Supplementary Information

A homogeneous polypyridine-based manganese catalytic system: Reducing CO_2 to CO under visible light

Yu-mei Chen, Ke-Xin Zhou, Quan-Qing Xu* and Zhi-Yang*

Faculty of Chemistry and Chemical Engineering, Yunnan Normal University, Kunming 650 050, P R China

*E-mail: qqxu1977@163.com (QQX), yangzhi@ynnu.edu.cn (Z-Y)

A Homogeneous polypyridine-based Manganese Catalytic System: Reducing CO_2 to CO under Visible Light

Photocatalytic effect of several recent Mn-based complex catalysts that have been reported

Catalyst	Photosensitizer	TON_{CO}	Selectivity	Reference
fac-[Mn(phen)$(CO)_3$Br]	ZnTPP	64	86.2%	*Applied Catalysis A: General,* ***2016,*** 522, 145-151.
[Mn{κ^2-(Ph_2P)NMe(NC_5H_4)}$(CO)_3$Br]	$[Ru(bpy)_3]^{2+}$	55	>99.0%	*Inorganic chemistry, 2018,*
g-C_3N_4/MnP	**g**-C_3N_4/MnP	75.7	---	*Chemical Engineering Science,* **2021,** 229, 116042
$C_{32}H_{32}Br_2MnN_4$	$[Ru(bpy)_3]^{2+}$	1038	99.2%	**This work**

2. Synthesis method for Mn-bpy,Mn-dmbpyand Mn-phen, Mn-tmphen

All chemicals were purchased from company such as Sigma-Aldrich and used as received.

Synthesis of Mn-bpy

2, 2'-Bipyridine (222 mg, 0.71 mmol) and [$Mn(CO)_5Br$] (199 mg, 0.72 mmol) were dissolved in 30 mL of diethyl ether, stirred, and then heated under reflux for 3 h. After cooling to room temperature, a yellow powder was obtained, which was filtered, washed with diethyl ether, and then dried under vacuum. Yield: 312 mg (0.59 mmol) (83.4%). ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 9.16 (s, 4H), 8.62 (s, 5H), 8.19 (s, 4H), 7.69 (s, 4H). Elemental analysis results for **Mn-bpy**: calculated: C, 45.57; H, 3.06; N, 10.63; found: C 45.19, H 3.04, N 10.49.

Synthesis of Mn-dmbpy

4, 4-Dimethyl-2,2-bipyridine (130 mg, 0.71 mmol) and [$Mn(CO)_5Br$] (113 mg, 0.41 mmol) were dissolved in 30 mL of diethyl ether, stirred, and maintained under reflux for 2 h. After cooling to room temperature, a yellow powder was obtained by precipitation, which was then washed with ether and dried under vacuum. Yield: 184 mg (0.32 mmol) (90.1%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.95 (s, 4H), 8.48 (s, 4H), 7.50 (s, 4H), 2.48 (s, 12H). Elemental analysis results of **Mn-dmbpy**: calculated: C 49.43, H 4.15, N 9.61; found: C 49.06, H 4.06, N 9.49.

Synthesis of Mn-phen

1, 10-Phenanthroline (232 mg, 1.29 mmol) and [$Mn(CO)_5Br$] (200 mg, 0.72 mmol) were dissolved in 50 mL of methanol stirred for 2 h. A yellow powder was obtained by precipitation, which was washed with methanol and then dried under vacuum. Yield: 340 mg (0.59 mmol) (92.4%). ^{1}H NMR (500 MHz,

DMSO-d_6, ppm): δ 9.55 (s, 4H), 8.33 (s, 4H), 8.24 (s, 4H), 8.05 (s, 4H). Elemental analysis results for **Mn-phen**: calculated: C 50.12, H 2.80, N 9.74; found: C 49.56, H 2.78, N 9.27.

Synthesis Mn-tmphen

3,4,7,8-Tetramethyl-1,10-phenanthroline (343.8 mg, 1.45 mmol) and [$Mn(CO)_5Br$] (200 mg, 0.72 mmol) were dissolved in 50 mL of methanol stirred for 2 h. A yellow powder was obtained by precipitation,

which was washed with methanol and dried under vacuum. Yield: 460 mg (0.67 mmol) (92.9%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.92 (s, 4H), 8.03 (s, 4H), 2.72-2.52 (m, 24H). Elemental analysis results for **Mn-tmphen**: calculated: C 55.92, H 4.69, N 8.15; found: C 55.56, H 4.58, N 8.28.

Crystallographic Data Collection and Refinement

Single crystals of **Mn-bpy**, **Mn-dmbpy**, **Mn-phen**, **Mn-tmphen** wereobtained. A suitable crystal was selected andon a**Xcalibur, Eos, Gemini**diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex2[1], the structure was solved with the SHELXT[2] structure solution program using Intrinsic Phasing and refined with the SHELXL[3] refinement package using Least Squares minimisation.

Single-crystal X-ray diffraction analysis (XRD) revealed that the four catalysts exhibit almost the same structure with crystallographic centers of symmetry (Fig. 1.). The **Mn-bpy, Mn-dmbpy** and **Mn-phen** structures have been reported before; however, a different solvent was adopted in our experimental study, affording higher yields. Table S1 lists key crystallographic data for these Four catalysts. Powder XRD (PXRD) patterns of **Mn-phen** and **Mn-tmphen** were measured at room temperature. The theoretical and experimental PXRD patterns were consistent (Fig. S2a ~ Fig. S2d).The symmetric unit of **Mn-tmphen** comprised **Mn (II)** with two **tmphen** units and two **Br$^-$**, the **Mn (II)** atom was present on a crystallographical center of symmetry. The coordination number of the manganese was six, with two **Br$^-$,** and with two chelating **tmphen** as ligands, and two nitrogen atoms on **tmphen** coordinate with metal centers.

Crystal data and structure refinement is summarized in Table S1. Crystallographic data for **Mn-tmphen** have been deposited in the Cambridge Crystallographic Data Center with CCDC reference number2109759, respectively. Whereas, crystallographic data for **Mn-bpy, Mn-dmbpy, Mn-phen,** have been reported with CCDC reference number 669826, 238626, 248718, respectively.

3. Experimental details for Photocatalytic CO_2 Reduction

Experimental details for Photocatalytic CO_2 Reduction

The system was purged with 10 min N_2 flow and then inlet 20 min CO_2, then the tube was sealed with a rubber septum. The system was then irradiated 12 h by a LED lamp (blue light, 18 modules, centered at 460 nm). The photocatalytic products of H_2 and CO, in the head-space were analyzed by GC/TCD (SHIMADZU 2014C). The generated gases were analyzed by a gas chromatography (GC-2014C, TDX-01 molecular sieve column (3 m × 2 mm), INJ 90 °C, TCD 60 °C, column temperature 60 °C, carrier gas flow 30 mL/min). The amounts of products were determined using the external standard method as the basis for quantitative analysis. Continuous illumination (the gas in the same reaction tube

was analyzed by GC every hour) for 12 h at room temperature, at this 12 h time point, the maximum value of CO from CO_2 was achieved, subsequent irradiation does not produce CO anymore. A calibration curves were obtained by filling pure H_2 and CO gas to a tube with a graduated gas tight syringe.

Photocatalytic reduction of CO_2 to CO was conducted under 1 atm of CO_2 atmosphere at room temperature. The reaction mixture had a total volume of 6 mL, containing the catalyst, **[Ru]**, BIH, and CH_3CN / TEOA (V / V = 7 / 1). Before irradiation, the solution was bubbled with N_2 for 10 min, then CO_2 for 20 min. The reaction mixture was continuously stirred with a magnetic stir bar and irradiated under the blue LED light.

The generated gases were analyzed by gas chromatography (GC-TCD), using calibration curves for H_2 and CO that were established separately. The molar amounts of H_2 and CO in the sample headspace were determined using the GC peak area and these calibration curves, taking into account of the irradiated sample volume.

