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Kinetic Resolution of Racemic Ferrocenylphosphine Compounds by Enantioselective Oxidation Using Cyclic Selenoxides Having a Chiral Ligand

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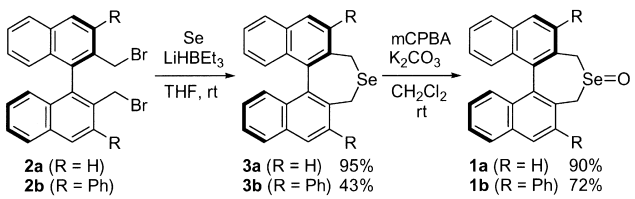
Cyclic selenoxides having an optically active binaphthyl skeleton work as the reagents for enantioselective oxidation of phosphines to the corresponding phosphine oxides. Treatment of a racemic 2-oxazolin-2-ylferrocenylphosphine with one of the selenoxides in carbon tetrachloride in the presence of phenol affords the corresponding phosphine oxide together with the unreacted starting phosphine, both with moderate enantioselectivities (the phosphine oxide, up to 13% ee; the phosphine, up to 29% ee).

Ferrocene and its derivatives play an important role in many areas of synthetic and material chemistry, and thus, they have been incorporated into complex structures which display unusual properties.[1] From the viewpoint of stereochemistry, ferrocenes with planar chirality have been widely investigated. They are of increasing importance as chiral ligands in transition metal-catalyzed asymmetric reactions.[2] Ferrocenes with planar chirality have mainly been prepared by two methods: the optical resolution of racemic ferrocenes and the diastereoselective *ortho*-lithiation of ferrocenes having an optically active directing group.[3] Recently, several groups have reported examples of direct asymmetric synthesis of ferrocenes bearing only planar chirality, where the enantioselective *ortho*-lithiation of prochiral ferrocenes[4] and enantioselective intramolecular insertion of carbenoids into C–H bonds of ferrocenes[5] have been investigated.

Organic selenoxides are known to be the reagents for oxidation of phosphines to the corresponding phosphine oxides.[6] However, no successful report on the enantioselective oxidation of racemic phosphines using selenoxides has appeared so far.[7] We now report the preparation of cyclic selenoxides **1** having an optically active binaphthyl skeleton[8] and the application of **1** to the kinetic resolution of racemic ferrocenylphosphine compounds with planar chirality, namely enantioselective oxidation of the phosphine compounds.

Results and Discussion

At first, we designed and prepared C_2-symmetric cyclic selenides having an optically active binaphthyl skeleton and converted them into the corresponding selenoxides (Scheme 1). In these selenoxides, it might not be necessary to consider the configuration around the selenium atom at the oxidation step because of the C_2-symmetric binaphthyl skeleton.[9] The dibromides **2** were prepared from the corresponding (*R*)-BINOLs[10] in three steps according to the literature method.[11] The reaction of **2** with selenium anion afforded the corresponding cyclic selenides **3**, which were then oxidized with *m*-chloroperbenzoic acid (mCPBA) to the selenoxides **1** having an optically active binaphthyl skeleton, in good yields. The molecular structure of the selenoxide **1a** was unambiguously clarified by X-ray structural determination, an ORTEP drawing being shown in Fig. 1.



Scheme 1.

