me-DPPN))(OOtBu](BPh<sub>4</sub>)•Et<sub>2</sub>O (**4a**).

**Table S-20.** Atomic coordinates ( x 10<sup>4</sup>) and equivalent isotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for [Mn<sup>III</sup>(S<sup>Me<sup>2</sup></sup>N<sub>4</sub>(6-Me-DPPN))(OOtBu](BPh<sub>4</sub>)•Et<sub>2</sub>O (**4a**).

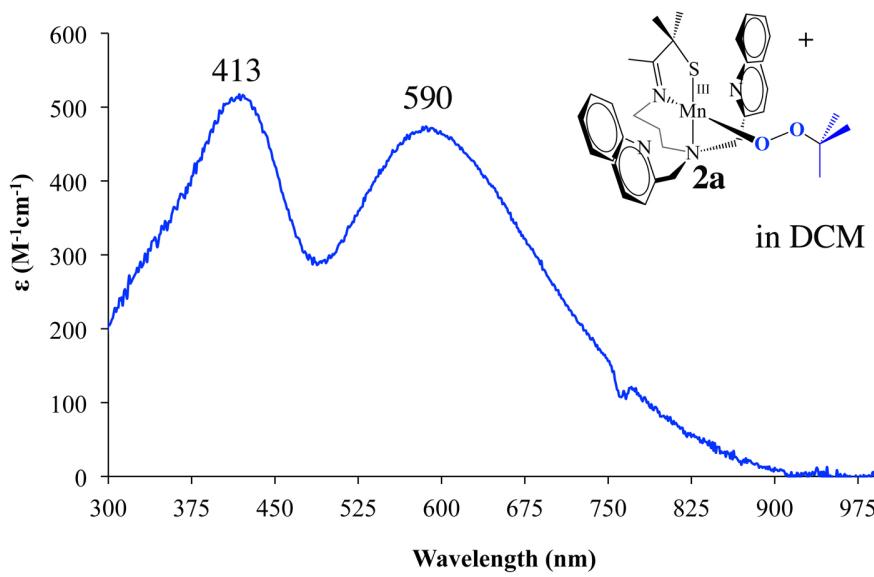
**Table S-21.** Bond lengths [Å] and angles [°] for [Mn<sup>III</sup>(S<sup>Me<sup>2</sup></sup>N<sub>4</sub>(6-Me-DPPN))(OOtBu](BPh<sub>4</sub>)•Et<sub>2</sub>O (**4a**).

**Table S-22.** Anisotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for [Mn<sup>III</sup>(S<sup>Me<sup>2</sup></sup>N<sub>4</sub>(6-Me-DPPN))(OOtBu](BPh<sub>4</sub>)•Et<sub>2</sub>O (**4a**). The anisotropic displacement factor exponent takes the form: -2p<sup>2</sup>[ h<sup>2</sup>a\*<sup>2</sup>U<sup>11</sup> + ... + 2 h k a\* b\* U<sup>12</sup> ]

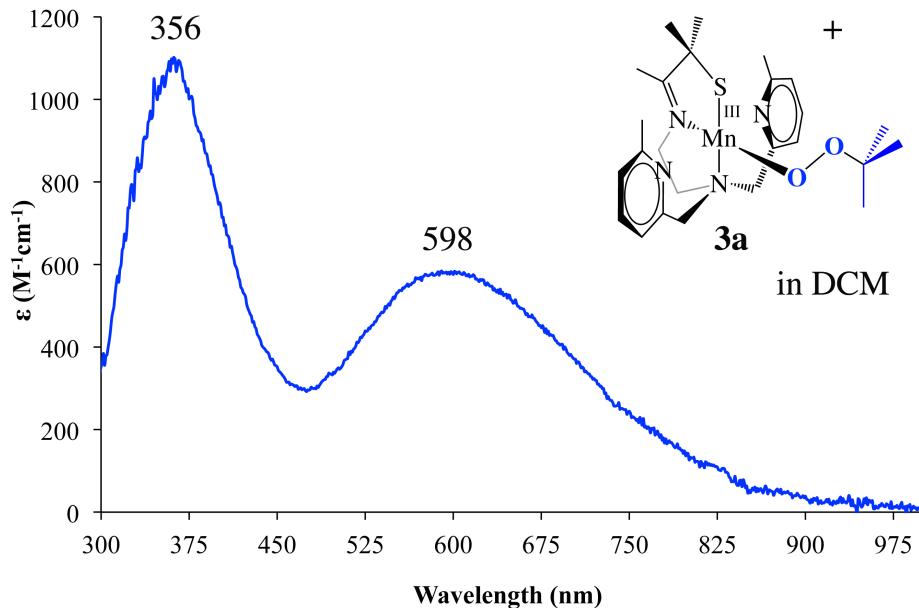
**Table S-23.** Hydrogen coordinates ( x 10<sup>4</sup>) and isotropic displacement parameters (Å<sup>2</sup>x 10<sup>3</sup>) for [Mn<sup>III</sup>(S<sup>Me<sup>2</sup></sup>N<sub>4</sub>(6-Me-DPPN))(OOtBu](BPh<sub>4</sub>)•Et<sub>2</sub>O (**4a**).



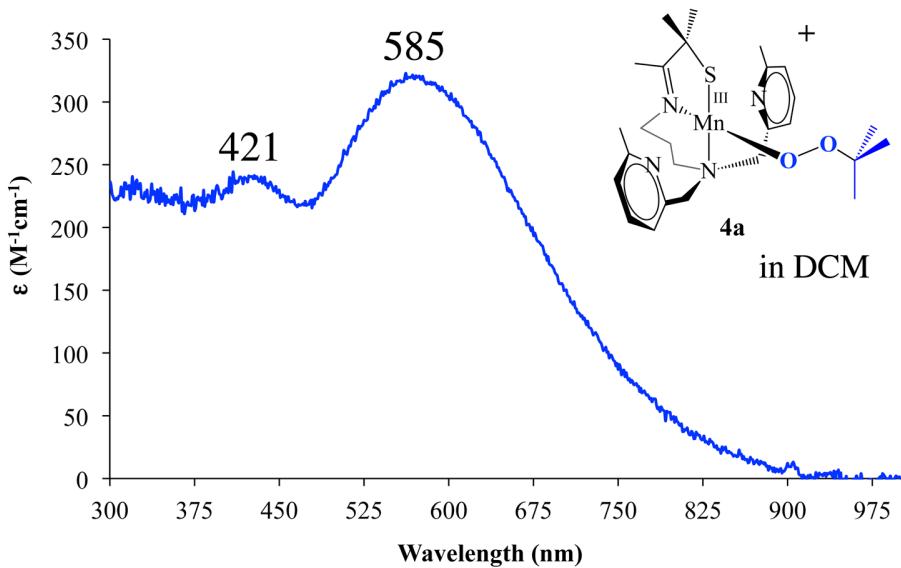
**Figure S-1.** Quantitative UV/vis of  $[\text{Mn}^{\text{III}}(\text{SMe}_2\text{N}_4(\text{QuinoEN}))(\text{OO}^{\text{tBu}})](\text{BPh}_4)$  (**1a**) in  $\text{CH}_2\text{Cl}_2$  at 258 K. Extinction coefficient matches that obtained via *in situ* stoichiometric titrations, and is estimated based on a MW that includes the counterion + complex.



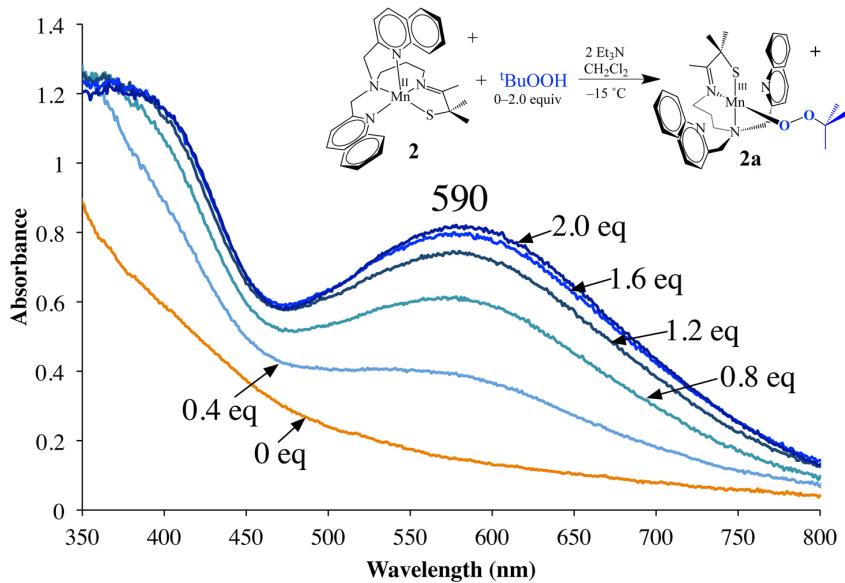
**Figure S-2.** Quantitative UV-vis spectrum of  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4\text{(QuinoPN)})(\text{OOtBu})](\text{PF}_6)$ •pentane (**2a**) in  $\text{CH}_2\text{Cl}_2$  at 258 K. Extinction coefficient matches that obtained via in situ stoichiometric titrations, and is estimated based on a MW that includes the counterion + complex, but not solvent of crystallization.



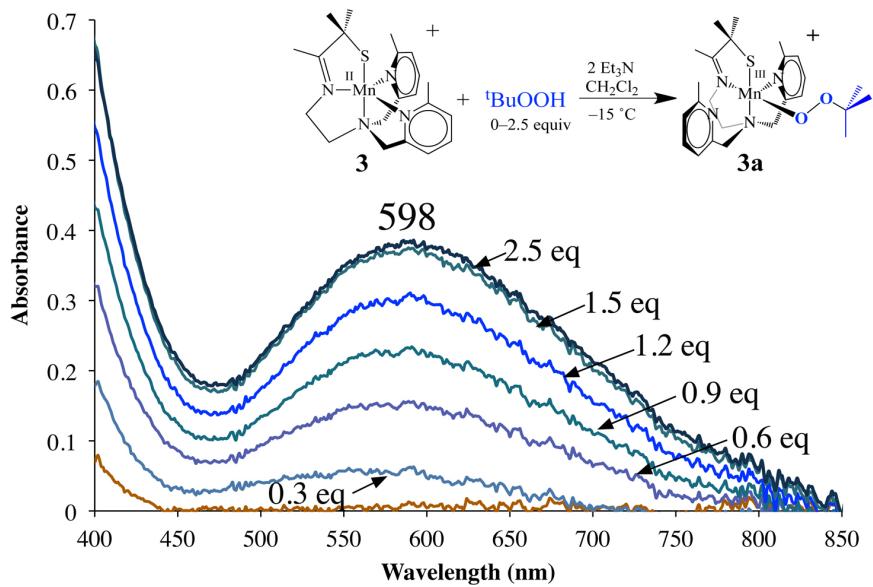
**Figure S-3.** Quantitative UV-vis spectrum of  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(6\text{-MeDPEN}))(\text{OOtBu})](\text{BPh}_4)$ •Et<sub>2</sub>O (**3a**) in  $\text{CH}_2\text{Cl}_2$  at 258 K. Extinction coefficient matches that obtained via in situ stoichiometric titrations, and is estimated based on a MW that includes the counterion + complex, but not solvent of crystallization.



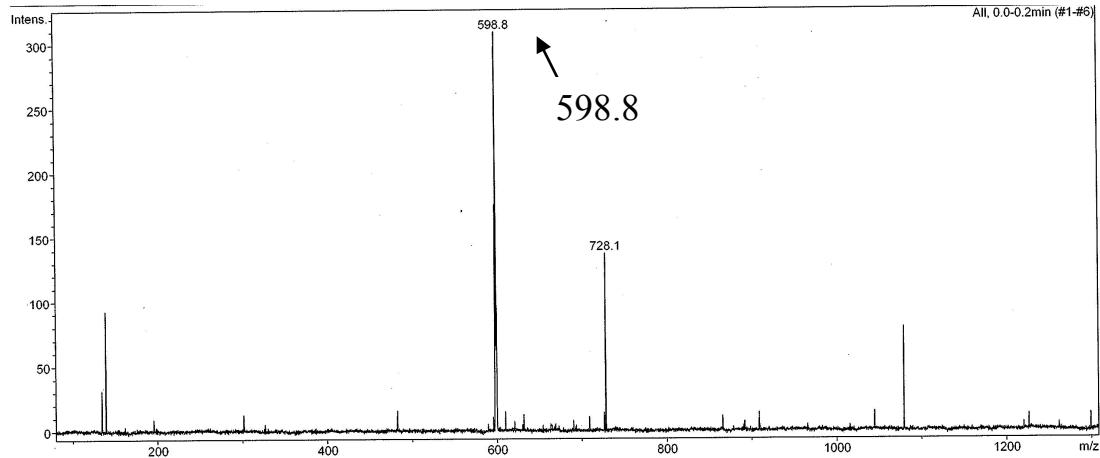
**Figure S-4.** UV/vis of  $[Mn^{III}(S^{Me_2}N_4(6\text{-Me-DPPN}))(OOtBu](BPh_4)\bullet Et_2O$  (**4a**) in  $CH_2Cl_2$  at 258 K. Extinction coefficient matches that obtained via *in situ* stoichiometric titrations, and is estimated based on a MW that includes the counterion + complex, but not solvent of crystallization.



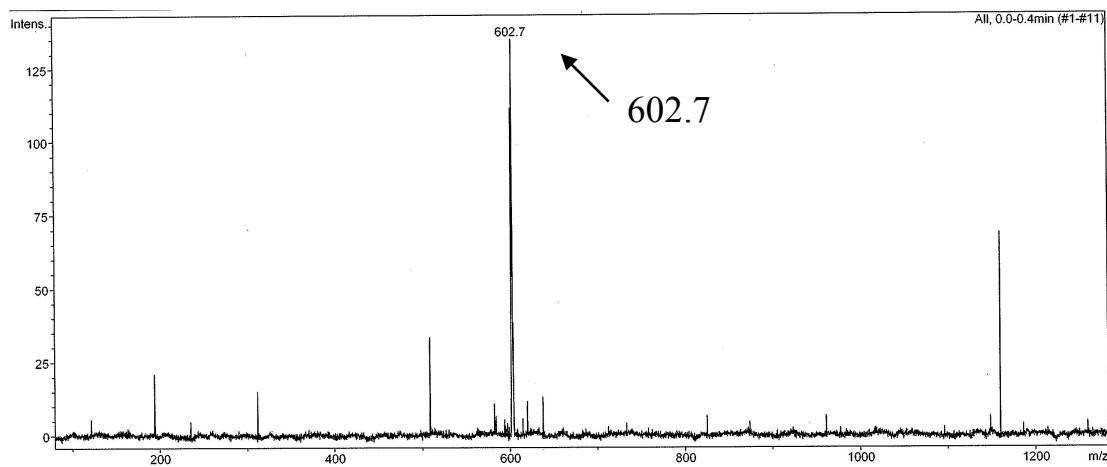
**Figure S-5.** Titration of 0-2.0 equiv of tBuOOH (in 0.4 equiv aliquots) to a  $CH_2Cl_2$  solution  $[Mn^{II}(S^{Me_2}N_4(2\text{-QuinoPN}))](PF_6)$  (**2**; 2.1 mM), in the presence of 2 equiv of  $Et_3N$ , at -15 °C as monitored by visible absorption spectroscopy.



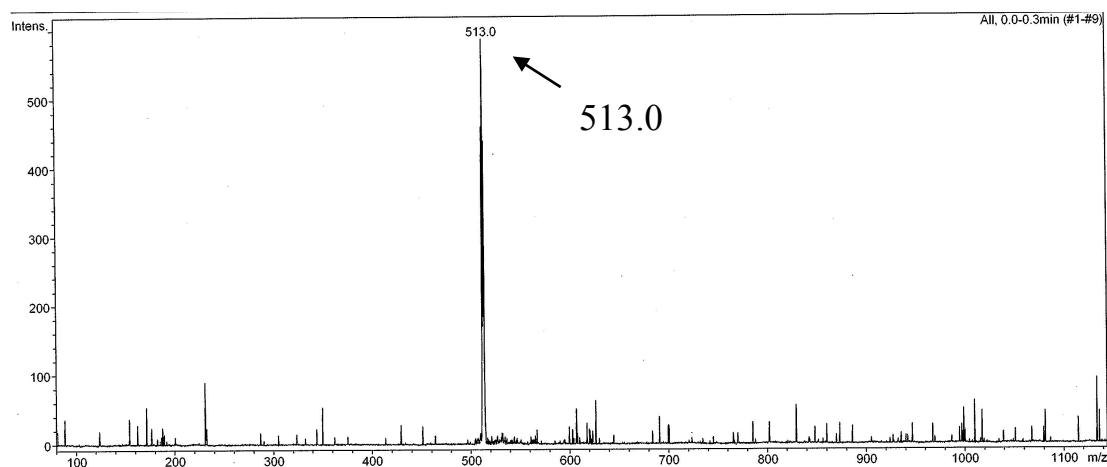
**Figure S-6.** Titration of 0-2.5 equiv of tBuOOH (in 0.3 equiv aliquots) to a CH<sub>2</sub>Cl<sub>2</sub> solution [Mn<sup>II</sup>(S<sup>Me<sub>2</sub></sup>N<sub>4</sub>(6-Me-DPEN))](BPh<sub>4</sub>) (**3**; 1.1 mM), in the presence of 2 equiv of Et<sub>3</sub>N, at -15 °C as monitored by visible absorption spectroscopy.



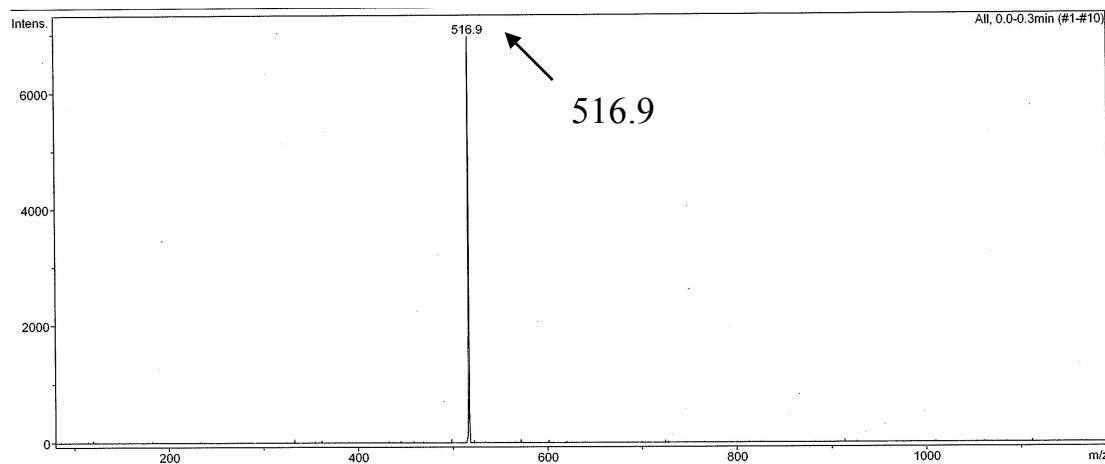
**Figure S-7.** ESI-MS of [Mn<sup>III</sup>(S<sup>Me<sub>2</sub></sup>N<sub>4</sub>(QuinoPN))(<sup>16</sup>O<sup>16</sup>O<sup>t</sup>Bu)]<sup>+</sup> (**2a**).



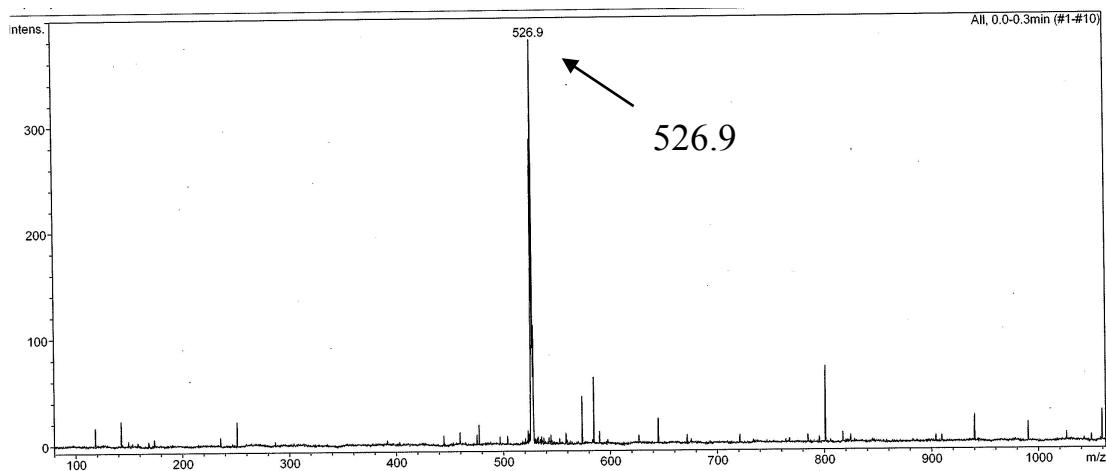
**Figure S-8.** ESI-MS of  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(\text{QuinoPN}))(\text{O}^{18}\text{O}^{\text{tBu}})]^+$  (**2a**).



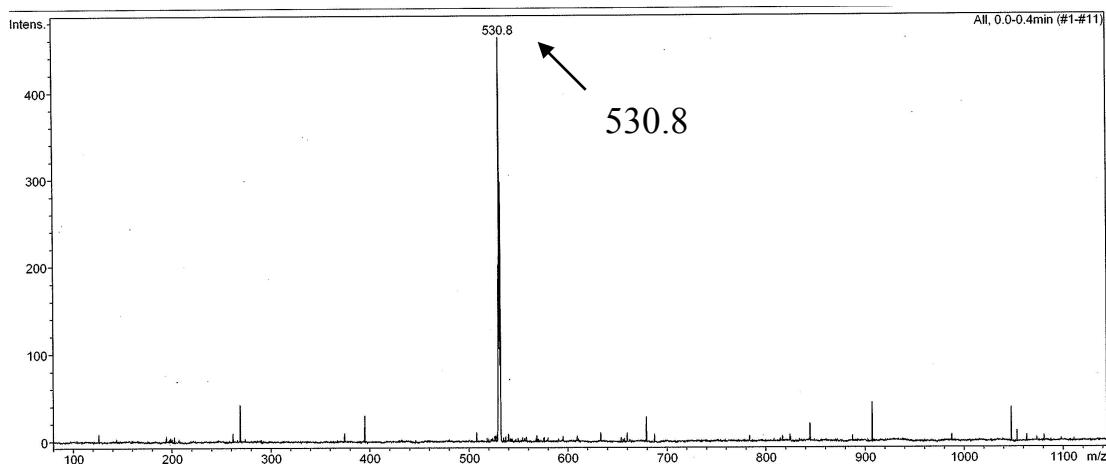
**Figure S-9.** ESI-MS of  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(6\text{-Me-DPEN}))(\text{O}^{16}\text{O}^{\text{tBu}})]^+$  (**3a**).



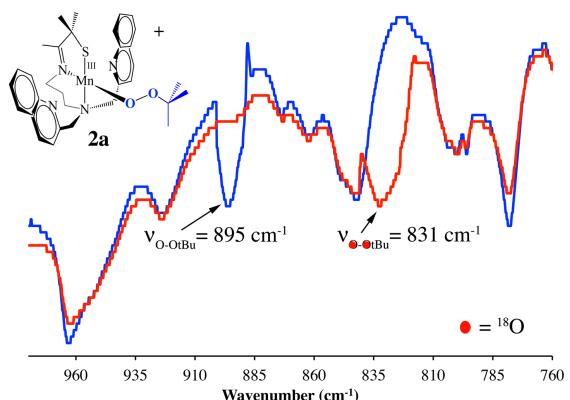
**Figure S-10.** ESI-MS of  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(6\text{-Me-DPEN}))(\text{O}^{18}\text{O}^{\text{tBu}})]^+$  (**3a**).



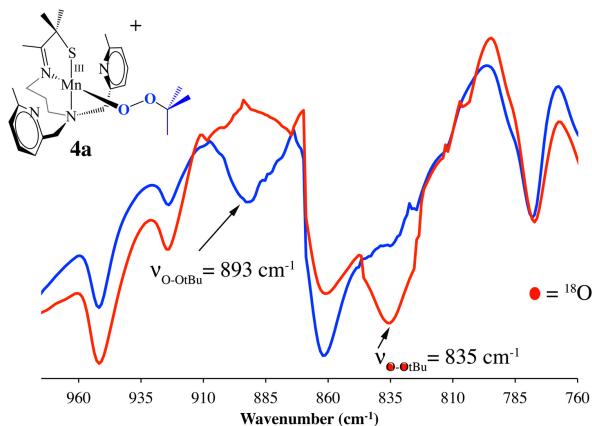
**Figure S-11.** ESI-MS of  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(6\text{-Me-DPPN}))(\text{O}^{16}\text{O}^{\text{t}}\text{Bu})]^+$  (**4a**).



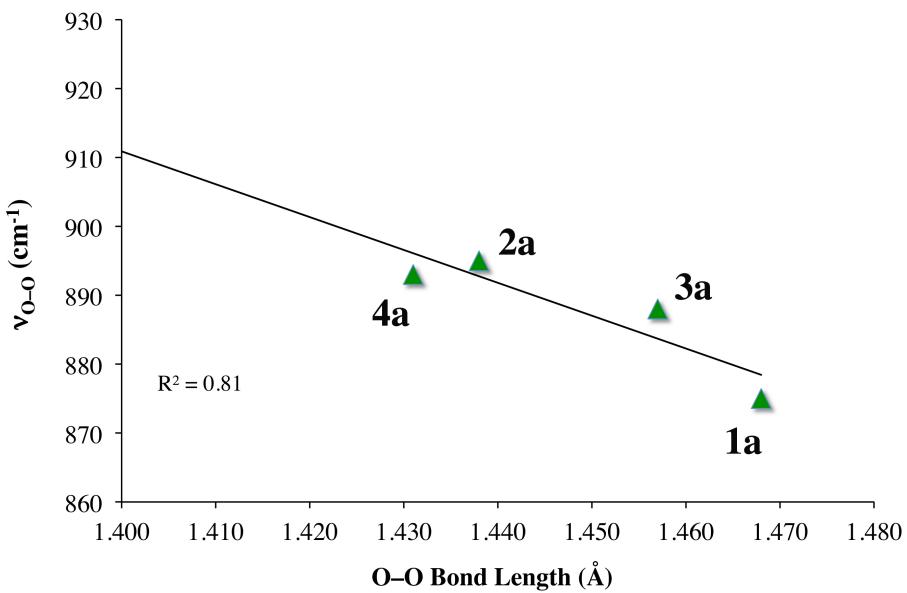
**Figure S-12.** ESI-MS of  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(6\text{-Me-DPPN}))(\text{O}^{18}\text{O}^{\text{t}}\text{Bu})]^+$  (**4a**).



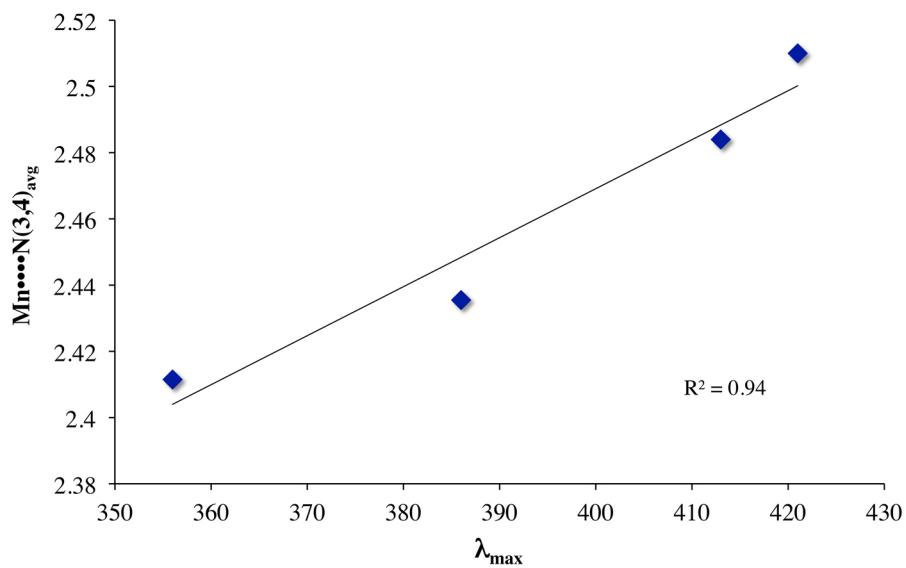
**Figure S-13.** FT-IR (nujol mull) of metastable versus metastable  $[Mn^{III}(SMe_2N_4(\text{QuinoPN}))({}^{16}\text{O}{}^{16}\text{O}^t\text{Bu})](\text{BPh}_4)$  (2a)  $[Mn^{III}(SMe_2N_4(\text{QuinoPN}))({}^{18}\text{O}{}^{18}\text{O}^t\text{Bu})](\text{BPh}_4)$  (2a).



