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Reaction of 1,4-Benzoquinones with PH-Phosphonium Salts

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Abstract—A novel approach has been proposed to the synthesis of phosphonium salts containing a 1,4-dihydroxybenzo fragment via reaction of 2-methyl-1,4-benzoquinone or 2-isopropyl-5-methyl-1,4-benzoquinone with PH-phosphonium salts generated *in situ* from triphenylphosphine and trifluoromethanesulfonic or trifluoroacetic acid. The structure of the synthesized phosphonium salts was determined by NMR spectroscopy and X-ray analysis.

Keywords: tertiary phosphine, PH-phosphonium salt, tetraarylphosphonium salt, 1,4-benzoquinone, thymoquinone, trifluoromethanesulfonic acid, trifluoroacetic acid

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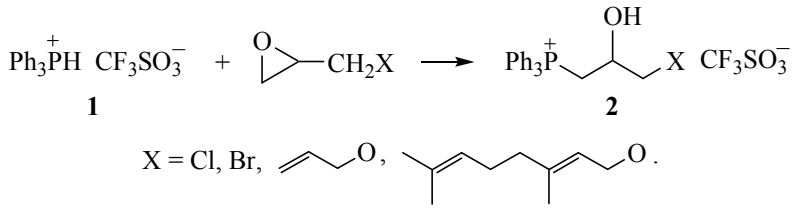
In recent years tri- and tetraarylphosphonium salts have attracted researchers' attention not only due to their application in organic synthesis but also as biologically active compounds [1–7]. Phosphonium group possesses a positive charge and fairly high lipophilicity and readily penetrates both cell and mitochondrial membranes, thus ensuring efficient targeted delivery of the corresponding drug or contrast compound for visualization of mitochondria and tumor cells [8–12]. A number of methods have been proposed for the introduction of a phosphonium moiety into organic molecules, including molecules of known medicines. These methods mostly involve alkylation of phosphines with various alkyl halides, diazonium salts, unsaturated carboxylic acids and their derivatives, etc. [13–17]. A particular place is occupied by the approach developed by us in recent years, which is based on the addition of readily accessible PH-phosphonium salts to epoxides and 1,4-naphthoquinone and its derivatives.

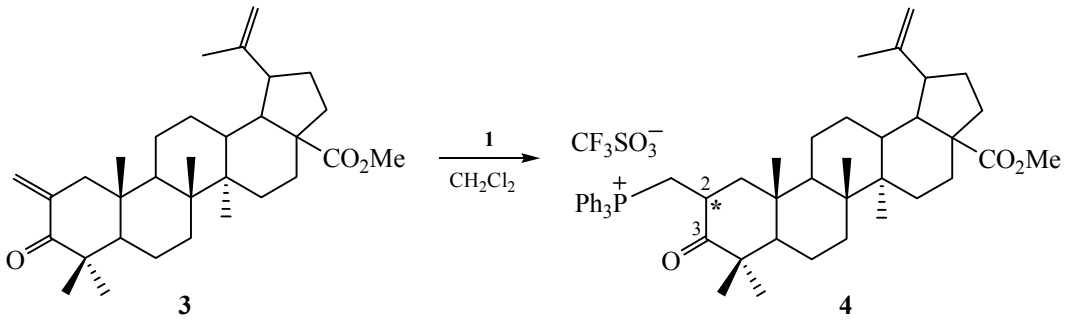
For instance, reactions of epyhalohydrins and allyl glycidyl ether with triphenylphosphonium trifluoromethanesulfonate (**1**) lead to the formation of phosphonium salts **2** in almost quantitative yield (Scheme 1) [18]. Triphenylphosphonium trifluoromethanesulfonate (**1**) readily adds to sterically crowded methyl 2-methylidene-3-oxolup-20(29)-en-28-oate (**3**) to give γ-oxoalkylphosphonium salt containing a terpene fragment, 28-methoxy-3,28-dioxo-lup-20(29)-en-2-yl(triphenyl)phosphonium trifluoromethanesulfonate (**4**) as a mixture of two epimers at a ratio of 2 : 1 with an overall yield of 90% (Scheme 2) [19].

