Bis(pentafluorophenyl)phosphinous acid in the synthesis of *P*,*P*-bis(pentafluorophenyl)phosphorylalkanones and -alkanediones*

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Addition of bis(pentafluorophenyl)phosphinous acid to α,β-alkenones and α,β,β′-alkenediones in anhydrous Et_2O (the solvent, in which the P—OH tautomeric form predominates) proceeds rapidly and regiospecifically at the C=C bond of the substrate at room temperature in the absence of catalysts. The reaction leads to bis(pentafluorophenyl)phosphorylated alkanones and alkanediones, as a rule, in the yields close to quantitative and can be considered as a highly efficient method for the synthesis of the corresponding functionalized phosphine oxides. The structures of obtained compounds were established by IR and NMR spectroscopy and X-ray diffraction analysis.

Key words: phosphinous acid *P*,*P*-bis(pentafluorophenyl)-substituted, addition to C=C bonds, ylidenealkanones(alkanediones), phosphorylalkanones(alkanediones), *P*,*P*-bis(pentafluorophenyl)-substituted, synthesis, IR spectroscopy, NMR spectroscopy, X-ray diffraction studies.

Though the first representatives of β-diphenylphosphorylalkanones were synthesized already at the beginning of 20th century,[1] this type of functionalized phosphine oxides became of special interest relatively recently.

It was found that such phosphorylated ketones can extract actinides and lanthanides from acidic solutions more efficiently than known organophosphorus mono- and bidentate extractants.[2,3] Besides, phosphoryl-containing compounds of this type, as it was demonstrated for 4-methyl-4-(diphenylphosphoryl)pentan-2-one as an example, are antipyrenes for poly(vinyl chloride).[4] Phosphorylated alkanones can be used in the design of various organophosphorus heterocyclic systems,[5—8] in which the presence of the phosphoryl fragment can be a factor increasing biological activity of corresponding compounds.[9]

From the practical point of view, it seemed potentially very promising to modify the named phosphoryl ketones by the replacement of the phenyl groups at the phosphorus atom with the pentafluorophenyl fragments. In fact, the perfluorination of the phenyl rings in the diphenylphosphoryl substituent of phosphorylalkanones can provide a high degree of affinity with fluorine-containing diluents (for example, with *m*-nitrobenzotrifluoride used in modern extraction technologies), as well as considerably enhance the antipyrene properties of such compounds as compared to nonfluorinated analogues. Finally, it is well known that replacement of hydrogen atoms with fluorine atoms is a powerful modificator influencing the character of biological activity of organic compounds (see, for example, Ref. 10 and references cited therein).

By now, only one compound of this type, $(C_6F_5)_2P(O)CHPhCH_2C(O)C_6H_4OMe$-*p*, is described in the literature, which was obtained by the reaction of bis(pentafluorophenyl)phosphinous acid (**1**) with the corresponding substituted chalcone in refluxing chloroform.[11] The purpose of the present study is to determine to which extent the reaction of acid **1** with α,β-enones can be considered as a general method for the synthesis of such phosphoryl ketones and develop a possibly simple and efficient process for their preparation, *i.e.*, to achieve the objectives, which could not be achieved in the work[11] because of its preliminary character.

It should be noted that acid **1** is a diarylhydrophosphoryl compound, which according to NMR spectroscopy can exist in solutions either as a P(O)H form (which is observed for the overwhelming majority of this type of compounds[12]), or as a mixture of P(O)H and P—OH forms. Since the P—OH form of hydrophosphoryl compounds is the most active toward electrophiles,[13] compound **1** potentially gives a golden opportunity for increasing reactivity only *via* the variation of the nature of organic solvents used as a medium in the reactions with α,β-enones.

* Dedicated to Academician of the Russian Academy of Sciences Yu. N. Bubnov on the occasion of his 80th birthday.

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However, it turned out that the literature data on the behavior of compound **1** in solutions are contradictory. Thus, in the work[14] it was indicated that the ^{1}H NMR spectra in deuterochloroform showed that this acid exists as a mixture of P(O)H and P—OH tautomers, whereas in hexadeuterodimethylsulfoxide only the P—OH form is present. On the contrary, the latest studies[15] allowed one to draw a conclusion that a solution of **1** in chloroform contains only the P(O)H isomer, whereas in dimethylsulfoxide both tautomers were present, though the P—OH tautomer was a predominant one (76%). It was also shown[15] that in such solvents, as toluene, CH_2Cl_2, and acetonitrile, acid **1** exists as a P(O)H tautomer, whereas in the case of MeOH, THF, DMF, dimethoxyethane, and diethyl ether both the P(O)H and the P—OH forms are present in solutions, though, the concentrations of acid **1** in these experiments were not specified. In this connection, in order to obtain the correct data on the behavior of acid **1** in the listed organic solvents we determined the position of tautomeric equilibrium of this hydrophosphoryl compound in the 0.05 *M* solutions in $CDCl_3$, CD_2Cl_2, CD_3CN, $(CD_3)_2SO$, MeOH, and diethyl ether and, if it was possible by a simultaneous use of both ^{31}P and ^{1}H NMR spectroscopy. In the case of first five solvents, our results turned out to be very similar to those given in the work,[15] that can indicate the absence of noticeable influence of the concentration factor on the position of tautomeric equilibrium in these solvents. Conversely, the content of the P—OH form in 0.05 *M* solution of **1** in diethyl ether (71%) turned out to be considerably higher than that reported in the work[15] (60%) and became actually the same as the content of this form in DMSO/DMSO-d_6.*

Besides, we determined the position of tautomeric equilibrium in 0.05 *M* solutions of acid **1** in a number of other synthetically important solvents (CCl_4, C_6D_6, and CD_3NO_2), which were not studied earlier. We found that the ^{1}H and ^{31}P NMR spectra of solutions of acid **1** exhibit only one doublet each in the regions δ 8.23—8.95 and −(18.97—23.57), respectively, which have the spin-spin coupling constants in the range 567—583 Hz virtually identical for each solvent, *i.e.*, the spin-spin coupling constant values characteristic of the $^1J_{H,P}$. The results obtained unambiguously indicate that compound **1** in these three solvents is present exclusively as the P(O)H tautomer.

To sum up, based on the available data a grounded suggestion can be made that among studied organic solvents diethyl ether, dimethylsulfoxide, and *N*-methylpyrrolidone are the most promising for the use as a medium to carry out the reactions of acid **1** with α,β-enones, since in these solvents the highest content of the POH form of this acid is observed.

