Supporting Information

An end-on bis(*μ*-hydroxido) dimanganese(II,III) azide complex for C–H bond and O–H bond activation reactions

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Experimental Section

Materials and Instrumentation. Commercially available chemicals were used without further purification unless otherwise indicated. Solvents were dried according to published procedures and distilled under Ar prior to use.[S1] Doubly labeled cumyl^{18}O^{18}OH (90 % ^{18}O-enriched) was synthesized by reacting cumene and $^{18}O_2$ in hexane at 85 ^{o}C according to the procedure of Finn and Sharpless.[S2] The nonheme manganese(II) complex was prepared according to the literature methods.[S3] UV-vis spectra were recorded on a Hewlett Packard Agilent Cary 8454 UV-visible spectrophotometer equipped with a T2/sport temperature controlled cuvette holder. Electrospray ionization mass spectra (ESI MS) were collected on a Thermo Finnigan (San Jose, CA, USA) LTQ^{TM} XL ion trap instrument, by infusing samples directly into the source at 5.0 μL/min using a syringe pump. The spray voltage was set at 4.7 kV and the capillary temperature at 200 ^{o}C. X-band EPR spectra were recorded at 4 K and 80 K using an X-band Bruker EMX-plus spectrometer equipped with a dual mode cavity (ER 4116DM) and a JEOL X band spectrometer (JESFA100). Low temperatures were achieved and controlled with an Oxford Instruments ESR900 liquid He quartz cryostat with an Oxford Instruments ITC503 temperature and gas flow controller. The experimental parameters for electron paramagnetic resonance (EPR) spectra were as follows: Microwave frequency = 9.647 GHz, microwave power = 1.0 mW, modulation amplitude = 10 G, gain = 1×10^4, modulation frequency = 100 kHz, time constant = 40.96 ms and conversion time = 81.00 ms. Resonance Raman (rRaman) spectral data were collected with the UniDRON (UniNanoTech, Korea) Microscope Raman chamber with 20x long working objective lens and SR500i-A Raman spectrometer in combination with the DU420A-BU2 (ANDOR, UK) TE cooled CCD detector, cooled to –45 ℃. The LD laser (532 nm Diode laser set, CNI laser, China) beam at the wavelength of 532 nm was used as the light source. The laser beam was focused using an objective lens with a magnifying power of 10. The frozen sample solution in NMR tube was put into a QUARTZ Large 150 mL Dewar Flasks (inner diameter 5.4 mm, outer diameter 10.5 mm, CortecNet, France), was filled by liquid N_2, and the data acquisition time was normally 10 s and the data was accumulated for 12 times. The wavenumber of the Raman spectra measured in this work was calibrated by using well-known Raman peaks of a cyclohexane (C_6H_{12}) solution. ^{1}H NMR spectra were measured with Bruker AVANCE III 400

MHz spectrometer. ATR-IR spectra were recorded by using an Thermo Fisher Scientific Nicolet IS50. Product analysis was performed with Agilent Technologies 6890N gas chromatograph (GC) and HPLC.

Synthesis and Characterization of Mononuclear Manganese(II), Dinuclear Manganese(II,II) and Manganese(II,III) Complexes. The mononuclear manganese(II) complex bearing HN3O2 ligand, $[Mn^{II}(HN3O2)(ClO_4)](ClO_4)$, was prepared by reacting HN3O2 ligand and equimolar of $Mn(ClO_4)_2{\cdot}xH_2O$ in ethanol. The dimanganse(II) complex, $[\{Mn^{II}(N_3)(\mu\text{-}N_3)_2Mn^{II}(N_3)\}(HN3O2)_2]$ (**1**), was obtained by reacting $[Mn^{II}(HN3O2)(ClO_4)](ClO_4)$ with 5.0 equiv of sodium azide in CH_3CN at 20 ℃. The dimanganse(II,III) complex, $[\{Mn^{II}(N_3)(\mu\text{-}OH)_2Mn^{III}(N_3)\}(HN3O2)_2]^+$ (**2**), was synthesized by treating the solution of **1** with 4.0 equiv of peracetic acid in CH_3CN at 20 ^oC. ^{18}O labeling experiments were performed by using cumyl$^{18}O^{18}OH$.

X-Ray Structural Analysis. Single crystals of mononuclear and dinuclear manganese(II) complexes $[Mn^{II}(HN3O2)(ClO_4)](ClO_4)$ and **1** suitable for X-ray crystallographic analysis were obtained by slow diffusion of Et_2O into a EtOH solution of $[Mn^{II}(HN3O2)(ClO_4)](ClO_4)$ and a CH_3CN solution of **1**, respectively. These crystals were taken from the solutions by a nylon loop (Hampton Research Co.) on a hand made copper plate and mounted on a goniometer head in a N_2 cryostream. The diffraction data for $[Mn^{II}(HN3O2)(ClO_4)](ClO_4)$ and **1** were collected at 120 K on a Bruker SMART AXS diffractometer equipped with a monochromator in the Mo *K*α (λ = 0.71073 Å) incident beam. Cell parameters were determined and refined by the SMART program.[S4] The CCD data were integrated and scaled using the Bruker-SAINT software package.[S5] An empirical absorption correction was applied using the SADABS program.[S6] The structures were solved by direct methods, and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 by using SHELXTL Ver. 6.14.[S7] Unless otherwise noted, hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. The O–H hydrogen atoms were located in difference density maps and freely refined. The crystallographic data and selected bond distances and angles are listed in Tables S1 and S2, respectively. Full

crystallographic details can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (CCDC 1979545 − 1979546).

Reactivity Studies. Kinetic measurements were performed on a Hewlett Packard 8453 photodiode-array spectrophotometer for the C−H bond and O−H bond activation reactions by **2** in CH_3CN at 20 ℃. Reactions were run in a 1.0 cm UV cuvette, monitoring UV-vis spectral changes of reaction solutions. Rate constants were determined under pseudo-first-order conditions (e.g., [substrate]/[**2**] > 10) by fitting the absorbance changes at 430 nm due to **2**. For the C−H bond and O−H bond activation reactions by **2**, the time dependence of the absorbance at 430 nm due to the decay of **2** was fitted with single exponential function to give k_{obs} (s^{-1}) under the pseudo-first-order conditions in CH_3CN at 20 ℃.
The kinetic experiments were run at least in triplicate, and the data reported represent the average of these reactions.

ATR-IR measurements. Solid IR signals for samples were recorded on an IR instrument (Remspec #: 626). Solid IR data of both **1** (12 mM) and **2** (12 mM) were obtained by isolating **1** and **2** under N_2 atmosphere, respectively.

Spin state measurements. The effective magnetic moment (μ_{eff}, BM) of the manganese dimer **1** and **2** were determined using the modified ^{1}H NMR method of Evans at room temperature.[S8,S9] A WILMAD® coaxial insert (sealed capillary) tube containing the blank acetonitrile-d_3 solvent only (with 1.0% tetramethylsilane (TMS)) was inserted into the normal NMR tube containing **1** and **2** (2.0 mM) dissolved in acetonitrile-d_3 (with 0.10% TMS). The chemical shift of the TMS peak (and/or solvent peak) in the presence of the paramagnetic metal complexes was compared to that of the TMS peak (and/or solvent peak) in the inner coaxial insert tube. The effective magnetic moment was calculated using the following equation:

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

where f is the oscillator frequency (MHz) of the superconducting spectrometer, T is the absolute temperature, M is the molar concentration of the metal ion, and $\Delta\nu$ is the difference in frequency (Hz) between the two reference signals. [S8,S9]

DFT Calculations.

Density functional theory (DFT) calculations[S10] were performed using Gaussian 16 suite of program[S11] with the hybrid functional B3LYP.[S12] The geometry optimizations were done at the B3LYP/Def2-SVP level of theory.[S12,S13] Frequency calculations on the optimized geometries were performed to confirm the nature of the stationary points and were carried out at the same level of theory as used for the geometry optimization. Single-point energy evaluations were also done using a triple-ζ basis set i.e. Def2-TZVPP.[S13] The conductor-like polarizable continuum model (CPCM)[S14] with UFF cavity, per G16 default, was used to include the solvent (acetonitrile) effects in all the calculations. However, in doing so, other problems will arise. Thermal contributions then becomes inaccurate, because the standard solvent models are parameterized to give good solvation free energies and not any other properties. This suggests that thermal effects are already included to a certain extent in the obtained electronic energies, therefore possibly double counting the thermal contributions.[S15] Dispersion corrections were evaluated at the converged geometries by use of the DFT-D3 program using the Becke-Johnson damping.[S16] The same problem of double-counting as in considering thermal effects also exists in the dispersion correction. On the other hand, the gas-phase frequency calculations on the optimized structure in solvation may not be meaningful since the structure may be not in a stationary point in the gas-phase. This leaves us in principle with no easily available options to calculate in a uniform manner the free energies and avoid the artificial errors of the DFT method at the same time, especially for highly charged systems (where self-interaction errors may be present), unless one is prepared to enlarge the model system with including counter ions.[S17] Adding counter ions into the model system however should be more time consuming and sometimes leading to its "reactions" with the transition metal complex, which may or may not be realistic. Therefore, the free energy barrier is not deemed to be reliable due to possible double counting of effects. Here, we mainly focus on the electronic energies without any corrections except for the solvent correction, which is included by default in all calculations. The energies cited in the text are electronic energies, which in our consistent and repetitive experiences gives the best agreement with experiments. But we also calculated the free energy barriers ΔG including the following terms: the electronic energy ($\Delta E_{(\mathrm{Def2TZVPP})}$), zero-point vibrational energy (ΔZ_0), enthalpy ($\Delta E_{\mathrm{thermal}}$), entropy ($-T\Delta S$) and dispersion effect (ΔDisp).

Table S1. Crystallographic Data and Refinements for [Mn(HN3O2)(ClO_4)](ClO_4), and **1**.

	[Mn(HN3O2)(ClO_4)](ClO_4)	**1**
Empirical formula	$C_{16}H_{21}N_3O_{10}C_{l2}Mn$	$C_{32}H_{42}N_{18}O_4Mn_2$
Formula weight	541.2	852.71
Temperature (K)	120(2)	120(2)
Wavelength (Å)	0.71073	0.71073
Crystal system/space group	triclinic, *P-1*	monoclinic, $P2_1/c$
Unit cell dimensions		
a (Å)	8.906(2)	10.8912(11)
b (Å)	9.306(3)	10.4204(11)
c (Å)	14.498(4)	16.9841(17)
α (°)	89.499(3)	90
$b\beta$ (°)	76.650(3)	99.8018(13)
γ (°)	65.347(3)	90
Volume ($Å^3$)	1057.4(5)	1899.4(3)
Z	2	2
Calculated density (g/cm^{-3})	1.700	1.491
Absorption coefficient (mm^{-1})	0.938	0.728
Reflections collected	9741	23415
Independent reflections	3754	3343
Goodness-of-fit on F^2	1.059	1.064
R [$F^2 > 2\text{sigma}(F^2)$]	0.0627	0.0435
wR^2	0.1900	0.1162

Table S2. Selected Bond Distances (Å) and Angles (°) for [Mn(HN3O2)(ClO_4)](ClO_4) and **1**.

	[Mn(HN3O2)(ClO_4)](ClO_4)	**1**
Bond Distances (Å)		
Mn1-N1	2.328(3)	2.387(2)
Mn1-N2	2.224(3)	2.281(3)
Mn1-N3	2.217(3)	2.243(3)
Mn1-O1	2.164(3)	-
Mn1-O2	2.270(3)	-
Mn1-O3	2.272(3)	-
Mn1-N4	-	2.154(3)
Mn1-N7	-	2.204(3)
Mn1-Mn2	-	3.528(7)
Bond Angles (°)		
O1-Mn1-N3	113.21(13)	-
O1-Mn1-N2	98.19(13)	-
N3- Mn1-N2	147.79(13)	108.41(9)
O1- Mn1-O2	71.76(11)	-
O1-Mn1-O3	78.21(11)	-
N4-Mn1-N7	-	107.67(11)
Mn1-N7-Mn2	-	104.583(10)
N7-Mn1-N3	-	157.56(10)
N4-Mn1-N2	-	93.43(10)
N7-Mn1-N2	-	86.99(9)
N3-Mn1-N2	-	108.41(9)
N4-Mn1-N1	-	152.35(10)
N7-Mn1-N1	-	95.37(10)
N3-Mn1-N1	-	74.87(9)

Table S3. Mulliken spin density distribution of $[Mn_2(BPA)_2(\mu\text{-}OH)_2(N_3)_2]^+$ (**2a**) and $[Mn_2(BPA)_2(\mu\text{-}N_3)_2(OH)_2]^+$ (**2b**) calculated at the B3LYP/Def2-TZVPP//Def2-SVP level.

Compound	Mn^{II}	Mn^{III}	OH(1)	OH(2)	N_3(1)	N_3(2)	Rest
^{2}**2a**	4.84	-3.87	0.02	0.00	0.06	-0.10	0.05
^{10}**2a**	4.82	3.95	-0.01	0.02	0.06	0.09	0.06
^{2}**2b**	4.79	-3.91	0.08	-0.00	-0.03	0.00	0.07
^{10}**2b**	4.81	3.94	0.08	0.00	0.09	0.03	0.05

Table S4. Relative energies (in kcal mol^{-1}) of $[Mn_2(BPA)_2(\mu\text{-}OH)_2(N_3)_2]^+$ (**2a**) and $[Mn_2(BPA)_2(\mu\text{-}N_3)_2(OH)_2]^+$ (**2b**) calculated at the B3LYP/Def2-TZVPP//Def2-SVP level.

Compound[a]	$\Delta E_{(Def2SVP)}$	ΔΔBS	$\Delta E_{(Def2TZVPP)}$[b]	ΔZ_0	$\Delta E_{thermal}$[c]	$-T\Delta S$[c]	ΔDisp	ΔG[d]
^{2}**2a**	0.63	-0.08	**0.55**	+0.07	-0.03	+1.23	-0.18	**1.65**
^{10}**2a**	0.00	+0.00	**0.00**	+0.00	+0.00	+0.00	+0.00	**0.00**
^{2}**2b**	14.98	-0.97	**14.01**	-0.12	-0.17	+2.66	-4.38	**12.00**
^{10}**2b**	14.66	-0.90	**13.76**	-0.17	-0.16	+1.67	-4.39	**10.71**

[a] The superscript indicate multiplicity (= 2*S*+1). [b] Sum of the two previous columns. [c] *T* = 298.15 K. [d] Sum of the five previous columns.

Table S5. Relative energies (in kcal mol^{-1}) of $[Mn_2(HN3O2)_2(\mu\text{-}OH)_2(N_3)_2]^+$ (**2a**) and $[Mn_2(HN3O2)_2(\mu\text{-}N_3)_2(OH)_2]^+$ (**2b**) calculated at the B3LYP/Def2-TZVPP//Def2-SVP level.

Compound[a]	$\Delta E_{(Def2SVP)}$	ΔΔBS	$\Delta E_{(Def2TZVPP)}$[b]	ΔZ_0	$\Delta E_{thermal}$[c]	$-T\Delta S$[c]	ΔDisp	ΔG[d]
^{2}**2a**	0.95	-0.16	**0.79**	+0.03	-0.02	+0.95	-0.22	**1.54**
^{10}**2a**	0.00	+0.00	**0.00**	+0.00	+0.00	+0.00	+0.00	**0.00**
^{2}**2b**	14.28	-2.49	**11.80**	-1.13	+0.35	-0.30	-2.09	**8.63**
^{10}**2b**	13.95	-2.38	**11.57**	-1.10	+0.31	+0.38	-2.15	**9.01**

[a] The superscript indicate multiplicity (= 2*S*+1). [b] Sum of the two previous columns. [c] *T* = 298.15 K. [d] Sum of the five previous columns.

Table S6. Relative energies (in kcal mol^{-1}) of $^{5}[Mn^{III}(HN3O2)(OH)(N_3)]^{+}$ C-H activation reaction of 1,4-cyclohexadiene calculated at the B3LYP/Def2-TZVPP//Def2-SVP level.

Compound	$\Delta E_{(Def2SVP)}$	ΔΔBS	$\boldsymbol{\Delta E_{(Def2TZVPP)}}^{a}$	ΔZ_0	$\Delta E_{thermal}{}^{b}$	$-T\Delta S^{b}$	ΔDisp	$\boldsymbol{\Delta G}^{c}$
RC	0.00	+0.00	**0.00**	+0.00	+0.00	+0.00	+0.00	**0.00**
TS	11.13	+11.12	**22.25**	-4.06	+-0.21	+2.23	-1.12	**19.08**
PC	-1.39	+1.89	**0.51**	-1.80	+0.73	-1.07	+1.47	**-0.16**

[a] Sum of the two previous columns. [b] T = 298.15 K. [c] Sum of the five previous columns.

Table S7. Relative energies (in kcal mol^{-1}) of $^{10}[Mn_2(HN3O2)_2(\mu\text{-}OH)_2(N_3)_2]^+$ (**2a**) in C-H activation reaction of 1,4-cyclohexadiene, performed by OH bound to the both Mn, calculated at the B3LYP/Def2-TZVPP//Def2-SVP level.

