Supporting Information for

A Bio-inspired Mononuclear Manganese Catalyst for Electrochemical Hydrogen Production with High Rate

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4. Crystallographic Structure Determinations

The single-crystal X-ray diffraction data were collected with an Bruker Smart Apex II CCD diffractometer with agraphite-monochromated Mo-*K* radiation (= 0.071073 Å) at 196 K using the $\omega - 2\theta$ scan mode. Data processing was accomplished with the SAINT processing program [S1]. Intensity data were corrected for absorption by the SADABS program [S2]. All structures were solved by direct methods and refined on F^2 against full-matrix least-squares methods by using the SHELXTL 2014 program package [S3]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located by geometrical calculation. Crystallographic data and selected bond lengths and angles for **2** are listed below. CCDC-2036461 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

S1 G. M. Sheldrick, SHELXTL97 Program for the Refinement of Crystal Structure, University of Göttingen, Germany, 1997.

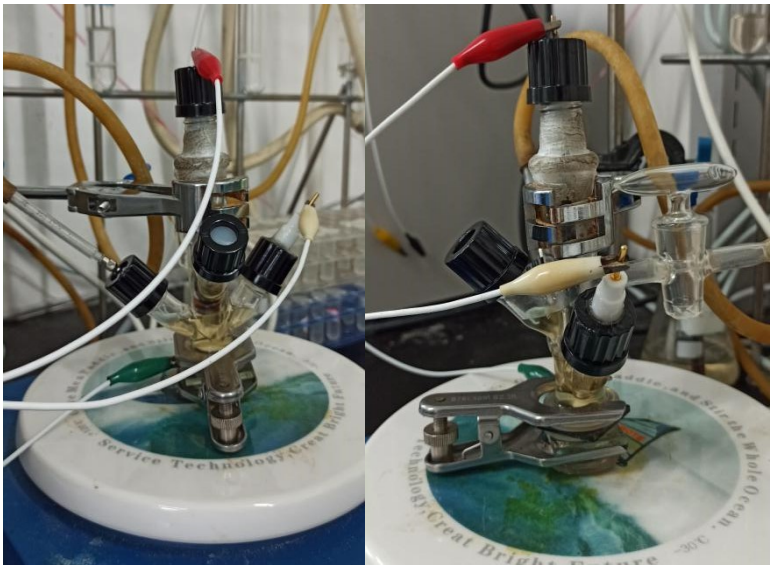
S2 Software packages SMART and SAINT, Siemens Energy & Automation Inc., Madison, Wisconsin, 1996.

S3 G. M. Sheldrick, SADABS Absorption Correction Program, University of Göttingen, Germany, 1996.

5. Electrochemistry Study Details

CV measurements in CH_3CN. Cyclic voltammetry experiments were carried out in a three-electrode cell under high-purity Ar using CHI 760E potentiostat. The working electrode was a glassy carbon disc (diameter 3 mm) polished with 0.5 mm diamond pastes, then sonicated in ion-free water for 15 min and washed with MeCN prior to use. The reference electrode was a Ag^+/Ag electrode (0.01 M $AgNO_3$ in CH_3CN) and the counter electrode was platinum wire. A solution of 0.1 M $^nBu_4NPF_6$ (Fluka, electrochemical grade) in CH_3CN/DMF (5:1, **All of the electrochemistry studies were performed in this mixture solution, owing to the poor solubility of complex 1 in pure CH_3CN**.) was used as supporting electrolyte, which was degassed by bubbling with dry Ar for 5 min before measurement. The ferricinium/ferrocene ($Fc^{+/0}$) couple was used as an internal reference and ***all potentials given in this work are referred to $Fc^{+/0}$***.

Controlled potential electrolysis experiments (CPE). Controlled potential electrolysis experiments were carried out in a custom 18 mL cell designed in our laboratory. The setup included a carbon plate working electrode, graphite rod counter electrode separated from the solution by a porous glass frit, and $Ag/AgNO_3$ pseudoreference electrode. For the catalytic electrolysis studies, the cell was charged with Mn catalyst (0.2 mM) and anilinium tetrafluoroborate (0.2 M) in 0.1 M tetra-n-butylammonium hexafluorophosphate solution CH_3CN/DMF (5:1). Hydrogen evolution was quantified by analyzing 50 μL aliquots of the headspace on a Beifen 6890A Series gas chromatograph. The partial pressure of H_2 in the headspace was determined by comparison to gas standard samples. Henry's Law was used to calculate the total H_2 production, given as the sum of headspace and dissolved hydrogen.

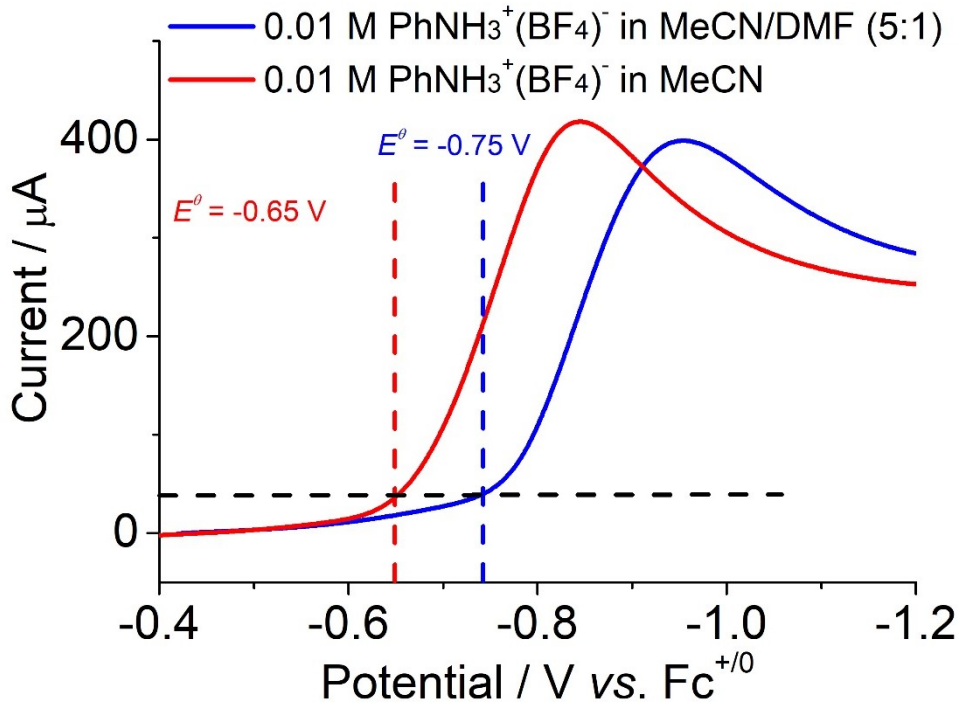


Typical Experimental Conditions:

Purity of the electrolyte medium was confirmed over the available electrochemical window through background scans taken prior to addition of analyte. 1.03 mg (0.0016 mmol) of **1** and 0.288 g (160 mmol) of anilinium tetrafluoroborate were weighed into an 18 mL glass vial and dissolved in 8 mL of a supporting electrolyte solution (0.1 M [^{n}Bu$_4$N][PF$_6$] / CH$_3$CN/DMF (5:1)).

6. Determination of the Standard Potentials for the H_2 Evolution Half Reaction with anilinium tetrafluoroborate in CH_3CN /DMF (5:1) Mixture Solution

The standard potentials is roughly estimated by linear sweep voltammograms for 0.01 M anilinium tetrafluoroborate in pure CH_3CN and CH_3CN/DMF mixture (5:1) solution with **Pt working electrode** (Inorg. Chem. **2006**, 45, 9181-9184). As shown in below, the standard potentials the H_2 Evolution Half Reaction with anilinium tetrafluoroborate in pure CH_3CN is –0.65 V vs. $Fc^{+/0}$ (Inorg. Chem. **2010,** 49, 10338–10347). The mixture solution CH_3CN/DMF (5:1) results in the standard potentials cathodic shifting to –0.75 V vs. $Fc^{+/0}$, about –0.1 V versus that in pure CH_3CN.



Condition: Pt wire working electrode, 25°C, scan rate, 100 mV/s, 0.1 M ^{n}Bu$_4$NPF$_6$ as supporting electrolyte.

7. Gas Analysis

Gas analysis for bulk electrolysis experiments were performed using 50 μL sample injections on a Beifen 6890A series gas chromatograph. Gas sample H_2 was analyzed using thermal conductivity detector (TCD), stainless-steel column packed with molecular sieves (5 Å ×3 m), and Ar as the carrier gas (flow rate = 30 mL min^{-1}). Gas chromatography calibration curves were made by sampling known volumes of H_2 gas. The operating temperatures of the injection port, the oven/column, and detector were 50°C, 50°C and 180°C, respectively. Aliquots (50 μL) of the gas headspace were injected into the GC every time to analyze the gas products formed.

8. Determination of Faradaic Efficiency

Gas chromatographic analysis (Beifen 6890A) of the electrolysis-cell headspace was made following controlled potential electrolysis experiments. The amount of hydrogen generated was determined by the external standard method metioned above.

Calculation for Faradaic Efficiency.

$$Faradaic\ yieldp\ roduct\ (\%) = 100 \times n_{prod} / (Q / F / 2)$$

Where F is the Faraday constant (C mol^{-1}), n_{prod} (mol) is the amount of H_2 in the headspace determined by GC, and Q (C) is the charged passed during electrolysis (Fig. S15).

9. Experiment Section

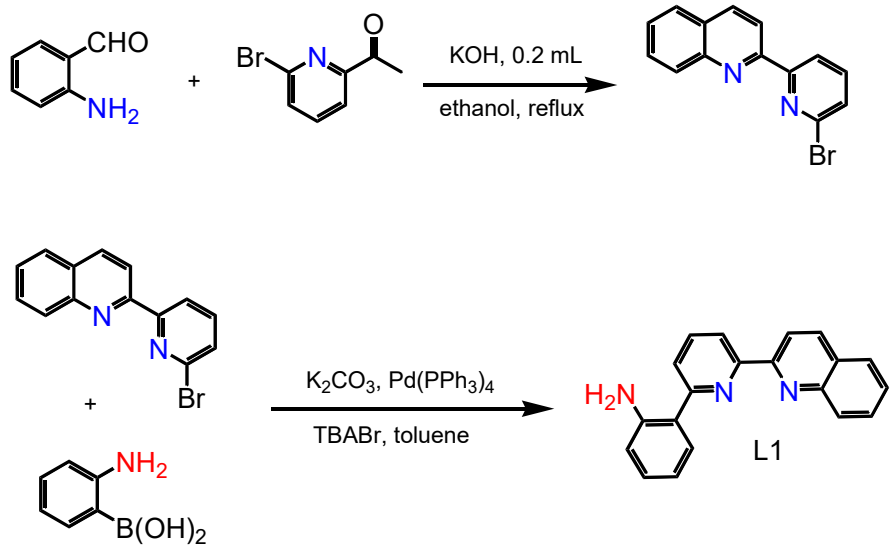
Materials and Instruments

All manipulations for preparation and handling of organometallic complexes were carried out under air. All the solvents were used as received. Other commercially available chemicals such as $Mn(CO)_5Br$, 2-aminobenzaldehyde, 1-(6-bromopyridin-2-yl)ethanone, benzoyl chloride, 2-aminephenylboronic acid, $Pd(PPh_3)_4$ were purchased from local suppliers and used as received. Water was deionized with the Millipore Milli-Q UF Plus system. Glass carbon disc (3 mm), Ag^+/Ag electrode and platinum wire were purchased from CHI for electrochemical studies.

NMR Spectra were collected with a varian INOVA 600 NMR spectrometer. Mass spectra were recorded with HP 1100 HPL/ESI-DAD-MS and Waters/Micromass LC/Q-TOF-MS instruments. Elemental analyses were performed with a Thermoquest-Flash EA 1112 elemental analyzer.Synthesis.

Spectroelectrochemical experiments were carried out using an Tensor 227 FTIR spectrometer (Bruker). A model CHI 760E potentiostat was used to control electrode potential. The SEC experiments were performed by using a purpose-designed three-neck cell in Ar saturated CH_3CN/DMF (5:1) mixed solution. The working electrode was a glassy carbon disk of 10 mm in diameter, the counter electrode was a platinum foil. The Ag^+/Ag reference electrode was put into the SEC cell, which contains the target complex and 0.1 M $^n Bu_4NPF_6$ in CH_3CN. The IR-SEC spectra were collected in single beam mode at 4 cm^{-1}.

1) Preparation of L1.



Scheme S 1 Preparation of target ligands **L1**.

a) Preparation of **L1a. L1a** was obtained according to literature procedures (Bera, J. K. *et. al. Inorg. Chem*., **2006**, *45 (10)*, 4007–4015).

L1 was obtained according to literature procedures (Solan, G. A. *et. al. Organometallics* **2013***, 32,* 249−259). The product L1 was obtained as a pale yellow solid (80%). ^{1}H NMR (600 MHz, DMSO) δ 8.57 (d, 1H), 8.49 (d, 1H), 8.45 (d, 1H), 8.15 (d, 1H), 8.10 (t, 1H), 8.06 (d, 1H), 7.90 (d, 1H), 7.84 (t, 1H), 7.67 (t, 1H), 7.62 (d, 1H), 7.16 (t, 1H), 6.85 (d, 1H), 6.69 (t, 1H), 6.57 (s, 2H).ESI-MS: Calcd for $[M+H]^{+}$: *m*/*z* 298.16; found: 298.15.

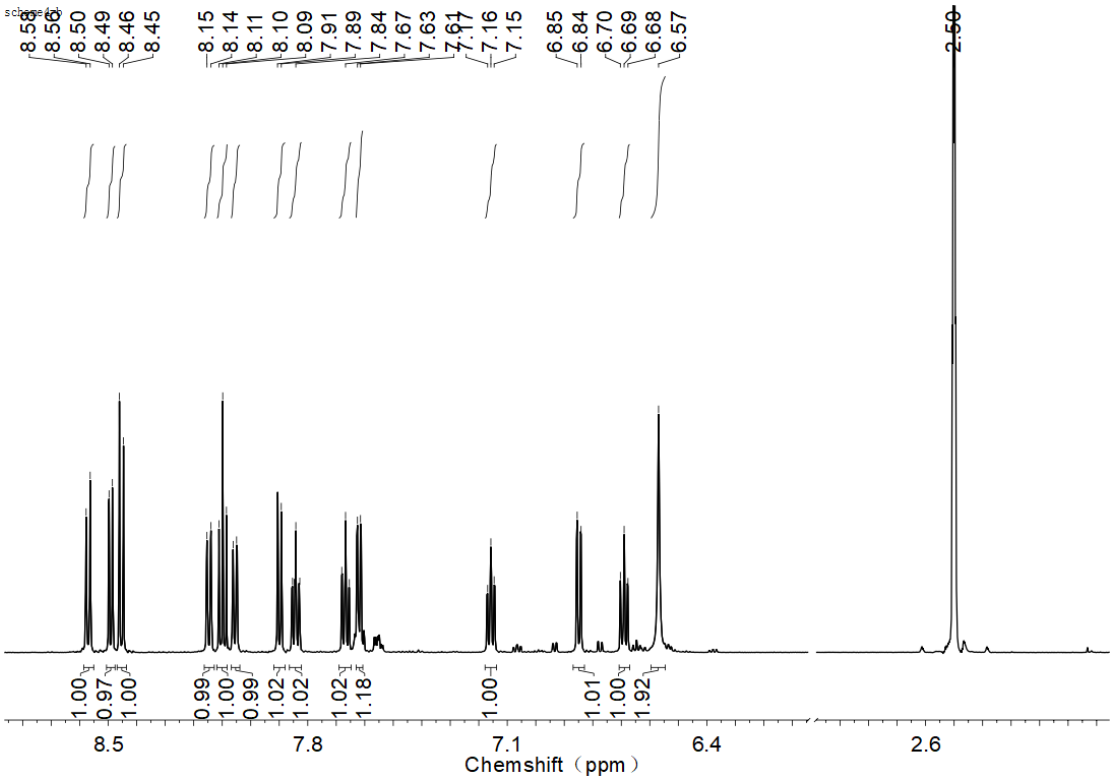
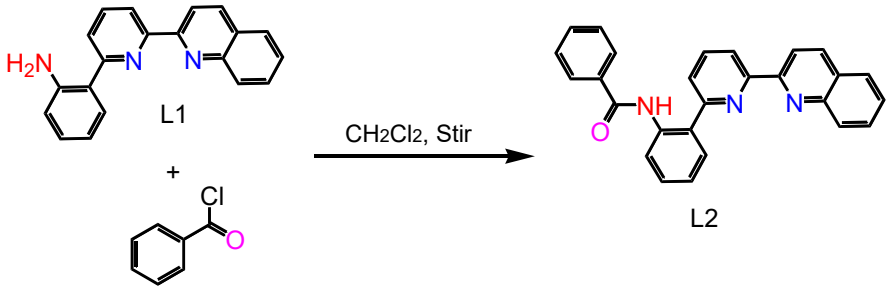


Figure S 1 ^{1}H NMR spectrum of **L1**.

2) Preparation of L2.



Scheme S 2 Preparation of target ligands **L2.**

Excess benzoyl chloride was slowly added to the 100 mL CH_2Cl_2 solution of **L1** (5 mmol). The resulted mixture was stirred under room temperature for 1 hour followed by addition of excess triethylamine. After stirring for another 2 hours, the reaction was terminated by addition of 100 mL water. The organic layer was washed with water for three times and collected. Following drying with anhydrous sodium sulfate, the volatiles were removed under reduced pressure to give an orange-brown residue. The residues were purified using a short silica gel column employing dichloromethane/methanol ether (100/5) as eluting solvent. After the solvent was removed under reduced pressure, The product **L2** was obtained as a pale yellow solid (96%). ^{1}H NMR (600 MHz, DMSO) δ 11.78 (s, 1H), 8.54 (d, Hz, 1H), 8.45 (q, Hz, 2H), 8.29 (d, 1H), 8.20 (t, 1H), 8.16 (d, 1H), 8.08 (d, 1H), 7.99 (d, 1H), 7.90 (d, 1H), 7.86 (t, 1H), 7.70 (t, 3H), 7.56 (t, 2H), 7.38 (t, 1H), 7.26 (t, 1H), 6.98 (t, 2H). ESI-MS: Calcd for $[M+H]^+$: *m/z* 402.16; found: 402.15.

