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Synthesis of novel phosphonium betaines and bis-betaines derived from hexafluoro-1,4-naphthoquinone

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ABSTRACT

Reactions of hexafluoro-1,4-naphthoquinone with phosphorus-centered bis-phenylphosphanes with structure $Ph_2P(CH_2)_nPPh_2$ (where n = 1–5) and $Et_2P(CH_2)_2PEt_2$ in various solvents (anhydrous C_6H_6, aq. C_6H_6, aq. dioxane, aq. DMSO, or MeOH) were investigated. It was shown that the use of aqueous dioxane and DMSO leads to target products of phosphanodefluorination (i.e., phosphorus-containing betaines and bis-betaines) with high yields. We found that the betaines upon purification by thin-layer chromatography underwent various transformations such as a ring contraction (thus yielding novel polyfluorinated indenones) or addition of an acetone molecule at the C═O bond of the fluorinated 1,4-naphthoquinone. According to X-ray diffraction analysis, there were intermolecular F···π interactions in the crystal packing of all the obtained betaines. The interactions are characterized by short distances F···Cg from 3.151(5) to 3.831(2) Å (where Cg is a centroid of π-system).

1. Introduction

The 1,4-naphthoquinone structure occurs frequently in numerous synthesized and natural compounds associated with antibacterial, antifungal, antiviral, antitumor, and antimalarial activities [1–3]. Recently, it was shown that polyfluorinated functionalized 1,4-naphthoquinones can also be inhibitors of cancer cells growth [4a–f]. In our group, it has been found that a number of polyfluorinated 1,4-naphthoquinone derivatives containing one phosphorus atom possess an antitumor activity [5–7]. In addition to imparting antitumor activity to derivatives, such 1,4-naphthoquinones can be effective antioxidants protecting bacterial cells from H_2O_2-induced and spontaneous mutagenesis [6,7].

Lately, we reported that reactions of hexafluoro-1,4-naphthoquinone (**1**) with PPh_3 or various other phosphorus-centered phenylphosphanes PPh_2R (Me, Ph, etc.) lead to phosphorus-containing betaines with phosphonium structure **A** and **B** (Chart 1) [5–8]. The common pattern of these reactions is nucleophilic substitution of the fluorine atom at position 2 of 1,4-naphthoquinone **1** with initial formation, in case of PPh_3, of highly reactive intermediate **C** in dry C_6H_6. As it turned out, this compound is unstable and quickly reacts with water or aniline, thus yielding corresponding phosphobetaines **A** and **B** [7].

In light of the obtained data, it was interesting to determine how the reaction will proceed if to expand the range of phosphorus-centered nucleophiles to bis-phosphanes $Ph_2P(CH_2)_nPPh_2$ with different lengths of the hydrocarbon chain between the two phosphorus atoms and $Et_2P(CH_2)_2PEt_2$. In this regard, we performed a series of experiments to synthesize new phosphonium betaine derivatives of hexafluoro-1,4-naphthoquinone; these compounds hold promise as anticancer agents. We also established a correlation between the structure of the initial nucleophile, the solvent in which the reaction was carried out, and the reaction product. Besides, a ring contraction of a polyfluorinated 1,4-naphthoquinone was found to give rise to novel fluorinated indenone betaines. Their structures were unambiguously proved by X-ray diffraction (XRD) analysis.

2. Results and discussion

2.1. Reactions of hexafluoro-1,4-naphthoquinone 1 with bis-phosphanes

In our previous paper, we reported that the reaction of hexafluoro-1,4-naphthoquinone **1** with methyldiphenylphosphane, PPh_3, or various other fluorinated phenylphosphanes $PPhR_1R_2$ (R_1 = Me, Ph; R_2 = 3,5-$F_2C_6H_3$, 2,5-$F_2C_6H_3$) in MeOH or DMSO gives phosphonium betaines with a high yield [7,8]. As it was shown earlier, the reaction of 1,4-naphthoquinone **1** with PPh_3 was carried out in thoroughly dried C_6H_6 in an atmosphere of dry argon and led to highly reactive intermediate **C**. In the latter, the presence of the > CF_2 group at position 3 indicates easy further substitution. The use of bis-phosphanes $Ph_2P(CH_2)_nPPh_2$ (especially with n = 2), could lead to not only the products

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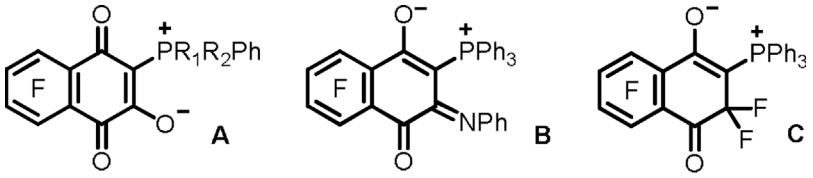


R^1 = Ph; R^2 = Me, Ph, 3,5-$F_2C_6H_3$, 2,5-$F_2C_6H_3$
R^1 = Me; R^2 = 3,5-$F_2C_6H_3$, 2,5-$F_2C_6H_3$

Chart 1. Structure A–C.

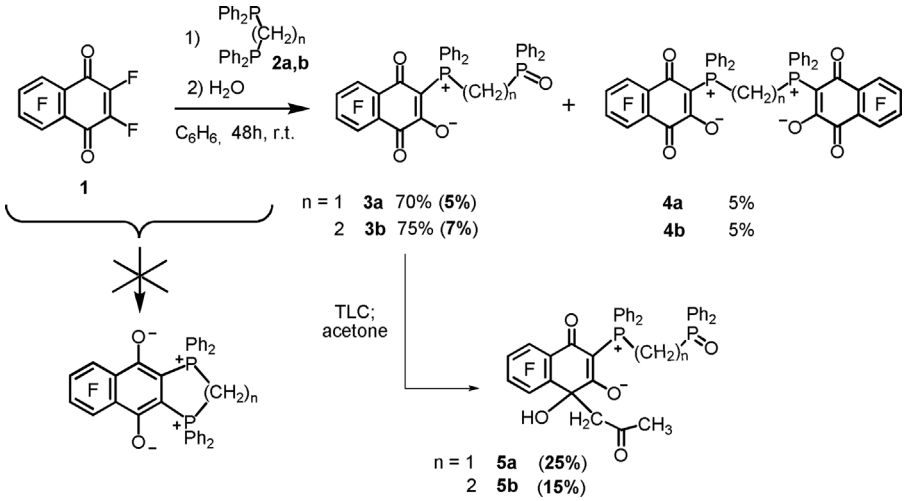
of monosubstitution but also intramolecular cyclization.

This assumption was tested on the reaction of hexafluoro-1,4-naphthoquinone **1** with one equivalent of bis(diphenylphosphano)methane (**2a**) as an example in dried C_6H_6 in the atmosphere of dry argon at room temperature. After 48 h, the reaction mixture was treated with water. According to the ^{19}F and $^{31}P\{^1H\}$ NMR spectra, the reaction mixture contained betaine 3-((((diphenylphosphoryl)methyl)diphenylphosphonio)-5,6,7,8-tetrafluoro-1,4-dioxo-1,4-dihydronaphthalen-2-olate (**3a**) as the main product (according to $^{31}P\{^1H\}$ NMR, the yield was ~70%, and isolated yield 5%, here and hereinafter, per initial bisphosphane). Besides, there were signals of 3,3′-(methylenebis(diphenylphosphonionediyl))bis(5,6,7,8-tetrafluoro-1,4-dioxo-1,4-dihydronaphthalen-2-olate) (**4a**) (according to $^{31}P\{^1H\}$ NMR, the yield was ~5%) and an oxide: bis(diphenylphosphoryl)methane (~20% NMR yield; Scheme 1). The structure of **3a** was solved by XRD analysis (SI, Fig. S1).

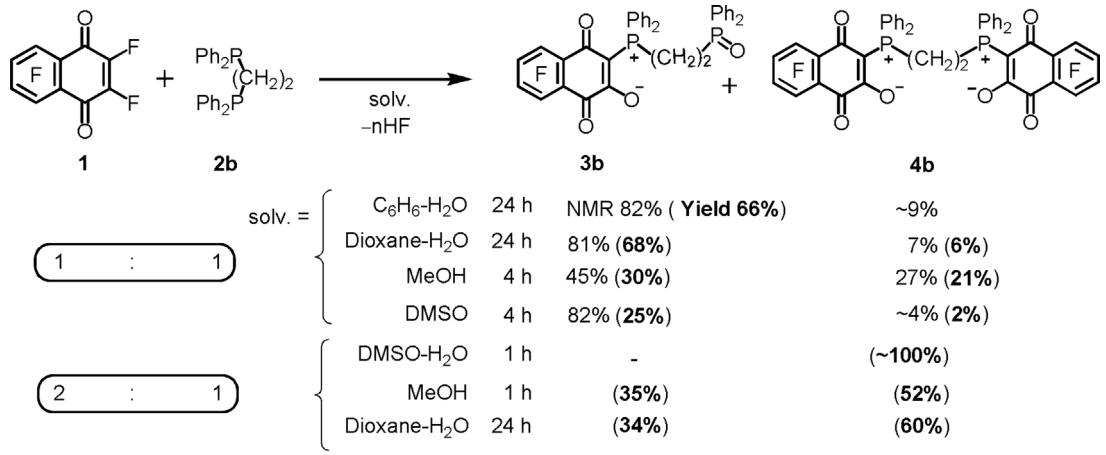
In agreement with the data obtained earlier [7,8], the formation of betaine **3a** is reasonably explained by the primarily occurring phosphanodefluorination of hexafluoro-1,4-naphthoquinone **1** producing the corresponding salt with two atoms of fluorine at position 3 as in salt **C**. **The** subsequent reaction with water leads to the observed betaine **3a**, wherein the second phosphorus atom at the end of the hydrocarbon chain group is oxidized by oxygen of air. Nonetheless, as we can see, the product of mono-phosphanodefluorination reacts via the PPh_2 group with another molecule of naphthoquinone **1** and yields a small amount of the corresponding bis-betaine **4a** (Scheme 1). Because the initial reagents were present in equivalent amounts, the remaining unreacted phosphane (usually its amount matched the bis-betaine content) is subsequently oxidized by air oxygen. Given that the phosphane oxides are not the products of the nucleophilic substitution of substrate **1**, here and later, we will not mention this observation in our schemes. Under similar conditions, the reaction of hexafluoro-1,4-naphthoquinone **1** with one equivalent of 1,2-bis(diphenylphosphano)ethane (**2b**) produces 3-((2-(diphenylphosphoryl)ethyl)diphenylphosphonio)-5,6,7,8-tetrafluoro-1,4-dioxo-1,4-dihydronaphthalen-2-olate (**3b**) (according to $^{31}P\{^1H\}$ NMR spectra, at ~75%, isolated yield 7%), 3,3′-(ethane-1,2-diylbis(diphenylphosphonionediyl))bis(5,6,7,8-tetrafluoro-1,4-dioxo-1,4-dihydronaphthalen-2-olate) (**4b**) (NMR yield ~5%), and 1,2-bis(diphenylphosphoryl)ethane (NMR yield ~15%) (Scheme 1). In all cases, the yields of the isolated products (**3a** and **3b**) were small; the reason was the fact that the betaines obtained in the reaction are not stable when isolated by thin-layer chromatography. For example, after TLC of the reaction mixture on silica gel in an acetone–hexane mixture and later in ethyl acetate, betaines 3-((((diphenylphosphoryl)methyl)diphenylphosphonio)-5,6,7,8-tetrafluoro-1-hydroxy-4-oxo-1-(2-oxopropyl)-1,4-dihydronaphthalen-2-olate (**5a**) and 3-((2-(diphenylphosphoryl)ethyl)diphenylphosphonio)-5,6,7,8-tetrafluoro-1-hydroxy-4-oxo-1-(2-oxopropyl)-1,4-dihydronaphthalen-2-olate (**5b**) were isolated in the form of the adduct of one molecule of acetone with 25% and 15% isolated yields, respectively (Scheme 1).

As we know from experience [7,9] the use of DMSO as a solvent noticeably increases the phosphanodefluorination reaction rate and consequently raises the yields of betaines. This notion is consistent with the results of the reaction of naphthoquinone **1** with phenylphosphane **2b** (1:1) in anhydrous DMSO in the atmosphere of dry argon at room temperature. After 24 h, the reaction mixture was quenched with water to produce betaines **3b** and **4b** (NMR yield ~82% and 4%, respectively) and oxide 1,2-bis(diphenylphosphoryl)ethane (NMR yield ~10%; Scheme 2). Unfortunately, the use of DMSO hindered isolation of the monosubstitution product, betaine **3b**, and lowered the yield of the product (Scheme 2).

According to the results of the experiments, the product of intramolecular cyclization in the quinone moiety of hexafluoro-1,4-naphthoquinone **1** did not form. Because one of the goals of our work was to obtain a variety of phosphorus-containing bis-betaines, we focused on finding the optimal conditions for the synthesis of the target products. We chose 1,2-bis(diphenylphosphano)ethane **2b** as a model reagent because of its availability and convenience. The presence of two



Scheme 1. Reaction of **1** with bis-phosphanes $Ph_2P(CH_2)_nPPh_2$, n = 1, 2, in dried C_6H_6 (here and below, isolated yields are given in parentheses).



