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Catalytic and asymmetric epoxidation by novel D_4-symmetric chiral porphyrin derived from C_2-symmetric diol

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Abstract

Novel D_4-symmetric chiral porphyrin **1c** was efficiently prepared by utilizing C_2-symmetric diol as the chiral source. Asymmetric epoxidation of styrene and *trans*-β-methylstyrene by the **1c**–Fe(Br)/PhIO system showed moderate enantioselectivity, and enantiomeric excesses were markedly increased by the introduction of electron-withdrawing groups at the aromatic rings of styrenes.

Keywords: D_4-symmetric chiral porphyrin; Asymmetric epoxidation

1. Introduction

Metalloporphyrins are of great interest as oxidation catalysts, e.g. for epoxidation or hydroxylation. Since application of chiral metalloporphyrins to asymmetric epoxidation was first reported in 1983 [1], many chiral porphyrins designed to catalyze asymmetric reactions have been synthesized [2-44]. Among these porphyrins, D_4-symmetric porphyrins [32–44] have several advantages: (1) as many as 8 *o*-positions of the *meso*-phenyl groups can be used to control the reaction; (2) separation of atropisomers is not required; (3) some reported chiral porphyrins require the addition of a large amount of ligand so as to prevent the reaction proceeding at an unfavorable site [29–31], but both surfaces of a D_4-symmetric porphyrin ring can be modified together to afford favorable reactive sites. Some D_4-symmetric metalloporphyrins have been reported to exhibit high enantioselectivity, but these porphyrins were prepared in low total yields or in many steps, so an efficient synthetic method for D_4-symmetrical porphyrins is still required for development of useful catalysts for stereospecific oxidation. We report here novel D_4-symmetric chiral porphyrin which can be easily synthesized in a few steps with high yield and the asymmetric epoxidation of aromatic olefins by this porphyrin catalyst.

2. Experimental

2.1. Syntheses of porphyrins *1a*, *1b* and *1c*

2.1.1. Preparation of (R,R)-2,3-butanediol cyclic sulfate (*2a*)

$SOCl_2$ (5.1 mL, 69 mmol) was added dropwise to a solution of (*R,R*)-2,3-butanediol (5.0 g, 50 mmol) in CCl_4 (39 mL) and this mixture was refluxed for 2 h. CCl_4 and the excess reactant were removed by evaporation and the residue was dissolved in CCl_4:CH_3CN:H_2O = 1:1:1.5 (138 mL). The solution was cooled to 0 °C, $RuCl_3$ (79 mg, 0.38 mmol) and $NaIO_4$ (24 g, 0.20 mol) were added, and the mixture was stirred for 2.5 h at 0 °C. The reaction mixture was poured into water and extracted with Et_2O. The organic layer was dried with Na_2SO_4 and passed through a short silica gel column to remove black material. Evaporation of the solvent afforded **2a** as a colorless oil (8.3 g, 54 mmol, 98% yield); ^{1}H NMR ($CDCl_3$) δ 1.32 (6H, d,

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J = 6.1 Hz), 4.68 (2H, m); ^{13}C NMR ($CDCl_3$) δ 16.4, 85.2.

*2.1.2. Preparation of (S,S)-2,3-hexanediol cyclic sulfate (**2b**)*

Prepared by the same method as **2a** (91% yield, colorless oil); ^{1}H NMR ($CDCl_3$) δ 1.10 (6H, t, J = 7.4 Hz), 1.84 (4H, m), 4.53 (2H, m); ^{13}C NMR ($CDCl_3$) δ 9.4, 25.2, 88.2.

*2.1.3. Preparation of (S,S)-1,4-dimethoxy-2,3-butanediol cyclic sulfate (**2c**)*

Prepared by the same method as **2a** (98% yield, colorless oil); ^{1}H NMR ($CDCl_3$) δ 3.34 (6H, s), 3.74 (4H, m), 4.91 (2H, m); ^{13}C NMR ($CDCl_3$) δ 59.7, 69.9, 81.5.

