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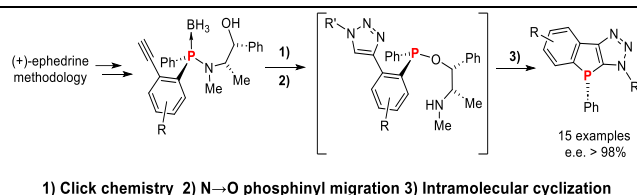
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Enantioselective Synthesis of P-chirogenic 1,2,3-triazolobenzophospholes

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ABSTRACT: An enantioselective synthesis of a new class of benzophosphole-based heterocycles bearing a fused triazole ring with enantioselectivities up to 99% is reported. The key steps of the synthesis are based on an innovative stereospecific phosphinyl N→O migration of aminophosphine-boranes into phosphinites, followed by an intramolecular cyclization. Five X-ray structures of P-chirogenic benzotriazolophospholes and gold(I) complex were established, for assigning absolute configurations, stereochemistry of reactions and the placement of the triazole substituent in *syn*-position of the P-center.

Dibenzophospholes and fused heteroaromatic derivatives have attracted increasing interest for their applications in organic optoelectronic materials¹, catalysis² and bioimaging.³ Chiral versions of dibenzophospholes or derivatives have been developed and proved to be suitable ligands^{2,4} or Lewis-bases⁵ in asymmetric catalysis or organocatalysis, respectively. In these cases, the chirality is located either on the carbon backbone or on the P-atom, or both, as in the examples **1-7** presented in Figure 1. So far, enantiomerically enriched P-chirogenic dibenzophospholes or derivatives have been scarcely described due to the lack of efficient stereoselective methods. Thus, phosphahelicene **4** was synthesized from enantiomerically pure 1-*H*-phosphindole-oxide, previously obtained by chemical resolution.⁶ Nevertheless, Leroux and our group have developed the stereoselective synthesis of P-chirogenic dibenzophospholes as borane complexes **5** using aryne chemistry.⁷ On the other hand, Cui, Xu and Duan *et al.* independently described the asymmetric synthesis of P-chirogenic dibenzophosphole-oxides **6** by desymmetrization of prochiral *o*-bromoaryl diarylphosphine-oxides using an intramolecular Pd-catalyzed C-H arylation.⁸ In addition, the desymmetrization of phosphole-diyne into P-chirogenic dibenzophosphole-oxides **7** was reported by Zhou *et al.* using an asymmetric Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC).⁹

In recent years, we described the synthesis of P-chirogenic *o*-functionalized arylphosphines,¹⁰ especially 1,2,3-triazole based-phosphine¹¹ using ephedrine methodology. In continuation of this work, we report herein the first enantioselective synthesis of a new class of P-chirogenic 1,2,3-triazolobenzophospholes **8** (Figure 1), based on the phosphole ring formation by an intramolecular cyclization.

The stereoselective synthesis of P-chirogenic 1,2,3-triazolobenzophospholes **8a-n** is described in Scheme 1 and was achieved in five steps from oxazaphospholidine borane **9**.¹² Reaction of **9** with organolithium reagents **10**¹³ resulted in the regio- and stereoselective cleavage of the P-O bond to provide corresponding aminophosphine-boranes **11a-d** in 60-78% yields, as single diastereomers and with retention of the configuration at the P-center.

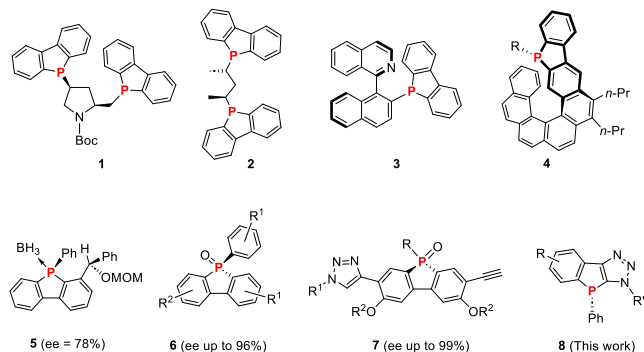
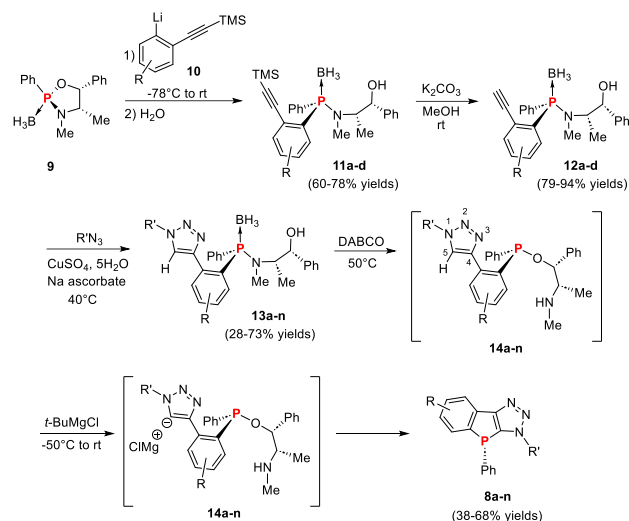


Figure 1. Representative chiral dibenzophospholes or derivatives and P-chirogenic 1,2,3-triazolobenzophospholes **8** from this work

The following desilylation with potassium carbonate in methanol/THF mixture affords terminal alkynes **12a-d** with yields up to 94%, which were subjected to Click Chemistry under modified Sharpless conditions (Scheme 1).¹⁴ Different azides R'-N₃, incorporating aromatic or aliphatic substituents with various steric and electronic properties, were used for the CuAAC cycloaddition (Figure 2). Thus, terminal alkynes **12a-d** reacted with azides R'-N₃ in presence of CuSO₄·5H₂O and sodium ascorbate in DMF/H₂O to give the triazolyl-aminophosphine-boranes **13a-n** in a 1,4-regioselective manner and with moderate to good yields (28-73%). Finally, P-chirogenic 1,2,3-triazolobenzophospholes **8a-n** were obtained by a one-pot two-step reaction from aminophosphine-boranes **13a-n**. Borane decomplexation of these compounds using DABCO at 50°C afforded stereoselectively the ephedrine phosphinite intermediates **14a-n** by an intramolecular P-chirogenic phosphinyl N→O migration, with retention of the configuration at the P-center.¹⁵ Finally, deprotonation of the triazole ring at the 5-*H* position with *t*-butylmagnesium chloride¹⁶ furnished the P-chirogenic 1,2,3-triazolobenzophospholes **8a-n** by an intramolecular cyclization (Scheme 1).

Scheme 1. Enantioselective synthesis of P-chirogenic 1,2,3-triazolobenzophospholes **8a-n**



After purification by column chromatography and, in some cases by crystallization, the P-chirogenic 1,2,3-triazolobenzophospholes **8a-n** were isolated in satisfactory yields, ranging from 38% to 68% (Figure 2).¹⁷ The best yields were obtained for **8b** ($R' = o\text{-An}$) and **8d** ($R' = p\text{-An}$) with respectively 67% and 68% whereas the compounds **8j** and **8k**, bearing bulky 2,6-dimethoxyphenyl and adamantyl substituents on the triazole ring gave the lower yields (50% and 38%, respectively). Moreover, when the aromatic cycle carried an electron-donating ($R = \text{Me}$) or electron-withdrawing ($R = \text{CF}_3$) group in meta or para position of the phosphorus center, the P-chirogenic 1,2,3-triazolobenzophospholes **8l**, **8m** and **8n** were isolated in 54%, 46% and 57% yields, respectively (Figure 2).

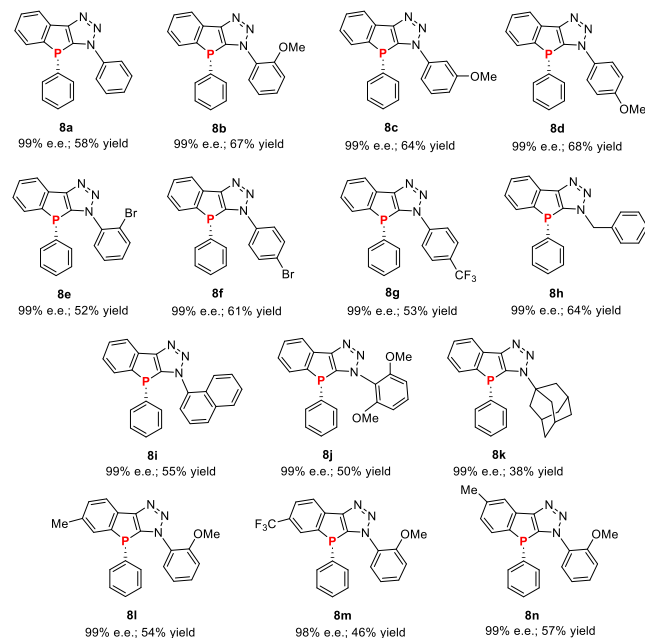


Figure 2. Structures of P-chirogenic 1,2,3-triazolobenzophospholes **8a-n**

The enantiomeric excesses of the 1,2,3-triazolobenzophospholes **8a-n** were determined by HPLC on chiral column (ee > 98%), proving that the two-step reaction sequence proceeds without racemization at the P-center.¹⁸ Moreover, single crystals of **8a** and **8j** were obtained by slow diffusion of hexane into dichloromethane and their structures were established by X-ray analysis (Figure 3).¹⁹

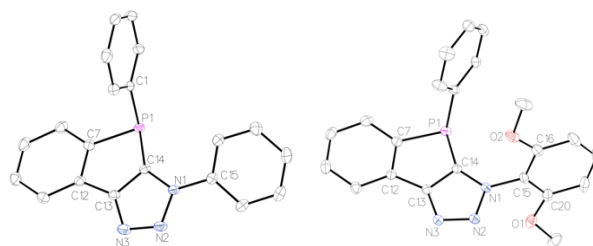
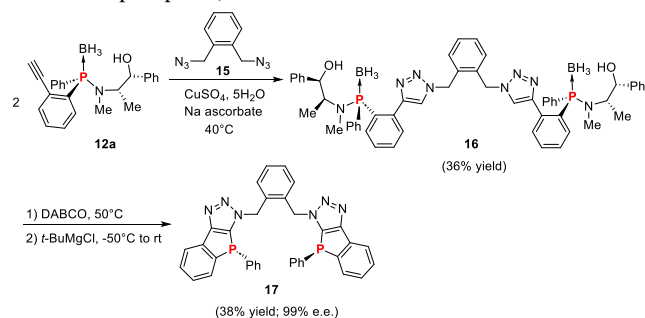


Figure 3. ORTEP view of compound **8a** (left) and **8j** (right). Thermal ellipsoids are drawn at 50% probability plot. H-atoms are omitted for clarity. Selected bond length (Å) and angle (°) in **8a/8j**: C7-P1 = 1.843(2)/1.851(2), C14-P1 = 1.819(2)/1.816(2), C1-P1 = 1.834(2)/1.836(2), C7-P1-C14 = 87.11(8)/86.70(8), C7-P1-C1 = 100.58(7)/102.75(8), C14-P1-C1 = 104.89(7)/103.21(8).

Both structures crystallize in non-centrosymmetric space group ($P1$ and $P2_12_12_1$), and the (R) absolute configuration at the P atom is supported by refinement of the Flack parameter. Consequently, as the borane decomplexation^{10,20} and the N→O phosphinyl migration¹⁵ proceed with retention of configuration at the P-center, the resulting stereochemistry of the P-chirogenic 1,2,3-triazolobenzophospholes **8** from aminophosphine-boranes **11** is consistent with inversion during the intramolecular cyclisation step. Noteworthy, the P-chirogenic 1,2,3-triazolobenzophospholes **8a-n** exhibit a small variation of the ³¹P chemical shifts, from -30.4 to -37.5 ppm, corresponding to cone angles estimated at 120-130°.²¹ Comparison with the cone angle of dibenzophosphole, *i.e.* 145°,^{2b} shows in a lesser contribution to the steric hindrance of the fused-triazolo moiety than the benzo moiety.

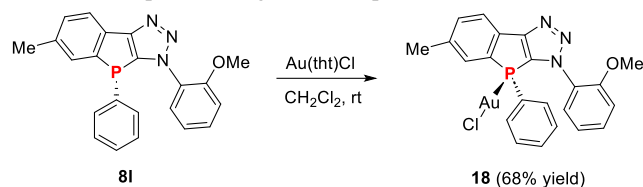
On the other hand, the synthesis of P-chirogenic bis(1,2,3-triazolobenzophosphole) was attempted by double CuAAC reaction of aminophosphine-boranes **12**. To the best of our knowledge, this approach has been applied only in the synthesis of chiral diphosphine dioxides with a bis(triazolyl) bridge.²² Thus, the reaction of bis-azide **15** with two equivalents of aminophosphine-borane **12a**, in presence of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and sodium ascorbate, led to the bis(triazolo)aminophosphine-borane **16** in 36% yield (Scheme 2). After decomplexation of borane and intramolecular phosphinyl N→O migration by heating with DABCO at 50°C, then deprotonation of the triazole ring with *t*-BuMgCl, the free P-chirogenic bis(1,2,3-triazolobenzophosphole) **17** was obtained in 38% yield as pure C_2 -symmetric epimer.²³

Scheme 2. Enantioselective synthesis of P-chirogenic bis(1,2,3-triazolobenzophosphole) **17**



Finally, the coordinative availability of the P-chirogenic 1,2,3-triazolobenzophospholes **8** was tested by the preparation of gold complex **18**. Thus, ligand **8l** reacted with $\text{Au}(\text{tht})\text{Cl}$ (tht = tetrahydrothiophene) in dichloromethane at room temperature to give gold(I)-complex **18** as a white powder in 68% yield (Scheme 3). Analysis by ³¹P NMR spectroscopy shows a clear shift of the phosphole signal (5.6 ppm for **18**) with respect to the free ligand (-32.1 ppm for **8l**), indicating the coordination of the P-atom to the metal center.

