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Synthesis of Enantiopure 1-*r*-Aryl-2-*c*,5-*t*-diphenylphospholane Oxides and Boranes by Pd-Catalyzed C–P Bond Formation

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New chiral enantiopure phospholane oxides **1** and boranes **5** were obtained from efficient carbon–phosphorus bond formation by organocuprate or palladium-catalyzed reactions. C–P cross-coupling reactions between chiral phosphane oxide **3** or borane **4** and various aryl derivatives are presented.

Introduction

The elaboration of new chiral phosphanes is of importance since they still play a major role as ligands in transition-metal-based asymmetric catalysis.[1] Although didentate phosphane ligands are the most documented, interest has grown recently in the use of monophosphanes as ligands for transition metals but also as organic catalysts.[2] Since organic catalysis mediated by phosphanes involves their nucleophilic properties, it appears of interest to synthesize new dialkylaryl- and trialkylphosphanes. The dialkyl or trialkyl substitution of the phosphorus atom provides an electron-rich and basic ligand that differs from the usual asymmetric mono- or diphosphanes, which possess two or three aryl substituents on phosphorus.[3]

With this in mind, we designed a new monophosphane ligand based on the 2,5-disubstituted phospholane framework, namely the new electron-rich, chiral, and enantiopure 1-*r*,2-*c*,5-*t*-triphenylphospholane, which was obtained by reduction of the corresponding phospholane oxide **1a**.[4] This monodentate phosphane shows high activity and selectivity (93% *ee*) in rhodium-catalyzed hydrogenation of methyl dehydrocinnamate.[5]

In order to investigate the influence of the nature of the P-substituent on the 2,5-diphenylphospholane moiety, we envisaged to set up methods to produce a range of enantiopure substituted *P*-aryl-2-*c*,5-*t*-diphenylphospholane oxides **1** and boranes **5**.

Results and Discussion

We initially developed a method to provide the arylation of the chiral, enantiopure *trans*-2,5-diphenylphospholane framework by substitution of the corresponding phosphinoyl chloride **2** with an organocuprate reagent. Since the phosphorus atom in **1** is not stereogenic, one does not have to pay attention to the stereochemistry of the substitution. The results are collected in Table 1.

A large variety of enantiopure *P*-aryl-2,5-diphenylphospholane oxides were thus obtained. However, since the substitution of heteroaryl groups such as 2-pyridyl and 2-benzothiophenyl failed, and the yields of substitution by 1- and 2-naphthyl groups were only moderate in this stoichiometric reaction, we looked for another, preferentially catalytic, procedure.

To the best of our knowledge, most of the coupling partners involved in palladium- or nickel-catalyzed C–P bond formation are not chiral mono- or diarylphosphanes or their derivatives (oxides, boranes),[6] and no example of a coupling reaction with a chiral secondary phosphane oxide exists.

We report here a palladium-catalyzed C–P bond formation by coupling a *chiral* dialkylphosphane oxide **3** with aryl and heteroaryl iodides, bromides and triflates. The reaction was carried out in the presence of 10 mol-% of palladium acetate, 12 mol-% of 1,3-bis(diphenylphosphanyl)propane (dppp) as ligand, and *i*Pr_2NEt as base in DMSO (Table 2). The synthesis of compound **3** was described in our previous paper.

The coupling reaction is quite general and clean, and can be used to prepare a wide variety of *P*-aryl-2,5-diphenylphospholane oxides. The yields recorded for **1a**–**f** were lower than those obtained from the method involving organocopper reagents. However, naphthyl and heteroaryl substrates afforded products **1g**–**j** in good yields. It is noteworthy that no epimerization at the benzylic carbon atoms of the phospholane ring, which would have led to diastereomeric or enantiomeric compounds, was observed.

In order to find out a further way of synthesizing *P*-arylphospholane compounds, we investigated the secondary

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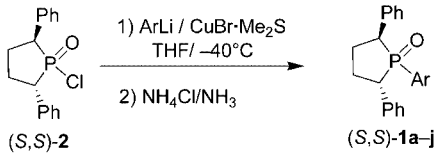
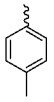
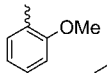
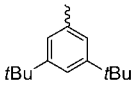
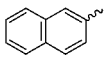
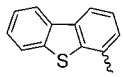
Table 1. Synthesis of (2*S*,5*S*)-1-aryl-1-oxo-2,5-diphenylphospholane **1a**–**j** by copper substitution.

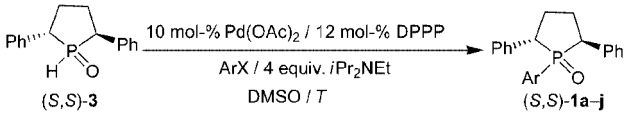


(*S*,*S*)-**2** (*S*,*S*)-**1a**–**j**

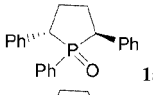
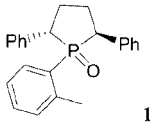
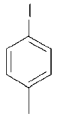
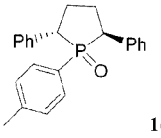
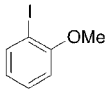
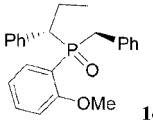
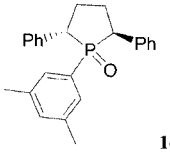
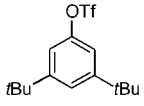
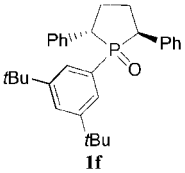
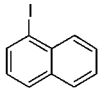
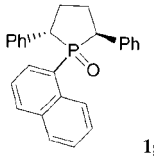
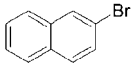
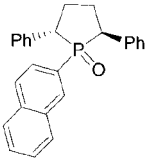
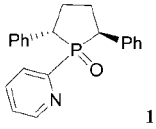
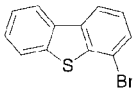
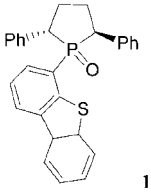
	1a	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**	**1i**	**1j**
Ar[b]	Ph									
Yield [%][a]	88	90	79	66	68	78	53	40	0	0

[a] Isolated yield. [b] Organolithium reagents were prepared from the corresponding aryl bromide and one equiv. of *n*BuLi in THF at –78 °C, except for **1e** and **1f**, where *t*BuLi was used.

Table 2. Synthesis of (2*S*,5*S*)-1-aryl-1-oxo-2,5-diphenylphospholanes **1a**–**j** by palladium-catalyzed cross-coupling of the secondary phospholane oxide **3**.



