The reaction of 2-R-benzo[*d*]-1,3,2-dioxaphosphorin-4-ones with arylidenemalonic acids diethyl- and bis(2,2,3,3-tetrafluoropropyl) esters. Synthesis, molecular and supramolecular structure of 2-aryl-2-R-benzo[*d*]-1,2-oxaphosphophepin-2,5-diones

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Dedicated to Professor Alexander I. Konovalov on the occasion of his 70th anniversary
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Abstract
The reaction of 2-R-benzo[*d*]-1,3,2-dioxaphosphorin-4-ones with arylidenemalonic acid diethyl- and bis(2,2,3,3-tetrafluoropropyl) esters has been found to give 2-aryl-2-R-benzo[*d*]-1,2-oxaphosphophepin-2,5-diones with high stereoselectivity under soft conditions. In all cases preferable diastereoisomers were isolated and the configuration of some of them was established by single crystal X-ray diffraction.

Keywords: Arylidenemalonic acid esters, 2-R-benzo[*d*]-1,3,2-dioxaphosphorin-4-ones, benzo[*d*]-1,2-oxaphosphophepine derivatives, stereoselective formation, crystal structure, quantum chemistry calculations

Introduction

Phosphorylated derivatives of salicylic acid (benzo[*d*]-1,3,2-dioxaphosphorin-4-ones or "salicylphosphites") obtained by Anshütz[1] more than one hundred years ago are of interest from several points of view. First, being the mixed anhydrides of phosphorous and carbonic acids they are attractive in the synthesis of the new types of organic phosphorus compounds.[2] Second, they as well as salicylic acid demonstrate versatile biological activity.[3] Third, they can be used in polymer chemistry.[4] And at last, salicylphosphites have considerable promise in biochemistry as phosphorylating reagents for introducing the phosphite moiety to the complex natural com-

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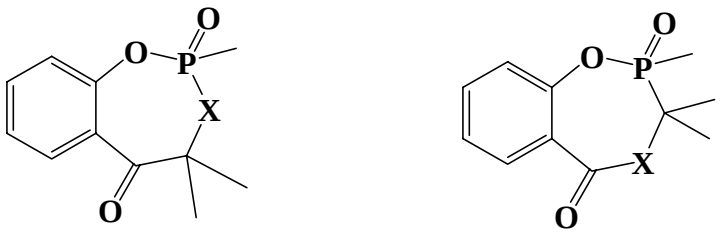
pounds.[5] Salicylphosphites have an interesting structural feature, namely, they are acylphosphites comprising a labile endocyclic fragment P-O-C(O). The presence of nucleophilic phosphorus atom and electrophilic carbonyl group in the same molecule leads to the appearance of unusual reactivity that is the possibility to react easily with both electrophiles and nucleophiles.

The presence of an essential positive charge on the carbon and phosphorus atoms has been shown by MNDO method for salicylfluorophosphite.[6] The first two ionization potentials determined by photoelectron spectroscopy method have been established to belong to two π-orbitals of a benzene ring and only the third potential corresponds to the lone electron pair of phosphorus[6]. The last potential is rather high, that is salicylphosphites are weaker nucleophiles than acyclic phosphites. Taking into consideration the photoelectron data it is easy to account for the reasons why the half-wave potentials $E_{1/2}$ of the first oxidation wave for salicylphosphites are practically not affected by the nature of the exocyclic substituent at phosphorus.[7] The removing of an electron proceeds from the π_1-orbital of the benzene ring and not from the phosphorus one.

The peculiarities of the electronic structure of salicylphosphites and their great ability to open a phosphorinane cycle under the attacks of electrophiles and nucleophiles are in accordance with their reactions with carbonyl compounds and imines. So, such electrophiles as hexafluoroacetone,[8] fluorinated α,β-diketones,[9] pyruvic acid methyl ester,[10] mezoxalic acid diethyl ester,[11] trifluoroacetone,[12] tetrachloro-*ortho*-quinone,[13] alkylcarbonylphosphonates,[14] hexafluoroacetone imine,[15] trifluoropyruvic acid methyl ester[16] easily react with salicylphosphites as nucleophiles. In these reactions the expansion of the phosphorinane cycle proceeds and the regio- and stereoselective formation of 6,7-benzo-1,3,2- and 6,7-benzo-1,4,2-dioxaphosphepines, 6,7-benzo-1,3,2- and 6,7-benzo-1,4,2-oxazaphosphepines (**I**, **II**) takes place.



I **X = O, NH** **II**

The reaction of 2-RO-5,6-benzophosphorin-4-ones containing the acceptor fluorinated exocyclic substituent R with aromatic aldimines proceeds *via* nucleophilic attack of the latter on the phosphorinone carbonyl group and leads to formation of 6,7-benzo-1,4,2-oxazaphosphepines with high regio- and stereoselectivity.[17]

It is necessary to note also that salicylphosphites contain a chiral phosphorus atom and are convenient substrates for investigation of the reactions with the prochiral carbonyl compounds, imines and alkenes.

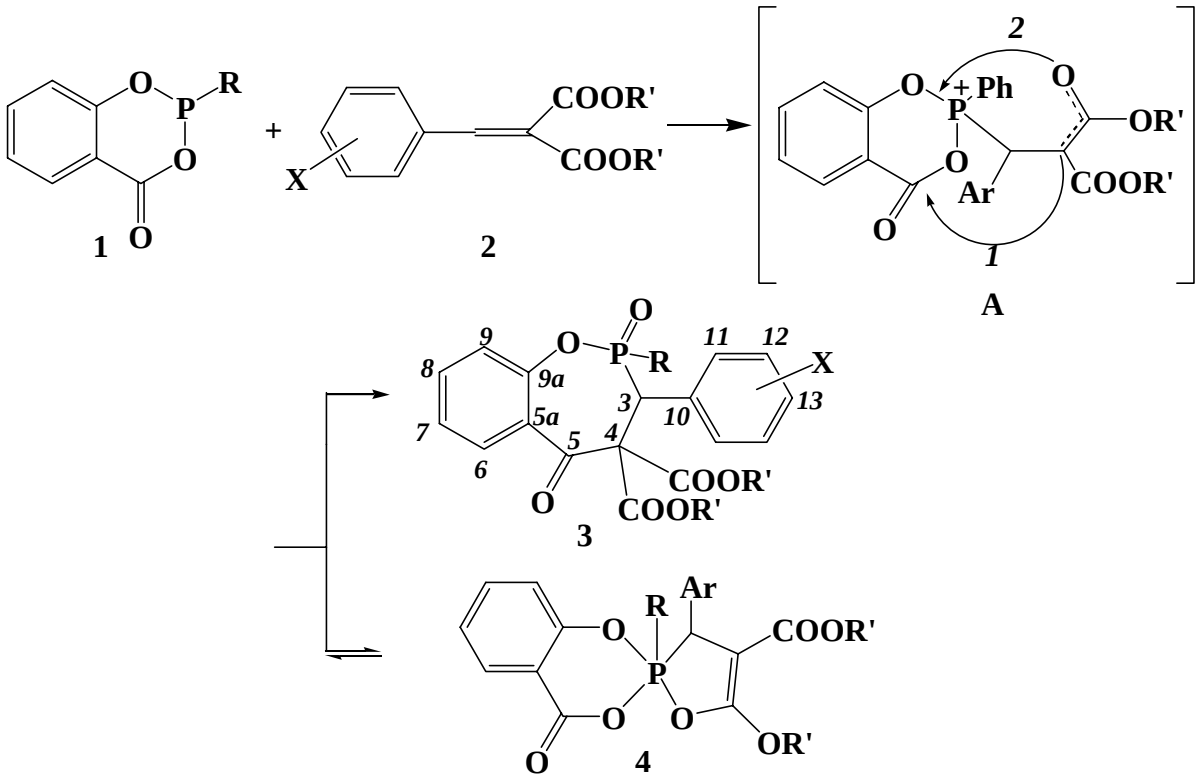
Here we for the first time demonstrate that salicylphosphites and -phosphonites are also capable to react with activated alkenes such as arylidenemalonic acids diethyl- and bis(2,2,3,3-

tetrafluoropropyl) esters to yield seven-membered heterocycles, 2-aryl-2-R-benzo[*d*]-1,2-oxaphosphepin-2,5-diones, with high regio- and stereoselectivity.

Results and Discussion

The interaction of the usual acyclic P(III) derivatives with alkylidene malonic acid esters leads to formation of 1,2-oxaphospholenes, containing pentacoordinated phosphorus atom.[18] We have found that 2-R-benzo[*d*]-1,3,2-dioxaphosphorin-4-ones **1** easily react with arylidenemalonic acid diethyl- and bis(2,2,3,3-tetrafluoropropyl) esters **2** via two directions. The first direction includes the formation of seven-membered heterocycles, 2-aryl-2-R-benzo[*d*]-1,2-oxaphosphepin-2,5-diones **3** (90-95 %) and the second one involves the usual formation of phosphorane derivatives **4** (5-10 %).

The second pathway is reversible and compounds **4** are converted to phosphepines **3** under light heating. The compound **1a** reacts faster than **1b, c**. Fluorinated derivatives **2b-d** exhibit higher reactivity than ethyl ester **2a**. These observations and literature data[18] indicate the nucleophilic attack of phosphorus on carbon-carbon bond and probable formation of intermediate bipolar ion **A**. Its further stabilization involves the intramolecular attack of anionic moiety on endocyclic carbonyl group and the formation of final compounds **3** (pathway ***1***). Owing to the presence of two electron-withdrawing substituents COOR and delocalization of the negative charge the nucleophilic attack of oxygen on phosphorus atom can also take place (pathway ***2***). This direction leads to formation of minor compounds **4**, which have characteristic signals in ^{31}P NMR spectra (δ_P –22 ÷ –24 ppm).



R = Ph (1a), OMe (1b), OEt (1c);
X, R' = H, Et (2a); R' = $OCH_2CF_2CHF_2$, X = H (2b), 4-Cl (2c), 2-Cl (2d), 4-Br (2e);
R, X, R' = Ph, H, Et (3a); R' = $OCH_2CF_2CHF_2$, R = OMe, X = H (3b), 4-Cl (3c), 2-Cl (3d),
R = OEt, X = H (3e), 4-Cl (3f), 2-Cl (3g), 4-Br (3h), R = Ph, X = H (3i), 4-Cl (3j), 4-Br (3k)

The formation of phosphepines **3** is remarkable for its high regio- (100 %) and stereoselectivity (93-97 %). The reasons of this phenomenon are incomprehensible and are the subject of quantum chemical calculations being carried out at present. Now it may be only said that preferable diastereoisomer of compound (**3f**) has higher energy than minor one (see figure 1). This unexpected result can indicate the kinetic reasons of high stereoselectivity. In all cases the preferred diastereoisomers are isolated. Its structure was confirmed by ^{1}H, ^{13}C, ^{19}F, ^{31}P NMR and IR spectroscopy.

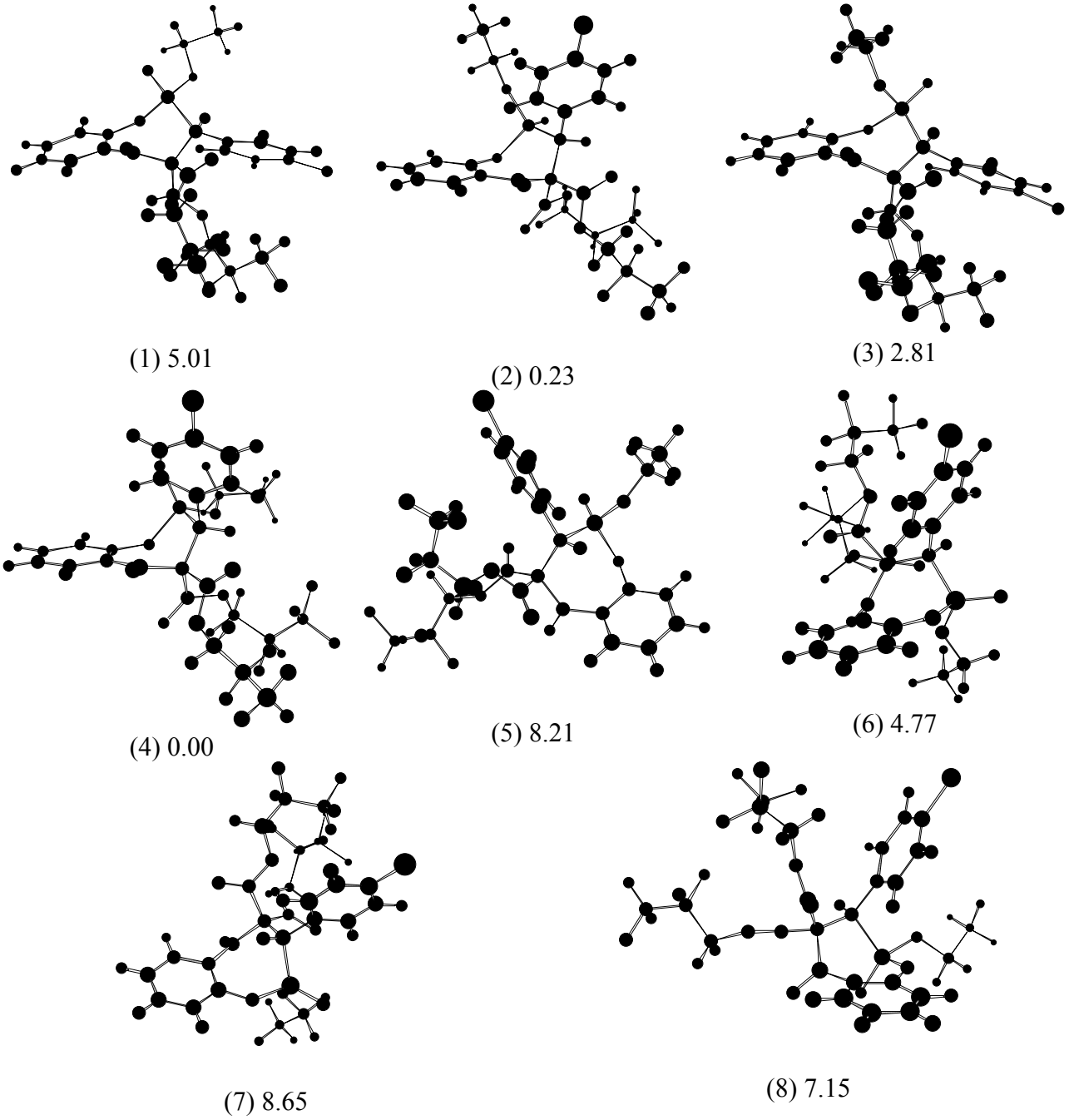


Figure 1. Structure and relative energy (kcal·mol^{-1}) of conformers for two diastereoisomers of compound (**3f**). (1) d_1 (P_RC_R), *twist-boat*, $(OEt)_{eq}$, $(ClC_6H_4)_{eq}$; (2) d_1 (P_SC_S), *boat*, $O^1C^{9a}C^{5a}C^5C^4$ planar fragment, $(OEt)_{ax}$, $(ClC_6H_4)_{ax}$; (3) d_2 (P_SC_R), *twist-boat*, $(OEt)_{ax}$, $(ClC_6H_4)_{eq}$; (4) d_2 (P_RC_S), *boat*, $O^1C^{9a}C^{5a}C^5C^4$ planar fragment, $(OEt)_{eq}$, $(ClC_6H_4)_{ax}$; (5) d_2 (P_RC_S), *boat*, $(OEt)_{eq}$, $(ClC_6H_4)_{eq}$; (6) d_2 (P_SC_R), *boat*, $P^2O^1C^{9a}C^{5a}C^5$ planar fragment, $(OEt)_{ax}$, $(ClC_6H_4)_{ax}$; (7) d_1 (P_SC_S), *boat*, $P^2O^1C^{9a}C^{5a}C^5$ planar fragment, $(OEt)_{ax}$, $(ClC_6H_4)_{eq}$; (8) d_1 (P_RC_R), *boat*, $P^2O^1C^{9a}C^{5a}C^5$ planar fragment, $(OEt)_{eq}$, $(ClC_6H_4)_{ax}$ (d_1 – main diastereoisomer, d_2 – minor one).

NMR data

The signals with δ_P 17.5-20.5 and δ_P 38.5-38.9 ppm belong to compounds (**3b-h**) and (**3a, 3i-k**) respectively and are consistent with the phosphorus atom nature (coordination number and the presence of one or two P–C bonds). The ^{13}C NMR data of phosphepines (7) recorded in two solvents (acetone-D_6 and $CDCl_3$) at various frequencies (150.9 and 100.6 MHz) are given in experimental part. In the up-field region of the ^{13}C NMR spectra there is a doublet of doublets with characteristic values of the $^1J_{PC}$ and $^1J_{HC}$ one-bond couplings (82.1-132.5 and 127.6-129.1 Hz respectively). In low-field region of the ^{13}C NMR spectra there are a singlet and two doublets that can be assigned to two types of carbonyl groups, namely C^5 (δ_C 186-188 ppm) and C^{16}, C^{20} (162-166 ppm). The chemical shift value of the latter carbons depends on the nature of substituents at P^2 and C^3, and also on the solvent. Figure 2 demonstrates these evidences for two solvents (acetone-D_6 and $CDCl_3$). The solvent influence is caused by the alteration of the seven-membered heterocycle conformation (this problem requires a separate investigation). According to Karplus equations[19,20] the small values of the $^3J_{PC}$ three-bond couplings ($^3J_{PC^3C^4C^{16,20}}$ 10-12 Hz) correspond to dihedral angle $PC^3C^4C^{16,20}$ of 40-60°, and values of 16-18 Hz are in agreement with the dihedral angle of 160-180°. This interpretation is confirmed by X-ray diffraction (see below). Other carbons in fluoroalkoxylic substituents are also non-equivalent in ^{13}C NMR spectra. The attention should be also drawn to the broadening of *ortho*-carbons ($C^{11,15}$) in aryl substituent connected with dynamic process in molecules (**3**) (it may be hindered rotation about the C^3–C^{10} bond). It is interesting that the signals of $C^{11,15}$ are clearly revealed in *ortho*-chlorophenyl substituent. The full interpretation of the spectra was made using the literature data for salicylic acid[21] and its phosphorylated derivatives,[8-12, 14-17] and also 2D NMR (COSY, HETCOR HMBC and HSQC) experiments. Made assignment is in good agreement with quantum chemical calculations (GIAO DFT) of carbon and proton chemical shifts. In all cases correlation coefficients lie within 0.96-0.98 (for *boat* conformations). Different shielding of fluoroalkoxylic substituents is manifested in ^1H and ^{19}F NMR spectra, where almost all nuclei are non-equivalent.

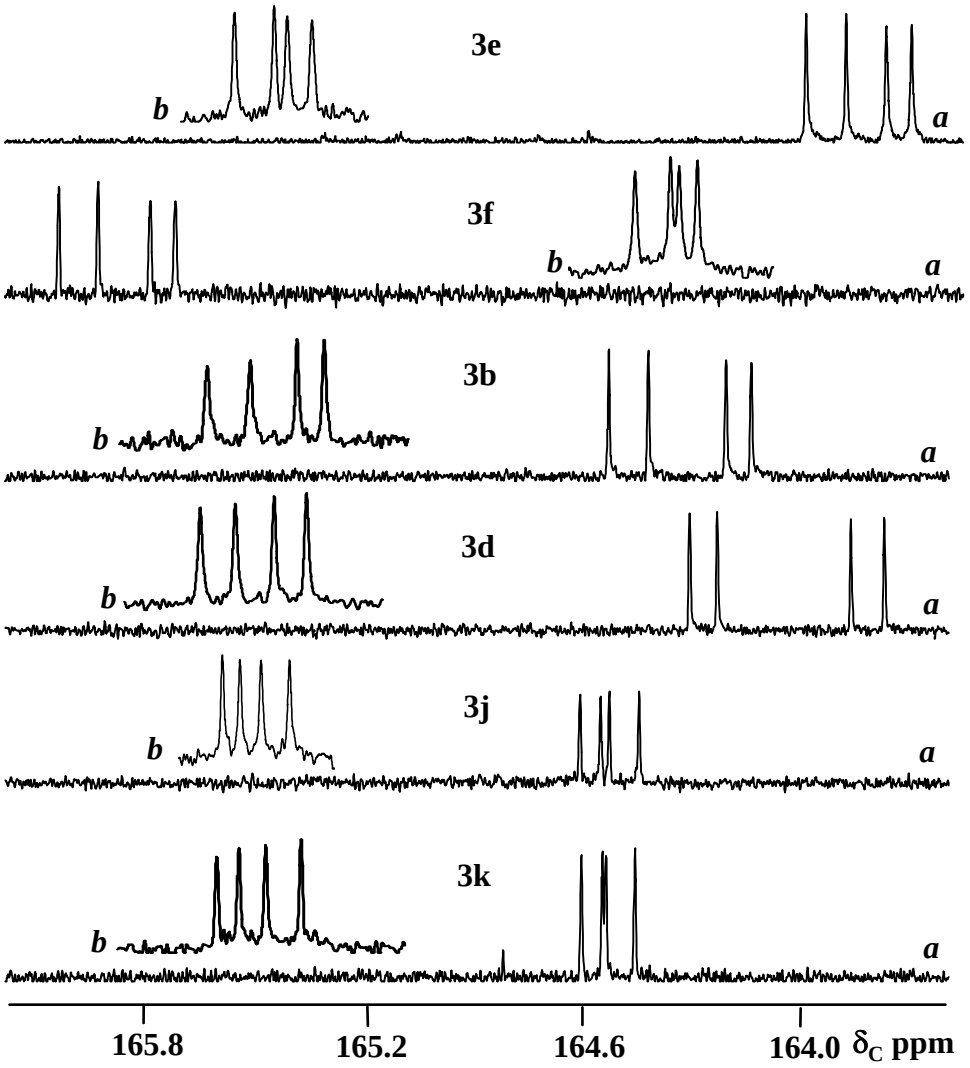


Figure 2. Low-field region of C-{H} NMR spectra of compounds (**3e**, **f**, **b**, **d, j**, **k**) recorded in CD_3COCD_3 (150.9 MHz) (***a***) and in $CDCl_3$ (100.6 MHz) (***b***).

Mass-spectrometry data

The structure of compounds (**3b-j**) was confirmed by high-resolution mass-spectrometry (electron impact). Mass-spectra of all compounds (**3b-j**) contain the molecular ion peaks $[M]^{+\bullet}$ (Tabl. 1). The cleavage of the C^4–C(X) bond and elimination of X (X = $C(O)OCH_2CF_2CHF_2$) leading to formation of ions $[M\text{-}X]^+$ are the common fragmentation pathway for these molecules. Another fragmentation pathway is connected with the formation of ions $[M - R]^+$ (R= $OCH_2CF_2CHF_2$). The process is accompanied with breaking of C–O bonds. Compounds (**3f, g, h**) containing ethoxy group at phosphorus give the ions $[M - OEt]^+$ and $[M - C_2H_4]^+$. Compounds (**3c, d, f, g, h, j**) containing halogen in aryl substituent at C^3 show the intensive peaks relating to ion $[M - Hal]^+$. Further the ion $[M - C_2H_4]^+$ can lose halogen in case of compounds

(**3f, g, h, j**) to yield the ion $[M - C_2H_4 - Hal]^+$. The most intensive peak with *m*/*z* 120 belongs to the ion $C_7H_4O_2$, which is formed in result of the P–C^3 and C^4–C^5 bonds cleavage.

