Reactions of 3,5-di(*tert*-butyl)-1,2-benzoquinone with terminal acetylenes in the presence of phosphorus trichloride. *ipso*-Substitution of the *tert*-butyl group*

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The reactions of 3,5-di(*tert*-butyl)-1,2-benzoquinone with aryl- and alkylacetylenes in the presence of phosphorus trichloride afford 4-aryl(alkyl)-8-*tert*-butyl-2,6-dichloro-2-oxo-2*H*-benzo[*e*][1,2]oxaphosphinines as the major *ipso*-substitution products of the *tert*-butyl group by the chlorine atom. 4-Aryl(alkyl)-6,8-di(*tert*-butyl)-2,5-dichloro-2-oxo- and 4-aryl(alkyl)-6-*tert*-butyl-2,8-dichloro-2-oxo-2*H*-benzo[*e*][1,2]oxaphosphinines were obtained as the minor products. The structures of the stable representatives of this series were confirmed by X-ray diffraction.

Key words: alkynes, 1,2-benzoquinones, phosphorus trichloride, 4,6-di(*tert*-butyl)-2,2,2-trichlorobenzo-1,3,2-dioxaphosphole, *ipso*-substitution, 2*H*-benzo[*e*][1,2]oxaphosphinine *P*-oxides, organophosphorus compounds, X-ray diffraction study.

The reactions of 2,2,2-trihalobenzo-1,3,2-dioxaphospholes with arylacetylenes are known to give 2-oxobenzo[*e*][1,2]oxaphosphinines or phosphacoumarin derivatives,[1—3] which are phosphorus-containing analogs of natural heterocycles (coumarins and α-chromenes) possessing diverse biological activities.[4] Recently, alternative approaches to the synthesis of phosphacoumarins and related phosphaisocoumarin derivatives have been developed. However, these procedures involve many steps and are based on the use of difficultly accessible starting compounds.[5—7] The resulting compounds inhibit protein tyrosine phosphatases and exhibit anticancer activity.[6,7]

A more convenient approach to the synthesis of 2-oxobenzo[*e*][1,2]oxaphosphinine derivatives is based on the reaction in a three-component system consisting of phenanthrenequinone, or tetrachloro-1,2-benzoquinone, or, alternatively, 3,6-di(*tert*-butyl)-1,2-benzoquinone, arylacetylene, and phosphorus trihalide.[8—15] The reaction pathway was found to strongly depend on the structure of the starting quinone. Thus, the reactions often afford, along with 2-oxobenzo[*e*][1,2]oxaphosphinine derivatives, other products. On the whole, the results of the reactions in the *ortho*-quinone—phosphorus trihalide—arylacetylene system differ from those of the reactions of 2,2,2-trihalobenzo-1,3,2-dioxaphospholes with arylacetylenes.

Results and Discussion

The aim of the present study was to reveal the characteristic features of the reactions in the three-component 3,5-di(*tert*-butyl)-1,2-benzoquinone (**1**)—monosubstituted acetylene—phosphorus trichloride system. Unlike *ortho*-quinones used earlier, compound **1** is unsymmetrical and contains bulky substituents in different positions with respect to the carbonyl groups. It appeared that the reaction of phosphorus trichloride with a mixture of quinone **1** and arylacetylene follows two pathways (Scheme 1) to form the *ipso*-substitution products of the *tert*-butyl group, **2** and **4**, and benzophosphinines **3** containing the chlorine atom at position 5 of the heterocyclic system. This is the difference between the reaction in the system under consideration and the earlier studied reaction of 3,5-di(*tert*-butyl)-2,2,2-trichlorobenzo-1,3,2-dioxaphosphole (**5**) with phenylacetylene,[2] which gives

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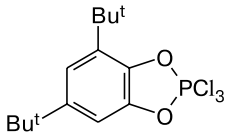
compound **2a** as the major product. In this case, phosphinines **2a**—**4a** are present in the reaction mixture in a ratio of 72 : 21 : 7. The reaction with the use of 4-chlorophenylacetylene produces these compounds in approximately the same ratio, whereas the reaction with 2-chlorophenylacetylene affords compound **2c** as the major product (>90%).



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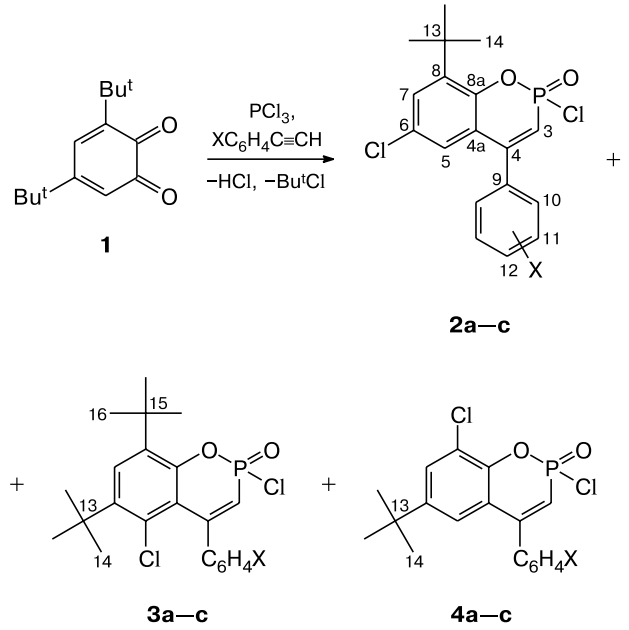
Scheme 1

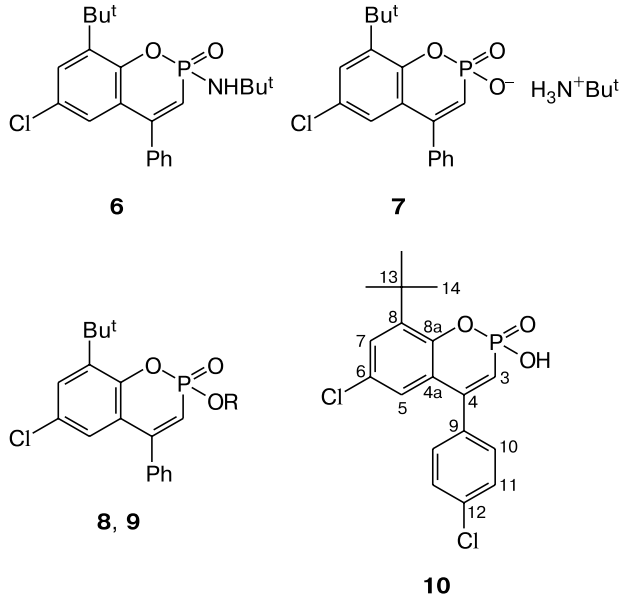


X = H (**a**), 4-Cl (**b**), 2-Cl (**c**)

The major portion of compounds **2a,b** can be separated after the storage of a mixture of the reaction products *in vacuo* (0.1 Torr, 120 °C) followed by the treatment of the glassy residue with dry hexane. These compounds are characterized by a doublet at δ_P 16.5—17.0 ($^2J_{PCH}$ = 24—25 Hz) in the ^{31}P NMR spectra ($CDCl_3$). An analogous doublet is observed in the ^{1}H NMR spectra ($CDCl_3$, δ 6.2—6.3, $^2J_{PCH}$ = 24—25 Hz). An analysis of the ^{1}H NMR spectra showed also that only one *tert*-butyl group is present in the molecules of these compounds. The *ipso*-substitution of the second *tert*-butyl group was established based on the ^{13}C—{^{1}H} NMR data. Thus, the spectrum of phosphinine **2b** shows only two signals at high field assigned to the carbon atoms of the $C(CH_3)_3$ fragment with the corresponding multiplicities. The complex appearance of the multiplet for the C(8) atom confirms the presence of the *tert*-butyl substituent at this atom. The multiplicity of the signal for the C(6) atom (a doublet of doublets) is consistent with the C(7)HC(6)(Cl)C(5)H structure.

The aminolysis of compound **2a** with *tert*-butylamine afforded *tert*-butylamide **6**. The hydrolysis of compound **2a** followed by the treatment of intermediate 8-*tert*-butyl-6-chloro-2-hydroxy-2-oxo-4-phenyl-2*H*-benzo[*e*]-[1,2]oxaphosphinine with *tert*-butylamine produced ammonium salt **7**. The alcoholysis of compound **2a** with ethanol and methanol afforded esters **8** and **9**. The hydrolysis of phosphinine **2b** gave cyclic phosphonic acid **10**. The structures of benzophosphinines **6**—**10** were established by spectroscopic methods. In all cases, the cyclic nature of the compounds is retained.

The structures of esters **8** and **9** were additionally confirmed by X-ray diffraction. The molecular structures and the atomic numbering schemes for esters **8** and **9** are presented in Figs 1 and 2, respectively. These figures give also selected geometric parameters of the molecules (bond lengths and bond angles).



R = Me (**8**), Et (**9**)

In molecules **8** and **9**, the heterocycle adopts a distorted (unsymmetrical) boat conformation with the planar (within 0.01(2) and 0.01(2) Å in molecule **8** and within 0.015(5) and 0.004(1) Å in molecule **9**) O(1)C(8a)C(4a)C(4) and P(2)C(3)C(4)C(4a) fragments. The dihedral angle between these fragments is 17(2) and 19.3(3)° in **8** and **9**, respectively. The P(2) and C(3) atoms deviate from the O(1)C(8a)C(4a)C(4) plane by 0.743(6) and 0.31(2) Å, respectively, in **8** and by −0.755(1) and −0.334(5) Å in **9**. The O(1) and C(8a) atoms deviate from the P(2)C(3)C(4)C(4a) plane by −0.68(2) and −0.35(2) Å (**8**) and by 0.677(3) and 0.360(5) Å (**9**), respectively. Therefore, these atoms deviate in the same direction, but the deviations are different in the magnitude, resulting in a distorted boat conformation. The phosphoryl group is in an equatorial position

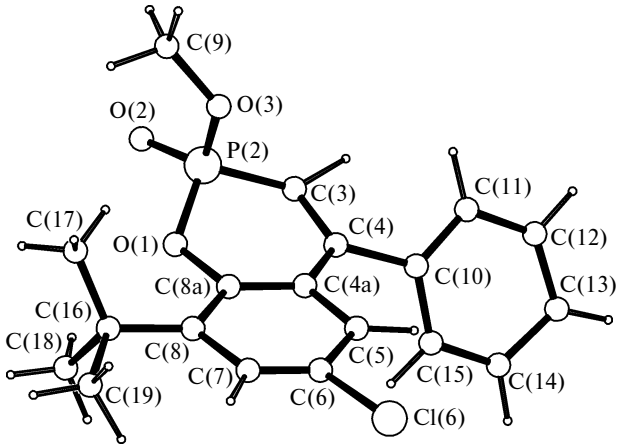


Fig. 1. Molecular geometry of compound **8** in the crystal structure. Selected bond lengths/Å: P(2)—O(1), 1.61(1); P(2)—O(2), 1.49(2); P(2)—O(3), 1.53(1); P(2)—C(3), 1.73(2); O(1)—C(8a), 1.39(2); C(3)—C(4), 1.33(3); C(4)—C(4a), 1.49(2). Selected bond angles/deg: O(1)—P(2)—O(2), 110.0(8); O(1)—P(2)—O(3), 105.4(8); O(1)—P(2)—C(3), 103.3(8); O(2)—P(2)—O(3), 113.6(9); O(2)—P(2)—C(3), 118.7(9); O(3)—P(2)—C(3), 104.6(9).

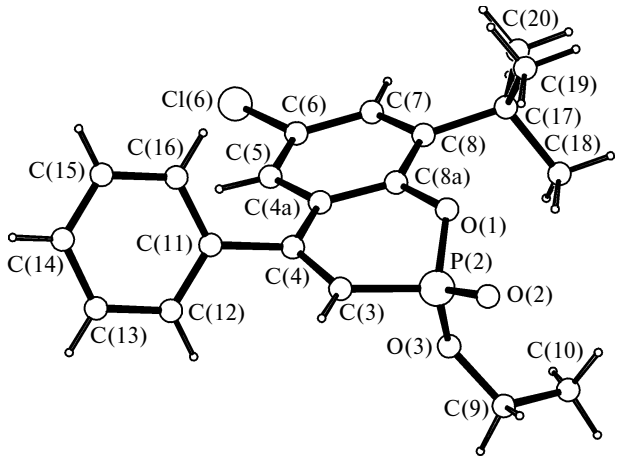
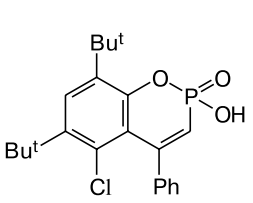


Fig. 2. Molecular geometry of compound **9** in the crystal structure. Selected bond lengths/Å: Cl(6)—C(6), 1.733(5); P(2)—O(1), 1.587(3); P(2)—O(2), 1.459(4); P(2)—O(3), 1.556(3); P(2)—C(3), 1.737(4); O(1)—C(8a), 1.395(5); O(3)—C(9), 1.431(7); C(3)—C(4), 1.342(6); C(4)—C(4a), 1.478(7); C(4)—C(11), 1.497(5); C(4a)—C(5), 1.396(6); C(4a)—C(8a), 1.398(5); C(5)—C(6), 1.368(7); C(6)—C(7), 1.386(5); C(7)—C(8), 1.374(6); C(8)—C(8a), 1.408(6). Selected bond angles/deg: O(1)—P(2)—O(2), 112.0(2); O(1)—P(2)—O(3), 103.3(2); O(1)—P(2)—C(3), 101.7(2); O(2)—P(2)—O(3), 114.9(2); O(2)—P(2)—C(3), 117.5(2); O(3)—P(2)—C(3), 105.9(2); P(2)—O(1)—C(8a), 122.8(2); P(2)—O(3)—C(9), 125.6(4).