*2.1.4. Preparation of (S,S,S,S)-2,3,6,7-tetramethyl-1,4,5,8-tetraoxa-1,2,3,4,5,6,7,8-octahydroanthracene (**3a**)*

Air dissolved in Cs_2CO_3 (36 g, 0.11 mol)-containing DMF (450 mL) was purged with argon gas for 30 min, and 1,2,4,5-tetrahydroxybenzene [45] (1.9 g, 14 mmol) and cyclic sulfate **2a** (5.0 g, 33 mmol) were added. The mixture was refluxed for 7 h under an argon atmosphere and then poured into ice-water. The aqueous solution was extracted with EtOAc and the organic layer was washed with water and dried with Na_2SO_4. The solvent was evaporated and purification of the residue by silica gel column chromatography (CH_2Cl_2:*n*-hexane) afforded **3a** (1.2 g, 5.0 mmol, 36% yield). The product was recrystallized from $CHCl_3$ to give colorless needles; mp 224–225 °C; ^{1}H NMR ($CDCl_3$) δ 1.24 (12H, d, J = 6.0 Hz), 3.71 (4H, m), 6.32 (2H, s); ^{13}C NMR ($CDCl_3$) δ 17.1, 74.3, 104.3, 137.4; MS (EI+) *m*/*z* (relative intensity) 166 (53), 167 (11), 195 (34), 196 (11), 250 (100), 251 (15); Anal. Calcd for $C_{14}H_{18}O_4$: C 67.18%, H 7.25%, Found: C 66.90%, H 7.29%; $[\alpha]_d^{20}$ −150.7 (c 0.010, $CHCl_3$).

*2.1.5. Preparation of (R,R,R,R)-2,3,6,7-tetraethyl-1,4,5,8-tetraoxa-1,2,3,4,5,6,7,8-octahydroanthracene (**3b**)*

Prepared by the same method as **3a** except that 1-methyl-2-pyrrolidone was used as the solvent (1.6 g, 5.1 mmol, 35% yield). Recrystallization from methanol gave colorless needles; mp 66–67 °C; ^{1}H NMR ($CDCl_3$) δ 1.04 (12H, t, J = 7.3 Hz), 1.69 (8H, m), 3.72 (4H, m), 6.39 (2H, s); ^{13}C NMR ($CDCl_3$) δ 9.2, 24.0, 76.8, 104.5, 136.8; MS (EI+) *m*/*z* (relative intensity) 142 (47), 224 (50), 306(100), 307(20); Anal. Calcd for $C_{18}H_{26}O_4$ C 70.56%, H 8.55%, Found C 70.31%, H 8.57%; $[\alpha]_d^{20}$ +161.4 (c 0.010, $CHCl_3$).

*2.1.6. Preparation of (R,R,R,R)-2,3,6,7-tetramethoxymethyl-1,4,5,8-tetraoxa-1,2,3,4,5,6,7,8-octahydro-anthracene (**3c**)*

Prepared by the same method as **3a** except that 1-methyl-2-pyrrolidone was used as the solvent (33% yield). Recrystallization from *n*-hexane gave colorless needles; mp 96–97 °C; ^{1}H NMR ($CDCl_3$) δ 3.41 (12H, s), 3.67 (8H, m), 4.15 (4H, m), 6.49 (2H, s); ^{13}C NMR ($CDCl_3$) δ 59.5, 71.2, 73.1, 105.0, 136.8; MS (EI+) *m*/*z* (relative intensity) 370 (100), 371 (21); Anal. Calcd for $C_{18}H_{26}O_8$: C 58.37%, H 7.08%, Found: C 58.20%, H 7.04%; $[\alpha]_d^{20}$ +76.6 (c 0.010, $CHCl_3$).

*2.1.7. Preparation of (S,S,S,S)-9-formyl-2,3,6,7-tetramethyl-1,4,5,8-tetraoxa-1,2,3,4,5,6,7,8-octahydro-anthracene (**4a**)*

A solution of **3a** (1.3 g, 5.4 mmol) in CH_2Cl_2 (40 mL) was cooled to −78 °C under an argon atmosphere. $TiCl_4$ (1.2 mL, 11 mmol) and dichloromethyl methyl ether (0.53 mL, 5.8 mmol) were sequentially added dropwise via a syringe and the reaction mixture was stirred at 0 °C for 2 h. The reaction mixture was poured into ice-water and extracted with CH_2Cl_2. The organic layer was washed with saturated $NaHCO_3$ aqueous solution and brine, and dried with Na_2SO_4. The solvent was evaporated and purification of the residue by silica gel column chromatography (CH_2Cl_2) afforded **4a** as yellow solid (1.4 g, 5.1 mmol, 96% yield); ^{1}H NMR ($CDCl_3$) δ 1.33 (6H, d, J = 6.0 Hz), 1.38 (6H, d, J = 6.0 Hz), 3.85 (4H, m), 6.63 (1H, s), 10.42 (1H, s); ^{13}C NMR ($CDCl_3$) δ 16.9, 17.0, 74.0, 74.7, 110.7, 113.3, 136.8, 139.3, 188.3.

