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 everincreasing 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 (ox-azaPB).^{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 Cumediated 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 CuCl₂-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 ¹H and ³¹P 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 (2R,4S,5R)-(+)-oxazaPB ring-

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



"Reagents and conditions: (i) s-BuLi, THF, -30 °C, 1 h, then CuCl₂, -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, H₂SO₄, 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) Et₂NH, 55–60 °C (93–99% yield); (vii) 50% aq H₂O₂, Me₂CO, 0 °C (98% yield).

Spectroscopic data (¹H, ¹³C, and ³¹P 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 4methoxy-9-phenyl-9,10-dihydro-9-phosphaphenanthrene-Pborane 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 ³¹P 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 BH₃ 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}



"Reagents and conditions: (i) s-BuLi, THF, -30 °C, then (R)-styrene oxide (70% yield); (ii) Et₂NH, 55-60 °C; (iii) 50% aq H₂O₂, Me₂CO, 0 °C (99% yield for two steps).

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 Et₂NH (55–60 °C) (step vi) furnished the corresponding homochiral dibenzophosphorinanes **5b**,c,e in 93–99% yield (³¹P NMR $\delta \sim$ –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 CuCl₂ 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·BH₃") (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, ¹H and ³¹P NMRs revealed the formation of a benzophospholane-*P*-borane **8b** (³¹P NMR $\delta \sim$ +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 CH₃ 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 ($\mathbb{R}'' \neq \mathbb{H}$), and in its absence ($\mathbb{R}'' = \mathbb{H}$) 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*-CH₂ 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



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

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.

EXPERIMENTAL SECTION

General Methods. All reactions were conducted under an inert atmosphere using anhydrous solvents. ¹H (300 MHz, internal Me₄Si), ¹³C (75 MHz, internal CDCl₃; J_{C-P} is indicated), and ³¹P NMR (120 MHz, external 85% H₃PO₄) were recorded for solutions in CDCl₃. 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-dimethoxybiphenyl, 2'-bromo-2,6-dimethoxybiphenyl, and (*R*)-styrene oxide (ee \geq 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-trimethoxybiphenyl²¹ 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

mmol) was slowly added, and the mixture was allowed to stir overnight at rt. After H₂O quenching and extraction with CH₂Cl₂, the crude was purified by recrystallization (*i*-Pr₂O/CH₂Cl₂) affording off-white crystals (11.50 g, 52%): mp 143–145 °C; R_f 0.49 (toluene/hexane 7:3); ¹H 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); ¹³C 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 C₁₅H₁₆⁷⁹BrO₂ [M⁺ + H] 307.0334, found 307.0345.

2'-Bromo-2,6-dimethylbiphenyl. To a solution of 1-bromo-2iodobenzene (8.49 g, 30.0 mmol) and Pd(PPh₃)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 Na₂CO₃ (19.08 g in 80 mL H₂O). The resulting mixture was stirred at 85 °C for 6 days. After toluene/H₂O 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; ¹H 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); ¹³C 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), K₂CO₃ (4.15 g, 30.0 mmol), and Pd(PPh_3)_4 (0.35 g, 0.3 mmol) in EtOH (1 mL)/ H₂O (4 mL)/dioxane (10 mL) was added a solution of 2-methoxy-1naphthaleneboronic 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 (CH2Cl2/hexane) afforded white crystals (1.65 g, 50%): mp 119-121 °C; R_f 0.36 (hexane/EtOAc 19:1); ¹H 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); ¹³C 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 C₁₇H₁₃⁷⁹BrO [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 Et₂O (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. CH₂Cl₂/H₂O 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; [*α*]²⁵_D +52.7 (*c* 1.2, CHCl₃) (*S*_p-enantiomer: [*α*]²⁰_D +64.9 (*c* 0.297, CH₂Cl₂)^{8a}); ¹H 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)-[(1R,2S)-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; $[\alpha]_{D}^{30}$ +80.9 (c 1.2, CHCl₃); ¹H 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, I = 8 Hz, 0.6H), 6.72-6.84 (m, 1.4H), 7.08-7.55 (m, 15H), 7.74 (m, 1H); ¹³C 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); ³¹P 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-2,6dimethoxybiphenyl (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; [α]³⁰_D +14.7 (*c* 1.0, CHCl₃); ¹H 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: ¹H 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 **Ia**. 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; [*α*]²⁵_D +11.9 (*c* 1.1, CHCl₃); ¹H 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); ¹³C 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; ³¹P NMR δ +71.7 (br m); MS (ESI) *m*/z 528.2 (38) [M⁺ – H]; HRMS (ESI) calcd for C₃₁H₃₆BNO₄P 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; [*α*]²⁵_D +16.4 (*c* 1.0, CHCl₃); ¹H 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); ¹³C 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; ³¹P NMR δ +72.0 (br m); MS (ESI) *m*/*z* 514.3 (42) [M⁺ + H]; HRMS (ESI) calcd for C₃₁H₃₈BNO₃P [M⁺ + H] 514.2682, found 514.2689.

