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Scope and Limitations of the Aromatic Anionic [1,3] P–O to P–C Rearrangement in the Synthesis of Chiral *o*-Hydroxyaryl Diazaphosphonamides

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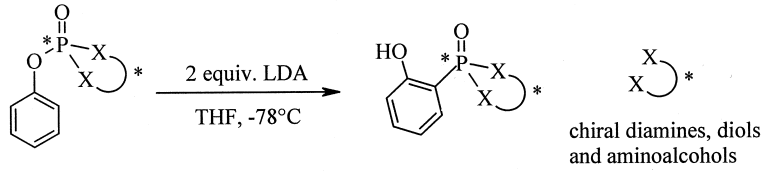
Abstract—The influence of numerous parameters in the aromatic anionic [1,3] P–O to P–C rearrangement in the synthesis of chiral *o*-hydroxyaryl diazaphosphonamides has been envisaged. Various strong bases such as LDA, *sec*-BuLi, *tert*-BuLi have been conveniently used. The scope of the regioselectivity of the rearrangement has been particularly studied varying the nature of the phenoxy group implied in this reaction. A totally diastereoselective P–O to P–C migration rearrangement has been observed starting from a thiophosphonamide precursor. Moreover, starting from a phenylthio substituted phosphonamide, a totally diastereoselective P–S to P–C rearrangement of the diazaphosphonamide moiety has also been demonstrated.

Introduction

In the last five years, numerous studies dealing with the use of non-organometallic phosphorus reagents in enantioselective catalysis have been described.[1] In the context of our work, we have recently reported the synthesis of a new class of chiral bi-functional compounds: the *ortho*-hydroxyarylphosphine oxides, and their successful use as catalysts[2] or ligands[3] in various asymmetric reactions. These compounds were easily obtained from various chiral diols, diamines or aminoalcohols through an original totally stereospecific P–O to P–C rearrangement.[4] An extension of this study has also demonstrated that this reaction is totally diastereoselective and regioselective (Scheme 1).[5,6]



Scheme 1.

In this paper, we will describe the scope and limitations of such a procedure studying more particularly the regio- and diastereoselectivity of the anionic [1,3] P–O to P–C rearrangement depending on the base used and the nature of the substrate.

Results and Discussion

Precursors **1a**–**g** were easily available by exchange reaction at 110°C in toluene between tris(dimethylamino)phosphine **2** and (*S*)-(+)-2-anilinomethylpyrrolidine **3** followed by addition of the desired phenol. Oxidation of crude phosphines **4** by *tert*-butyl hydroperoxide or sulphur afforded the expected compounds **1a**–**h** with chemical yields ranging from 55 to 87% (Scheme 2). Moreover, in all cases nearly only one diastereomer has been obtained and characterized as the thermodynamic *anti* diastereomer[7] (Table 1).

Since the pioneering work reported by Melvin,[8] lithium diisopropylamide (LDA) has appeared to be the best common base used in the rearrangement of arylphosphate into *o*-hydroxyarylphosphonate and related compounds. Only a few reports have mentioned the use of butyllithium

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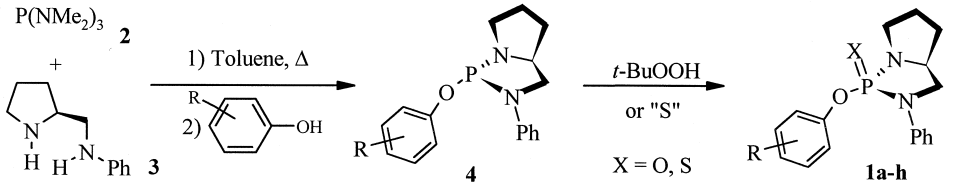
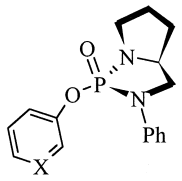
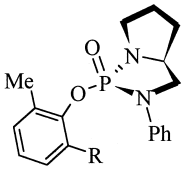
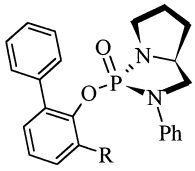
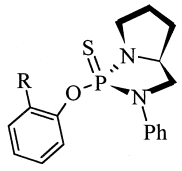


Scheme 2.

Table 1. Synthesis of precursors **1a–h**

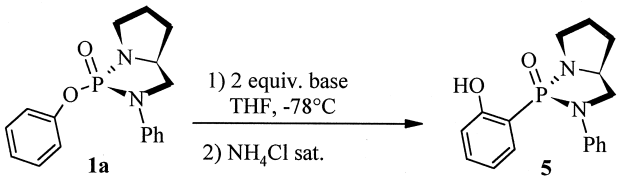
Entry	Product		Diastereomeric ratio (%)[a]	Yield (%)[b]
1		X=C **1a**	100/0	87
		X=N **1b**	100/0	63
2		R=H **1c**	100/0	55
		R=Me **1d**	90/10	55
3		R=H **1e**	95/5	70
		R=$SiEt_3$ **1f**	90/10	63
4		R=H **1g**	100/0	78
		R=Br **1h**	100/0	69

[a] Diastereomeric ratio determined by ^{31}P NMR spectroscopy.
[b] Isolated yield after column chromatography of *anti* diastereomer.

in such a reaction but a lower selectivity has been generally encountered. To our knowledge, neither study has been achieved dealing with the influence of the nature of the strong base used on the chemo- and stereoselectivity of the P–O to P–C migration rearrangement. The results of our investigations are summarized in Table 2 (Scheme 3).

Various amide bases have been tested in the rearrangement but whatever the experimental conditions applied, only LDA led to the expected product in excellent yields and with total diastereoselectivity. Moreover, in this case, it clearly appears that the amount of LDA used has dramatic effects on the outcome of the reaction (entries 1 and 2). The best results were obtained using 2 equiv. of LDA with respect to the precursor at −78°C (entry 1, 92% yield, 100% e.d.). On the other hand, the use of LHMDS or LTMP led to low results in terms of conversion, respectively, 0 and 11% (entries 3 and 4). The use of alkyllithium base has been also studied. Thus, the use of *n*-butyllithium or *n*-BuLi/TMEDA complex did not afford **5** and in these cases, only a product resulting from nucleophilic attack of the phosphorus atom by the base has been isolated in low yields (entries 5 and 6). Bulkier alkyllithium bases such as *sec*-BuLi or *tert*-BuLi led to the anionic [1,3] rearrangement product in a totally diastereoselective manner in high chemical yields (entries 7 and 8). Although these results are quite similar to those obtained with LDA, we will use this latter in the following parts.

The second part of our study deals with the regioselectivity of P–O to P–C migration rearrangement depending on the nature of the substrate considered. In this area, we have



Scheme 3.

