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1-Alkoxy-2,5-diphenylphospholane and -phospholanium Salts in Rhodium-Catalyzed Asymmetric Hydrogenation

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A series of chiral enantiopure phosphinites was synthesized in four steps starting from phosphinic acid. New species were obtained as alkoxyphosphonium compounds. They can be used in the asymmetric hydrogenation of functionalized alkenes.

Introduction

The elaboration of new chiral ligands is the key to developing new metal-catalyzed asymmetric processes. The design and synthesis of chiral phosphane ligands have played significant roles in the development of efficient metal-catalyzed asymmetric reactions.[1]

Monophosphorus ligands may be classified according to the nature of the atoms attached to the phosphorus atom. In most cases, these are carbon, nitrogen, or oxygen. For compounds that possess only P–C and P–O bonds, many combinations are possible (Figure 1).[2] Phosphanes constitute the main class with three P–C bonds.

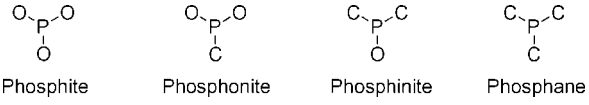

Figure 1. Phosphorus compounds containing P–C and/or P–O bonds.

Phosphite and phosphonite ligands have received much attention in the last several years. Reetz et al. developed new chiral phosphite and phosphonite ligands derived from BINOL in Rh-catalyzed asymmetric hydrogenation.[3] Alexakis et al. described a coupling reaction between allylic chloride and a Grignard reagent.[4] Phosphonites are less commonly used than phosphites as ligands in metal-catalyzed reactions. Börner et al. described an isomerization/hydroformylation of olefins with phosphorus ligands derived from biphenol.[5] Most of the chiral phosphinites used in enantioselective synthesis were prepared from chiral alcohols or diols and chlorodiphenylphosphane.[6] To the best of our knowledge, only one example of a chiral dialkylphosphinite containing chiral C-substituents was described by Zhang.[7]

In our effort to find efficient monodentate phosphorus ligands, we investigated the possibility of synthesizing compounds based on the chiral *trans*-2,5-diphenylphospholane frame **1** (Figure 2).

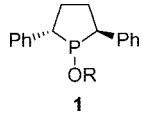

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Figure 2. 1-Alkoxy-2,5-*trans*-diphenylphospholane.

The structure of phosphinite **1** presents the following specific features: (i) a monodentate phosphorus nature, which is likely to offer more efficient activity,[8] (ii) a non-stereogenic phosphorus atom, which avoids problems of stereochemical integrity, (iii) chirality provided by the carbon moiety and not by the alcohol ligand, (iv) a five-membered cyclic chain, which could offer good enantioselectivity in asymmetric reactions, and (v) an electron-rich phosphorus atom compared to the diphenylphosphinyl radical usually found in the mono- or diphosphane ligands. We describe here the synthesis and use of new chiral enantiopure phosphinites.

Results and Discussion

Two proposed retrosynthetic routes to these chiral phosphinites from phospholanic acid **5**[9] are depicted in

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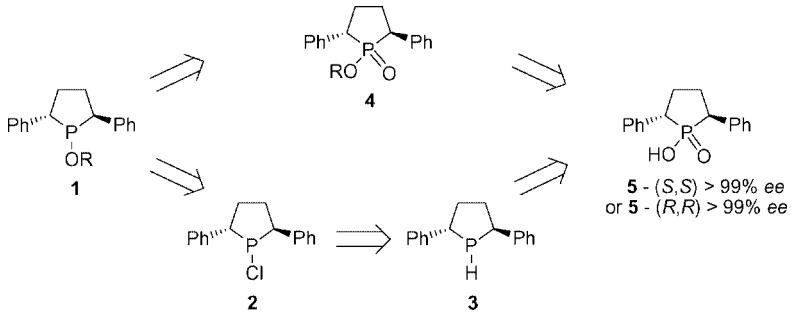
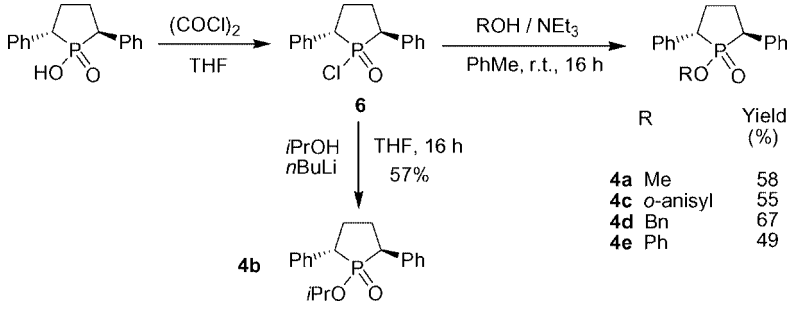


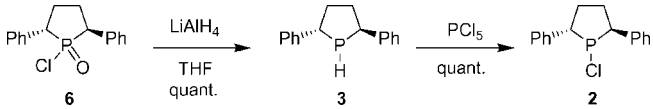
Scheme 1. Retrosynthesis of phosphinite **1**.



Scheme 2. Synthesis of phosphinates **4**.

Scheme 1. One way would involve the reduction of the corresponding phosphinate **4** with the Schwartz reagent, according to the method of Majoral et al.[10] The enantiopure phosphinates **4** were prepared through reaction of chloride **6** with alcohols (Scheme 2). In the case of isopropyl compound **4b**, the substitution occurs only with the lithium isopropoxide anion. Unfortunately, the reduction of the phosphinate with the Schwartz reagent was unsuccessful.

The second route to phosphinites consists of the nucleophilic substitution of the chlorophosphane **2**, which is obtained by chlorination of the secondary phosphane **3**. Secondary phosphanes usually result from the reduction of phosphinyl chlorides, phosphinates, or phosphinic acids by metal hydrides or silanes.[11] The enantiopure phosphinyl chloride **6** was reduced with lithium aluminum hydride to give the pure secondary phosphane **3** in quantitative yield (Scheme 3).



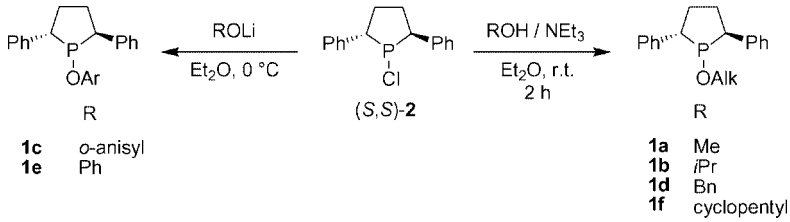
Scheme 3. Synthesis of secondary phosphane **3** and chlorophosphane **2**.

Chlorophosphanes are key intermediates in the formation of P–O or P–N bonds. They can be obtained from phosphorus compounds by their reaction with carbon tetrachloride,[12] *N*-chlorosuccinimide,[13] phosgene,[14] or dichlorotris(2,4,6-tribromophenoxy)phosphorane.[15] These methods were used on the secondary phosphane **3** without success. Oxalyl chloride, sulfuryl chloride, and thionyl chloride afforded a mixture of products. Finally, the chlorophosphane **2** was obtained quantitatively with the method developed by Rhodia with phosphorus pentachloride (Scheme 3).[16] Purification of **2** was not required since no non-volatile residue or by-product was formed.

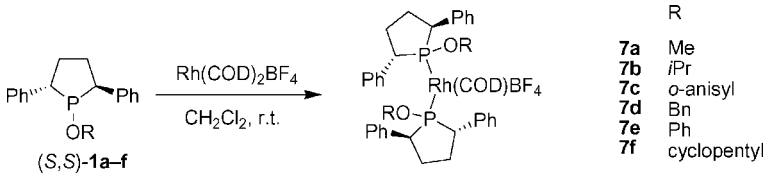
Chlorophosphane **2** reacted with alcohols in the presence of triethylamine to give the enantiomerically pure alkyl phosphinites **1** after filtration of the ammonium salt under argon. Aryl phosphinites were obtained by substitution with lithium aryloxides followed by filtration of the lithium chloride (Scheme 4).[14]

Compounds **6**, **3**, **2**, and **1** are oxygen- and moisture-sensitive. The synthesis of phosphinites **1** is a one-pot procedure carried out under argon, and the reagents were chosen in order to generate no by-products, to react with total conversion, and to be removed easily. Because of their instability, the phosphinites were characterized by NMR spectroscopy in a sealed tube under argon. Monitoring of the reaction by ^{31}P and ^{1}H NMR spectroscopy showed the complete consumption of the substrate and indicated a clean reaction without formation of by-products. To confirm the structure, the phosphinites were subjected to air oxidation. The corresponding products obtained were compared to the phosphinates **4**, confirming that the original structures were consistent with that of **1**.

Mixing of $Rh(COD)_2BF_4$ and 2 equiv. of phosphinite **1a** in dichloromethane gave the Rh complex as a powder after evaporation of the solvent in 70% yield (Scheme 5). The ^{31}P NMR spectrum of **7a** showed one clean sharp doublet (δ = 155 ppm, $J_{Rh\text{-}P}$ = 180 Hz), revealing the formation of the



Scheme 4. Synthesis of phosphinites **1a**–**f**.



Scheme 5. Synthesis of Rh phosphinite complexes **7**.

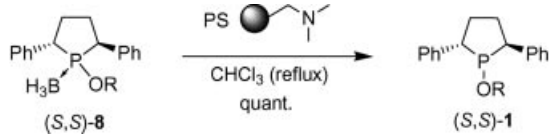
C_2-symmetric $[Rh(COD)(P^*)_2]BF_4$ complex. However, no crystal could be obtained for X-ray analysis. Complexes **7b**–**f** were contaminated by a small amount of the corresponding phosphinate.

