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# Chemo-, regio- and stereoselective conversion of *P*-chirogenic phosphorus borane complexes into their P=O or P=S derivatives

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**Abstract**—Chiral and achiral organophosphorus borane complexes are readily transformed into their corresponding phosphoryl or thiophosphoryl compounds in high yields using one-pot procedures with stereoselectivities reaching 100% in many cases. Both oxidation and sulfuration were performed under neutral or mild conditions and were applied to various organophosphorus borane complexes (phosphines, phosphinates, chlorophosphines, aminophosphines, etc.). In the case of the dissymmetric diphosphine or aminophosphine phosphinite ligands, the reaction of their diborane complexes proceeds regiospecifically to a single phosphorus group, affording the corresponding hybrid derivatives. 

## 1. Introduction

Introducing chirality at the phosphorus center of a phosphoryl compound is of particular importance in organophosphate agrochemistry,[1] the development of modified oligonucleotides[2] and in the synthesis of phosphamide anti-tumor agents.[3] The synthetic utility of P(IV)-chirogenic compounds has also been demonstrated using them as chiral auxiliaries,[4] ligands[5] or catalysts[6] in various asymmetric reactions, or as NMR derivatizing shift reagents.[7] Many of these compounds, which are obtained by condensation of a chlorophosphoryl reagent with a chiral amino alcohol or diamine, bear the chirality both at the phosphorus atom and at the carbon backbone. Nevertheless, chiral phosphoryl compounds can be prepared using racemate resolution processes or asymmetric synthesis,[8] but these methods generally require several steps and are not very versatile.

Recently, significant advances have been made in the asymmetric synthesis of P(III)-chirogenic phosphorus compounds, owing to the use of borane protecting groups.[9–13] Although decomplexation of organophosphorus borane complexes can be achieved in some cases with amines,[14] olefins,[15] EtOH[10g] or acids,[16] direct use of the complexes themselves in organic or organometallic synthesis would be of great interest,[17] since this would avoid the use of trivalent phosphorus compounds which are often difficult to purify.

In connection with our continued work on chiral ligand chemistry,[10] we have investigated both oxidation and sulfuration of organophosphorus borane complexes in order to prepare the corresponding (thio)phosphoryl derivatives. To date, the only direct use of organophosphorus borane complexes has been described by Imamoto et al.,[18] for a 'one-pot' synthesis of chiral or achiral phosphine oxides and phosphinates, using an excess of *m*-CPBA. However, these conditions are inappropriate for acid sensitive compounds such as aminophosphine boranes and for the preparation of hybrid ligands from diphosphine diboranes. We report herein alternative neutral or milder 'one-pot' decomplexation/oxidation (or sulfuration) procedures, allowing the chemo-, regio- and stereoselective synthesis of various organophosphorus *P*-oxides **2** (or *P*-sulfides **3**), from the borane complexes **1** (Scheme 1).

## 2. Results and discussion

Refluxing triphenylphosphine borane complex **1a** or dppe diborane **1b** in a mixture of *tert*-butyl hydroperoxide and butanone at 80°C (method A) led to the corresponding mono- and diphosphine oxides **2a** and **2b** in 94 and 85% isolated yields, respectively (Table 1, entries 1, 2).

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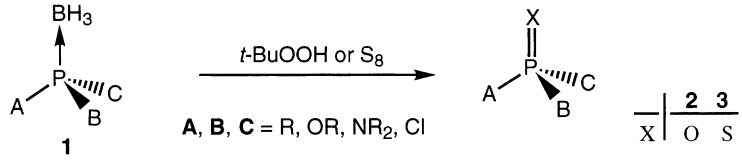
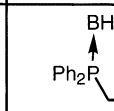
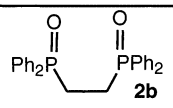
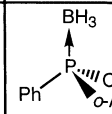
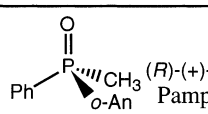
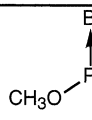
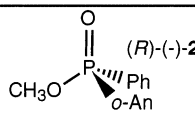
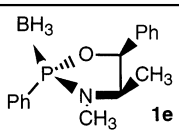
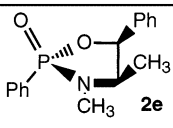
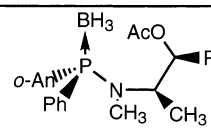
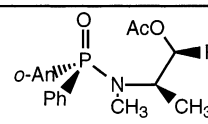



**Scheme 1.**

**Table 1.** Oxidation of organophosphorus borane complexes into their corresponding phosphoryl derivatives

| Entry | Borane complex | Method[a] | Product | Yield(%)[b] | d.e. (or e.e.) |
|---|---|---|---|---|---|
| 1 | $Ph_3PBH_3$ **1a** | A | $Ph_3P{=}O$ **2a** | 94 | - |
| 2 |  **1b** | A |  **2b** | 85 | - |
| 3 |  (*S*)-(+)-**1c** Pamp.$BH_3$ | A<br>B |  (*R*)-(+)-**2c** Pampo | 90<br>90 | 91[d]<br>100[d] |
| 4 |  (*R*)-(-)-**1d** | A<br>B |  (*R*)-(-)-**2d** | 90<br>97 | 45[d]<br>82[d] |
| 5 |  **1e** | B |  **2e** | 83 | 100[c] |
| 6 |  **1f** | B |  **2f** | 90 | 100[c] |

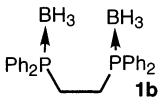
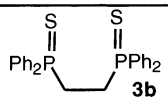
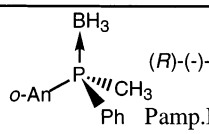
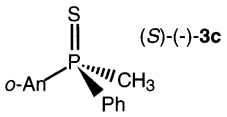
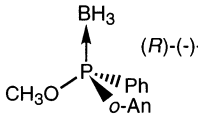
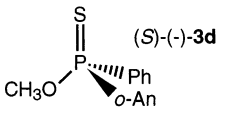
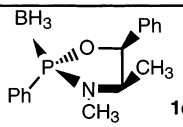
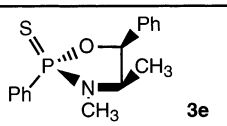
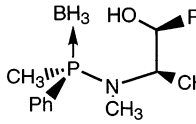
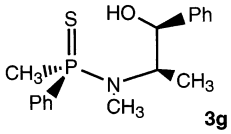
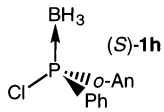
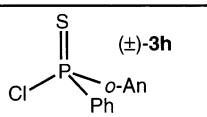
[a] Method A: *tert*-BuOOH/butanone, 80 °C; Method B: DABCO, 40 °C, then *tert*-BuOOH. [b] Isolated yields.
[c] Determined by NMR. [d]Determined by HPLC on a chiral column

