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# Enantiomeric resolution and determination of the absolute configuration of dibenzophosphole 5-oxides

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**Abstract**—The resolution of asymmetrically substituted dibenzophospholes via chromatographic separation of their cyclopalladium derivatives is described for the first time. The absolute configuration of the phosphorus atom was determined by X-ray crystallographic analysis in one case. A general NMR criterion for the complete determination of the configuration of this group of products is proposed. The enantiomeric excess of the resolved compounds was determined by NMR Eu(III) chemical displacement experiments and by HPLC using a chiral stationary phase. © 2001 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

Liquid crystals have been synthesized in recent years mainly because successful applications of liquid crystals have been developed, particularly in the area of electro-optical displays.[1] In this field, chiral nematic and smectic liquid crystals became the most important source of structures which have technological applications.

Our research group has worked on the synthesis of some chiral molecules in order to generate chiral liquid crystal macromolecular systems with ferroelectric properties (chiral smectic liquid crystals). It is known[2] that the introduction of a chiral group near the rigid core of the mesogene is directly related to higher spontaneous polarizability in these systems, and then with an improvement of their ferroelectric physical properties. As in previous studies on carbazole systems[3,4] we synthesized a similar structure derived from the dibenzophosphole **1c** with a stereogenic phosphorus atom in the rigid planar core.

From this synthesis we obtained a 1:1 mixture of two diastereomers, with different configuration on the phosphorus atom. The diastereomeric mixture of **1c** showed nematic liquid crystalline behaviour, and therefore chiral mesophases could be seen for the pure diastereomers (*S*,*S*)-**1c** and (*R*,*S*)-**1c**. The ($S_P$) and ($R_P$) diastereomers could not be separated directly by physical methods, so we had to find a new resolution method for this class of compounds. The literature only gave a resolution method of dibenzophospholes based on the synthesis of diastereomeric amides from a pure enantiomeric amine and racemic dibenzophospholes containing a carboxylic acid function,[5] and the separation was achieved by recrystallization. However, the most attractive resolution method for our system needs to be generally applicable for substituted dibenzophospholes and not just to dibenzophospholes bearing a carboxylic acid function. Therefore, we tried to find a new procedure, of general applicability, to resolve optically active dibenzophosphole 5-oxides.

## 2. Results and discussion

Dimeric cyclopalladium compounds react readily with a wide range of Lewis bases to afford monomeric complexes of formulae [Pd(C-N)ClL] or [Pd(C-N)$ClL_2$]. This simple reaction, using enantiomerically pure cyclopalladium dimers, is used for the resolution[6–19] and determination of the enantiomeric excess[20–23] of Lewis bases such as phosphines and amines. In addition, phosphine oxides are reduced to phosphines with trichlorosilane.[24] With these facts in mind we used the following procedure to resolve the new dibenzophosphole 5-oxides: the first step was the trichlorosilane reduction of these oxides (Scheme 1). Reaction of the

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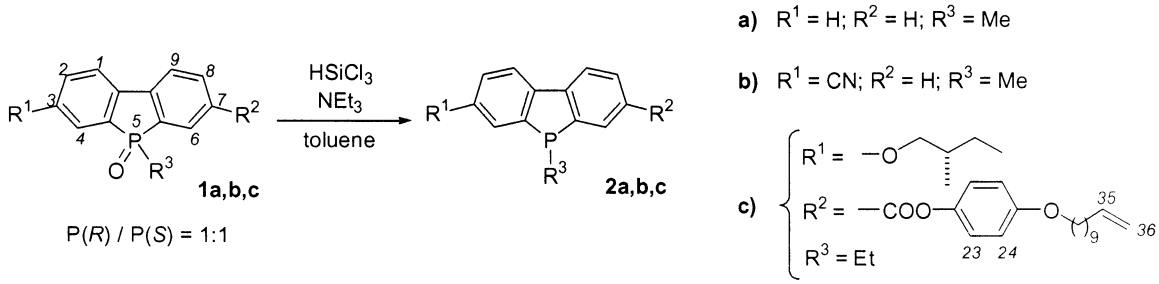
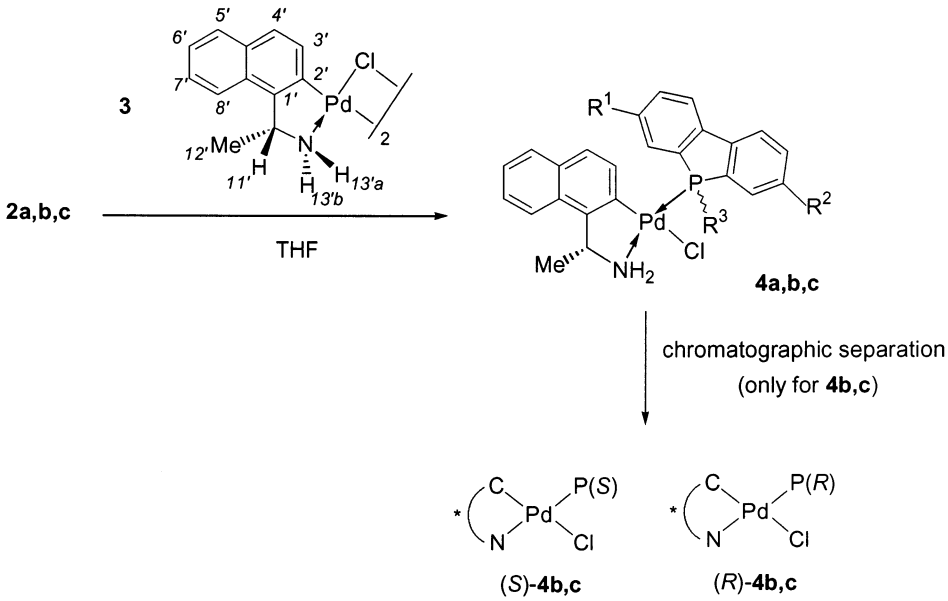



**Scheme 1.**

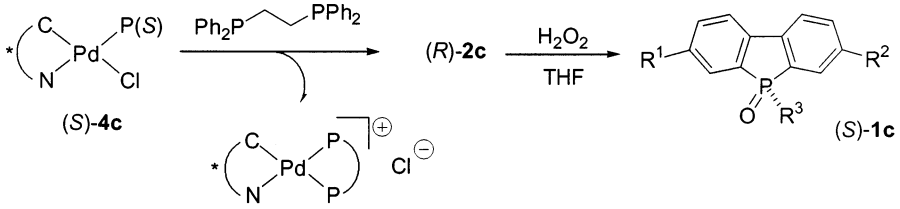
phosphines obtained with optically active cyclopalladium compounds then gave a mixture of diastereomers which were separated by column chromatography (Scheme 2); the third step was to decoordinate the dibenzophospholes by the reaction of the pure diastereomers with 1,2-bis(diphenylphosphino)ethane (dppe) and the last step of the resolution process was to oxidize the enantiomerically pure ligands using hydrogen peroxide (Scheme 3).

Cyclopalladium complexes derived from 1-(1-naphthyl)ethylamine and *N*,*N*-dimethyl-1-(1-(naphthyl)-ethylamine are the best resolving agents for the resolution of Lewis bases.[6] Their efficiency has been related to the locked asymmetric envelope conformation of the metallacycle, due to the methyl substituent of the stereogenic carbon adopting an axial disposition, which avoids the unfavourable interaction with naphthylic C(8′)H (see Scheme 2).[25–30] In this study we used the cyclopalladium derivative of (*R*)-(+)-1-(1-(naphthyl)-ethylamine as the resolving agent.

