DOI: 10.1002/ejoc.200500844

Diastereoselective Synthesis of New P-Stereogenic (*ortho*-Hydroxyaryl)-diazaphospholidine–Borane Complexes by a Totally Stereoselective P–O to P–C Migration Rearrangement

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Keywords: Asymmetric synthesis / Chiral ligand design / Organophosphorus compounds / P,O ligands / 1,3-Carbanionic rearrangements

The totally diastereoselective synthesis of new P-stereogenic (*o*-hydroxyaryl)diazaphospholidines, in the form of their borane complexes **4a**–**4h**, is described. The efficiency of this procedure is based both, on a one-pot and totally diastereoselective synthesis of the precursors (*ortho*-bromoaryloxy)diazaphosphospholidine–borane complexes **3a**–**3h**, and on a stereoselective P–O to P–C migration rearrangement. A X-ray diffraction study of the structures of the product **4f** and his precursor **3f** shows unambiguously the totally stereoselectivity of the P–O to P–C rearrangement with clean retention of the phosphorus configuration.

Introduction

During the last three decades, there was a great interest in the design and the development of numerous chiral organophosphorus compounds,[1] which have found broad applications in asymmetric catalysis, either as ligands of transition metals[2] or as catalysts.[3] In this area, chiral phosphanes,[4] bearing the chirality on the carbon backbone are the most commonly used. More recently, P-stereogenic phosphorus ligands, bearing the chirality closer to the metal centre, have been synthesised owing to the use of borane as protecting group,[5] and have received interest in catalysis.[6] By this way, the asymmetric induction of the catalyst may be increased.[7] In recent years, a new generation of ligands bearing two different sites of coordination appeared, such as P,N[8] or P,O[9] bidentate compounds, which are interesting because of their ability to offer a selection of hard–soft donors atoms that are capable of adapting to the character of the metal centre.[10] In this context, we were interested in the development and the applications in enantioselective catalysis of P-stereogenic bidentate organophosphorus compounds, such as chiral P-pyridine and P-quinoline phosphane ligands,[11] chiral (*ortho*-hydroxyaryl)phosphane oxides,[12] and more recently chiral (*ortho*-hydroxyaryl)-phosphane–borane complexes.[13]

These complexes are the protected forms of *ortho*-phosphanylphenols,[14] which are ambident molecules with two different nucleophilic sites, a hard oxygen atom and a soft phosphorus atom. Because they can react at oxygen or phosphorus or at both nucleophilic sites and also because their electronic and steric properties can easily be modulated by varying the substituents on the phosphorus atom and on the aromatic ring, they are of great interest in catalysis[15] and in complex chemistry.[16] However, only few synthetic approaches to *ortho*-phosphanylphenols have been developed. The preparation of these compounds could be achieved by the deprotection of suitable (*ortho*-phosphanylaryl)alkyl ethers[16a,16b] or trimethylsilyl ethers,[17] or by the reaction of a C,O-phenol dilithium reagent with a chlorophosphane.[18] On the basis of these results, we have recently reported a totally diastereoselective synthesis of (*ortho*-hydroxyaryl)diazaphospholidines, in the form of their borane complexes (Scheme 1).[13] Unless this approach represents the first accurate and totally diastereoselective method for the preparation of P-stereogenic 2-hydroxyarylphosphane ligands, it suffers from several limitations. For example, overall yields are quite good but not excellent, and the choice of the chiral auxiliary is limited to diamines.

Another general way of preparation of *ortho*-phosphanylphenols consists of an intramolecular 1,3-carbanionic rearrangement of *ortho*-metallated phenoxyphosphorus compounds (Scheme 2).[19]

In this context, Jugé et al. reported a stereoselective synthesis of P-stereogenic 2-hydroxyarylphosphane ligands, using the borane complexation methodology (Scheme 3).[20]

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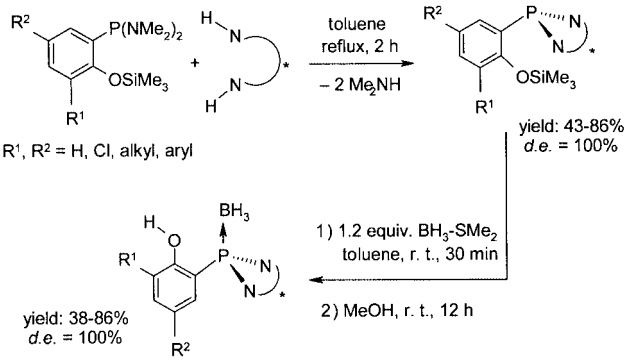
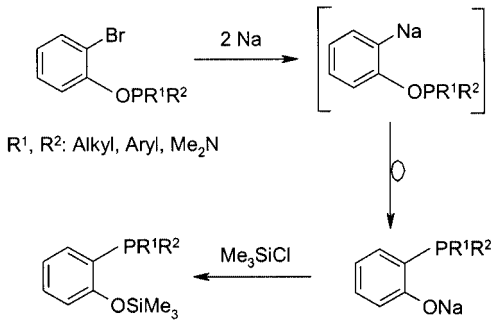
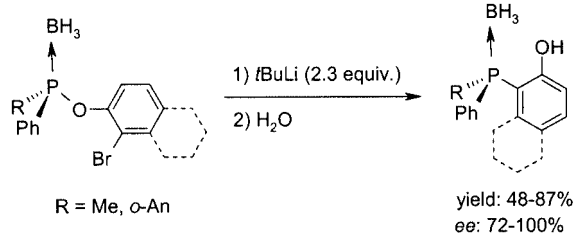


Scheme 1. Totally diastereoselective synthesis of (*ortho*-hydroxyaryl)diazaphospholidine–borane complexes.[13]



Scheme 2. Intramolecular 1,3-carbanionic rearrangement of *ortho*-metallated phenoxyphosphorus compounds.[19]

This method is based on an intramolecular *ortho*-Fries-like rearrangement of enantio-enriched *ortho*-bromoaryl phosphinite–borane complexes. Nevertheless, only one (*ortho*-hydroxyaryl)phosphane–borane complex could be obtained in pure enantiomeric form by this way. Although the P–O to P–C migration rearrangement proceeds with total retention of the configuration at the phosphorus atom, this approach suffers from the non-totally enantioselective preparation of the *ortho*-bromoaryl phosphinite–borane precursors.

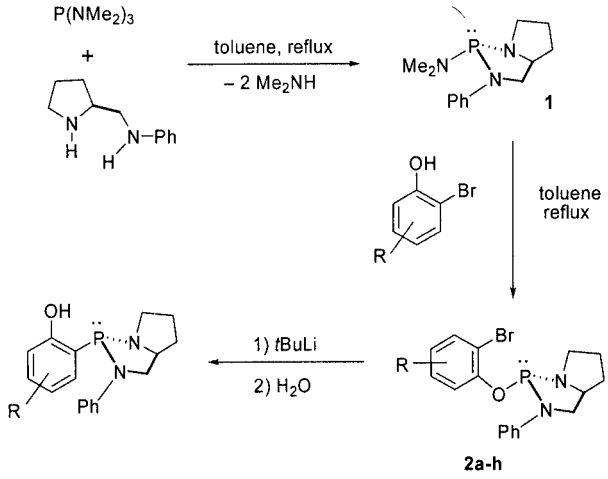


Scheme 3. Intramolecular *ortho*-Fries-like rearrangement of enantio-enriched *ortho*-bromoaryl phosphinite–borane complexes.[20]

In this paper, we wish to report a totally diastereoselective synthesis of new P-stereogenic (*o*-hydroxyaryl)diazaphospholidine–borane complexes, based on an intramolecular *ortho*-Fries-like rearrangement of diastereomerically pure (*ortho*-bromoaryloxy)diazaphospholidine–borane complexes. The X-ray diffraction of the structures of one product and its precursor shows unambiguously the stereoselectivity of the P–O to P–C rearrangement at the phosphorus atom.

