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# A novel catalytic system for oxygenation with molecular oxygen induced by transition metal complexes with a multidentate *N*-heterocyclic podand ligand

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**Abstract**

An efficient system for the catalytic epoxidation reaction of olefins with molecular oxygen was achieved by the utilization of $FeCl_2$ and the *N*-heterocyclic podand ligand, *N*,*N*′-bis{2-(4-imidazolyl)ethyl}-2,6-pyridinedicarboxamide (BIPA), without the need for a co-reductant. The pyridyl-substituted *N*-heterocyclic podand ligand, *N*,*N*′-bis{2-(2-pyridyl)ethyl}-2,6-pyridinedicarboxamide (2-BPEPA) was useful in the $Co(OAc)_2$-catalyzed selective oxygenation of phenols to the corresponding *p*- or *o*-quinones with molecular oxygen. Efficiency of the oxygenation catalysts largely depends on the coordination interaction with the heterocyclic moieties of the podand ligands.

*Keywords:* Epoxidation; Oxygenation; Quinone; Oxygen; Transition metal complex; Multidentate ligand; *N*-Heterocyclic ligand; Podand

## 1. Introduction

Catalytic oxygenation based on the redox of transition metal complexes is of importance from synthetic and biological viewpoints. A variety of complex catalysts and metalloenzyme models for cytochrome P-450 [1,2], tyrosinase [3–5], and other oxygenases have been investigated to develop an efficient system and elucidate the oxygenation mechanism [6]. Imidazoles serve as an axial *N*-ligand to elevate the monooxygenase activity of porphyrin complexes [2](a,j). The rate acceleration is similarly attained by the presence of lipophilic carboxylic acids and lipophilic heterocyclic bases [6](d), or aldehydes [6](b). A previous paper [7] demonstrated that *o*-quinones mediate the Mn(III)TPPCl-catalyzed epoxidation reaction with hydrogen peroxide.

Smooth electron transfer through reversible redox of transition metals is required for an efficient catalytic cycle. Since ligand coordination greatly contributes to their redox processes, ligand design is essential in the construction of a versatile redox system. Conformationally flexible ligands are considered to permit us to construct an efficient catalytic system rather than rigid ones. Such a system is correlated to non-heme oxygenases. Our system has been addressed by the design of multidentate *N*-hetero-

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cyclic podand ligands. The coordination interaction between $Mn(OAc)_2$ or $VO(OEt)Cl_2$ and *N*,*N*′-bis{2-(4-imidazolyl)ethyl}-2,6-pyridinedicarboxamide (BIPA) was revealed to play an important role in the oxygenation reactions of styrene derivatives with iodosylbenzene or molecular oxygen in the presence of a co-reductant [8]. The requisite complex is presumed to be formed for the efficient epoxidation.

Oxygenation with molecular oxygen in monooxygenases is usually achieved by reductive activation with an electron donor [1],[2](c), but the ruthenium-catalyzed epoxidation reaction has been reported to proceed in the absence of a co-reductant [9].

The complexation of transition metals with the flexible multidentate *N*-heterocyclic podand ligands is found to permit an efficient oxygenation system with molecular oxygen for the epoxidation without the need of a co-reductant and the oxygenation of phenols to quinones [10]. Herein we report the full scope of our catalytic system, in which a difference in heterocyclic coordination sites is reflected in the catalytic activity.

## 2. Results and discussion

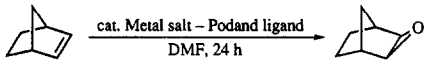
An efficient catalytic epoxidation reaction was performed by the use of an iron(II) com-

Table 1
Catalytic epoxidation of 2-norbornene [a]

| Metal salt | Ligand | Temp. (°C) | Atmosphere ($10^3$ kPa) | Yield (%) [b] |
|---|---|---|---|---|
| $FeCl_2$ | BIPA | 70 | $O_2$ (1.0) | 22 |
| $FeCl_2$ | – | 70 | $O_2$ (1.0) | 4 |
| $FeCl_2$ | BIPA | 70 | $O_2$ (0.1) | trace |
| $FeCl_2$ | BIPA | 70 | Ar (1.0) | no reaction |
| $FeCl_2$ | BIPA | 70 | air (1.0) | trace |
| $FeCl_2$ | BIPA | rt | $O_2$ (1.0) | 1 |
| $FeCl_2$ | 2-BPEPA | 70 | $O_2$ (1.0) | 17 |
| $FeCl_2$ | BPHEPA | 70 | $O_2$ (1.0) | 5 |
| $FeCl_2$ | 2-DPPA | 70 | $O_2$ (1.0) | 17 |
| $FeCl_2$ | 3-DPPA | 70 | $O_2$ (1.0) | 18 |
| $FeCl_2$ | DPHPA | 70 | $O_2$ (1.0) | 2 |
| $FeCl_2$ | 3-PPA [c] | 70 | $O_2$ (1.0) | 13 |
| $FeCl_3$ | BIPA | 70 | $O_2$ (1.0) | 6 |
| $FeCl_3$ | – | 70 | $O_2$ (1.0) | 2 |
| $Co(OAc)_2$ | BIPA | 70 | $O_2$ (1.0) | 24 |
| $Co(OAc)_2$ | 2-BPEPA | 70 | $O_2$ (1.0) | 7 |
| $Co(OAc)_2$ | BPHEPA | 70 | $O_2$ (1.0) | 5 |
| $Co(OAc)_2$ | – | 70 | $O_2$ (1.0) | 4 |
| $CoCl_2$ | BIPA | 70 | $O_2$ (1.0) | 13 |
| $CoCl_2$ | 2-BPEPA | 70 | $O_2$ (1.0) | 2 |
| $CoCl_2$ | BPHEPA | 70 | $O_2$ (1.0) | 6 |
| $CoCl_2$ | – | 70 | $O_2$ (1.0) | 3 |
| $CrCl_2$ | BIPA | 70 | $O_2$ (1.0) | 11 |
| $CrCl_2$ | – | 70 | $O_2$ (1.0) | 5 |
| $RhCl_3$ | BIPA | 70 | $O_2$ (1.0) | 6 |
| $RuCl_3$ | BIPA | 70 | $O_2$ (1.0) | 4 |
| $Ni(OAc)_2$ | BIPA | 70 | $O_2$ (1.0) | 1 |
| $Mn(OAc)_2$ | BIPA | 70 | $O_2$ (1.0) | trace |
| $Cu(OAc)_2$ | BIPA | 70 | $O_2$ (1.0) | trace |

[a] Metal salt, 0.02 mmol; ligand, 0.02 mmol; **1a**, 2.0 mmol, unless otherwise stated.
[b] GLC yields based on **1a**. Only *exo*-isomer was obtained.
[c] Ligand, 0.04 mmol.

plex with the multidentate *N*-heterocyclic podand ligand. Treatment of 2-norbornene (**1a**) with a catalytic amount of $FeCl_2$ and BIPA in DMF under molecular oxygen ($1.0 \times 10^3$ kPa) led to the stereoselective formation of *exo*-2,3-epoxynorbornane (**2a**, Eq. 1). The *endo*-isomer was not detected by $^1$H-NMR analysis. It should be noted that the existence of a co-reductant is not required for this catalytic oxygenation. The turnover number of the catalyst was more than 20 under the conditions employed here as listed in Table 1 although not optimized. The reaction under air ($1.0 \times 10^3$ kPa) or an atmospheric pressure of molecular oxygen gave only a trace amount of **2a**. No oxidized product was obtained under argon, supporting the incorporation of molecular oxygen to **2a**.