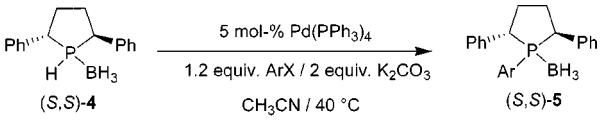
(*S*,*S*)-**3** (*S*,*S*)-**1a**–**j**

Entry	ArX	Product	*T* / time [°C] [h]	Yield [%][a]
1		 **1a**	100 / 24	78
2		 **1b**	110 / 24	72
3		 **1c**	110 / 24	76
4		 **1d**	110 / 24	62
5		 **1e**	110 / 24	54
6		 **1f**	110 / 60	47
7		 **1g**	110 / 48	75
8		 **1h**	110 / 48	81
9		 **1i**	105 / 48	77
10		 **1j**	105 / 48	65

[a] Isolated yield.

phosphane–borane complex **4** as a coupling partner.[7] This phosphane–borane was prepared from the enantiomerically pure 2,5-diphenylphospholane. The (*S*,*S*)-2,5-diphenylphospholane–borane **4** was coupled with various aryl halides and triflates in the presence of $[Pd(PPh_3)_4]$ as catalyst precursor and K_2CO_3 as base (Table 3).

Table 3. Palladium-catalyzed cross-coupling of secondary *trans*-2,5-diphenylphospholane–borane complex **4**.

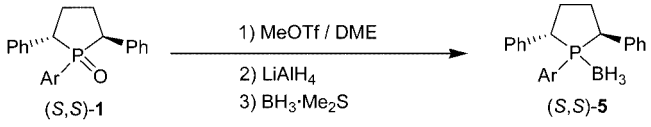


Entry	ArX	Product	Conv. [%][a]	Yield [%][b]
1	phenyl triflate	**5a**	90	78
2	5-iodo-*m*-xylene	**5e**	58	41
3	3,5-di-*tert*-butylphenyl triflate	**5f**	55	35
4	1-iodonaphthalene	**5h**	60	27
5	2-methoxyphenyl triflate	**5d**	80	60
6	4-methoxyphenyl triflate	**5k**	70	56
7	2-phenylphenyl triflate	**5l**	83	65

[a] Isolated yield. [b] Conversion determined by ^{1}H NMR spectroscopy.

In no case did we observe a total conversion, and the purification of products **5** was therefore more difficult. This poor reactivity was attributed to the low degradation of the substrate under the reaction conditions.

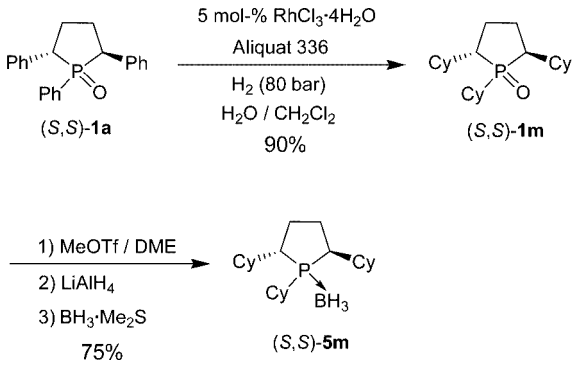
Phosphane–borane **5** could also be obtained by reduction of the phosphane oxide following Imamoto's procedure.[8] Treatment of the oxide with methyl triflate, followed by $LiAlH_4$ and borane, gave the enantiomerically pure phosphane–borane (Scheme 1).



5a: 90%, **5b**: 95%, **5c**: 92%, **5d**: 75%, **5e**: 61%, **5f**: 66%, **5g**: 84%, **5h**: 83%

Scheme 1. Synthesis of phosphane–borane **5**.

During the course of our investigation to synthesize more electron-rich ligands, we found that the phosphane oxide **1a** could be hydrogenated in the presence of $RhCl_3{\cdot}4H_2O$ catalyst under a high pressure of dihydrogen[9] to give the (2*S*,5*S*)-1,2,5-tricyclohexylphosphane oxide **1m** in excellent yield (Scheme 2). Reduction of this phosphane oxide followed by protection with borane offered enantiomerically pure electron rich (2*S*,5*S*)-1,2,5-tricyclohexylphosphane–borane **5m**.



Scheme 2. Synthesis of phosphane **5m** by Rh-catalyzed hydrogenation of **1a**.

Conclusions

In summary, several enantiopure ligand precursors based on the 1-aryl-*trans*-2,5-diphenylphospholane structure have been prepared by C–P bond construction using three efficient complementary methods from phospholanyl chloride, secondary phospholane oxide, or borane. The preparations of the corresponding phosphanes and their applications in asymmetric catalysis are currently underway.

Experimental Section

General Remarks: ^{1}H NMR spectra were recorded on Bruker 250, 360, or 400 MHz spectrometers. Chemical shifts are reported in ppm (δ) relative to tetramethylsilane as internal reference (δ = 0.0 ppm). ^{13}C NMR spectra were recorded on Bruker 250 MHz (62.9 MHz) or 300 MHz (75.45 MHz) spectrometers with complete proton decoupling. ^{31}P NMR spectra were recorded with a 101.2 MHz spectrometer with complete proton decoupling. The corresponding chemical shifts are reported in ppm (δ) relative to the residual deuterated solvent or external phosphoric acid (δ = 0.0 ppm). Flash column chromatography was performed using silica gel Merck (0.04–0.063 μm). Optical rotations were recorded at the sodium D line with a Perkin–Elmer 341 polarimeter. [α] is always given without the units (understood to be deg cm^2 g^{-1}). High-resolution mass spectra were obtained with a MAT95 Thermo-Finnigan spectrometer using electrospray analysis. All reactions were carried out in Schlenk tubes under argon. All solvents were distilled from appropriate drying agents prior to use. Palladium tetrakis(triphenylphosphane) and 4-bromodibenzothiophene[10] were prepared as described in the literature. Aryl triflates were prepared from the corresponding phenol and trifluoromethanesulfonic anhydride. All other reagents are available commercially and were used without further purification [CuBr–dimethylsulfide complex (Aldrich), copper iodide (Aldrich), borane–dimethyl sulfide complex (Aldrich), palladium acetate (Aldrich), $RhCl_3{\cdot}4H_2O$ (Prolabo)]. The synthesis and experimental data of products **1a**, **2**, and **3** were described in our previous paper.[4a]

General Procedure for Organocopper Substitution of (*S*,*S*)-2: A solution of the appropriate organolithium reagent in THF (7.3 mmol) was added slowly to a Schlenk tube containing a suspension of the CuBr–dimethylsulfide complex (1.5 g, 7.3 mmol) in THF (20 mL) at –40 °C. The resulting deep yellow solution was stirred for 10 min at –40 °C and then for 5 min at room temperature. After cooling down to –60 °C, the phenylcopper solution was added to a precooled (–60 °C) solution of phosphinoyl chloride (2*S*,5*S*)-**2**, prepared

from (–)-(2*S*,5*S*)-1-hydroxy-l-oxo-2,5-diphenylphospholane[4a] (2 g, 7.34 mmol). The mixture was stirred for 15 min at –60 °C, and from –60 °C to room temperature overnight. The reaction was quenched with a 1:1 mixture of a concentrated aqueous solution of ammonia and saturated NH_4Cl aqueous solution (50 mL) and diluted with dichloromethane. It was vigorously stirred until a dark blue color appeared. The blue solution was extracted with dichloromethane, the organic layer washed with brine, dried with anhydrous magnesium sulfate, and concentrated. The white solid was subjected to chromatographic purification on silica gel to give a white product, which was recrystallized from EtOAc/hexane to give the desired phosphane oxide **1**.