Phosphanes are most conveniently protected from air oxidation as their borane complexes. Since the protection of phosphinites in such a way has been reported,[17] treatment of phosphinites **1a**–**d** with borane–dimethyl sulfide complex led to phosphinite boranes **8a**–**d** (Scheme 6). The yields are given for the five-step procedure starting from phospholanic acid (**5**).

The relative stability of these compounds towards air oxidation allowed their characterization. They were, however, unstable to silica gel or alumina treatment. The two main methods currently used to deprotect phosphanes from their borane derivatives[18] are through displacement of the borane group with an amine (diethylamine, morpholine, or DABCO)[19] or by an acid treatment with methanesulfonic acid, trifluoromethanesulfonic acid, or tetrafluoroboric acid, followed by a basic treatment.[20]

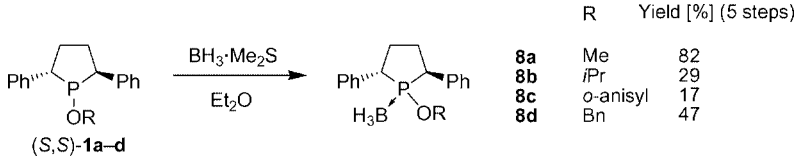
Deprotection of the phosphinite–boranes **8** with amines was not convenient, since it required a filtration through silica gel to remove the amine–borane complex formed. A method that does not necessitate an exposure to silica gel was then preferred; decoordination of the borane was realized by treatment of the phosphinite–borane adduct with an amino-grafted resin for an appropriate time, followed by filtration under argon to afford the phosphinite in a quantitative yield. Results for the deprotection of phosphinite–boranes **8** with the commercially available inexpensive [(dimethylamino)methyl]polystyrene (3–4 mmol g^{-1}) are shown (Table 1). The reaction took place in refluxing chloroform for a few days to ensure complete conversion without the recovery of any by-product or residue.

Table 1. Deprotection of phosphinite–borane complex **8** with amino-grafted polymer.



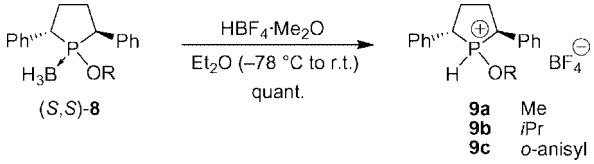
Substrate	R	Resin/phosphinite–borane	Reaction time [d]
8a	Me	5	2
8b	*i*Pr	10	5
8c	*o*-anisyl	5	3
8d	Bn	15	5

Assays for the deprotection of phosphinite–boranes with acids were conducted by treatment of **8a**–**c** with an excess of tetrafluoroboric acid–dimethyl ether complex. Oily, moisture- and air-sensitive products were obtained with complete conversion. The ^1H-coupled ^{31}P NMR spectrum showed for each product a clean doublet (δ = 90–100 ppm) with a coupling constant of about 500 Hz, indicative of a P–H bond, which was confirmed by the ^1H NMR spectra.



Scheme 6. Synthesis of phosphinite–borane complexes **8**.

The mass spectra (electrospray ionization) are consistent with the phosphonium tetrafluoroborate having the structure proposed for compounds **9a**–**c** (Scheme 7).



Scheme 7. Alkoxyphosphonium salt synthesis.

To the best of our knowledge, such a structure has never been described. Only a quaternary phospholanium compound, which possesses two methoxy groups on the phosphorus atom, has been reported.[21] Compounds **9** appear as oils, and no crystal could be obtained for X-ray crystal structure analysis. Treatment of the phosphinite–borane **8d** with an excess of tetrafluoroboric acid–dimethyl ether complex afforded quantitatively the secondary phospholane oxide–trifluoroborane complex **10**, likely as the result of the weakness of the benzylic C–O bond toward acid. Compound **10** could be obtained separately and quantitatively, as an air-stable solid, through reaction of the secondary phosphane oxide **11** (Scheme 8). The structure of **10** was confirmed by X-ray analysis (Figure 3).

The asymmetric Rh-catalyzed hydrogenation of methyl (*Z*)-2-acetamidocinnamate was investigated with complexes prepared by mixing ligands **7** and the cationic $Rh(COD)_2BF_4$ complex (Table 2).

Use of preformed **7a** as the catalyst and methanol as the solvent led to some decomposition of the complex and precipitation of Rh metal. This could be avoided by the use of dichloromethane without affecting the enantioselectivity. Good conversions of the substrate were recorded with all preformed complexes **7**.

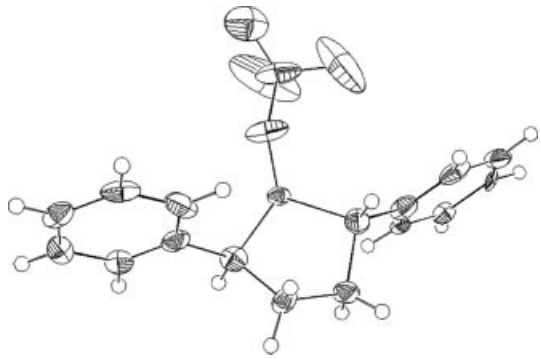


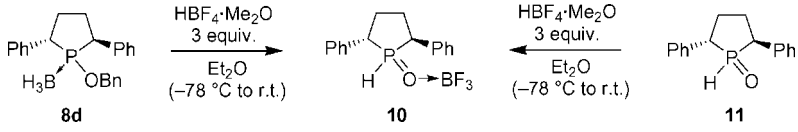
Figure 3. Molecular view of complex **10**.

These complexes are also effective in the hydrogenation of more bulky olefinic substrates such as *N*-(2-methyl-1-phenylprop-1-enyl)acetamide (Table 3).

Low conversions were recorded in methanol and toluene due to some decomposition of the catalyst. Better conversions and moderate enantioselectivities were obtained with dichloromethane as the solvent under an atmospheric pressure of hydrogen. No reaction took place with the phenyl-substituted phosphinite ligand **7e**.

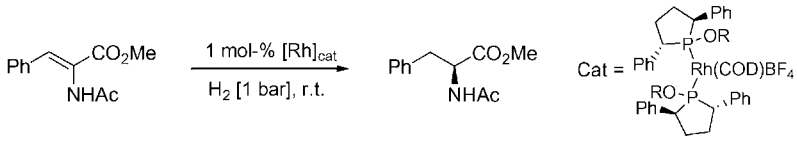
Complexes formed in situ from the $Rh(COD)_2BF_4$ complex and 2 equiv. of phosphinites **1** or alkoxyphosphonium salts **9** were examined as catalysts for the hydrogenation of methyl (*Z*)-2-acetamidocinnamate (Table 4). The hydrogenations were conducted in dichloromethane, under an atmospheric pressure of hydrogen at room temperature, with no sign of decomposition of the catalytic system.

Complete conversions were obtained in most cases. The products were obtained with moderate enantioselectivities. Interestingly, similar values for enantioselectivities were obtained irrespective of whether the chiral ligand precursor



Scheme 8. Formation of phospholane oxide complex **10**.

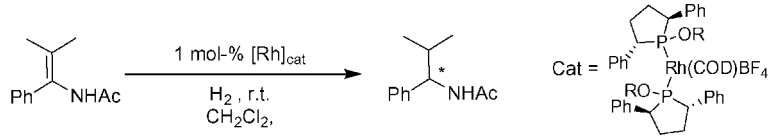
Table 2. Rh-catalyzed hydrogenation of methyl (*Z*)-2-acetamidocinnamate with complex **7**.[a]



R	Solvent	Conversion [%]	Reaction time [h]	*ee* [%]
Me	MeOH	100	0.5	31 (*S*)
	CH_2Cl_2	100	24	31 (*S*)
*i*Pr	CH_2Cl_2	100	0.8	75 (*S*)
Ph	CH_2Cl_2	78	6.5	11 (*S*)
o-anisyl	CH_2Cl_2	72	24	20 (*S*)
Bn	CH_2Cl_2	100	24	26 (*S*)

[a] All reactions were carried out at room temperature and under an atmospheric pressure of hydrogen with a preformed Rh catalyst. The absolute configuration of the ligand is (*S*,*S*).

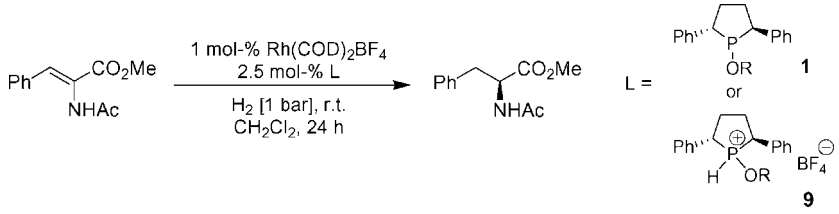
Table 3. Hydrogenation of *N*-(2-methyl-1-phenylpropenyl)acetamide.[a]



R	Hydrogen pressure [bar]	Solvent	Conversion [%]	Reaction time [h]	*ee* [%]
Me	1	MeOH	32	6.5	50 (*S*)
		CH_2Cl_2	76	21.5	47 (*S*)
		PhMe	53	24	44 (*S*)
*i*Pr	1	CH_2Cl_2	33	24	44 (*S*)
	40	CH_2Cl_2	59	24	51 (*S*)
Ph	40	CH_2Cl_2	0	48	–

[a] All reactions were carried out at room temperature with the preformed Rh catalyst. The absolute configuration of the ligand is (*S*,*S*).

