*Supporting Information for*

# Hangman Effect Boosts Hydrogen Production by a Manganese Terpyridine Complex

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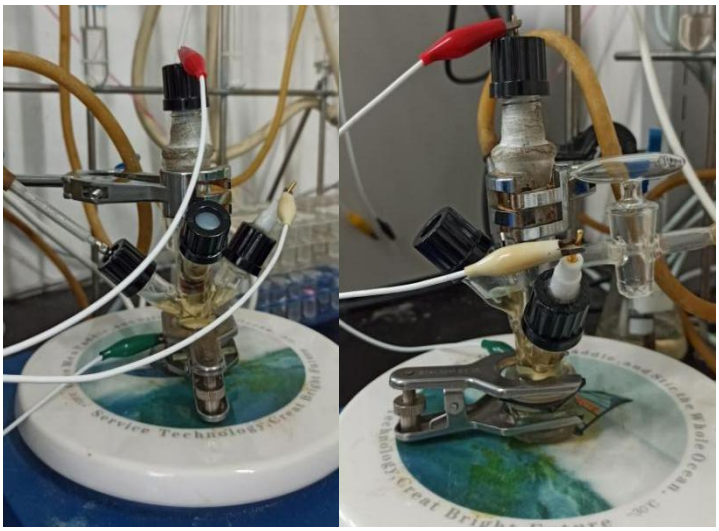
## 4. Electrochemistry Study Details

**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 μm diamond pastes, then sonicated in deionized 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 $CH_3CN$ 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 (0.5 mM) and phenol (1 M) in 0.1 M $^nBu_4NPF_6$ solution in $CH_3CN$. 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 $H_2$ and CO production, given as the sum of headspace and dissolved gases.



**Typical Experimental Conditions:**

Purity of the electrolyte medium was confirmed over the available electrochemical window through background scans taken prior to addition of analyte. 2.6 mg (0.004 mmol) of **1p** and 0.752 g (8 mmol) of phenol 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).

## 5. 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.

Table S 1 Information of calibration gas, sample gas and GC.

| | | | | |
|---|---|---|---|---|
| Composition and concentration of calibration gas | $CH_4$ (91.2 ppm), CO (103.6 ppm), $CO_2$ (115.2 ppm), $H_2$ (382.8 ppm), $O_2$ (381.8 ppm), Ar (bal) | | | |
| Purity of calibration gas | 99.999% | | | |
| Supplier of calibration gas | Chengdu Chenggang Messer Gas Products Co.,Ltd | | | |
| Detector type of GC | Thermal conductivity detector (TCD) for $H_2$ and $O_2$ detection,<br>Flame ionization detector (FID) for $CH_4$ and CO detection | | | |
| Calibration data (peak area for 1 mL calibration gas ) | $H_2$ | $O_2$ | $CH_4$ | CO |
| | 189046 | 83985 | 788817 | 755309 |
| | 189136 | 83554 | 787953 | 752459 |
| | 190374 | 84462 | 789010 | 752494 |

## 6. 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.**

$$\text{efficiency (\%)} = 100 \times n_{prod} \ / (Q / F / 2)$$

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.

Table S 2 Experimental results from controlled potential electrolysis.

| Sample Number | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| Coulombs (C) | 2.05 | 1.88 | 7.75 | 7.57 |
| Calc. moles $H_2$ (μmol) | 10.61 | 9.74 | 40.16 | 39.22 |
| Exp. moles $H_2$ (μmol) | 10.45 | 9.467 | 39.47 | 39.02 |
| Efficiency (%) | 98.5 | 97.2 | 98.3 | 99.5 |
| TON (moles $H_2$/moles cat) | 1.54 | 1.44 | 5.97 | 5.76 |

## 7. Calculation of $k_{obs}$, $TOF_{CV}$, $TON_{CPE}$ and $TOF_{CPE}$

The calculation uses the catalytic plateau current analysis method referred by Lee, K.; Elgrishi, N.; Kandemir, B. et al. (*Nat Rev Chem*. **2017**, 1(5), 1−14)

$$\frac{i_{pl}}{i_p} = \frac{n}{0.4463n'}\sqrt{\frac{R\,T\,k_{obs}}{n'\,F\,v}} \qquad \text{eq 1}$$

$$TOF_{CV} = k_{obs}\,[BH] \qquad \text{eq2}$$

from which $k_{obs}$ can be computed.

$i_{pl}$: the the idealized catalytic plateau current

$i_p$: the current observed in the absence of substrate

$n$ : the number of electrons involved in the catalytic reaction (for HER, $n$ = 2)

$n'$ : the number of electrons correponding to catalytic reaction in the absence of substrate ($n'$= 1).or the number of electrons in the non-catalytic peak used for ip.

F: Faraday's constant ($F$ = 96485.33 C mol$^{-1}$)

$k_{obs}$: the observed first order rate constant

$R$: the universal gas constant (8.314 J mol$^{-1}$ K$^{-1}$)

$T$: the temperature in Kelvin (298 K)

$v$: the scan rate (0.1 V s$^{-1}$)

*0.4463* is a constant determined by numerical solution of the diffusion equations.

[BH] is the substrate (phenol) concentration,

from which $k_{obs}$ can be computed to be 525.4 s$^{-1}$.

Since the $\boldsymbol{k_{obs}}$ is determined at the concentration of 1 M phenol, $TOF_{CV}$ can be calculated to be **525.4 s$^{-1}$.**

$$TON_{CPE} = \frac{n_{prod}}{n_{cat}} \qquad eq\ 3$$

$$TOF_{CPE} = \frac{TON_{CPE}}{t} \qquad eq4$$

Where $n_{prod}$ (mol) is the amount of $H_2$ in the head space determined by GC, $n_{cat}$ (mol) is the amount of total catalyst in the bulk solution, and t (hour) is the electrolysis times.

## 8. Experiment Section

### Materials and Instruments

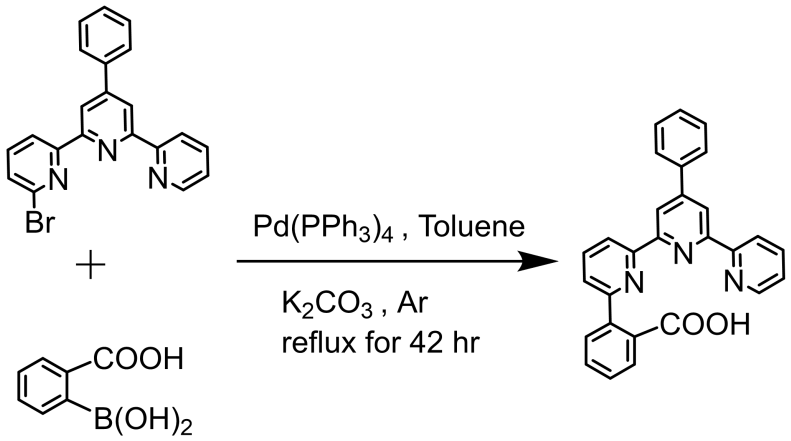
All manipulations for preparation and handling of organometallic complexes were carried out under air. All the solvents were used as received. Other commercially available chemicals such as $Mn(CO)_5Br$, $Pd(PPh_3)_4$, benzaldehyde, 1-(pyridin-2-yl)ethanone, potassium hydroxide, pyridine, Toluene, potassium carbonate, anhydrous methanol and iodine 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.

### Fourier-Transform Infrared Reflectance Spectroelectrochemistry (FTIR-SEC).

A homemade FTIR-SEC instrument was used for this study. The cell consists of a glass carbon working electrode (10 mm), a Pt counter (15 mm × 30 mm) electrode, and a $Ag/AgNO_3$ reference electrode and a $CaF_2$ plate as the optical window. The IR beam is directed to focus on the working electrode through the optical window, where it is reflected and ultimately directed to the Bruker Vertex 80 detector. The dry $CH_3CN$ solution (0.2 M TBAP) prepared under an atmosphere of Ar is used as the electrolyte.

**1) Preparation of L1**



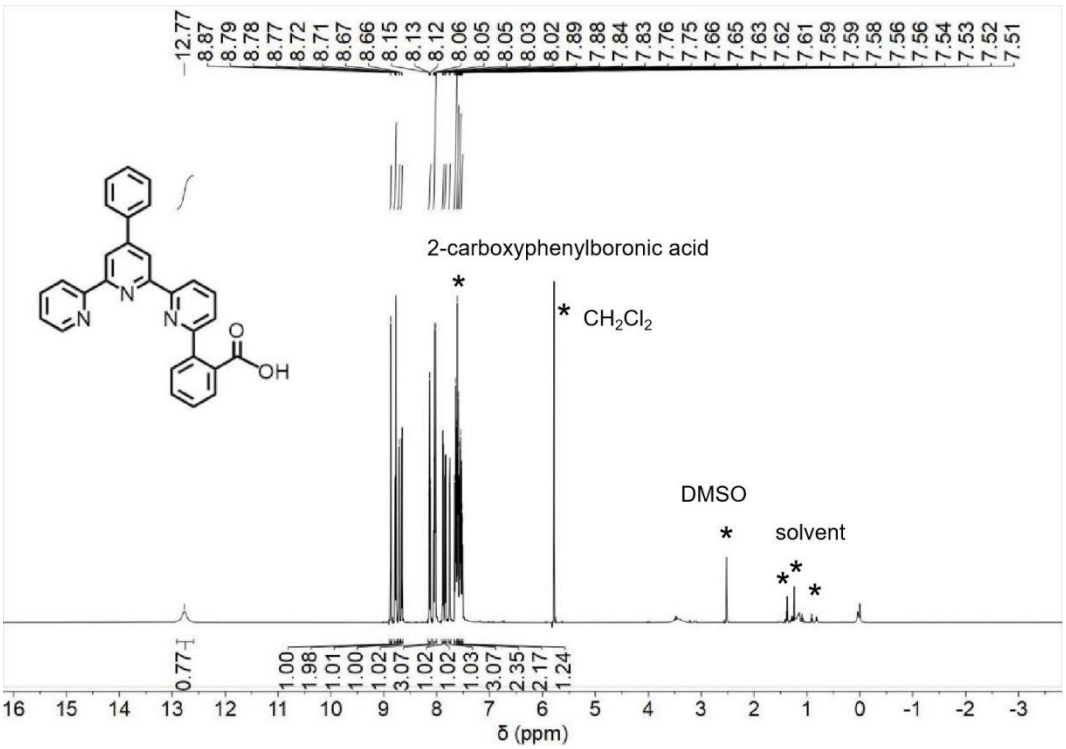

Scheme S 1 Preparation of target ligand **L1**.

2-bromo-6-(4-phenyl-6-(pyridin-2-yl)pyridin-2-yl)pyridine was obtained according to literature procedures. (Constable, E. C. *et. al. J. Chem. Soc., Dalton Trans.,* **1996**, *389*, 4207–4216).

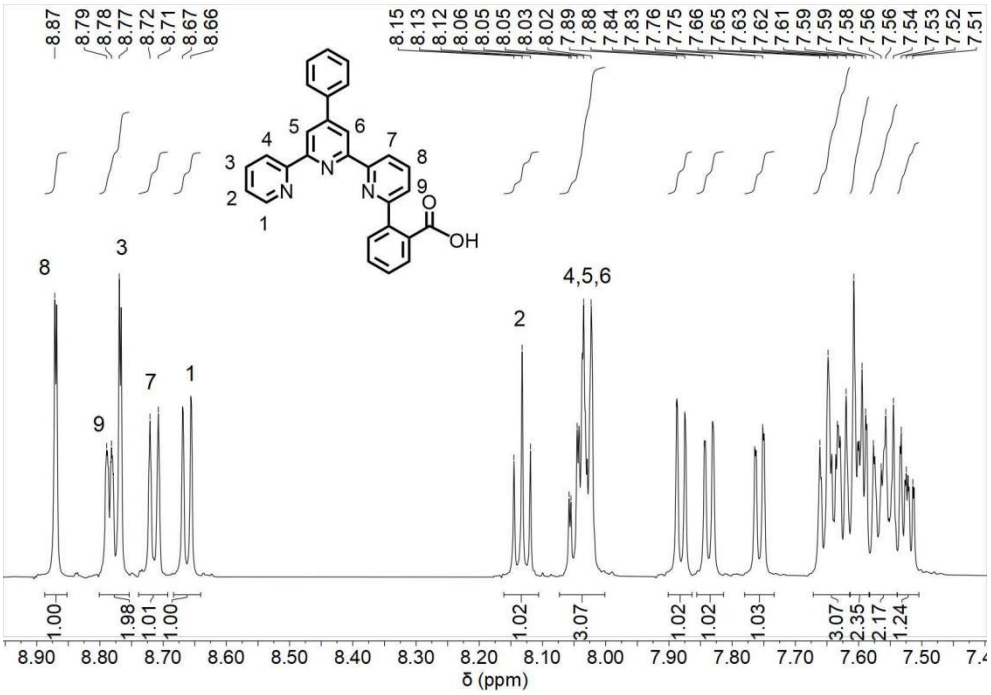
**L1** was obtained according to literature procedures (Solan, G. A. *et. al. Organometallics* **2013***, 32,* 249−259). The product **L1** was obtained as a pale yellow solid (80%). $^1$H NMR (600 MHz, DMSO): $\delta$ 12.77 (1H, s), 8.87 (1H, d), 8.79~8.77 (2H, m), 8.72~8.71 (1H, d), 8.67~8.66 (1H, d), 8.15~8.12 (1H, t), 8.06~8.02 (3H, m), 7.89~7.88 (1H, d), 7.84~7.83 (1H, d), 7.76~7.75 (1H, d), 7.64~7.51 (6H, m).

Besides **L1**, there are another two hydrogen atoms with chemical shift in the range of 7.64~7.51 ppm. These two atoms were assigned to the unpurity, which might be the reactant named 2-boronobenzoic acid, and the mole ratio of the ligand and the impurity is about 1:0.5. However, the impurity has no influence on the next reaction, since the metal-complex was collected as filtrate and the impurity remained in the methanol solvent. In addition, the purity of the ligand can't be improved any more by silica gel column separation and recrystallization, since the ligand was protonated by 2-boronobenzoic acid to generate an ionic complex.

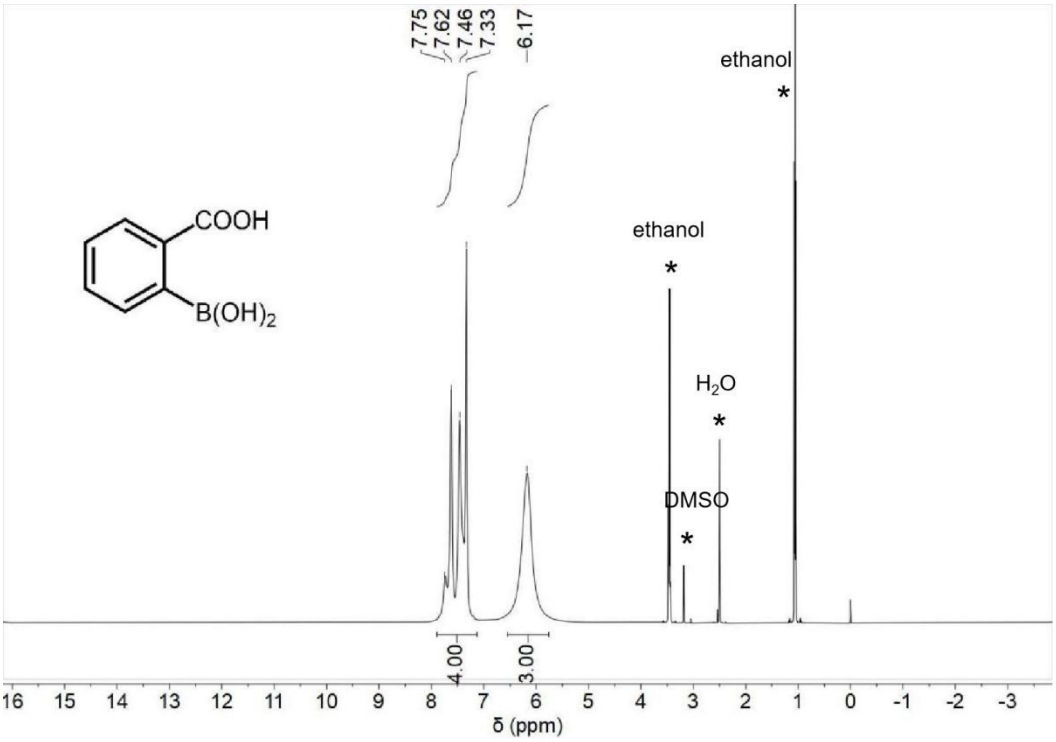
According to the HH-COSY (600 MHz, DMSO) spectrum of **L1**, we proposed an assignment of the chemical shift for the atoms on the pyridine moiety as shown in the magnified $^1$H NMR (600 MHz, DMSO) spectrum of **L1**.



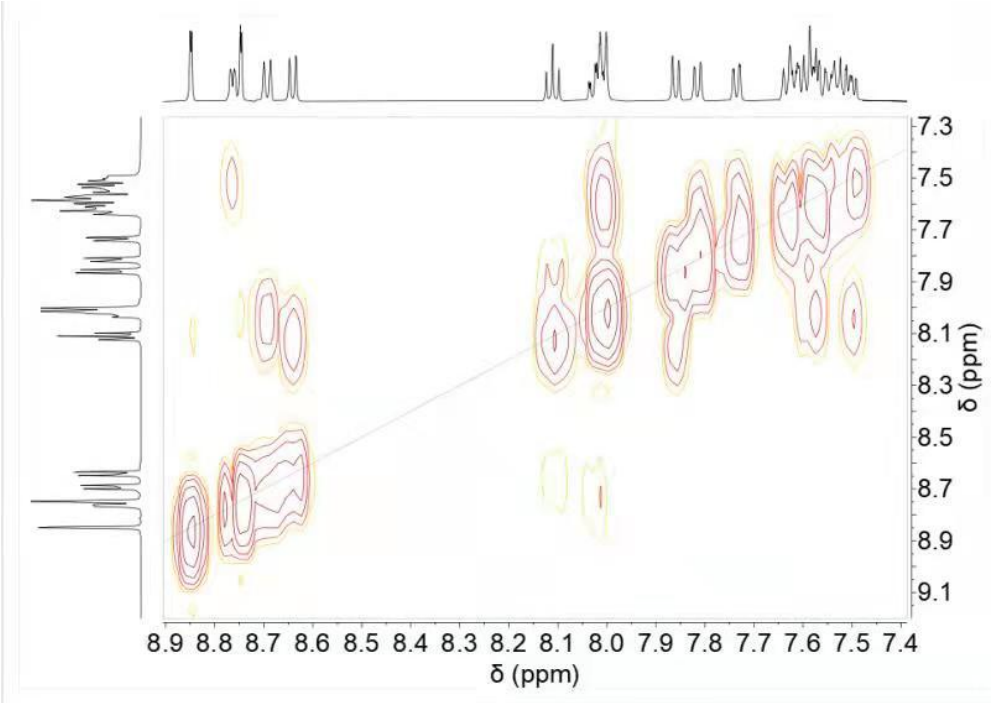

Entire $^{1}$H NMR (600 MHz, DMSO) spectrum of **L1**.