General Procedure for Palladium-Catalyzed Cross-Coupling of Secondary Phospholane Oxide 3: Palladium acetate (22.5 mg, 0.1 mmol) and 1,3-bis(diphenylphosphanyl)propane (dppp) (62 mg, 0.15 mmol) were dissolved in DMSO (1 mL) in a Schlenk tube under argon. The yellow solution was stirred for 15 min at room temperature. The solution was added to a solution of (*S*,*S*)-**3** (1 mmol), diisopropylethylamine (4 mmol), and the appropriate aryl halide or triflate (1.2 mmol) in DMSO (2 mL). The mixture was heated at 100–110 °C for the appropriate time. After cooling and hydrolysis with water, the aqueous phase was extracted with dichloromethane. The organic layer was washed with water (2 × 10 mL) and then dried with $MgSO_4$. Evaporation of the solvent gave a residue that was purified by flash chromatography on silica gel. The white product was recrystallized from EtOAc/hexane to give the desired phosphane oxide **1**.

General Procedure for Palladium-Catalyzed Cross-Coupling of Secondary Phospholane–Borane Complex 4: Tetrakis(triphenylphosphane)palladium (58 mg, 0.05 mmol), 2,5-diphenylphospholane–borane (**4**; 253 mg, 1 mmol), and the appropriate aryl triflate (1.2 mmol) were dissolved in CH_3CN (5 mL) in a Schlenk tube under argon. The solution was stirred for 5 min at room temperature and was then added to a solution of K_2CO_3 (2 mmol) in 5 mL of acetonitrile. The mixture was heated at 40 °C for 16 h. After cooling and hydrolysis with HCl solution (3 N), the aqueous phase was extracted with dichloromethane. The organic layer was washed with brine (10 mL) and then dried with $MgSO_4$. Evaporation of the solvent gave a residue that was purified by flash chromatography on silica gel using pentane/ethyl acetate (90:10) as eluent to give the desired phosphane–borane **5**.

General Procedure for Preparation of Phosphane–Borane 5 by Phosphane Oxide Reduction: Methyl trifluoromethanesulfonate (125 μL, 1.1 mmol) was added to the appropriate phosphane oxide **3** (1 mmol) dissolved in DME (10 mL) under argon. After 2 h the mixture was cooled down to 0 °C and lithium aluminum hydride (57 mg, 1.5 mmol) was added. The mixture was warmed to room temperature and stirred for an additional 15 h. After hydrolysis with a minimum amount of water, the mixture was filtered under argon through Celite via a cannula. Borane–dimethylsulfide complex (0.379 mL) was then added to the resulting solution at 0 °C and stirred for 2 h. After hydrolysis with HCl solution (1 N), the aqueous phase was extracted with dichloromethane. The organic layer was washed with brine (10 mL) and then dried with $MgSO_4$. Evaporation of the solvent gave a residue that was purified by flash chromatography on silica gel with heptane/ethyl acetate (95:5) to give the desired phosphane–borane **5**.

(2*S*,5*S*)-(–)-1-Oxo-2,5-diphenyl-1-(*o*-tolyl)phospholane (1b): The product was purified by flash chromatography on silica gel using CH_2Cl_2/MeOH (95:5) as eluent. Recrystallization from EtOAc/hexane gave the desired phosphane oxide as colorless needles. $[\alpha]_D^{20}$ = –135 (*c* = 1, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 6.90–7.60 (m, 14 H), 3.65–3.90 (m, 2 H), 2.40–2.80 (m, 3 H), 2.20 (s, 3 H), 2.00–2.20 (m, 1 H), 1.45 (m, 2 H) ppm. ^{13}C NMR (75.45 MHz, $CDCl_3$): δ = 21.5 (s), 30.65 (d, $J_{P,C}$ = 8 Hz), 31.85 (d, $J_{P,C}$ = 8 Hz), 45.40 (d, $J_{P,C}$ = 63 Hz), (s), 52.00 (d, $J_{P,C}$ = 62 Hz), 124.85(d, $J_{P,C}$ = 12 Hz), 126.35 (d, $J_{P,C}$ = 2.5 Hz), 126.85 (d, $J_{P,C}$ = 1.8 Hz), 127.9 (d, $J_{P,C}$ = 5 Hz), 128.00 (d, $J_{P,C}$ = 1.8 Hz), 128.50 (d, $J_{P,C}$ = 1 Hz), 129.10 (d, $J_{P,C}$ = 5 Hz), 130.60 (d, $J_{P,C}$ = 11.2 Hz), 131.50 (d, $J_{P,C}$ = 3 Hz), 131.65 (d, $J_{P,C}$ = 10.5 Hz), 136.30 (d, $J_{P,C}$ = 5 Hz), 137.25 (d, $J_{P,C}$ = 3 Hz), 144.00 (d, $J_{P,C}$ = 6.5 Hz) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 59.4 ppm. HRMS (IE): calcd. for $C_{23}H_{23}OP$ 346.1487; found 346.1486.

(2*S*,5*S*)-(–)-1-Oxo-2,5-diphenyl-1-(*p*-tolyl)phospholane (1c): The product was purified by flash chromatography on silica gel using CH_2Cl_2/MeOH (95:5) as eluent. Recrystallization from EtOAc/hexane gave the desired phosphane oxide as white crystals. $[\alpha]_D^{20}$ = –156 (*c* = 1, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 7.40–7.15 (m, 8 H), 7.10–7.95 (m, 6 H), 3.85 (ddd, *J* = 6.8, 12.7, 25.39 Hz, 1 H), 3.55 (s, 1 H), 2.80–2.40 (m, 3 H), 2.25 (m, 3 H), 2.30–2.10 (m, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.3 (d, $J_{P,C}$ = 1.5 Hz), 27.80 (d, $J_{P,C}$ = 8.5 Hz), 31.35 (d, $J_{P,C}$ = 7 Hz), 46.80 (d, $J_{P,C}$ = 62 Hz), 51.1 (d, $J_{P,C}$ = 61.5 Hz), 126.20 (d, $J_{P,C}$ = 2 Hz), 126.40 (s), 126.80 (d, $J_{P,C}$ = 2 Hz), 127.10 (d, $J_{P,C}$ = 5 Hz), 128.10 (d, $J_{P,C}$ = 2.5 Hz), 128.4 (d, $J_{P,C}$ = 1.5 Hz), 128.60 (d, $J_{P,C}$ = 4.5 Hz), 128.70 (d, $J_{P,C}$ = 3 Hz), 131.10 (d, $J_{P,C}$ = 9 Hz), 135.70 (d, $J_{P,C}$ = 5 Hz), 136.00 (d, $J_{P,C}$ = 3 Hz), 141.70 (d, $J_{P,C}$ = 3 Hz) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 53.4 ppm. HRMS (IE): calcd. for $C_{23}H_{23}OP$ 346.1487; found 346.1480.

