ISSN 1070-4280, Russian Journal of Organic Chemistry, 2014, Vol. 50, No. 6, pp. 864–887. © Pleiades Publishing, Ltd., 2014.
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Dedicated to Full Member of the Russian Academy of Sciences O.N. Chupakhin on his 80th anniversary

Reactions of Phenylenedioxytrihalophosphoranes with Arylacetylenes: XIII.* Reaction of 5-*tert*-Butyl-2,2,2-trihalo-1,3,2λ^5-benzodioxaphospholes with Acetylenes

V. F. Mironov, A. V. Nemtarev, E. N. Varaksina, A. A. Shtyrlina, A. T. Gubaidullin, I. A. Litvinov, and A. B. Dobrynin

Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences, ul. Arbuzova 8, Kazan, 420088 Tatarstan, Russia
e-mail: mironov@iopc.ru

Received April 24, 2014

Abstract—Reactions of 5-*tert*-butyl-2,2,2-trichloro-, 2,2,2-tribromo-5-*tert*-butyl-, and 2,2-dibromo-5-*tert*-butyl-2-fluoro-1,3,2λ^5-benzodioxaphospholes with aryl- and alkylacetylenes lead to quantitative formation of 2-halo-1,2λ^5-benzoxaphosphinine 2-oxides which may be regarded as phosphorus analogs of natural heterocyclic compounds, coumarin and chromene. The major products (>70%) are 4-aryl-7-*tert*-butyl-2,6-dichloro-, 4-aryl-2-bromo-7-*tert*-butyl-, and 4-aryl-7-*tert*-butyl-2-fluoro-1,2λ^5-benzoxaphosphinine 2-oxides. Hydrolysis of these compounds and their treatment with amines gives the corresponding 2-hydroxy and 2-amino derivatives, as well as ammonium salts. The structure of some compounds was proved by X-ray analysis.

DOI: 10.1134/S1070428014060190

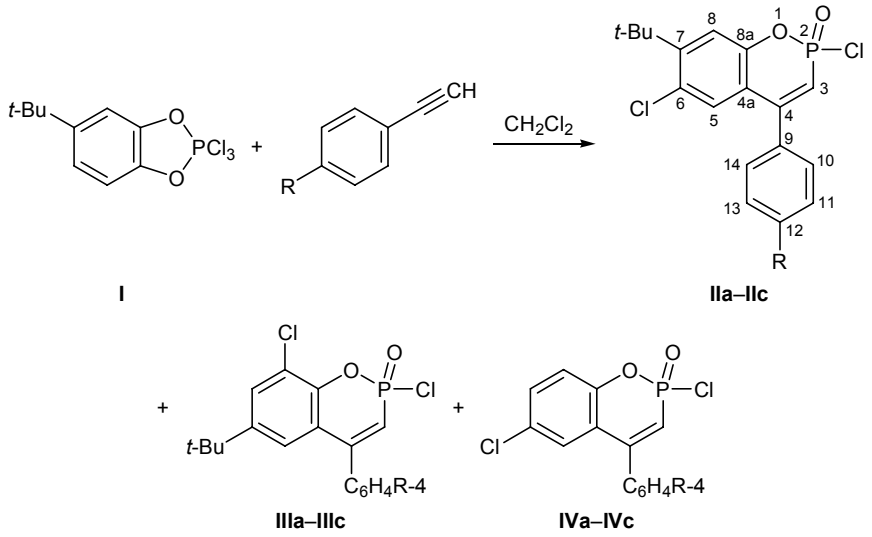
As we showed previously [2], reactions of arylacetylenes with 2,2,2-trichloro- and 2,2,2-tribromo-1,3,2λ^5-benzodioxaphospholes provide a convenient synthetic approach to 1,2λ^5-benzoxaphosphinine derivatives. The reaction direction did not change than the initial 2,2,2-trichloro-1,3,2λ^5-benzodioxaphospholes contained donor (5-methyl [3]) or acceptor substituent (5-chlorocarbonyl [4]) or halogen atoms (5-bromo, 5,6-dibromo, 4-fluoro [5–7]) in the aromatic ring; on the other hand, the regioselectivity in the substitution of oxygen atom and halogenation of the benzene ring was found to clearly depend on the substituent nature. The products of these reactions, 1,2λ^5-benzoxaphosphinine 2-oxide derivatives, were formed in high yields; they may be regarded as phosphorus-containing analogs of natural heterocycles, coumarin and chromene [8–12], whose chemical, biological, and other properties were extensively studied [13]. Therefore, interest in phosphorus analogs of coumarins appreciably increases [14–18], though these compounds remain so far difficultly accessible.

In this paper we report the results of our studies on reactions of aryl- and alkylacetylenes with 5-*tert*-butyl-2,2,2-trihalo-1,3,2λ^5-benzodioxaphospholes containing a bulky *tert*-butyl group in the *para* position with respect to one of the endocyclic oxygen atoms.

The reaction of 5-*tert*-butyl-2,2,2-trichloro-1,3,2λ^5-benzodioxaphosphole (**I**) with arylacetylenes in methylene chloride (10–20°C) was accompanied by liberation of hydrogen chloride (taking into account possible addition of the latter to multiple bond, 2 equiv of arylacetylene was used). The ^{31}P NMR spectra of the reaction mixtures contained doublets in the region δ_P 17–20 ppm with geminal coupling constants $^2J_{PH}$ of 23.4–25.5 Hz) typical of four-coordinate phosphorus derivatives, 1,2λ^5-benzoxaphosphinine 2-oxides. No possible products of classical electrophilic addition to the triple bond with unchanged configuration of the phosphorus atoms or other reaction paths were detected. The product structure was assigned by analysis of the ^{1}H, ^{13}C, and and ^{13}C–{^{1}H} NMR spectra of the product mixtures dried under reduced pressure. The reactions of **I** with arylacetylenes gave mainly (70–73%) 4-aryl-

* For communication XII, see [1].

Scheme 1.



R = H (**a**), Cl (**b**), Me (**c**).

7-*tert*-butyl-2,6-dichloro-1,2λ^5-benzoxaphosphinine 2-oxides **IIa**–**IIc** (Scheme 1).

The cyclic structure of **IIa**–**IIc** is confirmed by the presence in their $^{13}C-\{^1H\}$ NMR spectra of doublet signals from C^{4a}, C^{8a}, and C^8 (see Experimental) coupled with phosphorus, which is possible only when cyclic oxaphosphinine fragment is formed. The multiplicity of the same signals in the proton-coupled ^{13}C NMR spectrum indicated substitution at positions *6* and *7* of the heterocycle. The relative position of the *tert*-butyl group and chlorine atom introduced into the benzo fragment may be determined by comparing the chemical shifts of C^6, C^7 with account taken of substituent effects. The chlorine atom was thus localized on

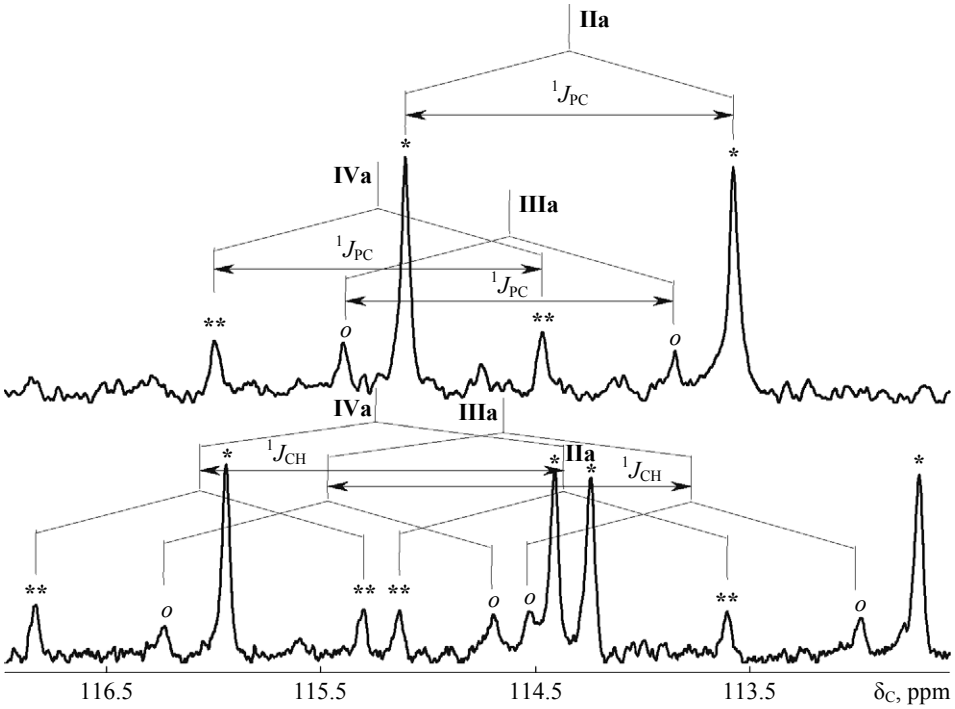
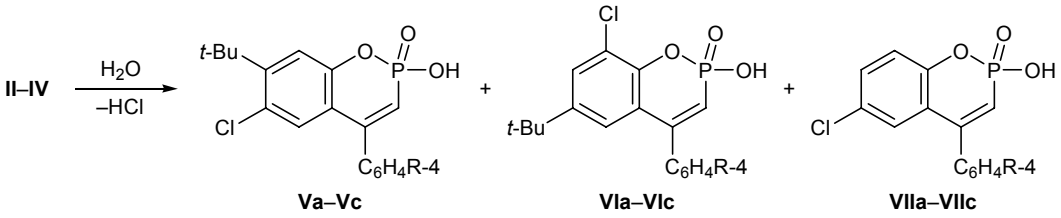


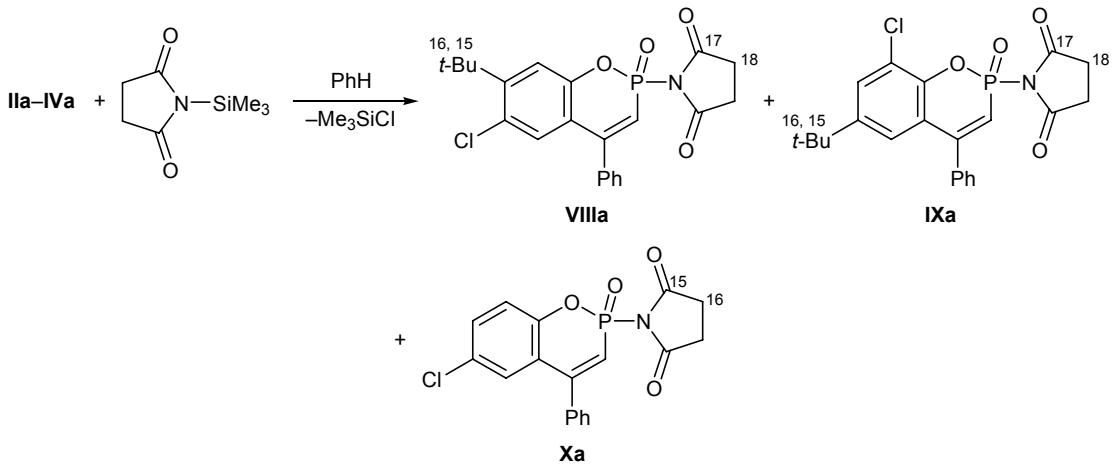
Fig. 1. Fragments of the ^{13}C and $^{13}C-\{^1H\}$ NMR spectra of the reaction mixture obtained from benzodioxaphosphole **I** and phenylacetylene (mixture of compounds **IIa**–**IVa**).

Scheme 2.



R = H (**a**), Cl (**b**), Me (**c**).

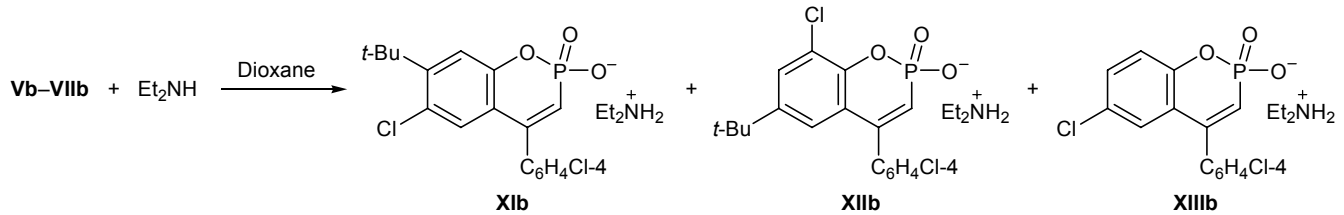
Scheme 3.



C^6. The C^3, C^4, and C^9 signals characteristically appeared in the spectrum as doublets due to coupling with the phosphorus nucleus. Figure 1 shows typical ^{13}C and $^{13}C–\{^1H\}$ NMR patterns for compounds **IIa**–**IVa** in the C^3 resonance region.

Minor 1,2λ^5-benzoxaphosphinine 2-oxides **III** and **IV** were formed at a ratio of ~1 : 1 in the reactions with phenyl- and 4-methylphenylacetylenes and at a ratio of 2 : 1 in the reaction with 4-chlorophenylacetylene. Their structure was assigned mainly on the basis of the chemical shifts of C^6 and C^8, as well as of the multiplicities of the C^{4a}, C^5, C^6, C^7, C^8, and C^{8a} signals. In the ^{13}C NMR spectrum of **IIIb**, the doublet signal of C^{4a} (δ_C 122.62 ppm, $^3J_{PC}$ = 17.7 Hz) is additionally split only into a doublet due to coupling with the 3-H proton ($^3J_{CH}$ = 8.2 Hz), indicating that the substituents are attached to C^6 and C^8. The lack of a direct $^{13}C–^1H$ coupling constant for C^8 (d.d.d, δ_C 128.83 ppm, $^3J_{PC}$ = 8.2, $^2J_{CH}$ = 5.4, $^4J_{CH}$ = 1.4 Hz) confirms the presence of chlorine in the *ortho* position with respect to the endocyclic oxygen atom. Another minor reaction path involves substitution of the *tert*-butyl group by chlorine. In our case, only the *tert*-butyl group in the *para* position to the endocyclic oxygen atom is replaced; products of substitution of the 7-*tert*-butyl group by chlorine were not detected. The ^{13}C and $^{13}C–\{^1H\}$ NMR spectra of **IVa** and **IVb** (recorded from product mixtures) were consistent with those reported for 4-aryl-2,6-dichloro-1,2λ^5-benzoxaphosphinines synthesized previously by reaction of 2,2,2-trichloro-1,3,2λ^5-benzodioxaphosphole with arylacetylenes [2]. Compound **IVc** was also synthesized independently by reaction of 2,2,2-trichloro-1,3,2λ^5-benzodioxaphosphole with 4-methylphenylacetylene.

Scheme 4.



With a view to isolating pure compounds, product mixtures **II**–**IV** were subjected to hydrolysis in benzene and, after removal of volatile compounds, were treated with diethyl ether (Scheme 2). By prolonged storage of hydroxyphosphinines **V**–**VII** in diethyl ether we succeeded in isolating crystalline cyclic hydrogen phosphonates **VII**. Their structure was confirmed by NMR spectroscopy, as well as by comparison of their spectral parameters with those given in [2]. We failed to separate isomeric compounds **V** and **VI** by crystallization from different solvents; therefore, we tried other chemical modification methods for **II**–**IV** to obtain isolable derivatives.

By treatment of mixture **IIa**–**IVa** in benzene with *N*-(trimethylsilyl)succinimide (Scheme 3) and subsequent fractional crystallization from diethyl ether we isolated compound **VIIIa** and a mixture of amides **VIIIa** and **Xa** at a ratio of 12:1; the structure of these compounds was determined by ^{13}C and $^{13}C-\{^1H\}$ NMR. Hydrogen phoshonates **Vb**–**VIIb** reacted with diethylamine to produce a mixture of ammonium salts **Xb**–**XIIb**; by fractional crystallization of the latter we succeeded in isolating pure salt **XIb** (Scheme 4).

The structure of **XIb** was proved by X-ray analysis (Fig. 2). Compound **XIb** in crystal is represented by the phosphorus-containing anion, diethylammonium cation, and one solvation water molecule. The oxaphosphinine heterocycle has a distorted *boat* conformation with the planar [within 0.001(6) Å] $O^1C^{8a}C^{4a}C^4$ four-atom fragment; the P^2 and C^3 atoms deviate from that plane toward one side by 0.803(2) and 0.400(6) Å, respectively. The negative charge is delocalized over the O^2 and O^3 atoms; the corresponding P–O bond lengths are leveled and are within the range typical of such bonds. The endocyclic bond angle at the phosphorus atom is 100.4(3)°. The chlorophenyl substituent on C^4 is turned with respect to the C^3=C^4 bond through a dihedral angle of 44(1)°, which weakens its conjugation with that π-bond.

The crystal structure of **XIb** is stabilized by classical N–H···O and O–H···O intermolecular hydrogen bonds. The hydrogen bonds N^1–H^{1b}···O^2 and N^1–H^{1a}···$O^{2'}$ link molecules **XIb** to form centrosymmetric dimers (including two anionic and two cationic species; Fig. 3). The dimers are linked through solvation water molecules by classical O–H···O hydrogen bonds, leading to infinite chains along one crystallographic axis, and these chains give rise to a layered structure with so-called chlorine channels.

Treatment of a mixture of hydrogen phosphonates **Vb**–**VIIb** with calcium oxide and subsequent crystallization afforded calcium salt **XIVb**. The 1,2-oxaphosphinine heterocycle in **VIIb** tured out to be unstable to hydrolysis in DMSO, and compound **VIIb** underwent partial opening with formation of acyclic phosphonic acid **XVb** (Scheme 5)

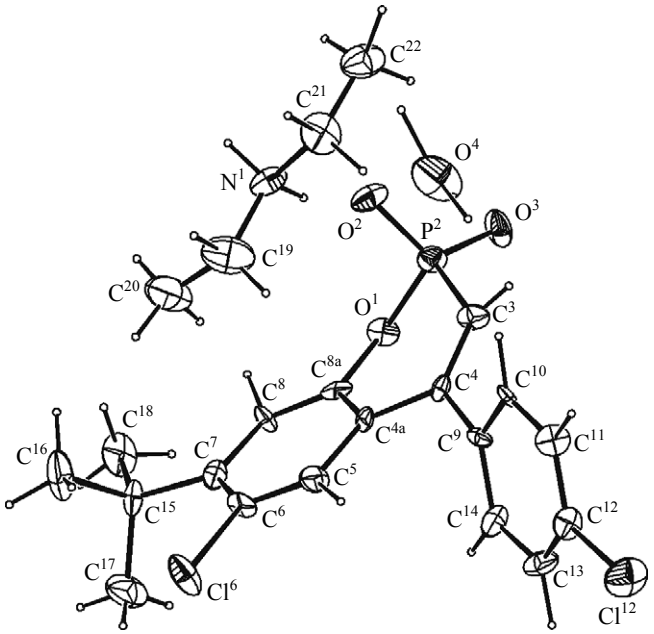


Fig. 2. Structure of diethylammonium 7-*tert*-butyl-6-chloro-4-(4-chlorophenyl)-2-oxo-1,2λ^5-benzoxaphosphinin-2-olate hydrate (**XIb**) in crystal according to the X-ray diffraction data (hereinafter, non-hydrogen atoms are shown as thermal vibration ellipsoids with a probability of 30%).

As with arylacetylenes, the reaction of benzodioxaphosphole **I** with terminal alkylacetylenes, namely pent-1-yne, hex-1-yne, and hept-1-yne, gave exclusively 1,2λ^5-benzoxaphosphinine derivatives (Scheme 6). According to the ^{31}P, ^1H, and ^{13}C NMR data, four products **XVI**–**XIX** were formed, and only three of them contained a *tert*-butyl group. As in the

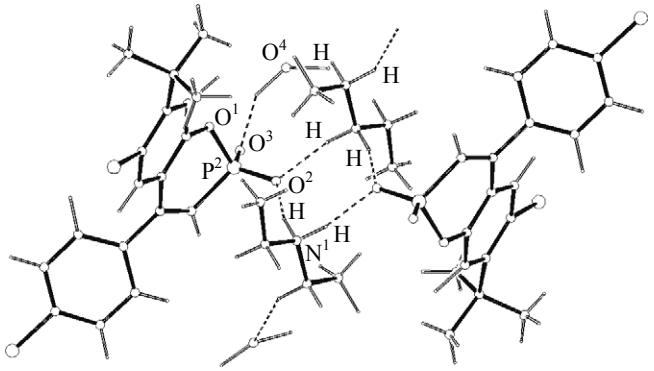
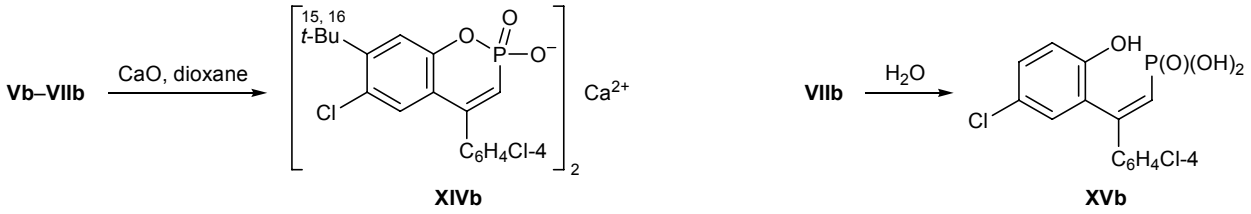
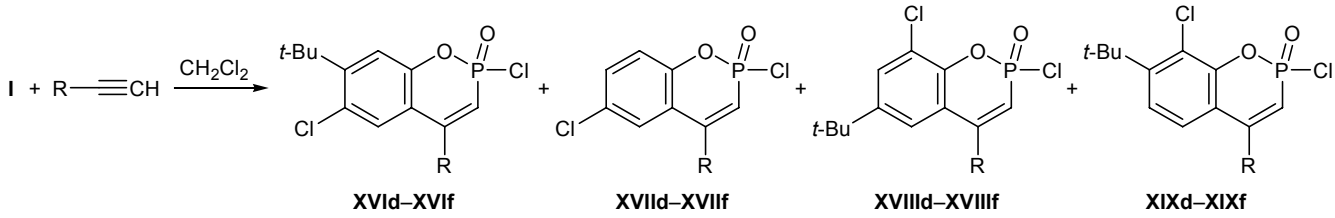


Fig. 3. Structure of centrosymmetric dimer formed by diethylammonium 7-*tert*-butyl-6-chloro-4-(4-chlorophenyl)-2-oxo-1,2λ^5-benzoxaphosphinin-2-olate hydrate (**XIb**) in crystal according to the X-ray diffraction data.