Under the same conditions, (*S*)-(+)-Pamp-$BH_3$ **1c** led to the corresponding (*R*)-(+)-Pampo **2c** in 90% yield, with significant retention of the configuration at the phosphorus center (91% e.e.; entry 3). However, **2c** was obtained stereospecifically when the Pamp-$BH_3$ **1c** was decomplexed by DABCO at 40°C, then oxidized using *tert*-BuOOH (method B; entry 3). In the case of the phosphinite borane (*R*)-**1d**, the oxidation method A gave the phosphinate (*R*)-**2d** with moderate stereoselectivity (45% e.e.), but when the decomplexation step was carried out with DABCO at 40°C (method B), the e.e. was 82% (entry 4). It should be pointed out that few publications mention the preparation of *P*-chirogenic acyclic phosphinites and, to our knowledge, their configurational stability seems to be lower than that of the phosphines.[19] Under the conditions in method B, the oxazaphospholidine and aminophosphine borane complexes **1e** and **1f** gave the corresponding diastereomerically pure compounds **2e** and **2f** isolated in good yields (entries 5, 6).

In addition, the one-pot sulfuration of borane complexes **1** has also been investigated to prepare *P*-chirogenic thiophosphoryl compounds (Table 2).

Thus, refluxing the triphenylphosphine borane complex **1a** or dppe diborane **1b**, in a mixture of THF/1-octene (2:1) and $S_8$ (method C), led to the corresponding mono- and diphosphine sulfides **3a** and **3b** in 90 and 88% isolated yields, respectively (Table 2, entries 1, 2). Under the same sulfuration conditions, (*R*)-(−)-Pamp-$BH_3$ **1c** gave (*S*)-(−)-Pamp-sulfide **3c** in 80% yield with complete retention of configuration at the phosphorus atom (entry 3). In the case of the sulfuration of the phosphinite borane (*R*)-**1d**, the thiophosphinite (*S*)-**3d** was obtained in 98% yield, and the analysis of the (*R*)-Pamp sulfide **3c** resulting from the reaction of **3d** with methyllithium indicated an e.e. of 90% (entry 4). Similarly, the oxazaphospholidine borane complex **1e** and the aminophosphine borane **1g** afforded the corresponding sulfides **3e** and **3g** with diastereoselectivities of 88 and 100%, respectively (entries 5, 6). However, a stereoselectivity >94% was obtained for **3e** by heating **1e** carefully in toluene at 40°C with a mixture of DABCO and sulfur (method D; entry 5). Interestingly, sulfuration of the chlorophosphine borane (*S*)-**1h**[10g] gave the thiophosphoryl derivative **3h** in good yield (entry 7). Unfortunately, compound **3h** was obtained as a racemic mixture, in spite of the neutral and

**Table 2.** Sulfuration of organophosphorus borane complexes into their corresponding thiophosphoryl derivatives

| Entry | Borane complex | Method[a] | Product | Yield(%)[b] | d.e.[c] (or e.e.) |
|---|---|---|---|---|---|
| 1 | $Ph_3PBH_3$ **1a** | C | $Ph_3P{=}S$ **3a** | 90 | - |
| 2 |  **1b** | C |  **3b** | 86 | - |
| 3 |  (*R*)-(-)-**1c** Pamp.$BH_3$ | C |  (*S*)-(-)-**3c** | 80 | 100 |
| 4 |  (*R*)-(-)-**1d** | C |  (*S*)-(-)-**3d** | 98 | 90[d] |
| 5 |  **1e** | C<br>D |  **3e** | 60<br>89 | 88<br>94 |
| 6 |  **1g** | C |  **3g** | 90 | 100 |
| 7 |  (*S*)-**1h** | C |  (±)-**3h** | 47<br>(90)[e] | 0[d] |

[a] Method C: 1-octene/$S_8$/THF; Method D: DABCO/toluene/40 °C/$S_8$. [b] Isolated yield. [c] Determined by NMR or by optical rotation. [d] Determined from optical rotation of phosphine sulfide **3c**, after reaction with MeLi. [e] Before chromatography

mild decomplexation conditions in 1-octene at 40°C; this is probably due to the weak configurational stability of the P(III) chlorophosphine intermediate.[20]

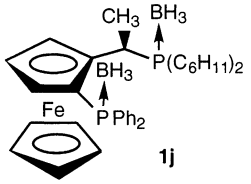
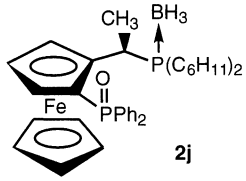
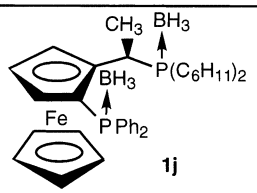
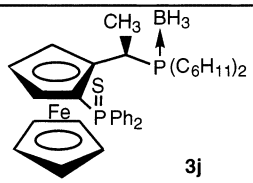
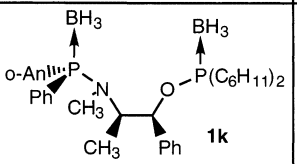
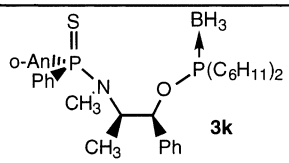
The chemoselectivity of both oxidation and sulfuration reactions was next investigated, in order to prepare hybrid (thio)phosphoryl compounds, starting from dissymmetric diborane phosphorus complexes (Table 3). Thus, when a mixture of triphenylphosphine and triethylphosphite borane complexes **1a** and **1i** (1:1) was treated with sulfur (method C), triphenylphosphine sulfide **3a** was obtained as a single product after refluxing in THF for 3 hours, while **1i** remained unchanged (entry 1). Under the reaction conditions of method B, the Josiphos[21] diborane complex **1j** afforded the phosphine oxide borane complex **2j** in 90% yield (entry 2), by regiospecific oxidation of the arylphosphino borane group. It should be pointed out that, on *m*-CPBA oxidation,[18] **1j** afforded a mixture of mono- and diphosphine oxide derivatives. Finally, the Josiphos diborane complex **1j** led regiospecifically to the phosphine sulfide borane complex **3j** under the sulfuration conditions of method C (entry 3).