4. Isotopic labeling experiment

The $^{13}CO_2$ isotopic labeling experiments were adopted using GC-MS (TSQ9000, Faculty of Chemistry and Chemical Engineering, Yunnan Normal University). The photocatalytic gas product was injected and then separated. Fig. S7 shows the GC-MS chromatograms of the peaks at m/z = 29.0 (^{13}CO). Herein, the peak at m/z = 45.2 attributed to $^{13}CO_2$, and the peak at m/z = 28.0 attributed to N_2 or small amount of ^{12}CO.

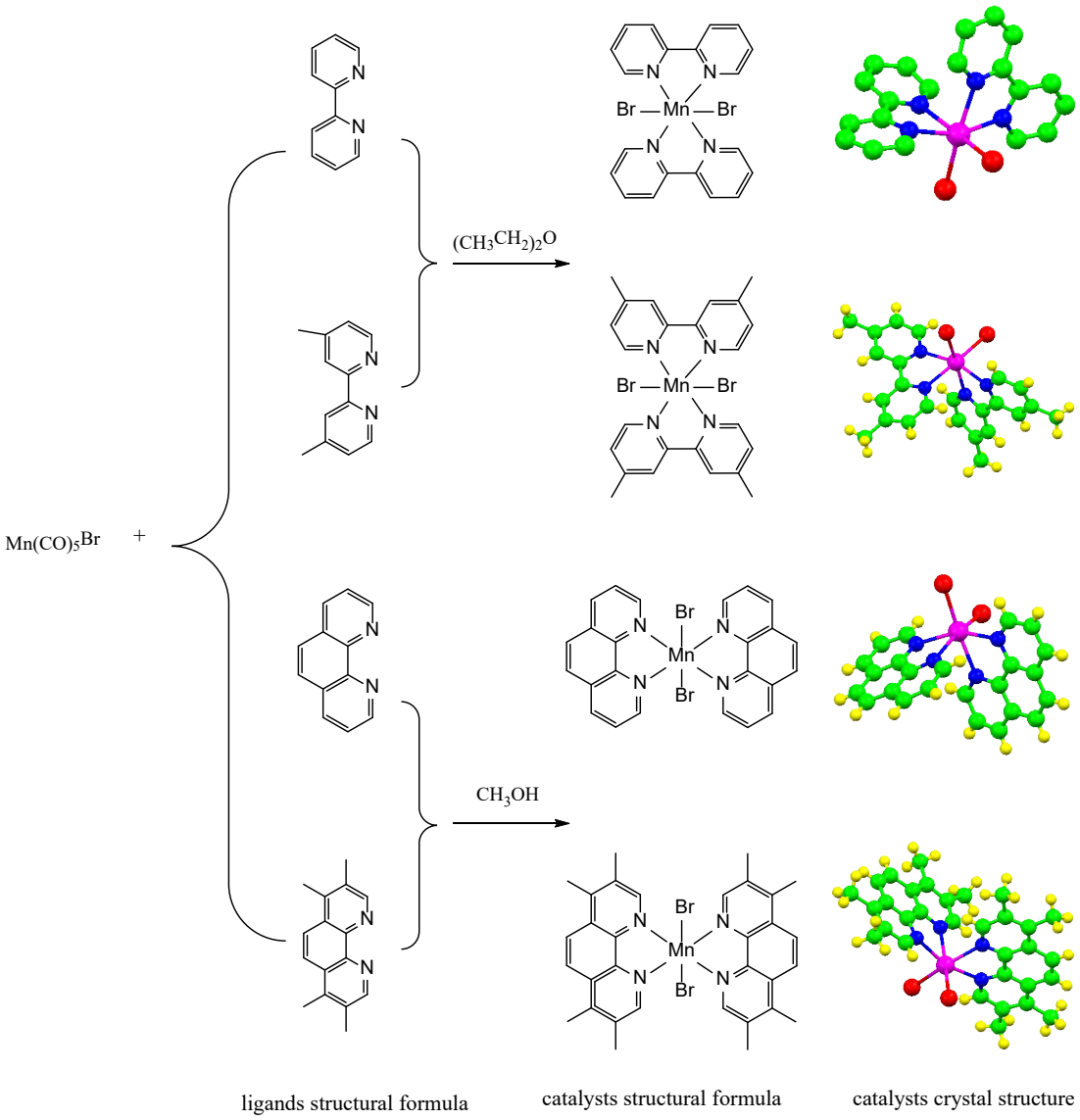
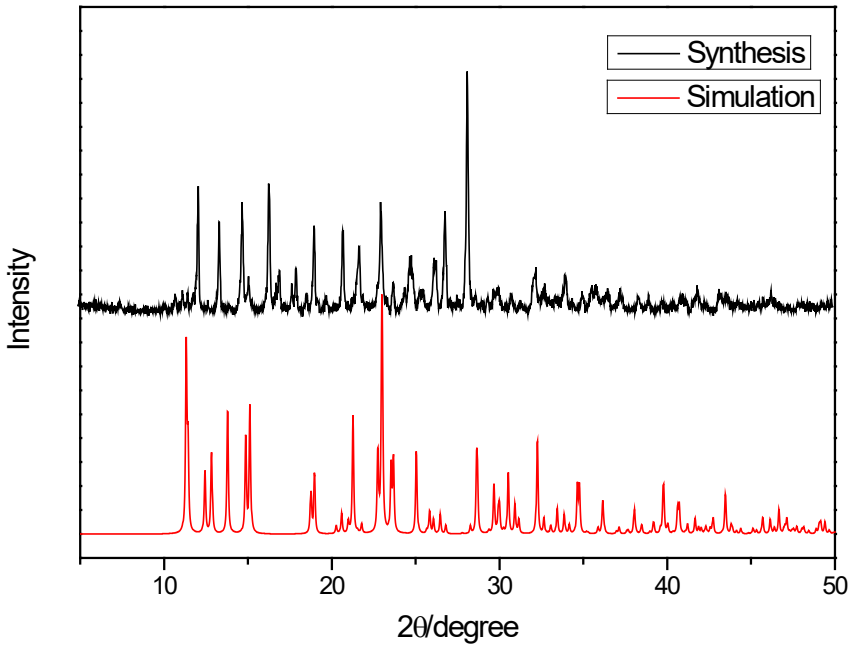


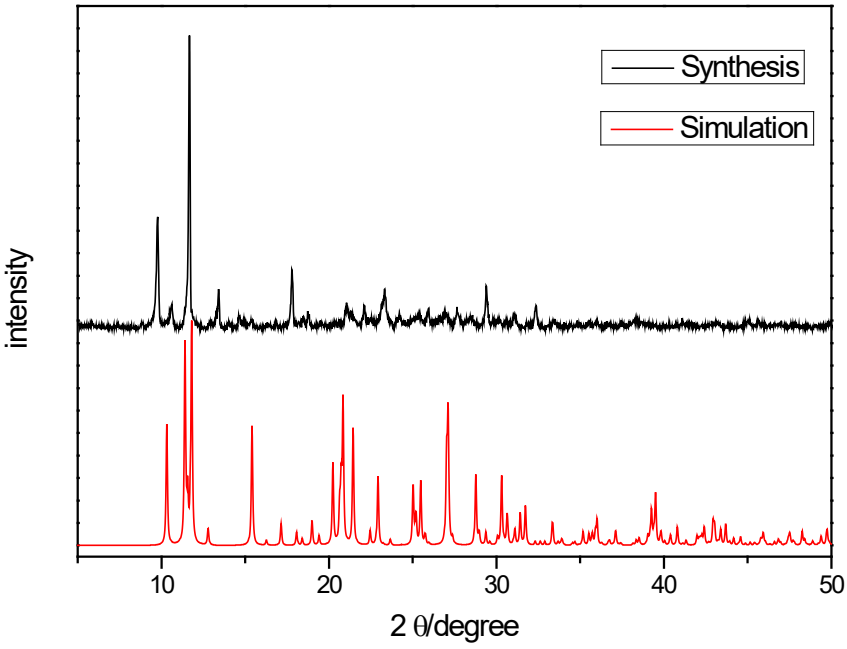
Fig. S1 — Ligands structural formulas (left), catalysts structural formulas (central) and catalysts crystal structure (right) of **Mn-bpy**, **Mn-dmbpy**, **Mn-phen** and **Mn-tmphen**, respectively

