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Synergetic oxidation of ethylbenzene to acetophenone catalyzed by manganese(II) complexes bearing pendant iodophenyl groups

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**Abstract:** Five tetradentate ligands,  $L_{1-5}$ , bearing the moiety of bis(pyridin-2-ylmethyl)amine (1) and their complexes with Mn(II) were prepared. All the compounds and metal complexes were appropriately characterized. The five manganese(II) complexes (3a-e) are of the formula,  $[Mn(II)L_xCl_2]$  (x = 1-5), as suggested by the crystal structure of complexes 3b and 3c. All the ligands except for  $L_3$  possess two iodobenzene groups *via* an ether linkage (except for  $L_1$ ) with various lengths. By using oxone as an oxidant, the catalytic activity of these complexes on the oxidation of ethylbenzene to acetophenone in acetonitrile / water at room temperature was studied. Our results showed that the pendant iodophenyl groups play a synergetic role with the metal center in the catalysis, and complex 3b possesses the most appropriate length of the linkage between the iodobenzene group and the metal center. EPR and FTIR data suggest that the metal center of the active species should be Mn(IV) after the oxidation of oxone under the reaction conditions. A catalytic mechanism was also proposed based on the experimental observations.

Keywords: Manganese complex • iodophenyl • oxone • ethylbenzene • acetophenone

# Introduction

Alkane oxidation is one of the most fundamental and important transformations in synthetic chemistry. Of the various alkane oxidation, the direct benzylic oxidation of alkylarenes into the corresponding carbonyl compounds has attracted considerable attention since the carbonyls could be key intermediates for the preparation of pharmaceuticals and agrochemicals [1-3]. However, the direct oxidation of a saturated sp<sup>3</sup> C-H bond under mild conditions poses a great challenge to organic chemists due to its notorious inactivity [4, 5]. Traditionally, benzylic oxidation often required the use of heavy metals oxidants in stoichiometric amounts, such as cerium triflate, potassium permanganate or potassium dichromate, which often leads to the formation of a lot of byproducts and the residual waste from the oxidants [6]. Recently, great progress has been made to improve the transformation [7-21]. Metal-based catalysts involving CrMCM-41, Mn(III), Co(OAc)<sub>2</sub>, Bi(0), RuCl<sub>3</sub>, RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>, Rh<sub>2</sub>(cap)<sub>4</sub>, FeCl<sub>3</sub> and Au have been reported [7-15]. Transition-metal-free oxidants, such as N-Hydroxyphthalimide (NHPI), 2-iodoxybenzoic acid (IBX), NaClO / TBHP, [PhIO]<sub>n</sub> / KBr and iodine-pyridine-tert-butylhydroperoxide (I<sub>2</sub>-Py-TBHP), avoided the involvement of heavy metals and were also employed in the transformation [16-21]. Despite the progress, employment of toxic and/or precious metal, harsh conditions are still involved in most of these systems. Therefore, direct benzylic oxidation of alkylarenes under mild and environmentally benign conditions with both economic and atomic efficiently remains highly desirable.

Hypervalent iodine compounds are a category of oxidants with availability, environmentally friendliness, mild reactivity, high stability and easy handling [22-33]. PhIO<sub>2</sub>, derived from PhI oxidation by oxone [34-37], is one of the common hypervalent iodine oxidants. Due to the distinct feature of PhIO<sub>2</sub> oxidant, it plays an important role in the oxidation of hydrocarbons and has received considerate attention in the past decades [38]. It is believed that the synergetic interaction of transition metal complexes with PhIO<sub>2</sub> could greatly improve its oxidizing capability due to the catalytic role of the metal complex. Indeed, immobilizing both hypervalent iodine and

RuCl<sub>3</sub> onto the surface of solid silica gel particles did improve the catalytic efficiency for ethylbenzene oxidation [39]. The improvement in catalysis was believed to be attributed to that both PhIO<sub>2</sub> and the metal center were brought into such a proximity by fixing them onto the surface of silica gel that they could act concertedly. However, the proximity created in this manner between the metal center and the hypervalent iodine could not appropriately be controlled and was arbitrary. If both the oxidant and the metal center are incorporated into a molecule, the proximity could be tuned well by molecular design and hence the catalytic efficiency could be well controlled.

