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Asymmetric Biarylphosphanes

Benzo/Naphtho-Anellated Dihydro-1,2-oxaphosphinines and Ring-Opening to P-Tertiary 2-Phosphanyl-1,1′-biaryl-2-ol Derivatives – Syntheses and Structures

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Dedicated to Professor Dr. Marian Mikołajczyk on the occasion of his 80th birthday

Abstract: Reaction of naphthylphenol **1a** and phenylnaphthol **1b**, respectively, with PCl_3 in the presence of $ZnCl_2$ gave mixed benzo- and naphtho-anellated 6-chloro-6*H*-1,2-oxaphosphinines **2a** and **2b**. Treatment with equimolar amounts of *t*BuLi led to 6-*t*Bu-substituted mixed-anellated oxaphosphinines **3a** and **3b**, respectively, and subsequent P–O-ring cleavage with methyllithium and quenching with $ClSiMe_3$ to 2-trimethylsilyloxy-biarylphosphanes **4a** and **4b**. NMR spectra indicated two data sets for **4a** but only one for **4b**, indicating higher diastereoselectivity in the ring opening of the 1,2-oxaphosphinine **3b** with oxygen in 2-position of naphthalene and the bulkier *t*BuMeP-group at the phenyl ring. Reaction of **2b** with *o*-anisyllithium (2 equiv.) and $ClSiMe_3$ led to the biarylsilyl ether **5b**. Further conversion with (1*S*)-camphanoyl chloride gave diastereoisomers of the 2′-phosphanylbiaryl camphanate **6b**. Structures were proven by characteristic multinuclear NMR spectroscopic data and for **2a** and **5d** by crystal structure analysis. **5b** and **6b** might be useful candidates for enantiomer separation and asymmetric transition metal catalysis.

Introduction

Phosphanes are among the most suitable ligands for a wide range of homogenously transition-metal-catalyzed organic reactions.[1] The use of biarylphosphanes for this purpose has been studied intensively in the last few decades,[2–4] whereas investigations of heterocyclic biaryl-type phosphanes have remained rather scarce. The main focus was on 6*H*-dibenzo-[5–7] and 6*H*-dinaphtho[c,e][1,2]oxaphosphinines,[8] which not only provided access to various achiral and chiral ligands and their use in homogeneous catalysis but also underwent ring opening reactions to O-functionalized 1,1′-biarylphosphane ligands.[5a,9] Whereas binaphthyl compounds with OR and PR_2 substituents in 2- and 2′-position are configuratively stable,[2] the barriers for the axial rotation of *o*,*o*′-biphenyl-O,P ligands are too low to prevent atropisomerization.[10] This raises the question whether the steric hindrance to rotation around the aryl–aryl-axis might already be sufficient for *o*,*o*′-substituted 1-phenylnaphthyl-O,P compounds to suppress atropisomerization and to open the way to a diastereoselective ring-opening of benzo-naphtho-anellated 6*H*-1,2-oxaphosphinines or to kinetic resolution by O-substitution with a chiral reagent. We report here the synthesis of 6*H*-1,2-oxaphosphinines with benzo- and naphtho-anellation, the first examples of P-substitution and ring-opening reactions of these compounds with RLi-reagents to phenylnaphthyl-O,P compounds and the structure and configuration of the products.

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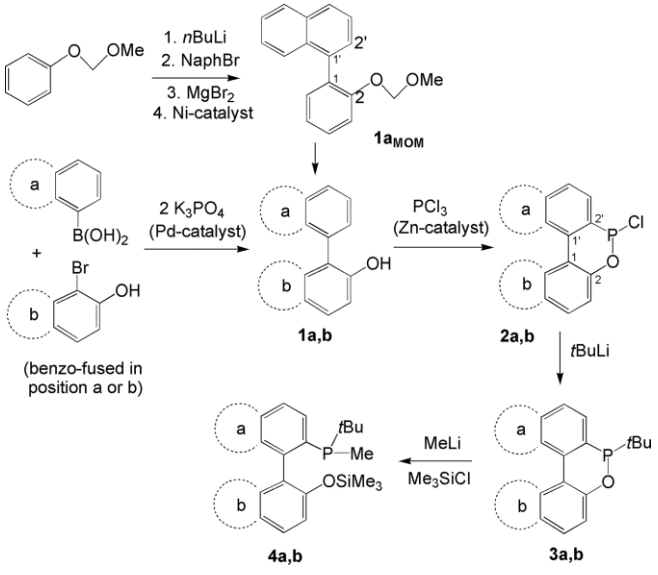
Results and Discussion

Synthesis

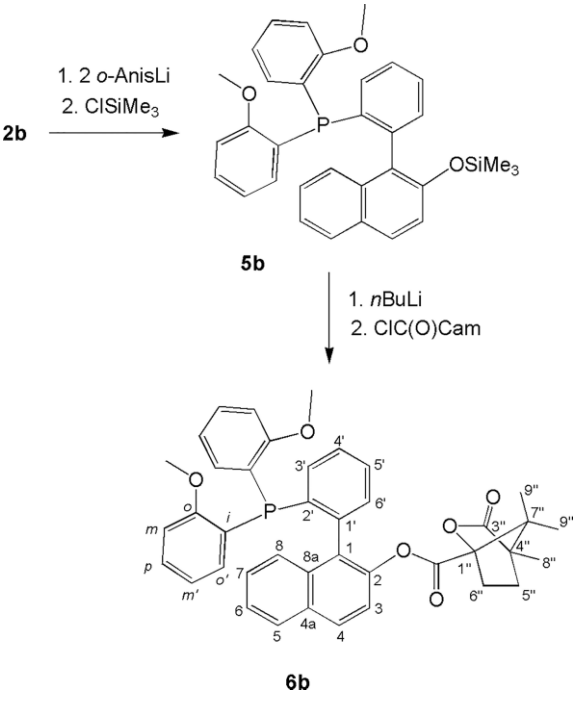
The synthesis of the mixed benzo/naphtho-anellated 6-chloro-6*H*-1,2-oxaphosphinines **2a** and **2b** was achieved by thermal condensation of naphthylphenol **1a** and phenylnaphthol **1b**, respectively, with PCl_3 in the presence of anhydrous $ZnCl_2$. Precursor **1a** was prepared initially by ortholithiation of methoxymethyl phenyl ether and Ni-catalyzed coupling with 1-bromonaphthalene in the presence of anhydrous $MgBr_2$ yielding $\mathbf{1a}_{MOM}$,[11] followed by acid-catalyzed deprotection. For repeated preparations of **2a** and for synthesis of **2b** we optimized the Suzuki–Miyaura-coupling of 2-bromophenol with 1-naphthylboronic acid and of 2-bromonaphth-1-ol with phenylboronic acid to give the products in up to 90 % yield.[12] The heterocyclic chlorophosphonites **2a** and **2b** are sensitive to hydrolysis and air oxidation but are thermally stable and can be separated