The enantiomerically pure cyclopalladium binuclear compound **3** was obtained from the optically active amine as reported.[31] Reaction of dimer **3** with the dibenzophosphole **2a** gave the mononuclear complex




**Scheme 2.** (Stereochemical descriptors refer only to the phosphorus atom.)




**Scheme 3.** (Stereochemical descriptors refer only to the phosphorus atom.)

[PdCl(C-N)(P*)] **4a** (see Scheme 2). The high-field shift of the aromatic protons of the metallated naphthyl group in **4a** compared with the aromatic protons of the phosphine indicates the *cis* disposition of the phosphorus atom relative to the metallated carbon atom.[32] This arrangement is usual in cyclopalladium compounds containing phosphines: the destabilizing effect of two soft ligands in mutual *trans* positions has been called antisymbiosis,[33–35] and recently the term transphobia has been proposed to describe the difficulty of coordinating mutually *trans* phosphine and aryl ligands in palladium complexes.[36,37]

The protons of the two aromatic rings of the dibenzophosphole appear at different $\delta$ values in compound **4a** in spite of the symmetry of the free phosphine. This can only be explained by the relative orientation of the plane determined by the naphthyl group and the phenyl groups of the dibenzophosphole ligand (see the geometry of related compound (*R*,*S*)-**4b** in Fig. 1). As a consequence of this arrangement, the shielding effects of the two aromatic rings of the phosphole by the π-system of the naphthyl group are very different, and the two equivalent protons in the free phosphine appear with different $\delta$ values in cyclopalladium compound **4a**. For example, of the two C(4)H protons (see Scheme 1) one is seen at 8.22 ppm, and the other is seen in the complex signal between 7.62 and 7.12 ppm, showing a difference in $\delta$ values of >0.6 ppm. The C(1)H protons give signals at 7.94 and 7.91 ppm, as two independent doublets. The $^{13}$C NMR spectra can be easily assigned using $^{13}$C–$^{31}$P coupling constants, and therefore HSQC bidimensional $^{1}$H–$^{13}$C heterocorrelation allows the total assignation of the $^{1}$H NMR spectra (see Section 3).

The reaction of dimer **3** with the dibenzophosphole **2b** afforded the mononuclear complex [PdCl(C-N)(P*)] **4b** (see Scheme 2) as a 1:1 mixture of diastereomers, (*R*,*S*)-**4b** and (*R*,*R*)-**4b**. $^{1}$H NMR analysis also shows the *cis* disposition of the phosphorus relative to the metallated carbon atom. It should be noted that some of the dibenzophosphole protons show an excellent diastereomeric peak separation. The $^{1}$H NMR spectra of (*R*,*S*)-**4b** and (*R*,*R*)-**4b** showed clear differences in the aromatic protons C(4)H and C(6)H, the nearest to the phosphorus atom in the dibenzophosphole ring (see Scheme 1). In (*R*,*S*)-**4b**, the $\delta$ values of these protons are 8.62 and 7.58 ppm, and in (*R*,*R*)-**4b** are 7.89 and 8.22 ppm, respectively. That is, the proton C(4)H appears in the diastereomer (*R*,*S*)-**4b** shifted to higher fields than in diastereomer (*R*,*R*)-**4b** ($\Delta\delta(H^4)=0.73$ ppm), and the opposite occurs in the case of the proton C(6)H ($\Delta\delta(H^6)=-0.64$ ppm). This is common in this kind of complex, for which reason cyclopalladium compounds have also been used for the determination of the enantiomeric excess of Lewis bases.[20–23]

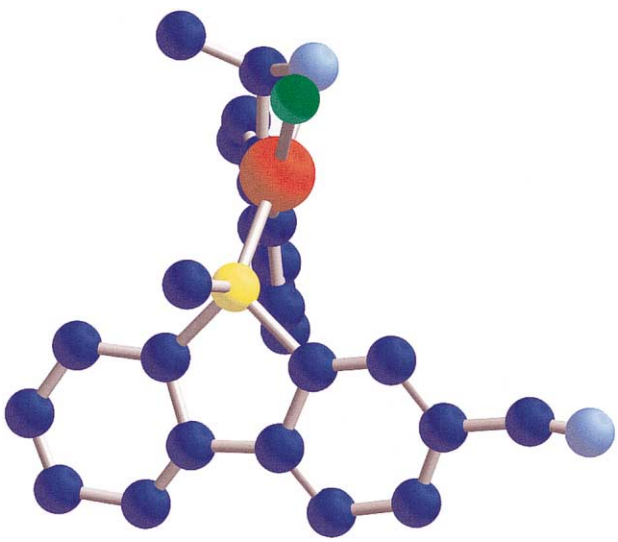


**Figure 1.** Relative positions of the naphthyl group and the dibenzophosphole ligand in the cyclopalladium derivative, (*R*,*S*)-**4b**.

Diastereomeric mixture **4b** (428 mg) was eluted at room temperature on a $SiO_2$ column with hexane–AcOEt (1:1) as eluent. The fractions eluted were checked by TLC. The first diastereomer eluted (*R*,*S*)-**4b** was obtained in 85% yield (182 mg), with a diastereomeric excess of >95%, and the second diastereomer (*R*,*R*)-**4b** was obtained with only 85% d.e.

In order to establish the absolute configuration of the phosphine, the crystal structure of (*R*,*S*)-**4b** was determined by X-ray diffraction (see Fig. 2). The crystal structure consists of discrete molecules separated by van der Waals distances. The structure, bond distances and angles are similar to those reported for related metallacycles[38,39] (see Table 1). The palladium atom is in a square-planar environment, coordinated to carbon, chlorine, nitrogen and phosphorus atoms. The phosphorus and nitrogen atoms adopt a *trans* arrangement. The methyl group of the stereogenic carbon atom occupies an axial position and the metallacycle adopts a δ conformation. The absolute configuration of the phosphorus atom in (*R*,*S*)-**4b** is (*S*).

Reaction of dimer **3** with the dibenzophosphole **2c** afforded the mononuclear complex [PdCl(C-N)(P*)] **4c** (see Scheme 2) as a 1:1 mixture of diastereomers,

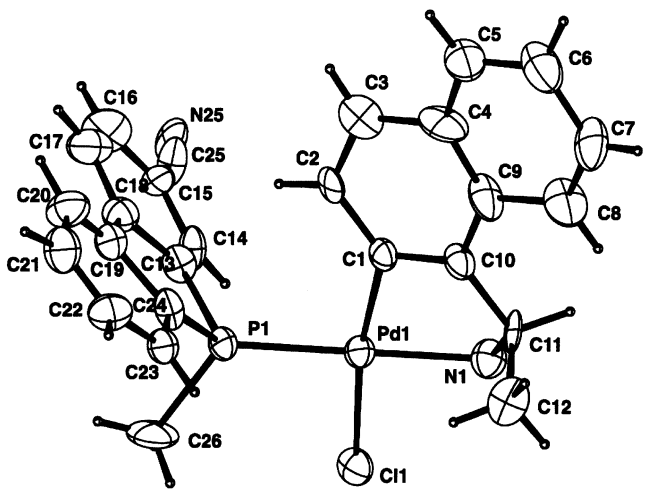



**Figure 2.** ORTEP plot of the structure of (*R*,*S*)-**4b**.

**Table 1.** Selected bond lengths (Å) and angles (°) for (*R*,*S*)-**4b**

| Atoms | Distance | Atoms | Distance |
|---|---|---|---|
| Pd(1)–C(1) | 2.032(7) | P(1)–C(24) | 1.729(19) |
| Pd(1)–N(1) | 2.114(16) | P(1)–C(13) | 1.807(9) |
| Pd(1)–P(1) | 2.234(4) | P(1)–C(26) | 1.899(15) |
| Pd(1)–Cl(1) | 2.393(2) | | |
| Atoms | Angle | Atoms | Angle |
| C(1)–Pd(1)–N(1) | 81.1(5) | C(26)–P(1)–Pd(1) | 123.4(10) |
| C(1)–Pd(1)–P(1) | 97.2(4) | C(24)–P(1)–C(13) | 91.4(6) |
| N(1)–Pd(1)–P(1) | 177.7(3) | C(11)–N(1)–Pd(1) | 105.0(10) |
| C(1)–Pd(1)–Cl(1) | 170.9(4) | C(2)–C(1)–Pd(1) | 126.1(8) |
| N(1)–Pd(1)–Cl(1) | 89.9(3) | C(12)–C(11)–C(10) | 113.9(14) |
| P(1)–Pd(1)–Cl(1) | 91.75(11) | C(12)–C(11)–N(1) | 110.5(10) |
| C(24)–P(1)–Pd(1) | 122.6(4) | C(10)–C(11)–N(1) | 107.2(9) |
| C(13)–P(1)–Pd(1) | 115.1(5) | | |
| Atoms | | Angle | |
| C(1)–Pd(1)–P(1)–C(13) | | 77.5(4) | |
| C(1)–Pd(1)–P(1)–C(24) | | −31.8(6) | |
| C(1)–Pd(1)–P(1)–C(26) | | −157.6(7) | |
| C(1)–Pd(1)–N(1)–C(11) | | 34.6(6) | |
| Pd(1)–N(1)–C(11)–C(10) | | −40.0(11) | |
| Pd(1)–N(1)–C(11)–C(12) | | 84.6(15) | |

(*R*,*S*,*S*)-**4c** and (*R*,*R*,*S*)-**4c**. $^1$H NMR data also showed the *cis* disposition of the phosphorus relative to the metallated carbon atom and significant differences in the $\delta$ values of both diastereomers: the $\delta$ values of C(4)H and C(6)H are 7.88 and 8.23 ppm in (*R*,*S*,*S*)-**4c** and 7.07 and 9.02 ppm in (*R*,*R*,*S*)-**4c** ($\Delta\delta(H^4)=0.88$ ppm and $\Delta\delta(H^6)=-0.79$ ppm), which shows that such criteria can be used for the determination of the absolute configuration of the phosphorus atom in our complexes.