Results and Discussion

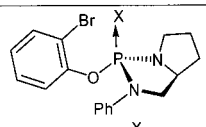
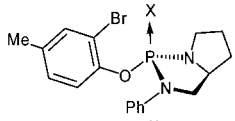
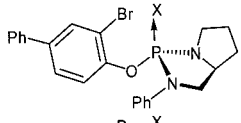
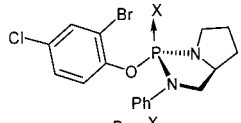
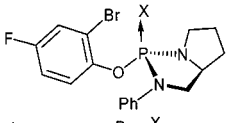
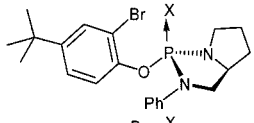
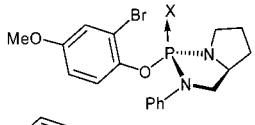
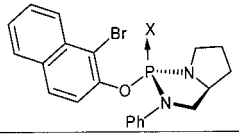
The new chiral ligands (*ortho*-hydroxyaryl)diazaphospholidines may be prepared according to the following general procedure (Scheme 4). On the basis of a previously described procedure,[12d] the precursors **2** could be obtained in a diastereomerically pure form from the (dimethylamino)-diazaphospholidine **1** and various mono- and disubstituted *ortho*-bromophenols. Halogen–metal exchange in the precursor **2** could lead to an unstable *ortho*-metallated intermediate, which could in turn undergo a fast 1,3-carbanionic rearrangement with cleavage of the P–O bond and formation of the new P–C bond, and with total retention of the configuration at the phosphorus atom.



Scheme 4. General procedure for the synthesis of chiral (*ortho*-hydroxyaryl)diazaphospholidines.

The synthesis of the precursors **2a**–**h** was readily achieved by the exchange reaction in refluxing toluene between tris(dimethylamino)phosphane and (*S*)-2-(anilinomethyl)pyrrolidine.[21] The reaction was monitored by ^{31}P NMR spectroscopy. After two hours, analysis revealed the presence of only one organophosphorus compound, with a δ_p value of 118.0 ppm, which was identified as the diazaphospholidine **1**.[22] Subsequent addition of one equivalent of the appropriated *ortho*-bromophenol led, after one hour in refluxing toluene, to the desired (*ortho*-bromoaryloxy)diazaphospholidine **2**. The products were purified by column chromatography on silica gel and isolated in good chemical yields (Scheme 4 and Table 1). In all cases, only one diastereomer was obtained, which was characterised as the thermodynamic *anti* diastereomer.[11,12] Moreover, these new P^{III}-stereogenic aryloxydiazaphospholidines are quite stable to air and moisture.

Table 1. One-pot synthesis of precursors **2a**–**h** and *o*-bromoaryloxydiazaphospholidine–borane complexes **3a**–**3h**.

Entry	Substituted 2-bromophenol	Product **2** (X = lone pair) or **3** (X = BH_3)	Yield (%)[a]
1	R = H		**2a**: 94 **3a**: 90
2	R = Me		**2b**: 91 **3b**: 85
3	R = Ph		**2c**: 85 **3c**: 85
4	R = Cl		**2d**: 93 **3d**: 88
5	R = F		**2e**: 95 **3e**: 83
6	R = *t*Bu		**2f**: 85 **3f**: 85
7	R = OMe		**2g**: 96 **3g**: 92
8	1-bromo-2-naphthol		**2h**: 60 **3h**: 70

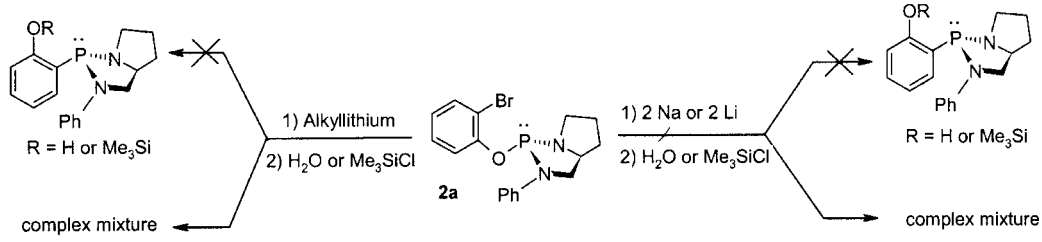
[a] Isolated yield after purification by column chromatography on silica gel.

The P–O to P–C migration rearrangement reaction was first tested with precursor **2a** as test substrate. On the basis of Heinicke's results,[19] the treatment of (*ortho*-bromoaryloxy)diazaphospholidine **2a** with two equivalents of an alkali metal such as sodium or lithium in dioxane, may lead to the corresponding free (*ortho*-hydroxyaryl)diazaphospholidine after hydrolysis. Unfortunately, all attempts gave complex mixtures of unidentified organophosphorus compounds (Scheme 5). The use of chlorotrimethylsilane instead of water to quench the reaction did not give the corresponding silylether, but the same complex mixture was obtained. The treatment of **2a** with alkyllithium compounds such as *n*-butyllithium, *sec*-butyllithium or *tert*-butyllithium was also unsucessful.

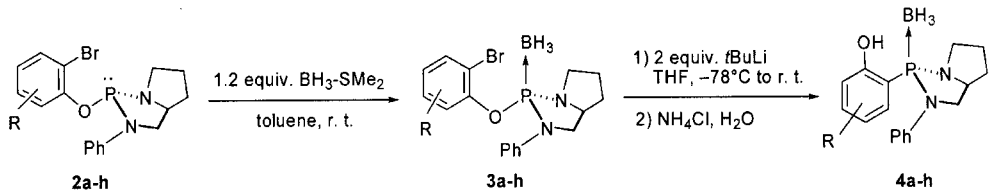
To overcome this problem, we decided to protect the phosphane moiety in the precursors **2** prior to the rearrangement procedure, with the borane complex methodology. Thus, after the completion of the exchange reaction leading to the diazaphospholidines **2** (Scheme 4), the reaction mixture was cooled to room temperature and 1.3 equivalent of borane–dimethyl sulfide was added (Scheme 6). After one hour stirring and evaporation of the solvent, the crude products were purified by column chromatography, affording the desired diastereomerically pure (*ortho*-bromoaryloxy)diazaphospholidine–borane complexes **3a**–**3h** in yields ranging from 70 to 92% (Table 1). These values can be considered as good to excellent owing to the one-pot procedure.

With these new chiral compounds **3a**–**3h** in hands, we studied the P–O to P–C rearrangement reaction. Treatment of precursors **3** with *tert*-butyllithium in THF at –78 °C resulted in the totally diastereoselective synthesis of *ortho*-hydroxyaryldiazaphospholidine–boranes **4a**–**h**, isolated in good yields (Scheme 6 and Table 2).

In all cases, only one diastereomer was formed, and the reaction was found to proceed with total retention of the configuration at the phosphorus atom, as particularly illus

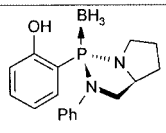
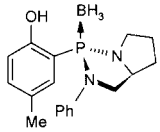
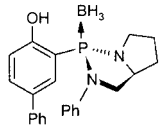
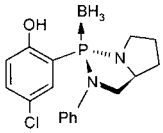
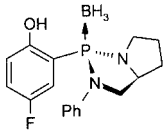
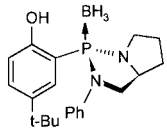
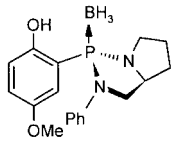
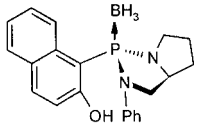


Scheme 5. Unsuccessful preliminary attempts for the P–O to P–C migration rearrangement.



Scheme 6. One-pot synthesis of (*ortho*-bromoaryloxy)diazaphospholidine–borane complexes **3a**–**3h** and totally diastereoselective P–O to P–C rearrangement.

Table 2. Diastereoselective synthesis of (*ortho*-hydroxyaryl)diazaphospholidine–boranes **4a**–**4h**.

Entry	Precursor **3**	Product **4**	Yield (%)[a]
1	**3a**	 **4a**	86
2	**3b**	 **4b**	70
3	**3c**	 **4c**	78
4	**3d**	 **4d**	76
5	**3e**	 **4e**	76
6	**3f**	 **4f**	80
7	**3g**	 **4g**	84
8	**3h**	 **4h**	40

[a] Isolated yield after purification by column chromatography on silica gel.

