Stereoselective PCO/POC-Rearrangement of P−C-Cage Phosphorane in the Reaction of 4,5-Dimethyl-2-(2-oxo-1,2-diphenyl)ethoxy-1,3,2-dioxaphospholane with Hexafluoroacetone

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ⓢ Supporting Information

ABSTRACT: Interaction of 4,5-dimethyl-2-(2-oxo-1,2-diphenyl)ethoxy-1,3,2-dioxaphospholane, bearing a carboxyl group in the γ-position with respect to the phosphorus atom and obtained from d,l-butanediol, with hexafluoroacetone (CCl₄, −40 °C) leads to the simultaneous formation of regio- and stereoisomeric cage-like phosphoranes with phosphorus−carbon and phosphorus−oxygen bonds with a high stereo-selectivity (>95%), whose structure was determined by 1D and 2D NMR spectroscopy and XRD. When stored as a solution in dichloromethane for one month, the PCO-isomer rearranges into the thermodynamically more stable POC-isomer of the cage-like phosphorane. Mild hydrolysis of the PCO/POC-isomers proceeds with a high chemoselectivity and leads to the formation of P(IV)-dioxaphospholane derivatives. Acidic hydrolysis of the POC-isomer leads to the formation of an oxirane derivative with an unexpectedly high stereoselectivity (>95%). DFT calculations (using the PBE functional) allowed us to obtain structures and energies of the initial phospholane, reaction products (PCO/POC-isomers), and an intermediate P(V)-oxaphosphirane.
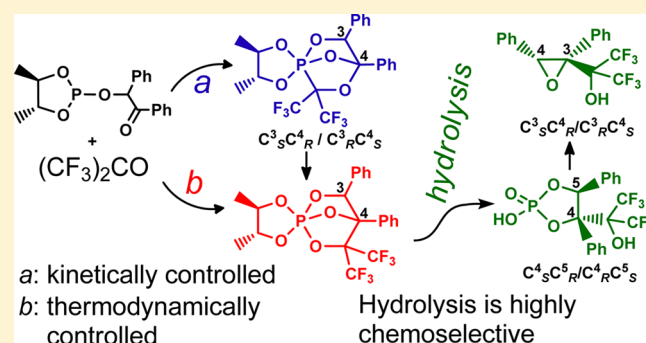
INTRODUCTION

Compounds of pentacoordinate phosphorus play an ultimate role in nature because they appear as intermediates or transition states in the phosphoryl group transport reactions, hydrolysis of RNA and phosphorus acid esters,[1−4] formation and phosphorylation of peptides,[5−7] and other catalytic processes.[8−10] The lifetime of a pentacoordinate intermediate of this type is relatively long, and it experiences a configuration stereo-isomerization (pseudorotation) leading to formation of an equilibrium mixture of several stereoisomers, which has a large influence on the stereochemical result and proportion of the products of chemical reactions.[11−14]

Compounds of pentacoordinate phosphorus are also intermediates in reactions of nucleophilic substitution at tetracoordinate phosphorus,[15,16] among which such important processes in organic synthesis as the Appel reaction[17,18] and Mitsunobu reaction[19,20] are worth noting. Therefore, much interest is paid to the questions of synthesis, chemical transformations, structure, and configuration stability of phosphoranes,[21−23] including molecular-level quantum chemical calculations of structure and properties.[24−28] Recently we proposed and developed a new approach to synthesis of compounds of pentacoordinate phosphorus with polycyclic (cage-like) structure containing several chiral centers.[29−34] It is based on interaction of derivatives of tricoordinated phosphorus, which have the exocyclic substituents containing a carbonyl or imino group in γ- or δ-position to the phosphorus atom, with systems containing activated multiple bonds (carbonyl compounds, alkynes). As carbonyl compounds, we used chloral, trifluoropyruvic and mesoxalic acid ethyl esters, and hexafluoroacetone. In all cases, cage phosphoranes with a phosphorus−carbon bond are formed. Scheme 1 illustrates this approach on the example of the reactions of benzodioxaphosphole 1 derivatives, which proceed with appearance of P−C phosphoranes 2−7. In all cases, bipolar ions containing the P⁺−C−O⁻ fragment arise followed by an attack of the alkoxide anion at the exocyclic substituent. This leads to formation of a longer bipolar anion, which is stabilized by cyclization into a cage phosphorane.

In these cases, cage phosphoranes that contained a P−O bond (products of a reaction similar to the phosphonate−phosphate rearrangement P−C−O → P−O−C) were not found. This rearrangement is readily performed in reactions of chloral,[35] hexafluoroacetone, and other activated carbonyl compounds with typical derivatives of P(III) (see refs 36 and 37).

**Scheme 1. Synthesis of Cage Phosphoranes Bearing P−C Bond**
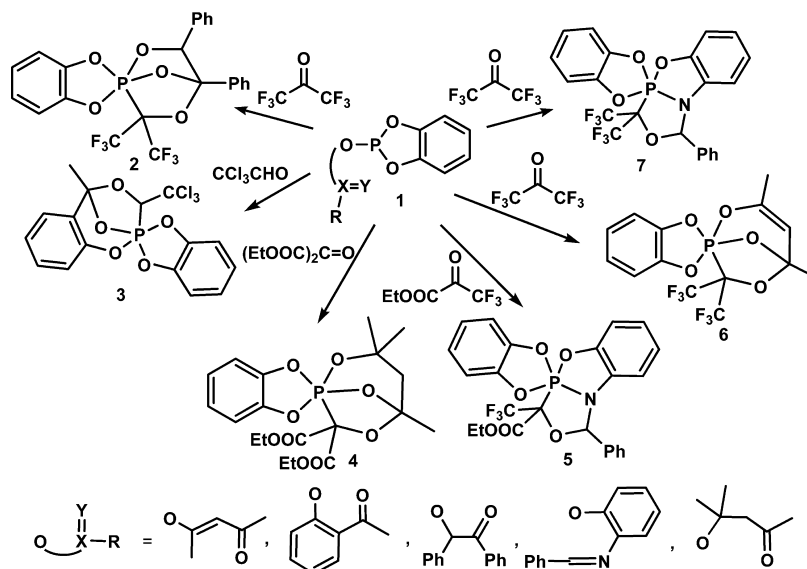
■ RESULTS AND DISCUSSION

Since the PCO/POC-rearrangement in the series of derivatives of tetracoordinate phosphorus is facilitated by electron-donor substituents at the phosphorus atoms,[38,39] we performed the reaction between hexafluoroacetone and 4,5-dimethyl-2-(2-oxo-1,2-diphenyl)ethoxy-1,3,2-dioxaphospholane **8**. Compound **8** contains a less electron-accepting cycle compared with the benzodioxaphosphol cycle, which still stabilizes the pentacoordinate state of phosphorus. Compound **8** was derived from the d,l-form of 2,3-butanediol as a mixture of two diastereoisomers in the ratio of 1:1. It turned out that the reaction of phosphite **8** with hexafluoroacetone in an inert atmosphere (CCl_4, −40 °C) proceeds with the formation of two regioisomeric phosphorane compounds **9** and **10** (Scheme 2), which are characterized by a group of close signals in the high-field region of the ^{31}P-$\{^1H\}$ NMR spectrum (162.0 MHz, CCl_4): two broadened quartets with δ_P = −22.8 and −24.2 ppm ($^3J_{PCCF}$ = 5.6 Hz) in the ratio of 1.1:0.8 (d_1 and d_2) and two singlets with δ_P = −23.9 and −24.0 ppm in the ratio of 1:1 (d_1 and d_2). The ratio of the summary integral intensities of the two quartets and the two singlets is 2:1; that is, the compound **9** showing quartets in the ^{31}P-$\{^1H\}$ NMR spectrum dominates in the solution. They were obtained by crystallization from CCl_4 in the ratio of 1:9 (d_1/d_2). Their structures were studied by one- and two-dimensional NMR spectroscopy (experiments ^1H, ^1H-$\{^{31}P\}$, ^{31}P, ^{31}P-$\{^1H\}$, ^{31}P-$\{^{19}F\}$, ^{19}F, ^{19}F-$\{^{31}P\}$, ^{13}C, ^{13}C-$\{^1H\}$, ^{13}C-$\{^{19}F\}$, ^{13}C-$\{^{31}P\}$, ^{13}C-$\{^{19}F,^{31}P\}$, ^{13}C-$\{^{19}F,^2H\}$, ($^{13}C,^{19}F$)-HMBC, ($^{13}C,^1H$)-HMBC, ($^{13}C,^{19}F$)-HSQC, and ($^{13}C,^1H$)-HSQC), IR spectroscopy, and EI mass-spectrometry. The EI mass spectrum contains a peak of a molecular ion corresponding to the addition product of the composition 1:1 (496 $[M]^{+\bullet}$). With the aid of the ^{31}P-$\{^{19}F\}$ experiment, scalar couplings of $^3J_{POCH}$ = 18.1 Hz for the dominant form (d_1) and 17.4 Hz for the minor form (d_2) were measured; these values agree with corresponding line splittings in the ^1H NMR spectrum. Information on chemical shifts of ^1H, ^{13}C, ^{31}P, and ^{19}F for compound **9** is summarized in Table 1 and Supporting Information. Figure 1 shows different variants of ^{31}P NMR spectra ($CDCl_3$) for the diastereoisomer mixture obtained by an additional crystallization from pentane in the ratio of 3:2 (d_1/d_2).

The key fragment P−$C(CF_3)_2$ was unambiguously identified using 2D spectra ($^{13}C,^{19}F$)-HMBC and ($^{13}C,^{19}F$)-HSQC obtained for the mixture of diastereoisomers of **9** in the ratio of 1:9. Signals of the groups $C^{23,24}F_3$ in proton-decoupled and coupled ^{13}C NMR spectra are quartets at δ_C = 121.3 and 122.4 ppm ($^1J_{CF} \approx$ 285 Hz). The signal of quaternary atom C^6 at $\delta \approx$ 77 ppm is a complex multiplet (due to spin−spin coupling with ^{19}F and ^{31}P nuclei) and overlaps with the solvent signal ($CDCl_3$). Step-by-step recording of spectra with decoupling in one (^{13}C-$\{^{19}F\}$) and two channels (^{13}C-$\{^{19}F\}$-$\{^{31}P\}$) allowed observation of a doublet with $^1J_{CP} \approx$ 150 Hz at δ_C = 77.15 ppm in the former spectrum and a singlet in the latter spectrum. It was attributed to the atom C^6 in the dominant isomer d_1. The weak signal of the minor form appears in the same region (δ_C = 77.3 ppm).

Vicinal proton−proton and phosphorus−proton scalar couplings from ^1H NMR spectra are known to provide the main information on the structure of the heterocycle in 1,3-dioxolanes and 1,3,2-dioxaphospholanes.[40,41] In rigid *envelope*-type conformations, they should be noticeably different; in the case of conformational equilibrium (alternating escape of the cycle members from its plane) and pseudorotation at the phosphorus atom, the scalar couplings should become similar due to averaging. In the ^1H NMR spectrum ($CDCl_3$, 15 °C) of **9**, the signals of protons H^7 and H^8 in the diastereoisomer d_1 are poorly resolved multiplets at δ = 4.24 and 4.12 ppm ($^3J_{H^7H^8} \approx$ 3.5 Hz and $^3J_{POCH^{7,8}}$ = 3.1 Hz). If we assume that the five-membered cycle in the pseudorotation process takes all *envelope* shapes with equal populations, then the average value of $^3J_{HH}$ should be ∼5.4 Hz.[40,41] Decrease in $^3J_{HH}$ to 3.5 Hz and inequality of chemical shifts δ ($H^{7,8}$) gives evidence of changes and redistribution of qualitative and quantitative compositions of the forms involved in the conformational equilibrium and in the pseudorotation process. The presence of the conformational equilibrium for **9** in solution was also confirmed by broadening of the signals of C^7 and C^8 carbons at δ_C = 77.46 and 74.75 ppm in the ^{13}C-$\{^1H\}$ and ^{13}C NMR spectra. Analysis of dynamic ^{19}F NMR spectra shows that at 30 °C the CF_3 groups are inequivalent, and one of them has a rather broad signal in each of the conformers while the other is a well resolved quartet. Upon lowering the temperature to −5 °C, all signals become broadened,

Scheme 2. Reaction of Phospholane 8 with Hexafluoroacetone and Diagram of Relative Energies of Molecules A, 8, 9, and 10[a]
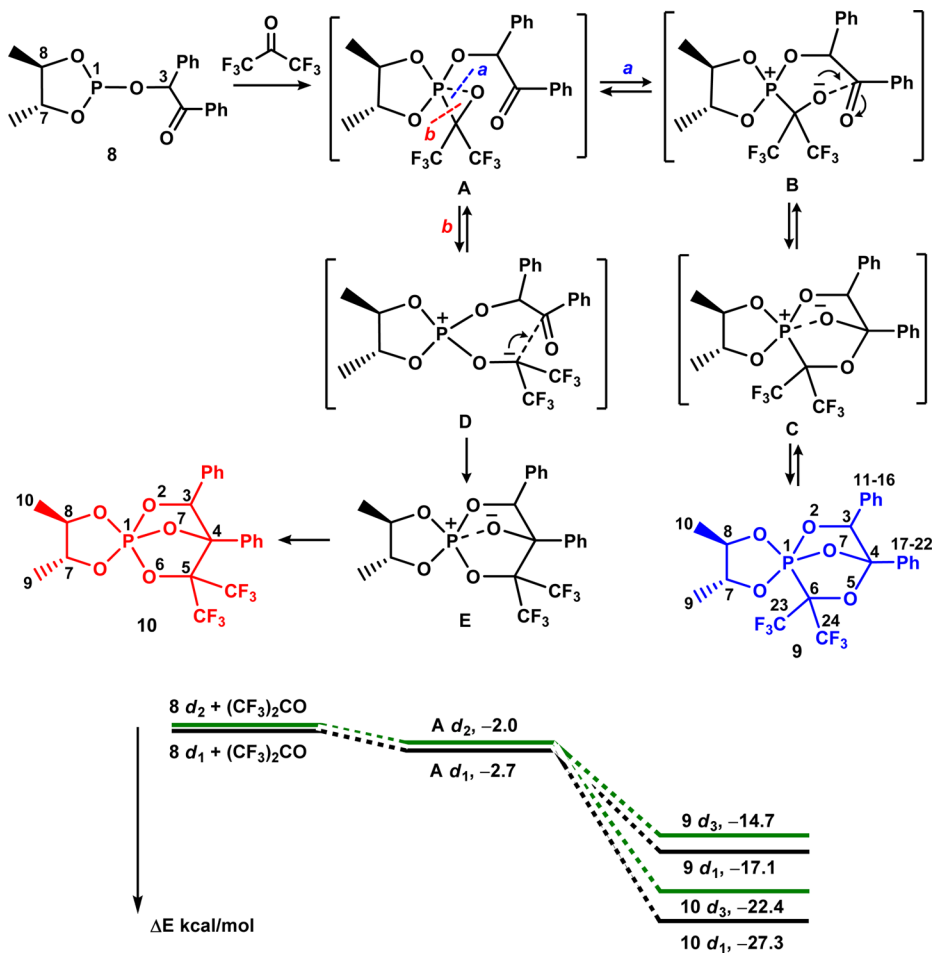
[a]Hereinafter the configuration of C^7 and C^8 atoms for one of the enantiomers of compound **8** is shown for clarity. The last one is a mixture of two diastereoisomers with configurations $C^3_R C^4_R C^6_S / C^3_S C^4_S C^6_R$ and $C^3_R C^4_R C^6_R / C^3_S C^4_S C^6_S$. The same numbering of the atoms in structures **8–10** is shown for convenience of discussion.

Table 1. Chemical Shifts (CDCl₃, 15°C, ppm) for Diastereoisomers d_1 and d_2 of Phosphorane 9[a]

atom no.	δ		atom no.	δ_C	
	d_1	d_2		d_1	d_2
3	5.53	5.54	3	86.41	87.29
			4	100.75	100.45
			6	77.25	77.36
7/8			7	77.46	77.33
8/7			8	74.75	75.83
9/10	1.51	1.48	9	18.39	18.35
10/9	1.57	1.64	10	17.52	18.32
			11	134.87	135.05
12,16	7.17	7.17	12,16	127.95	127.19
13,15	7.24	7.24	13,15	128.08	128.10
14	7.26	7.26	14	128.79	128.75
			17	132.98	133.06
18,22	7.38	7.38	18,22	125.75	125.64
19,21	7.27	7.27	19,21	128.01	127.99
20	7.31	7.31	20	129.33	129.28
			23	121.43	121.75
			24	122.47	122.31

[a]δ_P −25.05 ppm (d_1), −23.35 ppm (d_2); δ_F − 69.17 and −70.35 (br. q) ppm (d_1), −68.99 and −69.49 (br. q) ppm (d_2).
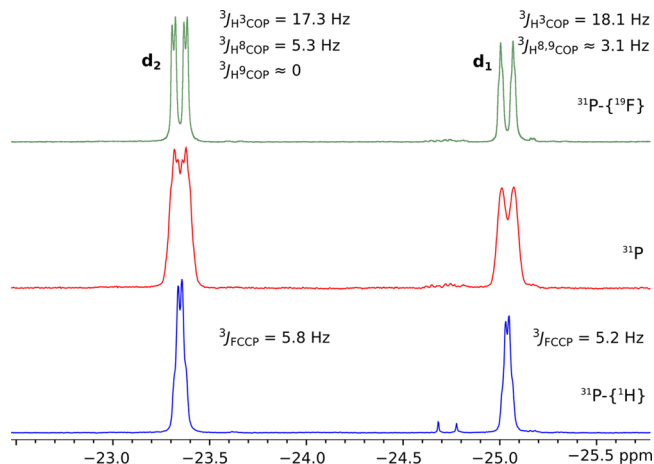

Figure 1. ^{31}P-{^1H}, ^{31}P, and ^{31}P-{^{19}F} NMR spectra (283.4 MHz, CDCl₃, 15 °C) of phosphorane **9**.

which occurs apparently due to retardation of the pseudorotation of the bipyramid formed by the bonds at the phosphorus atom. Signals of the phosphorus atoms in the ^{31}P NMR spectrum are also broadened.