*2.1.8. Preparation of (R,R,R,R)-9-formyl-2,3,6,7-tetraethyl-1,4,5,8-tetraoxa-1,2,3,4,5,6,7,8-octahydroanthracene (**4b**)*

Prepared by the same method as **4a** (93% yield, colorless solid); ^{1}H NMR ($CDCl_3$) δ 1.05 (6H, t, J = 7.5 Hz), 1.09 (6H, t, J = 7.5 Hz), 1.72 (8H, m), 3.81 (4H, m), 6.65 (1H, s), 10.45 (1H, s); ^{13}C NMR ($CDCl_3$) δ 9.1, 9.4, 23.9, 24.0, 77.4, 111.0, 113.8, 136.3, 138.8, 188.0.

*2.1.9. Preparation of (R,R,R,R)-9-formyl-2,3,6,7-tetramethoxymethyl-1,4,5,8-tetraoxa-1,2,3,4,5,6,7,8-octahydroanthracene (**4c**)*

A solution of **3c** (2.0 g, 5.4 mmol) in CH_2Cl_2 (114 mL) was cooled to 0 °C under an argon atmosphere. $SnCl_4$ (1.3 mL, 11 mmol) and dichloromethyl methyl ether (0.59 mL, 6.5 mmol) were sequentially added dropwise via a syringe and the reaction mixture was refluxed for 2 h. The reaction mixture was poured into ice-water and extracted with CH_2Cl_2. The organic layer was washed with saturated $NaHCO_3$ aqueous solution and brine, and dried with Na_2SO_4. The solvent was evaporated and purification of the residue by silica gel column chromatography (EtOAc:*n*-hexane) afforded **4c** as a yellow solid (1.9 g, 4.7 mmol, 86% yield); ^{1}H NMR ($CDCl_3$) δ 3.42 (6H, s), 3.43 (6H, s), 3.70 (4H, m), 3.74 (4H, m), 4.22 (4H, m), 6.76 (1H, s), 10.43 (1H, s); ^{13}C NMR ($CDCl_3$) δ 59.5, 59.7, 71.0, 71.1, 73.0, 73.6, 111.4, 113.7, 136.5, 139.0, 187.8.

*2.1.10. Preparation of 5,10,15,20-tetrakis((S,S,S,S)-2,3,6,7-tetramethyl-1,4,5,8-tetraoxa-1,2,3,4,5,6,7,8-octahydroanthracen-9-yl)porphyrin (**1a**)*

A solution of the aldehyde **4a** (2.0 g, 7.2 mmol) in $CHCl_3$ (713 mL) was purged with argon gas for 30 min. Under an

argon atmosphere, boron trifluoride diethyl etherate (0.30 mL, 2.4 mmol) and then pyrrole (0.50 mL, 7.2 mmol) were added slowly via a syringe and the mixture was stirred for 1 h. Chloranil (1.3 g, 5.4 mmol) was added to the mixture and the reaction was refluxed for another 1 h. Then the reaction mixture was cooled to room temperature and triethylamine (0.33 mL) and a pad of silica gel were added. The mixture was evaporated to dryness and passed through a short silica gel column (EtOAc). Purification by preparative HPLC (CH_3CN) afforded **1a** as a brown solid (20 mg, 15 μmol, <1% yield), which could not be purified adequately;[1] ^{1}H NMR ($CDCl_3$) δ −2.62 (2H, bs), 0.59 (24H, d, $J = 6.2$ Hz), 1.31 (24H, d, $J = 6.4$ Hz), 3.72 (8H, m), 3.92 (8H, m), 6.87 (4H, s), 8.82 (8H, s); LRMS (FAB, 3-nitrobenzyl alcohol) *m*/*z* (relative intensity) 1304 (100), 1305 (66).

