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P-Stereogenic Phospholanes or Phosphorinanes from *o*-Biarylylphosphines: Two Bridges Not Too Far

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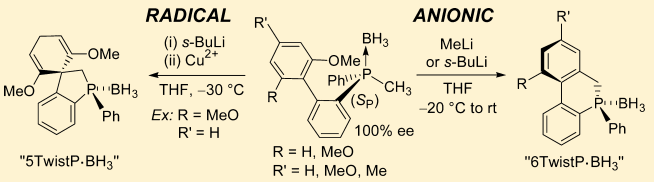
Supporting Information

ABSTRACT: The discovery of a concise regiodivergent asymmetric route to nonclassical *P*-stereogenic 5- or 6-membered benzophosphacycles, under conditions-dependent radical (oxidative addition) versus anionic (S_NAr) benzannulation, is reported.



INTRODUCTION

Enantiopure P-based organic compounds have been an ever-increasing research interest for over a century.[1] In particular, numerous phosphines were designed by an array of synthetic strategies encompassing chiral pool skeletal modification, resolution or desymmetrization techniques, and asymmetric synthesis.[2] Notably, backbone or P-atom stereogenic phosphacyclic motifs (Figure 1) have endowed excellent properties to transition-metal catalysts in a variety of asymmetric transformations.[3] Stereogenic mono- or di- (bridged) carbocyclic phosphetanes, phospholanes, and phosphepanes are predominantly encountered in the literature in contrast to phosphorinanes.[4,5]

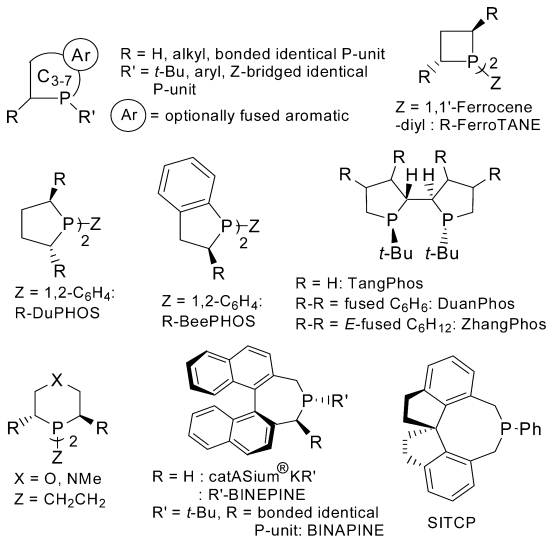


Figure 1. Generic representation of the most encountered cyclic phosphines in metal-catalyzed asymmetric hydrogenation and a selection thereof.

Of interest, the Jugé–Stephan asymmetric route to *P*-stereogenic phosphines via *P*-borane intermediates furnishes selectively either P-enantiomer in good overall yield. It relies upon the regio- and stereoselective two-step sequential displacement of the (+)- or (−)-ephedrine auxiliary from an enantiopure 1,3,2-oxazaphospholidine-2-borane complex (oxazaPB).[2b,e]

In our ongoing reasearch and development of (*P*-*ortho*-substituted aryl)-borne ethane-bridged diphosphines following the latter methodology,[6] we explored the synthesis of *P*-*o*-biarylyl congeners. The preparation of the basic enantiomeric 1,2-bis[(*o*-biphenylyl)(phenyl)phosphino]ethane diphosphine has been accomplished from its *P*-oxide derivative via a Cu-mediated dimerization.[7] Curiously, no reports existed on its preparation via the *P*-borane adduct variant, though *P*-*o*-biphenylyl-containing advanced *P*-borane intermediates have been earlier applied to various phosphines' syntheses by several research groups.[8]

RESULTS AND DISCUSSION

Our low-temperature $CuCl_2$-catalyzed attempted homocoupling of (S_P)-(*o*-biphenylyl)(methyl)(phenyl)phosphine-*P*-borane (**3a**) *P*-α-lithio anion gave rise, unfortunately, to a complex mixture (Scheme 1). Nevertheless, meticulous ^{1}H and ^{31}P NMR analyses identified the unexpected P-cyclic 9-phenyl-9,10-dihydro-9-phosphaphenanthrene-*P*-borane. This new chiral structure consists of a phosphorinane-*P*-borane wedged in the bay area of the biphenylic system, further bridging the two aryls. Unsubstituted phosphorinanes are inherently more flexible than phospholanes but a biphenyl-fused moiety confers a conformational restriction to the overall structure.

Following this discovery, the potential reactivity of such (*P*-*o*-biarylyl)-substituted (methyl)phosphine-*P*-boranes was investigated. Thus, screening the (2*R*,4*S*,5*R*)-(+)-oxazaPB ring-

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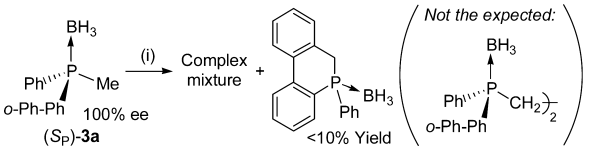
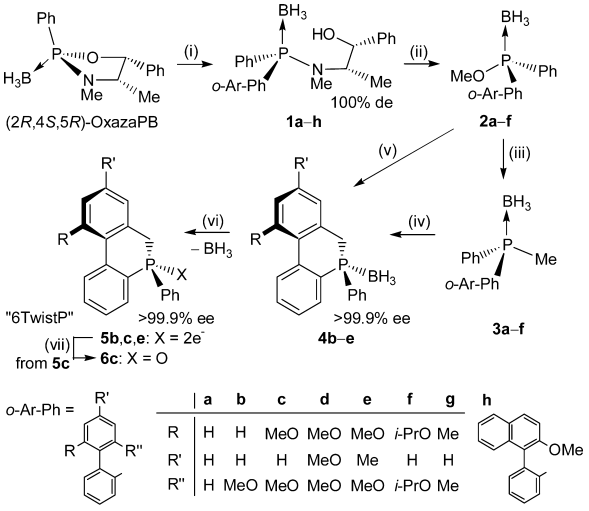
Scheme 1. Attempted Preparation of (S_P,S_P)-1,2-Bis[(*o*-biphenylyl)(phenyl)phosphino-*P*-borane]ethane Led to a Dibenzophosphorinane-*P*-borane[a]



[a]Reagents and conditions: (i) *s*-BuLi, THF, −30 °C, 1 h, then $CuCl_2$, −30 °C, 1 h.

opening with various *o*-biarylyllithiums, a series of (*o*-biarylyl)-(*N*-ephedrino)(phenyl)phosphine-*P*-boranes **1a−h** was prepared in 22−90% isolated yields (Scheme 2, step i).[9,10]

Scheme 2[a]



[a]Reagents and conditions: (i) *o*-Ar-PhLi, THF, −20 °C to rt (22−90% yield); (ii) MeOH, H_2SO_4, rt (40−83% yield); (iii) MeLi (1.2 equiv), THF, −20 °C (43−81% yield); (iv) *s*-BuLi (1.1 equiv) or MeLi (>1 equiv), THF, −30 °C to rt (81% yield for **4c** from **3c**); (v) MeLi (>2 equiv), THF, −20 °C to rt, o/n (73% yield for **4b**; 79% for **4c**; 10% for **4d** with 78% of **3d**; 77% for **4e**); (vi) Et_2NH, 55−60 °C (93−99% yield); (vii) 50% aq H_2O_2, Me_2CO, 0 °C (98% yield).

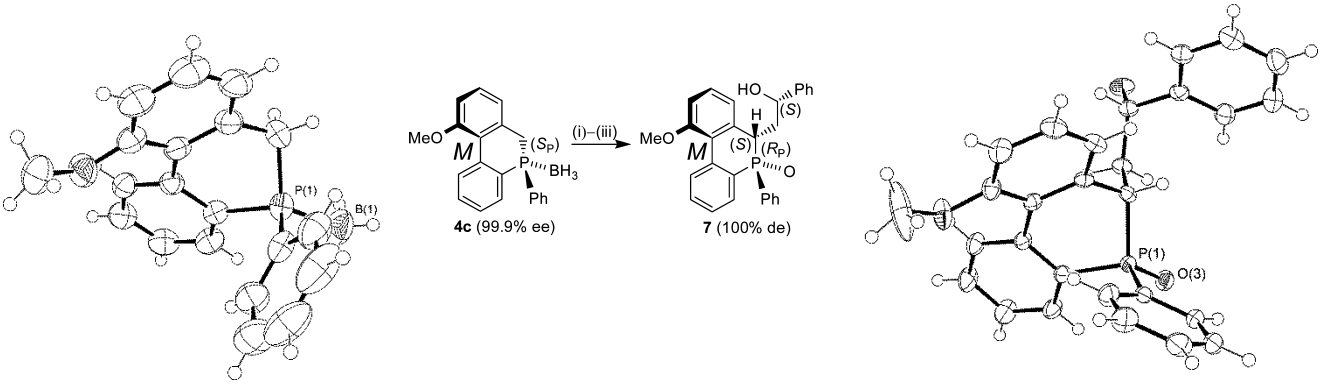
Spectroscopic data (^1H, ^{13}C, and ^{31}P NMR) of the crude indicated the formation of **1a−g** as a single diastereomer,[9c] and X-ray crystal-structure analysis of **1b** confirmed the retention of *P*-configuration.[11]

Following, H_2SO_4-promoted rt methanolysis of the (S_P)-aminophosphine-*P*-boranes **1a−f** (step ii) provided after recrystallization enantiomerically pure methyl (R_P)-phosphinite-*P*-boranes **2a−f** in 40−83% yield.[12,13]

Low-temperature displacement of the *P*-OMe group of (R_P)-**2a−f** with MeLi (1.2 equiv) afforded (S_P)-(methyl)phosphine-*P*-boranes **3a−f** in 43−81% (step iii).[12b] It was noticed with methyl phosphinite-*P*-borane **2c** that operating at up to rt with >2 equiv of MeLi (step v) induced the formation of the new 4-methoxy-9-phenyl-9,10-dihydro-9-phosphaphenanthrene-*P*-borane heterocycle (**4c**) by annulation onto the *o*-biarylyl group. An identical result was obtained with the generated *P*-α-lithio carbanion from the isolated (methyl)phosphine-*P*-borane **3c** (step iv). Clearly, a ready intramolecular nucleophilic aromatic substitution (S_NAr) of the activated C_{sp2}-OMe group was occurring. This displacement is accelerated by the MeO coordinative nature and suitable proximal disposition vis-à-vis the strongly reactive *P*-α-lithio anion with carbocyclization as a net result. Alternatively, in a convenient one-pot conversion via in situ formation of the reactive species, crystalline unsymmetrical dibenzophosphorinane-*P*-boranes **4b,c,e** were obtained in 73−79% yield upon treatment of **2b,c,e** with excess (>2 equiv) MeLi (step v).[14] Under the same conditions, compound **2d** gave a mixture of **4d** (10%) and **3d** (78%). Compound **4b** was found to have ^1H and ^{31}P NMR spectra identical to those of the phosphacycle of Scheme 1.

