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SYNTHESIS OF ASYMMETRIC DIBENZOPHOSPHOLE 5-OXIDES: THE FIRST DIBENZOPHOSPHOLE-BASED FAMILY OF COMPOUNDS WITH LIQUID CRYSTALLINE BEHAVIOUR

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Abstract - A synthesis of a new family of chiral dibenzophosphole 5-oxides is described. Using high-yield known reactions we report a method for the synthesis and optical resolution of chiral dibenzophospholes from an unsubstituted system. These molecules are the first examples of a new asymmetrically substituted dibenzophosphole-based group of systems with liquid crystal properties.

1. Introduction

Liquid crystal synthesis has been investigated in recent years mainly because successful applications of liquid crystals have been developed, particularly in the area of electro-optical displays.[1] Our research group has been working on the synthesis of certain chiral molecules in order to generate chiral liquid crystal macromolecular systems with ferroelectric properties for their possible use in optical devices for information storage. To develop chiral smectic mesogenes, it is known[2] that the introduction of a chiral group near the rigid core of the mesogene leads to higher spontaneous polarizability in these systems, and then to an improvement of their ferroelectric physical properties. Firstly, we studied carbazole systems[3] with chiral aliphatic chains attached to the aromatic rigid core, and then we attempted the synthesis of a similar structure derived from dibenzophosphole with the phosphorus atom in the same rigid planar core as the chiral centre (**10**), in order to study the effect that the introduction of the chiral centre into the rigid core of the mesogene has on the physical properties of these macromolecular systems. However, the synthesis of suitable molecules for our aims remained unresolved.

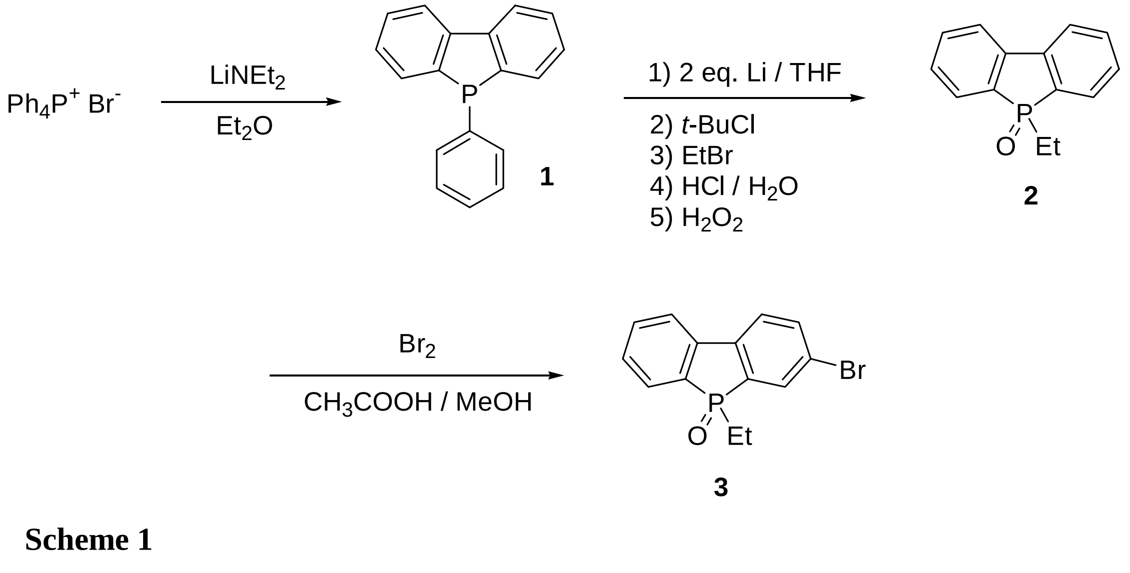
In spite of the common use of dibenzophosphole as a ligand in organometallic systems, there are no methods of synthesis of asymmetrically substituted dibenzophospholes in the literature, and there are no general methods of optical resolution of dibenzophospholes in order to obtain the chiral structures we want. The Cornforth[4a] method for dibenzophosphole synthesis is suitable for some symmetrically disubstituted 5-hydroxy-5*H*-dibenzophosphole 5-oxides. However, it is difficult to generalise this method to products of a different pattern of substitution and, furthermore, the introduction of an alkyl group onto the phosphorus atom requires several steps. A set of methods[4] using 2,2'-dibromobiphenyls as starting material is in all cases appropriate only for systems without substituents on the aromatic rings and/or with a phenyl group on the phosphorus atom. The adaptation of such methods to our requirements involves starting materials that are difficult to prepare; in addition, the overall yields described are very low. Attempts to generalise the Freedman and Doak method[5] were unsuccessful. We modified the method described by Campbell *et al.*[6] –formation of biphenyl-2-ylphenylphosphinic acid and its cyclisation by reaction with phosphorus pentachloride- despite the very low general yields, in some cases 3%. We were able to develop an improved method[7] for the general synthesis of 5-alkyl-5*H*-dibenzophospholes. However, we observed some problems in the cyclisation of phosphinic acids when this method was used to obtain asymmetrically substituted dibenzophospholes.

Hoffmann's method[8] consists of the treatment of tetraphenylphosphonium bromide with lithium diethylamide. The conversion of the 5-phenyl-5*H*-dibenzophosphole obtained into 5-methyl-5*H*-dibenzophosphole by treatment with lithium and methyl iodide is described by Ezzell and Freedman.[9] The yield from the commercial tetraphenylphosphonium bromide in 5-methyl-5*H*-dibenzophosphole is only 27%; and the method is impossible to generalise to systems substituted in the benzene rings. This method allowed synthesis of greater amounts of product than our previously improved method, and so we decided to use the Hoffmann and Ezzell methods to obtain 5-ethyl-5*H*-dibenzophosphole 5-oxide. Using high-yield known reactions we developed a method for the synthesis and optical resolution of chiral dibenzophospholes from an unsubstituted system.

2. Results and discussion

Following the Hoffmann method, we obtained 5-phenyl-5*H*-dibenzophosphole (**1**) from commercial tetraphenylphosphonium bromide in 80% yield (see Scheme 1). Using the method described by Ezzell and Freedman for 5-methyl-5*H*-dibenzophosphole 5-oxide, we converted **1** into 5-ethyl-5*H*-dibenzophosphole 5-oxide (**2**) by treatment with two equivalents of lithium in tetrahydrofuran, followed by addition of one equivalent of *tert*-butyl chloride. Then one equivalent of ethyl bromide was added, and the resulting 5-ethyl-5*H*-dibenzophosphole was oxidized with hydrogen peroxide after acidification to avoid decomposition of the peroxide, yielding the dibenzophosphole (**2**) in 96% yield, higher than 44% described by Ezzell for his compound. We found that, without addition of *tert*-butyl chloride, ethyl bromide firstly reacted with phenyllithium and the resulting ethylbenzene reacted with another molecule of phenyllithium. If a second equivalent of ethyl bromide was added to complete the reaction, 5,5-diethyl-5*H*-dibenzophospholium bromide was obtained as by-product. In order to avoid this, we added an equivalent of *tert*-butyl chloride that reacted with the phenyllithium formed in the reaction before the addition of only one equivalent of ethyl bromide.

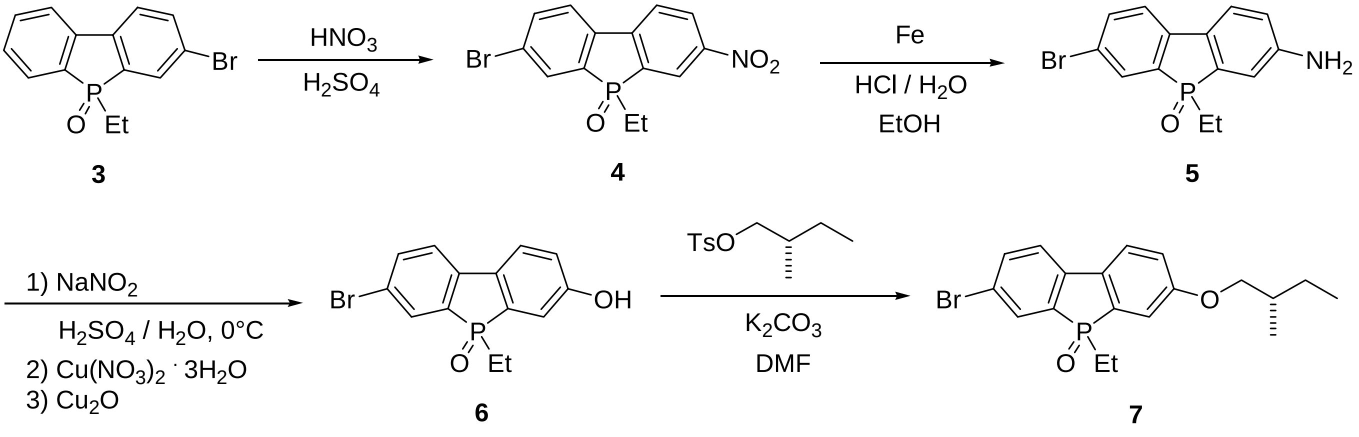
On studying some aromatic electrophilic substitution reactions over the dibenzophosphole system, we observed that bromination could be carried on under slow rate conditions that allowed the main formation of asymmetric 3-bromo-5-ethyl-5*H*-dibenzophosphole 5-oxide (**3**) as a racemic mixture. With a large excess of bromine -more than ten equivalents- in an acetic acid / methanol mixture at 45°C, compound (**3**) was obtained in 53% yield, and 33% of unreacted compound (**2**) was recovered after column chromatography. Only a small amount, less than 10%, of useless symmetric 3,7-dibromo-5-ethyl-5*H*-dibenzophosphole 5-oxide was obtained. Reaction conditions were essential: at lower temperatures the reaction became too slow and practically only unreacted compound (**2**) was recovered; at higher temperatures or longer reaction times, symmetric dibrominated compound became the main product obtained. Bromination of dibenzophospholes was only previously described by Cornforth[4a] at positions 2, 4, 6 and 8 of some activated 3,7-dihydroxydibenzophospholes, obtaining only symmetric products. This is the first report of a method to obtain asymmetric derivatives from symmetric dibenzophospholes, and compound (**3**) is the first asymmetric 5-alkyl dibenzophosphole described.



Scheme 1

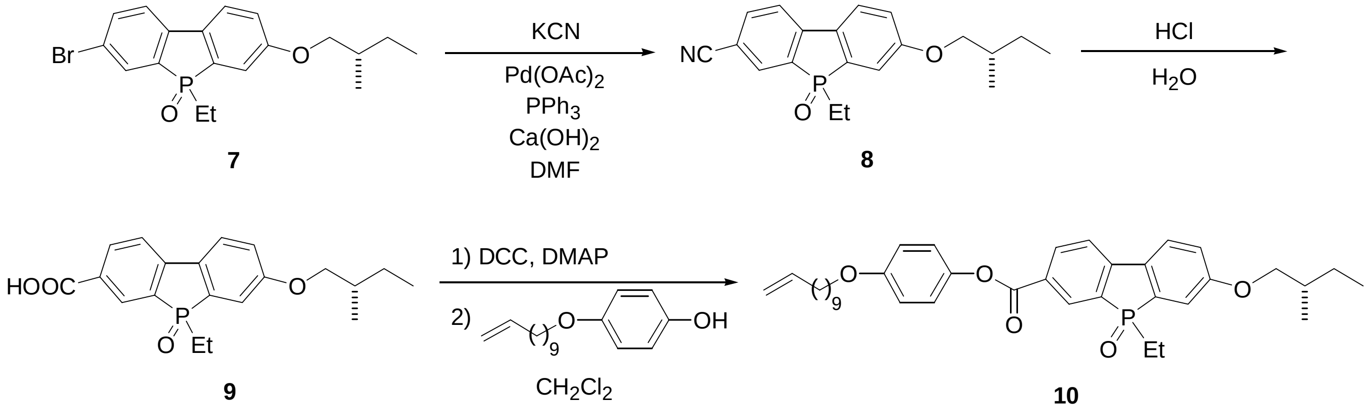
Nitration[10] of compound (**3**) in a fuming nitric / sulfuric acid mixture yields quantitatively 3-bromo-5-ethyl-7-nitro-5*H*-dibenzophosphole 5-oxide (**4**) after 10 min at 0°C (see Scheme 2). Higher temperatures or longer reaction times produced nitration in some positions of the brominated ring of dibenzophosphole (**3**). Reduction of compound (**4**) with iron in acidic conditions[11] yielded the corresponding amino compound (**5**) in 82% yield. Zinc was also valid as reductor for this reaction, but elimination of iron salts in the work-up process was easier. Catalytic Pd/C hydrogenation causes loss of bromine[12] together with nitro reduction.[13] Diazonium salt of compound (**5**) was obtained after treatment with sodium nitrite in a cooled sulfuric acid / water mixture, and its decomposition by adding copper(I) oxide in presence of a large excess of copper(II) salts[14] enabled the desired phenol (**6**) to be obtained in 87% yield. Other methods used for decomposition of diazonium salts[15] were unsuccessful and yielded untreatable polymeric by-products. We have observed that copper(I) in excess formed a water-soluble complex with phenol (**6**), which was lost after filtration. To avoid this yield decrease, the reaction was stirred overnight after copper(I) addition, allowing its air oxidation to copper(II).

After reaction of phenol (**6**) with *S*-(+)-2-methylbutyl tosylate in presence of potassium carbonate, ether (**7**) was obtained in 70% yield. Compound (**7**) was a mixture of two 1:1 diastereomers with different configurations on phosphorus atom, due to the incorporation of a second chiral centre in the structure, but these diastereomers were not separable using physical methods; furthermore, NMR chemical shifts of both diastereomers were identical. The chiral auxiliary agent used for resolution of dibenzophospholes is expensive, and so we decided to continue with the synthetic pathway and carry on the optical resolution process with the final product (**10**).



Scheme 2

Incorporation of the other lateral chain, in the position occupied by the bromine atom, was achieved in three steps (see Scheme 3) from compound (**7**). Cyano compound (**8**) was obtained in 92% yield using potassium cyanide in mild conditions with catalysis of a palladium(0) complex generated *in situ* from palladium(II) acetate, triphenylphosphine and calcium hydroxide.[16] Cyanation in absence of palladium catalyst needs higher temperatures and nucleophilic attack over phosphorus atom was observed, which caused the opening of the dibenzophosphole central ring. Hydrolysis of compound (**8**) in refluxing concentrated hydrochloric acid[17] yields acid (**9**) (80%). Basic hydrolysis conditions[18] are incompatible with the electrophilic character of the phosphorus atom, yielding the suitable phosphinic acid after opening of the dibenzophosphole central ring. Finally, compound (**10**) was obtained in 46% yield after activation of carboxylic acid (**9**) by reaction with dicyclohexylcarbodiimide[19] and ester formation with previously synthesized 4-undec-10-enoxyphenol.

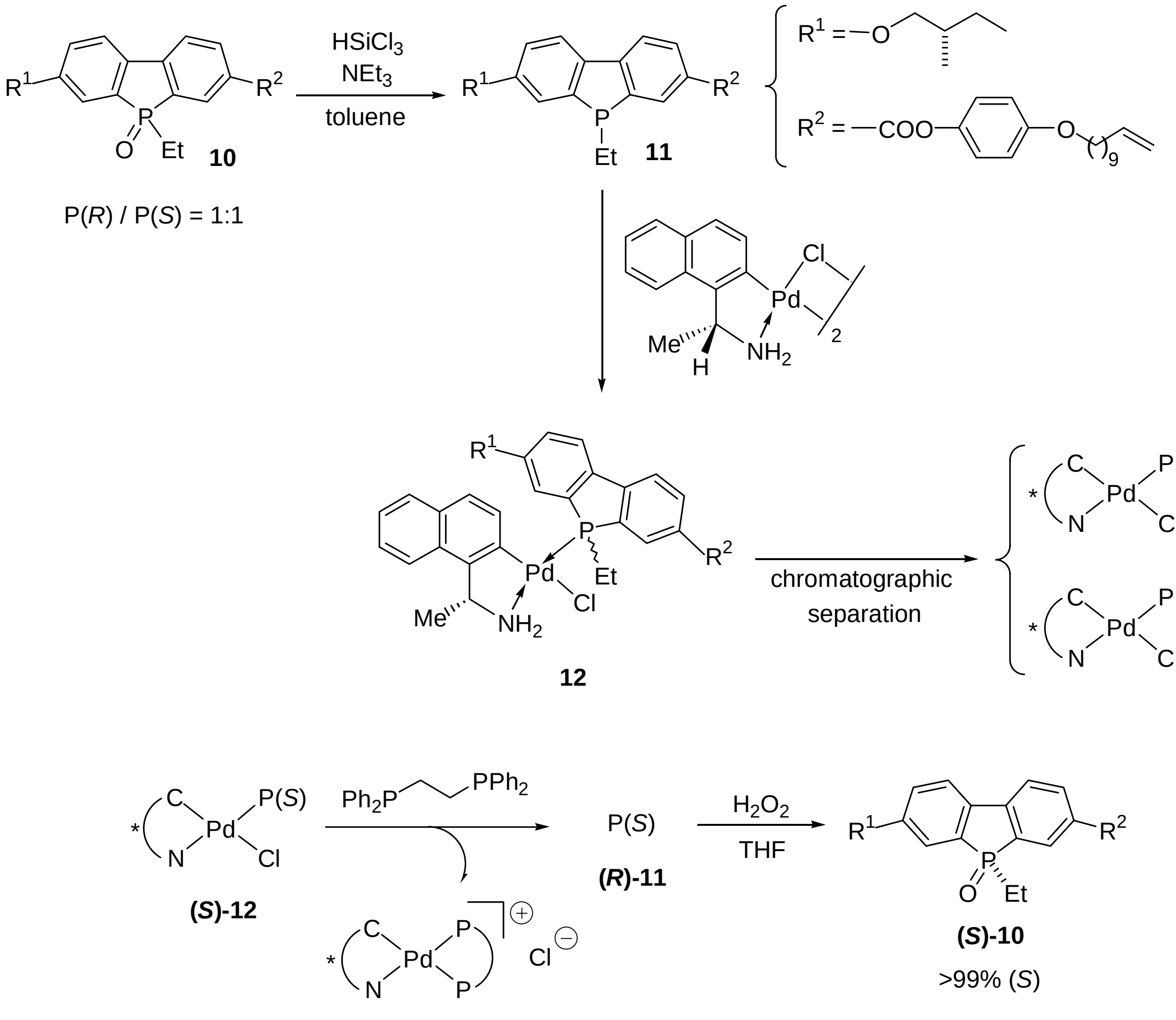


Scheme 3

Optical resolution of phosphorus at compound (**10**) was successfully carried out following the general procedure described in Scheme 4. The first step was to reduce the dibenzophosphole 5-oxide by use of trichlorosilane; next, the reaction between the resulting reduced phosphine (**11**) and an optically active dinuclear cyclopalladated compound derived from (*R*)-(+)-1-(1-naphthyl)ethylamine gave a mixture of diastereomers (**12**) that were separated by SiO_2 column chromatography, using $CHCl_3$-acetone (100:3) as eluent. Up to 85% of each diastereomer was isolated, with diastereomeric excess higher than 95%.