Table 2. Influence of the nature of the base on the P–O to P–C migration rearrangement

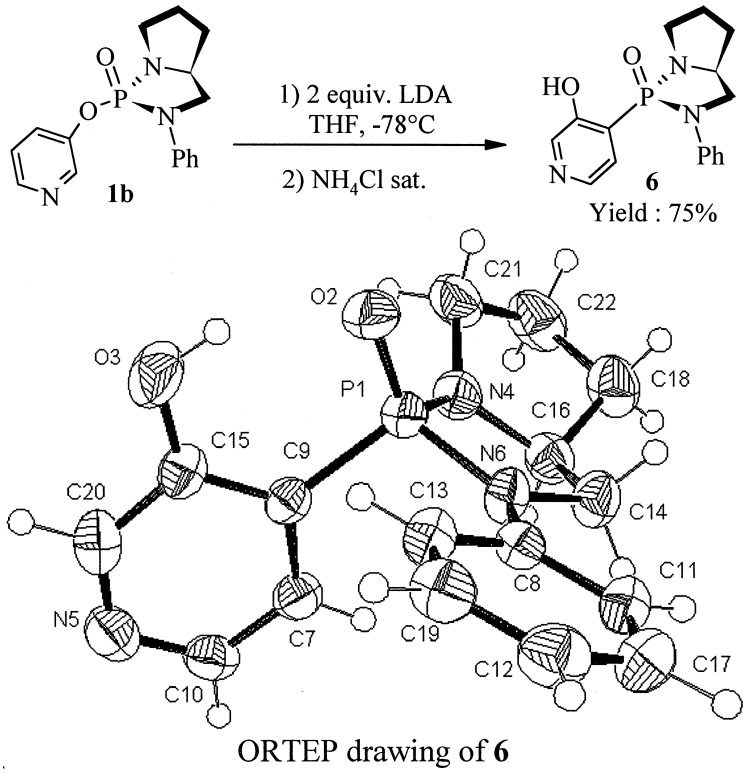
Entry	Strong base	Yield (conversion) (%)[a]	Diastereo-selectivity (%)[b]
1	LDA	92 (100)	100
2	LDA[c]	44 (50)	100
3	LHMDS[d]	0 (0)	–
4	LTMP[e]	11 (15)	100
5	*n*-BuLi	0 (10)	–
6	*n*-BuLi/TMEDA[f]	0 (6)	–
7	*sec*-BuLi	91 (100)	100
8	*tert*-BuLi	93 (100)	100

[a] Isolated yield after column chromatography.
[b] Diastereomeric ratio determined by ^{31}P NMR spectroscopy.
[c] One equivalent of LDA was used.
[d] LHMDS: lithium hexamethyldisilazane.
[e] LTMP: lithium tetramethylpiperidine.
[f] TMEDA: tetramethylethylenediamine.

recently clearly demonstrated the total regioselectivity of this process in the case of precursors bearing a substituent on the *para* or *meta* position of the phenoxy group.[5] Moreover, starting from precursors possessing a non-symmetrical substituted aromatic ring, the structure of the regiomer obtained is controlled by electronic or steric effects of the substituent. Thus, in order to generalize our assumptions, we have examined the regio- and stereoselectivity of the rearrangement of precursors possessing a heteroaromatic ring such as compound **1b**. The rearrangement of precursor **1b** was achieved using the standard conditions (2 equiv. LDA, THF, −78°C) and led to the expected product **6** in 75% yield. ^{31}P NMR analysis of the crude product demonstrates that only one isomer has been formed and the structure of **6** has been unambiguously determined by X-ray diffraction analysis (Scheme 4).[9]

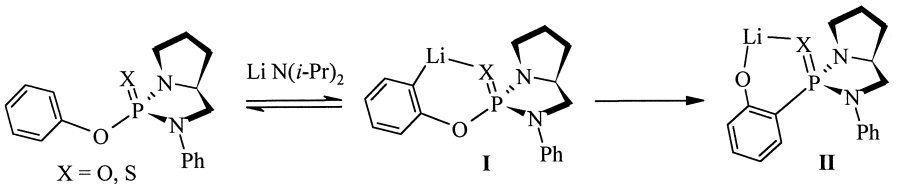
In this case, the relative configuration at the phosphorus atom is seen to be retained during the rearrangement implying that the steric course of the [1,3] migration from O to C of the chiral phosphorus atom is homofacial.[10] The phenyl ring (C8–C11) is almost coplanar with the atoms N6, P1, C14 and the bond distance N6–C8 is short (1.416 Å) suggesting an interaction between the lone pair of the nitrogen atom and the aromatic system. Moreover, there is evidently a strong hydrogen bond between the hydroxy group and the oxygen atom attached to the phosphorus moiety.

Diazaphospholidine oxide group has appeared to be an excellent activator for the direct metallation of the *ortho* position in an aromatic system. The efficiency of the phosphoryl group as DMG (Directed Metallation Group) could be due to the formation of a six-membered ring involving a coordination of lithium atom by the P=O group as outlined in **I** (Scheme 5). The driving force of

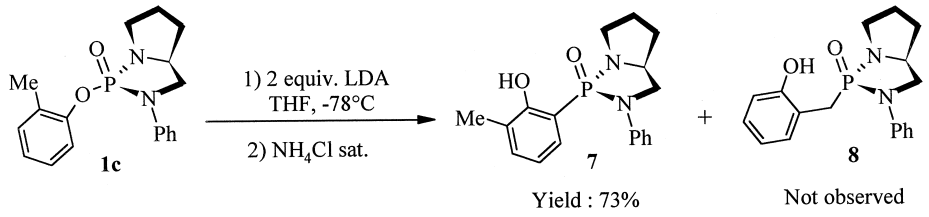


ORTEP drawing of **6**

Scheme 4. Bond length (Å): P1–O2, 1.481(1); P1–N4, 1.621(1); P1–N6, 1.669(1); P1–C9, 1.796(1); O3–C15, 1.348(2); N6–C8, 1.416(1). Angles (°): O2–P1–N4, 107.5(1); O2–P1–N6, 118.8(1); O2–P1–C9, 117.8(1); N4–P1–N6, 94.9(1); N4–P1–C9, 110.5(1); N6–P1–C9, 106.5(1); P1–N4–C21, 127.7(1); P1–N4–C16, 114.2(1); C16–N4–C21, 111.9(1); C8–N6–C14, 120.4(2); P1–N6–C8, 125.3(2); P1–N6–C14, 113.3(1).



Scheme 5.



Scheme 6.

the anionic [1,3] rearrangement could be the formation of the stable chelate complex **II** in which both oxygen atoms could interact with the lithium atom.

Nevertheless, possible competition between the lithiation of the *ortho* position of an aromatic ring and another position by formation of a seven or eight lithiated membered ring may be envisaged. With this purpose, we aim to achieve the rearrangement of various precursors bearing a methyl or a phenyl group on the *ortho* position of the aromatic ring.

Thus, treatment of precursor **1c** with 2 equiv. of LDA has been achieved (Scheme 6). In this case, only the formation of *o*-hydroxyaryl diazaphospholidine oxide **7** resulting from an anionic [1,3] rearrangement in 73% yield has been encountered and no trace of product **8** resulting from a [1,4] migration of the phosphoryl group on the benzylic position has been observed.