Structure of phosphorane **9** was also confirmed by XRD. The geometry of the molecule in a crystal and atom numbering are
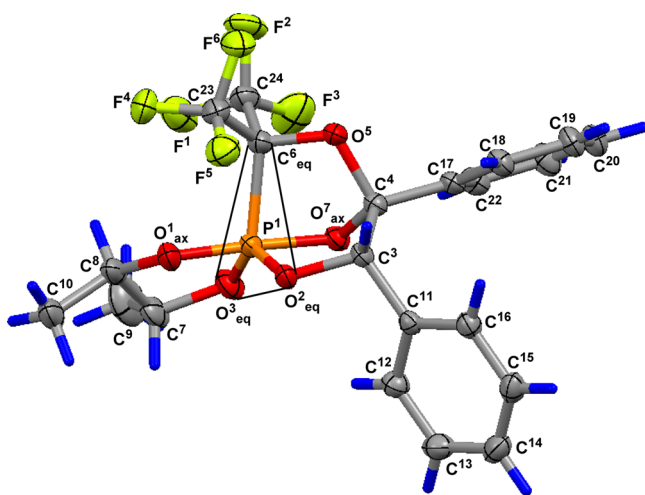
Figure 2. Geometry of molecule **9** in the crystal (diastereoisomer d_1, $P^1{}_SC^3{}_SC^4{}_RC^7{}_RC^8{}_R$-enantiomer). Hereinafter non-hydrogen atoms are shown in view of thermal ellipsoids with a probability of 30%; the trigonal pyramid base is outlined with thin lines. Selected bond lengths (Å) and bond and torsion angles (deg): $P^1–O^1$ 1.621(3), $P^1–O^2$ 1.604(3), $P^1–O^3$ 1.588(3), $P^1–O^7$ 1.707(2), $P^1–C^6$ 1.898(4), $O^1–P^1–O^2$ 89.9(1), $O^1–P^1–O^3$ 92.9(2), $O^1–P^1–O^7$ 177.1(1), $O^1–P^1–C^6$ 98.9(2), $O^2–P^1–O^3$ 132.2(2), $O^2–P^1–O^7$ 89.8(1), $O^2–P^1–C^6$ 101.7(2), $O^3–P^1–O^7$ 85.2(1), $O^3–P^1–C^6$ 124.8(2), $O^7–P^1–C^6$ 84.0(2), $C^9–C^7–C^8–C^{10}$ 91.8(5), $P^1–O^7–C^4–C^{17}$ −173.9(2), $C^{11}–C^3–C^4–C^{17}$ −47.5(4), $O^7–C^4–C^{17}–C^{18}$ −166.6(3).

shown in Figure 2; main geometrical parameters (bond lengths and bond and torsion angles) are listed in the figure caption. Configuration of the chiral atoms is $P^1{}_SC^3{}_SC^4{}_RC^7{}_RC^8{}_R$/$P^1{}_RC^3{}_RC^4{}_SC^7{}_SC^8{}_S$; a small deviation of the phosphorus atom from the $O^2O^3C^6$ plane (by −0.107(1) Å) allows us to conclude that the phosphorus polyhedron in the molecule **9** is a slightly distorted trigonal bipyramid with a planar base (within 0.079(1) Å) containing atoms P^1, O^2, O^3, and C^6. Atoms O^1 and O^7 occupy apical positions and deviate from $P^1O^2O^3C^6$ plane by −1.690(3) and 1.623(2) Å (the $O^1–P^1–O^7$ bond angle is 177.1(1)°). The carbon of one from the trifluoromethyl groups ($C^{24}F_3$) is lying almost exactly in this plane (its deviation from the plane is 0.233(5) Å). The $O^1–P^1–O^3$, $O^1–P^1–O^2$, $O^1–P^1–C^6$, $O^2–P^1–O^7$, $O^7–P^1–C^6$, and $O^3–P^1–O^7$ bond angles are of 82.0(2)−98.9(2)°, pointing at almost regular trigonal bipyramidal configuration of the phosphorus atom. That was further evidenced by the sum of the $O^2–P^1–C^6$, $O^2–P^1–O^3$, and $O^3–P^1–C^6$ bond angles in the base of the trigonal bipyramid, being equal to 358.7(2)°. The equatorial $P^1–O^2$ and $P^1–O^3$ bonds are slightly shorter (1.604(3) and 1.588(3) Å) than axial $P^1–O^1$ and $P^1–O^7$ ones (1.621(3) and 1.707(2) Å). Insignificant distortion of the trigonal bipyramid configuration was also confirmed by a slight discrepancy of the sums of $P^1–O^1$ and $P^1–O^7$ axial bonds lengths (which is 3.328(3) Å) with the $O^1\cdots O^7$ distance (3.327(3) Å). The equatorial $P^1–C^6$ bond length is 1.898(4) Å.

The five-membered dimethyl dioxaphospholane cycle occupies an axial−equatorial position in the trigonal bipyramid (Figure 3) (O^1 being axial, O^3 being equatorial); it has an *envelope* conformation with four atoms, O^1, P^1, O^3, and C^7, lying in one plane (which is planar within 0.012(3) Å) and the C^8 atom deviating from this plane by −0.439(3) Å. C^9 and C^{10} atoms deviate from this plane in different directions by −0.851(7) and 0.152(5) Å (and occupy equatorial positions in the cycle); O^2 and C^6 atoms are located at different sides from the $O^1P^1O^3C^7$
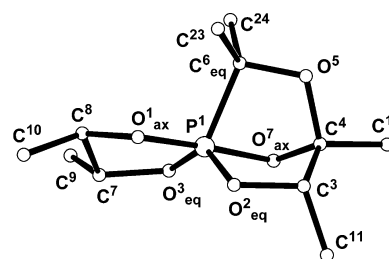

Figure 3. Conformation of the trioxaphosphabicycloheptane scaffold of molecule **9** in the crystal (hydrogen and fluorine atoms are omitted for clarity; C^{11} and C^{17} are shown instead of two phenyls).

plane in the equatorial and axial position in the five-membered cycle (at the distances of 1.213(2) and −1.489(3) Å). O^7 atom also lies nearly in the plane $O^1P^1O^3C^7$ (its deviation is 0.092(3) Å). The $O^1P^1O^3C^7$ planar fragment may also be considered as a part of the more extended $O^1P^1O^3C^7O^7C^4C^{17}$ seven-atom plane (which is planar within 0.043(2) Å). The plane of the phenyl substituent at position 4 is slightly turned with respect to this seven-atom fragment (the $O^7C^4C^{17}C^{22}$ torsion angle is 15.6(4)°). Conformation of the $P^1O^2C^3C^4O^7$ five-membered cycle of the rigid bicycloheptane scaffold of **9** is a slightly distorted *envelope* (Figure 3); it contains a planar within 0.014(3) Å $P^1O^2C^3C^4$ four-atom fragment, from which the O^7 atom is 0.768(2) Å apart. Substituents in the cycle (O^1, O^3, C^6, O^5, C^{11}, and C^{17}) deviate from the mentioned planar fragment by −0.628(3), 1.146(3), − 1.547(4), − 1.397(3), 1.242(3), and 0.314(3) Å, respectively. Deviation of atoms C^{11} and C^{17} to the same side points to the *cis*-orientation of phenyl rings in this five-membered cycle. Conformation of another five-membered cycle of the rigid bicycloheptane system of **9**, $P^1C^6O^5C^4O^7$, is a slightly distorted *envelope* (the $P^1C^6O^5C^4$ four-membered fragment is planar within 0.069(4) Å, and the atom O^7 deviates from this plane by 0.839(2) Å). Substituents in the cycle (O^1, O^2, O^3, C^3, C^{17}, C^{23}, and C^{24}) deviate from the mentioned planar fragment by −0.864(3), −1.384(3), 1.128(3). −1.321(3), 0.634(3), −1.079(5), and 1.433(6) Å, respectively.

Simultaneous appearance of phosphoranes **9** and **10** in very mild conditions (−40 °C) in nearly equal amounts may be evidence of two parallel four-stage pathways of their formation from one common intermediate, namely, a spirophosphorane with a three-membered oxaphosphirane cycle **A**, which is produced as a result of the cheletropic reaction of [1 + 2]-cycloaddition (see Scheme 2). Two bond disrupting processes are then equally probable: of the P−O bond (pathway a) and of the P−C bond (pathway b). The activation energy of these processes is quite small, since they occur at a very low temperature. The process a is reversible at room temperature in dichloromethane, which is more polar than tetrachloromethane (transition of phosphorane **9** into pentaalkoxyphosphorane **10** requires about 30 days at 20 °C but lasts approximately half an hour under heating in toluene). This reverse transformation is slower and more energy consuming since it should involve two consecutive disruptions of the P−O and C−O bonds (transition from phosphorane **9** to bipolar ions **C** and **B**, respectively). Apparently, the pathway a is kinetically controlled, and the pathway b is a thermodynamically controlled direction. The way b may also involve three stages, two of which are irreversible (consecutive transformation of **A** into intermediates **D**, **E**, and the reaction product **10**). Note that phosphorane **9** contains five chiral centers (P^1, C^3, C^4, C^7, and C^8) but only two chiral centers appear in the reaction (P^1 and C^4). This fact together with the observation that **9** is produced as a mixture of only two

diastereoisomers allows the conclusion that formation of one of these two centers is a highly stereoselective process. Apparently, this stereoselectivity pertains to the formation of C^4 due to hard steric requirements to the intramolecular attack of the alkoxide anion on the prochiral phenylcarbonyl substituent. Information on configurational stability of pentacoordinate phosphorus is inconsistent. On the one hand, processes of pseudorotation of phosphorus configuration are known, which lead to formation of different equilibrium forms;[42−44] on the other hand, stable penta-coordinate configurations were also reported.[45−51] It is possible that in the considered case stereoselectivity of formation of the phosphorus center is also high and is related to the configuration of the atom C^4. Formation of two diastereoisomers in the ratio of 1.1:0.8 for compound **9** and 1:1 for **10** is then solely connected with configurations of the atoms C^7, C^8 ($R,R/S,S$) and C^3 (R/S). If the stereoselectivity of formation of the phosphorane center was low (while its configurational stability was high), then the number of diastereoisomers should be four (d_1, d_2, d_3, d_4).

Structure of the phosphorane **10**, a viscous colorless oil consisting of two diastereoisomers (showing two singlets in the ^{31}P NMR spectrum (162.0 MHz, CCl$_4$) at $\delta_P = -23.9$ and -24.0 ppm with the intensity ratio of 1:1) was established by 1D and 2D NMR spectroscopy (^1H, ^1H-{^{31}P}, ^{31}P, ^{31}P-{^1H}, ^{31}P-{^{19}F}, ^{19}F, ^{19}F-{^{31}P}, ^{13}C, ^{13}C-{^1H}, ^{13}C-{^{19}F}, ^{13}C-{^{31}P}, ^{13}C-{^{19}F,^{31}P}, ^{13}C-{^{19}F,^2H}, (^{13}C,^{19}F)-HMBC, (^{13}C,^1H)-HMBC, (^{13}C,^{19}F)-HSQC, (^{13}C,^1H)-HSQC), IR spectroscopy, and EI mass-spectrometry. The EI mass spectrum contains a peak of a molecular ion corresponding to the addition product of the composition 1:1 (496 [M]$^{+•}$).

Signals of CF$_3$-groups in ^{19}F NMR spectra of **10** are two quartets ($^4J_{FF}$) at close frequencies. The spectrum has the same view also in the ^{19}F-{^{31}P} experiment, which proves the absence of scalar coupling between phosphorus and fluorine nuclei. Correlation experiments (^{13}C,^{19}F)-HMBC and (^{13}C,^{19}F)-HSQC allowed us to identify the C(CF$_3$)$_2$ fragment. Chemical shifts of the quaternary carbon C^5 in the two isomers are 83.7 (d_2) and 84.2 (d_1) ppm. Spectra ^{13}C-{^{19}F} and ^{13}C-{^{19}F}-{^{31}P} in this frequency range are identical showing thus that the coupling $^2J_{PC^5}$ is close to zero. Scalar coupling of the carbon C^3 ($\delta_C = 83.64$ ppm (d_2) and 83.63 ppm (d_1)) with phosphorus is unobservable, as well as in phosphorane **9**; at the same time, for C^4 ($\delta_C = 80.45$ and 80.50 ppm) the coupling $^2J_{PC^4} = -20.0$ Hz and also is close to the corresponding value in compound **9** (−24.0 Hz).

Thus, the absence of scalar coupling between the phosphorus nucleus, on the one hand, and the C^5 and F nuclei, on the other hand, is consistent with the proposed structure of the compound **10**. It was conclusively established from analysis of (^{13}C,^1H)-HMBC and (^{13}C,^1H)-HSQC spectra, which reveal a direct correlation between a proton and the carbon C^3 and long-range interaction of H^3 and C^4, C^5, and carbon nuclei of the aromatic substituents. The coupling $^2J_{C^4CH^3}$ is small and leads to broadening of the signal C^4 in ^{13}C NMR spectra. At the same time, peak of the atom C^6 in **9** or C^5 in **10** in analogous ^{13}C-{^{19}F}, ^{13}C-{^{19}F}-{^{31}P} spectra is a narrow singlet.

Additional information on the structure of the compound **10** can be obtained from analysis of ^{13}C NMR spectra of aromatic carbons. Spectra were obtained in different solvents (CCl$_4$ + 30% C$_6$D$_6$ and CDCl$_3$) to identify reliably the signals of *ortho*- and *meta*-atoms of the two phenyls. In both solvents, a small pairwise inequality and broadening of the *ortho*(C^{18,22})- and *meta*(C^{19,22})-carbon signals in the C^4-phenyl was observed, which was not the case for the carbon nuclei in the C^3-phenyl. This is probably due to the influence of trifluoromethyl groups, which hinder free

rotation around the C^4−C^{17} bond and thus broaden the carbon signals of this substituent. Signal broadening of one of the CF$_3$ groups and existence of long-range scalar coupling ($^5J_{FCCCCC} = 5.0$ Hz) with one of the *ortho*-carbons in the C^4-phenyl (C^{18}, $\delta_C = 127.47$ ppm) allowed assignment of the signals in these groups: C^{23}F$_3$ (121.86 and 121.88 ppm in both isomers) and C^{18} (127.47 ppm). Note that the signal of the second *ortho*-carbon (C^{22}, $\delta_C = 128.53$ ppm) is broadened (unresolved) due to hindered rotation around the C^4−C^{17} bond.

As well as the compound **9**, phosphorane **10** contains five chiral centers (P^1, C^3, C^4, C^7, C^8), only two of which arise during the reaction. Allowing for the fact than only two diastereoisomers of **10** arise, we can conclude that the process of formation of both these centers is characterized by a high stereoselectivity. This conclusion conforms to the results of investigation of spatial structure of the cyclic hydrolysis product **12** derived from phosphorane **10** (see below).

Structure and energy of the initial phospholane **8**, hexafluor-oacetone, obtained compounds **9** and **10**, and possible inter-mediate **A** were estimated by quantum chemical calculations. The calculated full energy of hexafluoroacetone is equal to −788.09758 Hartrees. Energies with respect to the initial compounds **8** and (CF$_3$)$_2$CO are shown in the bottom part of Scheme 2.

Figure 4 shows the geometry of the two diastereoisomers (d_1, d_2) of the initial 1,3,2-dioxaphospholane **8**. In both cases,
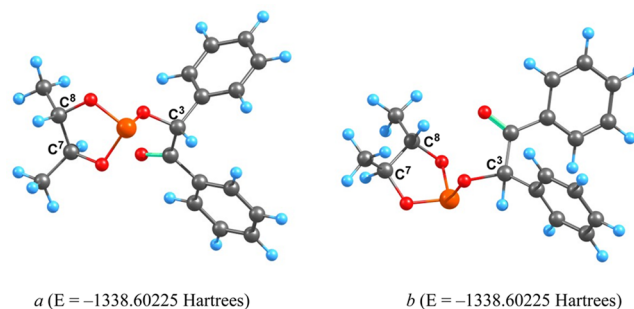

a (E = −1338.60225 Hartrees)   *b* (E = −1338.60225 Hartrees)

Figure 4. Calculated structure and energy for d_1- and d_2-diastereoisomers of phospholane (**8**). The view of C^3_RC^7_SC^8_S (d_1)- (a) and C^3_SC^7_SC^8_S (d_2)-enantiomers (b), differing by the configuration of the C^3 atom, is shown. These molecules' energies together with the energy of (CF$_3$)$_2$CO were taken as the zero level.

derivatives with the axial position of the exocyclic substituent and the *envelope* conformation of the dioxaphospholane cycle turn out to be the energetically preferable ones. Phosphorus has the pyramidal configuration. On the whole, structural parameters of the 1,3,2-dioxaphospholane cycle are close to the experimental ones, which were obtained by X-ray analysis of 2,2'-dioxybinaphthyl derivative of 4,5-dimethyl-1,3,2-dioxaphospholane.[52]

Optimized geometry for phospholane **9** calculated by the DFT method is presented in Figure 5. Evidently, the molecule has the form of a nearly perfect trigonal bipyramid with O^2, O^3, and C^6 atoms in its base (calculated sum of the O^2−P^1−O^3, O^2−P^1−C^6, and O^3−P^1−C^6 bond angles is 136.7° + 100.8° + 121.3° = 358.8°, which is close to the ideal value of 360.0°). Atoms O^1 and O^7 occupy apical positions, and the angle O^1−P^1−O^7 is 174.0°, which is also close to the experimental value of 177.1° found from XRD analysis. The O^1−P^1−O^2, O^1−P^1−O^3, O^1−P^1−C^6, O^7−P^1−O^2, O^7−P^1−O^3, and O^7−P^1−C^6 bond angles are within 84.0−98.9°, which also points to a close to the regular trigonal bipyramidal geometry of the phosphorus atom. Calculated the axial and equatorial P−O bonds lengths and those obtained by
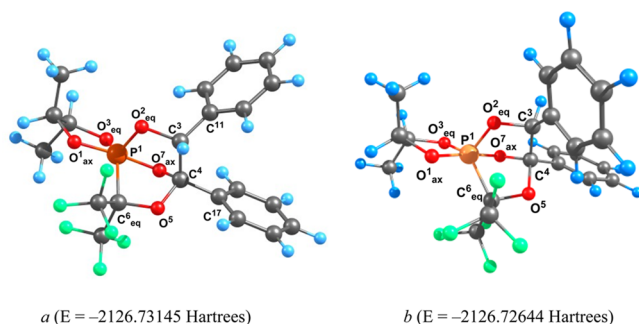
a (E = −2126.73145 Hartrees)　　　　　*b* (E = −2126.72644 Hartrees)

Figure 5. Calculated structure and energy for d_1- and d_3-diastereoisomers of phosphorane **9**. The view of $P^1_RC^3_RC^4_SC^7_SC^8_S$ (d_1)- (a) and $P^1_RC^3_SC^4_SC^7_SC^8_S$ (d_3)-enantiomers (b), differing by the configuration of the C^3 atoms, is shown. Relative energies: (a) −17.1, (b) −14.7 kcal/mol.

