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Synthesis of P-Stereogenic Phosphoramidite and Phosphorodiamidite Ligands and Their Application in Asymmetric Catalysis

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Keywords: Asymmetric catalysis / Ligand design / P ligands / P-chirality / Betti base

A series of *P*-stereogenic monodentate phosphoramidite (PNO_2) and phosphorodiamidite (PN_2O) ligands based on chiral Betti bases has been prepared by modular synthetic procedures. The chirality at the phosphorus can be controlled to a large extent by the synthetic route, leading to stereoselective access to single P-epimers. The absolute configuration of the P-atom was assigned by X-ray diffraction analysis. The new ligands were evaluated in asymmetric catalysis and the influence of the exocyclic amine or alcohol moiety as well as the interplay between the P-chirality and the stereocenters in the backbone were investigated. Enantioselectivities of up to 85 and 83 % *ee* were obtained in the Rh-catalyzed hydrogenation of dimethyl itaconate and in the Pd-catalyzed allylic amination of (*rac*)-(*E*)-1,3-diphenylallyl acetate with benzylamine, respectively. In the Ni-catalyzed hydrovinylation of styrene, *ee* values of up to 68 %, excellent chemoselectivities, and high activities (TOF_{av} up to 3000 h^{-1}) were achieved.

Introduction

The fruitful development of transition-metal-catalyzed asymmetric transformations is closely related to the availability of an increasing number of chiral phosphorus ligands.[1] The introduction of novel ligand structures has contributed greatly to the evolution of this field, resulting in a set of widely used tools for organic synthesis on both a laboratory and an industrial scale.[2] The overall chirality of the ligand environment can result from stereogenic elements in the ligand backbone and/or at the donor atom itself.

In 1961, Horner and co-workers isolated optically pure trivalent phosphines[3] and, some years later, Horner[4] and Knowles[5] demonstrated the potential of such compounds in asymmetric catalysis. Since these pioneering works, interest in phosphorus ligands bearing chirality at the phosphorus atom has expanded greatly, and the development of new efficient and stereoselective synthetic methodologies, particularly those using phosphine borane chemistry, has led to the availability of a large number of *P*-stereogenic ligands.[6] The choice of substituents at the P-atom allows not only fine-tuning of the ligand features but also affects the inversion barrier for the epimerization of the *P*-stereogenic center.[7]

Chiral phosphorus compounds in which the donor atom is surrounded by heteroatoms are finding increasing application in transition-metal-catalyzed asymmetric transformations.[1,8] Most of the monodentate ligands containing phosphorus–heteroatom bonds can be synthesized through simple condensation reactions and in high yields from a variety of chiral precursors, for example diols, amino alcohols, or diamines, allowing for the creation of ligand libraries to rapidly assess the optimum structure for a given application.[9] In particular, phosphoramidites have evolved into a versatile class of ligands since the first reports by Feringa and de Vries[10] showed excellent enantioselectivities in a variety of transition-metal-catalyzed asymmetric processes.[11] Phosphoramidites provide broad opportunities for fine tuning of their donor–acceptor and steric properties by the incorporation of appropriate substituents at the oxygen and nitrogen directly bound to the P-atom.[12] The large majority of reported phosphoramidites are composed of a C_2-symmetric diol backbone (especially BINOL or TADDOL) with a monoamine[13] and, hence, do not feature a *P*-stereogenic center. In general, the influence of P-chirality on the catalytic behavior in ligands of type PN_xO_y (x,y = 1,2) remains largely unexplored.

Apart from rare examples based on C_1-symmetric BINOL derivatives and a monoamine (compounds **1**–**3**; Figure 1),[14] *P*-stereogenic phosphoramidites have been prepared by combining an alcohol and an amino alcohol mostly derived from an amino acid or other natural product.[11c]

An early example of monodentate *P*-stereogenic phosphoramidites was reported by Pastor and Rodebaugh in 1988. Compounds **4** were synthesized from 2-(*N*-*tert*-butylamino)ethanol as an amino alcohol building block, but not tested in catalysis (Figure 2).[15] Polosukhin et al. synthesized monodentate phosphoramidites **5** from (*S*)-pro-

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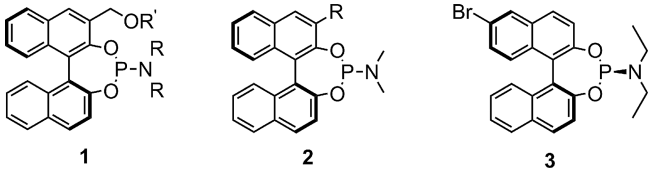

Figure 1. *P*-Stereogenic phosphoramidites derived from C_1-symmetric BINOL derivatives.[14]

linol and several alcohols, leading to diastereomeric mixtures of P-epimers, which were not separated.[16] Reetz and Bondarev used (*S*)-α,α-diphenylprolinol and several alcohols for the synthesis of phosphoramidites of type **6**, achivieng up to 95% *ee* in the Rh-catalyzed asymmetric hydrogenation.[17] A library of *P*-stereogenic phosphoramidites **7**–**11** possessing five- or six-membered phosphacycles and an exocyclic methoxy-substituent was synthesized by Benetsky et al. and applied in the Pd-catalyzed allylic substitution with up to 59% *ee*.[12] However, previous reports have either not investigated the impact of the P-chirality in catalysis as single diastereomers or diastereomeric mixtures have been employed as ligands for catalysis.

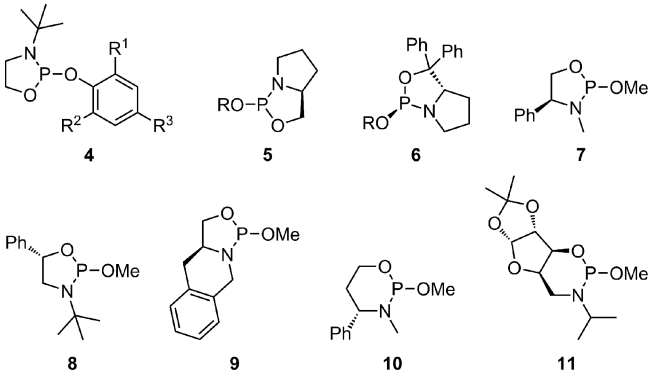

Figure 2. *P*-Stereogenic phosphoramidites synthesized from amino alcohols containing five- or six-membered 1,3,2-oxaazaphosphacycles.[12,15,16,17]

In a similar strategy, the combination of amino alcohols with monoamines results in phosphorodiamidites (diamidophosphites) containing two P–N and one P–O bond, which consequently possess a stereogenic P-atom.[18,19] Phosphorodiamidite ligands are underrepresented in the literature and their potential in catalysis has been assessed in very few cases.[20] For example, Bernard and Burgada reported phosphorodiamidites **12** prepared from an ephedrine derivative (Figure 3), but did not apply them in asymmetric catalysis.[21] Alexakis reported the synthesis and application of *P*-stereogenic phosphorodiamidites **12**–**15** based on ephedrine and prolinol in Cu-catalyzed 1,4-addition and achieved enantioselectivities of more than 95% *ee*.[22] Bondarev and Goddard described *P*-stereogenic phosphorodiamidites **16** derived from α,α-diphenylprolinol and their use in Rh-catalyzed asymmetric hydrogenation for which up to 91% *ee* was achieved.[23] Recently, we reported the synthesis of *N*-Phenyl-NOBIN derived phosphorodiamidites **17**. These ligands were tested in the nickel-catalyzed hydrovinylation of styrene without showing any catalytic activity.[24] In general, phosphorodiamidites derived from amino alcohols were obtained as single diastereomers and, hence, the effect in catalysis of the P-chirality could not be addressed.

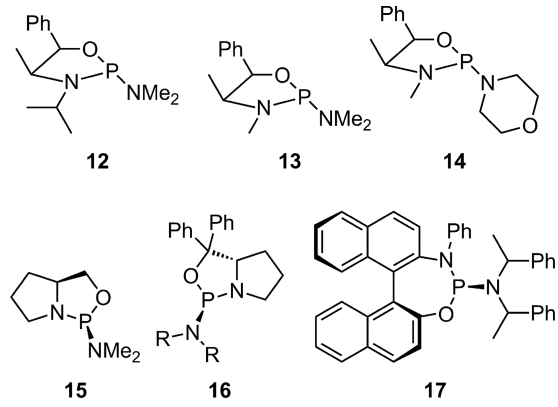

Figure 3. P-Stereogenic phosphorodiamidites synthesized from amino alcohols.[21–24]

As shown in the examples mentioned above, most of the reported *P*-stereogenic phosphoramidites and phosphorodiamidites were synthesized from amino alcohols derived from natural α-amino acids. These provide, in most cases, an inexpensive source of chirality but structural diversity is limited and typically only one enantiomer is accessible from the chiral pool.

An alternative source for chiral amino alcohols are the Betti bases **18**.[25] Betti bases are easily prepared on multigram scale from inexpensive starting materials by a simple and straightforward condensation between 2-naphthol, aryl aldehydes and ammonia or amines, which finally provides a broad structural variety of amino alcohols.[26] When enantiopure chiral amines are used in the synthesis of Betti bases, the reaction may proceed diastereoselectively, as was demonstrated for Betti base (*R*,*R*)-**19** (Figure 4).[27]

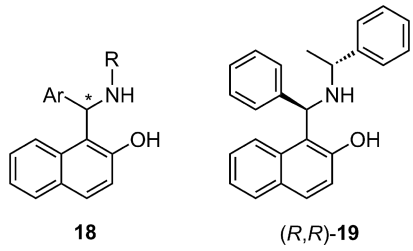

Figure 4. Betti bases containing one or two stereocenters.[25–27]

Betti bases and their derivatives have been applied in organic synthesis and asymmetric catalysis (Figure 5). For example, they were used as chiral auxiliaries for enantioseparation[28] or as ligands (**20**–**22**) in the asymmetric addition of organozinc compounds to aldehydes.[29] Furthermore, they have been used as chiral building blocks for phosphorus ligands **23**–**24**,[30] providing good to high levels of stereoselectivity in asymmetric catalysis, and thus encourage fur-

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ther investigations on the use of Betti base fragments as constituent of novel chiral ligands for asymmetric catalysis.[26] In none of the previously reported examples have *P*-stereogenic ligands been synthesized starting from a Betti base.

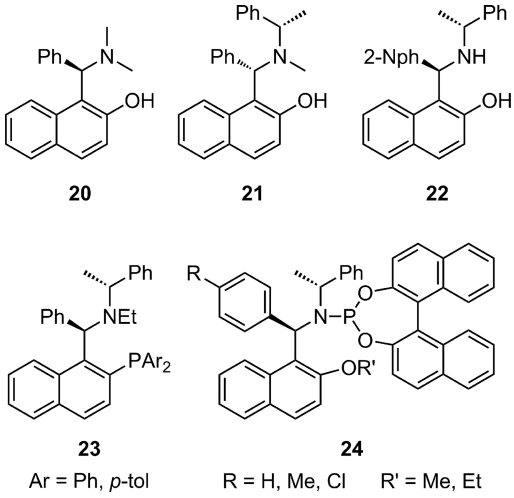


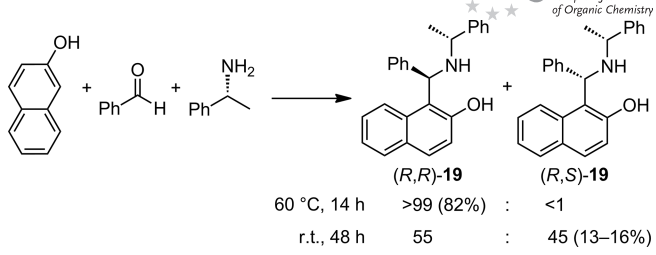
Figure 5. Chiral Betti bases and Betti-base-derived phosphorus ligands that have been applied successfully in asymmetric catalysis.[29,30]

Herein, we describe the synthesis of a series of new chiral phosphoramidite and phosphorodiamidite ligands based on Betti base **19** in a straightforward and modular synthetic protocol. The ligands include a stereogenic P-donor, and two different P-epimers are possible. The envisaged ligands are, in general, accessible by two different synthetic routes, which were compared and optimized for each ligand class. The predominantly formed P-epimer can be controlled to a large extent by the use of the appropriate synthetic route, allowing the isolation of both P-epimers in pure form for several ligands. Steric and electronic tuning of the ligand structure was accomplished by broad variation of the alcohol or amine component, including also chiral structures. All new ligands were tested in the asymmetric hydrogenation (Rh), allylic substitution (Pd), and hydrovinylation (Ni), for which the influence of the exocyclic O- or N-substituent at the P-atom (phosphoramidite vs. phosphorodiamidite) and the interplay of the different chiral centers in the Betti base backbone and the stereogenic phosphorus donor were evaluated.

Results and Discussion

Synthesis of Betti Bases

Betti base (*R*,*R*)-**19** was synthesized from 2-naphthol, benzaldehyde, and (*R*)-phenylethylamine by mixing and heating all components at 60 °C for 14 h according to a reported procedure.[31] The synthesis is diastereoselective, and (*R*,*R*)-**19** was obtained in > 99% *de* and 82% yield (Scheme 1).

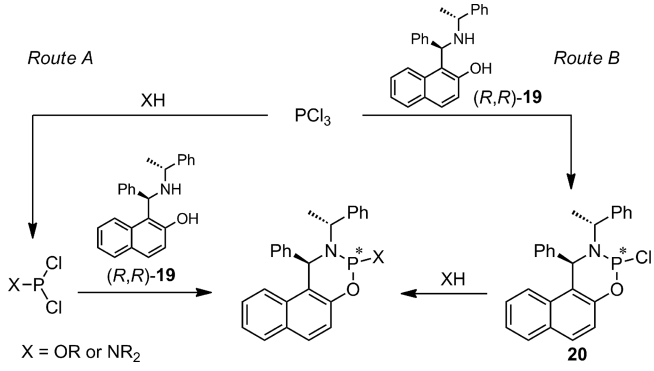


Scheme 1. Synthesis of Betti base (*R*,*R*)-**19** and (*R*,*S*)-**19**.

In contrast, the synthesis and isolation of (*R*,*S*)-**19** has not been previously reported; however, by simply performing the reaction at room temperature, an almost 1:1 mixture of (*R*,*R*)-**19** and (*R*,*S*)-**19** could be obtained (Scheme 1). Crystallization-induced asymmetric transformation[32] towards the exclusive formation of (*R*,*R*)-**19** was not observed under these reaction conditions. From the crude reaction mixture, pure (*R*,*S*)-**19** was isolated by multiple crystallization in low yields of 13–16%.[33]

Ligand Synthesis

Like other phosphorus ligands containing P–O and P–N bonds,[11b] the envisaged *P*-stereogenic phosphoramidites and phosphorodiamidites are, in principle, accessible by two convergent synthetic routes starting from phosphorus trichloride (Scheme 2).



Scheme 2. Possible synthetic routes for the preparation of *P*-stereogenic phosphoramidites and phosphorodiamidites.

Route A involves first the formation of a PCl_2-intermediate (dichlorophosphite or dichloramidophosphite), which is subsequently reacted with the amino alcohol to give the phosphoramidite or phosphorodiamidite, respectively. Here, the chirality at the phosphorus atom is generated in the second step. Alternatively, Route B first entails the synthesis of phosphoramidochloridite **20**, which is subsequently converted into the phosphoramidite or phosphorodiamidite by treatment with either an alcohol or a secondary amine. Thus, Route B involves the formation of a chiral center at the phosphorus atom in the first step of the synthesis. The subsequent substitution of the chloride may lead to inversion, retention, or even racemization of the configuration at the phosphorus. Therefore, temperature, solvent and hardness of the nucleophile can be impor-

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tant to control the stereochemistry at the P-atom during this synthesis route.

With the aim of developing a modular synthetic protocol, which also provides control of the P-chirality, both routes were investigated and compared for phosphoramidites and phosphorodiamidites. As will be shown in detail, the two synthetic routes are not equivalent but complementary.

Synthesis of Phosphoramidites by Route A

The reaction of (*R*,*R*)-**19** with commercially available dichloro(methoxy)phosphine in the presence of triethylamine in tetrahydrofuran (THF) led to the formation of two phosphorus-containing species, as indicated by $^{31}P\{^{1}H\}$ NMR analysis (δ_P = 136.6 ppm; 119.7 ppm) in a ratio of 80:20. MS and NMR analyses revealed their identical constitution but opposite configuration at the stereogenic phosphorus atom (Scheme 3).[34] The large difference in ^{31}P NMR shifts of the P-epimers **21a** indicates a significant difference in the environment at the P-atom.

Subsequent attempts to separate the P-epimers (*S*$_P$)-**21a** and (*R*$_P$)-**21a** either by crystallization or by chromatography were not successful. Therefore, the mixture of P-epimers was treated with a solution of BH_3·SMe_2 to give the borane adducts **21a**·BH_3 (Scheme 3). The resulting air-stable borane adducts were easily separated by column chromatography (silica; pentane/ethyl acetate) to give (*S*$_P$)-**21a**·BH_3 (^{31}P NMR: δ = 118.0 ppm) and (*R*$_P$)-**21a**·BH_3 (^{31}P NMR: δ = 110.5 ppm) in 63 and 12% yield,[35] respectively. The configuration of the P-atom was assigned by X-ray crystal structure analysis of suitable crystals of (*S*$_P$)-**21a**·BH_3, obtained by slow solvent evaporation at room temperature of an ethereal solution (Figure 6).

In the solid state, the 1,3,2-oxaazaphosphorinane ring of (*S*$_P$)-**21a**·BH_3 adopts an arrangement between a boat and a half-chair conformation. This is probably due to the incorporation in the cycle of heteroatoms with two, three, and four coordination number and an annulated naphthyl moiety. Additionally, a π-stacking of the phenyl ring of the phenylethyl fragment and the naphthyl moiety is observed. The average distance between the centroids is 3.731 and 3.884 Å, respectively, and the angle between the planes of the aryl rings is 13.8°. The bond lengths at the phosphorus atom are within the expected range, with the exocyclic O-atom exhibiting the shortest P–O bond length (Table 1). The phosphorus atom shows a nearly perfect tetrahedral

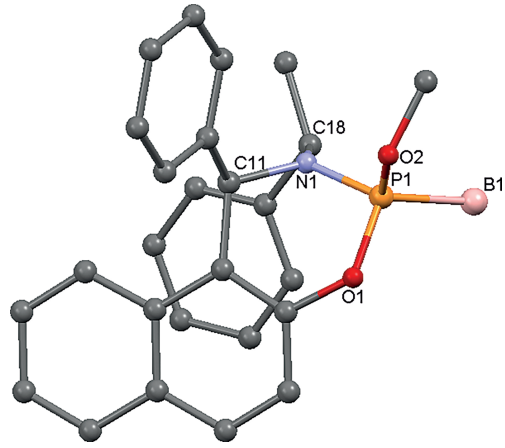


Figure 6. Molecular structure of (*S*$_P$)-**21a**·BH_3 in the solid state as determined from X-ray diffraction analysis. CCDC-1038401 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

geometry (sum of angles 654.50°), whereas the nitrogen atom in the oxazaphosphacycle has a trigonal-planar geometry (sum of angles 354.54°) and hence a high degree of sp^2-hybridization character (Table 2).

Table 1. Selected bond lengths [Å] in (*S*$_P$)-**21a**·BH_3.

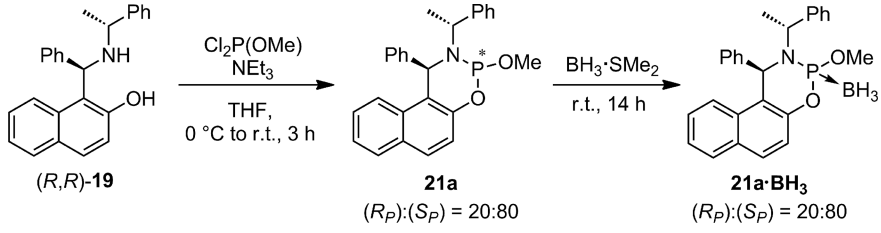
P1–N1	1.6443	P1–O1	1.6066
P1–B1	1.8876	P1–O2	1.5826

Table 2. Selected bond angles [°] in (*S*$_P$)-**21a**·BH_3.

P1–N1–C11	117.83	O1–P1–B1	114.02
P1–N1–C18	120.89	O2–P1–B1	114.26
C11–N1–C18	115.82	N1–P1–B1	116.89
O1–P1–O2	96.20	N1–P1–O2	109.06
O1–P1–N1	104.07		

The Betti base (*R*,*S*)-**19** was used for the synthesis of phosphoramidites, as described above, by dropwise addition of a solution of dichloro(methoxy)phosphine in CH_2Cl_2 to a cold solution (0 °C) of (*R*,*S*)-**19** and triethylamine in the same solvent. After 6 h, the two P-epimers (*R*$_P$)-**22a** and (*S*$_P$)-**22a** were obtained in a 62:38 ratio and protected by borane. Separation by column chromatography (silica; pentane/ethyl acetate) yielded both borane-protected P-epimers in 30 and 22% yield, respectively (Scheme 4).

The configuration of the P-atom was again assigned by X-ray crystal structure analysis of suitable crystals of (*R*$_P$)-



Scheme 3. Synthesis of phosphoramidites **21a** starting from (*R*,*R*)-**19** through Route A and protection as the borane adduct.

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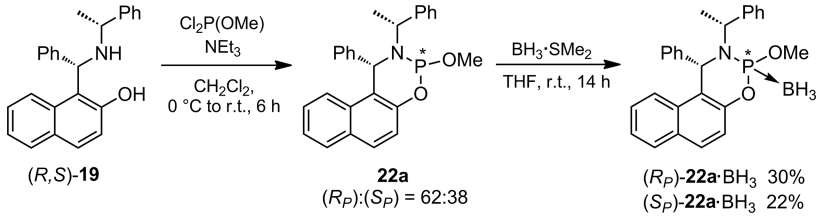


Scheme 4. Synthesis of phosphoramidite **22a** starting from (*R*,*S*)-**19** through Route A and protection as the borane adduct.

22a·BH_3 obtained by slow solvent evaporation at room temperature of an ethereal solution (Figure 7).

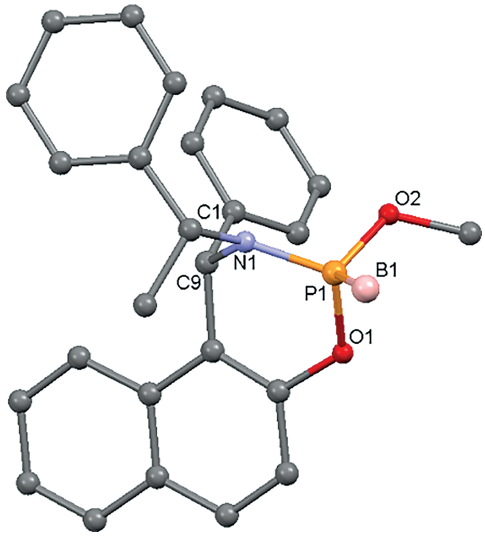


Figure 7. Structure of (R_P)-**22a**·BH_3 in the solid state as determined from X-ray diffraction.CCDC-1038402 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

In the solid-state crystal structure of (R_P)-**22a**·BH_3, the 1,3,2-oxaazaphosphorinane ring does not exhibit a definite conformation, as was also observed for (S_P)-**21a**·BH_3. The conformation adopted is again between boat and half-chair, but the half-chair conformation is more pronounced. A π-stacking is not observed and the phenylethyl substituent is oriented further away from the naphthyl moiety. All bond lengths on the P-atom are in the expected range and comparable to the values observed in (S_P)-**21a**·BH_3. Again, the exocyclic O-atom exhibits the shortest P–O bond length. The phosphorus atom has a nearly perfect tetrahedral geometry (sum of angles 655.09°), whereas the N-atom displays a trigonal-planar geometry (sum of angles 353.65°) (Table 3 and Table 4).

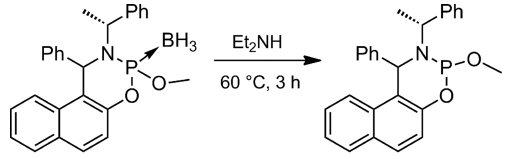
Table 3. Selected bond lengths [Å] in (R_P)-**22a**·BH_3.

P1–N1	1.6319	P1–O1	1.6198
P1–B1	1.8795	P1–O2	1.5876

To obtain the free ligands, diethylamine was added in large excess to the borane-phosphoramidites **21a**·BH_3 and **22a**·BH_3 and the resulting solutions were stirred for 3 h at 60 °C. Afterwards, all volatiles were removed in vacuo and the residue was washed with cold hexane to give phosphoramidites **21a** and **22a** in 64–97% yield (Scheme 5). Decomposition or epimerization of the *P*-configuration was not observed during the deprotection.

Table 4. Selected bond angles [°] in (R_P)-**22a**·BH_3.

P1–N1–C1	119.85	O1–P1–B1	111.28
P1–N1–C9	118.86	O2–P1–B1	114.56
C1–N1–C9	114.94	N1–P1–B1	118.19
O1–P1–O2	101.22	N1–P1–O2	104.77
O1–P1–N1	105.07		



(R_P)-**21a**-BH_3
(S_P)-**21a**-BH_3
(R_P)-**22a**-BH_3
(S_P)-**22a**-BH_3

(R_P)-**21a** 86%
(S_P)-**21a** 97%
(R_P)-**22a** 64%
(S_P)-**22a** 81%

Scheme 5. Deprotection of borane phosphoramidites **21a**·BH_3 and **22a**·BH_3 by reaction with diethylamine.

Synthesis of Phosphoramidites by Route B

After demonstrating that Route A was suitable for the synthesis of the (S_P)-epimer starting from (*R*,*R*)-**19**, Route B, comprising the generation of a phosphoramidochloridite in situ was evaluated by using different solvents and bases (Scheme 6). Compound (*R*,*R*)-**19** was dissolved in THF and the solution was cooled to 0 °C. After the addition of triethylamine, a solution of phosphorus trichloride was added slowly and the reaction was allowed to reach room temperature. After 3 h, the reaction was complete, as monitored by ^{31}P NMR spectroscopy, and the two P-epimers of phosphoramidochloridite **20** were formed in a 55:45 ratio [δ_P = 133.1 ppm (R_P); δ_P = 139.2 ppm (S_P)]. Methanol was then added slowly in the presence of triethylamine at 0 °C. After 6 h at room temperature, full conversion was achieved and phosphoramidites (R_P)-**21a** and (S_P)-**21a** were obtained with a high preference for the (S_P)-epimer in a ratio of 15:85, very similar to that obtained through Route A.[36]

When the same reaction sequence was carried out in CH_2Cl_2 with the same base triethylamine, phosphoramidochloridite **20** was formed in a similar R_P/S_P ratio of 60:40.

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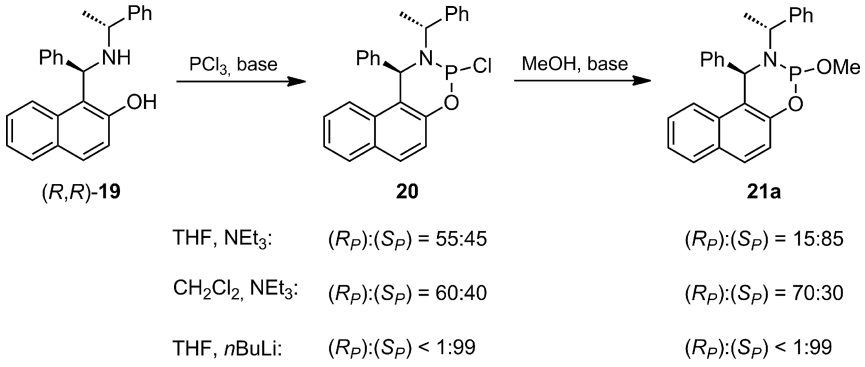
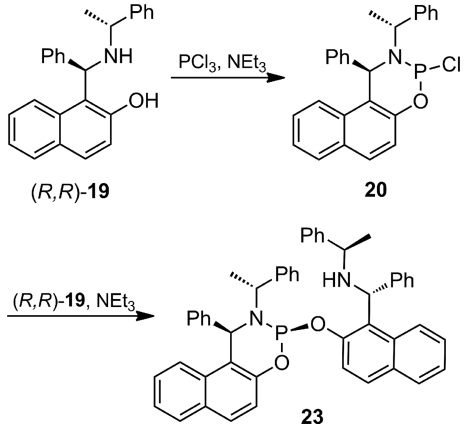


Scheme 6. Synthesis of *P*-stereogenic phosphoramidites by Route B using different solvents and bases.