Finally, the *P*-chirogenic thiophosphinamide phosphinite borane **3k** was obtained diastereospecifically from the AMPP diborane complex **1k**,[10f] according to a regio- and stereoselective sulfuration of the aminophosphine functionality (entry 4).

## 3. Conclusions

In summary, we have described chemo-, regio- and stereoselective methods affording phosphoryl or thiophosphoryl compounds in high yields either by direct oxidation or sulfuration of organophosphorus borane complexes. The mild and neutral conditions used were applied to various kinds of organophosphorus borane complexes, including chlorophosphines, aminophosphines and acid sensitive compounds. We have shown that both oxidation and sulfuration of *P*-chirogenic borane complexes proceeds with retention of configuration at the *P*-center and with stereoselectivities from 82 to 100% (excepting the chlorophosphine which gave a racemic thiophosphoryl derivative). These methods offer an alternative route to homochiral (thio)-phosphoryl compounds from phosphine borane complexes, which can be used in these reactions as easily handled and stable P(III) precursors.

**Table 3.** Preparation of hybrid (thio)phosphoryl compounds from the organophosphorus diborane complexes

| Entry | Borane complex | Method[a] | Product | Yield(%)[b] | d.e.[c] |
|---|---|---|---|---|---|
| 1 | $Ph_3PBH_3$ / $(EtO)_3PBH_3$ (1:1) **1a** **1i** | **C** | $Ph_3P{=}S$ **3a** | 100 | - |
| 2 |  **1j** | **B** |  **2j** | 90 | - |
| 3 |  **1j** | **C** |  **3j** | 60 | - |
| 4 |  **1k** | **C** |  **3k** | 80 | 100 |

[a] Method B: DABCO (1 equiv.)/toluene/40°C/11h, then *t*-BuOOH; Method C: 1-octene/$S_8$/THF. [b] Isolated yield. [c] Determined by NMR.

## 4. Experimental

### 4.1. General

All reactions were carried out under an argon or a nitrogen atmosphere in dried glassware. THF and toluene were dried and freshly distilled under a nitrogen atmosphere over sodium/benzophenone. Hexane and ethanol for HPLC were of chromatographic grade and were used without further purification. *n*-Butyllithium, 2-bromoanisole, 1-octene, *t*-butylhydroperoxide, $BH_3{\cdot}S(CH_3)_2$ and DABCO were purchased from Aldrich, Acros and Avocado. Commercially available 2-bromoanisole was distilled before use. HPLC analyses were performed on a Gilson 305/306 chromatograph equipped with a UV 116 detector. Flash chromatography was performed on silica gel (60AC.C, 35–70 μm; SDS) or neutral aluminum oxide (Carlo Erba; ref. 417241). All NMR spectral data were obtained on a Bruker DPX 250 spectrometer using TMS as internal reference for $^1H$ (250 MHz) and $^{13}C$ NMR (62.9 MHz) and 85% phosphoric acid as external reference for $^{31}P$ NMR (101.3 MHz). Melting points were measured on a Büchi melting point apparatus and are uncorrected. Optical rotation values were determined at 20°C on a Perkin–Elmer 241 polarimeter. Infrared spectra were recorded on a Bruker Equinox 55. Mass spectral analyses were performed on a JEOL MS 700 at the Mass Spectroscopy Laboratories of ENS Paris. Elemental analyses were measured with a precision greater than 0.4% at the Microanalysis Laboratories of P. & M. Curie University (Paris).

### 4.2. Preparation of the organophosphorus boranes 1

The triphenylphosphine borane **1a**, the 1,2-bis-(diphenylphosphino)ethane diborane **1b** and the triethylphosphite borane **1i** were prepared as described, from the corresponding P(III)-organophosphorus derivatives and borane dimethylsulfide in THF, then purified by recrystallization in cyclohexane or toluene for **1a** and **1b** or by distillation in the case of **1i**.

**1a**: mp = 189°C, lit.[22] mp = 189°C; **1b**: mp = 166–8°C, lit.[22b] mp = 162–167°C; **1i**: bp = 64°C (1 mmHg); $^1H$ NMR ($CDCl_3$) (lit.[23]) $\delta$ ppm, *J* Hz: 4.06 (6H, qt, $^3J_{HH} = {}^3J_{PH} = 7$, $OCH_2$), 1.31 (9H, dt, $^3J_{HH} = 7$, $^4J_{PH} = 1$, $CH_3$), 0.41 (3H, qd, $^1J_{BH} = 97$, $^2J_{PH} = 18$, $BH_3$); $^{13}C$ NMR ($CDCl_3$) $\delta$ ppm, *J* Hz: 62.5 (d, $^2J_{POC} = 4$, $OCH_2$), 16.2 (d, $^3J_{POCC} = 6$, $CH_3$); $^{31}P$ NMR ($CDCl_3$) $\delta$ ppm: +114.4 (q, $^1J_{PB} = 102$).

The (*R*)-(−)-*o*-anisyl methylphenylphosphinite borane **1c**, (2*S*,4*R*,5*S*)-(−)-3,4-dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine borane **1e**, (*S*p)-(+)-*N*-methyl-*N*-[(1*S*,2*R*)-(1-hydroxy-2-methyl-1-phenyl-prop-2-yl)]aminomethylphenylphosphine borane **1g**, (*R*)-*o*-anisylchlorophenylphosphine borane **1h**[10g] and (*R*p)-*N*-methyl-*N*-{(1*R*,2*S*)-[2-(dicyclohexylphosphinitoborane)-1-methyl-2-phenyl]ethyl}amino-*o*-anisylphenylphosphine borane **1k**[10f] complexes, were prepared from (+)-ephedrine according to the published procedure.[10c,10f] Likewise, the (*S*)-(+)-*o*-anisylmethylphenylphosphine borane **1c** and (*R*)-(−)-[(*O*-methyl)-*o*-anisylphenylphosphinite]-borane **1d** were obtained starting from (−)-ephedrine.

**4.2.1. (*R*p)-(−)-*N*-Methyl-*N*-[(1*S*,2*R*)-(1-acetoxy-2-methyl-1-phenyl-prop-2-yl)]amino-*o*-anisylphenylphosphine borane 1f**. A 100 mL round-bottomed flask equipped with a magnetic stirrer and an argon inlet was charged with a solution of 2.85 g of the oxazaphospholidine borane **1e** (15 mmol) in THF (15 mL). *o*-Anisyllithium reagent (1.5 equiv.) was added slowly at −78°C under stirring, and the reaction mixture was slowly warmed to 0°C until complex **1e** had completely disappeared. The reaction was monitored by TLC over silica (toluene/AcOEt 9:1). To this was added acetic anhydride (16.5 mmol, 1.65 equiv.). After stirring for 2 h, the mixture was warmed overnight to room temperature. The THF was removed under reduced pressure, the residue was hydrolyzed at room temperature and extracted with $CH_2Cl_2$. The combined extracts were dried over $MgSO_4$ and the solvent removed. The residue was purified by chromatography on silica gel using toluene, followed by a mixture of toluene/AcOEt (9:1) as eluent, yielding complex **1f** (2.85 g, 66% yield).