(1)

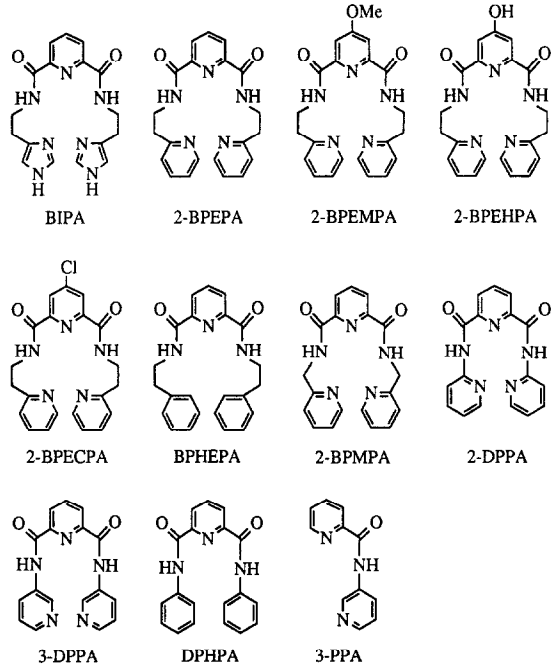



Fig. 1. Multidentate *N*-heterocyclic ligands used in the oxygenation reactions.

BIPA participates in the epoxidation reaction since the yield of **2a** decreased in the absence of BIPA. This finding suggests that the multidentate *N*-heterocyclic podand ligand forms an efficient complex catalyst. Other podand ligands derived from 2,6-pyridinedicarboxylic acid were examined (Fig. 1); the use of 2-BPEPA bearing the 2-pyridyl group instead of the 4-imidazolyl one lowered the epoxidation yield. A fatal decrease was observed in the case of BPHEPA bearing the phenyl group, indicating that the coordination of the 4-imidazolyl moieties of BIPA is essential for the epoxidation reaction. The pendant length is considered to be another factor for ligand design. The efficiency of 2-DPPA or 3-DPPA was lower than that of BIPA,

Table 2
Catalytic epoxidation of *trans*-β-methylstyrene [a]

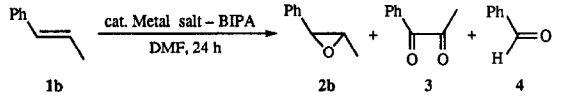
| Metal salt | Ligand | Temp. (°C) | $O_2$ ($10^3$ kPa) | Yield (%) [b] | | |
|---|---|---|---|---|---|---|
| | | | | **2b** [c] | **3** | **4** |
| $FeCl_2$ | BIPA | 70 | 1.0 | 16 | 3 | 40 |
| $FeCl_2$ | – | 70 | 1.0 | 7 | 1 | 28 |
| $FeCl_2$ | BIPA | 70 | 0.1 | 0.2 | – | 1 |
| $FeCl_2$ | – | 70 | 0.1 | – | – | 1 |
| $FeCl_2$ | BIPA | rt | 1.0 | 5 | 5 | 39 |
| $FeCl_2$ | – | rt | 1.0 | 0.2 | 0.1 | 6 |
| $Co(OAc)_2$ | BIPA | 70 | 1.0 | 14 | 7 | 36 |
| $Co(OAc)_2$ | – | 70 | 1.0 | 9 | 7 | 28 |
| $CoCl_2$ | BIPA | 70 | 1.0 | 0.4 | 0.3 | 5 |
| $CoCl_2$ | – | 70 | 1.0 | 0.8 | 0.3 | 6 |

[a] Metal salt, 0.02 mmol; BIPA, 0.02 mmol; **1b**, 2.0 mmol.
[b] GLC yields based on **1b**.
[c] Only *trans*-isomer was obtained.

but comparable to that of 2-BPEPA. A poor result was obtained with DPHPA as observed in BPHEPA. One pendant group of 3-PPA was not enough as compared with 3-DPPA.

A combination of $FeCl_3$, $RhCl_3$, $RuCl_3$, $Ni(OAc)_2$, $Mn(OAc)_2$, or $Cu(OAc)_2$ with BIPA did not form an efficient catalyst. The epoxidation reaction proceeded with $Co(OAc)_2$, but a more distinct difference between BIPA and 2-BPEPA was observed possibly due to the difference of coordination interaction. $CoCl_2$ was found to be inferior to $Co(OAc)_2$.

*trans*-β-Methylstyrene (**1b**) similarly underwent the $FeCl_2$–BIPA-catalyzed epoxidation reaction although the diketone **3** and benzaldehyde **4** via oxidative cleavage of the carbon–carbon double bond were obtained as byproducts (Eq. 2). The ligand effect of BIPA is also important to attain the high catalytic activity of the $FeCl_2$ or $Co(OAc)_2$ complex under molecular oxygen ($1.0 \times 10^3$ kPa) as shown in Tables 2 and 3.




(2)

The $FeCl_2$-catalyzed reaction of *trans*-stilbene (**1c**) proceeded well only with BIPA, but not with 2-BPEPA or BPHEPA. The $Co(OAc)_2$ complex did not induce the epoxidation of **1c** even in the presence of BIPA, indicating that the efficiency of the $Co(OAc)_2$–BIPA complex depends on substrates. *N,N*-Dimethylacetamide and 1-methyl-2-pyrrolidinone were suitable as a solvent, but **2c** was not obtained in pyridine. Although *cis*-stilbene (**1d**) is known to be more susceptible to epoxidation than the *trans*-isomer **1c**, the present epoxidation of **1d** did not occur under the conditions employed here. It suggests that a simple radical mechanism is not operating.

Although the iron(II) complex with BIPA has not been isolated yet, the coordination of the flexible multidentate *N*-heterocyclic ligand contributes to an efficient system for oxygenation. Cyclic voltammetry verified the formation of a complex of $FeCl_2$ with an equimolar amount of BIPA in methanol, resulting in the shift of the iron reduction wave from +0.35 to −0.35 V. A facile reduction of molecular oxygen was achieved with the more electron-rich iron species when molecular oxygen was introduced into the solution. In the case of $Co(OAc)_2$, the similar activation was observed with BIPA but not with 2-BPEPA. These findings are consistent with the above-mentioned results.

In the presumed octahedral geometry with two iron–nitrogen (amide) bonds, four nitrogen atoms of BIPA appear to exist approximately on the same plane as iron does. The optimized geometry based on ZINDO calculation (CAChe system) also refers to this structure. The second 4-imidazolyl group is capable of behaving as an anchored axial ligand to facilitate an oxidation process since the presence of excess amounts of the imidazole ligand has been reported to increase the activity of P-450 model catalysts [2](d,j).

Table 3
Catalytic epoxidation of olefins [a]

| Olefin | Metal salt | Ligand | Solvent | Product | Yield (%) [b] |
|---|---|---|---|---|---|
|  1b | $FeCl_2$ | BIPA | DMF |  2b | 16 (40) |
| | $FeCl_2$ | 2-BPEPA | DMF | [c] | 9 (35) |
| | $FeCl_2$ | BPHEPA | DMF | | 5 (23) |
| | $FeCl_2$ | — | DMF | | 7 (28) |
|  1c | $FeCl_2$ | BIPA | DMF |  2c | 21 (23) |
| | $FeCl_2$ | BIPA | DMAC [d] | [c] | 23 (32) |
| | $FeCl_2$ | BIPA | NMP [e] | | 31 (20) |
| | $FeCl_2$ | BIPA | pyridine | | 0 (0) |
| | $FeCl_2$ | 2-BPEPA | DMF | | 3 (5) |
| | $FeCl_2$ | BPHEPA | DMF | | 1 (3) |
| | $FeCl_2$ | — | DMF | | 1 (2) |
| | $Co(OAc)_2$ | BIPA | DMF | | 2 (5) |
| | $Co(OAc)_2$ | — | DMF | | trace (1) |
|  1d | $FeCl_2$ | BIPA | DMF |  2d | 0 (0) |
| | $FeCl_2$ | — | DMF | | 0 (0) |
| | $Co(OAc)_2$ | BIPA | DMF | | 0 (0) |
| | $Co(OAc)_2$ | — | DMF | | 0 (0) |

[a] Metal salt, 0.02 mmol; ligand, 0.02 mmol; **1**, 2.0 mmol.
[b] Based on **1**. The value in parenthesis is the turnover for the formation of benzaldehyde.
[c] Only *trans*-isomer was obtained.
[d] DMAC = *N,N*-dimethylacetamide.
[e] NMP = 1-methyl-2-pyrrolidinone.