Scheme 2. Reaction of **1** with bis-phosphane **2b** in different solvents.

methylene groups between phosphorus atoms ruled out the influence of steric and electrostatic factors on the course of the reactions.

The interaction of naphthoquinone **1** with 1,2-bis(diphenylphosphano)ethane **2b** (1:1) in system C_6H_6–H_2O (120:1) under argon gave a solution which, according to $^{31}P\{^1H\}$ NMR data, contained betaines **3b** and **4b** and a small amount of 1,2-bis(diphenylphosphoryl)ethane (yields 82%, 9%, and 9%, respectively; Scheme 2).

Reaction of 1,4-naphthoquinone **1** with bis-phenylphosphane **2b** (1:1) in methanol, along with the desired betaine **3b** (NMR yield ~45%, isolated yield 30%), produced a substantial amount of the corresponding bis-betaine **4b** (NMR ~27%, isolated yield 21%) and phosphane oxide (~28%). The system dioxane–H_2O (10:1) was selected as the best reaction medium for preparation of betaine **3b** because the NMR and isolated yields were the highest (81% and 68%, respectively; Scheme 2). The structure of **3b** was proved by XRD analysis (SI, Fig. S2).

As shown in Scheme 2, to obtain bis-betaine **4b** as the main product, we used 2 equivalents of 1,4-naphthoquinone **1**. Reactions in methanol or in the system dioxane–H_2O (10:1) yielded similar results (Scheme 2). In both cases, a significant amount of betaine **3b** was detected, even though the reaction was carried out under argon. Perhaps the considerable amounts of betaine **3b** are related to the fact that the initial 1,4-naphthoquinone **1** can act, in this case, as an oxidant and oxidizes the second PPh_2 group. The best result was achieved in a DMSO–water system. The interaction of naphthoquinone **1** with 1,2-bis(diphenylphosphano)ethane **2b** (2:1) in system DMSO–H_2O (20:1) under argon led to a single product, betaine **4b**, which precipitated from the solution as a bright yellow powder with **a** quantitative yield (~100%; Scheme 2). The structure of **4b** was proved by XRD analysis (SI, Fig. S3).

On the basis of these data, we can conclude that the most successful conditions for the preparation of monosubstituted betaine **3b** are the system dioxane–H_2O (10:1), whereas for bis-betaine **4b**: DMSO–H_2O (20:1). These conditions were applied to the synthesis of bis-betaines with different lengths of the polymethylene chain.

Equimolar amounts of naphthoquinone **1** and 1,3-bis(diphenylphosphano)propane (**2c**) in system dioxane–H_2O (10:1) were stirred under argon at room temperature for 24 h and then in open air for 48 h. According to $^{31}P\{^1H\}$ NMR data, the solution contained betaines 3-((3-(diphenylphosphoryl)propyl)diphenylphosphonio)-5,6,7,8-tetrafluoro-1,4-dioxo-1,4-dihydronaphthalen-2-olate (**3c**), 3,3′-(propane-1,3-diylbis(diphenylphosphonionediyl))bis(5,6,7,8-tetrafluoro-1,4-dioxo-1,4-dihydronaphthalen-2-olate) (**4c**) and 1,3-bis(diphenylphosphoryl)propane oxide (yields 70%, 15%, and ~15%, respectively). Betaines **3c** and **4c** were isolated with 65% and 13% yields, respectively (Scheme 3). Under similar conditions, target products of phosphanodefluorination, betaines 3-((4-(diphenylphosphoryl)butyl)diphenylphosphonio)-5,6,7,8-tetrafluoro-1,4-dioxo-1,4-dihydronaphthalen-2-olate (**3d**) and 3-((5-(diphenylphosphoryl)pentyl)diphenylphosphonio)-5,6,7,8-tetrafluoro-1,4-dioxo-1,4-dihydronaphthalen-2-olate (**3e**) were isolated with 50% and 53% yields, respectively. In addition, we isolated bis-betaines: 3,3′-(butane-1,4-diylbis(diphenylphosphonionediyl))bis(5,6,7,8-tetrafluoro-1,4-dioxo-1,4-dihydronaphthalen-2-olate) (**4d**) and 3,3′-(pentane-1,5-diylbis(diphenylphosphonionediyl))bis(5,6,7,8-tetrafluoro-1,4-dioxo-1,4-dihydronaphthalen-2-olate) (**4e**) with 18% and 7% yields, accordingly.

Impressive results were obtained in the DMSO–H_2O system for the synthesis of bis-betaines **4d-e**. Reactions of naphthoquinone **1** and phosphanes **2d-e** at the 2:1 initial ratio in system DMSO–H_2O (20:1) under argon led to the formation of pure bis-betaines **4d-e** with quantitative yields. A similar reaction of naphthoquinone **1** and phosphane **2c** led to bis-betaine **4c** as the main product with a small amount of betaine **3c**, with isolated yields 85% and 14%, respectively (Scheme 3).

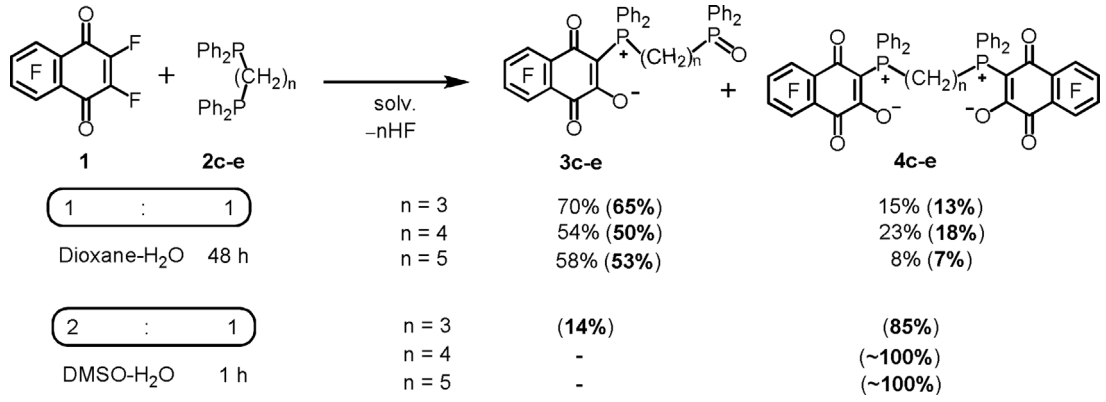
The reaction of 1,4-naphthoquinone **1** with bis(diphenylphosphano)methane **2a** (1:1) in aqueous dioxane (10:1) after 48 h produced desired betaine **3a** (NMR yield ~83%, isolated yield 79%), a small amount of betaine **4a** (NMR yield ~4%), and the corresponding phosphane oxide (~9%; Scheme 4). The same phosphonium betaine **3a** was formed (NMR yield ~70%) in the reaction of bis(diphenylphosphano)methane **2a** with two equivalents of 1,4-naphthoquinone **1** in system DMSO–H_2O (20:1) under argon at room temperature. According to $^{31}P\{^1H\}$ NMR data, the reaction mixture contained only 8% of desired bis-betaine **4a** (Scheme 4). The low yield of **4a** can be explained as follows. Initially, the reaction proceeds with formation of the intermediate mono-betaine in which nucleophilicity of the PPh_2 group is decreased due to the electron-withdrawing effect of a positively charged phosphorus atom that hinders the reaction of the mono-betaine with the next 1,4-naphthoquinone molecule.

An increase in temperature to 120 °C in aqueous DMSO as a solvent did not lead to significant changes in the set of products. Betaines **3a** and **4a** were isolated with 70% and 12% yields, respectively (Scheme 4). It turned out that betaines are very sensitive to heating. An increase in the temperature of the reaction mixture above 120 °C resulted in resinous unidentified products.

The highest yield of bis-betaine **4a** was achieved in the reaction of bis(diphenylphosphano)methane **2a** with two equivalents of 1,4-naphthoquinone **1** at reflux in system dioxane–H_2O (10:1). After 24 h, according to $^{31}P\{^1H\}$ NMR data, the solution contained betaines **3a** and **4a** (NMR yields ~51% and 27%), which were isolated with 43% and 21% yields, respectively (Scheme 4).

2.2. Reactions of hexafluoro-1,4-naphthoquinone 1 with bis-phosphane $Et_2P(CH_2)_2PEt_2$

The reaction of hexafluoro-1,4-naphthoquinone **1** with one



Scheme 3. The reaction of **1** with bis-phosphanes $Ph_2P(CH_2)_nPPh_2$, n = 3 to 5.

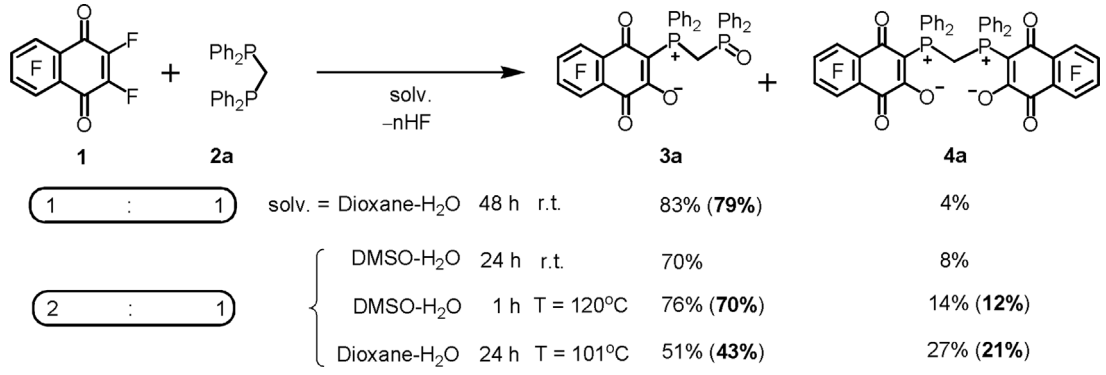
equivalent of 1,2-bis(diethylphosphano)ethane (**2f**) was carried out in dried C_6H_6 in an atmosphere of dry argon at room temperature. After 30 min, the reaction mixture was exposed to air and, according to $^{31}P\{^1H\}$ NMR data, the solution contained betaine 3-((2-(diethylphosphoryl)ethyl)diethylphosphonio)-5,6,7,8-tetrafluoro-1,4-dioxo-1,4-dihydronaphthalen-2-olate (**3f**) and 3,3′-(ethane-1,2-diylbis(diethylphosphonionediyl))bis(5,6,7,8-tetrafluoro-1,4-dioxo-1,4-dihydronaphthalen-2-olate) (**4f**) (NMR yields ~63% and 17%, isolated yields 48% and 12%, respectively). Additionally, there were signals of oxide 1,2-bis(diethylphosphoryl)ethane (according to $^{31}P\{^1H\}$ NMR, the yield was ~17%, Scheme 5). As in the previous case, we found that the product of cyclization did not form. Nonetheless, along with betaines **3f** and **4f** we isolated a small amount of an unexpected product – 5,6,7,8-tetrafluoro-1,4-dioxo-3-(triethylphosphonio)-1,4-dihydronaphthalen-2-olate (**6f**) – with a 3% isolated yield (Scheme 5). According to $^{31}P\{^1H\}$ NMR spectra of initial 1,2-bis(diethylphosphano) ethane **2f**, the reagent was pure, without obvious traces of triethylphosphane PEt_3. Accordingly, the latter product **6f** can be obtained only by breaking the P − CH_2 bond in the phosphonium betaine at any stage of product formation. As we found out, such a result can be seen only in the reaction carried out in dry C_6H_6. The structures of **4f** and **6f** were determined by XRD analysis (SI, Figs. S4 and S5). The replacement of dry C_6H_6 as a solvent with the usual system of dioxane–H_2O (10:1) led to similar results: formation of betaines **3f** and **4f** with isolated yields 37% and 20% yields, respectively.

The reaction of 1,4-naphthoquinone **1** with bis(diethylphosphano) ethane **2f** (2:1) in aqueous DMSO (20:1) led to strong heating and blackening of the reaction mixture. According to $^{31}P\{^1H\}$ NMR data, the solution consisted of only 1,4-naphthoquinone **1** and unidentified resinous products. The use of system dioxane–H_2O (10:1) gave betaines **3f** and **4f** (according to $^{31}P\{^1H\}$ NMR, the yields were ~46% and 14%, isolated yields 32% and 14%, respectively) and a small amount of **the** corresponding phosphane oxide (NMR yield ~26%). The low yields of bis-betaine **4f** can be explained by the strong propensity of initial bis(diethylphosphano)ethane **2f** to oxidation under the action of quinone **1**.