Scheme 3. Preparation of gold(I)-complex **18**



Moreover, the crystal structure of gold(I)-complex **18** was elucidated by X-ray crystallography (Figure 4).

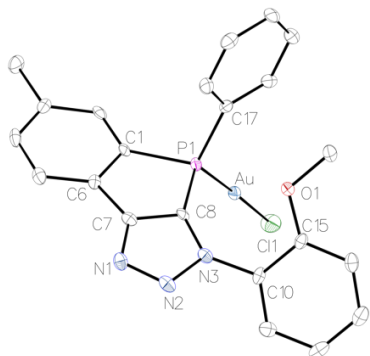


Figure 4. ORTEP view of compound **18**. Thermal ellipsoids are drawn at 50% probability plot. H-atoms are omitted for clarity. Selected bond length (Å) and angle (°): C1-P1 = 1.833(5), C8-P1 = 1.799(5), C17-P1=1.810(4), Au-P1 = 2.221(1), C1-P1-C8 = 89.1(2), C1-P1-C17 = 105.7(2), C8-P1-C17 = 109.7(2), Au-P1-C17 = 116.0(2), Cl1-Au-P1 = 177.9(1).

The ORTEP view shows that the phosphorus atom deviates slightly from a tetrahedral geometry, not quite reaching the expected 109.5° angle due to the C1 and C8 carbon atoms pulling the C1-P1-C8 bond closer to 90° . The Au metal center adopts a classical linear coordination scheme with an angle of $177.9(2)^\circ$.

In summary, we developed the first enantioselective synthesis of P-chirogenic 1,2,3-triazolobenzophospholes. This methodology uses an intramolecular phosphorus rearrangement based on innovative P*(III)-phosphinyl N→O migration followed by an intramolecular cyclisation as key steps. P-chirogenic triazolobenzophospholes were obtained with enantioselectivities up to 99% and their coordination chemistry has been preliminarily illustrated by the preparation of a gold(I)-complex. This synthetic method opens up a promising strategy in the stereoselective synthesis of dissymmetric benzophosphole-based heterocycle derivatives. Further developments of these new chiral 1,2,3-triazolobenzophospholes are currently underway.

EXPERIMENTAL SECTION

General Methods and Materials

All reactions were carried out under an atmosphere of argon using conventional Schlenk techniques. DCM, THF, toluene and pentane were dried using a MBRAUN SPS 800. Hexane was dried using a PureSolv MD5. Chromatographic grade hexane and isopropanol for HPLC analyses were used without further purification. Reagents were commercially available and used as received. $(2R_p,4S,5R)$ -(+)-3,4-dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine **9** was prepared from (-)-ephedrine according to published procedure.¹² 2-[2-(trimethylsilyl)ethynyl]-bromobenzene, 5-methyl-2-[2-(trimethylsilyl)ethynyl]-bromobenzene, 5-trifluoromethyl-2-[2-(trimethylsilyl)ethynyl]-bromobenzene and 4-methyl-2-[2-(trimethylsilyl)ethynyl]-bromobenzene were synthesized from literature procedure.²⁴ All azides,

except benzyl azide and adamantly azide which are purchased from commercial sources, were prepared using procedures described in literature.²⁵ Thin layer chromatography was performed on silica chromagel (60 μm F₂₅₄) and exposed by UV light ($\lambda = 254$ nm) or iodine treatment. Flash chromatography was carried out with the indicated solvents using silica gel 60 (60 AAC, 35-70 μm ; SDS). HPLC analyses were performed on a Shimadzu chromatograph equipped with a UV detector ($\lambda = 254$ nm) using the corresponding commercial Chiralpak or Lux columns. Melting points were measured on a Kofler melting points apparatus. Optical rotation values were determined at 20°C on a Perkin Elmer 241 polarimeter at 589 nm (sodium lamp). Following analyses were performed at the "Plateforme d'Analyses Chimiques de Synthèse Moléculaire de l'Université de Bourgogne". ^1H (and ^1H decoupled), ^{13}C and ^{31}P NMR spectra were recorded on Bruker 400 Avance Neo, Bruker 500 Avance Neo or Bruker 600 Avance HD spectrometers using tetramethylsilane as internal reference for ^1H and ^{13}C spectra, and phosphoric acid (85%) as external reference for ^{31}P NMR. The signals of ^{13}C NMR spectra were allocated using J-mod technology. Data were reported as follows: chemical shift (δ in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet, br.s = broad signal), coupling constants (Hz), integration. High Resolution Mass Spectra (HRMS) were performed under (ESI) conditions on a Bruker Daltonics micro TOF-Q or Thermo Fisher LTQ Orbitrap XL spectrometers. Elemental analyses were carried out on CHNS Thermo Fisher Scientific Flash EA 1112 analyzer.

Synthesis of aminophosphine-borane **11a**

To a solution of $(2R_p,4S,5R)$ -(+)-3,4-dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine **9** (1.0 g, 3.5 mmol) in dry THF (10 mL) was added, under argon at -78°C , a solution of 2-[2-(trimethylsilyl)ethynyl]phenyllithium in THF, previously prepared by reaction between 2-[2-(trimethylsilyl)ethynyl]-bromobenzene (1.33 g, 5.25 mmol) and *sec*-BuLi (1.4 M in cyclohexane) (3.8 mL, 5.25 mmol) in THF (5 mL) at -78°C during one hour. The resulting mixture was stirred until room temperature during 8 hours, then hydrolyzed with a saturated solution of NH_4Cl (20 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic phases were dried over MgSO_4 then filtered and the solvent was removed under vacuum to give the crude product, which was purified by column chromatography on silica gel using CH_2Cl_2 as eluent. White solid; yield 78% (1.252 g); mp $62\text{--}64^\circ\text{C}$ (dec); $R_f = 0.32$ (CH_2Cl_2); $[\alpha]_D^{25} = +59.3$ ($c = 0.4$, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ 7.84-7.79 (m, 1H), 7.66-7.63 (m, 1H), 7.55-7.36 (m, 12H), 5.03-5.01 (m, 1H), 4.48-4.41 (m, 1H), 2.68 (d, $J = 7.5$ Hz, 3H), 1.87 (d, $J = 3.5$ Hz, 1H), 1.31 (d, $J = 6.5$ Hz, 3H), 0.70-1.70 (m, 3H), 0.00 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CDCl_3): δ 143.3, 136.3 (d, $J = 7.7$ Hz), 133.9 (d, $J = 10.6$ Hz), 132.6 (d, $J = 57.7$ Hz), 132.4 (d, $J = 10.6$ Hz), 131.8 (d, $J = 68.3$ Hz), 131.2 (d, $J = 2.2$ Hz), 131.1 (d, $J = 2.5$ Hz), 129.1, 129.0 (d, $J = 10.6$ Hz), 128.8 (d, $J = 10.6$ Hz), 128.2, 127.2 (d, $J = 7.7$ Hz), 127.0, 104.0 (d, $J = 5.1$ Hz), 85.7, 79.6 (d, $J = 4.2$ Hz), 58.9 (d, $J = 10.7$ Hz), 31.8 (d, $J = 3.7$ Hz), 13.9 (d, $J = 2.7$ Hz), 0.0; $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, CDCl_3): δ +72.3 (br.s); HRMS (ESI-TOF) m/z : $[\text{M}-\text{BH}_3+\text{H}]^+$ Calcd for $\text{C}_{27}\text{H}_{33}\text{PNOSi}$ 446.2063; Found 446.2064. Anal. Calcd for $\text{C}_{27}\text{H}_{35}\text{PBNOSi}$: C, 70.58; H, 7.68; N, 3.05. Found C, 70.19; H, 7.65; N, 3.05.

Synthesis of aminophosphine-borane **11b**

To a solution of $(2R_p,4S,5R)$ -(+)-3,4-dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine **9** (0.5 g, 1.75 mmol) in dry THF (10

mL) was added, under argon at -78°C , a solution of 5-methyl-2-[2-(trimethylsilyl)ethynyl]phenyllithium in THF, previously prepared by reaction between 5-methyl-2-[2-(trimethylsilyl)ethynyl]-bromobenzene (0.70 g, 2.63 mmol) and *sec*-BuLi (1.4 M in cyclohexane) (1.9 mL, 2.63 mmol) in THF (5 mL) at -78°C during one hour. The resulting mixture was stirred until room temperature during 8 hours, then hydrolyzed with a saturated solution of NH_4Cl (10 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried over MgSO_4 then filtered and the solvent was removed under vacuum to give the crude product, which was purified by column chromatography on silica gel using CH_2Cl_2 as eluent. White solid; yield 60% (0.497 g); mp $68\text{--}70^{\circ}\text{C}$ (dec); $R_f = 0.41$ (CH_2Cl_2); $[\alpha]_D^{25} = +51.2$ ($c = 0.3$, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.66 (dd, $J = 0.8, 12.7$ Hz, 1H), 7.57–7.38 (m, 11H), 7.32 (br. d, $J = 7.9$ Hz, 1H), 5.04 (t, $J = 4.3$ Hz, 1H), 4.48–4.42 (m, 1H), 2.71 (d, $J = 8.0$ Hz, 3H), 2.49 (s, 3H), 1.89 (d, $J = 3.7$ Hz, 1H), 1.33 (d, $J = 6.8$ Hz, 3H), 0.70–1.70 (m, 3H), 0.00 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CDCl_3): δ 143.2, 139.2 (d, $J = 10.7$ Hz), 136.2 (d, $J = 6.9$ Hz), 134.6 (d, $J = 12.4$ Hz), 132.3 (d, $J = 30.2$ Hz), 132.3 (d, $J = 9.6$ Hz), 132.0 (d, $J = 1.8$ Hz), 131.8 (d, $J = 42.5$ Hz), 131.0 (d, $J = 2.7$ Hz), 129.0, 128.7 (d, $J = 11.0$ Hz), 128.2, 127.0, 124.1 (d, $J = 5.5$ Hz), 104.2 (d, $J = 4.2$ Hz), 102.9, 79.6 (d, $J = 4.3$ Hz), 58.9 (d, $J = 11.1$ Hz), 31.7 (d, $J = 3.5$ Hz), 22.3, 13.1 (d, $J = 2.8$ Hz), 0.0; $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, CDCl_3): δ +72.2 (br.s); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{28}\text{H}_{37}\text{BNOPSiNa}$ 496.2367; Found 496.2362. Anal. Calcd for $\text{C}_{28}\text{H}_{37}\text{BNOPSi}$: C, 71.03; H, 7.88; N, 2.96. Found C, 70.82; H, 7.61; N, 3.11.

Synthesis of aminophosphine-borane 11c

To a solution of $(2R_p,4S,5R)$ -(+)-3,4-dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine **9** (0.5 g, 1.75 mmol) in dry THF (10 mL) was added, under argon at -78°C , a solution of 5-trifluoromethyl-2-[2-(trimethylsilyl)ethynyl]phenyllithium in THF, previously prepared by reaction between 5-trifluoromethyl-2-[2-(trimethylsilyl)ethynyl]-bromobenzene (0.84 g, 2.63 mmol) and *sec*-BuLi (1.4 M in cyclohexane) (1.9 mL, 2.63 mmol) in THF (5 mL) at -78°C during one hour. The resulting mixture was stirred until room temperature during 8 hours, then hydrolyzed with a saturated solution of NH_4Cl (10 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried over MgSO_4 then filtered and the solvent was removed under vacuum to give the crude product, which was purified by column chromatography on silica gel using CH_2Cl_2 as eluent. White solid; yield 64% (0.591 g); mp $58\text{--}60^{\circ}\text{C}$ (dec); $R_f = 0.53$ (CH_2Cl_2); $[\alpha]_D^{25} = +44.2$ ($c = 0.3$, CHCl_3); $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 8.02 (d, $J = 11.4$ Hz, 1H), 7.75–7.74 (m, 2H), 7.55–7.52 (m, 3H), 7.47–7.38 (m, 7H), 5.03 (t, $J = 4.2$ Hz, 1H), 4.48–4.44 (m, 1H), 2.65 (d, $J = 7.5$ Hz, 3H), 1.87 (br.s, 1H), 1.36 (d, $J = 6.7$ Hz, 3H), 0.70–1.70 (m, 3H), 0.00 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CDCl_3): δ 143.4, 136.7 (d, $J = 6.9$ Hz), 134.7 (d, $J = 55.5$ Hz), 132.7 (d, $J = 10.6$ Hz), 131.8 (d, $J = 2.3$ Hz), 131.1–131.0 (m), 130.8 (d, $J = 68.6$ Hz), 130.8 (d, $J = 9.6$ Hz), 130.4–130.3 (m), 129.3, 129.1 (d, $J = 10.9$ Hz), 128.5, 128.0 (br.s), 127.2, 124.5 (q, $J = 271.7$ Hz), 107.9, 102.7 (d, $J = 3.5$ Hz), 79.7 (d, $J = 3.7$ Hz), 59.2 (d, $J = 10.7$ Hz), 31.8 (d, $J = 4.2$ Hz), 13.3 (d, $J = 3.4$ Hz), 0.0; $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, CDCl_3): δ +73.1 (br.s); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{28}\text{H}_{34}\text{BF}_3\text{NOPSiNa}$ 550.2085; Found 550.2099. Anal.

Calcd for $\text{C}_{28}\text{H}_{34}\text{BF}_3\text{NOPSi}$: C, 63.76; H, 6.50; N, 2.66. Found C, 63.48; H, 6.18; N, 2.57.