Triphenylphosphonium trifluoromethanesulfonate (**1**) is also capable of reacting with 1,4-naphthoquinone derivatives **5** and **6** to produce almost quantitatively tetraarylphosphonium salts **7**–**9** containing a 1,4-dihydroxynaphthalene fragment (Scheme 3) [20]. It should be noted that this reaction provides the mildest and

Scheme 1.

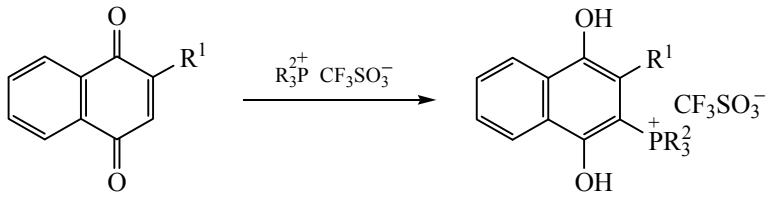


Scheme 2.



3 **4**

Scheme 3.



5, **6** **7**–**9**

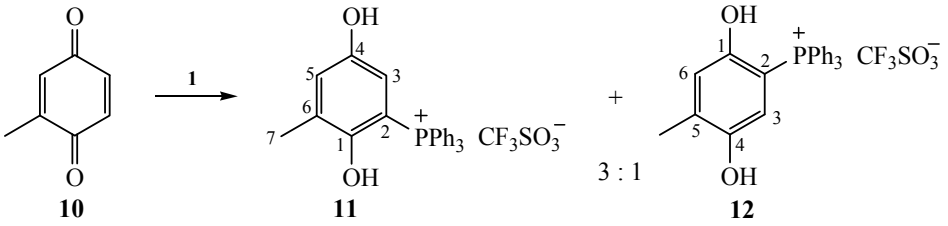
5, R^1 = H; **6**, R^1 = Me; **7**, R^1 = H, R^2 = Bu; **8**, R^1 = H, R^2 = Ph; **9**, R^1 = Me, R^2 = Ph.

most convenient method for the preparation of the corresponding dihydroxynaphthylphosphonium salt from 2-methyl-1,4-naphthoquinone since it cannot be obtained by direct reaction of the latter with triphenylphosphine.

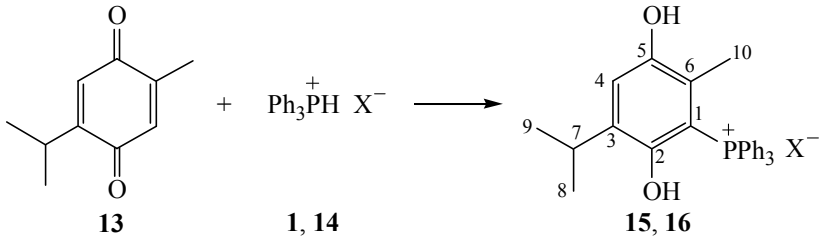
The results of the above reactions fairly strongly depend on the nucleophilicity of the phosphorus atom in the initial phosphine and steric load of the 1,4-quinone. For instance, the reaction of unsubstituted 1,4-naphthoquinone with PH-phosphonium salt derived from tributylphosphine requires a considerably longer time. 2-Methyl-1,4-naphthoquinone failed to react with tributylphosphonium trifluoromethanesulfonate even at elevated temperature. A probable reason is higher basicity of the phosphorus atom in tributylphosphine than in triphenylphosphine and, correspondingly, lower acidity of tributylphosphonium trifluoromethanesulfonate.