In view of the simultaneous determination of absolute *P*-configuration and anticipated axial chirality of **4**, α-functionalization using (*R*)-styrene oxide was performed. Its condensation with the preformed *P*-α-lithio carbanion of **4c**,[15] and subsequent BH_3 removal followed by P-oxidation,[16] furnished the *P*-oxide **7** which facilitated the growth of a single crystal (Scheme 3). X-ray crystal-structure analyses of **4c** and **7** confirmed the (S_P)-configuration of **4c**. With an identical *M*-atropisomery (or R_a) in both cases, the *P*-phenyl group occupies a less congested quasi-axial position. It is noteworthy that two structurally similar conformers (having *M*-atropisomery) were found in the **4c** cell unit. The twisted axial orientation is locked in all cases.[17]

Scheme 3. ORTEP Drawings of 4c (Left) and Its Derivative 7 (Right) at the 50% Probability Level and Preparation of 7[a]



[a]Reagents and conditions: (i) *s*-BuLi, THF, −30 °C, then (*R*)-styrene oxide (70% yield); (ii) Et_2NH, 55−60 °C; (iii) 50% aq H_2O_2, Me_2CO, 0 °C (99% yield for two steps).

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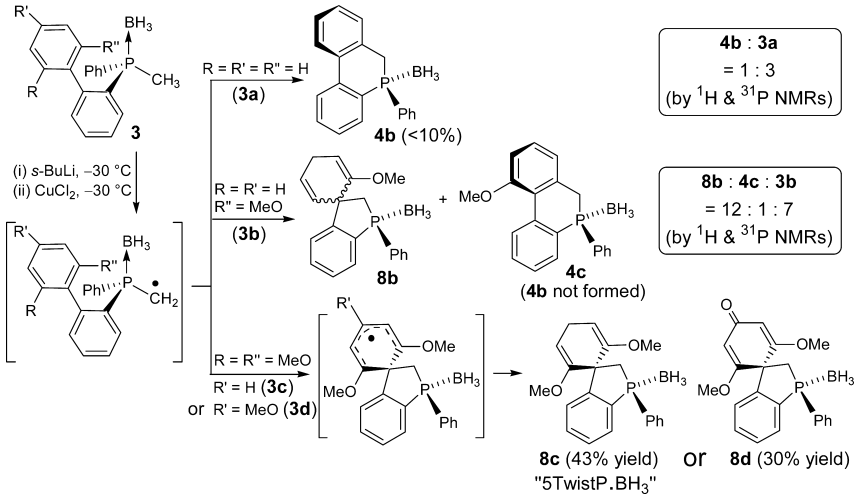
Scheme 4. Transformation Pathways of the *P*-α-Radical of (S_P)-3



Closing the synthetic sequence of Scheme 2, (S_P)-**4b,c,e** decomplexation under mild conditions in Et_2NH (55−60 °C) (step vi) furnished the corresponding homochiral dibenzophosphorinanes **5b,c,e** in 93−99% yield (^{31}P NMR δ ∼−40 ppm), and oxidation of **5c** gave **6c** (step vii).[14,16] The simplest free monophosphine **5b** was dubbed "6TwistP" alluding to its 6-membered twisted structure and reminiscent of the unexpected outcome of this chemistry.

In a second surprising turn of events, treatment of (S_P)-**3c** with *s*-BuLi and $CuCl_2$ did not lead to the expected dimerization product but instead gave the new unusual spiro[(2,6-dimethoxy-2,5-cyclohexadiene)-1,1′-(3-phenyl-3-phosphindane-*P*-borane)] chiral structure **8c** (dubbed "5TwistP·BH_3") (Scheme 4).[18]

This spiro benzophospholane-*P*-borane arose from favored *P*-α-radical trapping by the neighboring 2,6-dimethoxyphenyl ring and leading to its dearomatization. Analysis of this case coupled with Scheme 1 result with **3a** (Scheme 3, R = R′ = R″ = H) points out that, under the same reaction conditions, a switch in regioselectivity occurs depending on *o*′-MeO-substituents' availability on the top aryl. Investigating this reaction with **3b** led to a complex mixture. Nevertheless, ^{1}H and ^{31}P NMRs revealed the formation of a benzophospholane-*P*-borane **8b** (^{31}P NMR δ ∼+32 ppm; not isolated, with an unconfirmed geometry of the non-*meso*-cycle) and **4c** but not **4b**. Also, the spiro-dienonic structure (S_P)-**8d** was obtained from (S_P)-**3d** by loss of a CH_3 radical (Figure 2).

The polar cases experiments show that the *P*-α-radical preferentially adds intramolecularly onto the *ipso*-position of the top aryl furnishing a 5-membered ring (formal 5-*exo*-*trig* carbocyclization) if at least a substituent occupies an *o*′-position (R″ ≠ H), and in its absence (R″ = H) addition on the neighboring *o*′-position prevails leading to a 6-membered ring (6-*endo*-*trig*). The formation of compounds **4b,c** was accompanied by the partial recovery of starting **3**. This could have arguably formed in part via intermolecular quench of the *P*-CH_2 radical by H-abstraction from the transient cyclic radical evolving toward **4**. Such a pathway is excluded with **3c**.[19]

CONCLUSIONS

We have presented a controlled serendipitous divergent asymmetric synthesis of either 5- or 6-membered cyclic phosphine-*P*-boranes. The cascade reactions from methyl phosphinite-*P*-boranes **2** providing the biphenyl-fused phosphorinane-*P*-boranes **4** and the radical-initiated dearomatizing spirocyclization toward benzophospholane-*P*-boranes **8** represent a new twist in *P*-stereogenic cyclic phosphines' synthesis. Such "chiral or achiral" frameworks constitute interesting precursors for the elaboration of new diversified families of P-heterocycles. The progress of this ongoing research will be communicated in due course.

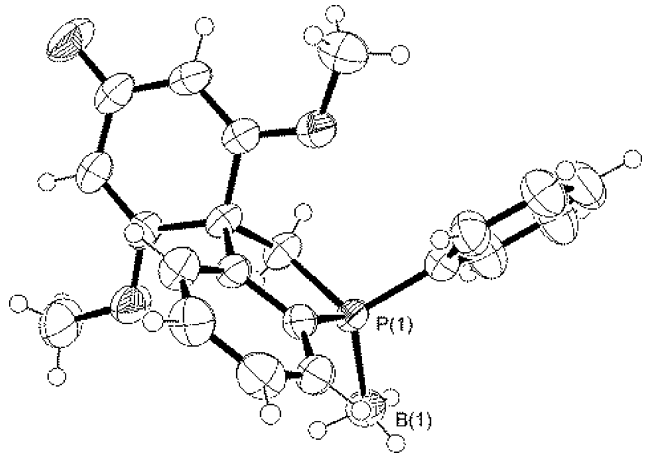


Figure 2. ORTEP drawing of (S_P)-**8d** at the 50% probability level.

EXPERIMENTAL SECTION

General Methods. All reactions were conducted under an inert atmosphere using anhydrous solvents. ^{1}H (300 MHz, internal Me_4Si), ^{13}C (75 MHz, internal $CDCl_3$; J_{C-P} is indicated), and ^{31}P NMR (120 MHz, external 85% H_3PO_4) were recorded for solutions in $CDCl_3$. High-resolution mass spectra were obtained with a Q-TOF instrument equipped with orthogonal Z-spray ESI interface. 2-Bromobiphenyl, 2′-bromo-2,6-dimethoxybiphenyl, 2′-bromo-2,6-diisopropoxybiphenyl, 2-methoxy-1-naphthaleneboronic acid, and (*R*)-styrene oxide (ee ≥98.0% (GC)) are commercially available. (2*R*,4*S*,5*R*)-(+)-3,4-Dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine-2-borane ((+)-oxazaPB derived from (1*R*,2*S*)-(−)-ephedrine),[2b] 2′-bromo-2-methoxybiphenyl,[20] and 2′-bromo-2,4,6-trimethoxybiphenyl[21] were prepared according to the literature.

2′-Bromo-2,6-dimethoxy-4-methylbiphenyl. To a solution of 1,3-dimethoxy-5-methylbenzene (11.00 g, 72.3 mmol) in THF (100 mL) was added under stirring *n*-BuLi (1.3 M in hexane, 56 mL) at rt. After 1 h, it was cooled to 0 °C, 1,2-dibromobenzene (17.05 g, 72.3

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mmol) was slowly added, and the mixture was allowed to stir overnight at rt. After H_2O quenching and extraction with CH_2Cl_2, the crude was purified by recrystallization (i-Pr_2O/CH_2Cl_2) affording off-white crystals (11.50 g, 52%): mp 143−145 °C; R_f 0.49 (toluene/hexane 7:3); ^{1}H NMR δ 2.42 (s, 3H), 3.72 (s, 6H), 6.47 (s, 2H), 7.14−7.24 (m, 2H), 7.30−7.36 (m, 1H), 7.64 (dd, J = 8, 1 Hz, 1H); ^{13}C NMR δ 22.2, 55.8, 104.9, 116.0, 125.4, 126.8, 128.3, 132.2, 132.5, 136.1, 139.6, 157.3; MS (ESI) m/z 307.0 (100) [M^+ + H]; HRMS (ESI) calcd for $C_{15}H_{16}{}^{79}BrO_2$ [M^+ + H] 307.0334, found 307.0345.

2′-Bromo-2,6-dimethylbiphenyl. To a solution of 1-bromo-2-iodobenzene (8.49 g, 30.0 mmol) and $Pd(PPh_3)_4$ (1.04 g, 0.9 mmol) in toluene (80 mL) was added 2,6-dimethylbenzeneboronic acid (5.85 g, 39.0 mmol) in EtOH (40 mL) then aq Na_2CO_3 (19.08 g in 80 mL H_2O). The resulting mixture was stirred at 85 °C for 6 days. After toluene/H_2O extraction, the product was purified on silica gel eluting with hexane (R_f 0.40) and recrystallized (hexane/MeOH) at 0 °C to afford white crystals (4.93 g, 63%): mp 47−50 °C; ^{1}H NMR δ 1.98 (s, 6H), 7.09−7.22 (m, 5H), 7.32−7.37 (m, 1H), 7.66 (dd, J = 8, 1 Hz, 1H); ^{13}C NMR δ 20.3, 123.9, 127.1, 127.6, 128.6, 130.5, 132.7, 135.8, 140.7, 141.7.

1-(2-Bromophenyl)-2-methoxynaphthalene. To a hot (85 °C) solution of 1-bromo-2-iodobenzene (4.24 g, 15.0 mmol), K_2CO_3 (4.15 g, 30.0 mmol), and $Pd(PPh_3)_4$ (0.35 g, 0.3 mmol) in EtOH (1 mL)/H_2O (4 mL)/dioxane (10 mL) was added a solution of 2-methoxy-1-naphthaleneboronic acid (2.02 g, 10.0 mmol) in dioxane (10 mL) over 4 h. The resulting mixture was stirred at 85 °C for 2 days. The reaction was allowed to cool to rt, quenched with 3 M HCl and extracted with EtOAc. Purification of the residue on silica gel eluting with hexane/EtOAc 19:1 and recrystallization (CH_2Cl_2/hexane) afforded white crystals (1.65 g, 50%): mp 119−121 °C; R_f 0.36 (hexane/EtOAc 19:1); ^{1}H NMR δ 3.84 (s, 3H), 7.19−7.43 (m, 7H), 7.72−7.76 (m, 1H), 7.79−7.85 (m, 1H), 7.90 (d, J = 9 Hz, 1H); ^{13}C NMR δ 56.6, 113.6, 123.6, 124.1, 124.6, 125.3, 126.6, 127.2, 127.9, 128.8, 128.9, 129.7, 132.4, 132.6, 132.9, 137.7, 153.8; MS (ESI) m/z 312.0 (93) [M^+]; HRMS (ESI) calcd for $C_{17}H_{13}{}^{79}BrO$ [M^+] 312.0150, found 312.0157.