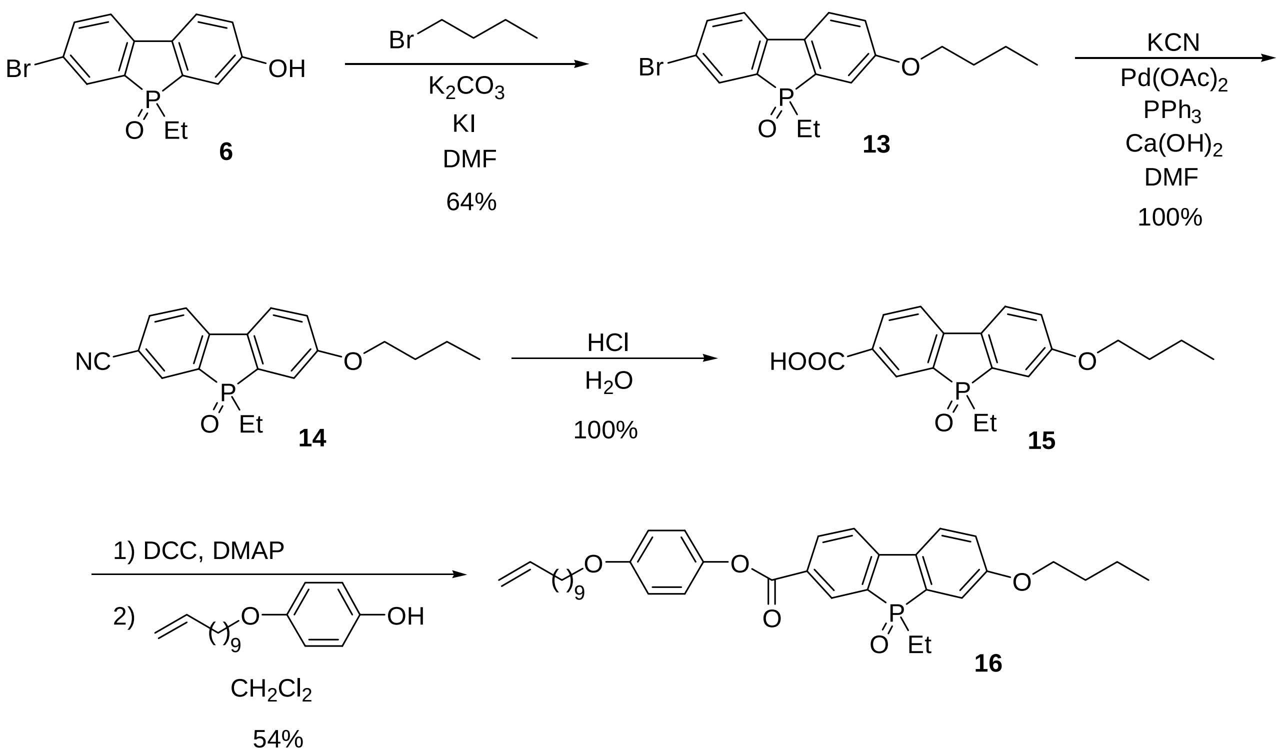
The third step of the resolution process was to decoordinate the dibenzophosphole through the reaction of each pure diastereomer (**12**) with 1,2-bis(diphenylphosphino)ethane (dppe). The action of dppe on the optically pure diastereomer ((*S*)-**12**) led to the enantiopure free dibenzophosphole ((*R*)-**11**). The displacement proceeds by retention of the configuration at the phosphorus atom, as verified by the quantitative regeneration of the starting material ((*S*)-**12**) from the free ligand ((*R*)-**11**) and the dinuclear cyclopalladated derivative. Change in nomenclature is due to priority changes of the phosphorus-attached groups.

The final step was to oxidate the optically pure ligand (**11**) with hydrogen peroxide, yielding the corresponding dibenzophosphole 5-oxides (**10**) with complete retention of configuration. HPLC with a CSP-1[20] chiral stationary phase derived from *N*-[*N*-(3,5-dinitrobenzoyl)-(*S*)-phenylalanyl]-(3-triethoxysilyl)propylamide was used to determine optical purity of each diastereomer. Very good resolution was achieved (R_S=1.41) using 1 mL/min flow of heptane-isopropanol (9:1), and 99% optical purity was measured. Full details of the resolution procedure, including the determination of the absolute configuration at phosphorus atom using ^{1}H NMR chemical shift regularities, have been recently described.[21]



Scheme 4

Related compounds 3-butoxy-5-ethyl-7-(4-undec-10-enoxyphenoxycarbonyl)-5*H*-dibenzophosphole 5-oxide (**16**) and 3-butoxy-5-methyl-7-(4-undec-10-enoxyphenoxycarbonyl)-5*H*-dibenzophosphole 5-oxide (**25**) were obtained following similar synthetic procedures. Dibenzophosphole (**16**) was obtained in 3 steps after the reaction between phenol (**6**) and 1-bromobutane (see Scheme 5).

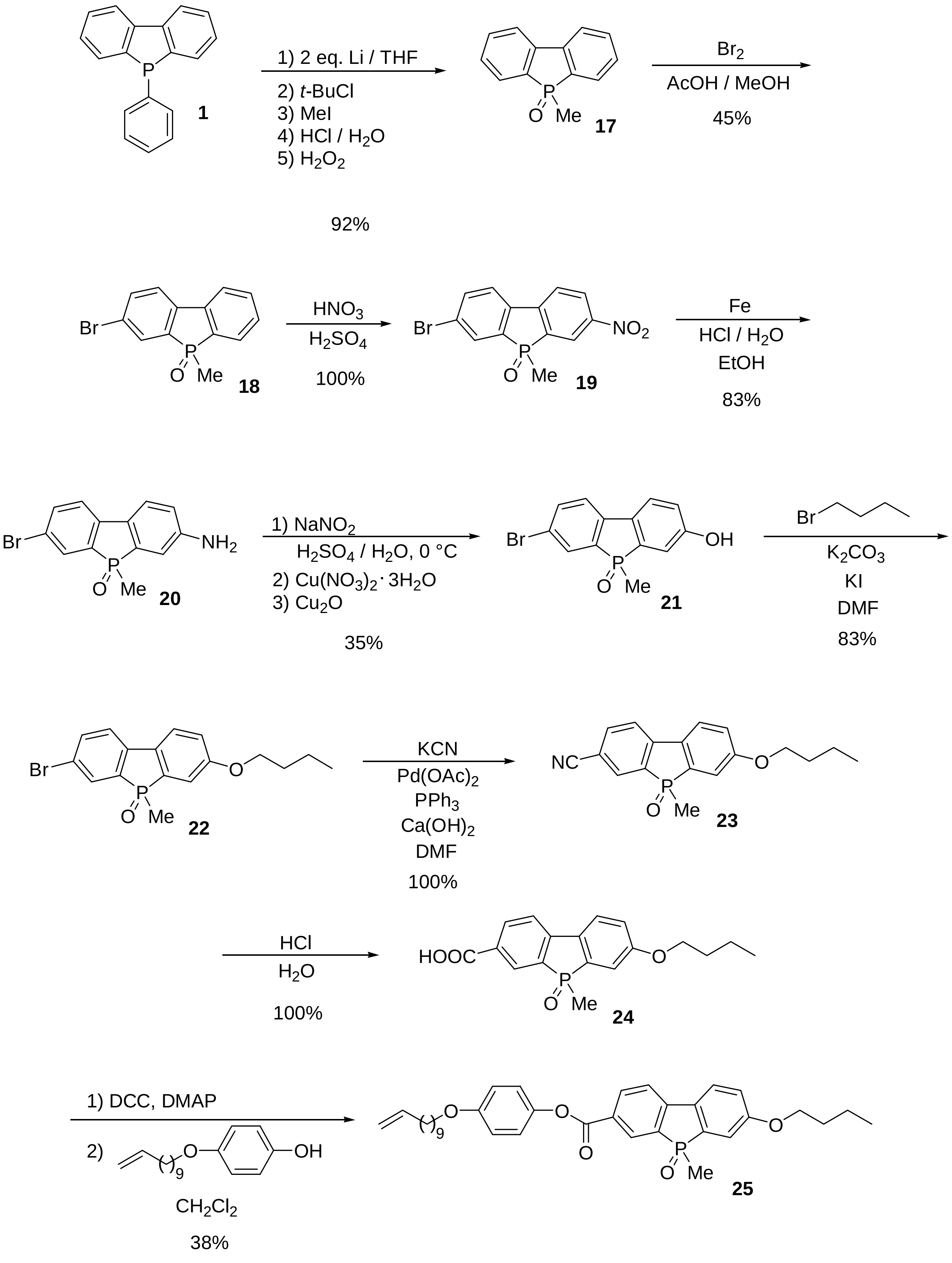


Scheme 5

Repeating the same synthetic pathway, but using iodomethane in the conversion of 5-phenyl-5*H*-dibenzophosphole (**1**) into 5-methyl-5*H*-dibenzophosphole 5-oxide (**17**), we obtained dibenzophosphole (**25**) after 9 steps (Scheme 6).

Optical resolution of compounds (**16**) and (**25**) was successfully realized following the general procedure described previously for compound (**10**), yielding the corresponding dibenzophosphole oxides with enantiomeric excess higher than 98% after chiral stationary phase HPLC analysis.

Just as practically no synthetic nor optical general resolution methods are described in the literature for the kind of molecules reported here, so these are the first examples of liquid-crystal dibenzophospholes.[22] The compounds were investigated with polarizing optical microscopy (POM), differential scanning calorimetry (DSC) and X-Ray diffraction with regard to their liquid crystal behaviour. Enantiopure compounds ((*S*)-**10**, (*S*)-**16** and (*S*)-**25**) showed stable chiral cholesteric phases, and compound ((*S*)-**25**) showed stable smectic-A and probably chiral smectic-C phases as well. Racemic mixtures of compounds (**16** and **25**) showed nematic and smectic-A phases, but complete crystallization of the mixture was observed some hours after preparation of the sample. All the compounds showed monotropic phases, which appeared only by cooling from the isotropic melt and not by heating the crystalline solid. Table 1 summarizes the thermal behavior of the synthesized dibenzophospholes.


1
1) 2 eq. Li / THF
2) t-BuCl
3) MeI
4) HCl / H2O
5) H2O2
92%
P
O
Me
17
Br2
AcOH / MeOH
45%
Br
18
HNO3
H2SO4
100%
NO2
19
Fe
HCl / H2O
EtOH
83%
NH2
20
1) NaNO2
H2SO4 / H2O, 0 °C
2) Cu(NO3)2 · 3H2O
3) Cu2O
35%
OH
21
K2CO3
KI
DMF
83%
22
KCN
Pd(OAc)2
PPh3
Ca(OH)2
DMF
100%
NC
23
HCl
H2O
100%
HOOC
24
1) DCC, DMAP
2)
( )9
OH
CH2Cl2
38%
25

Scheme 6

Compounds	**Phase behavior temp. in °C**
(*S*)-**10**	Cryst 42 (S_X –4) [0.8 J/g] (Ch 25) [0.6 J/g] I
(*S*)-**16**	Cryst 60 (S_X –10) [1.3 J/g] (Ch 40) [0.6 J/g] I
(*S*)-**25**	Cryst 136 (S_X -2) [0.5 J/g] (S_A 64) [1.6 J/g] (Ch 110) [0.2 J/g] I
16 (racemic)	Cryst 109 (S 1) [1.5 J/g] (N 81) [1.3 J/g] I
25 (racemic)	Cryst 121 (S_A 69) [0.3 J/g] (N 119) [2.6 J/g] I

Table 1

Chiral compound ((*S*)-**10**) showed a cholesteric phase even below room temperature. When the chiral, branched aliphatic chain was substituted by a non-chiral linear *n*-butyl chain in compound ((S)-**16**), the regime of existence of the cholesteric mesophase was stabilized. The most important aspect of this derivative is the stereocenter given by the phosphorus atom, which generates the chiral mesophase. No chiral substituents were necessary at the dibenzophosphole unit to induce chirality. The cholesteric phase of this compound was demonstrated by miscibility experiments and characterization of the helical pitch.

A broader cholesteric mesophase was observed for compound ((*S*)-**25**). This is related to the substituents at the pyramidal, pentavalent phosphorus. This effect, which is well known for lateral substituents of conventional liquid crystals, is caused by the short methyl chain in **25,** rather than the ethyl chain in **16,** which is attached to the phosphorus atom.

As expected, racemic mixtures show monotropic, nematic and smectic liquid crystalline phases in temperature intervals equivalent to that of the enantiopure compounds. Unfortunately, these mixtures show a strong tendency towards crystallization, which prevents a detailed analysis of the phase structure.

It should be noted that the dibenzophosphole oxides are thermally stable and no decomposition or racemization occurs when these derivatives are heated at about 160 °C for several days. However, further structural improvements have to be carried out in order to obtain enantiotropic, chiral mesophases. With respect to this problem, the reaction pathway described in this paper enables easy and numerous modifications of the dibenzophosphole oxide unit.

The synthetic procedure described in this paper is a general method for the synthesis and the optical resolution of asymmetrically substituted dibenzophosphole 5-oxides, and can be easily adapted to the synthesis of a large amount of related compounds with interesting properties.

3. EXPERIMENTAL

3.1. General

Melting points were determined in a Köfler apparatus provided with a Reichert Thermovar microscope and are uncorrected. TLC was carried out on SiO_2 (Alugram SIL G/UV_{254} Macherey-Nagel 0.25 mm) and spots were located with UV light. Flash chromatography was carried out on SiO_2 (Silica Gel 60 A CC, Merck). Organic extracts were dried over anhydrous $MgSO_4$, and solutions were evaporated under reduced pressure with a rotatory evaporator. IR spectra were recorded on a Nicolet 510 FT-IR spectrometer. NMR spectra were measured with Varian Gemini-200 (200 MHz), Varian Unity-300 (300 MHz) and Varian VXR-500 (500 MHz) spectrometers; data are given in δ/ppm, referenced to TMS for ^{1}H NMR, to $CDCl_3$ (77.0 ppm) for ^{13}C NMR and to $P(OMe)_3$ (140.18 ppm) for ^{31}P NMR, and J values are given in Hz. Optical rotations (c = g/100 mL) were determined at 20°C using a Perkin-Elmer 241-MC polarimeter at 589nm. HPLC experiments were carried out on a Hewlett-Packard HP 1090 liquid chromatograph equipped with a Philips PU4020 UV detector. The chiral stationary phase was packed into a stainless-steel tube (100 x 4.6 mm I.D.) by the slurry method according to Coq *et al.*[23] MS spectra were measured in chemical impact (CI, NH_3) mode with a Hewlett-Packard 5988A spectrometer, or with a Fisons VG-Quattro spectrometer, and then the samples were introduced into a matrix of 2-nitrobenzyl alcohol for FAB analysis and subjected to bombardment with cesium atoms. High-resolution MS spectra were performed on an Autospec/VG in chemical impact (CI, NH_3) mode by the Departament de Química Orgànica Biològica (C.S.I.C.), Barcelona and in chemical impact (CI, CH_4) mode by the Servicio de Espectrometría de Masas de la Facultad de Química (University of Córdoba). Elemental analyses were obtained with a FISONS Na-1500 apparatus, analyzing combustion gases by chromatography and using a thermal conductivity detector. Differential scanning calorimetry (DSC) was performed using a Mettler-Toledo DSC821 differential scanning calorimeter at heating rate of 10 K/min. For polarizing microscopy a Mettler FP 82 hot stage controlled by a Mettler FP 80 central processor was used together with a Leitz Ortholux II Pol-BK microscope. X-Ray diffractograms were monitored with an image plate system with Kiesig geometry.

3.2. Materials and Synthesis

All solvents were dried and degassed by standard methods. Ether and tetrahydrofuran were distilled over sodium benzophenone, under nitrogen, before use. Dichloromethane was distilled over calcium hydride under nitrogen. *N*,*N*-Dimethylformamide, *N*,*N*-dimethylacetamide and pyridine were distilled and stored over 4Å molecular sieves. All chemicals were of commercial grade and used as received.

5-Phenyl-5*H*-dibenzophosphole (1). Commercial bromobenzene (111.6 g, 711 mmol) was slowly added to a vigorously stirred suspension of lithium (9.2 g, 1325 mmol) in 800 mL of anhydrous ether under argon atmosphere, maintaining a gentle reflux for 2 h. After this time no lithium was present in the dark red solution of phenyllithium. Then, freshly distilled diethylamine (50.6 g, 692 mmol) was slowly added to obtain a solution of lithium diethylamide in ether. Commercial tetraphenylphosphonium bromide (82.7 g, 197 mmol) was added to this solution and the mixture was stirred at rt for 16 h. The reaction was quenched with the addition of aqueous 6M HCl (250 mL), first obtaining a yellow precipitate which rapidly dissolved, then a dark red solution. The organic layer was separated, and the aqueous acidic layer was extracted with CH_2Cl_2 (2 x 100 mL). All the organic extracts were dried. The solvent was removed and the resulting dark red oil was eluted with CH_2Cl_2 in a SiO_2 column to remove a residue with high polarity, obtaining a yellow solid which was recrystallized in methanol yielding 5-phenyl-5*H*-dibenzophosphole (**1**) (41.1 g, 80%) as a pale yellow solid; mp 94.9-95.7 ºC (from methanol) (lit.,[4a] 94.5-95 ºC); R_f (SiO_2, CH_2Cl_2) 0.72; ν_{max} (film)/cm^{-1} 3066 (arC-H s); δ_H ($CDCl_3$, 300 MHz) 7.95 (d, H^1, 2H, ^3J(H^1-H^2) = 7.8 Hz), 7.70 (ddd, H^4, 2H, ^3J(H^3-H^4) = 6.9 Hz, ^3J(H^4-P) = 5.1 Hz, ^4J(H^2-H^4) = 1.2 Hz), 7.47 (ddd, H^2, 2H, ^3J(H^1-H^2) = 7.8 Hz, ^3J(H^2-H^3) = 7.5 Hz, ^4J(H^2-H^4) = 1.2 Hz), 7.36-7.22 (complex signal, H^{3,15,16,17}, 7H); δ_C ($CDCl_3$, 75 MHz) 143.61 (s, C^{10}), 142.51 (s, C^{12}), 132.64 (d, C^{15}H, ^2J(C^2-P) = 19.7 Hz), 130.42 (d, C^{4}H, ^2J(C^4-P) = 21.9 Hz), 129.23 (s, C^{17}H), 128.63 (s, C^{2}H+C^{16}H), 127.56 (d, C^{3}H, ^3J(C^3-P) = 7.6 Hz), 121.35 (s, C^{1}H); δ_P ($CDCl_3$, 121 MHz) -9.68 (s); m/z (CI, NH_3) 261 (M + 1, 100%).

5-Ethyl-5*H*-dibenzophosphole 5-oxide (2). Small pieces of lithium (347 mg, 50.0 mmol) were added to a solution of 5-phenyl-5*H*-dibenzophosphole (**1**) (5032 mg, 19.3 mmol) in 100 mL of anhydrous THF under argon atmosphere, and the reaction mixture was vigorously stirred for 5 h at rt. After this time no more lithium was consumed and *tert*-butyl chloride (2.1 mL, 1.8 g, 19.3 mmol) was added to the dark red solution to destroy the phenyllithium generated in the reaction. After 15 min ethyl bromide (1.5 mL, 2.2 g, 20.1 mmol) was added. The mixture was stirred for 30 min at rt. The reaction was quenched with the addition of 10% HCl (10 mL), which destroys the excess of lithium, and then 30% H_2O_2 (4 mL, 35 mmol) was added for as long as the characteristic bromine colour persisted. After 30 min CH_2Cl_2 (100 mL) was added. The organic layer was extracted, washed with a saturated solution of $NaHSO_3$ (3 x 50 mL), dried over anhydrous $MgSO_4$, the solvent removed and the residue was purified by column chromatography eluting with CH_2Cl_2-CH_3OH, 96:4 yielding 5-ethyl-5*H*-dibenzophosphole 5-oxide (**2**) (4232 mg, 96%) as a white solid, identical to the product obtained from 5-methyl-5*H*-dibenzophosphole 5-oxide;[7] mp 126-128 ºC (from CH_2Cl_2); R_f (SiO_2, CH_2Cl_2-CH_3OH 96:4) 0.28; ν_{max} (film)/cm^{-1} 3056 (arC-H s), 2967 (C-H s), 1194 (P=O s); δ_H ($CDCl_3$, 200 MHz) 7.84 (dddd, H^4, 2H, ^3J(H^4-P) = 9.6 Hz, ^3J(H^3-H^4) = 7.5 Hz, ^4J(H^2-

H^{4}) = 1.2 Hz, ^{5}J(H^{1}-H^{4}) = 0.9 Hz), 7.79 (dddd, H^{1}, 2H, ^{3}J(H^{1}-H^{2}) = 7.8 Hz, ^{4}J(H^{1}-P) = 2.7 Hz, ^{4}J(H^{1}-H^{3}) = 0.9 Hz, ^{5}J(H^{1}-H^{4}) = 0.9 Hz), 7.59 (dddd, H^{2}, 2H, ^{3}J(H^{1}-H^{2}) = 7.8 Hz, ^{3}J(H^{2}-H^{3}) = 7.5 Hz, ^{5}J(H^{2}-P) = 1.5 Hz, ^{4}J(H^{2}-H^{4}) = 1.2 Hz), 7.43 (dddd, H^{3}, 2H, ^{3}J(H^{3}-H^{4}) = 7.5 Hz, ^{3}J(H^{2}-H^{3}) = 7.5 Hz, ^{4}J(H^{3}-P) = 3.6 Hz, ^{4}J(H^{1}-H^{3}) = 0.9 Hz), 2.12 (dq, H^{14}, 2H, ^{2}J(H^{14}-P) = 13.8 Hz, ^{3}J(H^{14}-H^{15}) = 7.6 Hz), 1.07 (dt, H^{15}, 3H, ^{3}J(H^{15}-P) = 18.8 Hz, ^{3}J(H^{14}-H^{15}) = 7.6 Hz); δ_{C} (CDCl$_3$, 50 MHz) 141.16 (d, C^{10}, ^{1}J(C^{10}-P) = 20.5 Hz), 133.07 (d, C^{2}, ^{4}J(C^{2}-P) = 2.3 Hz), 129.23 (d, C^{4}, ^{2}J(C^{4}-P) = 10.9 Hz), 129.02 (d, C^{3}, ^{3}J(C^{3}-P) = 9.6 Hz), 121.08 (d, C^{1}, ^{3}J(C^{1}-P) = 9.6 Hz), 23.19 (d, C^{14}, ^{1}J(C^{14}-P) = 70.1 Hz), 6.23 (d, C^{15}, ^{2}J(C^{15}-P) = 4.1 Hz); δ_{P} (CDCl$_3$, 121 MHz) 46.11 (s); m/z (CI, NH$_3$) 229 (M + 1, 100%), 246 (M + 18, 71%); HRMS (EI) 228.0711 (M^{+}), C$_{14}$H$_{13}$OP requires 228.0704.