 $(S_{P})-(2',6'-Diisopropoxybiphenyl-2-yl)[(1R,2S)-N-ephedrino]-$ (phenyl)phosphine P-Borane ((Sp)-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, CHCl₃); ¹H 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); ¹³C 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; ³¹P NMR δ +71.8 (br m); MS (ESI) m/z 556.3 (18) [M⁺ + H]; HRMS (ESI) calcd for C₃₄H₄₄BNO₃P [M⁺ + H] 556.3152, found 556.3142.

 $(S_p)-(2',6'-Dimethylbiphenyl-2-yl)[(1R,2S)-N-ephedrino]-(phenyl)phosphine$ *P* $-Borane ((<math>S_p$)-1g). From 2'-bromo-2,6-dimethylbiphenyl following procedure as for 1a. The organolithium was prepared as follows: to a cold solution ($-78 \,^{\circ}$ 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 $-78 \,^{\circ}$ C for 30 min, the temperature was gradually raised to $-50 \,^{\circ}$ C to ensure complete lithiation. Purification on silica gel eluting with

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%): [α]³⁰_D -7.6 (*c* 1.0, CHCl₃); ¹H 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); ¹³C 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); ³¹P NMR δ +72.2 (br m); MS (ESI) *m*/*z* 468.3 (100) [M⁺ + H]; HRMS (ESI) calcd for C₃₀H₃₆BNOP [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); $[α]^{25}_{\rm D}$ +63.6 (*c* 1.2, CHCl₃) ((*S*_p)-enantiomer, ^{9b} $[α]^{25}_{\rm D}$ –69.6 (*c* 1.0, CHCl₃)); ¹H 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); ³¹P NMR δ +105.3 (br m). NMR data were consistent with those reported in the literature.^{9b}

(S_P)-[(1R,2S)-N-Ephedrino][2-(2-methoxynaphth-1-yl)phenyl](phenyl)phosphine P-Borane ((S_P)-1h). From 1-(2bromophenyl)-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 ¹H NMR: R_f 0.52 (toluene/EtOAc 9:1); $[\alpha]^{25}_{D}$ +16.0 (c 1.1, CHCl₃); ¹H 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; ³¹P NMR δ +72.0 (br m); MS (ESI) m/z 520.3 (100) [M⁺ + H]; HRMS (ESI) calcd for C₃₃H₃₆BNO₂P [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 H₂SO₄ (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 CH₂Cl₂/ H₂O and purification on silica gel eluting with toluene/hexane 9:1 then toluene (R_f 0.76) and recrystallization (CH₂Cl₂/hexane) afforded white crystals (0.87 g, 71%): mp 119–121 °C; [α]²⁵_D –21.0 (*c* 1.2, CHCl₃) ((S_p)-enantiomer,^{8a} [α]²⁰_D +17.4 (*c* 0.945, CH₂Cl₂), >99% ee (HPLC)); ¹H 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); ³¹P 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, CHCl₃); ¹H 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); ¹³C 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; ³¹P NMR δ +109.1 (br m); MS (ESI) *m*/*z* 335.1 (100) [M⁺ – H]; HRMS (ESI) calcd for C₂₀H₂₁BO₂P [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 (CH₂Cl₂/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* $-Pr_2O/CH_2Cl_2) afforded <math>(-)-(2',6'-dimethoxybiphenyl-2-yl)(phenyl)-phosphine$ *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, CHCl₃) (R_p -enantiomer,^{10b} $[\alpha]_D$ +28.4 (c 0.9, CH₂Cl₂)); ¹H 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); ³¹P 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, CHCl₃); ¹H 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); ¹³C 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; ³¹P NMR δ +93.6 (br m); MS (ESI) *m/z* 351.1 (100) [M⁺ - H]; HRMS (ESI) calcd for C₂₀H₂₁BO₃P [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); $[\alpha]^{30}{}_{\rm D}$ –5.5 (*c* 1.3, CHCl₃); ¹H 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); ¹³C 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; ³¹P NMR δ +20.1 (s); MS (ESI) *m/z* 339.1 (100) [M⁺ + H]; HRMS (ESI) calcd for C₂₀H₂₀O₃P [M⁺ + H] 339.1150, found 339.1153.