Table S1 — Crystal data and structure refinements for **Mn-bpy**, **Mn-dmbpy**, **Mn-phen** and **Mn-tmphen**

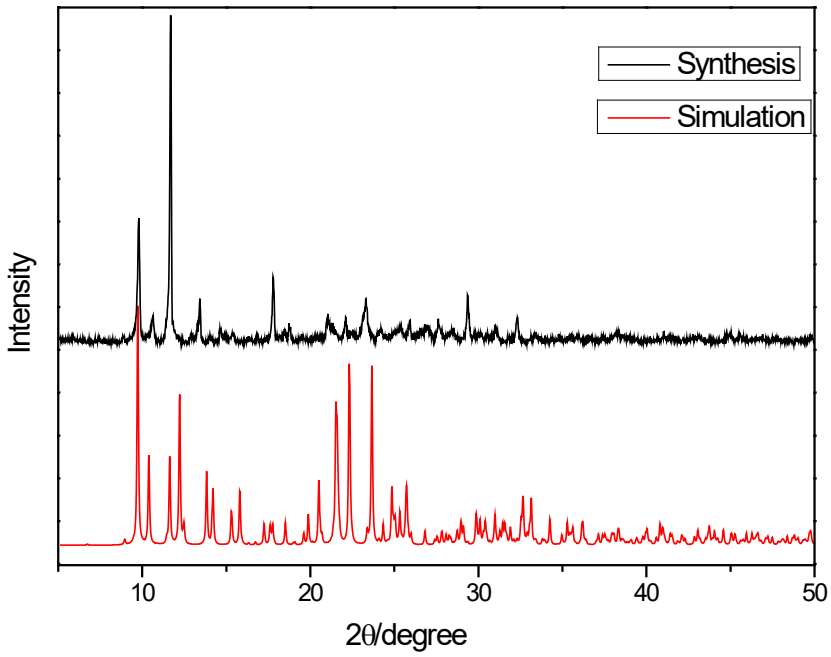
Compounds	**Mn-bpy**	**Mn-dmbpy**	**Mn-phen**	**Mn-tmphen**
Empirical formula	$C_{20}H_{16}Br_2MnN_4$	$C_{24}H_{24}Br_2MnN_4$	$C_{24}H_{16}Br_2MnN_4$	$C_{32}H_{32}Br_2MnN_4$
Formula weight	527.13	583.22	575.17	687.37
Temperature/K	293	293	293	293
Crystal system	Monoclinic	Orthorhombic	Triclinic	Orthorhombic
Space group	C2/c	Pbcn	C2/c	Pnna
a/Å	8.7589(18)	15.460(3)	9.3510 (15)	8.9062 (7)
b/Å	14.591(3)	10.297(2)	10.2285 (14)	18.2915 (17)
c/Å	15.892(3)	15.579(3)	12.7572 (14)	18.0577 (14)
α/°	90.00	90.00	78.355 (10)	90.00
β/°	97.89(3)	90.00	81.371 (11)	90.00
γ/°	90.00	90.00	69.827 (14)	90.00
Volume/$Å^3$	2011.9(7)	2479.9(9)	1117.5 (3)	2941.7 (4)
Z	4	31	2	4
μ/mm^{-1}	4.640	16.356	4.18	3.19
Radiation type	MoKα	MoKα	MoKα	MoKα


Synthesis
Simulation
Intensity
10
20
30
40
50
2θ/degree

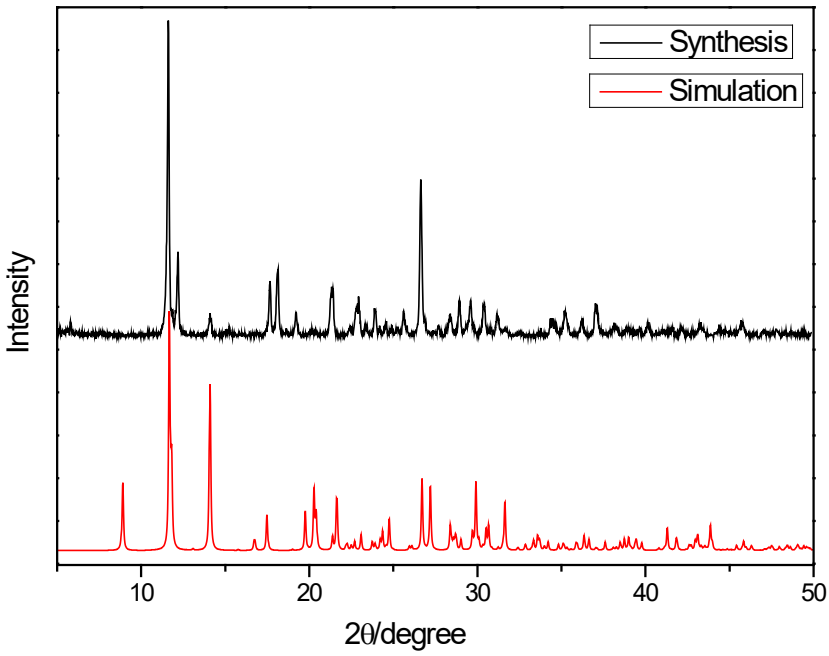
(a)


Synthesis
Simulation
intensity
10
20
30
40
50
2 θ/degree

(b)



(c)



(d)

Fig. S2 — PXRD patterns (black line indicates the as-synthesized, red line refers to simulated) of catalyst (a) **Mn-bpy**, (b) **Mn-dmbpy**, (c) **Mn-phen** and (d) **Mn-tmphen**

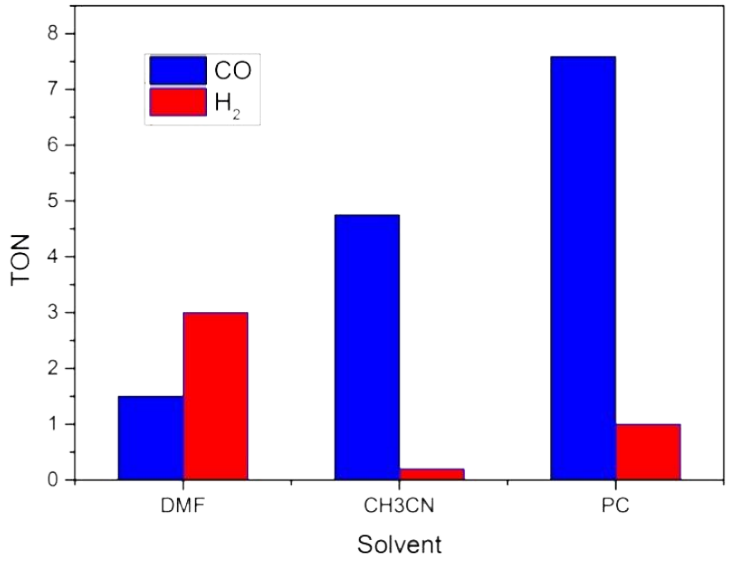


Fig. S3 — Photocatalytic reduction of CO_2 in different solvents of **$Mn(CO)_5Br$**

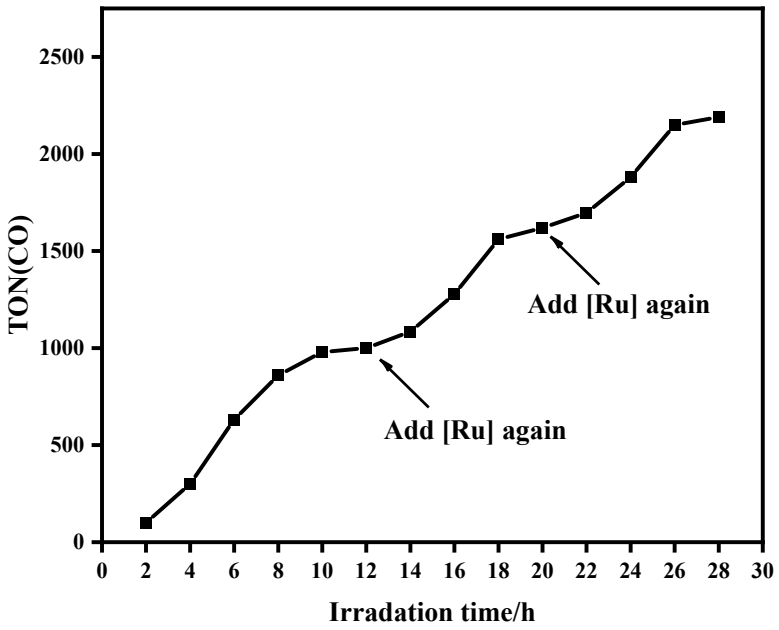


Fig. S4 — Photocatalytic CO_2 reduction in 6 mL CO_2-saturated CH_3CN / TEOA (7: 1 V: V, 6 mL total) solution with 0.1 mM catalyst, 0.45 mM [Ru], 0.052 M BIH, and irradiated with a 460 nm blue light