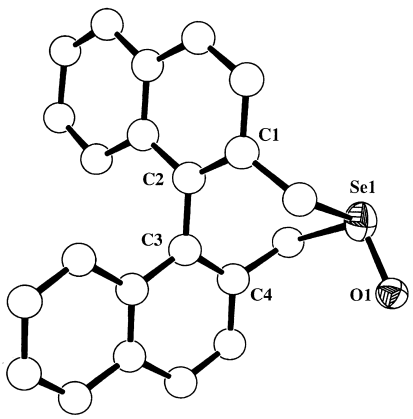
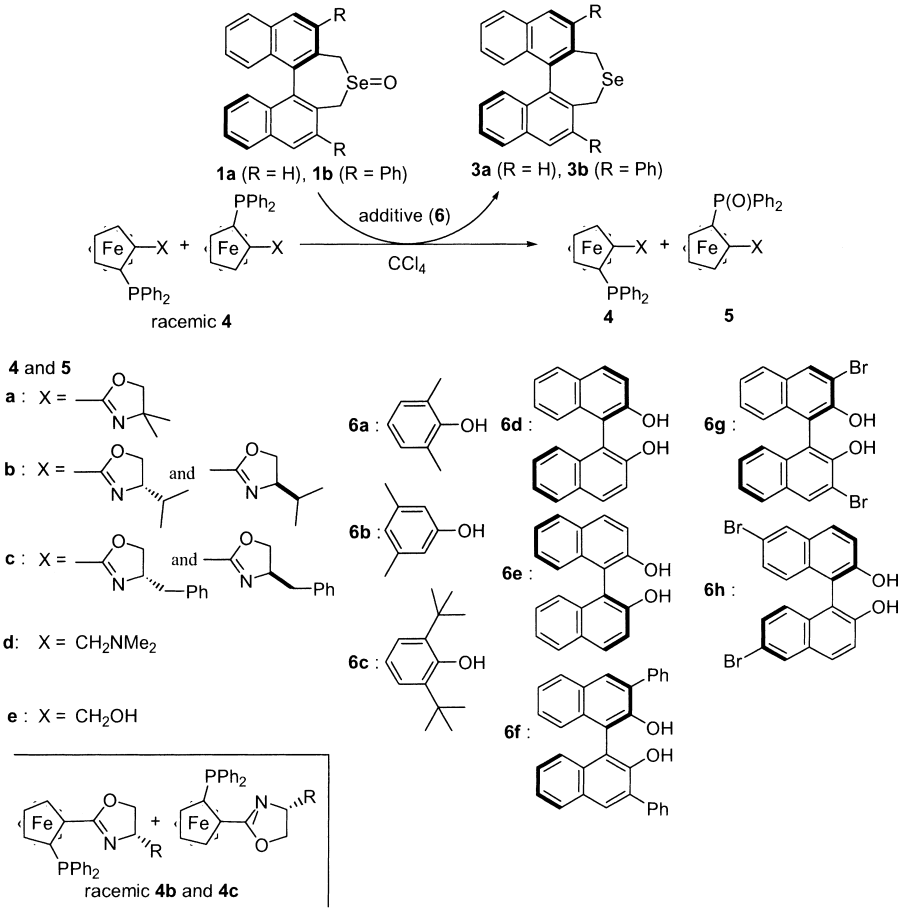


Fig. 1. An ORTEP drawing of **1a**. Selected bond lengths, torsion angle (Å, deg): Se1-O1 = 1.642 (9); C1-C2-C3-C4 = −68.0 (2).

First, we investigated kinetic resolution of racemic 2-oxazolin-2-ylferrocenylphosphine **4a** using the selenoxide **1a** (Scheme 2). Typical results are shown in Table 1. The reac-



Scheme 2.

Table 1. Kinetic Resolution of Oxazolinylferrocenylphosphine **4a** Using **1**[a)]

Entry	Additive	**4a**		**5a**	
		Recovered yield (%)[b)]	Ee (%)[c),d)]	Yield (%)[b)]	Ee (%)[c),e)]
1	—	35	15	53	12
2	H_2O	26	19	51	6
3	TfOH	41	4	58	5
4	Pyridine·HCl	44	17	56	8
5[f)]	PhOH	48	29	52	13
6[g)]	PhOH	45	18	35	15
7	**6a**	26	19	45	5
8	**6b**	31	16	53	7
9	**6c**	36	12	56	8
10	**6d**	36	18	57	11
11	**6e**	33	15	55	9
12	**6f**	30	13	49	8
13	**6g**	37	9	49	8
14	**6h**	34	8	50	6
15[h)]	PhOH	33	1	45	1

a) Reaction conditions: **4a** (0.2 mmol), **1a** (0.1 mmol), additive (0.1 mmol), CCl_4 (2 mL), at room temperature for 24 h. b) Determined by ^{31}P-NMR. c) Determined by HPLC analysis using suitable chiral columns (see experimental section). d) Absolute configuration is *S*. e) Absolute configuration is *R*. f) The efficiency of the kinetic resolution, the k_f/k_s value,[12] is estimated to be 2.3. g) At 0 °C. h) **1b** was used in place of **1a**.

tion of the racemic **4a** with **1a** (0.5 molar amount) in CCl_4 at room temperature for 24 h proceeded smoothly to give the corresponding phosphine oxide **5a** in 53% yield with 12% ee. The unreacted phosphine **4a** was recovered in 35% yield. It