Scheme 5.

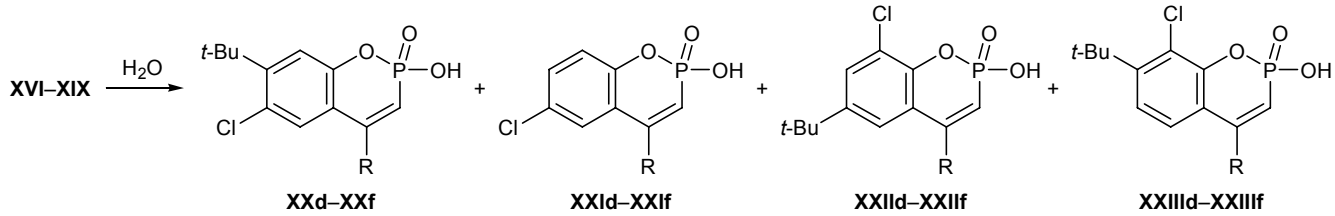


Scheme 6.



R = Pr (**d**), Bu (**e**), C_5H_{11} (**f**).

Scheme 7.



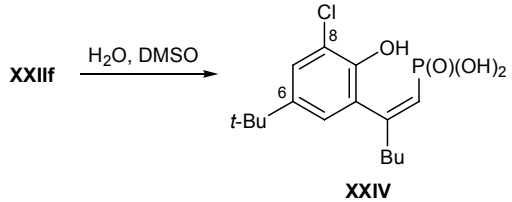
R = Pr (**d**), Bu (**e**), C_5H_{11} (**f**).

above considered reaction, the major products were 4-alkyl-7-*tert*-butyl-2,6-dichloro-1,2λ^5-benzoxaphosphinine 2-oxides **XVId**–**XVIf** with the chlorine atom occupying the *para* position with respect to the endocyclic oxygen atom. The C^8 signals of **XVId**–**XVIf** in the ^{13}C NMR spectra were doublets of doublets ($^3J_{PC}$, $^1J_{CH}$), and the C^{8a} signals, double doublets of doublets ($^2J_{PC}$, $^3J_{CH}$, $^2J_{CH}$), indicating substitution at the 6,7-positions.

The position of the *tert*-butyl group on C^7 is confirmed by the downfield shift of the C^7 resonance due to deshielding *ipso* effect of the *tert*-butyl group. Analysis of the ^{1}H and ^{13}C NMR spectra of the product mixture revealed formation of minor amounts of isomeric 6- and 7-*tert*-butyl-2,8-dichloro-4-alkyl-1,2λ^5-benzoxaphosphinine 2-oxides **XVIIId**–**XVIIIf** and **XIXd**–**XIXf**, as well as products of substitution of the *tert*-butyl group in the *para* position with respect to the endocyclic oxygen atom, 4-alkyl-2,6-dichloro-1,2λ^5-benzoxaphosphinine 2-oxides **XVIId**–**XVIIf**; the aromatic region of the ^{1}H NMR spectra of **XVIId**–**XVIIf** was typical of 1,2,4-substituted benzenes: 8-H (d, $^3J_{HH}$), 7-H (d.d, $^3J_{HH}$, $^4J_{HH}$), 5-H (d, $^4J_{HH}$).

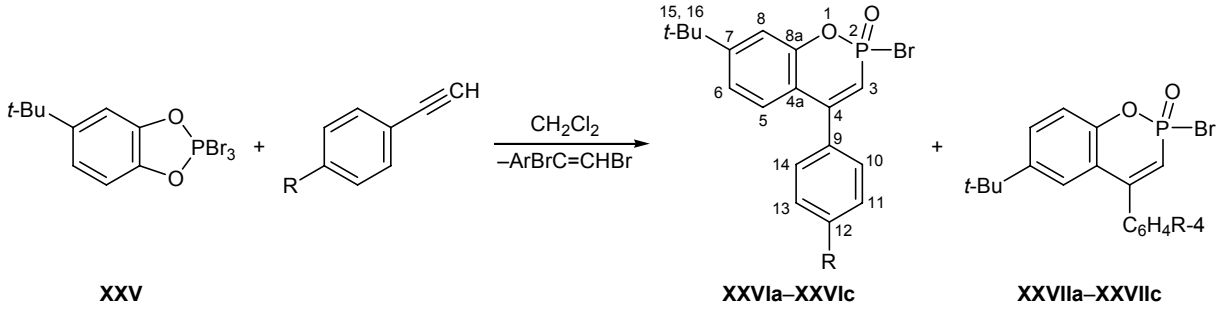
Hydrolysis of **XVI**–**XIX** with water gave mixtures of hydrogen phosphonates **XX**–**XXIII** (Scheme 7), from which pure compounds **XXIIe**, **XXIIf**, and **XXf** were isolated by fractional crystallization. Prolonged (4 months) storage of a solution of **XXIIf** in aqueous DMSO resulted in its partial (40%) conversion into phosphonic acid **XXIV** via opening of the oxaphosphinine ring (Scheme 8).

Scheme 8.



2,2,2-Tribromo-5-*tert*-butyl-1,3,2λ^5-benzodioxaphosphole (**XXV**) reacted with arylacetylenes more selectively than did trichloro analog **I**. Among two oxaphosphinine derivatives **XXVI** and **XXVII**, the major product (>80%) was 4-aryl-2-bromo-7-*tert*-butyl-1,2λ^5-benzoxaphosphinine **XXVI** (δ_P 9–10 ppm, $^2J_{PH}$ = 26.0–28.0 Hz; Scheme 9). Bromine liberated

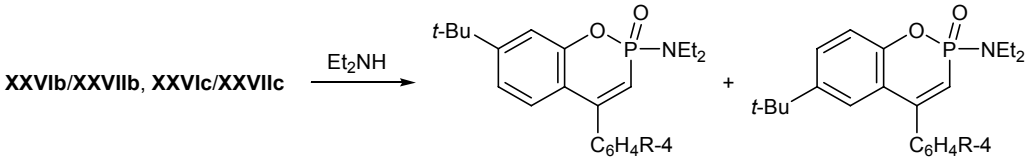
Scheme 9.



XXV **XXVIa–XXVIc** **XXVIIa–XXVIIc**

R = H (**a**), Cl (**b**), Me (**c**).

Scheme 10.



XXVIIIb, **XXVIIIc** **XXIXb**, **XXIXc**

R = Cl (**b**), Me (**c**).

during the reaction adds to the initial acetylene yielding 1-aryl-1,2-dibromoethenes. These results are consistent with the lower migrating ability of the bromine atom, which was noted previously in the reactions of 2,2,2-tribromo-1,3,2λ^5-benzodioxaphosphole with arylacetylenes [2]. However, in our case, no bromine migration was observed at all, which may be due to steric effect of the *tert*-butyl substituent. Furthermore, unlike reactions of **I** with arylacetylenes, there was no *ipso*-substitution of the *tert*-butyl group by bromine.

In the ^{13}C NMR spectra of **XXVI** the doublet signal of C^8 ($^3J_{PC}$ = 8.0–8.1 Hz) is additionally split into doublets due to couplings with 8-H ($^1J_{CH}$ = 161.5–162.0 Hz) and 6-H ($^3J_{CH}$ = 6.5–7.0 Hz). The C^8 signals of minor 6-*tert*-butyl derivatives **XXVII** were doublets of doublets with the coupling constants $^1J_{CH}$ = 164.9–165.0 and $^3J_{PC}$ = 8.1–8.3 Hz.

From 2-bromo-1,2-benzoxaphosphinines **XXVI** and **XXVII** and diethylamine we obtained amides **XXVIII** and **XXIX** (Scheme 10), and the structure of

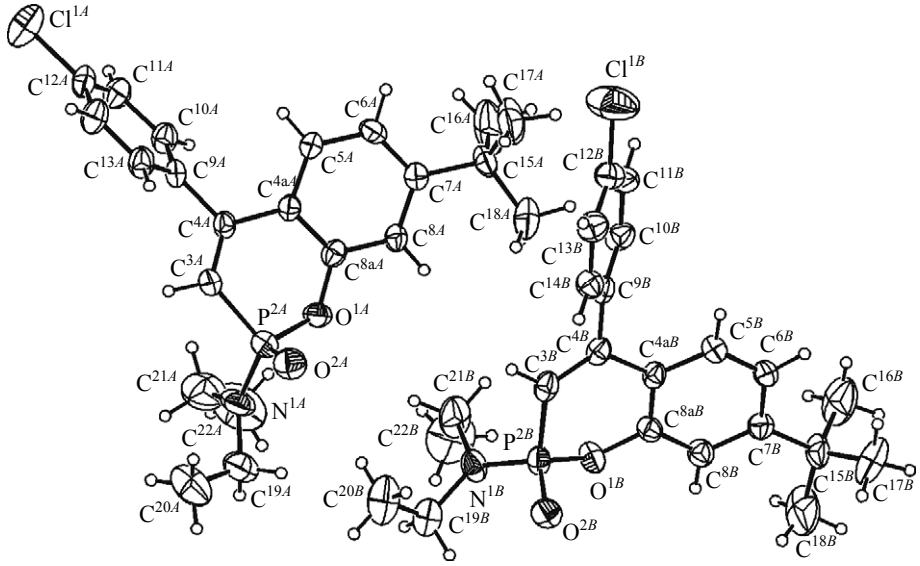


Fig. 4. Structure of two independent molecules **A** and **B** of 7-*tert*-butyl-4-(4-chlorophenyl)-2-diethylamino-1,2λ^5-benzoxaphosphinine 2-oxide (**XXVIIIb**) in crystal according to the X-ray diffraction data.

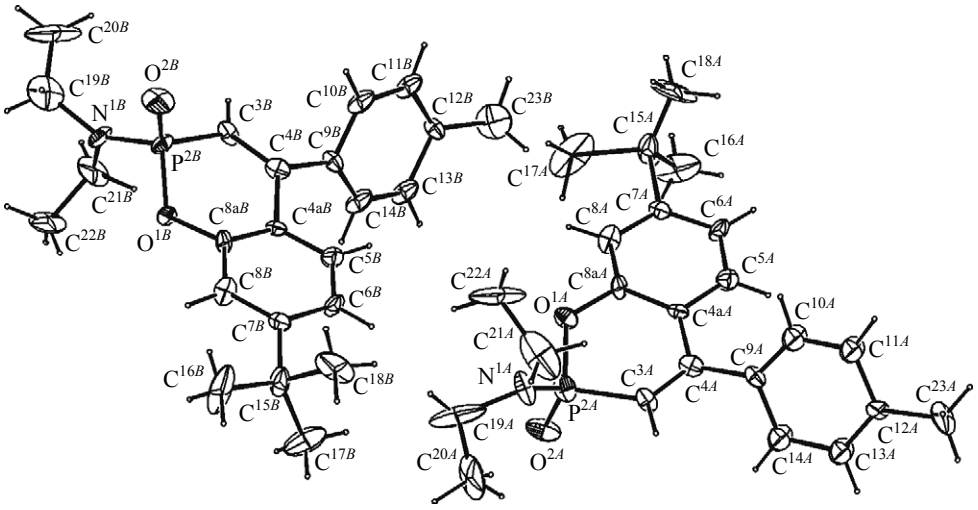
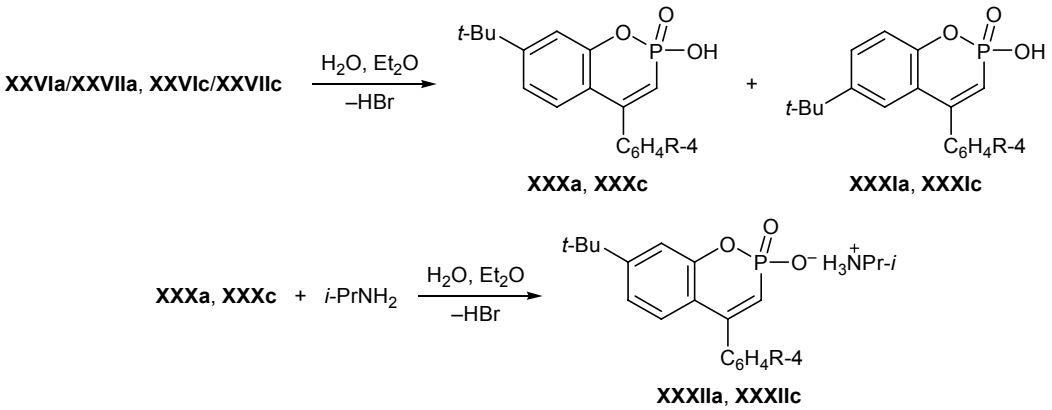


Fig. 5. Structure of two independent molecules **A** and **B** of 7-*tert*-butyl-2-diethylamino-4-(4-methylphenyl)-1,2λ^5-benzoxaphosphinine 2-oxide (**XXVIIIc**) in crystal according to the X-ray diffraction data.

XXVIIIb and **XXVIIIc** in crystal was determined by X-ray analysis. The unit cell of compound **XXVIIIb** contains two independent molecules (Fig. 4). The six-membered heterocycles in both independent molecules **A** and **B** adopt a distorted *boat* conformation with planar $O^1C^{8a}C^{4a}C^4$ and $P^2C^3C^4C^{4a}$ four-atom fragments (within 0.02 and 0.03 Å for molecules **A** and **B**, respectively); the P^2 and N^2 atoms appear at different sides with respect to the planar fragment, the corresponding deviations being –0.310(2) and 0.062(6) (**A**) and –0.324(1) and 0.072(4) Å (**B**). Intermolecular C–H···O interactions involving the phosphoryl group and diethylamine fragment give rise to cylindrical structures along the 0*c* crystallographic axis.

Amide **XXVIIIc** in crystal is also represented by two independent molecules (Fig. 5). The heterocycle in **A** and **B** contains two planar fragments $O^{1A}C^{8aA}C^{4aA}C^{4A}$ ($O^{1B}C^{8aB}C^{4aB}C^{4B}$) and $C^{4aA}C^{4A}C^{3A}P^{2A}$ ($C^{4aB}C^{4B}C^{3B}P^{2B}$) which form a dihedral angle of –22(1) (**A**) or –25(1)° (**B**) with respect to each other. The C^3 and P^2 atoms deviate from the first plane by –0.19(2) and –0.576(6) Å (**A**) and –0.18(2) and –0.542(6) Å (**B**), respectively; i.e., these atoms appear at the same side of the plane. The O^1 and C^{8a} atoms also deviate from the $C^{4a}C^4C^3P^2$ plane toward the same side but by different distances [0.53(1) and 0.29(2) Å in **A** and 0.47(1) and 0.11(2) Å in **B**]. These data suggest a distorted *boat* conformation of the oxaphosphinine heterocycle as well. The exocyclic O^2 and N^2 atoms deviate from the $O^1C^{8a}C^{4a}C^4$ plane by –2.00(1) and 0.45(2) Å in molecule **A** and by –1.94(1) and 0.39(2) Å, respectively, in molecule **B**, and the corresponding deviations from the $C^{4a}C^4C^3P^2$ plane are –1.32(1) and 1.21(2) Å in **A** and –1.31(1) and 1.14(2) Å in **B**. Thus the diethylamino group occupies equatorial position, and the phosphoryl oxygen atom is oriented

Scheme 11.



R = H (**a**), Me (**c**).

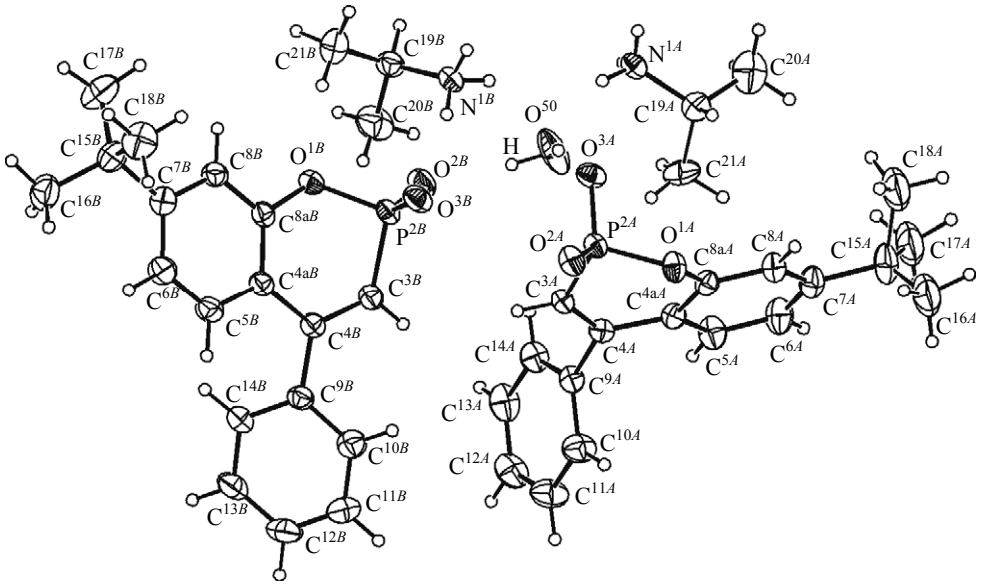


Fig. 6. Structure of two independent molecules **A** and **B** of 2-bromo-6-*tert*-butyl-4-phenyl-1,2λ^5-benzoxaphosphinine 2-oxide hydrate (**XXXIIa**) in crystal according to the X-ray diffraction data.

axially. The phenyl substituent on C^4 is turned with respect to the $C^3{=}C^4$ bond so that the torsion angle $C^3C^4C^{13}C^{17}$ is 55(2)° (mean value); therefore, conjugation between these fragments is hardly probable. The sum of the bond lengths at the nitrogen atom ($\angle P^2N^2C^{16}$, $P^2N^2C^2$, $C^2N^2C^{16}$) is 359(1)° (**A**, **B**); i.e., the nitrogen atom has a planar–trigonal configuration. The crystal packing of compound **XXVIIIc** is determined by van der Waals interactions.

Hydrolysis of mixtures of benzoxaphosphinines **XXVI** and **XXVII** (Scheme 11), followed by fractional crystallization, allowed us to separate hydrogen phosphonates **XXX** from minor isomers **XXXI**. The structure of the hydrolysis products was determined by ^{13}C NMR spectroscopy and by X-ray analysis of ammonium salt **XXXIIa** obtained from **XXXa** and isopropylamine.

Compound **XXXIIa** crystallizes as hydrate (Fig. 6), and its unit cell includes two independent phosphorus-containing anions, two isopropylammonium cations (the isopropyl group in one of which is disordered by two positions with equal populations; only one posi-

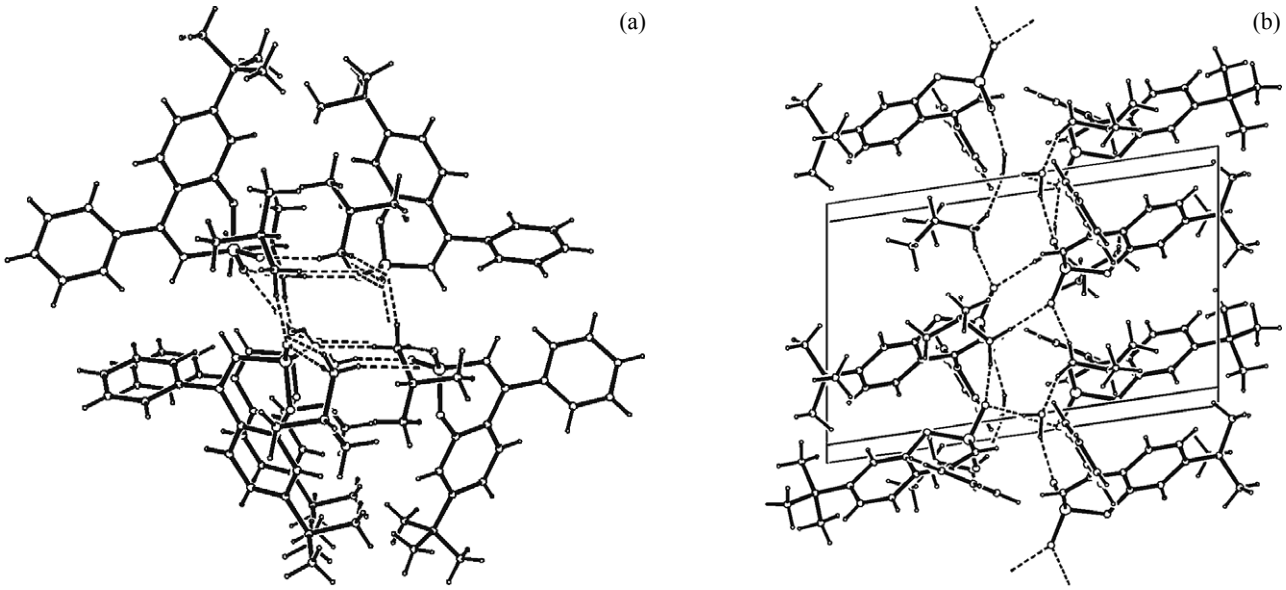


Fig. 7. Hydrogen bond system formed by 2-bromo-6-*tert*-butyl-4-phenyl-1,2λ^5-benzoxaphosphinine 2-oxide hydrate (**XXXIIa**) in crystal according to the X-ray diffraction data; views along the (a) 0*a* and (b) 0*b* axes.