(2*S*,5*S*)-(–)-1-(*o*-Anisyl)-1-oxo-2,5-diphenylphospholane (1d): The product was purified by flash chromatography on silica gel using CH_2Cl_2/MeOH (95:5) as eluent. Recrystallization from EtOAc/hexane gave the desired phosphane oxide as colorless needles. $[\alpha]_D^{20}$ = –140 (*c* = 1, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 7.80 (ddd, *J* = 12.7, 8, 2 Hz, 1 H), 6.80–7.40 (m, 12 H), 6.5 (dd, *J* = 8, 5.5 Hz, 1 H), 3.70–3.40 (m, 2 H), 2.35–3.80 (m, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 26.00 (d, $J_{P,C}$ = 7.6 Hz), 30.75 (d, $J_{P,C}$ = 7 Hz), 45.00 (d, $J_{P,C}$ = 63 Hz), 50.00 (d, $J_{P,C}$ = 64 Hz), 54.2 (s), 109.30 (d, $J_{P,C}$ = 6.5 Hz), 117.8 (s), 120.30 (d, $J_{P,C}$ = 10.5 Hz), 125.5 (d, $J_{P,C}$ = 2.4 Hz), 126 (s), 126.1(s), 127.00 (d, $J_{P,C}$ = 2 Hz), 127.8 (d, $J_{P,C}$ = 2 Hz), 128.3 (d, $J_{P,C}$ = 5 Hz), 133.40 (d, $J_{P,C}$ = 2 Hz), 135.10 (d, $J_{P,C}$ = 5 Hz), 135.70 (d, $J_{P,C}$ = 5.8 Hz), 135.9 (d, $J_{P,C}$ = 4 Hz), 158.3 (d, $J_{P,C}$ = 5 Hz) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 56.5 ppm. $C_{23}H_{23}O_2P$: calcd. C 76.23, H 6.40, P 8.55; found C 75.98, H 6.39, P 8.49. MS (IE): 385 [M + Na^+], 747 [2M + Na^+].

(2*S*,5*S*)-(–)-1-(3,5-Dimethylphenyl)-1-oxo-2,5-diphenylphospholane (1e): The product was purified by flash chromatography on silica gel using CH_2Cl_2/MeOH (98:2) as eluent. Recrystallization from EtOAc/hexane gave the desired phosphane oxide as fine colorless needles. $[\alpha]_D^{20}$ = –136 (*c* = 1, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 7.20–7.30 (m, 5 H), 6.80–7.10 (m, 8 H), 3.8 (m, 1 H), 3.55 (m, 1 H), 2.40–2.80 (m, 3 H), 2.30 (m, 1 H), 2.15 (s, 6 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.00 (s), 27.80 (d, $J_{P,C}$ = 8 Hz), 31.30 (d, $J_{P,C}$ = 7 Hz), 46.70 (d, $J_{P,C}$ = 61 Hz), 51.00 (d, $J_{P,C}$ = 61 Hz), 126.25 (d, $J_{P,C}$ = 3 Hz), 126.80 (d, $J_{P,C}$ = 3 Hz), 127.10 (d, $J_{P,C}$ = 4.5 Hz), 128.00 (d, $J_{P,C}$ = 2 Hz), 128.40 (d, $J_{P,C}$ = 2 Hz), 128.75 (d, $J_{P,C}$ = 2 Hz), 128.80 (s), 133.15 (d, $J_{P,C}$ = 3 Hz), 135.70 (d, $J_{P,C}$ = 5.5 Hz), 136.00 (d, $J_{P,C}$ = 3 Hz), 137.40 (d, $J_{P,C}$ = 13Hz) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 53.8 ppm. HRMS (IE): calcd. for $C_{24}H_{25}OP$ 360.1632; found 360.1643.

(2*S*,5*S*)-(+)-1-(3,5-Di-*tert*-butylphenyl)-1-oxo-2,5-diphenylphospholane (1f): The product was purified by flash chromatography on silica gel using CH_2Cl_2/MeOH (98:2) as eluent. Recrystallization from EtOAc/hexane gave the desired phosphane oxide as a white

solid. $[\alpha]_D^{20}$ = +103 (*c* = 1, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 7.10–7.40 (m, 8 H), 7.05 (m, 5 H), 3.70–4.00 (m, 1 H), 3.50–3.60 (m, 1 H), 2.40–2.80 (m, 3 H), 2.15–2.35 (m, 1 H), 1.2 (s, 18 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 28.28 (d, $J_{P,C}$ = 8.5 Hz), 31.40 (s), 31.60 (d, $J_{P,C}$ = 7.5 Hz), 35.00 (s), 46.50 (d, $J_{P,C}$ = 62 Hz), 51.20 (d, $J_{P,C}$ = 61 Hz), 125.30 (d, $J_{P,C}$ = 9 Hz), 125.70 (d, $J_{P,C}$ = 3.5 Hz), 126.35 (d, $J_{P,C}$ = 3 Hz), 127.10 (d, $J_{P,C}$ = 3 Hz), 127.35 (d, $J_{P,C}$ = 4.5 Hz), 128.35 (d, $J_{P,C}$ = 2 Hz), 128.75 (d, $J_{P,C}$ = 2 Hz), 129.10 (d, $J_{P,C}$ = 5.5 Hz), 130.50 (s), 136.15 (d, $J_{P,C}$ = 5.5 Hz), 136.70 (d, $J_{P,C}$ = 3.5 Hz). 150.65 (d, $J_{P,C}$ = 11 Hz) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 55.0 ppm. HRMS (IE): calcd. for $C_{30}H_{37}OP$ 444.2582; found 445.2576.