*2.1.11. Preparation of 5,10,15,20-tetrakis((R,R,R,R)-2,3,6,7-tetraethyl-1,4,5,8-tetraoxa-1,2,3,4,5,6,7,8-octahydroanthracen-9-yl)porphyrin (**1b**)*

Prepared by the same method as **1a**. A suspected peak of the product was detected by HPLC, but the product could not be characterized fully because of the poor yield (see footnote 1).

*2.1.12. Preparation of 5,10,15,20-tetrakis((R,R,R,R)-2,3,6,7-tetramethoxymethyl-1,4,5,8-tetraoxa-1,2,3,4,5,6,7,8-octahydroanthracen-9-yl)porphyrin (**1c**)*

Prepared by the same method as **1a**. Purification was carried out by preparative TLC (EtOAc:*n*-hexane) and **1c** was obtained as a brown solid (37% yield); ^{1}H NMR ($CDCl_3$) δ −2.71 (2H, bs), 2.66 (24H, s), 3.04 (8H, dd, $J = 4.6$ Hz, 11.1 Hz), 3.16 (8H, dd, $J = 3.7$ Hz, 11.0 Hz), 3.41 (24H, s), 3.71 (16H, d, $J = 4.4$ Hz), 3.97 (8H, m), 4.31 (8H, m), 7.02 (4H, s), 8.78 (8H, s); ^{13}C NMR ($CDCl_3$) δ 59.0, 59.5, 70.5, 71.4, 73.1, 73.2, 105.6, 106.9, 108.7, 109.2, 120.2, 136.7, 137.7; MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* (relative intensity) 1783 (100), 1784 (32); HRMS (FAB, 3-nitrobenzyl alcohol) Calcd for $C_{92}H_{110}N_4O_{32}$: 1782.7103, Found: 1782.6995; UV (CH_3CN) λ_{max} 415 nm ($\varepsilon = 239000\ cm^{-1}\ M^{-1}$), 510 (17000), 584 (6200).

*2.1.13. Preparation of bromo-[5,10,15,20-tetrakis((R,R,R,R)-2,3,6,7-tetramethoxymethyl-1,4,5,8-tetraoxa-1,2,3,4,5,6,7,8-octahydroanthracen-9-yl)porphyrinato]iron(III) (**1c**-Fe(Br))*

To a mixture of the porphyrin **1c** (150 mg, 84 μmol) and iodine (213 mg, 0.84 mmol) in toluene (15 mL) was added $Fe(CO)_5$ (1.9 mL, 15 mmol) via a syringe under an argon atmosphere. The mixture was refluxed for 5 h, then passed through an alumina short column (CH_2Cl_2). The porphyrin fraction was washed with 5% aqueous HBr solution and dried with KBr. The solvent was evaporated and recrystallization (CH_2Cl_2:*n*-hexane) afforded **1c**–Fe(Br) as a brown solid (88 mg, 46 μmol, 55% yield); MS (FAB, 3-nitrobenzyl alcohol) *m*/*z* (relative intensity) 1357 (100), 1358 (57); UV (CH_3CN) λ_{max} 416 nm ($\varepsilon = 60500\ cm^{-1}\ M^{-1}$), 508 (8500); HRMS (FAB, 3-nitrobenzyl alcohol) Calcd for C92H108FeN4O32: 1836.6296, Found: 1836.6250.

2.2. Typical procedure for asymmetric epoxidation of aromatic olefins

A mixture of styrene (28 μL, 0.25 mmol) and a catalyst (0.25 μmol) in a dry solvent (500 μL) was cooled to −20 °C under an argon atmosphere. Iodosylbenzene (5.5 mg, 25 μmol) was added and the reaction was stirred for 3 h. Then triphenylphosphine (33 mg, 0.13 mmol) in toluene (100 μL) was added to stop the reaction. The reaction mixture was analyzed by HPLC or the epoxide was purified by silica gel column chromatography and analyzed by ^{1}H NMR with (+)-Eu $(hfc)_3$. Absolute configuration was determined by comparison with an authentic sample.

