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Asymmetric hydroesterification of styrene using catalysts with planar-chiral ferrocene oxazoline ligands

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Abstract—Chiral *P*,*N*-ferrocene ligands, 1-diphenylphosphino-1′-[(*S*)-4-isopropyl-2.5-oxazolinyl]-2′-(S_p)-(trimethylsilyl)-ferrocene and its diastereomer, and 1-diphenylphosphino-1′-[(*S*)-4-isopropyl-2.5-oxazolinyl]-2′(S_p)-(diphenylphosphino)-ferrocene and its diastereomer were used in the palladium-catalyzed asymmetric hydroesterification of styrene. The role of these ligands, which contain central, axial, and planar chirality, on the stereochemical outcome was investigated. A significant effect of using $CuCl_2$ as a co-catalyst on the reaction was observed. Excellent regioselectivity (b/n >99:1) with low ee (28%) was obtained in the presence of $CuCl_2$; moderate enantioselectivity (64% ee) but low regioselectivity (b/n, 40/60) was obtained in the absence of $CuCl_2$.

1. Introduction

The hydroesterification of vinyl aromatics produces valuable intermediates for perfumes and pharmaceuticals. For example, the production of 2-arylpropionic acids, which constitute an important class of non-steroidal anti-inflammatory drugs (e.g. ibuprofen and naproxen),[1] is a scientifically interesting and potentially useful pursuit. Over the past three decades, excellent progress on asymmetric hydrogenation has been made. In contrast the progress on the asymmetric hydroesterification of vinyl aromatics is still limited. Hayashi's pioneering work using $Pd(dba)_2$-neomenthyldiphenylphosphine-trifluoroacetic acid in the asymmetric hydroesterification of α-methylstyrene showed moderate ee (42% ee; b/n = 94:6; dba = dibenzylideneacetone).[2] Recently, Inoue et al. used a chiral ferrocene ligand containing aminophosphine, (*S*)-1-[(*R*)-1′,2-bis(diphenylphosphino)-ferrocenyl]ethyldimethylamine, (*S*,*Rp*)-**BPPFA** (Fig. 1) in the reaction and achieved high ee (86%) but rather low yield and regioselectivity.[3] Chiral ligands containing central, axial, and planar chirality has not been reported for this reaction. As illustrated in Scheme 1, ligand **1** itself has no planar chirality on the ferrocene backbone. However, its coordination to a metal center gives rise to two diastereomeric complexes **2** and **3**, due to the opposite twists of the Cp rings in the ligand.[4] It is worth noting that by introducing planar chirality to ligand **1** and through its coordination to a metal center, three kinds of chiral elements (namely central, axial, and planar chirality) exist in one catalyst.

In this study, we investigated the role of central, axial, and planar chirality on the palladium-catalyzed asymmetric hydroesterification of styrene by using the new planar-chiral ferrocenyl oxazoline ligands **(*S*,*Sp*)-1**, **(*SRp*)-1**, **(*S*,*Sp*)-2**, and **(*S*,*Rp*)-2** (Fig. 1). In the meantime, the effects of different palladium sources and the use of $CuCl_2$ as a co-catalyst on the reaction were also studied. Excellent regioselectivity (b/n, >99:1) was obtained in the presence of $CuCl_2$ as a co-catalyst albeit with only 28% ee. In contrast, moderate enantioselectivity (64% ee) but low regioselectivity (b/n, 40/60) was obtained in the absence of $CuCl_2$.