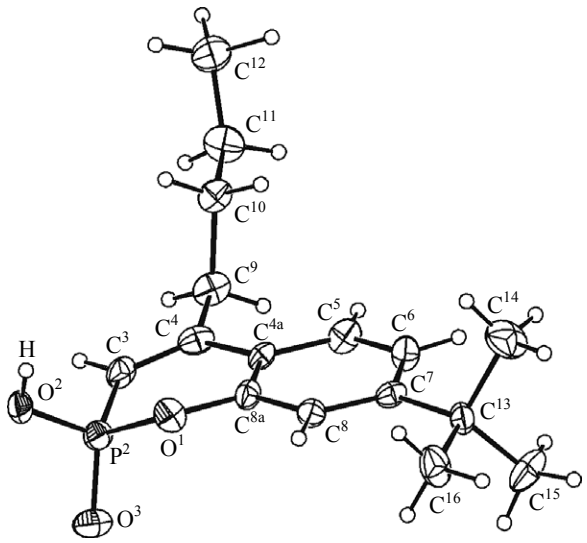


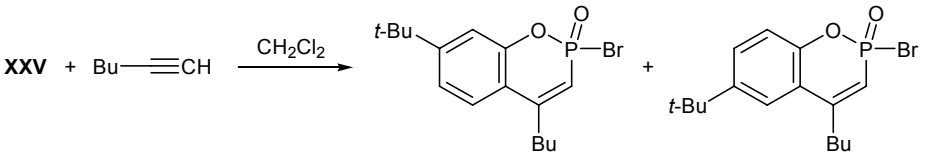
Fig. 8. Structure of the molecule of 4-butyl-7-*tert*-butyl-2-hydroxy-1,2λ^5-benzoxaphosphinine 2-oxide (**XXXV**) in crystal according to the X-ray diffraction data.

tion is shown in Fig. 6), and one water molecule. The six-membered heterocycles in both independent molecules **A** and **B** have a distrorted *boat* conformation; the $O^1C^{8a}C^{4a}C^4$ fragments are planar within 0.02 (**A**) and 0.01 Å (**B**), and the P^2 and C^3 atoms deviate from these planes toward one side by –0.722(1) and –0.330(4) (**A**) and 0.871(1) and 0.390(4) Å (**B**), respectively. Also, there is one more planar fragment, $P^2C^3C^4C^{4a}$. The P^2–O^1 bond lengths in molecules **A** and **B** do not differ from the corresponding reference values. The negative charge in the anionic species is delocalized over the O^2 and O^3 atoms, and the P^2–O^2 and P^2–O^3 bonds have similar lengths which fall into the range typical of such bonds. The endocyclic bond angle at the phosphorus atom is 100.6(2) (**A**) and 99.5(1)° (**B**).

The crystal structure of **XXXIIa** is stabilized by a hydrogen bond system involving the oxygen atoms in the anionic species and water molecules and all NH hydrogen atoms in the ammonium cations and hydrogen atoms in water molecules. The hydrogen bonds give rise to H-columns along the 0*a* crystallographic axis. The inner part of the columns contains hydrophilic parts of molecules, including ammonium cations and solvation water molecules, while the outer shell of the columns is composed of hydrophobic *tert*-butyl and aromatic fragments (Fig. 7a, b). On the whole, the crystal structure of **XXXIIa** may be represented as hexagonal packing of similar H-columns.

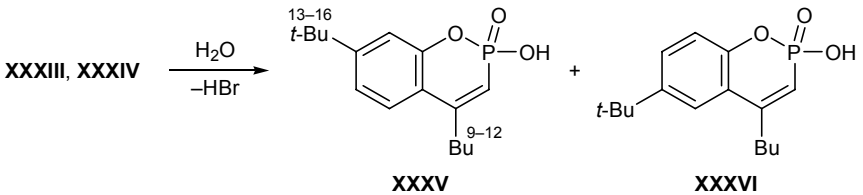
Tribromophosphorane **XXV** reacted with hex-1-yne to give two products **XXXIII** and **XXXIV** at a ratio of 2.8:1 (Scheme 12). Here, the major product was that containing *tert*-butyl group on C^7. Hydrolysis of mixture **XXXIII**/**XXXIV** and subsequent fractional crystallization afforded pure hydrogen phosphonate **XXXV** (Scheme 13). Figure 8 shows the structure of molecule **XXXV** according to the X-ray diffraction data. Like the above examined structures, the phosphorus atom in **XXXV** has a distorted tetrahedral configuration. The six-membered heteroring adopts a flattened distorted *boat* conformation with two planar fragments $C^4C^{4a}C^{8a}O^1$ and $P^2C^3S^4O^{4a}$ [within 0.017(2) and 0.006(2) Å, respectively] with the dihedral angle 11.6(1)° between them. The P^2 and C^3 atoms deviate from the first plane toward one side by –0.5466(5) and –0.235(2) Å, respectively, and the O^1 and C^{8a} atoms deviate from the second planar fragment by 0.471(2) and 0.193(2) Å respectively. These deviations are consistent with the distorted *boat* conformation of the heterocycle. The O^2 atom occupies equatorial position: the distances from O^2 to the $C^4C^{4a}C^{8a}O^1$ and $P^2C^3C^4O^{4a}$

Scheme 12.



XXXIII **XXXIV**

Scheme 13.



XXXV **XXXVI**

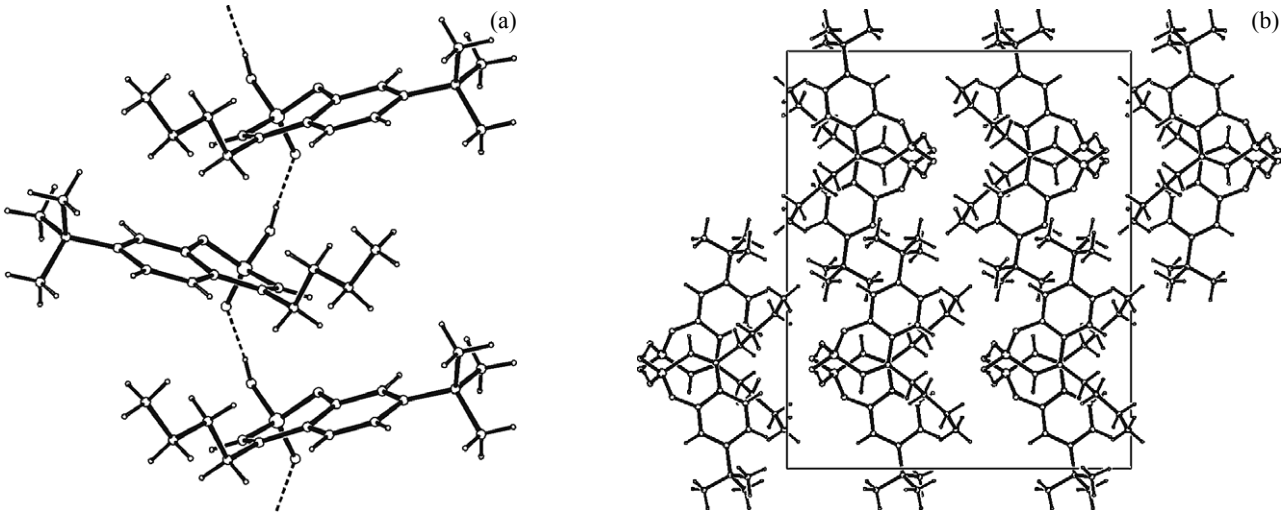


Fig. 9. Hydrogen bond system formed by molecules of 4-butyl-7-*tert*-butyl-2-hydroxy-1,2λ^5-benzoxaphosphinine 2-oxide (**XXXV**) in crystal according to the X-ray diffraction data; views along the (a) 0*b* and (b) 0*a* axes.

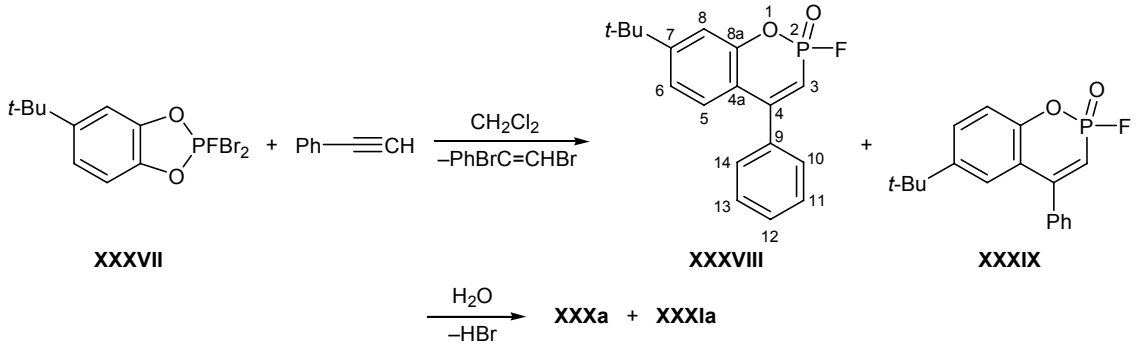
planes are 0.335(2) and 1.088(2) Å, respectively; the O^3 atom in the phosphoryl group is axial: its deviations from the $C^4C^{4a}C^{8a}O^1$ and $P^2C^3C^4O^{4a}$ planes are –1.960(2) and –1.309(1) Å, respectively.

Unlike compound **XXXIIa**, molecules **XXXV** in crystal are linked through only one classical hydrogen bond involving the phosphonate oxygen atoms and leading to formation of infinite H-bonded chains along the *0a* axis (Fig. 9a). These H-chains are packed antiparallel in a tetragonal mode (Fig. 9b) which ensures fairly high calculated packing factor (67.1%).

It was expected that replacement of one bromine atom on the phosphorus in **XXXV** by fluorine (compound **XXXVII**) should led to the formation of 1,2-benzoxaphosphinine derivatives containing bromine in the aromatic fragment, as was observed in the reaction of 2,2-dibromo-2-fluoro-1,3,2λ^5-benzodioxaphosphole with phenylacetylene [2]. However, dibromofluorophosphorane **XXXVII** reacted with phenylacetylene in methylene chloride at 10°C to produce a mixture of 7- and 6-*tert*-butyl-2-fluoro-4-phenyl-1,2λ^5-benzoxaphosphinine 2-oxides **XXXVIII** and **XXXIX** at a ratio of 3:1 (Scheme 14). The structure of **XXXVIII** and **XXXIX** was determined on the basis of their ^{13}C and $^{13}C-\{^1H\}$ NMR spectra in which the signals from these compounds were well resolved, so that their complete assignment was possible. Figure 10 shows the downfield fragments of the $^{13}C-\{^1H\}$ NMR spectrum of a mixture of compounds **XXXVIII** and **XXXIX**. Hydrolysis of the latter produced cyclic hydrogen phosphonates **XXXa** and **XXXIa**, and compound **XXXa** was isolated by fractional crystallization.

In summary, the reaction of 5-*tert*-butyl-2,2,2-trichloro-, 2,2,2-tribromo-5-*tert*-butyl-, and 2,2-dibromo-5-*tert*-butyl-2-fluoro-1,3,2λ^5-benzodioxaphospholes **I**, **XXV**, and **XXVII** with substituted acetylenes provides a convenient synthetic route to *tert*-butyl-substituted 1,2λ^5-benzoxaphosphinine 2-oxide derivatives. The presence of a bulky *tert*-butyl group in the aromatic fragment does not prevent introduction of a chlorine atom into that fragment with formation of 4-aryl-7-*tert*-butyl-2,6-dichloro-1,2λ^5-benzoxaphosphinine

Scheme 14.



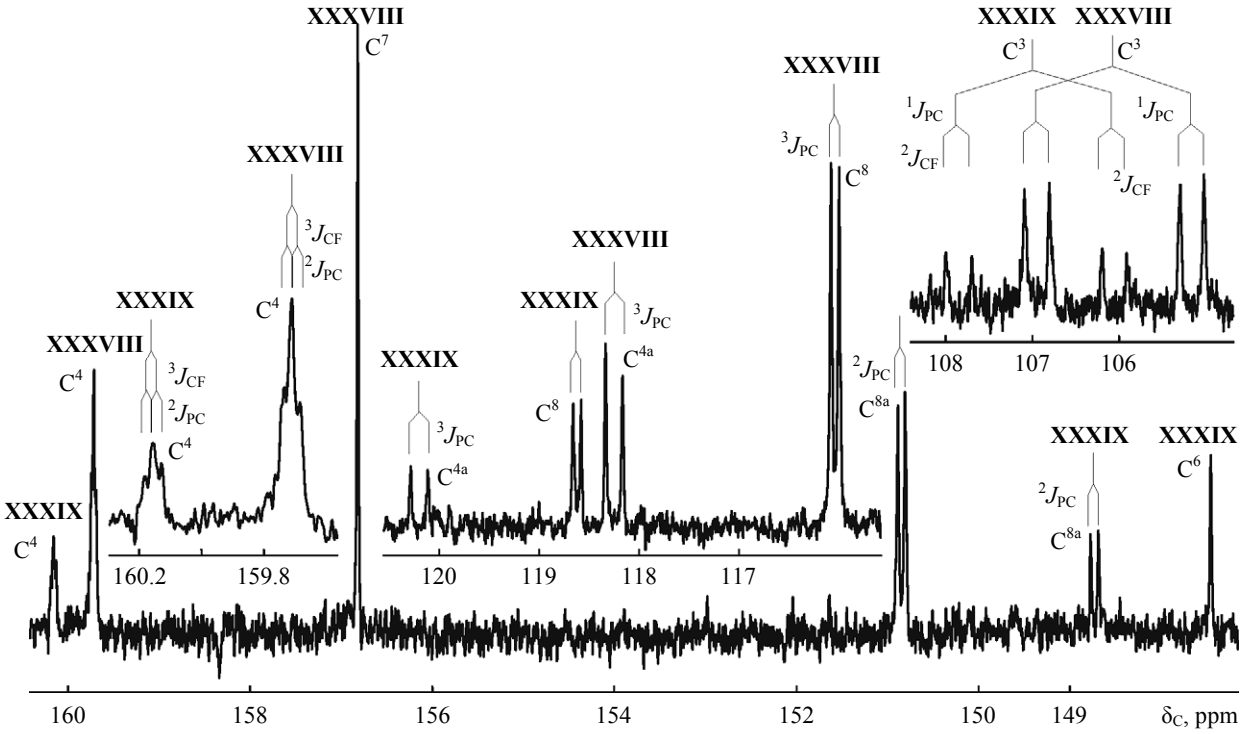


Fig. 10. Fragments of the $^{13}C–\{^1H\}$ NMR spectrum (100.6 MHz, $CDCl_3$) of a mixture of compounds **XXXVIII** and **XXXIX**.

2-oxides. The minor processes in the reactions of trichlorophosphole **I** with aryl- and alkylacetylenes are replacement of the *tert*-butyl group by chlorine to give 4-aryl-2,6-dichloro-1,2λ^5-benzoxaphosphinine 2-oxides and replacement of the oxygen atom in the *meta* position with respect to the *tert*-butyl group with subsequent chlorination of the *ortho* position relative to the endocyclic oxygen atom. The main direction in the reactions of bromobenzophospholes **XXV** and **XXXVII** with substituted acetylenes is the formation of 4-aryl-2-bromo(fluoro)-7-*tert*-butyl-1,2λ^5-benzoxaphosphinine 2-oxides having no bromine in the fused benzene ring.

EXPERIMENTAL

The ^1H, ^{13}C, $^{13}C–\{^1H\}$, ^{31}P, and $^{31}P–\{^1H\}$ NMR spectra were recorded on Bruker WM-250 (250 MHz, ^1H), Bruker MSL-400 (100.6 MHz, ^{13}C; 162.0 MHz, ^{31}P), Bruker Avance-600 (600 MHz, ^1H; 150.9 MHz, ^{13}C), Bruker Avance-400 (400 MHz, ^1H; 100.6 MHz, ^{13}C; **IIc**–**IVc**), Bruker Avance-500 (500 MHz, ^1H), and Bruker CXP-100 spectrometers (36.48 MHz, ^{31}P) at 25°C ($CDCl_3$, CH_2Cl_2) or 45°C (DMSO-d_6); the chemical shifts were determined relative to hexamethyldisiloxane (^1H, internal reference), solvent (^{13}C), or H_3PO_4 (^{31}P, external reference). The ^{13}C NMR spectra were recorded on a Bruker MSL-400 instrument using 10-mm glass ampules; otherwise, 5-mm glass ampules were used. The IR spectra were measured on UR-20, Bruker Vector-22, and Specord 75-IR instruments from samples dispersed in mineral oil. The mass spectra (electron impact, 70 eV) were obtained on Finnigan MAT TRACE MS and MKh-1310 high-resolution mass spectrometers (ion source temperature 200°C, direct sample admission into the ion source) coupled with an SM-4 computer. The mass spectra were processed using Xcalibur program.

5-*tert*-Butyl-2,2,2-trichloro-1,3,2λ^5-benzodioxaphosphole (I). 4-*tert*-Butylbenzene-1,2-diol, 33.6 g (0.20 mol), was added in portions under stirring to a solution of 51.7 g (0.25 mol) of phosphorus(V) chloride in 350 mL of benzene. After 24 h, excess PCl_5 crystallized from the solution; the liquid phase was separated by decanting, the solvent was distilled off, and the residue was distilled under reduced pressure. Yield 20 g (33%), yellowish transparent liquid, bp 168°C (0.5 mm). $^{31}P–\{^1H\}$ NMR spectrum (CH_2Cl_2): δ_P –25.3 ppm. Found, %: C 40.11; H 4.07; P 10.19. $C_{10}H_{12}Cl_{13}O_2P$. Calculated, %: C 39.80; H 3.98; P 10.28.

4-Phenyl-1,2λ^5-benzoxaphosphinine 2-oxides IIa–IVa. A solution of 4.7 mL (0.043 mol) of phenylacetylene in 5 mL of methylene chloride was added at 10–20°C in a stream of argon (which was intensely

Crystallographic parameters of compounds **XIb**, **XXVIIIb**, **XXVIIIc**, **XXXIIa**, and **XXXV** and conditions of X-ray diffraction experiments

Parameter	**XIa**	**XXVIIIb**	**XXVIIIc**	**XXXIIa**	**XXXV**
Color, habit	Colorless prismatic				
Formula	$C_{18}H_{16}Cl_2O_3P\cdot C_4H_{12}N^+\cdot H_2O$ ($C_{22}H_{30}Cl_2NO_4P$)	$C_{22}H_{27}ClNO_2P$	$C_{23}H_{30}NO_2P$	$2(C_{18}H_{18}O_3P^-)\cdot 2(C_3H_{10}N^+)\cdot H_2O$ ($C_{42}H_{58}N_2O_7P_2$)	$C_{16}H_{23}O_3P$
Crystal system	Monoclinic	Rhombic	Rhombic	Triclinic	Rhombic
Space group	$P2_1/a$	$Pna2_1$	$P2_12_12_1$	$P\bar{1}$	$Pbca$
Unit cell parameters					
a, Å	14.039(4)	17.262(6)	12.010(2)	9.319(3)	8.8633(6)
b, Å	9.949(2)	21.828(7)	17.083(5)	15.367(3)	17.012(1)
c, Å	17.704(5)	11.885(4)	21.933(6)	16.248(3)	20.658(1)
α, deg	90	90	90	69.38(2)	90
β, deg	104.97(3)	90	90	82.14(3)	90
γ, deg	90	90	90	87.38(3)	90
Volume, Å^3	2389.1(5)	4478(3)	4500(2)	2157.4(9)	3114.9(4)
Z	4	8	8	2	8
Temperature, K	294(2)	296(2)	294(2)	294(2)	296(2)
Molecular weight	474.34	403.87	383.45	764.84	294.31
d_{calc}, g/cm^3	1.319	1.198	1.132	1.177	1.255
μ, cm^{-1}	3.66	2.58	1.38	1.49	1.81
F(000)	1000	1712	1648	820	1264
Radiation source	MoK_α, λ 0.71073 Å				
θ range, deg	$2.12 \le \theta \le 24.63$	$2.21 \le \theta \le 27.0$	$2.78 \le \theta \le 22.77$	$2.21 \le \theta \le 26.23$	$1.97 \le \theta \le 28.71$
hkl range	$0 \le h \le 16$, $-11 \le k \le 9$, $-20 \le l \le 20$	$-22 \le h \le 22$, $-27 \le k \le 27$, $-15 \le l \le 15$	$-13 \le h \le 7$, $-16 \le k \le 18$, $-23 \le l \le 21$	$0 \le h \le 11$, $-18 \le k \le 19$, $-18 \le l \le 20$	$-11 \le h \le 11$, $-22 \le k \le 22$, $-26 \le l \le 25$
Total number of reflections	6825	24783	9213	7098	31491
Number of independent reflections	1811	9415	4624	6767	3927
Number of reflections with $I > 2\sigma(I)$	1811 [$I > 3\sigma(I)$]	4557	1699	4776	2484
R	0.050 ($F \ge 3\sigma$)	0.0693	0.0828	0.0485	0.0515
R_w ($F^2 \ge 2\sigma$)	0.047	0.1525	0.1807	0.1270	0.1420
Goodness of fit	1.131	0.979	0.959	1.037	1.002
Number of variables	271	498	440	500	188
CCDC entry no.	982941	982943	982940	982939	982942

bubbled through the mixture using a capillary) to a solution of 6.5 g (0.022 mol) of compound **I** in 10 mL of methylene chloride. Evolution of hydrogen chloride was observed. After 12 h, the mixture was evaporated under reduced pressure (12 mm and 0.1 mm) at 120°C, and the glassy residue, a mixture of compounds **IIa**–**IVa** at a ratio of 14 : 3 : 3 was analyzed by spectral methods.

7-*tert*-Butyl-2,6-dichloro-4-phenyl-1,2λ^5-benzoxaphosphinine 2-oxide (IIa). ^{1}H NMR spectrum (250 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 1.49 s (*t*-Bu), 6.30 d (3-H, $^2J_{PH}$ = 24.0), 7.22 br.s and 7.37 br.s (5-H, 8-H); 7.34 m, 7.49 m, 7.50 m (C_6H_5). ^{31}P–{^{1}H} NMR spectrum (162.0 MHz, $CDCl_3$): δ_P 16.9 ppm. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$), δ_C, ppm (*J*, Hz) (hereinafter, the multiplicity of the corresponding signal in the proton-decoupled ^{13}C NMR spectrum is given in parentheses): 114.58 d.d (d) (C^3, $^1J_{PC}$ = 154.1, $^1J_{CH}$ = 171.3), 155.23 m (d) (C^4, $^2J_{PC}$ = 1.7), 120.08 d.d.d (d) (C^{4a}, $^3J_{PC}$ = 17.8, $^3J_{C,3\text{-}H}$ = 8.7, $^3J_{C,8\text{-}H}$ = 6.0), 132.12 d.d (d) (C^5, $^1J_{CH}$ = 167.6, $^4J_{PC}$ = 1.3), 129.61 d.d.d (d) (C^6, $^3J_{CH}$ = 11.1, $^2J_{CH}$ = 4.5, $^5J_{PC}$ = 1.3), 151.91 m (s) (C^7), 119.17 d.d (d) (C^8, $^1J_{CH}$ = 163.9, $^3J_{PC}$ = 8.2), 149.36 d.d.d (d) (C^{8a}, $^2J_{PC}$ = 9.8, $^3J_{CH}$ = 10.0, $^2J_{CH}$ = 5.4), 136.40 d.t.d.t (d) (C^9, $^3J_{PC}$ = 20.7, $^3J_{C,11\text{-}H}$ = 7.5, $^3J_{C,3\text{-}H}$ = 6.7, $^2J_{CH}$ = 1.1), 128.24 br.d.d.d (s) (C^{10}, $^1J_{CH}$ = 162.1, $^3J_{C,14\text{-}H}$ = 7.8, $^3J_{C,12\text{-}H}$ = 7.7–7.8), 128.97 br.d.d (s) (C^{11}, $^1J_{CH}$ = 161.9, $^3J_{CH}$ = 6.5), 130.00 d.t (s) (C^{12}, $^1J_{CH}$ = 161.9, $^3J_{CH}$ = 7.9), 36.53 m (s) (C^{15}), 29.20 q.sept (s) (C^{16}, $^1J_{CH}$ = 126.7, $^3J_{CH}$ = 4.9).