(the O(2) atom deviates from the O(1)C(8a)C(4a)C(4) and P(2)C(3)C(4)C(4a) planes by 0.37(2) and −0.72(2) Å in **8** and by 0.701(5) and −0.394(5) Å in **9**). The alkoxy substituent occupies an axial position (the O(3) atom deviates from the O(1)C(8a)C(4a)C(4) and P(2)C(3)C(4)C(4a) planes by 2.25(2) and 1.48(2) Å in **8** and by −1.476(4) and −2.259(4) Å in **9**). The exocyclic O(3)—P(2) bond length (1.53(1) Å (**8**) and 1.558(4) Å (**9**)) is smaller than the endocyclic O(1)—P(2) bond length (1.61(1) Å (**8**) and 1.586(4) Å (**9**)), which is associated with the anomeric effect of the alkoxy substituent. The endocyclic angle at the phosphorus atom, O(1)—P(2)—C(3), is 103.3(8)° in **8** and 101.7(2)° in **9**. The phenyl substituent at the C(4) atom is twisted with respect to the plane of the phenylene fragment by 42(3)° in **8** and −55.6(7)° in **9**.

Acid **11** and amide **12** were obtained from minor products **3a** and **3b** after the treatment of the latter with water or isopropylamine, correspondingly, followed by the fractional crystallization. The structures of **11** and **12** were established by spectroscopic methods.



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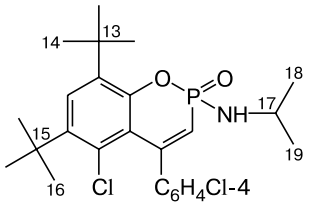

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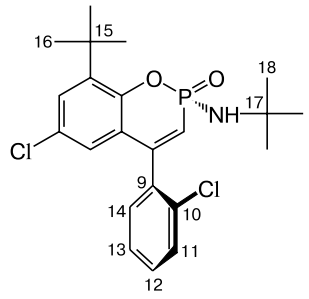
The reaction of quinone **1** with phosphorus trichloride in the presence of 2-chlorophenylacetylene followed by the treatment of intermediate **2c** with *tert*-butylamine produced a stable mixture of diastereomeric amides **13** and **13′** in a ratio of 2 : 1. The diastereomerism in this compound is associated with the presence of the chiral phosphorus atom and the atropoisomerism with respect to the C(4)—C(9) bond.



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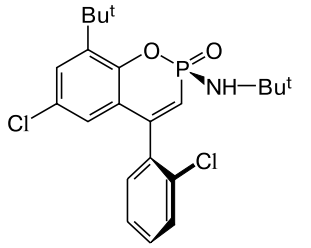
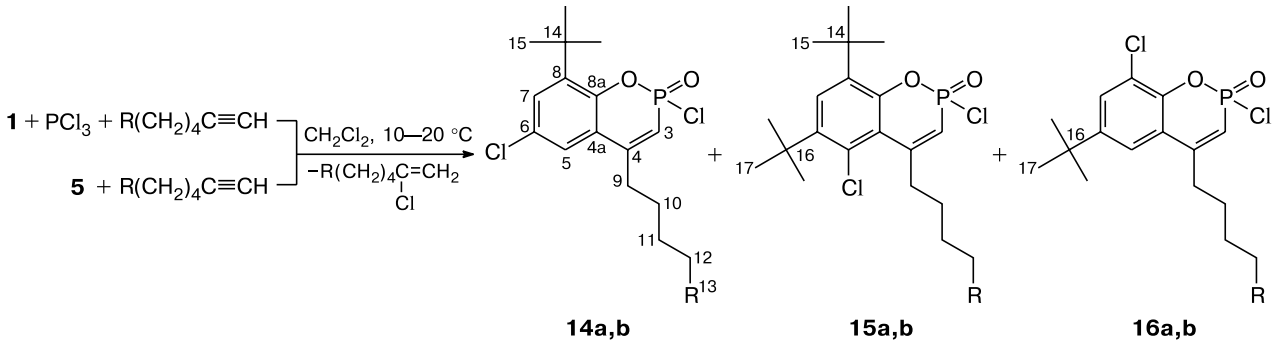


13′

Aliphatic alkynes, *viz.*, hex-1-yne and hept-1-yne, can also be involved in the reactions with quinone **1** and phosphorus trichloride (Scheme 2). The reactions proceed under mild conditions to give exclusively compounds of the benzophosphinine nature. These compounds are characterized by doublets at δ_P 18.5—19.1 ($^2J_{PCH}$ = 24.1—27.3 Hz) in the ^{31}P NMR spectra. An analysis of the ^{1}H, ^{13}C, and ^{13}C—{^{1}H} NMR spectra of the reaction

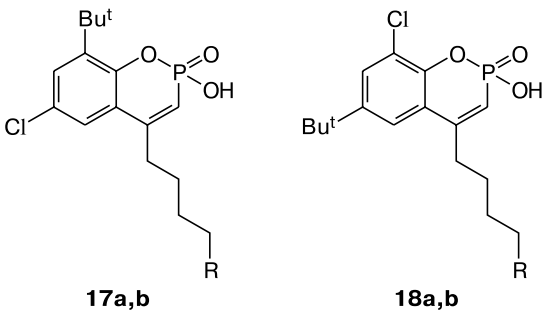
Scheme 2



R = H (**a**), Me (**b**)

mixtures, which were dried *in vacuo* to remove the solvent and 2-chloroalk-1-ene (the latter was formed as a result of the addition of HCl that was evolved to an excess of the starting acetylene), showed that the reaction produces phosphinines **14**—**16**. The percentage of these compounds in the reaction mixture was 55, 28, and 17% (for R = H) and 57, 27, and 16% (for R = Me), respectively.

In the $^{13}C—\{^1H\}$ NMR spectra, these reaction products are characterized by doublets of C(3), C(4a), C(8), C(8a), and C(9). Based on the multiplicities of these signals in the ^{13}C NMR spectra, these products were unambiguously identified as phosphinines **14**—**16**. Unlike the reactions of arylacetylenes, the latter reactions are less selective and afford the *ipso*-substitution products of either of the two *tert*-butyl groups. The same compounds were prepared by the reactions of phosphole **5** with hexyne and heptyne. These reactions also yield phosphinine **14** as the major product. Its percentage in the reaction mixture was 70% (**14a**) and 62% (**14b**). 1,2-Oxaphosphinines **15** and **16** are formed as by-products in approximately equal amounts (15%) in the reactions with hexyne and in 24 and 14% yields in the reactions with heptyne. Compounds **17** and **18** were isolated after the hydrolysis of the mixture. Their structures were established by ^1H and ^{13}C NMR spectroscopy.



R = H (**a**), Me (**b**)

To summarize, the involvement of unsymmetrical 3,5-di(*tert*-butyl)-1,2-benzoquinone (**1**) in the reactions with aryl- and alkylacetylenes in the presence of PCl_3 resulted in the formation of 2*H*-benzo[*e*][1,2]oxaphosphinine derivatives, with the *ipso*-substitution of the *tert*-butyl group in the *para* position with respect to the endocyclic oxygen atom predominating. The formation of benzo[*e*][1,2]phosphinines containing the chlorine atom at positions 5 and 8 of the heterocyclic system is a new unusual reaction pathway.

Experimental

The NMR spectra were recorded on Bruker Avance-600 (600 MHz for ^1H, 150.9 MHz for ^{13}C, and 242.8 MHz for ^{31}P), Bruker MSL-400 (400 MHz for ^1H and 100.6 MHz for ^{13}C), and Bruker CXP-100 (36.48 MHz for ^{31}P) instruments. The IR spectra were measured on a Bruker Vector-22 instrument in Nujol mulls. The mass spectra were obtained on a TRACE MS Finnigan MAT instrument; the ionizing electron energy was 70 eV; the ion source temperature was 200 °C. The evaporator tube was heated in the programmed mode from 35 to 150 °C with a step of 35 deg min^{-1}. The mass spectrometric data were processed with the use of the Xcalibur program.

Quinone **1** was supplied by V. K. Cherkasov (G. A. Razuvaev Institute of Organometallic Chemistry of the Russian Academy of Sciences). Compound **5** was synthesized according to a known procedure.[16] All aryl- and alkylacetylenes were synthesized and purified according to procedures described earlier.[17] Freshly distilled phosphorus trichloride was used.

Reaction of 3,5-di(*tert*-butyl)-1,2-benzoquinone (1) with phenylacetylene in the presence of phosphorus trichloride. A solution of phosphorus trichloride (0.8 mL, 0.0079 mol) in CH_2Cl_2 (1 mL) was added dropwise with stirring to a mixture of quinone **1** (1.5 g, 0.0068 mol), CH_2Cl_2 (20 mL), and phenylacetylene (1.1 mL, 0.01 mol) under argon. The reaction mixture was kept for 9 h. Then the solvent and excess phosphorus trichloride were removed by distillation. The residue was dried *in vacuo* (120 °C, 0.1 Torr). A mixture of 8-*tert*-butyl-2,6-dichloro-4-phenyl-2-oxo-2*H*-benzo[*e*][1,2]oxaphosphinine (**2a**) (72%), 6,8-di(*tert*-butyl)-2,5-dichloro-4-phenyl-2-oxo-2*H*-benzo[*e*][1,2]oxaphosphinine (**3a**) (21%), and 6-*tert*-butyl-2,8-dichloro-2-oxo-4-phenyl-2*H*-benzo[*e*][1,2]oxaphosphinine (**4a**) (7%) was obtained as a glassy yellowish substance. ^{31}P NMR ($CDCl_3$, 242.8 MHz), δ: 17.14 (d, $^2J_{PCH(3)}$ = 24.6 Hz) (**2a**); 17.89 (d,

$^2J_{PCH}$ = 25.4 Hz) (**3a**); 18.51 (d, $^2J_{PCH(3)}$ = 27.8 Hz) (**4a**). The reaction mixture was treated with hexane (10 mL) under argon. The white precipitate of oxaphosphinine **2a** that formed was filtered off. The yield was 1.36 g (60%), m.p. 195—197 °C (*cf.* lit. data[2]: m.p. 196 °C). The mass spectrum of compound **2a**, *m/z*: 370, 368, 366 ($C_{16}H_{17}{}^{35}Cl_2O_2P$) $[M]^{\bullet+}$, 351 [M – CH_3], 353 [M – CH]. The spectroscopic parameter of this compound are consistent with those described earlier.[2] The precipitate of compound **2a** was separated, and the filtrate was concentrated *in vacuo* (0.1 Torr). The glassy mixture consisting of phosphinines **2a** (14%), **3a** (71%), and **4a** (15%) was characterized by spectroscopic method. ^{1}H NMR of compound **3a** ($CDCl_3$, 600 MHz), δ: 7.67 (d, H(7), $^5J_{POCCCH(7)}$ = 1.7 Hz); 7.49—7.51 and 7.37—7.39 (both m, C_6H_5); 6.49 (d, H(3), $^2J_{PCH(3)}$ = 26.6 Hz); 1.47 and 1.53 (both s, H(14), H(16)). ^{1}H NMR of compound **4a** ($CDCl_3$, 600 MHz), δ: 7.58 (dd, H(7), $^4J_{H(5)CCCH(7)}$ = 2.4 Hz, $^5J_{POCCCH(7)}$ = 1.8 Hz); 7.11 (d, H(5), $^4J_{H(7)CCCH(5)}$ = 2.4 Hz); 7.49—7.51 and 7.37—7.39 (both m, C_6H_5); 6.49 (d, H(3), $^2J_{PCH(3)}$ = 26.6 Hz); 1.45 (s, H(14)). ^{13}C NMR of compound **4a** ($CDCl_3$, 150.9 MHz), δ:* 119.75 (dd [d], C(3), $^1J_{PC(3)}$ = 161.6 Hz, $^1J_{HC(3)}$ = 171.9 Hz); 157.76 (dt [s], C(4), $^2J_{HC(3)C(4)}$ = 3.7 Hz, $^3J_{HC(10)CC(4)}$ = 3.6 Hz); 123.65 (dd [d], C(4a), $^3J_{PCCC(4a)}$ = 18.4 Hz, $^3J_{HC(3)CC(4a)}$ = 8.1 Hz); 131.86 (dd [s], C(5), $^3J_{HC(7)CC(5)}$ = 12.0 Hz, $^4J_{POCCC(5)}$ = 1.5 Hz); 144.31 (m [s], C(6)); 128.62 (d [s], C(7), $^1J_{HC(7)}$ = 158.8 Hz); 137.65 (m [d], C(8), $^3J_{POCC(8)}$ = 6.5 Hz); 148.16 (dd [d], C(8a), $^2J_{POC(8a)}$ = 10.9 Hz, $^3J_{HCCC(8a)}$ = 11.6 Hz); 140.80 (dtd [d], C(9), $^3J_{PCCC(9)}$ = 20.5 Hz, $^3J_{HCCC(9)}$ = 7.2 Hz, $^3J_{HC(3)CC(9)}$ = 6.2 Hz); 128.29 (br.dm [br.s], C(10), $^1J_{HC(10)}$ = 161.0 Hz); 128.60 (br.dm [br.s], C(11), $^1J_{HC(11)}$ = 161.4 Hz); 129.05 (dt [s], C(12), $^1J_{HC(12)}$ = 161.2 Hz, $^2J_{HCC(12)}$ = 7.3 Hz); 35.33 (m [s], C(13), $^3J_{HCCC(13)}$ = 3.8 Hz, $^2J_{HCC(13)}$ = 3.7—3.8 Hz); 29.86 (q.sept [s], C(14), $^1J_{HC(14)}$ = 126.5 Hz, $^3J_{HCCC(14)}$ = 4.7 Hz); 36.78 (m [s], C(15), $^3J_{HCCC(15)}$ = 3.8 Hz, $^2J_{HCC(15)}$ = 3.8 Hz); 29.92 (q.sept [s], C(16), $^1J_{HC(16)}$ = 126.5 Hz, $^3J_{HCCC(16)}$ = 4.7 Hz).