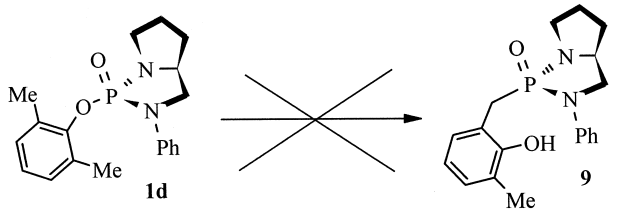
Moreover, starting from precursor **1d**, any products resulting from a migration of the phosphoryl group have not been encountered (Scheme 7). The use of bases such as alkyllithium afforded only by-products resulting from nucleophilic attack of the base at the phosphorus atom.

In order to explain these results, numerous attempts have been achieved to demonstrate the formation or not of a carbanion on the benzylic position. Thus, treatment of these precursors with strong bases such as *n*-BuLi, *tert*-BuLi and subsequent addition of various electrophiles did not lead to the formation of the expected substituted products. These results tend to probe the considerable degree of stabilization of the organolithium six-membered ring intermediate with respect to the other seven-membered ring.

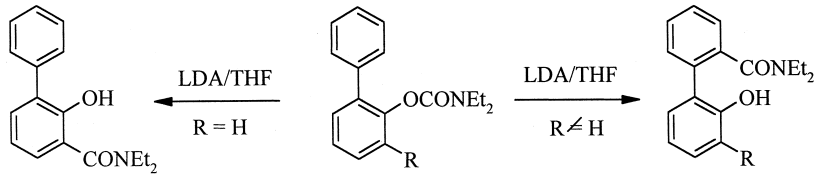
In the same area, Snieckus has demonstrated that in the presence of a phenyl substituent on the *ortho* position of the aromatic ring, an amide group can be transferred on the 2′ position of the biaryl system[11] (Scheme 8).

On the basis of these results, we have envisaged this strategy in the presence of the chiral diazaphospholidine group. Although precursor **1e** led as expected to the anionic [1,3] rearrangement product **10** clearly characterized by X-ray diffraction analysis[12] in 82% yield, any product resulting from a migration of the phosphoryl group on the 2′ position has been observed from the silylated compound **1f**. Moreover, subsequent addition of various electrophiles did not lead to a product resulting from lithiation of the 2′ position. These elements seem to indicate that the diazaphospholidine oxide group could not favour a complex-induced proximity effect (CIPE)[13] (Scheme 9).

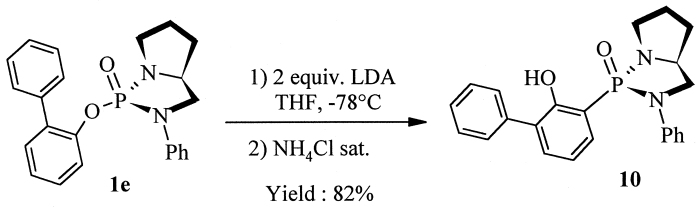
In the field of applications of phosphorus compounds such as P-DMG, few studies have concerned the anionic [1,3]

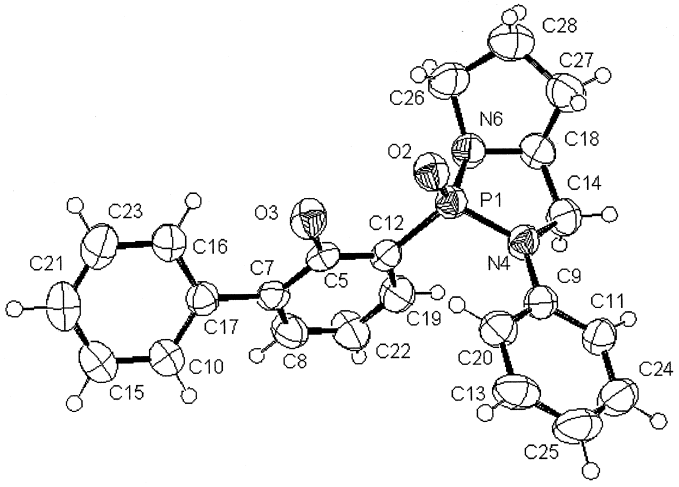


Scheme 7.



Scheme 8.





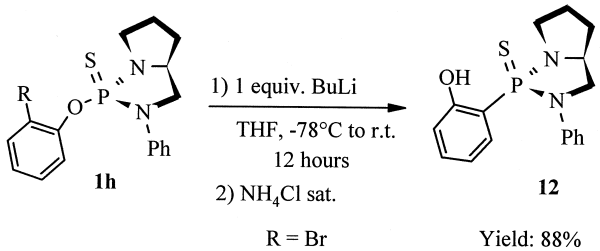
ORTEP drawing of **10**

Scheme 9. Bond length (Å): P1–O2, 1.487(3); P1–N4, 1.660(3); P1–N6, 1.660(2); P1–C12, 1.785(3); O3–C5, 1.367(4). Angles (°): O2–P1–N4, 116.9(2); O2–P1–N6, 117.4(2); O2–P1–C12, 107.7(3); N4–P1–N6, 94.6(2); N4–P1–C12, 110.2(2); N6–P1–C12, 109.5(3); P1–N4–C14, 113.3(3); P1–N4–C9, 125.2(3); C9–N4–C14, 120.7(3); C18–N6–C26, 106.7(3); P1–N6–C26, 118.1(3); P1–N6–C18, 111.8(3).

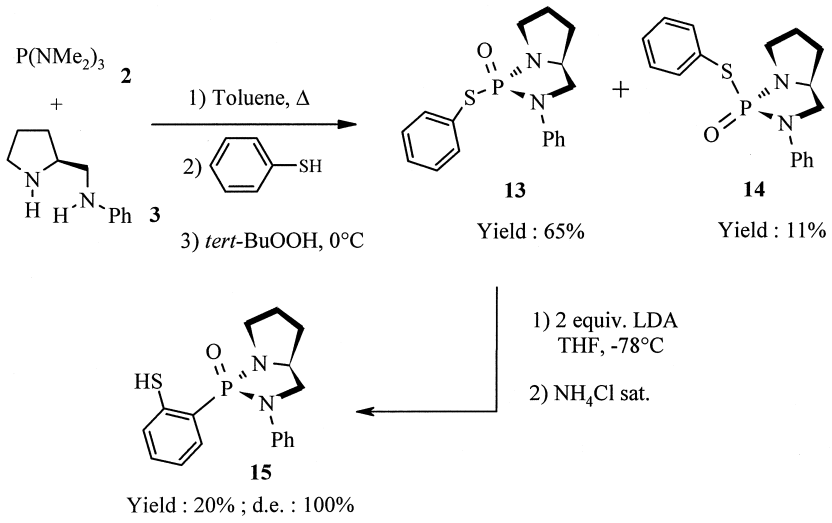
rearrangement of P=S derivatives.[14] Due to the weaker complexation of lithium atom by P=S group by comparison with P=O group, the DoM (Directed *ortho* Metallation) reactions are less favoured in these cases. Thus, we have investigated the possibility of realizing such a rearrangement using a precursor bearing a chiral diazaphospholidine moiety and a P=S function. Treatment of **1g** with 2 equiv. of LDA or other strong bases, did not lead to the expected product **12** whatever the conditions used. Presumably, due to the presence of the P=S moiety, the *ortho*-lithiated intermediate is not sufficiently stabilized to lead to the product of rearrangement **12**. In order to favour its formation, the parent compound **1h** has been prepared and treated with BuLi (1 equiv., THF, −78°C to RT, 12 h) leading to the metallation of the C–Br bond (Scheme 10).