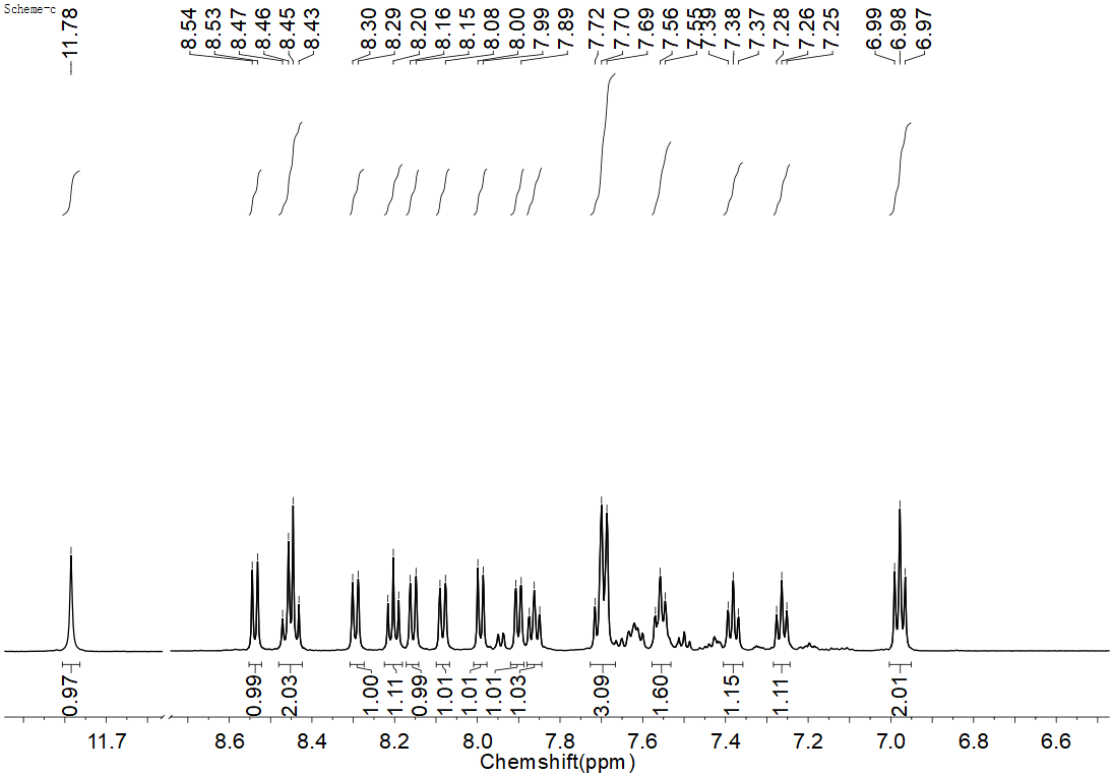
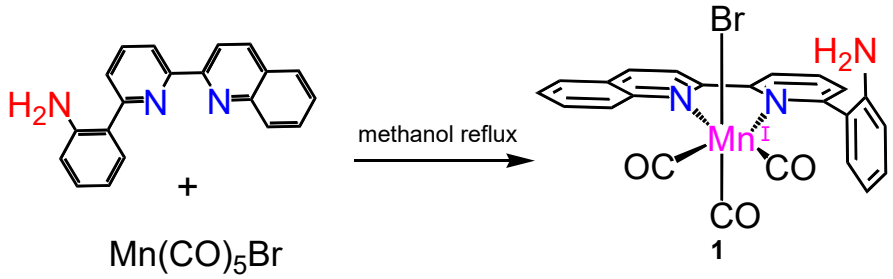


Figure S 2 ^{1}H NMR spectrum of **L2**.

3) Preparation of [Mn(L1)(CO)3]Br (1).



Scheme S 3 Preparation of target complex **1**.

$Mn(CO)_5Br$ (100 mg, 0.36 mmol) was added to 5 mL methanol under argon atmosphere. Ligand **L1** (107 mg, 0.36 mmol) was added to the mixture and heated to reflux. The solution turned orange within 30 min, and the product precipitated out of solution. The mixture was cooled to room temperature, and the precipitate was filtered off and washed with methanol. The orange solid was dried overnight under vacuum. The yield of $[Mn(L^1)(CO)_3]Br$ **(1)** was 149 mg (81%). The following were observed for the mixture of atropisomers (aniline adduct parallel and antiparallel to the axial plane) 1H NMR (600 MHz, DMSO) δ 8.97 (d, 1H), 8.84 (d, 1 H), 8.73 (s, 1H), 8.56~8.44 (m, 1 H), 8.28 (d, 2H), 8.14~8.05 (m, 2H), 7.90~7.84 (m, 1H), 7.67~6.69 (m, 4H), 6.57 (s, ~6.46 (s, 2H). IR (KBr, Figure S7) ν_{CO}: 2024 (s), 1926 (s), 1916 (s) cm^{-1}. Anal. Calcd for complex **1**， C23H15MnN3O3Br(%)： C, 53.51; H, 2.93;; N, 8.14; found: C, 53.52; H, 2.94; N, 8.07; MS (TOF-ES): m/z =436.0493 $[M-Br]^+$.

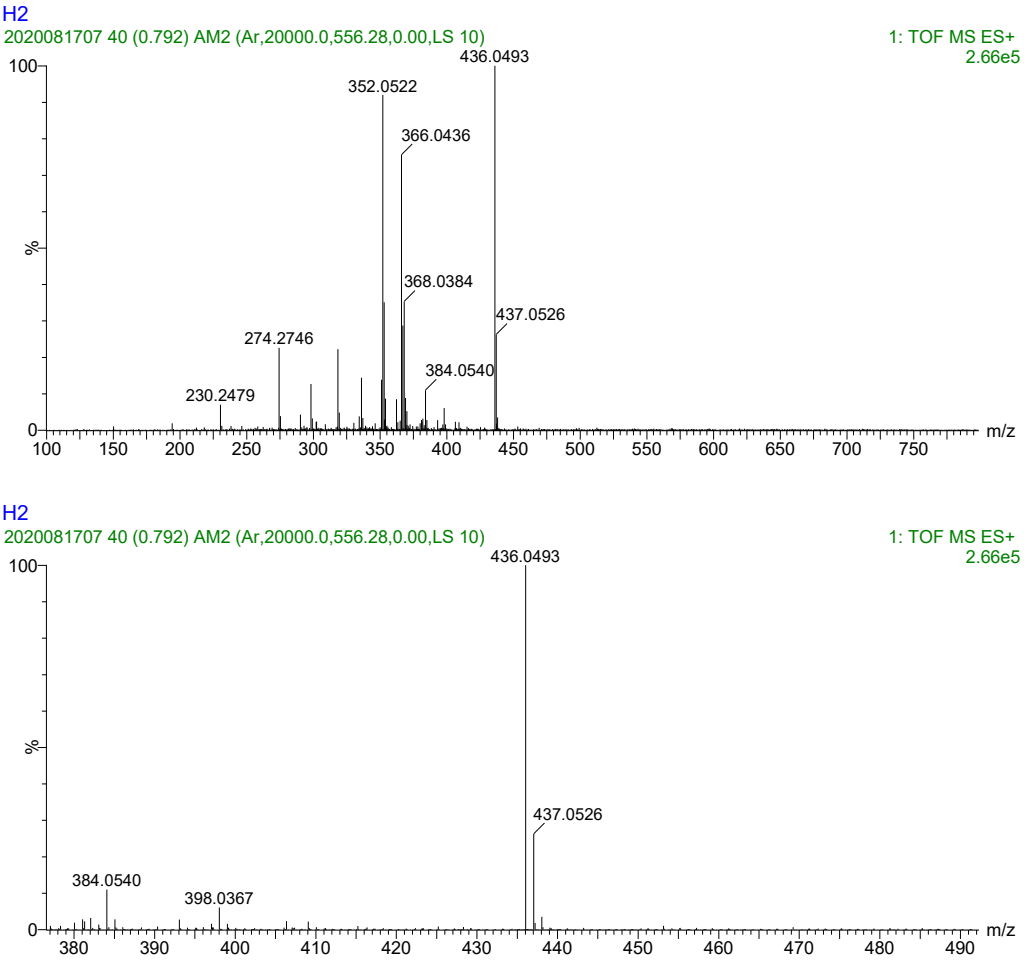


Figure S 3 High resolution mass spectrum of complex **1**.

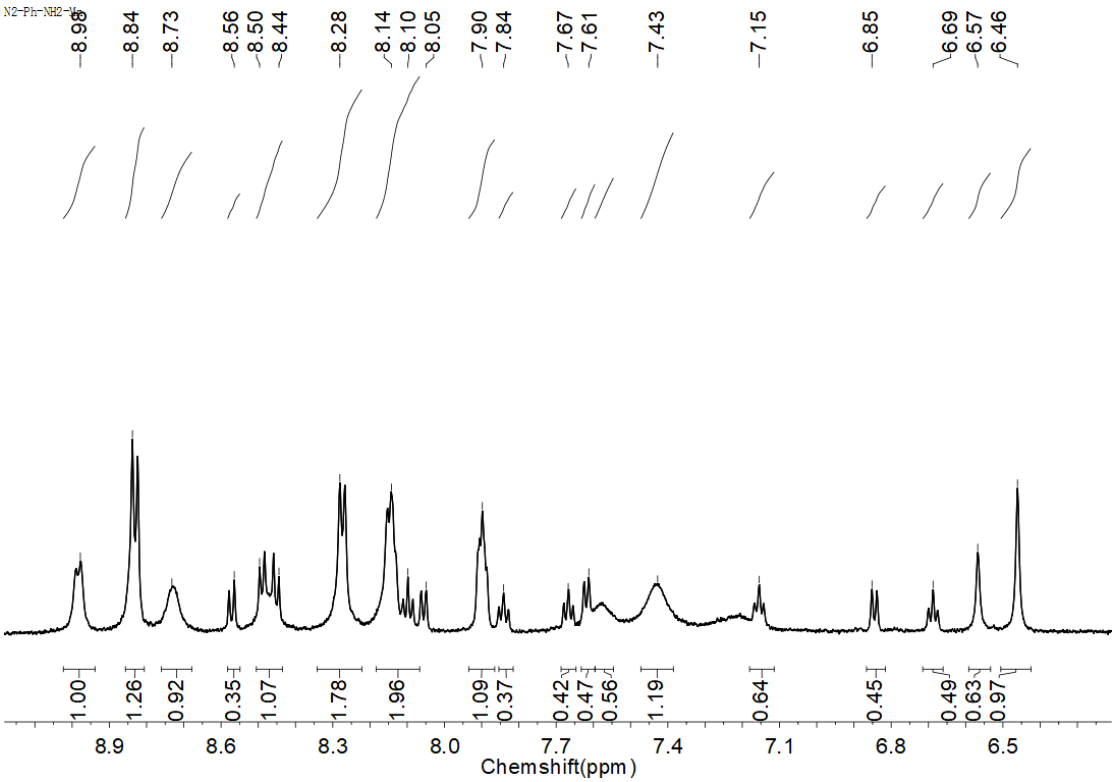


Figure S 4 ^{1}H NMR spectrum of complex **1**.

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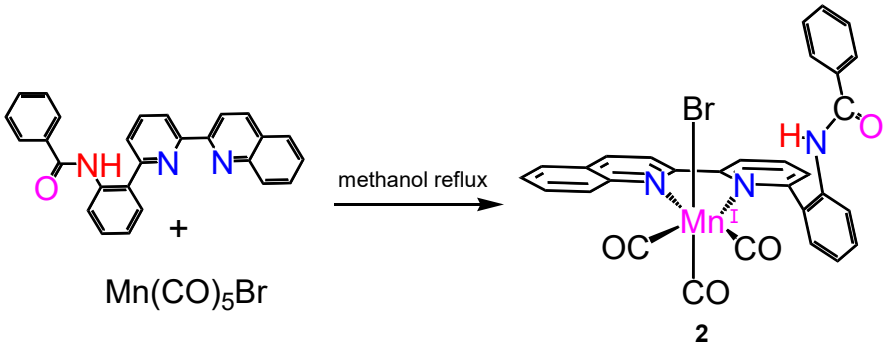
4) Preparation of [Mn(L2)(CO)3]Br (2).



Scheme S 4 Preparation of target complex **2**.

$Mn(CO)_5Br$ (100 mg, 0.36 mmol) was added to 5 mL methanol under argon atmosphere. Ligand **L2** (144 mg, 0.36 mmol) was added to the mixture and heated to reflux. The solution turned orange within 30 min, and the product precipitated out of solution. The mixture was cooled to room temperature, and the precipitate was filtered off and washed with methanol. The orange solid was dried overnight under vacuum. The yield of $[Mn(L^2)(CO)_3]Br$ **(2)** was 190 mg (85%). The following were observed for the mixture of atropisomers (the amide adduct parallel and antiparallel to the axial plane. ^1H NMR (600 MHz, DMSO) δ 8.90~8.87 (m, 1H), 8.82~8.79 (m, 1H), 8.76~8.68 (m, 1H), 8.54~8.42 (m,1H), 8.31~8.20 (m, 2H), 8.12~8.05 (m, 1H), 8.01~7.95 (m,1H), 7.89~7.63 (m, 4H), 7.59~7.46 (m, 3H), 7.40~7.36 (m, 1H), 7.09~6.79 (m, 1H). IR (KBr, Figure S7) v_{CO}: 2020 (s), 1936 (s), 1897 (s), 1640(s) cm^{-1}. Anal. Calcd for complex **2**, C30H19BrMnN3O4(%)： C, 58.09; H, 3.09; N, 6.77; found: C, 58.10; H, 3.10; N, 6.74; MS (TOF-ES): m/z =540.0753 $[M-Br]^+$; m/z =456.0895 $[M-Br-3CO]^+$;

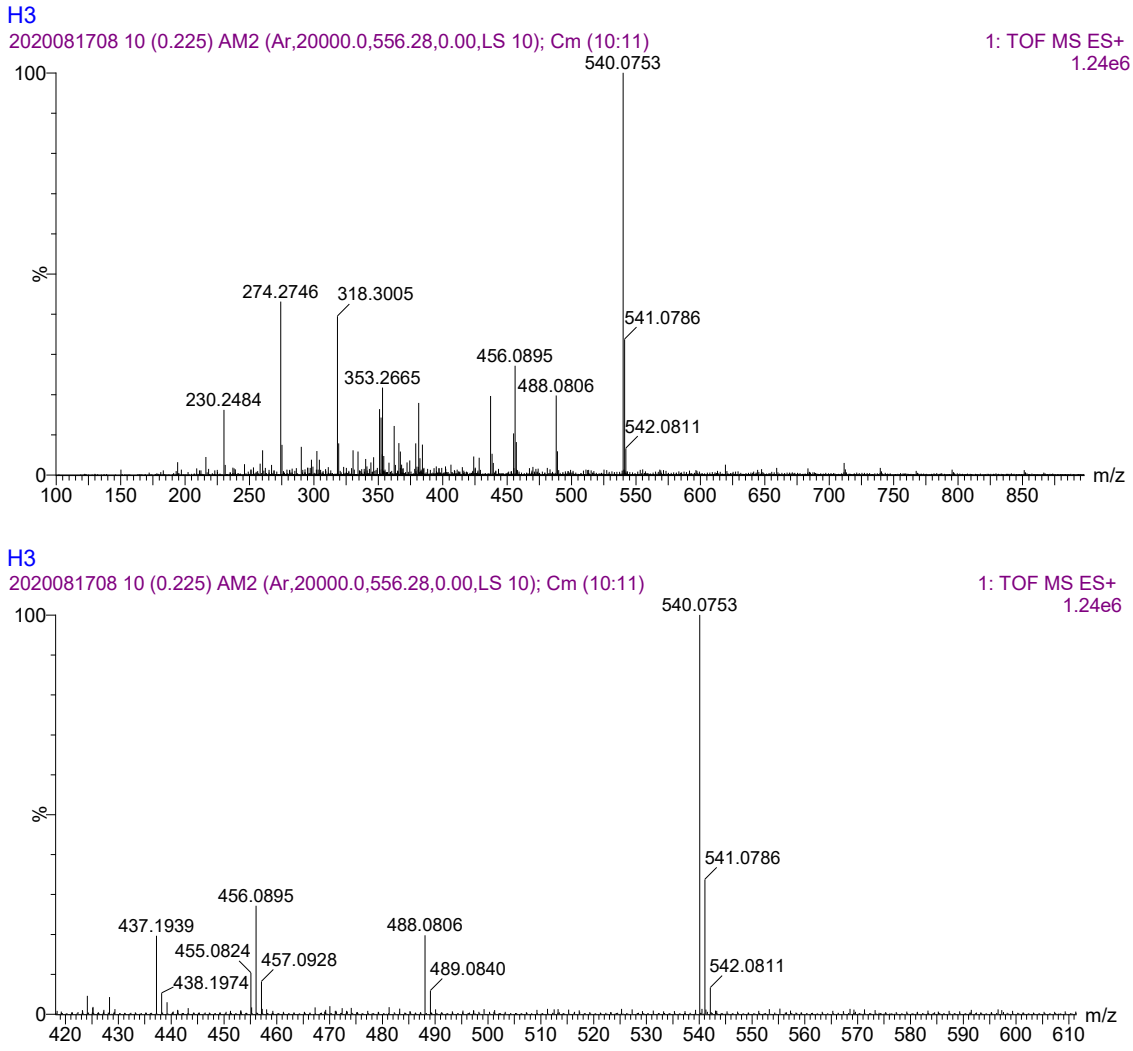


Figure S 5 High resolution mass spectrum of complex **2**.

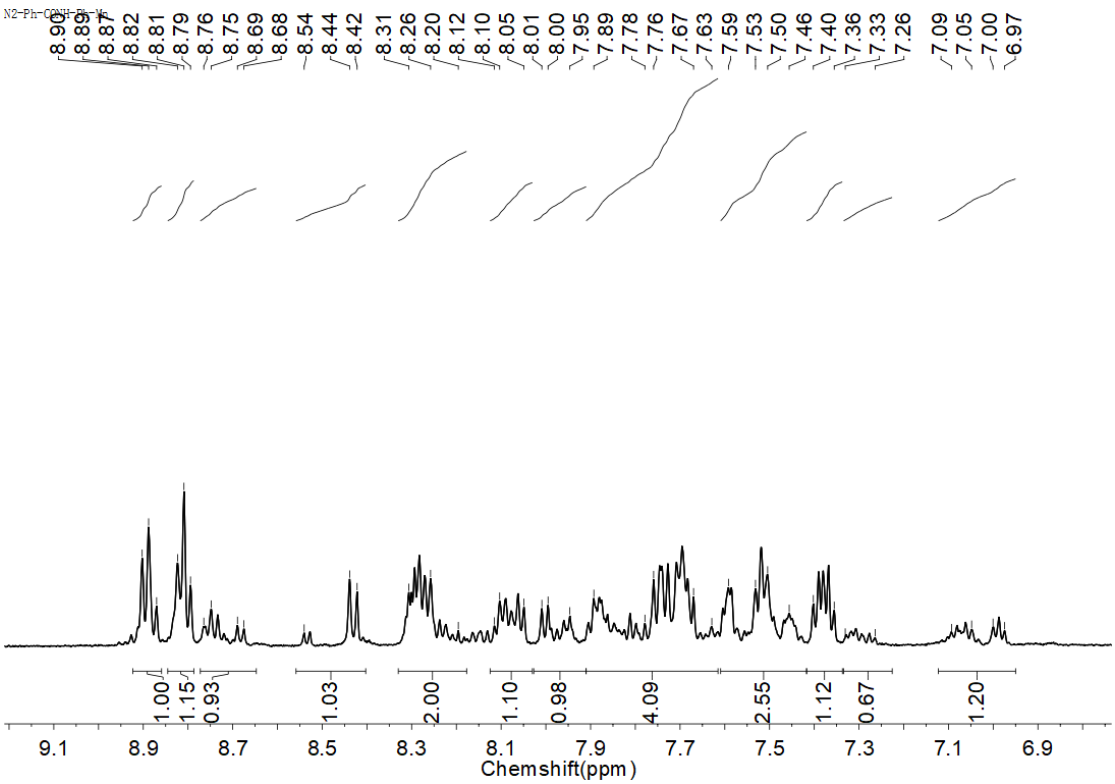


Figure S 6 ^{1}H NMR spectrum of complex **2**.