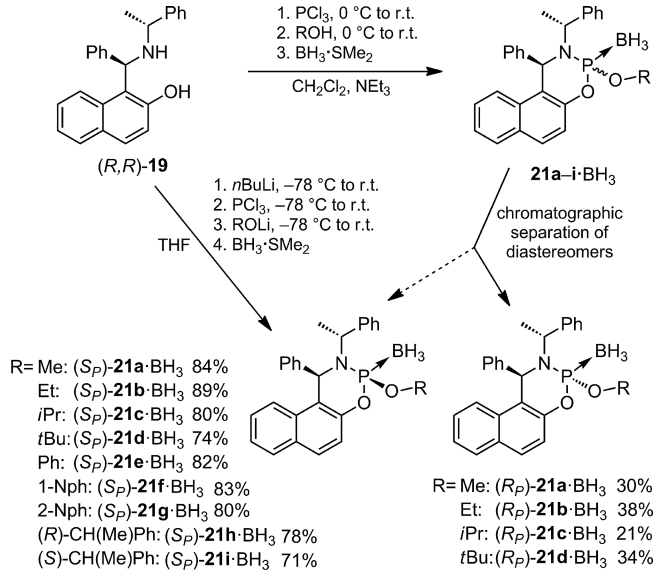
In the following reaction with methanol the P-epimers of the resulting phosphoramidite **21a** were obtained in a R_P/S_P ratio of 70:30 (Scheme 6). Consequently, the reaction in CH_2Cl_2 predominantly provided the (R_P)-epimer, whereas the reaction in THF led preferentially to the (S_P)-epimer. The reactions in CH_2Cl_2 proceeded more slowly than in THF; in particular, the formation of phosphoramidochloridite **20**. Additionally, an increased amount (usually 10–20%) of side product **23**, resulting from the reaction of phosphoramidochloridite **20** and (*R*,*R*)-Betti base **19**, was observed (Scheme 7).



Scheme 7. Formation of side product **23** from phosphoramidochloridite **20** and (*R*,*R*)-**19** in CH_2Cl_2.

Finally, when (*R*,*R*)-**19** was deprotonated using *n*-butyllithium as base in THF at –78 °C and then reacted with PCl_3, the stereoselective formation of (S_P)-phosphoramidochloridite (S_P)-**20** was observed (Scheme 6). The reaction of this intermediate (S_P)-**20** with the lithiated alcohol MeOLi at –78 °C led to the exclusive formation of (S_P)-**21a**. Thus, the substitution of the chloride by the alkoxide proceeded with complete inversion[36] of configuration at the P-atom, suggesting a S_N2-type mechanism. Hence, the same synthetic procedure using either CH_2Cl_2/NEt_3 or THF/*n*BuLi gave selective access to both P-epimers of the methoxy substituted phosphoramidite.

As a next step, the spectrum of alcohols used for the synthesis of phosphoramidites was extended. In addition to methanol, ethanol, isopropanol, *tert*-butanol, phenol, 1-naphthol, and 2-naphthol, as well as chiral alcohols (*R*)- and (*S*)-1-phenylethanol, were utilized. By using THF/*n*BuLi, phosphoramidites possessing (S_P)-configuration at the P-atom could be selectively prepared for all the alcohols employed in the synthesis. The ligands were purified by filtration through basic alumina to remove oxidized or hydrolyzed P-species and unreacted starting/intermediate materials. Afterwards, the ligands were protected by borane and purified by column chromatography (silica; pentane/ethyl acetate) to give (S_P)-**21a**–**i**·BH_3 in 71–89% yield (Scheme 8).



Scheme 8. Synthesis of borane phosphoramidites possessing different alkoxy substituents through Route B.

The procedure in CH_2Cl_2 using triethylamine as base was used for the preparation of (R_P)-**21** through the synthesis of a diastereomeric mixture followed by protection with BH_3 and separation. The preference towards the (R_P)-epimer, however, decreased with increasing steric bulk of the alcohols used for the synthesis. For example, the reaction using ethanol as the alcohol moiety provided both P-epimers in a R_P/S_P ratio of 60:40, whereas a 35:65 ratio was achieved when isopropanol was utilized. In addition, the R_f values of the two P-epimers became similar with increasing

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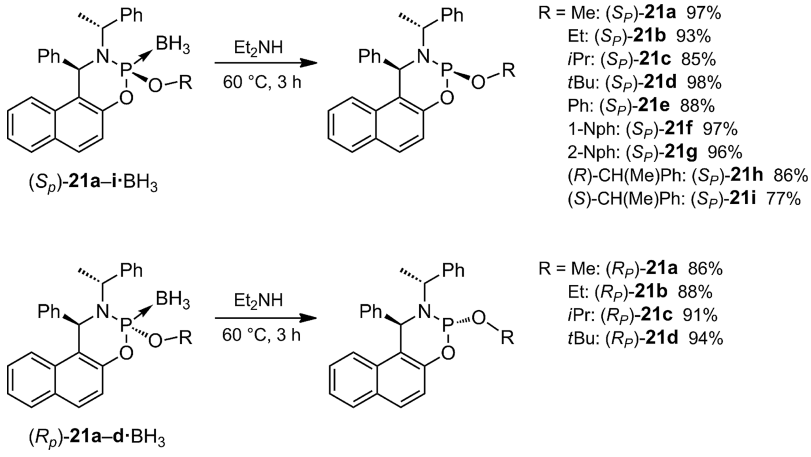

Scheme 9. Deprotection of borane phosphoramidites **21a**–**i**·BH_3 using diethylamine.

steric demand of the alcohols used and, hence, the chromatographic separation was more difficult. As a consequence, only (R_P)-**21a**–**d**·BH_3 could be successfully isolated in low to moderate yields of 21–38% (Scheme 9).

Finally, the borane-phosphoramidites **21a**–**i**·BH_3 were deprotected as described above by treatment with diethylamine. After the work-up, phosphoramidites **21a**–**i** were obtained in 77–98% yield (Scheme 9). Again, decomposition or epimerization of the *P*-configuration was not observed during the deprotection.

Each P-epimer presented very characteristic chemical shifts and coupling constants in ^{31}P, ^{1}H, and ^{13}C NMR spectra, and by comparison of these NMR data with that of (S_P)-**21a**, the structure of which was unequivocally determined by X-ray analysis, the *P*-configuration of all other deprotected ligands **21** was assigned. For example, ligands **21a**–**d** with (S_P)-configuration, gave a chemical shift of δ = 131.9–136.6 ppm in the ^{31}P NMR spectra, whereas ligands possessing (R_P)-configuration exhibit a chemical shift of δ = 114.1–120.0 ppm (Figure 8). The chemical shifts in the ^{1}H NMR spectra also provide characteristic information, particularly for the signals of the CH- and the CH_3-group of the phenylethyl moiety. In particular, the ligands with

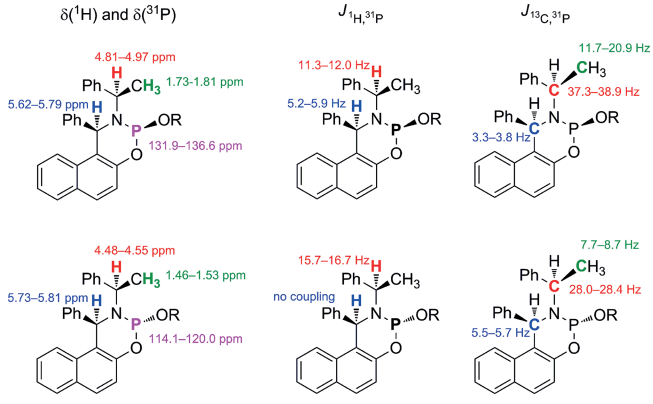

Figure 8. Comparison of characteristic chemical shifts (^{1}H,^{31}P) and coupling constants ($J_{H,P}$ and $J_{C,P}$) for both P-epimers of phosphoramidites **21a**–**d**.

(S_P)-configuration have a chemical shift in the range of δ = 1.73–1.81 ppm (CH_3) and δ = 4.81–4.97 (CH), whereas the ligands with (R_P)-configuration are shifted to higher field (δ = 1.46–1.53 ppm for CH_3, δ = 4.48–4.55 for CH). Very pronounced differences were also observed for the ^{1}H–^{31}P coupling constants of the two CH protons in the Betti base backbone. Coupling constants in the range of $^{3}J_{H,P}$ = 11.3–12.0 Hz for the exocyclic C–H in the 1-phenylethyl moiety and $^{3}J_{H,P}$ = 5.2–5.9 Hz for the endocyclic C–H were observed for the ligands with (S_P)-configuration, whereas the phosphoramidites with (R_P)-configuration showed a larger coupling constant of $^{3}J_{H,P}$ = 15.7–16.7 Hz for the exocyclic CH proton and no ^{1}H–^{31}P-coupling was observed for the endocyclic CH proton. Similar trends were observed in the ^{13}C NMR spectra. Here, especially the ^{13}C–^{31}P coupling constants are indicative for the *P*-configuration.

Synthesis of Phosphorodiamidites

The synthesis of phosphorodiamidites was also investigated by using both synthetic Routes A and B (Scheme 1). By following Route A, the reaction of (*R*,*R*)-Betti base **19** with commercially available dichloro-*N*,*N*-diethylaminophosphine in CH_2Cl_2 in the presence of triethylamine resulted in a mixture of the two P-epimers (R_P)-**24a** (δ = 135.4 ppm) and (S_P)-**24a** (δ = 114.7 ppm) in a 25:75 ratio, whereas when THF was used under the same conditions, formation of the (R_P)-epimer of **24a** was clearly favored (R_P/S_P ratio 75:25). Subsequent addition of BH_3/SMe_2 provided the borane adducts, which were separated by column chromatography in 30 and 18% yield, respectively (Scheme 10).

As already observed for the phosphoramidites, there was a considerable spread in the ^{31}P NMR chemical shift values (ca. 20 ppm), thus indicating the significant differences in the environment of the P-epimers of the phosphorodiamidites. In comparison to the phosphoramidites, ^{31}P NMR signals of the phosphorodiamidites were slightly shifted to higher field.

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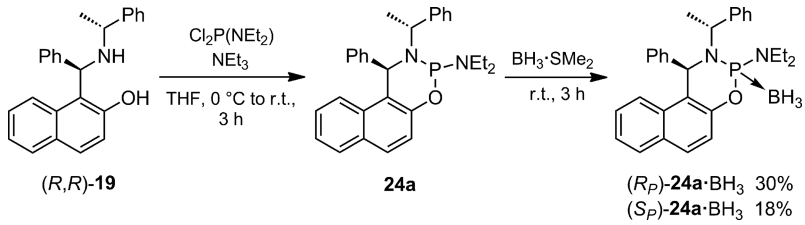


Scheme 10. Synthesis of borane-protected phosphorodiamidites **24a**·BH_3 by following Route A.

The configuration of the P-atom was unambiguously assigned by X-ray diffraction analysis of suitable crystals of (R_P)-**24a**·BH_3 obtained by slow solvent evaporation at room temperature from an ethereal solution (Figure 9).

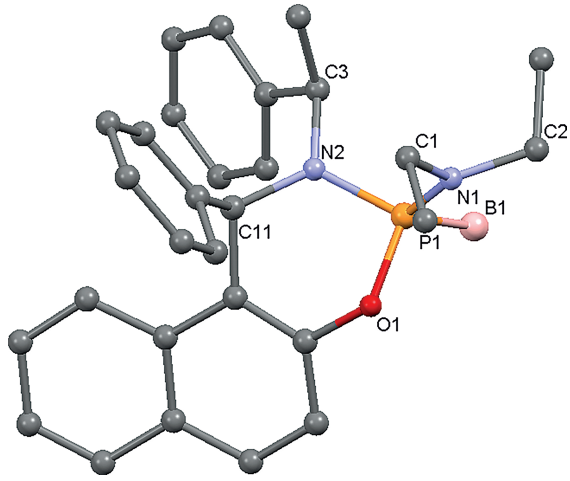


Figure 9. Structure of (R_P)-**24a**·BH_3 in the solid state as determined from X-ray diffraction.CCDC-1038400 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

It is important to note that the changes in CIP priority of the substituent at the phosphorus results in opposite stereodescriptors for the *P*-configuration of the phosphorodiamidites when compared with the phosphoramidites with the same spatial arrangement. For example, superimposing the (*R*,*R*)-Betti scaffold, the exocyclic NEt_2-substituent in (R_P)-**24a**·BH_3 will point in the same direction as the OEt-substituent in (S_P)-**21b**·BH_3.

In the solid state, the oxazaphosphacycle in (R_P)-**24a**·BH_3 exhibits a boat conformation and thus differs from the arrangement observed for phosphoramidite (S_P)-**21a**·BH_3. A π-stacking of the phenyl ring in the phenylethyl fragment and the naphthyl moiety is not present. The bond lengths at the P-atom are within the expected range. In comparison to the phosphoramidite (S_P)-**21a**·BH_3, the P1–O1 bond in (R_P)-**24a**·BH_3 is significantly longer. The P1–N1 bond is slightly shorter as compared with the P1–N2 bond in the oxazaphosphacycle. The phosphorus atom shows a nearly perfect tetrahedral geometry (sum of angles 655.19°) whereas both N-atoms adopt a trigonal-planar geometry (sum of angles 358.82°, 359.10°; Table 5 and Table 6).

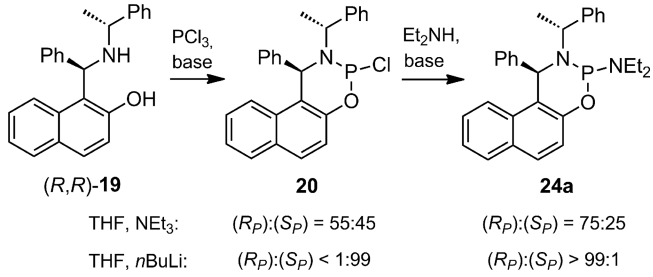
Table 5. Selected bond lengths [Å] in (R_P)-**24a**·BH_3.

P1–N1	1.6367	P1–O1	1.6207
P1–N2	1.6593	P1–B1	1.8864

Table 6. Selected bond angles [°] in (R_P)-**24a**·BH_3.

P1–N1–C1	122.98	N1–P1–O1	104.67
P1–N1–C2	120.77	N1–P1–N2	110.60
C1–N1–C2	115.35	N1–P1–B1	113.04
P1–N2–C3	115.55	N2–P1–O1	98.90
P1–N2–C11	125.08	N2–P1–B1	117.49
C3–N2–C11	118.19	O2–P1–B1	110.49

The synthesis of phosphorodiamidites through Route B was investigated using THF as solvent and triethylamine as base (Scheme 11). Both P-epimers of **24a** were obtained in a R_P/S_P ratio of 75:25, accompanied by the condensation product **23** (ca. 10%). When the reaction was carried out under kinetic control in THF at –78 °C using *n*-butyllithium as base, the (R_P)-epimer was again obtained stereoselectively.



Scheme 11. Synthesis of phosphorodiamidites **24a** following Route B.

In summary, Route A, using CH_2Cl_2/NEt_3 led preferentially to the (S_P)-epimer of phosphorodiamidites, whereas Route B, using THF/*n*BuLi, provided stereoselective access to the (R_P)-epimer. These findings were used to establish the conditions of the synthesis of phosphorodiamidites possessing different exocyclic amine substituents. In addition to diethylamine, diphenylamine and piperidine were utilized, as well as the chiral amines (*R*)- and (*S*)-*N*-methyl-1-phenylethylamine and (*R*,*R*)- and (*S*,*S*)-bis(1-phenylethyl)-amine.

Route B (THF/*n*BuLi) was used for the stereoselective synthesis of the (R_P)-epimers via (S_P)-phosphoramidochloridite (S_P)-**20** generated in situ and subsequent reaction with the respective lithiated amine. After filtration through basic alumina, the ligands were treated with borane-dimeth-

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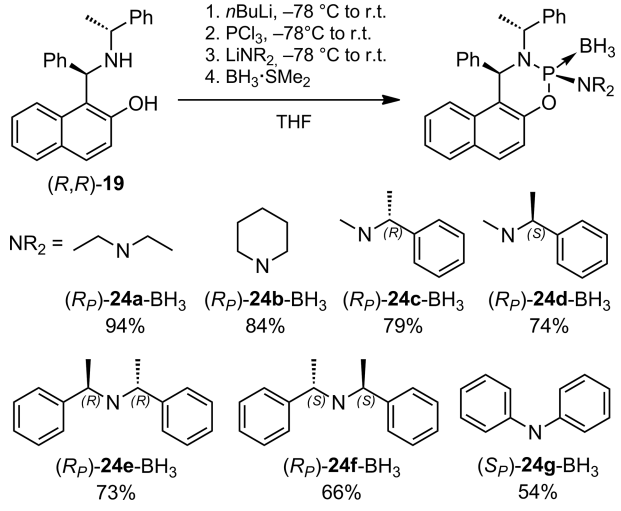
ylsulfide complex and purified by column chromatography (silica; pentane/ethyl acetate) to give the borane-phosphorodiamidites (R_P)-**24a**–**f**·BH_3 and (S_P)-**24g**·BH_3[37] in 54–94% yield (Scheme 12).

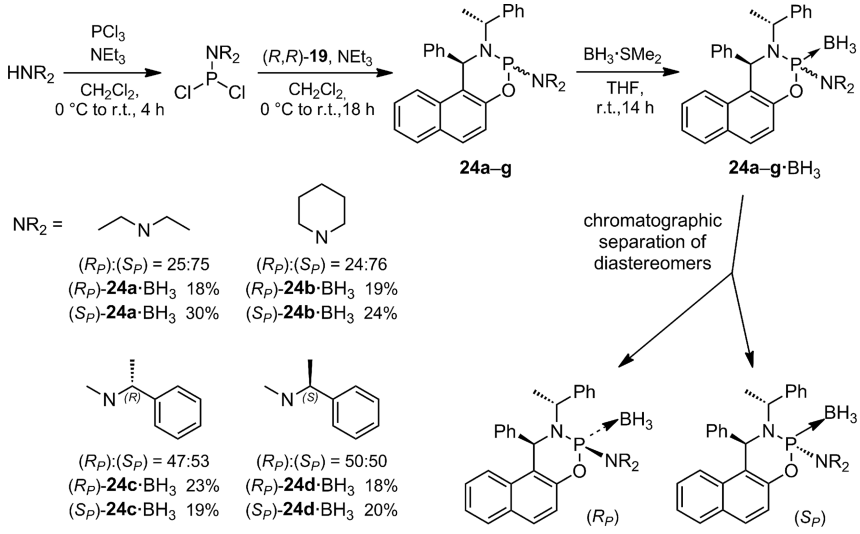


Scheme 12. Stereoselective synthesis of borane phosphorodiamidites (R_P)-**24a**–**f**·BH_3 and (S_P)-**24g**·BH_3[37] by following Route B (THF/*n*BuLi).

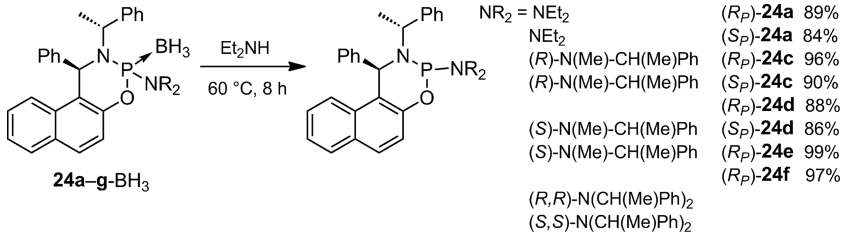
The (S_P)-epimers were obtained by Route A (CH_2Cl_2/NEt_3) via the respective dichloroaminophosphine formed in situ,[38] subsequent borane-protection of the mixture of P-epimers, and separation by column chromatography (silica; pentane/ethyl acetate) (Scheme 13). Similar to the trend observed for the phosphoramidites, the selectivity towards the (S_P)-epimer decreased with increasing steric demand of the amine moiety. For instance, the P-epimers synthesized from (*R*)-*N*-methyl-1-phenylethylamine were obtained in a ratio of R_P/S_P ratio of 47:53, whereas the synthesis using (*R*,*R*)-bis(1-phenylethyl)amine gave the P-epimers with a R_P/S_P ratio of only 88:12. In addition, the R_f-values of the two P-epimers converge with increasing steric bulk of the exocyclic amine substituent and rendered the isolation of the minor isomer arduous. Consequently, from the isomer mixture obtained by this route, only (S_P)-**24a**–**d**·BH_3 based on diethylamine, piperidine, and (*R*)- and (*S*)-*N*-methyl-1-phenylethylamine were successfully isolated (19–30% yield).

The BH_3-deprotection of phosphorodiamidites (R_P)-**24a**–**f**·BH_3 and (S_P)-**24a**–**d**,**g**·BH_3 was realized by treatment with a large excess of diethylamine at 60 °C, as described above. The phosphorodiamidites were obtained in 84–99% yield and without any epimerization during the deprotection procedure (Scheme 14).

Surprisingly, the deprotection was not effective for (R_P)- and (S_P)-**24b**·BH_3 and (S_P)-**24g**·BH_3. For the latter species, decomposition was observed, whereas (R_P)- and (S_P)-**24b**·BH_3 did not undergo deprotection using diethylamine or other bases such as morpholine or 1,4-diazabicyclo[2.2.2]octane (DABCO). Alternatively, (R_P)-**24b** was prepared according to Route B (THF/*n*BuLi) and used without further



Scheme 13. Synthesis of **24a**–**g**·BH_3 as mixtures of P-epimers by following Route A and their separation by column chromatography.



Scheme 14. Deprotection of borane phosphorodiamidites **24**·BH_3 by reaction with diethylamine.

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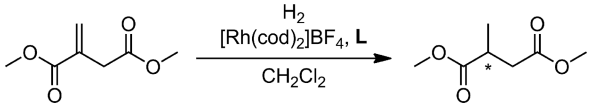
manipulation (purity ca. 88% as determined by ^{31}P NMR spectroscopic analysis) in catalysis.[39]

Rh-Catalyzed Hydrogenation

The newly synthesized *P*-stereogenic phosphoramidites **21a**–**i** and **22a**, and phosphorodiamidites **24a**–**f** were tested in a range of metal-catalyzed asymmetric transformations for which chiral monodentate phosphorus ligands are established lead structures. For the asymmetric hydrogenation of dimethyl itaconate, the catalysts were prepared in situ from $[Rh(cod)_2]BF_4$ by using a rhodium/phosphorus ratio of 1:2.05, and the reactions were carried out under standard conditions; the results are shown in Table 7.

Table 7. Asymmetric hydrogenation of dimethyl itaconate.[a]



Entry	Ligand	Exocycl. subst.	Conv. [%][b]	*ee* [%][c]
1	(S_P)-**21a**	OMe	4	70 (*S*)
2	(R_P)-**21a**	OMe	25	31 (*R*)
3	(S_P)-**21b**	OEt	5	61 (*S*)
4	(R_P)-**21b**	OEt	> 99	57 (*S*)
5	(S_P)-**21c**	O*i*Pr	10	37 (*S*)
6	(R_P)-**21c**	O*i*Pr	> 99	58 (*S*)
7	(S_P)-**21d**	O*t*Bu	28	3 (*S*)
8	(R_P)-**21d**	O*t*Bu	> 99	65 (*S*)
9	(S_P)-**21e**	OPh	32	33 (*S*)
10	(S_P)-**21f**	*O*-1-naphthyl	34	42 (*S*)
11	(S_P)-**21g**	*O*-2-naphthyl	24	46 (*S*)
12	(S_P)-**21h**	(*R*)-O–CH(Me)Ph	23	46 (*S*)
13	(S_P)-**21i**	(*S*)-O–CH(Me)Ph	27	37 (*S*)
14	(S_P)-**22a**	OMe	> 99	85 (*S*)
15	(R_P)-**22a**	OMe	6	50 (*R*)
16	(R_P)-**24a**	NEt_2	> 99	32 (*S*)
17	(S_P)-**24a**	NEt_2	42	45 (*S*)
18	(R_P)-**24b**	N-$(CH_2)_5$-	> 99	48 (*S*)
19	(R_P)-**24c**	(*R*)-N(Me)–CH(Me)Ph	47	63 (*S*)
20	(S_P)-**24c**	(*R*)-N(Me)–CH(Me)Ph	> 99	21 (*S*)
21	(R_P)-**24d**	(*S*)-N(Me)–CH(Me)Ph	57	50 (*S*)
22	(S_P)-**24d**	(*S*)-N(Me)–CH(Me)Ph	> 99	1 (*S*)
23	(R_P)-**24e**	(*R*,*R*)-N[CH(Me)Ph]$_2$	< 1	n.d.
24	(R_P)-**24f**	(*S*,*S*)-N[CH(Me)Ph]$_2$	2	7 (*S*)

[a] Reaction conditions: substrate (3 mmol), sub/Rh/L (1,000:1:2.05), CH_2Cl_2 (2 mL), $p(H_2)$ (40 bar), room temp., 14 h. [b] Determined by GC analysis. [c] Determined by chiral GC analysis.

Low conversions were obtained with all phosphoramidites **21a**–**i** possessing a (*S*)-configuration at the phosphorus atom (Table 7, entries 1, 3, 5, 7 and 9–13). In comparison, the (R_P)-counterparts (entries 2, 4, 6, and 8) were significantly more active and the ligands bearing ethyl, isopropyl, or *tert*-butyl substituents led to full conversion. For both P-epimers, an increasing steric bulk of the alcohol moiety resulted in higher activity.

The *ee* values obtained were low to moderate. All phosphoramidite ligands favored the formation of the (*S*)-enantiomer of the hydrogenation product with only two exceptions (see below) indicating that the enantiodiscrimination is dominated by the chiral information located at the carbon atoms of the ligand backbone rather than the chirality at the phosphorus atom. For the ligands possessing a (S_P)-configuration, a decrease in enantioselectivity was observed with increasing steric bulk of the alcohol moiety of the ligand. The highest *ee* value of 70% (*S*) was achieved by using the methyl-substituted ligand (S_P)-**21a** at very low conversion (Table 7, entry 1). In case of the ligands with (R_P)-configuration, an opposite trend was observed and the enantiomeric excesses raised with increasing steric demand of the exocyclic alkoxy substituents at the phosphorus atom (entries 2, 4, 6, and 8). No clear tendency was observed for ligands (S_P)-**21e**–**i**, which provided low conversions and moderate enantioselectivities.

Alteration of the stereochemistry on the backbone for ligands **22a**, synthesized from (*R*,*S*)-Betti base, was observed to have a significant influence on the catalytic properties of this system (Table 7, entries 14 and 15). Whereas (S_P)-**21a** provided only 4% conversion and 70% *ee* (*S*), the diastereomer (S_P)-**22a** led to full conversion and 85% *ee* (*S*). Higher enantioselectivity at low conversion was obtained with (R_P)-**22a** (50% *ee*) as compared with (R_P)-**21a** (31% *ee*). Interestingly, both of the latter phosphoramidites promoted the preferential formation of the (*R*)-enantiomer in contrast to all other ligands. Thus, the P-chirality appears to play a more important role in the enantiodiscrimination when the steric demand of the exocyclic substituent is particularly low.