(S_P)-(Biphenyl-2-yl)[(1*R*,2*S*)-*N*-ephedrino](phenyl)phosphine *P*-Borane ((S_P)-1a). To a cold solution (−78 °C) of 2-bromobiphenyl (2.50 g, 10.7 mmol) in Et_2O (35 mL) was added n-BuLi (1.5 M in hexane, 7.2 mL). After being stirred at −78 °C for 2 h, the reaction mixture was warmed to −20 °C for 15 min. To this suspension at −78 °C was added a solution of (+)-oxazaPB (2.37 g, 8.3 mmol) in THF (20 mL) then the suspension allowed to warm to rt with overnight stirring. CH_2Cl_2/H_2O extraction followed by purification on silica gel eluting with toluene then toluene/EtOAc 19:1 (R_f 0.51) afforded white crystals (2.70 g, 74%): mp 104−106 °C; $[\alpha]^{25}_D$ +52.7 (c 1.2, $CHCl_3$) (S_P-enantiomer: $[\alpha]^{20}_D$ +64.9 (c 0.297, CH_2Cl_2)[8a]); ^{1}H NMR δ 0.55−1.65 (br m, 3H), 0.68 (d, J = 7 Hz, 3H), 1.50 (br d, J = 4 Hz, 1H), 2.55 (d, J = 7 Hz, 3H), 3.94 (m, 1H), 4.84 (m, 1H), 7.13−7.49 (m, 17H), 7.64−7.72 (m, 2H). NMR data were consistent with those reported in the literature.[8a,b]

(S_P)-[(1*R*,2*S*)-*N*-Ephedrino](2′-methoxybiphenyl-2-yl)(phenyl)phosphine *P*-Borane ((S_P)-1b). To a cold solution (−78 °C) of 2′-bromo-2-methoxybiphenyl (5.00 g, 19.0 mmol) in THF (200 mL) was added n-BuLi (1.5 M in hexane, 12.7 mL). After being stirred at −78 °C for 1 h, a solution of (+)-oxazaPB (4.16 g, 14.6 mmol) in THF (20 mL) was slowly added. Treatment as for **1a** and purification on silica gel eluting with toluene then toluene/EtOAc 9:1 (R_f 0.53) followed by recrystallization (toluene/MeOH) afforded white crystals (7.13 g, 80%): mp 132−134 °C; $[\alpha]^{30}_D$ +80.9 (c 1.2, $CHCl_3$); ^{1}H NMR δ 0.40−1.55 (br m, 3H), 0.47 (d, J = 7 Hz, 1.2H), 1.13 (d, J = 7 Hz, 1.8H), 1.43 (br d, J = 4 Hz, 0.4H) 1.65 (br d, J = 4 Hz, 0.6H), 2.50 (d, J = 7 Hz, 1.2H), 2.70 (d, J = 7 Hz, 1.8H), 3.63 (s, 1.8H), 3.71 (s, 1.2H), 3.80 (m, 0.4H), 4.10 (m, 0.6H), 4.81 (m, 1H), 6.58 (d, J = 8 Hz, 0.6H), 6.72−6.84 (m, 1.4H), 7.08−7.55 (m, 15H), 7.74 (m, 1H); ^{13}C NMR δ 9.5 (d, J = 6 Hz), 10.8 (d, J = 5 Hz), 31.3 (d, J = 4 Hz), 31.6 (d, J = 4 Hz), 54.7, 54.9, 57.7 (d, J = 10 Hz), 58.0 (d, J = 10 Hz), 78.3, 78.8, 109.9, 110.2, 119.0, 119.4, 125.5−133.9 (m), 142.4−143.7 (m), 156.0 (d, J = 2 Hz); ^{31}P NMR δ +70.7 (br m); MS (ESI) m/z 470.2 (56) [M^+ + H]; HRMS (ESI) calcd for $C_{29}H_{34}BNO_2P$ [M^+ + H] 470.2420, found 470.2419.

(S_P)-(2′,6′-Dimethoxybiphenyl-2-yl)[(1*R*,2*S*)-*N*-ephedrino](phenyl)phosphine *P*-Borane ((S_P)-1c). From 2′-bromo-2,6-dimethoxybiphenyl (7.62 g, 26.0 mmol) following the procedure as for **1a**. Purification on silica gel eluting with toluene then toluene/EtOAc 9:1 (R_f 0.48) and recrystallization (toluene/MeOH) afforded white crystals (9.00 g, 90%). (S_P)-**1c**: mp 122−124 °C; $[\alpha]^{30}_D$ +14.7 (c 1.0, $CHCl_3$); ^{1}H NMR δ 0.57−1.56 (br m, 3H), 0.97 (d, J = 7 Hz, 3H), 1.80 (br d, J = 4 Hz, 1H), 2.65 (d, J = 8 Hz, 3H), 3.50 (s, 3H), 3.63 (s, 3H), 3.95 (m, 1H), 4.83 (m, 1H), 6.33 (d, J = 8 Hz, 1H), 6.42 (d, J = 8 Hz, 1H), 7.11−7.36 (m, 11H), 7.41−7.56 (m, 4H). NMR data were consistent with those reported in the literature.[10b] **2-Butyl-2′,6′-dimethoxybiphenyl** was also isolated: ^{1}H NMR δ 0.75 (t, J = 7 Hz, 3H), 1.17 (m, 2H), 1.40 (m, 2H), 2.35 (m, 2H), 3.69 (s, 6H), 6.63 (d, J = 8 Hz, 2H), 7.09 (m, 1H), 7.19−7.43 (m, 4H).

(S_P)-[(1*R*,2*S*)-*N*-Ephedrino](phenyl)(2′,4′,6′-trimethoxybiphenyl-2-yl)phosphine *P*-Borane ((S_P)-1d). From 2′-bromo-2,4,6-trimethoxybiphenyl (4.43 g, 13.7 mmol) following the procedure as for **1a**. Purification on silica gel eluting with toluene and then toluene/EtOAc 9:1 (R_f 0.38) and recrystallization (hexane/MeOH) afforded white crystals (4.79 g, 86%): mp 129−131 °C; $[\alpha]^{25}_D$ +11.9 (c 1.1, $CHCl_3$); ^{1}H NMR δ 0.45−1.50 (br m, 3H), 1.01 (d, J = 7 Hz, 3H), 1.72 (br d, J = 4 Hz, 1H), 2.66 (d, J = 8 Hz, 3H), 3.48 (s, 3H), 3.62 (s, 3H), 3.77 (s, 3H), 4.00 (m, 1H), 4.83 (m, 1H), 5.86 (d, J = 2 Hz, 1H), 5.96 (d, J = 2 Hz, 1H), 7.09−7.36 (m, 10H), 7.43−7.56 (m, 4H); ^{13}C NMR δ 10.7 (d, J = 4 Hz), 31.7 (d, J = 2 Hz), 54.8, 55.1, 55.2, 57.7 (d, J = 9 Hz), 78.7 (d, J = 2 Hz), 89.8, 89.9, 110.8 (d, J = 3 Hz), 125.8−133.9 (m), 139.8 (d, J = 11 Hz), 142.7, 158.2, 158.3, 161.0; ^{31}P NMR δ +71.7 (br m); MS (ESI) m/z 528.2 (38) [M^+ − H]; HRMS (ESI) calcd for $C_{31}H_{36}BNO_4P$ 528.2475 [M^+ − H], found 528.2496.

(S_P)-(2′,6′-Dimethoxy-4′-methylbiphenyl-2-yl)[(1*R*,2*S*)-*N*-ephedrino](phenyl)phosphine *P*-Borane ((S_P)-1e). From 2′-bromo-2,6-dimethoxy-4-methylbiphenyl (6.36 g, 20.7 mmol) following procedure as for **1a**. Purification on silica gel eluting with toluene then toluene/EtOAc 9:1 (R_f 0.52) and recrystallization (toluene/MeOH) afforded white crystals (7.35 g, 90%): mp 140−143 °C; $[\alpha]^{25}_D$ +16.4 (c 1.0, $CHCl_3$); ^{1}H NMR δ 0.45−1.50 (br m, 3H), 0.98 (d, J = 7 Hz, 3H), 1.74 (br d, J = 4 Hz, 1H), 2.27 (s, 3H), 2.65 (d, J = 8 Hz, 3H), 3.48 (s, 3H), 3.61 (s, 3H), 3.99 (m, 1H), 4.81 (m, 1H), 6.09 (s, 1H), 6.19 (s, 1H), 7.09−7.34 (m, 10H), 7.43−7.53 (m, 4H); ^{13}C NMR δ 10.5 (d, J = 4 Hz), 22.0, 31.7 (d, J = 2 Hz), 54.7, 55.1, 57.6 (d, J = 9 Hz), 78.6 (d, J = 2 Hz), 103.9, 115.1 (d, J = 3 Hz), 125.7−139.5 (m), 142.6, 157.3; ^{31}P NMR δ +72.0 (br m); MS (ESI) m/z 514.3 (42) [M^+ + H]; HRMS (ESI) calcd for $C_{31}H_{38}BNO_3P$ [M^+ + H] 514.2682, found 514.2689.

(S_P)-(2′,6′-Diisopropoxybiphenyl-2-yl)[(1*R*,2*S*)-*N*-ephedrino](phenyl)phosphine *P*-Borane ((S_P)-1f). From 2′-bromo-2,6-diisopropoxybiphenyl (8.00 g, 22.9 mmol) following procedure as for **1a**. Purification on silica gel eluting with toluene then toluene/EtOAc 9:1 (R_f 0.62) afforded a colorless syrup (7.93 g, 81%): $[\alpha]^{25}_D$ −40.4 (c 1.3, $CHCl_3$); ^{1}H NMR δ 0.45−1.55 (br m, 3H), 1.00 (d, J = 6 Hz, 3H), 1.03 (d, J = 7 Hz, 3H), 1.05 (d, J = 6 Hz, 3H), 1.14 (d, J = 6 Hz, 3H), 1.17 (d, J = 6 Hz, 3H), 1.86 (br s, 1H), 2.68 (d, J = 8 Hz, 3H), 4.06 (m, 1H), 4.32 (m, 2H), 4.84 (d, J = 3 Hz, 1H), 6.31 (d, J = 8 Hz, 1H), 6.33 (d, J = 8 Hz, 1H), 6.99−7.04 (m, 2H), 7.11−7.31 (m, 9H), 7.39 (m, 1H), 7.45−7.57 (m, 3H); ^{13}C NMR δ 10.5 (d, J = 4 Hz), 21.9, 22.4, 22.5, 32.2 (d, J = 3 Hz), 57.6 (d, J = 10 Hz), 69.8, 70.9, 79.0 (d, J = 2 Hz), 105.4, 106.3, 121.0 (d, J = 3 Hz), 125.8−134.5 (m), 140.9 (d, J = 11 Hz), 142.7, 156.7, 156.8; ^{31}P NMR δ +71.8 (br m); MS (ESI) m/z 556.3 (18) [M^+ + H]; HRMS (ESI) calcd for $C_{34}H_{44}BNO_3P$ [M^+ + H] 556.3152, found 556.3142.