Methyl $(R_{\rm P})$ -(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%). ($R_{\rm P}$)-2d: mp 136–138 °C; $R_{\rm f}$ 0.25 (toluene); $[\alpha]^{25}_{\rm D}$ +46.6 (c 1.1, CHCl₂); ¹H 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; ³¹P NMR δ +107.8 (br m); MS (ESI) m/z 395.2 (100) [M⁺ – H]; HRMS (ESI) calcd for C₂₂H₂₅BO₄P [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, CHCl₃); ¹H 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); ¹³C 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; ³¹P NMR δ +93.9 (br m); MS (ESI) *m*/z 381.1 (100) [M⁺ – H]; HRMS (ESI) calcd for C₂₁H₂₃BO₄P [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 (CH₂Cl₂/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, CHCl₃); ¹H 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); ¹³C 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; ³¹P NMR δ +107.7 (br m); MS (ESI) *m/z* 379.2 (100) [M⁺ – H]; HRMS (ESI) calcd for C₂₂H₂₅BO₃P [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, CHCl₃); ¹H 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); ¹³C NMR $\delta = 21.6, 21.9, 22.2, 22.3, 53.8$ (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; ³¹P NMR $\delta + 109.3$ (br m); MS (ESI) m/z 421.2 (100) [M⁺ – H]; HRMS (ESI) calcd for C₂₅H₃₁BO₃P [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); $[\alpha]^{25}{}_{\rm D}$ -15.7 (*c* 1.1, CHCl₃); ¹H 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); ¹³C 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; ³¹P NMR δ +19.4 (s); MS (ESI) *m*/*z* 395.2 (100) [M⁺ + H]; HRMS (ESI) calcd for C₂₄H₂₈O₃P [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 Et₂O, 4 mL, 1.5 equiv) and the resulting mixture allowed to warm to rt, stirred overnight, and then quenched with H₂O. Extraction with CH₂Cl₂ 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/ CH₂Cl₂ afforded the title compound²² as white crystals (1.02 g, 81%): mp 120–122 °C; [*α*]²⁵_D +50.7 (*c* 1.1, CHCl₃) ((*S*_p)-enantiomer,^{8c} [*α*]²⁵_D +54.8 (*c* 0.82, CHCl₃); (*R*_p)-enantiomer,^{8d} [*α*]_D²⁰ -42.1 (*c* 1, CHCl₃), 99% ee (HPLC)); ¹H 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); ¹³C 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); ³¹P 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 Et₂O, 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; [α]³⁰_D +34.3 (*c* 1.3, CHCl₃); ¹H 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); ¹³C 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; ³¹P NMR δ +12.8 (br m); MS (ESI) *m/z* 319.1 (100) [M⁺ – H]; HRMS (ESI) calcd for C₂₀H₂₁BOP [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, CHCl₃); ¹H 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); ³¹P 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, CHCl₃); ¹H 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); ¹³C 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; ³¹P NMR δ +11.2 (br m); MS (ESI) *m*/*z* 379.2 (100) [M⁺ – H]; HRMS (ESI) calcd for C₂₂H₂₅BO₃P [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, CHCl₃); ¹H 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); ¹³C 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; ³¹P NMR δ +11.4 (br m); MS (ESI) m/z 363.2 (100) [M⁺ – H]; HRMS (ESI) calcd for C₂₂H₂₅BO₂P [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, CHCl₃); ¹H 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); ¹³C 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); ³¹P NMR δ +12.8 (br m); MS (ESI) *m*/*z* 405.2 (100) [M⁺ – H]; HRMS (ESI) calcd for C₂₅H₃₁BO₂P [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 μ L) or MeLi (1.6 M in Et₂O, 250 μ L), and the resulting mixture was allowed to warm to rt overnight under stirring. Extraction with CH₂Cl₂/H₂O, purification on silica gel eluting with toluene/hexane 9:1 then toluene followed by recrystallization (CH₂Cl₂/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 Et₂O, 4.2 mL), and the resulting mixture was allowed to warm to rt overnight under stirring. Extraction with CH₂Cl₂/H₂O, purification on silica gel eluting with toluene/hexane 7:3 and then toluene, and recrystallization (CH₂Cl₂/hexane) afforded white crystals (0.35 g, 73%): mp 204–207 °C; *R*_f 0.51 (toluene/hexane 4:1); [*α*]²⁵_D +78.5 (*c* 1.0, CHCl₃); ¹H 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); ¹³C NMR δ = 29.3 (d, *J* = 38 Hz), 123.1–134.6 (m), 139.7; ³¹P NMR δ –1.9 (br m); MS (ESI) *m*/*z* 287.1 (100) [M⁺ – H]; HRMS (ESI) calcd for C₁₉H₁₇BP [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: [α]²⁵_D -14.3 (*c* 1.1, CHCl₃); 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 CH₂Cl₂/hexane in enantiopure form: mp 138–140 °C; [α]²⁵_D -14.6 (*c* 1.1, CHCl₃); >99.9% ee (HPLC); ¹H 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); ¹³C 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); ³¹P NMR δ –0.2 (br m);

