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Determination of the absolute configuration of chiral aryl–alkyl carbinols using organophosphorus diamine derivatizing agents by ^{31}P NMR spectroscopy

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Abstract—The prediction of the absolute configuration of chiral alcohols, namely phenylcarbinols, from the ^{31}P NMR spectra of the diastereoisomers obtained with organophosphorus diamino-derivatizing agents is presented. A simplified model based on NMR and crystallographic data is given, which associates the spatial location of the substituents of the stereogenic alcohol centre with the sign of the $\Delta\delta_{(R-S)}$ ($\Delta\delta_{(R-S)}$ representing the chemical shift difference between two diastereoisomers of the CDAs and the chiral secondary alcohol).

1. Introduction

NMR and chromatographic methods are widely used for the determination of enantiomeric purity, based on the formation of diastereomeric complexes or derivatives.[1–3] With the increasing development in enantioselective synthesis for its application in the pharmaceutical industry, it is of great interest to assign the absolute configuration of a studied organic or natural product. Several methods have been developed to determine the absolute configuration of primary or secondary chiral alcohols; most of these consist of their derivatisation with the (*R*)- or (*S*)-enantiomers of some auxiliary reagents (usually arylmethoxyacetic acids) and the comparison of the ^{1}H NMR spectra of the two resulting diastereoisomeric esters. A correlation exists between the spatial orientation of the aryl ring of the auxiliary reagent, whose absolute configuration is known, and the position of the stereogenic centre of the alcohol of which the absolute configuration has yet to be determined.[4–10] However, some limitations have been found with such compounds: these have been reviewed by Seco et al.[11] In some cases the chemical shift difference is very low, with little to no resolution at all; this is especially the case when using phenylcarbinol. For these reasons, Kelly reported a method based on the observation of the chemical shift of the benzylic proton of the MTPA-derivative, a method which also gives the absolute configuration of these secondary alcohols with satisfactory resolutions between the two diastereoisomers ($\Delta\delta \approx \pm 0.1$ ppm).[12] This method has been tested on previously reported compounds and gave good results for the assignment of the configuration in most cases. Nevertheless, it would be desirable to find another way of assigning the absolute configurations of chiral alcohols, including phenylcarbinols, through an easier, quickly prepared and more sensitive NMR method. It has been well established that ^{31}P is a very attractive nucleus to be used for NMR analysis because of the large chemical dispersion and the simplicity of the spectra.[13] Moreover many chiral phosphorus chemical derivatisation agents (CDAs) have been conveniently applied to the determination of the enantiomeric excesses of various chiral alcohols,[14–32] amines,[17,25,26,33,34] thiols[14,22,24,25,34,35] and aminoacids,[33,36,37] the majority of them containing an amine or a C_2-symmetric diamine moiety. In some cases, it has also been possible to determine the absolute configuration of the chiral alcohols.[1] In our laboratory, we have the expertise of developing such CDAs for determining the enantiomeric excess of various chiral compounds and we decided to investigate if it would be possible to use our CDAs for

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both ee determination and absolute configuration attribution. We focused on the use of three C_2-symmetric diamines as CDAs and coupled these diamines through organophosphorus derivatives with a large variety of chiral alcohols and, in particular, aryl–alkyl carbinols. Herein we report the results we observed, which can lead to a predictive method of determining their ee and absolute configuration.

1.1. Typical procedure for the preparation of the phosphorus CDAs

The reaction was performed in an NMR tube by adding under an argon atmosphere one equivalent of a diamine of already known absolute configuration (0.1 mmol) in $CDCl_3$ with 5 equiv of base (*N*,*N*-diethylaniline or pyridine) and 1 equiv of freshly distilled PCl_3. The formation of the P(III) derivatives was monitored by ^{31}P NMR. To this solution was added the chiral alcohol (0.1 mmol) as already described with other phosphorus derivatives.[30] The reaction occurred instantaneously, such that the ^{31}P and ^{1}H NMR spectra could be recorded immediately. Another way of synthesising the P(III) compound consisted of making the chiral alcohol react directly with the P-NMe_2 derivative, as described in Figure 1.[24] This compound was then diluted in $CDCl_3$, or nondeuterated benzene or toluene, with a few drops of C_6D_6 then added to lock the signal. The configuration of the alcohol was known: both pure/enriched (*R*)- and (*S*)-enantiomers were alternatively used. If only one enantiomer was commercially available, we used this and compared the results with the racemic mixture for the attribution of the chemical shifts, or we alternatively used both enantiomers of the diamine with the same enantiomer of the alcohol (for instance, the phosphorus CDAs obtained from a (*R*,*R*)-C_2-diamine and a (*S*)-alcohol had the same chemical shift of that obtained from the (*S*,*S*)-C_2-diamine and an (*R*)-alcohol since they are enantiomers). The observation of a 1:1 mixture of the diastereoisomer in the racemic case assured us that no kinetic resolution occurred during the derivatisation step. Sulfur could then be added directly to the NMR tube and the spectra recorded again after shaking the tube, without any further purification.[24,30] These stabilised compounds could also be isolated and purified by chromatography on silica gel (CH_2Cl_2/MeOH 99/1 v/v) while in some cases they could be crystallised with a quality suitable enough for the determination of their structure by X-ray diffraction.

The NMR data in the tables are presented with all the alcohols under the same relative configuration, the one dictated by (*R*)-phenyl-1-ethanol, whatever their official (*R*)- or (*S*)-CIP nomenclature. In the first column, the derivatisation was done with (*R*,*R*)-1,2-diamine whereas in the second column they are presented with the (*S*,*S*) one.

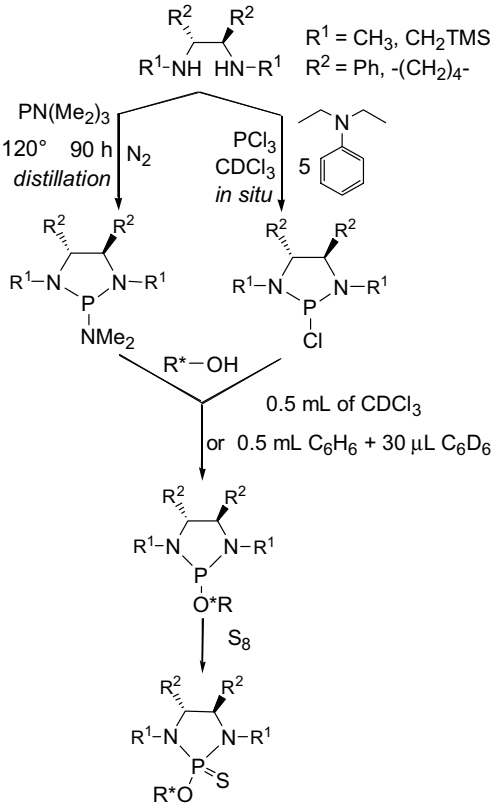


Figure 1. Preparation of the P(III) and P(V) derivatives.

2. Results and discussion

We extensively used (*R*,*R*)-*N*,*N*′-dimethyl-cyclohexane-1,2-diamine **A** (Fig. 2), as it was though that some kind of interaction may occur between the aromatic moiety of the alcohol and that of the *N*,*N*′-dimethyl-1,2-diphenyl-ethane-1,2-diamine **B** (Fig. 2). On the other hand, we also wanted to compare the influence of the methyl substituents of these amines so we substituted them with a methyl-trimethylsilyl moiety **C** (Fig. 2), a more bulky substituent.

In the case of (*R*,*R*)-*N*,*N*′-dimethyl-cyclohexane-1,2-diamine derivatives, the ^{31}P NMR spectra were recorded either in $CDCl_3$, as described above, or in distilled benzene (with a few drops of deuterated benzene to allow the lock), so that influence of the solvent could be tested. The results are summarised in Table 1. Chemical shift differences $\Delta\delta$ (ppm) of all P(III) derivatives were smaller when recorded in benzene when compared to

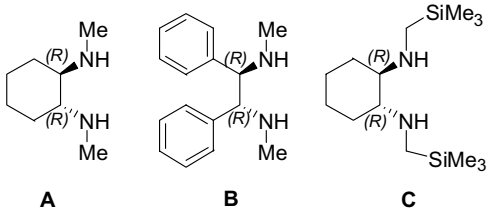


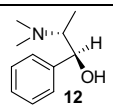
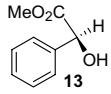
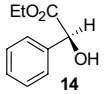
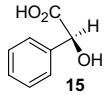
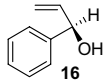
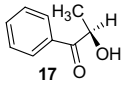
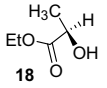
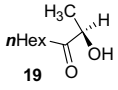
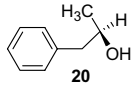
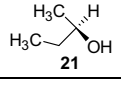
Figure 2. Different C_2-symmetric diamines used in this study.

Table 1. ^{31}P chemical shift δ, ^{1}H chemical shift of the benzylic proton (in italics) and chemical shift differences $\Delta\delta$ (ppm) of some (*R*)-phenylcarbinol P(III) and P(V) derivatives with (*R*,*R*)-*N*,*N*′-bis-cyclohexane-1,2-diamine **A** (in $CDCl_3$ and in benzene)

Entry		P(III)		$\Delta\delta_{(R-S)}$	P(V)		$\Delta\delta_{(R-S)}$
	A	(*R*,*R*)	(*S*,*S*)		(*R*,*R*)	(*S*,*S*)	
1	**1**	$CDCl_3$:138.05 *5.88* C_6D_6:138.78	143.96 *5.88* 142.30	−5.91 −3.52	87.03 *6.31* 87.69	85.94 *6.32* 86.99	1.09 0.70
2	**2**	$CDCl_3$:140.36 *5.28* C_6D_6:146.64	143.76 *5.28* 147.75	−3.40 −1.11	86.84 *5.73* 87.25	87.83 *5.76* 87.64	−0.99 −0.39
3	**3**	$CDCl_3$:134.89 *5.46* C_6D_6:140.63	140.21 *5.38* 142.80	−5.32 −2.17	85.60 *5.65* 84.20	86.00 *5.57* 86.85	−0.40 −2.65
4	**4**	$CDCl_3$:139.64 *5.11* C_6D_6:134.84	143.74 *5.11* 136.72	−4.10 −1.88	86.03 *5.49* 86.76	86.83 *5.57* 87.16	−0.80 −0.40
5	**5**	$CDCl_3$:136.00 *4.85* C_6D_6:140.58	146.54 *4.85* 142.29	−10.54 −1.71	85.84 *5.19* 87.13	87.14 *5.34* 88.07	−1.30 −0.94
6	**6**	$CDCl_3$:135.58 *4.90* C_6D_6:132.82	146.53 *4.90* 140.86	−10.95 −8.04	85.76 *5.19* 87.63	87.04 *5.43* 88.29	−1.28 −0.66
7	**7**	$CDCl_3$:133.81	147.50	−13.69	85.36 *4.91*	83.99 *5.02*	1.37
8	**8**	C_6D_6:135.28	144.23	−8.95	85.95	86.90	−0.95
9	**9**	$CDCl_3$:135.55 *4.86* C_6D_6:142.21	146.53 *4.86* 151.09	−10.98 −8.88	85.75 *5.18* 86.97	87.04 *5.40* 87.94	−1.29 −0.97
10	**10**	$CDCl_3$: 136.32 *5.14* C_6D_6:143.46	149.03 *5.14* 152.28	−12.71 −8.82	87.63 *5.55* 88.11	86.36 *5.45* 87.33	+1.27 +0.78
11	**11**	$CDCl_3$:135.51 *5.12* C_6D_6:141.54	146.47 *5.12* 151.34	−10.96 −9.80	86.75 *5.38* 86.95	87.06 *5.48* 88.06	−0.31 −1.11

(*continued on next page*)

Table 1 (*continued*)

Entry		P(III)		$\Delta\delta_{(R-S)}$	P(V)		$\Delta\delta_{(R-S)}$
	A	(*R*,*R*)	(*S*,*S*)		(*R*,*R*)	(*S*,*S*)	
12	 **12**	$CDCl_3$:135.57 C_6D_6:142.25	148.02 153.87	−12.45 −11.62	87.60 87.32	86.16 88.68	+1.44 −1.36
13	 **13**	$CDCl_3$:137.47	141.12	−3.65	88.07	88.37	−0.30
14	 **14**	$CDCl_3$:135.90 *5.26*	141.37 *5.41*	−5.47	88.28	87.04	+1.24
15	 **15**	$CDCl_3$:147.34	148.11	−0.77	86.99	88.37	−1.38
16	 **16**	$CDCl_3$:140.31 *5.31*	142.94 *5.98*	−2.63	87.49 *5.98*	86.61 *6.01*	0.88
17	 **17**	C_6D_6:145.97 C_6D_6:135.27	148.58 131.51	−2.61 +3.76	87.51 87.48	88.34 87.15	−0.83 +0.33
18	 **18**	C_6D_6:137.37	134.00	+3.37	87.69	87.35	+0.34
19	 **19**	C_6D_6:139.73	135.55	+4.18	86.21	85.94	+0.27
20	 **20**	$CDCl_3$:141.54	139.53	+2.01	87.16	87.36	−0.17
21	 **21**	$CDCl_3$:145.13 C_6D_6:145.32	141.27 141.43	+3.86 +3.89	86.41 87.18	86.11 87.41	+0.30 −0.23

those recorded in $CDCl_3$. However this value was always large enough to avoid any problem of overlapping peaks. In such conditions, preparing the P(III) derivatives can be done easily and readily since they do not require a deuterated solvent. This means that the alcohol to be studied could be directly taken out from the reaction solvent.

To simplify the nomenclature of the phosphorus derivatives with different alcohols, we used the system described below (Fig. 3). The (*R*,*R*)-C_2-diamine **A**, **B** or **C** were reacted with a chiral alcohol **1**–**16** [in its (*S*)- or (*R*)-configuration]: for example, (*R*,*R*)-*N*,*N*′-bis-cyclohexane-1,2-diamine **A** and (*R*)-1-(2-naphthyl)-ethanol provided the P(III) derivative (*R*)-**A1**, which in turn

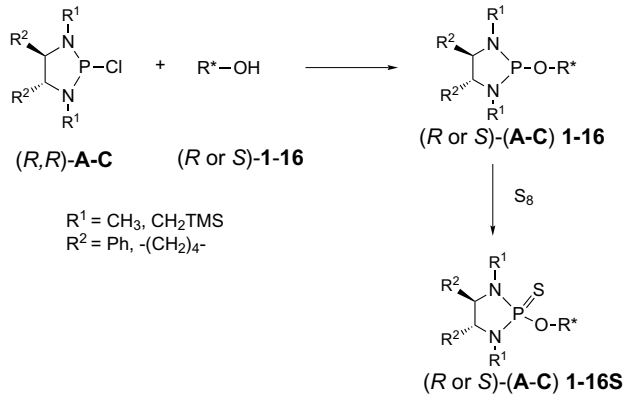


Figure 3. Numbering of the phosphorus derivatives with different chiral alcohols.

reacted with sulfur to give the P(V) derivative (*R*)-**A1S**.

The first step consisted of establishing a model in order to interpret the shielding effect observed between two diastereoisomers. In contrast to air-sensitive P(III) derivatives, P(V) derivatives are very stable and can be purified by chromatography. Several crystallographic structures have been elucidated, including both diastereoisomers obtained from 1-(2-naphthyl)-ethanol and (*R*,*R*)-*N*,*N*′-bis-cyclohexane-1,2-diamine (*R*)-**A2S** and (*S*)-**A2S** (see Fig. 4). In case of (*R*,*R*)-1,3-dimethyl-2-(*S*)-(1-naphthalen-2-yl-ethoxy)-octahydro-benzo[1,3,2]diazaphosphole 2-sulfide (*S*)-**A2S**, both independent molecules of the asymmetric unit showed the same configuration and differ essentially by the orientation of their naphthalene fragment (see Fig. 5).

In the case of the 1,3-dimethyl-2-(*S*)-(1-naphthalen-2-yl-ethoxy)-octahydro-benzo[1,3,2]diazaphosphole 2-sulfide compound (*R*)-**A2S**, obtained from (*R*)-2-naphthyl-ethanol, the aromatic moiety seemed to overlap with part of the C_2-diamine while there is a noticeable influence on nitrogen N5 whose hybridisation is closer to that of a sp^3 (sum of the dihedral angles: 346.3°, see Table 4). In contrast, N2 is closer to an sp^2 hybridisation (sum of the dihedral angles: 353.4°). The location of the naphthyl group is reversed in the case of (*S*)-2-naphthyl-ethanol, the aromatic moiety of (*S*)-**A2S** being far away from the C_2-diamine (sum of the dihedral angles: 347.0° for N2). In consequence the hybridisation of both nitrogen N1 and N2 shift towards an sp^2 hybridisation (346.3 → 344.0° and 353.4 → 351.0°). This could explain why in the ^{31}P NMR spectra there is such a shielding effect in the chemical shifts between the two diastereoisomers, with that of (*R*)-2-naphthyl-ethanol resonating upfield relative to that of the (*S*)-isomer (Fig. 6).

A huge similarity concerning the spatial orientation of the aromatic substituent of the phenylcarbinol has been observed with other compounds whose structures have been determined by X-ray crystallography: the normal hybridisation seems to be sp^2 but when a substituent is near the vicinity of one of the nitrogens, the hybridisations tends towards sp^3 hybridisation. The two examples of (*S*)-**B4S** and (*S*)-**B6S** are shown in Figure 7.

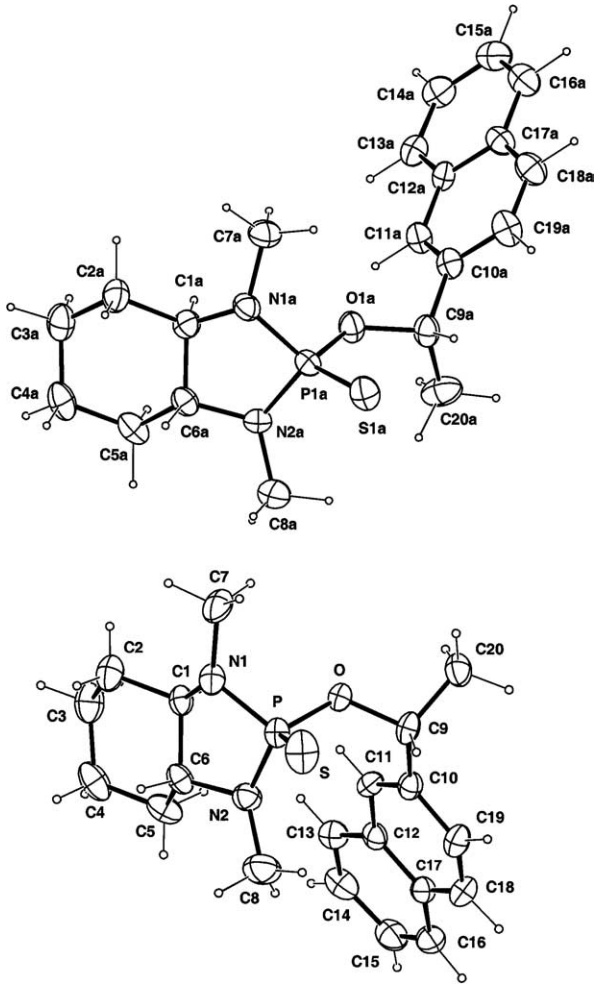


Figure 4. ORTEP view of the crystal structure of (*R*,*R*)-1,3-dimethyl-2-(*R*)-(1-naphthalen-2-yl-ethoxy)-octahydro-benzo[1,3,2]diazaphosphole 2-sulfide (*R*)-**A2S** (down side) and its diastereoisomer (*S*)-**A2S** (up side, molecule **a** of the asymmetric unit) with atom numbering (the numbering scheme of the molecule **b** is similar). Ellipsoids are represented with 40% probability.

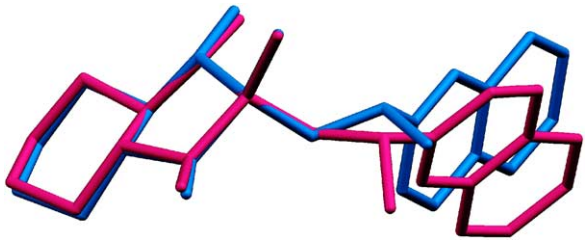


Figure 5. Superposition of both molecule of the asymmetric unit of (*R*,*R*)-1,3-dimethyl-2-(*R*)-(1-naphthalen-2-yl-ethoxy)-octahydro-benzo-[1,3,2]diazaphosphole 2-sulfide (*S*)-**A2S** showing the different orientation of their naphthalene fragment.

If we assume that the conformations seen in the solid state are similar to the ones in solution, we can, consequently, propose a model as depicted in Figure 8: in the case of 2-naphthyl-ethanol, R^1 represents the aromatic substituent and the R^2 methyl group. The configuration of the C_2-diamine is *R*,*R*.