(2*S*,5*S*)-(–)-1-(2-Naphthyl)-1-oxo-2,5-diphenylphospholane (1g): The product was purified by flash chromatography on silica gel using CH_2Cl_2/MeOH (98:2) as eluent. Recrystallization from EtOAc/hexane gave the desired phosphane oxide as a white solid. $[\alpha]_D^{20}$ = –148 (*c* = 1, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 13 Hz, 1 H), 7.60–7.80 (m, 3 H), 7.40–7.60 (m, 2 H), 7.10–7.40 (m, 8 H), 6.80–7.10 (m, 3 H), 3.40–4.10 (m, 1 H), 3.50–3.70 (m, 1 H), 2.50–2.90 (m, 3 H), 2.35 (m, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 28.35 (d, $J_{P,C}$ = 8 Hz), 31.60 (d, $J_{P,C}$ = 7 Hz), 47.65 (d, $J_{P,C}$ = 62 Hz), 51.15 (d, $J_{P,C}$ = 62 Hz), 125.60 (d, $J_{P,C}$ = 10 Hz), 126.70 (d, $J_{P,C}$ = 3 Hz), 126.90 (d, $J_{P,C}$ = 1.5 Hz), 127.30 (d, $J_{P,C}$ = 2 Hz), 127.45 (d, $J_{P,C}$ = 4.5 Hz), 127.85 (d, $J_{P,C}$ = 1 Hz), 127.90 (s), 128.00 (s), 128.25 (s), 128.55 (d, $J_{P,C}$ = 2 Hz), 128.85 (d, $J_{P,C}$ = 2 Hz), 129–129.10 (2C, m), 132.40 (d, $J_{P,C}$ = 12 Hz), 134.40 (d, $J_{P,C}$ = 6.5 Hz). 134.5 (d, $J_{P,C}$ = 2 Hz), 135.75 (d, $J_{P,C}$ = 5.5 Hz), 136.00 (d, $J_{P,C}$ = 3 Hz) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 53.4 ppm. HRMS (IE): calcd. for $C_{26}H_{23}OP$ 382.1487; found 382.1480.

(2*S*,5*S*)-(–)-1-(1-Naphthyl)-1-oxo-2,5-diphenylphospholane (1h): The product was purified by flash chromatography on silica gel using CH_2Cl_2/MeOH (95:5) as eluent. Recrystallization from EtOAc/hexane gave the desired phosphane oxide as colorless crystals. $[\alpha]_D^{20}$ = –206 (*c* = 1, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 8.60 (d, *J* = 9 Hz, 1 H), 7.80 (d, *J* = 8.2 Hz, 1 H), 7.65 (ddd, *J* = 14, 6.75, 1 Hz, 1 H), 7.45 (d, *J* = 8.25 Hz, 1 H), 7.20–7.40 (m, 6 H), 7.00 (m, 2 H), 6.85 (m, 3 H), 4.05 (m, 1 H), 3.80 (m, 1 H), 2.50–2.90 (m, 3 H), 2.10–2.40 (m, 1 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 29.50 (d, $J_{P,C}$ = 8.5 Hz), 31.80 (d, $J_{P,C}$ = 8 Hz), 46.00 (d, $J_{P,C}$ = 63 Hz), 52.00 (d, $J_{P,C}$ = 62 Hz), 123.70 (d, $J_{P,C}$ = 14 Hz), 126.15 (s), 126.20 (d, $J_{P,C}$ = 2.8 Hz), 126.65 (s), 126.95 (d, $J_{P,C}$ = 2 Hz), 127.25 (d, $J_{P,C}$ = 4 Hz), 127.50 (d, $J_{P,C}$ = 5 Hz), 127.85 (d, $J_{P,C}$ = 5 Hz), 128.15 (d, $J_{P,C}$ = 2.5 Hz), 128.55 (d, $J_{P,C}$ = 2 Hz), 129.20 (d, $J_{P,C}$ = 5.2 Hz), 130.60 (d, $J_{P,C}$ = 10 Hz), 132.75 (d, $J_{P,C}$ = 3 Hz), 133.35 (d, $J_{P,C}$ = 12 Hz), 134.00 (d, $J_{P,C}$ = 7 Hz). 136.30 (d, $J_{P,C}$ = 5 Hz), 136.80 (d, $J_{P,C}$ = 3 Hz) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 59.0 ppm. $C_{26}H_{23}O_2P$: calcd. C 81.66, H 6.06, P 8.10; found C 82.24, H 6.08, P 8.05. MS (IE): *m*/*z* = 383 [MH^+], 405 [M + Na^+], 787 [2M + Na^+].

(2*S*,5*S*)-(–)-1-Oxo-2,5-diphenyl-1-(2-pyridyl)phospholane (1i): The product was purified by flash chromatography on silica gel using CH_2Cl_2/MeOH (98:2) as eluent. Recrystallization from EtOAc/hexane gave the desired phosphane oxide as colorless crystals. $[\alpha]_D^{20}$ = –136 (*c* = 1, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 8.60 (m, 1 H), 7.65 (m, 1 H), 6.80–7.50 (m, 12 H), 4.20–4.50 (s, 1 H), 3.60–3.90 (m, 1 H), 2.60–2.90 (m, 1 H), 2.20–2.60 (m, 3 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 27.60 (d, $J_{P,C}$ = 8.3 Hz), 32.10 (d, $J_{P,C}$ = 7.5 Hz), 42.80 (d, $J_{P,C}$ = 63Hz), 51.50 (d, $J_{P,C}$ = 59 Hz), 120.80 (s), 123.45 (s), 124.75 (d, $J_{P,C}$ = 3.2 Hz), 126.00 (d, $J_{P,C}$ = 3 Hz), 126.55 (d, $J_{P,C}$ = 2 Hz), 127.15 (d, $J_{P,C}$ = 4.5 Hz), 127.75 (d, $J_{P,C}$ = 3 Hz), 128.30 (d, $J_{P,C}$ = 2 Hz), 128.50 (s), 128.90 (d, $J_{P,C}$ = 5.5 Hz), 135.25 (d, $J_{P,C}$ = 8 Hz), 136.15 (d, $J_{P,C}$ = 5 Hz), 149.10 (d, $J_{P,C}$ = 20 Hz), 153.55 (s), 155.70 (s) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 54.5 ppm. HRMS (IE): calcd. for $C_{21}H_{20}NOP$ 333.1279; found 333.1279.

