ANGEWANDTE CHEMIE
A Journal of the Gesellschaft Deutscher Chemiker

Supporting Information

for

Angew. Chem. Int. Ed. Z19488

69451 Weinheim, Germany

Application of a New Family of P,N-Ligands to the Highly Enantioselective Hydrosilylation of Arylalkyl and Dialkyl Ketones

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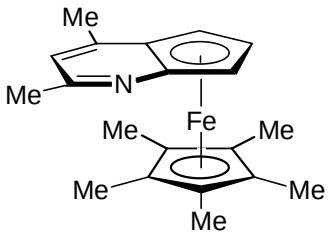
Supporting Information

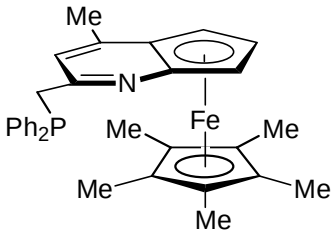
I. General

Unless otherwise noted, all reagents were purchased and used without further purification. The ketone substrates were purified by distillation or by column chromatography. Solvents were distilled from the indicated drying agents: benzene (sodium/benzophenone); THF (sodium/benzophenone); CH_2Cl_2 (CaH_2); Et_2O (sodium/benzophenone); toluene (molten sodium).
All reactions were carried out under an atmosphere of nitrogen or argon in oven-dried glassware, unless otherwise indicated.

II. Preparation of Ligand 1 (Figure 1)



Compound 3. In a glove box, Ni(dppp)Cl_2 (252 mg, 0.465 mmol) was added to a solution of **2**[1] (1.52 g, 4.27 mmol) in Et_2O (80 mL). The mixture was cooled to –30 °C, and then MeMgBr (3.0 M in Et_2O; 1.96 mL, 5.9 mmol) was added. The reaction mixture was stirred at room temperature for 20 hours. Then, NEt_3 (30 mL) was added, and the reaction mixture was removed from the glove box and filtered through a plug of silica gel. The silica gel was washed with NEt_3/EtOAc/hexanes (1:9:9) until all of a purple band had been collected. The resulting solution was concentrated to a purple solid, which was purified by column chromatography (5% EtOAc/hexanes), which provided 1.15 g (80%) of a purple solid. ^{1}H NMR (500 MHz, C_6D_6) δ 6.31 (s, 1H), 4.71 (dd, 1H, J = 0.6, 2.4), 4.00 (d, 1H, J = 2.8), 3.63 (t, 1H, J = 2.4), 2.45 (s, 3H), 2.05, (s, 3H), 1.56 (s, 15H). ^{13}C NMR (126 MHz, C_6D_6) δ 10.5, 19.5, 26.2, 61.8, 67.7, 75.7, 78.6, 81.5, 110.0, 114.9, 149.5, 159.8. FTIR (neat) 2966, 2900, 2849, 1595, 1373, 1028 cm^{-1}. HRMS (EI, *m/e*) calcd for $C_{20}H_{25}FeN$ (M^+) 335.1331, found 335.1349.



Compound 1. In a glove box, *n*-BuLi (1.61 M in hexanes; 2.13 mL, 3.43 mmol) was added by syringe over ~2 minutes to a –30 °C solution of complex **3** (1.15 g, 3.43 mmol) in Et_2O (100 mL). The mixture was stirred at room temperature for 10 minutes, and then it was cooled to –30 °C and $ClPPh_2$ (757 mg, 3.43 mmol) was added. This reaction mixture was stirred at room temperature for 3 hours and then filtered through a plug of silica gel. The silica gel was washed with NEt_3/EtOAc/hexanes (1:9:9) until all of a purple band had been collected. The resulting solution was concentrated to a purple solid, which was purified by column chromatography (17% Et_2O/pentane), which furnished 1.27 g (71%) of a purple solid.