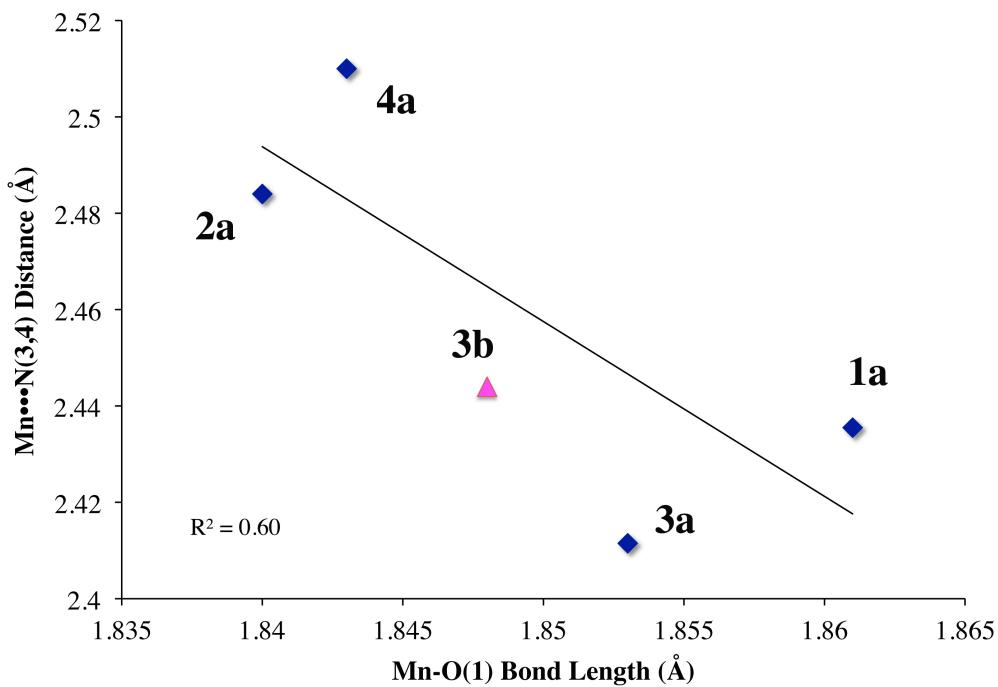
**Figure S-14.** FT-IR (nujol mull) of metastable versus metastable  $[Mn^{III}(SMe_2N_4(6\text{-Me-DPPN}))({}^{16}\text{O}{}^{16}\text{O}^t\text{Bu})](\text{BPh}_4)$  (4a)  $[Mn^{III}(SMe_2N_4(6\text{-Me-DPPN}))({}^{18}\text{O}{}^{18}\text{O}^t\text{Bu})](\text{BPh}_4)$  (4a).



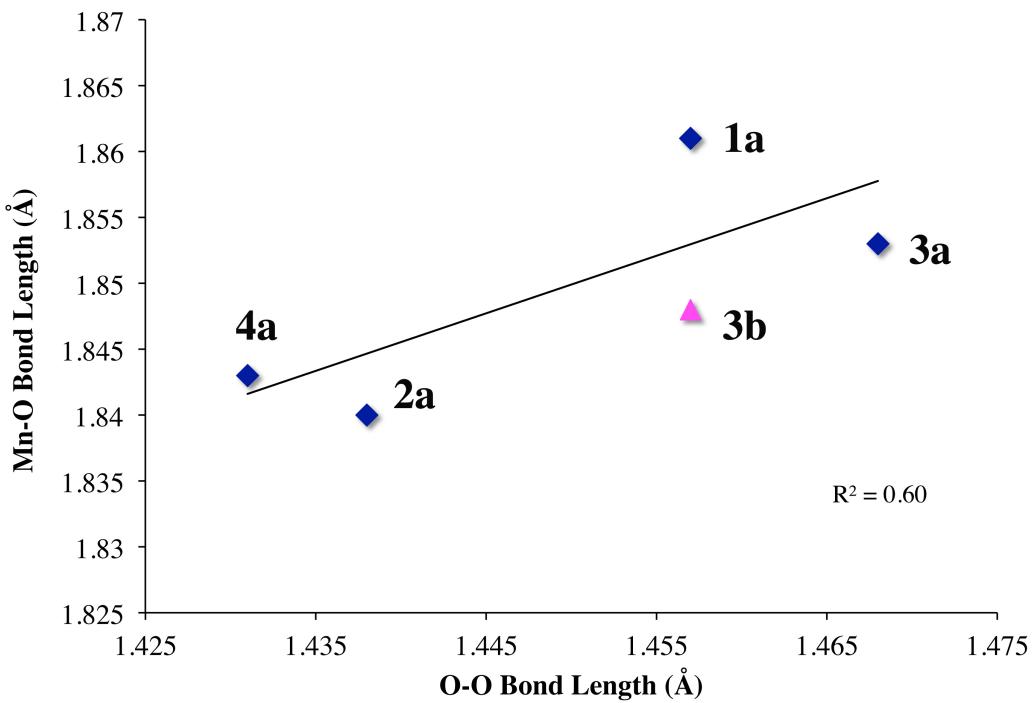
**Figure S-15.** Plot of  $\nu(\text{O-O})$  ( $\text{cm}^{-1}$ ) versus O(1)-O(2) bond length ( $\text{\AA}$ ) for **1a-4a**.



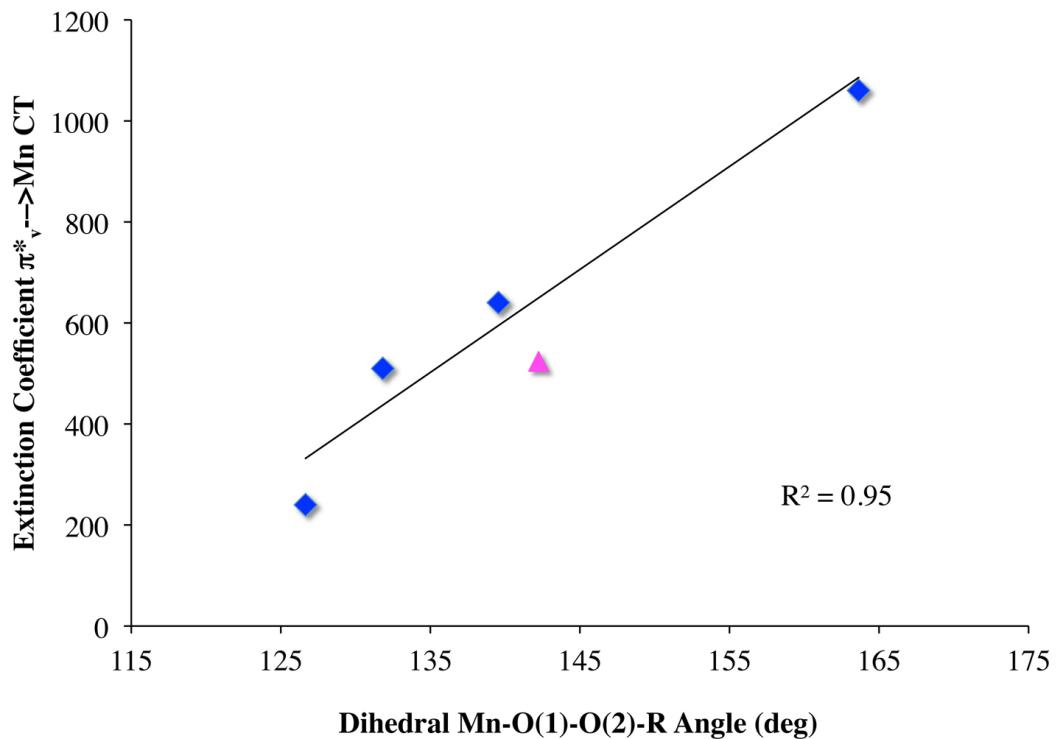
**Figure S-16.** Correlation between the highest energy electronic absorption bands associated with complexes **1a-4a** and the average Mn...N(3,4) distance.



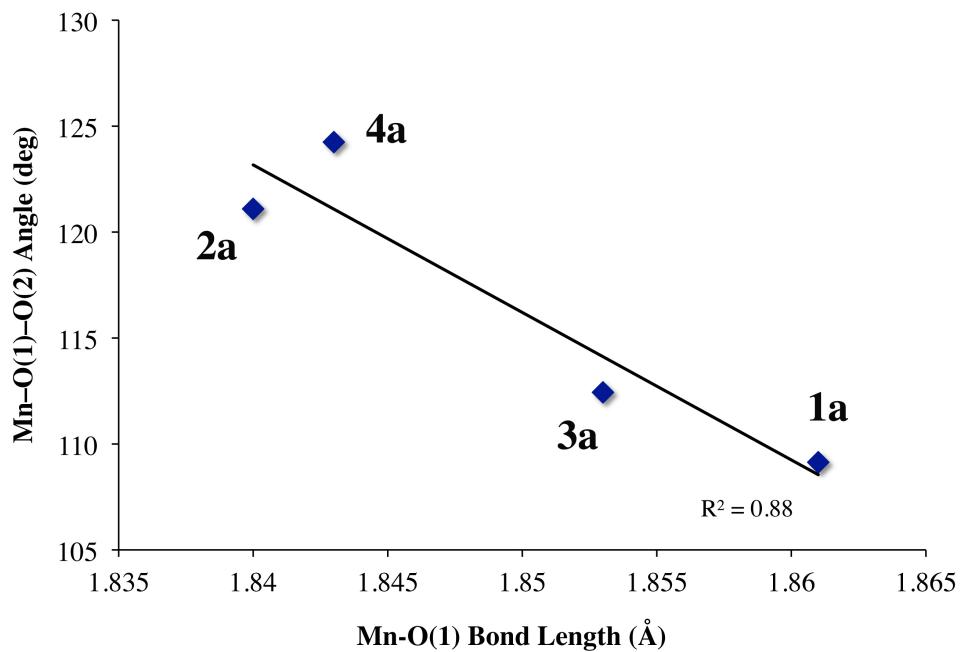
**Figure S-17.** Plot of Mn(III)-O(1) bond length ( $\text{\AA}$ ) versus Mn(III)-N(3,4)<sub>ave</sub> distance ( $\text{\AA}$ ) for **1a-4a**. Data for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(6\text{-Me-DPEN}))(\text{OOCm})](\text{BPh}_4)$  (**3b**) is represented by the pink triangle and is not included in the linear fit correlation coefficient ( $R^2$ ).



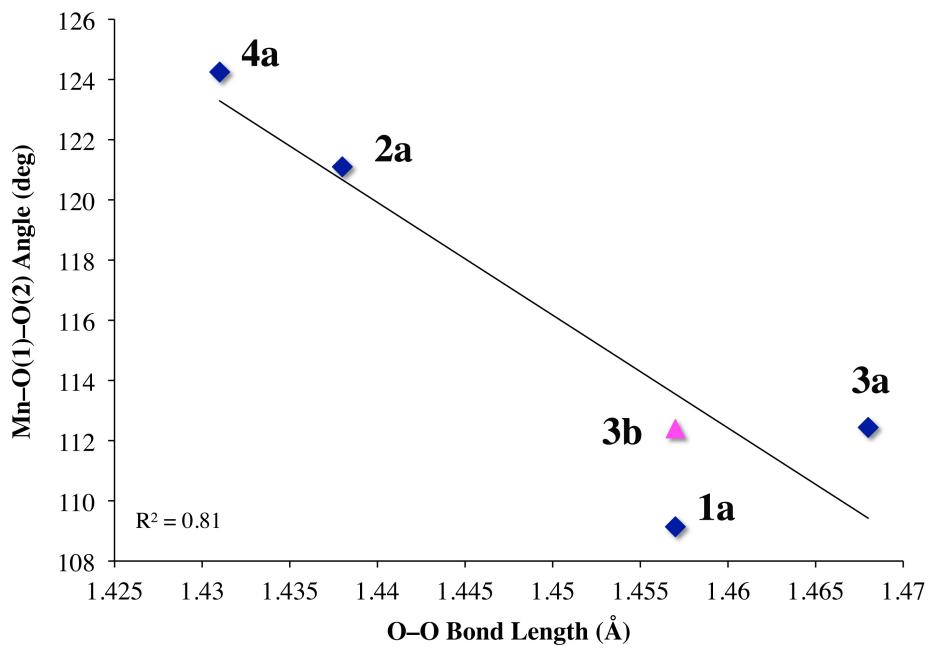
**Figure S-18.** Plot of Mn(III)-O(1) (Å) versus O(1)-O(2) bond length (Å) for **1a-4a**. Data for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4\text{(6-Me-DPEN)})(\text{OOCl})(\text{BPh}_4)]$  (**3b**) is represented by the pink triangle and is not included in the linear fit correlation coefficient ( $R^2$ ).



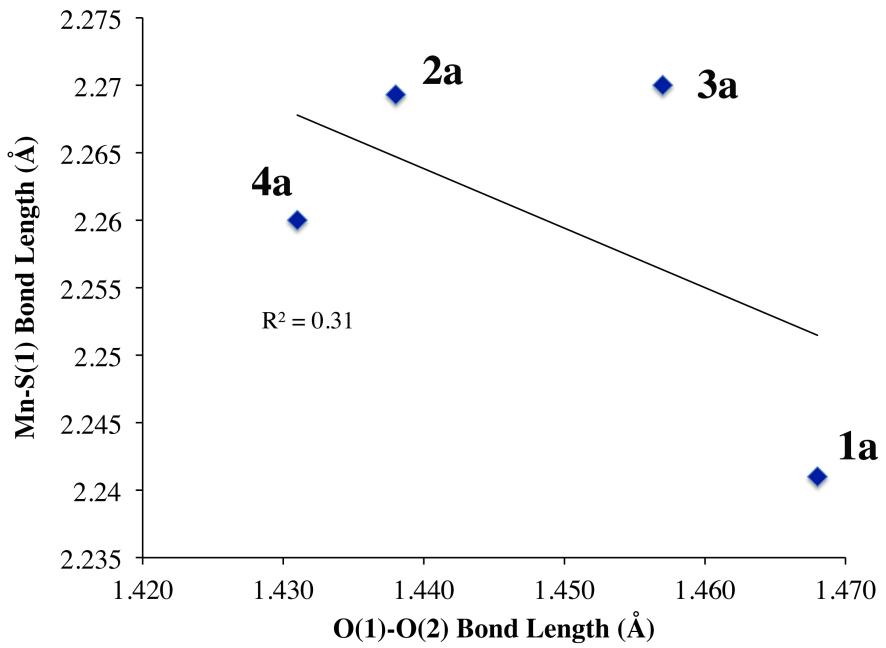
**Figure S-19.** Plot of Mn(III)-O(1)-O(2)-R dihedral angle (degrees) versus extinction coefficient of the high energy absorption band exhibited by **1a-4a**. Data for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4\text{(6-Me-DPEN)})(\text{OOCl})(\text{BPh}_4)]$  (**3b**) is represented by the pink triangle and is not included in the linear fit correlation coefficient ( $R^2$ ).



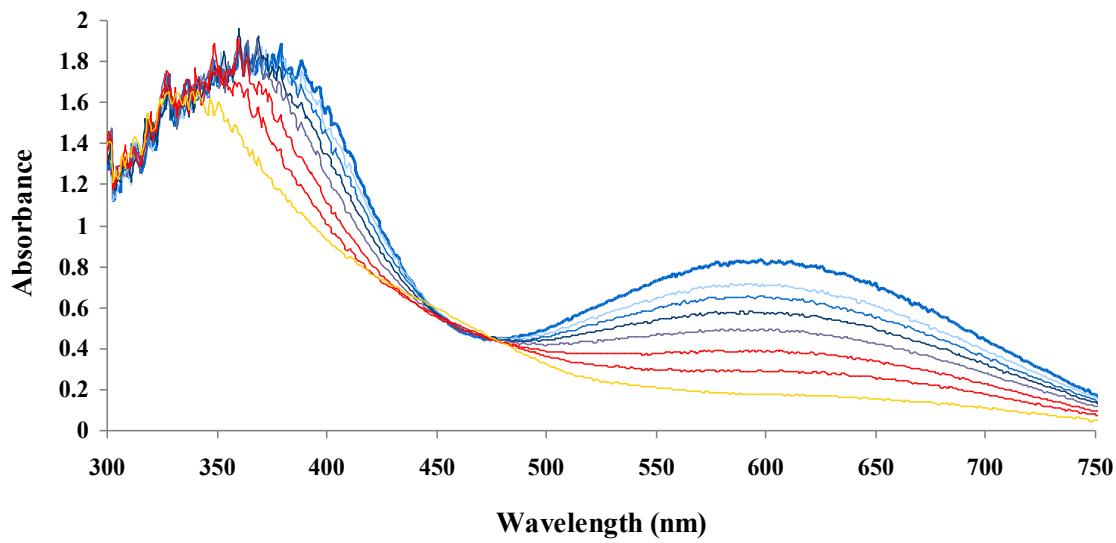
**Figure S-20.** Plot of Mn(III)-O(1)-O(2) bond angle (degrees) versus Mn(III)-O(1) bond length ( $\text{\AA}$ ) for **1a-4a**.



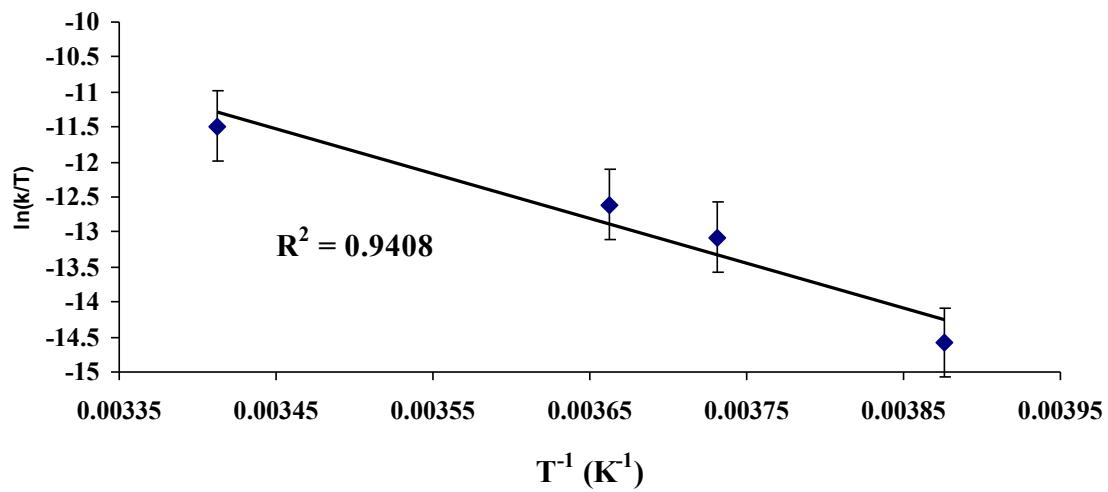
**Figure S-21.** Plot of Mn(III)-O(1)-O(2) bond angle (degrees) versus O(1)-O(2) bond length ( $\text{\AA}$ ) for **1a-4a**. Data for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4\text{-6-Me-DPEN})(\text{OOcm})(\text{BPh}_4)]$  (**3b**) is represented by the pink triangle and is not included in the linear fit correlation coefficient ( $R^2$ ).



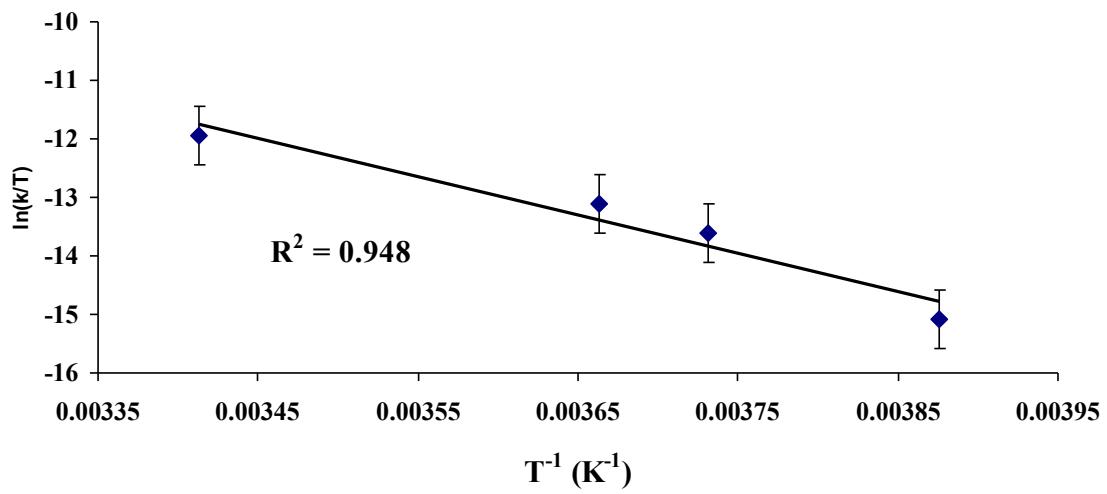
**Figure S-22.** Plot of Mn(III)-S(1) bond length ( $\text{\AA}$ ) versus O(1)-O(2) bond length ( $\text{\AA}$ ) for **1a-4a** showing that there is very little correlation between these two parameters.



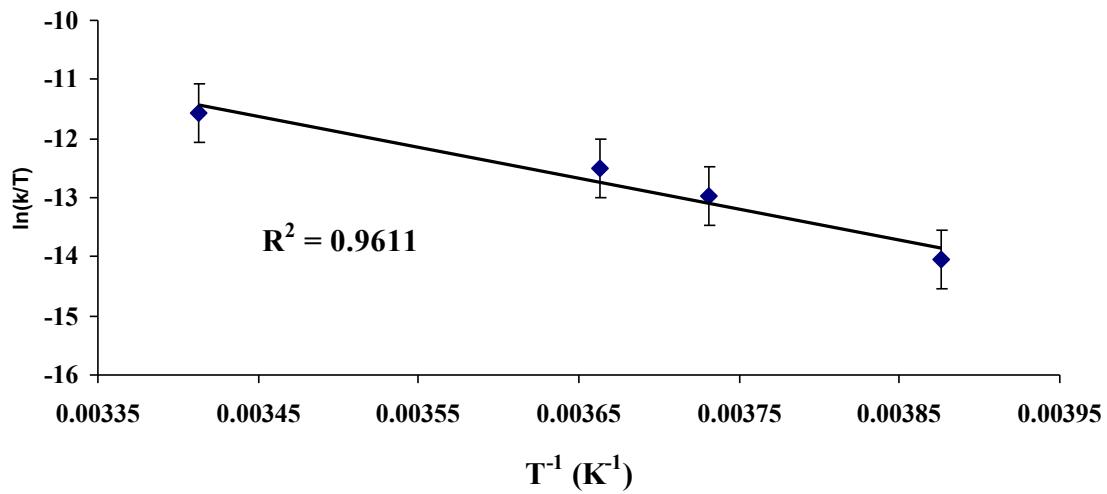
**Figure S-23.** Electronic absorption spectra demonstrating the thermal decay of **3a** at 268 K in  $\text{CH}_2\text{Cl}_2$  with each scan representing 30 minute intervals. Rate constants were calculated from monitoring the time-dependent absorbance value changes at 594 nm.



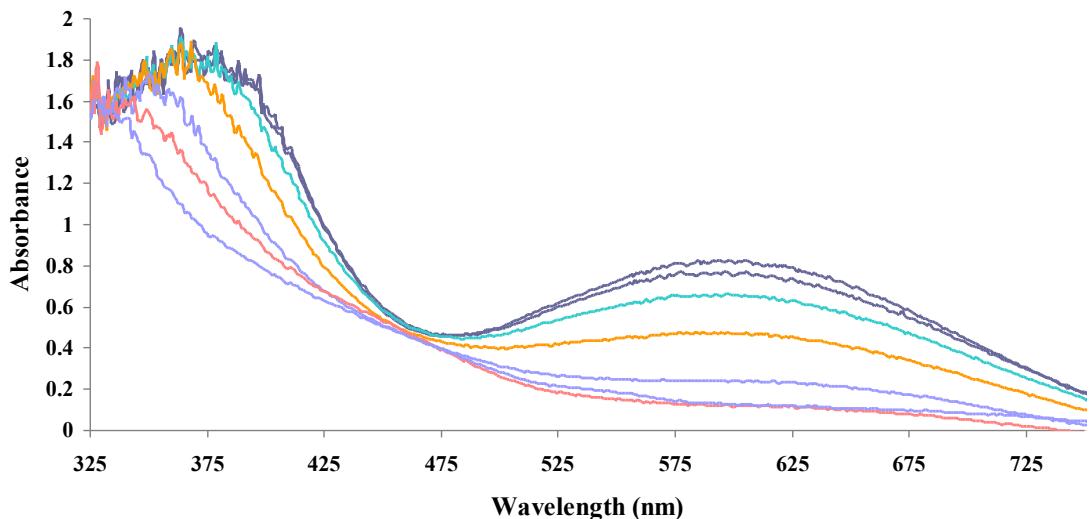
**Figure S-24.** Eyring plot from the variable-temperature thermal decay kinetics data for **1a** in  $\text{CH}_2\text{Cl}_2$ .



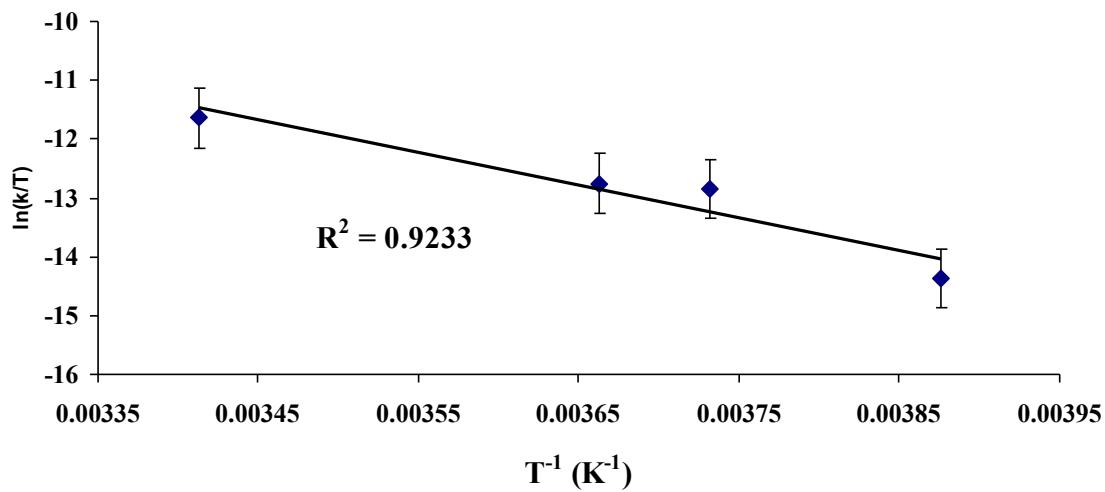
**Figure S-25.** Eyring plot from the variable-temperature thermal decay kinetics data for **3a** in  $\text{CH}_2\text{Cl}_2$ .



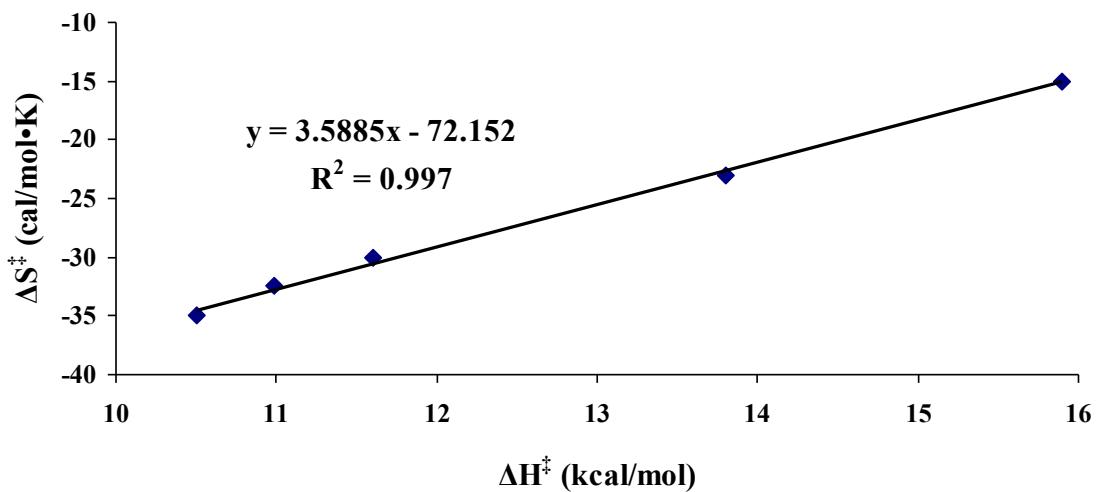
**Figure S-26.** Eyring plot from the variable-temperature thermal decay kinetics data for **4a** in  $\text{CH}_2\text{Cl}_2$ .