3-Bromo-5-ethyl-5*H*-dibenzophosphole 5-oxide (3). Bromine (6 mL, 18.7 g, 117.1 mmol) was added to a solution of 5-ethyl-5*H*-dibenzophosphole 5-oxide (**2**) (2281 mg, 9.99 mmol) in 25 mL of acetic acid and 10 mL of methanol. The mixture was heated to 45ºC for 2.5 h. The reaction was quenched over a 10% solution of NaHSO$_3$ in cold water. Dichloromethane (100 mL) was added to dissolve the white organic solid formed, and the organic layer was extracted and washed with a 10% solution of NaOH till the basic aqueous layer remains. The resulting organic layer was dried over anhydrous MgSO$_4$ and the solvent was removed. 3-Bromo-5-ethyl-5*H*-dibenzophosphole 5-oxide (**3**) (1614 mg, 53%) was isolated as a white solid after purification of the residue by column chromatography in SiO$_2$ (200 g) and eluting with AcOEt-CH$_3$OH 99:1. Unreacted 5-ethyl-5*H*-dibenzophosphole 5-oxide (**2**) (752 mg, 33%) was also recovered; mp 160-161 ºC (from CH$_2$Cl$_2$); R_{f} (SiO$_2$, AcOEt-CH$_3$OH 99:1) 0.21; ν_{max} (film)/cm^{-1} 3054 (arC-H s), 2971 (C-H s), 1191 (P=O s); δ_{H} (CDCl$_3$, 300 MHz) 7.96 (ddd, H^{4}, 1H, ^{3}J(H^{4}-P) = 9.0 Hz, ^{4}J(H^{2}-H^{4}) = 1.8 Hz, ^{5}J(H^{1}-H^{4}) = 0.6 Hz), 7.85 (dddd, H^{6}, 1H, ^{3}J(H^{6}-P) = 9.0 Hz, ^{3}J(H^{6}-H^{7}) = 7.5 Hz, ^{4}J(H^{6}-H^{8}) = 1.2 Hz, ^{5}J(H^{6}-H^{9}) = 0.6 Hz), 7.76 (ddd, H^{1}, 1H, ^{3}J(H^{1}-H^{2}) = 8.1 Hz, ^{4}J(H^{1}-P) = 3.0 Hz, ^{5}J(H^{1}-H^{4}) = 0.6 Hz), 7,71 (ddd, H^{2}, 1H, ^{3}J(H^{1}-H^{2}) = 8.1 Hz, ^{4}J(H^{2}-H^{4}) = 1.8 Hz, ^{5}J(H^{2}-P) = 1.2 Hz), 7.65 (dd, H^{9}, 1H, ^{3}J(H^{8}-H^{9}) = 7.5 Hz, ^{4}J(H^{9}-P) = 2.4 Hz), 7.60 (dddd, H^{8}, 1H, ^{3}J(H^{8}-H^{9}) = 7.5 Hz, ^{3}J(H^{7}-H^{8}) = 7.5 Hz, ^{4}J(H^{6}-H^{8}) = 1.2 Hz, ^{5}J(H^{8}-P) = 1.2 Hz), 7.46 (dddd, H^{7}, 1H, ^{3}J(H^{6}-H^{7}) = 7.5 Hz, ^{3}J(H^{7}-H^{8}) = 7.5 Hz, ^{4}J(H^{7}-P) = 3.6 Hz, ^{4}J(H^{7}-H^{9}) = 0.9 Hz), 2.18 (dq, H^{14}, 2H, ^{2}J(H^{14}-P) = 13.8 Hz, ^{3}J(H^{14}-H^{15}) = 7.5 Hz), 1.06 (dt, H^{15}, 3H, ^{3}J(H^{15}-P) = 19.2 Hz, ^{3}J(H^{14}-H^{15}) = 7.5 Hz); δ_{C} (CDCl$_3$, 75 MHz) [140.40 (d, ^{2}J(C-P) = 20.0 Hz), 139.41 (d, ^{2}J(C-P) = 20.6 Hz)] (C^{10}, C^{11}), 136.20 (s, C^{2}H), 133.50 (s, C^{8}H), 132.43 (d, C^{4}H, ^{2}J(C^{4}-P) = 10.1 Hz), 129.63 (d, C^{7}H, ^{3}J(C^{7}-P) = 9.8 Hz), 129.39 (d, C^{6}H, ^{2}J(C^{6}-P) = 9.5 Hz), 123.33 (d, C^{3}, ^{3}J(C^{3}-P) = 13.7 Hz), 122.68 (d, C^{1}H, ^{3}J(C^{1}-P) = 10.0 Hz), 121.23 (d, C^{9}H, ^{3}J(C^{9}-P) = 9.4 Hz), 22.94 (d, C^{14}H$_2$, ^{1}J(C^{14}-P) = 70.4 Hz), 6.08 (d, C^{15}H$_3$, ^{2}J(C^{15}-P) = 3.7 Hz); δ_{P} (CDCl$_3$, 121 MHz) 46.76 (s); m/z (CI, NH$_3$) 307 (M + 1, ^{79}Br, 56%), 309 (M + 1, ^{81}Br, 56%), 324 (M + 18, ^{79}Br, 100%), 326 (M + 18, ^{81}Br, 96%); HRMS (EI)

305.9811 (M^+), $C_{14}H_{12}OBrP$ requires 305.9809; Anal. Calcd for $C_{14}H_{12}OBrP$: C 54.75, H 3.94. Found: C 54.71, H 3.89.

3-Bromo-5-ethyl-7-nitro-5*H*-dibenzophosphole 5-oxide (4). 3-Bromo-5-ethyl-5*H*-dibenzophosphole 5-oxide (**3**) (1789 mg, 5.83 mmol) was dissolved in 40 mL of 96% H_2SO_4 and the solution was cooled to 0ºC. 6 mL of 100% HNO_3 were added to the solution and the resulting mixture was stirred at 0ºC for 10 min. The reaction was quenched over 200 mL of crushed ice, and dichloromethane (100 mL) was added. The organic layer was extracted and dried over anhydrous $MgSO_4$, and the solvent was removed. Pure 3-bromo-5-ethyl-7-nitro-5*H*-dibenzophosphole 5-oxide (**4**) (2047 mg, 100%) was obtained as a yellow solid; mp 209-210 ºC (from CH_2Cl_2); R_f (SiO_2, CH_2Cl_2-CH_3OH 96:4) 0.57; ν_{max} (film)/cm^{-1} 3085 (arC-H s), 2975 (C-H s), 1526 (NO_2 s. as), 1345 (NO_2 s. si), 1192 (P=O s); δ_H ($CDCl_3$, 300 MHz) 8.66 (ddd, H^6, 1H, $^3J(H^6\text{-}P)$ = 9.3 Hz, $^4J(H^6\text{-}H^8)$ = 2.1 Hz, $^5J(H^6\text{-}H^9)$ = 0.6 Hz), 8.46 (ddd, H^8, 1H, $^3J(H^8\text{-}H^9)$ = 8.7 Hz, $^4J(H^6\text{-}H^8)$ = 2.1 Hz, $^5J(H^8\text{-}P)$ = 0.9 Hz), 8.01 (ddd, H^4, 1H, $^3J(H^4\text{-}P)$ = 9.3 Hz, $^4J(H^2\text{-}H^4)$ = 1.8 Hz, $^5J(H^1\text{-}H^4)$ = 0.9 Hz), 7.94 (ddd, H^9, 1H, $^3J(H^8\text{-}H^9)$ = 8.7 Hz, $^4J(H^9\text{-}P)$ = 2.7 Hz, $^5J(H^6\text{-}H^9)$ = 0.6 Hz), 7.78 (complex signal, $H^{1,2}$, 2H), 2.23 (dq, H^{14}, 2H, $^2J(H^{14}\text{-}P)$ = 15.0 Hz, $^3J(H^{14}\text{-}H^{15})$ = 7.5 Hz), 1.12 (dt, H^{15}, 3H, $^3J(H^{15}\text{-}P)$ = 19.8 Hz, $^3J(H^{14}\text{-}H^{15})$ = 7.5 Hz); δ_C ($CDCl_3$, 75 MHz) 148.21 (d, C^7, $^3J(C^7\text{-}P)$ = 12.2 Hz), 145.89 (d, C^{11}, $^2J(C^{11}\text{-}P)$ = 19.4 Hz), 137.68 (d, C^{10}, $^2J(C^{10}\text{-}P)$ = 18.5 Hz), 136.80 (d, C^2H, $^4J(C^2\text{-}P)$ = 2.1 Hz), 134.85 (d, C^{12}, $^1J(C^{12}\text{-}P)$ = 97.7 Hz), 132.77 (d, C^{13}, $^1J(C^{13}\text{-}P)$ = 98.6 Hz), 132.77 (d, C^4H, $^2J(C^4\text{-}P)$ = 10.0 Hz), 128.81 (d, C^8H, $^4J(C^8\text{-}P)$ = 1.8 Hz), 125.65 (d, C^3, $^3J(C^3\text{-}P)$ = 13.7 Hz), 124.77 (d, C^6H, $^2J(C^6\text{-}P)$ = 11.3 Hz), 124.07 (d, C^1H, $^3J(C^1\text{-}P)$ = 9.7 Hz), 122.06 (d, C^9H, $^3J(C^9\text{-}P)$ = 9.7 Hz), 22.87 (d, $C^{14}H_2$, $^1J(C^{14}\text{-}P)$ = 71.0 Hz), 6.00 (d, $C^{15}H_3$, $^2J(C^{15}\text{-}P)$ = 4.5 Hz); δ_P ($CDCl_3$, 121 MHz) 44.19 (s); m/z (CI, NH_3) 351 (M + 1 - H, ^{79}Br, 16%), 353 (M + 1 - H, ^{81}Br, 16%), 368 (M + 18 - H, ^{79}Br, 100%), 370 (M + 18 - H, ^{81}Br, 100%); HRMS (EI) 350.9665 (M^+), $C_{14}H_{11}NO_3BrP$ requires 350.9660; Anal. Calcd for $C_{14}H_{11}NO_3BrP$: C 47.75, H 3.15, N 3.98. Found: 47.62, H 3.29, N 4.07.

7-Amino-3-bromo-5-ethyl-5*H*-dibenzophosphole 5-oxide (5). 3-Bromo-7-nitro-5-ethyl-5*H*-dibenzophosphole 5-oxide (**4**) (2047 mg, 5.81 mmol) was dissolved in a mixture of 75 mL of ethanol, 15 mL of 35% HCl and 10 mL of water, and the solution was heated to reflux. Iron turnings (8 g, 143 mmol) were added to the solution, and the mixture was vigorously stirred for 2.5 h at reflux temperature. After this time, the solution was basified with 10% NaOH and the abundant dark brown suspension of iron oxide obtained was removed by centrifugation. The resulting clear solution was decanted and the solvent was evaporated to obtain a mixture of organic compound and some inorganic salts. The organic product mixed with iron oxide was recovered by continuous Soxhlet extraction with methanol, and then added to the previously obtained mixture. Inorganic salts were removed and 7-amino-3-bromo-5-ethyl-5*H*-dibenzophosphole 5-oxide (**5**) (1530 mg, 82%) was isolated as a fluorescent green solid by column chromatography through neutral Al_2O_3 eluting with CH_2Cl_2-CH_3OH 96:4; mp 113-115ºC (decomp) (from CH_2Cl_2); R_f (Al_2O_3, pH 7.0, CH_2Cl_2-CH_3OH 96:4) 0.34; ν_{max} (film)/cm^{-1} [3330, 3218] (NH_2 s), 2973 (C-H s), 1603 (NH_2 δ), 1179 (P=O s); δ_H ($CDCl_3$, 300 MHz) 7.79 (dd, H^4, 1H, $^3J(H^4\text{-}P)$ = 9.6 Hz, $^4J(H^2\text{-}H^4)$ = 1.8 Hz), 7.60 (dd, H^2, 1H, $^3J(H^1\text{-}H^2)$ = 8.1 Hz, $^4J(H^2\text{-}H^4)$ = 1.8 Hz), 7.46 (complex signal, $H^{1,9}$, 2H), 7.02 (dd, H^6, 1H, $^3J(H^6\text{-}P)$ = 10.8 Hz, $^4J(H^6\text{-}H^8)$ = 2.4 Hz), 6.82 (dd, H^8, 1H, $^3J(H^8\text{-}H^9)$ = 8.1 Hz, $^4J(H^6\text{-}H^8)$ = 2.4 Hz), 2.07 (dq, H^{14}, 2H, $^2J(H^{14}\text{-}P)$ = 14.4 Hz, $^3J(H^{14}\text{-}H^{15})$ = 7.5 Hz), 1.01 (dt, H^{15}, 3H, $^3J(H^{15}\text{-}P)$ = 19.2 Hz, $^3J(H^{14}\text{-}H^{15})$ = 7.5 Hz); δ_C ($CDCl_3$, 75 MHz) 148.64 (d, C^7, $^3J(C^7\text{-}P)$ = 13.1 Hz), 141.15 (d, C^{10}, $^2J(C^{10}\text{-}P)$ = 20.9 Hz), 136.18 (s, C^2H), 131.79 (d, C^4H, $^2J(C^4\text{-}P)$ = 10.3 Hz), 131.39 (d, C^{12}, $^1J(C^{12}\text{-}P)$ = 102.0 Hz), 130.54 (d, C^{13}, $^1J(C^{13}\text{-}P)$ = 137.2 Hz), 122.44 (d, C^1H, $^3J(C^1\text{-}P)$ = 11.3 Hz), 121.31 (d, C^9H, $^3J(C^9\text{-}P)$ = 10.3 Hz), 120.77 (d, C^3, $^3J(C^3\text{-}P)$ = 14.0 Hz), 119.12 (s, C^8H), 114.67 (d, C^6H, $^2J(C^6\text{-}P)$ = 11.0 Hz), 22.65 (d, $C^{14}H_2$, $^1J(C^{14}\text{-}P)$ = 72.8 Hz), 5.68 (d, $C^{15}H_3$, $^2J(C^{15}\text{-}P)$ = 4.4 Hz); δ_P ($CDCl_3$, 121 MHz) 48.69 (s); m/z (CI, NH_3) 321 (M + 1 - H, ^{79}Br, 73%), 323 (M + 1 - H, ^{81}Br, 67%), 338 (M + 18 - H, ^{79}Br, 100%), 340 (M + 18 - H, ^{81}Br, 95%); HRMS (EI) 320.9924 (M^+), $C_{14}H_{13}NOBrP$ requires 320.9918; Anal. Calcd for $C_{14}H_{13}NOBrP$: C 52.20, H 4.07, N 4.35. Found: C 52.43, H 4.18, N 4.37.

3-Bromo-5-ethyl-7-hydroxy-5*H*-dibenzophosphole 5-oxide (6). A solution of sodium nitrite (337 mg, 4.88 mmol) in 5 mL of water was slowly added to a previously cooled to 0ºC solution of 7-amino-3-bromo-5-ethyl-5*H*-dibenzophosphole 5-oxide (**5**) (1142 mg, 3.55 mmol) in a mixture of 4 mL of 96% H_2SO_4 and 6 mL of water, maintaining the temperature during the addition below 5ºC. After the addition, the orange solution obtained was stirred at 0ºC for 5 min and then a small amount of urea was added to destroy the excess of sodium nitrite. The resulting diazonium salt was added to a solution of copper(II) nitrate (12.8 g, 53.1 mmol) in 100 mL of water, and immediately copper(I) oxide (530 mg, 3.70 mmol) was added. The mixture was vigorously stirred at rt overnight and an abundant evolution of N_2 was observed, with formation of a brown precipitate. This precipitate was filtered, washed with water and dried in presence of P_2O_5. After column chromatography eluting with CH_2Cl_2-CH_3OH 96:4, 3-bromo-5-ethyl-7-hydroxy-5*H*-dibenzophosphole 5-oxide (**6**) (995 mg, 87%) was isolated as a fluorescent yellow solid; mp 279-280ºC (from CH_2Cl_2); R_f (SiO_2, CH_2Cl_2-CH_3OH 96:4) 0.09; ν_{max} (film)/cm^{-1} 3050 (broad, OH s), 2930 (C-H s), 1434 (OH δ ip), 1164 (P=O s); δ_H (CD_3OD, 300 MHz) 8.01 (ddd, H^4, 1H, $^3J(H^4\text{-}P)$ = 9.3 Hz, $^4J(H^2\text{-}H^4)$ = 1.8 Hz, $^5J(H^1\text{-}H^4)$ = 0.6 Hz), 7.83 (complex signal, $H^{1,2,9}$, 3H), 7.30 (dd, H^6, 1H, $^3J(H^6\text{-}P)$ = 10.2 Hz, $^4J(H^6\text{-}H^8)$ = 2.4 Hz), 7.14 (ddd, H^8, 1H, $^3J(H^8\text{-}H^9)$ = 8.7 Hz, $^4J(H^6\text{-}H^8)$ = 2.4 Hz,

${}^5J$(H^8-P) = 0.9 Hz), 2.28 (dq, H^{14}, 2H, ${}^2J$(H^{14}-P) = 14.7 Hz, ${}^3J$(H^{14}-H^{15}) = 7.8 Hz), 1.07 (dt, H^{15}, 3H, ${}^3J$(H^{15}-P) = 19.8 Hz, ${}^3J$(H^{14}-H^{15}) = 7.8 Hz); δ_C (CD_3OD, 75 MHz) 160.81 (d, C^7, ${}^3J$(C^7-P) = 17.3 Hz), 142.53 (d, C^{10}, ${}^2J$(C^{10}-P) = 24.6 Hz), 137.90 (s, C^{2}H), 133.15 (d, C^{4}H, ${}^2J$(C^4-P) = 12.2 Hz), 133.14 (d, C^{13}, ${}^1J$(C^{13}-P) = 120.0 Hz), 124.48 (d, C^{1}H, ${}^3J$(C^1-P) = 13.7 Hz), 123.51 (d, C^{9}H, ${}^3J$(C^9-P) = 12.3 Hz), 122.58 (d, C^3, ${}^3J$(C^3-P) = 16.7 Hz), 121.98 (s, C^{8}H), 116.85 (d, C^{6}H, ${}^2J$(C^6-P) = 13.0 Hz), 23.13 (d, C^{14}H$_2$, ${}^1J$(C^{14}-P) = 84.5 Hz), 6.17 (d, C^{15}H$_3$, ${}^2J$(C^{15}-P) = 4.4 Hz); δ_P (CD_3OD, 121 MHz) 53.78 (s); m/z (CI, NH_3) 322 (M + 1 - H, ^{79}Br, 18%), 323 (M + 1, ^{79}Br, 43%), 324 (M + 1 - H, ^{81}Br, 39%), 325 (M + 1, ^{81}Br, 32%), 339 (M + 18 - H, ^{79}Br, 100%), 341 (M + 18 - H, ^{81}Br, 97%); HRMS (CI, CH_4) 321.9751 (M$^+$), $C_{14}H_{12}O_2BrP$ requires 321.9758; Anal. Calcd for $C_{14}H_{12}O_2BrP$: C 52.04, H 3.74. Found: C 52.37, H 3.90.