To this end, we attempted to design a serial of multi-dentate ligands bearing iodobenzene motif to achieve this controlled regulation, in which the iodobenzene group is expected to be oxidized into PhIO<sub>2</sub> motif in situ. It is hoped that a synergetic interaction between the hypervalent iodine and the metal center could be achieved in oxidation. Herein, we report the synthesis and characterization of four tetradentate ligands bearing iodobenzene moiety with various proximity (L1-2, L4-5) and their complexes with Mn(II) (3a-b, 3d-e). For comparison, ligand  $L_3$  which bears no iodo groups and is analogous to  $L_2$  and its manganese complex (3c) were also synthesized. Of the five complexes, **3b** and **3c** were crystallographically analyzed. The catalysis of these complexes on the oxidation of ethylbenzene was assessed by using oxone as an oxidant. Our results demonstrated that the integration of the hyperiodine derived from the in-situ oxidation of iodobenzene and the metal center improved significantly the catalysis. It turned out that the proximity between the hyperiodine and the catalyst controlled by the chain length of their link dictated the synergetic catalysis. Based on LC-MS analysis, a catalytic mechanism was proposed and highest oxidation state Mn(IV) is possibly involved during the catalysis as suggested by EPR and FTIR analysis.

## **Results and Discussion**

#### Synthesis

The synthetic routes of ligands  $L_{1-5}$  and complexes 3a-e are shown in Schemes 1 and 2, respectively. The building blocks 2a-d of L<sub>2-5</sub> were prepared from 2-iodophenol (or phenol) and 1,2-dibromoethane (or 1,4-dibromohexane, or 1,6-dibromohexane) in refluxing acetone by using potassium carbonate as a base. Compound 1 was synthesized from ethylenediamine and picolinaldehyde in refluxing methanol and subsequent reduction by NaBH<sub>4</sub>. Then compound 1 reacted with 1-(bromomethyl)-2-iodobenzene (or 2a-d) to afford ligand  $L_1$  (or  $L_{2-5}$ ) in refluxing acetonitrile in the presence of potassium iodide by using potassium carbonate as a base. Reacting ligands  $L_{1-5}$  with MnCl<sub>2</sub>·4H<sub>2</sub>O produced manganese (II) complexes **3a–e**, respectively.



Scheme 1 Synthesis of ligands  $L_{1-5}$  and their Mn(II) complexes 3a-e.

# Structural analysis

The spectroscopic data, elemental analyses for complexes **3a-e** and the crystal structures of complexes **3b** and **3c** allow the assignment of the suggested structures (Scheme 1). The structures of complexes **3b** and **3c** were analyzed by X-ray single crystal diffraction (Figs. 1 and 2). Crystallographic data and structural parameters are

presented in Tables S1 and S2, respectively. As shown in Figs. 1 and 2, the two complexes adopt an octahedral geometry with the donor-set "N<sub>4</sub>Cl<sub>2</sub>". Similar to other multidentate pyridinyl manganese complexes [40-44], the distances of the Mn–N(Py) bond in complexes **3b** and **3c** are about 0.12 Å shorter than the Mn–N (methylene) bonds.



Fig. 1 Crystal structure of complex 3b (Mn1–N1 = Mn1–N1A = 2.280(2) Å, Mn1–N2 = Mn1–N2A = 2.403(2) Å, Mn1–Cl1 = Mn1–Cl1A = 2.4404(8) Å).



Fig. 2 Crystal structure of complex 3c (Mn1–N1 = Mn1–N1A = 2.2715(13) Å, Mn1–N2 = Mn1–N2A = 2.4069(13) Å, Mn1–Cl1 = Mn1–Cl1A = 2.4451(4) Å).

### Optimization of reaction conditions of ethylbenzene oxidation

The catalytic activity of the complexes was assessed using the alkane oxidation reaction. To optimize the reaction conditions, complex **3b** and the ethylbenzene was employed as the catalyst and substrate, respectively. The reaction was found to give the best result in the mixture of CH<sub>3</sub>CN and H<sub>2</sub>O to react for 16 h. In this reaction medium, both the dosage of the catalyst and an oxidant were examined. The reaction was analyzed by a gas chromatography. It turned out that 0.1 equivalent of the catalyst and 6 equivalent of the oxidant gave the best result (Table 1, entry 2). The best ratio of CH<sub>3</sub>CN over H<sub>2</sub>O for the reaction is 1:1 ratio (Table 1). Screening Oxidants showed that oxone is the most appropriate oxidant compared to other ones, H<sub>2</sub>O<sub>2</sub>, TBHP (*tert*-butyl hydroperoxide), CAN [Ce(NH<sub>4</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub>], NaIO<sub>4</sub> and I<sub>2</sub>O<sub>5</sub> (entries 2 and 7–11, Table 1).

