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Stereoselective Synthesis of P-Chirogenic Dibenzophosphole–Boranes via Aryne Intermediates

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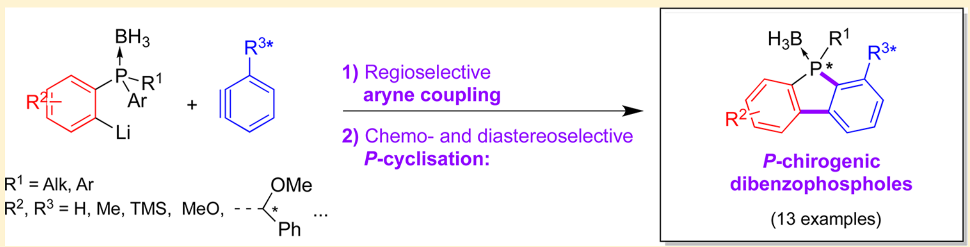
Supporting Information



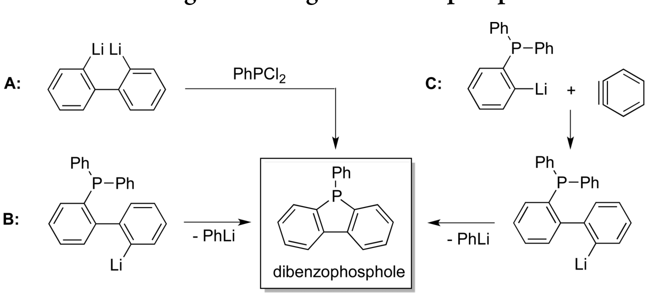
ABSTRACT: A new aryne-mediated tandem cross-coupling/P-cyclization sequence starting from tertiary phosphine–boranes and 1,2-dibromobenzenes is reported. P-chirogenic dibenzophospholes become accessible in a regio-, chemo-, and diastereoselective way.

INTRODUCTION

Dibenzophospholyl derivatives are useful P(III) subunits for the development of catalytic processes requiring achiral[1−4] or chiral σ-donor/π-acceptor ligands.[2,5−10] Although dibenzophosphole derivatives have found some applications in synthetic organic chemistry,[11,12] they have recently been shown, in the free or oxidized state, as promising outlets in material science, via the elaboration of liquid crystals[13] or optoelectronic devices.[14,15] Until today, chiral phospholes or derivatives have rarely been described in the literature, and their application in asymmetric catalysis is still scarce.[16−22]

So far, dibenzophospholes have only been prepared in racemic form by electrophilic trapping of 2,2′-dilithiobiphenyl with dichlorophenylphosphine (Scheme 1, pathway A)[10,14,23−25] or via intramolecular cyclization of lithiomonophosphines (Scheme 1, pathway B).[26−28] In the latter case, the

Scheme 1. Strategies Leading to Dibenzophospholes



2-biphenyllithium attacks in an S_N2-type way the PPh_2 substituent at the 2′-position with elimination of PhLi. Both approaches required the preliminary synthesis of functionalized biaryl subunits.[23,24]

Our group recently reported on a new, transition-metal-free aryl–aryl coupling (aryne coupling) which allows the construction of a wide range of di-, tri-, and tetrasubstituted biaryls.[29−33] The key step of this protocol is the nucleophilic addition of an aryllithium on a transient aryne generated from a 1,2-dibromobenzene derivative. In situ transfer of bromine from the remaining 1,2-dibromobenzene to the 2-biaryllithium intermediate then provides the desired 2-bromobiaryl (Scheme 2).

In both cases (i.e., the synthesis of dibenzophospholes via 2-lithio-2′-diphenylphosphinobiphenyl and aryne coupling), 2-lithiobiaryl intermediates are involved. Therefore, we envisioned combining both methodologies as a means to constructing the aryl–aryl bond and five-membered ring of the dibenzophosphole in one pot (Scheme 1, pathway C). In this way, so far unknown, dissymmetrically substituted and thus P-chirogenic phospholes possessing different steric and electronic effects should become accessible.

RESULTS AND DISCUSSION

In a model reaction, 2-bromophenylphosphine–borane (**1a**)[34,35] was submitted to a bromine/lithium exchange with

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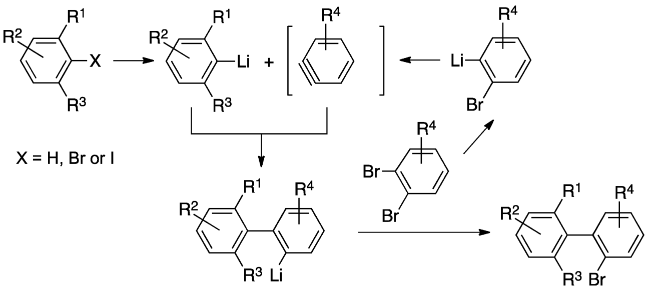
Scheme 2. Aryne Coupling Methodology



tert-butyllithium (2 equiv) at −78 °C, followed by the addition of 1,2-dibromobenzene at −35 °C. The dibenzophosphole−borane **3a** was obtained in a yield of 60% (Scheme 3), and its chemical structure was definitively assigned by single-crystal X-ray analysis.[36]

Next, we applied this coupling protocol to the synthesis of a wide range of dibenzophosphole−borane complexes. As depicted in Tables 1−3, various *o*-bromophenylphosphine−borane complexes (**1a**−**f**), obtained as for **1a** via a new aryne-mediated approach,[34,35] have been combined with different aryne precursors (**2b**−**j**). The later became accessible via efficient protocols our laboratory has recently developed, involving polyhalogenated intermediates.[29] Following this strategy, 1,2-dibromobenzenes **2g**, **2h**,**i** and **2j** have been synthesized by O protection of the corresponding benzyl alcohols **4**−**6**, respectively, as shown in Scheme 4. The *R* enantiomerically enriched alcohol **5** has been prepared by asymmetric reduction of (2,3-dibromophenyl)phenylmethanone (**7**) according to the procedure developed by Touet et al.,[37,38] whereas the racemic benzyl alcohols **4**−**6** have been prepared by regioselective magnesiation of 1,2-dibromo-3-iodobenzene (**8**) followed by electrophilic trapping with hexanal, benzaldehyde, and pivalaldehyde, respectively.

Both parts of the dibenzophosphole moiety can be easily modified, starting either from functionalized *o*-bromophenylphosphine−boranes or from functionalized 1,2-dibromobenzenes (Scheme 5).

Dibenzophospholes **3b**−**g** were isolated in moderate yields (from 34% to 60%) due to the concomitant formation in varying proportions of the P starting material **1** (resulting from direct bromine/lithium exchange between the intermediate aryllithium and the 1,2-dibromobenzene) and its deshalogenated derivative. Note that (a) the perfect regioselectivity of the reaction starting from dissymmetrically substituted 1,2-dibromobenzenes (Table 1, entries 4−6) was confirmed by single-crystal X-ray analysis in the case of dibenzophosphole **3f**[36] and (b) the free dibenzophospholes can be readily isolated by decomplexation of their borane complex.[39]

In the next step, we decided to study the leaving group ability of the phosphorus substituents in the cyclization step. As outlined in Scheme 1, the S_N2-type mechanism affords PhLi elimination. We therefore decided to study the influence of the relative basicity of the eliminated organolithium moiety on the outcome of the reaction. First, mixed alkyl/phenyl *o*-bromophenylphosphine−boranes were employed. In all cases, only PhLi has been eliminated. Compounds **1c**,**d**, bearing respectively *tert*-butyl and cyclohexyl groups, were successfully converted into dibenzophospholes **3h**,**i** with chemoselective cleavage of the P−Ph bond (Table 2, entries 1 and 2).

Then, we were pleased to notice that such a chemoselectivity can also be obtained when two different aryl groups with different relative basicities were used, as shown with **1e**. The dibenzophosphole−borane **3c** was obtained from the selective departure of *o*-anisyllithium (Table 2, entry 3).

In fact, a OMe group stabilizes an aryllithium carbanion at the ortho position by 2.8 kcal/mol.[40] Thus, the formation of *o*-AnLi is thermodynamically more favorable than the release of PhLi. In contrast, when two alkyl groups are present at phosphorus, no intramolecular cyclization takes place and only the aryne cross-coupling product is obtained, as shown for **9** (Table 2, entry 4). Crystals of **9** allowed confirming its structure by single-crystal X-ray analysis.[36] In this case, the elimination of an alkyllithium is thermodynamically unfavorable.

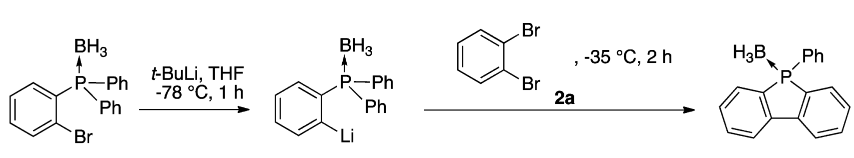
We tried then to exploit this chemoselective cyclization in the synthesis of enantiomerically pure P-chirogenic dibenzophospholes using enantiomerically pure 2-bromophenylphosphine−borane ((*S*)-**1e**).[34] Unfortunately, only racemic **3c** was obtained by reaction with the 1,2-dibromobenzene species **2c**. This result indicates that the intramolecular cyclization is probably not a concerted mechanism, since this would imply the formation of enantiomerically pure dibenzophosphole **3c**. Thus, we decided to introduce a chiral auxiliary at the 1,2-dibromobenzene part.