The desired product of rearrangement **12** has been obtained in 88% yield and, as already observed for the O=P–O to O=P–C migration, *this rearrangement proceeds by a totally diastereoselective reaction at the phosphorus atom*.

As an extension of this study, Masson et al. have recently described a P–S to P–C migration rearrangement to prepare *ortho*-thiohydroxyarylphosphonates.[15] Watanabe et al. have also prepared various *ortho*-thiohydroxyarylphosphonamides involving a rearrangement of the corresponding thioarylester.[16] Despite these works, no studies have been devoted to the diastereoselective P–S to P–C migration rearrangement. Thus, we have considered the rearrangement of the



Scheme 10.



Scheme 11.

diastereoisomerically pure precursor **13** easily obtained from an exchange reaction between phosphine **2**, diamine **3** and thiophenol, followed by a subsequent oxidation by *tert*-BuOOH. A mixture of the two diastereomers **13** and **14** has been obtained and separated by column chromatography in, respectively, 65 and 11% yield (Scheme 11).

Under the standard conditions (2 equiv. LDA, THF, −78°C), treatment of precursor **13** led to the expected *o*-thioaryl diazaphospholidine oxide **15** in only 20% yield. It is noteworthy that ^{31}P NMR analysis of the crude product indicates the presence of numerous by-products, but no trace of the other epimer at the phosphorus atom has been detected. Nevertheless, as already observed for the P–O to P–C rearrangement, *this migration proceeds with total retention of configuration at the phosphorus atom*.

Conclusion

The influence of numerous parameters in the aromatic anionic [1,3] P–O to P–C rearrangement in the synthesis of chiral *o*-hydroxyaryl diazaphosphonamides has been examined. The regioselectivity of the rearrangement has been particularly studied varying the nature of the phenoxy group implied in this reaction. A total diastereoselective P–O to P–C migration rearrangement has been observed starting from a thiophosphonamide precursor. Although a diastereoselective P–S to P–C migration rearrangement of the diazaphosphonamide moiety as P-DoM group has been also demonstrated, it has been established that this latter is less effective with respect to P–O to P–C rearrangement. Further studies implying these new compounds as chiral ligands or catalysts in asymmetric reactions are under current investigation.

Experimental

Tetrahydrofuran (THF) and toluene were distilled from sodium/benzophenone ketyl immediately prior to use. Ethylacetate and petroleum ether (35–60°C) were purchased from SDS and used without any further purification. Column chromatography was performed on SDS silica gel (70–230 mesh). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution at 200.00 MHz and 50.30 MHz on a Bruker AC200 instrument, ^{31}P NMR spectra were recorded in $CDCl_3$ solution at 40.50 MHz on a Bruker AC100 (the usual abbreviations are used: s=singlet, d=doublet, t=triplet, q=quadruplet, m=multiplet). The positive chemical shift values are given in ppm, the coupling constants in Hertz. Specific rotations were determined with a Perkin Elmer Polarimeter 341. Elemental analyses were performed by the 'Service de Microanalyse de la Faculté des Sciences de St Jérôme (Marseille)'. X-Ray diffraction analyses were performed at the 'Service de Cristallographie de la Faculté des Sciences de St Jérôme (Marseille)'.

General procedure for the synthesis of precursors 1b–h

In a two-necked round flask an equimolar mixture of tris(dimethylamino)phosphine **2** (5 mmol, 0.82 g) and (*S*)-(+)-2-anilinomethylpyrrolidine **3** (5 mmol, 0.88 g) were placed in dry toluene (10 mL) under argon atmosphere and warmed at 110°C for 3 h. Then 1 equiv. of desired phenol was added at room temperature and the mixture was warmed at 110°C for 1 h. The mixture was allowed to cool to room temperature and the toluene was removed in vacuo. The crude phosphine was diluted with dichloromethane (15 mL) and the mixture cooled to 0°C. *tert*-Butyl hydroperoxide 0.9 mL (5.5 M, decane) (in the case of precursors **1g**–**h**, sulphur, 0.2 g (6.2 mmol)), was slowly added and the mixture was stirred for 3 h. After removing the solvent in vacuo, the crude product was purified by column chromatography or crystallization.

(2*R*,5*S*)-2-(3-Pyridinoxy)-3-phenyl-1,3-diaza-2-phosphabicyclo-[3.3.0]-octane 2-oxide 1b. Purification by crystallization (mixture of ethyl acetate and petroleum ether) afforded **1b** as a white solid in 63% yield. Mp: 126°C; $[\alpha]_D^{20}=-76.6$ (c=0.15, CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.63–1.74 (m, 1H), 1.87–2.06 (m, 3H), 3.04–3.15 (m, 1H), 3.26–3.35 (m, 1H), 3.47–3.61 (m, 2H),

3.76–3.87 (m, 1H), 7.00 (t, $^3J_{HH}$=7.2 Hz, 1H), 7.11–7.37 (m, 6H), 8.34 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ=26.1 (d, $^3J_{PC}$= 3.1 Hz), 32.5 (d, $^3J_{PC}$=2.6 Hz), 46.8 (d, $^3J_{PC}$= 2.6 Hz), 49.7 (d, $^2J_{PC}$=17.9 Hz), 57.1 (d, $^2J_{PC}$=10.2 Hz), 116.3 (d, $^3J_{PC}$= 4.6 Hz, 2C), 122.0 (s), 124.0 (s), 128.5 (d, $^3J_{PC}$=3.5 Hz), 129.5 (s, 2C), 140.8 (d, $^2J_{PC}$=5.0 Hz), 143.4 (d, $^3J_{PC}$=4.4 Hz), 146.0 (s), 148.0 (d, $^2J_{PC}$=9.7 Hz); ^{31}P NMR (40.5 MHz, $CDCl_3$) δ=16.8. $C_{16}H_{18}N_3O_2P$ (315.23): calcd. C 60.95, H 5.75, N 13.33, P 9.82; found C 60.89, H 5.72, N 13.44, P 9.78.