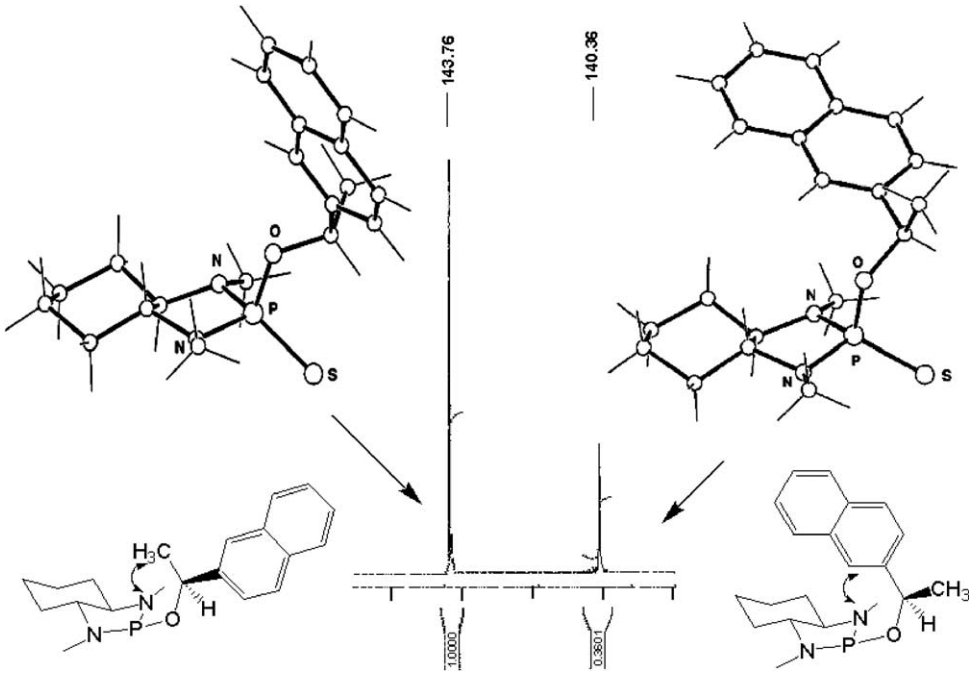


Figure 6. ^{31}P NMR spectrum of (*R*)-**A2** and (*S*)-**A2** diastereoisomers with crystallographic representations of their (*R*)-**A2S** and (*R*)-**A2S** derivatives.

According to this predictive model, all of the arylcarbinols, the stereogenic centres of which contain a methyl and an aryl moiety, should have the same spatial orientation. In such a case, the priority order for determining the absolute configuration is $OH > R^1$ (aryl) $> R^2$ (methyl) $>$ H meaning that relative and absolute configuration are the same. The diastereoisomer from the (*R*)-alcohol enantiomer would be expected to resonate upfield relative to the (*S*)-alcohol. In other words, the chemical shift difference $\Delta\delta_{(R-S)} = \delta_R - \delta_S$ should be negative. Indeed, this fact is confirmed by experimental data (Tables 1–3, entries 1–4).

In terms of steric hindrance, one can estimate that the aromatic moiety is planar so that the surface near the vicinity of the organophosphorus diamino-derivatizing agent (and namely its nitrogen) is less important when compared to that of the bulky three-dimensional methyl. This is confirmed in the case of the 2-bromo-α-methylbenzyl-alcohol for which the presence of the bulky bromine *ortho*-substituent does not interfere with the C_2-diamine according to the predictive model, since $\Delta\delta_{(R-S)} < 0$ (Tables 1–3, entry 3) with the values being close than that of the derivative of 1-phenyl-ethanol (Tables 1–3, entry 4). Consequently, the nature of the aromatic moiety is not important for the shielding effect: $\Delta\delta_{(R-S)}$ always has the same sign and about the same value (Tables 1–3, entries 1–4).

In the case of P(III) derivatives of (*R*,*R*)-*N*,*N*′-dimethyl-1,2-diphenyl-ethane-1,2-diamine, two counter examples exist; alcohols 1-naphthyl ethanol and 1-phenyl-ethanol (Table 2, entries 2 and 4), were $\Delta\delta_{(R-S)} > 0$. First of all, we have to take into account the fact that the shielding effect is not so important: $\Delta\delta_{(R-S)} \approx 1$–2 ppm while $\Delta\delta_{(R-S)} \geqslant 3$ ppm with the other diamines **A** and **C**. We observed that the less discrimination there is between R^1 and R^2, the smaller the $\Delta\delta_{(R-S)}$ value is. Secondly we have to reject the idea of some interaction between the aromatic moiety of the alcohol and that of the *N*,*N*′-dimethyl-1,2-diphenyl-ethane-1,2-diamine **B**. It is hard to understand why there would be an interaction with 1-naphthyl ethanol (Table 2, entry 1) and not with 2-naphthyl ethanol (entry 2). Furthermore, a crystallographic structure was obtained with a derivative of **B** and phenylbutanol (*S*)-**B6S** (Fig. 7) and no interaction could be evidenced between the alcohol phenyl moiety and those of diamine **B**. In fact, it appears that there is an important difference between derivatives of **A** and **C**, for which only one conformation exists, due to rigidity of the cyclohexane ring, and those of **B**, for which almost two main conformations occur, according to Figure 9. Conformation **a** corresponds to the same that is depicted in Figure 8, giving a negative $\Delta\delta_{(R-S)}$ value, while in the case of conformation **b**, it is the opposite nitrogen, which now tends towards sp^3 hybridisation. This results in a change of sign of $\Delta\delta_{(R-S)}$. The energy to convert **a** to **b** form is not important in the case of 1-phenyl ethanol and 1-naphthyl ethanol, for which there is not important enough discrimination between the aryl and the methyl substituent. Except for these two examples, which do not fit with our predictive model, all the other studied alcohols gave the same results as those observed with the two others diamines **A** and **C**. This is why we consider the diamine **B** as a reliable one.

In the case of the P(V) derivatives, hybridisation of the phosphorus was different with the spatial orientation of the aryl and alkyl substituent interfering differently than in the cases of the P(III) derivatives, leading in some cases to an inversion of the $\Delta\delta_{(R-S)}$ sign, as presented in Tables 1–3. It is not predictable whether or not $\Delta\delta_{(R-S)}$ of P(V) derivative will have the same sign than that of the corresponding P(III) one. This is why the following

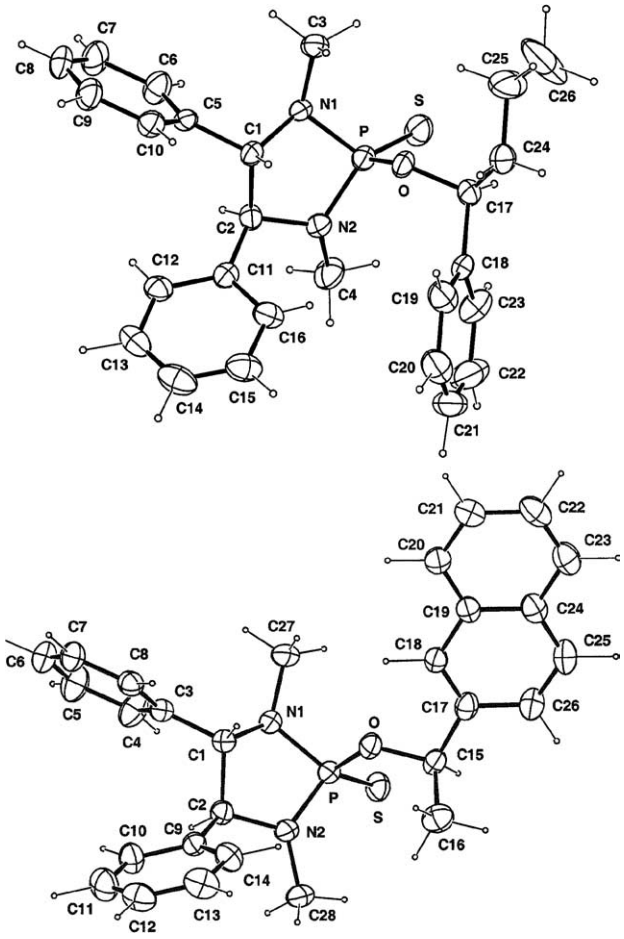


Figure 7. ORTEP view of the crystal structure of (*S*,*S*)-1,3-dimethyl-4,5-diphenyl-2-(*S*)-(1-phenyl-butoxy)-[1,3,2]diazaphospholidine 2-sulfide (*S*)-**B4S** (up side) and (*S*,*S*)-1,3-dimethyl-4,5-diphenyl-2-(*S*)-(1-phenyl-butoxy)-[1,3,2]diazaphospholidine 2-sulfide (*S*)-**B6S** (down side) with atom numbering. Ellipsoids are represented with 40% probability.

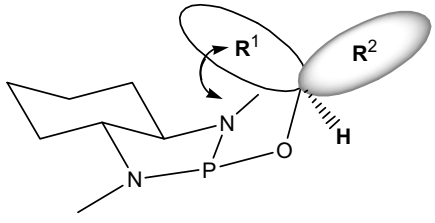


Figure 8. Model for the spatial orientation of R^1 and R^2 resulting in a shielding effect in the chemical shifts between the two diastereoisomers of the same chiral alcohol.

comparison of the data of Tables 1–3 will be conducted with the P(III) ones. Nevertheless, the predictive model of Figure 8 is based on the observation of crystallographic structures of P(V) derivatives for which the sign of $\Delta\delta_{(R-S)}$ is the same as that of the P(III) ones.

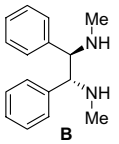
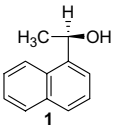
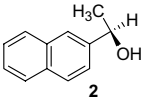
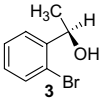
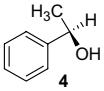
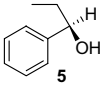
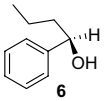
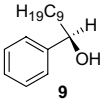
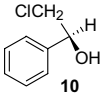
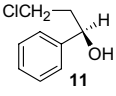
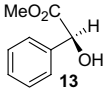
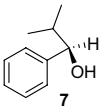
After varying the nature of the aromatic substituent of the chiral alcohol, we studied the influence of the alkyl groups. The length of the alkyl chain had no influence on the $\Delta\delta_{(R-S)}$ sign (Table 1, entries 4–9 and Tables 2, entries 4–7 and 3), but $\Delta\delta_{(R-S)}$ increased when the length of the carbon chain increased with asymptotic trends after four carbons. The same phenomenon was observed in the case of branched alkyl chains, namely in the case of isopropyl or 2-dimethylamino-1-phenyl-propan-1-ol versus methyl (Table 1, entries 7 and 12 and Table 2, entry 11). This can be explained either by a steric or an electronic effect: the bulkiness of an ethyl or a propyl is important when compared to that of a methyl. However when the length was increased too much, the influence was not so important relative to the stereogenic centre, which can be reasoned in terms of electronic effect, as alkyl groups are electron-donating; however the inductive effect is rarely transmitted up beyond two C–C bonds.

We also introduced some chlorinated compounds (Table 1, entries 10–11 and Tables 2, entries 8–9 and 3); in both cases, $\Delta\delta_{(R-S)} < 0$. Since the sign of $\Delta\delta_{(R-S)}$ is the same as that of 1-phenylethanol (Tables 1–3, entry 4) where there is no electronic influence of the chlorine. When comparing a methyl-chlorine versus an ethyl-chlorine substituent, there was only a change of the order of magnitude of the chemical shift difference, with it being only a little bit higher in the case of 2-chloro-1-phenyl-ethanol. However care had to be taken in establishing the absolute configurations of these alcohols. According to the model presented in Figure 8, in both cases the phenyl moiety is at the R^1 position and the chlorinated substituent at the R^2 position: the two compounds have the same relative configuration. However, if one takes into account that the priority rules are $-CH_2-Cl > \text{phenyl} > -CH_2-CH_2-Cl$ for the absolute configuration determination, it means that the chloro-phenyl-methanol derivative has an (*S*)-configuration, opposite to the one previously observed in the case of alcohols **1**–**9** and **11** of Table 1.

To confirm the effect of a heteroatom at the R^2 position, we also studied the case of (−)-*N*-methylephedrine derivatives (Table 1, entry 12). Once more we had no electronic influence and experimentally found only a negative sign of $\Delta\delta_{(R-S)}$.

We then replaced the alkyl group with a carboxyl of a carboxylic acid or ester. If the factor, which influenced the spatial orientation, is an electronic one, we would expect significant changes since we have now introduced an electron acceptor group, the previous ones being electron donors. This was not the case since again we observed that $\Delta\delta_{(R-S)}$ has a negative sign in all cases (Table 1, entries 13–14 and Tables 2, entry 10 and 3), and that these values were of the same order of magnitude when compared to the previous ones. In terms of steric hindrance, a phenyl or a naphthyl moiety has an important surface while it is planar, contrary to an ester whose carboxyl is an sp^2 planar carbon but bound to a tetrahedral methyl or an ethyl sp^3 hybridised. Experimentally, we observed that the preferred orientation was still the one in which the phenyl is at the R^1 position. This was the case even when R^2 was a carboxylic or an ethylene moiety, which is more difficult to predict just from the bulkiness of these substituents compared to

Table 2. ^{31}P chemical shift δ and chemical shift differences $\Delta\delta$ (ppm) of some (*R*)-phenylcarbinol P(III) and P(V) derivatives with (*R*,*R*)-*N*,*N*′-dimethyl-1,2-diphenyl-ethane-1,2-diamine **C** (in $CDCl_3$)

Entry		P(III)		$\Delta\delta_{(R-S)}$	P(V)		$\Delta\delta_{(R-S)}$
		(*R*,*R*)	(*S*,*S*)		(*R*,*R*)	(*S*,*S*)	
	 **B**						
1	 **1**	139.26 *5.65*	140.39 *5.83*	−1.13 *−0.18*	82.82 *5.60*	83.26 *5.87*	−0.44 *−0.27*
2	 **2**	141.16 *5.39*	139.65 *5.45*	+1.51 *−0.06*	82.92 *5.82*	82.89 *5.90*	+0.03 *−0.08*
3	 **3**	137.90 *5.61*	139.25 *5.63*	−1.35 *−0.02*	82.95 *5.94*	82.68 *5.98*	+0.27 *−0.04*
4	 **4**	139.93 *5.67*	139.46 *5.67*	+0.47 *0.00*	82.57 *5.72*	82.29 *5.67*	+0.28 *+0.05*
5	 **5**	139.85 *5.35*	141.60 *4.89*	−1.75 *+0.46*	83.01 *5.54*	82.52 *5.51*	+0.49 *+0.03*
6	 **6**	139.04 *5.03*	141.83 *4.68*	−2.79 *+0.35*	82.75 *5.49*	82.92 *5.57*	−0.17 *−0.08*
7	 **9**	139.22 *5.01*	142.36 *4.71*	−3.14 *+0.30*	82.82 *5.39*	83.26 *5.57*	−0.44 *−0.18*
8	 **10**	140.25 *5.00*	144.10 *5.18*	−3.85 *−0.18*	83.04 *5.00*	83.25 *5.71*	−0.21 *−0.71*
9	 **11**	140.01 *5.30*	146.64 *5.35*	−6.63 *−0.05*	83.00 *5.62*	83.41 *5.64*	−0.41 *−0.02*
10	 **13**	138.30	139.09	−0.79	83.04	83.14	−0.10
11	 **7**	138.82 *4.75*	143.79 *4.77*	−4.97 −0.02	82.73 *5.06*	83.10 *5.19*	−0.37 *−0.13*

(*continued on next page*)

Table 2 (*continued*)

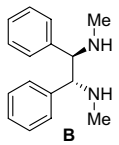
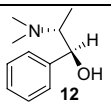
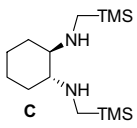
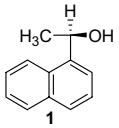
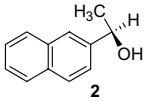
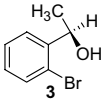
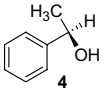
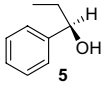
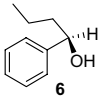
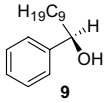
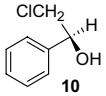
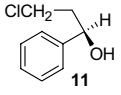
Entry		P(III)		$\Delta\delta_{(R-S)}$	P(V)		$\Delta\delta_{(R-S)}$
		(*R*,*R*)	(*S*,*S*)		(*R*,*R*)	(*S*,*S*)	
	 **B**						
12	 **12**	142.31	146.05	−3.74	83.66	82.39	+1.27

Table 3. ^{31}P chemical shift δ, ^{1}H chemical shift of the benzylic proton (in italics) and chemical shift differences $\Delta\delta$ (ppm) of some (*R*)-phenylcarbinol P(III) and P(V) derivatives with (*R*,*R*)-*N*,*N*′-bis-trimethylsilanylmethyl-cyclohexane-1,2-diamine **B** (in $CDCl_3$)

Entry		P(III)		$\Delta\delta_{(R-S)}$	P(V)		$\Delta\delta_{(R-S)}$
		(*R*,*R*)	(*S*,*S*)		(*R*,*R*)	(*S*,*S*)	
	 **C**						
1	 **1**	130.45	136.05	−5.60	89.34	86.99	2.35
2	 **2**	132.57	136.20	−3.63	87.11	89.06	−1.95
3	 **3**	128.47	132.95	−4.48	87.29	88.73	
4	 **4**	132.30	136.53	−4.23	87.09	88.98	1.90
5	 **5**	129.31	138.79	−9.48	86.45	88.80	−2.35
6	 **6**	133.31	138.93	−5.62	86.22	88.91	−2.69
7	 **9**	128.95	138.44	−9.49	85.76	88.03	−2.27
8	 **10**	129.95	135.23	−5.28	88.41	86.61	+1.80
9	 **11**	131.23	138.55	−7.32	85.79	88.16	−2.37

(*continued on next page*)

Table 3 (*continued*)

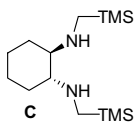
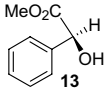
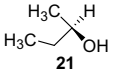
Entry		P(III)		$\Delta\delta_{(R-S)}$	P(V)		$\Delta\delta_{(R-S)}$
		(*R*,*R*)	(*S*,*S*)		(*R*,*R*)	(*S*,*S*)	
	 **C**						
10	 **13**	130.36	133.92	−43.56	88.45	89.05	−0.6
11	 **21**	131.73	130.45	1.28	87.99	88.14	0.15

Table 4. Selected bond lengths, distances (Å) and bond angles (°) for (*R*,*R*)-1,3-dimethyl-2-(*R*)-(1-naphthalen-2-yl-ethoxy)-octahydro-benzo[1,3,2]diazaphosphole 2-sulfide (*R*)-**A2S**, (*R*,*R*)-1,3-dimethyl-2-(*S*)-(1-naphthalen-2-yl-ethoxy)-octahydro-benzo[1,3,2]diazaphosphole 2-sulfide (*S*)-**A2S**, (*R*,*R*)-1,3-dimethyl-4,5-diphenyl-2-(*R*)-(1-phenyl-butoxy)-[1,3,2]diazaphospholidine-2-sulfide (*S*)-**B4S** and (*R*,*R*)-1,3-dimethyl-4,5-diphenyl-2-(*S*)-(1-phenyl-butoxy)-[1,3,2]diazaphospholidine-2-sulfide (*S*)-**B6S**

	(*R*)-**A2S**	(*S*)-**A2S**		(*S*)-**B4S**	(*S*)-**B6S**
		Molecule **a**	Molecule **b**		
P–N(1)	1.658(3)	1.655(5)	1.671(5)	1.660(3)	1.659(5)
P–N(2)	1.658(3)	1.671(5)	1.642(5)	1.649(3)	1.645(5)
P–S	1.937(1)	1.941(2)	1.938(2)	1.935(2)	1.925(2)
P–O	1.614(2)	1.595(4)	1.602(4)	1.596(3)	1.601(4)
N(1)–P–N(2)	95.7(1)	95.8(3)	95.0(3)	94.5(2)	95.2(3)
N(1)–P–O	102.7(1)	103.9(2)	108.7(2)	102.2(2)	101.6(2)
N(2)–P–O	108.4(1)	107.0(2)	102.6(2)	108.6(2)	108.9(2)
N(1)–P–S	119.1(1)	117.8(2)	116.1(2)	119.7(1)	118.8(2)
N(2)–P–S	118.1(1)	118.0(2)	120.4(2)	117.5(1)	117.4(2)
O–P–S	111.07(9)	112.2(2)	112.0(2)	112.0(1)	112.6(2)
P–N(1)–C	107.4(2)	108.4(4)	108.5(4)	108.8(3)	107.1(4)
P–N(1)–C_{methyl}	121.2(2)	118.6(4)	117.8(4)	117.8(2)	118.4(4)
C–N(1)–C_{methyl}	117.7(3)	117.7(5)	117.7(5)	117.1(3)	117.3(5)
Σ of angles at N(1)	346.3	344.7	344.0	343.7	342.8
N(1)...plane$_{(P,C,C\ methyl)}$	0.328(4)	0.350(6)	0.355(6)	0.360(4)	0.371(6)
P–N(2)–C	110.8(2)	109.1(4)	111.4(4)	112.8(3)	112.3(4)
P–N(2)–C_{methyl}	123.7(3)	120.6(5)	122.4(4)	122.9(3)	124.4(4)
C–N(2)–C_{methyl}	118.9(3)	117.3(5)	117.2(5)	118.5(3)	116.8(5)
Σ of angles at N(2)	353.4	347.0	351.0	354.2	353.5
N(2)...plane$_{(P,C,Cmethyl)}$	0.227(4)	0.321(6)	0.267(6)	0.213(4)	0.227(6)

that of a phenyl (Table 1, entries 15–16). As already observed in the case of the derivatives of alcohols **10**, the relative configurations of the alcohols are still the ones observed with (*R*)-phenyl-1-ethanol but have opposite absolute configurations.