7-*tert*-Butyl-2,8-dichloro-4-phenyl-1,2λ^5-benzoxaphosphinine 2-oxide (IIIa). ^{1}H NMR spectrum (250 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 1.51 s (*t*-Bu), 6.35 d (3-H, $^2J_{PH}$ = 24.4), 7.16 br.d (5-H, $^4J_{HH}$ = 2.3), 7.56 d.d (7-H, $^4J_{HH}$ = 2.3, $^5J_{PH}$ = 2.0). ^{31}P–{^{1}H} NMR spectrum (162.0 MHz, $CDCl_3$): δ_P 16.8 ppm. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$), δ_C, ppm (*J*, Hz): 114.65 d.d (d) (C^3, $^1J_{PC}$ = 155.5, $^1J_{CH}$ = 172.4), 156.71 m (d) (C^4, $^2J_{PC}$ = 1.6), 122.62 d.d (d) (C^{4a}, $^3J_{PC}$ = 17.7, $^3J_{CH}$ = 8.2), 125.39 d.d.d (d) (C^5, $^1J_{CH}$ = 160.7, $^3J_{CH}$ = 7.1, $^4J_{PC}$ = 1.6), 148.27 m (s) (C^6), 128.87 d.d (s) (C^7), 124.22 d.d.d (d) (C^8, $^3J_{PC}$ = 8.2, $^3J_{CH}$ = 5.4, $^4J_{CH}$ = 1.4), 144.72 d.d.d (d) (C^{8a}, $^2J_{PC}$ = 10.0, $^3J_{CH}$ = 10.0, 10.0), 136.38 m (d) (C^9, $^3J_{PC}$ = 21.3), 128.38 (s) (C^{10}), 128.82 (s) (C^{11}), 130.14 (s) (C^{12}), 34.47 m (s) (C^{15}), 39.73 q.sept (s) (C^{16}, $^1J_{CH}$ = 126.0, $^3J_{CH}$ = 4.3 Hz); the coupling constants for C^7, C^{10}, C^{11}, and C^{12} were not determined because of signal overlap.

The NMR spectra of **IVa** were identical to those reported in [2].

4-(4-Chlorophenyl)-1,2λ^5-benzoxaphosphinine 2-oxides IIb–IVb. A solution of 7.3 g (0.053 mol) of 4-chlorophenylacetylene in 15 mL of methylene chloride was added at 10–20°C in a stream of argon (which was intensely bubbled through the mixture using a capillary) to a solution of 8.9 g (0.03 mol) of compound **I** in 20 mL of methylene chloride. After 12 h, the mixture was evaporated under reduced pressure (0.1 mm) at 150°C. The residue was a light yellow thick oily mixture of compounds **IIb**–**IVb** at a ratio of 7:2:1. ^{31}P–{^{1}H} NMR spectrum (162.0 MHz, CH_2Cl_2), ppm: δ_P 17.1 (**IIb**), 17.0 (**IIIb**), 16.9 (**IVb**).

7-*tert*-Butyl-2,6-dichloro-4-(4-chlorophenyl)-1,2λ^5-benzoxaphosphinine 2-oxide (IIb). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 1.49 s (*t*-Bu), 6.29 d (3-H, $^2J_{PH}$ = 23.5), 7.16 s (8-H), 7.37 s (5-H), 7.31 m and 7.48 m (10-H, 11-H, *AA′BB′*, $^3J_{AB}$ = $^3J_{A'B'}$ = 8.6). ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$), δ_C, ppm (*J*, Hz): 114.86 d.d (d) (C^3, $^1J_{PC}$ = 154.4, $^1J_{CH}$ = 171.5), 153.92 m (d) (C^4, $^2J_{PC}$ = 1.8), 119.72 d.d.d (d) (C^{4a}, $^3J_{PC}$ = 18.0, $^3J_{C,3\text{-}H}$ = 8.4, $^3J_{C,8\text{-}H}$ = 5.9), 131.76 d.d (d) (C^5, $^1J_{CH}$ = 166.4, $^4J_{PC}$ = 1.3), 129.70 d.d (s) (C^6, $^2J_{C,8\text{-}H}$ = 11.2, $^2J_{C,5\text{-}H}$ = 3.9), 152.07 m (s) (C^7), 119.28 d.d (d) (C^8, $^1J_{CH}$ = 163.7, $^3J_{PC}$ = 8.6), 149.22 d.d.d (d) (C^{8a}, $^3J_{CH}$ = 10.1, $^2J_{PC}$ = 9.8, $^2J_{CH}$ = 5.5), 134.91 d.t.d (d) (C^9, $^3J_{PC}$ = 21.1, $^3J_{C,11\text{-}H}$ = 7.8, $^3J_{C,3\text{-}H}$ = 6.1), 129.65 d.d (s) (C^{10}, $^1J_{CH}$ = 163.5, $^3J_{CH}$ = 7.0), 129.26 d.d (s) (C^{11}, $^1J_{CH}$ = 166.9, $^3J_{CH}$ = 5.3), 136.21 t.t (s) (C^{12}, $^3J_{CH}$ = 10.4, $^2J_{CH}$ = 3.4), 36.52 m (s) (C^{15}), 29.09 q.sept (s) (C^{16}, $^1J_{CH}$ = 126.9, $^3J_{CH}$ = 4.6).

7-*tert*-Butyl-2,8-dichloro-4-(4-chlorophenyl)-1,2λ^5-benzoxaphosphinine 2-oxide (IIIb). ^{1}H NMR spectrum (250 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 1.30 s (*t*-Bu), 6.35 d (3-H, $^2J_{PH}$ = 23.9), 7.57 d.d (7-H, $^4J_{CH}$ = 2.1, $^5J_{PH}$ = 2.0). ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$), δ_C, ppm: 115.20 d.d (d) (C^3, $^1J_{PC}$ = 152.6, $^1J_{CH}$ = 171.5), 155.20 br.m (br.s) (C^4), 120.32 m (d) (C^{4a}, $^3J_{PC}$ = 19.0), 125.02 br.d.d (d) (C^5, $^1J_{CH}$ = 161.0, $^3J_{CH}$ = 7.2, $^4J_{PC}$ = 1.2), 148.37 m (s) (C^6), 128.95 (s) (C^7), 124.25 d.d (d) (C^8, $^3J_{PC}$ = 7.5, $^2J_{CH}$ = 3.7), 136.29 m (s) (C^{12}), 145.05 m (d) (C^{8a}, $^2J_{PC}$ = 9.0), 134.89 m (d) (C^9, $^3J_{PC}$ = 21.3), 34.48 m (s) (C^{15}), 30.73 q.sept (s) (C^{16}, $^1J_{CH}$ = 126.8, $^3J_{CH}$ = 4.0); signals from C^{10} and C^{11} were not identified because of overlap.

2,6-Dichloro-4-(4-chlorophenyl)-1,2λ^5-benzoxaphosphinine 2-oxide (IVb). ^{1}H NMR spectrum (250 MHz, $CDCl_3$): δ 6.37 ppm, d (3-H, $^2J_{PH}$ = 23.4 Hz). ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 115.77 d.d (d) (C^3, $^1J_{PC}$ = 154.4, $^1J_{CH}$ = 172.3), 155.35 m (d) (C^4, $^2J_{PC}$ = 1.5), 122.40 m (d) (C^{4a}, $^3J_{PC}$ = 17.5), 129.68 d.d (s) (C^5, $^1J_{CH}$ = 167.0, $^3J_{CH}$ = 6.0), 130.32 m (s) (C^6), 132.31 d.d (s) (C^7, $^1J_{CH}$ = 169.6, $^3J_{CH}$ = 5.9), 121.21 d.d (d) (C^8, $^1J_{CH}$ = 160.7, $^3J_{PC}$ = 7.9), 149.41 m (d) (C^{8a}, $^2J_{PC}$ = 10.3), 135.55 m (d) (C^9, $^3J_{PC}$ = 20.9), 129.68 (s) (C^{10}), 129.32 (s) (C^{11}), 136.31 m (s) (C^{12}).

4-(4-Methylphenyl)-1,2λ^5-benzoxaphosphinine 2-oxides IIc–IVc. A solution of 5.32 g (0.046 mol) of 4-methylphenylacetylene in 20 mL of methylene

chloride was added to a solution of 6.8 g (0.023 mol) of compound **I** in 20 mL of methylene chloride while bubbling argon through the mixture using a thin capillary. Evolution of hydrogen chloride was observed. After 12 h, the mixture was evaporated under reduced pressure (0.1 mm) at 150°C to obtain a light yellow thick oily mixture of compounds **IIc**–**IVc** at a ratio of 15:4:1. $^{31}P-\{^1H\}$ NMR spectrum (162.0 MHz, CH_2Cl_2): δ_P 17.4 (**IIc**), 17.3 (**IIIc**), 17.2 ppm (**IVc**).

7-*tert*-Butyl-2,6-dichloro-4-(4-methylphenyl)-1,2λ^5-benzoxaphosphinine 2-oxide (IIc). ^1H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 1.50 s (*t*-Bu), 2.43 s (CH_3), 6.27 d (3-H, $^2J_{PH}$ = 24.3 Hz), 7.26–7.28 m (10-H, 11-H), 7.36 br.s and 7.28 br.s (5-H, 8-H). ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$), δ_C, ppm (*J*, Hz): 113.71 d.d (d) (C^3, $^1J_{PC}$ = 154.6, $^1J_{CH}$ = 171.1), 155.38 m (d) (C^4, $^2J_{PC}$ = 4.0), 120.05 m (d) (C^{4a}, $^3J_{PC}$ = 17.9, $^3J_{C,3-H}$ = 8.2, $^3J_{C,8-H}$ = 5.4), 132.10 d (s) (C^5, $^1J_{CH}$ = 166.7), 129.49 d.d (s) (C^6, $^3J_{CH}$ = 11.0, $^2J_{CH}$ = 3.9), 151.54 m (s) (C^7), 119.03 d.d (d) (C^8, $^1J_{CH}$ = 163.2, $^3J_{PC}$ = 8.3), 149.17 d.d.d (d) (C^{8a}, $^2J_{PC}$ = 9.7, $^3J_{CH}$ = 9.7, $^2J_{CH}$ = 5.2), 133.50 m (d) (C^9, $^3J_{PC}$ = 20.9, $^3J_{C,11-H}$ = 7.5, $^3J_{C,3-H}$ = 6.5), 128.10 d.d (s) (C^{10}, $^1J_{CH}$ = 160.2, $^3J_{CH}$ = 6.0), 129.26 d.d.q (s) (C^{11}, $^1J_{CH}$ = 159.1, $^3J_{C,13-H}$ = 6.0, $^3J_{C,Me}$ = 5.0–6.0), 140.22 m (s) (C^{12}, $^3J_{CH}$ = 6.0, $^2J_{CH}$ = 6.0), 36.38 m (s) (C^{15}), 29.04 q.sept (s) (C^{16}, $^1J_{CH}$ = 127.0, $^3J_{CH}$ = 4.0), 21.19 q.t (s) (C^{23}, $^1J_{CH}$ = 126.6, $^3J_{CH}$ = 4.0).

6-*tert*-Butyl-2,8-dichloro-4-(4-methylphenyl)-1,2λ^5-benzoxaphosphinine 2-oxide (IIIc). ^1H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 1.21 s (*t*-Bu), 2.33 s (CH_3), 6.32 d (3-H, $^2J_{PH}$ = 24.7), 7.55 d.d (7-H, $^4J_{HH}$ = 3.2, $^5J_{PH}$ = 2.8). ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$), δ_C, ppm (*J*, Hz): 113.80 d.d (d) (C^3, $^1J_{PC}$ = 154.2, $^1J_{CH}$ = 170.4), 156.67 m (s) (C^4), 122.07 d.d (d) (C^{4a}, $^3J_{PC}$ = 17.9, $^3J_{CH}$ = 8.2), 125.25 d.d (s) (C^5, $^1J_{CH}$ = 160.7, $^3J_{CH}$ = 8.1), 147.92 m (s) (C^6), 129.74 d.d (s) (C^7, $^1J_{CH}$ = 163.2, $^3J_{CH}$ = 8.4), 123.82 br.d.d (d) (C^8, $^3J_{PC}$ = 7.7, $^2J_{CH}$ = 3.7–3.8, $^4J_{CH}$ = 1.7), 144.29 d.d.d (d) (C^{8a}, $^2J_{PC}$ = 8.8, $^3J_{C.5-H}$ = 9.0, $^3J_{C,7-H}$ = 9.0), 133.35 m (d) (C^9, $^3J_{PC}$ = 21.0), 128.07 d.d (s) (C^{10}, $^1J_{CH}$ = 160.2, $^3J_{CH}$ = 6.0), 129.20 d.d.q (s) (C^{11}, $^1J_{CH}$ = 160.0, $^3J_{C,13-H}$ = 6.0, $^3J_{C,Me}$ = 6.0), 140.05 m (s) (C^{12}), 34.38 m (s) (C^{15}), 30.59 q.sept (s) (C^{16}, $^1J_{CH}$ = 127.0, $^3J_{CH}$ = 4.0), 21.00 q.t (C^{23}, $^1J_{CH}$ = 126.5, $^3J_{CH}$ = 4.0–5.0).

2,6-Dichloro-4-(4-methylphenyl)-1,2λ^5-benzoxaphosphinine 2-oxide (IVc) was synthesized according to the procedure described in [1] from 2,2,2-trichloro-1,3,2λ^5-benzodioxaphosphole and 4-methylphenylacetylene in methylene chloride at 10–20°C. Yield 98%, light yellow oily substance. ^{31}P NMR spectrum (36.48 MHz, CH_2Cl_2): δ_P 17.9 ppm, d ($^2J_{PH}$ = 24.5 Hz). ^1H NMR spectrum (600 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 2.37 s (CH_3), 6.29 d (3-H, $^2J_{PH}$ = 24.3), 7.05 d (5-H, $^4J_{HH}$ = 2.7), 7.36 br.d (7-H, $^3J_{HH}$ = 8.5), 7.20–7.22 m (8-H, 10-H, 11-H). ^{13}C NMR spectrum (150.9 MHz, $CDCl_3$), δ_C, ppm (*J*, Hz): 114.66 d.d (d) (C^3, $^1J_{PC}$ = 154.3, $^1J_{CH}$ = 171.3), 155.46 m (s) (C^4), 122.65 d.d.d (d) (C^{4a}, $^3J_{PC}$ = 17.6, $^3J_{C,3-H}$ = 8.5, $^3J_{C,8-H}$ = 5.8), 129.10 d.d (s) (C^5, $^1J_{CH}$ = 163.9, $^3J_{CH}$ = 6.2), 130.06 m (s) (C^6, $^5J_{PC}$ = 0.6), 131.86 d.d (s) (C^7, $^1J_{CH}$ = 167.4, $^3J_{CH}$ = 6.5), 120.86 d.d (d) (C^8, $^1J_{CH}$ = 166.1, $^3J_{PC}$ = 8.0), 149.32 d.d.d.d (d) (C^{8a}, $^2J_{PC}$ = 10.0, $^3J_{C,7-H}$ = $^3J_{C,5-H}$ = 10.0, $^2J_{CH}$ = 4.2), 133.43 d.t.d (d) (C^9, $^3J_{PC}$ = 20.7, $^3J_{C,11-H}$ = 7.3, $^3J_{C,3-H}$ = 6.5), 128.03 d.d (s) (C^{10}, $^1J_{CH}$ = 160.2, $^3J_{CH}$ = 6.4), 129.50 d.d.q (s) (C^{11}, $^1J_{CH}$ = 159.5, $^3J_{C,13-H}$ = 6.4, $^3J_{C.Me}$ = 5.1), 140.18 m (s) (C^{12}), 21.06 q.t (s) (C^{23}, $^1J_{CH}$ = 126.9, $^3J_{CH}$ = 4.2).

2-Hydroxy-4-phenyl-1,2λ^5-benzoxaphosphinine 2-oxides Va–VIIa. Glassy mixture **IIa**–**IVa**, 1.62 g, was dissolved in 10 mL of benzene, 0.1 mL of water was added, the mixture was evaporated, the residue was dissolved in diethyl ether, and the solution was kept for 21 days at 20°C. The precipitate of 6-chloro-2-hydroxy-4-phenyl-1,2λ^5-benzoxaphosphinine 2-oxide (**VIIa**) was filtered off and dried in air. Yield 0.20 g (21%), mp 240–242°C; the spectral parameters of **VIIa** coincided with published data [2]. After separation of **VIIa**, the filtrate was evaporated under reduced pressure (12 mm) to isolate a yellowish oily mixture of compounds **Va** and **VIa** at a ratio of 14:3.

7-*tert*-Butyl-6-chloro-2-hydroxy-4-phenyl-1,2λ^5-benzoxaphosphinine 2-oxide (Va). ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 112.02 d.d (d) (C^3, $^1J_{PC}$ = 177.2, $^1J_{CH}$ = 165.1), 154.06 m (br.s) (C^4), 120.21 d.d.d (d) (C^{4a}, $^3J_{PC}$ = 16.7, $^3J_{C,3-H}$ = 8.2, $^3J_{C,8-H}$ = 6.7), 131.37 d (s) (C^5, $^1J_{CH}$ = 165.5), 128.05 d.d (s) (C^6, $^3J_{CH}$ = 11.0, $^2J_{CH}$ = 4.1), 150.27 m (s) (C^7), 118.82 d.d (d) (C^8, $^1J_{CH}$ = 162.6, $^3J_{PC}$ = 8.2), 149.27 d.d.d (d) (C^{8a}, $^2J_{PC}$ = 6.3, $^3J_{CH}$ = 9.8, $^2J_{CH}$ = 5.2), 137.64 d.t.d (d) (C^9, $^3J_{PC}$ = 19.6, $^3J_{C,11-H}$ = 7.3, $^3J_{C,3-H}$ = 6.3), 128.13 br.d.d.d (s) (C^{10}, $^1J_{CH}$ = 160.2, $^3J_{C,14-H}$ = 6.0, $^3J_{C,12-H}$ = 5.5–6.0), 128.55 br.d.d (s) (C^{11}, $^1J_{CH}$ = 162.3, $^3J_{CH}$ = 6.2), 129.11 d.t (s) (C^{12}, $^1J_{CH}$ = 160.9, $^3J_{CH}$ = 7.2), 36.16 m (s) (C^{15}, $^2J_{CH}$ = 3.2), 29.07 q.sept (s) (C^{16}, $^1J_{CH}$ = 126.5, $^3J_{CH}$ = 4.6). $^{31}P-\{^1H\}$ NMR spectrum (162.0 MHz, ethanol-d_6): δ_P 10.0 ppm.

6-*tert*-Butyl-8-chloro-2-hydroxy-4-phenyl-1,2λ^5-benzoxaphosphinine 2-oxide (VIa). ^{13}C NMR spec-

trum (100.6 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 112.68 d.d (d) (C^3, $^1J_{PC}$ = 177.5, $^1J_{CH}$ = 164.3), 155.16 m (s) (C^4), 122.38 d.d (d) (C^{4a}, $^3J_{PC}$ = 16.6, $^3J_{CH}$ = 8.3), 124.67 d.d (d) (C^5, $^1J_{CH}$ = 159.5, $^3J_{CH}$ = 7.6), 146.56 m (s) (C^6), 130.83 d.d (s) (C^7, $^1J_{CH}$ = 166.5, $^3J_{CH}$ = 6.2), 123.58 d.d (d) (C^8, $^3J_{PC}$ = 7.0, $^3J_{CH}$ = 4.6), 144.81 d.d.d (d) (C^{8a}, $^2J_{PC}$ = 5.8–6.0, $^3J_{C,5\text{-}H}$ = 9.0, $^3J_{C,7\text{-}H}$ = 8.3), 137.92 m (d) (C^9, $^3J_{PC}$ = 19.5), 128.19 d.d.d (s) (C^{10}, $^1J_{CH}$ = 160.0, $^3J_{CH}$ = 6.0–7.0, 6.0–7.0), 128.61 (s) (C^{11}, $^1J_{CH}$ = 162.0, $^3J_{CH}$ = 6.0–6.5), 129.05 d.t (s) (C^{12}, $^1J_{CH}$ = 160.0, $^3J_{CH}$ = 7.3), 34.36 m (s) (C^{15}, $^2J_{CH}$ = 3.6), 30.84 q.sept (s) (C^{16}, $^1J_{CH}$ = 125.9, $^3J_{CH}$ = 4.6). $^{31}P–\{^1H\}$ NMR spectrum (162.0 MHz, ethanol-d_6): δ_P 9.8 ppm.