(2*R*,5*S*)-2-(2-Methylphenoxy)-3-phenyl-1,3-diaza-2-phosphabicyclo-[3.3.0]-octane 2-oxide 1c. Purification by column chromatography (silica gel; ethylacetate/petroleum ether 75:25) afforded **1c** as a white solid in 55% yield. Mp: 128°C; $[\alpha]_D^{25}$=−24 (*c*=0.2, CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.66–2.06 (m, 4H), 2.22 (s, 3H), 3.02–3.11 (m, 1H), 3.31–3.35 (m, 1H), 3.55–3.66 (m, 2H), 3.82–3.87 (m, 1H), 6.69–7.21 (m, 5H), 7.22–7.37 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ=16.4 (s), 26.0 (d, $^3J_{PC}$=3.8 Hz), 32.4 (d, $^3J_{PC}$=2.7 Hz), 46.7 (d, $^2J_{PC}$=2.6 Hz), 49.7 (d, $^2J_{PC}$= 17.6 Hz), 56.9 (d, $^2J_{PC}$=10.1 Hz), 116.3 (d, $^3J_{PC}$=4.3 Hz, 2C), 120.3 (d, $^3J_{PC}$=2.5 Hz), 121.5 (s), 124.6 (s), 126.7 (s), 129.3 (s, 2C), 130.3 (d, $^3J_{PC}$=4.4 Hz), 131.1 (s), 141.2 (d, $^2J_{PC}$=5.7 Hz), 149.6 (d, $^2J_{PC}$=9.0 Hz); ^{31}P NMR (40.5 MHz) δ=15.6. $C_{18}H_{21}N_2O_2P$ (328.13): calcd. C 65.84, H 6.45, N 8.53, P 9.43; found C 65.89, H 6.72, N 8.33, P 9.48.

(2*R*,5*S*)-2-(2,6-Dimethylphenoxy)-3-phenyl-1,3-diaza-2-phosphabicyclo-[3.3.0]-octane 2-oxide 1d. Purification by column chromatography (silica gel; ethylacetate/petroleum ether 80:20) afforded **1d** as a white solid in 55% yield (product obtained as a mixture of two diastereomers 90/10). ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.68–2.12 (m, 4H), 2.24 (s, 6H), 2.89–3.07 (m, 1H), 3.35–3.41 (m, 1H), 3.68–3.85 (m, 3H), 6.89–7.34 (m, 8H); ^{13}C NMR (50 MHz, $CDCl_3$) δ=17.4 (s, 2C), 26.0 (d, $^3J_{PC}$=4.2 Hz), 32.4 (s), 47.3 (d, $^2J_{PC}$=2.6 Hz), 49.9 (d, $^2J_{PC}$=18.8 Hz), 56.8 (d, $^2J_{PC}$=10.2 Hz), 117.2 (d, $^3J_{PC}$=4.3 Hz, 2C), 121.9 (s), 124.6 (s), 129.0 (s, 2C), 129.2 (s, 2C), 130.3 (d, $^3J_{PC}$=3.0 Hz, 2C), 141.2 (d, $^2J_{PC}$=5.7 Hz), 149.6 (d, $^2J_{PC}$=9.0 Hz); ^{31}P NMR (40.5 MHz, $CDCl_3$) δ=17.2 (*anti*) and 9.4 (*syn*). $C_{19}H_{23}N_2O_2P$ (342.13): calcd. C 66.65, H 6.77, N 8.18, P 9.05; found C 66.89, H 6.72, N 8.33, P 9.18.

(2*R*,5*S*)-2-(2-Phenylphenoxy)-3-phenyl-1,3-diaza-2-phosphabicyclo-[3.3.0]-octane 2-oxide 1e. Purification by column chromatography (silica gel; ethylacetate/petroleum ether 67:33) afforded **1e** as a white solid in 70% yield (product obtained as a mixture of two diastereomers 95/5). ^{1}H NMR (200 MHz) δ=1.44–1.90 (m, 4H), 2.15–2.29 (m, 1H), 3.08–3.40 (m, 4H), 6.98 (t, $^3J_{HH}$=7.2 Hz, 1H), 7.12–7.38 (m, 12H), 7.62 (dd, $^3J_{HH}$=8.0 Hz, $^4J_{HH}$=1.4 Hz, 2H); ^{13}C NMR (50 MHz) *δ*=26.0 (d, $^3J_{PC}$=4.3 Hz), 30.5 (d, $^3J_{PC}$=2.8 Hz), 45.5 (d, $^2J_{PC}$=2.8 Hz), 49.5 (d, $^2J_{PC}$= 17.4 Hz), 56.5 (d, $^2J_{PC}$=11.3 Hz), 116.1 (d, $^3J_{PC}$=4.3 Hz, 2C), 121.4 (s), 122.1 (d, $^3J_{PC}$=2.8 Hz), 125.3 (s), 127.0 (s), 127.9 (s), 128.2 (s, 2C), 128.4 (s), 128.9 (s), 129.3 (s, 2C), 130.9 (s), 134.8 (d, $^3J_{PC}$=4.4 Hz), 138.1 (s), 141.3 (d, $^2J_{PC}$=5.8 Hz), 148.0 (d, $^2J_{PC}$=8.9 Hz); ^{31}P NMR (40.5 MHz, $CDCl_3$) δ=16.8 (*anti*) and 11.1 (*syn*). $C_{23}H_{23}N_2O_2P$ (390.15): calcd. C 70.76, H 5.94, N 7.18, P 7.93; found C 70.95, H 6.02, N 7.25, P 7.98.

(2*R*,5*S*)-2-(2-Phenyl-6-triethylsilylphenoxy)-3-phenyl-1,3-diaza-2-phosphabicyclo-[3.3.0]-octane 2-oxide 1f. Purification by column chromatography (silica gel; ethylacetate/petroleum ether 67:33) afforded **1f** as a white solid in 70% yield (product obtained as a mixture of two diastereomers 90/10). ^{1}H NMR (200 MHz) δ=0.78–0.95 (m, 15H), 1.44–1.90 (m, 4H), 2.15–2.29 (m, 1H), 3.08–3.40 (m, 4H), 6.98 (t, $^3J_{HH}$=7.2 Hz, 1H), 7.12–7.38 (m, 11H), 7.62 (dd, $^3J_{HH}$=8.0 Hz, $^4J_{HH}$=1.4 Hz, 2H); ^{13}C NMR (50 MHz) δ=5.6 (s, 3C), 7.7 (s, 3C), 26.1 (d, $^3J_{PC}$= 4.5 Hz), 30.4 (d, $^3J_{PC}$=2.7 Hz), 45.3 (d, $^2J_{PC}$=2.7 Hz), 49.3 (d, $^2J_{PC}$=16.9 Hz), 56.2 (d, $^2J_{PC}$=11.1 Hz), 116.1 (d, $^3J_{PC}$=4.4 Hz, 2C), 121.3 (s), 122.6 (d, $^3J_{PC}$=2.5 Hz), 125.4 (s), 126.8 (s), 127.8 (s), 128.0 (s, 2C), 128.4 (s), 129.0 (s), 129.4 (s, 2C), 130.7 (s), 134.8 (d, $^3J_{PC}$=4.4 Hz), 138.1 (s), 141.2 (d, $^2J_{PC}$=5.5), 148.2 (d, $^2J_{PC}$=9.1 Hz); ^{31}P NMR (40.5 MHz) δ=16.7 (*anti*) and 11.0 (*syn*). $C_{29}H_{37}N_2O_2PSi$ (504.68): calcd. C 69.02, H 7.39, N 5.55, P 6.14, Si 5.57; found C 68.95, H 7.22, N 5.45, P 6.12, Si 5.48.