XRD are relatively close. According to the calculations, the 4,5-dimethyl-1,3,2-dioxaphospholane cycle has almost regular *envelope* conformation: C^8, P^1, O^1, and O^3 atoms lie in the plane, and C^7 is outside the plane. Methyl groups are situated in the axial positions of this five-membered cycle. Disagreement with the X-ray data for molecule **9**, where diequatorial arrangement of these groups is observed, may be caused by two reasons: first, the calculations were performed in the gas phase; second, five-membered phosphorus cycles show a certain conformational flexibility,[53,54] and the forms with diaxial and diequatorial arrangement of methyl groups possess similar energies. The concerned geometry is more favorable than an analogous geometry with different relative disposition of phenyl groups at atoms C^3 and C^4 ($P^1_RC^3_SC^4_SC^7_SC^8_S/P^1_SC^3_RC^4_RC^7_RC^8_R$-diastereoisomer d_3) (see Figure 5). Calculations show that the energy of the $P^1_RC^3_RC^4_SC^7_SC^8_S/P^1_SC^3_SC^4_RC^7_RC^8_R$ (d_1)-diastereoisomer is lower than that of the d_3 diastereoisomer by 3.14 kcal/mol. However, this difference cannot provide the high stereoselectivity of the d_1 and d_2 diastereoisomer formation (which differ by configuration of the atoms C^3, C^7, and C^8: *R,S,S/S,R,R* and *R,R,R/S,S,S*. Apparently, stereoselectivity results from kinetic reasons.

As well as the compound **9**, the molecule of pentaalkoxy-phosphorane **10** has a close to ideal trigonal bipyramidal phosphorus configuration with O^7 and O^1 atoms in apical positions and atoms O^2, O^3, and O^6 in equatorial positions (geometry of the $P^1_RC^3_RC^4_SC^7_SC^8_S$ (d_1)-diastereoisomer is shown in Figure 6a).

a (E = −2126.74765 Hartrees)　　　　　*b* (E = −2126.73876 Hartrees)
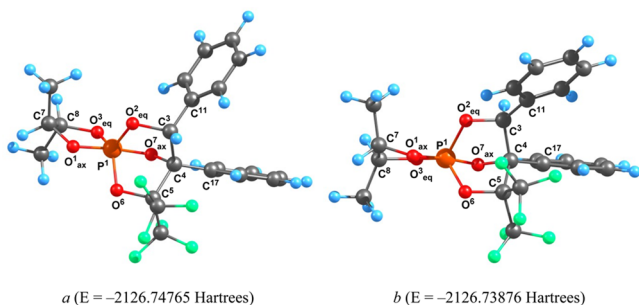
Figure 6. Calculated structure and energy for d_1- and d_3-diastereoisomers of phosphorane **10**. The view of $P^1_RC^3_RC^4_SC^7_SC^8_S$ (d_1)- (a) and $P^1_RC^3_SC^4_SC^7_SC^8_S$ (d_3)-enantiomers (b), differing by the configuration of the C^3 atoms, is shown. Relative energies: (a) −27.3, (b) −22.4 kcal/mol.

The sum of O^2−P^1−O^6, O^2−P^1−O^3, and O^3−P^1−O^6 bond angles in the base of the pyramid is also close to the ideal value of 360° (104.9° + 121.7° + 133.0° = 359.6°). The bond angle O^1−P^1−O^7 of 173.7° also certifies the almost regular trigonal pyramidal

configuration of phosphorus. Calculated axial P^1−O^1 and P^1−O^7 bonds lengths are equal to 1.659 and 1.715 Å and thus are slightly longer than equatorial P^1−O^2, P^1−O^3, and P^1−O^6 ones (1.651, 1.645, and 1.681 Å). Conformation of the 4,5-dimethyl-1,3,2-dioxaphospholane cycle is an *envelope* (four atoms O^1, P^1, O^3, and C^8 lie in one plane, and atom C^7 is slightly apart); methyl groups occupy axial positions. Energy of the $P^1_RC^3_RC^4_SC^7_SC^8_S$ (d_1)-diastereoisomer is more favorable than that of the $P^1_RC^3_SC^4_SC^7_SC^8_S$ (d_3)-diastereoisomer by 5.58 kcal/mol. As in the case of the molecule **9**, this difference cannot provide a high stereoselectivity of the formation of d_1 and d_2 diastereoisomers (which differ by configurations of the atoms C^3, C^7, and C^8: *R,S,S/S,R,R* and *R,R,R/S,S,S*); probably, the one is caused by kinetic reasons. On the whole, formation of **10** is more favorable by 10.17 kcal/mol compared with compound **9**. Allowing for reversibility of arising of **9**, we can conclude that its formation is kinetically controlled, whereas formation of phosphorane **10** is a thermodynamically controlled process.

Figure 7 presents the calculated geometry of the supposed intermediate **A**, which is probably the initial product in the
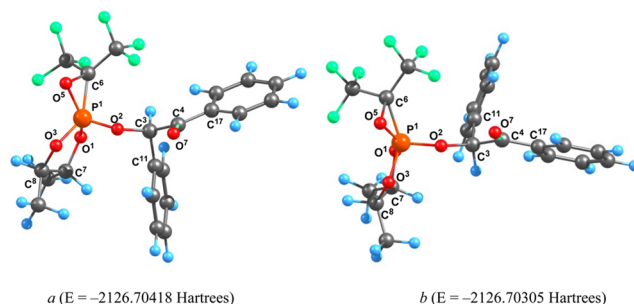

a (E = −2126.70418 Hartrees)　　　　　*b* (E = −2126.70305 Hartrees)

Figure 7. Calculated structure and energy for intermediate **A** in the reaction of phospholane **8** with hexafluoroacetone. The view of $C^3_RC^7_SC^8_S$ (d_1)- (a) and $C^3_SC^7_SC^8_S$ (d_2)-enantiomers (b), differing by the configuration of the C^3 atoms, is shown. Relative energies: (a) −2.7, (b) −2.0 kcal/mol.

reaction of phospholane **8** with hexafluoroacetone if this reaction proceeds via [1 + 2]-cycloaddition (a similar situation takes place in the reaction of 2-methoxybenzo[*d*]-1,3,2-dioxaphosphinin-4-one with chloral, for which the similar intermediate of the P(V)-oxaphosphirane type was revealed by quantum chemistry[55]). Its energy is substantially less favorable compared with the energies of phosphoranes **9** and **10**, by 17.12 and 27.28 kcal/mol, respectively. Its structure is intermediate between the trigonal bipyramidal and square pyramidal species. Among bond angles, O^1−P^1−C^6 (144.3°) is the biggest one (O^3−P^1−O^5 and O^1−P^1−O^5 angles are 94.3° and 134.3°). According to the apicophilicity rule, the five-membered and three-membered cycles should occupy the axial−equatorial position. In light of this fact, the deviation of the angle between axial substituents from the ideal value of 180° is rather high (35.7°). Concerning the bonds at the phosphorus atom, the O^1−P^1 (1.650(1) Å) and C^6−P^1 (1.848 Å) bonds are longer than the O^3−P^1 (1.642 Å), O^2−P^1 (1.623 Å), and O^5−P^1 (1.639 Å) bonds, which can also be explained by a strong distortion of the trigonal bipyramidal phosphorus configuration. Conformation of the 4,5-dimethyl-1,3,2-dioxaphospholane cycle is an *envelope* with the C^7 atom deviating from the plane. Methyl groups occupy the diequatorial position.

The phosphorane with the P−C bond, **9**, gives dioxaphospholane **11** and hexafluoroisopropanol (Scheme 3) during the

Scheme 3. Hydrolysis Reactions of Phosphorane 9
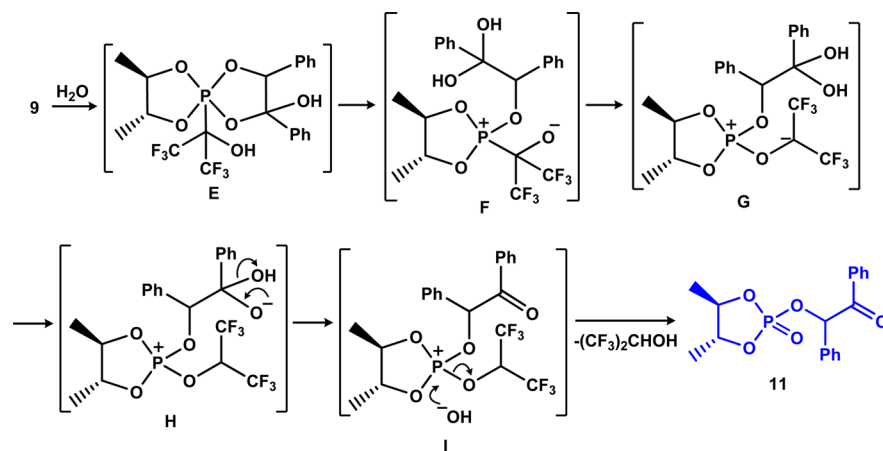
soft hydrolysis process (diethyl ether, in air, at 20 °C). Apparently, hydrolysis proceeds with opening of the dioxaphosphabicycloheptane scaffold of the molecule at the acetal fragment, which forms a spirophosphorane intermediate **E**. The leaving group is the most electronegative hexafluoroisopropanol substituent (a cleavage of the C^4–O^5 bond); transition of a proton from this group (which is the most acidic among the present hydroxyl groups) to the second acetal oxygen leads to the formation of a bipolar-type pattern **F**. Arising of this betaine is necessary for subsequent rearrangement into a bipolar intermediate of the POC-type, **G**. Further transition of a proton from the HO-acetal fragment to the C-carbanion center and removal of the hydroxide anion lead to the formation of the quasiphosphonium intermediate **I**, in which the most electronegative hexafluoroisopropanol substituent is the best leaving group at the attack of a hydroxide anion on the phosphorus atom. The structure of hexafluoroisopropanol obtained was confirmed by NMR. Note that hydrolysis is characterized by a high chemoselectivity.

Structure of the phosphorus hydrolysis product **11** was established by XRD on one of the diastereoisomers obtained by crystallization. Molecular geometry in the crystal and atom numbering is shown in Figure 8; main geometrical parameters
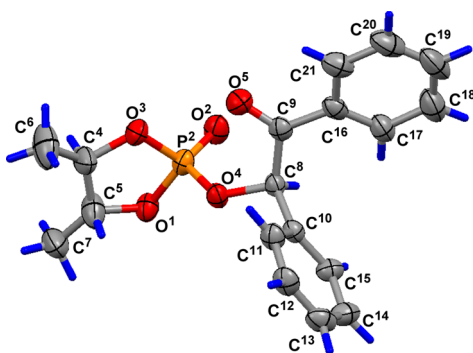

Figure 8. Geometry of molecule **11** in the crystal ($C^4_SC^5_SC^8_S$-enantiomer is shown). Selected bond lengths (Å) and bond and torsion angles (deg): P^2–O^1 1.576(3), P^2–O^2 1.446(3), P^2–O^3 1.564(3), P^2–O^4 1.570(2), O^1–P^2–O^2 115.4(2), O^1–P^2–O^3 98.2(1), O^1–P^2–O^4 103.1(1), O^2–P^2–O^3 117.5(2), O^3–P^2–O^1–C^5 −13.7(3), C^6–C^4–C^5–C^7 49.9(9).

(bond lengths and valence and torsion angles) are listed in the figure caption. Phosphorus has a distorted tetrahedral configuration; configuration of the chiral atoms is $C^4_SC^5_SC^8_S/C^4_RC^5_RC^8_R$.

Conformation of the dioxaphospholane cycle is an *envelope* containing the planar (within 0.023(2) Å) $O^1P^2O^3C^4$ four-atom fragment (Figure 9), from which the C^5 atom deviates by
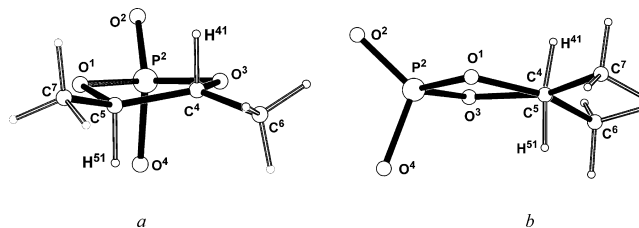

Figure 9. Conformation of the dioxaphospholane ring of molecule **11** in the crystal: view from the side of the C^4–C^5 bond (a); view from the side of the P^2–O^1–C^4 fragment (b) (for simplicity, substituent at the atom O^4 is omitted).

−0.253(5) Å. The O^4 atom is in the axial position (and deviates from the $O^1P^2O^3C^4$ plane by −1.485(2) Å). The O^2, C^6, and C^7 atoms occupy equatorial positions. They deviate from this plane at distances of 1.000(2), −0.385(6), and −0.029(6) Å. Although the C^6 and C^7 atoms deviate in the same direction, they are in the *trans*-configuration. Their unusual skew to the same side arises because deviation of the C^7 atom from the $O^1P^2O^3C^4$ plane is partially compensated by deviation of the C^5 atom from this plane in the same direction. Dimethyl dioxaphospholane cycle with different coordination of the phosphorus atom (III, IV, VI) usually possesses a flattened *envelope* conformation with a small deviation of either phosphorus or carbon atom from the ring plane.[42,56−58]

Behavior of pentaalkoxyphosphorane **10** (a mixture of two diastereoisomers) in the hydrolysis reaction differs from that of the P−C isomer **9** (Scheme 4). Dioxaphospholane **12** was unexpectedly obtained as the first produced compound in the form of a single diastereoisomer, which proves the above made assumption on a high stereoselectivity of the formation of the C^4 chiral center in compound **10**. When chirality at the phosphorus atom disappears due to hydrolysis, configuration of atoms C^3 and C^4 in **10** do not change (in compound **12** these are atoms C^4 and C^5). In this case, hydrolysis proceeds preferably at the phosphorus atom with cleavage of the P^1–O^6 bond in dioxaphosphabicyclooctane system, since the most electron withdrawing hexafluoroisopropoxyl substituent is the better leaving group. As an intermediate, apparently, hydroxyphosphorane **J** is produced, in which electron transfer to the endocyclic

Scheme 4. Hydrolysis Reactions of Phosphorane 10
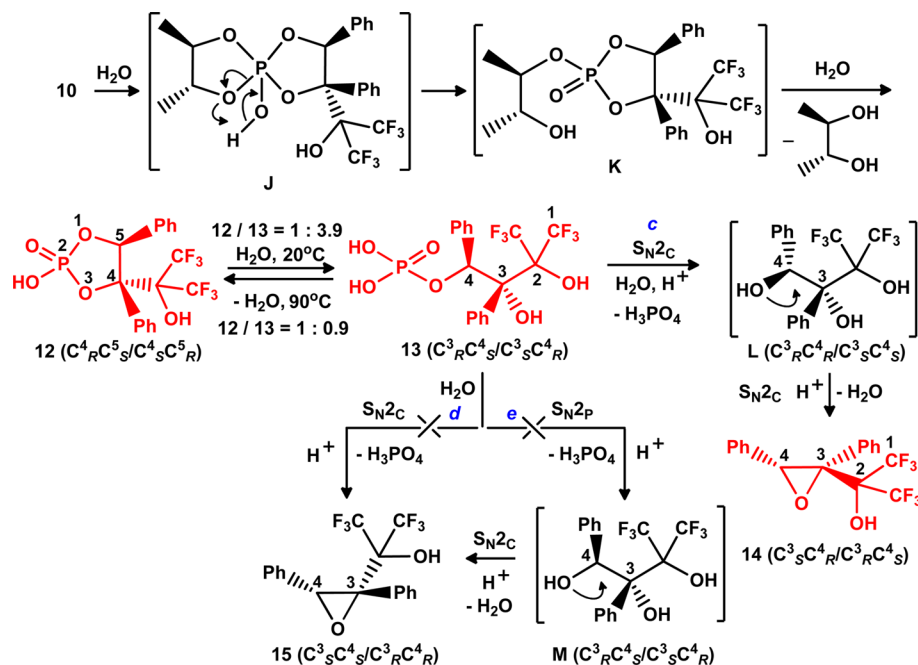
oxygen atom occurs and a phosphoryl group is formed (dioxaphospholane intermediate **K**). Despite the presence of a five-membered cycle, the structure **K** easily loses its exocyclic substituent and affords 2,3-butanediol (*d,l*-form) during further hydrolysis. Long-term storage of **12** in DMSO (at 20 °C) leads to the formation of the phosphoric acid monoester **13** as a single diastereoisomer; its structure was determined by spectroscopic methods. Acidic hydrolysis of **12** does not yield triol **L**, as could be expected, but with a high stereoselectivity (more than 95%) leads to the formation of the oxirane derivative **14**.

Structure of compounds **12** and **14** was also proved by XRD. Molecular geometries in the crystalline state are presented in Figures 10 and 11, and selected geometrical parameters are

Figure 11. Geometry of molecule **14** in the crystal ($C^3_R C^4_S$-enantiomer is shown). Selected bond lengths (Å) and bond and torsion angles (deg): O^1–C^3 1.440(3), O^1–C^4 1.450(4), C^3–C^4 1.480(4), C^4–C^{12} 1.474(4), C^3–O^1–C^4 61.6(1), O^1–C^3–C^4 59.5(2), O^1–C^4–C^3 58.9(1), C^6–C^3–C^4–C^{12} 2.1(4).

envelope and contains a planar (within 0.004(2) Å) $O^3 P^2 O^1 C^5$ four-atom fragment (O^3–P^2–O^1–C^5 torsion angle is 0.7(2)°), from which the C^4 atom deviates by −0.247(2) Å. O^4, C^9, and C^{15} atoms are in the axial positions and deviate from the $O^3 P^2 O^1 C^5$ fragment by 1.349(2), −1.686(2), and −1.002(2) Å, respectively. Conformation of phenyl substituents is close to the eclipsed one with respect to the C^4–C^5 bond (the C^9–C^4–C^5–C^{15} torsion angle is −16.7(2)°); O^2 and C^6 atoms are in the equatorial positions and are located at lesser distances from this fragment (−1.145(2) and 0.833(2) Å, respectively).

