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Efficient Oxidative Resolution of 1-Phenylphosphol-2-Ene and Diels–Alder Synthesis of Enantiopure Bicyclic and Tricyclic P-Stereogenic C-P Heterocycles

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Received: 4 February 2020; Accepted: 24 February 2020; Published: 1 March 2020

Abstract: 1-Phenylphosphol-2-ene 1-oxide is effectively resolved by L-menthyl bromoacetate to afford both S_P and R_P enantiomers of 1-phenylphosphol-2-ene 1-oxide on a multigram scale. The resolved 1-phenylphosphol-2-ene oxide has been found to undergo face-selective and endo-selective cycloadditions with a series of acyclic and cyclic dienes to produce enantiopure P-stereogenic C-P heterocycles of hexahydrophosphindole and hexahydrobenzophosphindole as well as phospha[5.2.1.$0^{2,6}$]decene and phospha[5.2.2.$0^{2,6}$]undecene structures. Conversions of these cycloadducts to the fully saturated heterocyclic systems as well as to their P (III), P = S, P = Se and P-BH_3 derivatives have been demonstrated to occur with retention of configuration and preservation of configurational homogeneity at P. A perplexing case of stereomutation at P during reduction of a tricyclic β-hydroxy phosphine oxide by $PhSiH_3$ at 80 °C has been recorded.

Keywords: P-stereogenicity; 1-phenylphosphol-2-ene 1-oxide; resolution; [4+2] cycloaddition; polycyclic phosphorus heterocycles; P = O reduction; optically active phosphines

1. Introduction

Optically active P-stereogenic organophosphorus compounds are of great importance in organic synthesis [1–4]. The most spectacular example of their utility has been the use of (S_P)-PAMP {*o*-anisylmethylphenylphosphine} and (R_P,R_P)-DIPAMP {1,2-bis(*o*-anisylmethylphenylphosphine)ethane} di as chiral ligands in rhodium-catalyzed asymmetric hydrogenation of enamides [5] which led to the first application of such a process in the industrial production, i.e., the Monsanto L-DOPA process [6] However, P-stereogenicity is not a natural phenomenon, and, from the very beginning [7], it had to be generated in the lab. Despite many developed asymmetric syntheses [1,7–18], desymmetrizations [14,19–27] and kinetic resolutions [28–34], practical preparations of optically active P-stereogenic compounds are still relying in great part on classical resolution of racemates [7,8,35–40]. The latter has the advantage to rely on cheap and often recoverable chiral auxiliaries, uses crystallization for separation of the P-epimers and,

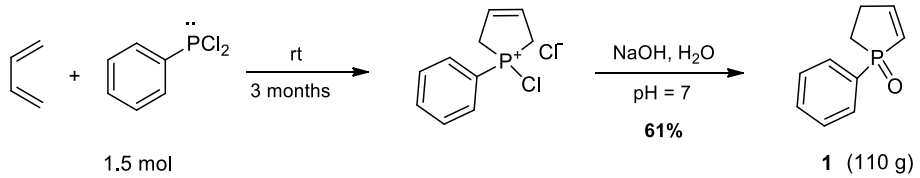
by avoiding chromatography, usually secures convenient access to resolved P-stereogenic compounds in multigram quantities [41]. In our studies, we have found that several synthetically useful P-stereogenic compounds could be readily resolved into enantiomers by the use of L-menthyl bromoacetate as the chiral auxiliary [38,39,42,43]. Due to versatility of its acetate function, it could serve either as the latent methyl group mounted on P during the resolution process [43,44], or it could be used as the classical chiral auxiliary that is removed in the last step as the whole [38,39].

In this paper, we wish to present the use of L-menthyl acetate auxilliary for efficient resolution of racemic 1-phenyl-phosphol-2-ene 1-oxide (**1**), one of the parent five-members of P-C-heterocycles readily available on the multigram scale by the McCormack process [45]. The chemistry of **1** is very rich and offers the possibility of transforming it into many other organophosphorus compounds through the use of its double bond functionality in Michael-type additions [45], Diels–Alder cycloadditions [46,47], 1,3-dipolar cycloadditions [28,30,48,49], and Heck reactions [24,33,50,51]. The utility of the resolved **1** as a dienophile in stereoselective Diels–Alder synthesis of a series of optically active bicyclic and tricyclic C-P-heterocyclic systems will be demonstrated.

2. Results and Discussions

2.1. Synthesis and Resolution of 1-Phenylphosphol-2-Ene 1-Oxide

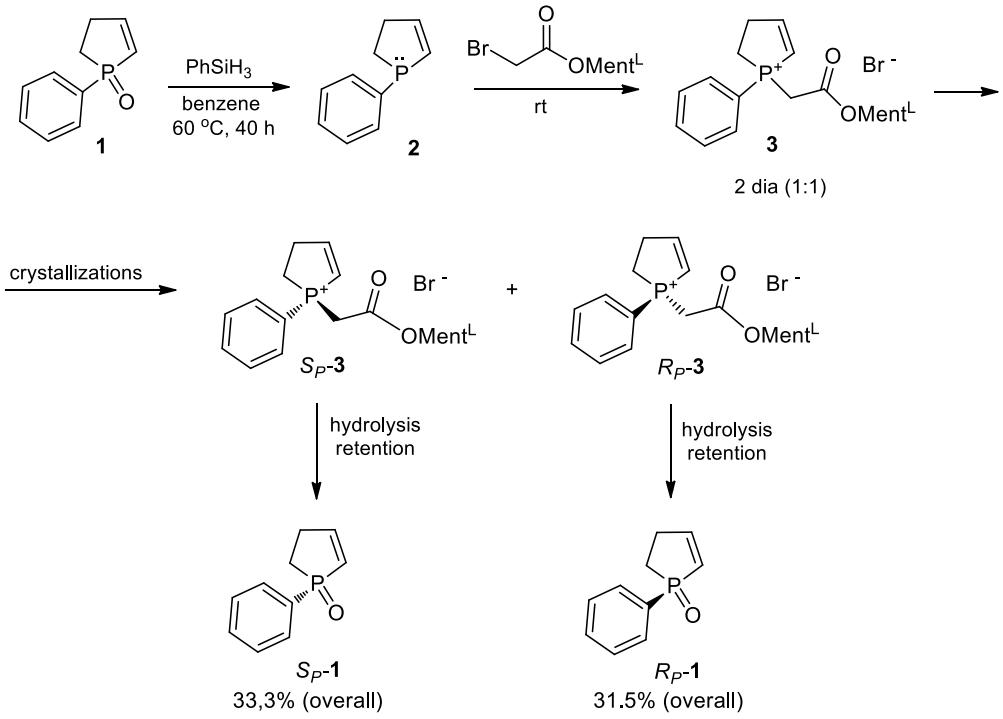
Racemic **1** was synthesized from butadiene and *P,P-dichlorophenylphosphine* via intermediate cyclic chlorophosphonium chloride (a 1,4-cycloadduct) which after a hydrolytic work-up afforded *rac*-**1** in good yield (Scheme 1).



Scheme 1. Synthesis of racemic 1-phenylphosphol-2-ene 1-oxide (**1**) by the McCormack route.

The subsequent resolution of *rac*-**1** started with its reduction to the corresponding phosphine **2** by treatment with $PhSiH_3$ at the temperature not exceeding 60 °C in order to avoid concomitant reduction of the double bond (Scheme 2). Then, the resulting phosphine **2** was quaternized by L-menthyl bromoacetate at room temperature to afford a ca. 1:1 mixture of the two P-epimeric quaternary phosphonium salts **3**. One of them, the (S_P)-**3**, crystallized out from the reaction mixture in great predominance over the more soluble (R_P)-**3** (>9:1). Recrystallization of the filtered crystals from AcOEt-EtOH (10:1) yielded pure S_P-**3** epimer in 37% yield. Evaporation of the filtrate and recrystallization of the residue from benzene-hexane (10:1), or from toluene, yielded in turn pure R_P-**3** epimer in 32% yield. Conversion of the P-epimeric phosphonium salts to the corresponding enantiopure phospholene oxides was conveniently achieved by removal of the auxilliary L-menthyl acetate group either by the Wittig reaction with benzaldehyde as originally applied [7,10] or, as found later [38], by simple alkaline hydrolysis. According to the literature, clean retention of configuration at P could have been expected in both cases [7,52–54]. In this way, over 20 g amounts of each enantiomer of **1** can be obtained in a single bench-top batch.

The assignment of the S configuration to the dextrorotatory **1** and the R configuration to the levorotatory **1** follows from the previous unequivocal X-ray based assignment of (S_P)-(+)-**1** [29]. The enantiomeric purity of the synthesized enantiomers of **1** was determined by running their ^1H and ^{31}P NMR spectra in the presence of equimolar amounts of (*S*)-3,5-dinitro-*N*-α-phenylethyl-benzamide as a chiral solvating agent (Kagan's reagent) according to the described procedure [55]. Because the presence of any signals of the opposite enantiomer could not be detected in either of the spectrums, the enantiomeric purity of both (S_P)-**1** and (R_P)-**1** was assigned to be more than 98% ee.

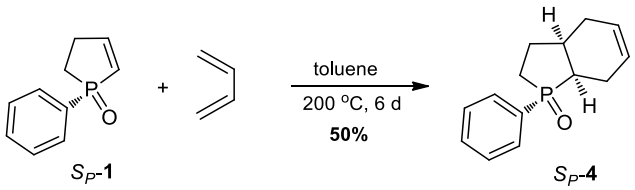


Scheme 2. Resolution protocol for 1-phenylphosphol-2-ene 1-oxide (**1**).

2.2. Synthesis of Optically Active Bicyclic and Tricyclic P-Sterogenic Phospholene Derivatives

Ready synthesis of enantiomers of **1** opens up the possibility of synthesizing also other optically active P-stereogenic heterocyclic compounds by employment of the conjugated double bond functionality present in its structure [24,28,30,33,45–50]. To illustrate this potential, we decided to use (S_P)-**1** as a dienophile in the Diels–Alder reactions with acyclic and cyclic dienes to synthesize optically active bicyclic and tricyclic C,P-heterocycles [56–60]. The additions of *rac*-**1** to acyclic dienes have been already described to occur at 260 °C and to afford the endo cycloadduct [46]. The required elevated temperature clearly indicated that phosphol-2-ene oxide is a rather poor dienophile. Our efforts to optimize the conditions of this reaction using *rac*-**1** and butadiene led us eventually to conclude that the best way to conduct the cycloaddition is to use a glass reactor (to avoid possible metal catalysis in equilibration of (S_P)-**1** with its symmetrical phosphol-3-ene counterpart), use toluene as solvent, carry out the reaction at 190–200 °C, and use 6–9 equiv. of the diene added in two or three portions over a period of 2–6 days. Interestingly, attempted Lewis acid catalysis by $FeCl_3$, $SnCl_4$, or $AlCl_3$ proved inefficient. Even with $AlCl_3$, which appeared to be the best of the three, the reaction temperature could be in some cases lowered to 100 °C, but the achieved overall yields were still inferior to those observed under the optimized thermal conditions.

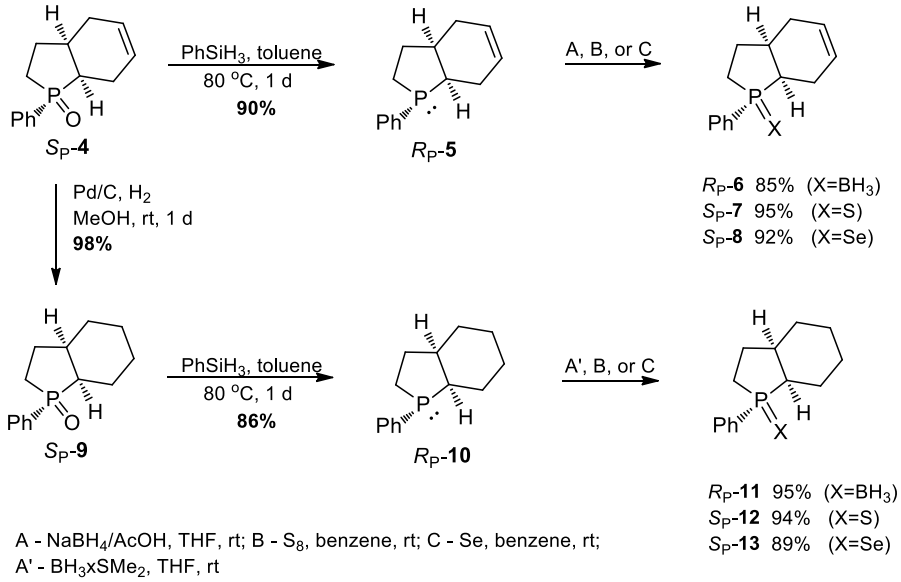
When (S_P)-**1** was reacted with butadiene under the optimized conditions, the (S_P)-*cis*-hexahydro-1-phenylphosphindole 1-oxide (**4**) was obtained in 50% isolated yield (Scheme 3).



Scheme 3. Cycloaddition of (S_P)-**1** to butadiene.

Enantiomeric purity of (S_P)-**4** was determined by ^{1}H NMR using Kagan's solvating agent [55] to be >98% ee. The confirmation of the very high enantiomeric purity of the synthesized (S_P)-**4** has also attested to the fact that racemizing of the starting (S_P)-**1** through its possible reversible equilibration with symmetrical 1-phenylphosphol-3-ene 1-oxide under such demanding thermal conditions has been negligible, if any.

Next, to check the possibility of steroselective conversion of (S_P)-**4** to the corresponding P,C-stereogenic enantiopure phosphine (R_P)-**5**, (S_P)-**4** was treated with $PhSiH_3$ at 80 °C to yield the desired phosphine in 92% isolated yield (Scheme 4). To confirm the expected retention of configuration at P in the reduction step [61,62], the resulting phosphine was reoxidized by 30% H_2O_2, known as a stereoretentive oxidant in phosphorus chemistry [7,63]. The oxidation gave back (S_P)-**4** of practically the same specific rotation sign and value as the starting one, attesting thus to the clean retention of configuration at P in the reduction step. Protection of (R_P)-**5** by BH_3 was best achieved by using $NaBH_4$/AcOH [64] yielding phosphine-borane (R_P)-**6** in 76% yield, while, with BH_3xTHF (or BH_3xSMe_2), it was much less efficient (ca. 36% or less) probably due to interfering reactivity of the double bond present in its structure. In turn, oxidation of (R_P)-**5** by elemental sulfur and selenium gave the corresponding phosphine sulfide (R_P)-**7** and phosphine selenide (R_P)-**8**, respectively, in practically quantitative yield (Scheme 4). In addition, these conversions have been known to occur with clean retention of configuration at P [7], and the synthesized sulfide and selenide derivatives of (R_P)-**5** should be considered as virtually enantiopure as well.



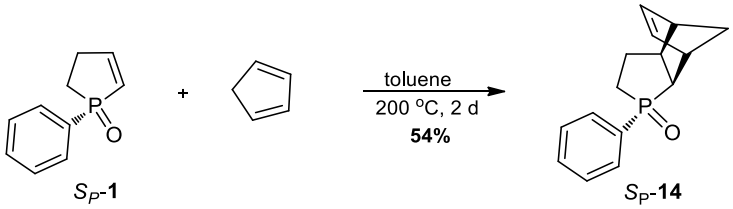
Scheme 4. Conversion of (S_P)-**4** to other unsaturated P-derivatives and their saturated counterparts.

