Manganese Catalysts with Tetradentate N-donor Pyridine-Appended Bipiperidine Ligands for Olefin Epoxidation Reactions: Ligand Electronic Effect and Mechanism

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1. Characterization of SR-mesoPYBP Ligand

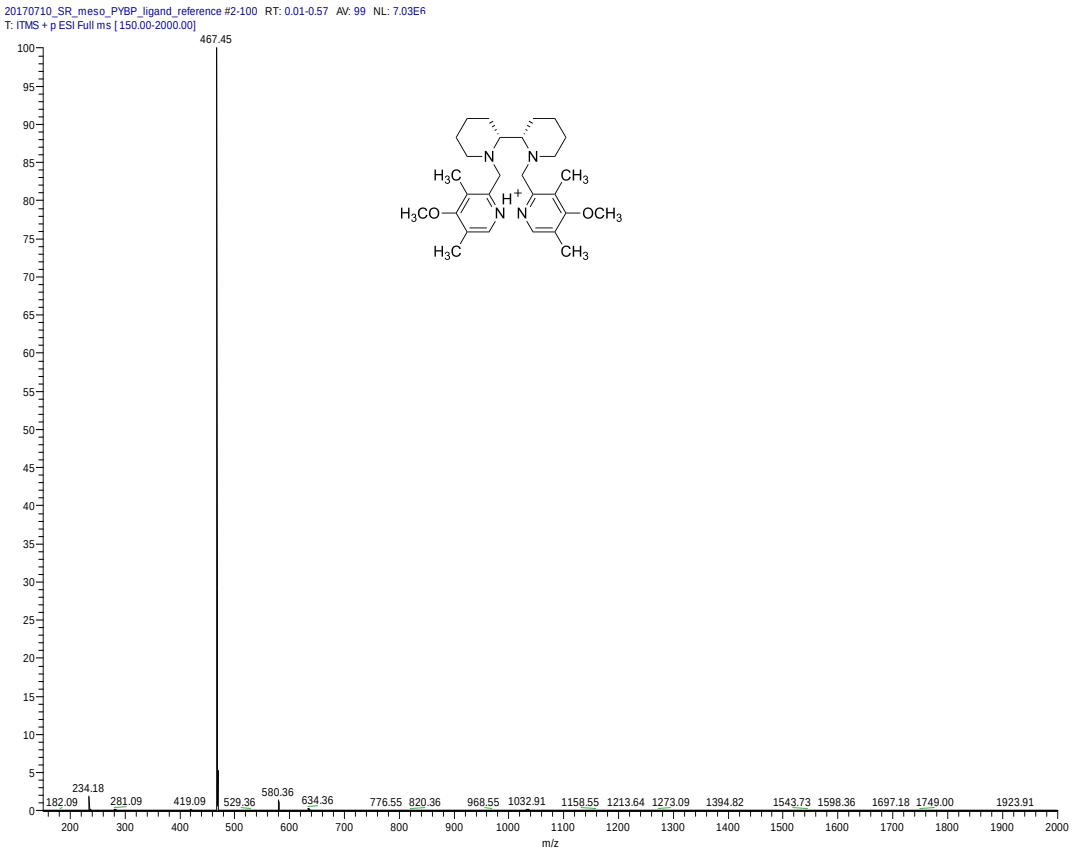

Figure S1. ESI-MS of SR-mesoPYBP ligand

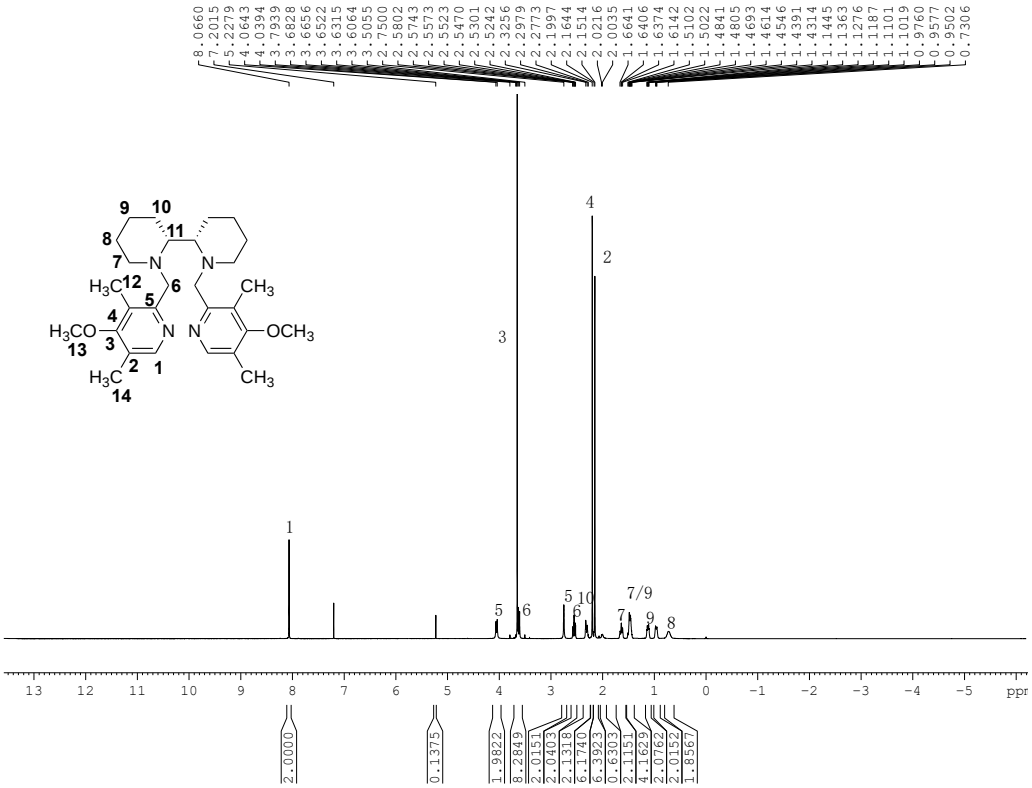

Figure S2. ^{1}H NMR of SR-mesoPYBP ligand

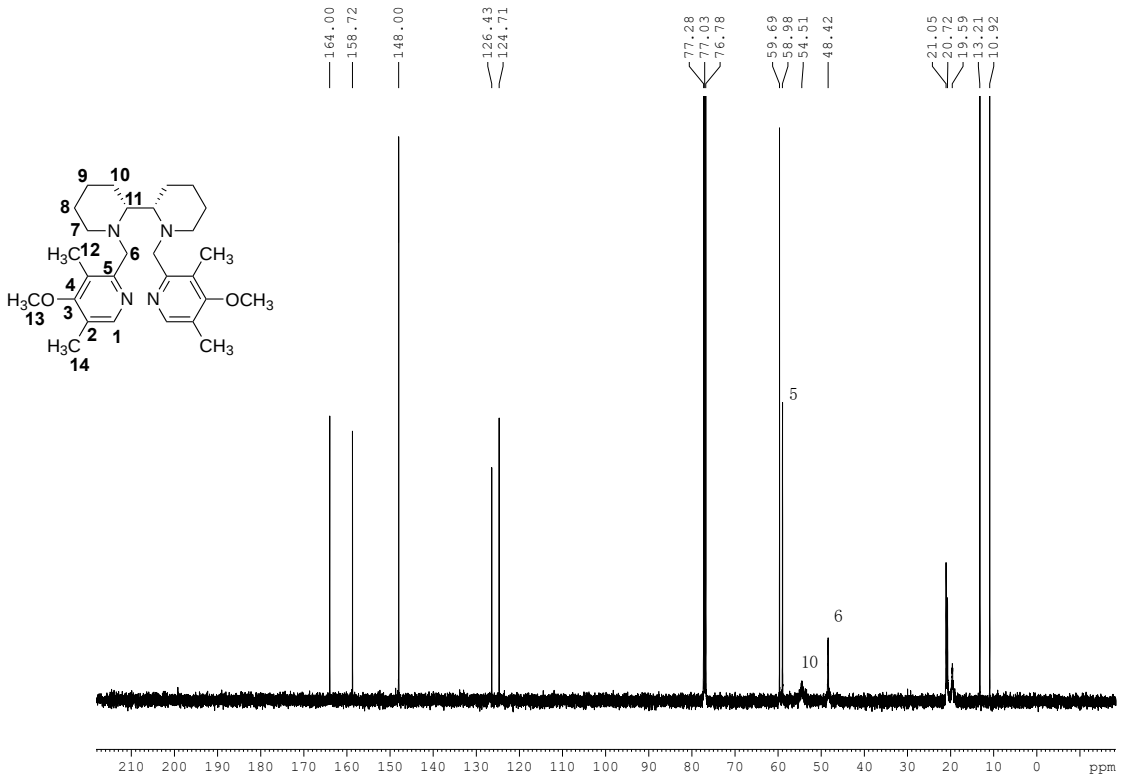

Figure S3. ^{13}C NMR of SR-mes*o*PYBP ligand

2. Characterization of Manganese SR-mesoPYBP Complex

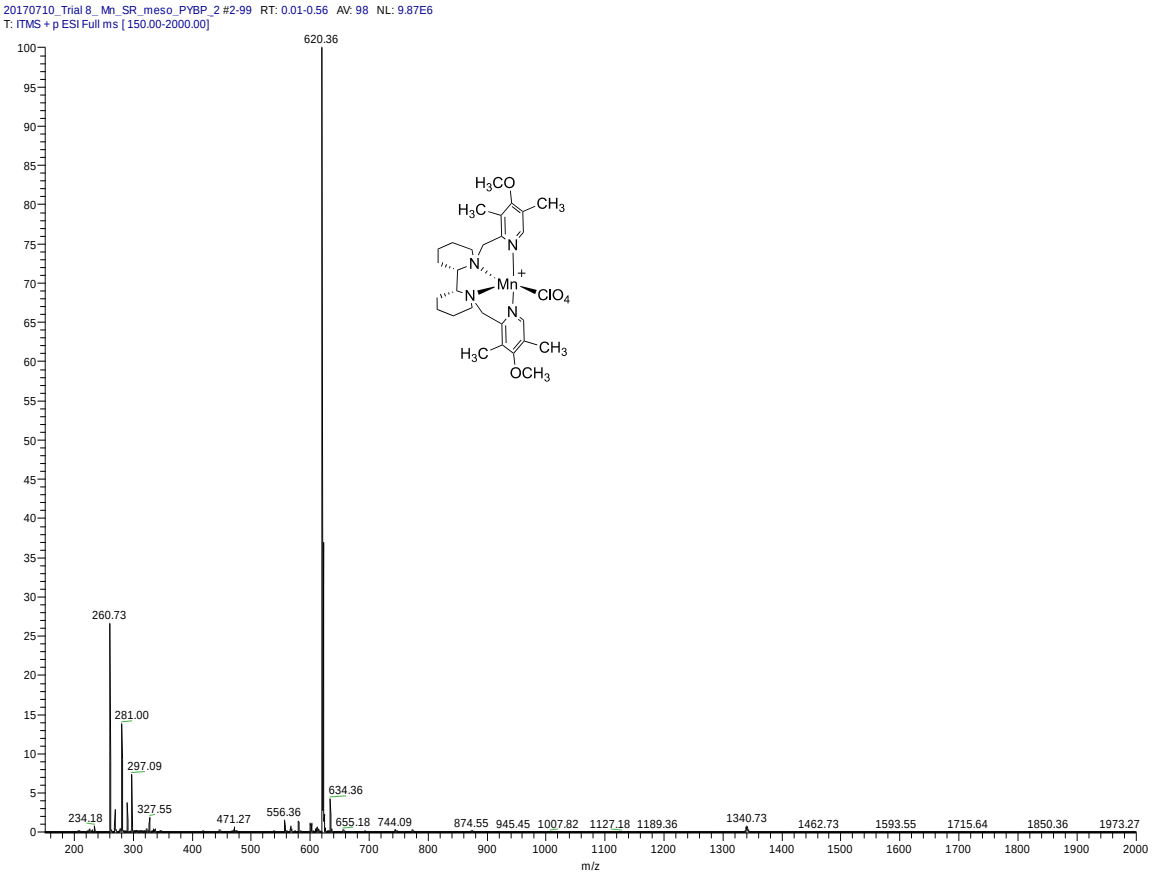

Figure S4. ESI-MS of complex **2**

3. Catalysis

Catalysis studies of Manganese *meso*PYBP(ClO_4)$_2$ **(1)** and Manganese SR-*meso*PYBP(ClO_4)$_2$ **(2)** have been investigated using cyclooctene as substrate. GC calibration and general catalysis procedures were adopted.[2]

Calibration and Method Development for Cyclooctene Epoxide as Olefin

Prepare stock solutions & samples: Separately prepared 1mL 1M solutions of olefin (cyclooctene epoxide, COE), epoxide (cyclooctene oxide, COX) and internal standard (chlorobenzene) as Pre-stock solution. Used the pre-stock solution to prepare stock solution shown in the table below (unit: uL).