***S*-(+)-2-Methylbutyl tosylate.** (*S*)-2-Methylbutanol (11.3 g, 128 mmol) was dissolved in 20 mL of anhydrous pyridine. The solution was cooled to 0ºC and *p*-toluensulfonyl chloride (tosyl chloride) (29.6 g, 155 mmol) was added with vigorous stirring at 0ºC. After addition, the mixture was stirred at 0ºC for 3 h. A white precipitate of pyridine hydrochloride was obtained and was removed by filtration. The resulting solution was extracted with dichloromethane, and the organic layer washed with water. After column chromatography eluting with hexane-dichloromethane 1:1, *S*-(+)-2-methylbutyl tosylate (29.4 g, 95%) was obtained as a colorless oil; R_f (SiO_2, hexane-CH_2Cl_2 1:1) 0.25; $[\alpha]_D^{20}$ +3.47º (*c* 1.2, $CHCl_3$); ν_{max} (film)/cm^{-1} 3040 (arC-H s), 2968 (C-H s), [1362, 1177] (S=O s); δ_H ($CDCl_3$, 200 MHz) 7.79 (d, H^7, 2H, ${}^3J$(H^7-H^8) = 8.0 Hz), 7.35 (d, H^8, 2H, ${}^3J$(H^7-H^8) = 8.0 Hz), 3.85 (complex signal, H^1, 2H), 2.45 (s, H^{10}, 3H), 1.69 (complex signal, H^2, 1H), 1.37 (complex signal, H^{3a}, 1H), 1.14 (complex signal, H^{3b}, 1H), 0.86 (d, H^5, 3H, ${}^3J$(H^2-H^5) = 6.8 Hz), 0.82 (t, H^4, 3H, ${}^3J$(H^3-H^4) = 7.0 Hz); δ_C ($CDCl_3$, 50 MHz) 144.55 (C^9), 132.96 (C^6), 129.70 (C^{8}H), 127.74 (C^{7}H), 74.78 (C^{1}H$_2$), 34.30 (C^{2}H), 25.39 (C^{3}H$_2$), 21.61 (C^{10}H$_3$), 15.94 (C^{5}H$_3$), 10.95 (C^{4}H$_3$); m/z (CI, NH_3) 242 (M + 1, 4%), 260 (M + 18, 100%); HRMS (CI, CH_4) 243.1041 ([M+H]$^+$), $C_{12}H_{19}O_3S$ requires 243.1055; Anal. Calcd for $C_{12}H_{18}O_3S$: C 59.47, H 7.49, S 13.23. Found: C 59.23, H 7.52, S 13.39.

(*S*$_C$)-3-Bromo-5-ethyl-7-(2-methylbutoxy)-5*H*-dibenzophosphole 5-oxide (7). 3-Bromo-5-ethyl-7-hydroxy-5*H*-dibenzophosphole 5-oxide (**6**) (879 mg, 2.72 mmol) was dissolved in 25 mL of anhydrous *N*,*N*-dimethylformamide. Anhydrous potassium carbonate (682 mg, 4.94 mmol) and *S*-(+)-2-methylbutyl tosylate (772 mg, 3.19 mmol) were added and the mixture was heated under anhydrous atmosphere to 130ºC for 8 h. Solvent was removed by vacuum distillation at rt (2 mmHg) and (*S*$_C$)-3-bromo-5-ethyl-7-(2-methylbutoxy)-5*H*-dibenzophosphole 5-oxide (**7**) (749 mg, 70%) was isolated as a pale yellow oil by column chromatography, eluting with CH_2Cl_2-CH_3OH 96:4; R_f (SiO_2, CH_2Cl_2-CH_3OH 96:4) 0.46; $[\alpha]_D^{20}$ +5.82° (*c* 1.44, acetone); ν_{max} (film)/cm^{-1} 2966 (C-H s), 1256 (C-O-C as. s), 1185 (P=O s); δ_H ($CDCl_3$, 300 MHz) 7.85 (dd, H^{4}, 1H, ^{3}J(H^{4}-P) = 9.0 Hz, ^{4}J(H^{2}-H^{4}) = 1.8 Hz), 7.60 (complex signal, H^{2,9}, 2H), 7.49 (dd, H^{1}, 1H, ^{3}J(H^{1}-H^{2}) = 8.1 Hz, ^{4}J(H^{1}-P) = 3.0 Hz), 7.29 (dd, H^{6}, 1H, ^{3}J(H^{6}-P) = 10.5 Hz, ^{4}J(H^{6}-H^{8}) = 2.4 Hz), 7.05 (dd, H^{8}, 1H, ^{3}J(H^{8}-H^{9}) = 8.7 Hz, ^{4}J(H^{6}-H^{8}) = 2.4 Hz), 3.81 (complex signal, H^{16}, 2H), 2.09 (dq, H^{14}, 2H, ^{2}J(H^{14}-P) = 15.0 Hz, ^{3}J(H^{14}-H^{15}) = 7.5 Hz), 1.86 (complex signal, H^{17}, 1H), 1.55 (complex signal, H^{18a}, 1H), 1.26 (complex signal, H^{18b}, 1H), 1.04 (dt, H^{15}, 3H, ^{3}J(H^{15}-P) = 18.9 Hz, ^{3}J(H^{14}-H^{15}) = 7.5 Hz), 1.01 (d, H^{20}, 3H, ^{3}J(H^{17}-H^{20}) = 7.5 Hz); δ_C ($CDCl_3$, 75 MHz) 160.61 (d, C^{7}, ^{3}J(C^{7}-P) = 13.6 Hz), 140.41 (d, C^{10}, ^{2}J(C^{10}-P) = 19.7 Hz), 136.03 (d, C^{2}H, ^{4}J(C^{2}-P) = 1.8 Hz), 132.16 (d, C^{4}H, ^{2}J(C^{4}-P) = 10.3 Hz), 122.48 (d, C^{1}H, ^{3}J(C^{1}-P) = 11.5 Hz), 121.87 (d, C^{9}H, ^{3}J(C^{9}-P) = 10.3 Hz), 120.00 (d, C^{8}H, ^{4}J(C^{8}-P) = 2.1 Hz), 114.51 (d, C^{6}H, ^{2}J(C^{6}-P) = 10.7 Hz), 73.41 (s, C^{16}H$_2$), 34.60 (s, C^{17}H), 26.03 (s, C^{18}H$_2$), 23.21 (d, C^{14}H$_2$, ^{1}J(C^{14}-P) = 70.1 Hz), 16.42 (s, C^{20}H$_3$), 11.21 (s, C^{19}H$_3$), 6.09 (d, C^{15}H$_3$, ^{2}J(C^{15}-P) = 4.3 Hz); δ_P ($CDCl_3$, 121 MHz) 43.01 (s); m/z (CI, NH_3) 392 (M + 1 - H, ^{79}Br, 70%), 394 (M + 1 - H, ^{81}Br, 70%), 410 (M + 18, ^{79}Br, 72%), 412 (M + 18, ^{81}Br, 70%); HRMS (CI, CH_4) 394.0523 (M^{+}), $C_{19}H_{22}O_2BrP$ requires 394.0520; Anal. Calcd for $C_{19}H_{22}O_2BrP$: C 58.03, H 5.64. Found: C 58.15, H 5.55.

(S_C)-7-Cyano-5-ethyl-3-(2-methylbutoxy)-5*H*-dibenzophosphole 5-oxide (8). (S_C)-3-Bromo-5-ethyl-7-(2-methylbutoxy)-5*H*-dibenzophosphole 5-oxide (**7**) (2216 mg, 5.64 mmol) was dissolved in 50 mL of anhydrous *N*,*N*-dimethylformamide. Potassium cyanide (848 mg, 13.0 mmol), palladium(II) acetate (267 mg, 1.19 mmol), triphenylphosphine (460 mg, 1.75 mmol) and calcium hydroxide (115 mg, 1.55 mmol) were added and the resulting mixture was heated to 100°C for 2 h under an inert atmosphere. Solvent was removed by vacuum distillation at rt (2 mmHg) and (S_C)-7-cyano-5-ethyl-3-(2-methylbutoxy)-5*H*-dibenzophosphole 5-oxide (**8**) (1763 mg, 92%) was isolated as a pale yellow oil by column chromatography, eluting with CH_2Cl_2-CH_3OH 96:4; R_f (SiO_2, CH_2Cl_2-CH_3OH 96:4) 0.43; $[\alpha]_D^{20}$ +6.65° (*c* 1.73, CH_2Cl_2); ν_{max} (film)/cm^{-1} 2966 (C-H s), 2229 (C≡N s), 1260 (C-O-C as. s), 1183 (P=O s); δ_H ($CDCl_3$, 200 MHz) 8.04 (dd, H^{6}, 1H, ^{3}J(H^{6}-P) = 9.2 Hz, ^{4}J(H^{6}-H^{8}) = 1.2 Hz), 7.81-7.48 (complex signal, H^{1,8,9}, 3H), 7.40 (dd, H^{4}, 1H, ^{3}J(H^{4}-P) = 10.4 Hz, ^{4}J(H^{2}-H^{4}) = 2.4 Hz), 7.15 (ddd, H^{2}, 1H, ^{3}J(H^{1}-H^{2}) = 8.8 Hz, ^{4}J(H^{2}-H^{4}) = 2.4 Hz, ^{5}J(H^{2}-P) = 0.8 Hz), 3.89 (complex signal, H^{16}, 2H), 2.17 (dq, H^{14}, 2H, ^{2}J(H^{14}-P) = 15.0 Hz, ^{3}J(H^{14}-H^{15}) = 7.5 Hz), 1.93 (complex signal, H^{17}, 1H), 1.61 (complex signal, H^{18a}, 1H), 1.34 (complex signal, H^{18b}, 1H), 1.10 (dt, H^{15}, 3H, ^{3}J(H^{15}-P) = 18.9 Hz, ^{3}J(H^{14}-H^{15}) = 7.5 Hz), 1.08 (d, H^{20}, 3H, ^{3}J(H^{17}-H^{20}) = 7.5 Hz); δ_C ($CDCl_3$, 50 MHz) 161.40 (d, C^{3}, ^{3}J(C^{3}-P) = 13.7 Hz), 145.38 (d, C^{11}, ^{2}J(C^{11}-P) = 20.1 Hz), 136.84 (d, C^{8}H, ^{4}J(C^{8}-P) = 1.9 Hz), 132.57 (d, C^{6}H, ^{2}J(C^{6}-P) = 10.5 Hz), 123.72 (d, C^{1}H, ^{3}J(C^{1}-P) = 11.4 Hz), 120.95 (d, C^{9}H, ^{3}J(C^{9}-P) = 9.6 Hz), 120.01 (d, C^{2}H, ^{4}J(C^{2}-P) = 1.8 Hz), 118.11 (d, C≡N,

^{4}J(C^{CN}-P) = 1.4 Hz), 114.60 (d, C^{4}H, ^{2}J(C^{4}-P) = 11.0 Hz), 110.92 (d, C^{7}, ^{3}J(C^{7}-P) = 12.8 Hz), 73.35 (s, C^{16}H$_2$), 34.49 (s, C^{17}H), 25.95 (s, C^{18}H$_2$), 22.80 (d, C^{14}H$_2$, ^{1}J(C^{14}-P) = 70.4 Hz), 16.32 (s, C^{20}H$_3$), 11.26 (s, C^{19}H$_3$), 6.05 (d, C^{15}H$_3$, ^{2}J(C^{15}-P) = 4.2 Hz); δ_P (CDCl$_3$, 121 MHz) 42.41 (s); m/z (CI, NH$_3$) 340 (M + 1, 100%), 356 (M + 18 - H, 92%), 357 (M + 18, 22%); HRMS (CI, CH$_4$) 340.1471 ([M+H]$^+$), $C_{20}H_{23}NO_2P$ requires 340.1466; Anal. Calcd for $C_{20}H_{22}NO_2P$: C 70.78, H 6.53, N 4.13. Found: C 70.63, H 6.59, N 4.21.

(*S*$_C$)-7-Carboxy-5-ethyl-3-(2-methylbutoxy)-5*H*-dibenzophosphole 5-oxide (9). (*S*$_C$)-7-Cyano-5-ethyl-3-(2-methylbutoxy)-5*H*-dibenzophosphole 5-oxide (**8**) (861 mg, 2.54 mmol) was suspended in 40 mL of 35% HCl and the mixture was heated to reflux for 2 h. The solvent was removed and the solid residue was digested with dichloromethane. The resultant fluorescent blue solution was dried over anhydrous MgSO$_4$ and the solvent was evaporated, yielding (*S*$_C$)-7-carboxy-5-ethyl-3-(2-methylbutoxy)-5*H*-dibenzophosphole 5-oxide (**9**) (731 mg, 80%) as a white solid; mp 197-198ºC (from CH$_2$Cl$_2$); $[\alpha]_D^{20}$ +7.89º (*c* 1.74, CH$_3$OH); ν_{max} (film)/cm^{-1} 3400 (broad, COO-H s), 2966 (C-H s), 1700 (C=O s), 1260 (C-O-C as. s), 1160 (P=O s); δ_H (CD$_3$OD, 300 MHz) 8.41 (d, H^{6}, 1H, ^{3}J(H^{6}-P) = 9.9 Hz), 8.25 (d, H^{8}, 1H, ^{3}J(H^{8}-H^{9}) = 8.4 Hz), 7.92 (dd, H^{9}, 1H, ^{3}J(H^{8}-H^{9}) = 8.4 Hz, ^{4}J(H^{9}-P) = 3.3 Hz), 7.58 (complex signal, H^{1}, 1H), 7.42 (dd, H^{4}, 1H, ^{3}J(H^{4}-P) = 10.5 Hz, ^{4}J(H^{2}-H^{4}) = 1.8 Hz), 7.22 (dd, H^{2}, 1H, ^{3}J(H^{1}-H^{2}) = 8.4 Hz, ^{4}J(H^{2}-H^{4}) = 1.8 Hz), 3.92 (complex signal, H^{16}, 2H), 2.25 (complex signal, H^{14}, 2H), 1.88 (complex signal, H^{17}, 1H), 1.61 (complex signal, H^{18a}, 1H), 1.31 (complex signal, H^{18b}, 1H), 1.04 (dt, H^{15+20}, 6H), 0.97 (t, H^{19}, 3H, ^{3}J(H^{18}-H^{19}) = 7.5 Hz); δ_C (CD$_3$OD, 75 MHz) 168.40 (s, COOH), 162.85 (d, C^{3}, ^{3}J(C^{3}-P) = 14.0 Hz), 147.28 (d, C^{11}, ^{2}J(C^{11}-P) = 20.3 Hz), 136.56 (s, C^{8}H), 133.07 (d, C^{6}H, ^{2}J(C^{6}-P) = 10.1 Hz), 129.96 (d, C^{7}, ^{3}J(C^{7}-P) = 12.5 Hz), 125.19 (d, C^{1}H, ^{3}J(C^{1}-P) = 10.9 Hz), 121.94 (d, C^{9}H, ^{3}J(C^{9}-P) = 9.7 Hz), 121.37 (s, C^{2}H), 116.11 (d, C^{4}H, ^{2}J(C^{4}-P) = 10.6 Hz), 74.57 (s, C^{16}H$_2$), 36.02 (s, C^{17}H), 27.11 (s, C^{18}H$_2$), 23.08 (d, C^{14}H$_2$, ^{1}J(C^{14}-P) = 70.4 Hz), 16.77 (s, C^{20}H$_3$), 11.64 (s, C^{19}H$_3$), 6.25 (s, C^{15}H$_3$); δ_P (CD$_3$OD, 121 MHz) 51.24 (s); m/z (CI, NH$_3$) 358 (M + 1 - H, 100%), 359 (M + 1, 22%), 375 (M + 18 - H, 12%); HRMS (CI, CH$_4$) 358.1336 (M$^+$), $C_{20}H_{23}O_4P$ requires 358.1334. Anal. Calcd for $C_{20}H_{23}O_4P$: C 67.03, H 6.47. Found: C 66.74, H 6.26.

4-(Undec-10-enoxy)anisole. 4-Methoxyphenol (3.4 g, 27.4 mmol) was dissolved in 50 mL of anhydrous *N*,*N*-dimethylacetamide. Anhydrous potassium carbonate (5.3 g, 38.1 mmol), undec-10-enyl bromide (6.5 g, 27.9 mmol) and a catalytic amount of potassium iodide were added to the solution, and the resulting mixture was heated to 160°C for 24 h. The solution was extracted with ether and washed with a 10%

aqueous solution of NaOH. The organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated. 4-(Undec-10-enoxy)anisole (5.4 g, 71%) was isolated as a white solid after column chromatography eluting with a hexane-CH_2Cl_2 1:1 mixture; mp 47-48°C (from CH_2Cl_2); R_f (SiO_2, hexane-CH_2Cl_2 1:1) 0.49; ν_{max} (film)/cm^{-1} 3072 (arC-H s), 2925 (C-H s), 1233 (C-O-C as. s); δ_H ($CDCl_3$, 200 MHz) 6.82 (s, H^{2+3}, 4H), 5.81 (complex signal, H^{14}, 1H), 4.97 (complex signal, H^{15}, 2H), 3.89 (t, H^5, 2H, $^3J(H^5\text{-}H^6)$ = 6.3 Hz), 3.76 (s, H^{16}, 3H), 2.04 (complex signal, H^{13}, 2H), 1.75 (complex signal, H^6, 2H), 1.29 (complex signal, $H^{7\text{-}12}$, 12H); δ_C ($CDCl_3$, 50 MHz) 153.53 (C^1), 153.18 (C^4), 139.11 ($C^{14}H$), 115.31 (C^3H), 114.50 (C^2H), 114.05 ($C^{15}H_2$), 68.59 (C^5H_2), 55.68 ($C^{16}H_3$), 33.84 ($C^{13}H_2$), [29.55, 29.42, 29.15, 28.96] (C^6H_2, C^8H_2-$C^{12}H_2$), 26.08 (C^7H_2); m/z (CI, NH_3) 277 (M + 1, 13%), 294 (M + 18, 100%); Anal. Calcd for $C_{18}H_{28}O_2$: C 78.21, H 10.21. Found: C 78.22, H 10.29.