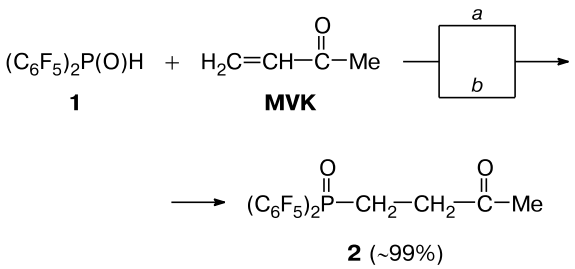
* As it was recently demonstrated,[16] yet higher content of the P—OH tautomer (90%) is observed in solution of **1** in *N*-methylpyrrolidone (for the concentration of ~0.56 mol L^{-1}).

Since in the cases of DMSO and *N*-methylpyrrolidone, there would be, undoubtedly, certain difficulties in the step of the isolation of target products in the individual state, diethyl ether is a preferable choice for the reactions of acid **1** with α,β-enones.

The studies of the synthetic potential of the reactions of bis(pentafluorophenyl)phosphinous acid with α,β-enones started from the simplest representative of this class of compounds, methyl vinyl ketone (**MVK**).

It was found that the reaction of acid **1** with **MVK** (the ratio 1 : 1.05, respectively) in anhydrous diethyl ether proceeded at very high rate even at room temperature,** and, according to the ^{31}P NMR spectroscopy, already after 1 h the signals of the starting hydrophosphoryl compound are absent in the reaction mixture (Scheme 1, *a*).

Scheme 1



a. 20 °C, 1 h, anhydrous Et_2O; *b*. 20 °C, 8 h, anhydrous $CHCl_3$.

The reaction was not accompanied by the formation of any side products, and the earlier unknown 4-[bis(pentafluorophenyl)phosphoryl]butan-2-one (**2**) was isolated in almost quantitative yield.

A control experiment (see Scheme 1, *b*), in which the reaction of acid **1** and **MVK** was carried out in anhydrous chloroform (where the named phosphinous acid exists exclusively as a P(O)H form), rather than in diethyl ether showed a sharp decrease in the rate of the process (the ^{31}P NMR spectroscopy showed that the signals of the starting organophosphorus compound disappear only after 8 h), which is in full agreement with the conclusions[13] on the relative reactivities of the P(O)H and the P—OH forms of hydrophosphoryl compounds.

The phosphorylalkanone **2** is a low-melting white crystalline compound stable in air in both the solid state and in solution. The composition of this compound was confirmed by elemental analysis, its structure was confirmed by IR spectroscopy and NMR spectroscopy (^{1}H, ^{1}H{^{31}P}, ^{13}C{^{1}H}, ^{19}F{^{1}H}, and ^{31}P{^{1}H}) (see Experimental), as well as by X-ray diffraction studies (Fig. 1).

** In the case of nonfluorinated analog **1**, diphenylphosphinous acid, the reaction with **MVK** proceeds at a comparable rate under much more drastic conditions: at 95 °C and under influence of microwave irradiation.[17]

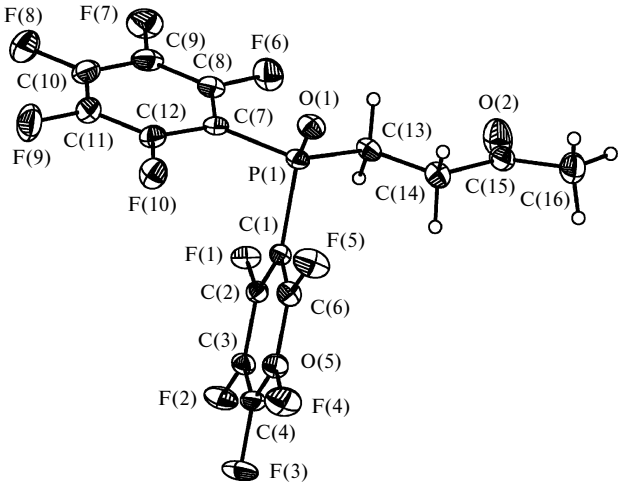


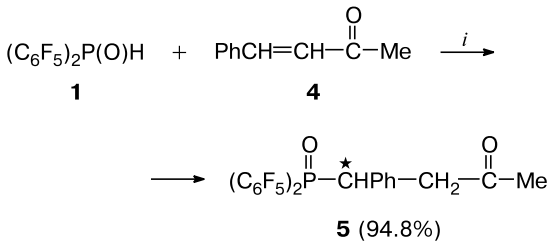
Fig. 1. General view of the structure of 4-[bis(pentafluorophenyl)phosphoryl]butan-2-one (**2**) in representation of atoms by ellipsoids of thermal vibrations ($p = 50\%$).

A comparison of the IR spectroscopy data for ketone **2** and its nonfluorinated analog $Ph_2P(O)CH_2CH_2C(O)Me$ (**3**) indicates that in the series of β-(diarylphosphoryl)-alkanones a replacement of *P*-phenyl fragments with the pentafluorophenyl substituents possessing a pronounced electron-withdrawing effect, causes a considerable shift of the P=O group vibrational frequency: from 1180 for **3** (see Ref. 5) to 1219 cm^{-1} for **2**, while for the C=O groups such a replacement expectedly results in much less changes and the corresponding Δν value is only 8 cm^{-1}.

Similarly to the IR spectra, a total replacement of hydrogen atoms with the fluorine atoms in the diphenylphosphoryl fragment of ketone **3** (see Ref. 17) results in a considerable (~12 ppm) upfield shift of the signal in the $^{31}P\{^1H\}$ NMR spectrum. In the ^1H NMR spectrum, the signals for the methylene fragments are found as the doublets of triplets, which in the $^1H\{^{31}P\}$ NMR spectrum are transformed to triplets. To correctly assign the signals for the protons of the CH_2P and the $CH_2C(O)$ groups with close positions in the ^1H NMR spectrum, we used the corresponding $^1H—^{13}C$-correlation (HMQC). The signals for the nuclei of ^{13}C (see Ref. 18) and ^{19}F atoms[19] were assigned based on the data published earlier. In the $^{13}C\{^1H\}$ NMR spectrum of phosphoryl ketone **2**, the signal for the carbonyl carbon atom was found as a doublet with a spin-spin coupling constant $^3J_{C,P} = 12.9$ Hz, that indicates[20] the *trans*-arrangement of the C=O and the P=O groups. It should be emphasized that this conclusion, obtained based on the results of spectral studies, is in full agreement with the results of X-ray diffraction studies for phosphoryl ketone **2**.

