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The crystal structure and characteristic chemical property of 1,2-bis(3-guaiazulenylmethylium)benzene bishexafluorophosphate

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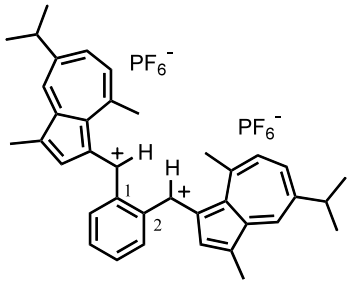
Abstract—Reaction of guaiazulene (**1**) with a 0.5 molar amount of phthalaldehyde in a mixed solvent of acetonitrile and diethyl ether in the presence of hexafluorophosphoric acid at 25°C under aerobic conditions rapidly gives the title dicarbocation compound, 1,2-bis(3-guaiazulenylmethylium)benzene bishexafluorophosphate (**2**) in 98% yield. Reduction of **2** with a large excess of $NaBH_4$ in a mixed solvent of acetonitrile and ethanol at 25°C quantitatively affords a unique *intra*-molecular cycloaddition compound **9** via the intermediate **8**. The crystal structure and characteristic chemical property of **2** are reported.

As a series of basic studies on the creation of novel functional materials with naturally occurring guaiazulene (**1**), we have been working on an efficient preparation, the molecular and crystal structures, and the spectroscopic and characteristic chemical properties and electrochemical behavior of carbocations stabilized by a guaiazulenyl group for the past several years. We have reported the chemistry of the dicarbocation compounds, 1,2- and 1,4-bis(3-guaiazulenylmethylium)-benzene bishexafluorophosphates (**2**[1] and **3**[1,2]), except their crystal structures. During the course of our investigations, we recently clarified the crystal structures of two monocarbocation compounds, 1-isopropyl-4-(3-guaiazulenylmethylium)benzene and 1-dimethylamino-4-(3-guaiazulenylmethylium)benzene tetrafluoroborates (**4**[3] and **5**[4]), as the first examples for monocarbocations stabilized by an azulenyl group, which formed a unique π-stacking structure in the single crystal, respectively. Now, our interest has been focused on the X-ray crystallographic analysis of the title dicarbocation com-



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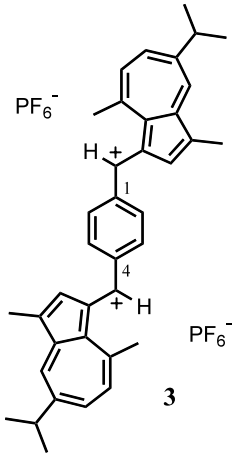

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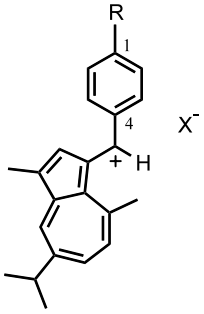

4: R = $(CH_3)_2CH$, $X^- = BF_4^-$

5: R = $(CH_3)_2N$, $X^- = BF_4^-$

6: R = H, $X^- = PF_6^-$

Keywords: azulenes; carbonium ions; X-ray crystal structures; reduction.