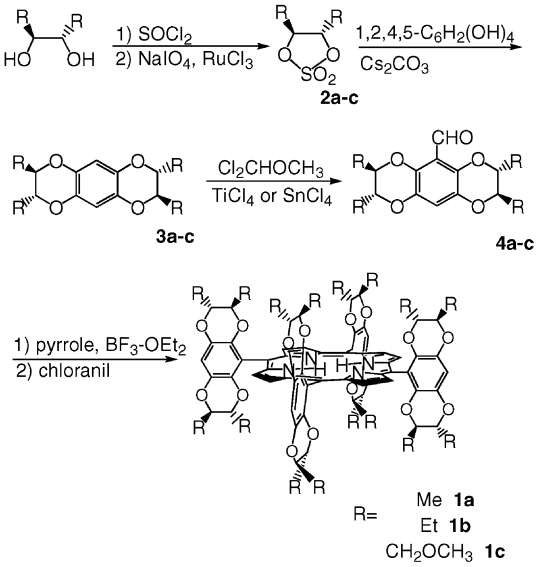
3. Results and discussion

3.1. Design and synthesis of porphyrin *1*

To design the new chiral D_4-symmetric porphyrins, we used C_2-symmetric diols as a source of the chiral center, because many diols can be easily obtained from commercial suppliers or by the asymmetric dihydroxylation of *trans*-olefins. The porphyrins **1**, which were to be synthesized from the C_2-symmetric diols, can have a reactive cavity on both sides of the porphyrin ring (Scheme 1). The chiral cavities over the porphyrin rings can be changed variously by the substituents of the diols, and the porphyrins do not have any atropisomers, thus making unnecessary a potentially difficult separation procedure. Such porphyrins are expected to be of practical use as catalysts.

The cyclic sulfates **2a–c** and 1,2,4,5-tetrahydroxybenzene were condensed to obtain **3a–c**. These compounds were confirmed to be single isomers by ^{1}H NMR. Unfortunately, the condensations did not proceed when the other diols were used. The chirality of **3a–c** must be reversed, because the cyclic sulfates react with stereospecific inversion of the configuration as reported by Sharpless et al.[46] Then **3a–c** were formylated to afforded the benzaldehydes **4a–c**, and the Lindsey method [47] was applied to obtain the porphyrins **1a–c**. The yield of **1a** and **1b** were too low and the catalytic ability could not be examined. On the other hand, the yield of **1c** was 37%, which is better for porphyrin synthesis from a 2,6-disubstituted benzaldehyde. It was suggested that the ether linkage of **4c** might have some interaction with BF_3–Et_2O and the yield was improved, because the ether linkage is the only significant difference between **4a–c** (see

[1] Low solubility of **1a** and **1b** was the possible reason for the low yields. However, we obtained small amount of **1a** and **1b**, which could not be purified for practical use, and confirmed that they have good solubility to most organic solvents.



R	2a-c	3a-c	4a-c	1a-c
Me[1)]	98%	36%	96%	< 1%
Et	91%	35%	93%	< 1%
CH_3OCH_2	98%	33%	86%	37%

1) (R, R)-diol was used.

Scheme 1. Synthetic scheme for novel D_4-symmetric chiral porphyrins.

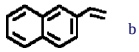
footnote 1). Only **1c** could be synthesized among the designed porphyrins, but **1c** was synthesized in only four steps with high total yield (10%). This synthesis of **1c** is the easiest among reported syntheses of chiral porphyrins.

3.2. Asymmetric reactions catalyzed by *1c*

Next, asymmetric epoxidation of styrene by metal inserted **1c** was examined under various conditions. The **1c**–Mn(Br)/PhIO and **1c**–$Ru(O)_2$/2,6-dichloropyridine *N*-oxide systems which we have found and extensively investigated [48] showed moderate enantioselectivity below 0 °C, but the reactivity became extremely low. The best enantiomeric excess (48% ee, 68% yield) was obtained with the **1c**–Fe(Br)/PhIO system in toluene at −20 °C, and it was maintained until turnover numbers over 600.