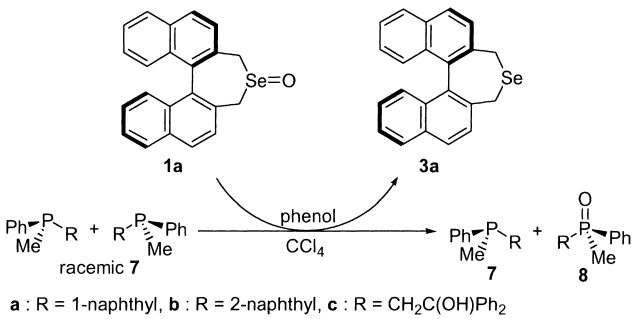
Table 2. Kinetic Resolution of **4** Using **1a**[a)]

Entry	Substrate	Additive	**4**		**5**	
			Recovered yield (%)[b)]	Ee (%)[c)]	Yield (%)[b)]	Ee (%)[c)]
1	**4b**	—	42	9	47	13
2	**4b**	PhOH	49	18	43	21
3	**4c**	—	49	6	39	12
4	**4c**	PhOH	67	9	33	22
5	**4d**	PhOH	59	6[d)]	41	1[e)]
6[f)]	**4e**	—	28	1	46	3
7[f),g)]	**4e**	—	48	8	41	10
8[f),h)]	**4e**	—	48	8	41	9
9[f),i)]	**4e**	—	14	13	46	5

a) Reaction conditions: **4** (0.2 mmol), **1a** (0.1 mmol), CCl_4 (2 mL), at room temperature for 24 h. b) Determined by ^{31}P-NMR. c) Determined by HPLC analysis using suitable chiral columns. d) Determined by optical rotation. e) Determined by optical rotation after conversion to the corresponding phosphine **4d**. f) For 3 h. g) CH_2Cl_2 was used in place of CCl_4. h) $ClCH_2CH_2Cl$ was used in place of CCl_4. i) C_6H_5Cl was used in place of CCl_4.

was revealed to be an enantiomer rich compound of 15% ee (Table 1, Entry 1). Then the effect of additives on the enantioselectivity of either or both compounds was examined; eventually it was disclosed that the addition of phenol was slightly effective for improving it (Table 1, Entries 2–14). Thus, **4a** was recovered with 29% ee and **5a** was obtained with 13% ee (Table 1, Entry 5). The efficiency of the kinetic resolution, the k_f/k_s value,[12] is estimated to be 2.3. When phenol was added to the reaction mixture before the addition of racemic **4a**, a white precipitate was produced, while the mixture changed to a clear solution when the reaction was completed. The white precipitate might be the adduct between **1a** and phenol[13] and the existence of interaction such as hydrogen bonding[8,14] between the oxygen atom of **1a** and the hydroxy group of phenol was expected. At present we consider that the interaction may change the chiral environment around the selenoxide. The reactions in other solvents such as tetrahydrofuran (THF), dichloromethane and 1,2-dichloroethane were slow and low enantioselectivities were obtained. When the selenoxide **1b** was used as an oxidant instead of **1a**, no asymmetric induction occurred, unfortunately (Table 1, Entry 15). In some cases, the formation of some unidentified products was observed by ^{31}P-NMR.

Other racemic oxazolinylferrocenylphosphines (**4b** and **4c**) and *N*,*N*-dimethylaminomethylferrocenylphosphine (**4d**) were investigated for this kinetic resolution by using **1a**. Typical results are shown in Table 2. In all cases, the addition of phenol was revealed to be slightly effective for enantioselectivity, but higher enantioselectivity than that obtained using **4a** was not observed. Treatment of racemic **4d** under similar reaction conditions afforded **5d** in 41% yield with only 1% ee and the unreacted **4d** was recovered in 59% yield with 6% ee (Table 2, Entry 5). Interestingly, the reaction of racemic ferrocenylphosphine having a hydroxy group (**4e**) proceeded faster than that of **4a** (Table 2, Entry 6). The reaction of **4e** in a variety of solvents such as dichloromethane, 1,2-dichloroethane and chlorobenzene also proceeded smoothly to give **5e**, but the enantioselectivity was lower than that obtained using **4a** (Table 2, Entries 7–9). The hydrogen bonding between the oxygen atom of **1a** and the hydroxy group of **4e** probably accelerated the reaction rate.