For the last examples of studied alcohols (entries 17–21), we observed positive sign for $\Delta\delta_{(R-S)}$. According to steric factors we would expect that in the case of a totally planar –COPh moiety versus a methyl, the preferred orientation would be that for which the methyl is represented by R^2. Surprisingly we experimentally found $\Delta\delta_{(R-S)} < 0$, meaning that it is placed at the R^1 position in Figure 8. It is more easy to understand that when we increase the bulkiness of the substituent with a partially planar benzyl, CO_2Et or –CO-*n*-hex or even a sp^3 hybridised ethyl, versus a methyl; this latter substituent preferentially occupying the R^1 position.

Table 5 shows the relative positions R^1 and R^2 preferentially occupied by the different substituents of secondary alcohols, summarizing these results.

According to these results, predictions can be carried out to predict which substituent would occupy which position of the model presented in Figure 8: for instance, we can assume that every kind of aromatic moiety (Table 5, entry 1) will preferentially occupy the R^1 position, compared to every kind of alkyl or derivative such as presented in entry 2 (R^2 position), leading to a negative sign of $\Delta\delta_{(R-S)}$. Starting from the relative configuration given by this model, one can immediately deduce the absolute configuration of the chiral alcohol, by applying the CIP rules.

Alongside this study, we also focused on the shielding effect, which could be observed in the ^{1}H NMR spectra

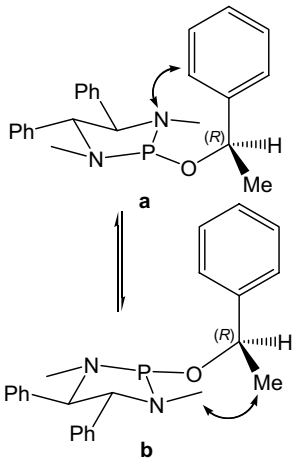


Figure 9. Conformational equilibrium of derivatives of (*R,R*)-1,3-dimethyl-4,5-diphenyl-2-(*R*)-(1-phenyl-ethoxy)-[1,3,2]diazaphospholidine (*R*)-**B4**.

Table 5. Relative R^1 and R^2 positions preferentially occupied by the different substituents of secondary alcohols, according to the model depicted in Figure 8

Entry	R^1	R^2
1	Phenyl 1-Naphthyl 2-Naphthyl *m*-Bromo-phenyl	$-CH_3$
2	Phenyl	Me, Et, Pr, Ipr, Bu, $-C_9H_{19}$ $-CH_2-Cl$, $-CH_2-CH_2-Cl$ $-CH(CH_3)-N(CH_3)_2$ $-CO_2H$, $-CO_2Me$, $-CO_2Et$, $-CH=CH_2$
3	$-CH_3$	$-CH_2Ph$,, –COPh, $-CO_2Et$, –CO–*n*-Hex $-C_2H_5$

of the two diastereoisomers of the same chiral alcohol with one (*R,R*)-diamine. The area studied was the one for which the benzylic proton of the alcohol was resonating, because it is the most often devoid of other signals (for instance the *N*-methyl substituents of diamine **A** and **B** could be of interest but the proton signals overlap with other signals). The results are shown in Tables 1 and 2, the value being in italic. Interestingly, the $\Delta\delta_{(R-S)}$ signal was usually negative for P(III) and P(V) derivatives, meaning that this benzylic proton is sensitive to the environment induced by the chiral phosphorus chemical derivatisation agent. The best agreement was obtained with P(V) derivatives of diamine **A**, for which the only two counter examples detected were 2-bromo-α-methylbenzyl-alcohol and 2-chloro-1-phenyl-ethanol (Table 1, entries 3 and 11). Consequently, the observation of these proton chemical shift differences cannot be another tool for the determination of the relative and absolute configuration of phenyl-aryl-carbinols, and only ^{31}P NMR can be reliably considered.

3. Conclusion

In conclusion, we have presented here a reliable and efficient way of determining the absolute configurations of chiral secondary alcohols, especially aryl and alkyl carbinols, with ^{31}P NMR, after derivatisation of these alcohols with phosphorus compounds. In the same way, their enantiomeric composition can be determined, as previously established.[24,30] For simplicity, the following method should be applied for an easy determination of chiral alcohol absolute configuration: the sample should be prepared in the NMR tube as described in the typical procedure described above; the preferred diamine should be cyclohexane-diamine (*R,R*)-**A** (see Fig. 2), due to its easy synthesis, and low cost, and where the rigidity of the cyclohexane ring provides wide chemical shifts.[43] When the alcohol to be studied is a mixture of two enantiomers, two signals are observed with (*R,R*)-diamine and the absolute configuration can be immediately determined by ^{31}P-NMR. When the alcohol to be studied is a single enantiomer, two measures have to be done, one with the (*R,R*)-diamine and one with the (*S,S*)-diamine, in order to obtain the chemical shift value of the second diastereoisomer. The upfield signal corresponds to the *R* enantiomer (unless the CIP rules agree with $R1 < R2$). This method has been applied to 16 alcohols and 3 different chiral diamines and gave a good correlation. Work is now being extended to other chiral alcohols.

4. Experimental part

4.1. X-ray crystallographic analysis

Cell dimensions and intensities were measured at 200 K on a Stoe IPDS diffractometer with graphite-monochromated Mo[Kα] radiation ($\lambda = 0.71073$ Å) for (*R*)-**A2S**, (*S*)-**A2S** and (*S*)-**B6S** and on a Stoe STADI4 diffractometer with graphite-monochromated Cu[Kα] radiation ($\lambda = 1.5418$ Å) for (*S*)-**B4S**. Data were corrected for Lorentz and polarisation effects and for absorption. The structures were solved by direct method (SIR97)[38] while all other calculations were performed with an XTAL system[39] and ORTEP[40] programs. (*R*)-**A2S**: $C_{20}H_{27}N_2OPS$, $M = 374.5$, $d_x = 1.264\,g\,cm^{-3}$, monoclinic, $P2_1$, $Z = 2$, $a = 8.1358(8)$, $b = 13.6526(9)$, $c = 9.0304(8)$ Å, $\beta = 101.277(11)°$, $U = 983.69(16)$ Å^3; 12239 measured reflections, 3796 unique reflections of which 3172 were observables $\{|Fo| > 4\sigma(Fo)\}$; Full-matrix least-squares refinement based on *F* gave final values $R = 0.028$, $\omega R = 0.031$ and Flack parameter[41,42] $x = -0.02(9)$. Hydrogen atoms were observed and refined. (*R*)-**A2S**: $C_{20}H_{27}N_2OPS$, $M = 374.5$, $d_x = 1.219\,g\,cm^{-3}$, monoclinic, $P2_1$, $Z = 4$, $a = 10.4469(4)$, $b = 8.5533(6)$, $c = 22.8413(12)$ Å, $\beta = 90.316(6)°$, $U = 2041.0(2)$ Å^3; 25737 measured reflections, 7648 unique reflections of which 4884 were observables $\{|Fo| > 4\sigma(Fo)\}$; Full-matrix least-squares refinement based on *F* gave final values $R = 0.037$, $\omega R = 0.041$ and Flack parameter $x = 0.02(11)$. Hydrogen atoms were calculated. (*S*)-B6S: $C_{26}H_{31}N_2OPS$, $M = 450.6$, $d_x = 1.203\,g\,cm^{-3}$, orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 9.2661(5)$, $b = 15.725(10)$, $c = 17.0800(10)$ Å,

$U = 2488.7(3)$ Å^3; 3550 measured reflections, 3072 unique reflections of which 2568 were observables $\{|Fo| > 4\sigma(Fo)\}$; Full-matrix least-squares refinement based on F gave final values $R = 0.044$, $\omega R = 0.043$ and Flack parameter $x = 0.04(4)$. Hydrogen atoms were observed and refined. (*S*)-B4S: $C_{28}H_{29}N_2OPS$, $M = 472.6$, $d_x = 1.229\,g\,cm^{-3}$, orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 8.3118(4)$, $b = 11.0919(4)$, $c = 27.7131(15)$ Å, $U = 2555.0(3)$ Å^3; 32380 measured reflections, 5000 unique reflections of which 3544 were observables $\{|Fo| > 4\sigma(Fo)\}$; Full-matrix least-squares refinement based on F gave final values $R = 0.036$, $\omega R = 0.039$ and Flack parameter $x = -0.03(11)$. Hydrogen atoms were calculated.

Crystallographic data (excluding structure factors) have been deposited to the Cambridge Crystallographic Data Centre [CCDC214464, CCDC214465, CCDC214466 and CCDC218666 for (*R*)-**A2S**, (*S*)-**A2S**, (*S*)-**B4S** and (*S*)-**B6S**, respectively]. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. + 44 (1223) 336-033; e-mail: deposit@ccdc.cam.ac.uk).

4.2. Preparation of the phosphorus derivatives

The syntheses of diamines **A**, **B**[30] and **C**[43] have already been reported, as well as the preparation of the phosphorus derivatives. NMR studies were performed on a Bruker-AM-400 instrument. The enriched chiral alcohols were purchased from Acros and Fluka. The NMR data for compounds (*RS*)-**A8** and **17**–**19** and their thio derivatives have also already been reported.[24]

4.2.1. (*R*,*R*)-1,3-Dimethyl-2-(*R*)-(1-naphthalen-1-yl-ethoxy)-octahydro-benzo[1,3,2]diazaphosphole (*R*)-A1. NMR ^{31}P: $\delta = 138.05$ ppm ($CDCl_3$), 138.78 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 7.85$ ppm (1H, H_{arom}); $\delta = 7.70$ ppm (2H, H_{arom}); $\delta = 7.47$ ppm (4H, H_{arom}); $\delta = 5.88$ ppm (qd, 1H, O–CH); $\delta = 2.81$ ppm (td, 1H, N–CH); $\delta = 2.68$ ppm (td, 1H, N–CH); $\delta = 2.43$ ppm (d, 3H, N–CH–CH_3); $\delta = 2.23$ ppm (d, 3H, N–CH_3); $\delta = 1.96$ ppm (m, 2H, –CH_2–); $\delta = 1.81$ ppm (m, 2H, –CH_2–); $\delta = 1.67$ ppm (d, 3H, –CH_3); $\delta = 1.20$ ppm (m, 4H, –CH_2–).

4.2.2. (*R*,*R*)-1,3-Dimethyl-2-(*R*)-(1-naphthalen-1-yl-ethoxy)-octahydro-benzo[1,3,2]diazaphosphole-2-sulfide (*R*)-A1S. NMR ^{31}P: $\delta = 87.03$ ppm ($CDCl_3$), 87.69 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 7.85$ ppm (1H, H_{arom}); $\delta = 7.51$ ppm (2H, H_{arom}); $\delta = 7.48$ ppm (4H, H_{arom}); $\delta = 6.21$ ppm (qd, 1H, O–CH); $\delta = 2.81$ ppm (td, 1H, N–CH); $\delta = 2.68$ ppm (td, 1H, N–CH); $\delta = 2.44$ ppm (d, 3H, N–CH_3); $\delta = 2.04$ ppm (d, 3H, N–CH_3); $\delta = 1.96$ ppm (m, 2H, –CH_2–); $\delta = 1.81$ ppm (m, 2H, –CH_2–); $\delta = 1.65$ ppm (d, 3H, –CH_3); $\delta = 1.32$ ppm (m, 4H, –CH_2–).

4.2.3. (*R*,*R*)-1,3-Dimethyl-2-(*S*)-(1-naphthalen-1-yl-ethoxy)-octahydro-benzo[1,3,2]diazaphosphole (*S*)-A1. NMR ^{31}P: $\delta = 143.96$ ppm ($CDCl_3$), 142.30 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 7.85$ ppm (1H, H_{arom}); $\delta = 7.72$ ppm (2H, H_{arom}); $\delta = 7.49$ ppm (4H, H_{arom}); $\delta = 5.88$ ppm (qd, 1H, O–CH); $\delta = 2.81$ ppm (td, 1H, N–CH); $\delta = 2.67$ ppm (td, 1H, N–CH); $\delta = 2.58$ ppm (d, 3H, N–CH_3); $\delta = 2.31$ ppm (d, 3H, N–CH_3); $\delta = 1.96$ ppm (m, 2H, –CH_2–); $\delta = 1.84$ ppm (m, 2H, –CH_2–); $\delta = 1.65$ ppm (d, 3H, –CH_3); $\delta = 1.26$ ppm (m, 4H, –CH_2–).

4.2.4. (*R*,*R*)-1,3-Dimethyl-2-(*S*)-(1-naphthalen-1-yl-ethoxy)-octahydro-benzo[1,3,2]diazaphosphole-2-sulfide (*S*)-A1S. NMR ^{31}P: $\delta = 85.94$ ppm ($CDCl_3$), 86.99 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 7.59$ ppm (1H, H_{arom}); $\delta = 7.49$ ppm (2H, H_{arom}); $\delta = 7.43$ ppm (4H, H_{arom}); $\delta = 6.32$ ppm (qd, 1H, O–CH); $\delta = 2.79$ ppm (td, 1H, N–CH); $\delta = 2.63$ ppm (td, 1H, N–CH); $\delta = 2.50$ ppm (d, 3H, N–CH_3); $\delta = 2.17$ ppm (d, 3H, N–CH_3); $\delta = 2.00$ ppm (m, 2H, –CH_2–); $\delta = 1.83$ ppm (m, 2H, –CH_2–); $\delta = 1.67$ ppm (d, 3H, –CH_3); $\delta = 1.31$ ppm (m, 4H, –CH_2–).

4.2.5. (*R*,*R*)-1,3-Dimethyl-2-(*R*)-(1-naphthalen-2-yl-ethoxy)-octahydro-benzo[1,3,2]diazaphosphole (*R*)-A2. NMR ^{31}P: $\delta = 140.36$ ppm ($CDCl_3$), 146.64 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 7.80$ ppm (4H, H_{arom}); $\delta = 7.46$ ppm (3H, H_{arom}); $\delta = 5.28$ ppm (qd, 1H, O–CH); $\delta = 2.81$ (td, 1H, N–CH); $\delta = 2.65$ ppm (td, 1H, N–CH); $\delta = 2.57$ ppm (d, 3H, N–CH_3); $\delta = 2.39$ ppm (d, 3H, N–CH_3); $\delta = 2.06$ ppm (m, 2H, –CH_2–); $\delta = 1.85$ ppm (m, 2H, –CH_2–); $\delta = 1.63$ ppm (d, 3H, –CH_3); $\delta = 1.32$ ppm (m, 4H, –CH_2–).

4.2.6. (*R*,*R*)-1,3-Dimethyl-2-(*R*)-(1-naphthalen-2-yl-ethoxy)-octahydro-benzo[1,3,2]diazaphosphole-2-sulfide (*R*)-A2S. NMR ^{31}P: $\delta = 86.84$ ppm ($CDCl_3$), 87.25 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 7.82$ ppm (4H, H_{arom}); $\delta = 7.54$ ppm (3H, H_{arom}); $\delta = 5.73$ ppm (qd, 1H, O–CH); $\delta = 2.77$ ppm (td, 1H, N–CH); $\delta = 2.70$ ppm (td, 1H, N–CH); $\delta = 2.51$ ppm (d, 3H, N–CH_3); $\delta = 2.31$ ppm (d, 3H, N–CH_3); $\delta = 2.12$ ppm (m, 2H, –CH_2–); $\delta = 1.91$ ppm (m, 2H, –CH_2–); $\delta = 1.63$ ppm (d, 3H, –CH_3); $\delta = 1.51$ ppm (m, 4H, –CH_2–).

4.2.7. (*R*,*R*)-1,3-Dimethyl-2-(*S*)-(1-naphthalen-2-yl-ethoxy)-octahydro-benzo[1,3,2]diazaphosphole (*S*)-A2. NMR ^{31}P: $\delta = 143.76$ ppm ($CDCl_3$), 147.75 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 7.83$ ppm (4H, H_{arom}); $\delta = 7.48$ ppm (3H, H_{arom}); $\delta = 5.28$ ppm (qd, 1H, O–CH); $\delta = 2.81$ (td, 1H, N–CH); $\delta = 2.65$ ppm (td, 1H, N–CH); $\delta = 2.63$ ppm (d, 3H, N–CH_3); $\delta = 2.32$ ppm (d, 3H, N–CH_3); $\delta = 2.05$ ppm (m, 2H, –CH_2–); $\delta = 1.83$ ppm (m, 2H, –CH_2–); $\delta = 1.60$ ppm (d, 3H, –CH_3); $\delta = 1.31$ ppm (m, 4H, –CH_2–).

4.2.8. (*R*,*R*)-1,3-Dimethyl-2-(*S*)-(1-naphthalen-2-yl-ethoxy)-octahydro-benzo[1,3,2]diazaphosphole-2-sulfide (*S*)-A2S. NMR ^{31}P: $\delta = 87.83$ ppm ($CDCl_3$), 87.64 ppm

(C_6D_6). NMR ^1H ($CDCl_3$): $\delta = 7.83$ ppm (4H, H_{arom}); $\delta = 7.50$ ppm (3H, H_{arom}); $\delta = 5.76$ ppm (qd, 1H, O–CH); $\delta = 2.75$ ppm (td, 1H, N–CH); $\delta = 2.71$ ppm (td, 1H, N–CH); $\delta = 2.58$ ppm (d, 3H, N–CH_3); $\delta = 2.23$ ppm (d, 3H, N–CH_3); $\delta = 2.20$ ppm (m, 2H, –CH_2–); $\delta = 1.98$ ppm (m, 2H, –CH_2–); $\delta = 1.65$ ppm (d, 3H, –CH_3); $\delta = 1.60$ ppm (m, 4H, –CH_2–).

4.2.9. 2-(*R*)-[1-(2-Bromo-phenyl)-ethoxy]-(*R*,*R*)-1,3-dimethyl-octahydro-benzo[1,3,2]diazaphosphole (*R*)-A3. NMR ^{31}P: $\delta = 134.89$ ppm ($CDCl_3$), 140.63 ppm (C_6D_6). NMR ^1H ($CDCl_3$): $\delta = 7.60$ ppm (1H, H_{arom}); $\delta = 7.47$ ppm (1H, H_{arom}); $\delta = 7.33$ ppm (1H, H_{arom}); $\delta = 7.08$ ppm (1H, H_{arom}); $\delta = 5.46$ ppm (qd, 1H, O–CH); $\delta = 2.65$ (td, 1H, N–CH); $\delta = 2.58$ ppm (td, 1H, N–CH); $\delta = 2.52$ ppm (d, 3H, N–CH_3); $\delta = 2.35$ ppm (d, 3H, N–CH_3); $\delta = 2.04$ ppm (m, 2H, –CH_2–); $\delta = 1.80$ ppm (m, 2H, –CH_2–);$\delta = 1.43$ ppm (d, 3H, –CH_3); $\delta = 1.39$ ppm (m, 2H, –CH_2–); $\delta = 1.22$ ppm (m, 2H, –CH_2–).