Hydrogenation of the double bond in (S_P)-**4** gave in turn fully saturated *cis*-octahydrophosphindole oxide (S_P)-**9**. As before, reduction of (S_P)-**9** by $PhSiH_3$ gave the corresponding saturated phosphine (R_P)-**10**, which could be further transformed to phosphine-borane (R_P)-**11** as well as to the phosphine sulfide (S_P)-**12** and phosphine selenide (S_P)-**13** by boranation, and oxidation by sulfur and selenium, respectively. This time, however, boranation of (R_P)-**10** by BH_3xSMe_2 gave the best results and proved more efficient than $NaBH_4$/AcOH (95% vs. 87%, respectively) (Scheme 4).

With the protocols for the cycloaddition and for the basic transformations of the cycloaddition product established, we turned our attention towards using these protocols for synthesis of the more rigid enantiopure P-stereogenic phosphines which could have potential relevance to asymmetric catalysis [2,4]. Towards this end, we selected cyclopentadiene, cyclohexadiene, and anthracene as well as hydroxybenzocyclobutene as dienes in order to prepare polycyclic phosphines containing rigidified bridged skeleton [65,66]. As with butadiene, also with these dienes, all the cycloadditions as

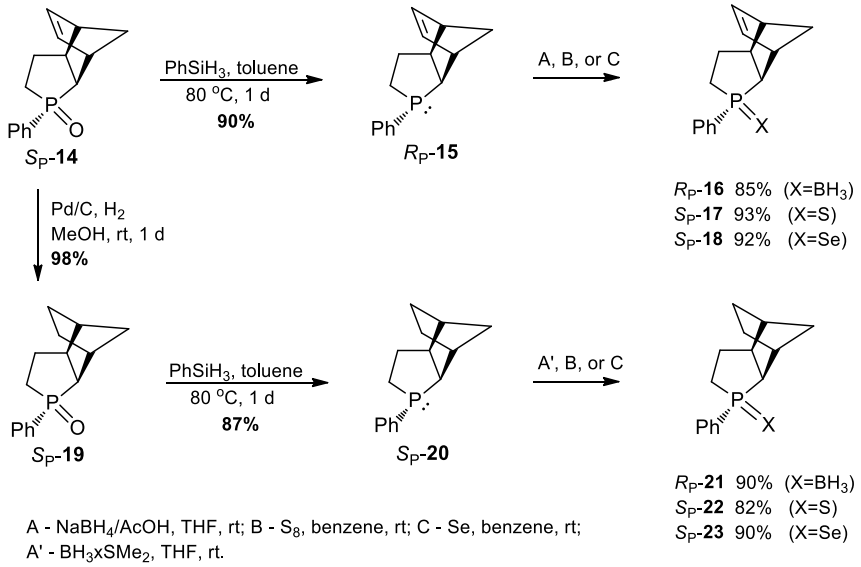
well as the following transformations were tested first for conditions and efficiency using *rac*-**1** as the substrate. Thus, the reaction conditions and yields of the syntheses starting with (S_P)-**1** which follow below should be considered as the optimized ones.

The cycloaddition reaction of (S_P)-**1** to cyclopentadiene is shown in Scheme 5. In spite of the fact that with this reactive diene the reaction could be carried out at the temperature lowered to 160 °C, the best results were obtained by running it at 200 °C for two days and by adding an extra portion of fresh cyclopentadiene after one day. In this way, (S_P)-**14** was obtained in 54% isolated yield after chromatographic separation from some minor products (one of those, not isolated, was identified by GC-MS analysis as being derived from the primary cycloadduct by sequential addition of another molecule of cyclopentadiene).



Scheme 5. Cycloaddition of (S_P)-**1** to cyclopentadiene.

The enantiomeric purity of (S_P)-**14** was confirmed by ^{1}H NMR using Kagan's solvating agent [55] to be >98% ee. Similar to before, reduction of (S_P)-**14** by $PhSiH_3$ at 80 °C gave saturated phosphine (S_P)-**15** which after boranation with $NaBH_4$/AcOH and oxidation by sulfur and selenium gave phosphine-borane (S_P)-**16**, sulfide (S_P)-**17**, and selenide (S_P)-**18**, respectively, in very good yields (Scheme 6). Reoxidation of the phosphine by H_2O_2 gave back (S_P)-**14** of practically the same specific rotation sign and value as the starting one, confirming again the clean retention of configuration at P in the reduction step.



Scheme 6. Conversion of (S_P)-**14** to other unsaturated P-derivatives and their saturated counterparts.

Hydrogenation of the double bond in (S_P)-**14** gave the fully saturated tricyclic phosphine oxide (S_P)-**19** in 98% yield. As before, reduction of (R_P)-**19** by $PhSiH_3$ at 80 °C gave saturated phosphine (R_P)-**20** which after boranation with BH_3xSMe_2 and oxidation by sulfur and selenium gave phosphine-borane (R_P)-**21**, sulfide (S_P)-**22**, and selenide (S_P)-**23**, respectively, in very good yields (Scheme 6).

Finally, the endo stereochemistry of the cycloaddition of (S_P)-**1** to cyclopentadiene was unequivocally confirmed by X-ray analysis of the saturated oxide *rac*-**19** obtained in preliminary optimizing reactions starting with *rac*-**1** (Figure 1).

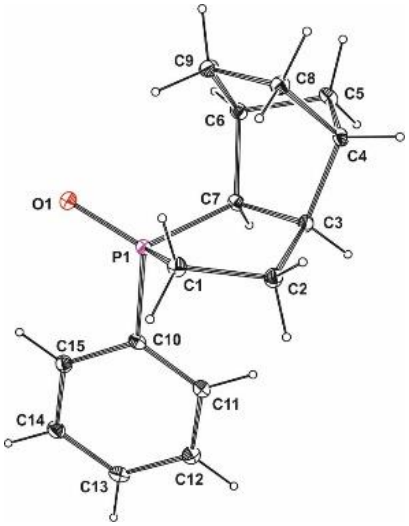
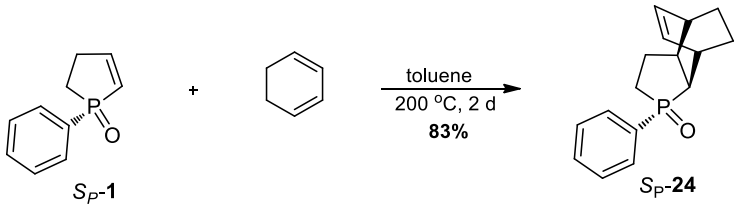


Figure 1. Molecular structure of *rac*-**19** with thermal ellipsoids set at 40% probability.

Cycloaddition of (S_P)-**1** to cyclohexadiene at 190 °C was studied next, which gave the tricyclic phosphaundecene oxide (S_P)-**24** in 80% isolated yield (Scheme 7). The enantiomeric purity of (S_P)-**24** of more than 98% ee was again confirmed by ^{1}H NMR using Kagan's solvating agent [55].

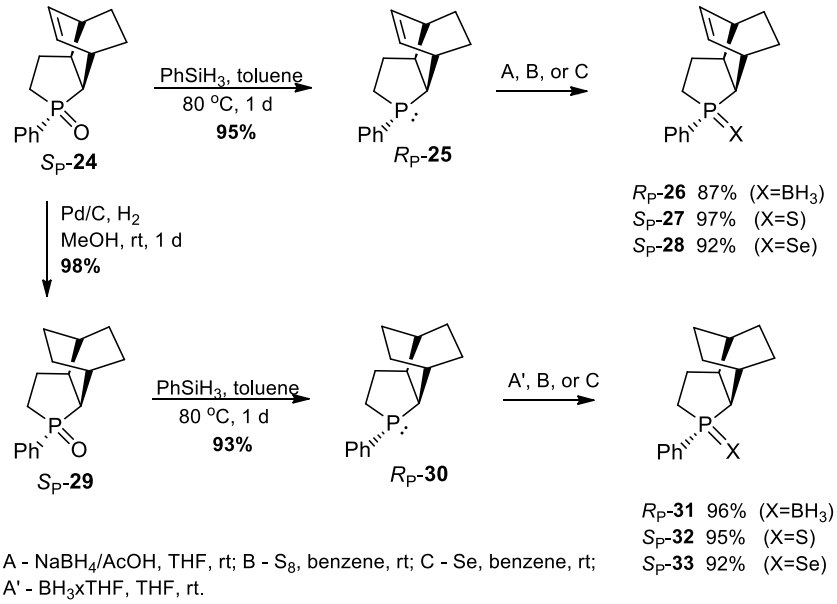


Scheme 7. Cycloaddition of (S_P)-**1** to cyclohexadiene.

Stereoretentive conversion of (S_P)-**24** to the corresponding tricyclic phosphine (R_P)-**25**, phosphine-borane (R_P)-**26**, sulfide (S_P)-**27** and selenide (S_P)-**28** in very good yields is shown in Scheme 8. Reoxidation of the phosphine by H_2O_2 gave back (S_P)-**24** of practically the same specific rotation sign and value as the starting one, confirming again the clean retention of configuration at P in the reduction step.

As before, to characterize also the corresponding fully saturated tricyclic phosphaundecane derivatives, (S_P)-**24** was hydrogenated over Pd/C and gave saturated oxide (S_P)-**29** in 98% isolated yield. Subsequent reduction of (S_P)-**29** by $PhSiH_3$ gave saturated phosphine (R_P)-**30** from which (R_P)-**31**, (S_P)-**32**, and (S_P)-**33** were obtained by complexation with BH_3xTHF, and oxidation with S_8 and Se, respectively (Scheme 8).

The expected endo stereocourse of the cycloadditon of cyclohexadiene to **1** was confirmed by an X-ray analysis of phosphine-borane *rac*-**26** available from preliminary optimizing experiments starting with *rac*-**1** (Figure 2).



Scheme 8. Conversion of (S_P)-**24** to other unsaturated P-derivatives and their saturated counterparts.

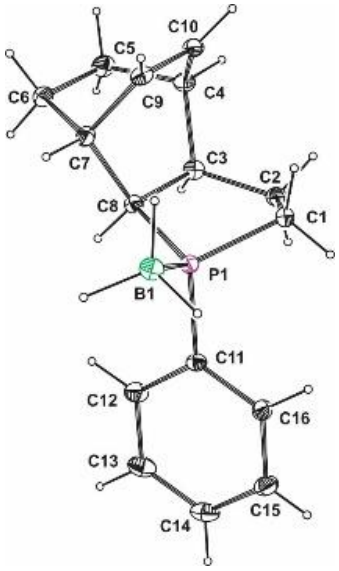
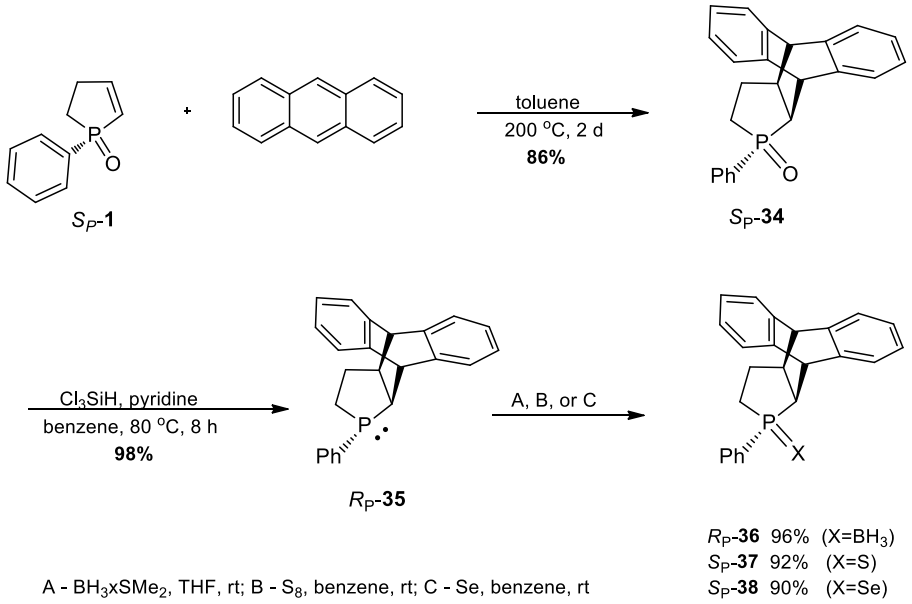


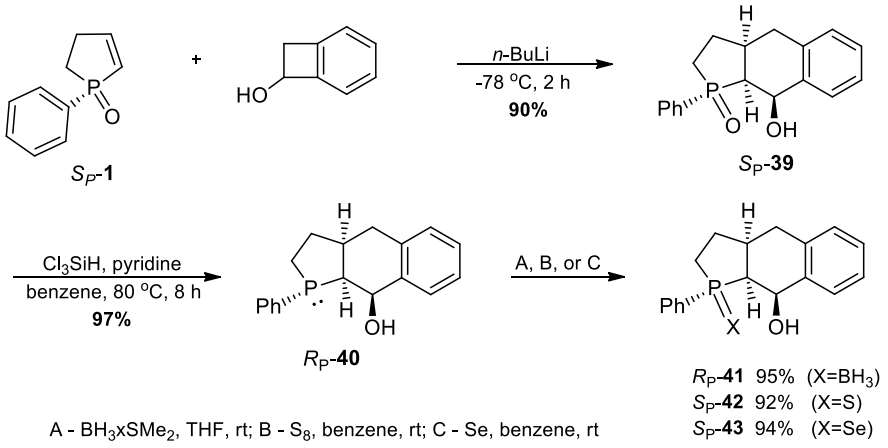
Figure 2. Molecular structure of *rac*-**26** with thermal ellipsoids set at 40% probability.

In turn, extending the cyclohexadiene structure to anthracene enabled to produce a pentacyclic cycloadduct (S_P)-**34** possessing still more sterically congested phosphorus center. As shown in Scheme 9, the pentacyclic cycloadduct (S_P)-**34** was obtained in a good 86% yield. In addition, in this case, more than 98% ee enantiomeric purity of the cycloadduct was confirmed by its ^{1}H NMR spectra recorded in the presence of the Kagan's solvating agent. Subsequently, (S_P)-**34** was reduced to the corresponding phosphine (R_P)-**35** from which the other virtually enantiopure P-derivatives (R_P)-**36**, (S_P)-**37**, and (S_P)-**38** were obtained with retention of configuration at P. In this case, however, reduction of (S_P)-**34** by Cl_3SiH/pyridine and boranation of (R_P)-**35** by BH_3xSMe_2 gave somewhat better results than use of $PhSiH_3$ and BH_3xTHF (or $NaBH_4$/AcOH), respectively. As before, reoxidation of (R_P)-**35** by H_2O_2 gave back (S_P)-**34** of practically the same specific rotation sign and value as the starting one, confirming again the clean retention of configuration at P in the reduction step.



Scheme 9. Cycloaddition of (S_P)-**1** to anthracene and synthesis of other cycloadduct P-derivatives.

Next, (S_P)-**1** was subjected to a reaction with highly reactive lithiated α-oxy-*o*-xylilene generated in situ from benzocyclobutenol and *n*-BuLi [67,68]. The reaction was effectively carried out at −78 °C and provided hexahydrobezophosphindole (S_P)-**39** in 90% isolated yield and of very high (>98% ee) enantiomeric purity, as confirmed by its ^{1}H NMR spectra recorded in the presence of the Kagan's solvating agent [55] (Scheme 10).