4-(Undec-10-enoxy)phenol. Sodium hydride (2.1 g, 60%, 52.0 mmol) was suspended in 20 mL of anhydrous *N*,*N*-dimethylformamide under argon atmosphere, and the mixture was cooled to 0°C. Ethanethiol (4.0 mL, 3.3 g, 53.1 mmol) was slowly added and the resulting sodium ethanethiolate solution was stirred at 0°C for 15 min. 4-(Undec-10-enoxy)anisole (826 mg, 2.99 mmol) was added and the mixture was heated to 120°C for 24 h. The reaction was quenched with 20 mL of 10% HCl aqueous solution, and then was extracted with AcOEt. The organic layer was washed with water, dried over anhydrous $MgSO_4$ and the solvent carefully evaporated due to the presence of ethanethiol. 4-(Undec-10-enoxy)phenol (619 mg, 79%) was isolated as a white solid after column chromatography eluting with CH_2Cl_2; mp 66-67°C (from CH_2Cl_2); R_f (SiO_2, CH_2Cl_2) 0.20; ν_{max} (film)/cm^{-1} 3377 (O-H s); 3082 (arC-H s), 2921 (C-H s), 1235 (C-O-C as. s); δ_H ($CDCl_3$, 200 MHz) 6.76 (s, H^{2+3}, 4H), 5.82 (complex signal, H^{14}, 1H), 4.97 (complex signal, H^{15}, 2H), 3.89 (t, H^5, 2H, $^3J(H^5\text{-}H^6)$ = 6.6 Hz), 2.04 (complex signal, H^{13}, 2H), 1.75 (complex signal, H^6, 2H), 1.29 (complex signal, $H^{7\text{-}12}$, 12H); δ_C ($CDCl_3$, 50 MHz) 153.12 (C^4), 149.24 (C^1), 139.15 ($C^{14}H$), 115.93 (C^2H), 115.56 (C^3H), 114.05 ($C^{15}H_2$), 68.74 (C^5H_2), 33.84 ($C^{13}H_2$), [29.52, 29.43, 29.40, 29.37, 29.13, 28.93] (C^6H_2, C^8H_2-$C^{12}H_2$), 26.08 (C^7H_2); m/z (CI, NH_3) 262 (M + 1 - H, 36%), 280 (M + 18, 100%); HRMS (CI, CH_4) 262.1931 (M^+), $C_{17}H_{26}O_2$ requires 262.1933; Anal. Calcd for $C_{17}H_{26}O_2$: C 77.82, H 9.99. Found: C 77.76, H 10.09.

(*S*$_C$)-5-Ethyl-3-(2-methylbutoxy)-7-(4-undec-10-enoxyphenoxycarbonyl)-5*H*-dibenzophosphole 5-oxide (10). (*S*$_C$)-7-Carboxy-5-ethyl-3-(2-methylbutoxy)-5*H*-dibenzophosphole 5-oxide (**9**) (743 mg, 2.07 mmol) was dissolved in 40 mL of anhydrous CH_2Cl_2. Dicyclohexylcarbodiimide (513 mg, 2.49 mmol) and *N*,*N*-dimethyl-4-aminopyridine (107 mg, 0.88 mmol) were added and the resulting solution was stirred at 0ºC for 30 min under anhydrous atmosphere. 4-Undec-10-enoxyphenol (619 mg, 2.36 mmol) was dissolved in 20 mL of anhydrous CH_2Cl_2 and was added to the reaction mixture, which was stirred at rt for 18 h. The solvent was removed and (S_C)-5-ethyl-3-(2-methylbutoxy)-7-(4-undec-10-enoxyphenoxycarbonyl)-5*H*-dibenzophosphole 5-oxide (**10**) (575 mg, 46%) was isolated as a yellow oil by column chromatography eluting with AcOEt; R_f (SiO_2, AcOEt) 0.58; ν_{max} (film)/cm^{-1} 2927 (C-H s), 1733 (C=O s), 1262 (C-O-C as. s), 1192 (P=O s); δ_H ($CDCl_3$, 500 MHz) 8.55 (dd, H^{6}, 1H, ^{3}J(H^{6}-P) = 10.0 Hz, ^{4}J(H^{6}-H^{8}) = 1.5 Hz), 8.28 (dd, H^{8}, 1H, ^{3}J(H^{8}-H^{9}) = 8.0 Hz, ^{5}J(H^{8}-P) = 1.0 Hz), 7.70 (complex signal, H^{1,9}, 2H), 7.33 (dd, H^{4}, 1H, ^{3}J(H^{4}-P) = 10.0 Hz, ^{4}J(H^{2}-H^{4}) = 2.5 Hz), 7.07 (complex signal, H^{2,23}, 3H), 6.87 (d, H^{24}, 2H, ^{3}J(H^{23}-H^{24}) = 7.0 Hz), 5.76 (complex signal, H^{35}, 1H), 4.91 (complex signal, H^{36}, 2H), 3.90 (t, H^{26}, 2H, ^{3}J(H^{26}-H^{27}) = 7.0 Hz), 3.81 (complex signal, H^{16}, 2H), 2.12 (dq, H^{14}, 2H, ^{2}J(H^{14}-P) = 14.5 Hz, ^{3}J(H^{14}-H^{15}) = 7.5 Hz), 1.99 (complex signal, H^{34}, 2H), 1.85 (complex signal, H^{17}, 1H), 1.73 (complex signal, H^{27}, 2H), 1.52 (complex signal, H^{18a}, 1H), 1.40 (complex signal, H^{18b,28}, 3H), 1.26 (complex signal, H$^{29\text{-}33}$, 10H), 1.03 (dt, H^{15}, 3H, ^{3}J(H^{15}-P) = 19.0 Hz, ^{3}J(H^{14}-H^{15}) = 7.5 Hz), 0.98 (complex signal, H^{20}, 3H), 0.91 (t, H^{19}, 3H, ^{3}J(H^{18}-H^{19}) = 7.5 Hz); δ_C ($CDCl_3$, 62.5 MHz) 164.34 (d, C^{21}, ^{4}J(C^{21}-P) = 1.7 Hz), 161.18 (d, C^{3}, ^{3}J(C^{3}-P) = 13.3 Hz), 156.83 (s, C^{25}), 146.12 (d, C^{11}, ^{2}J(C^{11}-P) = 20.4 Hz), 143.92 (s, C^{22}), 139.01 (s, C^{35}H), 135.18 (s, C^{8}H), 134.18 (d, C^{13}, ^{1}J(C^{13}-P) = 99.3 Hz), 131.40 (d, C^{12}, ^{1}J(C^{12}-P) = 117.9 Hz), 130.92 (d, C^{6}H, ^{2}J(C^{6}-P) = 10.3 Hz), 128.74 (d, C^{7}, ^{3}J(C^{7}-P) = 10.9 Hz), 123.46 (d, C^{1}H, ^{3}J(C^{1}-P) = 11.4 Hz), 122.10 (s, C^{23}H), 120.27 (d, C^{9}H, ^{3}J(C^{9}-P) = 9.6 Hz), 119.92 (s, C^{2}H), 114.95 (s, C^{24}H), 114.52 (d, C^{4}H, ^{2}J(C^{4}-P) = 10.2 Hz), 113.99 (s, C^{36}H$_2$), 73.30 (s, C^{16}H$_2$), 68.24 (s, C^{26}H$_2$), 34.47 (s, C^{17}H), 33.67 (s, C^{34}H$_2$), [29.36, 29.26, 29.21, 29.11, 28.95, 28.76] (s, C^{27}H$_2$, C^{29}H$_2$-C^{33}H$_2$), 25.90 (s, C^{18}H$_2$, C^{28}H$_2$), 22.98 (d, C^{14}H$_2$, ^{1}J(C^{14}-P) = 70.4 Hz), 16.32 (s, C^{20}H$_3$), 11.13 (s, C^{19}H$_3$), 6.05 (d, C^{15}H$_3$, ^{2}J(C^{15}-P) = 4.2 Hz); δ_P ($CDCl_3$, 121 MHz) 44.72 (s); m/z (positive FAB) 603 (M$^+$); HRMS (CI, CH_4) 603.3236 ([M+H]$^+$), $C_{37}H_{48}O_5P$ requires 603.3239; Anal. Calcd for $C_{37}H_{47}O_5P$: C 73.73, H 7.86. Found: C 73.65, H 7.84.

(S_C)-5-Ethyl-3-(2-methylbutoxy)-7-(4-undec-10-enoxyphenoxycarbonyl)-5*H*-dibenzophosphole (11). (S_C)-5-Ethyl-3-(2-methylbutoxy)-7-(4-undec-10-enoxyphenoxycarbonyl)-5*H*-dibenzophosphole 5-oxide (**10**) (699 mg, 1.16 mmol), a mixture of 50% (R_P) and 50% (S_P) product, was dissolved in anhydrous toluene (20 mL) under an inert atmosphere at rt. Distilled triethylamine (0.23 mL, 167 mg, 1.65 mmol) and then trichlorosilane (0.35 mL, 470 mg, 3.47 mmol) were added and the resulting solution was heated under reflux for 2 h. A 30% NaOH aqueous solution (20 mL) was purged with nitrogen and then added to the reaction mixture previously cooled to 0°C. After vigorous stirring for 0.5 h the organic layer was separated under nitrogen, dried over anhydrous $MgSO_4$ and the solvent removed. (S_C)-5-Ethyl-3-(2-

methylbutoxy)-7-(4-undec-10-enoxyphenoxycarbonyl)-5*H*-dibenzophosphole was isolated as a colorless oil which was rapidly converted into cyclopalladate (**12**) due to its rapid oxidation in contact with air.

Bis[(*R*)-1-(1-aminoethyl)naphthyl-*C*^{2},*N*]di-μ-chlorodipalladium(II). Palladium(II) acetate (1.9 g, 8.62 mmol) was dissolved in acetic acid (100 mL). *R*-(+)-1-(1-Naphthyl)ethylamine (1.5 g, 8.91 mmol) was added and the solution was stirred under an argon atmosphere at 60°C for 5 h. The solvent was removed and the resulting residue was dissolved in dichloromethane and filtered with Celite. The green solid obtained after dichloromethane evaporation was dissolved in acetone (120 mL) and lithium chloride (752 mg, 17.7 mmol) was added. The solution was stirred at rt for 30 min. Water (300 mL) was added, the pale brown solution was stirred for 0.5 h and a green precipitate was obtained. After filtering and drying in a low-pressure oven, bis[(*R*)-1-(1-aminoethyl)naphthyl-*C*^{2},*N*]di-μ-chlorodipalladium(II) (2.7 g, 100%) was isolated as a pale green solid, which was found to be identical by ^{1}H NMR to the described compound.[24]

Synthesis of 12 and separation of (*R*)-12 and (*S*)-12. Bis[(*R*)-1-(1-aminoethyl)naphthyl-*C*^{2},*N*]di-μ-chlorodipalladium(II) (362 mg, 0.58 mmol) was added to a solution of (S_C)-5-ethyl-3-(2-methylbutoxy)-7-(4-undec-10-enoxyphenoxycarbonyl)-5*H*-dibenzophosphole (**11**) previously obtained into anhydrous tetrahydrofuran (50 mL). The resulting solution was stirred under nitrogen at rt for 15 min. The solvent was removed and the oil obtained was purified by SiO_2 column chromatography (200 g), eluting with $CHCl_3$–acetone 49:1. Firstly, (R_C11’,S_P,S_C17)-[1-(1-aminoethyl)naphthyl-*C*^{2},*N*][chloro][5-ethyl-3-(2-methylbutoxy)-7-(4-undec-10-enoxyphenoxycarbonyl)-5*H*-dibenzophosphole-*P*]palladium(II) ((*S*)-**12**) (400 mg, 77%), and then (R_C11’,R_P,S_C17)-[1-(1-aminoethyl)naphthyl-*C*^{2},*N*][chloro][5-ethyl-3-(2-methylbutoxy)-7-(4-undec-10-enoxyphenoxycarbonyl)-5*H*-dibenzophosphole-*P*]palladium(II) ((*R*)-**12**) (227 mg, 44%) were isolated as yellow solids.

((*S*)-12); R_f (SiO_2, $CHCl_3$–acetone 49:1) 0.24; $[\alpha]_D^{20}$ –139.0° (*c* 1.29, CH_2Cl_2); δ_H ($CDCl_3$, 500 MHz) 8.29 (ddd, ^3J(H^8-H^9) = 8.5 Hz, ^4J(H^6-H^8) = 1.5 Hz, ^5J(H^8-P) = 1.5 Hz, 1 H, H^8), 8.23 (dd, ^3J(H^6-P) = 8.5 Hz, ^4J(H^6-H^8) = 1.5 Hz, 1 H, H^6), 7.88 (complex signal, 3 H, H^1+H^4+H^9), 7.53 (d, ^3J(H$^{7’}$-H$^{8’}$) = 8.0 Hz, 1 H, H$^{8’}$), 7.47 (d, ^3J(H$^{5’}$-H$^{6’}$) = 8.0 Hz, 1 H, H$^{5’}$), 7.28 (ddd, ^3J(H$^{7’}$-H$^{8’}$) = 8.0 Hz, ^3J(H$^{6’}$-H$^{7’}$) = 7.0 Hz, ^4J(H$^{5’}$-H$^{7’}$) = 1.0 Hz, 1 H, H$^{7’}$), 7.22 (ddd, ^3J(H$^{5’}$-H$^{6’}$) = 8.0 Hz, ^3J(H$^{6’}$-H$^{7’}$) = 7.0 Hz, ^4J(H$^{6’}$-H$^{8’}$) = 1.0 Hz, 1 H, H$^{6’}$), 7.17 (ddd, ^3J(H^1-H^2) = 9.0 Hz, ^4J(H^2-H^4) = 1.5 Hz, ^5J(H^2-P) = 1.5 Hz, 1 H, H^2), 6.91 (d, ^3J(H^{23}-H^{24}) = 9.0 Hz, 2 H, H^{23}), 6.81 (d, ^3J(H^{23}-H^{24}) = 9.0 Hz, 2 H, H^{24}), 6.75 (d, ^3J(H$^{3’}$-H$^{4’}$) = 8.5 Hz, 1 H, H$^{4’}$), 6.00 (dd, ^3J(H$^{3’}$-H$^{4’}$) = 8.5 Hz, ^4J(H$^{3’}$-P) = 6.5 Hz, 1 H, H$^{3’}$), 5.80 (complex signal, 1 H, H^{35}), 5.12 (q, ^3J(H$^{11’}$-

H$^{12'}$) = 6.5 Hz, 1 H, H$^{11'}$), 4.95 (complex signal, 2 H, H^{36}), 4.13 (complex signal, 1 H, H$^{13'a}$), 3.93 (complex signal, 2 H, H^{16}), 3.89 (t, ^{3}J(H^{26}-H^{27}) = 6.5 Hz, 2 H, H^{26}), 3.55 (complex signal, 1 H, H$^{13'b}$), 2.70 (dq, ^{2}J(H^{14a}-P) = 15.0 Hz, ^{3}J(H^{14a}-H^{15}) = 7.5 Hz, 1 H, H^{14a}), 2.46 (complex signal, 1 H, H^{14b}), 2.03 (complex signal, 2 H, H^{34}), 1.96 (d, ^{3}J(H$^{11'}$-H$^{12'}$) = 6.5 Hz, 3 H, H$^{12'}$), 1.90 (complex signal, 1 H, H^{17}), 1.74 (complex signal, 2 H, H^{27}), 1.60 (complex signal, 1 H, H^{18a}), 1.45–1.24 (complex signal, 13 H, H^{18b}+H$^{28–33}$), 1.03 (d, ^{3}J(H^{17}-H^{20}) = 6.5 Hz, 3 H, H^{20}), 0.96 (t, ^{3}J(H^{18}-H^{19}) = 7.5 Hz, 3 H, H^{19}), 0.84 (dt, ^{3}J(H^{15}-P) = 18.5 Hz, ^{3}J(H^{14}-H^{15}) = 7.5 Hz, 3 H, H^{15}); δ$_C$ (CDCl$_3$, 75 MHz) 164.66 (s, C=O), 161.19 (d, ^{3}J(C^{3}-P) = 12.8 Hz, C^{3}), 156.85 (s, C^{25}), 151.16 (s) [C$^{1'}$,C$^{2'}$, C$^{9'}$, C$^{10'}$], 149.19 (d, ^{2}J(C^{11}-P) = 7.4 Hz, C^{11}), 147.44 (s) [C$^{1'}$,C$^{2'}$,C$^{9'}$,C$^{10'}$], 144.03 (s, C^{22}), 139.19 (s, C^{35}H), 137.06 (d, ^{1}J(C^{13}-P) = 46.1 Hz, C^{13}), 134.81 (d, ^{2}J(C^{10}-P) = 7.0 Hz, C^{10}), 134.60 (d, ^{3}J(C$^{3'}$-P) = 12.2 Hz, C$^{3'}$H), 133.91 (d, ^{1}J(C^{12}-P) = 50.1 Hz, C^{12}), 133.24 (s, C^{8}H), 132.98 (d, ^{2}J(C^{6}-P) = 14.9 Hz, C^{6}H), 131.05 (s) [C$^{1'}$,C$^{2'}$,C$^{9'}$,C$^{10'}$], 128.38 (s, C^{7}), 128.01 (d, ^{6}J(C$^{5'}$-P) = 10.7 Hz, C$^{5'}$H), 125.70 (s, C$^{7'}$H), 125.21 (d, ^{4}J(C$^{4'}$-P) = 5.2 Hz, C$^{4'}$H), 124.13 (s, C$^{6'}$H), 123.31 (s, C^{1}H+C$^{8'}$H), 122.25 (s, C^{23}H), 120.26 (d, ^{3}J(C^{9}-P) = 5.1 Hz, C^{9}H), 119.10 (s, C^{2}H), 116.50 (d, ^{2}J(C^{4}-P) = 15.8 Hz, C^{4}H), 114.99 (s, C^{24}H), 114.12 (s, C^{36}H$_2$), 73.35 (s, C^{16}H$_2$), 68.35 (s, C^{26}H$_2$), 57.38 (s, C$^{11'}$H), 34.75 (s, C^{17}H), 33.73 (s, C^{34}H$_2$), [29.43, 29.34, 29.29, 29.19, 29.04, 28.86] (s, C^{27}H$_2$+C$^{29–33}$H$_2$), [26.06, 25.95, 25.69] (s, C$^{12'}$H$_3$+C^{18}H$_2$+C^{28}H$_2$), 23.08 (d, ^{1}J(C^{14}-P) = 27.3 Hz, C^{14}H$_2$), 16.50 (s, C^{20}H$_3$), 11.32 (s, C^{19}H$_3$), 8.44 (d, ^{2}J(C^{15}-P) = 4.8 Hz, C^{15}H$_3$); δ$_P$ (CDCl$_3$, 121 MHz) 29.30 (s).