^1H NMR (500 MHz, C_6D_6) δ 7.61-7.66 (m, 4H), 7.00-7.12 (m, 6H), 6.64 (s, 1H), 4.75, (s, 1H), 3.99 (s, 1H), 3.62-3.99 (m, 3H), 2.00 (s, 3H), 1.57 (s, 15H). ^{13}C NMR (126 MHz, C_6D_6) δ10.6, 19.5, 41.4, 61.8, 67.8, 76.0, 78.7, 81.8, 110.0, 118.1, 128.7, 129.0, 129.1, 133.7, 133.8, 140.3, 140.5, 149.9, 158.3, 160.4. FTIR (neat) 3072, 2903, 1584, 1433, 740, 696 cm^{-1}. HRMS (EI, *m/e*) calcd for $C_{32}H_{34}FeNP$ (M^+) 519.1773, found 519.1761.

The enantiomers of the catalyst were separated by semi-preparative HPLC (Regis (*R,R*)-Whelk-O 2, 1 cm x 25 cm, chloroform/hexanes/diethylamine/ethanol 50:50:0.4:1, 3.0 mL/min). Enantiomer (+)-**1** ($[\alpha]^{20}_D$ = +680° (c = 0.100, THF);

enantiomerically pure by analytical chiral HPLC) was collected from 4.8 minutes to 5.6 minutes, and enantiomer (–)-**1** ($[\alpha]^{20}_{D}$ = –690° (c = 0.100, THF); enantiomerically pure by analytical chiral HPLC) was collected from 6.3 minutes to 7.4 minutes.

III. Catalytic Asymmetric Hydrosilylation of Acetophenone: Enantioselectivity as a Function of the Silane (Table 1)

For Methods Used to Assay Enantiomeric Excess, see Section VI.

General procedure (Table 1, entry 1). In a glove box, a solution of ligand (+)-**1** (3.1 mg, 0.0060 mmol) in CH_2Cl_2 (2 mL) was added slowly to a stirring solution of $[RhCl(cod)]_2$ (1.2 mg, 0.0025 mmol) in CH_2Cl_2 (2 mL). The resulting mixture was stirred for ~40 minutes. The solvent was then removed, and a solution of acetophenone (12 mg, 0.10 mmol) in THF (1.5 mL) was added. The resulting mixture was cooled to –30 °C, and *n*-octylSiH_3 (39 μL, 29 mg, 0.20 mmol) was added. The reaction mixture was stirred at room temperature for ~18 hours. It was then cooled to 0 °C, and 1 N HCl (2 mL) and then acetone (2 mL) were slowly added. The mixture was stirred for 2 hours at 0 °C and then 30 minutes at room temperature. A solution of saturated sodium bicarbonate was added, and the reaction mixture was extracted with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The catalyst was removed by passing the residue through a plug of silica gel. GC analysis showed 1% ee in favor of (*R*)-*sec*-phenethyl alcohol.

When ligand (–)-**1** was used, (*S*)-*sec*-phenethyl alcohol was obtained in 5% ee.

Table 1, entry 2. The general procedure was followed with ligand (+)-**1** and $PhSiH_3$, affording (*R*)-*sec*-phenethyl alcohol in 6% ee. When ligand (–)-**1** was used, (*S*)-*sec*-phenethyl alcohol was obtained in 10% ee.

Table 1, entry 3. The general procedure was followed with ligand (+)-**1** and Et_2SiH_2, affording (*R*)-*sec*-phenethyl alcohol in 2% ee. When ligand (–)-**1** was used, (*S*)-*sec*-phenethyl alcohol was obtained in 0% ee.

Table 1, entry 4. The general procedure was followed with ligand (+)-**1** and $PhMeSiH_2$, affording (*R*)-*sec*-phenethyl alcohol in 64% ee.

When ligand (–)-**1** was used, (*S*)-*sec*-phenethyl alcohol was obtained in 67% ee.

Table 1, entry 5. The general procedure was followed with ligand (+)-**1** and Ph_2SiH_2, affording (*R*)-*sec*-phenethyl alcohol in 79% ee. When ligand (–)-**1** was used, (*S*)-*sec*-phenethyl alcohol was obtained in 80% ee.