Scheme 3.

Next, we attempted the kinetic resolution of racemic phosphines **7**, hoping to obtain *P*-chiral phosphines, which have recently been shown to be effective ligands for the rhodium-catalyzed asymmetric hydrogenation (Scheme 3).[15] Treatment of the racemic methyl(1-naphthyl)phenylphosphine (**7a**) with **1a** (0.5 molar amount) in the presence of phenol (0.5 equiv) in CCl_4 at room temperature for 3 h gave the corresponding phosphine oxide **8a** in 62% yield with 5% ee. The unreacted phosphine **7a** was recovered in 38% yield, but only with 5% ee. Typical results are shown in Table 3. Similarly, no satisfactory results were obtained in the oxidation of racemic methyl(2-naphthyl)phenylphosphine (**7b**) or (2-hydroxy-2,2-diphenylethyl)methyl(phenyl)phosphine (**7c**) (Table 3, Entries 3–5).

In summary, we have prepared cyclic selenoxides **1** having an optically active binaphthyl skeleton and attempted the kinetic resolution of racemic ferrocenylphosphine **4** using **1** as oxidants. Although the enantioselectivity of the produced phosphine is not yet high (up to 29% ee), this conceptually novel methodology may be interesting for the preparation of optically active ferrocene derivatives with only planar chirality.

Experimental

General Procedures. ^{1}H- and ^{13}C-NMR spectra were recorded on 300 or 400 and 100 MHz FT-NMR spectrometer, respectively. ^{31}P NMR spectra were recorded on a 160 MHz FT-NMR spectrometer using $P(OMe)_3$ as an external standard. ^{77}Se NMR spec-

Table 3. Kinetic Resolution of **7** Using **1a**[a)]

Entry	Substrate	Additive	Time (h)	**7**		**8**	
				Recovered yield (%)[b)]	Ee (%)[c)]	Yield (%)[b)]	Ee (%)[d)]
1	**7a**	—	3	38	5	62	5
2	**7a**	phenol	3	37	0	63	2
3	**7b**	—	3	10	16	14	—[e)]
4	**7b**	phenol	3	57	0	43	9
5	**7c**	—	0.1	22	5	30	19

a) Reaction conditions: **7** (0.2 mmol), **1a** (0.1 mmol), additive (0.1 mmol), CCl_4 (2 mL), at room temperature. b) Determined by ^{31}P-NMR. c) Determined by HPLC analysis using suitable chiral columns after conversion to the corresponding phosphine-borane. Absolute configuration is not determined. d) Determined by HPLC analysis using suitable chiral columns. Absolute configuration is not determined. e) Not determined.

tra were recorded on a 76 MHz FT-NMR spectrometer using Me_2Se as an external standard. Chemical shifts are reported in ppm relative to TMS in the solvents specified. High-resolution mass spectra (HRMS) were obtained with a JEOL JMS-SX102A spectrometer. Melting points are uncorrected. Column chromatographies on SiO_2 were performed with Merck silica gel 60. HPLC analyses were carried out on a HITACHI L-7100 and an L-7400 UV detector using Daicel Chiralcel OD, AD, and OJ columns at 30 °C. Elemental analyses were performed at the Microanalytical Center of Kyoto University. All reactions were performed in oven-dried or flame-dried glassware under an atmosphere of N_2 unless otherwise noted. Solvents and chemicals were obtained commercially and purified by standard procedures. Racemic phosphine compounds (**4a**,[16] **4b**,[17] **4c**,[17] **4d**,[18] **4e**,[18,19] **7a**,[20] **7b**,[20] and **7c**[21]) were prepared according to literature procedures. Optically active BINOLs were commercially available compounds.