6-Chloro-4-(4-chlorophenyl)-2-hydroxy-1,2λ^5-benzoxaphosphinine 2-oxide (VIIb). Water, 0.5 mL, was added to a solution of 6.8 g of a mixture of compounds **IIb**–**IVb** in 30 mL of dioxane. After 24 h, the precipitate was filtered off and dried in air. Yield 4.4% (0.4 g), mp 294°C. IR spectrum, ν, cm^{-1}: 3436, 3051, 2924, 2855, 2541 v.br, 2255 v.br, 1657, 1596, 1548, 1488, 1468, 1401, 1377, 1337, 1249, 1193, 1113, 1095, 1015, 962, 913, 884, 832, 807, 741, 714, 657, 631, 558, 484, 454. ^1H NMR spectrum (250 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 6.42 d (1H, 3-H, $^2J_{PH}$ = 17.0), 7.00 d (1H, 5-H, $^4J_{HH}$ = 2.6), 7.41 d and 7.57 d (4H, 10-H, 11-H, *AA′BB′*, $^3J_{AB} = {}^3J_{A'B'}$ = 8.5). ^{13}C NMR spectrum (100.6 MHz, DMSO-d_6), δ_C, ppm (*J*, Hz): 117.60 d.d (d) (C^3, $^1J_{PC}$ = 168.2, $^1J_{CH}$ = 163.3), 149.18 m (d) (C^4, $^2J_{PC}$ = 1.6), 123.11 m (d) (C^{4a}, $^3J_{PC}$ = 16.0), 127.19 d.d (s) (C^5, $^1J_{CH}$ = 165.9, $^3J_{CH}$ = 5.5), 130.32 d.d.d.d (s) (C^6, $^3J_{CH}$ = 9.5, $^2J_{C,5\text{-}H}$ = 4.3, $^2J_{C,7\text{-}H}$ = 4.3, $^5J_{PC}$ = 1.1–1.3), 130.41 d.d (s) (C^7, $^1J_{CH}$ = 169.5, $^3J_{CH}$ = 6.4), 121.52 d.d (d) (C^8, $^1J_{CH}$ = 168.5, $^3J_{PC}$ = 6.4), 149.88 m (d) (C^{8a}, $^2J_{PC}$ = 7.3), 136.47 m (d) (C^9, $^3J_{PC}$ = 19.3), 129.96 d.d (s) (C^{10}, $^1J_{CH}$ = 164.3, $^3J_{CH}$ = 7.0), 129.32 d.d (s) (C^{11}, $^1J_{CH}$ = 168.5, $^3J_{CH}$ = 5.1), 136.31 t.t (s) (C^{12}, $^3J_{CH}$ = 11.0, $^2J_{CH}$ = 4.0). ^{31}P NMR spectrum (162.0 MHz, dioxane): δ_P 6.3 ppm, d ($^2J_{PH}$ = 17.0 Hz). Found, %: C 51.48; H 2.75; P 9.82. $C_{14}H_9Cl_2O_3P$. Calculated, %: C 51.38; H 2.75; P 9.48.

6-Chloro-2-hydroxy-4-(4-methylphenyl)-1,2λ^5-benzoxaphosphinine 2-oxide (VIIc) was synthesized by hydrolysis of compound **IVc** in diethyl ether. Yield 97%, mp >250°C. ^1H NMR spectrum (600 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 2.38 s (CH_3), 6.32 d (3-H, $^2J_{PH}$ = 17.5), 7.03 d (5-H, $^4J_{HH}$ = 2.6), 7.48 d.d.d (7-H, $^3J_{HH}$ = 8.7, $^4J_{HH}$ = 2.6, $^5J_{PH}$ = 1.3), 7.31 d (8-H, $^3J_{HH}$ = 8.7), 7.26 m and 7.31 m (10-H, 11-H, *AA′BB′*, $^3J_{HH}$ = 8.1), 6.85 v.br.s (OH). ^{13}C NMR spectrum (100.6 MHz, DMSO-d_6), δ_C, ppm (*J*, Hz): 116.89 d.d (d) (C^3, $^1J_{PC}$ = 168.4, $^1J_{CH}$ = 63.5), 150.52 m (d) (C^4, $^2J_{PC}$ = 1.7), 123.71 d.d.d.d.d (d) (C^{4a}, $^3J_{PC}$ = 16.3, $^3J_{C,3\text{-}H}$ = 8.9, $^3J_{C,8\text{-}H}$ = 6.0, $^2J_{CH}$ = 1.2–1.3, $^4J_{CH}$ = 0.6), 129.10 br.d.d (s) (C^5, $^1J_{CH}$ = 165.5, $^3J_{CH}$ = 5.8, $^4J_{PC}$ = 0.9–1.0), 127.01 d.d.d.d.d (s) (C^6, $^3J_{CH}$ = 11.4, $^2J_{CH}$ = 4.5, 3.5, $^5J_{PC}$ = 1.1–1.2, $^5J_{CH}$ = 0.9–1.0), 131.57 br.d.d (d) (C^7, $^1J_{CH}$ = 169.7, $^3J_{CH}$ = 6.1, $^4J_{PC}$ = 0.4), 121.31 d.d (d) (C^8, $^1J_{CH}$ = 167.5, $^3J_{PC}$ = 7.0), 149.83 d.d.d.d (d) (C^{8a}, $^2J_{PC}$ = 7.3, $^3J_{CH}$ = 10.5, 8.7, $^2J_{CH}$ = 3.8), 135.00 d.t.d (d) (C^9, $^3J_{PC}$ = 18.4, $^3J_{C,11\text{-}H}$ = 7.2, $^3J_{C,3\text{-}H}$ = 6.7), 128.26 br.d.d (d) (C^{10}, $^1J_{CH}$ = 160.2, $^3J_{CH}$ = 6.2–6.3, $^4J_{PC}$ = 0.9–1.0), 129.44 d.d.q (s) (C^{11}, $^1J_{CH}$ = 159.3, $^3J_{C,13\text{-}H}$ = 6.0, $^3J_{C,Me}$ = 5.1), 138.74 br.t.q (s) (C^{12}, $^3J_{CH}$ = 6.0–7.0, $^2J_{CH}$ = 6.0), 20.86 q.t (s) (C^{23}, $^1J_{CH}$ = 126.6, $^3J_{CH}$ = 4.2). Mass spectrum, *m*/*z*: 306 $[M]^+$, 291 [*M* – Me], 290 [*M* – Me – H], 289 [*M* – OH], 271 [*M* – Cl], 243 [*M* – PO_2], 242 [*M* – PO_2H] ($C_5H_{11}O$), 207 [*M* – PO_2H – Cl]. Found, %: C 58.65; H 4.07; Cl 11.33; P 10.29. $C_{15}H_{12}ClO_3P$. Calculated, %: C 58.73; H 3.92; Cl 11.58; P 10.14. *M* 306.69.

1-(6-Chloro-2-oxo-4-phenyl-1,2λ^5-benzoxaphosphinin-2-yl)pyrrolidine-2,5-diones VIIIa and Xa. A solution of 5.5 g of mixture **IIa**–**IVa** and 2.84 g of *N*-(trimethylsilyl)succinimide in 20 mL of benzene was heated for 3 h under reflux. The mixture was evaporated at a bath temperature not exceeding 110°C, the residue was cooled and dissolved in 15 mL of diethyl ether, and the solution was kept for 3 days. A crystalline solid gradually separated and was filtered off, washed with diethyl ether, and dried under reduced pressure (12 mm) to obtain 6.3 g of a mixture of compounds **VIIIa** and **Xa** at a ratio of 12:1. Compound **VIIIa** was isolated by repeated crystallizations from diethyl ether.

1-(7-*tert*-Butyl-6-chloro-2-oxo-4-phenyl-1,2λ^5-benzoxaphosphinin-2-yl)pyrrolidine-2,5-dione (VIIIa). Yield 0.18 g (14%), mp 173–176°C. IR spectrum, ν, cm^{-1}: 3147, 1704, 1590, 1195, 1115, 1069, 993, 867, 807, 760, 700, 639, 602, 548, 520, 454, 426. ^1H NMR spectrum (250 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 1.46 s (*t*-Bu, 9H), 2.74 s (4H, CH_2), 6.35 d (1H, 3-H, $^2J_{PH}$ = 18.7), 7.10 s and 7.33 s (2H, 5-H, 8-H), 7.40–7.41 m (2H, 9-H), 7.54–7.56 m (3H, 10-H, 11-H). ^{13}C NMR spectrum (100.6 MHz, CH_2Cl_2, D_2O in an inner capillary), δ_C, ppm (*J*, Hz): 111.44 d.d (d) (C^3, $^1J_{PC}$ = 156.2, $^1J_{CH}$ = 169.7), 155.02 m (d) (C^4, $^2J_{PC}$ = 2.2), 120.07 d.d.d (d) (C^{4a}, $^3J_{PC}$ = 17.5, $^3J_{C,3\text{-}H}$ = 8.4, $^3J_{C,8\text{-}H}$ = 6.8), 131.78 d.d (d) (C^5, $^1J_{CH}$ = 166.0, $^4J_{PC}$ = 1.3), 128.78 d.d (s) (C^6, $^3J_{CH}$ = 11.6, $^2J_{CH}$ = 4.4), 151.24 m (s) (C^7), 119.22 d.d (d) (C^8, $^1J_{CH}$ = 162.8,

$^3J_{PC}$ = 8.7), 149.71 d.d.d (d) (C^{8a}, $^2J_{PC}$ = 8.4, $^3J_{CH}$ = 10.5, $^2J_{CH}$ = 5.5), 137.57 m (d) (C^9, $^3J_{PC}$ = 19.7), 128.39 br.d.d.d (s) (C^{10}, $^1J_{CH}$ = 160.9, $^3J_{CH}$ = 6.0–7.0, 6.0–7.0), 128.91 br.d.d (s) (C^{11}, $^1J_{CH}$ = 161.0, $^3J_{CH}$ = 7.1), 129.66 d.t (s) (C^{12}, $^1J_{CH}$ = 161.0, $^3J_{CH}$ = 7.6), 36.50 m (s) (C^{15}, $^2J_{CH}$ = 3.3), 29.11 q.sept (s) (C^{16}, $^1J_{CH}$ = 126.0, $^3J_{CH}$ = 4.6), 177.16 m (d) (C^{17}, $^2J_{PC}$ = 1.3), 30.12 t.d.t (d) (C^{18}, $^1J_{CH}$ = 135.5, $^3J_{PC}$ = 5.0, $^2J_{CH}$ = 4.2). $^{31}P–\{^1H\}$ NMR spectrum (162.0 MHz, CH_2Cl_2): δ_P 1.6 ppm. Found, %: C 60.23; H 5.18; Cl 8.14; N 3.52; P 6.98. $C_{22}H_{21}ClNO_4P$. Calculated, %: C 61.47; H 4.92; Cl 8.25; N 3.26; P 7.21.

1-(6-Chloro-2-oxo-4-phenyl-1,2λ^5-benzoxaphosphinin-2-yl)pyrrolidine-2,5-dione (Xa). ^1H NMR spectrum (250 MHz, $CDCl_3$): δ 6.39 ppm, d (3-H, $^2J_{PH}$ = 18.7 Hz). ^{13}C NMR spectrum (100.6 MHz, CH_2Cl_2, D_2O in an inner capillary), δ_C, ppm (*J*, Hz): 112.35 d.d (d) (C^3, $^1J_{PC}$ = 156.1, $^1J_{CH}$ = 170.4), 156.36 m (d) (C^4, $^2J_{PC}$ = 2.2), 122.70 d.d.d (d) (C^{4a}, $^3J_{PC}$ = 17.5, $^3J_{C,3\text{-}H}$ = 8.4, $^3J_{C,8\text{-}H}$ = 6.5–6.8), 128.96 (s) (C^5), 129.44 d.d.d (s) (C^6, $^3J_{CH}$ = 12.3, $^2J_{C,5\text{-}H}$ = $^2J_{C,7\text{-}H}$ = 4.0), 131.71 d.d (s) (C^7, $^1J_{CH}$ = 169.3, $^3J_{CH}$ = 6.5), 121.08 d.d (d) (C^8, $^1J_{CH}$ = 167.7, $^3J_{PC}$ = 8.4), 149.99 m (d) (C^{8a}, $^2J_{PC}$ = 8.6), 137.55 m (d) (C^9, $^3J_{PC}$ = 19.7), 128.44 br.d.d.d (s) (C^{10}, $^1J_{CH}$ = 161.0, $^3J_{C,14\text{-}H}$ = $^3J_{C,12\text{-}H}$ = 6.0–7.0), 128.96 br.d.d (s) (C^{11}, $^1J_{CH}$ = 161.0, $^3J_{CH}$ = 7.1), 129.74 d.t (s) (C^{12}, $^1J_{CH}$ = 161.1, $^3J_{CH}$ = 7.6), 177.18 m (d) (C^{15}, $^2J_{PC}$ = 1.3), 30.12 t.d.t (d) (C^{16}, $^1J_{CH}$ = 135.5, $^3J_{PC}$ = 5.0, $^2J_{CH}$ = 4.2). $^{31}P–\{^1H\}$ NMR spectrum (162.0 MHz, $CDCl_3$): δ_P 1.1 ppm.

Diethylammonium 7-*tert*-butyl-6-chloro-4-(4-chlorophenyl)-2-oxo-1,2λ^5-benzoxaphosphinin-2-olate (XIb) was isolated by evaporation under reduced pressure (0.1 mm) of the dioxane filtrate obtained after hydrolysis of mixture **IIb**–**IVb** and partial separation of compound **VIIb** (see the procedure for the synthesis of **VIIb**). The filtrate contained 7-*tert*-butyl-6-chloro- and 6-*tert*-butyl-8-chloro-4-(4-chlorophenyl)-2-hydroxy-1,2λ^5-benzoxaphosphinine 2-oxides **Vb** and **VIb** [^{31}P NMR spectrum (162.0 MHz), δ_P, ppm: 6.6 d ($^2J_{PH}$ = 18.0 Hz) (**Vb**); 6.2 d ($^2J_{PH}$ = 18.0 Hz) (**VIb**)] and compound **VIIb**. The glassy residue, 4.1 g, was dissolved in 30 mL of dioxane, 10 mL of diethylamine was added while bubbling argon through the mixture using a thin capillary, and the precipitate was filtered off, washed with dioxane, and dried under reduced pressure (12 mm). Yield 1.9 g (13%), mp 172°C. IR spectrum, ν, cm^{-1}: 3493, 3415, 3287, 2925, 2855, 2518, 1635, 1591, 1563, 1461, 1397, 1371, 1333, 1258, 1217, 1195, 1139, 1116, 1072, 1015, 988, 917, 898, 872, 847, 807, 757, 735, 716, 650, 616, 597, 546, 528, 491, 455, 414. ^1H NMR spectrum (400 MHz, DMSO-d_6), ppm (*J*, Hz): 1.14 t (6H, CH_3, $^3J_{HH}$ = 7.2), 1.42 s (9H, *t*-Bu), 2.83 q (4H, CH_2, $^3J_{HH}$ = 7.2), 6.10 d (1H, 3-H, $^2J_{PH}$ = 15.9), 6.86 s (1H, 8-H), 7.07 s (1H, 5-H), 7.32 m and 7.59 m (4H, 10-H, 11-H, *AA′XX′*, $^3J_{AX}$ = $^3J_{A'X'}$ = 8.4). ^{13}C NMR spectrum (100.6 MHz, DMSO-d_6), δ_C, ppm (*J*, Hz): 125.08 d.d (d) (C^3, $^1J_{PC}$ = 162.2, $^1J_{CH}$ = 156.5), 147.23 m (s) (C^4), 122.59 d.d.d (d) (C^{4a}, $^3J_{PC}$ = 14.9, $^3J_{C,3\text{-}H}$ = 8.4, $^3J_{C,8\text{-}H}$ = 6.1), 129.59 d (s) (C^5, $^1J_{CH}$ = 162.7), 124.37 d.d (s) (C^6, $^3J_{CH}$ = 11.3, $^2J_{CH}$ = 3.8), 143.08 m (s) (C^7), 118.85 d.d (d) (C^8, $^1J_{CH}$ = 159.7, $^3J_{PC}$ = 5.0), 152.06 m (d) (C^{8a}, $^2J_{PC}$ = 6.5), 138.40 br.d.t.d (d) (C^9, $^3J_{PC}$ = 16.6, $^3J_{C,11\text{-}H}$ = 7.8–8.0, $^3J_{C,3\text{-}H}$ = 6.8), 130.12 d.d (s) (C^{10}, $^1J_{CH}$ = 164.3, $^3J_{CH}$ = 6.8), 128.73 d.d (s) (C^{11}, $^1J_{CH}$ = 168.2, $^3J_{CH}$ = 5.0), 133.01 t.t (s) (C^{12}, $^3J_{CH}$ = 10.7, $^2J_{CH}$ = 3.1), 35.64 m (s) (C^{15}, $^2J_{CH}$ = 3.6), 29.31 q.sept (s) (C^{16}, $^1J_{CH}$ = 126.4, $^2J_{CH}$ = 4.6), 41.29 br.t.m (C^{19}, $^1J_{CH}$ = 142.1), 10.85 br.q.m. (C^{20}, $^1J_{CH}$ = 127.7, $^2J_{CH}$ = 3.3). ^{31}P NMR spectrum (36.48 MHz, DMSO-d_6): δ_P –1.2 ppm, d ($^2J_{PH}$ = 15.7 Hz). Found, %: C 57.84; H 6.39; Cl 15.99; N 3.05; P 6.15. $C_{22}H_{28}Cl_2NO_3P$. Calculated, %: C 57.89; H 6.14; Cl 15.57; N 3.07; P 6.80.

Calcium bis[7-*tert*-butyl-6-chloro-4-(4-chlorophenyl)-2-oxo-1,2λ^5-benzoxaphosphinin-2-olate] (XIVb). Calcium oxide, 0.2 g, was added to a solution of 1.8 g of mixture **Vb**–**VIIb** (after partial separation of **VIIb**) in 25 mL of dioxane, the mixture was heated to the boiling point and cooled, and the white precipitate was filtered off and dried. Yield 0.5 g, mp >350°C. IR spectrum, ν, cm^{-1}: 3530, 3039, 2960, 2925, 2855, 2346, 2251, 1918, 1655, 1601, 1561, 1528, 1480, 1464, 1398, 1372, 1334, 1247, 1214, 1185, 1117, 1073, 1005, 992, 923, 876, 851, 812, 758, 738, 715, 665, 636, 614, 597, 583, 571, 547, 531, 491, 479, 461, 411. ^1H NMR spectrum (250 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 6.24 d (1H, 3-H, $^2J_{PH}$ = 16.4), 6.92 s (1H, 8-H), 7.33 d and 7.50 d (4H, 10-H, 11-H, *AA′BB′*, $^3J_{AB}$ = $^3J_{A'B'}$ = 8.4). ^{13}C NMR spectrum (100.6 MHz, DMSO-d_6), δ_C, ppm (*J*, Hz): 125.09 d.d (d) (C^3, $^1J_{PC}$ = 162.2, $^1J_{CH}$ = 156.5), 147.23 m (s) (C^4), 122.60 d.d.d (d) (C^{4a}, $^3J_{PC}$ = 14.9, $^2J_{CH}$ = 8.3, $^3J_{CH}$ = 6.2), 129.59 d (s) (C^5, $^1J_{CH}$ = 162.7), 124.37 d.d (s) (C^6, $^3J_{CH}$ = 11.3, $^2J_{CH}$ = 3.2), 143.08 m (s) (C^7), 118.85 d.d (d) (C^8, $^1J_{CH}$ = 159.7, $^3J_{PC}$ = 5.2), 152.06 m (d) (C^{8a}, $^2J_{PC}$ = 6.4), 138.41 br.d.t.d (d) (C^9, $^3J_{PC}$ = 16.6, $^3J_{C,11\text{-}H}$ = 6.8–7.2, $^3J_{C,3\text{-}H}$ = 6.4–6.6), 128.73 d.d (s) (C^{10}, $^1J_{CH}$ = 168.1, $^3J_{CH}$ = 5.0), 130.12 d.d (s) (C^{11}, $^1J_{CH}$ = 164.1, $^3J_{CH}$ = 7.0), 133.01 m (s) (C^{12}, $^3J_{CH}$ = 10.5, $^2J_{CH}$ = 3.6), 35.64 m (s) (C^{15}), 29.31 q.sept (s) (C^{16}, $^1J_{CH}$ = 126.4, $^2J_{CH}$ = 4.8). ^{31}P NMR spectrum (36.48 MHz,

DMSO-d_6): δ_P 0.4 ppm, d ($^2J_{PH}$ = 15.3 Hz). Found, %: C 53.63; H 3.98; Cl 17.36; P 7.36. $C_{36}H_{32}CaCl_4O_6P_2$. Calculated, %: C 53.73; H 3.98; Cl 17.66; P 7.71.

2-(5-Chloro-2-hydroxyphenyl)-2-(4-chlorophenyl)prop-1-en-1-ylphosphonic acid (XVb). Phosphonic acid **XVb** was formed when compound **VIIb** was kept in aqueous DMSO. It was characterized by spectral methods. ^{1}H NMR spectrum (600 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 6.28 d (3-H, $^2J_{PH}$ = 13.0), 6.79 d (8-H, $^3J_{HH}$ = 8.5), 7.14 d (5-H, $^4J_{HH}$ = 2.7), 7.17 d.d (7-H, $^3J_{HH}$ = 8.5, $^4J_{HH}$ = 2.7), 7.22 m and 7.34 m (10-H, 11-H, *AA'MM'*, $^3J_{AM}$ = $^3J_{A'M'}$ = 8.7). ^{13}C NMR spectrum (150.9 MHz, DMSO-d_6), δ_C, ppm (*J*, Hz): 122.48 d.d (d) (C^3, $^1J_{PC}$ = 183.8, $^1J_{CH}$ = 149.4), 150.34 m (d) (C^4, $^2J_{PC}$ = 5.4), 128.12 m (d) (C^{4a}, $^3J_{PC}$ = 7.2), 129.31 d.d (s) (C^5, $^1J_{CH}$ = 165.1, $^3J_{CH}$ = 6.0), 122.39 d.d.d (s) (C^6, $^3J_{CH}$ = 11.5–12.0, $^2J_{C,7\text{-}H}$ = 3.6, $^2J_{C,5\text{-}H}$ = 3.6), 131.06 d.d.d.d (d) (C^7, $^1J_{CH}$ = 165.2, $^3J_{CH}$ = 6.2, $^2J_{CH}$ = 2.5, $^6J_{PC}$ = 1.3), 117.53 d (s) (C^8, $^1J_{CH}$ = 160.9), 154.08 br.d.d (s) (C^{8a}, $^3J_{C,5\text{-}H}$ = 10.5, $^3J_{C,7\text{-}H}$ = 10.5–11.0), 140.00 d.t.d (d) (C^9, $^3J_{PC}$ = 21.6, $^3J_{C,11\text{-}H}$ = 7.4, $^3J_{C,3\text{-}H}$ = 6.7), 128.70 br.d.d (s) (C^{10}, $^1J_{CH}$ = 162.8, $^3J_{CH}$ = 7.7), 128.83 d.d (s) (C^{11}, $^1J_{CH}$ = 168.8, $^3J_{CH}$ = 4.7), 133.71 t.t (s) (C^{12}, $^3J_{CH}$ = 11.1, $^2J_{CH}$ = 3.3–3.4). ^{31}P NMR spectrum (162.0 MHz, DMSO-d_6): δ_P 10.1 ppm, d ($^2J_{PH}$ = 13.0 Hz).