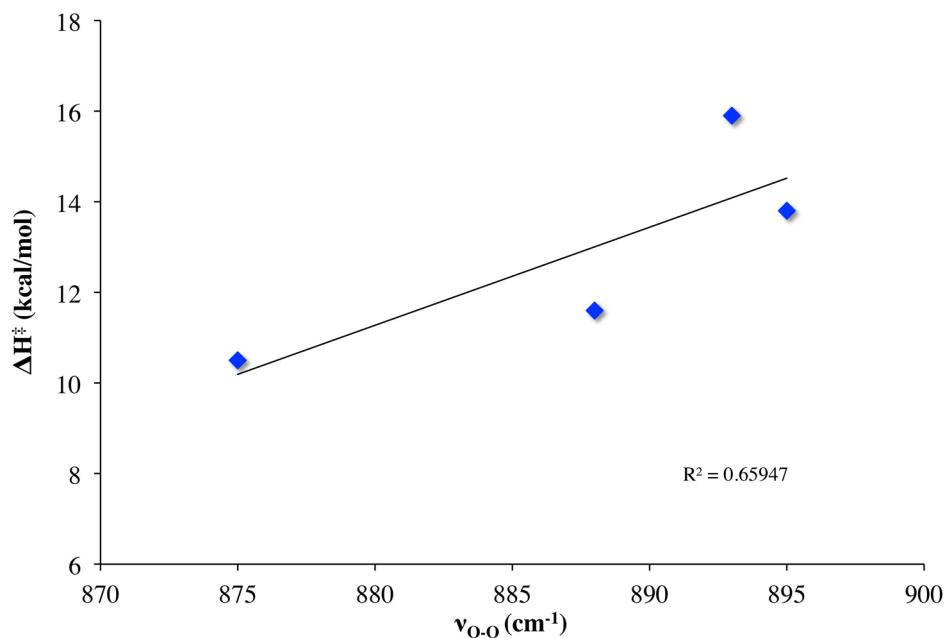
**Figure S-27.** Electronic absorption spectra demonstrating the thermal decay of **3b** at 268 K in  $\text{CH}_2\text{Cl}_2$ . Rate constants were calculated from monitoring the time-dependent absorbance value changes at 590 nm.



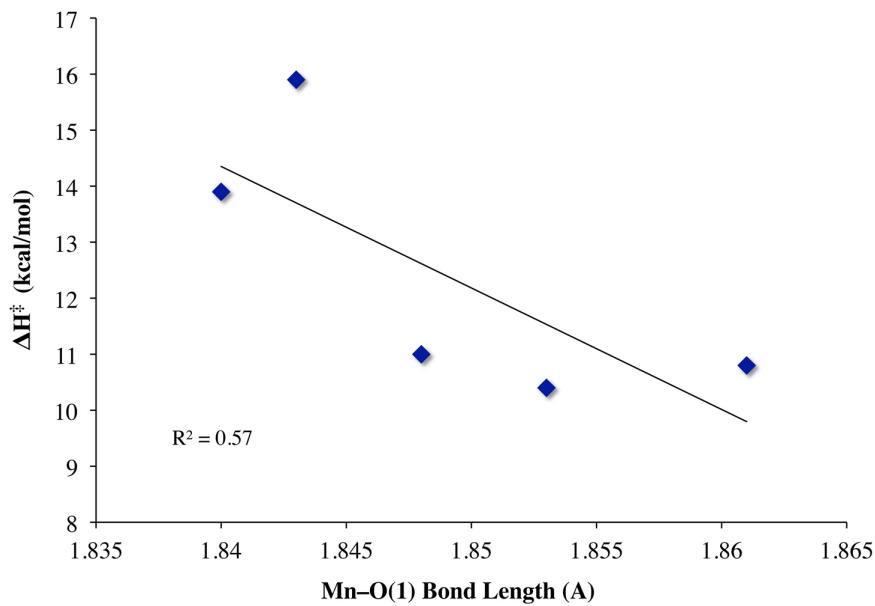
**Figure S-28.** Eyring plot from the variable-temperature thermal decay kinetics data for **3b** in  $\text{CH}_2\text{Cl}_2$ .



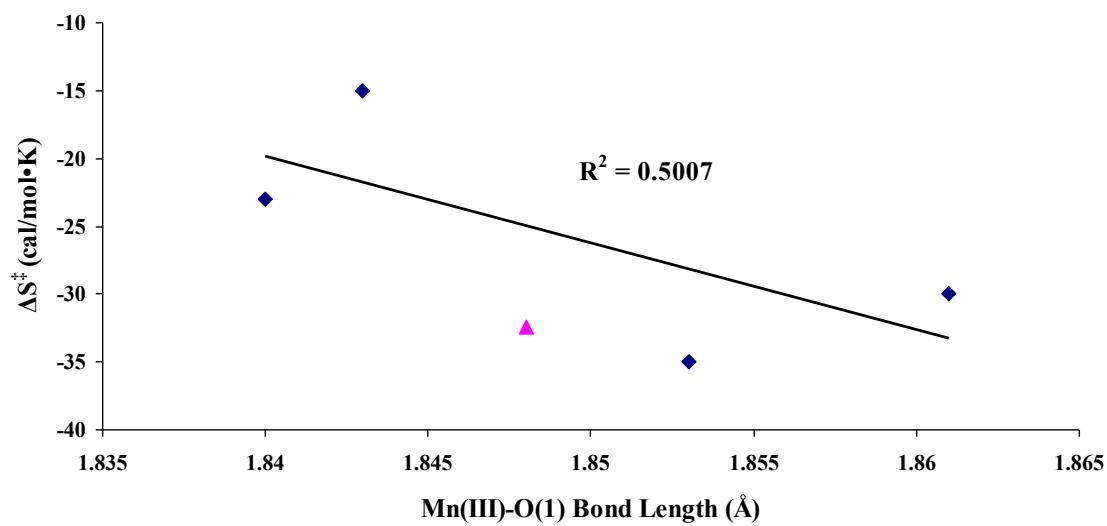
**Figure S-29.** Isokinetic plot from the variable-temperature kinetics data for **1a-4a** and **3b**.



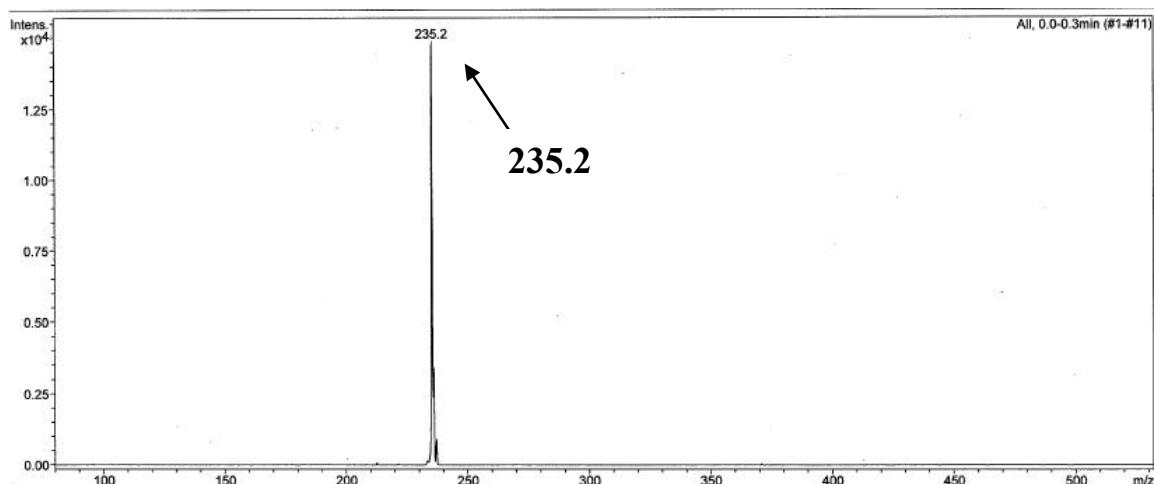
**Figure S-30.** Plot of activation parameter  $\Delta H^\ddagger$  versus IR stretching frequency  $\nu_{O-O}$  for **1a-4a**.



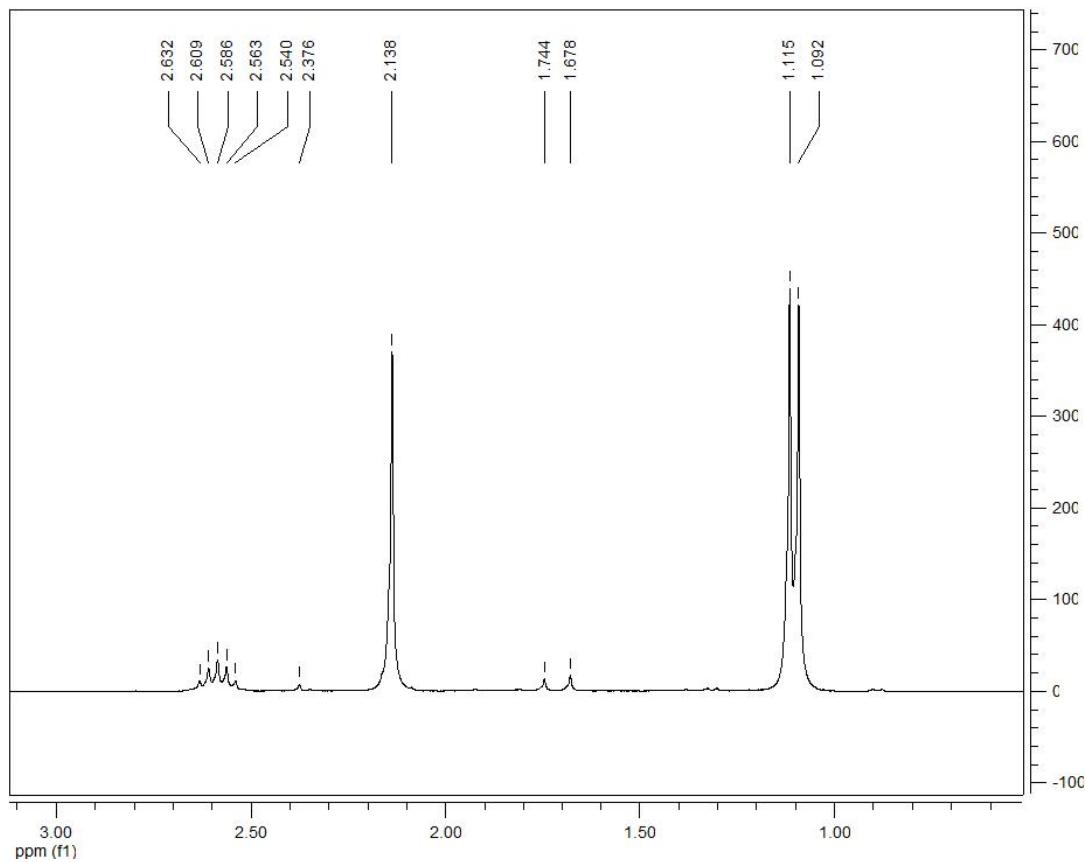
**Figure S-31.** Plot of activation enthalpy (kcal/mol) for thermal decay versus Mn-O(2) bond length (Å) for **1a-4a** and **3b**.



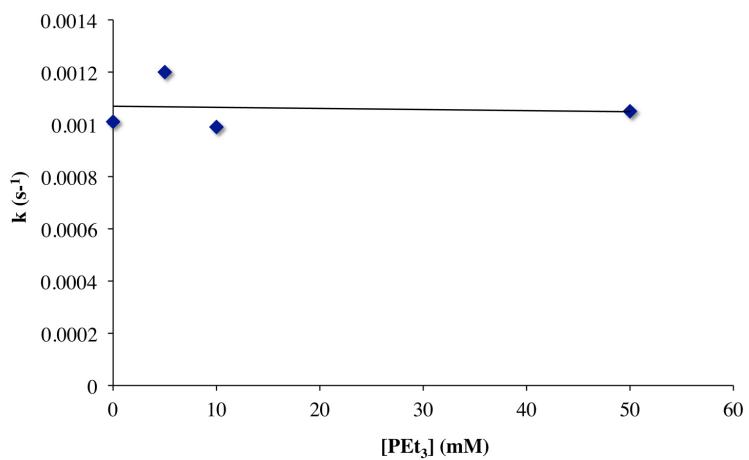
**Figure S-32.** Plot of activation entropy (cal/mol·K) from the thermal decay kinetics versus Mn-O(2) bond length (Å). Data for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(6\text{-Me-DPEN}))(\text{OOCm})(\text{BPh}_4)]$  (**3b**) is represented by the pink triangle and is not included in the linear fit correlation coefficient ( $R^2$ ).



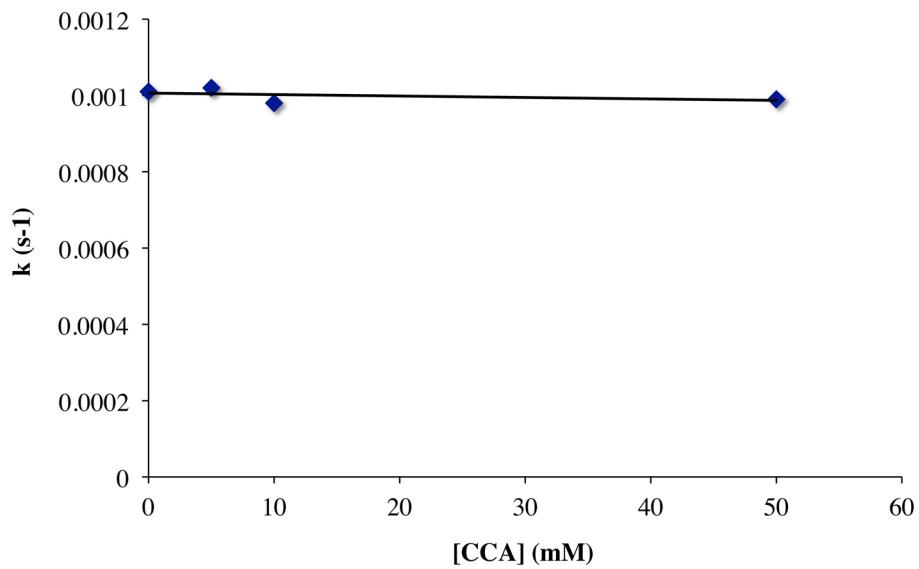
**Figure S-33.** ESI-MS of 3-methyl-2-butanone-3-disulfide, which was obtained in high yield from the thermal decay of **1a-4a**.



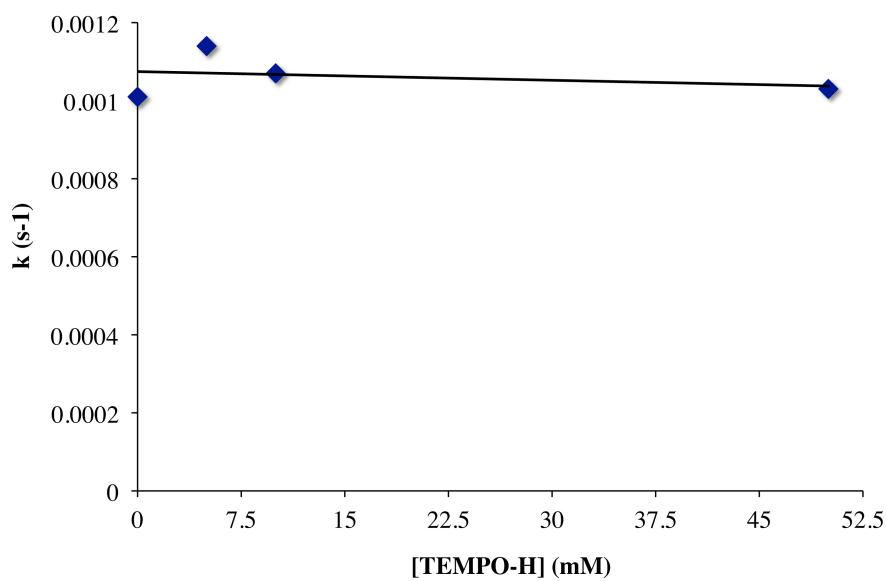
**Figure S-34.**  $^1\text{H}$  NMR spectrum of 3-methyl-2-butanone-3-disulfide obtained in high yield from the thermal decay of **1a-4a**.



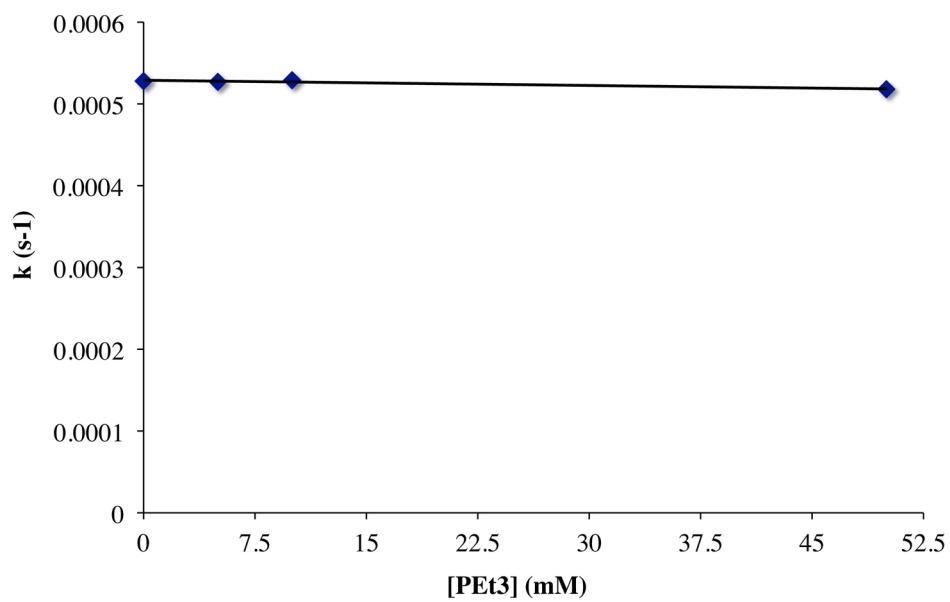
**Figure S-35.** Rate constant ( $k_{\text{obs}}$ ) versus  $\text{PEt}_3$  concentration plot for the decay of **1a** in the presence of  $\text{PEt}_3$  showing zero order dependence on substrate.



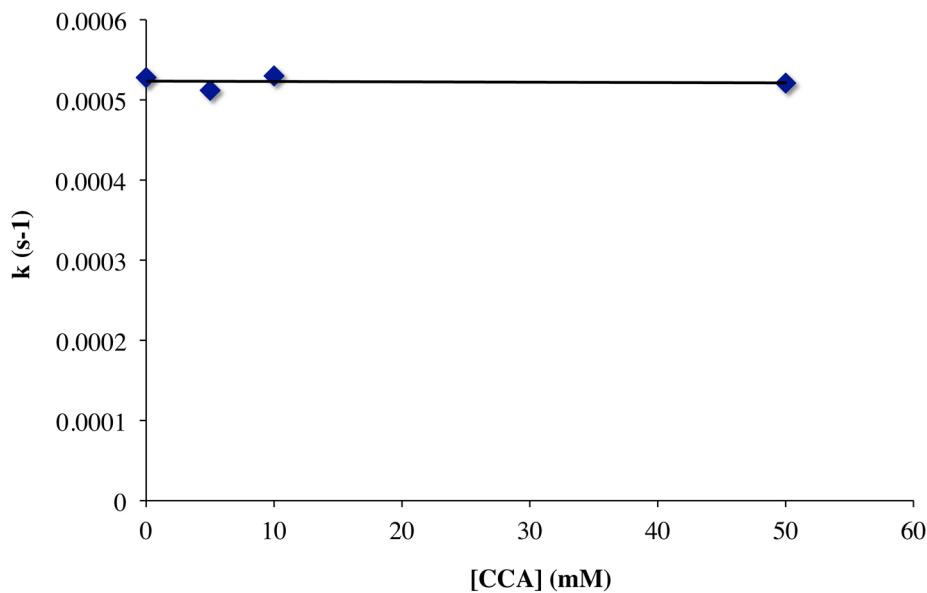
**Figure S-36.** Rate constant ( $k_{\text{obs}}$ ) versus cyclohexanecarboxaldehyde (CCA) concentration plot for the decay of **1a** in the presence of CCA showing zero order dependence on substrate.



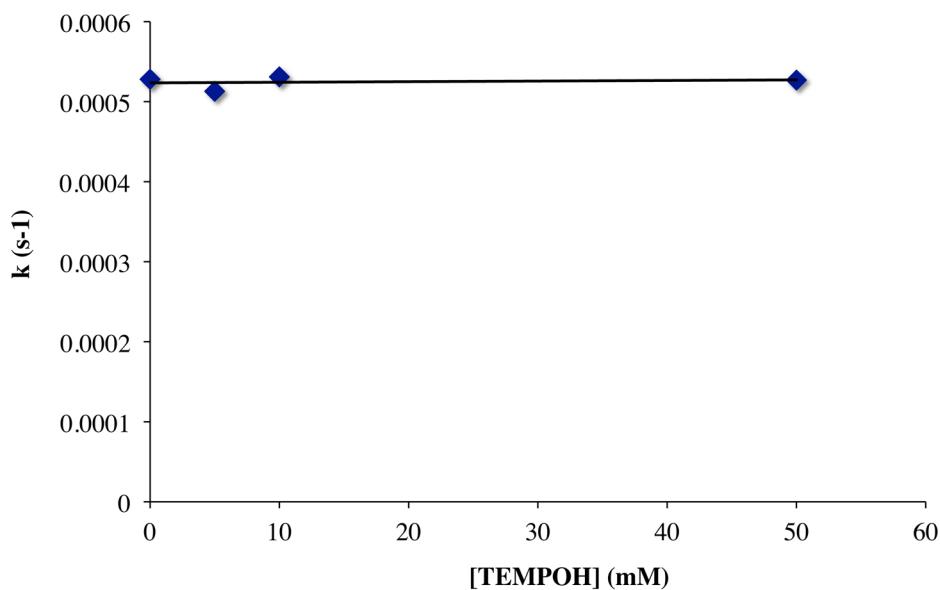
**Figure S-37.** Rate constant ( $k_{\text{obs}}$ ) versus TEMPOH concentration plot for the decay of **1a** in the presence of TEMPOH showing zero order dependence on substrate.



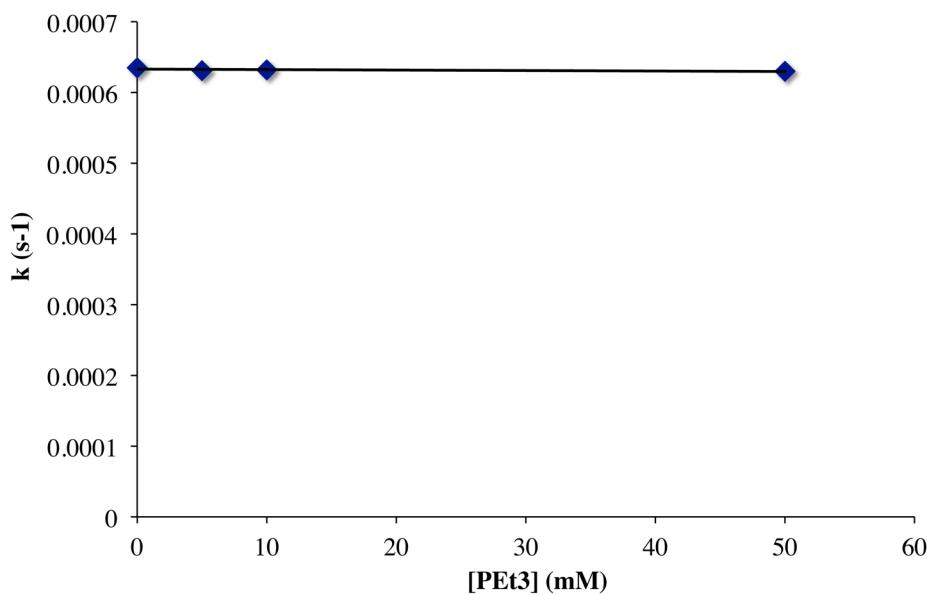
**Figure S-38.** Rate constant ( $k_{\text{obs}}$ ) versus PEt<sub>3</sub> concentration plot for the decay of **2a** in the presence of PEt<sub>3</sub> showing zero order dependence on substrate.



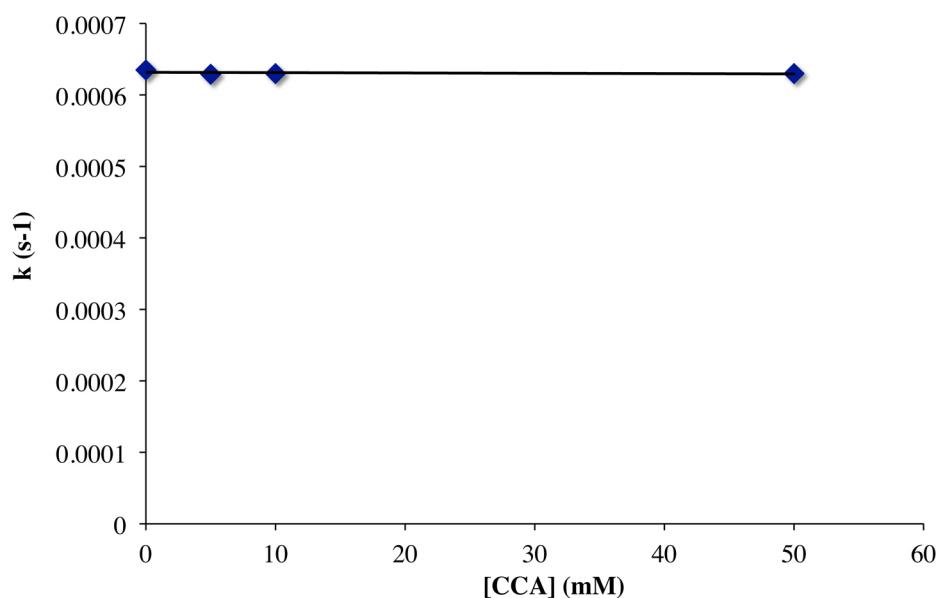
**Figure S-39.** Rate constant ( $k_{\text{obs}}$ ) versus cyclohexanecarboxaldehyde (CCA) concentration plot for the decay of **2a** in the presence of CCA showing zero order dependence on substrate.



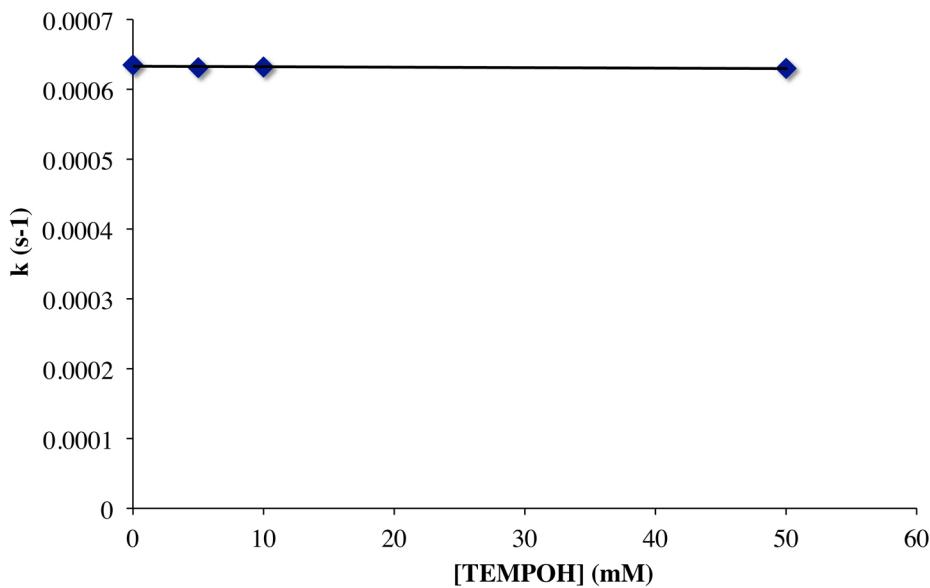
**Figure S-40.** Rate constant ( $k_{\text{obs}}$ ) versus TEMPOH concentration plot for the decay of **2a** in the presence of TEMPOH showing zero order dependence on substrate.



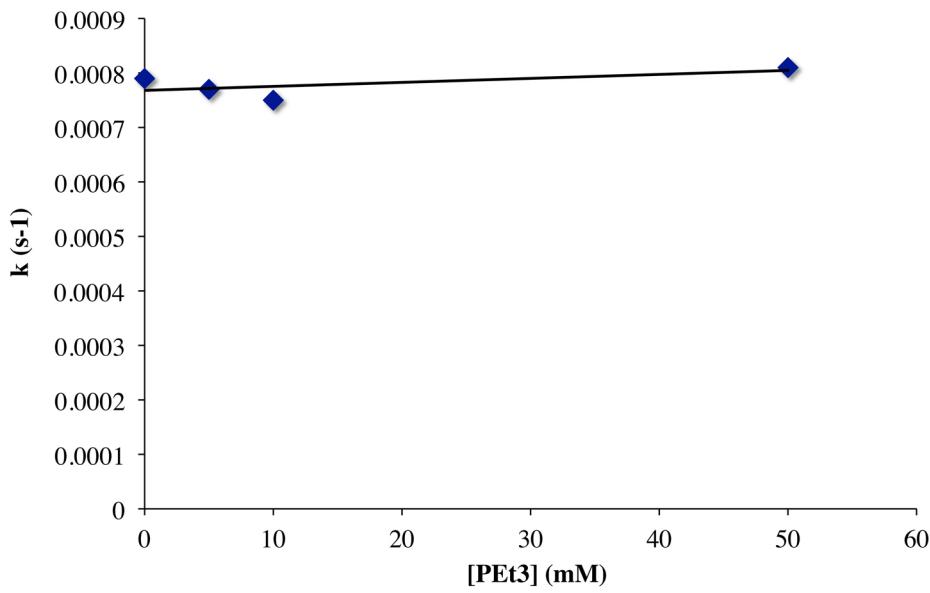
**Figure S-41.** Rate constant ( $k_{\text{obs}}$ ) versus  $\text{PEt}_3$  concentration plot for the decay of **3a** in the presence of  $\text{PEt}_3$  showing zero order dependence on substrate.