In this work, the above procedure for the synthesis of phosphonium salts was extended to 1,4-benzoquinone derivatives such as 2-methyl-1,4-benzoquinone (toluquinone) and 2-isopropyl-5-methyl-1,4-benzoquinone (thymoquinone) whose various derivatives exhibit antitumor activity [21–24]. Triphenylphosphonium trifluoromethanesulfonate and trifluoroacetate generated *in situ* were used as PH-phosphonium salts [25]. The developed approach turned out to be quite efficient. We thus isolated phosphonium salts **11**, **12**, **15**, and **16**, which contained a 1,4-dihydroxybenzene fragment. All reactions were carried out under mild conditions, in methylene chloride at room temperature (15 min). However, the reaction of 2-methyl-1,4-benzoquinone (**10**) with phosphonium salt (**1**) was not selective, and it afforded a mixture of regioisomeric phosphonium salts **11** and **12** at a ratio of 3:1 (Scheme 4). The structure of **11** and **12** was determined by NMR spectroscopy. The formation of a 1,4-dihydroxyphenylphosphonium fragment and new phosphorus–carbon bond followed primarily from the change of the position and multiplicity of the ^{31}P signal. Unlike initial PH-phosphonium salt **1**, no direct ^{31}P–^{1}H coupling was observed in the ^{31}P NMR spectra of **11** and **12**, and the ^{31}P signals appeared as multiplets. The ^{1}H NMR spectrum of a mixture of **11** and **12** contained a double set of signals. The 3-H and 5-H protons of **11** resonated as a doublet of doublets and doublet, respectively, with coupling constants $^{4}J_{HH}$ of 2.8 Hz. The multiplicity of the 3-H signal (d.d) confirmed that the phosphorus atom entered the 2-position of the *p*-phenylene fragment ($^{3}J_{PH}$ = 15.5 Hz). Unlike isomer **11**, the 3-H and 6-H signals in the ^{1}H NMR spectrum of **12** were doublets due to coupling only with the phosphorus atom through three and four bonds, respectively (3-H, $^{3}J_{PH}$ = 15.3 Hz; 6-H, $^{4}J_{PH}$ = 6.8 Hz). The formation of new P–C bond in **11** and **12**

Scheme 4.



Scheme 5.



1, **15**, X = CF_3SO_3; **14**, **16**, X = CF_3COO.

unambiguously followed from the presence in the $^{13}C–\{^1H\}$ NMR spectrum of doublets due to C^2 at δ_C 104.11 (**11**) and 98.46 ppm (**12**) with direct coupling constants $^1J_{PC}$ of 93.3 and 95.4 Hz, respectively.

Unlike 2-methyl-1,4-benzoquinone, thymoquinone (**13**) reacted with triphenylphosphonium trifluoromethanesulfonate (**1**) in a selective manner to form compound **15** as the only product (Scheme 5) which was isolated in a fairly high yield (90%). The IR spectrum of **15** showed a broadened absorption band at 3370 cm^{-1} due to OH stretchings. The multiplicities of signals in the ^{13}C NMR spectrum of **15** and the number of CH and quaternary carbon atoms indicated that the phosphorus atom is located *ortho* with respect to the methyl group. This also follows from the $^{13}C–^{31}P$ coupling through three bonds ($^3J_{CP}$ = 4.8 Hz) for the CH_3 carbon nucleus (δ_C 14.05 ppm, C^{10}) in the $^{13}C–\{^1H\}$ spectrum, and from the presence of only one CH signal (C^5, δ_C 121.24 ppm, $^1J_{CH}$ = 157.4 Hz) of the 1,4-dihydroxybenzene fragment in the ^{13}C NMR spectrum. The $^{13}C–\{^1H\}$ spectrum of **15** also displayed a doublet at δ_C 104.91 ppm (C^2, $^1J_{PC}$ 93.2 Hz), which confirmed the formation of P–C bond. The C–OH carbon signals were located most downfield, at δ_C 150.95 (C^4, $^3J_{PC}$ = 17.2) and 150.68 ppm (C^1), and only one of them was split due to coupling with phosphorus through three bonds.