Vial #	**1**	**2**	**3**	**4**	**5**	**6**
Olefin	196	160	120	80	40	4
Epoxide	4	40	80	120	160	196
Standard	80	80	80	80	80	80
Acetonitrile	720	720	720	720	720	720

GC-MS Method Development: Injected 5μL of each stock solution into 1mL Et_2O. Label the GC vials accordingly. Ran GC-MS under a developed method setting.

Set 3 runs for each prepared sample. GC peaks for standard, olefin (COE) and epoxide (COX) appeared approximately at 5.5, 6.0, 9.0 min. For data analysis, integrated the chosen peak area under qualitative integration (TIC), copied area% column into qualitative table (TIC). Calculated the average area% ratio of olefin:standard, and epoxide:standard. Generated calibration curve with relative concentration

(olefin:standard and epoxide:standard) as X-axis and relative area% ratio (olefin:standard and epoxide:standard) as Y-axis. Set the trendline as Y= aX+ b (intercept b = 0) with R≥0.99.

General Catalysis Procedure

Cyclooctene epoxide as olefin 1.3224 g (12 mmol) of cyclooctene and 0.5403 g (4.8 mmol) of chlorobenzene (internal standard) were combined and dissolved in acetonitrile to a 3 mL solution. 25 μL of the substrate stock solution contains 100 μmol cyclooctene and 40 μmol chlorobenzene.