First, a pentyl-substituted benzyl methyl ether in its racemic form has been chosen. A diastereomeric excess of 15% has been obtained for **3j** (Table 3, entry 1). Next, the steric hindrance around the benzyl methyl ether part has been increased by changing from the pentyl group in **3j** to a phenyl group in **3k**, which led to an enhanced de value of 48% (Table 3, entry 2). Crystals of the major diastereoisomer were grown which allowed for the determination of the X-ray structure and the ORTEP plot, the latter of which is depicted in Figure 1.

Increasing the coordinating properties of the ether part by changing from a methoxy to a methoxymethyl (MOM) group lead to an increased de of 70% in **3l** (Table 3, entry 3, and Figure 2). Finally, by combining both steric hindrance and chelation properties, we exclusively detected one diastereoisomer of **3m** (de >96%, Table 3, entry 4, and Figure 3).

These results clearly indicate that (a) the nucleophilic reaction of the aryllithium moiety occurs regioselectively on the sterically less hindered side of the aryne, in accordance with our previous works on model substrates,[30] (b) the intramolecular cyclization at phosphorus is perfectly chemoselective (Table 2), and (c) the chiral auxiliaries in ortho positions control the diastereoselectivity of the cyclization (Table 3). We therefore

Scheme 3. Synthesis of Dibenzophospholes via Aryne Coupling



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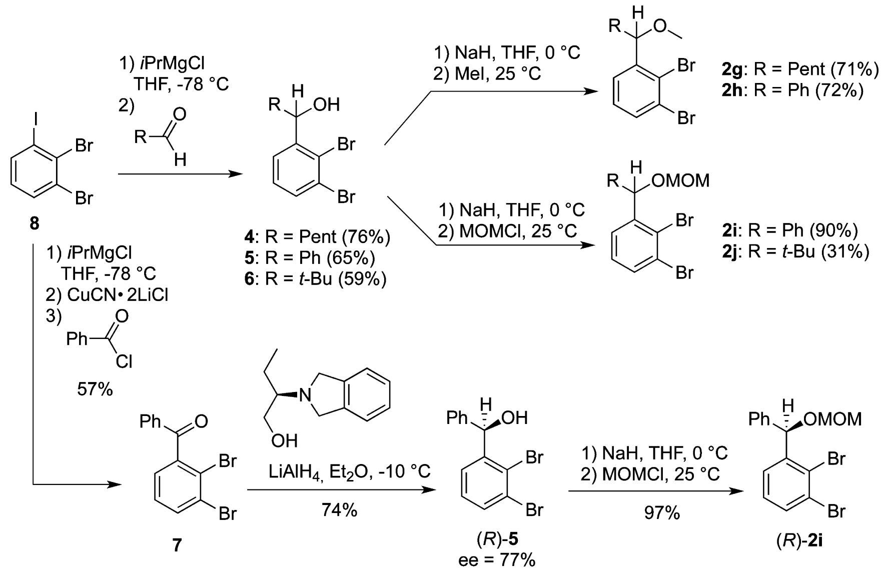
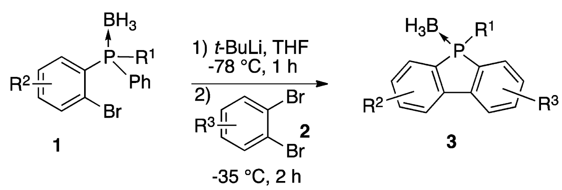
Scheme 4. Synthesis of Functionalized 1,2-Dibromobenzenes



Scheme 5. Access to Dibenzophospholes



tentatively postulate a mechanism which implies attack of the chelated biphenylyllithium species **I** at phosphorus, affording the intermediate lithium phosphoranide **II**, a species belonging to a class of compounds discovered by Hellwinkel.[41,42] Elimination of PhLi leads then to the final phospholes **III** (Scheme 6).

Next we decided to perform this reaction with an enantiomerically enriched 1,2-dibromobenzene. As a proof of concept, we were pleased to see that the reaction performed with the enantiomerically enriched 1,2-dibromobenzene (*R*)-**2i** (ee 77%) afforded the dibenzophosphole−borane (*R*,R_p)-**3l** with a de of 72%, previously in racemic form (entry 3) and now in 78% ee (entry 5). Crystallization from acetonitrile at −20 °C gave the enantiomerically pure dibenzophosphole−borane **3l**, and its X-ray analysis revealed the *R*,R_p configuration (Figure 4).

■ CONCLUSION

In conclusion, we reported the first chemo-, regio-, and diastereoselective synthesis of P-chirogenic dibenzophosphole-boranes based on a transition-metal-free aryne cross-coupling methodology. In this way, the simultaneous creation of the aryl−aryl bond and the five-membered ring of the dibenzophosphole moiety were realized. Preliminary tests in catalytic hydroformylation are very encouraging and will be reported in due course.

■ EXPERIMENTAL SECTION

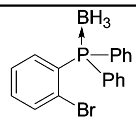
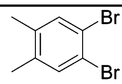
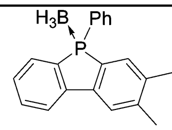
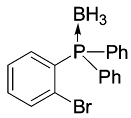
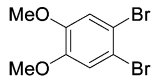
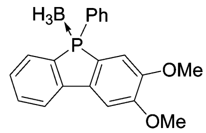
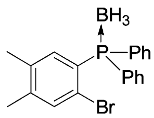
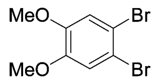
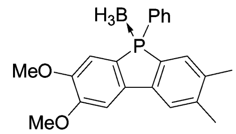
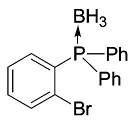
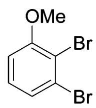
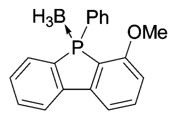
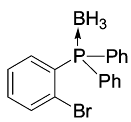
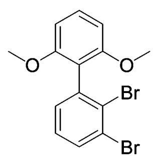
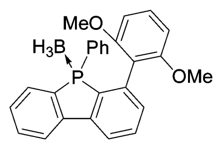
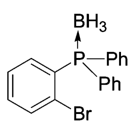
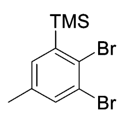
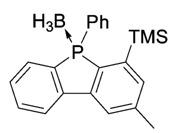
General Considerations. Starting materials, if commercial, were purchased and used as such, provided that adequate checks (melting ranges, refractive indices, and gas chromatography) had confirmed the claimed purity. When known compounds had to be prepared according to literature procedures, pertinent references are given. Air- and moisture-sensitive materials were stored in Schlenk tubes. They were protected by and handled under an atmosphere of argon, using appropriate glassware. Tetrahydrofuran and diethyl ether were dried by distillation from sodium using benzophenone as indicator. Column chromatography was carried out on a column packed with silica gel 60N spherical neutral size 63−210 μm. ^{1}H and (^{1}H decoupled) ^{13}C and ^{31}P nuclear magnetic resonance (NMR) spectra were recorded at 400 or 300 MHz and 101 or 75 and 162 MHz, respectively. Chemical shifts are reported in δ units (parts per million, ppm) and were measured relative to the signals for residual chloroform (7.26 ppm for ^{1}H NMR and 77.00 ppm for ^{13}C NMR). Coupling constants *J* are given in Hz. Coupling patterns are abbreviated as s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sp (septuplet), td (triplet of doublets), m (multiplet), app s (apparent singlet), and br (broad). MS experiments were performed with a TOF spectrometer equipped with an orthogonal electrospray (ESI) interface. Calibration was performed using a solution of 10 mM sodium formate. Sample solutions were introduced into the spectrometer source with a syringe pump with a flow rate of 5 μL min^{-1}. Values are given in *m*/*z* units.

Synthesis of the Starting Materials. 1,2-Dibromobenzenes **2a**−**c** are commercially available. 2-Bromophenylphosphine boranes **1a**−**f** as well as 1,2-dibromobenzenes **2d**−**f**, **4**, **5** (in racemic mixture), **7**, and **8** were synthesized as previously reported in the literature.[29,35]

*1,2-Dibromo-3-(1-methoxyhexyl)benzene (**2g**).* To a suspension of NaH (0.63 g, 26.4 mmol) in anhydrous THF (9.00 mL) was added dropwise, at 0 °C, a solution of 1-(2,3-dibromophenyl)hexan-1-ol (**4**; 2.96 g, 8.81 mmol) in anhydrous THF (18.0 mL). The reaction mixture was stirred at 25 °C for 1 h, and MeI (2.20 mL, 35.3 mmol) was then added. After 18 h of stirring at 25 °C, the reaction mixture was carefully hydrolyzed with water (100 mL) and was extracted with Et_2O (3 × 75 mL). The combined organic layers were dried over Na_2SO_4, and solvents were removed under reduced pressure. Purification of the crude product by column chromatography (cyclohexane/CH_2Cl_2 9/1) provided compound **2g** (2.18 g) as a colorless oil. Yield: 71%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.88 (m, 3 H), 1.21−1.72 (m, 8 H), 3.23 (s, 3 H), 4.60 (dd, 1 H, *J* = 7.9, 4.0 Hz), 7.21 (t, 1 H, *J* = 7.8 Hz), 7.37 (dd, 1 H, *J* = 7.8, 1.6 Hz), 7.55 (dd, 1 H, *J* = 7.8, 1.6 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.0, 22.6, 25.4, 31.7, 37.0, 57.2, 83.6, 125.1, 125.8, 125.9, 128.6, 132.4, 145.2. HRMS (ESI^+): calcd for $C_{13}H_{18}{}^{79}Br_2O$ $[M]^+$ 347.9724, found 347.9769; calcd for $C_{13}H_{18}{}^{79}Br^{81}BrO$ $[M]^+$ 349.9704, found 349.9749.