2-*tert*-Butylamino-8-*tert*-butyl-6-chloro-2-oxo-4-phenyl-2*H*-benzo[*e*][1,2]oxaphosphinine (6). *tert*-Butylamine (0.6 mL, 0.006 mol) was added to a solution of phosphinine **2a** (1.0 g, 0.003 mol) in CH_2Cl_2 (10 mL). The reaction mixture was kept for 10 h. Then the solvent was removed *in vacuo* (12 Torr) until a cotton-like white substance was obtained. The latter was treated with diethyl ether (10 mL). The white precipitate of *tert*-butylammonium chloride was filtered off, and the ethereal filtrate was concentrated until compound **6** was obtained as a white precipitate. The yield was 0.9 g (75%), m.p. 165—167 °C. Found (%): C, 65.17; H, 6.77; N, 3.37; P, 7.55. $C_{22}H_{27}ClNO_2P$. Calculated (%): C, 65.42; H, 6.69; N, 3.47; P, 7.68. ^{1}H NMR ($CDCl_3$, 600 MHz), δ: 6.17 (d, H(3), $^2J_{PCH(3)}$ = 19.1 Hz); 7.00 (d, H(5), $^4J_{H(7)CCCH(5)}$ = 2.5 Hz); 7.34 (dd, H(7), $^4J_{H(7)CCCH(5)}$ = 2.5 Hz, $^5J_{POCCCH(7)}$ = 1.5 Hz); 7.29, 7.31, and 7.43 (all m, C_6H_5); 3.56 (d, PNH, $^2J_{PNH}$ = 6.1 Hz); 1.52 (s, H(14)); 1.29 (s, H(16)). ^{31}P NMR ($CDCl_3$, 36.48 MHz), δ: 6.9 (dd, $^2J_{PCH(3)}$ = 19.2 Hz, $^2J_{PNH}$ = 6.2 Hz). ^{13}C NMR ($CDCl_3$, 150.9 MHz), δ: 117.51 (dd [d], C(3), $^1J_{PC(3)}$ = 158.0 Hz, $^1J_{HC(3)}$ = 163.0 Hz); 153.31 (m [d], C(4), $^2J_{PCC(4)}$ = 1.7 Hz); 123.99 (dd [d], C(4a), $^3J_{PCCC(4a)}$ = 15.3 Hz, $^3J_{HC(3)CC(4a)}$ = 8.3 Hz); 116.99 (dd [s], C(5), $^1J_{HC(5)}$ = 167.3 Hz, $^3J_{HC(7)CC(5)}$ = 5.7 Hz); 128.34 (dd [s], C(6), $^2J_{HCC(6)}$ = 4.5 Hz, $^2J_{HCC(6)}$ = 4.5 Hz); 128.78 (dd [s], C(7), $^1J_{HC(7)}$ = 164.5, $^3J_{HC(5)CC(7)}$ = 7.2); 141.97 (m [d], C(8), $^3J_{POCC(8)}$ = 6.2 Hz); 149.08 (ddd [d], C(8a), $^2J_{POC(8a)}$ = 8.7 Hz, $^3J_{HCCC(8a)}$ = 9.0—9.2 Hz, $^3J_{HCCC(8a)}$ = 9.0—9.2 Hz); 139.31 (dtd [d], C(9), $^3J_{PCCC(9)}$ = 18.2 Hz, $^3J_{HC(11)CC(9)}$ = 7.5 Hz, $^3J_{HC(3)CC(9)}$ = 6.5 Hz); 128.30 (ddd [s], C(10), $^1J_{HC(10)}$ = 158.5 Hz, $^3J_{HCCC(10)}$ = 5.6—6.0 Hz, $^3J_{HCCC(10)}$ = 5.6—6.0 Hz); 128.79 (dd [s], C(11), $^1J_{HC(11)}$ = 159.6 Hz, $^3J_{HCCC(11)}$ = 6.0 Hz); 128.92 (dt [s], C(12), $^1J_{HC(12)}$ = 161.3 Hz, $^3J_{HC(10)CC(12)}$ = 7.4 Hz); 35.33 (m [s], C(13)); 30.0 (qm [s], C(14), $^1J_{HC(14)}$ = 126.5 Hz, $^3J_{HCCC(14)}$ = 4.7 Hz); 51.70 (m [d], C(15), $^2J_{PNC(15)}$ = 1.8 Hz); 32.02 (qm [d], C(16), $^1J_{HC(16)}$ = 126.2 Hz, $^3J_{PNCC(16)}$ = 4.3 Hz, $^3J_{HCCC(16)}$ = 2.3 Hz).

***tert*-Butylammonium 8-*tert*-butyl-6-chloro-2-oxo-4-phenyl-2*H*-benzo[*e*][1,2]oxaphosphinin-2-oate (7)** was prepared by hydrolysis of compound **2a** (0.3 mmol) followed by mixing with *tert*-butylamine (0.03 mL, 0.3 mmol) in CH_2Cl_2, the removal of the solvent, washing of the precipitate that formed with diethyl ether, and drying in air. The yield was 0.09 g (69%), m.p. 218—219 °C. Found (%): C, 63.57; H, 6.94; N, 3.41; P, 7.39. $C_{22}H_{29}ClNO_3P$. Calculated (%): C, 62.63; H, 6.88; N, 3.32; P, 7.35. ^{1}H NMR ($CDCl_3$, 600 MHz), δ: 6.28 (br.d, H(3), $^2J_{PCH(3)}$ = 18.5 Hz); 6.90 (d, H(5), $^4J_{H(7)CCCH(5)}$ = 2.5 Hz); 7.22 (br.d, H(7), $^4J_{H(5)CCCH(7)}$ = 2.5 Hz); 7.29—7.31 and 7.43—7.45 (both m, C_6H_5); 1.46 (s, H(14)); 1.33 (br.s, H(16)); 8.49 (br.s, N^+H_3). ^{31}P NMR ($CDCl_3$, 36.48 MHz), δ: 1.7 (d, $^2J_{PCH(3)}$ = 18.3 Hz). ^{13}C NMR ($CDCl_3$, 150.9 MHz), δ: 121.15 (dd [d], C(3), $^1J_{PC(3)}$ = 166.4 Hz, $^1J_{HC(3)}$ = 160.0 Hz); 149.07 (m [s], C(4)); 125.53 (dd [d], C(4a), $^3J_{PCCC(4a)}$ = 15.3 Hz, $^3J_{HC(3)CC(4a)}$ = 8.3 Hz); 125.48 (dd [s], C(5), $^1J_{HC(5)}$ = 165.7 Hz, $^3J_{HC(7)CC(5)}$ = 5.7 Hz); 126.35 (dd [s], C(6), $^2J_{HC(7)C(6)}$ = 4.5 Hz, $^2J_{HC(5)C(6)}$ = 4.5 Hz); 128.13 (dd [s], C(7), $^1J_{HC(7)}$ = 163.0—164.0 Hz, $^3J_{HC(5)CC(7)}$ = 6.4 Hz); 141.42 (m [d], C(8), $^3J_{POCC(8)}$ = 5.1 Hz); 150.74 (ddd [d], C(8a), $^2J_{POC(8a)}$ = 8.7 Hz, $^3J_{HCCC(8a)}$ = 8.5—8.7 Hz, $^3J_{HCCC(8a)}$ = 8.5—8.7 Hz); 140.29 (m [d], C(9), $^3J_{PCCC(9)}$ = 17.5 Hz); 128.56 (ddd [s], C(10), $^1J_{HC(10)}$ = 159.0 Hz, $^3J_{HCCC(10)}$ = 7.0 Hz, $^3J_{HCCC(10)}$ = 7.0 Hz); 128.48 (dd [s], C(11), $^1J_{HC(11)}$ = 160.3 Hz, $^3J_{HCCC(11)}$ = 5.4 Hz); 128.13 (dt [s], C(12), $^1J_{HC(12)}$ = 161.0 Hz, $^3J_{HC(10)CC(12)}$ = 7.2 Hz); 35.32 (m [s], C(13)); 30.20 (qm [s], C(14), $^1J_{HC(14)}$ = 126.3 Hz, $^3J_{HCCC(14)}$ = 4.7 Hz); 51.61 (m [s], C(15)); 27.90 (br.q [s], C(16), $^1J_{HC(16)}$ = 127.1 Hz).

8-*tert*-Butyl-6-chloro-2-methoxy-2-oxo-4-phenyl-2*H*-benzo[*e*][1,2]oxaphosphinine (8). Anhydrous MeOH (2 mL) was added to phosphinine **2a** (0.4 g), and the reaction mixture was stirred. The reaction was accompanied by vigorous evolution of HCl. After heating at 65 °C for 30 min, the reaction mixture was cooled and kept for 10 h. The precipitate of phosphinine **8** was filtered off and washed with diethyl ether. The yield was 0.38 g (90%), m.p. 175 °C. Found (%): C, 63.01; H, 5.76; P, 8.49. $C_{19}H_{20}ClO_3P$. Calculated (%): C, 62.90; H, 5.52; P, 8.55. MS, *m/z*: 364, 362 ($C_{19}H_{20}{}^{35}ClO_3P$) $[M]^{\bullet+}$, 347 [M – CH_3], 327 [M – Cl], 297 [M – Cl – OCH_3], 241 [M – Cl – OCH_3 – C_4H_8], 56 [C_4H_8]. IR, ν/cm^{-1}: 1595, 1553, 1419, 1335, 1279, 1254, 1214, 1148, 1045, 923, 879, 865, 823, 792, 754, 701, 637, 559, 538. ^{1}H NMR ($CDCl_3$, 600 MHz), δ: 6.12 (d, H(3), $^2J_{PCH(3)}$ = 18.6 Hz); 7.03 (d, H(5), $^4J_{H(7)CCCH(5)}$ = 2.5 Hz); 7.38 (dd, H(7), $^4J_{H(5)CCCH(7)}$ = 2.5 Hz, $^5J_{POCCCH(7)}$ = 1.6 Hz); 7.32—7.33 and 7.46 (both m, C_6H_5); 1.50 (s, H(17)); 3.88 ($POCH_3$, $^3J_{POCH}$ = 11.8 Hz). ^{31}P—{^{1}H} NMR ($CDCl_3$, 36.48 MHz), δ: 10.2. ^{13}C NMR ($CDCl_3$, 150.9 MHz), δ: 111.70

* Hereinafter, the multiplicities of the signals in the ^{13}C—{^{1}H} NMR spectra are given in brackets.

(dd [d], C(3), $^1J_{PC(3)}$ = 175.0 Hz, $^1J_{HC(3)}$ = 166.3 Hz); 156.75 (m [s], C(4)); 123.73 (dd [d], C(4a), $^3J_{PCCC(4a)}$ = 15.7 Hz, $^3J_{HC(3)CC(4a)}$ = 8.3 Hz); 127.21 (ddd [s], C(5), $^1J_{HC(5)}$ = 167.8 Hz, $^3J_{HC(7)CC(5)}$ = 5.7 Hz, $^4J_{HC(3)CCC(5)}$ = 0.9 Hz); 128.54 (dd [s], C(6), $^2J_{HC(5)C(6)}$ = 4.5 Hz, $^2J_{HC(7)C(6)}$ = 4.5 Hz); 129.45 (dd [s], C(7), $^1J_{HC(7)}$ = 164.6 Hz, $^3J_{HC(5)CC(7)}$ = 6.2 Hz); 141.88 (m [d], C(8), $^3J_{POCC(8)}$ = 6.1 Hz); 149.20 (ddd [d], C(8a), $^2J_{POC(8a)}$ = 8.7 Hz, $^3J_{HCCC(8a)}$ = 10.0 Hz, $^3J_{HCCC(8a)}$ = 10.0 Hz); 53.69 (qd [d], C(9), $^1J_{HC(9)}$ = 148.4 Hz, $^2J_{POC(9)}$ = 6.6 Hz); 138.79 (dtd [d], C(10), $^3J_{PCCC(10)}$ = 19.8 Hz, $^3J_{HC(12)CC(10)}$ = 7.5 Hz, $^3J_{HC(3)CC(10)}$ = 6.2 Hz); 128.43 (dm [s], C(11), $^1J_{HC(11)}$ = 160.4 Hz, $^3J_{HCCC(11)}$ = 6.3—7.0 Hz, $^3J_{HCCC(11)}$ = 6.3—7.0 Hz); 128.90 (br.dd [s], C(12), $^1J_{HC(12)}$ = 162.2 Hz, $^3J_{HCCC(12)}$ = 5.5—6.0 Hz); 129.41 (dt [s], C(13), $^1J_{HC(13)}$ = 161.0 Hz, $^3J_{HC(11)CC(13)}$ = 7.7 Hz); 35.49 (m [s], C(16), $^2J_{HC(17)C(16)}$ = 3.8 Hz); 29.88 (q.sept [s], C(17), $^1J_{HC(17)}$ = 126.6 Hz, $^3J_{HCCC(17)}$ = 4.8 Hz).