At room temperature, 25 μL of an olefin stock solution was injected into 0.5 mL of 1 mM complex **1** or **2** with pipet, followed by the appropriate amount of HOAc as additive. The solution was well mixed and 5 μL was taken to inject into 1 mL of diethyl ether as initial sample. Appropriate amount of H_2O_2 was then injected into solution in 5 portions; a 5 μL solution was injected into 1 mL of ether at 5 or 30 min as final sample. The samples along with initial control samples were quantitatively analyzed by GC-MS. All samples were run at least 3 times, and the arithmetic means were used to report the data.

Entry	H_2O_2 (eq)	HOAc (eq)	Time (min)	Cat.	Yield (%)[c]	TON
1	500	2000	5	**1**	0	0
				2	75	248
2	500	2000	30	**1**	0	0
				2	76	250
3	300	2000	5	**1**	0	0
				2	62	220
4	300	5000	5	**1**	0	0
				2	59	213
5	300	5000	30	**1**	0	0
				2	58	211
6	400	2000	5	**1**	0	0
				2	67	246
7	400	2000	30	**1**	0	0
				2	66	246

Table S1. Complex **1** or **2** catalyzed olefin epoxidation reaction

[a]Reaction conditions: Catalyst (0.5 μmol), cyclooctene (100 μmol), chlorobenzene internal standard (40 μmol), H_2O_2 (30% aqueous solution), HOAc (glacial) in 0.5 mL of acetonitrile, room temperature. [b]H_2O_2 were added in equal five portions in the first 4 mins. [c]GC yield.