Entry	Cat. / Ox. (eq.)	Solvents	<sup>b</sup> Yield (%)	Conversion (%)
1	<b>3b</b> / Oxone = 0.05 / 6	MeCN-H <sub>2</sub> O	12	23
		(1:1)		
2	3b / Oxone = 0.1 / 6	MeCN-H <sub>2</sub> O	89	91
		(1:1)		
3	3b / Oxone = 0.15 / 6	MeCN-H <sub>2</sub> O	68	75
		(1:1)		
4	3b / Oxone = 0.1 / 3	MeCN-H <sub>2</sub> O	34	40
		(1:1)		
5	<b>3b</b> /Oxone = 0.1 / 6	MeCN-H <sub>2</sub> O	24	28
	Y	(4:1)		
6	3b / Oxone = 0.1 / 6	MeCN-H <sub>2</sub> O	10	40
		(1:2)		
7	$3b$ / $H_2O_2 = 0.1$ / 6	MeCN-H <sub>2</sub> O	0	0
		(1:1)		

Table 1 Optimization of reaction conditions using complex 3b as the catalyst.<sup>a</sup>

	ACC	CEPTED MAN	USCRIPT	
8	<b>3b</b> / TBHP = 0.1 / 6	MeCN-H <sub>2</sub> O	41	43
		(1:1)		
9	<b>3b</b> / CAN = 0.1 / 6	MeCN-H <sub>2</sub> O	3	8
		(1:1)		
10	<b>3b</b> / NaIO <sub>4</sub> = $0.1 / 6$	MeCN-H <sub>2</sub> O	14	20
		(1:1)		
11	<b>3b</b> /I <sub>2</sub> O <sub>5</sub> = 0.1 / 6	MeCN-H <sub>2</sub> O	0	0
		(1:1)		A Y
12	<b>3b</b> (0.1)	MeCN-H <sub>2</sub> O	0	0
		(1:1)		

<sup>*a*</sup> Reaction conditions: ethylbenzene (0.5 mmol), solvents (4 mL), 25 °C, 16 h in open air.

<sup>b</sup> Yield by GC analysis.

# Synergetic catalysis on the oxidation of ethylbenzene

To confirm whether synergetic interaction exists for the manganese(II) complexes bearing iodobenzene motif, four ligands ( $L_{1-2}$ ,  $L_{4-5}$ ) pendant with two iodobenzene groups derived from a tetradentate ligand (1) were designed and synthesized. In the four ligands, between the iodo group and secondary amine N atom is separated by the distance of 4, 6, 8, 10 bonds. Their complexes (**3a**, **3b**, **3d**, **3e**) with Mn(II) were analogously prepared. Under the same reaction conditions described in previous section, their catalytic efficiency towards the oxidation of ethylbenzene was examined. The results shown in Table 2 indicate clearly that the length of the linkage between the iodo group and the coordinating sphere matters so much that the conversion of the reaction catalyzed by **3a** decreased by nearly 50% compared to **3b** (Table 2, entries 1 and 2). In complexes **3d** and **3e**, the linkage was further lengthened, the conversion of the reaction declined slightly (Table 2, entries 5 and 6).

The variation in conversion rate with the length of the linkage suggests straightforward that both metal center and the hyperiodo derived from the oxidation of

the iodobenzene act concertedly on the catalytic oxidation of ethylbenzene. To reveal how important such concerting interaction is in the catalysis, ligand with no iodobenzene group ( $L_3$ ), an analogue of ligand  $L_2$ , and its Mn (II) complex (3c) were synthesized. Complex **3c** gave 17% conversion rate (Table 2, entry 4). By adding two equivalents of iodobenzene to constitute equivalent system analogous to complex **3b**, the reaction conversion rate was doubled (Table 2, entry 3), which is still lower than half of that obtained by complex **3b**. These results suggest that most contribution of the conversion is attributed to the concerting intermolecular interaction between the metal complex and PhIO<sub>2</sub>. In other word, the intramolecular concerted interaction in the catalysis dominates the catalysis. Despite that using MnCl<sub>2</sub> alone produced better result than complex 3c, incorporating iodobenzene into the complexes enhances significantly their catalytic efficiency (Table 2, entries 3, 4 and 10). It is not surprising that either ligand  $L_2$  or iodobenzene alone produced no detectable products (Table 2, entries 7 and 8). No product was detected without catalyst (Table 2, entry 9). Under the acidic condition resulted from the addition of excess oxone, it is possible that the manganese (II) catalysts collapse in the oxidation reaction to form  $MnO_2$  which could catalyse the oxidation, too. Since we cannot rule out the possibility of forming MnO<sub>2</sub>, confirming the catalytic activity of MnO<sub>2</sub> becomes important. As shown by the results (Table 2, entries 12-14), MnO<sub>2</sub> does show some activity but both yield and conversion rate are much less than those observed for catalyst 3b (Table 2, entry 2). By considering that forming  $MnO_2$  during the catalysis is not significant, its contribution to the catalysis can be neglected.