2-Chloro-4-propyl-1,2λ^5-benzoxaphosphinine 2-oxides XVId–XIXd. Pent-1-yne, 2.1 mL (1.9 g, 28.0 mmol), was added to a solution of 4.2 g (14.0 mmol) of compound **I** in 10 mL of methylene chloride, argon was bubbled through the mixture over a period of 20 min, the mixture was evaporated by half under atmospheric pressure and was evaporated to dryness under reduced pressure (15 mm). The residue was a brown glassy mixture of compounds **XIVd**–**XIXd** at a ratio of 3.6:1.5:1.07:1. ^{31}P NMR spectrum (36.48 MHz, CH_2Cl_2), δ, ppm: 19.9 d ($^2J_{PH}$ = 24.5 Hz), 19.2 d ($^2J_{PH}$ = 22.3 Hz) (**XVId**, **XVIId**); 19.6 d ($^2J_{PH}$ = 23.4 Hz), 19.4 d ($^2J_{PH}$ = 24.5 Hz) (**XVIIId**, **XIXd**). The spectral parameters of **XVIId** were consistent with those reported in [1].

7-*tert*-Butyl-2,6-dichloro-4-propyl-1,2λ^5-benzoxaphosphinine 2-oxide (XVId). ^{1}H NMR spectrum (600 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 0.87 m (11-H, $^3J_{HH}$ = 7.5), 1.17 s (*t*-Bu), 1.50 m (10-H, $^3J_{HH}$ = 7.4), 2.49 m (9-H, $^3J_{HH}$ = 7.8), 6.07 d (3-H, $^2J_{PH}$ = 24.5), 7.12 s (8-H), 7.38 s (5-H). ^{13}C NMR spectrum (150.9 MHz, $CDCl_3$), δ_C, ppm (*J*, Hz): 112.88 d.d.t (d) (C^3, $^1J_{PC}$ = 155.6, $^1J_{CH}$ = 156.2, $^3J_{CH}$ = 5.7), 155.43 m (s) (C^4), 119.75 m (d) (C^{4a}, $^3J_{PC}$ = 19.2, $^3J_{CH}$ = 3.3), 129.24 d.d (s) (C^5, $^1J_{CH}$ = 164.3, $^4J_{PC}$ = 1.2), 129.66 d.d (s) (C^6, $^3J_{CH}$ = 11.0, $^2J_{CH}$ = 4.5), 151.34 m (s) (C^7), 119.13 d.d (d) (C^8, $^1J_{CH}$ = 163.3, $^3J_{PC}$ = 8.3), 149.09 d.d.d (d) (C^{8a}, $^3J_{CH}$ = 10.1, $^2J_{PC}$ = 9.8, $^2J_{CH}$ = 5.3), 36.21 t.d.m (d) (C^9, $^3J_{PC}$ = 19.2, $^1J_{CH}$ = 128.0, $^2J_{CH}$ = 5.6), 20.97 t.m (s) (C^{10}, $^1J_{CH}$ = 127.8, $^2J_{CH}$ = 4.5), 13.62 q.t (s) (C^{11}, $^1J_{CH}$ = 125.9, $^2J_{CH}$ = 3.9), 36.43 br.s (s) (C^{12}), 29.16 q.m (s) (C^{13}, $^1J_{CH}$ = 126.8, $^2J_{CH}$ = 4.7).

6-*tert*-Butyl-2,8-dichloro-4-propyl-1,2λ^5-benzoxaphosphinine 2-oxide (XVIIId). ^{1}H NMR spectrum (600 MHz, $CDCl_3$), ppm (*J*, Hz): 0.87 t (11-H, $^3J_{HH}$ = 7.3), 1.33 s (*t*-Bu), 1.51 m (10-H, overlapped by the 10-H signal of **XVId**), 2.53 m (9-H, $^3J_{HH}$ = 7.8), 6.09 d (3-H, $^2J_{PH}$ = 23.4), 7.34 d (7-H, $^4J_{HH}$ = 2.1), 7.37 s (5-H, $^4J_{HH}$ = 2.1). ^{13}C NMR spectrum (150.9 MHz, $CDCl_3$), δ_C, ppm (*J*, Hz): 112.65 d.t.m (d) (C^3, $^1J_{PC}$ = 158.6, $^1J_{CH}$ = 156.2, $^3J_{CH}$ = 5.4), 156.56 m (s) (C^4), 121.79 m (d) (C^{4a}, $^3J_{PC}$ = 19.1, $^3J_{CH}$ = 3.3), 121.72 d.d (s) (C^5, $^1J_{CH}$ = 161.2, $^3J_{CH}$ = 7.4), 151.45 m (s) (C^6), 121.86 d.d (s) (C^7, $^1J_{CH}$ = 158.1, $^3J_{CH}$ = 7.4), 124.15 d.d.d (d) (C^8, $^3J_{PC}$ = 7.8, $^2J_{CH}$ = 7.4), 144.45 d.d.d (d) (C^{8a}, $^3J_{C,7\text{-}H}$ = 9.0–9.5, $^3J_{C,5\text{-}H}$ = 9.0–9.5, $^2J_{PC}$ = 9.5), 36.75 d.m (s) (C^9, $^3J_{PC}$ = 19.7, $^1J_{CH}$ = 128.0), 21.27 t.m (s) (C^{10}, $^1J_{CH}$ = 128.0, $^2J_{CH}$ = 4.4), 13.66 m (s) (C^{11}, overlapped by the C^{11} signal of **XVId**), 34.76 br.s (s) (C^{12}), 29.40 q.m (s) (C^{13}, $^1J_{CH}$ = 126.9, $^2J_{CH}$ = 4.8).

7-*tert*-Butyl-2,8-dichloro-4-propyl-1,2λ^5-benzoxaphosphinine 2-oxide (XIXd). ^{1}H NMR spectrum (600 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 0.85 t (11-H, $^3J_{HH}$ = 7.5), 1.13 s (*t*-Bu), 1.50 m (10-H, overlapped by the 10-H signal of **XVId**), 2.62 m (9-H, $^3J_{HH}$ = 7.8), 6.12 d (3-H, $^2J_{PH}$ = 24.5), 7.21 d (6-H, $^3J_{HH}$ = 8.7), 7.31 s (5-H, $^3J_{HH}$ = 8.7). ^{13}C NMR spectrum (150.9 MHz, $CDCl_3$), δ_C, ppm (*J*, Hz): 113.30 d.t.m (d) (C^3, $^1J_{PC}$ = 156.3, $^1J_{CH}$ = 156.2, $^3J_{CH}$ = 5.6), 156.85 m (s) (C^4), 120.18 m (d) (C^{4a}, $^3J_{PC}$ = 18.5), 124.09 d (s) (C^5, $^1J_{CH}$ = 163.3), 123.19 d (s) (C^6, $^1J_{CH}$ = 163.9), 149.2 m (s) (C^7), 124.65 d.d (d) (C^8, $^3J_{PC}$ = 8.0, $^3J_{CH}$ = 9.6), 147.56 d.d (d) (C^{8a}, $^3J_{CH}$ = 9.5, $^2J_{PC}$ = 9.0), 36.80 d.m (s) (C^9, $^3J_{PC}$ = 19.5; overlapped by the C^9 signal of **XVId**), 21.20 t.m (s) (C^{10}, $^1J_{CH}$ = 127.5, $^2J_{CH}$ = 4.4), 13.65 m (s) (C^{11}, $^1J_{CH}$ = 127.0), 35.04 br.s (s) (C^{12}), 31.32 q.m (s) (C^{13}, $^1J_{CH}$ = 130.8, $^2J_{CH}$ = 4.8).

4-Butyl-2-chloro-1,2λ^5-benzoxaphosphinine 2-oxides XVIe–XIXe. A solution of 2.85 mL (2.04 g, 33.2 mmol) of hex-1-yne in 10 mL of methylene chloride was added to a solution of 5 g (16.6 mmol) of benzodioxaphosphole **I** in 10 mL of methylene

chloride. ^{31}P NMR spectrum of the reaction mixture (36.48 MHz, CH_2Cl_2), δ_P, ppm: 19.1 d ($^2J_{PH}$ = 23.6 Hz), 18.5 d ($^2J_{PH}$ = 23.6 Hz) (**XVIe**, **XVIIe**); 18.9 d ($^2J_{PH}$ = 23.9 Hz), 18.6 d ($^2J_{PH}$ = 23.6 Hz) (**XVIIIe**, **XIXe**). The mixture was evaporated under reduced pressure (15 mm) to obtain a brown glassy mixture of compounds **XVIe**–**XIXe** at a ratio of 4.8:2.1:1.9:1.

2-Chloro-4-pentyl-1,2λ^5-benzoxaphosphinine 2-oxides XVIf–XIXf. A solution of 3.3 mL (2.4 g, 33.2 mmol) of hept-1-yne was added to a solution of 5 g (16.6 mmol) of compound **I** in 10 mL of methylene chloride. ^{31}P NMR spectrum of the reaction mixture (36.48 MHz, CH_2Cl_2), δ, ppm: 19.4 d ($^2J_{PH}$ = 24.5 Hz), 19.2d ($^2J_{PH}$ = 22.3 Hz) (**XVIf**, **XVIIf**); 19.6 d ($^2J_{PH}$ = 23.4 Hz), 19.4 d ($^2J_{PH}$ = 24.5 Hz) (**XVIIIf**, **XIXf**). The mixture was evaporated under reduced pressure at a bath temperature of 130°C. The residue was a brown glassy mixture of benzoxaphosphinine oxides **XVIf**–**XIXf** at a ratio of 7.4:2.6:2.1:1.

7-*tert*-Butyl-6-chloro-2-hydroxy-3-propyl-1,2λ^5-benzoxaphosphinine 2-oxide (XXd) and 7-*tert*-butyl-8-chloro-2-hydroxy-3-propyl-1,2λ^5-benzoxaphosphinine 2-oxide (XXIIId). Water, 2 mL, was added to a solution of 4.3 g of compounds **XVId**–**XIXd** in 10 mL of dioxane. After several days, a white solid precipitated and was filtered off. Yield 1.85 g, a mixture of compounds **XXd** and **XXIIId** at a ratio of 3.5:1.0.

Compound **XXd**. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 0.92 t (11-H, $^3J_{HH}$ = 7.0), 1.42 s (*t*-Bu), 1.52 m (10-H, $^3J_{HH}$ = 7.6), 2.58 m (9-H, $^3J_{HH}$ = 7.5), 6.16 d (3-H, $^2J_{PH}$ = 17.5), 7.18 s (8-H), 7.55 s (7-H). ^{13}C NMR spectrum (100.6 MHz, DMSO-d_6), δ_C, ppm (*J*, Hz): 114.10 d.d.t (d) (C^3, $^1J_{PC}$ = 170.2, $^1J_{CH}$ = 161.4, $^3J_{CH}$ = 5.9), 150.32 m (s) (C^4), 120.96 m (d) (C^{4a}, $^3J_{PC}$ = 17.6, $^3J_{CH}$ = 3.7), 128.80 d (s) (C^5, $^1J_{CH}$ = 164.3), 126.85 d.d (s) (C^6, $^3J_{CH}$ = 11.0, $^2J_{CH}$ = 4.4), 148.62 m (s) (C^7, $^2J_{CH}$ = 3.7), 118.85 d.d (d) (C^8, $^1J_{CH}$ = 162.1, $^3J_{PC}$ = 7.0), 149.70 d.d.d (d) (C^{8a}, $^3J_{CH}$ = 7.2–7.3, $^2J_{PC}$ = 7.3, $^2J_{CH}$ = 5.1), 35.43 t.d.m (d) (C^9, $^3J_{PC}$ = 17.6, $^1J_{CH}$ = 125.2, $^2J_{CH}$ = 3.7), 20.90 t.m (s) (C^{10}, $^1J_{CH}$ = 124.7, $^2J_{CH}$ = 3.7), 13.69 q.m (s) (C^{11}, $^1J_{CH}$ = 124.6, $^2J_{CH}$ = 3.7), 36.00 m (s) (C^{12}, $^2J_{CH}$ = 3.0), 29.16 q.m (s) (C^{13}, $^1J_{CH}$ = 126.3, $^2J_{CH}$ = 4.2–4.4). ^{31}P NMR spectrum (162 MHz, DMSO-d_6): δ_P 7.16 ppm, d ($^2J_{PH}$ = 17.5 Hz).

Compound **XXIIId**. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 0.91 t (11-H, $^3J_{HH}$ = 7.0), 1.32 s (*t*-Bu), 1.52 m (10-H, $^3J_{HH}$ = 7.5), 2.60 m (9-H, $^3J_{HH}$ = 7.3–7.5), 6.20 d (3-H, $^2J_{PH}$ = 17.5), 7.26 d (6-H, $^3J_{HH}$ = 8.5), 7.52 d (5-H, $^3J_{HH}$ = 8.5). ^{13}C NMR spectrum (100.6 MHz, DMSO-d_6), δ_C, ppm (*J*, Hz): 113.83 d.t.m (d) (C^3, $^1J_{PC}$ = 170.9, $^1J_{CH}$ = 162.0, $^3J_{CH}$ = 5.4), 151.33 m (s) (C^4), 123.24 m (d) (C^{4a}, $^3J_{PC}$ = 17.2), 131.85 d (s) (C^5, $^1J_{CH}$ = 162.4), 124.37 d (s) (C^6, $^1J_{CH}$ = 162.1), 148.69 m (s) (C^7), 122.52 d.d (d) (C^8, $^3J_{PC}$ = 7.0, $^3J_{CH}$ = 3.4), 147.82 d.d (d) (C^{8a}, $^2J_{PC}$ = 7.2, $^3J_{CH}$ = 6.6), 36.37 t.d.m (s) (C^9, $^3J_{PC}$ = 17.6, $^1J_{CH}$ = 125.1), 21.21 t.m (s) (C^{10}, $^1J_{CH}$ = 125.1, $^2J_{CH}$ = 3.7), 13.68 m (s) (C^{11}, $^1J_{CH}$ = 124.6, $^2J_{CH}$ = 3.7), 36.02 m (s) (C^{12}), 29.39 q.m (s) (C^{13}, $^1J_{CH}$ = 126.0, $^2J_{CH}$ = 4.2–4.4). ^{31}P NMR spectrum (162 MHz, DMSO-d_6): δ_P 7.30 ppm, d ($^2J_{PH}$ = 17.5 Hz).

4-Butyl-6-*tert*-butyl-8-chloro-2-hydroxy-1,2λ^5-benzoxaphosphinine 2-oxide (XXIIe). Water, 2 mL, was added to a solution of 5.5 g of mixture **XVIe**–**XIXe** in 10 mL of acetone. After 7 days, the white crystalline precipitate was filtered off. Yield 0.56 g (53%), mp 74–76°C. IR spectrum (KBr), ν, cm^{-1}: 3530, 2312, 1605, 1563, 1467, 1365, 1172, 1005, 934, 843, 718, 615, 588, 506, 416. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 0.86 t (12-H, $^3J_{HH}$ = 6.5), 1.31 m (11-H, $^3J_{HH}$ = 6.7–7.0), 1.47 m (10-H, $^3J_{HH}$ = 6.7–7.0), 2.63 br.t (9-H, $^3J_{HH}$ = 7.0), 6.20 d (3-H, $^2J_{PH}$ = 17.6), 7.31 br.s (5-H), 7.51 br.d (7-H, $^4J_{HH}$ = 2.0). ^{13}C NMR spectrum (100.6 MHz, DMSO-d_6), δ_C, ppm (*J*, Hz): 114.32 d.d.t (d) (C^3, $^1J_{PC}$ = 171.3, $^1J_{CH}$ = 162.1, $^3J_{CH}$ = 5.1), 151.20 m (s) (C^4), 123.83 m (d) (C^{4a}, $^3J_{PC}$ = 16.5, $^3J_{C,3\text{-}H}$ = 8.1, $^3J_{C,9\text{-}H}$ = 3.7), 123.70 d.d (s) (C^5, $^1J_{CH}$ = 167.3, $^3J_{CH}$ = 4.4), 137.03 m (s) (C^6), 127.39 d.d (s) (C^7, $^1J_{CH}$ = 164.3, $^3J_{CH}$ = 6.6), 126.84 d.d (d) (C^8, $^3J_{PC}$ = 4.4, $^2J_{CH}$ = 4.4), 148.87 d.d.d (d) (C^{8a}, $^3J_{C,7\text{-}H}$ = $^3J_{C,5\text{-}H}$ = 8.4, $^2J_{PC}$ = 8.4), 34.12 t.d.m (d) (C^9, $^1J_{CH}$ = 126.1, $^3J_{PC}$ = 17.6, $^2J_{CH}$ = 4.4), 27.29 t.m (s) (C^{10}, $^1J_{CH}$ = 124.8, $^2J_{CH}$ = 4.4), 21.84 t.m (s) (C^{11}, $^1J_{CH}$ = 125.5, $^2J_{CH}$ = 4.4), 13.72 q.m (s) (C^{12}, $^1J_{CH}$ = 124.7), 34.85 m (s) (C^{13}), 29.30 q.m (s) (C^{14}, $^1J_{CH}$ = 126.1, $^2J_{CH}$ = 4.4). ^{31}P NMR spectrum (36.48 MHz, CH_2Cl_2): δ_P 5.9 ppm, d ($^2J_{PH}$ = 17.6 Hz). Found, %: C 57.83; H 6.94; Cl 10.02; P 9.32. $C_{16}H_{22}ClO_3P$. Calculated, %: C 58.45; H 6.74; Cl 10.78; P 9.42.

7-*tert*-Butyl-6-chloro-2-hydroxy-4-pentyl-1,2λ^5-benzoxaphosphinine 2-oxide (XXf) and 6-*tert*-butyl-8-chloro-2-hydroxy-4-pentyl-1,2λ^5-benzoxaphosphinine 2-oxide (XXIIf). Glassy mixture **XVIf**–**XIXf**, 6 g, was subjected to hydrolysis in moist diethyl ether. The white precipitate of compound **XXIIf** was filtered off, the filtrate was evaporated, and 10 mL of dioxane

was added to the oily residue. After several days, the white precipitate of **XXf** was filtered off.

Compound **XXf**. Yield 1.5 g (47%), mp 123°C. IR spectrum (mineral oil), ν, cm^{-1}: 2176, 1661, 1596, 1561, 1203, 1176, 1134, 1034, 999, 954, 882, 853, 822, 789, 613, 536, 478. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 0.86 t (13-H, $^3J_{HH}$ = 6.5), 1.29 m (12-H, $^3J_{HH}$ = 5.5), 1.31 m (11-H, $^3J_{HH}$ = 5.5), 1.43 br.s (*t*-Bu), 1.51 br.s (10-H, $^3J_{HH}$ = 7.0), 2.68 m (2H, 9-H, $^3J_{HH}$ = 7.5), 6.16 d (1H, 3-H, $^2J_{PH}$ = 17.5), 7.18 s (8-H), 7.55 s (5-H). ^{13}C NMR spectrum (150.9 MHz, $CDCl_3$), δ_C, ppm (*J*, Hz): 113.75 d.d.t (d) (C^3, $^1J_{PC}$ = 170.2, $^1J_{CH}$ = 161.4, $^3J_{CH}$ = 5.9), 150.33 m (s) (C^4), 120.71 m (d) (C^{4a}, $^3J_{PC}$ = 17.2, $^2J_{CH}$ = 3.7), 128.55 d (s) (C^5, $^1J_{CH}$ = 164.3), 126.58 d.d (s) (C^6, $^3J_{C,7\text{-}H}$ = 11.0, $^3J_{C,5\text{-}H}$ = 3.7), 148.36 m (s) (C^7, $^3J_{CH}$ = 2.9), 118.59 d.d (d) (C^8, $^1J_{CH}$ = 162.1, $^3J_{PC}$ = 7.3), 149.46 d.d.d (d) (C^{8a}, $^3J_{CH}$ = 7.2–7.3, $^2J_{PC}$ = 7.3, $^2J_{CH}$ = 4.4), 33.20 d.t.m (s) (C^9, $^3J_{PC}$ = 17.6, $^1J_{CH}$ = 125.2), 30.75 t.m (s) (C^{10}, $^1J_{CH}$ = 124.9, $^2J_{CH}$ = 4.4), 27.11 t.m (s) (C^{11}, $^1J_{CH}$ = 122.5, $^2J_{CH}$ = 3.7), 21.82 t.m (s) (C^{12}, $^1J_{CH}$ = 125.4, $^2J_{CH}$ = 3.7), 13.84 q.t (s) (C^{13}, $^1J_{CH}$ = 124.7, $^2J_{CH}$ = 3.7), 35.77 m (s) (C^{14}, $^2J_{CH}$ = 2.9), 28.91 q.m (s) (C^{15}, $^1J_{CH}$ = 126.2, $^2J_{CH}$ = 4.4). ^{31}P NMR spectrum (36.48 MHz, CH_2Cl_2): δ_P 7.2 ppm, d ($^2J_{PH}$ = 17.5 Hz). Found, %: C 59.03; H 7.98; Cl 9.74; P 8.77. $C_{17}H_{24}ClO_3P$. Calculated, %: C 59.56; H 7.06; Cl 10.34; P 9.04.