Compound **4c** (1061 mg) was eluted at room temperature, from a $SiO_2$ column with $CHCl_3$–acetone (100/3) as eluent. The first diastereomer eluted (*R*,*S*,*S*)-**4c** was obtained in 77% yield (400 mg), with a d.e. of >95%, and the second diastereomer (*R*,*R*,*S*)-**4c** was obtained in 44% yield with d.e. of 91%

Unfortunately neither of the two diastereomers of **4c** afforded crystals suitable for the determination of their structure by X-ray diffraction. Nevertheless we can propose the absolute configuration of both diastereomers on the basis of $^1$H NMR data.

NOE techniques[40–45] or NMR chemical shift regularities[46,47] can be used to determine the absolute configuration of coordinated chiral diphosphines. Dunina et al.[48] have recently extended these studies to the monodentate *P*-stereogenic ligand, *tert*-butylphenyl(4-bromophenyl)phosphine. They show that the absolute configuration of this phosphine can be assigned through NMR techniques by using the homochiral palladacycle as a reference point. The difference in $\delta$ values of the aromatic protons of the dibenzophosphole, C(4)H and C(6)H, in compounds **4** is almost independent of the substituents of the aromatic ring and is great enough to preclude possible mistakes in the assignment of the absolute configuration of the phosphine (see Figs. 3 and 4). This difference can be explained by the relative disposition of the planes determined by the naphthyl group and by the phenyl groups of the dibenzophosphole ligand (see Fig. 1). In all cases the proton located near the naphthyl group appears at lower fields than the proton located on the other side. As a consequence, $\delta$ values of C(4)H and C(6)H can be used to assign the absolute configuration of the phosphine in the cyclopalladium derivatives.

The action of dppe on the enantiomerically pure cyclopalladium diastereomers **4c** led to the enantiopure free dibenzophospholes **2c**. The displacement proceeds with

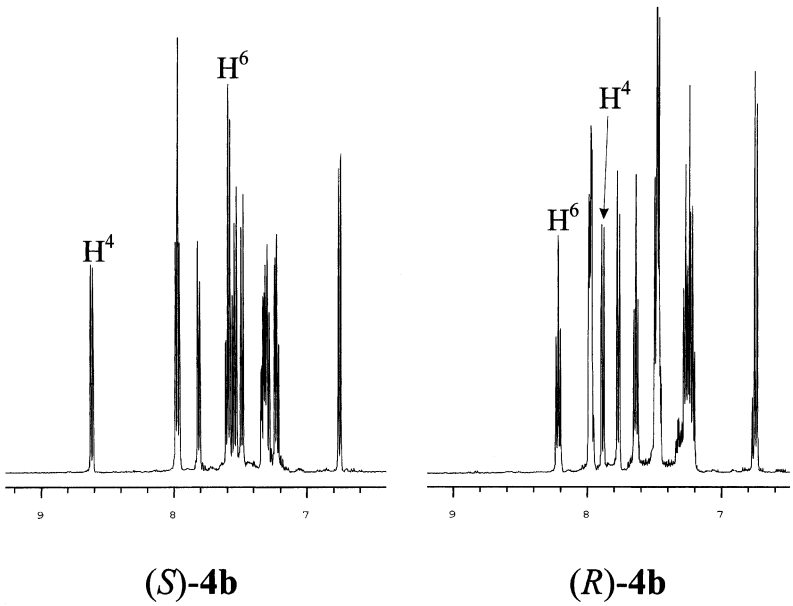



**Figure 3.** C(6)H in compound (*R*,*S*)-**4b**, and C(4)H in (*R*,*R*)-**4b** appear at lower fields than that in the other diastereomer due to its proximity to the naphthyl group, and can be used to assign the absolute configuration of the phosphine in the cyclopalladium derivative (stereochemical descriptors refer only to the phosphorus atom).

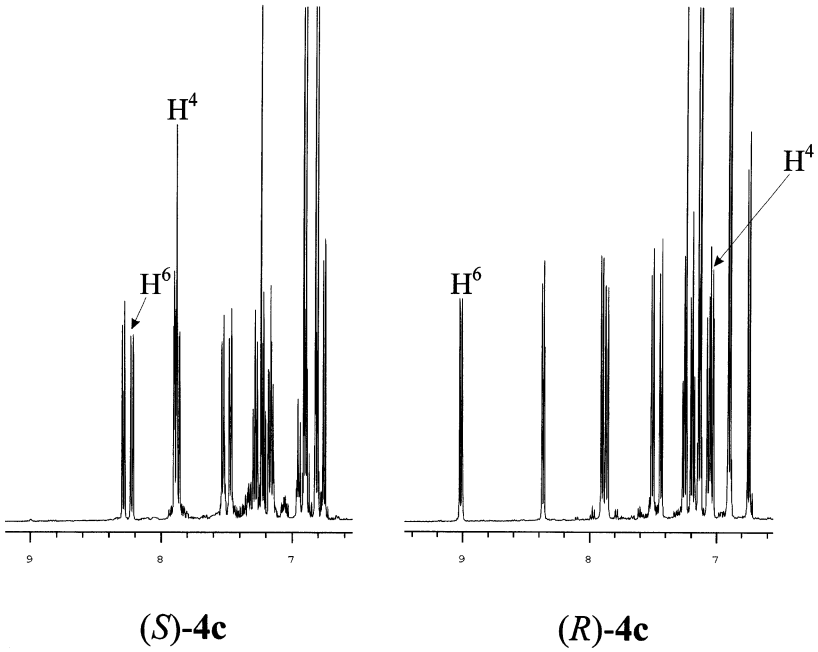



**Figure 4.** C(6)H in compound (*R*,*S*,*S*)-**4c**, and C(4)H in (*R*,*R*,*S*)-**4c** appear at lower fields than that in the other diastereomer due to its proximity to the naphthyl group, and can be used to assign the absolute configuration of the phosphine in the cyclopalladium derivative (stereochemical descriptors refer only to the phosphorus atom).

retention of the configuration at phosphorus as verified by the quantitative regeneration of the starting material **4c** from the free ligand and the binuclear cyclopalladium derivative **3**.

The oxidation of free dibenzophospholes **2c** afforded the corresponding oxides **1c** with complete retention of configuration.[49] The enantiomeric excess of (*S*,*S*)-**1c** was determined by $^1$H NMR and adding 0.6 equiv. of europium(III) tris{3-(heptafluoropropylhydroxymethylene)-(+)-camphorate} as resolving agent. The aromatic signals for C(23)H and C(24)H showed different $\delta$ values for each diastereomer (see Fig. 5) and can be used to confirm that hydrogen peroxide oxidizes with

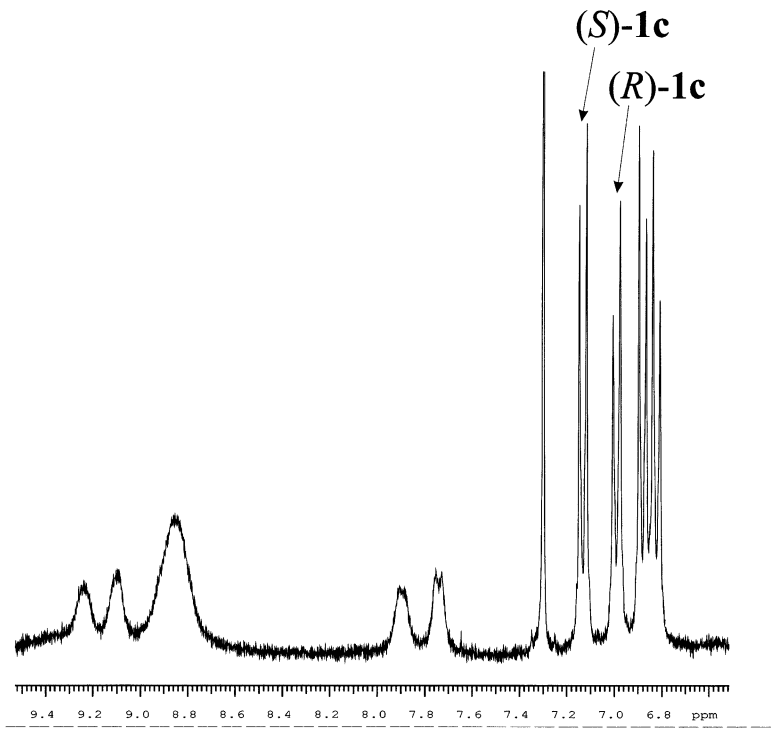



**Figure 5.** C(23)H shows different $\delta$ values for each diastereomer by addition of europium(III) tris{3-(heptafluoropropylhydroxymethylene)-(+)-camphorate} to a mixture of (*R*,*S*)-**1c** and (*S*,*S*)-**1c** in $CDCl_3$ (stereochemical descriptors refer only to the phosphorus atom).

complete retention of configuration. (*R*,*S*)-**1c** diastereomer was not detected after the oxidation of enantiomerically pure (*R*,*S*)-**2c**. Also HPLC with a CSP-1[50] chiral stationary phase derived from *N*-[*N*-(3,5-dinitrobenzoyl)-(*S*)-phenylalanyl]-(3-triethoxysilyl) propylamide was used to determine the enantiomeric excess of (*R*,*S*)-**1c**. Very good resolution was achieved ($R_S = 1.41$) using 1 mL/min flow of heptane–*iso*-propanol (9:1), and enantiomeric excess of 98% was measured for (*S*)-**1c**.