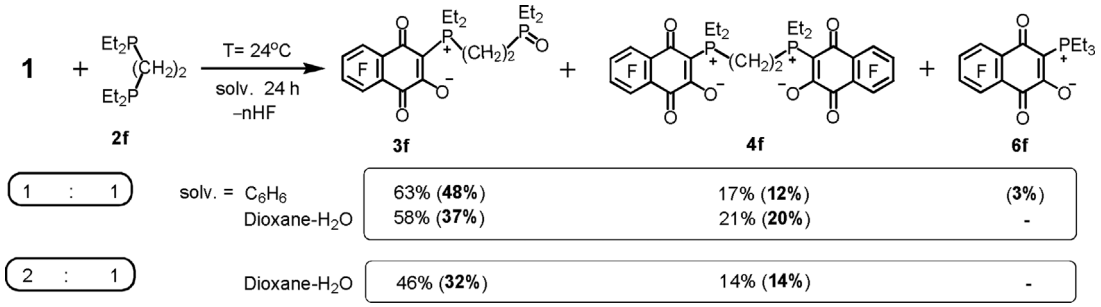
2.3. Oxidative rearrangement of bis-betaine derivatives of hexafluoro-1,4-naphthoquinone

In the course of this work, it turned out that the resulting betaines are not always stable when purified by chromatography on a column. For example, during chromatography on silica gel, the elution of betaines **3c** and **4c** with a dioxane–hexane mixture led to two fractions: the first fraction contained a mixture of betaines **3c** and 2-((3-(diphenylphosphoryl)propyl)diphenylphosphonio)-4,5,6,7-tetrafluoro-1-oxo-1H-inden-3-olate (**7c**) in the 1:1 ratio (according to ^{19}F NMR data), the second contained impure 2,2′-(propane-1,3-diylbis(diphenylphosphonionediyl))bis(4,5,6,7-tetrafluoro-1-oxo-1H-inden-3-olate) (**8c**). Further purification by TLC gave pure compounds **7c** and **8c** with yields 12% and 4%, respectively (Scheme 6). Accordingly, betaine **3d** was found to transform into 2-((4-(diphenylphosphoryl)butyl)diphenylphosphonio)-4,5,6,7-tetrafluoro-1-oxo-1H-inden-3-olate (**7d**) isolated with a low (8%) yield. The structures of betaines **7c**, **8c**, and **7d** were unambiguously proved by XRD (SI, Figs. S6 and S7).

The rearrangement leading to the quinone ring contraction is typical for the hydroxyquinone family [10a–d]. It was hypothesized that the transformation can be induced in the presence of O_2 or H_2O_2, by the action of a base, halogen, or even quinone itself [10a–d]. In this work, for the first time, a ring contraction was observed in quinone-based phosphonium betaines. In agreement with the literature, a putative scheme of this transformation may include oxidation of the quinone moiety with formation of intermediate **A**, then its benzylic-acid-type rearrangement and subsequent oxidative decarboxylation of intermediate **B** (Scheme 7).



Scheme 4. The reaction of **1** with $Ph_2PCH_2PPh_2$.



Scheme 5. Reactions of **1** with bis-phosphane $Et_2P(CH_2)_2PEt_2$.

3. Conclusions

We showed that bis-phosphanes $Ph_2P(CH_2)_nPPh_2$ (where n = 1–5) and $Et_2P(CH_2)_2PEt_2$ effectively participate in the reaction with hexafluoro-1,4-naphthoquinone and thus give access to a variety of new phosphonium betaines and bis-betaines. The effect of solvents (C_6H_6, aq. C_6H_6, aq. dioxane, MeOH, or aq. DMSO) on the observed transformations was investigated. It was demonstrated that in most cases, the use of aqueous dioxane or aqueous DMSO leads to the highest yields of polyfluoro-1,4-naphthoquinone-substituted phosphonium betaines and bis-betaines, respectively. The interaction of bis-phosphanes $Ph_2PCH_2PPh_2$ and $Ph_2P(CH_2)_2PPh_2$ with hexafluoro-1,4-naphthoquinone did not lead to formation of intramolecular cyclization products. It was revealed that upon TLC under appropriate conditions, the betaines underwent transformations such as addition of an acetone molecule to the C═O bond to form a stable adduct or the ring contraction affording novel polyfluorinated indenones.

4. Experimental section

4.1. Materials and methods

Benzene was dried by distillation over P_2O_5 and stored over molecular sieves (3 Å). Hexafluoro-1,4-naphthoquinone (**1**) was prepared as reported in the literature [11]. All phosphanes were purchased from Aldrich and Acros Organics. Solvents were of reagent quality. Unless specified otherwise, reactions of quinone **1** with phosphanes were carried out at room temperature under argon; crude betaines were purified by TLC on Sorbfil.

The NMR spectra were recorded on Bruker AV-300 (^{1}H: 300.13 MHz, $^{13}C\{^1H\}$: 75.47 MHz, ^{19}F: 282.36 MHz, $^{31}P\{^1H\}$: 121.49 MHz), AV-400 (^{1}H: 400.13 MHz, $^{13}C\{^1H\}$: 100.61 MHz), and AV-500 ($^{13}C\{^1H\}$: 125.76 MHz) spectrometers. ^{1}H chemical shifts are reported relative to residual protons of deuterated acetone (δ_H 2.07 ppm, δ_C 29.80 ppm), chloroform (δ_H 7.25 ppm, δ_C 77.00 ppm), and DMSO-d_6 (δ_H 2.50 ppm, δ_C 39.50 ppm) and relative to external Me_4Si (δ_H = 0.00 ppm). $^{31}P\{^1H\}$ chemical shifts (δ_P) are reported relative to an unlocked, external sample of H_3PO_4 (δ_P = 0.0 ppm); ^{19}F chemical shifts (δ_F) are reported relative to external $CFCl_3$ (δ_F = 0.00 ppm); and $^{13}C\{^1H\}$ chemical shifts (δ_C) relative to external Me_4Si (δ_C = 0.00 ppm). High-resolution mass spectra (HRMS) were acquired by means of a DFS Thermo Scientific instrument (EI, 70 eV). The melting points were determined on an FP 900 Thermosystem microscope melting-point apparatus (Mettler-Toledo International Inc., Zürich, Switzerland).

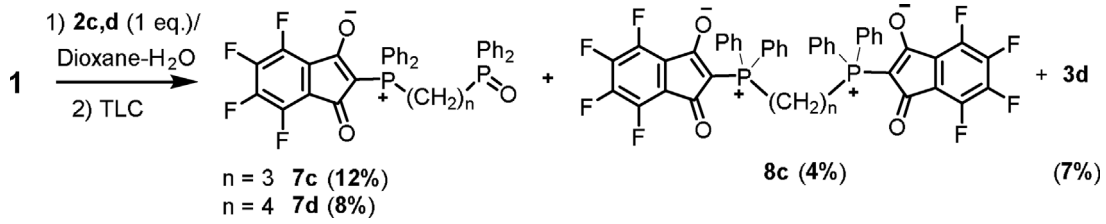
X-ray crystallographic analyses of the crystals of betaines were carried out on a Bruker Kappa Apex II CCD diffractometer using φ,ω-scans of narrow (0.5°) frames with Mo K_α radiation (λ = 0.71073 Å) and a graphite monochromator. The structures were solved by direct methods and refined by the full-matrix least-squares method against all F2 in anisotropic approximation using the SHELX-97 software suite [12]. The obtained crystallographic data are presented in Table S1 (SI). The positions of hydrogen atoms were calculated using the riding model. Absorption corrections were applied by the empirical multiscan method in the SADABS software [13]. The resultant crystal structures were analyzed for short contacts between nonbonded atoms in software packages PLATON [14] and MERCURY [15]. A table listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles can be obtained free of charge as CCDC 1578657 (3a), 1578658 (3b), 1578659 (4b), 1578660 (4f), 1578661 (6f), 1578662 (7c), 1578663 (7d), 1578664 (8c) via http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e mail: deposit@ccdc cam ac uk

4.2. The reaction of quinone 1 with $Ph_2PCH_2PPh_2$ 2a in different solvents (anhydrous C_6H_6, water-containing dioxane, or DMSO)

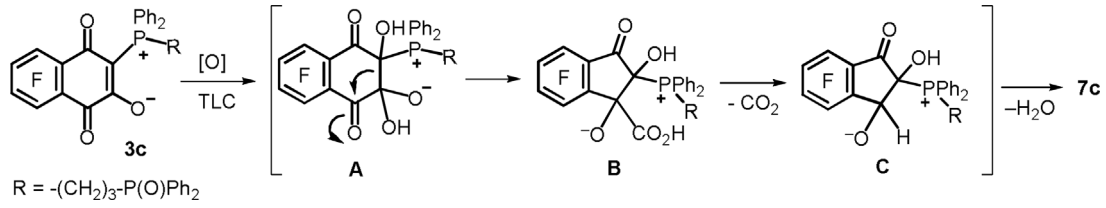
A solution of bis(diphenylphosphano)methane (**2a**; 144 mg, 0.376 mmol) in anhydrous C_6H_6 (2.0 mL) was added to a stirred solution of quinone **1** (100 mg, 0.376 mmol) in C_6H_6 (6.0 mL). After mixing at room temperature for 30 min, the reaction mixture changed color from cherry to yellow-green. The resulting solution was stirred for 48 h, then water (0.2 mL) was added, and the mixture was stirred for another 3 h. The solvent was distilled off, the dry residue was crystallized from ethyl acetate and then purified by TLC to obtain betaine **3a** (13 mg, 5%).

A mixture of **1** (50 mg, 0.188 mmol), **2a** (72 mg, 0.188 mmol), dioxane (1.0 mL), and H_2O (0.1 mL) was stirred for 48 h. The precipitate was centrifuged off, and air dried to produce compound **3a** (67 mg, 56%). From the mother liquid, an additional amount of **3a** was isolated by TLC; the total yield was 95 mg (79%).

A mixture of two eq. of **1** (138 mg, 0.520 mmol), **2a** (100 mg, 0.260 mmol), dioxane (2.0 mL), and H_2O (0.2 mL) was heated for 24 h



Scheme 6. Betaines detected after TLC purification on silica gel with a dioxane–hexane eluent.



Scheme 7. Oxidative rearrangement of betaine **3c**.

at 101 °C. The solvent was distilled off, the residue was purified by TLC to prepare betaines **3a** (72 mg, 43%) and **4a** (47 mg, 21%).

A mixture of **1** (100 mg, 0.376 mmol), **2a** (72 mg, 0.188 mmol), DMSO (1.0 mL), and H_2O (0.05 mL) was sealed in an NMR ampoule and heated for 1 h at 120 °C. After addition of water (200 mL), the precipitate was centrifuged off, washed with water (3 × 5 mL), and air dried. The aqueous fraction was extracted with chloroform (3 × 50 mL) and ethyl acetate (1 × 20 mL). The combined extracts were dried over $MgSO_4$, filtered, and evaporated. The combined crude product was purified by TLC to isolate betaines **3a** (85 mg, 70%) and **4a** (20 mg, 12%).

For TLC, the use of the 1:1 acetone–hexane mixture instead of diethyl ether as the eluent led to conversion of **3a** into **5a**.

3-(((Diphenylphosphoryl)methyl)diphenylphosphonio)-5,6,7,8-tetrafluoro-1,4-dioxo-1,4-dihydronaphthalen-2-olate (3a): bright yellow crystals, R_f = 0.8 (Sorbfil, diethyl ether), m.p. 136.8 °C followed by decomposition. ^{1}H NMR ($CDCl_3$): δ = 7.74–7.85 (m, 4H, C_6H_5), 7.49–7.60 (m, 4H, C_6H_5), 7.38–7.49 (m, 4H, C_6H_5), 7.28–7.38 (m, 8H, C_6H_5), 4.43 [dd, $^2J_{HP}$ = 16.4 Hz, $^2J_{HP}$ = 11.4 Hz, 2H, CH_2] ppm. ^{19}F NMR ($CDCl_3$): δ = −139.4, −142.7, −151.9, −156.7 [ddd, 1F, $^{ortho}J_{FF}$ 20.0 ÷ 21.0 Hz $^{meta}J_{FF}$ 3.7 ÷ 8.5 Hz, $^{para}J_{FF}$ 13.0 ÷ 13.2 Hz] ppm.^{31}P{^{1}H} ($CDCl_3$): δ = 23.50 [d, 1P, $^2J_{PP}$ = 13.9 Hz], 13,13 [d, 1P, $^2J_{PP}$ = 13.9 Hz] ppm. IR (neat): 3504 w, 3444 m, 3059 w, 3030 vw, 2991 vw, 2960 w, 2908 w, 1701 m, 1618 m, 1579 vs, 1504 m, 1485 w, 1470 w, 1439 m, 1371 s, 1336 m, 1277 m, 1200 m, 1165 m, 1115 m, 1074 w, 1045 w, 999 w, 953 w, 893 w, 822 w, 795 w, 769 m, 742 m, 692 m, 663 vw, 602 vw, 550 w, 501 m cm^{-1}. HRMS: calcd. for $C_{35}H_{22}F_4O_4P_2$ [M] 644.0924; found 644.0923; Anal. calcd. for $C_{35}H_{22}F_4O_4P_2{*}2C_3H_6O$ (acetone): C, 64.74; H, 4.51; found: C, 64.37; H, 4.15. Crystals suitable for XRD analysis were grown in acetone–heptane (1:1) in a refrigerator in an open flask at −5 °C.