White solid; mp 128–129°C; $R_f$=0.4 (toluene); $[\alpha]_D^{20}$=−14.3 (*c* 1.5, $CHCl_3$); $^1$H NMR ($CDCl_3$) $\delta$ ppm, *J* Hz: 7.54–7.36 (4H, m, *H* arom.), 7.26–7.05 (6H, m, *H* arom.), 6.98–6.79 (4H, m, *H* arom.), 5.76 (1H, d, $^3J_{HH}$=8, PhC*H*), 4.45 (1H, m, MeC*H*N), 3.47 (3H, s, C$H_3$O), 2.38 (3H, d, $^3J_{PH}$=8, NC$H_3$), 1.99 (3H, s, C$H_3$CO), 1.17 (3H, d, $^3J_{HH}$=7), 1.6–0.0 (3H, br, B$H_3$); $^{13}$C NMR ($CDCl_3$) $\delta$ ppm, *J* Hz: 170.0 (*C* arom.), 161.0 (d, $J_{PC}$=2, *C* arom.), 138.4 (*C* arom.), 135.1 (d, $J_{PC}$=11, *C* arom.), 133.4–127.7 (*C* arom.), 122.7–112.3 (*C* arom.), 111.5 (d, $J_{PC}$=5, *C* arom.), 78.9 (d, $^3J_{PNCC}$=7, Ph*C*HO), 56.4 (d, $^2J_{PNC}$=12, N*C*HMe), 55.0 (*C*$H_3$O), 30.1 (d, $^2J_{PNC}$=4, N*C*$H_3$), 21.3 (*C*$H_3$CO), 14.2 (*C*$H_3$CH); $^{31}$P NMR ($CDCl_3$) $\delta$ ppm: +70.5 (m, $^1J_{PB}$=69); HRMS (DCI, $CH_4$) calcd for $C_{25}H_{30}BNO_3P$ [M−H$^+$]: 434.2057; found: 434.2053; Anal. calcd for $C_{25}H_{31}BNO_3P$ (435.3): C, 68.98; H, 7.18; N, 3.22; found: C, 68.85; H, 7.29; N, 3.28%.

**4.2.2. (*R*)-(−)-1-(Dicyclohexylphosphinoborane)-1-[2-(diphenylphosphinoborane)ferrocenyl]ethane 1j**. This diborane complex was prepared by addition of $BH_3$·S$(CH_3)_2$ in a 0.5 M THF solution of the Josiphos complex.[21]

Orange solid; mp 186–187°C; $R_f$=0.7 (cyclohexane/AcOEt 4:1); $[\alpha]_D^{20}$=−129 (*c* 1, $CHCl_3$); $^1$H NMR ($CDCl_3$) $\delta$ ppm: 7.79–7.61 (4H, m, *H* arom.), 7.44–7.30 (6H, m, *H* arom.), 5.16 (1H, s, $C_5H_3$), 4.62 (1H, t, $J_{PH}$=2.5, $C_5H_3$), 4.24 (5H, s, $C_5H_5$), 4.21 (1H, m, $C_5H_3$), 3.66 (1H, qd, *J*=7, *J*=14, C*H*CH$_3$), 1.94 (3H, dd, *J*=7.2, *J*=13, CHC$H_3$), 2.10–0.58 (28H, m, B$H_3$, $C_6H_{11}$); $^{13}$C NMR ($CDCl_3$) $\delta$ ppm, *J* Hz: 133.2 (d, *J*=9.5, *C* arom.), 132.7 (d, *J*=9.5, *C* arom.), 131.6 (*C* arom.), 130.9 (d, $J_{PC}$=3, *C* arom.), 130.8 (d, $J_{PC}$=3, *C* arom.), 130.3 (d, $J_{PC}$=31, *C* arom.), 128.6 (d, $J_{PC}$=10, *C* arom.), 128.2 (d, $J_{PC}$=10, *C* arom.), 98.7 (dd, $J_{PC}$=4, $J_{PC}$=17, *C* arom.), 73.8 (dd, $J_{PC}$=4, $J_{PC}$=8, $C_5H_3$), 71.4 (d, $J_{PC}$=3, $C_5H_3$), 70.5 ($C_5H_5$), 69.8 (d, $J_{PC}$=6, $C_5H_3$), 67.4 (dd, $J_{PC}$=4, $J_{PC}$=64, $C_5H_3$), 32.3 (d, $J_{PC}$=2), 32.0, 28.2–25.6, 24.0, 22.4 (d, $J_{PC}$=27); $^{31}$P NMR ($CDCl_3$) $\delta$ ppm: +38.6 (m, *P*$C_6H_{11}$), +11.1 (m, *P*$C_6H_5$). HRMS (DCI, $CH_4$) calcd for $C_{36}H_{49}B_2FeP_2$ [M−H$^+$]: 621.2845; found: 621.2842.

### 4.3. Oxidation of organophosphorus boranes

#### 4.3.1. Typical procedures

**4.3.1.1. Method A**. A mixture of organophosphorus borane complex (0.5 mmol), *tert*-BuOOH (0.2 mL; 2 mmol) and butanone (2 mL) was heated at 80°C and the reaction was monitored by TLC. After between 6 and 24 h, the mixture was cooled to 0°C and was then poured into a solution of $FeSO_4$ (1.5 mL, 1.8 mmol) and tartaric acid (0.9 mmol). After stirring for 10 min, the mixture was extracted with $CH_2Cl_2$, and the organic extracts were successively washed with NaOH (0.3 M) and water and finally dried with $MgSO_4$. The solvent was removed and the residue was purified by chromatography on silica gel, using a mixture of cyclohexane/AcOEt (4:1) as eluent.

**4.3.1.2. Method B**. A mixture of Josiphos diborane complex (0.115 mmol), DABCO (0.115 mmol) and toluene (2 mL) was heated under argon at 40°C for 11 h, to which *t*-BuOOH (0.52 mmol) was added at room temperature. After 2 h, the solvent was removed and the residue was purified by chromatography on silica gel, using a mixture of cyclohexane/AcOEt (4:1) as eluent.