Scheme 10. Synthesis of cycloadduct (S_P)-**39** and its other P-derivatives **41**–**43**.

Attempted confirmation of the expected regio and endo selectivity of the cycloaddition by X-ray structural determination of *rac*-**39** was only partially successful. The collected data could not be fully refined because of poor quality of the monocrystals obtained. However, the data were sufficiently accurate to provide confirmation of the expected stereochemistry of the process as judged from the obtained unoptimized molecular structures which are displayed in Figure 3.

To enable characterization of other hexahydrobenzophosphindole P-derivatives, oxide (S_P)-**39** was subjected to reduction by Cl_3SiH/pyridine to yield the corresponding phosphine (R_P)-**40** from which the phosphine-borane (R_P)-**41**, phosphine sulfide (S_P)-**42**, and phosphine selenide (S_P)-**43** were obtained (Scheme 10). The phosphine (R_P)-**40** was also reoxidized by H_2O_2 and provided (S_P)-**39** of practically the same specific rotation sign and value as the starting oxide.

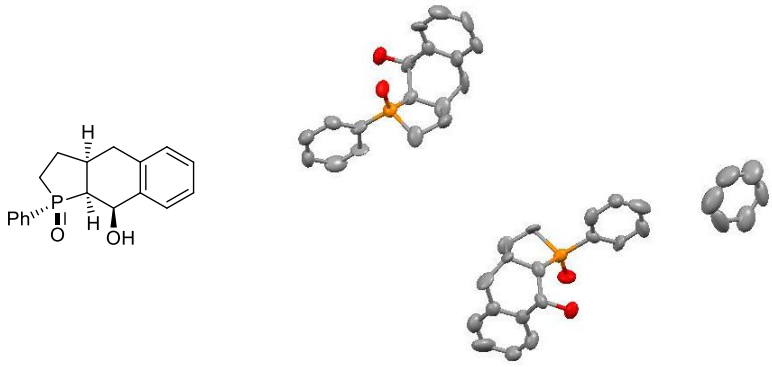


Figure 3. Molecular structure of *rac*-**39**: an overview picture.

It is important to note, however, that attempted reduction of (S_P)-**39** by $PhSiH_3$ at 80 °C for two days led unexpectedly to the formation of two reduction products as revealed by the ^{31}P NMR spectrum showing two phosphine signals at δ_P −8.35 and −3.67 ppm in a 7:3 ratio, respectively. Most probably, the observed loss of configurational integrity at P can be ascribed to an apparently lowered inversion barrier of the produced phosphine causing its substantial epimerization at P even at 80 °C. As shown in Scheme 10, using a stronger stereoretentive reductant, e.g., Cl_3SiH, instead of $PhSiH_3$, allowed to completely avoid the P-epimerization by carrying out the reduction at lower temperature and in shorter time (60 °C, 9 h).

Finally, in the course of efforts to obtain a better crystallizing derivative, *rac*-**39** was reacted with triflic acid and DCC in dry pyridine/DMSO mixture. A few crystals, which were fished out from the post-reaction mixture, were found suitable for an X-ray analysis. The solved molecular structure of this product is shown in Figure 4.

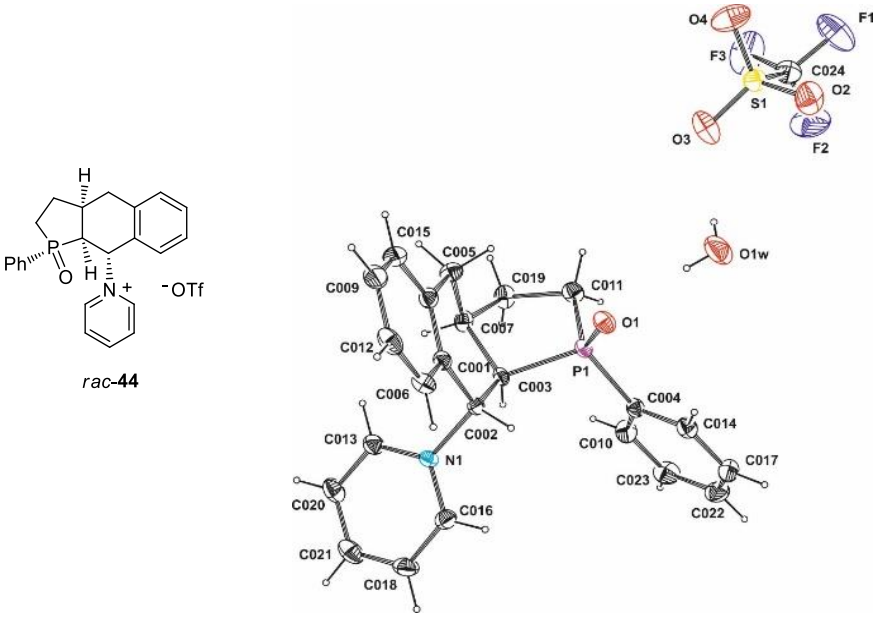
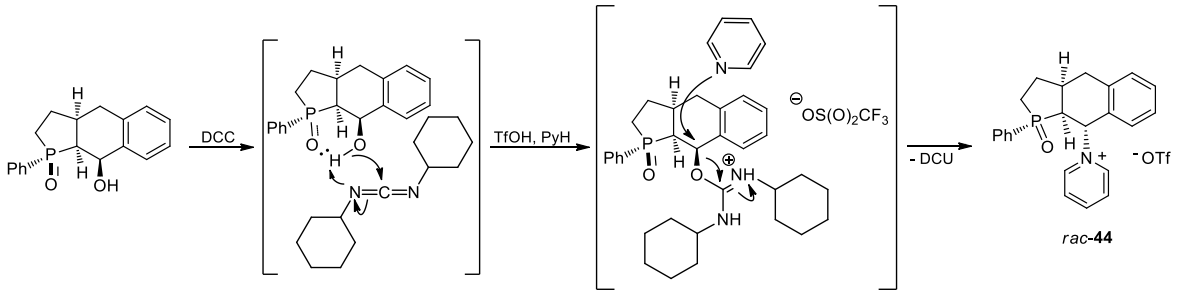


Figure 4. Molecular structure of *rac*-**44** with thermal ellipsoids set at 40% probability.

As can be seen, it turned out to be a (hexahydrobenzophosphindole-9-yl)pyridinium triflate **44**, which was formed from **39** and pyridine, most probably, via a modified Steglich esterification process [69] as visualized in Scheme 11.



Scheme 11. A plausible synthetic path for **44**.

The revealed structure of **44** eventually provided the sought unequivocal confirmation of the endo stereocourse of the cycloaddition step. Thus, it has been proven that, also with α-oxy-*o*-xylilene, (S_P)-**1** undergoes the face- and regioselective cycloaddition in the endo mode.

3. Materials and Methods

3.1. General Information

The reagents were purchased from commercial suppliers and used without further purification. Solvents were dried and distilled under argon before use. All of the reactions involving formation and further conversions of phosphines were carried out under argon atmosphere with attempted complete exclusion of air from the reaction vessels and solvents, including those used in the work-up. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV300 (^{1}H 300 MHz, ^{31}P 121.5 MHz, ^{13}C NMR 75 MHz) and Bruker AV500 (^{1}H 500 MHz, ^{31}P 202 MHz, ^{13}C NMR 126 MHz) spectrometers (Bruker; Billerica, Ma., USA). All spectra were obtained in $CDCl_3$ solutions, unless mentioned otherwise, and the chemical shifts (δ) are expressed in ppm using internal reference to TMS and external reference to 85% H_3PO_4 in D_2O for ^{31}P. Coupling constants (J) are given in Hz. The abbreviations of signal patterns are as follows: s-singlet, d-doublet, t-triplet, q-quartet, m-multiplet, b-broad, and i-intensive. NMR determinations of enantiomeric purity of phosphine oxides were performed in $CDCl_3$ in the presence of 1.1 equivalents of (*S*)-3,5-dinitro-*N*-α-phenylethyl-benzamide as described before. [55]. Elemental analyses were measured on the PerkinElmer CHN 2400. Optical rotations were measured in a 1 dm cell on a PerkinElmer 341LC digital polarimeter at ambient temperature. Thin-layer chromatography (TLC) was carried out on silica gel (Kieselgel 60, F254 on aluminum sheet, Merck). All separations and purifications by column chromatography were conducted by using Merck Silica gel 60 (230–400 mesh), unless noted otherwise. The X-ray data were collected at 100(2) K on a Nonius Kappa CCD diffractometer using graphite monochromated MoKα radiation (λ = 0.71073 Å) and on an Enraf Nonius MACH3 diffractometer using graphite monochromated CuKα radiation (λ = 1.54178 Å).

3.2. Synthesis and Spectral Data

3.2.1. Synthesis of 1-Phenylphosphol-2-ene 1-oxide (**1**)

To a 300 mL (4.02 mol) of butadiene condensed in a 2 L round-bottom flask cooled to −78 °C was added 2 g of 2,6-di-*tert*-butyl-2-methylphenol (polymerization inhibitor) followed by a solution of 136 mL (179 g, 1 mol) of *P*,*P-dichlorophenylphosphine* dissolved in 650 mL of dry petroleum ether. The flask was tightly closed and left at rt for 3 months. After this time, 300 mL of H_2O was slowly added to the stirred reaction mixture. Then, 70 mL of 5% aqueous solution of $NaHCO_3$ and ca. 160 mL of 30% of aqueous solution of NaOH were gradually added with care to reach the pH range of 6.5–7.0. Then, the resulting layers were separated and the water layer was washed four times with $CHCl_3$ (4 × 100 mL). The combined organic layers were dried over $MgSO_4$, concentrated under reduced pressure and distilled at 167–192 °C/2 mmHg to afford 110 g (61.8%) of 1-phenylphosphol-2-ene 1-oxide (**1**) which

solidified after cooling into a white solid: mp = 79 °C. ^{1}H NMR (300 MHz) δ 2.05–2.25 (m, 2H), 2.65–2.8 (m, 1H), 2.9–3.05 (m, 1H), 6.2–6.4 (dm, 1H), 7.0–7.25 (dm, 1H), 7.45–7.55 (m, 3H), 7.6–7.75 (m, 1H), ^{13}C NMR (75 MHz) δ 26.1 (d, J = 71.77), 30.45 (d, J = 10.57), 126.0 (s), 127.3 (s), 129 (d, J = 12.09), 130.85 (d, J = 10.43), 132.15 (d, J = 2.94), 133.3 (s), 134.6 (s), 153.1(d, J = 24.38), ^{31}P NMR (121 MHz) δ 61.2. Elemental Anal. Calcd. for $C_{10}H_{11}OP$: C 67.41, H 6.22, found C 67.3, H 6.31. This product typically contains a small amount of isomeric 1-phenylphosphol-3-lene 1-oxide (typically less then 3–5% as revealed by its ^{1}H and ^{31}P NMR spectra by the presence of pertinent signals: ^{1}H NMR (300 MHz) δ 6.0 (d, $^{3}J_{\text{P-H}}$ = 40 H); ^{31}P NMR (121 MHz) δ 56.3). It can be recrystallized from toluene when needed, but, for the purpose of resolution, it has been used as such.

3.2.2. Resolution of 1-Phenylphosphol-2-ene 1-oxide (**1**)

Step 1. Reduction of *rac*-**1**.

In a 250 mL three-neck round-bottom flask equipped with a reflux condenser and an addition funnel was placed 32.5 g (0.183 mol) of racemic 1-phenylphosphol-2-ene 1-oxide (**1**) dissolved in 20 mL of dry benzene. The solution was degassed, purged with argon, and heated to 60 °C. Then, 25.15 mL (0.2 mol) of $PhSiH_3$ dissolved in 20 mL of benzene was added dropwise over a period of 2 h. After the addition of $PhSiH_3$, the reaction mixture was heated at 60 °C for additional 40 h. After this time, the reaction mixture was allowed to cool to room temperature, the volatiles were removed under reduced pressure and the residue was distilled under reduced pressure at 80–100 °C/0.8 mmHg to yield 26 g (88%) of 1-phenylphosphol-2-ene (**2**), as a colorless oil which was directly used for preparation of salts in step 2.

Step 2. Quaternization of 1-Phenylphosphol-2-ene (**2**) by L-menthyl bromoacetate.

In a 2 L round-bottom flask was dissolved 44.5 g (0.16 mol) of L-menthyl bromoacetate in 25 mL of dry ethanol and 780 mL of dry ethyl acetate. The solution was degassed and placed under argon atmosphere. Then, 26 g (0.16 mol) of *rac*-**2** dissolved in 40 mL of ethyl acetate was added dropwise over a period of 8 h with magnetic stirring. During the addition, after ca. 2 h, a white precipitate started to accumulate slowly. After the addition was completed, the reaction mixture was stirred at room temperature overnight. The formed crystalline precipitate was filtered off and was found to contain the (S_P) epimer of **3** in great predominance (>90%). Crystallization of the precipitate from AcOEt-EtOH (10:1) was repeated (1–4 times) until ^{1}H NMR monitoring showed that the resulting crystals contained only a single, diastereomerically pure, salt (S_P)-**3**. The second P-epimer, (R_P)-**3**, was obtained by repeated recrystallizations of the residue from dry benzene-hexane 10:1 (or from toluene), until ^{1}H NMR monitoring showed that the resulting crystals contained only the single, diastereomerically pure, salt (R_P)-**3**:

(S_P)-**3**: 25.9 g (37%), white crystals: mp = 197–199 °C, $[\alpha]_D$ = −13.65 (c 2.15, $CHCl_3$). ^{1}H NMR (300 MHz) δ 0.59 (d, J = 6.9, 3H), 0.77 (d, J = 6.9, 3H), 0.83 (d, J = 6.5, 3H), 0.8–1.0 (m, 2H), 1.2–1.3 (m, 1H), 1.3–1.4 (m, 1H), 1.45–1.55 (m, 1H), 1.6–1.7 (m, 2H), 1.7–1.75 (m, 1H), 2.7–2.85 (m, 1H), 3.1–3.2 (m, 1H), 3.45–3.6 (m,1H), 3.75–3.9 (m, 1H), 4.64 (dt, J = 4.4, J = 10.9, 1H), 4.67 (dd, J = 14.0, J = 17.3, 1H), 4.9 (dd, J = 13.5, J = 17.3, 1H), 6.75 (dddd, J = 2.2, J = 2.3, J = 8, J = 20.3, 1H), 7.53 (dddd, J = 2.6, J = 2.7, J = 8.0, J = 36.4, 1H), 7.55–7.65 (m, 2H), 7.7–7.75 (m, 1H), 7.9–8.1 (m, 2H); ^{13}C NMR (75 MHz) δ 15.8 (s), 20.8 (s), 21.3 (s), 21.8 (s), 22.9 (s), 25.8 (s), 31.4 (s), 33.8 (d, J = 34), 33.83 (s), 34.1 (d, J = 12), 40.5 (s), 113.35 (d, J = 81), 120.3 (d, J = 88), 129.95 (d, J = 14), 132.18 (d, J = 11), 134.5 (s), 162.9 (d, J = 23), 164.93 (d, J = 4); ^{31}P NMR (121 MHz) δ 52.91, Elemental Anal. for $C_{22}H_{32}BrO_2P$: calcd. C 60.14, H 7.34, found C 59.95, H 7.4.