Table 1. Mass-spectra of compounds (**3b, c, d, f-j**)

Ion	*m*/*z* ($I_{relat.}$, %)*			
	3b	**3c**	**3d**	**3f**
$[M]^{+\bullet}$	618(6.2)	652(1.1)	652(0.30)	666(1.4)
$[M - OEt]^+$	-	-	-	621(0.04)
$[M - R]^+$	487(6.0)	521(1.0)	521(0.64)	535(1.4)
$[M - X]^+$	459(10.9)	493(1.7)	493(0.80)	507(1.5)
$[M - C_2H_4]^+$	-	-	-	638(0.04)
$[M - Hal]^+$	-	617(1.8)	617(13.2)	631(1.7)
$[M - C_2H_4 - X]^+$	-	-	479(0.18)	479(0.45)
$[M - C_2H_4 - Hal]^+$	-	-	-	603(0.16)
$[C_7H_4O_2]^+$	120(100.0)	120(100.0)	120(100.0)	120(100.0)

Ion	*m*/*z* ($I_{relat.}$, %)*			
	3g	**3h**	**3i**	**3j**
$[M]^{+\bullet}$	666(0.17)	710(5.3)	664(3.1)	698 (4.1)
$[M - OEt]^+$	621(0.06)	665(0.1)	-	-
$[M - R]^+$	535(0.97)	579(5.1)	533(2.8)	567(5.5)
$[M - X]^+$	507(0.49)	551(4.9)	505(1.3)	539(4.3)
$[M - C_2H_4]^+$	638(0.01)	682(0.18)	-	-
$[M - Hal]^+$	631(13.3)	631(12.5)	-	663 (5.9)
$[M - C_2H_4 - X]^+$	-	523(5.8)	-	-
$[M - C_2H_4 - Hal]^+$	603(3.1)	603(2.3)	-	-
$[C_7H_4O_2]^+$	120(100)	120(100.0)	120(11.8)	120(18.5)

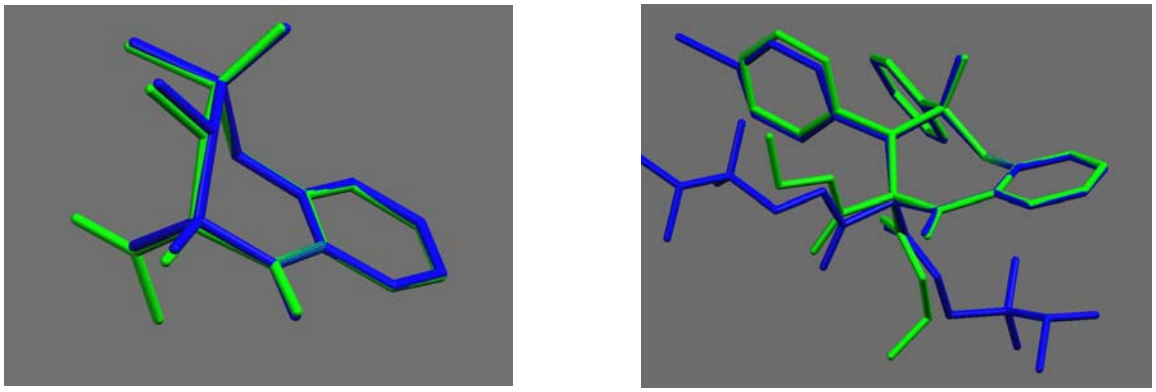
*The values of *m*/*z* are given for ions containing the most widespread isotopes; X = $C(O)OCH_2CF_2CHF_2$, R = $OCH_2CF_2CHF_2$; Hal = Cl.

X-ray diffraction data

In view of the fact that the reliable assignment of the configuration to phosphepines **3** is impossible using only NMR we have studied the structure of the isolated preferable diastereoisomers by single-crystal X-ray diffraction. The geometry of molecules **3a, c, d, g, j** is shown in figures 3-8, as well as their selected bond lengths, bond and torsion angles. The primary diastereoisomers of the compounds have the configuration R_PR_C (S_PS_C) (**3a, c, g, j**), R_PS_C (S_PR_C) (**3d**). The cycle conformation may be described as asymmetrical (distorted) *boat*. The $O^1C^{9a}C^{5a}C^5O^5C^4$ fragment is planar within 0.085(6) **Å** (**3a**), 0.073(3) **Å** (**3c, A**), 0.044(2) **Å** (**3c, B**), 0.085(6) **Å** (**3d**), 0.064(2) **Å** (**3g**) and 0.026(3) **Å** (**3j**). Deviations of the P^2, C^3 atoms from this plane are equal to 1.193(3), 1.312(8) **Å** (3**a**), –1.361(1), –1.243(4) **Å** (**3c**, **A**), –1.3524(9), –1.263(3) **Å** (**3c, B**), 1.193(3),

1.312(8) **Å** (**3d**), 1.2255(9), 1.348(3) **Å** (**3g**), 1.2505(9) and 1.310(3) **Å** (**3j**), that is, the two atoms are on the one side of the plane and at different distances from it. Atom O^2 occupies pseudoaxial position (its deviation from this plane is 2.448(6) **Å** (**3a**), –2.649(3) **Å** (**3c**, **A**), –2.598(2) **Å** (**3c, B**), 2.448(6) **Å** (**3d**), 2.461(3) **Å** (**3g**), 2.529(2) **Å** (**3j**)). Aryl group at C^3 and alkoxyl or phenyl substituent at P^2 are pseudoequatorial (deviation of C^{10} from plane $O^1C^{9a}C^{5a}C^5O^5C^4$ is equal to 1.883(8) **Å** (**3a**), –1.695(4) **Å** (**3c**, **A**), –1.648(4) **Å** (**3c, B**), 1.883(8) **Å** (**3d**), 1.953(3) **Å** (**3g**), 1.935(3) **Å** (**3j**); deviation of O^3 from the same plane is equal to –0.932(3) **Å** (**3c**, **A**), –0.978(2) **Å** (**3c, B**), 0.657(3) **Å** (**3g**)). It is interesting to note that 2-chlorophenyl substituent in molecules (**3d**, **g**) has a conformation, in which chlorine and proton at C^3 are in *cis*-orientation and approximately in one plane (dihedral angle $H^3C^3C^{10}C^{11}$ is 11.9(3)° (**3d**), 19.8(3)° (**3g**)). Moreover there is a hydrogen bond between Cl and H^3 (C^3–H^3...Cl1, C^3–H^3 1.06 **A**, H^3...Cl1 2.44 **Å**, C^3...Cl^1 3.084(3) **Å**, 118 (**3d**); C^3–H^3...Cl^1, C^3–H^3 1.13 **Å**, H^3...Cl^1 2.45 **Å**, C^3...Cl^1 3.079(4) **Å**, $C^3H^3Cl^1$ 114 (**3g**)). Such arrangement is not likely to be accidental and can be connected with reaction mechanism. The molecules have also a fragment $O^1P^2C^3C^4$ which is planar within 0.09(8) **Å** (**3a**), 0.03(4) **Å** (**3c, A**), 0.02(8) **Å** (**3c, B**), 0.10(3) **Å** (**3d**), 0.09(3) **Å** (**3g**) and 0.08(4) **Å** (**3j**). Atoms C^5, C^{5a} and C^{9a} deviate from this plane on the one side and by different distances (–1.22(8), –1.84(1), –1.28(1) **Å** (3**a**), –1.353(4), –1.797(4), –1.173(5) **Å** (**3c**, **A**), –1.352(4), –1.831(3), –1.194(4) **Å** (**3c, B**), –1.271(3), –1.870(3), –1.305(3) **Å** (**3d**), 1.263(4), 1.872(4), 1.322(3) **Å** (**3g**), 1.289(4), 1.850(4) and 1.280(4) **Å** (**3j**)). The deviations of numerated atoms on the one side from two planes ($O^1C^{9a}C^{5a}C^5O^5C^4$ and $O^1P^2C^3C^4$) are characteristic for *boat* conformation. The dihedral angles between planes $O^1C^{9a}C^{5a}C^5O^5C^4$ and $O^1P^2C^3C^4$ are equal to 122.0(4)° (**3a**), 119.4(2)° (**3c**, **A**), 119.2(2)° (**3c, B**), 119.1(1)° (**3d**), 119.5(1)° (**3g**), 119.0(2)° (**3j**). The carbons C^{16} (**3a**, **3c**, **A**, **B**, **3d**, **3j**) or C^{20} (**3g**) of equatorial fluoroalkoxylic groups are situated practically in six-atomic planar fragment $O^1C^{9a}C^{5a}C^5O^5C^4$ (deviations are 0.20(1) **A** (**3a**), 0.174(4) **Å** (**3c**, **A**), 0.152(4) **Å** (**3c, B**), –0.066(4) **Å** (**3d**), 0.089(4) **Å** (**3g**), 0.003(3) **Å** (**3j**)). The fluoroalkoxylic substituents at C^4 have different conformation in these molecules. So, along C^{17}–C^{18} (C^{21}–C^{22}) bond in axial group the *synclinal* conformation in molecules (**3c, j**) and *antiperiplanar* in molecules (**3d**, **g**) are realized. Equatorial group in theses molecules has *synclinal* conformation in molecules (**3c, d, g**) and *antiperiplanar* one only in molecule (**3j**). Such variety may be connected with crystal packing for these compounds. It should be noted also that some of fluoroalkoxylic substituents have rather long planar moiety ($C^4C^{16}(O^{16})O^{17}C^{17}C^{18}F^1$, ± 0.02(6) **Å** (**3d**), ± 0.04(8) **Å** (**3c, A**); $C^4C^{20}(O^{20})O^{21}C^{21}C^{22}F^6$, ± 0.09(6) **Å** (**3g**), ± 0.09(6) **Å** (**3c, A**).

The superposition of molecules (**3a**, **j**) is shown in fig. 8a, b. It is obvious that the molecules have the same conformation of heterocycles. There are the differences concerning the fluorocarboxylic substituens conformation. The superposition of heterocyclic moiety of molecules (**3c, d, g**) is shown in fig. 9. One can see that molecules (**3d, g**) have more folded conformation than (**3c, A, B**).



a ***b***

Figure 8. Superposition of molecules (**3a** – green) and (**3j** – blue). Hydrogen atoms are omitted (***a*** – heterocyclic parts of molecules, ***b*** – full molecules).

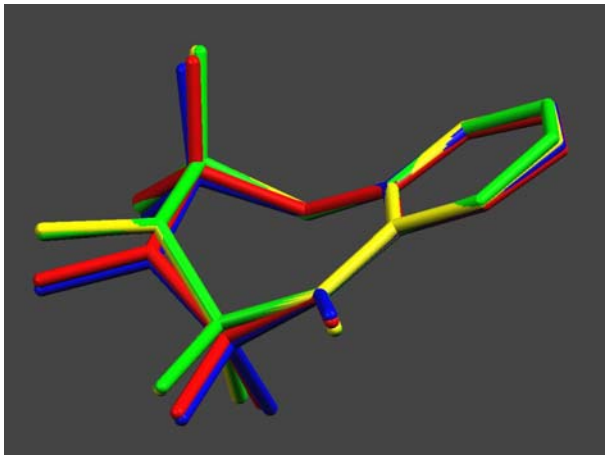
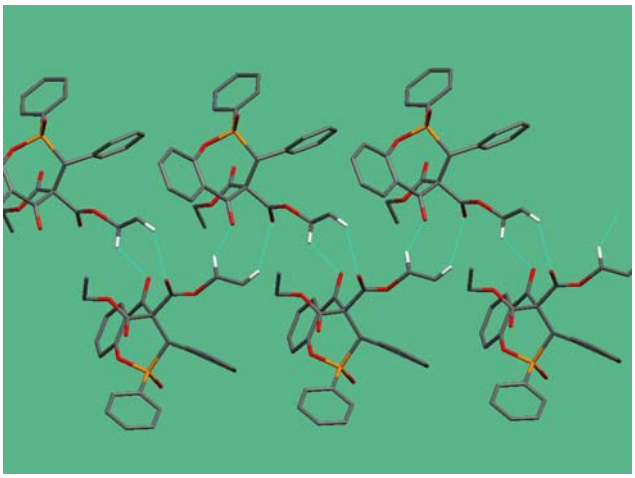
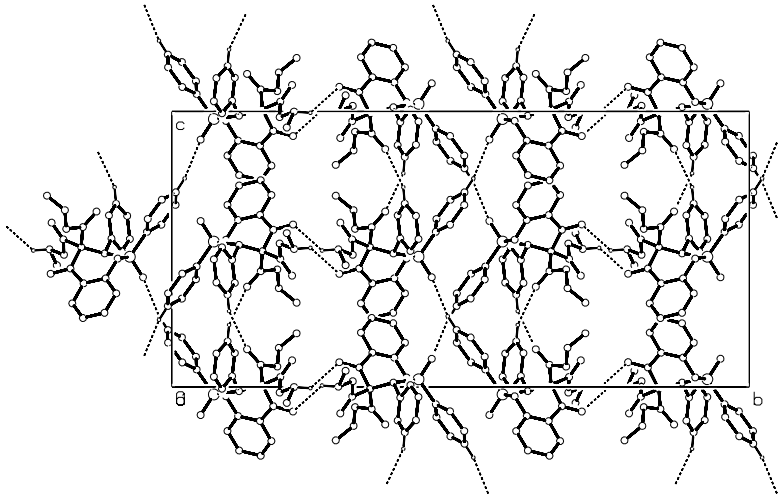


Figure 9. Superposition of heterocyclic parts of molecules (**3g** – green) and (**3d** – yellow), (**3c** – two independent molecules – red and blue). Hydrogen atoms are omitted.

The view of a fragment of the crystal structure of (**3a**) along *0c* and *0a* axis is shown in fig. 10a, b. The C–H...O contacts of the methylene (H^{172}) and methyl (H^{182}) H-atoms with carboxyl oxygen (O^5 and O^{16}) unite molecules into continuous layers along *0a* axis. Parameters of the H-bonds are as follows: distance $H^{172}...O^{5'}$ 2.56 **Å**, < C^{17}–$H^{172}...O^{5'}$ 122°, distance $H^{182}...O^{16'}$ 2.64 **Å**, < C^{18}–$H^{182}...O^{16'}$ 139°. (‘ = 1/2 + *x*, 1/2 – *y*, –*z*). The layers are united into a 3D framework due to the contacts of bridging H^{12} and H^{27} atoms with carboxyl oxygen O^{20} and phosphoryl oxygen O^2 respectively, distance $H^{12}...O^{20''}$ 2.50 **Å**, < C^{12}–$H^{12}...O^{20''}$ 157° (” = 1/2 + *x*, *y*, 1/2 – *z*), distance $H^{27}...O^{2'''}$ 2.48 **Å**, < C^{27}–$H^{27}...O^{2'''}$ 166°. (”’ = 3/2 – *x*, –*y*, 1/2 + *z*). In the crystal of (**3j**) intermolecular C–H...O interactions combine molecules into 3D frame. Hydrogen bonds parameters are listed in Table 2.



a



b

Figure 10. View of a fragment of the crystal structure of (**3a**) along *0c* axis (***a***). View along *0a* axis (***b***). Hydrogen atoms, which do not participated in intermolecular contacts, are omitted for clarity.

Table 2. Hydrogen bonds for **(3j)** (**Å** and deg.)

D–H...A	*d* (D–H)	*d* (H...A)	*d* (D...A)	< DHA
C^{19}–H^{19}...O^{2} (*)	0.98	2.32	3.180(7)	146
C^{17}–H^{171}...O^{2} (*)	0.97	2.58	3.370(7)	138
C^{17}–H^{172}...O^{5} (**)	0.97	2.49	3.349(7)	148
C^{21}–H^{212}...O^{2} (***)	0.97	2.32	3.257(6)	161

Equivalent positions: (*) 1 - *x*, 1 – *y*, 1 – *z*; (**) –*x*, 1 – *y*, 1 – *z*; (***) –1 + *x*, *y*, *z*.

Intermolecular interactions in the crystal of (**3c**) are shown in figure 11. The independent molecules **A** and **B** form the similar supramolecular motifs by C–H...π-interactions. These motifs are formed either by molecules **A**, or by molecules **B**. Parameters of the H-bonds are as follows (Cg1 – center of gravity of benzene ring $C^{5Aa}C^{6A\text{-}9A}C^{9Aa}$, Cg2 – center of gravity of benzene ring $C^{5Ba}C^{6B\text{-}9B}C^{9Ba}$): C^{12B}–H...Cg2' (1 – *x*, 1 – *y*, –*z*), distance H...Cg2' 3.11 **Å**, distance from H to plane Cg2' 2.80 **Å**, < C^{12B}–H...Cg2' 135°, distance C^{12B}...Cg2' 3.823(5) **Å**; C^{14A}–H...Cg1" (–*x*, –*y*, 1 – *z*), distance H...Cg1" 3.06 **Å**, distance from H to plane Cg1" 2.76 **Å**, < C^{14A}–H...Cg1" 137°, distance C^{14A}...Cg1" 3.800(6). Centrosymmetric dimers, formed by C–H...π-interactions, constitute the lamellar motifs by C–H...O interactions (Figure 12).

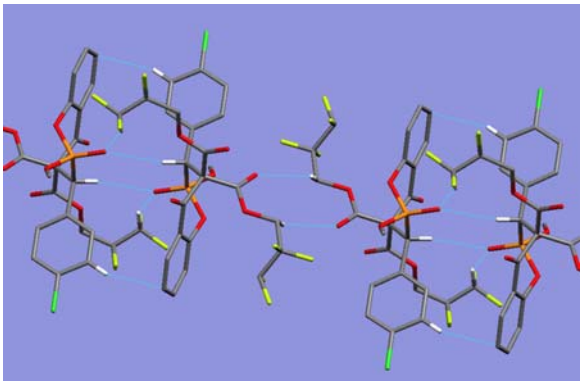


Figure 11. Intermolecular interactions in the crystal of (**3c**). View along *0c* axis. Hydrogen atoms, which do not participated in intermolecular contacts, are omitted for clarity.

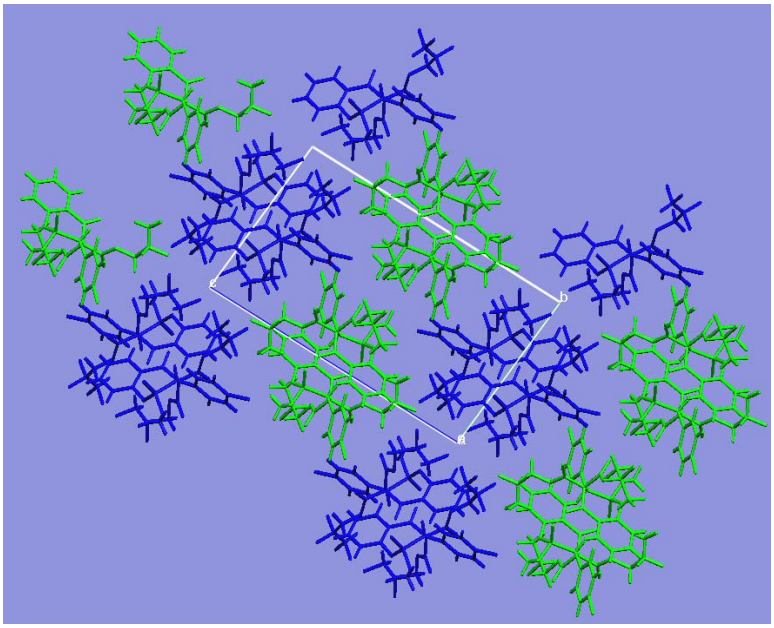


Figure 12. Crystal packing diagram in the crystal of (**3c, A**, **B**). View along *0a* axis. Molecules (**3c, A**) are blue and ones (**3c, B**) are green.

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Crystal packing of compound (**3d**) have 3D supramolecular structure (as in crystal of compound **3a**) determined by C–H...O- and C–H...F-interactions. The localization of fluorine atoms in the small volumes (see fig. 13) is observed.

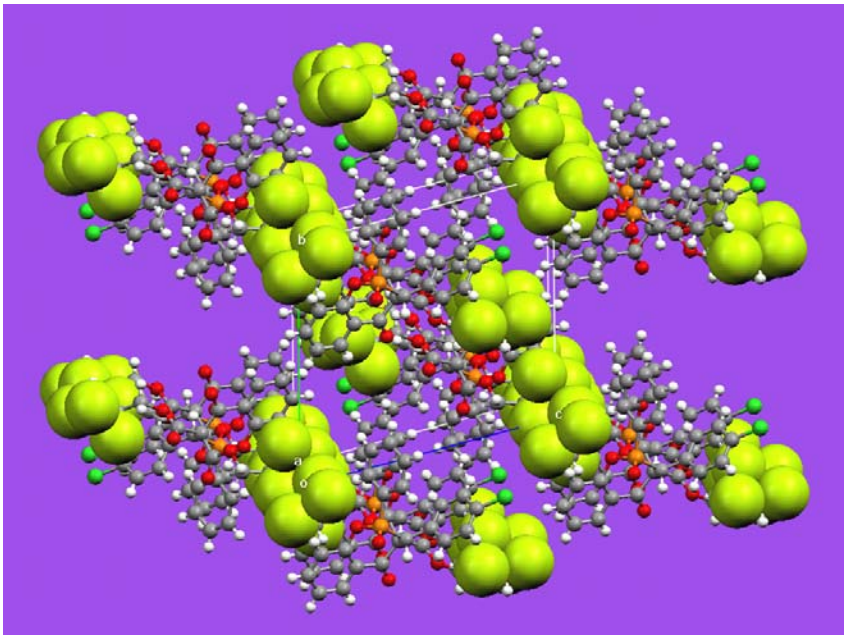
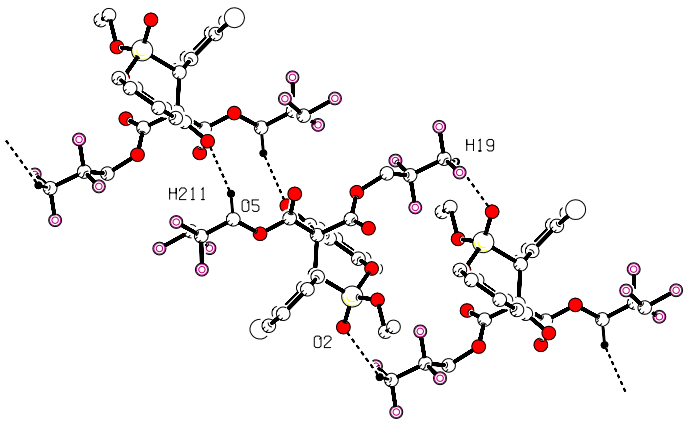
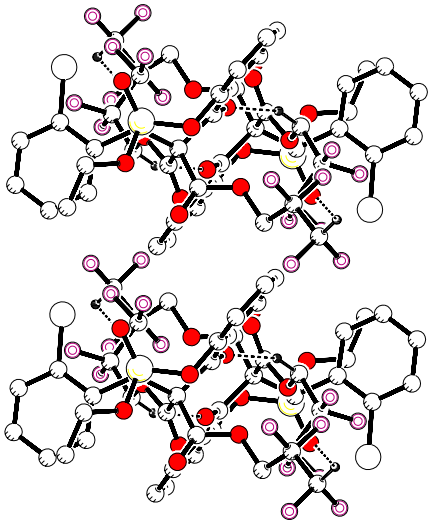


Figure 13. Crystal packing diagram in the crystal of (**3d**). View along *0a* axis. Fluorine atoms are shown as space-filled.