*1,2-Dibromo-3-(methoxy(phenyl)methyl)benzene (**2h**).* To a suspension of NaH (0.69 g, 28.7 mmol) in anhydrous THF (10.0

Table 1. Access to Dibenzophospholes via Aryne Coupling

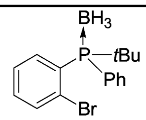
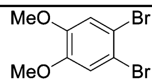
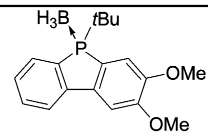
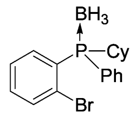
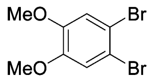
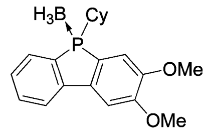
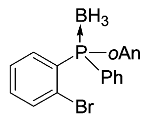
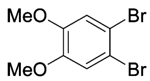
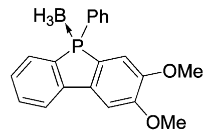
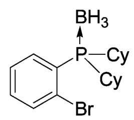
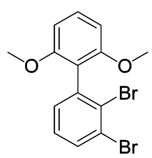
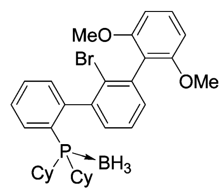
Entry	1	2	Product	Yield
1	 **1a**	 **2b**	 **3b**	34%
2	 **1a**	 **2c**	 **3c**	60%
3	 **1b**	 **2c**	 **3d**	42%
4	 **1a**	 **2d**	 **3e**	38%
5	 **1a**	 **2e**	 **3f**	46%
6	 **1a**	 **2f**	 **3g**	40%

mL) was added dropwise, at 0 °C, a solution of racemic (2,3-dibromophenyl)phenylmethanol (**5**; 3.27 g, 9.56 mmol) in anhydrous THF (20.0 mL). The reaction mixture was stirred at 25 °C for 1 h, and MeI (2.39 mL, 38.3 mmol) was then added. After 18 h of stirring at 25 °C, the reaction mixture was carefully hydrolyzed with water (100 mL) and was extracted with Et_2O (3 × 75 mL). The combined organic layers were dried over Na_2SO_4, and solvents were removed under reduced pressure. Purification of the crude product by column chromatography (cyclohexane/CH_2Cl_2 9/1) provided compound **2h** (2.45 g) as a colorless oil. Yield: 72%. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.40 (s, 3 H), 5.71 (s, 1 H), 7.22 (t, J = 7.8 Hz, 1 H), 7.26−7.39 (m, 5 H), 7.51 (br d, J = 7.7 Hz, 1 H), 7.57 (br d, J = 7.8 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 57.3, 84.7, 125.7, 126.0, 127.0, 127.5, 127.9, 128.4, 128.6, 132.8, 139.9, 143.9. HRMS (ESI$^+$): calcd for $C_{14}H_{12}{}^{79}Br_2O$ $[M]^+$ 353.9255, found 353.9289; calcd for $C_{14}H_{12}{}^{79}Br^{81}BrO$ $[M]^+$ 355.9234, found 355.9267; calcd for $C_{14}H_{12}{}^{81}Br_2O$ $[M]^+$ 357.9214, found 357.9256.

1,2-Dibromo-3-((methoxymethoxy)(phenyl)methyl)benzene (***2i***). To a suspension of NaH (4.80 mmol, 115 mg) in anhydrous THF (7.00 mL) was added dropwise, at 0 °C and under an inert atmosphere, a solution of racemic (2,3-dibromophenyl)-phenylmethanol **5** (3.43 mmol, 1.17 g) in anhydrous THF (4.00 mL). The reaction mixture was stirred at 25 °C for 1 h, and MOMCl (5.14 mmol, 0.39 mL) was then added dropwise. After 18 h of stirring at 25 °C, the reaction mixture was carefully hydrolyzed with water (100 mL) and was extracted with Et_2O (3 × 100 mL). The combined organic layers were dried over Na_2SO_4, and solvents were evaporated under reduced pressure. Purification of the crude product by column chromatography (cyclohexane/CH_2Cl_2 7/3) provided compound **2i** (1.20 g) as a colorless oil. Yield: 90%. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.38 (s, 3 H), 4.64−4.70 (m, 2 H), 6.16 (s, 1 H), 7.21−7.39 (m, 6 H),

dx.doi.org/10.1021/jo3009098 | J. Org. Chem. 2012, 77, 6117−6127

Table 2. Chemoselectivity of the Aryne Coupling

Entry	1	2	Product	Yield
1	 **1c**	 **2c**	 **3h**	27%
2	 **1d**	 **2c**	 **3i**	33%
3	 **1e**	 **2c**	 **3c**	44%
4	 **1f**	 **2e**	 **9**	20%

7.58 (dd, J = 7.9, 1.5 Hz, 1 H), 7.63 (dd, J = 7.7, 1.5 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.9, 78.6, 94.4, 125.4, 126.0, 127.3, 127.8, 127.9, 128.4, 128.5, 132.8, 139.8, 143.9. Anal. Calcd for $C_{15}H_{14}Br_2O_2$ (383.94): C, 46.66; H, 3.65. Found: C, 46.82; H, 3.68.

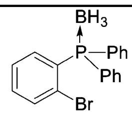
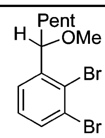
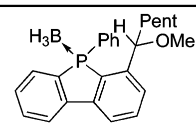
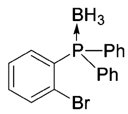
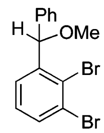
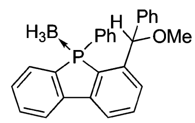
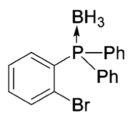
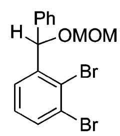
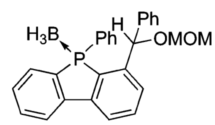
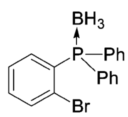
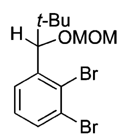
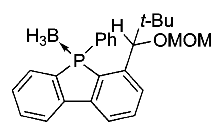
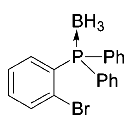
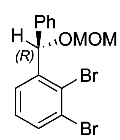
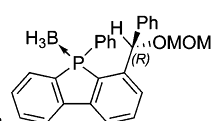
1,2-Dibromo-3-(1-methoxymethoxy-2,2-dimethylpropyl)benzene ***(2j)***. To a suspension of NaH (0.69 g, 28.9 mmol) in anhydrous THF (20.0 mL) was added dropwise, at 0 °C and under an inert atmosphere, a solution of 1-(2,3-dibromophenyl)-2,2-dimethylpropan-1-ol (**6**; 3.11 g, 9.65 mmol) in anhydrous THF (20.0 mL). The reaction mixture was stirred at 25 °C for 2 h, and MOMCl (2.34 mL, 30.8 mmol) was then added dropwise. After 18 h of stirring at 25 °C, the reaction mixture was carefully hydrolyzed with water (400 mL) and was extracted with Et_2O (3 × 200 mL). The combined organic layers were dried over Na_2SO_4, and solvents were removed under reduced pressure. Purification of the crude by column chromatography (cyclohexane/CH_2Cl_2 7/3) provided compound **2j** (1.10 g) as a colorless solid. Yield: 31%. An analytically pure sample was obtained by crystallization in acetonitrile at −20 °C. Mp: 53−54 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.99 (s, 9 H), 3.33 (s, 3 H), 4.36 (d, 1 H, J = 6.6 Hz), 4.47 (d, 1 H, J = 6.6 Hz), 5.01 (s, 1 H), 7.16 (t, 1 H, J = 7.8 Hz), 7.40 (dd, 1 H, J = 7.8, 1.6 Hz), 7.56 (dd, 1 H, J = 7.8, 1.6 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 26.3, 36.9, 56.1, 84.1, 95.2, 125.7, 127.5, 127.5, 128.6, 132.7, 142.7. Anal. Calcd for $C_{13}H_{18}Br_2O_2$ (366.09): C, 42.65; H, 4.96. Found: C, 42.40; H, 4.75.