Synthesis of aminophosphine-borane 11d

To a solution of $(2R_p,4S,5R)$ -(+)-3,4-dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine **9** (0.5 g, 1.75 mmol) in dry THF (10 mL) was added, under argon at -78°C , a solution of 4-methyl-2-[2-(trimethylsilyl)ethynyl]phenyllithium in Et_2O , previously prepared by reaction between 4-methyl-2-[2-(trimethylsilyl)ethynyl]-bromobenzene (0.70 g, 2.63 mmol) and *sec*-BuLi (1.4 M in cyclohexane) (1.9 mL, 2.63 mmol) in Et_2O (5 mL) at -78°C during 30 minutes then at room temperature during two hours. The resulting mixture was stirred until room temperature overnight, then hydrolyzed with a saturated solution of NH_4Cl (10 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried over MgSO_4 then filtered and the solvent was removed under vacuum to give the crude product, which was purified by column chromatography on silica gel using CH_2Cl_2 as eluent. White solid; yield 73% (0.605 g); mp $68\text{--}70^{\circ}\text{C}$ (dec); $R_f = 0.47$ (CH_2Cl_2); $[\alpha]_D^{25} = +48.9$ ($c = 0.3$, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.73 (dd, $J = 8.1, 12.3$ Hz, 1H), 7.56–7.54 (m, 2H), 7.50–7.37 (m, 9H), 7.31 (br. d, $J = 7.9$ Hz, 1H), 5.02 (t, $J = 4.9$ Hz, 1H), 4.49–4.40 (m, 1H), 2.69 (d, $J = 8.2$ Hz, 3H), 2.44 (s, 3H), 1.86 (d, $J = 4.4$ Hz, 1H), 1.30 (d, $J = 7.5$ Hz, 3H), 0.70–1.70 (m, 3H), 0.00 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3): δ 143.2, 141.6 (d, $J = 2.0$ Hz), 136.9 (d, $J = 7.2$ Hz), 134.2 (d, $J = 12.6$ Hz), 132.4 (d, $J = 10.3$ Hz), 132.1 (d, $J = 68.3$ Hz), 131.1 (d, $J = 2.4$ Hz), 130.0 (d, $J = 11.1$ Hz), 129.2 (d, $J = 58.8$ Hz), 129.0, 128.7 (d, $J = 11.1$ Hz), 128.2, 127.0, 126.9, 104.3 (d, $J = 4.6$ Hz), 103.3, 79.6 (d, $J = 4.4$ Hz), 58.8 (d, $J = 10.3$ Hz), 31.7 (d, $J = 4.4$ Hz), 21.6, 13.1 (d, $J = 3.2$ Hz), 0.0; $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, CDCl_3): δ +71.4–71.7 (m); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{28}\text{H}_{37}\text{BNOPSiNa}$ 496.2367; Found 496.2363. Anal. Calcd for $\text{C}_{28}\text{H}_{37}\text{BNOPSi}$: C, 71.03; H, 7.88; N, 2.96. Found C, 70.67; H, 7.96; N, 3.01.

Synthesis of alkyne 12a

To a solution of aminophosphine-borane **11a** (0.92 g, 2 mmol) in a mixture of MeOH/THF (2:1) (15 mL) was added K_2CO_3 (0.28 g, 2 mmol). The mixture was stirred at room temperature during four hours and the solvent was evaporated. Water (10 mL) and CH_2Cl_2 (20 mL) were added and organic phase was separated then washed with water (10 mL) and finally dried over MgSO_4 . After filtration and evaporation of the solvent, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate 3:1 as eluent. White solid; yield 91% (0.710 g); mp $<50^{\circ}\text{C}$ (dec); $R_f = 0.34$ (petroleum ether/ethyl acetate 3:1); $[\alpha]_D^{25} = +72.6$ ($c = 0.3$, CHCl_3); $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.61–7.56 (m, 1H), 7.51–7.49 (m, 1H), 7.37–7.34 (m, 7H), 7.28–7.18 (m, 5H), 4.83 (d, $J = 4.9$ Hz, 1H), 4.30–4.26 (m, 1H), 2.84 (s, 1H), 2.58 (d, $J = 8.0$ Hz, 3H), 1.17 (d, $J = 7.2$ Hz, 3H), 0.60–1.60 (m, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CDCl_3): δ 142.5, 135.6 (d, $J = 6.4$ Hz), 133.3 (d, $J = 11.0$ Hz), 133.0 (d, $J = 59.5$ Hz), 131.8 (d, $J = 10.1$ Hz), 131.2, 130.7 (d, $J = 2.4$ Hz), 130.6 (d, $J = 1.8$ Hz), 128.7 (d, $J = 10.1$ Hz), 128.4, 128.2 (d, $J = 10.4$ Hz), 127.6, 126.3, 125.5 (d, $J = 6.4$ Hz), 85.1, 82.0 (d, $J = 3.9$ Hz), 79.0 (d, $J = 3.9$ Hz), 58.4 (d, $J = 10.3$ Hz), 31.3 (d, $J = 4.2$ Hz), 12.0 (d, $J = 4.3$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, CDCl_3): δ +71.4–71.8 (m); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{24}\text{H}_{27}\text{PBNO}$ 410.1815; Found 410.1821. Anal. Calcd for $\text{C}_{24}\text{H}_{27}\text{PBNO}$: C, 74.43; H, 7.03; N, 3.62. Found C, 74.64; H, 7.35; N, 3.63.

Synthesis of alkyne 12b

To a solution of aminophosphine-borane **11b** (0.47 g, 1 mmol) in a mixture of MeOH/THF (2:1) (7.5 mL) was added K_2CO_3 (0.14 g, 1 mmol). The mixture was stirred at room temperature during four hours and the solvent was evaporated. Water (5 mL) and CH_2Cl_2 (10 mL) were added and organic phase was separated then washed with water (5 mL) and finally dried over $MgSO_4$. After filtration and evaporation of the solvent, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate 2:1 as eluent. White solid; yield 89% (0.356 g); mp 56-58°C (dec); $R_f = 0.55$ (petroleum ether/ethyl acetate 2:1); $[\alpha]_D^{25} = +62.3$ (c = 0.3, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$): δ 7.44-7.31 (m, 7H), 7.27-7.15 (m, 6H), 4.84 (t, $J = 3.8$ Hz, 1H), 4.31-4.24 (m, 1H), 2.77 (s, 1H), 2.58 (d, $J = 7.9$ Hz, 3H), 2.30 (s, 3H), 1.72 (d, $J = 3.2$ Hz, 1H), 1.16 (d, $J = 7.1$ Hz, 3H), 0.50-1.60 (m, 3H); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 142.5, 139.0 (d, $J = 9.5$ Hz), 135.5 (d, $J = 7.1$ Hz), 134.0 (d, $J = 11.2$ Hz), 132.6 (d, $J = 58.9$ Hz), 131.7 (d, $J = 10.6$ Hz), 131.6 (d, $J = 66.5$ Hz), 131.5 (d, $J = 1.8$ Hz), 130.5 (d, $J = 2.4$ Hz), 128.4, 128.1 (d, $J = 10.0$ Hz), 127.6, 126.3, 122.5 (d, $J = 5.8$ Hz), 84.1, 82.1 (d, $J = 3.8$ Hz), 79.0 (d, $J = 3.8$ Hz), 58.4 (d, $J = 9.9$ Hz), 31.3 (d, $J = 3.9$ Hz), 21.7, 12.0 (d, $J = 3.4$ Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ +71.7 (br.s); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{29}BNOPNa$ 424.1972; Found 424.1961. Anal. Calcd for $C_{25}H_{29}BNOP$: C, 74.83; H, 7.28; N, 3.49. Found C, 74.45; H, 6.95; N, 3.60.

Synthesis of alkyne **12c**

To a solution of aminophosphine-borane **11c** (0.43 g, 1 mmol) in a mixture of MeOH/THF (2:1) (7.5 mL) was added K_2CO_3 (0.14 g, 1 mmol). The mixture was stirred at room temperature during four hours and the solvent was evaporated. Water (5 mL) and CH_2Cl_2 (10 mL) were added and organic phase was separated then washed with water (5 mL) and finally dried over $MgSO_4$. After filtration and evaporation of the solvent, the crude product was purified by column chromatography on silica gel using dichloromethane as eluent. White solid; yield 79% (0.360 g); mp 50-52°C (dec); $R_f = 0.41$ (dichloromethane); $[\alpha]_D^{25} = +60.7$ (c = 0.3, $CHCl_3$); 1H NMR (500 MHz, $CDCl_3$): δ 7.94 (d, $J = 11.5$ Hz, 1H), 7.71-7.70 (m, 2H), 7.49-7.43 (m, 5H), 7.40-7.28 (m, 5H), 4.94 (t, $J = 4.2$ Hz, 1H), 4.42-4.35 (m, 1H), 3.07 (s, 1H), 2.66 (d, $J = 7.7$ Hz, 3H), 1.82 (d, $J = 3.5$ Hz, 1H), 1.31 (d, $J = 6.6$ Hz, 3H), 0.70-1.70 (m, 3H); $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): δ 142.3, 136.0 (d, $J = 5.5$ Hz), 134.9 (d, $J = 56.9$ Hz), 131.9 (d, $J = 10.2$ Hz), 131.0 (d, $J = 1.8$ Hz), 130.6 (dq, $J = 8.2, 32.8$ Hz), 130.1 (d, $J = 67.2$ Hz), 129.7-129.5 (m), 129.2 (d, $J = 6.2$ Hz), 128.5, 128.3 (d, $J = 10.0$ Hz), 127.7, 127.3 (br.q, $J = 1.8$ Hz), 126.3, 123.5 (q, $J = 273.4$ Hz), 87.9, 80.8 (d, $J = 3.8$ Hz), 78.9 (d, $J = 3.5$ Hz), 58.5 (d, $J = 11.1$ Hz), 31.2 (d, $J = 4.5$ Hz), 12.1 (d, $J = 3.5$ Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ +72.3-72.6 (m); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{26}BF_3NOPNa$ 478.1689; Found 478.1693. Anal. Calcd for $C_{25}H_{26}BF_3NOP$: C, 65.96; H, 5.76; N, 3.08. Found C, 65.72; H, 5.86; N, 3.00.

Synthesis of alkyne **12d**

To a solution of aminophosphine-borane **11d** (0.47 g, 1 mmol) in a mixture of MeOH/THF (2:1) (7.5 mL) was added K_2CO_3 (0.14 g, 1 mmol). The mixture was stirred at room temperature during four hours and the solvent was evaporated. Water (5 mL) and CH_2Cl_2 (10 mL) were added and organic phase was separated then washed with water (5 mL) and finally dried over $MgSO_4$. After filtration and evaporation of the solvent, the crude product was purified by column chromatography on silica

gel using dichloromethane as eluent. White solid; yield 94% (0.377 g); mp 66-68°C (dec); $R_f = 0.49$ (CH_2Cl_2); $[\alpha]_D^{25} = +67.4$ (c = 0.3, $CHCl_3$); 1H NMR (500 MHz, $CDCl_3$): δ 7.50 (dd, $J = 7.9, 12.0$ Hz, 1H), 7.37-7.31 (m, 6H), 7.26-7.23 (m, 4H), 7.21-7.15 (m, 2H), 4.83 (t, $J = 4.4$ Hz, 1H), 4.31-4.23 (m, 1H), 2.80 (s, 1H), 2.57 (d, $J = 7.8$ Hz, 3H), 2.28 (s, 3H), 1.73 (d, $J = 3.9$ Hz, 1H), 1.15 (d, $J = 6.9$ Hz, 3H), 0.60-1.60 (m, 3H); $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): δ 142.5, 141.1 (d, $J = 1.7$ Hz), 136.2 (d, $J = 6.4$ Hz), 133.5 (d, $J = 11.5$ Hz), 131.8 (d, $J = 9.7$ Hz), 131.7 (d, $J = 66.2$ Hz), 130.5 (d, $J = 1.8$ Hz), 129.6 (d, $J = 11.5$ Hz), 129.2, 128.4, 128.2 (d, $J = 10.6$ Hz), 127.6, 126.4, 125.3 (d, $J = 6.2$ Hz), 84.4, 82.2 (d, $J = 4.1$ Hz), 79.0 (d, $J = 3.8$ Hz), 58.3 (d, $J = 10.7$ Hz), 31.2 (d, $J = 4.0$ Hz), 21.0, 12.1 (d, $J = 3.6$ Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ +70.8-71.2 (m); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{29}BNOPNa$ 424.1972; Found 424.1973. Anal. Calcd for $C_{25}H_{29}BNOP$: C, 74.83; H, 7.28; N, 3.49. Found C, 74.99; H, 7.28; N, 3.48.

General procedure for the synthesis of aminophosphine-borane **13a-k.** To a solution of alkyne **12a** (0.327 g, 0.84 mmol) and azide (0.84 mmol) in DMF (2 mL) was added a solution of $CuSO_4 \cdot 5H_2O$ (13.5 mg, 0.084 mmol) and sodium ascorbate (50.2 mg, 0.252 mmol) in H_2O (2 mL). The solution was stirred at 40°C in an oil bath during 2-3 hours then CH_2Cl_2 (10 mL), NH_4OH (25% in water) (2 mL) and water (5 mL) were added at room temperature. The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (2 x 5 mL). The combined organic phases were dried over $MgSO_4$, filtered and the solvent was evaporated. The crude product was purified by column chromatography on silica gel.