4.2.10. 2-(*R*)-[1-(2-Bromo-phenyl)-ethoxy]-(*R*,*R*)-1,3-dimethyl-octahydro-benzo[1,3,2]diazaphosphole-2-sulfide (*R*)-A3S. NMR ^{31}P: $\delta = 85.60$ ppm ($CDCl_3$), 84.20 ppm (C_6D_6). NMR ^1H ($CDCl_3$): $\delta = 7.49$ ppm (1H, H_{arom}); $\delta = 7.42$ ppm (1H, H_{arom}); $\delta = 7.26$ ppm (1H, H_{arom}); $\delta = 7.04$ ppm (1H, H_{arom}); $\delta = 5.65$ ppm (qd, 1H, O–CH); $\delta = 2.59$ ppm (td, 1H, N–CH); $\delta = 2.42$ ppm (td, 1H, N–CH); $\delta = 2.37$ ppm (d, 3H, N–CH_3); $\delta = 2.25$ ppm (d, 3H, N–CH_3); $\delta = 1.91$ ppm (m, 2H, –CH_2–); $\delta = 1.75$ ppm (m, 2H, –CH_2–); $\delta = 1.43$ ppm (d, 3H, –CH_3); $\delta = 1.38$ ppm (m, 2H, –CH_2–); $\delta = 1.23$ ppm (m, 2H, –CH_2–).

4.2.11. 2-(*S*)-[1-(2-Bromo-phenyl)-ethoxy]-(*R*,*R*)-1,3-dimethyl-octahydro-benzo[1,3,2]diazaphosphole (*S*)-A3. NMR ^{31}P: $\delta = 140.21$ ppm ($CDCl_3$), 142.80 ppm (C_6D_6). NMR ^1H ($CDCl_3$): $\delta = 7.59$ ppm (1H, H_{arom}); $\delta = 7.46$ ppm (1H, H_{arom}); $\delta = 7.32$ ppm (1H, H_{arom}); $\delta = 7.09$ ppm (1H, H_{arom}); $\delta = 5.38$ ppm (qd, 1H, O–CH); $\delta = 2.65$ ppm (td, 1H, N–CH); $\delta = 2.61$ ppm (td, 1H, N–CH); $\delta = 2.49$ ppm (d, 3H, N–CH_3); $\delta = 2.41$ ppm (d, 3H, N–CH_3); $\delta = 2.39$ ppm (m, 2H, –CH_2–); $\delta = 2.02$ ppm (m, 2H, –CH_2–); $\delta = 1.95$ ppm (m, 2H, –CH_2–); $\delta = 1.46$ ppm (d, 3H, –CH_3); $\delta = 1.04$ ppm (m, 2H, –CH_2–).

4.2.12. 2-(*S*)-[1-(2-Bromo-phenyl)-ethoxy]-(*R*,*R*)-1,3-dimethyl-octahydro-benzo[1,3,2]diazaphosphole-2-sulfide (*S*)-A3S. NMR ^{31}P: $\delta = 86.00$ ppm ($CDCl_3$), 86.85 ppm (C_6D_6). NMR ^1H ($CDCl_3$): $\delta = 7.56$ ppm (1H, H_{arom}); $\delta = 7.50$ ppm (1H, H_{arom}); $\delta = 7.35$ ppm (1H, H_{arom}); $\delta = 7.11$ ppm (1H, H_{arom}); $\delta = 5.72$ ppm (qd, 1H, O–CH); $\delta = 2.85$ ppm (td, 1H, N–CH); $\delta = 2.62$ ppm (td, 1H, N–CH); $\delta = 2.45$ ppm (d, 3H, N–CH_3); $\delta = 2.31$ ppm (d, 3H, N–CH_3); $\delta = 1.95$ ppm (m, 2H, –CH_2–); $\delta = 1.83$ ppm (m, 2H, –CH_2–); $\delta = 1.32$ ppm (m, 2H, –CH_2–); $\delta = 1.28$ ppm (d, 3H, –CH_3); $\delta = 1.26$ ppm (m, 2H, –CH_2–).

4.2.13. (*R*,*R*)-1,3-Dimethyl-2-(*R*)-(1-phenyl-ethoxy)-octahydro-benzo[1,3,2]diazaphosphole (*R*)-A4. NMR ^{31}P: $\delta = 139.65$ ppm ($CDCl_3$), 134.84 ppm (C_6D_6). NMR ^1H ($CDCl_3$): $\delta = 7.36$–7.21 ppm (5H, H_{arom}); $\delta = 5.11$ ppm (qd, 1H, O–CH); $\delta = 2.71$ ppm (td, 1H, N–CH); $\delta = 2.62$ ppm (td, 1H, N–CH); $\delta = 2.39$ ppm (d, 3H, N–CH_3); $\delta = 2.45$ ppm (d, 3H, N–CH_3); $\delta = 2.01$ ppm (m, 2H, –CH_2–); $\delta = 1.79$ ppm (m, 2H, –CH_2–); $\delta = 1.46$ ppm (d, 3H, –CH_3); $\delta = 1.26$ ppm (m, 2H, –CH_2–); $\delta = 1.04$ ppm (m, 2H, –CH_2–).

4.2.14. (*R*,*R*)-1,3-Dimethyl-2-(*R*)-(1-phenyl-ethoxy)-octahydro-benzo[1,3,2]diazaphosphole-2-sulfide (*R*)-A4S. NMR ^{31}P: $\delta = 86.02$ ppm ($CDCl_3$), 86.76 ppm (C_6D_6). NMR ^1H ($CDCl_3$): $\delta = 7.36$–7.24 ppm (5H, H_{arom}); $\delta = 5.49$ ppm (qd, 1H, O–CH); $\delta = 2.68$ ppm (td, 1H, N–CH); $\delta = 2.51$ ppm (td, 1H, N–CH); $\delta = 2.46$ ppm (d, 3H, N–CH_3); $\delta = 2.19$ ppm (d, 3H, N–CH_3); $\delta = 1.95$ ppm (m, 2H, –CH_2–); $\delta = 1.80$ ppm (m, 2H, –CH_2–); $\delta = 1.30$ ppm (d, 3H, –CH_3); $\delta = 1.28$ ppm (m, 2H, –CH_2–); $\delta = 1.16$ ppm (m, 2H, –CH_2–).

4.2.15. (*R*,*R*)-1,3-Dimethyl-2-(*S*)-(1-phenyl-ethoxy)-octahydro-benzo[1,3,2]diazaphosphole (*S*)-A4. NMR ^{31}P: $\delta = 143.74$ ppm ($CDCl_3$), 136.72 ppm (C_6D_6). NMR ^1H ($CDCl_3$): $\delta = 7.38$–7.20 ppm (5H, H_{arom}); $\delta = 5.11$ ppm (qd, 1H, O–CH); $\delta = 2.71$ ppm (td, 1H, N–CH); $\delta = 2.65$ ppm (td, 1H, N–CH); $\delta = 2.67$ ppm (d, 3H, N–CH_3); $\delta = 2.32$ ppm (d, 3H, N–CH_3); $\delta = 2.03$ ppm (m, 2H, –CH_2–); $\delta = 1.81$ ppm (m, 2H, –CH_2–); $\delta = 1.49$ ppm (d, 3H, –CH_3); $\delta = 1.22$ ppm (m, 2H, –CH_2–); $\delta = 1.06$ ppm (m, 2H, –CH_2–).

4.2.16. (*R*,*R*)-1,3-Dimethyl-2-(*S*)-(1-phenyl-ethoxy)-octahydro-benzo[1,3,2]diazaphosphole-2-sulfide (*S*)-A4S. NMR ^{31}P: $\delta = 86.83$ ppm ($CDCl_3$), 87.16 ppm (C_6D_6). NMR ^1H ($CDCl_3$): $\delta = 7.38$–7.28 ppm (5H, H_{arom}); $\delta = 5.57$ ppm (qd, 1H, O–CH); $\delta = 2.71$ ppm (td, 1H, N–CH); $\delta = 2.51$ ppm (td, 1H, N–CH); $\delta = 2.47$ ppm (d, 3H, N–CH_3); $\delta = 2.23$ ppm (d, 3H, N–CH_3); $\delta = 1.97$ ppm (m, 2H, –CH_2–); $\delta = 1.82$ ppm (m, 2H, –CH_2–); $\delta = 1.53$ ppm (d, 3H, –CH_3); $\delta = 1.30$ ppm (m, 2H, –CH_2–); $\delta = 1.18$ ppm (m, 2H, –CH_2–).

4.2.17. (*R*,*R*)-1,3-Dimethyl-2-(*R*)-(1-phenyl-propoxy)-octahydro-benzo[1,3,2]diazaphosphole (*R*)-A5. NMR ^{31}P: $\delta = 136.00$ ppm ($CDCl_3$), 140.58 ppm (C_6D_6). NMR ^1H ($CDCl_3$): $\delta = 7.35$–7.21 ppm (5H, H_{arom}); $\delta = 4.85$ ppm (td, 1H, O–CH); $\delta = 2.71$ ppm (td, 1H, N–CH); $\delta = 2.59$ ppm (td, 1H, N–CH); $\delta = 2.53$ ppm (d, 3H, N–CH_3); $\delta = 2.28$ ppm (d, 3H, N–CH_3); $\delta = 2.02$–1.67 ppm (m, 7H, –CH_2–); $\delta = 1.21$ ppm (m, 2H, –CH_2–); $\delta = 0.90$ ppm (d, 3H, –CH_3).

4.2.18. (*R*,*R*)-1,3-Dimethyl-2-(*R*)-(1-phenyl-propoxy)-octahydro-benzo[1,3,2]diazaphosphole-2-sulfide (*R*)-A5S. NMR ^{31}P: $\delta = 85.84$ ppm ($CDCl_3$), 87.13 ppm (C_6D_6). NMR ^1H ($CDCl_3$): $\delta = 7.33$–7.24 ppm (5H, H_{arom});

$\delta = 5.19$ ppm (td, 1H, O–CH); $\delta = 2.67$ ppm (td, 1H, N–CH); $\delta = 2.49$ ppm (td, 1H, N–CH); $\delta = 2.42$ ppm (d, 3H, N–CH_3); $\delta = 2.08$ ppm (d, 3H, N–CH_3); $\delta = 1.93$–1.73 ppm (m, 8H, –CH_2–); $\delta = 1.27$ ppm (m, 2H, –CH_2–); $\delta = 1.60$ ppm (m, 2H, –CH_2–); $\delta = 0.90$ ppm (d, 3H, –CH_3).

4.2.19. (*R*,*R*)-1,3-Dimethyl-2-(*S*)-(1-phenyl-propoxy)-octahydro-benzo[1,3,2]diazaphosphole (*S*)-A5. NMR ^{31}P: $\delta = 146.55$ ppm ($CDCl_3$), 142.29 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 7.35$–7.21 ppm (5H, H_{arom}); $\delta = 4.85$ ppm (td, 1H, O–CH); $\delta = 2.69$ ppm (td, 1H, N–CH); $\delta = 2.59$ ppm (td, 1H, N–CH); $\delta = 2.65$ ppm (d, 3H, N–CH_3); $\delta = 2.20$ ppm (d, 3H, N–CH_3); $\delta = 2.02$–1.67 ppm (m, 7H, –CH_2–); $\delta = 1.21$ ppm (m, 2H, –CH_2–); $\delta = 0.90$ ppm (d, 3H, –CH_3).

4.2.20. (*R*,*R*)-1,3-Dimethyl-2-(*S*)-(1-phenyl-propoxy)-octahydro-benzo[1,3,2]diazaphosphole-2-sulfide (*S*)-A5S. NMR ^{31}P: $\delta = 87.14$ ppm ($CDCl_3$), 88.07 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 7.33$–7.24 ppm (5H, H_{arom}); $\delta = 5.34$ ppm (td, 1H, O–CH); $\delta = 2.69$ (td, 1H, N–CH); $\delta = 2.51$ ppm (td, 1H, N–CH); $\delta = 2.48$ ppm (d, 3H, N–CH_3); $\delta = 2.12$ ppm (d, 3H, N–CH_3); $\delta = 1.93$–1.75 ppm (m, 8H, –CH_2–); $\delta = 1.28$ ppm (m, 2H, –CH_2–); $\delta = 1.62$ ppm (m, 2H, –CH_2–); $\delta = 0.91$ ppm (d, 3H, –CH_3).

4.2.21. (*R*,*R*)-1,3-Dimethyl-2-(*R*)-(1-phenyl-butoxy)-octahydro-benzo[1,3,2]diazaphosphole (*R*)-A6. NMR ^{31}P: $\delta = 135.58$ ppm ($CDCl_3$), 132.82 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 7.32$–7.22 ppm (5H, H_{arom}); $\delta = 4.90$ ppm (td, 1H, O–CH); $\delta = 2.64$ ppm (td, 2H, N–CH); $\delta = 2.51$ ppm (d, 3H, N–CH_3); $\delta = 2.23$ ppm (d, 3H, N–CH_3); $\delta = 1.98$ ppm (m, 2H, –CH_2–); $\delta = 1.84$–1.63 ppm (m, 4H, –CH_2–); $\delta = 1.52$ ppm (m, 2H, –CH_2–); $\delta = 1.42$–1.20 ppm (m, 4H, –CH_2–); $\delta = 0.89$ ppm (d, 3H, –CH_3).

4.2.22. (*R*,*R*)-1,3-Dimethyl-2-(*R*)-(1-phenyl-butoxy)-octahydro-benzo[1,3,2]diazaphosphole-2-sulfide (*R*)-A6S. NMR ^{31}P: $\delta = 85.76$ ppm ($CDCl_3$), 87.63 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 7.28$–7.16 ppm (5H, H_{arom}); $\delta = 5.19$ ppm (td, 1H, O–CH); $\delta = 2.70$ ppm (d, 3H, N–CH_3); $\delta = 2.33$ ppm (td, 2H, N–CH); $\delta = 1.98$ ppm (d, 3H, N–CH_3); $\delta = 1.89$ ppm (m, 2H, –CH_2–); $\delta = 1.83$–1.72 ppm (m, 4H, –CH_2–); $\delta = 1.26$ ppm (m, 2H, –CH_2–); $\delta = 1.24$–1.17 ppm (m, 4H, –CH_2–); $\delta = 0.86$ ppm (d, 3H, –CH_3).

4.2.23. (*R*,*R*)-1,3-Dimethyl-2-(*S*)-(1-phenyl-butoxy)-octahydro-benzo[1,3,2]diazaphosphole (*S*)-A6. NMR ^{31}P: $\delta = 146.53$ ppm ($CDCl_3$), 140.86 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 7.32$–7.22 ppm (5H, H_{arom}); $\delta = 4.90$ ppm (td, 1H, O–CH); $\delta = 2.69$ ppm (td, 2H, N–CH); $\delta = 2.65$ ppm (d, 3H, N–CH_3); $\delta = 2.19$ ppm (d, 3H, N–CH_3); $\delta = 2.01$ ppm (m, 2H, –CH_2–); $\delta = 1.82$–1.67 ppm (m, 4H, –CH_2–); $\delta = 1.48$ ppm (m, 2H, –CH_2–); $\delta = 1.36$–1.22 ppm (m, 4H, –CH_2–); $\delta = 0.94$ ppm (d, 3H, –CH_3).

4.2.24. (*R*,*R*)-1,3-Dimethyl-2-(*S*)-(1-phenyl-butoxy)-octahydro-benzo[1,3,2]diazaphosphole-2-sulfide (*S*)-A6S. NMR ^{31}P: $\delta = 87.04$ ppm ($CDCl_3$), 88.29 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 7.38$–7.27 ppm (5H, H_{arom}); $\delta = 5.43$ ppm (td, 1H, O–CH); $\delta = 2.71$ ppm (d, 3H, N–CH_3); $\delta = 2.46$ ppm (td, 2H, N–CH); $\delta = 2.09$ ppm (d, 3H, N–CH_3); $\delta = 1.98$ ppm (m, 2H, –CH_2–); $\delta = 1.87$–1.68 ppm (m, 4H, –CH_2–); $\delta = 1.43$ ppm (m, 2H, –CH_2–); $\delta = 1.37$–1.25 ppm (m, 4H, –CH_2–); $\delta = 0.95$ ppm (d, 3H, –CH_3).

4.2.25. (*R*,*R*)-1,3-Dimethyl-2-(*R*)-(2-methyl-1-phenyl-propoxy)-octahydro-benzo[1,3,2]diazaphosphole (*R*)-A7. NMR ^{31}P: $\delta = 133.81$ ppm ($CDCl_3$). NMR ^{1}H ($CDCl_3$): $\delta = 7.38$–7.27 ppm (5H, H_{arom}); $\delta = 4.88$ ppm (td, 1H, O–CH); $\delta = 2.73$ ppm (td, 2H, N–CH); $\delta = 2.31$ ppm (d, 3H, N–CH_3); $\delta = 2.27$ ppm (d, 3H, N–CH_3); $\delta = 1.88$ ppm (m, 2H, –CH_2–); $\delta = 1.35$ ppm (m, 3H, –CH_2–); $\delta = 1.21$ ppm (m, 4H, –CH_2–); $\delta = 0.75$ ppm (d, 3H, –CH_3); $\delta = 0.55$ ppm (d, 3H, –CH_3).

4.2.26. (*R*,*R*)-1,3-Dimethyl-2-(*R*)-(2-methyl-1-phenyl-propoxy)-octahydro-benzo[1,3,2]diazaphosphole-2- sulfide (*R*)-A7S. NMR ^{31}P: $\delta = 85.36$ ppm ($CDCl_3$). NMR ^{1}H ($CDCl_3$): $\delta = 7.31$–7.22 ppm (5H, H_{arom}); $\delta = 4.91$ ppm (td, 1H, O–CH); $\delta = 2.69$ (d, 2H, N–CH); $\delta = 2.39$ ppm (d, 3H, N–CH_3); $\delta = 2.38$ ppm (d, 3H, N–CH_3); $\delta = 1.82$ ppm (m, 2H, –CH_2–); $\delta = 1.28$ ppm (m, 3H, –CH_2–); $\delta = 1.12$ ppm (m, 4H, –CH_2–); $\delta = 0.01$ ppm (d, 3H, –CH_3); $\delta = 0.77$ ppm (d, 3H, –CH_3).

4.2.27. (*R*,*R*)-1,3-Dimethyl-2-(*S*)-(2-methyl-1-phenyl-propoxy)-octahydro-benzo[1,3,2]diazaphosphole (*S*)-A7. NMR ^{31}P: $\delta = 147.50$ ppm ($CDCl_3$). NMR ^{1}H ($CDCl_3$): $\delta = 7.38$–7.27 ppm (5H, H_{arom}); $\delta = 4.88$ ppm (td, 1H, O–CH); $\delta = 2.71$ (td, 2H, N–CH); $\delta = 2.39$ ppm (d, 3H, N–CH_3); $\delta = 2.27$ ppm (d, 3H, N–CH_3); $\delta = 1.85$ ppm (m, 2H, –CH_2–); $\delta = 1.33$ ppm (m, 3H, –CH_2–); $\delta = 1.24$ ppm (m, 4H, –CH_2–); $\delta = 0.79$ ppm (d, 3H, –CH_3); $\delta = 0.52$ ppm (d, 3H, –CH_3).

4.2.28. (*R*,*R*)-1,3-Dimethyl-2-(*S*)-(2-methyl-1-phenyl-propoxy)-octahydro-benzo[1,3,2]diazaphosphole-2- sulfide (*S*)-A7S. NMR ^{31}P: $\delta = 83.99$ ppm ($CDCl_3$). NMR ^{1}H ($CDCl_3$): $\delta = 7.31$–7.22 ppm (5H, H_{arom}); $\delta = 5.02$ ppm (td, 1H, O–CH); $\delta = 2.68$ ppm (td, 2H, N–CH); $\delta = 2.65$ ppm (d, 3H, N–CH_3); $\delta = 2.42$ ppm (d, 3H, N–CH_3); $\delta = 1.80$ ppm (m, 2H, –CH_2–); $\delta = 1.28$ ppm (m, 3H, –CH_2–); $\delta = 1.11$ ppm (m, 4H, –CH_2–); $\delta = 0.98$ ppm (d, 3H, –CH_3); $\delta = 0.71$ ppm (d, 3H, –CH_3).

4.2.29. (*R*,*R*)-1,3-Dimethyl-2-(*R*)-(1-phenyl-pentyloxy)-octahydro-benzo[1,3,2]diazaphosphole (*R*)-A8. NMR ^{31}P: $\delta = 135.28$ ppm (C_6D_6).

4.2.30. (*R*,*R*)-1,3-Dimethyl-2-(*R*)-(1-phenyl-pentyloxy)-octahydro-benzo[1,3,2]diazaphosphole-2-sulfide (*R*)-A8S. NMR ^{31}P: $\delta = 85.95$ ppm (C_6D_6).

4.2.31. (*R*,*R*)-1,3-Dimethyl-2-(*S*)-(1-phenyl-pentyloxy)-octahydro-benzo[1,3,2]diazaphosphole (*S*)-A8. NMR ^{31}P: $\delta = 144.23$ ppm (C_6D_6).

4.2.32. (*R*,*R*)-1,3-Dimethyl-2-(*S*)-(1-phenyl-pentyloxy)-octahydro-benzo[1,3,2]diazaphosphole-2-sulfide (*S*)-A8S. NMR ^{31}P: $\delta = 86.90$ ppm (C_6D_6).