The reaction of acid **1** with 4-phenylbut-3-en-2-one (**4**) in anhydrous ether at ~20 °C proceeds at a slightly lower rate than in the case of **MVK**, which, most likely, is caused by an increase of sterical hindrance. However, this reaction is not virtually accompanied by the formation of any noticeable amounts of side products either* and leads to the desired 4-[bis(pentafluorophenyl)phosphoryl]-4-phenylbutan-2-one (**5**) in the yield close to quantitative (Scheme 2).

Scheme 2

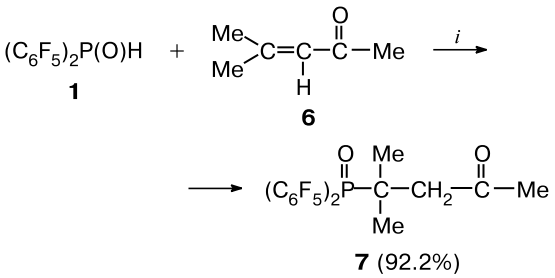


i. 20 °C, 2 h, anhydrous Et_2O.

The structure of phosphoryl ketone **5** was confirmed by IR spectroscopy and NMR spectroscopy (^1H, $^1H\{^{31}P\}$, $^{13}C\{^1H\}$, $^{19}F\{^1H\}$, and $^{31}P\{^1H\}$). Note that a 10 ppm difference in the chemical shifts of the singlet signals in the $^{31}P\{^1H\}$ NMR spectra of ketone **5** ($\delta_P = 23.6$) and its nonfluorinated analog $Ph_2P(O)CHPhCH_2C(O)Me$ ($\delta_P = 33.6$)[22] is slightly less than in the case of the pair of phosphoryl ketones **2**—**3**. Due to the presence in the molecule of ketone **5** of the asymmetric benzyl carbon atom, the hydrogen atoms of the neighboring methylene fragment become diastereotopic and, as a consequence, anisochronic (*i.e.*, having different chemical shifts) in the achiral medium. For a similar reason, both pentafluorophenyl fragments attached to the phosphorus atom are anisochronic, that is indicated by the doubling of the signals for the corresponding indicative nuclei in the $^{13}C\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectra (see Experimental).

The studies of the reaction of acid **1** with mesityl oxide (**6**) in anhydrous diethyl ether at ~20 °C (Scheme 3)

Scheme 3



i. 20 °C, 48 h, anhydrous Et_2O.

* It should be noted that, as it has been shown earlier,[21] the reaction of benzylideneacetone **4** with a number of diorganylphosphinous acids, including diphenylphosphinous acid, in Et_2O at room temperature leads to the products of addition of hydrophosphoryl compounds exclusively at the C=O bond of the starting enone.

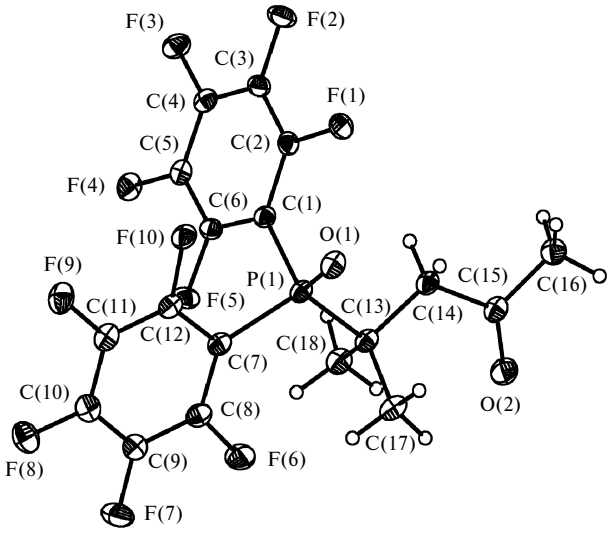


Fig. 2. General view of the structure of 4-[bis(pentafluorophenyl)phosphoryl]-4-methylpentan-2-one (**7**) in representation of atoms by ellipsoids of thermal vibrations (p = 50%).

showed that the presence of two substituents at the terminal atom of the C=C bond of α,β-enone leads to a further, though noncritical, decrease in the rate of the reaction, thus confirming our suggestion on the sterical character of such an effect.

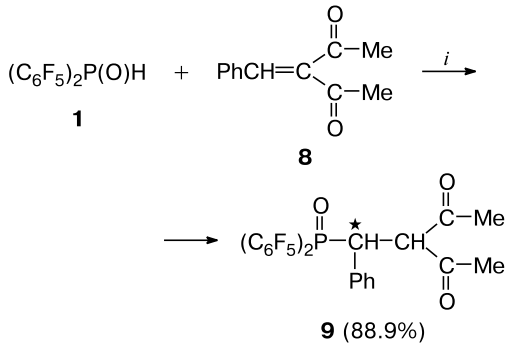
This reaction, like in the case of α,β-enones studied earlier, retains its regioselectivity,* which results in the isolation of 4-[bis(pentafluorophenyl)phosphoryl]-4-methylpentan-2-one (**7**) in 92.2% yield.

The structure of phosphoryl ketone **7** was confirmed by IR spectroscopy, NMR spectroscopy (^{1}H, ^{1}H{^{31}P}, ^{13}C{^{1}H}, ^{19}F{^{1}H}, and ^{31}P{^{1}H}) (see Experimental), and X-ray diffraction studies (Fig. 2). In this case, it is noticeable that the chemical shifts of the signals in the ^{31}P{^{1}H} NMR spectra of the fluorine-containing phosphoryl ketone **7** (δ_P = 34.9) and its nonfluorinated analog $Ph_2P(O)CMe_2CH_2C(O)Me$ (δ_P = 37.2)[5] are already virtually the same. Like in the case of the simplest β-[bis(pentafluorophenyl)phosphoryl]alkanone **2**, a suggestion on the transoid arrangement of the P=O and the C=O fragments in the molecule of fluorophosphorus-containing ketone **7**, made based on the spin-spin coupling constant $^3J_{C,P}$ (17.6 Hz) of the carbon atom of the carbonyl group of this compound, is confirmed by the X-ray diffraction data. The results obtained indicate that in the series of β-diorganylphosphorylalkanones parameters of the corresponding spin-spin coupling constant can serve as a reliable instrument for finding a mutual arrangement of the P=O and the C=O groups in the molecule of phosphorylated ketone independent of the nature of the organyl substituent at the phosphorus atom.

The reaction of acid **1** with the corresponding α,β-unsaturated alkenediones in anhydrous Et_2O at ~20 °C can be successfully used for the preparation of bis(pentafluorophenyl)phosphorylated alkanediones.