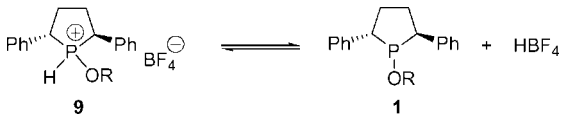
Table 4. Hydrogenation of methyl (*Z*)-2-acetamidocinnamate.[a]



Entry	R	Ligand	Conversion [%][b]	*ee* [%][c]
1	Me	**1a**	100	34 (*S*)
2		**9a**	100	31 (*S*)
3	*i*Pr	**1b**	15	–[d]
4		**9b**	100	28 (*S*)
5	*o*-anisyl	**1f**	100	25 (*S*)
6		**9c**	100	23 (*S*)
7	Bn	**1d**	100	23 (*S*)

[a] All reactions were carried out at room temperature and under an atmospheric pressure of hydrogen with 1 mol-% of $Rh(COD)_2BF_4$ and 2.5 mol-% of ligand. The absolute configuration of the ligand is (*S*,*S*). [b] Determined by ^1H NMR spectroscopy. [c] Determined by chiral HPLC analysis on a Chiralcel ODH column with hexanes/2-propanol (9:1) as the eluent. [d] Not determined.

was a phosphinite or an alkoxyphosphonium salt (Table 4, Entries 1–2 and 5–6). These results suggest an equilibrium between the active ligand and its corresponding phosphonium salt (Scheme 9). The presence of free acid seems to have no influence on the course of the hydrogenation. This is in agreement with our results with chiral phospholane ligands in Rh-catalyzed asymmetric hydrogenation.[22] Thus, alkoxyphosphonium salts appear to be of practical use as precursors of phosphinite ligands.

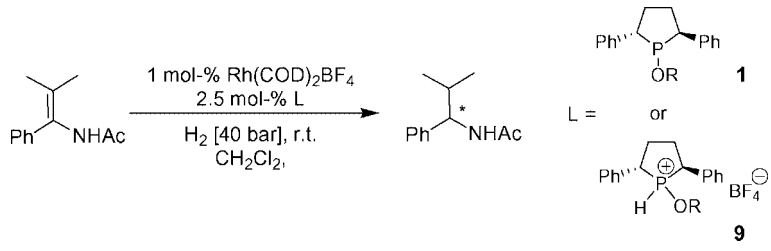


Scheme 9. Equilibrium between phosphinite and phosphonium species.

The same catalytic systems were investigated in the asymmetric hydrogenation of tetrasubstituted olefins (Table 5).

A higher hydrogen pressure (40 bar) and longer reaction times were required to ensure good conversions. The best enantioselectivities were obtained for methyl phosphinite **1a** and the corresponding salt **9a** (47% *ee* and 49% *ee*, respectively, Table 5, Entries 1 and 2). Both an inversion of configuration and a decrease in enantioselectivity and yield were recorded for phosphinite **1b** compared to the phosphonium salt **9b** (8% *ee* vs. 41% *ee*, Table 5, Entries 3 and 4). We suppose a rapid decomposition of isopropyl phosphinite **1b**, which generated another catalytic species. However, as reported above, the enantioselectivities were similar when we used the phosphinite or the corresponding tetrafluoroborate salt. The enantioselectivities were also similar to those obtained with the preformed Rh complexes as catalysts (Table 3).

Table 5. Hydrogenation of *N*-(2-methyl-1-phenylpropenyl)acetamide.[a]



Entry	R	Ligand	Conversion [%][b]	*ee* [%][c]
1	Me	**1a**	100	47 (*S*)
2		**9a**	57	49 (*S*)
3	*i*Pr	**1b**	46	8 (*R*)
4		**9b**	100	41 (*S*)
5	*o*-anisyl	**1c**	100	26 (*S*)
6		**9c**	100	32 (*S*)
7	Bn	**1d**	100	35 (*S*)

[a] All reactions were carried out at room temperature and under hydrogen (40 bar) with 1 mol-% of $Rh(COD)_2BF_4$ and 2.5 mol-% of ligand. The absolute configuration of the ligand is (*S*,*S*). [b] Determined by ^1H NMR spectroscopy. [c] Determined by chiral GC.

Conclusions

Several new chiral enantiopure phosphinites **1** have been prepared in four steps from *trans*-2,5-diphenylphospholanic acid **5**. We described a clean and useful deprotecting method for phosphorus–borane complexes with an amino-grafted polymer. We discovered chiral alkoxyphosphonium compounds **9** as new structures. These compounds present the asymmetric element in the phospholane moiety, contrary to the usual phosphinites previously reported. Phosphinites and alkoxyphosphonium salts have an interesting potential as ligands for transition metals in asymmetric catalysis.

Experimental Section

General Considerations: All reactions were carried out under argon in oven-dried glassware with magnetic stirring. Solvents were distilled before use: THF and diethyl ether from sodium metal/benzophenone ketyl and dichloromethane (DCM) and toluene from calcium hydride. All other reagents are available commercially and were used without further purification. ^1H NMR spectra were recorded with a Bruker AM 200 (200 MHz) or AC 250 (250 MHz) spectrometer as $CDCl_3$ solutions, and data are reported in ppm relative to TMS. ^{13}C NMR spectra were recorded with a Bruker AC 250 (62.9 MHz) spectrometer as $CDCl_3$ solutions and data are reported in ppm relative to the solvent (δ = 77.0 ppm). ^{31}P NMR spectra were recorded with a Bruker AC 250 (101.2 MHz) spectrometer as $CDCl_3$ solutions, and data are reported in ppm relative to H_3PO_4. Optical rotations were measured as solutions in 10 cm cells at the sodium D line with a Perkin–Elmer 241 polarimeter. IR spectra were recorded as KBr disks with a Perkin–Elmer spectrometer. Melting points were measured with a Reichert instrument. Gas chromatography was performed with a FISONS 9000 gas chromatograph with a BP1 column (15 m × 0.32 mm × 0.5 μm). High-resolution mass spectra were recorded with a Finningan MAT 95 S spectrometer. HPLC analyses were carried out with a Perkin–Elmer chromatograph equipped with a diode array UV detector with a Chiracel ODH column. Synthesis of compounds **5**, **6**, and **10** is described in our previous paper.[9a]

(*S*,*S*)-2,5-*trans*-Diphenylphospholane (3): Lithium aluminum hydride (212 mg, 5.6 mmol) was added to a suspension of enantiopure (*S*,*S*)-phosphinyl chloride **6** (831 mg, 2.8 mmol) in dry diethyl ether (20 mL) at 0 °C in a Schlenk tube under argon. The mixture was stirred from 0 °C to room temperature overnight. Degassed water was slowly added to aggregate the metallic salts in a gum. The solution was transferred by cannula through a magnesium sulfate layer under argon, and the solvent was removed under reduced pressure. The secondary phosphane **3** was isolated quantitatively as a white solid. ^1H NMR (250 MHz, $CDCl_3$): δ = 7.20 (d, $J_{H\text{-}P}$ = 156 Hz, 1 H, H-P), 7.27–7.10 (m, 10 H, Ph), 3.93–3.84 (m, 1 H, CH), 3.42–3.22 (m, 1 H, CH), 2.60–2.39 (m, 2 H, CH_2), 2.14–1.74 (m, 2 H, CH_2) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = –17.8 ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 145.3 (d, $J_{C\text{-}P}$ = 17 Hz, C_{quat}), 141.7 (C_{quat}), 128.5 (CH_{Ph}), 127.5 (d, $J_{C\text{-}P}$ = 4 Hz, CH_{Ph}), 126.2 (d, $J_{C\text{-}P}$ = 1 Hz, CH_{Ph}), 125.9 (d, $J_{C\text{-}P}$ = 2 Hz, CH_{Ph}), 44.7 (d, $J_{C\text{-}P}$ = 17 Hz, CH), 41.1 (d, $J_{C\text{-}P}$ = 11 Hz, CH), 39.1 (CH_2), 38.8 (d, $J_{C\text{-}P}$ = 6 Hz, CH_2) ppm. HRMS (GC): calcd. for $C_{16}H_{17}P$ 240.1068; found 240.1063. $[a]_D^{25}$ = +141.1 (*c* = 1.75, CH_2Cl_2).

(*S*,*S*)-1-Chloro-2,5-*trans*-diphenylphospholane (2): A suspension of pentachlorophosphorus (580 mg, 2.8 mmol) in dry toluene (10 mL) was added by cannula to a solution of enantiopure (*S*,*S*)-phosphane **3** (670 mg, 2.8 mmol) in dry toluene (10 mL) at room temperature in a Schlenk tube under argon. The mixture was stirred for 2 h. The yellow suspension became immediately limpid. The solvent was removed under reduced pressure giving the chlorophosphane quantitatively as a yellow oil. ^1H NMR (250 MHz, $CDCl_3$): δ = 7.34–7.10 (m, 10 H, Ph), 3.93–3.37 (m, 2 H, CH), 2.63–1.90 (m, 4 H, CH_2) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 138.0 ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 141.8 (C_{quat}), 134.9 (C_{quat}), 128.8 (d, $J_{C\text{-}P}$ = 3 Hz, CH_{Ph}), 128.4 (CH_{Ph}), 127.9 (CH_{Ph}), 126.8 (CH_{Ph}), 58.1 (d, $J_{C\text{-}P}$ = 32 Hz, CH), 53.6 (d, $J_{C\text{-}P}$ = 32 Hz, CH), 34.9 (CH_2), 32.0 (CH_2) ppm.