by high-vacuum distillation. Reaction with one equivalent of *t*BuLi in pentane/toluene led quantitatively to selective substitution of chloride and detection of reasonably pure crude products **3a** and **3b**, respectively. Further conversions with methyllithium and subsequently with chlorotrimethylsilane furnished the P-asymmetrically substituted 2-trimethylsiloxy-biarylphosphanes **4a** and **4b** in good to moderate yield (Scheme 1). Notably, P–O-ring cleavage with MeLi led for **3a** with *t*BuP at the naphthyl group to two pairs of diastereoisomers (δ^{31}P = –20.5, –24.2 ppm), molar ratio roughly 2:1, whereas application of the same procedure to **3b** with *t*BuP at the phenyl group provided only one pair of diastereoisomers. This may be explained by rotation of the 2-RO-phenyl group (R = Li, $SiMe_3$) across the 1,1′-bonded naphth-2-ylphosphane part of **4a** or its Li-precursor $\mathbf{4a_{Li}}$, whereas the more bulky 2-*t*BuMeP-phenyl group of **4b** or $\mathbf{4b_{Li}}$ is unable to surmount the barrier set up by the benzo-fusion and the 2-substituent at opposite sides of the RO-naphthyl fragment.



Scheme 1. Synthesis of benzo/naphtho-6*H*-1,2-oxaphosphinines **2a**,**b** and **3a**,**b** and ring opening to trimethylsiloxy-biarylphosphanes **4a**,**b**.

Reaction of the benzo/naphtho-anellated oxaphosphinine **2b** with two equivalents of *o*-anisyllithium and work-up via trimethylsilylation provided racemic dianisyl-trimethylsiloxy-naphthylphenylphosphane **5b** in good yield. To examine whether the configuratively more stable 1-phosphanylphenyl-2-naphthol derivatives can undergo enantiomer separation by esterification with a chiral acid, the silyl ether **5b** was converted with *n*BuLi and, subsequently, with (1*S*)-camphanic acid chloride to the phosphanylbiaryl camphanic acid ester **6b** (Scheme 2). The solution NMR spectroscopic data reveal a roughly 1:1 mixture of two diastereoisomers with no hint of atropisomerization to minor solution isomers as observed for related but sterically less hindered biphenyl compounds.[10b] However, all attempts at separation by crystallization have failed so far, as has growing suitable single crystals for XRD to ascertain whether co-crystallization occurs, as was observed for some of the (1*S*)-camphanoyloxy-biphenylphosphanes.[10b]



Scheme 2. Synthesis of 1-di-*o*-anisylphosphanylphenyl-naphthyl-silyl ether **5b** and -camphanic acid ester **6b**.

Structures

The structures of the mixed benzo- and naphtho-fused 2*H*-1,2-oxaphosphinines **2a**,**b** and **3a**,**b** were confirmed by characteristic ^{31}P, ^{1}H and in part (**2a**,**b**) by ^{13}C solution NMR spectroscopic data. For **2a** in-depth information was obtained by single-crystal X-ray diffraction. Solid **2a** forms twin crystals which contain one of two possible pairs of diastereoisomers (Figure 1). The molecules possess S_PS_{ax}- and R_PR_{ax}-configuration and are invers to each other. Phosphorus is pyramidal with an angle sum of 301.55(11)°. The 1,2-oxaphosphinine rings are non-planar and display an interplanar angle of the two aryl ring planes around the C1–C11 axis of 33.8°. This is close to the average of the biaryl angles observed in 6-diethylamino-6-oxo-6*H*-dibenzo[*c*,*e*][1,2]oxaphosphinine (13.7°)[6b] and 6-phenyl-6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinine–borane complex (50.7°)[8] and reflects a considerably stronger steric impact of naphtho-compared to benzo-anellation.

The solution NMR spectra of the anellated 6*H*-1,2-oxaphosphinines **2a**,**b** and **3a**,**b** also displayed only one phosphorus resonance and one set of ^{1}H and ^{13}C signals. This is consistent with two enantiomers of the four possible isomers. While the barrier to inversion at phosphorus is generally high,[13] the barrier for interconversion of the configuration at the biaryl C–C axis within the six-membered ring might be sufficiently low to allow atropisomerization and formation of equilibrium amounts of the R_PS_{ax}- and S_PR_{ax}-isomers in solution. To investigate this, VT-^{31}P and ^{1}H-NMR spectroscopic experiments were performed. In the temperature range from ca. –60 to +40 °C, however, apart from moderate upfield-shifts of some proton signals with temperature, neither a second signal set nor significant signal broadening was detectable (see Supporting Information). This