8-*tert*-Butyl-6-chloro-2-ethoxy-2-oxo-4-phenyl-2*H*-benzo[*e*][1,2]oxaphosphinine (9). The reaction of phosphinine **2a** (1 g) with ethanol was carried out analogously. The yield of compound **9** was 0.9 g (87%), m.p. 140 °C. Found (%): C, 63.82; H, 6.07; P, 8.37. $C_{20}H_{22}ClO_3P$. Calculated (%): C, 63.75; H, 5.84; P, 8.23. MS, *m/z*: 378, 376 ($C_{20}H_{22}{}^{35}ClO_3P$) $[M]^{\bullet+}$, 361 [M – CH_3], 341 [M – Cl], 333 [M – C_3H_7]. IR, ν/cm^{-1}: 1596, 1556, 1421, 1337, 1276, 1253, 1213, 1150, 1043, 955, 920, 867, 822, 803, 760, 720, 700, 638, 585, 560, 539. ^{1}H NMR ($CDCl_3$, 600 MHz), δ: 6.11 (d, H(3), $^2J_{PCH(3)}$ = 18.5 Hz); 7.01 (d, H(5), $^4J_{H(7)CCCH(5)}$ = 2.6 Hz); 7.37 (dd, H(7), $^4J_{H(5)CCCH(7)}$ = 2.6 Hz, $^5J_{POCCCH(7)}$ = 1.5 Hz); 4.26—4.29 (POC(9)H_AH_B, $^2J_{H_AH_B}$ = 10.6—11.0 Hz, $^3J_{PH_A}$ = 10.0—10.2 Hz, $^3J_{PH_B}$ = 9.6—10.0 Hz, $^3J_{H_XH}$ = 7.1 Hz); 1.38 (t, C(10)H_X, $^3J_{HH_X}$ = 7.1); 7.29—7.31 and 7.43—7.44 (both m, C_6H_5); 1.49 (s, H(18)). ^{1}H NMR (acetone-d_6, 600 MHz), δ: 6.31 (d, H(3), $^2J_{PCH(3)}$ = 18.2 Hz); 7.02 (d, H(5), $^4J_{H(7)CCCH(5)}$ = 2.6 Hz); 7.46 (dd, H(7), $^4J_{H(5)CCCH(7)}$ = 2.6 Hz, $^5J_{POCCCH(7)}$ = 1.7 Hz); 7.42—7.44 and 7.53—7.54 (both m, C_6H_5); 1.51 (s, H(14)); 4.23—4.27 (m, AB part of an $ABMX_3$ system, POC(9)H_AH_B, $^2J_{H_AH_B}$ = 10.2 Hz, $^3J_{POCH_A}$ = 7.3 Hz, $^3J_{POCH_B}$ = 7.3 Hz, $^3J_{H_XH}$ = 7.0 Hz); 1.36 (t, C(10)H_X, $^3J_{HH_X}$ = 7.0 Hz). ^{31}P—{^{1}H} NMR ($CDCl_3$, 36.48 MHz), δ: 7.5. ^{13}C NMR ($CDCl_3$, 150.9 MHz), δ: 112.51 (dd [d], C(3), $^1J_{PC(3)}$ = 174.7 Hz, $^1J_{HC(3)}$ = 165.9 Hz); 156.01 (m [d], C(4), $^2J_{PCC(4)}$ = 1.5 Hz); 123.70 (dd [d], C(4a), $^3J_{PCCC(4a)}$ = 15.6 Hz, $^3J_{HC(3)CC(4a)}$ = 8.4 Hz); 127.09 (dd [s], C(5), $^1J_{HC(5)}$ = 167.3 Hz, $^3J_{HC(7)CC(5)}$ = 5.7 Hz); 127.84 (s, C(6), overlap with the component of the signal of C(12)); 129.25 (dd [s], C(7), $^1J_{HC(7)}$ = 164.3 Hz, $^3J_{HC(5)CC(7)}$ = 5.5 Hz); 141.77 (m [d], C(8), $^3J_{POCC(8)}$ = 6.8 Hz); 149.17 (ddd [d], C(8a), $^2J_{POC(8a)}$ = 8.9 Hz, $^3J_{HCCC(8a)}$ = 8.9 Hz, $^3J_{HCCC(8a)}$ = 8.9 Hz); 63.59 (tdq [d], C(9), $^1J_{HC(9)}$ = 148.2 Hz, $^2J_{POC(9)}$ = 6.6 Hz, $^2J_{HCC(9)}$ = 4.4 Hz); 16.62 (qdt [d], C(10), $^1J_{HC(10)}$ = 127.4 Hz, $^3J_{POCC(10)}$ = 5.9 Hz, $^2J_{HCC(10)}$ = 2.4 Hz); 138.82 (dtd [d], C(11), $^3J_{PCCC(9)}$ = 19.4 Hz, $^3J_{HC(13)CC(11)}$ = 7.4 Hz, $^3J_{HC(3)CC(11)}$ = 6.2 Hz); 128.37 (ddd [s], C(12), $^1J_{HC(12)}$ = 159.0 Hz, $^3J_{HCCC(12)}$ = 5.8—6.0 Hz, $^3J_{HCCC(12)}$ = 5.8—6.0 Hz); 128.82 (dd [s], C(13), $^1J_{HC(13)}$ = 160.5 Hz, $^3J_{HCCC(13)}$ = 6.0 Hz); 129.27 (dt [s], C(14), $^1J_{HC(14)}$ = 162.0 Hz, $^3J_{HC(12)CC(14)}$ = 7.1 Hz); 35.39 (m [s], C(17)); 29.83 (qm [s], C(18), $^1J_{HC(18)}$ = 126.1 Hz, $^3J_{HCCC(18)}$ = 4.6 Hz).

Reaction of quinone 1 with 4-chlorophenylacetylene in the presence of phosphorus trichloride. The reaction was carried out analogously with the use of quinone **1** (1 g), CH_2Cl_2 (20 mL), 4-chlorophenylacetylene (0.92 g), and a solution of phosphorus trichloride (0.8 mL) in CH_2Cl_2 (1 mL). As described above, the reaction mixture was kept over a period of time. The solvent and excess phosphorus trichloride were removed. The residue was dried *in vacuo* (120 °C, 0.1 Torr) and treated with hexane. The white precipitate of **8-*tert*-butyl-2,6-dichloro-4-(4-chlorophenyl)-2-oxo-2*H*-benzo[*e*][1,2]oxaphosphinine** (**2b**) was filtered off. The yield was 1.2 g (65%). ^{31}P NMR ($CDCl_3$, 36.48 MHz), δ: 16.50 (d, $^2J_{PCH}$ = 24.4 Hz). ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 6.34 (d, H(3), $^2J_{PCH(3)}$ = 24.4 Hz); 7.00 (d, H(5), $^4J_{H(7)CCCH(5)}$ = 2.5 Hz); 7.45 (d, H(7), $^4J_{H(5)CCCH(7)}$ = 2.5 Hz); 7.29 and 7.46 (both m, AA´BB´ system, H(10), H(11), $^3J_{HCCH}$ = 8.5 Hz); 1.48 (s, H(14)). ^{13}C NMR ($CDCl_3$, 150.9 MHz), δ: 115.62 (dd [d], C(3), $^1J_{PC(3)}$ = 156.0 Hz, $^1J_{HC(3)}$ = 172.1 Hz); 155.69 (m [d], C(4), $^2J_{PCC(4)}$ = 2.2 Hz, $^2J_{HC(3)C(4)}$ = 3.0—3.2 Hz, $^3J_{HC(5)CC(4)}$ = 3.5—4.0 Hz); 124.58 (dd [d], C(4a), $^3J_{PCCC(4a)}$ = 15.8 Hz, $^3J_{HC(3)CC(4a)}$ = 8.1—8.2 Hz); 126.20 (dd [s], C(5), $^1J_{HC(5)}$ = 166.1 Hz, $^3J_{HC(7)CC(5)}$ = 5.7 Hz); 127.23 (dd [s], C(6), $^2J_{HCC(6)}$ = 4.6 Hz, $^2J_{HCC(6)}$ = 4.6 Hz); 128.47 (dd [s], C(7), $^1J_{HC(7)}$ = 164.4 Hz, $^3J_{HC(5)CC(7)}$ = 5.8 Hz); 142.18 (m [d], C(8), $^3J_{POCC(8)}$ = 6.0 Hz); 149.62 (ddd [d], C(8a), $^2J_{POC(8a)}$ = 8.1 Hz, $^3J_{HCCC(8a)}$ = 8.4 Hz, $^3J_{HCCC(8a)}$ = 9.6 Hz); 137.83 (ddt [d], C(9), $^3J_{PCCC(9)}$ = 18.9 Hz, $^3J_{HC(11)CC(9)}$ = 7.6 Hz, $^3J_{HC(3)CC(9)}$ = 6.1 Hz); 130.59 (dd [s], C(10), $^1J_{HC(10)}$ = 162.5 Hz, $^3J_{HCCC(10)}$ = 6.2—6.3 Hz); 129.28 (two ddd [s], C(11), $^1J_{HC(11)}$ = 163.8 Hz, $^3J_{HCCC(11)}$ = 4.4 Hz, $^2J_{HC(10)C(11)}$ = 3.6 Hz); 134.38 (tt [s], C(12), $^3J_{HC(10)CC(12)}$ = 10.8 Hz, $^3J_{HC(10)CC(12)}$ = 3.3 Hz); 35.55 (m [s], C(13), $^3J_{HC(7)CC(13)}$ = 7.4 Hz, $^2J_{HC(14)C(13)}$ = 3.8 Hz); 29.94 (q.sept [s], C(14), $^1J_{HC(14)}$ = 126.7 Hz, $^3J_{HCCC(14)}$ = 4.7 Hz).

The filtrate obtained after the isolation of compound **2b** was concentrated *in vacuo* (100 °C, 0.2 Torr). **6,8-Di(*tert*-butyl)-2,5-dichloro-4-(4-chlorophenyl)-2-oxo-2*H*-benzo[*e*][1,2]oxaphosphinine** (**3b**) was obtained as a glassy compound (~90%). ^{31}P NMR ($CDCl_3$, 36.48 MHz), δ: 17.3 (d, $^2J_{PCH}$ = 26.6 Hz). ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 6.34 (d, H(3), $^2J_{PCH(3)}$ = 24.4 Hz); 7.00 (d, H(5), $^4J_{H(7)CCCH(5)}$ = 2.5 Hz); 7.45 (d, H(7), $^4J_{H(5)CCCH(7)}$ = 2.5 Hz); 7.29 and 7.46 (both m, AA´BB´ system, H(10), H(11), $^3J_{HCCH}$ = 8.5 Hz); 1.48 (s, H(14)).

8-*tert*-Butyl-6-chloro-4-(4-chlorophenyl)-2-hydroxy-2-oxo-2*H*-benzo[*e*][1,2]oxaphosphinine (10). Compound **2b** (1.5 g) was dissolved in wet diethyl ether and kept in air. After evaporation of the solvent, compound **10** was obtained as a white powder in quantitative yield, m.p. 125 °C. Found (%): C, 56.25; H, 4.73; Cl, 18.74; P, 7.98. $C_{18}H_{17}Cl_2O_3P$. Calculated (%): C, 56.40; H, 4.44; Cl, 18.54; P, 8.09. MS, *m/z*: 382 $[M]^{\bullet+}$ ($C_{18}H_{17}{}^{35}Cl_2O_3P$). IR, ν/cm^{-1}: 3300—3400, 2740, 2370—2250, 1670—1770, 1598, 1555, 1422, 1335, 1257, 1217, 1148, 1125, 1091, 1013, 932, 865, 834, 806, 770, 734, 718, 685, 600, 566, 520, 485, 454. ^{31}P NMR (DMSO-d_6, 36.48 MHz), δ: 2.9 (d, $^2J_{PCH}$ = 16.6 Hz). ^{1}H NMR (DMSO-d_6, 600 MHz), δ: 6.38 (d, H(3), $^2J_{PCH(3)}$ = 17.8 Hz); 6.86 (d, H(5), $^4J_{H(7)CCCH(5)}$ = 2.5 Hz); 7.36 (br.m, H(7)); 7.38 and 7.54 (both m, AA´BB´ system, H(10), H(11), $^3J_{HCCH}$ = 8.5 Hz); 1.44 (s, H(14)). ^{13}C NMR (DMSO-d_6, 150.9 MHz), δ: 118.11 (dd [d], C(3), $^1J_{PC(3)}$ = 169.4 Hz, $^1J_{HC(3)}$ = 164.0 Hz); 150.58 (m [d], C(4), $^2J_{PCC(4)}$ = 1.5 Hz, $^2J_{HC(3)C(4)}$ = 3.5 Hz, $^3J_{HC(5)CC(4)}$ = 3.5—4.0 Hz); 123.53 (br.dd [d], C(4a), $^3J_{PCCC(4a)}$ = 17.2 Hz, $^3J_{HC(3)CC(4a)}$ = 8.5 Hz); 127.54 (ddd [d], C(5), $^1J_{HC(5)}$ = 168.3 Hz, $^3J_{HC(7)CC(5)}$ = 5.9 Hz, $^4J_{POCCC(5)}$ = 1.7 Hz); 130.23 (ddd [d], C(6), $^5J_{POCCCC(6)}$ = 1.7 Hz, $^2J_{HCC(6)}$ = 4.4 Hz,

$^2J_{HCC(6)}$ = 5.7 Hz); 130.80 (dd [s], C(7), $^1J_{HC(7)}$ = 165.4 Hz, $^3J_{HC(5)CC(7)}$ = 5.9 Hz); 143.06 (m [d], C(8), $^3J_{POCC(8)}$ = 7.2 Hz, $^4J_{HC(5)CCC(8)}$ = 1.5 Hz, $^2J_{HC(7)C(8)}$ = 3.2 Hz, $^3J_{HCCC(8)}$ = 4.2 Hz); 148.92 (ddd [d], C(8a), $^2J_{POC(8a)}$ = 11.3 Hz, $^3J_{HCCC(8a)}$ = 10.4—10.5 Hz, $^3J_{HCCC(8a)}$ = 8.6—8.7 Hz); 136.06 (dtd [d], C(9), $^3J_{PCCC(9)}$ = 21.3 Hz, $^3J_{HC(11)CC(9)}$ = 7.8 Hz, $^3J_{HC(3)CC(9)}$ = 6.1 Hz); 130.59 (dd [s], C(10), $^1J_{HC(10)}$ = 162.5 Hz, $^3J_{HCCC(10)}$ = 6.2—6.3 Hz); 129.28 (two ddd [s], C(11), $^1J_{HC(11)}$ = 163.8 Hz, $^3J_{HCCC(11)}$ = 4.4 Hz, $^2J_{HC(10)C(11)}$ = 3.6 Hz); 134.38 (tt [s], C(12), $^3J_{HC(10)CC(12)}$ = 10.8 Hz, $^3J_{HC(11)C(12)}$ = 3.3 Hz); 35.44 (d.dec [s], C(13), $^3J_{HC(7)CC(13)}$ = 7.5 Hz, $^2J_{HC(14)C(13)}$ = 3.7 Hz); 29.94 (q.sept [s], C(14), $^1J_{HC(14)}$ = 126.5 Hz, $^3J_{HC(14)CC(14)}$ = 4.7 Hz).