(R)-(2,3-Dibromophenyl)phenylmethanol ***(5)***. To a solution of $LiAlH_4$ (4.80 mmol) in anhydrous diethyl ether (4.80 mL) was added dropwise, over 3 h, with stirring and at 25 °C, a solution of (R)-(−)-2-(2-isoindolinyl)butan-1-ol[38] (12.0 mmol, 2.29 g) in anhydrous diethyl ether (32.0 mL). After the reaction mixture was cooled to −10 °C, a solution of (2,3-dibromophenyl)phenylmethanone (**7**; 4.00 mmol, 1.36 g) in anhydrous diethyl ether (4.80 mL) was added (2 h) with stirring. After a period of 15 min, the reaction mixture was hydrolyzed with aqueous 1 N NaOH and diluted with an additional fraction of diethyl ether (100 mL). The organic layer was separated, washed successively with 1 N HCl (2 × 100 mL), 1 N NaOH (1 × 100 mL), and water (1 × 100 mL) and dried over Na_2SO_4. After evaporation of the solvent under reduced pressure, purification of the crude by column chromatography (cyclohexane/EtOAc 9/1) followed by crystallization from hexane at −20 °C provided the benzyl alcohol (R)-**5** (1.02 g) as a colorless solid. Yield: 74%. ee: 77%. The NMR data matched those quoted in the literature.[29] ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.00 (br s, 1 H), 6.23 (s, 1 H), 7.24 (t, J = 7.9 Hz, 1 H), 7.29−7.39 (m, 5 H), 7.58−7.61 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): 75.9, 124.9, 126.1, 127.0, 127.2, 128.0, 128.5, 128.6, 132.9, 141.7, 145.3.

1-(2,3-Dibromophenyl)-2,2-dimethylpropan-1-ol ***(6)***. To 1,2-dibromo-3-iodobenzene (**8**; 20.0 mmol, 7.24 g) in anhydrous THF (60.0 mL) was added dropwise, under Ar and at −78 °C, a solution of iPrMgCl (21.0 mmol) in THF (21.0 mL). The reaction mixture was stirred for 2 h at −78 °C, and pivalaldehyde (24 mmol, 2.60 mL) was added dropwise. The reaction mixture was allowed to reach 25 °C overnight and was then hydrolyzed with saturated NH_4Cl and extracted with Et_2O (3 × 100 mL). The combined organic layers were dried over Na_2SO_4, and solvents were removed under reduced pressure. Purification of the crude product by column chromatography (cyclohexane/EtOAc 9/1) provided compound **6** (3.83 g) as a colorless solid. Yield: 59%. Mp: 72−74 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.00 (s, 9 H), 1.72 (br s, 1 H), 7.19 (t, 1 H, J = 7.9 Hz), 7.49 (dd, 1 H, J = 7.9, 1.6 Hz), 7.57 (dd, 1 H, J = 7.9, 1.6 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 25.9, 37.3, 80.2, 125.7, 126.1, 127.7, 128.3, 132.7, 144.7. HRMS (ESI$^+$): calcd for $C_{11}H_{14}{}^{79}Br^{81}BrO$ $[M]^+$ 321.9391,

dx.doi.org/10.1021/jo3009098 | J. Org. Chem. 2012, 77, 6117−6127

Table 3. Diastereoselective Dibenzophosphole Synthesis

Entry	1	2	Product	Yield[a]
1	 **1a**	 **2g**	 **3j:** *de* = 15%	44% [a]
2	 **1a**	 **2h**	 **3k:** *de* = 48%	37% [a]
3	 **1a**	 **2i**	 **3l:** *de* = 70%	38% [a]
4	 **1a**	 **2j**	 **3m:** *de* >96%[c]	34% [b]
5	 **1a**	 (*R*-)**2i** *ee* = 77%	 (*R*,*R*P)-**3l** *de* = 72% *ee* = 78%	15% [b]

[a]Yield of both diastereoisomers. [b]Yield of the major diastereoisomer. [c]Only one diastereoisomer has been detected in the crude NMR mixture.

found 321.9360; calcd for $C_{14}H_{12}{}^{81}Br_2O$ $[M]^+$ 323.9371, found 323.9353.

Aryne-Mediated Cross-Coupling Leading to Dibenzophosphole–Boranes 3a–m and to Biaryl 9. *General Procedure.* To a solution of tertiary phosphine–borane **1** (1 equiv) in anhydrous THF (10 mL/mmol) was added dropwise, at −78 °C and under an inert atmosphere, a solution of *t*-BuLi (2 equiv) in hexane. After 1 h of stirring at −78 °C, the temperature of the reaction mixture was increased to −35 °C and 1,2-dibromobenzene (**2**; 1.2–1.4 equiv), dissolved in anhydrous THF in the case of solid compounds, was added dropwise. The temperature was maintained at −35 °C for 2 h before the reaction mixture was slowly warmed to 25 °C. Water was then added. and the reaction mixture was extracted with CH_2Cl_2 (3×). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude product by column chromatography and/or crystallization provided the dibenzophosphole–borane **3** or the biaryl **9**.

*5-Phenyl-5H-dibenzophosphole–Borane (**3a**).* The general procedure was applied starting from (2-bromophenyl)-diphenylphosphine–borane (**1a**; 3.00 mmol, 1.06 g) and 1,2-dibromobenzene (**2a**; 3.60 mmol, 0.43 mL). Purification of the crude product by column chromatography (cyclohexane/CH_2Cl_2 75/25) provided dibenzophosphole–borane **3a** (0.50 g) as a colorless solid. Yield: 60%. Mp: 146–148 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ 0.5–1.8 (br 3 H), 7.31–7.47 (m, 5 H), 7.52–7.63 (m, 4 H), 7.71 (t, *J* = 7.9 Hz, 2 H), 7.94 (d, *J* = 7.8 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 121.7 (d, *J* = 6.2 Hz), 128.0 (d, *J* = 50.6 Hz), 128.9 (d, *J* = 10.3 Hz), 129.1 (d, *J* = 10.4 Hz), 130.5 (d, *J* = 12.5 Hz), 131.7 (d, *J* = 2.6 Hz), 131.9 (d, *J* = 1.8 Hz), 132.2 (d, *J* = 10.3 Hz), 133.6 (d, *J* = 61.0 Hz), 143.4 (d, *J* = 9.8 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 26.2 (br). Anal. Calcd for $C_{18}H_{16}BP$ (274.10): C, 78.87; H, 5.88. Found: C, 79.05; H, 5.41.

*2,3-Dimethyl-5-phenyl-5H-dibenzophosphole–Borane (**3b**).* The general procedure was applied starting from (2-bromophenyl)-diphenylphosphine–borane (**1a**; 3.00 mmol, 1.06 g) and 1,2-dibromobenzene (**2b**; 4.20 mmol, 1.11 g). Purification of the crude product by column chromatography (cyclohexane/CH_2Cl_2 75/25) followed by crystallization from a mixture of EtOAc and diisopropyl

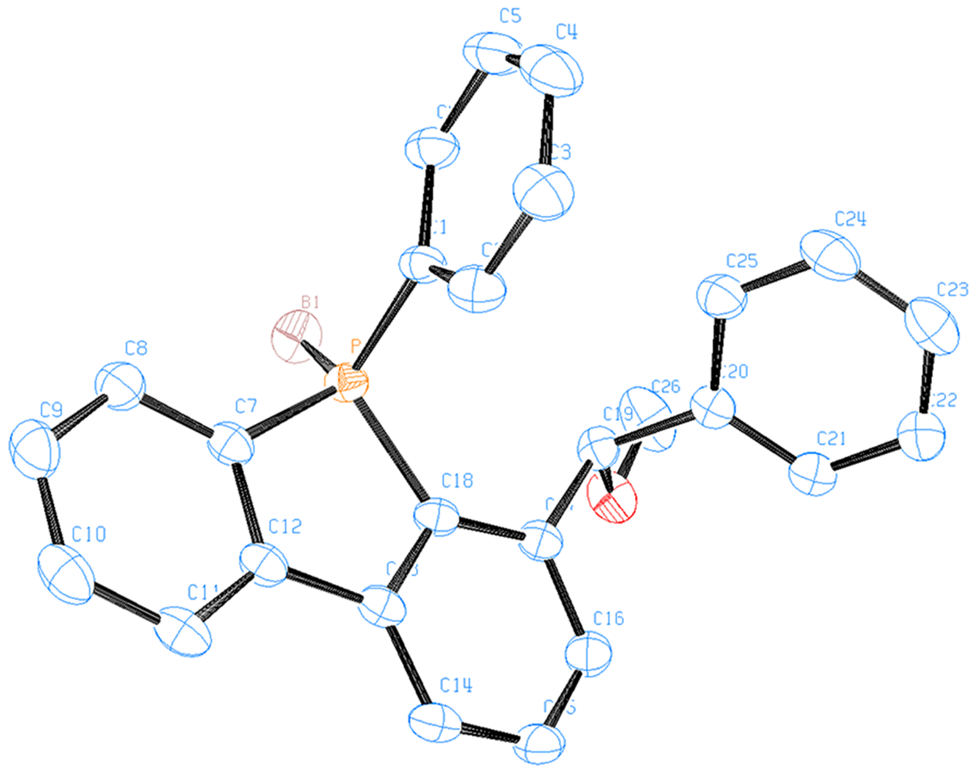


Figure 1. ORTEP view of **3k**, showing thermal ellipsoids at the 50% probability level.[36]