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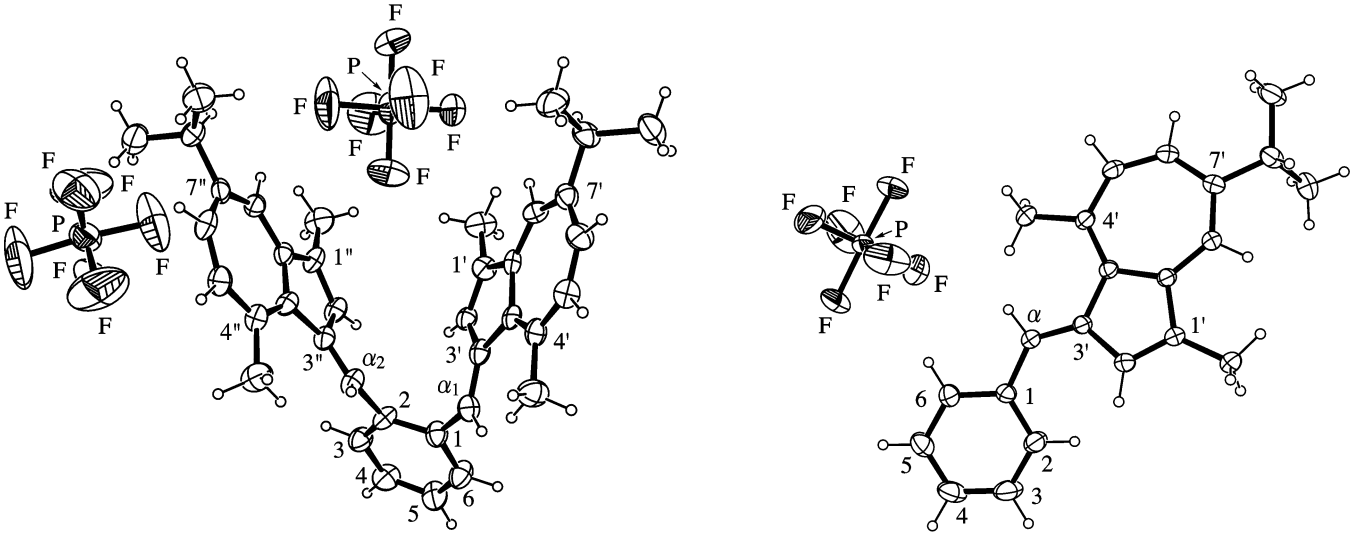
pound **2**[5] possessing larger steric hindrance and repulsion between the two adjacent 3-guaiazulenylmethyl cations and the benzene ring in comparison with the molecular structure of 3-guaiazulenylmethyliumbenzene hexafluorophosphate (**6**),[6] and further, possessing electrostatic repulsion between the two adjacent carbocations. We now wish to report our detailed studies on the X-ray crystal structure of **2**, as the first example for dicarbocations stabilized by an azulenyl group, compared with that of **6**, and on the characteristic chemical property of **2** compared with that of **3**.

The modified preparation method of the title compound **2**, which we reported previously,[1] is shown in Ref. 5: Although compound **2**, which we reported previously,[1] was a dihydrate, compound **2**, which we prepared this time, was an anhydride (98% isolated yield), and was a reddish-orange powder, mp >130°C [decomp., determined by thermal analysis (TGA and DTA)]. The elemental analysis confirmed the molecular formula $C_{38}H_{40}F_{12}P_2$ (Found: C, 58.05; H, 4.93%. Calcd for $C_{38}H_{40}F_{12}P_2$: C, 58.02; H, 5.13%.). The powdered sample **2** obtained was recrystallized from acetonitrile–diethyl ether (1:5 vol/vol) to provide stable single crystals (dark red prisms) suitable for X-ray crystallographic analysis. The crystal structure of **2** was determined by means of X-ray diffraction, producing accurate structural parameters.[7] The ORTEP drawing of **2**, indicating the molecular structure of the title dicarbocation compound, is shown in Fig. 1 together with the selected bond distances. As the result, the structural parameters of **2** revealed that: (1) contrary to anticipation,[1] the two 3-guaiazulenylmethylium substituents twisted to the same side from the benzene ring. From the dihedral angles between the least-squares planes, it was found that the plane of the 3′-guaiazulenyl group twisted by 63.0° from the plane of the benzene ring and the plane of the 3″-guaiazulenyl group twisted by 74.9° from the plane of the benzene ring, respectively, which were larger than the dihedral angle observed for that of 3-guaiazulenylmethyliumbenzene hexafluorophosphate (**6**) (21.3°);[8] (2) although the 3′-guaiazulenylmethylium substituent was planar, which coincided with that of **6**,[8] the 3″-guaiazulenylmethylium substituent was not planar. The dihedral angle between the least-squares planes of C7″–C8″–C8a″–C3a″ and C8a″–C3a″–C4″–C5″ was 3.8°, and further, the plane of the 3″-guaiazulenyl group twisted by 24.8° from the plane of C3″-Cα_2-H(Cα_2); (3) the plane of C2–C3–C4–C5 twisted by 2.1° from the plane of C1–C6–C5–C4, indicating the benzene ring is slightly twisted; (4) similarly, as in the case of **6**[8] (Fig. 1), the two 3-guaiazulenylmethylium substituents clearly indicated the bond alternation between the single and double bonds in comparison with the bond distances of the parent azulene;[9] (5) although the average C–C bond distances for the seven-membered rings of the 3′- and 3″-guaiazulenyl groups (1.40 and 1.39 Å) coincided