Compound **XXIIf**. Yield 0.2 g (22%). mp 156°C. IR spectrum, ν, cm^{-1}: 3448, 2926, 2854, 2724, 2287, 1655, 1596, 1560, 1461, 1377, 1333, 1302, 1271, 1203, 1176, 1134, 1070, 1034, 1011, 1000, 954, 907, 881, 853, 822, 789, 737, 725, 648, 613, 584, 536, 493. ^{1}H NMR spectrum (600 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 0.86 t (3H, 13-H, $^3J_{HH}$ = 3.8), 1.31–1.34 m (4H, 11-H, 12-H), 1.52 m (2H, 10-H, $^3J_{HH}$ = 3.8), 2.69 m (2H, 9-H, $^3J_{HH}$ = 7.8), 6.23 d (1H, 3-H, $^2J_{PH}$ = 18.2), 7.48 d (1H, 7-H, $^4J_{HH}$ = 1.9), 7.55 br.s (1H, 5-H). ^{13}C NMR spectrum (150.9 MHz, $CDCl_3$), δ_C, ppm (*J*, Hz): 114.18 d.d.t (d) (C^3, $^1J_{PC}$ = 170.9, $^1J_{CH}$ = 157.1, $^3J_{CH}$ = 5.7), 151.83 m (s) (C^4), 122.42 m (d) (C^{4a}, $^3J_{PC}$ = 16.9), 121.67 d.d (s) (C^5, $^1J_{CH}$ = 158.0, $^3J_{CH}$ = 7.5), 146.14 m (s) (C^6), 127.71 d.d (s) (C^7, $^1J_{CH}$ = 163.7, $^3J_{CH}$ = 8.0), 122.29 d.m (d) (C^8, $^3J_{PC}$ = 6.7), 144.60 d.d.d (d) (C^{8a}, $^3J_{C,7\text{-}H}$ = $^3J_{C,5\text{-}H}$ = 7.2, $^2J_{PC}$ = 6.5), 33.98 d.t.m (s) (C^9, $^3J_{PC}$ = 17.9, $^1J_{CH}$ = 126.2), 30.81 t.m (s) (C^{10}, $^1J_{CH}$ = 126.2), 27.47 t.m (s) (C^{11}, $^1J_{CH}$ = 126.2), 21.78 t.m (s) (C^{12}, $^1J_{CH}$ = 125.0), 13.66 m (s) (C^{13}, $^1J_{CH}$ = 124.5, $^2J_{CH}$ = 3.3). ^{31}P NMR spectrum (36.48 MHz, CH_2Cl_2): δ_P 5.9 ppm, d ($^2J_{PH}$ = 18.2 Hz). Found, %: C 58.97; H 7.34; Cl 10.12; P 8.89. $C_{17}H_{24}ClO_3P$. Calculated, %: C 59.56; H 7.06; Cl 10.34; P 9.04.

2-(5-*tert*-Butyl-3-chloro-2-hydroxyphenyl)hex-1-en-1-ylphosphonic acid (XXIV). Phosphonic acid **XXIV** was formed when compound **XXIIf** was kept in aqueous DMSO. The product was characterized by spectral data. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 0.75 t (12-H, $^3J_{HH}$ = 6.5), 6.00 d (3-H, $^2J_{PH}$ = 18.6), 6.98 br.s (5-H), 7.21 br.d (7-H). ^{13}C NMR spectrum (100.6 MHz, DMSO-d_6), δ_C, ppm (*J*, Hz): 121.05 d.d.m (d) (C^3, $^1J_{PC}$ = 183.0, $^1J_{CH}$ = 162.0), 150.77 d (s) (C^4, $^2J_{CH}$ = 10.3), 122.32 m (d) (C^{4a}), 123.91 d (s) (C^5, $^1J_{CH}$ = 155.2), 128.34 d.d (s) (C^6, $^2J_{C,7\text{-}H}$ = $^2J_{C,5\text{-}H}$ = 4.0–4.5), 127.39 d.d (s) (C^7, $^1J_{CH}$ = 155.3), 116.24 m (br.s) (C^8), 155.72 m (d) (C^{8a}, $^4J_{PC}$ = 2.5), 31.36 t.d.m (d) (C^9, $^3J_{PC}$ = 18.0, $^1J_{CH}$ = 126.0), 26.29 t.m (s) (C^{10}, $^1J_{CH}$ = 124.5), 21.94 t.m (s) (C^{11}, $^1J_{CH}$ = 125.4), 13.71 q.m (s) (C^{12}, $^1J_{CH}$ = 124.5), 35.59 m (s) (C^{13}), 29.84 q.m (s) (C^{14}, $^1J_{CH}$ = 126.0). ^{31}P NMR spectrum (36.48 MHz, CH_2Cl_2): δ_P 14.6 ppm, d ($^2J_{PH}$ = 18.6 Hz).

2,2,2-Tribromo-5-*tert*-butyl-1,3,2λ^5-benzodioxaphosphole (XXV). A mixture of 20 g (0.12 mol) of 4-*tert*-butylbenzene-1,2-diol, 12.6 mL (35.9 g, 0.13 mol) of phosphorus(III) bromide, and several drops of water was stirred for 1 h at 100–120°C. Distillation gave 20.1 g (55%) of 2-bromo-5-*tert*-butyl-1,3,2-benzodioxaphosphole as a colorless transparent liquid with bp 93°C (2 mm). ^{31}P–{^{1}H} NMR spectrum (CH_2Cl_2): δ_P 196.7 ppm.

A solution of 7.18 g (0.026 mol) of 2-bromo-5-*tert*-butyl-1,3,2-benzodioxaphosphole in 20 mL of methylene chloride was cooled to –40°C, and a solution of 1.33 mL (0.026 mol) of bromine in 15 mL of methylene chloride was added while bubbling argon through a capillary. Tribromobenzodioxaphosphole **XXV** thus formed was used in further syntheses without isolation. ^{31}P–{^{1}H} NMR spectrum (36.48 MHz, CH_2Cl_2): δ_P –188.6 ppm.

2-Bromo-7(6)-*tert*-butyl-2-oxo-4-phenyl-1,2λ^5-benzoxaphosphinine 2-oxides XXVIa and XXVIIa. Phenylacetylene, 6.7 mL (0.06 mol), was added dropwise under argon to 13.1 g (0.03 mol) of freshly prepared compound **XXV** in 20 mL of methylene chloride. After 24 h, the mixture was evaporated under reduced pressure (0.1 mm) to obtain a light brown mixture of compounds **XXVIa** and **XXVIIa** at a ratio of 4:1.

Compound **XXVIa**. ^{1}H NMR spectrum (250 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 1.32 s (*t*-Bu), 6.26 d (3-H,

$^2J_{PC}$ = 26.4). ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 115.43 d.d (d) (C^3, $^1J_{PC}$ = 142.1, $^1J_{CH}$ = 171.5), 156.03 m (d) (C^4, $^2J_{PC}$ = 2.0), 118.76 m (d) (C^{4a}, $^3J_{PC}$ = 18.0), 129.67 br.d (d) (C^5, $^1J_{CH}$ = 162.4, $^4J_{PC}$ = 1.3), 122.33 d.d (s) (C^6, $^1J_{CH}$ = 160.7, $^3J_{CH}$ = 7.1), 157.35 m (s) (C^7), 116.58 d.d.d (d) (C^8, $^1J_{CH}$ = 161.5, $^3J_{PC}$ = 8.0, $^3J_{CH}$ = 6.5), 151.34 m (d) (C^{8a}, $^3J_{PC}$ = 8.0, $^3J_{CH}$ = 9.1, $^2J_{CH}$ = 5.7, $^4J_{CH}$ = 1.7), 137.41 m (d) (C^9, $^3J_{PC}$ = 21.1, $^3J_{C,11\text{-}H}$ = 7.5, $^3J_{C,3\text{-}H}$ = 6.0–7.0), 128.49 br.d.d.d (s) (C^{10}, $^1J_{CH}$ = 160.5, $^3J_{C,12\text{-}H}$ = 6.8, $^3J_{C,14\text{-}H}$ = 6.5–6.8), 128.88 br.d.d (s) (C^{11}, $^1J_{CH}$ = 161.8, $^3J_{CH}$ = 6.8), 129.82 d.t (s) (C^{12}, $^1J_{CH}$ = 161.5, $^3J_{CH}$ = 7.6), 35.33 m (s) (C^{15}, $^2J_{CH}$ = 3.3), 31.07 q.sept (s) (C^{16}, $^1J_{CH}$ = 126.1, $^3J_{CH}$ = 4.5). ^{31}P NMR spectrum (36.48 MHz, CH_2Cl_2): δ_P 9.2 ppm, d ($^2J_{PH}$ = 26.5 Hz).

Compound **XXVIIa**. ^{1}H NMR spectrum (250 MHz, $CDCl_3$), ppm (*J*, Hz): 1.20 s (9H, *t*-Bu), 6.29 d (3-H, $^2J_{PH}$ = 26.2). ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$), δ_C, ppm (*J*, Hz): 116.21 d.d (d) (C^3, $^1J_{PC}$ = 142.5, $^1J_{CH}$ = 171.3), 156.54 m (d) (C^4, $^2J_{PC}$ = 1.6), 120.95 m (d) (C^{4a}, $^3J_{PC}$ = 18.6), 126.92 br.d.d (s) (C^5, $^1J_{CH}$ = 162.5, $^3J_{CH}$ = 5.0–6.0), 148.19 m (d) (C^6, $^5J_{PC}$ = 1.4), 129.99 (s) (C^7), 119.31 d.d (d) (C^8, $^1J_{CH}$ = 164.9, $^3J_{PC}$ = 8.1), 149.11 m (d) (C^{8a}, $^3J_{PC}$ = 10.5), 137.37 m (d) (C^9, $^3J_{PC}$ = 20.9), 128.57 (s) (C^{10}), 128.88 (s) (C^{11}), 129.80 (s) (C^{12}), 34.70 m (s) (C^{15}), 31.47 q.sept (s) (C^{16}, $^1J_{CH}$ = 126.7, $^3J_{CH}$ = 4.4); the coupling constants for C^7, C^{10}, C^{11}, and C^{12} were not determined because of signal overlap. ^{31}P NMR spectrum (36.48 MHz, CH_2Cl_2): δ_P 9.4 ppm, d ($^2J_{PH}$ = 26.4 Hz).

7- and 6-*tert*-Butyl-4-(4-chlorophenyl)-2-(diethylamino)-1,2λ^5-benzoxaphosphinine 2-oxides XXVIb and XXVIIb. A solution of 12 g (0.09 mol) of 4-chlorophenylacetylene in 30 mL of methylene chloride was added to a solution of 17.2 g (0.04 mol) of freshly prepared compound **XXV** in 30 mL of methylene chloride, and the mixture was stirred for 1.5 h by bubbling argon through a capillary. After 3 days, the mixture was evaporated, and the residue was dried under reduced pressure (0.1 mm) to obtain a brown oily mixture of compounds **XXVIb** and **XXVIIb** at a ratio of 9 : 2. ^{31}P NMR spectrum (36.48 MHz, CH_2Cl_2), δ_P, ppm: 8.6 d ($^2J_{PH}$ = 25.8 Hz) (**XXVIb**); 9.7 d ($^2J_{PH}$ = 28.0 Hz) (**XXVIIb**).

2-Bromo-7- and -6-*tert*-butyl-4-(4-methylphenyl)-1,2λ^5-benzoxaphosphinine 2-oxides XXVIc and XXVIIc. A solution of 6.64 mL (0.052 mol) of 4-methylphenylacetylene in 30 mL of methylene chloride was added dropwise to a solution of 11.4 g (0.026 mol) of compound **XXV** in 35 mL of methylene chloride. After 8 h, the solvent was distilled off, and volatile impurities were then removed at 150°C under reduced pressure (0.1 mm). The residue was a mixture of compounds **XXVIc** and **XXVIIc** at a ratio of 9 : 1. ^{31}P NMR spectrum (36.48 MHz, CH_2Cl_2), δ_P, ppm: 8.3 d ($^2J_{PH}$ = 26.0 Hz) (**XXVIc**); 9.4 d ($^2J_{PH}$ = 27.5 Hz) (**XXVIIc**).

7- and 6-*tert*-Butyl-4-(4-chlorophenyl)-2-diethylamino-1,2λ^5-benzoxaphosphinine 2-oxides XXVIIIb and XXIXb. Diethylamine, 7 mL, was added under stirring to a solution of 10 g of mixture **XXVIb**/**XXVIIb** in 45 mL of benzene. The precipitate was filtered off, combined with the precipitate obtained after partial evaporation of the filtrate under reduced pressure (12 mm), washed with a solution of sodium carbonate with pH 8.0 and with water, and dried in air to obtain a mixture of compounds **XXVIIIb** and **XXIXb** at a ratio of 9 : 1. Repeated recrystallization from aqueous acetone gave pure compound **XXVIIIb**.

Compound **XXVIIIb**. mp 173°C. IR spectrum, ν, cm^{-1}: 3426, 2127, 1664, 1614, 1591, 1536, 1344, 1244, 1223, 1202, 1174, 1086, 1033, 1008, 976, 918, 878, 837, 788, 636, 547, 530, 509, 476, 451. ^{1}H NMR spectrum (250 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 1.07 t (CH_3, $^2J_{HH}$ = 7.1), 1.27 s (*t*-Bu), 3.05 d.q (CH_2, $^2J_{PH}$ = 12.3, $^2J_{HH}$ = 7.0), 6.04 d (3-H, $^2J_{PH}$ = 17.5), 7.15 m and 7.09 m (5-H, 6-H, *AB*, $^3J_{AB}$ = 8.3), 7.52 m and 7.40 m (10-H, 11-H, *AA′BB′*, $^3J_{AB}$ = $^3J_{A'B'}$ = 8.4). ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$), δ_C, ppm (*J*, Hz): 116.75 d.d (d) (C^3, $^1J_{PC}$ = 143.0, $^1J_{CH}$ = 171.0), 156.64 m (d) (C^4, $^2J_{PC}$ = 2.2), 117.75 m (d) (C^{4a}, $^3J_{PC}$ = 17.8), 129.63 d (s) (C^5, $^1J_{CH}$ = 163.4), 121.54 d.d (s) (C^6, $^1J_{CH}$ = 160.1, $^3J_{CH}$ = 6.5), 156.22 m (s) (C^7), 116.47 d.m (d) (C^8, $^1J_{CH}$ = 160.0, $^3J_{PC}$ = 8.1, $^3J_{CH}$ = 8.0), 151.01 m (d) (C^{8a}, $^3J_{PC}$ = 9.8), 136.77 m (d) (C^9, $^3J_{PC}$ = 21.0), 129.71 d.d (s) (C^{10}, $^1J_{CH}$ = 163.3, $^3J_{CH}$ = 7.9), 128.87 d.d (s) (C^{11}, $^1J_{CH}$ = 168.5, $^3J_{CH}$ = 5.4), 135.52 m (s) (C^{12}), 34.85 m (s) (C^{15}), 30.84 q.sept (s) (C^{16}, $^1J_{CH}$ = 126.1, $^3J_{CH}$ = 4.4). ^{31}P–{^{1}H} NMR spectrum (36.48 MHz, DMSO-d_6): δ_P 12.0 ppm. Found, %: C 64.82; H 7.04; N 3.93; P 7.48. $C_{22}H_{27}ClNO_2P$. Calculated, %: C 65.42; H 6.74; 3.47; P 7.67.

Compound **XXIXb**. ^{1}H NMR spectrum (250 MHz, DMSO-d_6), δ, ppm: 5.95 d (3-H, $^2J_{PH}$ = 17.7 Hz). ^{31}P–{^{1}H} NMR spectrum (36.48 MHz, DMSO-d_6): δ_P 12.5 ppm.

7-*tert*-Butyl-2-diethylamino-4-(4-methylphenyl)-1,2λ^5-benzoxaphosphinine 2-oxide (XXIXc). Diethylamine, 12 mL, was added to 10.43 g of a mixture of compounds **XXVIc** and **XXVIIc** in 30 mL of ben-

zene. The precipitate was filtered off, combined with the precipitate obtained after partial evaporation of the filtrate under reduced pressure (12 mm), washed with a solution of sodium carbonate with pH 8.0 and with water, and dried in air. Yield 6.4 g (70%), mp 163°C. IR spectrum, ν, cm^{-1}: 2926, 2858, 1926, 1615, 1591, 1539, 1502, 1463, 1406, 1381, 1345, 1302, 1281, 1247, 1224, 1204, 1180, 1133, 1106, 1087, 1039, 969, 919, 876, 840, 795, 773, 716, 693, 673, 643, 626, 598, 548, 510, 473, 431. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), ppm (*J*, Hz): 1.31 s (9H, *t*-Bu), 1.15 t (6H, $CH_2C\mathbf{H}_3$, $^3J_{HH}$ = 7.2), 2.42 s (3H, CH_3), 3.14 q.d and 3.16 q.d (4H, NCH_2, $^3J_{PH}$ = 8.9–9.0, $^3J_{HH}$ = 7.2), 5.88 d (1H, 3-H, $^2J_{PH}$ = 18.1), 7.04 d.d (1H, 6-H, $^3J_{HH}$ = 8.4, $^4J_{HH}$ = 1.9), 7.15 d (1H, 5-H, $^3J_{HH}$ = 8.4), 7.22 d (1H, 8-H, $^4J_{HH}$ = 1.9), 7.26 m (4H, 10-H, 11-H, *AA′BB′*, $^3J_{AB}$ = $^3J_{A'B'}$ = 8.3). ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$), δ_C, ppm (*J*, Hz): 113.31 d.d (d) (C^3, $^1J_{PC}$ = 160.4, $^1J_{CH}$ = 160.8), 155.12 m (d) (C^4, $^2J_{PC}$ = 1.9), 118.82 br.d.d.d.d (d) (C^{4a}, $^3J_{PC}$ = 15.2, $^3J_{C,3\text{-}H}$ = 8.0–9.0, $^3J_{C,8\text{-}H}$ = $^3J_{C,6\text{-}H}$ = 6.5–7.0), 128.64 d (s) (C^5, $^1J_{CH}$ = 161.1), 120.13 d.d (s) (C^6, $^1J_{CH}$ = 159.4, $^3J_{CH}$ = 7.4), 155.10 m (s) (C^7), 116.56 br.d.d.d (d) (C^8, $^1J_{CH}$ = 159.9, $^3J_{PC}$ = 7.1, $^3J_{CH}$ = 6.7), 152.18 br.d.d.d (d) (C^{8a}, $^3J_{CH}$ = 9.1, $^2J_{PC}$ = 8.5, $^2J_{CH}$ = 3.9), 136.56 d.t.d (d) (C^9, $^3J_{PC}$ = 18.3, $^3J_{C,11\text{-}H}$ = 7.7, $^3J_{C,3\text{-}H}$ = 6.8), 128.49 d.d (s) (C^{10}, $^1J_{CH}$ = 159.8, $^3J_{CH}$ = 5.7), 129.25 d.d.q (s) (C^{11}, $^1J_{CH}$ = 158.1, $^3J_{C,13\text{-}H}$ = $^3J_{C,Me}$ = 5.4), 138.69 t.q (s) (C^{12}, $^3J_{CH}$ = 6.4, $^2J_{CH}$ = 6.4), 35.00 m (s) (C^{15}), 31.16 q.sept (s) (C^{16}, $^1J_{CH}$ = 126.0, $^3J_{CH}$ = 4.6), 39.21 t.d.q (d) (C^{17}, $^1J_{CH}$ = 136.7, $^2J_{PC}$ = 5.3, $^2J_{CH}$ = 4.0), 14.70 q.d.t (d) (C^{18}, $^1J_{CH}$ = 126.0, $^3J_{PC}$ = 2.0, $^2J_{CH}$ = 2.0–2.2), 21.33 q.t (s) (C^{23}, $^1J_{CH}$ = 126.5, $^3J_{CH}$ = 4.1). ^{31}P NMR spectrum (36.48 MHz, C_6H_6): δ_P 11.1 ppm, d.q ($^2J_{PH}$ = 14.1, $^3J_{PH}$ = 9.0 Hz). Found, %: C 71.84; H 8.02; N 3.53; P 7.96. $C_{23}H_{30}NO_2P$. Calculated, %: C 72.04; H 7.89; N 3.65; P 8.08.

7-*tert*-Butyl-2-hydroxy-4-phenyl-1,2λ^5-benzoxaphosphinine 2-oxide (XXXa). *a*. A mixture of 4.1 g of compounds **XXVIa** and **XXVIIa** was treated with 0.2 mL of water in diethyl ether on cooling. The white precipitate was filtered off, recrystallized from diethyl ether, and dried. Yield 1.9 g (20%), mp 215–218°C. IR spectrum, ν, cm^{-1}: 3322 v.br, 3076, 3028, 2960, 2925, 2857, 2600, 2385, 2354, 2287, 1843, 1753, 1616, 1585, 1537, 1463, 1405, 1368, 1344, 1234, 1194, 1085, 1008, 981, 932, 878, 838, 807, 786, 759, 701, 671, 640, 574, 543, 508, 465, 437. ^{1}H NMR spectrum (250 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 1.33 s (9H, *t*-Bu), 6.13 d (1H, 3-H, $^2J_{PH}$ = 18.0), 7.10 d and 7.14 d.d (2H, 5-H, 6-H, *AB*, $^3J_{AB}$ = 8.7, $^4J_{HH}$ = 1.7), 7.31 d (1H, 8-H, $^4J_{HH}$ = 1.6). ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$), δ_C, ppm (*J*, Hz): 110.86 d.d (d) (C^3, $^1J_{PC}$ = 180.1, $^1J_{CH}$ = 165.0), 155.88 m (d) (C^4, $^2J_{PC}$ = 2.6), 119.09 m (d) (C^{4a}, $^3J_{PC}$ = 16.8), 129.03 d (s) (C^5, $^1J_{CH}$ = 161.6), 120.90 d.d (s) (C^6, $^1J_{CH}$ = 159.5, $^3J_{CH}$ = 7.0), 155.72 m (s) (C^7), 116.63 d.d.d (d) (C^8, $^1J_{CH}$ = 159.7, $^3J_{PC}$ = 7.9, $^3J_{CH}$ = 6.3), 151.43 m (d) (C^{8a}, $^3J_{PC}$ = 6.8, $^3J_{CH}$ = 8.7, $^2J_{CH}$ = 5.2, $^4J_{C,6\text{-}H}$ = $^4J_{C,3\text{-}H}$ = 1.2), 138.99 m (d) (C^9, $^3J_{PC}$ = 19.6), 128.60 br.d.d.d (s) (C^{10}, $^1J_{CH}$ = 160.9, $^3J_{C,14\text{-}H}$ = $^3J_{C,12\text{-}H}$ = 7.1–7.2), 128.68 d.d (s) (C^{11}, $^1J_{CH}$ = 161.5, $^3J_{CH}$ = 8.2–8.3), 129.09 d.t (s) (C^{12}, $^1J_{CH}$ = 159.1, $^3J_{CH}$ = 7.7), 35.15 m (s) (C^{15}), 31.18 q.sept (s) (C^{16}, $^1J_{CH}$ = 126.1, $^3J_{CH}$ = 4.7). ^{31}P NMR spectrum (36.48 MHz, $CDCl_3$): δ_P 12.6 ppm, d ($^2J_{PH}$ = 17.5 Hz). Found, %: C 68.46; H 6.37. $C_{18}H_{19}O_3P$. Calculated, %: C 68.78; H 6.05.

b. Compound **XXXa** was synthesized in a similar way from mixture **XXXVIII**/**XXXIX**. The product showed no depression of the melting point on mixing with a sample obtained as described in *a*.