The present system for epoxidation does not formally require a co-reductant. The consumption of molecular oxygen was almost in accord with the amount of an epoxide. If DMF served as an electron donor, $FeCl_3$ should have worked similarly as $FeCl_2$. The large difference in their catalytic activities indicates an alternate reaction course rather than the reported monooxygenase mechanism [2,9,11]. The μ-peroxodiiron intermediate seems to be involved in this system as reported in the aromatic hydroxylation [12]. The equilibrium is considered to be readily shifted to the μ-peroxo intermediate under the high pressure of molecular oxygen.

Milder reaction conditions for epoxidation were achieved by use of an additive. The presence of 4-ethoxycarbonyl-3-methyl-2-cyclohexen-1-one (**5**) in the reaction of **1b**, **1c** with molecular oxygen catalyzed by $FeCl_2$ and BIPA in DMF led to a facile oxidation to **2b**, **2c** (Eq. 3 and Table 4). The reaction even proceeded at room temperature under molecular oxygen ($1.0 \times 10^3$ kPa). Furthermore, **2c** was obtained under an atmospheric pressure of molecular oxygen when the reaction temperature was raised to 50°C. The *cis*-olefin **1d** was poorly oxidized under the conditions employed here, only giving the *trans*-epoxide **2c** in a low yield. The *cis*-isomer **2d** and the isomerized *trans*-stilbene (**1c**) were not detected by $^1$H-NMR. These results also suggest that a simple radical mechanism is not operating in this system.

Table 4
Catalytic epoxidation of olefins in the presence of **5** [a]

| Olefin | Ligand | Temp. (°C) | $O_2$ ($10^3$ kPa) | **5** (Molar equiv.) [b] | Product | Yield (%) [c] |
|---|---|---|---|---|---|---|
| Ph, Ph (**1b**) | BIPA | 50 | 0.1 | 20 | Ph, O, d (**2b**) | 10 (10) |
| | — | 50 | 0.1 | 20 | | 1 (6) |
| Ph, Ph (**1c**) | BIPA | rt | 1.0 | 10 | Ph, O, Ph, d (**2c**) | 9 (14) |
| | — | rt | 1.0 | 10 | | 0 (0) |
| | BIPA | rt | 1.0 | 20 | | 12 (15) |
| | BIPA | rt | 1.0 | 100 | | 11 (17) |
| | BIPA | 50 | 0.1 | 10 | | 10 (3) |
| | — | 50 | 0.1 | 10 | | tracc (0) |
| | BIPA | 50 | 0.1 | 20 | | 22 (5) |
| | BIPA | 50 | 0.1 | 50 | | 30 (7) |
| | BIPA [e] | 50 | 0.1 | 50 | | 11 (3) |
| | BIPA | 50 | 0.1 | 100 | | 10 (4) |
| Ph, Ph (**1d**) | BIPA | rt | 1.0 | 10 | Ph, O, Ph, d (**2c**) | 4 (4) [f] |

[a] $FeCl_2$, 0.01 mmol; BIPA, 0.01 mmol; **1**, 1.0 mmol.
[b] Based on **1**.
[c] Based on **1**. Value in parentheses is the turnover for the formation of benzaldehyde.
[d] Only *trans*-isomer was obtained.
[e] $FeCl_3$ was used instead of $FeCl_2$.
[f] The *cis*-epoxide **2d** and the isomerized olefin **1c** were not detected by $^1$H-NMR.

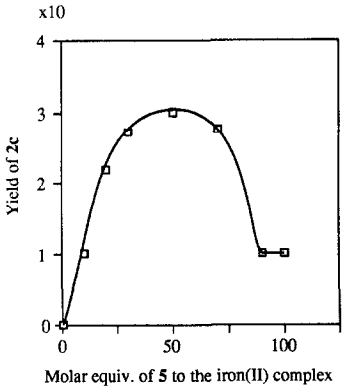
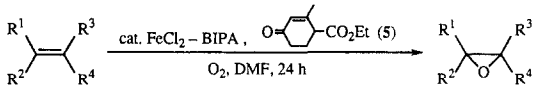



Fig. 2. Effect of **5** on the epoxidation of **1c** at 50°C under an atmospheric pressure of molecular oxygen.




(3)

The formation of **2c** is dependent on the amount of **5** as shown in Table 4 and Fig. 2. When the reaction was carried out under an atmospheric pressure of molecular oxygen, the epoxidation yield was raised by the increase in the amount of **5**, but was lowered by the addition of more than 70 molar equiv. of **5**.

It remains obscure why **5** facilitates the epoxidation reaction. The peak at 530 nm in the UV–Vis spectra attributable to the iron complex with BIPA in DMF disappeared on addition of **5** (5 molar equiv.) as shown in Fig. 3. It suggests that there is an electrical interaction-like coordination between the iron species and **5**. Such an interaction is assumed to enhance a step of the catalytic cycles. On the contrary, the existence of excess amounts of **5** is likely to disturb olefin coordination. The use of dimethyl maleate or 2-cyclohexen-1-one instead of **5** resulted in no epoxidation, indicating that the role of **5** is not

simply based on a property of an electron-deficient olefin.

Another possibility to be checked is that **5** serves as an electron donor. If this is so, $FeCl_3$ could be used as a catalyst with equal ease. The serious decrease in the yield of **2c** was, however, observed with $FeCl_3$–BIPA–**5**. The dehydrogenation product, 4-ethoxycarbonyl-3-methylphenol, was not detected in the reaction mixture, suggesting that the contribution of **5** only as an electron donor is not always reasonable. 2-Cyclohexen-1-one was not oxidized to phenol under similar conditions, without formation of the epoxide. Although almost half the amount of **5** or 2-cyclohexen-1-one (50 molar equiv. were used in each case) was recovered, a small amount of the oxygenated alcohol of **5** was formed as a sole detectable product by GLC and $^1$H-NMR. Molecular oxygen is assumed to be activated to afford a peroxide at the α-position of the ethoxycarbonyl group of **5** [13].

These findings imply that there is not necessarily only one interaction and path which is responsible for the catalytic system involving **5**. It is undeniable that these factors are considered to be correlated each other.

An efficient catalytic system for phenolase and catecholase is achieved by a cobalt(II) complex with multidentate *N*-heterocyclic podand ligands. Treatment of 2,6-di-*t*-butylphenol (**6a**) with 5 mol% of $Co(OAc)_2$ and 2-BPEPA in DMF under an atmospheric pressure of molecular oxygen led to the selective formation of the corresponding *p*-benzoquinone **7a** in a good yield with a small amount of the dehydrogenative coupling product **8a** (Eq. 4 and Table 5). DMF was superior to *N*,*N*-dimethylacetamide and 1-methyl-2-pyrrolidinone as a solvent. $Cu(OAc)_2$ did not induce the oxygenation reaction, to give only the diphenoquinone **8a**, even in the presence of 2-BPEPA.