((*R*)-12); *R*$_f$ (SiO$_2$, CHCl$_3$–acetone 49:1) 0.16; [α]$_D^{20}$ –9.05° (*c* 1.05, CH$_2$Cl$_2$); δ$_H$ (CDCl$_3$, 500 MHz) 9.02 (dd, ^{3}J(H^{6}-P) = 8.5 Hz, ^{4}J(H^{6}-H^{8}) = 1.5 Hz, 1 H, H^{6}), 8.37 (ddd, ^{3}J(H^{8}-H^{9}) = 8.5 Hz, ^{4}J(H^{6}-H^{8}) = 1.5 Hz, ^{5}J(H^{8}-P) = 1.5 Hz, 1 H, H^{8}), 7.90 (dd, ^{3}J(H^{8}-H^{9}) = 8.5 Hz, ^{4}J(H^{9}-P) = 1.0 Hz, 1 H, H^{9}), 7.87 (dd, ^{3}J(H^{1}-H^{2}) = 8.5 Hz, ^{4}J(H^{1}-P) = 2.0 Hz, 1 H, H^{1}), 7.51 (d, ^{3}J(H$^{7'}$-H$^{8'}$) = 8.0 Hz, 1 H, H$^{8'}$), 7.44 (d, ^{3}J(H$^{5'}$-H$^{6'}$) = 8.0 Hz, 1 H, H$^{5'}$), 7.25 (ddd, ^{3}J(H$^{7'}$-H$^{8'}$) = 8.0 Hz, ^{3}J(H$^{6'}$-H$^{7'}$) = 7.5 Hz, ^{4}J(H$^{5'}$-H$^{7'}$) = 1.0 Hz, 1 H, H$^{7'}$), 7.19 (ddd, ^{3}J(H$^{5'}$-H$^{6'}$) = 8.0 Hz, ^{3}J(H$^{6'}$-H$^{7'}$) = 7.5 Hz, ^{4}J(H$^{6'}$-H$^{8'}$) = 1.0 Hz, 1 H, H$^{6'}$), 7.14 (d, ^{3}J(H^{23}-H^{24}) = 9.5 Hz, 2 H, H^{23}), 7.07 (ddd, ^{3}J(H^{1}-H^{2}) = 8.5 Hz, ^{4}J(H^{2}-H^{4}) = 1.5 Hz, ^{5}J(H^{2}-P) = 1.5 Hz, 1 H, H^{2}), 7.04 (dd, ^{3}J(H^{4}-P) = 9.5 Hz, ^{4}J(H^{2}-H^{4}) = 1.5 Hz, 1 H, H^{4}), 6.90 (d, ^{3}J(H^{23}-H^{24}) = 9.5 Hz, 2 H, H^{24}), 6.75 (d, ^{3}J(H$^{3'}$-H$^{4'}$) = 8.5 Hz, 1 H, H$^{4'}$), 6.00 (dd, ^{3}J(H$^{3'}$-H$^{4'}$) = 8.5 Hz, ^{4}J(H$^{3'}$-P) = 6.5 Hz, 1 H, H$^{3'}$), 5.80 (complex signal, 1 H, H^{35}), 5.09 (q, ^{3}J(H$^{11'}$-H$^{12'}$) = 6.5 Hz, 1 H, H$^{11'}$), 4.95 (complex signal, 2 H, H^{36}), 4.17 (complex signal, 1 H, H$^{13'a}$), 3.93 (t, ^{3}J(H^{26}-H^{27}) = 6.5 Hz, 2 H, H^{26}), 3.61 (d, ^{3}J(H^{16}-H^{17}) = 6.0 Hz, 2 H, H^{16}), 3.56 (complex signal, 1 H, H$^{13'b}$), 2.66 (dq, ^{2}J(H^{14a}-P) = 15.0 Hz, ^{3}J(H^{14a}-H^{15}) = 7.5 Hz, 1 H, H^{14a}), 2.47 (complex signal, 1 H, H^{14b}), 2.03 (complex signal, 2 H, H^{34}), 1.92 (d, ^{3}J(H$^{11'}$-H$^{12'}$) = 6.5 Hz, 3 H, H$^{12'}$), 1.77 (complex signal, 2 H, H^{27}), 1.61 (complex signal, 1 H, H^{17}), 1.47–1.00 (complex signal, 14 H, H^{18}+H$^{28–33}$), 0.84 (d, ^{3}J(H^{17}-H^{20}) = 6.5 Hz, 3 H, H^{20}), 0.79 (complex signal, 3 H, H^{15}), 0.75 (t, ^{3}J(H^{18}-H^{19}) = 7.5 Hz, 3 H, H^{19}); δ$_C$ (CDCl$_3$, 75 MHz) 164.90 (s, C=O), 160.44 (d, ^{3}J(C^{3}-P) = 13.4 Hz, C^{3}), 156.85 (s, C^{25}), 151.18 (s) [C$^{1'}$,C$^{2'}$,C$^{9'}$,C$^{10'}$], 148.45 (d, ^{2}J(C^{11}-P) = 7.3 Hz, C^{11}), 147.45 (s) [C$^{1'}$,C$^{2'}$,C$^{9'}$,C$^{10'}$], 144.22 (s, C^{22}), 139.16 (s, C^{35}H), 137.37 (d, ^{1}J(C^{13}-P) = 48.9 Hz, C^{13}), 135.45 (d, ^{2}J(C^{10}-P) = 6.7 Hz, C^{10}), 134.64 (d, ^{3}J(C$^{3'}$-P) = 12.2 Hz, C$^{3'}$H), 133.54 (s, C^{8}H), 133.50 (d, ^{1}J(C^{12}-P) = 47.0 Hz, C^{12}), 133.32 (d, ^{2}J(C^{6}-P) = 15.2 Hz, C^{6}H), 130.96 (s) [C$^{1'}$,C$^{2'}$,C$^{9'}$,C$^{10'}$], 128.63 (d, ^{6}J(C$^{5'}$-P) = 10.7 Hz, C$^{5'}$H), 128.27 (d, ^{3}J(C^{7}-P) = 2.4 Hz, C^{7}), 125.60 (s, C$^{7'}$H), 125.12 (d, ^{4}J(C$^{4'}$-P) = 5.2 Hz, C$^{4'}$H), 124.03 (s, C$^{6'}$H), 123.26 (s, C^{1}H+C$^{8'}$H), 122.35 (s, C^{23}H), 120.37 (d, ^{3}J(C^{9}-P) = 5.5 Hz, C^{9}H), 118.67 (s, C^{2}H), 116.45 (d, ^{2}J(C^{4}-P) = 15.2 Hz, C^{4}H), 115.03 (s, C^{24}H), 114.07 (s, C^{36}H$_{2}$), 73.20 (s, C^{16}H$_{2}$), 68.37 (s, C^{26}H$_{2}$), 57.31 (s, C$^{11'}$H), 34.25 (s, C^{17}H), 33.75 (s, C^{34}H$_{2}$), [29.46, 29.37, 29.32, 29.24, 29.06, 28.88] (s, C^{27}H$_{2}$+C$^{29–33}$H$_{2}$), [25.99, 25.85, 25.69] (s, C$^{12'}$H$_{3}$+C^{18}H$_{2}$+C^{28}H$_{2}$), 23.03 (d, ^{1}J(C^{14}-P) = 27.3 Hz, C^{14}H$_{2}$), 16.31 (s, C^{20}H$_{3}$), 11.05 (s, C^{19}H$_{3}$), 8.23 (d, ^{2}J(C^{15}-P) = 4.9 Hz, C^{15}H$_{3}$); δ_{P} (CDCl$_{3}$, 121 MHz) 29.30 (s).

Discoordination of (*S*)-12 and oxidation of (*R)*-11 to obtain (*S*$_{C}$,*S*$_{P}$)-5-ethyl-3-(2-methylbutoxy)-7-(4-undec-10-enoxyphenoxycarbonyl)-5*H*-dibenzophosphole 5-oxide ((*S*)-10). (*R*$_{C}$11',*S*$_{P}$,*S*$_{C}$17)-[1-(1-Aminoethyl)naphthyl-*C*^{2},*N*][chloro][5-ethyl-3-(2-methylbutoxy)-7-(4-undec-10-enoxyphenoxycarbonyl)-5*H*-dibenzophosphole-*P*]palladium(II) ((*S*)-**12**) (227 mg, 0.25 mmol) was dissolved in anhydrous tetrahydrofuran (50 mL), and 1,2-bis(diphenylphosphino)ethane (110 mg, 0.28 mmol) was added to the solution. The resulting mixture was stirred at rt under an inert atmosphere for 3 h. The solution was evaporated, the residue dissolved in benzene and filtered through Celite. 30% H$_{2}$O$_{2}$ (1 mL) was added and the solution was stirred for a further 2 h. Dichloromethane (100 mL) and water (100 mL) were added. The organic layer was washed, dried over anhydrous MgSO$_{4}$ and the solvent removed. The residue was purified by column chromatography eluting with hexane–AcOEt 4:6, yielding (*S*$_{C}$,*S*$_{P}$)-5-ethyl-3-(2-methylbutoxy)-7-(4-undec-10-enoxyphenoxycarbonyl)-5*H*-dibenzophosphole 5-oxide (142 mg, 93%) as a yellow solid; mp 44.7°C (from benzene); R_{f} (SiO$_{2}$, AcOEt) 0.58; $[\alpha]_{D}^{20}$ +20.2° (*c* 1.03, CH$_{2}$Cl$_{2}$); ν_{max} (film)/cm^{-1} 2927 (C-H s), 1733 (C=O s), 1262 (C-O-C as. s), 1192 (P=O s); δ_{H} (CDCl$_{3}$, 500 MHz) 8.55 (dd, H^{6}, 1H, ^{3}J(H^{6}-P) = 10.0 Hz, ^{4}J(H^{6}-H^{8}) = 1.5 Hz), 8.28 (dd, H^{8}, 1H, ^{3}J(H^{8}-H^{9}) = 8.0 Hz, ^{5}J(H^{8}-P) = 1.0 Hz), 7.70 (complex signal, H^{1,9}, 2H), 7.33 (dd, H^{4}, 1H, ^{3}J(H^{4}-P) = 10.0 Hz, ^{4}J(H^{2}-H^{4}) = 2.5 Hz), 7.07 (complex signal, H^{2,23}, 3H), 6.87 (d, H^{24}, 2H, ^{3}J(H^{23}-H^{24}) = 7.0 Hz), 5.76 (complex signal, H^{35}, 1H), 4.91 (complex signal, H^{36}, 2H), 3.90 (t, H^{26}, 2H, ^{3}J(H^{26}-H^{27}) = 7.0 Hz), 3.81 (complex signal, H^{16}, 2H), 2.12 (dq, H^{14}, 2H, ^{2}J(H^{14}-P) = 14.5 Hz, ^{3}J(H^{14}-H^{15}) = 7.5 Hz), 1.99 (complex signal, H^{34}, 2H), 1.85 (complex signal, H^{17}, 1H), 1.73 (complex signal, H^{27}, 2H), 1.52 (complex signal, H^{18a}, 1H), 1.40 (complex signal, H^{18b,28}, 3H), 1.26 (complex signal, H$^{29-33}$, 10H), 1.03 (dt, H^{15}, 3H, ^{3}J(H^{15}-P) = 19.0 Hz, ^{3}J(H^{14}-H^{15}) = 7.5 Hz), 0.98 (complex signal, H^{20}, 3H), 0.91 (t, H^{19}, 3H, ^{3}J(H^{18}-H^{19}) = 7.5 Hz); δ_{C} (CDCl$_{3}$, 62.5 MHz) 164.34 (d, C^{21}, ^{4}J(C^{21}-P) = 1.7 Hz), 161.18 (d, C^{3}, ^{3}J(C^{3}-P) = 13.3 Hz), 156.83 (s, C^{25}), 146.12 (d, C^{11},

^2J(C^{11}-P) = 20.4 Hz), 143.92 (s, C^{22}), 139.01 (s, C^{35}H), 135.18 (s, C^{8}H), 134.18 (d, C^{13}, ^1J(C^{13}-P) = 99.3 Hz), 131.40 (d, C^{12}, ^1J(C^{12}-P) = 117.9 Hz), 130.92 (d, C^{6}H, ^2J(C^6-P) = 10.3 Hz), 128.74 (d, C^7, ^3J(C^7-P) = 10.9 Hz), 123.46 (d, C^{1}H, ^3J(C^1-P) = 11.4 Hz), 122.10 (s, C^{23}H), 120.27 (d, C^{9}H, ^3J(C^9-P) = 9.6 Hz), 119.92 (s, C^{2}H), 114.95 (s, C^{24}H), 114.52 (d, C^{4}H, ^2J(C^4-P) = 10.2 Hz), 113.99 (s, C^{36}H$_2$), 73.30 (s, C^{16}H$_2$), 68.24 (s, C^{26}H$_2$), 34.47 (s, C^{17}H), 33.67 (s, C^{34}H$_2$), [29.36, 29.26, 29.21, 29.11, 28.95, 28.76] (s, C^{27}H$_2$, C^{29}H$_2$-C^{33}H$_2$), 25.90 (s, C^{18}H$_2$, C^{28}H$_2$), 22.98 (d, C^{14}H$_2$, ^1J(C^{14}-P) = 70.4 Hz), 16.32 (s, C^{20}H$_3$), 11.13 (s, C^{19}H$_3$), 6.05 (d, C^{15}H$_3$, ^2J(C^{15}-P) = 4.2 Hz); δ_P (CDCl$_3$, 121 MHz) 44.72 (s); m/z (positive FAB) 603 (M$^+$); HRMS (CI, CH$_4$) 603.3236 ([M+H]$^+$), $C_{37}H_{48}O_5P$ requires 603.3239; Anal. Calcd for $C_{37}H_{47}O_5P$: C 73.73, H 7.86. Found: C 73.65, H 7.84.

3-Bromo-7-butoxy-5-ethyl-5*H*-dibenzophosphole 5-oxide (13). 3-Bromo-5-ethyl-7-hydroxy-5*H*-dibenzophosphole 5-oxide (**6**) (749 mg, 2.32 mmol) was dissolved in 20 mL of anhydrous *N,N*-dimethylformamide. Anhydrous potassium carbonate (875 mg, 6.33 mmol), potassium iodide (20 mg, 0.12 mmol) and 1-bromobutane (1.9 g, 14.1 mmol) were added and the mixture was heated under anhydrous atmosphere to 100ºC for 20 h. Solvent was removed by vacuum distillation at rt (2 mmHg) and 3-bromo-7-butoxy-5-ethyl-5*H*-dibenzophosphole 5-oxide (**13**) (564 mg, 64%) was isolated as a pale yellow solid by column chromatography, eluting with CH_2Cl_2-CH_3OH 96:4; mp 112-113°C (from CH_2Cl_2); R_f (SiO$_2$, CH_2Cl_2-CH_3OH 96:4) 0.43; $[\alpha]_D^{20}$+5.82º (*c* 1.44, acetone); ν_{max} (film)/cm^{-1} 2968 (C-H s), 1256 (C-O-C as. s), 1182 (P=O s); δ_H (CDCl$_3$, 300 MHz) 7.85 (dd, H^4, 1H, ^3J(H^4-P) = 9.3 Hz, ^4J(H^2-H^4) = 1.8 Hz), 7.61 (complex signal, H^{2,9}, 2H), 7.50 (dd, H^1, 1H, ^3J(H^1-H^2) = 8.1 Hz, ^4J(H^1-P) = 3.0 Hz), 7.29 (dd, H^6, 1H, ^3J(H^6-P) = 10.5 Hz, ^4J(H^6-H^8) = 2.4 Hz), 7.05 (ddd, H^8, 1H, ^3J(H^8-H^9) = 8.7 Hz, ^4J(H^6-H^8) = 2.4 Hz, ^5J(H^8-P) = 0.9 Hz), 4.03 (t, H^{16}, 2H, ^3J(H^{16}-H^{17}) = 6.3 Hz), 2.09 (dq, H^{14}, 2H, ^2J(H^{14}-P) = 15.0 Hz, ^3J(H^{14}-H^{15}) = 7.5 Hz), 1.77 (s.c., H^{17}, 2H), 1.48 (s.c., H^{18}, 2H), 1.04 (dt, H^{15}, 3H, ^3J(H^{15}-P) = 19.2 Hz, ^3J(H^{14}-H^{15}) = 7.5 Hz), 0.91 (t, H^{19}, 3H, ^3J(H^{18}-H^{19}) = 7.5 Hz); δ_C (CDCl$_3$, 75 MHz) 160.48 (d, C^7, ^3J(C^7-P) = 13.7 Hz), 140.42 (d, C^{10}, ^2J(C^{10}-P) = 20.1 Hz), 136.06 (d, C^{2}H, ^4J(C^2-P) = 1.8 Hz), 132.20 (d, C^{4}H, ^2J(C^4-P) = 10.1 Hz), 122.51 (d, C^{1}H, ^3J(C^1-P) = 11.6 Hz), 121.88 (d, C^{9}H, ^3J(C^9-P) = 10.4 Hz), 120.03 (d, C^{8}H, ^4J(C^8-P) = 2.2 Hz), 114.51 (d, C^{6}H, ^2J(C^6-P) = 10.6 Hz), 68.31 (s, C^{16}H$_2$), 31.13 (s, C^{17}H$_2$), 23.24 (d, C^{14}H$_2$, ^1J(C^{14}-P) = 70.1 Hz), 19.16 (s, C^{18}H$_2$), 13.76 (s, C^{19}H$_3$), 6.09 (d, C^{15}H$_3$, ^2J(C^{15}-P) = 4.3 Hz); δ_P (CDCl$_3$, 121 MHz) 43.01 (s); m/z (CI, NH$_3$) 378 (M + 1 - H, ^{79}Br, 98%), 380 (M + 1 - H, ^{81}Br, 100%), 395 (M + 18 - H, ^{79}Br, 78%), 397 (M + 18 - H, ^{81}Br, 73%); HRMS (CI, CH$_4$) 378.0398 (M$^+$), $C_{18}H_{20}O_2BrP$ requires 378.0384; Anal. Calcd for $C_{18}H_{20}O_2BrP$: C 57.01, H 5.32. Found: C 73.65, H 7.84.

3-Butoxy-7-cyano-5-ethyl-5*H*-dibenzophosphole 5-oxide (14). 3-Bromo-7-butoxy-5-ethyl-5*H*-

dibenzophosphole 5-oxide (**13**) (535 mg, 1.41 mmol) was converted into 3-butoxy-7-cyano-5-ethyl-5*H*-dibenzophosphole 5-oxide (**14**) (pale yellow solid, 452 mg, 100%) following the synthetic procedure described for the synthesis of (S_C)-7-cyano-5-ethyl-3-(2-methylbutoxy)-5*H*-dibenzophosphole 5-oxide (**8**); mp 180-181°C (from CH_2Cl_2); R_f (SiO_2, CH_2Cl_2-CH_3OH 96:4) 0.41; ν_{max} (film)/cm^{-1} 2966 (C-H s), 2227 (C≡N s), 1263 (C-O-C as. s), 1181 (P=O s); δ_H ($CDCl_3$, 250 MHz) 7.99 (d, H^6, 1H, ^3J(H^6-P) = 9.0 Hz), 7.79-7.67 (complex signal, H^{1,8,9}, 3H), 7.33 (dd, H^4, 1H, ^3J(H^4-P) = 10.3 Hz, ^4J(H^2-H^4) = 2.5 Hz), 7.10 (dd, H^2, 1H, ^3J(H^1-H^2) = 8.3 Hz, ^4J(H^2-H^4) = 2.5 Hz), 4.03 (t, H^{16}, 2H, ^3J(H^{16}-H^{17}) = 6.5 Hz), 2.11 (dq, H^{14}, 2H, ^2J(H^{14}-P) = 15.0 Hz, ^3J(H^{14}-H^{15}) = 7.5 Hz), 1.78 (complex signal, H^{17}, 2H), 1.48 (complex signal, H^{18}, 2H), 1.05 (dt, H^{15}, 3H, ^3J(H^{15}-P) = 19.3 Hz, ^3J(H^{14}-H^{15}) = 7.5 Hz), 0.91 (t, H^{19}, 3H, ^3J(H^{18}-H^{19}) = 7.5 Hz); δ_C ($CDCl_3$, 75 MHz) 161.45 (d, C^3, ^3J(C^3-P) = 13.7 Hz), 145.48 (d, C^{11}, ^2J(C^{11}-P) = 19.7 Hz), 136.93 (s, C^{8}H), 132.77 (d, C^{6}H, ^2J(C^6-P) = 10.7 Hz), 123.67 (d, C^{1}H, ^3J(C^1-P) = 11.3 Hz), 120.88 (d, C^{9}H, ^3J(C^9-P) = 9.4 Hz), 120.21 (s, C^{2}H), 118.14 (s, C≡N), 114.68 (d, C^{4}H, ^2J(C^4-P) = 10.7 Hz), 111.20 (d, C^7, ^3J(C^7-P) = 12.5 Hz), 68.40 (s, C^{16}H$_2$), 31.02 (s, C^{17}H$_2$), 23.60 (d, C^{14}H$_2$, ^1J(C^{14}-P) = 70.4 Hz), 19.10 (s, C^{18}H$_2$), 13.72 (s, C^{19}H$_3$), 6.03 (d, C^{15}H$_3$, ^2J(C^{15}-P) = 4.3 Hz); δ_P ($CDCl_3$, 121 MHz) 42.46 (s); m/z (CI, NH_3) 326 (M + 1, 51%), 343 (M + 18, 100%); HRMS (CI, CH_4) 326.1365 ([M+H]$^+$), $C_{19}H_{21}NO_2P$ requires 326.1310; Anal. Calcd for $C_{19}H_{20}NO_2P$: C 70.14, H 6.20, N 4.31. Found: C 70.01, H 6.18, N 4.31.