Table 1, entry 6. The general procedure was followed with ligand (+)-**1** and (*o*-tol)$PhSiH_2$, affording (*R*)-*sec*-phenethyl alcohol in 94% ee.

When ligand (–)-**1** was used, (*S*)-*sec*-phenethyl alcohol was obtained in 95% ee.

Table 1, entry 7. The general procedure was followed with ligand (+)-**1** and $(o\text{-tol})_2SiH_2$, affording (*R*)-*sec*-phenethyl alcohol in 91% ee.

When ligand (–)-**1** was used, (*S*)-*sec*-phenethyl alcohol was obtained in 93% ee.

Table 1, entry 8. The general procedure was followed with ligand (+)-**1** and $MesPhSiH_2$, affording (*R*)-*sec*-phenethyl alcohol in 98% ee.

When ligand (–)-**1** was used, (*S*)-*sec*-phenethyl alcohol was

obtained in 98% ee.

Table 1, entry 9. The general procedure was followed with ligand (+)-**1** and Mes_2SiH_2. No reduction of acetophenone was observed. When ligand (–)-**1** was used, again no reduction of acetophenone was observed.

IV. Catalytic Asymmetric Hydrosilylation of Arylalkyl Ketones (Table 2)

For Methods Used to Assay Enantiomeric Excess, see Section VI.

General procedure (Table 2, entry 1). In a glove box, a solution of ligand (+)-**1** (12.5 mg, 0.0241 mmol) in CH_2Cl_2 (2 mL) was added slowly to a stirring solution of $[RhCl(cod)]_2$ (4.9 mg, 0.010 mmol) in CH_2Cl_2 (2 mL). The resulting mixture was stirred for ~40 minutes. The solvent was then removed,[2] and a solution of acetophenone (120 mg, 0.999 mmol) in THF (1.0 mL) was added. The resulting mixture was cooled to –30 °C, and $MesPhSiH_2$ (453 mg, 2.0 mmol) was added. The reaction mixture was stirred at room temperature for 24 hours. It was then cooled to 0 °C, and 1 N HCl (10 mL) and then acetone (10 mL) were slowly added. The mixture was stirred for 2 hours at 0 °C and then 30 minutes at room temperature. A solution of saturated sodium bicarbonate was added, and the reaction mixture was extracted with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The product was purified by silica gel chromatography (5-10% Et_2O/pentane), which afforded 114 mg (93%) of (*R*)-*sec*-phenethyl alcohol. GC analysis showed 98% ee.

The general procedure was repeated with ligand (–)-**1**, affording 115 mg (94%) of (*S*)-*sec*-phenethyl alcohol in 98% ee.

Table 2, entry 2. The general procedure was followed with ligand (+)-**1**. After 24 hours, the reaction mixture was quenched with 1% K_2CO_3 in MeOH rather than HCl/acetone. Yield: 144 mg (95%) of (*R*)-4-methoxy-α-methylbenzyl alcohol in 97% ee ($[\alpha]^{20}_D$ = +42.3°,

c = 1.06, toluene).

When ligand (–)-**1** was used, 150 mg (99%) of (*S*)-4-methoxy-α-methylbenzyl alcohol was obtained in 97% ee.

Table 2, entry 3. The general procedure was followed with ligand (+)-**1**, affording 174 mg (92%) of (*R*)-α-methyl-4-(trifluoromethyl)benzyl alcohol in 96% ee after 24 hours of reaction time ($[\alpha]^{20}_D$ = +29.5°, c = 1.05, MeOH).

When ligand (–)-**1** was used, 160 mg (84%) of (*S*)-α-methyl-4-(trifluoromethyl)benzyl alcohol was obtained in 96% ee.

Table 2, entry 4. The general procedure was followed with ligand (+)-**1**, affording 168 mg (98%) of (*R*)-α-methyl-1-naphthalenemethanol in 99% ee after 24 hours of reaction time.

When ligand (–)-**1** was used, 165 mg (96%) of (*S*)-α-methyl-1-naphthalenemethanol was obtained in 99% ee.