A pronounced influence of the P-chirality on the catalyst activity was also observed for the phosphorodiamidites **24a**–**f**. For instance, the diethylamine substituted (R_P)-**24a** led to full conversion, whereas only moderate conversion was achieved with the epimeric ligand (S_P)-**24a** (Table 7, entries 16 and 17). The opposite trend was observed for **24c** and **24d** bearing the bulkier chiral *N*-methyl-1-phenylethylamine moiety for which the (R_P)-epimers were significantly more active than the (S_P)-epimers. A further increase of the steric hindrance of the amine synthon in (R_P)-**24e** and (R_P)-**24f** resulted in almost inactive Rh-catalysts (entries 23 and 24).

Low to moderate enantiomeric excesses were achieved with the phosphorodiamidite ligands **24**, all of which led preferentially to the (*S*)-enantiomer (Table 7, entries 16–24). The configuration of the phosphorus has a minor impact on the enantiodiscrimination, as was also observed in case of the phosphoramidites. In general, an increase in the steric demand of the amine substituent in (R_P)-**24** results in slightly higher enantioselectivities (entries 16, 18, 19, and 21). A direct comparison of the P-epimers of **24c** and **24d** based on the chiral (*R*)- or (*S*)-*N*-methyl-1-phenylethylamine, respectively, clearly show synergies of the different chiral centers (entries 19–22). The highest enantioselectivity of all tested phosphorodiamidites (63% *ee*) was achieved by using (R_P)-**24c**.

Pd-Catalyzed Allylic Substitution

P-Stereogenic phosphoramidites and phosphorodiamidites have been successfully applied in this transformation,

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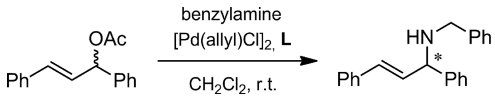
for which excellent enantioselectivities of up to 99% were achieved for the allylic amination, alkylation, and sulfonylation.[12,18b,18g]

The newly synthesized ligands were tested in the Pd-catalyzed asymmetric allylic amination of (*rac*)-(*E*)-1,3-diphenylallyl acetate with benzylamine. The catalyst was generated in situ from $[Pd(allyl)Cl]_2$ and the respective ligand with a palladium/phosphorus ratio of 1:2.1; the results are summarized in Table 8.

Table 8. Asymmetric allylic amination of (*rac*)-(*E*)-1,3-diphenylallyl acetate.[a]



Entry	Ligand	Exocyclic substituent	Conv. [%][b]	*ee* [%][c]
1	(S_P)-**21a**	OMe	> 99	22 (*S*)
2	(R_P)-**21a**	OMe	> 99	44 (*R*)
3	(S_P)-**21b**	OEt	> 99	38 (*S*)
4	(R_P)-**21b**	OEt	> 99	22 (*R*)
5	(S_P)-**21c**	O*i*Pr	> 99	23 (*S*)
6	(R_P)-**21c**	O*i*Pr	> 99	12 (*R*)
7	(S_P)-**21d**	O*t*Bu	39	13 (*R*)
8	(R_P)-**21d**	O*t*Bu	91	16 (*R*)
9	(S_P)-**21e**	OPh	> 99	48 (*R*)
10	(S_P)-**21f**	O-1-naphthyl	67	54 (*R*)
11	(S_P)-**21g**	O-2-naphthyl	73	51 (*R*)
12	(S_P)-**21h**	(*R*)-O–CH(Me)Ph	> 99	55 (*R*)
13	(S_P)-**21i**	(*S*)-O–CH(Me)Ph	58	17 (*S*)
14	(S_P)-**22a**	OMe	97	78 (*S*)
15	(R_P)-**22a**	OMe	93	11 (*R*)
16	(R_P)-**24a**	NEt_2	48	40 (*S*)
17	(S_P)-**24a**	NEt_2	> 99	70 (*R*)
18	(R_P)-**24b**	N-$(CH_2)_5$-	90	32 (*S*)
19	(R_P)-**24c**	(*R*)-N(Me)–CH(Me)Ph	56	37 (*R*)
20	(S_P)-**24c**	(*R*)-N(Me)–CH(Me)Ph	18	26 (*R*)
21	(R_P)-**24d**	(*S*)-N(Me)–CH(Me)Ph	> 99	83 (*S*)
22	(S_P)-**24d**	(*S*)-N(Me)–CH(Me)Ph	2	n.d.
23	(R_P)-**24e**	(*R*,*R*)-N[CH(Me)Ph]$_2$	12	6 (*S*)
24	(R_P)-**24f**	(*S*,*S*)-N[CH(Me)Ph]$_2$	6	45 (*S*)

[a] Reaction conditions: substrate (0.75 mmol), sub/Pd/L (50:1:1.05), CH_2Cl_2 (2 mL), room temp., 36 h. [b] Determined by ^{1}H NMR spectroscopic analysis. [c] Determined by chiral HPLC analysis.

Independently of the stereochemistry at the P-donor, high conversions were obtained with most phosphoramidites **21a**–**i**, especially with those ligands possessing sterically less demanding alkoxy groups (Table 8, entries 1–13). The configuration at the phosphorus atom played a dominant role in the enantiodiscrimination for the ligands with small alkoxy substituents. In particular, the (S_P)-diastereomer produced the (*S*)-enantiomer preferentially, whereas the ligands with (R_P)-configuration gave the (*R*)-product (entries 1–6). Low *ee* values were obtained with both *t*Bu-substituted ligands (R_P)- and (S_P)-**21d**, whereas enantioselectivities around 50% *ee* were achieved with the aryloxy derivatives (S_P)-**21e**–**g** and (S_P)-**21h**, bearing the chiral (*R*)-1-phenylethoxy group.

Similar high conversions and very different enantioselectivities have been observed for the phosphoramidites derived from the (*R*,*S*)-Betti base (Table 8, entries 14 and 15). Poor enantioselectivity (17% *ee*) towards the *S*-product was achieved with (R_P)-**22a**. Thus, as already observed in the hydrogenation, the combination of (*R*,*S*)-Betti base and S_P-chirality resulted in the machted ligand structure for (S_P)-**22a** (Table 8, cf. entry 14 with entries 15, 1, and 2).

The stereochemistry of the P-donor in the phosphorodiamidite ligands had a significant impact both on the catalyst activity and enantioselectivity. For instance, 48% conversion and 40% *ee* (*S*) was obtained with (R_P)-**24a**, whereas the use of (S_P)-**24a** led to full conversion and 70% *ee* (*R*) (Table 8, entries 16 and 17). Of the four diastereomers derived from *N*-methyl-1-phenylethylamine, (R_P)-**24c**, (S_P)-**24c**, (S_P)-**24d**, and (R_P)-**24d** (entries 19–22), the latter ligand possessed the matched structure for this reaction leading to quantitative conversion and 83% *ee* (*S*). Again, low conversions were observed with both diastereomers derived from the bulky bis(1-phenylethyl)amine (R_P)-**24e** and (R_P)-**24f** (entry 23–24).

Ni-Catalyzed Hydrovinylation

The Ni-catalyzed hydrovinylation of styrene, in which a single ligand is bound to the active metal species, was then investigated. In particular, phosphoramidites have been shown to provide catalyst systems with high levels of activities and enantioselectivities for this transformation,[40,41] whereas NOBIN-based *P*-stereogenic phosphorodiamidites did not afforded active catalysts.[24]

Nickel catalysts were generated in situ from the respective ligand, $[Ni(allyl)Br]_2$, and NaBArF as activator. Since first exploratory studies indicated a very high activity for these catalysts, the experiments were conducted at low temperature (–50 °C) with a catalyst loading of 0.1 mol-%, and the reactions were stopped after 20 min; the results are summarized in Table 9.

In general, the catalyst activity with the phosphoramidite ligands bearing alkoxy substituents correlated inversely with the steric demand of the alcohol moiety irrespective of the configuration at the P-donor (Table 9, entries 1–8). Thus, ligands (S_P)-**21a** and (R_P)-**21a**, bearing the smallest group (i.e., OMe), provided the highest activity and gave almost full conversion within 20 min, corresponding to a TOF_{av} of 3000 h^{-1} (entries 1 and 2). High selectivities (≥ 97%) towards the desired product 3-phenyl-1-butene were obtained with all tested phosphoramidite ligands, indicating that the corresponding catalysts did not promote consecutive reactions (isomerization or oligomerization) under these conditions even at high conversions.

The preferred stereochemistry of the product was determined by the configuration of the P-donor, where ligands possessing (S_P)-configuration favored the formation of the (*R*)-product, and diastereomers with (R_P)-configuration afforded the (*S*)-product. Similar observations have been made in the Pd-catalyzed allylic substitution and are again in contrast to the results obtained in the Rh-catalyzed hydrogenation for which the configuration at the P-atom had a large impact on the catalyst activity but a minor in-

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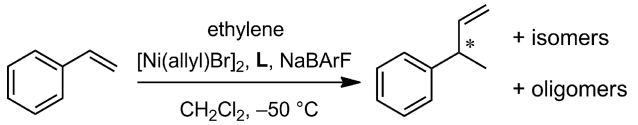
Table 9. Asymmetric hydrovinylation of styrene.[a]



Entry	Ligand	Exocyclic substituent	Conv. [%][b]	*p*:*i*:*o*[b]	*ee* [%][c]
1	(S_P)-**21a**	OMe	97	98:1:1	13 (*R*)
2	(R_P)-**21a**	OMe	> 99	96:3:1	27 (*S*)
3	(S_P)-**21b**	OEt	72	98:1:1	15 (*R*)
4	(R_P)-**21b**	OEt	67	99:0:1	24 (*S*)
5	(S_P)-**21c**	O*i*Pr	66	99:0:1	7 (*R*)
6	(R_P)-**21c**	O*i*Pr	54	100:0:0	12 (*S*)
7	(S_P)-**21d**	O*t*Bu	36	100:0:0	5 (*R*)
8	(R_P)-**21d**	O*t*Bu	20	100:0:0	56 (*S*)
9	(S_P)-**21e**	OPh	5	100:0:0	21 (*R*)
10	(S_P)-**21f**	O-1-naphthyl	15	98:1:1	26 (*R*)
11	(S_P)-**21g**	O-2-naphthyl	24	97:1:2	21 (*R*)
12	(S_P)-**21h**	(*R*)-O–CH(Me)Ph	57	97:2:1	4 (*S*)
13	(S_P)-**21i**	(*S*)-O–CH(Me)Ph	81	98:1:1	2 (*R*)
14	(S_P)-**22a**	OMe	23	93:6:1	7 (*R*)
15	(R_P)-**22a**	OMe	> 99	91:7:2	18 (*R*)
16	(R_P)-**24a**	NEt_2	30	98:2:0	18 (*S*)
17	(S_P)-**24a**	NEt_2	93	98:2:0	66 (*S*)
18	(R_P)-**24b**	N-$(CH_2)_5$-	37	98:1:1	32 (*S*)
19	(R_P)-**24c**	(*R*)-N(Me)–CH(Me)Ph	51	94:6:0	41 (*S*)
20	(S_P)-**24c**	(*R*)-N(Me)–CH(Me)Ph	84	99:1:0	68 (*S*)
21	(R_P)-**24d**	(*S*)-N(Me)–CH(Me)Ph	40	92:8:0	29 (*S*)
22	(S_P)-**24d**	(*S*)-N(Me)–CH(Me)Ph	11	100:0:0	47 (*S*)
23	(R_P)-**24e**	(*R*,*R*)-N[CH(Me)Ph]$_2$	< 1	n.d.	n.d.
24	(R_P)-**24f**	(*S*,*S*)-N[CH(Me)Ph]$_2$	< 1	n.d.	n.d.

[a] Reaction conditions: substrate (12 mmol), sub/Ni/L/NaBArF (1000:1:1.02:1.05), CH_2Cl_2 (2.5 mL), $p(C_2H_4)$ (1.2 bar), –50 °C, 20 min. [b] *p*:*i*:*o* = product/isomers/oligomers; determined by GC analysis with ethylbenzene as internal standard. [c] Determined by chiral GC analysis.

fluence in the enantioselectivity. Low to moderate enantioselectivities have been achieved with the phosphoramidite ligands and a clear trend with respect to the steric demand of the alkoxy substituent was not observed. Furthermore, the change in the configuration of the Betti base backbone from (*R*,*R*) to (*R*,*S*) in (S_P)-**22a** and (R_P)-**22a** did not result in a major improvement compared with (S_P)-**21a** and (R_P)-**21a** (*cf* Table 9, entries 1–2 and 14–15). The best result was obtained by using (R_P)-**21d**, with 56% *ee* (*S*) and full selectivity towards the desired product (entry 8).

The phosphorodiamidites provided similar activities and selectivities to those of the phosphoramidites, with the exception of (R_P)-**24e** and (R_P)-**24f**, which did not generate active catalysts under the conditions applied (Table 8, entries 16–24). No clear relationship between the steric demand of the exocyclic amine substituent and the catalyst activity was observed for this transformation. In contrast to the phosphoramidites, all phosphorodiamidites led to the formation of the (*S*)-enantiomer preferentially and indicated that the enantiodiscrimination was dominated by the configuration of the ligand backbone. The phosphorodiamidites with (S_P)-configuration led to higher enantiomeric excesses compared with their (R_P)-epimers. In more detail, the diethylamino-substituted ligand (S_P)-**24a** gave the most active catalyst among the tested phosphorodiamidites, with 93% conversion within 20 min accompanied by 98% selectivity and 66% *ee* (*S*) (Table 9, entry 17). Slightly higher enantioselectivity of 68% *ee* (*S*) and 99% selectivity at 84% conversion were achieved with (S_P)-**24c**, containing the chiral (*R*)-*N*-methyl-phenylethylamine (entry 20).

Conclusions

A library of novel phosphoramidite and phosphorodiamidite ligands based on chiral Betti bases has been prepared through a modular synthetic one-pot procedure from readily available starting materials. The new ligands possess a stereogenic phosphorus atom, and thus each ligand can be formed as a mixture of two P-epimers. We have shown that the ratio between the two P-epimers can be controlled to a large extent by the selected synthetic route and the reaction parameters (i.e., solvent, base, temperature).

Both P-epimers of the phosphoramidites could be accessed by using Route B, which comprises the formation of the phosphoramidochloridite of the Betti base as key intermediate. The (R_P)-epimer was obtained preferentially when the reaction of the phosphoramidochloridite with the corresponding alcohol was performed in CH_2Cl_2 using triethylamine as base. In contrast, when the reaction was carried out under kinetic control using THF as solvent and *n*-butyllithium as base at –78 °C, the (S_P)-epimer was obtained stereoselectively. The latter procedure was also used for the synthesis of phosphorodiamidites, where the (R_P)-epimer was selectively obtained. For the preferential synthesis of the (S_P)-epimer of the phosphorodiamidites, the reaction via the dichloramidophosphite (Route A) was the most suitable.

The P-epimers were separated by column chromatography as their borane adducts and subsequently deprotected by reaction with diethylamine. The configuration at the *P*-stereocenter was assigned by X-ray diffraction analysis of the borane adducts of two phosphoramidites and a phosphorodiamidite ligand. By comparison of the characteristic NMR chemical shifts and coupling constants, the configuration at the phosphorus of all other ligands was assigned.

The new ligands were evaluated in three metal-catalyzed asymmetric transformations, and the role of the exocyclic amine or alcohol substituent was examined as well as the interplay of the different chiral elements (Betti base backbone, *P*-stereochemistry, and chirality at the exocyclic substituent, if present). Considering the broad structural variation of the ligands and the very diverse catalytic applications chosen, involving different metals and active species with two phosphorus ligands at the metal center (hydrogenation and allylic alkylation) or with only one (hydrovinylation), no general guidelines but rather trends can be identified within similar ligand structures and for each catalytic application.

In the Rh-catalyzed hydrogenation, a large impact of the P-chirality on the catalyst activity was observed, whereas the influence on the enantioselectivity was more subtle. Using the optimum combination of the chirality at the Betti

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base, *P*-stereochemistry, and the smallest OMe exocyclic substituent in (S_P)-**22a** turned out to be decisive for obtaining good enantioselectivities (85% *ee*).

High conversions were obtained in the Pd-catalyzed allylic alkylation with most ligands. The configuration at the P-donor exerted a major control on the enantioselectivity when ligands with small substituents were applied. Two very different ligands afforded the best results as the "small" methoxy substituted phosphoramidite (S_P)-**22a** (97% conv., 78% *ee*) and the bulky phosphorodiamidite ligand (R_P)-**24d** bearing the chiral group (*R*)-*N*-methyl-1-phenylethylamine as exocyclic substituent (99% conv., 83% *ee*) were the most selective catalysts.

In the Ni-catalyzed hydrovinylation, low enantioselectivities were achieved with phosphoramidite ligands for which the configuration at the P-donor determined the preferred chirality of the product. However, this exerted no influence on the catalytic activity. The more bulky phosphorodiamidites were superior in this reaction and high chemo- (98–99%) and enantioselectivities (66–68% *ee*) at high conversion (84–93%) were obtained both with the NEt_2 and (*S*)-*N*-methyl-1-phenylethylamine substituted ligand (S_P)-**24a** and (S_P)-**24c**, respectively.

As a general observation, the influence of the P-chirality was significant and even became the dominating factor for the enantiodiscrimination and/or for the catalyst activity, when alkoxy- or amine-substituents with low steric demand were incorporated into the ligand structure. When chiral moieties are included in the structure, additional synergistic effects of the different chiral elements were observed leading to individual matched combinations for each catalytic application.

In conclusion, we have demonstrated that chiral Betti bases provide an easily accessible and versatile synthon for the synthesis of diverse phosphorus ligands with good properties in catalysis. The impact of the *P*-stereochemistry in phosphoramidite and phosphorodiamidite ligands was assessed in detail in this study. The ease of manipulation of the lead structure allows for a great variety for tailoring the ligand features. For instance, the use of this backbone for bidentate phosphorus ligands is under investigation in our group and will be reported in due course.

Experimental Section

General Considerations: All reactions and manipulations were performed either using standard Schlenk techniques or in a glovebox under an argon atmosphere. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with a Bruker AV 600 (600, 150 and 243 MHz, respectively), Bruker AV 400 (400, 100, 162 MHz, respectively), or Bruker AV 300 (300, 75, 121 MHz, respectively). Chemical shifts were referenced to residual solvent peaks (^{1}H NMR, ^{13}C NMR) or H_3PO_4 85% as external standard (^{31}P NMR). Mass spectra were recorded with a Finnigan MAT 8200 (MS + HRMS-EI) or a Bruker FTICR-Apex III (HRMS-ESI). Optical rotations were measured with a Jasco P-1020 polarimeter. The concentrations used for measuring specific rotations are given as grams per 100 mL. CH_2Cl_2, toluene, and *n*-pentane were dried with alumina and molecular sieves with a solvent purification system from Innovative Technology. THF, diethyl ether and NEt_3 were distilled from KOH and dried with molecular sieves. PCl_3 was freshly distilled. $CDCl_3$ was degassed through freeze-pump-thaw cycles and stored over molecular sieves. All solvents and substances were stored over molecular sieves under an atmosphere of argon. Silica gel (SiO_2 60, 0.04–0.063 mm, 230–400 mesh) and basic alumina (Al_2O_3 90 basic, pH 8.5–10.5, 0.063–0.2 mm) were purchased from Roth. [Ni(allyl)Br]$_2$ was prepared according to a reported procedure.[42] All other chemicals were purchased from Sigma–Aldrich, ABCR, TCI, or Alfa-Aesar and used as received.

General Procedure for the Synthesis of Borane-Protected Phosphoramidite and Phosphorodiamidite Ligands via in-situ-Generated Phosphoramidochloridite Using *n*-Butyllithium (GP-Syn1): 1-((*R*)-phenyl{[(*R*)-1-phenylethyl]amino}methyl)naphthalen-2-ol (4.0 mmol, 1.0 equiv.) was dissolved in THF (15 mL) and the solution was cooled to –78 °C. *n*-Butyllithium (1.6 M in hexanes, 2.0 equiv.) was added dropwise within 15 min and the mixture was stirred for 1 h at –78 °C and 1 h at room temperature. The solution was cooled again to –78 °C and a solution of phosphorous trichloride (1.05 equiv.) in THF (5 mL) was added dropwise within 20 min. The mixture was stirred for 1.5 h at –78 °C and then allowed to slowly reach room temperature. After another 1.5 h at room temperature, all volatiles were removed under reduced pressure. THF (10 mL) was added to the residue, and the resulting suspension was filtered through a PTFE membrane. In another Schlenk flask the respective alcohol (1.0 equiv.) or amine (1.0 equiv.) was dissolved in THF (10 mL) and *n*-butyllithium (1.6 M in hexanes, 1.0 equiv.) was added dropwise within 15 min. The mixture was stirred for 1 h at –78 °C and 1 h at room temperature. The solution was cooled again to –78 °C and the solution of the phosphoramidochloridite was added dropwise within 20 min. The mixture was stirred for 1 h at –78 °C and then allowed to slowly reach room temperature. After 1–3 h at room temperature, the solution was concentrated to a volume of 10 mL and filtered through basic alumina. After elution with THF (5 mL), borane–dimethylsulfide complex (2.0 M in THF, 1.5 equiv.) was added and the mixture was stirred overnight at room temperature. All volatiles were removed under reduced pressure to give a colorless foam, which was dried under high vacuum for 3 h and then subjected to column chromatography (silica; pentane/ethyl acetate, 4:1). After removal of the solvent, the borane-protected ligands were obtained as colorless solids. Recrystallization from diethyl ether by slow evaporation of the solvent resulted in colorless crystals that were suitable for X-ray crystal structure analysis.

General Procedure for the Synthesis of Borane-Protected Phosphoramidite and Phosphorodiamidite Ligands via in-situ-Generated Phosphoramidochloridite Using Triethylamine (GP-Syn2): 1-((*R*)-phenyl{[(*R*)-1-phenylethyl]amino}methyl)naphthalen-2-ol (2.0 mmol, 1.0 equiv.) was dissolved in THF or CH_2Cl_2 (10 mL) and triethylamine (2.5 equiv.) was added. The solution was cooled to 0 °C and a solution of phosphorous trichloride (1.02 equiv.) in THF or CH_2Cl_2 was added dropwise within 15 min. The mixture was stirred for 1 h at 0 °C and overnight at room temperature. All volatiles were removed under reduced pressure and the residue was redissolved in either THF or CH_2Cl_2 (10 mL) and the solution was cooled to 0 °C. A solution of the respective alcohol (1.0 equiv.) or amine (1.0 equiv.) and triethylamine (1.5 equiv.) in THF or CH_2Cl_2 (5 mL) was added dropwise within 15 min. The mixture was stirred for 1 h at 0 °C and 1–16 h at room temperature. Toluene (1 mL) was added and all volatiles were removed under high vacuum. The residue was dissolved in THF (8 mL) and filtered through basic alumina. After elution with THF (5 mL), borane–dimethylsulfide complex (2.0 M in THF, 1.5 equiv.) was added and the mixture was

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stirred overnight at room temperature. All volatiles were removed under reduced pressure to give a colorless foam, which was dried under high vacuum for 3 h and then subjected to column chromatography (silica; pentane/ethyl acetate, 9:1). After removal of the solvent, the borane-protected phosphorus-epimers were obtained as colorless solids. Recrystallization from diethyl ether by slow evaporation of the solvent resulted in colorless crystals that were suitable for X-ray crystal structure analysis.

General Procedure for the Synthesis of Borane-Protected Phosphorodiamidite Ligands via in-situ-Generated Dichlorophosphine Using Triethylamine (GP-Syn3): To a solution of phosphorus trichloride (2.04 mmol, 1.02 equiv.) in either CH_2Cl_2 or THF (10 mL), was added triethylamine (1.5 equiv.) and the solution was cooled to 0 °C. A solution of the respective amine (1.0 equiv.) in CH_2Cl_2 or THF (5 mL) was added dropwise within 5 min and the mixture was stirred for 15 min at 0 °C and 2–6 h at room temperature. Toluene (1 mL) was added and all volatiles were removed at high vacuum. The residue was redissolved in CH_2Cl_2 or THF (8 mL) and the solution was cooled to 0 °C. A solution of 1-((*R*)-phenyl{[(*R*)-1-phenylethyl]amino}methyl)naphthalen-2-ol (1.0 equiv.) and triethylamine (2.5 equiv.) in CH_2Cl_2 or THF (10 mL) was added dropwise within 15 min and the mixture was stirred for 1 h at 0 °C and overnight at room temperature. Toluene (1 mL) was added and all volatiles removed under high vacuum. THF (10 mL) was added to the residue, and the resulting suspension was filtered through a PTFE membrane and basic alumina consecutively. After elution with THF (5 mL), the borane–dimethylsulfide complex (2.0 M in THF, 1.5 equiv.) was added and the mixture was stirred overnight at room temperature. All volatiles were removed under reduced pressure to give colorless foam, which was dried under high vacuum for 3 h and then subjected to column chromatography (silica; pentane/ethyl acetate, 9:1). After removal of the solvent, the borane-protected phosphorus-epimers were obtained as colorless solids. Recrystallization from diethyl ether by slow evaporation of the solvent resulted in colorless crystals that were suitable for X-ray crystal structure analysis.

General Procedure for the Deprotection of Borane-Protected Ligands (GP-Syn4): The borane-protected ligand (typically ca. 1.0 mmol) was dissolved in diethylamine (3–5 mL)[43] and the solution was warmed to 60 °C for 3–18 h. After cooling to room temperature, all volatiles were removed under reduced pressure and the residue was dried at 60 °C and high vacuum for 3 h. The residue was washed with (cold) *n*-hexane (3 × 3 mL) and finally dried at high vacuum to yield the ligand as colorless solid or highly viscous oil, which crystallized upon standing.

General Procedure for the Catalytic Hydrogenation of Dimethyl Itaconate: To a solution of $[Rh(cod)_2]BF_4$ (1.22 mg, 3.0 μmol, 1.0 equiv.) in CH_2Cl_2 (1 mL) was added a solution of the ligand (6.15 μmol, 2.05 equiv.) in CH_2Cl_2 (1 mL). The mixture was stirred for 15 min at room temperature and then transferred into a 10 mL stainless steel autoclave, equipped with a glass inlet, magnetic stirring bar, and containing dimethyl itaconate (474.5 mg, 3.0 mmol, 1000 equiv.), under an argon atmosphere. After stirring for 10 min, the autoclave was pressurized with hydrogen (40 bar) and the mixture was stirred for 14 h at room temperature. After carefully releasing the pressure, the reaction mixture was filtered through a short plug of silica and analyzed by NMR and chiral GC.

General Procedure for the Catalytic Hydrovinylation of Styrene: To a solution of $[Ni(allyl)Br]_2$ (2.16 mg, 6.0 μmol, 0.5 equiv.) in CH_2Cl_2 (1 mL) was added a solution of the ligand (12.2 μmol, 1.02 equiv.) in CH_2Cl_2 (1 mL). The solution was stirred for 15 min at room temperature and then cooled to –50 °C. Styrene (1.37 mL, 12.0 mmol, 1000 equiv.) and a solution of $NaBAr^F$ (11.2 mg, 12.6 μmol, 1.05 equiv.) in CH_2Cl_2 (0.5 mL) were added sequentially, leading to a deep-red or purple solution. The reaction mixture was saturated with ethylene and stirred for 20 min. The ethylene pressure was kept constant at 1.2 bar within the reaction. The reaction was quenched by addition of aqueous ammonia (8 mL). The organic phase was washed with water (3 × 2 mL), dried with sodium sulfate, and analyzed by GC (ethylbenzene as internal standard) and chiral GC.

General Procedure for the Catalytic Asymmetric Allylic Amination: To a solution of $[Pd(allyl)Cl]_2$ (5.5 mg, 15.0 μmol, 1.0 equiv.) in CH_2Cl_2 (1 mL) was added a solution of the ligand (31.5 μmol, 2.1 equiv.) in CH_2Cl_2 (1 mL) and the mixture was stirred for 30 min at room temperature. (*rac*)-(*E*)-1,3-Diphenylallyl acetate (189.2 mg, 750 μmol, 50 equiv.) was added and the solution was stirred for 15 min. Benzylamine (245 μL, 2.25 mmol, 150 equiv.) was added and the mixture was stirred for 36 h at room temperature. The reaction was stopped by removal of all volatiles at high vacuum and the residue was analyzed by NMR and chiral HPLC (after purification by column chromatography).