4.2.33. (*R*,*R*)-1,3-Dimethyl-2-(*R*)-(1-phenyl-decyloxy)-octahydro-benzo[1,3,2]diazaphosphole (*R*)-A9. NMR ^{31}P: $\delta = 135.55$ ppm ($CDCl_3$), 142.21 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 7.27$–7.16 ppm (5H, H_{arom}); $\delta = 4.86$ ppm (td, 1H, O–CH); $\delta = 2.69$ ppm (td, 2H, N–CH); $\delta = 2.63$ ppm (d, 3H, N–CH_3); $\delta = 2.28$ ppm (d, 3H, N–CH_3); $\delta = 2.48$ ppm (m, 2H, –CH_2–); $\delta = 2.02$ ppm (m, 4H, –CH_2–); $\delta = 1.97$ ppm (m, 2H, –CH_2–); $\delta = 1.69$ ppm (m, 2H, –CH_2–); $\delta = 1.26$ ppm (m, 10H, –CH_2–); $\delta = 1.01$ ppm (m, 4H, –CH_2–); $\delta = 0.89$ ppm (d, 3H, –CH_3).

4.2.34. (*R*,*R*)-1,3-Dimethyl-2-(*R*)-(1-phenyl-decyloxy)-octahydro-benzo[1,3,2]diazaphosphole-2-sulfide (*R*)-A9S. NMR ^{31}P: $\delta = 85.75$ ppm ($CDCl_3$), 86.97 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 7.27$–7.16 ppm (5H, H_{arom}); $\delta = 5.18$ ppm (td, 1H, O–CH); $\delta = 2.71$ ppm (td, 2H, N–CH); $\delta = 2.33$ ppm (d, 3H, N–CH_3); $\delta = 1.98$ ppm (d, 3H, N–CH_3); $\delta = 1.84$ ppm (m, 2H, –CH_2–); $\delta = 1.81$ ppm (m, 4H, –CH_2–); $\delta = 1.19$ ppm (m, 18H, –CH_2–); $\delta = 0.81$ ppm (d, 3H, –CH_3).

4.2.35. (*R*,*R*)-1,3-Dimethyl-2-(*S*)-(1-phenyl-decyloxy)-octahydro-benzo[1,3,2]diazaphosphole (*S*)-A9. NMR ^{31}P: $\delta = 146.53$ ppm ($CDCl_3$), 151.09 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 7.36$–7.21 ppm (5H, H_{arom}); $\delta = 4.86$ ppm (td, 1H, O–CH); $\delta = 2.69$ ppm (td, 2H, N–CH); $\delta = 2.63$ ppm (d, 3H, N–CH_3); $\delta = 2.28$ ppm (d, 3H, N–CH_3); $\delta = 2.48$ ppm (m, 2H, –CH_2–); $\delta = 2.02$ ppm (m, 4H, –CH_2–); $\delta = 1.97$ ppm (m, 2H, –CH_2–); $\delta = 1.69$ ppm (m, 2H, –CH_2–); $\delta = 1.26$ ppm (m, 10H, –CH_2–); $\delta = 1.01$ ppm (m, 4H, –CH_2–); $\delta = 0.89$ ppm (d, 3H, –CH_3).

4.2.36. (*R*,*R*)-1,3-Dimethyl-2-(*S*)-(1-phenyl-decyloxy)-octahydro-benzo[1,3,2]diazaphosphole-2-sulfide (*S*)-A9S. NMR ^{31}P: $\delta = 87.04$ ppm ($CDCl_3$), 87.94 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 7.36$–7.26 ppm (5H, H_{arom}); $\delta = 5.40$ ppm (td, 1H, O–CH); $\delta = 2.80$ ppm (td, 2H, N–CH); $\delta = 2.49$ ppm (d, 3H, N–CH_3); $\delta = 2.11$ ppm (d, 3H, N–CH_3); $\delta = 2.47$ ppm (m, 2H, –CH_2–); $\delta = 2.11$ ppm (m, 4H, –CH_2–); $\delta = 2.08$ ppm (m, 2H, –CH_2–); $\delta = 1.24$ ppm (m, 16H, –CH_2–); $\delta = 0.89$ ppm (d, 3H, –CH_3).

4.2.37. 2-(*R*)-(2-Chloro-1-phenyl-ethoxy)-(*R*,*R*)-1,3-dimethyl-octahydro-benzo[1,3,2]diazaphosphole (*R*)-A10. NMR ^{31}P: $\delta = 149.03$ ppm ($CDCl_3$), 152.28 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 7.39$–7.25 ppm (5H, H_{arom}); $\delta = 5.14$ ppm (td, 1H, O–CH); $\delta = 3.57$ ppm (m, 2H, –CH_2–Cl); $\delta = 2.71$ ppm (td, 2H, N–CH); $\delta = 2.52$ ppm (d, 3H, N–CH_3); $\delta = 2.38$ ppm (d, 3H, N–CH_3); $\delta = 1.99$ ppm (m, 2H, –CH_2–); $\delta = 1.79$ ppm (m, 2H, –CH_2–); $\delta = 1.22$ ppm (m, 4H, –CH_2–).

4.2.38. 2-(*R*)-(2-Chloro-1-phenyl-ethoxy)-(*R*,*R*)-1,3-dimethyl-octahydro-benzo[1,3,2]diazaphosphole-2-sulfide (*R*)-A10S. NMR ^{31}P: $\delta = 87.63$ ppm ($CDCl_3$), 88.11 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 7.45$–7.22 ppm (5H, H_{arom}); $\delta = 5.55$ ppm (td, 1H, O–CH); $\delta = 3.70$ ppm (m, 2H, –CH_2–Cl); $\delta = 2.70$ ppm (td, 2H, N–CH); $\delta = 2.45$ ppm (d, 3H, N–CH_3); $\delta = 2.05$ ppm (d, 1H, N–CH_3); $\delta = 1.95$ ppm (m, 2H, –CH_2–); $\delta = 1.80$ ppm (m, 2H, –CH_2–); $\delta = 1.23$ ppm (m, 4H, –CH_2–).

4.2.39. 2-(*S*)-(2-Chloro-1-phenyl-ethoxy)-(*R*,*R*)-1,3-dimethyl-octahydro-benzo[1,3,2]diazaphosphole (*S*)-A10. NMR ^{31}P: $\delta = 136.32$ ppm ($CDCl_3$), 143.46 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 7.40$–7.28 ppm (5H, H_{arom}); $\delta = 5.14$ ppm (td, 1H, O–CH); $\delta = 3.60$ ppm (m, 2H, –CH_2–Cl); $\delta = 2.71$ ppm (td, 2H, N–CH); $\delta = 2.60$ ppm (d, 3H, N–CH_3); $\delta = 2.31$ ppm (d, 3H, N–CH_3); $\delta = 1.92$ ppm (m, 2H, –CH_2–); $\delta = 1.77$ ppm (m, 2H, –CH_2–); $\delta = 1.24$ ppm (m, 4H, –CH_2–).

4.2.40. 2-(*S*)-(2-Chloro-1-phenyl-ethoxy)-(*R*,*R*)-1,3-dimethyl-octahydro-benzo[1,3,2]diazaphosphole-2-sulfide (*S*)-A10S. NMR ^{31}P: $\delta = 86.36$ ppm ($CDCl_3$), 87.33 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 7.46$–7.28 ppm (5H, H_{arom}); $\delta = 5.45$ ppm (td, 1H, O–CH); $\delta = 3.68$ ppm (m, 2H, –CH_2–Cl); $\delta = 2.76$ ppm (td, 2H, N–CH); $\delta = 2.52$ ppm (d, 3H, N–CH_3); $\delta = 2.13$ ppm (d, 3H, N–CH_3); $\delta = 1.97$ ppm (m, 2H, –CH_2–); $\delta = 1.82$ ppm (m, 2H, –CH_2–); $\delta = 1.30$ ppm (m, 4H, –CH_2–).

4.2.41. 2-(*R*)-(3-Chloro-1-phenyl-propoxy)-(*R*,*R*)-1,3-dimethyl-octahydro-benzo[1,3,2]diazaphosphole (*R*)-A11. NMR ^{31}P: $\delta = 135.51$ ppm ($CDCl_3$), 141.54 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 7.38$–7.20 ppm (5H, H_{arom}); $\delta = 5.12$ ppm (qd, 1H, O–CH); $\delta = 3.65$ ppm (m, 2H, –CH_2–Cl); $\delta = 2.70$ ppm (td, 2H, N–CH); $\delta = 2.51$ ppm (d, 3H, N–CH_3); $\delta = 2.25$ ppm (d, 3H, N–CH_3); $\delta = 2.18$ ppm (m, 4H, –CH_2–); $\delta = 2.01$ ppm (m, 4H, –CH_2–); $\delta = 1.24$ ppm (m, 2H, –CH_2–).

4.2.42. 2-(*R*)-(3-Chloro-1-phenyl-propoxy)-(*R*,*R*)-1,3-dimethyl-octahydro-benzo[1,3,2]diazaphosphole-2-sulfide (*R*)-A11S. NMR ^{31}P: $\delta = 87.63$ ppm ($CDCl_3$), 88.11 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 7.37$–7.19 ppm (5H, H_{arom}); $\delta = 5.38$ ppm (qd, 1H, O–CH); $\delta = 3.56$ ppm (m, 2H, –CH_2–Cl); $\delta = 2.61$ ppm (td, 2H, N–CH); $\delta = 2.32$ ppm (d, 3H, N–CH_3); $\delta = 2.23$ ppm (d, 3H, N–CH_3); $\delta = 2.15$ ppm (m, 2H, –CH_2–);

$\delta = 1.98$ ppm (m, 2H, –CH_2–); $\delta = 1.80$ ppm (m, 2H, –CH_2–); $\delta = 1.25$ ppm (m, 4H, –CH_2–).

4.2.43. 2-(*S*)-(3-Chloro-1-phenyl-propoxy)-(*R*,*R*)-1,3-dimethyl-octahydro-benzo[1,3,2]diazaphosphole (*S*)-A11. NMR ^{31}P: $\delta = 146.47$ ppm ($CDCl_3$), 151.34 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 7.37$–7.24 ppm (5H, H_{arom}); $\delta = 5.12$ ppm (qd, 1H, O–CH); $\delta = 3.71$ ppm (m, 2H, –CH_2–Cl); $\delta = 2.70$ ppm (td, 2H, N–CH); $\delta = 2.61$ ppm (d, 3H, N–CH_3); $\delta = 2.25$ ppm (d, 3H, N–CH_3); $\delta = 2.20$ ppm (m, 4H, –CH_2–); $\delta = 2.00$ ppm (m, 4H, –CH_2–); $\delta = 1.24$ ppm (m, 2H, –CH_2–).

4.2.44. 2-(*S*)-(3-Chloro-1-phenyl-propoxy)-(*R*,*R*)-1,3-dimethyl-octahydro-benzo[1,3,2]diazaphosphole-2-sulfide (*S*)-A11S. NMR ^{31}P: $\delta = 87.06$ ppm ($CDCl_3$), 88.06 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 7.37$–7.28 ppm (5H, H_{arom}); $\delta = 5.48$ ppm (qd, 1H, O–CH); $\delta = 3.55$ ppm (m, 2H, –CH_2–Cl); $\delta = 2.61$ ppm (td, 2H, N–CH); $\delta = 2.44$ ppm (d, 3H, N–CH_3); $\delta = 2.21$ ppm (d, 3H, N–CH_3); $\delta = 2.16$ ppm (m, 2H, –CH_2–); $\delta = 1.98$ ppm (m, 2H, –CH_2–); $\delta = 1.82$ ppm (m, 2H, –CH_2–); $\delta = 1.27$ ppm (m, 4H, –CH_2–).

4.2.45. [2-(*R*,*R*)-(1,3-Dimethyl-octahydro-benzo[1,3,2]diazaphosphol-(*R*)-2-yloxy)-(*S*)-1-methyl-2-phenyl-ethyl]dimethyl-amine (*R*)-A12. NMR ^{31}P: $\delta = 148.02$ ppm ($CDCl_3$), 153.87 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 7.34$–7.20 ppm (5H, H_{arom}); $\delta = 4.89$ ppm (m, 1H, O–CH); $\delta = 2.76$ ppm (td, 2H, N–CH–); $\delta = 2.66$ ppm (td, 2H, N–CH–); $\delta = 2.65$ ppm (s, 3H, N–$(CH_3)_2$); $\delta = 2.56$ ppm (d, 1H, –CH–); $\delta = 2.54$ ppm (d, 3H, N–CH_3); $\delta = 2.46$ ppm (d, 3H, N–CH_3); $\delta = 2.14$ ppm (s, 3H, N–$(CH_3)_2$); $\delta = 2.51$–2.36 ppm (m, 4H, –CH_2–); $\delta = 1.78$ ppm (m, 2H, –CH_2–); $\delta = 1.20$ ppm (m, 4H, –CH_2–); $\delta = 1.03$ ppm (d, 3H, –CH_3).

4.2.46. [2-(*R*,*R*)-(1,3-Dimethyl-2-thioxo-octahydro-2λ5-benzo[1,3,2]diazaphosphol-(*R*)-2-yloxy)-(*S*)-1-methyl-2-phenyl-ethyl]dimethyl-amine (*R*)-A12S. NMR ^{31}P: $\delta = 86.16$ ppm ($CDCl_3$), 88.68 ppm (C_6D_6).

4.2.47. [2-(*R*,*R*)-(1,3-Dimethyl-octahydro-benzo[1,3,2]diazaphosphol-(*S*)-2-yloxy)-(*R*)-1-methyl-2-phenyl-ethyl]dimethyl-amine (*S*)-A12. NMR ^{31}P: $\delta = 135.57$ ppm ($CDCl_3$), 142.25 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 7.34$–7.20 ppm (5H, H_{arom}); $\delta = 5.01$ ppm (m, 1H, O–CH); $\delta = 2.80$ ppm (td, 2H, N–CH–); $\delta = 2.68$ ppm (td, 2H, N–CH–); $\delta = 2.62$ ppm (s, 3H, N-$(CH_3)_2$); $\delta = 2.56$ ppm (d, 1H, -CH–); $\delta = 2.51$ ppm (d, 3H, N–CH_3); $\delta = 2.48$ ppm (d, 3H, N–CH_3); $\delta = 2.12$ ppm (s, 3H, N–$(CH_3)_2$); $\delta = 2.41$–2.16 ppm (m, 4H, –CH_2–); $\delta = 1.79$ ppm (m, 2H, –CH_2–); $\delta = 1.20$ ppm (m, 4H, –CH_2–); $\delta = 1.04$ ppm (d, 3H, –CH_3).

4.2.48. [2-(*R*,*R*)-(1,3-Dimethyl-2-thioxo-octahydro-2λ5-benzo[1,3,2]diazaphosphol-(*S*)-2-yloxy)-(*R*)-1-methyl-2-phenyl-ethyl]dimethyl-amine (*S*)-A12S. NMR ^{31}P: $\delta = 87.60$ ppm ($CDCl_3$), 87.32 ppm (C_6D_6).

4.2.49. (*R*,*R*)-(1,3-Dimethyl-octahydro-benzo[1,3,2]diazaphosphol-(*R*)-2-yloxy)-phenyl-acetic acid methyl ester (*R*)-A13. NMR ^{31}P: $\delta = 141.12$ ppm ($CDCl_3$).

4.2.50. (*R*,*R*)-(1,3-Dimethyl-2-thioxo-octahydro-2λ5-benzo[1,3,2]diazaphosphol-(*R*)-2-yloxy)-phenyl-acetic acid methyl ester (*R*)-A13S. NMR ^{31}P: $\delta = 88.37$ ppm ($CDCl_3$).

4.2.51. (*R*,*R*)-(1,3-Dimethyl-octahydro-benzo[1,3,2]diazaphosphol-(*S*)-2-yloxy)-phenyl-acetic acid methyl ester (*S*)-A13. NMR ^{31}P: $\delta = 137.47$ ppm ($CDCl_3$).

4.2.52. (*R*,*R*)-(1,3-Dimethyl-2-thioxo-octahydro-2λ5-benzo[1,3,2]diazaphosphol-(*S*)-2-yloxy)-phenyl-acetic acid methyl ester (*S*)-A13S. NMR ^{31}P: $\delta = 88.07$ ppm ($CDCl_3$).

4.2.53. (*R*,*R*)-(1,3-Dimethyl-octahydro-benzo[1,3,2]diazaphosphol-(*R*)-2-yloxy)-phenyl-acetic acid ethyl ester (*R*)-A14. NMR ^{31}P: $\delta = 141.37$ ppm ($CDCl_3$). NMR ^{1}H ($CDCl_3$): $\delta = 7.39$–7.21 ppm (5H, H_{arom}); $\delta = 5.26$ ppm (d, 1H, O–CH); $\delta = 4.16$ ppm (td, 1H. N–CH–); $\delta = 4.08$ ppm (td, 1H, N–CH–); $\delta = 2.60$ ppm (qd, 1H, –CH_2–); $\delta = 2.54$ ppm (d, 3H, N–CH_3); $\delta = 2.28$ ppm (d, 3H, N–CH_3); $\delta = 2.36$ ppm (s, 3H, –CH_3),); $\delta = 2.51$–2.36 ppm (m, 4H, –CH_2–); $\delta = 1.93$ ppm (m, 2H, –CH_2–), $\delta = 1.74$ ppm (m, 2H, –CH_2–); $\delta = 1.10$ ppm (d, 3H, –CH_3).

4.2.54. (*R*,*R*)-(1,3-Dimethyl-2-thioxo-octahydro-2λ5-benzo[1,3,2]diazaphosphol-(*R*)-2-yloxy)-phenyl-acetic acid ethyl ester (*R*)-A14S. NMR ^{31}P: $\delta = 87.04$ ppm ($CDCl_3$).

4.2.55. (*R*,*R*)-(1,3-Dimethyl-octahydro-benzo[1,3,2]diazaphosphol-(*S*)-2-yloxy)-phenyl-acetic acid ethyl ester (*S*)-A14. NMR ^{31}P: $\delta = 135.90$ ppm ($CDCl_3$). NMR ^{1}H ($CDCl_3$): $\delta = 7.39$–7.21 ppm (5H, H_{arom}); $\delta = 5.41$ ppm (d, 1H, O–CH); $\delta = 4.15$ ppm (td, 1H. N–CH–); $\delta = 4.06$ ppm (td, 1H, N–CH–); $\delta = 2.61$ ppm (qd, 1H, –CH_2–); $\delta = 2.54$ ppm (d, 3H, N–CH_3); $\delta = 2.28$ ppm (d, 3H, N–CH_3); $\delta = 2.35$ m (s, 3H, –CH_3),); $\delta = 2.51$–2.36 m (m, 4H, –CH_2–); $\delta = 1.93$ m (m, 2H, –CH_2–), $\delta = 1.74$ m (m, 2H, –CH_2–); $\delta = 1.09$ m (d, 3H, –CH_3).

4.2.56. (*R*,*R*)-(1,3-Dimethyl-2-thioxo-octahydro-2λ5-benzo[1,3,2]diazaphosphol-(*S*)-2-yloxy)-phenyl-acetic acid ethyl ester (*S*)-A14S. NMR ^{31}P: $\delta = 88.28$ ppm ($CDCl_3$).

4.2.57. (*R*,*R*)-(1,3-Dimethyl-octahydro-benzo[1,3,2]diazaphosphol-(*R*)-2-yloxy)-phenyl-acetic acid (*R*)-A15. NMR ^{31}P: $\delta = 148.11$ ppm ($CDCl_3$).

4.2.58. (*R*,*R*)-(1,3-Dimethyl-2-thioxo-octahydro-2λ5-benzo[1,3,2]diazaphosphol-(*R*)-2-yloxy)-phenyl-acetic acid (*R*)-A15S. NMR ^{31}P: $\delta = 88.37$ ppm ($CDCl_3$).

4.2.59. (*R*,*R*)-(1,3-Dimethyl-octahydro-benzo[1,3,2]diazaphosphol-(*S*)-2-yloxy)-phenyl-acetic acid (*S*)-A15. NMR ^{31}P: $\delta = 147.34$ ppm ($CDCl_3$).

4.2.60. (*R*,*R*)-(1,3-Dimethyl-2-thioxo-octahydro-2λ5-benzo[1,3,2]diazaphosphol-(*S*)-2-yloxy)-phenyl-acetic acid (*S*)-A15S. NMR ^{31}P: $\delta = 86.99$ ppm ($CDCl_3$).