4. Limiting reagent test

For entry 1-7, 200 equiv. olefin stock solution was injected into 0.5 mL of 1 mM complex **2** with pipet, followed by 2000 equiv. HOAc as additive. The solution was well mixed and 5 μL was taken to inject into 1 mL of diethyl ether as initial sample. 500 equiv. H_2O_2 was then injected into solution in 5 portions. A 5 μL reaction solution was injected into 1 mL of ether at 30 mins as final sample 1. Then, different reagents (COE, H_2O_2, HOAc, fresh catalyst, manganese salts) were added in the solution accordingly as limiting reagent to resume the expoxidation reaction. After 30 mins, 5 μL of solution was taken from the reaction and injected into 1 mL of ether as final sample 2. Those samples along with initial control samples were quantitatively analyzed by GC-MS. All samples were run at least 3 times, and the arithmetic means were used to report the data. For entry 8 and 9, 0.5 mL of 1 mM complex **1** or manganese (II) salts were added in the reaction instead of complex **2**.

Entry	Cat.	Cat. loading	COE (eq)	H_2O_2 (eq)	HOAc (eq)	Time (min)	Yield %	TON
1	SR-meso	0.50%	200	500	2000	0-30	47	91
			200			30-60	54	104
2	SR-meso	0.50%	200	500	2000	0-30	47	89

				500		30-60	55	103
3	SR-meso	0.50%	200	500	2000	0-30	46	86
			200	500		30-60	53	100
4	SR-meso	0.50%	200	500	2000	0-30	43	80
		0.50%				30-60	66	124
5	SR-meso	0.50%	200	500	2000	0-30	44	85
		0.50%		500		30-60	77	150
6	SR-meso	0.50%	200	500	2000	0-30	26	38
	$Mn(ClO_4)_2$	0.50%				30-60	31	45
7	SR-meso	0.50%	200	500	2000	0-30	26	38
	$Mn(ClO_4)_2$	0.50%		500		30-60	28	42
8	meso	0.50%	200	500	2000	0-30	1	2
						30-60	1	3
9	$Mn(ClO_4)_2$	0.50%	200	500	2000	0-30	0	0
		0.50%				30-60	0	0

Table S2. Limiting reagent test

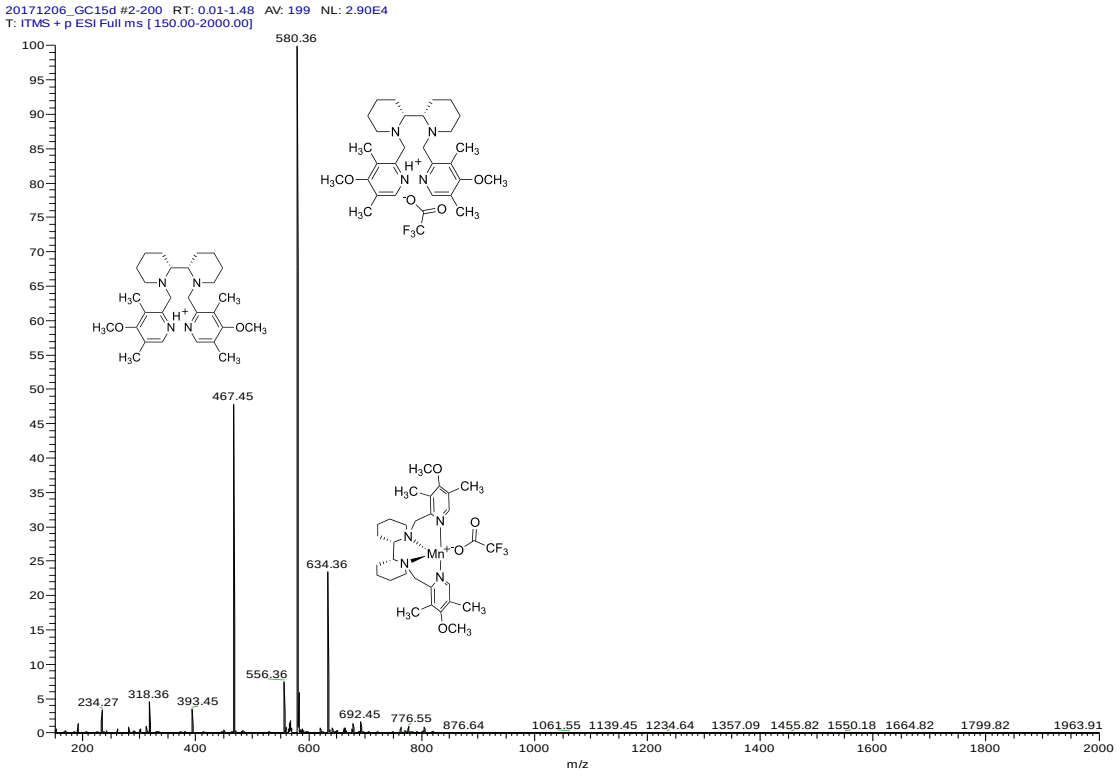

Figure S5. ESI-MS of Entry 1 solution after 60 min reaction time

5. Cyclic Voltammetry study

Cyclic votamintary was utilized to detect the redox reversibility of the manganese catalysts. The experiments were performed under argon protection in the glove box by using glassy carbon as working electrode and platinum wires as counter and reference electrode. The cell was filled by 0.1 mM Ferrocene,

0.1 M Tetra-n-butylammonium hexafluorophosphate, 2.8 mM Tetra- n-butylammonium chloride and 1 mM Mn-SR-*meso*PYBP(ClO_4)$_2$ or Mn-SR-*meso*PYBP(ClO_4)$_2$. 0.1 mV/s scan rates were used.