(R_P)-**3**: 23.1 g (33%), white tiny needles: mp = 76–77 °C, $[\alpha]_D$ = −55.55 (c 2.14, $CHCl_3$). ^{1}H NMR (300 MHz) δ 0.52 (d, J = 6.9, 3H), 0.78 (d, J = 6.9, 3H), 0.86 (d, J = 6.3, 3H), 0.8–1.0 (m, 2H), 1.2–1.3 (m, 1H), 1.3–1.45 (m, 1H), 1.55–1.55 (m, 1H), 1.6–1.7 (m, 2H), 1.75–1.8 (m, 1H), 2.7–2.85 (m, 1H), 3.1–3.2 (m, 1H), 3.45–3.55 (m,1H), 3.8–3.9 (m, 1H), 4.55 (dt, J = 4.5, J = 11.2, 1H), 4.8 (d, J = 13.5, 2H), 6.73 (dddd, J = 1.8, J = 2.1, J = 8, J = 28, 1H), 7.58 (dddd, J = 2.1, J = 2.5, J = 8.4, J = 37.3, 1H), 7.6–7.7 (m, 2H),

7.7–7.75 (m, 1H), 7.95–8.1 (m, 2H). ^{13}C NMR (75 MHz) δ 15.8 (s), 20.7 (s), 20.9 (d, J = 57), 21.85 (s), 22.9 (s), 25.9 (s), 31.4 (s), 33.75 (d, J = 34), 33.83 (s), 34.09 (d, J = 13), 40.4 (s), 46.6 (s), 113.0 (d, J = 80), 120.3 (d, J = 84), 129.95 (d, J = 12.5), 132.1 (d, J = 11), 134.6 (s), 163.1 (d, J = 22), 165.02 (d, J = 4). ^{31}P NMR (121 MHz) δ 53.03. Elemental Anal. For $C_{22}H_{32}BrO_2P$: calcd. C 60.14, H 7.34, found C 59.86, H 7.41.

Step 3. Hydrolysis of the resolved phosphonium salts (S_P)-**3** and (R_P)-**3**.

In a 500 mL round-bottom flask was dissolved 25 g (56.9 mmol) of (S_P)-**3** in 45 mL of CH_2Cl_2. To the solution was added 130 mL of H_2O and 120 mL of 1M NaOH, and the reaction mixture was stirred at rt for 12 h. The two phases were separated and the water phase was washed twice with CH_2Cl_2 (2 × 30 mL). The combined dichloromethane layers were dried over $MgSO_4$ and concentrated. The residue was purified by crystallization from toluene which afforded 9.1 g (90%) of (S_P)-1-phenylphosphol-2-ene-1-oxide (S_P-**1**) as white crystals, mp = 83–84 °C, $[\alpha]_D$ = +306.6 (*c* 1.3, $CHCl_3$).

The (R_P)-1-phenylphosphol-2-ene-1-oxide (R_P-**1**) was prepared from (R_P)-**3** analogously as described for the S_P isomer. White crystals: mp = 84–85 °C, $[\alpha]_D$ = −302.4 (*c* 1.42, $CHCl_3$).

The enantiomeric purity of the synthesized enantiomers of phospholene oxide **1** was determined by running their ^{1}H and ^{31}P NMR spectra in the presence of equimolar amounts of (*S*)-3,5-dinitro-*N*-α-phenylethyl-benzamide as a chiral solvating agent (Kagan's reagent) according to the described procedure [56]. As no presence of signals of the opposite enantiomer could be detected in either spectrum, the enantiomeric purity of both (S_P)-**1** and (R_P)-**1** was assigned to be at least 98% ee.

3.2.3. Synthesis of (S_P)-1-Phenyl-2,3,3a,4,7,7a-heksahydrophosphindole 1-oxide (S_P-**4**): Typical Procedure

Two grams (0.011 mol) of (S_P)-**1**, 3 g (0.056 mol) of 1.3-butadiene, and 0.019 g (0.089 mmol) of 2,6-di-*tert*-butyl-4-methylphenol (polymerization inhibitor) dissolved in 7 mL of toluene were placed in a tightly closed glass ampoule and heated at 200 °C for 48 h. During that time, two additional portions of the diene were added after controlling the progress of cycloaddition by TLC. After completion of heating, the reaction mixture was dissolved in 75 mL of methanol and filtered to remove the polymeric side-products formed. Then, 150 mL of 15% hydrochloric acid was added and the resulting mixture was washed with benzene (2 × 75 mL). The organic layers were combined, dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified on silica gel column using ethyl acetate/methanol (25:1) as eluent to give a white solid which was recrystallized from toluene/hexane mixture to yield 1.3 g (51%) of cycloadduct (S_P)-**4** as white crystals. Mp = 95–96 °C, $[\alpha]_D$ = −42.30 (*c* 1.13, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.80–7.73 (m, 2H); 7.52–7.28 (m, 3H); 5.81–5.70 (m, 2H); 2.52–2.03 (m, 10H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 134.3 (d, J = 88.1 Hz); 131.5 (d, J = 2.8 Hz); 130.0 (d, J = 9.2 Hz); 128.5 (d, J = 11.2 Hz); 124.7 (d, J = 0.9 Hz); 124.5 (d, J = 6.7 Hz); 35.7 (d, J = 69 Hz); 34.0 (d, J = 12.2 Hz); 27.9 (d, J = 5.6 Hz); 26.7 (d, J = 8.1 Hz); 25.8 (d, J = 65 Hz); 19.2 (d, J = 3.2 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 63.29 (s). Elemental Anal. for $C_{14}H_{17}OP$: calcd. C, 72.39; H, 7.37; found C, 72.47; H, 7.34.

3.2.4. Synthesis of (R_P)-1-Phenyl-2,3,3a,4,7,7a-heksahydrophosphindole (**5**): Typical Procedure

In a Schlenk flask protected from air was placed 1 g (0.0043 mol) of (S_P)-**4** and 5 mL of toluene and then 0.7 g (0.0064 mol) of $PhSiH_3$ was added. The mixture was heated under argon atmosphere at 75–80 °C for 24 h. Then, the reaction mixture was concentrated and distilled under reduced pressure to give 0.83 g (90%) of phosphine (R_P)-**5** as a colorless oil. Bp = 160 °C/0.2 mmHg, $[\alpha]_D$ = +75.22 (c 0.9, $CHCl_3$). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 3.84 (s). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.50–7.38 (m, 2H); 7.34–7.21 (m, 3H); 5.77–5.53 (m, 2H); 2.40–1.97 (m, 9H); 1.74–1.39 (m, 1H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 141.8 (d, J = 23 Hz); 130.7 (d, J = 15.4 Hz); 128.3 (d, J = 5.1 Hz); 127.5 (s); 125.4 (d, J = 13.8 Hz); 125.4 (d, J = 0.9 Hz); 38.3 (d, J = 8 Hz); 37.6 (d, J = 2.8 Hz); 31.4 (d, J = 3.4 Hz); 26.5 (d, J = 2.4 Hz); 25.7

(d, *J* = 28.6 Hz); 22.7 (d, *J* = 14 Hz). The configuration and high enantiomeric purity of (R_P)-**5** was confirmed by its oxidation by H_2O_2 which afforded back (S_P)-**4** of $[\alpha]_D$ = −42.26 (*c* 0.97, $CHCl_3$).

3.2.5. Synthesis of (R_P)-1-Phenyl-2,3,3a,4,7,7a-heksahydrophosphindole-borane (**6**): Typical Procedure

To a solution of 1 g (0.0046 mol) of (R_P)-**5** in dry THF (4 mL) kept under argon at 0 °C was added 0.26 g (0.0069 mol) of solid $NaBH_4$ in one portion. Then, 0.46 g (0.0077 mol) of acetic acid dissolved in THF (1.9 mL) was added dropwise within 30 min. The resulting mixture was left at room temperature for 1 h, and the conversion was checked by TLC. Then, water (4.5 mL) was added slowly, followed by 0.44 g (0.42 mL) of acetic acid dissolved in 5.6 mL of water. The reaction mixture was evaporated and the residue was passed through a silica gel column using CH_2Cl_2/hexane (2:3) to give 0.9 g (85%) of borane (R_P)-**6** as white crystals. Mp = 62–63 °C, $[\alpha]_D$ = −10.46 (*c* 1.04, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.75–7.68 (m, 2H); 7.49–7.40 (m, 3H); 5.75–5.60 (m, 2H); 2.50–1.85 (m, 10H); 1.10–0.20 (m, 3H, BH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 132 (d, *J* = 10.1 Hz); 131.6 (d, *J* = 8.4 Hz); 131.2 (d, *J* = 2.4 Hz); 129.2 (d, *J* = 9.4 Hz); 125 (d, *J* = 8.7 Hz); 37.4 (d, *J* = 3.1 Hz); 35.4 (d, *J* = 35 Hz); 30.6; 26.7 (d, *J* = 5.1 Hz); 23.0 (d, *J* = 35.2 Hz); 22.1 (d, *J* = 4.9 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 40.11. Elemental Anal. For $C_{14}H_{20}BP$: calcd. C, 73.08; H, 8.76; found C, 72.99; H, 8.36.

3.2.6. Synthesis of (S_P)-1-Phenyl-2,3,3a,4,7,7a-heksahydrophosphindole 1-sulfide (**7**): Typical Procedure

To a solution of 1 g (0.0046 mole) of phosphine (R_P)-**5** in 6 mL of benzene under argon was added 0.14 g (0.0046 mol) of sublimed sulfur. The reaction mixture was stirred at room temperature for 24 h. After this time, the reaction mixture was concentrated and the crude product was purified by column chromatography using CH_2Cl_2/hexane (2:3) followed by crystallization from methanol to yield 1.10 g (96%) of sulfide **7** as white crystals. Mp = 90–91 °C, $[\alpha]_D$ = −19.08 (*c* 1.13, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.93–7.85 (m, 2H); 7.55–7.45 (m, 3H); 5.83–5.70 (m, 2H); 2.71–2.62 (m, 1H); 2.50–1.95 (m, 9H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 135 (d, *J* = 70.1 Hz); 131.7 (d, *J* = 3 Hz); 130.8 (d, *J* = 9.8 Hz); 129 (d, *J* = 11.5 Hz); 125.2 (d, *J* = 7.6 Hz); 125.1 (d, *J* = 1.3 Hz); 39.0 (d, *J* = 53 Hz); 36.3 (d, *J* = 10.3 Hz); 32.5 (d, *J* = 52.7 Hz); 29.9 (d, *J* = 3.7 Hz); 27.3 (d, *J* = 7.2 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 65.56 (s). Elemental Anal. For $C_{14}H_{17}SP$: calcd. 67.71; H, 6.89; found C, 67.57; H, 6.85.

3.2.7. Synthesis of (S_P)-1-Phenyl-2,3,3a,4,7,7a-heksahydrophosphindole 1-Selenide (**8**): Typical Procedure

To a solution of 1 g (0.0046 mole) of phosphine (R_P)-**5** in 6 mL of benzene under argon was added 0.36 g (0.0046 mol) of selenium. The reaction mixture was magnetically stirred at room temperature for 24 h. After this time, the reaction mixture was concentrated and the crude product was purified by column chromatography using CH_2Cl_2/hexane (2:3) followed by crystallization from methanol to yield 1.25 g (92%) of selenide **8** as white crystals. Mp = 63 °C, $[\alpha]_D$ = −15.05 (*c* 1.65, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.92–7.84 (m, 2H); 7.50–7.45 (m, 3H); 5.82–5.69 (m, 2H); 2.89–2.80 (m, 1H); 2.52–2.04 (m, 9H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 132 (d, *J* = 70.1 Hz); 131.7 (d, *J* = 3 Hz); 131.1 (d, *J* = 9.8 Hz); 129 (d, *J* = 11.5 Hz); 125.1 (d, *J* = 8.5 Hz); 125.0 (d, *J* = 1.5 Hz); 38.5 (d, *J* = 45.8 Hz); 36.6 (d, *J* = 9.5 Hz); 32.9 (d, *J* = 46.3 Hz); 30.4 (d, *J* = 2.7 Hz); 27.2 (d, *J* = 7.2 Hz); 23.3. ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 53.81 (s). Elemental Anal. For $C_{14}H_{17}SeP$: calcd. C, 56.95; H, 5.80; found C, 56.79; H, 5.70.

3.2.8. Synthesis of (S_P)-1-Phenyl-octahydrophosphindole 1-oxide (**9**): Typical Procedure

To a flask containing 1 g (0.0043 mol) of (S_P)-**5** dissolved in 15 mL of methanol was added 0.045 g (0.00043 mol) of Pd/C. Argon was passed through the flask for 10 min., and the flask was capped with a balloon filled with hydrogen. Then, the reaction mixture was magnetically stirred at room temperature for 24 h, filtered through Celite and the filtrate was evaporated. The resulting solid residue was recrystallized from toluene/hexane to give 0.99 g (98%) of saturated oxide (S_P)-**9** as white crystals. Mp = 96–98 °C, $[\alpha]_D$ = −27.65(*c* 1.34, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.79–7.71 (m,

2H); 7.54–7.43 (m, 3H); 2.29–2.03 (m, 5H); 1.93–1.59 (m, 7H); 1.44–1.37 (m, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 135.1 (d, J = 87 Hz); 131.4 (d, J = 2.8 Hz); 129.9 (d, J = 9.2 Hz); 128.5 (d, J = 11.1 Hz); 39.7 (d, J = 68.2 Hz); 38.2 (d, J = 11.4 Hz); 28.10 (d, J = 6.8 Hz); 27.5 (d, J = 64.7 Hz); 27.2 (d, J = 5.8 Hz); 24.3 (d, J = 6.9 Hz); 22.6; 21.50 (d, J = 3.3 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 60.01 (s). Elemental Anal. For $C_{14}H_{19}OP$: calcd. C, 71.77; H, 8.17; found C, 71.62; H, 8.10.

3.2.9. Synthesis of (R_P)-1-Phenyl-octahydrophosphindole (**10**)

(R_P)-**10** was obtained in 86% yield according to typical procedure described in Section 3.2.4. (R_P)-**10**: a colorless oil, bp = 136 °C/0.2 mmHg, $[\alpha]_D$ = +26.61 (*c* 1.1, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.50–7.43 (m, 2H); 7.36–7.26 (m, 3H); 2.32–2.17 (m, 3H); 2.05–1.78 (m, 5H); 1.60–1.41 (m, 6H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 135(d, J = 11.6 Hz); 131.0 (d, J = 16.5 Hz); 128.6 (d, J = 5.4 Hz); 127.8 (s); 44.5 (d, J = 8.9 Hz); 41.4 (d, J = 1.4 Hz); 31.6 (d, J = 3.1 Hz); 28.1 (d, J = 2.2 Hz); 27.8 (d, J = 26.1 Hz); 25.5 (d, J = 13.1 Hz); 23.8 (d, J = 12.1 Hz); 23.1. ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ -1.38 (s). The configuration and high enantiomeric purity of (R_P)-**10** was confirmed by its oxidation by H_2O_2 which afforded back (S_P)-**9** of $[\alpha]_D$ = −27.71 (*c* 1.1, $CHCl_3$).