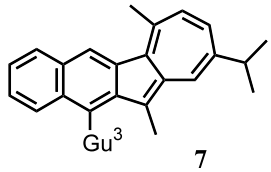


2 **6**

Figure 1. The ORTEP drawings with the numbering scheme (30% probability thermal ellipsoids) of **2** and **6**. The selected bond distances (Å) of **2** are as follows: C1–C2; 1.38(1), C2–C3; 1.39(1), C3–C4; 1.39(1), C4–C5; 1.37(1), C5–C6; 1.39(1), C6–C1; 1.39(1), C1–Cα_1; 1.48(1), Cα_1–C3′; 1.39(1), C1′–C2′; 1.33(1), C2′–C3′; 1.47(1), C3′–C3a′; 1.47(1), C3a′–C4′; 1.38(1), C4′–C5′; 1.41(1), C5′–C6′; 1.34(1), C6′–C7′; 1.42(1), C7′–C8′; 1.40(1), C8′–C8a′; 1.38(1), C8a′–C1′; 1.46(1), C8a′–C3a′; 1.47(1), C2–Cα_2; 1.49(1), Cα_2–C3″; 1.35(1), C1″–C2″; 1.39(1), C2″–C3″; 1.43(1), C3″–C3a″; 1.47(1), C3a″–C4″; 1.38(1), C4″–C5″; 1.41(1), C5″–C6″; 1.39(1), C6″–C7″; 1.36(1), C7″–C8″; 1.36(1), C8″–C8a″; 1.42(1), C8a″–C1″; 1.43(1) and C8a″–C3a″; 1.45(1). The selected bond distances (Å) of **6** are as follows: C1–C2; 1.407(4), C2–C3; 1.376(5), C3–C4; 1.379(5), C4–C5; 1.380(5), C5–C6; 1.384(4), C6–C1; 1.393(4), C1–Cα; 1.461(4), Cα–C3′; 1.361(4), C1′–C2′; 1.345(4), C2′–C3′; 1.449(3), C3′–C3a′; 1.481(3), C3a′–C4′; 1.398(3), C4′–C5′; 1.408(4), C5′–C6′; 1.375(4), C6′–C7′; 1.393(4), C7′–C8′; 1.394(4), C8′–C8a′; 1.389(3), C8a′–C1′; 1.459(3) and C8a′–C3a′; 1.450(3).

with the bond distance observed for that of **6** (1.40 Å),[8] the bond distances of the 3-guaiazulenylmethylium substituent which combined with the C1 carbon atom were slightly different in comparison with those of the other 3-guaiazulenylmethylium substituent which combined with the C2 carbon atom, as shown in Figure 1 caption; and (6) the two counter anions (PF_6^-) were located near the seven-membered rings of the two 3-guaiazulenylmethyl cations, respectively. Thus, from the results of the bond distances and the dihedral angles between the least-squares planes, the following point is noteworthy: the crystal structure of **2** was distorted owing to the influence of larger steric hindrance and repulsion between the two adjacent 3-guaiazulenylmethylium substituents and the benzene ring in comparison with the crystal structure of **6**,[8] and further, owing to the influence of electrostatic repulsion between the two adjacent carbocations.