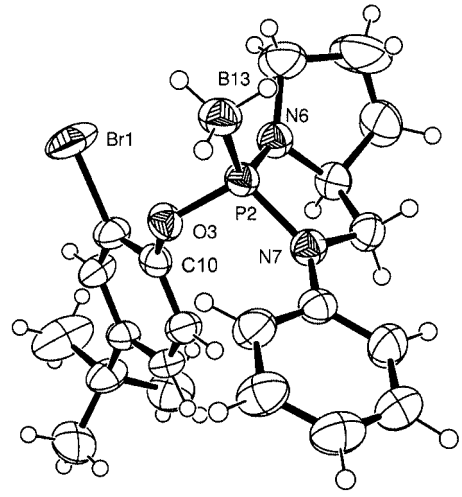


Figure 1. ORTEP drawing of the crystal structure of compound **3f** (the numbering does not correspond with the correct nomenclature); selected bond lengths [Å] and angles [°]: P2–B13 1.883, P2–N6 1.639, P2–N7 1.682, P2–O3 1.610, O3–C10 1.390; B13–P2–N6 119.2, B13–P2–N7 121.1, B13–P2–O3 106.0, N6–P2–N7 94.0, O3–P2–N6 109.8, O3–P2–N7 105.8, P2–O3–C10 125.1. The sum of the bond angles around N6 and N7 is 351.5° and 358.6°, respectively.

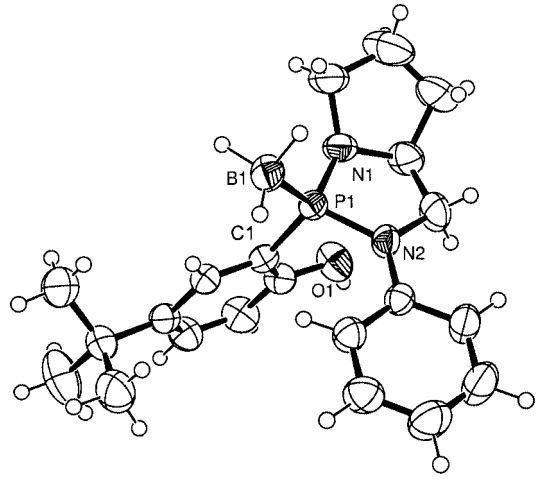
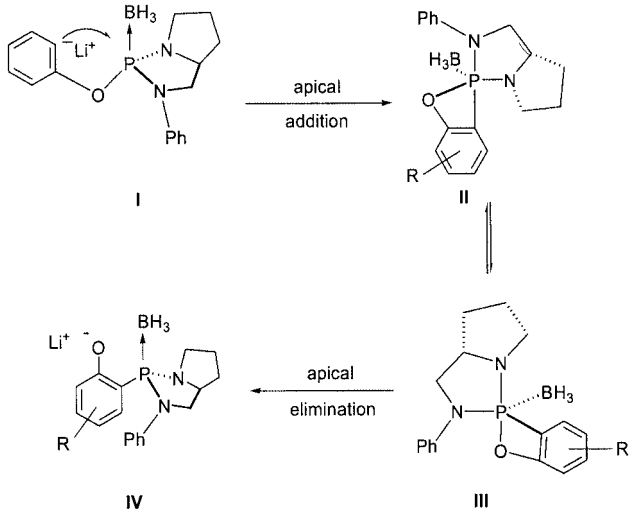


Figure 2. ORTEP drawing of the crystal structure of compound **4f**; selected bond lengths [Å] and angles [°]: P1–B1 1.906, P1–N1 1.651, P1–N2 1.683, P1–C1 1.808; B1–P1–N1 113.6, B1–P1–N2 117.5, B1–P1–C1 111.3, N1–P1–N2 94.8, N2–P1–C1 108.1, N1–P1–C1 110.3. The sum of the bond angles around N1 and N2 is 348.0° and 358.7°, respectively.

trated for the rearrangement of precursor **3f**. X-ray analysis of borane complex **3f**[23] (Figure 1) and borane complex **4f**[24] (Figure 2), obtained through treatment of **3f** with *tert*-butyllithium, shows unambiguously that these two compounds present the same R_P configuration.

These results show similar stereospecificity of the rearrangement for the diazaphospholidine–borane complexes, with respect to the phosphate series[25] or the phosphinite–borane complexes.[20,26] As previously described,[12c,20,26] a mechanism involving a trigonal-bipyramidal (TBP) intermediate can be postulated (Scheme 7). This retention of configuration may be explained in terms of an apical addition to the phosphorus of the anion *ortho* to the aryloxy substituent, generated by halogen–metal exchange. This intramolecular nucleophilic attack may result in the formation of a trigonal-bipyramidal intermediate **II** spanning both diazaphospholidine and oxaphosphetene rings in apical-equatorial positions. The isomerisation by pseudorotation of this intermediate **II** into **III** maintains the equatorial P–BH_3 bond as pivot and allows to place the oxygen ring in a favourable apical position. The loss of the aryloxy leaving group from **III** leads to the observed product with a retention of stereochemistry at phosphorus. An inversion of stereochemistry at phosphorus from the intermediate **II** or **III** would involve energetically unfavourable placement of the rings in the diequatorial positions.[27]



Scheme 7. Mechanism for the P–O to P–C rearrangement.

Conclusion

In this paper, we have described a totally diastereoselective synthesis of new P-stereogenic (*o*-hydroxyaryl)diazaphospholidines, in the form of their borane complexes. The efficiency of this procedure is based on two key steps: firstly, a *one-pot* and totally diastereoselective synthesis of the precursors (*ortho*-bromoaryloxy)diazaphospholidine–borane complexes **3a**–**3h**; secondly, a stereoselective P–O to P–C migration rearrangement. The stereospecificity of the rearrangement has been clearly illustrated by X-ray analysis of the product **4f** and his precursor **3f**, showing unambiguously that these two compounds present the same R_P configuration. We are currently extending this procedure to the use of other chiral auxiliaries such as amino alcohols and diols. In the same time, investigations of the catalytic activity of these new chiral compounds **4a**–**h** in enantioselective processes are in progress. In this context, tests are directed to the use of these compounds either as ligands or as nonmetallic catalysts.

Experimental Section

General: All reactions are conducted under dry argon by using the Schlenk techniques. All solvents were purified according to reported procedures, and reagents were used as commercially available. Ethyl acetate and petroleum ether (35–65 °C) were purchased from SDS and used without any further purification. Column chromatography was performed on SDS silica gel (70–230 mesh). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution at 200.00 and 50.30 MHz with a Bruker AC200 spectrometer. ^{31}P NMR spectra were recorded in $CDCl_3$ solution at 40.50 MHz with a Bruker AC100 spectrometer (the usual abbreviations are used: s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet). The chemical shift values are given in ppm, and were determined, relative to TMS (^{1}H), $CDCl_3$ (^{13}C), and 85% H_3PO_4 (^{31}P). IR spectra were recorded with a Perkin–Elmer 298 IR spectrometer. Optical rotations were determined with a Perkin–Elmer 241 MC polarimeter. All melting points were taken with a Büchi apparatus, and are uncorrected.

General Procedure for the Synthesis of Compounds 2a–2h: In a 25-.mL two-necked round-bottomed flask was added tris(dimethylamino)phosphane (5 mmol) and (*S*)-2-anilinomethylpyrrolidine (5 mmol), each dissolved in 2.5 mL of dry toluene. The solution was heated to reflux for two hours, and the reaction was monitored by ^{31}P NMR spectroscopy. After completion of the reaction, 1 equiv. (5 mmol) of the appropriate *ortho*-bromophenol[28] dissolved in 2.5 mL of dry toluene was added. After one hour stirring and evaporation of the solvent, the crude products were purified by column chromatography (eluent: ethyl acetate/petroleum ether, 20:80), affording the diastereomerically pure (*ortho*-bromoaryloxy)-diazaphospholidines **2a**–**2h**.