This work provides a general application procedure to resolve racemic and diastereomeric mixtures of dibenzophosphole 5-oxides using enantiomerically pure cyclopalladates derived from (*R*)-1-(1-naphthyl)-ethylamine, to assign the absolute configuration of phosphorus atom using $^1$H NMR chemical shift regularities, and to determine the enantiomeric excess of dibenzophosphole 5-oxides using europium shift reagents in $^1$H NMR and HPLC with a chiral stationary phase.

## 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 using a rotary 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 $\delta$/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. HPLC experiments were carried out on an Hewlett–Packard HP 1090 liquid chromatograph equipped with a Philips PU4020 UV detector. The chiral stationary phase was packed into a stainless-steel tube (100×4.6 mm I.D.) by the slurry method according to Coq et al.[51] The volume of sample injected was 5 μL (1 mg/mL), the flow-rate of the pump was 1 mL/min and the detection wavelength was 254 nm. Optical rotations (*c* g/100 mL) were determined at 20°C using a Perkin–Elmer 241-MC polarimeter at 589 nm. Mass spectra were measured in chemical-impact (CI, $NH_3$) mode with an Hewlett–Packard 5988A spectrometer, or with a Fisons VG-Quattro spectrometer. Then the samples were introduced into a matrix of 2-nitrobenzyl alcohol for FAB analysis and subjected to bombardment with caesium atoms. High-resolution mass spectra were performed on an Autospec/VG in chemical-impact (CI, $NH_3$) mode by the Departament de Química Orgànica Biològica (CSIC), Barcelona and in chemical-impact (CI, $CH_4$) mode by the Servicio de Espectrometría de Masas de la Facultad de Química (University of Córdoba).

### 3.2. Materials and synthesis

All the reactions involving free phosphines were carried out using Schlenk techniques under an argon atmosphere. All solvents were dried and degassed by standard methods. Tetrahydrofuran and toluene were distilled from sodium benzophenone, under nitrogen, before use. Dimethylformamide was distilled and stored over 4 Å molecular sieves. All chemicals were of commercial grade and used as received. Compounds **1a** and **1c** were prepared according to procedures described elsewhere.[52]

### 3.3. Synthesis of 3-cyano-5-methyl-5*H*-dibenzophosphole 5-oxide 1b

3-Bromo-5-methyl-5*H*-dibenzophosphole 5-oxide (750 mg, 2.56 mmol), prepared according to the procedure described elsewhere,[52] was dissolved in anhydrous *N*,*N*-dimethylformamide (20 mL). Potassium cyanide (300 mg, 4.61 mmol), palladium(II) acetate (98 mg, 0.44 mmol), triphenylphosphine (235 mg, 0.90 mmol) and calcium hydroxide (32 mg, 0.44 mmol) were added and the resulting mixture was heated to 100°C for 1 h under an inert atmosphere. Solvent was removed by vacuum distillation at rt (2 mmHg) and 3-cyano-5-methyl-5*H*-dibenzophosphole 5-oxide (540 mg, 88%) was isolated as a white solid by column chromatography, eluting with $CH_2Cl_2$–$CH_3OH$ 24:1; mp 185°C decomp. (from $CH_2Cl_2$); TLC ($SiO_2$, $CH_2Cl_2$–$CH_3OH$ 96:4): $R_f = 0.31$; IR (film): $\nu = 3056$ (arC–H s), 2908 (C–H s), 2229 (C≡N s), 1188 (P=O s) cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$, 25°C, TMS): $\delta = 8.04$ (ddd, $^3J(H,P) = 9.3$ Hz, $^4J(H^2,H^4) = 1.7$ Hz, $^5J(H^1,H^4) = 0.8$ Hz, 1 H, $H^4$), 7.87–7.76 (complex signal, 4 H, $H^1$+$H^2$+$H^6$+$H^9$), 7.59 (dddd, $^3J(H^8,H^9) = 7.5$ Hz, $^3J(H^7,H^8) = 7.5$ Hz, $^5J(H,P) = 1.5$ Hz, $^4J(H^6,H^8) = 1.2$ Hz, 1 H, $H^8$), 7.48 (dddd, $^3J(H^6,H^7) = 7.5$ Hz, $^3J(H^7,H^8) = 7.5$ Hz, $^4J(H,P) = 3.6$ Hz, $^4J(H^7,H^9) = 0.9$ Hz, 1 H, $H^7$), 1.84 (d, $^2J(H,P) = 13.8$ Hz, 3 H, $H^{14}$) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$, 25°C): $\delta = 144.47$ (d, $^2J(C,P) = 21.2$ Hz, $C^{10}$), 138.62 (d, $^2J(C,P) = 20.3$ Hz, $C^{11}$), 136.86 (d, $^4J(C,P) = 1.8$ Hz, $C^2H$), 134.01 (d, $^1J(C,P) = 101.3$ Hz, $C^{12}$), 133.69 (d, $^4J(C,P) = 2.1$ Hz, $C^8H$), 133.19 (d, $^1J(C,P) = 104.0$ Hz, $C^{13}$), 132.49 (d, $^2J(C,P) = 10.6$ Hz, $C^4H$), 130.84 (d, $^2J(C,P) = 10.9$ Hz, $C^6H$), 129.20 (d, $^3J(C,P) = 10.0$ Hz, $C^7H$), 122.35 (d, $^3J(C,P) = 9.7$ Hz, $C^9H$), 121.92 (d, $^3J(C,P) = 9.4$ Hz, $C^1H$), 117.83 (d, $^4J(C,P) = 1.8$ Hz, C≡N), 112.66 (d, $^3J(C,P) = 12.5$ Hz, $C^3$), 16.11 (d, $^1J(C,P) = 71.9$ Hz, $C^{14}H_3$) ppm; $^{31}$P NMR (121 MHz, $CDCl_3$, 25°C, $P(OMe)_3$): $\delta = 35.99$ (s) ppm; MS (70 eV, CI, $NH_3$): *m*/*z* (%): 240 (15) $[M+1]^+$, 257 (100) $[M+18]^+$, 274 (15) $[M+35]^+$; HRMS (70 eV, EI): *m*/*z*: 239.0505 $[M]^+$, $C_{14}H_{10}NOP$ requires 239.0500.