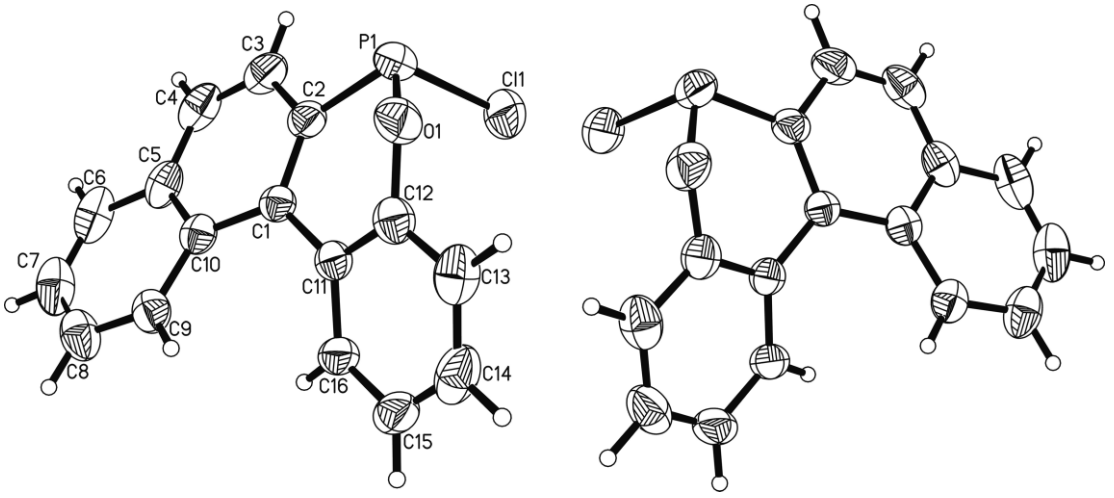


Figure 1. Molecular structure of **2a** in the twin crystal, left with S_PS_{ax}-, right with R_PR_{ax}-configuration (ellipsoids with 50 % probability). Selected bond lengths [Å] and angles [°]: P1–C2 1.792(3), O1–P1 1.623(2), Cl1–P1 2.0835(11), C1–C11 1.474(3), C1–C2 1.388(3), C2–C3 1.415(4), C3–C4 1.356(5); C2–P1–O1 99.56(11), O1–P1–Cl1 101.07(9).

suggests that, as for dinaphtho[c,e][1,2]oxaphosphinine derivatives,[8] only the R_PS_{ax}- and S_PR_{ax}-stereoisomers are formed. B3LYP/6-31G(d)-optimized calculations for the diastereoisomers of 6-chloro-6*H*-dinaphtho[c,e][1,2]oxaphosphinine show about 7 kcal/mol lower total energy, that is, higher stability, for the R_PR_{ax}- and S_PS_{ax}-diastereoisomers relative to those of the unobserved R_PS_{ax}- and S_PR_{ax}-diastereoisomers. Based on a comparison of bond lengths and angles a greater steric strain was anticipated in the latter isomers.[8]

An unambiguous structure proof of the 6*H*-1,2-oxaphosphinines **2a**,**b** and **3a**,**b** in solution was provided by characteristic $^{13}C\{^1H\}$ NMR spectroscopic data. Tentative assignments (see Scheme 1 for the numbering), based on typical chemical shift ranges and J_{PC} coupling constants, correlation with CH-COSY and HH-COSY spectra (see Supporting Information) and a CH-coupled ^{13}C NMR spectrum of **2a** are given in the experimental part. The $^2J_{PC}$ coupling constants of C-3′ (ca. 56 Hz) are remarkable, being considerably larger than $^2J_{PC}$ values for *o*-^{13}C nuclei in various types of phenylphosphanes (16-31 Hz[14]) or for ^{13}C-3′ nuclei in 2-hydroxy- or 2-camphanoyloxybiphenylphosphanes (3–6 Hz[10]) and **4b** (6.5 Hz). The $^3J_{PC}$ values for C-4′ are also somewhat increased compared to $^3J_{PC}$ values of *m*-^{13}C phenyl nuclei. It is assumed that the large $^2J_{PC}$ coupling values for C-3′ are caused by the close proximity of the P electron lone-pair[14] which is forced to this position by the chlorine atom in the axial position (cf. Figure 1). C-1′ is then remote from the P lone-pair and exhibits very small $^2J_{PC}$ couplings (0–3 Hz).

The molecular structures of the mixed benzo- and naphthoanellated 2-trimethylsilyloxy- and (1*S*)-camphanoyloxy-biarylphosphanes **4a** and **4b**–**6b** were likewise elucidated by characteristic chemical shifts and coupling constants in the ^{31}P, ^1H and ^{13}C NMR spectra. The signals were tentatively assigned by comparison with corresponding data of 2-hydroxybiphenylphosphanes[10] and **4b**, which were analyzed by HH- and CH-COSY spectra (see Supporting Information) and estimations of the chemical shifts using increment methods. Detailed information on the solid-state structure of **5b** was provided by XRD of single crystals of the toluene solvate, grown by diffusion of diethyl ether into a toluene solution. Figure 2 shows the almost perpendicular orientation of the naphthyl to the biaryl–phenyl plane in the molecule (interplanar angle 88.8°), with an *R*-configuration around the C11–C21 axis. The second molecule in the triclinic unit cell of the racemic **5b** necessarily displays the *S*-configuration. The three *o*-substituted P-phenyl groups of the depicted molecule exhibit a right turning propeller-like twisting. The P–C22 bond is longer than P–C2 in **2a** because of the lack of electronegative atoms at phosphorus and the P–C angle sum is slightly larger [303.48(6)°]. Other bond lengths and an-

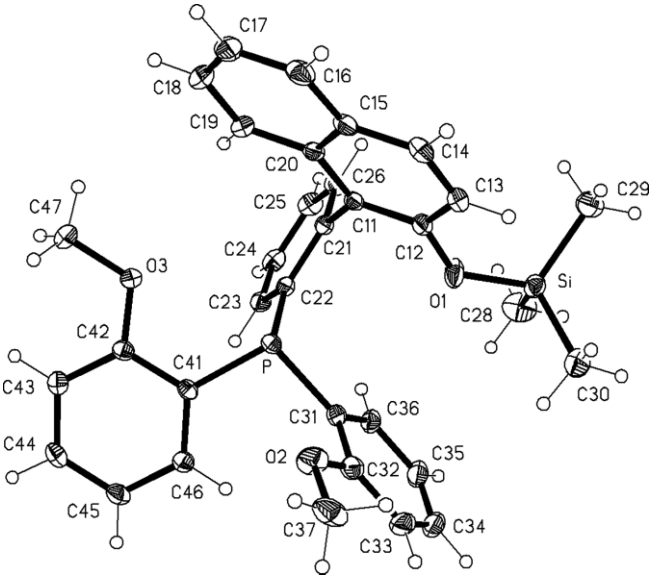


Figure 2. Molecular structure of (R_{ax})-**5b** in the crystal of *rac*-**5b** (ellipsoids with 30 % probability; solvent molecule omitted). Selected bond lengths [Å] and torsion angles [°]: P–C22 1.8353(13), P–C41 1.8398(13), P–C31 1.8416(13), C11–C21 1.4907(17), C21–C22 1.4060(17); C12–C11–C21–C22 88.23(16), C21–C22–P–C41 153.73(9), C21–C22–P–C31 103.26(10), C22–P–C41–C42 73.95(10), C22–P–C31–C32 168.50(10), C31–P–C41–C42 177.73(10), C41–P–C31–C32 86.65(11).

gles are unexceptional. The phosphorus electron lone pair is directed roughly parallel to the bond C21–C11.