3,3′-(Methylenebis(diphenylphosphonionediyl))bis(5,6,7,8-tetrafluoro-1,4-dioxo-1,4-dihydronaphthalen-2-olate) (4a): yellow powder, R_f = 0.5 (ethyl acetate), decomposes without melting. ^{1}H NMR ($CDCl_3$): δ = 7.63–7.73 (m, 8H, C_6H_5), 7.48–7.56 (m, 4H, C_6H_5), 7.36–7.45 (m, 8H, C_6H_5), 5.86 [t, $^2J_{HP}$ = 17.0 Hz, 2H, CH_2) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 178.1 (m, C^{1or4}), 177.7 (m, C^{1or4}), 174.1 (m, C^2), 147.3 [ddm, $^1J_{CF}$ ~ 273 Hz, $^2J_{CF}$ ~ 11 Hz, C^{6or7}], 146.4 [ddm, $^1J_{CF}$ ~ 270 Hz, $^2J_{CF}$ ~ 10 Hz, C^{6or7}], 144.8 [ddd, $^1J_{CF}$ ~ 220 Hz, $^2J_{CF}$ ~ 10 Hz, $^3J_{CF}$ ~ 5 Hz, C^{5or8}], 142.9 [ddd, $^1J_{CF}$ ~ 263 Hz, $^2J_{CF}$ ~ 17 Hz, $^3J_{CF}$ ~ 12 Hz, C^{5or8}], 133.6 (br. s, C_6H_5), 133.1 [m, $^3J_{CP}$ = 11.3 Hz, C_6H_5], 129.0 [m, $^2J_{CP}$ = 13.5 Hz, C_6H_5], 120.9 [d, $^1J_{CP}$ = 95.7 Hz, C_6H_5], 118.8 (m, $C_{10}F_4O_2$), 116.0 (m, $C_{10}F_4O_2$), 88.3 [dd, $^1J_{CP}$ = 99.9 Hz, $^3J_{CP}$ = 3.0 Hz, C^3], 18.4 [t, $^1J_{CP}$ = 52.6 Hz, CH_2] ppm. ^{19}F NMR ($CDCl_3$): δ = −138.2, −140.7, −144.6, −149.2 [ddd, 1F, $^{ortho}J_{FF}$ 19.5 ÷ 20.1 Hz $^{meta}J_{FF}$ 9.3 ÷ 11.3 Hz, $^{para}J_{FF}$ 13.5 ÷ 13.6 Hz] ppm.^{31}P{^{1}H} ($CDCl_3$): δ = 12.04 (s) ppm. IR (neat): 3427 w, 3061 w, 2956 w, 2929 w, 2872 w, 2857 w, 1704 m, 1618 s, 1580 vs, 1570 vs, 1506 s, 1485 m, 1472 m, 1439 m, 1371 s, 1335 m, 1274 s, 1166 m, 1106 m, 1046 m, 1029 w, 999 w, 954 m, 935 w, 894 w, 821 w, 798 w, 769 m, 742 m, 723 w, 689 m, 647 vw, 602 w, 549 vw, 527 w, 497 w, 473 w cm^{-1}. HRMS: calcd. for $C_{45}H_{22}F_8O_6P_2$ [M] 872.0758; found 872.0774; Anal. calcd. for $C_{45}H_{22}F_8O_6P_2{*}C_4H_8O_2$ (ethyl acetate): C, 61.26; H, 3.15; found: C, 61.30; H, 2.99.

3-(((Diphenylphosphoryl)methyl)diphenylphosphonio)-5,6,7,8-tetrafluoro-1-hydroxy-4-oxo-1-(2-oxopropyl)-1,4-dihydronaphthalen-2-olate (5a): white powder, R_f = 0.5 (acetone–hexane, 1:1), m.p. 92.0 °C followed by decomposition. ^{1}H NMR ($CDCl_3$): δ = 7.83–7.90 (m, 2H, C_6H_5), 7.72–7.80 (m, 2H, C_6H_5), 7.54–7.64 (m, 4H, C_6H_5), 7.22–7.52 (m, 12H, C_6H_5), 4.80 (br. s, 1H, OH), 4.14–4.45 (m, 2H, CH_2), 3.02–3.34 (m, 2H, $C\underline{H}_2C(O)$), 2.21 (s, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 206.4 (s, C═O), 191.8 [d, $^2J_{CP}$ = 4.1 Hz, C^2], 178.7 [dm, $^2J_{CP}$ = 6.7 Hz, C^4], 146.7 [ddm, $^1J_{CF}$ ~ 264 Hz, $^2J_{CF}$ ~ 10 Hz, C^{6or7}], 145.2 [ddm, $^1J_{CF}$ = 264 Hz, $^2J_{CF}$ ~ 10 Hz, C^{6or7}], 142.7 [dm, $^1J_{CF}$ ~ 280 Hz, C^{5or8}], 140.7 [dm, $^1J_{CF}$ ~ 255 Hz, C^{5or8}], 133.5 [d, $^4J_{CP}$ = 3.4 Hz, C_6H_5], 132.5 [d, $^4J_{CP}$ = 3.4 Hz, C_6H_5], 133.1 [d, $^2J_{CP}$ = 11.4 Hz, C_6H_5], 132.9 [d, $^2J_{CP}$ = 11.5 Hz, C_6H_5], 132.8 [d, $^4J_{CP}$ = 3.2 Hz, C_6H_5], 131.9 [d, $^4J_{CP}$ = 2.3 Hz, C_6H_5], 131.9 [d, $^3J_{CP}$ = 10.7 Hz, C_6H_5], 131.8 [d, $^3J_{CP}$ = 10.7 Hz, C_6H_5], 130.5 [d, $^3J_{CP}$ = 10.0 Hz, C_6H_5], 130.3 [d, $^3J_{CP}$ = 9.7 Hz, C_6H_5], 128.8 [d, $^2J_{CP}$ = 13.4 Hz, C_6H_5], 128.7 [d, $^2J_{CP}$ = 12.3 Hz, C_6H_5], 128.6 [d, $^2J_{CP}$ = 12.6 Hz, C_6H_5], 125.4 [ddd, $^2J_{CF}$ = 9.6 Hz, $^3J_{CF}$ = 4.2 Hz, $^3J_{CP}$ = 1.5 Hz, $C_{10}F_4O_2$], 121.8 [dd, $^1J_{CP}$ = 91.1 Hz, $^3J_{CP}$ = 1.5 Hz, C_6H_5], 121.2 [dd, $^1J_{CP}$ = 93.1 Hz, $^3J_{CP}$ = 1.3 Hz, C_6H_5], 116.3 [dm, $^2J_{CF}$ ~ 9 Hz, $C_{10}F_4O_2$], 83.5 [dd, $^1J_{CP}$ = 104.9 Hz, $^3J_{CP}$ = 1.6 Hz, C^3], 73.5 [dm, $^3J_{CF}$ ~ 10 Hz, C^1], 55.5 (br. s, $\underline{C}H_2C(O)$), 31.8 (br. s, $C(O)\underline{C}H_3$), 25.9 [dd, $^1J_{CP}$ = 60.0 Hz, $^1J_{CP}$ = 52.0 Hz, CH_2] ppm. ^{19}F NMR ($CDCl_3$): δ = −139.4, −142.7, −151.8, −156.7 [ddd, 1F, $^{ortho}J_{FF}$ 19.8 ÷ 21.2 Hz $^{meta}J_{FF}$ 3.7 ÷ 8.5 Hz, $^{para}J_{FF}$ 13.1 ÷ 13.2 Hz] ppm.^{31}P{^{1}H} ($CDCl_3$): δ = 23.6 [d, 1P, $^2J_{PP}$ = 14.0 Hz], 13.1 [d, 1P, $^2J_{PP}$ = 14.0 Hz] ppm. IR (neat): 3356 w, 3253 w, 3059 w, 3030 w, 3012 w, 2993 w, 2962 w, 2926 w, 2902 w, 2858 w, 1782 vw, 1709 m, 1618 m, 1566 vs, 1508 s, 1485 m, 1473 m, 1466 m, 1439 s, 1398 m, 1365 s, 1338 s, 1275 m, 1184 s, 1107 s, 1072 w, 1055 m, 1028 w, 999 w, 976 w, 933 m, 876 w, 787 m, 777 m, 744 s, 692 s, 661w, 617 vw, 550 w, 527 w, 500 m, 478 w, 419 w cm^{-1}. HRMS: calcd. for $C_{38}H_{28}F_4O_5P_2$ [M] 702.1343; found 702.1336; Anal. calcd. for $C_{38}H_{28}F_4O_5P_2$: C, 64.96; H, 4.02; found: C, 64.93; H, 4.18.

4.3. The reaction of quinone 1 with $Ph_2P(CH_2)_2PPh_2$ 2b in different solvents (anhydrous C_6H_6 or DMSO; water-containing C_6H_6, dioxane or DMSO, and MeOH)

A mixture of quinone **1** (100 mg, 0.376 mmol), phosphane **2b** (150 mg, 0.376 mmol), and anhydrous C_6H_6 (6.0 mL) was stirred for 48 h at room temperature. The solvent was distilled off, and the residue was purified by TLC to isolate betaine **3b** (17 mg, 7%).

A solution of **2b** (150 mg, 0.376 mmol) in anhydrous DMSO (1.5 mL) was added to a stirred solution of **1** (100 mg, 0.376 mmol) in anhydrous DMSO (1.5 mL). The resulting solution was stirred for 24 h. After addition of water (100 mL), the precipitate was separated by centrifugation, washed with water (4 × 5 mL), and air dried. The product was purified by TLC to obtain betaines **3b** (62 mg, 25%) and **4b** (7 mg, 2%).

A solution of **1** (50 mg, 0.188 mmol) in C_6H_6 (2.0 mL) and H_2O (0.1 mL) was added to a stirred solution of **2b** (75 mg, 0.188 mmol) in C_6H_6 (10.0 mL). The reaction mixture was stirred for 24 h at room temperature. The solvent was distilled off, the crude product was purified by column chromatography to isolate betaine **3b** with yield 82 mg (66%).

A solution of **1** (100 mg, 0.376 mmol) in dioxane (10.0 mL) and H_2O (1.0 mL) was added slowly to a stirred solution of **2b** (150 mg, 0.376 mmol) in dioxane (4.0 mL) and H_2O (0.4 mL). After stirring for

24 h, the solvent was distilled off, and the crude product was purified by TLC to obtain betaines **3b** (168 mg, 68%) and **4b** (20 mg, 6%).

A mixture of **1** (30 mg, 0.113 mmol), **2b** (45 mg, 0.113 mmol), and MeOH (1.0 mL) was stirred for 4 h at room temperature. A precipitate was centrifuged off, and purified by TLC to isolate betaine **4b** with a yield of 21 mg (21%). The mother liquid was evaporated, and the residue was purified by TLC (Sorbfil, acetone) to isolate betaine **3b** (22 mg, 30%).

A mixture of two eq. of quinone **1** (100 mg, 0.376 mmol), **2b** (75 mg, 0.188 mmol), DMSO (2.0 mL), and H_2O (0.1 mL) was stirred for 1 h at room temperature. A precipitate was centrifuged off, washed with water (4 × 5 mL), and air dried to obtain compound **4b** (166 mg, 100%).

A mixture of **1** (50 mg, 0.188 mmol), **2b** (37 mg, 0.094 mmol), and methanol (1.0 mL) was stirred for 5 h at room temperature. A precipitate was centrifuged off and crystallized from methanol (1 mL) to isolate betaine **4b** (10 mg, 12%). The mother liquid was evaporated, the residue was purified by TLC to obtain **4b** (33 mg, 40%) and an additional amount of **3b** (22 mg, 35%). The total yield of betaine **4b** was 43 mg (52%).

A mixture of **1** (50 mg, 0.188 mmol), **2b** (37 mg, 0.094 mmol), dioxane (1.0 mL), and H_2O (0.1 mL) was stirred for 24 h at room temperature. Water (~4 mL) was added; the precipitate was centrifuged off, washed with water (3 × 5 mL), and air dried to obtain compound **4b** (50 mg, 60%). The aqueous fraction was extracted with chloroform (4 × 20 mL). The extract was dried over $MgSO_4$ and evaporated to obtain a residue, which was purified by TLC. The yield of betaine **3b** was 21 mg (34%).

For TLC, the use of the 1:1 acetone–hexane mixture instead of ethyl acetate as the eluent led to conversion of **3b** into **5b**.