(2*R*,5*S*)-2-Phenoxy-3-phenyl-1,3-diazaphosphabicyclo-[3.3.0]-octane 2-thioxide 1g. Purification by column chromatography (silica gel; ethylacetate/petroleum ether 25:75) afforded **1g** as a white solid in 78% yield. Mp: 122°C; $[\alpha]_D^{25}$=−8.3 (*c*=1, CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.48–1.62 (m, 1H), 1.73–2.00 (m, 3H), 2.91–3.09 (m, 1H), 3.13–3.31 (m, 1H), 3.41–3.56 (m, 2H), 3.80–3.97 (m, 1H), 6.93–7.36 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$) δ=26.1 (d, $^3J_{PC}$=4.8 Hz), 31.8 (d, $^3J_{PC}$=3.9 Hz), 47.4 (d, $^2J_{PC}$=6.1 Hz), 52.4 (d, $^2J_{PC}$=13.3 Hz), 58.7 (d, $^2J_{PC}$= 6.2 Hz), 117.0 (d, $^3J_{PC}$=4.3 Hz, 2C), 121.6 (s), 121.8 (d, $^3J_{PC}$=8.8 Hz, 2C), 125.0 (s), 129.1 (s, 2C), 129.3 (s, 2C), 141.3 (d, $^2J_{PC}$=7.2 Hz), 151.3 (d, $^2J_{PC}$=12.8 Hz); ^{31}P NMR (40.5 MHz, $CDCl_3$) δ=71.5. $C_{17}H_{19}N_2OPS$ (330.10): calcd. C 61.80, H 5.80, N 8.48, P 9.38, S 9.71; found C 61.50, H 5.80, N 8.42, P 9.42, S 9.68.

(2*R*,5*S*)-2-(2-Bromophenoxy)-3-phenyl-1,3-diazaphosphabicyclo-[3.3.0]-octane 2-thioxide 1h. Purification by column chromatography (silica gel; ethylacetate/petroleum ether 25:75) afforded **1h** as a pale yellow solid in 69% yield. Mp: 88°C; $[\alpha]_D^{25}$=−9.2 (*c*=0.6, CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.67–1.78 (m, 1H), 1.86–2.07 (m, 3H), 3.11–3.22 (m, 1H), 3.36–3.44 (m, 1H), 3.63–3.83 (m, 2H), 3.94–4.05 (m, 1H), 7.06–7.51 (m, 8H), 7.62 (d, $^3J_{HH}$=7.9 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ=26.1 (d, $^3J_{PC}$=5.4 Hz), 31.8 (d, $^3J_{PC}$=3.2 Hz), 47.8 (d, $^2J_{PC}$=6.7 Hz), 52.6 (d, $^2J_{PC}$=14.0 Hz), 58.7 (d, $^2J_{PC}$=7.2 Hz), 116.8 (d, $^3J_{PC}$=5.7 Hz), 117.5 (d, $^3J_{PC}$=5.6 Hz, 2C), 121.9 (s), 122.6 (d, $^3J_{PC}$=4.2 Hz), 126.1 (s), 128.2 (s), 129.1 (s, 2C), 133.6 (s), 141.1 (d, $^2J_{PC}$=6.0 Hz), 148.9 (d, $^2J_{PC}$=11.6 Hz); ^{31}P NMR (40.5 MHz, $CDCl_3$) δ=71.7. $C_{17}H_{18}N_2OPSBr$ (408.04): calcd. C 49.89, H 4.43, N 6.84, P 7.57, S 7.83, Br 19.52; found C 50.95, H 4.52, N 6.78, P 7.63, S 7.78, Br 20.01.

General procedure for the anionic [1,3] rearrangement

To a stirred solution of the corresponding compounds **1a**–**h** (2.5 mmol) in dry THF (25 mL) under argon atmosphere was slowly added at −78°C a solution of LDA (5 mmol, 2 M in THF, 2.5 mL). The mixture was allowed to warm to room temperature and quenched by addition of a saturated solution of NH_4Cl (20 mL). The product was extracted with

ethylacetate (3×10 mL). The combined organic phases were dried over $MgSO_4$, filtered and evaporated under reduced pressure. The residue was purified by chromatography or crystallization.

(2*S*,5*S*)-2-(2-Hydroxy-4-pyridinyl)-3-phenyl-1,3-diaza-2-phosphabicyclo-[3.3.0]-octane 2-oxide 6. Purification by crystallization in diethylether afforded **6** as a pale yellow solid in 75% yield. Mp: 176°C; $[\alpha]_D^{25}=+43.6$ (c=0.28, CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.74–1.87 (m, 1H), 1.94–2.23 (m, 3H), 2.95–3.04 (m, 1H), 3.53–3.60 (m, 1H), 3.68–3.79 (m, 1H), 3.91–4.11 (m, 2H), 6.90 (t, $^3J_{HH}$=7.6 Hz, 1H), 6.96 (d, $^3J_{HH}$=7.5 Hz, 2H), 6.96–7.20 (m, 1H), 7.21 (dd, $^3J_{HH}$=7.6 Hz, $^3J_{HH}$=7.5 Hz, 2H), 8.03 (dd, $^3J_{HH}$=4.8 Hz, $^3J_{PH}$=4.2 Hz, 1H), 8.37 (d, $^3J_{PH}$= 7.4 Hz, 1H), 10.92 (s, OH); ^{13}C NMR (50 MHz, $CDCl_3$) δ=26.7 (d, $^3J_{PC}$=2.5 Hz), 32.3 (s), 44.6 (s), 49.7 (d, $^2J_{PC}$= 14.4 Hz), 60.1 (d, $^2J_{PC}$=5.8 Hz), 116.7 (d, $^3J_{PC}$=4.6 Hz), 120.7 (d, $^1J_{PC}$=159.6 Hz), 122.6(s), 123.8 (d, $^2J_{PC}$= 5.8 Hz), 129.5 (s, 2C), 140.1 (d, $^3J_{PC}$=11.6 Hz), 140.5 (d, $^2J_{PC}$=5.4 Hz), 141.5 (d, $^3J_{PC}$=9.1 Hz), 157.6 (d, $^2J_{PC}$=5.4 Hz); ^{31}P NMR (40.5 MHz, $CDCl_3$) δ=30.0. $C_{16}H_{18}N_3O_2P$ (315.23): calcd. C 60.95, H 5.75, N 13.33, P 9.82; found C 60.92, H 5.82, N 13.44, P 9.88.