Conclusions

Mixed benzo- and naphtho-fused 6-chloro-6*H*-1,2-oxaphosphinines **2a** and **2b** are available by $ZnCl_2$-catalyzed condensation and ring-closure of 2-OH-substituted 1-phenylnaphthyl compounds with PCl_3. Structural data gave evidence of exclusive or preferred formation of R_P,R_{ax}- and S_P,S_{ax}-diastereoisomers (at least for **2a**). Treatment with one equivalent of RLi allows selective substitution of chlorine. Subsequent reaction with a second equivalent of an organolithium reagent (another or the same) opens a synthetic route to the respective 2-RO-substituted biaryl-2′-phosphanes. The reaction of the oxaphosphinine **2b** with oxygen at the naphthalene ring was more diastereoselective and provided only one pair of diastereoisomers. Reaction of the Me_3SiO-biaryl-2′-dianisylphosphane **5b** with BuLi followed by (1*S*)-camphanoyl chloride furnished a diastereoisomeric mixture of the corresponding camphanoyloxybiarylphosphane **6b**. The lack of any minor atropisomeric NMR signals in solution, such as were found in related biphenyl derivatives, hints at a higher configurational stability and suggests that P,OR-biaryl derivatives of this type can be used as an alternative to binaphthylphosphane ligands in asymmetric homogeneous transition-metal-catalyzed organic reactions. First attempts at separation of the diastereoisomers of **6b** failed, possibly because of cocrystallization, as observed already for some (1*S*)-camphanoyloxybiphenylphosphanes, but further studies using other separation methods or alternative asymmetric substituents at oxygen may overcome this problem. The paper presented here paves the way for such studies and subsequent ligand screenings in (asymmetric) catalytic organic reactions.

Experimental Section

All operations were performed under argon atmosphere. Solvents were dried by standard techniques and freshly distilled before use. 2-(Naphth-1-yl)phenol (**1a**) and 1-phenyl-naphth-2-ol (**1b**) were prepared by Suzuki–Miyaura coupling of 2-bromophenol and naphthylboronic acid and 1-bromo-naphth-2-ol and phenylboronic acid,[12] respectively, **1a** also via the methoxymethyl-protected $\mathbf{1a_{MOM}}$[11] by an organometallic route (for procedure and NMR spectroscopic data see supporting information). Commercial $ClSiMe_3$ and PCl_3 were recondensed under vacuum before use. Other chemicals were used as purchased. NMR spectroscopic data were measured on a multinuclear FT-NMR spectrometer ARX 300 (Bruker) at 300.1 (^{1}H), 75.5 (^{13}C), and 121.5 (^{31}P) MHz or an AVANCE 600 (Bruker) 600.1 (^{1}H) and (^{13}C) 151 MHz, with reference to TMS and H_3PO_4 (85 %), respectively. Assignments are tentative and based on HH- and CH-COSY experiments of selected compounds, comparison of chemical shifts, P-H and P–C-coupling constants (Tables S1–S4) and supplementing increment estimations. Assignment numbers are indicated in Scheme 1 and Scheme 2 and the Supporting Information. Mass spectra (EI, 70 eV) were measured on a single-focusing sector field mass spectrometer AMD40 (Intectra). Elemental analyses were determined using a Leco CHNS-932 analyzer under standard conditions. Melting points were determined in closed capillaries under argon using a Sanyo Gallenkamp melting point apparatus and are uncorrected.

6-Chloro-*6H*-benzo[*e*]naphtho[2,1-*c*]-1,2-oxaphosphinine (6-Chloro-*6H*-5-oxa-6-phospha-benzo[*c*]phenanthrene) (2a): 2-(Naphth-1-yl)phenol (**1a**) (1.77 g, 8.04 mmol) was placed in a 25 mL flask, equipped with a reflux condenser and bubble counter at the top. Then PCl_3 (0.90 mL, 10.3 mmol) was added, the mixture slowly warmed up and refluxed at a bath temperature of 140 °C until the evolution of HCl gas stopped (about 4 h). After cooling to room temperature anhydrous $ZnCl_2$ (14 mg, 0.1 mmol) was added. The mixture was again heated slowly (45 °C/h) up to 220 °C and stirred at this temperature until HCl gas evolution ceased. Then excess PCl_3 was removed under vacuum and the product separated by high vacuum distillation (8×10^{-5} Torr/bath temperature 140–160 °C). For further purification it was recrystallized from hexane yielding 0.69 g (30 %) pale yellow twin crystals. $C_{16}H_{10}ClOP$ (284.68): calcd. C 67.51, H 3.54; found C 67.31, H 3.52. MS (EI, 70 eV, 25 °C): *m/e* (%) = 287 (1.2), 286 (19) [$M(^{37}Cl)]^+$, 285 (9), 284 (62) [$M(^{35}Cl)]^+$, 250 (16), 249 (100) [M – Cl]$^+$, 202 (35), 126 (12). ^{1}H NMR (HH-COSY) ($CDCl_3$): δ = 7.36 (superimp. td, ^3J = 7–8, ^4J = 1.4 Hz, 1 H, 5-H), 7.38 (superimp. dbr, ^3J = 7–8 Hz, 1 H, 3-H), 7.48 (td, ^3J = 7–8, ^4J = 1.6 Hz, 4-H), 7.60 (superimp. td, ^3J = 6.8, ^4J = 2 Hz, 7′-H), 7.63 (superimp. td, ^3J = 6.6, ^4J = 1.7 Hz, 1 H, 6′-H), 7.73 (dd, ^3J = 8.2, $^3J_{PH}$ = 10.2 Hz, 1 H, 3′-H), 7.94 (superimp. dd, ^3J = 8, $^4J_{PH}$ = 3.3 Hz, 1 H, 4′-H), 7.95 (superimp. dd, ^3J = 7–8, ^4J = 1–2 Hz, 1 H, 5′-H), 8.12 (dd, ^3J = 7.6, ^4J = 1.6 Hz, 1 H, 6-H), 8.62 (d br, $^3J \approx$ 7 Hz, 1 H, 8′-H) ppm. $^{13}C\{^1H\}$, (CH-COSY) and proton-coupled ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 121.03 (dd, J_{CH} = 165, 7–8 Hz, CH-3), 122.84 (d, $^3J_{PC}$ = 5.3 Hz, no or small J_{CH}, C_q-1), 123.93 (dd, J_{CH} = 162, 7–8 Hz, CH-5), 124.34 (dd, J_{CH} = 162–163, $^2J_{PC}$ = 56.1 Hz, CH-3′), 126.89 (superimp. dd, $J_{CH} \approx$ 162, 6 Hz, CH-8′), 127.15 (dd, J_{CH} = 161, 8 Hz, CH, CH-7′), 127.66 (dd, J_{CH} = 161, 8 Hz, CH-5′), 128.44 (ddd, J_{CH} = 163, 5, $^3J_{PC}$ = 14.3 Hz, CH-4′), 128.88 (superimpos. dt br, $J_{CH} \approx$ 162, 6 Hz, CH-6′), 129.28 (superimpos. s br, no or small J_{CH}, C_q-4a or C_q-1′), 129.60 (partly superimpos. dd, J_{CH} = 162, 8 Hz, CH-4), 130.44 (partly superimpos. dd, J_{CH} = 163, 7 Hz, CH-6), 130.77 (no or small J_{CH}, C_q-1′ or C_q-4a), 132.70 (ddd, J_{PC} = 38.5, J_{CH} = 8, 2.6 Hz, C_q-2′), 136.58 (d br, estimated $J_{CH} \approx$ 8, 2 Hz, no detectable J_{PC}, C_q-8a), 149.63 (dd br, $J_{CH} \approx$ 8, $^2J_{PC}$ = 6.6 Hz, C_q-2) ppm; δ-values and J_{PC} from $^{13}C\{^1H\}$ measurement. ^{31}P NMR ($CDCl_3$): δ = 132.2 ppm.