(2*S*,5*S*)-(–)-1-(4-Dibenzothiophenyl)-1-oxo-2,5-diphenylphospholane (1j): The product was purified by flash chromatography on silica gel using heptane/EtOAc (50:50) as eluent. Recrystallization from EtOAc/hexane gave the desired phosphane oxide as colorless crystals. $[\alpha]_D^{18}$ = –193 (*c* = 0.425, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 8.00–8.20 (m, 2 H), 7.80 (m, 1 H), 7.10–7.50 (m, 11 H), 6.80–7.00 (m, 3 H), 3.70–4.15 (m, 2 H), 2.30–2.90 (m, 4 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 27.85 (d, $J_{P,C}$ = 8 Hz), 31.25 (d, $J_{P,C}$ = 8 Hz), 46.00 (d, $J_{P,C}$ = 62 Hz), 51.00 (d, $J_{P,C}$ = 62 Hz), 121.2 (s), 122.30 (s), 123.40 (d, $J_{P,C}$ = 11.5 Hz), 124.90 (s), 126.30 (s), 126.85 (s), 126.95 (s),127.95 (s), 128.50 (s), 128.85 (d, $J_{P,C}$ = 5.25 Hz), 129.20 (d, $J_{P,C}$ = 9.5 H), 133.45 (s), 135.40 (s), 136.50 (d, $J_{P,C}$ = 9 Hz), 140.85 (s), 143.60 (d, $J_{P,C}$ = 5 Hz) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 57.6 ppm. HRMS (IE): calcd. for $C_{28}H_{23}OPS$ 438.1207; found 438.1207.

(2*S*,5*S*)-(+)-1,2,5-Tricyclohexyl-1-oxophospholane (1m): A solution of (2*S*,5*S*)-1-oxo-1,2,5-triphenylphospholane **1a** (1 mmol), $RhCl_3 \cdot 4H_2O$ (0.05 mmol), and aliquot 336 (0.0625 mmol) in dichloromethane (10 mL) and water (2 mL) was placed in an autoclave under 80 bar of dihydrogen for two days. The aqueous phase was then extracted with dichloromethane. The organic layer was washed with water (2 × 10 mL) and then dried with $MgSO_4$. Evaporation of the solvent gave a residue that was purified by flash chromatography on silica gel using heptane/ethyl acetate (40:60) as eluent. Recrystallization from EtOAc/hexane gave the desired phosphane oxide as fine, colorless needles. $[\alpha]_D^{20}$ = +20.8 (*c* = 0.52, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 2.00–2.3 (m, 4 H), 1.45–2.00 (m, 19 H), 1.10–1.50 (m, 12 H), 0.80–1.10 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 50.50 (d, $J_{P,C}$ = 59 Hz), 39.45 (s), 38.45 (s), 38.10 (s), 37.70 (d, $J_{P,C}$ = 2 Hz), 37.50 (s), 36.51 (s), 33.60 (d, $J_{P,C}$ = 1.5 Hz), 33.30 (d, $J_{P,C}$ = 3 Hz), 32.40 (d, $J_{P,C}$ = 11 Hz), 31.25 (d, $J_{P,C}$ = 9 Hz), 27.95 (d, $J_{P,C}$ = 6.5 Hz), 27.60 (d, $J_{P,C}$ = 2.25 Hz), 26.60 (d, $J_{P,C}$ = 12 Hz), 26.50 (d, $J_{P,C}$ = 12.5 Hz), 26.20 (s), 26.15 (s), 26.05 (s), 26.00 (s), 25.95 (s), 25.93 (s), 25.90 (s), 25.80 (d, $J_{P,C}$ = 4 Hz), 25.65 (s) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 66.8 ppm. HRMS (IE): calcd. for $C_{22}H_{40}OP$ [MH^+] 351.2811; found 351.2815.

(2*S*,5*S*)-(–)-2-*c*,5-*t*-Diphenylphospholane–Borane (4): $BH_3 \cdot SMe_2$ (3 mmol) was added at 0 °C to a Schlenk tube containing a solution of (2*S*,5*S*)-(+)-2,5-diphenylphospholane (1 mmol) in Et_2O (10 mL). The resulting solution was stirred for 16 h until it reached room temperature. The solvent was then evaporated and the residue was purified by flash chromatography on silica gel using pentane/diethyl ether (90:10) as eluent. The product was isolated as a white solid. $[\alpha]_D^{18}$ = –15.5 (*c* = 1, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 7.20–7.40 (m, 10 H), 4.80 (d, $J_{P,H}$ = 360 Hz), 3.80–4.15 (m, 1 H), 3.50 (m, 1 H), 2.50–2.70 (m, 2 H), 2.15–2.25 (m, 2 H), 0.1–0.9 (broad, 3 H, BH_3) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 33.80 (d, $J_{P,C}$ = 1 Hz), 34.50 (d, $J_{P,C}$ = 4 Hz), 40.50 (d, $J_{P,C}$ = 29 Hz), 44.40 (d, $J_{P,C}$ = 33 Hz), 127.15 (d, $J_{P,C}$ = 2.5 Hz), 127.25 (d, $J_{P,C}$ = 2 Hz), 127.28 (d, $J_{P,C}$ = 5 Hz), 128.40 (d, $J_{P,C}$ = 2 Hz), 128.60 (d, $J_{P,C}$ = 5.25 Hz), 128.90 (d, $J_{P,C}$ = 2 Hz), 136.50 (d, $J_{P,C}$ = 2 Hz), 137.70 (d, $J_{P,C}$ = 5.25 Hz) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 29.4 (d, $J_{P,B}$ = 46 Hz) ppm. HRMS (IE): calcd. for $C_{16}H_{20}BP$ 254.1396; found 240.1063 (corresponding to $C_{16}H_{17}P$, i.e. [M – BH_3]).

(2*S*,5*S*)-(+)-2,5-Diphenylphospholane:[11] (2*S*,5*S*)-(–)-1-Chloro-1-oxo-2,5-diphenylphospholane (**2**; 1 mmol) was suspended in freshly

distilled diethyl ether (10 mL) after sonication and cooled to 0 °C. Lithium aluminum hydride (1.5 mmol) was then added portionwise. The solution was stirred at room temperature for 16 h, then hydrolyzed with a minimum of water and filtered under argon to give a colorless solution. The solvent was removed in vacuo and the phospholane was obtained as a white solid that was stored in a glove box without further purification. $[\alpha]_D^{20}$ = +104 (*c* = 0.95, $CHCl_3$). ^1H NMR (360 MHz, $CDCl_3$): δ = 7.25 (m, 9 H), 7.10 (m, 1 H), 3.90 (m, 1 H), 3.35 (ddd, $J_{P,H}$ = 190, $J_{H,H}$ = 11 and 11 Hz, 1 H), 3.35 (m, 1 H), 2.45–2.55 (m, 2 H), 2.00–2.15 (m, 1 H), 1.75–1.90 (m, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 38.80 (d, $J_{P,C}$ = 5 Hz), 39 (s), 41.10 (d, $J_{P,C}$ = 9 Hz), 44.80 (d, $J_{P,C}$ = 12 Hz), 126.00 (d, $J_{P,C}$ = 13 Hz), 127.15 (d, $J_{P,C}$ = 14 Hz), 127.65 (d, $J_{P,C}$ = 8 Hz), 128.55 (s) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = –17.8 (d, $J_{P,H}$ = 190 Hz) ppm. HRMS (IE): calcd. for $C_{16}H_{17}P$ 240.1068; found 240.1063.