(2*S*,5*S*)-2-(2-Hydroxy-3-methylphenyl)-3-phenyl-1,3-diaza-2-phosphabicyclo-[3.3.0]-octane 2-oxide 7. Purification by column chromatography (silica gel; ethylacetate/petroleum ether 80:20) afforded **7** as a white solid in 70% yield. Mp: 202°C; $[\alpha]_D^{25}=+37.7$ (c=1.34, CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.73–2.23 (m, 4H), 2.15 (s, 3H), 2.93–3.03 (m, 1H), 3.54–3.61 (m, 1H), 3.71–3.79 (m, 1H), 3.88–4.08 (m, 2H), 6.67 (ddd, $^3J_{HH}$=7.6 Hz, $^3J_{HH}$= 7.4 Hz, $^4J_{PH}$=3.4 Hz, 1H), 6.89 (t, $^3J_{HH}$=7.2 Hz, 1H), 6.98 (d, $^3J_{HH}$=8.4 Hz, 2H), 7.06 (d, $^3J_{HH}$=7.6 Hz, 1H), 7.18 (dd, $^3J_{HH}$=8.4 Hz, $^3J_{HH}$=7.2 Hz, 2H), 7.15–7.26 (m, 1H), 11.26 (s, OH); ^{13}C NMR (50 MHz, $CDCl_3$) δ=16.2 (s, CH_3), 26.7 (s), 32.3 (s), 44.6 (s), 49.7 (d, $^2J_{PC}$=13.3 Hz), 60.0 (d, $^2J_{PC}$= 5.9 Hz), 112.2 (d, $^1J_{PC}$=162.9 Hz), 116.5 (d, $^3J_{PC}$=5.4 Hz, 2C), 118.9 (d, $^3J_{PC}$=14.9 Hz), 121.8 (s), 126.6 (d, $^3J_{PC}$= 11.4 Hz), 128.9 (d, $^2J_{PC}$=7.3 Hz), 129.3 (s, 2C), 135.1 (d, $^4J_{PC}$=2.6 Hz), 141.2 (d, $^2J_{PC}$=6.9 Hz), 161.1 (d, $^2J_{PC}$= 7.2 Hz); ^{31}P NMR (40.5 MHz, $CDCl_3$) δ=33.9. $C_{18}H_{21}N_2O_2P$ (328.13): calcd. C 65.84, H 6.45, N 8.53, P 9.43; found C 65.79, H 6.72, N 8.43, P 9.50.

(2*S*,5*S*)-2-(2-Hydroxy-3-biphenyl)-3-phenyl-1,3-diaza-2-phosphabicyclo-[3.3.0]-octane 2-oxide 10. Purification by column chromatography (silica gel; ethylacetate/petroleum ether 50:50) afforded **10** as a white solid in 82% yield. Mp: 152°C; $[\alpha]_D^{20}=+237$ (c=0.18, CH_2Cl_2); ^{1}H NMR (200 MHz) δ=1.80–2.20 (m, 4H), 3.00–3.05 (m, 1H), 3.58–3.65 (m, 1H), 3.77–3.85 (m, 1H), 3.94–4.15 (m, 2H), 6.81–6.93 (m, 2H), 7.06 (d, J=8.2 Hz, 2H), 7.14–7.26 (m, 3H), 7.35–7.49 (m, 4H), 7.62 (ddd, $^3J_{HH}$=8.4 Hz, $^4J_{HH}$=2.0 Hz, $^4J_{HH}$=1.6 Hz, 2H), 11.55 (s, OH); ^{13}C NMR (50 MHz) δ=26.7 (d, $^3J_{PC}$=2.3 Hz), 32.4 (s), 44.7 (d, $^2J_{PC}$= 2.2 Hz), 49.7 (d, $^2J_{PC}$=13.4 Hz), 60.0 (d, $^3J_{PC}$=5.6 Hz), 113.3 (d, $^1J_{PC}$=162.3 Hz), 116.6 (d, $^3J_{PC}$=4.7 Hz, 2C), 119.4 (d, $^3J_{PC}$=14.6 Hz), 121.9 (s), 127.2 (s), 128.1 (s, 2C),129.4 (s, 2C) 129.5 (s, 2C), 130.3 (d, $^3J_{PC}$=11.5 Hz), 130.8 (d, $^2J_{PC}$=7.3 Hz), 135.3 (d, $^4J_{PC}$=2.3 Hz), 137.9 (d, $^4J_{PC}$=2.7 Hz), 141.2 (d, $^2J_{PC}$=5.8 Hz), 160.0 (d, $^2J_{PC}$= 8.0 Hz); ^{31}P NMR (40.5 MHz) δ=33.9. $C_{23}H_{23}N_2O_2P$ (390.15): calcd. C 70.76, H 5.94, N 7.18, P 7.93; found C 70.91, H 6.02, N 7.12, P 7.98.

(2*S*,5*S*)-2-(2-Hydroxyphenyl)-3-phenyl-1,3-diazaphosphabicyclo-[3.3.0]-octane 2-thioxide 12. To a stirred solution of **1g** (530 mg, 1.3 mmol) in dry THF (15 mL) under argon atmosphere was slowly added at −78°C a solution of *n*-BuLi (1.4 mmol, 2.5 M in hexanes, 0.56 mL). The mixture was allowed to warm to room temperature and stirred overnight. After quenching by addition of a saturated solution of NH_4Cl (10 mL), the product was extracted with dichloromethane (3×10 mL). The combined organic phases were dried over $MgSO_4$, filtered and evaporated under reduced pressure. Purification by column chromatography (silica gel; ethylacetate/petroleum ether 50:50) afforded **12** as a white solid in 88% yield. Mp: 147°C; $[\alpha]_D^{25}=+95$ (c=1.38, CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.86–2.26 (m, 4H), 2.96–3.09 (m, 1H), 3.47–3.57 (m, 1H), 3.85–4.06 (m, 1H), 4.18–4.25 (m, 1H), 6.87–7.02 (m, 2H), 7.07 (dd, $^3J_{HH}$=7.9 Hz, $^4J_{HH}$=1.0 Hz, 2H), 7.27 (dd, $^3J_{HH}$=7.6 Hz, $^3J_{PH}$=7.3 Hz, 2H), 7.36–7.59 (m, 3H), 10.35 (s, OH); ^{13}C NMR (50 MHz, $CDCl_3$) δ=26.8 (d, $^3J_{PC}$=3.0 Hz), 31.5 (s), 45.8 (d, $^2J_{PC}$= 3.4 Hz), 51.7 (d, $^2J_{PC}$=12.8 Hz), 61.1 (d, $^2J_{PC}$=2.8 Hz), 101.0 (d, $^1J_{PC}$=151.0 Hz), 118.1 (d, $^3J_{PC}$=5.2 Hz, 2C), 118.8 (d, $^3J_{PC}$=9.8 Hz), 119.6 (d, $^3J_{PC}$=13.1 Hz), 122.1 (s), 129.0 (s, 2C), 131.4 (d, $^2J_{PC}$=8.2 Hz), 134.3 (s), 141.4 (d, $^2J_{PC}$=5.8 Hz), 160.7 (d, $^2J_{PC}$=8.7 Hz); ^{31}P NMR (40.5 MHz, $CDCl_3$) δ=70.2. $C_{17}H_{19}N_2OPS$ (330.10): calcd. C 61.80, H 5.80, N 8.48, P 9.38, S 9.71; found C 61.75, H 5.75, N 8.43, P 9.28, S 9.63.