1-((*R*)-Phenyl{[(*R*)-1-phenylethyl]amino}methyl)naphthalen-2-ol [(*R*,*R*)-19]: 2-Naphthol (14.5 g, 100.3 mmol, 1.0 equiv.) was dissolved in benzaldehyde (12.1 mL, 120.0 mmol, 1.2 equiv.), (*R*)-phenylethylamine (13.3 mL, 105.0 mmol, 1.05 equiv.) was added, and the mixture was gently stirred for 30 min at room temperature and overnight at 60 °C, leading to a solid material. After cooling to room temperature. ethanol (15–25 mL) was added and the mixture was ground in a mortar. The resulting suspension was filtered through a frit and the remaining solid was washed with small portions of ethanol (8 × 10 mL). The residue was dried at 50 °C under high vacuum overnight. The product was obtained as a colorless solid, yield 30.1 g (82.3 mmol, 82.1%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.46 (d, $J_{H,H}$ = 6.8 Hz, 3 H, CH_3), 2.26 (br. s, 1 H, NH), 3.86 (q, $J_{H,H}$ = 6.7 Hz, 1 H, CH), 5.43 (s, 1 H, CH), 7.17 (m, 10 H, Ar), 7.34 (m, 4 H, Ar), 7.70 (m, 2 H, Ar), 13.71 (br. s, 1 H, OH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 22.9 (CH_3), 56.6 (CH), 60.2 (CH), 113.0 (C_q, Ar), 120.0 (CH, Ar), 121.1 (CH, Ar), 122.4 (CH, Ar), 126.3 (CH, Ar), 126.7 (2 × CH, Ar), 127.6 (2 × CH, Ar), 127.8 (CH, Ar), 127.9 (CH, Ar), 128.6 (C_q, Ar), 128.7 (CH, Ar), 128.9 (2 × CH, Ar), 129.0 (2 × CH, Ar), 129.7 (CH, Ar), 132.6 (C_q, Ar), 141.4 (C_q, Ar), 143.0 (C_q, Ar), 157.3 (C_q, Ar) ppm. The analytical data are in accordance with the literature.[44]

1-((*S*)-Phenyl{[(*R*)-1-phenylethyl]amino}methyl)naphthalen-2-ol [(*R*,*S*)-19]: 2-Naphthol (14.5 g, 100.3 mmol, 1.0 equiv.) was dissolved in benzaldehyde (12.1 mL, 120.0 mmol, 1.2 equiv.). The solution was cooled to 0 °C and (*R*)-phenylethylamine (13.3 mL, 105.0 mmol, 1.05 equiv.) was added. The mixture was gently stirred for 20 min at 0 °C and for 48 h at room temperature, leading to a viscous material. The (*R*,*S*)-diastereomer was isolated in three different manners. *Method A*: Ethanol (2–5 mL) was added carefully until a colorless precipitate formed. The precipitate [(*R*,*R*)-diastereomer] was collected by filtration. The mother liquor was concentrated at the rotary evaporator until a colorless precipitate [(*R*,*S*)-diastereomer] formed. The precipitate was collected by filtration, washed with small portions of ethanol and dried under high vacuum. The product was obtained as a colorless solid (2.46 g, 7.0 mmol, 6.9%). *Method B*: Ethanol (15 mL) was added slowly, leading to a colorless precipitate. The precipitate (mixture of diastereomers) was collected by filtration and the filtrate left at room temperature overnight, leading to a crystalline precipitate [(*R*,*S*)-diastereomer], which was also collected by filtration, washed with ethanol, and dried under high vacuum. The product was obtained

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as a colorless solid (1.35 g, 3.8 mmol, 3.8%). *Method C*: Ethanol (30 mL) was added slowly, leading to a colorless precipitate. The precipitate was collected by filtration, washed with ethanol (8× 10 mL) and dried at high vacuum. The residue was recrystallized several times from boiling toluene or acetonitrile and the crystalline product [diastereomerically enriched/pure (*R*,*S*)-diastereomer] was collected. After drying under high vacuum, the product was obtained as colorless crystalline solid (1.91 g, 5.4 mmol, 5.4%). $[a]_D^{26}$ = 191.9 (*c* = 0.5, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.56 (d, $J_{H,H}$ = 6.7 Hz, 3 H, CH_3), 3.96 (q, $J_{H,H}$ = 6.7 Hz, 1 H, CH), 5.86 (s, 1 H, CH), 7.12 (d, $J_{H,H}$ = 8.9 Hz, 1 H, Ar), 7.16–7.42 (m, 12 H, Ar), 7.69 (m, 3 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 21.0 (CH_3), 55.4 (CH), 60.1 (CH), 114.3 (C_q, Ar), 120.2 (CH, Ar), 121.0 (CH, Ar), 122.4 (CH, Ar), 126.5 (3×CH, Ar), 127.5 (CH, Ar), 127.87 (2×CH, Ar), 127.94 (CH, Ar), 128.59 (C_q, Ar), 128.64 (2×CH, Ar), 128.8 (CH, Ar), 129.0 (2×CH, Ar), 129.7 (CH, Ar), 132.3 (C_q, Ar), 141.3 (C_q, Ar), 143.0 (C_q, Ar), 156.6 (C_q, Ar) ppm. MS (EI): *m*/*z* (%) = 354.2 (30), 353.2 (69), 233.1 (16), 232.1 (50), 231.1 (100), 202.1 (11), 106.1 (13), 105.1 (10). HRMS (ESI): *m*/*z* calcd. for $C_{25}H_{24}NO^+$ $[M + H]^+$ 354.18524; found 354.18445.

(1*R*,3*S*)-3-Chloro-1-phenyl-2-[(*R*)-1-phenylethyl]-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(*S*$_P$)-20]: 1-((*R*)-Phenyl{[(*R*)-1-phenylethyl]amino}methyl)naphthalen-2-ol (1.77 g, 5.01 mmol, 1.0 equiv.) was dissolved in THF (15 mL) and the solution was cooled to –78 °C. *n*-Butyllithium (2.5M in hexanes, 10.25 mmol, 4.1 mL, 2.0 equiv.) was added dropwise within 15 min and the mixture was stirred for 1 h at –78 °C and 1 h at room temperature. The solution was cooled again to –78 °C and a solution of phosphorus trichloride (5.10 mmol, 0.48 mL, 1.1 equiv.) in THF (5 mL) was added dropwise within 15 min. The mixture was stirred for 1.5 h at –78 °C and for 2 h at room temperature. All volatiles were removed under reduced pressure and the residue was redissolved in THF (10 mL) and filtered through Celite. The solvent was removed under reduced pressure and the residue was dried under high vacuum. The product was obtained as a colorless solid, yield 1.87 g (4.47 mmol, 89%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.71 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 4.62 (dq, $^3J_{H,H}$ = 7.0, $^3J_{H,P}$ = 20.6 Hz, 1 H, CH), 5.90 (s, 1 H, CH), 7.13–7.49 (m, 13 H, Ar), 7.72–7.80 (m, 2 H, Ar), 7.87 (m, 1 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 17.5 (d, *J* = 9.5 Hz, CH_3), 56.4 (d, *J* = 26.0 Hz, CH), 57.6 (d, *J* = 7.0 Hz, CH), 120.1 (d, *J* = 8.3 Hz, C_q, Ar), 120.5 (d, *J* = 1.3 Hz, CH, Ar), 122.1 (CH, Ar), 124.7 (CH, Ar), 126.8 (CH, Ar), 127.9 (CH, Ar), 128.0 (CH, Ar), 128.1 (CH, Ar), 128.2 (CH, Ar), 128.5 (2×CH, Ar), 128.6 (2×CH, Ar), 128.7 (2×CH, Ar), 129.0 (CH, Ar), 129.7 (CH, Ar), 130.3 (C_q, Ar), 131.3 (C_q, Ar), 139.7 (d, *J* = 6.3 Hz, C_q, Ar), 142.0 (d, *J* = 2.9 Hz, C_q, Ar), 145.5 (d, *J* = 3.8 Hz, C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 140.1 ppm.

Borane Adduct of (1*R*,3*S*)-3-Methoxy-1-phenyl-2-[(*R*)-1-phenylethyl]-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(*S*$_P$)-21a·BH$_3$]: The compound was synthesized by following the general procedure GP-Syn1 for ligand synthesis starting from 1-((*R*)-phenyl{[(*R*)-1-phenylethyl]amino}methyl)naphthalen-2-ol (2.0 mmol, 1.0 equiv.) and methanol (2.0 mmol, 1.0 equiv.). The product was obtained as a colorless solid, yield 717.8 mg (1.68 mmol, 84%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.85 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 3.35 (d, $^3J_{H,H}$ = 11.9 Hz, 3 H, OCH_3), 5.38 (dq, $^3J_{H,H}$ = 6.9, $^3J_{H,P}$ = 12.2 Hz, 1 H, CH), 5.69 (d, $^3J_{H,P}$ = 15.0 Hz, 1 H, CH), 6.79 (t, $^3J_{H,H}$ = 7.2 Hz, 1 H, Ar), 6.87 (m, 2 H, Ar), 7.08 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H, Ar), 7.15–7.29 (m, 10 H, Ar), 7.69 (m, 2 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 20.2 (d, *J* = 3.7 Hz, CH_3), 52.8 (d, *J* = 2.4 Hz, OCH_3), 53.7 (d, *J* = 3.8 Hz, CH), 55.4 (d, *J* = 15.3 Hz, CH), 119.3 (d, *J* = 6.6 Hz, CH, Ar), 120.3 (d, *J* = 9.0 Hz, C_q, Ar), 121.8 (CH, Ar), 124.5 (CH, Ar), 126.6 (CH, Ar), 127.3 (CH, Ar), 127.5 (2×CH, Ar), 127.6 (CH, Ar), 127.9 (2×CH, Ar), 128.25 (2×CH, Ar), 128.30 (3×CH, Ar), 129.7 (CH, Ar), 129.98 (C_q, Ar), 130.02 (C_q, Ar), 139.0 (d, *J* = 4.2 Hz, C_q, Ar), 140.9 (C_q, Ar), 147.5 (d, *J* = 9.1 Hz, C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 118.0 ppm.

Borane Adduct of (1*R*,3*R*)-3-Methoxy-1-phenyl-2-[(*R*)-1-phenylethyl]-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(*R*$_P$)-21a·BH$_3$]: The compound was synthesized by following the general procedure GP-Syn2 for ligand synthesis starting from 1-((*R*)-phenyl{[(*R*)-1-phenylethyl]amino}methyl)naphthalen-2-ol (4.0 mmol, 1.0 equiv.) and methanol (4.4 mmol, 1.1 equiv.). The product was obtained as a colorless solid, yield 517.9 mg (1.21 mmol, 30%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.36 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 3.71 (d, $^3J_{H,H}$ = 11.4 Hz, 3 H, OCH_3), 5.09 (dq, $^3J_{H,H}$ = 6.9, $^3J_{H,P}$ = 11.8 Hz, 1 H, CH), 5.66 (d, $^3J_{H,P}$ = 9.1 Hz, 1 H, CH), 7.10–7.45 (m, 11 H, Ar), 7.52 (m, 3 H, Ar), 7.74 (m, 2 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 19.2 (d, *J* = 4.1 Hz, CH_3), 54.1 (d, *J* = 1.9 Hz, OCH_3), 54.3 (d, *J* = 3.1 Hz, CH), 55.2 (d, *J* = 12.7 Hz, CH), 119.4 (d, *J* = 3.5 Hz, CH, Ar), 121.7 (CH, Ar), 124.5 (d, *J* = 11.4 Hz, C_q, Ar), 125.1 (CH, Ar), 127.1 (2×CH, Ar), 127.2 (CH, Ar), 127.6 (CH, Ar), 127.8 (CH, Ar), 128.0 (2×CH, Ar), 128.7 (4×CH, Ar), 129.0 (CH, Ar), 129.4 (C_q, Ar), 130.0 (CH, Ar), 131.2 (C_q, Ar), 139.6 (d, *J* = 2.7 Hz, C_q, Ar), 143.5 (C_q, Ar), 144.1 (d, *J* = 9.8 Hz, C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 110.5 ppm.

Borane Adduct of (1*R*,3*S*)-3-Ethoxy-1-phenyl-2-[(*R*)-1-phenylethyl]-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(*S*$_P$)-21b·BH$_3$]: The compound was synthesized by following the general procedure GP-Syn1 for ligand synthesis starting from 1-((*R*)-phenyl{[(*R*)-1-phenylethyl]amino}methyl)naphthalen-2-ol (2.0 mmol, 1.0 equiv.) and ethanol (2.0 mmol, 1.0 equiv.). The product was obtained as a colorless solid, yield 784.6 mg (1.78 mmol, 89%). $[a]_D^{27}$ = –181.8 (*c* = 0.5, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.96 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 1.85 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 3.65 (m, 1 H, OCH_2), 3.93 (m, 1 H, OCH_2), 5.39 (dq, $^3J_{H,H}$ = 7.1, $^3J_{H,P}$ = 12.1 Hz, 1 H, CH), 5.70 (d, $^3J_{H,P}$ = 15.3 Hz, 1 H, CH), 6.72–6.89 (m, 3 H, Ar), 7.04–7.31 (m, 11 H, Ar), 7.63–7.72 (m, 2 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 15.8 (d, *J* = 7.1 Hz, CH_3), 20.2 (d, *J* = 3.5 Hz, CH_3), 53.6 (d, *J* = 4.0 Hz, CH), 55.3 (d, *J* = 15.8 Hz, CH), 62.6 (d, *J* = 2.1 Hz, OCH_2), 119.4 (d, *J* = 6.7 Hz, CH, Ar), 120.5 (d, *J* = 8.3 Hz, C_q, Ar), 121.8 (CH, Ar), 124.4 (CH, Ar), 126.6 (CH, Ar), 127.3 (CH, Ar), 127.5 (3×CH, Ar),127.9 (2×CH, Ar), 128.2 (2×CH, Ar), 128.3 (3×CH, Ar), 129.6 (CH, Ar), 129.96 (C_q, Ar), 130.03 (C_q, Ar), 139.1 (d, *J* = 4.6 Hz, C_q, Ar), 140.9 (C_q, Ar), 147.6 (d, *J* = 9.6 Hz, C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 115.8 ppm.

Borane Adduct of (1*R*,3*R*)-3-Ethoxy-1-phenyl-2-[(*R*)-1-phenylethyl]-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(*R*$_P$)-21b·BH$_3$]: The compound was synthesized by following the general procedure GP-Syn2 for ligand synthesis starting from 1-((*R*)-phenyl{[(*R*)-1-phenylethyl]amino}methyl)naphthalen-2-ol (3.0 mmol, 1.0 equiv.) and ethanol (3.6 mmol, 1.2 equiv.). The product was obtained as a colorless solid, yield 503.1 mg (1.14 mmol, 38%). $[a]_D^{27}$ = –110.9 (*c* = 0.5, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.24 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, CH_3), 1.37 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 4.05–4.21 (m, 2 H, OCH_2), 5.07 (dq, $^3J_{H,H}$ = 7.0, $^3J_{H,P}$ = 11.8 Hz, 1 H, CH), 5.64 (d, $^3J_{H,P}$ = 9.3 Hz, 1 H, CH), 7.01–7.44 (m, 11 H, Ar), 7.52 (m, 3 H, Ar), 7.69–7.77 (m, 2 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 16.4 (d, *J* = 4.8 Hz, CH_3), 19.2 (d, *J* = 4.0 Hz, CH_3), 54.0 (d, *J* = 1.8 Hz,

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CH), 55.1 (d, J = 12.5 Hz, CH), 63.8 (d, J = 3.1 Hz, OCH_2), 119.4 (d, J = 2.8 Hz, CH, Ar), 121.7 (CH, Ar), 124.7 (d, J = 11.4 Hz, C_q, Ar), 125.0 (CH, Ar), 127.0 (3×CH, Ar), 127.5 (CH, Ar), 127.6 (CH, Ar), 128.0 (2×CH, Ar), 128.58 (2×CH, Ar), 128.61 (2×CH, Ar), 128.9 (CH, Ar), 129.4 (C_q, Ar), 129.8 (CH, Ar), 131.1 (C_q, Ar), 139.7 (d, J = 2.5 Hz, C_q, Ar), 143.6 (C_q, Ar), 144.1 (d, J = 10.4 Hz, C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 108.5 ppm.

Borane Adduct of (1*R*,3*S*)-3-Isopropoxy-1-phenyl-2-[(*R*)-1-phenylethyl]-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(S_P)-21c·BH_3]: The compound was synthesized by following the general procedure GP-Syn1 for ligand synthesis starting from 1-((*R*)-phenyl{[(*R*)-1-phenylethyl]amino}methyl)naphthalen-2-ol (2.0 mmol, 1.0 equiv.) and isopropanol (2.0 mmol, 1.0 equiv.). The product was obtained as a colorless solid, yield 728.5 mg (1.60 mmol, 80%). $[\alpha]_D^{27}$ = –157.3 (c = 0.5, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.11 (d, $^3J_{H,H}$ = 6.7 Hz, 3 H, CH_3), 1.13 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3), 1.76 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 4.69 (dsept, $^3J_{H,H}$ = 6.2, $^3J_{H,P}$ = 14.2 Hz, 1 H, OCH), 5.40 (dq, $^3J_{H,H}$ = 7.0, $^3J_{H,P}$ = 11.6 Hz, 1 H, CH), 5.67 (d, $^3J_{H,P}$ = 16.4 Hz, 1 H, CH), 6.82–6.96 (m, 3 H, Ar), 7.06–7.37 (m, 11 H, Ar), 7.64–7.73 (m, 2 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 19.9 (d, J = 2.5 Hz, CH_3), 23.7 (d, J = 5.1 Hz, CH_3), 23.8 (d, J = 3.0 Hz, CH_3), 54.2 (d, J = 4.5 Hz, CH), 55.1 (d, J = 15.4 Hz, CH), 72.4 (d, J = 2.2 Hz, OCH), 119.4 (d, J = 6.6 Hz, CH, Ar), 121.75 (CH, Ar), 121.84 (d, J = 7.4 Hz, C_q, Ar), 124.4 (CH, Ar), 126.6 (CH, Ar), 127.3 (CH, Ar), 127.4 (CH, Ar), 127.7 (2×CH, Ar), 128.0 (2×CH, Ar), 128.1 (2×CH, Ar), 128.3 (CH, Ar), 128.5 (2×CH, Ar), 129.5 (CH, Ar), 129.9 (C_q, Ar), 130.1 (C_q, Ar), 139.2 (d, J = 5.2 Hz, C_q, Ar), 141.2 (C_q, Ar), 147.4 (d, J = 8.8 Hz, C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 114.1 ppm.

Borane Adduct of (1*R*,3*R*)-3-Isopropoxy-1-phenyl-2-[(*R*)-1-phenylethyl]-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(R_P)-21c·BH_3]: The compound was synthesized by following the general procedure GP-Syn2 for ligand synthesis starting from 1-((*R*)-phenyl{[(*R*)-1-phenylethyl]amino}methyl)naphthalen-2-ol (3.0 mmol, 1.0 equiv.) and isopropanol (3.6 mmol, 1.2 equiv.). The product was obtained as a colorless solid, yield 290.0 mg (0.64 mmol, 21%). $[\alpha]_D^{27}$ = –128.2 (c = 0.5, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.24 (m, 6 H, 2 CH_3), 1.38 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 4.85 (dsept, $^3J_{H,H}$ = 6.2, $^3J_{H,P}$ = 13.9 Hz, 1 H, OCH), 5.03 (dq, $^3J_{H,H}$ = 7.0, $^3J_{H,P}$ = 11.8 Hz, 1 H, CH), 5.61 (d, $^3J_{H,P}$ = 9.5 Hz, 1 H, CH), 7.06–7.56 (m, 14 H, Ar), 7.66–7.77 (m, 2 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 19.1 (d, J = 4.1 Hz, CH_3), 23.6 (d, J = 5.9 Hz, CH_3), 23.8 (d, J = 1.3 Hz, CH_3), 53.9 (d, J = 1.3 Hz, CH), 54.9 (d, J = 12.2 Hz, CH), 72.4 (d, J = 2.5 Hz, OCH), 119.5 (d, J = 3.3 Hz, CH, Ar), 121.7 (CH, Ar), 124.7 (d, J = 11.5 Hz, C_q, Ar), 124.8 (CH, Ar), 126.97 (CH, Ar), 127.04 (2×CH, Ar), 127.4 (CH, Ar), 127.6 (CH, Ar), 127.9 (2×CH, Ar), 128.53 (2×CH, Ar), 128.56 (2×CH, Ar), 128.8 (CH, Ar), 129.4 (C_q, Ar), 129.7 (CH, Ar), 131.0 (C_q, Ar), 139.8 (d, J = 4.6 Hz, C_q, Ar), 143.7 (C_q, Ar), 144.0 (d, J = 10.1 Hz, C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 107.1 ppm.

Borane Adduct of (1*R*,3*S*)-3-(*tert*-Butoxy)-1-phenyl-2-[(*R*)-1-phenylethyl]-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(S_P)-21d·BH_3]: The compound was synthesized by following the general procedure GP-Syn1 for ligand synthesis starting from 1-((*R*)-phenyl{[(*R*)-1-phenylethyl]amino}methyl)naphthalen-2-ol (2.0 mmol, 1.0 equiv.) and *tert*-butanol (2.0 mmol, 1.0 equiv.). The product was obtained as a colorless solid, yield 694.6 mg (1.48 mmol, 74%). $[\alpha]_D^{27}$ = –124.0 (c = 0.5, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.33 (s, 9 H, 3 CH_3), 1.79 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 5.47 (dq, $^3J_{H,H}$ = 7.0, $^3J_{H,P}$ = 11.7 Hz, 1 H, CH), 5.66 (d, $^3J_{H,P}$ = 16.2 Hz, 1 H, CH), 6.77–6.91 (m, 3 H, Ar), 7.04–7.34 (m, 11 H, Ar), 7.70 (d, $^3J_{H,H}$ = 8.6 Hz, 2 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 19.8 (d, J = 2.2 Hz, CH_3), 30.1 (d, J = 2.9 Hz, 3×CH_3), 53.9 (d, J = 4.4 Hz, CH), 54.8 (d, J = 16.1 Hz, CH), 83.7 (d, J = 6.3 Hz, OC_q), 119.6 (d, J = 6.7 Hz, CH, Ar), 121.6 (d, J = 7.4 Hz, C_q, Ar), 121.8 (CH, Ar), 124.3 (CH, Ar), 126.5 (CH, Ar), 127.1 (CH, Ar), 127.2 (CH, Ar), 127.7 (2×CH, Ar), 127.8 (2×CH, Ar), 128.0 (2×CH, Ar), 128.2 (CH, Ar), 128.5 (2×CH, Ar), 129.4 (CH, Ar), 129.9 (C_q, Ar), 130.1 (C_q, Ar), 139.4 (d, J = 5.8 Hz, C_q, Ar), 141.3 (C_q, Ar), 147.6 (d, J = 9.0 Hz, C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 108.6 ppm.

Borane Adduct of (1*R*,3*R*)-3-(*tert*-Butoxy)-1-phenyl-2-[(*R*)-1-phenylethyl]-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(R_P)-21d·BH_3]: The compound was synthesized by following the general procedure GP-Syn2 for ligand synthesis starting from 1-((*R*)-phenyl{[(*R*)-1-phenylethyl]amino}methyl)naphthalen-2-ol (3.0 mmol, 1.0 equiv.) and *tert*-butanol (3.0 mmol, 1.0 equiv.). The product was obtained as a colorless solid, yield 484.4 mg (1.03 mmol, 34%). $[\alpha]_D^{27}$ = –125.8 (c = 0.5, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.30 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 1.38 (s, 9 H, 3 CH_3), 5.00 (dq, $^3J_{H,H}$ = 6.9, $^3J_{H,P}$ = 12.0 Hz, 1 H, CH), 5.55 (d, $^3J_{H,P}$ = 8.7 Hz, 1 H, CH), 7.01–7.38 (m, 11 H, Ar), 7.43–7.49 (m, 3 H, Ar), 7.62–7.72 (m, 2 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 19.3 (d, J = 5.3 Hz, CH_3), 30.1 (d, J = 2.8 Hz, 3×CH_3), 54.0 (d, J = 2.3 Hz, CH), 54.9 (d, J = 11.5 Hz, CH), 82.9 (d, J = 6.9 Hz, OC_q), 119.6 (d, J = 3.3 Hz, CH, Ar), 121.9 (CH, Ar), 124.7 (d, J = 12.1 Hz, C_q, Ar), 124.9 (CH, Ar), 127.0 (CH, Ar), 127.2 (2×CH, Ar), 127.4 (CH, Ar), 127.5 (CH, Ar), 128.0 (2×CH, Ar), 128.50 (2×CH, Ar), 128.54 (2×CH, Ar), 128.9 (CH, Ar), 129.5 (C_q, Ar), 129.6 (CH, Ar), 131.1 (C_q, Ar), 140.3 (d, J = 1.9 Hz, C_q, Ar), 144.0 (d, J = 10.3 Hz, C_q, Ar), 144.1 (C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 100.8 ppm.

Borane Adduct of (1*R*,3*S*)-3-Phenoxy-1-phenyl-2-[(*R*)-1-phenylethyl]-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(S_P)-21e·BH_3]: The compound was synthesized by following the general procedure GP-Syn1 for ligand synthesis starting from 1-((*R*)-phenyl{[(*R*)-1-phenylethyl]amino}methyl)naphthalen-2-ol (2.0 mmol, 1.0 equiv.) and phenol (2.0 mmol, 1.0 equiv.). The product was obtained as a colorless solid, yield 801.6 mg (1.64 mmol, 82%). $[\alpha]_D^{27}$ = –154.4 (c = 0.5, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.84 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 5.50 (dq, $^3J_{H,H}$ = 6.9, $^3J_{H,P}$ = 12.0 Hz, 1 H, CH), 5.77 (d, $^3J_{H,P}$ = 15.6 Hz, 1 H, CH), 6.81–6.95 (m, 5 H, Ar), 7.05–7.40 (m, 14 H, Ar), 7.66–7.77 (m, 2 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 20.1 (d, J = 2.6 Hz, CH_3), 54.4 (d, J = 4.3 Hz, CH), 55.8 (d, J = 16.1 Hz, CH), 119.3 (d, J = 6.6 Hz, CH, Ar), 121.1 (d, J = 3.8 Hz, 2×CH, Ar), 121.4 (d, J = 7.6 Hz, C_q, Ar), 121.7 (CH, Ar), 124.7 (CH, Ar), 124.8 (CH, Ar), 126.8 (CH, Ar), 127.5 (CH, Ar), 127.6 (2×CH, Ar), 127.8 (CH, Ar), 128.1 (2×CH, Ar), 128.4 (3×CH, Ar), 128.6 (2×CH, Ar), 129.3 (2×CH, Ar), 129.82 (CH, Ar), 129.87 (C_q, Ar), 130.2 (C_q, Ar), 138.8 (d, J = 5.6 Hz, C_q, Ar), 140.3 (C_q, Ar), 147.2 (d, J = 9.1 Hz, C_q, Ar), 150.7 (d, J = 4.1 Hz, OC_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 114.3 ppm.