(2*R*,5*R*)-(+)-2,5-Diphenyl-1-(*o*-tolyl)phospholane–Borane (5b): $[\alpha]_D^{20}$ = +75.6 (*c* = 1, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 2.05 (s, 3 H), 2.15–2.80 (m, 4 H), 3.80–4.25 (m, 2 H), 6.86–7.30 (m, 13 H), 7.60 (m, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 22.80 (s), 31.20 (s), 32.65 (d, $J_{P,C}$ = 6.5 Hz), 45.20 (d, $J_{P,C}$ = 30.5 Hz), 47.85 (d, $J_{P,C}$ = 32 Hz), 125.50 (d, $J_{P,C}$ = 9 Hz), 126.55 (s), 127.00 (s), 127.80 (d, $J_{P,C}$ = 5 Hz), 128.00 (s), 128.25 (s), 128.40 (d, $J_{P,C}$ = 5 Hz), 131.20 (s), 131.50 (d, $J_{P,C}$ = 9 Hz), 133.55–133.70 (m, 2 C), 136.65 (m, 1 C), 137.50 (d, $J_{P,C}$ = 5 Hz) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 40.00 (d, *J* = 61 Hz) ppm. HRMS (IE): calcd. for $C_{23}H_{23}P$ 330.1532; found 330.1518.

(2*R*,5*R*)-(+)-2-*c*,5-*t*,-Diphenyl-1-*r*-(*p*-tolyl)phospholane–Borane (5c): $[\alpha]_D^{20}$ = +131 (*c* = 1, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 0.30–1.40 (broad, 3 H, BH_3), 2.05 (s, 3 H, C*H*$_3$), 2.05–2.70 (m, 4 H), 3.50–4.00 (m, 2 H), 6.70–7.15 (m, 12 H), 7.15–7.30 (m, 2 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.00 (s), 3.80 (s), 31.30(d, $J_{P,C}$ = 6 Hz), 45.70 (d, $J_{P,C}$ = 30 Hz), 47.00 (d, $J_{P,C}$ = 31 Hz), 123.15 (d, $J_{P,C}$ = 45 Hz), 126.40 (d, $J_{P,C}$ = 28 Hz), 127.20 (d, $J_{P,C}$ = 4 Hz), 127.70–128.00 (m, 5 C), 128.70 (d, $J_{P,C}$ = 9 Hz), 135.90 (d, $J_{P,C}$ = 5 Hz), 136.40 (s), 141.20 (s) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 40.54 (s large) ppm. HRMS (IE): calcd. for $C_{23}H_{23}P$ 330.1532; found 330.1519.

(2*S*,5*S*)-(–)-1-(*o*-Anisyl)-2,5-diphenylphospholane–Borane (5d): $[\alpha]_D^{20}$ = –99.4 (*c* = 0.68, CH_2Cl_2). ^1H NMR (250 MHz, $CDCl_3$): δ = 0.10–0.91 (m, 3 H, BH_3), 2.46–2.72 (m, 4 H), 3.61 (s, 3 H), 3.96–4.07 (m, 1 H), 4.38–4.53 (m, 1 H), 6.58 (dd, *J* = 8, 3 Hz, 1 H), 6.85–7.19 (m, 12 H), 7.81 (dd, *J* = 14, 7 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 29.80 (d, $^2J_{P,C}$ = 6 Hz), 31.27 (d, $^2J_{P,C}$ = 6.6 Hz), 42.50 (d, $^1J_{P,C}$ = 31 Hz), 45.51 (d, $^1J_{P,C}$ = 35 Hz), 54.77 (s), 109.75 (d, $J_{P,C}$ = 4 Hz), 113.79 (d, $^1J_{P,C}$ = 40.3 Hz), 121.00 (d, $J_{P,C}$ = 12.6 Hz), 126.02 (d, $J_{P,C}$ = 2 Hz), 126.8 (d, $J_{P,C}$ = 2 Hz), 126.83 (d, $J_{P,C}$ = 4.5 Hz), 127.49 (d, $J_{P,C}$ = 1.8 Hz), 128.14 (d, $J_{P,C}$ = 3 Hz), 128.2 (d, $J_{P,C}$ = 4.5 Hz), 133.94 (d, $J_{P,C}$ = 2 Hz), 137.00 (d, $J_{P,C}$ = 1.5 Hz), 137.36 (d, $J_{P,C}$ = 19.5 Hz), 138.20 (d, $J_{P,C}$ = 15.5 Hz), 160.27 (d, $J_{P,C}$ = 2.6 Hz) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 43.05 (d, *J* = 71 Hz) ppm. HRMS (IE): calcd. for $C_{23}H_{23}OP$ 346.1481; found 346.1483.

(2*S*,5*S*)-(–)-1-(3,5-Dimethylphenyl)-2,5-diphenylphospholane–Borane (5e): $[\alpha]_D^{20}$ = –101 (*c* = 1, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 0.20–0.90 (broad, 3 H, BH_3), 2.15 (s, 6 H), 2.30–2.80 (m, 4 H), 3.70–4.10 (m, 2 H), 6.90–7.20 (m, 7 H), 7.20–7.60 (m, 6 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.00 (s, 2 C), 30.90 (s), 31.60 (d, $J_{P,C}$ = 5 Hz), 45.60 (d, $J_{P,C}$ = 30 Hz), 47.30 (d, $J_{P,C}$ = 32 Hz), 126.00 (s), 126.35 (d, *J* = 2.5 Hz), 126.70 (s), 126.90 (d, *J* = 2.5 Hz), 127.45 (d, $J_{P,C}$ = 4 Hz), 127.85 (d, *J* = 2.5 Hz), 128.15 (s), 128.20 (d, *J* = 3 Hz), 130.50 (d, $J_{P,C}$ = 9 Hz), 132.80 (d, $J_{P,C}$ = 3 Hz), 136.20 (d, $J_{P,C}$ = 5 Hz), 136.60 (d, $J_{P,C}$ = 2 Hz), 137.50 (d, $J_{P,C}$ = 10 Hz), 147.15 (s) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 40.90 (d, *J* = 46 Hz) ppm. HRMS (IE): calcd. for $C_{24}H_{25}P$ 344.1688; found 344.1684.