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; [α]²⁵_D +34.3 (*c* 1.0, CHCl₃); ¹H 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); ¹³C 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; ³¹P NMR δ –1.3 (br m); MS (ESI) *m/z* 347.1 (100) [M⁺ – H]; HRMS (ESI) calcd for C₂₁H₂₁BO₂P [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 (CH₂Cl₂/hexane) afforded white crystals (0.49 g, 77%): mp 140–142 °C; [α]²⁵_D +10.9 (*c* 1.1, CHCl₃); ¹H 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); ¹³C 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); ³¹P NMR δ –0.4 (br m); MS (ESI) *m*/*z* 331.1 (100) [M⁺ – H]; HRMS (ESI) calcd for C₂₁H₂₁BOP [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 Et₂NH (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, CHCl₃); ¹H 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); ¹³C NMR δ 29.5 (d, *J* = 11 Hz), 125.8–136.6 (m), 139.2; ³¹P NMR δ –41.7 (s); MS (ESI) *m/z* 275.2 (100) [M⁺ + H]; HRMS (ESI) calcd for C₁₉H₁₆P [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, CHCl₃); ¹H 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, SH), 7.26 (m, 1H), 7.44 (m, 1H), 7.61 (m, 1H), 8.20 (d, *J* = 8 Hz, 1H); ¹³C NMR δ 30.9 (d, *J* = 11 Hz), 55.8, 110.5, 122.2–136.5 (m), 156.7 (d, *J* = 4 Hz); ³¹P NMR δ –39.9 (s); MS (ESI) *m*/z 305.1 (100) [M⁺ + H]; HRMS (ESI) calcd for C₂₀H₁₈OP [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, CHCl₃); ¹H 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); ¹³C 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); ³¹P NMR δ –39.3 (s); MS (ESI) *m*/z 319.1 (100) [M⁺ + H]; HRMS (ESI) calcd for C₂₁H₂₀OP [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 H₂O₂ (50 wt % in H₂O, 90 μ L) and the mixture stirred for 3 h at 0 °C. Extraction with EtOAc/H₂O and purification on silica gel eluting with EtOAc (*R*_f 0.36) afforded a white foam (97 mg, 98%): [α]²⁵_D +37.5 (*c* 1.2, CHCl₃); ¹H 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); ¹³C 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); ³¹P NMR δ +23.5 (s); MS (ESI) m/z 321.1 (100) [M⁺ + H]; HRMS (ESI) calcd for C₂₀H₁₈O₂P 321.1044 [M⁺ + H], found 321.1050.