### 3.4. Synthesis of 5-methyl-5*H*-dibenzophosphole 2a

Distilled triethylamine (0.74 mL, 537 mg, 7.33 mmol) was added to a solution of 5-methyl-5*H*-dibenzophosphole 5-oxide **1a** (783 mg, 3.66 mmol) in anhydrous

toluene (20 mL) under an inert atmosphere at rt. Trichlorosilane (1.1 mL, 1.48 g, 7.90 mmol) was added and the mixture was heated under reflux for 2 h. 30% aqueous NaOH solution (20 mL) was deoxygenated and then added to the reaction mixture previously cooled to 0°C. After vigorous stirring for 0.5 h the organic layer was extracted under nitrogen, dried and the solvent removed. 5-Methyl-5*H*-dibenzophosphole (672 mg, 93%) was isolated as a colourless oil which was checked only by NMR spectroscopy due to its rapid oxidation in contact with air. Previously described[53,54] $^{13}$C NMR spectroscopy assignation for this compound is not consistent with our COSY and HSQC spectra; $^1$H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta=7.93$ (ddd, $^3J(H^1,H^2)=7.8$ Hz, $^4J(H^1,H^3)=1.2$ Hz, $^5J(H^1,H^4)=0.9$ Hz, 2 H, $H^1$), 7.73 (dddd, $^3J(H^3,H^4)=7.5$ Hz, $^3J(H,P)=5.0$ Hz, $^4J(H^2,H^4)=1.2$ Hz, $^5J(H^1,H^4)=0.9$ Hz, 2 H, $H^4$), 7.46 (ddd, $^3J(H^1,H^2)=7.8$ Hz, $^3J(H^2,H^3)=7.5$ Hz, $^4J(H^2,H^4)=1.2$ Hz, 2 H, $H^2$), 7.35 (dddd, $^3J(H^3,H^4)=7.5$ Hz, $^3J(H^2,H^3)=7.5$ Hz, $^4J(H,P)=2.7$ Hz, $^4J(H^1,H^3)=1.2$ Hz, 2 H, $H^3$), 1.43 (d, $^2J(H,P)=1.8$ Hz, 3 H, $H^{14}$) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$, 25°C): $\delta=145.08$ (d, $^2J(C,P)=4.0$ Hz, $C^{10}$), 143.30 (d, $^2J(C,P)=1.8$ Hz, $C^{12}$), 129.58 (d, $^2J(C,P)=21.5$ Hz, $C^4H$), 128.36 (s, $C^2H$), 127.24 (d, $^3J(C,P)=7.7$ Hz, $C^3H$), 121.47 (s, $C^1H$), 14.06 (d, $^1J(C,P)=20.3$ Hz, $C^{14}H_3$) ppm; $^{31}$P NMR (121 MHz, $CDCl_3$, $P(OMe)_3$): $\delta=-27.52$ (s) ppm.

### 3.5. Synthesis of 3-cyano-5-methyl-5*H*-dibenzophosphole 2b

3-Cyano-5-methyl-5*H*-dibenzophosphole 5-oxide **1b** (178 mg, 0.80 mmol), a mixture of 50% ($R_P$) and 50% ($S_P$) product, was dissolved in anhydrous toluene (10 mL) under an inert atmosphere at rt. Distilled triethylamine (0.30 mL, 218 mg, 2.16 mmol) and then trichlorosilane (0.20 mL, 269 mg, 1.99 mmol) were added and the resulting solution was heated under reflux for 2 h. 30% NaOH aqueous solution (10 mL) was deoxygenated and then added to the reaction mixture previously cooled to 0°C. After vigorous stirring for 0.5 h the organic layer was extracted under nitrogen, dried and the solvent removed. Reduced 3-cyano-5-methyl-5*H*-dibenzophosphole was isolated as an orange oil which was rapidly converted into cyclopalladate **3b** due to its rapid oxidation in contact with air.

### 3.6. Synthesis of ($S_C$)-5-ethyl-3-(2-methylbutoxy)-7-(4-undec-10-enoxyphenoxycarbonyl)-5*H*-dibenzophosphole 2c

($S_C$)-5-Ethyl-3-(2-methylbutoxy)-7-(4-undec-10-enoxyphenoxycarbonyl)-5*H*-dibenzophosphole 5-oxide **1c** (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. 30% NaOH aqueous solution (20 mL) was deoxygenated and then added to the reaction mixture previously cooled to 0°C. After vigorous stirring for 0.5 h the organic layer was extracted under nitrogen, dried and the solvent removed. ($S_C$)-5-Ethyl-3-(2-methylbutoxy)-7-(4-undec-10-enoxyphenoxycarbonyl)-5*H*-dibenzophosphole was isolated as a colourless oil which was rapidly converted into cyclopalladate **3c** due to its rapid oxidation in contact with air.

### 3.7. Synthesis of bis[(*R*)-1-(1-aminoethyl)-naphthyl-$C^2$,*N*]di-μ-chlorodipalladium(II) 3

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 spectroscopy to the previously described compound.[31]

### 3.8. Synthesis of (*R*)-[1-(1-aminoethyl)-naphthyl-$C^2$,*N*][chloro][5-methyl-5*H*-dibenzophosphole-*P*]palladium(II) 4a

5-Methyl-5*H*-dibenzophosphole **2a** (159 mg, 0.80 mmol) was dissolved in anhydrous tetrahydrofuran (10 mL). Bis[(*R*)-1-(1-aminoethyl)naphthyl-$C^2$,*N*]di-μ-chlorodipalladium(II) **3** (250 mg, 0.40 mmol) was added and the resulting solution was stirred under nitrogen at rt for 15 min. The solvent was removed and (*R*)-[1-(1-aminoethyl)naphthyl-$C^2$,*N*][chloro][5-methyl-5*H*-dibenzophosphole-*P*]palladium(II) (339 mg, 83%) was isolated as a yellow solid after column chromatography eluting with $CHCl_3$–$CH_3OH$ 100:3; mp 220°C decomp. (from $CH_2Cl_2$); TLC ($SiO_2$, $CHCl_3$–$CH_3OH$ 100:3): $R_f=0.63$; IR (film): $\nu=3210$ ($NH_2$ s), 3040 (arC–H s), 2950 (C–H s), 1570 ($NH_2$ $\delta$) cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$, 25°C, TMS): $\delta=8.22$ (dd, $^3J(H,P)=8.4$ Hz, $^3J(H^3,H^4)=8.4$ Hz, 1 H, [$H^{4a}$, $H^{4b}$]), 7.94 (d, $^3J(H^1,H^2)=8.7$ Hz, 1 H, [$H^{1a}$, $H^{1b}$]), 7.91 (d, $^3J(H^1,H^2)=8.7$ Hz, 1 H, [$H^{1a}$, $H^{1b}$]), 7.62–7.17 (complex signal, 9 H, $H^2$+$H^3$+[$H^{4a}$, $H^{4b}$]+$H^{5'}$+$H^{6'}$+$H^{7'}$+$H^{8'}$), 6.71 (d, $^3J(H^{3'},H^{4'})=8.5$ Hz, 1 H, $H^{4'}$), 5.93 (dd, $^3J(H^{3'},H^{4'})=8.5$ Hz, $^4J(H,P)=7.2$ Hz, 1 H, $H^{3'}$), 5.06 (q, $^3J(H^{11'},H^{12'})=6.3$ Hz, 1 H, $H^{11'}$), 4.31 (complex signal, 1 H, $H^{13'a}$), 3.54 (complex signal, 1 H, $H^{13'b}$), 1.93 (d, $^2J(H,P)=10.8$ Hz, 3 H, $H^{14}$), 1.90 (d, $^3J(H^{11'},H^{12'})=6.3$ Hz, 3 H, $H^{12'}$) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$, 25°C): $\delta=$[151.32 (s), 147.33 (s)] [$C^{1'}$, $C^{2'}$, $C^{9'}$, $C^{10'}$], [143.13 (d, $^2J(C,P)=8.2$ Hz), 142.58 (d, $^2J(C,P)=8.6$ Hz)] [$C^{10a}$, $C^{10b}$], [136.38 (d, $^1J(C,P)=52.5$ Hz), 135.87 (d, $^1J(C,P)=48.9$ Hz)] [$C^{12a}$, $C^{12b}$], 134.64 (d, $^3J(C,P)=12.8$ Hz, $C^{3'}H$), 131.74 (d, $^2J(C,P)=14.3$ Hz) [$C^{4a}H$, $C^{4b}H$], [131.28 (s), 131.05 (s)] [$C^{2a}H$, $C^{2b}H$], 130.86 (d, $^2J(C,P)=14.0$ Hz) [$C^{4a}H$, $C^{4b}H$], [128.81 (d,

$^3J$(C,P)=10.6 Hz), 128.51 (d, $^3J$(C,P)=11.0 Hz)] [$C^{3a}$H, $C^{3b}$H], 128.23 (s, $C^{5'}$H), 125.53 (s, $C^{7'}$H), 124.94 (d, $J_{C-P}$ 5.5, $C^{4'}$H), 123.98 (s, $C^{6'}$H), 123.32 (s, $C^{8'}$H), [121.50 (d, $^3J$(C,P)=5.8 Hz), 121.32 (d, $^3J$(C,P)=5.8 Hz)] [$C^{1a}$H, $C^{1b}$H], 57.06 (s, $C^{11'}$H), 25.65 (s, $C^{12'}H_3$), 16.08 (d, $^1J$(C,P)=29.8 Hz, $C^{14}H_3$) ppm; $^{31}$P NMR (121 MHz, $CDCl_3$, $P(OMe)_3$): $\delta$=16.92 (s) ppm; MS (10 kV, positive FAB, Cs, NBA): $m/z$: 474 $[M-Cl]^+$.