Preparation of (*R*)-3,5-Dihydrodinaphtho[2,1-*c*:1′,2′-*e*]selenepin (3a). A solution of (*R*)-2,2′-bis(bromomethyl)-1,1′-binaphthalene (2a)[11a] (2.640 g, 6.00 mmol) and *tert*-butyl alcohol (0.35 mL, 3.00 mmol) in THF (4 mL) was added at room temperature to Li_2Se[22] (5.55 mmol) suspended in THF (8 mL), and the mixture was stirred at room temperature for 12 h. Then the reaction mixture was taken up in Et_2O/H_2O. After separation, the aqueous layer was extracted with Et_2O (2 × 40 mL). The ether layer was dried over $MgSO_4$ and concentrated under vacuum. Purification by column chromatography on SiO_2 with hexane/CH_2Cl_2 (20/1) as an eluent gave the title compound **3a** (1.90 g, 5.29 mmol, 95%): A white solid; mp 169.1–170.0 °C; $[\alpha]_D^{25}$ −7.47 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.46 (d, J = 10.8 Hz, 2H), 3.51 (d, J = 10.8 Hz, 2H), 7.18–7.25 (m, 4H), 7.40–7.45 (m, 2H), 7.54 (d, J = 8.0 and 13.6 Hz, 2H), 7.92 (dd, J = 7.8 and 13.6 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.7, 125.4, 126.1, 126.3, 126.6, 128.2, 129.1, 132.0, 132.8, 133.4, 134.5; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 438.2. Found: C, 73.50; H, 4.79%. Calcd for $C_{22}H_{16}Se$: C, 73.54; H, 4.49%.

(*R*)-2,6-Diphenyl-3,5-dihydrodinaphtho[2,1-*c*:1′,2′-*e*]selenepin (3b). The compound was similarly prepared from **2b**.[11b] A pale yellow solid; 43%; mp 175.5–176.1 °C; $[\alpha]_D^{25}$ −66.5 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.38 (d, J = 11.4 Hz, 2H), 3.61 (d, J = 11.4 Hz, 2H), 7.11–7.20 (m, 2H), 7.20–7.27 (m, 2H), 7.35–7.51 (m, 8H), 7.67 (brs, 4H), 7.81–7.92 (m, 4H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.2, 125.8, 126.0, 126.7, 127.1, 127.3, 128.1, 128.2, 129.7, 130.1, 131.4, 132.3, 132.5, 134.3, 139.0, 141.2; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 440.6. HRMS *m*/*z* Found: 512.1049. Calcd for $C_{34}H_{24}Se$ M^+: 512.1046. Found: C, 80.31; H, 5.24%. Calcd for $C_{34}H_{24}Se$: C, 79.83; H, 4.73%.

Preparation of (*R*)-3,5-Dihydrodinaphtho[2,1-*c*:1′,2′-*e*]selenepin 4-Oxide (1a). To a solution of **3a** (0.359 g, 1.00 mmol) in CH_2Cl_2 (30 mL) were added mCPBA (80%, 0.237 g, 1.1 mmol) and saturated aqueous K_2CO_3 solution (6 mL) and the resulting solution was stirred at room temperature for 10 min. The mixture was poured into saturated aqueous Na_2CO_3 solution and extracted with CH_2Cl_2 (2 × 30 mL). The combined organic layer was then dried over $MgSO_4$ and concentrated under vacuum to leave a crude product. Purification by column chromatography on SiO_2 with ethyl acetate/MeOH (1/1) as an eluent gave the title compound **1a** (0.336 g, 0.90 mmol, 90%). A white solid; mp 84.2–85.5 °C; $[\alpha]_D^{25}$ −43.4 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.18 (d, J = 10.8 Hz, 1H), 3.55 (d, J = 12.5 Hz, 1H), 3.81 (d, J = 12.5 Hz, 1H), 4.36 (d, J = 10.8 Hz, 1H), 7.21–7.34 (m, 4H), 7.48–7.55 (m, 3H), 7.63–7.65 (m, 1H), 7.93–8.04 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 48.9, 54.2, 126.2, 126.5, 126.9, 126.9, 128.0, 128.3, 128.5, 128.8, 129.0, 129.0, 129.1, 131.8, 132.4, 133.6, 133.7, 134.4, 134.6; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 1033.3. HRMS *m*/*z* Found: 377.0446. Calcd for $C_{22}H_{17}OSe$ M^+: 377.0446. Found: C, 69.55. H, 4.73%. Calcd for $C_{22}H_{17}OSe$: C, 70.40; H, 4.30%.

X-ray Structural Analysis of 1a. Single crystals of **1a** ($C_{22}H_{16}OSe{\cdot}C_6H_6$) suitable for X-ray analysis were prepared by recrystallization from benzene. Diffraction data were collected on a Rigaku RAXIS imaging plate area detector with Mo K_α (λ = 0.711 Å) radiation and a graphite monochromator at 23 °C. Details of crystal and data collection parameters are summarized in Table 4. For a structure analysis and refinement, computations were performed using the CrystalStructure[23] crystallographic software package of Molecular Structure. Neutral atom scattering factors were taken from Ref. 24. Anomalous dispersion effects were included in F_{calc}^{25}; the values of $\Delta f'$ and $\Delta f''$ were those of Ref. 26. The structure was solved by direct methods (SIR92). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included, but not refined.