(2*R*,5*S*)-2-(2-Bromophenoxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0^{1,5}]octane (2a): Prepared by the general procedure from 2-bromophenol (0.87 g, 5 mmol) in 94% yield (1.77 g). White solid, m.p. 64–66 °C. $[\alpha]_D^{25}$ = –304.1 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.4–1.5 (m, 1 H), 1.7–1.9 (m, 3 H), 3.0–3.1 (m, 1 H), 3.2–3.3 (m, 1 H), 3.5–3.7 (m, 3 H), 6.8–7.5 (m, 9 H) ppm. ^{13}C NMR (50.30 MHz, $CDCl_3$): δ = 26.7 (d, *J* = 5 Hz), 31.9, 48.2 (d, *J* = 35 Hz), 54.2 (d, *J* = 8 Hz), 62.9 (d, *J* = 13 Hz), 115.6 (d, *J* = 13 Hz), 117.1, 119.6, 123.2 (d, *J* = 7 Hz), 124.3, 128.1, 129.3, 133.0, 145.3 (d, *J* = 16 Hz), 151.4 (d, *J* = 6 Hz) ppm. ^{31}P NMR (40.50 MHz, $CDCl_3$): δ = 123.9 ppm. $C_{17}H_{18}BrN_2OP$ (377.22): calcd. C 54.13, H 4.81; found C 54.07, H 4.75.

(2*R*,5*S*)-2-(2-Bromo-4-methylphenoxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0^{1,5}]octane (2b): Prepared by the general procedure from 2-bromo-4-methylphenol (0.94 g, 5 mmol) in 91% yield (1.78 g). White solid, m.p. 90–94 °C. $[\alpha]_D^{25}$ = –443.3 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.4–1.5 (m, 1 H), 1.7–1.9 (m, 3 H), 2.2 (s, 3 H), 3.0–3.1 (m, 1 H), 3.2–3.3 (m, 1 H), 3.4–3.6 (m, 3 H), 6.7–7.3 (m, 8 H) ppm. ^{13}C NMR (50.30 MHz, $CDCl_3$): δ = 20.3, 26.5 (d, *J* = 4 Hz), 31.9, 47.8 (d, *J* = 34 Hz), 54.0 (d, *J* = 8 Hz), 62.7 (d, *J* = 9 Hz), 115.3 (d, *J* = 13 Hz), 116.5, 119.4, 122.7 (d, *J* = 6 Hz), 128.7, 129.1, 133.0, 134.0, 145.1 (d, *J* = 16 Hz), 148.8 (d, *J* = 8 Hz) ppm. ^{31}P NMR (40.50 MHz, $CDCl_3$): δ = 125.7 ppm. $C_{18}H_{20}BrN_2OP$ (391.24): calcd. C 55.26, H 5.15; found C 55.23, H 5.12.

(2*R*,5*S*)-2-(2-Bromo-4-phenylphenoxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0^{1,5}]octane (2c): Prepared by the general procedure from 3-bromo-4-hydroxybiphenyl (1.25 g, 5 mmol) in 85% yield (1.92 g). White solid, m.p. 88–90 °C. $[\alpha]_D^{25}$ = –429.6 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.5–1.7 (m, 1 H), 1.8–2.1 (m, 3 H), 3.1–3.3 (m, 1 H), 3.3–3.5 (m, 1 H), 3.6–3.9 (m, 3 H), 6.9–8.0 (m, 13 H) ppm. ^{13}C NMR (50.30 MHz, $CDCl_3$): δ = 26.6 (d, *J* = 4 Hz), 31.9, 47.8 (d, *J* = 34 Hz), 54.0 (d, *J* = 8 Hz), 62.8 (d, *J* = 8 Hz), 115.5 (d, *J* = 13 Hz), 116.4, 117.4, 119.6 (d, *J* = 2 Hz), 123.2 (d, *J* = 6 Hz), 126.6, 126.7, 126.8, 127.3, 128.8, 129.2, 131.4, 137.4 (d, *J* = 1 Hz), 139.4, 145.0 (d, *J* = 16 Hz), 150.7 (d, *J* = 5 Hz) ppm. ^{31}P NMR (40.50 MHz, $CDCl_3$): δ = 124.6 ppm. $C_{23}H_{22}BrN_2OP$ (453.31): calcd. C 60.94, H 4.89; found C 61.05, H 4.93.

(2*R*,5*S*)-2-(2-Bromo-4-chlorophenoxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0^{1,5}]octane (2d): Prepared by the general procedure from 2-bromo-4-chlorophenol (1.04 g, 5 mmol) in 93% yield (1.91 g). Yellow oil. $[\alpha]_D^{25}$ = –415.8 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.6–1.7 (m, 1 H), 1.9–2.1 (m, 3 H), 3.2–3.3 (m, 1 H), 3.4–3.5 (m, 1 H), 3.6–3.9 (m, 3 H), 6.8–7.8 (m, 8 H) ppm. ^{13}C NMR (50.30 MHz, $CDCl_3$): δ = 26.5, 31.7, 47.5 (d, *J* = 35 Hz), 53.8 (d, *J* = 9 Hz), 62.6 (d, *J* = 9 Hz), 115.2 (d, *J* = 14 Hz), 117.4, 119.6 (d, *J* = 1 Hz), 123.6 (d, *J* = 7 Hz), 127.9, 128.3 (d, *J* = 1 Hz), 129.1, 132.2, 144.6 (d, *J* = 16 Hz), 150.2 (d, *J* = 6 Hz) ppm. ^{31}P

NMR (40.50 MHz, $CDCl_3$): δ = 123.5 ppm. $C_{17}H_{17}BrClN_2OP$ (411.66): calcd. C 49.60, H 4.16; found C 49.75, H 4.21.

(2*R*,5*S*)-2-(2-Bromo-4-fluorophenoxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0^{1,5}]octane (2e): Prepared by the general procedure from 2-bromo-4-fluorophenol (0.96 g, 5 mmol) in 95% yield (1.88 g). Colorless oil. $[\alpha]_D^{25}$ = –423.6 (c = 1.0, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.5–1.7 (m, 1 H), 1.7–2.1 (m, 3 H), 2.9–3.2 (m, 2 H), 3.3–3.5 (m, 2 H), 3.6–3.8 (m, 1 H), 6.4–7.5 (m, 8 H). ^{13}C NMR (50.30 MHz, $CDCl_3$): δ = 23.6, 27.8, 44.6, 44.8, 59.3, 109.4 (d, J = 10 Hz), 112.7, 115.1 (d, J = 22 Hz), 115.3, 116.3 (d, J = 8 Hz), 117.7, 119.2 (d, J = 25 Hz), 129.2, 147.5, 150.0 (d, J = 3 Hz). ^{31}P NMR (40.50 MHz, $CDCl_3$): δ = 123.2 ppm. $C_{17}H_{17}BrFN_2OP$ (395.21): calcd. C 51.66, H 4.34; found C 51.43, H 4.36.

(2*R*,5*S*)-2-(2-Bromo-4-*tert*-butylphenoxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0^{1,5}]octane (2f): Prepared by the general procedure from 2-bromo-4-*tert*-butylphenol (1.15 g, 5 mmol) in 85% yield (1.84 g). White solid, m.p. 126–130 °C. $[\alpha]_D^{25}$ = –408.5 (c = 1.0, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.3 (s, 9 H), 1.5–1.8 (m, 1 H), 1.9–2.1 (m, 3 H), 3.2–3.3 (m, 1 H), 3.4–3.5 (m, 1 H), 3.6–3.8 (m, 3 H), 7.4–7.8 (m, 8 H) ppm. ^{13}C NMR (50.30 MHz, $CDCl_3$): δ = 26.5 (d, J = 4 Hz), 31.3, 31.9, 34.3, 47.8 (d, J = 35 Hz), 54.0 (d, J = 8 Hz), 62.7 (d, J = 9 Hz), 115.5 (d, J = 13 Hz), 116.3 (d, J = 2 Hz), 119.4 (d, J = 2 Hz), 122.2 (d, J = 7 Hz), 125.1, 129.1, 129.9, 145.2 (d, J = 16 Hz), 147.5, 148.7 (d, J = 4 Hz) ppm. ^{31}P NMR (40.50 MHz, $CDCl_3$): δ = 126.5 ppm. $C_{21}H_{26}BrN_2OP$ (433.32): calcd. C 58.21, H 6.05, N 6.46; found C 57.90, H 6.21; N. 6.55.