10. v_{CO} stretch absorption for complexes 1 and 2

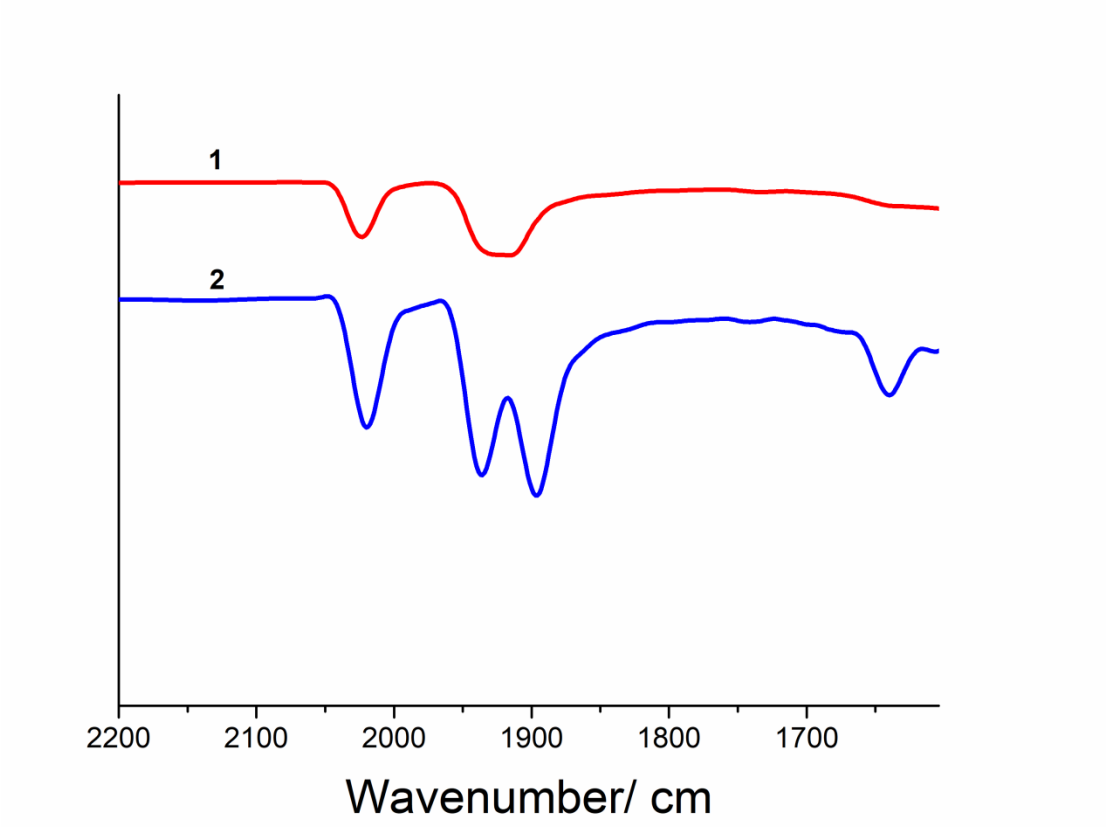


Figure S 7 Experimental FTIR spectra of **1** and **2** recorded in KBr displaying characteristic v_{CO} stretching modes for their facial tricarbonyl geometries.

11. Tables of Crystallographic Data and Selected Bond Lengths and Angles

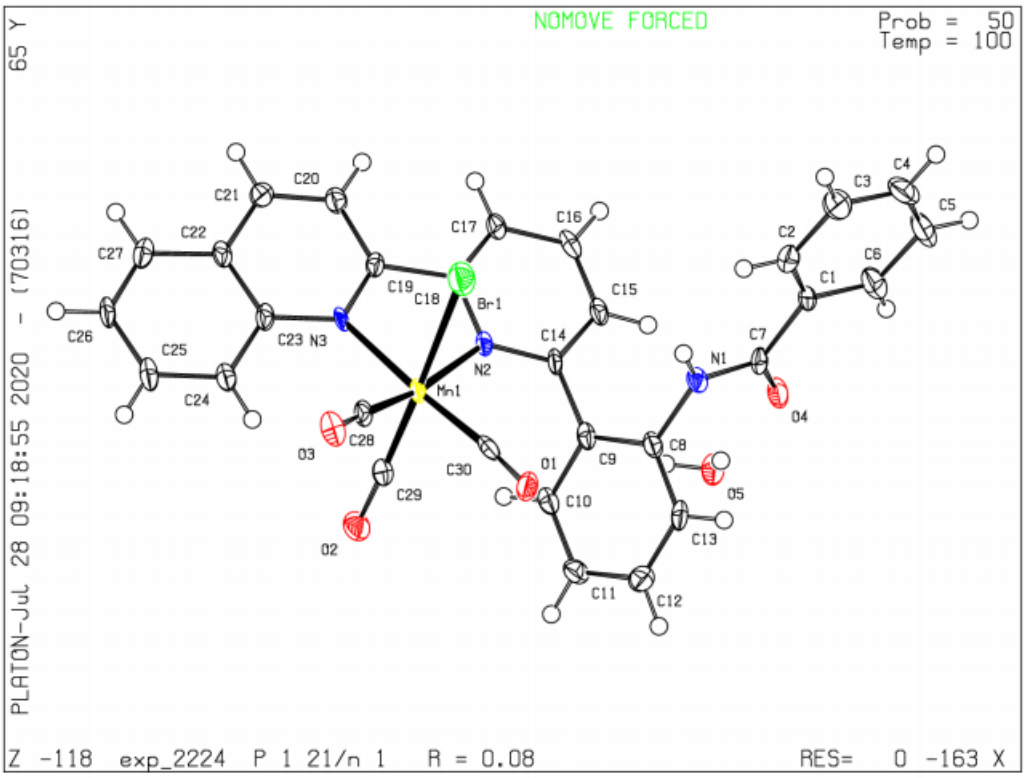


Table S 1 **Crystal data and structure refinement for complex 2**

Identification code	Complex 2
Empirical formula	$C_{30}H_{21}BrMnN_3O_5$
Formula weight	638.35
Temperature/K	99.99(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	7.1335(3)
b/Å	27.4408(10)
c/Å	13.4270(6)
α/°	90
β/°	91.758(4)
γ/°	90
Volume/Å^3	2627.08(19)
Z	4
ρ_{calc}g/cm^3	1.614
μ/mm^{-1}	6.265
F(000)	1288.0
Crystal size/mm^3	0.13 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)

2Θ range for data collection/°	6.442 to 147.082
Index ranges	$-8 \le h \le 8$, $-33 \le k \le 29$, $-16 \le l \le 16$
Reflections collected	9917
Independent reflections	5137 [R_{int} = 0.0655, R_{sigma} = 0.0920]
Data/restraints/parameters	5137/0/364
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0825, wR_2 = 0.2187
Final R indexes [all data]	R_1 = 0.1030, wR_2 = 0.2433
Largest diff. peak/hole / e $Å^{-3}$	1.97/-1.51

Table S 2 **Bond Lengths for complex 2**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	Mn1	2.4995(12)	C5	C6	1.393(10)
Mn1	N2	2.098(5)	C8	C9	1.388(9)
Mn1	N3	2.083(5)	C8	C13	1.379(10)
Mn1	C28	1.801(7)	C9	C10	1.398(9)
Mn1	C29	1.788(7)	C9	C14	1.483(9)
Mn1	C30	1.826(7)	C10	C11	1.375(10)
O1	C30	1.148(8)	C11	C12	1.398(10)
O2	C29	1.152(8)	C12	C13	1.371(10)
O3	C28	1.138(8)	C14	C15	1.410(9)
O4	C7	1.239(8)	C15	C16	1.365(10)
N1	C7	1.347(8)	C16	C17	1.403(9)
N1	C8	1.457(8)	C17	C18	1.376(9)
N2	C14	1.345(8)	C18	C19	1.481(8)
N2	C18	1.360(8)	C19	C20	1.415(9)
N3	C19	1.328(8)	C20	C21	1.344(9)
N3	C23	1.370(8)	C21	C22	1.420(9)
C1	C2	1.387(10)	C22	C23	1.431(9)
C1	C6	1.386(10)	C22	C27	1.418(9)
C1	C7	1.510(9)	C23	C24	1.407(9)
C2	C3	1.383(10)	C24	C25	1.382(9)
C3	C4	1.359(11)	C25	C26	1.391(10)
C4	C5	1.373(12)	C26	C27	1.371(10)

Table S 3 **Bond Angles for complex 2**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N2	Mn1	Br1	83.35(14)	C13	C8	C9	120.9(6)
N3	Mn1	Br1	87.27(14)	C8	C9	C10	118.0(6)
N3	Mn1	N2	78.5(2)	C8	C9	C14	123.3(6)
C28	Mn1	Br1	85.7(2)	C10	C9	C14	118.6(6)
C28	Mn1	N2	168.8(2)	C11	C10	C9	121.1(6)
C28	Mn1	N3	98.4(3)	C10	C11	C12	119.8(6)
C28	Mn1	C30	82.9(3)	C13	C12	C11	119.3(6)
C29	Mn1	Br1	176.3(2)	C12	C13	C8	120.7(7)
C29	Mn1	N2	100.3(2)	N2	C14	C9	120.0(6)
C29	Mn1	N3	93.2(3)	N2	C14	C15	120.5(6)
C29	Mn1	C28	90.6(3)	C15	C14	C9	119.4(6)
C29	Mn1	C30	90.4(3)	C16	C15	C14	120.7(6)
C30	Mn1	Br1	89.2(2)	C15	C16	C17	118.2(6)
C30	Mn1	N2	99.5(2)	C18	C17	C16	119.2(6)
C30	Mn1	N3	176.2(2)	N2	C18	C17	122.4(6)
C7	N1	C8	120.2(5)	N2	C18	C19	115.1(5)
C14	N2	Mn1	128.0(4)	C17	C18	C19	122.4(6)
C14	N2	C18	119.0(5)	N3	C19	C18	116.2(5)
C18	N2	Mn1	111.1(4)	N3	C19	C20	122.4(6)
C19	N3	Mn1	112.4(4)	C20	C19	C18	121.3(6)
C19	N3	C23	119.0(6)	C21	C20	C19	119.9(6)
C23	N3	Mn1	128.0(4)	C20	C21	C22	119.7(6)
C2	C1	C6	119.8(7)	C21	C22	C23	117.8(6)
C2	C1	C7	123.4(6)	C27	C22	C21	122.4(6)
C6	C1	C7	116.7(6)	C27	C22	C23	119.8(6)
C3	C2	C1	119.0(7)	N3	C23	C22	120.9(6)
C4	C3	C2	120.9(7)	N3	C23	C24	121.1(6)
C3	C4	C5	121.1(7)	C24	C23	C22	118.0(6)
C4	C5	C6	118.7(7)	C25	C24	C23	120.4(7)
C1	C6	C5	120.4(7)	C24	C25	C26	121.6(7)
O4	C7	N1	122.1(6)	C27	C26	C25	119.7(6)
O4	C7	C1	120.7(6)	C26	C27	C22	120.4(6)
N1	C7	C1	117.2(6)	O3	C28	Mn1	175.6(6)
C9	C8	N1	121.2(6)	O2	C29	Mn1	174.0(6)
C13	C8	N1	117.9(6)	O1	C30	Mn1	172.5(6)

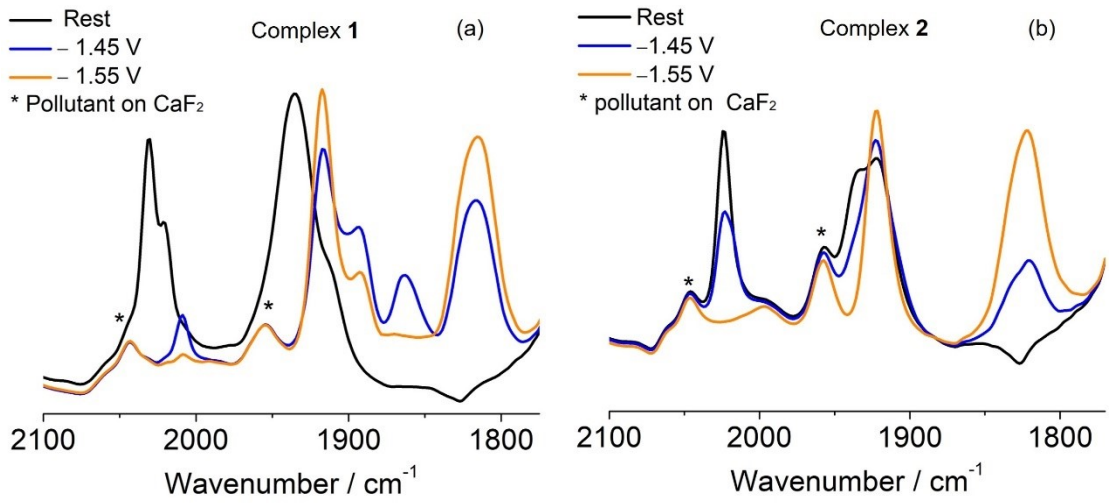


Figure S 8 (a) IR-SEC of 3 mM **1** in MeCN/DMF (1:1) mixture with 0.1 M $TBAPF_6$ electrolyte under an atmosphere of Ar. The resting species (black, 1) has two ν_{CO} stretches at 2029 and 1935 cm^{-1}. Upon initial reduction at approximately −1.45 V (blue), singly reduced species of **1** (2008, 1893, 1862 cm^{-1}) and doubly reduced species (1917 and 1814 cm^{-1}) formed. When the voltage of the cell is held at approximately −1.55 V for more than 1 min, all species are converted to doubly reduced species (orange). (b) IR-SEC of 3 mM **2** in MeCN/DMF (1:1) mixture with 0.1 M $TBAPF_6$ electrolyte under an atmosphere of Ar. The resting species (black, **2**) has three ν_{CO} stretches at 2023, 1934 and 1922 cm^{-1}. Upon initial reduction at approximately −1.45 V (blue), almost no singly reduced species formation. When the voltage of the cell is held at approximately −1.55 V for more than 1 min, all species are converted to doubly reduced species (1922 and 1821 cm^{-1}, orange).

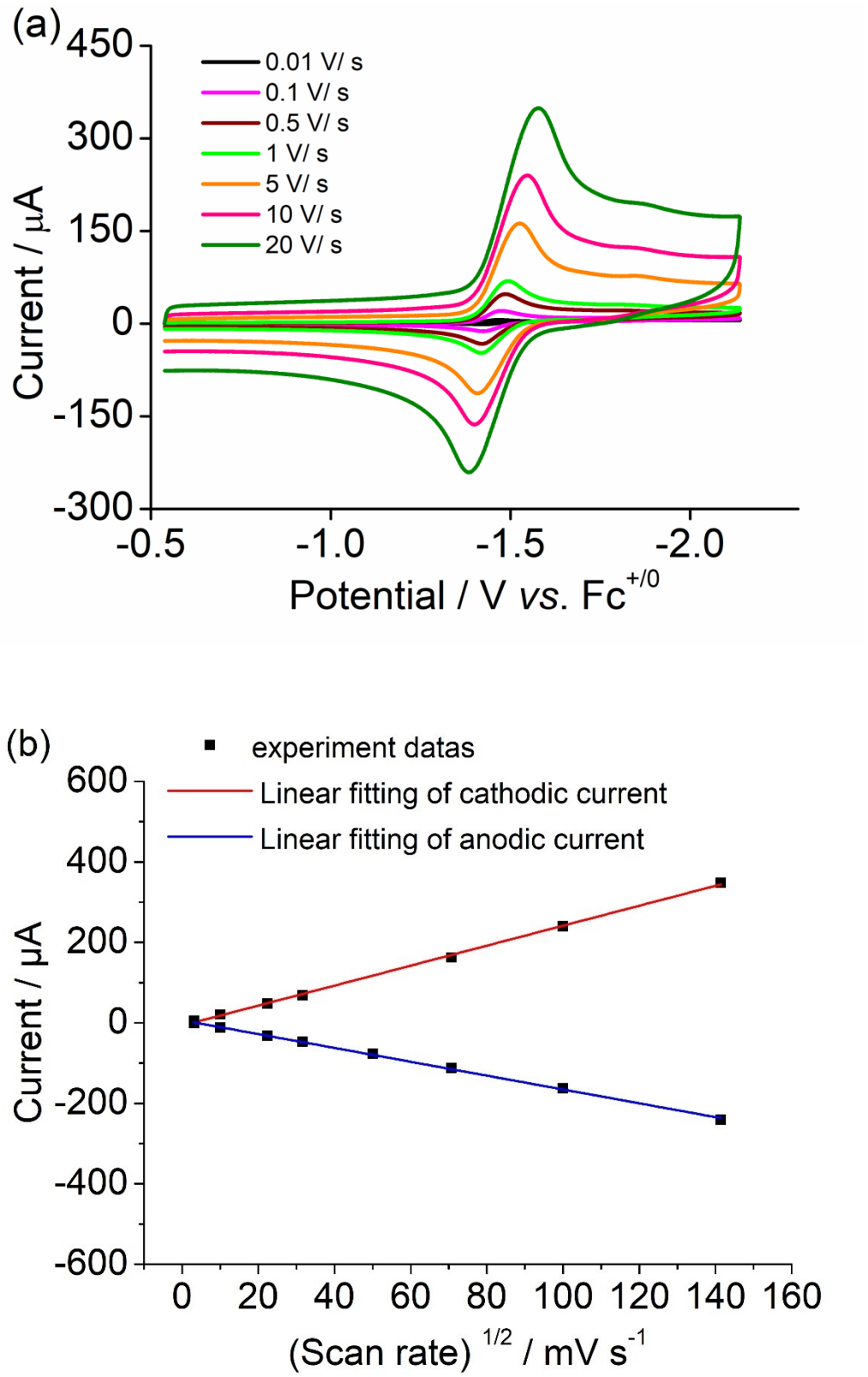


Figure S 9 (a) The CVs of complex **1** (0.5 mM) in $^{n}Bu_4NPF_6$ (0.1 M) CH_3CN/DMF (5:1) solution with scan rate (v) varied from 0.01 V/s to 20 V/s under Ar; (b) Plot of anodic and cathodic peak current (i_p) vs. $v^{1/2}$ for **1**.

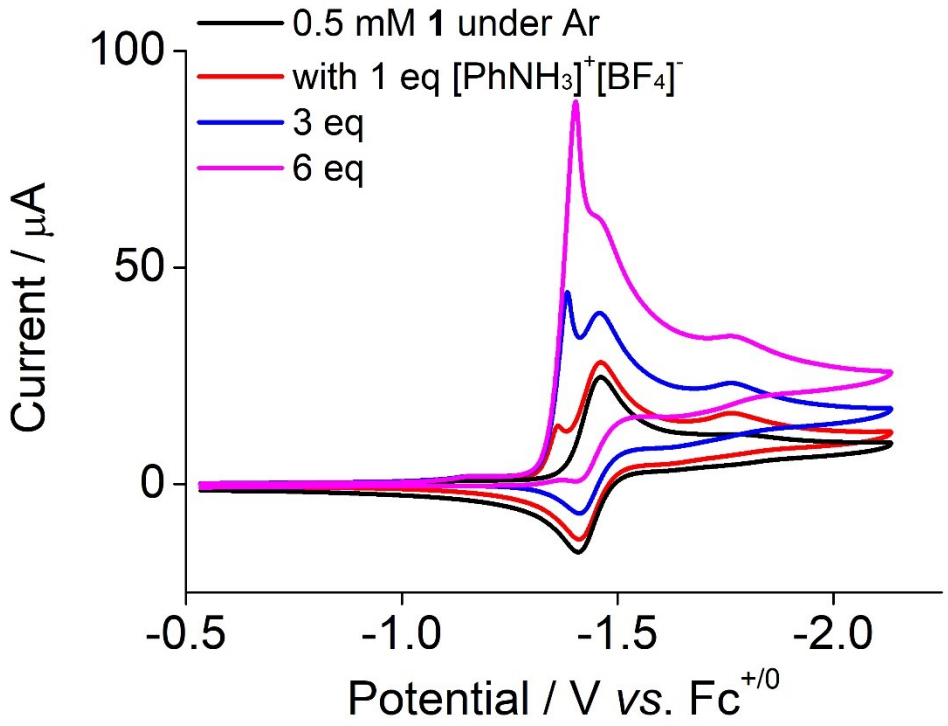


Figure S 10 Cyclic voltammograms of 0.5 mM **1** with anilinium tetrafluoroborate (0 ~ 3 mM from bottom to top) under Ar. Condition: 3 mm glassy-carbon working electrode; 25°C; scan rate, 100 mV/s.; 0.1 M $^{n}Bu_4NPF_6$ as supporting electrolyte in CH_3CN/DMF (5:1).