Compound	$\Delta E_{(Def2SVP)}$	ΔΔBS	$\boldsymbol{\Delta E_{(Def2TZVPP)}}^a$	ΔZ_0	$\Delta E_{thermal}{}^b$	$-T\Delta S^b$	ΔDisp	$\boldsymbol{\Delta G}^c$
RC	0.00	+0.00	**0.00**	+0.00	+0.00	+0.00	+0.00	**0.00**
TS	7.65	+20.95	**28.61**	-4.00	-0.16	+1.57	+0.69	**26.71**

[a] Sum of the two previous columns. [b] T = 298.15 K. [c] Sum of the five previous columns.

Table S8. Relative energies (in kcal mol^{-1}) of $[Mn_2(HN3O2)_2(\mu\text{-}OH)_2(N_3)_2]^+$ (**2a**) in C-H activation reaction of 1,4-cyclohexadiene in a two-step mechanism, calculated at the B3LYP/Def2-TZVPP//Def2-SVP level.

Compound	$\Delta E_{(Def2SVP)}$	ΔΔBS	$\Delta E_{(Def2TZVPP)}$[a]	ΔZ_0	$\Delta E_{thermal}$[b]	$-T\Delta S$[b]	ΔDisp	ΔG[c]
^{2}**2a**	0.43	-0.03	**0.40**	-0.09	+0.04	+0.16	-0.08	**0.43**
^{2}**TS1**	1.83	-1.36	**0.47**	+0.28	-0.66	+2.80	+1.34	**4.23**
^{2}**IM1**	-0.50	-1.41	**-1.91**	+0.24	-0.05	+1.04	+2.77	**2.09**
^{2}**TS2**	16.10	+2.65	**18.75**	-3.85	-0.31	+4.33	+1.04	**19.96**
^{2}**IM2**	-9.84	+2.56	**-7.28**	-2.26	+0.80	+0.12	+4.17	**-4.45**
^{10}**2a**	0.00	+0.00	**0.00**	+0.00	+0.00	+0.00	+0.00	**0.00**
^{10}**TS1**	1.86	-1.42	**0.44**	+0.24	-0.62	+1.64	+1.53	**3.22**
^{10}**IM1**	-0.32	-1.35	**-1.67**	+0.39	-0.22	+2.30	+2.84	**3.65**
^{10}**TS2**	16.47	+2.66	**19.13**	-3.87	-0.30	+3.39	+1.23	**19.58**
^{10}**IM2**	-9.45	+2.50	**-6.95**	-2.05	+0.68	+0.47	+4.37	**-3.48**

[a] Sum of the two previous columns. [b] T = 298.15 K. [c] Sum of the five previous columns.

Table S9. Mulliken spin density distribution of $[Mn_2(HN3O2)_2(\mu\text{-}OH)_2(N_3)_2]^+$ (**2a**) and $[Mn_2(HN3O2)_2(\mu\text{-}N_3)_2(OH)_2]^+$ (**2b**) calculated at the B3LYP/Def2-TZVPP//Def2-SVP level.

Compound	Mn^{II}	Mn^{III}	OH(1)	OH(2)	N_3(1)	N_3(2)	Rest
^{2}**2a**	4.83	-3.89	-0.01	0.04	0.06	-0.03	0.01
^{10}**2a**	4.81	4.02	0.02	-0.03	0.06	0.03	0.09
^{2}**2b**	4.79	-3.92	0.08	0.00	-0.03	0.01	0.07
^{10}**2b**	4.81	3.95	0.08	-0.00	0.09	0.02	0.05

Table S10. Mulliken spin density distribution of $^{5}[Mn^{III}(HN3O2)(OH)(N_3)]^{+}$ C-H activation reaction of 1,4-cyclohexadiene calculated at the B3LYP/Def2-TZVPP//Def2-SVP level.

Compound	Mn^{III}	OH	N_3	Substrate	Rest
RC	3.95	0.01	0.02	0.00	0.02
TS	4.58	0.01	-0.16	-0.48	0.05
PC	4.86	0.05	-0.00	-0.98	0.08

Table S11. Mulliken spin density distribution of $^{10}[Mn_2(HN3O2)_2(\mu\text{-}OH)_2(N_3)_2]^+$ (**2a**) in C-H activation reaction of 1,4-cyclohexadiene performed by OH bound to the both Mn, calculated at the B3LYP/Def2-TZVPP//Def2-SVP level.

Compound	Mn^{II}	Mn^{III}	OH(1)	OH(2)	N_3(1)	N_3(2)	Substrate	Rest
RC	4.83	3.99	-0.01	0.03	0.06	-0.03	0.00	0.12
TS	4.84	4.59	0.04	-0.17	0.06	-0.03	-0.44	0.11

Table S12. Mulliken spin density distribution of $[Mn_2(HN3O2)_2(\mu\text{-}OH)_2(N_3)_2]^+$ (**2a**) in C-H activation reaction of 1,4-cyclohexadiene in a two-step mechanism, calculated at the B3LYP/Def2-TZVPP//Def2-SVP level.

Compound	Mn^{II}	Mn^{III}	OH(1)	OH(2)	N_3(1)	N_3(2)	Substrate	Rest
^{2}**2a**	4.84	-3.87	0.00	0.01	0.05	-0.09	----	0.06
^{2}**TS1**	4.82	-3.85	-0.01	0.01	0.05	-0.08	----	0.06
^{2}**IM1**	4.84	-3.85	-0.02	0.00	0.05	-0.07	0.00	0.06
^{2}**TS2**	4.83	-4.49	0.20	0.01	0.05	-0.05	0.41	0.03
^{2}**IM2**	4.83	-4.83	0.00	0.01	0.05	-0.05	0.99	0.00
^{10}**2a**	4.84	3.95	0.00	0.01	0.05	0.09	----	0.05
^{10}**TS1**	4.85	3.91	0.02	0.03	0.05	0.08	----	0.05
^{10}**IM1**	4.85	3.90	0.03	0.03	0.05	0.07	0.00	0.06
^{10}**TS2**	4.85	4.53	-0.19	0.04	0.05	0.05	-0.41	0.09
^{10}**IM2**	4.85	4.86	0.00	0.06	0.05	0.05	-0.99	0.11

Table S13. Selected geometries of $[Mn_2(BPA)_2(\mu\text{-}OH)_2(N_3)_2]^+$ (**2a**) and $[Mn_2(BPA)_2(\mu\text{-}N_3)_2(OH)_2]^+$ (**2b**) calculated at the B3LYP/Def2-TZVPP//Def2-SVP level.

Compound	Mn^{II}-Mn^{III}	Mn^{II}-[μ-X(1)]	Mn^{II}-[μ-X(2)]	Mn^{III}-[μ-X(1)]	Mn^{III}-[μ-X(2)]	$\angle$ Mn^{II}-[μ-X(1)]-Mn^{III}	$\angle$ Mn^{II}-[μ-X(2)]-Mn^{III}
^{2}**2a**	3.22	2.25	2.16	1.88	1.91	102.41	104.77
^{10}**2a**	3.25	2.21	2.16	1.89	1.91	104.50	105.76
^{2}**2b**	3.53	2.24	2.45	2.26	2.04	103.56	103.18
^{10}**2b**	3.52	2.24	2.43	2.25	2.05	103.53	103.26

Table S14. Selected geometries of $[Mn_2(HN3O2)_2(\mu\text{-}OH)_2(N_3)_2]^+$ (**2a**) and $[Mn_2(HN3O2)_2(\mu\text{-}N_3)_2(OH)_2]^+$ (**2b**) calculated at the B3LYP/Def2-SVP level.

Compound	Mn^{II}-Mn^{III}	Mn^{II}-[μ-X(1)]	Mn^{II}-[μ-X(2)]	Mn^{III}-[μ-X(1)]	Mn^{III}-[μ-X(2)]	$\angle$ Mn^{II}-[μ-X(1)]-Mn^{III}	$\angle$ Mn^{II}-[μ-X(2)]-Mn^{III}
^{2}**2a**	3.26	2.16	2.22	1.94	1.88	105.06	104.93
^{10}**2a**	3.27	2.15	2.18	1.96	1.90	105.56	106.46
^{2}**2b**	3.55	2.23	2.44	2.26	2.04	104.64	104.28
^{10}**2b**	3.55	2.23	2.43	2.25	2.05	104.68	104.32

Table S15. Selected geometries of $^{5}[Mn^{III}(HN3O2)(OH)(N_3)]^{+}$ C-H activation reaction of 1,4-cyclohexadiene calculated at the B3LYP/Def2-SVP level.

Compound	Mn^{III}-O	O-H(Subs)	H-C(subs)	∠ Mn^{III}-O-H(Subs)
RC	1.83	2.56	1.11	136.19
TS	2.01	1.33	1.29	155.30
PC	2.26	0.97	2.28	142.45

Table S16. Selected geometries of $^{10}[Mn_2(HN3O2)_2(\mu\text{-}OH)_2(N_3)_2]^+$ (**2a**) in C-H activation reaction of 1,4-cyclohexadiene performed by OH bound to the both Mn, calculated at the B3LYP/Def2-SVP level.

Compound	Mn^{II}-Mn^{III}	Mn^{II}-[μ-OH(1)]	Mn^{II}-[μ-OH(2)]	Mn^{III}-[μ-OH(1)]	Mn^{III}-[μ-OH(2)]	OH(1)-H(Subs)	H-C(subs)
RC	3.26	2.23	2.16	1.89	1.95	3.18	1.11
TS	3.75	2.06	3.35	2.03	2.06	1.33	1.30

Table S17. Selected geometries of $[Mn_2(HN3O2)_2(\mu\text{-}OH)_2(N_3)_2]^+$ (**2a**) in C-H activation reaction of 1,4-cyclohexadiene in a two-step mechanism, calculated at the B3LYP/Def2-SVP level.

Compound	Mn^{II}-Mn^{III}	Mn^{II}-OH(1)	Mn^{II}-[μ-O(2)]	Mn^{III}-OH(1)	Mn^{III}-[μ-O(2)]	OH(1)-H(Subs)	H-C(subs)
^{2}**2a**	3.22	2.29	2.17	1.87	1.90	----	----
^{2}**TS1**	3.47	2.93	2.09	1.81	1.94	----	----
^{2}**IM1**	3.87	3.87	2.10	1.79	1.99	2.50	1.11
^{2}**TS2**	3.92	3.96	2.07	1.97	2.07	1.34	1.28
^{2}**IM2**	3.91	3.84	2.05	2.21	2.11	0.97	2.45
^{10}**2a**	3.24	2.27	2.17	1.88	1.91	----	----
^{10}**TS1**	3.50	2.96	2.10	1.81	1.95	----	----
^{10}**IM1**	3.86	3.85	2.11	1.79	1.99	2.52	1.11
^{10}**TS2**	3.94	3.98	2.08	1.97	2.07	1.34	1.28
^{10}**IM2**	3.96	3.90	2.05	2.21	2.12	0.97	2.45

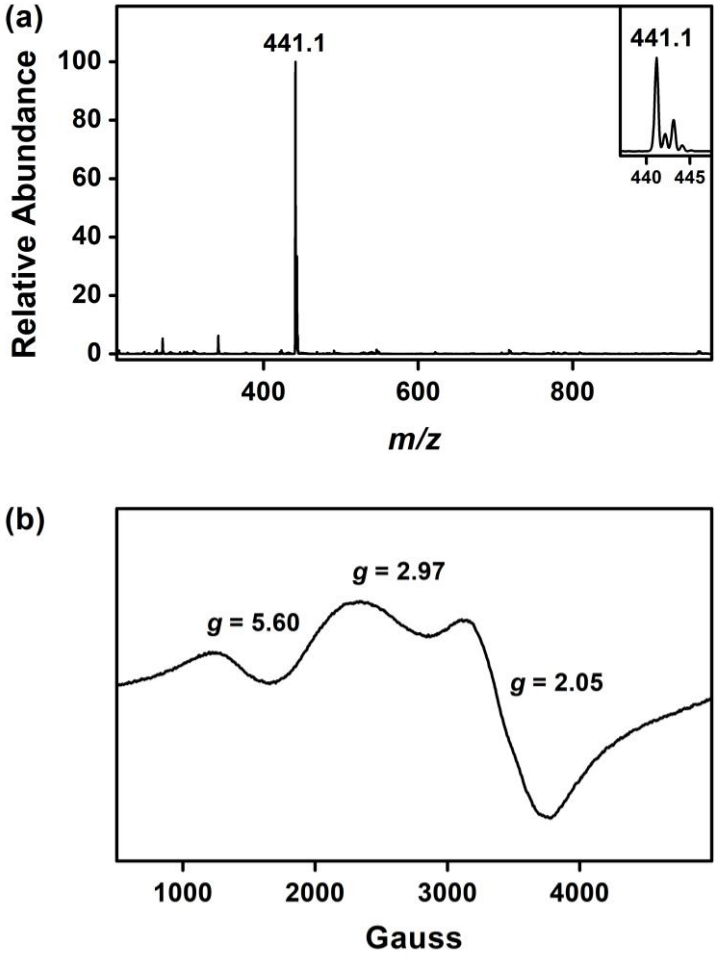

Figure S1. (a) ESI-MS spectrum of [Mn(HN3O2)(ClO_4)](ClO_4) in CH_3CN at 20 ^oC. A prominent peak at *m/z* of 441.1 corresponds to mass and isotope distribution pattern of [Mn(HN3O2)(ClO_4)]$^+$ (calculated *m/z* of 441.1). Inset shows the observed isotope distribution pattern for [Mn(HN3O2)(ClO_4)](ClO_4) at *m/z* of 441.1. (b) X-band EPR spectrum of a frozen CH_3CN-solution of [Mn(HN3O2)(ClO_4)](ClO_4) recorded at 4 K.

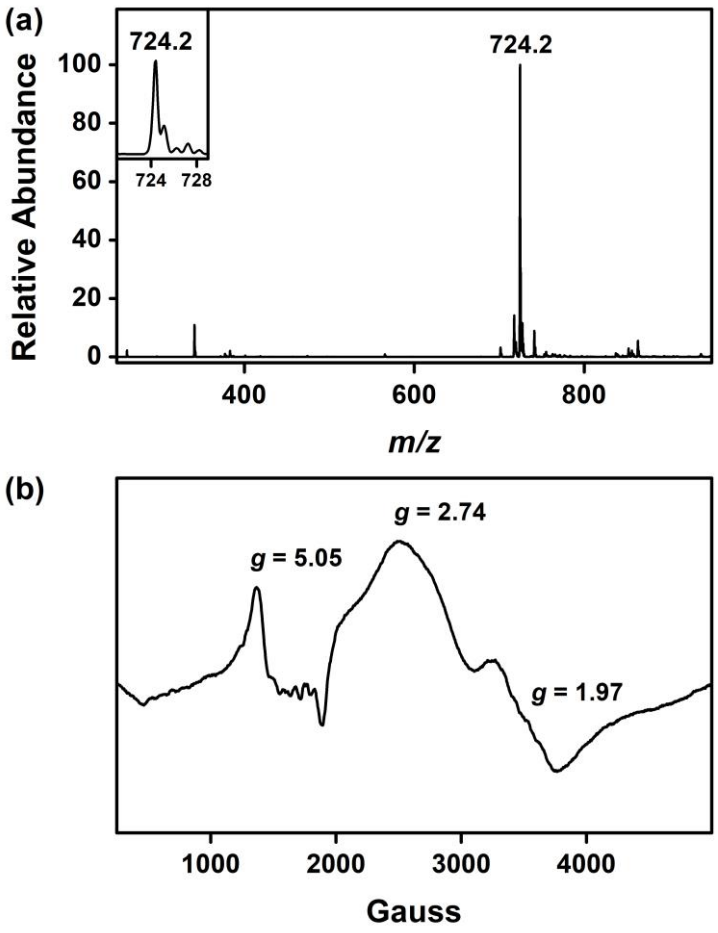

Figure S2. (a) ESI-MS spectrum of **1** in CH_3CN at 20 ^oC. A prominent peak at *m/z* of 724.2 corresponds to mass and isotope distribution pattern of $[Mn_2(N3O2)_2(N_3)]^+$ (calculated *m/z* of 724.2). Inset shows the observed isotope distribution pattern for **1** at *m/z* of 724.2. (b) X-band EPR spectra of a frozen CH_3CN-solution of **1** recorded at 4 K.

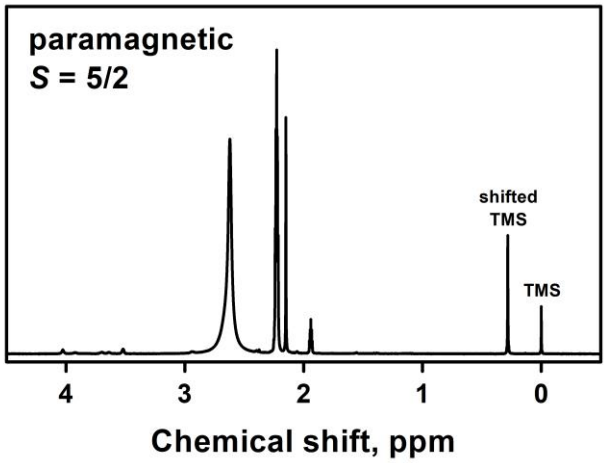

Figure S3. Paramagnetic ^{1}H NMR spectrum of **1** in CD_3CN at 20 ^{o}C.