Entry	Catalyst (eq.)	<sup>b</sup> Yield (%)	Conversion (%)
1	<b>3a</b> (0.1)	46	58
2	<b>3b</b> (0.1)	89	91
3	<b>3c</b> (0.1) + PhI (0.2)	24	39
4	<b>3c</b> (0.1)	9	17

Table 2 The reaction efficiency under various catalytic conditions.<sup>a</sup>

ACCEPTED MAN	NUSCRI	IPT
5 <b>3d</b> (0.1)	82	88
6 <b>3e</b> (0.1)	75	84
7 $L_2(0.1)$	0	0
8 PhI (0.1)	0	0
9 none	0	0
10 MnCl <sub>2</sub> (0.1)	17	30
11 $MnCl_2(0.1) + PhI(0.2)$	12	41
$12^c$ MnO <sub>2</sub> (0.1)	0	25
13 MnO <sub>2</sub> ( 0.1 )	46	66
14 $MnO_2(0.1) + PhI(0.2)$	16	34

<sup>*a*</sup> Ethylbenzene (0.5 mmol) in MeCN-H<sub>2</sub>O (1:1), oxone ( 6.0 eq.), 25 °C, 16 h in open air.

<sup>b</sup> Yield by GC analysis.

<sup>c</sup> Without oxone.

To understand how the pendant iodobenzene groups play a role in the synergetic catalysis, we first examined the oxidation products of ligand  $L_2$ , complexes **3b** and **3c** using high-resolution LG-MS. The mass spectra are shown in Figs. S1-3. By common knowledge in oxidation chemistry, one major oxidation product for the oxidations is tentatively proposed in Scheme S1 and in Table S3, further fragments are also proposed. For comparison, we used ChemDraw software to predict the peak distribution of those proposed fragments. As shown in Table S3, for all the proposed fragments, there are generally good agreements between the predicted signals and the observed ones.

The fragments found in the MS spectra indicate that the iodo is oxidized to high valent iodine (ArIO<sub>2</sub>). Under the oxidative condition, the metal center is likely oxidized to Mn(IV) to form Mn(IV)=O bond as suggested by the EPR spectrum of the oxidation product (Fig. S4) [45] and its IR absorption band at 921 cm<sup>-1</sup> (Fig. S5) [46]. These observed fragments suggest also that under the oxidation conditions two

bound chlorides were cleaved despite the report that such a chloride could involve in reaction with the iodobenzene [47]. Oxidizing the analogue (3c) produced metal-free fragments (Scheme S1 and Table S3). This suggests strongly that the high valent iodine stabilizes the oxidized product *via* direct interaction between the metal center and hyperiodide. This may explain how the high valent iodine involves in the synergetic catalysis between the iodine and the metal center and why the linkage length matters in the catalysis. This is the ground for us to proposed a mechanism for the catalysis (*vide infra*). It is particularly noteworthy that examining the LC-MS spectrum of the catalytic reaction reveals a fragment which may bear the half-oxidized intermediate (**3b**-P, Scheme S1 and Table S3). Very likely, the substrate is bound at the iodo center rather than the metal center.

### Proposed mechanism for the synthesis of acetophenone

The oxidation of ethylbenzene into ketone involves oxo transfer insertion and hydrogen abstraction. The hypervalent iodine must involve in either process. Since iodine is more electronegative than manganese, the oxo group of the hypervalent iodine ought to be less nucleophilic than that of Mn(IV)=O. Bearing with this argument in mind, it is feasible to speculate that the metal oxo undertake the proton abstraction from the substrate while the hypervalent iodine helps complete the second electron transfer from the substrate to form the product, ketone. With above mechanistic outline, a mechanism for the synergetic oxidation of ethylbenzene is proposed (Scheme 2).



Scheme 2 Possible mechanism for the concerted oxidation of ethylbenzene (sol = solvent).