Aminophosphine-borane **13a**

The reaction was performed using phenyl azide (0.100 g). Purification was accomplished by column chromatography on silica gel using petroleum ether/ethyl acetate 1:1 as eluent. White solid; yield 72% (0.306 g); mp 92-94°C (dec); $R_f = 0.46$ (petroleum ether/ethyl acetate 1:1); $[\alpha]_D^{25} = +86.4$ (c = 0.3, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.62-7.52 (m, 11H), 7.26-7.06 (m, 8H), 4.62 (br.s, 1H), 4.07-3.95 (m, 1H), 2.70 (br.s, 1H), 2.63 (d, $J = 8.9$ Hz, 3H), 1.03 (d, $J = 6.8$ Hz, 3H), 0.30-1.40 (m, 3H); $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 146.4 (d, $J = 3.1$ Hz), 142.3, 136.8, 135.1 (d, $J = 10.4$ Hz), 133.4 (d, $J = 7.9$ Hz), 132.8 (d, $J = 7.9$ Hz), 131.7 (d, $J = 10.3$ Hz), 131.2 (d, $J = 2.0$ Hz), 131.2 (d, $J = 60.9$ Hz), 130.7 (d, $J = 2.0$ Hz), 130.2 (d, $J = 64.2$ Hz), 129.6, 128.7, 128.6 (d, $J = 9.3$ Hz), 128.3 (d, $J = 10.3$ Hz), 128.1, 127.1, 125.7, 122.8, 120.7, 77.5, 58.4 (d, $J = 6.3$ Hz), 31.5, 11.7 (d, $J = 4.3$ Hz); $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$): δ +69.2 (br.s); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{32}PBN_4ONa$ 529.2299; Found 529.2311. Anal. Calcd for $C_{30}H_{32}PBN_4O$: C, 71.16; H, 6.37; N, 11.06. Found C, 70.80; H, 6.71; N, 10.77.

Aminophosphine-borane **13b**

The reaction was performed using 2-methoxyphenyl azide (0.125 g). Purification was accomplished by column chromatography on silica gel using petroleum ether/ethyl acetate 3:2 as eluent. Pale yellow solid; yield 40% (0.180 g); mp 82-84°C (dec); $R_f = 0.41$ (petroleum ether/ethyl acetate 3:2); $[\alpha]_D^{25} = +100.8$ (c = 0.3, $CHCl_3$); 1H NMR (500 MHz, $CDCl_3$): δ 8.34 (s, 1H), 7.61-7.58 (m, 2H), 7.53-7.45 (m, 4H), 7.42-7.39 (m, 1H), 7.33-7.23 (m, 4H), 7.15-7.07 (m, 5H), 7.01-6.95 (m, 2H), 4.63 (d, $J = 3.4$ Hz, 1H), 3.96-3.92 (m, 1H), 3.77 (s, 3H), 2.64 (d, $J = 8.7$ Hz, 3H), 0.92 (d, $J = 6.6$ Hz, 3H), 0.40-1.40 (m, 3H); $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): δ 151.0, 145.5 (d, $J = 2.8$ Hz), 142.3, 135.7 (d, $J = 7.8$ Hz), 133.5 (d, $J = 9.0$ Hz), 133.1

(d, $J = 7.8$ Hz), 131.9 (d, $J = 10.3$ Hz), 131.5, 131.1 (d, $J = 2.3$ Hz), 130.6 (d, $J = 2.3$ Hz), 130.2 (d, $J = 65.5$ Hz), 129.9, 128.3 (d, $J = 9.4$ Hz), 128.2 (d, $J = 10.5$ Hz), 128.1, 127.0, 126.4, 126.1, 125.7, 125.4, 121.0, 112.2, 77.4, 58.3 (d, $J = 4.9$ Hz), 55.8, 31.8, 11.3 (d, $J = 4.7$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, CDCl_3): $\delta +69.3$ (br.s); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{31}\text{H}_{34}\text{PBN}_4\text{O}_2\text{Na}$ 559.2405; Found 559.2410.

Aminophosphine-borane 13c

The reaction was performed using 3-methoxyphenyl azide (0.125 g). Purification was accomplished by column chromatography on silica gel using petroleum ether/ethyl acetate 2:1 as eluent. White solid; yield 28% (0.126 g); mp 64–66°C (dec); $R_f = 0.19$ (petroleum ether/ethyl acetate 2:1); $[\alpha]_D^{25} = +48.5$ ($c = 0.3$, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 8.00 (s, 1H), 7.62–7.59 (m, 1H), 7.55–7.51 (m, 2H), 7.45–7.39 (m, 5H), 7.26–7.21 (m, 3H), 7.16–7.02 (m, 5H), 6.90 (d, $J = 9.0$ Hz, 2H), 4.62–4.61 (m, 1H), 4.01–3.96 (m, 1H), 3.79 (s, 3H), 2.63 (d, $J = 8.9$ Hz, 3H), 1.03 (d, $J = 6.2$ Hz, 3H), 0.30–1.40 (m, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ 159.8, 146.3, 142.3, 135.2 (d, $J = 10.9$ Hz), 133.4 (d, $J = 7.3$ Hz), 132.8 (d, $J = 9.1$ Hz), 131.7 (d, $J = 10.9$ Hz), 131.2 (d, $J = 60.1$ Hz), 131.2, 130.6, 130.2 (d, $J = 65.1$ Hz), 130.2, 128.5 (d, $J = 9.1$ Hz), 128.2 (d, $J = 10.9$ Hz), 128.1, 127.1, 125.7, 123.0, 122.4, 114.7, 77.4, 58.4 (d, $J = 4.0$ Hz), 55.6, 31.6, 11.7; $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): $\delta +69.2$ (br.s); HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{31}\text{H}_{35}\text{PBN}_4\text{O}_2$ 537.2585; Found 537.2563. Anal. Calcd for $\text{C}_{31}\text{H}_{34}\text{PBN}_4\text{O}_2$: C, 69.41; H, 6.39; N, 10.44. Found C, 69.03; H, 6.40; N, 10.38.

Aminophosphine-borane 13d

The reaction was performed using 4-methoxyphenyl azide (0.125 g). Purification was accomplished by column chromatography on silica gel using petroleum ether/ethyl acetate 1:1 as eluent. White solid; yield 70% (0.315 g); mp 88–90°C (dec); $R_f = 0.51$ (petroleum ether/ethyl acetate 1:1); $[\alpha]_D^{25} = +88.6$ ($c = 0.3$, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 8.00 (s, 1H), 7.61–7.39 (m, 8H), 7.25–7.08 (m, 8H), 6.90 (d, $J = 9.0$ Hz, 2H), 4.62 (d, $J = 4.0$ Hz, 1H), 4.02–3.97 (m, 1H), 3.79 (s, 3H), 2.63 (d, $J = 8.9$ Hz, 3H), 1.03 (d, $J = 6.0$ Hz, 3H), 0.30–1.40 (m, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3): δ 159.8, 146.3 (d, $J = 3.0$ Hz), 142.3, 135.3 (d, $J = 9.9$ Hz), 133.4 (d, $J = 7.8$ Hz), 132.8 (d, $J = 7.8$ Hz), 131.7 (d, $J = 10.2$ Hz), 131.3 (d, $J = 60.6$ Hz), 131.2 (d, $J = 1.7$ Hz), 130.6 (d, $J = 2.0$ Hz), 130.3, 130.2 (d, $J = 64.5$ Hz), 128.5 (d, $J = 8.3$ Hz), 128.3 (d, $J = 9.9$ Hz), 128.1, 127.1, 125.7, 123.0, 122.4, 114.7, 77.4, 58.4 (d, $J = 6.0$ Hz), 55.6, 31.6, 11.7 (d, $J = 4.2$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): $\delta +69.1$ (br.s); HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{31}\text{H}_{35}\text{PBN}_4\text{O}_2$ 537.2585; Found 537.2559. Anal. Calcd for $\text{C}_{31}\text{H}_{34}\text{PBN}_4\text{O}_2$: C, 69.41; H, 6.39; N, 10.44. Found C, 69.35; H, 6.72; N, 10.09.

Aminophosphine-borane 13e

The reaction was performed using 2-bromophenyl azide (0.166 g). Purification was accomplished by column chromatography on silica gel using petroleum ether/ethyl acetate 2:1 as eluent. Pale yellow solid; yield 73% (0.270 g); mp 88–90°C (dec); $R_f = 0.61$ (petroleum ether/ethyl acetate 2:1); $[\alpha]_D^{25} = +99.8$ ($c = 0.3$, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 8.05 (s, 1H), 7.66–7.61 (m, 2H), 7.56–7.50 (m, 2H), 7.47–7.25 (m, 9H), 7.16–7.06 (m, 5H), 4.62 (br.s, 1H), 3.97–3.92 (m, 1H), 3.07 (br.s, 1H), 2.69 (d, $J = 9.4$ Hz, 3H), 1.09 (d, $J = 6.9$ Hz, 3H), 0.20–1.30 (m, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CDCl_3): δ 145.9 (d, $J = 4.2$ Hz), 142.2, 136.3, 135.2 (d, $J = 10.8$ Hz), 133.8, 133.5 (d, $J = 7.5$ Hz), 133.2 (d, $J = 7.5$ Hz), 131.7 (d, $J = 9.7$ Hz), 131.3, 131.1,

130.6 (d, $J = 1.5$ Hz), 130.6 (d, $J = 63.5$ Hz), 128.6 (d, $J = 8.6$ Hz), 128.4 (d, $J = 10.8$ Hz), 128.3 (d, $J = 3.2$ Hz), 128.1, 127.0, 126.2, 125.7, 118.5, 77.1, 58.4 (d, $J = 4.1$ Hz), 31.8 (d, $J = 1.5$ Hz), 11.9 (d, $J = 4.1$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (162.0 MHz, CDCl_3): $\delta +69.5$ (br.s); HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{30}\text{H}_{32}\text{PBN}_4\text{OBr}$ 585.1585; Found 585.1590. Anal. Calcd for $\text{C}_{30}\text{H}_{31}\text{PBN}_4\text{OBr}$: C, 61.56; H, 5.34; N, 9.57. Found C, 61.64; H, 5.73; N, 9.32.

Aminophosphine-borane 13f

The reaction was performed using 4-bromophenyl azide (0.166 g). Purification was accomplished by column chromatography on silica gel using petroleum ether/ethyl acetate 3:1 as eluent. White solid; yield 73% (0.270 g); mp 84–86°C (dec); $R_f = 0.28$ (petroleum ether/ethyl acetate 3:1); $[\alpha]_D^{25} = +64.7$ ($c = 0.3$, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ 8.06 (s, 1H), 7.62–7.59 (m, 1H), 7.56–7.52 (m, 4H), 7.47–7.39 (m, 4H), 7.22–7.11 (m, 9H), 4.62 (d, $J = 3.8$ Hz, 1H), 4.03–3.98 (m, 1H), 2.61 (d, $J = 8.6$ Hz, 3H), 1.04 (d, $J = 7.3$ Hz, 3H), 0.40–1.40 (m, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ 146.6 (d, $J = 3.1$ Hz), 142.2, 135.7, 134.7 (d, $J = 10.4$ Hz), 133.4 (d, $J = 8.1$ Hz), 132.8 (2s), 131.7 (d, $J = 10.4$ Hz), 131.2, 130.8, 130.7, 130.1 (d, $J = 64.8$ Hz), 128.7 (d, $J = 9.3$ Hz), 128.3 (d, $J = 10.4$ Hz), 128.2, 127.2, 125.8, 122.7, 122.4, 122.0, 77.5, 58.4 (d, $J = 6.1$ Hz), 31.5, 11.7 (d, $J = 4.6$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, CDCl_3): $\delta +69.0$ (br.s); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{30}\text{H}_{31}\text{PBN}_4\text{OBrNa}$ 607.1394; Found 607.1404. Anal. Calcd for $\text{C}_{30}\text{H}_{31}\text{PBN}_4\text{OBr}$: C, 61.56; H, 5.34; N, 9.57. Found C, 61.22; H, 5.63; N, 9.27.

Aminophosphine-borane 13g

The reaction was performed using 4-(trifluoromethyl)phenyl azide (0.158 g). Purification was accomplished by column chromatography on silica gel using petroleum ether/ethyl acetate 2:1 as eluent. White solid; yield 52% (0.251 g); mp 68–70°C (dec); $R_f = 0.32$ (petroleum ether/ethyl acetate 2:1); $[\alpha]_D^{25} = +64.7$ ($c = 0.3$, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ 8.24 (s, 1H), 7.80–7.75 (m, 5H), 7.67–7.63 (m, 2H), 7.58–7.50 (m, 3H), 7.33–7.18 (m, 8H), 4.73 (t, $J = 3.9$ Hz, 1H), 4.14–4.10 (m, 1H), 2.71 (d, $J = 8.5$ Hz, 3H), 2.58 (br.s, 1H), 1.15 (d, $J = 6.5$ Hz, 3H), 0.60–1.50 (m, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CDCl_3): δ 146.8 (d, $J = 2.8$ Hz), 142.2, 139.1, 134.5 (d, $J = 9.2$ Hz), 133.4 (d, $J = 7.7$ Hz), 132.8 (d, $J = 7.7$ Hz), 131.7 (d, $J = 9.9$ Hz), 131.2 (d, $J = 2.2$ Hz), 130.8, 130.7 (d, $J = 1.7$ Hz), 130.7 (q, $J = 33.2$ Hz), 130.2 (d, $J = 64.2$ Hz), 128.8 (d, $J = 9.2$ Hz), 128.3 (d, $J = 10.8$ Hz), 128.2, 127.3, 127.0 (q, $J = 3.7$ Hz), 125.7, 123.6 (q, $J = 272.5$ Hz), 122.7, 120.5, 77.6, 58.4 (d, $J = 6.3$ Hz), 31.4, 11.8 (d, $J = 4.5$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, CDCl_3): $\delta +69.0$ (br.s); HRMS (ESI-TOF) m/z : $[\text{M}-\text{BH}_3+\text{Na}]^+$ Calcd for $\text{C}_{31}\text{H}_{28}\text{PF}_3\text{N}_4\text{ONa}$ 583.1845; Found 583.1840. Anal. Calcd for $\text{C}_{31}\text{H}_{31}\text{PF}_3\text{N}_4\text{O}$: C, 64.82; H, 5.44; N, 9.75. Found C, 64.61; H, 5.84; N, 9.84.