Borane Adduct of (1*R*,3*S*)-3-(Naphthalen-1-yloxy)-1-phenyl-2-[(*R*)-1-phenylethyl]-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(S_P)-21f·BH_3]: The compound was synthesized by following the general procedure GP-Syn1 for ligand synthesis starting from 1-((*R*)-phenyl{[(*R*)-1-phenylethyl]amino}methyl)naphthalen-2-ol (1.0 mmol, 1.0 equiv.) and 1-naphthol (1.0 mmol, 1.0 equiv.). The product was obtained as a colorless solid, yield 447.7 mg

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(0.83 mmol, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.97 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 5.64 (dq, $^3J_{H,H}$ = 6.9, $^3J_{H,P}$ = 11.9 Hz, 1 H, CH), 5.84 (d, $^3J_{H,P}$ = 16.1 Hz, 1 H, CH), 6.87 (m, 1 H, Ar), 6.93 (m, 2 H, Ar), 7.00 (m, 1 H, Ar), 7.05 (m, 2 H, Ar), 7.12 (m, 1 H, Ar), 7.17 (m, 1 H, Ar), 7.27 (m, 1 H, Ar), 7.30–7.40 (m, 8 H, Ar), 7.42 (m, 1 H, Ar), 7.60 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H, Ar), 7.69 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, Ar), 7.75 (m, 2 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 20.3 (d, $J_{C,P}$ = 2.4 Hz, CH_3), 54.5 (d, $J_{C,P}$ = 4.3 Hz, CH), 55.7 (d, $J_{C,P}$ = 16.1 Hz, CH), 115.5 (d, $J_{C,P}$ = 3.9 Hz, CH, Ar), 119.2 (d, $J_{C,P}$ = 6.7 Hz, CH, Ar), 121.71 (CH, Ar), 121.74 (d, $J_{C,P}$ = 5.7 Hz, C_q, Ar), 122.3 (CH, Ar), 124.6 (CH, Ar), 124.7 (CH, Ar), 125.2 (CH, Ar), 125.8 (CH, Ar), 126.4 (CH, Ar), 126.73 (d, $J_{C,P}$ = 4.6 Hz, C_q, Ar), 126.76 (CH, Ar), 127.45 (CH, Ar), 127.51 (CH, Ar), 127.58 (CH, Ar), 127.63 (2×CH, Ar), 128.1 (2×CH, Ar), 128.27 (2×CH, Ar), 128.30 (2×CH, Ar), 128.35 (CH, Ar), 129.8 (CH, Ar), 129.9 (C_q, Ar), 130.2 (C_q, Ar), 134.6 (C_q, Ar), 138.7 (d, $J_{C,P}$ = 5.7 Hz, C_q, Ar), 140.2 (C_q, Ar), 147.1 (d, $J_{C,P}$ = 10.0 Hz, C_q, Ar), 147.2 (d, $J_{C,P}$ = 4.8 Hz, C_q, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 115.3 ppm.

Borane Adduct of (1*R*,3*S*)-3-(Naphthalen-2-yloxy)-1-phenyl-2-[(*R*)-1-phenylethyl]-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(S_P)-21g·BH_3]: The compound was synthesized by following the general procedure GP-Syn1 for ligand synthesis starting from 1-((*R*)-phenyl{[(*R*)-1-phenylethyl]amino}methyl)naphthalen-2-ol (1.0 mmol, 1.0 equiv.) and 2-naphthol (1.0 mmol, 1.0 equiv.). The product was obtained as a colorless solid, yield 431.0 mg (0.80 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.84 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 5.52 (dq, $^3J_{H,H}$ = 6.9, $^3J_{H,P}$ = 12.1 Hz, 1 H, CH), 5.79 (d, $^3J_{H,P}$ = 15.5 Hz, 1 H, CH), 6.83 (m, 1 H, Ar), 6.90 (m, 2 H, Ar), 6.99 (dd, $^3J_{H,H}$ = 8.9, $^4J_{H,H}$ = 1.8 Hz, 1 H, Ar), 7.09 (m, 1 H, Ar), 7.13–7.21 (m, 5 H, Ar), 7.23–7.31 (m, 3 H, Ar), 7.34 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H, Ar), 7.36–7.45 (m, 4 H, Ar), 7.67 (m, 3 H, Ar), 7.74 (m, 2 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 20.1 (d, $J_{C,P}$ = 2.6 Hz, CH_3), 54.3 (d, $J_{C,P}$ = 4.4 Hz, CH), 55.8 (d, $J_{C,P}$ = 16.2 Hz, CH), 117.5 (d, $J_{C,P}$ = 4.3 Hz, CH, Ar), 119.2 (d, $J_{C,P}$ = 6.9 Hz, CH, Ar), 121.1 (d, $J_{C,P}$ = 3.2 Hz, CH, Ar), 121.2 (d, $J_{C,P}$ = 7.2 Hz, C_q, Ar), 121.6 (CH, Ar), 124.6 (CH, Ar), 125.3 (CH, Ar), 126.4 (CH, Ar), 126.7 (CH, Ar), 127.43 (CH, Ar), 127.46 (CH, Ar), 127.55 (2×CH, Ar), 127.62 (CH, Ar), 127.8 (CH, Ar), 128.0 (2×CH, Ar), 128.3 (CH, Ar), 128.4 (2×CH, Ar), 128.7 (2×CH, Ar), 129.2 (CH, Ar), 129.79 (CH, Ar), 129.80 (C_q, Ar), 130.1 (C_q, Ar), 130.8 (C_q, Ar), 133.7 (C_q, Ar), 138.7 (d, $J_{C,P}$ = 5.5 Hz, C_q, Ar), 140.2 (C_q, Ar), 147.2 (d, $J_{C,P}$ = 9.2 Hz, C_q, Ar), 148.2 (d, $J_{C,P}$ = 4.5 Hz, C_q, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 114.5 ppm.

Borane Adduct of (1*R*,3*S*)-1-Phenyl-3-[(*R*)-1-phenylethoxy]-2-[(*R*)-1-phenylethyl]-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(S_P)-21h·BH_3]: The compound was synthesized by following the general procedure GP-Syn1 for ligand synthesis starting from 1-((*R*)-phenyl{[(*R*)-1-phenylethyl]amino}methyl)naphthalen-2-ol (1.0 mmol, 1.0 equiv.) and (*R*)-1-phenylethanol (1.0 mmol, 1.0 equiv.). The product was obtained as a colorless solid, yield 403.1 mg (0.78 mmol, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.36 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 1.40 (d, $^3J_{H,H}$ = 6.5 Hz, 3 H, CH_3), 5.16 (dq, $^3J_{H,H}$ = 7.0, $^3J_{H,P}$ = 11.5 Hz, 1 H, CH), 5.55 (m, 2 H, CH), 6.81 (m, 3 H, Ar), 7.01 (m, 3 H, Ar), 7.07 (m, 1 H, Ar), 7.11–7.20 (m, 9 H, Ar), 7.23 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H, Ar), 7.27 (m, 2 H, Ar), 7.60 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H, Ar), 7.63 (d, $^3J_{H,H}$ = 9.0 Hz, 1 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 19.5 (d, $J_{C,P}$ = 1.2 Hz, CH_3), 24.8 (d, $J_{C,P}$ = 2.9 Hz, CH_3), 54.3 (d, $J_{C,P}$ = 4.0 Hz, CH), 55.0 (d, $J_{C,P}$ = 16.1 Hz, CH), 77.1 (CH), 119.3 (d, $J_{C,P}$ = 6.4 Hz, CH, Ar), 121.6 (CH, Ar), 122.4 (d, $J_{C,P}$ = 6.8 Hz, C_q, Ar), 124.4 (CH, Ar), 125.8 (2×CH, Ar), 126.6 (CH, Ar), 127.3 (CH, Ar), 127.4 (CH, Ar), 127.6 (2×CH, Ar), 127.8 (CH, Ar), 128.0 (2×CH, Ar), 128.14 (2×CH, Ar), 128.26 (2×CH, Ar), 128.29 (CH, Ar), 128.5 (2×CH, Ar), 129.5 (CH, Ar), 129.8 (C_q, Ar), 130.1 (C_q, Ar), 139.1 (d, $J_{C,P}$ = 6.0 Hz, C_q, Ar), 141.1 (C_q, Ar), 142.2 (d, $J_{C,P}$ = 5.4 Hz, C_q, Ar), 147.2 (d, $J_{C,P}$ = 8.7 Hz, C_q, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 116.0 ppm.

Borane Adduct of (1*R*,3*S*)-1-Phenyl-3-[(*S*)-1-phenylethoxy]-2-[(*R*)-1-phenylethyl]-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(S_P)-21i·BH_3]: The compound was synthesized by following the general procedure GP-Syn1 for ligand synthesis starting from 1-((*R*)-phenyl{[(*R*)-1-phenylethyl]amino}methyl)naphthalen-2-ol (1.0 mmol, 1.0 equiv.) and (*S*)-1-phenylethanol (1.0 mmol, 1.0 equiv.). The product was obtained as a colorless solid, yield 368.9 mg (0.71 mmol, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.46 (d, $^3J_{H,H}$ = 6.4 Hz, 3 H, CH_3), 1.77 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 5.44 (dq, $^3J_{H,H}$ = 6.9, $^3J_{H,P}$ = 11.5 Hz, 1 H, CH), 5.59 (dq, $^3J_{H,H}$ = 6.5, $^3J_{H,P}$ = 8.4 Hz, 1 H, CH), 5.67 (d, $^3J_{H,P}$ = 16.7 Hz, 1 H, CH), 6.86 (m, 3 H, Ar), 7.05–7.34 (m, 16 H, Ar), 7.64 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H, Ar), 7.65 (d, $^3J_{H,H}$ = 7.9 Hz, 1 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 19.9 (d, $J_{C,P}$ = 1.5 Hz, CH_3), 24.7 (d, $J_{C,P}$ = 4.2 Hz, CH_3), 54.3 (d, $J_{C,P}$ = 3.9 Hz, CH), 55.1 (d, $J_{C,P}$ = 15.7 Hz, CH), 77.0 (CH), 119.4 (d, $J_{C,P}$ = 6.5 Hz, CH, Ar), 121.6 (CH, Ar), 121.7 (d, $J_{C,P}$ = 7.2 Hz, C_q, Ar), 124.4 (CH, Ar), 125.8 (2×CH, Ar), 126.5 (CH, Ar), 127.3 (CH, Ar), 127.4 (CH, Ar), 127.6 (2×, CH, Ar), 127.7 (CH, Ar), 128.0 (2×CH, Ar), 128.2 (4×CH, Ar), 128.3 (CH, Ar), 128.5 (2×CH, Ar), 129.4 (CH, Ar), 129.7 (C_q, Ar), 130.0 (C_q, Ar), 139.0 (d, $J_{C,P}$ = 5.8 Hz, C_q, Ar), 141.2 (C_q, Ar), 141.9 (d, $J_{C,P}$ = 3.7 Hz, C_q, Ar), 147.1 (d, $J_{C,P}$ = 8.8 Hz, C_q, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 115.0 ppm.

(1*R*,3*S*)-3-Methoxy-1-phenyl-2-[(*R*)-1-phenylethyl]-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(S_P)-21a]: The compound was synthesized from the borane adduct (1.0 mmol) by following the general procedure GP-Syn4 for deprotection of ligands. The product was obtained as a colorless solid, yield 401.0 mg (0.97 mmol, 97%). $[\alpha]_D^{25}$ = –98.0 (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.73 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 2.86 (d, $^3J_{H,P}$ = 13.1 Hz, 3 H, OCH_3), 4.81 (dq, d, $^3J_{H,H}$ = 7.0, $^3J_{H,P}$ = 11.4 Hz, 1 H, CH), 5.62 (d, $^3J_{H,P}$ = 5.2 Hz, 1 H, CH), 6.82 (m, 1 H, Ar), 6.90 (m, 2 H, Ar), 7.02–7.21 (m, 11 H, Ar), 7.59 (m, 2 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 21.4 (d, *J* = 11.7 Hz, CH_3), 49.3 (d, *J* = 16.0 Hz, OCH_3), 54.1 (d, *J* = 3.3 Hz, CH), 58.8 (d, *J* = 37.3 Hz, CH), 118.2 (d, *J* = 8.0 Hz, C_q, Ar), 120.7 (d, *J* = 2.9 Hz, CH, Ar), 122.0 (CH, Ar), 123.5 (CH, Ar), 126.3 (CH, Ar), 126.7 (CH, Ar), 127.1 (CH, Ar), 127.3 (2×CH, Ar), 127.8 (2×CH, Ar), 128.0 (2×CH, Ar), 128.3 (CH, Ar), 128.4 (2×CH, Ar), 128.9 (CH, Ar), 129.5 (C_q, Ar), 131.3 (C_q, Ar), 141.8 (d, *J* = 4.5 Hz, C_q, Ar), 142.8 (C_q, Ar), 148.4 (d, *J* = 8.0 Hz, C_q, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 136.6 ppm. MS (EI): *m*/*z* (%) = 279.2 (19), 167.1 (34), 149.1 (100), 71.3 (13). HRMS (ESI): *m*/*z* calcd. for $C_{26}H_{24}NO_2P^+$ [M^+] 413.15392; found 413.15411.

(1*R*,3*R*)-3-Methoxy-1-phenyl-2-[(*R*)-1-phenylethyl]-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(R_P)-21a]: The compound was synthesized from the borane adduct (0.7 mmol) by following the general procedure GP-Syn4 for deprotection of ligands. The product was obtained as a colorless solid, yield 248.9 mg (0.60 mmol, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.53 (d, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH_3), 3.30 (d, $^3J_{H,P}$ = 11.9 Hz, 3 H, OCH_3), 4.55 (dq, $^3J_{H,H}$ = 7.2, $^3J_{H,P}$ = 15.7 Hz, 1 H, CH), 5.81 (s 1 H, CH), 7.09–7.33 (m, 10 H, Ar), 7.38 (m, 1 H, Ar), 7.48 (m, 2 H, Ar), 7.68 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H, Ar), 7.73 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H, Ar),

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7.86 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 19.7 (d, J = 7.8 Hz, CH_3), 50.5 (d, J = 13.6 Hz, OCH_3), 55.6 (d, J = 28.3 Hz, CH), 56.5 (d, J = 5.6 Hz, CH), 120.7 (CH, Ar), 122.0 (CH, Ar), 122.4 (d, J = 8.2 Hz, C_q, Ar), 124.0 (CH, Ar), 126.4 (CH, Ar), 127.1 (CH, Ar), 127.2 (CH, Ar), 128.0 (2×CH, Ar), 128.2 (2×CH, Ar), 128.3 (4×CH, Ar), 128.8 (CH, Ar), 129.3 (CH, Ar), 130.3 (C_q, Ar), 130.7 (C_q, Ar), 141.6 (d, J = 4.5 Hz, C_q, Ar), 144.0 (d, J = 2.0 Hz, C_q, Ar), 144.8 (d, J = 3.3 Hz, C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 120.1 ppm. MS (EI): *m*/*z* (%) = 308.1 (14), 279.2 (18), 167.1 (33), 149.1 (100), 144.1 (68), 115.2 (31), 106.2 (16), 105.2 (15), 91.2 (11), 73.3 (36), 72.3 (26), 71.3 (13). HRMS (ESI): *m*/*z* calcd. for $C_{26}H_{24}NO_2P^+$ [M^+] 413.15392; found 413.15399.

(1*R*,3*S*)-3-Ethoxy-1-phenyl-2-[(*R*)-1-phenylethyl]-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(S_P)-21b]: The compound was synthesized from the borane adduct (0.7 mmol) by following the general procedure GP-Syn4 for deprotection of ligands. The product was obtained as a colorless solid, yield 278.3 mg (0.65 mmol, 93%). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.83 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 1.81 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 3.14 (m, 1 H, OCH_2), 3.51 (m, 1 H, OCH_2), 4.87 (dq, $^3J_{H,H}$ = 7.0, $^3J_{H,P}$ = 11.3 Hz, 1 H, CH), 5.70 (d, $^3J_{H,P}$ = 5.3 Hz, 1 H, CH), 6.90 (m, 1 H, Ar), 6.97 (m, 2 H, Ar), 7.09–7.30 (m, 11 H, Ar), 7.62–7.71 (m, 2 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 16.3 (d, J = 7.3 Hz, CH_3), 21.3 (d, J = 12.4 Hz, CH_3), 54.0 (d, J = 3.8 Hz, CH), 58.5 (d, J = 18.4 Hz, OCH_2), 58.7 (d, J = 37.6 Hz, CH), 118.2 (d, J = 8.3 Hz, C_q, Ar), 120.7 (d, J = 3.7 Hz, CH, Ar), 122.0 (CH, Ar), 123.4 (CH, Ar), 126.2 (CH, Ar), 127.0 (CH, Ar), 127.2 (2×CH, Ar), 127.7 (2×CH, Ar), 127.9 (2×CH, Ar), 128.2 (2×CH, Ar), 128.4 (2×CH, Ar), 128.8 (CH, Ar), 129.4 (C_q, Ar), 131.3 (C_q, Ar), 141.8 (d, J = 4.3 Hz, C_q, Ar), 142.7 (C_q, Ar), 148.5 (d, J = 8.5 Hz, C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 135.3 ppm. MS (EI): *m*/*z* (%) = 279.3 (20), 167.1 (35), 150.1 (10), 149.1 (100), 144.2 (24), 115.2 (11), 113.3 (10), 106.2 (10), 86.2 (35), 85.2 (11), 72.3 (10), 71.3 (17), 70.3 (29). HRMS (ESI): *m*/*z* calcd. for $C_{27}H_{26}NO_2P^+$ [M^+] 427.16957; found 427.16934.

(1*R*,3*R*)-3-Ethoxy-1-phenyl-2-[(*R*)-1-phenylethyl]-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(R_P)-21b]: The compound was synthesized from the borane adduct (0.5 mmol) by following the general procedure GP-Syn4 for deprotection of ligands. The product was obtained as a colorless solid, yield 188.1 mg (0.44 mmol, 88%). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.99 (t, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH_3), 1.46 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 3.55 (m, 1 H, OCH_2), 3.67 (m, 1 H, OCH_2), 4.48 (dq, $^3J_{H,H}$ = 7.1, $^3J_{H,P}$ = 15.9 Hz, 1 H, CH), 5.73 (s, 1 H, CH), 7.00–7.48 (m, 13 H, Ar), 7.59 ($^3J_{H,H}$ = 8.9 Hz, 1 H, Ar), 7.65 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H, Ar), 7.78 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 17.1 (d, J = 4.8 Hz, CH_3), 19.5 (d, J = 8.0 Hz, CH_3), 55.6 (d, J = 28.0 Hz, CH), 56.5 (d, J = 5.7 Hz, CH), 59.4 (d, J = 16.9 Hz, OCH_2), 120.9 (CH, Ar), 122.1 (CH, Ar), 122.5 (d, J = 8.1 Hz, C_q, Ar), 123.9 (CH, Ar), 126.3 (CH, Ar), 127.07 (CH, Ar), 127.12 (CH, Ar), 127.97 (CH, Ar), 128.00 (CH, Ar), 128.1 (2×CH, Ar), 128.3 (4×CH, Ar), 128.7 (CH, Ar), 129.1 (CH, Ar), 130.3 (C_q, Ar), 130.6 (C_q, Ar), 141.8 (d, J = 4.2 Hz, C_q, Ar), 144.2 (d, J = 2.1 Hz, C_q, Ar), 145.1 (d, J = 2.9 Hz, C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 119.1 ppm. MS (EI): *m*/*z* (%) = 279.3 (18), 196.2 (10), 167.2 (33), 149.1 (100), 113.3 (10). HRMS (ESI): *m*/*z* calcd. for $C_{27}H_{26}NO_2P^+$ [M^+] 427.16957; 427.17011.

(1*R*,3*S*)-3-Isopropoxy-1-phenyl-2-[(*R*)-1-phenylethyl]-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(S_P)-21c]: The compound was synthesized from the borane adduct (0.6 mmol) by following the general procedure GP-Syn4 for deprotection of ligands. The product was obtained as a colorless solid, yield 225.2 mg (0.51 mmol, 85%). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.77 (d, $^3J_{H,H}$ = 6.2 Hz, 3 H, CH_3), 1.03 (d, $^3J_{H,H}$ = 6.1 Hz, 3 H, CH_3), 1.79 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 4.00 (dsept, $^3J_{H,H}$ = 6.2, $^3J_{H,P}$ = 12.3 Hz, 1 H, OCH), 4.87 (dq, $^3J_{H,H}$ = 7.0, $^3J_{H,P}$ = 11.7 Hz, 1 H, CH), 5.71 (d, $^3J_{H,P}$ = 5.5 Hz, 1 H, CH), 6.87–7.02 (m, 3 H, Ar), 7.10–7.31 (m, 11 H, Ar), 7.62–7.71 (m, 2 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 21.3 (d, J = 12.0 Hz, CH_3), 23.8 (d, J = 4.5 Hz, CH_3), 24.1 (d, J = 4.4 Hz, CH_3), 54.5 (d, J = 3.6 Hz, CH), 58.8 (d, J = 38.9 Hz, CH), 67.5 (d, J = 19.8 Hz, OCH), 118.6 (d, J = 7.8 Hz, C_q, Ar), 120.8 (d, J = 2.9 Hz, CH, Ar), 122.0 (CH, Ar), 123.3 (CH, Ar), 126.1 (CH, Ar), 126.5 (CH, Ar), 126.9 (CH, Ar), 127.25 (CH, Ar), 127.28 (CH, Ar), 127.6 (2×CH, Ar), 127.8 (2×CH, Ar), 128.2 (CH, Ar), 128.7 (CH, Ar), 128.8 (2×CH, Ar), 129.4 (C_q, Ar), 131.3 (C_q, Ar), 142.0 (d, J = 5.0 Hz, C_q, Ar), 142.7 (C_q, Ar), 148.5 (d, J = 8.3 Hz, C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 134.8 ppm. MS (EI): *m*/*z* (%) = 279.3 (17), 167.2 (34), 149.1 (100), 71.3 (13), 70.3 (15). HRMS (ESI): *m*/*z* calcd. for $C_{28}H_{28}NO_2P^+$ [M^+] 441.18522; found 441.18568,

(1*R*,3*R*)-3-Isopropoxy-1-phenyl-2-[(*R*)-1-phenylethyl]-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(R_P)-21c]: The compound was synthesized from the borane adduct (0.42 mmol) by following the general procedure GP-Syn4 for deprotection of ligands. The product was obtained as a colorless solid, yield 168.7 mg (0.38 mmol, 91%). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.98 (d, $^3J_{H,H}$ = 6.2 Hz, 3 H, CH_3), 1.14 (d, $^3J_{H,H}$ = 6.2 Hz, 3 H, CH_3), 1.53 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 4.26 (dsept, $^3J_{H,H}$ = 6.2, $^3J_{H,P}$ = 9.3 Hz, 1 H, OCH), 4.53 (dq, $^3J_{H,H}$ = 7.1, $^3J_{H,P}$ = 16.2 Hz, 1 H, CH), 5.79 (s, 1 H, CH), 7.07–7.26 (m, 9 H, Ar), 7.30 (m, 1 H, Ar), 7.37 (m, 1 H, Ar), 7.48 (m, 2 H, Ar), 7.67 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H, Ar), 7.73 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H, Ar), 7.84 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 19.3 (d, J = 7.7 Hz, CH_3), 24.3 (d, J = 2.0 Hz, CH_3), 24.6 (d, J = 5.5 Hz, CH_3), 55.5 (d, J = 28.4 Hz, CH), 56.4 (d, J = 5.5 Hz, CH), 67.2 (d, J = 20.6 Hz, OCH), 121.2 (CH, Ar), 122.1 (CH, Ar), 122.7 (d, J = 8.4 Hz, C_q, Ar), 123.8 (CH, Ar), 126.2 (CH, Ar), 127.0 (CH, Ar), 127.1 (CH, Ar), 128.01 (CH, Ar), 128.03 (CH, Ar), 128.06 (2×CH, Ar), 128.25 (2×CH, Ar), 128.33 (2×CH, Ar), 128.7 (CH, Ar), 128.9 (CH, Ar), 130.4 (C_q, Ar), 130.5 (C_q, Ar), 142.1 (d, J = 7.2 Hz, C_q, Ar), 143.0 (d, J = 2.2 Hz, C_q, Ar), 144.3 (d, J = 3.1 Hz, C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 119.5 ppm. MS (EI): *m*/*z* (%) = 231.3 (19), 209.4 (25), 208.3 (31), 194.3 (17), 167.3 (19), 149.2 (50), 144.3 (85), 116.3 (12), 115.3 (42), 109.2 (40), 106.3 (23), 105.3 (100), 104.3 (12), 89.3 (10), 83.2 (52), 79.3 (11), 77.3 (18). HRMS (ESI): *m*/*z* calcd. for $C_{28}H_{28}NO_2P^+$ [M^+] 441.18522; found 441.18549.

(1*R*,3*S*)-3-(*tert*-Butoxy)-1-phenyl-2-[(*R*)-1-phenylethyl]-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(S_P)-21d]: The compound was synthesized from the borane adduct (0.7 mmol) by following the general procedure GP-Syn4 for deprotection of ligands. The product was obtained as a colorless solid, yield 312.5 mg (0.69 mmol, 98%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.33 (s, 9 H, 3 CH_3), 1.79 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 4.97 (dq, $^3J_{H,H}$ = 6.9, $^3J_{H,P}$ = 12.0 Hz, 1 H, CH), 5.79 (d, $^3J_{H,P}$ = 5.9 Hz, 1 H, CH), 7.00–7.12 (m, 3 H, Ar), 7.17–7.49 (m, 11 H, Ar), 7.66 (m, 2 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 20.1 (d, J = 20.9 Hz, CH_3), 30.1 (d, J = 2.9 Hz, 3×CH_3), 54.3 (d, J = 3.7 Hz, CH), 58.1 (d, J = 38.1 Hz, CH), 83.0 (d, J = 20.1 Hz, OC_q), 117.9 (d, J = 7.4 Hz, C_q, Ar), 119.6 (d, J = 6.7 Hz, CH, Ar), 121.8 (CH, Ar), 124.3 (CH, Ar), 126.5 (CH, Ar), 127.1 (CH, Ar), 127.2 (CH, Ar), 127.7 (2×CH, Ar), 127.8 (2×CH, Ar), 128.0 (2×CH, Ar), 128.2 (CH, Ar), 128.5 (2×CH, Ar), 129.4 (CH, Ar), 130.0 (C_q, Ar), 131.6 (C_q, Ar), 139.4 (d, J = 5.8 Hz, C_q, Ar), 141.3 (C_q, Ar), 147.5 (d, J =

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9.0 Hz, C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 131.9 ppm. MS (EI): *m*/*z* (%) = 399.2 (27), 322.1 (17), 294.1 (37), 280.1 (11), 234.2 (13), 231.1 (26), 218.1 (60), 215.2 (10), 209.2 (22), 208.1 (11), 194.2 (15), 167.1 (14), 149.1 (35), 144.1 (51), 115.2 (24), 106.2 (29), 105.2 (100), 104.2 (13), 91.2 (14), 83.1 (19), 79.2 (14), 77.2 (20). HRMS (ESI): *m*/*z* calcd. for $C_{29}H_{30}NO_2P^+$ [M^+] 455.20087; found 455.20027.

(1*R*,3*R*)-3-(*tert*-Butoxy)-1-phenyl-2-[(*R*)-1-phenylethyl]-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(R_P)-21d]: The compound was synthesized from the borane adduct (0.6 mmol) by following the general procedure GP-Syn4 for deprotection of ligands. The product was obtained as a colorless solid, yield 256.9 mg (0.56 mmol, 94%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.25 (s, 9 H, 3 CH_3), 1.51 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 4.52 (dq, $^3J_{H,H}$ = 7.0, $^3J_{H,P}$ = 16.7 Hz, 1 H, CH), 5.77 (s, 1 H, CH), 7.07–7.33 (m, 10 H, Ar), 7.34–7.41 (m, 1 H, Ar), 7.45–7.50 (m, 2 H, Ar), 7.67 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H, Ar), 7.74 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, Ar), 7.84 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 19.2 (d, *J* = 8.7 Hz, CH_3), 30.8 (d, *J* = 8.6 Hz, 3 × CH_3), 55.2 (d, *J* = 28.2 Hz, CH), 55.9 (d, *J* = 5.7 Hz, 1 CH), 75.4 (d, *J* = 6.4 Hz, OC_q), 121.4 (CH, Ar), 122.2 (CH, Ar), 122.8 (d, *J* = 8.7 Hz, C_q, Ar), 123.7 (CH, Ar), 126.1 (CH, Ar), 126.8 (CH, Ar), 126.9 (CH, Ar), 128.0 (4 × CH, Ar), 128.2 (2 × CH, Ar), 128.4 (2 × CH, Ar), 128.7 (2 × CH, Ar), 130.5 (2 × C_q, Ar), 142.3 (d, *J* = 3.6 Hz, C_q, Ar), 144.7 (d, *J* = 2.7 Hz, C_q, Ar), 145.0 (d, *J* = 3.5 Hz, C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 114.1 ppm. MS (EI): *m*/*z* (%) = 399.2 (36), 384.2 (13), 356.1 (10), 322.1 (21), 295.1 (10), 294.1 (49), 280.1 (17), 279.2 (20), 234.2 (17), 231.1 (16), 218.1 (91), 215.1 (14), 167.1 (34), 150.1 (10), 149.1 (100), 105.2 (49), 104.2 (12). HRMS (ESI): *m*/*z* calcd. for $C_{29}H_{30}NO_2P^+$ [M^+] 455.20087; found 455.20157.