4.2.61. (*R*,*R*)-1,3-Dimethyl-(*R*)-2-(1-phenyl-allyloxy)-octahydro-benzo[1,3,2]diazaphosphole (*R*)-A16. NMR ^{31}P: $\delta = 140.31$ ppm ($CDCl_3$), 145.97 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 7.37$–7.26 ppm (5H, H_{arom}); $\delta = 5.31$ ppm (m, 1H, CH_{allyl}); $\delta = 5.32$ ppm (dd, 1H, O–CH); $\delta = 5.27$ and 5.19 ppm (dd, 2H, CH_{2allyl}); $\delta = 2.79$ ppm (td, 1H, N–CH–); $\delta = 2.52$ ppm (td, 1H, N–CH–); $\delta = 2.46$ ppm (d, 3H, N–CH_3); $\delta = 2.26$ ppm (d. 3H. N–CH_3); $\delta = 2.19$ ppm (m, 2H, –CH_2–), $\delta = 1.99$ ppm (m, 2H, –CH_2–); $\delta = 1.30$ ppm (d, 4H, –CH_3).

4.2.62. (*R*,*R*)-1,3-Dimethyl-(*R*)-2-(1-phenyl-allyloxy)-octahydro-benzo[1,3,2]diazaphosphole-2-sulfide (*R*)-A16S. NMR ^{31}P: $\delta = 87.49$ ppm ($CDCl_3$), 87.51 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 7.36$–7.26 ppm (5H, H_{arom}); $\delta = 5.98$ ppm (m, 1H, CH_{allyl}); $\delta = 5.89$ ppm (dd, 1H, O–CH); $\delta = 5.29$ and 5.18 ppm (dd, 2H, CH_{2allyl}); $\delta = 2.65$ ppm (td, 2H, N–CH–); $\delta = 2.48$ ppm (d, 3H, N–CH_3); $\delta = 2.20$ ppm (d, 3H, N–CH_3); $\delta = 1.97$ ppm (m, 2H, –CH_2–), $\delta = 1.80$ ppm (m, 2H, –CH_2–); $\delta = 1.19$ ppm (d, 4H, –CH_3).

4.2.63. (*R*,*R*)-1,3-Dimethyl-(*S*)-2-(1-phenyl-allyloxy)-octahydro-benzo[1,3,2]diazaphosphole (*S*)-A16. NMR ^{31}P: $\delta = 142.94$ ppm ($CDCl_3$), 148.58 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 7.38$–7.24 ppm (5H, H_{arom}); $\delta = 5.98$ ppm (m, 1H, CH_{allyl}); $\delta = 5.46$ ppm (dd, 1H, O–CH); $\delta = 5.20$ and 5.10 ppm (dd, 2H, CH_{2allyl}); $\delta = 2.65$ ppm (td, 2H, N–CH–); $\delta = 2.63$ ppm (d, 3H, N–CH_3); $\delta = 2.43$ ppm (d, 3H, N–CH_3); $\delta = 2.06$ ppm (m, 2H, –CH_2–), $\delta = 1.80$ ppm (m, 2H, –CH_2–); $\delta = 1.24$ ppm (d, 4H, –CH_3).

4.2.64. (*R*,*R*)-1,3-Dimethyl-(*S*)-2-(1-phenyl-allyloxy)-octahydro-benzo[1,3,2]diazaphosphole-2-sulfide (*S*)-A16S. NMR ^{31}P: $\delta = 86.61$ ppm ($CDCl_3$), 88.34 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 7.39$–7.26 ppm (5H, H_{arom}); $\delta = 6.01$ ppm (m, 1H, CH_{allyl}); $\delta = 5.35$ ppm (dd, 1H, O–CH); $\delta = 5.24$ and 5.22 ppm (dd, 2H, CH_{2allyl}); $\delta = 2.65$ ppm (td, 2H, N–CH–); $\delta = 2.31$ ppm (d, 3H, N–CH_3); $\delta = 2.25$ ppm (d, 3H, N–CH_3); $\delta = 2.21$ ppm (m, 2H, –CH_2–), $\delta = 1.84$ ppm (m, 2H, –CH_2–); $\delta = 1.25$ ppm (d, 4H, –CH_3).

4.2.65. (*R*,*R*)-1,3-Dimethyl-(*R*)-2-(1-methyl-2-phenyl-ethoxy)-octahydro-benzo[1,3,2]diazaphosphole (*R*)-A20. NMR ^{31}P: $\delta = 141.54$ ppm ($CDCl_3$).

4.2.66. (*R*,*R*)-1,3-Dimethyl-(*R*)-2-(1-methyl-2-phenyl-ethoxy)-octahydro-benzo[1,3,2]diazaphosphole-2-sulfide (*R*)-A20S. NMR ^{31}P: $\delta = 87.16$ ppm ($CDCl_3$). NMR ^{1}H ($CDCl_3$): $\delta = 7.25$–7.14 ppm (5H, H_{arom}); $\delta = 4.03$ ppm (m, 1H, O–CH); $\delta = 2.73$ ppm (td, 1H, N–CH); $\delta = 2.58$ ppm (td, 1H, N–CH); $\delta = 2.44$ ppm (d, 2H, –CH_2–); $\delta = 2.42$ ppm (d, 3H, N–CH_3); $\delta = 2.29$ ppm (d, 3H, N–CH_3); $\delta = 1.90$ ppm (m, 2H, –CH_2–); $\delta = 1.73$ ppm (m, 2H, –CH_2–); $\delta = 1.26$–1.19 ppm (m, 4H, –CH_2–); $\delta = 1.21$ ppm (d, 3H, –CH_3).

4.2.67. (*R*,*R*)-1,3-Dimethyl-(*S*)-2-(1-methyl-2-phenyl-ethoxy)-octahydro-benzo[1,3,2]diazaphosphole (*S*)-A20S. NMR ^{31}P: $\delta = 139.53$ ppm ($CDCl_3$).

4.2.68. (*R*,*R*)-1,3-Dimethyl-(*S*)-2-(1-methyl-2-phenyl-ethoxy)-octahydro-benzo[1,3,2]diazaphosphole-2-sulfide (*S*)-A20S. NMR ^{31}P: $\delta = 87.36$ ppm ($CDCl_3$). NMR ^{1}H ($CDCl_3$): $\delta = 7.25$–7.14 ppm (5H, H_{arom}); $\delta = 3.63$ ppm (m, 1H, O–CH); $\delta = 2.71$ ppm (td, 1H, N–CH); $\delta = 2.55$ ppm (td, 1H, N–CH); $\delta = 2.51$ ppm (d, 2H, –CH_2–); $\delta = 2.34$ ppm (d, 3H, N–CH_3); $\delta = 2.23$ ppm (d, 3H, N–CH_3); $\delta = 1.92$ ppm (m, 2H, –CH_2–); $\delta = 1.72$ ppm (m, 2H, –CH_2–); $\delta = 1.29$–1.25 ppm (m, 4H, –CH_2–); $\delta = 1.26$ ppm (d, 3H, –CH_3).

4.2.69. (*R*)-2-*sec*-Butoxy-(*R*,*R*)-1,3-dimethyl-octahydro-benzo[1,3,2]diazaphosphole (*R*)-A21. NMR ^{31}P: $\delta = 145.13$ ppm ($CDCl_3$), 145.32 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 3.91$ ppm (m, 1H, O–CH); $\delta = 2.71$ ppm (d, 3H, N–CH_3); $\delta = 2.64$ ppm (td, 1H, N–CH); $\delta = 2.53$ ppm (d, 3H, N–CH_3); $\delta = 2.42$ ppm (td, 1H, N–CH); $\delta = 2.01$ ppm (m, 2H, –CH_2–); $\delta = 1.74$ ppm (m, 2H, –CH_2–); $\delta = 1.45$ ppm (m, 2H, –CH_2–); $\delta = 1.21$ ppm (m, 2H, –CH_2–); $\delta = 1.71$ ppm (d, 3H, –CH_3); $\delta = 0.90$ ppm (t, 3H, –CH_3).

4.2.70. (*R*)-2-*sec*-Butoxy-(*R*,*R*)-1,3-dimethyl-octahydro-benzo[1,3,2]diazaphosphole-2-sulfide (*R*)-A21S. NMR ^{31}P: $\delta = 86.41$ ppm ($CDCl_3$), 87.18 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 4.32$ ppm (m, 1H, O–CH); $\delta = 2.68$ ppm (d, 3H, N–CH_3); $\delta = 2.50$ ppm (d, 3H, N–CH_3); $\delta = 2.45$ ppm (td, 1H, N–CH); $\delta = 2.38$ ppm (td, 1H, N–CH); $\delta = 1.98$ ppm (m, 2H, –CH_2–); $\delta = 1.81$ ppm (m, 2H, –CH_2–); $\delta = 1.57$ ppm (m, 2H, –CH_2–); $\delta = 1.30$ ppm (m, 2H, –CH_2–); $\delta = 1.26$ ppm (d, 3H, –CH_3); $\delta = 0.89$ ppm (t, 3H, –CH_3).

4.2.71. (*S*)-2-*sec*-Butoxy-(*R*,*R*)-1,3-dimethyl-octahydro-benzo[1,3,2]diazaphosphole (*S*)-A21. NMR ^{31}P: $\delta = 141.27$ ppm ($CDCl_3$), 141.43 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 3.91$ ppm (m, 1H, O–CH); $\delta = 2.71$ ppm (d, 3H, N–CH_3); $\delta = 2.63$ ppm (td, 1H, N–CH);

$\delta = 2.54$ ppm (d, 3H, N–CH_3); $\delta = 2.41$ ppm (td, 1H, N–CH); $\delta = 2.01$ ppm (m, 2H, –CH_2–); $\delta = 1.74$ ppm (m, 2H, –CH_2–); $\delta = 1.45$ ppm (m, 2H, –CH_2–); $\delta = 1.21$ ppm (m, 2H, –CH_2–); $\delta = 1.73$ ppm (d, 3H, –CH_3); $\delta = 0.88$ ppm (t, 3H, –CH_3).

4.2.72. (*S*)-2-*sec*-Butoxy-(*R*,*R*)-1,3-dimethyl-octahydrobenzo[1,3,2]diazaphosphole-2-sulfide (*S*)-A21S. NMR ^{31}P: $\delta = 86.11$ ppm ($CDCl_3$), 87.41 ppm (C_6D_6). NMR ^{1}H ($CDCl_3$): $\delta = 4.22$ ppm (m, 1H, O–CH); $\delta = 2.65$ ppm (d, 3H, N–CH_3); $\delta = 2.51$ ppm (d, 3H, N–CH_3); $\delta = 2.46$ ppm (td, 1H, N–CH); $\delta = 2.42$ ppm (td, 1H, N–CH); $\delta = 1.95$ ppm (m, 2H, –CH_2–); $\delta = 1.75$ ppm (m, 2H, –CH_2–); $\delta = 1.51$ ppm (m, 2H, –CH_2–); $\delta = 1.33$ ppm (m, 2H, –CH_2–); $\delta = 1.21$ ppm (d, 3H, –CH_3); $\delta = 0.87$ ppm (t, 3H, –CH_3).

4.2.73. (*R*,*R*)-1,3-Dimethyl-2-(*R*)-(1-naphthalen-1-yl-ethoxy)-4,5-diphenyl-[1,3,2]diazaphospholidine (*R*)-B1. NMR ^{31}P ($CDCl_3$): $\delta = 139.26$ ppm. NMR ^{1}H ($CDCl_3$): $\delta = 6.97$–8.23 ppm (17H, H_{arom}); $\delta = 5.65$ ppm (qd, 1H, O–CH); $\delta = 4.11$ ppm (dd, 1H, –CH–N–) $\delta = 3.97$ ppm (dd, 1H, –CH–N–); $\delta = 2.41$ ppm (d, 3H, N–CH_3); $\delta = 2.23$ ppm (d, 3H, N–CH_3); $\delta = 1.58$ ppm (d, 3H, –CH_3).

4.2.74. (*R*,*R*)-1,3-dimethyl-2-(*R*)-(1-naphthalen-1-yl-ethoxy)-4,5-diphenyl-[1,3,2]diazaphospholidine-2-sulfide (*R*)-B1S. NMR ^{31}P ($CDCl_3$): $\delta = 82.82$ ppm. NMR ^{1}H ($CDCl_3$): $\delta = 6.67$–7.62 ppm (17H, H_{arom}); $\delta = 5.60$ ppm (qd, 1H, O–CH); $\delta = 4.02$ ppm (dd, 1H, –CH–N–) $\delta = 3.87$ ppm (dd, 1H, –CH–N–); $\delta = 2.59$ ppm (d, 3H, N–CH_3); $\delta = 1.89$ ppm (d, 3H, N–CH_3); $\delta = 1.58$ ppm (d, 3H, –CH_3).

4.2.75. (*R*,*R*)-1,3-dimethyl-2-(*S*)-(1-naphthalen-1-yl-ethoxy)-4,5-diphenyl-[1,3,2]diazaphospholidine (*S*)-B1. NMR ^{31}P ($CDCl_3$): $\delta = 140.39$ ppm. NMR ^{1}H ($CDCl_3$): $\delta = 7.48$–6.81 ppm (17H, H_{arom}); $\delta = 5.83$ ppm (qd, 1H, O–CH); $\delta = 4.14$ ppm (dd, 1H, –CH–N–); $\delta = 3.51$ ppm (dd, 1H, –CH–N–); $\delta = 2.48$ ppm (d, 3H, N–CH_3); $\delta = 2.30$ ppm (d, 3H, N–CH_3); $\delta = 1.71$ ppm (d, 3H, –CH_3).

4.2.76. (*R*,*R*)-1,3-Dimethyl-2-(*S*)-(1-naphthalen-1-yl-ethoxy)-4,5-diphenyl-[1,3,2]diazaphospholidine-2-sulfide (*S*)-B1S. NMR ^{31}P ($CDCl_3$): $\delta = 83.26$ ppm NMR ^{1}H ($CDCl_3$): $\delta = 8.32$–7.20 ppm (17H, H_{arom}); $\delta = 5.87$ ppm (qd, 1H, O–CH); $\delta = 4.10$ ppm (dd, 1H, –CH–N–) $\delta = 3.93$ ppm (dd, 1H, –CH–N–); $\delta = 2.48$ ppm (d, 3H, N–CH_3); $\delta = 2.01$ ppm (d, 3H, N–CH_3); $\delta = 1.65$ ppm (d, 3H, –CH_3).

4.2.77. (*R*,*R*)-1,3-Dimethyl-2-(*R*)-(1-naphthalen-2-yl-ethoxy)-4,5-diphenyl-[1,3,2]diazaphospholidine (*R*)-B2. NMR ^{31}P ($CDCl_3$): $\delta = 141.16$ ppm. NMR ^{1}H ($CDCl_3$): $\delta = 6.97$–7.76 ppm (17H, H_{arom}); $\delta = 5.39$ ppm (qd, 1H, O–CH); $\delta = 4.18$ ppm (dd, 1H, –CH–N–); $\delta = 3.89$ ppm (dd, 1H, –CH–N–); $\delta = 2.32$ ppm (d, 3H, N–CH_3); $\delta = 2.23$ ppm (d, 3H, N–CH_3); $\delta = 1.62$ ppm (d, 3H, –CH_3).

4.2.78. (*R*,*R*)-1,3-Dimethyl-2-(*R*)-(1-naphthalen-2-yl-ethoxy)-4,5-diphenyl-[1,3,2]diazaphospholidine-2-sulfide (*R*)-B2S. NMR ^{31}P ($CDCl_3$): $\delta = 82.92$ ppm. NMR ^{1}H ($CDCl_3$): $\delta = 6.83$–7.42 ppm (17H, H_{arom}); $\delta = 5.82$ ppm (qd, 1H, O–CH); $\delta = 4.00$ ppm (dd, 1H, –CH–N–); $\delta = 3.80$ ppm (dd, 1H, –CH–N–); $\delta = 2.34$ ppm (d, 3H, N–CH_3); $\delta = 1.98$ ppm (d, 3H, N–CH_3); $\delta = 1.66$ ppm (d, 3H, –CH_3).

4.2.79. (*R*,*R*)-1,3-Dimethyl-2-(*S*)-(1-naphthalen-2-yl-ethoxy)-4,5-diphenyl-[1,3,2]diazaphospholidine (*S*)-B2. NMR ^{31}P ($CDCl_3$): $\delta = 139.65$ ppm. NMR ^{1}H ($CDCl_3$): $\delta = 6.75$–7.86 ppm (17H, H_{arom}); $\delta = 5.45$ ppm (qd, 1H, O–CH); $\delta = 4.25$ ppm (dd, 1H, –CH–N–); $\delta = 4.05$ ppm (dd, 1H, –CH–N–); $\delta = 2.62$ ppm (d, 3H, N–CH_3); $\delta = 2.22$ ppm (d, 3H, N–CH_3); $\delta = 1.73$ ppm (d, 3H, –CH_3).

4.2.80. (*R*,*R*)-1,3-Dimethyl-2-(*S*)-(1-naphthalen-2-yl-ethoxy)-4,5-diphenyl-[1,3,2]diazaphospholidine-2-sulfide (*S*)-B2S. NMR ^{31}P ($CDCl_3$): $\delta = 82.89$ ppm. NMR ^{1}H ($CDCl_3$): $\delta = 6.82$–7.94 ppm (17H, H_{arom}); $\delta = 5.90$ ppm (qd, 1H, O–CH); $\delta = 4.08$ ppm (dd, 1H, –CH–N–); $\delta = 4.01$ ppm (dd, 1H, –CH–N–); $\delta = 2.23$ ppm (d, 3H, N–CH_3); $\delta = 1.97$ ppm (d, 3H, N–CH_3); $\delta = 1.61$ ppm (d, 3H, –CH_3).

4.2.81. (*R*,*R*)-2-[1-(*R*)-(2-Bromo-phenyl)-ethoxy]-1,3-dimethyl-4,5-diphenyl-[1,3,2]diazaphospholidine (*R*)-B3. NMR ^{31}P ($CDCl_3$): $\delta = 137.90$ ppm. NMR ^{1}H ($CDCl_3$): $\delta = 6.77$–7.44 ppm (14H, H_{arom}); $\delta = 5.61$ ppm (qd, 1H, O–CH); $\delta = 4.20$ ppm (dd, 1H, –CH–N–); $\delta = 3.88$ ppm (dd, 1H, –CH–N–); $\delta = 2.44$ ppm (d, 3H, N–CH_3); $\delta = 2.12$ ppm (d, 3H, N–CH_3); $\delta = 1.49$ ppm (d, 3H, –CH_3).

4.2.82. (*R*,*R*)-2-[1-(*R*)-(2-Bromo-phenyl)-ethoxy]-1,3-dimethyl-4,5-diphenyl-[1,3,2]diazaphospholidine-2-sulfide (*R*)-B3S. NMR ^{31}P ($CDCl_3$): $\delta = 82.95$ ppm. NMR ^{1}H ($CDCl_3$): $\delta = 6.76$–7.44 ppm (14H, H_{arom}); $\delta = 5.94$ ppm (qd, 1H, O–CH); $\delta = 4.07$ ppm (dd, 1H, –CH–N–); $\delta = 3.82$ ppm (dd, 1H, –CH–N–); $\delta = 2.20$ ppm (d, 3H, N–CH_3); $\delta = 2.17$ ppm (d, 3H, N–CH_3); $\delta = 1.53$ ppm (d, 3H, –CH_3).

4.2.83. (*R*,*R*)-2-[1-(*S*)-(2-Bromo-phenyl)-ethoxy]-1,3-dimethyl-4,5-diphenyl-[1,3,2]diazaphospholidine (*S*)-B3. NMR ^{31}P ($CDCl_3$): $\delta = 139.25$ ppm. NMR ^{1}H ($CDCl_3$): $\delta = 7.45$–7.05 ppm (14H, H_{arom}); $\delta = 5.63$ ppm (qd, 1H, O–CH); $\delta = 4.21$ ppm (dd, 1H, –CH–N–); $\delta = 3.92$ ppm (dd, 1H, –CH–N–); $\delta = 2.16$ ppm (d, 3H,

N–CH_3); $\delta = 1.51$ ppm (d, 3H, N–CH_3); $\delta = 1.44$ ppm (d, 3H, –CH_3).

4.2.84. (*R*,*R*)-2-[1-(*S*)-(2-Bromo-phenyl)-ethoxy]-1,3-dimethyl-4,5-diphenyl-[1,3,2]diazaphospholidine-2-sulfide (*S*)-B3S. NMR ^{31}P ($CDCl_3$): $\delta = 82.68$ ppm. NMR ^{1}H ($CDCl_3$): $\delta = 6.76$–7.44 ppm (14H, H_{arom}); $\delta = 5.98$ ppm (qd, 1H, O–CH); $\delta = 4.11$ ppm (dd, 1H, –CH–N–); $\delta = 3.87$ ppm (dd, 1H, –CH–N–); $\delta = 2.29$ ppm (d, 3H, N–CH_3); $\delta = 2.25$ ppm (d, 3H, N–CH_3); $\delta = 1.542$ ppm (d, 3H, –CH_3).