In crystals **9** and **11**, there is no opportunity to form classical hydrogen bonds, and their crystal structures are stabilized by intermolecular contacts of C−H···O-type and π−π-interactions. In the crystal of **12** due to the classical hydrogen bond O^6−H^6···O^2 (parameters are the following: O^6−H^6 0.88(3) Å, H^6···O^2 1.76(3) Å, O^6···O^2 2.635(3) Å, angle O^6−H^6−O^2 175(4)°, the symmetry operation *x*, 3/2 − *y*, −1/2 + *z*), infinite chains along the 0*c* crystallographic axis are formed (Supporting Information). The molecule of solvent is connected with the
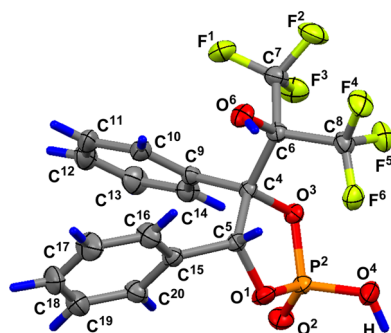

Figure 10. Geometry of molecule **12** in the crystal ($P^1_R C^4_S C^5_R$-enantiomer is shown). Selected bond lengths (Å) and bond and torsion angles (deg): P^1–O^1 1.565(2), P^1–O^2 1.459(2), P^1–O^3 1.586(2), P^1–O^4 1.526(2), O^1–P^1–O^2 113.9(1), O^1–P^1–O^3 97.94(8), O^1–P^1–O^4 109.6(1), O^2–P^1–O^3 115.0(1), O^2–P^1–O^4 114.1(1), O^3–P^1–O^4 104.9(1), P^1–O^3–C^4 114.1(1), C^9–C^4–C^5–C^{15} −16.4(2), C^6–C^4–C^5–C^{15} 110.7(2).

described in the figure captions. The molecule **12** forms a solvate with a diethyl ether molecule with the composition of 1:1. The diethyl ether molecule, which is disordered at two positions, is not shown in the figure for the sake of simplicity. The five-membered heterocycle of **12** has the conformation of a flattened
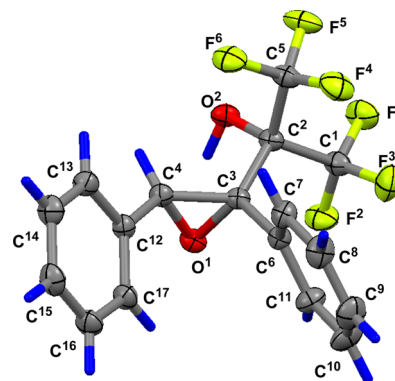
compound molecule **12** by the O^4−H^4···O^{50} hydrogen bond in every chain (parameters are the following: O^4−H^4 0.98(4) Å, H^4···O^{50} 1.56(4) Å, O^4···O^{50} 2.531(3) Å, angle O^4−H^4−O^{50} 173(3)°, the symmetry operation x, y, $1 + z$). Molecules of **14** in the crystal form dimers via the O^2−H^2···O^1 hydrogen bond (parameters are the following: O^2−H^2 0.89(3) Å, H^2···O^1 2.04(3) Å, O^2···O^1 2.841(4) Å, angle O^2−H^2−O^1 149(3)°, the symmetry operation $1 − x$, $− y$, $1 − z$) (see Supporting Information).

The configuration of chiral atoms in **12** is $P^1_R C^4_S C^5_R$/ $P^1_S C^4_R C^5_S$, and configuration of atoms $C^4_S C^5_R$/ $C^4_R C^5_S$ is similar to that of analogous atoms $C^4_S C^3_R$/$C^4_R C^3_S$ in the molecule of phosphorane **9**. We can conclude that in the initial compound **10**, from which dioxaphospholane **12** is obtained, configuration of these atoms is the same. Thus, in the rearrangement process that turns the PCO-phosphorane **9** into the POC-phosphorane **10**, as well as in the hydrolysis of the latter to the phosphate **12**, configuration of atoms C^4 and C^5 (or C^4 and C^3) remains unchanged. Regarding the configuration of the phosphorus atom in **12**, its chirality is lost in solution due to easy transition of a proton between oxygen atoms.

Configuration of chiral atoms in the oxirane molecule **14** is $C^3_S C^4_R$/$C^3_R C^4_S$, which is the same as of analogous chiral centers in molecules **9** and **12**. This conforms to the hydrolysis mechanism proposed in Scheme 4 as pathway c, which involves nucleophilic substitution of the phosphoric acid residue by water in the acidic catalysis following the S_N2 mechanism with inversion of the configuration of the atom C^4 and formation of triol **L**. After that, acid-catalyzed intramolecular nucleophilic substitution of the hydroxyl at the atom C^3 in the intermediate **L** under the influence of the hydroxyl group at the atom C^4 occurs, which, apparently, also follows the S_N2 mechanism with inversion of the atom C^3 and leads to the oxirane **14** derivative. Thus, double nucleophilic substitution at the atoms C^4 and C^3 keeps the relative configuration of the chiral centers in oxirane **14** the same as those of analogous atoms in the structures **9** and **12**. Evidently, we should exclude the pathway d, which is acid-catalyzed intramolecular nucleophilic substitution of the phosphate group by a low-reactive hydroxyl at the ternary atom C^3. In a separate experiment, we revealed that hydrolysis of this type does not take place at heating in DMSO. Instead, there is equilibrium of cyclic and acyclic forms **12** and **13**, which shows the content ratio of 1:3.9 after a month-long exposure at 20 °C. After heating (100 °C, 1 h), the ratio of the phosphates **12** and **13** becomes 1:0.9. Oxirane **15** with another relative configuration of atoms C^3 and C^4 ($R,R/S,S$) was not found by spectral methods (^{1}H, ^{19}F, and ^{13}C NMR, chromato-mass-spectrometry). Probable ways of production of **15**, which involve nucleophilic substitution at the phosphorus atom (S_N2_P) with formation of triol **M** (which is a diastereoisomer of **L**) and subsequent acid-catalyzed intramolecular substitution of the hydroxyl group at the ternary atom C^3 by the C^4-hydroxyl (pathway e), as well as nucleophilic substitution of the phosphate group at C^4 (pathway d), do not take place in the considered process.

CONCLUSIONS

Interaction of 4,5-dimethyl-2-(2-oxo-1,2-diphenyl)ethoxy-1,3,2-dioxaphospholane **8**, containing a carbonyl group in the γ-position with respect to the phosphorus atom, with hexafluoroacetone leads to simultaneous formation of regio- and stereoisomeric cage-like phosphoranes (**9** and **10**, Scheme 2) containing phosphorus−carbon and phosphorus−oxygen bonds. Despite the presence of several chiral centers, the process

proceeds with a high stereoselectivity. A stereoselective rearrangement of the PCO-isomer **9** into the POC-isomer **10** of the cage-like phosphorane was revealed; structure and energy of a possible intermediate of this intramolecular process, a pentacoordinate derivative with the oxaphosphirane cycle (**A**, Scheme 2), were determined by means of quantum chemistry. Hydrolysis of the PCO- and POC-isomers proceeds with a high stereoselectivity and leads to the formation of dioxaphospholane derivatives (**11** and **12**, Schemes 3 and 4). Acid-catalyzed hydrolysis of the POC-isomer **10** leads to the formation of an oxirane derivative (**14**, Scheme 4) with a high stereoselectivity (>95%). Our findings are of great importance for questions concerning C−C bond creation in a series of more complex organic compounds.

■ EXPERIMENTAL SECTION

One- and two-dimensional NMR spectra were recorded using the 700 MHz (^{1}H, 700.13 MHz; ^{31}P, 283.42 MHz; ^{19}F, 658.78 MHz; ^{13}C, 176.05 MHz), 500 MHz (^{1}H, 500 MHz; ^{31}P, 202.4 MHz; ^{19}F, 470.5 MHz; ^{13}C, 125.7 MHz), and 400 MHz (^{1}H, 400 MHz; ^{31}P, 162.0 MHz; ^{19}F, 376.5 MHz; ^{13}C, 100.6 MHz) spectrometers. The samples were prepared by dissolution of the studied compounds in $CDCl_3$, mix of C_6D_6 and CCl_4, DMSO-d_6, or acetone-d_6. Experiments on a 700 MHz instrument were made on a quadruple cryoprobe QCI at a stabilized sample temperature of 288 K. Number of scans in ^{19}F spectra was 16 or 32, in ^{31}P 64, and in ^{13}C 128. Spectral windows used in 1D spectra were 237 or 20 ppm in ^{19}F spectra, from 400 to 20 ppm in ^{31}P, and 161 or 40 ppm in ^{13}C spectra. The 2D heteronuclear spectra were optimized for observation of direct scalar couplings of $^1J_{HC} = 145$ and $^1J_{FC} = 286$ Hz and long-range scalar couplings (in HMBC) of $^nJ_{H···C} = 8$ and $^nJ_{F···C} = 30$ Hz. The chemical shifts were measured relative to the residual signals of the solvent. The following abbreviations are used to designate signal multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad. The IR spectra were recorded for thin films in Nujol or KBr pellets. High-resolution mass spectra (HRMS) were measured in ESI and EI modes with quadrupole and magnetic mass analyzers.

Quantum Chemical Calculations. Calculations of the spatial structure and energy of the studied organophosphorus molecules were carried out by optimizing geometry parameters in the Priroda program[59] within the density functional theory (DFT). The functional PBE and the basis set 6-311 G(2d,p) were used.

X-ray Investigations. Crystal structure was determined by X-ray diffraction of suitable monocrystal. Crystal data were collected at 296 K using graphite monochromated Mo Kα (0.71073 Å) radiation and ω-scan. Data collection images were indexed, integrated, and scaled using the APEX2 data reduction package.[60] Multiscan empirical absorption corrections were applied to all data sets, where appropriate, using the program SADABS.[61] The structure was solved and refined using SHELX[62] program. All pictures of crystal structures were created using Mercury CSD 2.4.[63]

Crystallographic Data for 9. $C_{21}H_{19}F_6O_5P$, colorless prism, formula weight 496.33, monoclinic, $P2_1/c$, $a = 15.079(5)$ Å, $b = 9.051(3)$ Å, $c = 15.770(5)$ Å, $\beta = 90.259(4)°$, $V = 2152(1)$ Å^3, $Z = 4$, $\rho_{calc} = 1.53$ g cm^{-3}, $\mu(\lambda_{MoK\alpha}) = 2.11$ cm^{-1}, $F(000) = 1016$, reflections unique = 4198, full matrix least-squares on F^2, parameters = 303, restraints = 0. Final indices $R_1 = 0.0517$, $wR_2 = 0.1498$ for 3580 reflections with $I > 2\sigma(I)$; $R_1 = 0.0620$, $wR_2 = 0.1683$ for all data, goodness-of-fit on $F^2 = 1.093$, refined as a four-component twin, largest difference in peak and hole 0.214 and $−0.526$ e Å^{-3}.

Crystallographic Data for 11. $C_{18}H_{19}O_5P$, colorless prism, formula weight 346.30, monoclinic, $P2_1/n$, $a = 9.297(5)$ Å, $b = 12.571(6)$ Å, $c = 15.387(7)$ Å, $\beta = 101.619(7)°$, $V = 1762(2)$ Å^3, $Z = 4$, $\rho_{calc} = 1.31$ g cm^{-3}, $\mu(\lambda_{MoK\alpha}) = 1.80$ cm^{-1}, $F(000) = 728$, reflections collected = 13485, unique = 3460, $R_{(int)} = 0.0617$, full matrix least-squares on F^2, parameters = 219, restraints = 0. Final indices $R_1 = 0.0584$, $wR_2 = 0.1535$ for 1838 reflections with $I > 2\sigma(I)$; $R_1 = 0.1218$, $wR_2 = 0.1880$ for all data,

goodness-of-fit on F^2 = 1.000, largest difference in peak and hole 0.194 and −0.237 e Å^{-3}.

Crystallographic Data for 12. $C_{21}H_{23}F_6O_6P$, colorless prism, formula weight 516.36, monoclinic, $P2_1/c$, a = 14.973(6) Å, b = 11.931(4) Å, c = 13.665(5) Å, β = 109.548(5)°, V = 2301(2) Å^3, Z = 4, ρ_{calc} = 1.49 g cm^{-3}, $\mu(\lambda_{MoK\alpha})$ = 2.03 cm^{-1}, F(000) = 1064, reflections collected = 17518, unique = 4526, $R_{(int)}$ = 0.0557, full matrix least-squares on F^2, parameters = 356, restraints = 80. Final indices R_1 = 0.0472, wR_2 = 0.1351 for 3357 reflections with $I > 2\sigma(I)$; R_1 = 0.0649, wR_2 = 0.1559 for all data, goodness-of-fit on F^2 = 0.981, largest difference in peak and hole 0.436 and −0.313 e Å^{-3}.

Crystallographic Data for 14. $C_{17}H_{12}F_6O_2$, colorless prism, formula weight 362.27, triclinic, $P\bar{1}$, a = 6.964(7) Å, b = 11.28(1) Å, c = 11.33(1) Å, α = 71.02(1)°, β = 82.78(1)°, γ = 75.33(1)°, V = 813(1) Å^3, Z = 2, ρ_{calc} = 1.48 g cm^{-3}, $\mu(\lambda_{MoK\alpha})$ = 1.42 cm^{-1}, F(000) = 368, reflections collected = 8265, unique = 3180, $R_{(int)}$ = 0.0450, full matrix least-squares on F^2, parameters = 230, restraints = 0. Final indices R_1 = 0.0534, wR_2 = 0.0938 for 1873 reflections with $I > 2\sigma(I)$; R_1 = 0.0953, wR_2 = 0.1040 for all data, goodness-of-fit on F^2 = 1.489, largest difference in peak and hole 0.183 and −0.226 e Å^{-3}.

Crystallographic data (excluding structure factors) for the structures **9**, **11**, **12**, and **14** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC 1451980−1451983. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk).

Preparation of Phosphoranes 9 and 10. 2-Chloro-4,5-dimethyl-1,3,2-dioxaphospholane (5.54 g, 35.86 mmol) in anhydrous ether (10 mL) was added dropwise during 30 min to a mixture of benzoin (7.61 g, 35.90 mmol) and triethylamine (3.80 g, 37.62 mmol) in ether (10 mL) with stirring under argon at room temperature. After all the chlorophosphite was added, the reaction mixture was stirred for another 2 h. A precipitate was filtered off and washed with ether (5 mL). The solvent was evaporated from the filtrate *in vacuo* (12 Torr). The resultant white precipitate (phosphite **8**) was used without further purification. NMR ^{31}P-$\{^1$H$\}$ spectrum (ether): δ_P 140.7 ppm. Compound **8** was dissolved in 100 mL of dry CCl$_4$. The resulting solution was condensed (−40 °C) of hexafluoroacetone (6.36 g, 38.31 mmol) by weight gain. The reaction mixture was allowed to warm to 20 °C over a period of 10 h. The precipitate formed (compound **9**) was filtered and dried *in vacuo* (12 Torr). The yield of **9** was 3.1 g (17%), mp 124−126 °C. Found, %: C, 51.21, H, 3.68, P, 6.61. $C_{21}H_{19}F_6O_5P$ Calcd, %: C, 50.81, H, 3.83, P, 6.25. The filtrate was concentrated *in vacuo* (12 Torr) in an argon flow. The residue as a viscous oil on storage under a layer of pentane was gradually crystallized. By filtration and drying *in vacuo* (12 Torr) an additional 7.46 g (42%) phosphorane **9** was isolated. The pentane filtrate was evaporated, and in the residue, 5.2 g (29%) of a mixture of two diastereoisomers of compound **10** as viscous transparent oil was obtained. Found, %: C, 51.17; H, 3.89; P, 6.15. $C_{21}H_{19}O_5F_6P$ Calcd, %: C, 50.81; H, 3.83; P, 6.25.