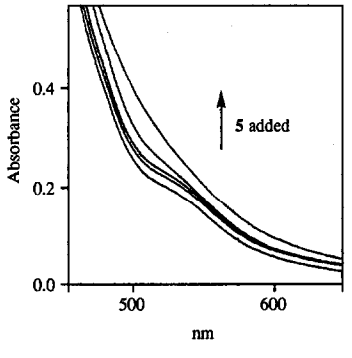
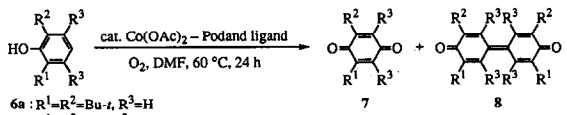



Fig. 3. UV–Vis spectra of $FeCl_2$–BIPA with **5**. [$FeCl_2$–BIPA] = $1.0\times10^{-3}$ M; [**5**] = 0, 1.0, 2.0, 3.0, $5.0\times10^{-3}$ M; solv. DMF; under nitrogen.

Table 5
Catalytic oxidation of phenols [a]

| | Ligand | Solvent | Yield (%) [b] | |
|---|---|---|---|---|
| | | | **7** | **8** |
| **6a** | BIPA | DMF | 10 | 41 |
| | 2-BPEPA | DMF | 86, 82 [c] | 9 |
| | 2-BPEPA [d] | DMF | 92 | 6 |
| | 2-BPEPA [e] | DMF | 0 | 93 |
| | BPHEPA | DMF | 0 | 38 |
| | 2-BPMPA | DMF | 3 | 3 |
| | 2-DPPA | DMF | 0 | 0 |
| | – | DMF | 0 | 45 |
| | 2-BPEPA | DMAC [f] | 54 | 10 |
| | 2-BPEPA | NMP [g] | 76 | 7 |
| **6b** | BIPA | DMF | 1 | 0 |
| | 2-BPEPA | DMF | 77, 71 [c] | 1 |
| | 2-BPEMPA | DMF | 82 | 0 |
| | 2-BPEHPA | DMF | 60 | trace |
| | 2-BPECPA | DMF | 78 | trace |
| | BPHEPA | DMF | 0 | 0 |
| | – | DMF | 0 | 0 |
| **6c** | BIPA | DMF | 0 | 0 |
| | 2-BPEPA | DMF | 70 | 0 |
| | 2-BPEMPA | DMF | 69 | 0 |
| | BPHEPA | DMF | 0 | 0 |
| | – | DMF | 0 | 0 |

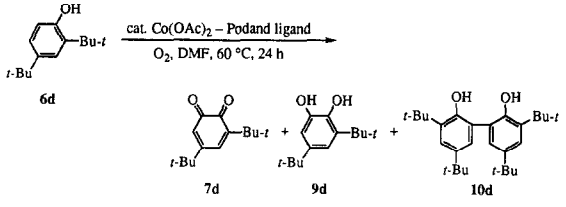
[a] $Co(OAc)_2$, 0.01 mmol; ligand, 0.01 mmol; **6**, 0.20 mmol.
[b] GLC yields based on **6**.
[c] Isolated yield.
[d] Use of the isolated complex.
[e] $Cu(OAc)_2$ was used instead of $Co(OAc)_2$.
[f] DMAC = *N*,*N*-dimethylacetamide.
[g] NMP = 1-methyl-2-pyrrolidinone.




(4)

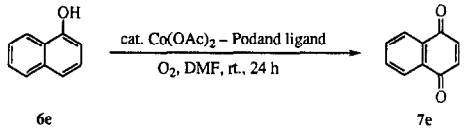
These results are in sharp contrast to the poor combination of $Co(OAc)_2$ and 2-BPEPA in the epoxidation reaction as mentioned above (Table 1). It should be noted that the oxygenation reactions are also effected by the podand ligands. The use of BIPA bearing the 4-imidazolyl group, which is effective in the $FeCl_2$-catalyzed epoxidation reaction with molecular oxygen, was found to drastically lower the conversion to **7a** with the predominant formation of **8a**. BPHEPA bearing the phenyl group instead was an inefficient ligand for the oxygenation to **7a**. Taking them into consideration, the 4-imidazolyl and 2-pyridyl groups are considered to play a respective important role in each oxygenation system possibly due to the difference of the coordination interaction. A more distinct difference was observed in the oxygenation of the less readily oxidizable phenol, 2,6-dimethylphenol (**6b**), to the quinone **7b**. Furthermore, the oxygenation of 2,3,5-trimethylphenol (**6c**) to **7c** was selectively accomplished only by the presence of 2-BPEPA. A combination of 2-BPMPA or 2-DPPA and $Co(OAc)_2$ was useless in the oxygenation reaction of **6a**. The shorter pendant group is considered to form no efficient complex catalyst. A substituent on the pyridyl ring of podand ligands is expected to effect the efficiency of a catalyst. 2-BPEMPA, bearing an electron-releasing methoxyl group, gave a better result than 2-BPEPA as shown in Table 5.

The phenol **6d** blocked at the para position underwent the selective $Co(OAc)_2$–2-BPEPA-catalyzed oxygenation to the *o*-benzoquinone **7d** (Eq. 5 and Table 6). BIPA and BPHEPA did not serve as a ligand either.




(5)

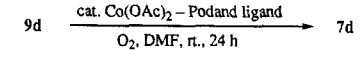
1-Naphthol (**6e**) similarly underwent the oxygenation to the *p*-quinone **7e** in the presence of $Co(OAc)_2$ and 2-BPEPA derivative although yields were not so high (Eq. 6).




(6)

Podand ligand : 2-BPEPA 36 %
2-BPEMPA 45 %
— 0 %

The facile dehydrogenation of 3,5-di-*t*-butylcatechol (**9d**) to **7d** was performed by the catalyst consisting of $Co(OAc)_2$ and 2-BPEPA or BIPA under the milder conditions (Eq. 7). This finding indicates that the introduction of the hydroxyl group is the rate-determining step in the oxygenation of **6** to **7**.




(7)

Podand ligand:

| | | | |
|---|---|---|---|
| BIPA | 96% | BPHEPA | 33% |
| 2-BPEPA | 93% | – | 34% |

The complexation of $Co(OAc)_2$ with 2-BPEPA was verified by the following observations. The new cobalt reversible reduction wave was observed at −0.07 V in cyclic voltamo-

Table 6
Catalytic oxidation 2,4-di-*t*-butylphenol [a]

| Ligand | Yield (%) [b] | | |
|---|---|---|---|
| | **7d** | **9d** | **10d** |
| BIPA | 0 | 0 | 9 |
| 2-BPEPA | 72, 69 [c] | 5 | trace |
| BPHEPA | 0 | 0 | 0 |
| 2-BPMPA | 0 | 0 | 0 |
| 2-DPPA | 0 | 0 | 0 |
| — | 0 | 0 | 0 |

[a] $Co(OAc)_2$, 0.01 mmol; ligand, 0.01 mmol; **6d**, 0.20 mmol.
[b] GLC yields based on **6d**.
[c] Isolated yield.

gram of $Co(OAc)_2$ with an equimolar amount of 2-BPEPA in methanol. This potential is reasonable for tyrosinase model catalysts [14]. The reduction potentials of the cobalt(II) complexes depend on the podand ligands possibly due to the difference of the coordination interaction. In the case of other podand ligands except 2-BPEPA, the reversible reduction wave was not observed, being consistent with the catalytic activity. A new absorption at 317 nm appeared in the UV–Vis spectrum of a solution of $Co(OAc)_2$ and 2-BPEPA in DMF, which also supports the complexation.

The cobalt complex was isolated by treatment of $Co(OAc)_2$ with an equimolar amount of 2-BPEPA in methanol. The higher catalytic activity was attained by use of the thus-isolated complex in the oxygenation of **6a** to **7a** (Table 5). The spectral data showed the substitution of cobalt with two amide moieties. It should be noted that two different kinds of the pyridylethyl protons were observed in $^1$H-NMR, indicating the different coordination of two podand 2-pyridyl groups. One of them is assumed to behave as an intramolecular axial ligand as proposed in the Fe(II)–BIPA complex. This coordination mode is likely to contribute to the efficiency of the complex catalyst.