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers CCDC-196734.

(*R*)-2,6-Diphenyl-3,5-dihydrodinaphtho[2,1-*c*:1′,2′-*e*]selenepin 4-Oxide (1b). The compound was similarly prepared from **3b**. A pale yellow solid; 72%; mp 76.1–77.0 °C; $[\alpha]_D^{25}$ −5.30 (c 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.30 (d, J = 12.8 Hz, 1H), 3.35 (d, J = 10.8 Hz, 1H), 4.28 (d, J = 12.8 Hz, 1H), 4.47 (d, J = 10.8 Hz, 1H), 7.00–8.15 (m, 20H); ^{13}C NMR (100 MHz,

Table 4. Summary of Crystallographic Data of **1a**

Empirical formula	$C_{22}H_{16}OSe{\cdot}C_6H_6$
Fw	453.44
Crystal system	orthorhombic
Space group	$P2_12_12_1$(#19)
Crystal color	colorless
a/Å	8.0215(7)
b/Å	12.529(1)
c/Å	21.105(2)
V/(Å^3)	2121.1(3)
Z	4
D_{calc}/g cm^{-3}	1.420
μ(Mo K_α)/cm^{-1}	1.95
F(000)	928.00
Radiation	Mo K_α (λ = 0.71069 Å) graphite monochromated
Temp/°C	23.0
Scan type	ω
Max. 2θ/°	55.0
No. of rflns measd	18857
No. of observns ($I > 3.00\ \sigma(I)$)	1349
Structure soln	direct methods (SIR92)
Refinement	full-matrix least squares
No. of variables	287
Reflection/parameter ratio	4.70
Residuals: R ; R_w	0.039; 0.044
GOF	0.70
Max shift/error in final cycle	3.58
Maximum peak in final diff map (e Å^{-3})	0.58
Minimum peak in final diff map (e Å^{-3})	−0.64

$CDCl_3$) δ 44.2, 51.3, 126.3, 126.4, 126.6, 126.7, 126.9, 127.1, 127.3, 127.9, 128.2, 128.3, 128.7, 129.3, 129.6, 130.0, 131.3, 131.6, 132.8, 132.9, 135.5, 135.7, 139.4, 140.1, 141.5. Found: C, 77.50; H, 4.84%. Calcd for $C_{34}H_{24}OSe$: C, 77.41; H, 4.59%.

Typical Procedure for Kinetic Resolution of Racemic Ferrocenylphosphine Compounds. A solution of **1a** (37.5 mg, 0.1 mmol) and phenol (9.4 mg, 0.1 mmol) in carbon tetrachloride (1 mL) was stirred under nitrogen atmosphere at room temperature. After 15 min, the racemic **4a** (93.5 mg, 0.2 mmol) in carbon tetrachloride (1 mL) was added to the solution and the resulting solution was stirred at room temperature for 24 h. Yields of phosphine and phosphine oxide were determined by integration of the ^{31}P resonances against $P(OMe)_3$ added as an internal reference. Purification of the crude products by SiO_2 chromatography gave the corresponding ferrocenylphosphine and ferrocenylphosphine oxide in a pure form.

[2-(4,4-Dimethyl-2-oxazolin-2-yl)ferrocenyl]diphenylphosphine (4a). Enantiomeric excess was determined by Daicel Chiralcel AD, 30 °C, 0.5 mL/min, hexane/2-propanol = 95/5, t_1 = 9.27 (*S*) min, t_2 = 11.28 min (*R*).[16]