Thus, according to the ^{31}P NMR spectroscopy data, the reaction of acid **1** with 3-benzylidenepentane-2,4-dione (**8**) under these conditions comes to completion within 24 h in the absence of any initiators or catalysts,** which results in the isolation of 3-{α-[bis(pentafluorophenyl)phosphoryl]benzyl}pentane-2,4-dione (**9**) in high yield (Scheme 4).

Scheme 4



i. 20 °C, 24 h, anhydrous Et_2O.

The structure of compound **9** was confirmed by IR spectroscopy, NMR spectroscopy (^{1}H, ^{1}H{^{31}P}, ^{19}F{^{1}H}, ^{13}C{^{1}H}, ^{31}P{^{1}H}), and X-ray diffraction studies (Fig. 3).

In the IR spectrum of diketone **9**, two vibrational bands for the carbonyl groups are found at 1712 and 1732 cm^{-1}. Earlier,[22] a similar effect was also observed in the case of nonfluorinated diketone $Ph_2P(O)CHPhCH[C(O)Me]_2$. In this case, the quantum chemical calculations of the vibrational frequencies in the conformation of the global minimum showed that the vibrations of the C=O groups of compound under consideration are bound both in-phase and in-antiphase. It is possible that similar situation is also in place in the case of decafluorinated phosphoryl diketone **9**.

In the molecule of diketone **9,** there are present an asymmetric benzyl carbon atom, included in the composition of the P(O)CH fragment, and two prochiral centers: the phosphorus atom and the methine carbon atom bonded to

* According to the literature data,[23] the addition of diorganylphosphinous acids containing no fluorine atoms to mesityl oxide **6** at room temperature, like in the case of another nonterminal α,β-enone **4**, proceeds exclusively at the C=O bond of the starting unsaturated ketone.

** Earlier we have shown,[7] that an efficient addition of diphenylphosphinous acid (nonfluorinated analog of **1**) at ~20 °C to enedione **8** becomes feasible only in the presence of 1,5,7-triazabicyclo[4.4.0]dec-5-ene as a catalyst.

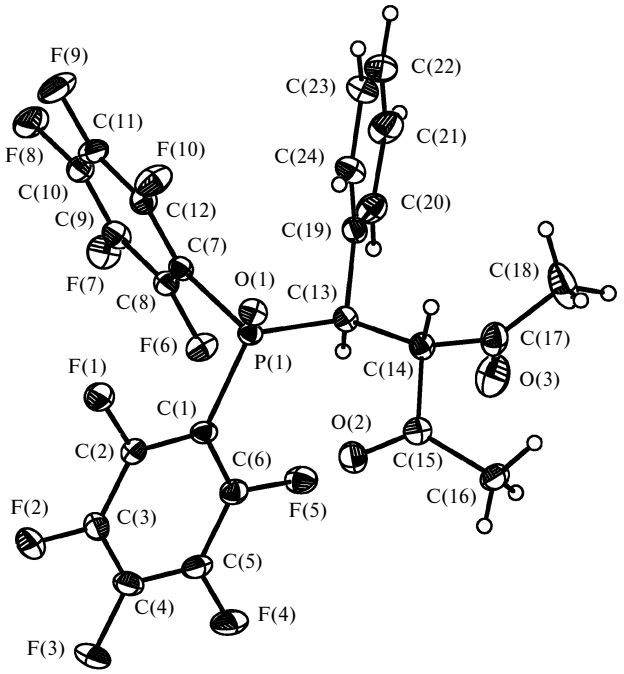


Fig. 3. General view of the structure of 3-{α-[bis(pentafluorophenyl)phosphoryl]benzyl}pentane-2,4-dione (**9**) in representation of atoms by ellipsoids of thermal vibrations (p = 50%).

the acyl groups. In this connection, both the *P*-pentafluorophenyl substituents and the COMe groups are diastereotopic and magnetically nonequivalent in achiral medium, which can be seen in the $^1H/^1H\{^{31}P\}$, $^{19}F\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra as a doubling of signals of the corresponding indicative nuclei.* In particular, the signals for the carbon atoms of the C=O groups are found as two doublets at δ_P = 200.74 ($^3J_{C,P}$ = 14.7 Hz) and 201.74 ($^3J_{C,P}$ = 1.5 Hz). Taking into account a high reliability of the correlation between the corresponding spin-spin coupling constant and a mutual arrangement of the carbonyl and the phosphoryl fragments confirmed for diorganylphosphorylated monoketones, the high-field signal can be assigned to the C=O fragment of the phosphoryl diketone molecule **9**, which is in the transoid position with respect to the phosphoryl group, whereas the low-field signal can be assigned to the cisoid C=O fragment. Note that according to the X-ray diffraction data, the phenyl substituent at the C(13) atom is *cis*-oriented relative to the phosphoryl group and in close proximity to the perfluorophenyl substituent C(7)—C(12) (C(7)...C(19) 2.955(1) Å). By all accounts, this specific feature of the structure of phosphoryl diketone **9** is a cause of the effect observed in the ^1H, ^{13}C and ^{19}F NMR spectra of this compound (see Experimental): the signals for a number of the corresponding nuclei which compose the Ph and one of the C_6F_5 substituents are found as the broad signals, rather than as expected multiplets.

In conclusion, the addition of bis(pentafluorophenyl)-phosphinous acid to α,β-alkenones and α,β,β′-alkenediones in anhydrous Et_2O proceeds regiospecifically at the C=C bond of the substrate at high rate at ~20 °C in the absence of any catalysts and usually in the yields close to quantitative and leads to bis(pentafluorophenyl)phosphorylated alkanones and alkanediones, which allows one to consider this process as a highly efficient method for the synthesis of the corresponding functionalized phosphine oxides.

To increase the practical importance of this method, we suggested a new simple and efficient version for the synthesis of the starting acid **1**, consisting in the aqueous hydrolysis of bromobis(pentafluorophenyl)phosphine (**10**) (Scheme 5).

Scheme 5

$$(C_6F_5)_2PBr \xrightarrow{H_2O} (C_6F_5)_2P(O)H$$

10 **1** (84%)

This approach is favorably distinguished from the classic[14] method for the preparation of acid **1**: the starting organophosphorus compound is not bis(pentafluorophenyl)chlorophosphine (**11**), but synthetically more available** analog **10**.