## 3. Conclusion

The complexation of $FeCl_2$ with the flexible multidentate podand ligand, BIPA, is shown to permit the epoxidation reaction with molecular oxygen in the absence of a co-reductant. The coexistence of 4-ethoxycarbonyl-3-methyl-2-cyclohexen-1-one results in the facile epoxidation reaction with molecular oxygen under milder conditions. The cobalt(II) complex with 2-BPEPA serves as an efficient catalyst for the selective oxygenation of phenols to the corresponding quinones. A combination of *N*-heterocyclic podand ligands and transition metals is a critical factor to construct an efficient catalytic system for oxygenation based on the multidentate coordination interaction.

## 4. Experimental section

Melting points were measured using a Yanagimoto micromelting point apparatus. Infrared spectra were obtained with a Perkin Elmer Model 1605 FT-IR. $^1$H-NMR spectra were recorded using Bruker AM-600 (600 MHz), JEOL JNM-GSX-400 (400 MHz), and JEOL JNM-EX-270 (270 MHz) spectrometers with tetramethylsilane as an internal standard. UV–Vis spectra were recorded using a Hitachi U-3000. The fast atom bombardment mass spectra were recorded using a JEOL JMS-DX303HF spectrometer. Recycling preparative HPLC analysis was performed on a JAI LC-908 with synthetic polymer packed column (JAIGEL-1H and JAIGEL-2H). The standard electrochemical instrumentation consisting of a Hokuto Denko potentiostat/galvanostat HA-301S and a Hokuto Denko function generator HB-104S with a three-electrode system consisting of a glassy carbon working electrode, a platinum auxiliary electrode, and a KCl–saturated calomel reference electrode. Cyclic voltammograms were recorded with a Graphtec WX 1000.

### *4.1. General procedure for the synthesis of multidentate N-heterocyclic podand ligands*

2,6-Pyridinedicarboxylic acid (3.34 g, 20.0 mmol) was treated with thionyl chloride (11.9 g, 100 mmol) and benzene (9 ml) at 80°C for 35 h. Excess thionyl chloride and benzene were then removed under reduced pressure to give the crude acid chloride as a white solid. A solution of the thus-obtained acid chloride in dichloromethane (35 ml) was slowly added to a solution of the corresponding amine (40.0 mmol) and triethylamine (15.0 ml, 108 mmol) in dichloromethane (15 ml) at 0°C. The mixture was stirred at 0°C for 7 h and at room temperature for 17 h. In the case of BIPA, 3-DPPA, and DPHPA, the white precipitate was filtered off and was washed successively with dichloromethane, saturated $NaHCO_3$ aqueous solution, and water. In the case of 2-BPEPA,

BPHEPA, 2-BPMPA, and 2-DPPA, the resulting mixture was diluted with dichloromethane (30 ml), washed with saturated $NaHCO_3$ aqueous solution and brine, and dried over $MgSO_4$. The white solid was obtained by evaporation of the dichloromethane solution in vacuo. Recrystallization gave the pure product in both cases.

*4.1.1. N,N'-Bis{2-(4-imidazolyl)ethyl}-2,6-pyridinedicarboxamide (BIPA)*

A white needle (recrystallization from methanol); 92% yield; mp 118–119°C (uncorrected); $R_f = 0.29$ (chloroform–methanol v/v 1:1); IR (KBr) 3204 (NH), 1594 (C=O) $cm^{-1}$; $^1H$ NMR (400 MHz, $CD_3OD$) δ 8.24 (d, 1H, $J = 8.3$ Hz), 8.25 (d, 1H, $J = 7.1$ Hz), 8.13 (dd, 1H, $J = 8.3$, 7.1 Hz), 7.58 (d, 2H, $J = 1.1$ Hz), 6.87 (d, 2H, $J = 1.1$ Hz), 3.68 (t, 4H, $J = 7.5$ Hz), 2.94 (t, 4H, $J = 7.5$ Hz); MS (EI) $m/z$ 353 ($M^+$); Anal. Calcd for $C_{17}H_{19}N_7O_2 \cdot H_2O$: C, 54.98; H, 5.70; N, 26.40. Found: C, 54.90; H, 5.66; N, 26.52.

*4.1.2. N,N'-Bis{2-(2-pyridyl)ethyl}-2,6-pyridinedicarboxamide (2-BPEPA)*

A white needle (recrystallization from dichloromethane); 98% yield; mp 116–117°C (uncorrected); $R_f = 0.59$ (methanol); IR (KBr) 3343 (NH), 1672 (C=O) $cm^{-1}$; $^1H$ NMR (270 MHz, $CDCl_3$) δ 8.73 (br, 2H), 8.50 (ddd, 2H, $J = 4.9$, 1.6, 1.1 Hz), 8.32 (d, 1H, $J = 8.1$ Hz), 8.31 (d, 1H, $J = 7.5$ Hz), 8.00 (dd, 1H, $J = 8.1$, 7.5 Hz), 7.61 (dt, 2H, $J = 7.5$, 1.1 Hz), 7.21 (dt, 2H, $J = 7.5$, 1.1 Hz), 7.15 (ddd, 2H, $J = 7.5$, 4.9, 1.1 Hz), 3.93 (dt, 4H, $J = 6.2$, 6.2 Hz), 3.15 (t, 4H, $J = 6.2$ Hz); MS (EI) $m/z$ 375 ($M^+$); Anal. Calcd for $C_{21}H_{21}N_5O_2 \cdot 0.5H_2O$: C, 65.61; H,5.77; N, 18.22. Found: C, 65.90; H, 5.54; N, 18.26.

*4.1.3. N,N'-Bis(2-phenylethyl)-2,6-pyridinedicarboxamide (BPHEPA)*

A white plate (recrystallization from chloroform); 89% yield; mp 66–67°C (uncorrected); $R_f = 0.60$ (ethyl acetate); IR (KBr) 3308 (NH), 1640 (C=O) $cm^{-1}$; $^1H$ NMR (270 MHz, $CDCl_3$) δ 8.34 (d, 1H, $J = 8.1$ Hz), 8.33 (d, 1H, $J = 7.3$ Hz), 8.02 (dd, 1H, $J = 8.1$, 7.3 Hz), 7.49 (br, 2H), 7.36–7.22 (m, 10H), 3.73 (dt, 4H, $J = 7.0$, 7.0 Hz), 2.93 (t, 4H, $J = 7.0$ Hz); MS (EI) $m/z$ 373 ($M^+$); Anal. Calcd for $C_{23}H_{23}N_3O_2 \cdot H_2O$: C,70.57; H, 6.44; N, 10.73. Found: C, 70.64; H, 6.41; N, 10.65.

*4.1.4. N,N'-Bis{(2-pyridyl)methyl}-2,6-pyridinedicarboxamide (2-BPMPA)*

A white needle (recrystallization from dichloromethane); 98% yield; mp 151–153°C (uncorrected); $R_f = 0.28$ (ethyl acetate–methanol v/v 5:1); IR (KBr) 3305 (NH), 1676 (C=O) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 9.15 (br, 2H), 8.52 (ddd, 2H, $J = 4.9$, 1.8, 0.6 Hz), 8.37 (d, 2H, $J = 7.8$ Hz), 8.03 (t, 1H, $J = 7.8$ Hz), 7.69 (dt, 2H, $J = 7.7$, 1.8 Hz), 7.39 (dt, 2H, $J = 7.7$, 0.6 Hz), 7.21 (ddd, 2H, $J = 7.7$, 4.9, 0.6 Hz), 4.82 (d, 4H, $J = 5.9$ Hz); MS (EI) $m/z$ 347 ($M^+$); Anal. Calcd for $C_{19}H_{17}N_5O_2 \cdot 0.5H_2O$: C, 64.04; H, 5.09; N, 19.65. Found: C, 63.64; H, 5.00; N, 19.52.