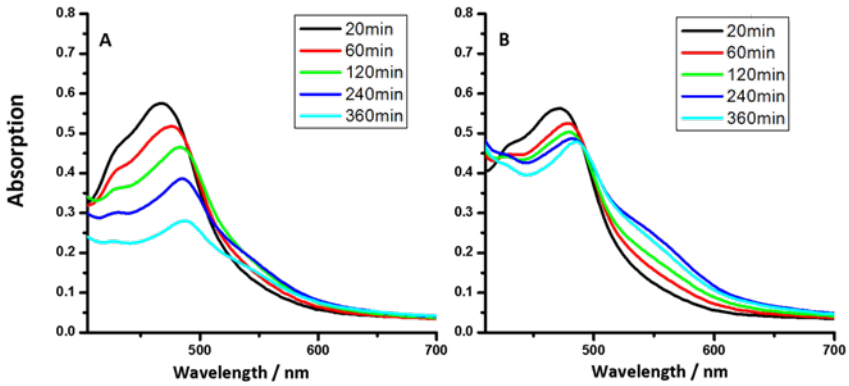


Fig. S5 — The electronic absorption spectra at different irradiation times: **[Ru]** (4×10^{-5} M); solvent was CH_3CN : TEOA = 7 : 1 (*V* / *V*), [A]without catalyst **Mn-dmbpy** and [B]with catalyst **Mn-dmbpy** (1×10^{-5} M); the blue lamp produced a spectrum within the range of 460 ≤λ≤ 465 nm. Each sample were deoxygenated with N_2 before measuring the emission spectra

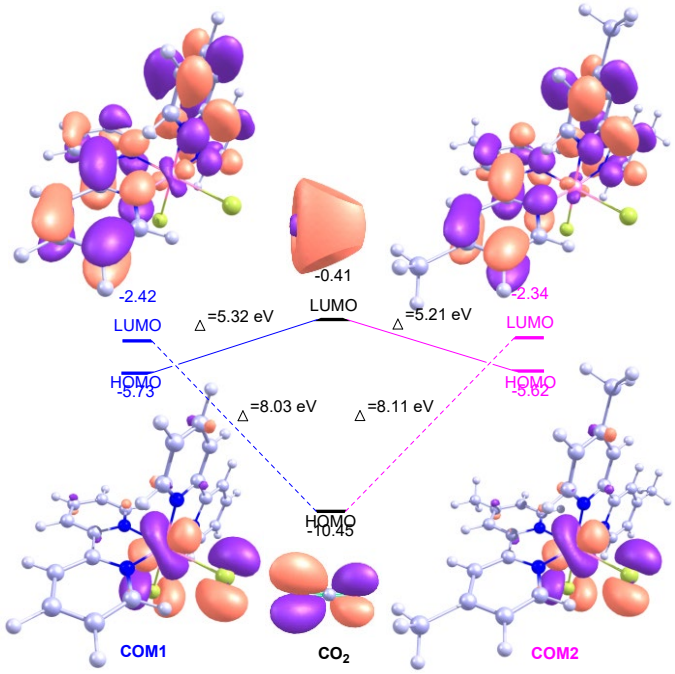
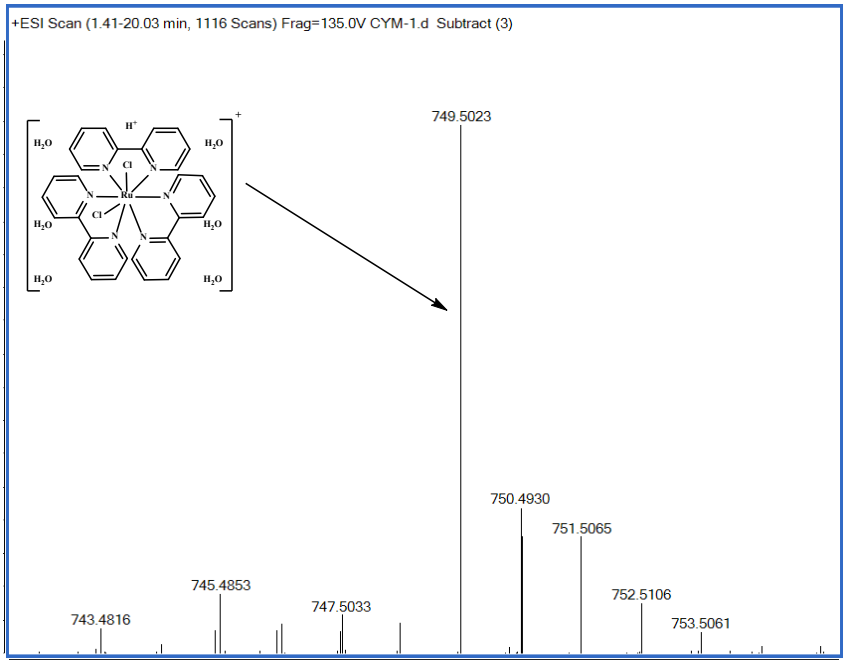
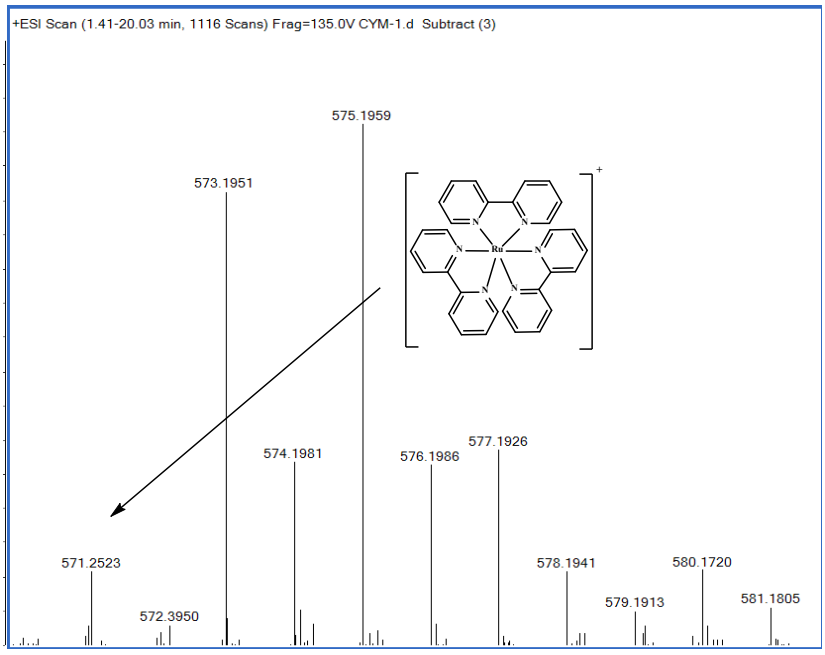