(1*R*,3*S*)-3-Phenoxy-1-phenyl-2-[(*R*)-1-phenylethyl]-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(S_P)-21e]: The compound was synthesized from the borane adduct (0.5 mmol) by following the general procedure GP-Syn4 for deprotection of ligands. The product was obtained as a colorless solid, yield 209.2 mg (0.44 mmol, 88%). $[a]_D^{24}$ = +21.5 (*c* = 0.5, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.79 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 4.95 (dq, $^3J_{H,H}$ = 6.9, $^3J_{H,P}$ = 12.0 Hz, 1 H, CH), 5.80 (d, $^3J_{H,P}$ = 5.9 Hz, 1 H, CH), 6.64 (m, 2 H, Ar), 6.91–7.04 (m, 4 H, Ar), 7.11–7.36 (m, 13 H, Ar), 7.68–7.73 (m, 2 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 21.3 (d, *J* = 11.0 Hz, CH_3), 55.0 (d, *J* = 3.8 Hz, CH), 59.1 (d, *J* = 38.1 Hz, CH), 118.5 (d, *J* = 7.4 Hz, C_q, Ar), 119.6 (2 × CH, Ar), 120.5 (d, *J* = 3.5 Hz, CH, Ar), 122.0 (CH, Ar), 122.6 (CH, Ar), 123.7 (CH, Ar), 126.3 (CH, Ar), 126.9 (CH, Ar), 127.2 (CH, Ar), 127.32 (CH, Ar), 127.34 (CH, Ar), 127.8 (2 × CH, Ar), 128.0 (2 × CH, Ar), 128.3 (CH, Ar), 128.9 (2 × CH, Ar), 129.1 (CH, Ar), 129.2 (2 × CH, Ar), 129.7 (C_q, Ar), 131.0 (C_q, Ar), 141.4 (d, *J* = 5.9 Hz, C_q, Ar), 142.1 (C_q, Ar), 147.7 (d, *J* = 9.2 Hz, C_q, Ar), 153.1 (d, *J* = 8.9 Hz, OC_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 129.9 ppm. MS (EI): *m*/*z* (%) = 382.2 (13), 279.2 (21), 278.1 (12), 167.1 (41), 150.1 (11), 149.1 (100), 105.2 (20), 71.3 (15). HRMS (ESI): *m*/*z* calcd. for $C_{31}H_{26}NO_2P^+$ [M^+] 475.16957; found 475.16988.

(1*R*,3*S*)-3-(Naphthalen-1-yloxy)-1-phenyl-2-[(*R*)-1-phenylethyl]-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(S_P)-21f]: The compound was synthesized from the borane adduct (0.6 mmol) by following the general procedure GP-Syn4 for deprotection of ligands. The product was obtained as a colorless solid, yield 305.9 mg (0.58 mmol, 97%). $[a]_D^{23}$ = –2.1 (*c* = 0.5, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.81 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 5.00 (dq, $^3J_{H,H}$ = 6.8, $^3J_{H,P}$ = 12.4 Hz, 1 H, CH), 5.86 (d, $^3J_{H,P}$ = 5.9 Hz, 1 H, CH), 6.93–7.47 (m, 20 H, Ar), 7.69 (m, 3 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 21.6 (d, $J_{C,P}$ = 11.1 Hz, CH_3), 55.8 (d, $J_{C,P}$ = 4.1 Hz, CH), 59.6 (d, $J_{C,P}$ = 39.2 Hz, CH), 112.6 (d, $J_{C,P}$ = 16.8 Hz, CH, Ar), 118.7 (d, $J_{C,P}$ = 6.9 Hz, C_q, Ar), 120.4 (d, $J_{C,P}$ = 3.6 Hz, CH, Ar), 122.1 (CH, Ar), 122.4 (CH, Ar), 122.9 (CH, Ar), 123.7 (CH, Ar), 125.0 (CH, Ar), 125.5 (CH, Ar), 126.1 (CH, Ar), 126.4 (CH, Ar), 127.0 (CH, Ar), 127.16 (CH, Ar), 127.23 (CH, Ar), 127.25 (C_q, Ar), 127.41 (CH, Ar), 127.44 (CH, Ar), 128.08 (2 × CH, Ar), 128.12 (2 × CH, Ar), 128.34 (CH, Ar), 129.0 (2 × CH, Ar), 129.2 (CH, Ar), 129.7 (C_q, Ar), 131.0 (C_q, Ar), 134.6 (C_q, Ar), 141.4 (d, $J_{C,P}$ = 6.4 Hz, C_q, Ar), 142.2 (C_q, Ar), 147.7 (d, $J_{C,P}$ = 9.2 Hz, C_q, Ar), 149.7 (d, $J_{C,P}$ = 9.2 Hz, C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 128.7 ppm. MS (EI): *m*/*z* (%) = 234.2 (10), 196.2 (16), 149.1 (26), 145.1 (11), 144.1 (100), 116.1 (34), 115.1 (78), 106.2 (56), 105.2 (40), 91.2 (22), 89.2 (10), 79.2 (13). HRMS (ESI): *m*/*z* calcd. for $C_{35}H_{28}NO_2P^+$ [M^+] 525.18522; found 525.18545.

(1*R*,3*S*)-3-(Naphthalen-2-yloxy)-1-phenyl-2-[(*R*)-1-phenylethyl]-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(S_P)-21g]: The compound was synthesized from the borane adduct (0.6 mmol) by following the general procedure GP-Syn4 for deprotection of ligands. The product was obtained as a colorless solid, yield 302.7 mg (0.58 mmol, 96%). $[a]_D^{25}$ = +46.7 (*c* = 0.5, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.79 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 4.96 (dq, $^3J_{H,H}$ = 6.9, $^3J_{H,P}$ = 12.1 Hz, 1 H, CH), 5.83 (d, $^3J_{H,P}$ = 5.7 Hz, 1 H, CH), 6.70 (dd, $^3J_{H,H}$ = 8.8, $^4J_{H,H}$ = 2.0 Hz, 1 H, Ar), 6.90–7.06 (m, 4 H, Ar), 7.12–7.42 (m, 13 H, Ar), 7.62 (m, 2 H, Ar), 7.71 (d, $^3J_{H,H}$ = 8.2 Hz, 3 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 21.3 (d, $J_{C,P}$ = 11.2 Hz, CH_3), 55.2 (d, $J_{C,P}$ = 3.8 Hz, CH), 59.3 (d, $J_{C,P}$ = 38.4 Hz, CH), 114.8 (d, $J_{C,P}$ = 12.6 Hz, CH, Ar), 118.4 (d, $J_{C,P}$ = 7.5 Hz, C_q, Ar), 120.5 (d, $J_{C,P}$ = 3.6 Hz, CH, Ar), 121.0 (d, $J_{C,P}$ = 6.6 Hz, CH, Ar), 122.0 (CH, Ar), 123.7 (CH, Ar), 124.2 (CH, Ar), 126.1 (CH, Ar), 126.4 (CH, Ar), 126.99 (CH, Ar), 127.00 (CH, Ar), 127.21 (CH, Ar), 127.37 (CH, Ar), 127.41 (CH, Ar), 127.56 (CH, Ar), 127.93 (2 × CH, Ar), 128.06 (2 × CH, Ar), 128.33 (CH, Ar), 128.93 (2 × CH, Ar), 129.10 (CH, Ar), 129.14 (CH, Ar), 129.7 (C_q, Ar), 129.9 (C_q, Ar), 131.1 (C_q, Ar), 134.1 (C_q, Ar), 141.4 (d, $J_{C,P}$ = 5.9 Hz, C_q, Ar), 142.2 (C_q, Ar), 147.8 (d, $J_{C,P}$ = 9.0 Hz, C_q, Ar), 150.8 (d, $J_{C,P}$ = 8.5 Hz, C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 129.8 ppm. MS (EI): *m*/*z* (%) = 382.4 (30), 278.3 (32), 115.3 (19), 105.3 (100). HRMS (ESI): *m*/*z* calcd. for $C_{35}H_{29}NO_2P^+$ [M + H^+] 526.19304; found 526.19336.

(1*R*,3*S*)-1-Phenyl-3-[(*R*)-1-phenylethoxy]-2-[(*R*)-1-phenylethyl]-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(S_P)-21h]: The compound was synthesized from the borane adduct (0.4 mmol) by following the general procedure GP-Syn4 for deprotection of ligands. The product was obtained as a semicrystalline colorless solid, yield 173.2 mg (0.34 mmol, 86%). $[a]_D^{25}$ = –25.4 (*c* = 0.63, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.21 (d, $^3J_{H,H}$ = 6.5 Hz, 3 H, CH_3), 1.54 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 4.70 (dq, $^3J_{H,H}$ = 6.9, $^3J_{H,P}$ = 11.5 Hz, 1 H, CH), 4.92 (dq, $^3J_{H,H}$ = 6.5, $^3J_{H,P}$ = 9.0 Hz, 1 H, CH), 5.63 ($^3J_{H,P}$ = 5.9 Hz, 1 H, CH), 6.79–6.87 (m, 5 H, Ar), 7.04–7.25 (m, 14 H, Ar), 7.63 (m, 2 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 21.3 (d, $J_{C,P}$ = 12.5 Hz, CH_3), 25.5 (d, $J_{C,P}$ = 3.7 Hz, CH_3), 55.1 (d, $J_{C,P}$ = 4.0 Hz, CH), 59.1 (d, $J_{C,P}$ = 38.6 Hz, CH), 73.6 (d, $J_{C,P}$ = 23.9 Hz, OCH), 119.1 (d, $J_{C,P}$ = 7.3 Hz, C_q, Ar), 120.7 (d, $J_{C,P}$ = 3.0 Hz, CH, Ar), 122.0 (CH, Ar), 123.4 (CH, Ar), 125.7 (2 × CH, Ar), 126.2 (CH, Ar), 126.6 (CH, Ar), 126.9 (CH, Ar), 127.0 (CH, Ar), 127.23 (CH, Ar), 127.25 (CH, Ar), 127.7 (2 × CH, Ar), 127.9 (2 × CH, Ar), 128.0 (2 × CH, Ar), 128.2 (CH, Ar), 128.8 (CH, Ar), 129.0 (2 × CH, Ar), 129.4 (C_q, Ar), 131.2 (C_q, Ar), 142.0 (d, $J_{C,P}$ = 5.2 Hz, C_q, Ar), 142.5 (C_q,

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Ar), 144.3 (d, $J_{C,P}$ = 4.9 Hz, C_q, Ar), 148.3 (d, $J_{C,P}$ = 8.6 Hz, C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 136.2 ppm. MS (EI): *m*/*z* (%) = 503.1 (15), 426.1 (20), 400.1 (29), 399.1 (100), 398.0 (51), 357.0 (23), 356.0 (91), 322.0 (31), 295.0 (19), 294.0 (95), 231.1 (11), 218.0 (10), 215.1 (11), 105.1 (75), 79.2 (10). HRMS (ESI): *m*/*z* calcd. for $C_{33}H_{31}NO_2P^+$ [M + H$^+$] 504.20869; found 504.20880.

(1*R*,3*S*)-1-Phenyl-3-[(*S*)-1-phenylethoxy]-2-[(*R*)-1-phenylethyl]-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(*S*$_P$)-21i]: The compound was synthesized from the borane adduct (0.33 mmol) by following the general procedure GP-Syn4 for deprotection of ligands. The product was obtained as a semicrystalline colorless solid, yield 128.0 mg (0.25 mmol, 77%). $[\alpha]_D^{25}$ = +29.9 (*c* = 0.1, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.94 (d, $^3J_{H,H}$ = 6.5 Hz, 3 H, CH_3), 1.73 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 4.73 (dq, $^3J_{H,H}$ = 6.5, $^3J_{H,P}$ = 9.0 Hz, 1 H, CH), 4.80 (dq, $^3J_{H,H}$ = 6.9, $^3J_{H,P}$ = 11.8 Hz, 1 H, CH), 5.68 ($^3J_{H,P}$ = 5.6 Hz, 1 H, CH), 6.82 (m, 1 H, Ar), 6.89 (m, 2 H, Ar), 7.01–7.25 (m, 16 H, Ar), 7.55 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H, Ar), 7.60 (m, 1 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 21.2 (d, $J_{C,P}$ = 11.4 Hz, CH_3), 24.8 (d, $J_{C,P}$ = 5.0 Hz, CH_3), 54.5 (d, $J_{C,P}$ = 3.5 Hz, CH), 58.8 (d, $J_{C,P}$ = 39.2 Hz, CH), 72.9 (d, $J_{C,P}$ = 21.0 Hz, OCH), 118.5 (d, $J_{C,P}$ = 7.8 Hz, C_q, Ar), 120.7 (d, $J_{C,P}$ = 3.4 Hz, CH, Ar), 121.9 (CH, Ar), 123.4 (CH, Ar), 125.9 (2×CH, Ar), 126.1 (CH, Ar), 126.7 (CH, Ar), 126.9 (CH, Ar), 127.16 (CH, Ar), 127.26 (CH, Ar), 127.28 (CH, Ar), 127.84 (2×CH, Ar), 127.88 (2×CH, Ar), 128.1 (2×CH, Ar), 128.2 (CH, Ar), 128.7 (CH, Ar), 128.8 (2×CH, Ar), 129.4 (C_q, Ar), 131.2 (C_q, Ar), 141.8 (d, $J_{C,P}$ = 4.7 Hz, C_q, Ar), 142.6 (C_q, Ar), 144.1 (d, $J_{C,P}$ = 3.3 Hz, C_q, Ar), 148.4 (d, $J_{C,P}$ = 8.8 Hz, C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 135.7 ppm. MS (EI): *m*/*z* (%) = 399.2 (12), 294.1 (11), 279.2 (22), 218.1 (26), 167.1 (44), 150.1 (12), 149.1 (100), 113.2 (11), 105.2 (21), 104.2 (12). HRMS (ESI): *m*/*z* calcd. for $C_{33}H_{30}NO_2P^+$ [M$^+$] 503.20087; found 503.20127.

Borane Adduct of (1*S*,3*R*)-3-Methoxy-1-phenyl-2-[(*R*)-1-phenylethyl]-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(*R*$_P$)-22a·BH$_3$]: The compound was synthesized by following the general procedure GP-Syn3 for ligand synthesis starting from 1-((*S*)-phenyl{[(*R*)-1-phenylethyl]amino}methyl)naphthalen-2-ol (2.0 mmol, 1.0 equiv.). Deviating from the general procedure, commercially available dichloro(methoxy)phosphine (2.0 mmol, 1.0 equiv.) was used. The product was obtained as a colorless solid, yield 257.2 mg (0.60 mmol, 30%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.29 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 3.07 (d, $^3J_{H,P}$ = 12.0 Hz, 3 H, OCH_3), 5.27 (dq, $^3J_{H,H}$ = 7.0, $^3J_{H,P}$ = 10.9 Hz, 1 H, CH), 5.94 (d, $^3J_{H,P}$ = 13.7 Hz, 1 H, CH), 6.28 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, Ar), 6.93 (t, $^3J_{H,H}$ = 7.4 Hz, 2 H, Ar), 7.02 (t, $^3J_{H,H}$ = 7.3 Hz, 1 H, Ar), 7.36 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H, Ar), 7.43 (m, 4 H, Ar), 7.54 (m, 4 H, Ar), 7.86 (m, 2 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 17.1 (CH_3), 51.5 (d, $J_{C,P}$ = 3.9 Hz, CH), 52.1 (d, $J_{C,P}$ = 2.0 Hz, OCH_3), 56.7 (d, $J_{C,P}$ = 15.3 Hz, CH), 119.1 (d, $J_{C,P}$ = 9.7 Hz, C_q, Ar), 119.8 (d, $J_{C,P}$ = 7.0 Hz, CH, Ar), 121.9 (CH, Ar), 124.8 (CH, Ar), 127.3 (CH, Ar), 127.5 (CH, Ar), 127.8 (2×CH, Ar), 128.0 (2×CH, Ar), 128.3 (CH, Ar), 128.6 (2×CH, Ar), 128.9 (CH, Ar), 129.0 (2×CH, Ar), 130.1 (CH, Ar), 130.2 (C_q, Ar), 130.5 (C_q, Ar), 139.8 (C_q, Ar), 141.2 (d, $J_{C,P}$ = 9.1 Hz, C_q, Ar), 148.1 (d, $J_{C,P}$ = 8.9 Hz, C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 118.5 ppm.

Borane Adduct of (1*S*,3*S*)-3-Methoxy-1-phenyl-2-[(*R*)-1-phenylethyl]-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(*S*$_P$)-22a·BH$_3$]: The compound was synthesized by following the general procedure GP-Syn3 for ligand synthesis starting from 1-((*S*)-phenyl{[(*R*)-1-phenylethyl]amino}methyl)naphthalen-2-ol (2.0 mmol, 1.0 equiv.). Deviating from the general procedure, commercially available dichloro(methoxy)phosphine (2.0 mmol, 1.0 equiv.) was used. The product was obtained as a colorless solid, yield 189.6 mg (0.44 mmol, 22%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.68 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 3.73 (d, $^3J_{H,P}$ = 11.5 Hz, 3 H, OCH_3), 4.87 (dq, $^3J_{H,H}$ = 7.0, $^3J_{H,P}$ = 9.9 Hz, 1 H, CH), 5.76 (d, $^3J_{H,P}$ = 10.6 Hz, 1 H, CH), 6.98 (m, 3 H, Ar), 7.13 (m, 5 H, Ar), 7.28 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, Ar), 7.37 (m, 3 H, Ar), 7.46 (m, 1 H, Ar), 7.77 (m, 3 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 18.9 (CH_3), 54.0 (d, $J_{C,P}$ = 3.1 Hz, CH), 55.2 (d, $J_{C,P}$ = 1.4 Hz, OCH_3), 55.6 (d, $J_{C,P}$ = 10.3 Hz, CH), 119.2 (d, $J_{C,P}$ = 3.4 Hz, CH, Ar), 121.6 (CH, Ar), 124.7 (d, $J_{C,P}$ = 11.1 Hz, C_q, Ar), 125.1 (CH, Ar), 127.0 (CH, Ar), 127.1 (2×CH, Ar), 127.3 (CH, Ar), 127.5 (CH, Ar), 127.8 (2×CH, Ar), 128.1 (2×CH, Ar), 128.2 (2×CH, Ar), 129.0 (CH, Ar), 129.4 (C_q, Ar), 130.0 (CH, Ar), 131.1 (C_q, Ar), 140.6 (d, $J_{C,P}$ = 6.2 Hz, C_q, Ar), 141.0 (C_q, Ar), 144.3 (d, $J_{C,P}$ = 10.4 Hz, C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 111.7 ppm.

(1*S*,3*S*)-3-Methoxy-1-phenyl-2-[(*R*)-1-phenylethyl]-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(*S*$_P$)-22a]: The compound was synthesized from the borane adduct (0.5 mmol) by following the general procedure GP-Syn4 for deprotection of ligands. The product was obtained as a colorless solid, yield 167.4 mg (0.41 mmol, 81%). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.63 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 3.42 (d, $^3J_{H,P}$ = 12.0 Hz, 3 H, OCH_3), 4.21 (dq, $^3J_{H,H}$ = 6.9, $^3J_{H,P}$ = 12.9 Hz, 1 H, CH), 5.56 (s, 1 H, CH), 6.79 (m, 1 H, Ar), 7.05–7.53 (m, 12 H, Ar), 7.61–7.79 (m, 3 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 23.1 (d, $J_{C,P}$ = 19.0 Hz, CH_3), 48.2 (d, $J_{C,P}$ = 17.3 Hz, OCH_3), 52.0 (d, $J_{C,P}$ = 5.6 Hz, CH), 58.4 (d, $J_{C,P}$ = 26.6 Hz, CH), 119.8 (CH, Ar), 121.9 (C_q, Ar), 122.3 (CH, Ar), 123.7 (CH, Ar), 126.3 (CH, Ar), 126.5 (CH, Ar), 127.0 (CH, Ar), 127.2 (2×CH, Ar), 127.5 (2×CH, Ar), 128.5 (CH, Ar), 128.8 (CH, Ar), 128.9 (CH, Ar), 129.0 (2×CH, Ar), 129.3 (CH, Ar), 130.2 (C_q, Ar), 131.3 (C_q, Ar), 141.7 (d, $J_{C,P}$ = 4.5 Hz, C_q, Ar), 143.7 (C_q, Ar), 146.9 (d, $J_{C,P}$ = 7.4 Hz, C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 116.7 ppm. MS (EI): *m*/*z* (%) = 308.1 (13), 279.2 (31), 167.1 (62), 150.1 (12), 149.1 (100), 115.2 (30), 113.2 (11), 105.2 (11), 73.3 (14), 72.3 (12). HRMS (ESI): *m*/*z* calcd. for $C_{26}H_{25}NO_2P^+$ [M + H$^+$] 414.16174; found 414.16207.

(1*S*,3*R*)-3-Methoxy-1-phenyl-2-[(*R*)-1-phenylethyl]-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(*R*$_P$)-22a]: The compound was synthesized from the borane adduct (0.32 mmol) by following the general procedure GP-Syn4 for deprotection of ligands. The product was obtained as a colorless solid, yield 84.7 mg (0.20 mmol, 64%). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.48 (dd, $^3J_{H,H}$ = 7.0, $^4J_{H,P}$ = 1.1 Hz, 3 H, CH_3), 3.01 (d, $^3J_{H,P}$ = 13.0 Hz, 3 H, OCH_3), 4.92 (dq, $^3J_{H,H}$ = 7.0, $^3J_{H,P}$ = 7.5 Hz, 1 H, CH), 5.60 (d, $^3J_{H,P}$ = 5.4 Hz, 1 H, CH), 6.76 (m, 2 H, Ar), 7.06 (m, 3 H, Ar), 7.22–7.50 (m, 9 H, Ar), 7.76 (d, $^3J_{H,H}$ = 8.6 Hz, 2 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 21.3 (d, $J_{C,P}$ = 16.5 Hz, CH_3), 49.2 (d, $J_{C,P}$ = 15.5 Hz, OCH_3), 53.0 (d, $J_{C,P}$ = 3.5 Hz, CH), 58.4 (d, $J_{C,P}$ = 35.9 Hz, CH), 120.9 (d, $J_{C,P}$ = 3.1 Hz, CH, Ar), 122.4 (CH, Ar), 123.7 (CH, Ar), 123.8 (C_q, Ar), 126.5 (CH, Ar), 126.7 (CH, Ar), 127.6 (3×CH, Ar), 127.7 (2×CH, Ar), 128.5 (CH, Ar), 128.6 (2×CH, Ar), 128.8 (2×CH, Ar), 129.2 (CH, Ar), 129.9 (C_q, Ar), 132.3 (C_q, Ar), 141.8 (d, $J_{C,P}$ = 4.5 Hz, C_q, Ar), 142.3 (C_q, Ar), 145.9 (d, $J_{C,P}$ = 13.6 Hz, C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ = 132.6 ppm. MS (EI): *m*/*z* (%) = 279.2 (22), 167.1 (43), 150.1 (12), 149.1 (100), 73.3 (11), 71.3 (12). HRMS (ESI): *m*/*z* calcd. for $C_{26}H_{25}NO_2P^+$ [M + H$^+$] 414.16174; found 414.16196.

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Borane Adduct of (*R*)-1-Phenyl-*N*-{(*R*)-phenyl[2-({(1*R*,3*S*)-1-phenyl-2-[(*R*)-1-phenylethyl]-1,2-dihydro-3*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinin-3-yl}oxy)naphthalen-1-yl]methyl}ethan-1-amine (23·BH$_3$): The compound was isolated by column chromatography as a side-product in the syntheses following the general procedure GP-Syn2 and GP-Syn3 for ligand synthesis starting from 1-((*R*)-phenyl{[(*R*)-1-phenylethyl]amino}methyl)naphthalen-2-ol. The product was obtained as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.21 (br. s, 3 H, CH_3), 1.63 (d, $^3J_{H,H}$ = 6.5 Hz, 3 H, CH_3), 3.72 (q, $^3J_{H,H}$ = 6.3 Hz, 1 H, CH), 5.26 (m, 1 H, CH), 5.65 (br. d, $^3J_{H,P}$ = 8.7 Hz, 1 H, CH), 5.74 (d, $^3J_{H,P}$ = 16.7 Hz, 1 H, CH), 6.76–7.80 (m, 32 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 20.0 (CH_3), 25.7 (CH_3), 54.8 (d, J = 3.5 Hz, CH), 55.4 (d, J = 15.8 Hz, CH), 55.5 (CH), 56.1 (CH), 119.3 (d, J = 6.5 Hz, CH, Ar), 120.4 (CH, Ar), 121.6 (CH, Ar), 122.0 (C_q, Ar), 124.7 (CH, Ar), 124.8 (CH, Ar), 125.9 (CH, Ar), 126.3 (CH, Ar), 126.6 (CH, Ar), 126.8 (CH, Ar), 127.1 (5 × CH, Ar), 127.4 (4 × CH, Ar), 127.8 (4 × CH, Ar), 128.0 (2 × CH, Ar), 128.2 (2 × CH, Ar), 128.4 (3 × CH, Ar), 128.68 (C_q, Ar), 128.73 (CH, Ar), 128.78 (CH, Ar), 129.7 (C_q, Ar), 129.8 (CH, Ar), 130.3 (C_q, Ar), 131.5 (C_q, Ar), 132.8 (C_q, Ar), 138.9 (d, J = 4.7 Hz, C_q, Ar), 140.4 (C_q, Ar), 143.8 (C_q, Ar), 146.2 (C_q, Ar), 146.8 (d, J = 8.6 Hz, C_q, Ar), 147.7 (d, J = 2.1 Hz, C_q, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 116.3 ppm.