Fig. 14a, b demonstrates the intermolecular interactions in the crystal of (**3g**). The pairs of C–H...O contacts between methylene H^{211} atoms and oxygen O^5 atoms combine two molecules into centrosymmetrical dimers, which are, in turn, combined into continuous layers along [110] crystallographic direction due to symmetric C^{19}–H^{19}...O^2 contacts between dimers. Parameters of the H-bonds are as following: distance H^{211}...O^5 2.35 **Å**, < C^{21}–H^{211}...$O^{5'}$ 154° (‘ = 1 – *x*, –*y* ,–*z*); distance H^{19}...O^2 2.53 **Å**, < (C^{19}–H^{19}...$O^{2''}$) 126° (“ = –*x*, 1 – *y*, –*z*). The layers are combined into 3D frame by the weaker π–π-contacts.



a



b

Figure 14. Intermolecular interactions in the crystal of (**3g**) – (***a***) view along *0c* axis (diagonal *a0b*), (***b***) top view along [110] on the layers. Hydrogen atoms, which do not participated in intermolecular contacts, are omitted for clarity.

Experimental Section

General Procedures. Solvents and commercially available reagents were purified by conventional methods before use. All experiments were performed under an atmosphere of dry argon. Melting points are uncorrected. Measurements involved "Boetius" melting point apparatus (manufacturing of DDR). NMR spectra were recorded on Varian Unity-300 (300 MHz, ^{1}H; 121.4 MHz, ^{31}P; 282.0 MHz, ^{19}F), Bruker MSL-400 (100.6 MHz, ^{13}C), Bruker Avance-600 (600 MHz, ^{1}H; 150.9 MHz, ^{13}C) spectrometers. The δ_P values were determined relative to external standard (H_3PO_4). The δ_C and δ_H values were determined relative to internal standard (HMDS).

The δ_F values were determined relative to internal standard C_6F_6 and then recalculated relative to $CFCl_3$. Infrared spectra were registered on a Specord M-80 spectrometer in Nujol between KBr plates. The EI mass spectra were obtained on a MAT–212 (Finnigan) instrument; the energy of ionizing electrons was 70 eV. The masses were precisely determined by fitting to the reference peaks of perfluorokerosene. The temperature of the ion source was 120 °C. The samples were introduced into the ion source using a direct inlet system. The temperature of the evaporator tube was 100°C. The mass-spectrometric data were processed using the MASPEC 2 system program.

The starting 2-RO-5,6-benzophosphorin-4-ones were prepared as described previously[8a,22].

X-ray crystallography. The X-Ray diffraction data for the crystals of (**3a**, **c, d, g**, **j)** were collected on a CAD4 Enraf-Nonius automatic diffractometer using graphite monochromatic radiation. The stability of crystals and experimental conditions was checked every 2 hours using three control reflections, while the orientation was monitored every 200 reflections by centering two standards. No significant decay was observed. Corrections for Lorentz and polarization effects were applied. Absorption correction was applied for (**3c, d, g**, **j**). The structure was solved by direct method using the SIR[23] program and refined by full-matrix least squares using SHELXL97[24] program. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters and hydrogen atoms bonded to carbon were inserted at calculated positions using a riding model. All calculations were performed on a PC using WinGX[25] set of programs. Data collection and data reduction were performed on Alpha Station 200 computer using MoLEN[26] program. A summary of the crystal data, data collection and refinement procedures are given in Table 3.

Table 3. Crystal data and structure refinement for (**3a, c, d, g, j**)

	3a	**3c**	**3d**	**3g**	**3j**
Empirical formula	$C_{27}H_{25}O_7P$	$C_{24}H_{18}ClF_8O_8P$	$C_{24}H_{18}ClF_8O_8P$	$C_{25}H_{20}ClF_8O_8P$	$C_{29}H_{19}ClF_8O_7P$
Empirical formula weight	492.47	652.80	652.82	666.85	697.88
Temperature (K)			293(2)		
Wavelength (**Å**)	0.71073	1.54180	1.54180	1.54180	1.54180
Crystal system	Orthorhombic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	Pbca	P-1	P-1	$P2_1/c$	P-1
			Unit cell dimensions		
a (**Å**)	9.536(2)	11.770(2)	9.639(2)	9.847(9)	9.10(1)
b (**Å**)	33.148(2)	12.304(3)	11.918(2)	12.332(9)	13.00(1)
c (**Å**)	15.85(4)	19.865(3)	12.502(3)	23.24(2)	13.97(2)
α (deg)	90.00	93.65(2)	102.68(1)	90.00	75.4(1)
β (deg)	90.00	90.70(1)	90.80(2)	99.83(3)	89.0(1)
γ (deg)	90.00	105.84(1)	101.15(2)	90.00	73.9(1)
Volume (**Å**^{3})	5008(3)	2760.4(9)	1372.5(5)	2780(4)	1535(4)
Z	8	2	2	4	2
Density (calculated) (Mg/m^3)	1.305	1.571	1.580	1.593	1.513
Absorption coefficient (cm^{-1})	1.54	27.10	27.26	27.04	24.57
F(000)	2064	1320	660	1352	708
Crystal size (mm)	0.4 × 0.4 × 0.4	0.3 × 0.3 × 0.2	0.4 × 0.3 × 0.2	0.2 × 0.2 × 0.2	0.2 × 0.2 × 0.15
Scan mode	ω-scan	ω/2θ-scan	ω/2θ-scan	ω/2θ-scan	ω-scan
Theta range for data collection (deg)	3.82 to 22.70	4.22 to 74.12	3.88 to 64.92	3.86 to 74.27	3.27 to 74.30
Index ranges	$-10 \le h \le 0$, $0 \le k \le 32$, $0 \le l \le 15$	$-13 \le h \le 7$, $-14 \le k \le 14$, $-24 \le l \le 24$	$0 \le h \le 11$, $-13 \le k \le 12$, $-13 \le l \le 14$	$-4 \le h \le 12$, $-15 \le k \le 0$, $-29 \le l \le 28$	$0 \le h \le 9$, $-12 \le k \le 9$, $-13 \le l \le 13$
Reflections collected	2528	9709	4103	5993	4425
Independent reflections	2527 [R(int) = 0.1081]	6522 [R(int) = 0.0751]	3565 [R(int) = 0.0251]	5611 [R(int) = 0.0352]	3500 [R(int) = 0.1815]
Refinement method			Full-matrix least-squares on F^2		
Data / restraints / parameters	2527 / 0 / 341	9709 / 12 / 809	4103 / 0 / 396	5611 / 0 / 409	4425 / 0 / 416
Goodness-of-fit on F 2	1.035	1.025	1.042	1.028	1.061
Final R indices [I > 2 sigma (I)]	R1 = 0.0632 wR2 = 0.1453	R1 = 0.0632 wR2 = 0.1678	R1 = 0.0544 wR2 = 0.1519	R1 = 0.0770 wR2 = 0.2104	R1 = 0.0747 wR2 = 0.2023

Table 3. Continued

R indices (all data)	R1 = 0.1996 wR2 =0.2108	R1 = 0.1052 wR2 = 0.1959	R1 = 0.0624 wR2 = 0.1604	R1 = 0.1089 wR2= 0.2479	R1 = 0.0747 wR2 = 0.2023
Extinction coefficient	0.00	0.00	0.00	0.0133(11)	0.032(3)
Largest diff. peak and hole ($e \cdot Å^{-3}$)	0.30 and –0.40	0.62 and –0.46	0.47 and –0.44	0.58 and –0.52	0.56 and –0.38

Ab initio quantum calculations were carried out using the GAUSSIAN98 program package[27] on a computer cluster at the A.E.Arbuzov Institute of Organic and Physical Chemistry of the Kazan Research Center of the Russian Academy of Sciences consisting of nine Compaq Alpha DS10L workstations (Alpha-264-466MHz/256 Mb/10 Gb) and an Alpha DS20E workstation (2*Alpha-264-667MHz/512 Mb/20 Gb) with 100 Mbps Fast Ethernet system. All molecular geometries were optimized at the HF/6–31G level of theory. The absolute values of shielding were calculated by the DFT/GIAO (density functional theory/gauge including atomic orbital) method with the 6–31G(d) basis set and the B3LYP functional. All data were referred to TMS chemical shifts that were calculated in the same conditions. Calculations were carried out for the isolated molecule in the gas phase without regard for the solvent effects.

Malonic acid bis(2,2,3,3-tetrafluoropropyl) ester was prepared by refluxing the benzene solution of a malonic acid with a double equivalent amount of 2,2,3,3-tetrafluoropropanol in the presence of a catalytic amount of p-toluenesulfonic acid. Yield 92 %, b. p. 132°C (15 mmHg).

General procedure for preparation of malonates (2b-e)

The mixture of malonic acid bis(2,2,3,3-tetrafluoropropyl) ester (22 g, 66 mmol) and equimolar amount of aldehyde was refluxed in 25 mL of benzene in the presence of catalytic amount of piperidine for 4 hours in a Dean and Stark apparatus. After the reaction was completed and cooled to 20°C, 10 mL of C_6H_6 was added. The reaction mixture washed with 20 mL H_2O, 20 mL 1M HCl and then 20 mL solution of Na_2CO_3. The organic phase was separated and dried with Na_2SO_4 overnight. The solvent was removed by distillation and the residue was distilled in *vacuo*.

Benzylidenmalonic acid bis(2,2,3,3-tetrafluoropropyl) ester (2b). Yield 21 g (88 %), b. p. 130 °C (0.03 mmHg). ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm, J Hz): 7.93 s (CH, *1H*); 7.43 m (C_6H_5, *5H*); 5.88 t. t (CHF_2, *1H*, $^2J_{HCF}$ 53.0, $^3J_{FCCH}$ 3.5-3.7); 5.69 t. t (CHF_2, *1H*, $^2J_{HCF}$ 52.9, $^3J_{FCCH}$ 4.2); 4.65 t. t (OCH_2, *2H*, $^3J_{HCCF}$ 12.6, $^4J_{FCCCH}$ 1.3); 4.63 t. t (OCH_2, *2H*, $^3J_{HCCF}$ 12.7, $^4J_{FCCCH}$ 1.5).

4-Chlorobenzylidenmalonic acid bis(2,2,3,3-tetrafluoropropyl) ester (2c). Yield 17 g (78 %), b. p. 138°C (0.02 mmHg). ^{13}C NMR (acetone-d_6, 150.9 MHz, δ ppm, J Hz) (description of a signal in ^{13}C-{^{1}H} NMR spectrum is in parentheses): 164.57 two d. t (s) (COO-*cis*, $^3J_{HCCC}$ 4.4, $^3J_{HCOC}$ 2.9; COO-*trans* $^3J_{HCCC}$ 9.8, $^3J_{HCOC}$ 2.9); 144.86 br. d. t (s) (CH=, $^1J_{HC}$ 157.4, $^3J_{HCoCC}$ 4.4); 136.26 t. t (s) (C^p, $^3J_{HoCCCp}$ 10.8, $^2J_{HCmCp}$ 3.3); 132. 2 t. d (s) (C^i, $^3J_{HmCCCi}$ 7.0, $^3J_{HCoCi}$ 7.0); 129.12 d. d. d (s) (C^o, $^1J_{HCo}$ 161.9, $^2J_{HCmCo}$ 6.6, $^3J_{HCCCo}$ 5.6); 128.8 d. d (s), (C^m, $^1J_{HCm}$ 167.3, $^2J_{HCoCm}$

5.1); 116.63 br. s (s) (C=); 114.06 t. t. d. t (t. t) (CF_2, $^1J_{FC}$ 249.7, $^2J_{FCC}$ 27.5, $^2J_{HCC}$ 4.1, $^2J_{HCC}$ 3.0); 109.75 t. d. t (t. t) (HCF_2, $^1J_{FC}$ 250.0, $^1J_{HC}$ 193.1, $^2J_{FCC}$ 36.0); 59.3 t. t (t) (CH_2, $^1J_{HC}$ 150.6, $^2J_{FCC}$ 29.0).

2-Chlorobenzylidenmalonic acid bis(2,2,3,3-tetrafluoropropyl) ester (2d). Yield 18 g (79 %), b. p. 138 °C (0.02 mmHg). NMR ^1H ($CDCl_3$, 300 MHz, δ ppm, J Hz): 8.23 s (CH, *1H*); 7.34-7.52 m (C_6H_4, *4H*); 5.97 t. t (CHF_2, *1H*, $^2J_{HCF}$ 53.0, $^3J_{FCCH}$ 3.6); 5.71 t. t (CHF_2, *1H*, $^2J_{HCF}$ 52.9, $^3J_{FCCH}$ 4.0); 4.73 t. t (OCH_2, *2H*, $^3J_{HCCF}$ 12.6, $^4J_{FCCCH}$ 1.3); 4.60 t. t (OCH_2, *2H*, $^3J_{HCCF}$ 12.6, $^4J_{FCCCH}$ 1.4).

4-Bromobenzylidenmalonic acid bis(2,2,3,3-tetrafluoropropyl) ester (2e). Yield 18 g (82 %), b. p. 140 °C (0.03 mmHg). NMR ^1H ($CDCl_3$, 300 MHz, δ ppm, J Hz): 7.96 s (CH, *1H*); 7.66 and 7.42 two m (C_6H_4, *4H*); 6.01 t. t (CHF_2, *1H*, $^2J_{HCF}$ 53.0, $^3J_{FCCH}$ 3.4); 5.91 t. t (CHF_2, *1H*, $^2J_{HCF}$ 53.0, $^3J_{FCCH}$ 3.9); 4.76 br. t (OCH_2, *2H*, $^3J_{HCCF}$ 12.6-13.0); 4.72 br. t (OCH_2, *2H*, $^3J_{HCCF}$ 12.6-13.0).

2,5-Dioxo-2,3-diphenyl-4,4-bis(ethoxycarbonyl)-6,7-benzo-1,2-oxaphosphepine (3a). was obtained by heating the mixture of salicylphosphonite (**1a**) (5.0 g) with benzylidenmalonic acid diethyl ester (**2a**) (5.02 g) and 10 mL CH_2Cl_2 under reflux (5 h) in argon atmosphere with the following precipitation of reaction mixture into ether. Yield 70 %, m. p. 166°C. Anal. Calcd for $C_{27}H_{25}O_7P$: C 65.85; H 5.08; P 6.30. Found: C 65.48; H 4.94; P 6.10. IR (cm^{-1}): 1740 and 1770 (COO), 1690 (C=O), 1610, 1575, 1500, 1480, 1395, 1287 (P=O), 1246, 1212, 1195, 1165, 1125, 1100, 1070, 1040, 923, 890, 865, 840, 825, 770, 746, 700, 640, 620, 605, 565, 545, 509, 463. ^1H NMR ($CDCl_3$, δ ppm, J Hz): 4.47 d (H^3, $^2J_{PCH}$ 27.5), 4.29 and 4.14 two m (OCH_AH_B, A- and B-parts of ABX_3-spectrum, $^3J_{HBCCH_X}$ 7.0, $^3J_{HACCH_X}$ 7.0, $^2J_{HACH_B}$ 10.8), 3.79 and 3.84 two m (OCH_AH_B, A- and B-parts of ABX_3-spectrum, $^3J_{HACCH_X}$ 7.1, $^3J_{HBCCH_X}$ 7.1, $^2J_{HACH_B}$ 10.7), 1.50 and 0.74 two t (CH_3, two X_3-parts of ABX_3-spectra, $^3J_{HA,BCCH_X}$ 7.0, $^3J_{HA,BCCH_X}$ 7.1]. ^{13}C NMR ($CDCl_3$, 100.6 MHz, δ ppm, J Hz) (here and below the description of a signal in ^{13}C-{^1H} NMR spectrum is given in parentheses): 188.05 d. d. d (d) (C^5, $^3J_{PCCC}$ 0.96, $^3J_{HCCC}$ 5.8-5.9, $^3J_{HCCC}$ 4.6-4.8); 165.80 d. t (d) (COO, $^3J_{PCCC}$ 14.1, $^3J_{HCOC}$ 3.1, $^3J_{HC^3CC}$ 0); 165.79 d. d. t (d) (COO, $^3J_{HC^3CC}$ 9.3, $^3J_{PCCC}$ 6.6, $^3J_{HCOC}$ 3.6); 148.74 d. d. d. d. d (d) (C^{9a}, $^2J_{POC^{9a}}$ 8.1, $^3J_{HCCC^{9a}}$ 9.7-9.8, $^3J_{HCCC^{9a}}$ 9.7-9.8, $^2J_{HC^9C^{9a}}$ 4.0, $^4J_{HC^7CCC^{9a}}$ 1.8); 136.13 d. d. d. d. d (d) (C^8, $^1J_{HC^8}$ 160.3, $^3J_{HC^6CC^8}$ 9.3, $^2J_{HC^9C^8}$ 1.5, $^2J_{HC^7C^8}$ 1.5, $^4J_{POCCC^8}$ 1.4); 132.51 d. m (d) (C^{27}, $^1J_{HC^{27}}$ 164.6, $^4J_{PC^{24}CCC^{27}}$ 2.9); 132.48 t. d. d (d) (C^{10}, $^3J_{HC^{12,14}CC^{10}}$ 7.9, $^2J_{HC^3C^{10}}$ 7.9, $^2J_{PC^3C^{10}}$ 2.7); 132.34 d. m (br. d) (C^6, $^1J_{HC^6}$ 166.4, $^4J_{POCCC^6}$ 1.4); 132.31 d. m (d) (C^{25}, $^1J_{HC^{25}}$ 164.5, $^2J_{PC^{24}C^{25}}$ 9.3); 130.41 very br. d. m (very br. s) (C^{11}); 128.43 br. d. d. m (d) (C^{12}, $^1J_{HC^{12}}$ 160.3, $^3J_{HC^{14}CC^{12}}$ 8.4, $^4J_{PC^3CCC^{12}}$ 2.9); 127.61 d. m. d (d) (C^{13}, $^1J_{HC^{13}}$ 160.5-161.0, $^3J_{HC^{11,15}CC^{17}}$ 7.5, $^5J_{PC^3CCCC^{13}}$ 3.2); 127.37 d. m (d) (C^{24}, $^1J_{PC^{24}}$ 141.6); 127.19 d. m (d) (C^{26}, $^1J_{HC^{26}}$ 160.0-161.0, $^3J_{PC^{24}CC^{26}}$ 13.8, $^3J_{HC^{28}CC^{26}}$ 6.6-6.7); 126.49 d. d. d. d (d) (C^7, $^1J_{HC^7}$ 163.2, $^3J_{HC^9CC^7}$ 8.4, $^5J_{POCCCC^7}$ 2.4, $^2J_{HCC^7}$ 1.4); 126.41 m (d) (C^{5a}, $^3J_{POC^{9a}C^{5a}}$ 1.5); 124.17 d. d. d. d (d) (C^9, $^1J_{HC^9}$ 165.4, $^3J_{HC^7CC^9}$ 7.7, $^3J_{POC^{9a}C^9}$ 3.2, $^2J_{HC^8C^9}$ 1.5); 50.84 d. d. t (d) (C^3, $^1J_{PC^3}$ 84.2, $^1J_{HC^3}$ 126.9, $^3J_{HC^{11}CC^3}$ 4.4), 74.58 d. d (d) (C^4, $^2J_{PCC^4}$ 1.8, $^2J_{HCC^4}$ 5.4), 62.71 and 62.17 two t. q (s) (OCH_2, $^1J_{HC}$ 148.8, $^3J_{HCC}$ 4.5), 13.59 and 13.06 two t. q (s) (CH_3, $^1J_{HC}$ 127.5, $^3J_{HCC}$ 2.6).

Typical procedure for the synthesis of compounds (3b-k). Malonic derivative (**2b**) (756 mg, 18 mmol) was added to a stirring solution of compound (**1b**) (372 mg, 18 mmol) in CH_2Cl_2 (10 ml) at room temperature under argon. After addition the mixture was stirred for 1 h to yield colorless solution and stand at room temperature for two months (for **3b-h**) and 7 days (for **3i-k**). After solvent removal, the residue was recrystallized from diethyl ether/pentane (1 : 1) to yield (**3b-k**) as colorless crystalline solid. Individual crystals for X-ray diffraction were obtained by crystallization from acetone.