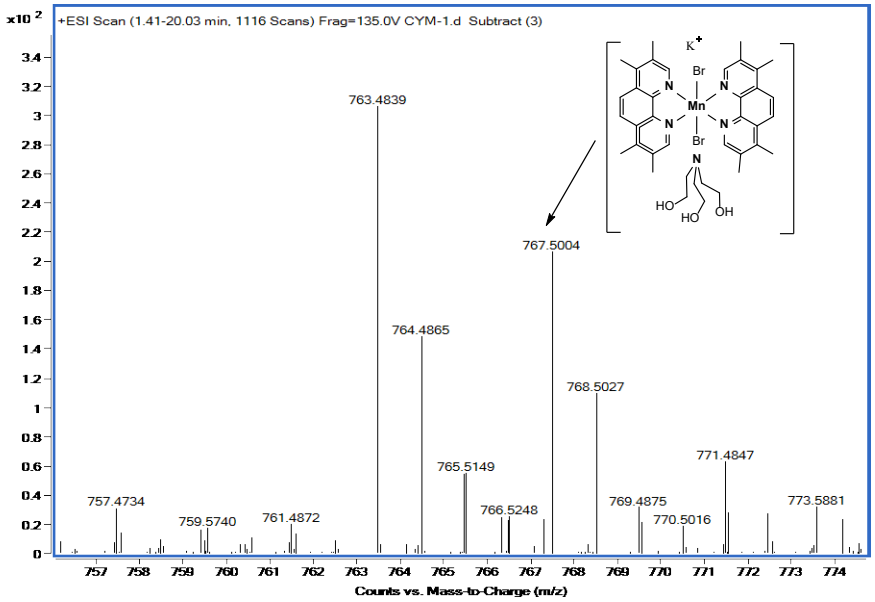
Fig. S6 — Theoretical calculation of CO_2 Bonding with M1, M2. **(**M1=**Mn-bpy,** M2=**Mn-dmbpy)**


+ESI Scan (1.41-20.03 min, 1116 Scans) Frag=135.0V CYM-1.d Subtract (3)
749.5023
750.4930
751.5065
745.4853
752.5106
747.5033
743.4816
753.5061

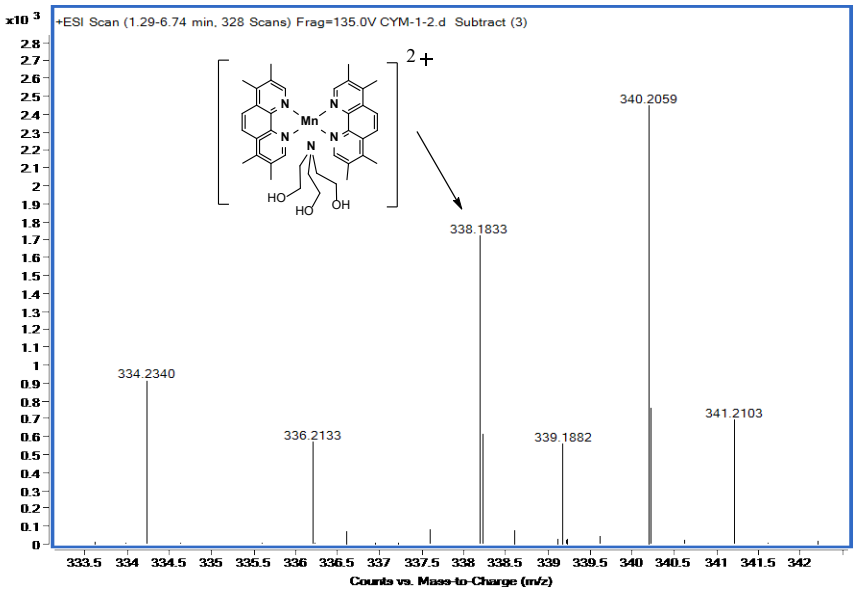
(a)


+ESI Scan (1.41-20.03 min, 1116 Scans) Frag=135.0V CYM-1.d Subtract (3)
575.1959
573.1951
574.1981
577.1926
576.1986
571.2523
578.1941
580.1720
572.3950
579.1913
581.1805

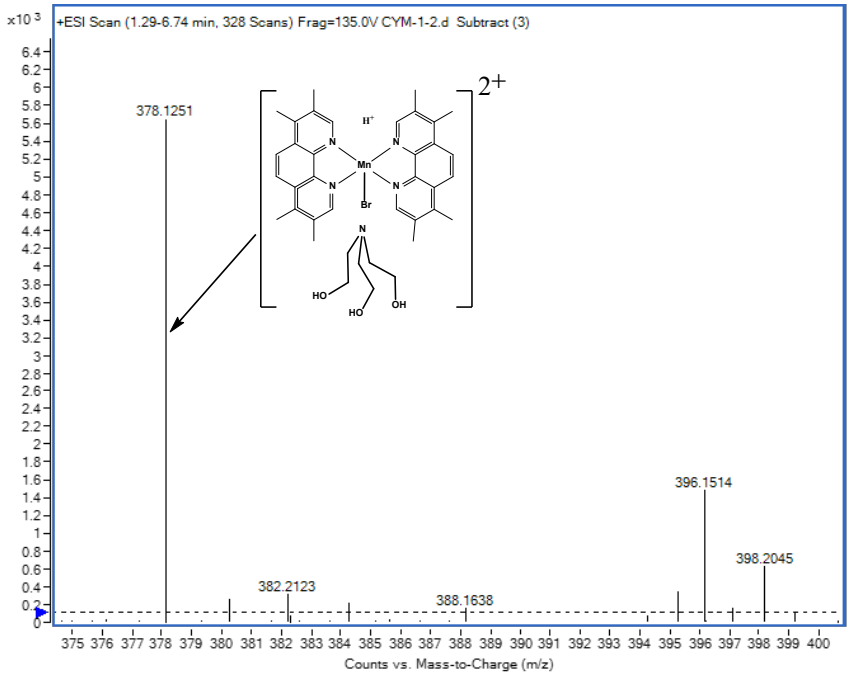
(b)


x10 2
+ESI Scan (1.41-20.03 min, 1116 Scans) Frag=135.0V CYM-1.d Subtract (3)
763.4839
767.5004
764.4865
768.5027
765.5149
771.4847
757.4734
759.5740
761.4872
766.5248
769.4875
770.5016
773.5881
Counts vs. Mass-to-Charge (m/z)

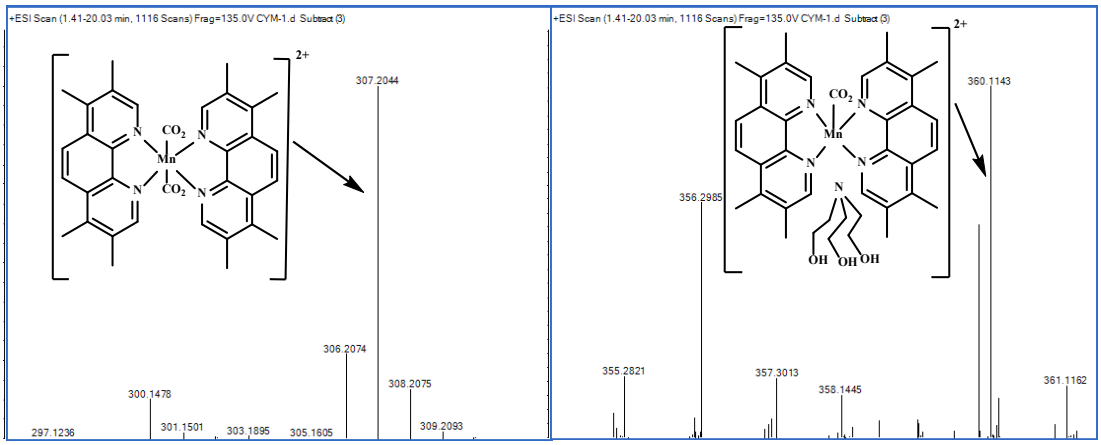
(c)


x10 3
+ESI Scan (1.29-6.74 min, 328 Scans) Frag=135.0V CYM-1-2.d Subtract (3)
340.2059
338.1833
334.2340
341.2103
336.2133
339.1882
Counts vs. Mass-to-Charge (m/z)

(d)



(e)



(f)