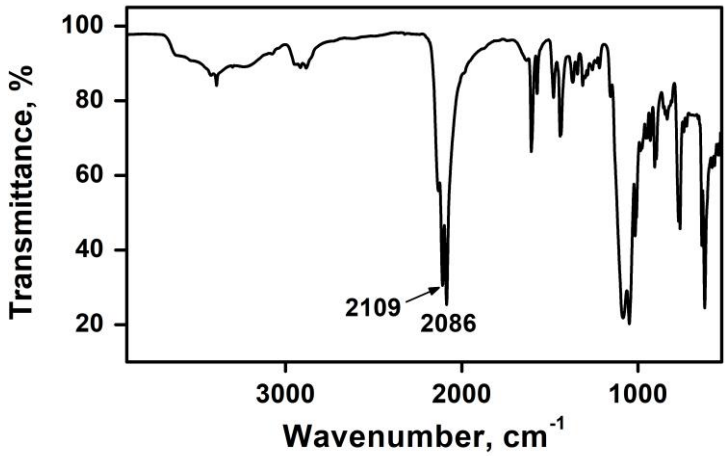

Figure S4. ATR-IR spectra of the isolated **1** collected from the reaction between [Mn(HN3O2)(ClO_4)](ClO_4) (12 mM) and 2.2 equiv of NaN_3 in CH_3CN at 20 ^oC. The spectrum was recorded from **1** deposited on the ATR crystal.

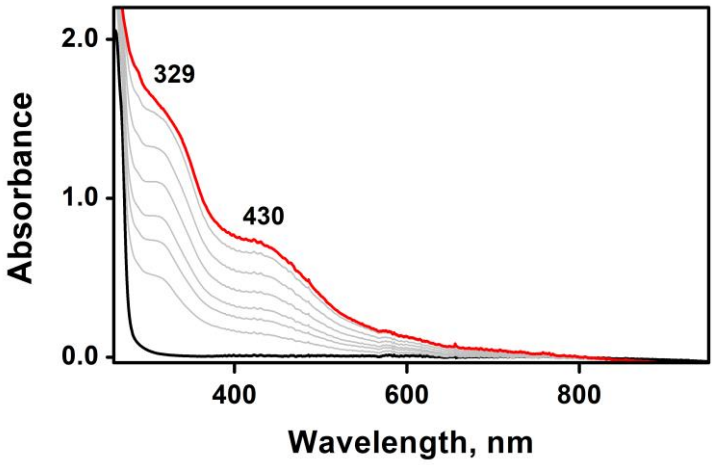

Figure S5. UV-vis spectral change observed in the reaction of **1** (0.25 mM) and cumylhydroperoxide (0.40 mM) in CH_3CN at 20 ^oC.

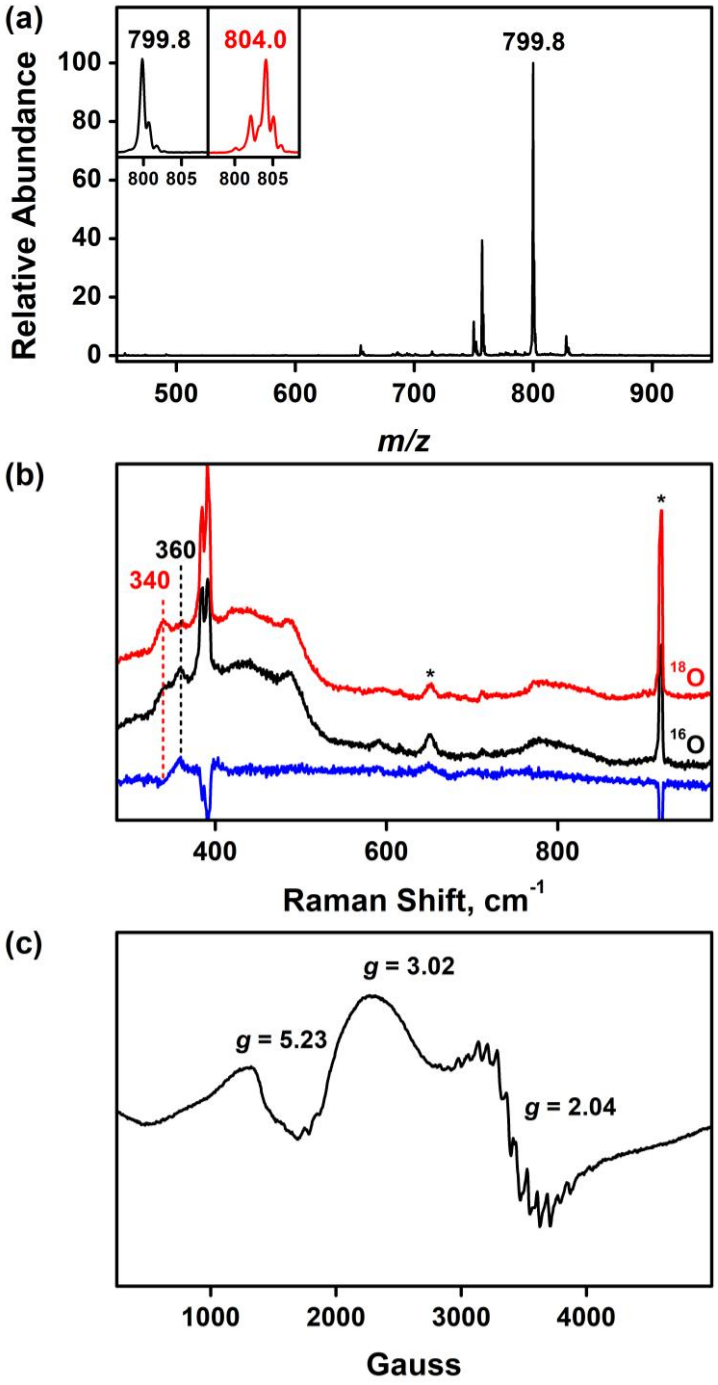

Figure S6. (a) ESI-MS spectrum of **2** obtained in CH_3CN at 20 °C. A prominent peak at *m/z* of 799.8 corresponds to $[Mn_2(HN3O2)(N3O2)(OH)_2(N_3)(CH_3CN)]^+$ (calculated *m/z* of 800.2). Insets show the observed isotope distribution pattern for **2**-^{16}O (left panel) and **2**-^{18}O (right panel). (b) rRaman spectrum of **2**-^{16}O (16 mM, black line) and **2**-^{18}O (16 mM, red line) in CH_3CN at -40 °C upon 532 nm-excitation. The isotopically sensitive band at 360 cm^{-1} correspond to Mn-OH bond stretching frequency. * indicates solvent peaks. (c) X-band EPR spectra of a frozen CH_3CN-solution of **2** recorded at 4 K.

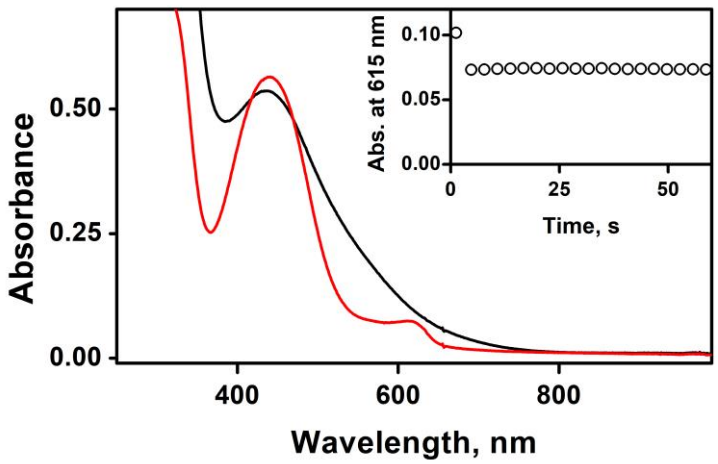

Figure S7. UV-vis spectral change observed in the reaction between **2** (0.25 mM) and ferrocene (5.0 mM) in CH_3CN at 20 ^oC. The appearance of absorption band at 615 nm due to the formation of 1.0 equiv of ferrocenium ion was observed.

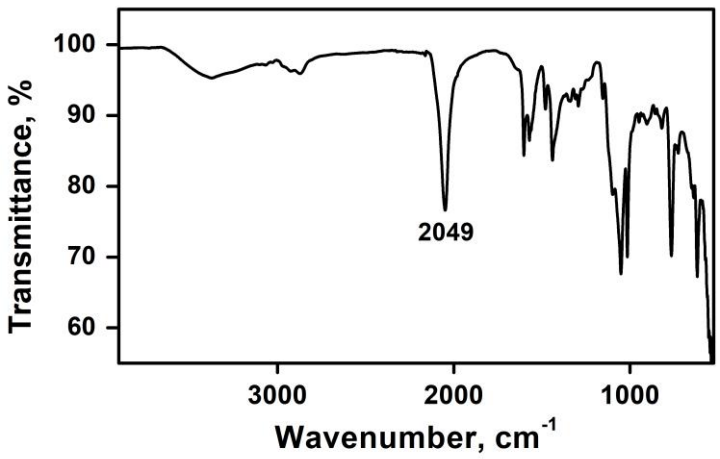

Figure S8. ATR-IR spectra of the isolated **2** collected from the reaction between **1** (12 mM) and 4.0 equiv of peracetic acid in CH_3CN at 20 ^oC. The spectrum was recorded from **2** deposited on the ATR crystal.

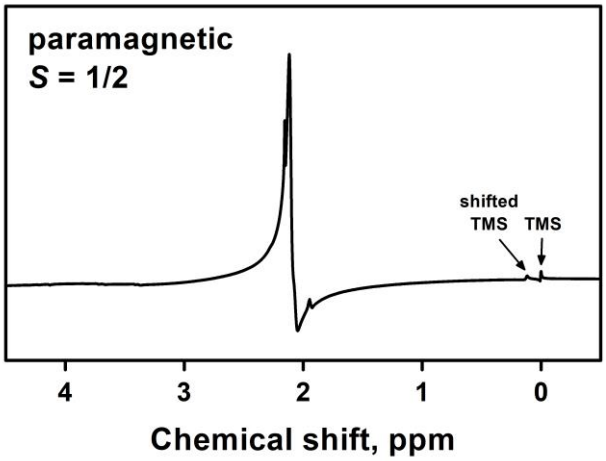

Figure S9. Paramagnetic ^{1}H NMR spectrum of **2** in CD_3CN at 20 ^{o}C

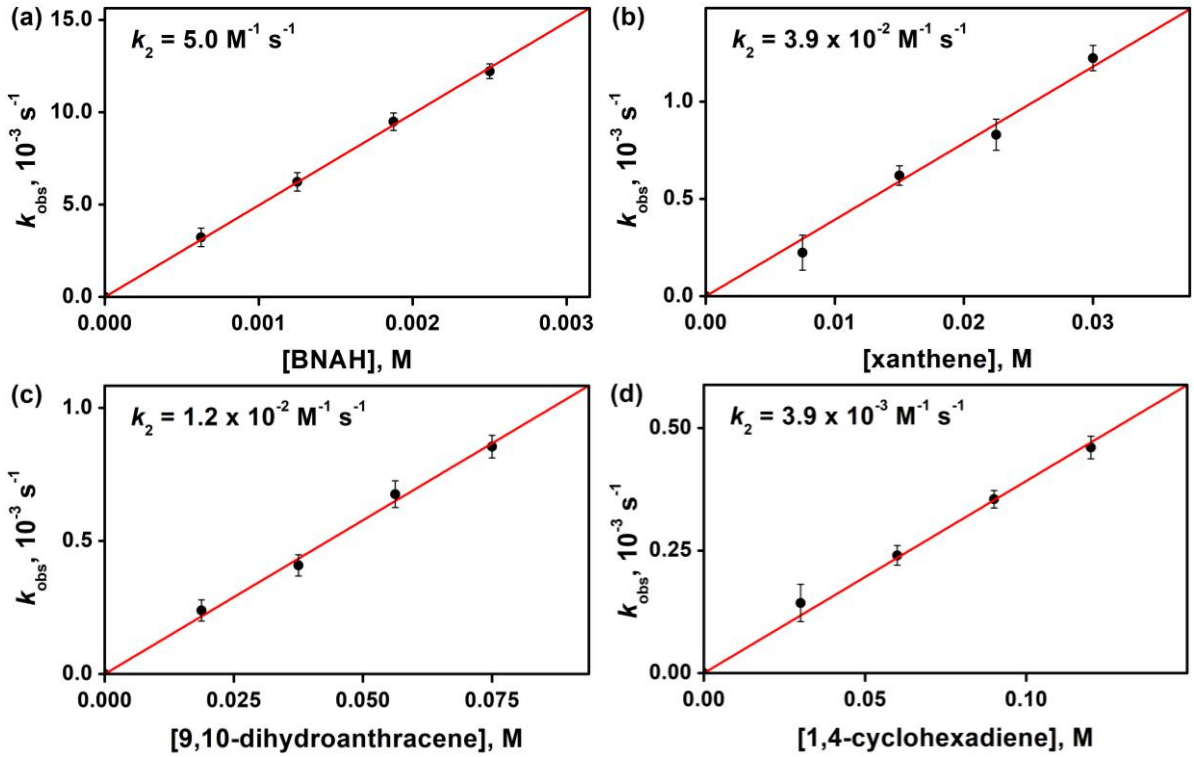

Figure S10. Plot of pseudo-first-order rate constants (k_{obs}) against the concentration of substrates [(a) BNAH, (b) xanthene, (c) 9,10-dihydroanthracene, (d) cyclohexadiene] in order to determine a second-order rate constant (k_2) in the C–H bond activation by **2** (0.25 mM) in CH_3CN at 20 ^oC.

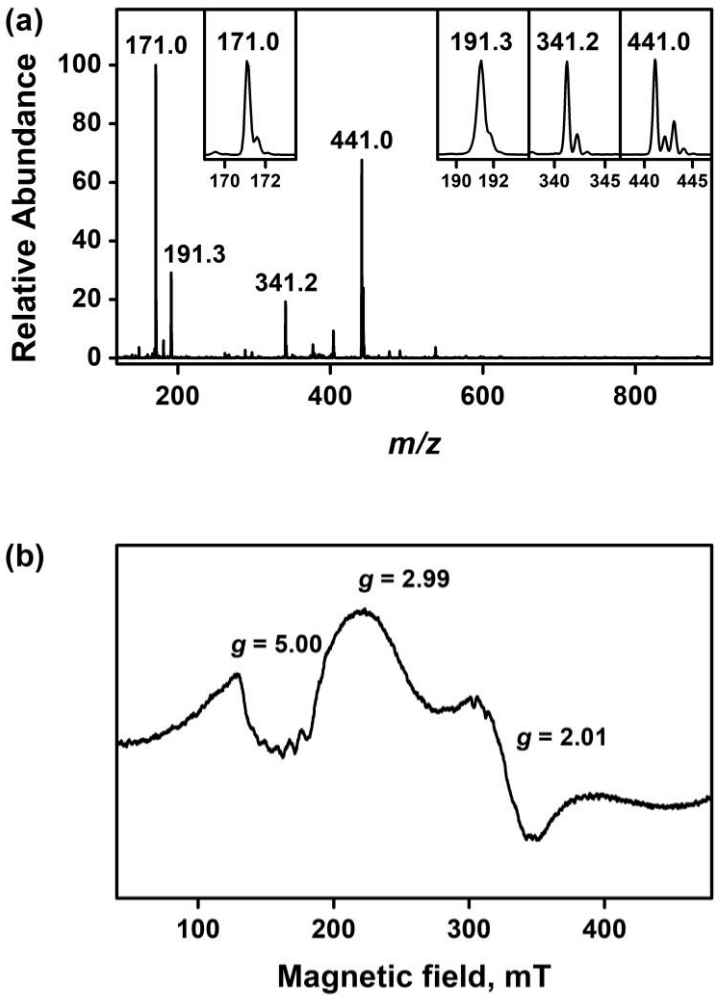

Figure S11. (a) ESI-MS spectrum obtained after the completion of the C-H bond activation of xanthene (1.0 mM) by **2** (0.10 mM) in CH_3CN at 20 °C. The peaks at *m/z* = 171.0, 191.3, 341.2 and 441.0 correspond to $[Mn(HN3O2)]^{2+}$ (calculated *m/z* = 171.1), $[Mn(HN3O2)(CH_3CN)]^{2+}$ (calculated *m/z* = 191.5), $[Mn(N3O2)]^{+}$ (calculuated *m/z* = 341.1), and $[Mn(HN3O2)(ClO_4)]^{+}$ (calculated *m/z* = 441.1), respectively. (b) X-band EPR spectrum obtained after the completion of the C–H bond activation of xanthene (5.0 mM) by **2** (0.5 mM) in CH_3CN at 20 °C recorded at 80 K.

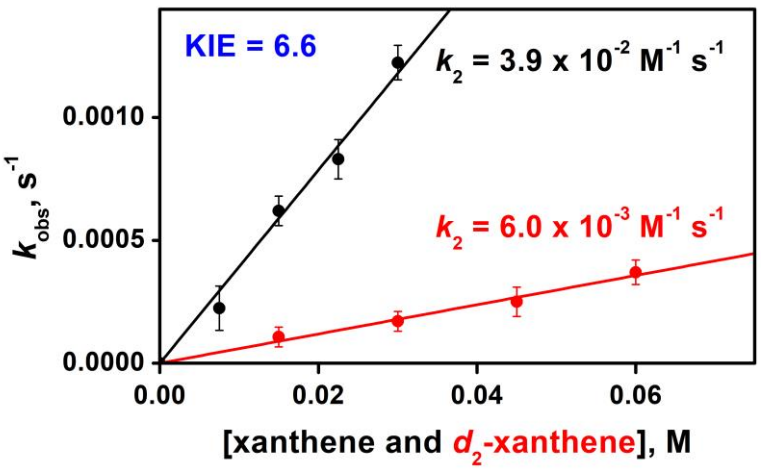

Figure S12. Plots of k_{obs} against concentrations of xanthene (black) and xanthene-d_2 (red) in order to determine k_2 in the C–H bond activation by **2** in CH_3CN at 20 °C.