The triphenylphosphine oxide **2a** and dppe dioxide **2b** exhibit satisfactory analytical data in agreement with the literature. **2a**: $^{31}$P NMR ($CDCl_3$) $\delta$ ppm: +29.3; lit.[24] $\delta$ ppm: +32; **2b**: $^1$H NMR (lit.[25]).

**4.3.2. *o*-Anisylmethylphenylphosphine oxide (Pampo) 2c[26]**. Uncrystallized, colorless; $^1$H NMR ($CDCl_3$) $\delta$ ppm, *J* Hz: 7.88 (1H, ddd, *J*=2, *J*=8, *J*=13, *H* arom.), 7.67 (2H, ddd, *J*=2, *J*=8, *J*=13, *H* arom.), 7.43–7.33 (4H, m, *H* arom.), 7.03 (1H, t, *J*=7, *H* arom.), 6.82 (1H, dd, *J*=5, *J*=8, *H* arom.), 3.65 (3H, s, C$H_3$O), 2.00 (3H, d, $^2J_{PH}$=14, C$H_3$P); $^{13}$C NMR ($CDCl_3$) $\delta$ ppm: 159.8 (d, $J_{PC}$=4, *C* arom.), 135.5–133.7 (*C* arom.), 131.2 (d, $J_{PC}$=3, *C* arom.), 130.1 (d, $J_{PC}$=10, *C* arom.), 128.1 (d, $J_{PC}$=12, *C* arom.), 121.1 (d, $J_{PC}$=100, *C* arom.), 120.9 (d, $J_{PC}$=11, *C* arom.), 110.8 (d, $J_{PC}$=7, *C* arom.), 55.2 (*C*$H_3$O), 16.0 (d, $^1J_{PC}$=75, *C*$H_3$P); $^{31}$P NMR ($CDCl_3$) $\delta$ ppm: +30.1.

The enantiomeric excess of the Pampo **2c** was determined by HPLC on a Chiralcel OD column (Daicel), with a hexane/EtOH (98:2) mixture as eluent, flow rate 1 mL min$^{-1}$ and UV detection $\lambda$=254 nm: (*R*)-enantiomer $t_R$=50.6 min, (*S*)-enantiomer $t_R$=55.3 min.

**4.3.3. (*R*)-(−)-(*O*-Methyl)-*o*-anisylphenylphosphinate 2d[27c]**. Uncrystallized, colorless; $R_f$=0.26 (cyclohexane/acetone 6:4); $[\alpha]_D^{20}$=−10.5 (*c* 1, $CHCl_3$), 45% e.e.; $^1$H NMR ($CDCl_3$) $\delta$ ppm, *J* Hz: 7.91 (1H, ddd, *J*=2, *J*=8, *J*=13, *H* arom.), 7.78 (2H, ddd, *J*=2, *J*=8, *J*=13, *H* arom.), 7.46–7.20 (4H, m, *H* arom.), 7.00 (1H, td, *J*=2, *J*=7, *H* arom.), 6.80 (1H, dd, *J*=6, *J*=8, *H* arom.), 3.64 (3H, s, C$H_3$O); $^{13}$C NMR ($CDCl_3$) $\delta$ ppm: 160.9 (d, $J_{PC}$=4, *C* arom.), 134.7 (d, $J_{PC}$=6, *C* arom.), 134.4

(d, $J_{PC}=2$, *C* arom.), 133.0 (*C* arom.), 131.8 (d, $J_{PC}=3$, *C* arom.), 131.7 (d, $J_{PC}=11$, *C* arom.), 128.0 (d, $J_{PC}=14$, *C* arom.), 120.6 (d, $J_{PC}=12$, *C* arom.), 118.7 (d, $J_{PC}=136$, *C* arom.), 111.2 (d, $J_{PC}=8$, *C* arom.), 55.5 (*C*$H_3$O), 51.4 (d, $^2J_{PC}=6$, *C*$H_3$OP); $^{31}$P NMR ($CDCl_3$) $\delta$ ppm: +32.5.

The enantiomeric excess of the phosphinate **2d** was determined by HPLC on a Chiralcel OD column (Daicel), with a hexane/EtOH (98:2) mixture as eluent, flow rate 1 mL min$^{-1}$ and UV detection $\lambda=254$ nm: (*S*)-enantiomer $t_R=32.4$ min, (*R*)-enantiomer $t_R=34.2$ min.

**4.3.4. (2*S*,4*R*,5*S*)-(+)-3,4-Dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine 2-oxide 2e**[27]. White solid; mp 154–155°C; $R_f=0.25$ (cyclohexane/AcOEt 1:1); $[\alpha]_D^{20}=+26.2$ (*c* 1, $CHCl_3$); $^1$H NMR ($CDCl_3$) $\delta$ ppm, *J* Hz: 7.90 (2H, ddd, $J=2$, $J=8$, $J=13$, *H* arom.), 7.60–7.20 (8H, m, *H* arom.), 5.63 (1H, dd, $J=5$, $J=6$, PhC*H*O), 3.79 (1H, qd, $^3J_{HH}=6$, $^3J_{PNCH}=14$, MeC*H*N), 2.64 (3H, d, $^3J_{PNCH}=10$, C$H_3$N), 0.92 (3H, d, $^3J_{HH}=7$, C$H_3$CH); $^{13}$C NMR ($CDCl_3$) $\delta$ ppm: 136.2 (d, $J_{PC}=5$, *C* arom.), 132.3–126.2 (*C* arom.), 82.6 (d, $^2J_{POC}=2$, PO*C*H), 59.2 (d, $^2J_{PNC}=10$, PN*C*H), 28.6 (d, $^2J_{PNC}=6$, PN*C*$H_3$), 14.5 (d, $^3J_{PNCC}=2$, *C*$H_3$CH); $^{31}$P NMR ($CDCl_3$) $\delta$ ppm: +34.