Experimental

^1H, $^1H\{^{31}P\}$, $^{13}C\{^1H\}$, $^{19}F\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker AV-400 (400.13 (^1H and $^1H\{^{31}P\}$), 100.61 ($^{13}C\{^1H\}$), 376.49 ($^{19}F\{^1H\}$), and 161.98 MHz ($^{31}P\{^1H\}$)) and Bruker AV-600 (in the case of ^1H and $^{13}C\{^1H\}$ NMR spectra of compound **2**) (600.22 (^1H) and 150.925 MHz (^{13}C)). The signals for the residual protons of the deuterated solvent (in the case of CCl_4, the signals for the residual protons of D_2O (capillary)) were used as a reference for the ^1H and $^1H\{^{31}P\}$ NMR spectra, for $^{13}C\{^1H\}$ NMR spectra the reference was the signals for the carbon atom nuclei of the deuterated solvent, external standards for $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were $CFCl_3$ and 85% H_3PO_4, respectively.

* In this case, if in the $^{13}C\{^1H\}$ NMR spectrum such a doubling is observed for the signals of all four types of nuclei of carbon atoms (*ortho*-, *meta*-, *para*-, and *ipso*-) of pentafluorophenyl fragments, in the $^{19}F\{^1H\}$ NMR spectrum such an effect is observed only for the nuclei of the fluorine atoms located at *ortho*- and *para*-positions of these substituents.

** According to the recent data,[24] bromophosphine **10** can be easily synthesized in one step by the reaction of C_6F_5MgBr with PCl_3, whereas a two-step process remains the only method for the synthesis of chlorophosphine **11**, reliably leading to the individual product: $C_6F_5MgX \rightarrow (C_6F_5)_2PNRR' \rightarrow$ **11** (see, for example, Ref. 18).

IR spectra were recorded on a Bruker Tensor 37 Fourier-transform spectrometer (resolution 2 cm^{-1}) in the region of 400—4000 cm^{-1}. Samples were prepared in KBr pellets.

The crystals of bis(pentafluorophenyl)phosphorylalkanones **2**, **7**, and **9** suitable for X-ray diffraction studies were obtained by evaporation of solutions of the corresponding compounds in anhydrous diethyl ether at ~20 °C.

X-ray diffraction studies of compounds **2** and **7** were carried out on a Smart APEX2 DUO CCD diffractometer, compound **9** was studies on a Smart APEX2 CCD diffractometer (Mo-Kα radiation, graphite monochromator, ω-scan technique). The structures were solved by direct method and refined by least squares method in anisotropic full-matrix approximation on F^2_{hkl}. Positions of hydrogen atoms were calculated geometrically and refined in isotropic approximation using a riding model. Principal crystallographic data and parameters of refinement are given in Table 1. All the calculations were carried out using the SHELXTL PLUS software.

The starting bromopentafluorobenzene (Acros) was dried with anhydrous $CaCl_2$ and distilled before the reaction; phosphorus trichloride, methyl vinyl ketone, and mesityl oxide **6** (Acros) were distilled before the reaction; 4-phenylbut-3-en-2-one **4** (Acros) and 3-benzylidenepentane-2,4-dione **8** (Alfa Aesar) were used without additional purification. The basic Brockmann I Al_2O_3 (50—200 μm, Acros) was used.

Organic solvents used in the work were purified according to the standard procedures.[25]

Deuterated solvents for the recording NMR spectra ($CDCl_3$, CD_2Cl_2, C_6D_6, CD_3CN, CD_3NO_2, and DMSO-d_6) produced by the FGUP Russian Scientific Center of Applied Chemistry, Saint Petersburg) were used without additional purification.

Reaction progress of addition of **1** to unsaturated carbonyl compounds was monitored by ^{31}P NMR spectroscopy.

Elemental analysis was performed in the Laboratory of Microanalysis of A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences.

Bromobis(pentafluorophenyl)phosphine (10). The Grignard reagent was obtained by a standard method from bromopentafluorobenzene (60 g, 0.243 mol) and magnesium turnings (6.1 g, 0.251 mol) in anhydrous diethyl ether (210 mL) and was filtered through a porous glass filter under argon. The ethereal solution of the Grignard reagent was placed into a 500-mL round-bottom three-neck glass flask equipped with a mechanical stirrer, dropping funnel, and an alcohol thermometer, cooled to –50 °C, followed by a dropwise addition of a solution of freshly distilled phosphorus trichloride (14.5 g, 0.106 mol) in anhydrous diethyl ether (10 mL) at this temperature over 0.5 h. The reaction mixture was stirred for 2 h, gradually raising temperature to ~20 °C, allowed to stand for 3 days, filtered through a porous glass filter under argon. A precipitate was washed with anhydrous diethyl ether (2×50 mL), the ether from the combined filtrates was evaporated, the residue was distilled *in vacuo*, collecting a fraction with b.p. 80—130 °C (~1 Torr), the fraction obtained was redistilled *in vacuo*. The yield was 28.4 g (67%), b.p. 119—121 °C (0.5 Torr) (*cf.* Ref. 26: b.p. 100—104 °C (0.1 Torr)). ^{31}P NMR (MeCN (anhydrous)), δ: 12.81 (quint, $^3J_{P,F} = 37.1$ Hz).

Bis(pentafluorophenyl)phosphinous acid (1). Bromobis(pentafluorophenyl)phosphine (**10**) (10 g, 22.5 mmol) was added drop-

Table 1. Principal crystallographic data and parameters refinement for compounds **2**, **7**, and **9**

Parameter	**2**	**7**	**9**
Molecular formula	$C_{16}H_7F_{10}O_2P$	$C_{18}H_{11}F_{10}O_2P$	$C_{24}H_{13}F_{10}O_3P$
Molecular weight	452.19	480.24	570.31
T/K	120	100	120
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	P-1
Z	4	4	2
a/Å	10.4562(19)	9.9196(4)	10.2732(17)
b/Å	15.837(3)	11.4783(4)	10.4596(18)
c/Å	10.3974(19)	15.9353(6)	11.5429(19)
α/deg	90.00	90.00	87.627(3)
β/deg	100.499(3)	99.4720(10)	69.131(3)
γ/deg	90.00	90.00	78.278(3)
V/Å^3	1692.9(5)	1789.66(12)	1134.1(3)
d_{calc}/g cm^{-3}	1.774	1.782	1.670
μ/cm^{-1}	2.78	2.69	2.3
F(000)	896	960	572
$2\theta_{max}$/deg	58	60	56
Reflections collected	12024	19667	12426
Number of independent reflections	4479	5216	5448
Number of reflections with $I > 2\sigma(I)$	3763	4601	4344
Number of refined parameters	263	283	345
R_1	0.0339	0.0304	0.0493
wR_2	0.0907	0.0839	0.1444
GOOF	1.013	1.031	1.018
Residual electron density/e Å^{-3}, ρ_{max}/ρ_{min}	0.443/–0.343	0.422/–0.363	1.201/–0.637