Aminophosphine-borane 13h

The reaction was performed using benzyl azide (0.112 g). Purification was accomplished by column chromatography on silica gel using petroleum ether/ethyl acetate 2:1 as eluent. White solid; yield 54% (0.236 g); mp 82–84°C (dec); $R_f = 0.21$ (petroleum ether/ethyl acetate 2:1); $[\alpha]_D^{25} = +96.8$ ($c = 0.3$, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 7.58 (s, 1H), 7.47–7.38 (m, 6H), 7.29–7.05 (m, 13H), 5.30 (AB syst., $J = 14.6$ Hz, 2H), 4.57 (t, $J = 3.4$ Hz, 1H), 3.85–3.80 (m, 1H), 3.15 (br.s, 1H), 2.65 (d, $J = 9.7$ Hz, 3H), 0.95 (d, $J = 7.3$ Hz, 3H), 0.20–1.30 (m, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3): δ 146.4 (d, $J = 3.5$ Hz), 142.2, 135.8 (d, $J = 10.5$ Hz), 134.2, 133.5 (d, $J = 7.0$ Hz), 132.9

(d, $J = 7.9$ Hz), 131.8 (d, $J = 61.5$ Hz), 131.6 (d, $J = 9.7$ Hz), 131.1 (d, $J = 2.6$ Hz), 130.5 (d, $J = 1.8$ Hz), 130.4 (d, $J = 63.2$ Hz), 129.1, 128.7, 128.4, 128.3 (d, $J = 8.9$ Hz), 128.2 (d, $J = 10.2$ Hz), 128.1, 127.0, 125.7, 124.2, 77.1, 58.3 (d, $J = 4.4$ Hz), 54.1, 31.9 (d, $J = 2.0$ Hz), 11.5 (d, $J = 4.3$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ +69.4 (br.s); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{31}\text{H}_{34}\text{PBN}_4\text{ONa}$ 543.2455; Found 543.2441. Anal. Calcd for $\text{C}_{31}\text{H}_{34}\text{PBN}_4\text{O}$: C, 71.55; H, 6.59; N, 10.77. Found C, 71.35; H, 6.42; N, 10.59.

Aminophosphine-borane 13i

The reaction was performed using α -naphthyl azide (0.142 g). Purification was accomplished by column chromatography on silica gel using petroleum ether/ethyl acetate 1:1 as eluent. White solid; yield 49% (0.229 g); mp 112-114°C (dec); $R_f = 0.44$ (petroleum ether/ethyl acetate 1:1); $[\alpha]_D^{25} = +112.1$ ($c = 0.3$, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 8.17 (s, 1H), 8.02 (d, $J = 8.2$ Hz, 1H), 7.96 (d, $J = 7.2$ Hz, 1H), 7.79-7.76 (m, 1H), 7.69-7.53 (m, 9H), 7.47-7.36 (m, 4H), 7.27-7.17 (m, 5H), 4.75 (t, $J = 3.9$ Hz, 1H), 4.11-4.06 (m, 1H), 3.24 (br.s, 1H), 2.82 (d, $J = 9.2$ Hz, 3H), 1.21 (d, $J = 6.4$ Hz, 3H), 0.40-1.50 (m, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ 146.2 (d, $J = 2.6$ Hz), 142.2, 135.4 (d, $J = 11.5$ Hz), 134.1, 133.6 (d, $J = 6.5$ Hz), 133.4, 133.1 (d, $J = 8.6$ Hz), 131.7 (d, $J = 10.0$ Hz), 131.6, 131.3, 131.0 (d, $J = 63.8$ Hz), 130.7, 130.3, 128.6 (d, $J = 8.3$ Hz), 128.4 (d, $J = 10.0$ Hz), 128.2, 128.1, 127.8, 127.0, 126.6, 125.7, 124.9, 123.6, 122.7, 77.1, 58.4 (d, $J = 4.8$ Hz), 31.7, 11.9 (d, $J = 3.4$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ +69.5 (br.s); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{34}\text{H}_{34}\text{PBN}_4\text{ONa}$ 579.2455; Found 579.2435. Anal. Calcd for $\text{C}_{34}\text{H}_{34}\text{PBN}_4\text{O}$: C, 73.39; H, 6.16; N, 10.07. Found C, 73.07; H, 5.78; N, 9.86.

Aminophosphine-borane 13j

The reaction was performed using 2,6-(dimethoxy)phenyl azide (0.150 g). Purification was accomplished by column chromatography on silica gel using petroleum ether/ethyl acetate 1:2 as eluent. White solid; yield 60% (0.285 g); mp 120-122°C (dec); $R_f = 0.49$ (petroleum ether/ethyl acetate 1:2); $[\alpha]_D^{25} = +110.8$ ($c = 0.3$, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ 7.85 (s, 1H), 7.63-7.49 (m, 4H), 7.42-7.28 (m, 6H), 7.15-7.07 (m, 5H), 6.56 (d, $J = 9.0$ Hz, 2H), 4.65 (t, $J = 3.6$ Hz, 1H), 3.85-3.82 (m, 1H), 3.63 (s, 6H), 3.15 (br.s, 1H), 2.75 (d, $J = 9.2$ Hz, 3H), 0.95 (d, $J = 6.9$ Hz, 3H), 0.50-1.30 (m, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CDCl_3): δ 155.7, 145.1 (d, $J = 3.3$ Hz), 142.4, 136.2 (d, $J = 10.5$ Hz), 133.7 (d, $J = 8.1$ Hz), 133.5 (d, $J = 8.1$ Hz), 132.8 (d, $J = 60.5$ Hz), 131.8 (d, $J = 10.5$ Hz), 131.2, 131.0 (d, $J = 1.3$ Hz), 130.6 (d, $J = 62.8$ Hz), 130.5 (d, $J = 2.3$ Hz), 128.3 (d, $J = 10.5$ Hz), 128.1, 128.0, 127.5, 126.8, 125.7, 115.2, 104.3, 77.1, 58.3 (d, $J = 3.3$ Hz), 56.0, 32.3 (d, $J = 2.2$ Hz), 11.0 (d, $J = 3.5$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, CDCl_3): δ +70.2 (br.s); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{32}\text{H}_{36}\text{BN}_4\text{O}_3\text{PNa}$ 589.2510; Found 589.2485. Anal. Calcd for $\text{C}_{32}\text{H}_{36}\text{BN}_4\text{O}_3\text{P}$: C, 67.85; H, 6.41; N, 9.89. Found C, 67.48; H, 6.67; N, 9.74.

Aminophosphine-borane 13k

The reaction was performed using 1-adamantyl azide (0.149 g). Purification was accomplished by column chromatography on silica gel using dichloromethane/acetone 15:1 as eluent. White solid; yield 43% (0.204 g); mp 88-90°C (dec); $R_f = 0.29$ (dichloromethane/acetone 15:1); $[\alpha]_D^{25} = +88.0$ ($c = 0.3$, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ 7.84 (s, 1H), 7.66-7.57 (m, 3H), 7.51-7.48 (m, 3H), 7.41-7.38 (m, 1H), 7.35-7.32 (m, 2H), 7.26-7.23 (m, 2H), 7.21-7.18 (m, 3H), 4.70 (t, $J = 4.0$ Hz, 1H), 4.05-4.02 (m, 1H), 3.29 (br.s, 1H), 2.71 (d, $J = 9.4$ Hz, 3H), 2.24

(br.s, 3H), 2.16-2.10 (m, 6H), 1.81-1.75 (m, 6H), 1.15 (d, $J = 7.1$ Hz, 3H), 0.40-1.40 (m, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CDCl_3): δ 144.9 (d, $J = 2.9$ Hz), 142.4, 136.3 (d, $J = 10.6$ Hz), 133.3 (d, $J = 8.4$ Hz), 132.8 (d, $J = 8.4$ Hz), 131.7 (d, $J = 10.0$ Hz), 131.3 (d, $J = 62.4$ Hz), 131.1 (d, $J = 1.4$ Hz), 130.4 (d, $J = 1.6$ Hz), 130.0 (d, $J = 63.7$ Hz), 128.3 (d, $J = 10.0$ Hz), 128.2, 128.1, 127.0, 125.7, 121.0, 77.0, 59.5, 58.3 (d, $J = 4.6$ Hz), 42.8, 35.9, 31.6 (d, $J = 1.6$ Hz), 29.4, 11.9 (d, $J = 3.7$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, CDCl_3): δ +69.5 (br.s); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{34}\text{H}_{42}\text{BN}_4\text{OPNa}$ 587.3081; Found 587.3065.

Synthesis of aminophosphine-borane 13l

To a solution of alkyne **12b** (0.428 g, 1.07 mmol) and 2-methoxyphenyl azide (0.160 g, 1.07 mmol) in DMF (2.5 mL) was added a solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (17 mg, 0.107 mmol) and sodium ascorbate (64 mg, 0.321 mmol) in H_2O (2.5 mL). The solution was stirred at 40°C in an oil bath during 2-3 hours then CH_2Cl_2 (15 mL), NH_4OH (25% in water) (3 mL) and water (10 mL) were added at room temperature. The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic phases were dried over MgSO_4 , filtered and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate 3:2 as eluent. White solid; yield 60% (0.353 g); mp 74-76°C (dec); $R_f = 0.42$ (ether/ethyl acetate 3:2); $[\alpha]_D^{25} = +94.7$ ($c = 0.3$, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ 8.40 (s, 1H), 7.68 (dd, $J = 1.6, 7.7$ Hz, 1H), 7.61-7.57 (m, 3H), 7.43-7.32 (m, 6H), 7.25-7.18 (m, 5H), 7.10-7.04 (m, 2H), 4.74 (t, $J = 3.6$ Hz, 1H), 4.05-4.02 (m, 1H), 3.86 (s, 3H), 2.77 (br.s, 1H), 2.73 (d, $J = 8.7$ Hz, 3H), 2.40 (s, 3H), 1.01 (d, $J = 7.1$ Hz, 3H), 0.60-1.40 (m, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CDCl_3): δ 151.0, 145.5 (d, $J = 3.3$ Hz), 142.4, 138.2 (d, $J = 8.2$ Hz), 133.9 (d, $J = 8.7$ Hz), 133.1 (d, $J = 8.7$ Hz), 132.7 (d, $J = 9.8$ Hz), 131.9 (d, $J = 10.9$ Hz), 131.8, 131.8 (d, $J = 60.9$ Hz), 130.6 (d, $J = 2.2$ Hz), 129.9, 129.8 (d, $J = 65.2$ Hz), 128.2 (d, $J = 10.9$ Hz), 128.1, 127.0, 126.3, 126.1, 125.7, 125.4, 121.0, 112.1, 77.4, 58.3 (d, $J = 5.5$ Hz), 55.8, 31.7, 21.5, 11.3 (d, $J = 4.9$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, CDCl_3): δ +69.2 (br.s); HRMS (ESI-TOF) m/z : $[\text{M}-\text{BH}_3+\text{Na}]^+$ Calcd for $\text{C}_{32}\text{H}_{33}\text{N}_4\text{O}_2\text{PNa}$ 559.2233; Found 559.2235. Anal. Calcd for $\text{C}_{32}\text{H}_{36}\text{BN}_4\text{O}_2\text{P}$: C, 69.83; H, 6.59; N, 10.18. Found C, 69.45; H, 6.60; N, 9.88.

Synthesis of aminophosphine-borane 13m

To a solution of alkyne **12c** (0.487 g, 1.07 mmol) and 2-methoxyphenyl azide (0.160 g, 1.07 mmol) in DMF (2.5 mL) was added a solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (34 mg, 0.214 mmol) and sodium ascorbate (128 mg, 0.642 mmol) in H_2O (2.5 mL). The solution was stirred at 40°C during 2-3 hours then CH_2Cl_2 (15 mL), NH_4OH (25% in water) (3 mL) and water (10 mL) were added at room temperature. The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic phases were dried over MgSO_4 , filtered and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using dichloromethane/acetone 15:1 as eluent. White solid; yield 38% (0.246 g); mp 80-82°C (dec); $R_f = 0.54$ (dichloromethane/acetone 15:1); $[\alpha]_D^{25} = +73.3$ ($c = 0.3$, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ 8.47 (s, 1H), 7.92-7.87 (m, 3H), 7.59 (d, $J = 7.5$ Hz, 1H), 7.50-7.37 (m, 4H), 7.30-7.20 (m, 7H), 7.09-7.04 (m, 2H), 4.78 (br.s, 1H), 4.19 (br.s, 1H), 3.86 (s, 3H), 2.63 (d, $J = 8.0$ Hz, 3H), 2.33 (br.s, 1H), 1.12 (d, $J = 6.8$ Hz, 3H), 0.60-1.60 (m, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CDCl_3): δ 150.8, 144.2 (d, $J = 2.4$ Hz), 144.2, 139.0 (d, $J = 9.4$ Hz), 133.5 (d, $J = 7.9$ Hz),

131.0 (d, $J = 1.9$ Hz), 130.5 (qd, $J = 9.1, 32.9$ Hz), 130.1-130.0 (m), 129.7 (d, $J = 61.7$ Hz), 128.3 (d, $J = 10.5$ Hz), 128.2, 127.6 (br.s), 127.3, 126.9, 125.8, 125.7, 125.2, 123.8 (q, $J = 271.6$ Hz), 121.0, 112.1, 78.0, 58.5 (d, $J = 7.3$ Hz), 55.8, 31.2, 11.5 (d, $J = 4.6$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, CDCl_3): $\delta +70.2$ (br.s); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{32}\text{H}_{33}\text{BF}_3\text{N}_4\text{O}_2\text{PNa}$ 627.2278; Found 627.2275.