Table 2, entry 5. The general procedure was followed with ligand (+)-**1**, affording 143 mg (95%) of (*R*)-2,4-dimethyl-α-methylbenzyl alcohol in 97% ee after 24 hours of reaction time ($[\alpha]^{20}_D$ = +59.0°, c = 1.05, EtOH).

When ligand (–)-**1** was used, 148 mg (99%) of (*S*)-2,4-dimethyl-α-methylbenzyl alcohol was obtained in 92% ee.

Table 2, entry 6. The general procedure was followed with ligand (+)-**1**. After 72 hours, the reaction mixture was quenched with 1% K_2CO_3 in MeOH rather than HCl/acetone. Yield: 162 mg (99%) of (*R*)-α-methyl-2,4,6-(trimethyl)benzyl alcohol in 97% ee ($[\alpha]^{20}_D$ = +47.7°, c = 1.10, $CHCl_3$).

When ligand (–)-**1** was used, 162 mg (99%) of (*S*)-α-methyl-2,4,6-(trimethyl)benzyl alcohol was obtained in 99% ee.

Table 2, entry 7. The general procedure was followed with ligand (+)-**1**, affording 140 mg (95%) of (*R*)-1,2,3,4-tetrahydro-1-naphthol in 98% ee after 72 hours of reaction time ($[\alpha]^{20}_D$ = –32.5°, c = 2.51, $CHCl_3$).

When ligand (–)-**1** was used, 140 mg (95%) of (*S*)-1,2,3,4-tetrahydro-1-naphthol was obtained in 97% ee.

Table 2, entry 8. The general procedure was followed with ligand (+)-**1**, affording 135 mg (98%) of (*R*)-1-phenyl-1-propanol in 98% ee after 72 hours of reaction time ($[\alpha]^{20}_D$ = +47.2°, c = 5.02, $CHCl_3$).

When ligand (–)-**1** was used, 128 mg (94%) of (*S*)-1-phenyl-1-propanol was obtained in 98% ee.

Table 2, entry 9. The general procedure was followed with ligand (+)-**1**, affording 82 mg (75%) of (*S*)-benzyl alcohol-α-*d* in 95% ee (derivatized with (*R*)-Mosher acid chloride; major isomer: δ 5.31; minor isomer: δ 5.36)[3] after 17 h of reaction time.

When ligand (–)-**1** was used, 80 mg (73%) of (*R*)-benzyl alcohol-α-*d* was obtained in 94% ee.

V. Catalytic Asymmetric Hydrosilylation of Dialkyl Ketones (Table 3)

For Methods Used to Assay Enantiomeric Excess, see Section VI.

General procedure (Table 3, entry 2). In a glove box, a solution of ligand (+)-**1** (12.5 mg, 0.0241 mmol) in CH_2Cl_2 (2 mL) was added slowly to a stirring solution of $[RhCl(cod)]_2$ (4.9 mg, 0.010 mmol) in CH_2Cl_2 (2 mL). The resulting mixture was stirred for ~40 minutes. The solvent was then removed,[2] and a solution of cyclohexylmethyl ketone (126 mg, 0.998 mmol) in THF (1.0 mL) was added. The resulting mixture was cooled to –30 °C, and (*o*-tol)$_2SiH_2$ (424 mg, 2.00 mmol) was added. The reaction mixture was stirred at 0 °C for 48 hours, and then 1 N HCl (10 mL) and acetone (10 mL) were slowly added. The mixture was stirred for 2 hours at 0 °C and then 30 minutes at room temperature. A solution of saturated sodium bicarbonate was added, and the reaction mixture was extracted with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The product was purified by silica gel chromatography (5-10% Et_2O/pentane), which afforded 111 mg (87%) of (*R*)-1-cyclohexylethanol. GC analysis showed 94% ee ($[\alpha]^{20}_D$ = –6.69°, c = 3.05, Et_2O).

The general procedure was repeated with ligand (–)-**1**, affording 122 mg (95%) of (*S*)-1-cyclohexylethanol in 94% ee.