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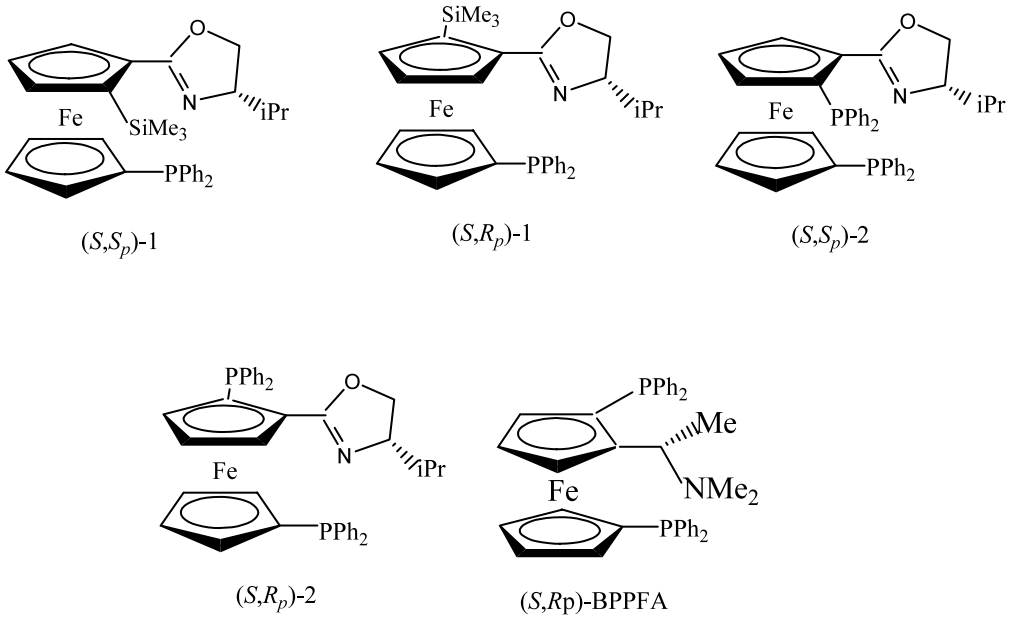


Figure 1.

2. Results and discussion

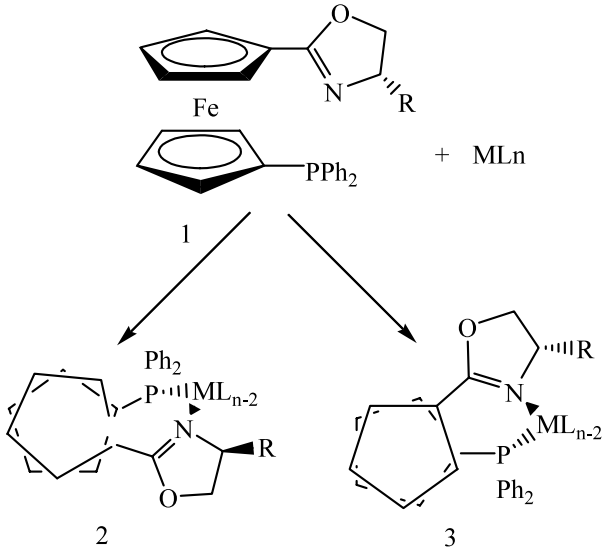
The hydroesterification of styrene is shown in Scheme 2. Enantiomeric branched ester (b) is the desired product while the linear ester (n) is considered to be a byproduct. The effects of different reaction conditions on the hydroesterification of styrene using CO and methanol are summarized in Table 1.

Chiral *P*,*N*-ligands have been proved to be effective in several metal-catalyzed asymmetric reactions.[5–8] Von Matt and Pfaltz,[9a] Sprinz and Helmchen,[9b] and Dawson et al.[9c] established that the oxazoline center chirality of bidentate *P*,*N*-ligands furnishes exceptional stereocontrol in palladium-catalyzed allylic alkylations (up to 99% ee). Ahn[10a,b] and Helmchen[11] reported that the central chirality of the oxazoline subunit, not the planar-chirality, is the primary determinant factor of the stereochemical outcome of alkylation catalyzed by Pd complexes.

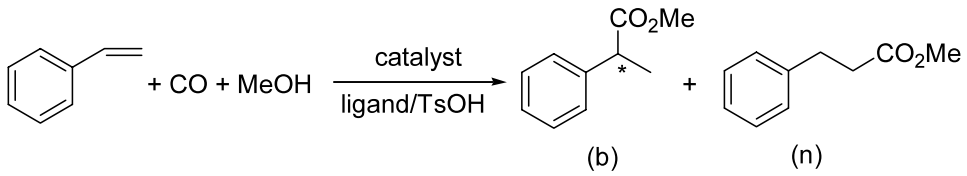
In the present study we also found that the central chirality of the oxazoline subunit, not the planar-chirality, was the primary determinant factor for the enantioselectivity (Table 1, entries 1–5).

Ligand **(*S*,*Sp*)-1** gave moderate enantioselectivity (45% ee) with a regioselectivity (b/n) of 79/21 (Table 1, entry 3), while ligand **(*S*,*Rp*)-1** gave the best regioselectivity (b/n, >99/1) (Table 1, entries 4 and 5). A comparison of the results of using ligand **(*S*,*Sp*)-2** and **(*S*,*Rp*)-2** clearly showed that the enantioselectivity of the catalyst was predominantly influenced by the planar-chirality of the ferrocene unit, and the central chirality of oxazoline was a minor factor. The higher ee from the reaction using ligand **(*S*,*Rp*)-2**, relative to that from the reaction using ligand **(*S*,*Sp*)-2**, indicated that for ligand **(*S*,*Rp*)-2** the planar-chirality and the central-chirality of the oxazoline were working in concert to preferentially generating the (*R*)-product (Table 1, entries 11 and 15).