*4.1.5. N,N'-Di-2-pyridyl-2,6-pyridinedicarboxamide (2-DPPA)*

A white needle (recrystallization from ethanol); 95% yield; mp 193–194°C (uncorrected); $R_f = 0.63$ (ethyl acetate); IR (KBr) 3300 (NH), 1700 (C=O) $cm^{-1}$; $^1H$ NMR (270 MHz, $CDCl_3$) δ 11.20 (br, 2H), 8.54 (dt, 2H, $J = 8.8$, 1.0 Hz), 8.53 (d, 1H, $J = 8.1$ Hz), 8.52 (d, 1H, $J = 7.6$ Hz), 8.40 (ddd, 2H, $J = 4.9$, 2.0, 1.0 Hz), 8.17 (dd, 1H, $J = 8.1$, 7.6 Hz), 7.82 (ddd, 2H, $J = 8.8$, 7.3, 2.0 Hz), 7.13 (ddd, 2H, $J = 7.3$, 4.9, 1.0 Hz); MS (EI) $m/z$ 319 ($M^+$); Anal. Calcd for $C_{17}H_{13}N_5O_2 \cdot H_2O$: C, 60.53; H, 4.48; N, 20.76. Found: C, 60.54; H, 4.39; N, 20.67.

*4.1.6. N,N'-Di-3-pyridyl-2,6-pyridinedicarboxamide (3-DPPA)*

A white plate (recrystallization from ethanol); 99% yield; mp 245–246°C (uncorrected); $R_f = 0.34$ (ethyl acetate–methanol v/v 5:1); IR (KBr) 3256 (NH), 1692 (C=O) $cm^{-1}$; $^1H$ NMR (270

MHz, $CD_3OD$) δ 9.19 (m, 2H), 8.67 (d, 1H, $J = 8.3$ Hz), 8.66 (d, 1H, $J = 7.3$ Hz), 8.57–8.52 (m, 4H), 8.45 (dd, 1H, $J = 8.3$, 7.3 Hz), 7.71–7.67 (m, 2H); MS (EI) $m/z$ 319 ($M^+$); Anal. Calcd for $C_{17}H_{13}N_5O_2$: C, 63.95; H, 4.10; N, 21.93. Found: C, 63.74; H, 4.02; N, 21.84.

*4.1.7. N,N'-Diphenyl-2,6-pyridinedicarboxamide (DPHPA)*

A white solid; 98% yield; mp 285–286°C (uncorrected); $R_f = 0.71$ (ethyl acetate); IR (KBr) 3276 (NH), 1662 (C=O) $cm^{-1}$; $^1H$ NMR (270 MHz, $CDCl_3$) δ 11.14 (br, 2H), 8.52 (d, 1H, $J = 7.5$ Hz), 8.51 (d, 1H, $J = 6.2$ Hz), 8.41 (dd, 1H, $J = 7.5$, 6.2 Hz), 8.03 (dd, 4H, $J = 7.5$, 1.1 Hz), 7.56 (t, 4H, $J = 7.5$ Hz), 7.30 (dd, 2H, $J = 7.5$, 1.1 Hz); MS (EI) $m/z$ 317 ($M^+$); Anal. Calcd for $C_{19}H_{15}N_3O_2$: C, 71.91; H, 4.76; N, 13.24. Found: C, 71.81; H, 4.71; N, 13.23.

*4.2. Synthesis of N,N'-bis{2-(2-pyridyl)ethyl}-4-hydroxy-2,6-pyridinedicarboxamide (2-BPEHPA) and N,N'-bis{2-(2-pyridyl)ethyl}-4-chloro-2,6-pyridinedicarboxamide (2-BPECPA)*

A mixture of chelidamic acid (2.20 g, 12.0 mmol) and thionyl chloride (94.6 g, 795 mmol) was heated at reflux temperature for 48 h. Excess thionyl chloride was then removed under reduced pressure to give the crude acid chloride as a white solid. A solution of the thus-obtained acid chloride in dichloromethane (35 ml) was slowly added to a solution of 2-(2-aminoethyl)pyridine (2.9 g, 24 mmol) and triethylamine (7.0 ml, 50 mmol) in dichloromethane (15 ml) at 0°C. The mixture was stirred at 0°C for 4 h and at room temperature for 40 h. The resulting mixture was diluted with dichloromethane (30 ml), washed with saturated $NaHCO_3$ aqueous solution and brine, and dried over $MgSO_4$. The white solid was obtained by evaporation of the dichloromethane solution in vacuo. 2-BPEHPA and 2-BPECPA were isolated in 22% and 16% yields, respectively, by recycling preparative HPLC eluting with chloroform and recrystallized from dichloromethane.

*4.2.1. 2-BPEHPA*

A white plate; mp 101–103°C (uncorrected); $R_f = 0.45$ (ethyl acetate–methanol v/v 5:1); IR (KBr) 3312 (NH), 1661 (C=O) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.86 (br, 2H), 8.45 (ddd, 2H, $J = 5.0$, 1.8, 1.0 Hz), 7.61 (s, 2H), 7.59 (dt, 2H, $J = 7.8$, 1.8 Hz), 7.21 (dt, 2H, $J = 7.8$, 1.0 Hz), 7.11 (ddd, 2H, $J = 7.8$, 5.0, 1.0 Hz), 3.81 (dt, 4H, $J = 6.4$, 6.4 Hz), 3.13 (t, 4H, $J = 6.4$ Hz); MS (EI) $m/z$ 391 ($M^+$); Anal. Calcd for $C_{21}H_{21}N_5O_3 \cdot H_2O$: C, 61.60; H, 5.66; N, 17.11. Found: C, 61.20; H, 5.62; N, 17.00.

*4.2.2. 2-BPECPA*

A white–yellow needle; mp 164–166°C (uncorrected); $R_f = 0.47$ (ethyl acetate–methanol v/v 5:1); IR (KBr) 3259 (NH), 1664 (C=O) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.78 (br, 2H), 8.49 (ddd, 2H, $J = 5.0$, 1.8, 0.9 Hz), 8.30 (s, 2H), 7.63 (dt, 2H, $J = 7.7$, 1.8 Hz), 7.22 (dt, 2H, $J = 7.7$, 0.9 Hz), 7.16 (ddd, 2H, $J = 7.7$, 5.0, 0.9 Hz), 3.93 (dt, 4H, $J = 6.5$, 6.5 Hz), 3.15 (t, 4H, $J = 6.5$ Hz); MS (EI) $m/z$ 409 ($M^+$); Anal. Calcd for $C_{21}H_{20}N_5O_2Cl$: C, 61.54; H, 4.92; N, 17.09. Found: C, 61.63; H, 5.06; N, 17.04.

*4.3. Synthesis of N,N'-bis{2-(2-pyridyl)ethyl}-4-methoxy-2,6-pyridinedicarboxamide (2-BPEMPA)*

To a solution of 2-BPECPA (0.408 g, 1.0 mmol) in methanol (50 ml) was added a solution of NaOH (0.623 g, 15.0 mmol) in methanol at room temperature. The mixture was stirred at 50°C for 48 h and at reflux temperature for 3 h. The mixture was extracted with dichloromethane (20 ml) and dried over $MgSO_4$. The white solid was obtained by evaporation of the dichloromethane solution in vacuo. 2-BPEMPA was isolated in 59% yield by recycling preparative HPLC eluting with chloroform and recrystallized from dichloromethane.