(S_P)-(2′,6′-Dimethylbiphenyl-2-yl)[(1*R*,2*S*)-*N*-ephedrino](phenyl)phosphine *P*-Borane ((S_P)-1g). From 2′-bromo-2,6-dimethylbiphenyl following procedure as for **1a**. The organolithium was prepared as follows: to a cold solution (−78 °C) of 2′-bromo-2,6-dimethylbiphenyl (0.23 g, 0.88 mmol) in THF (10 mL) was added t-BuLi (1.5 M in pentane, 1.17 mL). After the solution was stirred at −78 °C for 30 min, the temperature was gradually raised to −50 °C to ensure complete lithiation. Purification on silica gel eluting with

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toluene/hexane 4:1 and then toluene afforded (R_P)-*trans*-(*N*-methylamino)(phenyl)(1-phenyl-1-propenyloxy)phosphine *P*-borane as white crystals (0.12 g, 73%). Further elution with toluene/EtOAc (19:1) then toluene/EtOAc 9:1 (R_f 0.56) afforded **1g** as a white foam (61 mg, 22%): $[\alpha]^{30}_D$ −7.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR δ 0.35−1.50 (br m, 3H), 1.04 (d, *J* = 7 Hz, 3H), 1.87 (s, 3H), 1.96 (s, 3H), 2.75 (d, *J* = 7 Hz, 3H), 3.96 (m, 1H), 4.99 (d, *J* = 3 Hz, 1H), 6.87 (d, *J* = 7 Hz, 1H), 6.95 (d, *J* = 7 Hz, 1H), 7.14−7.29 (m, 2H), 7.31−7.65 (m, 13H); ^{13}C NMR δ 10.3 (d, *J* = 5 Hz), 21.3, 21.4, 31.9 (d, *J* = 3 Hz), 57.8 (d, *J* = 10 Hz), 79.2, 125.8−136.6 (m), 140.0 (d, *J* = 3 Hz), 142.6, 146.2 (d, *J* = 14 Hz); ^{31}P NMR δ +72.2 (br m); MS (ESI) *m*/*z* 468.3 (100) [M^+ + H]; HRMS (ESI) calcd for $C_{30}H_{36}BNOP$ [M^+ + H] 468.2628, found 468.2638.

(R_P)-*trans*-(*N*-Methylamino)(phenyl)(1-phenyl-1-propenyloxy)phosphine *P*-Borane: mp 65−68 °C; R_f 0.52 (toluene); $[\alpha]^{25}_D$ +63.6 (*c* 1.2, $CHCl_3$) ((S_P)-enantiomer,[9b] $[\alpha]^{25}_D$ −69.6 (*c* 1.0, $CHCl_3$)); ^{1}H NMR δ 0.23−1.30 (br m, 3H), 1.78 (dd, *J* = 7, 3 Hz, 3H), 2.30 (dd, *J* = 11, 6 Hz, 3H), 2.89 (m, 1H), 5.67 (dq, *J* = 7, 3 Hz, 1H), 7.29−7.41 (m, 3H), 7.43−7.54 (m, 5H), 7.76−7.83 (m, 2H); ^{31}P NMR δ +105.3 (br m). NMR data were consistent with those reported in the literature.[9b]

(S_P)-[(1*R*,2*S*)-*N*-Ephedrino][2-(2-methoxynaphth-1-yl)-phenyl](phenyl)phosphine *P*-Borane ((S_P)-1h). From 1-(2-bromophenyl)-2-methoxynaphthalene (1.10 g, 3.51 mmol) following the procedure as for **1a**. Purification on silica gel eluting with toluene then toluene/EtOAc 9:1 afforded a colorless solid foam (1.09 g, 90%). The compound was obtained as a mixture of two atropo-diastereomers in ∼1:1 ratio as revealed by ^{1}H NMR: R_f 0.52 (toluene/EtOAc 9:1); $[\alpha]^{25}_D$ +16.0 (*c* 1.1, $CHCl_3$); ^{1}H NMR δ 0.35−1.25 (br m, 3H), 0.62 (d, *J* = 7 Hz, 1.4H), 0.83 (d, *J* = 7 Hz, 1.6H), 1.66 (br s, 1H), 2.61 (d, *J* = 8 Hz, 1.6H), 2.72 (d, *J* = 7 Hz, 1.4H), 3.69 (s, 1.3H), 3.75−3.76 (m, 1.8H), 3.89 (m, 0.5H), 4.66 (d, *J* = 4 Hz, 0.5H), 4.77 (d, *J* = 3 Hz, 0.5H), 6.94−7.69 (m, 20H); ^{13}C NMR δ 9.8 (d, *J* = 5 Hz), 10.4 (d, *J* = 5 Hz), 32.0 (d, *J* = 2 Hz), 32.3 (d, *J* = 3 Hz), 55.2, 55.8, 57.5 (d, *J* = 10 Hz), 57.8 (d, *J* = 9 Hz), 78.5, 79.1, 112.2, 112.5, 122.5−134.6 (m), 141.3 (d, *J* = 10 Hz), 141.5 (d, *J* = 11 Hz), 142.5, 153.86, 153.90; ^{31}P NMR δ +72.0 (br m); MS (ESI) *m*/*z* 520.3 (100) [M^+ + H]; HRMS (ESI) calcd for $C_{33}H_{36}BNO_2P$ [M^+ + H] 520.2577, found 520.2563.

Methyl (R_P)-(Biphenyl-2-yl)(phenyl)phosphinite *P*-Borane ((R_P)-2a). To a solution of ((S_P)-**1a** (1.76 g, 4.00 mmol) in MeOH (30 mL) was added H_2SO_4 (96%, 0.40 g, 3.96 mmol) at rt under stirring. After being stirred for 1 day, the reaction mixture was filtered through a pad of silica gel and concentrated. Extraction with CH_2Cl_2/H_2O and purification on silica gel eluting with toluene/hexane 9:1 then toluene (R_f 0.76) and recrystallization (CH_2Cl_2/hexane) afforded white crystals (0.87 g, 71%): mp 119−121 °C; $[\alpha]^{25}_D$ −21.0 (*c* 1.2, $CHCl_3$) ((S_P)-enantiomer,[8a] $[\alpha]^{20}_D$ +17.4 (*c* 0.945, CH_2Cl_2), >99% ee (HPLC)); ^{1}H NMR δ 0.30−1.50 (br m, 3H), 3.56 (d, *J* = 12 Hz, 3H), 6.89−6.93 (m, 2H), 7.10 (m, 2H), 7.17−7.38 (m, 7H), 7.45−7.56 (m, 2H), 8.05 (m, 1H); ^{31}P NMR δ +109.7 (br m). NMR data were consistent with those reported in the literature.[8a,b]

Methyl (R_P)-(2′-Methoxybiphenyl-2-yl)(phenyl)phosphinite *P*-Borane ((R_P)-2b). From (S_P)-**1b** (2.11 g, 4.50 mmol) following the procedure as for **2a**. Purification on silica gel eluting with toluene (R_f 0.49) and then toluene/EtOAc 19:1 and recrystallization (MeOH/hexane) afforded white crystals (1.25 g, 83%): mp 80−82 °C; $[\alpha]^{25}_D$ −2.2 (*c* 1.4, $CHCl_3$); ^{1}H NMR δ 0.30−1.50 (br m, 3H), 3.34 (s, 1.5H), 3.39 (s, 1.5H), 3.55 (d, *J* = 12 Hz, 1.5H), 3.57 (d, *J* = 12 Hz, 1.5H), 6.54 (m, 1H), 6.68−6.87 (m, 2H), 7.13−7.38 (m, 7H), 7.44−7.56 (m, 2H), 8.03−8.19 (m, 1H); ^{13}C NMR δ 53.4 (d, *J* = 2 Hz), 53.7 (d, *J* = 2 Hz), 54.5, 54.6, 109.3, 109.8, 118.9, 119.2, 126.8−134.0 (m), 142.6 (d, *J* = 9 Hz), 142.9 (d, *J* = 5 Hz), 156.2, 156.4; ^{31}P NMR δ +109.1 (br m); MS (ESI) *m*/*z* 335.1 (100) [M^+ − H]; HRMS (ESI) calcd for $C_{20}H_{21}BO_2P$ [M^+ − H] 335.1372, found 335.1377.

Methyl (R_P)-(2′,6′-Dimethoxybiphenyl-2-yl)(phenyl)-phosphinite *P*-Borane ((R_P)-2c). From (S_P)-**1c** (8.00 g, 16.0 mmol) following the procedure as for **2a**. Purification on silica gel eluting with toluene and then toluene/EtOAc (19:1) and recrystallization (CH_2Cl_2/hexane) afforded **2c** as white crystals (4.63 g, 79%). Further elution with toluene/EtOAc 4:1 and recrystallization (CH_2Cl_2/hexane) afforded (−)-(2′,6′-dimethoxybiphenyl-2-yl)-(hydroxy)(phenyl)phosphine *P*-borane as white crystals (0.34 g, 6%). Further elution with EtOAc/MeOH and recrystallization (*i*-Pr_2O/CH_2Cl_2) afforded (−)-(2′,6′-dimethoxybiphenyl-2-yl)(phenyl)-phosphine *P*-oxide as white crystals (0.54 g, 10%).

(R_P)-**2c**: mp 108−110 °C; R_f 0.35 (toluene); $[\alpha]^{30}_D$ +38.6 (*c* 1.1, $CHCl_3$) (R_P-enantiomer,[10b] $[\alpha]_D$ +28.4 (*c* 0.9, CH_2Cl_2)); ^{1}H NMR δ 0.30−1.45 (br m, 3H), 3.32 (s, 3H), 3.40 (s, 3H), 3.57 (d, *J* = 12 Hz, 3H), 6.26 (d, *J* = 8 Hz, 1H), 6.38 (d, *J* = 8 Hz, 1H) 7.10−7.37 (m, 7H), 7.48 (tt, *J* = 8, 2 Hz, 1H), 7.56 (tt, *J* = 7, 1 Hz, 1H), 8.16 (ddd, *J* = 12, 8, 1 Hz, 1H); ^{31}P NMR δ +107.8 (br m). NMR data were consistent with those reported in the literature.[10b]

(−)-(2′,6′-Dimethoxybiphenyl-2-yl)(hydroxy)(phenyl)-phosphine *P*-Borane: mp 129−132 °C; R_f 0.52 (toluene/EtOAc 4:1); $[\alpha]^{25}_D$ −11.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR δ 0.40−1.60 (br m, 3H), 3.20 (s, 3H), 3.74 (s, 3H), 6.10 (d, *J* = 8 Hz, 1H), 6.63 (d, *J* = 8 Hz, 1H), 6.71 (br s, 1H), 7.05−7.24 (m, 7H), 7.57 (m, 2H), 8.50 (m, 1H); ^{13}C NMR δ 54.8, 57.2, 105.0, 105.2, 119.0 (d, *J* = 3 Hz), 127.3−137.2 (m), 155.3, 157.4; ^{31}P NMR δ +93.6 (br m); MS (ESI) *m*/*z* 351.1 (100) [M^+ − H]; HRMS (ESI) calcd for $C_{20}H_{21}BO_3P$ [M^+ − H] 351.1321, found 351.1314.