### 3.9. Synthesis of 4b and separation of (*R*,*S*)-4b and (*R*,*R*)-4b

Bis[(*R*)-1-(1-aminoethyl)naphthyl-$C^2$,*N*]di-μ-chlorodipalladium(II) **3** (250 mg, 0.40 mmol) was added to a solution of **2b** previously obtained in anhydrous tetrahydrofuran (50 mL) and the resulting solution was stirred under nitrogen at rt for 15 min. The solvent was removed and the yellow solid obtained was purified by column chromatography eluting with hexane–AcOEt 1:1. Firstly, ($R_C$,$S_P$)-[1-(1-aminoethyl)naphthyl-$C^2$,*N*]-[chloro][3-cyano-5-methyl-5*H*-dibenzophosphole-*P*]-palladium(II) (*R*,*S*)-**4b** (182 mg, 85%) was isolated as a yellow solid. Finally ($R_C$,$R_P$)-[1-(1-aminoethyl)-naphthyl-$C^2$,*N*][chloro][3-cyano-5-methyl-5*H*-dibenzophosphole-*P*]palladium(II) (*R*,*R*)-**4b** was obtained with a small amount of the (*R*,*S*)-**4b** product.

**3.9.1. (*R*,*S*)-4b**. TLC ($SiO_2$, hexane–AcOEt 6:4): $R_f$=0.40; $[\alpha]_D^{20}$=+99.8 (*c* 1.02, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta$=8.62 (d, $^3J$(H,P)=8.5 Hz, 1 H, $H^4$), 7.98 (complex signal, 2 H, $H^1$+$H^9$), 7.81 (d, $^3J$($H^1$,$H^2$)=8.5 Hz, 1 H, $H^2$), 7.58 (complex signal, 2 H, $H^6$+$H^8$), 7.54 (d, $^3J$($H^{7'}$,$H^{8'}$)=8.5 Hz, 1 H, $H^{8'}$), 7.49 (complex signal, 1 H, $H^{7'}$), 7.28 (complex signal, 3 H, $H^{5'}$+$H^{6'}$+$H^{7'}$), 6.76 (d, $^3J$($H^{3'}$,$H^{4'}$)=8.5 Hz, 1 H, $H^{4'}$), 5.87 (dd, $^3J$($H^{3'}$,$H^{4'}$)=8.5 Hz, $^4J$(H,P)=7.0 Hz, 1 H, $H^{3'}$), 5.10 (q, $^3J$($H^{11'}$,$H^{12'}$)=6.5 Hz, 1 H, $H^{11'}$), 4.33 (complex signal, 1 H, $H^{13'a}$), 3.58 (complex signal, 1 H, $H^{13'b}$), 1.96 (d, $^2J$(H,P)=11.0 Hz, 3 H, $H^{14}$), 1.93 (d, $^3J$($H^{11'}$,$H^{12'}$)=6.5 Hz, 3 H, $H^{12'}$) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$, 25°C): $\delta$=151.49 (s) [$C^{1'}$, $C^{2'}$, $C^{9'}$, $C^{10'}$], 147.22 (s) [$C^{1'}$, $C^{2'}$, $C^{9'}$, $C^{10'}$], 146.14 (d, $^2J$(C,P)=8.2 Hz) [$C^{10}$, $C^{11}$], 141.33 (d, $^2J$(C,P)=7.3 Hz) [$C^{10}$, $C^{11}$], 137.49 (d, $^1J$(C,P)=46.4 Hz) [$C^{12}$, $C^{13}$], 136.97 (d, $^1J$(C,P)=50.4 Hz) [$C^{12}$, $C^{13}$], 135.35 (d, $^2J$(C,P)=15.2 Hz, $C^4$H), 134.93 (s, $C^2$H), 134.73 (d, $^3J$(C,P)=12.4 Hz, $C^{3'}$H), 131.53 (s, $C^8$H), 131.32 (d, $^2J$(C,P)=14.3 Hz, $C^6$H), 130.95 (s) [$C^{1'}$, $C^{2'}$, $C^{9'}$, $C^{10'}$], 129.97 (d, $^6J$(C,P)=10.9 Hz, $C^{5'}$H), 128.28 (s, $C^{7'}$H), 125.80 (s, $C^7$H), 125.09 (d, $^4J$(C,P)=5.5 Hz, $C^{4'}$H), 124.23 (s, $C^{6'}$H), 123.41 (s, $C^{8'}$H), 122.51 (d, $^3J$(C,P)=5.5 Hz) [$C^1$H, $C^9$H], 122.00 (d, $^3J$(C,P)=5.5 Hz) [$C^1$H, $C^9$H], 118.25 (s, C≡N), 112.08 (d, $^3J$(C,P)=11.9 Hz, $C^3$), 57.45 (s, $C^{11'}$H), 25.64 (s, $C^{12'}H_3$), 15.96 (d, $^1J$(C,P)=29.7 Hz, $C^{14}H_3$) ppm; $^{31}$P NMR (121 MHz, $CDCl_3$, $P(OMe)_3$): $\delta$=18.99 (s) ppm.

**3.9.2. (*R*,*R*)-4b**. TLC ($SiO_2$, hexane–AcOEt 6:4): $R_f$=0.33; $^1$H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta$=8.22 (dd, $^3J$($H^6$,$H^7$)=8.0 Hz, $^3J$(H,P)=8.0 Hz, 1 H, $H^6$), 7.98 (complex signal, 2 H, $H^1$+$H^9$), 7.89 (dd, $^3J$(H,P)=8.5 Hz, $^4J$($H^2$,$H^4$)=1.0 Hz, 1 H, $H^4$), 7.77 (ddd, $^3J$($H^1$,$H^2$)=8.0 Hz, $^5J$(H,P)=1.0 Hz, $^4J$($H^2$,$H^4$)=1.0 Hz, 1 H, $H^2$), 7.64 (dddd, $^3J$($H^7$,$H^8$)=7.5 Hz, $^3J$($H^8$,$H^9$)=7.5 Hz, $^4J$($H^6$,$H^8$)=1.0 Hz, $^5J$(H,P)=1.0 Hz, 1 H, $H^8$), 7.47 (complex signal, 3 H, $H^7$+$H^{5'}$+$H^{7'}$), 7.27 (ddd, $^3J$($H^{6'}$,$H^{7'}$)=7.0 Hz, $^3J$($H^{5'}$,$H^{6'}$)=7.0 Hz, $^4J$($H^{6'}$,$H^{8'}$)=1.0 Hz, 1 H, $H^{6'}$), 7.23 (dd, $^3J$($H^{7'}$,$H^{8'}$)=8.0 Hz, $^4J$($H^{6'}$,$H^{8'}$)=1.0 Hz, 1 H, $H^{8'}$), 6.74 (d, $^3J$($H^{3'}$,$H^{4'}$)=8.5 Hz, 1 H, $H^{4'}$), 5.87 (dd, $^3J$($H^{3'}$,$H^{4'}$)=8.5 Hz, $^4J$(H,P)=7.0 Hz, 1 H, $H^{3'}$), 5.06 (q, $^3J$($H^{11'}$,$H^{12'}$)=6.5 Hz, 1 H, $H^{11'}$), 4.44 (complex signal, 1 H, $H^{13'a}$), 3.57 (complex signal, 1 H, $H^{13'b}$), 1.92 (d, $^2J$(H,P)=11.0 Hz, 3 H, $H^{14}$), 1.90 (d, $^3J$($H^{11'}$,$H^{12'}$)=6.5 Hz, 3 H, $H^{12'}$); $^{13}$C NMR (75 MHz, $CDCl_3$, 25°C): $\delta$=151.68 (s) [$C^{1'}$, $C^{2'}$, $C^{9'}$, $C^{10'}$], 146.84 (d, $^2J$(C,P)=7.9 Hz) [$C^{10}$, $C^{11}$], 146.67 (s) [$C^{1'}$, $C^{2'}$, $C^{9'}$, $C^{10'}$], 140.75 (d, $^2J$(C,P)=7.6 Hz) [$C^{10}$, $C^{11}$], 138.24 (d, $^1J$(C,P)=49.7 Hz) [$C^{12}$, $C^{13}$], 136.77 (d, $^1J$(C,P)=47.3 Hz) [$C^{12}$, $C^{13}$], 134.71 (s, $C^2$H), 134.39 (d, $^2J$(C,P)=15.5 Hz, $C^4$H), 134.02 (d, $^3J$(C,P)=12.5 Hz, $C^{3'}$H), 131.94 (d, $^2J$(C,P)=14.3 Hz, $C^6$H), 131.70 (s, $C^8$H), 130.99 (s) [$C^{1'}$, $C^{2'}$, $C^{9'}$, $C^{10'}$], 130.37 (d, $^6J$(C,P)=10.7 Hz, $C^{5'}$H), 128.30 (s, $C^{7'}$H), 125.85 (s, $C^{6'}$H), 125.14 (d, $^4J$(C,P)=5.5 Hz, $C^{4'}$H), 124.29 (s, $C^{8'}$H), 123.39 (s, $C^7$H), 122.64 (d, $^3J$(C,P)=5.4 Hz) [$C^1$H, $C^9$H], 121.86 (d, $^3J$(C,P)=5.5 Hz) [$C^1$H, $C^9$H], 118.08 (s, C≡N), 111.81 (d, $^3J$(C,P)=12.2 Hz, $C^3$), 57.39 (s, $C^{11'}$H), 25.66 (s, $C^{12'}H_3$), 15.77 (d, $^1J$(C,P)=29.5 Hz, $C^{14}$H) ppm; $^{31}$P NMR (121 MHz, $CDCl_3$, $P(OMe)_3$): $\delta$=18.77 (s) ppm.