3.2.10. Synthesis of (R_P)-1-Phenyl-octahydrophosphindole-borane (**11**): Typical Procedure

To a solution of 1 g (0.0046 mol) of phosphine (R_P)-**10** in 6 mL of benzene under argon atmosphere was added 0.50 g (0.0066 mol) of BH_3-SMe_2 complex and the reaction mixture was stirred at room temperature for 24 h. At the end of the reaction, the mixture was concentrated and the crude product was passed through a silica gel column using CH_2Cl_2/hexane (2:3) as eluent to give 0.96 g (95%) of phosphine-borane (R_P)-**11** white solid. Mp = 68–69 °C, $[\alpha]_D$ = −5.04 (*c* 1.15, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.74–7.86 (m, 2H); 7.47–7.45 (m, 3H); 2.29–1.32 (m, 14H); 1.25–0.40 (m, 3H, BH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 132.7 (d, J = 46.5 Hz); 131.6 (d, J = 8.4 Hz); 131.2 (d, J = 2.5 Hz); 129.1 (d, J = 9.4 Hz); 40.9 (d, J = 3.0 Hz); 39.7 (d, J = 33.8 Hz); 29.5; 27.8 (d, J = 5 Hz); 25.2 (d, J = 10.5 Hz); 24.3 (d, J = 35.7 Hz); 24.0 (d, J = 3.9 Hz); 22.3. ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 37.3. Elemental Anal. For $C_{14}H_{22}BP$: calcd. C, 72.44; H, 9.55; found C, 72.23; H, 9.55.

3.2.11. Synthesis of (S_P)-1-Phenyl-octahydrophosphindole 1-sulfide (**12**)

(S_P)-**12** was obtained in 94% yield according to typical procedure described in Section 3.2.6. (S_P)-**12**: white crystals, mp = 82–84 °C, $[\alpha]_D$ = − 4.03 (*c* 1.15, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.94–7.86 (m, 2H); 7.50–7.47 (m, 3H); 2.68–2.59 (m, 1H); 2.42–2.19 (m, 4H); 2.00–1.90 (m, 3H); 1.73–1.65 (m, 3H); 1.51–1.48 (m, 2H); 1.35–1.29 (m, 1H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 135.5 (d, J = 69.5 Hz); 131.6 (d, J = 3 Hz); 130.6 (d, J = 10 Hz); 129 (d, J = 11.4 Hz); 41.8 (d, J = 52 Hz); 39.5 (d, J = 9.9 Hz); 34.7 (d, J = 52.2 Hz); 28.3 (d, J = 8.2 Hz); 28.0 (d, J = 3.7 Hz); 25.1 (d, J = 10.4 Hz); 23.5 (d, J = 1.6 Hz); 22.0. ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 64,87 (s). Elemental Anal. For $C_{14}H_{19}SP$: calcd. C, 67.17; H, 7.65; found C, 67.09; H, 7.55.

3.2.12. Synthesis of (S_P)-1-Phenyl-octahydrophosphindole 1-selenide (**13**)

(S_P)-**13** was obtained in 89% yield according to typical procedure described in Section 3.2.7. (S_P)-**13**: white crystals, mp = 67–68 °C, $[\alpha]_D$ = −0.95 (*c* 0.97, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.93–7.83 (m, 2H); 7.49–7.47 (m, 3H); 2.84–2.74 (m, 1H); 2.56–1.35 (m, 13H). ^{13}C NMR ($CDCl_3$, 75,5 MHz): δ 134.5 (d, J = 61.4 Hz); 131.6 (d, J = 3 Hz); 131.0 (d, J = 9.8 Hz); 129.0 (d, J = 11.3 Hz); 41.3 (d, J = 44.8 Hz); 39.5 (d, J = 8.8 Hz); 33.9 (d, J = 45.9 Hz); 28.3 (d, J = 2.8 Hz); 28.0 (d, J = 8.3 Hz); 25.3 (d, J = 11.7 Hz); 25.0; 21.7. ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 52.96 (s). Elemental Anal. For $C_{14}H_{19}SeP$: calcd C, 56.57; H, 6.44; found C, 56.40; H, 6.40.

3.2.13. Synthesis of (S_P)-3-Phenyl-3-phosphatricyclo[5.2.1.0^{2,6}]dec-8-ene 3-oxide (**14**)

(S_P)-**14** was obtained in 54% yield according to typical procedure described in Section 3.2.3. (S_P)-**14**: white crystals, mp = 100–101 °C, $[\alpha]_D$ = −21.23 (*c* 1.02, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.72–7.66 (m, 2H); 7.49–7.46 (m, 3H); 6.64–6.61 (m, 1H); 6.25–6.22 (m, 1H); 3.32 (s, 1H); 3.04 (m, 2H); 2.73–2.70 (m, 1H); 1.96–1.85 (m, 5H); 1.58–1.55 (m, 1H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 138.4 (d, *J* = 4.97 Hz); 135.0 (d, *J* = 89.1 Hz); 133.7(s); 131.5 (d, *J* = 2.7 Hz); 129.8 (d, *J* = 9.1 Hz); 128.7 (d, *J* = 11.0 Hz); 53.0 (d, *J* = 9.6 Hz); 48.2 (d, *J* = 2.1 Hz); 46.4 (d, *J* = 2.1 Hz); 45.1 (d, *J* = 30.8 Hz); 44.5 (d, *J* = 32.6 Hz); 29.4 (d, *J* = 67.3 Hz); 23.5 (d, *J* = 9.8 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 61.43 (s). Elemental Anal. for $C_{15}H_{17}OP$: calcd. C, 73.75; H, 7.01; found C, 73.60; H, 6.98.

3.2.14. Synthesis of (R_P)-3-Phenyl-3-phosphatricyclo[5.2.1.0^{2,6}]dec-8-ene (**15**)

(R_P)-**15** was obtained in 89% yield according to typical procedure described in Section 3.2.4. (R_P)-**15**: a colorless oil, bp = 150 °C/0.2 mmHg, $[\alpha]_D$ = −16.8 (*c* 0.9, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.42–7.37 (m, 2H); 7.34–7.24 (m, 3H); 6.38–6.35 (m, 1H); 6.16–6.13 (m, 1H); 3.18–3.17 (m, 2H); 3.04–3.0 (m, 1H); 2.90 (s, 1H); 1.85–1.78 (m, 4H); 1.47–1.65 (m, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 141.6 (d, *J* = 19.4 Hz); 136.7 (d, *J* = 9.2 Hz); 135.5(s); 131.1 (d, *J* = 15.4 Hz); 128.3 (d, *J* = 5.3 Hz); 127.3 (s); 52.9 (d, *J* = 6.2 Hz); 51.2 (d, *J* = 9.1 Hz); 50.4 (d, *J* = 3.4 Hz); 48.5 (s); 47.3 (d, *J* = 21.3 Hz); 30.1 (d, *J* = 4.1 Hz); 28.8 (d, *J* = 12.3 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ -6.84 (s). The configuration and high enantiomeric purity of (R_P)-**15** was confirmed by its oxidation by H_2O_2 which afforded back (S_P)-**14** of $[\alpha]_D$ = −21.2 (*c* 1.21, $CHCl_3$).

3.2.15. Synthesis of (R_P)-3-Phenyl-3-phosphatricyclo[5.2.1.0^{2,6}]dec-8-ene-borane (**16**)

(R_P)-**16**: a colorless oil, $[\alpha]_D$ = −32.1 (*c* 1.04, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.70–7.62 (m, 2H); 7.46–7.43 (m, 3H); 6.58–6.55 (m, 1H); 6.19–6.16 (m, 1H); 3.32–3.21 (m, 2H); 3.01–2.95 (m, 2H); 1.92–1.91 (m, 4H); 1.6–1.58 (m, 1H); 1.56–1.48 (m, 1H); 1.01–0.66 (m, 3H, BH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 137.8 (d, *J* = 3.78 Hz); 134.4 (s); 131.3 (d, *J* = 7.8 Hz); 130.6 (d, *J* = 2.4 Hz); 128.8 (d, *J* = 9.1 Hz); 53.3 (d, *J* = 9.2 Hz); 48.4 (d, *J* = 1.9 Hz); 48.0 (d, *J* = 1.5 Hz);46.6 (d, *J* = 4.5 Hz); 46.0 (s); 28.1 (d, *J* = 33.6 Hz); 27.7 (d, *J* = 2.2 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 35.89. Elemental Anal. For $C_{15}H_{20}BP$: calcd. C, 74.41; H, 8.32; found C, 74.31; H, 8.29.

3.2.16. Synthesis of (S_P)-3-Phenyl-3-phosphatricyclo[5.2.1.0^{2,6}]dec-8-ene 3-sulfide (**17**)

(S_P)-**17** was obtained in 93% yield according to typical procedure described in Section 3.2.6. (S_P)-**17**: white crystals, mp = 103–105 °C, $[\alpha]_D$ = −33.01 (*c* 1.03, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.87–7.79 (m, 2H); 7.48–7.47 (m, 3H); 6.81–6.78 (m, 1H); 6.23–6.21 (m, 1H); 3.36 (s, 1H); 3.20–3.14 (m, 1H); 3.07–3.02 (m, 2H); 2.10–1.91 (m, 4H); 1.64–1.49 (m, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 138.1 (d, *J* = 5.1 Hz); 135.1 (d, *J* = 71.1 Hz); 133.75 (s); 131.2 (d, *J* = 2.85 Hz); 130.4 (d, *J* = 9.54 Hz); 128.7 (d, *J* = 11.2 Hz); 52.6 (d, *J* = 10.3 Hz); 49.5 (d, *J* = 60.89 Hz); 47.6 (d, *J* = 10.8 Hz); 47.2 (s); 35.7 (d, *J* = 52.8 Hz); 25.9 (d, *J* = 6.0 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 62.19 (s). Elemental Anal. For $C_{15}H_{17}SP$: calcd. C, 69.20; H, 6.58; found C, 69.10; H, 6.55.

3.2.17. Synthesis of (S_P)-3-Phenyl-3-phosphatricyclo[5.2.1.0^{2,6}]dec-8-ene 3-selenide (**18**)

(S_P)-**17** was obtained in 92% yield according to typical procedure described in Section 3.2.7. (1.2:1) as eluent followed by crystallization from methanol to yield 1.24 g (92%) of selenide (S_P)-**18**: white crystals, mp = 93–94 °C, $[\alpha]_D$ = −39.98 (*c* 1.09, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.87–7.80 (m, 2H); 7.46–7.45 (m, 3H); 6.90–6.88 (m, 1H); 6.23–6.20 (m, 1H); 3.39 (s, 1H); 3.25–3.23 (m, 1H); 3.22–3.10 (m, 2H); 2.21–2.14 (m, 2H); 1.95–1.90 (m, 2H); 1.58–1.52 (m, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 137.7 (d, *J* = 5.3 Hz); 133.9 (d, *J* = 63 Hz); 133.8 (s); 131.3 (d, *J* = 2.9 Hz); 130.9 (d, *J* = 9.5 Hz); 128.7 (d, *J* = 11.1 Hz); 52.6 (d, *J* = 10.5 Hz); 49.8 (d, *J* = 53.6 Hz); 49.4 (d, *J* = 1.9 Hz); 48.7 (d, *J* = 9.2 Hz); 47.7 (s); 36.1 (d,

J = 45.9 Hz); 27.1 (d, J = 4.2 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 47.22 (s). Elemental Anal. For $C_{15}H_{17}SeP$: calcd. C, 58.63; H, 5.57; found C, 58.45; H, 5.53.

3.2.18. Synthesis of (S_P)-3-Phenyl-3-phosphatricyclo[5.2.1.0^{2,6}]decane 3-oxide (**19**)

(S_P)-**19** was obtained in 98% yield according to typical procedure described in Section 3.2.8. The resulting solid residue was recrystallized from toluene/hexane to give 0.98 g (98%) of saturated oxide (S_P)-**19**: white crystals, mp = 105–106 °C, $[\alpha]_D$ = −20.57 (c 1.08, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.73–7.65 (m, 2H); 7.54–7.43 (m, 3H); 2.79–2.67 (m, 2H); 2.40–2.30 (m, 3H); 2.12–2.00 (m, 3H); 1.85–1.75 (m, 2H); 1.69–1.52 (m, 5H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 135.7 (d, J = 88.9 Hz); 131.7 (d, J = 2.6 Hz); 129.9 (d, J = 8.9 Hz); 129.0 (d, J = 10.8 Hz); 44.2 (d, J = 15.7 Hz); 43.8 (d, J = 12.0 Hz); 43.4 (d, J = 2.3 Hz); 42.6 (d, J = 73.6 Hz); 40.7 (d, J = 2.4 Hz); 29.4 (d, J = 65.3 Hz); 25.4 (d, J = 6.2 Hz); 23.5; 21.45 (d, J = 10.4 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 60.03 (s). Elemental Anal. For $C_{15}H_{19}OP$: calcd. C, 73.15; H, 7.77; found C, 73.15; H, 7.74.

3.2.19. Synthesis of (R_P)-3-Phenyl-3-phosphatricyclo[5.2.1.0^{2,6}]decane (**20**)

(R_P)-**20** was obtained in 87% yield according to typical procedure described in Section 3.2.4. (R_P)-**20**: a colorless oil, bp = 210 °C/0.3 mmHg, $[\alpha]_D$ = −11.62 (c 0.9, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.62–7.12 (m, 5H); 2.78–2.67 (m, 2H); 2.44 (s, 1H); 2.16 (s, 1H); 1.99–1.82 (m, 2H); 1.77–1.67 (m, 2H); 1.52–1.44 (m, 2H); 1.40–1.18 (m, 4H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 142.0 (d, J = 16.2 Hz); 131.4 (d, J = 15.46 Hz); 128.6 (d, J = 5.4 Hz); 127.69 (s); 50.8 (d, J = 10.6 Hz); 48.9 (d, J = 4.1 Hz); 43.6 (d, J = 6.5 Hz); 43.4 (s); 42.1 (d, J = 18.1 Hz); 29.2 (d, J = 12.5 Hz); 28.7 (d, J = 4.9 Hz); 25.7 (d, J = 17.7 Hz); 23.9 (s). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ -9.90 (s). The configuration and high enantiomeric purity of (R_P)-**20** was confirmed by its oxidation by H_2O_2 which afforded back (S_P)-**19** of $[\alpha]_D$ = −20.52 (c 1.2, $CHCl_3$).

3.2.20. Synthesis of (R_P)-3-Phenyl-3-phosphatricyclo[5.2.1.0^{2,6}]decane-borane (**21**)

To a solution of 1 g (0.004 mol) of phosphine **(R_P)-20** in 6 mL of benzene under argon atmosphere was added 0.49 g (0.0065 mol) of the BH_3-SMe_2 complex, and the reaction mixture was stirred at room temperature for 24 h. At the end of the reaction, the mixture was concentrated and the crude product was passed through a silica gel column using CH_2Cl_2/hexane (1:2) as eluent to yield 0.95 g (90%) of phosphine-borane **(R_P)-21** as an oil. $[\alpha]_D$ = −42.24 (c 0.98, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.65–7.55 (m, 2H); 7.47–7.37 (m, 3H); 2.92–2.84 (m, 1H); 2.72–2.66 (m, 2H); 2.36 (s, 1H); 2.15–1.95 (m, 5H); 1.58–1.36 (m, 5H); 1.25–0.30 (m, 3H, BH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 132 (d, J = 49.1 Hz); 131.3 (d, J = 7.8 Hz); 130.9 (d, J = 2.3 Hz); 129.1 (d, J = 9.2 Hz); 47.3 (d, J = 2.6 Hz); 45.1 (d, J = 35.7 Hz); 43.8 (d, J = 10.8 Hz); 43.1 (d, J = 1.4 Hz); 40.8 (d, J = 3.7 Hz); 28.2 (d, J = 32.3 Hz); 25.9 (d, J = 2.0 Hz); 25.3 (d, J = 6.0 Hz); 23.3 (s). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 33.16. Elemental Anal. For $C_{15}H_{22}BP$: calcd. C, 73.80; H, 9.08; found C, 73.70; H, 9.01.