(*R*)-1-Phenyl-*N*-{(*R*)-phenyl[2-({(1*R*,3*S*)-1-phenyl-2-[(*R*)-1-phenylethyl]-1,2-dihydro-3*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinin-3-yl}oxy)naphthalen-1-yl]methyl}ethan-1-amine (23): The compound was synthesized from the borane adduct (0.6 mmol) by following the general procedure GP-Syn4 for deprotection of ligands. The product was obtained as a colorless solid, yield 427.7 mg (0.58 mmol, 97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.15 (d, $^3J_{H,H}$ = 6.4 Hz, 3 H, CH_3), 1.72 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 3.52 (m, 1 H, CH), 4.64 (m, 1 H, CH), 5.54 (m, 1 H, CH), 5.71 (d, $^3J_{H,P}$ = 6.0 Hz, 1 H, CH), 6.83–7.38 (m, 28 H, Ar), 7.65–7.82 (m, 4 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 20.9 (d, J = 9.0 Hz, CH_3), 25.7 (CH_3), 54.1 (d, J = 4.5 Hz, CH), 55.4 (CH), 55.8 (CH), 58.0 (d, J = 42.5 Hz, CH), 120.4 (d, J = 3.3 Hz, CH, Ar), 121.7 (d, J = 9.5 Hz, C_q, Ar), 121.9 (CH, Ar), 123.7 (CH, Ar), 124.1 (CH, Ar), 125.9 (CH, Ar), 126.0 (d, J = 4.4 Hz, C_q, Ar), 126.1 (CH, Ar), 126.2 (CH, Ar), 126.7 (CH, Ar), 126.8 (CH, Ar), 127.05 (2 × CH, Ar), 127.06 (3 × CH, Ar), 127.10 (CH, Ar), 127.2 (2 × CH, Ar), 127.7 (2 × CH, Ar), 127.9 (2 × CH, Ar), 128.06 (2 × CH, Ar), 128.17 (2 × CH, Ar), 128.23 (CH, Ar), 128.50 (3 × CH, Ar), 128.54 (2 × CH, Ar), 128.8 (d, J = 3.7 Hz, C_q, Ar), 128.7 (C_q, Ar), 129.0 (CH, Ar), 129.6 (C_q, Ar), 130.8 (C_q, Ar), 141.1 (d, J = 4.8 Hz, C_q, Ar), 141.9 (C_q, Ar), 144.6 (C_q, Ar), 146.3 (C_q, Ar), 147.9 (d, J = 8.7 Hz, C_q, Ar), 149.4 (d, J = 8.0 Hz, C_q, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 133.7 ppm. MS (EI): *m*/*z* (%) = 382.2 (31), 363.3 (18), 287.2 (12), 286.2 (65), 285.2 (14), 279.2 (18), 278.1 (32), 234.2 (17), 231.2 (48), 218.1 (13), 215.2 (12), 202.2 (15), 182.2 (49), 181.2 (13), 167.1 (26), 149.1 (68), 106.2 (52), 105.2 (100), 91.2 (10), 79.2 (17), 77.2 (16). HRMS (ESI): *m*/*z* calcd. for $C_{50}H_{43}N_2O_2P^+$ [M$^+$] 734.30567; found 734.30641.

Borane Adduct of (1*R*,3*R*)-*N*,*N*-Diethyl-1-phenyl-2-[(*R*)-1-phenylethyl]-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine-3(2*H*)-amine [(*R*$_P$)-24a·BH$_3$]: The compound was synthesized by following the general procedure GP-Syn1 for ligand synthesis starting from 1-((*R*)-phenyl{[(*R*)-1-phenylethyl]amino}methyl)naphthalen-2-ol (4.0 mmol, 1.0 equiv.). Deviating from the general procedure, commercially available 1,1-dichloro-*N*,*N*-diethylphosphinamine (4.0 mmol, 1.0 equiv.) was used. The product was obtained as a colorless solid, yield 1.757 g (3.75 mmol, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14 (t, $^3J_{H,H}$ = 7.0 Hz, 6 H, CH_3), 1.44 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 2.95 (m, 2 H, CH_2), 3.40 (m, 2 H, CH_2), 5.07 (dq, $^3J_{H,H}$ = 7.0, $^3J_{H,P}$ = 11.2 Hz, 1 H, CH), 5.62 (d, $^3J_{H,P}$ = 16.9 Hz, 1 H, CH), 7.04 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H, Ar), 7.15 (m, 2 H, Ar), 7.23 (m, 6 H, Ar), 7.32 (m, 3 H, Ar), 7.54 (d, $^3J_{H,H}$ = 7.4 Hz, 2 H, Ar), 7.71 (t, $^3J_{H,H}$ = 9.4 Hz, 2 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 14.4 (2 × CH_3), 18.5 (CH_3), 39.0 (d, $J_{C,P}$ = 6.3 Hz, 2 × CH_2), 54.2 (d, $J_{C,P}$ = 14.3 Hz, CH), 56.7 (CH), 120.0 (d, $J_{C,P}$ = 4.8 Hz, CH, Ar), 121.4 (CH, Ar), 123.9 (d, $J_{C,P}$ = 6.7 Hz, C_q, Ar), 124.5 (CH, Ar), 126.6 (CH, Ar), 127.5 (CH, Ar), 127.6 (CH, Ar), 128.4 (4 × CH, Ar), 128.5 (2 × CH, Ar), 128.6 (CH, Ar), 128.7 (2 × CH, Ar), 129.3 (C_q, Ar), 129.7 (CH, Ar), 130.6 (C_q, Ar), 139.6 (d, $J_{C,P}$ = 4.8 Hz, C_q, Ar), 142.9 (C_q, Ar), 148.1 (d, $J_{C,P}$ = 6.1 Hz, C_q, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 111.5 ppm.

Borane Adduct of (1*R*,3*S*)-*N*,*N*-Diethyl-1-phenyl-2-[(*R*)-1-phenylethyl]-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine-3(2*H*)-amine [(*S*$_P$)-24a·BH$_3$]: The compound was synthesized by following the general procedure GP-Syn3 for ligand synthesis starting from 1-((*R*)-phenyl{[(*R*)-1-phenylethyl]amino}methyl)naphthalen-2-ol (4.0 mmol, 1.0 equiv.). Deviating from the general procedure, commercially available 1,1-dichloro-*N*,*N*-diethylphosphinamine (4.0 mmol, 1.0 equiv.) was used. The product was obtained as a colorless solid, yield 562.1 mg (1.20 mmol, 30%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (t, $^3J_{H,H}$ = 7.0 Hz, 6 H, CH_3), 1.38 (d, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3), 3.02 (m, 4 H, CH_2), 4.85 (dq, $^3J_{H,H}$ = 7.1 Hz, $^3J_{H,P}$ = 10.7 Hz, 1 H, CH), 5.82 (d, $^3J_{H,P}$ = 12.4 Hz, 1 H, CH), 7.16 (m, 1 H, Ar), 7.25 (m, 3 H, Ar), 7.34 (m, 2 H, Ar), 7.39 (m, 5 H, Ar), 7.69 (m, 5 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 13.4 (2 × CH_3), 19.7 (CH_3), 38.5 (d, $J_{C,P}$ = 4.4 Hz, 2 × CH_2), 54.9 (CH), 56.1 (d, $J_{C,P}$ = 13.6 Hz, CH), 119.7 (d, $J_{C,P}$ = 3.5 Hz, CH, Ar), 121.6 (CH, Ar), 123.7 (d, $J_{C,P}$ = 9.2 Hz, C_q, Ar), 124.6 (CH, Ar), 127.0 (CH, Ar), 127.6 (CH, Ar), 127.9 (3 × CH, Ar), 128.4 (2 × CH, Ar), 128.56 (2 × CH, Ar), 128.59 (2 × CH, Ar), 128.9 (CH, Ar), 129.2 (C_q, Ar), 129.6 (CH, Ar), 130.7 (C_q, Ar), 140.1 (d, $J_{C,P}$ = 4.5 Hz, C_q, Ar), 143.9 (C_q, Ar), 145.8 (d, $J_{C,P}$ = 11.5 Hz, C_q, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 100.7 ppm.

Borane Adduct of (1*R*,3*R*)-1-Phenyl-2-[(*R*)-1-phenylethyl]-3-(piperidin-1-yl)-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(*R*$_P$)-24b·BH$_3$]: The compound was synthesized by following the general procedure GP-Syn1 for ligand synthesis starting from 1-((*R*)-phenyl{[(*R*)-1-phenylethyl]amino}methyl)naphthalen-2-ol (2.0 mmol, 1.0 equiv.) and piperidine (2.0 mmol, 1.0 equiv.). The product was obtained as a colorless solid, yield 809.0 mg (1.68 mmol, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.49 (m, 3 H, CH_3, 6 H, CH_2), 3.06 (m, 4 H, CH_2), 5.04 (dq, $^3J_{H,H}$ = 7.0 Hz, $^3J_{H,P}$ = 11.6 Hz, 1 H, CH), 5.62 (d, $^3J_{H,P}$ = 16.2 Hz, 1 H, CH), 7.04–7.22 (m, 9 H, Ar), 7.29 (m, 3 H, Ar), 7.45 (m, 2 H, Ar), 7.66 (m, 2 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 19.0 (CH_3), 24.5 (CH_2), 26.4 (d, $J_{C,P}$ = 2.8 Hz, 2 × CH_2), 45.4 (d, $J_{C,P}$ = 3.9 Hz, 2 × CH_2), 54.6 (d, $J_{C,P}$ = 13.4 Hz, CH), 56.6 (CH), 119.9 (d, $J_{C,P}$ = 4.9 Hz, CH, Ar), 121.4 (CH, Ar), 123.4 (d, $J_{C,P}$ = 7.3 Hz, C_q, Ar), 124.4 (CH, Ar), 126.6 (CH, Ar), 127.3 (CH, Ar), 127.5 (CH, Ar), 128.29 (4 × CH, Ar), 128.39 (2 × CH, Ar), 128.48 (CH, Ar), 128.54 (2 × CH, Ar), 129.4 (C_q, Ar), 129.6 (CH, Ar), 130.4 (C_q, Ar), 139.6 (d, $J_{C,P}$ = 4.1 Hz, C_q, Ar), 142.7 (C_q, Ar), 148.1 (d, $J_{C,P}$ = 6.4 Hz, C_q, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 108.6 ppm.

Borane Adduct of (1*R*,3*S*)-1-Phenyl-2-[(*R*)-1-phenylethyl]-3-(piperidin-1-yl)-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(*S*$_P$)-24b·BH$_3$]: The compound was synthesized by following the general procedure GP-Syn3 for ligand synthesis starting from 1-

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((*R*)-phenyl{[(*R*)-1-phenylethyl]amino}methyl)naphthalen-2-ol (2.0 mmol, 1.0 equiv.) and piperidine (2.0 mmol, 1.0 equiv.). The product was obtained as a colorless solid, yield 227.7 mg (0.47 mmol, 24%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (m, 4 H, CH_2), 1.37 (d, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3), 1.47 (m, 2 H, CH_2), 2.86 (m, 2 H, CH_2), 3.06 (m, 2 H, CH_2), 4.85 (dq, $^3J_{H,H}$ = 7.2 Hz, $^3J_{H,P}$ = 10.4 Hz, 1 H, CH), 5.83 (d, $^3J_{H,P}$ = 12.5 Hz, 1 H, CH), 7.07–7.42 (m, 11 H, Ar), 7.66 (m, 5 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 19.6 (d, $J_{C,P}$ = 1.0 Hz, CH_3), 24.2 (CH_2), 26.2 (d, $J_{C,P}$ = 3.1 Hz, 2×CH_2), 46.1 (d, $J_{C,P}$ = 1.9 Hz, 2×CH_2), 54.9 (CH), 56.2 (d, $J_{C,P}$ = 13.0 Hz, CH), 119.5 (d, $J_{C,P}$ = 3.5 Hz, CH, Ar), 121.4 (CH, Ar), 123.8 (d, $J_{C,P}$ = 9.1 Hz, C_q, Ar), 124.6 (CH, Ar), 127.0 (CH, Ar), 127.5 (CH, Ar), 127.7 (3×CH, Ar), 128.2 (2×CH, Ar), 128.4 (2×CH, Ar), 128.5 (2×CH, Ar), 128.8 (CH, Ar), 129.1 (C_q, Ar), 129.6 (CH, Ar), 130.6 (C_q, Ar), 140.1 (d, $J_{C,P}$ = 4.3 Hz, C_q, Ar), 143.8 (C_q, Ar), 145.9 (d, $J_{C,P}$ = 11.1 Hz, C_q, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 98.7 ppm.

Borane Adduct of (1*R*,3*R*)-*N*-Methyl-1-phenyl-*N*,2-bis[(*R*)-1-phenylethyl]-1*H*-naphtho[1,2-*e*][1,3,2]oxaza-phosphinine-3(2*H*)-amine [(R_P)-24c·BH_3]: The compound was synthesized by following the general procedure GP-Syn1 for ligand synthesis starting from 1-((*R*)-phenyl{[(*R*)-1-phenylethyl]amino}methyl)naphthalen-2-ol (2.0 mmol, 1.0 equiv.) and (*R*)-*N*-methyl-1-phenylethanamine (2.0 mmol, 1.0 equiv.). The product was obtained as a colorless solid, yield 841.3 mg (1.59 mmol, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.21 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 1.67 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 2.30 (d, $^3J_{H,P}$ = 8.1 Hz, 3 H, NCH_3), 5.21 (dq, $^3J_{H,H}$ = 7.1 Hz, $^3J_{H,P}$ = 10.7 Hz, 1 H, CH), 5.41 (dq, $^3J_{H,H}$ = 6.9 Hz, $^3J_{H,P}$ = 11.6 Hz, 1 H, CH), 5.62 (d, $^3J_{H,P}$ = 17.3 Hz, 1 H, CH), 7.00 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H, Ar), 7.07 (m, 1 H, Ar), 7.14 (m, 3 H, Ar), 7.20–7.33 (m, 9 H, Ar), 7.40 (m, 3 H, Ar), 7.58 (m, 2 H, Ar), 7.71 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H, Ar), 7.76 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 16.7 (CH_3), 18.3 (CH_3), 25.9 (d, $J_{C,P}$ = 3.7 Hz, NCH_3), 54.1 (d, $J_{C,P}$ = 16.2 Hz, CH), 54.3 (d, $J_{C,P}$ = 14.1 Hz, CH), 56.6 (CH), 120.0 (d, $J_{C,P}$ = 4.7 Hz, CH, Ar), 121.4 (CH, Ar), 123.9 (d, $J_{C,P}$ = 6.7 Hz, C_q, Ar), 124.5 (CH, Ar), 126.7 (CH, Ar), 127.3 (CH, Ar), 127.5 (CH, Ar), 127.6 (CH, Ar), 127.7 (2×CH, Ar), 128.2 (2×CH, Ar), 128.4 (2×CH, Ar), 128.5 (2×CH, Ar), 128.6 (CH, Ar), 128.7 (2×CH, Ar), 129.0 (2×CH, Ar), 129.2 (C_q, Ar), 129.8 (CH, Ar), 130.7 (C_q, Ar), 139.6 (d, $J_{C,P}$ = 5.0 Hz, C_q, Ar), 140.9 (d, $J_{C,P}$ = 8.4 Hz, C_q, Ar), 142.5 (C_q, Ar), 148.1 (d, $J_{C,P}$ = 6.3 Hz, C_q, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 111.2 ppm.

Borane Adduct of (1*R*,3*S*)-*N*-Methyl-1-phenyl-*N*,2-bis[(*R*)-1-phenylethyl]-1*H*-naphtho[1,2-*e*][1,3,2]oxaza-phosphinine-3(2*H*)-amine [(S_P)-24c·BH_3]: The compound was synthesized by following the general procedure GP-Syn3 for ligand synthesis starting from 1-((*R*)-phenyl{[(*R*)-1-phenylethyl]amino}methyl)naphthalen-2-ol (2.0 mmol, 1.0 equiv.) and (*R*)-*N*-methyl-1-phenylethanamine (2.0 mmol, 1.0 equiv.). The product was obtained as a colorless solid, yield 204.4 mg (0.39 mmol, 19%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.41 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 1.55 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 1.66 (d, $^3J_{H,P}$ = 7.8 Hz, 3 H, NCH_3), 4.94 (dq, $^3J_{H,H}$ = 7.1 Hz, $^3J_{H,P}$ = 10.7 Hz, 1 H, CH), 5.51 (dq, $^3J_{H,H}$ = 6.7 Hz, $^3J_{H,P}$ = 13.0 Hz, 1 H, CH), 5.89 (d, $^3J_{H,P}$ = 11.9 Hz, 1 H, CH), 6.98 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, Ar), 7.14 (m, 1 H, Ar), 7.22–7.43 (m, 12 H, Ar), 7.50 (m, 3 H, Ar), 7.60 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H, Ar), 7.68 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H, Ar), 7.77 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 16.2 (d, $J_{C,P}$ = 6.8 Hz, CH_3), 19.6 (d, $J_{C,P}$ = 1.8 Hz, CH_3), 27.4 (d, $J_{C,P}$ = 5.3 Hz, NCH_3), 53.8 (d, $J_{C,P}$ = 13.6 Hz, CH), 54.6 (CH), 56.4 (d, $J_{C,P}$ = 13.4 Hz, CH), 119.0 (d, $J_{C,P}$ = 3.4 Hz, CH, Ar), 121.4 (CH, Ar), 124.2 (d, $J_{C,P}$ = 9.2 Hz, C_q, Ar), 124.6 (CH, Ar), 127.0 (CH, Ar), 127.2 (CH, Ar), 127.48 (2×CH, Ar), 127.52 (2×CH, Ar), 127.57 (CH, Ar), 128.0 (CH, Ar), 128.2 (2×CH, Ar), 128.4 (2×CH, Ar), 128.57 (2×CH, Ar), 128.61 (2×CH, Ar), 128.8 (CH, Ar), 129.0 (C_q, Ar), 129.9 (CH, Ar), 130.6 (C_q, Ar), 139.8 (d, $J_{C,P}$ = 3.9 Hz, C_q, Ar), 140.7 (d, $J_{C,P}$ = 1.7 Hz, C_q, Ar), 144.1 (C_q, Ar), 146.1 (d, $J_{C,P}$ = 10.8 Hz, C_q, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 101.4 ppm.

Borane Adduct of (1*R*,3*R*)-*N*-Methyl-1-phenyl-2-[(*R*)-1-phenylethyl]-*N*-[(*S*)-1-phenylethyl]-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine-3(2*H*)-amine [(R_P)-24d·BH_3]: The compound was synthesized by following the general procedure GP-Syn1 for ligand synthesis starting from 1-((*R*)-phenyl{[(*R*)-1-phenylethyl]amino}methyl)-naphthalen-2-ol (2.0 mmol, 1.0 equiv.) and (*S*)-*N*-methyl-1-phenylethanamine (2.0 mmol, 1.0 equiv.). The product was obtained as a colorless solid, yield 785.1 mg (1.48 mmol, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.47 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 1.53 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 2.27 (d, $^3J_{H,P}$ = 7.9 Hz, 3 H, NCH_3), 5.17 (dq, $^3J_{H,H}$ = 7.1 Hz, $^3J_{H,P}$ = 11.1 Hz, 1 H, CH), 5.47 (dq, $^3J_{H,H}$ = 6.7 Hz, $^3J_{H,P}$ = 13.1 Hz, 1 H, CH), 5.65 (d, $^3J_{H,P}$ = 16.8 Hz, 1 H, CH), 7.01–7.10 (m, 2 H, Ar), 7.14 (m, 3 H, Ar), 7.18–7.31 (m, 7 H, Ar), 7.39 (m, 3 H, Ar), 7.52 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H, Ar), 7.58 (d, $^3J_{H,H}$ = 7.3 Hz, 2 H, Ar), 7.69 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, Ar), 7.73 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 17.0 (d, $J_{C,P}$ = 4.6 Hz, CH_3), 18.7 (CH_3), 26.4 (d, $J_{C,P}$ = 3.7 Hz, NCH_3), 53.5 (d, $J_{C,P}$ = 16.6 Hz, CH), 54.2 (d, $J_{C,P}$ = 14.4 Hz, CH), 56.8 (CH), 120.0 (d, $J_{C,P}$ = 4.7 Hz, CH, Ar), 121.4 (CH, Ar), 123.9 (d, $J_{C,P}$ = 6.7 Hz, C_q, Ar), 124.5 (CH, Ar), 126.7 (CH, Ar), 127.1 (CH, Ar), 127.4 (2×CH, Ar), 127.5 (CH, Ar), 127.6 (CH, Ar), 128.3 (2×CH, Ar), 128.45 (2×CH, Ar), 128.48 (2×CH, Ar), 128.6 (3×CH, Ar), 128.9 (2×CH, Ar), 129.2 (C_q, Ar), 129.7 (CH, Ar), 130.7 (C_q, Ar), 139.5 (d, $J_{C,P}$ = 4.8 Hz, C_q, Ar), 140.9 (d, $J_{C,P}$ = 3.6 Hz, C_q, Ar), 142.7 (C_q, Ar), 148.0 (d, $J_{C,P}$ = 6.0 Hz, C_q, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 111.4 ppm.

Borane Adduct of (1*R*,3*S*)-*N*-Methyl-1-phenyl-2-[(*R*)-1-phenylethyl]-*N*-[(*S*)-1-phenylethyl]-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine-3(2*H*)-amine [(S_P)-24d·BH_3]: The compound was synthesized by following the general procedure GP-Syn3 for ligand synthesis starting from 1-((*R*)-phenyl{[(*R*)-1-phenylethyl]amino}methyl)-naphthalen-2-ol (2.0 mmol, 1.0 equiv.) and (*S*)-*N*-methyl-1-phenylethanamine (2.0 mmol, 1.0 equiv.). The product was obtained as a colorless solid, yield 211.1 mg (0.40 mmol, 20%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.39 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 1.61 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 1.66 (d, $^3J_{H,P}$ = 8.0 Hz, 3 H, NCH_3), 4.98 (dq, $^3J_{H,H}$ = 7.2 Hz, $^3J_{H,P}$ = 10.9 Hz, 1 H, CH), 5.48 (dq, $^3J_{H,H}$ = 6.9 Hz, $^3J_{H,P}$ = 10.6 Hz, 1 H, CH), 5.86 (d, $^3J_{H,P}$ = 11.3 Hz, 1 H, CH), 7.13–7.48 (m, 16 H, Ar), 7.66 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H, Ar), 7.71 (d, $^3J_{H,H}$ = 8.6 Hz, 2 H, Ar), 7.79 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 16.1 (CH_3), 19.6 (d, $J_{C,P}$ = 2.1 Hz, CH_3), 27.0 (d, $J_{C,P}$ = 5.5 Hz, NCH_3), 54.0 (d, $J_{C,P}$ = 13.7 Hz, CH), 54.5 (CH), 56.5 (d, $J_{C,P}$ = 12.9 Hz, CH), 119.2 (d, $J_{C,P}$ = 3.4 Hz, CH, Ar), 121.6 (CH, Ar), 124.1 (d, $J_{C,P}$ = 9.5 Hz, C_q, Ar), 124.7 (CH, Ar), 127.0 (CH, Ar), 127.4 (CH, Ar), 127.5 (2×CH, Ar), 127.6 (CH, Ar), 127.8 (2×CH, Ar), 127.9 (CH, Ar), 128.3 (2×CH, Ar), 128.4 (2×CH, Ar), 128.6 (2×CH, Ar), 128.7 (2×CH, Ar), 129.0 (CH, Ar), 129.2 (C_q, Ar), 130.0 (CH, Ar), 130.8 (C_q, Ar), 139.5 (d, $J_{C,P}$ = 3.8 Hz, C_q, Ar), 140.7 (d, $J_{C,P}$ = 10.0 Hz, C_q, Ar), 144.3 (C_q, Ar), 146.2 (d, $J_{C,P}$ = 10.5 Hz, C_q, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 101.4 ppm.

Borane Adduct of (1*R*,3*R*)-1-Phenyl-*N*,*N*,2-tris[(*R*)-1-phenylethyl]-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine-3(2*H*)-amine [(R_P)-24e·BH_3]: The compound was synthesized by following the general

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procedure GP-Syn1 for ligand synthesis starting from 1-((*R*)-phenyl{[(*R*)-1-phenylethyl]amino}methyl)naphthalen-2-ol (2.0 mmol, 1.0 equiv.) and (*R*)-bis[(*R*)-1-phenylethyl]amine (2.0 mmol, 1.0 equiv.). The product was obtained as a colorless solid, yield 907.3 mg (1.46 mmol, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (d, $^3J_{H,H}$ = 7.2 Hz, 6 H, CH_3), 1.96 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 5.01 (dq, $^3J_{H,H}$ = 7.1 Hz, $^3J_{H,P}$ = 12.6 Hz, 2 H, CH), 5.55 (dq, $^3J_{H,H}$ = 7.0 Hz, $^3J_{H,P}$ = 11.6 Hz, 1 H, CH), 5.86 (d, $^3J_{H,P}$ = 18.4 Hz, 1 H, CH), 6.80 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H, Ar), 6.99 (m, 3 H, Ar), 7.10 (m, 4 H, Ar), 7.22–7.36 (m, 13 H, Ar), 7.55 (m, 3 H, Ar), 7.78 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H, Ar), 7.87 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 19.4 (2×CH_3), 21.7 (CH_3), 53.1 (d, $J_{C,P}$ = 7.9 Hz, 2×CH), 55.5 (d, $J_{C,P}$ = 17.7 Hz, CH), 57.2 (d, $J_{C,P}$ = 2.1 Hz, CH), 120.1 (d, $J_{C,P}$ = 5.2 Hz, CH, Ar), 121.4 (CH, Ar), 124.60 (d, $J_{C,P}$ = 6.3 Hz, C_q, Ar), 124.62 (CH, Ar), 126.5 (CH, Ar), 127.2 (2×CH, Ar), 127.58 (CH, Ar), 127.61 (CH, Ar), 127.8 (4×CH, Ar), 128.4 (7×CH, Ar), 128.67 (2×, CH, Ar), 128.69 (4×CH, Ar), 129.3 (C_q, Ar), 129.7 (CH, Ar), 130.6 (C_q, Ar), 139.5 (d, $J_{C,P}$ = 4.4 Hz, C_q, Ar), 141.7 (C_q, Ar), 142.1 (d, $J_{C,P}$ = 4.9 Hz, 2×C_q, Ar), 149.3 (d, $J_{C,P}$ = 6.6 Hz, C_q, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 117.6 ppm.

Borane Adduct of (1*R*,3*R*)-1-Phenyl-2-[(*R*)-1-phenylethyl]-*N*,*N*-bis[(*S*)-1-phenylethyl]-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine-3(2*H*)-amine [(*R*$_P$)-24f·BH$_3$]: The compound was synthesized by following the general procedure GP-Syn1 for ligand synthesis starting from 1-((*R*)-phenyl{[(*R*)-1-phenylethyl]amino}methyl)-naphthalen-2-ol (2.0 mmol, 1.0 equiv.) and (*S*)-bis[(*S*)-1-phenylethyl]amine (2.0 mmol, 1.0 equiv.). The product was obtained as a colorless solid, yield 824.1 mg (1.33 mmol, 66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16 (d, $^3J_{H,H}$ = 7.2 Hz, 6 H, CH_3), 1.76 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 5.06 (dq, $^3J_{H,H}$ = 7.1 Hz, $^3J_{H,P}$ = 7.0 Hz, 2 H, CH), 5.16 (m, 1 H, CH), 5.83 (d, $^3J_{H,P}$ = 18.3 Hz, 1 H, CH), 6.80 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H, Ar), 6.96 (t, $^3J_{H,H}$ = 7.4 Hz, 1 H, Ar), 7.05 (m, 10 H, Ar), 7.15 (m, 7 H, Ar), 7.30 (d, $^3J_{H,H}$ = 7.4 Hz, 2 H, Ar), 7.45 (m, 3 H, Ar), 7.67 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H, Ar), 7.75 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 21.0 (d, $J_{C,P}$ = 1.1 Hz, 2×CH_3), 21.5 (CH_3), 53.2 (d, $J_{C,P}$ = 7.5 Hz, 2×CH), 55.4 (d, $J_{C,P}$ = 17.3 Hz, CH), 57.4 (d, $J_{C,P}$ = 2.0 Hz, CH), 120.0 (d, $J_{C,P}$ = 4.9 Hz, CH, Ar), 121.3 (CH, Ar), 124.2 (d, $J_{C,P}$ = 6.2 Hz, C_q, Ar), 124.6 (CH, Ar), 126.6 (CH, Ar), 127.3 (2×CH, Ar), 127.5 (5×CH, Ar), 127.9 (CH, Ar), 128.47 (3×CH, Ar), 128.49 (2×CH, Ar), 128.6 (2×CH, Ar), 129.03 (3×CH, Ar), 129.05 (3×CH, Ar), 129.14 (C_q, Ar), 129.7 (CH, Ar), 130.6 (C_q, Ar), 139.6 (d, $J_{C,P}$ = 4.8 Hz, C_q, Ar), 141.5 (d, $J_{C,P}$ = 4.4 Hz, 2×C_q, Ar), 142.2 (C_q, Ar), 149.0 (d, $J_{C,P}$ = 6.6 Hz, C_q, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 120.5 ppm.