### 3.10. Synthesis of 4c and separation of (*R*,*S*,*S*)-4c and (*R*,*R*,*S*)-4c

Bis[(*R*)-1-(1-aminoethyl)naphthyl-$C^2$,*N*]di-μ-chlorodipalladium(II) **3** (362 mg, 0.58 mmol) was added to a solution of the **2c** compound 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_C$11′,$S_P$,$S_C$17)-[1-(1-aminoethyl)naphthyl-$C^2$,*N*][chloro][5-ethyl-3-(2-methylbutoxy)-7-(4-undec-10-enoxyphenoxycarbonyl)-5*H*-dibenzophosphole-*P*]palladium(II) (*R*,*S*,*S*)-**4c** (400 mg, 77%), and then ($R_C$11′,$R_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) (*R*,*R*,*S*)-**4c** (227 mg, 44%) were isolated as yellow solids.

**3.10.1. (*R*,*S*,*S*)-4c**. TLC ($SiO_2$, $CHCl_3$–acetone 49:1): $R_f$=0.24; $[\alpha]_D^{20}$=−139.0 (*c* 1.29, $CH_2Cl_2$); $^1$H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta$=8.29 (ddd, $^3J$($H^8$,$H^9$)=8.5 Hz, $^4J$($H^6$,$H^8$)=1.5 Hz, $^5J$(H,P)=1.5 Hz, 1 H, $H^8$), 8.23 (dd, $^3J$(H,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,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,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, $^3J$(H$^{26}$,H$^{27}$) = 6.5 Hz, 2 H, H$^{26}$), 3.55 (complex signal, 1 H, H$^{13'b}$), 2.70 (dq, $^2J$(H,P) = 15.0 Hz, $^3J$(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, $^3J$(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, $^3J$(H$^{17}$,H$^{20}$) = 6.5 Hz, 3 H, H$^{20}$), 0.96 (t, $^3J$(H$^{18}$,H$^{19}$) = 7.5 Hz, 3 H, H$^{19}$), 0.84 (dt, $^3J$(H,P) = 18.5 Hz, $^3J$(H$^{14}$,H$^{15}$) = 7.5 Hz, 3 H, H$^{15}$) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$, 25°C): $\delta$ = 164.66 (s, C=O), 161.19 (d, $^3J$(C,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, C$^{11}$, $^2J$(C,P) = 7.4 Hz), 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, $^1J$(C,P) = 46.1 Hz, C$^{13}$), 134.81 (d, $^2J$(C,P) = 7.0 Hz, C$^{10}$), 134.60 (d, $^3J$(C,P) = 12.2 Hz, C$^{3'}$H), 133.91 (d, $^1J$(C,P) = 50.1 Hz, C$^{12}$), 133.24 (s, C$^8$H), 132.98 (d, $^2J$(C,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, $^6J$(C,P) = 10.7 Hz, C$^{5'}$H), 125.70 (s, C$^{7'}$H), 125.21 (d, $^4J$(C,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, $^3J$(C,P) = 5.1 Hz, C$^9$H), 119.10 (s, C$^2$H), 116.50 (d, $^2J$(C,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, $^1J$(C,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, $^2J$(C,P) = 4.8 Hz, C$^{15}$H$_3$) ppm; $^{31}$P NMR (121 MHz, $CDCl_3$, $P(OMe)_3$): $\delta$ = 29.30 (s) ppm.

**3.10.2. (*R*,*R*,*S*)-4c**. TLC ($SiO_2$, $CHCl_3$–acetone 49:1): $R_f$ = 0.16; $[\alpha]_D^{20}$ = −9.05 (*c* 1.05, $CH_2Cl_2$); $^1$H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta$ = 9.02 (dd, $^3J$(H,P) = 8.5 Hz, $^4J$(H$^6$,H$^8$) = 1.5 Hz, 1 H, H$^6$), 8.37 (ddd, $^3J$(H$^8$,H$^9$) = 8.5 Hz, $^4J$(H$^6$,H$^8$) = 1.5 Hz, $^5J$(H,P) = 1.5 Hz, 1 H, H$^8$), 7.90 (dd, $^3J$(H$^8$,H$^9$) = 8.5 Hz, $^4J$(H,P) = 1.0 Hz, 1 H, H$^9$), 7.87 (dd, $^3J$(H$^1$,H$^2$) = 8.5 Hz, $^4J$(H,P) = 2.0 Hz, 1 H, H$^1$), 7.51 (d, $^3J$(H$^{7'}$,H$^{8'}$) = 8.0 Hz, 1 H, H$^{8'}$), 7.44 (d, $^3J$(H$^{5'}$,H$^{6'}$) = 8.0 Hz, 1 H, H$^{5'}$), 7.25 (ddd, $^3J$(H$^{7'}$,H$^{8'}$) = 8.0 Hz, $^3J$(H$^{6'}$,H$^{7'}$) = 7.5 Hz, $^4J$(H$^{5'}$,H$^{7'}$) = 1.0 Hz, 1 H, H$^{7'}$), 7.19 (ddd, $^3J$(H$^{5'}$,H$^{6'}$) = 8.0 Hz, $^3J$(H$^{6'}$,H$^{7'}$) = 7.5 Hz, $^4J$(H$^{6'}$,H$^{8'}$) = 1.0 Hz, 1 H, H$^{6'}$), 7.14 (d, $^3J$(H$^{23}$,H$^{24}$) = 9.5 Hz, 2 H, H$^{23}$), 7.07 (ddd, $^3J$(H$^1$,H$^2$) = 8.5 Hz, $^4J$(H$^2$,H$^4$) = 1.5 Hz, $^5J$(H,P) = 1.5 Hz, 1 H, H$^2$), 7.04 (dd, $^3J$(H,P) = 9.5 Hz, $^4J$(H$^2$,H$^4$) = 1.5 Hz, 1 H, H$^4$), 6.90 (d, $^3J$(H$^{23}$,H$^{24}$) = 9.5 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,P) = 6.5 Hz, 1 H, H$^{3'}$), 5.80 (complex signal, 1 H, H$^{35}$), 5.09 (q, $^3J$(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, $^3J$(H$^{26}$,H$^{27}$) = 6.5 Hz, 2 H, H$^{26}$), 3.61 (d, $^3J$(H$^{16}$,H$^{17}$) = 6.0 Hz, 2 H, H$^{16}$), 3.56 (complex signal, 1 H, H$^{13'b}$), 2.66 (dq, $^2J$(H,P) = 15.0 Hz, $^3J$(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, $^3J$(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, $^3J$(H$^{17}$,H$^{20}$) = 6.5 Hz, 3 H, H$^{20}$), 0.79 (complex signal, 3 H, H$^{15}$), 0.75 (t, $^3J$(H$^{18}$,H$^{19}$) = 7.5 Hz, 3 H, H$^{19}$) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$, 25°C): $\delta$ = 164.90 (s, C=O), 160.44 (d, $^3J$(C,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, $^2J$(C,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, $^1J$(C,P) = 48.9 Hz, C$^{13}$), 135.45 (d, $^2J$(C,P) = 6.7 Hz, C$^{10}$), 134.64 (d, $^3J$(C,P) = 12.2 Hz, C$^{3'}$H), 133.54 (s, C$^8$H), 133.50 (d, $^1J$(C,P) = 47.0 Hz, C$^{12}$), 133.32 (d, $^2J$(C,P) = 15.2 Hz, C$^6$H), 130.96 (s) [C$^{1'}$, C$^{2'}$, C$^{9'}$, C$^{10'}$], 128.63 (d, $^6J$(C,P) = 10.7 Hz, C$^{5'}$H), 128.27 (d, $^3J$(C,P) = 2.4 Hz, C$^7$), 125.60 (s, C$^{7'}$H), 125.12 (d, $^4J$(C,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, $^3J$(C,P) = 5.5 Hz, C$^9$H), 118.67 (s, C$^2$H), 116.45 (d, $^2J$(C,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, $^1J$(C,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, $^2J$(C,P) = 4.9 Hz, C$^{15}$H$_3$) ppm; $^{31}$P NMR (121 MHz, $CDCl_3$, $P(OMe)_3$): $\delta$ = 29.30 (s) ppm.