(*S*,*S*)-1-Methoxy-2,5-*trans*-diphenylphospholane (1a): A Schlenk tube was charged with enantiopure (*S*,*S*)-chlorophosphane **2** (383 mg, 1.4 mmol) and dry diethyl ether (10 mL) under argon. Triethylamine (210 μL, 1.5 mmol) and MeOH (170 μL, 4.2 mmol) were added by syringe at 0 °C. The mixture was stirred at room temperature for 2 h and then filtered under argon to eliminate the ammonium salt. The solvent was removed under reduced pressure giving quantitatively the methyl phosphinite as a pale yellow oil.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.40–7.22 (m, 10 H, Ph), 3.52–3.02 (m, 2 H, CH), 3.00 (d, $J_{H\text{-}P}$ = 13 Hz, 3 H, CH_3), 2.63–1.82 (m, 4 H, CH_2) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 162.8 ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 138.5 (C_{quat}), 128.9 (CH_{Ph}), 128.6 (CH_{Ph}), 128.2 (CH_{Ph}), 126.2 (CH_{Ph}), 58.3 (d, $J_{C\text{-}P}$ = 20 Hz, CH), 57.2 (d, $J_{C\text{-}P}$ = 20 Hz, CH), 54.5 (d, $J_{C\text{-}P}$ = 23 Hz, CH_3), 35.5 (CH_2), 32.5 (d, $J_{C\text{-}P}$ = 2 Hz, CH_2) ppm.

(*S*,*S*)-1-Isopropoxy-2,5-*trans*-diphenylphospholane (1b): A Schlenk tube was charged with enantiopure (*S*,*S*)-chlorophosphane **2** (353 mg, 1.3 mmol) and dry diethyl ether (10 mL) under argon. Triethylamine (200 μL, 1.4 mmol) and freshly distilled *i*PrOH (200 μL, 2.6 mmol) were added by syringe at 0 °C. The mixture was stirred at room temperature for 2 h and then filtered under argon to eliminate the ammonium salt. The solvent was removed under reduced pressure, giving quantitatively the isopropyl phosphinite as a pale yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.34–7.05 (m, 10 H, Ph), 3.48–3.33 (m, 2 H, CH), 3.17–2.98 (m, 1 H, CH), 2.65–1.73 (m, 4 H, CH_2), 1.03 (d, $J_{H\text{-}H}$ = 6 Hz, 3 H, CH_3), 0.61 (d, $J_{H\text{-}H}$ = 6 Hz, 3 H, CH_3) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 151.3 ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 143.1 (d, $J_{C\text{-}P}$ = 19 Hz, C_{quat}), 138.7 (C_{quat}), 128.7 (CH_{Ph}), 128.6 (CH_{Ph}), 128.0 (d, $J_{C\text{-}P}$ = 1 Hz, CH_{Ph}), 127.8 (CH_{Ph}), 127.7 (CH_{Ph}), 125.9 (d, $J_{C\text{-}P}$ = 2 Hz, CH_{Ph}), 125.8 (d, $J_{C\text{-}P}$ = 2 Hz, CH_{Ph}), 74.1 (d, $J_{C\text{-}P}$ = 20 Hz, CH), 57.7 (d, $J_{C\text{-}P}$ = 22 Hz, CH), 53.8 (d, $J_{C\text{-}P}$ = 21 Hz, CH), 34.9 (CH_2), 32.3 (d, $J_{C\text{-}P}$ = 2 Hz, CH_2), 24.3 (d, $J_{C\text{-}P}$ = 4 Hz, CH_3), 23.4 (d, $J_{C\text{-}P}$ = 5 Hz, CH_3) ppm.

(*S*,*S*)-1-(*o*-Methoxyphenoxy)-2,5-*trans*-diphenylphospholane (1c): A Schlenk tube was charged with freshly distilled guaiacol (150 μL, 1.3 mmol), diethyl ether (3 mL), and lithium granules (15 mg, 2.2 mmol). At the end of the reaction, the suspension was transferred by cannula to a suspension of enantiopure (*S*,*S*)-chlorophosphane **2** (353 mg, 1.3 mmol) in dry diethyl ether (7 mL) under argon at 0 °C. The mixture was stirred at room temperature for 3 h and then filtered under argon to eliminate the lithium salt. The solvent was removed under reduced pressure, giving quantitatively the phosphinite as a brown oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.44–7.12 (m, 10 H, Ph), 6.92–6.50 (m, 4 H, Ar), 3.82–3.07 (m, 2 H, CH), 3.53 (s, 3 H, CH_3), 2.73–1.80 (m, 4 H, CH_2) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 167.3 ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 151.0 (d, $J_{C\text{-}P}$ = 3 Hz, C_{quat}), 147.3 (d, $J_{C\text{-}P}$ = 7 Hz, C_{quat}), 142.9 (d, $J_{C\text{-}P}$ = 19 Hz, C_{quat}), 138.3 (C_{quat}), 128.7 (d, $J_{C\text{-}P}$ = 4 Hz, CH_{Ph}), 128.6 (CH_{Ph}), 128.3 (d, $J_{C\text{-}P}$ = 1 Hz, CH_{Ph}), 126.1 (d, $J_{C\text{-}P}$ = 2 Hz, CH_{Ph}), 126.0 (d, $J_{C\text{-}P}$ = 2 Hz, CH_{Ph}), 123.3 (d, $J_{C\text{-}P}$ = 1 Hz, CH_{Ph}), 120.9 (d, $J_{C\text{-}P}$ = 7 Hz, CH_{Ph}), 120.7 (CH_{Ph}), 111.9 (CH_{Ph}), 57.8 (d, $J_{C\text{-}P}$ = 25 Hz, CH), 55.5 (CH_3), 54.7 (d, $J_{C\text{-}P}$ = 20 Hz, CH), 35.8 (CH_2), 32.2 (CH_2) ppm.

(*S*,*S*)-1-Benzyloxy-2,5-*trans*-diphenylphospholane (1d): A Schlenk tube was charged with enantiopure (*S*,*S*)-chlorophosphane **2** (316 mg, 1.1 mmol) and dry diethyl ether (10 mL) under argon. Triethylamine (170 μL, 1.2 mmol) and freshly distilled benzyl alcohol (120 μL, 1.2 mmol) were added by syringe at 0 °C. The mixture was stirred at room temperature for 2.5 h and then filtered under argon to eliminate the ammonium salt. The solvent was removed under reduced pressure, giving quantitatively the benzyl phosphinite as a pale yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.40–6.97 (m, 15 H, Ph), 4.36–3.98 (m, 2 H, CH_2), 3.48–3.00 (m, 2 H, CH), 2.53–1.73 (m, 4 H, CH_2) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 161.1 ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 150.5 (C_{quat}), 138.1 (C_{quat}), 128.5 (CH_{Ph}), 128.3 (t, $J_{C\text{-}P}$ = 2 Hz, CH_{Ph}), 128.1(CH_{Ph}), 127.7 (CH_{Ph}), 127.3 (CH_{Ph}), 126.8 (CH_{Ph}), 125.8 (CH_{Ph}), 72.5 (d, $J_{C\text{-}P}$ = 20 Hz, CH_2), 56.8 (d, $J_{C\text{-}P}$ = 21 Hz, CH), 54.0 (d, $J_{C\text{-}P}$ = 22 Hz, CH), 34.8 (CH_2), 32.0 (d, $J_{C\text{-}P}$ = 2 Hz, CH_2) ppm.

(*S*,*S*)-1-Phenoxy-2,5-*trans*-diphenylphospholane (1e): A Schlenk tube under argon was charged with phenol (145 mg, 1.5 mmol), diethyl ether (3 mL), and lithium granules (15 mg, 2.2 mmol). At the end of the reaction, the suspension was transferred by cannula to a suspension of enantiopure (*S*,*S*)-chlorophosphane **2** (405 mg, 1.5 mmol) in dry diethyl ether (7 mL) at 0 °C. The mixture was stirred at room temperature for 2 h and then filtered under argon to eliminate the lithium salt. The solvent was removed under reduced pressure, giving quantitatively the phenyl phosphinite as pale yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.39–6.51 (m, 15 H, Ph), 3.68–3.63 (m, 1 H, CH), 3.25–3.10 (m, 1 H, CH), 2.75–1.86 (m, 4 H, CH_2) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 158.2 ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 157.9 (d, $J_{C\text{-}P}$ = 8 Hz, C_{quat}), 142.3 (d, $J_{C\text{-}P}$ = 20 Hz, C_{quat}), 138.0 (C_{quat}), 129.2 (CH_{Ph}), 128.9 (d, $J_{C\text{-}P}$ = 1 Hz, CH_{Ph}), 128.6 (CH_{Ph}), 128.4 (d, $J_{C\text{-}P}$ = 1 Hz, CH_{Ph}), 128.0 (CH_{Ph}), 127.9 (CH_{Ph}), 126.2 (d, $J_{C\text{-}P}$ = 2 Hz, CH_{Ph}), 122.2 (d, $J_{C\text{-}P}$ = 1 Hz, CH_{Ph}), 119.0 (d, $J_{C\text{-}P}$ = 9 Hz, CH_{Ph}), 57.3 (d, $J_{C\text{-}P}$ = 24 Hz, CH), 54.6 (d, $J_{C\text{-}P}$ = 21 Hz, CH), 35.3 (d, $J_{C\text{-}P}$ = 1 Hz, CH_2), 32.7 (d, $J_{C\text{-}P}$ = 2 Hz, CH_2) ppm.