(*M*,95_P,105)-4-Methoxy-9-phenyl-10-[(25)-2-phenyl-2-hydroxyethyl]-9,10-dihydro-9-phosphaphenanthrene P-Borane. To a cold solution (–78 $^{\circ}\text{C})$ 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 H2O. Extraction with CH2Cl2/H2O and purification on silica gel eluting with CH₂Cl₂/hexane 9:1 then CH₂Cl₂ afforded the title compound (0.34 g, 70%): R_f 0.32 (toluene/EtOAc 19:1); $[\alpha]^{25}_{D}$ +41.4 (c 1.2, CHCl₃); ¹H 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); ¹³C 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); ³¹P NMR δ +9.2 (br m); MS (ESI) m/z 437.2 (100) [M⁺ – H]; HRMS (ESI) calcd for $C_{28}H_{27}BO_{2}P$ 437.1842 [M⁺ – H], found 437.1841.

(*M*,9*R*_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 Et₂NH (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_2 , 50 μ L). After stirring at 0 °C for 3 h, the reaction mixture was partitioned between EtOAc and H₂O. Purification on silica gel eluting with EtOAc and recrystallization (i-Pr₂O/CH₂Cl₂) afforded yellowish crystals (65 mg, 99%): mp 179–181 °C; $R_f 0.60$ (EtOAc); $[\alpha]^{25}_{D}$ +94.5 (c 1.0, CHCl₃); ¹H 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); ³¹P NMR δ +31.1 (s); MS (ESI) m/z 441.2 (100) [M⁺ + H]; HRMS (ESI) calcd for $C_{28}H_{26}O_{3}P$ 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 $-30\ ^\circ C$ 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 NH4OH, and brine. The organic phase was washed twice with aq NH₄OH and once with brine. Purification on silica gel eluting with toluene/hexane 3:2 containing 1% of Et₃N 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, CHCl₃); ¹H 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); ¹³C 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); ³¹P 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 CH₂Cl₂ and then hexane/EtOAc (gradient

elution from 80:20 to 20:80) and recrystallization (CH₂Cl₂/EtOAc) afforded yellow crystals (0.19 g, 30%): mp 188–192 °C; R_f 0.50 (EtOAc); [α]²⁵_D +110.5 (*c* 1.1, CHCl₃); ¹H 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); ¹³C 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; ³¹P NMR δ +41.8 (br m); MS (ESI) *m/z* 365.1 (25) [M⁺ + H]; HRMS (ESI) calcd for C₂₁H₂₃BO₃P [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). ¹H and ¹³C 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 2,6dialkoxyaryllithiums or by Suzuki cross-coupling. (b) OxazaPB ringopening with the bulky g-Li reagent gave rise to 1g in low yield (22%) accompanied by (R_p)-*trans*-(*N*-methylamino)(phenyl)(1-phenyl-1propenyloxy)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) ¹H and ¹³C 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".

denotes the stereodescriptor pius . (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 BH₃ loss were formed with compound**2c**. <math>(-)-(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) ¹H and ¹³C 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_a-OH.

(16) Phosphine-*P*-borane deprotection with Et_2NH or phosphine Poxidation with H_2O_2 proceeds with retention of *P*-stereochemistry.^{2a} Because of CIP stereochemistry rules, the switch from "BH₃" (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 CuCl₂ in THF at rt.

(19) For *N*-Me-*N*-Bn-anilines, a 5-*exo-trig* radical carbocyclization followed by a ring-strain transposition to a 6-membered ring has been proposed. For this, see: Roman, D. S.; Takahashi, Y.; Charette, A. B. *Org. Lett.* **2011**, *13*, 3242–3245.

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