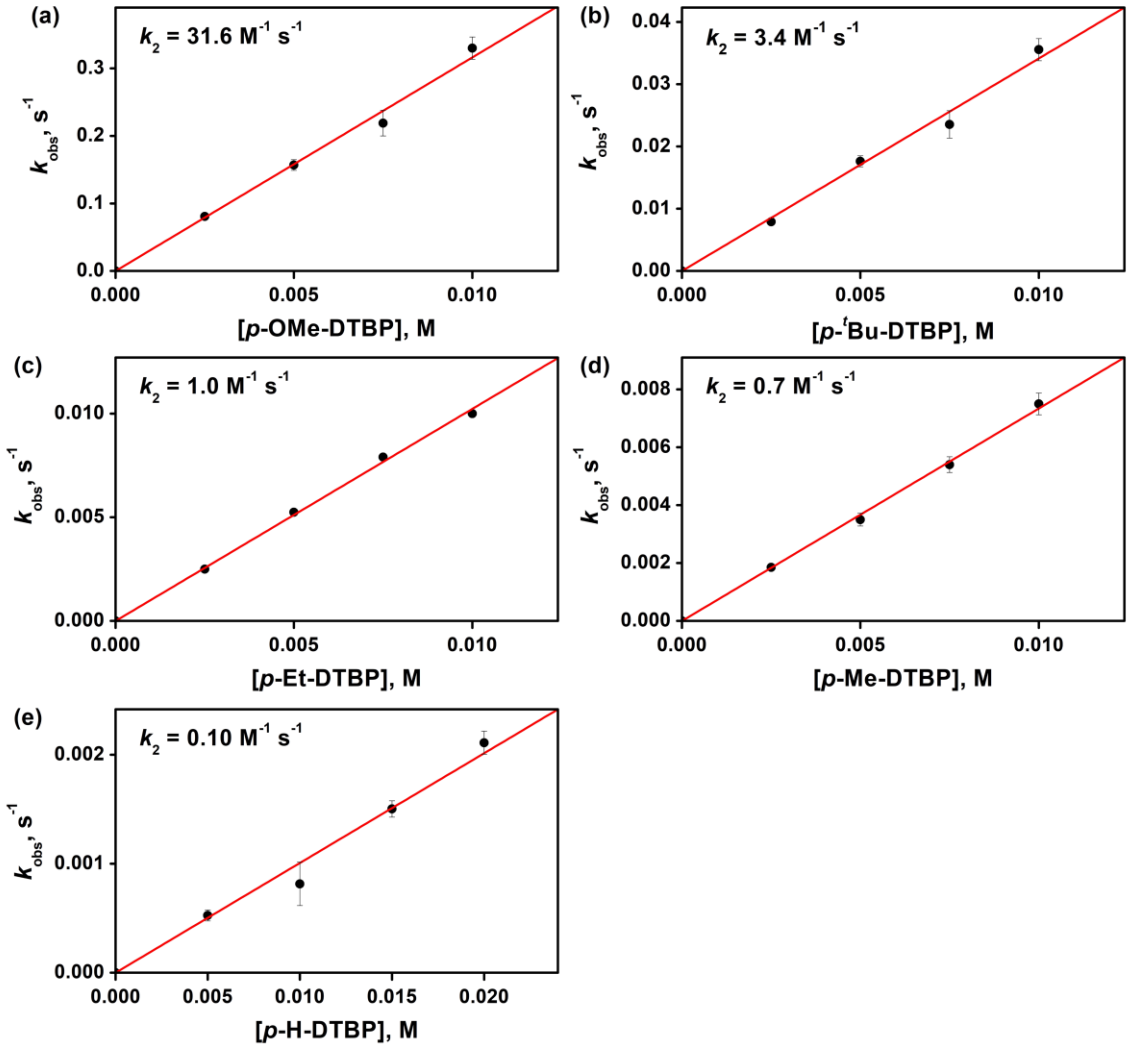

Figure S13. Plot of pseudo-first-order rate constants (k_{obs}) against the concentration of *p*-X-DTBP (X = OMe, ^{t}Bu, Et, Me, H) in order to determine a second-order rate constant (k_2) in the C–H bond activation by **2** (0.25 mM) in CH_3CN at 20 ^{o}C.

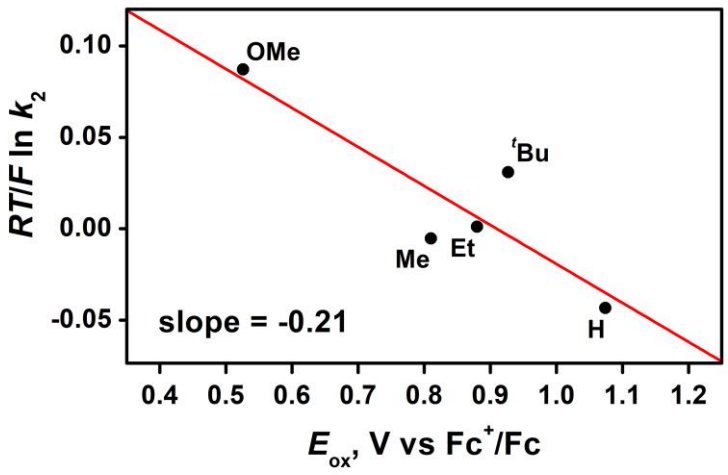

Figure S14. Plot of RT/F ln k_2 against E_{ox} of *p*-X-DTBP for the O–H bond activation reaction by **2** in CH_3CN at 20 °C.

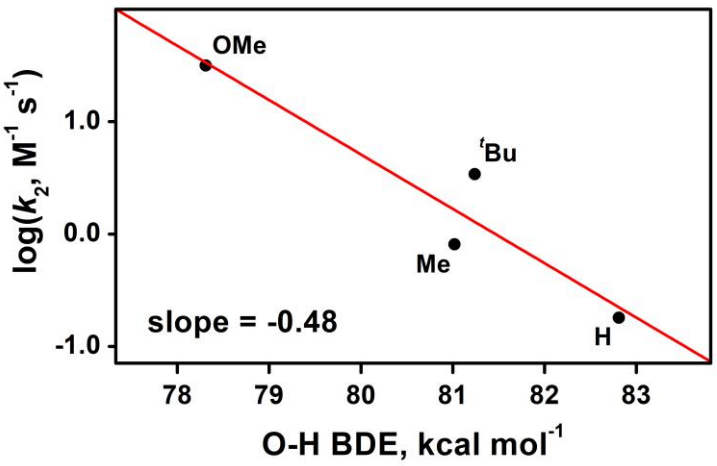

Figure S15. Plot of log k_2 against BDE of *p*-X-DTBP for the O–H bond activation reaction by **2** in CH_3CN at 20 °C.

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DFT Calculated Coordinates

All the coordinates follow the *.xyz file format. The (charge/multiplicity) is specified in the comment field.

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H -1.98473 0.62011 3.09061
N -0.06084 -1.38620 -0.02139
N -0.20295 -2.49836 -0.46024
N -0.33637 -3.56439 -0.87908
N -3.23920 -1.61145 0.59356
C -3.60573 -2.19324 1.74457
H -3.08860 -1.81956 2.63379
C -4.57032 -3.19869 1.79519
H -4.84313 -3.65170 2.74999
C -5.17422 -3.59885 0.59983
H -5.94022 -4.37795 0.59791
C -4.79281 -2.98516 -0.59513
H -5.25129 -3.26924 -1.54452
C -3.80789 -1.99146 -0.56135
C -3.29064 -1.32487 -1.82040
H -2.40503 -1.88563 -2.16362
H -4.04333 -1.40857 -2.62766
N -2.83673 2.02443 0.43274
C -2.58698 3.04761 1.26227
H -1.86511 2.84883 2.05987
C -3.20571 4.28937 1.12835
H -2.97545 5.09619 1.82610
C -4.11245 4.46593 0.08013
H -4.61170 5.42645 -0.06714
C -4.37257 3.39801 -0.78081
H -5.07733 3.50244 -1.60819
C -3.72013 2.17850 -0.56728
C -4.04090 0.94555 -1.38681
H -4.80997 0.38251 -0.83221
H -4.50365 1.23818 -2.34783
N -2.88080 0.06655 -1.59137
C -2.02530 0.55646 -2.67772
H -1.11073 -0.05037 -2.72745
H -1.74039 1.60019 -2.48422
H -2.53635 0.51301 -3.65913
Mn 1.71185 -0.06251 -0.46867
O 1.56936 -0.07065 -2.28118
H 0.94381 0.59378 -2.60507
N 0.29140 1.36416 -0.13432
N 0.40361 2.56599 -0.19350
N 0.47356 3.71123 -0.23730
N 2.85784 -1.85187 -0.51724
C 3.27053 -2.45408 -1.64218
H 3.04837 -1.92456 -2.57186
C 3.93183 -3.67967 -1.61159
H 4.25865 -4.14570 -2.54219
C 4.16082 -4.28498 -0.37338
H 4.67967 -5.24420 -0.31384
C 3.72552 -3.65032 0.79293
H 3.89680 -4.09475 1.77466
C 3.06693 -2.42486 0.68680
C 2.51838 -1.66073 1.86743
H 1.47239 -1.95716 2.03942
H 3.08680 -1.88501 2.78569
N 3.39192 1.47258 -0.46337
C 3.57349 2.42374 -1.38977
H 2.96192 2.34273 -2.29203
C 4.49521 3.45578 -1.22110
H 4.61867 4.21198 -1.99789
C 5.24031 3.49578 -0.03974
H 5.96352 4.29590 0.13311
C 5.05172 2.49946 0.92073
H 5.62218 2.49780 1.85116
C 4.11901 1.49071 0.66558
C 3.93190 0.29844 1.56777
H 4.59016 -0.50062 1.19198
H 4.25809 0.51878 2.59618
N 2.52588 -0.20425 1.57667
C 1.73969 0.54237 2.59196
H 0.67427 0.25659 2.57959
H 1.81844 1.61707 2.38015
H 2.16390 0.35496 3.59409

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2b without sidechain (1/10)
Mn -1.64336 0.05656 0.59574
O -1.39600 0.05608 2.56087
H -1.99481 0.59996 3.08901
N -0.04954 -1.38253 -0.02431
N -0.18732 -2.49835 -0.45604
N -0.31725 -3.56776 -0.86773
N -3.21938 -1.62556 0.58645
C -3.57666 -2.21383 1.73712
H -3.05825 -1.83890 2.62511
C -4.53366 -3.22649 1.78849
H -4.79896 -3.68471 2.74292
C -5.13985 -3.62702 0.59443
H -5.90017 -4.41167 0.59320
C -4.76810 -3.00660 -0.60010
H -5.22860 -3.29083 -1.54847
C -3.79024 -2.00593 -0.56724
C -3.28282 -1.33175 -1.82625
H -2.39422 -1.88480 -2.17427
H -4.03774 -1.41905 -2.63108
N -2.84966 2.01210 0.43927
C -2.60650 3.03380 1.27253
H -1.88318 2.83658 2.06922
C -3.23361 4.27190 1.14352
H -3.00860 5.07758 1.84429
C -4.14183 4.44635 0.09623
H -4.64758 5.40404 -0.04726
C -4.39514 3.37990 -0.76857
H -5.10096 3.48267 -1.59525
C -3.73452 2.16395 -0.55980
C -4.04819 0.93181 -1.38340
H -4.81168 0.36110 -0.82891
H -4.51577 1.22486 -2.34199
N -2.88258 0.06189 -1.59457
C -2.03369 0.56135 -2.68150
H -1.11653 -0.04110 -2.73749
H -1.75303 1.60548 -2.48400
H -2.54772 0.51997 -3.66147
Mn 1.71156 -0.05706 -0.46988
O 1.56882 -0.06648 -2.28111
H 0.93216 0.58843 -2.60305
N 0.27542 1.36390 -0.13426
N 0.38207 2.56670 -0.18978
N 0.44736 3.71250 -0.23027
N 2.86884 -1.84561 -0.51468
C 3.28506 -2.44930 -1.63741
H 3.06109 -1.92401 -2.56909
C 3.95240 -3.67156 -1.60291
H 4.28198 -4.13892 -2.53189
C 4.18383 -4.27188 -0.36269
H 4.70743 -5.22831 -0.29996
C 3.74491 -3.63575 0.80143
H 3.91800 -4.07629 1.78460
C 3.08024 -2.41385 0.69094
C 2.52756 -1.64894 1.86929
H 1.48347 -1.95087 2.04315
H 3.09775 -1.86678 2.78803
N 3.37500 1.48673 -0.46757
C 3.54735 2.43784 -1.39583
H 2.93320 2.35169 -2.29581
C 4.46314 3.47578 -1.23143
H 4.57915 4.23180 -2.00953
C 5.21207 3.52176 -0.05274
H 5.93086 4.32657 0.11673
C 5.03319 2.52537 0.90953
H 5.60698 2.52843 1.83789
C 4.10602 1.51050 0.65902
C 3.92900 0.31813 1.56284
H 4.59170 -0.47709 1.18671
H 4.25550 0.54173 2.59042
N 2.52604 -0.19320 1.57456
C 1.73698 0.55104 2.58946
H 0.67330 0.25849 2.58043
H 1.80857 1.62567 2.37487
H 2.16453 0.36879 3.59111

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2a with sidechain (1/2)
Mn -0.92117 -1.51613 0.21659
O 0.12651 0.05766 -0.82599
H 0.30639 -0.04828 -1.77739
N 0.08208 -3.36049 -0.12760
N 1.03973 -3.87676 0.36721
N 1.96761 -4.39818 0.83177
N -2.34557 -1.90631 -1.54934
C -2.24646 -2.98232 -2.34433
H -1.46024 -3.69478 -2.07906
C -3.08893 -3.18641 -3.43635
H -2.97502 -4.07598 -4.05826
C -4.07509 -2.23237 -3.70068
H -4.76033 -2.35792 -4.54230
C -4.18153 -1.11940 -2.86562
H -4.94843 -0.36103 -3.03532
C -3.28966 -0.98188 -1.79516
C -3.32235 0.23713 -0.89584
H -2.60567 0.97516 -1.29041
H -4.31632 0.71132 -0.94624
N -2.02524 -2.14058 2.14799
C -1.44492 -2.88404 3.10183
H -0.42698 -3.22931 2.90008
C -2.08708 -3.20607 4.29653
H -1.57816 -3.81427 5.04613
C -3.38267 -2.72566 4.50288
H -3.91828 -2.94906 5.42845
C -3.98286 -1.94797 3.51149
H -4.99138 -1.55082 3.64221
C -3.27353 -1.67882 2.33572
C -3.89216 -0.90623 1.18891
H -4.29210 -1.64226 0.47206
H -4.76326 -0.33233 1.55041
N -2.91451 -0.06860 0.48246
C -2.48402 1.11653 1.25297
H -1.68701 1.61029 0.67981
H -2.02479 0.76342 2.18837
C -3.53312 2.16199 1.61648
H -3.05397 2.88443 2.30869
H -4.38102 1.71490 2.17392
O -3.99246 2.81941 0.45673
C -4.93092 3.84329 0.71438
H -5.83918 3.43047 1.19830
H -4.49979 4.59445 1.40711
C -5.32576 4.52320 -0.57781
H -5.68929 3.75565 -1.28956
H -6.17813 5.19612 -0.35720
O -4.21606 5.23185 -1.09386
H -4.48495 5.64460 -1.92513
Mn 1.31282 0.83795 0.49885
O 0.59444 -0.56673 1.52676
H 0.45612 -0.30299 2.44789
N 0.84165 2.15408 1.96981
N 1.54539 2.95583 2.52707
N 2.18324 3.73468 3.08706
N 1.79085 2.43061 -0.81739
C 1.26793 3.66090 -0.64133
H 0.63662 3.79443 0.23752
C 1.50199 4.70519 -1.52841
H 1.05527 5.68278 -1.34228
C 2.31524 4.46918 -2.63921
H 2.53266 5.26801 -3.35159
C 2.84497 3.19409 -2.82547
H 3.48045 2.96857 -3.68359
C 2.55432 2.18279 -1.90358
C 3.00277 0.76307 -2.13596
H 2.22286 0.25167 -2.71901
H 3.90221 0.75932 -2.77596
N 3.31497 0.48683 1.85873
C 3.24893 0.36508 3.19167
H 2.28427 0.58487 3.65633
C 4.33933 -0.01730 3.97145
H 4.23485 -0.10072 5.05451
C 5.55002 -0.29104 3.33077
H 6.42714 -0.60033 3.90377
C 5.61815 -0.17189 1.94260
H 6.54254 -0.38661 1.40287
C 4.47528 0.22573 1.23910
C 4.48696 0.42975 -0.25565
H 4.65287 1.50307 -0.44758
H 5.34374 -0.09977 -0.70871
N 3.20994 0.04444 -0.87330
C 3.02913 -1.42563 -0.95312
H 1.95036 -1.62585 -0.98907
H 3.38764 -1.85392 -0.00587
C 3.70034 -2.16475 -2.11466
H 3.70052 -3.24450 -1.87276
H 4.75288 -1.86187 -2.23436
O 3.07025 -1.92639 -3.36237
C 1.85384 -2.62220 -3.58322
H 2.05055 -3.57684 -4.10919
H 1.34593 -2.86772 -2.63356
C 0.92404 -1.78207 -4.43170
H 1.45746 -1.44732 -5.33928
H 0.07177 -2.41102 -4.74760
O 0.46937 -0.66008 -3.67621
H 0.00738 -0.04933 -4.26730