(2*R*,5*S*)-2-(2-Bromo-4-methoxyphenoxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0^{1,5}]octane (2 g): Prepared by the general procedure from 2-bromo-4-methoxyphenol (1.02 g, 5 mmol) in 96% yield (1.95 g). White solid, m.p. 66–68 °C. $[\alpha]_D^{25}$ = –309.4 (c = 1.0, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.5–1.7 (m, 1 H), 1.7–2.1 (m, 3 H), 3.1–3.2 (m, 1 H), 3.3–3.5 (m, 1 H), 3.5–3.7 (m, 3 H), 3.8 (s, 3 H), 6.6–7.5 (m, 8 H) ppm. ^{13}C NMR (50.30 MHz, $CDCl_3$): δ = 26.6 (d, J = 5 Hz), 31.9, 47.7 (d, J = 35 Hz), 54.0 (d, J = 8 Hz), 55.6, 62.6 (d, J = 8 Hz), 113.8, 115.2 (d, J = 13 Hz), 117.0 (d, J = 2 Hz), 117.8, 119.4, 123.3 (d, J = 5 Hz), 129.1, 144.7 (d, J = 6 Hz), 145.1 (d, J = 16 Hz), 155.7 ppm. ^{31}P NMR (40.50 MHz, $CDCl_3$): δ = 125.1 ppm. $C_{18}H_{20}BrN_2O_2P$ (407.24): calcd. C 53.09, H 4.95; found C 53.21, H 4.87.

(2*S*,5*R*)-2-(1-Bromo-2-naphthoxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0^{1,5}]octane (2h): Prepared by the general procedure from 1-bromonaphth-2-ol (1.16 g, 5 mmol) in 60% yield (1.28 g). Uncoloured oil. $[\alpha]_D^{25}$ = –433.5 (c = 1.0, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.4–1.6 (m, 1 H), 1.7–2.0 (m, 3 H), 3.0–3.3 (m, 1 H), 3.3–3.5 (m, 1 H), 3.6–3.8 (m, 3 H), 7.0–7.9 (m, 11 H) ppm. ^{13}C NMR (50.30 MHz, $CDCl_3$): δ = 26.6 (d, J = 4 Hz), 31.9, 47.8 (d, J = 34 Hz), 54.0 (d, J = 8 Hz), 62.8 (d, J = 8 Hz), 115.3 (d, J = 13 Hz), 117.0, 119.4, 124.7, 126.6, 127.0, 127.4 (d, J = 8 Hz), 127.7, 128.0, 129.0, 130.8 (d, J = 1 Hz), 132.8, 145.0 (d, J = 16 Hz), 149.5 (d, J = 6 Hz) ppm. ^{31}P NMR (40.50 MHz, $CDCl_3$): δ = 124.3 ppm. $C_{21}H_{20}BrN_2OP$ (427.27): calcd. C 59.03, H 4.72; found C 59.09, H 4.80.

General Procedure for the Synthesis of Compounds 3a–3h: After completion of the exchange reaction leading to the (*ortho*-bromoaryloxy)diazaphospholidines **2**, the reaction mixture was cooled to room temperature and 1.3 equiv. of borane–dimethyl sulfide was added. After one hour stirring and evaporation of the solvent, the crude products were purified by column chromatography (eluent: ethyl acetate/petroleum ether, from 5:95 to 20:80), affording the diastereomerically pure (*ortho*-bromoaryloxy)diazaphospholidine–borane complexes **3a**–**3h**.

(2*R*,5*S*)-2-(2-Bromophenoxy)-3-phenyl-1,3-diaza-2-phosphabicyclo-[3.3.0^{1,5}]octane–Borane (3a): Yield 90% (1.75 g). White solid, m.p. 102 °C. $[\alpha]_D^{25}$ = –171.8 (c = 1, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.0–1.5 (m, 3 H), 1.6–1.7 (m, 1 H), 1.9–2.1 (m, 3 H), 3.2–3.5 (m, 3 H), 3.6–3.7 (m, 1 H), 3.8–4.0 (m, 1 H), 6.5–7.7 (m, 9 H) ppm. ^{13}C NMR (50.30 MHz, $CDCl_3$): δ = 26.4 (d, J = 5 Hz), 31.5 (d, J = 3 Hz), 46.9 (d, J = 11 Hz), 54.1, 59.8, 116.8 (d, J = 6 Hz), 117.0 (d, J = 4 Hz), 121.5, 122.5 (d, J = 4 Hz), 126.0 (d, J = 2 Hz), 128.3 (d, J = 2 Hz), 129.2, 133.4 (d, J = 2 Hz), 141.7 (d, J = 10 hz), 143.8 (d, J = 15 Hz) ppm. ^{31}P NMR (40.50 MHz, $CDCl_3$): δ = 108.9 (broad) ppm. IR (neat, cm^{-1}): $\tilde{\nu}$ = 884 (s), 1050 (s), 1136 (s), 1222 (s), 1293 (s), 1467 (s), 1497 (s), 1602 (s), 1631 (m), 2339 (m, BH), 2366 (m, BH), 2422 (m, BH), 2885 (m), 2916 (m), 2984 (m), 3039 (w). $C_{17}H_{21}BBrN_2OP$ (391.05): calcd. C 52.21, H 5.41; found C 52.16, H 5.36.

(2*R*,5*S*)-2-(2-Bromo-4-methylphenoxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0^{1,5}]octane–Borane (3b): Yield 85% (1.72 g). White solid, m.p. 102–103 °C. $[\alpha]_D^{25}$ = –167.6 (c = 1, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.0–1.4 (m, 2 H), 1.5–1.7 (m, 1 H), 1.8–2.1 (m, 4 H), 2.3 (s, 3 H), 3.1–3.5 (m, 3 H), 3.6–3.7 (m, 1 H), 3.8–4.0 (m, 1 H), 6.7–7.1 (m, 3 H), 7.2–7.6 (m, 5 H) ppm. ^{13}C NMR (50.30 MHz, $CDCl_3$): δ = 20.4, 26.5 (d, J = 5 Hz), 31.6 (d, J = 3 Hz), 47.0 (d, J = 10 Hz), 54.1, 59.9, 116.5, 116.9 (d, J = 6 Hz), 121.5, 122.1 (d, J = 3 Hz), 128.9 (d, J = 2 Hz), 129.3, 133.7 (d, J = 2 Hz), 136.0 (d, J = 2 Hz), 149.1 (d, J = 10 Hz), 146.0 (d, J = 15 Hz) ppm. ^{31}P NMR (40.50 MHz, $CDCl_3$): δ = 110.7 (broad) ppm. IR (neat, cm^{-1}): $\tilde{\nu}$ = 884 (s), 1050 (s), 1136 (s), 1222 (s), 1293 (s), 1467 (s), 1497 (s), 1602 (s), 1631 (m), 2339 (m, BH), 2366 (m, BH), 2422 (m, BH), 2885 (m), 2916 (m), 2984 (m), 3039 (w). $C_{18}H_{23}BBrN_2OP$ (405.08): calcd. C 53.37, H 5.72; found C 53.31, H 5.69.

(2*R*,5*S*)-2-(2-Bromo-4-phenylphenoxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0^{1,5}]octane–Borane (3c): Yield 85% (1.99 g). White solid, m.p. 136–142 °C. $[\alpha]_D^{25}$ = –141.7 (c = 1, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.1–1.6 (m, 3 H), 1.2–2.2 (m, 4 H), 2.3 (s, 3 H), 3.2–3.5 (m, 3 H), 3.6–3.7 (m, 1 H), 3.7–3.8 (m, 1 H), 6.9–7.8 (m, 13 H) ppm. ^{13}C NMR (50.30 MHz, $CDCl_3$): δ = 26.4 (d, J = 2 Hz), 31.6, 47.1 (d, J = 10 Hz), 54.1, 59.9, 116.9 (d, J = 5 Hz), 117.4 (d, J = 3 Hz), 121.4, 122.7, 126.8, 127.8, 128.7, 128.9, 129.3, 131.8, 138.7, 139.2, 141.9 (d, J = 10 Hz), 147.7 (d, J = 15 Hz) ppm. ^{31}P NMR (40.50 MHz, $CDCl_3$): δ = 108.2 (broad) ppm. IR (neat, cm^{-1}): $\tilde{\nu}$ = 884 (s), 1050 (s), 1136 (s), 1222 (s), 1293 (s), 1467 (s), 1497 (s), 1602 (s), 1631 (m), 2339 (m, BH), 2366 (m, BH), 2422 (m, BH), 2885 (m), 2916 (m), 2984 (m), 3039 (w). $C_{23}H_{25}BBrN_2OP$ (467.15): calcd. C 59.13, H 5.39; found C 59.04, H 5.44.