*4.3.1. 2-BPEMPA*

A white needle; mp 95–97°C (uncorrected); $R_f = 0.38$ (ethyl acetate–methanol v/v 5:1); IR (KBr) 3296 (NH), 1656 (C=O) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.71 (br, 2H), 8.51 (ddd, 2H, $J = 4.9$, 1.8, 1.1 Hz), 7.82 (s, 2H), 7.62 (dt, 2H, $J = 7.7$, 1.8 Hz), 7.22 (dt, 2H, $J = 7.7$, 1.1 Hz), 7.16 (ddd, 2H, $J = 7.7$, 4.9, 1.1 Hz), 3.96 (s, 3H), 3.92 (dt, 4H, $J = 6.4$, 6.4 Hz), 3.15 (t, 4H, $J = 6.4$ Hz); MS (EI) $m/z$ 405 ($M^+$); Anal. Calcd for $C_{22}H_{23}N_5O_3 \cdot H_2O$: C, 62.40; H, 5.95; N, 16.54. Found: C, 62.29; H, 5.81; N, 16.70.

*4.4. Synthesis of 3-pyridyl-2-pyridinecarboxamide (3-PPA)*

Picolinic acid (2.46 g, 20.0 mmol) was treated with thionyl chloride (5.9 g, 50 mmol) in benzene (4.5 ml) at 80°C for 35 h. Excess thionyl chloride and benzene were then removed under reduced pressure to give the crude acid chloride as a white solid. A solution of the thus-obtained acid chloride in dichloromethane (35 ml) was slowly added to a solution of 3-aminopyridine (1.88 g, 20.0 mmol) and triethylamine (10 ml, 72 mmol) in dichloromethane (15 ml) at 0°C. The mixture was stirred at 0°C for 7 h and at room temperature for 17 h. The resulting mixture was diluted with dichloromethane (30 ml), washed with saturated $NaHCO_3$ aqueous solution and brine, and dried over $MgSO_4$. The white solid was obtained by evaporation of the dichloromethane solution in vacuo. 3-PPA was isolated in 78% yield as a white needle by recrystallization from dichloromethane.

*4.4.1. 3-PPA*

A white needle; mp 82–83°C (uncorrected); $R_f = 0.31$ (ethyl acetate); IR (KBr) 3336 (NH), 1682 (C=O) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 10.10 (br, 1H), 8.84 (d, 1H, $J = 2.7$ Hz), 8.65 (ddd, 1H, $J = 4.8$, 1.7, 1.1 Hz), 8.43–8.40 (m, 2H), 8.31 (dt, 1H, $J = 7.8$, 1.1 Hz), 7.95 (dt, 1H, $J = 7.8$, 1.7 Hz), 7.53 (ddd, 1H, $J = 7.8$, 4.8, 1.1 Hz), 7.35 (dd, 1H, $J = 7.8$, 4.8 Hz); MS (EI) $m/z$ 199 ($M^+$); Anal. Calcd for $C_{11}H_9N_3O$: C, 66.32; H, 4.55; N, 21.09. Found: C, 66.21; H, 4.42; N, 21.15.

*4.5. Isolation of Co–2-BPEPA complex*

A mixture of 2-BPEPA (37.5 mg, 0.1 mmol) and $Co(OAc)_2$ (17.7 mg, 0.1 mmol) in methanol (1.0 ml) was stirred under nitrogen at room temperature for 24 h. After evaporation of the methanol solution in vacuo, the complex was separated in 76% yield by chromatography on a silica gel column eluting with methanol.

*4.5.1. Co–2-BPEPA complex*

A brown plate (recrystallization from methanol); mp 205–207°C (uncorrected); $R_f = 0.08$ (chloroform–methanol v/v 1:1); IR (KBr) 3396 (OH), 1594 (C=O) $cm^{-1}$; $^1H$ NMR (600 MHz, $CD_3OD$) δ 9.57 (dd, 1H, $J = 5.9$, 1.5 Hz), 8.33 (t, 1H, $J = 7.8$ Hz), 8.15 (dd, 1H, $J = 7.8$, 0.9 Hz), 8.11 (dt, 1H, $J = 7.7$, 1.5 Hz), 8.01 (dd, 1H, $J = 5.9$, 1.5 Hz), 7.90 (dd, 1H, $J = 7.8$, 0.9 Hz), 7.72 (ddd, 1H, $J = 7.7$, 5.9, 0.9 Hz), 7.71 (dt, 1H, $J = 7.7$, 1.5 Hz), 7.56 (dd, 1H, $J = 7.7$, 0.9 Hz), 7.25 (dd, 1H, $J = 7.7$, 0.9 Hz), 7.14 (ddd, 1H, $J = 7.7$, 5.9, 0.9 Hz), 4.2–4.1 (m, 2H), 4.07 (dd, 1H, $J = 13.1$, 9.0 Hz), 3.27 (dt, 1H, $J = 14.3$, 2.6 Hz), 3.16 (dt, 1H, $J = 14.3$, 2.6 Hz), 3.00 (dd, 1H, $J = 15.0$, 6.4 Hz), 2.47 (ddd, 1H, $J = 15.0$, 11.9, 9.0 Hz), 2.18 (dt, 1H, $J = 14.3$, 4.0 Hz); $^{13}C$ NMR (150 MHz, $CD_3OD$) δ 172.0, 171.7, 165.1, 163.1, 158.2, 157.0, 151.7, 142.0, 141.5, 141.1, 128.9, 127.2, 125.4, 125.2, 125.0, 124.5, 41.5, 40.5, 37.4, 36.7; MS (FAB) $m/z$ 433 ($M^+ + 1$); UV–Vis 317 nm ([Co–2–BPEPA complex] = $4.0 \times 10^{-4}$ M, solv. DMF, under nitrogen); cyclic voltammetry $E_p = -0.07$ V vs. SCE ([Co–2-BPEPA complex] = $2.0 \times 10^{-3}$ M, [$Bu_4NClO_4$] = 0.1 M, solv. methanol, scan rate = 50 mV/s). This complex was diamagnetic. The further characterization with a UV–Vis spectrum was unsuccessful to elucidate the proper cobalt species.

### 4.6. General procedure for the epoxidation of olefins

A mixture of a metal salt (0.02 mmol) and podand ligand (0.02 mmol) in DMF (0.8 ml) was stirred in a glass vessel under nitrogen at room temperature for 24 h. After the addition of an olefin (2.0 mmol) in DMF (0.2 ml) to the resulting solution, the vessel was put in a stainless steel autoclave. The epoxidation reaction was carried out under molecular oxygen ($1.0 \times 10^3$ kPa) at 70°C for 24 h (the conditions are safety in a laboratory level). The mixture was diluted with ether (30 ml), washed with 1.5 M HCl solution and brine, dried over $MgSO_4$, and concentrated. The formation of products was detected by $^1$H-NMR and GLC (Tables 1–3). Melting points and spectral data for the products were identical with those of commercially available samples.

#### 4.6.1. 1-Phenyl-1,2-propanedione (3)

Bp 101–103°C/14 mm; IR (neat) 1716 (MeC=O), 1677 (PhC=O) $cm^{-1}$; $^1$H NMR (270 MHz, $CDCl_3$) δ 8.02 (d, 2H, $J = 7.6$ Hz), 7.65 (t, 1H, $J = 7.6$ Hz), 7.50 (t, 2H, $J = 7.6$ Hz), 2.53 (s, 3H); MS (EI) $m/z$ 148 ($M^+$).

### 4.7. Epoxidation of olefins in the presence of 4-ethoxycarbonyl-3-methyl-2-cyclohexen-1-one

To a mixture of an olefin (1.0 mmol) and BIPA (3.53 mg, 0.01 mmol) was added $FeCl_2$ (1.27 mg, 0.01 mmol) in DMF (0.8 ml), and then the resulting mixture was stirred under nitrogen at room temperature for 24 h. 4-Ethoxycarbonyl-3-methyl-2-cyclohexen-1-one (**5**) (0.10–1.00 mmol) was added to the resultant mixture. The reaction vessel was refilled with molecular oxygen. The mixture was stirred under an atmospheric pressure of molecular oxygen at 50°C for 24 h. The mixture was diluted with ether (30 ml), washed with 1.5 M HCl solution and brine, dried over $MgSO_4$, and concentrated. The formation of products was detected by $^1$H-NMR and GLC (Table 4). Melting points and spectral data for the products were identical with those of commercially available samples.