Wan et al. reported that polymer-supported PVP–$PdCl_2$–$4CuCl_2$–PPh_3 bimetallic system [PVP = poly(*N*-vinyl-2-pyrrolidone)] was effective for the hydroesterification of styrene with CO and methanol, and the addition of $CuCl_2$ was essential for obtaining higher regioselectivity in the corresponding reaction.[12] Lee et al. studied the effects of promoters and reaction conditions on the regioselectivity of palladium complex-catalyzed hydroesterification of 4-methylstyrene and found that $PdCl_2$–$CuCl_2$–PPh_3 dissolved in a nonpolar solvent provided nearly regiospecific conversion to the branched ester in high rates at 100°C and under 41 bar of CO pressure.[13] In this study we found that in the



Scheme 1.



Scheme 2.

Table 1. Asymmetric hydroesterification of styrene using $PdCl_2$–$CuCl_2$–ligands–*p*-toluenesulfonic acid system[a]

Entry	Ligands	Cu/Pd (M/M)	Conv.[b] (%)	Yield[b] (%)	b/n[b]	Ee (abs. conf.)[b]
1	**(*S*,*Sp*)-1**	0/1	68	62	38/62	22 (*R*)
2	**(*S*,*Sp*)-1**	3/1	72	63	89/11	42 (*R*)
3	**(*S*,*Sp*)-1**	5/1	37	33	79/21	45 (*R*)
4	**(*S*,*Rp*)-1**	3/1	16	8.2	>99/1	12 (*R*)
5	**(*S*,*Rp*)-1**	5/1	12	5.7	>99/1	28 (*R*)
6	**(*S*,*Rp*)-BPPFA**	0/1	>99	>99	29/71	63 (*S*)
7	**(*S*,*Rp*)-BPPFA**	1/1	>99	>99	43/57	40 (*S*)
8	**(*S*,*Rp*)-BPPFA**	3/1	94	93	58/42	16 (*S*)
9	**(*S*,*Rp*)-BPPFA**	5/1	84	81	70/30	9.0 (*S*)
10	**(*S*,*Sp*)-2**	0/1	>99	>99	16/84	10 (*S*)
11	**(*S*,*Sp*)-2**	3/1	92	91	39/61	38 (*S*)
12	**(*S*,*Sp*)-2**	5/1	63	61	40/60	36 (*S*)
13	**(*S*,*Rp*)-2**	0/1	74	74	23/77	37 (*R*)
14	**(*S*,*Rp*)-2**	3/1	14	14	65/35	43 (*R*)
15	**(*S*,*Rp*)-2**	5/1	5.8	5.8	69/31	48 (*R*)

[a] Reaction conditions: 25 μL, 0.225 mmol styrene; 2 mg $PdCl_2$ (0.01125 mmol); 21.5 mg toluenesulfonic acid (0.1125 mmol); 6.25 mg ligands (0.01125 mmol); 1.0 mL methanol; 1.0 mL 1.4-dioxane; 1800 psi CO; reaction temperature = 80°C; reaction time = 20 h.

[b] The data on conversion and yields of the asymmetric hydroesterification products were determined by GC–MS on a Bexs column (30 m×0.25 mm I.D.) using acetophenone as an internal standard. The enantiomeric excess of the chiral product was determined by GC with a Chrompack Chirasil-Dex CB column (50 m×0.25 mm I.D.). The absolute configuration of methyl 2-phenylpropionate was determined by the comparison of the retention time with that of a pure authentic sample.

absence of copper salt, both the branched/linear ratio and the ee of branched product were substantially lower when ligands **(*S*,*Sp*)-1**, **(*S*,*Rp*)-2**, and **(*S*,*Sp*)-2** were used (Table 1, entries 1, 10, and 13). It is worth noting that by increasing the molar ratio of copper(II) to palladium(II) from 0/1 to 5/1 brought about a marked decrease in the conversion and a significant increase in regioselectivity and enantioselectivity (Table 1, entries 1–3; 4–5; 10–12; 13–15). This effect was in sharp contrast with the **(*S*,*Rp*)-BPPFA** ligand system, in which the addition of copper salt lowered the product ee (Table 1, entries 6–9). It appeared that the Pd/Cu mixed metal catalyst system exhibited a synergistic effect, although the role of $CuCl_2$ is still not fully understood.