Table 3, entry 1. The general procedure was followed with ligand (+)-**1**, affording 160 mg (89%) (*R*)-(1-adamantanyl)ethanol in 94% ee ($[\alpha]^{20}_D$ = +18.9°, c = 0.54, CCl_4).

When ligand (–)-**1** was used, 175 mg (95%) of (*S*)-1-(adamantanyl)ethanol was obtained in 97% ee.

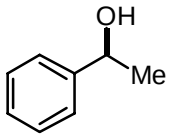
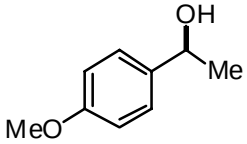
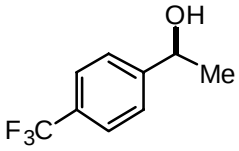
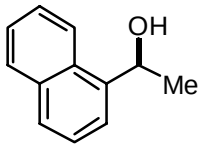
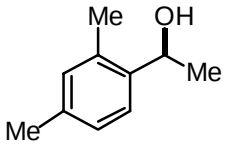
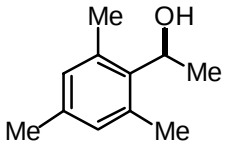
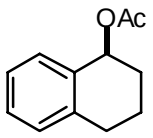
Table 3, entry 3. The general procedure was followed with ligand (+)-**1**, affording 147 mg (98%) of (*R*)-4-phenyl-2-butanol in 83% ee ($[\alpha]^{20}_{D}$ = –14.3°, c = 6.57, $CHCl_3$).

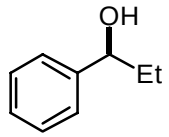
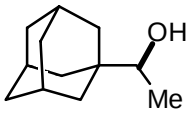
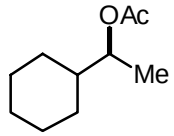
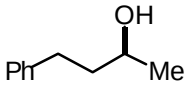
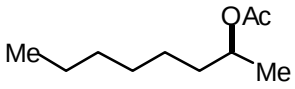
When ligand (–)-**1** was used, 146 mg (97%) of (*S*)-4-phenyl-2-butanol was obtained in 80% ee.

Table 3, entry 4. The general procedure was followed at –20 °C with ligand (+)-**1**, affording 105 mg (81%) of (*R*)-2-octanol in 71% ee.

When ligand (–)-**1** was used, 106 mg (81%) of (*S*)-2-octanol was obtained in 72% ee.

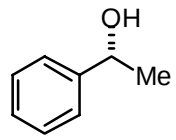
VI. Methods Used to Assay Enantiomeric Excess

Product or its Derivative	ee Assay	Conditions	Retention Time of Isomer with Indicated Configuration (min)	Retention Time of Isomer with Opposite Configuration (min)
	GC Chiraldex BPH	70 °C; 1.0 mL/min carrier gas flow	35.79	34.97
	GC Chiraldex GTA	100 °C; 1.0 mL/min carrier gas flow	26.18	24.58
	GC Chiraldex GTA	100 °C; 1.0 mL/min carrier gas flow	7.66	6.91
	Chiralcel OD Column	10:90 isopropanol : hexanes	10.01	15.50
	GC Chiraldex GTA	105 °C; 1.0 mL/min carrier gas flow	14.85	12.53
	GC Chiraldex BPH	120 °C; 1.0 mL/min carrier gas flow	13.62	13.16
	GC Chiraldex GTA	110 °C; 1.0 mL/min carrier gas flow	20.00	19.45

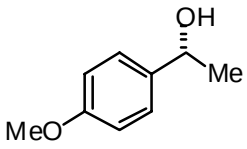
	GC Chiralde x GTA	90 °C; 1.0 mL/min carrier gas flow	15.64	13.95
	GC Chiralde x BPH	110 °C; 1.0 mL/min carrier gas flow	40.05	38.94
	GC Chiralde x GTA	70 °C; 1.0 mL/min carrier gas flow	17.64	19.90
	GC Chiralde x GTA	90 °C; 1.0 mL/min carrier gas flow	21.45	22.29
	GC Chiralde x GTA	70 °C; 1.0 mL/min carrier gas flow	11.36	12.80

VII. Assignment of Absolute Stereochemistry

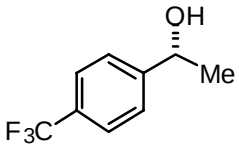
For those alcohols not listed below, the assignment of absolute configuration is based on analogy.