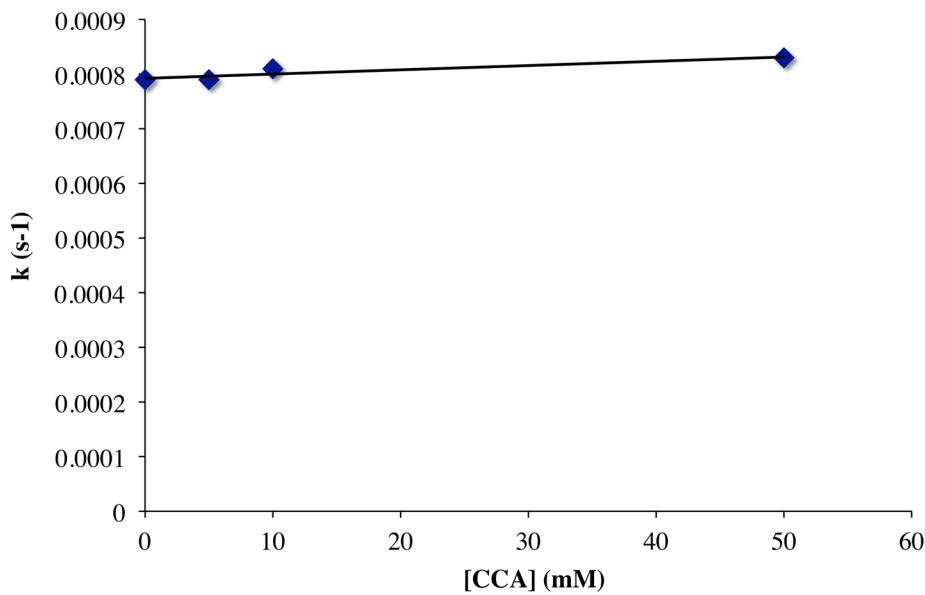
**Figure S-42.** Rate constant ( $k_{\text{obs}}$ ) versus cyclohexanecarboxaldehyde (CCA) concentration plot for the decay of **3a** in the presence of CCA showing zero order dependence on substrate.



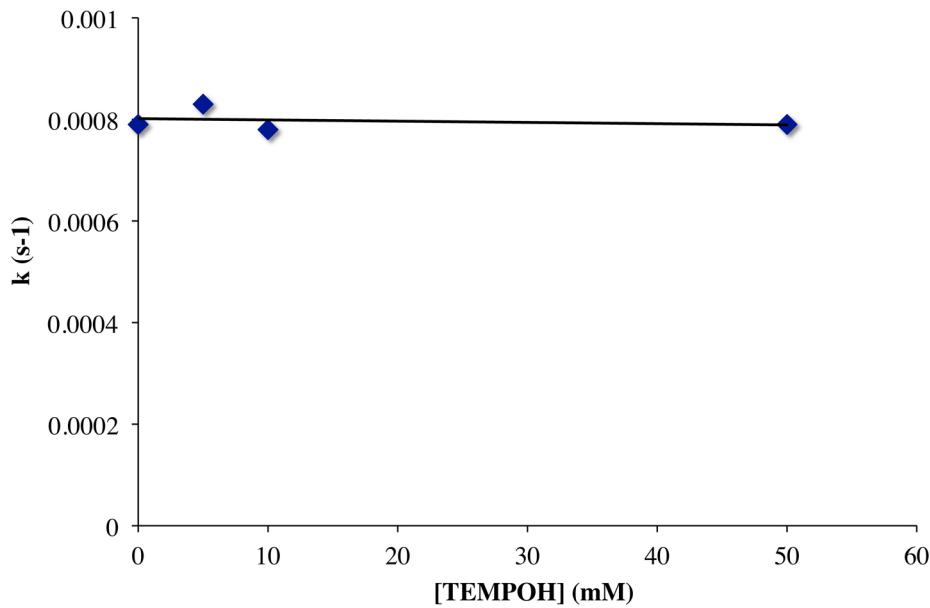
**Figure S-43.** Rate constant ( $k_{\text{obs}}$ ) versus TEMPOH concentration plot for the decay of **3a** in the presence of TEMPOH showing zero order dependence on substrate.



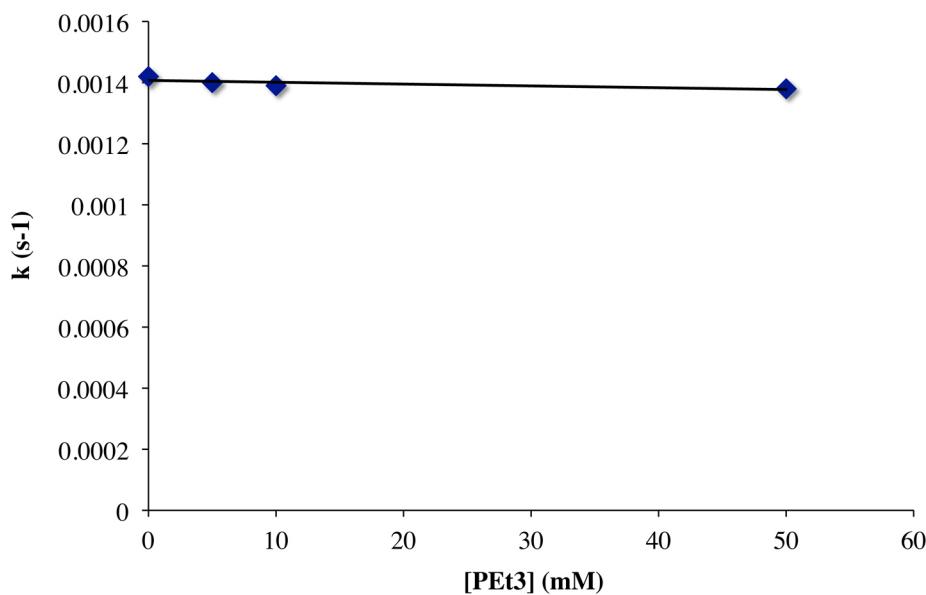
**Figure S-44.** Rate constant ( $k_{\text{obs}}$ ) versus PEt<sub>3</sub> concentration plot for the decay of **3b** in the presence of PEt<sub>3</sub> showing zero order dependence on substrate.



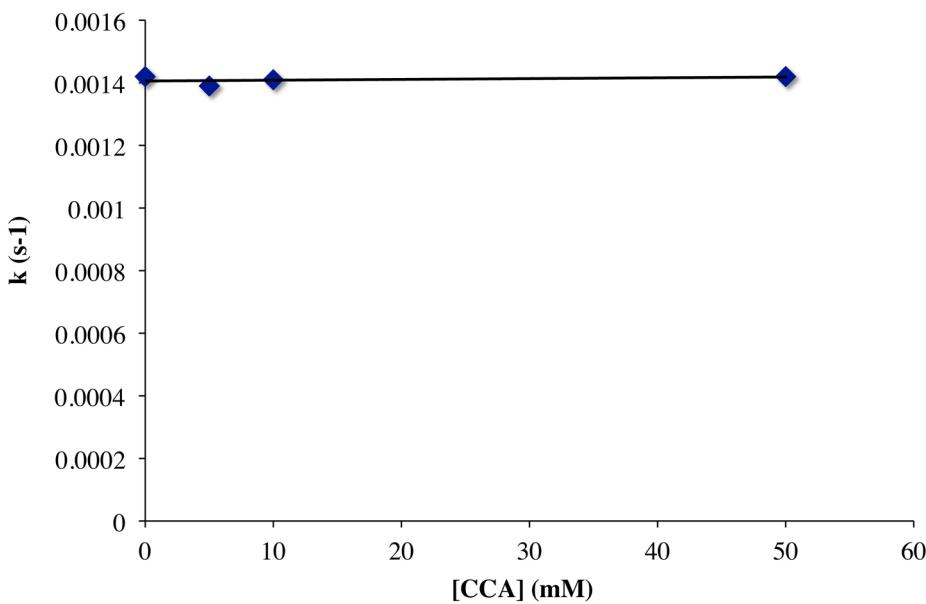
**Figure S-45.** Rate constant ( $k_{\text{obs}}$ ) versus cyclohexanecarboxaldehyde (CCA) concentration plot for the decay of **3b** in the presence of CCA showing zero order dependence on substrate.



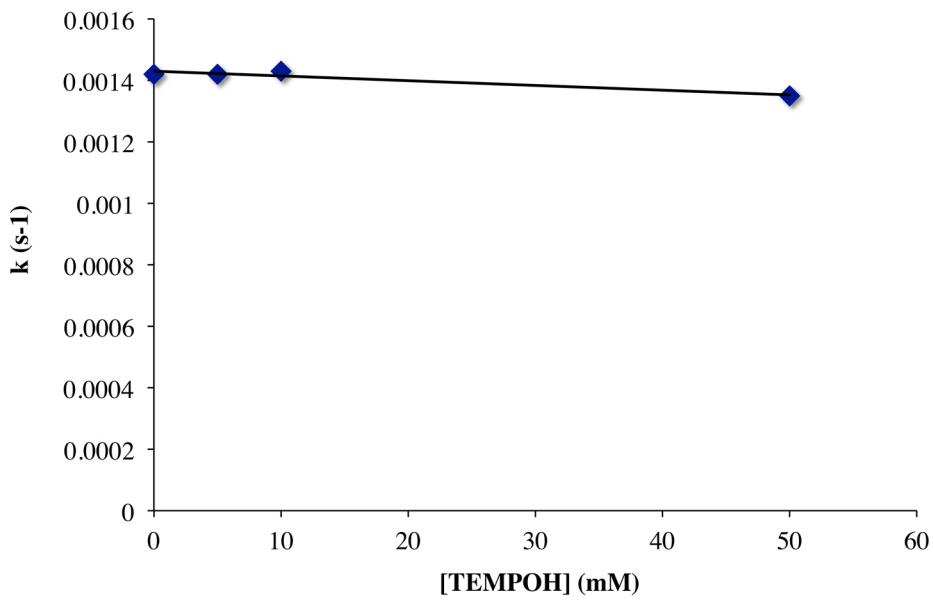
**Figure S-46.** Rate constant ( $k_{\text{obs}}$ ) versus TEMPOH concentration plot for the decay of **3b** in the presence of TEMPOH showing zero order dependence on substrate.



**Figure S-47.** Rate constant ( $k_{\text{obs}}$ ) versus PEt<sub>3</sub> concentration plot for the decay of **4a** in the presence of PEt<sub>3</sub> showing zero order dependence on substrate.



**Figure S-48.** Rate constant ( $k_{\text{obs}}$ ) versus cyclohexanecarboxaldehyde (CCA) concentration plot for the decay of **4a** in the presence of CCA showing zero order dependence on substrate.



**Figure S-49.** Rate constant ( $k_{\text{obs}}$ ) versus TEMPOH concentration plot for the decay of **4a** in the presence of TEMPOH showing zero order dependence on substrate.

**Table S-1.** DFT calculated geometric parameters for compounds **1a-4a**. Table shows crystal structure bond distances and angles followed by geometry optimized structures without the Van der Waals correction (vdw10) and with the correction. The last two lines of each section show the difference between calculated structural parameters and the crystal structure.

No.	Description	N <sub>2</sub>	N <sub>3,4</sub>	< N <sub>3,4</sub> MnN <sub>1</sub>	N <sub>1</sub>	S <sub>1</sub>	O <sub>1</sub>	O-O	O-C	< MnOO
1a	[Mn <sup>III</sup> (S <sup>Me<sup>2</sup></sup> N <sub>4</sub> (QuinoEN))(OO <sup>t</sup> Bu)] <sup>+</sup>	2.173	2.522 2.349	94.2 87	2.034	2.27	1.861	1.457	1.449	109.2
	Geometry Optimized	2.18	2.55 2.40	97.70 85.60	2.04	2.27	1.84	1.48	1.47	113.20
	Geometry Optimized w/ vdw10	2.18	2.47 2.37	97.80 85.30	2.03	2.27	1.84	1.48	1.47	111.40
		ΔN <sub>2</sub>	ΔN <sub>3,4</sub>	Δ< N <sub>3,4</sub> MnN <sub>1</sub>	ΔN <sub>1</sub>	ΔS <sub>1</sub>	ΔO <sub>1</sub>	ΔO-O	ΔO-C	Δ< MnOO
	Geometry Optimized	0.01	0.03 0.05	3.5 -1.4	0.00	0.00	-0.02	0.02	0.02	4.00
	Geometry Optimized w/ vdw10	0.00	-0.05 0.02	3.6 -1.7	0.00	0.00	-0.03	0.02	0.02	2.20
2a	[Mn <sup>III</sup> (S <sup>Me<sup>2</sup></sup> N <sub>4</sub> (QuinoPN))(OO <sup>t</sup> Bu)] <sup>+</sup>	2.182	2.518 2.450	91.5 91.4	2.046	2.269	1.84	1.438	1.452	121.1
	Geometry Optimized	2.21	2.56 2.45	94.90 92.90	2.09	2.26	1.85	1.48	1.47	114.50
	Geometry Optimized w/ vdw10	2.21	2.51 2.45	96.20 86.40	2.07	2.27	1.84	1.47	1.47	120.10
		ΔN <sub>2</sub>	ΔN <sub>3,4</sub>	Δ< N <sub>3,4</sub> MnN <sub>1</sub>	ΔN <sub>1</sub>	ΔS <sub>1</sub>	ΔO <sub>1</sub>	ΔO-O	ΔO-C	Δ< MnOO
	Geometry Optimized	0.02	0.04 0.00	3.4 1.5	0.05	-0.01	0.01	0.04	0.01	-6.60
	Geometry Optimized w/ vdw10	0.03	-0.01 0.00	4.7 -5.0	0.02	0.00	0.00	0.03	0.02	-1.00
3a	[Mn <sup>III</sup> (S <sup>Me<sup>2</sup></sup> N <sub>4</sub> (6-Me-DPEN))(OOtBu)] <sup>+</sup>	2.163	2.471 2.351	103.7 101.1	2.015	2.241	1.853	1.468	1.435	112.4
	Geometry Optimized	2.18	2.52 2.43	100.5 97.7	2.03	2.26	1.84	1.48	1.46	114.1
	Geometry Optimized w/ vdw10	2.18	2.46 2.38	104.4 97.8	2.02	2.25	1.84	1.48	1.46	113.0
		ΔN <sub>2</sub>	ΔN <sub>3,4</sub>	Δ< N <sub>3,4</sub> MnN <sub>1</sub>	ΔN <sub>1</sub>	ΔS <sub>1</sub>	ΔO <sub>1</sub>	ΔO-O	ΔO-C	Δ< MnOO
	Geometry Optimized	0.02	0.04 0.08	-3.2 -3.4	0.02	0.02	-0.01	0.01	0.01	0.03
	Geometry Optimized w/ vdw10	0.02	-0.01 0.02	0.7 -3.3	0.01	0.01	-0.01	0.01	0.02	0.6
4a	[Mn <sup>III</sup> (S <sup>Me<sup>2</sup></sup> N <sub>4</sub> (6-Me-DPPN))(OOtBu)] <sup>+</sup>	2.178	2.517 2.504	94.1 87	2.061	2.26	1.843	1.431	1.466	124.2
	Geometry Optimized	2.20	2.60 2.46	95.70 90.80	2.09	2.26	1.85	1.48	1.47	113.40
	Geometry Optimized w/ vdw10	2.20	2.58 2.46	95.20 87.4	2.07	2.26	1.84	1.47	1.47	120.90
		ΔN <sub>2</sub>	ΔN <sub>3,4</sub>	Δ< N <sub>3,4</sub> MnN <sub>1</sub>	ΔN <sub>1</sub>	ΔS <sub>1</sub>	ΔO <sub>1</sub>	ΔO-O	ΔO-C	Δ< MnOO
	Geometry Optimized	0.02	0.08 -0.05	1.6 3.8	0.03	0.00	0.00	0.05	0.00	-10.80
	Geometry Optimized w/ vdw10	0.02	0.06 -0.05	1.1 0.4	0.00	0.00	-0.01	0.03	0.00	-3.30

**Table S-2.** Mulliken charge densities for Van der Waals corrected, geometry optimized compounds **1a-4a**.

No.	Description	N <sub>2</sub>	N <sub>3,4</sub>	N <sub>1</sub>	S <sub>1</sub>	O <sub>1</sub>	O <sub>2</sub>	Mn
1a	[Mn <sup>III</sup> (S <sup>Me<sub>2</sub></sup> N <sub>4</sub> (QuinoEN))(OO <sup>t</sup> Bu)] <sup>+</sup>	-0.33 -0.52	-0.58	-0.29	-0.30	-0.39	-0.19	0.49
2a	[Mn <sup>III</sup> (S <sup>Me<sub>2</sub></sup> N <sub>4</sub> (QuinoPN))(OO <sup>t</sup> Bu)] <sup>+</sup>	-0.39 -0.58	-0.57	-0.37	-0.22	-0.38	-0.20	0.48
3a	[Mn <sup>III</sup> (S <sup>Me<sub>2</sub></sup> N <sub>4</sub> (6-Me-DPEN))(OOtBu)] <sup>+</sup>	-0.40 -0.59	-0.54	-0.26	-0.28	-0.38	-0.20	0.42
4a	[Mn <sup>III</sup> (S <sup>Me<sub>2</sub></sup> N <sub>4</sub> (6-Me-DPPN))(OOtBu)] <sup>+</sup>	-0.41 -0.52	-0.58	-0.37	-0.19	-0.39	-0.21	0.50

**Table S-3.** Geometry optimized structural parameters and Mulliken charges derived from relaxed surface scans over the 1.1 to 1.6 O-O bond range for compound **3a** and **4a**.

No.	Description	N <sub>2</sub>	N <sub>3,4</sub>	< N <sub>3,4</sub> MnN <sub>1</sub>	N <sub>1</sub>	S <sub>1</sub>	O <sub>1</sub>	O-O	O-C	< MnOO
3a	[Mn <sup>III</sup> (S <sup>Me<sup>2</sup></sup> N <sub>4</sub> (6-Me-DPEN))(OOtBu)] <sup>+</sup>	2.27	2.48 2.46	99.7 97.4	2.11	2.30	1.92	1.10	1.62	131.80
		2.22	2.50 2.46	99.4 97.4	2.05	2.27	1.87	1.20	1.53	126.70
		2.20	2.52 2.44	99.6 97.6	2.04	2.26	1.86	1.30	1.49	121.10
		2.19	2.52 2.43	100.0 97.7	2.03	2.26	1.85	1.40	1.48	116.70
		2.18	2.52 2.42	100.5 97.8	2.03	2.26	1.84	1.50	1.46	113.50
		2.18	2.52 2.42	100.9 97.9	2.03	2.26	1.83	1.60	1.45	111.50
Mulliken Population Analysis		N <sub>2</sub>	N <sub>3,4</sub>	N <sub>1</sub>	S <sub>1</sub>	O <sub>1</sub>	O <sub>2</sub>	Mn		
		-0.40	-0.55 -0.60	-0.34	-0.37	-0.22	-0.05	0.49		
			-0.38 -0.59	-0.30	-0.33	-0.29	-0.10	0.46		
			-0.38 -0.58	-0.29	-0.31	-0.33	-0.14	0.46		
			-0.38 -0.58	-0.28	-0.31	-0.36	-0.17	0.47		
			-0.38 -0.58	-0.28	-0.30	-0.38	-0.20	0.48		
			-0.39 -0.57	-0.28	-0.30	-0.40	-0.22	0.49		
No.	Description	N <sub>2</sub>	N <sub>3,4</sub>	< N <sub>3,4</sub> MnN <sub>1</sub>	N <sub>1</sub>	S <sub>1</sub>	O <sub>1</sub>	O-O	O-C	< MnOO
4a	[Mn <sup>III</sup> (S <sup>Me<sup>2</sup></sup> N <sub>4</sub> (6-Me-DPPN))(OOtBu)] <sup>+</sup>	2.26	2.58 2.55	95.1 90.3	2.14	2.29	1.91	1.10	1.63	135.20
		2.24	2.59 2.48	95.5 91.5	2.11	2.27	1.87	1.20	1.53	126.90
		2.22	2.60 2.47	95.5 91.3	2.09	2.26	1.86	1.30	1.50	120.40
		2.21	2.60 2.46	95.6 90.9	2.09	2.26	1.85	1.40	1.48	116.00
		2.20	2.60 2.46	95.8 90.7	2.09	2.26	1.85	1.50	1.46	112.80
		2.20	2.61 2.45	95.7 90.6	2.09	2.26	1.84	1.60	1.45	110.80
Mulliken Population Analysis		N <sub>2</sub>	N <sub>3,4</sub>	N <sub>1</sub>	S <sub>1</sub>	O <sub>1</sub>	O <sub>2</sub>	Mn		
		-0.41	-0.59 -0.54	-0.42	-0.29	-0.20	-0.10	0.51		
			-0.40 -0.54	-0.40	-0.27	-0.30	-0.10	0.54		
			-0.39 -0.54	-0.39	-0.26	-0.34	-0.13	0.55		
			-0.38 -0.53	-0.39	-0.25	-0.36	-0.16	0.56		
			-0.38 -0.53	-0.39	-0.25	-0.39	-0.19	0.57		
			-0.38 -0.53	-0.39	-0.25	-0.40	-0.21	0.58		

**Table S-4.** Crystal data and structure refinement for [Mn<sup>III</sup>(S<sup>Me<sub>2</sub></sup>N<sub>4</sub>(QuinoPN))(OOtBu)](PF<sub>6</sub>)•pentane (**2a**).

Identification code	ben07_0m	
Empirical formula	C <sub>69</sub> H <sub>92</sub> F <sub>12</sub> Mn <sub>2</sub> N <sub>8</sub> O <sub>4</sub> P <sub>2</sub> S <sub>2</sub>	
Formula weight	1561.45	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 10.5559(8) Å	a = 90°.
	b = 14.0937(10) Å	b = 94.560(4)°.
	c = 23.9583(16) Å	g = 90°.
Volume	3553.0(4) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.460 Mg/m <sup>3</sup>	
Absorption coefficient	0.545 mm <sup>-1</sup>	
F(000)	1628	
Crystal size	0.15 x 0.15 x 0.05 mm <sup>3</sup>	
Theta range for data collection	1.68 to 25.45°.	
Index ranges	-12<=h<=12, -17<=k<=17, -28<=l<=28	
Reflections collected	49617	
Independent reflections	6557 [R(int) = 0.0875]	
Completeness to theta = 25.00°	100.0 %	

Max. and min. transmission	0.9733 and 0.9227
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	6557 / 7 / 449
Goodness-of-fit on $F^2$	1.013
Final R indices [ $I > 2\sigma(I)$ ]	R1 = 0.0688, wR2 = 0.1692
R indices (all data)	R1 = 0.1382, wR2 = 0.2088
Largest diff. peak and hole	0.833 and -0.718 e. $\text{\AA}^{-3}$

**Table S-5.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}2}\text{N}_4\text{(QuinoPN)})(\text{OOtBu})](\text{PF}_6)\bullet\text{pentane}$  (**2a**). U(eq) is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

	x	y	z	U(eq)
C(1)	9988(6)	10117(4)	3142(2)	51(2)
C(2)	9618(10)	9830(6)	3724(3)	103(3)
C(3)	11387(7)	10433(6)	3217(4)	96(3)
C(4)	9163(5)	10913(4)	2927(2)	40(1)
C(5)	9256(7)	11809(5)	3256(3)	73(2)
C(6)	7717(5)	11672(4)	2266(2)	45(1)
C(7)	6489(6)	11470(4)	1931(2)	48(2)
C(8)	6568(6)	11090(4)	1358(2)	50(2)
C(9)	7504(7)	9948(5)	773(2)	58(2)
C(10)	8732(8)	10443(5)	762(3)	65(2)
C(11)	9071(9)	10874(6)	266(3)	86(2)
C(12)	10176(11)	11295(7)	262(4)	97(3)
C(13)	11035(7)	11296(5)	719(4)	68(2)
C(14)	12239(9)	11719(6)	765(4)	93(3)
C(15)	12988(7)	11734(6)	1253(4)	86(3)
C(16)	12625(9)	11301(7)	1729(5)	129(4)

C(17)	11423(8)	10856(7)	1710(4)	105(3)
C(18)	10636(7)	10851(5)	1225(3)	71(2)
C(19)	5856(6)	9423(4)	1304(2)	51(2)
C(20)	5394(6)	9265(4)	1868(2)	47(2)
C(21)	4082(6)	9113(5)	1934(3)	59(2)
C(22)	3709(6)	8890(5)	2437(3)	61(2)
C(23)	4590(7)	8821(4)	2906(3)	57(2)
C(24)	4251(8)	8577(5)	3452(3)	65(2)
C(25)	5182(10)	8504(5)	3873(3)	79(2)
C(26)	6460(9)	8632(5)	3781(3)	69(2)
C(27)	6803(7)	8865(4)	3263(2)	52(2)
C(28)	5876(6)	8974(4)	2817(2)	40(1)
C(35)	9784(7)	7274(5)	1410(2)	54(2)
C(36)	10286(9)	6398(6)	1706(4)	105(3)
C(37)	10762(8)	7930(7)	1276(4)	89(3)
C(38)	8927(8)	6966(6)	912(3)	98(3)
C(39)	7285(14)	5356(11)	-71(6)	73(4)
C(40)	8338(17)	4702(13)	-231(9)	86(7)
C(41)	10838(18)	4590(20)	-32(15)	162(7)
C(42)	12040(20)	5025(17)	234(9)	88(6)
C(43)	9593(19)	5090(30)	10(20)	161(7)
N(3)	6264(4)	9213(3)	2291(2)	40(1)
N(4)	9473(5)	10439(4)	1231(2)	61(2)

N(2)	6974(4)	10074(3)	1316(2)	43(1)
N(1)	8440(4)	10821(3)	2469(2)	34(1)
O(1)	8363(4)	8503(3)	1591(2)	55(1)
O(2)	9000(4)	7673(3)	1823(2)	54(1)
F(1)	6938(4)	12367(3)	154(2)	84(1)
F(2)	5072(5)	12703(3)	471(1)	81(1)
F(3)	4094(3)	12424(3)	-393(1)	63(1)
F(4)	5979(4)	12086(4)	-705(2)	87(1)
F(5)	5656(4)	13481(3)	-275(2)	94(2)
F(6)	5332(4)	11315(2)	43(1)	72(1)
P(1)	5519(2)	12404(1)	-119(1)	53(1)
S(1)	9833(2)	9106(1)	2661(1)	53(1)
Mn(1)	8359(1)	9620(1)	1988(1)	37(1)

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**Table S-6.** Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for  
 $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4\text{(QuinoPN)})(\text{OOtBu})](\text{PF}_6)\bullet\text{pentane } (\textbf{2a})$ .