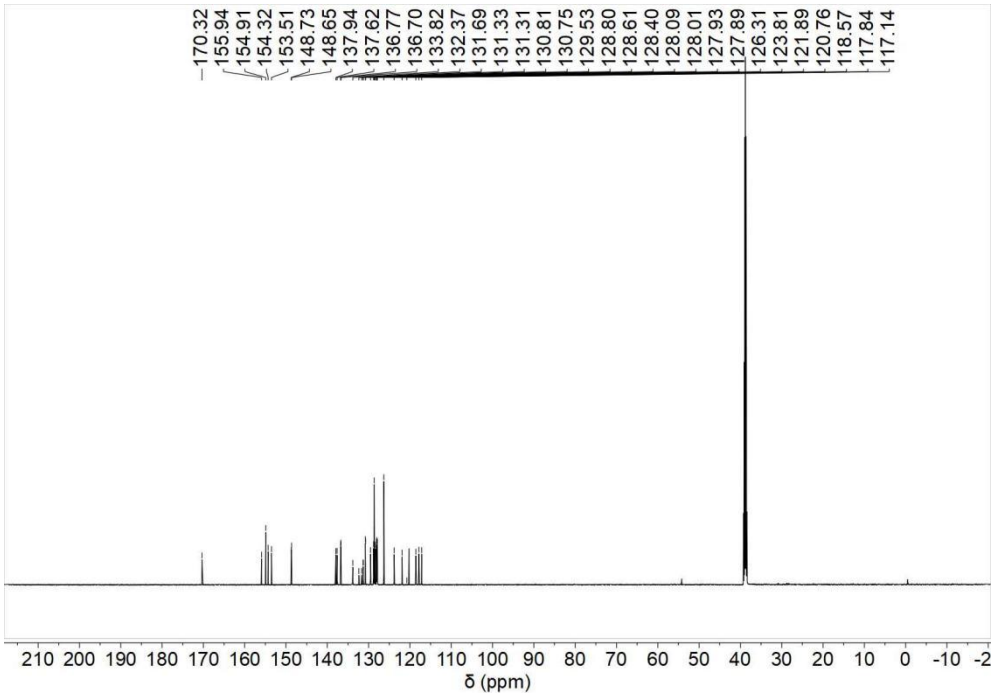

Magnified $^{1}$H NMR (600 MHz, DMSO) spectrum of **L1**



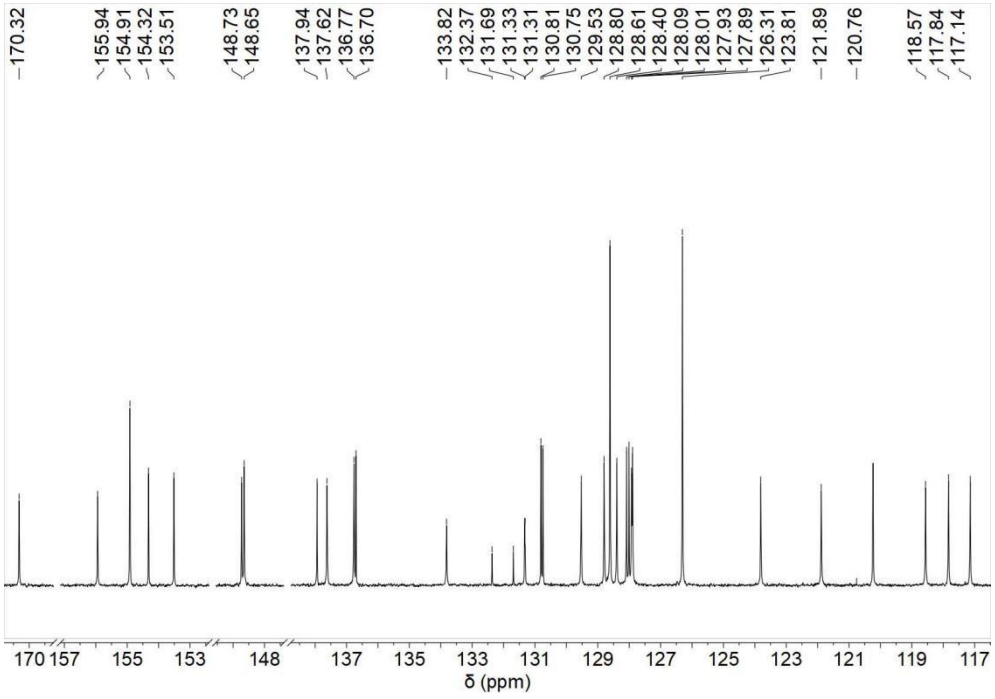

$^{1}$H NMR (600 MHz, DMSO) spectrum of the reactant 2-boronobenzoic acid




HH-COSY (600 MHz, DMSO) spectrum of **L1**

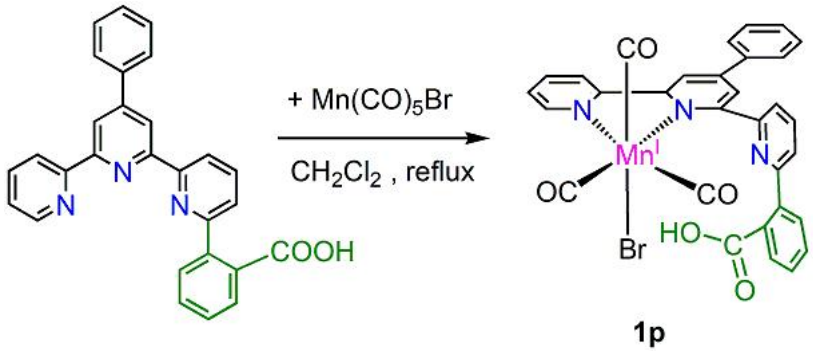



Entire $^{13}$C NMR (600 MHz, DMSO) spectrum of **L1**.



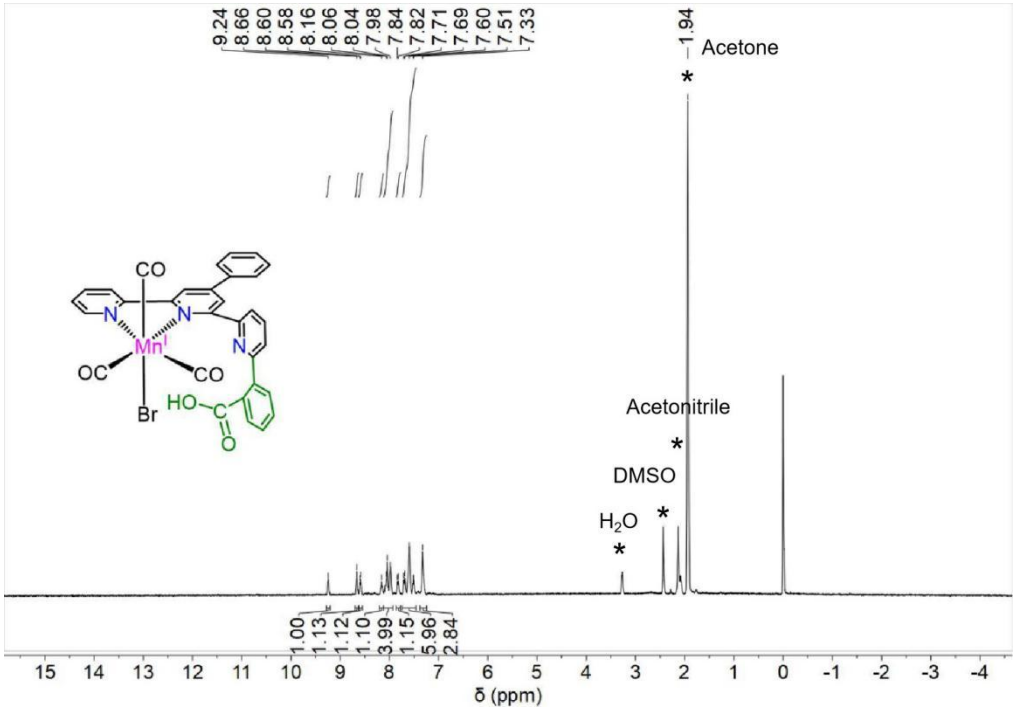

Magnified $^{13}$C NMR (600 MHz, DMSO) spectrum of **L1**

**2) Preparation of complex 1p**

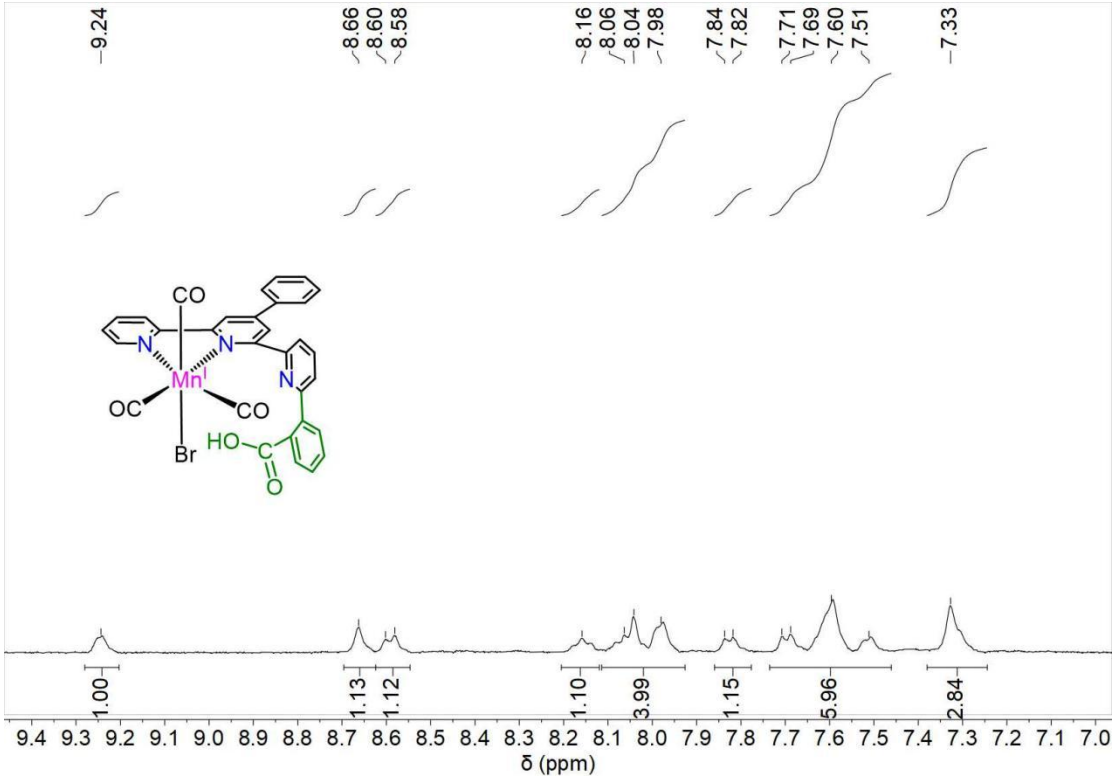



Scheme S 2 Preparation of the precursor **1p**.

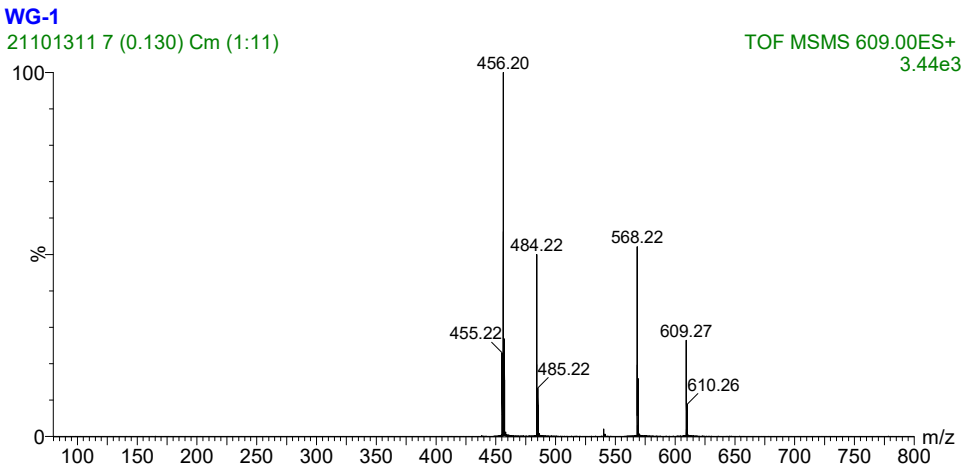
Compound $Mn(CO)_5Br$ (0.2 g, 0.73 mmol) was added to a degassed dichloromethane solution (20 mL) of **L1** (0.31g, 0.73 mmol). The resulting yellow solution was heated to reflux for 3 hours under argon, then allowed to cool to room temperature before filtration. The yellow solid was collected, then washed with petroleum ether and dried in vacuo to afford 0.377 g (80% yield). $^1$H NMR (400 MHz, DMSO): $\delta$ 9.24 (1H, d), 8.66 (1H, s), 8.60~8.58 (1H, d), 8.16 (1H, t), 8.06~7.98 (4H, m), 7.84~7.82 (1H, d), 7.71~7.51 (6H, m) 7.33 (3H, m). Anal. Calcd for **1p**, C31H19MnBrN3O5: C, 57.42; H, 2.93; N, 6.48; Found: C, 56.31; H, 4.27; N, 6.44; MS (TOF-MS): m/z = 568.22, [M–Br$^-$]; 609.27, [M–Br$^-$+$CH_3CN$]. IR: $\nu_{CO}$ (KBr) = 2023, 1946, 1903 and 1714 cm$^{-1}$.



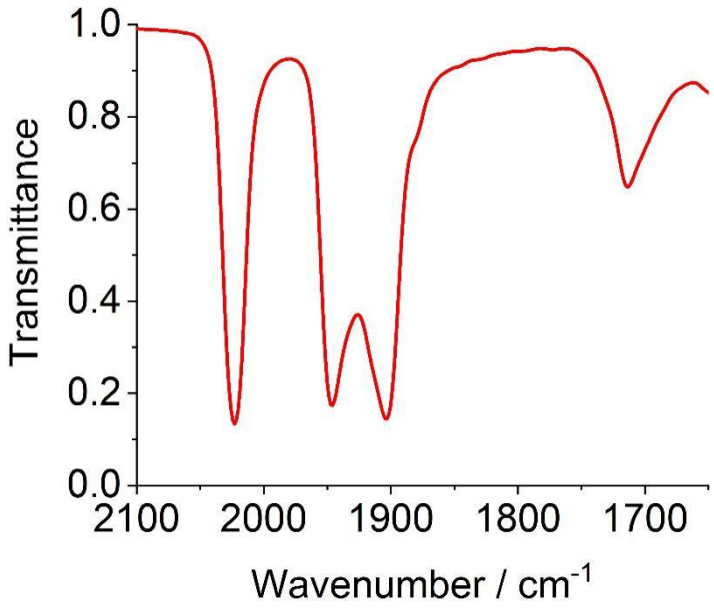

Entire [1]H NMR (400 MHz, DMSO) spectrum of complex **1p**




Magnified [1]H NMR (400 MHz, DMSO) spectrum of complex **1p**

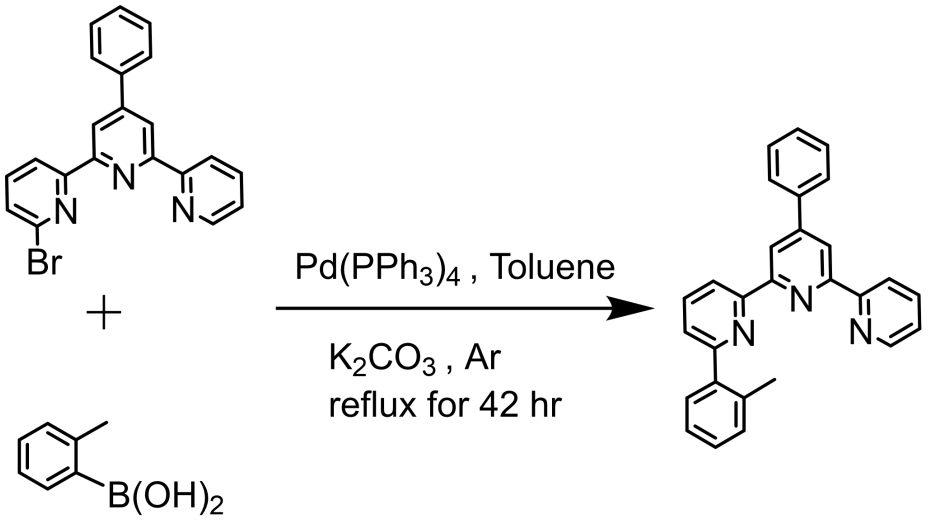



Mass spectrum of complex **1p**.




Experimental FTIR spectra of **1p** recorded in KBr displaying characteristic $\boldsymbol{\nu_{CO}}$ stretching modes for their facial tricarbonyl geometries.