6. EPR Study

1 mM of complex **1** or **2** solution in dry acetonitrile were prepared in the glove box. 20 eq H_2O_2 and HOAc were prepared, as mixed solution. With stirring, the solutions were combined, and transferred to EPR tubes. Each EPR tube with reaction mixture was quenched in liquid nitrogen at a predefined time (6 min, 30 min, 1 day or more than 1 day), and EPR spectra were acquired at 120 K.

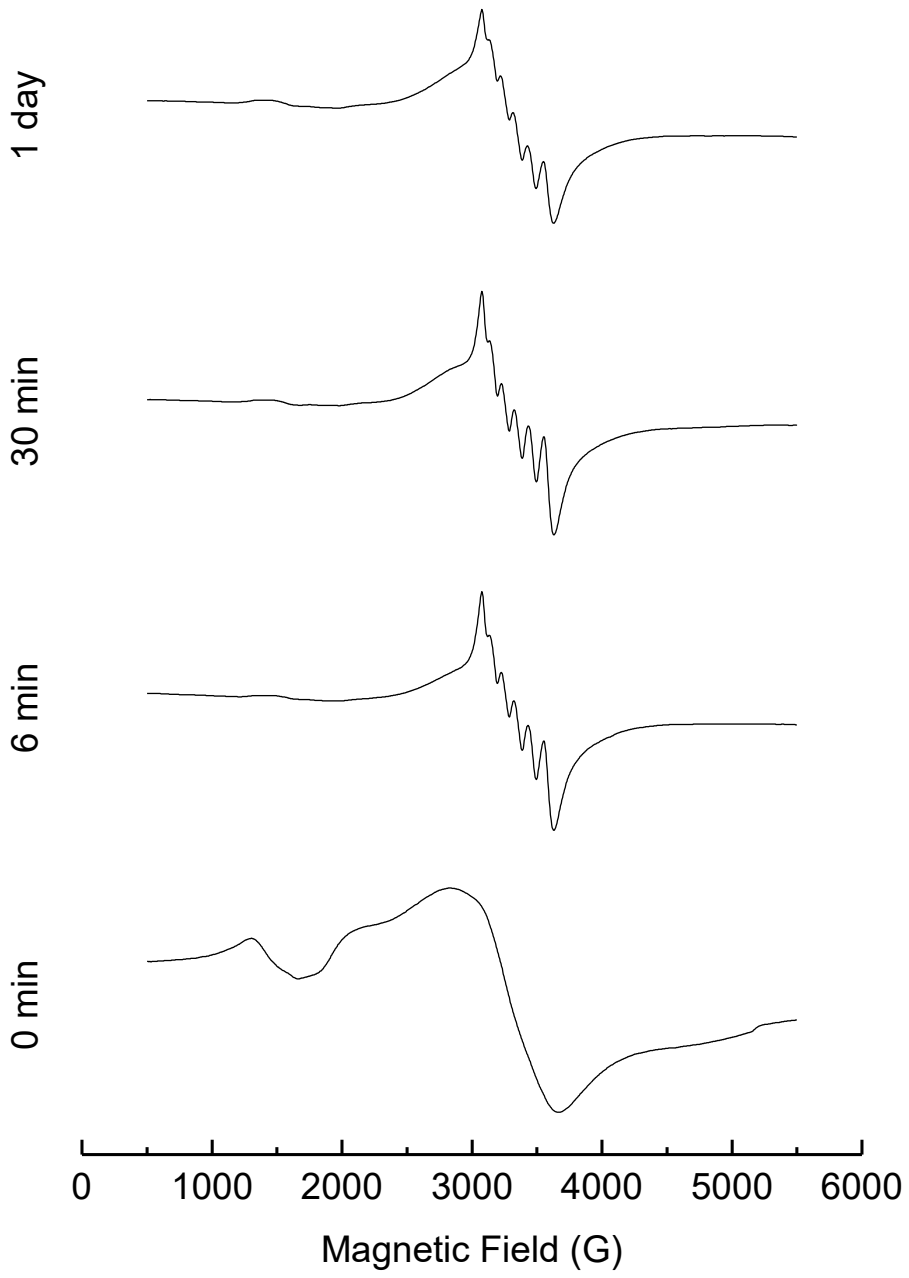

Figure S6. EPR spectrum for complex **1** at 120K at 6 min, 30 min, 1 day or more than 1 day