(*S*,*S*)-1-Cyclopentoxy-2,5-*trans*-diphenylphospholane (1f): A Schlenk tube was charged with enantiopure (*S*,*S*)-chlorophosphane **2** (424 mg, 1.5 mmol) and dry diethyl ether (10 mL) under argon. Triethylamine (240 μL, 1.7 mmol) and freshly distilled cyclopentanol (170 μL, 1.8 mmol) were added by syringe at 0 °C. The mixture was stirred at room temperature for 2 h and then filtered under argon to eliminate the ammonium salt. The solvent was removed under reduced pressure, giving quantitatively the cyclopentyl phosphinite as a pale yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.40–7.05 (m, 10 H, Ph), 4.31–3.20 (m, 2 H, CH), 3.14–2.90 (m, 1 H, CH), 2.60–2.08 (m, 4 H, CH_2), 1.78–1.17 (m, 8 H, CH_2) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 151.2 ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 151.1 (C_{quat}), 147.2 (C_{quat}), 128.6 (CH_{Ph}), 128.1 (CH_{Ph}), 127.7 (CH_{Ph}), 126.8 (CH_{Ph}), 125.8 (CH_{Ph}), 57.3 (CH), 53.8 (d, $J_{C\text{-}P}$ = 20 Hz, CH), 45.8 (CH), 35.6 (CH_2), 34.9 (CH_2), 34.5 (CH_2), 32.5 (CH_2), 29.7 (CH_2), 23.1 (CH_2) ppm.

Typical Procedure for Synthesis of Rh Complexes 7: A Schlenk tube was charged with the desired enantiopure (*S*,*S*)-alkyl phosphinite **1** (1.8 mmol) in freshly distilled DCM (5 mL), and this solution was added at room temperature by cannula to a solution of $Rh(COD)_2BF_4$ (347 mg, 0.8 mmol) in DCM (5 mL). The mixture was stirred overnight, and the solvent was removed under reduced pressure, giving a powder.

(Cycloocta-1,5-diene)bis[(*S*,*S*)-1-methoxy-2,5-*trans*-diphenylphospholane]rhodium Tetrafluoroborate (7a): The powder was washed with cold diethyl ether, giving the complex as an orange solid (501 mg, 70% yield over 5 steps). ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 7.24–7.12 (m, 20 H, Ph), 5.11–5.01 (m, 2 H, CH), 4.22–4.10 (m, 1 H, CH), 3.92–3.78 (m, 1 H, CH), 3.46 (d, J = 10 Hz, 6 H, CH_3), 3.12–2.98 (m, 4 H, CH), 2.70–2.49 (m, 4 H, CH_2), 2.22–2.00 (m, 4 H, CH_2), 2.00–1.88 (m, 4 H, CH_2), 1.80–1.48 (m, 4 H, CH_2) ppm. ^{31}P NMR (101.2 MHz, CD_2Cl_2): δ = 155.1 (d, $J_{Rh\text{-}P}$ = 180 Hz) ppm. ^{13}C NMR (90.6 MHz, CD_2Cl_2): δ = 140.1 (CH_{Ph}), 137.1 (CH_{Ph}), 129.4 (CH_{Ph}), 129.1 (CH_{Ph}), 128.6 (CH_{Ph}), 127.7 (CH_{Ph}), 127.6 (CH_{Ph}), 107.9 (*C*H=CH), 102.0 (*C*H=CH), 97.8 (*C*H=CH), 49.6 (CH phosphinite), 48.8 (CH phosphinite), 47.9 (CH phosphinite), 34.8 (CH_2), 33.2 (CH_2), 32.3 (CH_2), 30.0 (CH_2), 28.3 (CH_2), 27.7 (CH_2) ppm. ESI-MS: *m*/*z* (%) = 643.0 (100) [$C_{34}H_{38}O_2P_2Rh$ = RhL_2], 481.1 (71) [$C_{25}H_{31}OPRh$ = RhL(COD)].

(Cycloocta-1,5-diene)bis[(*S*,*S*)-1-isopropoxy-2,5-*trans*-diphenylphospholane]rhodium Tetrafluoroborate (7b): The powder was washed with cold diethyl ether, giving an oil, which was extracted with DCM. The solvent was removed under reduced pressure, giving the

complex as an impure brown solid contaminated by a small amount of **4b**. ^{1}H NMR (250 MHz, CD_2Cl_2) was poorly resolved. ^{31}P NMR (101.2 MHz, CD_2Cl_2): δ = 148.0 (d, J_{Rh-P} = 175 Hz) ppm. ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ = 139.7 (C_{quat}), 136.5 (C_{quat}), 129.0 (CH_{Ph}), 128.6 (CH_{Ph}), 127.7 (CH_{Ph}), 127.2 (CH_{Ph}), 108.8 (*C*H=CH), 108.0 (*C*H=CH), 107.9 (*C*H=CH), 74.3 (CH_{iPr}), 71.5 (CH_{iPr}), 47.7 (CH phosphane), 46.7 (CH phosphane), 46.0 (CH phosphane), 45.1 (CH phosphane), 32.2 (CH_2), 31.3 (CH_2), 30.0 (CH_2), 27.7 (CH_2), 24.7 (CH_3), 23.2 (CH_3) ppm. ESI-MS: *m*/*z* (%) = 509.3 (100) [$C_{27}H_{35}OPRh$ = RhL(COD)].

(Cycloocta-1,5-diene)bis[(*S*,*S*)-1-(*o*-methoxyphenoxy-2,5-*trans*-diphenylphospholane)rhodium Tetrafluoroborate (7c): The powder was washed with cold diethyl ether and diisopropyl ether, giving an impure orange solid contaminated by a small amount of **4c**. ^{1}H NMR (250 MHz, CD_2Cl_2): poorly resolved. ^{31}P NMR (101.2 MHz, CD_2Cl_2): δ = 163.9 (d, J_{Rh-P} = 188 Hz) ppm.

(Cycloocta-1,5-diene)bis[(*S*,*S*)-1-benzyloxy-2,5-*trans*-diphenylphospholane]rhodium Tetrafluoroborate (7d): The powder was washed with cold diethyl ether and diisopropyl ether, giving an impure brown solid contaminated by a small amount of **4d**. ^{1}H NMR (250 MHz, $CDCl_3$): poorly resolved. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 153.8 (d, J_{Rh-P} = 185 Hz) ppm.

(Cycloocta-1,5-diene)bis[(*S*,*S*)1-phenoxy-2,5-*trans*-diphenylphospholane]rhodium Tetrafluoroborate (7e): The powder was washed with cold diethyl ether, diisopropyl ether, and hexanes, giving an impure orange solid contaminated by a small amount of **4e**. ^{1}H NMR (250 MHz, $CDCl_3$): poorly resolved. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 158.7 (d, J_{Rh-P} = 178 Hz) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 135.9 (C_{quat}), 130.9 (CH_{Ph}), 130.4 (CH_{Ph}), 129.6 (CH_{Ph}), 128.9 (CH_{Ph}), 127.4 (CH_{Ph}), 124.7 (CH_{Ph}), 120.4 (CH_{Ph}), 115.5 (CH_{Ph}), 105.7 (*C*H=CH), 94.9 (*C*H=CH), 47.4 (CH phosphane), 45.8 (CH phosphane), 44.1 (CH phosphane), 40.5 (CH phosphane), 31.5 (CH_2), 29.8 (CH_2), 28.6 (CH_2), 27.6 (CH_2), 24.9 (CH_2), 21.9 (CH_2) ppm. ESI-MS: *m*/*z* (%) = 543.2 (100) [$C_{30}H_{33}OPRh$ = RhL(COD)].

Typical Procedure for Synthesis of Phosphinite–Boranes 8: A Schlenk tube was charged with enantiopure (*S*,*S*)-phosphinite **1** (1 mmol) in freshly distilled diethyl ether. Borane–dimethyl sulfide complex (3 mmol) was added by syringe. The yellow solution became white, and the mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure, giving a residue, which was purified by flash chromatography on silica gel to give the desired phosphinite–borane **8**.

(*S*,*S*)-1-Methoxy-2,5-*trans*-diphenylphospholane–Borane (8a): The crude oil was purified by flash chromatography on silica gel with heptane/AcOEt (90:10) as the eluent, giving the product as a white solid (882 mg, 3.1 mmol, 82% yield). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.39–7.30 (m, 10 H, Ph), 3.58–3.24 (m, 2 H, CH), 3.04 (d, J_{P-H} = 11 Hz, 3 H, CH_3), 2.52–2.04 (m, 4 H, CH_2), 0.90–0.70 (BH_3) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 145.0 (d, J_{P-B} = 69 Hz) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 136.3 (d, J_{C-P} = 3 Hz, C_{quat}), 135.0 (d, J_{C-P} = 5 Hz, C_{quat}), 128.5 (d, J_{C-P} = 2 Hz, CH_{Ph}), 128.4 (CH_{Ph}), 128.3 (d, J_{C-P} = 2 Hz, CH_{Ph}), 128.2 (CH_{Ph}), 127.0 (d, J_{C-P} = 3 Hz, CH_{Ph}), 126.9 (d, J_{C-P} = 3 Hz, CH_{Ph}), 54.8 (d, J_{C-P} = 4 Hz, CH_3), 51.0 (d, J_{C-P} = 35 Hz, CH), 48.6 (d, J_{C-P} = 30 Hz, CH), 30.6 (CH_2) ppm. HRMS (GC): calcd. for $C_{17}H_{19}OP$ 270.1168; found 270.1153. $[a]_D^{25}$ = –38.1 (*c* = 0.5, $CHCl_3$).