7-*tert*-Butyl-2-hydroxy-4-(4-methylphenyl)-1,2λ^5-benzoxaphosphinine 2-oxide (XXXc). Water, 0.16 mL, was added to 3.28 g of a mixture of compounds **XXVIc** and **XXVIIc** in 20 mL of methylene chloride while bubbling argon through a capillary. The solvent was removed by distillation, the thick viscous residue was dried under reduced pressure (12 mm) at 150°C and treated with diethyl ether, and the white precipitate was filtered off. Yield 1.73 g (70%), mp 217°C. IR spectrum, ν, cm^{-1}: 3448, 3026, 2924, 2855, 2366, 1660, 1615, 1583, 1535, 1506, 1462, 1404, 1364, 1344, 1301, 1230, 1199, 1134, 1085, 1003, 918, 876, 842, 822, 792, 768, 717, 673, 631, 599, 546, 508, 469, 435. ^{1}H NMR spectrum (250 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 1.34 s (9H, *t*-Bu), 2.44 s (3H, CH_3), 6.13 d (1H, 3-H, $^2J_{PH}$ = 18.3), 7.14 d and 7.17 d.d (2H, 5-H, 6-H, *AB*, $^3J_{AB}$ = 8.7, $^4J_{HH}$ = 1.6), 7.29 m (4H, 10-H, 11-H, *AA′BB′*), 7.32 d (2H, 8-H, $^4J_{HH}$ = 1.6). ^{13}C NMR spectrum (100.6 MHz, DMSO-d_6), δ_C, ppm (*J*, Hz): 120.44 d.d (d) (C^3, $^1J_{PC}$ = 178.6, $^1J_{CH}$ = 165.6), 155.88 m (d) (C^4, $^2J_{PC}$ = 2.8), 119.20 d.d.d.d (d) (C^{4a}, $^3J_{PC}$ = 16.5, $^3J_{C,3\text{-}H}$ = 8.5, $^3J_{C,8\text{-}H}$ = 6.5–7.0, $^3J_{C,6\text{-}H}$ = 4.8–5.0), 129.06 d (s) (C^5, $^1J_{CH}$ = 161.7), 120.79 d.d (s) (C^6, $^1J_{CH}$ = 159.2, $^3J_{CH}$ = 7.0), 155.72 m (s) (C^7), 116.58 d.d.d (d) (C^8, $^1J_{CH}$ = 159.2, $^3J_{PC}$ = 8.1, $^3J_{CH}$ = 7.2), 151.42 m (d) (C^{8a}, $^2J_{PC}$ = 6.6, $^3J_{CH}$ = 10.5, $^2J_{CH}$ = 2.6, $^4J_{CH}$ = 1.0), 136.07 m (d) (C^9, $^3J_{PC}$ = 19.9, $^3J_{C,11\text{-}H}$ = 7.4, $^3J_{C,3\text{-}H}$ = 6.8), 128.53 d.d (s) (C^{10}, $^1J_{CH}$ = 160.0, $^3J_{CH}$ = 5.3), 129.32 d.d.q (s) (C^{11}, $^1J_{CH}$ = 158.1, $^3J_{C,13\text{-}H}$ = 6.0, 5.2), 139.07 m (s) (C^{12}, $^3J_{CH}$ = 7.0, $^2J_{CH}$ = 6.5), 34.88 m (s) (C^{15}, $^3J_{C,8\text{-}H}$ =

$^3J_{C,6\text{-}H}$ = 4.2, $^2J_{CH}$ = 3.8), 31.15 q.sept (s) (C^{16}, $^1J_{CH}$ = 126.2, $^3J_{CH}$ = 4.6), 21.38 q.t (s) (C^{23}, $^1J_{CH}$ = 125.5, $^3J_{CH}$ = 4.2). ^{31}P NMR spectrum (36.48 MHz, $CDCl_3$): δ_P 13.0 ppm, d ($^2J_{PH}$ = 18.4 Hz). Found, %: C 69.38; H 6.22. $C_{19}H_{21}O_3P$. Calculated, %: C 69.51; H 6.41.

Isopropylammonium 7-*tert*-butyl-2-oxo-4-phenyl-1,2λ^5-benzoxaphosphinin-2-olate (XXXIIa). Isopropylamine, 0.2 mL, was added to a solution of 0.6 g of compound **XXXa** in 15 mL of diethyl ether. After 3 days, the colorless crystals were filtered off. Yield 76% (0.52 g), mp 202°C. IR spectrum, ν, cm^{-1}: 3366, 2924, 2854, 2574, 2346, 2161, 1959, 1895, 1752, 1720, 1642, 1612, 1591, 1572, 1548, 1522, 1492, 1461, 1406, 1385, 1378, 1359, 1344, 1296, 1280, 1258, 1228, 1200, 1170, 1131, 1078, 1066, 1036, 1000, 965, 929, 908, 878, 845, 834, 824, 810, 778, 753, 718, 700, 669, 641, 625, 602, 576, 554, 541, 518, 475, 441, 420. ^{1}H NMR spectrum (250 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 1.20 m (*i*-Pr), 1.23 s (*t*-Bu), 3.47 q (CH), 6.17 d (3-H, $^2J_{PH}$ = 18.2), 6.94 d.d and 7.02 d (5-H, 6-H, *AB*, $^3J_{AB}$ = 8.3, $^4J_{HH}$ = 1.8), 7.16 d (8-H, $^4J_{HH}$ = 1.8), 7.34 s (5H, C_6H_5). Found, %: C 67.26; H 7.89; N 3.93; P 8.32. $C_{21}H_{28}NO_3P$. Calculated, %: C 67.56; H 7.51; N 3.75; P 8.31.

Isopropylammonium 7-*tert*-butyl-4-(4-methylphenyl)-2-oxo-1,2λ^5-benzoxaphosphinin-2-olate (XXXIIc). Isopropylamine, 0.2 mL, was added to a solution of 1.1 g of compound **XXXc** in 15 mL of diethyl ether; a white solid immediately precipitated. Yield 0.53 g (49%), mp 187°C. IR spectrum, ν, cm^{-1}: 3449, 2924, 2854, 2758, 2665, 2580, 2346, 2175, 1925, 1736, 1719, 1637, 1613, 1591, 1562, 1509, 1498, 1460, 1405, 1396, 1379, 1338, 1301, 1280, 1260, 1232, 1199, 1171, 1130, 1111, 1081, 1066, 1021, 970, 961, 914, 882, 853, 834, 819, 797, 761, 714, 672, 645, 630, 593, 555, 511, 489, 445, 420. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 1.15 d (6H, CH_3, $^3J_{HH}$ = 6.5), 1.27 s (9H, *t*-Bu), 3.17 m (1H, CH, $^3J_{HH}$ = 6.5), 5.92 d (1H, 3-H, $^2J_{PH}$ = 16.7), 6.90 m and 6.92 m (2H, 6-H, 5-H, *AB* part of *ABM*, $^2J_{AB}$ = 8.2, $^4J_{BM}$ = 1.9), 6.98 d (1H, 8-H, *M* part of *ABM*, $^4J_{BM}$ = 1.9), 7.17 m and 7.23 m (4H, 10-H, 11-H, *AA′BB′*, $^3J_{AB}$ = $^3J_{A'B'}$ = 8.7). ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$), δ_C, ppm (*J*, Hz): 113.11 d.d (d) (C^{13}, $^1J_{PC}$ = 160.5, $^1J_{CH}$ = 160.5), 154.92 m (d) (C^4, $^2J_{PC}$ = 1.8), 116.26 m (d) (C^{4a}, $^3J_{PC}$ = 15.2), 128.43 d (s) (C^5, $^1J_{CH}$ = 161.1), 119.93 d.d (s) (C^6, $^1J_{CH}$ = 159.4, $^3J_{CH}$ = 7.6), 154.90 m (s) (C^7), 116.36 br.d.d.d (d) (C^8, $^1J_{CH}$ = 159.5, $^3J_{PC}$ = 7.1, $^3J_{CH}$ = 6.9), 151.99 d.d.d (d) (C^{8a}, $^3J_{CH}$ = 9.1, $^3J_{PC}$ = 8.4, $^2J_{CH}$ = 4.0), 136.36 br.d.t.d (d) (C^9, $^3J_{PC}$ = 18.3, $^3J_{C,11\text{-}H}$ = 7.8, $^3J_{C,3\text{-}H}$), 128.29 d.d (s) (C^{10}, $^1J_{CH}$ = 159.6, $^3J_{CH}$ = 5.5), 129.05 d.d.q (s) (C^{11}, $^1J_{CH}$ = 158.0, $^3J_{C,13\text{-}H}$ = 5.2, $^3J_{C,Me}$ = 5.2), 138.48 t.q (s) (C^{12}, $^3J_{CH}$ = $^2J_{CH}$ = 6.4–6.6), 34.81 m (s) (C^{15}), 30.96 q.sept (s) (C^{16}, $^1J_{CH}$ = 126.0, $^3J_{CH}$ = 4.7), 21.13 q.t (s) (C^{23}, $^1J_{CH}$ = 126.8, $^3J_{CH}$ = 3.8). ^{31}P NMR spectrum (36.48 MHz, DMSO-d_6): δ_P –0.6 ppm, d ($^2J_{PH}$ = 16.7 Hz). Found, %: C 68.01; H 7.46; N 3.64; P 8.22. $C_{22}H_{30}NO_3P$. Calculated, %: C 68.21; H 7.75; N 3.61; P 8.01.

2-Bromo-4-butyl-7- and -6-*tert*-butyl-1,2λ^5-benzoxaphosphinine 2-oxides XXXIII and XXXIV. A solution of 4.6 mL (3.29 g, 0.04 mol) of hex-1-yne was added to a solution of 8.65 g (0.0199 mol) of freshly prepared benzodioxaphosphole **XXV** in 200 mL of methylene chloride. ^{31}P NMR spectrum of the reaction mixture (36.48 MHz, CH_2Cl_2), δ_P, ppm: 10.3 d ($^2J_{PH}$ = 25.8 Hz) (**XXXIII**), 9.3 d ($^2J_{PH}$ = 27.9 Hz) (**XXXIV**). The mixture was evaporated under reduced pressure (water-jet pump) at a bath temperature of 130°C. The residue was a brown glassy mixture of compounds **XXXIII** and **XXXIV** at a ratio of 2.8:1.0.

Compound **XXXIII**. ^{13}C NMR spectrum (150.9 MHz, $CDCl_3$), δ_C, ppm (*J*, Hz): 113.76 d.d.t (d) (C^3, $^1J_{PC}$ = 144.2, $^1J_{CH}$ = 144.8, $^3J_{CH}$ = 6.6), 156.75 m (s) (C^4), 118.21 m (d) (C^{4a}, $^3J_{PC}$ = 18.6), 126.4 d (s) (C^5, $^1J_{CH}$ = 159.2), 122.48 d.d (s) (C^6, $^1J_{CH}$ = 159.8, $^3J_{CH}$ = 7.2), 149.25 m (s) (C^7), 116.63 d.d (d) (C^8, $^3J_{PC}$ = 8.4, $^1J_{CH}$ = 161.0, $^3J_{CH}$ = 7.2), 150.97 m (d) (C^{8a}, $^2J_{PC}$ = 19.8), 34.39 t.d.m (d) (C^9, $^1J_{CH}$ = 127.8, $^3J_{PC}$ = 19.8), 30.17 t.m (s) (C^{10}, $^1J_{CH}$ = 125.0), 22.3 t.m (s) (C^{11}, $^1J_{CH}$ = 125.1), 13.87 q.t (s) (C^{12}, $^1J_{CH}$ = 125.0, $^2J_{CH}$ = 3.9).

Compound **XXXIV**. ^{13}C NMR spectrum (150.9 MHz, $CDCl_3$), δ_C, ppm (*J*, Hz): 114.64 d.d (d) (C^3, $^1J_{PC}$ = 144.2, $^1J_{CH}$ = 145.0), 156.50 m (s) (C^4), 120.14 m (d) (C^{4a}, $^3J_{PC}$ = 18.6), 123.23 d.d (s) (C^5, $^1J_{CH}$ = 156.8, $^3J_{CH}$ = 7.2), 148.09 m (s) (C^6), 129.51 d.d (s) (C^7, $^1J_{CH}$ = 159.2, $^3J_{CH}$ = 7.8), 119.3 m (d) (C^8, $^3J_{PC}$ = 7.8), 148.77 m (d) (C^{8a}, $^2J_{PC}$ = 10.2), 35.03 t.d.m (s) (C^9, $^3J_{PC}$ = 18.63, $^1J_{CH}$ = 127.0), 30.17 m (s) (C^{10}), 22.34 m (s) (C^{11}), 13.9 q.t (s) (C^{12}, $^1J_{CH}$ = 125.0, $^2J_{CH}$ = 4.2).

4-Butyl-7-*tert*-butyl-2-hydroxy-1,2λ^5-benzoxaphosphinine 2-oxide (XXXV). Water, 5 mL, was added to 7 g of a mixture of compounds **XXXIII** and **XXXIV** in 20 mL of diethyl ether. The white precipitate was filtered off and dried. Yield 20%, mp 166°C. IR spectrum, ν, cm^{-1}: 3435, 2958, 2854, 2725, 2670, 2273, 2150, 1959, 1925, 1702, 1615, 1595, 1539, 1502, 1465, 1401, 1377, 1364, 1302, 1284, 1222,

1194, 1160, 1132, 1094, 1039, 1020, 972, 938, 926, 899, 879, 834, 802, 787, 755, 718, 678, 654, 629, 609, 546, 537, 514, 480, 451. ^{1}H NMR spectrum (600 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 0.92 t (3H, 12-H, $^3J_{HH}$ = 5.4), 1.29 br.s (3H, 14-H), 1.37 m (2H, 11-H, $^3J_{HH}$ = 5.6, 5.6), 1.51 m (2H, 10-H, $^3J_{HH}$ = 5.4, 7.0), 2.63 m (2H, 9-H, $^3J_{HH}$ = 7.0), 6.06 d (1H, 3-H, $^2J_{PH}$ = 18.1), 7.14 br.s (1H, 8-H), 7.23 br.d (1H, 6-H, $^3J_{HH}$ = 6.0), 7.55 d (1H, 5-H, $^3J_{HH}$ = 6.0).

2,2-Dibromo-5-*tert*-butyl-2-fluoro-1,3,2λ^5-benzodioxaphosphole (XXXVII). Several drops of water were added to a mixture of 64.5 g (0.32 mol) of 4-*tert*-butylbenzene-1,2-diol and 45 mL (0.51 mol) of PCl_3. The mixture was stirred for 2.5 h at 100–120°C and distilled to isolate 81.2 g (91%) of 5-*tert*-butyl-2-chloro-1,3,2-benzodioxaphosphole with bp 86–89°C (0.6 mm). ^{31}P–{^{1}H} NMR spectrum (162.0 MHz, CH_2Cl_2): δ_P 173.5 ppm.

Finely ground antimony trifluoride, 20 g (0.12 mol), was carefully added on cooling to 30.6 g (0.133 mol) of 5-*tert*-butyl-2-chloro-1,3,2-benzodioxaphosphole. The mixture was thoroughly mixed and slowly heated to 60–70°C, kept for 1 h at room temperature, and distilled under reduced pressure using a capillary to isolate 23.0 g (81%) of 5-*tert*-butyl-2-fluoro-1,3,2-benzodioxaphosphole as a colorless transparent liquid, bp 94–98°C (10 mm). ^{31}P–{^{1}H} NMR spectrum (CH_2Cl_2): δ_P 124.3 ppm, d ($^1J_{PF}$ = 1299.4 Hz).

A solution of 4.28 g (0.02 mol) of 5-*tert*-butyl-2-fluoro-1,3,2-benzodioxaphosphole in 8 mL of methylene chloride was cooled to –40°C, a solution of 1.07 mL (0.02 mol) of bromine in 3 mL of methylene chloride was added dropwise while bubbling argon through a capillary, and dibromofluorobenzodioxaphosphole **XXXVII** thus formed was used in further syntheses without isolation. ^{31}P–{^{1}H} NMR spectrum (36.48 MHz, CH_2Cl_2): δ_P –88.0 ppm ($^1J_{PF}$ = 1033.0 Hz).

7- and 6-*tert*-Butyl-2-fluoro-4-phenyl-1,2λ^5-benzoxaphosphinine 2-oxides XXXVIII and XXXIX. Phenylacetylene, 7.1 mL (0.064 mol), was added dropwise under argon to 10.2 g (0.032 mol) of freshly prepared phosphole **XXXVII** in 30 mL of methylene chloride. After 24 h, the mixture was evaporated under reduced pressure (0.1 mm) at a bath temperature of 150°C. The residue was a light brown mixture of compounds **XXXVIII** and **XXXIX** at a ratio of 4:1. Mass spectrum, *m*/*z*: 316 $[M]^+$. $C_{18}H_{18}FO_2P$. Found: *M* 316.31.

Compound **XXXVIII**. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$), δ_C, ppm (*J*, Hz): 106.05 d.d.d (d) (C^3, $^1J_{PC}$ = 179.3, $^1J_{CH}$ = 168.3, $^2J_{CF}$ = 28.0), 159.71 m (d.d) (C^4, $^3J_{CF}$ = 2.9, $^2J_{PC}$ = 2.4), 118.24 m (d) (C^{4a}, $^3J_{PC}$ = 17.1), 129.36 d (s) (C^5, $^1J_{CH}$ = 162.6), 121.68 d.d (s) (C^6, $^1J_{CH}$ = 160.6, $^3J_{CH}$ = 7.0), 156.82 m (s) (C^7), 116.03 d.d.d (d) (C^8, $^1J_{CH}$ = 160.8, $^3J_{PC}$ = 8.3, $^3J_{CH}$ = 6.0), 150.84 br.d.d.d (d) (C^{8a}, $^3J_{PC}$ = 8.4, $^3J_{CH}$ = 8.6, $^2J_{CH}$ = 5.0, $^4J_{CH}$ = 1.3–1.5), 137.50 m (d) (C^9, $^3J_{PC}$ = 20.6), 127.97 d.d.d (s) (C^{10}, $^1J_{CH}$ = 159.7, $^3J_{C,14\text{-}H}$ = 7.6, $^3J_{CH}$ = 7.5), 128.52 br.d.d (s) (C^{11}, $^1J_{CH}$ = 161.9, $^3J_{CH}$ = 6.0), 129.47 d.t (s) (C^{12}, $^1J_{CH}$ = 161.5, $^3J_{CH}$ = 7.6), 34.81 m (s) (C^{15}), 30.64 q.sept (s) (C^{16}, $^1J_{CH}$ = 126.2, $^3J_{CH}$ = 4.7). ^{31}P NMR spectrum (162.0 MHz, $CDCl_3$): δ_P 5.0 ppm, d.d ($^1J_{PF}$ = 1059.1, $^2J_{PH}$ = 19.2 Hz).

Compound **XXXIX**. ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$), δ_C, ppm (*J*, Hz): 106.94 d.d.d (d) (C^3, $^1J_{PC}$ = 180.6, $^1J_{CH}$ = 167.9, $^2J_{CF}$ = 29.8), 160.18 m (d.d) (C^4, $^3J_{CF}$ = 2.9, $^2J_{PC}$ = 2.5), 120.19 m (d) (C^{4a}, $^3J_{PC}$ = 17.0), 126.48 d.d (s) (C^5, $^1J_{CH}$ = 163.0, $^3J_{CH}$ = 6.8), 147.45 m (s) (C^6), 129.83 d.d (s) (C^7, $^3J_{CH}$ = 6.9), 118.81 d.d (d) (C^8, $^1J_{CH}$ = 164.4, $^3J_{PC}$ = 8.2), 148.72 m (d) (C^{8a}, $^3J_{PC}$ = 8.4), 137.21 m (d) (C^9, $^3J_{PC}$ = 21.0), 128.06 (s) (C^{10}), 128.52 (s) (C^{11}), 129.62 (s) (C^{12}), 34.20 m (s) (C^{15}), 30.87 q.sept (s) (C^{16}, $^1J_{CH}$ = 126.0, $^3J_{CH}$ = 4.8); the coupling constants for C^7, C^{10}, C^{11}, and C^{12} were not determined because of signal overlap. ^{31}P NMR spectrum (36.48 MHz, $CDCl_3$): δ_P 4.8 ppm, d.d ($^1J_{PF}$ = 1060.8 Hz, $^2J_{PH}$ = 19.3 Hz).

The X-ray diffraction data for single crystals of **XIb**, **XXVIIIb**, **XXVIIIc**, **XXXIIa**, and **XXXV** were obtained at the X-Ray Analysis Department, Joint Spectral and Analytical Center, Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences. The crystallographic parameters and parameters of X-ray diffraction experiments and structure refinement are given in table. The data were obtained on a Nonius B.V. CAD-4 automated four-circle diffractometer at 20°C (Mo*K* radiation, graphite monochromator) and were preliminarily processed using MolEN program [19] on an AlphaStation 200 PC. No drop in the intensity of three control reflections was observed during experiments. The structure of **XXVIIIc** was solved by the direct method using SIR program [20] and was refined first in isotropic and then in anisotropic approximation. Hydrogen atoms were localized from the difference electron density maps, and their contributions to structural amplitudes were included with fixed positional and temperature parameters in the final refinement step. All calculations were performed using MolEN software [19] in an Alpha Station 200 PC. The structures of **XIb** and **XXXIIa** were solved by the direct

method using SIR program [20] and were refined first in isotropic and then in anisotropic approximation using SHELXL-97 [21] and WinGX [22]. Hydrogen atoms were visualized by the difference electron density maps, and their positions were refined according to the riding model. Intermolecular interactions were analyzed, and the molecular structures were plotted, using PLATON program [23].

The coordinates of atoms in structures **XIb**, **XXVIIIb**, **XXVIIIc**, **XXXIIa**, and **XXXV**, and their temperature factors were deposited to the Cambridge Crystallographic Data Centre (http://www.ccdc.cam.ac.uk; for entry numbers, see table).**

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** Tabulated bond lengths and bond and torsion angles are available from the authors upon request by e-mail.