(−)-(2′,6′-Dimethoxybiphenyl-2-yl)(phenyl)phosphine *P*-Oxide: mp 166−168 °C; R_f 0.46 (EtOAc); $[\alpha]^{30}_D$ −5.5 (*c* 1.3, $CHCl_3$); ^{1}H NMR δ 3.19 (s, 3H), 3.72, (s, 3H), 6.29 (d, *J* = 8 Hz, 1H), 6.59 (d, *J* = 8 Hz, 1H), 7.16−7.29 (m, 6H), 7.36−7.42 (m, 1H), 7.54−7.62 (m, 2H), 7.62 (d, J_{P-H} = 492 Hz, 1H), 8.19 (m, 1H); ^{13}C NMR δ 54.8, 55.6, 103.2, 103.5, 115.3 (d, *J* = 6 Hz), 127.3−132.6 (m), 137.4 (d, *J* = 12 Hz), 156.9, 157.4; ^{31}P NMR δ +20.1 (s); MS (ESI) *m*/*z* 339.1 (100) [M^+ + H]; HRMS (ESI) calcd for $C_{20}H_{20}O_3P$ [M^+ + H] 339.1150, found 339.1153.

Methyl (R_P)-(Phenyl)(2′,4′,6′-trimethoxybiphenyl-2-yl)-phosphinite *P*-Borane ((R_P)-2d). From (S_P)-**1d** (2.06 g, 3.89 mmol) following the procedure as for **2a**. Purification on silica gel eluting with toluene and then toluene/EtOAc 19:1 afforded **2d** as white crystals (0.92 g, 60%). Further elution with toluene/EtOAc 9:1 then toluene/EtOAc 4:1 afforded (hydroxy)(phenyl)(2′,4′,6′-trimethoxybiphenyl-2-yl)phosphine *P*-borane as white crystals (0.15 g, 10%). (R_P)-**2d**: mp 136−138 °C; R_f 0.25 (toluene); $[\alpha]^{25}_D$ +46.6 (*c* 1.1, $CHCl_3$); ^{1}H NMR δ 0.30−1.50 (br m, 3H), 3.29 (s, 3H), 3.35 (s, 3H), 3.57 (d, *J* = 12 Hz, 3H), 3.79 (s, 3H), 5.81 (d, *J* = 2 Hz, 1H), 5.91 (d, *J* = 2 Hz, 1H), 7.10 (m, 1H), 7.19−7.25 (m, 2H), 7.30−7.36 (m, 3H), 7.45 (m, 1H), 7.53 (m, 1H), 8.16 (m, 1H); ^{13}C NMR δ 53.5 (d, *J* = 2 Hz), 54.7, 54.8, 55.2, 89.3, 89.4, 109.9 (d, *J* = 3 Hz), 126.7−133.8 (m), 139.2 (d, *J* = 8 Hz), 158.3 (d, *J* = 5 Hz), 161.3; ^{31}P NMR δ +107.8 (br m); MS (ESI) *m*/*z* 395.2 (100) [M^+ − H]; HRMS (ESI) calcd for $C_{22}H_{25}BO_4P$ [M^+ − H] 395.1584, found 395.1592.

(−)-(Hydroxy)(phenyl)(2′,4′,6′-trimethoxybiphenyl-2-yl)-phosphine *P*-Borane: mp 151−154 °C; R_f 0.45 (toluene/EtOAc 4:1); $[\alpha]^{30}_D$ −6.9 (*c* 1.1, $CHCl_3$); ^{1}H NMR δ 0.40−1.60 (br m, 3H), 3.17 (s, 3H), 3.68 (s, 3H), 3.77 (s, 3H), 5.64 (d, *J* = 2 Hz, 1H), 6.16 (d, *J* = 2 Hz, 1H), 6.62 (br s, 1H), 7.05−7.25 (m, 6H), 7.53 (m, 2H), 8.46 (m, 1H); ^{13}C NMR δ 54.7, 55.5, 57.2, 91.7, 92.0, 111.8 (d, *J* = 3.3 Hz), 127.2−135.1 (m), 137.3 (d, *J* = 2.0 Hz), 155.9, 158.0, 161.5; ^{31}P NMR δ +93.9 (br m); MS (ESI) *m*/*z* 381.1 (100) [M^+ − H]; HRMS (ESI) calcd for $C_{21}H_{23}BO_4P$ [M^+ − H] 381.1427, found 381.1428.

Methyl (R_P)-(2′,6′-Dimethoxy-4′-methylbiphenyl-2-yl)-(phenyl)phosphinite *P*-Borane ((R_P)-2e). From (S_P)-**1e** (3.00 g, 5.8 mmol) following procedure as for **2a**. Purification on silica gel eluting with toluene then toluene/EtOAc 19:1 and recrystallization (CH_2Cl_2/hexane) afforded white crystals (1.60 g, 73%): mp 121−123 °C; R_f 0.29 (toluene); $[\alpha]_D^{30}$ +41.0 (*c* 1.1, $CHCl_3$); ^{1}H NMR δ 0.25−1.40 (br m, 3H), 2.34 (s, 3H), 3.31 (s, 3H), 3.39 (s, 3H), 3.57 (d, *J* = 12 Hz, 3H), 6.06 (s, 1H), 6.19 (s, 1H), 7.12 (m, 1H), 7.19−7.37 (m, 5H), 7.47 (m, 1H), 7.55 (m, 1H), 8.16 (m, 1H); ^{13}C NMR δ 22.1, 53.6 (d, *J* = 2 Hz), 54.7, 54.8, 103.3, 103.8, 114.2 (d, *J* = 3 Hz), 126.7−133.9 (m), 139.4 (d, *J* = 7 Hz), 139.5, 157.4, 157.5; ^{31}P NMR δ +107.7 (br m); MS (ESI) *m*/*z* 379.2 (100) [M^+ − H]; HRMS (ESI) calcd for $C_{22}H_{25}BO_3P$ [M^+ − H] 379.1634, found 379.1625.

Methyl (R_P)-(2′,6′-Diisopropoxybiphenyl-2-yl)(phenyl)-phosphinite *P*-Borane ((R_P)-2f). From (S_P)-**1f** (1.97 g, 3.55

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mmol) following the procedure as for **2a**. Purification on silica gel eluting with toluene and then toluene/EtOAc 19:1 afforded **2f** as white crystals (0.51 g, 40%). Further elution with toluene/EtOAc 4:1 then EtOAc afforded (−)-(2′,6′-diisopropoxybiphenyl-2-yl)(phenyl)-phosphine *P*-oxide as white crystals (0.62 g, 45%).

(R_P)-**2f**: mp 84−86 °C; R_f 0.61 (toluene); $[\alpha]^{30}_D$ +17.1 (*c* 1.1, $CHCl_3$); ^{1}H NMR δ 0.25−1.40 (m, 3H), 0.99 (d, *J* = 6 Hz, 3H), 1.01 (d, *J* = 6 Hz, 3H), 1.03 (d, *J* = 6 Hz, 3H), 1.10 (d, *J* = 6 Hz, 3H), 3.48 (d, *J* = 12 Hz, 3H), 4.17 (sep, *J* = 6 Hz, 1H), 4.30 (sep, *J* = 6 Hz, 1H), 6.30 (d, *J* = 8 Hz, 1H), 6.46 (d, *J* = 8 Hz, 1H), 7.07 (m, 1H), 7.13 (m, 1H), 7.21−7.28 (m, 2H), 7.31−7.40 (m, 2H), 7.43−7.51 (m, 3H), 7.90 (m, 1H); ^{13}C NMR δ = 21.6, 21.9, 22.2, 22.3, 53.8 (d, *J* = 2 Hz), 69.6, 70.6, 105.4, 105.9, 120.6 (d, *J* = 3 Hz), 126.2−133.3 (m), 140.3 (d, *J* = 7 Hz), 156.6, 156.9; ^{31}P NMR δ +109.3 (br m); MS (ESI) *m*/*z* 421.2 (100) [M$^+$ − H]; HRMS (ESI) calcd for $C_{25}H_{31}BO_3P$ [M$^+$ − H] 421.2104, found 421.2089.

(−)-(2′,6′-Diisopropoxybiphenyl-2-yl)(phenyl)phosphine *P*-Oxide: mp 120−123 °C; R_f 0.58 (EtOAc); $[\alpha]^{25}_D$ −15.7 (*c* 1.1, $CHCl_3$); ^{1}H NMR δ 0.81 (d, *J* = 6 Hz, 3H), 1.06 (d, *J* = 6 Hz, 3H), 1.09 (d, *J* = 6 Hz, 3H), 1.28 (d, *J* = 6 Hz, 3H), 4.06 (sep, *J* = 6 Hz, 1H), 4.42 (sep, *J* = 6 Hz, 1H), 6.34 (d, *J* = 8 Hz, 1H), 6.58 (d, *J* = 8 Hz, 1H), 7.12−7.39 (m, 7H), 7.50 (m, 2H), 7.75 (d, J_{P-H} = 507 Hz, 1H), 8.09 (m, 1H); ^{13}C NMR δ 21.4, 21.8, 21.9, 22.0, 69.5, 70.9, 105.5, 106.0, 117.9 (d, *J* = 6 Hz), 126.7−132.8 (m), 137.9 (d, *J* = 12 Hz), 155.7, 156.2; ^{31}P NMR δ +19.4 (s); MS (ESI) *m*/*z* 395.2 (100) [M$^+$ + H]; HRMS (ESI) calcd for $C_{24}H_{28}O_3P$ [M$^+$ + H] 395.1776, found 395.1766.