The effect of using different palladium precursors is shown in Table 2. When $PdCl_2(NCPh)_2$ was used as the catalyst precursor in the absence of copper salt, ligand **(*S*,*Rp*)-2** gave similar conversion and yield but poorer

Table 2. Asymmetric hydroesterification of styrene using different palladium catalyst precursors–$CuCl_2$–ligands–*p*-toluenesulfonic acid system[a]

Entry	Pd source	Ligand	Cu/Pd (M/M)	Conv.[b] (%)	Yield[b] (%)	B/n[b]	Ee[b] (conf.)
1	$PdCl_2$	**(*S*,*Rp*)-2**	0/1	14	14	40/60	64 (*R*)
2	$PdCl_2(NCPh)_2$	**(*S*,*Rp*)-2**	0/1	14	8.1	46/54	35 (*R*)
3	$Pd(acac)_2$	**(*S*,*Sp*)-2**	0/1	70	70	39/61	34 (*R*)
4	$Pd(acac)_2$	**(*S*,*Sp*)-2**	3/1	10	10	65/35	20 (*S*)
5	$Pd(acac)_2$	**(*S*,*Sp*)-2**	5/1	13	13	64/36	22 (*S*)
6	$Pd(OAc)_2$	**(*S*,*Rp*)-2**	0/1	17	17	36/64	14 (*S*)
7	$Pd(OAc)_2$	**(*S*,*Rp*)-2**	3/1	11	11	54/46	33 (*R*)
8	$Pd(OAc)_2$	**(*S*,*Rp*)-2**	5/1	6.3	6.3	59/41	44 (*R*)

[a] Reaction conditions: 12.5 μL, 0.1125 mmol styrene; 0.00225 mmol Pd source; 4.28 mg toluenesulfonic acid (0.0225 mmol); 1.50 mg ligands (0.00225 mmol); 0.25 mL methanol; 0.25 mL 1,4-dioxane; 2500 psi CO; reaction temperature = 50°C; reaction time = 20 h.

[b] The data on conversion and yield, the enantiomeric excess, and the assignment of absolute configuration of the chiral product was determined using the same conditions as noted in Table 1.

enantioselectivity in comparison to the reaction using $PdCl_2$ as catalyst precursor (Table 2, entries 1–2). In the case of $Pd(acac)_2$ as catalyst precursor in the absence of copper salt, ligand **(*S*,*Sp*)-2** provided a moderate asymmetric induction of 34% ee (*R*) at high conversion and yield with low regioselectivity (b/n = 39/61, Table 2, entry 3).

It is interesting to note that by increasing the molar ratio of copper(II) and palladium(II) to 3/1, higher regioselectivity (b/n) of 65/35 with opposite enantioselectivity was observed (Table 2, entry 4). A slight improvement of enantioselectivity and regioselectivity were achieved by increasing the Cu/Pd molar ratio to 5/1 (Table 2, entry 5), but with substantial decrease in conversion and yield. In the case of $Pd(OAc)_2$/**(*S*,*Rp*)-2** as catalyst precursor in the absence of copper salt, the asymmetric induction decreased markedly to 14% ee (*S*) and low regioselectivity (b/n) of 39/61 was obtained (Table 2, entry 6). By increasing the Cu/Pd molar ratio to 3/1, an opposite enantioselectivity of 33% ee (*R*) and an enhanced regioselectivity (b/n) of 54/46 were observed (Table 2, entry 7). Slight improvements in enantioselectivity and regioselectivity were achieved by increasing the Cu/Pd molar ratio to 5/1, but with a decrease in the catalytic activity of the system (Table 2, entry 8).

3. Conclusion

It has been demonstrated in this study that palladium-catalyzed asymmetric hydroesterification of styrene using new planar-chiral ferrocenyl oxazoline ligands **(*S*,*Sp*)-1**, **(*S*,*Rp*)-1**, **(*S*,*Sp*)-2**, and **(*S*,*Rp*)-2** exhibit high regioselectivity and moderate asymmetric induction. In addition, the use of $CuCl_2$ as a co-catalyst enhances the regioselectivity (b/n) of this reaction.