(2*R*,5*S*)-2-(2-Bromo-4-chlorophenoxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0^{1,5}]octane (3d): Yield 88% (1.87 g). White solid, m.p. 82–87 °C. $[\alpha]_D^{25}$ = –137.9 (c = 1, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = –0.1–1.3 (m, 3 H), 1.4–1.6 (m, 1 H), 1.7–2.2 (m, 3 H), 3.0–3.4 (m, 3 H), 3.5–3.9 (m, 2 H), 6.7–7.6 (m, 8 H) ppm. ^{13}C NMR (50.30 MHz, $CDCl_3$): δ = 26.5 (d, J = 4 Hz), 31.6 (d, J = 3 Hz), 46.2 (d, J = 10 Hz), 54.1, 60.0, 117.0 (d, J = 5 Hz), 117.8 (d, J = 2 Hz), 121.9, 123.4 (d, J = 3 Hz), 128.4, 129.4, 130.7, 133.0, 141.7 (d, J = 10 Hz), 147.3 (d, J = 15 Hz) ppm. ^{31}P NMR (40.50 MHz, $CDCl_3$): δ = 111.2 (broad) ppm. IR (neat, cm^{-1}): $\tilde{\nu}$ = 884 (s), 1050 (s), 1136 (s), 1222 (s), 1293 (s), 1467 (s), 1497 (s), 1602 (s), 1631 (m), 2339 (m, BH), 2366 (m, BH), 2422 (m, BH), 2885 (m), 2916 (m), 2984 (m), 3039 (w). $C_{17}H_{20}BBrClN_2OP$ (425.5): calcd. C 47.99, H 4.74; found C 47.87, H 4.81.

(2*R*,5*S*)-2-(2-Bromo-4-fluorophenoxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0^{1,5}]octane (3e): Yield 83% (1.70 g). White solid, m.p. 100–105 °C. $[\alpha]_D^{25}$ = –153.8 (c = 1, CH_2Cl_2). ^{1}H NMR

(200 MHz, $CDCl_3$): δ = 0.1–1.4 (m, 3 H), 1.5–1.6 (m, 1 H), 1.7–1.9 (m, 3 H), 3.0–3.4 (m, 3 H), 3.5–3.6 (m, 1 H), 3.7–3.9 (m, 1 H), 6.7–7.4 (m, 8 H) ppm. ^{13}C NMR (50.30 MHz, $CDCl_3$): δ = 26.5 (d, *J* = 5 Hz), 31.6 (d, *J* = 3 Hz), 47.1 (d, *J* = 11 Hz), 54.1, 59.9, 115.2 (d, *J* = 22 Hz), 116.8 (d, *J* = 6 Hz), 117.4 (d, *J* = 10 Hz), 120.4 (d, *J* = 25 Hz), 121.8, 123.8 (d, *J* = 8 Hz), 129.4, 141.6 (d, *J* = 10 Hz), 144.8 (d, *J* = 18 Hz), 156.6 (d, *J* = 12 Hz) ppm. ^{31}P NMR (40.50 MHz, $CDCl_3$): δ = 110.9 (broad) ppm. IR (neat, cm^{-1}): $\tilde{\nu}$ = 884 (s), 1050 (s), 1136 (s), 1222 (s), 1293 (s), 1467 (s), 1497 (s), 1602 (s), 1631 (m), 2339 (m, BH), 2366 (m, BH), 2422 (m, BH), 2885 (m), 2916 (m), 2984 (m), 3039 (w). $C_{17}H_{20}BBrFN_2OP$ (409.04): calcd. C 49.92, H 4.93; found C 49.98, H 4.88.

(2*R*,5*S*)-2-(2-Bromo-4-*tert*-butylphenoxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0^{1,5}]octane–Borane (3f): Yield 85% (1.90 g). White solid, m.p. 136–142 °C. $[\alpha]_D^{25}$ = –139.4 (*c* = 1, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.0 (m, 3 H), 1.2 (s, 9 H), 1.4–1.6 (m, 1 H), 1.8–2.0 (m, 3 H), 3.0–3.2 (m, 3 H), 3.3–3.6 (m, 1 H), 3.7–3.8 (m, 1 H), 6.6–7.5 (m, 8 H) ppm. ^{13}C NMR (50.30 MHz, $CDCl_3$): δ = 26.4 (d, *J* = 4 Hz), 31.2, 32.0 (d, *J* = 3 Hz), 34.4, 47.0 (d, *J* = 11 Hz), 54.0, 59.8, 116.4 (d, *J* = 4 Hz), 116.8 (d, *J* = 5 Hz), 121.4, 121.8 (d, *J* = 3 Hz), 125.3, 129.2, 130.3, 141.9 (d, *J* = 10 Hz), 145.8 (d, *J* = 15 Hz), 149.4 ppm. ^{31}P NMR (40.50 MHz, $CDCl_3$): δ = 109.3 (broad) ppm. IR (neat, cm^{-1}): $\tilde{\nu}$ = 884 (s), 1050 (s), 1136 (s), 1222 (s), 1293 (s), 1467 (s), 1497 (s), 1602 (s), 1631 (m), 2339 (m, BH), 2366 (m, BH), 2422 (m, BH), 2885 (m), 2916 (m), 2984 (m), 3039 (w). $C_{21}H_{29}BBrN_2OP$ (447.16): calcd. C 56.41, H 6.54, N 6.26; found C 56, 55, H 6.38, N 6.51.

(2*R*,5*S*)-2-(2-Bromo-4-methoxyphenoxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0^{1,5}]octane–Borane (3 g): Yield, 92% (1.94 g). White solid, m.p. 103–108 °C. $[\alpha]_D^{25}$ = –123.2 (*c* = 1, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.3–1.3 (m, 3 H), 1.5–1.8 (m, 1 H), 1.9–2.1 (m, 3 H), 3.1–3.5 (m, 3 H), 3.6–3.7 (m, 1 H), 3.8 (s, 3 H), 3.8–4.2 (m, 1 H), 6.6–6.9 (m, 3 H), 7.0–7.2 (m, 2 H), 7.3–7.7 (m, 3 H) ppm. ^{13}C NMR (50.30 MHz, $CDCl_3$): δ = 26.4 (d, *J* = 5 Hz), 31.5 (d, *J* = 3 Hz), 46.9 (d, *J* = 11 Hz), 54.0, 55.6, 59.8, 113.8 (d, *J* = 2 Hz), 116.8 (d, *J* = 6 Hz), 117.2 (d, *J* = 4 Hz), 118.3 (d, *J* = 2 Hz), 121.5, 122.7 (d, *J* = 3 Hz), 129.2, 141.8 (d, *J* = 16 Hz), 141.9 (d, *J* = 10 Hz), 156.8 (d, *J* = 2 Hz) ppm. IR (neat, cm^{-1}): $\tilde{\nu}$ = 884 (s), 1028 (s), 1119 (s), 1199 (s), 1259 (m), 1298 (s), 1487 (m), 1503 (s), 1598 (s), 2339 (m, BH), 2366 (m, BH), 2422 (m, BH), 2832 (m), 2967 (m), 2975 (m), 3094 (w). $C_{18}H_{23}BBrN_2O_2P$ (420.08): calcd. C 51.34, H 5.51; found C 51.46, H 5.48.