Synthesis of aminophosphine-borane 13n

To a solution of alkyne **12d** (0.428 g, 1.07 mmol) and 2-methoxyphenyl azide (0.160 g, 1.07 mmol) in DMF (2.5 mL) was added a solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (17 mg, 0.107 mmol) and sodium ascorbate (64 mg, 0.321 mmol) in H_2O (2.5 mL). The solution was stirred at 40°C in an oil bath during 2-3 hours then CH_2Cl_2 (15 mL), NH_4OH (25% in water) (3 mL) and water (10 mL) were added at room temperature. The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic phases were dried over MgSO_4 , filtered and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate 3:2 as eluent. White solid; yield 60% (0.353 g); mp $98-100^\circ\text{C}$ (dec); $R_f = 0.34$ (ether/ethyl acetate 3:2); $[\alpha]_D^{25} = +102.2$ ($c = 0.3$, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ 8.33 (s, 1H), 7.58 (dd, $J = 1.8, 7.9$ Hz, 1H), 7.51-7.46 (m, 2H), 7.42 (dd, $J = 1.3, 3.6$ Hz, 1H), 7.36-7.19 (m, 6H), 7.14-7.05 (m, 5H), 7.00-6.94 (m, 2H), 4.64 (br.s, 1H), 3.97-3.92 (m, 1H), 3.75 (s, 3H), 2.68 (br.s, 1H), 2.61 (d, $J = 8.8$ Hz, 3H), 2.36 (s, 3H), 0.89 (d, $J = 6.9$ Hz, 3H), 0.40-1.40 (m, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3): δ 151.0, 145.6 (d, $J = 3.0$ Hz), 142.4, 141.5 (d, $J = 1.5$ Hz), 135.5 (d, $J = 9.8$ Hz), 133.8 (d, $J = 8.8$ Hz), 133.6 (d, $J = 8.8$ Hz), 132.0 (d, $J = 59.5$ Hz), 131.9 (d, $J = 9.8$ Hz), 130.5 (d, $J = 2.0$ Hz), 129.9, 129.0 (d, $J = 9.8$ Hz), 128.2 (d, $J = 10.7$ Hz), 128.1, 127.1, 127.0, 126.3, 126.2 (d, $J = 31.2$ Hz), 125.7, 125.4, 121.0, 112.2, 77.5, 58.3 (d, $J = 5.8$ Hz), 55.8, 31.7, 21.2, 11.3 (d, $J = 5.0$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, CDCl_3): $\delta +68.8$ (br.s); HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{32}\text{H}_{37}\text{BN}_4\text{O}_2\text{P}$ 551.2742; Found 551.2732. Anal. Calcd for $\text{C}_{32}\text{H}_{36}\text{BN}_4\text{O}_2\text{P}$: C, 69.83; H, 6.59; N, 10.18. Found C, 69.71; H, 6.59; N, 9.83.

General procedure for the synthesis of P-chirogenic 1,2,3-triazolobenzophospholes 8a-k. To a solution of aminophosphine-borane **13a-k** (0.5 mmol) in toluene (4 mL) was added DABCO (0.168 g, 1.5 mmol) and the resulting solution was stirred under argon atmosphere at 50°C overnight in an oil bath. At room temperature, THF (2 mL) was added then the solution was cooled to -50°C . $t\text{-BuMgCl}$ (2M in THF) (0.75 mL, 1.5 mmol) was slowly added and the reaction mixture was stirred until room temperature during five-six hours. Saturated solution of NH_4Cl (5 mL) and CH_2Cl_2 (10 mL) were added and the phases were separated. Aqueous phase was extracted with CH_2Cl_2 (2 x 5 mL) then the combined organic phases were dried over MgSO_4 , filtered and the solvent was evaporated. The crude product was purified by column chromatography on silica gel and recrystallization in some cases.

1,2,3-triazolobenzophosphole 8a

Purification was accomplished by column chromatography on silica gel using petroleum ether/ethyl acetate 3:1 as eluent and recrystallization in CH_2Cl_2 /hexane. White solid; yield 58% (0.095 g); mp $170-172^\circ\text{C}$; $R_f = 0.61$ (petroleum ether/ethyl acetate 3:1); $[\alpha]_D^{25} = -83.9$ ($c = 0.3$, CHCl_3); ^1H NMR (500 MHz, CD_2Cl_2): δ 8.10 (d, $J = 7.5$ Hz, 1H), 7.77 (d, $J = 8.0$ Hz, 2H), 7.62 (t, $J = 7.0$ Hz, 1H), 7.57 (t, $J = 7.5$ Hz, 1H), 7.52-7.49 (m, 2H), 7.45-7.32 (m, 7H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CD_2Cl_2):

δ 159.7 (d, $J = 7.1$ Hz), 145.6 (d, $J = 7.2$ Hz), 138.0 (d, $J = 17.7$ Hz), 137.5, 133.6 (d, $J = 22.1$ Hz), 131.1 (d, $J = 15.4$ Hz), 131.0, 130.8 (2s), 129.7, 129.4, 129.2 (d, $J = 7.7$ Hz), 128.4, 127.5 (d, $J = 7.7$ Hz), 121.2, 120.1 (d, $J = 3.6$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, CD_2Cl_2): $\delta -32.9$ (s); HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{15}\text{N}_3\text{P}$ 328.0998; Found 328.1004. Anal. Calcd for $\text{C}_{20}\text{H}_{14}\text{N}_3\text{P}$: C, 73.39; H, 4.31; N, 12.84. Found C, 73.79; H, 4.38; N, 12.91. The enantiomeric excess (99%) was determined by HPLC (Chiralpak IA, hexane/isopropanol = 95/5, flow rate = 1.0 mL/min, $\lambda = 254$ nm) $t_R = 18.9$ min (*R*), 21.8 min (*S*). Suitable crystals for X-ray structure were obtained by slow diffusion of hexane into dichloromethane. Structure of **8a** and crystallographic data were reported in SI.

1,2,3-triazolobenzophosphole 8b

Purification was accomplished by column chromatography on silica gel using petroleum ether/ethyl acetate 2:1 as eluent. White solid; yield 67% (0.120 g); mp $130-132^\circ\text{C}$; $R_f = 0.38$ (petroleum ether/ethyl acetate 2:1); $[\alpha]_D^{25} = -95.2$ ($c = 0.3$, CHCl_3); ^1H NMR (500 MHz, CD_2Cl_2): δ 7.94 (d, $J = 7.4$ Hz, 1H), 7.51 (dd, $J = 1.7, 8.3$ Hz, 1H), 7.45-7.39 (m, 2H), 7.36-7.33 (m, 1H), 7.24-7.14 (m, 6H), 6.97 (d, $J = 7.8$ Hz, 1H), 6.93 (d, $J = 8.3$ Hz, 1H), 3.40 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CD_2Cl_2): δ 158.8 (d, $J = 6.7$ Hz), 152.0, 146.3 (d, $J = 6.7$ Hz), 141.5 (d, $J = 15.7$ Hz), 133.9, 133.1, 132.9, 132.5 (d, $J = 16.2$ Hz), 130.8, 130.6 (2s), 130.0, 129.0, 128.8 (d, $J = 8.7$ Hz), 127.2 (d, $J = 7.9$ Hz), 126.5, 126.2, 121.1, 120.7, 112.0, 55.2; $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, CD_2Cl_2): $\delta -32.0$ (s); HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{17}\text{N}_3\text{OP}$ 358.1104; Found 358.1092. Anal. Calcd for $\text{C}_{21}\text{H}_{16}\text{N}_3\text{OP}$: C, 70.58; H, 4.51; N, 11.76. Found C, 70.19; H, 4.59; N, 11.53. The enantiomeric excess (99%) was determined by HPLC (Chiralpak IA, hexane/isopropanol = 95/5, flow rate = 1 mL/min, $\lambda = 254$ nm) $t_R = 31.5$ min (*R*), 36.1 min (*S*).

1,2,3-triazolobenzophosphole 8c

Purification was accomplished by column chromatography on silica gel using petroleum ether/ethyl acetate 3:1 as eluent. White solid; yield 64% (0.114 g); mp $138-140^\circ\text{C}$; $R_f = 0.40$ (petroleum ether/ethyl acetate 3:1); $[\alpha]_D^{25} = -113.0$ ($c = 0.3$, CHCl_3); ^1H NMR (500 MHz, CD_2Cl_2): δ 7.95 (d, $J = 8.1$ Hz, 1H), 7.53-7.41 (m, 4H), 7.29-7.19 (m, 6H), 6.87-6.85 (m, 2H), 3.73 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CD_2Cl_2): δ 159.7, 159.5 (d, $J = 7.4$ Hz), 145.6 (d, $J = 7.4$ Hz), 137.9 (d, $J = 17.9$ Hz), 133.8, 133.7, 133.5, 131.0, 130.9, 130.8 (d, $J = 7.1$ Hz), 129.3, 129.1 (d, $J = 8.5$ Hz), 127.4 (d, $J = 9.9$ Hz), 121.7 (d, $J = 2.8$ Hz), 121.2, 114.7, 55.6; $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, CD_2Cl_2): $\delta -33.8$ (s); HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{17}\text{N}_3\text{OP}$ 358.1104; Found 358.1107. Anal. Calcd for $\text{C}_{21}\text{H}_{16}\text{N}_3\text{OP}$: C, 70.58; H, 4.51; N, 11.76. Found C, 70.47; H, 4.43; N, 11.36. The enantiomeric excess (99%) was determined by HPLC (Lux 5μ cellulose-2, hexane/isopropanol = 80/20, flow rate = 1 mL/min, $\lambda = 254$ nm) $t_R = 10.7$ min (*R*), 14.8 min (*S*).

1,2,3-triazolobenzophosphole 8d

Purification was accomplished by column chromatography on silica gel using petroleum ether/ethyl acetate 3:1 as eluent and recrystallization in CH_2Cl_2 /hexane. White solid; yield 68% (0.122 g); mp $140-142^\circ\text{C}$; $R_f = 0.26$ (petroleum ether/ethyl acetate 3:1); $[\alpha]_D^{25} = -155.7$ ($c = 0.3$, CHCl_3); ^1H NMR (400 MHz, CD_2Cl_2): δ 7.95 (d, $J = 6.4$ Hz, 1H), 7.53-7.41 (m, 4H), 7.27-7.21 (m, 6H), 6.86 (d, $J = 7.8$ Hz, 2H), 3.73 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CD_2Cl_2): δ 159.7, 159.5 (d, $J = 6.2$ Hz), 145.6 (d, $J = 6.2$ Hz), 137.9 (d, $J = 17.5$ Hz), 133.8, 133.7, 133.5, 131.4 (d, $J = 15.4$ Hz), 131.1 (2s), 130.7 (d, $J = 4.5$ Hz),

129.3, 129.1 (d, $J = 8.4$ Hz), 127.4 (d, $J = 8.4$ Hz), 121.7 (d, $J = 2.7$ Hz), 121.2, 114.7, 55.6; $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2): δ -33.8 (s); HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{17}\text{N}_3\text{OP}$ 358.1109; Found 358.1101. Anal. Calcd for $\text{C}_{21}\text{H}_{16}\text{N}_3\text{OP}$: C, 70.58; H, 4.51; N, 11.76. Found C, 70.42; H, 4.63; N, 11.73. The enantiomeric excess (99%) was determined by HPLC (Chiralpak IA, hexane/isopropanol = 90/10, flow rate = 1 mL/min, $\lambda = 254$ nm) $t_{\text{R}} = 23.9$ min (R), 26.9 min (S).

1,2,3-triazolobenzophosphole 8e

Purification was accomplished by column chromatography on silica gel using petroleum ether/ethyl acetate 2:1 as eluent. Light yellow solid; yield 52% (0.106 g); mp 50–52°C; $R_f = 0.57$ (petroleum ether/ethyl acetate 2:1); $[\alpha]_{\text{D}}^{25} = +19.7$ (c = 0.3, CHCl_3); ^1H NMR (500 MHz, CD_2Cl_2): δ 7.98 (d, $J = 7.7$ Hz, 1H), 7.67–7.65 (m, 1H), 7.51 (t, $J = 6.9$ Hz, 1H), 7.46 (td, $J = 1.0, 7.6$ Hz, 1H), 7.33–7.23 (m, 4H), 7.16–7.08 (m, 5H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CD_2Cl_2): δ 158.5 (d, $J = 6.9$ Hz), 145.2 (d, $J = 9.2$ Hz), 142.4 (d, $J = 18.4$ Hz), 136.8, 134.3, 133.9, 133.2, 133.0, 131.6, 131.4, 131.3 (d, $J = 15.1$ Hz), 131.2, 130.5, 129.5, 129.0 (d, $J = 8.3$ Hz), 128.3, 128.1, 127.4 (d, $J = 9.1$ Hz), 121.3, 119.9; $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, CD_2Cl_2): δ -35.4 (s); HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{14}\text{N}_3\text{BrP}$ 406.0103; Found 406.0105. Anal. Calcd for $\text{C}_{20}\text{H}_{13}\text{N}_3\text{BrP}$: C, 59.14; H, 3.23; N, 10.34. Found C, 59.39; H, 3.61; N, 10.10. The enantiomeric excess (99%) was determined by HPLC (Chiralpak IA, hexane/isopropanol = 95/5, flow rate = 1 mL/min, $\lambda = 254$ nm) $t_{\text{R}} = 27.5$ min (R), 28.9 min (S).