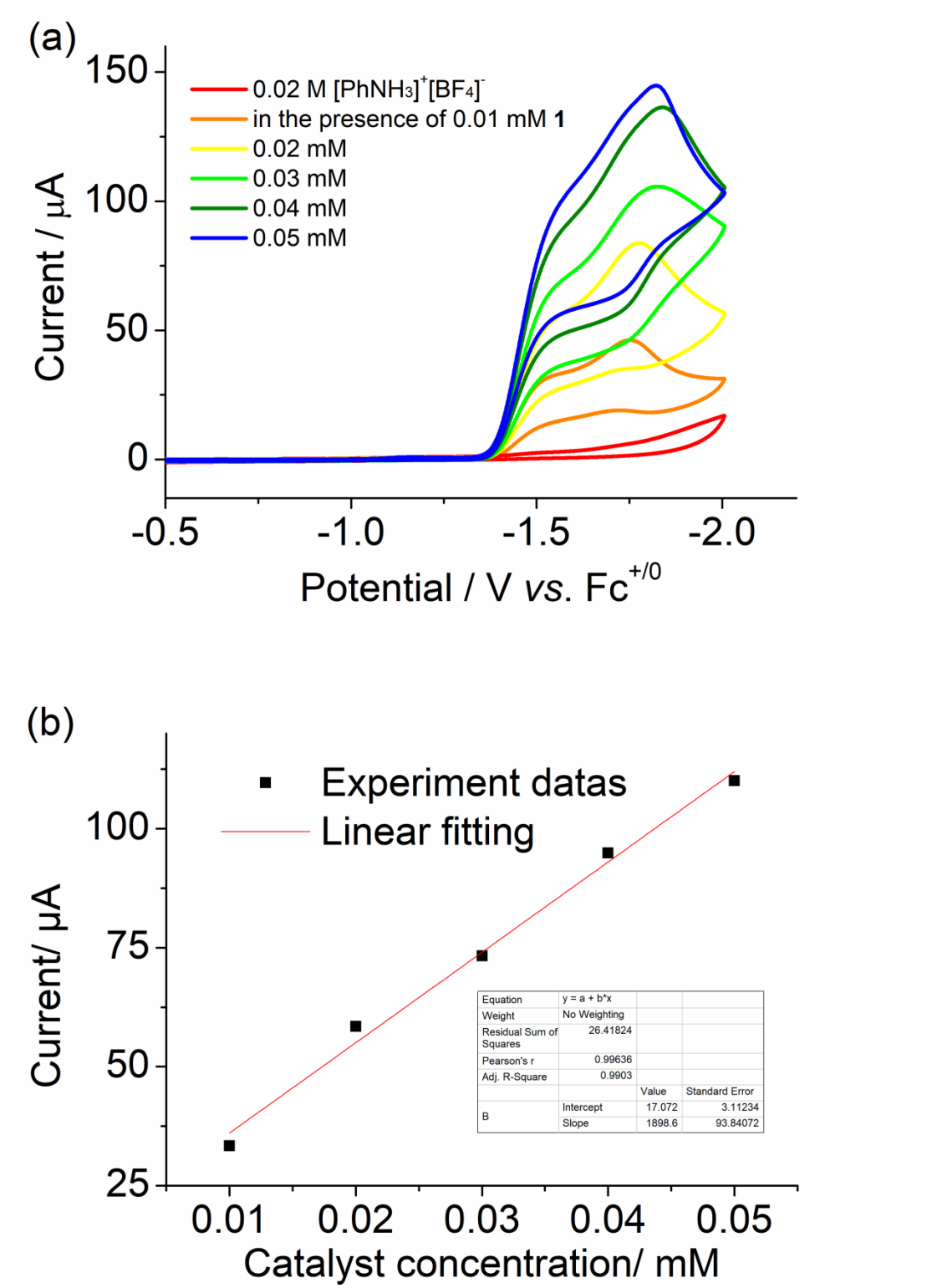


Figure S 11 (a) Cyclic voltammograms of 0.02 M $[PhNH_3]^+[BF_4]^-$ with varied concentrations of **1** (0 –0.05 mM) under Ar. (b) Plot of i_{cat} versus concentrations of complex **1**. Voltammograms are taken at a scan rate of 100 mV/s, in CH_3CN/DMF (5:1) with 0.1 M $^nBu_4NPF_6$.

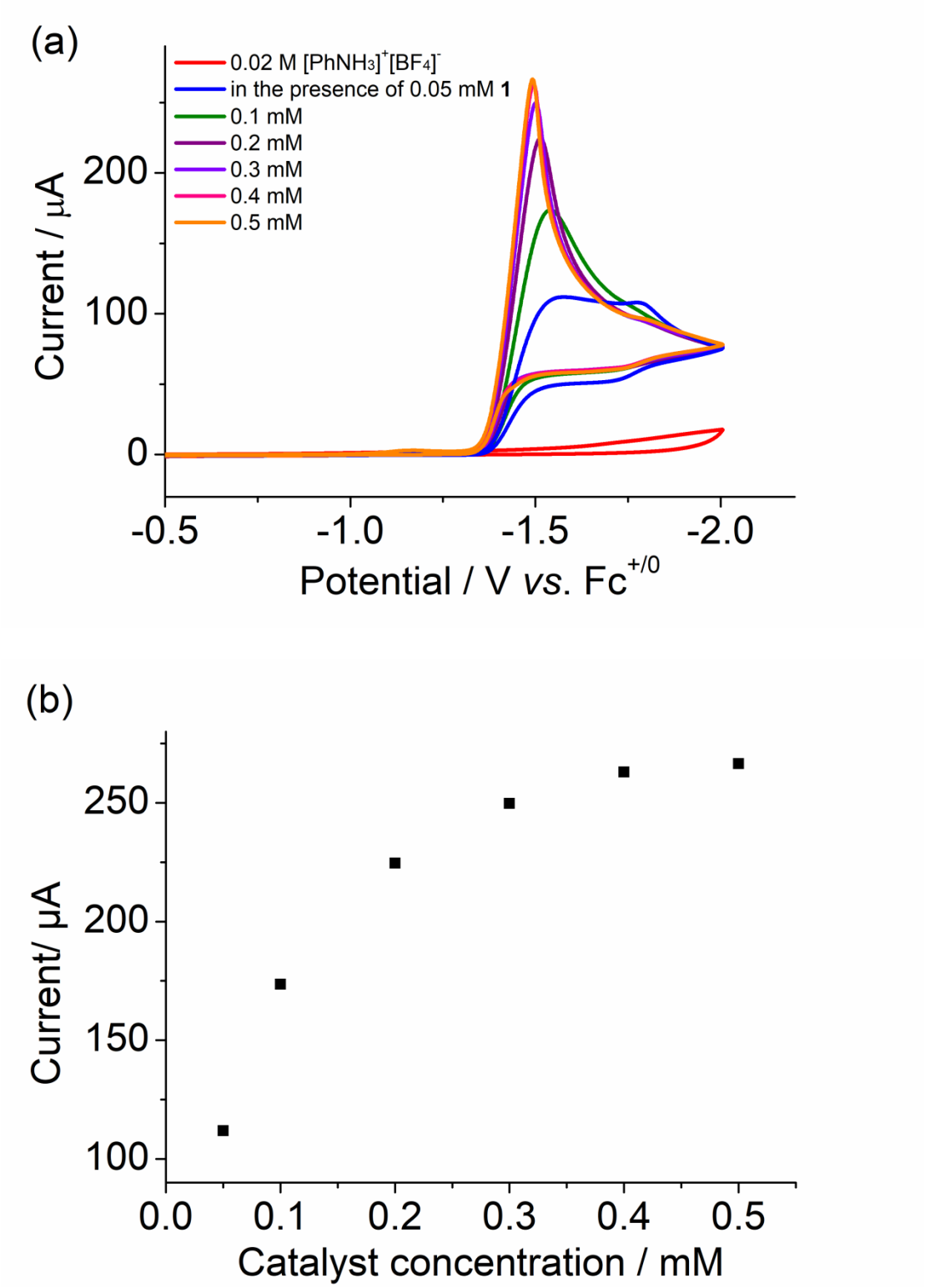


Figure S 12 (a) Cyclic voltammograms of 0.02 M $[PhNH_3]^+[BF_4]^-$ with varied concentrations of **1** (0.05 –0.5 mM) under Ar. (b) Plot of i_{cat} versus concentrations of complex **1**. Voltammograms are taken at a scan rate of 100 mV/s, in CH_3CN/DMF (5:1) with 0.1 M $^n Bu_4NPF_6$.

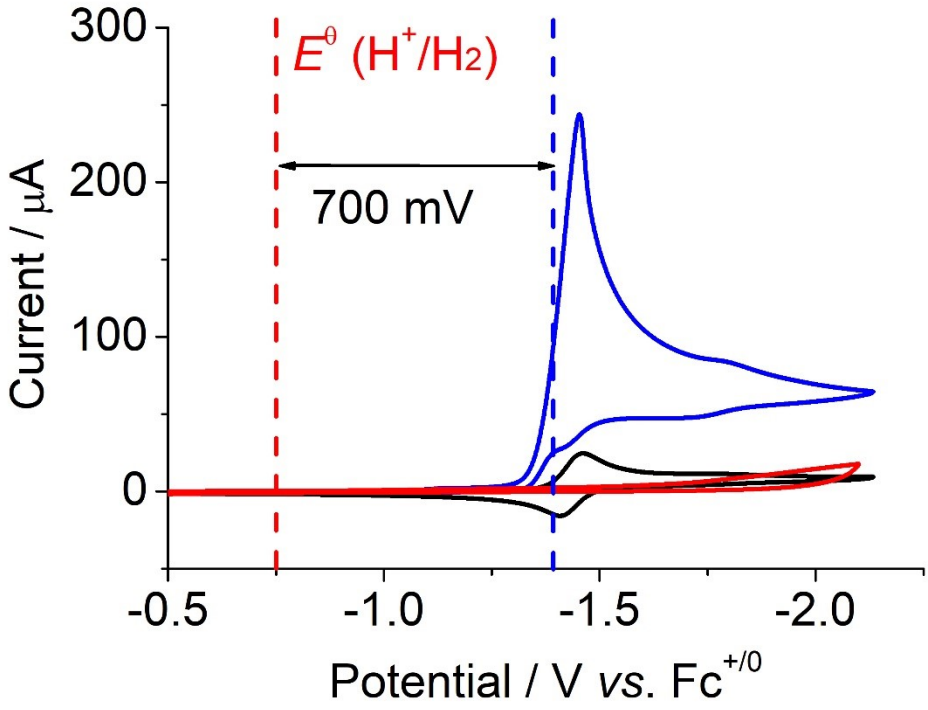


Figure S 13 The CVs of complex **1** (0.5 mM) in the presence (blue) and absence (black) of 0.01 M [$PhNH_3$][BF_4]. CV of 0.01 M [$PhNH_3$][BF_4 in the absence of catalyst (red). Voltammograms are taken at a scan rate of 100 mV/s, in CH_3CN/DMF (5:1) with 0.1 M $^{n}Bu_4NPF_6$ under Ar.

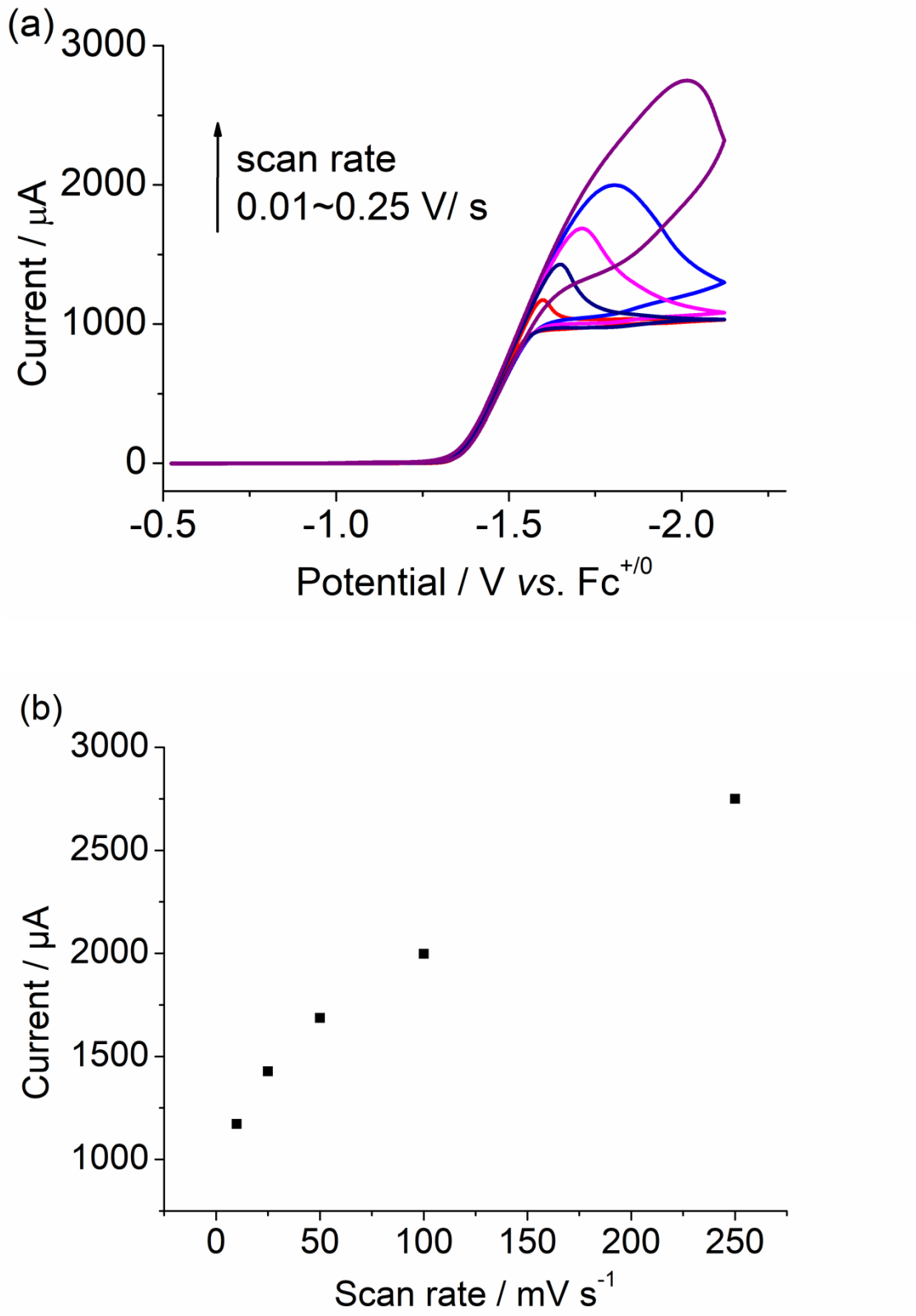


Figure S 14 (a) Cyclic voltammogram of 0.5 mM complexes **1** at varied scan rate from 10 mV/s to 250 mV/s in the presence of 0.2 M $[PhNH_3]^+[BF_4]^-$ under Ar. (b) the dependence of catalytic peak currents on the scan rates. Voltammograms are taken in CH_3CN/DMF (5:1) with 0.1 M $^n Bu_4NPF_6$.

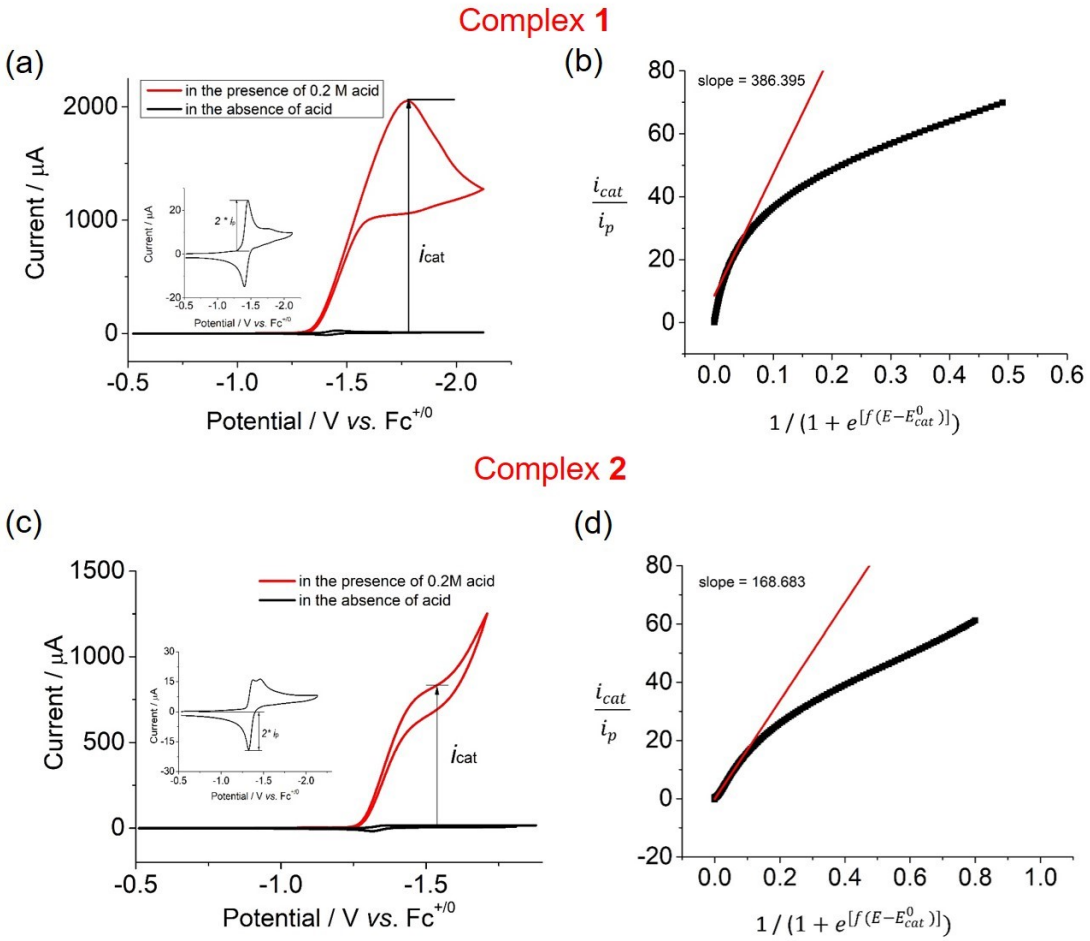


Figure S 15 (a) Cyclic voltammograms of 0.5 mM **1** in the absence and presence of 0.2 M $[PhNH_3]^+[BF_4]^-$ under Ar at scan rate 100 mV/s with 0.1 M $^nBu_4NPF_6$ in CH_3CN/DMF (5:1). Inset: magnification of the CV of **1**. (b) Foot-of the-wave analyses of the voltammograms in (a). (c) Cyclic voltammograms of 0.5 mM **1** in the absence and presence of 0.2 M $[PhNH_3]^+[BF_4]^-$ under the same condition as (a), Inset: magnification of the CV of **2**. (d) Foot-of the-wave analyses of the voltammograms in (c).

Calculation of TOF The calculation uses the **Foot-of-the-Wave Analysis (FOWA)** methods referred by Artero and Savéant (Energy & Enviromental Sicence, **2014**, *7(11)*, 3808-3814).