5-Chloro-*5H*-benzo[*c*]-naphtho[1,2-*e*]-1,2-oxaphosphinine (5-Chloro-5*H*-6-oxa-5-phospha-benzo[*c*]phenanthrene) (2b): 1-Phenyl-naphth-2-ol (**1b**) (3.57 g, 16.2 mmol) and PCl_3 (2.0 mL, 22.9 mmol) were slowly heated in a silicone bath and refluxed at 140 °C until the evolution of HCl gas ceased (about 4 h). After cooling to room temp. $ZnCl_2$ (21 mg, 0.15 mmol) was added to the mixture, the heating procedure repeated and excess PCl_3 removed under vacuum (cf. above). High vacuum distillation (8.7×10^{-5} Torr/bath temperature 200 °C) gave 2.45 g (53 %) of a slightly yellow viscous liquid, which solidified on storage and was subsequently recrystallized from hexane. $C_{16}H_{10}ClOP$ (284.68): calcd. C 67.51, H 3.54; found C 67.24, H 3.62. ^{1}H NMR (HH-COSY, $CDCl_3$): δ = 7.39 (dd, ^3J = 8.7, J = 0.7 Hz, 1 H, 3-H), 7.50 (superimp. td, ^3J = 7.0, ^4J = 1.2 Hz, 1 H, 6-H), 7.52 (superimp. tdd, ^3J = 7.5, $^4J_{PH}$ = 2.6, ^4J = 1.1 Hz, 4′-H), 7.58 (superimp. td, ^3J = 8.4, 6.9, ^4J = 1.5 Hz, 7-H), 7.68 (tdd, ^3J = 7.9, 7.6, ^4J = 1.5, J = 0.5 Hz, 1 H, 5′-H), 7.84 (superimp. dddd, $^3J_{PH}$ = 11.9, ^3J = 7.5, ^4J = 1.5, J = 0.5 Hz, 1 H, 3′-H), 7.87 (superimp. d, ^3J = 8.7 Hz, 1 H, 4-H), 7.91 (dd, ^3J = 7.6, ^4J = 1.4 Hz, 1 H, 5-H), 8.23 (d br, ^3J = 8.1 Hz, 1 H, 6′-H), 8.60 (d br, J = 8.4 Hz, 1 H, 8-H) ppm. $^{13}C\{^1H\}$ NMR (CH-COSY, DEPT. $CDCl_3$): δ = 118.86 (d, ^3J = 7.5 Hz, C_q-1), 120.30 (d, ^3J = 1.7 Hz, CH-3), 125.11 (CH-6), 125.71 (CH-8), 127.11 (CH-7), 127.25 (d, ^3J = 14.7 Hz) (CH-4′), 128.86 (CH-5), 129.28 (^3J = 1.1 Hz, CH-6′), 129.9 (d, ^2J = 55.6 Hz, CH-3′), 130.26 (C_q-4a), 130.78 (^4J =

1.1 Hz, CH-4), 130.92 (^2J = 3.1 Hz, C_q-1′), 131.87 (C_q-8a), 131.95 (CH-5′), 135.05 (d, ^1J = 34.7 Hz, C_q-2′), 147.12 (^2J = 8.3 Hz, C_q-2) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 128.6 ppm.