(*S*,*S*)-1-Isopropoxy-2,5-*trans*-diphenylphospholane–Borane (8b): The crude oil was purified by flash chromatography on silica gel with heptane/AcOEt (90:10) as the eluent, giving the product as a white solid (130 mg, 0.4 mmol, 29% yield). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.36–7.18 (m, 10 H, Ph), 4.08–4.00 (m, 1 H, CH), 3.50–3.28 (m, 2 H, CH), 2.47–1.99 (m, 4 H, CH_2), 1.06 (d, J_{H-H} = 6 Hz, 3 H, CH_3), 0.44 (d, J_{H-H} = 6 Hz, 3 H, CH_3), 0.90–0.70 (BH_3) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 139.2 (d, J_{P-B} = 69 Hz) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 136.5 (C_{quat}), 135.7 (d, J_{C-P} = 4 Hz, C_{quat}), 128.8 (CH_{Ph}), 128.4 (CH_{Ph}), 128.2 (CH_{Ph}), 126.9 (CH_{Ph}), 73.3 (CH), 52.1 (d, J_{C-P} = 34 Hz, CH), 48.5 (d, J_{C-P} = 33 Hz, CH), 30.5 (CH_2), 30.1 (d, J_{C-P} = 7 Hz, CH_2), 24.6 (CH_3), 22.8 (CH_3) ppm. HRMS (GC): calcd. for $C_{19}H_{23}OP$ 298.1481; found 298.1480. $[a]_D^{25}$ = –40.6 (*c* = 0.5, $CHCl_3$).

(*S*,*S*)-1-(*o*-Methoxyphenoxy)-2,5-*trans*-diphenylphospholane–Borane (8c): The crude oil was purified by flash chromatography on silica gel with heptane/AcOEt (90:10) as the eluent and precipitated in diethyl ether, giving the product as a white solid (84 mg, 0.2 mmol, 17% yield). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.48–7.24 (m, 10 H, Ph), 6.91 (t, *J* = 8 Hz, 1 H, Ar), 6.71 (d, *J* = 8 Hz, 1 H, Ar), 6.52 (t, *J* = 8 Hz, 1 H, Ar), 5.61 (d, *J* = 8 Hz, 1 H, Ar), 3.98–3.80 (m, 1 H, CH), 3.44 (s, 3 H, CH_3), 3.55–3.35 (m, 1 H, CH), 2.60–2.05 (m, 4 H, CH_2), 0.90–0.70 (BH_3) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 149.6 (d, J_{P-B} = 51 Hz) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 151.1 (d, J_{C-P} = 2 Hz, C_{quat}), 141.6 (d, J_{C-P} = 6 Hz, C_{quat}), 137.4 (d, J_{C-P} = 4 Hz, C_{quat}), 135.3 (d, J_{C-P} = 5 Hz, C_{quat}), 129.2 (d, J_{C-P} = 1 Hz, CH_{Ph}), 129.1 (CH_{Ph}), 128.6 (d, J_{C-P} = 2 Hz, CH_{Ph}), 128.3 (d, J_{C-P} = 2 Hz, CH_{Ph}), 127.3 (d, J_{C-P} = 2 Hz, CH_{Ph}), 127.0 (d, J_{C-P} = 2 Hz, CH_{Ph}), 125.3 (d, J_{C-P} = 2 Hz, CH_{Ph}), 122.0 (d, J_{C-P} = 3 Hz, CH_{Ph}), 120.4 (d, J_{C-P} = 1 Hz, CH_{Ph}), 111.7 (d, J_{C-P} = 1 Hz, CH_{Ph}), 55.2 (CH_3), 52.6 (d, J_{C-P} = 29 Hz, CH), 49.9 (d, J_{C-P} = 34 Hz, CH), 33.3 (d, J_{C-P} = 6 Hz, CH_2), 30.5 (CH_2) ppm. HRMS (GC): calcd. for $C_{23}H_{23}O_2P$ 362.14308; found 362.1431. $[a]_D^{25}$ = –63.4 (*c* = 0.5, $CHCl_3$).

(*S*,*S*)-1-Benzyloxy-2,5-*trans*-diphenylphospholane–Borane (8d): The crude oil was purified by flash chromatography on silica gel with heptane/AcOEt (90:10) as the eluent, giving the product as a white solid (194 mg, 0.5 mmol, 47% yield). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.37–6.94 (m, 15 H, Ph), 4.58 (dd, *J* = 7 Hz and 12 Hz, 1 H, CH_2), 3.83 (dd, *J* = 6 Hz and 12 Hz, 1 H, CH_2), 3.54–3.32 (m, 2 H, CH), 2.48–2.00 (m, 4 H, CH_2), 0.90–0.70 (BH_3) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 144.5 (d, J_{P-B} = 51 Hz) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 136.6 (d, J_{C-P} = 7 Hz, C_{quat}), 136.1 (d, J_{C-P} = 3 Hz, C_{quat}), 134.9 (d, J_{C-P} = 5 Hz, C_{quat}), 128.4 (d, J_{C-P} = 3 Hz, CH_{Ph}), 128.1 (d, J_{C-P} = 2 Hz, CH_{Ph}), 127.9 (CH_{Ph}), 127.6 (CH_{Ph}), 126.9 (CH_{Ph}), 126.8 (CH_{Ph}), 69.3 (d, J_{C-P} = 3 Hz, CH_2), 52.1 (CH_2), 51.0 (d, J_{C-P} = 34 Hz, CH), 48.5 (d, J_{C-P} = 31 Hz, CH), 30.2 (d, J_{C-P} = 7 Hz, CH_2) ppm. HRMS (GC): calcd. for $C_{23}H_{23}OP$ 346.1481; found 346.1487. $[a]_D^{25}$ = –56.6 (*c* = 0.5, $CHCl_3$).

General Procedure for the Deprotection of Phosphinite–Boranes on Solid Support: A Schlenk tube equipped with a refrigerant was charged with the phosphinite–borane, [(dimethylamino)methyl]-polystyrene, and chloroform under argon. The mixture was refluxed for the desired time, and it was filtered under an inert gas. The solvent was removed under reduced pressure, giving quantitatively the phosphinite **1** as a colorless liquid.

(*S*,*S*)-1-Methoxy-2,5-*trans*-diphenylphospholanium Tetrafluoroborate (9a): A Schlenk tube was charged with enantiopure (*S*,*S*)-methyl phosphinite–borane **8a** (7.1 mg, 0.025 mmol) in freshly distilled diethyl ether (2 mL). Tetrafluoroboric acid–dimethyl ether complex (8 μL, 0.075 mmol) was added by syringe at –78 °C. The mixture was warmed to room temperature overnight. The solvent was removed under reduced pressure, giving quantitatively the phosphonium salt as a colorless liquid. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.69 [d, J_{P-H} = 551 Hz, 1 H, H(P)], 7.52–7.24 (m, 10 H, Ph), 4.59–4.48 (m, 1 H, CH), 4.21–4.02 (m, 1 H, CH), 3.39 (d,

J = 12 Hz, 3 H, OCH_3), 2.87–2.26 (m, 4 H, CH_2) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 99.4 ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 133.2 (d, $J_{C\text{-}P}$ = 3 Hz, C_{quat}), 131.0 (d, $J_{C\text{-}P}$ = 4 Hz, C_{quat}), 129.8 (d, $J_{C\text{-}P}$ = 2 Hz, CH_{Ph}), 129.5 (d, $J_{C\text{-}P}$ = 2 Hz, CH_{Ph}), 129.3 (CH_{Ph}), 129.2 (CH_{Ph}), 128.9 (CH_{Ph}), 128.1 (CH_{Ph}), 128.0 (CH_{Ph}), 60.7 (d, $J_{C\text{-}P}$ = 10 Hz, CH_3), 45.0 (d, $J_{C\text{-}P}$ = 57 Hz, CH), 42.0 (d, $J_{C\text{-}P}$ = 53 Hz, CH), 32.0 (d, $J_{C\text{-}P}$ = 8 Hz, CH_2), 29.6 (d, $J_{C\text{-}P}$ = 16 Hz, CH_2) ppm. ESI-MS: m/z (%) = 271.1 (100) [$C_{17}H_{20}OP$].

(*S*,*S*)-1-Isopropoxy-2,5-*trans*-diphenylphospholanium Tetrafluoroborate (9b): A Schlenk tube was charged with enantiopure (*S*,*S*)-isopropyl phosphinite–borane **8b** (7.8 mg, 0.025 mmol) in freshly distilled diethyl ether (2 mL). Tetrafluoroboric acid–dimethyl ether complex (13 μL, 0.125 mmol) was added by syringe at –78 °C. The mixture was warmed to room temperature overnight. The solvent was removed under reduced pressure, giving quantitatively the phosphonium salt as a colorless liquid. ^1H NMR (250 MHz, $CDCl_3$): δ = 7.60 [d, $J_{P\text{-}H}$ = 539 Hz, 1 H, H(P)], 7.38–7.10 (m, 10 H, Ph), 4.38–4.12 (m, 1 H, $CH_{i\text{Pr}}$), 3.88–3.62 (m, 2 H, CH), 2.82–2.24 (m, 4 H, CH_2), 0.96 (d, J = 6 Hz, 3 H, CH_3), 0.67 (d, J = 6 Hz, 3 H, CH_3) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 91.0 ppm. ^{13}C NMR (62.9 MHz, DMSO): δ = 137.6 (C_{quat}), 137.1 (C_{quat}), 129.9 (CH_{Ph}), 129.5 (CH_{Ph}), 128.9 (CH_{Ph}), 128.2 (CH_{Ph}), 127.6 (CH_{Ph}), 127.2 (CH_{Ph}), 63.0 (CH), 48.5 (d, $J_{C\text{-}P}$ = 61 Hz, CH), 43.8 (d, $J_{C\text{-}P}$ = 59 Hz, CH), 32.8 (CH_2), 28.1 (d, $J_{C\text{-}P}$ = 12 Hz, CH_2), 25.9 (CH_3) ppm. ESI-MS: m/z (%) = 299.1 (28) [$C_{19}H_{24}OP$], 257.1 (100) [$C_{16}H_{18}OP$].