96
2a with sidechain (1/10)
Mn -0.98321 -1.51272 0.14544
O 0.12807 0.05249 -0.81553
H 0.29670 0.02417 -1.77459
N -0.02372 -3.36125 -0.29534
N 0.93405 -3.92679 0.14181
N 1.86079 -4.49536 0.55002
N -2.37412 -1.74025 -1.64774
C -2.28701 -2.76663 -2.50769
H -1.52346 -3.51416 -2.27486
C -3.11490 -2.87942 -3.62368
H -3.01223 -3.73091 -4.29852
C -4.07164 -1.88518 -3.84366
H -4.74421 -1.93970 -4.70288
C -4.16534 -0.82435 -2.94190
H -4.90963 -0.03694 -3.07607
C -3.29064 -0.77766 -1.85002
C -3.30931 0.38071 -0.87430
H -2.56204 1.12063 -1.20264
H -4.28778 0.88748 -0.91702
N -2.14471 -2.27047 1.97791
C -1.60684 -3.12127 2.86514
H -0.60136 -3.48819 2.64160
C -2.27697 -3.52566 4.01845
H -1.80185 -4.21984 4.71353
C -3.55567 -3.01521 4.25555
H -4.11197 -3.30078 5.15134
C -4.11197 -2.12746 3.33370
H -5.10646 -1.70501 3.49001
C -3.37747 -1.77938 2.19457
C -3.95692 -0.88516 1.11743
H -4.38343 -1.54021 0.33996
H -4.80605 -0.31047 1.52686
N -2.94372 -0.02927 0.48807
C -2.49871 1.08616 1.34769
H -1.64138 1.56410 0.85415
H -2.12121 0.65556 2.28698
C -3.50880 2.17270 1.70219
H -3.05579 2.80147 2.49580
H -4.43642 1.74647 2.13528
O -3.80352 2.95380 0.56543
C -4.68853 4.02425 0.82213
H -5.67399 3.64631 1.16224
H -4.28625 4.67069 1.62851
C -4.88055 4.85019 -0.43035
H -5.21097 4.18365 -1.25159
H -5.70326 5.56721 -0.23818
O -3.67052 5.51045 -0.74672
H -3.81134 6.02236 -1.55404
Mn 1.30836 0.78241 0.56505
O 0.46782 -0.63745 1.51030
H 0.32285 -0.44301 2.44776
N 0.86459 2.05521 2.09448
N 1.59605 2.78435 2.71152
N 2.26222 3.49421 3.32857
N 1.82359 2.42909 -0.68568
C 1.32084 3.65837 -0.45518
H 0.67777 3.75780 0.42015
C 1.59263 4.74266 -1.28171
H 1.16044 5.71804 -1.05411
C 2.42585 4.54856 -2.38590
H 2.67423 5.37897 -3.05049
C 2.93636 3.27481 -2.62740
H 3.58747 3.08217 -3.48178
C 2.60569 2.22266 -1.76651
C 3.03081 0.80756 -2.06445
H 2.24902 0.34331 -2.68346
H 3.93888 0.81881 -2.69236
N 3.25881 0.26808 1.91315
C 3.16522 0.05939 3.23395
H 2.19239 0.25444 3.69237
C 4.23792 -0.37952 4.00819
H 4.11109 -0.53434 5.08093
C 5.46054 -0.61560 3.37519
H 6.32476 -0.96626 3.94394
C 5.55771 -0.40468 1.99976
H 6.49256 -0.58715 1.46619
C 4.43110 0.04341 1.30048
C 4.47514 0.34295 -0.17808
H 4.66096 1.42360 -0.29802
H 5.33300 -0.17079 -0.64765
N 3.20446 0.01877 -0.83969
C 2.99389 -1.44058 -1.00140
H 1.91142 -1.61398 -1.05926
H 3.33275 -1.92827 -0.07584
C 3.66342 -2.12964 -2.19419
H 3.63895 -3.22066 -2.01145
H 4.72303 -1.84187 -2.28615
O 3.05264 -1.81163 -3.43399
C 1.82537 -2.46921 -3.70480
H 2.00909 -3.40060 -4.27536
H 1.29940 -2.75060 -2.77520
C 0.92446 -1.56796 -4.52121
H 1.47760 -1.19817 -5.40311
H 0.06510 -2.16280 -4.88117
O 0.48059 -0.47762 -3.71509
H 0.03976 0.17179 -4.28056

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2b with sidechain (1/2)
Mn 1.02673 1.37738 0.28839
O 0.00134 3.07825 0.19940
H 0.49442 3.89845 0.32877
N -0.06298 -0.08969 -0.99250
N 0.17455 -0.38697 -2.13449
N 0.39886 -0.67325 -3.22832
N 2.50041 1.81485 -1.41734
C 2.37968 2.93850 -2.13950
H 1.55299 3.59353 -1.85191
C 3.24588 3.25152 -3.18553
H 3.11416 4.17638 -3.74984
C 4.27891 2.35745 -3.47956
H 4.98441 2.56839 -4.28670
C 4.40472 1.19239 -2.72127
H 5.20615 0.47755 -2.91872
C 3.48638 0.94570 -1.69332
C 3.53415 -0.33268 -0.87902
H 2.86438 -1.07088 -1.34860
H 4.54584 -0.76916 -0.93794
N 2.18181 1.93825 2.18425
C 1.60127 2.73202 3.09656
H 0.62655 3.13888 2.81246
C 2.20158 3.02940 4.31897
H 1.69629 3.67901 5.03564
C 3.45228 2.47092 4.59473
H 3.95291 2.67016 5.54516
C 4.05758 1.65327 3.63844
H 5.03695 1.20618 3.82051
C 3.39394 1.41495 2.42955
C 4.04204 0.63619 1.30237
H 4.52237 1.37360 0.63796
H 4.86187 0.01385 1.70274
N 3.08352 -0.13708 0.50472
C 2.62923 -1.37126 1.17157
H 1.78607 -1.77431 0.59022
H 2.23247 -1.08505 2.15836
C 3.64277 -2.49230 1.38558
H 3.17862 -3.23999 2.06107
H 4.55229 -2.12756 1.90503
O 3.97929 -3.08547 0.15167
C 4.86767 -4.17736 0.26551
H 5.82963 -3.85586 0.71369
H 4.43772 -4.95546 0.92871
C 5.13338 -4.77377 -1.09885
H 5.49745 -3.97398 -1.77384
H 5.95383 -5.51073 -0.99016
O 3.94930 -5.37255 -1.58793
H 4.13691 -5.73428 -2.46406
Mn -1.58037 -1.03403 0.38583
O -0.67910 -2.54776 0.85614
H -0.03061 -2.37568 1.55407
N -0.57332 0.17529 1.69162
N -0.81950 0.39162 2.85507
N -1.02545 0.62496 3.96013
N -2.37803 -2.03145 -1.29077
C -2.16773 -3.33053 -1.55663
H -1.59832 -3.87959 -0.80295
C -2.64254 -3.92082 -2.72406
H -2.45887 -4.97943 -2.91277
C -3.35142 -3.12959 -3.63282
H -3.74148 -3.56225 -4.55677
C -3.56392 -1.77991 -3.34684
H -4.12104 -1.13881 -4.03188
C -3.05638 -1.25082 -2.15761
C -3.19436 0.20003 -1.77366
H -2.35470 0.78562 -2.18073
H -4.10333 0.63067 -2.22005
N -3.24818 -1.40056 1.89377
C -3.10636 -2.06192 3.05096
H -2.15773 -2.58540 3.19499
C -4.11157 -2.09126 4.01600
H -3.96219 -2.64255 4.94568
C -5.29699 -1.39585 3.76303
H -6.10250 -1.38544 4.50073
C -5.44261 -0.71312 2.55368
H -6.35821 -0.16610 2.32172
C -4.39227 -0.74931 1.63185
C -4.50428 -0.16512 0.24668
H -4.86540 -0.96794 -0.41512
H -5.26985 0.62386 0.21494
N -3.20558 0.33659 -0.28932
C -2.93708 1.73278 0.18274
H -1.87858 1.97370 0.02025
H -3.09219 1.72964 1.27231
C -3.79721 2.84801 -0.42234
H -3.63025 3.75180 0.19447
H -4.87308 2.61804 -0.35256
O -3.52792 3.10370 -1.78367
C -2.39331 3.92566 -2.04207
H -2.68853 4.99324 -1.99943
H -1.59443 3.75339 -1.29667
C -1.85473 3.61644 -3.42162
H -2.68655 3.63300 -4.15158
H -1.14502 4.41777 -3.70571
O -1.21448 2.34980 -3.39417
H -0.99287 2.08672 -4.29732

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2b with sidechain (1/10)
Mn 1.02083 1.38897 0.24464
O 0.00182 3.09020 0.09266
H 0.50251 3.91215 0.16933
N -0.06590 -0.12543 -0.98072
N 0.17447 -0.46514 -2.11036
N 0.40179 -0.79149 -3.19270
N 2.49037 1.75927 -1.48075
C 2.36275 2.85270 -2.24683
H 1.53188 3.51315 -1.98510
C 3.22694 3.12962 -3.30465
H 3.08936 4.03065 -3.90498
C 4.26566 2.23122 -3.56329
H 4.97011 2.41466 -4.37804
C 4.39820 1.09755 -2.75996
H 5.20376 0.38024 -2.92952
C 3.48112 0.88556 -1.72313
C 3.53508 -0.36155 -0.86232
H 2.86966 -1.11985 -1.30524
H 4.54899 -0.79493 -0.90507
N 2.18155 2.01999 2.11380
C 1.60214 2.84925 2.99477
H 0.62976 3.24889 2.69304
C 2.20104 3.18985 4.20660
H 1.69661 3.86755 4.89740
C 3.44912 2.63764 4.50576
H 3.94852 2.87019 5.44925
C 4.05351 1.78315 3.58162
H 5.03115 1.34017 3.78215
C 3.39163 1.50253 2.38088
C 4.04073 0.68229 1.28420
H 4.52303 1.39459 0.59428
H 4.85929 0.07434 1.70865
N 3.08329 -0.11871 0.51339
C 2.63107 -1.33034 1.22182
H 1.78513 -1.75138 0.65749
H 2.23921 -1.01218 2.20079
C 3.64480 -2.44475 1.46769
H 3.18435 -3.16867 2.17105
H 4.55783 -2.06342 1.96874
O 3.97355 -3.08021 0.25285
C 4.86623 -4.16486 0.39917
H 5.82945 -3.82483 0.83063
H 4.44268 -4.92089 1.09141
C 5.12681 -4.80740 -0.94507
H 5.48225 -4.02983 -1.64995
H 5.95202 -5.53568 -0.81581
O 3.94323 -5.42950 -1.40540
H 4.12649 -5.81745 -2.27120
Mn -1.57967 -1.01634 0.42517
O -0.67896 -2.50958 0.95537
H -0.02840 -2.30884 1.64366
N -0.57045 0.24747 1.68549
N -0.81437 0.50357 2.84170
N -1.01850 0.77470 3.93852
N -2.37501 -2.08005 -1.21568
C -2.16242 -3.38781 -1.43232
H -1.59024 -3.90678 -0.65963
C -2.63819 -4.02333 -2.57543
H -2.45253 -5.08796 -2.72409
C -3.35074 -3.26887 -3.51212
H -3.74185 -3.73724 -4.41804
C -3.56553 -1.90970 -3.27741
H -4.12558 -1.29653 -3.98518
C -3.05657 -1.33465 -2.11031
C -3.19587 0.12969 -1.78209
H -2.35724 0.69996 -2.21230
H -4.10577 0.54210 -2.24356
N -3.24333 -1.32623 1.94397
C -3.09841 -1.94217 3.12563
H -2.14887 -2.45870 3.28757
C -4.10168 -1.93500 4.09302
H -3.94993 -2.44977 5.04302
C -5.28824 -1.25093 3.81571
H -6.09229 -1.21271 4.55410
C -5.43701 -0.61564 2.58114
H -6.35363 -0.07898 2.32995
C -4.38857 -0.68648 1.65924
C -4.50345 -0.15642 0.25282
H -4.86596 -0.98405 -0.37698
H -5.26886 0.63116 0.19237
N -3.20539 0.32408 -0.30430
C -2.93750 1.73823 0.11185
H -1.87875 1.97222 -0.05901
H -3.09398 1.77856 1.20048
C -3.79672 2.82834 -0.53900
H -3.63298 3.75535 0.04322
H -4.87261 2.59986 -0.46444
O -3.52298 3.03200 -1.90830
C -2.38726 3.84318 -2.19444
H -2.68348 4.91131 -2.20019
H -1.59366 3.70434 -1.43670
C -1.83864 3.47528 -3.55560
H -2.66443 3.46377 -4.29250
H -1.12431 4.26228 -3.86683
O -1.20244 2.20924 -3.47024
H -0.97152 1.90888 -4.35937

Monomer with 1,4-cyclohexadiene

62
Reactant Complex (1/5)
Mn -0.63158 -0.12024 -0.47336
N -1.12646 -0.82170 -2.23135
N -1.74900 -0.24937 -3.09230
N -2.33684 0.24170 -3.94868
O 0.29974 1.33367 -1.06581
H 0.41329 1.38597 -2.02580
N 0.80870 -1.86954 -0.19178
O -2.74703 0.82328 -0.32455
C -0.95612 -0.18828 2.46789
N -0.40257 0.56475 1.49755
N -1.78448 -1.64433 0.60157
O -5.37907 2.15120 -1.01978
H -5.67541 2.66231 -0.25292
C 0.16315 1.74793 1.79477
H 0.57935 2.29425 0.94561
C -3.22750 -1.40827 0.30934
H -3.85748 -2.05037 0.94812
H -3.39764 -1.69769 -0.73628
C -0.96638 0.24313 3.79697
H -1.42700 -0.37784 4.56713
C 0.86726 -4.24052 0.13135
H 0.32658 -5.17106 0.31391
C 2.91138 -3.01118 -0.21322
H 3.99668 -2.95653 -0.31152
C 0.17061 -3.03459 0.01686
C 2.14409 -1.85081 -0.30420
H 2.61126 -0.87718 -0.47631
C -1.47796 -1.54169 2.05932
H -2.35848 -1.82144 2.65891
H -0.69711 -2.27875 2.30342
C -0.37723 1.46702 4.11455
H -0.37232 1.82201 5.14739
C -1.33992 -2.95900 0.07189
H -1.73307 -3.05289 -0.95142
H -1.75658 -3.78681 0.66853
C 2.25839 -4.22621 0.00934
H 2.82706 -5.15499 0.09356
C -3.62389 0.04486 0.48983
H -4.66606 0.18296 0.16802
H -3.54677 0.37243 1.54321
C 0.20159 2.23239 3.09789
H 0.67158 3.19447 3.30635
C -2.99268 2.23395 -0.39284
H -2.04079 2.67873 -0.71915
H -3.22735 2.61737 0.61712
C -4.08637 2.59990 -1.38525
H -4.05825 3.69753 -1.53051
H -3.85324 2.13306 -2.35562
C 4.31278 2.87201 -0.27963
C 5.29337 2.42314 0.51485
C 5.58864 0.42593 -0.97908
C 4.60784 0.87642 -1.77361
H 3.80789 3.81332 -0.03517
H 5.58018 3.00133 1.40027
H 6.10104 -0.50966 -1.22955
H 4.32903 0.30293 -2.66468
C 6.04820 1.14434 0.26232
H 7.13488 1.35361 0.19591
H 5.96223 0.47397 1.14099
C 3.84460 2.14868 -1.51483
H 2.76246 1.92631 -1.43069
H 3.91595 2.81790 -2.39567