6,8-Di(*tert*-butyl)-5-chloro-4-(4-chlorophenyl)-2-isopropylamino-2-oxo-2*H*-benzo[*e*][1,2]oxaphosphinine (12). Compound **3b** (0.6 g, 1.3 mmol) was dissolved in hexane (10 mL). Then isopropylamine (0.7 mL) was added dropwise under argon. The precipitate that formed was filtered off, washed with hexane and water (pH 8), and dried. Compound **12** was obtained in a yield of 0.14 g, m.p. 214 °C. Found (%): C, 62.43; H, 6.74; Cl, 14.86; N, 3.05; P, 6.29. $C_{22}H_{27}ClNO_3P$. Calculated (%): C, 62.50; H, 6.67; Cl, 14.79; N, 2.92; P, 6.46. MS, *m/z*: 483, 481, 479 ($C_{25}H_{32}{}^{35}Cl_2NO_2P$) $[M]^{\bullet+}$, 466 [M – CH], 464 [M – CH_3], 423 [M – C_4H_8], 422 [M – C_4H_9], 421 [M – NHC_3H_7], 57 [C_4H_9], 58 [NHC_3H_7]. IR, ν/cm^{-1}: 3153, 2618, 1584, 1554, 1485, 1464, 1368, 1339, 1228, 1169, 1140, 1073, 1013, 949, 919, 872, 833, 799, 746, 548, 487, 419. ^{31}P NMR (DMSO-d_6, 36.48 MHz), δ: 9.7 (ddd, $^2J_{H(3)CP}$ = 20.5 Hz, $^2J_{HNP}$ = 10.1 Hz, $^3J_{HCNP}$ = 10.6 Hz). ^{1}H NMR ($CDCl_3$—DMSO-d_6 (1 : 1), 600 MHz), δ: 6.47 (d, H(3), $^2J_{PCH(3)}$ = 21.3 Hz); 7.55 (s, H(7)); 7.23 (br.s, H(10)); 7.38 (br.m, H(11), $^3J_{H(10)CCH(11)}$ = 8.3 Hz); 1.46 (s, H(14)); 1.41 (s, H(16)); 5.53 (br.dd, NH, $^2J_{PNH}$ = 10.0 Hz, $^3J_{HCNH}$ = 10.0 Hz); 3.39 (m, H(17)); 1.13 and 1.15 (both d, H(18), H(19), $^3J_{H(17)CCH(18)}$ = 6.5 Hz, $^3J_{H(17)CCH(19)}$ = 6.6 Hz). ^{13}C NMR ($CDCl_3$—DMSO-d_6 (1 : 1), 150.9 MHz), δ: 122.50 (dd [d], C(3), $^1J_{PC(3)}$ = 161.0 Hz, $^1J_{HC(3)}$ = 163.7 Hz); 151.08 (dt [s], C(4), $^2J_{HC(3)C(4)}$ = 4.2 Hz, $^3J_{HC(10)CC(4)}$ = 4.2—4.3 Hz); 123.08 (ddd [d], C(4a), $^3J_{PCCC(4a)}$ = 15.2 Hz, $^3J_{HC(3)CC(4a)}$ = 8.9 Hz, $^4J_{HCCCC}$ = 1.0 Hz); 129.75 (dd [s], C(5), $^3J_{HC(7)CC(5)}$ = 12.3 Hz, $^4J_{POCCC(5)}$ = 1.8 Hz); 141.19 (m [s], C(6)); 126.43 (d [s], C(7), $^1J_{HC(7)}$ = 156.9 Hz); 139.78 (m [d], C(8), $^3J_{POCC(8)}$ = 4.8 Hz); 148.74 (dd [d], C(8a), $^2J_{POC(8a)}$ = 8.4 Hz, $^3J_{HCCC(8a)}$ = 12.0 Hz); 140.59 (ddt [d], C(9), $^3J_{PCCC(9)}$ = 18.0 Hz, $^3J_{HCCC(9)}$ = 7.5—7.7 Hz, $^3J_{HC(3)CC(9)}$ = 6.9 Hz); 127.57 (dd [s], C(10), $^1J_{HC(10)}$ = 161.9 Hz, $^3J_{HCCC(10)}$ = 8.0 Hz); 128.13 (br.dm [br.s], C(11), $^1J_{HC(11)}$ = 166.9 Hz); 132.46 (tt [s], C(12), $^3J_{HC(10)CC(12)}$ = 10.8 Hz, $^2J_{HCC(12)}$ = 3.5 Hz); 34.64 (m [s], C(13), $^3J_{HCCC(13)}$ = 7.0 Hz, $^2J_{HCC(13)}$ = 3.6—3.7 Hz); 29.26 (q.sept [s], C(14), $^1J_{HC(14)}$ = 126.5 Hz, $^3J_{HCCC(14)}$ = 4.7—4.8 Hz); 35.95 (m [s], C(15), $^3J_{HCCC(15)}$ = 7.0 Hz, $^2J_{HCC(15)}$ = 3.6—3.7 Hz); 29.48 (q.sept [s], C(16), $^1J_{HC(16)}$ = 126.4 Hz, $^3J_{HCCC(16)}$ = 4.7—4.8 Hz); 42.58 (d.sept [s], C(17), $^1J_{HC(17)}$ = 147.3 Hz, $^2J_{HCC(17)}$ = 4.6 Hz); 24.93 and 24.58 (two qm [two d], C(18), C(19), $^1J_{HC(18),C(19)}$ = 125.0—126.0 Hz, $^3J_{PNCC(18)}$ = 3.8 Hz, $^3J_{PNCC(19)}$ = 5.4 Hz). The signals of the carbons and protons were interpreted using the ^{1}H—^{13}C HETCOR experiment.

Reaction of quinone 1 with 2-chlorophenylacetylene in the presence of phosphorus trichloride. The reaction was carried out as described above for the reaction of 4-chlorophenylacetylene with the use of quinone **1** (1 g). The reaction mixture was dried at 110 °C (0.8 Torr). A mixture of diastereomers of **8-*tert*-butyl-2,6-dichloro-4-(2-chlorophenyl)-2-oxo-2*H*-benzo[*e*][1,2]oxaphosphinine** (**2c**) (~90%) and **6,8-di(*tert*-butyl)-2,5-dichloro-4-(2-chlorophenyl)-2-oxo-2*H*-benzo[*e*][1,2]oxaphosphinine** (**3c**) (~10%) was obtained as a glassy light-yellow substance. ^{31}P NMR ($CDCl_3$, 36.48 MHz), δ: 15.3 and 15.4 (two d, $^2J_{PCH(3)}$ = 23.6—24.0 Hz) (**2c**); 16.6 and 16.7 (two d, $^2J_{PCH(3)}$ = 24.0—25.0 Hz) (**3c**). The mixture was dissolved in CH_2Cl_2 (6 mL), and *tert*-butylamine (0.96 mL) was added with stirring. After 2 h, the solvent was removed in vacuo (12 Torr), and the viscous residue was washed with water and extracted with diethyl ether. The ethereal extract was concentrated, and the residue was triturated with wet acetone. The precipitate that formed was filtered off, washed with acetone, and dried. A 2 : 1 mixture of diastereomers of **2-*tert*-butylamino-8-*tert*-butyl-6-chloro-4-(2-chlorophenyl)-2-oxo-2*H*-benzo[*e*][1,2]oxaphosphinine** (**13** and **13′**) was obtained in a yield of 1.3 g (72%), m.p. 110 °C. Found (%): C, 60.03; H, 6.11; Cl, 16.13; N, 3.09; P, 7.14. $C_{22}H_{26}Cl_2NO_2P$. Calculated (%): C, 60.27; H, 5.94; Cl, 16.21; N, 3.20; P, 7.08. MS, *m/z*: 437 ($C_{22}H_{26}{}^{35}Cl_2NO_2P$) $[M]^{\bullet+}$, 424 [M – CH], 422 [M – CH_3], 381 [M – C_4H_8], 365 [M – C_4H_9NH]. Diastereomer **13**. ^{31}P NMR (DMSO-d_6, 36.48 MHz), δ: –2.8 (d, $^2J_{PCH}$ = 18.5 Hz). ^{1}H NMR ($CDCl_3$—DMSO-d_6 (1 : 1), 600 MHz), δ: 6.10 (d, H(3), $^2J_{PCH(3)}$ = 18.5 Hz); 6.54 (d, H(5), $^4J_{H(7)CCCH(5)}$ = 2.3 Hz); 7.24 (br.s, H(7)); 1.43 (s, H(8)); 7.41 (br.m, H(11), $^3J_{H(12)CCH(11)}$ = 7.3 Hz, $^4J_{H(14)CCCH(12)}$ = 1.6 Hz); 7.36 (m, H(12), $^3J_{H(12)CCH(11)}$ = 7.3 Hz, $^4J_{H(12)CCCH(14)}$ = 1.8 Hz); 7.37 (m, H(13), $^3J_{H(14)CCH(13)}$ = 7.0—7.1 Hz, $^4J_{H(11)CCCH(13)}$ = 1.6 Hz); 7.28 (br.m, H(14), $^3J_{H(14)CCH(13)}$ = 7.0 Hz, $^4J_{H(14)CCCH(12)}$ = 1.8 Hz); 4.64 (d, NH, $^2J_{PNH}$ = 6.8 Hz); 1.22 (s, H(16)). ^{13}C NMR ($CDCl_3$—DMSO-d_6 (1 : 1), 150.9 MHz), δ: 119.55 (dd [d], C(3), $^1J_{PC(3)}$ = 154.2 Hz, $^1J_{HC(3)}$ = 163.4 Hz); 150.29 (m [br.s], C(4), $^2J_{PC(3)C(4)}$ = 2.1 Hz); 122.92 (dd [d], C(4a), $^3J_{PCCC(4a)}$ = 15.0 Hz, $^3J_{HC(3)CC(4a)}$ = 8.0 Hz); 125.51 (dd [s], C(5), $^1J_{HC(5)}$ = 166.1 Hz, $^3J_{HCCC(5)}$ = 6.0 Hz); 127.66 (dd [s], C(6), $^2J_{HCC(6)}$ = 4.7 Hz, $^2J_{HCC(6)}$ = 4.7 Hz); 130.48 (dd [s], C(7), $^1J_{HC(7)}$ = 164.1 Hz, $^3J_{HC(5)CC(7)}$ = 8.1 Hz); 141.89 (m [d], C(8), $^3J_{POCC(8)}$ = 6.0 Hz, $^2J_{H(7)CC(8)}$ = 2.3—2.6 Hz); 148.64 (ddd [d], C(8a), $^2J_{POC(8a)}$ = 8.9 Hz, $^3J_{HCCC(8a)}$ = 9.3 Hz, $^3J_{HCCC(8a)}$ = 9.3 Hz); 137.54 (ddt [d], C(9), $^3J_{PCCC(9)}$ = 18.3 Hz, $^3J_{HC(3)CC(9)}$ = 6.8—7.0 Hz, $^3J_{HCCC(9)}$ = 7.3—7.4 Hz); 132.28 (br.dd [s], C(10), $^3J_{HCCC(10)}$ = 9.9—10.0 Hz, $^3J_{HCCC(10)}$ = 9.9—10.0 Hz); 129.91 (ddd [s], C(11), $^1J_{HC(11)}$ = 166.7 Hz, $^3J_{HCCC(11)}$ = 5.8—6.0 Hz, $^2J_{HCC(11)}$ = 1.5 Hz); 128.53 (dd [s], C(12), $^1J_{HC(12)}$ = 164.2 Hz, $^3J_{HC(14)CC(12)}$ = 5.8 Hz); 127.71 (dd [s], C(13), $^1J_{HC(13)}$ = 164.1 Hz, $^3J_{HC(11)CC(13)}$ = 7.8 Hz); 130.74 (br.dd [br.s], C(14), $^1J_{HC(14)}$ = 162.9 Hz, $^3J_{HCCC(14)}$ = 7.8 Hz); 35.28 (m [s], C(15), $^2J_{HCC(15)}$ = 3.6 Hz); 29.96 (qm [s], C(16), $^1J_{HC(16)}$ = 126.5 Hz, $^3J_{HCCC(16)}$ = 4.5 Hz); 51.52 (m [d], C(17), $^2J_{PNC(17)}$ = 1.8 Hz); 31.93 (qm [d], C(18), $^1J_{HC(18)}$ = 126.8 Hz, $^3J_{PNCC(18)}$ = 4.5 Hz, $^3J_{HCCC(18)}$ = 4.4 Hz, $^3J_{HNCC(18)}$ = 2.4 Hz). Diastereomer **13′**. ^{1}H NMR ($CDCl_3$—DMSO-d_6 (1 : 1), 600 MHz), δ: 6.07 (d, H(3), $^2J_{PCH(3)}$ = 17.7 Hz); 6.56 (d, H(5), $^4J_{H(7)CCCH(5)}$ = 2.2 Hz); 7.24 (br.s, H(7)); 1.43 (s, H(8)); 7.45 (br.d, H(11), $^3J_{H(12)CCH(11)}$ = 7.8 Hz); 7.36 (m, overlap with H(12) and H(13)); 7.32 (br.dd, H(13), $^3J_{H(14)CCH(13)}$ = 7.4 Hz); 7.14 (d, H(14), $^3J_{H(14)CCH(13)}$ = 7.4 Hz); 4.61 (d, NH, $^2J_{PNH}$ = 7.8 Hz); 1.24 (s, H(16)). ^{13}C NMR ($CDCl_3$—DMSO-d_6 (1 : 1), 150.9 MHz), δ: 119.62 (dd [d], C(3), $^1J_{PC(3)}$ = 154.5 Hz,