wise to an ice-cold water (50 mL) with vigorous stirring using a magnetic stirrer and cooling by ice, the mixture was stirred for 3 h with external cooling in an ice-water bath. A precipitate formed was separated, washed with ice-cold water (15 mL), thoroughly wrung out, dried in air for 1 h, kept over P_2O_5 *in vacuo* (~1 Torr) at 30 °C until the weight was constant, and recrystallized from hexane. The yield was 7.2 g (84%), m.p. 97—99 °C (*cf.* Ref. 14: m.p. 97—98 °C). ^{1}H NMR (CCl_4, c = 0.05 mol L^{-1}), δ: 8.66 (d, P(O)H, $^1J_{H,P}$ = 569.2 Hz). ^{31}P NMR (CCl_4, c = = 0.05 mol L^{-1}), δ: –22.93 (d, P(O)H, $^1J_{P,H}$ = 571.9 Hz). ^{1}H NMR (C_6D_6, c = 0.05 mol L^{-1}), δ: 8.23 (d, P(O)H, $^1J_{H,P}$ = = 566.7 Hz). ^{31}P NMR (C_6D_6, c = 0.05 mol L^{-1}), δ: –23.57 (d, P(O)H, $^1J_{P,H}$ = 566.7 Hz). ^{1}H NMR (CD_3NO_2, c = 0.05 mol L^{-1}), δ: 8.95 (d, P(O)H, $^1J_{H,P}$ = 583.1 Hz). ^{31}P NMR (CD_3NO_2, c = 0.05 mol L^{-1}), δ: –18.97 (d, P(O)H, $^1J_{P,H}$ = 583.0 Hz).

4-[Bis(pentafluorophenyl)phosphoryl]butan-2-one (2). ***A. In diethyl ether.*** A solution of acid **1** (2.292 g, 6 mmol) in anhydrous diethyl ether (24 mL) was added dropwise to a solution of freshly distilled **MVK** (0.44 g, 6.3 mmol) in anhydrous ether (6 mL). The reaction mixture was allowed to stand for 1 h at ~20 °C, concentrated to dryness, and kept *in vacuo* (~ 1 Torr) at 75 °C for 3.5 h. The yield was 2.675 g (98.6%), m.p. 87.5—89 °C (hexane—CCl_4). Found (%): C, 42.23; H, 1.47; F, 42.02; P, 6.71. $C_{16}H_7F_{10}O_2P$. Calculated (%): C, 42.50; H, 1.56; F, 42.01; P, 6.85. IR, ν/cm^{-1}: 1219 (P=O), 1728 (C=O). ^{31}P{^{1}H} NMR ($CDCl_3$, c = 0.1 mol L^{-1}), δ: 19.97 (s). ^{1}H NMR (Bruker AV-400, $CDCl_3$, c = 0.1 mol L^{-1}), δ: 2.23 (s, 3 H, Me); 2.87 (dt, 2 H, CH_2P, $^3J_{H,H}$ = 7.2 Hz, $^2J_{H,P}$ = 11.2 Hz); 3.02 (dt, 2 H, $C\underline{H}_2CH_2P$, $^3J_{H,H}$ = 7.2 Hz, $^3J_{H,P}$ = 13.4 Hz). ^{1}H NMR (Bruker AV-600, $CDCl_3$, c = 0.1 mol L^{-1}), δ: 2.23 (s, 3 H, Me); 2.87 (dt, 2 H, CH_2P, $^3J_{H,H}$ = 7.6 Hz, $^2J_{H,P}$ = 11.5 Hz); 3.01 (dt, 2 H, $C\underline{H}_2CH_2P$, $^3J_{H,H}$ = 7.4 Hz, $^3J_{H,P}$ = 13.4 Hz). ^{1}H{^{31}P} NMR ($CDCl_3$, c = 0.1 mol L^{-1}), δ: 2.23 (s, 3 H, Me); 2.88 (t, 2 H, CH_2P, $^3J_{H,H}$ = 7.2 Hz); 3.02 (t, 2 H, $C\underline{H}_2CH_2P$, $^3J_{H,H}$ = 7.3 Hz). ^{13}C{^{1}H} NMR (Bruker AV-600, $CDCl_3$, c = 0.1 mol L^{-1}), δ: 27.33 (d, CH_2P, $^1J_{C,P}$ = 81.8 Hz); 29.63 (s, Me); 34.58 (d, $\underline{C}H_2CH_2P$, $^2J_{C,P}$ = 4.4 Hz); 107.38 (dtm, *ipso*-C_6F_5, $^1J_{C,P}$ = = 95.1 Hz, $^2J_{C,F}$ = 21.0 Hz); 137.89 (dm, *m*-C_6F_5, $^1J_{C,F}$ = = 263.1 Hz); 144.59 (dm, *p*-C_6F_5, $^1J_{C,F}$ = 263.1 Hz); 147.11 (dm, *o*-C_6F_5, $^1J_{C,F}$ = 256.5 Hz); 204.52 (d, C=O, $^3J_{C,P}$ = 13.3 Hz). ^{19}F{^{1}H} NMR ($CDCl_3$, c = 0.1 mol L^{-1}), δ: –131.63 (d, 4 F, *o*-C_6F_5, $^3J_{F,F}$ = 21.3 Hz); –143.64 (t, 2 F, *p*-C_6F_5, $^3J_{F,F}$ = = 21.3 Hz); –(157.73—157.93) (m, 4 F, *m*-C_6F_5).

B. In chloroform. A solution of acid **1** (2.292 g, 6 mmol) in anhydrous chloroform (10 mL) was added dropwise to a solution of freshly distilled **MVK** (0.44 g, 6.3 mmol) in anhydrous chloroform (20 mL), kept for 8 h at ~20 °C, and treated afterwards as in the preceding case. The yield was 2.695 g (99.3%), m.p. 88—89 °C (hexane—CCl_4). The spectral characteristics of compound obtained are identical to the corresponding parameters of phosphoryl ketone **2** obtained by method ***A***.