[2-(4,4-Dimethyl-2-oxazolin-2-yl)ferrocenyl]diphenylphosphine Oxide·H_2O (5a·H_2O). A reddish brown solid; mp 115.1–116.0 °C; enantiomeric excess was determined by Daicel Chiralcel AD, 30 °C, 0.5 mL/min, hexane/2-propanol = 90/10, t_1 = 45.77 (*S*) min, t_2 = 48.65 min (*R*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03 (brs, 3H), 1.19 (brs, 3H), 1.35 (br, 2H, H_2O), 2.93 (brs, 1H), 3.95 (brs, 2H), 4.49 (m, 6H), 5.09 (brs, 1H), 7.41–7.70 (m, 10H); ^{31}P NMR (160 MHz, $CDCl_3$) δ 23.6. HRMS *m*/*z* Found: 484.1136. Calcd for $C_{27}H_{27}FeNO_2P$ M^+ + H: 484.1129. Found: C, 64.76; H, 5.43; N, 2.63%. Calcd for $C_{27}H_{26}FeNO_2P{\cdot}H_2O$: C, 64.69; H, 5.63; N, 2.79%. The presence of H_2O was confirmed by ^{1}H NMR spectroscopy.

[2-(4-Isopropyl-2-oxazolin-2-yl)ferrocenyl]diphenylphosphine (4b).[17] Enantiomeric excess was determined by Daicel Chiralcel AD, 30 °C, 0.5 mL/min, hexane/2-propanol = 95/5, t_1 = 8.20 min, t_2 = 9.82 min.

[2-(4-Isopropyl-2-oxazolin-2-yl)ferrocenyl]diphenylphosphine Oxide·H_2O (5b·H_2O). A reddish brown solid; mp 192.2–192.5 °C; enantiomeric excess was determined by Daicel Chiralcel AD, 30 °C, 1.0 mL/min, hexane/2-propanol = 90/10, t_1 = 31.84 min, t_2 = 41.72 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.61 (brs, 3H), 0.80 (brs, 3H), 1.47–1.53 (m, 1H), 2.05 (br, 2H, H_2O), 3.13 (m, 1H), 3.75 (m, 1H), 3.93 (brs, 1H), 4.21 (m, 1H), 4.49 (m, 1H), 4.50 (brs, 5H), 5.07 (brs, 1H), 7.27–7.74 (m, 10H); ^{31}P NMR (160 MHz, $CDCl_3$) δ 23.7. HRMS *m*/*z* Found: 498.1293. Calcd for $C_{28}H_{29}FeNO_2P$ M^+ + H: 498.1286. Found: C, 65.28; H, 5.62; N, 2.59%. Calcd for $C_{28}H_{28}FeO_2P{\cdot}H_2O$: C, 65.26; H, 5.87; N, 2.72%. The presence of H_2O was confirmed by ^{1}H NMR spectroscopy.

[2-(4-Benzyl-2-oxazolin-2-yl)ferrocenyl]diphenylphosphine (4c).[17] Enantiomeric excess was determined by Daicel Chiralcel AD, 30 °C, 0.5 mL/min, hexane/2-propanol = 95/5, t_1 = 11.29 min, t_2 = 14.78 min.

[2-(4-Benzyl-2-oxazolin-2-yl)ferrocenyl]diphenylphosphine Oxide·H_2O (5c·H_2O). A reddish brown solid; mp 193.2–193.7 °C; enantiomeric excess was determined by Daicel Chiralcel AD, 30 °C, 1.0 mL/min, hexane/2-propanol = 90/10, t_1 = 41.11 min, t_2 = 46.72 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.75 (br, 2H, H_2O), 2.12 (dd, J = 12.3 and 14.7 Hz, 1H), 3.00 (dd, J = 12.3 and 13.6 Hz, 1H), 3.06 (dd, J = 8.0 and 8.4 Hz, 1H), 3.98 (brs, 1H), 4.12 (dd, J = 8.0 and 8.4 Hz, 1H), 4.20 (m, 1H), 4.39 (brs, 1H), 4.50 (s, 5H), 5.05 (brs, 1H), 7.03–7.77 (m, 15H); ^{31}P NMR (160 MHz, $CDCl_3$) δ 23.7. HRMS *m*/*z* Found: 546.1273. Calcd for $C_{32}H_{29}FeNO_2P$ M^+ + H: 546.1286. Found: C, 68.79; H, 5.56; N, 2.40%. Calcd for $C_{32}H_{28}FeNO_2P{\cdot}H_2O$: C, 68.22; H, 5.37; N, 2.49%. The presence of H_2O was confirmed by ^{1}H NMR spectroscopy.