At the outset of each experiment, a cyclic voltammogram was measured of catalyst alone under inert atmosphere in the absence of proton source, from which E^0_{cat} could be determined. The half of the peak height of the formal **1**/(**1**$^{2-}$ - Br^-) couple, i_p, was determined by taking the difference between peak cathodic current and baseline current before this couple. Thus, proton reduction with complex **1** may be described as a EECC'

process, in which the rate-determining step involves pre-equilibrium H^+ binding to the nucleophilic Mn(0) center ($k_1 << k_2$).

$$LMn^{I} + e^- \xrightarrow{E_1} LMn^{0}$$

$$LMn^{0} + e^- \xrightarrow{E_2} \dot{L}\bar{M}n^{0}$$

$$\dot{L}\bar{M}n^{0} + H^+ \xrightarrow{k_1} \dot{L}\bar{M}n\text{-}H^-$$

$$\dot{L}\bar{M}n\text{-}H^- + H^+ \xrightarrow{k_2} H_2 + LMn^{I}$$

The following relationship may be derived:

$$\frac{i_{cat}}{i_p} = \frac{4.48\sqrt{\frac{k_{obs}}{fv}}}{1+e^{[f(E-E^0_{cat})]}} \qquad (1)$$

$$k_{obs} = (slope)^2 \times v \times 1.94 \qquad (2)$$

where i_{cat} is the catalytic current, E is the potential, v is the scan rate (V/s), k_{obs} is the observed rate constant, and f = F/RT = 38.94 V^{-1}. Thus, a "FOW" plot of $\frac{i_{cat}}{i_p}$ *versus* $\frac{1}{1+e^{[f(E-E^0_{cat})]}}$ yields a straight line with slope $4.48\sqrt{\frac{k_{obs}}{fv}}$, from which k_{obs} may be determined.

At 100 mv/s, the values of *slope* for complex **1** and **2** are 386 and 169， corresponding to TOFs of $2.89*10^4$ s^{-1} and $5.41*10^3$ s^{-1}, respectively.

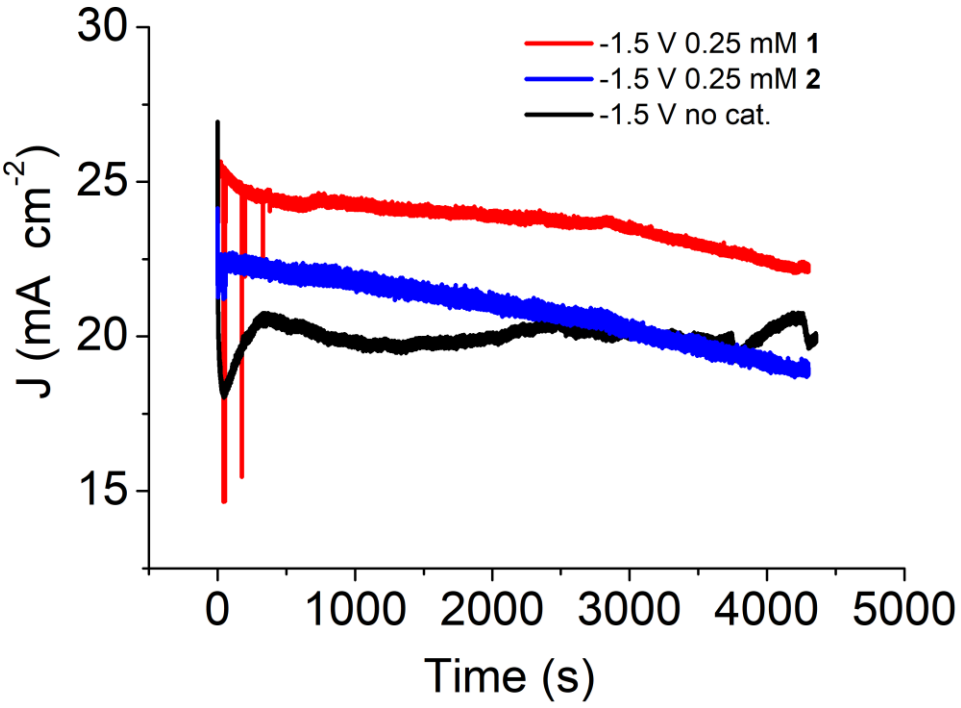


Figure S 16 Controlled potential electrolysis at –1.5 V *vs.* $Fc^{+/0}$ in the presence (red) of 0.25 mM **1** or **2** (blue) and in the absence of catalyst (black) under Ar. Conditions: 0.1 M $^{n}Bu_4NPF_6$ in CH_3CN/DMF (5:1) with 0.2 M $[PhNH_3]^+[BF_4]^-$, glassy carbon working electrode, graphite rod counter electrode, Ag^+/Ag reference electrode.

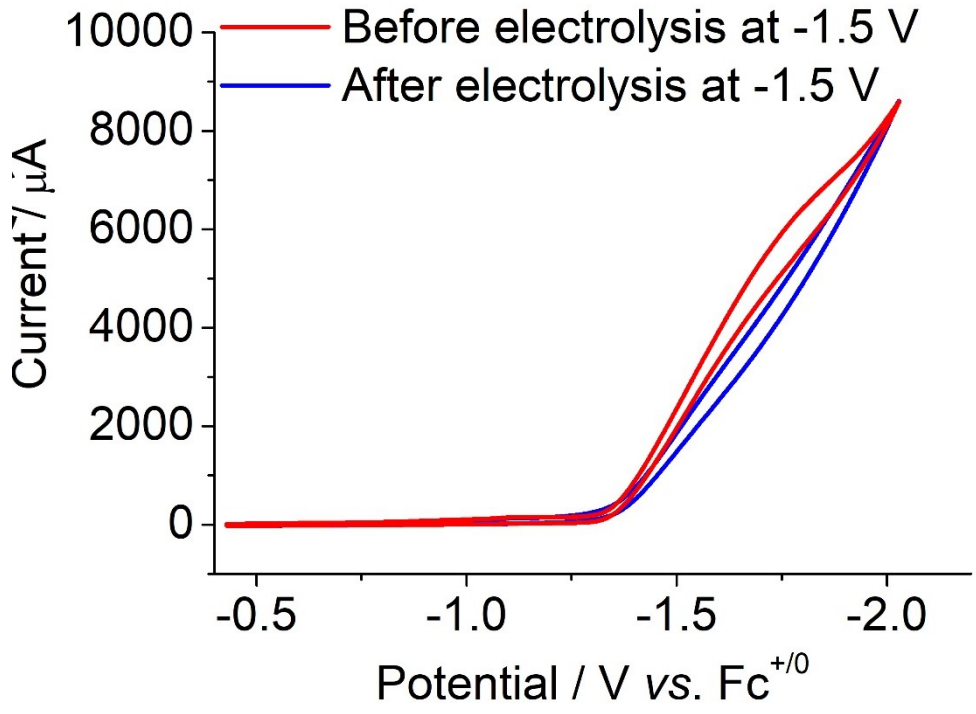


Figure S 17 Cyclic voltammograms of 0.25 mM **1** before (red line) and after (blue line) controlled potential electrolysis at –1.5 V *vs.* $Fc^{+/0}$ in the presence of 0.2 M $[PhNH_3]^+[BF_4]^-$ under Ar. Conditions: 0.1 M $^nBu_4NPF_6$ in CH_3CN/DMF (5:1) with 0.2 M $[PhNH_3]^+[BF_4]^-$, glassy carbon working electrode, graphite rod counter electrode, Ag^+/Ag reference electrode.

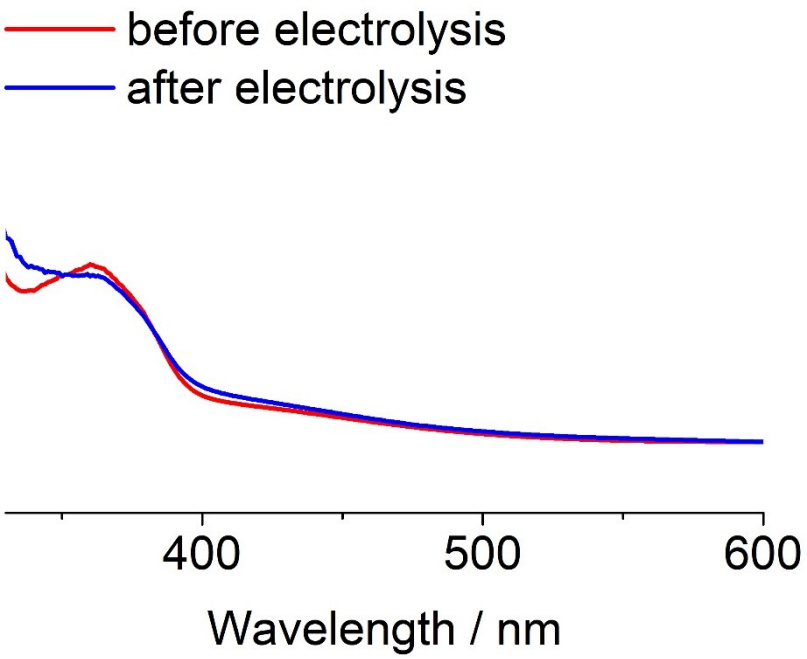


Figure S 18 Ultraviolet-visible absorption spectra of 0.25 mM **1** before (red line) and after (blue line) controlled potential electrolysis at –1.5 V *vs.* $Fc^{+/0}$ in the presence of 0.2 M $[PhNH_3]^+[BF_4]^-$ under Ar.

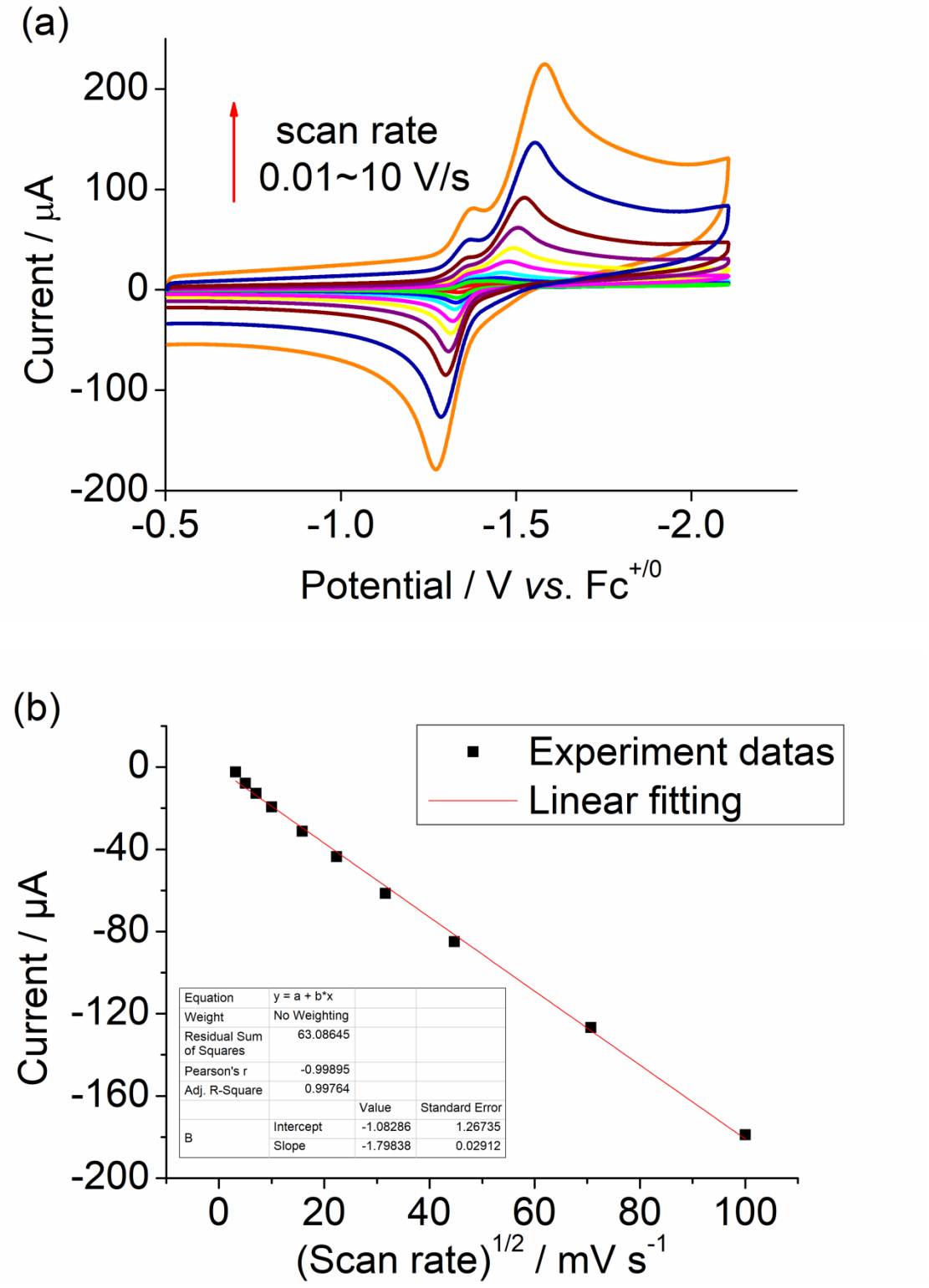


Figure S 19 (a) The CVs of complex **2** (0.5 mM) in $^{n}Bu_4NPF_6$ (0.1 M) CH_3CN/DMF (5:1) solution with scan rate varied from 0.01 V/s to 10 V/s under Ar; (b) Plot of anodic peak current (i_p) vs. $v^{1/2}$ for **2**

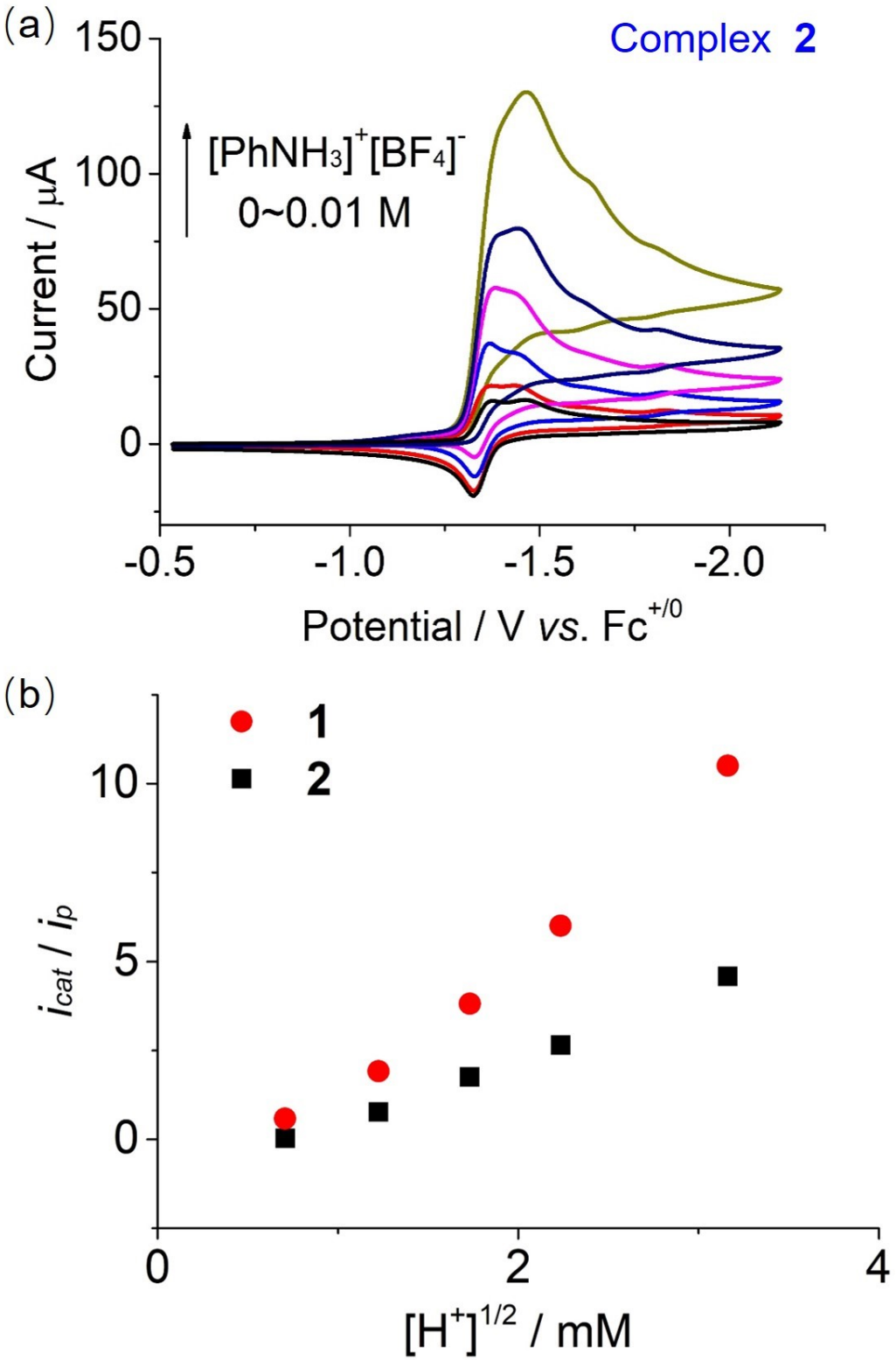


Figure S 20 (a) CVs of 0.5 mM **2** with anilinium tetrafluoroborate (0 ~ 0.01 M from bottom to top) under Ar. (b) Linear dependence of i_{cat}/i_p on the square root of acid concentration from 0.5 to 10 mM for **1** (red square) and **2** (black square). Condition: 3 mm glassy-carbon working electrode; 25°C; scan rate, 100 mV/s.; 0.1 M $^{n}Bu_4NPF_6$ as supporting electrolyte in CH_3CN/DMF (5:1).