4-[Bis(pentafluorophenyl)phosphoryl]-4-phenylbutan-2-one (5). A solution of acid **1** (1.146 g, 3 mmol) in anhydrous diethyl ether (12 mL) was added dropwise to a solution of 4-phenylbut-3-en-2-one (**4**) (0.46 g, 3.15 mmol) in anhydrous ether (3 mL), The reaction mixture was kept for 2 h at ~20 °C and concentrated to dryness, the residue was dissolved in anhydrous CH_2Cl_2 (5 mL). The solution obtained was filtered through a layer of basic Al_2O_3 (0.57 g), the Al_2O_3 was washed with anhydrous CH_2Cl_2 (6 mL). The combined filtrates were concentrated to dryness, triturated with a 2 : 1 mixture of hexane—ether (3 mL), a precipitate formed was separated, sequentially washed on the filter with a mixture of hexane—ether (2 : 1) (3×3 mL) and hexane (5 mL), and dried in air. The yield was 1.502 g (94.8%), m.p. 168.5—169.5 °C. Found (%): C, 49.69; H, 2.01; F, 35.31; P, 6.17. $C_{22}H_{11}F_{10}O_2P$. Calculated (%): C, 50.02; H, 2.10; F, 35.96; P, 5.86. IR, ν/cm^{-1}: 1219 (P=O), 1715 (C=O). ^{31}P{^{1}H} NMR ($CDCl_3$, c = 0.1 mol L^{-1}), δ: 23.62 (s). ^{1}H NMR ($CDCl_3$, c = 0.1 mol L^{-1}), δ: 2.16 (s, 3 H, Me); 3.32 (dd, $C\underline{H}_AH_B$, 1 H, $^2J_{H_A,H_B}$ = 18.2 Hz, $^3J_{H_A,P}$ = 12.4 Hz); 3.53 (ddd, $CH_A\underline{H}_B$, 1 H, $^2J_{H_B,H_A}$ = 18.0 Hz, $^3J_{H_B,H}$ = 9.8 Hz, $^3J_{H_B,P}$ = 6.4 Hz); 4.47—4.54 (m, 1 H, CHP); 7.18—7.27 (m, 3 H, *m*-Ph, *p*-Ph); 7.40—7.44 (m, 2 H, *o*-Ph). ^{1}H{^{31}P} NMR ($CDCl_3$, c = 0.1 mol L^{-1}), δ: 2.16 (s, 3 H, Me); 3.32 (d, $C\underline{H}_AH_B$, 1 H, $^2J_{H_A,H_B}$ = 17.7 Hz); 3.53 (dd, $CH_A\underline{H}_B$, 1 H, $^2J_{H_B,H_A}$ = 17.9 Hz, $^3J_{H_B,H}$ = 10.2 Hz); 4.51 (d, 1 H, CHP, $^3J_{H,H_B}$ = 9.2 Hz); 7.18—7.27 (m, 3 H, *m*-Ph, *p*-Ph); 7.42 (d, 2 H, *o*-Ph, $^3J_{H,H}$ = 6.9 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, c = 0.1 mol L^{-1}), δ: 30.26 (s, Me); 43.67 (s, CH_2); 44.50 (d, CHP, $^1J_{C,P}$ = 76.3 Hz); 106.16 (dm, *ipso*-C_6F_5, $^1J_{C,P}$ = 93.9 Hz); 108.40 (dm, *ipso*-C_6F_5, $^1J_{C,P}$ = 85.8 Hz); 128.57 (d, *p*-Ph, $^5J_{C,P}$ = 2.2 Hz); 129.04 (d, *m*-Ph, $^4J_{C,P}$ = 1.5 Hz); 129.16 (d, *o*-Ph, $^3J_{C,P}$ = 7.3 Hz); 134.54 (d, *ipso*-Ph, $^2J_{C,P}$ = 5.9 Hz); 137.32 (dm, *m*-C_6F_5, $^1J_{C,F}$ = 250.2 Hz); 137.93 (dm, *m*-C_6F_5, $^1J_{C,F}$ = = 256.0 Hz); 143.98 (dm, *p*-C_6F_5, $^1J_{C,F}$ = 260.4 Hz); 144.43 (dm, *p*-C_6F_5, $^1J_{C,F}$ = 246.5 Hz); 146.53 (dm, *o*-C_6F_5, $^1J_{C,F}$ = = 251.6 Hz); 146.90 (dm, *o*-C_6F_5, $^1J_{C,F}$ = 251.6 Hz); 203.33 (d, C=O, $^3J_{C,P}$ = 16.1 Hz). ^{19}F{^{1}H} NMR ($CDCl_3$, c = 0.1 mol L^{-1}), δ: –130.33 (d, 2 F, *o*-C_6F_5, $^3J_{F,F}$ = 16.5 Hz); –132.30 (d, 2 F, *o*-C_6F_5, $^3J_{F,F}$ = 16.5 Hz); –143.78 (t, 1 F, *p*-C_6F_5, $^3J_{F,F}$ = 20.6 Hz); –144.23 (t, 1 F, *p*-C_6F_5, $^3J_{F,F}$ = 20.6 Hz); –(157.43—157.70) (m, 2 F, *m*-C_6F_5); –(158.70—158.93) (m, 2 F, *m*-C_6F_5).

4-[Bis(pentafluorophenyl)phosphoryl]-4-methylpentan-2-one (7). A solution of acid **1** (1.146 g, 3 mmol) in anhydrous diethyl ether (12 mL) was added dropwise to a solution of mesityl oxide (**6**) (0.31 g, 3.15 mmol) in anhydrous ether (3 mL). The reaction mixture was allowed to stand for 48 h at ~20 °C and concentrated to dryness, the residue was dissolved in anhydrous CH_2Cl_2 (5 mL). The solution obtained was filtered through a layer of basic Al_2O_3 (0.57 g), the Al_2O_3 was washed with anhydrous CH_2Cl_2 (6 mL), the combined filtrates were concentrated to dryness and dried *in vacuo* (~1 Torr) at 50 °C over 1 h. The yield was 1.328 g (92.2%), m.p. 126—127.5 °C (hexane—CCl_4). Found (%): C, 44.97; H, 2.26; F, 39.43; P, 6.32. $C_{18}H_{21}F_{10}O_2P$. Calculated (%): C, 45.02; H, 2.31; F, 39.56; P, 6.45. IR, ν/cm^{-1}: 1212 (P=O), 1724 (C=O). ^{31}P{^{1}H} NMR ($CDCl_3$, c = 0.1 mol L^{-1}), δ: 34.87 (s). ^{1}H NMR ($CDCl_3$, c = 0.1 mol L^{-1}), δ: 1.57 (d, 6 H, MeCP, $^3J_{H,P}$ = 21.1 Hz); 2.23 (s, 3 H, MeC(O)); 2.99 (d, 2 H, CH_2, $^3J_{H,P}$ = 9.5 Hz). ^{1}H{^{31}P} NMR ($CDCl_3$, c = 0.1 mol L^{-1}), δ: 1.58 (s, 6 H, MeCP); 2.23 (s, 3 H, MeC(O)), 3.00 (s, 2 H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$, c = 0.1 mol L^{-1}), δ: 19.34 (s, $\underline{C}H_3CP$); 32.25 (d, $\underline{C}H_3C(O)$, $^4J_{C,P}$ = 2.2 Hz); 40.79 (d, Me$\underline{C}$P, $^1J_{C,P}$ = 74.8 Hz); 44.85 (s, CH_2); 107.48 (dtm, *ipso*-C_6F_5, $^1J_{C,P}$ = 82.9 Hz, $^2J_{C,F}$ = 20.9 Hz); 137.94 (dm, *m*-C_6F_5, $^1J_{C,F}$ = = 253.8 Hz); 144.29 (dm, *p*-C_6F_5, $^1J_{C,F}$ = 263.4 Hz); 146.87 (dm, *o*-C_6F_5, $^1J_{C,F}$ = 256.0 Hz); 205.04 (d, C=O, $^3J_{C,P}$ = 17.6 Hz). ^{19}F{^{1}H} NMR ($CDCl_3$, c = 0.1 mol L^{-1}), δ: –(126.79—127.01) (m, 4 F, *o*-C_6F_5); –144.00 (t, 2 F, *p*-C_6F_5, $^3J_{F,F}$ = 20.6 Hz); –157.72 (t, 4 F, *m*-C_6F_5, $^3J_{F,F}$ = 19.3 Hz).