4. Experimental

4.1. Reagents and materials

$PdCl_2(NCPh)_2$, $Pd(OAc)_2$, $PdCl_2$, and $Pd(acac)_2$ were purchased from Aldrich and were used without further purification. Styrene and methanol were distilled and degassed with dry N_2 before use. The enantiomerically pure ligand **(*S*,*Rp*)-BPPFA** was purchased from Aldrich. The other commercially available reagents were used as received without further purification. ^1H NMR and ^{31}P NMR were recorded on a Varian AS 500 at room temperature. ^1H NMR spectra are reported in ppm with TMS as an internal standard ($\delta = 0$ ppm). ^{31}P NMR spectra are reported in ppm with 85% H_3PO_4 as an external reference. Optical rotations were recorded on a Perkin–Elmer 241 MC polarimeter with a thermally jacketed 10 cm cell at 25°C. IR spectra were recorded in KBr and measured in inverse centimeters, using a Shimadzu IR-440 infrared spectrophotometer. Mass spectra were taken using HP 5989A mass spectrometers. Elemental analyses were performed on a Foss-Heraeus Vario EL instrument.

1 - Diphenylphosphino - 1′ - [(*S*) - 4 - isopropyl - 2.5 - oxazolinyl]-2′(S_p)-(trimethylsilyl)-ferrocene **(*S*,*Sp*)-1** and 1-diphenylphosphino-1′-[(*S*)-4-isopropyl-2.5-oxazolinyl]-2′(R_p)-(trimethylsilyl)-ferrocene **(*S*,*Rp*)-1** were synthesized according to a previously published methods.[4b]

4.2. 1-Diphenylphosphino-1′-[(*S*)-4-isopropyl-2.5-oxazolinyl]-2′-(S_p)-(diphenylphosphino)ferrocene, (*S*,*Sp*)-2

1-Diphenylphosphino-1′-[(*S*)-isopropyl-2.5-oxazolinyl]ferrocene (0.240 g, 0.5 mmol, synthesized according to a previously published methods[4b]) was dissolved in anhydrous Et_2O (6 mL) under a nitrogen at room temperature, TMEDA (0.1 mL, 0.7 mmol) was added to the solution using a syringe. *n*-BuLi (0.4 mL, 0.64 mmol, 1.6 M in hexane) was then slowly added to the mixture at −78°C. After stirring for 2 h, Ph_2PCl (0.14 mL, 0.8 mmol) was added and the mixture was stirred at 0°C for 20 min. The reaction was monitored by TLC and the mixture was quenched using saturated $NaHCO_3$ and extracted by Et_2O. The extract was washed by brine and dried using anhydrous Na_2SO_4. The solvents were removed and the residue was purified by column chromatography (10:1 petroleum ether/AcOEt). Yellow solid of **(*S*,*Sp*)-2** (0.230 g, 68% yield) was obtained. $[\alpha]_D^{20} = -65.5$ (*c* 0.15, $CHCl_3$). ^1H NMR: $\delta = 0.64$ (d, $J = 6.8$ Hz, 3H), 0.80 (d, $J = 6.8$ Hz, 3H), 1.63 (m, 1H), 3.44 (m, 1H), 3.70 (t, $J = 8.2$ Hz, 1H), 3.80–3.91 (m, 1H), 3.96 (s, 1H), 4.18–4.30 (m, 3H), 4.48–4.51 (m, 2H), 4.92 (t, $J = 1.2$ Hz, 1H), 7.17–7.48 (m, 20H) ppm. ^{31}P NMR: $\delta = -16.49$ (s, 1P), −17.28 (s, 1P) ppm. MS *m*/*z* (relative intensity) 666 (M^+, 100), 480 (70.4), 393 (38.6), 183 (39.6), 171 (44.8). IR (KBr) 2955, 1658, 1478, 1433, 1026, 980, 741, 695, 498 cm^{-1}. Anal. calcd for $C_{40}H_{37}NOP_2Fe$: C, 72.19; H, 5.60; N, 2.11. Found: C, 72.10; H, 5.60; N, 1.94.