(*S*,*S*)-1-(*o*-Methoxyphenoxy)-2,5-*trans*-diphenylphospholanium Tetrafluoroborate (9c): A Schlenk tube was charged with enantiopure (*S*,*S*)-phosphinite–borane **8c** (9.4 mg, 0.025 mmol) in freshly distilled diethyl ether (2 mL). Tetrafluoroboric acid–dimethyl ether complex (8 μL, 0.075 mmol) was added by syringe at –78 °C. The mixture was warmed to room temperature overnight. The solvent was removed under reduced pressure, giving quantitatively the phosphonium salt as a colorless liquid. ^1H NMR (250 MHz, $CDCl_3$): δ = 7.50–6.62 (m, 14 H, Ph), 4.11–3.88 (m, 2 H, CH), 3.30 (s, 3 H, CH_3), 2.83–2.37 (m, 4 H, CH_2) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 98.6 ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 147.0 (C_{quat}), 139.6 (d, $J_{C\text{-}P}$ = 13 Hz, C_{quat}), 132.1 (C_{quat}), 130.6 (CH_{Ph}), 129.6 (d, $J_{C\text{-}P}$ = 12 Hz, CH_{Ph}), 129.0 (CH_{Ph}), 128.7 (CH_{Ph}), 128.4 (CH_{Ph}), 127.2 (CH_{Ph}), 121.6 (CH_{Ph}), 119.8 (CH_{Ph}), 111.9 (CH_{Ph}), 55.4 (CH_3), 47.1 (d, $J_{C\text{-}P}$ = 50 Hz, CH), 43.7 (d, $J_{C\text{-}P}$ = 50 Hz, CH), 32.7 (CH_2), 30.6 (d, $J_{C\text{-}P}$ = 14 Hz, CH_2) ppm. ESI-MS: m/z (%) = 363.1 (100) [$C_{23}H_{24}O_2P$].

(*S*,*S*)-1-Oxo-2,5-*trans*-diphenylphospholane–Trifluoroborane (10): A Schlenk tube was charged with enantiopure (*S*,*S*)-phosphane oxide **11** (6.4 mg, 0.025 mmol) in freshly distilled diethyl ether (2 mL). Tetrafluoroboric acid–dimethyl ether complex (8 μL, 0.075 mmol) was added by syringe at –78 °C. The mixture was warmed to room temperature overnight. The solvent was removed under reduced pressure, giving quantitatively a white solid. Recrystallization in chloroform/hexanes offered pure crystals for analysis. ^1H NMR (250 MHz, DMSO): δ = 9.48 (s, 1 H, OH), 7.61–7.30 (m, 10 H, Ph), 7.17 [d, $J_{P\text{-}H}$ = 467 Hz, 1 H, H(P)], 3.78–3.57 (m, 2 H, CH), 2.60–2.04 (m, 4 H, CH_2) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 72.6 ppm. ^{13}C NMR (62.9 MHz, DMSO): δ = 138.5 (d, $J_{C\text{-}P}$ = 2 Hz, C_{quat}), 138.0 (d, $J_{C\text{-}P}$ = 6 Hz, C_{quat}), 130.6 (d, $J_{C\text{-}P}$ = 5 Hz, CH_{Ph}), 130.1 (CH_{Ph}), 129.5 (CH_{Ph}), 128.9 (d, $J_{C\text{-}P}$ = 6 Hz, CH_{Ph}), 128.1 (CH_{Ph}), 127.7 (CH_{Ph}), 49.2 (d, $J_{C\text{-}P}$ = 60 Hz, CH), 44.5 (d, $J_{C\text{-}P}$ = 59 Hz, CH), 33.6 (d, $J_{C\text{-}P}$ = 7 Hz, CH_2), 29.0 (d, $J_{C\text{-}P}$ = 12 Hz, CH_2) ppm. ESI-MS: m/z (%) = 257.1 (100) [$C_{16}H_{18}OP$].

(*S*,*S*)-1-Oxo-1-methoxy-2,5-*trans*-diphenylphospholane (4a): A Schlenk tube was charged with enantiopure (*S*,*S*)-phosphinyl chloride **6** (2.13 g, 7.3 mmol) and freshly distilled toluene (50 mL) under argon. MeOH (2.98 mL, 73.4 mmol) and triethylamine (1.33 mL, 9.5 mmol) were added by syringe. The mixture was stirred at room temperature overnight. The resulting suspension was washed with water and extracted with AcOEt. The combined organic phases were washed with brine and dried with $MgSO_4$, and the solvent was removed under reduced pressure. The residue was crystallized from AcOEt/heptane (50:50), giving the expected methyl phosphinate as a white solid (1.21 g, 4.2 mmol, 58% yield). ^1H NMR (200 MHz, $CDCl_3$): δ = 7.39–7.15 (m, 10 H, Ph), 3.60–3.41 (m, 1 H, CH), 3.32–3.10 (m, 1 H, CH), 3.14 (d, $J_{H\text{-}P}$ = 5 Hz, 3 H, CH_3), 2.55–2.28 (m, 2 H, CH_2), 2.20–2.05 (m, 2 H, CH_2) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 64.5 ppm. HPLC [Regis (*S*,*S*)-Whelk O1, hexanes/*i*PrOH/EtOH (63:27:10), flow = 0.65 mL min^{-1}, λ = 254 nm]: R_t (*S*,*S*) = 8.9 min, R_t (*R*,*R*) = 15.1 min.

(±)-1-Oxo-1-isopropoxy-2,5-*trans*-diphenylphospholane (4b): A Schlenk tube was charged with freshly distilled *i*PrOH (0.34 mL, 4.4 mmol) and THF (5 mL). After cooling at –78 °C, *n*BuLi (1.5 M in hexanes, 2.5 mL, 3.7 mmol) was added by syringe. The solution was warmed slowly to room temperature and was transferred by cannula to a solution of racemic phosphinyl chloride **6** (991 mg, 3.4 mmol) in freshly distilled THF (15 mL) under argon. The mixture was stirred at room temperature overnight. The resulting suspension was washed with water and extracted with AcOEt. The combined organic phases were washed with brine and dried with $MgSO_4$, and the solvent was removed under reduced pressure. The residue was crystallized from hexanes/AcOEt, giving the expected phosphinate as a white solid (609 mg, 1.9 mmol, 57% yield). ^1H NMR (250 MHz, $CDCl_3$): δ = 7.38–7.24 (m, 10 H, Ph), 4.32–4.24 (m, 1 H, CH), 3.49–3.33 (m, 1 H, CH), 3.22–3.00 (m, 1 H, CH), 2.52–2.06 (m, 4 H, CH_2), 1.11 (d, $J_{H\text{-}H}$ = 6 Hz, 3 H, CH_3), 0.60 (d, $J_{H\text{-}H}$ = 6 Hz, 3 H, CH_3) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 63.6 ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 136.5 (d, $J_{C\text{-}P}$ = 4 Hz, C_{quat}), 136.3 (d, $J_{C\text{-}P}$ = 7 Hz, C_{quat}), 128.6 (CH_{Ph}), 128.4 (CH_{Ph}), 128.2 (d, $J_{C\text{-}P}$ = 4 Hz, CH_{Ph}), 126.7 (CH_{Ph}), 70.1 (d, $J_{C\text{-}P}$ = 7 Hz, CH), 46.6 (d, $J_{C\text{-}P}$ = 84 Hz, CH), 46.2 (d, $J_{C\text{-}P}$ = 85 Hz, CH), 30.2 (d, $J_{C\text{-}P}$ = 13 Hz, CH_2), 27.6 (d, $J_{C\text{-}P}$ = 11 Hz, CH_2), 24.8 (CH_3), 23.0 (d, $J_{C\text{-}P}$ = 5 Hz, CH_3) ppm. M.p. 129 °C. ESI-MS: m/z (%) = 273.1 (100) [M – C_3H_6]$^+$, 315.2 (54) [M + H]$^+$, 337.2 (41) [M + Na]$^+$, 651.3 (52) [2 M + Na]$^+$. $C_{19}H_{23}O_2P$ (314.36): calcd. C 72.59, H 7.37, P 9.85; found C 72.60, H 7.44, P 9.93. HPLC [Regis (*S*,*S*)-Whelk O1, hexanes/*i*PrOH (75:25), flow = 0.8 mL min^{-1}, λ = 254 nm]: R_t (*S*,*S*) = 6.8 min, R_t (*R*,*R*) = 9.3 min.