(2*R*,5*S*)-2-Phenylthio-3-phenyl-1,3-diazaphosphabicyclo-[3.3.0]-octane 2-oxide 13 and (2*S*,5*S*)-2-phenylthio-3-phenyl-1,3-diazaphosphabicyclo-[3.3.0]-octane 2-oxide 14. In a two-necked round flask an equimolar mixture of tris(dimethylamino)phosphine **2** (5 mmol, 0.82 g) and (*S*)-(+)-2-anilinomethylpyrrolidine **3** (5 mmol, 0.88 g) were placed in dry toluene (10 mL) under argon atmosphere and warmed at 110°C for 3 h. Then 1 equiv. of thiophenol was added at room temperature and the mixture was warmed at 110°C for 1 h. The mixture was allowed to cool to room temperature and the toluene was removed in vacuo. The crude phosphine was diluted with dichloromethane (15 mL) and the mixture was cooled at 0°C. Then *tert*-butyl hydroperoxide 0.9 mL (5.5 M, decane), was slowly added and the mixture was stirred for 3 h. After removing the solvent in vacuo, the crude product was purified by chromatography (silica gel; ethylacetate/petroleum ether 75:25) and afforded the two diastereomers **13** and **14** as white solids in, respectively, 68 and 11% chemical yield. Analytical data for **13**: mp: 222°C; $[\alpha]_D^{25}=-155$ (c=0.985, CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.44–1.55 (m, 1H), 1.86–2.03 (m, 3H), 2.70–2.77 (m, 1H), 3.02–3.20 (m, 3H), 3.78–3.92 (m, 1H), 7.03 (t, $^3J_{HH}$=7.2 Hz, 1H), 7.16–7.21 (m, 5H), 7.22–7.37 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ=26.1 (d, $^3J_{PC}$=2.4 Hz), 32.7 (d, $^3J_{PC}$=2.7 Hz), 44.4 (d, $^2J_{PC}$=2.6 Hz), 48.5 (d, $^2J_{PC}$= 13.0 Hz), 58.3 (d, $^2J_{PC}$=6.5 Hz), 116.9 (d, $^3J_{PC}$=4.4 Hz, 2C), 121.9 (s), 128.1 (d, $^2J_{PC}$=6.5 Hz), 128.6 (d, $^4J_{PC}$=2.6 Hz, 2C), 129.0 (s, 2C), 129.1 (s),

136.1 (d, $^3J_{PC}$=4.3 Hz, 2C), 140.8 (d, $^2J_{PC}$=7.1 Hz); ^{31}P NMR (40.5 MHz, $CDCl_3$) δ=35.9. $C_{17}H_{19}N_2OPS$ (330.10): calcd. C 61.80, H 5.80, N 8.48, P 9.38, S 9.71; found C 60.75, H 5.75, N 8.33, P 9.28, S 9.62. Analytical data for **14**: mp: 216°C; $[\alpha]_D^{25}$=+140 (*c*=0.93, CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.72–2.03 (m, 4H), 2.55 (t, $^3J_{HH}$=8.6 Hz, 1H), 3.20–3.28 (m, 1H), 3.52–3.70 (m, 2H), 3.87–3.94 (m, 1H), 6.95–7.45 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$) δ=27.4 (d, $^3J_{PC}$=6.8 Hz), 31.3 (d, $^3J_{PC}$=4.2 Hz), 42.7 (d, $^2J_{PC}$=6.6 Hz), 52.4 (d, $^2J_{PC}$=10.9 Hz), 57.6 (d, $^2J_{PC}$=10.3 Hz), 116.5 (d, $^3J_{PC}$=4.7 Hz, 2C), 121.8 (s), 127.8 (d, $^2J_{PC}$=7.2 Hz), 129.1 (d, $^4J_{PC}$=2.3 Hz, 2C), 129.3 (s, 2C), 136.0 (d, $^3J_{PC}$=4.5 Hz, 2C), 141.8 (d, $^2J_{PC}$=7.0 Hz); ^{31}P NMR (40.5 MHz, $CDCl_3$) δ=26.5. $C_{17}H_{19}N_2OPS$ (330.10): calcd. C 61.80, H 5.80, N 8.48, P 9.38, S 9.71; found C 61.75, H 5.89, N 8.43, P 9.50, S 9.63.

(2*S*,5*S*)-2-(2-Sulfanylphenyl)-3-phenyl-1,3-diazaphosphabicyclo-[3.3.0]-octane 2-oxide 15. Classical procedure has been used for the preparation of **15** from diastereomerically pure precursor **13**. Purification by column chromatography (silica gel; ethylacetate/petroleum ether 25:75) afforded **15** as a white solid in 20% yield. Mp: 104°C; $[\alpha]_D^{25}$=+22.1 (*c*=1, CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.86–2.26 (m, 4H), 2.96–3.09 (m, 1H), 3.47–3.57 (m, 1H), 3.85–4.06 (m, 1H), 4.18–4.25 (m, 1H), 6.87–7.02 (m, 2H), 7.07 (dd, $^3J_{HH}$=7.9 Hz, $^4J_{HH}$=1.0 Hz, 2H), 7.27 (dd, $^3J_{HH}$=7.6 Hz, $^3J_{PH}$=7.3 Hz, 2H), 7.36–7.59 (m, 3H), 10.35 (s, OH); ^{13}C-NMR (50 MHz, $CDCl_3$) δ=26.8 (s), 32.3 (s), 44.5 (s), 49.6 (d, $^2J_{PC}$=11.5 Hz), 59.9 (s), 103.6 (d, $^1J_{PC}$=162.0 Hz), 116.4 (d, $^3J_{PC}$=5.4 Hz, 2C), 117.6 (d, $^3J_{PC}$=11.6 Hz), 119.3 (d, $^3J_{PC}$=14.1 Hz), 121.8 (s), 129.2 (s, 2C), 130.7 (d, $^2J_{PC}$= 6.7 Hz), 131.3 (d, $^2J_{PC}$=8.4 Hz), 134.3 (s), 141.4 (d, $^2J_{PC}$=5.7 Hz); ^{31}P NMR (40.5 MHz, $CDCl_3$) δ=30.9. $C_{17}H_{19}N_2OPS$ (330.10): calcd. C 61.80, H 5.80, N 8.48, P 9.38, S 9.71; found C 61.75, H 5.89, N 8.54, P 9.48, S 9.53.

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12. X-Ray analysis of **10**: A plate white monocrystal of $C_{23}H_{23}N_2O_2P$, obtained by recrystallization in ethylacetate, with approximate dimensions 0.4×0.3×0.2 mm was mounted on a glass capillary. All the measurements were made on a Rigaku diffractometer with Mo-Kα radiation. Cell constants and the orientation matrix for data collection were obtained from a least-square refinement using setting angles of 30 reflections in the range θ=1–25°, which corresponded to an orthorhombic cell with dimensions: *a*=9.620(1), *b*=9.675(1), *c*=21.729(1) Å. For *Z*=4 and *M*=390.42, ρ_{calcd}=1.25 g cm^{-3}. The space group was determined to be $P2_12_12_1$ from the systemic absences. A total of 2278 reflections were collected at *T*=298 K. The standards were measured after every 120 reflections. Among the first 200 pairs of reflections, the signs of the corresponding calculated differences, establishing that the molecule is described with the correct absolute configuration *S. CCDC 132970*
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