1,2,3-triazolobenzophosphole 8f

Purification was accomplished by column chromatography on silica gel using petroleum ether/ethyl acetate 3:1 as eluent and recrystallization in CH_2Cl_2 /hexane. White solid; yield 61% (0.124 g); mp 200–202°C; $R_f = 0.58$ (petroleum ether/ethyl acetate 3:1); $[\alpha]_{\text{D}}^{25} = -137.9$ (c = 0.3, CHCl_3); ^1H NMR (500 MHz, CD_2Cl_2): δ 7.97 (d, $J = 7.6$ Hz, 1H), 7.55–7.48 (m, 5H), 7.45 (td, $J = 1.1, 7.6$ Hz, 1H), 7.32–7.20 (m, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CD_2Cl_2): δ 159.8 (d, $J = 7.6$ Hz), 145.5 (d, $J = 6.8$ Hz), 138.1 (d, $J = 20.4$ Hz), 136.6, 133.8, 133.6, 132.8, 131.0 (d, $J = 4.6$ Hz), 131.0, 130.8, 130.7 (d, $J = 15.5$ Hz), 129.4, 129.2 (d, $J = 8.8$ Hz), 127.6 (d, $J = 8.8$ Hz), 121.9, 121.6 (d, $J = 3.8$ Hz), 121.3; $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, CD_2Cl_2): δ -32.7 (s); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{13}\text{N}_3\text{BrPNa}$ 427.9923; Found 427.9920. Anal. Calcd for $\text{C}_{20}\text{H}_{13}\text{N}_3\text{BrP}$: C, 59.14; H, 3.23; N, 10.34. Found C, 58.88; H, 3.15; N, 10.25. The enantiomeric excess (99%) was determined by HPLC (Chiralpak IA, hexane/isopropanol = 90/10, flow rate = 1 mL/min, $\lambda = 254$ nm) $t_{\text{R}} = 15.1$ min (R), 18.3 min (S). Suitable crystals for X-ray structure were obtained by slow diffusion of hexane into dichloromethane. Structure of **8f** and crystallographic data were reported in SI.

1,2,3-triazolobenzophosphole 8g

Purification was accomplished by column chromatography on silica gel using petroleum ether/ethyl acetate 2:1 as eluent and recrystallization in CH_2Cl_2 /hexane. Light yellow solid; yield 53% (0.105 g); mp 122–124°C; $R_f = 0.61$ (petroleum ether/ethyl acetate 2:1); $[\alpha]_{\text{D}}^{25} = -58.9$ (c = 0.3, CHCl_3); ^1H NMR (400 MHz, CD_2Cl_2): δ 8.12 (dd, $J = 0.7, 7.7$ Hz, 1H), 7.93 (d, $J = 8.5$ Hz, 2H), 7.78 (d, $J = 8.5$ Hz, 2H), 7.65–7.57 (m, 2H), 7.45–7.33 (m, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CD_2Cl_2): δ 160.0 (d, $J = 7.6$ Hz), 145.4 (d, $J = 6.9$ Hz), 140.1, 138.4 (d, $J = 19.8$ Hz), 133.9, 133.7, 133.3, 131.1, 131.0, 130.8, 130.5 (d, $J = 13.5$ Hz), 130.0 (q, $J = 32.8$ Hz), 129.5, 129.3 (d, $J = 7.7$ Hz), 127.8 (d, $J = 7.7$ Hz), 127.0 (q, $J = 3.9$ Hz), 123.7 (q, $J = 271.9$ Hz), 121.4,

120.2 (d, $J = 5.8$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, CD_2Cl_2): δ -32.1 (s); HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{14}\text{N}_3\text{F}_3\text{PNa}$ 396.0872; Found 396.0866. Anal. Calcd for $\text{C}_{21}\text{H}_{13}\text{N}_3\text{F}_3\text{P}$: C, 63.80; H, 3.31; N, 10.63. Found C, 63.59; H, 3.34; N, 10.36. The enantiomeric excess (99%) was determined by HPLC (Chiralpak IA, hexane/isopropanol = 90/10, flow rate = 1 mL/min, $\lambda = 254$ nm) $t_{\text{R}} = 11.8$ min (R), 14.5 min (S).

1,2,3-triazolobenzophosphole 8h

Purification was accomplished by column chromatography on silica gel using petroleum ether/ethyl acetate 2:1 as eluent. Light yellow oil; yield 64% (0.109 g); $R_f = 0.54$ (petroleum ether/ethyl acetate 2:1); $[\alpha]_{\text{D}}^{25} = +54.7$ (c = 0.3, CHCl_3); ^1H NMR (400 MHz, CD_2Cl_2): δ 8.00 (d, $J = 8.3$ Hz, 1H), 7.51–7.46 (m, 2H), 7.36–7.11 (m, 1H), 5.54 (2 AB system, $J = 14.7$ Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CD_2Cl_2): δ 159.5 (d, $J = 7.3$ Hz), 146.3 (d, $J = 7.9$ Hz), 139.6 (d, $J = 15.8$ Hz), 133.9 (d, $J = 22.8$ Hz), 133.5, 133.3, 131.1, 131.0, 130.8, 130.3, 129.1, 128.9, 128.8, 128.5 (d, $J = 6.3$ Hz), 127.2 (d, $J = 8.9$ Hz), 121.0, 54.6; $^{31}\text{P}\{^1\text{H}\}$ NMR (162.0 MHz, CD_2Cl_2): δ -37.5 (s); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{16}\text{N}_3\text{PNa}$ 364.0974; Found 364.0964. The enantiomeric excess (99%) was determined by HPLC (Lux 5 μ cellulose-2, hexane/isopropanol = 90/10, flow rate = 1 mL \cdot min $^{-1}$, $\lambda = 254$ nm) $t_{\text{R}} = 25.1$ min (R), 30.8 min (S).

1,2,3-triazolobenzophosphole 8i

Purification was accomplished by column chromatography on silica gel using petroleum ether/ethyl acetate 3:1 as eluent. White solid; yield 55% (0.104 g); mp 60–62°C; $R_f = 0.58$ (petroleum ether/ethyl acetate 3:1); $[\alpha]_{\text{D}}^{25} = +92.3$ (c = 0.3, CHCl_3); ^1H NMR (500 MHz, CD_2Cl_2): δ 8.16 (d, $J = 7.7$ Hz, 1H), 8.04 (d, $J = 8.3$ Hz, 1H), 7.99 (d, $J = 8.3$ Hz, 1H), 7.64–7.57 (m, 4H), 7.50 (t, $J = 7.0$ Hz, 1H), 7.44–7.31 (m, 4H), 7.24–7.17 (m, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CD_2Cl_2): δ 158.5 (d, $J = 7.8$ Hz), 145.1 (d, $J = 7.9$ Hz), 143.0 (d, $J = 19.8$ Hz), 134.4, 134.2, 133.9, 133.3, 133.2, 131.4 (d, $J = 14.9$ Hz), 131.3, 131.2, 130.5, 130.4, 129.5, 128.9 (d, $J = 9.9$ Hz), 128.2, 128.1, 127.5 (2s), 127.0, 124.8, 123.3, 122.7, 121.3; $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, CD_2Cl_2): δ -36.5 (s); HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{17}\text{N}_3\text{P}$ 378.1155; Found 378.1163. Anal. Calcd for $\text{C}_{24}\text{H}_{16}\text{N}_3\text{P}$: C, 76.38; H, 4.27; N, 11.13. Found C, 76.53; H, 4.41; N, 11.14. The enantiomeric excess (99%) was determined by HPLC (Chiralpak IA, hexane/2-propanol = 80/20, flow rate = 1 mL/min, $\lambda = 254$ nm) $t_{\text{R}} = 12.6$ min (S), 14.9 min (R).

1,2,3-triazolobenzophosphole 8j

Purification was accomplished by column chromatography on silica gel using petroleum ether/ethyl acetate 1:2 as eluent and recrystallization in CH_2Cl_2 /hexane. White solid; yield 50% (0.096 g); mp 184–186°C; $R_f = 0.54$ (petroleum ether/ethyl acetate 1:2); $[\alpha]_{\text{D}}^{25} = +29.5$ (c = 0.3, CHCl_3); ^1H NMR (400 MHz, CD_2Cl_2): δ 8.05 (br.d, $J = 7.8$ Hz, 1H), 7.61–7.53 (m, 2H), 7.45 (t, $J = 8.1$ Hz, 1H), 7.37–7.31 (m, 2H), 7.28–7.24 (m, 4H), 6.66 (d, $J = 8.7$ Hz, 2H), 3.56 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CD_2Cl_2): δ 158.2 (d, $J = 6.4$ Hz), 155.9, 145.5 (d, $J = 6.4$ Hz), 143.0 (d, $J = 15.9$ Hz), 134.7, 133.1, 132.9, 132.0 (d, $J = 14.9$ Hz), 131.6, 131.2, 131.0, 130.0, 129.2, 128.6 (d, $J = 8.7$ Hz), 127.0 (d, $J = 8.7$ Hz), 121.0, 114.9, 104.0, 55.8; $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, CD_2Cl_2): δ -37.3 (s); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{18}\text{N}_3\text{O}_2\text{PNa}$ 410.1029; Found 410.1031. Anal. Calcd for $\text{C}_{22}\text{H}_{18}\text{N}_3\text{O}_2\text{P}$: C, 68.21; H, 4.68; N, 10.85. Found C, 67.90; H, 4.82; N, 10.79. The enantiomeric excess (99%) was determined by HPLC (Chiralpak IA, hexane/isopropanol = 80:20, flow rate = 1 mL/min, $\lambda = 254$ nm) $t_{\text{R}} = 11.4$ min (R), 15.3 min (S). Suitable crystals for X-ray

structure were obtained by slow diffusion of hexane into dichloromethane. Structure of **8j** and crystallographic data were reported in SI.

1,2,3-triazolobenzophosphole **8k**

Purification was accomplished by column chromatography on silica gel using petroleum ether/ethyl acetate 2:1 as eluent and recrystallization in hexane. White solid; yield 38% (0.073 g); mp 186-188°C; $R_f = 0.58$ (petroleum ether/ethyl acetate 2:1); $[\alpha]_D^{25} = +3.7$ ($c = 0.3$, CHCl_3); $^1\text{H NMR}$ (500 MHz, CD_2Cl_2): δ 8.01 (d, $J = 7.7$ Hz, 1H), 7.51-7.48 (m, 2H), 7.41-7.40 (m, 1H), 7.37-7.29 (m, 5H), 2.25-2.23 (m, 3H), 2.17-2.15 (m, 6H), 1.86-1.58 (m, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CD_2Cl_2): δ 158.6 (d, $J = 7.7$ Hz), 146.3 (d, $J = 7.0$ Hz), 137.1 (d, $J = 18.2$ Hz), 134.0, 133.9, 133.8, 132.6 (d, $J = 15.1$ Hz), 130.6 (2s), 130.5, 129.0, 128.9 (d, $J = 7.6$ Hz), 127.0 (d, $J = 7.6$ Hz), 120.7, 61.0, 42.6 (2s), 35.7, 29.6; $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, CD_2Cl_2): δ -31.9 (s); HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{24}\text{H}_{24}\text{N}_3\text{PNa}$ 408.1600; Found 408.1602. Anal. Calcd for $\text{C}_{24}\text{H}_{24}\text{N}_3\text{P}$: C, 74.79; H, 6.28; N, 10.90. Found C, 74.81; H, 6.59; N, 11.11. The enantiomeric excess (99%) was determined by HPLC (Chiralpak IA, hexane/isopropanol = 80/20, flow rate = 1 mL/min, $\lambda = 254$ nm) $t_R = 9.1$ min (*R*), 13.1 min (*S*). Suitable crystals for X-ray structure were obtained by slow diffusion of hexane into dichloromethane. Structure of **8k** and crystallographic data were reported in SI.

Synthesis of P-chirogenic 1,2,3-triazolobenzophosphole **8l**

To a solution of aminophosphine-borane **13l** (0.138 g, 0.25 mmol) in toluene (2 mL) was added DABCO (0.084 g, 0.75 mmol) and the resulting solution was stirred under argon atmosphere at 50°C overnight in an oil bath. At room temperature, THF (1 mL) was added then the solution was cooled to -50°C. *t*-BuMgCl (2M in THF) (0.38 mL, 0.75 mmol) was slowly added and the reaction mixture was stirred until room temperature during five-six hours. Saturated solution of NH_4Cl (2.5 mL) and CH_2Cl_2 (5 mL) were added and the phases were separated. Aqueous phase was extracted with CH_2Cl_2 (2 x 5 mL) then the combined organic phases were dried over MgSO_4 , filtered and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using dichloromethane/acetone 15:1 as eluent. White solid; yield 54% (0.050 g); mp 48-50°C (dec); $R_f = 0.63$ (dichloromethane/acetone 15:1); $[\alpha]_D^{25} = -11.5$ ($c = 0.3$, CHCl_3); $^1\text{H NMR}$ (500 MHz, CD_2Cl_2): δ 7.95 (d, $J = 7.3$ Hz, 1H), 7.63 (d, $J = 7.3$ Hz, 1H), 7.48-7.28 (m, 8H), 7.11-7.04 (m, 2H), 3.52 (s, 3H), 2.40 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CD_2Cl_2): δ 158.9 (d, $J = 6.9$ Hz), 152.0, 146.4 (d, $J = 7.6$ Hz), 141.0 (d, $J = 15.2$ Hz), 137.3 (d, $J = 7.6$ Hz), 133.1, 133.0, 132.8 (d, $J = 17.0$ Hz), 131.2, 131.1 (2s), 130.5, 130.0, 129.9, 128.8 (d, $J = 7.7$ Hz), 126.5, 126.2, 120.7 (d, $J = 10.8$ Hz), 112.0, 55.2, 21.2; $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, CD_2Cl_2): δ -32.1 (s); HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{19}\text{N}_3\text{OP}$ 372.1260; Found 372.1268. Anal. Calcd for $\text{C}_{22}\text{H}_{18}\text{N}_3\text{OP}$: C, 71.15; H, 4.89; N, 11.31. Found C, 71.30; H, 4.51; N, 11.31. The enantiomeric excess (99%) was determined by HPLC (Lux 5 μ cellulose-2, hexane/isopropanol 80/20, flow rate = 1 mL/min, $\lambda = 254$ nm) $t_R = 14.2$ min (*S*), 17.1 min (*R*).