*3-((2-(Diphenylphosphoryl)ethyl)diphenylphosphonio)-5,6,7,8-tetrafluoro-1,4-dioxo-1,4-dihydronaphthalen-2-olate **(3b)***: orange powder, R_f = 0.4 (Sorbfil, ethyl acetate), m.p. 293.2 °C followed by decomposition. ^{1}H NMR (acetone-d_6): δ = 7.83–7.94 (m, 4H, C_6H_5), 7.67–7.77 (m, 6H, C_6H_5), 7.57–7.66 (m, 4H, C_6H_5), 7.44–7.57 (m, 6H, C_6H_5), 3.15–3.32 (m, 2H, CH_2), 2.42–2.56 (m, 2H, CH_2) ppm. ^{19}F NMR (acetone-d_6): δ = −140.3, −140.8, −146.8, −151.4 [ddd, 1F, $^{ortho}J_{FF}$ 18.7 ÷ 19.4 Hz $^{meta}J_{FF}$ 8.2 ÷ 9.8 Hz, $^{para}J_{FF}$ 13.7 Hz] ppm.^{31}P{^{1}H} (acetone-d_6): δ = 29.86 [d, 1P, $^3J_{PP}$ = 55.9 Hz], 20,76 [d, 1P, $^3J_{PP}$ = 55.9 Hz] ppm. IR (neat): 3442 w, 3054 w, 3025 vw, 2984 vw, 1698 m, 1617 m, 1592 s, 1581 vs, 1503 m, 1485 w, 1462 w, 1438 m, 1410 w, 1364 s, 1351 m, 1332 m, 1278 s, 1262 m, 1195 m, 1164 m, 1120 m, 1110 m, 1047 w, 998 w, 948 w, 892 w, 822 vw, 790 vw, 769 m, 755 m, 741 s, 732 s, 708 w, 692 m, 671 w, 600 w, 537 w, 527 m, 511 w, 500 m, 488 w, 480 w, 462 vw cm^{-1}. HRMS: calcd. for $C_{36}H_{24}F_4O_4P_2$ [M] 658.1081; found 658.1091; Anal. calcd. for $C_{36}H_{24}F_4O_4P_2$: C, 65.66; H, 3.67; F, 11.54; found: C, 65.96; H, 3.35; F, 11.54. Crystals suitable for XRD analysis were grown in acetone–heptane (1:1) in a refrigerator in an open flask at −5 °C.

*3,3′-(Ethane-1,2-diylbis(diphenylphosphonionediyl))bis(5,6,7,8-tetrafluoro-1,4-dioxo-1,4-dihydronaphthalen-2-olate) **(4b)***: bright yellow powder, R_f = 0.9 (Sorbfil, ethyl acetate); decomp. before melting. ^{1}H NMR (DMSO-d_6): δ = 7.66–7.77 (m, 12H, C_6H_5), 7.54–7.62 (m, 8H, C_6H_5), 3.10–3.16 (m, 4H, $2CH_2$) ppm. ^{13}C{^{1}H} NMR (DMSO-d_6): δ = 178.0 (m, C^{1or4}), 177.7 (m, C^{1or4}), 173.6 (m, C^2), 146.4 [ddm, $^1J_{CF}$ = 265.2 Hz, $^2J_{CF}$ = 10.8 Hz, C^{6or7}], 145.6 [ddm, $^1J_{CF}$ = 263.7 Hz, $^2J_{CF}$ = 10.2 Hz, C^{6or7}], 144.1 [ddd, $^1J_{CF}$ = 258.0 Hz, $^2J_{CF}$ ~ 19 Hz, $^3J_{CF}$ ~ 13 Hz, C^{5or8}], 141.9 [ddd, $^1J_{CF}$ ~ 257 Hz, $^2J_{CF}$ ~ 17 Hz, $^3J_{CF}$ ~ 11 Hz, C^{5or8}], 133.2 (br. s, C_6H_5), 132.2 [m, $^3J_{CP}$ = 10.5 Hz, C_6H_5], 129.3 [m, $^2J_{CP}$ = 12.7 Hz, C_6H_5], 121.7 [m, $^1J_{CP}$ = 90.2 Hz, C_6H_5], 119.2 (m, $C_{10}F_4O_2$), 117.0 (m, $C_{10}F_4O_2$), 87.6 [m, $^1J_{CP}$ = 97.1 Hz, C^3], 18.9 [m, $^1J_{CP}$ = 53.1 Hz, CH_2] ppm. ^{19}F NMR ($CDCl_3$): δ = −151.6, −154.2, −158.2, −162.9 [ddd, 1F, $^{ortho}J_{FF}$ 19.4 ÷ 20.1 Hz $^{meta}J_{FF}$ 9.1 ÷ 11.5 Hz, $^{para}J_{FF}$ 13.2 ÷ 13.6 Hz] ppm.^{31}P{^{1}H} ($CDCl_3$): δ = 20.36 (s) ppm. IR (neat): 3435 w, 2931 vw, 1703 m, 1618 s, 1579 vs, 1506 s, 1485 w, 1466 m, 1439 m, 1373 s, 1333 s, 1279 s, 1194 w, 1161 m, 1107 m, 1074 w, 1043 m, 999 w, 953 m, 887 w, 820 vw, 768 m, 741 m, 731 m, 714 w, 692 m, 667 w, 602 w, 517 m, 501 w, 486 w cm^{-1}. Anal. calcd. for $C_{46}H_{24}F_8O_6P_2$: C, 62.31; H, 2.73; F 17.14; found: C, 62.30; H, 2.58; F 17.14. Crystals suitable for XRD analysis were grown from acetone.

*3-((2-(Diphenylphosphoryl)ethyl)diphenylphosphonio)-5,6,7,8-tetrafluoro-1-hydroxy-4-oxo-1-(2-oxopropyl)-1,4-dihydronaphthalen-2-olate **(5b)***, white powder, m.p. 207.4 °C followed by decomposition. ^{1}H NMR ($CDCl_3$): δ = 7.55–7.81 (m, 10H, C_6H_5), 7.40–7.55 (m, 10H, C_6H_5), 4.45 [d, 1H, J = 2.6 Hz, OH), 2.90–3.30 (m, 4H, $2CH_2$), 2.32–2.62 (m, 2H, $C\underline{H}_2C(O)$), 2.12 (s, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 205.6 (s, C═O), 191.6 [d, $^2J_{CP}$ = 4.2 Hz, C^{2or4}], 179.5 [d, $^2J_{CP}$ = 6.1 Hz, C^{2or4}], 146.8 [ddm, $^1J_{CF}$ = 266.3 Hz, $^2J_{CF}$ ~ 10 Hz, C^{6or7}], 145.4 [ddd, $^1J_{CF}$ = 254.0 Hz, $^2J_{CF}$ = 10.7 Hz, $^3J_{CF}$ = 4.0 Hz, C^{6or7}], 142.7 [ddd, $^1J_{CF}$ = 257.0 Hz, $^2J_{CF}$ ~ 14 Hz, $^3J_{CF}$ ~ 3.0 Hz, C^{5or8}], 140.8 [ddd, $^1J_{CF}$ = 255.0 Hz, $^2J_{CF}$ = 13.4 Hz, $^3J_{CF}$ = 3.0 Hz, C^{5or8}], 133.1 [d, $^4J_{CP}$ = 1.7 Hz, C_6H_5], 132.3 [d, $^3J_{CP}$ = 9.4 Hz, C_6H_5], 132.2 [d, $^3J_{CP}$ = 9.5 Hz, C_6H_5], 132.1 [d, $^4J_{CP}$ = 3.0 Hz, C_6H_5], 132.1 [d, $^4J_{CP}$ = 2.9 Hz, C_6H_5], 130.9 [d, $^3J_{CP}$ = 9.5 Hz, C_6H_5], 130.9 [d, $^3J_{CP}$ = 9.6 Hz, C_6H_5], 129.5 [d, $^2J_{CP}$ = 13.0 Hz, C_6H_5], 129.4 [d, $^2J_{CP}$ = 12.9 Hz, C_6H_5], 128.8 [d, $^2J_{CP}$ = 11.9 Hz, C_6H_5], 128.7 [d, $^2J_{CP}$ = 11.9 Hz, C_6H_5], 125.2 [dd, $^2J_{CF}$ = 8.9 Hz, $^3J_{CF}$ = 3.2 Hz, $C_{10}F_4O_2$], 122.5 [d, $^1J_{CP}$ = 89.6 Hz, C_6H_5], 122.2 [d, $^1J_{CP}$ = 91.3 Hz, C_6H_5], 116.5 [dd, $^2J_{CF}$ = 8.6 Hz, $^3J_{CF}$ = 2.7 Hz, $C_{10}F_4O_2$], 81.4 [d, $^1J_{CP}$ = 100.8 Hz, C^3], 73.2 [d, $^3J_{CF}$ ~ 10 Hz, C^1], 55.5 (br. s, $\underline{C}H_2C(O)$), 31.9 (s, $C(O)\underline{C}H_3$), 22.8 [dd, $^1J_{CP}$ = 68.2 Hz, $^2J_{CP}$ = 4.0 Hz, CH_2], 19.5 [d, $^1J_{CP}$ = 56.4 Hz, CH_2] ppm. ^{19}F NMR ($CDCl_3$): δ = −139.3, −142.7, −151.6, −156.3 [ddd, 1F, $^{ortho}J_{FF}$ 20.0 ÷ 21.0 Hz $^{meta}J_{FF}$ 3.0 ÷ 8.6 Hz, $^{para}J_{FF}$ 13.0 ÷ 13.1 Hz] ppm.^{31}P{^{1}H} ($CDCl_3$): δ = 32.70 [d, 1P, $^3J_{PP}$ = 57.0 Hz], 19,30 [d, 1P, $^3J_{PP}$ = 57.0 Hz] ppm. IR (neat): 3392 vw, 3203 w, 3080 w, 3059 w, 3030 vw, 3012 vw, 2974 w, 2960 w, 2914 w, 2891 vw, 2858 vw, 1709 m, 1618 m, 1570 vs, 1508 m, 1483 w, 1462 m, 1437 m, 1417 w, 1394 w, 1362 s, 1325 m, 1302 w, 1273 m, 1200 m, 1173 m, 1138 w, 1120 m, 1107 m, 1059 w, 1024 w, 999 w, 978 w, 931 w, 891 w, 854 vw, 802 w, 787 vw, 739 m, 694 m, 677 w, 544 m, 519 m, 498 w, 482 w cm^{-1}. HRMS: calcd. for $C_{39}H_{30}F_4O_5P_2$ [M] 716.1500; found 716.1493; Anal. calcd. for $C_{39}H_{30}F_4O_5P_2$: C, 65.37; H, 4.22; F, 10.60; found: C, 65.83; H, 4.22; F, 10.61.

4.4. The reaction of quinone *1* with $Ph_2P(CH_2)_3PPh_2$ *2c* in water-containing dioxane or DMSO

A solution of quinone **1** (100 mg, 0.376 mmol) in dioxane (10.0 mL) and H_2O (1.0 mL) was added slowly to a stirred solution of phosphane **2c** (155 mg, 0.376 mmol) in dioxane (4.0 mL) and H_2O (0.4 mL). Within 2 h, the reaction mixture changed its color from yellow to orange. The solvents were evaporated, and the residue was purified by TLC to isolate betaines **3c** (164 mg, 65%) and **4c** (44 mg, 13%).

A mixture of **1** (200 mg, 0.752 mmol), **2c** (155 mg, 0.376 mmol), DMSO (2.0 mL), and H_2O (0.1 mL) was stirred for 1 h. Addition of water (~8 mL) gave a precipitate, which was centrifuged off, washed with water (4 × 5 mL), and dried. The aqueous fraction was extracted with chloroform (3 × 15 mL). The extracts were dried over $MgSO_4$, filtered, and evaporated. The residue was purified by TLC to give betaines **3c** (35 mg, 14%) and **4c** (287 mg, 85%).

For TLC, the use of the 1:1 dioxane–hexane mixture instead of ethyl acetate as the eluent led to conversion of **3c** and **4c** into **7c** and **8c**, respectively.