4,4-Bis(2,2,3,3-tetrafluoropropoxycarbonyl)-2-methoxy-2,5-dioxo-3-phenylbenzo[*f*]-1,2-oxaphosphepine (3b). Yield 92 % (102.2 mg, 16 mmol), m. p. 76-78°C. Anal. Calcd for $C_{24}H_{19}F_8O_8P$: C, 46.60; H, 3.07; P, 5.02. Found: C, 46.54; H, 3.09; P, 5.01. IR (Nujol): 1784, 1752, 1684, 1608, 1460, 1376, 1280, 1256,1232, 1224, 1192, 1108, 1076, 1064, 920, 896, 840, 792, 768, 680 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ: 8.20 d. d (H^6, *1H*, $^3J_{H6CCH7}$ 8.0, $^4J_{H8CCCH6}$ 1.75); 7.72 d. d. d. d (H^8, *1H*, $^3J_{H8CCH9}$ 8.2, $^3J_{H7CCH8}$ 7.3, $^4J_{H8CCCH6}$ 1.75, $^5J_{POCCCH8}$ 0.8); 7.61 b. m (H^{11}, *1H*); 7.44 d. d. d. d (H^7, *1H*, $^3J_{H6CCH7}$ 8.0, $^3J_{H7CCH8}$ 7.3, $^4J_{H7CCCH9}$ 1.2-1.3, $^6J_{POCCCCH7}$ 1.2); 7.34-7.35 m (H^{12}, H^{13}, *3H*); 7.29 d. d. d (H^9, *1H*, $^3J_{H8CCH9}$ 8.2, $^4J_{H9CCH7}$ 1.3, $^4J_{POCCH9}$ 1.3); 5.56 t. t (CHF_2, *1H*, $^2J_{HCF}$ 52.9, $^3J_{FCCH}$ 4.1); 5.43 t. t (CHF_2, *1H*, $^2J_{HCF}$ 52.8-52.9, $^3J_{FCCH}$ 4.3); 4.63 and 4.55 two m (OCH_AH_B, *2H*, AB-part of ABM_3N_2 spectrum, $^2J_{H_AH_B}$ 12.5, $^3J_{FCCH_A}$ 12.4-12.5, $^3J_{FCCH_B}$ 12.4-12.5, $^4J_{FCCCH_A}$ 1.4-1.3, $^4J_{FCCCH_B}$ 1.4-1.3); 4.45 d (PCH, *1H*, $^2J_{PCH}$ 26.2); 4.39 q. t (OCH_B, *1H*, B-part of ABM_3N_2 spectrum, $^3J_{H_BCCF}$ 12.3, $^2J_{H_ACH_B}$ 12.3, $^4J_{H_BCCCF}$ 1.4); 4.10 q. t (OCH_A, *1H*, A-part of ABM_3N_2 spectrum, $^3J_{H_ACCF}$ 12.3, $^2J_{H_ACH_B}$ 12.3, $^4J_{H_ACCCF}$ 1.4-1.3); 3.49 d (OCH_3, *3H*, $^2J_{POCH}$ 11.2). ^1H NMR (acetone-D_6, 600 MHz) δ: 8.18 d. d (H^6, *1H*, $^3J_{H6CCH7}$ 8.0, $^4J_{H8CCCH6}$ 1.7); 7.84 d. d. d. d (H^8, *1H*, $^3J_{H8CCH9}$ 8.3, $^3J_{H7CCH8}$ 7.4, $^4J_{H8CCCH6}$ 1.7, $^5J_{POCCCH8}$ 0.8); 7.70 br. d (H^{11}, *1H*, $^3J_{H12CCH11}$ 7.0-8.0); 7.55 d. d. d. d (H^7, *1H*, $^3J_{H6CCH7}$ 8.0, $^3J_{H7CCH8}$ 7.4, $^4J_{H7CCCH9}$ 1.2, $^6J_{POCCCCH7}$ 1.2); 7.39-7.37 m (H^{12}, H^{13}, *3H*); 7.37 d. d. d (H^9, *1H*, $^3J_{H8CCH9}$ 8.3, $^4J_{POCCH9}$ 1.6, $^4J_{H9CCH7}$ 1.2); 6.08 t. t (CHF_2, *1H*, $^2J_{HCF}$ 52.6, $^3J_{FCCH}$ 4.9); 6.16 t. t (CHF_2, *1H*, $^2J_{HCF}$ 52.1, $^3J_{FCCH}$ 5.4); 4.85 d (PCH, *1H*, $^2J_{PCH}$ 26.7); 4.83 br. d. t. t (OCH_B, *1H*, B-part of ABM_3N_2 spectrum, $^2J_{H_BCCF}$ 13.1-13.5, $^3J_{H_AH_B}$ 13.1-13.5, $^4J_{H_BCCCF}$ 1.3); 4.73 br. d. t (OCH_A, *1H*, A-part of ABM_3N_2 spectrum, $^2J_{H_ACCF}$ 13.1-13.5, $^3J_{H_AH_B}$ 13.1-13.5, $^4J_{H_ACCCF}$ 1.3); 4.56 br. d. t (OCH_B, *1H*, $^2J_{H_AH_B}$ 12.8, $^3J_{H_BCCF}$ 11.0, $^4J_{H_BCCCF}$ 2.0); 4.09 d. t. d (OCH_A, *1H*, A-part of ABM_3N_2 spectrum, $^3J_{H_ACCF}$ 12.6-12.7, $^2J_{H_AH_B}$ 12.6-12.7, $^4J_{H_ACCCF}$ 1.9); 3.52 d (OCH_3, *3H*, $^2J_{POCH}$ 11.2). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 186.98 br. d. d (s) (C^5, $^3J_{HC6CC5}$ 4.6, $^3J_{HC3CC5}$ 4.6); 164.31 br. d. t (d) (COO, $^3J_{PC3CC}$ 16.3, $^3J_{HCOC}$ 2.7-2.8, $^3J_{HC3CC}$ 0-0.5); 164.0 d. d. t (d) (COO, $^3J_{PCC4C}$ 10.3, $^3J_{HC3CC}$ 9.2, $^3J_{HCOC}$ 2.8-2.9); 149.01 m (d) (C^{9a}, $^2J_{POC9a}$ 5.2); 137.24 d. d. d. d (s) (C^8, $^1J_{HC8}$ 162.8, $^3J_{HC6CC8}$ 9.4, $^2J_{HC9C8}$ 1.7, $^2J_{HC7C8}$ 1.7); 132.24 d. d (s) (C^6, $^1J_{HC6}$ 166.1, $^3J_{HC8CC6}$ 7.9); 130.89 d. d. t (d) (C^{10}, $^3J_{HC12CC10}$ 7.8, $^2J_{HC3C10}$ 7.8, $^2J_{PC3C10}$ 7.5); 130.30 d. m (d) (C^{11}, $^1J_{HC11}$ 161.3, $^3J_{PC3CC11}$ 4.6); 129.19 br. d. d (d) (C^{12}, $^1J_{HC12}$ 161.4, $^3J_{HC15CC12}$ 8.0, $^4J_{PC3CCC12}$ 2.3); 128.62 d. t. d (d) (C^{13}, $^1J_{HC13}$ 161.1, $^3J_{HC11CC13}$ 7.5, $^5J_{PC3CCCC13}$ 2.7); 127.07 d. d (s) (C^7, $^1J_{HC7}$ 164.0, $^3J_{HC9CC7}$ 7.8); 125.40 m (d) (C^{5a}, $^3J_{POC9aC5a}$ 2.7); 123.82 d. m (d) (C^9, $^1J_{HC9}$ 165.8, $^3J_{HC7CC9}$ 7.7, $^3J_{POC9aC9}$ 3.4); 113.68 t. t. d. t (t. t) (CF_2, $^1J_{FC}$ 250.6, $^2J_{FCC}$ 28.0, $^2J_{HCC}$ 4.1-4.2, $^2J_{HCC}$ 4.1-4.2); 113.49 t. t. d. t (t. t) (CF_2, $^1J_{FC}$ 250.6, $^2J_{FCC}$ 28.0, $^2J_{HCC}$ 4.1-4.2, $^2J_{HCC}$ 4.1-4.2); 108.94 t. d. t. t (t. t) (CHF_2, $^1J_{FC}$ 250.6, $^1J_{HC}$ 193.5, $^2J_{FCC}$ 36.0, $^3J_{HCCC}$ 2.1-2.2); 108.83 t. d. t. t (t. t) (CHF_2, $^1J_{FC}$ 250.5, $^1J_{HC}$ 192.8, $^2J_{FCC}$

35.0, $^{3}J_{HCCC}$ 2.1-2.2); 74.01 d. d (d) (C^{4}, $^{2}J_{HC3C4}$ 5.4, $^{2}J_{PC3C4}$ 1.4); 61.34 t. t (t) (OCH_2, $^{1}J_{HC}$ 152.0, $^{2}J_{FCC}$ 30.5); 62.0 t. t (t) (OCH_2, $^{1}J_{HC}$ 152.6, $^{2}J_{FCC}$ 30.5); 55.10 q. d (d) (OCH_3, $^{2}J_{HC}$ 150.0, $^{2}J_{POC}$ 6.7); 46.16 d. d. t (d) (C^{3}, $^{1}J_{PC3}$ 131.5, $^{1}J_{HC3}$ 127.5, $^{3}J_{HC11CC3}$ 4.2). ^{13}C NMR (acetone-D_6, 150.9 MHz) δ: 187.20 br. d. d (s) (C^{5}, $^{3}J_{HC3CC5}$ 4.3-4.5, $^{3}J_{HC6CC5}$ 3.9-4.0); 164.51 d. d. t (d) (COO, $^{3}J_{PC3CC}$ 16.2, $^{3}J_{HCOC}$ 2.7, $^{3}J_{HC3C4C}$ 0); 164.20 d. d. t (d) (COO, $^{3}J_{PCC4C}$ 10.5, $^{3}J_{HC3CC}$ 9.0, $^{3}J_{HCOC}$ 2.6-2.7); 149.10 m (d) (C^{9a}, $^{2}J_{POC9a}$ 5.2); 137.04 d. d. d. d (d) (C^{8}, $^{1}J_{HC8}$ 163.8, $^{3}J_{HC6CC8}$ 9.3, $^{2}J_{HC9C8}$ 1.6, $^{2}J_{HC7C8}$ 1.6); 131.82 br. d. d (d) (C^{6}, $^{1}J_{HC6}$ 166.0, $^{3}J_{HC8CC6}$ 8.4, $^{4}J_{POCCC6}$ 1.5); 131.70 d. d. t (d) (C^{10}, $^{3}J_{HC12CC10}$ 7.6, $^{2}J_{HC3C10}$ 7.6, $^{2}J_{PC3C10}$ 7.4); 130.51 br. d. m (br. d) (C^{11}, $^{1}J_{HC11}$ 160.5, $^{3}J_{HC15CC11}$ 5.4-5.8, $^{3}J_{HC13CC11}$ 5.4-5.8, $^{3}J_{PC3CC11}$ 4.7); 128.72 br. d. d (d) (C^{12}, $^{1}J_{HC12}$ 160.5, $^{3}J_{HC14CC12}$ 7.4, $^{4}J_{PC3CCC12}$ 2.6); 128.17 d. t. d (d) (C^{13}, $^{1}J_{HC13}$ 161.3, $^{3}J_{HC11CC13}$ 7.8, $^{5}J_{PC3CCCC13}$ 3.2); 126.81 br. d. d (d) (C^{7}, $^{1}J_{HC7}$ 164.9, $^{3}J_{HC9CC7}$ 8.1, $^{5}J_{PO9aCCC7}$ 1.8); 125.75 m (d) (C^{5a}, $^{3}J_{HC7CC5}$ 5.2-5.3, $^{3}J_{HC9CC5a}$ 5.2-5.3, $^{3}J_{POC9aC5a}$ 2.7-2.8); 123.86 d. d. d. d. d (d) (C^{9}, $^{1}J_{HC9}$ 166.4, $^{3}J_{HC7CC9}$ 7.8, $^{3}J_{POC9aC9}$ 3.4, $^{2}J_{HC8C9}$ 1.5, $^{4}J_{HC6CCC9}$ 1.5); 114.10 t. t. d. t (t. t) (CF_2, $^{1}J_{FC}$ 250.0, $^{2}J_{FCC}$ 27.5, $^{2}J_{HCC}$ 3.0, $^{2}J_{HCC}$ 3.0); 113.92 t. t. d. t (t. t) (CF_2, $^{1}J_{FC}$ 249.6, $^{2}J_{FCC}$ 26.3, $^{2}J_{HCC}$ 3.0, $^{2}J_{HCC}$ 3.0); 109.27 br. t. d. t (t. t) (CHF_2, $^{1}J_{FC}$ 248.8, $^{1}J_{HC}$ 195.4, $^{2}J_{FCC}$ 33.8); 108.96 br. t. d. t (t. t) (CHF_2, $^{1}J_{FC}$ 248.4, $^{1}J_{HC}$ 196.3, $^{2}J_{FCC}$ 32.1); 74.06 d. d (d) (C^{4}, $^{2}J_{HC3C4}$ 5.4, $^{2}J_{PC3C4}$ 1.8); 61.52 br. d. d. d (d. d. t) (OCH_2, $^{1}J_{HC}$ 152.3, $^{2}J_{FCC}$ 32.5, $^{2}J_{FCC}$ 29.6, $^{3}J_{FCCC}$ 1.2); 61.50 br. t. t (t. t) (OCH_2, $^{1}J_{HC}$ 152.6, $^{2}J_{FCC}$ 28.5, $^{3}J_{FCCC}$ 1.2); 54.15 q. d (d) (OCH_3, $^{1}J_{HC}$ 149.8, $^{2}J_{POC}$ 6.8); 45.24 d. d. t (d) (C^{3}, $^{1}J_{PC3}$ 130.6, $^{1}J_{HC3}$ 127.8, $^{3}J_{HC11CC3}$ 3.8). ^{19}F NMR, ($CDCl_3$) δ_F: –125.22 t. d. t (CF_2, *2F*, $^{3}J_{HCCF}$ 12.2, $^{3}J_{HCCF}$ 4.0, $^{3}J_{FCCF}$ 3.5); –125.47 m (CF_2, *2F*, $^{3}J_{HXCCF}$ 13.5, $^{3}J_{HACCF}$ 12.2, $^{3}J_{HCCF}$ 4.2, $^{3}J_{FCCF}$ 3.8); –139.28 d. m (CHF_2, *2F*, $^{2}J_{HF}$ 53.0, $^{3}J_{FCCF}$ 3.8); –139.49 d. m (CHF_2, *2F*, $^{2}J_{HF}$ 53.0, $^{3}J_{FCCF}$ 3.5-3.6). ^{31}P-{^{1}H} NMR (CH_2Cl_2), δ_P: 20.4 ppm.

3-(4-Chlorophenyl)-4,4-bis(2,2,3,3-tetrafluoropropoxycarbonyl)-2-methoxy-2-oxobenzo[*f*]-1,2-oxaphosphepine (3c). Yield 91% (106.9 mg, 16 mmol), m. p. 88-90°C. Anal. Calcd for $C_{24}H_{18}ClF_8O_8P$: C, 44.14; H, 2.76; P, 4.75; Cl 5.44. Found: C, 44.17; H, 2.79; P, 4.76; Cl, 5.43. IR (Nujol): 1776, 1708, 1688, 1600, 1576, 1496, 1488, 1456, 1376, 1288, 1168, 1108, 976, 940, 824, 800, 776, 680, 664, 544 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.18 d. d (H^{6}, *1H*, $^{3}J_{H6CCH7}$ 8.0, $^{4}J_{H8CCCH6}$ 1.7-1.8); 7.71 d. d. d. d (H^{8}, *1H*, $^{3}J_{H8CCH9}$ 8.2, $^{3}J_{H7CCH8}$ 7.3, $^{4}J_{H8CCCH6}$ 1.6-1.7, $^{5}J_{POCCH8}$ 0.8-0.9); 7.56 br. d and 7.31 m (H^{11}, H^{12}, *2H*, AA'XX' spectrum, $^{3}J_{AX}$ 8.9, $^{3}J_{AX'}$ 8.9); 7.44 d. d. d. d (H^{7}, *1H*, $^{3}J_{H6CCH7}$ 8.0, $^{3}J_{H7CCH8}$ 7.3, $^{4}J_{H7CCCH9}$ 1.3, $^{6}J_{POCCCCH7}$ 1.2); 7.28 d. d. d (H^{9}, *1H*, $^{3}J_{H8CCH9}$ 8.2, $^{4}J_{H9CCCH7}$ 1.3, $^{4}J_{POCCH9}$ 1.2); 5.64 t. t (CHF_2, *1H*, $^{2}J_{HCF}$ 52.9, $^{3}J_{FCCH}$ 3.8-3.9); 5.58 t. t (CHF_2, *1H*, $^{2}J_{HCF}$ 52.9, $^{3}J_{FCCH}$ 3.8-3.9); 4.63 and 4.53 two br. m. (OCH_AH_B, *2H*, AB-parts of ABX_3 spectrum, $^{3}J_{HACCF}$ = $^{2}J_{HAHB}$ 12.5 and $^{3}J_{HBCCF}$ = $^{2}J_{HAHB}$ 12.5); 4.45 d (PCH, *1H*, $^{2}J_{PCH}$ 26.2); 4.44 and 4.13 two br. t. d (OCH_AH_B, *2H*, AB-parts of ABX_3 spectrum, $^{3}J_{HACCF}$ = $^{2}J_{HAHB}$ 12.6, $^{3}J_{HBCCF}$ = $^{2}J_{HAHB}$ 12.6); 3.58 d (OCH_3, *3H*, $^{2}J_{POCH}$ 11.3). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 186.86 br. d. d (s) (C^{5}, $^{3}J_{HC3CC5}$ 3.8-4.0, $^{3}J_{HC6CC5}$ 3.8-4.0); 164.07 br. d. t (d) (COO, $^{3}J_{PC3CC}$ 16.5, $^{3}J_{HCOC}$ 2.8-2.5, $^{3}J_{HC3CC}$ 0-0.5); 163.97 d. d. t (d) (COO, $^{3}J_{PCC4C}$ 10.2, $^{3}J_{HC3CC}$ 8.8-9.0, $^{3}J_{HCOC}$ 3.1-3.2); 148.85 m (d) (C^{9a}, $^{2}J_{POC9a}$ 5.3); 137.32 d. d (s) (C^{8}, $^{1}J_{HC8}$ 163.2, $^{3}J_{HC6CC8}$ 9.3); 134.94 t. t. d (d) (C^{13}, $^{3}J_{HC11CC13}$ 10.7, $^{5}J_{PC3CCCC13}$ 3.6, $^{2}J_{HC12C13}$ 3.5-3.6); 132.28 d. d (s) (C^{6}, $^{1}J_{HC6}$ 165.9, $^{3}J_{HC8CC6}$ 8.5); 131.92 br. d. d. d. d (d) (C^{11}, $^{1}J_{HC11}$ 163.4, $^{3}J_{HC15CC11}$ 5.7-6.0, $^{3}J_{HC3CC11}$ 5.7-6.0, $^{3}J_{PC3CC11}$ 5.1); 129.40 d. d. t (d) (C^{10}, $^{2}J_{PC3C10}$ 8.1, $^{3}J_{HC12CC10}$ 8.1, $^{2}J_{HC3C10}$ 8.1);

129.31 br. d. m (d) (C^{12}, $^{1}J_{HC12}$ 166.2, $^{3}J_{HC14CC12}$ 4.6-4.8, $^{4}J_{PC3CCC12}$ 2.4); 127.19 d. d (s) (C^{7}, $^{1}J_{HC7}$ 164.2, $^{3}J_{HC9CC7}$ 8.1); 125.40 m (d) (C^{5a}, $^{3}J_{POC9aC5a}$ 2.2); 123.72 br. d. d. d (d) (C^{9}, $^{1}J_{HC9}$ 166.0, $^{3}J_{HC7CC9}$ 7.0, $^{3}J_{POC9aC9}$ 3.5); 113.68 t. t. t. d (t. t) (CF_2, $^{1}J_{FC}$ 250.8, $^{2}J_{FCC}$ 28.3, $^{2}J_{HCC}$ 2.9-3.1, $^{2}J_{H2CC}$ 2.9-3.1); 113.54 t. t. t. d (t. t) (CF_2, $^{1}J_{FC}$ 250.5, $^{2}J_{FCC}$ 28.2, $^{2}J_{HCC}$ 2.9-3.1, $^{2}J_{H2CC}$ 2.9-3.1); 109.05 t. d. t. t (t. t) (CHF_2, $^{1}J_{FC}$ 250.4, $^{1}J_{HC}$ 192.5, $^{2}J_{FCC}$ 35.8, $^{2}J_{H2CCC}$ 2.2); 109.03 t. d. t. t (t. t) (CHF_2, $^{1}J_{FC}$ 250.4, $^{1}J_{HC}$ 192.5, $^{2}J_{FCC}$ 35.9, $^{2}J_{H2CCC}$ 2.2); 73.90 br. d (br. s) (C^{4}, $^{2}J_{HC3C4}$ 5.2); 61.69 t. t (t) (OCH_2, $^{1}J_{HC}$ 152.5, $^{2}J_{FCC}$ 29.7); 61.40 t. t (t) (OCH_2, $^{1}J_{HC}$ 153.0, $^{2}J_{FCC}$ 29.7); 55.16 q. d (d) ($POCH_3$, $^{1}J_{HC}$ 150.0, $^{2}J_{POC}$ 6.9); 45.59 d. d. t (d) (C^{3}, $^{1}J_{PC3}$ 132.4, $^{1}J_{HC3}$ 128.4, $^{3}J_{HC11CC3}$ 4.6). ^{19}F NMR ($CDCl_3$) δ_F: –124.89 br. m (CF_2, *2F*); –138.70 and –139.0 two m (CHF_2, *2F*, 2 AB spectrum). ^{31}P-{^{1}H} NMR (CH_2Cl_2) δ_P: 17.2 ppm.

3-(2-Chlorophenyl)-4,4-bis(2,2,3,3-tetrafluoropropoxycarbonyl)-2-methoxy-2-oxobenzo[*f*]-1,2-oxaphosphepine (3d). Yield 92 % (108.1 mg, 16 mmol), m. p. 96-98°C. Anal. Calcd for $C_{24}H_{18}ClF_8O_8P$: C, 44.14; H, 2.76; P, 4.75; Cl 5.44. Found: C, 44.19; H, 2.78; P, 4.76; Cl, 5.43. IR (Nujol): 1784, 1756, 1680, 1604, 1480, 1472, 1456, 1408, 1284, 1200, 1176, 1108, 1064, 936, 772 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.15 d. d (H^{6}, *1H*, $^{3}J_{H6CCH7}$ 8.0, $^{4}J_{H8CCCH6}$ 1.7); 7.98 m (H^{15}, *1H*, $^{3}J_{H15CCH14}$ 6.9-7.0, $^{4}J_{H15CCCH13}$ 3.4, $^{5}J_{H15CCCCH12}$ 2.5); 7.67 d. d. d. d (H^{8}, *1H*, $^{3}J_{H8CCH9}$ 8.1-8.2, $^{3}J_{H7CCH8}$ 7.4, $^{4}J_{H8CCCH6}$ 1.7, $^{5}J_{POCCCH8}$ 0.8); 7.41 d. d. d. d (H^{7}, *1H*, $^{3}J_{H6CCH7}$ 8.0, $^{3}J_{H7CCH8}$ 7.4, $^{4}J_{H7CCCH9}$ 1.2, $^{6}J_{POCCCCH7}$ 1.2); 7.39 m (H^{12}, *1H*); 7.25 d. d. d (H^{9}, *1H*, $^{3}J_{H8CCH9}$ 8.2, $^{4}J_{POCCH9}$ 1.4, $^{4}J_{H9CCH7}$ 1.2); 7.21-7.22 m (H^{14}, H^{13}, *2H*); 5.66 t. t (CHF_2, *1H*, $^{2}J_{HCF}$ 52.8, $^{3}J_{FCCH}$ 4.4); 5.53 t. t (CHF_2, *1H*, $^{2}J_{HCF}$ 52.9, $^{3}J_{FCCH}$ 4.1); 5.29 d (PCH, *1H*, $^{2}J_{PCH}$ 26.9); 4.57 and 4.50 two m (OCH_AH_B, *2H*, AB-part of ABX_3Y_2 spectrum, $^{2}J_{HAHB}$ 12.5, $^{3}J_{FCCH_A} = {}^{3}J_{FCCH_B}$ 12.5, $^{4}J_{FCCCH_A} = {}^{4}J_{FCCCH_B}$ 1.6); 4.40 and 4.10 two br. d. t (OCH_AH_B, *2H*, AB-part of ABX_3 spectrum, $^{3}J_{FCCH_A}$ 12.0-12.2, $^{3}J_{FCCH_X}$ 12.0-12.2, $^{2}J_{HAHX}$ 12.2); 3.59 d (OCH_3, *3H*, $^{2}J_{POCH}$ 11.3). ^{1}H NMR (acetone-D_6, 600 MHz) δ: 8.19 d. d (H^{6}, *1H*, $^{3}J_{H6CCH7}$ 8.0, $^{4}J_{H8CCCH6}$ 1.7); 7.92 br. d. d. d (H^{15}, *1H*, $^{3}J_{H15CCH14}$ 7.6, $^{4}J_{H15CCCH13}$ 1.6-1.7, $^{4}J_{PCCCH15}$ 1.6-1.7); 7.86 d. d. d. d (H^{8}, *1H*, $^{3}J_{H8CCH9}$ 8.2, $^{3}J_{H7CCH8}$ 7.4, $^{4}J_{H8CCCH6}$ 1.7, $^{5}J_{POCCCH8}$ 0.8); 7.57 d. d. d. d (H^{7}, *1H*, $^{3}J_{H6CCH7}$ 8.0, $^{3}J_{H7CCH8}$ 7.4, $^{4}J_{H7CCCH9}$ 1.2, $^{6}J_{POCCCCH7}$ 1.2); 7.52 br. d. d. d (H^{12}, *1H*, $^{3}J_{H12CCH13}$ 7.5-7.6, $^{4}J_{H14CCCH12}$ 1.1, $^{5}J_{PCCCCH12}$ 0.7); 7.41 d. d. d (H^{9}, *1H*, $^{3}J_{H8CCH9}$ 8.2, $^{4}J_{H9CCH7}$ 1.2, $^{4}J_{POCCH9}$ 1.2); 7.37 d. d. d. d (H^{13}, *1H*, $^{3}J_{H14CCH13}$ 7.5, $^{3}J_{H12CCH13}$ 7.5, $^{4}J_{H15CCCH13}$ 1.7, $^{6}J_{PCCCCCH13}$ 1.7); 7.34 d. d. d (H^{14}, *1H*, $^{3}J_{H13CCH14}$ 7.5, $^{4}J_{H15CCH14}$ 7.5-7.6, $^{4}J_{H12CCCH14}$ 1.2); 6.21 t. t (CHF_2, *1H*, $^{2}J_{HCF}$ 52.3, $^{3}J_{FCCH}$ 5.0-5.1); 6.10 t. t (CHF_2, *1H*, $^{2}J_{HCF}$ 52.4, $^{3}J_{FCCH}$ 4.7); 5.42 d (PCH, *1H*, $^{2}J_{PCH}$ 27.1); 4.78 and 4.74 two br. m (OCH_AH_B, *2H*, AB-part of ABX_3 spectrum, $^{2}J_{HACCF}$ 13.1-13.2, $^{3}J_{HAHX}$ 13.1-13.2, $^{3}J_{FCCH_B}$ 13.1-13.2); 4.62 and 4.33 two br. d. t (OCH_AH_B, *2H*, AB-part of ABX_3 spectrum, $^{2}J_{HBCCF}$ 12.5-12.6, $^{3}J_{HAHB}$ 12.5-12.6, $^{3}J_{FCCH_B}$ 12.5-12.6); 3.62 d (OCH_3, *3H*, $^{3}J_{POCH}$ 11.4). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 187.35 m (s) (C^{5}, $^{3}J_{HC3CC5}$ 6.0, $^{3}J_{HC6CC5}$ 4.7-4.8, $^{4}J_{HC7CCC5}$ 1.6); 164.12 d. t (d) (COO, $^{3}J_{PC3CC}$ 13.4, $^{3}J_{HCOC}$ 2.8, $^{3}J_{HC3CC}$ 0); 164.83 d. d. t (d) (COO, $^{3}J_{PCC4C}$ 12.5, $^{3}J_{HC3CC}$ 7.8, $^{3}J_{HCOC}$ 3.2); 148.81 m (d) (C^{9a}, $^{2}J_{POC9a}$ 5.7); 137.15 br. d. d (s) (C^{8}, $^{1}J_{HC8}$ 162.5, $^{3}J_{HC6CC8}$ 9.7); 135.87 m (d) (C^{11}, $^{3}J_{PC3CC11}$ 7.5); 132.15 br. d. d (s) (C^{6}, $^{1}J_{HC6}$ 166.0, $^{3}J_{HC8CC6}$ 8.6); 131.03 d. m (d) (C^{15}, $^{1}J_{HC15}$ 162.6, $^{3}J_{PCCC15}$ 4.1); 130.23 d. d. d. d (d) (C^{12}, $^{1}J_{HC12}$ 163.0, $^{3}J_{HC14CC12}$ 6.4, $^{2}J_{HC13C12}$ 5.6-5.7, $^{4}J_{PC3CCC12}$ 2.1); 129.75 br. d. d. d (d) (C^{13}, $^{1}J_{HC13}$ 165.9, $^{3}J_{HC15CC13}$ 8.6, $^{5}J_{PC3CCCC13}$ 2.7); 129.32 m (d) (C^{10}, $^{2}J_{PC3C10}$ 6.7); 127.45 d. d. d (d) (C^{14}, $^{1}J_{HC14}$ 166.7, $^{3}J_{HC12CC14}$