3.2.21. Synthesis of (S_P)-3-Phenyl-3-phosphatricyclo[5.2.1.0^{2,6}]decane 3-sulfide (**22**)

(S_P)-**22** was obtained in 82% yield according to typical procedure described in Section 3.2.6. (S_P)-**22**: white crystals, mp = 95–96 °C, $[\alpha]_D$ = −22.61 (c 1.72, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.82–7.75 (m, 2H); 7.50–7.42 (m, 3H); 2.85–2.74 (m, 2H); 2.70–2.65 (m, 1H); 2.56–2.53 (m, 1H); 2.44 (s, 1H); 2.31–2.22 (m, 1H); 2.19–2.07 (m, 2H); 1.95–1.79 (m, 1H); 1.66–1.46 (m, 5H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 135.2 (d, J = 72.2 Hz); 131.5 (d, J = 2.9 Hz); 130.3 (d, J = 9.5 Hz); 129.0 (d, J = 11.2 Hz); 46.3 (d, J = 48.6 Hz); 45.9 (d, J = 3.8 Hz); 44.1 (d, J = 2.1 Hz); 43.4 (d, J = 12.9 Hz); 41.3 (s); 35.6 (d, J = 51.0 Hz); 24.9 (d, J = 6.7 Hz); 23.9 (d, J = 6.6 Hz); 23.4 (s). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 59.32 (s). Elemental Anal. For $C_{15}H_{19}SP$: calcd. C, 68.67; H, 7.30; found C, 68.57; H, 7.27.

3.2.22. Synthesis of (S_P)-3-Phenyl-3-phosphatricyclo[5.2.1.$0^{2,6}$]decane 3-selenide (**23**)

(S_P)-**23** was obtained in 90% yield according to typical procedure described in Section 3.2.7. (S_P)-**23**: white crystals, mp = 118–119 °C, $[\alpha]_D$ = −45.87 (*c* 1.09, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.82–7.75 (m, 2H); 7.45–7.42 (m, 3H); 2.78–2.76 (m, 3H); 2.61–2.56 (m, 2H); 2.51–2.38 (m, 1H); 2.26–1.92 (m, 2H); 1.82–1.75 (m, 1H); 1.61–1.53 (m, 5H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 133.9 (d, *J* = 64.4 Hz); 131.6 (d, *J* = 2.9 Hz); 130.7 (d, *J* = 9.5 Hz); 129.0 (d, *J* = 11.1 Hz); 46.5 (d, *J* = 12.7 Hz); 46.1 (d, *J* = 26.1 Hz); 44.3 (d, *J* = 2.0 Hz); 43.4 (d, *J* = 13.0 Hz); 41.7 (s); 36.1 (d, *J* = 44.4 Hz); 25.1 (d, *J* = 4.7 Hz); 24.6 (d, *J* = 7.0 Hz); 23.4 (s). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 42.60 (s). Elemental Anal. For $C_{15}H_{19}SeP$: calcd. C, 58.25; H, 6.19; found C, 58.11; H, 6.15.

3.2.23. Synthesis of (S_P)-3-Phenyl-3-phosphatricyclo[5.2.2.$0^{2,6}$]undec-8-ene 3-oxide (**24**)

(S_P)-**24** was obtained in 83% yield according to typical procedure described for (S_P)-**4** in Section 3.2.3. This time, however, addition of cyclohexadiene was repeated three times (4+2+1 equiv.) and the reaction mixture was heated for 72 h. (S_P)-**24**: white crystals, mp = 88–89 °C, $[\alpha]_D$ = −18.3 (*c* 1.12, $CHCl_3$). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 61.45 (s). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.75–7.68 (m, 2H); 7.51–7.43 (m, 3H); 6.56 (ddd, 1H, *J* = 1.1 Hz; 6.6 Hz; 18 Hz); 6.28 (t, 1H, *J* = 7.4 Hz); 3.02 (s, 1H); 2.71–2.69 (m, 1H); 2.58–2.49 (m, 1H); 2.29 (dt, 1H, *J* = 2.5 Hz; 10.2 Hz); 2.08–1.88 (m, 4H); 1.54–1.49 (m, 2H); 1.36–1.31 (m, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 135.6 (d, *J* = 2.3 Hz); 134.8 (d, *J* = 87.2 Hz); 132.4; 131.9 (d, *J* = 2.8 Hz); 130.5 (d, *J* = 9 Hz); 129.0 (d, *J* = 10.9 Hz); 44.7 (d, *J* = 25.6 Hz); 44.2 (d, *J* = 36.5 Hz); 35.9 (d, *J* = 2.1 Hz); 30.4 (d, *J* = 2.8 Hz); 28.7 (d, *J* = 48.3 Hz); 28.2 (d, *J* = 5.4 Hz); 26.3 (d, *J* = 12.3 Hz); 25.1. Elemental Anal. For $C_{16}H_{19}OP$: calcd. C, 74.40; H, 7.41; found C, 74.25; H, 7.38.

3.2.24. Synthesis of (R_P)-3-Phenyl-3-phosphatricyclo[5.2.2.$0^{2,6}$]undec-8-ene (**25**)

(R_P)-**25** was obtained in 89% yield according to typical procedure described in Section 3.2.4. (R_P)-**25**: a colorless oil, bp = 150 °C/0.2 mmHg, $[\alpha]_D$ = −3.6 (*c* 1.67, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.39–7.34 (m, 2H); 7.31–7.18 (m, 3H); 6.38–6.26 (m, 2H); 2.97–2.94 (m, 1H); 2.61–2.48 (m, 3H); 2.05–1.96 (m, 1H); 1.85–1.69 (m, 3H); 1.58–1.51 (m, 2H); 1.31–1.19 (m, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 142.1 (d, *J* = 21.2 Hz); 135.0; 134.2 (d, *J* = 4.4 Hz); 130.8 (d, *J* = 15.1 Hz); 128.2 (d, *J* = 5.1 Hz); 127.4; 50.0 (d, *J* = 8.3 Hz); 47.3 (d, *J* = 2.9 Hz); 36.8 (s); 35.3 (d, *J* = 26.4 Hz); 35.0 (s); 26.6 (d, *J* = 10.1 Hz); 26.0 (d, *J* = 12.9 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 7.88. The configuration and high enantiomeric purity of (R_P)-**25** was confirmed by its oxidation by H_2O_2 which afforded back (S_P)-**24** of $[\alpha]_D$ = −18.35 (*c* 0.97, $CHCl_3$).

3.2.25. Synthesis of (R_P)-3-Phenyl-3-phosphatricyclo[5.2.2.$0^{2,6}$]undec-8-ene-borane (**26**)

(R_P)-**26** was obtained in 87% yield according to typical procedure described in Section 3.2.5. (R_P)-**26**: white crystals, mp = 90–91 °C, $[\alpha]_D$ = −31.98 (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.68–7.63 (m, 2H); 7.46–7.44 (m, 3H); 6.48–6.44 (m, 1H); 6.26–6.21 (m, 1H); 3.05–3.03 (m, 1H); 2.68–2.51 (m, 3H); 2.13–2.06 (m, 1H); 1.94–1.88 (m, 3H); 1.57–1.54 (m, 2H); 1.33–1.29 (m, 2H); 1.10–0.25 (m, 3H, BH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 135.4 (d, *J* = 1.49 Hz); 132.8 (s); 132.3 (d, *J* = 46.5 Hz); 131.7 (d, *J* = 8.0 Hz); 131.1 (d, *J* = 2.4 Hz); 129.1 (d, *J* = 9.1 Hz); 47.0 (s); 44.5 (d, *J* = 35.9 Hz); 36.3 (s); 32.2 (d, *J* = 3.0 Hz); 32.0 (d, *J* = 4.7 Hz); 26.8 (d, *J* = 12.4 Hz); 26.4 (d, *J* = 35.1 Hz); 25.1 (s). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 44.11. Elemental Anal. for $C_{16}H_{22}BP$: calcd. C, 75.03; H, 8.65; found C, 74.92; H, 8.61.

3.2.26. Synthesis of (S_P)-3-Phenyl-3-phosphatricyclo[5.2.2.$0^{2,6}$]undec-8-ene 3-sulfide (**27**)

(S_P)-**27** was obtained in 96% yield according to typical procedure described in Section 3.2.6. (S_P)-**27**: white crystals, mp = 13–131 °C, $[\alpha]_D$ = +6.36 (*c* 1.03, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.88–7.79 (m, 2H); 7.51–7.42 (m, 3H); 6.58 (t, 1H, *J* = 7.2 Hz); 6.25 (t, 1H, *J* = 7.2 Hz); 3.13 (m, 1H); 2.71–2.65 (m, 2H); 2.59–2.54 (m, 1H); 2.17–1.87 (m, 4H); 1.57–1.47 (m, 2H); 1.36–1.30 (m, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 135.0 (d, *J* = 2.4 Hz); 134.5 (d, *J* = 78.1 Hz); 131.8 (s); 131.2 (d, *J* = 2.9 Hz); 130.4 (d,

J = 9.6 Hz); 128.6 (d, *J* = 11.2 Hz); 47.19 (d, *J* = 54.8 Hz); 46.2 (d, *J* = 6.4 Hz); 36.4 (d, *J* = 1.9 Hz); 34.0 (d, *J* = 52.7 Hz); 31.6 (s); 29.6 (d, *J* = 10.6 Hz); 25.8 (d, *J* = 13.5 Hz); 24.6 (d, *J* = 1.1 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 67.98 (s). Elemental Anal. For $C_{16}H_{19}SP$: calcd. C, 70.04; H, 6.97; found C, 69.95; H, 6.95.

3.2.27. Synthesis of (S_P)-3-Phenyl-3-phosphatricyclo[5.2.2.0^{2,6}]undec-8-ene 3-selenide (**28**)

(S_P)-**28** was obtained in 92% yield according to typical procedure described in Section 3.2.7. (S_P)-**28**: white crystals, mp = 130–131 °C, $[\alpha]_D$ = +8.2 (*c* 1.09, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.88–7.79 (m, 2H); 7.51–7.42 (m, 3H); 6.58 (t, 1H, *J* = 7.2 Hz); 6.25 (t, 1H, *J* = 7.2 Hz); 3.13 (m, 1H); 2.71–2.65 (m, 2H); 2.59–2.54 (m, 1H); 2.17–1.87 (m, 4H); 1.57–1.47 (m, 2H); 1.36–1.30 (m, 2H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 135.0 (d, *J* = 2.4 Hz); 134.5 (d, *J* = 78.1 Hz); 131.8 (s); 131.2 (d, *J* = 2.9 Hz); 130.4 (d, *J* = 9.6 Hz); 128.6 (d, *J* = 11.2 Hz); 47.19 (d, *J* = 54.8 Hz); 46.2 (d, *J* = 6.4 Hz); 36.4 (d, *J* = 1.9 Hz); 34.0 (d, *J* = 52.7 Hz); 31.6 (s); 29.6 (d, *J* = 10.6 Hz); 25.8 (d, *J* = 13.5 Hz); 24.6 (d, *J* = 1.1 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 59.8 (s). Elemental Anal. For $C_{16}H_{19}SeP$: calcd. C, 59.82; H, 5.96; found C, 59.75; H, 5.94.

3.2.28. Synthesis of (S_P)-3-Phenyl-3-phosphatricyclo[5.2.2.0^{2,6}]undecane 3-oxide (**29**)

(S_P)-**29** was obtained in 98% yield according to typical procedure described in Section 3.2.8. (S_P)-**29**: white crystals, mp = 119–120 °C, $[\alpha]_D$ = −5.6 (*c* 1.08, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.77–7.70 (m, 2H); 7.54–7.45 (m, 3H); 2.33–2.00 (m, 7H); 1.95–1.82 (m, 2H); 1.79–1.63 (m, 3H); 1.56–1.46 (m, 4H). ^{13}C NMR ($CDCl_3$, 75,5 MHz): δ 134.9 (d, *J* = 87.4 Hz); 131.8 (d, *J* = 2.6 Hz); 130.4 (d, *J* = 9.1 Hz); 128.9 (d, *J* = 11.0 Hz); 41.7 (d, *J* = 8.1 Hz); 41.1 (d, *J* = 68.9 Hz); 29.9 (d, *J* = 65.4 Hz); 28.8 (d, *J* = 3.0 Hz); 27.6 (d, *J* = 13.6 Hz); 27.3 (s); 26.5 (d, *J* = 11.5 Hz); 25.1 (d, *J* = 3.3 Hz); 22.7 (d, *J* = 1.7 Hz); 20.9. ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 61.86 (s). Elemental Anal. For $C_{16}H_{21}OP$: calcd. C, 73.82; H, 8.13; found C, 73.72; H, 8.10.

3.2.29. Synthesis of (R_P)-3-Phenyl-3-phosphatricyclo[5.2.2.0^{2,6}]undecane (**30**)

(R_P)-**30** was obtained in 93% yield according to typical procedure described in Section 3.2.4. (R_P)-**30**: a colorless oil, bp = 180 °C/0.1 mmHg, $[\alpha]_D$ = −8.79 (*c* 1.8, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.66–7.30 (m, 2H); 7.26–7.13 (m, 3H); 2.42–2.31 (m, 2H); 2.04–1.81 (m, 6H); 1.61–1.28 (m, 8H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 142.6 (d, *J* = 20.7 Hz); 131.2 (d, *J* = 15.4 Hz); 128.6 (d, *J* = 5.4 Hz); 127.8; 46.8 (d, *J* = 9.9 Hz); 43.8 (d, *J* = 2 Hz); 33.0 (d, *J* = 2.3 Hz); 30.12; 29.5 (d, *J* = 23.2 Hz); 28.0 (d, *J* = 10.8 Hz); 27.7; 27.6 (d, *J* = 9 Hz); 22.8 (d, *J* = 10.8 Hz); 21.3. ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 2.85. The configuration and high enantiomeric purity of (R_P)-**30** was confirmed by its oxidation by H_2O_2 which afforded back (S_P)-**29** of $[\alpha]_D$ = −5.38 (*c* 1.24, $CHCl_3$).