**4.3.5. (*S*p)-(+)-*N*-Methyl-*N*-[(1*S*,2*R*)-(1-acetoxy-2-methyl-1-phenyl-prop-2-yl)]amino-*o*-anisylphenylphosphine oxide 2f**. Uncrystallized, colorless; $R_f=0.5$ (cyclohexane/AcOEt 1:1); $[\alpha]_D^{20}=+1.5$ (*c* 0.6, $CHCl_3$); $^1$H NMR ($CDCl_3$) $\delta$ ppm, *J* Hz: 7.82 (1H, ddd, $J=2$, $J=8$, $J=13$, *H* arom.), 7.51–7.19 (11H, m, *H* arom.), 7.00 (1H, td, $J=1$, $J=7$, *H* arom.), 6.88 (1H, dd, $J=6$, $J=8$, *H* arom.), 5.92 (1H, d, $^3J_{HH}=7$, PhC*H*O), 4.12 (1H, qd, $^3J_{HH}=7$, $^3J_{PH}=10$, NC*H*CH$_3$), 3.70 (3H, s, C$H_3$O), 2.52 (3H, d, $^3J_{PH}=11$, C$H_3$N), 2.06 (3H, s, C$H_3$CO), 1.25 (3H, d, $^3J_{HH}=7$, C$H_3$CH); $^{13}$C NMR ($CDCl_3$) $\delta$ ppm: 170.0 (CH$_3$*C*O), 160.4 (d, $J_{PC}=3$, *C* arom.), 138.5 (*C* arom.), 135.8 (d, $J_{PC}=7$, *C* arom.), 133.8 (*C* arom.), 132.5 (d, $J_{PC}=134$, *C* arom.), 132.0 (d, $J_{PC}=11$, *C* arom.), 131.2 (d, $J_{PC}=3$, *C* arom.), 128.2–127.2 (*C* arom.), 120.7 (d, $J_{PC}=12$, *C* arom.), 118.7 (*C* arom.), 110.7 (d, $J_{PC}=7$, *C* arom.), 78.7 (d, $^2J_{PC}=6$, Ph*C* HO), 55.0 (*C*$H_3$O), 53.2 (d, $^2J_{PC}=4$, N*C*H), 28.7 (d, $^2J_{PC}=5$, N*C*$H_3$), 21.2 (*C*$H_3$CO), 13.8 (*C*$H_3$CH); $^{31}$P NMR ($CDCl_3$) $\delta$ ppm: +32; HRMS (DCI, $CH_4$) calcd for $C_{25}H_{29}NO_4P$ [M+H$^+$]: 438.1834; found: 438.1830.

**4.3.6. (*R*)-(−)-1-(Dicyclohexylphosphino borane)-1-[2-(diphenylphosphino oxide)ferrocenyl]ethane 2j**. Orange solid; mp 250–251°C; $[\alpha]_D^{20}=-127.5$ (*c* 0.5, $CHCl_3$); IR (KBr, $\nu$ cm$^{-1}$): 2935, 2919, 2374, 2355, 2338, 2336, 1437, 1189, 1163, 1112, 754, 719, 705, 699; $^1$H NMR ($CDCl_3$) $\delta$ ppm, *J* Hz: 7.90–7.77 (4H, m, *H* arom.), 7.48–7.38 (6H, m, *H* arom.), 4.80 (1H, s, $C_5H_3$), 4.40 (1H, dd, $J=2$, $J=5$, $C_5H_3$), 4.23 (1H, s, $C_5H_3$), 3.97 (5H, s, $C_5H_5$), 3.81 (1H, m, C*H*CH$_3$), 1.81 (1H, m), 1.70 (3H, dd, $^3J_{HH}=7$, $^3J_{PH}=14$, C$H_3$), 1.7–0.4 (24H, m, $C_6H_{11}$); $^{13}$C NMR ($CDCl_3$) $\delta$ ppm, *J* Hz: 136.1 (d, $J_{PC}=14$), 134.5 (d, $J_{PC}=17$), 131.4 (d, $J_{PC}=2$), 131.3 (d, $J_{PC}=2$), 131.2 (d, $J_{PC}=9$), 130.8 (d, $J_{PC}=9$), 128.5 (d, $J_{PC}=12$), 128.3 (d, $J_{PC}=12$), 72.9 ($C_5H_3$), 71.0 ($C_5H_3$), 70.7 ($C_5H_3$), 70.3 ($C_5H_5$), 32.9 (d, $J_{PC}=28.4$), 30.0 (d, $J_{PC}=29$), 27.5–25.6, 22.7, 22.5 (d, $J_{PC}=24$); $^{31}$P NMR ($CDCl_3$) $\delta$ ppm, *J* Hz: 38.3 (m), 26.7; HRMS (EI) calcd for $C_{36}H_{47}BFeOP_2$ [M$^+$]: 624.2552; found: 624.2544.

### 4.4. Sulfuration of organophosphorus boranes

#### 4.4.1. Typical procedures

**4.4.1.1. Method C**. A mixture of organophosphorus borane complex (1 mmol), 1-octene (4 mmol) and THF (3 mL) was refluxed in the presence of sulfur (4 mmol) for 24 h. After cooling, the solvent was removed and the residue was purified by chromatography on silica gel, using a mixture of cyclohexane/AcOEt as eluent.

**4.4.1.2. Method D**. The borane complex (0.115 mmol), DABCO (0.115 mmol) and toluene (2 mL) were heated under argon at 40°C for 11 h in the presence of sulfur (4 mmol), after which the reaction mixture was treated as for method C.

The triphenylphosphine sulfide **3a** and dppe disulfide **3b** exhibit satisfactory analytical data in agreement with the literature. **3a**: $^{31}$P NMR ($CDCl_3$) $\delta$ ppm: +43; lit.[24] +44. **3b**: mp 223–225°C; $^{31}$P NMR ($CDCl_3$) $\delta$ ppm: +44; lit.[25] mp 224–225°C.

**4.4.2. (*S*)-(−)-*o*-Anisylmethylphenylphosphine sulfide 3c**[28]. White solid; $R_f=0.3$ (cyclohexane/AcOEt 85:15); $[\alpha]_D^{20}=-7.9$ (*c* 0.5, MeOH); $^1$H NMR ($CDCl_3$) $\delta$ ppm, *J* Hz: 8.22 (1H, ddd, $J=2$, $J=8$, $J=17$, *H* arom.), 7.73 (2H, m, *H* arom.), 7.55–7.35 (4H, m, *H* arom.), 7.26–7.09 (1H, m, *H* arom.), 6.87 (1H, dd, $J=6$, $J=8$, *H* arom.), 3.65 (3H, s, C$H_3$O), 2.36 (3H, d, $^2J_{PH}=14$, C$H_3$P); $^{13}$C NMR ($CDCl_3$) $\delta$ ppm, *J* Hz: 159.8 (d, $J_{PC}=2.5$, *C* arom.), 135.5 (d, $J_{PC}=10$, *C* arom.), 135.3 (d, $J_{PC}=86$, *C* arom.), 134.0 (d, $J_{PC}=2$, *C* arom.), 130.7 (d, $J_{PC}=3$, *C* arom.), 129.9 (d, $J_{PC}=11$, *C* arom.), 128.1 (d, $J_{PC}=13$, *C* arom.), 120.9 (d, $J_{PC}=13$, *C* arom.), 119.9 (d, $J_{PC}=80$, *C* arom.), 111.0 (d, $J_{PC}=6$, *C* arom.), 55.3 (*C*$H_3$O), 20.7 (d, $J_{PC}=61$, *C*$H_3$P); $^{31}$P NMR ($CDCl_3$) $\delta$ ppm: +36.5.