### 3.11. Discoordination of (*R*,*S*,*S*)-4c and oxidation of (*R*,*S*)-2c to obtain ($S_C$,$S_P$)-5-ethyl-3-(2-methylbutoxy)-7-(4-undec-10-enoxyphenoxycarbonyl)-5*H*-dibenzophosphole 5-oxide (*S*,*S*)-1c

($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) (*R*,*S*,*S*)-**4c** (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% $H_2O_2$ (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 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); TLC ($SiO_2$, AcOEt): $R_f$ = 0.58; $[\alpha]_D^{20}$ = +20.2 (*c* 1.03, $CH_2Cl_2$); IR (film): $\nu$ = 2927 (C–H s), 1733 (C=O s), 1262 (C–O–C as. s), 1192 (P=O s) cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta$ = 8.55 (dd, $^3J$(H,P) = 10.0 Hz, $^4J$(H$^6$,H$^8$) = 1.5 Hz, 1 H, H$^6$), 8.28 (dd, $^3J$(H$^8$,H$^9$) = 8.0 Hz, $^5J$(H,P) = 1.0 Hz, 1 H, H$^8$), 7.70 (complex signal, 2 H, H$^1$+H$^9$), 7.33 (dd, $^3J$(H,P) = 10.0 Hz, $^4J$(H$^2$,H$^4$) = 2.5 Hz, 1 H, H$^4$), 7.07 (complex signal, 3 H, H$^2$+H$^{23}$), 6.87 (d, $^3J$(H$^{23}$,H$^{24}$) = 7.0 Hz, 2 H, H$^{24}$), 5.76 (complex signal, 1 H, H$^{35}$), 4.91 (complex signal, 2 H, H$^{36}$), 3.90 (t, $^3J$(H$^{26}$,H$^{27}$) = 7.0 Hz, 2 H, H$^{26}$), 3.81 (complex signal, 2 H, H$^{16}$), 2.12 (dq, $^2J$(H,P) = 14.5 Hz, $^3J$(H$^{14}$,H$^{15}$) = 7.5 Hz, 2 H, H$^{14}$), 1.99 (complex signal, 2 H, H$^{34}$), 1.85 (complex signal, 1 H, H$^{17}$), 1.73 (complex signal, 2 H, H$^{27}$), 1.52 (complex

signal, 1 H, $H^{18a}$), 1.40 (complex signal, 3 H, $H^{18b}$+$H^{28}$), 1.26 (complex signal, 10 H, $H^{29-33}$), 1.03 (dt, $^3J$(H,P)=19.0 Hz, $^3J(H^{14},H^{15})$=7.5 Hz, 3 H, $H^{15}$), 0.98 (complex signal, 3 H, $H^{20}$), 0.91 (t, $^3J(H^{18},H^{19})$=7.5 Hz, 3 H, $H^{19}$) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$, 25°C): $\delta$=164.34 (d, $^4J$(C,P)=1.7 Hz, C=O), 161.18 (d, $^3J$(C,P)=13.3 Hz, $C^3$), 156.83 (s, $C^{25}$), 146.12 (d, $^2J$(C,P)=20.4 Hz, $C^{11}$), 143.92 (s, $C^{22}$), 139.01 (s, $C^{35}H$), 135.18 (s, $C^8H$), 134.18 (d, $^1J$(C,P)=99.3 Hz, $C^{13}$), 131.40 (d, $^1J$(C,P)=117.9 Hz, $C^{12}$), 130.92 (d, $^2J$(C,P)=10.3 Hz, $C^6H$), 128.74 (d, $^3J$(C,P)=10.9 Hz, $C^7$), 123.46 (d, $^3J$(C,P)=11.4 Hz, $C^1H$), 122.10 (s, $C^{23}H$), 120.27 (d, $^3J$(C,P)=9.6 Hz, $C^9H$), 119.92 (s, $C^2H$), 114.95 (s, $C^{24}H$), 114.52 (d, $^2J$(C,P)=10.2 Hz, $C^4H$), 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, $C^{27}H_2$+$C^{29-33}H_2$), 25.90 (s, $C^{18}H_2$+$C^{28}H_2$), 22.98 (d, $^1J$(C,P)=70.4 Hz, $C^{14}H_2$), 16.32 (s, $C^{20}H_3$), 11.13 (s, $C^{19}H_3$), 6.05 (d, $^2J$(C,P)=4.2 Hz, $C^{15}H_3$) ppm; $^{31}$P NMR (121 MHz, $CDCl_3$, $P(OMe)_3$): $\delta$=44.72 (s) ppm; MS (10 kV, positive FAB, Cs, NBA): $m/z$: 603 $[M]^+$; HRMS (70 eV, CI, $CH_4$): $m/z$: 603.3236 $[M+H]^+$, $C_{37}H_{48}O_5P$ requires 603.3239; HPLC (CSP-1[50] phase, heptane–*iso*-propanol 9:1, 1 mL/min, 40 bar, 254 nm) $t_1$=17.119 min (*R*,*S*)-**1c**, $t_2$=19.603 min (*S*,*S*)-**1c**, $t_0$=1.486 min, $\omega_1$=1.611 min, $\omega_2$=1.913 min, $k'_1$=10.52, $k'_2$=12.19, $\alpha$=1.16, $R_S$=1.41, 99% of (*S*,*S*)-**1c**.

### 3.12. Discoordination of (*R*,*R*,*S*)-4c and oxidation of (*S*,*S*)-2c to obtain ($S_C$,$R_P$)-5-ethyl-3-(2-methylbutoxy)-7-(4-undec-10-enoxyphenoxycarbonyl)-5*H*-dibenzophosphole 5-oxide (*R*,*S*)-1c

($R_C$11′,$R_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) (*R*,*R*,*S*)-**4c** (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% $H_2O_2$ (1 mL) was added and the solution was stirred for another 2 h. Then, dichloromethane (100 mL) and water (100 mL) were added. The organic layer was extracted, dried and the solvent removed. The residue was purified by column chromatography eluting with AcOEt, yielding ($S_C$,$R_P$)-5-ethyl-3-(2-methylbutoxy)-7-(4-undec-10-enoxyphenoxycarbonyl)-5*H*-dibenzophosphole 5-oxide (150 mg, 99%) as a yellow solid with all spectra identical to (*S*,*S*)-**1c**; HPLC (CSP-1[50] phase, heptane–*iso*-propanol 9:1, 1 mL/min, 40 bar, 254 nm) $t_1$=17.119 min (*R*,*S*)-**1c**, $t_2$=19.603 min (*S*,*S*)-**1c**, $t_0$=1.486 min, $\omega_1$=1.611 min, $\omega_2$=1.913 min, $k'_1$=10.52, $k'_2$=12.19, $\alpha$=1.16, $R_S$=1.41, 91% of (*R*,*S*)-**1c**.

### 3.13. Crystallographic studies

A yellow plate crystal of (*R*,*S*)-**4b** (0.3×0.3×0.1 mm) was selected, mounted on a glass fiber, and transferred to a Marresearch MAR345 diffractometer. Graphite-monochromatized Mo Kα radiation was used. Cell constants were obtained from least-squares refinement using the setting angles of 6085 reflections. The system was determined to be monoclinic, space group *C*2. Lorentz-polarization correction was applied. The structure was resolved using the SHELXS software package[55] and refined by least-squares using the complete matrix with the SHELXL software package.[56] The refined function was $\Sigma\omega(|F_o|^2-|F_c|^2)^2$, where $\omega=[\sigma^2(I)+(0.1206P)^2]^{-1}$, $P=(|F_o|^2+2|F_c|^2)/3$. $f$, $f'$ and $f''$ values were taken from International Tables of X-ray Crystallography.[57] The chirality of the structure was defined with Flack coefficient.[58] After isotropic refinement a difference map showed the presence of one ethyl acetate and one water molecule in the structure. Atom positions were calculated and refined with a global temperature factor. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-150264. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

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