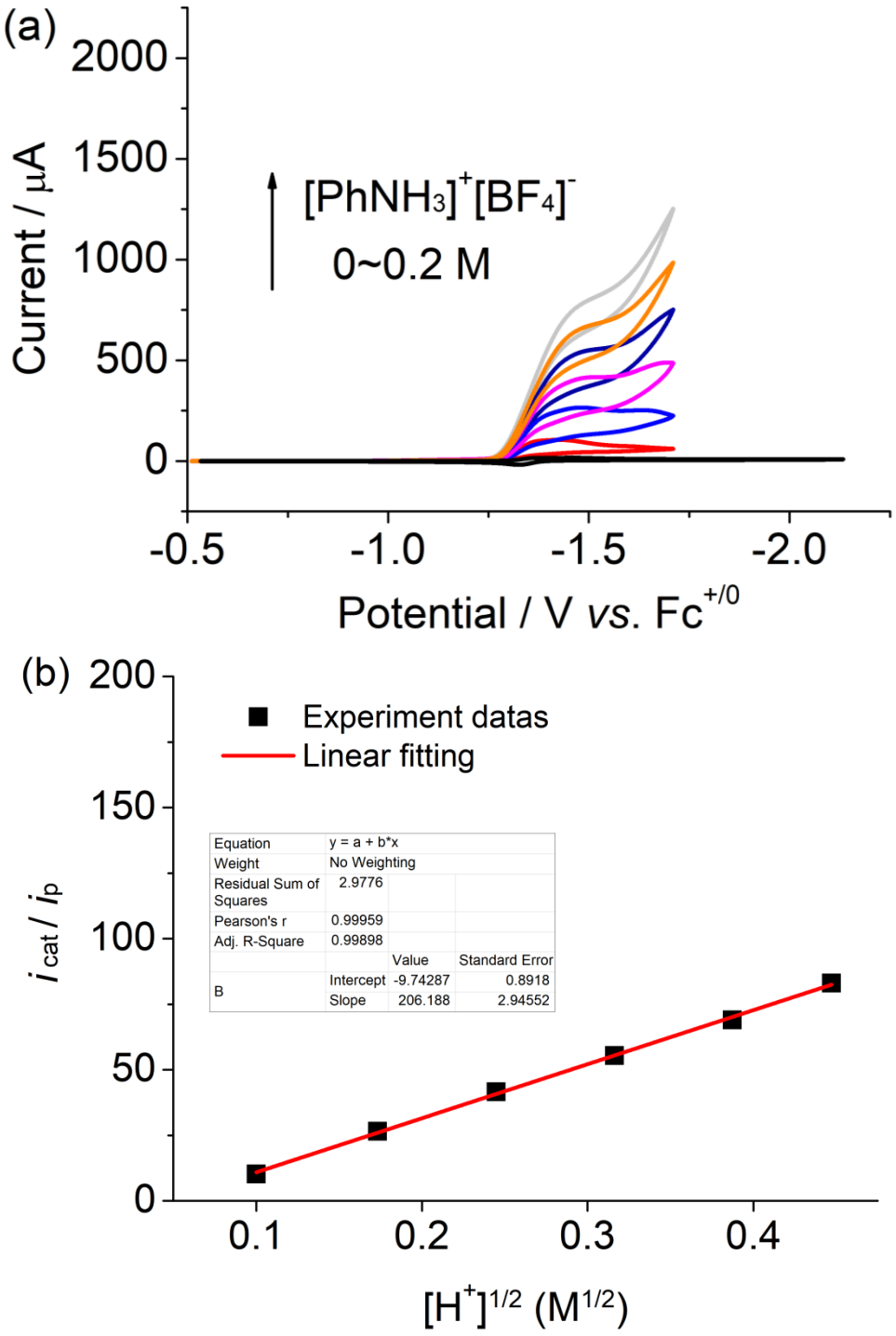


Figure S 21 (a) CVs of 0.5 mM **2** with anilinium tetrafluoroborate (0 ~ 0.2 M from bottom to top) under Ar. (b) linear dependence of i_{cat}/i_p on the square root of acid concentration from 0.01 to 0.2 M for **2**. Condition: 3 mm glassy-carbon working electrode; 25°C; scan rate, 100 mV/s.; 0.1 M ^{n}Bu$_4$NPF$_6$ as supporting electrolyte in CH$_3$CN/DMF (5:1).

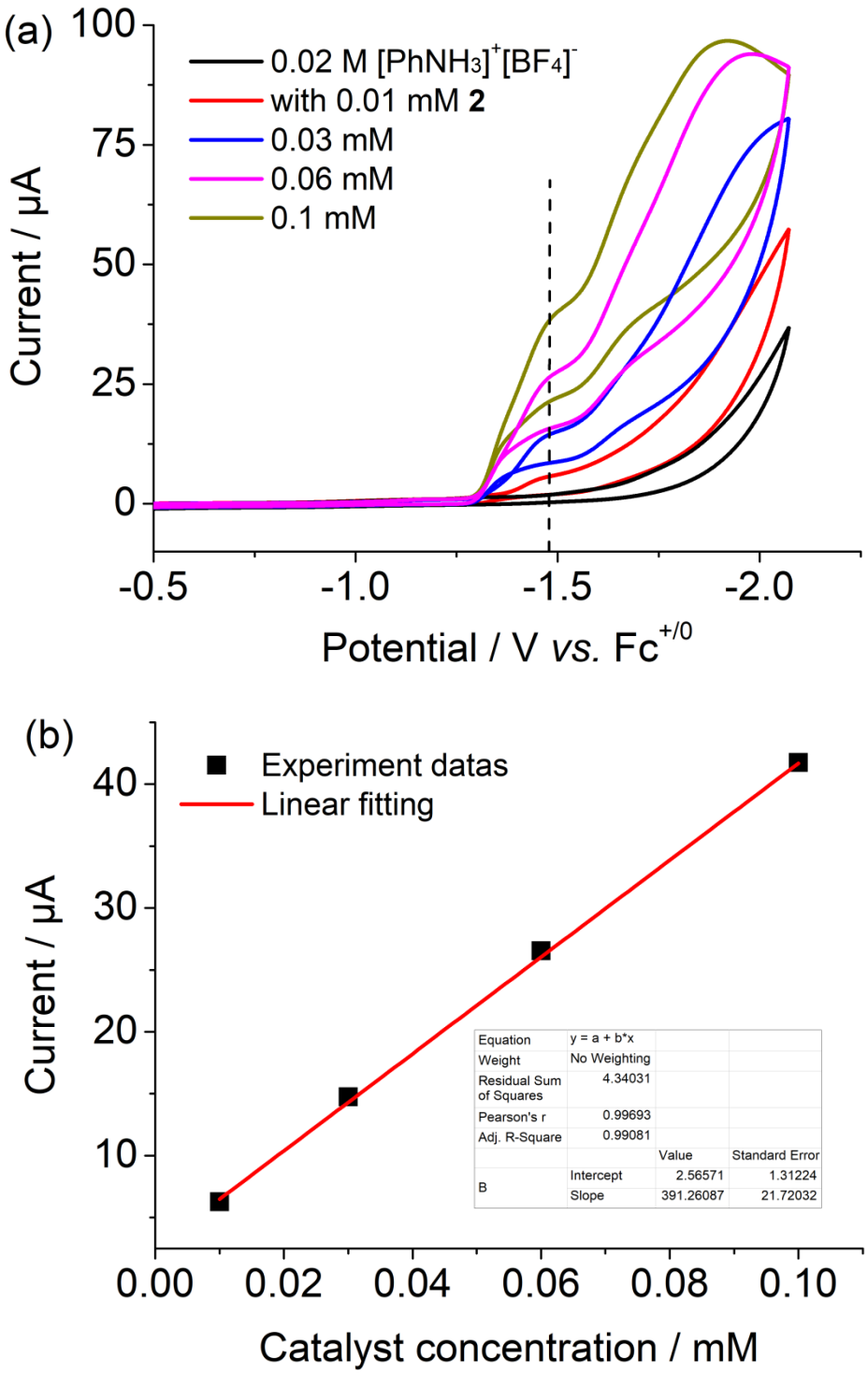


Figure S 22 (a) Cyclic voltammograms of 0.02 M $[PhNH_3]^+[BF_4]^-$ with varied concentrations of **2** (0 –0.1 mM) under Ar. (b) Plot of i_{cat} versus concentrations of complex **2**. Voltammograms are taken at a scan rate of 100 mV/s, in CH_3CN/DMF (5:1) with 0.1 M $^n Bu_4NPF_6$.

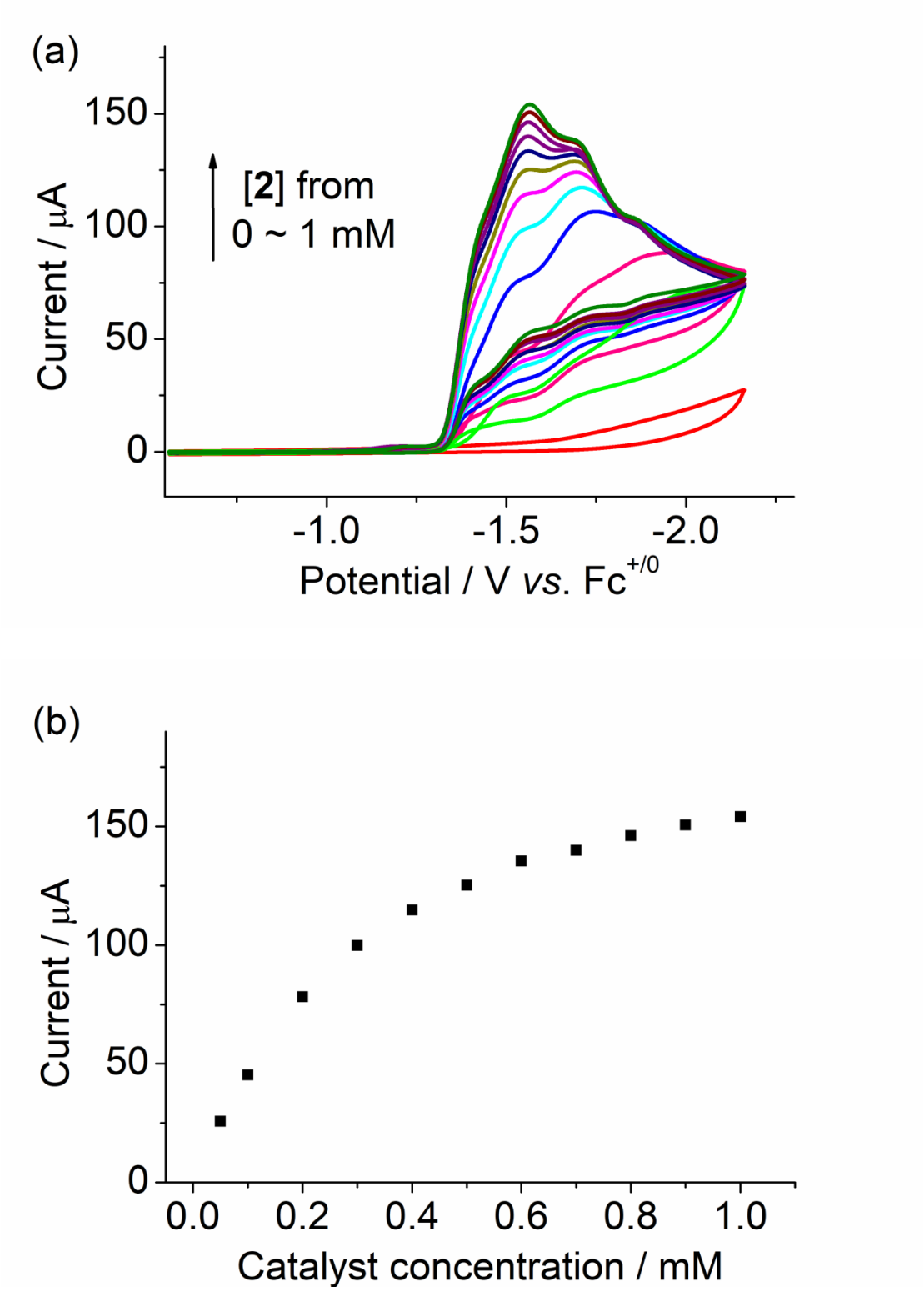


Figure S 23 (a) Cyclic voltammograms of 0.02 M $[PhNH_3]^+[BF_4]^-$ with varied concentrations of **2** (0.05 –1 mM) under Ar. (b) Plot of i_{cat} versus concentrations of complex **2.** Voltammograms are taken at a scan rate of 100 mV/s, in CH_3CN/DMF (5:1) with 0.1 M $^nBu_4NPF_6$.

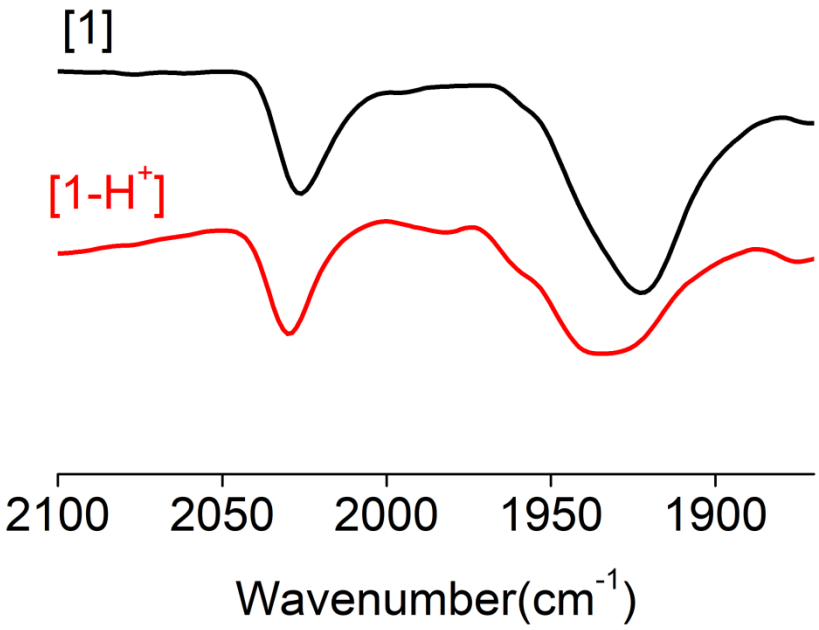


Figure S 24 Infrared spectra of complex **1** in the absence (black) and presence (red) of 10 equiv $[PhNH_3]^+[BF_4]^-$ in MeCN.

12. DFT Calculations

Computational Details.

All geometry optimizations and vibrational frequency calculations were obtained from density functional theory with the M06 exchange-correlation functional[1] computations as implemented in Gaussian 09[2]. Nonmetals (C, H, O, N) used 6-31G(d,p) basis set[3, 4] and SDD[5] was used for Mn. The single point energies of optimized structures were calculated at M06/[6-311++G(d,p) + SDD] level. All geometric structure optimizations, vibrational frequency calculations and single point energy calculations were obtained in acetonitrile solvent using the polarizable continuum model (CPCM)[6,7].

The reduction potential $E_{O|R}$ relative to the ferrocene/ferrocenium couple was

$$E_{O|R} = -\frac{\Delta G_{O|R}}{nF} - E_{SCE}^{ref} - 0.384V$$

calculated using the following formula:

ΔG is the total Gibbs free energy; n is the number of electrons involved in the electrochemistry reaction. F is Faraday's constant. E_{SCE}^{ref} is taken as -4.422 V[8], which is the absolute potential of saturated calomel electrode (SCE) in acetonitrile solution. -0.384V is the shift value of reduction potential for ferrocene/ferrocenium couple relative to SCE.[9] For the reactions involving the participation of electrons, the energy contributions due to the least negative reductive potential were added to all the species after each electronreduction step.

Refs

[1] Zhao, Y.; Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **2008**, 120, 215-241.

[2] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.;

Nakai, H.; Vreven, T.; Montgomery, J. J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision D.01; Gaussian, Inc.: Wallingford, CT, **2009**.

[3] Hehre, W. J.; Ditchfield, R.; Pople, J. A. Self-consistent molecular orbital methods. XII. Further extensions of gaussian-type basis sets for use in molecular orbital studies of organic molecules. *J. Chem. Phys.* **1972**, 56, 2257-2261.

[4] Hariharan, P. C.; Pople, J. A. The influence of polarization functions on molecular orbital hydrogenation energies. *Theor. Chim. Acta.* **1973**, 28, 213-222.

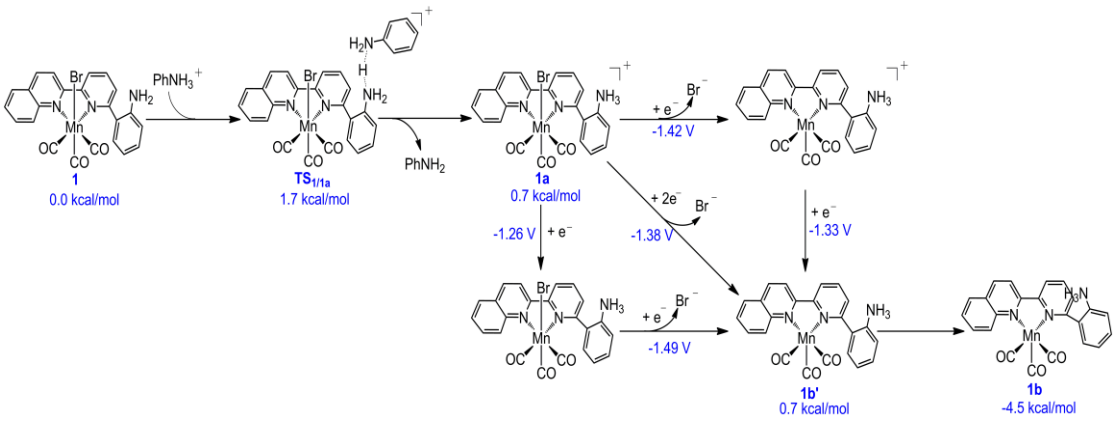
[5] Dolg M.; Wedig U.; Stoll H.; Preuss H. Energy-adjusted ab initio pseudopotentials for the first row transition elements. *J. Chem. Phys.* **1987**, 86, 866-872.

[6] Barone V.; Cossi M. Quantum calculation of molecular energies and energy gradients in solution by a conductor solvent model.*J. Phys. Chem. A.* **1998**, 102, 1995-2001.

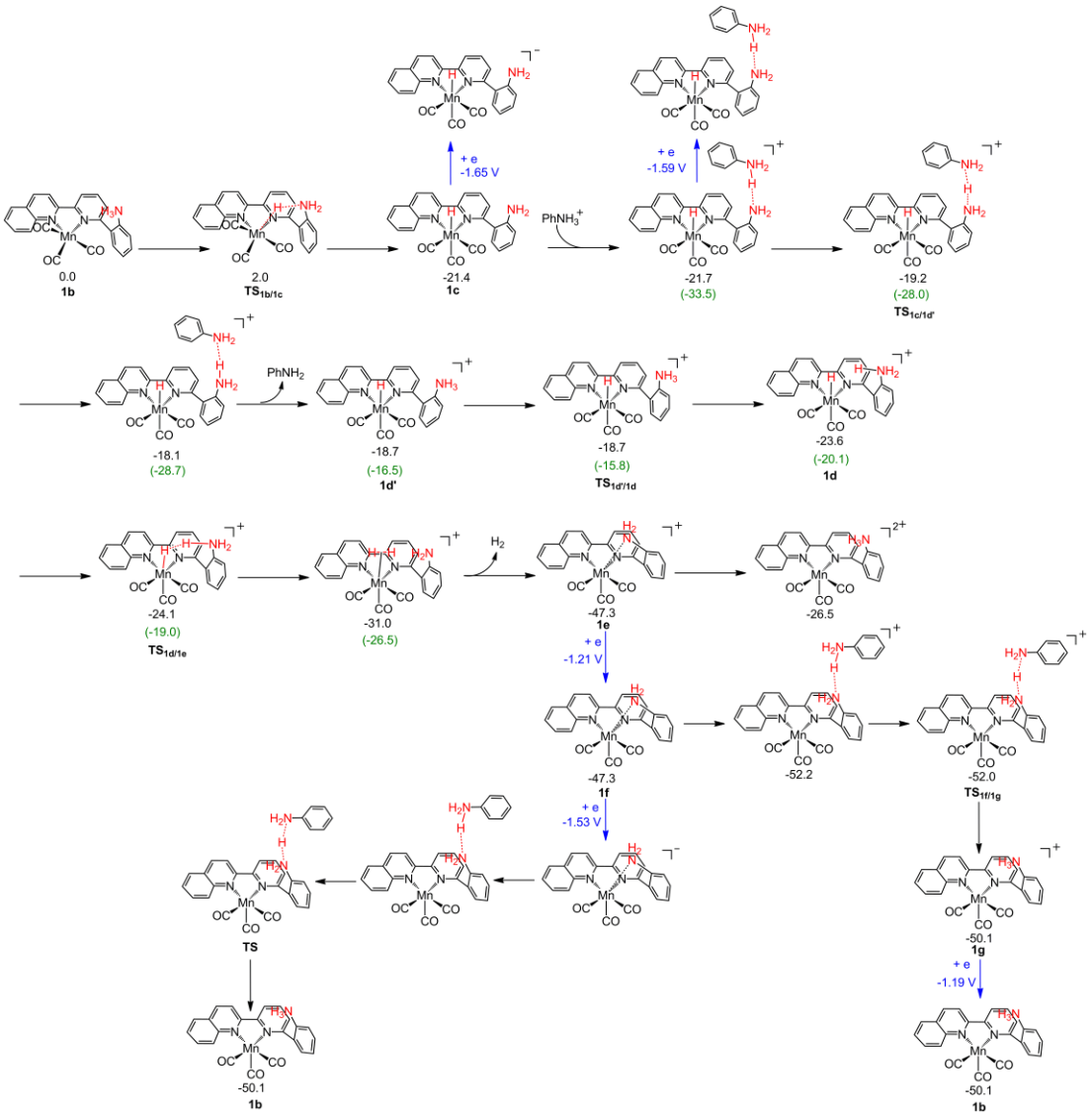
[7] Cossi M.; Rega N.; Scalmani G.; Barone V. Energies, structures, and electronic properties of molecules in solution with the C-PCM solvation model. *J. Comp. Chem.***2003**, 24, 669-681.