Compound (9). ^{1}H NMR (700.0 MHz, 15 °C, CDCl$_3$, d_1/d_2 = 31:4): δ 1.51 and 1.57 two d (H^9 and H^{10}, d_1, $^3J_{H^7CCH^9}$ = 6.2, $^3J_{H^8CCH^{10}}$ = 6.2, 6H), 1.48 and 1.64 two d (H^9 and H^{10}, d_2, $^3J_{H^7CCH^9}$ = 6.1, $^3J_{H^8CCH^{10}}$ = 6.1, 6H), 4.24 and 4.12 two m (H^7 and H^8, d_1, d_2, $^3J_{H^7H^8}$ ≈ 3.5 and $^3J_{POCH^{7,8}}$ = 3.0 for d_1), 5.53 d (H^3, d_1, $^3J_{POCH^3}$ = 18.1, 1H), 5.54 d (H^3, d_2, $^3J_{POCH^3}$ = 17.3, 1H), 7.17 m (H^{12,16}, d_1, d_2, $^3J_{H^{13}CCH^{12}}$ = $^3J_{H^{16}CCH^{15}}$ = 8.0, 2H), 7.24 m (H^{13,15}, d_1, d_2, $^3J_{H^{12,16}CCH^{13,15}}$ = 8.0, $^3J_{H^{14}CCH^{13,15}}$ = 7.2, $^4J_{H^{13}CCCH^{15}}$ = 1.8, $^4J_{H^{15}CCCH^{13}}$ = 1.8, 2H), 7.26 m (H^{14}, d_1, d_2, $^3J_{H^{13}CCH^{14}}$ = 7.2, $^3J_{H^{15}CCH^{14}}$ = 7.2, $^4J_{H^{12}CCCH^{14}}$ = 1.3, $^4J_{H^{16}CCCH^{14}}$ = 1.3, 1H), 7.27 m (H^{19,21}, d_1, d_2, $^3J_{H^{18,22}CCH^{19,21}}$ = 8.0, $^3J_{H^{20}CCH^{19,21}}$ = 7.2, 2H), 7.31 m (H^{20}, d_1, d_2, $^3J_{H^{19}CCH^{20}}$ = 7.2, $^3J_{H^{21}CCH^{20}}$ = 7.2, $^4J_{H^{18}CCCH^{20}}$ = 1.4, $^4J_{H^{22}CCCH^{20}}$ = 1.4, 1H), 7.38 m (H^{18,22}, d_1, d_2, $^3J_{H^{19}CCH^{18}}$ = $^3J_{H^{21}CCH^{22}}$ = 8.0). ^{13}C NMR (176.1 MHz, 15 °C, CDCl$_3$, d_1) (hereinafter a view of signal in ^{13}C-$\{^1$H$\}$ NMR spectrum is in parentheses): δ 17.52 qdd (d) (C^{10}, $^1J_{HC^{10}}$ = 127.5, $^2J_{POC^{10}}$ = 11.4, $^2J_{HC^7C^{10}}$ = 4.3, $^3J_{HC^7CC^{10}}$ = 0), 18.39 qdd (d) (C^9, $^1J_{HC^9}$ = 127.5, $^2J_{POC^9}$ = 9.0, $^2J_{HC^7C^9}$ = 4.3−4.4, $^3J_{HC^8CC^9}$ = 0), 74.75 br. d (br. s) (C^8, $^1J_{HC^8}$ = 146.5), 77.25 d. sept (d. sept) (C^6, $^1J_{PC^6}$ = 148.3, $^2J_{FC^{23,24}C^6}$ = 32.0), 77.46 br. d (d) (C^7, $^1J_{HC^7}$ = 146.5−147.0, $^2J_{POC^7}$ = 3.5), 86.41 br. d (d) (C^3, $^1J_{HC^3}$ = 157.0, $^3J_{H^{12,16}CCC^3}$ = 4.1, $^2J_{POC^3}$ = 2.5), 100.75 dtd (d) (C^4, $^2J_{POC^4}$ = 24.3, $^3J_{H^{18,22}CCC^4}$ = 4.4, $^2J_{HC^3C^4}$ = 3.5), 121.43 q (q) (C^{23},

$^1J_{FC^{23}}$ = 286.1), 122.47 qd (qd) (C^{24}, $^1J_{FC^{24}}$ = 284.4, $^2J_{PC^6C^{24}}$ = 1.7), 125.75 dt (s) (C^{18,22}, $^1J_{HC^{18,22}}$ = 163.3, $^3J_{HC^{20}CC^{18,22}}$ = 7.0, $^3J_{HC^{22}CC^{18}}$ = 7.0), 127.95 dddd (s) (C^{12,16}, $^1J_{HC^{12,16}}$ = 159.5, $^3J_{HC^{14}CC^{12,16}}$ = 7.0, $^3J_{HC^{16}CC^{12}}$ = 7.0, $^3J_{HC^3CC^{12,16}}$ = 4.4), 128.01 dd (s) (C^{19,21}, $^1J_{HC^{19,21}}$ = 162.1, $^3J_{HC^{21}CC^{19}}$ = 7.8), 128.08 dd (s) (C^{13,15}, $^1J_{HC^{13,15}}$ = 162.2, $^3J_{HC^{15}CC^{13}}$ = 7.8), 128.79 dt (s) (C^{14}, $^1J_{HC^{14}}$ = 161.3, $^3J_{HC^{12,16}CC^{14}}$ = 7.4), 129.33 dt (s) (C^{20}, $^1J_{HC^{20}}$ = 160.4, $^3J_{HC^{18,22}CC^{20}}$ = 7.4), 132.98 d. t (d) (C^{17}, $^3J_{POCC^{17}}$ = 12.2, $^3J_{HC^{19,21}CC^{17}}$ = 7.5), 134.87 br. t (s) (C^{11}, $^3J_{HC^{13,15}CC^{11}}$ = 6.6, $^2J_{HCC^{11}}$ = 1.7). ^{13}C NMR (176.1 MHz, 15 °C, CDCl$_3$, d_2): δ 18.32 qdd (d) (C^{10}, $^1J_{HC^{10}}$ = 127.5, $^2J_{POC^{10}}$ = 10.5, $^2J_{HC^8C^{10}}$ = 4.3, $^3J_{HC^7CC^{10}}$ = 0), 18.35 qdd (d) (C^9, $^1J_{HC^9}$ = 127.5, $^2J_{POC^9}$ = 9.5, $^2J_{HC^7C^9}$ = 4.3, $^3J_{HC^8CC^9}$ = 0), 75.83 dm (br. s) (C^8, $^1J_{HC^8}$ = 147.5, $^2J_{HC^{10}C^8}$ = 6.8, $^2J_{HC^9C^8}$ = 3.4, $^3J_{HC^{11}CC^8}$ = 3.3), 77.36 d. sept (d. sept) (C^6, $^1J_{PC^6}$ = 153.9, $^2J_{FC^{23,24}C^6}$ = 31.0), 77.33 br. d (d) (C^7, $^1J_{HC^7}$ = 146.5−147.0, $^2J_{POC^7}$ = 3.0), 87.29 dtd (d) (C^3, $^1J_{HC^3}$ = 156.0, $^3J_{HC^{12,16}CC^3}$ = 4.3, $^2J_{POC^3}$ = 3.5), 100.45 dtd (d) (C^4, $^2J_{POC^4}$ = 24.5, $^3J_{HC^{18,22}CC^4}$ = 4.3, $^2J_{HC^3C^4}$ = 3.5), 122.31 br. q (br. q) (C^{24}, $^1J_{FC^{24}}$ = 286.1), 121.75 q (q) (C^{23}, $^1J_{FC^{23}}$ = 287.0), 125.64 dt (s) (C^{18,22}, $^1J_{HC^{18,22}}$ = 163.0, $^3J_{HC^{20}CC^{18,22}}$ = 7.8, $^3J_{HC^{22}CC^{18}}$ = 7.0), 127.19 dddd (s) (C^{12,16}, $^1J_{HC^{12,16}}$ = 159.5, $^3J_{HC^{14}CC^{12,16}}$ = 7.0, $^3J_{HC^{16}CC^{12}}$ = 7.0, $^3J_{HC^3CC^{12,16}}$ = 4.4), 127.99 dd (s) (C^{19,21}, $^1J_{HC^{19,21}}$ = 160.4, $^3J_{HC^{21}CC^{19}}$ = 7.8), 128.10 dd (s) (C^{13,15}, $^1J_{HC^{13,15}}$ = 160.5, $^3J_{HC^{15}CC^{13}}$ = 7.8), 128.75 dt (s) (C^{14}, $^1J_{HC^{14}}$ = 160.5, $^3J_{HC^{12,16}CC^{14}}$ = 7.2), 129.28 dt (s) (C^{20}, $^1J_{HC^{20}}$ = 160.3, $^3J_{HC^{18,22}CC^{20}}$ = 7.2), 133.06 dtd (d) (C^{17}, $^3J_{POCC^{17}}$ = 12.2, $^3J_{HC^{19,21}CC^{17}}$ = 7.5), 135.05 td (s) (C^{11}, $^3J_{HC^{13,15}CC^{11}}$ = 7.0, $^2J_{HC^3C^{11}}$ = 1.7). ^{13}C-$\{^{19}$F$\}$ NMR (176.1 MHz, 15 °C, CDCl$_3$, d_1, d_2): δ 77.24 d (C^6, d_1, $^1J_{PC^6}$ = 148.3), 77.36 d (C^6, d_2, $^1J_{PC^6}$ = 153.9), 121.41 s (C^{23}, d_1), 121.75 (C^{23}, d_2), 122.31 d (C^{24}, d_2, $^2J_{PC^6C^{24}}$ = 1.7), 122.48 d (C^{24}, d_1, $^2J_{PC^6C^{24}}$ = 1.7). ^{13}C-$\{^1$H$\}$-$\{^{31}$P$\}$ NMR (176.1 MHz, 15 °C, CDCl$_3$, d_1, d_2): δ 17.52 s (C^{10}, d_1), 18.32 and 18.35 br. s (C^9 and C^{10}, d_2), 18.39 s (C^9, d_1), 74.75 s (C^8, d_1), 77.24 sept (C^6, d_1, $^2J_{FC^{23,24}C^6}$ = 32.0), 77.36 sept (C^6, d_2, $^2J_{FC^{23,24}C^6}$ = 30.4), 77.33 (C^7, d_2), 77.46 s (C^7, d_1), 86.41 s(C^3, d_1), 87.29 s (C^3, d_2), 100.75 s (C^4, d_1), 100.45 s (C^4, d_2), 121.43 q (C^{23}, d_1, $^1J_{FC^{23}}$ = 286.1), 121.75 q (C^{23}, d_2, $^1J_{FC^{23}}$ = 287.0), 122.31 q (C^{24}, d_2, $^1J_{FC^{24}}$ = 286.1), 122.47 q (C^{24}, d_1, $^1J_{FC^{24}}$ = 284.4), 132.98 s (C^{17}, d_1), 133.06 s (C^{17}, d_2). ^{19}F NMR (658.8 MHz, 30 °C, CDCl$_3$, d_1/d_2 = 31:4): δ −70.31 br. q (CF$_3$, d_1, $^4J_{FCCCF}$ = 10.3, 3F), −69.14 qd (CF$_3$, d_1, $^4J_{FCCCF}$ = 10.3, $^3J_{PCCF}$ = 5.3, 3F), −69.47 br. q (CF$_3$, d_2, $^4J_{FCCCF}$ = 9.8, 3F), −68.95 qd (CF$_3$, d_2, $^4J_{FCCCF}$ = 9.8, $^3J_{PCCF}$ = 6.1, 3F). ^{19}F NMR (658.8 MHz, 15 °C, CDCl$_3$, d_1/d_2 = 31:4): δ −70.35 br. s (CF$_3$, d_1, 3F), −69.17 br. qd (CF$_3$, d_1, $^4J_{FCCCF}$ = 10.3, $^3J_{PCCF}$ = 5.0, 3F), −69.49 br. q (CF$_3$, d_2, $^4J_{FCCCF}$ = 9.8, 3F), −68.99 qd (CF$_3$, d_2, $^4J_{FCCCF}$ = 9.8, $^3J_{PCCF}$ = 5.8, 3F). ^{19}F-$\{^{31}$P$\}$ NMR (658.8 MHz, 30 °C, CDCl$_3$, d_1/d_2 = 31:4): δ −70.35 br. q (CF$_3$, d_1, $^4J_{FCCCF}$ = 10.5, 3F), −69.17 q (CF$_3$, d_1, $^4J_{FCCCF}$ = 10.5, 3F), −69.47 br. q (CF$_3$, d_2, $^4J_{FCCCF}$ = 10.1, 3F), −68.95 q (CF$_3$, d_2, $^4J_{FCCCF}$ = 10.0, 3F). ^{31}P NMR (283.4 MHz, 15 °C, CDCl$_3$, d_1/d_2 = 31:4) (hereinafter a view of signal in ^{31}P-$\{^1$H$\}$ NMR spectrum is in parentheses): δ −25.05 br. dm (br. q) ($^3J_{H^3COP}$ = 18.1, d_1, $^3J_{FCCP}$ = 5.0), −23.35 br. dm (br. q) ($^3J_{H^3COP}$ = 17.3, d_2, $^3J_{FCCP}$ = 5.3). ^{31}P-$\{^{19}$F$\}$ NMR (283.4 MHz, 15 °C, CDCl$_3$, d_1/d_2 = 31:4): δ −25.05 ddd (d_1, $^3J_{H^3COP}$ = 18.1, $^3J_{H^7COP}$ = 3.0, $^3J_{H^8COP}$ = 3.0), −23.35 dd (d_2, $^3J_{H^3COP}$ = 17.3, $^3J_{H^7COP}$ = 5.3, $^3J_{H^8COP}$ = 0). HRMS (EI): *m/z* calcd for $C_{21}H_{19}F_6O_5P$ [M]$^+$ 496.0874, found 496.0880. IR spectrum, KBr pellet, ν, cm^{-1}: 545 w, 665 m, 706 m, 763 s, 798 s, 911 m, 968 v. s, 991 m, 1086 v. s, 1189 v. s, 1262 s, 1279 s, 1340 m, 1454 m, 2947 m. br, 2979 m. br.

Compound (10). ^{1}H NMR (700.0 MHz, 15 °C, CCl$_4$ + C$_6$D$_6$ (30%), d_1/d_2 = 1:1): δ 1.11 and 1.12 two d (H^9, d_1, d_2, $^3J_{H^7CCH^9}$ = 6.0, 3H), 1.19 and 1.20 two d (H^{10}, d_1, d_2, $^3J_{H^8CCH^{10}}$ = 6.0, 3H), 3.65−3.68, 3.68−3.72 and 3.72−3.78 three m (H^7 and H^8, d_1, d_2, $^3J_{H^9CCH^7}$ = 6.0, $^3J_{H^{10}CCH^8}$ = 6.0, $^2J_{H^7CH^8}$ = 9.1, $^3J_{POCH^7}$ = 7.8, $^3J_{POCH^8}$ = 5.2, 2H), 5.70 and 5.71 two d (two s in ^{1}H-$\{^{31}$P$\}$ NMR spectrum) (H^3, d_1, d_2, $^3J_{POCH^3}$ = 19.1 and 18.5, 1H), 6.91−6.93 m (H^{13,15}, H^{18}, d_1, d_2, 4H), 6.99 and 7.0 two m (H^{20}, d_1, d_2, $^3J_{H^{19}CCH^{20}}$ = 7.3, $^3J_{H^{21}CCH^{20}}$ = 7.3, 1H), 7.11−7.14 m (H^{12,16} and H^{14}, 3H), 7.21−7.23 m (H^{21}, H^{22}, d_1, d_2, 2H), 7.52 br. t (H^{19}, d_1, d_2, $^3J_{H^{18}CCH^{19}}$ = $^3J_{H^{20}CCH^{19}}$ 8.0−8.4, 1H). ^{1}H NMR (400.0 MHz, 25 °C, CDCl$_3$, d_1/d_2 = 1:1): 1.41, 1.38, 1.50, and 1.59 four d (H^9, H^{10}, d_1, d_2, $^3J_{H^7CCH^9}$ = 6.0−6.1, 6H), 3.98−4.02 and 4.09−4.11 two m (H^7 and H^8, d_1, d_2, $^3J_{H^9CCH^7}$ = 6.0, $^3J_{H^{10}CCH^8}$ = 6.0, 2H), 5.78 d (H^3, d_1, d_2, $^3J_{POCH^3}$ = 19.0, 1H), 7.09−7.11 m, 7.21−7.23 m, 7.31−7.33 m, 7.49−7.51 br. m (H$^{12−16}$, H$^{18−22}$, d_1, d_2, 10H). ^{13}C NMR (176.1 MHz, 15 °C, CCl$_4$ + C$_6$D$_6$ (30%), d_1): δ 18.70 qdd (d) (C^{10}, d_1, $^1J_{HC^{10}}$ = 127.2, $^2J_{POC^{10}}$ = 9.5, $^2J_{HC^8C^{10}}$ = 4.0, $^3J_{HC^7CC^{10}}$ = 0),