Thymoquinone (**13**) reacted with triphenylphosphonium trifluoroacetate (**14**) in a similar way, yielding phosphonium salt **16**. According to the ^{31}P NMR data, the reaction was highly regioselective (the ratio of regioisomers in the reaction mixture was 100:1). The major isomer (**16**) was isolated, and its structure was proved by NMR spectroscopy and X-ray analysis (Fig. 1). The bond lengths and bond and torsion angles in molecule **16** fall within the corresponding standard ranges. Trifluoroacetate anions in crystal are held by classical O–H···O hydrogen bonds to form infinite chains along the 0*a* axis (Fig. 2). The chains are linked together through weaker C–H···O interactions (see table).

In summary, we have proposed a new mild and efficient procedure for the synthesis of phosphonium salts containing a 1,4-dihydroxybenzene fragment by reaction of substituted 1,4-benzoquinones with PH-phosphonium salts.

EXPERIMENTAL

The ^1H, ^{13}C, $^{13}C–\{^1H\}$, ^{31}P, and $^{31}P–\{^1H\}$ NMR spectra were recorded on Bruker Avance-400 [400 (^1H), 162.0 (^{31}P), 100.6 MHz (^{13}C)] and Bruker Avance-600 [600 (^1H), 242.94 (^{31}P), 150.9 MHz (^{13}C)] spectrometers; the chemical shifts were measured relative to the solvent signals (^1H, ^{13}C) or H_3PO_4 (^{31}P, external standard). The IR spectra were recorded on a Bruker Vector-22 spectrometer from Nujol mulls or KBr discs. The elemental analyses were obtained on a

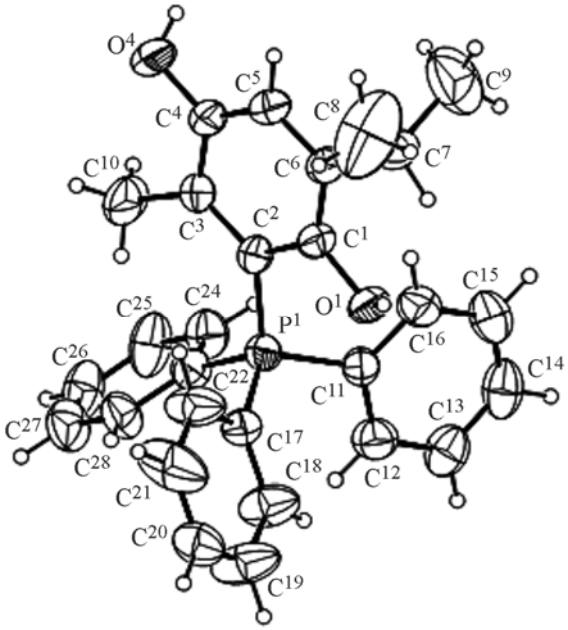


Fig. 1. Structure of the molecule of 2,5-dihydroxy-3-isopropyl-6-methylphenyl(triphenyl)phosphonium trifluoroacetate (**16**) in crystal according to the X-ray diffraction data. Non-hydrogen atoms are shown as thermal vibration ellipsoids with a probability of 30%.

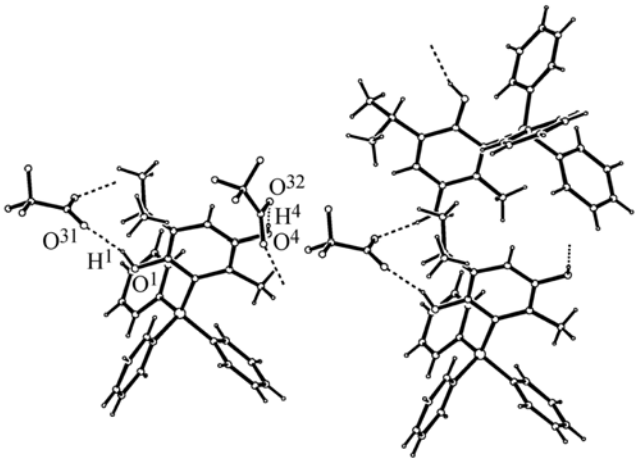


Fig. 2. O–H···O hydrogen bonds in the crystal structure of compound **16**.