$^1J_{HC(3)}$ = 163.5 Hz); 149.30 (m [br.s], C(4), $^2J_{PC(3)C(4)}$ = 2.1 Hz); 122.68 (dd [d], C(4a), $^3J_{PCCC(4a)}$ = 15.3 Hz, $^3J_{HC(3)CC(4a)}$ = 7.9—8.0 Hz); 125.78 (dd [s], C(5), $^1J_{HC(5)}$ = 165.8 Hz, $^3J_{HCCC(5)}$ = 6.0 Hz); 127.47 (dd [s], C(6), $^2J_{HCC(6)}$ = 4.4 Hz, $^2J_{HCC(6)}$ = 4.4 Hz); 130.32 (dd [s], C(7), $^1J_{HC(7)}$ = 164.3 Hz, $^3J_{HC(5)CC(7)}$ = 8.4 Hz); 141.69 (m [d], C(8), $^3J_{POCC(8)}$ = 5.9 Hz, $^2J_{H(7)CC(8)}$ = 2.3—2.6 Hz); 149.00 (ddd [d], C(8a), $^2J_{POC(8a)}$ = 9.2 Hz, $^3J_{HCCC(8a)}$ = 8.6—9.0 Hz, $^3J_{HCCC(8a)}$ = 8.6—9.0 Hz); 137.65 (m [d], C(9), $^3J_{PCCC(9)}$ = 18.0 Hz); 132.43 (br.dd [s], C(10), $^3J_{HCCC(10)}$ = 9.9—10.0 Hz, $^3J_{HCCC(10)}$ = 9.9—10.0 Hz); 130.07 (dd [s], C(11), $^1J_{HC(11)}$ = 166.8 Hz, $^3J_{HCCC(11)}$ = 7.8 Hz); 128.55 (dd [s], C(12), $^1J_{HC(12)}$ = 164.0 Hz, $^3J_{HC(14)CC(12)}$ = 5.5 Hz); 127.43 (dd [s], C(13), $^1J_{HC(13)}$ = 164.0 Hz, $^3J_{HC(11)CC(13)}$ = 8.0 Hz); 129.95 (br.dd [br.s], C(14), $^1J_{HC(14)}$ = 161.7 Hz, $^3J_{HCCC(14)}$ = 8.0 Hz); 35.28 (m [s], C(15), $^2J_{HCC(15)}$ = 3.6 Hz); 29.95 (qm [s], C(16), $^1J_{HC(16)}$ = 126.5 Hz, $^3J_{HCCC(16)}$ = 4.5 Hz); 51.52 (m [d], C(17), $^2J_{PNC(17)}$ = 1.9 Hz); 32.01 (qm [d], C(18), $^1J_{HC(18)}$ = 127.0 Hz, $^3J_{PNCC18)}$ = 4.5 Hz, $^3J_{HCCC(18)}$ = 4.4 Hz, $^3J_{HNCC(18)}$ = 2.4 Hz).

Reaction of dioxaphosphole 5 with hex-1-yne. A mixture of phosphole **5** (4.5 g, 0.0126 mol), CH_2Cl_2 (5 mL), and hex-1-yne (2.2 mL, 1.57 g, 0.019 mol) was kept at 10—20 °C for 12 h. Then the reaction mixture was dried in *vacuo* (130 °C, 12 Torr) to remove the solvent, excess alkyne, and 2-chlorohex-1-ene. The glassy light-brown residue, a mixture of phosphinines **14a**—**16a**, was obtained. ^{31}P NMR ($CDCl_3$, 242.8 MHz), δ: 18.09 (d, $^2J_{PCH}$ = 24.0 Hz) (**14a**, 70%); 18.84 (d, $^2J_{PCH}$ = 27.2 Hz) (**15a**, 15%); 19.35 (d, $^2J_{PCH}$ = 24.2 Hz) (**16a**, 15%).

4-Butyl-8-*tert*-butyl-2,6-dichloro-2-oxo-2*H*-benzo[*e*]-[1,2]oxaphosphinine (14a). MS, *m/z*: 350, 348, 346 ($C_{16}H_{21}{}^{35}Cl_2O_2P$) $[M]^{\bullet+}$, 331 [M – CH_3], 311 [M – Cl], 289 [M – C_4H_9], 57 [C_4H_9]. ^{13}C NMR ($CDCl_3$), δ: 113.28 (ddt [d], C(3), $^1J_{PC(3)}$ = 157.4 Hz, $^1J_{HC(3)}$ = 169.6 Hz, $^3J_{HC(9)CC(3)}$ = 6.0 Hz); 156.82 (m [s], C(4)); 123.09 (ddtd [d], C(4a), $^3J_{PCCC(4a)}$ = 18.0 Hz, $^3J_{HC(3)CC(4a)}$ = 7.8 Hz, $^3J_{HC(9)CC(4a)}$ = 3.1 Hz, $^2J_{HC(5)C(4a)}$ = 0.9 Hz); 124.37 (dd. [s], C(5), $^1J_{HC(5)}$ = 165.8 Hz, $^3J_{HC(7)CC(5)}$ = 5.4 Hz); 130.02 (dd [s], C(6), $^2J_{HCC(6)}$ = 4.8 Hz, $^2J_{HCC(6)}$ = 4.4 Hz); 129.89 (dd [s], C(7), $^1J_{HC(7)}$ = 165.4 Hz, $^3J_{HC(5)CC(7)}$ = 5.8 Hz); 142.53 (d [d], C(8), $^3J_{POCC(8)}$ = 7.4 Hz); 148.52 (ddd [d], C(8a), $^3J_{HC(5)CC(8a)}$ = 10.4 Hz, $^3J_{HC(7)CC(8a)}$ = 10.4 Hz, $^2J_{POC(8a)}$ = 11.4 Hz); 35.04 (tdm [d], C(9), $^3J_{PCCC(9)}$ = 19.8 Hz, $^1J_{HC(9)}$ = 127.8 Hz, $^3J_{HC(3)CC(9)}$ = 5.6—6.0 Hz, $^3J_{HC(11)CC(9)}$ = 3.9—4.0 Hz, $^2J_{HC(10)C(9)}$ = 3.9—4.0 Hz); 30.08 (tm [s], C(10), $^1J_{HC(10)}$ = 126.6 Hz, $^3J_{HCCC(10)}$ = 3.9—4.2 Hz, $^2J_{HCC(10)}$ = 3.9—4.2 Hz); 22.28 (tm [s], C(11), $^1J_{HC(11)}$ = 125.3 Hz, $^3J_{HCCC(11)}$ = 3.2—3.5 Hz, $^2J_{HCC(11)}$ = 3.2—3.5 Hz); 13.80 (qm [s], C(12), $^1J_{HC(12)}$ = 125.1 Hz, $^3J_{HCCC(12)}$ = 3.9—4.1 Hz, $^2J_{HCC(12)}$ = 3.9—4.1 Hz); 35.43 (m [s], C(13)); 29.83 (q.sept [s], C(15), $^1J_{HC(15)}$ = 126.7 Hz, $^3J_{HCCC(15)}$ = 4.6 Hz). ^{1}H NMR ($CDCl_3$), δ: 6.33 (d, H(3), $^2J_{PCH(3)}$ = 24.1 Hz); 7.47 and 7.49 (both d, H(7), H(5), $^4J_{H(5)CCCH(7)}$ = 1.7 Hz); 2.73 (m, AB part of an ABX_2 system, H(9)); 1.66 (m, H(10)); 1.49 (m, H(11)); 0.99 (t, H(12), $^3J_{HCCH(12)}$ = 7.3 Hz); 1.48 (s, H(15)).

4-Butyl-6,8-di(*tert*-butyl)-2,5-dichloro-2-oxo-2*H*-benzo[*e*][1,2]oxaphosphinine (15a). MS, *m/z*: 406, 404, 402 ($C_{20}H_{29}{}^{35}Cl_2O_2P$) $[M]^{\bullet+}$, 387 [M – CH_3], 367 [M – Cl], 345 [M – C_4H_9]. ^{1}H NMR ($CDCl_3$), δ: 6.48 (d, H(3), $^2J_{PCH(3)}$ = 27.3 Hz); 7.62 (s, H(7)); 2.85 and 3.22 (both br.ddd, C(9)H_AH_X, $^2J_{H_AHX}$ = 14.8 Hz, $^3J_{H_AH(10)}$ = 5.3 Hz, $^3J_{H_AH(10)}$ = 9.9 Hz, $^3J_{H_XH(10)}$ = 5.3 Hz, $^3J_{H_XH(10)}$ = 9.0 Hz); 0.89 (t, H(12), $^3J_{HH(12)}$ = 7.3 Hz); 1.46 and 1.58 (both s, H(15) and H(17)). ^{13}C NMR ($CDCl_3$), δ: 118.12 (ddt [d], C(3), $^1J_{PC(3)}$ = 162.8 Hz, $^1J_{HC(3)}$ = 169.7 Hz, $^3J_{HC(9)CC(3)}$ = 5.7 Hz); 161.07 (m [s], C(4)); 124.92 (m [d], C(4a), $^3J_{PCCC(4a)}$ = 19.2 Hz); 130.46 (d [s], C(5), $^3J_{HC(7)CC(5)}$ = 7.2 Hz); 143.90 (m [s], C(6)); 128.05 (d [s], C(7), $^1J_{HC(7)}$ = 158.9 Hz); 137.91 (m [d], C(8), $^3J_{POC(8a)C(8)}$ = 6.6 Hz); 147.24 (dd [d], C(8a), $^3J_{HC(7)CC(8a)}$ = 11.3 Hz, $^2J_{POC(8a)}$ = 11.4 Hz); 38.37 (tdm [s], C(9), $^1J_{HC(9)}$ = 129.8 Hz, $^3J_{PCCC(9)}$ = 18.6 Hz, $^3J_{HC(3)CC(9)}$ = 6.3 Hz); 30.08 (tm [s], C(10)); 22.28 (tm [s], C(11), $^1J_{HC(11)}$ = 125.3 Hz, $^3J_{HCCC(11)}$ = 3.2—3.5 Hz, $^2J_{HCC(11)}$ = 3.2—3.5 Hz); 13.80 (qm [s], C(12), $^1J_{HC(12)}$ = 125.0 Hz, $^3J_{HC(10)CC(12)}$ = 3.9—4.1 Hz, $^2J_{HC(11)C(12)}$ = 3.9—4.1 Hz); 35.43 (m [s], C(14)); 29.96 (q.sept [s], C(15), $^1J_{HC(15)}$ = 126.6 Hz, $^3J_{HCCC(15)}$ = 4.6 Hz); 37.02 (m [s], C(16)); 31.16 (q.sept [s], C(17), $^1J_{HC(17)}$ = 126.0 Hz, $^3J_{HCCC(17)}$ = 4.6 Hz).