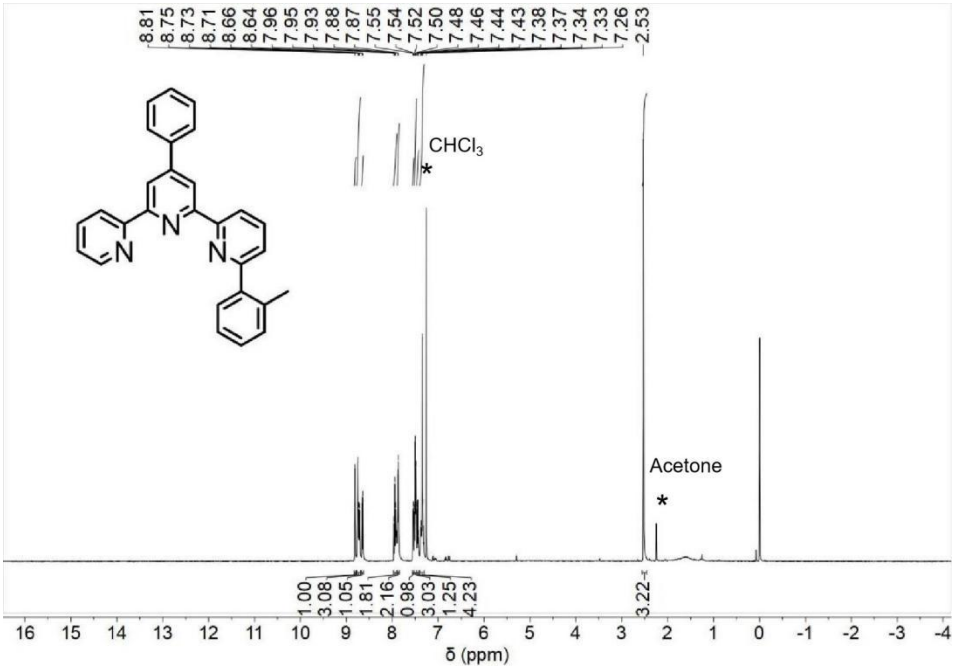
**3) Preparation of L2**



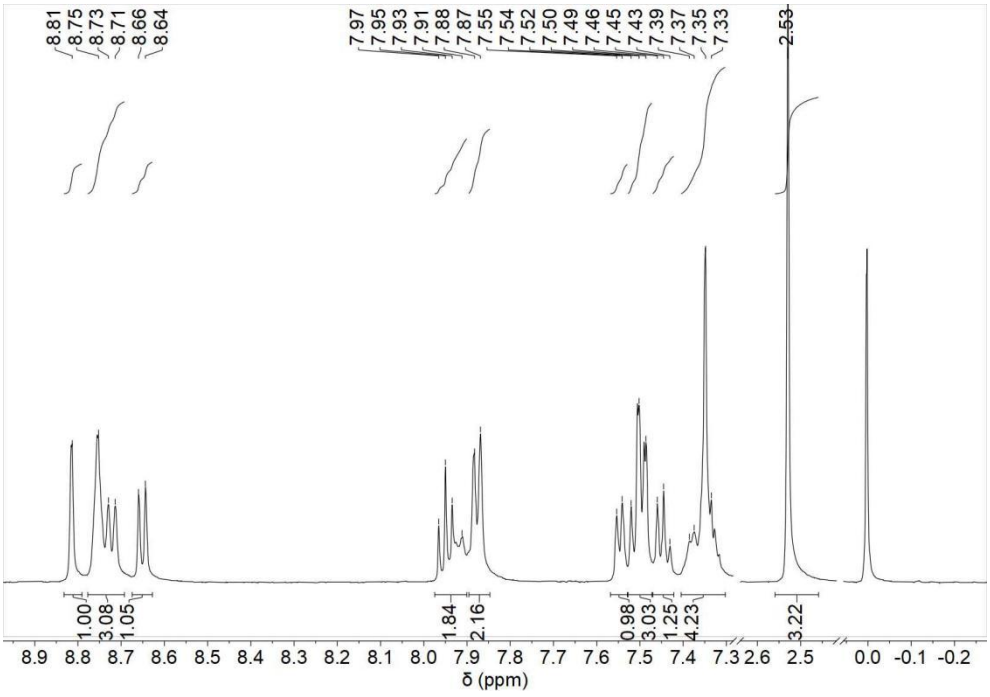

Scheme S 3 Preparation of target ligand **L2**.

2-bromo-6-(4-phenyl-6-(pyridin-2-yl)pyridin-2-yl)pyridine was obtained according to literature procedures. (Constable, E. C. *et. al. J. Chem. Soc., Dalton Trans.,* **1996**, *389*, 4207–4216).

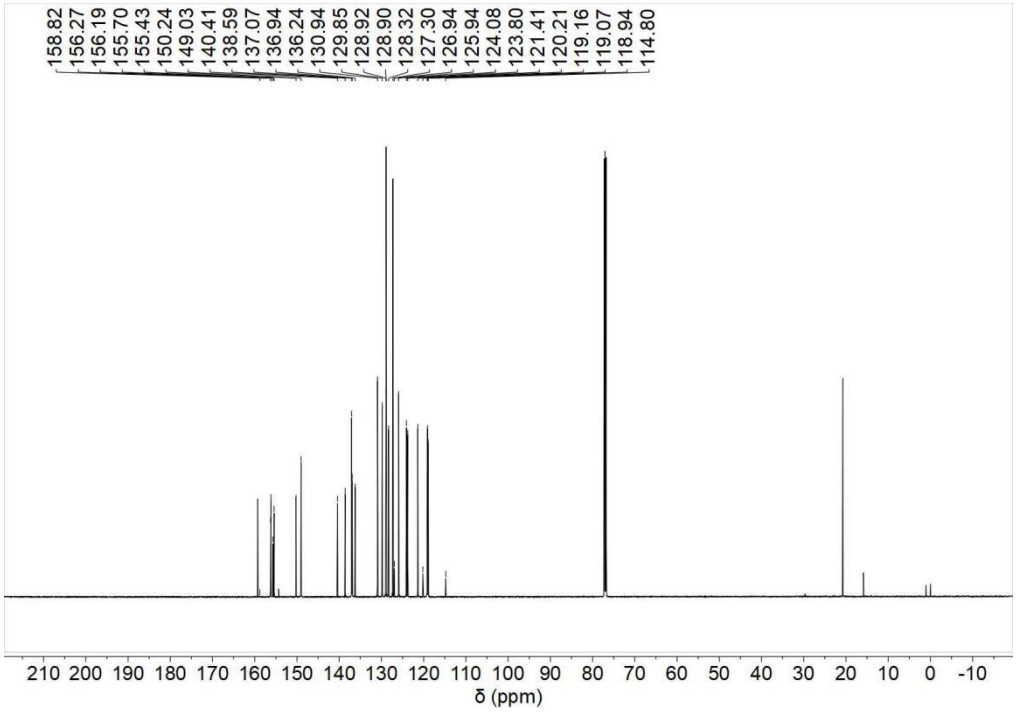
**L2** was obtained according to literature procedures (Solan, G. A. *et. al. Organometallics* **2013***, 32,* 249−259). The product **L2** was obtained as a white solid (80%). $^{1}$H NMR (600 MHz, $CDCl_3$): δ8.81 (1H, d), 8,75~8.71 (3H, m), 8.66~8.64 (1H, d), 7.97~7.91 (2H, m), 7.88~7.87 (2H, d), 7.55~7.54 (1H, d), 7.52~7.49 (3H, m), 7.46~7.43 (1H, t), 7.39~7.33 (4H, m), 2.53 (3H, s).



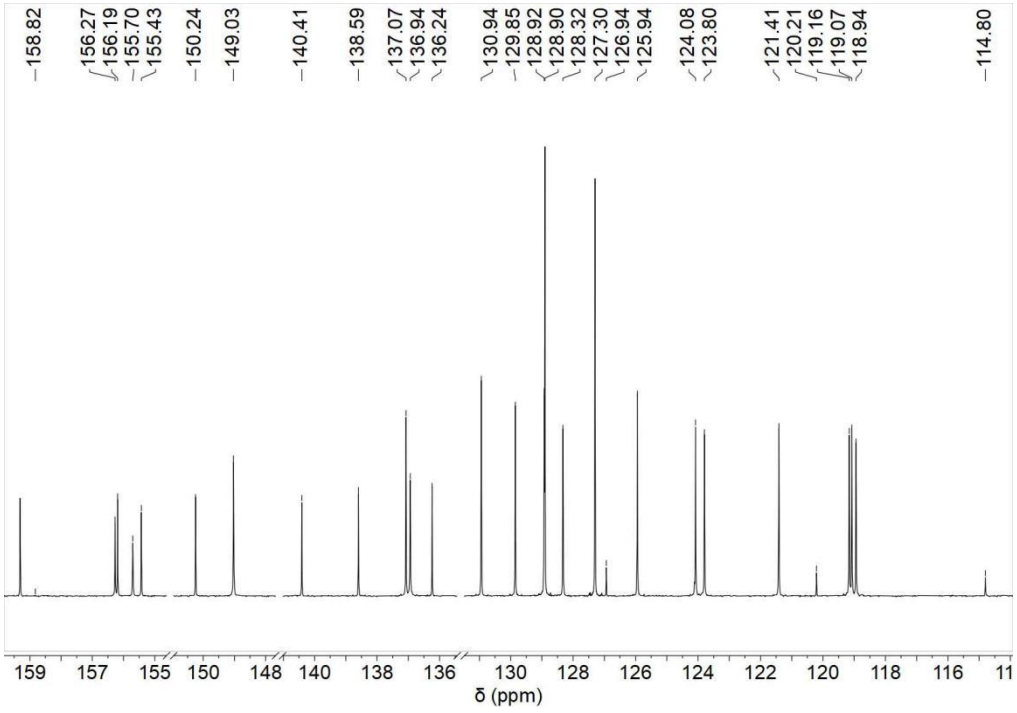

Entire $^{1}$H NMR (600 MHz, $DCCl_3$) spectrum of the ligand **L2**




Magnified $^{1}$H NMR (600 MHz, $DCCl_3$) spectrum of the ligand **L2**

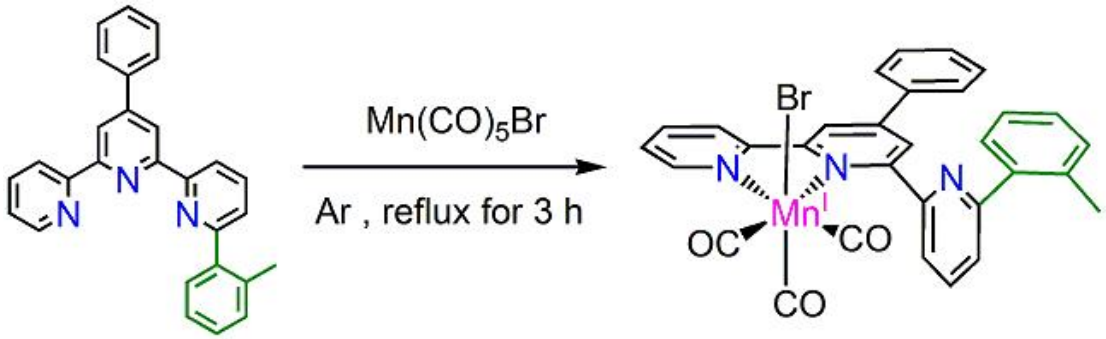



Entire $^{13}C$ NMR (600 MHz, $DCCl_3$) spectrum of the ligand **L2**




Magnified $^{13}C$ NMR (600 MHz, $DCCl_3$) spectrum of the ligand **L2**

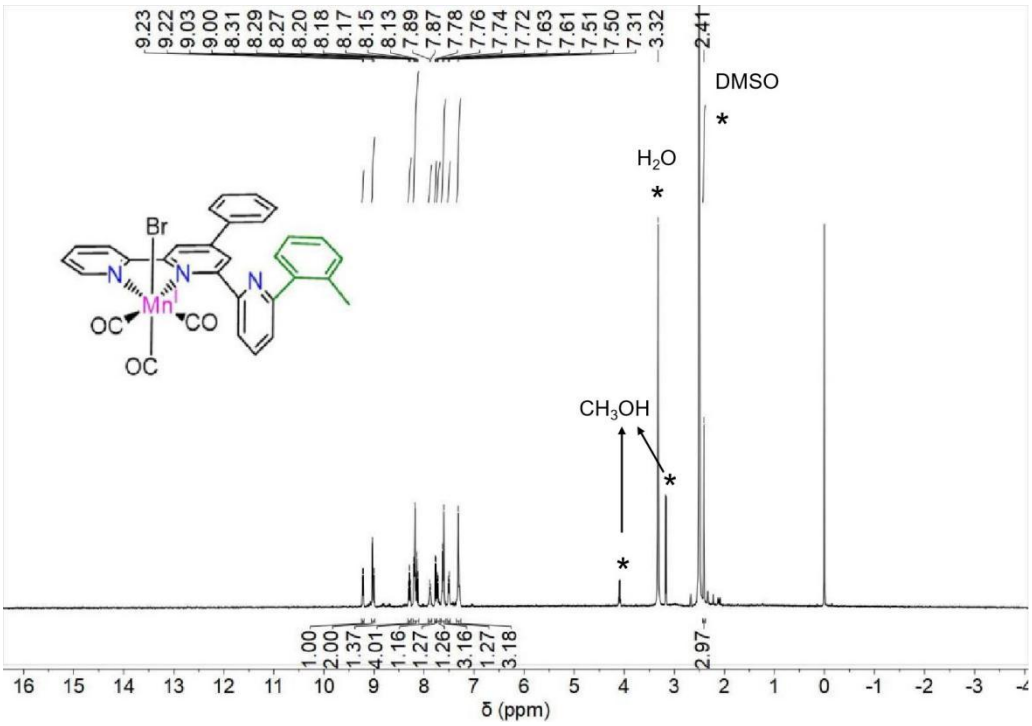
**4) Preparation of complex 2p**



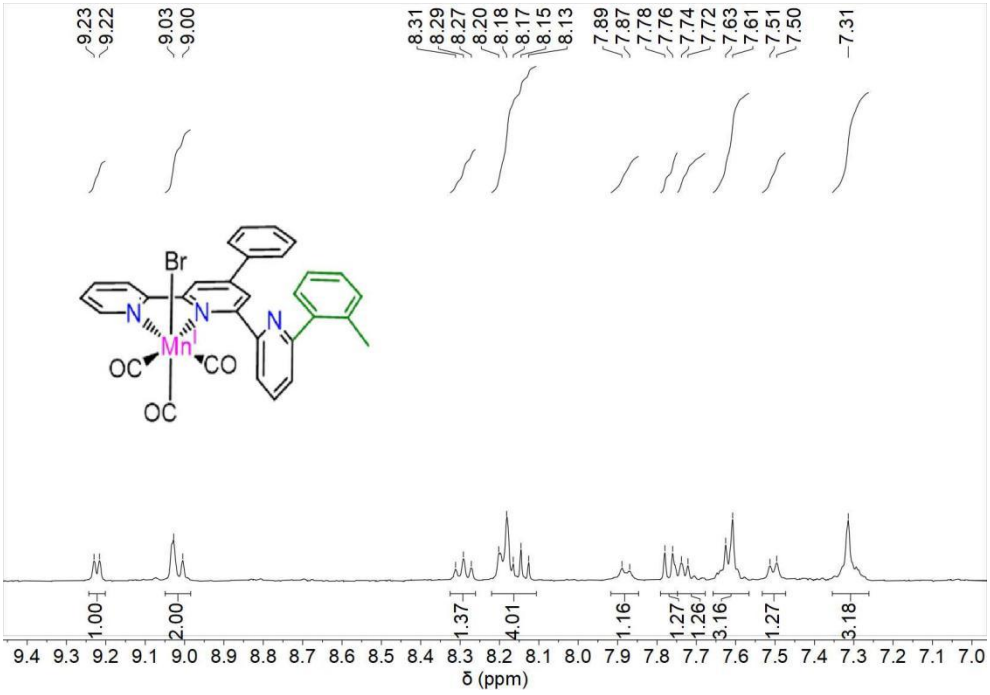

Scheme S 4 Preparation of the precursor **2p**.

The configuration of 2p is proposed according to our unpublished crystal (CCDC: 1964783), in which a mthoxyl group replaced the methyl group in **2p**.