[8] Isse A. A.; Gennaro A. Absolute potential of the standard hydrogen electrode and the problem of interconversion of potentials in different solvents. *J. Phys. Chem. B* **2010**, 114, 7894-7899.

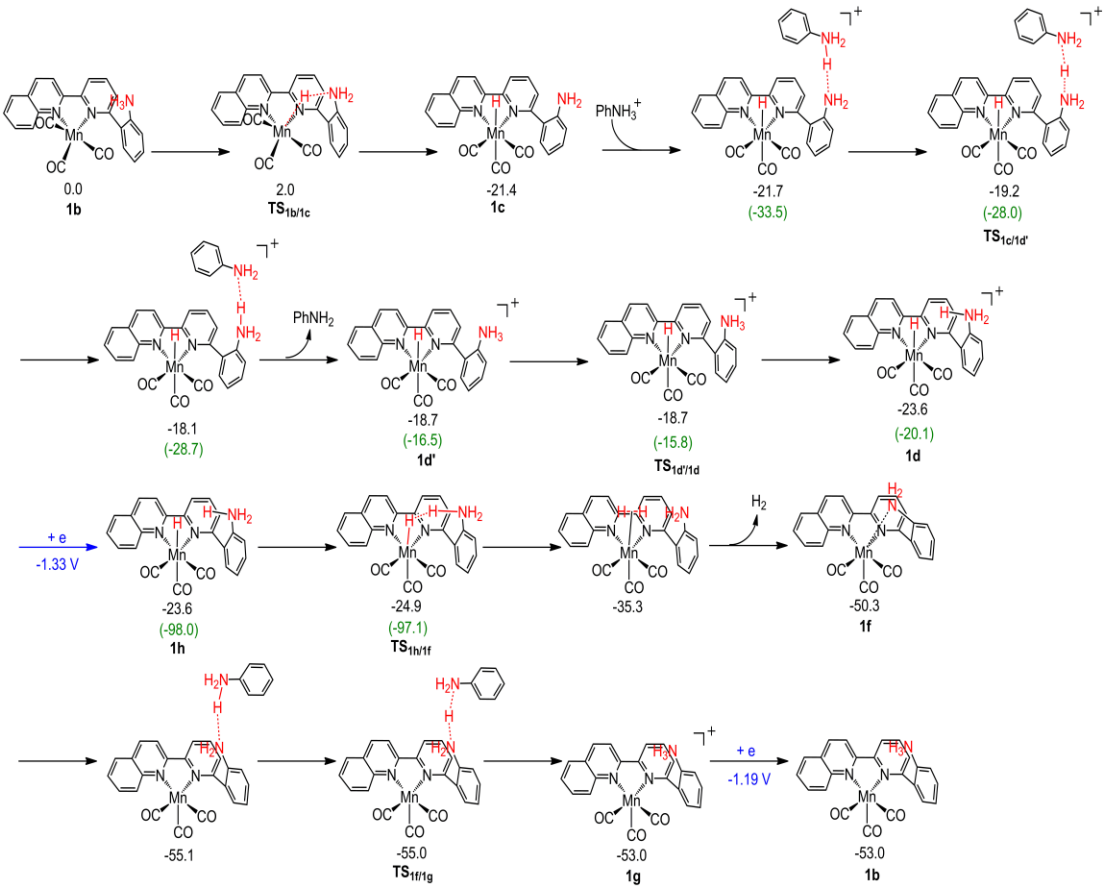
[9] Ngo K. T.; McKinnon M.; Mahanti B.; Narayanan R.; Grills D. C.; Ertem M. Z.; Rochford J. Turning on the protonation-first pathway for electrocatalytic CO_2 reduction by manganese bipyridyl tricarbonyl complexes. *J. Am. Chem. Soc.* **2017**, 139, 2604-2618.



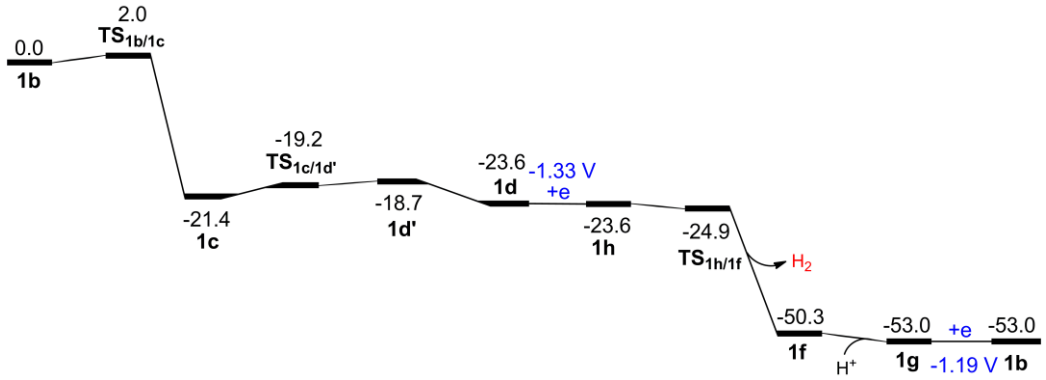
Scheme S 5 Computated reduction potentials (V *vs.* $Fc^{+/0}$) and free energies (kcal/mol) for the generation of active catalyst **1b**.



Scheme S 6 Detail mechanism for hydrogen evolution reaction via **path 1** along with the calculated free energies relative to **1b** (in kcal/mol). The values labled in green are electronic energies relative to **1b**.



Scheme S 7 Detail mechanism for hydrogen evolution reaction via **path 2** along with the calculated free energies relative to **1b** (in kcal/mol). The values labled in green are electronic energies relative to **1b**.



Scheme S 8 Free energy profile for hydrogen evolution reaction via **path 2**. Computated reduction potentials and free energies are given in V *vs.* $Fc^{+/0}$ and kcal/mol.

Cartesian coordinates of optimized key structures

1

Br	-0.07756600	0.34012500	2.37140500
Mn	-0.08502600	-0.77528100	0.07181000
O	-0.02251200	-2.07466300	-2.56290900
O	-1.39939000	-2.99990200	1.48558600
O	2.27634200	-2.27815400	0.99207900
N	0.71148900	1.05395000	-0.55573300
N	-1.82108100	0.31130500	-0.41468400
C	-0.04551600	-1.55613500	-1.52625300
C	-0.91622200	-2.13244800	0.88994700
C	1.41030300	-1.62365100	0.59081600
C	2.01147100	1.37397900	-0.68977600
C	2.42984300	2.70572700	-0.77442500
H	3.49230200	2.91192900	-0.86453500
C	1.49606000	3.72391200	-0.75157600
H	1.80124200	4.76360900	-0.82342000
C	0.15380400	3.38955400	-0.64717100
H	-0.59719600	4.17078100	-0.64146200
C	-0.20692200	2.05149600	-0.54492800
C	-1.61067100	1.62646200	-0.44107600
C	-2.66437700	2.56538400	-0.39210000
H	-2.45671000	3.62864400	-0.37811800
C	-3.95404100	2.11916700	-0.33662600
H	-4.78441100	2.81836900	-0.26741800
C	-4.21816000	0.73634300	-0.41037100
C	-3.11075900	-0.15775500	-0.48158600
C	3.05002400	0.32259300	-0.76611100
C	3.16953600	-0.46467800	-1.91345300
C	4.20423200	-1.38097600	-2.04942900
H	4.28914900	-1.98528000	-2.94828200
C	5.14470400	-1.49050900	-1.02477000
C	5.03789300	-0.71966100	0.12284800
H	5.76430700	-0.82756300	0.92685100
C	3.98249500	0.18841100	0.28124600
C	-3.37993500	-1.53328900	-0.67022900
C	-4.67350400	-1.99311600	-0.72631500
C	-5.76633000	-1.11223100	-0.59181300
C	-5.53812700	0.23191600	-0.44508800
H	-2.55679200	-2.22347100	-0.81336300
H	-4.85457900	-3.05273500	-0.88621000
H	-6.78109500	-1.49852900	-0.62576300

H	-6.36293500	0.93749500	-0.37013100
H	5.96987400	-2.19321700	-1.11765400
H	2.44030700	-0.33519700	-2.71250600
N	3.86478400	0.94526500	1.43694500
H	4.40162100	0.59993800	2.22155700
H	2.91868400	1.18800800	1.71170600

1a

Br	-0.04170300	-0.24176700	2.26289500
Mn	-0.08357900	-0.78847300	-0.22643300
O	-0.04986400	-1.32681600	-3.11881500
O	-1.36336400	-3.31115700	0.59815400
O	2.22340700	-2.56820000	0.18510500
N	0.72197800	1.14288600	-0.45420400
N	-1.83397500	0.38925000	-0.39595600
C	-0.07013200	-1.11904200	-1.98126000
C	-0.91013700	-2.31393900	0.22867400
C	1.38429400	-1.78986700	0.00983100
C	2.00738800	1.50499000	-0.62546400
C	2.39043400	2.83286100	-0.80715100
H	3.44200500	3.06265700	-0.95355000
C	1.42668600	3.82863100	-0.79104400
H	1.69752200	4.86905000	-0.94127400
C	0.10962500	3.46594700	-0.56784900
H	-0.66730200	4.22174600	-0.54997600
C	-0.21017300	2.12158000	-0.39634100
C	-1.59828900	1.68378100	-0.19506600
C	-2.60481200	2.59577900	0.18552100
H	-2.35761600	3.62845800	0.40375500
C	-3.88825400	2.14591800	0.32593400
H	-4.68065000	2.81233500	0.65897400
C	-4.19857900	0.81175600	-0.00476300
C	-3.13510900	-0.04964700	-0.40474300
C	3.08840300	0.48934400	-0.56674700
C	3.61572500	-0.06548900	-1.73226400
C	4.69705200	-0.93830400	-1.67295700
H	5.09397700	-1.36670900	-2.58871300
C	5.27608900	-1.25260300	-0.44833100
C	4.77145800	-0.70123700	0.72502900

H	5.21891500	-0.94255900	1.68632800
C	3.69171300	0.16151400	0.64897100
C	-3.46470800	-1.34565000	-0.86361600
C	-4.76792900	-1.77958300	-0.85611200
C	-5.80859300	-0.95096400	-0.38695200
C	-5.52649000	0.32706800	0.02149300
H	-2.68739400	-1.98046300	-1.27320500
H	-5.00026100	-2.77319000	-1.22985900
H	-6.83039200	-1.31938800	-0.37597300
H	-6.31568600	0.99890800	0.35195000
H	6.12518900	-1.92757000	-0.39963900
H	3.16600800	0.19720900	-2.68755100
N	3.14255900	0.72182600	1.89337300
H	3.68955400	0.41609300	2.70292200
H	3.15833900	1.74743600	1.90056700
H	2.14751700	0.42422300	2.06796600

1b

Mn	0.04877200	-0.72737400	0.34203600
O	1.31250000	-2.03069100	2.65279700
O	0.48879100	-2.87003900	-1.62321300
O	-2.27846100	-2.24274600	1.30894500
N	-0.74776400	1.10521000	0.16489900
N	1.72701000	0.37030000	0.00299700
C	0.80346500	-1.47858000	1.74999600
C	0.32098600	-1.97443300	-0.87663800
C	-1.40850400	-1.57842900	0.88730000
C	-2.07580500	1.49685800	0.16495300
C	-2.46824900	2.81378400	0.28709800
H	-3.53097000	3.04161300	0.29347600
C	-1.51551300	3.84110700	0.34027400
H	-1.81558700	4.87987900	0.43575300
C	-0.19582300	3.48708500	0.20690600
H	0.56979800	4.25606900	0.19446200
C	0.17585000	2.13627600	0.10259500
C	1.53379900	1.71394400	-0.02618300
C	2.60337200	2.63735500	-0.18343800
H	2.39524200	3.70169200	-0.21200600
C	3.87874700	2.19212600	-0.31105700

H	4.71064900	2.88183400	-0.43633600
C	4.13082700	0.79255900	-0.28530700
C	3.03388000	-0.09926900	-0.12691700
C	-3.15490600	0.50647700	-0.04461300
C	-4.23487500	0.43543100	0.84172700
C	-5.30111500	-0.42581700	0.61460500
H	-6.12030800	-0.46626400	1.32751100
C	-5.32067300	-1.23820800	-0.51478900
C	-4.26981800	-1.17651700	-1.42353700
H	-4.27367600	-1.79336800	-2.31963000
C	-3.22229200	-0.30425400	-1.18314600
H	-1.21231000	-0.48943900	-1.63186400
C	3.31840600	-1.48039200	-0.10467900
C	4.60987800	-1.95049000	-0.23077200
C	5.68703700	-1.06541200	-0.38660000
C	5.44013300	0.28879000	-0.41328700
H	2.50139000	-2.18094600	0.01775400
H	4.78867500	-3.02300700	-0.20886100
H	6.70076300	-1.44492900	-0.48547700
H	6.25446600	1.00186400	-0.53330900
H	-6.15094600	-1.91447700	-0.69551000
H	-4.21572000	1.05891900	1.73296500
N	-2.11792300	-0.24527400	-2.13815000
H	-1.99714700	0.68959900	-2.53937000
H	-2.24835500	-0.89847000	-2.91386400

$TS_{1b/1c}$

Mn	0.00925000	-0.71681000	0.39204400
O	1.36985200	-1.74662800	2.79279000
O	0.27847900	-2.98782800	-1.44172100
O	-2.30107700	-2.06351600	1.61330400
N	-0.75754900	1.15187500	0.16636700
N	1.70960400	0.36659600	-0.03233800
C	0.81677300	-1.27251800	1.87211100
C	0.19117100	-2.04067000	-0.73836000
C	-1.43250900	-1.48326500	1.08392500
C	-2.07404000	1.52632300	0.09097900
C	-2.46398500	2.85679700	0.16561900
H	-3.52330900	3.09460900	0.12164700

C	-1.50821800	3.86714000	0.23346200
H	-1.80150300	4.91095600	0.28899400
C	-0.17841100	3.50616900	0.15733300
H	0.58875500	4.27265000	0.13916100
C	0.17407300	2.15455800	0.10393700
C	1.54151700	1.70269100	-0.02540100
C	2.61969300	2.61334600	-0.16154800
H	2.43255200	3.68135300	-0.15040000
C	3.88759600	2.14541200	-0.31506200
H	4.73048500	2.82402900	-0.42555900
C	4.11266000	0.74681100	-0.33109600
C	2.99858200	-0.12633000	-0.18035200
C	-3.12718500	0.51813100	-0.14767700
C	-4.27678500	0.50535900	0.65202300
C	-5.30423600	-0.39920200	0.42785400
H	-6.17691100	-0.39793500	1.07536100
C	-5.20978400	-1.31204000	-0.62087600
C	-4.09432900	-1.30189600	-1.44645600
H	-4.01632900	-1.99856600	-2.27905900
C	-3.07469900	-0.38171800	-1.22587900
H	-0.91239200	-0.78032000	-1.30666800
C	3.24786200	-1.51618000	-0.18194800
C	4.52523800	-2.00860800	-0.33230300
C	5.62156300	-1.14188900	-0.48762600
C	5.41096500	0.21592900	-0.48594000
H	2.41290200	-2.19496200	-0.05596100
H	4.68414700	-3.08423200	-0.33012100
H	6.62398800	-1.54463400	-0.60628400
H	6.24082000	0.91103200	-0.60103000
H	-6.00837400	-2.02600300	-0.80268700
H	-4.33890600	1.20386400	1.48425800
N	-1.91126500	-0.41452400	-2.05584600
H	-1.63676700	0.50352300	-2.40575600
H	-2.01501600	-1.04505100	-2.84956100

1c

Mn	0.10784500	-0.75062800	-0.44425300
O	-0.03888100	-2.22980100	2.13729600

O	1.49744600	-2.81336800	-1.98853200
O	-2.26099600	-2.09986000	-1.53307500
N	-0.70331800	1.11422600	0.06738100
N	1.82274200	0.37452800	-0.00077300
C	0.01988900	-1.59493700	1.16455100
C	0.96471200	-2.01631300	-1.32637300
C	-1.36999800	-1.52105700	-1.05887700
C	-2.00120500	1.43908900	0.24246700
C	-2.42028500	2.77253700	0.28173900
H	-3.47532400	2.98421900	0.43624500
C	-1.49610200	3.79400900	0.15093000
H	-1.80590000	4.83454500	0.17428000
C	-0.15760400	3.45871500	0.02407200
H	0.58950400	4.24068300	-0.04738900
C	0.20912600	2.11617700	-0.00025500
C	1.61390800	1.69084300	-0.04645400
C	2.67059300	2.62824400	-0.09495300
H	2.46273600	3.68924700	-0.16901700
C	3.96162400	2.18506900	-0.06358400
H	4.79439200	2.88235900	-0.12305100
C	4.22018400	0.80682400	0.08725800
C	3.11054300	-0.08554600	0.13993800
C	-3.01726600	0.38263900	0.44863600
C	-2.96727200	-0.39923200	1.60509700
C	-3.93364000	-1.35855600	1.87264500
H	-3.88193600	-1.95462700	2.77966300
C	-4.98336600	-1.52322700	0.96769900
C	-5.05712800	-0.74947700	-0.17937000
H	-5.87413900	-0.89066700	-0.88550600
C	-4.07522500	0.21052400	-0.46661900
H	0.19829100	-0.08875500	-1.90111700
C	3.36946600	-1.45521300	0.38140900
C	4.65806400	-1.91130000	0.51972800
C	5.75607100	-1.03239700	0.41610500
C	5.53621100	0.30542800	0.20947700
H	2.53452800	-2.13840000	0.48792900
H	4.83141300	-2.96572700	0.71866100
H	6.76796900	-1.41513500	0.51640600
H	6.36483100	1.00824100	0.15033000
H	-5.75895600	-2.26101900	1.16167700
H	-2.15198500	-0.23253100	2.30751800
N	-4.10869700	0.89116400	-1.67090600
H	-3.60448700	1.76524300	-1.72276100