# The applicability of the complexes on the activation of sp<sup>3</sup> C–H bonds

To examine the applicability of the Mn(II) complexes on the activation of  $sp^3$  C–H bonds, we checked the catalysis of complex **3b** on a number of substrates which were arbitrarily chosen. As shown in Table 3, complex **3b** exhibited generally better catalytic performance on benzylic C–H bonds compared to cyclohexane. This is apparently due to that the benzylic C–H bonds are more reactive than aliphatic C–H bonds of cyclohexane. For those compounds of benzylic type C–H bonds, the reactivity is much lower compared to ethylbenzene, which may be attributed to both electronic and steric reasons.



Table 3 Oxidation of various hydrocarbons under the catalysis by complex **3b**.<sup>*a*</sup>

<sup>*a*</sup> Reaction conditions: substrate (1 eq.), complex **3b** (0.1 eq.), oxone (6 eq.), 4 mL MeCN-H<sub>2</sub>O (1:1, v/v), 25 °C, 16 h. <sup>*b*</sup> GC yield.

# Conclusions

In summary, we reported four tetradentate ligands  $L_{1-2}$ ,  $L_{4-5}$  and Mn(II) complexes **3a**, **3b**, **3d** and **3e**. Related compounds and complexes were fully characterized. In all the ligands, iodobenzene group was introduced to examine the synergetic catalysis on the ethylbenzene oxidation by oxone between the metal center and the hypervalent iodine. It was found that cooperation between the two functionalities enhanced greatly the reaction. The most striking evidence was that the linkage length between the tetradentate ligand moiety and the iodobenzene affects severely the reactivity. It turned out that ligand  $L_2$ 

presence the most appropriate linkage. Further evidence came for the poor performance of the analogue (3c) of complex 3b, in which a phenyl ring replaced the iodobenzene in  $L_2$ . EPR and FTIR data (Figs. S4 and S5) suggests Mn(IV) as the active oxidation state.

### **Experimental Section**

### **Materials and Methods**

All commercially available reagents and solvents were obtained from the commercial providers unless otherwise stated and used without further purification. Preparation and handling of air-sensitive compounds were performed under an argon atmosphere using standard Schlenk techniques or in an MBraunLabmaster 120 inert atmosphere (<1 ppm  $O_2$ , <1 ppm  $H_2O$ ) glovebox filled with nitrogen. Deoxygenation of solvents was effected by either repetitive freezing/pumping/thawing cycles or bubbling with argon for 45-60 min. Elemental analyses were performed on Quantitative Technologies, Inc. (QTI, Whitehouse, NJ) or Desert Analytics (Tucson, AZ). <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded using a Varian 400 MHz spectrometer. Chemical shifts were reported relative to internal tetramethylsilane (0.00 ppm) for <sup>1</sup>H and CDCl<sub>3</sub> (77.0 ppm) for <sup>13</sup>C. IR spectra were obtained on an Agilent 640 FT-IR spectrophotometer. High-resolution mass spectra were obtained on a Waters LCT Premier XE LC-MS spectrometer (ESI). GC analysis was performed on GC-2010 equipped with a flame ionization detector using a 0.2 mm  $\times$  30 m capillary column. Flash column chromatography was performed on 300-400 mesh silica gel. Crystallographic data of complexes 3b and 3c (CCDC 1522129 for 3b and 1522130 for 3c) were collected on a Bruker SMART CCD diffractometer with graphite-monochromated Mo–K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The crystal structures were solved using direct methods in SHELXS and refined by full-matrix least-squares routines, based on  $F^2$ , using the SHELXL package [48].

# Synthesis of ligands and complexes

Synthesis of N<sup>1</sup>,N<sup>2</sup>-bis(pyridin-2-ylmethyl)ethane-1,2-diamine (1) [49]: To a solution of ethylenediamine (1.50 g, 25 mmol) in CH<sub>3</sub>OH (60 mL) was added picolinaldehyde (5.35 g, 50 mmol). The clear yellow solution was stirred and refluxed at 80 °C for 12 h. At ice-temperature, NaBH<sub>4</sub> (1.43 g, 37.5 mmol) was added in small portions, and then refluxed at 80 °C for 17 h. When the reaction was completed as monitored by TLC, the solvent was evaporated to produce a residue to which water (50 mL) was added. The solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL). The organic phases were combined and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvents gave light-brown solid. Purification by silica flash chromatography (ethyl acetate / methanol / triethylamine = 5:1:0.1, v / v / v) gave the desired product as pale-yellow oil **1** (4.48 g, 74%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 8.48 (d, *J* = 4.4 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H) 7.11-7.06 (m, 2H), 3.86 (s, 4H), 2.77 (s, 4H), 2.54 (s, 2H).