### 4.8. General procedure for the oxygenation of phenols

To a mixture of the phenol **6** (0.2 mmol) and the podand ligand (0.01 mmol) was added $Co(OAc)_2$ (1.77 mg, 0.01 mmol) in DMF (0.2 ml) under nitrogen at room temperature. The reaction vessel was refilled with molecular oxygen. The resulting mixture was stirred under an atmospheric pressure of molecular oxygen at 60°C for 24 h. The mixture was diluted with ether (30 ml), washed with 1.5 M HCl solution and brine, and dried over $MgSO_4$. GLC analysis (1.0 m, 10% SE-30 column, 50–250°C) of the concentrated residue showed the formation of **7–10** (Tables 5 and 6). The quinone **7** was isolated by chromatography on a silica gel column eluting with hexane. Melting points and spectral data for the products were identical with those of authentic samples [3](a),[5](a).

#### 4.8.1. 2,6-Di-t-butyl-1,4-benzoquinone (7a)

A yellow needle (recrystallization from ether); mp 65–66°C (uncorrected); $R_f = 0.40$ (hexane–chloroform v/v 1:1); IR (KBr) 1654 (C=O) $cm^{-1}$; $^1$H NMR (600 MHz, $(CD_3)_2CO$) δ 6.49 (s, 2H), 1.29 (s, 18H); MS (EI) $m/z$ 220 ($M^+$) [3](a).

#### 4.8.2. 3,3',5,5'-Tetra-t-butyldiphenoquinone (8a)

A red–brown prism (recrystallization from ether); mp 242–243°C (uncorrected); $R_f = 0.55$ (hexane–chloroform v/v 1:1); IR (KBr) 1608 (C=O) $cm^{-1}$; $^1$H NMR (600 MHz, $(CD_3)_2CO$) δ 7.87 (s, 4H), 1.34 (s, 36H); MS (EI) $m/z$ 408 ($M^+$) [3](a).

#### 4.8.3. 2,6-Dimethyl-1,4-benzoquinone (7b)

A yellow needle (recrystallization from ether); mp 70–72°C (uncorrected); $R_f = 0.25$ (hexane–chloroform v/v 1:4); IR (KBr) 1656 (C=O) $cm^{-1}$; $^1$H NMR (600 MHz, $(CD_3)_2CO$)

δ 6.59 (s, 2H), 2.02 (s, 6H); MS (EI) *m/z* 136 ($M^+$) [3](a).

*4.8.4. 3,3',5,5'-Tetramethyldiphenoquinone (**8b**)*

A red–violet needle (recrystallization from ether); mp 208–210°C (uncorrected); $R_f = 0.10$ (hexane–chloroform v/v 1:4); IR (KBr) 1594 (C=O) $cm^{-1}$; $^1H$ NMR (600 MHz, $(CD_3)_2CO$) δ 8.09 (s, 4H), 2.08 (s, 12H); MS (EI) *m/z* 240 ($M^+$) [3](a).

*4.8.5. 2,3,5-Trimethyl-1,4-benzoquinone (**7c**)*

A yellow needle (recrystallization from ether); mp 29–30°C (uncorrected); $R_f = 0.40$ (chloroform); IR (KBr) 1650 (C=O) $cm^{-1}$; $^1H$ NMR (600 MHz, $CDCl_3$) δ 6.56 (s, 1H), 2.04 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H); MS (EI) *m/z* 150 ($M^+$) [3](a).

*4.8.6. 3,5-Di-t-butyl-1,2-benzoquinone (**7d**)*

A red brown prism (recrystallization from ether); mp 113–114°C (uncorrected); $R_f = 0.35$ (chloroform); IR (KBr) 1656 (C=O) $cm^{-1}$; $^1H$ NMR (600 MHz, $(CD_3)_2CO$) δ 7.10 (d, 1H, $J = 2.3$ Hz), 6.14 (d, 1H, $J = 2.3$ Hz), 1.27 (s, 9H), 1.25 (s, 9H); MS (EI) *m/z* 222 ($M^+ + 2$), 220 ($M^+$) [5](a).

*4.8.7. 3,3',5,5'-Tetra-t-butyl-2,2-dihydroxybiphenyl (**10d**)*

A yellow needle (recrystallization from ether); mp 188–190°C (uncorrected); $R_f = 0.75$ (chloroform); IR (KBr) 3540 (OH) $cm^{-1}$; $^1H$ NMR (600 MHz, $(CD_3)_2CO$) δ 7.38 (d, 2H, $J = 2.4$ Hz), 7.09 (d, 2H, $J = 2.4$ Hz), 1.46 (s, 18H), 1.32 (s, 18H); MS (EI) *m/z* 410 ($M^+$) [5](a).

*4.9. Oxygenation of 1-naphthol (**6e**)*

To a mixture of 1-naphthol (**6e**, 28.8 mg, 0.2 mmol) and a podand ligand (0.01 mmol) was added $Co(OAc)_2$ (1.77 mg, 0.01 mmol) in DMF (0.2 ml) under nitrogen at room temperature. The reaction vessel was refilled with molecular oxygen. The resulting mixture was stirred under an atmospheric pressure of molecular oxygen at room temperature for 24 h. The mixture was diluted with ether (30 ml), washed with 1.5 M HCl solution and brine, and dried over $MgSO_4$. GLC analysis (1.0 m, 10% OV-17 column, 50–250°C) of the concentrated residue showed the formation of **7e** (Eq. 6). The quinone **7e** was isolated by chromatography on a silica gel column eluting with hexane. Melting point and spectral data were identical with those of the authentic sample [4](b).

*4.9.1. 1,4-Naphthoquinone (**7e**)*

A yellow needle (recrystallization from ether); mp 120–121°C (uncorrected); $R_f = 0.45$ (chloroform); IR (KBr) 1661 (C=O) $cm^{-1}$; $^1H$ NMR (600 MHz, $CDCl_3$) δ 8.11 (dd, 2H, $J = 5.8$, 3.4 Hz), 7.78 (dd, 2H, $J = 5.8$, 3.4 Hz), 7.63 (s, 2H); MS (EI) *m/z* 158 ($M^+$) [4](b).

*4.10. Dehydrogenation of 3,5-di-t-butylcatechol (**9d**)*

To a mixture of the 3,5-di-*t*-butylcatechol (**9d**, 44.4 mg, 0.2 mmol) and the podand ligand (0.01 mmol) was added $Co(OAc)_2$ (1.77 mg, 0.01 mmol) in DMF (0.2 ml) under nitrogen at room temperature. The reaction vessel was refilled with molecular oxygen. The resulting mixture was stirred under an atmospheric pressure of molecular oxygen at room temperature for 24 h. The mixture was diluted with ether (30 ml), washed with 1.5 M HCl solution and brine, and dried over $MgSO_4$. GLC analysis (1.0 m, 10% SE-30 column, 50–250°C) of the concentrated residue showed the formation of **7d** (Eq. 7). The quinone **7d** was isolated by chromatography on a silica gel column eluting with hexane.

*4.11. UV–Vis spectra*

UV–Vis spectra were taken under nitrogen at 30°C after treatment of a metal salt and a podand ligand in DMF at room temperature for 24 h.

### 4.12. Electrochemical experiments

Cyclic voltammograms were obtained in methanol solution containing 0.1 M $Bu_4NClO_4$ as a supporting electrolyte.

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