Euro Vector 3000 analyzer (C, H) and by pyrolysis in a stream of oxygen (P, S).

X-Ray analysis of compound 16. The unit cell parameters and intensities of 38398 reflections (R_{int} = 0.2168) were measured on a Kappa Apex II CCD diffractometer (MoK_α radiation, graphite monochromator, ω-scanning, θ_{max} = 15.58°). Orthorhombic crystal system, space group *Pbca*; $C_{30}H_{28}F_3O_4P$, *M* 540.49; unit cell parameters [296(2) K]: *a* = 11.958(3), *b* = 18.999(5), *c* = 24.752(6) Å; *V* = 5624(2) Å^3; *Z* = 8; *F*(000) = 2256; d_{calc} = 1.277 g/cm^3; μ = 0.150 mm^{-1}. The structure was solved and refined first in isotropic and then in anisotropic approximation using SHELXL-97 program [26]. Hydrogen atoms were placed in geometrically calculated positions. Final divergence factors: R_1 = 0.0880 for 1684 independent reflections with $I > 2\sigma(I)$ and wR_2 = 0.3810 for all 5533 independent reflections. The crystallographic data for compound **16** were deposited to the Cambridge Crystallographic Data Centre (CCDC entry no. 1545689). Intermolecular interactions were analyzed, and molecular structures were plotted, using PLATON [27] and ORTEP [28].

Triphenylphosphonium trifluoromethanesulfonate (1). Trifluoromethanesulfonic acid, 0.16 mL (1.83 mmol), was slowly added dropwise to a solution of 0.48 g (1.83 mmol) of triphenylphosphine in 3 mL of methylene chloride while stirring and bubbling argon. The mixture was stirred for 30 min, and PH-phosphonium salt **1** thus obtained was then used without isolation.

Compounds 11 and 12 (mixture of regioisomers**).** A solution of 0.2 g (1.66 mmol) of 2-methyl-1,4-benzoquinone in 7 mL of methylene chloride was

Hydrogen bonds in the crystal structure of compound **16**

Hydrogen bond	Symmetry operation	D–H, Å	H···A, Å	D···A, Å	∠D–H···A, deg
O^1–H^1···O^{31}	*x*, 1 + *y*, *z*	0.82	1.84	2.617(9)	159
O^4–H^4···O^{32}	–1/2 + *x*, 1 + *y*, 1/2 – *z*	0.82	1.82	2.640(8)	172
C^7–H^7···O^1		0.98	2.42	2.935(11)	112
C^7–H^7···O^{31}	*x*, 1 + *y*, *z*	0.98	2.46	3.303(12)	144
C^{26}–H^{26}···O^3	1/2 – *x*, 1/2 + *y*, *z*	0.93	2.53	3.26(5)	135
C^{26}–H^{26}···O^{31}	1/2 – *x*, 1/2 + *y*, *z*	0.93	2.55	3.461(15)	165

added dropwise with continuous stirring while bubbling argon to a solution of 0.68 g (1.66 mmol) of phosphonium salt **1** in 5 mL of methylene chloride. The mixture turned colorless, and slight heat evolution was observed. The mixture was stirred for 30 min until complete decoloration and was left to stand for 24 h. The white finely crystalline solid (mixture **11**/**12** at a ratio of 3 : 1) was filtered off and dried under reduced pressure (14 mm). Yield 0.70 g (80%). IR spectrum, ν, cm^{-1}: 3253, 1588, 1412, 1289, 1237, 1227, 1195, 1174, 1157, 1108, 1030, 1013, 998, 877, 751, 733, 722, 690, 638, 560, 520, 509.