7.9, $^{4}J_{PC3CCC14}$ 2.6); 127.02 br. d. d (s) (C^{7}, $^{1}J_{HC7}$ 164.7, $^{3}J_{HC9CC7}$ 7.6); 123.52 d. d. d. d. d (d) (C^{9}, $^{1}J_{HC9}$ 166.3, $^{3}J_{HC7CC9}$ 7.4, $^{3}J_{POC9aC9}$ 3.7, $^{2}J_{HC8C9}$ 1.8, $^{4}J_{HC6CCC9}$ 1.8); 125.71 m (br. s) (C^{5a}, $^{3}J_{HC7CC5a}$ 6.0-7.0, $^{3}J_{HC9CC5a}$ 6.0-7.0, $^{2}J_{HC6C5a}$ 2.0, $^{3}J_{HC3CC5a}$ 1.6); 113.59 t. t. m (t. t) (CF_2, $^{1}J_{FC}$ 250.8, $^{2}J_{FCC}$ 28.0); 113.44 t. t. m (t. t) (CF_2, $^{1}J_{FC}$ 250.8, $^{2}J_{FCC}$ 28.0); 108.91 t. d. t. t (t. t) (CHF_2, $^{1}J_{FC}$ 250.5, $^{2}J_{FCC}$ 35.3, $^{3}J_{H2CCC}$ 1.6-1.7); 108.85 t. d. t. t (t. t) (CHF_2, $^{1}J_{FC}$ 250.7, $^{2}J_{FCC}$ 35.0, $^{3}J_{H2CCC}$ 1.6-1.7); 73.87 d (s) (C^{4}, $^{2}J_{HC3C4}$ 5.8); 61.48 t. t (t) (OCH_2, $^{1}J_{HC}$ 152.7, $^{2}J_{FCC}$ 30.7); 61.46 t. t (t) (OCH_2, $^{1}J_{HC}$ 152.7, $^{2}J_{FCC}$ 30.7); 54.77 q. d (d) (OCH_3, $^{1}J_{HC}$ 150.3, $^{2}J_{POC}$ 6.9); 41.23 d. d. d (d) (C^{3}, $^{1}J_{PC3}$ 133.4, $^{1}J_{HC3}$ 127.4, $^{3}J_{HC15CC3}$ 3.0). ^{13}C NMR (acetone-D_6, 151.0 MHz) δ: 187.99 br. m (br. s) (C^{5}, $^{3}J_{HC3CC5}$ 6.2, $^{3}J_{HC6CC5}$ 5.1, $^{4}J_{HC7CCC5}$ 1.5); 164.82 d. d. t (d) (COO, $^{3}J_{PCC4C}$ 14.1, $^{3}J_{HC3CC}$ 7.0, $^{3}J_{HCOC}$ 3.3-3.5); 164.27 d. t. d (d) (COO, $^{3}J_{PC3CC}$ 11.6, $^{3}J_{HCOC}$ 3.0, $^{3}J_{HC3CC}$ 1.3); 148.97 m (d) (C^{9a}, $^{2}J_{POC9a}$ 5.9); 137.16 d. d. d. d (d) (C^{8}, $^{1}J_{HC8}$ 164.0, $^{3}J_{HC6CC8}$ 9.3, $^{4}J_{POC9aCC8}$ 1.6-1.7, $^{2}J_{HC9C8}$ 1.6-1.7); 135.59 m (d) (C^{11}, $^{3}J_{PC3CC11}$ 7.5); 131.87 br. d. d (d) (C^{6}, $^{1}J_{HC6}$ 166.0, $^{3}J_{HC8CC6}$ 8.4, $^{4}J_{POC9aCC6}$ 1.5); 131.09 d. m (d) (C^{15}, $^{1}J_{HC15}$ 160.6, $^{3}J_{HC3CC15}$ 6.6, $^{3}J_{PCCC15}$ 4.2); 130.04 d. m (d) (C^{12}, $^{1}J_{HC12}$ 165.2, $^{3}J_{HC14CC12}$ 7.7, $^{2}J_{HC13C12}$ 3.1, $^{4}J_{PC3CCC12}$ 2.4); 129.79 br. d. d. d (d) (C^{13}, $^{1}J_{HC13}$ 162.9, $^{3}J_{HC15CC13}$ 8.7, $^{5}J_{PC3CCCC13}$ 2.8); 129.76 d. d. d. d (d) (C^{10}, $^{3}J_{HC12,14CC10}$ 6.7-6.8, $^{2}J_{HC3C10}$ 6.7-6.8, $^{2}J_{PC3C10}$ 6.5); 127.46 d. d. d (d) (C^{14}, $^{1}J_{HC14}$ 163.5, $^{3}J_{HC12CC14}$ 8.1, $^{4}J_{PC3CCC14}$ 2.8); 126.95 br. d. d (d) (C^{7}, $^{1}J_{HC7}$ 165.3, $^{3}J_{HC9CC7}$ 8.1, $^{5}J_{POC9aCCC7}$ 1.2); 126.26 m (br. d) (C^{5a}, $^{3}J_{POC9aC5a}$ 2.7); 123.60 d. d. d. d. d (d) (C^{9}, $^{1}J_{HC9}$ 166.6, $^{3}J_{HC7CC9}$ 7.7, $^{3}J_{POC9aC9}$ 3.7, $^{2}J_{HC8C9}$ 1.3, $^{4}J_{HC6CCC9}$ 1.3); 114.04 t. t. t. d (t. t) (CF_2, $^{1}J_{FC}$ 249.7, $^{2}J_{FCC}$ 27.3, $^{2}J_{HCC}$ 2.9-3.0, $^{2}J_{H2CC}$ 2.9-3.0); 113.88 t. t. t. d (t. t) (CF_2, $^{1}J_{FC}$ 249.9, $^{2}J_{FCC}$ 26.9, $^{2}J_{HCC}$ 2.9-3.0, $^{2}J_{H2CC}$ 2.9-3.0); 109.3 t. d. t. t (t. t) (CHF_2, $^{1}J_{FC}$ 248.7, $^{1}J_{HC}$ 195.4, $^{3}J_{H2CCC}$ 1.6-1.7); 109.17 t. d. t. t (t. t) (CHF_2, $^{1}J_{FC}$ 248.7, $^{1}J_{HC}$ 197.5, $^{3}J_{H2CCC}$ 1.6-1.7); 73.63 br. d (s) (C^{4}, $^{2}J_{HC3C4}$ 6.1); 61.60 br. t. t (t) (OCH_2, $^{1}J_{HC}$ 153.0, $^{2}J_{FCC}$ 29.6); 61.59 br. t. t (t) (OCH_2, $^{1}J_{HC}$ 152.7, $^{2}J_{FCC}$ 28.3); 54.23 q. d (d) (OCH_3, $^{1}J_{HC}$ 150.2, $^{2}J_{POC}$ 6.9); 41.57 d. d. d (d) (C^{3}, $^{1}J_{PC3}$ 132.9, $^{1}J_{HC3}$ 127.5, $^{3}J_{HC15CC3}$ 4.0). ^{19}F NMR ($CDCl_3$) δ_F: –125.16 m (CF_2, *2F*, $^{3}J_{FCCH}$ 12.4, $^{3}J_{FCCH}$ 4.0, $^{3}J_{FCCF}$ 3.6); –125.39 m (B-part of AB spectrum, $^{2}J_{FAFB}$ 276.9, $^{3}J_{HBCCFB}$ 13.6, $^{3}J_{HACCFB}$ 12.0, $^{3}J_{HCCFB}$ 4.1, $^{3}J_{FCCFB}$ 3.8); –125.71 m (A-part, $^{2}J_{FAFB}$ 276.9, $^{3}J_{HCCFA}$ 12.0, $^{3}J_{HCCFA}$ 4.1, $^{3}J_{FCCFA}$ 3.8); –139 15 br. d. m (CHF_2, *2F*, $^{2}J_{FCH}$ 52.8); –139.35 br. m (A-part of AB spectrum, $^{2}J_{FACFB}$ 304.4, $^{2}J_{FACH}$ 52.9, $^{3}J_{FCCFA}$ 3.6-3.7). ^{31}P NMR ($CDCl_3$) δ_P (ppm): 18.6 br. d. q ($^{2}J_{PCH}$ 26.9, $^{3}J_{POCH}$ 11.3).

2-Ethoxy-4,4-bis(2,2,3,3-tetrafluoropropoxycarbonyl)-2-oxo-3-phenylbenzo[*f*]-1,2-oxaphosphepine (3e). Yield 87 % (989.0 mg, 15 mmol), m. p. 72-74°C. Anal. Calcd for $C_{25}H_{21}F_8O_8P$: C, 47.47; H, 3.32; P, 4.91. Found: C, 46.51; H, 3.36; P, 4.92. IR (Nujol): 1784, 1768, 1744, 1680, 1600, 1456, 1332, 1100, 932, 848, 792, 768, 640, 608, 536 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.20 d. d (H^{6}, *1H*, $^{3}J_{H6CCH7}$ 8.0, $^{4}J_{H8CCCH6}$ 1.6-1.7); 7.73 d. d. d. d (H^{8}, *1H*, $^{3}J_{H8CCH9}$ 8.1, $^{3}J_{H7CCH8}$ 7.4, $^{4}J_{H8CCCH6}$ 1.6, $^{5}J_{POCCCH8}$ 1.0); 7.62 br. d. m (H^{11}, *1H*); 7.45 d. d. d. d (H^{7}, *1H*, $^{3}J_{H6CCH7}$ 8.0, $^{3}J_{H7CCH8}$ 7.4, $^{4}J_{H7CCCH9}$ 1.2, $^{6}J_{POCCCCH7}$ 1.2); 7.34-7.35 m (H^{12}, H^{13}, *3H*, ABB'-spectrum); 7.31 d. d. d (H^{9}, *1H*, $^{3}J_{H8CCH9}$ 8.1, $^{4}J_{POCCH9}$ 1.4, $^{4}J_{H9CCH7}$ 1.2); 5.57 t. t (CHF_2, *1H*, $^{2}J_{HCF}$ 52.9, $^{3}J_{FCCH}$ 4.1-4.2); 5.43 t. t (CHF_2, *1H*, $^{2}J_{HCF}$ 52.8, $^{3}J_{FCCH}$ 4.3-4.4); 4.63 d. t. t (CH_B, B-part of ABM_3N_2 spectrum, $^{2}J_{HAHB}$ 12.3-12.4, $^{3}J_{FCCHB}$ 12.3-12.4, $^{4}J_{FCCCHB}$ 1.3); 4.54 d. t. t (OCH_A, *2H*, A-part of ABM_3N_2 spectrum, $^{2}J_{HAHB}$ 12.3-12.4, $^{3}J_{FCCHA}$ 12.3-12.4, $^{4}J_{FCCCHB}$ 1.3), 4.45 d (PCH, *1H*, $^{2}J_{PCH}$ 26.2); 4.39 br. d. t (OCH_B, *1H*, B-part of ABM_3N_2 spectrum, $^{2}J_{HAHB}$ 12.2-12.5, $^{3}J_{HBCCF}$ 12.2-12.5,

$^{4}J_{HBCCCF}$ 1.5); 4.09 br. d. t. t (OCH_A, *1H*, A-part of ABM_3N_2 spectrum, $^{2}J_{HAHX}$ 12.0-12.3, $^{3}J_{HACCF}$ 12.0-12.3, $^{4}J_{HACCCF}$ 1.5); 4.04 d. d. t ($POCH_B$, *1H*, B-part of ABX_3 spectrum, $^{2}J_{HAHB}$ 10.0, $^{3}J_{POCHB}$ 9.5, $^{3}J_{HCCH}$ 7.0); 3.80 d. d. t ($POCH_A$, *1H*, A-part of ABX_3 spectrum, $^{2}J_{HAHB}$ 10.0, $^{3}J_{POCHA}$ 10.0, $^{3}J_{HCCH}$ 7.0); 1.07 q (CCH_3, *3H*, $^{3}J_{HCCH}$ 7.0). ^{1}H NMR (DMSO-D_6, 600 MHz) δ: 8.15 d. d (H^6, *1H*, $^{3}J_{H6CCH7}$ 8.0, $^{4}J_{H8CCCH6}$ 1.7); 7.65 br. d (H^{11}, *1H*, $^{3}J_{H11CCH12}$ 7.7); 7.83 d. d. d (H^8, *1H*, $^{3}J_{H8CCH9}$ 8.1, $^{3}J_{H7CCH8}$ 7.4, $^{4}J_{H8CCCH6}$ 1.7); 7.32-7.35 m (H^{12}, H^{13}); 7.38 d. d. d (H^9, *1H*, $^{3}J_{H8CCH9}$ 8.1, $^{3}J_{H7CCCH9}$ 1.1, $^{3}J_{POCCH9}$ 1.3); 6.33 t. t (CHF_2, *1H*, $^{2}J_{HCF}$ 52.0, $^{3}J_{FCCH}$ 5.5); 6.28 t. t (CHF_2, *1H*, $^{2}J_{HCF}$ 52.5, $^{3}J_{FCCH}$ 4.8); 5.04 d (PCH, *1H*, $^{2}J_{PCH}$ 26.7); 4.85 and 4.69 two br. d. t (OCH_AH_B, *2H*, A- and B-parts of ABX_3 spectrum, $^{3}J_{FCCHA} = {}^{2}J_{HAHB}$ 13.0, $^{3}J_{FCCHB} = {}^{2}J_{HAHB}$ 13.0); 4.52 and 4.09 two br. d. t (OCH_AH_M, *2H*, A- and M-parts of AMX_3 spectrum, $^{3}J_{FCCHA} = {}^{2}J_{HAHM}$ 12.5-12.6, $^{3}J_{FCCHM} = {}^{2}J_{HAHM}$ 12.5-12.6); 3.99 d. d. q ($POCH_M$, M-part of AMX_3 spectrum, $^{3}J_{HACOP}$ 8.6, $^{2}J_{HAHM}$ 10.3, $^{3}J_{HH}$ 7.0); 3.79 d. d. q ($POCH_A$, A-part of AMX_3 spectrum, $^{3}J_{HMCOP}$ 9.6, $^{2}J_{HAHM}$ 10.3, $^{3}J_{HCCH}$ 7.0); 1.01 t (CH_3, *3H*, $^{3}J_{HCCH}$ 7.0-7.1). ^{13}C NMR (DMSO-d_6, 100.6 MHz, 45°C) δ: 187.81 br. d (s) (C^5, $^{3}J_{HC3CC5}$ 6.0, $^{3}J_{HC6CC5}$ 3.8); 165.06 d. t (d) (COO, $^{3}J_{PC3CC}$ 16.5, $^{3}J_{HCOC}$ 2.7, $^{3}J_{HC3CC}$ 0); 164.88 d. d. t (d) (COO, $^{3}J_{PCC4C}$ 10.2, $^{3}J_{HC3CC}$ 9.8, $^{3}J_{HCOC}$ 2.7); 149.47 m (d) (C^{9a}, $^{2}J_{POC9a}$ 5.1); 137.91 br. d. d (s) (C^8, $^{1}J_{HC8}$ 164.0, $^{3}J_{HC6CC8}$ 9.1); 132.55 br. d. d (s) (C^6, $^{1}J_{HC6}$ 164.7, $^{3}J_{HC8CC6}$ 8.1); 132.49 d. d. t (d) (C^{10}, $^{2}J_{PC3C10}$ 7.6, $^{3}J_{HC12CC10}$ 7.5, $^{2}J_{HC3C10}$ 7.5); 131.16 d. m (d) (C^{11}, $^{1}J_{HC11}$ 160.3, $^{3}J_{PC3CC11}$ 5.1); 129.27 br. d. d (br. s) (C^{12}, $^{1}J_{HC12}$ 163.4, $^{3}J_{HC14CC12}$ 6.1); 128.77 d. t. d (d) (C^{13}, $^{1}J_{HC13}$ 160.8, $^{3}J_{HC11CC13}$ 7.6, $^{5}J_{PC3CCCC13}$ 4.0); 127.61 br. d. d (br. s) (C^7, $^{1}J_{HC7}$ 165.7, $^{3}J_{HC9CC7}$ 7.1); 126.24 br. s (m) (C^{5a}); 124.60 br. d. d. d (br. d) (C^9, $^{1}J_{HC9}$ 166.0, $^{3}J_{HC7CC9}$ 8.3, $^{3}J_{POC9aC9}$ 2.2); 114.76 t. t. m (t. t) (CF_2, $^{1}J_{FC}$ 249.5, $^{2}J_{FCC}$ 27.5, $^{2}J_{HCC}$ 3.5-3.6, $^{2}J_{H2CC}$ 3.5-3.6); 114.60 t. t. m (t. t) (CF_2, $^{1}J_{FC}$ 250.5, $^{2}J_{FCC}$ 27.0, $^{2}J_{HCC}$ 2.5-3.0, $^{2}J_{H2CC}$ 2.5-3.0); 109.88 br. t. d. t (t. t) (CHF_2, $^{1}J_{FC}$ 248.0, $^{1}J_{HC}$ 197.5, $^{2}J_{FCC}$ 33.1); 109.55 br. t. d. t (t. t) (CHF_2, $^{1}J_{FC}$ 248.0, $^{1}J_{HC}$ 198.4, $^{2}J_{FCC}$ 29.3); 72.52 br. d (s) (C^4, $^{2}J_{HC3C4}$ 4.8); 65.34 t. d. q (d) ($POCH_2$, $^{1}J_{HC}$ 150.0, $^{2}J_{POC}$ 6.4, $^{2}J_{HCC}$ 4.6); 62.32 t. t (t) (OCH_2, $^{1}J_{HC}$ 153.3, $^{2}J_{FCC}$ 30.3); 62.20 t. t (t) (OCH_2, $^{1}J_{HC}$ 152.6, $^{2}J_{FCC}$ 26.0); 45.34 d. d. t (d) (C^3, $^{1}J_{PC3}$ 132.4, $^{1}J_{HC3}$ 128.8, $^{3}J_{HC11CC3}$ 3.4); 16.42 q. d. t (d) (CCH_3, $^{1}J_{HC}$ 127.3, $^{3}J_{POCC}$ 5.1, $^{2}J_{HCC}$ 2.5). ^{19}F NMR ($CDCl_3$) δ_F: –125.17 t. d. t (CF_2, *2F*, $^{3}J_{HCCF}$ 12.2, $^{3}J_{HCCF}$ 4.1, $^{3}J_{FCCF}$ 3.4); –125.46 br. d. d. d. t (CF_2, *2F*, $^{3}J_{HBCCF}$ 15.1, $^{3}J_{HACCF}$ 11.9, $^{3}J_{HCCF}$ 4.3, $^{3}J_{FCCF}$ 3.5-3.4); –139.29 br. d. m (CHF_2, *2F*, $^{2}J_{HF}$ 52.9, $^{3}J_{FCCF}$ 3.4); –139.50 br. d. m (CHF_2, *2F*, $^{2}J_{HF}$ 52.9, $^{3}J_{FCCF}$ 3.5). ^{31}P-{^{1}H} NMR ($CDCl_3$), δ_P: 19.3 ppm.