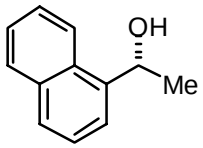
The absolute configuration of the alcohol produced in the presence of (+)-**1** has been assigned by comparing the retention time (GC) with (*R*)-*sec*-phenethyl ethanol from Aldrich.



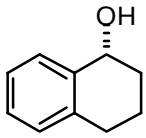
The sign of the optical rotation of the alcohol produced in the presence of (+)-**1** is positive; therefore, its absolute stereochemistry is *R*.[4]



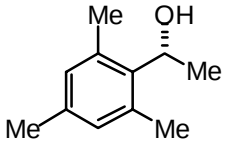
The sign of the optical rotation of the alcohol produced in the presence of (+)-**1** is positive; therefore, its absolute stereochemistry is *R*.[5]



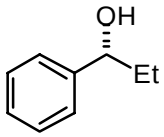
The absolute configuration of the alcohol produced in the presence of (+)-**1** has been assigned by comparing the retention time (HPLC) with (*R*)-α-methyl-1-naphthalenemethanol from Aldrich.



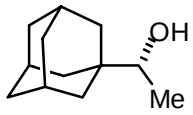
The sign of the optical rotation of the alcohol produced in the presence of (+)-**1** is negative; therefore, its absolute stereochemistry is *R*.[4]



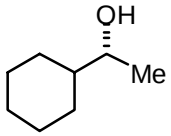
The sign of the optical rotation of the alcohol produced in the presence of (+)-**1** is positive; therefore, its absolute stereochemistry is *R*.[5]



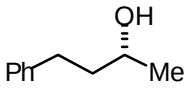
The sign of the optical rotation of the alcohol produced in the presence of (+)-**1** is positive; therefore, its absolute stereochemistry is *R*.[6]



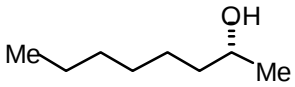
The sign of the optical rotation of the alcohol produced in the presence of (+)-**1** is positive; therefore, its absolute stereochemistry is *R*.[4]



The sign of the optical rotation of the alcohol produced in the presence of (+)-**1** is negative; therefore, its absolute stereochemistry is *R*.[4]



The sign of the optical rotation of the alcohol produced in the presence of (+)-**1** is negative; therefore, its absolute stereochemistry is *R*.[4]



The sign of the optical rotation of the alcohol produced in the presence of (+)-**1** is negative; therefore, its absolute stereochemistry is *R*.[4]

VIII. X-ray Crystal Structure of (–)-1•TsOH (011781s)

A colorless solution of (–)-**1**•TsOH in benzene was prepared. Crystals suitable for X-ray structural analysis were obtained by diffusing pentane into this solution at room temperature.

A blue-green plate of dimensions 0.4 x 0.2 x 0.09 mm^3 was mounted under STP and transferred to a Bruker AXS/CCD three-circle diffractometer (χ fixed at 54.78°) equipped with a cold stream of N_2 gas. An initial unit cell was determined by harvesting reflections I > 20 σ(I) from 45 x 10-s frames of 0.30° ω scan data with monochromated Mo K_α radiation (λ = 0.71073 Å). The cell thus determined was triclinic.