18.97 qdd (d) (C^9, d_1, $^1J_{HC^9}$ = 127.3, $^2J_{POC^9}$ = 9.6, $^2J_{HC^7C^9}$ = 4.0, $^3J_{HC^8CC^9}$ = 0), 18.76 qdd (d) (C^{10}, d_2, $^1J_{HC^{10}}$ = 127.3, $^2J_{POC^{10}}$ = 10.2, $^2J_{HC^8C^{10}}$ = 4.0, $^3J_{HC^7CC^{10}}$ = 0), 18.78 qdd (d) (C^9, d_2, $^1J_{HC^9}$ = 127.3, $^2J_{POC^9}$ = 10.6, $^2J_{HC^7C^9}$ = 4.0, $^3J_{HC^8CC^9}$ = 0), 74.37 dm (d) (C^8, d_2, $^1J_{HC^8}$ = 147.5–148.0, $^2J_{POC^8}$ = 4.6), 74.38 dm (d) (C^8, d_1, $^1J_{HC^8}$ = 147.5–148.0, $^2J_{POC^8}$ = 4.6), 76.89 dm (d) (C^7, d_2, $^1J_{HC^7}$ = 151.1, $^2J_{POC^7}$ = 3.5, $^2J_{HC^9C^7}$ = 4.0, $^2J_{HC^8C^7}$ = 4.0), 77.21 dm (d) (C^7, d_1, $^1J_{HC^7}$ = 150.6, $^2J_{POC^7}$ = 3.5, $^2J_{HC^9C^7}$ = 4.0, $^2J_{HC^8C^7}$ = 4.0), 80.45 d.t (d) (C^4, d_1, $^2J_{POC^4}$ = 20.0, $^3J_{HC^{18,22}CC^4}$ = 3.8), 80.50 dt (d) (C^4, d_2, $^2J_{POC^4}$ = 20.0, $^3J_{HC^{18,22}CC^4}$ = 3.8), 83.63 br. d (br. s) (C^3, d_1, $^1J_{HC^3}$ = 153.3), 83.64 br. d (br. s) (C^3, d_2, $^1J_{HC^3}$ = 155.2), 83.72 sept (sept) (C^5, d_2, $^2J_{FC^{23,24}C^5}$ = 29.5), 84.16 sept (sept) (C^5, d_1, $^2J_{FC^{23,24}C^5}$ = 29.5), 121.86 and 121.88 two qd (two qd) (C^{23}, d_1, d_2, $^1J_{FC^{23}}$ = 288.7, $^3J_{POCC^{23}}$ = 3.5), 123.20 qd (qd) (C^{24}, d_1, d_2, $^1J_{FC^{24}}$ = 286.4, $^2J_{PC^6C^{24}}$ = 7.2), 127.47 dm (br. m) (C^{18}, d_1, d_2, $^1J_{HC^{18}}$ = 162.0, $^3J_{HC^{20}CC^{18}}$ = 7.0, $^3J_{HC^{22}CC^{18}}$ = 7.0, $^5J_{FC^3C^5C^4C^{17}C^{18}}$ = 5.0), 128.53 dm (br. m) (C^{22}, d_1, d_2), 129.18 br. m (br. s) (C^{12,16}, d_1, d_2, $^1J_{HC^{12,16}}$ = 159.3), 127.67 br. dd (br. s) (C^{19}, d_2, d_1, $^1J_{HC^{19,21}}$ = 161.0, $^3J_{HC^{21}CC^{19}}$ = 7.0), 128.64 br. dd (br. s) (C^{21}, d_1, d_2, $^1J_{HC^{19,21}}$ = 159.6, $^3J_{HC^{21}CC^{19}}$ = 7.0), 128.28 dd (s) (C^{13,15}, d_1, d_2, $^1J_{HC^{13,15}}$ = 159.6, $^3J_{HC^{15}CC^{13}}$ = 7.0), 129.27 and 129.31 two dt (two s) (C^{14} and C^{20}, d_1, $^1J_{HC^{14,20}}$ = 161.5–162.0, $^3J_{HC^{12,16}CC^{14}}$ = 7.3–7.5, $^3J_{HC^{18,22}CC^{20}}$ = 7.3–7.5), 129.13 and 129.21 two dt (two s) (C^{14} and C^{20}, d_2, $^1J_{HC^{14,20}}$ = 161.5–162.0, $^3J_{HC^{12,16}CC^{14}}$ = 7.3–7.5, $^3J_{HC^{18,22}CC^{20}}$ = 7.3–7.5), 131.84 dt (d) (C^{17}, d_2, $^3J_{POCC^{17}}$ = 19.1, $^3J_{HC^{19,21}CC^{17}}$ = 7.4), 131.88 dt (d) (C^{17}, d_1, $^3J_{POCC^{17}}$ = 20.0, $^3J_{HC^{19,21}CC^{17}}$ = 7.4), 135.97 td (s) (C^{11}, d_2 $^3J_{HC^{13,15}CC^{11}}$ = 7.4, $^2J_{HC^3C^{11}}$ = 2.4), 136.01 td (s) (C^{11}, d_1, $^3J_{HC^{13,15}CC^{11}}$ = 7.4, $^2J_{HC^3C^{11}}$ = 2.4). ^{13}C-{^{19}F} NMR (176.1 MHz, 15 °C, CCl$_4$ + C$_6$D$_6$ (30%), d_1, d_2): δ 83.72 s (C^5, d_2), 84.16 s (C^5, d_1), 121.86 and 121.88 two s (C^{23}, d_1, d_2, $^3J_{POCC^{23}}$ = 3.5), 123.20 d (C^{24}, d_1, d_2, $^2J_{PC^6C^{24}}$ = 7.2), 127.47 dm (br. d) (C^{18}, d_1, d_2, $^1J_{HC^{18}}$ = 162.0, $^3J_{HC^{20}CC^{18}}$ = 7.0, $^3J_{HC^{22}CC^{18}}$ = 7.0). ^{13}C-{^{31}P} NMR (176.1 MHz, 15 °C, CCl$_4$ + C$_6$D$_6$ (30%), d_1, d_2): δ 18.70 q. d (C^{10}, d_1, $^1J_{HC^{10}}$ = 127.2, $^2J_{HC^8C^{10}}$ = 4.0), 18.97 qd (C^9, d_1, $^1J_{HC^9}$ = 127.3, $^2J_{HC^7C^9}$ = 4.0), 18.76 qd (C^{10}, d_2, $^1J_{HC^{10}}$ = 127.3, $^2J_{HC^8C^{10}}$ = 4.0), 18.78 qd (C^9, d_2, $^1J_{HC^9}$ = 127.3, $^2J_{HC^7C^9}$ = 4.0), 74.37 dm (C^8, d_2, $^1J_{HC^8}$ = 147.5–148.0), 74.38 dm (C^8, d_1, $^1J_{HC^8}$ = 147.5–148.0), 76.89 dm (C^7, d_2, $^1J_{HC^7}$ = 151.1, $^2J_{HC^9C^7}$ = 4.0, $^2J_{HC^8C^7}$ = 4.0), 77.21 dm (C^7, d_1, $^1J_{HC^7}$ = 151.1, $^2J_{HC^9C^7}$ = 4.0, $^2J_{HC^8C^7}$ = 4.0), 80.45 t (C^4, d_1, $^3J_{HC^{18,22}CC^4}$ = 3.8), 80.50 t (C^4, d_2, $^3J_{HC^{18,22}CC^4}$ = 3.8), 83.63 br. d (C^3, d_1, $^1J_{HC^3}$ = 153.3), 83.64 br. d (C^3, d_2, $^1J_{HC^3}$ = 155.2), 121.86 and 121.88 two q (C^{23}, d_1, d_2, $^1J_{FC^{23}}$ = 288.7), 123.20 q (C^{24}, d_1, d_2, $^1J_{FC^{24}}$ = 286.4), 131.84 t (C^{17}, d_2, $^3J_{HC^{19,21}CC^{17}}$ = 7.1), 131.88 t (C^{17}, d_1, $^3J_{HC^{19,21}CC^{17}}$ = 7.1). ^{13}C NMR (100.6 MHz, 25 °C, CDCl$_3$, d_1): δ 18.48 qdd (d) (C^9, C^{10}, d_2, $^1J_{HC^{10}}$ = 127.7, $^2J_{POC^{10}}$ = 9.5, $^2J_{HC^8C^{10}}$ = 4.0), 18.49 qdd (d) (C^{10}, d_1, $^1J_{HC^{10}}$ = 127.3, $^2J_{POC^{10}}$ = 8.1, $^2J_{HC^8C^{10}}$ = 4.0), 18.79 qdd (d) (C^9, d_1, $^1J_{HC^9}$ = 127.3, $^2J_{POC^9}$ = 8.2, $^2J_{HC^7C^9}$ = 4.0), 76.79 dm (d) (C^7, d_2, $^1J_{HC^7}$ = 151.9, $^2J_{POC^7}$ = 3.7, $^2J_{HC^9C^7}$ = 4.4), 76.98 dm (d) (C^7, d_1, $^1J_{HC^7}$ = 151.5, $^2J_{POC^7}$ = 3.7, $^2J_{HC^9C^7}$ = 4.4), 74.11 dm (d) (C^8, d_1, $^1J_{HC^8}$ = 151.1, $^2J_{POC^8}$ = 3.5, $^2J_{HC^{10}C^8}$ = 4.0, $^2J_{HC^9C^8}$ = 4.0), 74.21 dm (d) (C^8, d_2, $^1J_{HC^8}$ = 151.1, $^2J_{POC^8}$ = 3.5, $^2J_{HC^{10}C^8}$ = 4.0, $^2J_{HC^9C^8}$ = 4.0), 79.95 dt (d) (C^4, d_2, $^2J_{POC^4}$ = 20.2, $^3J_{HC^{18,22}CC^4}$ = 4.4), 80.0 dt (d) (C^4, d_1, $^2J_{POC^4}$ = 20.5, $^3J_{HC^{18,22}CC^4}$ = 4.4), 82.54 br. d (br. s) (C^3, d_1, $^1J_{HC^3}$ = 155.5), 83.22 br. d (br. s) (C^3, d_2, $^1J_{HC^3}$ = 155.5), 83.22 sept (sept) (C^5, d_2, $^2J_{FC^{23,24}C^5}$ = 30.4), 83.70 sept (sept) (C^5, d_1, $^2J_{FC^{23,24}C^5}$ = 30.4), 121.03 br. q (br. q) (C^{23}, d_1, d_2, $^1J_{FC^{23}}$ = 289.0), 122.37 qd (qd) (C^{24}, d_1, d_2, $^1J_{FC^{24}}$ = 286.1, $^2J_{PC^6C^{24}}$ = 8.5), 127.76–127.83 two d. m (two m) (C^{22}, d_1, d_2), 126.86 and 126.91 two d. m (two br. q) (C^{18}, d_1, d_2, $^1J_{HC^{18}}$ = 159.0–159.5, $^5J_{FC^{23}C^5C^4C^{17}C^{18}}$ = 5.0), 127.16 and 127.18 two br. dd (two br. s) (C^{19}, d_2, d_1, $^1J_{HC^{19}}$ = 160.0, $^3J_{HC^{21}CC^{19}}$ = 159.5), 127.98 and 128.0 two dm (two s) (C^{21}, d_1, d_2, $^1J_{HC^{21}}$ = 160.7, $^3J_{HC^{19}CC^{21}}$ = 7.0), 127.78 br. dm (s) (C^{13,15}, d_1, d_2, $^1J_{HC^{13,15}}$ = 161.0, $^3J_{HC^{15}CC^{13}}$ = 6.0–7.0), 128.69 and 127.72 two dt (two s) (C^{14} and C^{20}, d_1, $^1J_{HC^{14,20}}$ = 160.7–161.5, $^3J_{HC^{12,16}CC^{14}}$ = 7.3–7.5, $^3J_{HC^{18,22}CC^{20}}$ = 7.3–7.5), 128.62 and 126.58 two dm (two s) (C^{12} and C^{16}, d_1, d_2, $^1J_{HC^{12,16}}$ = 161.5, $^3J_{HC^{14}CC^{12,16}}$ = 7.3), 128.62 and 128. 50 two dm (two s) (C^{14} and C^{20}, d_2, $^1J_{HC^{14,20}}$ = 160.7–161.5), 130.87 dm (d) (C^{17}, d_2, $^3J_{POCC^{17}}$ = 18.7, $^3J_{HC^{19,21}CC^{17}}$ = 6.2, $^3J_{FCCC^{17}}$ = 1.5), 130.92 br. dt (d) (C^{17}, d_1, $^3J_{POCC^{17}}$ = 18.7, $^3J_{HC^{19,21}CC^{17}}$ = 6.2), 135.07 td (s) (C^{11}, d_2, $^3J_{HC^{13,15}CC^{11}}$ = 6.5, $^2J_{HC^3C^{11}}$ = 2.5), 135.21 (C^{11}, d_1, $^3J_{HC^{13,15}CC^{11}}$ = 6.5, $^2J_{HC^3C^{11}}$ = 2.5). ^{19}F NMR (658.8 MHz, 15 °C, CCl$_4$ + 30% C$_6$D$_6$, d_1/d_2 = 1:1): δ − 72.11 and −72.13 two q (CF$_3$, d_1, d_2, $^4J_{FCCCF}$ = 10.0, $^4J_{FCCCF}$ = 10.0, 3F), −68.27 and −68.30 two q (CF$_3$, d_1, d_2,

$^4J_{FCCCF}$ = 10.0, $^4J_{FCCCF}$ = 10.0, 3F). ^{19}F NMR (376.5 MHz, 25 °C, CDCl$_3$, δ$_F$ ppm, J Hz, d_1/d_2 = 1:1): −72.06 and −72.1 two q (CF$_3$, d_1, d_2, $^4J_{FCCCF}$ = 10.3, 3F), −68.22 br. q (CF$_3$, d_1, d_2, $^4J_{FCCCF}$ = 10.3, 3F), −69.17 br. qd (CF$_3$, d_1, $^4J_{FCCCF}$ = 9.7, $^3J_{PCCF}$ = 4.8, 3F). ^{31}P NMR (a view of signal in ^{31}P-{^{1}H} NMR (283.4 MHz, 15 °C, CCl$_4$ + C$_6$D$_6$ (30%), d_1/d_2 = 1:1): δ −24.38 dt (s) ($^3J_{HC^3OP}$ = 18.9, d_1, $^3J_{HC^{7,8}OP}$ = 7.5), −24.5 dt (s) ($^3J_{HC^3OP}$ = 18.9, d_2, $^3J_{HC^{7,8}OP}$ = 5.9). ^{31}P-{^{19}F} NMR (283.4 MHz, 15 °C, CCl$_4$ + C$_6$D$_6$ (30%), d_1/d_2 = 1:1): δ −24.38 dt ($^3J_{HC^3OP}$ = 18.9, d_1, $^3J_{HC^{7,8}OP}$ = 7.5), −24.5 dt ($^3J_{HC^3OP}$ = 18.9, d_2, $^3J_{HC^{7,8}OP}$ = 5.9). ^{31}P NMR spectrum (242.9 MHz, 25 °C, pentane + ether (40%), d_1/d_2 = 1:0.8): δ −23.32 dt (s) ($^3J_{HC^3OP}$ = 19.2, d_1, $^3J_{HC^{7,8}OP}$ = 8.9), −23.45 ddd (s) ($^3J_{HC^3OP}$ = 19.2, d_2, $^3J_{HC^7OP}$ = 7.2, $^3J_{HC^8OP}$ = 7.4). ^{31}P NMR (162.0 MHz, 25 °C, toluene, d_1/d_2 = 1:0.8): δ −23.94 dt (s) ($^3J_{HC^3OP}$ = 19.3, d_1, $^3J_{HC^{7,8}OP}$ = 9.0), −24.04 ddd (s) ($^3J_{HC^3OP}$ = 19.2, d_2, $^3J_{HC^{7,8}OP}$ = 7.8). ^{31}P NMR (162.0 MHz, 25 °C, CDCl$_3$, d_1/d_2 = 1:1): δ −24.05 dt (s) ($^3J_{HC^3OP}$ = 19.3, d_1, $^3J_{HC^{7,8}OP}$ = 8.9), −24.13 ddd (s) ($^3J_{HC^3OP}$ = 19.3, d_2, $^3J_{HC^7OP}$ = 7.0, $^3J_{HC^8OP}$ = 7.4). HRMS (EI): m/z calcd for C$_{21}$H$_{19}$F$_6$O$_5$P [M]$^+$ 496.0874, found 496.0879. Mass spectrum (EI), m/z (I_{rel}, %): 496 (12.8) [M]$^+$, 452 (0.25) [M − OC$_2$H$_4$]$^+$, 424 (3.7) [M − OC$_4$H$_8$]$^+$, 166 (30.5) [OC$_3$F$_6$]$^+$, 105 (100.0) [OC$_7$H$_5$] $^+$, 91 (3.9) [PhCH$_2$]$^+$, 77 (39.2) [Ph]$^+$, 69 (57.4) [CF$_3$] $^+$.

Rearrangement of Phosphorane 9 into Phosphorane 10. The phosphorane **9** (0.53 g, 1.06 mmol) in 10 mL of anhydrous toluene was boiled for 30 min. Next, after cooling to room temperature, the solvent was removed *in vacuo* (12 Torr). Spectral parameters of the residue (0.52 g, 99%) are similar to those of the phosphorane **10** (d_2) derived from the reaction of the phosphite **8** and hexafluoroacetone.

Hydrolysis of Phosphorane 9. The phosphorane **9** (2 g, 4.03 mmol) in a 5 mL mixture of CH$_2$Cl$_2$ and ether (1:1) under access of air was allowed to stand for 30 days (dichloromethane was added when necessary). The solvent was removed *in vacuo* (12 Torr). The residue, a colorless powder, was washed with pentane and dried *in vacuo* (12 Torr). The yield of **11** was 1.3 g (93%), mp 117–120 °C. ^{1}H NMR (25 °C, 500.1 MHz, CDCl$_3$, d_1/d_2 ≈ 1.9:0.7): δ 1.35 and 1.42 two d (H^{6,7}, d_1, $^3J_{HCCH}$ = 6.1), 1.32 and 1.41 two d (H^{6,7}, d_2, $^3J_{HCCH}$ = 6.1), 4.20–4.22 and 4.28–4.35 two m (H^{4,5}, d_1, d_2), 6.70 d (H^8, d_1, $^3J_{POCH}$ = 7.2), 6.71 d (H^8, d_2, $^3J_{POCH}$ = 7.2), 7.34–7.36 m (H^{13}, H^{18,20}, H^{12,14}, d_1, d_2, 5H), 7.47–7.49 m (H^{11,15}, H^{19}, d_1, d_2, 3H), 7.90 m (H^{17,21}, d_1, d_2, 2H). ^{1}H NMR (15 °C, 700.0 MHz, CDCl$_3$, d_1/d_2 ≈ 1.9:0.7): δ 1.41 d. d (H^6, d_2, $^3J_{H^4CCH^6}$ = 6.1, $^4J_{POCCH^6}$ = 1.7), 1.42 dd (H^6, d_1, $^3J_{H^4CCH^6}$ = 6.1, $^4J_{POCCH^6}$ = 1.7), 1.49 dd (H^7, d_2, $^3J_{H^5CCH^7}$ = 6.1, $^4J_{POCCH^7}$ = 1.7), 1.50 dd (H^7, d_1, $^3J_{H^5CCH^7}$ = 6.1, $^4J_{POCCH^7}$ = 1.7), 4.22 m (H^4, d_1, $^3J_{H^5CCH^4}$ = 8.4, $^3J_{H^6CCH^4}$ = 6.1, $^3J_{POCH^4}$ = 2.2), 4.29 m (H^4, d_2, $^3J_{H^5CCH^4}$ = 8.4, $^3J_{H^6CCH^4}$ = 6.1, $^3J_{POCH^4}$ = 3.6), 4.33 m (H^5, d_1, $^3J_{H^4CCH^5}$ = 8.4, $^3J_{H^7CCH^5}$ = 6.1, $^3J_{POCH^5}$ = 3.7), 4.37 m (H^5, d_2, $^3J_{H^4CCH^5}$ = 8.4, $^3J_{H^7CCH^5}$ = 6.1, $^3J_{POCH^5}$ = 2.2), 6.71 d (H^8, d_1, $^3J_{POCH}$ = 6.9), 6.73 d (H^8, d_2, $^3J_{POCH}$ = 6.8), 7.34–7.37 m (H^{13}, H^{18,20}, H^{12,14}, d_1, d_2, 5H), 7.47–7.49 m (H^{11,15}, H^{19}, d_1, d_2, 3H), 7.90–7.91 m (H^{17,21}, d_1, d_2, 2H). ^{1}H-{^{31}P} NMR (15 °C, 700.0 MHz, CDCl$_3$, d_1/d_2 ≈ 1.9:0.7): δ 1.41 d (H^6, d_2, $^3J_{H^4CCH^6}$ = 6.1), 1.42 d (H^6, d_1, $^3J_{H^4CCH^6}$ = 6.1), 1.49 d (H^7, d_2, $^3J_{H^5CCH^7}$ = 6.1), 1.50 d (H^7, d_1, $^3J_{H^5CCH^7}$ = 6.1), 4.23 dq (H^4, d_1, $^3J_{H^5CCH^4}$ = 8.4, $^3J_{H^6CCH^4}$ = 6.1), 4.30 dq (H^4, d_2, $^3J_{H^5CCH^4}$ = 8.4, $^3J_{H^6CCH^4}$ = 6.1), 4.33 dq (H^5, d_1, $^3J_{H^4CCH^5}$ = 8.4, $^3J_{H^7CCH^5}$ = 6.1), 4.37 dq (H^5, d_2, $^3J_{H^4CCH^5}$ = 8.4, $^3J_{H^7CCH^5}$ = 6.1), 6.71 s (H^8, d_1), 6.73 s (H^8, d_2). ^{1}H-{^{1}H^7} (H^7, 1.50 ppm) NMR (15 °C, 700.0 MHz, CDCl$_3$, d_1/d_2 ≈ 1.9:0.7): δ 1.41 dd (H^6, d_2, $^3J_{H^4CCH^6}$ = 6.1, $^4J_{POCCH^6}$ = 1.7), 1.42 dd (H^6, d_1, $^3J_{H^4CCH^6}$ = 6.1, $^4J_{POCCH^6}$ = 1.7), 4.23 m (H^4, d_1, $^3J_{H^5CCH^4}$ = 8.4, $^3J_{H^6CCH^4}$ = 6.1, $^3J_{POCH^4}$ = 2.2), 4.30 m (H^4, d_2, $^3J_{H^5CCH^4}$ = 8.4, $^3J_{H^6CCH^4}$ = 6.1, $^3J_{POCH^4}$ = 3.6), 4.33 dd (H^5, d_1, $^3J_{H^4CCH^5}$ = 8.4, $^3J_{POCH^5}$ = 3.7), 4.37 dd (H^5, d_2, $^3J_{H^4CCH^5}$ = 8.4, $^3J_{POCH^5}$ = 2.2). ^{1}H-{^{1}H^6} (H^6, 1.43 ppm) NMR (15 °C, 700.0 MHz, CDCl$_3$, d_1/d_2 ≈ 1.9:0.7): δ 1.49 dd (H^7, d_2, $^3J_{H^5CCH^7}$ = 6.1, $^4J_{POCCH^7}$ = 1.7), 1.50 dd (H^7, d_1, $^3J_{H^5CCH^7}$ = 6.1, $^4J_{POCCH^7}$ = 1.7), 4.23 dd (H^4, d_1, $^3J_{H^5CCH^4}$ = 8.4, $^3J_{POCH^4}$ = 2.2), 4.30 dd (H^4, d_2, $^3J_{H^5CCH^4}$ = 8.4, $^3J_{POCH^4}$ = 3.6), 4.33 m (H^5, d_1, $^3J_{H^4CCH^5}$ = 8.4, $^3J_{H^7CCH^5}$ = 6.1, $^3J_{POCH^5}$ = 3.7), $^3J_{POCH^4}$ = 3.6), 4.37 m (H^5, d_2, $^3J_{H^4CCH^5}$ = 8.4, $^3J_{H^7CCH^5}$ = 6.1, $^3J_{POCH^5}$ = 2.2). ^{13}C NMR (15 °C, 176.1 MHz, CDCl$_3$, d_1/d_2 ≈ 1.9:0.7): δ 17.84 qdd (d) (C^6, d_1, $^1J_{HC^6}$ = 128.1, $^3J_{POCC^6}$ = 9.2, $^2J_{HC^4C^6}$ = 3.7), 17.95 qm (d) (C^6, d_2, $^1J_{HC^6}$ = 128.6, $^3J_{POCC^6}$ = 8.3), 18.02 qdd (d) (C^7, d_1, $^1J_{HC^7}$ = 128.3, $^3J_{POCC^7}$ = 8.0, $^2J_{HC^5C^7}$ = 3.7), 18.04 qm (d) (C^7, d_2, $^1J_{HC^7}$ = 128.6, $^3J_{POCC^7}$ = 7.8), 81.30 dm (d) (C^4, d_1, $^1J_{HC^4}$ = 153.8,