3-(4-Chlorophenyl)-2-ethoxy-2-oxo-4,4-bis(2,2,3,3-tetrafluoropropoxycarbonyl)benzo-[*f*]-1,2-oxaphosphepine (3f). Yield 92 % (110.4 mg, 16 mmol), m. p. 105-107°C. Anal. Calcd for $C_{25}H_{20}ClF_8O_8P$: C, 45.01; H, 3.00; P, 4.65; Cl, 5.44. Found: C, 45.13; H, 3.11; P, 4.64; Cl, 5.41. IR (Nujol): 1780, 1752, 1688, 1608, 1480, 1472, 1460, 1376, 1304, 1284, 1204, 1156, 1096, 1044, 928, 896, 832, 784, 768, 736, 696 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.60 d. d (H^6, *1H*, $^{3}J_{H6CCH7}$ 8.0, $^{4}J_{H8CCCH6}$ 1.6-1.7); 8.28 d. d. d. d (H^8, *1H*, $^{3}J_{H8CCH9}$ 8.1, $^{3}J_{H7CCH8}$ 7.4, $^{4}J_{H8CCCH6}$ 1.7, $^{5}J_{POCCCH8}$ 0.7); 8.15 br. d. d ($H^{11,15}$, *1H*, XX'-part of AA'XX' spectrum, $^{3}J_{H12CCH11}$ 8.6, $^{4}J_{PCCCH11}$ 2.2); 7.98 d. d. d. d (H^7, *1H*, $^{3}J_{H6CCH7}$ 8.0, $^{3}J_{H7CCH8}$ 7.4, $^{4}J_{H7CCCH9}$ 1.2, $^{6}J_{POCCCCH7}$ 1.2); 7.85 br. d. m ($H^{12,14}$, *1H*, AA'-part of AA'XX' spectrum, $^{3}J_{H11CCH12}$ 8.6); 7.80 d. d. d (H^9, *1H*, $^{3}J_{H8CCH9}$ 8.1, $^{4}J_{POCCH9}$ 1.4; $^{4}J_{H9CCCH7}$ 1.2); 6.72 t. t. d (CHF_2, *1H*, $^{2}J_{HCF}$ 52.5, $^{3}J_{FCCH}$ 6.0-6.1, $^{3}J_{HCCF}$ 5.1-5.2); 6.54 t. t (CHF_2, *1H*, $^{2}J_{HCF}$ 52.4, $^{3}J_{HCCF}$ 4.8); 5.33 d (PCH, *1H*, $^{2}J_{PCH}$ 26.7); 5.29 d. t. t (OCH_AH_X,

1H, B-part of ABX_3Y_2 spectrum, $^2J_{H_AH_B}$ = $^3J_{FCCC_B}$ 13.2-14.4, $^4J_{FCCCH}$ 1.4); 5.16 d. t. t (OCH_B, *1H*, A-part of ABX_3Y_2 spectrum, $^2J_{H_AH_B}$ = $^3J_{FCCH_A}$ 13.7-14.4, $^4J_{FCCCH_A}$ 1.4); 5.03 br. d. t. m (OCH_M, *1H*, M-part of AMX_3Y_2 spectrum, $^2J_{H_AH_M}$ 12.4, $^3J_{FCCH_M}$ 12.8-13.5, $^4J_{HCCCH_M}$ 1.4, $^4J_{FCCCH_M}$ 0.8); 4.60 br. d. t. m (OCH_A, *1H*, A-part of AMX_3Y_2 spectrum,$^2J_{H_AH_M}$ = $^3J_{FCCH_A}$ 12.4, $^4J_{HCCCH_A}$ 1.4, $^4J_{FCCCH_A}$ 0.8); 4.53 and 4.36 two d. d. t ($POCH_AH_B$, *2H*, A- and B-parts of ABX_3 spectrum, $^2J_{H_AH_B}$ = $^3J_{POCH_A}$ 10.0, $^3J_{POCH_B}$ 8.5, $^3J_{HCCH}$ 7.0-7.1, $^3J_{HCCH}$ 7.0); 1.55 t. d (OCH_3, *3H*, $^3J_{HCCH}$ 7.0, $^4J_{POCCH}$ 0.7). ^{1}H NMR (acetone-D_6, 600 MHz) δ: 8.17 d. d (H^6, *1H*, $^3J_{H6CCH7}$ 8.0, $^4J_{H8CCCH6}$ 1.7); 7.84 br. d. d. d (H^8, *1H*, $^3J_{H8CCH9}$ 7.8, $^3J_{H7CCH8}$ 7.5, $^4J_{H8CCCH6}$ 1.7); 7.72 and 7.42 two br. d (C_6H_4Cl, *4H*, AA'XX' spectrum, $^3J_{H_AH_X}$ 8.2, $^3J_{H_A'H_X'}$ 8.2); 7.55 br. d. d (H^7, *1H*, $^3J_{H6CCH7}$ 8.0, $^3J_{H7CCH8}$ 7.5); 7.37 br. d (H^9, *1H*, $^3J_{H8CCH9}$ 7.8); 6.27 t. t (CHF_2, *1H*, $^2J_{HCF}$ 52.3, $^3J_{FCCH}$ 5.5); 6.10 t. t (CHF_2, *1H*, $^2J_{HCF}$ 52.5, $^3J_{FCCH}$ 4.7); 4.89 d (PCH, *1H*, $^2J_{PCH}$ 25.8); 4.87 br. d. t (OCH_AH_B, B-part of ABX_3 spectrum, *1H*, $^3J_{H_BCCF}$ = $^2J_{H_AH_B}$ 13.7); 4.73 br. d. t (OCH_AH_B, A-part of ABX_3 spectrum, *1H*, $^3J_{H_ACCF}$ = $^2J_{H_AH_B}$ 13.7); 4.59 br. d. t. d (OCH_M, M-part of AMX_3 spectrum, *1H*, $^2J_{H_AH_M}$ 12.2, $^3J_{FCCH_M}$ 12.5, $^4J_{HCCCH_M}$ 1.8); 4.19 br. d. t (OCH_A, A-part of AMX_3 spectrum, *1H*, $^2J_{H_AH_M}$ = $^3J_{FCCH_A}$ 12.2); 4.09 d. d. q ($POCH_AH_M$, M-part of AMQ_3X spectrum, *1H*, $^2J_{H_AH_M}$ 10.0, $^3J_{POCH_M}$ 8.5, $^3J_{HCCH}$ 7.0); 3.93 d. d. q ($POCH_AH_M$, A-part of AMQ_3X spectrum, *1H*, $^2J_{H_AH_M}$ 10.0, $^3J_{POCH_A}$ 8.5, $^3J_{HCCH}$ 7.0); 1.13 t (CH_3, *3H*, $^3J_{HCCH}$ 7.0). ^{13}C NMR (acetone-d_6, 150.9 MHz) δ: 188.82 br d. d. d (s) (C^5, $^3J_{HC3CC5}$ 5.8, $^3J_{HC6CC5}$ 4.2, $^4J_{HC7CCC5}$ 1.6); 166.0 d. t (d) (COO, $^3J_{PC3CC}$ 16.0, $^3J_{HCOC}$ 2.7, $^3J_{HC3CC}$ 0); 165.77 d. d. t (d) (COO, $^3J_{PC3CC}$ 10.4, $^3J_{HC3CC}$ 8.7-9.0, $^3J_{HCOC}$ 3.0); 150.79 m (d) (C^{9a}, $^2J_{POC^{9a}}$ 5.4), 138.67 d. d. d. d (d) (C^8, $^1J_{HC8}$ 163.7, $^3J_{HC6CC8}$ 8.8, $^4J_{POC9aCC8}$ 1.6, $^2J_{HCC8}$ 1.6); 135.44 t. d. t (d) (C^{13}, $^3J_{HC11,15CC13}$ 10.8, $^5J_{PC3CCCC13}$ 3.4, $^2J_{HC12,14C13}$ 3.3-3.4); 133.98 br. d. d. d. d (br. d) (C^{11}, $^1J_{HC11}$ 162.6, $^3J_{HC3CC11}$ 5.1-6.0, $^3J_{HC15CC11}$ 5.1-6.0, $^3J_{PC3CC11}$ 5.5); 133.42 d. d. d. d (d) (C^6, $^1J_{HC6}$ 166.0, $^3J_{HC8CC6}$ 8.4, $^4J_{POC9aCC6}$ 1.4, $^2J_{HC7C6}$ 1.4); 132.58 t. d. d (d) (C^{10}, $^3J_{HC12,14CC10}$ 7.8, $^2J_{HC3C10}$ 7.8, $^2J_{PC3C10}$ 7.4); 130.27 d. d. d (d) (C^{12}, $^1J_{HC12}$ 166.4, $^3J_{HC14CC12}$ 5.3, $^4J_{PC3CCC12}$ 2.5); 128.40 br. d. d (d) (C^7, $^1J_{HC7}$ 164.9, $^3J_{HC9CC7}$ 7.9-8.0, $^5J_{POC9aCCC7}$ 1.6); 127.39 m (d) (C^{5a}, $^3J_{HC9CC5a}$ 6.6-7.0, $^3J_{HC7CC5a}$ 6.6-7.0, $^3J_{POC9aC5a}$ 2.4); 125.49 d. d. d. d. d (d) (C^9, $^1J_{HC9}$ 166.6, $^3J_{HC7CC9}$ 7.7, $^3J_{POC9aC9}$ 3.6, $^2J_{HC8C9}$ 1.3, $^4J_{HC6CCC9}$ 1.3); 115.70 t. t. d. t (t. t) (CF_2, $^1J_{FC}$ 250.4, $^2J_{FCC}$ 26.8, $^2J_{HCC}$ 3.2-3.3, $^2J_{H2CC}$ 3.2-3.3); 115.58 t. t. d. t (t. t) (CF_2, $^1J_{FC}$ 250.1, $^2J_{FCC}$ 27.0, $^2J_{HCC}$ 3.2-3.4, $^2J_{H2CC}$ 3.2-3.4); 110.90 t. d. t. t (t. t) (CHF_2, $^1J_{FC}$ 248.7, $^1J_{HC}$ 194.4, $^2J_{FCC}$ 34.1, $^2J_{H2CCC}$ 1.8); 110.65 t. d. d. d. t (t. d. d) (CHF_2, $^1J_{FC}$ 248.1, $^1J_{HC}$ 195.1, $^2J_{FCC}$ 31.7, $^2J_{FCC}$ 32.9, $^2J_{H2CCC}$ 1.8); 75.56 d. d (d) (C^4, $^2J_{HC3C4}$ 5.4, $^2J_{PC3C4}$ 1.8); 66.38 t. d. q (d) ($POCH_2$, $^1J_{HC}$ 150.3, $^2J_{POC}$ 7.0-7.1, $^2J_{HCC}$ 4.5); 61.24 t. d. d (d. d) (OCH_2, $^1J_{HC}$ 153.3, $^2J_{FCC}$ 31.8, $^2J_{FCC}$ 30.6); 63.11 t. t (t) (OCH_2, $^1J_{HC}$ 153.3, $^2J_{FCC}$ 28.2); 46.35 d. d. t (d) (C^3, $^1J_{PC3}$ 131.7, $^1J_{HC3}$ 128.0, $^3J_{HC11CC3}$ 3.7-3.8); 11.04 q. d. t (d) (CCH_3, $^1J_{HC}$ 127.5, $^3J_{POCC}$ 5.5, $^2J_{HCC}$ 2.6). ^{19}F NMR ($CDCl_3$) δ_F: –124.09 t. t. d (CF_2, *2F*, $^3J_{H2CCF}$ 13.3, $^3J_{HCCF}$ 4.8, $^3J_{FCCF}$ 4.6); –125.47 m (CF_2, A'-part of spectrum A'B'M_2X_2Y, $^2J_{F_A'F_B'}$ 277.6-278.0); –124.73 m (CF_2, B'-part of spectrum A'B'M_2X_2Y, $^2J_{F_A'F_B'}$ 277.6-278.0); –137.95 d. m (CHF_2, *2F*, $^2J_{FCH}$ 52.3, $^3J_{FCCF}$ 4.5-4.6, $^4J_{H2CCCF}$ 1.5-1.7); –139.45 d. m (CHF_2, B-part of ABMM'XY_2 spectrum, $^2J_{F_AF_B}$ 302.6, $^2J_{FCH}$ 52.0, $^3J_{F_A'CCF_B}$ 8.5, $^3J_{F_B'CCF_B}$ 2.0, $^3J_{H2CCCF_B}$ 1.5); –140.20 m (A-part of ABMM'XY_2 spectrum, $^2J_{F_AF_B}$ 302.6, $^2J_{FCH}$ 52.0, $^3J_{F_B'CCF_A}$ 8.1-8.2, $^3J_{F_A'CCF_A}$ 2.3-2.5, $^3J_{H2CCCF_A}$ 1.5). ^{31}P-{^{1}H} NMR (CH_2Cl_2) δ_P: 19.0 ppm.

3-(2-Chlorophenyl)-2-ethoxy-4,4-bis(2,2,3,3-tetrafluoropropoxycarbonyl)-2-oxo-benzo[*f*]-1,2-oxaphosphepine (3g). Yield 92 % (110.4 mg, 16 mmol), m. p. 101-102°C. Anal. Calcd for $C_{25}H_{20}ClF_8O_8P$: C, 45.01; H, 3.00; P, 4.65; Cl, 5.44. Found: C, 45.06; H, 3.27; P, 4.77; Cl, 5.63. IR (Nujol): 1776, 1768, 1724, 1600, 1476, 1356, 1272, 1252, 1232, 1104, 976, 840, 752, 684, 656, 612, 536 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ: 8.31 d. d (H^6, *1H*, $^3J_{H6CCH7}$ 8.0, $^4J_{H8CCCH6}$ 1.7); 8.13 d. d. d (H^{15}, *1H*, $^3J_{H14CCH15}$ 6.9-7.0, $^4J_{H13CCCH15}$ 3.5, $^4J_{PCCCH15}$ 2.8); 7.83 d. d. d. d (H^8, *1H*, $^3J_{H8CCH9}$ 8.1, $^3J_{H7CCH8}$ 7.4, $^4J_{H8CCCH6}$ 1.7, $^5J_{POCCCH}$ 1.0); 7.57 d. d. d. d (H^7, *1H*, $^3J_{H6CCH7}$ 8.0, $^3J_{H7CCH8}$ 7.4, $^4J_{H7CCCH9}$ 1.2, $^6J_{POCCCCH7}$ 1.0); 7.56 m (H^{12}, *1H*); 7.41 d. d. d (H^9, *1H*, $^3J_{H8CCH9}$ 8.1, $^4J_{POCCH9}$ 1.4, $^4J_{H9CCCH7}$ 1.2); 7.35-7.39 m (H^{14}, H^{13}, *2H*, AB-part of ABMX spectrum); 5.81 t. t (CHF_2, *1H*, $^2J_{HCF}$ 52.5, $^3J_{FCCH}$ 4.3-4.4); 5.68 t. t (CHF_2, *1H*, $^2J_{HCF}$ 52.9-53.0, $^3J_{FCCH}$ 4.1); 5.43 d (PCH, *1H*, $^2J_{PCH}$ 26.9); 4.72 and 4.64 two d. t. t (OCH_AH_B, *2H*, A- and B-parts of ABX_3Y_2 spectrum, $^2J_{HAHB}$ 12.3-12.5, $^3J_{FCCCHB}$ 12.3-12.5, $^4J_{HCCCHB}$ 1.4 and $^3J_{FCCCHA}$ 12.3-12.5, $^4J_{FCCCHA}$ 1.5); 4.56 and 4.25 two br. d. t. d (OCH_AH_B, *2H*, A- and B-parts of $ABMX_3$ spectrum, $^2J_{HAHB}$ = $^3J_{FCCHA}$ = $^3J_{FCCHB}$ 12.3-12.5, $^4J_{HCCCHB}$ 1.6-1.7, $^4J_{HCCCHA}$ 1.6-1.7); 4.24 and 4.07 two t. t. d ($POCH_AH_B$, *2H*, A- and B-parts of ABM_3X spectrum, $^2J_{HAHB}$ 10.1, $^3J_{POCHA}$ 9.5, $^3J_{POCHB}$ 8.5, $^3J_{HCCHA}$ = $^3J_{HCCHM}$ 7.1); 1.25 t. d (CH_3, *3H*, $^3J_{HCCH}$ 7.0, $^4J_{POCCH}$ 0.6-0.7). ^1H NMR (acetone-D_6, 600 MHz) δ: 8.20 d. d (H^6, *1H*, $^3J_{H6CCH7}$ 8.0, $^4J_{H8CCCH6}$ 1.6-1.7); 7.96 br. d (H^{15}, *1H*, $^3J_{H14CCH15}$ 7.0-7.1); 7.78 d. d. d (H^8, *1H*, $^3J_{H8CCH9}$ 8.2, $^3J_{H7CCH8}$ 7.4, $^4J_{H8CCCH6}$ 1.6); 7.49-7.50 and 7.30-7.31 two m (H^7, H^{12}, H^{13}, H^{14}); 7.37 br. d (H^9, *1H*, $^3J_{H8CCH9}$ 8.2); 6.14 t. t (CHF_2, *1H*, $^2J_{HCF}$ 52.3, $^3J_{FCCH}$ 4.8); 6.03 t. t (CHF_2, *1H*, $^2J_{HCF}$ 52.5, $^3J_{FCCH}$ 4.5); 5.47 d (PCH, *1H*, $^2J_{PCH}$ 27.0); 4.76 and 4.72 two br. m (OCH_AH_B, *2H*, A- and B-parts of ABX_3 spectrum, $^3J_{FCCHA}$ = $^2J_{HAHB}$ 12.7-13.0, $^3J_{FCCHB}$ = $^2J_{HAHB}$ 12.7-13.0); 4.61 and 4.33 two br. d. t (OCH_AH_B, *2H*, A- and B-parts of ABX_3 spectrum, $^3J_{FCCHA}$ = $^2J_{HAHB}$ 12.7, $^3J_{FCCHB}$ = $^2J_{HAHB}$ 12.7); 4.09 t. t. q ($POCH_B$, *1H*, B-part of ABM_3X spectrum, $^3J_{HBCOP}$ 9.8, $^2J_{HAHB}$ 9.8, $^3J_{HCCH}$ 7.2); 3.97 t. t. q ($POCH_A$, A-part of ABM_3X spectrum, $^3J_{HACOP}$ 8.4, $^2J_{HAHB}$ 9.8, $^3J_{HCCH}$ 7.2); 1.08 t (CH_3, *3H*, $^3J_{HCCH}$ 7.2). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 186.27 br. d. d (s) (C^5, $^3J_{HC3CC5}$ 5.5, $^3J_{HC6CC5}$ 4.3); 162.88 d. t (d) (COO, $^3J_{PC3CC}$ 12.8, $^3J_{HCOC}$ 2.8); 162.45 d. d. t (d) (COO, $^3J_{PCC4C}$ 13.0, $^3J_{HC3CC}$ 7.5, $^3J_{HCOC}$ 2.8-3.0); 147.62 m (d) (C^{9a}, $^2J_{POC9a}$ 5.9); 135.70 br. d. d (br. s) (C^8, $^1J_{HC8}$ 162.4, $^3J_{HC6CC8}$ 9.2); 134.38 br. m (d) (C^{11}, $^3J_{PC3CC11}$ 7.5, $^3J_{HC3CC11}$ 6.5-7.0, $^3J_{HC13CC11}$ 6.7, $^3J_{HC15C11}$ 6.7); 130.63 br. d. d (s) (C^6, $^1J_{HC6}$ 163.8, $^3J_{HC8CC6}$ 8.3); 129.84 br. d. m (br. s) (C^{15}, $^1J_{HC15}$ 163.0); 128.72 br. d. m (s) (C^{13}, $^1J_{HC13}$ 163.4, $^3J_{HC15CC13}$ 9.6); 128.34 d. d. d (d) (C^{10}, $^2J_{PC3C10}$ 6.8-7.0, $^2J_{HC3C10}$ 6.8-7.0, $^3J_{HC14CC10}$ 6.8-7.0); 128.31 br. d. d (s) (C^{12}, $^2J_{HC12}$ 164.8, $^3J_{HC14CC12}$ 8.3); 125.90 br. d. d (s) (C^{14}, $^1J_{HC14}$ 163.2, $^3J_{HC12CC14}$ 7.8); 125.52 d. d (s) (C^7, $^1J_{HC7}$ 164.6, $^3J_{HC9CC7}$ 7.8-7.9); 124.52 m (br. s) (C^{5a}); 122.14 br. d. d (br. d) (C^9, $^1J_{HC9}$ 165.9, $^3J_{HC7CC9}$ 7.6, $^3J_{POC9aC9}$ 2.2); 112.28 br. t. t. m (t. t) (CF_2, $^1J_{FC}$ 250.9, $^2J_{FCC}$ 27.7, $^2J_{HCC}$ 3.6-3.8, $^2J_{H2CC}$ 3.6-3.8); 112.14 br. t. t. m (t. t) (CF_2, $^1J_{FC}$ 250.7, $^2J_{FCC}$ 27.1, $^2J_{HCC}$ 3.6-4.0, $^2J_{H2CC}$ 3.6); 107.57 br. t. d. t t. (t. t) (CHF_2, $^1J_{FC}$ 253.2, $^1J_{HC}$ 193.5, $^2J_{FCC}$ 35.5); 107.52 br. t. d. t (t. t) (CHF_2, $^1J_{FC}$ 251.3, $^1J_{HC}$ 193.1, $^2J_{FCC}$ 31.9); 72.47 br. d (s) (C^4, $^2J_{HC3C4}$ 5.9); 63.87 t. d. q (d) ($POCH_2$, $^1J_{HC}$ 150.2, $^2J_{POC}$ 6.6, $^2J_{HCC}$ 4.3); 60.12 t. t (t) (OCH_2, $^1J_{HC}$ 152.8, $^2J_{FCC}$ 30.5); 60.03 br. t. t (br. t) (OCH_2, $^1J_{HC}$ 152.9, $^2J_{FCC}$ 30.5); 41.21 d. d. d (d) (C^3, $^1J_{PC3}$ 133.2, $^1J_{HC3}$ 128.1, $^3J_{HC11CC3}$ 2.5); 14.35 q. d. t (d) (CCH_3, $^1J_{HC}$ 125.1, $^3J_{POCC}$ 5.6, $^2J_{HCC}$ 2.6-2.7). ^{13}C-{^1H} NMR (acetone-d_6, 150.9 MHz) δ: 187.97 s (C^5); 164.26 d (COO, $^3J_{PC3CC}$ 11.5); 163.79 d (COO,

$^{3}J_{PCC4C}$ 14.1); 149.05 d (C^{9a}, $^{2}J_{POC9a}$ 5.9); 137.05 s (C^{8}); 135.57 d (C^{11}, $^{3}J_{PC3CC11}$ 7.5); 131.79 d (C^{6}, $^{4}J_{POC9aCC6}$ 1.2); 131.21 d (C^{15}, $^{3}J_{PC3CC15}$ 3.9); 129.95 d (C^{10}, $^{2}J_{PC3C10}$ 6.4); 129.92 d (C^{13}, $^{5}J_{PC3CCCC13}$ 1.8); 129.64 d (C^{12}, $^{4}J_{PC3CCC12}$ 2.6); 127.24 d (C^{14}, $^{4}J_{PC3CCC14}$ 2.6); 126.82 s (C^{7}); 123.54 d (C^{9}, $^{2}J_{POC9aC9}$ 3.7); 126.19 br. d (C^{5a}, $^{3}J_{POC9aCC5a}$ 2.0); 113.92 t. t (CF_2, $^{1}J_{FC}$ 250.3, $^{2}J_{FCC}$ 27.2); 113.78 t. t (CF_2, $^{1}J_{FC}$ 250.2, $^{2}J_{FCC}$ 27.1); 109.19 t. t (CHF_2, $^{1}J_{FC}$ 249.3, $^{2}J_{FCC}$ 33.8); 109.08 t. t (CHF_2, $^{1}J_{FC}$ 248.2, $^{2}J_{FCC}$ 33.4); 73.65 s (C^{4}); 64.95 d ($POCH_2$, $^{2}J_{POC}$ 7.0); 61.53 br. t (OCH_2, $^{2}J_{FCC}$ 30.4); 61.50 br. t (OCH_2, $^{2}J_{FCC}$ 28.7); 41.51 d (C^{3}, $^{1}J_{PC3}$ 132.5); 15.36 d (CCH_3, $^{3}J_{POCC}$ 5.6). ^{19}F NMR ($CDCl_3$) δ_F: –124.87 m (CF_2, *2F*); –125.39 ÷ –125.44 m (CF_2, AB part of $ABMNXY_2$ spectrum); –138.87 br. d. m (CHF_2, *2F*, $^{2}J_{HCF}$ 52.0-53.0); –139.18 ÷ –139.47 two br. m (AB-part of $ABMNXY_2$ spectrum, $^{2}J_{HCF}$ 52.5-53.0). ^{31}P-{^{1}H} NMR (CH_2Cl_2) δ_P: 20.1 ppm.