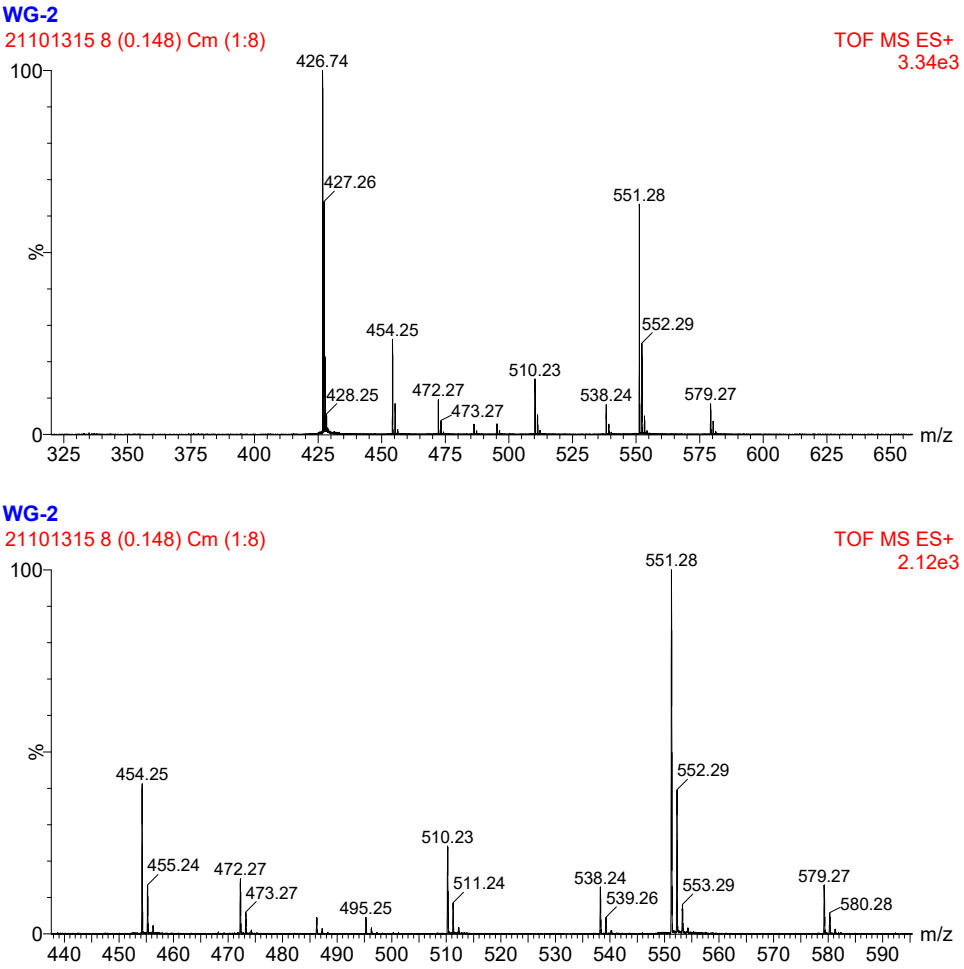
Compound $Mn(CO)_5Br$ (0.2 g, 0.73 mmol) was added to a degassed dichloromethane solution (20 mL) of **L2** (0.29g, 0.73 mmol). The resulting yellow solution was heated to reflux for 3 hours under argon, then allowed to cool to room temperature before filtration. The yellow solid was collected, then washed with $Et_2O$ and dried in vacuo to afford 0.34 g (75% yield). $^1H$ NMR (400 MHz, DMSO): $\delta$ 9.23~9.21 (1H, d), 9.03~9.00 (2H, m), 8.31~8.27 (1H, t), 8.20~8.12 (4H, m), 7.89~7.87 (1H, d), 7.78~7.76 (1H, d), 7.74~7.72 (1H, d), 7.62~7.61 (3H, m), 7.51~7.49 (1H, d), 7.31 (3H, m), 2.41 (3H,s). Anal. Calcd for **2p**, C31H21BrMnN3O3: C, 60.21; H, 3.42; N, 6.80; Found: C, 60.22; H, 3.44; N, 6.78; MS (TOF-MS): m/z = 538.24,.[M–$Br^-$]; 579.27, [M–$Br^-$+$CH_3CN$]; 551.28, [M–$Br^-$+$CH_3CN$-CO]. IR: $\nu_{CO}$ (KBr) = 2023, 1946, 1905 $cm^{-1}$.



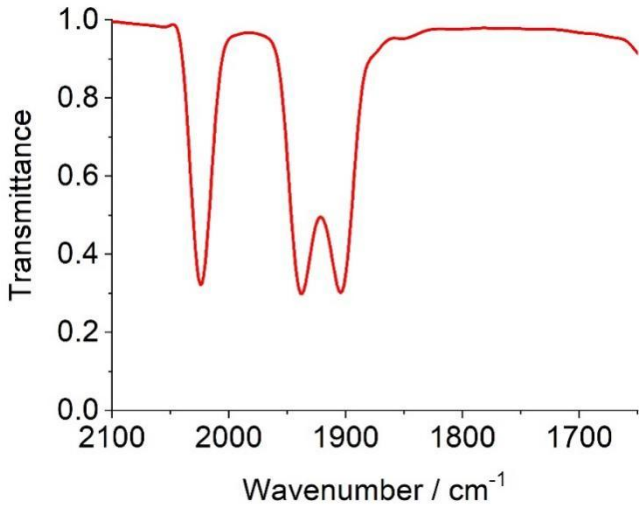

Entire $^{1}$H NMR (400 MHz, DMSO) spectrum of complex **2p**




Magnified $^{1}$H NMR (400 MHz, DMSO) spectrum of complex **2p**




Mass spectrum of complex **2p**.




Experimental FTIR spectra of **2p** recorded in KBr displaying characteristic $\boldsymbol{\nu_{CO}}$ stretching modes for their facial tricarbonyl geometries.

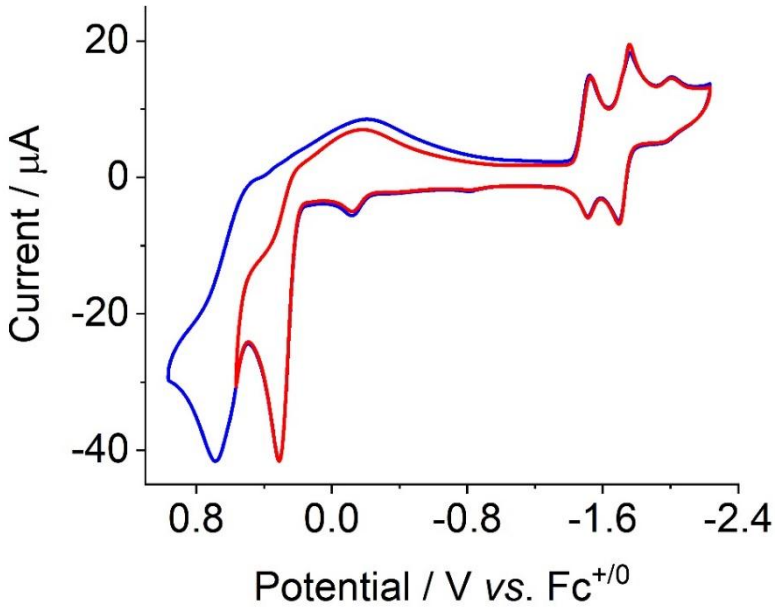
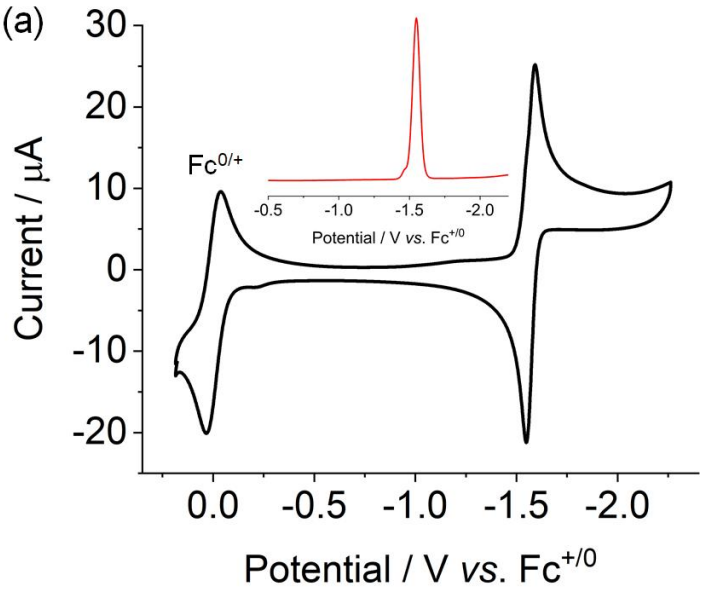
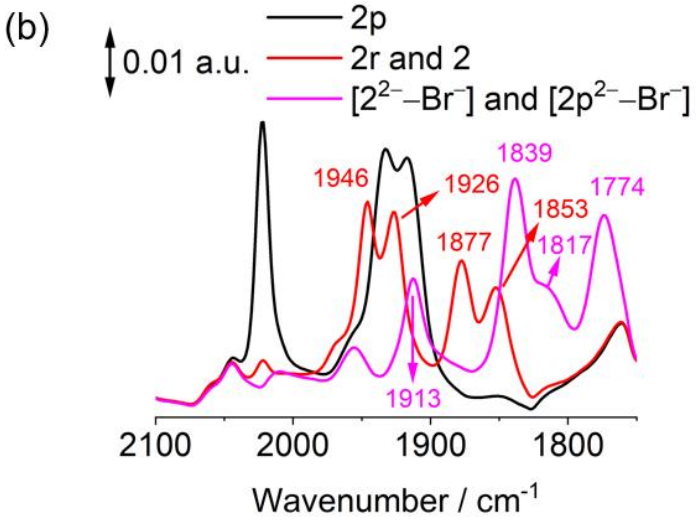
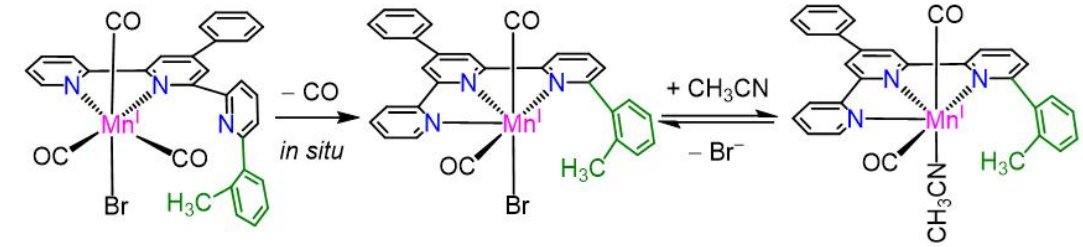



Figure S 1 Cyclic voltammogram of 0.5 mM **1p** in $CH_3CN$ at 100 mV/s under Ar. The scan range of the red line is from 0.55 V to -2.23 V, showing one oxidation peak at 0.31 V. The blue line ranges from 0.97 V to -2.23 V, featuring two oxidation peaks at 0.31 V and 0.69 V respectively.




**2p** ( 2024, 1938, 1905 $cm^{-1}$) **2** (1926, 1853 $cm^{-1}$) **2r** (1946, 1877 $cm^{-1}$)

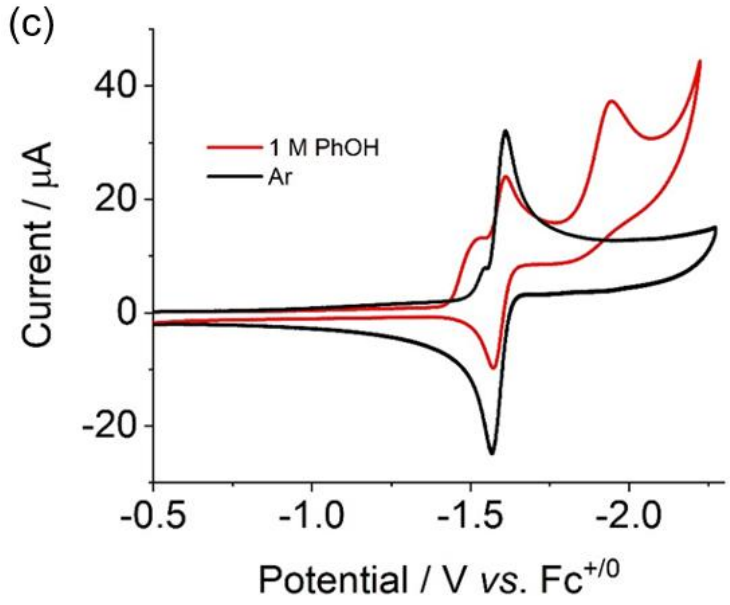
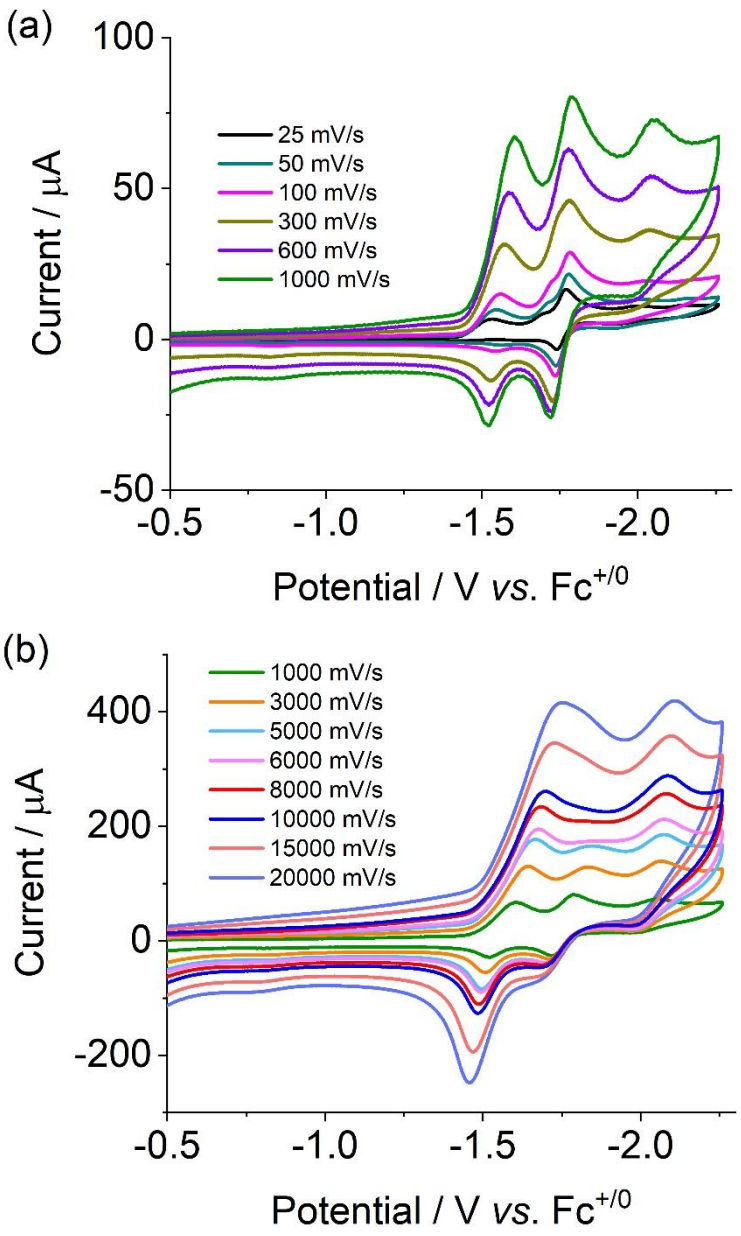



Figure S 2 (a) Cyclic voltammograms of **2p** under Ar, inset: DPV of **2p**. Voltammograms are taken at a scan rate of 100 mV/s with 0.1 M $^{n}Bu_4NPF_6$ in MeCN solution. Glassy carbon working electrode, $Ag^{+}/Ag$ reference electrode, and Pt wire counter electrode. (b) IR-SEC of 2 mM **2p** in $CH_3CN$ with 0.1 M $^{n}Bu_4NPF_6$ electrolyte under Ar. The resting species (**2p**, black line), the mixture of the dicarbonyl complexes **2** and **2r** (red line), and the mixture of the doubly reduced species [$\mathbf{2}^{2-}$–$Br^{-}$] (1839, 1774 $cm^{-1}$) and [$\mathbf{2p}^{2-}$–$Br^{-}$] (1913, 1817 $cm^{-1}$) (pink line) generated upon reduction at approximately −1.6 V. (c) Cyclic voltammograms of **2p** under Ar and in the presence of 1 M phenol. Glassy carbon working electrode, $Ag^{+}/Ag$ reference electrode, and Pt wire counter electrode.

**Comments on the CV and the IR-SEC spectrum of complex 2p**

Cyclic voltammetry (CV) of **2p** revealed one reversible wave with at −1.57 V under Ar (Figure S2). Compared to a peak-to-peak separation of 72 mV for $Fc^{+/0}$, this reversible couple shows a separation of 37 mV in the same CV, implying a two-electrons process. The changes in IR-SEC spectra of **2p** were recorded under the potential from −1.30 to −1.60 V. Complex **2p** at its initial state exhibits three IR-active carbonyl streches at 2023, 1934 and 1918 $cm^{-1}$ (black line, Figure S2), consistent with a fac-tricarbonyl coordination mode. Holding the potential at −1.40 V, these bands are replaced by absorption bands at 1946, 1926, 1877, and 1853 $cm^{-1}$ (red line, Figure 3b), indicating the *in situ* switch of coordination mode from $k^2-N,N'$ ($k^2$-tpy) to $k^3-N,N'N''$ ($k^3$-tpy). These absorption bands can be separated into two groups due to the partial replacement of $Br^-$ by acetonitrile molecule (red line, Figure S2). At the reduction peak potential (−1.55 V), these signals are further replaced by two prominent peaks at 1839 and 1774 $cm^{-1}$ (pink line, Figure S2), characterized as the doubly reduced species [$\mathbf{2}^{2-}$–**Br**$^-$] (*Dalton Trans*., **2016**, *45*, 17179–17186 ). Based on this finding, the reversible redox couple in the CV of **2p** could be assigned to a two-electron redox event (**2**/[$\mathbf{2}^{2-}$–**Br**$^-$] ,Scheme 2). Another group of IR absorption with weak intensity was also observed at 1913 and 1817 $cm^{-1}$, which is due to the doubly reduced species [$\mathbf{2p}^{2-}$–**Br**$^-$] (*Chem. Eur.J*., **2017**, *23*, 4782 –4793).


(a)
100
50
0
-50
Current / µA
25 mV/s
50 mV/s
100 mV/s
300 mV/s
600 mV/s
1000 mV/s
-0.5
-1.0
-1.5
-2.0
Potential / V vs. Fc+/0
(b)
400
200
0
-200
Current / µA
1000 mV/s
3000 mV/s
5000 mV/s
6000 mV/s
8000 mV/s
10000 mV/s
15000 mV/s
20000 mV/s
-0.5
-1.0
-1.5
-2.0
Potential / V vs. Fc+/0

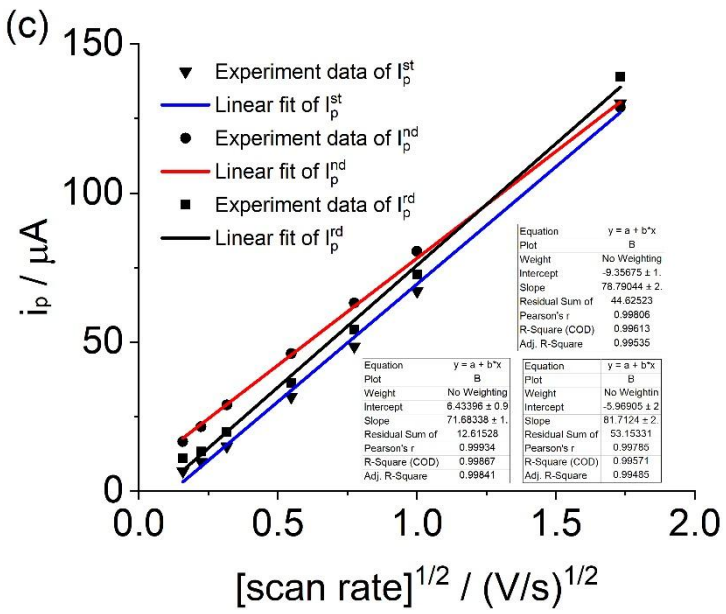



Figure S 3 (a) Cyclic voltammograms of complex **1p** (0.5 mM) with scan rate ($v$) varied from 0.025 V/s to 1 V/s under Ar and (b) from 1 V/s to 20 V/s under Ar. (c) Plot of the first, second and third reduction peak current ($i_p$) of complex **1p** *vs.* the square root of scan rate with the scan rate ($v$) varied from 0.025 V/s to 3 V/s. Voltammograms are taken in MeCN solution with 0.1 M $^n$Bu$_4$NPF$_6$. Glassy carbon working electrode, $Ag^+$/Ag reference electrode, and Pt wire counter electrode.