2-(*tert*-Butylmethylphosphanyl)naphth-1-yl-phenyl Trimethylsilyl Ether (4a) via 6-*tert*-Butyl-*6H*-benzo[*e*]-naphtho[2,1-*c*]-1,2-oxaphosphinine (3a): i) A solution of *t*BuLi in pentane (1.8 mL, 1.5 M, 2.70 mmol) was added dropwise at –90 °C to a solution of **2a** (0.764 g, 2.68 mmol) in toluene (20 mL). The mixture was warmed slowly to room temperature with stirring overnight, giving a pale yellow, later pale brown, solution. NMR monitoring of a sample (after removal of volatiles) indicated quantitative conversion of **2a** to **3a**. ^1H NMR ($CDCl_3$): δ = 0.84 (d, $^3J_{PH}$ = 13.0 Hz, 9 H, CMe_3), 7.15 (td, ^3J = 7–8, ^4J = 1.4 Hz, 1 H, 5-H), 7.21 (d br, $^3J \approx$ 8 Hz, 1 H, 3-H), 7.33 (td, ^3J = 8.3, 7.4, ^4J = 1.7 Hz, 1 H, 4-H), 7.48 (t, ^3J = 8.4 Hz, 1 H, 6′-H or 7′-H), 7.51–7.57 (m, 2 H, napth-H), 7.80 (dd, ^3J = 8.2, ^4J = 2.2 Hz, 1 H, 4′-H or 5′-H), 7.87 (superimp. dd, ^3J = 7.5, ^4J = 1.6 Hz, 1 H, 6-H), 7.87–7.93 (superimp. m, 1 H, 3′-H), 8.44–8.53 (m, 1 H, 8′-H) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 109.0 ppm.

ii) The solution of crude **3a** was cooled to –90 °C, an ether solution of MeLi (1.9 mL, 1.6 M, 3.04 mmol) was added and the reaction mixture warmed slowly to room temp. (12 h). NMR monitoring indicated P-methylation with ring cleavage to the respective lithium 2-phosphanylnaphthyl-phenolate (δ ^{31}P = –21.2, –23.2, 3:2 ppm). Then $ClSiMe_3$ (1.0 mL, 7.9 mmol) was added. After stirring for 3 h the precipitate was filtered off, washed with diethyl ether, and the solvent and excess $ClSiMe_3$ were removed under vacuum. The residue was distilled at 10^{-5} Torr/bath temperature 190 °C to give 677 mg (64 %) of a mixture of two diastereoisomers A and B (ca. 2:1) of **4a** as a viscous pale yellow liquid. (The product is oxidized by air to a solid, which is almost insoluble in ether. Contamination by this oxide after unintended air contact can be removed from ether solutions of **4a** by filtration to give pure **4a**.) $C_{24}H_{31}O_4PSi$ (394.56); found by MS (EI, 70 eV, 275 °C): *m/e* (%) = 395 (2.5), 394 (9) [M^+], 337 (7), 306 (21), 305 (100), 261 (11), 249 (36), 74 (42). ^1H NMR ($CDCl_3$): δ = –0.28 (s, 9 H, $SiMe_3$, A), –0.09 (s, 9 H, $SiMe_3$, B), 0.90 (d, $^3J_{PH}$ = 11.7 Hz, 9 H, CMe_3, A, B), 1.31 (d, $^2J_{PH}$ = 6 Hz, 3 H, Me, B), 1.33 (d, $^2J_{PH}$ = 5.7 Hz, 3 H, Me, A), 6.86 (dd, ^3J = 8.0, ^4J = 1 Hz, 1 H, 3-H, B), 6.97 (dd, ^3J = 8.0, ^4J = 1.0 Hz, 1 H, 3-H, A), 7.07 (td, ^3J = 7.5, ^4J = 1.1 Hz, 1 H, 5-H, A), 7.10 (td, ^3J = 7.4, ^4J = 1 Hz, 1 H, 5-H, B), 7.24 (dd, ^3J = 7.3, ^4J = 1.8 Hz, 1 H, 6-H, A), 7.27 (dd, ^3J = 7.4, ^4J = 1.7 Hz, 1 H, 6-H, B), 7.34 (superimp. tt, $^3J \approx$ 8, 7, ^4J = 1.4 Hz, 1 H, 4-H, A,B), 7.37 (superimp. t, $^3J \approx$ 7.7 Hz, 1 H, 7′-H, A,B), 7.45 (superimp. m, 4′-H, A,B), 7.48 (superimp. t br, ^3J = 8.4, 8 Hz, 1 H, 6′-H, A,B), 7.69 (dd, ^3J = 8.5, ^4J = 1.9 Hz, 1 H, 5′-H, A,B), 7.83 (superimp. dd, ^3J = 8.5, $^3J_{PH}$ = 6.8 Hz, 1 H, 3′-H, A, B), 7.86 (superimp. d br, ^3J = 7.7 Hz, 1 H, 8′-H, A, B) ppm; assigned tentatively by comparison with $\mathbf{1a_{MOM}}$ and other related compounds (Table S1). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = –20.5, –24.2 (integrals A:B 63:37) ppm.

***rac*-1-(2-*tert*-Butylmethylphosphanyl)phenyl-naphth-2-yl Trimethylsilyl Ether (4b) via 5-*tert*-Butyl-5*H*-benzo[*c*]-naphtho-[1,2-*e*]-1,2-oxaphosphinine (3b):** i) A solution of *t*BuLi in pentane (2.5 mL, 1.5 M, 3.75 mmol) was added dropwise at –90 °C to a solution of **2b** (1.06 g, 3.72 mmol mmol) in toluene (20 mL). The mixture was warmed slowly to room temperature with stirring overnight to give a pale brown solution. NMR monitoring indicated quantitative conversion of **2b** to **3b**. ^1H NMR ($CDCl_3$): δ = 0.90 (d, $^3J_{PH}$ = 13.5 Hz, 9 H, CMe_3), 7.33 (d, ^3J = 8.8 Hz, 1 H, 3-H), 7.44 (td, ^3J = 8.0, 6.8, ^4J = 1.2 Hz, 1 H, 6-H), 7.46 (tdd, ^3J = 7.5, $^4J_{PH}$ = 1.8, ^4J = 1.3 Hz, 4′-H), 7.53 (td, ^3J = 8.4, 6.8, ^4J = 1.5 Hz, 7-H), 7.57 (td, ^3J = 7.9, 7.6, ^4J = 1.5 Hz, 1 H, 5′-H), 7.63 (dddd, $^3J_{PH}$ = 10.6, ^3J = 7.43, ^4J = 1.4, J = 0.5 Hz, 1 H, 3′-H), 7.78 (d, ^3J = 8.7 Hz, 1 H, 4-H), 7.87 (ddd, ^3J = 8.0, ^4J = 1, J = 0.5 Hz, 1 H, 5-H), 8.09 (ddd, ^3J = 8.0, $^4J \approx J$ = 0.5 Hz, 1 H, 6′-H), 8.51 (d br, J = 8.6 Hz, 1 H, 8-H) ppm; superimposed aryl proton signals assigned by comparison with data of **2b** (see Table S3 and Figure S3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 106.9 ppm.