**4.4.3. (*S*)-(−)-(*O*-Methyl)-*o*-anisylphenylthiophosphinate 3d**. Yellow oil; $R_f=0.25$ (toluene); $[\alpha]_D^{20}=-42.5$ (*c* 1.4, $CHCl_3$), 90% e.e.; $^1$H NMR ($CDCl_3$) $\delta$ ppm, *J* Hz: 8.02 (1H, ddd, $J=2$, $J=8$, $J=16$, *H* arom.), 7.79 (2H, ddd, $J=2$, $J=8$, $J=14$, *H* arom.), 7.40–7.30 (4H, m, *H* arom.), 7.20–6.97 (2H, m, *H* arom.), 6.76 (1H, dd, $J=7$, $J=8$, *H* arom.), 3.61 (3H, d, $^3J_{PH}=14$, C$H_3$OP), 3.52 (3H, s, C$H_3$O); $^{13}$C NMR ($CDCl_3$) $\delta$ ppm, *J* Hz: 160.7 (d, $J_{PC}=4$, *C* arom.), 135.2 (d, $J_{PC}=114$, *C* arom.), 135.1 (d, $J_{PC}=9$, *C* arom.), 134.7 (d, $J_{PC}=2$, *C* arom.), 131.8 (d, $J_{PC}=3$, *C* arom.), 131.5 (d, $J_{PC}=12$, *C* arom.), 129.0 (d, $J_{PC}=51$, *C* arom.), 128.3 (d, $J_{PC}=14$, *C* arom.), 125.7 (*C* arom.), 121.9 (d, $J_{PC}=110$, *C* arom.), 121.0 (d, $J_{PC}=13$, *C* arom.), 112.1 (d, $J_{PC}=7$, *C* arom.), 56 (*C*$H_3$O), 51.5 (d, $J_{PC}=6$, *C*$H_3$P); $^{31}$P NMR ($CDCl_3$) $\delta$ ppm: +82.2.

**4.4.4. (2*R*,4*R*,5*S*)-(−)-3,4-Dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine 2-sulfide 3e[27d]**. Major isomer: white solid; mp 84°C; $R_f$=0.35 (toluene/AcOEt 7:3); $[\alpha]_D^{20}$=−21.1 (*c* 1, $CHCl_3$); $^1$H NMR ($CDCl_3$) $\delta$ ppm, *J* Hz: 7.90 (2H, ddd, *J*=2, *J*=8, *J*=13, *H* arom.), 7.60–7.20 (8H, m, *H* arom.), 5.58 (1H, dd, *J*=4, *J*=6, PhC*H*O), 3.72 (1H, m, MeC*H*N), 2.57 (3H, d, $^3J_{PNCH}$=12, C$H_3$N), 0.85 (3H, d, $^3J_{HH}$=7, C$H_3$CH); $^{13}$C NMR ($CDCl_3$) $\delta$ ppm: 136.1 (d, $J_{PC}$=6, *C* arom.), 134.8 (d, $J_{PC}$=128, *C* arom.), 132.1 (d, $J_{PC}$=3, *C* arom.), 131.1 (d, $J_{PC}$=12, *C* arom.), 128.5–126.4 (*C* arom.), 83.5 (d, $^2J_{POC}$=4, PO*C*H), 60.0 (d, $^2J_{PNC}$=8, PN*C*H), 29.2 (d, $^2J_{PNC}$=6, PN*C*$H_3$), 13.5 (d, $^3J_{PNCC}$=3, *C*$H_3$CH); $^{31}$P NMR ($CDCl_3$) $\delta$ ppm: +94.5; HRMS (EI) calcd for $C_{16}H_{18}NOPS$ [M$^+$]: 303.0847; found: 303.0846.

Minor isomer (2*S*,4*R*,5*S*): $R_f$=0.30 (toluene/AcOEt 7:3); $^1$H NMR ($CDCl_3$) $\delta$ ppm, *J* Hz: 7.97 (2H, ddd, *J*=2, *J*=8, *J*=15, *H* arom.), 7.52–7.19 (8H, m, *H* arom.), 5.85 (1H, d, *J*=7, PhC*H*O), 3.70 (1H, m, MeC*H*N), 2.69 (3H, d, $^3J_{PNCH}$=12, C$H_3$N), 0.77 (3H, d, $^3J_{HH}$=7, C$H_3$CH); $^{31}$P NMR ($CDCl_3$) $\delta$ ppm: +95.8.

**4.4.5. (*R*p)-(−)-*N*-Methyl-*N*-[(1*R*,2*S*)-1-hydroxy-1-phenyl-prop-2-yl]aminomethylphenyl-phosphine sulfide 3g[29]**. White solid; mp 126–127°C; $R_f$=0.5 (toluene/AcOEt 8:2); $[\alpha]_D^{20}$=−1.4 (*c* 0.5, $CHCl_3$); $^1$H NMR ($CDCl_3$) $\delta$ ppm, *J* Hz: 7.59 (2H, m, *H* arom.), 7.46–7.09 (8H, m, *H* arom.), 4.75 (1H, d, *J*=5, PhC*H*O), 3.84 (1H, m, MeC*H*N), 2.46 (3H, d, $^3J_{PNCH}$=13, C$H_3$N), 1.90 (3H, d, $^2J_{PCH}$=13, C$H_3$P), 1.12 (3H, d, $^3J_{HH}$=7, C$H_3$CH); $^{13}$C NMR ($CDCl_3$) $\delta$ ppm: 142.2 (*C* arom.), 134.1 (d, $J_{PC}$=102, *C* arom.), 131.4 (d, $J_{PC}$=3, *C* arom.), 130.8 (d, $J_{PC}$=11, *C* arom.), 128.4 (d, $J_{PC}$=13, *C* arom.), 128.2–126.2 (*C* arom.), 77.6 (PO*C*H), 56.3 (d, $^2J_{PNC}$=3, PN*C*H), 29.2 (d, $^2J_{PNC}$=3, PN*C*$H_3$), 21.4 (d, $^1J_{PC}$=73, P*C* $H_3$), 12.4 (d, $^3J_{PNCC}$=2, *C*$H_3$CH); $^{31}$P NMR ($CDCl_3$) $\delta$ ppm: +66.7; HRMS (EI) calcd for $C_{17}H_{23}NOPS$ [M+H$^+$]: 320.1238; found: 320.1237.