(*R*,*R*)-1-Oxo-1-(*o*-methoxyphenoxy)-2,5-*trans*-diphenylphospholane (4c): A Schlenk tube was charged with enantiopure (*R*,*R*)-phosphinyl chloride **6** (1.15 g, 3.9 mmol) and freshly distilled toluene (25 mL) under argon. Guaiacol (0.66 mL, 5.9 mmol) and triethylamine (0.72 mL, 5.1 mmol) were added by syringe. The mixture was stirred at room temperature overnight. The resulting suspension was washed with water and extracted with AcOEt. The combined organic phases were washed with brine and dried with $MgSO_4$, and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel with DCM/MeOH (gradient from 100:0 to 92:8) as the eluent. The residue was crystallized from AcOEt/heptane, giving the expected phosphinate as a white solid (812 mg, 2.1 mmol, 55% yield). ^1H NMR (250 MHz, $CDCl_3$): δ = 7.48–7.20 (m, 10 H, Ph), 6.95 (t, J = 8 Hz, 1 H, Ar), 6.78 (d, J = 8 Hz, 1 H, Ar), 6.63 (t, J = 8 Hz, 1 H, Ar), 6.39 (d, J = 8 Hz, 1 H, Ar), 3.58 (s, 3 H, CH_3), 3.60–3.43 (m, 2 H, CH), 2.67–2.13 (m, 4 H, CH_2) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 63.8 ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 150.5 (d, $J_{C\text{-}P}$ = 4 Hz, C_{quat}), 139.5 (d, $J_{C\text{-}P}$ = 10 Hz, C_{quat}), 137.2 (d, $J_{C\text{-}P}$ = 4 Hz, C_{quat}), 135.1 (d, $J_{C\text{-}P}$ = 7 Hz, C_{quat}),

128.9 (d, $J_{C\text{-}P}$ = 6 Hz, CH_{Ph}), 128.4 (CH_{Ph}), 126.7 (d, $J_{C\text{-}P}$ = 16 Hz, CH_{Ph}), 125.1 (CH_{Ph}), 121.9 (CH_{Ph}), 120.7 (CH_{Ph}), 112.3 (CH_{Ph}), 55.6 (CH_3), 46.8 (d, $J_{C\text{-}P}$ = 86 Hz, CH), 44.8 (d, $J_{C\text{-}P}$ = 82 Hz, CH), 31.6 (d, $J_{C\text{-}P}$ = 13 Hz, CH_2), 26.9 (d, $J_{C\text{-}P}$ = 11 Hz, CH_2) ppm. M.p. (±): 126 °C; m.p. (*R*,*R*): 113 °C. ESI-MS: *m*/*z* (%) = 379.2 (100) $[M + H]^+$, 401.1 (14) $[M + Na]^+$, 779.3 (18), $[2 M + Na]^+$. $C_{23}H_{23}O_3P$ (378.40): calcd. C 73.00, H 6.13, P 8.19; found C 72.91, H 6.08, P 8.23. HPLC [Regis (*S*,*S*)-Whelk O1, hexanes/*i*PrOH (95:5), flow = 1 mL min^{-1}, λ = 254 nm]: R_t (*R*,*R*) = 43.0 min, R_t (*S*,*S*) = 49.6 min. $[\alpha]_D^{25}$ = +56.6 (*c* = 0.5, $CHCl_3$).

(*R*,*R*)-1-Oxo-1-benzyloxy-2,5-*trans*-diphenylphospholane (4d): A Schlenk tube was charged with enantiopure (*R*,*R*)-phosphinyl chloride **6** (1.15 g, 3.9 mmol) and freshly distilled toluene (25 mL) under argon. Benzyl alcohol (0.72 mL, 5.9 mmol) and triethylamine (0.72 mL, 5.1 mmol) were added by syringe. The mixture was stirred at room temperature overnight. The resulting suspension was washed with water and extracted with AcOEt. The combined organic phases were washed with brine and dried with $MgSO_4$, and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel with DCM/MeOH (gradient from 100:0 to 95:5) as the eluent. The residue was crystallized from hexanes/AcOEt, giving the expected benzyl phosphinate as a white solid (947 mg, 2.6 mmol, 67% yield). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.39–7.00 (m, 15 H, Ph), 4.80 (dd, *J* = 7 Hz and 12 Hz, 1 H, CH_2), 4.02 (dd, *J* = 6 Hz and 12 Hz, 1 H, CH_2), 3.55–3.40 (m, 1 H, CH), 3.30–3.13 (m, 1 H, CH), 2.54–2.12 (m, 4 H, CH_2) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 65.6 ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 136.4 (d, $J_{C\text{-}P}$ = 7 Hz, C_{quat}), 136.1 (d, $J_{C\text{-}P}$ = 4 Hz, C_{quat}), 135.5 (d, $J_{C\text{-}P}$ = 6 Hz, C_{quat}), 128.6 (d, $J_{C\text{-}P}$ = 4 Hz, CH_{Ph}), 128.2 (CH_{Ph}), 128.0 (d, $J_{C\text{-}P}$ = 4 Hz, CH_{Ph}), 127.9 (CH_{Ph}), 127.6 (CH_{Ph}), 126.8 (d, $J_{C\text{-}P}$ = 4 Hz, CH_{Ph}), 66.3 (d, $J_{C\text{-}P}$ = 7 Hz, CH_2), 46.4 (d, $J_{C\text{-}P}$ = 82 Hz, CH), 45.2 (d, $J_{C\text{-}P}$ = 85 Hz, CH), 30.2 (d, $J_{C\text{-}P}$ = 13 Hz, CH_2), 27.4 (d, $J_{C\text{-}P}$ = 11 Hz, CH_2) ppm. M.p. (±): 114 °C; m.p. (*R*,*R*): 117 °C. ESI-MS: *m*/*z* (%) = 363.2 (100) $[M + H]^+$, 385.2 (42) $[M + Na]^+$, 747.3 (36) $[2 M + Na]^+$. $C_{23}H_{23}O_2P$ (362.40): calcd. C 76.23, H 6.40, P 8.55; found C 76.26, H 6.38, P 8.57. HPLC [Regis (*S*,*S*)–Whelk O1, hexanes/*i*PrOH (75:25), flow = 0.8 mL min^{-1}, λ = 254 nm]: R_t (*S*,*S*) = 9.7 min, R_t (*R*,*R*) = 16.5 min. $[\alpha]_D^{25}$ = +99.8 (*c* = 0.5, $CHCl_3$).

(*R*,*R*)-1-Oxo-1-phenoxy-2,5-*trans*-diphenylphospholane (4e): A Schlenk tube was charged with enantiopure (*R*,*R*)-phosphinyl chloride **6** (2.13 g, 7.3 mmol) and freshly distilled toluene (50 mL) under argon. Phenol (760 mg, 8.1 mmol) and triethylamine (1.33 mL, 9.5 mmol) were added. The mixture was stirred at room temperature overnight. The resulting suspension was washed with water and extracted with AcOEt. The combined organic phases were washed with brine and dried with $MgSO_4$, and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel with DCM/MeOH (gradient from 100:0 to 90:10) as the eluent. The residue was crystallized from AcOEt/heptane, giving the expected phenyl phosphinate as a white solid (1.25 g, 3.6 mmol, 49% yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.43–6.69 (m, 15 H, Ph), 3.57–3.34 (m, 2 H, CH), 2.33–2.04 (m, 4 H, CH_2) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 62.9 ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 150.6 (d, $J_{C\text{-}P}$ = 9 Hz, C_{quat}), 136.2 (d, $J_{C\text{-}P}$ = 4 Hz, C_{quat}), 134.8 (d, $J_{C\text{-}P}$ = 7 Hz, C_{quat}), 129.3 (CH_{Ph}), 128.8 (d, $J_{C\text{-}P}$ = 6 Hz, CH_{Ph}), 128.6 (d, $J_{C\text{-}P}$ = 2 Hz, CH_{Ph}), 128.5 (d, $J_{C\text{-}P}$ = 2 Hz, CH_{Ph}), 128.2 (d, $J_{C\text{-}P}$ = 5 Hz, CH_{Ph}), 127.0 (d, $J_{C\text{-}P}$ = 3 Hz, CH_{Ph}), 126.9 (d, $J_{C\text{-}P}$ = 2 Hz, CH_{Ph}), 124.2 (d, $J_{C\text{-}P}$ = 1 Hz, CH_{Ph}), 120.2 (d, $J_{C\text{-}P}$ = 4 Hz, CH_{Ph}), 46.5 (d, $J_{C\text{-}P}$ = 86 Hz, CH), 44.7 (d, $J_{C\text{-}P}$ = 83 Hz, CH), 30.7 (d, $J_{C\text{-}P}$ = 13 Hz, CH_2), 27.2 (d, $J_{C\text{-}P}$ = 11 Hz, CH_2) ppm. M.p. (±): 139 °C; m.p. (*R*,*R*): 138 °C. ESI-MS: *m*/*z* (%) = 349.1 (10) $[M + H]^+$, 371.1 (61) $[M + Na]^+$, 719.3 (100) $[2 M + Na]^+$. $C_{22}H_{21}O_2P$ (348.37): calcd. C 75.85, H 6.08, P 8.89; found C 75.14, H 6.04, P 8.80. HPLC [Regis (*S*,*S*)-Whelk O1, hexanes/*i*PrOH (95:5), flow = 1 mL min^{-1}, λ = 254 nm]: R_t (*R*,*R*) = 52.3 min, R_t (*S*,*S*) = 60.1 min. $[\alpha]_D^{25}$ = +61.9 (*c* = 0.5, $CHCl_3$).

X-ray Crystallography of Complex 10: X-ray diffraction data for **10** were collected with a Kappa X8 APPEX II Bruker diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The temperature of the crystal was maintained at the selected value (100 K) by means of a 700 series Cryostream cooling device to within an accuracy of ±1 K. The data were corrected for Lorentz, polarization and absorption effects. The structures were solved by direct methods with SHELXS-97[23] and refined against F^2 by full-matrix least-squares techniques with SHELXL-97[24] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations were performed with the Crystal Structure crystallographic software package WINGX.[25] CCDC-614521 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Crystal data for **10**: $C_{16}H_{16}BF_3OP$; M_r = 323.07; monoclinic; space group $P2_1$; *a* = 7.1183(15), *b* = 5.8400(14), *c* = 18.575(5), β = 93.349(6) Å; *V* = 770.9(3) Å^3; *Z* = 2, $\rho_{calcd.}$ = 1.392 g mm^{-3}, μ = 0.207; $2\theta_{max}$ = 69.96°; reflections collected/unique/used: 5978/5978 (R_{int} = 0.0224)/2926 [$I > 2\sigma(I)$]; parameters refined: 201; R/wR_2 (all data) = 0.0962/0.2433; GOF = 1.107; Δ/σ_{max} = 0.009, $[\Delta\rho]_{max}$ = 0.739, $[\Delta\rho]_{min}$ = –0.601; Flack′s parameter = 0.12(9).

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