$^2J_{POC^4} = 1.6$), 81.68 dm (d) (C^4, d_2, $^1J_{HC^4} = 153.7$, $^2J_{POC^4} = 1.6$), 81.52 ddt (d) (C^8, d_1, $^1J_{HC^8} = 149.6$, $^2J_{POC^8} = 5.4$, $^3J_{HC^{11,15}CC^8} = 4.4$), 81.55 ddt (d) (C^8, d_2, $^1J_{HC^8} = 149.4$, $^2J_{POC^8} = 5.6$, $^3J_{HC^{11,15}CC^8} = 4.5$), 81.48 dm (d) (C^5, d_2, $^1J_{HC^5} = 153.8$, $^2J_{POC^5} = 1.7$), 81.89 dm (d) (C^5, d_1, $^1J_{HC^5} = 154.2$, $^2J_{POC^5} = 1.4$), 128.39 dm (s) (C^{11,15}, d_1, $^1J_{HC^{11,15}} = 157.5$), 128.46 dm (s) (C^{11,15}, d_2, $^1J_{HC^{11,15}} = 158.0$), 128.66 dm (s) (C^{12,14}, d_1, $^1J_{HC^{12,14}} = 160.2$, $^3J_{HC^{4,12}CC^{12,14}} = 7.2$), 128.67 dm (s) (C^{12,14}, d_2, $^1J_{HC^{12,14}} = 160.2$, $^3J_{HC^{14,12}CC^{12,14}} = 7.2$), 129.05 dm (s) (C^{17,21}, d_2, $^1J_{HC^{17,21}} = 161.2$, $^3J_{HC^{19}CC^{17,21}} = 7.6$, $^3J_{HC^{21,17}CC^{17,21}} = 7.6$), 129.06 dm (s) (C^{17,21}, d_1, $^1J_{HC^{17,21}} = 161.2$, $^3J_{HC^{19}CC^{17,21}} = 7.6$, $^3J_{HC^{21,17}CC^{17,21}} = 7.6$), 129.21 dm (s) (C^{18,20}, d_2, $^1J_{HC^{18,20}} = 159.0$, $^3J_{HC^{20,18}CC^{18,20}} = 7.3$), 129.23 dm (s) (C^{18,20}, d_1, $^1J_{HC^{18,20}} = 159.0$, $^3J_{HC^{20,18}CC^{18,20}} = 7.3$), 129.59 br. dt (s) (C^{13}, d_1, d_2, $^1J_{HC^{13}} = 160.6$, $^3J_{HC^{11,15}CC^{13}} = 7.5$), 133.70 br. dt (s) (C^{19}, d_1, $^1J_{HC^{19}} = 161.3$, $^3J_{HC^{17,21}CC^{19}} = 6.5$), 133.73 br. dm (s) (C^{19}, d_2, $^1J_{HC^{19}} = 161.3$), 133.92 br. t (s) (C^{16}, d_2, $^3J_{HC^{18,20}CC^{16}} = 7.5$), 133.93 br. t (s) (C^{16}, d_1, $^3J_{HC^{18,20}CC^{16}} = 7.5$), 134.44 m (d) (C^{10}, d_2, $^3J_{POCC^{10}} = 7.6$), 134.46 m (d) (C^{10}, d_1, $^3J_{POCC^{10}} = 7.0$, $^3J_{HC^{12,14}CC^{10}} = 6.7$, $^2J_{HC^8CC^{10}} = 5.9$), 193.52 m (d) (C^9, d_2, $^3J_{POC^8C^9} = 3.4$), 193.36 m (d) (C^9, d_1, $^3J_{POC^8C^9} = 3.9$). ^{13}C-{^{1}H}-{^{31}P} NMR (176.1 MHz, 15 °C, CDCl$_3$, $d_1/d_2 \approx 1.9{:}0.7$): δ 17.84 s (C^6, d_1), 17.95 s (C^6, d_2), 18.02 s (C^7, d_1), 18.03 s (C^7, d_2), 81.30 s (C^4, d_1), 81.47 s (C^4, d_2), 81.52 s (C^8, d_1), 81.55 s (C^8, d_2), 81.67 s (C^5, d_2), 81.89 s (C^5, d_1), 193.52 s (C^9, d_2), 193.36 s (C^9, d_1). ^{31}P-{^{1}H} NMR (202.5 MHz, 25 °C, CDCl$_3$, $d_1/d_2 \approx 1.9{:}0.7$): δ 13.66 s, 13.68 s. Found, %: C, 62.81; H, 5.83; P, 9.39. C$_{18}$H$_{19}$O$_5$P Calcd, %: C, 62.43; H, 5.49; P, 8.96. HRMS (EI): m/z calcd for C$_{18}$H$_{19}$O$_5$P [M]$^+$ 346.0970, found 346.0977. HRMS (EI), m/z (I_{rel}, %): 346 (1.2) [M]$^+$, 258 (9.2) [M − C$_4$H$_8$O$_2$] $^+$, 241 (100.0) [M − PhCO]$^+$, 196 (1.8) [C$_{14}$H$_{12}$O]$^+$, 187 (12.6) [C$_8$H$_{12}$O$_3$P]$^+$, 165 (18.6) [C$_5$H$_{10}$O$_4$P]$^+$, 152 (7.2) [C$_4$H$_9$O$_4$P]$^+$, 105 (79.9) [PhCO]$^+$, 91 (7.5) [PhCH$_2$]$^+$, 77 (64.6) [Ph]$^+$, 55 (45.2) [C$_4$H$_7$] $^+$. IR spectrum, KBr pellet, ν, cm^{-1}: 694 s, 845 m, 905 m, 962 s, 1045 s, 1235 m, 1276 v. s, 1703 v. s, 2938 w, 2985 w.

Hydrolysis of Phosphorane 10. A mixture of phosphorane **10** (4 g, 8.06 mmol) in 10 mL of ether and water (0.4 g, 22.22 mmol) was allowed to stand at room temperature. On standing for 1 day, the reaction mixture was crystallized. The precipitate of phosphate **12** as a colorless powder was filtered off, washed with pentane, and dried *in vacuo* (12 Torr). Yield 3.02 g (85%), mp 144−146 °C. ^{1}H NMR (400.0 MHz, 25 °C, CDCl$_3$): δ 1.26 t (CH$_3$, $^3J_{HCCH} = 7.1$, 6H), 3.59 q (CH$_2$O, $^3J_{HCCH} = 7.1$ 4H), 6.55 d (singlet in ^{1}H-{^{31}P} spectrum) (H^5, $^3J_{POCH} = 7.1$, 1H), 6.53 and 7.83 two br. d (H^{14} and H^{10}, $^3J_{HCCH} = 6.9-7.2$, 2H), 6.65 and 7.32 two br. dd (H^{13} and H^{11}, $^3J_{HCCH} = 6.9-7.4$, 2H), 7.02 v. br. s (COH), 7.06−7.08 br. m (H^{16,20}, H^{17,19}), 7.12 t (H^{12}, $^3J_{HCCH} = 7.3$, the total integral intensity of the H^{12}, H^{16,20}, H^{17,19} and COH signals is equal to 6H), 7.18 t (H^{18}, $^3J_{HCCH} = 7.3$, 1H), 8.72 v. br. s (POH, 1H). ^{1}H NMR (700.0 MHz, 15 °C, CDCl$_3$): δ 1.24 t (CH$_3$, $^3J_{HCCH} = 7.1$, 6H), 3.56 q (CH$_2$O, $^3J_{HCCH} = 7.1$ 4H), 6.53 d (singlet in ^{1}H-{^{31}P} spectrum) (H^5, $^3J_{POCH} = 7.1$, 1H), 6.49 and 7.81 two br. d (H^{14} and H^{10}, $^3J_{HCCH} = 6.9-7.2$, 2H), 6.63 and 7.30 two br. dd (H^{13} and H^{11}, $^3J_{HCCH} = 6.9-7.4$, 2H), 7.0 v. br. s (COH), 7.06−7.08 br. m (H^{16,20}, H^{17,19}), 7.10 t (H^{12}, $^3J_{HCCH} = 7.3$, the total integral intensity of the H^{12}, H^{16,20}, H^{17,19} and COH signals is equal to 6H), 7.16 t (H^{18}, $^3J_{HCCH} = 7.3$, 1H), 8.48 v. br. s (POH, 1H). ^{1}H NMR (400.0 MHz, 25 °C, DMSO-d_6): δ 1.08 t (CH$_3$, $^3J_{HCCH} = 7.1$, 6H), 3.37 q (CH$_2$O, $^3J_{HCCH} = 7.1$ 4H), 6.31 d (singlet in ^{1}H-{^{31}P} spectrum) (H^5, $^3J_{POCH} = 7.0$, 1H), 6.51 and 7.72 two br. d (H^{14} and H^{10}, $^3J_{HCCH} = 7.5$, 2H), 6.59 and 7.28 two br. dd (H^{13} and H^{11}, $^3J_{HCCH} = 8.1$, $^3J_{HCCH} = 7.5$, 2H), 7.03−7.11 m (H^{16,20}, H^{17,19} and H^{12}, 5H), 7.13 m (H^{18}, $^3J_{HCCH} = 7.2$, 1H). ^{13}C NMR (100.6 MHz, 25 °C, CDCl$_3$): δ 14.82 qt (s) (CH$_3$, $^1J_{HC} = 126.2$, $^2J_{HCC} = 2.5$), 66.08 tq (s) (OCH$_2$, $^1J_{HC} = 141.6$, $^2J_{HCC} = 4.4$), 123.12 and 122.23 two q (two q) (C^{7,8}, $^1J_{FC^7} = 291.6$, $^1J_{FC^8} = 290.9$), 82.35 sept. d (sept. dd) (C^6, $^2J_{FC^{7,8}C^6} = 26.8$, $^3J_{POCC^6} = 7.0$, $^3J_{HC^5CC^6} = 2.2$), 89.93 m (d) (C^4, $^2J_{POC^4} = 3.0$), 86.25 br. d (br. s) (C^5, $^1J_{HC^5} = 159.2$), 125.46 and 127.53 two br. d (two br. s) (C^{13} and C^{11}, $^1J_{HC^{11,13}} = 159.0-159.3$), 126.51 and 129.79 two br. d (two br. s) (C^{10} and C^{14}, $^1J_{HC^{10,14}} = 159.0-159.5$), 127.80 s (C^{17,19}, $^1J_{HC^{17,19}} = 160.6$, $^3J_{HC^{19}CC^{17}} = 8.1$), 128.37 dt (s) (C^{12}, $^1J_{HC^{12}} = 161.4$, $^3J_{HC^{10,14}CC^{12}} = 7.7$), 128.88 dt (s) (C^{18}, $^1J_{HC^{18}} = 160.0$, $^3J_{HC^{16,20}CC^{18}} = 7.3$), 128.97 dm (s) (C^{16,20}, $^1J_{HC^{16,20}} = 160.6$, $^3J_{HC^{18}CC^{16,20}} = 6.5-7.5$, $^3J_{HC^{20}CC^{16}} = 6.5-7.5$), 132.82 m (d) (C^9, $^2J_{POC^4C^9} = 2.2$), 135.75 br. m (d) (C^{15}, $^3J_{HC^{17,20}CC^{15}} = 7.5$, $^3J_{POC^5C^{15}} = 6.6$, $^2J_{HC^5C^{15}} = 3.0$). ^{13}C (176.5 MHz, 15 °C, CDCl$_3$):

δ 14.92 q. t (s) (CH$_3$, $^1J_{HC} = 126.2$, $^2J_{HCC} = 2.5$), 66.08 tq (s) (OCH$_2$, $^1J_{HC} = 141.6$, $^2J_{HCC} = 4.4$), 123.09 and 122.21 two q (two q) (C^{7,8}, $^1J_{FC^7} = 291.6$, $^1J_{FC^8}$ 290.9), 82.33 sept. d (sept. dd) (C^6, $^2J_{FC^{7,8}C^6} = 26.6$, $^3J_{POCC^6}$ 6.3, $^3J_{HC^5CC^6} = 2.8$), 89.95 m (d) (C^4, $^2J_{POC^4} = 3.0$), 86.22 br. d (br. s) (C^5, $^1J_{HC^5} = 160.1$), 125.45 and 127.55 two br. dd (two br. s) (C^{13} and C^{11}, $^1J_{HC^{11,13}} = 160.6-159.1$, $^3J_{HC^{11,13}CC^{13,11}} = 8.0-8.5$), 126.53 and 129.73 two br. d. m (two br. s) (C^{10} and C^{14}, $^1J_{HC^{10,14}} = 163.0-163.5$, $^3J_{HC^{14,10}CC^{10,14}} = 6.6-7.0$, $^3J_{HC^{12}CC^{10,14}} = 6.6-7.0$), 127.82 (s) (C^{17,19}, $^1J_{HC^{17,19}} = 160.7$, $^3J_{HC^{19}CC^{17}} = 6.0$), 128.38 dt (s) (C^{12}, $^1J_{HC^{12}} = 160.3$, $^3J_{HC^{10,14}CC^{12}} = 7.5$), 128.89 dt (s) (C^{18}, $^1J_{HC^{18}} = 160.4$, $^3J_{HC^{16,20}CC^{18}} = 7.0$), 128.96 dm (s) (C^{16,20}, $^1J_{HC^{16,20}} = 158.7$, $^3J_{HC^{18}CC^{16,20}} = 6.5-7.5$, $^3J_{HC^{20}CC^{16}} = 6.5-7.5$), 132.79 br. t (d) (C^9, $^3J_{HC^{11,13}CC^9} = 7.6$, $^3J_{POC^4C^9} = 2.2$), 135.74 br. m (d) (C^{15}, $^3J_{HC^{17,20}CC^{15}} = 7.5$, $^3J_{POC^5C^{15}} = 6.6$, $^2J_{HC^5C^{15}} 3.0$). ^{13}C NMR (100.6 MHz, 25 °C, DMSO-d_6): δ 15.45 q. t (s) (CH$_3$, $^1J_{HC} = 125.5$, $^2J_{HCC} = 2.5$), 65.29 tq (s) (OCH$_2$, $^1J_{HC} = 140.2$, $^2J_{HCC} = 4.4$), 123.68 and 122.63 two q (two q) (C^{7,8}, $^1J_{FC^7} = 292.5$, $^1J_{FC^8} 291.8$), 82.34 sept. d (sept. dd) (C^6, $^2J_{FC^{7,8}C^6} = 25.5$, $^3J_{POCC^6}$ 7.6, $^3J_{HC^5CC^6}$ 2.2), 87.6 m (d) (C^4, $^2J_{POC^4} = 2.0$), 84.25 br. d (br. s) (C^5, $^1J_{HC^5} = 158.3$), 125.20 and 127.23 two br. d (two br. s) (C^{13} and C^{11}, $^1J_{HC^{11,13}} = 159.0-159.5$), 126.35 and 130.04 two br. d (two br. s) (C^{10} and C^{14}, $^1J_{HC^{10,14}} = 159.0-159.5$), 127.70 (s) (C^{17,19}, $^1J_{HC^{17,19}} = 160.6$, $^3J_{HC^{19}CC^{17}} = 8.1$), 128.17 dt (s) (C^{12}, $^1J_{HC^{12}} = 160.0$, $^3J_{HC^{10,14}CC^{12}} = 7.3$), 128.62 dt (s) (C^{18}, $^1J_{HC^{18}} = 161.4$, $^3J_{HC^{16,20}CC^{18}} = 7.7$), 128.87 dm (s) (C^{16,20}, $^1J_{HC^{16,20}} = 160.6$, $^3J_{HC^{18}CC^{16,20}} = 6.5-7.5$, $^3J_{HC^{20}CC^{16}} = 6.5-7.5$), 134.21 m (s) (C^9), 137.16 br. m (d) (C^{15}, $^3J_{HC^{17,20}CC^{15}} = 8.1$, $^3J_{POC^5C^{15}} = 6.6$, $^2J_{HC^5C^{15}} 3.0$). ^{19}F NMR (376.5 MHz, 25 °C, CDCl$_3$): δ −68.85 q (CF$_3$, $^4J_{FCCCF} = 10.9$, 3F), −67.63 q (CF$_3$, $^4J_{FCCCF} = 10.9$, 3F). ^{19}F NMR (658.8 MHz, 15 °C): δ −70.12 br. s (CF$_3$, 3F), −68.89 br. s (CF$_3$, 3F). ^{19}F NMR (376.5 MHz, 25 °C, DMSO-d_6): δ −66.55 q (CF$_3$, $^4J_{FCCCF} = 11.0$, 3F), −65.77 q (CF$_3$, $^4J_{FCCCF} = 11.0$, 3F). ^{31}P NMR (162.0 MHz, 25 °C, CDCl$_3$): δ 15.7 d (s) ($^3J_{HCOP} = 11.8$). ^{31}P NMR (162.0 MHz, 25 °C, DMSO-d_6): δ 13.0 d (s) ($^3J_{HCOP} = 5.9$). Found, %: C, 45.87; H, 3.28; P, 6.81. C$_{17}$H$_{13}$O$_5$F$_6$P Calcd, %: C, 46.15; H, 2.94; P, 7.01. HRMS (ESI): m/z calcd for C$_{17}$H$_{13}$O$_5$F$_6$P (M − H)$^-$ 441.0327, found 441.0322. IR spectrum, KBr pellet, ν, cm^{-1}: 725 m, 923 m, 1027 v. s, 1052 m, 1146 s, 1218 v. s, 1275 m, 1450 m, 2987 s. br, 3063 s. br.