62
Transition State (1/5)
Mn -0.50005 -0.27769 -0.57708
N -1.54042 -0.73763 -2.28267
N -2.29608 -0.07144 -2.93455
N -3.03253 0.52936 -3.59194
O 1.08494 0.40779 -1.59618
H 0.83753 0.33413 -2.53419
N 0.22806 -2.42096 -0.32421
O -2.21372 1.32635 -0.12497
C -0.32883 0.02570 2.46364
N 0.26564 0.49860 1.35301
N -1.90078 -1.26506 0.98199
O -4.43463 3.39332 -0.44374
H -4.35565 4.02401 0.28647
C 1.15340 1.50166 1.45021
H 1.60281 1.84764 0.51603
C -3.20573 -0.56567 0.92339
H -3.86292 -0.88692 1.75248
H -3.69210 -0.85625 -0.01852
C -0.04499 0.56069 3.72512
H -0.54647 0.16331 4.60956
C -0.38433 -4.62472 0.37628
H -1.12671 -5.29030 0.82065
C 1.78754 -4.21847 -0.58602
H 2.77293 -4.55404 -0.91334
C -0.67203 -3.26717 0.20608
C 1.42633 -2.87793 -0.71229
H 2.10745 -2.13654 -1.13849
C -1.25162 -1.16400 2.30877
H -2.00328 -1.16959 3.11642
H -0.63597 -2.06500 2.46080
C 0.88063 1.59852 3.82967
H 1.11631 2.03055 4.80481
C -2.02163 -2.67392 0.55358
H -2.64592 -2.69154 -0.35393
H -2.53225 -3.29183 1.31313
C 0.86229 -5.10562 -0.02996
H 1.11026 -6.16246 0.09197
C -3.07072 0.94551 0.95038
H -4.06397 1.40000 0.82282
H -2.65438 1.30932 1.90817
C 1.49476 2.07962 2.67020
H 2.22189 2.89241 2.70371
C -2.05459 2.73056 -0.34971
H -1.12497 2.83874 -0.92992
H -1.91213 3.24818 0.61751
C -3.19975 3.35296 -1.13737
H -2.87860 4.36326 -1.45904
H -3.36752 2.75310 -2.04606
C 3.67078 2.51009 -1.41379
C 4.37743 2.72587 -0.28107
C 5.13859 0.33186 -0.32507
C 4.42459 0.13771 -1.45636
H 3.14095 3.34084 -1.89024
H 4.42335 3.72985 0.15227
H 5.75927 -0.47545 0.07594
H 4.47006 -0.82909 -1.96770
C 5.14318 1.63805 0.41326
H 6.18654 1.96696 0.59712
H 4.74402 1.49204 1.44014
C 3.54897 1.17617 -2.01879
H 2.34451 0.79414 -1.74806
H 3.46066 1.16814 -3.11668

62
Product Complex (1/5)
Mn -0.59436 -0.27250 -0.53704
N -1.14097 -0.47246 -2.56551
N -2.16987 -0.42336 -3.17171
N -3.15165 -0.38434 -3.78648
O 1.22052 0.52651 -1.62923
H 0.94024 0.36813 -2.54728
N 0.26925 -2.34655 -0.17723
O -2.52650 1.02660 -0.25311
C -0.31833 0.46683 2.47929
N 0.13023 0.87882 1.28090
N -1.78542 -1.21975 1.31993
O -5.10367 2.58122 -0.77191
H -5.07945 3.38465 -0.23242
C 0.83210 2.02110 1.19353
H 1.16840 2.30422 0.19307
C -3.15484 -0.66080 1.30580
H -3.67118 -0.84281 2.26711
H -3.71860 -1.18907 0.52356
C -0.07213 1.20407 3.64365
H -0.45387 0.85001 4.60316
C 0.01094 -4.46875 0.89873
H -0.57998 -5.11958 1.54601
C 1.94752 -4.03534 -0.46411
H 2.89800 -4.33281 -0.90987
C -0.44251 -3.17893 0.60354
C 1.43359 -2.76172 -0.69862
H 1.96481 -2.04113 -1.32474
C -1.02794 -0.87134 2.53759
H -1.67391 -0.91502 3.43245
H -0.24768 -1.63590 2.68528
C 0.66160 2.38700 3.55585

H 0.86474 2.97765 4.45201
C -1.78558 -2.67477 1.09074
H -2.52980 -2.89167 0.30759
H -2.09943 -3.23791 1.98832
C 1.22026 -4.90346 0.35396
H 1.59249 -5.90752 0.56978
C -3.19798 0.82340 0.99203
H -4.24697 1.14121 0.90705
H -2.71995 1.43455 1.77895
C 1.12511 2.80676 2.30596
H 1.69883 3.72762 2.18974
C -2.64219 2.33427 -0.82609
H -1.80319 2.43146 -1.53184
H -2.51106 3.09681 -0.03589
C -3.94397 2.55366 -1.58568
H -3.83606 3.48683 -2.17297
H -4.07787 1.72834 -2.30315
C 4.33560 2.01224 -1.99498
C 4.59922 2.69939 -0.83881
C 5.09405 0.51038 0.29352
C 4.81975 -0.13182 -0.88543
H 4.04640 2.56104 -2.89600
H 4.52122 3.79021 -0.81797
H 5.39094 -0.06359 1.17605
H 4.90147 -1.22135 -0.93920
C 5.00717 2.00246 0.42589
H 5.97644 2.41036 0.79058
H 4.31113 2.27182 1.25156
C 4.43207 0.59152 -2.05065
H 2.19458 0.52362 -1.61372
H 4.25339 0.06425 -2.99055

2a reaction with 1,4-cyclohexadiene with bidentate OH

110
Reactant Complex (1/10)
Mn 0.94665 0.69298 1.65782
O -0.36520 1.50768 0.05347
H 0.14942 1.81159 -0.72168
N 0.11735 1.91835 3.20241
N -0.59916 2.86952 3.09732
N -1.29350 3.79787 3.02110
N 2.64535 2.20005 1.21458
C 2.68100 3.42748 1.75679
H 1.85528 3.68424 2.42393
C 3.70648 4.33569 1.49831
H 3.69145 5.32413 1.96054
C 4.74332 3.94140 0.64915
H 5.57132 4.61887 0.42774
C 4.71064 2.66175 0.09443
H 5.50896 2.31503 -0.56469
C 3.63722 1.81402 0.39299
C 3.51988 0.44490 -0.23941
H 2.87563 0.54544 -1.12549
H 4.51011 0.12344 -0.60647
N 1.82567 -0.72249 3.25385
C 1.13401 -1.03026 4.36097
H 0.20059 -0.48122 4.51143
C 1.57421 -1.97906 5.28283
H 0.97826 -2.19907 6.17015
C 2.78375 -2.63225 5.03488
H 3.16093 -3.38824 5.72750
C 3.50506 -2.30700 3.88505
H 4.45430 -2.79741 3.66041
C 2.99736 -1.33637 3.01394
C 3.77522 -0.87714 1.79777
H 4.33427 0.02764 2.08803
H 4.53650 -1.63286 1.53312
N 2.90568 -0.53699 0.66426
C 2.37075 -1.73580 -0.01429
H 1.46074 -1.44603 -0.55741
H 2.03830 -2.43073 0.76995
C 3.29728 -2.49124 -0.96191
H 2.87064 -3.49993 -1.13350
H 4.29756 -2.64665 -0.50900
O 3.41208 -1.79640 -2.18740
C 4.31909 -2.39610 -3.09082
H 5.33225 -2.44022 -2.64351
H 4.01149 -3.43710 -3.31641
C 4.39291 -1.60772 -4.37956
H 4.57296 -0.54165 -4.14152
H 5.26929 -1.97541 -4.94571
O 3.19842 -1.78327 -5.12475
H 3.29927 -1.32393 -5.96970
Mn -1.63975 0.14589 -0.25790
O -0.52936 -0.77222 1.05801
H -0.80778 -1.60758 1.45697
N -2.79793 -1.41432 -0.60960
N -3.26194 -2.15518 0.22045
N -3.73358 -2.88981 0.96992
N -1.16553 0.15194 -2.47721
C -0.01947 -0.32871 -2.98778
H 0.69488 -0.76620 -2.28799
C 0.27685 -0.29119 -4.34832
H 1.22552 -0.70578 -4.69828
C -0.66582 0.27695 -5.21150
H -0.47337 0.33601 -6.28522
C -1.85943 0.76558 -4.68233
H -2.62016 1.21009 -5.32698
C -2.08222 0.67967 -3.30287
C -3.41149 1.06511 -2.69504
H -3.94807 1.77009 -3.34992
H -4.01600 0.14501 -2.67779
N -3.16262 0.78389 1.38090
C -2.94914 0.68644 2.69988
H -1.96742 0.31619 2.99971
C -3.90993 1.05639 3.64097
H -3.69406 0.96346 4.70666
C -5.13316 1.55132 3.18527
H -5.90710 1.86106 3.89133
C -5.35346 1.64953 1.80991
H -6.29718 2.03130 1.41569
C -4.34262 1.24342 0.93401
C -4.54053 1.20368 -0.56129
H -4.82485 0.17440 -0.82668
H -5.37645 1.86267 -0.85468
N -3.30809 1.54049 -1.30566
C -3.04434 3.01247 -1.14189
H -2.45945 3.14672 -0.22101
H -4.01662 3.51119 -0.97983
C -2.39779 3.78829 -2.29090
H -2.54917 4.85818 -2.05500
H -2.92891 3.60594 -3.23670
O -1.03140 3.53631 -2.53565
C -0.12903 4.27467 -1.73037
H -0.25819 5.36371 -1.88696
H -0.29368 4.06184 -0.65854
C 1.27572 3.85834 -2.12605
H 1.50026 4.19882 -3.15202
H 2.00416 4.32416 -1.44589
O 1.44035 2.44507 -2.03030
H 0.98795 2.05329 -2.79168
C -1.31712 -5.02158 -1.52844
C -0.67785 -5.61221 0.82789
C -1.72123 -6.44872 0.90123
C -2.36246 -5.85570 -1.45360
H -1.13253 -4.46621 -2.45463
H -0.00842 -5.50524 1.68866
H -1.89524 -7.01723 1.82157
H -3.02254 -5.97481 -2.31998
C -2.69803 -6.65986 -0.22527
H -3.72349 -6.41317 0.11626
H -2.75473 -7.73679 -0.48122
C -0.35728 -4.78872 -0.39167
H 0.67964 -4.99696 -0.72391
H -0.34038 -3.71154 -0.12863

110
Transition State (1/10)
Mn 1.34618 -0.77516 1.40534
O -0.09556 0.40314 0.52216
H 0.15013 1.34716 0.56485
N 0.60999 -1.70511 3.13612
N 0.09422 -1.46484 4.18552
N -0.39926 -1.25712 5.21530
N 2.77200 0.67169 2.45677
C 2.80735 0.81566 3.79196
H 2.07951 0.23752 4.36580
C 3.71405 1.65780 4.43278
H 3.70440 1.74533 5.52037
C 4.62684 2.36884 3.64996
H 5.36028 3.03241 4.11378
C 4.59370 2.21286 2.26403
H 5.29752 2.74613 1.62212
C 3.64388 1.35721 1.69385
C 3.51591 1.21212 0.19267
H 2.72682 1.90250 -0.14102
H 4.45153 1.54514 -0.28927
N 2.52617 -2.65123 0.88121
C 2.06276 -3.87400 1.18643
H 1.11838 -3.90374 1.73572
C 2.74462 -5.03988 0.84341
H 2.33208 -6.01416 1.11049
C 3.95407 -4.92299 0.15315
H 4.51579 -5.81274 -0.14047
C 4.43546 -3.65105 -0.15899
H 5.37686 -3.52263 -0.69675
C 3.69540 -2.52830 0.22904
C 4.21055 -1.12201 0.00020
H 4.77381 -0.82803 0.90149
H 4.94262 -1.12224 -0.82701
N 3.13078 -0.14891 -0.20532
C 2.53136 -0.23788 -1.55414
H 1.53883 0.23229 -1.50584
H 2.35816 -1.30407 -1.75957
C 3.31420 0.34917 -2.72435
H 2.91299 -0.08168 -3.66378
H 4.38269 0.05641 -2.67776
O 3.18637 1.75598 -2.74072
C 3.99129 2.38076 -3.72111
H 5.06394 2.20024 -3.50801
H 3.77821 1.96063 -4.72456
C 3.74141 3.87214 -3.74591
H 3.80845 4.26699 -2.71392
H 4.55362 4.33880 -4.33476
O 2.47581 4.13781 -4.32836
H 2.34644 5.09588 -4.34960
Mn -1.84747 -0.03283 -0.40590
O -1.05690 -1.92730 -0.62460
H -1.75374 -2.56941 -0.40746
N -3.27546 -0.59943 -1.86113
N -3.63698 -1.72515 -2.05420
N -4.00598 -2.80602 -2.25220
N -1.76497 1.97185 -1.52327
C -0.63490 2.32732 -2.15573
H 0.20767 1.63695 -2.08467
C -0.50129 3.51157 -2.87830
H 0.45096 3.74249 -3.36267
C -1.60681 4.36356 -2.94703
H -1.55249 5.30562 -3.49789
C -2.78330 3.99453 -2.29590
H -3.66483 4.63831 -2.32583
C -2.83239 2.78740 -1.58697
C -4.11722 2.32045 -0.93251
H -4.82372 3.16700 -0.84905
H -4.57123 1.59790 -1.62735
N -3.12510 -0.91054 1.36561
C -2.63355 -1.85610 2.18073
H -1.60516 -2.17264 1.99142
C -3.37150 -2.40705 3.22901
H -2.92412 -3.16862 3.86940
C -4.67485 -1.95289 3.43416
H -5.28544 -2.35435 4.24636
C -5.18451 -0.96565 2.58882
H -6.19593 -0.57758 2.72413
C -4.38079 -0.46474 1.55946
C -4.88819 0.56932 0.58096
H -5.07626 0.05935 -0.37464
H -5.85372 0.97531 0.93939
N -3.90208 1.63063 0.34057
C -3.87477 2.52025 1.52269
H -3.48663 1.93823 2.37350
H -4.91585 2.79774 1.79326
C -3.12982 3.84996 1.42579
H -3.35722 4.39762 2.36177
H -3.52531 4.46021 0.60085
O -1.73578 3.78925 1.23036
C -0.97052 3.30779 2.31963
H -1.27823 3.78674 3.26948
H -1.08517 2.21362 2.42935
C 0.47613 3.64549 2.00856
H 0.62473 4.73988 2.04469
H 1.14181 3.18425 2.75178
O 0.84614 3.14058 0.72884
H 0.25336 3.56108 0.08525
C 0.03751 -2.94629 -3.58986
C -0.57858 -4.83295 -2.09402
C -1.49308 -5.26089 -2.99231
C -0.86746 -3.36009 -4.50430
H 0.68716 -2.09608 -3.82100
H -0.39483 -5.41644 -1.18598
H -2.04431 -6.18907 -2.81070
H -0.94252 -2.84790 -5.46892
C -1.79215 -4.51720 -4.26115
H -2.83972 -4.14769 -4.22486
H -1.78124 -5.20903 -5.12729
C 0.15842 -3.57145 -2.26360
H 1.17316 -3.56924 -1.83560
H -0.38108 -2.71572 -1.44817

2a μ-OH releasing the Mn^{II}-OH bond

96
2a (1/2) This **2a** is different from above as its side-chain locations have been adjusted to correspond to **TS1** and **IM1** to avoid artificial results.
Mn -1.38717 -0.91283 0.04135
O 0.65735 -0.96756 -0.99093
N -1.31653 -3.04448 0.42156
N -2.12345 -3.75117 0.96249
N -2.88967 -4.43902 1.48536
N -2.45023 -1.29673 -1.96003
C -2.29420 -2.46101 -2.61096
H -1.53652 -3.13921 -2.21156
C -3.04820 -2.80137 -3.73204
H -2.88283 -3.75695 -4.23241
C -4.01527 -1.89859 -4.18135
H -4.63827 -2.13414 -5.04732
C -4.17523 -0.68925 -3.50500
H -4.91886 0.04164 -3.82891
C -3.36096 -0.41293 -2.40003
C -3.40282 0.93733 -1.71641
H -2.62899 1.55083 -2.20592
H -4.37274 1.42391 -1.92324
N -2.69123 -0.71071 1.97903
C -2.29780 -1.19158 3.16670
H -1.34060 -1.72001 3.18372
C -3.05227 -1.03421 4.32862
H -2.69292 -1.44148 5.27515
C -4.26399 -0.34446 4.24353
H -4.88315 -0.19483 5.13105
C -4.66977 0.16092 3.00730
H -5.60561 0.71383 2.90575
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H -4.71734 -0.41719 -0.02352
H -5.03703 1.20694 0.59324
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N 0.68826 1.97631 -1.43011
N 0.15863 1.67372 -2.46812
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N 3.27139 0.25966 -1.38416
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H 6.18712 -0.38288 -3.85270
C 5.19922 -1.00284 -2.03159
H 5.88913 -1.82093 -1.81741
C 4.13995 -0.74823 -1.15584
C 3.92182 -1.58156 0.08366
H 3.26529 -2.42924 -0.15172
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C 3.32196 3.70998 3.04100
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H -2.27904 1.99063 1.29974
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H 1.10009 -2.40482 1.30430
O 2.62422 -3.82138 1.53150
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H 2.63512 -4.87348 -0.96477
H 1.13086 -5.80105 -0.76680
O 0.95647 -3.72437 -0.91890
H 0.09597 -3.63927 -0.42706
H 1.68198 4.96640 2.35172
H 0.90070 3.29341 0.70153
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C -1.06619 5.17912 -1.42383
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H -2.96063 5.97131 -0.76601
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O 0.19322 4.77848 -0.92432
H -0.94987 6.08671 -2.04859
H 0.37143 3.84770 -1.17545