3-(4-Bromophenyl)-2-ethoxy-4,4-bis(2,2,3,3-tetrafluoropropoxycarbonyl)-2-oxobenzo[*f*]-1,2-oxaphosphepine (3h). Yield 86 % (110.0 mg, 15 mmol), m. p. 103–105°C. Anal. Calcd for $C_{25}H_{20}BrF_8O_8P$: C, 42.20; H, 2.81; P, 4.36; Br, 11.24. Found: C, 42.31; H, 2.97; P, 4.22; Br, 11.09. IR (Nujol): 1776, 1764, 1752, 1688, 1452, 1400, 1284, 1224, 1200, 1152, 1100, 1056, 1040, 976, 928, 896, 768, 688, 536 cm^{-1}. ^{1}H NMR ($CDCl_3$, acetone-D_6, 300 MHz) δ: 8.08 d. d (H^{6}, *1H*, $^{3}J_{H6CCH7}$ 8.0, $^{4}J_{H8CCCH6}$ 1.7-1.8); 7.70 d. d. d. d (H^{8}, *1H*, $^{3}J_{H8CCH9}$ 8.1-8.2, $^{3}J_{H7CCH8}$ 7.4, $^{4}J_{H8CCCH6}$ 1.8, $^{5}J_{POCCCH8}$ 0.8); 7.51 and 7.42 two m (H^{11}, H^{12}, *2H*, AA'BB' spectrum, $^{3}J_{HAHB}$ 8.6, $^{3}J_{HA'HB'}$ 8.6, $^{4}J_{PCCCH}$ 2.0); 7.42 d. d. d. d (H^{7}, *1H*, $^{3}J_{H6CCH7}$ 8.0, $^{3}J_{H7CCH8}$ 7.4, $^{4}J_{H7CCCH9}$ 1.7, $^{6}J_{POCCCCH7}$ 0.8); 7.24 d. d. d (H^{9}, *1H*, $^{3}J_{H8CCH9}$ 8.1-8.2, $^{4}J_{H9CCCH7}$ 1.7-1.8, $^{4}J_{POCCH9}$ 1.4); 6.01 t. t (CHF_2, *1H*, $^{2}J_{HCF}$ 52.5, $^{3}J_{HCCF}$ 4.5-4.6); 5.83 t. t (CHF_2, *1H*, $^{2}J_{HCF}$ 52.6, $^{3}J_{HCCF}$ 4.5-4.6); 4.73 d (PCH, *1H*, $^{2}J_{PCH}$ 26.5); 4.69 d. t. t (OCH_B, *1H*, B-part of ABX_3Y_2 spectrum, $^{2}J_{HAHB} = {}^{3}J_{FCCH}$ 13.0, $^{4}J_{FCCCH}$ 1.4); 4.56 d. t. t (OCH_A, *1H*, A-part of ABX_3Y_2 spectrum, $^{2}J_{HAHB} = {}^{3}J_{FCCH}$ 13.0, $^{4}J_{FCCCH}$ 1.4); 4.45 and 4.05 two m (OCH_AH_M, *2H*, A- and M-parts of AMX_3Y_2 spectrum, $^{2}J_{HAHM}$ 12.4-12.7, $^{3}J_{FCCH_A}$ 12.5-13.0, $^{3}J_{FCCH_M}$ 12.5-13.0, $^{4}J_{HCCCF}$ 1.7); 4.02 d. d. q ($POCH_B$, *1H*, B-part of ABM_3X spectrum,$^{2}J_{HAHB}$ 10.1, $^{3}J_{POCH_B}$ 8.4, $^{3}J_{HCCH}$ 7.1); 3.85 d. d. q ($POCH_A$, *1H*, A-part of ABM_3X spectrum, $^{3}J_{HCCH}$ 7.1, $^{2}J_{HAHB}$ 10.1, $^{3}J_{POCH_A}$ 10.1, $^{3}J_{HCCH}$ 7.1); 1.06 t. d (CH_3, *3H*, $^{3}J_{HCCH}$ 7.1, $^{4}J_{POCCH}$ 0.6). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 187.05 d. d. d (d) (C^{5}, $^{3}J_{HC6CC5}$ 4.8-4.9, $^{3}J_{HC3CC5}$ 4.8, $^{3}J_{PC3CC5}$ 0.8); 164.14 d. d. t (d) (COO, $^{3}J_{PC3CC}$ 13.9, $^{3}J_{HCOC}$ 2.6-2.7, $^{3}J_{HC3CC}$ 2.5-2.6); 163.91 d. d. t (d) (COO, $^{3}J_{PCC4C}$ 10.6, $^{3}J_{HC3CC}$ 8.8, $^{3}J_{HCOC}$ 2.8-2.9); 149.0 m (d) (C^{9a}, $^{2}J_{POC9a}$ 5.3); 137.24 d. d. d. d (s) (C^{8}, $^{1}J_{HC8}$ 162.8, $^{3}J_{HC6CC8}$ 9.2, $^{2}J_{HCC8}$ 1.8, $^{2}J_{HCC8}$ 1.5); 132.28 d. d (s) (C^{6}, $^{1}J_{HC6}$ 163.3, $^{3}J_{HC8CC6}$ 8.2); 132.21 d. m (d) (C^{11}, $^{1}J_{HC11}$ 167.8, $^{3}J_{PC3CC11}$ 7.8-8.0); 132.17 d. m (s) (C^{12}, $^{1}J_{HC12}$ 167.9); 130.28 d. t. d (d) (C^{10}, $^{2}J_{PC3C10}$ 8.0, $^{3}J_{HC12CC10}$ 7.6, $^{2}J_{HC3C10}$ 7.6); 127.09 d. d (s) (C^{7}, $^{1}J_{HC7}$ 166.4, $^{3}J_{HC9CC7}$ 8.2); 125.53 m (s) (C^{5a}); 123.75 br. d. d. d (d) (C^{9}, $^{1}J_{HC9}$ 165.9, $^{3}J_{HC7CC9}$ 7.7, $^{3}J_{POC9aC9}$ 4.0); 122.98 m (d) (C^{13}, $^{5}J_{PC3CCCC13}$ 4.0); 113.70 t. t. m (t. t) (CF_2, $^{1}J_{FC}$ 250.8, $^{2}J_{FCC}$ 28.5, $^{2}J_{H2CC}$ 4.0, $^{2}J_{HCC}$ 4.0-4.2); 113.55 t. t. m (t. t) (CF_2, $^{1}J_{FC}$ 250.8, $^{2}J_{FCC}$ 28.5, $^{2}J_{HCC}$ 4.0, $^{2}J_{H2CC}$ 4.0-4.2); 109.05 t. d. t. t (t. t) (CHF_2, $^{1}J_{FC}$ 250.8, $^{1}J_{HC}$ 193.0, $^{2}J_{FCC}$ 35.8, $^{3}J_{H2CCC}$ 1.7-1.8); 109.03 t. d. t. t (t. t) (CHF_2, $^{1}J_{FC}$ 250.8, $^{1}J_{HC}$ 192.6, $^{2}J_{FCC}$ 35.8, $^{3}J_{H2CCC}$ 1.7-1.8); 73.86 d. d (d) (C^{4}, $^{2}J_{HC3C4}$ 6.3, $^{2}J_{PC3C4}$ 1.0); 65.71 t. d. q (d) ($POCH_2$, $^{1}J_{HC}$ 150.3, $^{2}J_{POC}$ 8.0, $^{2}J_{HCC}$ 4.2); 61.66 t (t. t) (OCH_2, $^{2}J_{HC}$ 152.8, $^{2}J_{FCC}$ 30.5); 61.42 t. t (t) (OCH_2, $^{1}J_{HC}$ 153.4, $^{2}J_{FCC}$ 30.5); 45.80 d. d. t (d) (C^{3}, $^{1}J_{PC3}$ 132.7, $^{1}J_{HC3}$ 127.9, $^{3}J_{HC11CC3}$ 3.8); 15.99 q. d. t (d) (CCH_3, $^{1}J_{HC}$ 127.6, $^{3}J_{POCC}$ 5.5, $^{2}J_{HCC}$ 2.6). ^{19}F NMR ($CDCl_3$, acetone-D_6) δ_F: –124.86 m (CF_2, *2F*, A_2-part of $A_2M_2X_2Y$ system,

$^{3}J_{HCCF}$ 12.5-13.0, $^{3}J_{FCCH}$ 4.3, $^{3}J_{FCCF}$ 4.3); –126.20 m (CF_2, A-part of spectrum $ABMNX_2Y$, $^{2}J_{F_AF_B}$ 277.0, $^{3}J_{F_ACCH}$ 12.5, $^{3}J_{F_ACCH}$ 4.5, $^{3}J_{F_ACCF_{M,N}}$ 5.5-5.6); –125.1 m (CF_2, B-part of spectrum ABM_2X_2Y, $^{2}J_{F_AF_B}$ 277.0, $^{3}J_{F_BCCH}$ 12.5-12.8, $^{3}J_{F_BCCF_M}$ 6.5, $^{3}J_{F_BCCH} = {}^{3}J_{F_BCCF_N}$ 4.5); –138.80 br. d. t (CHF_2, *2F*, $^{2}J_{HCF}$ 52.6, $^{3}J_{FCCF}$ 4.2-4.3); –140.4 br. m (CHF_2, M-part of spectrum ABM_2X_2Y, $^{2}J_{F_MF_N}$ 303.1, $^{2}J_{F_MCH}$ 52.3, $^{3}J_{FCCF}$ 5.5,$^{3}J_{FCCF}$ 4.5); –139.80 br. m (CHF_2, N-part of spectrum $ABMNX_2Y$, $^{2}J_{F_MF_N}$ 303.1, $^{2}J_{F_NCH}$ 52.3, $^{3}J_{F_ACCF_N}$ 5.5, $^{3}J_{F_BCCF_N}$ 4.5). ^{31}P NMR (CH_2Cl_2) δ_P: 17.5 ppm.

4,4-Bis(2,2,3,3-tetrafluoropropoxycarbonyl)-2-oxo-2,3-diphenylbenzo[*f*]-1,2-oxaphosphepine (3i). Yield 93 % (111.1 mg, 16 mmol), m. p. 124-125°C. Anal. Calcd for $C_{29}H_{21}F_8O_7P$: C, 52.41; H, 3.16; P, 4.67. Found: C, 52.27; H, 3.39; P, 4.90. IR (Nujol): 1784, 1724, 1692, 1600, 1456, 1376, 1368, 1360, 1276, 1108, 1032, 920, 836, 776, 752, 696 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.25 d. d. d (H^6, *1H*, $^{3}J_{H6CCH7}$ 8.0, $^{4}J_{H8CCCH6}$ 1.6, $^{5}J_{POCCCH6}$ 1.4); 7.76 d. d. d. d (H^8, *1H*, $^{3}J_{H8CCH9}$ 8.1, $^{3}J_{H7CCH8}$ 7.4, $^{4}J_{H8CCCH6}$ 1.6, $^{5}J_{POCCCH8}$ 1.2); 7.53 m (H^{27}, *1H*, $^{3}J_{H26CCH27}$ 7.4); 7.51 br. d. d. d (H^7, *1H*, $^{3}J_{H6CCH7}$ 8.0, $^{3}J_{H7CCH8}$ 7.4, $^{4}J_{H7CCCH9}$ 1.2); 7.26-7.38 m ($H^{11\text{-}13}$, H^9, H^{25}, H^{26}, *6H*); 5.55 br. t. t (CHF_2, *1H*, $^{2}J_{HCF}$ 53.0, $^{3}J_{FCCH}$ 4.4); 5.45 br. t. t (CHF_2, *1H*, $^{2}J_{HCF}$ 52.8, $^{3}J_{FCCH}$ 4.1); 4.77 d. t. d. t (OCH_B, *1H*, B-part of ABX_3Y_2 spectrum, $^{2}J_{H_AH_B}$ 12.5, $^{3}J_{H_BCCF}$ 12.5, $^{4}J_{HCCCH}$ 1.1, $^{4}J_{FCCCH}$ 1.1); 4.56 d (PCH, *1H*, $^{2}J_{PCH}$ 26.8); 4.50 d. t. d. t (OCH_2, *1H*, A-part of ABX_3Y_2 spectrum, $^{2}J_{H_AH_X}$ 12.5, $^{3}J_{H_ACCH}$ 12.5, $^{4}J_{HCCCH}$ 1.1, $^{4}J_{FCCH}$ 1.1); 4.43 t. d. t. d (OCH_B, *1H*, B-part of ABX_3Y_2 spectrum, $^{2}J_{H_AH_B}$ 12.3, $^{3}J_{FCCH_B}$ 12.3, $^{4}J_{HCCCH_B}$ 1.5, $^{4}J_{FCCCH_B}$ 1.3); 4.14 t. d. t. d (OCH_A, *1H*, A-part of ABX_3Y_2 spectrum,$^{2}J_{H_AH_B}$ 12.3, $^{3}J_{FCCH_A}$ 12.3, $^{4}J_{HCCCH}$ 1.5, $^{4}J_{FCCCH}$ 1.3). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 188.10 br. d. d. d (s) (C^5, $^{3}J_{HC3CC5}$ 5.3, $^{3}J_{HC6CC5}$ 4.4, $^{4}J_{HC7CCC5}$ 1.3); 164.53 d. t (d) (COO, $^{3}J_{PC3CC}$ 12.8, $^{3}J_{HCOC}$ 3.0, $^{3}J_{HC3CC}$ 0); 164.43 d. d. t (d) (COO, $^{3}J_{HC3CC}$ 8.8, $^{3}J_{PCC4C}$ 8.3, $^{3}J_{HCOC}$ 3.2); 148.55 d. d. d. d. d (d) (C^{9a}, $^{3}J_{HCCC9a}$ 10.3, $^{3}J_{HCCC9a}$ 8.7, $^{2}J_{POC9a}$ 8.2, $^{2}J_{HC9C9a}$ 4.2, $^{4}J_{HC7CCC9a}$ 1.7); 136.81 d. d (s) (C^8, $^{1}J_{HC8}$ 162.6, $^{3}J_{HC6CC8}$ 9.3); 133.15 d. t. d (d) (C^{27}, $^{1}J_{HC27}$ 161.1, $^{3}J_{HC25CC27}$ 8.4, $^{4}J_{PC24CCC27}$ 2.9); 132.60 br. d. d (s) (C^6, $^{1}J_{HC6}$ 164.5, $^{3}J_{HC8CC6}$ 8.4); 132.50 d. m (d) (C^{25}, $^{1}J_{HC25}$ 164.1, $^{2}J_{PC24C25}$ 9.5, $^{3}J_{HC29CC25}$ 6.9-7.0, $^{3}J_{HC27CC25}$ 6.9-7.0, $^{2}J_{HC26C25}$ 2.0); 131.81 m (d) (C^{10}, $^{2}J_{PC3C10}$ 3.2); 130.24 very br. m (very br. s) (C^{11}, $^{1}J_{HC11}$ 163.0-165.0); 129.01 d. d. d (d) (C^{12}, $^{1}J_{HC12}$ 161.0, $^{3}J_{HC14CC12}$ 6.6, $^{4}J_{PC3CCC12}$ 2.5); 128.36 d. t. d (d) (C^{13}, $^{1}J_{HC13}$ 161.5, $^{3}J_{HC11CC13}$ 7.3, $^{5}J_{PC3CCCC13}$ 3.1); 128.31 m (d) (C^{10}, $^{2}J_{PC3C10}$ 3.2); 127.73 d. d. d (d) (C^{26}, $^{1}J_{HC26}$ 161.0, $^{3}J_{PC24CC26}$ 13.8, $^{3}J_{HC28CC26}$ 6.2-6.3); 126.92 m (d) (C^{5a}, $^{3}J_{POC9aC5a}$ 2.3); 126.88 d. d (s) (C^7, $^{1}J_{HC7}$ 163.6, $^{3}J_{HC9CC7}$ 7.7); 126.84 d. t (d) (C^{24}, $^{1}J_{PC24}$ 142.6, $^{3}J_{HC26CC24}$ 7.7); 124.27 d. d. d. d. d (d) (C^9, $^{1}J_{HC9}$ 166.0, $^{3}J_{HC7CC9}$ 7.6, $^{3}J_{POC9aC9}$ 3.4, $^{2}J_{HC8C9}$ 1.5, $^{4}J_{HC6CCC9}$ 1.5); 113.63 t. t. d. t (t. t) (CF_2, $^{1}J_{FC}$ 250.8, $^{2}J_{FCC}$ 28.2, $^{2}J_{HCC}$ 4.8-5.0, $^{2}J_{H2CC}$ 4.0-4.2); 113.53 t. t. d. t (t. t) (CF_2, $^{1}J_{FC}$ 250.7, $^{2}J_{FCC}$ 27.2, $^{2}J_{HCC}$ 4.8-5.0, $^{2}J_{H2CC}$ 4.0-4.2); 108.93 t. d. t. t (t. t) (CHF_2, $^{1}J_{FC}$ 250.6, $^{1}J_{HC}$ 192.6, $^{2}J_{FCC}$ 35.6, $^{3}J_{H2CCC}$ 1.0); 108.85 t. d. t. t (t. t) (CHF_2, $^{1}J_{FC}$ 250.4, $^{1}J_{HC}$ 192.5, $^{2}J_{FCC}$ 35.0, $^{3}J_{H2CCC}$ 1.0); 74.72 d. d (d) (C^4, $^{2}J_{HC3C4}$ 4.8, $^{2}J_{PC3C4}$ 1.2); 61.48 t. t (t) (OCH_2, $^{1}J_{HC}$ 152.6, $^{2}J_{FCC}$ 30.5); (C^3,); 61.36 t. t (t) (OCH_2, $^{1}J_{HC}$ 152.6, $^{2}J_{FCC}$ 30.4); 51.07 d. d. t (d) (C^3, $^{1}J_{HC}$ 127.7, $^{1}J_{PC}$ 83.1, $^{3}J_{HC11CC3}$ 4.1). ^{19}F NMR ($CDCl_3$) δ: –125.26 t. t. d (CF_2, *2F*, $^{3}J_{HCCF}$ 12.5, $^{3}J_{FCCF}$ 5.5, $^{3}J_{HCCF}$ 4.0); –125.75 t. t. d (CF_2, *2F*, $^{3}J_{HCCF}$ 12.5, $^{3}J_{FCCF}$ 6.3, $^{3}J_{FCCH}$ 4.5); –138.72 br. d. m (CHF_2, *2F*, $^{2}J_{F_AF_B}$ 305.0, $^{2}J_{F_ACH}$ 52.8); –138.85 br. d. m (CHF_2, $^{2}J_{F_AF_B}$ 305.0, $^{2}J_{F_BCH}$ 52.8);

–139.25 br. m (CHF_2, $^2J_{FACH}$ 53.0); –139.27 br. m (CHF_2, $^2J_{FBCH}$ 53.0). ^{31}P-{^1H} NMR (CH_2Cl_2) δ_P: 38.5 ppm.

3-(4-Chlorophenyl)-4,4-bis(2,2,3,3-tetrafluoropropoxycarbonyl)-2-oxo-2-phenylbenzo[*f*]-1,2-oxaphosphepine (3j). Yield 93 % (116.9 mg, 16 mmol), m. p. 120–122°C. Calcd for $C_{29}H_{20}ClF_8O_7P$: C, 49.82; H, 2.86; P, 4.44; Cl, 5.08. Found: C, 49.65; H, 2.92; P, 4.24; Cl, 5.11. IR (Nujol): 1776, 1760, 1680, 1456, 1376, 1312, 1280, 1236, 1184, 1160, 1112, 1064, 928 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ: 8.20 d. d (H^6, *1H*, $^3J_{H6CCH7}$ 8.0, $^4J_{H8CCCH6}$ 1.7); 7.73 d. d. d. d (H^8, *1H*, $^3J_{H8CCH9}$ 8.1, $^3J_{H7CCH8}$ 7.4, $^4J_{H8CCCH6}$ 1.8, $^5J_{POCCCH}$ 0.7); 7.54 m (H^{27}, *1H*, $^3J_{H26CCH27}$ 7.2, $^4J_{H25CCCH27}$ 2.3, $^5J_{PCCCCH27}$ 1.3); 7.48 d. d. d. d (H^7, *1H*, $^3J_{H6CCH7}$ 8.0, $^3J_{H7CCH8}$ 7.4, $^4J_{H7CCCH9}$ 1.0, $^6J_{POCCCCH7}$ 1.0); 7.28-7.32 and 7.19 two br. m (H^{12}, H^{11}, H^{25}, H^{26}, 5*H*); 5.64 t. t (CHF_2, *1H*, $^2J_{HCF}$ 52.9, $^3J_{FCCH}$ 4.0); 5.53 t. t (CHF_2, *1H*, $^2J_{HCF}$ 52.9, $^3J_{FCCH}$ 4.0); 5.55 d (PCH, *1H*, $^2J_{PCH}$ 25.9); 4.74 br. d. t. t (OCH_B, B-part of ABX_3Y_2 spectrum, *1H*, $^3J_{HBCCF}$ 13.6, $^2J_{HAHB}$ 13.6, $^4J_{FCCCHB}$ 1.4); 4.46 b. d. t. t (OCH_A, A-part of ABX_3Y_2 spectrum, *1H*, $^3J_{HACCF}$ 13.6, $^2J_{HAHB}$ 13.6, $^4J_{FCCCHA}$ 1.4); 4.74 d. t. t (OCH_M, M-part of AMX_3Y_2 spectrum, *1H*, $^3J_{HMCCF}$ 12.7, $^2J_{HAHM}$ 12.7, $^4J_{FCCCHM}$ 1.3); 4.11 d. t. t (OCH_A, A-part of AMX_3Y_2 spectrum, *1H*, $^3J_{HACCF}$ 12.7, $^2J_{HAHM}$ 12.7, $^4J_{FCCCHA}$ 1.3). ^1H NMR (acetone-D_6, 600 MHz) δ: 8.20 d. d (H^6, *1H*, $^3J_{H6CCH7}$ 8.0, $^4J_{H8CCCH6}$ 1.7); 7.82 d. d. d (H^8, *1H*, $^3J_{H8CCH9}$ 8.0, $^3J_{H7CCH8}$ 7.4); 7.59 m (H^{27}, *1H*); 7.55 br. d. d (H^7, *1H*, $^3J_{H6CCH7}$ 8.0, $^3J_{H7CCH8}$ 7.4); 7.39 br. d (H^9, *1H*, $^3J_{H8CCH9}$ 8.0); 7.39-7.44 and 7.27 two br. m (H^{12}, H^{11}, H^{25}, H^{26}, 5*H*); 6.29 br. t. d. d (CHF_2, *2F*, $^2J_{HCF}$ 52.3, $^3J_{HCCF}$ 5.5, $^3J_{HCCF}$ 5.2-5.3); 6.07 t. t (CHF_2, *1H*, $^2J_{HCF}$ 52.4, $^3J_{FCCH}$ 4.5); 4.98 d (PCH, *1H*, $^2J_{PCH}$ 25.8); 4.94 t. d (OCH_M, *1H*, M-part of AMX_3 spectrum, $^3J_{HMCCF} = {}^2J_{HAHM}$ 13.3); 4.73 t. d (OCH_A, *1H*, A-part of AMX_3 spectrum, $^3J_{HACCF} = {}^2J_{HAHM}$ 13.3); 4.59 br. t. d (OCH_M, *1H*, M-part of AMX_3 spectrum, $^3J_{HMCCF} = {}^2J_{HAHM}$ 12.3-12.5); 4.24 br. t. d (OCH_A, *1H*, A-part of AMX_3 spectrum, $^3J_{HACCF} = {}^2J_{HAHM}$ 12.3-12.5). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 187.83 br. d. d (s) (C^5, $^3J_{HC3CC5}$ 4.0-5.0, $^3J_{HC6CC5}$ 3.4-3.5); 164.48 d. d. t (d) (COO, $^3J_{PCC4C}$ 8.0, $^3J_{HC3CC}$ 7.8-8.0, $^3J_{HCOC}$ 3.5); 164.28 d. t (d) (COO, $^3J_{PC3CC}$ 13.0, $^3J_{HCOC}$ 2.5, $^3J_{HC3CC}$ 0); 148.46 m (d) (C^{9a}, $^3J_{HCCC9a}$ 10.8-11.0, $^3J_{HCCC9a}$ 10.0-10.5, $^2J_{POC9a}$ 8.3, $^2J_{HC9C9a}$ 3.6); 136.99 br. d. d (s) (C^8, $^1J_{HC8}$ 162.8, $^3J_{HC6CC8}$ 9.5); 134.71 t. d. t (d) (C^{13}, $^3J_{HC11,15CC13}$ 7.3-7.5, $^5J_{PC3CCCC13}$ 3.8, $^2J_{HC12,14C13}$ 3.5-3.6); 133.50 d. t. d (d) (C^{27}, $^1J_{HC27}$ 161.8, $^3J_{HC25,29CC27}$ 7.8, $^4J_{PC24CCC27}$ 2.7); 132.66 d. d (s) (C^6, $^1J_{HC6}$ 166.2, $^3J_{HC8CC6}$ 8.2); 132.61 br. d. m (d) (C^{25}, $^1J_{HC25}$ 165.3, $^2J_{PC24C25}$ 9.7); 131.72 very br. d (very br. s) (C^{11}, $^1J_{HC11}$ 165.0-166.0); 130.37 t. d. d (d) (C^{10}, $^3J_{HC12,14CC10}$ 8.0, $^2J_{HC3C10}$ 8.0, $^2J_{PC3C10}$ 3.1); 129.17 br. d. d. d (d) (C^{12}, $^1J_{HC12}$ 164.4, $^3J_{HC14CC12}$ 4.0, $^4J_{PC3CCC12}$ 2.4); 127.96 d. d. m (d) (C^{26}, $^1J_{HC26}$ 161.4, $^3J_{PC24CC26}$ 13.6, $^3J_{HC28CC26}$ 5.0-6.0, $^2J_{HC25C26}$ 3.4, $^2J_{HC27C26}$ 3.4); 127.07 br. d. d (br. s) (C^7, $^1J_{HC7}$ 164.1, $^3J_{HC9CC7}$ 8.0); 126.77 m (d) (C^{5a}, $^3J_{POC9aC5a}$ 2.3); 126.46 br. d. m (d) (C^{24}, $^1J_{PC24}$ 143.0, $^3J_{HC26,28CC24}$ 7.9, $^3J_{HC3PC24}$ 4.8-5.0); 124.30 d. d. d (d) (C^9, $^1J_{HC9}$ 167.5, $^3J_{HC7CC9}$ 7.9, $^3J_{POC9aC9}$ 3.3); 113.57 t. t. m (t. t) (CF_2, $^1J_{FC}$ 248.0, $^2J_{FCC}$ 27.5); 113.63 t. t. m (t. t) (CF_2, $^1J_{FC}$ 248.1, $^2J_{FCC}$ 27.5); 109.0 t. d. t. t (t. t) (CHF_2, $^1J_{FC}$ 251.1, $^1J_{HC}$ 192.7, $^2J_{FCC}$ 36.0, $^3J_{H2CCC}$ 3.2); 109.07 t. d. t. t (t. t) (CHF_2, $^1J_{FC}$ 250.1, $^1J_{HC}$ 192.6, $^2J_{FCC}$ 36.0, $^3J_{H2CCC}$ 3.2); 74.66 br. d (s) (C^4, $^2J_{HC3C4}$ 5.2); 61.40 t. t (t) (OCH_2, $^1J_{HC}$ 152.4, $^2J_{FCC}$ 30.0); 61.55 t. t (t) (OCH_2, $^1J_{HC}$ 152.5, $^2J_{FCC}$ 30.0); 50.59 d. d. t (d) (C^3, $^1J_{HC3}$ 127.7, $^1J_{PC3}$ 83.0, $^3J_{HC11CC3}$ 3.5). ^{13}C NMR (acetone-d_6, 150.9 MHz) δ: 188.27 br. d. d. d (s) (C^5, $^3J_{HC3CC5}$ 5.0, $^3J_{HC6CC5}$ 4.6, $^4J_{HC7CCC5}$ 1.7); 164.62 d. d. t (d) (COO, $^3J_{PCC4C}$ 8.7, $^3J_{HC3CC}$ 8.7, $^3J_{HCOC}$ 3.3); 164.53 d. t (d) (COO, $^3J_{PC3CC}$