2,5-Dihydroxy-3-methylphenyl(triphenyl)phosphonium trifluoromethanesulfonate (11). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 10.32 s (2H, OH), 7.79 t.m (3H, 11-H), 7.66 d.d.d (6H, 10-H, $^3J_{HH}$ = 8.0, 8.0, $^4J_{PH}$ = 3.7), 7.58 d.d.d.d (6H, 9-H, $^3J_{PH}$ = 13.5, $^3J_{HH}$ = 8.0, $^4J_{HH}$ = 1.4, 0.7), 6.89 d (1H, 5-H, $^4J_{HH}$ = 2.8), 6.21 d.d (1H, 3-H, $^3J_{PH}$ = 15.5, $^4J_{HH}$ = 2.8), 2.21 s (3H, 7-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz) (hereinafter, the multiplicity of signal in the proton-decoupled spectrum is given in parentheses): 151.85 d.d.d (d) (C^4, $^3J_{CP}$ = 18.1, $^2J_{CH}$ = 3.5, 3.5), 151.65 d.d.d.d (d) (C^1, $^3J_{CH}$ = 8.8, 8.7, 8.3, $^2J_{CP}$ = 1.6), 134.67 d.m (d) (C^{11}, $^1J_{CH}$ = 164.0, $^4J_{CP}$ = 3.0), 134.02 d.m (d) (C^9, $^1J_{CH}$ = 164.5, $^2J_{CP}$ = 10.4), 130.13 d.d.d (d) (C^{10}, $^1J_{CH}$ = 165.9, $^3J_{CP}$ = 12.9, $^3J_{CH}$ = 7.3), 129.51 m (d) (C^6, $^3J_{CP}$ = 8.9), 127.08 d.m (d) (C^5, $^1J_{CH}$ = 158.2, $^4J_{CP}$ = 2.7), 120.85 q (q) (C^{12}, $^1J_{CP}$ = 320.9–321.3), 119.55 d.t (d) (C^8, $^1J_{CP}$ = 91.5, $^3J_{CH}$ = 7.9), 118.14 d.d.d (d) (C^3, $^1J_{CH}$ = 163.7, $^2J_{CP}$ = 10.8, $^3J_{CH}$ = 5.2), 104.11 d (d) (C^2, $^1J_{CP}$ = 93.3), 16.99 q.d (s) (C^7, $^1J_{CH}$ = 128.4, $^3J_{CH}$ = 5.2). ^{31}P NMR spectrum ($CDCl_3$): δ_P 22.8 ppm.

2,5-Dihydroxy-4-methylphenyl(triphenyl)phosphonium trifluoromethanesulfonate (12). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 9.48 s (2H, OH), 7.05 d (1H, 6-H, $^4J_{HP}$ = 6.8), 6.40 d (1H, 3-H, $^3J_{HP}$ = 15.3), 2.19 s (3H, 7-H); the 9-H, 10-H, and 11-H signals were overlapped by those of isomer **11**. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz): 153.98 d.d.d (d) (C^1, $^3J_{CH}$ = 8.5, $^2J_{CH}$ = 2.0–2.2, $^2J_{CP}$ = 1.9), 150.02 d.m (d) (C^4, $^3J_{CP}$ = 16.3), 137.31 d.m (d) (C^5, $^4J_{CP}$ = 2.6), 134.62 d.m (d) (C^{11}, $^1J_{CH}$ = 163.8, $^4J_{CP}$ = 3.2), 134.06 d.m (d) (C^9, $^1J_{CH}$ = 162.8, $^2J_{CP}$ = 10.4), 130.06 d.d.d (d) (C^{10}, $^1J_{CH}$ = 165.8, $^3J_{CP}$ = 13.0, $^3J_{CH}$ = 7.2), 119.84 m (d) (C^3, $^2J_{CP}$ = 9.2, overlapped by a component of the C^8 signal), 119.52 d.t (d) (C^8, $^1J_{CP}$ = 91.5, $^3J_{CH}$ = 8.1), 118.93 d.m (d) (C^6, $^1J_{CH}$ = 162.1, $^3J_{CP}$ = 11.0), 98.46 d (d) (C^2, $^1J_{CP}$ = 95.4), 16.97 q (s) (C^7, $^1J_{CH}$ = 128.0). ^{31}P NMR spectrum ($CDCl_3$): δ_P 21.7 ppm.