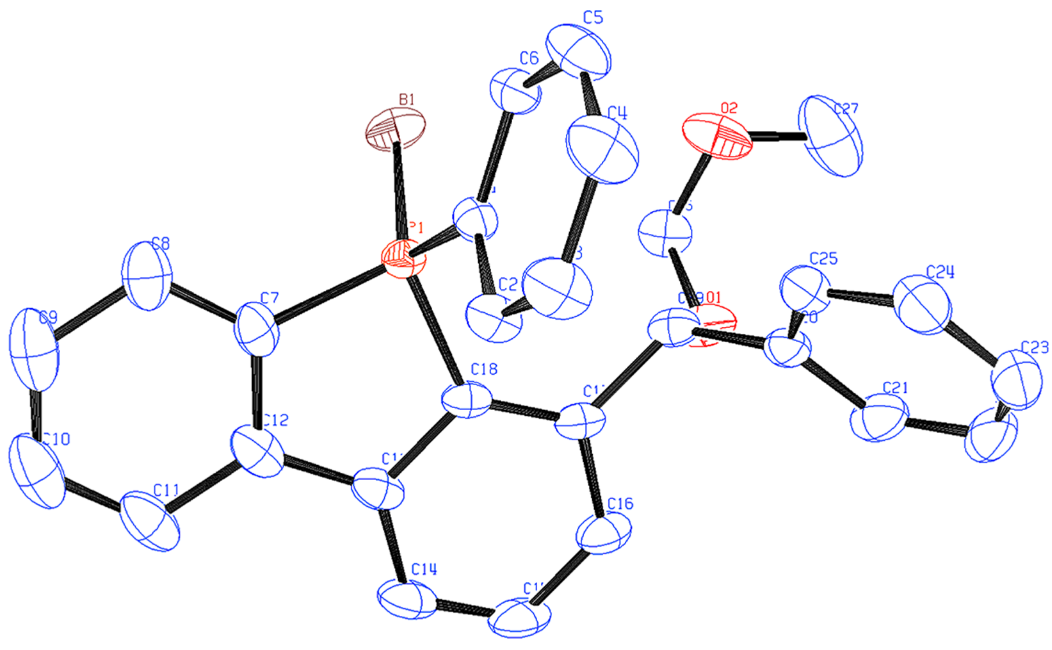


Figure 2. ORTEP view of **3l**, showing thermal ellipsoids at the 50% probability level.[36]

ether at −20 °C provided dibenzophosphole−borane **3b** (0.31 g) as a colorless solid. Yield: 34%. Mp: 149−150 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.4−1.9 (br 3 H), 2.30 (s, 3 H), 2.39 (s, 3 H), 7.31−7.49 (m, 5 H), 7.53−7.60 (m, 3 H), 7.64−7.70 (m, 2 H), 7.87 (br d, 1 H, J = 7.8 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 19.9, 20.4, 121.1 (d, J = 6.4 Hz), 122.8 (d, J = 6.8 Hz), 128.4 (d, J = 50.4 Hz), 128.5 (d, J = 10.4 Hz), 128.8 (d, J = 10.1 Hz), 130.4 (d, J = 12.5 Hz), 130.4 (d, J = 62.6 Hz), 131.1 (d, J = 12.7. Hz), 131.5 (d, J = 2.4 Hz), 131.8 (d, J = 1.9 Hz), 132.1 (d, J = 10.3 Hz), 133.6 (d, J = 61.4 Hz), 138.2 (d, J = 10.7 Hz), 141.2 (d, J = 2.0 Hz), 141.3 (d, J = 10.1 Hz), 143.6 (d, J = 10.2 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 24.1 (br). Anal. Calcd for $C_{20}H_{20}BP$ (302.14): C, 79.50; H, 6.67. Found: C, 79.12; H, 6.62.

2,3-Dimethoxy-5-phenyl-5H-dibenzophosphole−Borane (**3c**). The general procedure was applied starting from (2-bromophenyl)-(2-methoxyphenyl)phenylphosphine−borane (**1e**; 3.61 mmol, 1.39 g) and 1,2-dibromobenzene (**2c**; 4.33 mmol, 1.29 g). Purification of the crude product by column chromatography (cyclohexane/CH_2Cl_2 5/5) provided dibenzophosphole−borane **3c** (0.53 g) as a colorless solid. Yield: 44%. Mp: 208−210 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.4−1.8 (br 3 H), 3.90 (s, 3 H), 4.04 (s, 3 H), 7.11 (d, J = 8.6 Hz, 1 H), 7.29−7.48 (m, 5 H), 7.53−7.60 (m, 3 H), 7.65 (br t, J = 8.0 Hz, 1 H),

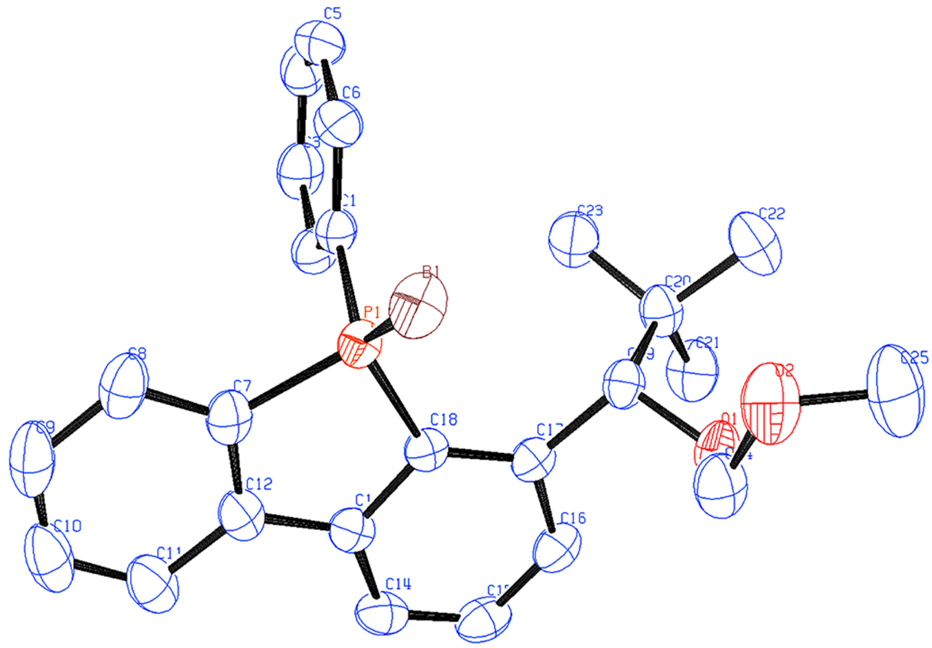
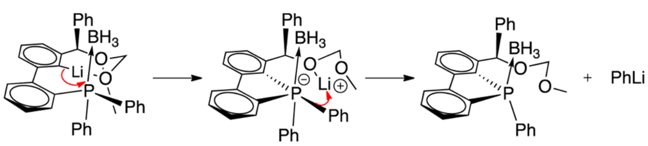


Figure 3. ORTEP view of **3m**, showing thermal ellipsoids at the 50% probability level.[36]

Scheme 6. Postulated Mechanism toward Dibenzophospholes



I II III

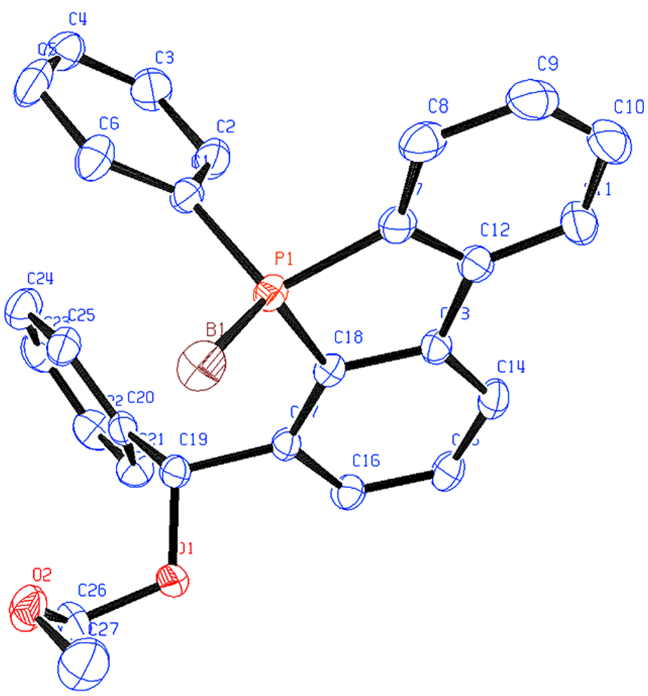


Figure 4. ORTEP view of (R,R_p)-**3l**, showing thermal ellipsoids at the 50% probability level.[36]

7.80 (br d, J = 7.8 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 56.1, 56.2, 104.4 (d, J = 8.5 Hz), 111.5 (d, J = 15.3 Hz), 120.7 (d, J = 6.3 Hz), 124.5 (d, J = 65.5 Hz), 127.9 (d, J = 10.4 Hz), 128.3 (d, J = 50.3 Hz), 128.9 (d, J = 10.2 Hz), 130.2 (d, J = 12.7 Hz), 131.6 (d, J = 2.5 Hz), 131.8 (d, J = 1.7 Hz), 132.1 (d, J = 10.3 Hz), 134.0 (d, J = 61.7 Hz), 137.2 (d, J = 10.4 Hz), 143.4 (d, J = 9.9 Hz), 150.4 (d, J = 13.0 Hz), 152.7 (d, J = 1.9 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 25.3 (br). Anal. Calcd for $C_{20}H_{20}BO_2P$ (334.16): C, 71.89; H, 6.03. Found: C, 72.06; H, 6.34.