ii) The solution of crude **3b** was cooled to –90 °C, an ether solution of MeLi (2.6 mL, 1.6 M, 4.16 mmol) was added and the reaction mixture warmed to room temperature overnight. NMR monitoring indicated P-methylation with ring cleavage to the corresponding lithium 2-phosphanylphenylnaphtholate , δ ^{31}P = –22.9 (vbr) ppm. Then $ClSiMe_3$ (1.0 mL, 8.0 mmol) was added. After stirring for 3 h the precipitate was filtered off and washed with diethyl ether. The volatiles were removed under vacuum. Slow diffusion of hexane into a THF solution of the viscous pale yellow residue provided 0.67 g (46 %) of pale yellow crystals of **4b**. $C_{24}H_{31}OPSi$ (394.56): calcd. C 73.06, H 7.92; found C 73.36, H 8.14 %. MS (EI, 70 eV, 275 °C): *m/z* (%) = 395 (4.5), 394 (17) [M^+], 337 (11), 306 (23), 305 (100), 292 (12), 249 (41), 233 (11), 146 (12), 73 (47), 57 (34). ^1H NMR and HH-COSY ($CDCl_3$): δ = 0.16 (s, 9 H, $SiMe_3$), 0.90 (d, $^3J_{PH}$ = 12.0 Hz, 9 H, CMe_3), 1.15 ($^2J_{PH}$ = 5.5 Hz, 3 H, PMe), 7.06–7.11 (m, 1 H, 8-H), 7.12 (d, ^3J = 8.8 Hz, 1 H, 3-H), 7.14–7.20 (m, 1 H, 3′-H), 7.24–7.29 (superimp. m, 1 H, 6-H), 7.27–7.32 (superimp. m, 1 H, 7-H), 7.39–7.45 (m, 2 H, 5′-H, 4′-H), 7.67–7.73 (m, 1 H, 6′-H), 7.76 (d, ^3J = 8.6 Hz, 1 H, 4-H), 7.76–7.82 (m, 1 H, 5-H) ppm. $^{13}C\{^1H\}$ NMR, DEPT135 and CH-COSY ($CDCl_3$): δ = 0.67 ($SiMe_3$), 7.66 (d, ^1J = 19.9 Hz, PMe), 27.48 (d, ^2J = 15.1 Hz, P*C*Me_3), 28.86 (d, ^1J = 13.6 Hz, P*C*Me_3), 120.02 (CH-3), 123.27 (CH-6), 125.38 (J = 2.9 Hz, CH-8), 125.94 (CH-7), 126.43 (CH-5′), 127.88 (CH-5), 128.06 (d, ^3J = 6.7 Hz, C_q-1), 128.47 (CH-4′), 128.54 (C_q-4a), 128.64 (CH-4), 131.55 (^2J = 6.5 Hz, CH-3′), 132.17 (^3J = 3.4 Hz, CH-6′), 134.56 (^4J = 2.9 Hz, C_q-8a), 138.58 (J = 21.0 Hz, C_q-2′ or C_q-1′), 144.46 (d, J = 33.5 Hz, C_q-1′ or C_q-2′), 150.15 (C_q-2) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = –23.1 ppm.

1-(Di-*o*-Anisylphosphanyl)phenyl-naphth-2-yl Trimethylsilyl Ether (5b): A pentane solution of *t*BuLi (12.8 mL, 1.5 M, 19.2 mmol) was added to 2-bromoanisole (3.54 g, 18.9 mmol) in diethyl ether (20 mL) at –70 °C. The mixture was warmed to room temperature. After 2 h the resulting *o*-anisyllithium solution was added at –90 °C to a solution of **2b** (2.45 g, 8.61 mmol) in THF (30 mL), the mixture warmed to room temp. and stirring continued overnight. Then $ClSiMe_3$ (2.5 mL, 19.7 mmol) was added (10 °C). After 2 h at room temp., the solvent was removed under vacuum. Dry toluene was added (30 mL) to the residue, the insoluble lithium salt was filtered off, and the solvent was evaporated under vacuum and warming yielding 3.95 g (85 %) of pale yellow crude product. $C_{33}H_{33}O_3PSi$ (536.67): calcd. C 73.85, H 6.20; found C 73.61, H 6.53. Crystals of the toluene solvate were obtained by overlayering the toluene solution with diethyl ether. Selected bond lengths and torsion angles determined by XRD are presented in Figure 2, crystal data in Table 1. MS (EI, 70 eV, 230 °C): *m/e* (%) = 538 (3), 536 (63) [M^+], 464 (6), 463 (8) 448 (34), 447 (100), 401 (8), 74 (24). ^1H NMR ($CDCl_3$): δ = 0.01 (s, 9 H, $SiMe_3$), 3.43 (s, 3 H, OMe), 3.59 (s, 3 H, OMe), 6.59 (dd, ^3J = 8.2, $^4J_{PH}$ = 4.6 Hz, 1 H, *m*-H), 6.68–6.76 (m, 2 H, anisyl-H), 6.81 (dd, ^3J = 8.2, $^4J_{PH}$ = 4.5 Hz, 1 H, *m*-H), 6.82–6.90 (m, 2 H, anisyl-H), 7.02 (d, ^3J = 8.8 Hz, 1 H, 3-H), 7.05–7.55 (m, 9 H, aryl-H), 7.70 (d, ^3J = 8.8 Hz, 1 H, 4-H), 7.73 (d, ^3J = 7.7 Hz, 1 H, aryl-H) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$): δ = 0.55 ($SiMe_3$), 55.07, 55.36 (2s, *o*-OMe), 109.89 (superimp. d, $^3J \leq$ 12 Hz, 2 CH-*m*), 120.30 (CH-3), 120.69, 120.96 (2s, CH-*m*′), 123.07 (CH-6), 125.30 (br., CH-8), 125.5 (br., 2 C_q-*i*), 126.06 (CH-7), 126.98, 127.38, 128.06 (CH-4′, CH-5′, CH-5), 128.19 (C_q-4a), 128.64 (CH-4), 129.05 (d, ^2J = 6.3 Hz, C_q-1), 129.50, 129.55 (2s, 2 CH-*p*), 131.24 (d, ^2J = 6.3 Hz, CH-3′), 134.05–134.25 (superimp. signals, 2 CH-*o*′, C_q-8a, C_q-2′ or C_q-1′), 135.00 (d, ^3J = 2.8 Hz, CH-6′), 143.16 (d, J = 34.3 Hz, C_q-1′ or C_q-2′), 150.55 (d, ^3J = 1.8 Hz, C_q-2), 161.17 (d, ^2J = 16.1 Hz, C_q-*o*), 161.44 (d, ^2J = 15.4 Hz, C_q-*o*) ppm; assignment

tentatively by comparison with data of **4b** (Table S4). $^{31}P\{H\}$ NMR ($CDCl_3$): δ = –34.6 ppm.