4-Butyl-6-*tert*-butyl-2,8-dichloro-2-oxo-2*H*-benzo[*e*]-[1,2]oxaphosphinine (16a). ^{1}H NMR ($CDCl_3$), δ: 6.31 (d, H(3), $^2J_{PCH(3)}$ = 24.0 Hz); 7.52 and 7.58 (both br.s, H(5) and H(7)); 2.70 and 2.82 (both m, AB part of an ABX_2 system, C(9)H_2); 1.00 (t, H(12), $^3J_{HCCH(12)}$ = 7.3 Hz); 1.37 (s, H(16)). ^{13}C NMR ($CDCl_3$), δ: 113.28 (ddt [d], C(3), $^1J_{PC(3)}$ = 157.4 Hz, $^1J_{HC(3)}$ = 169.6 Hz, $^3J_{HC(9)CC(3)}$ = 6.0 Hz); 157.06 (m [s], C(4)); 121.76 (m [d], C(4a), $^3J_{PCCC(4a)}$ = 18.3 Hz); 121.81 (dd. [s], C(5), $^1J_{HC(5)}$ = 158.0 Hz, $^3J_{HC(7)CC(5)}$ = 7.2 Hz); 148.30 (m [s], C(6)); 129.94 (dd [s], C(7), $^1J_{HC(7)}$ = 163.7 Hz, $^3J_{HC(5)CC(7)}$ = 7.2 Hz); 124.25 (ddd [d], C(8), $^3J_{POCC(8)}$ = 8.4 Hz, $^2J_{HC(7)C(8)}$ = 4.2 Hz, $^4J_{HC(5)CCC(8)}$ = 1.3 Hz); 144.52 (ddd [d], C(8a), $^3J_{HC(7)CC(8a)}$ = 8.7 Hz, $^3J_{HC(5)CC(8a)}$ = 8.7 Hz, $^2J_{POC(8a)}$ = 9.0 Hz); 34.69 (tdm [s], C(9), $^3J_{PCCC(9)}$ = 19.8 Hz, $^1J_{HC(9)}$ = 128.0 Hz); 30.08 (tm [s], C(10)); 22.28 (tm [s], C(11), $^1J_{HC(11)}$ = 125.3 Hz, $^3J_{HCCC(11)}$ = 3.2—3.5 Hz, $^2J_{HCC(11)}$ = 3.2—3.6 Hz); 13.80 (qm [s], C(12), $^1J_{HC(12)}$ = 125.0 Hz, $^2J_{HCC(12)}$ = 3.9—4.1 Hz, $^3J_{HCCC(12)}$ = 3.9—4.1 Hz).

4-Butyl-8-*tert*-butyl-6-chloro-2-hydroxy-2-oxo-2*H*-benzo[*e*][1,2]oxaphosphinine (17a). A glassy substance (a mixture of compounds **14a**—**16a**) was treated with water in diethyl ether. 1,2-Oxaphosphinine **17a** that precipitated was filtered off and dried *in vacuo*. The yield was 0.88 g (21%) (unoptimized), m.p. 164—166 °C. Found (%): C, 58.22; H, 6.81; P, 9.72. $C_{16}H_{22}ClO_3P$. Calculated (%): C, 58.45; H, 6.70; P, 9.44. IR, ν/cm^{-1}: 471, 492, 537, 582, 612, 648, 728, 747, 772, 822, 881, 891, 912, 952, 1001, 1016, 1052, 1072, 1110, 1135, 1176, 1206, 1236, 1271, 1319, 1377, 1428, 1462, 1561, 1597, 1667, 2330, 2670, 2725, 2854, 2925, 3469. ^{31}P NMR (DMSO-d_6, 36.48 MHz), δ: 7.1 (d, $^2J_{PCH(3)}$ = 18.4 Hz). ^{1}H NMR (DMSO-d_6), δ: 6.15 (d, H(3), $^2J_{PCH(3)}$ = 18.3 Hz); 7.31 (br.s, H(5)); 7.51 (d, H(7), $^4J_{HC(5)CCH(7)}$ = 2.4 Hz); 2.62 (br.t, H(9), $^3J_{HCCH(9)}$ = 7.6 Hz); 1.46 (m, H(10)); 1.34 (m, H(11)); 0.89 (t, H(12), $^3J_{HH(12)}$ = 7.3 Hz); 1.38 (s, H(14)). ^{13}C NMR (DMSO-d_6), δ: 114.13 (ddt [d], C(3), $^1J_{PC(3)}$ = 171.4 Hz, $^1J_{HC(3)}$ = 162.5 Hz, $^3J_{HC(9)CC(3)}$ = 5.6 Hz); 151.46 (m [s], C(4)); 123.79 (ddt [d], C(4a), $^3J_{PCCC(4a)}$ = 15.8 Hz, $^3J_{HC(3)CC(4a)}$ = 8.3 Hz, $^3J_{HC(9)CC(4a)}$ = 3.2—3.5 Hz); 123.74 (dd [s], C(5), $^1J_{HC(5)}$ = 165.3 Hz, $^3J_{HC(7)CC(5)}$ = 5.8 Hz); 126.90 (dd [s], C(6), $^2J_{HC(5)C(6)}$ = 4.9—5.0 Hz, $^2J_{HC(7)C(6)}$ = 4.9—5.0 Hz); 127.47 (dd [s], C(7), $^1J_{HC(7)}$ = 165.2 Hz, $^3J_{HC(5)CC(7)}$ = 5.8 Hz); 141.11 (dm [d], C(8), $^3J_{POCC(8)}$ = 5.6 Hz); 148.81 (ddd [d], C(8a), $^3J_{HC(7)CC(8a)}$ = 8.9—9.1 Hz, $^3J_{HC(5)CC(8a)}$ = 9.0 Hz, $^2J_{POC(8a)}$ = 8.1 Hz); 33.89 (tdm [s], C(9), $^1J_{HC(9)}$ = 127.9 Hz, $^3J_{PCCC(9)}$ = 17.8 Hz); 29.77 (m [s], C(10)); 21.67 (m [s], C(11),

$^1J_{HC(11)}$ = 127.8 Hz); 13.64 (qt [s], C(12), $^1J_{HC(12)}$ = 124.8 Hz, $^3J_{HCCC(12)}$ = 3.9 Hz, $^2J_{HCC(12)}$ = 3.9 Hz).

4-Butyl-6-*tert*-butyl-8-chloro-2-hydroxy-2-oxo-2*H*-benzo[*e*][1,2]oxaphosphinine (18a) was obtained by crystallization of the reaction mixture from hexane after the partial separation of compound **17a**. The yield was 0.1 g (2.4%), m.p. 174—176 °C. Found (%): C, 58.37; H, 7.09; P, 9.51. $C_{16}H_{22}ClO_3P$. Calculated (%): C, 58.45; H, 6.70; P, 9.44. ^{31}P NMR (DMSO-d_6, 36.48 MHz), δ: 7.0 (d, $^2J_{PCH(3)}$ = 18.2 Hz). ^{1}H NMR (DMSO-d_6), δ: 6.21 (d, H(3), $^2J_{PCH(3)}$ = 18.0 Hz); 7.53 (br.s, H(5)); 7.47 (d, H(7), $^4J_{HC(5)CCH(7)}$ = 2.0 Hz); 2.69 (br.m, C(9)H_2, $^3J_{HCCH(9)}$ = 7.4 Hz); 1.48 (m, H(10)); 1.37 (m, H(11)); 0.90 (t, C(12)H_3, $^3J_{HH(12)}$ = 7.2 Hz); 1.28 (s, H(14)). ^{13}C NMR (DMSO-d_6), δ: 114.13 (ddt [d], C(3), $^1J_{PC(3)}$ = 171.4 Hz, $^1J_{HC(3)}$ = 162.5 Hz, $^3J_{HC(9)CC(3)}$ = 5.6 Hz); 151.81 (m [s], C(4)); 122.39 (m [d], C(4a), $^3J_{PCCC(4a)}$ = 17.3 Hz); 121.64 (dd [s], C(5), $^1J_{HC(5)}$ = 158.2 Hz, $^3J_{HC(7)CC(5)}$ = 7.5 Hz); 146.14 (m [s], C(6)); 127.73 (dd [s], C(7), $^1J_{HC(7)}$ = 163.7 Hz, $^3J_{HC(5)CC(7)}$ = 8.1 Hz); 122.31 (dd [d], C(8), $^3J_{POCC(8)}$ = 7.1 Hz, $^2J_{HC(7)C(8)}$ = 5.9 Hz); 144.59 (ddd [d], C(8a), $^3J_{HC(7)CC(8a)}$ = 9.0 Hz, $^3J_{HC(5)CC(8a)}$ = 9.0 Hz, $^2J_{POC(8a)}$ = 6.8 Hz); 33.66 (tdm [s], C(9), $^1J_{HC(9)}$ = 128.0 Hz, $^3J_{PCCC(9)}$ = 17.8 Hz); 29.94 (tdm [s], C(10), $^1J_{HC(10)}$ = 127.0 Hz); 21.67 (m [s], C(11), $^1J_{HC(11)}$ = 127.8 Hz); 13.64 (qm [s], C(12), $^1J_{HC(12)}$ = 124.8 Hz, $^3J_{HCCC(12)}$ = 3.9 Hz, $^3J_{HCC(12)}$ = 3.9 Hz).

Reaction of quinone 1 with hex-1-yne in the presence of phosphorus trichloride. The reaction was carried out analogously to the reaction with phenylacetylene. A mixture of compounds **14a**—**16a** was obtained; the percentage of these compounds in the mixture was 55, 28, and 17%, respectively. The mixture was treated analogously to that obtained in the reaction of phosphole **5** with hex-1-yne. Hydroxyphosphinine **17a** was isolated in 22% yield.

Reaction of dioxaphosphole 5 with hept-1-yne. A mixture of phosphole **5** (4.5 g, 0.0126 mol), CH_2Cl_2 (12 mL), and hept-1-yne (2.5 mL, 1.81 g, 0.0189 mol) was kept at 10—20 °C for 12 h. Then the reaction mixture was dried *in vacuo* (130 °C, 12 Torr) to remove the solvent, excess alkyne, and 2-chlorohept-1-ene. A glassy light-brown mixture of phosphinines **14b**—**16b** was obtained. ^{31}P NMR, δ: 17.3 (d, $^2J_{PCH}$ = 24.2 Hz) (**14b**, 62%); 17.8 (d, $^2J_{PCH}$ = 27.3 Hz) (**15b**, 24%); 18.7 (d, $^2J_{PCH}$ = 24.2 Hz) (**16b**, 14%).

8-*tert*-Butyl-2,6-dichloro-4-pentyl-2-oxo-2*H*-benzo[*e*][1,2]oxaphosphinine (14b). ^{1}H NMR ($CDCl_3$), δ: 6.25 (d, H(3), $^2J_{PCH(3)}$ = 24.0 Hz); 7.39 (dd, H(7), $^4J_{H(5)CCCH(7)}$ = 2.1 Hz, $^5J_{POCCCH(7)}$ = 1.4 Hz); 7.40 (d, H(5), $^4J_{H(5)CCCH(7)}$ = 2.1 Hz); 2.63 (m, AB part of an ABX_2 system, H(9), $^2J_{H_ACH_B}$ = 11.5 Hz, $^2J_{H_XCH}$ = 7.4 Hz); 1.66 (m, H(10), $^3J_{H(9)CCH(10)}$ = 7.4 Hz, $^3J_{H(11)CCH(10)}$ = 7.0—7.4 Hz); 1.33—1.34 (m, H(11), H(12)); 0.86 (t, H(13), $^3J_{H(12)CCH(13)}$ = 7.0 Hz); 1.48 (H(15)). ^{13}C NMR ($CDCl_3$), δ: 113.19 (ddt [d], C(3), $^1J_{PC(3)}$ = 157.4 Hz, $^1J_{HC(3)}$ = 169.0 Hz, $^3J_{HC(9)CC(3)}$ = 5.7 Hz); 156.80 (m [s], C(4)); 123.04 (ddtd [d], C(4a), $^3J_{PCCC(4a)}$ = 18.0 Hz, $^3J_{HC(3)CC(4a)}$ = 8.0 Hz, $^3J_{HC(9)CC(4a)}$ = 3.1 Hz, $^2J_{HC(5)C(4a)}$ = 0.9 Hz); 124.30 (dd [s], C(5), $^1J_{HC(5)}$ = 166.1 Hz, $^3J_{HC(7)CC(5)}$ = 5.8 Hz); 129.98 (dd [s], C(6), $^2J_{HCC(6)}$ = 4.5—4.8 Hz, $^2J_{HCC(6)}$ = 4.5—4.8 Hz); 129.85 (dd [s], C(7), $^1J_{HC(7)}$ = 165.4 Hz, $^3J_{HC(5)CC(7)}$ = 5.9 Hz); 142.50 (d [d], C(8), $^3J_{POCC(8)}$ = 7.2 Hz); 148.47 (ddd [d], C(8a), $^3J_{HC(5)CC(8a)}$ = 10.2—10.5 Hz, $^3J_{HC(7)CC(8a)}$ = 10.2—10.5 Hz, $^2J_{POC(8a)}$ = 11.4 Hz); 35.24 (tdm [d], C(9), $^3J_{PCCC(9)}$ = 20.4 Hz, $^1J_{HC(9)}$ = 127.4 Hz); 31.23 (tm [s], C(10), $^1J_{HC(10)}$ = 123.9 Hz); 27.50 (tm [s], C(11), $^1J_{HC(11)}$ = 127.1 Hz, $^3J_{HCCC(11)}$ = 3.6—3.9 Hz, $^2J_{HCC(11)}$ = 3.6—3.9 Hz); 22.28 (tm [s], C(12), $^1J_{HC(12)}$ = 125.9 Hz, $^3J_{HCCC(12)}$ = 4.1—4.2 Hz, $^2J_{HCC(12)}$ = 4.1—4.2 Hz); 13.84 (qm [s], C(13), $^1J_{HC(13)}$ = 124.9 Hz, $^3J_{HCCC(13)}$ = 3.4—3.9 Hz, $^2J_{HCC(13)}$ = 3.4—3.9 Hz); 35.30 (m [s], C(14)); 29.77 (q.sept [s], C(15), $^1J_{HC(15)}$ = 126.8 Hz, $^3J_{HCCC(15)}$ = 4.7 Hz).