*3-((3-(Diphenylphosphoryl)propyl)diphenylphosphonio)-5,6,7,8-tetrafluoro-1,4-dioxo-1,4-dihydronaphthalen-2-olate **(3c)***: orange powder, R_f = 0.1 (ethyl acetate), m.p. 74.1 °C followed by decomposition. ^{1}H NMR ($CDCl_3$): δ = 7.44–7.64 (m, 10H, C_6H_5), 7.27–7.42 (m, 10H, C_6H_5), 3.06–3.19 (m, 2H, CH_2), 2.30–2.42 (m, 2H, CH_2), 1.58–1.74 (m, 2H, CH_2) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 178.2 (br. s, C^{1or4}), 178.1

(br. s, C^{1or4}), 173.6 [d, $^2J_{CP}$ = 3.7 Hz, C^2], 147.0 [ddm, $^1J_{CF}$ = 270.3 Hz, $^2J_{CF}$ = 10.1 Hz, C^{6or7}], 146.1 [ddm, $^1J_{CF}$ = 268.6 Hz, $^2J_{CF}$ = 11.1 Hz, C^{6or7}], 144.8 [dm, $^1J_{CF}$ ~ 238 Hz, $^2J_{CF}$ ~ 12 Hz, C^{5or8}], 142.2 [dm, $^1J_{CF}$ ~ 235 Hz, $^2J_{CF}$ ~ 11 Hz, C^{5or8}], 132.8 [d, $^4J_{CP}$ = 2.9 Hz, C_6H_5], 132,5 (s, C_6H_5), 131.8 [d, $^3J_{CP}$ = 10.2 Hz, C_6H_5], 131.6 [d, $^4J_{CP}$ = 2.5 Hz, C_6H_5], 131.5 [d, $^4J_{CP}$ = 2.8 Hz, C_6H_5], 130.3 [d, $^3J_{CP}$ = 9.4 Hz, C_6H_5], 129.0 [d, $^2J_{CP}$ = 12.8 Hz, C_6H_5], 128.4 [d, $^2J_{CP}$ = 11.7 Hz, C_6H_5], 121.6 [d, $^1J_{CP}$ = 90.2 Hz, C_6H_5], 119.0 [dm, $^2J_{CF}$ = 9.7 Hz, $C_{10}F_4O_2$], 116.2 (br. s, $C_{10}F_4O_2$), 88.9 [d, $^1J_{CP}$ = 94.2 Hz, C^3], 29.9 [dd, $^1J_{CP}$ = 70.9 Hz, $^3J_{CP}$ = 16.5 Hz, CH_2], 26.1 [dd, $^1J_{CP}$ = 53.9 Hz, $^3J_{CP}$ = 12.3 Hz, CH_2], 15.9 [t, $^2J_{CP}$ = 2.5 Hz, CH_2] ppm. ^{19}F NMR ($CDCl_3$): δ = –138.7, −141.2, −145.1, −150.0 [ddd, 1F, $^{ortho}J_{FF}$ 19.3 ÷ 20.1 Hz $^{meta}J_{FF}$ 9.0 ÷ 11.3 Hz, $^{para}J_{FF}$ 12.9 ÷ 13.0 Hz] ppm.^{31}P{^{1}H} ($CDCl_3$): δ = 32.44 [d, 1P, $^4J_{PP}$ = 3.6 Hz], 17,63 [d, 1P, $^4J_{PP}$ = 3.6 Hz] ppm. IR (neat): 3429 m, 3057 w, 2955 w, 2924 m, 2854 w, 1701 m, 1618 s, 1579 vs, 1504 s, 1485 m, 1468 m, 1437 m, 1371 s, 1336 m, 1277 s, 1165 s, 1113 s, 1072 m, 1045 m, 997 m, 951 m, 891 w, 823 vw, 748 s, 721 s, 694 s, 665 m, 602 w, 548 m, 505 m, 420 vw cm^{-1}. HRMS: calcd. for $C_{37}H_{26}F_4O_4P_2$ [M] 672.1237; found 672.1230; Anal. calcd. for $C_{37}H_{26}F_4O_4P_2$*2$CHCl_3$: C, 51.40; H, 3.10; found: C, 51.45; H, 3.13.

*3,3′-(Propane-1,3-diylbis(diphenylphosphonionediyl))-bis(5,6,7,8-tetrafluoro-1,4-dioxo-1,4-dihydronaphthalen-2-olate) (**4c**)*: yellow powder, R_f = 0.6 (ethyl acetate–hexane, 1:1), m.p. 145.9 °C followed by decomposition. ^{1}H NMR ($CDCl_3$): δ = 7.54–7.62 (m, 8H, C_6H_5), 7.48–7.54 (m, 4H, C_6H_5), 7.37–7.45 (m, 8H, C_6H_5), 3.05–3.20 (m, 4H, $2CH_2$), 1.23–1.34 (m, 2H, CH_2) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 178.2 (m, C^{1or4}), 178.1 (m, C^{1or4}), 173.6 (m, C^2), 147.1 [dd, $^1J_{CF}$ = 272.4 Hz, $^2J_{CF}$ = 9.2 Hz, C^{6or7}], 146.7 [dd, $^1J_{CF}$ = 268.5 Hz, $^2J_{CF}$ = 10.8 Hz, C^{6or7}], 144.9 [dt, $^1J_{CF}$ = 269.0 Hz, $^2J_{CF}$ = 15.0 Hz, C^{5or8}], 142.5 [dt, $^1J_{CF}$ = 261.6 Hz, $^2J_{CF}$ = 14.6 Hz, C^{5or8}], 132.9 (br. s, C_6H_5), 132.0 [m, $^3J_{CP}$ = 10.3 Hz, C_6H_5], 129.0 [m, $^2J_{CP}$ = 12.8 Hz, C_6H_5], 121.6 [d, $^1J_{CP}$ = 91.0 Hz, C_6H_5], 119.0 (m, $C_{10}F_4O_2$), 116.3 (m, $C_{10}F_4O_2$), 88.7 [d, $^1J_{CP}$ = 95.1 Hz, C^3], 25.8 [dd, $^1J_{CP}$ = 55.7 Hz, $^3J_{CP}$ = 17.1 Hz, CH_2], 18.0 (br. s, CH_2) ppm. ^{19}F NMR ($CDCl_3$): δ = −138.9, −141.2, −145.2, −150.1 [ddd, 1F, $^{ortho}J_{FF}$ 19.6 ÷ 20.1 Hz $^{meta}J_{FF}$ 9.0 ÷ 11.3 Hz, $^{para}J_{FF}$ 13.1 ÷ 13.4 Hz] ppm.^{31}P{^{1}H} ($CDCl_3$): δ = 17.62 (s) ppm. IR (neat): 3437 w, 3394 w, 3059 vw, 2956 w, 2926 w, 2856 vw, 1703 m, 1618 s, 1581 vs, 1504 s, 1485 w, 1468 m, 1439 m, 1369 s, 1335 m, 1275 s, 1190 w, 1163 m, 1111 m, 1074 vw, 1045 w, 999 vw, 968 w, 951 m, 891 w, 768 m, 748 w, 725 m, 690 m, 665 vw, 602 w, 548 vw, 527 w, 505 w cm^{-1}. HRMS: calcd. for $C_{47}H_{26}F_8O_6P_2$ [M] 900.1071; found 900.1065; Anal. calcd. for $C_{47}H_{26}F_8O_6P_2$: C, 62.68; H, 2.91; found: C, 62.93; H, 3.19.

*2-((3-(Diphenylphosphoryl)propyl)diphenylphosphonio)-4,5,6,7-tetrafluoro-1-oxo-1H-inden-3-olate (**7c**)*: yellow crystals, R_f = 0.2 (dioxane-hexane, 1:1), m.p. 216.1–216.8 °C. ^{1}H NMR ($CDCl_3$): δ = 7.54–7.69 (m, 10H, C_6H_5), 7.38–7.52 (m, 10H, C_6H_5), 3.07–3.20 (m, 2H, CH_2), 2.41–2.53 (m, 2H, CH_2), 1.79–1.95 (m, 2H, CH_2) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 186.5 [d, $^2J_{CP}$ = 11.5 Hz, $C^{1,3}$], 142.9 [dm, $^1J_{CF}$ ~ 260 Hz, $C^{4,7or5,6}$], 141.3 [dm, $^1J_{CF}$ ~ 263 Hz, $C^{4,7or5,6}$], 133.3 [d, $^4J_{CP}$ = 2.8 Hz, C_6H_5], 132.4 [d, $^3J_{CP}$ = 10.5 Hz, C_6H_5], 131.9 [d, $^4J_{CP}$ = 2.3 Hz, C_6H_5], 130.6 [d, $^3J_{CP}$ = 9.4 Hz, C_6H_5], 129.3 [d, $^2J_{CP}$ = 12.7 Hz, C_6H_5], 128.7 [d, $^2J_{CP}$ = 11.7 Hz, C_6H_5], 122.4 [d, $^1J_{CP}$ = 90.4 Hz, C_6H_5], 120.8 (m, $C_9F_4O_2$), 73.8 [d, $^1J_{CP}$ = 112.1 Hz, C^2], 30.1 [dd, $^1J_{CP}$ = 71.0 Hz, $^3J_{CP}$ = 16.9 Hz, CH_2], 29.7 [d, $^2J_{CP}$ = 3.4 Hz, CH_2], 22.6 [dd, $^1J_{CP}$ = 55.5 Hz, $^3J_{CP}$ = 11.3 Hz, CH_2] ppm. ^{19}F NMR ($CDCl_3$): δ = –145.1 (m, 2F), −150.4 (m, 2F) ppm. ^{31}P{^{1}H} ($CDCl_3$): δ = 32.5 [d, 1P, $^4J_{PP}$ 3.0 Hz], 11.3 [d, 1P, $^4J_{PP}$ 3.0 Hz] ppm. IR (neat): 3435 w, 3066 w, 3036 vw, 2937 w, 2922 w, 2868 vw, 2852 vw, 1641 s, 1612 vs, 1589 m, 1552 w, 1491 s, 1439 m, 1402 w, 1385 m, 1362 w, 1327 s, 1300 s, 1254 w, 1196 m, 1157 m, 1117 m, 1074 m, 1028 vw, 997 w, 968 w, 955 w, 922 m, 833 w, 764 w, 744 m, 715 m, 692 m, 665 w, 550 m, 523 m, 500 m, 474 w, 424 w cm^{-1}. HRMS: calcd. for $C_{36}H_{26}F_4O_3P_2$ [M] 644.1288; found 644.1285; Anal. calcd. for $C_{36}H_{26}F_4O_3P_2$: C, 67.09; H, 4.07; F, 11.79; found: C, 66.71; H, 4.37; F, 11.79. Crystals suitable for XRD analysis were grown from acetone–heptane (1:1) in the refrigerator in an open flask at −5 °C.

*2,2′-(Propane-1,3-diylbis(diphenylphosphonionediyl))bis(4,5,6,7-tetrafluoro-1-oxo-1H-inden-3-olate) (**8c**)*: yellow crystals, R_f = 0.8 (dioxane-hexane, 1:1), m.p. 240.8 °C followed by decomposition. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 186.4 (m, $C^{1,3}$), 143.0 [dm, $^1J_{CF}$ ~ 259 Hz, $C^{4,7or5,6}$], 141.3 [dm, $^1J_{CF}$ ~ 265 Hz, $C^{4,7or5,6}$], 133.4 [m, $^4J_{CP}$ = 3.0 Hz, C_6H_5], 132.4 [m, $^3J_{CP}$ = 10.7 Hz, C_6H_5], 129.4 [m, $^2J_{CP}$ = 12.8 Hz, C_6H_5], 122.1 [d, $^1J_{CP}$ = 91.1 Hz, C_6H_5], 120.7 (m, $C_{10}F_4O_2$), 73.4 [d, $^1J_{CP}$ = 112.6 Hz, C^2], 22.7 [dd, $^1J_{CP}$ = 57.3 Hz, $^3J_{CP}$ = 17.5 Hz, CH_2], 17.8 [br. s, CH_2] ppm. ^{19}F NMR ($CDCl_3$): δ = −145.0 (m, 2F), −150.2 (m, 2F) ppm. ^{31}P{^{1}H} ($CDCl_3$): δ = 11.3 (s) ppm. IR (neat): 3444 vw, 1710 w, 1678 w, 1640 s, 1611 vs, 1587 m, 1575 w, 1552 w, 1490 s, 1439 m, 1384 m, 1363 w, 1344 w, 1325 m, 1299 s, 1246 w, 1220 w, 1200 w, 1193 w, 1166 vw, 1130 w, 1114 m, 1075 m, 996 vw, 975 w, 924 m, 765 w, 742 w, 723 w, 703 w, 691 m, 672 w, 528 w, 501 m, 486 w, 479 w, 426 w cm^{-1}. HRMS: calcd. for $C_{45}H_{26}F_8O_4P_2$ [M] 844.1173; found 844.1175. Crystals suitable for XRD analysis were grown from acetone–heptane (1:1) in the refrigerator in an open flask at −5 °C.

*4.5. The reaction of quinone **1** with $Ph_2P(CH_2)_4PPh_2$ **2d** in water-containing dioxane or DMSO*

A solution of **1** (100 mg, 0.376 mmol) in dioxane (10.0 mL) and H_2O (1.0 mL) was added slowly to a stirred solution of **2d** (160 mg, 0.376 mmol) in dioxane (4.0 mL) and H_2O (0.4 mL) at room temperature. Within 1 h, the reaction mixture changed its color from yellow to orange. The solvents were distilled off, and the residue was purified by TLC to isolate betaines **3d** (129 mg, 50%) and **4d** (63 mg, 18%).

A mixture of **1** (200 mg, 0.752 mmol), **2d** (160 mg, 0.376 mmol), DMSO (2.0 mL), and H_2O (0.1 mL) was stirred for 1 h. Water (~8 mL) was added; a precipitate was centrifuged off, washed with water (4 × 5 mL), and air dried to obtain compound **4d** with a yield of 344 mg (100%).

For preparative chromatography on silica gel, the use of the 1:1 dioxane–hexane mixture instead of ethyl acetate as the eluent led to conversion of **3d** into **7d**.