In the previous paper,[1] we reported that the reduction of **2** with zinc powder in acetonitrile at 0°C under aerobic conditions rapidly afforded a unique rearrangement product, 6,11-dimethyl-12-(3-guaiazulenyl)-9-isopropylnaphtho[2,3-*a*]azulene (**7**) as a major product (11% isolated yield).[10] In addition to the reduction of **2** with zinc powder in acetonitrile, we studied the reduction of **2** with a large excess of $NaBH_4$ in a mixed solvent of acetonitrile and ethanol at 25°C with a view to a comparative study with that of **3**. The hydride-reduction of **2** was performed as follows: To a solution of $NaBH_4$ (40 mg, 1.06 mmol) in ethanol (5 mL) was added a solution of **2** (100 mg, 0.13 mmol) in acetonitrile (5 mL). The mixture was stirred at 25°C for 20 min and then evaporated in vacuo. The residue thus obtained was carefully separated by silica-gel column chromatography with hexane–ethyl acetate (95:5, vol/vol) as an eluant, providing a pure compound **9** (60 mg, 0.12 mmol, 92% yield), whose structure was established on the basis of the spectroscopic data [UV–vis, EI-MS (including exact MS) and NMR (700 MHz for ^1H and 176 MHz for ^{13}C) including 2D NMR (H–H COSY, HMQC = ^1H detected heteronuclear multiple quantum coherence and HMBC = ^1H detected heteronuclear multiple bond connectivity)]. Compound **9** was a blue paste [$R_f = 0.73$ on silica-gel TLC (benzene/AcOEt = 95/5, vol/vol)]. The UV–vis [λ_{max} (CH_3CN) nm (log ε)] spectrum appeared at 247 (4.44), 292 (4.57), 312sh (4.22), 356 (3.76), 373 (3.67), 614 (2.51) and 670sh (2.40). The characteristic absorption bands for guaiazulene were observed and the visible absorption maximum appeared at λ_{max} 614 nm. The EI-MS (70 eV) spectrum showed the molecular ion peak at m/z 498 (M^+, 100%) and the following nine fragment ion peaks: m/z 483 ([M–Me]$^+$, 20), 455 ([M–*i*-Pr]$^+$, 20), 300 ([M–**1**]$^+$, 32), 285 ([M–**1**–Me]$^+$, 64), 257 ([M–**1**–*i*-Pr]$^+$, 59), 242 ([M–**1**–*i*-Pr–Me]$^+$, 38), 228 ([M–**1**–*i*-Pr–Me–CH_2]$^+$, 19), 198 (**1**$^+$, 29) and 183 ([**1**–Me]$^+$, 15). The molecular formula $C_{38}H_{42}$ for **9** was determined by the exact EI-MS (70 eV) spectrum (Found: m/z 498.3238. Calcd for $C_{38}H_{42}$: M^+, m/z 498.3287.). The ^1H NMR (C_6D_6) spectrum showed signals for the 3-guaiazulenyl group at δ 1.177, 1.183 (3H each, d, $J = 6.8$ Hz, (CH_3)$_2$CH-7″), 2.47 (3H, s, Me-1″), 2.72 (3H, s, Me-4″), 2.75 (1H, sept, $J = 6.8$ Hz, Me_2CH-7″), 6.68 (1H, d, $J = 10.4$ Hz, H-5″), 7.07 (1H, dd, $J = 10.4$, 2.5 Hz, H-6″), 7.27 (1H, s, H-2″), 8.02 (1H, d, $J = 2.5$ Hz, H-8″), signals for the indane unit at δ 3.35, 3.65 (1H each, d, $J = 17.0$ Hz, CH_2-3), 6.044 (1H, s, H-1), 7.03 (1H, d, $J = 7.6$ Hz, H-4), 7.11 (1H, dd, $J = 7.6$, 7.4 Hz, H-5), 7.19 (1H, dd, $J = 7.6$, 7.4 Hz, H-6), 7.23 (1H, d, $J = 7.6$ Hz, H-7), and further, signals for the 1*H*,7*H*-3,8-dimethyl-5-isopropylazulene unit at δ 0.98, 0.99 (3H each, d, $J = 6.8$ Hz, (CH_3)$_2$CH-5′), 1.47 (3H, d, $J = 1.2$ Hz, Me-3′), 1.86 (3H, s, Me-8′), 2.27 (1H, dd, $J = 12.5$, 6.4 Hz, H(a)-7′), 2.33 (1H, sept, $J = 6.8$ Hz, Me_2CH-5′), 2.51 (1H, dd, $J = 12.5$, 7.6 Hz, H(e)-7′), 5.09 (1H, dd, $J = 7.6$, 6.4 Hz, H-6′), 5.65 (1H, q, $J = 1.2$ Hz, H-2′), 6.040 (1H, s, H-4′). The ^{13}C NMR (C_6D_6) spectrum exhibited the following 38 carbon signals: δ 149.9 (C-3a), 149.7 (C-3a′), 145.1 (C-4″), 144.9 (C-5′), 144.2 (C-8a′), 142.8 (C-7a), 141.0 (C-2″), 139.7 (C-2′), 139.6 (C-8a″), 139.2 (C-7″), 138.6 (C-3′), 133.6 (C-6″), 133.5 (C-3a″), 133.0 (C-8″), 129.1 (C-3″), 127.2 (C-5), 127.0 (C-6), 126.8 (C-5″), 126.3 (C-4), 125.8 (C-8′), 124.5 (C-7), 124.2 (C-1″), 118.6 (C-4′), 111.0 (C-6′), 62.8 (2-C-1′), 54.2 (C-1), 43.4 (C-3), 37.8 (Me_2**C**H-7″), 36.3 (C-7′), 34.3 (Me_2**C**H-5′), 27.9 (Me-4″), 24.62 and 24.59 ((CH_3)$_2$CH-7″), 23.3 and 23.2 ((CH_3)$_2$CH-5′), 22.5 (Me-8′), 13.2 (Me-1″) and 12.7 (Me-3′). The detailed analyses of these spectroscopic data for **9** led to the structure, spiro[1-(3-guaiazulenyl)indane-2,1′-1′*H*,7′*H*-3′,8′-dimethyl-5′-isopropylazulene]. Although **9** possesses two asymmetric carbons at the C-1 and 2-C-1′ positions, this compound is suggested to be a chromatographically inseparable mixture of two diastereoisomers along with two enantiomeric forms, because the NMR signals based on the methyl protons and carbons of the C-5′- and C-7″-isopropyl groups divided into two signals (a ratio of almost 1:1), respectively. A reaction pathway for the formation of **9** can be inferred to be: (1) this hydride-reduction of **2** quantitatively gives the intermediate **8**, in which a hydride ion rapidly attached to the C-5 position of a 3-guaiazulenylmethylium substituent of **2**; and (2) **8** yielded is rapidly converted into the *intra*-molecular cycloaddition compound **9**. On the other hand, the reduction of **3** with $NaBH_4$ under completely the same experimental procedure as **2** afforded 1,4-bis(3-guaiazulenylmethyl)benzene (**10**)[11] in 80% isolated yield. Thus, an apparent difference between the reductions of the isomers **2** and **3** with $NaBH_4$ was observed. This difference can be inferred to arise as follows: although the positive charges of **3** are mainly localized at the C-α_1 and C-α_2 carbon atoms of the two 3-guaiazulenylmethylium substituents which combined with the C-1 and C-4 positions of the benzene ring, the positive charges of **2** are mainly localized at the C-5 carbon atom of a 3-guaiazulenylmethylium substituent and the C-α carbon atom of the other 3-guaiazulenylmethylium substituent owing to the influence of electrostatic repulsion between the two adjacent carbocations.