3-{α-[Bis(pentafluorophenyl)phosphoryl]benzyl}pentane-2,4-dione (9). A solution of acid **1** (1.146 g, 3 mmol) in anhydrous diethyl ether (12 mL) was added dropwise to a solution of 3-benzylidenepentane-2,4-dione (**8**) (0.59 g, 3.15 mmol) in an-

hydrous ether (3 mL). The reaction mixture was allowed to stand for 24 h at ~20 °C and concentrated to dryness, the residue was dissolved in anhydrous CH_2Cl_2 (10 mL). The solution obtained was filtered through a layer of basic Al_2O_3 (1.14 g), the Al_2O_3 was washed with anhydrous CH_2Cl_2 (10 mL), the combined filtrates were concentrated to dryness, the residue was triturated with a 2 : 1 mixture of hexane—ether (6 mL). A precipitate formed was separated, sequentially washed on the filter with a 2 : 1 mixture of hexane—ether (2×3 mL) and hexane (5 mL), and dried in air. The yield was 1.52 g (88.9%), m.p. 165—167 °C (hexane—CCl_4). Found (%): C, 50.49; H, 2.28; F, 33.17; P, 5.49. $C_{24}H_{13}F_{10}O_3P$. Calculated (%): C, 50.54; H, 2.30; F, 33.31; P, 5.43. IR, ν/cm^{-1}: 1219 (P=O); 1712, 1732 (C=O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, c = 0.1 mol L^{-1}), δ: 26.04 (s). ^1H NMR ($CDCl_3$, c = 0.1 mol L^{-1}), δ: 2.05 (s, 3 H, Me); 2.34 (s, 3 H, Me); 4.98 (dd, 1 H, CHP, $^3J_{H,H}$ = 11.0 Hz, $^2J_{H,P}$ = 6.0 Hz); 5.08 (dd, 1 H, C<u>H</u>CHP, $^3J_{H,H}$ = 10.6 Hz, $^3J_{H,P}$ = 10.2 Hz); 7.15—7.26 (m, 3 H, *m*-Ph, *p*-Ph); 7.31 (br.s, 2 H, *o*-Ph). $^1H\{^{31}P\}$ NMR ($CDCl_3$, c = 0.1 mol L^{-1}), δ: 2.05 (s, 3 H, Me); 2.35 (s, 3 H, Me); 4.98 (d, 1 H, CHP, $^3J_{H,H}$ = 11.2 Hz); 5.08 (d, 1 H, C<u>H</u>CHP, $^3J_{H,H}$ = = 11.1 Hz); 7.16—7.26 (m, 3 H, *m*-Ph, *p*-Ph); 7.31 (br.s, 2 H, *o*-Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, c = 0.1 mol L^{-1}), δ: 29.62 (s, Me); 30.88 (s, Me); 49.41 (dt, CHP, $^1J_{C,P}$ = 76.3 Hz, $^4J_{C,F}$ = 5.5 Hz); 107.15 (dtm, *ipso*-C_6F_5, $^1J_{C,P}$ = 100.5 Hz, $^2J_{C,F}$ = 17.4 Hz); 110.03 (dtm, *ipso*-C_6F_5, $^1J_{C,P}$ = 88.8 Hz, $^2J_{C,F}$ = 17.8 Hz); 129.04 (d, *p*-C_6H_5, $^5J_{C,P}$ = 3.7 Hz); 129.15 (br.s, *o*-Ph); 129.27 (d, *m*-Ph, $^4J_{C,P}$ = 2.2 Hz); 133.37 (d, *ipso*-Ph, $^2J_{C,P}$ = 4.4 Hz); 137.07 (dm, *m*-C_6F_5, $^1J_{C,F}$ = 256.0 Hz); 137.64 (dm, *m*-C_6F_5, $^1J_{C,F}$ = 250.1 Hz); 143.71 (dm, *p*-C_6F_5, $^1J_{C,F}$ = 260.2 Hz); 144.18 (dm, *p*-C_6F_5, $^1J_{C,F}$ = 261.9 Hz); 146.06 (dm, *o*-C_6F_5, $^1J_{C,F}$ = = 250.9 Hz); 147.16 (dm, *o*-C_6F_5, $^1J_{C,F}$ = 250.9 Hz); 200.74 (d, C=O, $^3J_{C,P}$ = 14.7 Hz); 201.74 (d, C=O, $^3J_{C,P}$ = 1.5 Hz). $^{19}F\{^1H\}$ NMR ($CDCl_3$, c = 0.1 mol L^{-1}), δ: −128.97 (dm, 2 F, *o*-C_6F_5, $^3J_{F,F}$ = 14.3 Hz); −131.40 (br.s, 2 F, *o*-C_6F_5); −144.79 (tm, 1 F, *p*-C_6F_5, $^3J_{F,F}$ = 20.3 Hz); −145.41 (tt, 1 F, *p*-C_6F_5, $^3J_{F,F}$ = 20.3 Hz, $^4J_{F,F}$ = 6.5 Hz); −(159.08—159.33) (m, 4 F, *m*-C_6F_5).

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