Synthesis of P-chirogenic 1,2,3-triazolobenzophosphole **8m**

To a solution of aminophosphine-borane **13m** (0.151 g, 0.25 mmol) in toluene (2 mL) was added DABCO (0.084 g, 0.75 mmol) and the resulting solution was stirred under argon atmosphere at 50°C overnight in an oil bath. At room temperature, THF (1 mL) was added then the solution was cooled to -50°C. *t*-BuMgCl (2M in THF) (0.38 mL, 0.75 mmol) was slowly

added and the reaction mixture was stirred until room temperature during five-six hours. Saturated solution of NH_4Cl (2.5 mL) and CH_2Cl_2 (5 mL) were added and the phases were separated. Aqueous phase was extracted with CH_2Cl_2 (2 x 5 mL) then the combined organic phases were dried over MgSO_4 , filtered and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using dichloromethane/acetone 15:1 as eluent. White solid; yield 46% (0.049 g); mp < 50°C (dec); $R_f = 0.68$ (dichloromethane/acetone 15:1); $[\alpha]_D^{25} = -67.1$ ($c = 0.3$, CHCl_3); $^1\text{H NMR}$ (500 MHz, CD_2Cl_2): δ 8.06 (br.d, $J = 8.0$ Hz, 1H), 7.69-7.67 (m, 2H), 7.56 (dd, $J = 1.6$, 7.9 Hz, 1H), 7.37-7.34 (m, 1H), 7.28-7.25 (m, 1H), 7.19-7.14 (m, 4H), 6.98 (td, $J = 1.1$, 7.7 Hz, 1H), 6.93 (br.d, $J = 8.4$ Hz, 1H), 3.42 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CD_2Cl_2): δ 157.5 (d, $J = 7.1$ Hz), 151.8, 147.3 (d, $J = 10.8$ Hz), 142.6 (d, $J = 14.4$ Hz), 137.1, 133.3, 133.1, 130.9 (d, $J = 15.4$ Hz), 130.7, 130.5, 129.0 (2s), 128.7 (qd, $J = 8.2$, 32.3 Hz), 127.5 (dq, $J = 4.3$, 24.9 Hz), 126.2 (q, $J = 3.5$ Hz), 126.0, 123.2 (q, $J = 272.5$ Hz), 121.2, 120.8, 112.1, 55.2; $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, CD_2Cl_2): δ -30.4 (s); HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{16}\text{F}_3\text{N}_3\text{OP}$ 426.0978; Found 426.0959. The enantiomeric excess (98%) was determined by HPLC (Chiralpak IA, hexane/isopropanol = 90/10, flow rate = 1 mL/min, $\lambda = 254$ nm) $t_R = 11.9$ min (*S*), 13.9 min (*R*).

Synthesis of P-chirogenic 1,2,3-triazolobenzophosphole **8n**

To a solution of aminophosphine-borane **13n** (0.138 g, 0.25 mmol) in toluene (2 mL) was added DABCO (0.084 g, 0.75 mmol) and the resulting solution was stirred under argon atmosphere at 50°C overnight. At room temperature, THF (1 mL) was added then the solution was cooled to -50°C. *t*-BuMgCl (2M in THF) (0.38 mL, 0.75 mmol) was slowly added and the reaction mixture was stirred until room temperature during five-six hours. Saturated solution of NH_4Cl (2.5 mL) and CH_2Cl_2 (5 mL) were added and the phases were separated. Aqueous phase was extracted with CH_2Cl_2 (2 x 5 mL) then the combined organic phases were dried over MgSO_4 , filtered and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using dichloromethane/acetone 15:1 as eluent. White solid; yield 57% (0.053 g); mp 122-124°C (dec); $R_f = 0.55$ (dichloromethane/acetone 15:1); $[\alpha]_D^{25} = -83.6$ ($c = 0.3$, CHCl_3); $^1\text{H NMR}$ (500 MHz, CD_2Cl_2): δ 7.90 (s, 1H), 7.61 (dd, $J = 1.4$, 7.9 Hz, 1H), 7.49-7.43 (m, 2H), 7.36-7.33 (m, 1H), 7.27-7.26 (m, 4H), 7.16 (br.d, $J = 7.6$ Hz, 1H), 7.11-7.04 (m, 2H), 3.52 (s, 3H), 2.51 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, CD_2Cl_2): δ 158.7 (d, $J = 8.3$ Hz), 152.1, 142.7 (d, $J = 6.7$ Hz), 141.9 (d, $J = 16.8$ Hz), 139.5, 134.0, 133.0, 132.8, 132.8 (d, $J = 16.6$ Hz), 130.6, 130.4, 129.9, 128.8 (d, $J = 8.5$ Hz), 128.2 (d, $J = 8.5$ Hz), 126.5, 126.3, 121.8, 120.7, 112.0, 55.2, 21.3; $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, CD_2Cl_2): δ -32.5 (s); HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{19}\text{N}_3\text{OP}$ 372.1260; Found 372.1260. Anal. Calcd for $\text{C}_{22}\text{H}_{18}\text{N}_3\text{OP}$: C, 71.15; H, 4.89; N, 11.31. Found C, 71.53; H, 5.09; N, 11.28. The enantiomeric excess (99%) was determined by HPLC (Chiralpak IA, hexane/isopropanol = 80/20, flow rate = 1 mL/min, $\lambda = 254$ nm) $t_R = 15.5$ min (*S*), 14.6 min (*R*).

Synthesis of bis-aminophosphine-diborane **16**

To a solution of alkyne **12a** (0.375 g, 0.97 mmol) and 1,2-bis(azidomethyl)benzene (0.091 g, 0.484 mmol) in DMF (2.3 mL) was added a solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (31 mg, 0.194 mmol) and sodium ascorbate (115 mg, 0.581 mmol) in H_2O (2.3 mL). The solution was stirred at 40°C in an oil bath during 4 hours then CH_2Cl_2 (15 mL), NH_4OH (25% in water) (3 mL) and water

(10 mL) were added at room temperature. The phases were separated and the aqueous phase was extracted with CH₂Cl₂ (2 x 10 mL). The combined organic phases were dried over MgSO₄, filtered and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate 1:2 as eluent. White solid; yield 36% (0.168 g); mp 132-134°C (dec); R_f = 0.50 (petroleum ether/ethyl acetate 1:2); [α]_D²⁵ = +108.7 (c = 0.3, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 7.64 (s, 2H), 7.53-7.39 (m, 14H), 7.35-7.29 (m, 8H), 7.25-7.17 (m, 6H), 7.11-7.10 (m, 4H), 5.58 (AB syst., J = 15.5 Hz, 2H), 5.47 (AB syst., J = 15.5 Hz, 2H), 4.64 (t, J = 3.5 Hz, 2H), 3.85-3.91 (m, 2H), 3.50 (br.s, 2H), 2.79 (d, J = 9.5 Hz, 6H), 1.07 (d, J = 6.9 Hz, 6H), 0.30-1.10 (m, 6H); ¹³C{¹H} NMR (125.8 MHz, CDCl₃): δ 146.5 (d, J = 3.3 Hz), 142.2, 135.7 (d, J = 10.1 Hz), 133.5 (d, J = 7.0 Hz), 132.9 (d, J = 8.1 Hz), 132.9, 131.9 (d, J = 60.4 Hz), 131.5 (d, J = 10.5 Hz), 131.2, 130.8, 130.6 (d, J = 62.7 Hz), 130.5 (d, J = 2.3 Hz), 129.8, 128.3, 128.3 (d, J = 10.5 Hz), 128.1, 126.9, 125.7, 124.3, 76.8, 58.3 (d, J = 2.8 Hz), 51.3, 32.0 (d, J = 3.0 Hz), 11.7 (d, J = 3.5 Hz); ³¹P{¹H} NMR (202.5 MHz, CDCl₃): δ +69.2 (br.s); HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd for C₅₆H₆₃B₂N₈O₂P₂ 963.4730; Found 963.4736.

Synthesis of P-chirogenic bis(1,2,3-triazolobenzophosphole) **17**

To a solution of bis-aminophosphine diborane **16** (0.151 g, 0.16 mmol) in toluene (2 mL) was added DABCO (0.106 g, 0.94 mmol) and the resulting solution was stirred under argon atmosphere at 50°C overnight. At room temperature, THF (1 mL) was added then the solution was cooled to -50°C. *t*-BuMgCl (2M in THF) (0.47 mL, 0.94 mmol) was slowly added and the reaction mixture was stirred until room temperature during five-six hours. Saturated solution of NH₄Cl (2.5 mL) and CH₂Cl₂ (5 mL) were added and the phases were separated. Aqueous phase was extracted with CH₂Cl₂ (2 x 5 mL) then the combined organic phases were dried over MgSO₄, filtered and the solvent was evaporated. The crude product was purified by column chromatography on silica gel using dichloromethane/acetone 10:1 as eluent. White solid; yield 38% (0.036 g); mp 94-96°C (dec); R_f = 0.47 (dichloromethane/acetone 10:1); [α]_D²⁵ = +41.9 (c = 0.3, CHCl₃); ¹H NMR (400 MHz, CD₂Cl₂): δ 7.87 (dd, J = 0.7, 7.7 Hz, 2H), 7.39-7.30 (m, 4H), 7.22-7.13 (m, 4H), 7.07-7.03 (m, 4H), 6.94-6.88 (m, 6H), 6.74-6.72 (m, 2H), 5.31 (br.s, 4H); ¹³C{¹H} NMR (125.8 MHz, CD₂Cl₂): δ 159.6 (d, J = 7.2 Hz), 146.5 (d, J = 6.5 Hz), 139.7 (d, J = 17.2 Hz), 133.7, 133.5, 133.4, 132.4, 130.9 (d, J = 2.9 Hz), 130.7 (2s), 130.5, 129.6, 129.2, 128.8 (d, J = 9.1 Hz), 128.8, 127.3 (d, J = 9.1 Hz), 127.3, 121.1, 51.5; ³¹P{¹H} NMR (162 MHz, CD₂Cl₂): δ -37.5 (s); HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd for C₃₆H₂₇N₆P₂ 605.1761; Found 605.1767. Anal. Calcd for C₃₆H₂₆N₆P₂: C, 71.52; H, 4.33. Found C, 71.21; H, 3.97.

7. Synthesis of gold(I)-complex **18**

A solution of 1,2,3-triazolobenzophosphole **8l** (0.740 g, 0.20 mmol) and Au(tht)Cl (0.641 g, 0.20 mmol) in dichloromethane (5 mL) was stirred out of the light, under argon atmosphere at room temperature during one hour. After evaporation of the solvent, the white solid was washed with pentane (2 x 20 mL) then recrystallized in CH₂Cl₂/pentane. White solid; yield 68% (0.821 g); mp 210-212°C (dec); [α]_D²⁵ = +29.3 (c = 0.3, CHCl₃); ¹H NMR (500 MHz, CD₂Cl₂): δ 7.85 (dd, J = 2.9, 7.8 Hz, 1H), 7.50-7.29 (m, 9H), 7.00 (td, J = 0.8, 7.8 Hz, 1H), 6.94 (dd, J = 0.7, 8.3 Hz, 1H), 3.16 (s, 3H), 2.27 (s, 3H); ¹³C{¹H} NMR (125.8 MHz, CD₂Cl₂): δ 160.8 (d, J = 23.1 Hz), 152.0, 139.8 (d,

J = 13.2 Hz), 138.4 (d, J = 62.6 Hz), 133.9 (d, J = 15.6 Hz), 133.4 (d, J = 1.4 Hz), 133.2 (d, J = 2.9 Hz), 132.8 (d, J = 76.4 Hz), 132.5 (d, J = 15.6 Hz), 131.8, 130.8 (d, J = 4.7 Hz), 129.6 (d, J = 12.5 Hz), 126.6, 126.4, 125.6 (d, J = 71.7 Hz), 121.9 (d, J = 6.2 Hz), 121.2, 112.4, 55.7, 21.3; ³¹P{¹H} NMR (202.5 MHz, CD₂Cl₂): δ 5.6 (s); HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₂₂H₁₈AuClN₃OPNa 626.0433; Found 626.0446. Anal. Calcd for C₂₂H₁₈AuClN₃OP: C, 43.76; H, 3.00; N, 6.96. Found C, 43.78; H, 2.81; N, 6.94. Suitable crystals for X-ray structure were obtained by slow diffusion of pentane into dichloromethane. Structure of **18** and crystallographic data were reported in SI.

ASSOCIATED CONTENT

Data Availability statement

The data underlying this study are available in the published article and in its Supporting Information.

Accession Codes

All experimental data procedure and refinement are detailed in Supplementary Information. Data CCDC-**2309206-10** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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Notes

The authors declare no competing financial interest.

SUPPORTING INFORMATION

The Supporting Information is available free of charge on the ACS Publications website.

Copies of NMR spectra of all new compounds, copies of HPLC chromatograms of compounds **8a-n** and X-ray structures and crystallographic data of compounds **8a**, **8f**, **8j**, **8k** and **18** (PDF).

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- (17) Lower yields obtained for compounds **8** were explained by a poor reactivity during the cyclization step of the more hindered substrates, consequently the main by-products are starting material **14** and ephedrine. In other cases, the main by-product is ephedrine.
- (18) Triazolophospholes **8d** and **8g** were obtained with 99% ee after recrystallization in CH₂Cl₂/hexane.

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