*3-((4-(Diphenylphosphoryl)butyl)diphenylphosphonio)-5,6,7,8-tetrafluoro-1,4-dioxo-1,4-dihydronaphthalen-2-olate (**3d**)*: red powder, R_f = 0.2 (ethyl acetate), m.p. 95.3 °C followed by decomposition. ^{19}F NMR ($CDCl_3$): δ = −135.8, −138.2, −142.2, −147.2 [ddd, 1F, $^{ortho}J_{FF}$ 19.2 ÷ 20.4 Hz $^{meta}J_{FF}$ 8.9 ÷ 11.3 Hz, $^{para}J_{FF}$ 12.3 ÷ 13.1 Hz] ppm.^{31}P{^{1}H} ($CDCl_3$): δ = 32.54 (s), 18,29 (s) ppm. IR (neat): 3427 w, 3057 w, 3026 w, 3012 w, 2993 w, 2935 w, 2926 w, 2870 w, 1782 vw, 1703 m, 1616 s, 1581 vs, 1506 s, 1485 m, 1466 w, 1437 s, 1369 s, 1335 m, 1275 m, 1244 w, 1223 w, 1182 m, 1165 m, 1117 m, 1070 w, 1045 w, 1028 w, 997 w, 951 w, 924 vw, 893 w, 845 vw, 768 m, 746 m, 719 m, 694 s, 675 w, 602 w, 548 m, 509 m cm^{-1}. HRMS: calcd. for $C_{38}H_{28}F_4O_4P_2$ [M] 686.1394; found 686.1386; Anal. calcd. for $2C_{38}H_{28}F_4O_4P_2$*$CHCl_3$: C, 61.96; H, 3.85; found: C, 61.60; H, 3.67.

*3,3′-(Butane-1,4-diylbis(diphenylphosphonionediyl))-bis(5,6,7,8-tetrafluoro-1,4-dioxo-1,4-dihydronaphthalen-2-olate) (**4d**)*: bright yellow crystals, R_f = 0.9 (ethyl acetate), m.p. 234.6 °C followed by decomposition. ^{1}H NMR ($CDCl_3$): δ = 7.63–7.75 (m, 8H, C_6H_5), 7.55–7.63 (m, 4H, C_6H_5), 7.44–7.55 (m, 8H, C_6H_5), 2.84–3.05 (m, 4H, CH_2), 1.37–1.58 (m, 4H, CH_2) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 178.5 [d, J_{CP} = 12.9 Hz, C^{1or4}], 178.2 [d, J_{CP} = 5.1 Hz, C^{1or4}], 173.9 [d, $^2J_{CP}$ = 3.9 Hz, C^2], 147.2 [ddm, $^1J_{CF}$ = 272.0 Hz, $^2J_{CF}$ ~ 10 Hz, C^{6or7}], 146.4 [ddm, $^1J_{CF}$ = 268.0 Hz, $^2J_{CF}$ ~ 10 Hz, C^{6or7}], 145.0 [dm, $^1J_{CF}$ ~ 264 Hz, C^{5or8}], 142.7 [dm, $^1J_{CF}$ ~ 262.0 Hz, C^{5or8}], 133.0 [d, $^4J_{CP}$ = 3.1 Hz, C_6H_5], 132.2 [d, $^3J_{CP}$ = 10.2 Hz, C_6H_5], 129.2 [d, $^2J_{CP}$ = 12.8 Hz, C_6H_5], 122.1 [d, $^1J_{CP}$ = 90.2 Hz, C_6H_5], 119.4 [dm, $^2J_{CF}$ = 11.4 Hz, $C_{10}F_4O_2$], 116.5 (br. s, $C_{10}F_4O_2$), 89.1 [d, $^1J_{CP}$ = 94.2 Hz, C^3], 24.9 [d, $^1J_{CP}$ = 54.8 Hz, CH_2], 23.7 [dd, $^3J_{CP}$ = 17.7 Hz, $^2J_{CP}$ = 3.2 Hz, CH_2] ppm. ^{19}F NMR ($CDCl_3$):

δ = –138.7, −141.3, −145.2, −150.1 [ddd, 1F, $^{ortho}J_{FF}$ 19.4 ÷ 20.1 Hz $^{meta}J_{FF}$ 9.0 ÷ 11.1 Hz, $^{para}J_{FF}$ ~ 13.5 Hz] ppm.$^{31}P\{^{1}H\}$ ($CDCl_3$): δ = 18.47 (s) ppm. IR (neat): 3437 w, 3392 vw, 3080 vw, 3059 w, 2962 w, 2924 w, 2854 vw, 1701 m, 1618 s, 1579 vs, 1574 vs, 1504 s, 1485 w, 1462 w, 1439 m, 1373 s, 1365 s, 1335 m, 1275 s, 1221 w, 1190 w, 1163 m, 1115 m, 1074 vw, 1045 m, 1028 w, 999 w, 953 m, 893 w, 858 vw, 822 vw, 771 m, 746 m, 727 w, 721 w, 692 m, 675 w, 602 w, 550 w, 525 w, 507 w, 471 w, 417 vw cm^{-1}. HRMS: calcd. for $C_{48}H_{28}F_8O_6P_2$ [M] 914.1228; found 914.1231; Anal. calcd. for $C_{48}H_{28}F_8O_6P_2$: C, 63.03; H, 3.09; found: C, 63.03; H, 3.48.

2-((4-(Diphenylphosphoryl)butyl)diphenylphosphonio)-4,5,6,7-tetrafluoro-1-oxo-1H-inden-3-olate ***(7d)***: yellow oil, R_f = 0.8 (acetonitrile), m.p. 91.1 °C followed by decomposition. ^{1}H NMR ($CDCl_3$): δ = 7.58–7.72 (m, 10H, C_6H_5), 7.47–7.53 (m, 6H, C_6H_5), 7.41–7.46 (m, 4H, C_6H_5), 2.81–2.90 (m, 2H, CH_2), 2.23–2.32 (m, 2H, CH_2), 1.71–1.82 (m, 2H, CH_2), 1.54–1.64 (m, 2H, CH_2) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 186.4 [d, $^{2}J_{CP}$ = 11.6 Hz, $C^{1,3}$], 143.0 [ddd, $^{1}J_{CF}$ ~ 260 Hz, $^{2}J_{CF}$ ~ 14 Hz, $^{3}J_{CF}$ ~ 4 Hz, $C^{5,6}$], 141.4 [dm, $^{1}J_{CF}$ ~ 264 Hz, $C^{4,7}$], 133.3 [d, $^{4}J_{CP}$ = 3.0 Hz, C_6H_5], 132.4 [d, $^{3}J_{CP}$ = 10.4 Hz, C_6H_5], 131.8 [d, $^{4}J_{CP}$ = 2.6 Hz, C_6H_5], 130.7 [d, $^{3}J_{CP}$ = 9.3 Hz, C_6H_5], 129.3 [d, $^{2}J_{CP}$ = 12.6 Hz, C_6H_5], 128.7 [d, $^{2}J_{CP}$ = 11.6 Hz, C_6H_5], 122.6 [d, $^{1}J_{CP}$ = 90.2 Hz, C_6H_5], 120.9 (m, $C_{10}F_4O_2$), 74.0 [dt, $^{1}J_{CP}$ = 112.1 Hz, $^{4}J_{CF}$ = 1.4 Hz, C^{2}], 29.0 [d, $^{1}J_{CP}$ = 71.5 Hz, CH_2], 23.7 [dd, $^{3}J_{CP}$ = 14.5 Hz, $^{2}J_{CP}$ = 3.0 Hz, CH_2], 22.8 [dd, $^{3}J_{CP}$ = 18.4 Hz, $^{2}J_{CP}$ = 3.5 Hz, CH_2], 21.9 [d, $^{1}J_{CP}$ = 56.0 Hz, CH_2] ppm. ^{19}F NMR ($CDCl_3$): δ = −145.1 (m, 2F), −150.4 (m, 2F) ppm. $^{31}P\{^{1}H\}$ ($CDCl_3$): δ = 32.08 (s), 11.87 (s) ppm. IR (neat): 3425 w, 3295 w, 3059 w, 2938 w, 2930 w, 1686 w, 1642 s, 1612 vs, 1588 m, 1572 w, 1552 w, 1490 s, 1438 m, 1381 m, 1343 w, 1326 m, 1299 m, 1245 vw, 1183 m, 1168 w, 1114 m, 1072 m, 1027 w, 997 w, 954 w, 923 m, 841 vw, 763 w, 746 m, 721 m, 694 m, 550 m, 518 w, 504 m, 484 w cm^{-1}. HRMS: calcd. for $C_{37}H_{28}F_4O_3P_2$ [M] 658.1444; found 658.1446. Crystals suitable for XRD analysis were grown from methanol–heptane (1:2) in the refrigerator in an open flask at −5 °C.

4.6. The reaction of quinone ***1*** *with* $Ph_2P(CH_2)_5PPh_2$ ***2e*** *in water-containing dioxane or DMSO*

A soilution of **1** (100 mg, 0.376 mmol) in dioxane (5.0 mL) and H_2O (0.5 mL) was added to a stirred solution of phosphane **2e** (166 mg, 0.376 mmol) in dioxane (20.0 mL) and H_2O (2.0 mL). The reaction mixture was left open for 2 days, and a precipitate was separated by centrifugation and air dried to obtain **4e** with a yield of 24 mg (7%). The mother liquid was evaporated, the residue was purified by column chromatography on silica gel using ethyl acetate and then a mixture of ethanol with hexane (1:1) as eluents to isolate betaine **3e** (140 mg, 53%).

A mixture of **1** (200 mg, 0.752 mmol), **2e** (166 mg, 0.376 mmol), DMSO (2.0 mL), and H_2O (0.1 mL) was stirred for 1 h. After addition of water (~8 mL), the precipitate was centrifuged off, washed with water (3 × 6 mL), and air dried to obtain compound **4e** (260 mg, 74%). The aqueous fraction was extracted with chloroform (3 × 15 mL). The extracts were dried over $MgSO_4$, filtered, and evaporated. The residue was purified by TLC to form an additional amount of title compound **4e**, with a total yield of 349 mg (100%).

3-((5-(Diphenylphosphoryl)pentyl)diphenylphosphonio)-5,6,7,8-tetrafluoro-1,4-dioxo-1,4-dihydronaphthalen-2-olate ***(3e)***: orange powder, R_f = 0.2 (ethyl acetate), m.p. 79.2 °C followed by decomposition. ^{19}F NMR ($CDCl_3$): δ = –139.1, −143.1, −152.2, −156.8 [ddd, 1F, $^{ortho}J_{FF}$ 20.0 ÷ 21.3 Hz $^{meta}J_{FF}$ 2.7 ÷ 8.1 Hz, $^{para}J_{FF}$ 12.7 ÷ 13.1 Hz] ppm.$^{31}P\{^{1}H\}$ ($CDCl_3$): δ = 32.4 (s, 1P), 17.2 (s, 1P) ppm. IR (neat): 3415 m, 3232 w, 3076 w, 3074 w, 3057 w, 3014 w, 2991 w, 2931 m, 2866 w, 1709 m, 1616 m, 1578 vs, 1566 vs, 1508 m, 1481 m, 1464 m, 1437 s, 1398 m, 1362 s, 1335 s, 1273 m, 1223 w, 1176 s, 1113 s, 1070 w, 1053 m, 1028 w, 997 w, 976 w, 933 m, 868 vw, 796 w, 746 m, 719 m, 696 s, 675 w, 546 s, 515 m, 422 vw cm^{-1}. HRMS: calcd. for $C_{39}H_{30}F_4O_4P_2$ [M] 700.1550; found 700.1542; Anal. calcd. for $C_{39}H_{30}F_4O_4P_2{*}4C_3H_6O$ (acetone): C, 65.66; H, 5.83; found: C, 65.45; H, 5.86.

3,3′-(Pentane-1,5-diylbis(diphenylphosphonionediyl))-bis(5,6,7,8-tetrafluoro-1,4-dioxo-1,4-dihydronaphthalen-2-olate) ***(4e)***: R_f = 0.3 (ethyl acetate–hexane, 2:1), m.p. 308.1 °C followed by decomposition. ^{1}H NMR ($CDCl_3$): δ = 7.62–7.73 (m, 8H, C_6H_5), 7.53–7.60 (m, 4H, C_6H_5), 7.42–7.52 (m, 8H, C_6H_5), 2.80–2.90 (m, 4H, CH_2), 1.43–1.54 (m, 2H, CH_2), 1.21–1.35 (m, 4H, CH_2) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 178.3 [d, J_{CP} = 12.2 Hz, C^{1or4}], 178.1 [d, J_{CP} = 3.6 Hz, C^{1or4}], 173.6 [d, $^{2}J_{CP}$ = 3.5 Hz, C^{2}], 147.1 [dd, $^{1}J_{CF}$ = 271.2 Hz, $^{2}J_{CF}$ = 8.9 Hz, C^{6or7}], 146.3 [dd, $^{1}J_{CF}$ = 267.9 Hz, $^{2}J_{CF}$ = 10.1 Hz, C^{6or7}], 144.8 [dm, $^{1}J_{CF}$ = 264.0 Hz, $^{2}J_{CF}$ = 14.3 Hz, C^{5or8}], 142.4 [dm, $^{1}J_{CF}$ = 262.2 Hz, $^{2}J_{CF}$ = 14.0 Hz, C^{5or8}], 132.8 [d, $^{4}J_{CP}$ = 1.8 Hz, C_6H_5], 132.0 [d, $^{3}J_{CP}$ = 10.1 Hz, C_6H_5], 129.0 [d, $^{2}J_{CP}$ = 12.7 Hz, C_6H_5], 122.1 [d, $^{1}J_{CP}$ = 90.0 Hz, C_6H_5], 119.2 [d, $^{2}J_{CF}$ = 10.4 Hz, $C_{10}F_4O_2$], 116.2 (br. s, $C_{10}F_4O_2$), 89.2 [d, $^{1}J_{CP}$ = 94.2 Hz, C^{3}], 31.2 [t, $^{3}J_{CP}$ = 17.5 Hz, CH_2], 25.0 [d, $^{1}J_{CP}$ = 54.3 Hz, CH_2], 21.4 (br. s, CH_2) ppm. ^{19}F NMR ($CDCl_3$): δ = −135.8, −138.3, −142.3, −147.2 [ddd, 1F, $^{ortho}J_{FF}$ 19.5 ÷ 20.0 Hz $^{meta}J_{FF}$ 8.9 ÷ 11.2 Hz, $^{para}J_{FF}$ 13.2 ÷ 13.4 Hz] ppm.$^{31}P\{^{1}H\}$ ($CDCl_3$): δ = 18.31 (s) ppm. IR (neat): 3435 w, 3392 w, 3061 vw, 2937 vw, 2902 vw, 1703 m, 1618 m, 1581 vs, 1504 s, 1485 w, 1468 w, 1439 m, 1369 s, 1333 m, 1277 s, 1234 vw, 1190 w, 1165 m, 1113 m, 1045 w, 1028 w, 999 w, 951 m, 895 w, 820 vw, 769 m, 744 m, 725 m, 702 w, 690 m, 675 w, 600 w, 525 w, 501 w, 471 w cm^{-1}. HRMS: calcd. for $C_{49}H_{30}F_8O_6P_2$ [M] 928.1384; found 928.1387; Anal. calcd. for $C_{49}H_{30}F_8O_6P_2$: C, 63.37; H, 3.26; F, 16.37; P, 6.67; found: C, 63.14; H, 3.26; F, 16.31; P, 6.36.