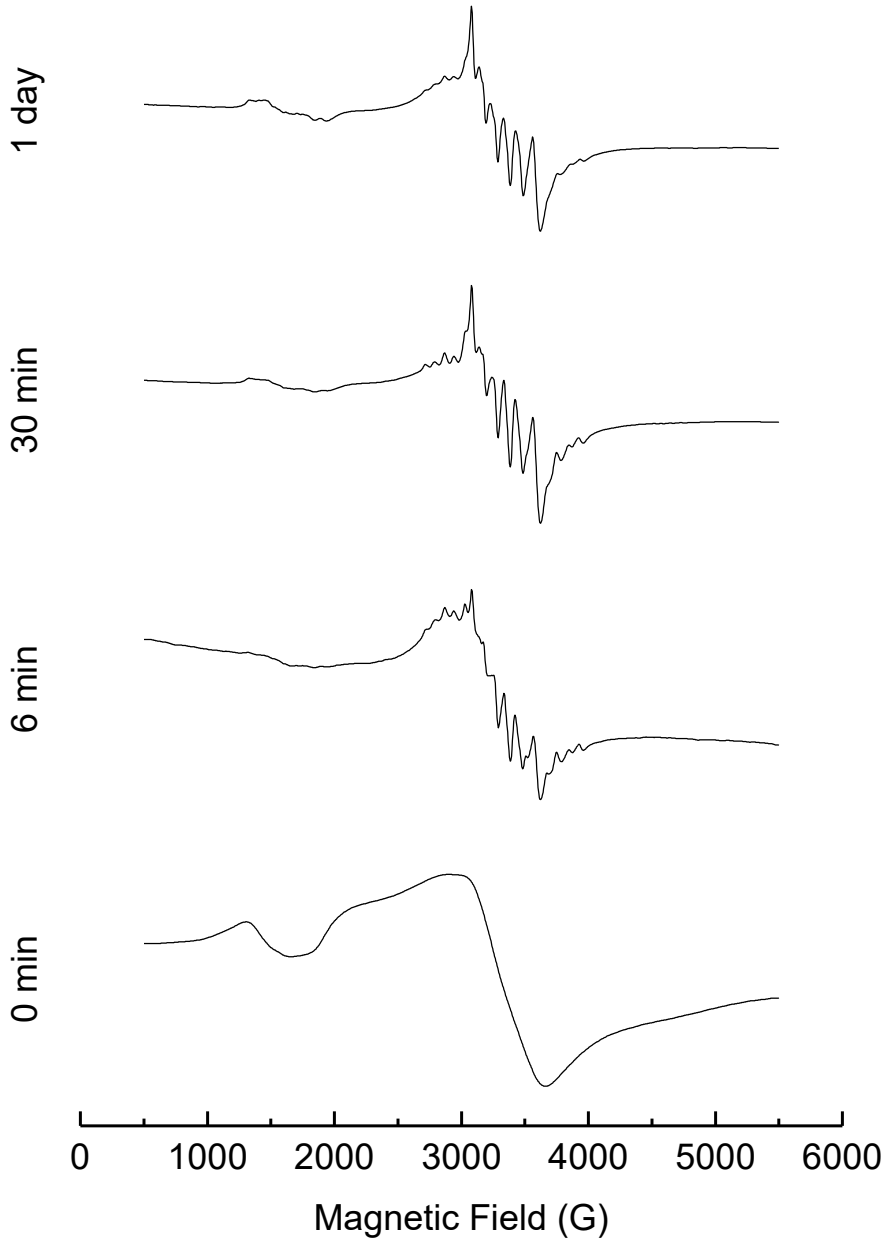

Figure S7. EPR spectrum for complex **2** at 120K at 6 min, 30 min, 1 day or more than 1 day

7. X-ray Crystallography Data

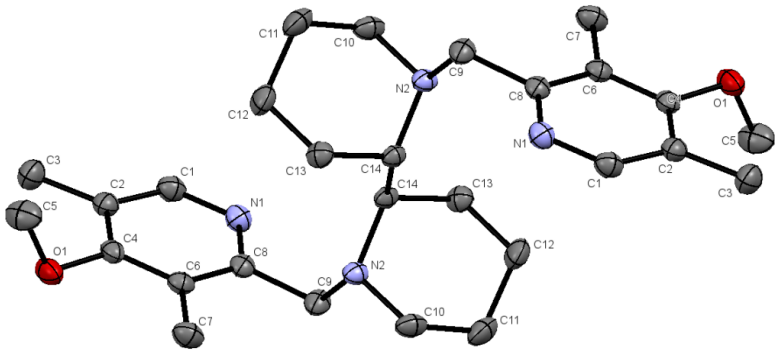

Figure S8. ORTEP diagram of SR-mesoPYBP ligand [2]

Crystal Data

$C_{14}H_{21}N_2O$	F(000) = 508.1984
M_r = 233.34	D_x = 1.228 Mg·m^{-3}
Monoclinic $P2_1/_c$	Mo Kα radiation, λ = 0.71073 Å
a = 9.407 (2) Å	Cell parameters from 6925 reflections
b = 15.950 (4) Å	θ = 2.7–31.5 °
c = 8.849 (2) Å	μ = 0.08 mm^{-1}
β = 108.033 (5)°	T=105K
V = 1262.4 (6) Å	Prism clear colourless
Z = 4	0.22 ×0.18 ×0.16 mm

Data Collection

Bruker D8-QUEST diffractometer	4232 independent reflections
Radiation source: sealed tube	2948 reflections with I > 2σ(I)
Graphite monochromator	R_{int} = 0.056
φ and ω scans	θ_{max} = 31.6 ° θ_{min} = 2.7 °
Absorption correction: multi-scan	h = −13→13
T_{min} = 0.704, T_{max} = 0.746	k = −23→23
27771 measured reflections	l = −13→13