Triphenylphosphonium trifluoroacetate (14). A solution of 0.18 mL (2.44 mmol) of trifluoroacetic acid in 2 mL of methylene chloride was gradually added dropwise while stirring and bubbling argon to a solution of 0.64 g (2.44 mmol) of triphenylphosphine in 3 mL of methylene chloride. The mixture was stirred for 2 h, and PH-phosphonium salt **14** thus obtained was used without isolation.

2,5-Dihydroxy-3-isopropyl-6-methylphenyl(triphenyl)phosphonium trifluoromethanesulfonate (15). A solution of 0.30 g (1.83 mmol) of thymoquinone in 10 mL of methylene chloride was added dropwise over a period of 20 min to a solution of 0.75 g (1.83 mmol) of phosphonium salt **1** in 5 mL of methylene chloride while stirring and continuously bubbling argon. The mixture was left to stand for 24 h, and it changed from orange to lilac. The precipitate was filtered off and dried under reduced pressure (14 mm). Yield 0.95 g (90%), mp 194°C. IR spectrum, ν, cm^{-1}: 3370, 2968, 1600, 1484, 1456, 1440, 1420, 1385, 1366, 1297, 1239, 1179, 1165, 1107, 1045, 1031, 991, 900, 815, 748, 734, 693, 638, 571, 558, 512, 445. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 9.55 s (1H, OH), 9.50 s (1H, OH), 7.83 m (3H, 14-H), 7.73 m (6H, 12-H, 13-H), 7.25 s (1H, 5-H), 3.12 sept (1H, 7-H, $^3J_{HH}$ = 6.9), 1.46 d (3H, 10-H, $^4J_{CH}$ = 0.8), 1.12 s (3H, 8-H), 1.10 s (3H, 9-H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm (*J*, Hz): 150.95 d.m (d) (C^4, $^3J_{CP}$ = 17.2, $^2J_{CH}$ = 2.9–3.3), 150.68 d.m (s) (C^1, $^3J_{CH}$ = 9.5, 2.6), 133.28 m (d) (C^3, $^2J_{CP}$ = 8.1), 134.46 d.m (s) (C^{14}, $^1J_{CH}$ = 163.6, $^3J_{CH}$ = 7.0, $^2J_{CH}$ = 4.4–4.8), 134.06 d.m (d) (C^{12}, $^1J_{CH}$ = 164.3–165.0, $^2J_{CP}$ = 10.6, $^3J_{CH}$ = 8.4, $^2J_{CH}$ = 5.5–6.6), 130.39 d.d.d.d (d) (C^{13}, $^1J_{CH}$ = 165.8, $^3J_{CP}$ = 12.8, $^3J_{CH}$ = 6.6, $^2J_{CH}$ = 5.1–5.6), 127.47 m (d) (C^6, $^3J_{CP}$ = 9.2), 122.93 d.t (d) (C^{11}, $^1J_{CP}$ = 90.2, $^3J_{CH}$ = 8.1), 121.24 br.d.d (d) (C^5, $^1J_{CH}$ = 157.4, $^4J_{CP}$ = 1.8), 121.18 q (q) (C^{15}, $^1J_{CF}$ = 322.4), 104.91 d.m (d) (C^2, $^1J_{CP}$ = 93.2), 25.93 d.m (d) (C^7, $^1J_{CH}$ = 128.7, $^4J_{CP}$ = 1.5), 23.03 d.q (s) (C^8, C^9, $^1J_{CH}$ = 126.5, $^3J_{CH}$ = 5.1), 14.05 d.d (d) (C^{10}, $^1J_{CH}$ = 129.5, $^3J_{CP}$ = 4.8). ^{31}P NMR spectrum (DMSO-d_6): δ_P 18.2 ppm. Found, %: C 60.29; H 4.80; P 5.42; S 5.50. $C_{29}H_{28}F_3O_5PS$. Calculated, %: C 60.41; H 4.89; P 5.37; S 5.56.