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C(1)-C(4)	1.487(7)
C(1)-C(2)	1.532(10)
C(1)-C(3)	1.539(9)
C(1)-S(1)	1.832(6)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(3)-H(3C)	0.9800
C(4)-N(1)	1.292(6)
C(4)-C(5)	1.487(8)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-N(1)	1.482(6)
C(6)-C(7)	1.496(8)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-C(8)	1.482(8)

C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-N(2)	1.501(7)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-N(2)	1.469(7)
C(9)-C(10)	1.475(10)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-N(4)	1.318(8)
C(10)-C(11)	1.406(10)
C(11)-C(12)	1.310(12)
C(11)-H(11)	0.9500
C(12)-C(13)	1.365(11)
C(12)-H(12)	0.9500
C(13)-C(14)	1.400(12)
C(13)-C(18)	1.456(10)
C(14)-C(15)	1.359(12)
C(14)-H(14)	0.9500
C(15)-C(16)	1.375(12)
C(15)-H(15)	0.9500
C(16)-C(17)	1.412(12)
C(16)-H(16)	0.9500

C(17)-C(18)	1.373(11)
C(17)-H(17)	0.9500
C(18)-N(4)	1.359(9)
C(19)-C(20)	1.489(8)
C(19)-N(2)	1.492(8)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(20)-N(3)	1.314(7)
C(20)-C(21)	1.423(9)
C(21)-C(22)	1.336(9)
C(21)-H(21)	0.9500
C(22)-C(23)	1.404(9)
C(22)-H(22)	0.9500
C(23)-C(28)	1.407(9)
C(23)-C(24)	1.426(9)
C(24)-C(25)	1.355(10)
C(24)-H(24)	0.9500
C(25)-C(26)	1.396(11)
C(25)-H(25)	0.9500
C(26)-C(27)	1.360(9)
C(26)-H(26)	0.9500
C(27)-C(28)	1.398(8)
C(27)-H(27)	0.9500

C(28)-N(3)	1.396(7)
C(35)-C(37)	1.442(10)
C(35)-O(2)	1.452(7)
C(35)-C(36)	1.499(9)
C(35)-C(38)	1.504(9)
C(36)-H(36A)	0.9800
C(36)-H(36B)	0.9800
C(36)-H(36C)	0.9800
C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800
C(38)-H(38A)	0.8000
C(38)-H(38B)	0.8000
C(38)-H(38C)	0.8000
C(39)-C(42)#1	1.00(2)
C(39)-C(40)	1.516(11)
C(39)-C(41)#1	1.98(2)
C(39)-H(39A)	0.9800
C(39)-H(39B)	0.9800
C(39)-H(39C)	0.9800
C(40)-C(42)#1	0.55(3)
C(40)-C(41)#1	1.44(4)
C(40)-C(43)	1.507(11)

C(40)-H(40A)	0.9900
C(40)-H(40B)	0.9900
C(41)-C(43)#1	0.65(5)
C(41)-C(40)#1	1.44(4)
C(41)-C(43)	1.504(11)
C(41)-C(42)	1.506(11)
C(41)-C(39)#1	1.98(2)
C(41)-H(41A)	0.8000
C(41)-H(41B)	0.8000
C(42)-C(40)#1	0.55(3)
C(42)-C(39)#1	1.00(2)
C(42)-C(43)#1	1.78(4)
C(42)-H(42A)	0.9800
C(42)-H(42B)	0.9800
C(42)-H(42C)	0.9800
C(43)-C(41)#1	0.65(5)
C(43)-C(43)#1	0.90(4)
C(43)-C(42)#1	1.78(4)
C(43)-H(43A)	0.9900
C(43)-H(43B)	0.9900
N(3)-Mn(1)	2.450(5)
N(4)-Mn(1)	2.518(5)
N(2)-Mn(1)	2.182(4)

N(1)-Mn(1)	2.046(4)
O(1)-O(2)	1.438(5)
O(1)-Mn(1)	1.840(4)
F(1)-P(1)	1.588(4)
F(2)-P(1)	1.583(4)
F(3)-P(1)	1.593(4)
F(4)-P(1)	1.585(4)
F(5)-P(1)	1.573(4)
F(6)-P(1)	1.599(4)
S(1)-Mn(1)	2.2693(15)

C(4)-C(1)-C(2)	109.2(6)
C(4)-C(1)-C(3)	110.6(5)
C(2)-C(1)-C(3)	106.4(6)
C(4)-C(1)-S(1)	110.4(4)
C(2)-C(1)-S(1)	110.5(4)
C(3)-C(1)-S(1)	109.6(5)
C(1)-C(2)-H(2A)	109.5
C(1)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
C(1)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5

C(1)-C(3)-H(3A)	109.5
C(1)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
C(1)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
N(1)-C(4)-C(5)	123.0(5)
N(1)-C(4)-C(1)	120.6(5)
C(5)-C(4)-C(1)	116.4(5)
C(4)-C(5)-H(5A)	109.5
C(4)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
N(1)-C(6)-C(7)	115.1(5)
N(1)-C(6)-H(6A)	108.5
C(7)-C(6)-H(6A)	108.5
N(1)-C(6)-H(6B)	108.5
C(7)-C(6)-H(6B)	108.5
H(6A)-C(6)-H(6B)	107.5
C(8)-C(7)-C(6)	117.0(5)
C(8)-C(7)-H(7A)	108.0

C(6)-C(7)-H(7A)	108.0
C(8)-C(7)-H(7B)	108.0
C(6)-C(7)-H(7B)	108.0
H(7A)-C(7)-H(7B)	107.3
C(7)-C(8)-N(2)	116.4(4)
C(7)-C(8)-H(8A)	108.2
N(2)-C(8)-H(8A)	108.2
C(7)-C(8)-H(8B)	108.2
N(2)-C(8)-H(8B)	108.2
H(8A)-C(8)-H(8B)	107.3
N(2)-C(9)-C(10)	110.8(5)
N(2)-C(9)-H(9A)	109.5
C(10)-C(9)-H(9A)	109.5
N(2)-C(9)-H(9B)	109.5
C(10)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	108.1
N(4)-C(10)-C(11)	123.4(8)
N(4)-C(10)-C(9)	116.5(6)
C(11)-C(10)-C(9)	120.1(7)
C(12)-C(11)-C(10)	119.1(9)
C(12)-C(11)-H(11)	120.4
C(10)-C(11)-H(11)	120.4
C(11)-C(12)-C(13)	122.1(9)

C(11)-C(12)-H(12)	119.0
C(13)-C(12)-H(12)	119.0
C(12)-C(13)-C(14)	127.2(9)
C(12)-C(13)-C(18)	116.7(7)
C(14)-C(13)-C(18)	116.1(8)
C(15)-C(14)-C(13)	122.4(8)
C(15)-C(14)-H(14)	118.8
C(13)-C(14)-H(14)	118.8
C(14)-C(15)-C(16)	121.7(8)
C(14)-C(15)-H(15)	119.1
C(16)-C(15)-H(15)	119.1
C(15)-C(16)-C(17)	118.6(9)
C(15)-C(16)-H(16)	120.7
C(17)-C(16)-H(16)	120.7
C(18)-C(17)-C(16)	120.8(8)
C(18)-C(17)-H(17)	119.6
C(16)-C(17)-H(17)	119.6
N(4)-C(18)-C(17)	118.6(7)
N(4)-C(18)-C(13)	120.9(7)
C(17)-C(18)-C(13)	120.4(7)
C(20)-C(19)-N(2)	113.0(4)
C(20)-C(19)-H(19A)	109.0
N(2)-C(19)-H(19A)	109.0

C(20)-C(19)-H(19B)	109.0
N(2)-C(19)-H(19B)	109.0
H(19A)-C(19)-H(19B)	107.8
N(3)-C(20)-C(21)	122.2(6)
N(3)-C(20)-C(19)	116.7(5)
C(21)-C(20)-C(19)	121.0(5)
C(22)-C(21)-C(20)	119.6(6)
C(22)-C(21)-H(21)	120.2
C(20)-C(21)-H(21)	120.2
C(21)-C(22)-C(23)	120.9(6)
C(21)-C(22)-H(22)	119.5
C(23)-C(22)-H(22)	119.5
C(22)-C(23)-C(28)	117.0(6)
C(22)-C(23)-C(24)	123.5(7)
C(28)-C(23)-C(24)	119.4(6)
C(25)-C(24)-C(23)	118.8(7)
C(25)-C(24)-H(24)	120.6
C(23)-C(24)-H(24)	120.6
C(24)-C(25)-C(26)	121.7(7)
C(24)-C(25)-H(25)	119.2
C(26)-C(25)-H(25)	119.2
C(27)-C(26)-C(25)	120.4(7)
C(27)-C(26)-H(26)	119.8

C(25)-C(26)-H(26)	119.8
C(26)-C(27)-C(28)	120.2(7)
C(26)-C(27)-H(27)	119.9
C(28)-C(27)-H(27)	119.9
N(3)-C(28)-C(27)	118.6(6)
N(3)-C(28)-C(23)	122.0(5)
C(27)-C(28)-C(23)	119.5(6)
C(37)-C(35)-O(2)	111.1(6)
C(37)-C(35)-C(36)	113.6(7)
O(2)-C(35)-C(36)	101.4(5)
C(37)-C(35)-C(38)	113.8(7)
O(2)-C(35)-C(38)	108.3(6)
C(36)-C(35)-C(38)	107.8(7)
C(35)-C(36)-H(36A)	109.5
C(35)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
C(35)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
C(35)-C(37)-H(37A)	109.5
C(35)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37B)	109.5
C(35)-C(37)-H(37C)	109.5

H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5
C(35)-C(38)-H(38A)	109.2
C(35)-C(38)-H(38B)	109.8
H(38A)-C(38)-H(38B)	109.5
C(35)-C(38)-H(38C)	109.4
H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5
C(42)#1-C(39)-C(40)	8.8(19)
C(42)#1-C(39)-C(41)#1	48.0(14)
C(40)-C(39)-C(41)#1	46.4(12)
C(42)#1-C(39)-H(39A)	107.9
C(40)-C(39)-H(39A)	109.8
C(41)#1-C(39)-H(39A)	155.9
C(42)#1-C(39)-H(39B)	102.5
C(40)-C(39)-H(39B)	109.2
C(41)#1-C(39)-H(39B)	81.0
H(39A)-C(39)-H(39B)	109.5
C(42)#1-C(39)-H(39C)	117.7
C(40)-C(39)-H(39C)	109.4
C(41)#1-C(39)-H(39C)	86.0
H(39A)-C(39)-H(39C)	109.5
H(39B)-C(39)-H(39C)	109.5

C(42)#1-C(40)-C(41)#1	86(4)
C(42)#1-C(40)-C(43)	111(4)
C(41)#1-C(40)-C(43)	25(2)
C(42)#1-C(40)-C(39)	16(3)
C(41)#1-C(40)-C(39)	84.0(14)
C(43)-C(40)-C(39)	108.8(17)
C(42)#1-C(40)-H(40A)	121.2
C(41)#1-C(40)-H(40A)	125.8
C(43)-C(40)-H(40A)	109.9
C(39)-C(40)-H(40A)	109.9
C(42)#1-C(40)-H(40B)	94.8
C(41)#1-C(40)-H(40B)	115.2
C(43)-C(40)-H(40B)	109.8
C(39)-C(40)-H(40B)	110.1
H(40A)-C(40)-H(40B)	108.4
C(43)#1-C(41)-C(40)#1	83(4)
C(43)#1-C(41)-C(43)	17(5)
C(40)#1-C(41)-C(43)	98(2)
C(43)#1-C(41)-C(42)	105(4)
C(40)#1-C(41)-C(42)	21.5(10)
C(43)-C(41)-C(42)	119(2)
C(43)#1-C(41)-C(39)#1	131(4)
C(40)#1-C(41)-C(39)#1	49.6(9)

C(43)-C(41)-C(39)#1	147.6(18)
C(42)-C(41)-C(39)#1	29.4(11)
C(43)#1-C(41)-H(41A)	106.4
C(40)#1-C(41)-H(41A)	113.2
C(43)-C(41)-H(41A)	107.3
C(42)-C(41)-H(41A)	107.4
C(39)#1-C(41)-H(41A)	86.1
C(43)#1-C(41)-H(41B)	123.1
C(40)#1-C(41)-H(41B)	121.8
C(43)-C(41)-H(41B)	107.9
C(42)-C(41)-H(41B)	107.3
C(39)#1-C(41)-H(41B)	95.4
H(41A)-C(41)-H(41B)	107.3
C(40)#1-C(42)-C(39)#1	155(5)
C(40)#1-C(42)-C(41)	72(4)
C(39)#1-C(42)-C(41)	103(2)
C(40)#1-C(42)-C(43)#1	52(3)
C(39)#1-C(42)-C(43)#1	122(3)
C(41)-C(42)-C(43)#1	20.7(19)
C(40)#1-C(42)-H(42A)	162.7
C(39)#1-C(42)-H(42A)	10.6
C(41)-C(42)-H(42A)	110.7
C(43)#1-C(42)-H(42A)	130.6

C(40)#1-C(42)-H(42B)	84.5
C(39)#1-C(42)-H(42B)	119.5
C(41)-C(42)-H(42B)	109.0
C(43)#1-C(42)-H(42B)	102.3
H(42A)-C(42)-H(42B)	109.5
C(40)#1-C(42)-H(42C)	54.7
C(39)#1-C(42)-H(42C)	107.1
C(41)-C(42)-H(42C)	108.7
C(43)#1-C(42)-H(42C)	93.7
H(42A)-C(42)-H(42C)	109.5
H(42B)-C(42)-H(42C)	109.5
C(41)#1-C(43)-C(43)#1	151(9)
C(41)#1-C(43)-C(41)	163(5)
C(43)#1-C(43)-C(41)	12(4)
C(41)#1-C(43)-C(40)	72(3)
C(43)#1-C(43)-C(40)	133(5)
C(41)-C(43)-C(40)	123(2)
C(41)#1-C(43)-C(42)#1	55(3)
C(43)#1-C(43)-C(42)#1	148(6)
C(41)-C(43)-C(42)#1	140(2)
C(40)-C(43)-C(42)#1	16.8(10)
C(41)#1-C(43)-H(43A)	58.0
C(43)#1-C(43)-H(43A)	95.5

C(41)-C(43)-H(43A)	106.7
C(40)-C(43)-H(43A)	106.6
C(42)#1-C(43)-H(43A)	94.2
C(41)#1-C(43)-H(43B)	74.3
C(43)#1-C(43)-H(43B)	105.5
C(41)-C(43)-H(43B)	106.1
C(40)-C(43)-H(43B)	106.5
C(42)#1-C(43)-H(43B)	100.3
H(43A)-C(43)-H(43B)	106.7
C(20)-N(3)-C(28)	118.1(5)
C(20)-N(3)-Mn(1)	110.5(4)
C(28)-N(3)-Mn(1)	131.3(3)
C(10)-N(4)-C(18)	117.7(6)
C(10)-N(4)-Mn(1)	109.7(5)
C(18)-N(4)-Mn(1)	132.6(5)
C(9)-N(2)-C(19)	105.4(5)
C(9)-N(2)-C(8)	107.8(4)
C(19)-N(2)-C(8)	111.0(5)
C(9)-N(2)-Mn(1)	109.8(3)
C(19)-N(2)-Mn(1)	108.5(3)
C(8)-N(2)-Mn(1)	114.1(3)
C(4)-N(1)-C(6)	116.9(4)
C(4)-N(1)-Mn(1)	123.8(4)

C(6)-N(1)-Mn(1)	119.1(3)
O(2)-O(1)-Mn(1)	121.1(3)
O(1)-O(2)-C(35)	109.1(4)
F(5)-P(1)-F(2)	89.7(3)
F(5)-P(1)-F(4)	91.3(3)
F(2)-P(1)-F(4)	178.8(3)
F(5)-P(1)-F(1)	91.6(2)
F(2)-P(1)-F(1)	88.8(2)
F(4)-P(1)-F(1)	90.6(2)
F(5)-P(1)-F(3)	89.2(2)
F(2)-P(1)-F(3)	91.4(2)
F(4)-P(1)-F(3)	89.2(2)
F(1)-P(1)-F(3)	179.1(2)
F(5)-P(1)-F(6)	178.1(3)
F(2)-P(1)-F(6)	89.2(2)
F(4)-P(1)-F(6)	89.8(2)
F(1)-P(1)-F(6)	90.0(2)
F(3)-P(1)-F(6)	89.2(2)
C(1)-S(1)-Mn(1)	102.73(18)
O(1)-Mn(1)-N(1)	176.12(16)
O(1)-Mn(1)-N(2)	84.16(17)
N(1)-Mn(1)-N(2)	99.72(17)
O(1)-Mn(1)-S(1)	93.69(12)

N(1)-Mn(1)-S(1)	82.44(12)
N(2)-Mn(1)-S(1)	177.62(13)
O(1)-Mn(1)-N(3)	89.54(17)
N(1)-Mn(1)-N(3)	91.41(16)
N(2)-Mn(1)-N(3)	73.70(16)
S(1)-Mn(1)-N(3)	107.36(11)
O(1)-Mn(1)-N(4)	89.99(19)
N(1)-Mn(1)-N(4)	91.48(18)
N(2)-Mn(1)-N(4)	70.06(18)
S(1)-Mn(1)-N(4)	108.98(14)
N(3)-Mn(1)-N(4)	143.61(16)

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Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z

**Table S-7.** Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4\text{(QuinoPN)})(\text{OOtBu})](\text{PF}_6)$ •pentane (**2a**). The anisotropic displacement factor exponent takes the form:  $-2p^2 [ h^2 a^*{}^2 U^{11} + \dots + 2 h k a^* b^* U^{12} ]$

	U <sup>11</sup>	U <sup>22</sup>	U <sup>33</sup>	U <sup>23</sup>	U <sup>13</sup>	U <sup>12</sup>
C(1)	59(4)	34(3)	57(4)	0(3)	-23(3)	2(3)
C(2)	185(10)	65(5)	51(4)	0(4)	-39(5)	-38(6)
C(3)	47(4)	81(6)	153(8)	-46(5)	-37(5)	3(4)
C(4)	36(3)	34(3)	50(3)	-2(3)	-1(3)	2(2)
C(5)	74(5)	56(4)	82(5)	-28(4)	-34(4)	21(4)
C(6)	45(4)	34(3)	53(3)	6(3)	-5(3)	9(3)
C(7)	52(4)	38(3)	51(3)	6(3)	-6(3)	12(3)
C(8)	57(4)	48(4)	43(3)	12(3)	-1(3)	18(3)
C(9)	69(5)	73(4)	32(3)	3(3)	1(3)	22(4)
C(10)	85(6)	66(5)	44(4)	9(3)	19(4)	29(4)
C(11)	100(7)	100(7)	60(5)	-3(4)	19(5)	-12(6)
C(12)	113(8)	109(8)	71(6)	-15(5)	28(6)	4(6)
C(13)	51(5)	57(5)	103(6)	6(4)	40(4)	11(4)
C(14)	91(7)	80(6)	116(7)	22(5)	46(6)	33(5)
C(15)	46(5)	65(5)	148(8)	43(5)	22(5)	13(4)
C(16)	69(6)	124(8)	190(11)	97(8)	-18(6)	18(6)
C(17)	47(5)	113(7)	153(8)	77(6)	-4(5)	-5(5)
C(18)	48(5)	68(5)	97(6)	26(4)	12(4)	29(4)

C(19)	46(4)	56(4)	47(3)	-4(3)	-22(3)	8(3)
C(20)	49(4)	37(3)	52(4)	1(3)	-15(3)	5(3)
C(21)	42(4)	59(4)	72(5)	5(3)	-14(3)	-2(3)
C(22)	48(4)	55(4)	80(5)	0(4)	5(4)	-5(3)
C(23)	70(5)	29(3)	70(4)	1(3)	2(4)	-2(3)
C(24)	86(6)	53(4)	58(4)	3(3)	21(4)	-11(4)
C(25)	124(8)	58(5)	57(5)	10(4)	17(5)	-1(5)
C(26)	112(7)	52(4)	43(4)	1(3)	-2(4)	12(4)
C(27)	75(5)	36(3)	43(3)	-1(3)	-9(3)	5(3)
C(28)	51(4)	23(3)	47(3)	-4(2)	4(3)	0(3)
C(35)	60(4)	58(4)	45(3)	-9(3)	3(3)	24(3)
C(36)	134(8)	92(7)	91(6)	13(5)	33(6)	65(6)
C(37)	75(6)	105(7)	89(6)	-20(5)	13(5)	-11(5)
C(38)	95(7)	100(7)	95(6)	-49(5)	-8(5)	9(5)
N(3)	46(3)	30(2)	44(3)	-3(2)	-4(2)	6(2)
N(4)	40(3)	59(3)	87(4)	21(3)	21(3)	20(3)
N(2)	51(3)	46(3)	31(2)	4(2)	-6(2)	13(2)
N(1)	31(2)	26(2)	45(3)	5(2)	-3(2)	0(2)
O(1)	57(3)	48(3)	56(2)	-8(2)	-15(2)	20(2)
O(2)	61(3)	43(2)	59(3)	-2(2)	4(2)	12(2)
F(1)	75(3)	103(3)	67(3)	10(2)	-41(2)	-21(2)
F(2)	131(4)	64(3)	46(2)	-19(2)	-7(2)	-14(2)
F(3)	61(2)	67(2)	59(2)	-5(2)	-16(2)	-3(2)

F(4)	65(3)	149(4)	46(2)	-9(2)	-8(2)	-4(3)
F(5)	119(4)	70(3)	85(3)	34(2)	-45(3)	-40(3)
F(6)	103(3)	49(2)	58(2)	1(2)	-33(2)	-11(2)
P(1)	68(1)	54(1)	34(1)	4(1)	-21(1)	-13(1)
S(1)	55(1)	35(1)	64(1)	-5(1)	-29(1)	13(1)
Mn(1)	38(1)	31(1)	41(1)	1(1)	-8(1)	6(1)

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**Table S-8.** Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}^2}\text{N}_4\text{(QuinoPN)})(\text{OOtBu})](\text{PF}_6)$ •pentane (**2a**).

	x	y	z	U(eq)
H(2A)	9853	10339	3992	155
H(2B)	10066	9246	3843	155
H(2C)	8699	9723	3710	155
H(3A)	11631	10718	2868	144
H(3B)	11928	9881	3311	144
H(3C)	11494	10901	3520	144
H(5A)	9709	12287	3051	109
H(5B)	9720	11690	3620	109
H(5C)	8400	12040	3313	109
H(6A)	8260	12053	2033	53
H(6B)	7536	12064	2593	53
H(7A)	6004	11011	2144	57
H(7B)	5991	12066	1902	57
H(8A)	7172	11489	1166	59
H(8B)	5724	11161	1152	59
H(9A)	6900	10200	472	70

H(9B)	7624	9263	702	70
H(11)	8504	10860	-63	103
H(12)	10387	11609	-69	116
H(14)	12544	12005	442	112
H(15)	13784	12052	1266	103
H(16)	13170	11302	2065	155
H(17)	11156	10557	2036	126
H(19A)	5157	9694	1054	61
H(19B)	6092	8805	1147	61
H(21)	3474	9170	1621	70
H(22)	2834	8777	2479	73
H(24)	3389	8468	3520	78
H(25)	4960	8361	4240	95
H(26)	7095	8557	4081	83
H(27)	7674	8952	3203	63
H(36A)	10879	6075	1475	157
H(36B)	9579	5972	1771	157
H(36C)	10730	6575	2066	157
H(37A)	10371	8530	1147	134
H(37B)	11240	7661	979	134
H(37C)	11339	8044	1610	134
H(38A)	8441	7386	824	146
H(38B)	8538	6503	989	146

H(38C)	9346	6849	657	146
H(39A)	6460	5106	-220	109
H(39B)	7413	5988	-227	109
H(39C)	7306	5399	338	109
H(40A)	8202	4056	-85	104
H(40B)	8338	4665	-644	104
H(41A)	10928	4522	-358	195
H(41B)	10781	4067	99	195
H(42A)	12786	4659	143	131
H(42B)	11996	5041	641	131
H(42C)	12109	5674	92	131
H(43A)	9684	5728	-147	194
<u>H(43B)</u>	<u>9509</u>	<u>5175</u>	<u>420</u>	<u>194</u>

**Table S-9.** Crystal data and structure refinement for [Mn<sup>III</sup>(S<sup>Me<sub>2</sub></sup>N<sub>4</sub>(6-Me-DPEN))(OOtBu)](BPh<sub>4</sub>)•Et<sub>2</sub>O (**3a**).

Identification code	ben04_0ma	
Empirical formula	C <sub>53</sub> H <sub>68</sub> B Mn N <sub>4</sub> O <sub>3</sub> S	
Formula weight	906.92	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P n a 2 <sub>1</sub>	
Unit cell dimensions	a = 17.265(2) Å b = 25.499(3) Å c = 11.2048(14) Å	⟨= 90°. @= 90°. © = 90°.
Volume	4932.7(11) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.221 Mg/m <sup>3</sup>	
Absorption coefficient	0.356 mm <sup>-1</sup>	
F(000)	1936	
Crystal size	0.15 x 0.10 x 0.05 mm <sup>3</sup>	
Theta range for data collection	1.99 to 25.35°.	
Index ranges	-20<=h<=20, -30<=k<=30, -13<=l<=13	
Reflections collected	76962	
Independent reflections	4716 [R(int) = 0.4200]	
Completeness to theta = 25.00°	98.9 %	

Max. and min. transmission	0.9824 and 0.9486
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	4716 / 1 / 579
Goodness-of-fit on $F^2$	1.000
Final R indices [ $I > 2\sigma(I)$ ]	R1 = 0.0696, wR2 = 0.0937
R indices (all data)	R1 = 0.1826, wR2 = 0.1246
Absolute structure parameter	0.06(4)
Extinction coefficient	0.0049(5)
Largest diff. peak and hole	0.401 and -0.378 e. $\text{\AA}^{-3}$

**Table S-10.** Atomic coordinates ( $x \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}^2}\text{N}_4(6\text{-Me-DPEN}))(\text{OOtBu})](\text{BPh}_4) \bullet \text{Et}_2\text{O}$  (**3a**). U(eq) is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

	x	y	z	U(eq)
C(1)	3502(6)	-1161(4)	-2528(7)	35(3)
C(2)	3421(5)	-1196(4)	-3903(7)	54(3)
C(3)	4090(5)	-1574(4)	-2100(9)	48(3)
C(4)	2713(5)	-1293(4)	-1956(8)	37(3)
C(5)	2340(6)	-1800(4)	-2220(9)	45(3)
C(6)	1650(5)	-1051(4)	-706(9)	38(3)
C(7)	1328(5)	-542(4)	-278(7)	32(2)
C(8)	1722(5)	307(4)	481(8)	42(3)
C(9)	1669(5)	582(3)	-719(8)	26(2)
C(10)	1259(5)	1047(4)	-825(10)	38(2)
C(11)	1289(5)	1293(4)	-1921(10)	42(3)
C(12)	1705(5)	1080(4)	-2855(9)	41(3)
C(13)	2073(6)	613(4)	-2679(8)	36(2)
C(14)	2511(5)	350(4)	-3669(8)	47(3)
C(15)	2061(5)	-478(4)	1564(7)	33(2)
C(16)	2853(6)	-372(3)	2020(7)	33(2)

C(17)	2986(5)	-249(4)	3192(7)	37(2)
C(18)	3737(6)	-194(4)	3593(8)	49(3)
C(19)	4325(6)	-274(4)	2784(8)	44(3)
C(20)	4174(6)	-379(4)	1598(9)	46(3)
C(21)	4809(5)	-458(4)	729(8)	55(3)
C(22)	547(5)	931(4)	3088(7)	29(2)
C(23)	11(5)	837(4)	2152(7)	30(2)
C(24)	-277(6)	338(4)	1896(8)	37(3)
C(25)	-48(5)	-83(4)	2575(8)	40(3)
C(26)	482(5)	-5(4)	3485(7)	31(2)
C(27)	753(5)	493(4)	3702(8)	35(3)
C(28)	1780(5)	1510(4)	3764(7)	29(2)
C(29)	2300(6)	1160(4)	3277(8)	37(3)
C(30)	3104(6)	1186(4)	3453(8)	44(3)
C(31)	3392(5)	1579(4)	4168(11)	54(3)
C(32)	2905(6)	1925(4)	4714(8)	49(3)
C(33)	2101(6)	1901(4)	4476(7)	38(3)
C(34)	347(5)	1754(4)	4534(7)	31(2)
C(35)	174(6)	2283(4)	4674(8)	46(3)
C(36)	-218(5)	2480(4)	5683(9)	48(3)
C(37)	-474(6)	2143(5)	6510(9)	50(3)
C(38)	-332(5)	1614(4)	6437(8)	42(3)
C(39)	98(5)	1438(4)	5450(8)	31(2)

C(40)	763(6)	1903(4)	2213(8)	35(3)
C(41)	1366(5)	2010(4)	1447(8)	39(3)
C(42)	1265(7)	2288(4)	397(9)	51(3)
C(43)	552(7)	2485(4)	69(9)	54(3)
C(44)	-57(7)	2395(4)	822(10)	55(3)
C(45)	40(6)	2107(4)	1886(10)	50(3)
C(47)	3892(5)	1177(4)	-846(10)	42(2)
C(48)	3219(6)	1439(4)	-219(9)	61(3)
C(49)	4126(6)	1478(4)	-1957(9)	56(3)
C(50)	4565(6)	1126(4)	25(8)	47(3)
C(51)	1396(6)	-1374(4)	4488(9)	57(3)
C(52)	1893(7)	-1810(4)	4009(10)	65(3)
C(53)	2817(8)	-2029(5)	2511(10)	78(4)
C(54)	3204(7)	-1843(4)	1401(11)	82(4)
N(1)	2420(4)	-938(3)	-1267(6)	32(2)
N(2)	1938(4)	-246(3)	351(6)	31(2)
N(3)	2076(4)	359(3)	-1597(7)	36(2)
N(4)	3428(4)	-436(3)	1234(6)	30(2)
O(1)	3480(3)	330(2)	-316(5)	39(2)
O(2)	3687(3)	673(3)	-1320(5)	44(2)
O(3)	2281(4)	-1654(3)	2947(6)	59(2)
B(1)	857(6)	1517(5)	3396(10)	35(3)
S(1)	3837(1)	-516(1)	-2131(2)	39(1)

Mn(1)	2943(1)	-262(1)	-802(1)	32(1)
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**Table S-11.** Bond lengths [ $\text{\AA}$ ] and angles [°] for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(6\text{-MeDPEN}))(\text{OOtBu})](\text{BPh}_4)\bullet\text{Et}_2\text{O}$  (**3a**).