12.3, $^{3}J_{HCOC}$ 2.8, $^{3}J_{HC3CC}$ 0); 148.52 d. d. d. d. d (d) (C^{9a}, $^{3}J_{HCCC9a}$ 10.5, $^{3}J_{HCCC9a}$ 8.7, $^{2}J_{POC9a}$ 8.1, $^{2}J_{HC9C9a}$ 4.2, $^{4}J_{HC7CCC9a}$ 1.8); 136.77 br. d. d (s) (C^{8}, $^{1}J_{HC8}$ 169.9, $^{3}J_{HC6CC8}$ 9.0); 133.83 t. d. t (d) (C^{13}, $^{3}J_{HC11,15CC13}$ 8.5, $^{5}J_{PC3CCCC13}$ 3.6, $^{2}J_{HC12,14C13}$ 3.5-3.6); 133.26 d. t. d (d) (C^{27}, $^{1}J_{HC27}$ 161.5, $^{3}J_{HC27CC25}$ 7.8, $^{4}J_{PC24CCC27}$ 2.8); 132.54 d. d. d. d (d) (C^{25}, $^{1}J_{HC25}$ 165.6, $^{2}J_{PC24C25}$ 9.5, $^{3}J_{HC29CC25}$ 7.2-7.3, $^{3}J_{HC27CC25}$ 7.2); 132.32 br. d. d (d) (C^{6}, $^{1}J_{HC6}$ 166.8, $^{3}J_{HC8CC6}$ 8.4, $^{4}J_{POC9aCC6}$ 0.6); 132.30 very br. d (very br. s) (C^{11}, $^{2}J_{HC11}$ 165.0-166.0); 131.37 d. t. d (d) (C^{10}, $^{3}J_{HC12,14CC10}$ 8.1, $^{2}J_{HC3C10}$ 8.1, $^{2}J_{PC3C10}$ 3.3); 128.72 d. d. d (d) (C^{12}, $^{1}J_{HC12}$ 166.4, $^{3}J_{HC14CC12}$ 5.4, $^{4}J_{PC3CCC12}$ 2.5); 127.87 br. d. d. d (d) (C^{26}, $^{1}J_{HC26}$ 163.0, $^{3}J_{PC24CC26}$ 13.7, $^{3}J_{HC28CC26}$ 6.9-7.0); 127.19 m br. (s) (C^{5a}); 126.79 br. d. d (d) (C^{7}, $^{1}J_{HC7}$ 164.4, $^{3}J_{HC9CC7}$ 8.4, $^{5}J_{POC9aCCC7}$ 0.9); 126.79 br. d. t (d) (C^{24}, $^{1}J_{PC24}$ 141.9, $^{3}J_{HC26,28CC24}$ 7.3-7.4); 124.30 d. d. d. d. d (d) (C^{9}, $^{1}J_{HC9}$ 166.3, $^{3}J_{HC7CC9}$ 7.9-8.0, $^{3}J_{POC9aC9}$ 3.3, $^{2}J_{HC8C9}$ 1.2, $^{4}J_{HC6CCC9}$ 1.2); 115.66 t. t. m (t. t) (CF_2, $^{1}J_{FC}$ 250.2, $^{2}J_{FCC}$ 26.7); 115.70 t. t. m (t. t) (CF_2, $^{1}J_{FC}$ 250.2, $^{2}J_{FCC}$ 26.6); 109.31 t. d. t. t (t. t) (CHF_2, $^{1}J_{FC}$ 248.8, $^{1}J_{HC}$ 195.2, $^{2}J_{FCC}$ 34.3, $^{3}J_{H2CCC}$ 2.0-2.1); 109.11 t. d. d. d. t (t. d. d) (CHF_2, $^{1}J_{FC}$ 251.2, $^{1}J_{HC}$ 195.0, $^{2}J_{FCC}$ 32.7, $^{2}J_{FCC}$ 32.7, $^{3}J_{H2CCC}$ 2.0-2.1); 74.49 br. d (d) (C^{4}, $^{2}J_{HC3C4}$ 5.3, $^{2}J_{PC3C4}$ 1.2); 61.65 br. t. t (t) (OCH_2, $^{1}J_{HC}$ 152.6, $^{2}J_{FCC}$ 28.2); 61.68 d. br. t. d. d (d) (OCH_2, $^{1}J_{HC}$ 152.9, $^{2}J_{FCC}$ 31.4, $^{2}J_{FCC}$ 30.2); 49.69 d. d. t (d) (C^{3}, $^{1}J_{PC3}$ 82.6, $^{1}J_{HC3}$ 129.1, $^{3}J_{HC11CC3}$ 4.0-4.1). ^{19}F NMR ($CDCl_3$) δ_F: –124.92 and –124.97 two m (CF_2, *2F*, $^{3}J_{HCCF}$ 12.5-13.5, $^{3}J_{HCCF}$ 4.0); –139.05 and –138.84 two br. m (CHF_2, *2F*, $^{2}J_{FCH}$ 53.0); –139.05 and –138.70 two br. m (CHF_2, *2F*, $^{2}J_{FCH}$ 53.0). ^{31}P-{^{1}H} NMR ($CDCl_3$) δ_P: 38.9 ppm.

3-(4-Bromophenyl)-4,4-bis(2,2,3,3-tetrafluoropropoxycarbonyl)-2-oxo-2-phenylbenzo[*f*]-1,2-oxaphosphepine (3k). Yield 90 % (120.3 mg, 16 mmol), m. p. 115–117°C. Calcd for $C_{29}H_{20}BrF_8O_7P$: C, 46.84; H, 2.69; P, 4.17; Br, 10.76. Found: C, 46.72; H, 2.88; P, 4.21; Br, 10.55. IR (Nujol): 1776, 1704, 1684, 1600, 1576, 1456, 1392, 1384, 1376, 1280, 1264, 1236, 1168, 1136, 1008, 968, 928, 896, 864, 848, 816, 768, 748, 692, 656, 536, 512 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.23 d. d (H^{6}, *1H*, $^{3}J_{H6CCH7}$ 8.0, $^{4}J_{H8CCCH6}$ 1.7); 7.75 d. d. d (H^{8}, *1H*, $^{3}J_{H8CCH9}$ 8.1, $^{3}J_{H7CCH8}$ 7.3, $^{4}J_{H8CCCH6}$ 1.7); 7.58 m (H^{27}, *1H*, $^{3}J_{H26CCH27}$ 7.1, $^{4}J_{H25CCCH27}$ 1.7, $^{5}J_{PCCCCH27}$ 1.6); 7.50 d. d. d. d (H^{7}, *1H*, $^{3}J_{H6CCH7}$ 8.0, $^{3}J_{H7CCH8}$ 7.3, $^{4}J_{H7CCCH9}$ 1.1, $^{6}J_{POCCCCH7}$ 1.1); 7.38-7.33 m (H^{12}, H^{11}, H^{25}, H^{26}, *4H*); 7.26 d. d. d (H^{9}, *1H*, $^{3}J_{H8CCH9}$ 8.1, $^{4}J_{POCCH9}$ 1.3; $^{4}J_{H9CCH7}$ 1.1); 5.68 t. t (CHF_2, *1H*, $^{2}J_{HCF}$ 52.9, $^{3}J_{FCCH}$ 3.9); 5.58 t. t (CHF_2, *1H*, $^{2}J_{HCF}$ 52.9, $^{3}J_{FCCH}$ 3.9); 4.60 d (PCH, *1H*, $^{2}J_{PCH}$ 25.9); 4.77 br. d. t. t (OCH_B, *1H*, B-part of ABX_3Y_2 spectrum, $^{3}J_{HBCCF}$ 12.5, $^{2}J_{HAHB}$ 12.5, $^{4}J_{FCCCHB}$ 1.3); 4.49 br. d. t. t (OCH_A, *1H*, A-part of ABX_3Y_2 spectrum, $^{3}J_{HACCF}$ = $^{2}J_{HAHB}$ 12.5, $^{4}J_{FCCCHA}$ 1.3); 4.48 d. t. t (OCH_B, *1H*, B-part of ABX_3Y_2 spectrum,$^{3}J_{HBCCF}$ = $^{2}J_{HAHB}$ 12.3, $^{4}J_{FCCCHB}$ 1.3); 4.15 d. t. t (OCH_A, *1H*, A-part of ABX_3Y_2 spectrum, $^{3}J_{HACCF}$ = $^{2}J_{HAHB}$ 12.3, $^{4}J_{FCCCHA}$ 1.3). ^{1}H NMR (acetone-D_6, 600 MHz) δ: 8.18 d. d (H^{6}, *1H*, $^{3}J_{H6CCH7}$ 8.0, $^{4}J_{H8CCCH6}$ 1.6-1.7); 7.83 d. d. d (H^{8}, *1H*, $^{3}J_{H8CCH9}$ 8.0, $^{3}J_{H7CCH8}$ 7.4, $^{4}J_{H6CCCH8}$ 1.7-1.8); 7.60 m (H^{27}, *1H*); 7.56 d. d. d. d (H^{7}, *1H*, $^{3}J_{H6CCH7}$ 8.0, $^{3}J_{H7CCH8}$ 7.4, $^{4}J_{H7CCCH9}$ 1.0, $^{6}J_{POCCCCH7}$ 0.8-1.0); 7.36 d. d. d (H^{9}, *1H*, $^{3}J_{H8CCH9}$ 8.0, $^{4}J_{POCCH9}$ 1.6, $^{3}J_{H7CCCH9}$ 1.0); 7.39-7.42 m (H^{12}, H^{11}, H^{25}, H^{26}, *4H*); 6.29 br. t. t (CHF_2, *2F*, $^{2}J_{HCF}$ 52.3, $^{3}J_{HCCF}$ 5.5-5.6, $^{3}J_{HCCF}$ 5.1-5.2); 6.07 t. t (CHF_2, *1H*, $^{2}J_{HCF}$ 52.5, $^{3}J_{FCCH}$ 4.6-4.7); 4.94 d (PCH, *1H*, $^{2}J_{PCH}$ 25.5); 4.92 br. t. d (OCH_AH_M, *1H*, M-part of AMX_3 spectrum, $^{3}J_{HMCCF}$ = $^{2}J_{HAHM}$ 13.1); 4.72 br. t. d (CH_A, *1H*, A-part of AMX_3 spectrum, $^{3}J_{HACCF}$ = $^{2}J_{HAHM}$ 13.1); 4.58 and 4.23 two br. d. t. d (OCH_AH_M, *2H*, A- and M-parts of $AMNX_3Y_2$ spectrum, $^{3}J_{HACCF}$ = $^{3}J_{HMCCF}$ 12.6, $^{2}J_{HAHM}$ 12.6-12.8, $^{4}J_{HCCCH}$ 1.8, $^{4}J_{FCCCH}$ 0.8-0.9). ^{13}C NMR ($CDCl_3$, 100.6

MHz) δ: 187.82 br. d. d (s) (C^5, $^3J_{HC3CC5}$ 5.0, $^3J_{HC6CC5}$ 4.5,); 164.40 d. d. t (d) (COO, $^3J_{HC3CC}$ 8.5, $^3J_{PC3CC}$ 8.2, $^3J_{HCOC}$ 3.3); 164.20 d. t (d) (COO, $^3J_{PCC4C}$ 13.1, $^3J_{HCOC}$ 2.7); 148.34 d. d. d. d. d (d) (C^{9a}, $^3J_{HCCC9a}$ 11.1, $^3J_{HCCC9a}$ 8.2, $^3J_{POC9a}$ 8.2, $^2J_{HC9C9a}$ 4.0); 136.90 br. d. d (s) (C^8, $^1J_{HC8}$ 163.0, $^3J_{HC6CC8}$ 9.3); 133.43 d. t. d (d) (C^{27}, $^1J_{HC27}$ 161.5, $^3J_{HC25CC27}$ 8.6, $^4J_{PC24CCC27}$ 2.8); 132.55 br. d. d (s) (C^6, $^1J_{HC6}$ 166.2, $^3J_{HC8CC6}$ 7.6); 132.53 d. m (d) (C^{25}, $^1J_{HC25}$ 164.0, $^2J_{PC24C25}$ 9.7); 132.04 d. d. d (d) (C^{12}, $^1J_{HC12}$ 165.7, $^3J_{HC14CC12}$ 5.2, $^4J_{PC3CCC12}$ 2.5); 131.99 very br. d. m (very br. s) (C^{11}, $^2J_{HC11}$ 165.0-166.0); 130.88 d. t. d (d) (C^{10}, $^2J_{HC3C10}$ 7.8-7.9, $^3J_{HC12CC10}$ 7.8-7.9, $^2J_{PC3C10}$ 3.1); 127.88 d. d. m (d) (C^{26}, $^1J_{HC26}$ 161.3, $^3J_{PC24CC26}$ 13.8, $^3J_{HC28CC26}$ 5.8); 126.97 br. d. d (s) (C^7, $^1J_{HC7}$ 164.1, $^3J_{HC9CC7}$ 7.9); 126.71 m (s) (C^{5a}); 126.36 br. d. m (d) (C^{24}, $^1J_{PC24}$ 142.9, $^3J_{HC26,28CC24}$ 6.3, $^3J_{HC3PC24}$ 5.4); 124.18 br. d. d. d (d) (C^9, $^1J_{HC9}$ 165.6, $^3J_{HC7CC9}$ 7.4, $^3J_{POC9aC9}$ 3.4); 122.68 t. d. t (d) (C^{13}, $^3J_{HC11CC13}$ 10.6, $^5J_{PC3CCCC13}$ 4.1, $^3J_{HC12CC13}$ 3.6-3.7); 113.56 t. t. d. t (t. t) (CF_2, $^1J_{FC}$ 251.0, $^2J_{FCC}$ 28.3, $^2J_{HCC}$ 4.2-4.3, $^2J_{H2CC}$ 3.2); 113.50 t. t. d. t (t. t) (CF_2, $^1J_{FC}$ 250.6, $^2J_{FCC}$ 27.6, $^2J_{HCC}$ 4.2-4.3, $^2J_{H2CC}$ 3.2); 108.99 t. d. t. t (t. t) (CHF_2, $^1J_{FC}$ 250.3, $^1J_{HC}$ 193.0, $^2J_{FCC}$ 35.8, $^3J_{H2CCC}$ 1.1-1.2); 108.92 t. d. t. t (t. t) (CHF_2, $^1J_{FC}$ 250.5, $^1J_{HC}$ 192.6, $^2J_{FCC}$ 36.0, $^3J_{H2CCC}$ 1.1-1.2); 74.51 br. d (s) (C^4, $^2J_{HC3C4}$ 5.1); 61.46 t. t (t) (OCH_2, $^1J_{HC}$ 151.9, $^2J_{FCC}$ 30.2); 61.32 t. t (t) (OCH_2, $^1J_{HC}$ 152.7, $^2J_{FCC}$ 29.8); 50.58 d. d. t (d) (C^3, $^1J_{HC3}$ 127.6, $^1J_{PC3}$ 82.9, $^3J_{HC11CC3}$ 3.1). ^{13}C NMR (acetone-d_6, 150.9 MHz) δ: 188.34 br. d. d (s) (C^5, $^3J_{HC3CC5}$ 5.6-5.8, $^3J_{HC6CC5}$ 4.5,); 164.58 d. d. t (d) (COO, $^3J_{PC3CC}$ 8.9, $^3J_{HC3CC}$ 8.9, $^3J_{HCOC}$ 3.0-3.1); 164.50 br. d. t (d) (COO, $^3J_{PCC4C}$ 12.5, $^3J_{HCOC}$ 2.5); 148.48 d. d. d. d. d (d) (C^{9a}, $^3J_{HCCC9a}$ 11.3, $^3J_{HCCC9a}$ 9.1, $^2J_{POC9a}$ 8.1 ; $^2J_{HC8C9a}$ 3.6, $^4J_{H7CCC9a}$ 1.6); 136.69 br. d. d (s) (C^8, $^1J_{HC8}$ 164.1, $^3J_{HC6CC8}$ 9.3); 133.22 d. t. d (d) (C^{27}, $^1J_{HC27}$ 159.6, $^3J_{HC25CC27}$ 8.6, $^4J_{PC24CCC27}$ 3.0); 132.31 br. d. d (d) (C^6, $^1J_{HC6}$ 166.0, $^3J_{HC8CC6}$ 8.4, $^4J_{POC9aCC6}$ 0.9); 132.56 d. d. d. d. d. d (d) ($C^{25,}$ $^1J_{HC25}$ 164.2, $^2J_{PC24C25}$ 9.3, $^3J_{HC25CC29}$ 8.2 ; $^3J_{HC27CC25}$ 5.5 ; $^2J_{HC26C25}$ 1.6 ; $^4J_{HC28CCC25}$ 1.6); 131.92 m (d) (C^{10}, $^2J_{PC3C10}$ 3.3); 131.68 d. d. d (d) (C^{12}, $^1J_{HC12}$ 168.3, $^3J_{HC14CC12}$ 5.3-5.4, $^4J_{PC3CCC12}$ 2.7); 131.5-132.5 very br. d. m (very br. s) (C^{11}); 127.85 d. d. d (d) (C^{26}, $^1J_{HC26}$ 162.8, $^3J_{POC24CC26}$ 13.7, $^3J_{HC26CC28}$ 5.4); 126.75 br. d. d (d) (C^7, $^1J_{HC7}$ 164.9, $^3J_{HC9CC7}$ 8.1 ; $^5J_{POC9aCCC7}$ 1.0); 127.29 m (s) (C^{5a}); 127.25 d (d. d. t) (C^{24}, $^1J_{PC24}$ 141.9, $^3J_{HC3PC24}$ 4.7-4.8, $^3J_{HC26CC24}$ 4.5-4.6); 124.28 d. d. d. d. d (d) (C^9, $^1J_{HC9}$ 166.9, $^3J_{HC7CC9}$ 7.8, $^3J_{POC9aC9}$ 3.3, $^2J_{HC8C9}$ 1.6, $^4J_{HC6CCC9}$ 1.6); 121.91 t. d. t (d) (C^{13}, $^3J_{HC11CC13}$ 10.8, $^5J_{PC3CCCC13}$ 4.0, $^3J_{HC12CC13}$ 3.5-3.6); 114.04 t. t. d. t (t. t) (CF_2, $^1J_{FC}$ 250.1, $^2J_{FCC}$ 27.5, $^2J_{HCC}$ 4.0-4.2, $^2J_{H2CC}$ 3.0-3.2); 114.0 t. t. d. t (t. t) (CF_2, $^1J_{FC}$ 250.1, $^2J_{FCC}$ 27.5, $^2J_{HCC}$ 4.0-4.2, $^2J_{H2CC}$ 3.0-3.2); 109.29 t. d. t (t. t) (CHF_2, $^1J_{FC}$ 249.0, $^1J_{HC}$ 195.4, $^2J_{FCC}$ 34.2); 109.08 t. d. t (t. t) (CHF_2, $^1J_{FC}$ 248.2, $^1J_{HC}$ 196.1, $^2J_{FCC}$ 32.4); 74.38 br. d (d) (C^4, $^2J_{HC3C4}$ 5.4, $^2J_{PC3C4}$ 1.2); 61.68 t. t (t) (OCH_2, $^1J_{HC}$ 152.9, $^2J_{FCC}$ 30.8); 61.64 t. t (t) (OCH_2, $^1J_{HC}$ 152.7, $^2J_{FCC}$ 28.2); 49.75 d. d. t (d) (C^3, $^1J_{HC3}$ 129.1, $^1J_{PC3}$ 82.1, $^3J_{HC11CC3}$ 3.0-3.1). ^{19}F NMR ($CDCl_3$) δ_F: –124.95 and –124.90 two m ($2CF_2$, *4F*, $^3J_{FCCH}$ 12.5-13.0, $^3J_{FCCH}$ 3.9); –139.10 and –138.80 two m ($2CHF_2$, *4F*, two AB-parts of $ABMN_2X_2$ systems, $^2J_{HCF}$ 52.9-53.0). ^{31}P-{^{1}H} NMR ($CDCl_3$) δ_P: 38.9 ppm.

Supplementary Materials Available

Crystallographic data (excluding structural factors) for the structures (**3a**, **c**, **d**, **g**, **j**) reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC 251677-251681 – respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0) 1223-336033 or e-mail: deposit@ccdc.cam.ac.uk]. See Page 170

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