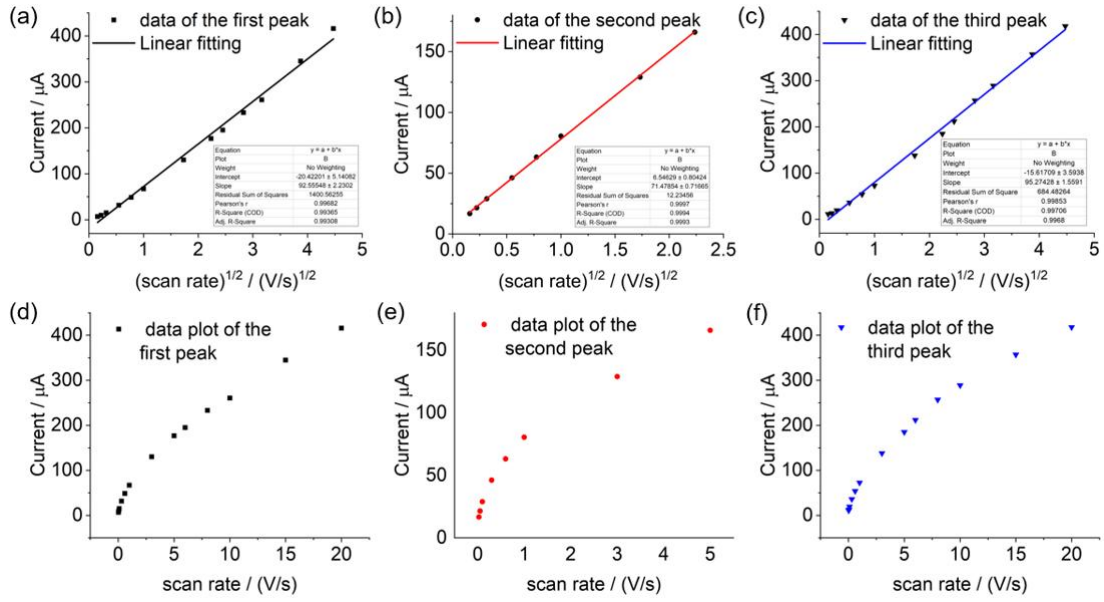



Figure S 4 (a), (b) and (c) are plot of the first, second and third reduction peak current ($i_p$) of complex **1p** *vs.* the square root of scan rate with the scan rate ($v$) varied from 0.025 V/s to 20 V/s, 0.025 V/s to 5 V/s and 0.025 V/s to 20 V/s, respectively. (d), (e) and (f) are plot of the first, second and third reduction peak current ($i_p$) of complex **1p** *vs.* the scan rate with the scan rate ($v$) varied from 0.025 V/s to 20 V/s, 0.025 V/s to 5 V/s and 0.025 V/s to 20 V/s, respectively. Voltammograms are taken in MeCN solution with 0.1 M $^n$Bu$_4$NPF$_6$. Glassy carbon working electrode, Ag$^+$/Ag reference electrode, and Pt wire counter electrode.

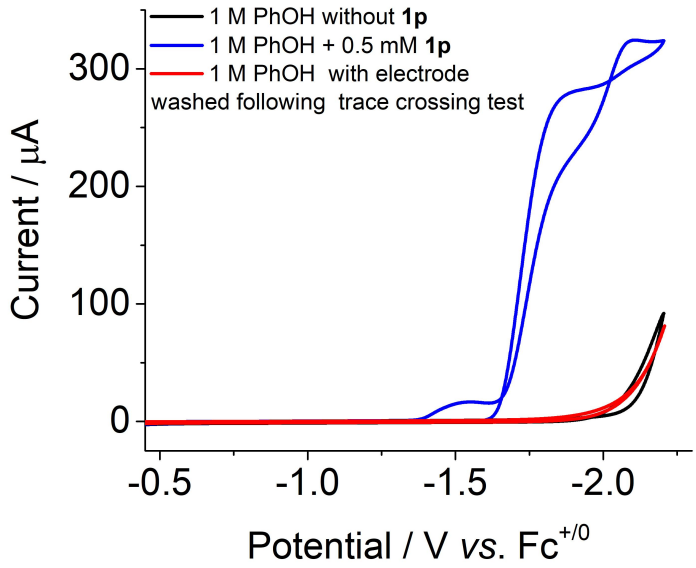



Figure S 5 black line: Cyclic voltammogram of 1 M phenol in the absence of **1p.** blue line: Cyclic voltammogram of 1 M phenol in the presence of **1p**. red line: Cyclic voltammogram of 1 M phenol in the absence of **1p** but with the electrode washed following the trace crossing test. Voltammograms are taken at a scan rate of 100 mV/s with 0.1 M $^{n}Bu_4NPF_6$ in MeCN solution under Ar. Glassy carbon working electrode, $Ag^{+}/Ag$ reference electrode, and Pt wire counter electrode.

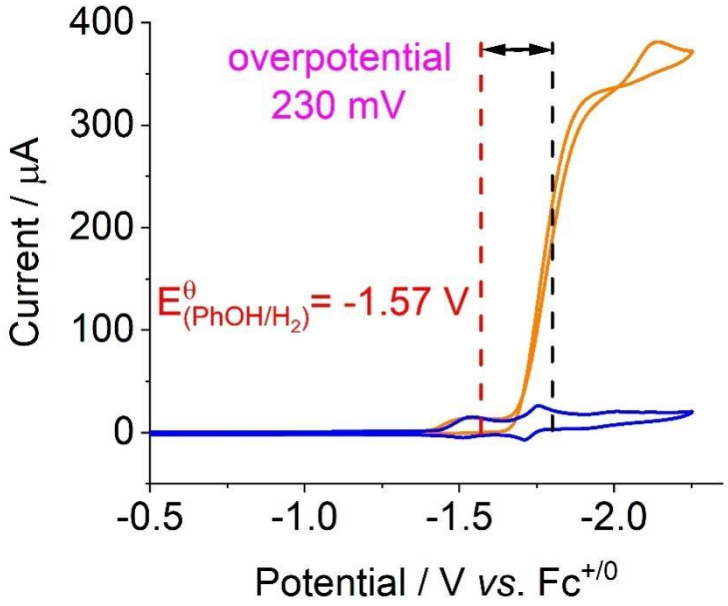



Figure S 6 Cyclic voltammograms of complex **1p** (0.5 mM) in the absence of phenol (blue line) and in the presence of 1 M phenol (orange line, pKa=25.4) under Ar. $E^{\theta}(PhOH/H_2)$ = –1.57 V and $E_{cat/2}$ = –1.80 V. Voltammograms are taken at a scan rate of 100 mV/s with 0.1 M $^{n}Bu_4NPF_6$ in MeCN solution. Glassy carbon working electrode, $Ag^{+}/Ag$ reference electrode, and Pt wire counter electrode.

**Estimation of $E^{\theta}_{BH}$ of phenol in acetonitrile (***ACS Catal.* **2018**, *8*, 9596−9603**)**

Phenol is known to undergo significant homoconjugation in acetonitrile ($K_c = 10^{4.2}$) which lowers its effective $pK_a$ and thereby shifts the thermodynamic potential for reduction for proton reduction more positive. To more accurately estimate the thermodynamic potential for the reduction of $H^{+}$ from phenol for use in the calculation of upper benchmarks of hydricities and for determination of overpotentials, $E_{1/2(BH/B^{-})}$ of phenol at various concentrations can be estimated according to Artero et al. by the following equation:

$$E^o_{BH} = E^o_{H^+/H_2} - \frac{2.303RT}{F} pK_a + \varepsilon_d + \frac{RT}{2F} \ln(2K_c{}^2 C_0 C^0_{H_2})$$

Where,

$E^o_{H^+/H_2}$ = -0.07 V vs. $Fc^{+/0}$ (ref 2)

R = 8.314 J $mol^{-1}$ $K^{-1}$

T = temperature in Kelvin

F = 96485.3 C $mol^{-1}$

$pK_a$ = 29.12 (phenol in acetonitrile)[3]

$\varepsilon_d$ = 40 ± 5 $mV^2$

$K_c$ = homoconjugation formation constant

$C_0$ = concentration of acid

$C^0_{H_2}$ = 3.3 mM in acetonitrile[4]

Therefore, at

0.1 M phenol: $E^o_{BH}$ = -1.60 V vs $Fc^{+/0}$

1.0 M phenol: $E^o_{BH}$ = -1.57 V vs $Fc^{+/0}$

---

Using these values to estimate effective $pK_a$ by the Nernst equation:

$$E^o_{BH} = E^o_{H^+/H_2} - \frac{2.303RT}{F} pK_a$$

Gives,

0.1 M phenol: $pK_a$ = 25.9

1.0 M phenol: $pK_a$ = 25.4

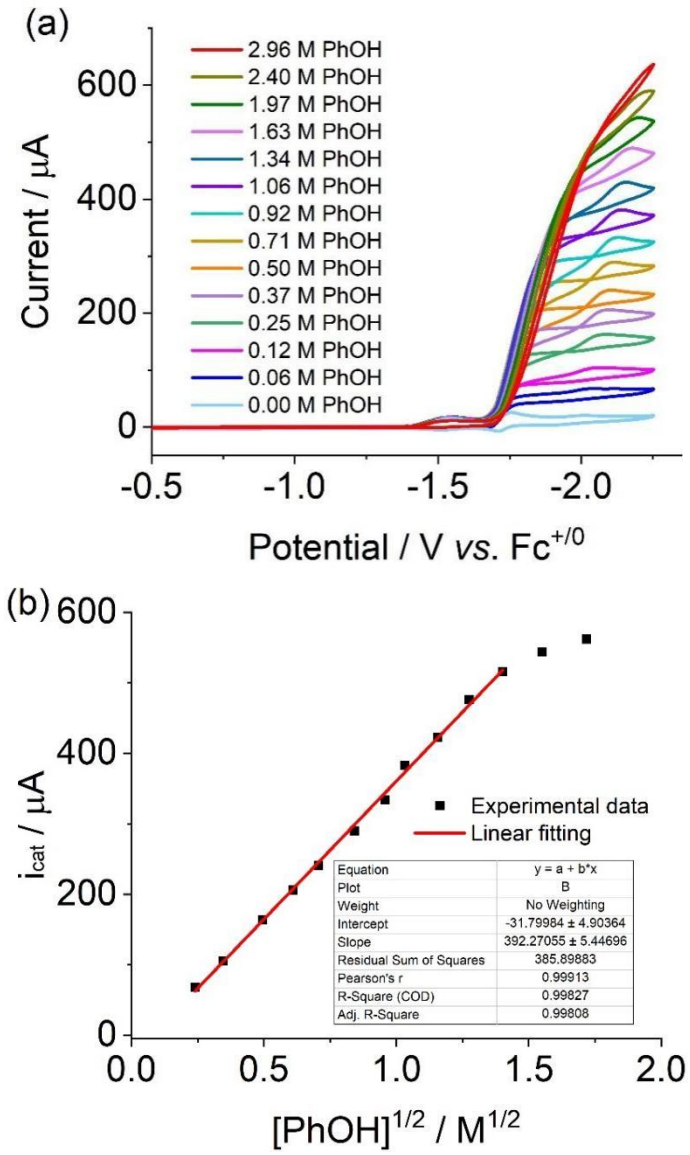
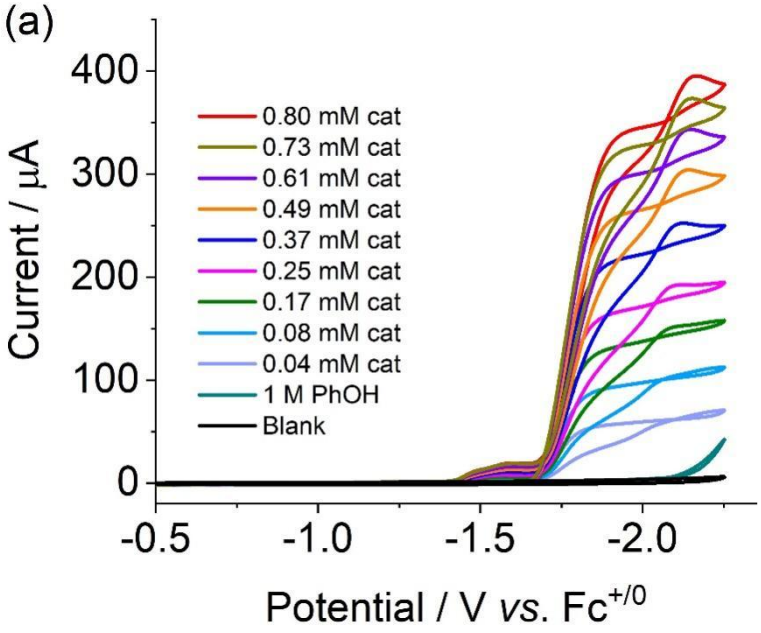
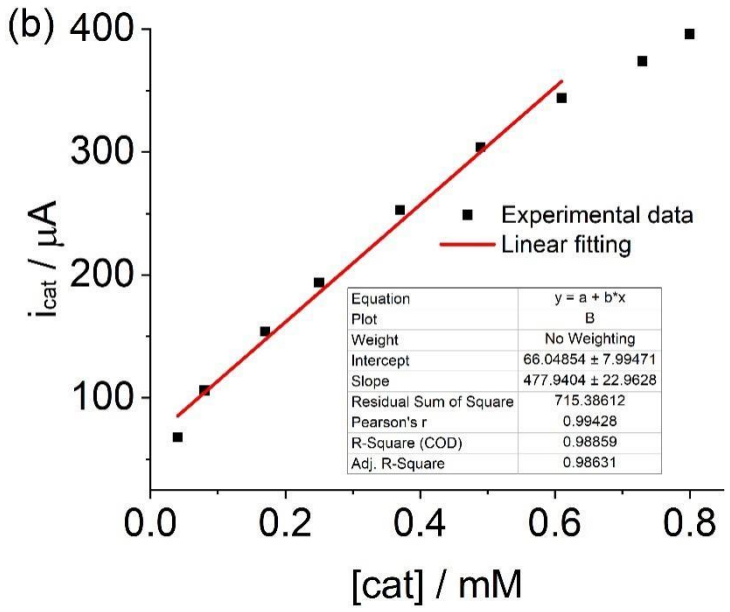



Figure S 7 (a) Cyclic voltammograms show 0.5 mM **1p** with varied amounts of phenol (from 0 M to 2.96 M) under Ar. (b)The linear dependence of catalytic Current ($i_{cat}$) on the square root of the concentration of phenol. Voltammograms are taken at a scan rate of 100 mV/s with 0.1 M $^{n}Bu_4NPF_6$ in MeCN solution. Glassy carbon working electrode, $Ag^{+}/Ag$ reference electrode, and Pt wire counter electrode.

**Comment:** In the low concentration section, the current displayed a linear relation with square root of phenol concentration, suggesting a first-order in phenol and then leveling off with larger concentrations of phenol, implying saturation kinetics in which concentration of phenol is sufficiently high so that it is not depleted during the course of the experiment.