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C(1)-C(3)	1.538(12)
C(1)-C(4)	1.543(12)
C(1)-C(2)	1.550(11)
C(1)-S(1)	1.800(10)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(3)-H(3C)	0.9800
C(4)-N(1)	1.292(10)
C(4)-C(5)	1.475(12)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-C(7)	1.492(11)
C(6)-N(1)	1.500(9)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-N(2)	1.473(10)

C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-N(2)	1.467(10)
C(8)-C(9)	1.518(12)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-N(3)	1.335(11)
C(9)-C(10)	1.386(11)
C(10)-C(11)	1.381(13)
C(10)-H(10)	0.9500
C(11)-C(12)	1.381(12)
C(11)-H(11)	0.9500
C(12)-C(13)	1.364(12)
C(12)-H(12)	0.9500
C(13)-N(3)	1.373(10)
C(13)-C(14)	1.501(12)
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-C(16)	1.484(11)
C(15)-N(2)	1.496(10)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900

C(16)-N(4)	1.337(10)
C(16)-C(17)	1.369(11)
C(17)-C(18)	1.379(12)
C(17)-H(17)	0.9500
C(18)-C(19)	1.376(12)
C(18)-H(18)	0.9500
C(19)-C(20)	1.380(12)
C(19)-H(19)	0.9500
C(20)-N(4)	1.358(10)
C(20)-C(21)	1.481(12)
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-C(27)	1.358(11)
C(22)-C(23)	1.419(11)
C(22)-B(1)	1.626(14)
C(23)-C(24)	1.395(11)
C(23)-H(23)	0.9500
C(24)-C(25)	1.373(12)
C(24)-H(24)	0.9500
C(25)-C(26)	1.385(11)
C(25)-H(25)	0.9500
C(26)-C(27)	1.375(11)

C(26)-H(26)	0.9500
C(27)-H(27)	0.9500
C(28)-C(29)	1.379(11)
C(28)-C(33)	1.390(11)
C(28)-B(1)	1.647(13)
C(29)-C(30)	1.403(12)
C(29)-H(29)	0.9500
C(30)-C(31)	1.377(12)
C(30)-H(30)	0.9500
C(31)-C(32)	1.363(12)
C(31)-H(31)	0.9500
C(32)-C(33)	1.414(12)
C(32)-H(32)	0.9500
C(33)-H(33)	0.9500
C(34)-C(39)	1.374(11)
C(34)-C(35)	1.389(12)
C(34)-B(1)	1.663(13)
C(35)-C(36)	1.410(12)
C(35)-H(35)	0.9500
C(36)-C(37)	1.338(13)
C(36)-H(36)	0.9500
C(37)-C(38)	1.374(13)
C(37)-H(37)	0.9500

C(38)-C(39)	1.406(12)
C(38)-H(38)	0.9500
C(39)-H(39)	0.9500
C(40)-C(41)	1.377(11)
C(40)-C(45)	1.401(12)
C(40)-B(1)	1.658(13)
C(41)-C(42)	1.386(13)
C(41)-H(41)	0.9500
C(42)-C(43)	1.379(13)
C(42)-H(42)	0.9500
C(43)-C(44)	1.367(13)
C(43)-H(43)	0.9500
C(44)-C(45)	1.410(13)
C(44)-H(44)	0.9500
C(45)-H(45)	0.9500
C(47)-O(2)	1.434(10)
C(47)-C(49)	1.518(13)
C(47)-C(48)	1.515(12)
C(47)-C(50)	1.524(12)
C(48)-H(48A)	0.9800
C(48)-H(48B)	0.9800
C(48)-H(48C)	0.9800
C(49)-H(49A)	0.9800

C(49)-H(49B)	0.9800
C(49)-H(49C)	0.9800
C(50)-H(50A)	0.9800
C(50)-H(50B)	0.9800
C(50)-H(50C)	0.9800
C(51)-C(52)	1.504(12)
C(51)-H(51A)	0.9800
C(51)-H(51B)	0.9800
C(51)-H(51C)	0.9800
C(52)-O(3)	1.423(12)
C(52)-H(52A)	0.9900
C(52)-H(52B)	0.9900
C(53)-O(3)	1.418(11)
C(53)-C(54)	1.489(14)
C(53)-H(53A)	0.9900
C(53)-H(53B)	0.9900
C(54)-H(54A)	0.9800
C(54)-H(54B)	0.9800
C(54)-H(54C)	0.9800
N(1)-Mn(1)	2.015(8)
N(2)-Mn(1)	2.163(7)
N(3)-Mn(1)	2.354(8)
N(4)-Mn(1)	2.471(7)

O(1)-O(2)	1.468(7)
O(1)-Mn(1)	1.853(6)
S(1)-Mn(1)	2.241(3)
C(3)-C(1)-C(4)	107.8(7)
C(3)-C(1)-C(2)	109.4(7)
C(4)-C(1)-C(2)	108.7(8)
C(3)-C(1)-S(1)	109.6(7)
C(4)-C(1)-S(1)	112.3(6)
C(2)-C(1)-S(1)	109.0(7)
C(1)-C(2)-H(2A)	109.5
C(1)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
C(1)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
C(1)-C(3)-H(3A)	109.5
C(1)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
C(1)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
N(1)-C(4)-C(5)	124.4(9)

N(1)-C(4)-C(1)	116.2(9)
C(5)-C(4)-C(1)	119.5(9)
C(4)-C(5)-H(5A)	109.5
C(4)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(7)-C(6)-N(1)	107.2(7)
C(7)-C(6)-H(6A)	110.3
N(1)-C(6)-H(6A)	110.3
C(7)-C(6)-H(6B)	110.3
N(1)-C(6)-H(6B)	110.3
H(6A)-C(6)-H(6B)	108.5
N(2)-C(7)-C(6)	109.5(7)
N(2)-C(7)-H(7A)	109.8
C(6)-C(7)-H(7A)	109.8
N(2)-C(7)-H(7B)	109.8
C(6)-C(7)-H(7B)	109.8
H(7A)-C(7)-H(7B)	108.2
N(2)-C(8)-C(9)	111.8(7)
N(2)-C(8)-H(8A)	109.3
C(9)-C(8)-H(8A)	109.3

N(2)-C(8)-H(8B)	109.3
C(9)-C(8)-H(8B)	109.3
H(8A)-C(8)-H(8B)	107.9
N(3)-C(9)-C(10)	124.7(9)
N(3)-C(9)-C(8)	115.1(8)
C(10)-C(9)-C(8)	120.0(9)
C(11)-C(10)-C(9)	116.5(10)
C(11)-C(10)-H(10)	121.8
C(9)-C(10)-H(10)	121.8
C(10)-C(11)-C(12)	121.0(9)
C(10)-C(11)-H(11)	119.5
C(12)-C(11)-H(11)	119.5
C(13)-C(12)-C(11)	118.5(9)
C(13)-C(12)-H(12)	120.8
C(11)-C(12)-H(12)	120.8
C(12)-C(13)-N(3)	122.6(9)
C(12)-C(13)-C(14)	121.1(9)
N(3)-C(13)-C(14)	116.2(9)
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5

H(14B)-C(14)-H(14C)	109.5
C(16)-C(15)-N(2)	111.9(7)
C(16)-C(15)-H(15A)	109.2
N(2)-C(15)-H(15A)	109.2
C(16)-C(15)-H(15B)	109.2
N(2)-C(15)-H(15B)	109.2
H(15A)-C(15)-H(15B)	107.9
N(4)-C(16)-C(17)	122.4(9)
N(4)-C(16)-C(15)	115.8(7)
C(17)-C(16)-C(15)	121.7(8)
C(16)-C(17)-C(18)	119.5(9)
C(16)-C(17)-H(17)	120.2
C(18)-C(17)-H(17)	120.2
C(19)-C(18)-C(17)	117.6(8)
C(19)-C(18)-H(18)	121.2
C(17)-C(18)-H(18)	121.2
C(18)-C(19)-C(20)	121.6(9)
C(18)-C(19)-H(19)	119.2
C(20)-C(19)-H(19)	119.2
N(4)-C(20)-C(19)	119.3(9)
N(4)-C(20)-C(21)	119.4(8)
C(19)-C(20)-C(21)	121.3(9)
C(20)-C(21)-H(21A)	109.5

C(20)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(20)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(27)-C(22)-C(23)	114.0(9)
C(27)-C(22)-B(1)	124.2(8)
C(23)-C(22)-B(1)	121.8(9)
C(24)-C(23)-C(22)	122.6(9)
C(24)-C(23)-H(23)	118.7
C(22)-C(23)-H(23)	118.7
C(25)-C(24)-C(23)	119.7(9)
C(25)-C(24)-H(24)	120.1
C(23)-C(24)-H(24)	120.1
C(24)-C(25)-C(26)	119.0(9)
C(24)-C(25)-H(25)	120.5
C(26)-C(25)-H(25)	120.5
C(27)-C(26)-C(25)	119.2(9)
C(27)-C(26)-H(26)	120.4
C(25)-C(26)-H(26)	120.4
C(22)-C(27)-C(26)	125.4(9)
C(22)-C(27)-H(27)	117.3
C(26)-C(27)-H(27)	117.3

C(29)-C(28)-C(33)	115.5(9)
C(29)-C(28)-B(1)	122.6(8)
C(33)-C(28)-B(1)	121.4(9)
C(28)-C(29)-C(30)	124.0(9)
C(28)-C(29)-H(29)	118.0
C(30)-C(29)-H(29)	118.0
C(31)-C(30)-C(29)	118.2(9)
C(31)-C(30)-H(30)	120.9
C(29)-C(30)-H(30)	120.9
C(32)-C(31)-C(30)	120.6(9)
C(32)-C(31)-H(31)	119.7
C(30)-C(31)-H(31)	119.7
C(31)-C(32)-C(33)	119.6(9)
C(31)-C(32)-H(32)	120.2
C(33)-C(32)-H(32)	120.2
C(28)-C(33)-C(32)	122.0(9)
C(28)-C(33)-H(33)	119.0
C(32)-C(33)-H(33)	119.0
C(39)-C(34)-C(35)	114.7(8)
C(39)-C(34)-B(1)	121.7(8)
C(35)-C(34)-B(1)	123.6(9)
C(34)-C(35)-C(36)	122.6(9)
C(34)-C(35)-H(35)	118.7

C(36)-C(35)-H(35)	118.7
C(37)-C(36)-C(35)	119.1(10)
C(37)-C(36)-H(36)	120.5
C(35)-C(36)-H(36)	120.5
C(36)-C(37)-C(38)	121.9(10)
C(36)-C(37)-H(37)	119.0
C(38)-C(37)-H(37)	119.0
C(37)-C(38)-C(39)	117.1(9)
C(37)-C(38)-H(38)	121.5
C(39)-C(38)-H(38)	121.5
C(34)-C(39)-C(38)	124.4(9)
C(34)-C(39)-H(39)	117.8
C(38)-C(39)-H(39)	117.8
C(41)-C(40)-C(45)	115.9(9)
C(41)-C(40)-B(1)	122.8(9)
C(45)-C(40)-B(1)	121.1(9)
C(40)-C(41)-C(42)	122.4(9)
C(40)-C(41)-H(41)	118.8
C(42)-C(41)-H(41)	118.8
C(43)-C(42)-C(41)	121.7(10)
C(43)-C(42)-H(42)	119.1
C(41)-C(42)-H(42)	119.1
C(44)-C(43)-C(42)	117.4(10)

C(44)-C(43)-H(43)	121.3
C(42)-C(43)-H(43)	121.3
C(43)-C(44)-C(45)	121.2(11)
C(43)-C(44)-H(44)	119.4
C(45)-C(44)-H(44)	119.4
C(40)-C(45)-C(44)	121.3(10)
C(40)-C(45)-H(45)	119.3
C(44)-C(45)-H(45)	119.3
O(2)-C(47)-C(49)	102.5(8)
O(2)-C(47)-C(48)	112.2(8)
C(49)-C(47)-C(48)	111.2(8)
O(2)-C(47)-C(50)	110.5(8)
C(49)-C(47)-C(50)	111.4(8)
C(48)-C(47)-C(50)	109.0(8)
C(47)-C(48)-H(48A)	109.5
C(47)-C(48)-H(48B)	109.5
H(48A)-C(48)-H(48B)	109.5
C(47)-C(48)-H(48C)	109.5
H(48A)-C(48)-H(48C)	109.5
H(48B)-C(48)-H(48C)	109.5
C(47)-C(49)-H(49A)	109.5
C(47)-C(49)-H(49B)	109.5
H(49A)-C(49)-H(49B)	109.5

C(47)-C(49)-H(49C)	109.5
H(49A)-C(49)-H(49C)	109.5
H(49B)-C(49)-H(49C)	109.5
C(47)-C(50)-H(50A)	109.5
C(47)-C(50)-H(50B)	109.5
H(50A)-C(50)-H(50B)	109.5
C(47)-C(50)-H(50C)	109.5
H(50A)-C(50)-H(50C)	109.5
H(50B)-C(50)-H(50C)	109.5
C(52)-C(51)-H(51A)	109.5
C(52)-C(51)-H(51B)	109.5
H(51A)-C(51)-H(51B)	109.5
C(52)-C(51)-H(51C)	109.5
H(51A)-C(51)-H(51C)	109.5
H(51B)-C(51)-H(51C)	109.5
O(3)-C(52)-C(51)	111.1(9)
O(3)-C(52)-H(52A)	109.4
C(51)-C(52)-H(52A)	109.4
O(3)-C(52)-H(52B)	109.4
C(51)-C(52)-H(52B)	109.4
H(52A)-C(52)-H(52B)	108.0
O(3)-C(53)-C(54)	111.4(9)
O(3)-C(53)-H(53A)	109.3

C(54)-C(53)-H(53A)	109.3
O(3)-C(53)-H(53B)	109.3
C(54)-C(53)-H(53B)	109.3
H(53A)-C(53)-H(53B)	108.0
C(53)-C(54)-H(54A)	109.5
C(53)-C(54)-H(54B)	109.5
H(54A)-C(54)-H(54B)	109.5
C(53)-C(54)-H(54C)	109.5
H(54A)-C(54)-H(54C)	109.5
H(54B)-C(54)-H(54C)	109.5
C(4)-N(1)-C(6)	117.5(8)
C(4)-N(1)-Mn(1)	125.4(7)
C(6)-N(1)-Mn(1)	117.0(6)
C(8)-N(2)-C(7)	111.0(7)
C(8)-N(2)-C(15)	109.0(7)
C(7)-N(2)-C(15)	109.6(7)
C(8)-N(2)-Mn(1)	106.2(5)
C(7)-N(2)-Mn(1)	106.2(5)
C(15)-N(2)-Mn(1)	114.9(5)
C(9)-N(3)-C(13)	116.7(8)
C(9)-N(3)-Mn(1)	109.9(6)
C(13)-N(3)-Mn(1)	130.7(7)
C(16)-N(4)-C(20)	119.5(8)

C(16)-N(4)-Mn(1)	109.5(5)
C(20)-N(4)-Mn(1)	125.4(6)
O(2)-O(1)-Mn(1)	112.4(4)
C(47)-O(2)-O(1)	108.0(6)
C(53)-O(3)-C(52)	114.0(8)
C(22)-B(1)-C(28)	111.2(8)
C(22)-B(1)-C(40)	110.1(8)
C(28)-B(1)-C(40)	107.5(8)
C(22)-B(1)-C(34)	108.9(8)
C(28)-B(1)-C(34)	108.9(8)
C(40)-B(1)-C(34)	110.3(8)
C(1)-S(1)-Mn(1)	102.0(3)
O(1)-Mn(1)-N(1)	175.7(3)
O(1)-Mn(1)-N(2)	102.2(3)
N(1)-Mn(1)-N(2)	79.1(3)
O(1)-Mn(1)-S(1)	94.9(2)
N(1)-Mn(1)-S(1)	83.6(2)
N(2)-Mn(1)-S(1)	162.6(2)
O(1)-Mn(1)-N(3)	83.2(3)
N(1)-Mn(1)-N(3)	101.1(3)
N(2)-Mn(1)-N(3)	72.8(3)
S(1)-Mn(1)-N(3)	112.4(2)
O(1)-Mn(1)-N(4)	72.9(2)

N(1)-Mn(1)-N(4)	103.7(3)
N(2)-Mn(1)-N(4)	74.0(2)
S(1)-Mn(1)-N(4)	109.13(18)
N(3)-Mn(1)-N(4)	133.3(3)

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Symmetry transformations used to generate equivalent atoms:

**Table S-11.** Bond lengths [ $\text{\AA}$ ] and angles [°] for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(6\text{-Me-DPEN}))(\text{OOtBu})](\text{BPh}_4)\bullet\text{Et}_2\text{O}$  (**3a**).

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{23}$	$U^{13}$	$U^{12}$
C(1)	41(6)	49(7)	14(5)	-4(4)	16(4)	22(6)
C(2)	31(6)	95(9)	35(6)	0(6)	-1(5)	3(6)
C(3)	34(6)	57(7)	53(6)	-11(6)	-1(6)	8(6)
C(4)	27(6)	63(8)	19(5)	3(5)	-3(5)	-5(5)
C(5)	46(7)	45(7)	45(6)	-6(6)	3(6)	4(6)
C(6)	14(5)	75(8)	26(5)	-3(6)	6(5)	-10(5)
C(7)	27(6)	42(6)	29(5)	0(5)	-2(4)	0(5)
C(8)	29(6)	57(8)	39(6)	-10(6)	-13(5)	-3(6)
C(9)	26(5)	32(6)	20(5)	-4(6)	-9(5)	-2(4)
C(10)	28(6)	51(7)	36(6)	-5(7)	-14(6)	-6(5)
C(11)	30(6)	29(6)	68(8)	-5(6)	-14(6)	3(5)
C(12)	40(7)	42(8)	41(6)	12(6)	-7(5)	0(6)
C(13)	27(6)	42(7)	39(6)	-1(5)	0(5)	-7(6)
C(14)	25(5)	90(9)	27(5)	10(6)	-6(5)	10(6)
C(15)	23(5)	58(7)	19(5)	6(4)	3(4)	-2(6)
C(16)	46(7)	32(7)	21(5)	5(4)	-7(5)	2(5)
C(17)	28(6)	51(7)	33(5)	3(5)	7(5)	-1(6)
C(18)	42(7)	75(9)	30(6)	-6(6)	-24(5)	-8(7)

C(19)	33(6)	61(7)	38(6)	11(6)	-15(5)	-11(6)
C(20)	33(6)	61(9)	44(7)	11(6)	-13(5)	-3(6)
C(21)	25(6)	100(10)	41(6)	18(6)	7(5)	4(6)
C(22)	20(5)	43(7)	24(5)	-2(5)	5(4)	-5(5)
C(23)	17(5)	53(7)	21(5)	4(5)	6(4)	5(5)
C(24)	32(6)	58(8)	21(5)	-10(6)	6(4)	2(6)
C(25)	23(6)	45(7)	52(7)	1(6)	14(5)	-10(5)
C(26)	18(6)	47(7)	28(5)	1(5)	4(4)	13(5)
C(27)	32(6)	42(7)	30(5)	-3(5)	6(4)	-5(6)
C(28)	24(6)	49(7)	12(5)	1(5)	-2(4)	0(5)
C(29)	44(7)	34(7)	33(6)	-7(5)	-5(5)	-4(6)
C(30)	40(8)	44(7)	47(6)	-12(5)	7(5)	-1(6)
C(31)	19(6)	78(9)	64(7)	-14(8)	-2(7)	1(6)
C(32)	34(7)	69(8)	44(6)	-9(6)	-6(6)	-16(7)
C(33)	32(6)	56(7)	26(6)	1(5)	2(5)	0(6)
C(34)	16(5)	42(7)	34(7)	4(5)	-9(4)	2(5)
C(35)	42(7)	55(8)	41(7)	10(6)	-2(5)	4(6)
C(36)	40(7)	56(8)	47(7)	-3(7)	6(6)	9(6)
C(37)	38(7)	71(9)	41(7)	2(7)	9(6)	-5(7)
C(38)	19(6)	67(9)	39(6)	18(6)	4(5)	-7(6)
C(39)	21(6)	49(7)	22(5)	-3(5)	-9(4)	3(5)
C(40)	29(6)	49(7)	26(6)	-9(5)	-9(5)	-7(5)
C(41)	28(6)	61(8)	27(6)	-1(5)	1(5)	-7(5)

C(42)	61(9)	58(8)	34(7)	-2(6)	9(6)	-7(7)
C(43)	65(9)	55(8)	42(7)	10(6)	-17(7)	-8(7)
C(44)	42(7)	52(9)	71(9)	5(7)	-17(7)	-4(6)
C(45)	39(8)	55(8)	56(7)	11(6)	-17(6)	-12(6)
C(47)	33(6)	47(7)	44(6)	-6(7)	-11(6)	0(5)
C(48)	45(8)	65(8)	73(8)	-12(7)	3(6)	3(7)
C(49)	43(7)	63(8)	62(8)	22(7)	6(6)	5(6)
C(50)	32(7)	48(8)	62(8)	-9(6)	5(6)	-3(6)
C(51)	49(7)	78(8)	44(7)	3(6)	-9(5)	10(7)
C(52)	62(8)	93(9)	39(8)	4(7)	-17(6)	-4(7)
C(53)	94(11)	81(10)	57(9)	3(7)	12(8)	41(9)
C(54)	103(12)	75(10)	68(9)	-4(7)	12(8)	29(8)
N(1)	24(5)	47(6)	27(4)	-1(4)	7(4)	2(4)
N(2)	20(4)	42(5)	30(4)	5(4)	-8(3)	4(4)
N(3)	20(4)	54(6)	35(5)	0(4)	-2(4)	-3(5)
N(4)	10(4)	57(6)	24(4)	4(4)	2(4)	-4(4)
O(1)	29(4)	57(5)	31(4)	7(4)	-1(3)	1(4)
O(2)	34(4)	59(6)	37(4)	-1(4)	-1(3)	-7(4)
O(3)	52(5)	78(6)	46(4)	9(4)	0(4)	4(4)
B(1)	21(7)	49(9)	35(7)	11(6)	5(5)	14(6)
S(1)	24(1)	54(2)	39(2)	-5(1)	9(1)	-3(1)
Mn(1)	20(1)	48(1)	27(1)	-1(1)	3(1)	2(1)

**Table S-13.** Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $\text{Mn}^{\text{III}}(\text{S}^{\text{Me}^2}\text{N}_4(6\text{-Me-DPEN}))(\text{OOtBu})(\text{BPh}_4)\bullet\text{Et}_2\text{O}$  (**3a**).

	x	y	z	U(eq)
H(2A)	3903	-1080	-4279	81
H(2B)	2994	-970	-4165	81
H(2C)	3313	-1559	-4134	81
H(3A)	4075	-1596	-1227	72
H(3B)	4612	-1472	-2356	72
H(3C)	3959	-1916	-2443	72
H(5A)	2219	-1981	-1471	68
H(5B)	2693	-2017	-2696	68
H(5C)	1862	-1740	-2670	68
H(6A)	1296	-1212	-1297	46
H(6B)	1712	-1297	-29	46
H(7A)	1137	-335	-965	39
H(7B)	888	-606	268	39
H(8A)	2112	487	982	50
H(8B)	1216	331	892	50
H(10)	971	1188	-177	46

H(11)	1020	1614	-2034	51
H(12)	1734	1254	-3603	49
H(14A)	3052	301	-3428	71
H(14B)	2491	570	-4386	71
H(14C)	2277	8	-3840	71
H(15A)	1677	-328	2124	40
H(15B)	1977	-861	1526	40
H(17)	2564	-201	3725	45
H(18)	3844	-104	4399	59
H(19)	4847	-258	3049	53
H(21A)	4768	-809	379	83
H(21B)	5309	-423	1136	83
H(21C)	4772	-194	96	83
H(23)	-159	1124	1682	37
H(24)	-629	289	1254	44
H(25)	-251	-423	2423	48
H(26)	657	-292	3954	37
H(27)	1115	535	4334	42
H(29)	2103	886	2792	44
H(30)	3440	938	3090	53
H(31)	3936	1611	4280	64
H(32)	3103	2180	5251	59
H(33)	1770	2159	4813	46

H(35)	325	2521	4065	55
H(36)	-299	2846	5774	57
H(37)	-762	2274	7168	60
H(38)	-516	1378	7027	50
H(39)	225	1076	5414	37
H(41)	1870	1888	1646	47
H(42)	1697	2345	-110	61
H(43)	486	2677	-651	65
H(44)	-555	2528	624	66
H(45)	-393	2050	2392	60
H(48A)	2787	1481	-779	92
H(48B)	3381	1785	72	92
H(48C)	3053	1223	457	92
H(49A)	4583	1313	-2315	84
H(49B)	4248	1841	-1742	84
H(49C)	3698	1474	-2533	84
H(50A)	4975	912	-334	71
H(50B)	4384	959	762	71
H(50C)	4770	1476	209	71
H(51A)	1727	-1088	4773	85
H(51B)	1080	-1507	5151	85
H(51C)	1056	-1244	3854	85
H(52A)	2280	-1912	4618	78

H(52B)	1566	-2120	3840	78
H(53A)	2543	-2362	2345	93
H(53B)	3214	-2098	3129	93
H(54A)	2832	-1848	739	123
H(54B)	3641	-2073	1213	123
H(54C)	3393	-1484	1519	123

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**Table S-14.** Crystal data and structure refinement for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(6\text{-Me-DPEN}))(\text{OOCm})(\text{BPh}_4)]$  (**3b**).

Identification code	twin4	
Empirical formula	C56 H64.65 B Cl1.34 Mn N4 O2.33 S	
Formula weight	976.36	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 12.8928(18) Å b = 14.433(2) Å c = 15.069(3) Å	a = 71.085(10)°. b = 77.463(10)°. g = 82.463(9)°.
Volume	2583.7(7) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.255 Mg/m <sup>3</sup>	
Absorption coefficient	0.411 mm <sup>-1</sup>	
F(000)	1032	
Crystal size	0.10 x 0.05 x 0.05 mm <sup>3</sup>	
Theta range for data collection	1.97 to 25.57°.	
Index ranges	-15<=h<=15, -16<=k<=17, 0<=l<=18	
Reflections collected	9356	
Independent reflections	9356 [R(int) = 0.1265]	
Completeness to theta = 25.00°	98.8 %	

Max. and min. transmission	0.9798 and 0.9601
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	9356 / 9 / 619
Goodness-of-fit on $F^2$	0.952
Final R indices [ $I > 2\sigma(I)$ ]	R1 = 0.1004, wR2 = 0.1919
R indices (all data)	R1 = 0.2391, wR2 = 0.2365
Largest diff. peak and hole	0.697 and -0.506 e. $\text{\AA}^{-3}$

**Table S-15.** Atomic coordinates ( $x \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}^2}\text{N}_4(6\text{-Me-DPEN}))(\text{OOCm})(\text{BPh}_4)]$  (**3b**). U(eq) is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

	x	y	z	U(eq)
C(1)	5406(5)	1057(5)	2867(5)	43(2)
C(2)	4502(5)	1006(6)	3779(5)	60(2)
C(3)	4960(6)	694(5)	2186(5)	59(2)
C(4)	5735(6)	2066(5)	2375(4)	33(2)
C(5)	4883(5)	2894(5)	2239(5)	46(2)
C(6)	7111(5)	3166(5)	1588(5)	41(2)
C(7)	8206(5)	3042(4)	987(4)	35(2)
C(8)	9476(5)	2613(5)	2085(5)	43(2)
C(9)	8798(5)	2798(5)	2945(5)	34(2)
C(10)	8884(6)	3576(5)	3221(5)	45(2)
C(11)	8266(7)	3685(6)	4043(6)	63(2)
C(12)	7592(7)	2995(7)	4580(6)	69(3)
C(13)	7554(6)	2193(6)	4292(5)	51(2)
C(14)	6869(7)	1351(6)	4910(5)	76(3)
C(15)	9706(5)	1855(5)	843(5)	41(2)
C(16)	9204(5)	1290(5)	399(5)	36(2)

C(17)	9544(5)	1369(5)	-561(5)	42(2)
C(18)	9124(6)	771(5)	-922(5)	46(2)
C(19)	8403(6)	122(5)	-340(5)	43(2)
C(20)	8103(5)	86(5)	601(5)	41(2)
C(21)	7369(6)	-681(6)	1274(5)	59(2)
C(23)	12159(5)	3993(5)	1781(4)	30(2)
C(24)	12019(5)	3087(5)	2467(5)	33(2)
C(25)	12154(5)	2215(5)	2255(5)	35(2)
C(26)	12459(5)	2194(5)	1311(5)	39(2)
C(27)	12600(5)	3078(5)	604(5)	37(2)
C(28)	12455(5)	3944(5)	840(5)	40(2)
C(29)	12848(5)	5797(5)	1357(4)	29(2)
C(30)	13884(5)	5517(5)	987(4)	36(2)
C(31)	14665(5)	6147(6)	474(5)	40(2)
C(32)	14434(5)	7140(6)	290(4)	40(2)
C(33)	13422(6)	7482(5)	625(5)	41(2)
C(34)	12645(5)	6812(5)	1146(4)	31(2)
C(35)	12115(5)	4788(4)	3155(4)	31(2)
C(36)	11294(5)	4546(4)	3947(4)	36(2)
C(37)	11460(5)	4297(4)	4873(4)	35(2)
C(38)	12457(6)	4264(5)	5041(5)	52(2)
C(39)	13293(6)	4480(6)	4301(5)	62(2)
C(40)	13121(6)	4762(5)	3363(5)	45(2)

C(41)	10770(5)	5514(5)	1879(4)	35(2)
C(42)	10167(5)	6120(5)	2405(4)	36(2)
C(43)	9152(5)	6518(5)	2282(4)	38(2)
C(44)	8668(5)	6345(5)	1638(4)	34(2)
C(45)	9238(5)	5783(5)	1074(5)	41(2)
C(46)	10242(5)	5381(5)	1216(4)	39(2)
C(47)	9390(6)	-1065(5)	4120(5)	41(2)
C(48)	8540(6)	-1629(5)	4007(5)	60(2)
C(49)	9396(6)	-1260(6)	5181(5)	61(2)
C(50)	10498(6)	-1242(5)	3617(5)	36(2)
C(51)	11186(6)	-508(6)	3202(5)	48(2)
C(52)	12220(6)	-678(6)	2767(5)	48(2)
C(53)	12574(6)	-1603(7)	2721(5)	57(2)
C(54)	11900(7)	-2353(6)	3147(5)	56(2)
C(55)	10866(6)	-2181(6)	3591(5)	46(2)
N(1)	6741(4)	2175(4)	2113(3)	29(1)
N(2)	8916(4)	2244(4)	1531(4)	33(1)
N(3)	8461(4)	685(4)	981(4)	39(1)
N(4)	8128(5)	2086(4)	3463(4)	39(2)
O(1)	9023(3)	228(3)	2819(3)	42(1)
O(2)	9076(3)	-28(3)	3828(3)	45(1)
B(1)	11992(6)	5021(5)	2036(5)	32(2)
S(1)	6513(1)	193(1)	3290(1)	43(1)

Mn(1)	7905(1)	1131(1)	2494(1)	36(1)
Cl(1)	5987(3)	5351(3)	2880(3)	82(2)
C(22)	5035(10)	6390(10)	2772(10)	71(4)
Cl(2)	5611(3)	7412(3)	2761(4)	126(2)
C(56)	5610(20)	7650(20)	4240(20)	117(6)
C(57)	5380(30)	7440(20)	3370(20)	117(6)
O(3)	5776(15)	6481(15)	3332(14)	117(6)
C(58)	5600(30)	6260(20)	2540(20)	117(6)
C(59)	5980(30)	5240(20)	2470(30)	117(6)

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**Table S-16.** Bond lengths [ $\text{\AA}$ ] and angles [°] for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(6\text{-Me-DPEN}))(\text{OOCm})(\text{BPh}_4)]$  (**3b**).