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct method
Least-squares matrix: full	H atom site location: mixed
R[$F^2 > 2\sigma(F^2)$] = 0.070	H-atom treated by a mixture of independent and constrained refinement
wR(F^2) = 0.210	w = 1/[σ2(F_o^2) + (0.1P)^2]
S = 1.37	where P = (F_o^2 + 2F_c^2)/3
4232 reflections	$(\Delta/\sigma)_{max}$ =13.601 –3
157 parameters	$\Delta\rho_{max}$ = 0.67e Å
0 restraints	$\Delta\rho_{min}$ = −0.47 e Å^{-3}
31 constraints	Absolute structure parameters: -0.2 (4)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
O1	0.47080 (14)	0.78716 (7)	0.54158 (13)	0.0302 (3)
N1	0.55213 (14)	1.00843 (9)	0.79906 (16)	0.0239 (3)
N2	0.90464 (13)	1.02213 (8)	0.78306 (15)	0.0203 (3)
C1	0.44127 (18)	0.95669 (11)	0.80345 (19)	0.0253 (3)
H1	0.38193 (18)	0.97229 (11)	0.86841 (19)	0.0303 (4)*
C2	0.40708 (17)	0.88212 (10)	0.72003 (18)	0.0234 (3)
C3	0.27196 (19)	0.83161 (12)	0.7191 (2)	0.0320 (4)
H3a	0.3006 (4)	0.77276 (19)	0.7417 (16)	0.0479 (6)*
H3b	0.2309 (9)	0.8532 (5)	0.8006 (11)	0.0479 (6)*
H3c	0.1963 (6)	0.8359 (7)	0.6146 (5)	0.0479 (6)*
C4	0.50049 (17)	0.85919 (10)	0.63161 (17)	0.0214 (3)
C5	0.5175 (2)	0.71213 (11)	0.6307 (2)	0.0364 (4)
H5a	0.4825 (13)	0.66354 (12)	0.5641 (6)	0.0546 (7)*
H5b	0.4752 (13)	0.7086 (4)	0.6650 (14)	0.0546 (7)*
H5c	0.6269 (2)	0.7126 (4)	0.7241 (9)	0.0546 (7)*
C6	0.61834 (17)	0.91028 (10)	0.62484 (17)	0.0210 (3)
C7	0.71751 (19)	0.88639 (11)	0.52693 (19)	0.0285 (4)
H7a	0.7036 (11)	0.8268 (2)	0.4989 (13)	0.0427 (6)*
H7b	0.6913 (10)	0.9202 (6)	0.4297 (7)	0.0427 (6)*
H7c	0.8222 (2)	0.8966 (8)	0.5885 (6)	0.0427 (6)*
C8	0.63647 (16)	0.98625 (10)	0.70822 (17)	0.0205 (3)
C9	0.75199 (17)	1.04926 (10)	0.69634 (19)	0.0245 (3)
H9a	0.73191 (17)	1.10363 (10)	0.73975 (19)	0.0294 (4)*
H9b	0.74355 (17)	1.05780 (10)	0.58307 (19)	0.0294 (4)*
C10	1.01656 (18)	1.06282 (11)	0.72439 (19)	0.0262 (4)
H10a	1.11222 (18)	1.03208 (11)	0.76579 (19)	0.0315 (4)*
H10b	0.98424 (18)	1.05853 (11)	0.60703 (19)	0.0315 (4)*
C11	1.0436 (2)	1.15503 (11)	0.7709 (2)	0.0316 (4)
H11a	1.1238 (2)	1.17776 (11)	0.7320 (2)	0.0380 (5)*
H11b	0.9513 (2)	1.18776 (11)	0.7220 (2)	0.0380 (5)*
C12	1.0888 (2)	1.16253 (11)	0.9512 (2)	0.0312 (4)
H12a	1.1867 (2)	1.13483 (11)	0.9992 (2)	0.0374 (5)*
H12b	1.0995 (2)	1.22243 (11)	0.9820 (2)	0.0374 (5)*
C13	0.97122 (18)	1.12164 (10)	1.01353 (19)	0.0234 (3)
H13a	1.00676 (18)	1.12265 (10)	1.13116 (19)	0.0281 (4)*
H13b	0.87782 (18)	1.15482 (10)	0.97764 (19)	0.0281 (4)*
C14	0.93732 (15)	1.03075 (9)	0.95707 (17)	0.0179 (3)
H14	0.84530 (15)	1.01336 (9)	0.98279 (17)	0.0215 (4)*

Atomic displacement parameters (Å2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0430 (7)	0.0221 (6)	0.0211 (6)	−0.0023 (5)	0.0036 (5)	−0.0025 (4)
N1	0.0219 (6)	0.0245 (7)	0.0238 (7)	0.0016 (5)	0.0050 (5)	−0.0009 (5)
N2	0.0168 (6)	0.0244 (7)	0.0186 (6)	0.0013 (5)	0.0039 (5)	0.0047 (5)
C1	0.0236 (7)	0.0300 (9)	0.0226 (7)	0.0016 (6)	0.0077 (6)	0.0005 (6)