*2,3-Dimethoxy-7,8-dimethyl-5-phenyl-5H-dibenzophosphole–Borane (**3d**).* The general procedure was applied starting from (2-bromo-4,5-dimethylphenyl)diphenylphosphine–borane (**1b**; 2.50 mmol, 0.96 g) and 1,2-dibromobenzene (**2c**; 3.50 mmol, 1.04 g). Purification of the crude product by column chromatography (cyclohexane/EtOAc 8/2) followed by crystallization from a mixture of EtOAc and cyclohexane provided dibenzophosphole–borane **3d** (0.38 g) as a colorless solid. Yield: 42%. Mp: 212–214 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.4–1.8 (br, 3 H), 2.27 (s, 3 H), 2.36 (s, 3 H), 3.89 (s, 3 H), 4.03 (s, 3 H), 7.08 (d, 1 H, J = 8.6 Hz), 7.31–7.46 (m, 5 H), 7.53–7.60 (m, 3 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 19.8, 20.4, 56.1, 56.2, 104.1 (d, J = 8.5 Hz), 111.6 (d, J = 15.3 Hz), 122.0 (d, J = 7.0 Hz), 124.4 (d, J = 66.0 Hz), 128.8 (d, J = 10.1 Hz), 128.9 (d, J = 50.1 Hz), 130.9 (d, J = 63.3 Hz), 131.0 (d, J = 12.8 Hz), 131.5 (d, J = 2.5 Hz), 132.1 (d, J = 10.3 Hz), 137.0 (d, J = 10.7 Hz), 137.5 (d, J = 10.6 Hz), 141.0 (d, J = 1.9 Hz), 141.4 (d, J = 9.9 Hz), 149.9 (d, J = 13.0 Hz), 152.6 (d, J = 2.0 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 24.3 (br). Anal. Calcd for $C_{22}H_{24}BO_2P$ (362.21): C, 72.95; H, 6.68. Found: C, 72.80; H, 6.734.

*4-Methoxy-5-phenyl-5H-dibenzophosphole–Borane (**3e**).* The general procedure was applied starting from (2-bromophenyl)-diphenylphosphine–borane (**1a**; 4.00 mmol, 1.42 g) and 1,2-dibromobenzene **2d** (4.80 mmol, 1.27 g). Purification of the crude by column chromatography (cyclohexane/CH_2Cl_2 7/3) provided dibenzophosphole–borane **3e** (0.46 g) as a colorless solid. Yield: 38%. Mp: 158–160 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.4–1.9 (br 3 H), 3.82 (s, 3 H), 6.84–6.89 (m, 1 H), 7.31–7.46 (m, 4 H), 7.51–7.64 (m, 5 H), 7.70 (br t, 1 H, J = 7.7 Hz), 7.89 (br d, 1 H, J = 7.8 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.9, 111.0 (d, J = 5.5 Hz), 114.3 (d, J = 6.2 Hz), 119.7 (d, J = 61.2 Hz), 121.9 (d, J = 6.2 Hz), 127.4 (d, J = 51.5 Hz), 128.6 (d, J = 10.3 Hz), 129.1 (d, J = 10.2 Hz), 130.3 (d, J = 12.2 Hz), 131.3 (d, J = 2.5 Hz), 131.6 (d, J = 1.6 Hz), 132.1 (d, J = 10.3 Hz), 134.3 (d, J = 61.5 Hz), 134.3 (d, J = 1.2 Hz), 143.1 (d, J = 10.0 Hz), 145.3 (d, J = 8.6 Hz), 161.6 (d, J = 5.9 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 24.8 (br). Anal. Calcd for $C_{19}H_{18}BOP$ (304.13): C, 75.03; H, 5.97. Found: C, 74.78; H, 6.34.

*4-(2,6-Dimethoxyphenyl)-5-phenyl-5H-dibenzophosphole–Borane (**3f**).* The general procedure was applied starting from (2-bromophenyl)diphenylphosphine–borane (**1a**; 4.00 mmol, 1.42 g) and 1,2-dibromobenzene **2e** (4.80 mmol, 1.78 g). Purification of the crude product by column chromatography (cyclohexane/CH_2Cl_2 7/3) provided dibenzophosphole–borane **3f** (0.75 g) as a colorless solid. Yield: 46%. Analytically pure crystals were obtained by crystallization from acetonitrile. Mp: 210–212 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.2–1.5 (br 3 H), 2.85 (s, 3 H), 3.78 (s, 3 H), 6.17 (d, 1 H, J = 8.2 Hz), 6.66 (d, 1 H, J = 8.4 Hz), 7.14–7.19 (m, 5 H), 7.29 (t, 1 H, J = 8.3 Hz), 7.30–7.39 (m, 2 H), 7.56–7.60 (m, 2 H), 7.65 (td, 1 H, J = 7.6, 1.2 Hz), 7.92–7.96 (m, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 54.5, 55.5, 102.1, 103.5, 116.1 (d, J = 2.8 Hz), 120.4 (d, J = 6.0 Hz), 121.4 (d, J = 6.1 Hz), 127.6 (d, J = 53.6 Hz), 127.9 (d, J = 10.4 Hz), 128.9 (d, J = 10.0 Hz), 129.8, 130.4 (d, J = 11.9 Hz), 130.8 (d, J = 2.1 Hz), 131.2 (d, J = 8.3 Hz), 131.7, 132.1, 132.8 (d, J = 10.4 Hz), 134.2 (d, J = 59.1 Hz), 134.4 (d, J = 62.8 Hz), 139.7 (d, J = 11.2 Hz), 143.8, 143.8 (d, J = 2.7 Hz), 157.1, 158.4. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 24.6 (br). Anal. Calcd for $C_{26}H_{24}BO_2P$ (410.25): C, 76.12; H, 5.90. Found: C, 75.83; H, 5.85.

*2-Methyl-5-phenyl-4-trimethylsilanyl-5H-dibenzophosphole–Borane (**3g**).* The general procedure was applied starting from (2-bromophenyl)diphenylphosphine–borane (**1a**; 2.00 mmol, 0.71 g) and 1,2-dibromobenzene **2f** (2.40 mmol, 0.77 g). Purification of the crude product by column chromatography (cyclohexane/CH_2Cl_2 9/1) provided dibenzophosphole–borane **3g** (0.29 g) as a colorless solid. Yield: 40%. Mp: 212–214 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.16 (s, 9 H), 0.6–2.1 (br, 3 H), 2.52 (s, 3 H), 7.26–7.43 (m, 4 H), 7.48–7.56 (m, 4 H), 7.60 (br t, 1 H, J = 7.6 Hz), 7.80 (br s, 1 H), 7.86 (br d, 1 H, J = 7.8 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 0.5, 21.8, 121.1 (d, J = 6.2 Hz), 123.0 (d, J = 6.4 Hz), 128.7 (d, J = 10.0 Hz), 129.0 (d, J = 10.1 Hz), 129.7 (d, J = 48.7 Hz), 129.7(d, J = 11.8 Hz), 131.4 (m), 132.1 (d, J = 9.9 Hz), 134.3 (d, J = 58.6 Hz), 135.8 (d, J = 64.0 Hz), 136.8 (d, J = 13.1 Hz), 141.2 (d, J = 2.2 Hz), 141.8 (d, J = 9.5 Hz), 145.2 (d, J = 1.8 Hz), 145.4 (d, J = 8.9 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 25.6 (br). Anal. Calcd for $C_{22}H_{26}BPSi$ (360.31): C, 73.34; H, 7.27. Found: C, 73.21; H, 7.36.