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C(1)-C(4)	1.475(9)
C(1)-C(3)	1.530(9)
C(1)-C(2)	1.586(9)
C(1)-S(1)	1.847(7)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(3)-H(3C)	0.9800
C(4)-N(1)	1.286(7)
C(4)-C(5)	1.507(8)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-N(1)	1.477(7)
C(6)-C(7)	1.526(8)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-N(2)	1.507(7)

C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-N(2)	1.467(7)
C(8)-C(9)	1.479(9)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(10)	1.343(9)
C(9)-N(4)	1.353(8)
C(10)-C(11)	1.363(9)
C(10)-H(10)	0.9500
C(11)-C(12)	1.342(10)
C(11)-H(11)	0.9500
C(12)-C(13)	1.371(10)
C(12)-H(12)	0.9500
C(13)-N(4)	1.352(9)
C(13)-C(14)	1.521(10)
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-N(2)	1.483(8)
C(15)-C(16)	1.486(8)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900

C(16)-N(3)	1.345(8)
C(16)-C(17)	1.388(9)
C(17)-C(18)	1.375(9)
C(17)-H(17)	0.9500
C(18)-C(19)	1.362(9)
C(18)-H(18)	0.9500
C(19)-C(20)	1.372(9)
C(19)-H(19)	0.9500
C(20)-N(3)	1.353(8)
C(20)-C(21)	1.509(9)
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(23)-C(24)	1.384(8)
C(23)-C(28)	1.410(8)
C(23)-B(1)	1.626(10)
C(24)-C(25)	1.378(8)
C(24)-H(24)	0.9500
C(25)-C(26)	1.400(9)
C(25)-H(25)	0.9500
C(26)-C(27)	1.376(9)
C(26)-H(26)	0.9500
C(27)-C(28)	1.387(9)

C(27)-H(27)	0.9500
C(28)-H(28)	0.9500
C(29)-C(30)	1.393(8)
C(29)-C(34)	1.396(8)
C(29)-B(1)	1.617(10)
C(30)-C(31)	1.374(9)
C(30)-H(30)	0.9500
C(31)-C(32)	1.374(9)
C(31)-H(31)	0.9500
C(32)-C(33)	1.381(8)
C(32)-H(32)	0.9500
C(33)-C(34)	1.405(9)
C(33)-H(33)	0.9500
C(34)-H(34)	0.9500
C(35)-C(40)	1.392(8)
C(35)-C(36)	1.394(8)
C(35)-B(1)	1.648(9)
C(36)-C(37)	1.380(8)
C(36)-H(36)	0.9500
C(37)-C(38)	1.355(8)
C(37)-H(37)	0.9500
C(38)-C(39)	1.359(9)
C(38)-H(38)	0.9500

C(39)-C(40)	1.397(9)
C(39)-H(39)	0.9500
C(40)-H(40)	0.9500
C(41)-C(46)	1.397(8)
C(41)-C(42)	1.415(8)
C(41)-B(1)	1.674(9)
C(42)-C(43)	1.385(8)
C(42)-H(42)	0.9500
C(43)-C(44)	1.361(8)
C(43)-H(43)	0.9500
C(44)-C(45)	1.392(8)
C(44)-H(44)	0.9500
C(45)-C(46)	1.378(8)
C(45)-H(45)	0.9500
C(46)-H(46)	0.9500
C(47)-O(2)	1.446(7)
C(47)-C(50)	1.497(9)
C(47)-C(48)	1.516(9)
C(47)-C(49)	1.532(9)
C(48)-H(48A)	0.9800
C(48)-H(48B)	0.9800
C(48)-H(48C)	0.9800
C(49)-H(49A)	0.9800

C(49)-H(49B)	0.9800
C(49)-H(49C)	0.9800
C(50)-C(51)	1.371(9)
C(50)-C(55)	1.386(9)
C(51)-C(52)	1.381(9)
C(51)-H(51)	0.9500
C(52)-C(53)	1.372(10)
C(52)-H(52)	0.9500
C(53)-C(54)	1.377(10)
C(53)-H(53)	0.9500
C(54)-C(55)	1.385(9)
C(54)-H(54)	0.9500
C(55)-H(55)	0.9500
N(1)-Mn(1)	2.018(5)
N(2)-Mn(1)	2.145(5)
N(3)-Mn(1)	2.499(6)
N(4)-Mn(1)	2.389(5)
O(1)-O(2)	1.457(5)
O(1)-Mn(1)	1.848(4)
S(1)-Mn(1)	2.268(2)
Cl(1)-C(22)	1.796(13)
C(22)-Cl(2)	1.731(13)
C(22)-H(22A)	0.9900

C(22)-H(22B)	0.9900
C(56)-C(57)	1.528(18)
C(56)-H(56A)	0.9800
C(56)-H(56B)	0.9800
C(56)-H(56C)	0.9800
C(57)-O(3)	1.426(18)
C(57)-H(57A)	0.9900
C(57)-H(57B)	0.9900
O(3)-C(58)	1.397(18)
C(58)-C(59)	1.511(19)
C(58)-H(58A)	0.9900
C(58)-H(58B)	0.9900
C(59)-H(59A)	0.9800
C(59)-H(59B)	0.9800
C(59)-H(59C)	0.9800
C(4)-C(1)-C(3)	109.3(5)
C(4)-C(1)-C(2)	111.7(6)
C(3)-C(1)-C(2)	107.7(6)
C(4)-C(1)-S(1)	112.7(5)
C(3)-C(1)-S(1)	108.9(5)
C(2)-C(1)-S(1)	106.4(4)
C(1)-C(2)-H(2A)	109.5

C(1)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
C(1)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
C(1)-C(3)-H(3A)	109.5
C(1)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
C(1)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
N(1)-C(4)-C(1)	116.9(6)
N(1)-C(4)-C(5)	124.7(6)
C(1)-C(4)-C(5)	118.4(6)
C(4)-C(5)-H(5A)	109.5
C(4)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
N(1)-C(6)-C(7)	107.5(5)
N(1)-C(6)-H(6A)	110.2
C(7)-C(6)-H(6A)	110.2

N(1)-C(6)-H(6B)	110.2
C(7)-C(6)-H(6B)	110.2
H(6A)-C(6)-H(6B)	108.5
N(2)-C(7)-C(6)	112.6(5)
N(2)-C(7)-H(7A)	109.1
C(6)-C(7)-H(7A)	109.1
N(2)-C(7)-H(7B)	109.1
C(6)-C(7)-H(7B)	109.1
H(7A)-C(7)-H(7B)	107.8
N(2)-C(8)-C(9)	114.4(5)
N(2)-C(8)-H(8A)	108.7
C(9)-C(8)-H(8A)	108.7
N(2)-C(8)-H(8B)	108.7
C(9)-C(8)-H(8B)	108.7
H(8A)-C(8)-H(8B)	107.6
C(10)-C(9)-N(4)	122.7(7)
C(10)-C(9)-C(8)	122.9(7)
N(4)-C(9)-C(8)	114.3(6)
C(9)-C(10)-C(11)	120.1(7)
C(9)-C(10)-H(10)	120.0
C(11)-C(10)-H(10)	120.0
C(12)-C(11)-C(10)	119.3(7)
C(12)-C(11)-H(11)	120.4

C(10)-C(11)-H(11)	120.4
C(11)-C(12)-C(13)	119.0(8)
C(11)-C(12)-H(12)	120.5
C(13)-C(12)-H(12)	120.5
N(4)-C(13)-C(12)	123.0(7)
N(4)-C(13)-C(14)	115.7(7)
C(12)-C(13)-C(14)	121.3(8)
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
N(2)-C(15)-C(16)	112.0(5)
N(2)-C(15)-H(15A)	109.2
C(16)-C(15)-H(15A)	109.2
N(2)-C(15)-H(15B)	109.2
C(16)-C(15)-H(15B)	109.2
H(15A)-C(15)-H(15B)	107.9
N(3)-C(16)-C(17)	123.3(6)
N(3)-C(16)-C(15)	116.6(6)
C(17)-C(16)-C(15)	120.0(7)
C(18)-C(17)-C(16)	118.1(7)

C(18)-C(17)-H(17)	121.0
C(16)-C(17)-H(17)	121.0
C(19)-C(18)-C(17)	119.9(7)
C(19)-C(18)-H(18)	120.1
C(17)-C(18)-H(18)	120.1
C(18)-C(19)-C(20)	118.8(7)
C(18)-C(19)-H(19)	120.6
C(20)-C(19)-H(19)	120.6
N(3)-C(20)-C(19)	123.5(7)
N(3)-C(20)-C(21)	117.0(6)
C(19)-C(20)-C(21)	119.5(7)
C(20)-C(21)-H(21A)	109.5
C(20)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(20)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(24)-C(23)-C(28)	113.8(6)
C(24)-C(23)-B(1)	123.2(6)
C(28)-C(23)-B(1)	123.0(6)
C(25)-C(24)-C(23)	123.4(6)
C(25)-C(24)-H(24)	118.3
C(23)-C(24)-H(24)	118.3

C(24)-C(25)-C(26)	121.2(6)
C(24)-C(25)-H(25)	119.4
C(26)-C(25)-H(25)	119.4
C(27)-C(26)-C(25)	117.5(6)
C(27)-C(26)-H(26)	121.3
C(25)-C(26)-H(26)	121.3
C(26)-C(27)-C(28)	120.0(7)
C(26)-C(27)-H(27)	120.0
C(28)-C(27)-H(27)	120.0
C(27)-C(28)-C(23)	124.1(7)
C(27)-C(28)-H(28)	117.9
C(23)-C(28)-H(28)	117.9
C(30)-C(29)-C(34)	113.6(6)
C(30)-C(29)-B(1)	123.1(6)
C(34)-C(29)-B(1)	123.1(6)
C(31)-C(30)-C(29)	125.3(7)
C(31)-C(30)-H(30)	117.4
C(29)-C(30)-H(30)	117.4
C(30)-C(31)-C(32)	119.2(6)
C(30)-C(31)-H(31)	120.4
C(32)-C(31)-H(31)	120.4
C(31)-C(32)-C(33)	119.2(6)
C(31)-C(32)-H(32)	120.4

C(33)-C(32)-H(32)	120.4
C(32)-C(33)-C(34)	119.8(6)
C(32)-C(33)-H(33)	120.1
C(34)-C(33)-H(33)	120.1
C(29)-C(34)-C(33)	122.9(6)
C(29)-C(34)-H(34)	118.6
C(33)-C(34)-H(34)	118.6
C(40)-C(35)-C(36)	115.2(6)
C(40)-C(35)-B(1)	119.2(6)
C(36)-C(35)-B(1)	125.5(6)
C(37)-C(36)-C(35)	122.8(6)
C(37)-C(36)-H(36)	118.6
C(35)-C(36)-H(36)	118.6
C(38)-C(37)-C(36)	120.0(6)
C(38)-C(37)-H(37)	120.0
C(36)-C(37)-H(37)	120.0
C(37)-C(38)-C(39)	120.2(7)
C(37)-C(38)-H(38)	119.9
C(39)-C(38)-H(38)	119.9
C(38)-C(39)-C(40)	119.8(7)
C(38)-C(39)-H(39)	120.1
C(40)-C(39)-H(39)	120.1
C(35)-C(40)-C(39)	122.0(7)

C(35)-C(40)-H(40)	119.0
C(39)-C(40)-H(40)	119.0
C(46)-C(41)-C(42)	112.9(6)
C(46)-C(41)-B(1)	124.1(6)
C(42)-C(41)-B(1)	123.0(5)
C(43)-C(42)-C(41)	122.9(6)
C(43)-C(42)-H(42)	118.5
C(41)-C(42)-H(42)	118.5
C(44)-C(43)-C(42)	121.5(6)
C(44)-C(43)-H(43)	119.3
C(42)-C(43)-H(43)	119.3
C(43)-C(44)-C(45)	118.2(6)
C(43)-C(44)-H(44)	120.9
C(45)-C(44)-H(44)	120.9
C(46)-C(45)-C(44)	119.5(6)
C(46)-C(45)-H(45)	120.2
C(44)-C(45)-H(45)	120.2
C(45)-C(46)-C(41)	124.9(6)
C(45)-C(46)-H(46)	117.6
C(41)-C(46)-H(46)	117.6
O(2)-C(47)-C(50)	109.8(5)
O(2)-C(47)-C(48)	109.1(5)
C(50)-C(47)-C(48)	116.2(6)

O(2)-C(47)-C(49)	101.4(5)
C(50)-C(47)-C(49)	109.1(5)
C(48)-C(47)-C(49)	110.1(6)
C(47)-C(48)-H(48A)	109.5
C(47)-C(48)-H(48B)	109.5
H(48A)-C(48)-H(48B)	109.5
C(47)-C(48)-H(48C)	109.5
H(48A)-C(48)-H(48C)	109.5
H(48B)-C(48)-H(48C)	109.5
C(47)-C(49)-H(49A)	109.5
C(47)-C(49)-H(49B)	109.5
H(49A)-C(49)-H(49B)	109.5
C(47)-C(49)-H(49C)	109.5
H(49A)-C(49)-H(49C)	109.5
H(49B)-C(49)-H(49C)	109.5
C(51)-C(50)-C(55)	118.0(7)
C(51)-C(50)-C(47)	122.1(6)
C(55)-C(50)-C(47)	119.8(7)
C(50)-C(51)-C(52)	122.1(8)
C(50)-C(51)-H(51)	118.9
C(52)-C(51)-H(51)	118.9
C(53)-C(52)-C(51)	119.7(8)
C(53)-C(52)-H(52)	120.2

C(51)-C(52)-H(52)	120.2
C(52)-C(53)-C(54)	119.0(8)
C(52)-C(53)-H(53)	120.5
C(54)-C(53)-H(53)	120.5
C(53)-C(54)-C(55)	121.1(8)
C(53)-C(54)-H(54)	119.4
C(55)-C(54)-H(54)	119.4
C(54)-C(55)-C(50)	120.0(7)
C(54)-C(55)-H(55)	120.0
C(50)-C(55)-H(55)	120.0
C(4)-N(1)-C(6)	119.1(5)
C(4)-N(1)-Mn(1)	125.7(4)
C(6)-N(1)-Mn(1)	114.8(4)
C(8)-N(2)-C(15)	109.3(5)
C(8)-N(2)-C(7)	111.5(5)
C(15)-N(2)-C(7)	108.8(5)
C(8)-N(2)-Mn(1)	109.0(4)
C(15)-N(2)-Mn(1)	111.4(4)
C(7)-N(2)-Mn(1)	106.9(4)
C(16)-N(3)-C(20)	116.2(6)
C(16)-N(3)-Mn(1)	108.3(4)
C(20)-N(3)-Mn(1)	134.9(5)
C(13)-N(4)-C(9)	116.0(6)

C(13)-N(4)-Mn(1)	132.3(5)
C(9)-N(4)-Mn(1)	109.6(4)
O(2)-O(1)-Mn(1)	112.4(3)
C(47)-O(2)-O(1)	105.6(4)
C(29)-B(1)-C(23)	112.4(6)
C(29)-B(1)-C(35)	108.9(5)
C(23)-B(1)-C(35)	108.7(5)
C(29)-B(1)-C(41)	108.4(5)
C(23)-B(1)-C(41)	107.8(5)
C(35)-B(1)-C(41)	110.7(5)
C(1)-S(1)-Mn(1)	99.8(2)
O(1)-Mn(1)-N(1)	176.9(2)
O(1)-Mn(1)-N(2)	94.23(19)
N(1)-Mn(1)-N(2)	82.8(2)
O(1)-Mn(1)-S(1)	99.92(14)
N(1)-Mn(1)-S(1)	83.11(16)
N(2)-Mn(1)-S(1)	164.95(14)
O(1)-Mn(1)-N(4)	94.71(18)
N(1)-Mn(1)-N(4)	83.59(18)
N(2)-Mn(1)-N(4)	76.4(2)
S(1)-Mn(1)-N(4)	107.23(16)
O(1)-Mn(1)-N(3)	80.87(18)
N(1)-Mn(1)-N(3)	99.25(18)

N(2)-Mn(1)-N(3)	73.82(19)
S(1)-Mn(1)-N(3)	103.28(15)
N(4)-Mn(1)-N(3)	149.5(2)
Cl(2)-C(22)-Cl(1)	110.8(7)
Cl(2)-C(22)-H(22A)	109.5
Cl(1)-C(22)-H(22A)	109.5
Cl(2)-C(22)-H(22B)	109.5
Cl(1)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	108.1
C(57)-C(56)-H(56A)	109.5
C(57)-C(56)-H(56B)	109.5
H(56A)-C(56)-H(56B)	109.5
C(57)-C(56)-H(56C)	109.5
H(56A)-C(56)-H(56C)	109.5
H(56B)-C(56)-H(56C)	109.5
O(3)-C(57)-C(56)	112.5(19)
O(3)-C(57)-H(57A)	109.1
C(56)-C(57)-H(57A)	109.1
O(3)-C(57)-H(57B)	109.1
C(56)-C(57)-H(57B)	109.1
H(57A)-C(57)-H(57B)	107.8
C(58)-O(3)-C(57)	114.9(18)
O(3)-C(58)-C(59)	117(2)

O(3)-C(58)-H(58A)	108.0
C(59)-C(58)-H(58A)	108.0
O(3)-C(58)-H(58B)	108.0
C(59)-C(58)-H(58B)	108.0
H(58A)-C(58)-H(58B)	107.3
C(58)-C(59)-H(59A)	109.5
C(58)-C(59)-H(59B)	109.5
H(59A)-C(59)-H(59B)	109.5
C(58)-C(59)-H(59C)	109.5
H(59A)-C(59)-H(59C)	109.5
H(59B)-C(59)-H(59C)	109.5

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Symmetry transformations used to generate equivalent atoms:

**Table S-17.** Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}2}\text{N}_4(6\text{-MeDPEN}))(\text{OOCm})(\text{BPh}_4)]$  (**3b**). The anisotropic displacement factor exponent takes the form:  $-2p^2 [ h^2 a^* U^{11} + \dots + 2 h k a^* b^* U^{12} ]$

	U <sup>11</sup>	U <sup>22</sup>	U <sup>33</sup>	U <sup>23</sup>	U <sup>13</sup>	U <sup>12</sup>
C(1)	27(4)	56(5)	43(4)	-5(4)	-11(4)	-11(4)
C(2)	42(5)	78(6)	41(5)	5(4)	-4(4)	0(4)
C(3)	51(5)	51(5)	69(6)	0(4)	-27(4)	-4(4)
C(4)	37(5)	27(4)	33(4)	-2(3)	-11(3)	-1(4)
C(5)	22(4)	41(5)	64(5)	-5(4)	-3(4)	0(3)
C(6)	36(5)	34(5)	46(4)	-6(4)	-7(4)	8(4)
C(7)	45(5)	21(4)	30(4)	0(3)	-3(3)	4(3)
C(8)	34(4)	54(5)	46(5)	-21(4)	-3(4)	-8(4)
C(9)	33(4)	30(5)	43(4)	-11(4)	-14(4)	1(4)
C(10)	53(5)	46(5)	34(4)	-12(4)	-6(4)	-11(4)
C(11)	86(7)	66(7)	54(6)	-36(5)	-16(5)	-14(5)
C(12)	91(7)	83(7)	46(5)	-34(5)	2(5)	-34(6)
C(13)	56(6)	58(6)	35(5)	-7(4)	-7(4)	-13(4)
C(14)	88(7)	99(8)	45(5)	-22(5)	-2(5)	-31(6)
C(15)	30(4)	47(5)	40(4)	-5(4)	-6(3)	0(3)
C(16)	37(5)	33(5)	37(4)	-13(4)	-9(4)	3(4)
C(17)	39(5)	40(5)	35(5)	-3(4)	0(4)	4(4)
C(18)	61(6)	39(5)	37(4)	-17(4)	-14(4)	23(4)

C(19)	51(5)	36(5)	45(5)	-14(4)	-23(4)	10(4)
C(20)	33(5)	43(5)	46(5)	-10(4)	-7(4)	-2(4)
C(21)	61(6)	67(6)	57(5)	-28(5)	-16(4)	1(5)
C(23)	22(4)	37(5)	30(4)	-11(4)	-4(3)	5(3)
C(24)	26(4)	39(5)	35(4)	-19(4)	-4(3)	5(3)
C(25)	22(4)	35(5)	44(5)	-10(4)	-2(3)	-4(3)
C(26)	27(4)	46(5)	55(5)	-30(4)	-18(4)	13(3)
C(27)	35(4)	41(5)	35(4)	-11(4)	-13(3)	11(3)
C(28)	43(5)	36(5)	42(5)	-13(4)	-7(3)	0(3)
C(29)	30(4)	32(5)	20(3)	-5(3)	-6(3)	5(3)
C(30)	29(5)	42(5)	33(4)	-9(4)	-4(3)	6(4)
C(31)	18(4)	54(6)	45(4)	-24(4)	3(3)	14(4)
C(32)	23(4)	56(6)	29(4)	-9(4)	8(3)	2(4)
C(33)	54(6)	26(4)	33(4)	-1(3)	0(4)	-2(4)
C(34)	26(4)	46(5)	17(3)	-13(3)	0(3)	8(4)
C(35)	28(4)	28(4)	37(4)	-14(3)	-2(3)	4(3)
C(36)	31(4)	35(5)	36(4)	-8(3)	0(3)	-8(3)
C(37)	38(5)	35(5)	28(4)	-9(3)	-1(3)	3(3)
C(38)	45(5)	81(6)	32(4)	-19(4)	-9(4)	-7(4)
C(39)	38(5)	104(7)	41(5)	-15(5)	-6(4)	-21(5)
C(40)	40(5)	56(5)	37(4)	-14(4)	1(4)	-12(4)
C(41)	46(5)	36(4)	21(4)	-4(3)	-3(3)	-12(3)
C(42)	47(5)	38(5)	24(4)	-10(3)	-4(3)	-8(4)

C(43)	34(5)	42(5)	31(4)	-9(3)	1(3)	4(4)
C(44)	21(4)	40(5)	33(4)	-6(3)	-3(3)	6(3)
C(45)	34(5)	50(5)	40(4)	-15(4)	-9(3)	1(4)
C(46)	44(5)	41(5)	28(4)	-9(3)	-1(3)	-5(4)
C(47)	49(5)	27(5)	41(4)	-4(4)	-10(4)	0(4)
C(48)	55(6)	61(6)	57(5)	-2(4)	-17(4)	-11(4)
C(49)	50(5)	76(6)	42(5)	-2(4)	-4(4)	0(4)
C(50)	44(5)	31(5)	33(4)	-9(4)	-16(4)	12(4)
C(51)	50(6)	55(6)	33(4)	-4(4)	-11(4)	0(4)
C(52)	32(5)	59(6)	52(5)	-15(4)	-12(4)	-1(4)
C(53)	46(6)	71(7)	59(6)	-30(5)	-21(4)	16(5)
C(54)	62(6)	43(6)	61(5)	-17(4)	-18(5)	15(5)
C(55)	44(5)	55(6)	39(5)	-14(4)	-10(4)	4(4)
N(1)	26(4)	27(3)	36(3)	-2(3)	-15(3)	-9(3)
N(2)	36(4)	27(3)	39(3)	-19(3)	3(3)	0(3)
N(3)	39(4)	34(4)	44(4)	-10(3)	-11(3)	3(3)
N(4)	49(4)	38(4)	34(4)	-8(3)	-15(3)	-7(3)
O(1)	42(3)	54(3)	25(3)	-4(2)	-10(2)	-5(2)
O(2)	49(3)	54(4)	28(3)	-10(2)	-8(2)	0(2)
B(1)	33(5)	30(5)	31(4)	-7(4)	-6(4)	3(4)
S(1)	36(1)	46(1)	40(1)	-1(1)	-8(1)	-4(1)
Mn(1)	32(1)	39(1)	33(1)	-5(1)	-6(1)	-2(1)
Cl(1)	43(2)	77(3)	119(4)	-23(2)	-13(2)	-3(2)

C(22)	67(10)	83(10)	67(9)	-23(7)	-21(8)	-6(8)
Cl(2)	71(3)	79(4)	232(7)	-39(3)	-43(4)	-16(2)

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**Table S-18.** Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}^2}\text{N}_4(6\text{-Me-DPEN}))(\text{OOCm})(\text{BPh}_4)]$  (**3b**).

	x	y	z	U(eq)
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—				
H(2A)	4678	1406	4136	90
H(2B)	4451	324	4188	90
H(2C)	3819	1258	3578	90
H(3A)	4320	1103	2018	88
H(3B)	4779	11	2498	88
H(3C)	5496	736	1606	88
H(5A)	4830	3222	2726	69
H(5B)	4199	2632	2300	69
H(5C)	5067	3367	1603	69
H(6A)	7160	3518	2042	49
H(6B)	6607	3550	1172	49
H(7A)	8117	2883	417	42
H(7B)	8554	3670	764	42
H(8A)	9792	3231	1666	52
H(8B)	10068	2130	2283	52
H(10)	9376	4052	2842	53

H(11)	8312	4242	4233	75
H(12)	7148	3061	5151	83
H(14A)	6184	1443	4700	114
H(14B)	6747	1339	5578	114
H(14C)	7234	729	4849	114
H(15A)	10256	1424	1178	49
H(15B)	10063	2407	336	49
H(17)	10051	1823	-956	50
H(18)	9336	811	-1577	55
H(19)	8112	-299	-581	51
H(21A)	7676	-1334	1254	88
H(21B)	6674	-561	1079	88
H(21C)	7282	-646	1925	88
H(24)	11820	3066	3118	39
H(25)	12038	1616	2758	42
H(26)	12564	1592	1164	47
H(27)	12798	3095	-46	44
H(28)	12560	4543	335	49
H(30)	14064	4834	1098	44
H(31)	15357	5899	248	48
H(32)	14965	7587	-62	48
H(33)	13252	8167	503	49
H(34)	11951	7061	1363	37

H(36)	10591	4553	3845	43
H(37)	10875	4150	5391	42
H(38)	12571	4088	5679	62
H(39)	13994	4440	4421	74
H(40)	13708	4940	2852	54
H(42)	10473	6260	2863	43
H(43)	8785	6921	2655	45
H(44)	7961	6600	1576	41
H(45)	8937	5678	595	49
H(46)	10601	4984	834	46
H(48A)	7836	-1388	4280	90
H(48B)	8659	-2329	4340	90
H(48C)	8574	-1534	3327	90
H(49A)	9948	-892	5246	92
H(49B)	9544	-1963	5481	92
H(49C)	8699	-1048	5495	92
H(51)	10944	139	3214	57
H(52)	12684	-157	2501	57
H(53)	13274	-1724	2400	68
H(54)	12147	-3000	3137	67
H(55)	10410	-2707	3877	56
H(22A)	4759	6532	2174	85
H(22B)	4428	6235	3314	85

H(56A)	5317	8306	4247	176
H(56B)	6385	7604	4209	176
H(56C)	5286	7161	4827	176
H(57A)	4604	7509	3398	141
H(57B)	5713	7932	2786	141
H(58A)	5953	6742	1958	141
H(58B)	4827	6349	2542	141
H(59A)	5803	5172	1898	176
H(59B)	5630	4750	3038	176
<u>H(59C)</u>	<u>6753</u>	<u>5149</u>	<u>2436</u>	<u>176</u>

**Table S-19.** Crystal data and structure refinement for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}^2}\text{N}_4(6\text{-Me-DPPN}))(\text{OOtBu})(\text{BPh}_4)\bullet\text{Et}_2\text{O}$  (**4a**).