4.3. 1-Diphenylphosphino-1′-[(*S*)-4-isopropyl-2.5-oxazolinyl]-2′(R_p)-(diphenylphosphino)-ferrocene, (*S*,*Rp*)-2

(*S*,*Sp*)-1 (0.276 g, 0.5 mmol) was dissolved in anhydrous THF (4 mL) under nitrogen at room temperature, *n*-BuLi (0.4 mL, 0.64 mmol, 1.6 M in hexane) was then slowly added to the mixture at −78°C. After stirring for 2 h, Ph_2PCl (0.13 mL, 0.7 mmol) was added and the mixture was stirred at 0°C for 20 min. The reaction was monitored by TLC and the mixture was quenched with water and extracted by Et_2O. The extract was washed by brine and dried using anhydrous Na_2SO_4. The solvents were removed and the residue was purified by column chromatography (30:1 petroleum ether/AcOEt). 1-Diphenylphosphino-1′-[(*S*)-4-isopropyl-2.5-oxazolinyl]-2′(R_p)-(diphenylphosphino)-5′-(trimethylsilyl)ferrocene (0.538 g, 73% yield) was obtained as an orange solid. $[\alpha]_D^{20} = 192.7$ (*c* 0.51, $CHCl_3$). ^1H NMR: $\delta = 0.30$ (s, 9H), 0.56 (d, $J = 6.7$ Hz, 3H), 0.63 (d, $J = 6.7$ Hz, 3H), 1.42 (m, 1H), 3.25 (d, $J = 2.4$ Hz, 1H), 3.72–4.05 (m, 4H), 4.21 (d,

$J=6.7$ Hz, 1H), 4.36 (s, 1H), 4.42 (s, 1H), 4.74 (s, 1H), 7.02–7.24 (m, 20H). MS m/z (relative intensity) 737 (M^+, 100.0), 694 (16.7), 660 (23.1), 652 (28.9). IR (KBr) 2954, 1650, 1478, 1433, 1244, 1160, 994, 836, 740, 695 cm^{-1}. Anal. calcd for $C_{43}H_{45}NOSiP_2Fe$: C, 70.01; H, 6.15; N, 1.89. Found: C, 70.06; H, 6.30; N, 1.84.

1-Diphenylphosphino-1′-[(*S*)-4-isopropyl-2.5-oxazolinyl]-2′(R_p)-(diphenylphosphino)-5′-(trimethylsilyl)-ferrocene (0.074 g, 0.1 mmol) was dissolved in anhydrous THF (1 mL) under nitrogen, TBAF (1 mL, 1 mmol, 1.0 M in THF) was then added and the mixture was stirred under reflux for 5 h. The reaction was monitored by TLC and the mixture was quenched with water and extracted by Et_2O. The extract was washed by brine and dried using anhydrous Na_2SO_4. The solvents were removed and the residue was purified by column chromatography (10:1 petroleum ether/AcOEt). Yellowish orange solid of **(*S*,*Rp*)-2** (0.066 g, 98% yield) was obtained. $[\alpha]_D^{20}=161.0$ (c 0.16, $CHCl_3$). ^{1}H NMR: $\delta=0.61$ (d, $J=6.2$ Hz, 6H), 1.55 (m, 1H); 3.47 (m, 1H), 3.85–4.05 (m, 4H), 4.16 (t, $J=2.5$ Hz, 1H), 4.26 (m, 1H), 4.50 (t, $J=1.8$ Hz, 2H), 4.87 (m, 1H), 7.1–7.50 (m, 20H) ppm. ^{31}P NMR: $\delta=-17.38$ (s, 1P), −17.70 (s, 1P) ppm. MS m/z (relative intensity) 665 (M^+, 100.0), 622 (16.33), 588 (13.7), 518 (13.7), 480 (32.4), 305 (15.2). IR (KBr) 2955, 1657, 1478, 1433, 1027, 981, 742, 695, 487 cm^{-1}. Anal. calcd for $C_{40}H_{37}NOP_2Fe$: C, 72.19; H, 5.60; N, 2.11. Found: C, 72.14; H, 5.80; N, 2.22.

4.4. General procedure for the asymmetric hydroesterification of styrene

A 50 mL stainless steel autoclave was charged with ρ-toluenesulfonic acid, a chosen source of palladium salt, ligand, styrene, and methanol under an atmosphere of N_2. The autoclave was pressurized with CO and heated to the desired reaction temperature. The reaction mixture was stirred well with a magnetic stirrer. After a prescribed reaction time, the autoclave was cooled to room temperature and the residue gas was released. The data on conversion and yield were determined by GC-MS using acetophenone as an internal standard on an HPG 1800c GCD system on a Bexs column (30 m×0.25 m I.D.). The enantiomeric excess of the product was determined by GC using an HP5890 gas chromatograph equipped with a Chrompack Chirasil-Dex CB column (50 m×0.25 mm). The absolute configuration of methyl 2-phenylpropionate was determined by the comparison of the retention time with those of pure authentic samples.

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