Borane Adduct of (1*R*,3*S*)-*N*,*N*,1-Triphenyl-2-[(*R*)-1-phenylethyl]-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine-3(2*H*)-amine [(*S*$_P$)-24g·BH$_3$]: The compound was synthesized by following the general procedure GP-Syn1 for ligand synthesis starting from 1-((*R*)-phenyl{[(*R*)-1-phenylethyl]amino}methyl)naphthalen-2-ol (2.0 mmol, 1.0 equiv.) and diphenylamine (2.0 mmol, 1.0 equiv.). The product was obtained as a colorless solid, yield 607.4 mg (1.08 mmol, 54%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.81 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 5.66 (dq, $^3J_{H,H}$ = 6.9 Hz, $^3J_{H,P}$ = 13.0 Hz, 1 H, CH), 5.70 (d, $^3J_{H,P}$ = 15.1 Hz, 1 H, CH), 6.76 (m, 1 H, Ar), 6.82–6.92 (m, 6 H, Ar), 6.94–7.25 (m, 15 H, Ar), 7.39 (d, $^3J_{H,H}$ = 7.7 Hz, 2 H, Ar), 7.66 (m, 2 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 19.5 (d, $J_{C,P}$ = 4.5 Hz, CH_3), 54.5 (d, $J_{C,P}$ = 3.3 Hz, CH), 55.6 (d, $J_{C,P}$ = 15.6 Hz, CH), 119.7 (d, $J_{C,P}$ = 6.2 Hz, CH, Ar), 120.8 (d, $J_{C,P}$ = 8.7 Hz, C_q, Ar), 121.9 (CH, Ar), 124.4 (CH, Ar), 125.4 (2×CH, Ar), 126.5 (CH, Ar), 126.9 (CH, Ar), 127.2 (CH, Ar), 127.73 (2×, CH, Ar), 127.78 (2×CH, Ar), 127.87 (2×CH, Ar), 127.90 (2×CH, Ar), 127.98 (2×CH, Ar), 128.01 (2×CH, Ar), 128.2 (CH, Ar), 128.6 (4×CH, Ar), 129.6 (CH, Ar), 129.9 (C_q, Ar), 130.0 (C_q, Ar), 139.2 (d, $J_{C,P}$ = 2.9 Hz, C_q, Ar), 139.8 (C_q, Ar), 144.0 (d, $J_{C,P}$ = 5.8 Hz, 2×C_q, Ar), 147.7 (d, $J_{C,P}$ = 7.5 Hz, C_q, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 108.5 ppm.

(1*R*,3*R*)-*N*,*N*-Diethyl-1-phenyl-2-[(*R*)-1-phenylethyl]-1*H*-naphtho-[1,2-*e*][1,3,2]oxaza-phosphinine-3(2*H*)-amine [(*R*$_P$)-24a]: The compound was synthesized from the borane adduct (0.7 mmol) by following the general procedure GP-Syn4 for deprotection of ligands. The product was obtained as a colorless solid, yield 283.2 mg (0.62 mmol, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.96 (t, $^3J_{H,H}$ = 7.0 Hz, 6 H, CH_3), 1.61 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 2.68 (m, 2 H, CH_2), 2.99 (m, 2 H, CH_2), 4.88 (dq, $^3J_{H,H}$ = 7.0 Hz, $^3J_{H,P}$ = 11.2 Hz, 1 H, CH), 5.67 (d, $^3J_{H,P}$ = 7.9 Hz, 1 H, CH), 6.93 (m, 1 H, Ar), 7.01 (m, 2 H, Ar), 7.08–7.33 (m, 11 H, Ar), 7.66 (m, 2 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 15.0 (d, $J_{C,P}$ = 3.0 Hz, 2×CH_3), 19.9 (d, $J_{C,P}$ = 5.0 Hz, CH_3), 38.3 (d, $J_{C,P}$ = 21.8 Hz, 2×CH_2), 56.3 (d, $J_{C,P}$ = 2.6 Hz, CH), 56.6 (d, $J_{C,P}$ = 38.0 Hz, CH), 121.2 (d, $J_{C,P}$ = 3.1 Hz, CH, Ar), 123.5 (CH, Ar), 124.7 (d, $J_{C,P}$ = 6.0 Hz, C_q, Ar), 126.1 (CH, Ar), 126.58 (CH, Ar), 126.61 (CH, Ar), 127.47 (CH, Ar), 127.53 (CH, Ar), 127.9 (2×CH, Ar), 128.1 (2×CH, Ar), 128.2 (CH, Ar), 128.4 (2×CH, Ar), 128.5 (CH, Ar), 128.7 (CH, Ar), 129.4 (C_q, Ar), 130.4 (C_q, Ar), 142.1 (d, $J_{C,P}$ = 3.7 Hz, C_q, Ar), 144.5 (C_q, Ar), 150.3 (d, $J_{C,P}$ = 3.5 Hz, C_q, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 135.4 ppm. MS (EI): *m*/*z* (%) = 279.2 (19), 232.1 (16), 231.1 (38), 167.1 (36), 150.1 (10), 149.1 (100), 144.1 (10), 106.2 (50), 105.2 (39), 104.1 (10), 91.2 (10), 79.2 (12). HRMS (ESI): *m*/*z* calcd. for $C_{29}H_{31}N_2OP^+$ [M^+] 454.21685; found 454.21659.

(1*R*,3*S*)-*N*,*N*-Diethyl-1-phenyl-2-[(*R*)-1-phenylethyl]-1*H*-naphtho-[1,2-*e*][1,3,2]oxaza-phosphinine-3(2*H*)-amine [(*S*$_P$)-24a]: The compound was synthesized from the borane adduct (0.5 mmol) by following the general procedure GP-Syn4 for deprotection of ligands. The product was obtained as a colorless solid, yield 190.9 mg (0.42 mmol, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.82 (t, $^3J_{H,H}$ = 7.0 Hz, 6 H, CH_3), 1.45 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 2.87 (m, 4 H, CH_2), 4.51 (dq, $^3J_{H,H}$ = 7.0 Hz, $^3J_{H,P}$ = 12.4 Hz, 1 H, CH), 5.87 (s, 1 H, CH), 7.13 (m, 2 H, Ar), 7.18–7.33 (m, 8 H, Ar), 7.42 (m, 1 H, Ar), 7.61 (m, 3 H, Ar), 7.72 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H, Ar), 7.84 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 14.0 (d, $J_{C,P}$ = 3.0 Hz, 2×CH_3), 19.0 (d, $J_{C,P}$ = 4.2 Hz, CH_3), 38.2 (d, $J_{C,P}$ = 19.9 Hz, 2×CH_2), 56.3 (d, $J_{C,P}$ = 33.2 Hz, CH), 56.6 (d, $J_{C,P}$ = 8.3 Hz, CH), 120.9 (CH, Ar), 121.4 (CH, Ar), 123.6 (CH, Ar), 123.8 (d, $J_{C,P}$ = 8.0 Hz, C_q, Ar), 126.4 (CH, Ar),126.98 (CH, Ar), 127.02 (CH, Ar), 127.67 (CH, Ar), 127.70 (CH, Ar), 128.07 (2×CH, Ar), 128.21 (CH, Ar), 128.24 (CH, Ar), 128.31 (2×CH, Ar), 128.8 (CH, Ar), 128.9 (CH, Ar), 129.9 (C_q, Ar), 130.0 (C_q, Ar), 141.9 (d, $J_{C,P}$ = 3.8 Hz, C_q, Ar), 145.2 (C_q, Ar), 147.6 (d, $J_{C,P}$ = 5.8 Hz, C_q, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 114.7 ppm. MS (EI): *m*/*z* (%) = 349.2 (32), 279.2 (22), 278.1 (16), 167.1 (34), 149.1 (100), 105.2 (26). HRMS (ESI): *m*/*z* calcd. for $C_{29}H_{31}N_2OP^+$ [M^+] 454.21685; found 454.21741.

(1*R*,3*R*)-1-Phenyl-2-[(*R*)-1-phenylethyl]-3-(piperidin-1-yl)-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine [(*R*$_P$)-24b]: The compound was synthesized by following the general procedure GP-Syn1 for ligand synthesis starting from 1-((*R*)-phenyl{[(*R*)-1-phenylethyl]amino}methyl)naphthalen-2-ol (0.5 mmol, 1.0 equiv.) and piperidine (0.5 mmol, 1.0 equiv.), without purification via the bor-

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ane adduct. The product was obtained as a colorless solid, yield 181.8 mg (0.39 mmol, 78%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.46 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 1.52 (m, 6 H, CH_2), 2.87 (m, 4 H, CH_2), 4.48 (dq, $^3J_{H,H}$ = 7.1 Hz, $^3J_{H,P}$ = 11.5 Hz, 1 H, CH), 5.56 (d, $^3J_{H,P}$ = 6.8 Hz, 1 H, CH), 6.92–7.38 (m, 12 H, Ar), 7.51–7.71 (m, 4 H, Ar) ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = 135.4 ppm.

(1*R*,3*S*)-*N*-Methyl-1-phenyl-*N*,2-bis[(*R*)-1-phenylethyl]-1*H*-naphtho-[1,2-*e*][1,3,2]oxazaphosphinine-3(2*H*)-amine [(S_P)-24c]: The compound was synthesized from the borane adduct (0.5 mmol) by following the general procedure GP-Syn4 for deprotection of ligands. The product was obtained as a colorless solid, yield 232.5 mg (0.45 mmol, 90%). $[\alpha]_D^{25}$ = –338.3 (c = 0.2, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.41 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 1.42 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 1.63 (d, $^3J_{H,P}$ = 3.7 Hz, 3 H, NCH_3), 4.54 (dq, $^3J_{H,H}$ = 7.0 Hz, $^3J_{H,P}$ = 12.8 Hz, 1 H, CH), 4.80 (dq, $^3J_{H,H}$ = 7.0 Hz, $^3J_{H,P}$ = 10.1 Hz, 1 H, CH), 5.84 (s, 1 H, CH), 6.80 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, Ar), 7.07 (m, 1 H, Ar), 7.13–7.39 (m, 14 H, Ar), 7.42 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, Ar), 7.57 (d, $^3J_{H,H}$ = 7.7 Hz, 3 H, Ar), 7.77 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 17.5 (d, $J_{C,P}$ = 9.4 Hz, CH_3), 19.0 (d, $J_{C,P}$ = 4.0 Hz, CH_3), 27.1 (d, $J_{C,P}$ = 7.7 Hz, NCH_3), 55.5 (d, $J_{C,P}$ = 46.8 Hz, CH), 56.4 (d, $J_{C,P}$ = 6.3 Hz, CH), 56.6 (d, $J_{C,P}$ = 18.7 Hz, CH), 120.2 (CH, Ar), 121.3 (CH, Ar), 123.6 (CH, Ar), 124.1 (d, $J_{C,P}$ = 8.0 Hz, C_q, Ar), 126.4 (CH, Ar), 126.7 (CH, Ar), 127.0 (CH, Ar), 127.2 (CH, Ar), 127.55 (2×CH, Ar), 127.57 (CH, Ar), 127.59 (CH, Ar), 128.0 (2×CH, Ar), 128.2 (2×CH, Ar), 128.30 (CH, Ar), 128.32 (CH, Ar), 128.37 (2×CH, Ar), 128.7 (CH, Ar), 129.2 (CH, Ar), 129.8 (C_q, Ar), 130.0 (C_q, Ar), 141.8 (d, $J_{C,P}$ = 3.9 Hz, C_q, Ar), 142.5 (C_q, Ar), 145.3 (C_q, Ar), 148.0 (d, $J_{C,P}$ = 4.9 Hz, C_q, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 114.2 ppm. MS (EI): m/z (%) = 518.2 (38), 517.2 (100), 354.2 (13), 233.1 (10). HRMS (ESI): m/z calcd. for $C_{34}H_{34}N_2OP^+$ [M + H$^+$] 517.24033; found 517.23999.

(1*R*,3*R*)-*N*-Methyl-1-phenyl-*N*,2-bis[(*R*)-1-phenylethyl]-1*H*-naphtho-[1,2-*e*][1,3,2]oxazaphosphinine-3(2*H*)-amine [(R_P)-24c]: The compound was synthesized from the borane adduct (0.7 mmol) by following the general procedure GP-Syn4 for deprotection of ligands. The product was obtained as a colorless solid, yield 347.2 mg (0.67 mmol, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.52 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 1.64 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 1.80 (d, $^3J_{H,P}$ = 4.9 Hz, 3 H, NCH_3), 4.79 (dq, $^3J_{H,H}$ = 7.0 Hz, $^3J_{H,P}$ = 10.1 Hz, 1 H, CH), 5.01 (dq, $^3J_{H,H}$ = 7.0 Hz, $^3J_{H,P}$ = 11.6 Hz, 1 H, CH), 5.68 (d, $^3J_{H,P}$ = 7.5 Hz, 1 H, CH), 6.85 (m, 1 H, Ar), 6.94 (m, 2 H, Ar), 7.03 (m, 3 H, Ar), 7.12–7.37 (m, 13 H, Ar), 7.67 (m, 2 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 18.6 (d, $J_{C,P}$ = 6.8 Hz, CH_3), 19.8 (d, $J_{C,P}$ = 5.6 Hz, CH_3), 26.2 (NCH_3), 55.5 (d, $J_{C,P}$ = 3.1 Hz, CH), 55.8 (d, $J_{C,P}$ = 44.8 Hz, CH), 57.0 (d, $J_{C,P}$ = 40.9 Hz, CH), 121.1 (d, $J_{C,P}$ = 3.1 Hz, CH, Ar), 121.5 (CH, Ar), 123.5 (CH, Ar),124.3 (d, $J_{C,P}$ = 4.3 Hz, C_q, Ar), 126.0 (CH, Ar), 126.6 (2×CH, Ar), 126.7 (CH, Ar), 127.30 (CH, Ar), 127.36 (CH, Ar), 127.41 (2×CH, Ar), 127.8 (2×CH, Ar), 128.03 (2×CH, Ar), 128.05 (2×CH, Ar), 128.14 (CH, Ar), 128.4 (2×CH, Ar), 128.7 (CH, Ar), 129.3 (C_q, Ar), 130.6 (C_q, Ar), 142.0 (d, $J_{C,P}$ = 3.5 Hz, C_q, Ar), 143.00 (C_q, Ar), 143.08 (C_q, Ar), 143.9 (C_q, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 134.2 ppm. MS (EI): m/z (%) = 518.2 (14), 517.2 (100), 354.2 (34), 279.2 (11), 167.1 (24), 149.1 (43), 113.2. HRMS (ESI): m/z calcd. for $C_{34}H_{34}N_2OP^+$ [M + H$^+$] 517.24033; found 517.24012.

(1*R*,3*R*)-*N*-Methyl-1-phenyl-2-[(*R*)-1-phenylethyl]-*N*-[(*S*)-1-phenyl-ethyl]-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine-3(2*H*)-amine [(R_P)-24d]: The compound was synthesized from the borane adduct (0.7 mmol) by following the general procedure GP-Syn4 for deprotection of ligands. The product was obtained as a colorless solid, yield 318.2 mg (0.62 mmol, 88%). $[\alpha]_D^{25}$ = 121.8 (c = 0.0275, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.46 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 1.69 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 1.74 (d, $^3J_{H,P}$ = 4.4 Hz, 3 H, NCH_3), 4.82 (dq, $^3J_{H,H}$ = 7.0 Hz, $^3J_{H,P}$ = 10.8 Hz, 1 H, CH), 4.99 (dq, $^3J_{H,H}$ = 7.0 Hz, $^3J_{H,P}$ = 11.6 Hz, 1 H, CH), 5.71 (d, $^3J_{H,P}$ = 7.3 Hz, 1 H, CH), 6.87 (m, 1 H, Ar), 6.96 (m, 2 H, Ar), 7.06 (m, 1 H, Ar), 7.11–7.36 (m, 13 H, Ar), 7.39 (m, 2 H, Ar), 7.66 (m, 2 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 18.2 (d, $J_{C,P}$ = 6.0 Hz, CH_3), 20.4 (d, $J_{C,P}$ = 5.8 Hz, CH_3), 26.0 (d, $J_{C,P}$ = 4.2 Hz, NCH_3), 54.9 (d, $J_{C,P}$ = 48.4 Hz, CH), 55.8 (d, $J_{C,P}$ = 2.8 Hz, CH), 57.1 (d, $J_{C,P}$ = 40.5 Hz, CH), 121.2 (d, $J_{C,P}$ = 3.2 Hz, CH, Ar), 121.5 (CH, Ar), 123.5 (CH, Ar),124.3 (d, $J_{C,P}$ = 6.1 Hz, C_q, Ar), 126.0 (CH, Ar), 126.58 (CH, Ar), 126.63 (CH, Ar), 126.65 (CH, Ar), 127.28 (CH, Ar), 127.29 (CH, Ar), 127.41 (CH, Ar), 127.45 (CH, Ar), 127.8 (2×CH, Ar), 128.1 (4×CH, Ar), 128.2 (CH, Ar), 128.5 (2×CH, Ar), 128.7 (CH, Ar), 129.4 (C_q, Ar), 130.6 (C_q, Ar), 142.1 (d, $J_{C,P}$ = 3.4 Hz, C_q, Ar), 142.9 (d, $J_{C,P}$ = 5.7 Hz, C_q, Ar), 144.1 (C_q, Ar), 150.5 (d, $J_{C,P}$ = 3.9 Hz, C_q, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 133.5 ppm. MS (EI): m/z (%) = 279.2 (24), 167.1 (49), 150.1 (12), 149.1 (100), 113.2 (11). HRMS (ESI): m/z calcd. for $C_{34}H_{33}N_2OP^+$ [M$^+$] 516.23250; found 516.23272.

(1*R*,3*S*)-*N*-Methyl-1-phenyl-2-[(*R*)-1-phenylethyl]-*N*-[(*S*)-1-phenyl-ethyl]-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine-3(2*H*)-amine [(S_P)-24d]: The compound was synthesized from the borane adduct (0.45 mmol) by following the general procedure GP-Syn4 for deprotection of ligands. The product was obtained as a colorless solid, yield 200.0 mg (0.39 mmol, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.44 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 1.53 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 1.69 (d, $^3J_{H,P}$ = 3.1 Hz, 3 H, NCH_3), 4.59 (dq, $^3J_{H,H}$ = 7.0 Hz, $^3J_{H,P}$ = 13.3 Hz, 1 H, CH), 4.79 (dq, $^3J_{H,H}$ = 7.0 Hz, $^3J_{H,P}$ = 9.8 Hz, 1 H, CH), 5.92 (s, 1 H, CH), 7.11–7.44 (m, 17 H, Ar), 7.62 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, Ar), 7.65 (d, $^3J_{H,H}$ = 7.1 Hz, 1 H, Ar), 7.70 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, Ar), 7.85 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H, Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 18.2 (d, $J_{C,P}$ = 5.4 Hz, CH_3), 18.8 (d, $J_{C,P}$ = 4.1 Hz, CH_3), 27.8 (d, $J_{C,P}$ = 7.9 Hz, NCH_3), 55.7 (d, $J_{C,P}$ = 43.3 Hz, CH), 56.5 (d, $J_{C,P}$ = 3.6 Hz, CH), 56.6 (d, $J_{C,P}$ = 28.3 Hz, CH), 120.4 (CH, Ar), 121.3 (CH, Ar), 123.6 (CH, Ar), 123.9 (d, $J_{C,P}$ = 7.8 Hz, C_q, Ar), 126.4 (CH, Ar), 126.7 (CH, Ar), 127.0 (CH, Ar), 127.1 (CH, Ar), 127.3 (2×CH, Ar), 127.62 (CH, Ar), 127.64 (CH, Ar), 127.9 (2×CH, Ar), 128.0 (2×CH, Ar), 128.20 (CH, Ar), 128.22 (CH, Ar), 128.3 (2×CH, Ar), 128.7 (CH, Ar), 129.2 (CH, Ar), 129.9 (C_q, Ar), 130.1 (C_q, Ar), 141.6 (d, $J_{C,P}$ = 3.9 Hz, C_q, Ar), 142.7 (d, $J_{C,P}$ = 11.0 Hz, C_q, Ar), 145.2 (C_q, Ar), 147.9 (d, $J_{C,P}$ = 4.2 Hz, C_q, Ar) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 112.1 ppm. MS (EI): m/z (%) = 278.1 (15), 149.1 (14), 121.2 (14), 120.2 (100), 106.2 (10), 105.2 (70). HRMS (ESI): m/z calcd. for $C_{34}H_{33}N_2OP^+$ [M$^+$] 516.23250; found 516.23274.

(1*R*,3*R*)-1-Phenyl-*N*,*N*,2-tris[(*R*)-1-phenylethyl]-1*H*-naphtho[1,2-*e*]-[1,3,2]oxazaphosphinine-3(2*H*)-amine [(R_P)-24e]: The compound was synthesized from the borane adduct (0.7 mmol) by following the general procedure GP-Syn4 for deprotection of ligands. The product was obtained as a colorless solid, yield 420.5 mg (0.69 mmol, 99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.44 (d, $^3J_{H,H}$ = 6.9 Hz, 6 H, CH_3), 1.88 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 4.31 (dq, $^3J_{H,H}$ = 7.0 Hz, $^3J_{H,P}$ = 12.0 Hz, 2 H, CH), 5.02 (dq, $^3J_{H,H}$ = 6.9 Hz, $^3J_{H,P}$ = 12.3 Hz, 1 H, CH), 5.76 (d, $^3J_{H,P}$ = 8.4 Hz, 1 H, CH), 6.78 (m, 1 H, Ar), 6.86 (m, 2 H, Ar), 6.97 (m, 1 H, Ar), 7.00–7.10 (m, 13 H, Ar), 7.16 (m, 2 H, Ar), 7.24 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, Ar), 7.31 (m, 4 H, Ar), 7.62 (m, 2 H, Ar) ppm. ^{13}C{^{1}H} NMR

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(100 MHz, $CDCl_3$): δ = 21.0 (d, $J_{C,P}$ = 5.1 Hz, CH_3), 22.1 (br. CH_3), 22.2 (CH_3), 52.4 (d, $J_{C,P}$ = 11.8 Hz, 2×CH), 56.2 (d, $J_{C,P}$ = 3.0 Hz, CH), 56.4 (d, $J_{C,P}$ = 47.9 Hz, CH), 121.0 (d, $J_{C,P}$ = 3.0 Hz, CH, Ar), 121.2 (CH, Ar), 123.4 (CH, Ar), 125.7 (CH, Ar), 125.9 (2×CH, Ar), 126.0 (d, $J_{C,P}$ = 5.4 Hz, C_q, Ar), 126.5 (CH, Ar), 126.7 (CH, Ar), 127.3 (4×CH, Ar), 127.39 (CH, Ar), 127.45 (CH, Ar), 127.54 (2×CH, Ar), 127.8 (4×CH, Ar), 128.0 (CH, Ar), 128.1 (2×CH, Ar), 128.3 (2×CH, Ar), 128.4 (CH, Ar), 129.3 (C_q, Ar), 130.0 (C_q, Ar), 141.6 (d, $J_{C,P}$ = 2.8 Hz, C_q, Ar), 143.7 (br., 2×C_q, Ar), 143.8 (C_q, Ar), 151.2 (d, $J_{C,P}$ = 1.6 Hz, C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 137.4 ppm. MS (EI): *m*/*z* (%) = 501.5 (19), 278.3 (16), 231.3 (10), 210.4 (39), 200.3 (10), 106.3 (26), 105.3 (100), 79.3 (11), 77.3 (14). HRMS (ESI): *m*/*z* calcd. for $C_{41}H_{40}N_2OP^+$ [M + H^+] 607.28728; found 607.29012.

(1*R*,3*R*)-1-Phenyl-2-[(*R*)-1-phenylethyl]-*N*,*N*-bis[(*S*)-1-phenylethyl]-1*H*-naphtho[1,2-*e*][1,3,2]oxazaphosphinine-3(2*H*)-amine [(R_P)-24f]: The compound was synthesized from the borane adduct (0.7 mmol) by following the general procedure GP-Syn4 for deprotection of ligands. The product was obtained as a colorless solid, yield 412.0 mg (0.68 mmol, 97%). $[\alpha]_D^{25}$ = –218.7 (*c* = 0.5, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.53 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 1.64 (d, $^3J_{H,H}$ = 7.0 Hz, 6 H, CH_3), 4.25 (dq, $^3J_{H,H}$ = 7.0 Hz, $^3J_{H,P}$ = 11.3 Hz, 1 H, CH), 4.37 (dq, $^3J_{H,H}$ = 7.0 Hz, $^3J_{H,P}$ = 11.9 Hz, 2 H, CH), 5.73 (d, $^3J_{H,P}$ = 9.4 Hz, 1 H, CH), 6.76 (m, 1 H, Ar), 6.82 (m, 2 H, Ar), 6.87–7.16 (m, 17 H, Ar), 7.20 (m, 1 H, Ar), 7.25 (m, 3 H, Ar), 7.60 (m, 2 H, Ar) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 20.9 (d, $J_{C,P}$ = 6.0 Hz, CH_3), 22.5 (d, $J_{C,P}$ = 10.4 Hz, 2×CH_3), 52.7 (d, $J_{C,P}$ = 10.9 Hz, 2×CH), 56.23 (d, $J_{C,P}$ = 40.0 Hz, CH), 56.29 (d, $J_{C,P}$ = 2.4 Hz, CH), 121.0 (d, $J_{C,P}$ = 2.4 Hz, CH, Ar), 121.2 (CH, Ar), 123.5 (CH, Ar), 125.8 (CH, Ar), 126.3 (2×CH, Ar), 126.4 (d, $J_{C,P}$ = 5.6 Hz, C_q, Ar), 126.5 (CH, Ar), 126.7 (CH, Ar), 127.33 (CH, Ar), 127.39 (CH, Ar), 127.43 (4×CH, Ar), 127.6 (2×CH, Ar), 128.03 (2×CH, Ar), 128.05 (2×CH, Ar), 128.08 (2×CH, Ar), 128.11 (CH, Ar), 128.58 (CH, Ar), 128.62 (2×CH, Ar), 129.5 (C_q, Ar), 129.9 (C_q, Ar), 142.1 (d, $J_{C,P}$ = 2.0 Hz, C_q, Ar), 143.9 (C_q, Ar), 144.2 (2×C_q, Ar), 151.1 (d, $J_{C,P}$ = 1.8 Hz, C_q, Ar) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 144.8 ppm. MS (EI): *m*/*z* (%) = 279.2 (18), 210.2 (42), 167.1 (34), 149.1 (100), 106.2 (29), 105.2 (44), 86.2 (27). HRMS (ESI): *m*/*z* calcd. for $C_{41}H_{39}N_2OP^+$ [M^+] 606.27945; found 606.27935.

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[34] Since the reaction in THF and with triethylamine as base provided only a small amount of the R_P epimer, other solvents (CH_2Cl_2, toluene) and bases (*n*-butyllithium) were tested. However, no significant differences in the preferred configuration at the phosphorus atom ore side reactions were observed.

[35] The yields reported in the experimental part always refer to the synthetic procedure leading to maximum yield and may not be coincident with the values reported here.

[36] It is important to note that the change in CIP priority from the Cl- to OMe-substituent results in the same stereodescriptor for the phosphorus atom (S_P) although the relative spatial arrangement is inverted.

[37] Here, the N-atom of NPh_2 has a higher CIP priority compared with the N-atom in the Betti base backbone. This leads to a change in the CIP nomenclature of the configuration of the P-atom to (S_P). The relative spatial orientation of the NPh_2 substituent is the same as for the other amine-substituents of the ligands with R_P configuration.

[38] It should be noted that, whereas dichloroaminophosphines can be directly generated from PCl_3 and the corresponding amine, an analogous in situ approach for the synthesis of dichlorophosphite from PCl_3 and an alcohol leads to significant amounts of chlorophosphite and phosphite even by slow alcohol addition and under high dilution. Pure dichlorophosphite are usually synthesized through a two-step procedure from the condensation of, for example, $ClP(NEt_2)_2$ with an alcohol followed by substitution of the amino moieties via anhydrous HCl.

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