Hydrolysis of Phosphate 12. A mixture of phosphate **12** (0.2 g, 0.45 mmol), 2 mL of DMSO-d_6, and 0.1 mL of water was allowed to stand at the room temperature for 30 days. The equilibrium ratio of phosphates **12** and **13** was 1:3.9. HRMS (ESI): m/z calcd for C$_{17}$H$_{15}$O$_6$F$_6$P (**13**) (M − H)$^-$ 459.0432, found 459.0428; m/z calcd for C$_{17}$H$_{13}$O$_5$F$_6$P (**12**) (M − H)$^-$ 441.0327, found 441.0325.

Compound (13). ^{1}H NMR (400.0 MHz, 25 °C, DMSO-d_6): δ 5.93 d (singlet in ^{1}H-{^{31}P} spectrum) (H^4, $^3J_{POCH} = 9.8$, 1H), 7.02, 7.11−7.14, 6.98 three br. m (H^{13,17}, H^{14,16}, H^9, H^{8,10}, H^{12}, 8H), 7.37 br. m (H^{7,11}, 2H). ^{1}H NMR (400.0 MHz, 35 °C, DMSO-d_6): δ 5.97 d (singlet in ^{1}H-{^{31}P} spectrum) (H^4, $^3J_{POCH} = 9.0$, 1H), 7.02−7.04, 7.08−7.10, two br. m (H^9, H^{8,10}, H^{12}, H^{13,17}, H^{14,16}, 8H), 7.39 br. m (H^{7,11}, 2H). ^{13}C NMR (100.6 MHz, 25 °C, DMSO-d_6): δ 124.01 q (q) (C^1, $^1J_{FC^1} = 292.6$), 123.41 br. q (br. q) (C^5, $^1J_{FC^5} = 292.3$), 83.48 sept (sept) (C^2, $^2J_{FC^1C^2} = 25.4$), 81.03 m (d) (C^3, $^3J_{POC^4C^3} = 6.2$), 80.34 br. d (br. s) (C^4, $^1J_{HC^4} = 146.4$), 128.90 and 127.30 two v. br. d (two v. br. s) (C^{7,11} and C^{8,10}), 126.74 dd (s) (C^{14,16}, $^1J_{HC^{14,16}} = 159.6$, $^3J_{HC^{14,16}CC^{14,16}} = 6.5$), 127.56 and 127.52 two dt (two s) (C^{9,15}, $^1J_{HC^{9,15}} = 160.0$, $^3J_{HCCC^{9,15}} = 7.6$), 129.91 dm (s) (C^{13,17}, $^1J_{HC^{13,17}} = 161.2$, $^3J_{HC^{15}CC^{13,17}} = 6.5-7.0$, $^3J_{HC^{17}CC^{13}} = 6.5-7.0$, $^3J_{HC^4CC^{13,17}} = 4.8$), 137.81 m (d) (C^{12}, $^3J_{POCC^{12}} = 2.4$), 138.38 br. m (br. s) (C^6). ^{13}C-{^{1}H} NMR (100.6 MHz, 35 °C, DMSO-d_6): δ 123.93 q (C^1, $^1J_{FC^1} = 291.6$), 123.35 q (C^5, $^1J_{FC^5} = 291.7$), 83.47 sept (C^2, $^2J_{FC^1C^2} = 24.5$), 81.0 d (C^3, $^3J_{POC^4C^3} = 6.6$), 80.47 br. s (C^4), 128.40 and 126.46 two v. br. s (C^{7,11} and C^{8,10}), 126.71 s (C^{14,16}), 127.52 s (C^{9,15}), 129.89 s (C^{13,17}), 137.73 d (C^{12}, $^3J_{POCC^{12}} = 2.4$), 138.26 s (C^6). ^{19}F NMR (376.5 MHz, 25 °C, DMSO-d_6): δ −65.77 q (CF$_3$, $^4J_{FCCCF} = 11.0$, 3F), −66.96 q (CF$_3$, $^4J_{FCCCF} = 11.0$, 3F). ^{31}P NMR (a view of signal in ^{31}P-{^{1}H} NMR spectrum is in parentheses, 162.0 MHz, 25 °C, DMSO-d_6): δ 0.2 d (s) ($^3J_{HCOP} = 9.8$). ^{19}F NMR (376.5 MHz, 35 °C, DMSO-d_6): δ −65.90 q (CF$_3$, $^4J_{FCCCF} = 10.9$, 3F), −66.83 q (CF$_3$, $^4J_{FCCCF} = 10.9$, 3F). ^{31}P NMR (162.0 MHz, 35 °C, DMSO-d_6): δ 0.2 d (s) ($^3J_{HCOP} = 9.8$).

Hydrolysis of Phosphate 12 and Isolation of Oxirane 14. To a solution of phosphate **12** (1 g, 2.26 mmol) in a 6 mL mixture of ethanol and water (1:1), 4 drops of concentrated HCl were added. The reaction

mixture was boiled for 4 h. On cooling to 20 °C, colorless oil was separated from the reaction mixture, which was crystallized for 7 days. The crystals were filtered off, washed with water, and dried *in vacuo* (12 Torr) at 80 °C. The yield of compound **14** was 0.58 g (70%), mp 90−91 °C. ^{1}H NMR (600.0 MHz, 25 °C, acetone-d_6): δ 4.75 s (H^4, 1H), 4.77 br. s (OH), 6.75 br. s (H^7, the total integral intensity of the OH and H^7 is equal to 2H), 6.99 br. s (H^8), 6.97 m (H^{13,17}, $^3J_{HCCH}$ = 7.7, the total integral intensity of the H^8 and H^{13,17} signals is equal to 3H), 7.13 m (H^{14,16}, $^3J_{HCCH}$ = 7.7, $^3J_{HCCH}$ = 7.1), 7.16 m (H^{15}, $^3J_{HCCH}$ = 7.1, $^4J_{HCCCH}$ = 1.4, the total integral intensity of the H^{15} and H^{14,16} signals is equal to 3H), 7.24 br. t (H^9, $^3J_{HCCH}$ = 7.3, 1H), 7.41 br. s (H^{10}, 1H), 7.65 two br. s (H^{11}, 1H). ^{1}H NMR (400.0 MHz, 25 °C, CDCl$_3$): δ 3.80 v. br. s (OH, 1H), 4.65 s (H^4, 1H), 6.76 and 7.65 two br. d (H^7 and H^{11}, $^3J_{HCCH}$ = 7.3 and 7.7, 2H), 7.0 and 7.39 two br. dd (H^8 and H^{10}, $^3J_{HCCH}$ = 7.3−7.7 and 7.5, 2H), 6.94 m (H^{13,17}, $^3J_{HCCH}$ = 7.7, 2H), 7.14 m (H^{14,16}, $^3J_{HCCH}$ = 7.7, $^3J_{HCCH}$ = 7.1, 2H), 7.18 m (H^{15}, $^3J_{HCCH}$ = 7.1, $^4J_{HCCCH}$ = 1.4, 1H), 7.24 tt (H^9, $^3J_{HCCH}$ = 7.4, $^4J_{HCCCH}$ = 1.1, 1H). ^{1}H NMR (700.0 MHz, 15 °C, CDCl$_3$): δ 4.07 v. br. s (OH, 1H), 4.75 s (H^4, 1H), 6.87 and 7.76 two br. d (H^7 and H^{11}, $^3J_{HCCH}$ = 7.6−7.7, 2H), 7.10 and 7.49 two br. dd (H^8 and H^{10}, $^3J_{HCCH}$ = 7.6−7.7 and 7.5, 2H), 7.04 br. d (H^{13,17}, $^3J_{HCCH}$ = 7.5, 2H), 7.24 br. dd (H^{14,16}, $^3J_{HCCH}$ = 7.5, $^3J_{HCCH}$ = 7.3, 2H), 7.29 m (H^{15}, $^3J_{HCCH}$ = 7.3, 1H), 7.34 t (H^9, $^3J_{HCCH}$ = 7.5, 1H). ^{13}C NMR (150.9 MHz, 25 °C, acetone-d_6): δ 123.05 q (q) and 122.79 br. q (br. q) (C^{1,5}, $^1J_{FC^{1,5}}$ = 289.4 and 285.6), 77.72 sept (sept) (C^2, $^2J_{FC^{1,5}C^2}$ = 28.5), 58.74 br. s (br. d) (C^4, $^1J_{HC^4}$ = 179.4), 133.11 td (s) (C^{12}, $^3J_{HC^{14,16}CC^{12}}$ = 7.2, $^2J_{HC^4C^{12}}$ = 4.7), 130.81 br. t (s) (C^6, $^3J_{HC^{8,10}CC^6}$ = 8.0), 129.63 and 130.44 two br. d (two br. s) (C^{7,11}, $^1J_{HC^{7,11}}$ = 161.0), 126.91 and 127.77 two br. d (two br. s) (C^{8,10}, $^1J_{HC^{8,10}}$ = 159.5), 128.16 d. t (s) (C^9, $^1J_{HC^9}$ = 159.5, $^3J_{HC^{7,11}CC^9}$ = 7.6), 126.58 br dddd (s) (C^{13,17}, $^1J_{HC^{13,17}}$ = 160.0, $^3J_{HC^{17,13}CC^{13,17}}$ = 7.0, $^3J_{HC^{15}CC^{13,17}}$ = 7.0, $^3J_{HC^4CC^{13,17}}$ = 2.7), 127.76 dd (s) (C^{14,16}, $^1J_{HC^{14,16}}$ = 159.5, $^3J_{HC^{16,14}CC^{14,16}}$ = 7.3), 128.03 dt (s) (C^{15}, $^1J_{HC^{15}}$ = 161.0, $^3J_{HC^{13,17}CC^{15}}$ = 7.6). ^{13}C NMR (100.6 MHz, 25 °C, CDCl$_3$): δ 122.62 q (q) and 122.39 qq (qq) (C^{1,5}, $^1J_{FC^1}$ = 289.0, $^1J_{FC^5}$ = 285.6, $^3J_{FC^1CC^5}$ 1.1), 77.04 sept (sept) (C^2, $^2J_{FC^{1,5}C^2}$ = 29.0), 64.62 br. td (s) (C^3, $^3J_{HC^{7,11}CC^3}$ = 3.3, $^2J_{HC^4CC^3}$ = 3.3), 59.92 q (br. d) (C^4, $^1J_{HC^4}$ = 178.0, $^4J_{FCCCC^4}$ = 1.8), 132.02 td (s) (C^{12}, $^3J_{HC^{14,16}CC^{12}}$ = 7.0, $^2J_{HC^4C^{13}}$ = 4.0), 129.73 br. t (s) (C^6, $^3J_{HC^{8,10}CC^6}$ = 7.2), 129.73 and 130.33 two br. d (two br. s) (C^{7,11}, $^1J_{HC^{7,11}}$ = 158.0), 127.40 and 128.08 two br. d (two br. s) (C^{8,10}, $^1J_{HC^{8,10}}$ = 160.0), 129.06 dt (s) (C^9, $^1J_{HC^9}$ = 161.0, $^3J_{HC^{7,11}CC^9}$ = 7.3), 126.73 br dddd (s) (C^{13,17}, $^1J_{HC^{13,17}}$ = 162.1, $^3J_{HC^{17,13}CC^{13,17}}$ = 7.0, $^3J_{HC^{15}CC^{13,17}}$ = 7.0, $^3J_{HC^4CC^{13,17}}$ = 2.8), 128.07 dm (s) (C^{14,16}, $^1J_{HC^{14,16}}$ = 161.4, $^3J_{HC^{16}CC^{14}}$ = 7.3), 128.62 dt (s) (C^{15}, $^1J_{HC^{15}}$ = 160.6, $^3J_{HC^{13,17}CC^{15}}$ = 7.5). ^{13}C NMR (176.5 MHz, 15 °C, CDCl$_3$): δ 122.56 q (q) and 122.32 br. q (br. q) (C^{1,5}, $^1J_{FC^1}$ = 288.7, $^1J_{FC^5}$ = 286.1), 76.92 sept (sept) (C^2, $^2J_{FC^{1,5}C^2}$ = 29.5), 64.56 br. td (s) (C^3, $^3J_{HC^{7,11}CC^3}$ = 3.5, $^2J_{HC^4CC^3}$ = 3.5), 59.84 br. dt (br. s) (C^4, $^1J_{HC^4}$ = 178.7, $^4J_{HC^{13,17}CC^4}$ = 5.0), 131.91 tdd (s) (C^{12}, $^3J_{HC^{8,10}CC^{12}}$ = 7.8, $^3J_{HC^4CC^{12}}$ = 4.0, $^4J_{HC^{15}CCC^{12}}$ 1.2), 129.61 br. t (s) (C^6, $^3J_{HC^{8,10}CC^6}$ = 7.2), 129.47 and 130.28 two br. ddd (two br. s) (C^7 and C^{11}, $^1J_{HC^{7,11}}$ = 159.6, $^3J_{HC^9CC^7}$ = $^3J_{HC^{11}CC^7}$ = 7.6, $^3J_{HC^9CC^{11}}$ = 7.6, $^3J_{HC^7CC^{11}}$ = 6.5), 127.39 and 128.09 two br. d (two br. s) (C^8 and C^{10}, $^1J_{HC^{8,10}}$ = 160.0−160.5, $^3J_{HC^{10,8}CC^{8,10}}$ = 7.6), 129.05 dtt (s) (C^9, $^1J_{HC^9}$ = 159.5, $^3J_{HC^{7,11}CC^9}$ = 7.5, $^2J_{HC^{8,10}C^9}$ = 1.3), 126.68 ddddd (s) (C^{13,17}, $^1J_{HC^{13,17}}$ = 159.3, $^3J_{HC^{17,13}CC^{13,17}}$ = 7.0, $^3J_{HC^{15}CC^{13,17}}$ = 7.0, $^3J_{HC^4CC^{13,17}}$ = 2.8, $^2J_{HC^{14,16}CC^{13,17}}$ = 1.3), 128.05 dd (s) (C^{14,16}, $^1J_{HC^{14,16}}$ = 160.5, $^3J_{HC^{14,16}CC^{16,14}}$ = 7.3), 128.61 dt (s) (C^{15}, $^1J_{HC^{15}}$ = 160.8, $^3J_{HC^{13,17}CC^{15}}$ = 7.5). ^{13}C-{^{19}F} NMR (176.5 MHz, 15 °C, CDCl$_3$): δ 122.54 and 122.31 two s (C^{1,5}), 76.92 s (C^2). ^{19}F NMR (376.5 MHz, 25 °C, CDCl$_3$): δ −72.44 q (CF$_3$, $^4J_{FCCCF}$ = 9.2, 3F), −70.94 q (CF$_3$, $^4J_{FCCCF}$ = 9.2, 3F). ^{19}F NMR (658.8 MHz, 15 °C, CDCl$_3$): δ −72.41 q (CF$_3$, $^4J_{FCCCF}$ = 8.9, 3F), −70.93 q (CF$_3$, $^4J_{FCCCF}$ = 8.9, 3F). Found, %: C, 56.68; H, 3.62. C$_{17}$H$_{12}$O$_2$F$_6$ Calcd, %: C, 56.35; H, 3.31. HRMS (ESI): *m/z* calcd for C$_{17}$H$_{12}$O$_2$F$_6$ (M − H)$^-$ 361.0673, found 361.0679. Mass spectrum (EI), *m/z* (I_{rel}, %): 362 (15.7) [M]$^+$, 346 (0.90) [M − O]$^+$, 343 (0.12) [M − F]$^+$, 293 (1.9) [M − CF$_3$]$^+$, 275 (1.1) [M − CF$_3$ − H$_2$O]$^+$, 195 (43.7) [M − C(OH)(CF$_3$)$_2$]$^+$, 167 (100.0) [CH(Ph)C(Ph)O]$^+$, 105 (35.6) [PhCO]$^+$, 91 (3.7) [PhCH$_2$]$^+$, 77 (18.3) [Ph]$^+$, 69 (7.1) [CF$_3$]$^+$. IR spectrum, KBr pellet, ν, cm^{-1}: 561 m, 697 s, 742 m, 909 m, 1147 s, 1220 v. s, 1284 s, 1386 m, 1450 m, 3422 v. s. br.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00356.

> X-ray data of compounds **9**, **11**, **12**, and **14** and quantum chemical calculations (atom coordinates and absolute energies) of hexafluoroacetone, molecules **8**−**10**, and intermediate **A** (PDF)
> NMR spectra of compounds **9**−**11** (PDF)
> NMR Spectra of Compounds **12** and **13** (PDF)
> NMR Spectra of Compound **14** (PDF)
> Crystallographic data for compounds **9**, **11**, **12**, **14** (CIF)
> Check CIF data-validation report (PDF)

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Notes

The authors declare no competing financial interest.

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