(a)
Current / μA
400
300
200
100
0
0.80 mM cat
0.73 mM cat
0.61 mM cat
0.49 mM cat
0.37 mM cat
0.25 mM cat
0.17 mM cat
0.08 mM cat
0.04 mM cat
1 M PhOH
Blank
-0.5
-1.0
-1.5
-2.0
Potential / V vs. Fc+/0


(b)
icat / μA
400
300
200
100
Experimental data
Linear fitting
Equation y = a + b*x
Plot B
Weight No Weighting
Intercept 66.04854 ± 7.99471
Slope 477.9404 ± 22.9628
Residual Sum of Square 715.38612
Pearson's r 0.99428
R-Square (COD) 0.98859
Adj. R-Square 0.98631
0.0
0.2
0.4
0.6
0.8
[cat] / mM

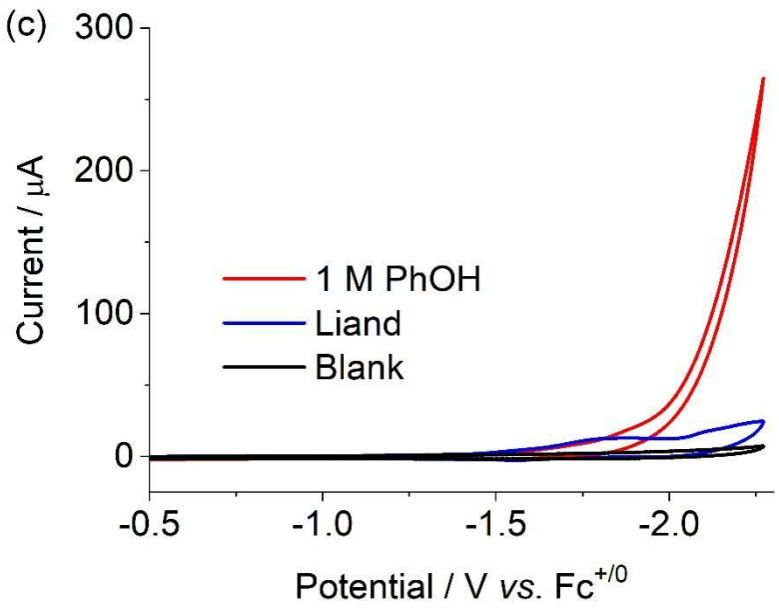
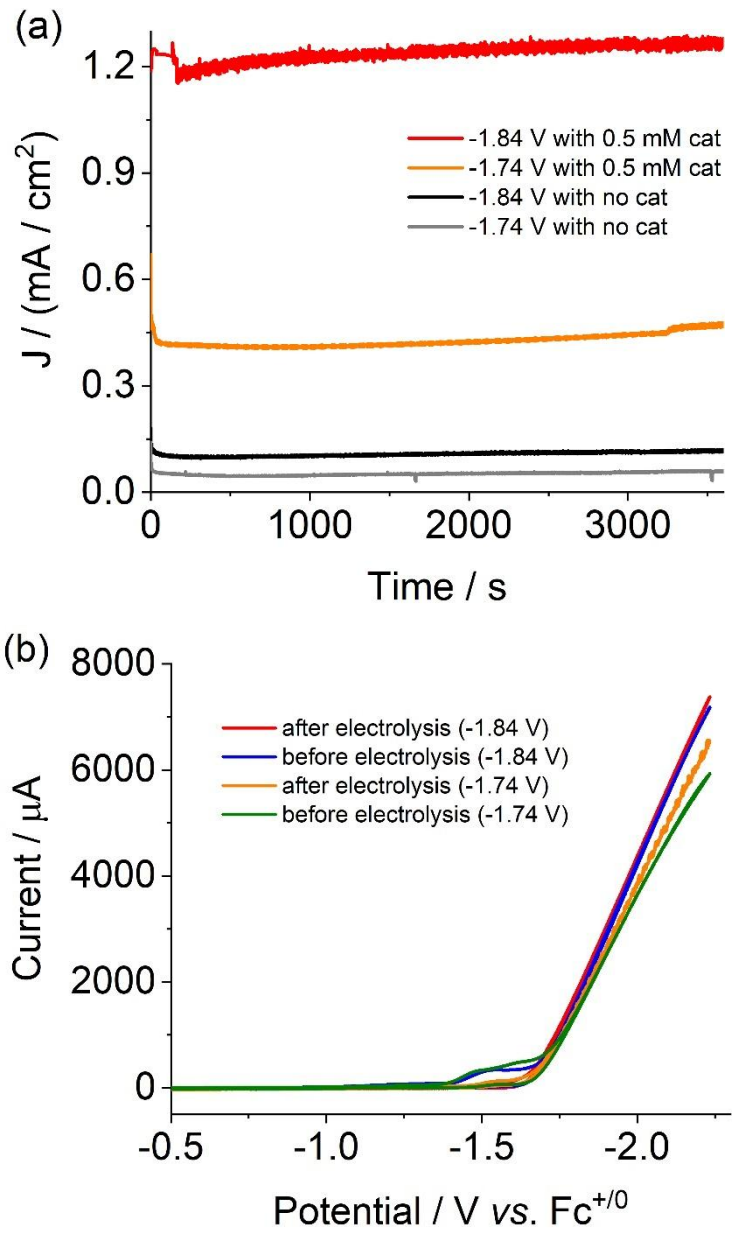



Figure S 8 (a) Cyclic voltammograms of **1p** (from 0.04 mM to 0.80 mM) in the presence of 1 M phenol under Ar. (b) The linear dependence of catalytic Current ($i_{cat}$) on the concentration of the catalyst. (c) Cyclic voltammograms of 0.5 mM Ligand **(L1)** in the absence of phenol (blue line) and in the presence of 1 M phenol (red line) under Ar. Voltammograms are taken at a scan rate of 100 mV/s with 0.1 M $^{n}Bu_4NPF_6$ in MeCN solution. Glassy carbon working electrode, $Ag^{+}/Ag$ reference electrode, and Pt wire counter electrode.

**Comment**: The catalytic current shows a linear dependence on the catalyst concentration in low concentration section and then leveling off with larger concentrations of catalyst owing to the saturation solubility of catalyst in the pure acetonitrile.


(a)
1.2
0.9
0.6
0.3
0.0
J / (mA / cm$^2$)
-1.84 V with 0.5 mM cat
-1.74 V with 0.5 mM cat
-1.84 V with no cat
-1.74 V with no cat
0
1000
2000
3000
Time / s
(b)
8000
6000
4000
2000
0
Current / µA
after electrolysis (-1.84 V)
before electrolysis (-1.84 V)
after electrolysis (-1.74 V)
before electrolysis (-1.74 V)
-0.5
-1.0
-1.5
-2.0
Potential / V vs. Fc$^{+/0}$

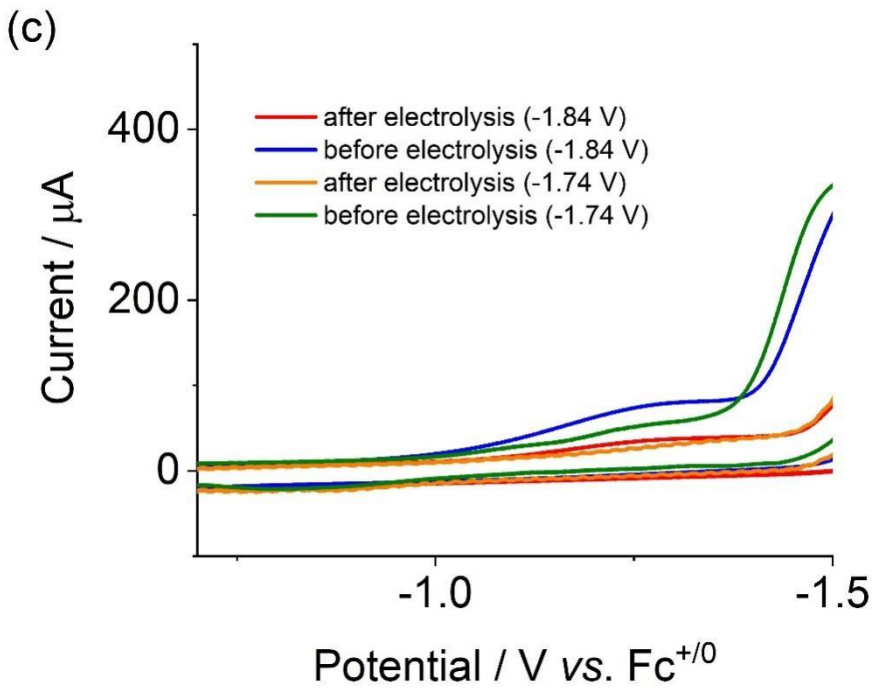



Figure S 9 (a) Controlled potential electrolysis in the presence and absence of **1p** under Ar. at -1.74 V *vs.* $Fc^{+/0}$ and -1.84 V *vs.* $Fc^{+/0}$ (b) Cyclic voltammograms show 0.5 mM **1p** before and after electrolysis at -1.74 V *vs.* $Fc^{+/0}$ and -1.84 V *vs.* $Fc^{+/0}$ in the presence of 1 M phenol. (c) Enlargation of figure S7b in the region between -0.7 and -1.5 V. Voltammograms are taken at a scan rate of 100 mV/s. Conditions: 0.1 M $TBAPF_6$ in $CH_3CN$ with 1 M phenol, glassy carbon working electrode, graphite rod counter electrode, $Ag^+/Ag$ reference electrode.

Table S 3 Collected electrochemical data of some hydrogen evolution catalysts with weak acid.

| catalyst | appl potential | solvent | proton source | FE | $TOF_{max}$ | TON | η | ref |
|---|---|---|---|---|---|---|---|---|
| $[Co^{III}(dmgH)_2pyCl]^a$ | -0.9 V vs AgCl | DMF (0.1 M n-$Bu_4NBF_4$) | $Et_3NHCl$ ($pK_a$ = 10.75) | 85-100% | $10^4$ | 100 ± 3 (2.5 h) | 0.03 V | 1 |
| $[Ni(bdt)(dppf)]^b$ | -1.28 V[c] ($E_{1/2}$) vs SCE | THF (0.3 M $TBAPF_6$) | HOAc ($pK_a$ = 22.48) | 99% | 1240 $s^{-1}$ [d] ( 100 mV/s) | ____[e] | 0.265 V[f] | 2 |
| $[Ni(bis\text{-}NHC)(dRpe)]^{2+}$ [g] | −1.9 V vs $Fc^+/Fc$ | MeCN (0.1 M $Bu_4NPF_6$) | PhOH ($pK_a$ = 29.14) | 112 ± 5% | ~1000 $s^{-1}$ (0.2 M $H^+$) | ≧1 (25 min) | 0.4 V | 3 |
| $[Ni(L)_2Cl]Cl$ [h] | -2.5 V vs Ag/ $Ag^+$ | MeCN (0.1 M n-$Bu_4NClO_4$) | HOAc ($pK_a$ = 22.3) | 89.8% | 8400 $s^{-1}$ (0.29 M $H^+$) | ____[e] | 0.59 V | 4 |
| $L^{N2S2}Ni^{II}Fe^{II}$ [i] | −1.85 V vs $Fc^+/Fc$ | MeCN (0.1 M n-$Bu_4NClO_4$) | $Et_3NHBF_4$ ($pK_a$ = 18.6) | 70% | 250 $s^{-1}$ (10 mM $H^+$) | 16 (100 min) | ~0.8 V | 5, 6 |
| Mn-tpy-COOH | −1.84 V vs $Fc^+/Fc$ | $CH_3CN$ (0.1 M $TBAPF_6$) | PhOH ($pK_a$ = 25.4) | 100 ± 5% | 525 $s^{-1}$ (1 M $H^+$) | 6 (60 min) | 0.23 V | This work |

[a] dmgH = dimethylglyoxime; py = pyridine.

[b] bdt=1,2-benzenedithiolate, dppf= 1,1'bis(diphenylphosphino)ferrocene.

[c] The applied potential was not clearly stated during electrolysis.

[d] the $i_c/i_p$ data are also independent of both catalyst concentration and the potential scan rate of the cyclic voltammogram. The $i_c/i_p$ values of 80 in the acid independent region (for a scan rate of 100 mV $s^{-1}$) indicate an acid-independent rate constant of 1240 $s^{-1}$.

[e] "____" means the turnover number (TON) was not been reported in corresponding reference.

[f] This value ranges from 265 mV at low acid concentration to 500 mV at high acid concentration.

[g] (bis-NHC)(dRpe). R = methyl; bis-NHC = 1,l':3,3'-bis(1,3-propanediyl)dibenzimidazolin-2,2′-diylidene.

[h] L is 6-((diphenylphosphino)methyl)pyridin-2-amine.

[i] $L^{N2S2}$ is the bipyridine–bisthiolate ligand.

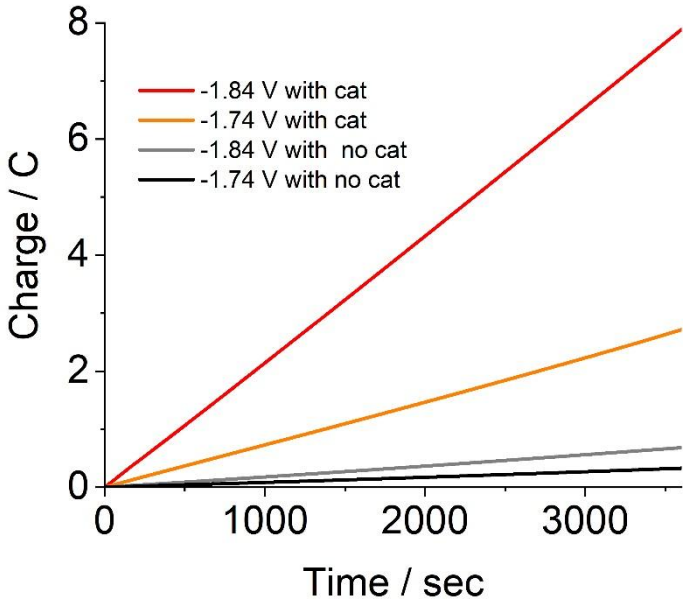



Figure S 10 The integral of charge after electrolysis at -1.74 V *vs.* $Fc^{+/0}$ and -1.84 V *vs.* $Fc^{+/0}$ in the absence and presence of 0.5 mM **1p**, respectively. Conditions: 0.1 M $TBAPF_6$ in $CH_3CN$ with 1 M phenol, glassy carbon working electrode, graphite rod counter electrode, $Ag^+/Ag$ reference electrode.

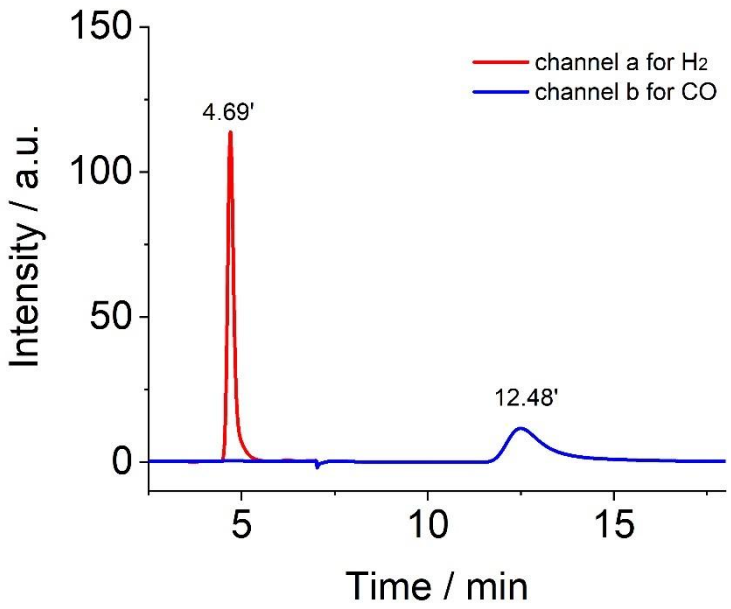



Figure S 11 Gas chromatography shows the production of $H_2$ and trace amount of CO dissociated from **1p** after electrolysis at -1.84 V *vs.* $Fc^{+/0}$ in the presence of 1 M phenol. Conditions: 0.1 M $TBAPF_6$ in $CH_3CN$ with 1 M phenol, glassy carbon working electrode, graphite rod counter electrode, $Ag^+/Ag$ reference electrode. Retention time for $H_2$ and CO is 4.69 min and 12.48 min, respectively.

## 9. DFT Calculations

**Computational Details.**

All geometry optimizations and vibrational frequency calculations were obtained computationally from density functional theory with the M06 exchange-correlation functional[7] computations as implemented in Gaussian 09[8]. Nonmetals (C, H, O, N, Br) used 6-31G(d,p) basis set[9,10] and SDD[11] was used for Mn. Harmonic vibrational frequencies were computed to determine free energies and to verify the nature of stationary points. The minimum-energy structures have positive eigenvalues of the Hessian matrix, whereas the transition states have only one negative eigenvalue. 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)[12,13]. The relative free energies ΔG in Figure S12 is the free energies changes of intermediates/transition states relative to active catalyst **1**.

The reduction potential $E_{O|R}$ relative to the ferrocene/ferrocenium couple was calculated using the following formula:

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

$\Delta G$ 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[14], 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.[15]

For the reactions involving the participation of electrons, the energy contributions due to the application of electrode potential, $\phi$, were simulated by adding $-e\phi$ to all the species after each electroreduction step.

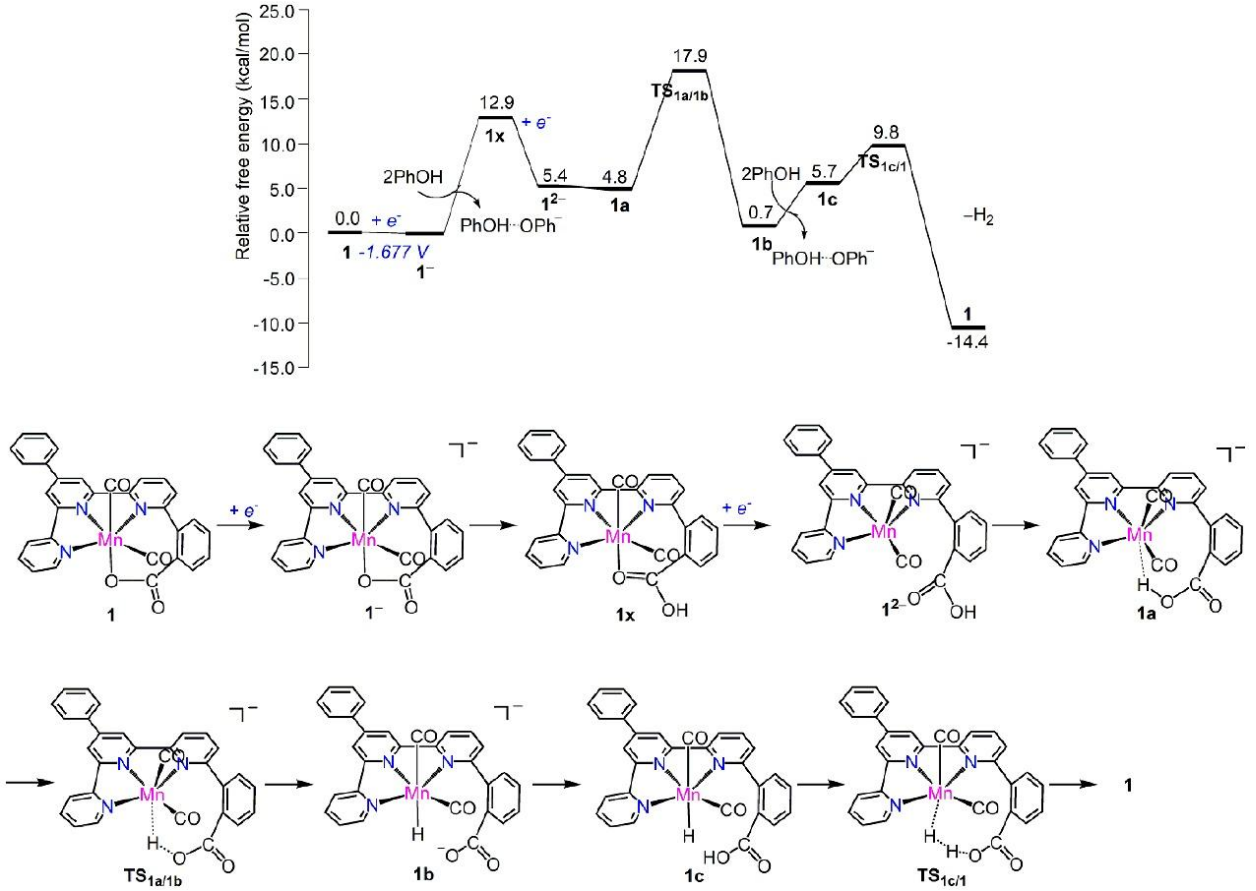



Figure S 12 The mechanism and free energy profile for the reduction of phenol to hydrogen mediated by **1** at the applied potentials of –1.677 V vs. $Fc^{+/0}$. Here, –1.677 V is the reduction potential of **1** according to DFT computations.