(2*R*,5*R*)-(+)-1-(3′,5′-Di-*tert*-butylphenyl)-2,5-diphenylphospholane–Borane (5f): $[\alpha]_D^{20}$ = +81.9 (*c* = 0.77, CH_2Cl_2). ^1H NMR (250 MHz, $CDCl_3$): δ = 0.10–0.97 (m, 3 H, BH_3), 1.28 (s, 18 H), 2.38–2.76 (m, 4 H), 3.88–3.96 (m, 1 H), 4.09–4.15 (m, 1 H), 6.95–7.11 (m, 5 H), 7.32–7.47 (m, 8 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 31.00(s, 6C), 31.10 (d, $J_{P,C}$ = 6 Hz), 31.65 (d, $^2J_{P,C}$ = 6 Hz), 34.65 (s, 2 C), 44.75 (d, $^1J_{P,C}$ = 29 Hz), 47.25 (d, $^1J_{P,C}$ = 31 Hz), 124.92 (d, $J_{P,C}$ = 3 Hz), 125.50 (d, $^1J_{P,C}$ = 44 Hz), 126.17 (d, $J_{P,C}$ = 2 Hz), 126.66 (d, $J_{P,C}$ = 9 Hz), 126.82 (d, $J_{P,C}$ = 3 Hz), 127.36 (d, $J_{P,C}$ = 4 Hz), 127.86 (d, $J_{P,C}$ = 3 Hz), 128.08 (d, $J_{P,C}$ = 2 Hz), 128.24 (d, $J_{P,C}$ = 4 Hz), 136.46 (d, $J_{P,C}$ = 5 Hz), 136.59 (d, $J_{P,C}$ = 2 Hz), 150.39 (d, $J_{P,C}$ = 9 Hz) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 42.70 (broad) ppm. HRMS (IE): calcd. for $C_{30}H_{37}P$: 428.2627; found 428.2629.

(2*S*,5*S*)-(–)-1-(2-Naphthyl)-2,5,-diphenylphospholane–Borane (5g): $[\alpha]_D^{20}$ = –147 (*c* = 1, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 0.30–1.40 (broad, 3 H, BH_3) 2.40–2.90 (m, 4 H), 3.90–4.20 (m, 2 H), 6.80–7.10 (m, 3 H), 7.10–7.40 (m, 8 H), 7.40–7.60 (m, 2 H), 7.70 (m, 1 H), 7.75 (m, 2 H), 8.15 (d, *J* = 13 Hz, 2 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 31.00 (s), 31.45 (d, $J_{P,C}$ = 6 Hz), 46.20 (d, $J_{P,C}$ = 30 Hz), 47.00 (d, $J_{P,C}$ = 31 Hz), 124.20 (d, $J_{P,C}$ = 43 Hz), 126.30 (d, $J_{P,C}$ = 3 Hz), 126.45 (s), 126.80 (d, $J_{P,C}$ = 3 Hz), 127.25 (d, $J_{P,C}$ = 4 Hz), 127.35 (s), 127.60 (s), 127.90 (d, $J_{P,C}$ = 3 Hz), 127.95 (s), 128.00 (s), 128.05 (s), 128.35 (s), 132.05 (d, $J_{P,C}$ = 11 Hz), 133.80 (d, $J_{P,C}$ = 3 Hz), 135.50 (d, $J_{P,C}$ = 11 Hz), 135.85 (d, $J_{P,C}$ = 5 Hz), 136.25 (d, $J_{P,C}$ = 2 Hz) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 41.76 (broad) ppm. HRMS (IE): calcd. for $C_{26}H_{23}P$ 366.1532; found 366.1519.

(2*S*,5*S*)-(–)-1-(1-Naphthyl)-2,5-diphenylphospholane–Borane (5h): $[\alpha]_D$ = –136 (*c* = 1, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 0.10–1.10 (broad, 3 H, BH_3), 2.55–2.89 (m, 4 H), 4.20–4.38 (m, 2 H), 6.88 (d, $J_{H,H}$ = 7 Hz, 3 H), 7.10 (d, $J_{H,H}$ = 7 Hz, 2 H), 7.20–7.50 (m, 8 H), 7.70 (d, $J_{H,H}$ = 7 Hz, 1 H), 7.85 (d, $J_{H,H}$ = 7 Hz, 1 H), 7.95 (dd, $J_{H,H}$ = 15, $J_{H,H}$ = 7 Hz, 1 H), 8.15 (d, $J_{H,H}$ = 7 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 31.80 (d, $J_{P,C}$ = 7 Hz), 31.92 (s), 45.57 (d, $J_{P,C}$ = 30 Hz), 47.53 (d, $J_{P,C}$ = 32 Hz), 124.34 (s), 124.55 (d, $J_{P,C}$ = 11 Hz), 124.65 (d, $J_{P,C}$ = 34 Hz), 124.93 (s), 126.06 (d, $J_{P,C}$ = 6 Hz), 126.39 (d, $J_{P,C}$ = 2 Hz), 126.99 (d, $J_{P,C}$ = 3 Hz), 127.05 (s), 127.52 (d, $J_{P,C}$ = 4 Hz), 127.84 (d, $J_{P,C}$ = 2 Hz), 128.22 (d, $J_{P,C}$ = 2 Hz), 128.58 (d, $J_{P,C}$ = 11 Hz), 128.73 (s), 132.6 (d, $J_{P,C}$ = 3 Hz), 133.36 (s), 133.50 (s), 133.34 (d, $J_{P,C}$ = 9 Hz), 136.76 (d, $J_{P,C}$ = 2 Hz), 137.13 (d, $J_{P,C}$ = 5 Hz) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 42.00 ppm. HRMS (IE): calcd. for $C_{26}H_{23}P$ 366.1532; found 366.1534.

(2*R*,5*R*)-(–)-1,2,5-Tricyclohexylphospholane–Borane (5m): $[\alpha]_D^{20}$ = –40.8 (*c* = 0.805, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 0.10–0.80 (broad, 3 H, BH_3), 0.75–1.00 (m, 4 H), 1.00–1.35 (m, 14 H), 1.35–1.50 (m, 1 H), 1.50–1.85 (m, 15 H), 1.85–1.95 (m, 1 H), 1.95–2.15 (m, 4 H) ppm. ^{13}C NMR (90.5 MHz, $CDCl_3$): δ = 47.60 (d, *J* = 33 Hz, CH), 40.00 (d, $J_{P,C}$ = 29 Hz, CH), 37.50 (d, $J_{P,C}$ = 4 Hz, CH), 34.45 (d, $J_{P,C}$ = 3 Hz), 34.25 (s), 32.60 (d, $J_{P,C}$ = 24.5 Hz, CH), 32.30 (d, $J_{P,C}$ = 9 Hz), 31.25 (d, $J_{P,C}$ = 9 Hz), 30.95 (s), 29.65 (d, $J_{P,C}$ = 2.5 Hz), 29.25 (d, $J_{P,C}$ = 5 Hz), 27.85 (s), 27.20 (d, $J_{P,C}$ = 12 Hz), 26.85(d, $J_{P,C}$ = 8.5 Hz), 26.10 (s), 26.00 (s), 25.95 (s), 25.93 (s), 25.85 (s, 2 C), 25.75 (s) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 36.55 ppm. HRMS (IE): calcd. for $C_{22}H_{39}P$ [MH^+] 334.2784, found 344.2783.

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