(2*R*,5*S*)-2-(2-Bromo-1-naphthoxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0^{1,5}]octane–Borane (3h): Yield 70% (1.54 g). White solid, m.p. 150–152 °C. $[\alpha]_D^{25}$ = –88.0 (*c* = 1, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.1–1.3 (m, 3 H), 1.5–1.6 (m, 1 H), 1.8–2.0 (m, 3 H), 3.0–3.4 (m, 3 H), 3.5–3.7 (m, 1 H), 3.8–3.9 (m, 1 H), 7.0–7.8 (m, 11 H) ppm. ^{13}C NMR (50.30 MHz, $CDCl_3$): δ = 26.4 (d, *J* = 5 Hz), 31.5 (d, *J* = 2 Hz), 46.9 (d, *J* = 10 Hz), 53.9, 59.8, 115.6 (d, *J* = 6 Hz), 116.9 (d, *J* = 6 Hz), 121.2 (d, *J* = 3 Hz), 121.6, 126.0, 127.1, 127.7, 128.0, 128.6, 129.3, 131.6, 132.8, 141.9 (d, *J* = 10 Hz), 146.5 (d, *J* = 15 Hz) ppm. IR (neat, cm^{-1}): $\tilde{\nu}$ = 884 (s), 1050 (s), 1136 (s), 1222 (s), 1293 (s), 1467 (s), 1497 (s), 1602 (s), 1631 (m), 2339 (m, BH), 2366 (m, BH), 2422 (m, BH), 2885 (m), 2916 (m), 2984 (m), 3039 (w). $C_{21}H_{23}BBrN_2OP$ (441.11): calcd. C 57.18, H 5.26; found C 57.25, H 5.32.

General Procedure for the Synthesis of Compounds 4a–4h: To a 25-mL two-necked round -bottomed flask were added compound **3** (2.5 mmol) dissolved in dry THF (10 mL). The solution was cooled to –78 °C and 2 equiv. of *tert*-butyllithium (1.7 M in diethyl ether) were added dropwise. The solution was stirred overnight at room temperature and then hydrolysed with 10 mL of an aqueous saturated solution of NH_4Cl. The product was extracted with CH_2Cl_2. The combined organic phases were dried with $MgSO_4$ and the solvent was removed in vacuo. The residue was purified by column chromatography (eluent: ethyl acetate/petroleum ether, from 5:95 to 20:80), affording the corresponding *o*-hydroxyphenyldiazaphospholidine–borane complex **4**. In all cases only one diastereoisomer was obtained.

(2*R*,5*S*)-2-(2-Hydroxyphenyl)-3-phenyl-1,3-diaza-2-phosphabicyclo-[3.3.0^{1,5}]octane–Borane (4a): Prepared by general procedure from **3a** (0.98 g, 2.5 mmol) in 86% yield (0.67 g). White solid, m.p. 115–122 °C. $[\alpha]_D^{25}$ = +164.2 (*c* = 1, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.1–1.1 (m, 3 H), 1.7–2.2 (m, 4 H), 3.1–3.4 (m, 2 H), 3.6–3.9 (m, 2 H), 4.0–4.1 (m, 1 H), 6.7–7.6 (m, 9 H), 9.8 (s, 1 H) ppm. ^{13}C NMR (50.30 MHz, $CDCl_3$): δ = 26.3 (d, *J* = 4 Hz), 31.7, 48.6 (d, *J* = 4 Hz), 52.4 (d, *J* = 3 Hz), 61.9 (d, *J* = 3 Hz), 116.5 (d, *J* = 35 Hz), 117.7 (d, *J* = 5 Hz), 118.9 (d, *J* = 4 Hz), 119.8 (d, *J* = 19 Hz), 122.3, 129.4, 132.1 (d, *J* = 15 Hz), 134.0, 142.0 (d, *J* = 7 Hz), 159.2 ppm. ^{31}P NMR (40.50 MHz, $CDCl_3$): δ = 106.5 (broad) ppm. IR (neat, cm^{-1}): $\tilde{\nu}$ = 1187 (s), 1287 (s), 1310 (s), 1501 (s), 1602 (s), 1630 (m), 2348 (m, BH), 2387 (s, BH), 2883 (m), 2950 (m), 2975 (m), 3095 (m), 3470 (s, OH). $C_{17}H_{22}BN_2OP$ (312.15): calcd. C 65.41, H 7.10; found C 65.33, H 7.07.

(2*R*,5*S*)-2-(2-Hydroxy-5-methylphenyl)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0^{1,5}]octane–Borane (4b): Prepared by the general procedure from **3b** (1.02 g, 2.5 mmol) in 70% yield (0.57 g). White solid, m.p. 124–126 °C. $[\alpha]_D^{25}$ = –187.5 (*c* = 1, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.5–1.5 (m, 2 H), 1.6–1.9 (m, 5 H), 2.0 (s, 3 H), 3.0–3.3 (m, 2 H), 3.5–3.7 (m, 2 H), 3.9 (m, 1 H), 6.7–7.3 (m, 8 H), 9.9 (s, 1 H) ppm. ^{13}C NMR (50.30 MHz, $CDCl_3$): δ = 16.0, 26.3 (d, *J* = 4 Hz), 31.7 (d, *J* = 3 Hz), 48.6 (d, *J* = 4 Hz), 52.4, 61.9 (d, *J* = 3 Hz), 115.5 (d, *J* = 56 Hz), 118.9 (d, *J* = 4 Hz), 119.5 (d, *J* = 12 Hz), 122.3, 126.5 (d, *J* = 5 Hz), 129.1, 129.7 (d, *J* = 15 Hz), 135.0 (d, *J* = 2 Hz), 142.2 (d, *J* = 6 Hz), 157.4 (d, *J* = 3 Hz) ppm. ^{31}P NMR (40.50 MHz, $CDCl_3$): δ = 105.6 (broad) ppm. IR (neat, cm^{-1}): $\tilde{\nu}$ = 1187 (s), 1287 (s), 1310 (s), 1501 (s), 1602 (s), 1630 (m), 2348 (m, BH), 2387 (s, BH), 2883 (m), 2950 (m), 2975 (m), 3095 (m), 3470 (s, OH). $C_{18}H_{24}BN_2OP$ (326.18): calcd. C 66.28, H 7.42; found C 66.31, H 7.45.

(2*R*,5*S*)-2-(2-Hydroxy-5-phenylphenyl)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0^{1,5}]octane–Borane (4c): Prepared by the general procedure from **3c** (1.17 g, 2.5 mmol) in 78% yield (0.76 g). White solid, m.p. 132–134 °C. $[\alpha]_D^{25}$ = –172.0 (*c* = 1, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.9 (m, 1 H); 1.1–1.5 (m, 2 H), 2.4–2.6 (m, 4 H), 3.1–3.5 (m, 2 H), 3.5–3.9 (m, 2 H), 3.9–4.2 (m, 1 H), 6.7–7.9 (m, 13 H), 9.9 (s, 1 H) ppm. ^{13}C NMR (50.30 MHz, $CDCl_3$): δ = 26.3, 31.7, 48.8, 52.0, 60.0, 116.2 (d, *J* = 55 Hz), 117.9, 119.2, 122.5, 126.2, 126.7, 128.4, 129.2, 130.3 (d, *J* = 15 Hz), 132.4, 132.7, 139.6, 141.8 (d, *J* = 7 Hz), 158.6 (d, *J* = 3 Hz) ppm. ^{31}P NMR (40.50 MHz, $CDCl_3$): δ = 107.6 (broad) ppm. IR (neat, cm^{-1}): $\tilde{\nu}$ = 1187 (s), 1287 (s), 1310 (s), 1501 (s), 1602 (s), 1630 (m), 2348 (m, BH), 2387 (s, BH), 2883 (m), 2950 (m), 2975 (m), 3095 (m), 3470 (s, OH). $C_{23}H_{26}BN_2OP$ (388.25): calcd. C 71.15, H 6.75; found C 71.23, H 6.83.