A hemisphere of data was then collected using ω scans of 0.30° and 30-s frames. The raw data frames were integrated using the Bruker program SAINT+ for NT version 6.01. An initial background was determined from the first 12° of data. Actual integration was performed with constant spot sizes of 1.6° in the detector plane and 0.6° in ω. Backgrounds were then calculated as a continuing average over 8 frames of data. The data that were collected (7202 total reflections, 5915 unique, R_{int} = 0.0263) had the following Miller index ranges: –12 to 12 in h, –12 to 12 in k, and –15 to 8 in l. The data were corrected for Lorentz and polarization effects. SADABS absorption correction was applied with μ=0.56 mm^{-1}.

All aspects of the solution and refinement were handled by SHELXTL NT version 5.10.[7] The structure was solved by direct methods in the chiral triclinic space group P1, a = 11.3695(10)

Å; b = 11.3787(10) Å; c = 14.1642(12) Å; α = 78.384(2)°; β = 86.377(2)°; γ = 86.2590(10)°, and refined using standard difference Fourier techniques. Final, full-matrix least-squares refinement (5915 data for 843 parameters) on F^2 yielded residuals of R_1 and wR_2.[8] of 0.0462 and 0.1116 for data $I > 2\sigma(I)$, and 0.0524 and 0.1156, respectively, for all data. During the final refinement, all non-hydrogen atoms were treated anisotropically. Hydrogen atoms were included in calculated positions and refined isotropically on a riding model. No secondary extinction coefficient was used in the refinement. Residual electron density amounted to a maximum of 0.535 e/Å^3 and a minimum of -0.285 e/Å^3. The absolute structure (Flack) parameter for the correct enantiomer is 0.047(19). The structure was inverted and refined in order to confirm the initial assignment of absolute stereochemistry.

Table 1 provides a summary of the crystallographic data for the X-ray structure.

Table 1. Crystal data and structure refinement for 011781s.

Identification code	011781s	
Empirical formula	C39 H42 Fe N O3 P S	
Formula weight	691.62	
Temperature	183(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 11.3695(10) Å	a= 78.384(2)°.
	b = 11.3787(10) Å	b= 86.377(2)°.
	c = 14.1642(12) Å	g = 86.2590(10)°.
Volume	1788.7(3) $Å^3$	
Z	2	
Density (calculated)	1.284 Mg/m^3	
Absorption coefficient	0.562 mm^{-1}	
F(000)	728	
Crystal size	0.4 x 0.2 x 0.09 mm^3	
Theta range for data collection	2.63 to 23.29°.	
Index ranges	-12<=h<=12, -12<=k<=12, -15<=l<=8	
Reflections collected	7202	
Independent reflections	5915 [R(int) = 0.0263]	
Completeness to theta = 23.29•	97.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5915 / 3 / 843	
Goodness-of-fit on F^2	1.038	
Final R indices [I>2sigma(I)]	R1 = 0.0462, wR2 = 0.1116	
R indices (all data)	R1 = 0.0524, wR2 = 0.1157	
Absolute structure parameter	0.047(19)	
Largest diff. peak and hole	0.535 and -0.285 $e.Å^{-3}$	

IX. References

(1) Rios, R.; Liang, J.; Lo, M. M.-C.; Fu, G. C. *Chem. Commun.* **2000**, 377-378.

(2) We subsequently determined that the catalyst can also be prepared directly in THF, thus making this solvent switch unnecessary.

(3) Yamada, I.; Noyori, R. *Org. Lett.* **2000**, *2*, 3425-3427.

(4) Kuwano, R.; Sawamura, M.; Shirai, J.; Takahashi, M.; Ito, Y,. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 485-496.

(5) Nakamura, K.; Matsuda, T. *J. Org. Chem.* **1998**, *63*, 8957-8964.

(6) Kasai, M.; Froussios, C.; Ziffer, H. *J. Org. Chem.* **1983**, *48*, 459-464.

(7) SHELXTL: Bruker AXS, Inc., SHELXTLTM Reference Manual Version 5.1, 1997.

(8) $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$

$wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$

$w = 1/[\sigma^2(F_o)^2 + (0.0746 * P)^2 + 0.8299 * P]$

where $P = [Max(F_o^2, 0) + 2 * F_c^2]/3$