4.2.85. (*R*,*R*)-1,3-Dimethyl-4,5-diphenyl-2-(*R*)-(1-phenyl-ethoxy)-[1,3,2]diazaphospholidine (*R*)-B4. NMR ^{31}P ($CDCl_3$): $\delta = 139.93$ ppm. NMR ^{1}H ($CDCl_3$): $\delta = 7.2$–7.4 ppm (15H, H_{arom}); $\delta = 5.67$ ppm (qd, 1H, O–CH, $^{3}J_{H-H} = 6.4$ Hz, $^{3}J_{H-P} = 12.8$ Hz); $\delta = 4.02$ ppm (dd, 1H, –CH–N–, $^{3}J_{H-H} = 9$ Hz, $^{3}J_{H-P} < 0.5$ Hz); $\delta = 3.78$ ppm (dd, 1H, –CH–N–, $^{3}J_{H-H} = 9$ Hz, $^{3}J_{H-P} = 2$ Hz); $\delta = 2.40$ ppm (d, 3H, N–CH_3, $^{3}J_{H-P} = 12.1$ Hz); $\delta = 2.11$ ppm (d, 3H, N–CH_3, $^{3}J_{H-P} = 12.4$ Hz); $\delta = 1.67$ ppm (d, 3H, –CH_3, $^{3}J_{H-H} = 6.6$ Hz).

4.2.86. (*R*,*R*)-1,3-Dimethyl-4,5-diphenyl-2-(*R*)-(1-phenyl-ethoxy)-[1,3,2]diazaphospholidine-2-sulfide (*R*)-B4S. NMR ^{31}P ($CDCl_3$): $\delta = 82.57$ ppm. NMR ^{1}H ($CDCl_3$): $\delta = 7.4$–6.5 ppm (15H, H_{arom}); $\delta = 5.72$ ppm (qd, 1H, O–CH, $^{3}J_{H-H} = 6.4$ Hz; $^{3}J_{H-P} = 12.1$ Hz); $\delta = 4.04$ ppm (dd, 1H, –CH–N–, $^{3}J_{H-H} = 8.37$ Hz, $^{3}J_{H-P} < 0.5$ Hz); $\delta = 3.97$ ppm (dd, 1H, –CH–N–, $^{3}J_{H-H} = 8.37$ Hz, $^{3}J_{H-P} = 1.97$ Hz); $\delta = 2.50$ ppm (d, 3H, N–CH_3; $^{3}J_{H-P} = 11.8$ Hz); $\delta = 2.19$ ppm (d, 3H, N–CH_3; $^{3}J_{H-P} = 12.3$ Hz); $\delta = 1.67$ ppm (d, 3H, –CH_3, $^{3}J_{H-H} = 6.4$ Hz). NMR ^{13}C ($CDCl_3$): $\delta = 142.92$, 142.86, 138.66, 138.59, 137.80, 137.70 ppm ($C_{IV\,arom}$); $\delta = 128.80$, 128.75, 128.49, 128.39, 128.21, 128.09, 127.98, 127.79, 127.67, 127.60, 126 ppm (C_{arom}); $\delta = 76.3$ ppm (O–CH); $\delta = 73$ and 71.5 ppm (N–CH–CH–N–); $\delta = 31.2$ and 29.5 ppm (N–CH_3); $\delta = 24.7$ ppm (–CH_3).

4.2.87. (*R*,*R*)-1,3-Dimethyl-4,5-diphenyl-2-(*S*)-(1-phenyl-ethoxy)-[1,3,2]diazaphospholidine (*S*)-B4. NMR ^{31}P ($CDCl_3$): $\delta = 139.46$ ppm. NMR ^{1}H ($CDCl_3$): $\delta = 7.2$–7.4 ppm (15H, H_{arom}); $\delta = 5.35$ ppm (qd, 1H, O–CH, $^{3}J_{H-H} = 6.9$ Hz, $^{3}J_{H-H} = 8.86$ Hz); $\delta = 4.04$ ppm (dd, 1H, –CH–N–, $^{3}J_{H-H} = 9$ Hz, $^{3}J_{H-P} = 3$ Hz); $\delta = 3.97$ ppm (dd, 1H, –CH–N–, $^{3}J_{H-H} = 9$ Hz, $^{3}J_{H-P} = 1.5$ Hz); $\delta = 2.49$ ppm (d, 3H, N–CH_3, $^{3}J_{H-P} = 11$ Hz); $\delta = 2.16$ ppm (d, 3H, N–CH_3, $^{3}J_{H-P} = 14$ Hz); $\delta = 1.60$ ppm (d, 3H, –CH_3, $^{3}J_{H-H} = 6.4$ Hz).

4.2.88. (*R*,*R*)-1,3-Dimethyl-4,5-diphenyl-2-(*S*)-(1-phenyl-ethoxy)-[1,3,2]diazaphospholidine-2-sulfide (*S*)-B4S. NMR ^{31}P ($CDCl_3$): $\delta = 82.29$ ppm. NMR ^{1}H ($CDCl_3$): $\delta = 7.4$–6.5 ppm (15H, H_{arom}); $\delta = 5.67$ ppm (qd, 1H, O–CH, $^{3}J_{H-H} = 6.9$ Hz, $^{3}J_{H-P} = 12.8$ Hz); $\delta = 3.97$ ppm (dd, 1H, –CH–N–, $^{3}J_{H-H} = 8.37$ Hz, $^{3}J_{H-P} < 0.5$ Hz); $\delta = 3.89$ ppm (dd, 1H, –CH–N–, $^{3}J_{H-H} = 8.37$ Hz, $^{3}J_{H-P} = 1.48$ Hz); $\delta = 2.36$ ppm (d, 3H, N–CH_3, $^{3}J_{H-P} = 12.3$ Hz); $\delta = 2.11$ ppm (d, 3H, N–CH_3, $^{3}J_{H-P} = 11.8$ Hz); $\delta = 1.59$ ppm (d, 3H, –CH_3, $^{3}J_{H-H} = 6.9$ Hz).

4.2.89. (*R*,*R*)-1,3-Dimethyl-4,5-diphenyl-2-(*R*)-(1-phenyl-propoxy)-[1,3,2]diazaphospholidine (*R*)-B5. NMR ^{31}P ($CDCl_3$): $\delta = 139.85$ ppm. NMR ^{1}H ($CDCl_3$): $\delta = 7.2$–7.4 ppm (15H, H_{arom}); $\delta = 5.05$ ppm (td, 1H, O–CH, $^{3}J_{H-H} = 6.4$ Hz, $^{3}J_{H-P} = 8.9$ Hz); $\delta = 4.09$ ppm (dd, 1H, –CH–N–, $^{3}J_{H-H} = 9.35$ Hz, $^{3}J_{H-P} = 3.2$ Hz); $\delta = 3.88$ ppm (dd, 1H. –CH–N–, $^{3}J_{H-H} = 9.35$ Hz, $^{3}J_{H-P} = 1.7$ Hz); $\delta = 2.31$ ppm (d, 3H, N–CH_3, $^{3}J_{H-P} = 12.31$ Hz); $\delta = 2.20$ ppm (d, 3H, N–CH_3, $^{3}J_{H-P} = 13.8$ Hz); $\delta = 1.95$ ppm (m, 2H, –CH_2–, $^{3}J_{H-H} = 6.89$ and 6.4 Hz); $\delta = 0.9$ ppm (d, 3H, –CH_3, $^{3}J_{H-H} = 6.89$ Hz).

4.2.90. (*R*,*R*)-1,3-Dimethyl-4,5-diphenyl-2-(*R*)-(1-phenyl-propoxy)-[1,3,2]diazaphospholidine-2-sulfide (*R*)-B5S. NMR ^{31}P ($CDCl_3$): $\delta = 83.01$ ppm. NMR ^{1}H ($CDCl_3$): $\delta = 7.2$–7.4 ppm (15H, H_{arom}); $\delta = 5.54$ ppm (td, 1H, O–CH, $^{3}J_{H-H} = 6.39$ Hz, $^{3}J_{H-P} = 12.8$ Hz); $\delta = 4.04$ ppm (dd, 1H, –CH–N–, $^{3}J_{H-H} = 8.37$ Hz, $^{3}J_{H-P} < 0.5$ Hz); $\delta = 3.98$ ppm (dd, 1H, –CH–N–, $^{3}J_{H-H} = 8.37$ Hz, $^{3}J_{H-P} < 0.5$ Hz); $\delta = 2.53$ ppm (d, 3H. N–CH_3, $^{3}J_{H-P} = 12.31$ Hz); $\delta = 2.50$ ppm (d, 3H, N–CH_3, $^{3}J_{H-P} = 12$ Hz); $\delta = 1.97$ ppm (m, 2H, –CH_2, $^{3}J_{H-H} = 6.39$ and 7.39 Hz); $\delta = 1.02$ ppm (d. 3H, –CH_3, $^{3}J_{H-H} = 7.39$ Hz). NMR ^{13}C ($CDCl_3$): $\delta = 138.61$, 137.72, 137.62 ppm ($C_{IV\,arom}$); $\delta = 129.22$, 128.81, 128.48, 128.26, 128.18, 128.08, 127.01, 127.63, 126.79 ppm (C_{arom}); $\delta = 81.87$ ppm (O–CH); $\delta = 72.96$ and $\delta = 71.49$ ppm (–CH–N–); $\delta = 31.31$ and 31.21 ppm (N–CH_3); $\delta = 31.26$ ppm (–CH_2–); $\delta = 8.88$ ppm (–CH_3).

4.2.91. (*R*,*R*)-1,3-Dimethyl-4,5-diphenyl-2-(*S*)-(1-phenyl-propoxy)-[1,3,2]diazaphospholidine (*S*)-B5. NMR ^{31}P ($CDCl_3$): $\delta = 141.60$ ppm. NMR ^{1}H ($CDCl_3$): $\delta = 6.9$–7.7 ppm (15H, H_{arom}); $\delta = 4.89$ ppm (td, 1H, O–CH, $^{3}J_{H-H} = 6.89$ Hz, $^{3}J_{H-P} = 8.86$ Hz); $\delta = 4.01$ ppm (dd, 1H, –CH–N–, $^{3}J_{H-H} = 9.37$ Hz, $^{3}J_{H-P} = 2.95$ Hz); $\delta = 3.85$ ppm (dd, 1H, –CH–N–, $^{3}J_{H-H} = 9.37$ Hz, $^{3}J_{H-P} < 0.5$ Hz); $\delta = 2.46$ ppm (d, 3H, N–CH_3, $^{3}J_{H-P} = 11.8$ Hz); $\delta = 1.89$ ppm (d, 3H, N–CH_3, $^{3}J_{H-P} = 14.3$ Hz); $\delta = 1.78$ ppm (m, 2H, CH_2–, $^{3}J_{H-H} = 6.89$ and 7.38 Hz); $\delta = 0.9$ ppm (d, 3H, –CH_3, $^{3}J_{H-H} = 7.38$ Hz).

4.2.92. (*R*,*R*)-1,3-Dimethyl-4,5-diphenyl-2-(*S*)-(1-phenyl-propoxy)-[1,3,2]diazaphospholidine-2-sulfide (*S*)-B5S. NMR ^{31}P ($CDCl_3$): $\delta = 82.52$ ppm. NMR ^{1}H ($CDCl_3$): $\delta = 6.9$–7.7 ppm (15H, H_{arom}); $\delta = 5.51$ ppm (td, 1H, O–CH, $^{3}J_{H-H} = 6.9$ Hz, $^{3}J_{H-P} = 12$ Hz); $\delta = 4.02$ ppm (dd, 1H, –CH–N–, $^{3}J_{H-H} = 8$ Hz, $^{3}J_{H-P} < 0.5$ Hz); $\delta = 3.96$ ppm (d, 1H, –CH–N–, $^{3}J_{H-H} = 8$ Hz, $^{3}J_{H-P} = 2$ Hz); $\delta = 2.48$ ppm (d, 3H, N–CH_3, $^{3}J_{H-P} = 12$ Hz); $\delta =$

2.04 ppm (d, 3H, N–CH_3, $^3J_{H-P} = 12$ Hz); $\delta = 1.94$ ppm (m, 2H, CH_2–, $^3J_{H-H} = 6.9$ and 7.4 Hz); $\delta = 1$ ppm (d, 3H, –CH_3, $^3J_{H-H} = 7.4$ Hz). NMR ^{13}C ($CDCl_3$): $\delta = 138.61$, 137.72, 137.62 ppm ($C_{IV\,arom}$); $\delta = 129.2$–126.8 ppm (C_{arom}); $\delta = 81.9$ ppm (O–CH); $\delta = 72.9$ and 71.5 ppm (–CH–N–); $\delta = 31.3$ and 29.3 ppm (N–CH_3); $\delta = 31.2$ ppm (–CH_2–); $\delta = 9.9$ ppm (–CH_3).

4.2.93. (*R*,*R*)-1,3-Dimethyl-4,5-diphenyl-2-(*R*)-(1-phenyl-butoxy)-[1,3,2]diazaphospholidine (*R*)-B6. NMR ^{31}P ($CDCl_3$): $\delta = 139.04$ ppm. NMR ^1H ($CDCl_3$): $\delta = 7.39$–6.96 ppm (15H, H_{arom}); $\delta = 5.03$ ppm (td, 1H, O–CH); $\delta = 4.12$ ppm (dd, 1H, –CH–N–); $\delta = 3.97$ ppm (dd, 1H, –CH–N–); $\delta = 2.22$ ppm (d, 3H, N–CH_3); $\delta = 1.15$ ppm (d, 3H, N–CH_3); $\delta = 1.85$ ppm (m, 2H, CH_2); $\delta = 1.35$ ppm (m, 2H, –CH_2–); $\delta = 0.86$ ppm (t, 3H, –CH_3).

4.2.94. (*R*,*R*)-1,3-Dimethyl-4,5-diphenyl-2-(*R*)-(1-phenyl-butoxy)-[1,3,2]diazaphospholidine-2-sulfide (*R*)-B6S. NMR ^{31}P ($CDCl_3$): $\delta = 82.75$ ppm. NMR ^1H ($CDCl_3$): $\delta = 7.31$–6.88 ppm (15H, H_{arom}); $\delta = 5.49$ ppm (td, 1H, O–CH, $^3J_{H-H} = 7.38$ Hz, $^3J_{H-P} = 12.31$ Hz); $\delta = 4.01$ ppm (dd, 1H, –CH–N–, $^3J_{H-H} = 8.86$ Hz, $^3J_{H-P} = 0$ Hz); $\delta = 3.84$ ppm (dd, 1H, –CH–N–, $^3J_{H-H} = 8.86$ Hz, $^3J_{H-P} < 0.5$ Hz); $\delta = 2.37$ ppm (d, 3H, N–CH_3, $^3J_{H-P} = 11.8$ Hz); $\delta = 1.95$ ppm (d, 3H, N–CH_3, $^3J_{H-P} = 12.31$ Hz); $\delta = 1.80$ ppm (m, 2H, CH_2–); $\delta = 1.52$ ppm (m, 2H, –CH_2–); $\delta = 1.37$ ppm (t, 3H, –CH_3, $^3J_{H-H} = 7.38$ Hz).

4.2.95. (*R*,*R*)-1,3-Dimethyl-4,5-diphenyl-2-(*S*)-(1-phenyl-butoxy)-[1,3,2]diazaphospholidine (*S*)-B6. NMR ^{31}P ($CDCl_3$): $\delta = 141.83$ ppm. NMR ^1H ($CDCl_3$): $\delta = 7.41$–6.96 ppm (15H, H_{arom}); $\delta = 4.68$ ppm (td, 1H, O–CH, $^3J_{H-H} = 7.35$ Hz, $^3J_{H-P} = 7.88$ Hz); $\delta = 4.11$ ppm (dd, 1H, –CH–N–, $^3J_{H-H} = 8.86$ Hz, $^3J_{H-P} = 3.44$ Hz); $\delta = 3.96$ ppm (dd, 1H, –CH–N–, $^3J_{H-H} = 8.86$ Hz. $^3J_{H-P} = 1.97$ Hz); $\delta = 2.54$ ppm (d, 3H, N–CH_3, $^3J_{H-P} = 11.3$ Hz); $\delta = 1.99$ ppm (d, 3H, N–CH_3, $^3J_{H-P} = 14.3$ Hz); $\delta = 1.73$ ppm (m, 2H, CH_2–); $\delta = 1.37$ ppm (m, 2H, –CH_2–); $\delta = 0.97$ ppm (t, 3H, –CH_3, $^3J_{H-H} = 7.39$ Hz).

4.2.96. (*R*,*R*)-1,3-Dimethyl-4,5-diphenyl-2-(*S*)-(1-phenyl-butoxy)-[1,3,2]diazaphospholidine-2-sulfide (*S*)-B6S. NMR ^{31}P ($CDCl_3$): $\delta = 82.92$ ppm. NMR ^1H ($CDCl_3$): $\delta = 7.46$–7.09 ppm (15H, H_{arom}); $\delta = 5.57$ ppm (td, 1H, O–CH, $^3J_{H-H} = 6.89$ Hz, $^3J_{H-P} = 13.29$ Hz); $\delta = 4.00$ ppm (dd, 1H, –CH–N–, $^3J_{H-H} = 8.37$ Hz, $^3J_{H-P} = 0.4$ Hz); $\delta = 3.94$ ppm (dd, 1H, –CH–N–, $^3J_{H-H} = 8.37$ Hz, $^3J_{H-P} < 0.5$ Hz); $\delta = 2.48$ ppm (d, 3H, N–CH_3, $^3J_{H-P} = 12.8$ Hz); $\delta = 2.03$ ppm (d, 3H, N–CH_3, $^3J_{H-P} = 12.3$ Hz); $\delta = 1.81$ ppm (m, 2H, CH_2–); $\delta = 1.42$ ppm (m, 2H, –CH_2–); $\delta = 0.97$ ppm (t, 3H, –CH_3, $^3J_{H-H} = 7.39$ Hz). NMR ^{13}C ($CDCl_3$): $\delta = 141.99$, 138.62, 137.72 ppm ($C_{IV\,arom}$); $\delta = 128.02$–126.68 ppm (C_{arom}); $\delta = 80.54$ ppm (O–CH); $\delta = 72.96$ and 71.48 ppm (–CH–N–); $\delta = 31.29$ and 29.24 ppm (N–CH_3); $\delta = 40.45$ ppm (CH_2–); $\delta = 18.70$ ppm (–CH_2–), 13.93 ppm (–CH_3).

4.2.97. (*R*,*R*)-1,3-Dimethyl-4,5-diphenyl-2-(*R*)-(1-phenyl-decyloxy)-[1,3,2]diazaphospholidine (*R*)-B9. NMR ^{31}P ($CDCl_3$): $\delta = 139.22$ ppm. NMR ^1H ($CDCl_3$): $\delta = 7.39$–6.94 ppm (15H, H_{arom}); $\delta = 5.01$ ppm (td, 1H, O–CH); $\delta = 4.12$ ppm (dd, 1H.–CH–N–); $\delta = 3.97$ ppm (dd, 1H, –CH–N–); $\delta = 2.22$ ppm (d, 3H, N–CH_3); $\delta = 2.15$ ppm (d, 3H, N–CH_3); $\delta = 1.80$ ppm (m, 2H, CH_2); $\delta = 1.28$–1.11 ppm (m, 12H, CH_2); $\delta = 0.79$ ppm (t, 3H, –CH_3).

4.2.98. (*R*,*R*)-1,3-Dimethyl-4,5-diphenyl-2-(*R*)-(1-phenyl-decyloxy)-[1,3,2]diazaphospholidine-2-sulfide (*R*)-B9S. NMR ^{31}P ($CDCl_3$): $\delta = 82.82$ ppm. NMR ^1H ($CDCl_3$): $\delta = 7.28$–6.80 ppm (15H, H_{arom}); $\delta = 5.39$ ppm (td, 1H, O–CH); $\delta = 4.91$ ppm (dd, 1H, –CH–N–); $\delta = 3.75$ ppm (dd, 1H, –CH–N–); $\delta = 2.28$ ppm (d, 3H, N–CH_3); $\delta = 1.97$ ppm (d, 3H, N–CH_3); $\delta = 1.96$ ppm (m, 2H, CH_2); 1.40–1.15 ppm (m, 12H, CH_2); $\delta = 0.76$ ppm (t, 3H, –CH_3).

4.2.99. (*R*,*R*)-1,3-Dimethyl-4,5-diphenyl-2-(*S*)-(1-phenyl-decyloxy)-[1,3,2]diazaphospholidine (*S*)-B9. NMR ^{31}P ($CDCl_3$): $\delta = 142.36$ ppm. NMR ^1H ($CDCl_3$): $\delta = 7.41$–6.76 ppm (15H, H_{arom}); $\delta = 4.71$ ppm (td, 1H, O–CH); $\delta = 4.13$ ppm (dd, 1H, –CH–N–); $\delta = 3.98$ ppm (dd, 1H, –CH–N–); $\delta = 2.60$ ppm (d, 3H, N–CH_3); $\delta = 2.05$ ppm (d, 3H, N–CH_3); $\delta = 1.97$–1.19 ppm (m, 14H, CH_2); $\delta = 0.90$ ppm (t, 3H, –CH_3).