H	-5.01052700	0.93576400	-2.12455200

$TS_{1c/1d'}$

Mn	0.45647000	-0.21481100	-0.73430100
O	0.94292100	-2.44722400	-2.65260800
O	1.31426600	2.05895000	-2.36885300
O	-2.10813000	0.41580000	-2.00488500
N	-0.13532400	-1.23798000	0.98882500
N	2.27240300	-0.43172700	0.30069000
C	0.76937500	-1.61534400	-1.86114000
C	1.01179500	1.11695700	-1.75618900
C	-1.12243200	0.11608800	-1.45383400
C	-1.35115400	-1.74692800	1.27441300
C	-1.71095400	-2.13082400	2.56589600
H	-2.70124400	-2.54472600	2.73796700
C	-0.79622600	-2.00011400	3.59933700
H	-1.05654700	-2.28473300	4.61408100
C	0.46795100	-1.52351000	3.30097800
H	1.20910700	-1.43594100	4.08673600
C	0.77455500	-1.16218600	1.99010800
C	2.11548000	-0.71405100	1.59428300
C	3.17294000	-0.63263600	2.52746600
H	3.00104300	-0.84044900	3.57700600
C	4.41895600	-0.27719100	2.09641500
H	5.24759200	-0.18601000	2.79503200
C	4.64437300	-0.06203600	0.72141000
C	3.53720600	-0.16995400	-0.16993700
C	-2.33967600	-1.95244400	0.18764100
C	-2.12123000	-2.94383500	-0.77317200
C	-3.06630100	-3.20293100	-1.75634900
H	-2.88087800	-3.97952900	-2.49301900
C	-4.25517900	-2.47738200	-1.78786900
C	-4.49081600	-1.48868800	-0.84180300
H	-5.40766200	-0.90313500	-0.86579100
C	-3.53807300	-1.24046100	0.13766300
H	0.20634400	1.06129200	0.19375800
C	3.78501000	-0.03833900	-1.55662900
C	5.05154400	0.22253600	-2.02060800
C	6.13552700	0.37575100	-1.13155600

C	5.93221100	0.22942600	0.21658100
H	2.96757500	-0.17681500	-2.25491700
H	5.21957400	0.30571300	-3.09119000
H	7.12714200	0.59328400	-1.51846800
H	6.75571300	0.31945300	0.92198000
H	-4.99994200	-2.67773200	-2.55272500
H	-1.19835000	-3.51832200	-0.73017600
N	-3.77962100	-0.12684900	1.04271600
H	-3.03650200	-0.02728500	1.73819900
H	-4.65484000	-0.24094900	1.55901900
C	-2.70789700	3.28934600	1.42952200
C	-1.63849400	4.06011100	1.87324900
C	-0.66368500	4.49206600	0.97665700
C	-0.76715600	4.15364400	-0.36942100
C	-1.83822400	3.39011000	-0.82290900
C	-2.80800100	2.95919900	0.07846500
H	-3.47226100	2.94976700	2.12745000
H	-1.56702300	4.32155200	2.92609900
H	0.17257000	5.09173300	1.32673500
H	-0.00939100	4.48186200	-1.07668400
H	-1.91805300	3.12193000	-1.87483400
N	-3.89293400	2.11759700	-0.34600400
H	-3.85462200	0.86823900	0.43433600
H	-4.79814700	2.55987100	-0.19279900
H	-3.81562700	1.88543000	-1.33511400

1d'

Mn	0.11925500	-0.71880300	-0.55889900
O	-0.25766100	-2.35820700	1.90877900
O	1.54354900	-2.76500400	-2.10581900
O	-2.24444600	-1.60475400	-2.03044100
N	-0.67756300	1.12416800	0.02982700
N	1.82463200	0.36538900	0.00167400
C	-0.10131600	-1.66535000	0.99147100
C	0.99311800	-1.97982400	-1.44974800
C	-1.32426800	-1.28024700	-1.37996900
C	-1.97239900	1.45167200	0.20761400
C	-2.41209100	2.77352900	0.17193600
H	-3.46313800	2.99377900	0.34205100

C	-1.49005700	3.79079400	-0.03399600
H	-1.80918100	4.82722000	-0.08293100
C	-0.14823200	3.46171200	-0.12329600
H	0.59402800	4.24380600	-0.23645100
C	0.23124800	2.12185800	-0.06560200
C	1.63377000	1.68568400	-0.04158100
C	2.69619500	2.61319500	-0.00281000
H	2.50066000	3.67790000	-0.05788800
C	3.97928500	2.15424100	0.10258000
H	4.82040100	2.84368700	0.11540200
C	4.21499900	0.77076300	0.23495100
C	3.09583000	-0.11199300	0.20179100
C	-2.94026300	0.38376300	0.56862400
C	-2.83195000	-0.21643800	1.82602700
C	-3.74968000	-1.16966000	2.24585800
H	-3.64256400	-1.62382900	3.22673600
C	-4.80731300	-1.53533400	1.41798300
C	-4.94092200	-0.94924300	0.16549100
H	-5.75297700	-1.23570000	-0.49847200
C	-4.01539100	0.00305900	-0.23170000
H	0.30416600	0.02235400	-1.95656800
C	3.32542100	-1.49104700	0.41816400
C	4.59898400	-1.96490700	0.61707500
C	5.70947900	-1.09463500	0.60320100
C	5.51657700	0.25054500	0.42127600
H	2.47868800	-2.16757800	0.45618000
H	4.75127900	-3.02629000	0.79433600
H	6.70974300	-1.49180300	0.75153600
H	6.35470700	0.94424200	0.42956400
H	-5.53011400	-2.27741000	1.74314600
H	-2.01233600	0.08184500	2.47585800
N	-4.11553100	0.51851100	-1.60631700
H	-3.71309300	1.45606100	-1.71043500
H	-5.08760700	0.56986100	-1.92462700
H	-3.60249300	-0.11365800	-2.24344600

$TS_{1d'/1d}$

Mn	0.08192900	-0.78617700	-0.27324000
O	-0.00238900	-1.86785000	2.50652500

O	1.42894000	-2.98184200	-1.66970500
O	-2.23367800	-2.40051100	-1.05839400
N	-0.68871300	1.12097700	0.09799200
N	1.83183000	0.35522900	0.01062900
C	0.04638700	-1.40625300	1.44348800
C	0.92382700	-2.12970800	-1.06076000
C	-1.36761800	-1.70036000	-0.71307100
C	-1.97176800	1.47953600	0.29647100
C	-2.37221400	2.80910900	0.41034900
H	-3.42278900	3.03208900	0.57682000
C	-1.42477900	3.81653500	0.31417400
H	-1.70894700	4.86079600	0.39809800
C	-0.10332600	3.45624000	0.12000200
H	0.66079600	4.22260400	0.06181000
C	0.23714000	2.10828700	0.02082500
C	1.63100000	1.66749400	-0.10516400
C	2.68419200	2.58819300	-0.29991800
H	2.47580000	3.64155200	-0.44692800
C	3.97131100	2.13211000	-0.33173400
H	4.80144800	2.81207000	-0.50929400
C	4.23125300	0.76742000	-0.09106700
C	3.12264100	-0.10699500	0.10518200
C	-3.03387800	0.44465800	0.38256800
C	-3.36245300	-0.15232000	1.59884800
C	-4.42901100	-1.04138300	1.68301900
H	-4.67035900	-1.50232500	2.63652400
C	-5.19515600	-1.32941400	0.55799200
C	-4.88424900	-0.74578200	-0.66553900
H	-5.46225100	-0.97984000	-1.55599900
C	-3.81234700	0.12605500	-0.72756800
H	0.10421100	-0.26670300	-1.79186600
C	3.38930600	-1.45385300	0.44621400
C	4.68176000	-1.91029100	0.53650500
C	5.77497600	-1.05583100	0.28362700
C	5.54976200	0.26272700	-0.01795200
H	2.56153000	-2.11642900	0.67272000
H	4.86278700	-2.94500600	0.81545300
H	6.78903800	-1.44037800	0.34746400
H	6.37636300	0.94906400	-0.18954800
H	-6.03410800	-2.01521900	0.62624300
H	-2.77326500	0.09231200	2.47996500
N	-3.41844000	0.68089300	-2.03697500
H	-3.51767700	1.70167800	-2.08403800

H	-3.99014600	0.29240300	-2.79348800
H	-2.43691500	0.46063100	-2.26080000

1d

Mn	0.04087900	-0.80000100	0.50315600
O	0.27731800	0.12843300	3.32378000
O	1.32004300	-3.33114300	1.25101600
O	-2.38151600	-2.34835300	1.11607500
N	-0.77166000	1.09066600	-0.03616600
N	1.73391100	0.28840600	-0.12690200
C	0.19033900	-0.20125200	2.21800100
C	0.84575700	-2.31733500	0.94059300
C	-1.46417300	-1.68280200	0.86246800
C	-2.06759300	1.45593200	-0.11663500
C	-2.46698700	2.78746500	0.01332100
H	-3.52071100	3.03600800	-0.06870200
C	-1.51190300	3.76851000	0.21580700
H	-1.80057400	4.80839400	0.33360400
C	-0.17427900	3.40380800	0.22581900
H	0.59090200	4.16170500	0.34737100
C	0.16703700	2.06324900	0.07996200
C	1.56285600	1.60656200	-0.01404100
C	2.63748700	2.52076900	-0.04180500
H	2.46201800	3.58394700	0.07271100
C	3.90993600	2.04893400	-0.20528000
H	4.76150800	2.72551300	-0.19968800
C	4.11864500	0.67366900	-0.43139600
C	2.98532100	-0.19139700	-0.42234100
C	-3.10763000	0.44276900	-0.40042600
C	-4.25271600	0.37875800	0.39779000
C	-5.26949000	-0.52677300	0.12161700
H	-6.14306400	-0.56772400	0.76565900
C	-5.16901400	-1.37635900	-0.97463500
C	-4.04994300	-1.31552900	-1.79801600
H	-3.96706400	-1.96488200	-2.66655200
C	-3.04394700	-0.40910600	-1.50811300
H	-1.01596800	-0.73971900	-1.83191300
C	3.17638400	-1.54727300	-0.77420700

C	4.43320300	-2.02487900	-1.05477500
C	5.56316200	-1.18199400	-0.99344300
C	5.40373300	0.14731400	-0.69760700
H	2.31044700	-2.19124200	-0.87139600
H	4.55627700	-3.06642600	-1.33987200
H	6.55008400	-1.58389600	-1.20481700
H	6.25451300	0.82517100	-0.67949700
H	-5.96191000	-2.08385200	-1.19767400
H	-4.32721300	1.03802500	1.25960600
H	-0.01481000	-1.37350300	-1.01604600
N	-1.86766400	-0.37202400	-2.37390100
H	-1.64549200	0.57159300	-2.70414800
H	-1.99691300	-0.95816600	-3.20168200

$TS_{1d/1e}$

Mn	0.01474900	-0.77417200	0.51294100
O	0.38842000	0.20156400	3.29065900
O	1.28188800	-3.31655100	1.27162500
O	-2.42420000	-2.20960400	1.33841800
N	-0.78048200	1.10151300	-0.03680400
N	1.71294200	0.28915000	-0.13810400
C	0.23871900	-0.16482700	2.20569800
C	0.81232300	-2.30608100	0.95394100
C	-1.50568400	-1.59938000	0.98382000
C	-2.07506300	1.45965300	-0.15866600
C	-2.47240800	2.79629700	-0.06397300
H	-3.52299600	3.04587600	-0.17670700
C	-1.52053800	3.77932700	0.13832900
H	-1.81059600	4.82181700	0.22651800
C	-0.18135200	3.41672200	0.17996100
H	0.58228500	4.17793200	0.29108700
C	0.15944300	2.07423800	0.07041500
C	1.55344200	1.60836500	-0.01195900
C	2.63735200	2.51027100	-0.02285900
H	2.47282700	3.57336500	0.10783300
C	3.90519400	2.02545900	-0.18972200
H	4.76392500	2.69270800	-0.17337300
C	4.10082800	0.65106200	-0.43162000
C	2.95916500	-0.20297400	-0.43178900

C	-3.09949700	0.43506100	-0.44740500
C	-4.27984200	0.40927900	0.30256000
C	-5.27559500	-0.52159800	0.04154800
H	-6.17561800	-0.53551500	0.64933800
C	-5.11408000	-1.43566400	-0.99549500
C	-3.96350900	-1.40820200	-1.77357200
H	-3.83896900	-2.10668100	-2.59831000
C	-2.97009400	-0.47352500	-1.50880100
H	-0.82076700	-0.92070300	-1.58044100
C	3.13618800	-1.55842700	-0.79180100
C	4.38845500	-2.04626100	-1.07506800
C	5.52637500	-1.21452200	-1.00841600
C	5.38057000	0.11397000	-0.70202100
H	2.26593100	-2.19633200	-0.89381800
H	4.50157500	-3.08708800	-1.36651000
H	6.50910100	-1.62465000	-1.22312400
H	6.23824600	0.78275800	-0.67797300
H	-5.88844300	-2.16702800	-1.20836000
H	-4.39515500	1.11579500	1.12173100
H	-0.04410900	-1.36699500	-1.03817300
N	-1.77048200	-0.48878600	-2.30003600
H	-1.48742500	0.43617400	-2.62688000
H	-1.86359500	-1.09301200	-3.11599400

1e

Mn	-0.16690000	-0.65333800	0.59530500
O	0.97299800	0.16739800	3.19406500
O	0.88349900	-3.38808600	0.98214700
O	-2.55232100	-1.56888900	2.07332600
N	-0.84447600	1.21917000	0.07074500
N	1.55205300	0.33741800	-0.23400500
C	0.52145100	-0.15832300	2.18298000
C	0.49675800	-2.31118400	0.81862100
C	-1.63538100	-1.20983200	1.46856900
C	-2.10744000	1.51566700	-0.27988300
C	-2.49838500	2.84967200	-0.42990500
H	-3.51597600	3.08597300	-0.72464000
C	-1.56228700	3.85502000	-0.24845400
H	-1.85374600	4.89651300	-0.34548000

C	-0.22820700	3.52143600	-0.03385100
H	0.53566000	4.29132500	-0.00752100
C	0.10339500	2.17853100	0.08048000
C	1.47626500	1.65144900	0.01567600
C	2.60988200	2.47848800	0.11209400
H	2.50025800	3.53001300	0.35558700
C	3.84905200	1.92717000	-0.08276900
H	4.74846500	2.53161200	0.01064500
C	3.96376100	0.56895300	-0.44231600
C	2.77185300	-0.20870500	-0.52798700
C	-3.00234200	0.39073400	-0.59557400
C	-4.37916400	0.48884900	-0.38185700
C	-5.23079900	-0.56628900	-0.68240200
H	-6.29564000	-0.47579100	-0.48919700
C	-4.71004600	-1.73580500	-1.22415000
C	-3.34337000	-1.84844100	-1.46154600
H	-2.93535600	-2.76312900	-1.88730700
C	-2.48754300	-0.80134400	-1.14687700
C	2.86586900	-1.54714600	-0.97166800
C	4.08919500	-2.09578300	-1.26737100
C	5.27521100	-1.34158600	-1.13186800
C	5.21098700	-0.03088200	-0.73406700
H	1.95619200	-2.12125900	-1.11685600
H	4.14398400	-3.12186400	-1.62081200
H	6.23347200	-1.79882500	-1.36131300
H	6.11038200	0.57490500	-0.64818900
H	-5.36523700	-2.56830800	-1.46517700
H	-4.78242500	1.39681000	0.06088900
N	-1.06438200	-0.98985200	-1.29660200
H	-0.65157200	-0.29727300	-1.92386900
H	-0.88403700	-1.90168600	-1.71188600

1f

Mn	-0.15071900	-0.62196500	0.65643100
O	0.99827200	0.31717200	3.19678600
O	0.90247500	-3.33334800	1.17121300
O	-2.55801700	-1.49856400	2.12351200
N	-0.85367100	1.20750700	0.07699300
N	1.52006400	0.31436900	-0.21202600

C	0.53153700	-0.06034200	2.20613900
C	0.52185700	-2.26114200	0.94356100
C	-1.63169000	-1.15555000	1.51523400
C	-2.11850000	1.49543700	-0.30635400
C	-2.53242000	2.80942100	-0.45832300
H	-3.53912400	3.03124300	-0.79892500
C	-1.60559100	3.84366200	-0.22406000
H	-1.92099200	4.88102900	-0.29853400
C	-0.28278500	3.53965500	0.00418300
H	0.46063200	4.32887900	0.07746600
C	0.10797200	2.18641000	0.06429600
C	1.43697700	1.68012600	-0.02684200
C	2.59459100	2.49315400	0.00787000
H	2.49207200	3.55716100	0.20731600
C	3.82469000	1.94247700	-0.19786400
H	4.72735300	2.54912300	-0.16076500
C	3.93346300	0.55154600	-0.51601700
C	2.73916000	-0.23058000	-0.53109400
C	-2.98617100	0.35097300	-0.64374400
C	-4.37088900	0.42325200	-0.47178000
C	-5.19932700	-0.64683500	-0.78554100
H	-6.27130000	-0.56839700	-0.62656500
C	-4.64585000	-1.81777700	-1.29174600
C	-3.27069700	-1.90976900	-1.48211200
H	-2.83339500	-2.82477300	-1.87852100
C	-2.43895300	-0.84277300	-1.16190500
C	2.84119800	-1.57916900	-0.93023200
C	4.06584900	-2.14581800	-1.23980200
C	5.24056200	-1.38800800	-1.17667900
C	5.16228500	-0.05023000	-0.82730500
H	1.93138100	-2.16547700	-1.02575100
H	4.10758100	-3.18811200	-1.54848300
H	6.19965800	-1.83928200	-1.41758200
H	6.05959300	0.56709100	-0.79688200
H	-5.28016200	-2.66472600	-1.53956100
H	-4.79877600	1.33032900	-0.05025100
N	-1.01463500	-1.01823600	-1.26295000
H	-0.57160200	-0.30054000	-1.83667500
H	-0.80267700	-1.92070800	-1.68256700

1g

Mn	0.03890400	-0.69034700	0.55596200
O	1.49213800	-2.12968100	2.70274400
O	0.03795800	-2.98721600	-1.34230200
O	-2.35526500	-1.85854600	1.82137300
N	-0.78388300	1.18019900	0.06582300
N	1.73251500	0.37303200	0.01282200
C	0.92490400	-1.55077100	1.86794600
C	0.04472200	-2.04559400	-0.64876600
C	-1.43753900	-1.36025600	1.30193700
C	-2.08621200	1.55208200	0.03211500
C	-2.47892800	2.87426100	0.21717400
H	-3.53387700	3.12768400	0.17422100
C	-1.51397100	3.84794900	0.43162800
H	-1.79873300	4.88204300	0.59933700
C	-0.17827900	3.48465600	0.38987500
H	0.59204400	4.23469400	0.52838700
C	0.15913900	2.14949600	0.17990900
C	1.54898200	1.69662100	0.03897300
C	2.60416200	2.62063200	-0.11809900
H	2.40914300	3.68660400	-0.09935800
C	3.87309300	2.15661000	-0.31817000
H	4.70605400	2.84442700	-0.44446800
C	4.10647900	0.76708800	-0.38007000
C	3.00097900	-0.11563000	-0.20948300
C	-3.11991600	0.53155900	-0.24585200
C	-4.24269900	0.43042600	0.57759600
C	-5.22832600	-0.51890200	0.33363500
H	-6.08462200	-0.58694500	0.99818400
C	-5.11505800	-1.38323100	-0.74862700
C	-4.01929700	-1.28565400	-1.60158400
H	-3.93013700	-1.94023100	-2.46544400
C	-3.05190800	-0.33128600	-1.34416100
C	3.24026700	-1.50652100	-0.28303600
C	4.50682500	-1.98717300	-0.51427100
C	5.60002100	-1.11175000	-0.67679500
C	5.39890500	0.24311500	-0.61044000
H	2.40943300	-2.19233200	-0.16259000
H	4.66593200	-3.06074800	-0.57234900
H	6.59378100	-1.51290100	-0.85492900
H	6.22454700	0.94048500	-0.73552400
H	-5.87974800	-2.12952400	-0.94088400
H	-4.31981200	1.08823100	1.44021300

N	-1.91719700	-0.22018600	-2.27105100
H	-1.02077800	-0.33665700	-1.75164700
H	-1.95401600	-0.94433500	-2.99400300
H	-1.88856700	0.68405000	-2.75448500