(S_P)-(Biphenyl-2-yl)(methyl)(phenyl)phosphine *P*-Borane ((S_P)-3a). To a cold solution (−20 °C) of (R_P)-**2a** (1.33 g, 4.34 mmol) in THF (15 mL) was added MeLi (1.6 M in Et_2O, 4 mL, 1.5 equiv) and the resulting mixture allowed to warm to rt, stirred overnight, and then quenched with H_2O. Extraction with CH_2Cl_2 and purification on silica gel eluting with hexane/EtOAc 19:1 and then hexane/EtOAc 9:1 (R_f 0.40) and recrystallization from hexane/CH_2Cl_2 afforded the title compound[22] as white crystals (1.02 g, 81%): mp 120−122 °C; $[\alpha]^{25}_D$ +50.7 (*c* 1.1, $CHCl_3$) ((S_P)-enantiomer,[8c] $[\alpha]^{25}_D$ +54.8 (*c* 0.82, $CHCl_3$); (R_P)-enantiomer,[8d] $[\alpha]_D{}^{20}$ −42.1 (*c* 1, $CHCl_3$), 99% ee (HPLC)); ^{1}H NMR δ 0.30−1.45 (br m, 3H), 1.42 (d, *J* = 10 Hz, 3H), 6.90 (d, *J* = 7 Hz, 2H), 7.13 (m, 2H), 7.19−7.40 (m, 7H), 7.48 (m, 2H), 7.98 (m, 1H); ^{13}C NMR δ 11.9 (d, *J* = 41 Hz), 127.2 −132.3 (m), 134.3 (d, *J* = 15 Hz), 140.5 (d, *J* = 3 Hz), 146.9 (d, *J* = 4 Hz); ^{31}P NMR δ +13.7 (br m).

(S_P)-(2′-Methoxybiphenyl-2-yl)(methyl)(phenyl)phosphine *P*-Borane ((S_P)-3b). From (R_P)-**2b** (1.30 g, 3.87 mmol) and MeLi (1.6 M in Et_2O, 2.9 mL, 1.2 equiv) at 0 °C. Workup as for **3a** and purification on silica gel eluting with toluene/hexane 4:1 (R_f 0.44) and then toluene afforded white crystals (0.53 g, 43%): mp 93−96 °C; $[\alpha]^{30}_D$ +34.3 (*c* 1.3, $CHCl_3$); ^{1}H NMR δ 0.30−1.50 (br m, 3H), 1.47−1.54 (m, 3H), 3.39 (s, 1.3H), 3.55 (s, 1.7H), 6.56−6.68 (m, 2H), 6.88 (m, 0.5H), 7.00 (m, 0.5H), 7.14−7.55 (m, 9H), 7.89 (m, 0.5H), 8.10 (m, 0.5H); ^{13}C NMR δ 11.0 (d, *J* = 42 Hz), 12.2 (d, *J* = 41 Hz), 54.7 (d, *J* = 9 Hz), 109.7, 110.1, 119.3, 119.5, 127.2−134.4 (m), 143.0 (d, *J* = 3 Hz), 143.1 (d, *J* = 4 Hz), 156.2, 156.5; ^{31}P NMR δ +12.8 (br m); MS (ESI) *m*/*z* 319.1 (100) [M$^+$ − H]; HRMS (ESI) calcd for $C_{20}H_{21}BOP$ [M$^+$ − H] 319.1423, found 319.1414.

(S_P)-(2′,6′-Dimethoxybiphenyl-2-yl)(methyl)(phenyl)-phosphine *P*-Borane ((S_P)-3c). From (R_P)-**2c** (2.00 g, 5.50 mmol) following the procedure as for **3b**. Purification on silica gel eluting with hexane/EtOAc (9:1) and then hexane/EtOAc 3:1 (R_f 0.30) afforded a colorless foam (1.16 g, 60%): $[\alpha]^{25}_D$ −1.9 (*c* 1.2, $CHCl_3$); ^{1}H NMR δ 0.40−1.50 (br m, 3H), 1.52 (d, *J* = 10 Hz, 3H), 3.18 (s, 3H), 3.57 (s, 3H), 6.25 (dd, *J* = 8, 1 Hz, 1H), 6.48 (dd, *J* = 8, 1 Hz, 1H), 7.06−7.10 (m, 1H), 7.19−7.34 (m, 6H), 7.43 (tt, *J* = 8, 2 Hz, 1H), 7.51 (tt, *J* = 7, 2 Hz, 1H), 8.11 (ddd, *J* = 14, 8, 1 Hz, 1H); ^{31}P NMR δ +11.3 (br m). NMR data were in accordance with those reported in the literature.[10b]

(S_P)-(Methyl)(phenyl)(2′,4′,6′-trimethoxybiphenyl-2-yl)-phosphine *P*-Borane ((S_P)-3d). From (R_P)-**2d** (1.00 g, 2.52 mmol) following the procedure as for **3b**. Purification on silica gel eluting with hexane/EtOAc 9:1 afforded a yellow solid foam (0.777 g, 81%): R_f 0.27 (hexane/EtOAc 4:1); $[\alpha]^{25}_D$ +8.5 (*c* 1.1, $CHCl_3$); ^{1}H NMR δ 0.30−1.50 (br m, 3H), 1.55 (d, *J* = 10 Hz, 3H), 3.19 (s, 3H), 3.56 (s, 3H), 3.83 (s, 3H), 5.83 (d, *J* = 2 Hz, 1H), 6.06 (d, *J* = 2 Hz, 1H), 7.07 (m, 1H), 7.22−7.51 (m, 8H) 8.08 (m, 1H); ^{13}C NMR δ 10.5 (d, *J* = 41 Hz), 54.7, 55.1, 55.3, 89.6, 89.7, 110.4 (d, *J* = 3 Hz), 127.0−134.8 (m), 139.4 (d, *J* = 3 Hz), 158.3, 158.3, 161.5; ^{31}P NMR δ +11.2 (br m); MS (ESI) *m*/*z* 379.2 (100) [M$^+$ − H]; HRMS (ESI) calcd for $C_{22}H_{25}BO_3P$ [M$^+$ − H] 379.1634, found 379.1628.

(S_P)-(2′,6′-Dimethoxy-4′-methylbiphenyl-2-yl)(methyl)-(phenyl)phosphine *P*-Borane ((S_P)-3e). From (R_P)-**2e** (0.71 g, 1.87 mmol) following the procedure as for **3b**. Purification on silica gel eluting with toluene and then toluene/EtOAc 19:1 afforded white crystals (0.44 g, 64%): mp 106−109 °C; R_f 0.39 (hexane/EtOAc 4:1); $[\alpha]^{30}_D$ +9.9 (*c* 1.2, $CHCl_3$); ^{1}H NMR δ 0.30−1.50 (br m, 3H), 1.52 (d, *J* = 10 Hz, 3H), 2.36 (s, 3H), 3.19 (s, 3H), 3.58 (s, 3H), 6.07 (s, 1H), 6.31 (s, 1H), 7.07 (m, 1H), 7.20−7.36 (m, 5H), 7.43 (m, 1H), 7.51 (m, 1H), 8.09 (m, 1H); ^{13}C NMR δ 10.4 (d, *J* = 41 Hz), 22.2, 54.6, 55.0, 103.6, 103.9, 114.7 (d, *J* = 3 Hz), 126.9−134.8 (m), 139.5 (d, *J* = 3 Hz), 140.0, 157.3; ^{31}P NMR δ +11.4 (br m); MS (ESI) *m*/*z* 363.2 (100) [M$^+$ − H]; HRMS (ESI) calcd for $C_{22}H_{25}BO_2P$ [M$^+$ − H] 363.1685, found 363.1676.

(S_P)-(2′,6′-Diisopropoxybiphenyl-2-yl)(methyl)(phenyl)-phosphine *P*-Borane ((S_P)-3f). From (R_P)-**2f** (0.64 g, 1.52 mmol) following procedure as for **3b**. Purification on silica gel eluting with toluene/hexane 9:1 then toluene afforded a colorless oil (0.42 g, 68%): R_f 0.6 (hexane/EtOAc 4:1); $[\alpha]^{25}_D$ +58.8 (*c* 1.2, $CHCl_3$); ^{1}H NMR δ 0.40−1.55 (br m, 3H), 0.97 (d, *J* = 6 Hz, 3H), 1.02 (d, *J* = 6 Hz, 3H), 1.07 (d, *J* = 6 Hz, 3H), 1.22 (d, *J* = 6 Hz, 3H), 1.46 (d, *J* = 11 Hz, 3H), 4.17 (sep, *J* = 6 Hz, 1H), 4.40 (sep, *J* = 6 Hz, 1H), 6.31 (d, *J* = 8 Hz, 1H), 6.53 (d, *J* = 8 Hz, 1H), 7.01 (m, 1H), 7.14−7.49 (m, 8H), 7.93 (m, 1H); ^{13}C NMR δ 11.1 (d, *J* = 40 Hz), 21.5, 21.8, 22.20, 22.22, 69.8, 70.5, 105.76, 105.80, 120.8 (d, *J* = 3 Hz), 126.6 −134.5 (m), 139.7 (d, *J* = 2 Hz), 156.6 (*J* = 11 Hz); ^{31}P NMR δ +12.8 (br m); MS (ESI) *m*/*z* 405.2 (100) [M$^+$ − H]; HRMS (ESI) calcd for $C_{25}H_{31}BO_2P$ [M$^+$ − H] 405.2155, found 405.2157.

(*M*,S_P)-4-Methoxy-9-phenyl-9,10-dihydro-9-phosphaphenanthrene *P*-Borane ((*M*,S_P)-4c) (Scheme 2, step iv). To a cold solution (−20 °C) of (S_P)-**3c** (0.10 g, 0.285 mmol) in THF (20 mL) was added *s*-BuLi (1.4 M in cyclohexane, 225 μL) or MeLi (1.6 M in Et_2O, 250 μL), and the resulting mixture was allowed to warm to rt overnight under stirring. Extraction with CH_2Cl_2/H_2O, purification on silica gel eluting with toluene/hexane 9:1 then toluene followed by recrystallization (CH_2Cl_2/hexane) afforded white crystals (74 mg, 81%) possessing the same characteristics as described below.

(*P*,S_P)-9-Phenyl-9,10-dihydro-9-phosphaphenanthrene *P*-Borane ((*P*,S_P)-4b) (Scheme 2, Step v). To a cold solution (−20 °C) of (R_P)-**2b** (0.56 g, 1.67 mmol) in THF (10 mL) was added MeLi (1.6 M in Et_2O, 4.2 mL), and the resulting mixture was allowed to warm to rt overnight under stirring. Extraction with CH_2Cl_2/H_2O, purification on silica gel eluting with toluene/hexane 7:3 and then toluene, and recrystallization (CH_2Cl_2/hexane) afforded white crystals (0.35 g, 73%): mp 204−207 °C; R_f 0.51 (toluene/hexane 4:1); $[\alpha]^{25}_D$ +78.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR δ 0.40−1.65 (br m, 3H), 3.31 (dd, *J* = 16, 8 Hz, 1H), 3.44 (dd, *J* = 16, 8 Hz, 1H), 7.10−7.35 (m, 8H), 7.45 (m, 1H), 7.65 (m, 1H), 7.75 (d, *J* = 8 Hz, 1H), 7.91 (m, 1H), 8.00 (m, 1H); ^{13}C NMR δ = 29.3 (d, *J* = 38 Hz), 123.1−134.6 (m), 139.7; ^{31}P NMR δ −1.9 (br m); MS (ESI) *m*/*z* 287.1 (100) [M$^+$ − H]; HRMS (ESI) calcd for $C_{19}H_{17}BP$ [M$^+$ − H] 287.1161, found 287.1158.