3.2.30. Synthesis of (R_P)-3-Phenyl-3-phosphatricyclo[5.2.2.0^{2,6}]undecane-borane (**31**)

(R_P)-**31** was obtained in 96% yield according to typical procedure described in Section 3.2.9. with using 1M BH_3-THF instead of BH_3-SMe_2. **(R_P)-31**: a white solid, mp = 60–62 °C, $[\alpha]_D$ = −9.3 (*c* 1.2, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.73–7.63 (m, 2H); 7.48–7.39 (m, 3H); 2.73–2.37 (m, 2H); 2.20–2.01 (m, 6H); 1.76–1.68 (m, 4H); 1.64–1.51 (m, 3H); 1.47–1.29 (m, 1H); 1.29–0.30 (m, 3H, BH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 135.4 (d, *J* = 1.49 Hz); 132.8 (s); 132.3 (d, *J* = 46.5 Hz); 131.7 (d, *J* = 8.0 Hz); 131.1 (d, *J* = 2.4 Hz); 129.1 (d, *J* = 9.1 Hz); 47.0 (s); 44.5 (d, *J* = 35.9 Hz); 36.3 (s); 32.2 (d, *J* = 3.0 Hz); 32.0 (d, *J* = 4.7 Hz); 26.8 (d, *J* = 12.4 Hz); 26.4 (d, *J* = 35.1 Hz); 25.1 (s). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 39.35. Elemental Anal. For $C_{16}H_{24}BP$: calcd. C, 74.44; H, 9.37; found C, 74.22; H, 9.34.

3.2.31. Synthesis of (S_P)-3-Phenyl-3-phosphatricyclo[5.2.2.0^{2,6}]undecane 3-sulfide (**32**)

(S_P)-**32** was obtained in 95% yield according to typical procedure described in Section 3.2.6. (R_P)-32: white crystals, mp = 124–125 °C, $[\alpha]_D$ = +2.8 (*c* 1.03, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.90–7.82 (m, 2H); 7.50–7.47 (m, 3H); 2.52–2.49 (m, 1H); 2.41–2.06 (m,7H); 1.74–1.44 (m, 8H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 135.2 (d, *J* = 70.0 Hz); 131.5 (d, *J* = 2.9 Hz); 130.6 (d, *J* = 9.7 Hz); 129.0 (d,

J = 11.3 Hz); 43.1 (d, *J* = 24.7 Hz); 42.6 (d, *J* = 20.2 Hz); 35.6 (d, *J* = 52.0 Hz); 30.0 (d, *J* = 2.73 Hz); 28.1 (d, *J* = 10.6 Hz); 27.5 (d, *J* = 14.6 Hz); 26.4 (d, *J* = 70.8 Hz); 22.1 (d, *J* = 2.1 Hz); 20.6. ^{31}P NMR ($CDCl_3$, 121,5 MHz): δ 65.93. Elemental Anal. For $C_{16}H_{21}SP$: calcd. C, 69.53; H, 7.65; found C, 69.43; H, 7.63.

3.2.32. Synthesis of (S_P)-3-Phenyl-3-phosphatricyclo[5.2.2.0^{2,6}]undecane 3-selenide (**33**)

(S_P)-**33** was obtained in 95% yield according to typical procedure described in Section 3.2.7. (S_P)-**33**: white crystals, mp = 146–147 °C, $[\alpha]_D$ = −0.95 (*c* 0.97, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.87–7.84 (m, 2H); 7.52–7.46 (m, 3H); 2.53–2.34 (m, 5H); 2.22–2.05 (m, 3H); 1.74–1.42 (m, 8H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 134.0 (d, *J* = 62.2 Hz); 131.6 (d, *J* = 2.9 Hz); 131.0 (d, *J* = 9.7 Hz); 129.0 (d, *J* = 11.2 Hz); 43.1 (d, *J* = 6.0 Hz); 42.6 (d, *J* = 44.6 Hz); 36.0 (d, *J* = 45.7 Hz); 30.2 (d, *J* = 2.5 Hz); 29.0 (d, *J* = 9.3 Hz); 27.5 (d, *J* = 14.9 Hz); 26.9; 26.8 (d, *J* = 1.2 Hz); 21.8 (d, *J* = 2.3 Hz); 20.5 (s). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 52.94. Elemental Anal. For $C_{16}H_{21}SeP$: calcd. C, 59.44; H, 6.54; found C, 59.22; H, 6.50.

3.2.33. Synthesis of (S_P)-Dibenzo[a,d]-3-Phenyl-3-phosphatricyclo[5.2.2.02.6]undeca-8,10-diene 3-oxide (**34**)

In a tightly closed glass ampoule was placed 2 g (0.011 mol) of (S_P)-**4**, 3.9 g (0.022 mol) of anthracene, and 0.019g (0.089 mmol) of 2.6-di-*tert*-butyl-4-methylphenol in 7 mL of toluene. The reaction mixture was then heated at 200 °C for 48 h. After that time, the reaction mixture was evaporated under reduced pressure and the residue was passed through a silica gel column using AcOEt/CH_3OH (30:1) as eluent to give a white solid which was recrystallized from toluene/hexane to yield 3.4 g (86%) of (S_P)-**34**: white crystals, mp = 251–252 °C, $[\alpha]_D$ = −12.3 (*c* 1.1, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.63–7.56 (m, 3H); 7.5–7.37 (m, 3H); 7.32–7.08 (m, 7H); 4.87 (t, 1H, *J* = 2.9 Hz); 4.29 (bs, 1H); 2.93–2.81 (m, 1H); 2.61–2.55 (m, 1H); 1.87–1.70 (m, 2H); 1.52–1.23 (m, 1H); 0.28–0.13 (m, 1H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 143.6 (d, *J* = 1.6 Hz); 143.4; 141.0; 140.6 (d, *J* = 2.6 Hz);134.3 (d, *J* = 88.3 H); 131.7 (d, *J* = 2.7 Hz); 129.8 (d, *J* = 9 Hz); 128.8 (d, *J* = 11 Hz); 126.9; 126.6; 126.4; 126.2; 126.0; 124.6; 123.8; 123.0; 51.1 (d, *J* = 1.5 Hz); 44.1 (d, *J* = 1.6 Hz); 42.4 (d, *J* = 13.8 Hz); 41.9 (d, *J* = 70 Hz); 26.4 (d, *J* = 66 Hz); 24.5 (d, *J* = 11.6 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 58.65 (s). Elemental Anal. For $C_{24}H_{21}OP$: calcd. C, 80.88; H, 5.94; found C, 80.70; H, 5.90.

3.2.34. Synthesis of (R_P)-Dibenzo[a,d]-3-Phenyl-3-phosphatricyclo[5.2.2.02.6]undeca-8,10-diene (**35**)

A three-neck flask equipped with a reflux condenser and a septum was charged with 2.7 g (0.034 mol) of pyridine in 68 mL of benzene. Then, 1.54 g (0.011 mole) of Cl_3SiH was added followed by 0.81 g (0.0022 mol) of oxide (S_P)-**34** dissolved in benzene, and the reaction mixture was heated at 80 °C for 8 h. After the reaction mixture was cooled to room temperature, 20 mL of 30% NaOH was added slowly over a period of 1 h. The organic layer was separated, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was crystallized from methanol and yielded 0.76 g (98%) of phosphine (R_P)-**35**: white crystals, mp = 189–190 °C, $[\alpha]_D$ = −6.38 (*c* 1.5, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.42–6.96 (m, 13H); 4.51 (dd, 1H, *J* = 2.4 Hz, 4.3 Hz); 4.12 (d, 1H, *J* = 2.5 Hz); 2.88–2.76 (m, 2H); 1.9–1.7 (m, 2H); 1.31 (ddd, 1H, *J* = 2 Hz, 6.5 Hz, 14 Hz); 0.07–0.12 (m, 1H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 144.5 (d, *J* = 12.9 Hz); 144.0; 141.7; 141.4 (d, *J* = 3.1 Hz); 140.2 (d, *J* = 23 Hz); 129.0 (d, *J* = 15.4 Hz,); 128.3; 128.2; 126.4; 125.9 (d, *J* = 12.7 Hz); 125.8;125.3 (d, *J* = 2 Hz); 124.9; 123.5; 123.2; 51.1; 49.0 (d, *J* = 27 Hz); 48.5 (d, *J* = 14.3 Hz); 47.4 (d, *J* = 4.4 Hz); 32.9 (d, *J* = 4.4 Hz); 26.4 (d, *J* = 12.5 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 4.12. The configuration and high enantiomeric purity of (R_P)-**30** was confirmed by its oxidation by H_2O_2 which afforded back (S_P)-**29** of $[\alpha]_D$ = −11.95 (*c* 0.88, $CHCl_3$).

3.2.35. Synthesis of (R_P)-Dibenzo[a,d]-3-Phenyl-3-phosphatricyclo[5.2.2.02.6]undeca-8,10-diene -borane (**36**)

(R_P)-**36** was obtained in 96% yield according to typical procedure described in Section 3.2.9. **(R_P)-36**: a crystalline solid, mp = 243–244 °C, $[\alpha]_D$ = −25.95 (*c* 1.3, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.63 (m, 1H); 7.57–7.5 (m, 1H); 7.42–7.13 (m, H); 4.83 (dd, 1H, *J* = 2.2 Hz, 3.9 Hz); 4.29 (d, 1H, *J* = 3.3 Hz);

3.07–3.00 (m, 1H); 2.86–2.81 (m, 1H); 2.01–1.84 (m, 2H); 1.65 (m, 1H); 0.39–0.26 (m, 1H); 1.50–0.6 (m, 3H, BH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 144.7 (d, J = 12.4 Hz);143.7; 141.6; 140.2 (d, J = 1.5 Hz); 131.4 (d, J = 44.6 Hz); 131.3 (d, J = 8 Hz); 131.1 (d, J = 2.4 Hz); 129.2 (d, J = 9.2 Hz); 126.8; 126.6; 126.5; 125.1; 124.4; 123.4; 50.9; 45.8 (d, J = 1.5 Hz); 45.3 (d, J = 3.1 Hz); 44.1 (d, J = 31.6 Hz); 30.0; 25.5 (d, J = 32 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 42.56.

3.2.36. Synthesis of (S_P)-Dibenzo[a,d]-3-Phenyl-3-phosphatricyclo[5.2.2.02.6]undeca-8,10-diene 3-sulfide (**37**)

(S_P)-**37** was obtained in 92% yield according to typical procedure described in Section 3.2.6. (R_P)-**37**: white crystals, mp = 259–260 °C, $[\alpha]_D$ = +14.02 (*c* 1.32, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.75–7.65 (m, 3H); 7.43–7.05 (m, 11H); 5.04 (dd, 1H, J = 1.7 Hz, 4.5 Hz); 4.30 (s, 1H); 3.10–2.95 (m, 1H); 2.85–2.75 (m, 1H); 1.97–1.70 (m, 3H); 0.36–0.25 (m, 1H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 143.8 (d, J = 13 Hz); 143.5; 141.3; 139.8 (d, J = 2.3 Hz); 134.5 (d, J = 71.8 Hz); 131.3 (d, J = 2.8 Hz); 130.1 (d, J = 9.6 Hz); 128.7 (d, J = 11.3 Hz); 128.6; 126.4; 126.4; 126.1; 124.6; 123.9; 123.2; 51.2 (d, J = 1.5 Hz); 45.0 (d, J = 21.5 Hz); 44.7 (d, J = 31.2 Hz); 44.3 (d, J = 10.7 Hz); 32.2 (d, J = 50.6 Hz); 27.2 (d, J = 7.6 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 63.30. Elemental Anal. for $C_{24}H_{21}SP$: calcd. C, 77.39; H, 5.68; found C, 77.29; H, 5.64.

3.2.37. Synthesis of (S_P)-Dibenzo[a,d]-3-Phenyl-3-phosphatricyclo[5.2.2.02.6]undeca-8,10-diene 3-selenide (**38**)

(S_P)-**38** was obtained in 95% yield according to typical procedure described in Section 3.2.7. To the solution of 2 g (0.0058 mol) of (R_P)-**35** in 10 mL of benzene was added 0.46 g (0.0058 mol) of selenium under argon and the reaction mixture was stirred at room temperature for 24 h. After this time, the reaction mixture was concentrated and the crude product was purified by column chromatography using CH_2Cl_2/hexane (1:1) as eluent followed by crystallization from methanol to yield 2.21 g (90%) of selenide (S_P)-**38**: white crystals, mp = 248–249 °C, $[\alpha]_D$ = +15.07 (*c* 1.04, $CHCl_3$)). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.74–7.66 (m, 3H); 7.41–7.15 (m, 10H); 5.10 (dd, 1H, J = 2.4 Hz, 5.4 Hz); 4.3 (dd, 1H, J = 2.4 Hz, 2.7 Hz); 3.05–2.98 (m, 1H); 2.90–2.85 (m, 1H); 1.92–1.80 (m, 3H); 0.42–0.34 (m, 1H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 144.2 (d, J = 13.4 Hz); 143.9; 141.7; 139.8 (d, J = 2.2 Hz); 133.9 (d, J = 63.7 Hz); 131.6 (d, J = 3 Hz); 130.7 (d, J = 9.5 Hz); 129.5; 129.1 (d, J = 11.3 Hz); 128.8 (d, J = 3 Hz); 126.8 (d, J = 3 Hz); 126.8; 126.7; 126.4; 124.9; 124.3; 123.6; 51.4 (d, J = 1.3 Hz); 46.0 (d, J = 1.4 Hz); 45.3 (d, J = 1.2 Hz); 44.8 (d, J = 37 Hz); 33.0 (d, J = 44 Hz); 28.8 (d, J = 5.5 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 49.52 (s). Elemental Anal. For $C_{24}H_{21}SeP$: calcd. C, 77.39; H, 5.68; found C, 77.29; H, 5.64.

3.2.38. Synthesis of (S_P)-1-Phenyl-2,3,3a,4,9,9a-hexahydrophosphacyclopenta[b]naphthalen-9-ol 1-oxide (**39**)

In a Schlenk flask under argon atmosphere was placed 0.8 g (0.0067 mol) of benzocyclobutenol dissolved in 120 mL of THF, and all of it was cooled down to −78 °C with stirring. After 1 h, 5 mL of 1.6 M *n*-BuLi (1.1 equiv.) was added dropwise and the resulting mixture was stirred at −78 °C for 0.5 h. Then, 1 g (0.0056 mol) of (S_P)-**4** in THF was added dropwise and the reaction mixture was stirred at −78 °C for 2 h, and then at 0 °C for 1 h. Next, the volatiles were removed from the reaction mixture and the residue was dissolved in CH_2Cl_2 (120 mL) and washed with saturated aq. NH_4Cl (50 mL) and H_2O (2 × 35 mL). The separated organic layer was dried over anhydrous $MgSO_4$, filtered and evaporated under reduced pressure. The residue was purified by column chromatography using $CHCl_3$/acetone (35:1) as eluent to yield 1.5 g (90%) of oxide (S_P)-**39**: a white crystalline solid. mp = 145–147 °C, $[\alpha]_D$ = −46.95 (*c* 1.22, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.8–7.72 (m, 2H); 7.55–7.51 (m, 3H); 7.31–7.2 (m, 4H); 5.22 (dd, 1H, J = 4 Hz; 8.8 Hz); 4.97 (d, 1H, J = 7.9 Hz); 3.14 (dd, 1H, J = 8 Hz; 14.5 Hz); 3.0(ddd, 1H, J = 1.3 Hz, 6.8 Hz, 15.7 Hz); 2.66–2.63 (m, 1H); 2.55–2.33 (m, 2H); 2.2–2.1 (m, 2H); 1.98–1.86 (m, 1H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 139.5 (d, J = 8.2 Hz); 137.7; 132.8 (d, J = 90 Hz); 132.6 (d, J = 2.8 Hz); 130.6 (d, J = 9.9 Hz); 129.4 (d, J = 11.4 Hz); 128.5; 128.4; 126.9; 126.8; 70.6 (d, J = 5.5 Hz); 43.7

(d, *J* = 67 Hz); 38.0 (d, *J* = 10.4 Hz); 34.3 (d, *J* = 4.4 Hz); 32.2 (d, *J* = 8.7 Hz); 30.0 (d, *J* = 65.3 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 65.17 (s). Elemental Anal. For $C_{18}H_{19}O_2P$: calcd. C, 72.47; H, 6.42; found C, 72.37; H, 6.40.