*5-tert-Butyl-2,3-dimethoxy-5H-dibenzophosphole–Borane (**3h**).* The general procedure was applied starting from (2-bromophenyl)-*tert*-butylphenylphosphine–borane (**1c**; 4.00 mmol, 1.34 g) and 1,2-dibromobenzene **2c** (4.80 mmol, 1.42 g). Purification of the crude product by column chromatography (cyclohexane/CH_2Cl_2 4/6) provided dibenzophosphole–borane **3h** (0.34 g) as a colorless solid. Yield: 27%. Mp: 144–146 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.1–1.8 (br 3 H), 1.12 (d, J = 14.5 Hz, 9 H), 3.98 (s, 3 H), 4.02 (s, 3 H), 7.17 (d, J = 7.2 Hz, 1 H), 7.33–7.41 (m, 2 H), 7.55 (br t, J = 7.6 Hz, 1 H), 7.68–7.80 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 25.1 (d, J = 2.8 Hz), 30.7 (d, J = 28.8 Hz), 56.1, 56.3, 104.3 (d, J = 7.7 Hz), 112.2 (d, J = 13.8 Hz), 120.6 (d, J = 5.8 Hz), 122.7 (d, J = 58.1 Hz), 127.3 (d, J = 9.7 Hz), 130.7 (d, J = 11.4 Hz), 131.6 (d, J = 1.8 Hz), 131.7 (d, J = 54.9 Hz), 137.8 (d, J = 8.1 Hz), 144.2 (d, J = 7.6 Hz), 149.8 (d, J = 12.1 Hz), 152.4 (d, J = 1.8 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 44.6 (br). Anal. Calcd for $C_{18}H_{24}BO_2P$ (314.17): C, 68.81; H, 7.70. Found: C, 68.78; H, 7.78.

*5-Cyclohexyl-2,3-dimethoxy-5H-dibenzophosphole–Borane (**3i**).* The general procedure was applied starting from (2-bromophenyl)-cyclohexylphenylphosphine–borane (**1d**; 4.00 mmol, 1.44 g) and 1,2-dibromobenzene **2c** (4.80 mmol, 1.42 g). Purification of the crude product by column chromatography (cyclohexane/CH_2Cl_2 4/6) provided dibenzophosphole–borane **3i** (0.46 g) as a colorless solid. Yield: 33%. Mp: 152–154 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.1–1.4 (br 3 H), 0.95–1.33 (m, 5 H), 1.52–2.06 (m, 6 H), 3.99 (s, 3 H), 4.01 (s, 3 H), 7.15 (d, J = 7.6 Hz, 1 H), 7.32–7.39 (m, 2 H), 7.54 (br t, J = 7.7 Hz, 1 H), 7.68–7.76 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 25.6 (d, J = 1.2 Hz), 26.4–26.5 (m), 26.6 (d, J = 1.5 Hz), 36.4 (d, J = 30.0 Hz), 56.1, 56.3, 104.4 (d, J = 7.8 Hz), 111.9 (d, J = 14.2 Hz), 120.6 (d, J = 6.0 Hz), 122.7 (d, J = 59.9 Hz), 127.4 (d, J = 9.9 Hz), 130.4 (d, J = 11.6 Hz), 131.5 (d, J = 1.7 Hz), 131.6 (d, J = 56.6 Hz), 137.5 (d, J = 8.7 Hz), 143.9 (d, J = 8.3 Hz), 150.0 (d, J = 12.3 Hz), 152.5 (d, J = 2.0 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 34.6 (br). Anal. Calcd for $C_{20}H_{26}BO_2P$ (340.20): C, 70.61; H, 7.70. Found: C, 70.68; H, 7.65.

*4-(1-Methoxyhexyl)-5-phenyl-5H-dibenzophosphole–Borane (**3j**).* The general procedure was applied starting from (2-bromophenyl)diphenylphosphine–borane (**1a**; 4.00 mmol, 1.42 g) and racemic 1,2-dibromobenzene **2g** (4.80 mmol, 1.68 g). Diastereoisomers of the dibenzophosphole–borane **3j** (dr = 57/43 according to NMR analysis of the crude product) were separated by column chromatography (cyclohexane/CH_2Cl_2 8/2). The main diastereoisomer (racemic mixture of (R,R_p)-**3j** and (S,S_p)-**3j** assuming configurations similar to **3k–m**) was isolated in 26% yield (0.40 g), whereas the minor diastereoisomer (racemic mixture of (S,R_p)-**3j** and (R,S_p)-**3j**) was recovered in 18% yield (0.28 g).

Main Diastereoisomer. Mp: 97–99 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.50–2.03 (m, 14 H), 3.24 (s, 3 H), 4.57 (dd, 1 H, J = 9.2, 2.8 Hz), 7.30–7.46 (m, 5 H), 7.52–7.70 (m, 5 H), 7.87–7.98 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.2, 22.4, 25.7, 31.5, 38.0, 57.1, 81.2 (d, J = 5.2 Hz), 120.8 (d, J = 6.1 Hz), 121.5 (d, J = 6.2 Hz), 126.3 (d, J = 8.3 Hz), 127.6 (d, J = 50.3 Hz), 128.9 (d, J = 10.3 Hz), 129.2 (d, J = 10.3 Hz), 130.3 (d, J = 12.5 Hz), 131.8 (d, J = 56.9 Hz), 131.8 (d, J = 2.4 Hz), 131.9 (d, J = 1.8 Hz), 132.6–132.8 (m), 134.1 (d, J = 63.8 Hz), 143.2 (d, J = 9.8 Hz), 143.7 (d, J = 10.3 Hz), 147.8 (d, J = 10.7 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 22.3 (br). HRMS (ESI$^+$): calcd for $C_{25}H_{30}{}^{10}BNaOP^+$ ([M + Na]$^+$) 410.2056, found 410.2059.

Minor Diastereoisomer. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.71–1.85 (m, 14 H), 2.48 (s, 3 H), 4.21 (dd, 1 H, J = 8.8, 3.2 Hz), 7.28–7.50 (m, 5 H), 7.52–7.70 (m, 5 H), 7.84–7.96 (m, 2 H). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 22.7 (br).

*4-(Methoxy(phenyl)methyl)-5-phenyl-5H-dibenzophosphole–Borane (**3k**).* The general procedure was applied starting from (2-bromophenyl)diphenylphosphine borane (**1a**; 4.00 mmol, 1.42 g) and racemic 1,2-dibromobenzene **2h** (4.80 mmol, 1.71 g). Diastereoisomers of the dibenzophosphole–borane **3k** (dr = 74/26 according to NMR analysis of the crude product) were separated by column chromatography (cyclohexane/CH_2Cl_2 8/2). The main diastereoisomer (racemic mixture of (R,R_p)-**3k** and (S,S_p)-**3k** according to single-crystal X-ray analysis) was isolated in 30% yield (0.48 g), whereas the minor diastereoisomer (racemic mixture of (S,R_p)-**3k** and (R,S_p)-**3k**) was recovered in 7% yield (0.11 g).

Main Diastereoisomer. An analytically pure sample was obtained by crystallization in acetonitrile. Mp: 175–177 °C. ^{1}H NMR ($CDCl_3$ 300 MHz): δ 0.6–2.3 (br 3 H), 3.35 (s, 3 H), 5.65 (s, 1H), 6.75–6.78 (m, 2 H), 6.95–7.08 (m, 3 H), 7.16–7.22 (m, 2 H), 7.32–7.51 (m, 5 H), 7.57 (br t, 1 H, J = 7.6 Hz), 7.64 (br t, 2 H, J = 7.7 Hz), 7.88–7.93 (m, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 56.8, 82.4 (d, J = 4.5 Hz), 121.0 (d, J = 6.0 Hz), 121.5 (d, J = 6.2 Hz), 127.1, 127.4, 127.6 (d, J = 51.3 Hz), 127.8 (d, J = 8.1 Hz), 128.1, 128.9 (d, J = 10.5 Hz), 129.3 (d, J = 10.3 Hz), 130.2 (d, J = 12.2 Hz), 131.5 (d, J = 57.5 Hz), 131.6 (d, J = 2.1 Hz), 131.9 (d, J = 1.0 Hz), 132.4 (d, J = 10.3 Hz), 132.8, 134.6 (d, J = 62.9 Hz), 140.3, 142.7 (d, J = 9.4 Hz), 144.3 (d, J = 10.3 Hz), 146.2 (d, J = 9.9 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 23.7 (br). Anal. Calcd for $C_{26}H_{24}BOP$ (394.25): C, 79.21; H, 6.14. Found: C, 79.08; H, 6.08.

Minor Diastereoisomer. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.6–2.1 (br 3 H), 2.72 (s, 3 H), 5.59 (s, 1 H), 7.06 (dd, 1 H, J = 7.7, 4.4 Hz), 7.22–7.63 (m, 11 H), 7.60–7.72 (m, 3 H), 7.86 (br d, 1 H, J = 7.7 Hz), 7.91 (br d, 1 H, J = 7.8 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 56.2, 82.5 (d, J = 3.9 Hz), 121.0 (d, J = 6.2 Hz), 121.5 (d, J = 6.1 Hz), 127.2, 127.6, 128.4, 128.5 (d, J = 7.9 Hz), 128.7 (d, J = 52.2 Hz), 128.7 (d, J = 10.5 Hz), 129.2 (d, J = 10.1 Hz), 130.1 (d, J = 12.2 Hz), 131.5 (d, J = 2.4 Hz), 131.7 (d, J = 1.7 Hz), 131.8 (d, J = 58.7 Hz), 132.4 (d, J = 10.3 Hz), 132.7 (d, J = 1.6 Hz), 135.0 (d, J = 62.2 Hz), 140.3, 142.6 (d, J = 9.6 Hz), 144.4 (d, J = 10.4 Hz), 146.3 (d, J = 9.8 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 24.4 (br).