Fig. S7 — HRMS of the peaks related to (a) **[Ru]**$^{2+}$(m/z = 749.5023), **(b) [Ru]** $^{+}$(m/z = 571.2523), **(c) [Mn + K^{+} + TEOA]**$^{+}$ (m/z = 767.5004), (d) **[Mn + TEOA]**$^{2+}$(m/z = 338.1833), (e) **[Mn + H^{+} + TEOA]**$^{+}$(m/z = 378.1251), (f) **[Mn + 2CO+ TEOA]** $^{2+}$ **(**m/z =307.2044) and **[Mn + 2HCO+ TEOA]**$^{2+}$ (m/z = 360.1143) intermediate measured with the photocatalytic solution (**Mn-tmphen** as catalyst) after 2 h illumination

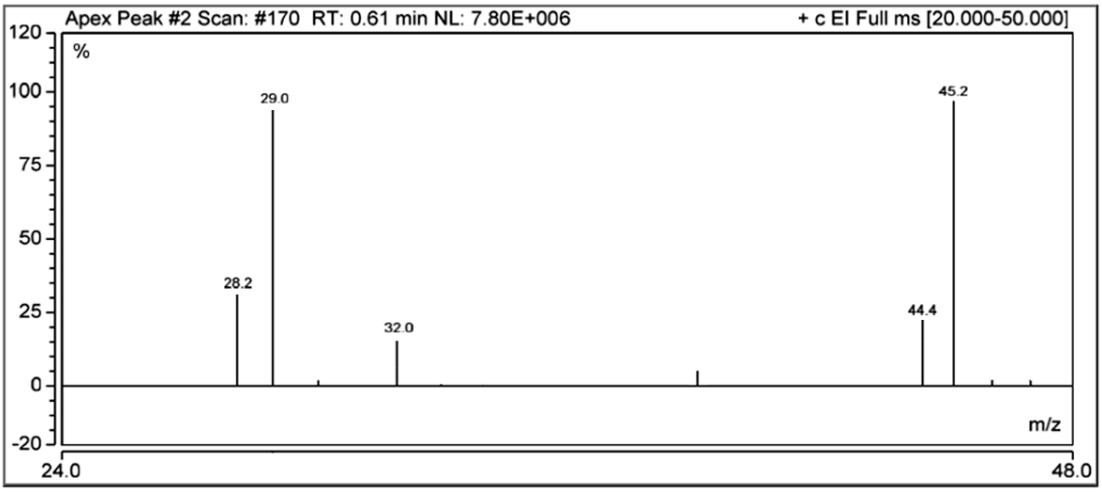
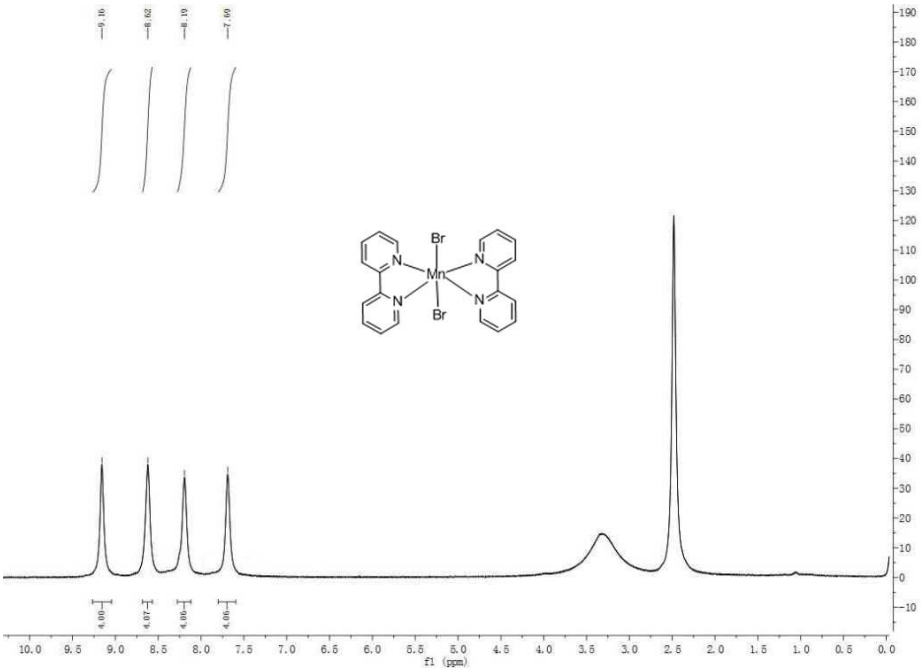
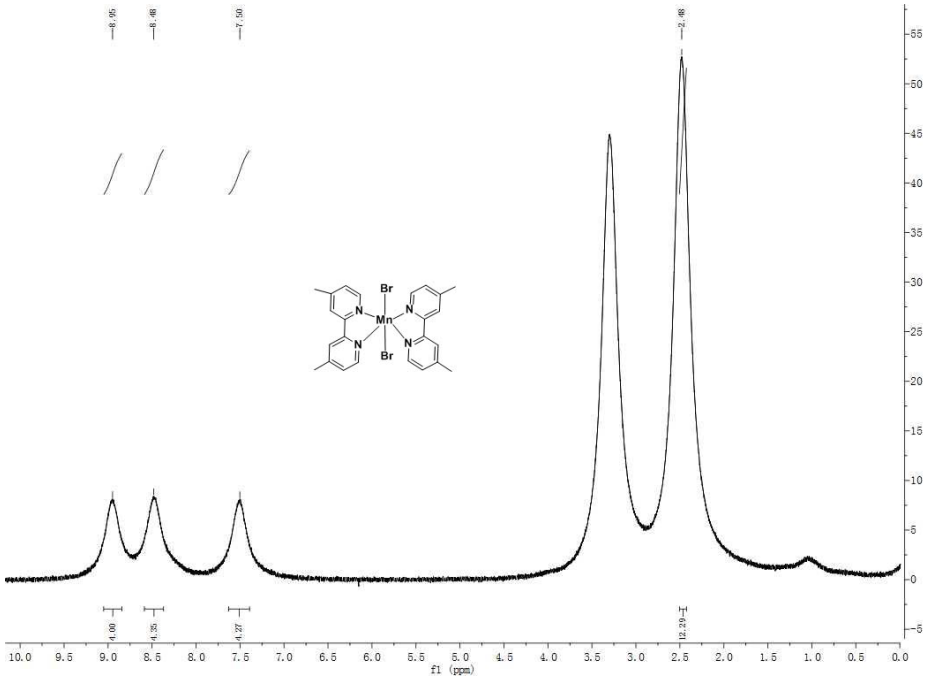


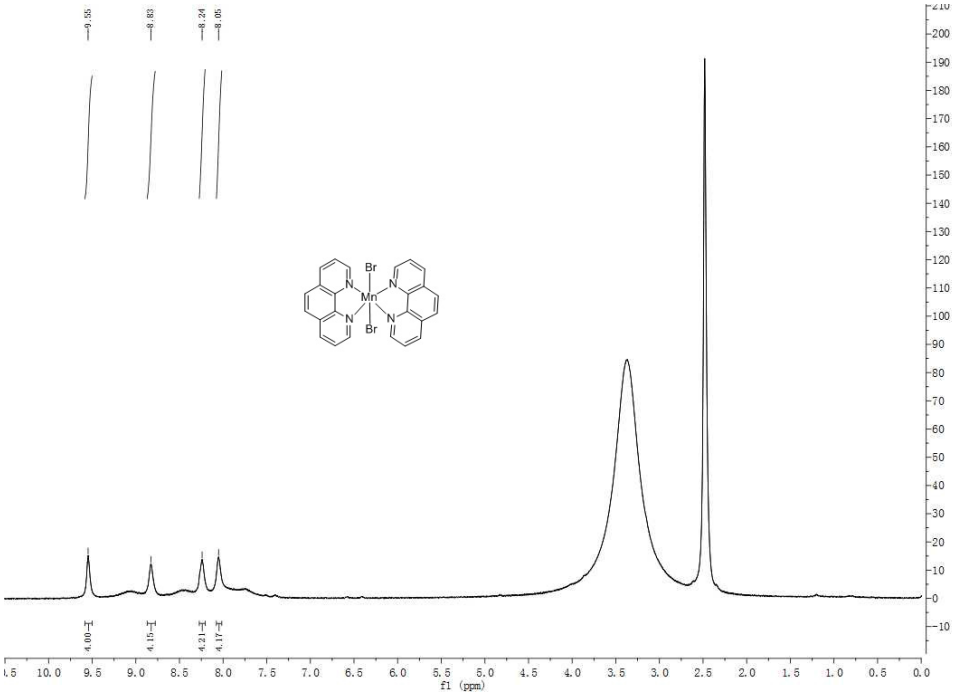
Fig. S8 — GC-MS chromatograms of CO obtained from the photocatalytic CO_2 reduction system, under $^{13}CO_2$ atmosphere with $^{13}CO_2$-saturated CH3CN / TEOA (V / V = 7 / 1) solution and 0.45 mM **[Ru]**, 0.052 M BIH with CO_2 saturation after 12 hours irradiation at 460 nm. The peak in the figure is 29.0, indicating that CO is detected