4.2.100. (*R*,*R*)-1,3-Dimethyl-4,5-diphenyl-2-(*S*)-(1-phenyl-decyloxy)-[1,3,2]diazaphospholidine-2-sulfide (*S*)-B9S. NMR ^{31}P ($CDCl_3$): $\delta = 83.26$ ppm. NMR ^1H ($CDCl_3$): $\delta = 7.65$–6.82 ppm (15H, H_{arom}); $\delta = 4.69$ ppm (td, 1H, O–CH); $\delta = 4.14$ ppm (dd, 1H.–CH–N–); $\delta = 3.97$ ppm (dd, 1H, –CH–N–); $\delta = 2.56$ ppm (d, 3H, N–CH_3); $\delta = 2.05$ ppm (d, 3H, N–CH_3); $\delta = 1.82$–1.19 ppm (m, 14H, CH_2); $\delta = 0.90$ ppm (t, 3H, –CH_3).

4.2.101. (*R*)-2-(2-Chloro-1-phenyl-ethoxy)-(*R*,*R*)-1,3-dimethyl-4,5-diphenyl-[1,3,2]diazaphospholidine (*R*)-B10. NMR ^{31}P ($CDCl_3$): $\delta = 144.10$ ppm. NMR ^1H ($CDCl_3$): $\delta = 6.97$–7.03 ppm (15H, H_{arom}); $\delta = 5.18$ ppm (td, 1H, O–CH); $\delta = 4.07$ ppm (dd, 1H, –CH–N–); $\delta = 3.73$ ppm (d, 2H, –CH_2–Cl); $\delta = 3.71$ ppm (dd, 1H, –CH–N–); $\delta = 2.55$ ppm (d, 3H, N–CH_3); $\delta = 1.98$ ppm (d, 2H, CH_2-Cl).

4.2.102. (*R*)-2-(2-Chloro-1-phenyl-ethoxy)-(*R*,*R*)-1,3-dimethyl-4,5-diphenyl-[1,3,2]diazaphospholidine-2-sulfide (*R*)-B10S. NMR ^{31}P ($CDCl_3$): $\delta = 83.04$ ppm. NMR ^1H ($CDCl_3$): $\delta = 7.37$–7.06 ppm (15H, H_{arom}); $\delta = 5.71$ ppm (td, 1H, O–CH); $\delta = 3.90$ ppm (dd, 1H, –CH–N–): $\delta = 3.73$ ppm (dd, 1H, –CH–N–); $\delta = 3.66$ ppm (d, 3H,

N–CH_3); $\delta = 2.45$ ppm (d, 2H, –CH_2–Cl); $\delta = 1.98$ ppm (d, 3H, N–CH_3).

4.2.103. (*S*)-2-(2-Chloro-1-phenyl-ethoxy)-(*R*,*R*)-1,3-dimethyl-4,5-diphenyl-[1,3,2]diazaphospholidine (*S*)-B10. NMR ^{31}P ($CDCl_3$): $\delta = 140.25$ ppm. NMR ^{1}H ($CDCl_3$): $\delta = 7.36$–7.05 ppm (15H, H_{arom}); $\delta = 5.72$ ppm (td, 1H, O–CH); $\delta = 3.92$ ppm (dd, 1H, –CH–N–); $\delta = 3.74$ ppm (dd, 1H, –CH–N–); $\delta = 3.68$ ppm (d, 3H, N–CH_3); $\delta = 2.43$ ppm (d, 2H, –CH_2–Cl); $\delta = 1.92$ ppm (d, 3H, N–CH_3).

4.2.104. (*S*)-2-(2-Chloro-1-phenyl-ethoxy)-(*R*,*R*)-1,3-dimethyl-4,5-diphenyl-[1,3,2]diazaphospholidine-2-sulfide (*S*)-B10S. NMR ^{31}P ($CDCl_3$): $\delta = 83.25$ ppm. NMR ^{1}H ($CDCl_3$): $\delta = 7.39$–7.01 ppm (15H, H_{arom}); $\delta = 5.74$ ppm (td, 1H, O–CH); $\delta = 3.92$ ppm (dd, 1H, –CH–N–); $\delta = 3.71$ ppm (dd, 1H, –CH–N–); $\delta = 3.67$ ppm (d, 3H, N–CH_3); $\delta = 2.44$ ppm (d, 2H, –CH_2–Cl); $\delta = 1.96$ ppm (d, 3H, N–CH_3).

4.2.105. (*R*)-2-(3-Chloro-1-phenyl-propoxy)-(*R*,*R*)-1,3-dimethyl-4,5-diphenyl-[1,3,2]diazaphospholidine (*R*)-B11. NMR ^{31}P ($CDCl_3$): $\delta = 140.01$ ppm. NMR ^{1}H ($CDCl_3$): $\delta = 7.40$–6.97 ppm (15H, H_{arom}); $\delta = 5.30$ ppm (td, 1H, O–CH); $\delta = 4.02$ ppm (dd, 1H, –CH–N–); $\delta = 3.73$ ppm (dd, 1H, –CH–N–); $\delta = 3.70$ ppm (d, 2H, CH_2–Cl); $\delta = 2.21$ ppm (d, 2H, –CH_2–); $\delta = 2.17$ ppm (d, 3H, N–CH_3); $\delta = 2.10$ ppm (d, 3H, N–CH_3).

4.2.106. (*R*)-2-(3-Chloro-1-phenyl-propoxy)-(*R*,*R*)-1,3-dimethyl-4,5-diphenyl-[1,3,2]diazaphospholidine-2-sulfide (*R*)-B11S. NMR ^{31}P ($CDCl_3$): $\delta = 83.00$ ppm NMR ^{1}H ($CDCl_3$): $\delta = 7.43$–6.80 ppm (15H, H_{arom}); $\delta = 5.62$ ppm (td, 1H, O–CH); $\delta = 3.90$ ppm (dd, 1H, –CH–N–); $\delta = 3.76$ ppm (dd, 1H, –CH–N–); $\delta = 3.76$ ppm (d, 2H, CH_2–Cl); $\delta = 2.16$ ppm (d, 3H, N–CH_3); $\delta = 2.13$ ppm (d, 2H, –CH_2–); $\delta = 1.90$ ppm (d, 3H, N–CH_3).

4.2.107. (*S*)-2-(3-Chloro-1-phenyl-propoxy)-(*R*,*R*)-1,3-dimethyl-4,5-diphenyl-[1,3,2]diazaphospholidine (*S*)-B11. NMR ^{31}P ($CDCl_3$): $\delta = 146.64$ ppm. NMR ^{1}H ($CDCl_3$): $\delta = 7.43$–7.0 ppm (15H, H_{arom}); $\delta = 5.35$ ppm (td, 1H, O–CH); $\delta = 4.05$ ppm (dd, 1H, –CH–N–); $\delta = 3.89$ ppm (dd, 1H, –CH–N–); $\delta = 3.54$ ppm (d, 2H, CH_2–Cl); $\delta = 2.25$ ppm (d, 3H, N–CH_3); $\delta = 2.19$ ppm (d, 2H, –CH_2–).

4.2.108. (*S*)-2-(3-Chloro-1-phenyl-propoxy)-(*R*,*R*)-1,3-dimethyl-4,5-diphenyl-[1,3,2]diazaphospholidine-2-sulfide (*S*)-B11S. NMR ^{31}P ($CDCl_3$): $\delta = 83.25$ ppm. NMR ^{1}H ($CDCl_3$): $\delta = 7.38$–6.85 ppm (15H, H_{arom}); $\delta = 5.64$ ppm (td, 1H, O–CH); $\delta = 3.96$ ppm (dd, 1H, –CH–N–); $\delta = 3.81$ ppm (dd, 1H, –CH–N–); $\delta = 3.65$ ppm (d, 2H, CH_2–Cl); $\delta = 2.27$ ppm (d, 3H, N–CH_3); $\delta = 1.98$ ppm (d, 2H, –CH_2–).

4.2.109. (*R*,*R*)-(1,3-Dimethyl-4,5-diphenyl-[1,3,2]diazaphospholidin-2-(*R*)-(-yloxy)-phenyl-acetic acid methyl ester (*R*)-B13. NMR ^{31}P ($CDCl_3$): $\delta = 139.09$ ppm.

4.2.110. (*R*,*R*)-(1,3-Dimethyl-4,5-diphenyl-2-thioxo-2λ^5-[1,3,2]diazaphospholidin-2-(*R*)-(-yloxy)-phenyl-acetic acid methyl ester (*R*)-B13S. NMR ^{31}P ($CDCl_3$): $\delta = 83.14$ ppm.

4.2.111. (*R*,*R*)-(1,3-Dimethyl-4,5-diphenyl-[1,3,2]diazaphospholidin-2-(*S*)-(-yloxy)-phenyl-acetic acid methyl ester (*S*)-B13. NMR ^{31}P ($CDCl_3$): $\delta = 138.30$ ppm.

4.2.112. (*R*,*R*)-(1,3-Dimethyl-4,5-diphenyl-2-thioxo-2λ^5-[1,3,2]diazaphospholidin-2-(*S*)-(-yloxy)-phenyl-acetic acid methyl ester (*S*)-B13S. NMR ^{31}P ($CDCl_3$): $\delta = 83.04$ ppm.

4.2.113. (*R*,*R*)-1,3-Dimethyl-2-(*R*)-(2-methyl-1-phenyl-propoxy)-4,5-diphenyl-[1,3,2]diazaphospholidine (*R*)-B7. NMR ^{31}P ($CDCl_3$): $\delta = 138.82$ ppm ($CDCl_3$). NMR ^{1}H ($CDCl_3$): NMR ^{1}H ($CDCl_3$): $\delta = 7.45$–6.75 ppm (15H, H_{arom}); $\delta = 4.75$ ppm (dd, 1H, O–CH, $^3J_{H-H} = 7.38$ Hz, $^3J_{H-P} = 8.74$ Hz); $\delta = 3.96$ ppm (dd, 1H, N–CH–, $^3J_{H-H} = 9.35$ Hz, $^3J_{H-P} < 0.5$ Hz); $\delta = 3.78$ ppm (dd, 1H, N–CH–, $^3J_{H-H} = 9.35$ Hz, $^3J_{H-P} = 2.95$ Hz); $\delta = 2.28$ ppm (d, 3H, N–CH_3, $^3J_{H-P} = 13.3$ Hz); $\delta = 2.25$ ppm (d, 3H, N–CH_3, $^3J_{H-P} = 14.27$ Hz); $\delta = 2.14$ ppm (m, 1H, –CH–, $^3J_{H-H} = 6.89$ and 7.38 Hz); $\delta = 1.12$ ppm (d, 3H, –$(CH_3)_2$, $^3J_{H-H} = 6.89$ Hz), $\delta = 0.91$ ppm (d, 3H, –$(CH_3)_2$, $^3J_{H-H} = 6.89$ Hz).

4.2.114. (*R*,*R*)-1,3-Dimethyl-2-(*R*)-(2-methyl-1-phenyl-propoxy)-4,5-diphenyl-[1,3,2]diazaphospholidine-2-sulfide (*R*)-B7S . NMR ^{31}P ($CDCl_3$): $\delta = 82.73$ ppm. NMR ^{1}H ($CDCl_3$): $\delta = 6.8$–7.8 ppm (15H, H_{arom}); $\delta = 5.06$ ppm (dd, 1H, O–CH, $^3J_{H-H} = 7$ Hz, $^3J_{H-P} = 8$ Hz); $\delta = 3.95$ ppm (dd, 1H, N–CH–, $^3J_{H-H} = 9$ Hz, $^3J_{H-P} < 0.5$ Hz); $\delta = 3.78$ ppm (dd, 1H, N–CH–, $^3J_{H-H} = 9$ Hz, $^3J_{H-P} < 0.5$ Hz); $\delta = 2.30$ ppm (d, 3H, N–CH_3, $^3J_{H-P} = 12$ Hz); $\delta = 1.79$ ppm (d, 3H, N–CH_3, $^3J_{H-P} = 13$ Hz); $\delta = 2.14$ ppm (m, 1H, –CH–, $^3J_{H-H} = 7$ Hz); $\delta = 1.07$ ppm (d, 3H, –$(CH_3)_2$, $^3J_{H-H} = 7$ Hz); $\delta = 0.93$ ppm (d, 3H, –$(CH_3)_2$, $^3J_{H-H} = 7$ Hz). NMR ^{13}C ($CDCl_3$): $\delta = 143.65$, 140.3, 137.99 ppm ($C_{IV\,arom}$); $\delta = 129.01$–126.29 ppm (C_{arom}); $\delta = 88.40$ ppm (O–CH); $\delta = 79.27$ and 72.90 ppm (–CH–N–); $\delta = 31.46$ and 30.83 ppm (N–CH_3); $\delta = 31.2$ ppm (–CH–); $\delta = 17.91$ and 18.89 ppm (–$(CH_3)_2$).

4.2.115. (*R*,*R*)-1,3-Dimethyl-2-(*S*)-(2-methyl-1-phenyl-propoxy)-4,5-diphenyl-[1,3,2]diazaphospholidine (*S*)-B7. NMR ^{31}P ($CDCl_3$): $\delta = 143.79$ ppm. NMR ^{1}H ($CDCl_3$): $\delta = 7.41$–6.96 ppm (15H, H_{arom}); $\delta = 4.75$ ppm (dd, 1H, O–CH, $^3J_{H-H} = 7.87$ Hz, $^3J_{H-P} = 8.37$ Hz); $\delta = 4.10$ ppm (dd, 1H, N–CH–, $^3J_{H-H} = 8.86$ Hz, $^3J_{H-P} = 2.46$ Hz); $\delta = 3.86$ ppm (dd, 1H, N–CH–, $^3J_{H-H} = 8.86$ Hz,

$^3J_{H-P} < 0.5$ Hz); $\delta = 2.20$ ppm (d, 3H, N–CH_3, $^3J_{H-P} = 11.81$ Hz); $\delta = 2.16$ ppm (d, 3H, N–CH_3, $^3J_{H-P} = 13.29$ Hz); $\delta = 2.05$ ppm (m, 1H, –CH–, $^3J_{H-H} = 7.87$ Hz, $^3J_{H-H} = 6.89$ Hz); $\delta = 0.97$ ppm (d, 3H, –$(CH_3)_2$, $^3J_{H-H} = 6.89$ Hz); $\delta = 0.82$ ppm (d, 3H, –$(CH_3)_2$, $^3J_{H-H} = 7$ Hz).

4.2.116. (*R*,*R*)-1,3-Dimethyl-2-(*S*)-(2-methyl-1-phenyl-propoxy)-4,5-diphenyl-[1,3,2]diazaphospholidine-2-sulfide (*S*)-B7S. NMR ^{31}P ($CDCl_3$): $\delta = 83.10$ ppm. NMR ^{1}H ($CDCl_3$): $\delta = 6,8$–7.8 ppm (15H, H_{arom}); $\delta = 5.19$ ppm (dd, 1H, O–CH, $^3J_{H-H} = 7.39$ Hz, $^3J_{H-P} = 13.79$ Hz); $\delta = 3,93$ ppm (dd, 1H, N–CH, $^3J_{H-H} = 8.37$ Hz, $^3J_{H-P} < 0.5$ Hz) = 3.86 ppm (dd, 1H, N–CH, $^3J_{H-H} = 8.37$ Hz, $^3J_{H-P} = 2.46$ Hz); $\delta = 2.40$ ppm (d, 3H, N–CH_3, $^3J_{H-P} = 12.3$ Hz); $\delta = 1.80$ ppm (d, 3H, N–CH_3, $^3J_{H-P} = 12.3$ Hz); $\delta = 2.13$ ppm (m, 1H, –CH–, $^3J_{H-H} = 6.89$ Hz, $^3J_{H-H} = 7.39$ Hz), $\delta = 1,04$ ppm (d, 3H, –$(CH_3)_2$, $^3J_{H-H} = 6.89$ Hz); $\delta = 0.79$ ppm (d, 3H, –$(CH_3)_2$, $^3J_{H-H} = 6,89$ Hz).

4.2.117. [2-(*R*,*R*)-(1,3-Dimethyl-4,5-diphenyl-[1,3,2]diazaphospholidin-(*R*)-2-yloxy)-(*S*)-1-methyl-2-phenyl-ethyl]-dimethyl-amine (*R*)-B12. NMR ^{31}P ($CDCl_3$): $\delta = 146.05$ ppm. NMR ^{1}H ($CDCl_3$): $\delta = 7.45$–7.01 ppm (15H, H_{arom}); $\delta = 5.93$ ppm (d, 1H, O–CH); $\delta = 4.15$ ppm (dd, 1H, N–CH); $\delta = 3.87$ ppm (dd, 1H, N–CH); $\delta = 2.92$ ppm (s, 3H, –$N(CH_3)_2$); $\delta = 2.82$ ppm (s, 3H, –$N(CH_3)_2$); $\delta = 2.55$ ppm (d, 3H, N–CH_3); $\delta = 2.45$ ppm (m, 3H, –CH–); $\delta = 1.83$ ppm (d, 3H, N–CH_3); $\delta = 1.40$ ppm (d, 3H, –CH_3).

4.2.118. [2-(*R*,*R*)-(1,3-Dimethyl-4,5-diphenyl-2-thioxo-2λ5-[1,3,2]diazaphospholidin-(*R*)-2-yloxy)-(*S*)-1-methyl-2-phenyl-ethyl]-dimethyl-amine (*R*)-B12S. NMR ^{31}P ($CDCl_3$): $\delta = 82.39$ ppm. NMR ^{1}H ($CDCl_3$): $\delta = 7.40$–7.05 ppm (15H, H_{arom}); $\delta = 6.11$ ppm (d, 1H, O–CH); $\delta = 4.05$ ppm (dd, 1H, N–CH); $\delta = 3.97$ ppm (dd, 1H, N–CH); $\delta = 3.32$ ppm (s, 3H, –$N(CH_3)_2$); $\delta = 2.94$ ppm (s, 3H, –$N(CH_3)_2$); $\delta = 2.48$ ppm (d, 3H, N–CH_3); $\delta = 2.44$ ppm (m, 3H, –CH–); $\delta = 1.58$ ppm (d, 3H, N–CH_3); $\delta = 1.56$ ppm (d, 3H, –CH_3).

4.2.119. [2-(*R*,*R*)-(1,3-Dimethyl-4,5-diphenyl-[1,3,2]diazaphospholidin-(*S*)-2-yloxy)-(*R*)-1-methyl-2-phenyl-ethyl]-dimethyl-amine (*S*)-B12. NMR ^{31}P ($CDCl_3$): $\delta = 142.31$ ppm. NMR ^{1}H ($CDCl_3$): $\delta = 7.52$–7.00 ppm (15H, H_{arom}); $\delta = 5.92$ ppm (d, 1H, O–CH); $\delta = 4.04$ ppm (dd, 1H, N–CH); $\delta = 3.84$ ppm (dd, 1H, N–CH); $\delta = 2.89$ ppm (s, 3H, –$N(CH_3)_2$); $\delta = 2.80$ ppm (s, 3H, –$N(CH_3)_2$); $\delta = 2.42$ ppm (m, 3H, –CH–); $\delta = 2.30$ ppm (d, 3H, N–CH_3); $\delta = 2.20$ ppm (d, 3H, N–CH_3); $\delta = 1.42$ ppm (d, 3H, –CH_3).

4.2.120. [2-(*R*,*R*)-(1,3-Dimethyl-4,5-diphenyl-2-thioxo-2λ5-[1,3,2]diazaphospholidin-(*S*)-2-yloxy)-(*R*)-1-methyl-2-phenyl-ethyl]-dimethyl-amine (*S*)-B12S. NMR ^{31}P ($CDCl_3$): $\delta = 83.66$ ppm. NMR ^{1}H ($CDCl_3$): $\delta = 7.49$–7.04 ppm (15H, H_{arom}); $\delta = 6.10$ ppm (d, 1H, O–CH); $\delta = 4.19$ ppm (dd, 1H, N–CH); $\delta = 3.80$ ppm (dd, 1H, N–CH); $\delta = 3.35$ ppm (s, 3H, –$N(CH_3)_2$); $\delta = 2.91$ ppm (s, 3H, –$N(CH_3)_2$); $\delta = 2.45$ ppm (d, 3H, N–CH_3); $\delta = 2.41$ ppm (m, 3H, –CH–); $\delta = 1.70$ ppm (d, 3H, N–CH_3); $\delta = 1.58$ ppm (d, 3H, –CH_3).

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