Synthesis of 2a, 2c and 2d: To a solution of 2-iodophenol (4.4 g, 20 mmol) and 1, 2-dibromoethane (or 1, 4-dibromoethane, or 1,6-dibromohexane) (120 mmol) in acetone (50 mL) was added potassium carbonate (5.52 g, 40 mmol). The mixture was refluxed at 80 °C for 24 h. After being cooled to room temperature, any insoluable solids were filtered off and the solvent was evaporated from the filtrate to give a residue which was purified by column chromatography (ethyl acetate / petroleum ether = 1:50, v / v) to afford the desired product 2a ( or 2c, or 2d).

**1-(2-Bromoethoxy)-2-iodobenzene** (**2a**): pale-yellow oil ( 4.44 g, 68%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 7.77 (d, *J* = 7.6 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.74 (t, *J* = 7.6Hz, 1H), 4.29 (t, *J* = 6.4 Hz, 2H), 3.66 (t, *J* = 6.4 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 156.7, 139.7, 129.6, 123.4, 112.9, 87.0, 69.2, 29.7. IR (neat, cm<sup>-1</sup>): 3065, 2926, 2854, 1582, 1475, 1439, 1246, 1050, 1018, 650, 579.

**1-(4-bromobutoxy)-2-iodobenzene** (**2c**) [50]: yellow oil ( 6.10 g, 85%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 7.76 (d, J = 8.0 Hz, 1H), 7.27 (t, J = 7.2 Hz, 1H), 6.77 (d, J = 8.4 Hz, 1H), 6.70 (t, J = 7.6Hz, 1H), 4.02 (t, J = 5.8 Hz, 2H), 3.53 (t, J = 6.6 Hz, 2H), 2.20-2.08 (m, 2H), 2.03-1.92 (m, 2H).

**1-(6-Bromohexyloxy)-2-iodobenzene** (**2d**) [50]: yellow oil (5.97 g, 78%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 7.75 (d, J = 8.0 Hz, 1H), 7.26 (t, J = 7.8 Hz, 1H), 6.78 (d, J = 8.0 Hz, 1H), 6.68 (t, J = 7.6Hz, 1H), 4.00 (t, J = 6.0 Hz, 2H), 3.42 (t, J = 6.8 Hz, 2H),1.95-1.75 (m, 4H), 1.65-1.45 (m, 4H).

Synthesis of (2-bromoethoxy) benzene (2b) [51]:To a solution of phenol (1.88 g, 20 mmol) and 1,2-dibromoethane (22.56 g, 120 mmol) in acetone (50 mL) was added potassium carbonate (5.52 g, 40 mmol ) under stirring. The mixture was refluxed at 80 °C for 24 h. After being cooled to room temperature, any insoluable solids were filtered off and the solvent was evaporated from the filtrate to give a residue which was purified by column chromatography (ethyl acetate / petroleum ether = 1:50, v / v ) to afford the desired product as pale-yellow oil (2b) (1.11 g, 44%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 7.29 (t, *J* = 8.0 Hz, 2H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.28 (t, *J* = 6.2 Hz, 2H), 3.63 (t, *J* = 6.4 Hz, 2H).

Synthesis of N<sup>1</sup>,N<sup>2</sup>-bis(2-iodobenzyl)-N<sup>1</sup>,N<sup>2</sup>-bis((pyridin-2-yl)methyl) ethane-1,2diamine  $(L_1)$ : To a solution of compound 1 (0.73 g, 3 mmol) and 1-(bromomethyl)-2-iodobenzene (1.78 g, 6 mmol) in acetonitrile (50 mL) were added potassium carbonate (1.66 g, 12 mmol) and potassium iodide (0.01g, 0.06 mmol) under stirring. The mixture was refluxed at 80 °C for 15 h. After being cooled to room temperature, any insoluable solids were filtered off and the solvent was evaporated from the filtrate to give a residue which was purified by column chromatography (petroleum ether / ethyl acetate / triethylamine = 20:5:4, v / v / v ) to afford the desired product as yellow oil (L<sub>1</sub>) (0.55 g, 27%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$ =8.44 (d, J = 4.0 Hz, 2H), 7.75 (d, J = 8.0 Hz, 2H), 7.51 (t, J = 7.6 Hz, 2H), 7.44 (d, J= 7.6 Hz, 2H), 7.39 (d, J = 7.6 Hz, 2H), 7.19 (t, J = 7.6 Hz, 2H), 7.06 (t, J = 5.8 Hz, 2H ), 6.87 (t, J = 7.4 Hz, 2H ), 3.73 (s, 4H), 3.62 (s, 4H), 2.72 (s, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta = 159.7$  (2C), 148.8 (2C), 141.3 (2C), 139.3 (2C), 136.4 (2C), 130.0 (2C), 128.6 (2C), 128.0 (2C), 122.7 (2C), 121.9 (2C), 100.1 (2C), 63.6 (2C), 60.6 (2C), 52.2 (2C). IR (neat, cm<sup>-1</sup>): 3061, 2927, 2823, 1591, 1570, 1474, 1436, 1363, 1147, 1046, 617.