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TS1 (1/2)
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N -1.80908 -2.92149 0.36043
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H -3.80283 -3.29990 -4.21208
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C -3.43172 0.09352 -2.44363
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H -2.21351 1.79940 -2.24126
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C -4.73439 0.93130 2.89751
H -5.49697 1.70516 2.79113
C -3.94750 0.57058 1.79852
C -4.16182 1.18510 0.43049
H -4.83841 0.52177 -0.13512
H -4.68837 2.15076 0.53173
N -2.90859 1.30574 -0.32889
C -1.98390 2.32837 0.19858
Mn 1.61386 0.14837 -0.16414
O 0.02913 -0.10485 0.93258
H 0.00613 0.33699 1.79233
N 1.09450 1.87903 -1.41338
N 0.52379 1.72346 -2.46070
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C 4.99738 0.55541 -3.02290
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C 5.76555 -0.58630 -2.78288
H 6.64037 -0.80983 -3.39755
C 5.41011 -1.42879 -1.73035
H 6.00170 -2.31505 -1.49355
C 4.28450 -1.12315 -0.95874
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H 3.19821 -2.79636 -0.15495
H 4.75275 -2.50325 0.62050
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C 3.08434 3.08970 3.47709
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H -0.98191 2.10622 -0.19092
H -1.92947 2.21200 1.29086
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H 0.77337 -2.58793 1.16172
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H 1.93543 -5.03452 -1.28787
H 0.35372 -5.82242 -1.08774
O 0.39084 -3.73323 -1.07202
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H 1.57596 4.46228 2.71508
H 0.98126 2.98328 0.81534
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O -1.19119 4.52520 0.44876
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C 0.14566 5.36204 -1.44826
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H -1.63464 6.27065 -0.61123

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O 1.36070 4.75520 -1.06399
H 0.37300 6.32177 -1.94917
H 1.28019 3.78366 -1.16032

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IM1 (1/2)
Mn -1.95867 -0.72804 0.08473
O 1.38573 -1.37251 -1.39559
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C -4.20666 -2.20074 -3.55010
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H -5.41407 -1.08566 -4.96414
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H -4.80253 1.12796 -3.95374
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H 7.17215 -0.80818 -2.83187
C 5.75007 -1.51316 -1.36276
H 6.31497 -2.40997 -1.10118
C 4.53480 -1.24650 -0.72334
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H 4.79138 -2.71554 0.82642
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Mn -1.41325 -0.91532 0.04703
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H -0.80857 6.12836 -2.04452
H 0.48813 3.87230 -1.16442

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TS1 (1/10)
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H 5.27293 1.22502 -3.81682
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C 5.41689 -1.45722 -1.72206
H 6.00352 -2.34618 -1.48300
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H -0.35462 4.74510 -2.19845
O 1.39553 4.75165 -1.06202
H 0.41603 6.31960 -1.95399
H 1.31314 3.78023 -1.15847

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IM1 (1/10)
Mn -1.96498 -0.73111 0.08319
O 1.37968 -1.36667 -1.40177
N -2.29104 -2.77875 0.61444
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N -2.80649 1.49531 -0.42636
C -1.73300 2.40575 0.01911
Mn 1.76211 -0.09369 -0.20061
O -0.00126 -0.29154 0.68942
H 0.02061 0.01872 1.60591
N 1.31004 1.59060 -1.52123
N 0.72344 1.40718 -2.55421
N 0.15394 1.25205 -3.54836
N 3.81897 -0.14501 -1.02070
C 4.27974 0.73020 -1.92837
H 3.65095 1.60447 -2.10929
C 5.48069 0.53451 -2.60629
H 5.82091 1.27144 -3.33548
C 6.22451 -0.61442 -2.32651
H 7.17047 -0.80401 -2.83887
C 5.75028 -1.51110 -1.36895
H 6.31689 -2.40682 -1.10742
C 4.53491 -1.24682 -0.72885
C 3.97000 -2.17896 0.31714
H 3.33485 -2.93560 -0.16352
H 4.79598 -2.71831 0.81752
N 2.33802 1.25391 1.35404
C 1.97046 3.27612 2.59197
C 2.84326 2.83712 3.58861
H 3.03744 3.44949 4.47200
C 3.46625 1.59834 3.43877
H 4.15895 1.22213 4.19348
C 3.20085 0.82815 2.30291
C 3.93692 -0.46287 2.04480
H 4.83755 -0.20438 1.46652
H 4.30241 -0.88906 2.99402
N 3.13594 -1.44596 1.28571
C 2.43492 -2.34117 2.23786
H 1.97303 -1.69788 3.00191
H 3.17706 -2.97777 2.75915
C 1.33008 -3.21917 1.68152
H 0.73523 -2.06595 -1.14500
C 1.74223 2.45396 1.49235
C -1.81609 3.87882 -0.39022
H -0.78230 2.01358 -0.36495
H -1.67397 2.35457 1.11621
H 0.78590 -3.63949 2.55083
H 0.61457 -2.60927 1.11278
O 1.86034 -4.27637 0.89810
C 0.89753 -5.19154 0.40339
H 0.05675 -5.28293 1.11804
H 1.38458 -6.18016 0.34398
C 0.37365 -4.83843 -0.98412
H 1.21882 -4.80440 -1.69132
H -0.29568 -5.65746 -1.31539
O -0.27353 -3.58324 -1.06586
H -1.01998 -3.51246 -0.41916
H 1.45948 4.23773 2.65576
H 1.07490 2.77625 0.69370
H -2.72959 4.37452 -0.00779
H -1.83043 3.97119 -1.49019
O -0.66130 4.49130 0.15737
C -0.11098 5.57128 -0.58322
C 0.77876 5.12253 -1.74122
H 0.50001 6.14796 0.13008
H -0.90938 6.23963 -0.96032
H 0.18308 4.54831 -2.47658
O 1.91140 4.39678 -1.31688
H 1.12051 6.03520 -2.26414
H 1.70215 3.43858 -1.34000

C-H activation by **2a** with Mn^{III}-OH in dimer

110
IM1 with substrate (1/2)
Mn -2.06689 -0.54355 0.80602
O 1.77566 -0.80943 0.39860
N -1.98973 -1.48269 2.71941
N -2.26646 -1.14497 3.83756
N -2.52434 -0.84109 4.92244
N -2.48144 -2.52608 -0.20964
C -2.49189 -3.68771 0.46606
H -2.19510 -3.63157 1.51572
C -2.86747 -4.89348 -0.12246
H -2.85780 -5.81343 0.46422
C -3.26163 -4.88538 -1.46265
H -3.57369 -5.80780 -1.95768
C -3.26173 -3.67647 -2.15915
H -3.57286 -3.63003 -3.20448
C -2.85633 -2.51001 -1.50157
C -2.75574 -1.18939 -2.23355
H -1.71577 -1.09812 -2.59003
H -3.39753 -1.21858 -3.13172
N -3.88542 0.77443 1.16639
C -4.10914 1.41597 2.32563
H -3.37648 1.26314 3.12220
C -5.21598 2.23770 2.52657
H -5.35766 2.73916 3.48518
C -6.12103 2.40050 1.47519
H -6.99813 3.04141 1.58988
C -5.88539 1.73779 0.27007
H -6.56829 1.84818 -0.57436
C -4.75533 0.92262 0.14941
C -4.48549 0.12678 -1.11106
H -4.92303 -0.87680 -0.97443
H -5.02103 0.58307 -1.96203
N -3.04821 -0.03493 -1.37275
C -2.37926 1.20409 -1.81272
Mn 1.44177 0.92835 0.12553
O -0.43820 0.78528 0.76485
H -0.74540 1.64712 1.08211
N 1.10971 0.74919 -2.01757
N 0.94981 -0.33331 -2.51534
N 0.78616 -1.36427 -3.01191
N 3.62545 1.10533 -0.25463
C 4.17156 1.12003 -1.48060
H 3.47519 1.24962 -2.31180
C 5.54128 0.97035 -1.68561
H 5.94606 0.99007 -2.69865
C 6.36714 0.79924 -0.57176
H 7.44603 0.67738 -0.69176
C 5.79608 0.80161 0.70096
H 6.41282 0.69280 1.59511
C 4.41155 0.95633 0.82710
C 3.73360 0.96118 2.17718
H 3.45946 -0.06530 2.45655
H 4.43826 1.33180 2.94505
N 1.18939 3.04440 0.01098
C 0.04676 4.95788 -0.87779
C 0.61523 5.76769 0.10662
H 0.38571 6.83447 0.15475

C 1.48456 5.19102 1.03221
H 1.95293 5.79147 1.81391
C 1.76215 3.82318 0.95543
C 2.78289 3.18170 1.86162
H 3.75487 3.25970 1.35029
H 2.88670 3.76556 2.79123
N 2.49507 1.75988 2.14844
C 1.72292 1.66591 3.41194
H 0.91771 2.41359 3.35280
H 2.37120 1.95822 4.26154
C 1.06010 0.33825 3.72512
H 1.23402 -1.29504 1.06318
H 2.92239 -2.97235 -0.12849
C 3.01106 -4.05799 -0.32824
C 1.63549 -4.63954 -0.51965
C 1.26227 -5.31209 -1.61640
C 2.17692 -5.56769 -2.78607
C 3.55081 -4.97892 -2.59750
C 3.92242 -4.30566 -1.50056
H 0.91964 -4.47000 0.29142
H 0.24042 -5.70051 -1.69142
H 1.72077 -5.16792 -3.71419
H 4.26707 -5.12055 -3.41465
H 4.93989 -3.90405 -1.43315
H 3.46728 -4.46626 0.59672
H 2.25496 -6.65703 -2.97768
C 0.35665 3.60117 -0.88969
C -2.57273 1.65039 -3.26425
H -1.30144 1.07437 -1.65120
H -2.70217 2.02187 -1.15131
H 0.36219 0.51919 4.56653
H 0.45927 0.00957 2.86564
O 2.01545 -0.64008 4.10364
C 1.46507 -1.88879 4.48763
H 0.46984 -1.74095 4.95033
H 2.12255 -2.31318 5.26601
C 1.38083 -2.89792 3.34766
H 2.39134 -3.07126 2.94378
H 1.02730 -3.85994 3.76864
O 0.57634 -2.49324 2.25407
H -0.33715 -2.25506 2.54776
H -0.63590 5.35701 -1.62912
H -0.06296 2.94731 -1.65370
H -3.63513 1.84249 -3.51183
H -2.21206 0.86887 -3.95568
O -1.81445 2.83939 -3.40012
C -1.30088 3.11037 -4.69644
C -0.01151 2.35263 -5.00828
H -1.09064 4.19199 -4.71929
H -2.05954 2.89730 -5.47451
H -0.20159 1.26211 -5.00594
O 1.04983 2.69211 -4.14336
H 0.28049 2.61401 -6.04231
H 1.05111 2.06954 -3.38549

110
TS2 with substrate (1/2)
Mn -2.18774 -0.67734 0.67822
O 1.70224 -1.22947 0.19394
N -2.17051 -1.89715 2.44499
N -2.43695 -1.69047 3.59666
N -2.68648 -1.51312 4.71182
N -2.62613 -2.48800 -0.63210
C -2.68536 -3.73839 -0.14444
H -2.43646 -3.84987 0.91344
C -3.04823 -4.83116 -0.92893
H -3.07927 -5.83081 -0.49257
C -3.37713 -4.60818 -2.26837
H -3.67688 -5.43689 -2.91394
C -3.32722 -3.30700 -2.76918
H -3.58649 -3.09446 -3.80815
C -2.93711 -2.26386 -1.92172
C -2.78030 -0.84904 -2.43973
H -1.72894 -0.73368 -2.75424
H -3.39443 -0.72424 -3.34942
N -3.98502 0.62336 1.18120
C -4.23779 1.09319 2.41433
H -3.53941 0.80496 3.20429
C -5.33346 1.90594 2.69716
H -5.50018 2.26445 3.71410
C -6.19497 2.24601 1.65161
H -7.06185 2.88616 1.83041
C -5.92886 1.76180 0.37032
H -6.57745 2.01344 -0.47093
C -4.81290 0.94299 0.16864
C -4.51453 0.33326 -1.18603
H -4.98031 -0.66661 -1.21398
H -5.00756 0.92515 -1.97716
N -3.07269 0.17030 -1.42283
C -2.35976 1.44336 -1.64160
Mn 1.44105 0.72437 0.18309
O -0.51352 0.52864 0.82221
H -0.76551 1.33434 1.29635
N 1.18315 0.94360 -1.97369
N 0.92144 0.02983 -2.70586
N 0.65827 -0.83666 -3.42809
N 3.74490 0.78517 -0.10822
C 4.35357 0.92690 -1.29436
H 3.70625 1.19816 -2.13252
C 5.72504 0.73851 -1.45915
H 6.18176 0.86814 -2.44176
C 6.48552 0.38645 -0.34103
H 7.56337 0.23022 -0.42711
C 5.85077 0.25119 0.89432
H 6.41741 -0.00295 1.79236
C 4.46859 0.45907 0.97631
C 3.72674 0.31857 2.28753
H 3.38212 -0.71850 2.40440
H 4.41909 0.52479 3.12592
N 1.27797 2.94919 0.50279
C 0.14683 5.03142 0.12532
C 0.75427 5.57810 1.25683
H 0.54446 6.60576 1.56236
C 1.63787 4.78920 1.99493
H 2.13637 5.18330 2.88248
C 1.88644 3.47551 1.58442
C 2.91827 2.61506 2.27550
H 3.84983 2.70940 1.69723
H 3.14006 3.01810 3.27887
N 2.53775 1.18819 2.34371
C 1.73378 0.96992 3.56995
H 0.98048 1.77166 3.60479
H 2.37777 1.09648 4.46327
C 0.97598 -0.33895 3.68578
H 1.12650 -1.73084 0.82531
H 2.38859 -2.28084 -0.27411
C 2.94225 -3.36988 -0.64760
C 1.86388 -4.17761 -1.24415
C 1.75776 -4.37049 -2.57587
C 2.75341 -3.82258 -3.55777
C 3.93379 -3.16257 -2.90499
C 4.02217 -2.97992 -1.56971
H 1.10747 -4.58944 -0.56910
H 0.92114 -4.95027 -2.97907
H 2.24667 -3.09468 -4.22565
H 4.75009 -2.83336 -3.55613
H 4.90948 -2.49880 -1.14634
H 3.28599 -3.71719 0.34012
H 3.09453 -4.62134 -4.24720
C 0.43392 3.71011 -0.21482
C -2.51293 2.13446 -2.99853
H -1.28981 1.26086 -1.47901
H -2.67691 2.15006 -0.86020
H 0.26533 -0.22454 4.52821
H 0.38091 -0.50686 2.77625
O 1.85189 -1.42395 3.95194
C 1.20506 -2.66288 4.18783
H 0.21019 -2.49340 4.64336
H 1.80854 -3.21627 4.92833
C 1.08329 -3.53372 2.94232
H 2.09197 -3.74381 2.55161
H 0.64156 -4.50424 3.24298
O 0.35352 -2.94895 1.87801
H -0.55528 -2.68602 2.16990
H -0.54567 5.60931 -0.48880
H -0.01516 3.25867 -1.10184
H -3.56903 2.36614 -3.23986
H -2.12825 1.48704 -3.80632
O -1.75987 3.32990 -2.89748
C -1.21605 3.83578 -4.10714
C 0.08915 3.15588 -4.51684
H -1.01724 4.90483 -3.92666
H -1.95121 3.76442 -4.93240
H -0.08995 2.08296 -4.72035
O 1.12306 3.33432 -3.57387
H 0.40404 3.60497 -5.47755
H 1.13974 2.55775 -2.97449