Table 1 shows the results of the epoxidation of various aromatic olefins by the **1c**–Fe(Br)/PhIO systems. Epoxidation of styrene and *trans*-β-methylstyrene by **1c**–Fe(Br) showed moderate enantioselectivity. The configuration in these reactions can be rationalized as follows. When the double bond of the olefins reacts perpendicularly to the reactive species in the "side-on approach" transition state [49–51], large and small groups of the substrate are recognized by steric interaction in the same way as in the reported examples [34,35] (Fig. 1). Although the chiral centers of **1c** are rather separated from the catalytic center than the reported D_4-symmetric porphyrins that showed moderate to high enantioselectivity, the methoxymethyl groups would

Table 1
Epoxidation of aromatic olefins catalyzed by **1c**–Fe(Br)

Run	Substrate	**1c**–Fe(Br) Ee (yield) (%)	Configuration	TON
1		47 (68)	*S*	68
2	 [a]	45 (64)	*S*	638
3	 [b]	31 (73)	1*S*, 2*R*	73
4	 [b]	38 (66)	*S*	66
5		8 (70)	1*S*, 2*R*	70
6		42 (45)	1*S*, 2*S*	45
7		52 (59)	ND[c]	59
8	 [b]	78 (62)	ND[c]	62

Reactions were typically run for 3 h at −20 °C with 0.25 μmol of catalyst, 25 μmol of PhIO, and 250 μmol of substrate in 500 μL of toluene. Ees and yields (based on PhIO) were determined by HPLC analysis except for 1,2-didhydronaphthalene, 2-vinylnaphthalene and 3-nitrostyrene.

[a] Reaction was run for 6 h at −20 °C with 0.25 μmol of catalyst, 250 μmol of PhIO, and 1.5 mmol of substrate in 1 mL of toluene.

[b] Isolated yields. Ees were determined by ^{1}H NMR with (+)-Eu(hfc)$_3$.

[c] Not determined.

be large enough to cause the steric interaction. However, the methoxymethyl groups are long and flexible, therefore the ees would become rather low. Interestingly, epoxidation of *trans*-β-methylstyrene by **1c**–Fe(Br) showed higher enantioselectivity than that of *cis*-β-methylstyrene contrary to the tendency of most porphyrin catalysts [16,17]. The methyl group of *cis*-β-methylstyrene, which would stand up on the porphyrin ring in the "side-on approach" transition state unlike *trans*-β-methylstyrene, might interact the methoxymethyl group of **1c**–Fe(Br) and the selectivity decreased.

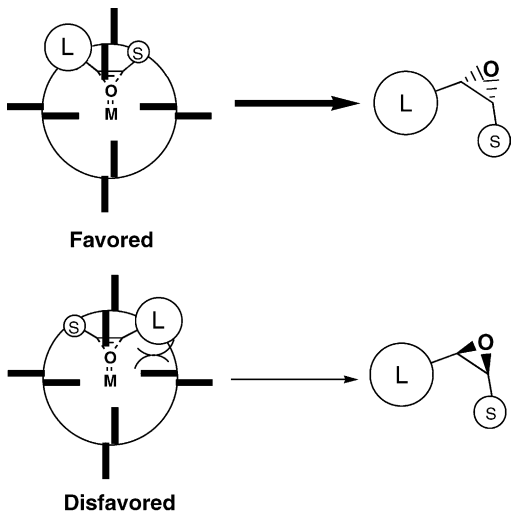


Fig. 1. Mechanism of observed enantioselectivity.

Especially, the enantioselectivity of aromatic olefins was markedly improved by introduction of electron-withdrawing groups at the aromatic rings and the best result was obtained in the case of 3-nitrostyrene (78% ee). These improvements are dramatically, and we are currently investigating the reasons of this electronic effect. We will report our findings in near future.

4. Conclusions

Novel D_4-symmetric chiral porphyrin **1c** was synthesized in a few steps with high yield from commercially available C_2-symmetric diols as the chiral source. Synthesis of **1c** is easier than that of other reported chiral porphyrins because separation of isomers is not required and the chiral cavity can be easily constructed by utilizing cyclic sulfates. The best enantiomeric excess in the epoxidation of styrene was obtained with the **1c**–Fe(Br)/PhIO system in toluene at $-20\,^{\circ}C$. Under these conditions, a turnover number in excess of 600 could be achieved without decrease of the enantiomeric excess. Notably, epoxidation of *trans*-β-methylstyrene showed higher enantioselectivity than that of *cis*-β-methylstyrene contrary to the tendency of most metalloporphyrin catalysts. The presence of electron-withdrawing substituents greatly increased the enantioselectivity, and the highest enantiomeric excess was achieved in the case of 3-nitrostyrene (78% ee).

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