3.2.39. Synthesis of (R_P)-1-Phenyl-2,3,3a,4,9,9a-hexahydrophosphacyclopenta[b]naphthalen-9-ol (**40**)

(R_P)-**40** was obtained in 97% yield according to procedure described in Section 3.2.32. (R_P)-**40**: a thick oil, $[\alpha]_D$ = −10.8 (*c* 1.5, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.8–7.72 (m, 2H); 7.55–7.51 (m, 3H); 7.31–7.2 (m, 4H); 5.22 (dd, 1H, *J* = 4 Hz; 8.8 Hz); 4.97 (d, 1H, *J* = 7.9 Hz); 3.14 (dd, 1H, *J* = 8 Hz; 14.5 Hz); 3.0(ddd, 1H, *J* = 1.3 Hz, 6.8 Hz, 15.7 Hz); 2.66–2.63 (m, 1H); 2.55–2.33 (m, 2H); 2.2–2.1 (m, 2H); 1.98–1.86 (m, 1H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 139.5 (d, *J* = 8.2 Hz); 137.7; 132.8 (d, *J* = 90 Hz); 132.6 (d, *J* = 2.8 Hz); 130.6 (d, *J* = 9.9 Hz); 129.4 (d, *J* = 11.4 Hz); 128.5; 128.4; 126.9; 126.8; 70.6 (d, *J* = 5.5 Hz); 43.7 (d, *J* = 67 Hz); 38.0 (d, *J* = 10.4 Hz); 34.3 (d, *J* = 4.4 Hz); 32.2 (d, *J* = 8.7 Hz); 30.0 (d, *J* = 65.3 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ -8.82. The configuration and high enantiomeric purity of (R_P)-**40** was confirmed by its oxidation by H_2O_2 which afforded back (S_P)-**39** of $[\alpha]_D$ = −46.6 (*c* 1.05, $CHCl_3$).

It is important to note in this place that a primarily attempted reduction of (S_P)-**39** by $PhSiH_3$ under our standard conditions (toluene, 80 °C, 24 h) led to the formation of two P-epimeric phosphine products as revealed by ^{31}P NMR spectrum of the crude post-reduction mixture showing two signals at −8.35 and −3.67 ppm (7:3) indicating that a partial inversion at P in (R_P)-**40** had taken place already at 80 °C.

3.2.40. Synthesis of
(R_P)-1-Phenyl-2,3,3a,4,9,9a-hexahydrophosphacyclopenta[b]naphthalen-9-ol-borane (**41**)

(R_P)-**41** was obtained in 95% yield according to typical procedure described in Section 3.2.9. with using 1M BH_3-THF instead of BH_3-SMe_2. (R_P)-**41**: white crystals, mp = 104–105 °C, $[\alpha]_D$ = −34.86 (c 1.3, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.77–7.73 (m, 2H); 7.51–7.44 (m, 3H); 7.33–7.21 (m, 4H); 5.24–5.20 (m, 1H -OH); 3.1–2.92 (m, 2H); 2.85–2.72 (m, 3H); 2.50–2.0 (m, 4H); 1.29–0.30 (m, 3H, BH_3). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 139.2 (d, *J* = 8.2 Hz); 137.4; 132.0 (d, *J* = 8.8 Hz); 131.8 (d, *J* = 2.5 Hz); 131.0 (d, *J* = 50.3 Hz); 129.4 (d, *J* = 9.8 Hz); 128.6; 128.6; 127.0; 126.9; 70.8 (d, *J* = 1.1 Hz, C-OH); 46.2 (d, *J* = 34.5 Hz); 39.7 (d, *J* = 5.4 Hz); 34.9 (d, *J* = 4.5 Hz); 33.5 (d, *J* = 3.4 Hz); 26.7 (d, *J* = 37.3 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 32.80. Elemental Anal. For $C_{18}H_{22}BOP$: calcd. C, 73.00; H, 7.48; found C, 72.91; H, 7.44.

3.2.41. Synthesis of (S_P)-1-Phenyl-2,3,3a,4,9,9a-hexahydrophosphacyclopenta[b]naphthalen-9-ol 1-sulfide (**42**)

(S_P)-**42** was obtained in 92% yield according to typical procedure described in Section 3.2.6. (S_P)-**42**: white crystals, mp = 141–142 °C, $[\alpha]_D$ = +17.59 (*c* 1.02, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.93–7.85 (m, 2H); 7.60–7.45 (m, 3H); 7.32–7.20 (m, 4H); 5.31 (dd, 1H, *J* = 3.1 Hz, 8.7 Hz); 5.03 (bs, 1H-OH); 3.21 (dd, 1H, *J* = 8 Hz, 14.6 Hz); 3.06 (ddd, 1H, *J* = 2.4 Hz, 7.3 Hz, 14.7 Hz); 2.85–2.71 (m, 1H); 2.70–2.65 (m, 1H); 2.53–2.35 (m, 4H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 139 (d, *J* = 10.9 Hz); 137,7; 133.2 (d, *J* = 71.3 Hz); 132.2 (d, *J* = 3 Hz); 130.9 (d, *J* = 9.8 Hz); 129.2 (d, *J* = 11.9 Hz); 128.7; 128.5; 127.2; 126.8; 70.8 (d, *J* = 3.9 Hz); 47.2 (d, *J* = 55 Hz); 39.6 (d, *J* = 10.8 Hz); 36.3 (d, *J* = 52.4 Hz); 34.3 (d, *J* = 5.1 Hz); 33.9 (d, *J* = 8.2 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 61.08. Elemental Anal. For $C_{18}H_{19}SOP$: calcd. C, 68.76; H, 6.09; found C, 68.65; H, 6.05.

3.2.42. Synthesis of (S_P)-1-Phenyl-2,3,3a,4,9,9a-hexahydrophosphacyclopenta[b]naphthalen-9-ol 1-selenide (**43**)

(S_P)-**42** was obtained in 92% yield according to typical procedure described in Section 3.2.6. (S_P)-**43**: white crystals, mp = 119–120 °C, $[\alpha]_D$ = +20.07 (*c* 1.02, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.95–7.86 (m, 2H); 7.55–7.46 (m, 3H); 7.31–7.2 (m, 4H); 5.32 (dd, 1H, *J* = 2.3 Hz, 8.1 Hz); 4.95 (bs, 1H-OH), 3.21 (dd, 1H, *J* = 7.8 Hz, 15 Hz); 3.2–3.05 (m, 1H); 2.81–2.78 (m, 6H). ^{13}C NMR ($CDCl_3$, 75.5 MHz):

δ 138.4 (d, J = 10 Hz); 137.3 (d, J = 0.7 Hz); 131.8 (d, J = 62.9 Hz); 131.1 (d, J = 10.5 Hz); 128.9 (d, J = 11.8 Hz); 128.4; 128.1; 126.9; 126.4; 71.9 (d, J = 3.0 Hz); 46.8 (d, J = 46.3 Hz); 39.2 (d, J = 10.3 Hz); 36.3 (d, J = 46.5 Hz); 33.8 (d, J = 1.2 Hz); 33.7 (d, J = 3.9 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 46.27. Elemental Anal. for $C_{18}H_{19}SeOP$: calcd. C, 59.84; H, 5.30; found C, 59.68; H, 5.28.

3.2.43. Synthesis of *rac*-1-[1-Oxido-1-phenyl-2,3,3a,4,9,9a-hexahydro-1H-benzo[f]phosphindol-9-yl]pyridinium Triflate (*rac*-**44**)

In a flask equipped with a magnetic stirrer septum were placed 15 mL of dry DMSO and 10 mL of pyridine. The stirred mixture was chilled to 0 °C and 170 µL (300 mg, 2 mmol) of triflic acid was added. Then, 300 mg (1 mmol) of *rac*-**39** disolved in 5 mL of DMSO was slowly added, and 400 mg (1.9 mmol) DCC was added in one portion at 0 °C. The resulting reaction mixture was then stirred for 24 h at room temperature and, at the end, heated to 60 °C for additional 2 h. The end point of the reaction was detected by NMR, which indicated a nearly complete conversion of *rac*-**39**. The formed DCU was removed by filtration through a syringe filter and a small part of the product crystallized out from the filtrate during cooling to ambient temperature. Due to a minute amount of isolated hardly soluble crystalline *rac*-**44**, it was not fully characterized except for an X-ray diffraction analysis which unambiguously confirmed its molecular structure.

3.3. X-Ray Crystallographic Data

The X-ray data for compounds *rac*-**19** and *rac*-**26** were collected at 100(2) K on a Nonius Kappa CCD diffractometer [70] using graphite monochromated MoKα radiation (λ = 0.71073 Å). The crystals were mounted in a nylon loop in a drop of silicon oil to prevent the possibility of decay of the crystal during data collection. The unit cells' parameters were determined from ten frames and then refined on all data. The data were processed with *DENZO* and *SCALEPACK* (*HKL2000* package) [71]. The structures were solved by direct methods using the SHELXS-97 [72] program and was refined by full matrix least–squares on F^2 using the program SHELXL-97 [73]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at geometrically idealized coordinates with a fixed isotropic displacement parameter equal to 1.5 (methyl groups) times the value of the equivalent isotropic displacement parameter of the parent carbon.

The X-ray data for complex *rac*-**39a** were collected at 293(2) K on an Enraf Nonius MACH3 diffractometer [71] using graphite monochromated CuKα radiation (λ = 1.54178 Å). The unit cell parameters were determined from ten frames and then refined on all data. The data were processed with *OpenMolEN, Nonius BV*. The structure was solved by direct methods using the SHELXS97 [71] program and was refined by full matrix least–squares on F^2 using the program SHELXL 97 [73] All of the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at geometrically idealized coordinates with a fixed isotropic displacement parameter equal to 1.5 (methyl groups) times the value of the equivalent isotropic displacement parameter of the parent carbon.

Crystallographic data for compounds *rac*-**19,** *rac*-**26** and *rac*-**44** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication.: CCDC–1981155 (*rac*-**19**), CCDC–1981156 (*rac*-**26**) and CCDC–239150 (*rac*-**44**). Copies of the data can be obtained free of charge on application to CCDC via www.ccdc.cam.ac.uk/data_request/cif, or by e-mail data_request@ccdc.cam.ac.uk.

Crystal data for *rac*-**19**: $C_{15}H_{19}P_1O_1$: M = 246.27, orthorhombic, space group $P\,2_12_12_1$ (no. 19), a = 9.4360(2) Å, b = 11.3710(2) Å, c = 11.5660(2) Å, U = 1240.99(4) Å^3, Z = 4, F(000) = 528, D_c = 1.318 g cm^{-3}, T = 100(2)K, μ(Mo-Kα) = 0.202 mm^{-1}, θ_{max} = 27.505°, 2833 unique reflections. Refinement converged at $R1$ = 0.0346, $wR2$ = 0.0816 for all data and 154 parameters ($R1$ = 0.0317, $wR2$ = 0.0803 for 2716 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on F^2 was equal 1.052. A weighting scheme

$w = [\sigma^2(F_o)^2 + (0.0418P)^2 + 3.1964P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the final stage of refinement. The residual electron density = +0.24/−0.24 eÅ^{-3}.

Crystal data for *rac*-**26**: $C_{16}H_{22}P_1B_1$: M = 256.11, monoclinic, space group P 21 (no. 4), a = 6.37100(10) Å, b = 13.5760(3) Å, c = 8.4160(2) Å, β = 101.4930(10)°, U = 713.33(3) Å^3, Z = 2, $F(000)$ = 276, D_c = 1.192 g cm^{-3}, T = 100(2)K, μ(Mo-Kα) = 0.172 mm^{-1}, θ_{max} = 27.471°, 2639 unique reflections. Refinement converged at $R1$ = 0.0367, $wR2$ = 0.0946 for all data and 180 parameters ($R1$ = 0.0352, $wR2$ = 0.0924 for 2566 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on F^2 was equal 1.063. A weighting scheme $w = [\sigma^2(F_o)^2 + (0.0418P)^2 + 3.1964P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the final stage of refinement. The residual electron density = +0.25/−0.30 eÅ^{-3}.

Crystal data for *rac*-**44**: $C_{24}H_{25}P_1S_1F_3N_1O_5$: M = 246.27, triclinic, space group P -1 (no. 2), a = 9.6444(6) Å, b = 11.0887(7) Å, c = 11.7985(7), Å, α = 95.281(5)°, β = 105.384(5)°, γ = 95.097(5)°, U = 1202.94(13) Å^3, Z = 2, F(000) = 548, D_c = 1.456 g cm^{-3}, μ(Mo-Kα) = 2.363 mm^{-1}, θ_{max} = 74.24°, 3948 unique reflections. Refinement converged at R1 = 0.0858, wR2 = 0.1772 for all data and 337 parameters. The goodness-of-fit on F^2 was equal 1.430. A weighting scheme $w = [\sigma^2(F_o)^2 + (0.0418P)^2 + 3.1964P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$ was used in the final stage of refinement. The residual electron density = +0.67/−0.31 eÅ^{-3}.

Crystal data for rac-**39**: *There are no complete crystallographic data for rac-**39**. The overview picture was built based on the RES file whose quality was sufficient to determine the relative configuration of the substituents.*

4. Conclusions

In summary, an efficient procedure for accessing gram quantities of both enantiomers of 1-phenylphosphole-2-ene 1-oxide (**1**) in a single resolution process has been optimized and is described in full reproducible details. The resolved **1** has been shown to undergo stereoselective Diels–Alder cycloadditions with cyclic dienes. The dienes approach the phospholene oxide in the endo mode and exclusively from its P = O bearing side. The cycloadditions led to synthesis of virtually enantiopure bicyclic and polycyclic phosphine oxides of the phosphindole, functionalized benzophosphindole, phospha[5.2.1.0^{2,6}]decane, phospha[5.2.2.0^{2,6}]undecane and dibenzophospha[5.2.2.0^{2,6}]undecane ring systems containing resolved P-stereogenic centre embeded in the five-membered ring. The cycloadducts were shown to undergo fully stereoselective conversions to the corresponding bicyclic and polycyclic phosphines as well as to their borane, sulfide, and selenide derivatives with complete retention of configuration at P. Unexpectedly, for a tricyclic phosphine (R_P)-**40** bearing a β-hydroxy substituent, an apparently lowered P-inversion barrier has been revealed during its attempted synthesis from oxide (S_P)-**39** by stereoretentive reduction with $PhSiH_3$ at 80 °C. The synthesized enantiomerically pure polycyclic P (III) derivatives have the potential to serve as the P-stereogenic monophosphine ligands in asymmetric catalysis. Studies along these lines are currently in progress in our laboratories.

Author Contributions: Conceptualization and supervision, K.M.P.; investigation, M.K., Z.D., R.P., E.Ł., and O.M.D.; X-ray analyses, I.J.; writing, K.M.P.; review and editing, E.Ł. and O.M.D. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

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