110
IM2 with substrate (1/2)
Mn -2.08517 -0.82296 0.68182
O 1.71929 -1.23797 0.34656
N -1.96194 -1.96688 2.51381
N -2.29124 -1.74399 3.64601
N -2.59825 -1.54703 4.74358
N -2.46315 -2.70282 -0.54182
C -2.41164 -3.93470 -0.00843
H -2.10601 -3.98829 1.03927
C -2.73345 -5.07886 -0.73538
H -2.67421 -6.06102 -0.26359
C -3.13862 -4.92981 -2.06423
H -3.40943 -5.80098 -2.66518
C -3.20255 -3.64836 -2.61226
H -3.52354 -3.49436 -3.64431
C -2.84767 -2.54907 -1.82197
C -2.81356 -1.14733 -2.39613
H -1.78716 -0.97144 -2.76200
H -3.47353 -1.10056 -3.28108
N -3.95345 0.38540 1.22274
C -4.17889 0.89704 2.44418
H -3.42792 0.69055 3.21095
C -5.30995 1.65337 2.74477
H -5.45169 2.04839 3.75196
C -6.23900 1.89009 1.72915
H -7.13596 2.48303 1.92197
C -6.00102 1.36430 0.45873
H -6.70171 1.53675 -0.36041
C -4.84526 0.60749 0.23894
C -4.56856 -0.04028 -1.10246
H -4.96149 -1.07072 -1.06576
H -5.14064 0.47933 -1.89142
N -3.13220 -0.11238 -1.40434
C -2.51820 1.19671 -1.69628
Mn 1.36092 0.92084 0.04511
O -0.59146 0.57227 0.76699
H -0.93007 1.37639 1.18525
N 1.09481 0.92258 -2.12801
N 0.83075 -0.01942 -2.82015
N 0.56454 -0.91497 -3.50739
N 3.69247 0.92056 -0.22843
C 4.30144 0.93776 -1.42366
H 3.64404 1.05055 -2.29010
C 5.68335 0.82011 -1.56517
H 6.13673 0.84039 -2.55764
C 6.45828 0.68260 -0.41072
H 7.54500 0.59137 -0.47648
C 5.82477 0.67768 0.83242
H 6.40119 0.58997 1.75555
C 4.43052 0.79683 0.88872
C 3.69478 0.76505 2.21068
H 3.40808 -0.27158 2.43839
H 4.37843 1.09007 3.01870
N 1.03844 3.20431 0.31764
C -0.27471 5.18511 -0.01469
C 0.33734 5.78686 1.08599
H 0.05937 6.79677 1.39659
C 1.31400 5.07672 1.78710
H 1.81740 5.51613 2.65044
C 1.64736 3.78410 1.36909
C 2.76842 3.00373 2.02053
H 3.64827 3.09852 1.36550
H 3.04642 3.47166 2.98209
N 2.46165 1.56972 2.19125
C 1.65925 1.39315 3.42331
H 0.85121 2.13957 3.38866
H 2.27836 1.63382 4.31149
C 0.99319 0.04511 3.63761
H 1.29705 -1.83272 1.02680
H 2.45430 -1.74607 -0.03144
C 3.73346 -3.77646 -0.53212
C 2.44525 -4.26000 -0.90074
C 2.03048 -4.25674 -2.20690
C 2.89210 -3.72810 -3.31585
C 4.24460 -3.26495 -2.85902
C 4.61557 -3.29196 -1.54003
H 1.77387 -4.62827 -0.11985
H 1.03573 -4.62952 -2.46804
H 2.35875 -2.89303 -3.82393
H 4.93816 -2.88910 -3.61706
H 5.60944 -2.93786 -1.25091
H 4.05535 -3.80717 0.51128
H 2.99503 -4.48596 -4.12350
C 0.10450 3.88801 -0.36281
C -2.78300 1.83071 -3.06342
H -1.43179 1.09446 -1.57700
H -2.84696 1.90682 -0.92305
H 0.25242 0.18036 4.45025
H 0.43820 -0.24559 2.73317
O 1.93713 -0.94421 4.02416
C 1.37898 -2.18944 4.40626
H 0.35508 -2.04608 4.80202
H 1.99051 -2.58895 5.23439
C 1.38099 -3.22885 3.29135
H 2.41674 -3.39676 2.95497
H 1.01293 -4.18521 3.71027
O 0.63890 -2.86696 2.13713
H -0.30066 -2.63424 2.36181
H -1.03826 5.70308 -0.59761
H -0.34329 3.39378 -1.22904
H -3.86409 1.95981 -3.26785
H -2.37233 1.19585 -3.86828
O -2.13899 3.09198 -3.02529
C -1.63894 3.58260 -4.25916
C -0.28368 2.99210 -4.64343
H -1.52776 4.67167 -4.12996
H -2.36606 3.41364 -5.07743
H -0.37578 1.89988 -4.79305
O 0.73184 3.29781 -3.71312
H -0.00958 3.41747 -5.62776
H 0.85772 2.52582 -3.12061

110
IM1 with substrate (1/10)
Mn -2.08136 -0.41185 0.82510
O 1.70881 -0.92746 0.42807
N -2.05729 -1.31836 2.75995
N -2.32748 -0.93097 3.86391
N -2.57954 -0.57988 4.93560
N -2.70127 -2.37129 -0.13180
C -2.82660 -3.50774 0.57419
H -2.52974 -3.45125 1.62401
C -3.31484 -4.68651 0.01423
H -3.39728 -5.58744 0.62427
C -3.70024 -4.67564 -1.32858
H -4.09796 -5.57636 -1.80167
C -3.58025 -3.49131 -2.05643
H -3.88067 -3.44255 -3.10476
C -3.06668 -2.35282 -1.42625
C -2.83687 -1.06605 -2.18834
H -1.79051 -1.07888 -2.53830
H -3.47309 -1.05644 -3.09103
N -3.76700 1.09587 1.15909
C -3.92323 1.79798 2.29393
H -3.20147 1.60817 3.09271
C -4.94893 2.72463 2.46794
H -5.03697 3.27247 3.40740
C -5.84308 2.93014 1.41480
H -6.65690 3.65274 1.50840
C -5.67809 2.20340 0.23504
H -6.35407 2.34379 -0.61053
C -4.62825 1.28412 0.14127
C -4.44160 0.42030 -1.08918
H -4.95918 -0.53745 -0.91031
H -4.94757 0.88774 -1.95196
N -3.02509 0.13109 -1.35647
C -2.26160 1.29849 -1.83717
Mn 1.50901 0.82525 0.11653
O -0.38137 0.83098 0.75235
H -0.63432 1.72165 1.03626
N 1.17223 0.62049 -2.02926
N 0.93380 -0.45703 -2.50547
N 0.69556 -1.48300 -2.98228
N 3.69681 0.83430 -0.26073
C 4.24261 0.78168 -1.48601
H 3.55641 0.93834 -2.32092
C 5.59874 0.53361 -1.68534
H 6.00343 0.50076 -2.69807
C 6.41124 0.33376 -0.56657
H 7.47922 0.13525 -0.68187
C 5.84202 0.40695 0.70480
H 6.45055 0.27850 1.60195
C 4.47137 0.65912 0.82567
C 3.79671 0.74419 2.17475
H 3.45091 -0.25340 2.47836
H 4.52696 1.08166 2.93401
N 1.40945 2.95085 -0.04713
C 0.41439 4.92047 -0.98908
C 1.03912 5.71073 -0.02297
H 0.88960 6.79251 -0.00294
C 1.86076 5.09494 0.92065
H 2.37113 5.67863 1.68870
C 2.03625 3.70869 0.87979
C 3.00547 3.01852 1.80720
H 3.98311 3.01686 1.30046
H 3.14524 3.61633 2.72324
N 2.61842 1.62802 2.12591
C 1.83841 1.61643 3.38766
H 1.08426 2.41363 3.30687
H 2.50171 1.88581 4.23328
C 1.08842 0.34315 3.72926
H 1.14713 -1.35907 1.11295
H 2.71656 -3.16331 -0.14831
C 2.71810 -4.25201 -0.35285
C 1.29604 -4.73806 -0.44646
C 0.80016 -5.37466 -1.51571
C 1.60889 -5.68101 -2.74940
C 3.03094 -5.19232 -2.65641
C 3.52539 -4.55514 -1.58679
H 0.65211 -4.52537 0.41339
H -0.24869 -5.69191 -1.51846
H 1.11738 -5.23935 -3.63970
H 3.67638 -5.37813 -3.52227
H 4.57105 -4.22702 -1.59010
H 3.21007 -4.69348 0.53782
H 1.59561 -6.77087 -2.95300
C 0.62254 3.54464 -0.96540
C -2.42972 1.71752 -3.29986
H -1.19645 1.08929 -1.67663
H -2.51369 2.15887 -1.19967
H 0.39988 0.58985 4.56160
H 0.47132 0.03290 2.87447
O 1.97629 -0.68540 4.13771
C 1.34454 -1.88553 4.55035
H 0.35897 -1.66164 5.00297
H 1.96975 -2.33090 5.34350
C 1.20034 -2.91653 3.43616
H 2.19959 -3.16479 3.04320
H 0.78440 -3.84270 3.88005
O 0.42782 -2.48989 2.32844
H -0.47213 -2.19108 2.61029
H -0.23453 5.35025 -1.75329
H 0.15705 2.90414 -1.71421
H -3.47760 1.97400 -3.55123
H -2.12394 0.89621 -3.97144
O -1.59429 2.84956 -3.46657
C -1.06787 3.05503 -4.76969
C 0.17167 2.21124 -5.06171
H -0.79117 4.12064 -4.82043
H -1.83976 2.86952 -5.54174
H -0.08614 1.13505 -5.03311
O 1.25232 2.50466 -4.20387
H 0.47946 2.42891 -6.10123
H 1.20890 1.90714 -3.42718

110
TS2 with substrate (1/10)
Mn -2.19959 -0.67204 0.68065
O 1.70800 -1.23850 0.19422
N -2.17853 -1.89072 2.44716
N -2.44037 -1.68231 3.59965
N -2.68545 -1.50342 4.71547
N -2.65355 -2.47774 -0.62668
C -2.72397 -3.72706 -0.13756
H -2.48296 -3.83821 0.92224
C -3.08796 -4.81861 -0.92312
H -3.12833 -5.81744 -0.48565
C -3.40569 -4.59552 -2.26525
H -3.70571 -5.42333 -2.91186
C -3.34436 -3.29540 -2.76754
H -3.59490 -3.08280 -3.80863
C -2.95405 -2.25339 -1.91881
C -2.78603 -0.84008 -2.43757
H -1.73320 -0.73151 -2.74968
H -3.39714 -0.71172 -3.34882
N -3.99171 0.63337 1.18105
C -4.24510 1.10139 2.41480
H -3.55118 0.80629 3.20615
C -5.33613 1.92071 2.69650
H -5.50366 2.27737 3.71395
C -6.19193 2.26976 1.64920
H -7.05495 2.91533 1.82713
C -5.92508 1.78747 0.36736
H -6.56922 2.04600 -0.47523
C -4.81417 0.96160 0.16680
C -4.51596 0.35336 -1.18850
H -4.98833 -0.64326 -1.22020
H -5.00274 0.95043 -1.97954
N -3.07450 0.18160 -1.42183
C -2.35388 1.45056 -1.63968
Mn 1.45602 0.71695 0.17998
O -0.50721 0.52105 0.81525
H -0.75235 1.32790 1.29140
N 1.19527 0.94342 -1.97829
N 0.92326 0.03464 -2.71280
N 0.65030 -0.82692 -3.43745
N 3.75430 0.77043 -0.10615
C 4.36344 0.91075 -1.29234
H 3.71636 1.18104 -2.13097
C 5.73491 0.72204 -1.45633
H 6.19192 0.85044 -2.43895
C 6.49495 0.37128 -0.33754
H 7.57281 0.21486 -0.42301
C 5.85974 0.23766 0.89774
H 6.42607 -0.01530 1.79630
C 4.47760 0.44563 0.97930
C 3.73581 0.30670 2.29070
H 3.38828 -0.72952 2.40691
H 4.42928 0.51036 3.12883
N 1.29249 2.94210 0.50631
C 0.16223 5.02524 0.13100
C 0.76965 5.57037 1.26326
H 0.56016 6.59774 1.56996
C 1.65285 4.78027 2.00056
H 2.15135 5.17317 2.88866
C 1.90100 3.46693 1.58868
C 2.93209 2.60515 2.27950
H 3.86364 2.69822 1.70092
H 3.15473 3.00818 3.28274
N 2.54935 1.17928 2.34746
C 1.74339 0.96146 3.57218
H 0.99318 1.76606 3.60809
H 2.38663 1.08324 4.46677
C 0.97986 -0.34454 3.68349
H 1.12691 -1.73602 0.82356
H 2.38427 -2.29062 -0.27652

C 2.93273 -3.38368 -0.65438
C 1.84923 -4.18462 -1.25038
C 1.73868 -4.37323 -2.58239
C 2.73413 -3.82670 -3.56543
C 3.91940 -3.17430 -2.91362
C 4.01203 -2.99625 -1.57794
H 1.09259 -4.59495 -0.57464
H 0.89825 -4.94787 -2.98504
H 2.22889 -3.09430 -4.22955
H 4.73553 -2.84680 -3.56584
H 4.90276 -2.52066 -1.15545
H 3.27673 -3.73415 0.33209
H 3.06964 -4.62476 -4.25844
C 0.44897 3.70423 -0.21064
C -2.49999 2.14159 -2.99740
H -1.28549 1.26240 -1.47342
H -2.66962 2.15956 -0.85976
H 0.26866 -0.22955 4.52537
H 0.38537 -0.50734 2.77256
O 1.85086 -1.43402 3.94780
C 1.19848 -2.67022 4.18258
H 0.20487 -2.49666 4.63933
H 1.80009 -3.22742 4.92176
C 1.07130 -3.53900 2.93617
H 2.07855 -3.75321 2.54401
H 0.62556 -4.50788 3.23624
O 0.34302 -2.94974 1.87334
H -0.56452 -2.68430 2.16632
H -0.52992 5.60410 -0.48260
H 0.00016 3.25406 -1.09846
H -3.55453 2.37645 -3.24257
H -2.11447 1.49273 -3.80366
O -1.74356 3.33459 -2.89378
C -1.20023 3.84274 -4.10272
C 0.10407 3.16262 -4.51482
H -1.00032 4.91121 -3.92004
H -1.93611 3.77382 -4.92755
H -0.07601 2.09026 -4.72035
O 1.13883 3.33840 -3.57228
H 0.41855 3.61343 -5.47487
H 1.15541 2.56047 -2.97463

110
IM2 with substrate (1/10)
Mn -2.12542 -0.76458 0.79555
O 1.72255 -1.23926 0.37244
N -1.95820 -1.81123 2.67590
N -2.25587 -1.52534 3.80293
N -2.53238 -1.26785 4.89593
N -2.47567 -2.71137 -0.32842
C -2.39916 -3.91262 0.26849
H -2.08786 -3.90583 1.31583
C -2.70192 -5.09919 -0.39585
H -2.62193 -6.05391 0.12650
C -3.11528 -5.02790 -1.72862
H -3.37178 -5.93435 -2.28178
C -3.20512 -3.77847 -2.34274
H -3.53230 -3.68492 -3.38010
C -2.86739 -2.63277 -1.61307
C -2.85665 -1.26434 -2.26298
H -1.83613 -1.09929 -2.64920
H -3.52529 -1.27351 -3.14249
N -4.01336 0.44023 1.27422
C -4.24591 1.00726 2.46944
H -3.49904 0.83752 3.24918
C -5.38013 1.77439 2.72795
H -5.52894 2.21495 3.71503
C -6.30289 1.96294 1.69655
H -7.20162 2.56300 1.85621
C -6.05681 1.37941 0.45309
H -6.75277 1.51303 -0.37728
C -4.89918 0.61443 0.27562
C -4.61523 -0.09794 -1.03100
H -5.00252 -1.12736 -0.94236
H -5.18889 0.37718 -1.84621
N -3.17766 -0.17844 -1.32761
C -2.57252 1.11471 -1.69973
Mn 1.37169 0.89636 -0.05946
O -0.57950 0.58388 0.71289
H -0.88898 1.42020 1.08959
N 1.06204 0.77860 -2.22339
N 0.78227 -0.20356 -2.85071
N 0.50114 -1.13919 -3.47570
N 3.69412 0.88135 -0.36190
C 4.28491 0.83329 -1.56540
H 3.61326 0.88512 -2.42670
C 5.66609 0.72505 -1.72094
H 6.10445 0.69097 -2.71975
C 6.45979 0.66801 -0.57258
H 7.54661 0.58736 -0.64954
C 5.84484 0.73020 0.67843
H 6.43605 0.70644 1.59602
C 4.45023 0.83498 0.74939
C 3.73408 0.87633 2.08179
H 3.45027 -0.14580 2.37071
H 4.42948 1.24498 2.86047
N 1.03997 3.19176 0.09318
C -0.28755 5.14489 -0.33381
C 0.34324 5.81477 0.71569
H 0.06720 6.84094 0.96952
C 1.33655 5.15178 1.43932
H 1.85502 5.64485 2.26388
C 1.66691 3.83692 1.09486
C 2.80245 3.10019 1.77136
H 3.66965 3.15542 1.09528
H 3.09733 3.62655 2.69703
N 2.50072 1.67951 2.03514
C 1.72063 1.57956 3.28983
H 0.91464 2.32636 3.22670
H 2.35683 1.86927 4.15090
C 1.05302 0.25009 3.59441
H 1.29284 -1.77965 1.09192
H 2.47020 -1.76866 0.05305
C 3.75936 -3.81729 -0.29788
C 2.48604 -4.35412 -0.64386
C 2.06758 -4.41120 -1.94744
C 2.90908 -3.89668 -3.07840
C 4.24678 -3.37309 -2.64370
C 4.62241 -3.34123 -1.32596
H 1.82905 -4.71601 0.15206
H 1.08436 -4.82434 -2.19088
H 2.34797 -3.10011 -3.61769
H 4.92568 -3.00227 -3.41729
H 5.60499 -2.94485 -1.05370
H 4.08449 -3.79947 0.74475
H 3.03555 -4.68134 -3.85667
C 0.09060 3.83019 -0.60957
C -2.84354 1.65889 -3.10395
H -1.48556 1.02345 -1.57730
H -2.90353 1.86896 -0.97019
H 0.32908 0.43587 4.41230
H 0.47951 -0.08846 2.71860
O 1.99994 -0.72069 4.01844
C 1.44329 -1.93713 4.48542
H 0.43228 -1.76167 4.90100
H 2.07504 -2.29505 5.31735
C 1.40482 -3.03739 3.43115
H 2.42945 -3.23572 3.07763
H 1.03867 -3.96456 3.91271
O 0.63604 -2.73162 2.27826
H -0.29568 -2.48056 2.51414
H -1.06461 5.62346 -0.93234
H -0.37125 3.28359 -1.43589
H -3.92513 1.78401 -3.30851
H -2.44551 0.96717 -3.86719
O -2.18764 2.91318 -3.15754
C -1.71827 3.32270 -4.43264
C -0.37727 2.69957 -4.81541
H -1.59763 4.41688 -4.37504
H -2.46833 3.10805 -5.21888
H -0.47894 1.60069 -4.89232
O 0.66509 3.05716 -3.93468
H -0.12879 3.05936 -5.83223
H 0.80661 2.32136 -3.30097