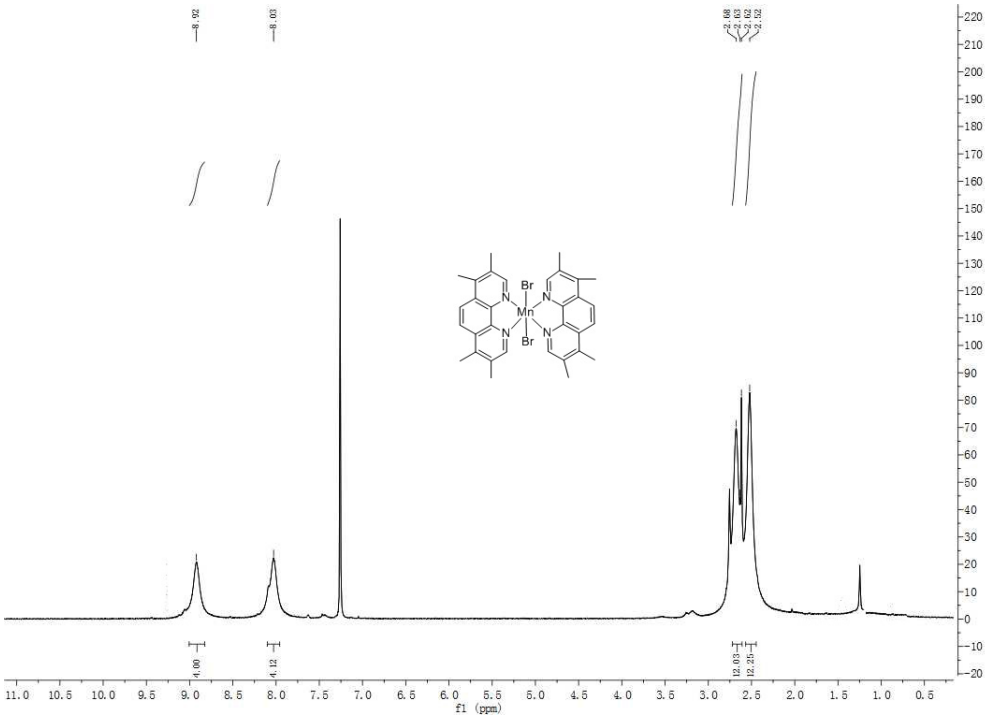
(a)


8.95
8.49
7.50
2.48
Br
Mn
Br
4.00
4.35
4.27
12.29
f1 (ppm)

(b)


9.55
8.83
8.24
8.05
Br
Mn
Br
4.00
4.15
4.21
4.17
f1 (ppm)

(c)



(d)

Fig. S9 — [1]HNMR spectra of (a) **Mn-bpy, (b) Mn-dmbpy,** and (c) **Mn-phen** in DMSO solution and (d) **Mn-tmphen**in $CDCl_3$ solution

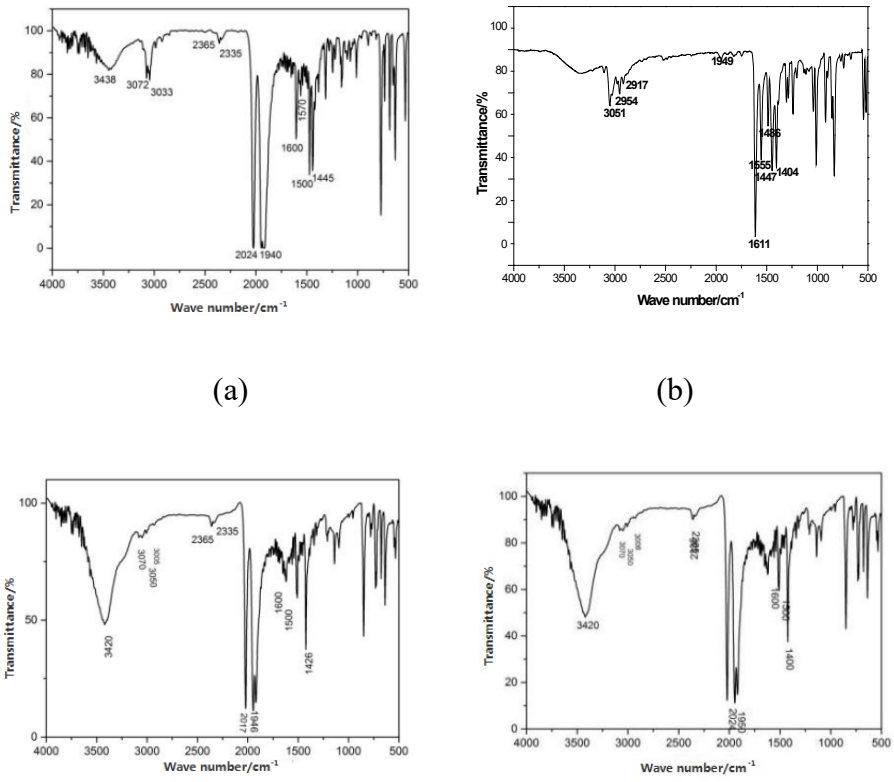
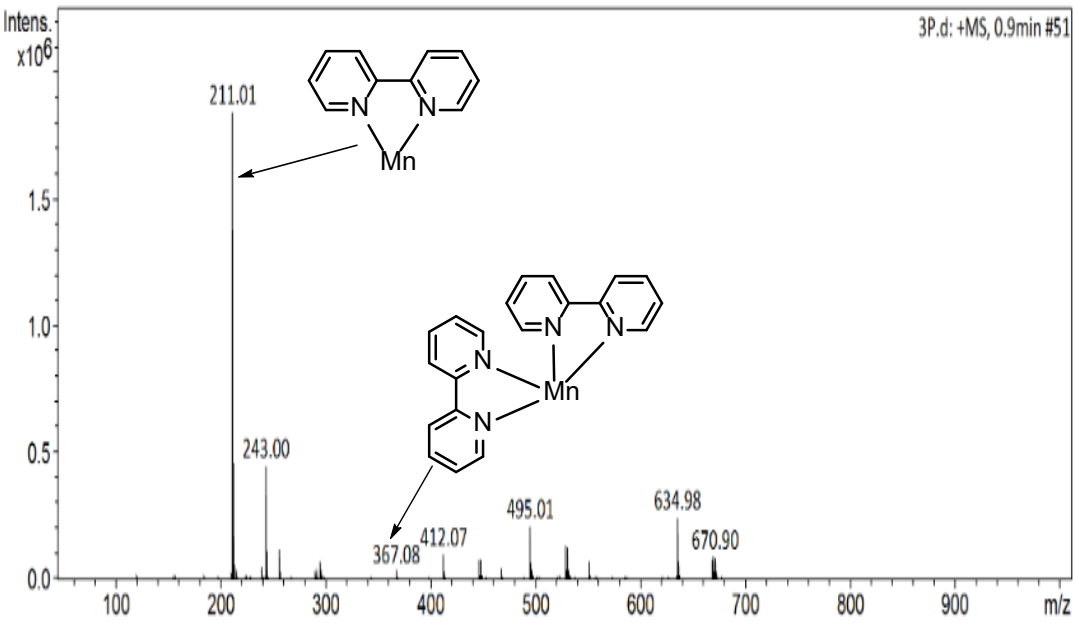
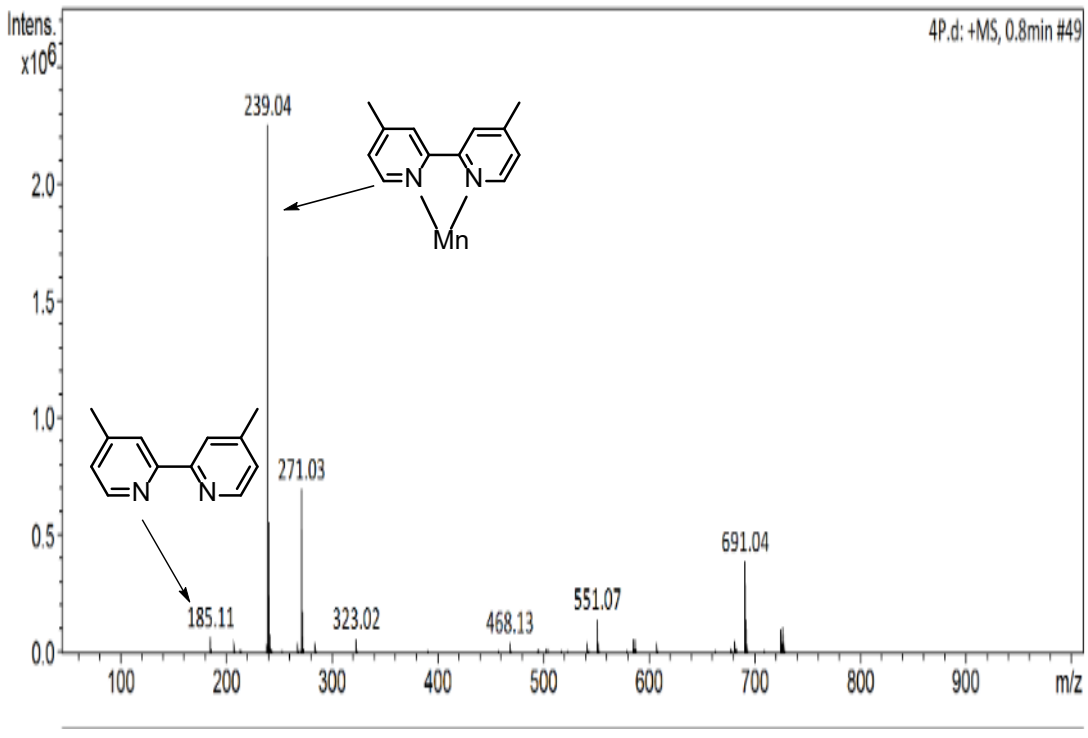