Identification code	michael054_0m	
Empirical formula	C50 H60 B Mn N4 O2 S	
Formula weight	846.83	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	$a = 9.5420(7)$ Å	$\alpha = 77.689(4)^\circ$ .
	$b = 14.5846(11)$ Å	$\beta = 83.682(4)^\circ$ .
	$c = 16.4547(13)$ Å	$\gamma = 78.144(4)^\circ$ .
Volume	2184.3(3) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.288 Mg/m <sup>3</sup>	
Absorption coefficient	0.395 mm <sup>-1</sup>	
F(000)	900	
Crystal size	0.25 x 0.20 x 0.10 mm <sup>3</sup>	
Theta range for data collection	1.45 to 25.34°.	
Index ranges	$-11 \leq h \leq 11, -14 \leq k \leq 17, -19 \leq l \leq 19$	
Reflections collected	32127	
Independent reflections	7856 [R(int) = 0.0766]	

Completeness to theta = 25.00°	98.0 %
Max. and min. transmission	0.9616 and 0.9077
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	7856 / 10 / 540
Goodness-of-fit on F <sup>2</sup>	1.008
Final R indices [I>2sigma(I)]	R1 = 0.0667, wR2 = 0.1448
R indices (all data)	R1 = 0.1436, wR2 = 0.1786
Largest diff. peak and hole	0.487 and -0.722 e.Å <sup>-3</sup>

**Table S-20.** Atomic coordinates ( $x \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}^2}\text{N}_4(6\text{-Me-DPPN}))(\text{OOtBu})(\text{BPh}_4)\bullet\text{Et}_2\text{O}$  (**4a**).

	x	y	z	U(eq)
C(1)	5887(6)	43(3)	2853(3)	45(1)
C(2)	4564(6)	1595(4)	2147(3)	51(1)
C(3)	5897(5)	1122(3)	2626(3)	34(1)
C(4)	7197(5)	1371(3)	2075(3)	34(1)
C(5)	7556(6)	940(4)	1310(3)	52(1)
C(6)	9119(5)	2226(3)	1655(3)	36(1)
C(7)	9483(5)	3175(4)	1693(3)	44(1)
C(8)	10235(5)	3194(4)	2442(3)	40(1)
C(9)	8701(5)	4174(4)	3340(3)	44(1)
C(10)	7472(5)	4630(3)	2810(3)	35(1)
C(11)	7300(6)	5572(4)	2408(4)	56(2)
C(12)	6104(7)	5984(4)	1994(4)	68(2)
C(13)	5094(6)	5446(4)	1985(3)	48(1)
C(14)	5309(5)	4493(3)	2389(3)	40(1)
C(15)	4172(6)	3912(4)	2427(5)	84(2)
C(16)	10274(5)	2759(4)	3944(3)	47(1)
C(17)	10791(5)	1710(4)	4008(3)	45(1)

C(18)	12090(6)	1267(5)	4350(3)	61(1)
C(19)	12442(6)	282(5)	4459(4)	69(2)
C(20)	11561(6)	-220(5)	4204(3)	63(1)
C(21)	10300(6)	275(4)	3853(3)	48(1)
C(22)	9339(6)	-231(4)	3534(4)	61(2)
C(23)	5296(6)	2949(4)	5440(4)	57(2)
C(24)	4318(7)	3543(4)	4785(4)	70(2)
C(25)	6056(8)	3556(5)	5796(4)	84(2)
C(26)	4624(8)	2318(5)	6128(4)	77(2)
C(27)	8584(4)	3328(3)	-955(3)	28(1)
C(28)	8871(5)	4225(3)	-915(3)	38(1)
C(29)	8045(6)	4823(3)	-410(3)	46(1)
C(30)	6874(6)	4550(4)	60(3)	46(1)
C(31)	6522(5)	3692(4)	21(3)	43(1)
C(32)	7360(5)	3101(3)	-477(3)	31(1)
C(33)	11231(4)	2290(3)	-1081(3)	24(1)
C(34)	12327(5)	1602(3)	-1346(3)	37(1)
C(35)	13634(5)	1326(3)	-1016(3)	40(1)
C(36)	13948(5)	1705(3)	-373(3)	36(1)
C(37)	12892(5)	2368(3)	-72(3)	38(1)
C(38)	11580(5)	2650(3)	-422(3)	30(1)
C(39)	9795(5)	3171(3)	-2485(3)	33(1)
C(40)	10796(7)	2806(5)	-3081(3)	68(2)

C(41)	10799(9)	3171(6)	-3919(4)	85(2)
C(42)	9874(11)	3940(6)	-4212(4)	85(2)
C(43)	8860(8)	4351(4)	-3697(4)	73(2)
C(44)	8829(6)	3953(4)	-2823(3)	50(1)
C(45)	8963(4)	1675(3)	-1493(3)	24(1)
C(46)	8191(6)	1584(4)	-2132(3)	48(1)
C(47)	7533(6)	804(4)	-2098(3)	55(2)
C(48)	7618(5)	99(4)	-1412(3)	45(1)
C(49)	8352(5)	149(3)	-762(3)	44(1)
C(50)	9013(5)	922(3)	-813(3)	34(1)
N(1)	9346(4)	3185(3)	3245(2)	33(1)
N(2)	7907(4)	1954(3)	2253(2)	30(1)
N(3)	6509(4)	4074(2)	2788(2)	32(1)
N(4)	9907(4)	1235(3)	3758(2)	39(1)
O(1)	7304(3)	2643(3)	4446(2)	46(1)
O(2)	6342(4)	2230(3)	5082(2)	61(1)
B(1)	9655(5)	2622(3)	-1500(3)	25(1)
S(1)	5816(1)	1545(1)	3612(1)	32(1)
Mn(1)	7621(1)	2377(1)	3387(1)	29(1)

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**Table S-21.** Bond lengths [ $\text{\AA}$ ] and angles [°] for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(6\text{-Me-DPPN}))(\text{OOtBu})(\text{BPh}_4)\bullet\text{Et}_2\text{O}$  (**4a**).

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C(1)-C(3)	1.540(6)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-C(3)	1.531(6)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-C(4)	1.513(7)
C(3)-S(1)	1.842(4)
C(4)-N(2)	1.287(6)
C(4)-C(5)	1.500(6)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-N(2)	1.495(6)
C(6)-C(7)	1.510(7)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-C(8)	1.501(7)

C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-N(1)	1.488(6)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-N(1)	1.482(6)
C(9)-C(10)	1.495(7)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-N(3)	1.352(6)
C(10)-C(11)	1.377(7)
C(11)-C(12)	1.358(8)
C(11)-H(11)	0.9500
C(12)-C(13)	1.364(8)
C(12)-H(12)	0.9500
C(13)-C(14)	1.391(7)
C(13)-H(13)	0.9500
C(14)-N(3)	1.350(5)
C(14)-C(15)	1.496(7)
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-N(1)	1.479(6)

C(16)-C(17)	1.493(7)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-N(4)	1.342(6)
C(17)-C(18)	1.393(7)
C(18)-C(19)	1.383(9)
C(18)-H(18)	0.9500
C(19)-C(20)	1.371(9)
C(19)-H(19)	0.9500
C(20)-C(21)	1.386(7)
C(20)-H(20)	0.9500
C(21)-N(4)	1.352(6)
C(21)-C(22)	1.487(8)
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-O(2)	1.466(6)
C(23)-C(26)	1.476(8)
C(23)-C(25)	1.493(8)
C(23)-C(24)	1.508(8)
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800

C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(27)-C(32)	1.392(6)
C(27)-C(28)	1.405(6)
C(27)-B(1)	1.635(6)
C(28)-C(29)	1.399(6)
C(28)-H(28)	0.9500
C(29)-C(30)	1.366(7)
C(29)-H(29)	0.9500
C(30)-C(31)	1.376(7)
C(30)-H(30)	0.9500
C(31)-C(32)	1.388(6)
C(31)-H(31)	0.9500
C(32)-H(32)	0.9500
C(33)-C(34)	1.395(6)
C(33)-C(38)	1.398(6)
C(33)-B(1)	1.661(6)
C(34)-C(35)	1.365(6)
C(34)-H(34)	0.9500

C(35)-C(36)	1.379(6)
C(35)-H(35)	0.9500
C(36)-C(37)	1.375(6)
C(36)-H(36)	0.9500
C(37)-C(38)	1.384(6)
C(37)-H(37)	0.9500
C(38)-H(38)	0.9500
C(39)-C(44)	1.368(7)
C(39)-C(40)	1.401(7)
C(39)-B(1)	1.651(7)
C(40)-C(41)	1.368(8)
C(40)-H(40)	0.9500
C(41)-C(42)	1.314(10)
C(41)-H(41)	0.9500
C(42)-C(43)	1.346(9)
C(42)-H(42)	0.9500
C(43)-C(44)	1.431(8)
C(43)-H(43)	0.9500
C(44)-H(44)	0.9500
C(45)-C(50)	1.389(6)
C(45)-C(46)	1.392(6)
C(45)-B(1)	1.645(6)
C(46)-C(47)	1.396(7)

C(46)-H(46)	0.9500
C(47)-C(48)	1.352(7)
C(47)-H(47)	0.9500
C(48)-C(49)	1.364(7)
C(48)-H(48)	0.9500
C(49)-C(50)	1.384(6)
C(49)-H(49)	0.9500
C(50)-H(50)	0.9500
N(1)-Mn(1)	2.178(4)
N(2)-Mn(1)	2.061(4)
N(3)-Mn(1)	2.517(4)
N(4)-Mn(1)	2.504(4)
O(1)-O(2)	1.431(5)
O(1)-Mn(1)	1.843(3)
S(1)-Mn(1)	2.2603(13)

C(3)-C(1)-H(1A)	109.5
C(3)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(3)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(3)-C(2)-H(2A)	109.5

C(3)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
C(3)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
C(4)-C(3)-C(2)	107.7(4)
C(4)-C(3)-C(1)	113.7(4)
C(2)-C(3)-C(1)	107.0(4)
C(4)-C(3)-S(1)	110.1(3)
C(2)-C(3)-S(1)	111.0(3)
C(1)-C(3)-S(1)	107.3(3)
N(2)-C(4)-C(5)	123.0(5)
N(2)-C(4)-C(3)	120.2(4)
C(5)-C(4)-C(3)	116.8(4)
C(4)-C(5)-H(5A)	109.5
C(4)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
N(2)-C(6)-C(7)	114.4(4)
N(2)-C(6)-H(6A)	108.7
C(7)-C(6)-H(6A)	108.7

N(2)-C(6)-H(6B)	108.7
C(7)-C(6)-H(6B)	108.7
H(6A)-C(6)-H(6B)	107.6
C(8)-C(7)-C(6)	115.8(4)
C(8)-C(7)-H(7A)	108.3
C(6)-C(7)-H(7A)	108.3
C(8)-C(7)-H(7B)	108.3
C(6)-C(7)-H(7B)	108.3
H(7A)-C(7)-H(7B)	107.4
N(1)-C(8)-C(7)	116.8(4)
N(1)-C(8)-H(8A)	108.1
C(7)-C(8)-H(8A)	108.1
N(1)-C(8)-H(8B)	108.1
C(7)-C(8)-H(8B)	108.1
H(8A)-C(8)-H(8B)	107.3
N(1)-C(9)-C(10)	114.1(4)
N(1)-C(9)-H(9A)	108.7
C(10)-C(9)-H(9A)	108.7
N(1)-C(9)-H(9B)	108.7
C(10)-C(9)-H(9B)	108.7
H(9A)-C(9)-H(9B)	107.6
N(3)-C(10)-C(11)	122.5(5)
N(3)-C(10)-C(9)	115.8(4)

C(11)-C(10)-C(9)	121.6(4)
C(12)-C(11)-C(10)	119.9(5)
C(12)-C(11)-H(11)	120.1
C(10)-C(11)-H(11)	120.1
C(11)-C(12)-C(13)	118.7(5)
C(11)-C(12)-H(12)	120.7
C(13)-C(12)-H(12)	120.7
C(12)-C(13)-C(14)	120.0(5)
C(12)-C(13)-H(13)	120.0
C(14)-C(13)-H(13)	120.0
N(3)-C(14)-C(13)	121.6(5)
N(3)-C(14)-C(15)	117.9(4)
C(13)-C(14)-C(15)	120.4(5)
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
N(1)-C(16)-C(17)	112.6(4)
N(1)-C(16)-H(16A)	109.1
C(17)-C(16)-H(16A)	109.1
N(1)-C(16)-H(16B)	109.1

C(17)-C(16)-H(16B)	109.1
H(16A)-C(16)-H(16B)	107.8
N(4)-C(17)-C(18)	123.4(5)
N(4)-C(17)-C(16)	116.2(4)
C(18)-C(17)-C(16)	120.4(5)
C(19)-C(18)-C(17)	117.3(6)
C(19)-C(18)-H(18)	121.3
C(17)-C(18)-H(18)	121.3
C(20)-C(19)-C(18)	120.4(5)
C(20)-C(19)-H(19)	119.8
C(18)-C(19)-H(19)	119.8
C(19)-C(20)-C(21)	118.8(6)
C(19)-C(20)-H(20)	120.6
C(21)-C(20)-H(20)	120.6
N(4)-C(21)-C(20)	122.2(6)
N(4)-C(21)-C(22)	116.8(4)
C(20)-C(21)-C(22)	120.9(5)
C(21)-C(22)-H(22A)	109.5
C(21)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(21)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5

O(2)-C(23)-C(26)	99.7(5)
O(2)-C(23)-C(25)	110.0(5)
C(26)-C(23)-C(25)	109.2(5)
O(2)-C(23)-C(24)	109.9(5)
C(26)-C(23)-C(24)	116.0(5)
C(25)-C(23)-C(24)	111.4(5)
C(23)-C(24)-H(24A)	109.5
C(23)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(23)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(23)-C(25)-H(25A)	109.5
C(23)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(23)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(23)-C(26)-H(26A)	109.5
C(23)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(23)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5

H(26B)-C(26)-H(26C)	109.5
C(32)-C(27)-C(28)	114.3(4)
C(32)-C(27)-B(1)	124.4(4)
C(28)-C(27)-B(1)	121.3(4)
C(29)-C(28)-C(27)	123.3(5)
C(29)-C(28)-H(28)	118.4
C(27)-C(28)-H(28)	118.4
C(30)-C(29)-C(28)	119.6(5)
C(30)-C(29)-H(29)	120.2
C(28)-C(29)-H(29)	120.2
C(29)-C(30)-C(31)	119.2(5)
C(29)-C(30)-H(30)	120.4
C(31)-C(30)-H(30)	120.4
C(30)-C(31)-C(32)	120.6(5)
C(30)-C(31)-H(31)	119.7
C(32)-C(31)-H(31)	119.7
C(31)-C(32)-C(27)	123.0(5)
C(31)-C(32)-H(32)	118.5
C(27)-C(32)-H(32)	118.5
C(34)-C(33)-C(38)	113.5(4)
C(34)-C(33)-B(1)	122.6(4)
C(38)-C(33)-B(1)	123.9(4)
C(35)-C(34)-C(33)	123.5(4)

C(35)-C(34)-H(34)	118.2
C(33)-C(34)-H(34)	118.2
C(34)-C(35)-C(36)	121.3(4)
C(34)-C(35)-H(35)	119.3
C(36)-C(35)-H(35)	119.3
C(37)-C(36)-C(35)	117.6(4)
C(37)-C(36)-H(36)	121.2
C(35)-C(36)-H(36)	121.2
C(36)-C(37)-C(38)	120.3(4)
C(36)-C(37)-H(37)	119.9
C(38)-C(37)-H(37)	119.9
C(37)-C(38)-C(33)	123.7(4)
C(37)-C(38)-H(38)	118.1
C(33)-C(38)-H(38)	118.1
C(44)-C(39)-C(40)	113.1(5)
C(44)-C(39)-B(1)	123.2(4)
C(40)-C(39)-B(1)	123.1(4)
C(41)-C(40)-C(39)	124.2(6)
C(41)-C(40)-H(40)	117.9
C(39)-C(40)-H(40)	117.9
C(42)-C(41)-C(40)	120.5(7)
C(42)-C(41)-H(41)	119.7
C(40)-C(41)-H(41)	119.7

C(41)-C(42)-C(43)	120.4(7)
C(41)-C(42)-H(42)	119.8
C(43)-C(42)-H(42)	119.8
C(42)-C(43)-C(44)	119.0(6)
C(42)-C(43)-H(43)	120.5
C(44)-C(43)-H(43)	120.5
C(39)-C(44)-C(43)	122.7(6)
C(39)-C(44)-H(44)	118.6
C(43)-C(44)-H(44)	118.6
C(50)-C(45)-C(46)	113.9(4)
C(50)-C(45)-B(1)	122.3(4)
C(46)-C(45)-B(1)	123.7(4)
C(45)-C(46)-C(47)	123.3(5)
C(45)-C(46)-H(46)	118.4
C(47)-C(46)-H(46)	118.4
C(48)-C(47)-C(46)	119.6(5)
C(48)-C(47)-H(47)	120.2
C(46)-C(47)-H(47)	120.2
C(47)-C(48)-C(49)	120.0(5)
C(47)-C(48)-H(48)	120.0
C(49)-C(48)-H(48)	120.0
C(48)-C(49)-C(50)	119.5(5)
C(48)-C(49)-H(49)	120.3

C(50)-C(49)-H(49)	120.3
C(49)-C(50)-C(45)	123.8(4)
C(49)-C(50)-H(50)	118.1
C(45)-C(50)-H(50)	118.1
C(16)-N(1)-C(9)	107.2(4)
C(16)-N(1)-C(8)	109.2(3)
C(9)-N(1)-C(8)	110.2(4)
C(16)-N(1)-Mn(1)	107.5(3)
C(9)-N(1)-Mn(1)	108.1(3)
C(8)-N(1)-Mn(1)	114.4(3)
C(4)-N(2)-C(6)	117.8(4)
C(4)-N(2)-Mn(1)	122.7(3)
C(6)-N(2)-Mn(1)	118.9(3)
C(14)-N(3)-C(10)	117.3(4)
C(14)-N(3)-Mn(1)	134.6(3)
C(10)-N(3)-Mn(1)	107.6(3)
C(17)-N(4)-C(21)	117.8(4)
C(17)-N(4)-Mn(1)	108.3(3)
C(21)-N(4)-Mn(1)	133.2(3)
O(2)-O(1)-Mn(1)	124.2(3)
O(1)-O(2)-C(23)	112.7(4)
C(27)-B(1)-C(45)	109.9(4)
C(27)-B(1)-C(39)	109.8(4)

C(45)-B(1)-C(39)	106.3(3)
C(27)-B(1)-C(33)	108.6(3)
C(45)-B(1)-C(33)	109.9(3)
C(39)-B(1)-C(33)	112.3(4)
C(3)-S(1)-Mn(1)	102.45(16)
O(1)-Mn(1)-N(2)	174.27(15)
O(1)-Mn(1)-N(1)	85.02(14)
N(2)-Mn(1)-N(1)	99.84(14)
O(1)-Mn(1)-S(1)	91.79(11)
N(2)-Mn(1)-S(1)	83.32(11)
N(1)-Mn(1)-S(1)	176.78(11)
O(1)-Mn(1)-N(4)	91.71(14)
N(2)-Mn(1)-N(4)	87.03(13)
N(1)-Mn(1)-N(4)	71.43(14)
S(1)-Mn(1)-N(4)	108.32(10)
O(1)-Mn(1)-N(3)	90.11(14)
N(2)-Mn(1)-N(3)	94.08(13)
N(1)-Mn(1)-N(3)	74.60(13)
S(1)-Mn(1)-N(3)	105.87(9)
N(4)-Mn(1)-N(3)	145.67(13)

Symmetry transformations used to generate equivalent atoms:

**Table S-22.** Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}_2}\text{N}_4(6\text{-Me-DPPN}))(\text{OOtBu})(\text{BPh}_4)\bullet\text{Et}_2\text{O}$  (**4a**). The anisotropic displacement factor exponent takes the form:  $-2p^2[h^2a^*{}^2U^{11} + \dots + 2hka^*b^*U^{12}]$

	U <sup>11</sup>	U <sup>22</sup>	U <sup>33</sup>	U <sup>23</sup>	U <sup>13</sup>	U <sup>12</sup>
C(1)	56(3)	30(3)	52(3)	-11(2)	3(3)	-13(2)
C(2)	58(3)	42(3)	58(4)	-16(3)	-24(3)	-6(3)
C(3)	44(3)	22(2)	39(3)	-10(2)	-6(2)	-6(2)
C(4)	49(3)	26(3)	26(3)	-5(2)	-8(2)	-3(2)
C(5)	82(4)	39(3)	39(3)	-13(2)	4(3)	-23(3)
C(6)	34(3)	38(3)	29(3)	-2(2)	2(2)	-3(2)
C(7)	37(3)	48(3)	42(3)	-1(2)	-2(2)	-8(2)
C(8)	25(3)	46(3)	45(3)	0(2)	-2(2)	-11(2)
C(9)	40(3)	47(3)	51(3)	-16(3)	-3(3)	-19(3)
C(10)	31(3)	31(3)	44(3)	-7(2)	2(2)	-10(2)
C(11)	44(3)	32(3)	86(4)	-2(3)	16(3)	-15(3)
C(12)	61(4)	34(3)	81(5)	21(3)	29(4)	4(3)
C(13)	47(3)	40(3)	42(3)	2(2)	4(3)	10(3)
C(14)	39(3)	31(3)	48(3)	-13(2)	-17(2)	10(2)
C(15)	67(4)	25(3)	167(7)	-18(4)	-79(5)	11(3)
C(16)	24(3)	80(4)	42(3)	-7(3)	-12(2)	-21(3)
C(17)	29(3)	69(4)	27(3)	3(3)	-1(2)	-2(3)
C(18)	31(3)	105(3)	37(3)	1(3)	-9(3)	-1(3)

C(19)	37(3)	106(3)	41(3)	7(3)	-11(3)	22(3)
C(20)	46(3)	75(3)	41(3)	7(3)	0(2)	24(2)
C(21)	41(3)	50(3)	36(3)	13(2)	-2(2)	5(2)
C(22)	56(4)	37(3)	76(4)	2(3)	-2(3)	7(3)
C(23)	46(3)	69(4)	58(4)	-23(3)	8(2)	-12(3)
C(24)	61(4)	68(4)	73(4)	-10(3)	-6(3)	2(3)
C(25)	87(5)	93(5)	84(5)	-34(4)	5(4)	-29(4)
C(26)	97(5)	64(4)	65(4)	-1(3)	6(4)	-22(4)
C(27)	23(2)	26(2)	31(3)	1(2)	-6(2)	3(2)
C(28)	26(3)	29(3)	57(3)	-12(2)	2(2)	2(2)
C(29)	42(3)	27(3)	68(4)	-17(3)	-7(3)	6(2)
C(30)	37(3)	45(3)	47(3)	-18(3)	-2(3)	18(3)
C(31)	31(3)	49(3)	40(3)	-2(2)	1(2)	4(2)
C(32)	25(2)	30(3)	32(3)	0(2)	-4(2)	4(2)
C(33)	26(2)	18(2)	28(2)	-3(2)	2(2)	-9(2)
C(34)	27(3)	35(3)	52(3)	-22(2)	-7(2)	0(2)
C(35)	27(3)	32(3)	65(4)	-22(3)	-8(2)	2(2)
C(36)	26(3)	30(3)	50(3)	1(2)	-14(2)	-5(2)
C(37)	40(3)	36(3)	41(3)	-11(2)	-10(2)	-8(2)
C(38)	29(3)	27(2)	31(3)	-7(2)	-4(2)	3(2)
C(39)	33(3)	38(3)	31(3)	-1(2)	-5(2)	-16(2)
C(40)	71(4)	91(5)	32(3)	-2(3)	11(3)	-11(4)
C(41)	113(6)	95(6)	39(4)	-3(4)	13(4)	-23(5)

C(42)	156(8)	74(5)	37(4)	-7(4)	13(5)	-67(6)
C(43)	109(6)	46(4)	68(5)	16(3)	-51(4)	-31(4)
C(44)	61(4)	47(3)	41(3)	13(3)	-20(3)	-20(3)
C(45)	20(2)	28(2)	24(2)	-5(2)	0(2)	-2(2)
C(46)	56(3)	56(3)	36(3)	6(2)	-13(3)	-32(3)
C(47)	59(4)	78(4)	41(3)	-8(3)	-10(3)	-43(3)
C(48)	38(3)	48(3)	57(4)	-15(3)	-1(3)	-22(3)
C(49)	36(3)	36(3)	58(4)	6(2)	-13(3)	-15(2)
C(50)	34(3)	34(3)	33(3)	4(2)	-12(2)	-13(2)
N(1)	24(2)	45(2)	30(2)	-4(2)	-6(2)	-10(2)
N(2)	29(2)	30(2)	29(2)	-4(2)	-3(2)	0(2)
N(3)	33(2)	27(2)	35(2)	-6(2)	-7(2)	-5(2)
N(4)	29(2)	48(3)	34(2)	1(2)	-5(2)	0(2)
O(1)	39(2)	74(2)	26(1)	-10(2)	-4(1)	-17(2)
O(2)	68(3)	61(2)	48(2)	-11(2)	21(2)	-13(2)
B(1)	23(3)	27(3)	24(3)	-2(2)	-1(2)	-5(2)
S(1)	34(1)	28(1)	35(1)	-5(1)	-2(1)	-11(1)
Mn(1)	26(1)	34(1)	29(1)	-6(1)	-3(1)	-9(1)

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**Table S-23.** Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{Mn}^{\text{III}}(\text{S}^{\text{Me}^2}\text{N}_4(6\text{-Me-DPPN}))(\text{OOtBu})(\text{BPh}_4)\bullet\text{Et}_2\text{O}$  (**4a**).

	x	y	z	U(eq)
H(1A)	5791	-189	2348	68
H(1B)	5077	-73	3256	68
H(1C)	6787	-296	3097	68
H(2A)	4539	2284	1985	76
H(2B)	3701	1477	2504	76
H(2C)	4600	1325	1647	76
H(5A)	7537	1451	813	77
H(5B)	6849	549	1278	77
H(5C)	8515	539	1337	77
H(6A)	8870	2248	1082	43
H(6B)	9982	1722	1769	43
H(7A)	10098	3373	1187	52
H(7B)	8583	3656	1676	52
H(8A)	11031	2635	2519	48
H(8B)	10669	3774	2321	48
H(9A)	9454	4571	3198	53
H(9B)	8365	4169	3932	53

H(11)	8018	5933	2420	67
H(12)	5972	6634	1715	82
H(13)	4245	5722	1703	57
H(15A)	4458	3283	2780	125
H(15B)	4047	3835	1863	125
H(15C)	3265	4239	2661	125
H(16A)	9731	2875	4472	56
H(16B)	11113	3079	3868	56
H(18)	12709	1626	4503	73
H(19)	13300	-49	4712	83
H(20)	11811	-895	4266	75
H(22A)	8337	28	3688	91
H(22B)	9558	-915	3778	91
H(22C)	9489	-141	2925	91
H(24A)	4871	3926	4355	104
H(24B)	3549	3968	5044	104
H(24C)	3899	3122	4531	104
H(25A)	6765	3146	6168	127
H(25B)	5358	3966	6110	127
H(25C)	6543	3955	5342	127
H(26A)	4313	1823	5908	115
H(26B)	3791	2695	6386	115
H(26C)	5321	2016	6546	115

H(28)	9666	4435	-1249	46
H(29)	8297	5416	-394	56
H(30)	6309	4948	409	55
H(31)	5699	3502	338	51
H(32)	7085	2515	-493	37
H(34)	12154	1310	-1779	44
H(35)	14343	864	-1233	48
H(36)	14860	1515	-146	43
H(37)	13063	2634	379	45
H(38)	10877	3114	-203	36
H(40)	11518	2272	-2891	82
H(41)	11477	2866	-4292	102
H(42)	9920	4207	-4792	101
H(43)	8175	4897	-3911	87
H(44)	8107	4243	-2463	61
H(46)	8108	2076	-2616	57
H(47)	7029	769	-2554	66
H(48)	7166	-431	-1383	54
H(49)	8410	-344	-278	52
H(50)	9530	938	-356	40

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