(*M*,S_P)-4-Methoxy-9-phenyl-9,10-dihydro-9-phosphaphenanthrene *P*-Borane ((*M*,S_P)-4c). From (R_P)-**2c** (3.54 g, 9.7 mmol) following the procedure as for **4b**. Purification on silica gel eluting with toluene/hexane 9:1 (R_f 0.49) and then toluene afforded a white solid: $[\alpha]^{25}_D$ −14.3 (*c* 1.1, $CHCl_3$); 98% ee by HPLC on a Daicel Chiralsil AD-H column, hexane/2-PrOH 95:5, 1 mL/min, UV detection (λ = 254 nm), t_R 9.3 min (S_P), 10.8 min (R_P). White crystals (2.44 g, 79%) from CH_2Cl_2/hexane in enantiopure form: mp 138−140 °C; $[\alpha]^{25}_D$ −14.6 (*c* 1.1, $CHCl_3$); >99.9% ee (HPLC); ^{1}H NMR δ 0.40−1.55 (br m, 3H), 3.28 (m, 2H), 3.85 (s, 3H), 6.72 (d, *J* = 7 Hz, 1H), 6.88 (d, *J* = 8 Hz, 1H), 7.11−7.44 (m, 7H), 7.61 (m, 1H), 8.01 (m, 1H), 8.29 (m, 1H); ^{13}C NMR δ 30.3 (d, *J* = 38 Hz), 55.7, 111.4 (d, *J* = 1 Hz), 122.7−133.3 (m), 136.9, 156.8 (d, *J* = 2 Hz); ^{31}P NMR δ −0.2 (br m);

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MS (ESI) m/z 317.1 (100) [$M^+ - H$]; HRMS (ESI) calcd for $C_{20}H_{19}BOP$ [$M^+ - H$] 317.1267, found 317.1265.

(*M*,S_P)-2,4-Dimethoxy-9-phenyl-9,10-dihydro-9-phosphaphenanthrene *P*-Borane ((*M*,S_P)-4d). From (R_P)-**2d** (0.89 g, 2.25 mmol) following the procedure as for **4b**. Purification on silica gel eluting with toluene then toluene/EtOAc 50:1 afforded off-white crystals (0.08 g, 10%). Further elution with toluene/EtOAc 19:1 and then 9:1 (R_f 0.38) afforded (S_P)-**3d** (0.67 g, 78%; its characteristics are as described above). (*M*,S_P)-**4d**: mp 105−107 °C; $[\alpha]^{25}_D$ +34.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR δ 0.45−1.60 (br m, 3H), 3.19 (dd, J = 16 and 8 Hz, 1H), 3.29 (dd, J = 16 and 8 Hz, 1H), 3.74 (s, 3H), 3.82 (s, 3H), 6.25 (d, J = 2 Hz, 1H), 6.43 (d, J = 2 Hz, 1H), 7.17−7.40 (m, 6H), 7.57 (m, 1H), 7.97 (m, 1H), 8.22 (m, 1H); ^{13}C NMR δ 30.8 (d, J = 38 Hz), 55.2, 55.7, 98.5 (d, J = 1 Hz), 107.3 (d, J = 6 Hz), 117.0 (d, J = 7 Hz), 123.5−133.2 (m), 137.2, 158.3 (d, J = 2 Hz), 160.0; ^{31}P NMR δ −1.3 (br m); MS (ESI) m/z 347.1 (100) [$M^+ - H$]; HRMS (ESI) calcd for $C_{21}H_{21}BO_2P$ [$M^+ - H$] 347.1372, found 347.1378.

(*M*,S_P)-4-Methoxy-2-methyl-9-phenyl-9,10-dihydro-9-phosphaphenanthrene *P*-Borane ((*M*,S_P)-4e). From (R_P)-**2e** (0.71 g, 1.9 mmol) following the procedure as for **4b**. Purification on silica gel eluting with toluene/hexane 9:1 (R_f 0.53) and then toluene and recrystallization (CH_2Cl_2/hexane) afforded white crystals (0.49 g, 77%): mp 140−142 °C; $[\alpha]^{25}_D$ +10.9 (*c* 1.1, $CHCl_3$); ^{1}H NMR δ 0.45−1.50 (br m, 3H), 2.25 (s, 3H), 3.24 (m, 2H), 3.82 (s, 3H), 6.54 (s, 1H), 6.68 (s, 1H), 7.16−7.42 (m, 6H), 7.58 (m, 1H), 7.98 (m, 1H), 8.27 (m, 1H); ^{13}C NMR δ 21.3, 30.2 (d, J = 38 Hz), 55.6, 112.4 (d, J = 1 Hz), 120.8−133.1 (m), 137.1, 139.5, 157.3 (d, J = 2 Hz); ^{31}P NMR δ −0.4 (br m); MS (ESI) m/z 331.1 (100) [$M^+ - H$]; HRMS (ESI) calcd for $C_{21}H_{21}BOP$ [$M^+ - H$] 331.1423, found 331.1425.

(*P*,S_P)-9-Phenyl-9,10-dihydro-9-phosphaphenanthrene ((*P*,S_P)-5b). A solution of (*P*,S_P)-**4b** (0.10 g, 0.35 mmol) in Et_2NH (3.5 mL) was refluxed for 2 h. Purification on silica gel eluting with toluene/hexane 3:2 under an inert atmosphere afforded a pale yellow oil (0.09 g, 93%): R_f 0.63 (toluene/hexane 1:1); $[\alpha]^{25}_D$ −203.0 (*c* 1.1, $CHCl_3$); ^{1}H NMR δ 3.07 (dd, J = 15, 10 Hz, 1H), 3.22 (dd, J = 15, 3 Hz, 1H), 6.99−7.18 (m, 8H), 7.28 (m, 1H), 7.45 (m, 1H), 7.55−7.67 (m, 2H), 7.82 (d, J = 8 Hz, 1H); ^{13}C NMR δ 29.5 (d, J = 11 Hz), 125.8−136.6 (m), 139.2; ^{31}P NMR δ −41.7 (s); MS (ESI) m/z 275.2 (100) [$M^+ + H$]; HRMS (ESI) calcd for $C_{19}H_{16}P$ [$M^+ + H$] 275.0990, found 275.0996.

(*M*,S_P)-4-Methoxy-9-phenyl-9,10-dihydro-9-phosphaphenanthrene ((*M*,S_P)-5c). From (*M*,S_P)-**4c** (0.34 g, 1.10 mmol) following the procedure as for **5b**. Purification on silica gel eluting with toluene afforded a pale yellow oil (0.32 g, 99%): R_f 0.66 (toluene/hexane 4:1); $[\alpha]^{30}_D$ −244.0 (*c* 1.3, $CHCl_3$); ^{1}H NMR δ 2.95 (dd, J = 15, 9 Hz, 1H), 3.21 (dd, J = 15, 4 Hz, 1H), 3.77 (s, 3H), 6.68 (d, J = 7 Hz, 1H), 6.76 (d, J = 8 Hz, 1H), 7.03 (m, 1H), 7.09−7.19 (m, 5H), 7.26 (m, 1H), 7.44 (m, 1H), 7.61 (m, 1H), 8.20 (d, J = 8 Hz, 1H); ^{13}C NMR δ 30.9 (d, J = 11 Hz), 55.8, 110.5, 122.2−136.5 (m), 156.7 (d, J = 4 Hz); ^{31}P NMR δ −39.9 (s); MS (ESI) m/z 305.1 (100) [$M^+ + H$]; HRMS (ESI) calcd for $C_{20}H_{18}OP$ [$M^+ + H$] 305.1095, found 305.1102.

(*M*,S_P)-4-Methoxy-2-methyl-9-phenyl-9,10-dihydro-9-phosphaphenanthrene ((*M*,S_P)-5e). From (*M*,S_P)-**4e** (0.19 g, 0.58 mmol) following the procedure as for **5b**. Purification on silica gel eluting with toluene afforded a pale yellow oil (0.18 g, 99%): R_f 0.68 (toluene/hexane 4:1); $[\alpha]^{30}_D$ −176.1 (*c* 1.7, $CHCl_3$); ^{1}H NMR δ 2.22 (s, 3H), 2.90 (dd, J = 15, 9 Hz, 1H), 3.18 (dd, J = 15, 3 Hz, 1H), 3.74 (s, 3H), 6.52 (s, 1H), 6.58 (s, 1H), 7.10−7.24 (m, 6H), 7.40 (dt, J = 8, 2 Hz, 1H), 7.54 (m, 1H), 8.17 (d, J = 8 Hz, 1H); ^{13}C NMR δ 21.3, 30.8 (d, J = 11 Hz), 55.7, 111.4, 121.9−138.3 (m), 156.7 (d, J = 1 Hz); ^{31}P NMR δ −39.3 (s); MS (ESI) m/z 319.1 (100) [$M^+ + H$]; HRMS (ESI) calcd for $C_{21}H_{20}OP$ [$M^+ + H$] 319.1252, found 319.1254.

(*M*,R_P)-4-Methoxy-9-phenyl-9,10-dihydro-9-phosphaphenanthrene *P*-Oxide ((*M*,R_P)-6c). To a cold solution (0 °C) of (S_P)-**5c** (94 mg, 0.309 mmol) in acetone (3 mL) was added H_2O_2 (50 wt % in H_2O, 90 μL) and the mixture stirred for 3 h at 0 °C. Extraction with EtOAc/H_2O and purification on silica gel eluting with EtOAc (R_f 0.36) afforded a white foam (97 mg, 98%): $[\alpha]^{25}_D$ +37.5 (*c* 1.2, $CHCl_3$); ^{1}H NMR δ 3.36 (dd, J = 15, 14 Hz, 1H), 3.60 (dd, J = 21, 15 Hz, 1H), 3.84 (s, 3H), 6.76 (d, J = 7 Hz, 1H), 6.91 (d, J = 8 Hz, 1H), 7.13−7.61 (m, 8H), 7.96 (m, 1H), 8.23 (m, 1H); ^{13}C NMR δ 34.9 (d, J = 69 Hz), 55.7, 111.6 (d, J = 2 Hz), 123.3, 123.5−131.7 (m), 137.3 (d, J = 7 Hz), 156.8 (d, J = 3 Hz); ^{31}P NMR δ +23.5 (s); MS (ESI) m/z 321.1 (100) [$M^+ + H$]; HRMS (ESI) calcd for $C_{20}H_{18}O_2P$ 321.1044 [$M^+ + H$], found 321.1050.