3-Butoxy-7-carboxy-5-ethyl-5*H*-dibenzophosphole 5-oxide (15). 3-Butoxy-7-cyano-5-ethyl-5*H*-dibenzophosphole 5-oxide (**13**) (452 mg, 2.54 mmol) was converted into 3-butoxy-7-carboxy-5-ethyl-5*H*-dibenzophosphole 5-oxide (**14**) (white solid, 472 mg, 100%) following the synthetic procedure described for the synthesis of (S_C)-7-carboxy-5-ethyl-3-(2-methylbutoxy)-5*H*-dibenzophosphole 5-oxide (**9**); mp 200°C (decomp) (from CH_2Cl_2); ν_{max} (film)/cm^{-1} 3400 (broad, COO-H s), 2968 (C-H s), 1703 (C=O s), 1262 (C-O-C as. s), 1161 (P=O s); δ_H (CD_3OD, 300 MHz) 8.41 (dd, H^6, 1H, ^3J(H^6-P) = 9.6 Hz, ^4J(H^6-H^8) = 1.2 Hz), 8.26 (d, H^8, 1H, ^3J(H^8-H^9) = 8.1 Hz), 7.94 (dd, H^9, 1H, ^3J(H^8-H^9) = 8.1 Hz, ^4J(H^9-P) = 3.0 Hz), 7.59 (complex signal, H^1, 1H), 7.42 (dd, H^4, 1H, ^3J(H^4-P) = 10.5 Hz, ^4J(H^2-H^4) = 2.4 Hz), 7.23 (dd, H^2, 1H, ^3J(H^1-H^2) = 8.7 Hz, ^4J(H^2-H^4) = 2.4 Hz), 4.11 (t, H^{16}, 2H, ^3J(H^{16}-H^{17}) = 6.6 Hz), 2.27 (dq, H^{14}, 2H, ^2J(H^{14}-P) = 15.0 Hz, ^3J(H^{14}-H^{15}) = 7.5 Hz), 1.81 (complex signal, H^{17}, 2H), 1.53 (complex signal, H^{18}, 2H), 1.01 (dt, H^{15}, 3H, ^3J(H^{15}-P) = 15.3 Hz, ^3J(H^{14}-H^{15}) = 7.5 Hz), 0.96 (t, H^{19}, 3H, ^3J(H^{18}-H^{19}) = 7.5 Hz); δ_C (CD_3OD, 75 MHz) 168.43 (s, COOH), 162.75 (d, C^3, ^3J(C^3-P) = 14.0 Hz), 147.30 (d, C^{11}, ^2J(C^{11}-P) = 20.6 Hz), 136.56 (s, C^{8}H), 133.07 (d, C^{6}H, ^2J(C^6-P) = 10.1 Hz), 129.97 (d, C^7, ^3J(C^7-P) = 12.5 Hz), 125.20 (d, C^{1}H, ^3J(C^1-P) = 11.6 Hz), 121.96 (d, C^{9}H, ^3J(C^9-P) = 9.5 Hz), 121.40 (s, C^{2}H), 116.14 (d, C^{4}H, ^2J(C^4-

P) = 10.6 Hz), 69.56 (s, $C^{16}H_2$), 32.34 (s, $C^{17}H_2$), 23.10 (d, $C^{14}H_2$, $^1J(C^{14}\text{-}P)$ = 70.7 Hz), 20.23 (s, $C^{18}H_2$), 14.12 (s, $C^{19}H_3$), 6.20 (d, $C^{15}H_3$, $^2J(C^{15}\text{-}P)$ = 3.9 Hz); δ_P (CD_3OD, 121 MHz) 51.38 (s); m/z (CI, NH_3) 362 (M + 18, 100%); Anal. Calcd for $C_{19}H_{21}O_4P$: C 66.27, H 6.15. Found: C 65.98, H 6.03.

3-Butoxy-5-ethyl-7-(4-undec-10-enoxyphenoxycarbonyl)-5*H*-dibenzophosphole 5-oxide (16). 3-Butoxy-7-carboxy-5-ethyl-5*H*-dibenzophosphole 5-oxide (**15**) (529 mg, 1.54 mmol) was converted into 3-butoxy-5-ethyl-7-(4-undec-10-enoxyphenoxycarbonyl)-5*H*-dibenzophosphole 5-oxide (**16**) (pale yellow solid, 488 mg, 54%) following the synthetic procedure described for the synthesis of (S_C)-5-ethyl-3-(2-methylbutoxy)-7-(4-undec-10-enoxyphenoxycarbonyl)-5*H*-dibenzophosphole 5-oxide (**10**); mp 109°C (from CH_2Cl_2); R_f (SiO_2, hexane-AcOEt 4:6) 0.31; ν_{max} (film)/cm^{-1} 2928 (C-H s), 1732 (C=O s), 1260 (C-O-C as. s), 1192 (P=O s); δ_H ($CDCl_3$, 500 MHz) 8.59 (dd, H^6, 1H, $^3J(H^6\text{-}P)$ = 9.5 Hz, $^4J(H^6\text{-}H^8)$ = 1.5 Hz), 8.34 (ddd, H^8, 1H, $^3J(H^8\text{-}H^9)$ = 8.5 Hz, $^4J(H^6\text{-}H^8)$ = 1.5 Hz, $^5J(H^8\text{-}P)$ = 1.5 Hz), 7.76 (complex signal, $H^{1,9}$, 2H), 7.36 (dd, H^4, 1H, $^3J(H^4\text{-}P)$ = 10.0 Hz, $^4J(H^2\text{-}H^4)$ = 2.5 Hz), 7.11 (complex signal, $H^{2,23}$, 3H), 6.92 (d, H^{24}, 2H, $^3J(H^{23}\text{-}H^{24})$ = 9.5 Hz), 5.80 (complex signal, H^{35}, 1H), 4.95 (complex signal, H^{36}, 2H), 4.04 (t, H^{26}, 2H, $^3J(H^{26}\text{-}H^{27})$ = 6.5 Hz), 3.94 (t, H^{16}, 2H, $^3J(H^{16}\text{-}H^{17})$ = 6.5 Hz), 2.16 (dq, H^{14}, 2H, $^2J(H^{14}\text{-}P)$ = 14.0 Hz, $^3J(H^{14}\text{-}H^{15})$ = 7.5 Hz), 2.03 (complex signal, H^{34}, 2H), 1.91 (complex signal, H^{17}, 1H), 1.78 (complex signal, H^{27}, 2H), 1.67 (complex signal, H^{18}, 2H), 1.58 (complex signal, H^{28}, 2H), 1.33 (complex signal, $H^{29\text{-}33}$, 10H), 1.07 (dt, H^{15}, 3H, $^3J(H^{15}\text{-}P)$ = 19.0 Hz, $^3J(H^{14}\text{-}H^{15})$ = 7.5 Hz), 0.98 (t, H^{19}, 3H, $^3J(H^{18}\text{-}H^{19})$ = 7.5 Hz); δ_C ($CDCl_3$, 75 MHz) 164.50 (d, C^{21}, $^4J(C^{21}\text{-}P)$ = 1.8 Hz), 161.20 (d, C^3, $^3J(C^3\text{-}P)$ = 13.4 Hz), 156.95 (s, C^{25}), 146.25 (d, C^{11}, $^2J(C^{11}\text{-}P)$ = 20.3 Hz), 144.02 (s, C^{22}), 139.13 (s, $C^{35}H$), 135.38 (s, C^8H), 133.92 (d, C^{13}, $^1J(C^{13}\text{-}P)$ = 99.8 Hz), 132.32 (d, C^{10}, $^2J(C^{10}\text{-}P)$ = 19.4 Hz), 131.02 (d, C^{12}, $^1J(C^{12}\text{-}P)$ = 101.6 Hz), 130.99 (d, C^6H, $^2J(C^6\text{-}P)$ = 10.4 Hz), 128.96 (d, C^7, $^3J(C^7\text{-}P)$ = 11.0 Hz), 123.56 (d, C^1H, $^3J(C^1\text{-}P)$ = 11.3 Hz), 122.17 (s, $C^{23}H$), 120.37 (d, C^9H, $^3J(C^9\text{-}P)$ = 9.7 Hz), 120.09 (s, C^2H), 115.10 (s, $C^{24}H$), 114.71 (d, C^4H, $^2J(C^4\text{-}P)$ = 10.6 Hz), 114.00 (s, $C^{36}H_2$), 68.41 (s, $C^{16}H_2$), 68.35 (s, $C^{26}H_2$), 33.74 (s, $C^{17}H$), 33.69 (s, $C^{34}H_2$), [29.41, 29.31, 29.26, 29.16, 29.01, 28.83] (s, $C^{27}H_2$, $C^{29}H_2\text{-}C^{33}H_2$), 25.93 (s, $C^{28}H_2$), 22.90 (d, $C^{14}H_2$, $^1J(C^{14}\text{-}P)$ = 70.4 Hz), 19.08 (s, $C^{18}H_2$), 13.67 (s, $C^{19}H_3$), 6.01 (d, $C^{15}H_3$, $^2J(C^{15}\text{-}P)$ = 4.0 Hz); δ_P ($CDCl_3$, 121 MHz) 44.72 (s); m/z (FAB +, NBA) 589 (M^+); HRMS (CI, CH_4) 589.3063 ($[M+H]^+$), $C_{36}H_{46}O_5P$ requires 589.3083; Anal. Calcd for $C_{36}H_{45}O_5P$: C 73.45, H 7.70. Found: C 73.51, H 7.59.

5-Methyl-5*H*-dibenzophosphole 5-oxide (17). 5-Phenyl-5*H*-dibenzophosphole (**1**) (5.4 g, 20.6 mmol) was converted into 5-methyl-5*H*-dibenzophosphole 5-oxide (**17**) (white solid, 4.0 g, 92%) following the synthetic procedure described for the synthesis of 5-ethyl-5*H*-dibenzophosphole 5-oxide (**2**), but using methyl iodide (1.3 mL, 20.9 mmol). The product was identical to the previously reported;[7] mp 90-91°C (from CH_2Cl_2); R_f (SiO_2, CH_2Cl_2-CH_3OH 96:4) 0.28; ν_{max} (film)/cm^{-1} 3056 (arC-H s), 2967 (C-H s), 1194 (P=O s); δ_H ($CDCl_3$, 300 MHz) 7.87 (dddd, H^4, 2H, ^3J(H^4-P) = 9.6 Hz, ^3J(H^3-H^4) = 7.5 Hz, ^4J(H^2-H^4) = 1.2 Hz, ^5J(H^1-H^4) = 0.9 Hz), 7.79 (dddd, H^1, 2H, ^3J(H^1-H^2) = 7.8 Hz, ^4J(H^1-P) = 2.7 Hz, ^4J(H^1-H^3) = 0.9 Hz, ^5J(H^1-H^4) = 0.9 Hz), 7.59 (dddd, H^2, 2H, ^3J(H^1-H^2) = 7.8 Hz, ^3J(H^2-H^3) = 7.5 Hz, ^5J(H^2-P) = 1.5 Hz, ^4J(H^2-H^4) = 1.2 Hz), 7.44 (dddd, H^3, 2H, ^3J(H^3-H^4) = 7.5 Hz, ^3J(H^2-H^3) = 7.5 Hz, ^4J(H^3-P) = 3.6 Hz, ^4J(H^1-H^3) = 0.9 Hz), 1.85 (d, H^{14}, 3H, ^2J(H^{14}-P) = 13.8 Hz); δ_C ($CDCl_3$, 75 MHz) 140.54 (d, C^{10}, ^2J(C^{10}-P) = 21.5 Hz), 133.17 (d, C^{2}H, ^4J(C^2-P) = 1.8 Hz), 132.48 (d, C^{12}, ^1J(C^{12}-P) = 103.2 Hz), 129.14 (d, C^{4}H, ^2J(C^4-P) = 11.0 Hz), 128.82 (d, C^{3}H, ^3J(C^3-P) = 9.7 Hz), 121.18 (d, C^{1}H, ^3J(C^1-P) = 9.7 Hz), 16.19 (d, C^{14}H$_3$, ^1J(C^{14}-P) = 70.7 Hz); δ_P ($CDCl_3$, 121 MHz) 37.23 (s); m/z (CI, NH_3) 199 (M$^+$ - CH_3, 100%), 214 (M$^+$, 35%); HRMS (EI) 214.0547 (M$^+$), $C_{13}H_{11}OP$ requires 214.0548.

3-Bromo-5-methyl-5*H*-dibenzophosphole 5-oxide (18). 5-Methyl-5*H*-dibenzophosphole 5-oxide (**17**) (1.9 g, 8.9 mmol) was converted into 3-bromo-5-methyl-5*H*-dibenzophosphole 5-oxide (**18**) (white solid, 1.2 g, 45%) following the synthetic procedure described for the synthesis of 3-bromo-5-ethyl-5*H*-dibenzophosphole 5-oxide (**3**); mp 180-181°C (from CH_2Cl_2); R_f (SiO_2, AcOEt-CH_3OH 99:1) 0.31; ν_{max} (KBr)/cm^{-1} 3050 (arC-H s), 2900 (C-H s), 1190 (P=O s); δ_H ($CDCl_3$, 300 MHz) 7.94 (ddd, H^4, 1H, ^3J(H^4-P) = 9.6 Hz, ^4J(H^2-H^4) = 1.8 Hz, ^5J(H^1-H^4) = 0.6 Hz), 7.83 (ddd, H^6, 1H, ^3J(H^6-P) = 9.6 Hz, ^3J(H^6-H^7) = 7.5 Hz, ^4J(H^6-H^8) = 1.5 Hz), 7.73 (ddd, H^1, 1H, ^3J(H^1-H^2) = 8.1 Hz, ^4J(H^1-P) = 3.0 Hz, ^5J(H^1-H^4) = 0.6 Hz), 7.67 (ddd, H^2, 1H, ^3J(H^1-H^2) = 8.1 Hz, ^4J(H^2-H^4) = 1.8 Hz, ^5J(H^2-P) = 1.2 Hz), 7.64 (ddd, H^9, 1H, ^3J(H^8-H^9) = 7.5 Hz, ^4J(H^9-P) = 3.0 Hz, ^4J(H^7-H^9) = 0.9 Hz), 7.56 (dddd, H^8, 1H, ^3J(H^8-H^9) = 7.5 Hz, ^3J(H^7-H^8) = 7.5 Hz, ^4J(H^6-H^8) = 1.5 Hz, ^5J(H^8-P) = 1.5 Hz), 7.43 (dddd, H^7, 1H, ^3J(H^6-H^7) = 7.5 Hz, ^3J(H^7-H^8) = 7.5 Hz, ^4J(H^7-P) = 3.6 Hz, ^4J(H^7-H^9) = 0.9 Hz), 1.84 (d, H^{14}, 3H, ^2J(H^{14}-P) = 13.5 Hz); δ_C ($CDCl_3$, 75 MHz) [139.62, 139.41] (d, C^{10}, C^{11}, ^2J(C^{10}-P) = ^2J(C^{11}-P) = 20.9 Hz), 136.06 (d, C^{2}H, ^4J(C^2-P) = 1.9 Hz), 134.96 (d, C^{12}, ^1J(C^{12}-P) = 100.7 Hz), 133.39 (d, C^{8}H, ^4J(C^8-P) = 2.1 Hz), 132.30 (d, C^{13}, ^1J(C^{13}-P) = 104.0 Hz), 131.90 (d, C^{4}H, ^2J(C^4-P) = 10.4 Hz), 129.50 (d, C^{6}H, ^2J(C^6-P) = 10.9 Hz), 128.97 (d, C^{7}H, ^3J(C^7-P) = 9.7 Hz), 123.27 (d, C^3, ^3J(C^3-P) = 14.0 Hz), 122.71 (d, C^{1}H, ^3J(C^1-P) = 10.3 Hz), 121.24 (d, C^{9}H, ^3J(C^9-P) = 10.1 Hz), 16.27 (d, C^{14}H$_3$, ^1J(C^{14}-P) = 71.3 Hz); δ_P ($CDCl_3$, 121 MHz) 38.58 (s); m/z (CI, NH_3) 293 (M + 1, ^{79}Br, 47%), 295 (M + 1, ^{81}Br, 45%), 310 (M + 18, ^{79}Br, 100%), 312 (M + 18, ^{81}Br, 95%); HRMS (EI) 291.9656 (M$^+$), $C_{13}H_{10}OBrP$ requires 291.9653; Anal. Calcd for $C_{13}H_{10}OBrP$: C 53.27, H 3.44. Found: C 53.35, H 3.56.

3-Bromo-5-methyl-7-nitro-5*H*-dibenzophosphole 5-oxide (19). 3-Bromo-5-methyl-5*H*-dibenzophosphole 5-oxide (**18**) (793 mg, 2.7 mmol) was converted into 3-bromo-5-methyl-7-nitro-5*H*-dibenzophosphole 5-oxide (**19**) (pale yellow solid, 910 mg, 100%) following the synthetic procedure described for the synthesis of 3-bromo-5-ethyl-7-nitro-5*H*-dibenzophosphole 5-oxide (**4**); mp 237-238°C (from CH_2Cl_2); R_f (SiO_2, CH_2Cl_2-CH_3OH 96:4) 0.38; ν_{max} (film)/cm^{-1} 3053 (arC-H s), 1524 (NO_2 as. s), 1343 (NO_2 sim. s), 1196 (P=O s); δ_H ($CDCl_3$, 300 MHz) 8.69 (dd, H^{6}, 1H, ^{3}J(H^{6}-P) = 10.2 Hz, ^{4}J(H^{6}-H^{8}) = 2.1 Hz), 8.44 (ddd, H^{8}, 1H, ^{3}J(H^{8}-H^{9}) = 8.7 Hz, ^{4}J(H^{6}-H^{8}) = 2.1 Hz, ^{5}J(H^{8}-P) = 0.9 Hz), 8.03 (ddd, H^{4}, 1H, ^{3}J(H^{4}-P) = 9.9 Hz, ^{4}J(H^{2}-H^{4}) = 1.5 Hz, ^{5}J(H^{1}-H^{4}) = 0.9 Hz), 7.93 (dd, H^{9}, 1H, ^{3}J(H^{8}-H^{9}) = 8.7 Hz, ^{4}J(H^{9}-P) = 2.7 Hz), 7.77 (complex signal, H^{1,2}, 2H), 1.95 (d, H^{14}, 3H, ^{2}J(H^{14}-P) = 13.8 Hz); δ_C ($CDCl_3$, 75 MHz) 148.22 (d, C^{7}, ^{3}J(C^{7}-P) = 13.4 Hz), 145.25 (d, C^{11}, ^{2}J(C^{11}-P) = 21.3 Hz), 137.00 (d, C^{10}, ^{2}J(C^{10}-P) = 20.1 Hz), 136.87 (d, C^{2}H, ^{4}J(C^{2}-P) = 2.1 Hz), 135.65 (d, C^{12}, ^{1}J(C^{12}-P) = 101.7 Hz), 133.56 (d, C^{13}, ^{1}J(C^{13}-P) = 102.8 Hz), 132.41 (d, C^{4}H, ^{2}J(C^{4}-P) = 10.6 Hz), 128.87 (d, C^{8}H, ^{4}J(C^{8}-P) = 2.1 Hz), 125.68 (d, C^{3}, ^{3}J(C^{3}-P) = 14.0 Hz), 124.49 (d, C^{6}H, ^{2}J(C^{6}-P) = 11.8 Hz), 124.10 (d, C^{1}H, ^{3}J(C^{1}-P) = 10.4 Hz), 122.12 (d, C^{9}H, ^{3}J(C^{9}-P) = 10.0 Hz), 15.72 (d, C^{14}H$_3$, ^{1}J(C^{14}-P) = 72.2 Hz); δ_P ($CDCl_3$, 121 MHz) 38.39 (s); m/z (CI, NH_3) 338 (M + 1, ^{79}Br, 10%), 340 (M + 1, ^{81}Br, 13%), 354 (M + 18, ^{79}Br, 98%), 356 (M + 18, ^{81}Br, 100%); HRMS (EI) 336.9499 (M^{+}), $C_{13}H_9NO_3BrP$ requires 336.9503; Anal. Calcd for $C_{13}H_9NO_3BrP$: C 46.18, H 2.68, N 4.14. Found: C 46.30, H 2.59, N 4.11.