(2*R*,5*S*)-2-(5-Chlorophenyl-2-hydroxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0^{1,5}]octane–Borane (4d): Prepared by the general procedure from **3d** (1.06 g, 2.5 mmol) in 76% yield (0.66 g). White solid, m.p. 80–85 °C– $[\alpha]_D^{25}$ = –171.8 (*c* = 1, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.1–1.2 (m, 3 H), 1.7–2.2 (m, 4 H), 3.0–3.4 (m, 2 H), 3.5–3.9 (m, 2 H), 4.0 (m, 1 H), 6.7–7.4 (m, 8 H), 9.2 (s, 1 H) ppm. ^{13}C NMR (50.30 MHz, $CDCl_3$): δ = 26.3, 31.8, 48.5 (d, *J* = 4 Hz), 52.5, 62.0, 118.7 (d, *J* = 4 Hz), 119.3 (d, *J* = 5 Hz), 122.5, 124.8 (d, *J* = 15 Hz), 129.4, 131.2 (d, *J* = 15 Hz), 133.8,

141.7 (d, J = 10 Hz), 157.7 (d, J = 3 Hz) ppm. ^{31}P NMR (40.50 MHz, $CDCl_3$): δ = 105.1 (broad) ppm. IR (neat, cm^{-1}): $\tilde{\nu}$ = 1187 (s), 1287 (s), 1310 (s), 1501 (s), 1602 (s), 1630 (m), 2348 (m, BH), 2387 (s, BH), 2883 (m), 2950 (m), 2975 (m), 3095 (m), 3470 (s, OH). $C_{17}H_{21}BClN_2OP$ (346.6): calcd. C 58.91, H 6.11; found C 58.95, H 6.18.

(2*R*,5*S*)-2-(5-Fluorophenyl-2-hydroxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0^{1,5}]octane–Borane (4e): Prepared by the general procedure from **3e** (1.02 g, 2.5 mmol) in 76% yield (0.63 g). White solid, m.p. 80–85 °C. $[\alpha]_D^{25}$ = –171.8 (c = 1, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.0–0.8 (m, 1 H), 1.0–1.2 (m, 2 H), 1.7–2.1 (m, 4 H), 3.1–3.4 (m, 2 H), 3.6–3.9 (m, 2 H), 4.0–4.1 (m, 1 H), 6.7–7.2 (m, 8 H), 9.3 (s, 1 H) ppm. ^{13}C NMR (50.30 MHz, $CDCl_3$): δ = 26.4 (d, J = 3 Hz), 31.8, 48.6 (d, J = 4 Hz), 52.5 (d, J = 2 Hz), 62.1, 116.4 (d, J = 35 Hz), 117.3 (d, J = 3 Hz), 18.7 (d, J = 2 Hz), 119.1 (d, J = 2 Hz), 119.3, 120.9 (d, J = 15 Hz), 122.4, 129.2, 141.7 (d, J = 6 Hz), 157.9 ppm. ^{31}P NMR (40.50 MHz, $CDCl_3$): δ = 105.4 (broad) ppm. IR (neat, cm^{-1}): $\tilde{\nu}$ = 1187 (s), 1287 (s), 1310 (s), 1501 (s), 1602 (s), 1630 (m), 2348 (m, BH), 2387 (s, BH), 2883 (m), 2950 (m), 2975 (m), 3095 (m), 3470 (s, OH). $C_{17}H_{21}BFN_2OP$ (330.14): calcd. C 61.85, H 6.41; found C 61.78, H 6.56.

(2*R*,5*S*)-2-(5-*tert*-Butylphenyl-2-hydroxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0^{1,5}]octane–Borane (4f): Prepared by the general procedure from **3f** (1.12 g, 2.5 mmol) in 80% yield (0.74 g). White solid, m.p. 134–140 °C. $[\alpha]_D^{25}$ = –170.0 (c = 1, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.2–1.0 (m, 2 H), 1.0 (s, 9 H), 1.1–1.3 (m, 1 H), 1.6–2.2 (m, 4 H), 3.1–3.4 (m, 2 H), 3.6–3.8 (m, 1 H), 3.8–3.9 (m, 1 H), 4.0–4.1 (m, 1 H), 6.6–6.7 (m, 1 H), 6.9–7.3 (m, 7 H), 9.8 (m, 1 H) ppm. ^{13}C NMR (50.30 MHz, $CDCl_3$): δ = 26.3, 31.0, 31.9, 33.8, 48.9 (d, J = 4 Hz), 51.7, 62.1 (d, J = 4 Hz), 114.3 (d, J = 54 Hz), 116.8 (d, J = 3 Hz), 119.4 (d, J = 2 Hz), 122.6, 128.5 (d, J = 16 Hz), 129.0, 131.0, 141.9, 142.0 (d, J = 5 Hz), 156.9 ppm. ^{31}P NMR (40.50 MHz, $CDCl_3$): δ = 107.5 (broad) ppm. IR (neat, cm^{-1}): $\tilde{\nu}$ = 1187 (s), 1287 (s), 1310 (s), 1501 (s), 1602 (s), 1630 (m), 2348 (m, BH), 2387 (s, BH), 2883 (m), 2950 (m), 2975 (m), 3095 (m), 3470 (s, OH). $C_{21}H_{30}BN_2OP$ (368.26): calcd. C 68.49, H 8.21; 7.61; found C 68.36, H 8.32, N 7.56.

(2*R*,5*S*)-2-(2-Hydroxy-5-methoxyphenyl)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0^{1,5}]octane–Borane (4 g): Prepared by the general procedure from **3 g** (1.05 g, 2.5 mmol) in 84% yield (0.72 g). White solid, m.p. 129–134 °C ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.1–1.1 (m, 3 H), 1.7–2.2 (m, 4 H), 3.1–3.5 (m, 2 H), 3.5 (s, 3 H), 3.6–4.1 (m, 3 H), 6.6–7.3 (m, 8 H), 8.5 (s, 1 H) ppm. ^{13}C NMR (50.30 MHz, $CDCl_3$): δ = 26.3 (d, J = 3 Hz), 31.8 (d, J = 1 Hz), 48.6 (d, J = 4 Hz), 52.2 (d, J = 2 Hz), 55.4, 62.0 (d, J = 3 Hz), 114.7 (d, J = 15 Hz), 116.2 (d, J = 32 Hz), 118.6 (d, J = 6 Hz), 119.0 (d, J = 4 Hz), 121.0 (d, J = 2 Hz), 122.4, 129.1, 142.0 (d, J = 6 Hz), 152.4 (d, J = 14 Hz), 153.0 (d, J = 3 Hz) ppm. ^{31}P NMR (40.50 MHz, $CDCl_3$): δ = 104.9 (broad) ppm. IR (neat, cm^{-1}): $\tilde{\nu}$ = 1187 (s), 1287 (s), 1310 (s), 1501 (s), 1602 (s), 1630 (m), 2348 (m, BH), 2387 (s, BH), 2883 (m), 2950 (m), 2975 (m), 3095 (m), 3470 (s, OH). $C_{18}H_{24}BN_2O_2P$ (342.18): calcd. C 63.18, H 7.07; found C 63.26, H 6.96.

(2*R*,5S)-2-(1-Hydroxy-2-naphthyl)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0^{1,5}]octane–Borane (4h): Prepared by the general procedure from **3h** (1.10 g, 2.5 mmol) in 40% yield (0.36 g). White solid, m.p. 146–152 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.3–1.1 (m, 3 H), 1.6–2.2 (m, 4 H), 3.3–3.7 (m, 3 H), 3.9–4.1 (m, 2 H), 6.8–7.8 (m, 11 H), 12.7 (s, 1 H) ppm. ^{31}P NMR (40.50 MHz, $CDCl_3$): δ = 108.9 (broad) ppm. IR (neat, cm^{-1}): $\tilde{\nu}$ = 1187 (s), 1287 (s), 1310 (s), 1501 (s), 1602 (s), 1630 (m), 2348 (m, BH), 2387 (s, BH), 2883 (m), 2950 (m), 2975 (m), 3095 (m), 3470 (s, OH). $C_{21}H_{24}BN_2OP$ (362.17): calcd. C 69.63, H 6.68; found C 69.72, H 6.56.

Acknowledgments

The authors would like to thank Inspec Fine Chemical Company and Dr. Brigitte Saliva for financial support. Thanks are also due to Dr. Michel Giorgi for his kind assistance with X-ray analysis of compounds **3f** and **4f**. C. J. N. thanks CNRS and Region PACA for a doctoral fellowship.

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[23] CCDC-287827 (for **3f**) contains 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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Received: October 28, 2005
Published Online: December 30, 2005