4.7. The reaction of quinone ***1*** *with* $Et_2P(CH_2)_2PEt_2$ ***2f*** *in anhydrous* C_6H_6 *or water-containing dioxane*

A solution of **1** (585 mg, 2.199 mmol) in anhydrous C_6H_6 (15.0 mL) was added to a stirred solution of phosphane **2f** (454 mg, 2.199 mmol) in anhydrous C_6H_6 (15.0 mL). After stirring for 30 min, the reaction mixture changed color from yellow to red. The solvent was distilled off, the residue was purified by TLC to give compounds **3f** (494 mg, 48%), **4f** (184 mg, 12%) and **6f** (26 mg, 3%).

A solution of **1** (141 mg, 0.528 mmol) in dioxane (5.0 mL) and H_2O (0.5 mL) was added to a stirred solution of **2f** (109 mg, 0.528 mmol) in dioxane (20.0 mL) and H_2O (2.0 mL). Then the reaction mixture was left open for 2 days. The solvents were evaporated, and the rest was purified by TLC to isolate betaines **3f** (91 mg, 37%) and **4f** (73 mg, 20%). The same reaction of 2 eq. of quinone **1** (384 mg, 1.444 mmol) with **2f** (149 mg, 0.722 mmol) also gave betaines **3f** (107 mg, 32%) and **4f** (68 mg, 14%).

3-((2-(Diethylphosphoryl)ethyl)diethylphosphonio)-5,6,7,8-tetrafluoro-1,4-dioxo-1,4-dihydronaphthalen-2-olate ***(3f)***: yellow powder, R_f = 0.3 (ethanol-ethyl acetate, 1:2), m.p. 153.2 °C followed by decomposition. ^{1}H NMR ($CDCl_3$): δ = 2.49–2.65 (m, 2H, CH_2), 2.24–2.49 (m, 4H, $2CH_2$), 1.63–1.86 (m, 6H, $3CH_2$), 0.99–1.26 (m, 12H, $4CH_3$) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 179.3 [dm, J_{CP} = 6.1 Hz, C^{1or4}], 178.1 [dm, J_{CP} = 11.2 Hz, C^{1or4}], 174.3 [dm, $^{2}J_{CP}$ = 3.5 Hz, C^{2}], 147.2 [ddm, $^{1}J_{CF}$ = 273.0 Hz, $^{2}J_{CF}$ = 11.0 Hz, C^{6or7}], 146.5 [ddm, $^{1}J_{CF}$ = 268.7 Hz, $^{2}J_{CF}$ = 9.3 Hz, C^{6or7}], 145.2 [ddm, $^{1}J_{CF}$ = 236.4 Hz, $^{2}J_{CF}$ = 14.3 Hz, C^{5or8}], 142.4 [ddm, $^{1}J_{CF}$ = 236.0 Hz, $^{2}J_{CF}$ = 13.8 Hz, C^{5or8}], 119.0 [dm, $^{2}J_{CF}$ = 10.5 Hz, $C_{10}F_4O_2$], 116.2 (m, $C_{10}F_4O_2$), 86.7 [d, $^{1}J_{CP}$ = 88.2 Hz, C^{3}], 20.0 [d, $^{1}J_{CP}$ = 66.9 Hz, CH_2], 19.5 [dd, $^{1}J_{CP}$ = 60.2 Hz, $^{2}J_{CP}$ = 5.2 Hz, CH_2], 14.3 [d, $^{1}J_{CP}$ = 52.9 Hz, CH_2], 13.8 [dd, $^{1}J_{CP}$ = 52.4 Hz, $^{2}J_{CP}$ = 3.3 Hz, CH_2], 6.1 [d, $^{2}J_{CP}$ = 5.1 Hz, CH_3], 5.6 [d, $^{2}J_{CP}$ = 4.8 Hz, CH_3] ppm. ^{19}F NMR ($CDCl_3$): δ = –138.6, −141.8, −145.1, −150.0 [ddd, 1F, $^{ortho}J_{FF}$ 19.4 ÷ 20.0 Hz $^{meta}J_{FF}$ 9.1 ÷ 11.2 Hz, $^{para}J_{FF}$ 13.4 ÷ 13.5 Hz] ppm.$^{31}P\{^{1}H\}$ ($CDCl_3$): δ = 51.4 [d, 1P, $^{3}J_{PP}$ = 45.0 Hz], 32.3 [d, 1P, $^{3}J_{PP}$ = 45.0 Hz] ppm. IR (neat): 3431 w, 2976 w, 2945 w, 2920 w, 2885 w, 1703 m, 1620 m, 1572 vs, 1504 m, 1462 m, 1402 w, 1369 s, 1331 m, 1277 m, 1244 w, 1198 w, 1167 s, 1113 w, 1047 w, 1032 m, 1024 m, 1005 w, 951 m, 899 w, 879

vw, 818 vw, 810 vw, 777 m, 764 m, 750 m, 729 w, 696 w, 652 w, 600 vw, 463 vw, 436 vw cm^{-1}. HRMS: calcd. for $C_{20}H_{24}F_4O_4P_2$ [M] 466.1081; found 466.1087.

*3,3′-(Ethane-1,2-diylbis(diethylphosphonionediyl))bis(5,6,7,8-tetrafluoro-1,4-dioxo-1,4-dihydronaphthalen-2-olate) (**4f**)*: red powder, R_f = 0.5 (ethanol-ethyl acetate, 1:2), m.p. 229.6–231.2 °C. ^{1}H NMR ($CDCl_3$): δ = 2.64 [d, 4H, $^2J_{HP}$ = 4.9 Hz, $2CH_2$], 2.35–2.58 (m, 8H, $4CH_2$), 1.12–1.30 (m, 12H, $4CH_3$) ppm. $^{13}C\{^1H\}$ NMR (acetone-d_6): δ = 179.5 (br. s, C^{1or4}), 179.0 (br. s, C^{1or4}), 175.2 (br. s, C^2), 147.7 [ddm, $^1J_{CF}$ = 266.8 Hz, $^2J_{CF}$ = 10.5 Hz, C^{6or7}], 147.1 [ddd, $^1J_{CF}$ = 265.0 Hz, $^2J_{CF}$ = 11.0 Hz, $^3J_{CF}$ = 3.3 Hz, C^{6or7}], 145.5 [dddd, $^1J_{CF}$ = 259.1 Hz, $^2J_{CF}$ = 17.0 Hz, $^3J_{CF}$ = 12.4 Hz, $^4J_{CF}$ = 3.3 Hz, C^{5or8}], 143.2 [dddd, $^1J_{CF}$ = 257.6 Hz, $^2J_{CF}$ = 16.6 Hz, $^3J_{CF}$ = 12.5 Hz, $^4J_{CF}$ = 2.7 Hz, C^{5or8}], 120.7 (m, $C_{10}F_4O_2$), 117.8 (m, $C_{10}F_4O_2$), 87.1 [d, $^1J_{CP}$ = 88.0 Hz, C^3], 15.0 [d, $^1J_{CP}$ = 49.0 Hz, CH_2], 14.6 [d, $^1J_{CP}$ = 52.8 Hz, CH_2], 6.4 [d, $^2J_{CP}$ = 2.3 Hz, CH_3], 6.4 [d, $^2J_{CP}$ = 2.3 Hz, CH_3] ppm. ^{19}F NMR ($CDCl_3$): δ = −135.2, −138.5, −141.6, −146.4 [ddd, 1F, $^{ortho}J_{FF}$ 19.4 ÷ 22.2 Hz $^{meta}J_{FF}$ 9.2 ÷ 11.3 Hz, $^{para}J_{FF}$ 12.5 ÷ 13.4 Hz] ppm.$^{31}P\{^1H\}$ ($CDCl_3$): δ = 32.61 (s) ppm. IR (neat): 3446 vw, 2983 w, 2966 w, 2947 w, 1703 m, 1643 m, 1630 s, 1616 m, 1574 vs, 1504 s, 1462 m, 1412 m, 1369 s, 1335 m, 1281 s, 1238 w, 1200 w, 1163 m, 1111 w, 1045 m, 1032 w, 993 vw, 951 m, 887 w, 822 vw, 775 m, 764 m, 748 w, 723 vw, 696 vw, 625 vw, 598 w cm^{-1}. HRMS: calcd. for $C_{30}H_{24}F_8O_6P_2$ [M] 694.0915; found 694.0920; Anal. calcd. for $C_{30}H_{24}F_8O_6P_2$: C, 51.89; H, 3.48; F, 21.89; found: C, 51.96; H, 3.56; F, 21.91. Crystals suitable for XRD analysis were grown from chloroform.

*5,6,7,8-Tetrafluoro-1,4-dioxo-3-(triethylphosphonio)-1,4-dihydronaphthalen-2-olate (**6f**)*: orange powder, R_f = 0.8 (ethyl acetate), m.p. 145.6 °C followed by decomposition. ^{1}H NMR ($CDCl_3$): δ = 2.31–2.49 (m, 6H, $3CH_2$), 1.10–1.27 (m, 9H, $3CH_3$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 179.3 [d, J_{CP} = 5.9 Hz, C^{1or4}], 178.4 [d, J_{CP} = 10.7 Hz, C^{1or4}], 174.7 [d, $^2J_{CP}$ = 2.7 Hz, C^2], 147.3 [ddm, $^1J_{CF}$ = 270.0 Hz, $^2J_{CF}$ = 10.6 Hz, C^{6or7}], 146.6 [ddm, $^1J_{CF}$ = 267.0 Hz, $^2J_{CF}$ = 11.0 Hz, C^{6or7}], 145.1 [ddd, $^1J_{CF}$ = 263.6 Hz, $^2J_{CF}$ = 17.1 Hz, $^3J_{CF}$ = 12.3 Hz, $^4J_{CF}$ = 3.0 Hz, C^{5or8}], 142.7 [ddd, $^1J_{CF}$ = 261.7 Hz, $^2J_{CF}$ = 15.9 Hz, $^3J_{CF}$ = 12.5 Hz, $^4J_{CF}$ = 3.0 Hz, C^{5or8}], 119.4 [dm, $^2J_{CF}$ = 10.6 Hz, $C_{10}F_4O_2$], 116.4 (m, $C_{10}F_4O_2$), 86.9 [d, $^1J_{CP}$ = 88.5 Hz, C^3], 13.6 [d, $^1J_{CP}$ = 53.0 Hz, CH_2], 6.2 [d, $^2J_{CP}$ = 4.9 Hz, CH_3] ppm. ^{19}F NMR ($CDCl_3$): δ = −138.8, −142.1, −145.3, −150.4 [ddd, 1F, $^{ortho}J_{FF}$ 19.3 ÷ 20.1 Hz $^{meta}J_{FF}$ 9.0 ÷ 11.0 Hz, $^{para}J_{FF}$ = 13.6 Hz] ppm.$^{31}P\{^1H\}$ ($CDCl_3$): δ = 32.49 (s) ppm. IR (neat): 2978 w, 2943 w, 2885 w, 1711 m, 1628 m, 1566 vs, 1504 s, 1462 w, 1410 w, 1365 s, 1338 m, 1275 s, 1238 w, 1159 m, 1107 w, 1045 m, 1012 w, 949 w, 887 w, 820 vw, 766 m, 744 w, 725 w, 694 w, 623 w, 600 vw cm^{-1}. HRMS: calcd. for $C_{16}H_{15}F_4O_3P$ [M] 362.0690; found 362.0693. Crystals suitable for XRD analysis were grown from acetone–heptane (1:1) in the refrigerator in an open flask at −5 °C.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jfluchem.2017.11.010.

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