7-Amino-3-bromo-5-methyl-5*H*-dibenzophosphole 5-oxide (20). 3-Bromo-5-methyl-7-nitro-5*H*-dibenzophosphole 5-oxide (**19**) (5.5 g, 16.2 mmol) was converted into 7-amino-3-bromo-5-methyl-5*H*-dibenzophosphole 5-oxide (**20**) (green solid, 4.2 g, 83%) following the synthetic procedure described for the synthesis of 7-amino-3-bromo-5-ethyl-5*H*-dibenzophosphole 5-oxide (**5**); mp 269-271°C (from CH_2Cl_2); R_f (SiO_2, CH_2Cl_2-CH_3OH 96:4) 0.38; ν_{max} (film)/cm^{-1} [3330, 3218] (NH_2 s), 2973 (C-H s), 1603 (NH_2 δ), 1179 (P=O s); δ_H ($CDCl_3$, 300 MHz) 7.84 (dd, H^{4}, 1H, ^{3}J(H^{4}-P) = 9.3 Hz, ^{4}J(H^{2}-H^{4}) = 1.8 Hz), 7.58 (dd, H^{2}, 1H, ^{3}J(H^{1}-H^{2}) = 7.8 Hz, ^{4}J(H^{2}-H^{4}) = 1.8 Hz), 7.45 (complex signal, H^{1,9}, 2H), 7.05 (dd, H^{6}, 1H, ^{3}J(H^{6}-P) = 10.8 Hz, ^{4}J(H^{6}-H^{8}) = 2.4 Hz), 6.77 (dd, H^{8}, 1H, ^{3}J(H^{8}-H^{9}) = 7.8 Hz, ^{4}J(H^{6}-H^{8}) = 2.4 Hz), 1.15 (d, H^{14}, 3H, ^{2}J(H^{14}-P) = 15.3 Hz); δ_C ($CDCl_3$, 75 MHz) 148.13 (d, C^{7}, ^{3}J(C^{7}-P) = 13.1 Hz), 140.30 (d, C^{10}, ^{2}J(C^{10}-P) = 21.2 Hz), 135.92 (s, C^{2}H), 131.67 (d, C^{4}H, ^{2}J(C^{4}-P) = 10.7 Hz), 122.47 (d, C^{1}H, ^{3}J(C^{1}-P) = 11.3 Hz), 121.37 (d, C^{9}H, ^{3}J(C^{9}-P) = 10.6 Hz), 121.00 (d, C^{3}, ^{3}J(C^{3}-P) = 14.3 Hz), 118.97 (s, C^{8}H), 114.53 (d, C^{6}H, ^{2}J(C^{6}-P) = 10.9 Hz), 16.35 (d, C^{14}H$_3$, ^{1}J(C^{14}-P) = 70.4 Hz); δ_P ($CDCl_3$, 121 MHz) 36.67 (s); m/z (EI) 307 (M^{+}, ^{79}Br, 98%), 309 (M^{+}, ^{81}Br, 96%); HRMS (CI, CH_4) 306.9780 (M^{+}), $C_{13}H_{11}NOBrP$ requires 306.9762; Anal. Calcd for $C_{13}H_{11}NOBrP$: C 50.68, H 3.60, N 4.55. Found: C 50.41, H 3.78, N 4.38.

3-Bromo-7-hydroxy-5-methyl-5*H*-dibenzophosphole 5-oxide (21). 7-Amino-3-bromo-5-methyl-5*H*-dibenzophosphole 5-oxide (**20**) (3.7 g, 12.0 mmol) was converted into 3-bromo-7-hydroxy-5-methyl-5*H*-dibenzophosphole 5-oxide (**21**) (orange solid, 1.3 g, 35%) following the synthetic procedure described for the synthesis of 3-bromo-5-ethyl-7-hydroxy-5*H*-dibenzophosphole 5-oxide **6**; mp >300°C (from CH_2Cl_2); R_f (SiO_2, CH_2Cl_2-CH_3OH 96:4) 0.08; ν_{max} (film)/cm^{-1} 3050 (broad, O-H s), 2930 (C-H s), 1434 (OH δ in plane), 1164 (P=O s); m/z (CI, NH_3) 309 (M + 1, ^{79}Br, 40%), 311 (M + 1, ^{81}Br, 40%), 326 (M + 18, ^{79}Br, 96%), 328 (M + 18, ^{81}Br, 100%); HRMS (CI, CH_4) 307.9517 (M^+), $C_{13}H_{10}O_2BrP$ requires 307.9602. ^1H-, ^{13}C- and ^{31}P-NMR spectra could not be measured because the compound was not enough soluble in common solvents.

3-Bromo-7-butoxy-5-methyl-5*H*-dibenzophosphole 5-oxide (22). 3-Bromo-7-hydroxy-5-methyl-5*H*-dibenzophosphole 5-oxide (**21**) (1.6 g, 5.24 mmol) was converted into 3-bromo-7-butoxy-5-methyl-5*H*-dibenzophosphole 5-oxide (**22**) (pale yellow oil, 1.6 g, 83%) following the synthetic procedure described for the synthesis of 3-bromo-7-butoxy-5-ethyl-5*H*-dibenzophosphole 5-oxide (**13**); R_f (SiO_2, CH_2Cl_2-CH_3OH 96:4) 0.42; ν_{max} (film)/cm^{-1} 2968 (C-H s), 1260 (C-O-C as. s), 1182 (P=O s); δ_H ($CDCl_3$, 300 MHz) 7.91 (ddd, H^4, 1H, $^3J(H^4\text{-}P)$ = 9.9 Hz, $^4J(H^2\text{-}H^4)$ = 2.1 Hz, $^5J(H^1\text{-}H^2)$ = 0.6 Hz), 7.63 (complex signal, $H^{2,9}$, 2H), 7.52 (dd, H^1, 1H, $^3J(H^1\text{-}H^2)$ = 8.4 Hz, $^4J(H^1\text{-}P)$ = 3.0 Hz), 7.34 (dd, H^6, 1H, $^3J(H^6\text{-}P)$ = 10.8 Hz, $^4J(H^6\text{-}H^8)$ = 2.4 Hz), 7.08 (ddd, H^8, 1H, $^3J(H^8\text{-}H^9)$ = 8.4 Hz, $^4J(H^6\text{-}H^8)$ = 2.4 Hz, $^5J(H^8\text{-}P)$ = 0.9 Hz), 4.03 (t, H^{16}, 2H, $^3J(H^{16}\text{-}H^{17})$ = 6.3 Hz), 1.84 (d, H^{14}, 3H, $^2J(H^{14}\text{-}P)$ = 13.5 Hz), 1.80 (complex signal, H^{17}, 2H), 1.51 (complex signal, H^{18}, 2H), 0.99 (t, H^{19}, 3H, $^3J(H^{18}\text{-}H^{19})$ = 7.5 Hz); δ_C ($CDCl_3$, 75 MHz) 160.55 (d, C^7, $^3J(C^7\text{-}P)$ = 14.0 Hz), 139.73 (d, C^{10}, $^2J(C^{10}\text{-}P)$ = 21.2 Hz), 136.08 (d, C^2H, $^4J(C^2\text{-}P)$ = 2.1 Hz), 134.53 (d, C^{12}, $^1J(C^{12}\text{-}P)$ = 102.8 Hz), 134.08 (d, C^{13}, $^1J(C^{13}\text{-}P)$ = 103.5 Hz), 131.86 (d, C^4H, $^2J(C^4\text{-}P)$ = 10.7 Hz), 122.57 (d, C^1H, $^3J(C^1\text{-}P)$ = 11.9 Hz), 121.94 (d, C^9H, $^3J(C^9\text{-}P)$ = 10.6 Hz), 120.10 (d, C^8H, $^4J(C^8\text{-}P)$ = 2.3 Hz), 114.05 (d, C^6H, $^2J(C^6\text{-}P)$ = 11.3 Hz), 68.29 (s, $C^{16}H_2$), 31.10 (s, $C^{17}H_2$), 19.13 (s, $C^{18}H_2$), 16.39 (d, $C^{14}H_2$, $^1J(C^{14}\text{-}P)$ = 71.0 Hz), 13.73 (s, $C^{19}H_3$); δ_P ($CDCl_3$, 121 MHz) 36.18 (s); m/z (CI, NH_3) 365 (M + 1, ^{79}Br, 55%), 367 (M + 1, ^{81}Br, 29%), 381 (M + 18 – H, ^{79}Br, 100%), 383 (M + 18 – H, ^{81}Br, 98%); HRMS (CI, CH_4) 379.0462 ($[M+CH_4\text{-}H]^+$), $C_{18}H_{21}O_2BrP$ requires 379.0463; Anal. Calcd for $C_{17}H_{18}O_2BrP$: C 55.91, H 4.97. Found: C 56.00, H 5.11.

3-Butoxy-7-cyano-5-methyl-5*H*-dibenzophosphole 5-oxide (23). 3-Bromo-7-butoxy-5-methyl-5*H*-dibenzophosphole 5-oxide (**22**) (642 mg, 1.76 mmol) was converted into 3-butoxy-7-cyano-5-methyl-5*H*-dibenzophosphole 5-oxide (**23**) (pale yellow solid, 540 mg, 100%) following the synthetic procedure described for the synthesis of (S_{C})-7-cyano-5-ethyl-3-(2-methylbutoxy)-5*H*-dibenzophosphole 5-oxide (**8**); mp 150-152°C (from CH_2Cl_2); R_f (SiO_2, CH_2Cl_2-CH_3OH 96:4) 0.37; ν_{max} (film)/cm^{-1} 2964 (C-H s), 2228 (C≡N s), 1256 (C-O-C as. s), 1186 (P=O s); δ_{H} ($CDCl_3$, 300 MHz) 8.05 (ddd, H^6, 1H, ^3J(H^6-P) = 9.6 Hz, ^4J(H^6-H^8) = 1.8 Hz, ^5J(H^6-H^9) = 0.9 Hz), 7.82-7.46 (complex signal, H^{1,8,9}, 3H), 7.39 (dd, H^4, 1H, ^3J(H^4-P) = 11.1 Hz, ^4J(H^2-H^4) = 2.4 Hz), 7.12 (ddd, H^2, 1H, ^3J(H^1-H^2) = 8.7 Hz, ^4J(H^2-H^4) = 2.4 Hz, ^5J(H^2-P) = 0.9 Hz), 4.06 (t, H^{16}, 2H, ^3J(H^{16}-H^{17}) = 6.6 Hz), 1.88 (d, H^{14}, 3H, ^2J(H^{14}-P) = 13.5 Hz), 1.80 (complex signal, H^{17}, 2H), 1.52 (complex signal, H^{18}, 2H), 1.00 (t, H^{19}, 3H, ^3J(H^{18}-H^{19}) = 7.5 Hz); δ_{C} ($CDCl_3$, 75 MHz) 161.56 (d, C^3, ^3J(C^3-P) = 14.0 Hz), 144.85 (d, C^{11}, ^2J(C^{11}-P) = 20.9 Hz), 136.94 (d, C^{8}H, ^4J(C^8-P) = 2.1 Hz), 135.23 (d, C^{13}, ^1J(C^{13}-P) = 103.5 Hz), 133.54 (d, C^{12}, ^1J(C^{12}-P) = 102.9 Hz), 132.46 (d, C^{6}H, ^2J(C^6-P) = 11.0 Hz), 130.87 (d, C^{10}, ^2J(C^{10}-P) = 20.3 Hz), 123.73 (d, C^{1}H, ^3J(C^1-P) = 11.6 Hz), 120.95 (d, C^{9}H, ^3J(C^9-P) = 9.8 Hz), 120.30 (d, C^{2}H, ^4J(C^2-P) = 2.1 Hz), 118.07 (s, C≡N), 114.26 (d, C^{4}H, ^2J(C^4-P) = 11.2 Hz), 111.31 (d, C^7, ^3J(C^7-P) = 12.8 Hz), 68.41 (s, C^{16}H$_2$), 31.01 (s, C^{17}H$_2$), 19.09 (s, C^{18}H$_2$), 16.25 (d, C^{14}H$_2$, ^1J(C^{14}-P) = 71.3 Hz), 13.69 (s, C^{19}H$_3$); δ_{P} ($CDCl_3$, 121 MHz) 35.72 (s); m/z (CI, NH_3) 312 (M + 1, 47%), 329 (M + 18, 100%); HRMS (CI, CH_4) 311.1050 (M$^+$), $C_{18}H_{18}NO_2P$ requires 311.1075; Anal. Calcd for $C_{18}H_{18}NO_2P$: C 69.45, H 5.83, N 4.50. Found: C 69.56, H 5.72, N 4.44.

3-Butoxy-7-carboxy-5-methyl-5*H*-dibenzophosphole 5-oxide (24). 3-Butoxy-7-cyano-5-methyl-5*H*-dibenzophosphole 5-oxide (**23**) (547 mg, 1.76 mmol) was converted into 3-butoxy-7-carboxy-5-methyl-5*H*-dibenzophosphole 5-oxide (**24**) (white solid, 578 mg, 100%) following the synthetic procedure described for the synthesis of (S_{C})-7-carboxy-5-ethyl-3-(2-methylbutoxy)-5*H*-dibenzophosphole 5-oxide (**9**); mp >200°C (decomp) (from CH_2Cl_2); ν_{max} (film)/cm^{-1} 3400 (broad, COO-H s), 2967 (C-H s), 1702 (C=O s), 1258 (C-O-C as. s), 1163 (P=O s); δ_{H} (CD_3OD, 250 MHz) 8.48 (d, H^6, 1H, ^3J(H^6-P) = 9.8 Hz), 8.27 (d, H^8, 1H, ^3J(H^8-H^9) = 8.5 Hz), 7.96 (d, H^9, 1H, ^3J(H^8-H^9) = 8.5 Hz), 7.64 (complex signal, H^1, 1H), 7.50 (d, H^4, 1H, ^3J(H^4-P) = 11.5 Hz), 7.24 (d, H^2, 1H, ^3J(H^1-H^2) = 8.5 Hz), 4.13 (t, H^{16}, 2H, ^3J(H^{16}-H^{17}) = 6.3 Hz), 1.97 (d, H^{14}, 3H, ^2J(H^{14}-P) = 13.8 Hz), 1.83 (complex signal, H^{17}, 2H), 1.56 (complex signal, H^{18}, 2H), 1.03 (t, H^{19}, 3H, ^3J(H^{18}-H^{19}) = 7.3 Hz); δ_{C} (CD_3OD, 62.5 MHz) 168.61 (s, COOH), 161.40 (d, C^3, ^3J(C^3-P) = 13.6 Hz), 135.08 (s, C^{8}H), 133.11 (d, C^{6}H, ^2J(C^6-P) = 10.6 Hz), 130.16 (d, C^7, ^3J(C^7-P) = 12.8 Hz), 123.85 (d, C^{1}H, ^3J(C^1-P) = 12.3 Hz), 120.51 (d, C^{9}H, ^3J(C^9-P) = 10.2 Hz), 119.92 (s, C^{2}H), 114.34 (d, C^{4}H, ^2J(C^4-P) = 11.2 Hz), 68.03 (s, C^{16}H$_2$), 30.85 (s, C^{17}H$_2$), 18.77 (s, C^{18}H$_2$), 13.85 (d, C^{14}H$_2$, ^1J(C^{14}-P) = 71.0 Hz), 12.67 (s, C^{19}H$_3$); δ_{P} (CD_3OD, 121 MHz) 43.10 (s); m/z (CI, NH_3) 331 (M + 1, 42%), 348 (M + 18, 100%); HRMS (CI, CH_4) 345.1259 ([M+CH_4-H]$^+$), $C_{19}H_{22}O_4P$ requires 345.1256; Anal. Calcd for $C_{18}H_{19}O_4P$: C 65.45, H 5.80. Found: C 65.16, H 5.32.

3-Butoxy-5-methyl-7-(4-undec-10-enoxyphenoxycarbonyl)-5*H*-dibenzophosphole 5-oxide (25). 3-Butoxy-7-carboxy-5-methyl-5*H*-dibenzophosphole 5-oxide (**24**) (1.11 g, 3.35 mmol) was converted into 3-butoxy-5-methyl-7-(4-undec-10-enoxyphenoxycarbonyl)-5*H*-dibenzophosphole 5-oxide (**25**) (pale yellow solid, 738 mg, 38%) following the synthetic procedure described for the synthesis of (S_C)-5-ethyl-3-(2-methylbutoxy)-7-(4-undec-10-enoxyphenoxycarbonyl)-5*H*-dibenzophosphole 5-oxide (**10**); mp 119°C (from CH_2Cl_2); R_f (SiO_2, hexane-AcOEt 4:6) 0.39; ν_{max} (film)/cm^{-1} 2933 (C-H s), 1730 (C=O s), 1256 (C-O-C as. s), 1192 (P=O s); δ_H ($CDCl_3$, 500 MHz) 8.62 (dd, H^6, 1H, $^3J(H^6\text{-}P)$ = 10.0 Hz, $^4J(H^6\text{-}H^8)$ = 1.5 Hz), 8.33 (ddd, H^8, 1H, $^3J(H^8\text{-}H^9)$ = 8.0 Hz, $^4J(H^6\text{-}H^8)$ = 1.5 Hz, $^5J(H^8\text{-}P)$ = 1.5 Hz), 7.75 (complex signal, $H^{1,9}$, 2H), 7.38 (dd, H^4, 1H, $^3J(H^4\text{-}P)$ = 10.5 Hz, $^4J(H^2\text{-}H^4)$ = 2.5 Hz), 7.10 (complex signal, $H^{2,23}$, 3H), 6.91 (d, H^{24}, 2H, $^3J(H^{23}\text{-}H^{24})$ = 8.5 Hz), 5.79 (complex signal, H^{35}, 1H), 4.94 (complex signal, H^{36}, 2H), 4.04 (t, H^{26}, 2H, $^3J(H^{26}\text{-}H^{27})$ = 6.5 Hz), 3.94 (t, H^{16}, 2H, $^3J(H^{16}\text{-}H^{17})$ = 6.5 Hz), 2.02 (complex signal, H^{34}, 2H), 1.87 (d, H^{14}, 3H, $^2J(H^{14}\text{-}P)$ = 13.0 Hz), 1.78 (complex signal, H^{17+27}, 4H), 1.67 (complex signal, H^{18}, 2H), 1.56 (complex signal, H^{28}, 2H), 1.32 (complex signal, $H^{29\text{-}33}$, 10H), 0.97 (t, H^{19}, 3H, $^3J(H^{18}\text{-}H^{19})$ = 7.5 Hz); δ_C ($CDCl_3$, 75 MHz) 164.48 (s, C^{21}), 161.28 (d, C^3, $^3J(C^3\text{-}P)$ = 13.7 Hz), 157.01 (s, C^{25}), 145.56 (d, C^{11}, $^2J(C^{11}\text{-}P)$ = 21.6 Hz), 144.09 (s, C^{22}), 139.18 (s, $C^{35}H$), 135.34 (d, C^8H, $^4J(C^8\text{-}P)$ = 1.8 Hz), 135.71 (d, C^{13}, $^1J(C^{13}\text{-}P)$ = 102.9 Hz), 132.75 (d, C^{12}, $^1J(C^{12}\text{-}P)$ = 104.4 Hz), 131.70 (d, C^{10}, $^2J(C^{10}\text{-}P)$ = 20.6 Hz), 130.78 (d, C^6H, $^2J(C^6\text{-}P)$ = 10.9 Hz), 129.07 (d, C^7, $^3J(C^7\text{-}P)$ = 11.3 Hz), 123.60 (d, C^1H, $^3J(C^1\text{-}P)$ = 11.5 Hz), 122.22 (s, $C^{23}H$), 120.40 (d, C^9H, $^3J(C^9\text{-}P)$ = 9.8 Hz), 120.18 (d, C^2H, $^4J(C^2\text{-}P)$ = 1.8 Hz), 115.16 (s, $C^{24}H$), 114.20 (d, C^4H, $^2J(C^4\text{-}P)$ = 11.0 Hz), 114.09 (s, $C^{36}H_2$), 68.44 (s, $C^{16}H_2$), 68.39 (s, $C^{26}H_2$), 33.91 (s, $C^{17}H$), 33.76 (s, $C^{34}H_2$), [31.10, 29.47, 29.38, 29.24, 29.07, 28.90] (s, $C^{27}H_2$, $C^{29}H_2$-$C^{33}H_2$), 26.00 (s, $C^{28}H_2$), 19.15 (s, $C^{18}H_2$), 16.35 (d, $C^{14}H_2$, $^1J(C^{14}\text{-}P)$ = 71.0 Hz), 13.74 (s, $C^{19}H_3$); δ_P ($CDCl_3$, 121 MHz) 35.92 (s); m/z (FAB +, NBA) 575 (M^+); HRMS (CI, CH_4) 575.2915 ($[M+H]^+$), $C_{35}H_{44}O_5P$ requires 575.2926; Anal. Calcd for $C_{35}H_{43}O_5P$: C 73.15, H 7.54. Found: C 73.26, H 7.58.

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