## 10. Cartesian coordinates of optimized structures

**1**

| | | | |
|---|---|---|---|
| Mn | -1.06166600 | 0.63979800 | 0.53195400 |
| O | -0.57784200 | 0.67949500 | 3.42354600 |
| O | -3.73855600 | 1.58753700 | 1.30742300 |
| N | 0.83239700 | 0.19941100 | 0.16890800 |
| N | -1.10894100 | -1.41637900 | 0.39016400 |
| N | -0.28864100 | 2.48689000 | 0.16169900 |
| C | 3.51942300 | -0.37871500 | -0.05674800 |
| C | 3.05567600 | 0.93605700 | -0.18809700 |
| H | 3.75474100 | 1.73907500 | -0.40402000 |
| C | 1.69665100 | 1.19480100 | -0.05985600 |
| C | 2.58515800 | -1.39478800 | 0.18485400 |
| H | 2.92034800 | -2.42108900 | 0.30763600 |
| C | 1.23790400 | -1.07196100 | 0.28250600 |
| C | 1.03843600 | 2.50639600 | -0.13396800 |
| C | 1.69766800 | 3.68071000 | -0.47650100 |
| H | 2.75793500 | 3.66329100 | -0.71055700 |
| C | 0.98385500 | 4.87024400 | -0.52621300 |
| H | 1.48112600 | 5.79759500 | -0.79459200 |
| C | -0.37246100 | 4.84933700 | -0.22932400 |
| H | -0.97356200 | 5.75237400 | -0.25576700 |
| C | -0.96607000 | 3.64049200 | 0.10893100 |
| C | 0.11337700 | -2.00913600 | 0.43186600 |
| C | 0.26091100 | -3.38629400 | 0.50702700 |
| H | 1.24861000 | -3.83379900 | 0.56112800 |
| C | -0.87947600 | -4.18164300 | 0.48882800 |
| H | -0.79673800 | -5.26215300 | 0.55910100 |
| C | -2.11327800 | -3.58004000 | 0.30948800 |
| H | -3.01539000 | -4.17345600 | 0.19318100 |
| C | -2.19807200 | -2.18481400 | 0.22996900 |
| C | -2.71326300 | 1.15428000 | 0.95316600 |
| C | -0.74863300 | 0.67025100 | 2.26791700 |
| C | -3.47794700 | -1.53558500 | -0.11253700 |
| C | -3.56273700 | -0.59660600 | -1.16068600 |
| C | -4.64112000 | -1.94205800 | 0.54961400 |
| C | -4.82234700 | -0.10560900 | -1.51032900 |
| C | -5.87831200 | -1.40511900 | 0.21879300 |
| H | -4.56282500 | -2.67788500 | 1.34842100 |
| C | -5.96728100 | -0.48079100 | -0.81788200 |
| H | -4.89227500 | 0.58751000 | -2.34588300 |

| | | | |
|---|---|---|---|
| H | -6.76795000 | -1.71357200 | 0.76182900 |
| H | -6.93142300 | -0.06309900 | -1.09783600 |
| C | 4.95633100 | -0.68595300 | -0.17685300 |
| C | 5.91855200 | 0.21530400 | 0.29461100 |
| C | 5.38213000 | -1.88191600 | -0.76750600 |
| C | 7.27258600 | -0.07379500 | 0.17932200 |
| H | 5.60403200 | 1.13631400 | 0.78182200 |
| C | 6.73678900 | -2.16677500 | -0.88666700 |
| H | 4.64871000 | -2.58067200 | -1.16525400 |
| C | 7.68532500 | -1.26456600 | -0.41261000 |
| H | 8.00770000 | 0.63089900 | 0.55994800 |
| H | 7.05271600 | -3.09404300 | -1.35803300 |
| H | 8.74510600 | -1.48901100 | -0.50444700 |
| C | -2.40676400 | -0.11175200 | -2.02685400 |
| O | -1.42442300 | 0.50314100 | -1.47749400 |
| O | -2.52378100 | -0.28904100 | -3.24328100 |
| H | -2.02413500 | 3.58850500 | 0.35196300 |

**1**$^{-}$

| | | | |
|---|---|---|---|
| Mn | -1.05603200 | 0.64742800 | 0.53509400 |
| O | -0.47046500 | 0.63743300 | 3.39490800 |
| O | -3.69774700 | 1.61972700 | 1.37992000 |
| N | 0.81829400 | 0.21325600 | 0.09999400 |
| N | -1.11935700 | -1.39539800 | 0.38286800 |
| N | -0.27171100 | 2.49597100 | 0.14999800 |
| C | 3.52471200 | -0.39136600 | -0.09591100 |
| C | 3.05989800 | 0.95249300 | -0.21325200 |
| H | 3.76064800 | 1.75892600 | -0.41065400 |
| C | 1.70765300 | 1.20135100 | -0.09910300 |
| C | 2.58747400 | -1.39372000 | 0.13365300 |
| H | 2.91973500 | -2.42217700 | 0.26333700 |
| C | 1.22241500 | -1.09078300 | 0.22753000 |
| C | 1.05827000 | 2.51656400 | -0.14698200 |
| C | 1.71465200 | 3.70251500 | -0.46788500 |
| H | 2.77480200 | 3.68444400 | -0.70478300 |
| C | 1.00533500 | 4.89322500 | -0.49323600 |
| H | 1.50353600 | 5.82523300 | -0.74485800 |
| C | -0.35453200 | 4.86903700 | -0.19431000 |
| H | -0.95453600 | 5.77356000 | -0.20416200 |
| C | -0.94613300 | 3.65586800 | 0.11938900 |
| C | 0.13041900 | -1.99580500 | 0.40426100 |
| C | 0.24872900 | -3.39524800 | 0.51509000 |
| H | 1.23509300 | -3.84644500 | 0.59519700 |
| C | -0.88182500 | -4.17720700 | 0.49049600 |
| H | -0.80595000 | -5.25871400 | 0.57133200 |
| C | -2.13337400 | -3.56512400 | 0.29191900 |
| H | -3.03285400 | -4.15668200 | 0.14756900 |
| C | -2.20591100 | -2.17819700 | 0.22528100 |
| C | -2.68502300 | 1.16765400 | 0.99353200 |
| C | -0.69054600 | 0.65314400 | 2.24190000 |
| C | -3.49679900 | -1.53075100 | -0.09968300 |
| C | -3.61009700 | -0.60008400 | -1.15230800 |
| C | -4.64832500 | -1.93350300 | 0.58483600 |
| C | -4.87982000 | -0.12629300 | -1.49012400 |
| C | -5.89841800 | -1.41752500 | 0.26416700 |
| H | -4.54926600 | -2.65879100 | 1.39118500 |
| C | -6.01409000 | -0.50759300 | -0.78210800 |
| H | -4.96749600 | 0.55785100 | -2.33204300 |
| H | -6.77665000 | -1.73085200 | 0.82377600 |
| H | -6.98683600 | -0.10442900 | -1.05494600 |
| C | 4.95907900 | -0.70171700 | -0.19698800 |
| C | 5.92993900 | 0.23078000 | 0.20087600 |

| | | | |
|---|---|---|---|
| C | 5.40204700 | -1.93779500 | -0.69402900 |
| C | 7.28526800 | -0.06364400 | 0.11292700 |
| H | 5.61761800 | 1.18893300 | 0.61230200 |
| C | 6.75661100 | -2.23269800 | -0.77864900 |
| H | 4.67373300 | -2.66683100 | -1.04480400 |
| C | 7.70769700 | -1.29726000 | -0.37622700 |
| H | 8.01652400 | 0.67387600 | 0.43678100 |
| H | 7.07237900 | -3.19567100 | -1.17418700 |
| H | 8.76825000 | -1.52670900 | -0.44649800 |
| C | -2.47054100 | -0.10496800 | -2.03387300 |
| O | -1.50221800 | 0.53915000 | -1.50502500 |
| O | -2.59986200 | -0.30687700 | -3.24991900 |
| H | -2.00475700 | 3.59842300 | 0.36188400 |

**1x**

| | | | |
|---|---|---|---|
| Mn | 1.00928800 | 0.64828100 | -0.57921800 |
| O | 0.43938900 | 0.69339800 | -3.42969500 |
| O | 3.69252200 | 1.59344800 | -1.33685900 |
| N | -0.84427100 | 0.20282000 | -0.13267800 |
| N | 1.09315800 | -1.37893000 | -0.40276900 |
| N | 0.23644300 | 2.48856400 | -0.15944000 |
| C | -3.54732000 | -0.40936800 | 0.09031000 |
| C | -3.08686900 | 0.93054700 | 0.19709400 |
| H | -3.79170400 | 1.73332300 | 0.39639700 |
| C | -1.74036100 | 1.19452600 | 0.07092300 |
| C | -2.60382500 | -1.41236100 | -0.13885700 |
| H | -2.93268400 | -2.44313500 | -0.25555500 |
| C | -1.24751800 | -1.09995600 | -0.24250100 |
| C | -1.10077700 | 2.50763400 | 0.11750600 |
| C | -1.76475300 | 3.69477500 | 0.42255000 |
| H | -2.82869400 | 3.67577600 | 0.64164300 |
| C | -1.05907400 | 4.88522100 | 0.45450200 |
| H | -1.56307400 | 5.81709100 | 0.69451600 |
| C | 0.30737100 | 4.86387300 | 0.17568400 |
| H | 0.90446200 | 5.77007500 | 0.19083300 |
| C | 0.90689500 | 3.65337600 | -0.12565500 |
| C | -0.14367600 | -2.00033900 | -0.41648200 |
| C | -0.24507700 | -3.39670900 | -0.52277300 |
| H | -1.22549000 | -3.86185500 | -0.59119400 |
| C | 0.89639300 | -4.16577800 | -0.51312400 |
| H | 0.83504800 | -5.24750800 | -0.59286500 |
| C | 2.13910200 | -3.53493900 | -0.32803600 |
| H | 3.04810100 | -4.11420800 | -0.19526900 |
| C | 2.19318800 | -2.15061700 | -0.25629600 |
| C | 2.65761200 | 1.16171000 | -0.99454800 |
| C | 0.66827000 | 0.68568500 | -2.28085000 |
| C | 3.48870400 | -1.50635200 | 0.06094100 |
| C | 3.66601100 | -0.61911900 | 1.14706900 |
| C | 4.61923900 | -1.90109700 | -0.65790100 |
| C | 4.94976200 | -0.18289300 | 1.48511400 |
| C | 5.88711400 | -1.42685100 | -0.34069000 |
| H | 4.48959000 | -2.59058600 | -1.48923200 |
| C | 6.05617300 | -0.56666300 | 0.73726300 |
| H | 5.07489300 | 0.48265700 | 2.33498400 |
| H | 6.74326000 | -1.73740800 | -0.93407000 |
| H | 7.04339800 | -0.19808200 | 1.00148000 |
| C | -4.97940400 | -0.72285200 | 0.21090000 |
| C | -5.95532600 | 0.19771800 | -0.20090600 |

| | | | |
|---|---|---|---|
| C | -5.41139000 | -1.94782700 | 0.74186700 |
| C | -7.30860700 | -0.09678800 | -0.08917500 |
| H | -5.65004900 | 1.14538900 | -0.64097100 |
| C | -6.76459400 | -2.24221100 | 0.85116400 |
| H | -4.67736100 | -2.66681600 | 1.10151100 |
| C | -7.72145500 | -1.31839600 | 0.43671800 |
| H | -8.04535200 | 0.62989000 | -0.42435200 |
| H | -7.07456200 | -3.19540100 | 1.27368200 |
| H | -8.78053700 | -1.54821500 | 0.52474500 |
| C | 2.55781600 | -0.06656000 | 1.97069700 |
| O | 1.52676900 | 0.45641300 | 1.56325300 |
| O | 2.82240200 | -0.12095600 | 3.27158300 |
| H | 2.10244700 | 0.33212700 | 3.74254000 |
| H | 1.96840100 | 3.59995300 | -0.35548400 |

**$1^{2-}$**

| | | | |
|---|---|---|---|
| Mn | 0.77827400 | 0.82931100 | -0.14554400 |
| O | 2.52182400 | 1.94124100 | -2.21540300 |
| O | 2.83536100 | 1.38749700 | 1.85975400 |
| N | -1.03026100 | 0.31612000 | -0.08181800 |
| N | 0.93970300 | -1.18933300 | -0.34484200 |
| N | -0.11394500 | 2.59286000 | 0.07545100 |
| C | -3.75992800 | -0.44423000 | -0.00790600 |
| C | -3.37053100 | 0.90599800 | 0.07689400 |
| H | -4.12655300 | 1.67981200 | 0.20002300 |
| C | -2.03771500 | 1.26678600 | 0.04743900 |
| C | -2.72879500 | -1.39869800 | -0.12788900 |
| H | -2.98296000 | -2.45251100 | -0.22686900 |
| C | -1.40264900 | -1.01729300 | -0.16869400 |
| C | -1.49237500 | 2.58320900 | 0.14074900 |
| C | -2.22625700 | 3.77506300 | 0.27976700 |
| H | -3.31188900 | 3.72564100 | 0.32531000 |
| C | -1.57466600 | 4.98306700 | 0.35606700 |
| H | -2.13239900 | 5.90952300 | 0.46318700 |
| C | -0.16633700 | 4.99232600 | 0.29245400 |
| H | 0.39577400 | 5.91997900 | 0.34876400 |
| C | 0.50288700 | 3.80103100 | 0.15562500 |
| C | -0.26329200 | -1.87220400 | -0.31307400 |
| C | -0.33337400 | -3.26970900 | -0.41844800 |
| H | -1.30536000 | -3.75550300 | -0.37917000 |
| C | 0.81629500 | -4.00663800 | -0.57395300 |
| H | 0.78044300 | -5.08895000 | -0.66334500 |
| C | 2.03891100 | -3.32061100 | -0.61872200 |
| H | 2.97987300 | -3.85120900 | -0.74158400 |
| C | 2.06344200 | -1.94602300 | -0.48584800 |
| C | 2.01534200 | 1.12408100 | 1.04728800 |
| C | 1.84707000 | 1.41815100 | -1.39699200 |
| C | 3.38612100 | -1.27498700 | -0.61254300 |
| C | 4.26247600 | -1.02589300 | 0.45895300 |
| C | 3.81304800 | -0.97995200 | -1.90825800 |
| C | 5.51228900 | -0.44673700 | 0.20911300 |
| C | 5.05720000 | -0.41151400 | -2.14823900 |
| H | 3.13875200 | -1.18921500 | -2.73716900 |
| C | 5.90893200 | -0.13406600 | -1.08304000 |
| H | 6.17695800 | -0.24745900 | 1.04418200 |
| H | 5.36101200 | -0.18458300 | -3.16740900 |
| H | 6.88424500 | 0.31260000 | -1.25854800 |
| C | -5.17213800 | -0.83975900 | 0.02376500 |
| C | -6.18422300 | 0.02771600 | -0.42310000 |

| | | | |
|---|---|---|---|
| C | -5.56734900 | -2.10157600 | 0.50103800 |
| C | -7.52176600 | -0.34623300 | -0.39066600 |
| H | -5.91443000 | 1.00118700 | -0.82912000 |
| C | -6.90454800 | -2.47784800 | 0.52578100 |
| H | -4.81499500 | -2.78934200 | 0.88384000 |
| C | -7.89387600 | -1.60279700 | 0.08228600 |
| H | -8.27950600 | 0.34691100 | -0.75091200 |
| H | -7.17716400 | -3.46004300 | 0.90690600 |
| H | -8.94064200 | -1.89631500 | 0.10381200 |
| C | 3.87474000 | -1.35901000 | 1.84969400 |
| O | 2.82370000 | -1.85892200 | 2.19527300 |
| O | 4.84004400 | -1.07078100 | 2.74105000 |
| H | 4.49290900 | -1.32530400 | 3.60990100 |
| H | 1.58957400 | 3.77227600 | 0.10263000 |

**1a**

| | | | |
|---|---|---|---|
| Mn | 0.82572700 | 0.85306100 | -0.20917100 |
| O | 2.44476800 | 1.80008500 | -2.45473300 |
| O | 2.94878300 | 1.73916900 | 1.60109000 |
| N | -0.98065700 | 0.32284000 | -0.11010100 |
| N | 0.98922800 | -1.16396900 | -0.44556200 |
| N | -0.07675400 | 2.61049000 | 0.02880500 |
| C | -3.70286600 | -0.45088000 | -0.00555600 |
| C | -3.31589200 | 0.89971500 | 0.11299100 |
| H | -4.07148800 | 1.66646100 | 0.27414600 |
| C | -1.98688200 | 1.26371400 | 0.05868500 |
| C | -2.67935800 | -1.39245000 | -0.19857800 |
| H | -2.93467100 | -2.44109100 | -0.33955600 |
| C | -1.35085500 | -1.00495500 | -0.25614900 |
| C | -1.44812500 | 2.58689800 | 0.14734900 |
| C | -2.18970500 | 3.76705600 | 0.32255700 |
| H | -3.27132300 | 3.70411500 | 0.41608400 |
| C | -1.54900600 | 4.98335400 | 0.37206400 |
| H | -2.11167400 | 5.90278400 | 0.50797400 |
| C | -0.14802600 | 5.00891500 | 0.23889100 |
| H | 0.40528300 | 5.94299100 | 0.26637800 |
| C | 0.52944700 | 3.82542700 | 0.07242400 |
| C | -0.21915000 | -1.84560200 | -0.47214600 |
| C | -0.28889900 | -3.22837000 | -0.71188100 |
| H | -1.26250900 | -3.71218700 | -0.72836100 |
| C | 0.85606000 | -3.95118300 | -0.93422700 |
| H | 0.81662300 | -5.01867000 | -1.13116400 |
| C | 2.08770400 | -3.27230500 | -0.88444300 |
| H | 3.02799100 | -3.79893800 | -1.02583300 |
| C | 2.11753700 | -1.91920300 | -0.62826700 |
| C | 2.12013200 | 1.30661700 | 0.87540200 |
| C | 1.80722500 | 1.37202100 | -1.55839900 |
| C | 3.44731500 | -1.26199800 | -0.52183400 |
| C | 4.11749700 | -1.10221200 | 0.70451500 |
| C | 4.11268700 | -0.92124000 | -1.70045200 |
| C | 5.41659900 | -0.58850500 | 0.72042700 |
| C | 5.39425800 | -0.38449200 | -1.67239200 |
| H | 3.60485100 | -1.07967900 | -2.65001100 |
| C | 6.04887400 | -0.21144300 | -0.45535900 |
| H | 5.91857600 | -0.48853400 | 1.67950300 |
| H | 5.88747100 | -0.11317300 | -2.60273500 |
| H | 7.05433900 | 0.20032700 | -0.42558200 |
| C | -5.11429900 | -0.85165700 | 0.05729600 |
| C | -6.13739000 | 0.01743700 | -0.35669800 |