C2	0.0224 (7)	0.0268 (8)	0.0192 (7)	−0.0010 (6)	0.0040 (6)	0.0029 (6)
C3	0.0292 (9)	0.0341 (10)	0.0329 (9)	−0.0069 (7)	0.0102 (7)	0.0028 (7)
C4	0.0250 (8)	0.0194 (7)	0.0166 (7)	−0.0002 (6)	0.0014 (6)	0.0009 (5)
C5	0.0491 (11)	0.0270 (9)	0.0325 (9)	0.0098 (8)	0.0119 (8)	0.0031 (7)
C6	0.0199 (7)	0.0243 (8)	0.0170 (7)	0.0028 (6)	0.0032 (5)	0.0019 (5)
C7	0.0291 (8)	0.0353 (9)	0.0225 (8)	0.0024 (7)	0.0101 (6)	−0.0018 (7)
C8	0.0173 (7)	0.0222 (7)	0.0193 (7)	0.0020 (5)	0.0016 (5)	0.0037 (5)
C9	0.0201 (7)	0.0247 (8)	0.0254 (8)	0.0004 (6)	0.0021 (6)	0.0070 (6)
C10	0.0228 (8)	0.0354 (9)	0.0228 (8)	0.0025 (6)	0.0105 (6)	0.0065 (7)
C11	0.0292 (9)	0.0314 (9)	0.0373 (9)	−0.0042 (7)	0.0146 (7)	0.0106 (7)
C12	0.0337 (9)	0.0224 (8)	0.0372 (9)	−0.0084 (7)	0.0104 (7)	0.0030 (7)
C13	0.0264 (8)	0.0197 (7)	0.0246 (7)	0.0024 (6)	0.0086 (6)	0.0012 (6)
C14	0.0153 (6)	0.0206 (7)	0.0188 (7)	0.0005 (5)	0.0066 (5)	0.0036 (5)

Geometric parameters (Å,°)

O1—C4	1.3765 (19)	C7—H7a	0.9800
O1—C5	1.426 (2)	C7—H7b	0.9800
N1—C1	1.340 (2)	C7—H7c	0.9800
N1—C8	1.3400 (19)	C8—C9	1.508 (2)
N2—C9	1.4683 (19)	C9—H9a	0.9900
N2—C10	1.462 (2)	C9—H9b	0.9900
N2—C14	1.480 (2)	C10—H10a	0.9900
C1—H1	0.9500	C10—H10b	0.9900
C1—C2	1.384 (2)	C10—C11	1.527 (2)
C2—C3	1.503 (2)	C11—H11a	0.9900
C2—C4	1.394 (2)	C11—H11b	0.9900
C3—H3a	0.9800	C11—C12	1.523 (3)
C3—H3b	0.9800	C12—H12a	0.9900
C3—H3c	0.9800	C12—H12b	0.9900
C4—C6	1.392 (2)	C12—C13	1.527 (2)
C5—H5a	0.9800	C13—H13a	0.9900
C5—H5b	0.9800	C13—H13b	0.9900
C5—H5c	0.9800	C13—C14	1.534 (2)
C6—C7	1.506 (2)	C14—C14	1.541 (3)
C6—C8	1.401 (2)	C14—H14	1.0000
C5—O1—C4	114.08 (12)	C9—C8—C6	120.84 (14)
C8—N1—C1	117.74 (14)	C8—C9—N2	112.11 (12)
C10—N2—C9	112.26 (12)	H9a—C9—N2	109.19 (9)
C14—N2—C9	111.77 (12)	H9a—C9—C8	109.19 (9)
C14—N2—C10	112.80 (12)	H9b—C9—N2	109.19 (8)
H1—C1—N1	117.69 (9)	H9a—C9—C8	109.19 (8)
C2—C1—N1	124.62 (15)	H9b—C9—H9a	107.9
C2—C1—H1	117.69 (9)	H10a—C10—N2	108.71 (8)
C3—C2—C1	121.32 (15)	H10b—C10—N2	108.71 (8)
C4—C2—C1	116.23 (14)	H10a—C10—H10b	107.6
C4—C2—C3	122.37 (15)	C11—C10—N2	114.18 (13)
H3c—C3—C2	109.5	C11—C10—H10b	108.71 (9)
H3b—C3—H3a	109.5	C11—C10—H10a	108.71 (9)
H3a—C3—H3c	109.5	H11a—C11—C10	109.86 (9)
H3b—C3—C2	109.5	H11b—C11—C10	109.86 (9)
H3b—C3—H3c	109.5	H11a—C11—H11b	108.3

H3a—C3—C2	109.5	C12—C11—C10	109.11 (13)
C2—C4—O1	119.57 (14)	C12—C11—H11a	109.86 (9)
C6—C4—O1	119.03 (14)	C12—C11—H11b	109.86 (10)
C6—C4—C2	121.28 (14)	H12a—C12—C11	109.61 (10)
H5b—C5—O1	109.5	H12b—C12—C11	109.61 (9)
H5c—C5—O1	109.5	H12b—C12—H12a	108.1
H5c—C5—H5b	109.5	C13—C12—C11	110.23 (14)
H5a—C5—O1	109.5	C13—C12—H12a	109.61 (9)
H5a—C5—H5b	109.5	C13—C12—H12b	109.61 (9)
H5a—C5—H5c	109.5	H13a—C13—C12	109.04 (9)
C7—C6—C4	121.35 (14)	H13b—C13—C12	109.04 (9)
C8—C6—C4	116.89 (14)	H13a—C13—H13b	107.8
C8—C6—C7	121.72 (14)	C14—C13—C12	112.75 (13)
H7a—C7—C6	109.5	C14—C13—H13a	109.04 (8)
H7b—C7—C6	109.5	C14—C13—H13b	109.04 (8)
H7b—C7—H7a	109.5	C13—C14—N2	112.45 (12)
H7c—C7—C6	109.5	C14—C14—N2	109.54 (14)
H7c—C7—H7a	109.5	C14—C14—C13	113.00 (15)
H7c—C7—H7b	109.5	H14—C14—N2	107.17 (7)
C6—C8—N1	123.09 (14)	H14—C14—C13	107.17 (8)
C9—C8—N1	116.05 (14)		

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2 G. Yang, PhD thesis, Tufts University, 2017.