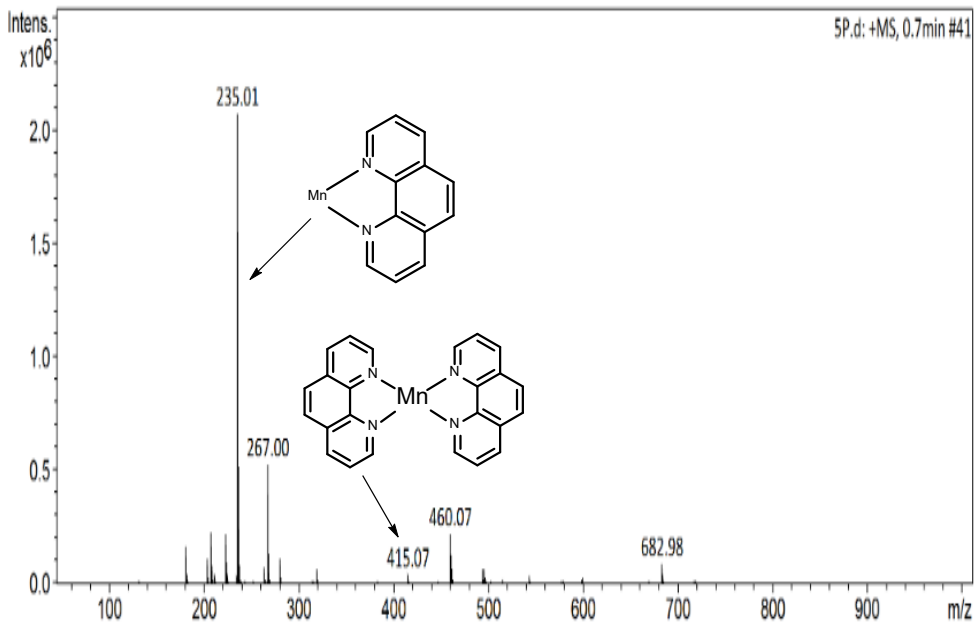
Fig. S10 — FTIR spectra of (a) **Mn-bpy** (b)**Mn-dmbpy**, (c) **Mn-phen** and (d)**Mn-tmphen**


Intens.
x10^6
3P.d: +MS, 0.9min #51
211.01
243.00
367.08
412.07
495.01
634.98
670.90
Mn
m/z

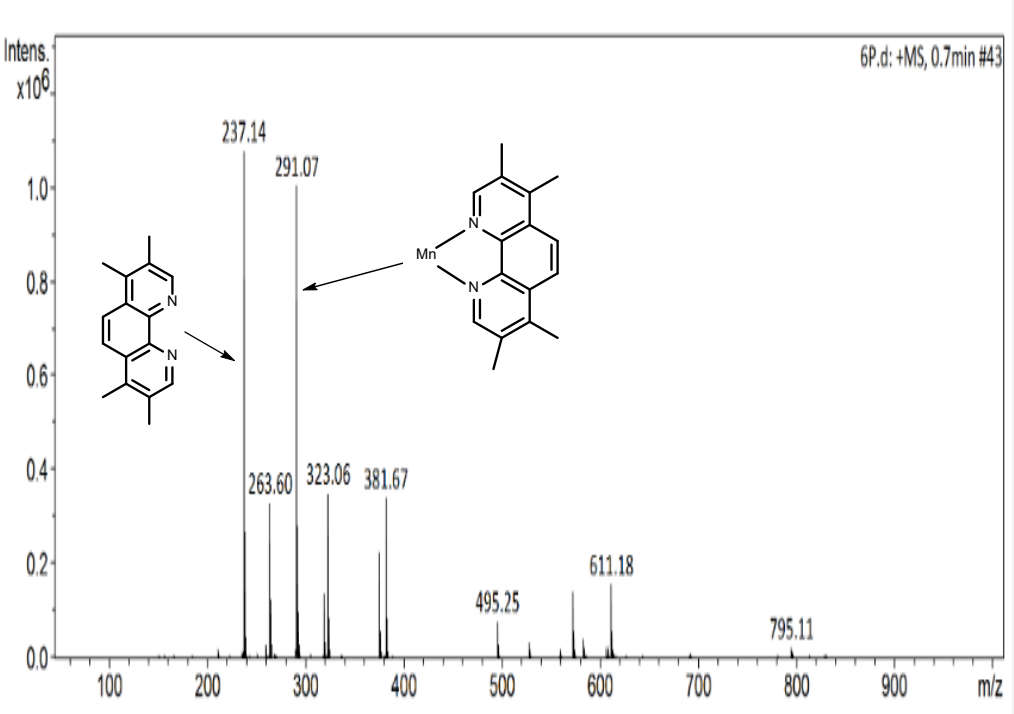
(a)


Intens.
x10^6
4P.d: +MS, 0.8min #49
239.04
271.03
185.11
323.02
468.13
551.07
691.04
Mn
m/z

(b)



(c)



(d)

Fig. S11 — Electrospray ionization mass spectra (ESI-MS) of catalyst (a) **Mn-bpy, (b) Mn-dmbpy, (c) Mn-phen** and (d) **Mn-tmphen**

Reference

1 Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.https://doi.org/10.1107/S0021889808042726

2 Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.https://doi.org/10.1107/S2053273314026370

3 Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.http://dx.doi.org/10.1107/S2053229614024218