2,5-Dihydroxy-3-isopropyl-6-methylphenyl(triphenyl)phosphonium trifluoroacetate (16). A solution of 0.40 g (2.44 mmol) of thymoquinone in 10 mL of methylene chloride was added dropwise over a period of 20 min to a solution of 0.75 g (1.83 mmol) of triphenylphosphonium trifluoroacetate in 5 mL of methylene chloride while stirring and continuously

bubbling argon. The reaction was accompanied by a slight heat evolution. ^{31}P NMR spectrum (CH_2Cl_2), δ_P, ppm: 18.3, 17.6 (100:1). After 24 h, the lilac mixture was evaporated under reduced pressure (14 mm), the glassy residue was dissolved in 5 mL of anhydrous acetone, and the white crystalline solid was filtered off and dried under reduced pressure (14 mm). Yield 1.05 g (81%), mp 197–198°C. IR spectrum, ν, cm^{-1}: 3074, 2962, 1678, 1594, 1441, 1319, 1202, 1164, 1132, 1104, 998, 750, 716, 692, 520, 499. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 9.82 s (1H, OH), 9.73 s (1H, OH), 7.82 t (3H, 14-H, $^3J_{CH}$ = 6.0), 7.73 m (6H, 12-H, 13-H), 7.35 s (1H, 5-H), 3.14 sept (1H, 7-H, $^3J_{HH}$ = 6.6), 1.46 s (3H, 10-H), 1.11 s (3H, 8-H), 1.09 s (3H, 9-H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm (*J*, Hz): 158.45 q (C^{16}, $^2J_{CF}$ = 30.7) 151.17 d.m (d) (C^4, $^3J_{CP}$ = 17.2, $^2J_{CH}$ = 3.0), 150.77 d (s) (C^1, $^3J_{CH}$ = 7.5), 136.55 br.m (d) (C^3, $^2J_{CP}$ = 7.7), 134.44 d.m (s) (C^{14}, $^1J_{CH}$ = 165.8, $^3J_{CH}$ = 7.2, $^2J_{CH}$ = 3.9), 134.09 d.d.d.d (d) (C^{12}, $^1J_{CH}$ = 165.0, $^2J_{CP}$ = 10.2, $^3J_{CH}$ = 7.3, $^2J_{CH}$ = 6.6), 130.38 d.d.d (d) (C^{13}, $^1J_{CH}$ = 166.4, $^3J_{CP}$ = 13.0, $^3J_{CH}$ = 7.2), 127.30 m (d) (C^6, $^3J_{CP}$ = 8.8), 123.05 d.t (d) (C^{11}, $^1J_{CP}$ = 90.4, $^3J_{CH}$ = 8.3), 121.48 br.d (s) (C^5, $^1J_{CH}$ = 157.3), 117.80 q (q) (C^{15}, $^1J_{CF}$ = 300.5), 104.95 d.d (d) (C^2, $^1J_{CP}$ = 93.4, $^4J_{CH}$ = 3.3), 25.97 br.d (s) (C^7, $^1J_{CH}$ = 128.5), 23.07 d.q (s) (C^8, C^9, $^1J_{CH}$ = 126.3, $^3J_{CH}$ = 4.9), 14.11 d.d (d) (C^{10}, $^1J_{CH}$ = 129.1, $^3J_{CP}$ = 4.4). ^{31}P NMR spectrum (DMSO-d_6): δ_P 18.27 ppm. Found, %: C 66.29; H 5.20; P 5.72. $C_{30}H_{28}F_3O_4P$. Calculated, %: C 66.66; H 5.22; P 5.73.

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