(*M*,9S_P,10*S*)-4-Methoxy-9-phenyl-10-[(2*S*)-2-phenyl-2-hydroxyethyl]-9,10-dihydro-9-phosphaphenanthrene *P*-Borane. To a cold solution (−78 °C) of (S_P)-**4c** (0.66 g, 2.1 mmol) in THF (20 mL) was added *s*-BuLi (1.3 M in hexane, 1.6 mL). After the solution was stirred at −78 °C for 1 h, a solution of (*R*)-(+)-styrene oxide (0.13 g, 1.1 mmol) in THF (4 mL) was slowly added, and the resulting mixture was allowed to warm to rt and stirred for 24 h before quenching with H_2O. Extraction with CH_2Cl_2/H_2O and purification on silica gel eluting with CH_2Cl_2/hexane 9:1 then CH_2Cl_2 afforded the title compound (0.34 g, 70%): R_f 0.32 (toluene/EtOAc 19:1); $[\alpha]^{25}_D$ +41.4 (*c* 1.2, $CHCl_3$); ^{1}H NMR δ 0.50−1.60 (br m, 3H), 1.76 (m, 1H), 1.85 (br s, 1H), 2.33 (m, 1H), 3.23 (m, 1H), 3.82 (s, 3H), 4.90 (m, 1H), 6.51 (d, J = 7 Hz, 1H), 6.82 (d, J = 8 Hz, 1H), 7.03 (m, 1H), 7.08−7.37 (m, 10H), 7.46 (m, 1H), 7.63 (m, 1H), 8.08 (m, 1H), 8.26 (m, 1H); ^{13}C NMR δ 36.4 (d, J = 36 Hz), 38.5 (d, J = 4 Hz), 55.7, 72.9 (d, J = 9 Hz), 111.4, 121.2−131.7 (m), 134.9 (d, J = 16 Hz), 136.7, 137.2 (d, J = 9 Hz), 143.1, 156.9 (d, J = 1 Hz); ^{31}P NMR δ +9.2 (br m); MS (ESI) m/z 437.2 (100) [$M^+ - H$]; HRMS (ESI) calcd for $C_{28}H_{27}BO_2P$ 437.1842 [$M^+ - H$], found 437.1841.

(*M*,9R_P,10*S*)-4-Methoxy-9-phenyl-10-[(2*S*)-2-phenyl-2-hydroxyethyl]-9,10-dihydro-9-phosphaphenanthrene *P*-Oxide (7). A solution of the previous compound (65 mg, 0.15 mmol) in Et_2NH (1.5 mL) was refluxed for 2 h under the inert atmosphere then allowed to cool to rt and concentrated. Rapid purification of the concentrated residue on silica gel eluting with toluene/EtOAc 4:1 under the inert atmosphere afforded the free phosphine as pale yellow oil (64 mg, 0.15 mmol). To this compound in acetone (2 mL) was added H_2O_2 (50 wt % in H_2O, 50 μL). After stirring at 0 °C for 3 h, the reaction mixture was partitioned between EtOAc and H_2O. Purification on silica gel eluting with EtOAc and recrystallization (*i*-Pr_2O/CH_2Cl_2) afforded yellowish crystals (65 mg, 99%): mp 179−181 °C; R_f 0.60 (EtOAc); $[\alpha]^{25}_D$ +94.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR δ 2.15 (m, 1H), 2.47 (m, 1H), 3.21 (m, 1H), 3.83 (s, 3H), 5.03 (m, 1H), 5.17 (m, 1H), 6.26 (d, J = 8 Hz, 1H), 6.82 (d, J = 8 Hz, 1H), 7.00 (m, 1H), 7.16−7.44 (m, 10H), 7.52 (m, 1H), 7.66 (m, 1H), 8.09−8.21 (m, 2H); ^{13}C NMR δ 39.3 (d, J = 61 Hz), 39.7 (d, J = 10 Hz), 55.7, 71.4 (d, J = 4 Hz), 111.7 (d, J = 1 Hz), 123.0−132.2 (m), 137.0 (d, J = 6 Hz), 137.1 (d, J = 10 Hz), 143.9, 156.8 (d, J = 2 Hz); ^{31}P NMR δ +31.1 (s); MS (ESI) m/z 441.2 (100) [$M^+ + H$]; HRMS (ESI) calcd for $C_{28}H_{26}O_3P$ 441.1620 [$M^+ + H$], found 441.1613.

(S_P)-Spiro[(2,6-dimethoxy-2,5-cyclohexadiene)-1,1′-(3-phenyl-3-phosphindane-*P*-Borane)] ((S_P)-8c). To a cold solution (−20 °C) of (S_P)-**3c** (1.00 g, 2.86 mmol) in THF (15 mL) was added *s*-BuLi (1.3 M in cyclohexane/hexane, 2.20 mL). After the solution was stirred at −30 °C for 1 h, $CuCl_2$ (0.42 g, 3.15 mmol) was added and the reaction mixture allowed to stir for 2 h at −20 °C. The reaction mixture was quenched with H_2O at −20 °C, brought to rt, and then diluted with EtOAc, aq NH_4OH, and brine. The organic phase was washed twice with aq NH_4OH and once with brine. Purification on silica gel eluting with toluene/hexane 3:2 containing 1% of Et_3N afforded a pale yellow oil (0.43 g, 43%): R_f 0.28 (hexane/EtOAc 9:1); $[\alpha]^{25}_D$ +69.3 (*c* 1.2, $CHCl_3$); ^{1}H NMR δ 0.50−1.70 (br m, 3H), 2.66 (dd, J = 15, 12 Hz, 1H), 2.81 (dd, J = 15, 2 Hz, 1H), 2.94 (m, 1H), 3.06 (m, 1H), 3.31 (s, 3H), 3.44 (s, 3H), 4.80 (app t, J = 4 Hz, 1H), 4.87 (app t, J = 4 Hz, 1H), 7.20−7.26 (m, 1H), 7.29−7.47 (m, 6H), 7.69−7.76 (m, 2H); ^{13}C NMR δ 24.2, 34.4 (d, J = 37 Hz), 54.3, 54.6, 56.4 (d, J = 3 Hz), 90.7, 92.1, 124.7 (d, J = 9 Hz), 128.1−133.1 (m), 152.6 (d, J = 14 Hz), 155.0 (d, J = 2 Hz), 155.7 (d, J = 3 Hz); ^{31}P NMR δ +36.6 (br m); MS (ESI) m/z 349.2 (100) [$M^+ - H$]; HRMS (ESI) calcd for $C_{21}H_{23}BO_2P$ 349.1529 [$M^+ - H$], found 349.1535.

(S_P)-Spiro[(2,6-dimethoxy-4-oxo-2,5-cyclohexadiene)-1,1′-(3-phenyl-3-phosphindane *P*-borane)] ((S_P)-8d). From (S_P)-**3d** (0.67 g, 1.76 mmol) following the procedure as for **8c**. Purification on silica gel eluting with CH_2Cl_2 and then hexane/EtOAc (gradient

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elution from 80:20 to 20:80) and recrystallization (CH_2Cl_2/EtOAc) afforded yellow crystals (0.19 g, 30%): mp 188−192 °C; R_f 0.50 (EtOAc); $[\alpha]^{25}_D$ +110.5 (*c* 1.1, $CHCl_3$); ^{1}H NMR δ 0.50−1.70 (br m, 3H), 2.75 (dd, *J* = 15, 12 Hz, 1H), 2.91 (dd, *J* = 15, 1.4 Hz, 1H), 3.45 (s, 3H), 3.64 (s, 3H), 5.54 (d, *J* = 1 Hz, 1H), 5.58 (d, *J* = 1 Hz, 1H), 7.12 (m, 1H), 7.39−7.60 (m, 6H), 7.69 (m, 2H); ^{13}C NMR δ 34.1 (d, *J* = 35 Hz), 55.9, 56.2, 58.0 (d, *J* = 3 Hz), 99.8, 100.7, 123.9 (d, *J* = 8 Hz), 128.4−133.6 (m), 147.8 (d, *J* = 13 Hz), 172.1 (d, *J* = 2 Hz), 173.3 (d, *J* = 3 Hz), 187.6; ^{31}P NMR δ +41.8 (br m); MS (ESI) *m*/*z* 365.1 (25) [M^+ + H]; HRMS (ESI) calcd for $C_{21}H_{23}BO_3P$ [M^+ + H] 365.1478, found 365.1479.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

HPLC chromatograms of **4c**. X-ray crystallographic data for **1b**, **4c**, **7**, and **8d** (CIF). ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(9) (a) The corresponding 2-bromobiaryls were prepared from *o*-bromohalobenzenes either by S_NAr using *O*,*O*′-doubly stabilized 2,6-dialkoxyaryllithiums or by Suzuki cross-coupling. (b) OxazaPB ring-opening with the bulky **g**-Li reagent gave rise to **1g** in low yield (22%) accompanied by (R_P)-*trans*-(*N*-methylamino)(phenyl)(1-phenyl-1-propenyloxy)phosphine *P*-borane (73%) resulting from a competitive attack on the ephedrino moiety. Therefore, reactions with **1g** were not pursued further. For reaction of oxazaPB with bulky aryllithiums, see: Stephan, M.; Šterk, D.; Modec, B.; Mohar, B. *J. Org. Chem.* **2007**, *72*, 8010−8018. (c) The unsymmetrical **h**-Li led to a 1:1 atropodiastereomeric mixture **1h**.

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(11) ^{1}H and ^{13}C NMRs showed rotational isomers for (S_P)-**1b** but its X-ray structure analysis revealed only *P*-atropisomery (or S_a). "*P*" here denotes the stereodescriptor "plus".

(12) (a) The P-stereochemistry was assigned according to the general stereochemical course of the Jugé−Stephan route,[2b,e] X-ray structure analyses of (S_P)-**3a** (derived from (−)-ephedrine),[8e] and **4c** (this work). (b) Ee's of **2a**[8a] and **3a**[8d] were determined by chiral HPLC.

(13) Partial P-OMe hydrolysis arose following an unoptimized workup procedure. For example, (−)-(2′,6′-dimethoxybiphenyl-2-yl)(hydroxy)(phenyl)phosphine *P*-borane (6%) and (−)-(2′,6′-dimethoxybiphenyl-2-yl)(phenyl)phosphine *P*-oxide (10%) ensuing from its slow BH_3 loss were formed with compound **2c**. (−)-(Hydroxy)(phenyl)(2′,4′,6′-trimethoxybiphenyl-2-yl)phosphine *P*-borane (10%) formed with **2d**. (−)-(2′,6′-Diisopropoxybiphenyl-2-yl)(phenyl)phosphine *P*-oxide (45%) formed with **2f**.

(14) (a) ^{1}H and ^{13}C NMRs showed a single atropisomer for **4**, **5**, and **6**. (b) Ee (>99.9%) of **4c** was determined by chiral HPLC.

(15) (a) P-α-Alkylation at the bridge-junction occurred with high *trans*-stereoselectivity, and the results of an ongoing broader study will be presented elsewhere. (b) Due to CIP stereochemistry rules, (*R*)-styrene oxide ring-opening at the terminal position leads in this case to reversal of configuration at the resulting C_α-OH.

(16) Phosphine-*P*-borane deprotection with Et_2NH or phosphine P-oxidation with H_2O_2 proceeds with retention of *P*-stereochemistry.[2a] Because of CIP stereochemistry rules, the switch from "BH_3" (small) to "O" (big) reverses the *P*-configuration.
(17) (a) On this basis, only compounds **4b** and **5b** of the prepared phosphacyclic series would have *P*-atropisomery (CIP rules). (b) The biaryl dihedral angles found in (M,S_P)-**4c** are 33.6 (1)° and 34.8(1)° and in (M,9R_P,10S)-**7** is 33.52(8)°.
(18) No cyclization took place when (S_P)-**3c** was left for 24 h in presence of anhydrous $CuCl_2$ in THF at rt.
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