Synthesis of L<sub>2-5</sub>: To a solution of compound 1 (0.73 g, 3 mmol) and compound 2a (2b, 2c, 2d) (9 mmol) in acetonitrile (50 mL) were added potassium carbonate (1.66 g, 12 mmol) and potassium iodide (0.015 g, 0.09 mmol) under stirring. The mixture was refluxed at 80 °C for 15 h. After being cooled to room temperature, any insoluable solids were filtered off and the solvent was evaporated from the filtrate to give a residue which was purified by column chromatography (ethyl acetate / methanol / triethylamine = 50:5:4, v / v / v ) to afford the desired product L<sub>2</sub> (L<sub>3</sub>, L<sub>4</sub>, L<sub>5</sub>).

N<sup>1</sup>,N<sup>2</sup>-bis(2-(2-iodophenoxy)ethyl)-N<sup>1</sup>,N<sup>2</sup>-bis(pyridin-2-ylmethyl) ethane-1,2diamine (L<sub>2</sub>): yellow oil (1.04 g, 47%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 8.45 (d, *J* = 4.8 Hz, 2H), 7.70 (d, *J* = 7.6 Hz, 2H), 7.55-7.45 (m, 4H), 7.18 (t, *J* = 7.6 Hz, 2H), 7.06 (t, *J* = 5.4 Hz, 2H), 6.69-6.60 (m, 4H), 4.01 (t, *J* = 5.6 Hz, 4H), 3.90 (s, 4H), 3.01 (t, *J* = 5.6 Hz, 4H), 2.87 (s, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 160.1 (2C), 157.4 (2C), 148.8 (2C), 139.4 (2C), 136.3 (2C), 129.3 (2C), 123.0 (2C), 122.4 (2C), 121.8 (2C), 111.9 (2C), 86.5 (2C), 67.8 (2C), 61.5 (2C), 53.6 (2C), 53.5 (2C). IR (neat, cm<sup>-1</sup>): 3062, 2932, 2825, 1583, 1470, 1438, 1365, 1275, 1122, 1050, 617.

N<sup>1</sup>,N<sup>2</sup>-bis(2-phenoxyethyl)-N<sup>1</sup>,N<sup>2</sup>-bis(pyridin-2-ylmethyl)ethane-1,2-diamine (L<sub>3</sub>): brown oil (0.64 g, 44%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 8.45 (d, *J* = 4.8 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 8.0 Hz, 4H), 7.09 (d, *J* = 6.0 Hz, 2H), 6.87 (t, *J* = 7.4 Hz, 2H), 6.76 (d, *J* = 8.0 Hz, 4H), 4.01 (t, *J* = 5.6 Hz, 4H), 3.92 (s, 4H), 3.01 (t, *J* = 5.0 Hz, 4H), 2.91 (s, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 158.5 (2C), 148.9 (2C), 136.5 (2C), 129.35 (4C), 123.1 (2C), 122.1 (2C), 120.7 (2C), 114.4 (4C), 65.9 (2C), 53.5 (2C), 52.9 (2C), 45.8 (4C). IR (neat, cm<sup>-1</sup>): 3159, 2985, 2927, 1599, 1497, 1474, 1390, 1244, 1173, 1038.

# N<sup>1</sup>,N<sup>2</sup>-bis(4-(2-iodophenoxy)butyl)-N<sup>1</sup>,N<sup>2</sup>-bis(pyridin-2-ylmethyl)

ethane-1,2-diamine (L<sub>4</sub>): yellow oil (0.26 g, 11%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  =8.45 (d, *J* = 3.2 Hz, 2H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 6.8 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 6.6 Hz, 2H), 7.08 (t, *J* = 5.2 Hz, 2H), 6.72-6.63 (m, 4H), 3.90 (t, *J* = 6.0 Hz, 4H), 3.77 (s, 4H), 2.73 (s, 4H), 2.57 (s, 4H), 1.80-1.65 (m, 8H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 157.4 (2C), 157.0 (2C), 148.8 (2C),

139.3 (2C), 136.4 (2C), 129.4 (2C), 123.0 (2C), 122.3 (2C), 121.9 (2C), 112.0 (2C), 86.7 (2C), 68.8 (2C), 60.6 (2C), 54.4 (2C), 52.2 (2C), 26.9 (2C), 23.7 (2C).