*4-(Methoxymethoxy(phenyl)methyl)-5-phenyl-5H-dibenzophosphole–Borane (**3l**). Synthesis of **3l** Starting from a Racemic Mixture of 1,2-Dibromobenzene **2i**.* The general procedure was applied starting from (2-bromophenyl)diphenylphosphine–borane (**1a**; 2.52 mmol, 0.89 g) and racemic 1,2-dibromobenzene **2i** (3.03 mmol, 1.17 g). Diastereoisomers of dibenzophosphole–borane **3l** (dr

= 85/15 according to NMR analysis of the crude product) were separated by column chromatography (cyclohexane/CH_2Cl_2 8/2). The main diastereoisomer (racemic mixture of (R,R_p)-**3l** and (S,S_p)-**3l** according to single-crystal X-ray analysis) was isolated in 32% yield (0.34 g), whereas the minor diastereoisomer (racemic mixture of (S,R_p)-**3l** and (R,S_p)-**3l**) was recovered in 6% yield (0.07 g).

*Synthesis of **3l** Starting from the R Enantiomerically Enriched 1,2-Dibromobenzene **2i**.* The general procedure was applied starting from (2-bromophenyl)diphenylphosphine−borane (**1a**; 2.17 mmol, 0.77 g) and *R* enantiomerically enriched 1,2-dibromobenzene **2i** (2.62 mmol, 1.01 g, ee 77%). The main diastereoisomer of dibenzophosphole−borane **3l** (dr = 86/14 according to NMR analysis of the crude product) was isolated by column chromatography (cyclohexane/CH_2Cl_2 8/2) in 15% yield (0.14 g, ee 78%). An optically pure sample of (R,R_p)-**3l** was obtained by crystallization from acetonitrile at −20 °C.

Main Diastereoisomer. Mp: 160−162 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.7−2.0 (br 3 H), 3.17 (s, 3 H), 4.56 (d, J = 6.6 Hz, 1 H), 4.64 (d, J = 6.6 Hz, 1 H), 6.05 (s, 1 H), 6.91−7.08 (m, 5 H), 7.09−7.20 (m, 2 H), 7.26−7.41 (m, 4 H), 7.51−7.71 (m, 4 H), 7.90 (br d, J = 7.5 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.6, 77.4 (m), 94.0, 120.8 (d, J = 6.1 Hz), 121.4 (d, J = 6.2 Hz), 127.5, 128.0 (d, J = 51.9 Hz), 127.9−128.1 (m), 128.7 (d, J = 10.4 Hz), 129.2 (d, J = 10.0 Hz), 130.1 (d, J = 56.9 Hz), 130.1 (d, J = 12.1 Hz), 131.2 (d, J = 2.5 Hz), 131.6 (d, J = 1.8 Hz), 132.1 (d, J = 10.3 Hz), 132.6 (d, J = 1.5 Hz), 135.0 (d, J = 62.5 Hz), 139.5, 142.3 (d, J = 9.4 Hz), 144.6 (d, J = 10.0 Hz), 146.3 (d, J = 9.6 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 24.3 (br). Anal. Calcd for $C_{27}H_{26}BO_2P$ (424.28): C, 76.43; H, 6.18. Found: C, 76.25; H, 6.36. HPLC (column Lux 5u Cellulose-2, UV−visible detector λ 210 nm, eluent hexane/*i*PrOH 90/10, flow rate 0.5 mL/min): t_R = 19.9 min for (S,S_p)-**3l**, 23.0 min for (R,R_p)-**3l**. (R,R_p)-**3l**: $[\alpha]_D$ = −127° (c 0.5, $CHCl_3$).

Minor Diastereoisomer. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.5−2.1 (br 3 H), 2.94 (s, 3 H), 4.11 (d, J = 6.5 Hz, 1 H), 4.19 (d, J = 6.5 Hz, 1 H), 5.88 (s, 1 H), 7.17−7.47 (m, 10 H), 7.53−7.69 (m, 5 H), 7.85−7.91 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.7, 78.1 (d, J = 3.9 Hz), 94.8, 121.0 (d, J = 6.0 Hz), 121.4 (d, J = 6.1 Hz), 127.2, 127.5, 128.0 (d, J = 51.2 Hz), 128.2, 128.8−129.1 (m), 129.3 (d, J = 10.3 Hz), 130.2 (d, J = 12.3 Hz), 131.2 (d, J = 57.0 Hz), 131.7 (d, J = 2.5 Hz), 131.8 (d, J = 1.8 Hz), 132.7−132.8 (m), 134.8 (d, J = 62.9 Hz), 141.0, 142.6 (d, J = 9.3 Hz), 144.3 (d, J = 10.3 Hz), 146.3 (d, J = 9.8 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 24.1 (br).

*4-(1-Methoxymethoxy-2,2-dimethylpropyl)-5-phenyl-5H-dibenzophosphole−Borane (**3m**).* The general procedure was applied starting from (2-bromophenyl)diphenylphosphine−borane (**1a**; 2.71 mmol, 0.96 g) and racemic 1,2-dibromobenzene **2j** (3.25 mmol, 1.19 g). A single diastereoisomer (racemic mixture of (R,R_p)-**3m** and (S,S_p)-**3m** according to single-crystal X-ray analysis) was detected in the crude by NMR analysis and was isolated by column chromatography (cyclohexane/CH_2Cl_2 5/5) as a colorless solid with 34% yield (0.37 g). Analytically pure crystals were obtained by crystallization from acetonitrile at −20 °C. Mp: 135−137 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.50 (s, 9 H), 0.2−2.1 (br 3 H), 3.36 (s, 3 H), 4.51 (d, 1 H, J = 5.7 Hz), 4.63 (s, 1 H), 4.74 (d, 1 H, J = 5.7 Hz), 7.30−7.48 (m, 4 H), 7.56−7.64 (m, 6 H), 7.90−7.95 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 26.2, 36.1, 56.1, 83.9 (d, J = 5.2 Hz), 96.0, 121.1−121.4 (m), 128.3 (d, J = 50.4 Hz), 128.9−129.2 (m), 129.3 (d, J = 10.4 Hz), 130.1 (d, J = 12.4 Hz), 131.9−132.1 (m), 133.3 (d, J = 10.3 Hz), 133.6 (d, J = 50.4 Hz), 134.1 (d, J = 65.6 Hz), 143.2 (d, J = 9.8 Hz), 143.5 (d, J = 11.2 Hz), 146.0 (d, J = 10.7 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 23.6 (br) ppm. HRMS (ESI$^+$): calcd for $C_{25}H_{34}{}^{10}BNO_2P^+$ ($[M + NH_4]^+$) 421.2451, found 421.2458.

*(2′-Bromo-2″,6″-dimethoxy[1,1′;3′,1″]terphenyl-2-yl)-dicyclohexylphosphine−Borane (**9**).* The general procedure was applied starting from (2-bromophenyl)dicyclohexylphosphine−borane (**1f**; 4.00 mmol, 1.47 g) and 1,2-dibromobenzene **2e** (4.80 mmol, 1.78 g). Purification of the crude product by column chromatography (cyclohexane/CH_2Cl_2 6/4) provided compound **9** (0.48 g) as a colorless solid. Yield: 20%. Analytically pure crystals were obtained by crystallization from cyclohexane. Mp: 180−182 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.1−1.2 (br 3 H), 1.04−2.05 (m, 22 H), 3.76 (s, 3H), 3.80 (s, 3 H), 6.67 (d, 1 H, J = 7.6 Hz), 6.69 (d, 1 H, J = 7.6 Hz), 7.13 (dd, 1 H, J = 7.6, 1.8 Hz), 7.30−7.33 (m, 2 H), 7.43 (t, 1 H, J = 8.4 Hz), 7.42−7.53 9 (m, 2H), 8.13 (ddd, 1 H, J = 13.1, 7.7, 1.1 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 25.7−25.8 (m), 26.5−27.0 (m), 27.6, 27.8, 28.3, 29.3, 33.0 (d, J = 33.0 Hz), 34.5 (d, J = 31.1 Hz), 55.5, 56.1, 103.8, 103.9, 119.1, 125.6 (d, J = 44.8 Hz), 126.0, 126.9, 127.4 (d, J = 11.4 Hz), 129.0, 129.5, 130.1 (d, J = 2.2 Hz), 132.0, 133.0 (d, J = 6.3 Hz), 137.3 (d, J = 14.7 Hz), 137.8, 142.2 (d, J = 2.1 Hz), 145.3, 157.3, 157.8. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 35.1 (br). HRMS (ESI$^+$): calcd for $C_{32}H_{45}{}^{10}B^{79}BrNO_2P^+$ ($[M + NH_4]^+$) 595.2495, found 595.2487.

■ ASSOCIATED CONTENT

Supporting Information

Figures, tables, and CIF files giving ^{1}H, ^{13}C, and ^{31}P NMR and HPLC spectra and crystallographic details (CCDC 868763−868769) of compounds **3a,f,k,l**, **9**, and (R,R_p)-**3l**. 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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