6,8-Di(*tert*-butyl)-2,5-dichloro-2-oxo-4-pentyl-2*H*-benzo[*e*][1,2]oxaphosphinine (15b). ^{1}H NMR ($CDCl_3$), δ: 6.40 (d, H(3), $^2J_{PCH(3)}$ = 27.3 Hz); 7.54 (br.s, H(7)); 2.74 (br.ddd, C(9)H_A, $^2J_{H_AH_X}$ = 15.3 Hz, $^3J_{H_AH(10)}$ = 6.2 Hz, $^3J_{H_AH(10)}$ = 9.1 Hz); 3.16 (br.ddd, C(9)H_X, $^2J_{H_XH_A}$ = 15.3 Hz, $^3J_{H_XH(10)}$ = 9.5—10.0 Hz, $^3J_{H_AH(10)}$ = 16.1—16.8 Hz); 1.19—1.20 (m, H(11), H(12)); 0.77 (t, H(13), $^3J_{HH(13)}$ = 7.2 Hz); 1.46 and 1.58 (both s, H(15), H(17)). ^{13}C NMR ($CDCl_3$), δ: 118.07 (ddt [d], C(3), $^1J_{PC(3)}$ = 162.8 Hz, $^1J_{HC(3)}$ = 169.1 Hz, $^3J_{HC(9)CC(3)}$ = 5.6 Hz); 161.05 (m [s], C(4)); 124.84 (m [d], C(4a), $^3J_{PCCC(4a)}$ = 19.2 Hz); 130.43 (d [s], C(5), $^3J_{HC(7)CC(5)}$ = 7.2 Hz); 143.85 (m [s], C(6)); 128.00 (d [s], C(7), $^1J_{HC(7)}$ = 159.1 Hz); 137.88 (m [d], C(8), $^3J_{POC(8a)C(8)}$ = 6.6 Hz); 147.19 (dd [d], C(8a), $^3J_{HC(7)CC(8a)}$ = 11.6 Hz, $^2J_{POC(8a)}$ = 10.8 Hz); 38.62 (tdm [s], C(9), $^1J_{HC(9)}$ = 129.2 Hz, $^3J_{PCCC(9)}$ = 18.6 Hz); 29.90 (tm [s], C(10)); 28.86 (tm [s], C(11), $^1J_{HC(11)}$ = 126.2 Hz); 22.19 (tm [s], C(12), $^1J_{HC(12)}$ = 124.9 Hz); 13.84 (qm [s], C(13), $^1J_{HC(13)}$ = 125.0 Hz); 35.38 (m [s], C(14)); 29.89 (q.sept [s], C(15), $^1J_{HC(15)}$ = 126.6 Hz, $^3J_{HCCC(15)}$ = 4.8 Hz); 36.97 (m [s], C(16)); 30.03 (q.sept [s], C(17), $^1J_{HC(17)}$ = 126.3 Hz, $^3J_{HCCC(17)}$ = 4.8 Hz).

6-*tert*-Butyl-2,8-dichloro-2-oxo-4-pentyl-2*H*-benzo[*e*][1,2]oxaphosphinine (16b). ^{1}H NMR ($CDCl_3$), δ: 6.24 (d, H(3), $^2J_{PCH(3)}$ = 23.7 Hz); 7.44 (H(5), $^4J_{H(7)CCCH(5)}$ = 2.1 Hz); 7.50 (dd, H(7), $^4J_{H(5)CCCH(7)}$ = 2.1 Hz, $^5J_{POCCCH(7)}$ = 1.4 Hz); 2.63 (m, C(9)H_2, AB part of the ABX_2 system); 0.86 (t, H(13), $^3J_{HCC(13)}$ = 7.2 Hz); 1.29 (s, H(17)). ^{13}C NMR ($CDCl_3$), δ: 113.19 (ddt [d], C(3), $^1J_{PC(3)}$ = 157.4 Hz, $^1J_{HC(3)}$ = 169.0 Hz, $^3J_{HC(9)CC(3)}$ = 5.4 Hz); 157.04 (m [s], C(4)); 121.72 (m [d], C(4a), $^3J_{PCCC(4a)}$ = 18.0 Hz); 121.73 (dd [s], C(5), $^1J_{HC(5)}$ = 158.2 Hz, $^3J_{HC(7)CC(5)}$ = 7.5 Hz); 148.25 (m [s], C(6)); 129.89 (dd [s], C(7), $^1J_{HC(7)}$ = 163.7 Hz, $^3J_{HC(5)CC(7)}$ = 7.5 Hz); 124.23 (m [d], C(8), $^3J_{POCC(8)}$ = 7.8 Hz); 144.48 (ddd [d], C(8a), $^3J_{HC(7)CC(8a)}$ = 9.0 Hz, $^3J_{HC(5)CC(8a)}$ = 9.0 Hz, $^2J_{POC(8a)}$ = 10.2 Hz); 34.95 (tdm [s], C(9), $^3J_{PCCC(9)}$ = 19.2 Hz, $^1J_{HC(9)}$ = 130.7 Hz); 30.03 (tm [s], C(10)); 27.70 (tm [s], C(11), $^1J_{HC(11)}$ = 126.8 Hz, $^3J_{HCCC(11)}$ = 4.1—4.7 Hz, $^2J_{HCC(11)}$ = 4.1—4.7 Hz); 22.3 (tm [s], C(12), $^1J_{HC(12)}$ = 124.9 Hz, $^2J_{HCC(12)}$ = 3.4—3.9 Hz, $^3J_{HCCC(12)}$ = 3.4—3.9 Hz); 13.80 (qm [s], C(13), $^1J_{HC(13)}$ = 125.0 Hz).

6-*tert*-Butyl-8-chloro-2-hydroxy-2-oxo-4-pentyl-2*H*-benzo[*e*][1,2]oxaphosphinine (18b). A glassy substance (a mixture of compounds **14b**—**16b**) was treated with water in diethyl ether. 1,2-Oxaphosphinine **18b** that precipitated was filtered off and dried *in vacuo*. The yield was 0.26 g (6%) (unoptimized), m.p. 185—186 °C. Found (%): C, 59.17; H, 7.33; P, 8.79. $C_{17}H_{24}ClO_3P$. Calculated (%): C, 59.56; H, 7.01; P, 9.05. MS, *m/z*: 344, 342 ($C_{17}H_{24}{}^{35}ClO_3P$) $[M]^{\bullet+}$, 327 [M – CH_3], 286 [M – C_4H_8], 271 [M – C_5H_{11}]. IR, ν/cm^{-1}: 431, 494, 537, 586, 613, 68, 725, 737, 789, 822, 853, 881, 908, 953, 1000, 1011, 1034, 1069, 1134, 1176, 1209, 1271, 1280, 1302, 1333, 1377, 1426, 1460, 1560, 1596, 1659, 2284, 2670, 2723, 2854, 2924, 3437. ^{31}P NMR (DMSO-d_6, 36.48 MHz), δ: 6.5 (d, $^2J_{PCH(3)}$ = 18.4 Hz). ^{1}H NMR (DMSO-d_6), δ: 6.22 (d, H(3), $^2J_{PCH(3)}$ = 18.2 Hz); 7.48 (br.s, H(5)); 7.55 (d, H(7), $^4J_{HC(5)CCH(7)}$ =

2.0 Hz); 2.69 (br.m, H(9), $^3J_{HCCH(9)}$ = 7.7 Hz); 1.51 (m, H(10), $^3J_{HCCH(10)}$ = 7.3—7.7 Hz); 1.31—1.32 (m, H(11), H(12)); 0.86 (t, H(13), $^3J_{HH(13)}$ = 7.0 Hz); 1.29 (s, H(17)). ^{13}C NMR (DMSO-d_6), δ: 114.18 (ddt [d], C(3), $^1J_{PC(3)}$ = 170.9 Hz, $^1J_{HC(3)}$ = 160.1 Hz, $^3J_{HC(9)CC(3)}$ = 5.7 Hz); 151.83 (m [s], C(4)); 122.40 (m [d], C(4a), $^3J_{PCCC(4a)}$ = 16.9 Hz); 121.67 (dd [s], C(5), $^1J_{HC(5)}$ = 158.0 Hz, $^3J_{HC(7)CC(5)}$ = 7.5 Hz); 146.12 (m [s], C(6)); 127.72 (dd [s], C(7), $^1J_{HC(7)}$ = 163.7 Hz, $^3J_{HC(5)CC(7)}$ = 7.8 Hz); 122.29 (dm [d], C(8), $^3J_{POCC(8)}$ = 6.7 Hz, $^2J_{HC(7)C(8)}$ = 4.6 Hz); 144.60 (ddd [d], C(8a), $^3J_{HC(7)CC(8a)}$ = 8.6 Hz, $^3J_{HC(5)CC(8a)}$ = 8.6 Hz, $^2J_{POC(8a)}$ = 6.5 Hz); 34.00 (tdm [s], C(9), $^1J_{HC(9)}$ = 125.9 Hz, $^3J_{PCCC(9)}$ = 17.9 Hz); 30.78 (m [s], C(10)); 27.47 (tm [s], C(11), $^1J_{HC(11)}$ = 127.4 Hz); 21.78 (tm [s], C(12), $^1J_{HC(12)}$ = 125.2 Hz); 13.77 (qt [s], C(13), $^1J_{HC(13)}$ = 124.5 Hz, $^3J_{HCCC(13)}$ = 3.0—4.0 Hz, $^2J_{HCC(13)}$ = 3.0—4.0 Hz); 34.36 (m [s], C(16)); 30.81 (q.sept [s], C(17), $^1J_{HC(17)}$ = 125.9 Hz, $^3J_{HCCC(17)}$ = 4.7 Hz).

8-*tert*-Butyl-6-chloro-2-hydroxy-2-oxo-4-pentyl-2*H*-benzo[*e*][1,2]oxaphosphinine (17b). After the separation of the precipitate of oxaphosphinine **18b**, compound **17b** gradually precipitated from the hydrolyzed reaction mixture of phosphinines **14b**—**16b**. The precipitate was filtered off, washed with diethyl ether, and dried in air. The yield was 0.21 g (5%) (unoptimized), m.p. 173—175 °C. Found (%): C, 59.17; H, 7.33; P, 8.79. $C_{17}H_{24}ClO_3P$. Calculated (%): C, 59.56; H, 7.01; P, 9.05. MS, *m/z*: 344, 342 ($C_{17}H_{24}{}^{35}ClO_3P$) $[M]^{\bullet+}$, 327 [M − CH_3], 286 [M − C_4H_8], 271 [M − C_5H_{11}]. ^{31}P NMR (DMSO-d_6, 36.48 MHz), δ: 5.6 (d, $^2J_{PCH(3)}$ = 18.4 Hz).

Reaction of quinone 1 with hept-1-yne in the presence of phosphorus trichloride. The reaction was carried out analogously to the reaction with phenylacetylene. Compounds **14b**, **15b**, and **16b** were obtained in percentage of 57, 27, and 16%, respectively. Then the reaction mixture was treated analogously to that obtained in the reaction of phosphole **5** with hex-1-yne. Hydroxyphosphinines **17b** and **18b** were isolated in 27 and 5% yields, respectively.

X-ray diffraction study of compounds 8 and 9 was performed on an automated four-circle Enraf-Nonius CAD-4 diffractometer (Mo-Kα and Cu-Kα radiation). The unit cell parameters were determined and the X-ray data collection and preliminary processing were performed with the use of the MolEN program package.[18] Crystals of compound **8** ($C_{19}H_{20}ClO_3P$) are colorless, transparent, prismatic-shaped, monoclinic, space group $P2_1/c$. At 20 °C, a = 8.859(2) Å, b = 15.672(7) Å, c = 13.005(7) Å, β = 98.35(6)°, V = 1786(2) Å^3, d_{calc} = 1.41 g cm^{-3}, Z = 4. The unit cell parameters and the intensities of 2679 independent reflections, of which 812 reflections were with $I > 3\sigma(I)$, were measured at 20 °C (λ(MoKα) radiation, graphite monochromator, ω/2θ-scanning technique, θ ≤ 24.63°). The intensities of three check reflections showed no decrease in the course of X-ray data collection. No absorption correction was applied because of the low absorption coefficient (μ(Mo) = 4.6 cm^{-1}). The structure was solved by direct methods using the SIR program[19] and refined first isotropically and then anisotropically. The hydrogen atoms were located in difference electron density maps. Their contributions to the structure amplitudes were taken into account in the final step of the refinement with fixed positional and thermal parameters. The final R factors were R = 0.086, R_w = 0.085 based on 737 independent reflections with $F^2 \geq 3\sigma$. All calculations were carried out on an Alpha Station 200.

Crystals of compound **9** ($C_{20}H_{22}ClO_3P$) are colorless, triclinic, space group $P\bar{1}$, at 20 °C a = 8.745(1) Å, b = 9.751(2) Å, c = 12.857(2) Å, α = 93.71(2)°, β = 107.04(2)°, γ = 113.26(2)°, V = 942.4(3) Å^3, d_{calc} = 1.33 g cm^{-3}, Z = 2. The unit cell parameters and the intensities of 3799 reflections, of which 2051 reflections were with $I \geq 2\sigma$, were measured at 20 °C (λ(CuKα) radiation, graphite monochromator, ω/2θ-scanning technique, θ ≤ 74.24°). The intensities of three check reflections showed no decrease in the course of X-ray data collection. The empirical absorption correction was applied (μ(Cu) = 27.26 cm^{-1}). The structure was solved by direct methods using the SIR program[19] and refined first isotropically and then anisotropically with the use of the SHELXL-97 program package.[20] The coordinates of the hydrogen atoms were calculated based on the stereochemical criteria and refined using a riding model. The final R factors were R = 0.063, R_w = 0.166 based on 2051 reflections with $F^2 \geq 4\sigma$. All calculations were carried out with the use of the WinGX program.[21] The figures were drawn with the use of the PLATON program.[22]

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