[2-(*N*,*N*-Dimethylaminomethyl)ferrocenyl]diphenylphosphine (4d). Enantiomeric excess was determined by optical rotation.[18]

[2-(*N*,*N*-Dimethylaminomethyl)ferrocenyl]diphenylphosphine Oxide·H_2O (5d·H_2O). A reddish brown solid; mp 59.2–59.9 °C; enantiomeric excess of **5d** was determined by optical rotation after the reduction of **5d** into the corresponding phosphine[18]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.96 (s, 6H), 3.00 (br, 2H, H_2O), 3.43 (d, J =13.0, 2H), 3.94 (s, 1H), 4.20 (s, 5H), 4.36 (s, 1H), 4.67 (s, 1H), 7.21–7.92 (m, 10H); ^{31}P NMR (160 MHz, $CDCl_3$) δ 23.3. HRMS *m*/*z* Found: 444.1183. Calcd for $C_{25}H_{27}FeNOP$ M^+ + H: 444.1180. Found: C, 65.47; H, 5.93; N, 2.70%. Calcd for $C_{25}H_{26}FeNOP{\cdot}H_2O$: C, 65.09; H, 6.12; N, 3.04%. The presence of H_2O was confirmed by ^{1}H NMR spectroscopy.

[2-(Hydroxymethyl)ferrocenyl]diphenylphosphine (4e).[18,19] Enantiomeric excess was determined by Daicel Chiralcel AD, 30 °C, 0.5 mL/min, hexane/2-propanol = 95/5, t_1 = 22.77 min, t_2 = 29.04 min.

[2-(Hydroxymethyl)ferrocenyl]diphenylphosphine Oxide·H_2O (5e·H_2O). A reddish brown solid; mp 91.5–92.3 °C; enantiomeric excess was determined by Daicel Chiralcel OD, 30 °C, 0.5 mL/min, hexane/2-propanol = 95/5, t_1 = 31.96 min, t_2 = 37.96 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.93 (s, 1H), 4.24–4.36

(m, 3H), 4.27 (s, 5H), 4.55 (s, 1H), 5.51 (s, 1H), 7.25–7.81 (m, 10H); ^{31}P NMR (160 MHz, $CDCl_3$) δ 30.9. HRMS *m/z* Found: 416.0627. Calcd for $C_{23}H_{21}FeO_2P$ M^+: 416.0629. Found: C, 65.94; H, 5.25%. Calcd for $C_{23}H_{21}FeO_2P$: C, 66.37; H, 5.09%.

Methyl(1-naphthyl)phenylphosphine (7a).[20] Enantiomeric excess of **7a** was determined by Daicel Chiralcel OD, 30 °C, 1.0 mL/min, hexane/2-propanol = 90/10, t_1 = 6.41 min, t_2 = 6.98 min, after the transformation of **7a** into the corresponding phosphine-borane.[20c]

Methyl(1-naphthyl)phenylphosphine Oxide (8a).[20] Enantiomeric excess was determined by Daicel Chiralcel OJ, 30 °C, 1.0 mL/min, hexane/2-propanol = 90/10, t_1 = 33.50 min, t_2 = 37.90 min.

Methyl(2-naphthyl)phenylphosphine (7b).[20] Enantiomeric excess of **7b** was determined by Daicel Chiralcel OD, 30 °C, 1.0 mL/min, hexane/2-propanol = 90/10, t_1 = 15.98 min, t_2 = 19.80 min, after the transformation of **7b** into the corresponding phosphine-borane.[20c]

Methyl(2-naphthyl)phenylphosphine Oxide (8b).[20] Enantiomeric excess was determined by Daicel Chiralcel AD, 30 °C, 0.5 mL/min, hexane/2-propanol = 90/10, t_1 = 28.78 min, t_2 = 32.97 min.

(2-Hydroxy-2,2-diphenylethyl)methyl(phenyl)phosphine (7c).[21] Enantiomeric excess of **7c** was determined by Daicel Chiralcel OD, 30 °C, 0.5 mL/min, hexane/2-propanol = 92/8, t_1 = 26.42 min, t_2 = 33.54 min, after the transformation of **7c** into the corresponding phosphine-borane.[20c]

(2-Hydroxy-2,2-diphenylethyl)methyl(phenyl)phosphine Oxide (8c).[21] Enantiomeric excess was determined by Daicel Chiralcel OD, 30 °C, 0.5 mL/min, hexane/2-propanol = 85/15, t_1 = 28.40 min, t_2 = 36.18 min.

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