N<sup>1</sup>,N<sup>2</sup>-bis(6-(2-iodophenoxy)hexyl)-N<sup>1</sup>,N<sup>2</sup>-bis((pyridin-2-ylmethyl) ethane-1,2diamine (L<sub>5</sub>): yellow oil (1.19 g, 47%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 8.43 (d, *J* = 4.8 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 7.0 Hz, 2H), 7.04 (t, *J* = 6.2 Hz, 2H), 6.70 (d, *J* = 8.4 Hz, 2H), 6.61 (t, *J* = 7.6 Hz, 2H), 3.89 (t, *J* = 6.2 Hz, 4H), 3.68 (s, 4H), 2.60 (s, 4H), 2.43 (t, *J* = 7.4 Hz, 4H), 1.77-1.67 (m, 4H), 1.50-1.35 (m, 8H), 1.33-1.21 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 160.6 (2C), 157.5 (2C), 148.8 (2C), 139.3 (2C), 136.2 (2C), 129.3 (2C), 122.7 (2C), 122.3 (2C), 121.7 (2C), 112.1 (2C), 86.8 (2C), 69.0 (2C), 61.0 (2C), 54.9 (2C), 52.5 (2C), 29.0 (2C), 27.1 (2C), 27.0 (2C), 26.0 (2C). IR (neat, cm<sup>-1</sup>): 3064, 3013, 2931, 2829, 1592, 1571, 1471, 1439, 1366, 1277, 1247, 1122, 1050, 621, 540.

Synthesis of metal complexes 3a-e: To a solution of compound  $L_1$  (or  $L_2$ ,  $L_3$ ,  $L_4$ ,  $L_5$ ) (0.2 mmol) in methanol (2 mL) was added slowly the solution of manganese chloride tetrahydrate (0.04 g, 0.2 mmol) in methanol (1 mL) under stirring. After being stirred at room temperature for 1 h, a precipitate was collected by filtration, washed with diethyl ether and dried under vacuum overnight and got the desired complex 3a (or 3b, 3c, 3d, 3e).

**3a** (0.14 g, 90%). Calcd. for C<sub>28</sub>H<sub>28</sub>Cl<sub>2</sub>I<sub>2</sub>MnN<sub>4</sub> (FW = 800.20): N 7.00%; C 42.03%; H 3.53%; Found: N 6.32 %; C 41.74%; H 3.78%.

**3b** (0.13 g, 74%). Calcd. for  $C_{30}H_{32}Cl_2I_2MnN_4O_2$  (FW = 860.25): N 6.51%; C 41.89%; H 3.75%; Found: N 6.39%; C 41.68%; H 3.80%.

**3c** (0.051 g, 42%). Calcd. for C<sub>30</sub>H<sub>34</sub>Cl<sub>2</sub>MnN<sub>4</sub>O<sub>2</sub> (FW = 607.14): N 9.21%; C 59.22%; H 5.63%; Found: N 8.7%; C 58.97%; H 5.57%.

**3d** (0.094 g, 51%). Calcd. for  $C_{34}H_{40}Cl_2I_2MnN_4O_2$  (FW = 916.36): N 6.11%; C 44.56%; H 4.40%; Found: N 5.95%; C 44.42%; H 4.29%.

**3e** (0.12 g, 63%). Calcd. for  $C_{38}H_{48}Cl_2I_2MnN_4O_2$  (FW = 972.47): N 5.76%; C 46.93%; H 4.98%; Found: N 5.64%; C 46.61%; H 4.86%.

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#### Appendix A. Supplementary data

Crystallographic data of the complexes, related spectra for oxidations, possible oxidation products, synthesis and characterization of compounds 4 and LC-MS signal analysis for oxidations. Supplementary data associated with this article can be found in the online version.

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# Highlights

- Oxidation of ethylbenzene to acetophenone catalyzed by Mn(II) complexes in good yield under mild conditions.
- The pendant iodophenyl groups in Mn(II) complexes play a synergetic role with the metal center in the catalysis.
- The linkage length between the tetradentate ligand moiety and the iodobenzene affects severely the catalytic reactivity.

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