**4.4.6. (±)-*o*-Anisylchlorophenylthiophosphoryl 3h**. White solid; mp 89°C; $R_f$=0.20 (cyclohexane/AcOEt 99:1); $^1$H NMR ($CDCl_3$) $\delta$ ppm, *J* Hz: 8.17 (1H, ddd, *J*=2, *J*=8, *J*=18, *H* arom.), 7.90 (2H, ddd, *J*=1, *J*=8, *J*=16, *H* arom.), 7.59–7.41 (4H, m, *H* arom.), 7.12 (1H, td, *J*=3, *J*=8, *H* arom.), 6.90 (1H, t, *J*=8, *H* arom.), 3.61 (3H, s, C$H_3$O); $^{13}$C NMR ($CDCl_3$) $\delta$ ppm, *J* Hz: 159.9 (d, $J_{PC}$=4, *C* arom.), 136.8 (d, $J_{PC}$=101, *C* arom.), 135.4 (d, $J_{PC}$=2, *C* arom.), 134.5 (d, $J_{PC}$=11, *C* arom.), 131.9 (d, $J_{PC}$=3, *C* arom.), 130.3 (d, $J_{PC}$=13, *C* arom.), 128.7–127.2 (*C* arom.), 122.3 (d, $J_{PC}$=96, *C* arom.), 120.6 (d, $J_{PC}$=21, *C* arom.), 112.2 (d, $J_{PC}$=7, *C* arom.), 55.7 (*C*$H_3$O); $^{31}$P NMR ($CDCl_3$) $\delta$ ppm: +78. HRMS (DCI, $CH_4$) calcd for $C_{13}H_{12}OSPCl$ [M+H$^+$]: 285.0084; found: 285.0073.

**4.4.7. (*R*)-(−)-1-(Dicyclohexylphosphino borane)-1-[2-(diphenylphosphino sulfide)ferrocenyl]ethane 3j**. Orange solid; mp 232–233°C; $R_f$=0.6 (cyclohexane/AcOEt 9:1); $[\alpha]_D^{20}$=−6.6 (*c* 0.7, $CHCl_3$); $^1$H NMR ($CDCl_3$) $\delta$ ppm, *J* Hz: 7.96–7.80 (4H, m, *H* arom.), 7.45–7.36 (6H, m, *H* arom.), 4.81 (1H, m, $C_5H_3$), 4.32 (1H, dd, *J*=2, *J*=4, $C_5H_3$), 4.11 (5H, s, $C_5H_5$), 4.04–3.89 (2H, m, $C_5H_3$, CpC*H*), 1.75 (3H, dd, *J*=7, *J*=13, C$H_3$CH), 1.7–0.6 (25H, m, $C_6H_{11}$); $^{13}$C NMR ($CDCl_3$) $\delta$ ppm, *J* Hz: 134.8 (d, $J_{PC}$=42, *C* arom.), 133.4 (d, $J_{PC}$=44, *C* arom.), 132.6 (d, $J_{PC}$=11, *C* arom.), 132.5 (d, $J_{PC}$=12, *C* arom.), 131.7 (*C* arom.), 131.6 (*C* arom.), 128.8 (d, $J_{PC}$=12, *C* arom.), 128.4 (d, $J_{PC}$=12, *C* arom.), 74.8 ($C_5H_3$), 72.9 (d, $J_{PC}$=12, $C_5H_3$), 71.8 ($C_5H_3$), 71.1 ($C_5H_5$), 69.1 (d, $J_{PC}$=11, $C_5H_3$), 32.3 (d, *J*=29), 32.2 (d, $J_{PC}$=30), 28.3–26.1, 23.8, 22.6 (d, $J_{PC}$=26); $^{31}$P NMR ($CDCl_3$) $\delta$ ppm: +40.2, +38.5 (m); HRMS (FAB) calcd for $C_{36}H_{46}BFeP_2S$ [M$^+$−H]: 639.2245; found: 639.2233; anal. calcd for $C_{36}H_{47}BFeP_2S$ (640): C, 67.50; H, 7.34; found: C, 67.27; H, 7.34.

**4.4.8. (*S*p)-(−)-*N*-Methyl-*N*-{(1*R*,2*S*)-[1-(dicyclohexylphosphinito borane)-1-phenyl]prop-2-yl}amino-*o*-anisyl phenylphosphine sulfide 3k**. White solid; mp 152–153°C; $R_f$=0.7 (cyclohexane/AcOEt 8:2); $[\alpha]_D^{20}$=−16.2 (*c* 1, $CHCl_3$); $^1$H NMR ($CDCl_3$): $\delta$ 7.8–6.8 (14H, m, *H* arom.), 5.15 (1H, t, *J*=9, PhC*H*O), 4.93 (1H, m, C*H*Me), 3.60 (3H, s, C$H_3$O), 2.47 (3H, d, $^3J_{PH}$=12, NC$H_3$), 1.40 (3H, d, $^2J_{PH}$=7, PC$H_3$), 2.1–0.6 (25H, m); $^{13}$C NMR ($CDCl_3$) $\delta$ ppm, *J* Hz: 160.3 (*C* arom.), 139.5 (*C* arom.), 135.8–127.5 (*C* arom.), 122.0–120.3 (*C* arom.), 111.5 (d, $J_{PC}$=7, *C* arom.), 111.0 (*C* arom.), 82.4 (d, $^2J_{PC}$=5, PhCHO), 55.1 (*C*$H_3$O), 54.2 (dd, $^2J$=6, $^3J$=14, N*C*H), 37.6–14.1 (*C*$H_3$CH, N*C*$H_3$, $C_6H_{11}$); $^{31}$P NMR ($CDCl_3$) $\delta$ ppm, *J* Hz: +135.8 (m), +68.1; MS (EI) *m*/*z* (relative intensity): 622 (M$^+$+H; 5), 394 (10), 362 (10), 305 (30), 304 (100), 247 (100), 215 (30), 183 (10), 91 (20); HRMS (DCI, $CH_4$) calcd for $C_{35}H_{51}BNO_2P_2S$ [M$^+$+H]: 622.3209; found: 622.3222.

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