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|---|---|---|---|
| C | -5.49057200 | -2.11858400 | 0.53303000 |
| C | -7.47252300 | -0.36245900 | -0.29694000 |
| H | -5.87973500 | 0.99623400 | -0.75783100 |
| C | -6.82547600 | -2.50053200 | 0.58593500 |
| H | -4.72560300 | -2.80538200 | 0.89191500 |
| C | -7.82719300 | -1.62488000 | 0.17300000 |
| H | -8.24172600 | 0.33050400 | -0.63185600 |
| H | -7.08595000 | -3.48670800 | 0.96481800 |
| H | -8.87205000 | -1.92262500 | 0.21665700 |
| C | 3.55124300 | -1.48561900 | 2.03282200 |
| O | 4.25389100 | -1.86984300 | 2.94527600 |
| O | 2.22917700 | -1.39593500 | 2.21084100 |
| H | 1.78829300 | -0.90425700 | 1.48013400 |
| H | 1.61230900 | 3.81247500 | -0.03160500 |

**$TS_{1a/1b}$**

| | | | |
|---|---|---|---|
| Mn | 0.85612200 | 0.79605700 | -0.23640000 |
| O | 2.26715300 | 1.43191600 | -2.72702000 |
| O | 3.12681600 | 1.93607900 | 1.19580800 |
| N | -0.97856100 | 0.29359600 | -0.11268800 |
| N | 0.97499200 | -1.22020000 | -0.46123100 |
| N | -0.02587100 | 2.56849400 | -0.00097600 |
| C | -3.69971100 | -0.43159800 | -0.00322000 |
| C | -3.29500800 | 0.90029400 | 0.14407200 |
| H | -4.03663800 | 1.67513900 | 0.32676400 |
| C | -1.95274600 | 1.24341400 | 0.08132900 |
| C | -2.69265000 | -1.38925500 | -0.22178600 |
| H | -2.96393000 | -2.43062700 | -0.38023900 |
| C | -1.36355300 | -1.01324100 | -0.27138900 |
| C | -1.39010700 | 2.56000200 | 0.16047900 |
| C | -2.11766700 | 3.74473100 | 0.34879400 |
| H | -3.19514500 | 3.69078800 | 0.48237200 |
| C | -1.46638600 | 4.95704300 | 0.35852500 |
| H | -2.01639700 | 5.88227300 | 0.50467900 |
| C | -0.07445500 | 4.96921800 | 0.16851900 |
| H | 0.48598800 | 5.89919100 | 0.15847200 |
| C | 0.59034100 | 3.77854400 | -0.00419000 |
| C | -0.22517900 | -1.88059900 | -0.46019900 |
| C | -0.31130500 | -3.27019800 | -0.58820600 |
| H | -1.28659500 | -3.74896200 | -0.59289100 |
| C | 0.84335800 | -4.01518200 | -0.69240100 |
| H | 0.80196400 | -5.09555400 | -0.79754000 |
| C | 2.06893800 | -3.34873200 | -0.63600100 |
| H | 3.00814500 | -3.89304700 | -0.68559500 |
| C | 2.10540500 | -1.96903900 | -0.50252600 |
| C | 2.24031500 | 1.36789000 | 0.64479400 |
| C | 1.66453900 | 1.16012100 | -1.75582500 |
| C | 3.44222500 | -1.32179700 | -0.43091700 |
| C | 4.07757400 | -1.04918500 | 0.79221800 |
| C | 4.13923000 | -1.12720300 | -1.62639600 |
| C | 5.39443100 | -0.58756700 | 0.77899900 |
| C | 5.43367300 | -0.62077200 | -1.62480700 |
| H | 3.64497000 | -1.36410400 | -2.56795000 |
| C | 6.06708300 | -0.35342100 | -0.41363800 |
| H | 5.87700600 | -0.40457500 | 1.73648700 |
| H | 5.95200800 | -0.45398700 | -2.56629500 |
| H | 7.08608800 | 0.02660900 | -0.40072000 |
| C | -5.11976200 | -0.81306100 | 0.06098400 |
| C | -6.12261100 | 0.06148600 | -0.38267700 |

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|---|---|---|---|
| C | -5.51065600 | -2.06029900 | 0.56971100 |
| C | -7.46379300 | -0.29601100 | -0.31704900 |
| H | -5.84563700 | 1.02365700 | -0.81009400 |
| C | -6.85203700 | -2.41901000 | 0.63122700 |
| H | -4.75599400 | -2.74789700 | 0.94791600 |
| C | -7.83645600 | -1.53861100 | 0.18956500 |
| H | -8.22194000 | 0.39723200 | -0.67470000 |
| H | -7.13034300 | -3.38910900 | 1.03701300 |
| H | -8.88583400 | -1.81899600 | 0.23844400 |
| C | 3.39889200 | -1.19571800 | 2.13974000 |
| O | 4.08314400 | -1.58318200 | 3.09517800 |
| O | 2.15668000 | -0.88070600 | 2.19840100 |
| H | 1.71566200 | 0.11392600 | 1.19877600 |
| H | 1.66778800 | 3.75705800 | -0.14592400 |

**1b**

| | | | |
|---|---|---|---|
| Mn | -0.79766400 | 0.93334400 | 0.04989100 |
| O | -1.37549700 | 1.64449600 | 2.86444400 |
| O | -3.37885100 | 2.00631300 | -0.81919500 |
| N | 1.06776400 | 0.33094300 | 0.05706100 |
| N | -1.03136300 | -1.12118500 | 0.30899300 |
| N | 0.18570500 | 2.66544500 | -0.29494300 |
| C | 3.71100100 | -0.51958800 | -0.00711200 |
| C | 3.38631800 | 0.83115000 | -0.17345700 |
| H | 4.17002500 | 1.56088000 | -0.35868700 |
| C | 2.05526800 | 1.22582800 | -0.13754000 |
| C | 2.66272000 | -1.42860900 | 0.17502800 |
| H | 2.88131400 | -2.48234600 | 0.32349500 |
| C | 1.34856200 | -0.97614100 | 0.19415900 |
| C | 1.54442000 | 2.58041400 | -0.32722700 |
| C | 2.35039100 | 3.69765900 | -0.53444700 |
| H | 3.43122800 | 3.59033500 | -0.55275800 |
| C | 1.76227600 | 4.93893700 | -0.71433100 |
| H | 2.37374000 | 5.82123300 | -0.87818700 |
| C | 0.37322100 | 5.02713700 | -0.67982300 |
| H | -0.13677500 | 5.97585400 | -0.81521800 |
| C | -0.36918600 | 3.87752400 | -0.46916700 |
| C | 0.15129400 | -1.80641800 | 0.33990700 |
| C | 0.21995200 | -3.18431600 | 0.48943900 |
| H | 1.18330400 | -3.68477100 | 0.50933500 |
| C | -0.95685200 | -3.90963200 | 0.62236100 |
| H | -0.93211100 | -4.98804700 | 0.75101100 |
| C | -2.15436400 | -3.22330400 | 0.58960600 |
| H | -3.10595400 | -3.73959500 | 0.68350700 |
| C | -2.16750500 | -1.83499700 | 0.41406600 |
| C | -2.38756900 | 1.51740000 | -0.42573700 |
| C | -1.08904500 | 1.32473100 | 1.77321000 |
| C | -3.48356800 | -1.15091000 | 0.50174500 |
| C | -4.40900200 | -1.14946500 | -0.55188700 |
| C | -3.84034200 | -0.61279200 | 1.74291600 |
| C | -5.66164800 | -0.57306900 | -0.33506100 |
| C | -5.08931800 | -0.03530600 | 1.93686800 |
| H | -3.12549200 | -0.65220600 | 2.56399500 |
| C | -6.00687300 | -0.01398300 | 0.88858400 |
| H | -6.35950600 | -0.58622400 | -1.16912400 |
| H | -5.34942700 | 0.38280500 | 2.90701700 |
| H | -6.99023700 | 0.42997200 | 1.03118500 |
| C | 5.11487600 | -0.97077900 | -0.03310900 |
| C | 6.13386400 | -0.15987600 | 0.48231700 |

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|---|---|---|---|
| C | 5.45749500 | -2.21590200 | -0.57510500 |
| C | 7.45709300 | -0.58338300 | 0.45840500 |
| H | 5.88377800 | 0.79956400 | 0.93137800 |
| C | 6.78141600 | -2.63768100 | -0.59980400 |
| H | 4.68473300 | -2.84885900 | -1.00728700 |
| C | 7.78567700 | -1.82336900 | -0.08316100 |
| H | 8.23389900 | 0.05569000 | 0.87115900 |
| H | 7.03014300 | -3.60348400 | -1.03288200 |
| H | 8.82129700 | -2.15368100 | -0.10256900 |
| C | -4.09044300 | -1.72986800 | -1.93222200 |
| O | -5.04462100 | -1.79298400 | -2.73948400 |
| O | -2.89990800 | -2.08417700 | -2.12720100 |
| H | -0.80174800 | 0.67392600 | -1.56458600 |
| H | -1.45512700 | 3.91138400 | -0.44087800 |

**1c**

| | | | |
|---|---|---|---|
| Mn | 0.77087500 | 0.93924200 | -0.03428800 |
| O | 1.32540200 | 1.69693900 | -2.84261700 |
| O | 3.35902900 | 1.97746500 | 0.85988900 |
| N | -1.09076900 | 0.32709000 | -0.04031500 |
| N | 1.01231100 | -1.10723400 | -0.30810600 |
| N | -0.22104700 | 2.66492200 | 0.33458500 |
| C | -3.73020800 | -0.53659700 | 0.00515400 |
| C | -3.41168500 | 0.81465300 | 0.18093400 |
| H | -4.20016600 | 1.53971600 | 0.36382500 |
| C | -2.08271800 | 1.21636000 | 0.15540900 |
| C | -2.67687200 | -1.44109400 | -0.16995200 |
| H | -2.88923500 | -2.49534200 | -0.32378300 |
| C | -1.36569400 | -0.98066100 | -0.17905000 |
| C | -1.57886600 | 2.57217900 | 0.35934900 |
| C | -2.39139200 | 3.68264000 | 0.57464300 |
| H | -3.47172300 | 3.57045500 | 0.58620400 |
| C | -1.80975100 | 4.92465700 | 0.77132500 |
| H | -2.42630100 | 5.80208800 | 0.94178100 |
| C | -0.42146700 | 5.02033400 | 0.74538400 |
| H | 0.08314300 | 5.96988400 | 0.89382400 |
| C | 0.32777700 | 3.87647000 | 0.52512000 |
| C | -0.16277200 | -1.80280500 | -0.31782400 |
| C | -0.21548400 | -3.18735100 | -0.42942800 |
| H | -1.17385400 | -3.69744300 | -0.42499000 |
| C | 0.96408200 | -3.90554200 | -0.54098800 |
| H | 0.94986900 | -4.98781600 | -0.62770900 |
| C | 2.15894100 | -3.20535500 | -0.54940900 |
| H | 3.11272900 | -3.71715500 | -0.64726900 |
| C | 2.15148100 | -1.81591700 | -0.43342300 |
| C | 2.36059600 | 1.51406300 | 0.45374300 |
| C | 1.04790700 | 1.36257000 | -1.75451200 |
| C | 3.45246100 | -1.10666000 | -0.55157100 |
| C | 4.45420100 | -1.12732400 | 0.43445800 |
| C | 3.73238700 | -0.50825500 | -1.78259200 |
| C | 5.69557100 | -0.53939300 | 0.16757400 |
| C | 4.96332900 | 0.08499900 | -2.03023500 |
| H | 2.96373200 | -0.51001100 | -2.55249000 |
| C | 5.95334100 | 0.06764600 | -1.05103800 |
| H | 6.45195400 | -0.56630000 | 0.94716900 |
| H | 5.15345000 | 0.54837200 | -2.99525200 |
| H | 6.92224700 | 0.52239100 | -1.23902300 |
| C | -5.13270300 | -0.99195500 | 0.01390600 |
| C | -6.14711300 | -0.18237400 | -0.51237800 |

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|---|---|---|---|
| C | -5.47777400 | -2.23922500 | 0.54904800 |
| C | -7.46924700 | -0.60978200 | -0.50568300 |
| H | -5.89413200 | 0.77863500 | -0.95640500 |
| C | -6.80077200 | -2.66446400 | 0.55700100 |
| H | -4.70856000 | -2.87087600 | 0.98936000 |
| C | -7.80068200 | -1.85173300 | 0.02956400 |
| H | -8.24275100 | 0.02775200 | -0.92680900 |
| H | -7.05234300 | -3.63167600 | 0.98512400 |
| H | -8.83554400 | -2.18483100 | 0.03581500 |
| C | 4.29898200 | -1.70173300 | 1.79517500 |
| O | 3.02919700 | -1.94460800 | 2.14845700 |
| O | 5.22657400 | -1.91387800 | 2.54940800 |
| H | 0.78041000 | 0.65931300 | 1.57496900 |
| H | 3.05137300 | -2.30551200 | 3.04950300 |
| H | 1.41360500 | 3.91641900 | 0.50090400 |

**$TS_{1c/1}$**

| | | | |
|---|---|---|---|
| Mn | 0.89816100 | 0.83158500 | -0.26405000 |
| O | 0.77936900 | 1.16181900 | -3.18522700 |
| O | 3.56854600 | 2.05169200 | -0.41590800 |
| N | -0.99038000 | 0.28197200 | -0.05792100 |
| N | 1.04662200 | -1.22537700 | -0.39114200 |
| N | -0.00203500 | 2.61349400 | 0.15715000 |
| C | -3.65218500 | -0.45397500 | 0.04555700 |
| C | -3.26838100 | 0.87966900 | 0.23115400 |
| H | -4.01862700 | 1.63774800 | 0.43758300 |
| C | -1.92334700 | 1.21810200 | 0.16726600 |
| C | -2.65021800 | -1.40741900 | -0.17446300 |
| H | -2.91774000 | -2.44673300 | -0.34241200 |
| C | -1.32056600 | -1.00685200 | -0.21199000 |
| C | -1.35030200 | 2.55938800 | 0.32555500 |
| C | -2.09954600 | 3.69070600 | 0.62640900 |
| H | -3.17442900 | 3.61288400 | 0.75876100 |
| C | -1.45921700 | 4.91503200 | 0.75779100 |
| H | -2.02771400 | 5.80925900 | 0.99495500 |
| C | -0.08306700 | 4.97086800 | 0.58074600 |
| H | 0.46319300 | 5.90410100 | 0.67136200 |
| C | 0.60331300 | 3.80279900 | 0.28205000 |
| C | -0.14878300 | -1.87666300 | -0.38222600 |
| C | -0.24393100 | -3.25893000 | -0.46563700 |
| H | -1.21621900 | -3.74170900 | -0.45607700 |
| C | 0.91967100 | -4.01056700 | -0.54437900 |
| H | 0.87430000 | -5.09308600 | -0.61657000 |
| C | 2.13718700 | -3.35174500 | -0.50576300 |
| H | 3.07596000 | -3.89737000 | -0.53612300 |
| C | 2.17055700 | -1.95900200 | -0.41109600 |
| C | 2.55029200 | 1.48599900 | -0.34929400 |
| C | 0.79556400 | 1.03345200 | -2.02729300 |
| C | 3.49657400 | -1.29569600 | -0.34994200 |
| C | 4.11540100 | -0.98198500 | 0.87099800 |
| C | 4.19195700 | -1.12134600 | -1.54877500 |
| C | 5.42465000 | -0.49755600 | 0.85108500 |
| C | 5.47835500 | -0.59603900 | -1.55181800 |
| H | 3.70746000 | -1.39833900 | -2.48446900 |
| C | 6.09849900 | -0.28574600 | -0.34452900 |
| H | 5.90329400 | -0.28883000 | 1.80486600 |
| H | 6.00099300 | -0.44723200 | -2.49358700 |
| H | 7.11160700 | 0.10910600 | -0.33594700 |
| C | -5.07440300 | -0.84010500 | 0.07930500 |
| C | -6.05570300 | 0.02581200 | -0.41868200 |

| | | | |
|---|---|---|---|
| C | -5.46828800 | -2.07544000 | 0.60770300 |
| C | -7.39678400 | -0.33612500 | -0.39053300 |
| H | -5.76427300 | 0.97733200 | -0.85931100 |
| C | -6.81062900 | -2.43330400 | 0.63954800 |
| H | -4.72260600 | -2.74981900 | 1.02428000 |
| C | -7.77807300 | -1.56554300 | 0.14017400 |
| H | -8.14564700 | 0.34265900 | -0.79089800 |
| H | -7.10262400 | -3.39115300 | 1.06263800 |
| H | -8.82777500 | -1.84733600 | 0.16343400 |
| C | 3.46022600 | -1.18148000 | 2.22008000 |
| O | 2.18966100 | -0.98346000 | 2.30640700 |
| O | 4.17735900 | -1.52570400 | 3.16279600 |
| H | 1.03070300 | 0.71550200 | 1.44438400 |
| H | 1.56426200 | -0.01221700 | 1.62223300 |
| H | 1.67999200 | 3.81236100 | 0.13699100 |

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