Camphanic Acid 1-(Di-*o*-anisylphosphanyl)phenyl-naphth-2-yl Ester (6b): A solution of *n*BuLi in hexane (0.7 mL, 1.6 M, 1.1 mmol) was added dropwise to a cold (–85 °C) solution of **5b** (0.564 g, 1.05 mmol) in THF (8 mL). The mixture was warmed to room temperature and stirred for 2 h. Then, after cooling again to –85 °C, a solution of (1*S*)-camphanoyl chloride (0.24 g, 1.1 mmol) in THF (4 mL) was added, followed by warming to room temp. and removal of the solvent under vacuum after 1 d. The product was dissolved in toluene and LiCl extracted with water (3 × 2 mL). The organic layer was dried with anhydrous magnesium sulfate, filtered and the solution concentrated under vacuum to give 0.65 g (96 %) of solid crude product, containing two pairs of diastereoisomers (ca. 1:1). Attempts at diastereoisomer separation by crystallization from toluene/diethyl ether or toluene/hexane failed. $C_{40}H_{37}O_6P$ (644.96): calcd. C 74.52, H 5.78; found C 74.62, H 6.06. ^1H NMR ($CDCl_3$): δ = 0.64, 0.70, 0.88, 0.91 (4s, 6 H, 2 9′′-Me), 1.06 (s, 3 H, 8′′-Me), 1.55–2.20 (m, 2 5′′-H, 2 6′′-H), 3.53, 3.55, 3.56, 3.57 (4s, 6 H, OMe), 6.68–6.95 (m, 6 H, anisyl-H), 7.11 (d, ^3J = 8.8 Hz, 3-H), 7.14 (d, ^3J = 8.8 Hz, 3-H), 7.14–7.42 (m, 10 H, aryl-H), 7.81 (d, ^3J = 8.8 Hz, 4-H), 7.84 (d, ^3J = 8.8 Hz, 4-H) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = –34.5, –35.0 (1:1) ppm.

Crystal Structure Analysis of 2a and 5b: A crystal of **2a** was mounted on a glass fiber in inert paraffin oil. Data were recorded at 170 K on a STOE-IPDS 2 T diffractometer with graphite-monochromated Mo-K_α-radiation (λ = 0.71073 Å). The structure was solved by direct methods (SHELXT-2016) and refined by full-matrix least-squares techniques (SHELXL-2016).[15] All non-hydrogen-atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined isotropically at calculated positions using a riding model with their U_{iso} values constrained to 1.2 U_{eq} of their pivot atoms. The structure was a racemic twin. The data from a crystal of **5b**·C_7H_8 were recorded at 133 K on a Bruker SMART 1000 CCD diffractometer using Mo-K_α-radiation (λ = 0.71073 Å). The structure was refined as above but using SHELXL-97.[16] The toluene molecule was well ordered. Crystal data are summarized in Table 1.

CCDC 1558150 (for **2a**) and 1555546 (for **5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Supporting Information (see footnote on the first page of this article): Tables S1–S4 of selected ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data of the new and some closely related compounds for data correlation; Figures S1–S6 of HH- and CH-COSY NMR spectra of **2a**, **2b**,

Table 1. Crystal data and structure refinement for **2a** and **5b**.

Compound	**2a**	**5b C_7H_8**
Empirical formula	$C_{16}H_{10}ClOP$	$C_{40}H_{41}O_3PSi$
Formula weight	284.66	452.50
Temperature [K]	170(2)	133(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	orthorhombic	triclinic
Space group	$P2_12_12_1$	$P\bar{1}$
Unit cell dimensions		
a [Å]	7.6655(15)	11.3939(14)
b [Å]	9.1681(18)	12.7531(14)
c [Å]	18.750(4)	13.4758(16)
α [°]	90	73.682(4)
β [°]	90	68.328(4)
γ [°]	90	88.289(4)
Volume [Å^3]	1317.7(5)	1740.4(4)
Z	4	2
Density (calculated) [Mg/m^3]	1.435	1.200
Absorption coefficient [mm^{-1}]	0.398	0.150
F(000)	584	668
Crystal size	0.45 × 0.385 × 0.28 mm^3	0.37 × 0.25 × 0.20 mm^3
ϑ range for data collection	3.433 to 29.205°	1.67 to 30.51°
Index ranges	$-10 \le h \le 10$,	$-16 \le h \le 16$,
	$-11 \le k \le 12$,	$-18 \le k \le 18$,
	$-25 \le l \le 25$	$-19 \le l \le 19$
Reflections collected	14189	31263
Independent reflections	3572	10549
	[*R*(int) = 0.0384]	[*R*(int) = 0.0396]
Completeness	99.7 % to ϑ = 25.24°	99.4 % to ϑ = 30.00°
Absorption correction	Numerical	None
Max. and min. transmission	0.9650 and 0.7951	
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3572/0/173	10549/0/412
Goodness-of-fit on F^2	1.078	1.047
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0376,	*R*1 = 0.0430,
	*wR*2 = 0.0933	*wR*2 = 0.1110
R indices (all data)	*R*1 = 0.0487,	*R*1 = 0.0720,
	*wR*2 = 0.1052	*wR*2 = 0.1232
Absolute structure parameter	0.50(10)	–
Largest diff. peak and hole	0.303 and –0.309 e Å^{-3}	0.411 and –0.225 e Å^{-3}

4a, and **4b**; selected NMR spectra of **1a**,**b**, **2a**,**b**, **3a**,**b**, **4a**,**b**, **5b** and **6b**.

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Keywords: P,O heterocycles · Phosphanes · P ligands · Chirality · Diastereoisomers

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