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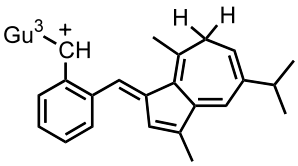

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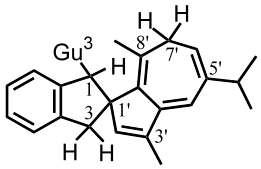

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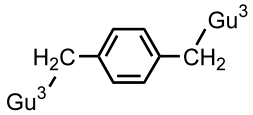

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Gu3: 3-guaiazulenyl group

Acknowledgements

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3. Takekuma, S.; Tanizawa, M.; Sasaki, M.; Matsumoto, T.; Takekuma, H. *Tetrahedron Lett*. **2002**, *43*, 2073–2078. Crystallographic data of compound **4** have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number CCDC 184618.
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5. Compound **2** was prepared by the following procedure: To a solution of guaiazulene (**1**) (30 mg, 0.15 mmol) in acetonitrile (0.2 mL) was added a solution of phthalaldehyde (10 mg, 0.07 mmol) in diethyl ether (1.0 mL) and then the mixture was stirred at 25°C under aerobic conditions. Addition of hexafluorophosphoric acid (60% aqueous solution, 0.27 mL) to the mixture led to a precipitation of a reddish-orange solid, which was centrifuged at 2 krpm for 1 min. The crude product thus obtained was carefully washed with diethyl ether and dried well in a vacuum desiccator to provide pure **2** as a reddish-orange powder (54 mg, 68.6 μmol, 98% yield). The powdered sample **2** was recrystallized from acetonitrile–diethyl ether (1:5, vol/vol) to provide stable single crystals (dark red prisms) suitable for X-ray crystallographic analysis. Compound **2**: The 500 MHz ^{1}H NMR (CD_3CN) spectrum was assigned as follows using the 2D NMR (H–H COSY) technique and the computer-assisted simulation analysis using the software, gNMR, which was developed by Adept Scientific plc: δ 1.43 (12H, d, $J=6.9$ Hz, $(CH_3)_2$CH-7′,7″), 2.40 (6H, brd d, $J=0.9$ Hz, Me-1′,1″), 3.22 (6H, s, Me-4′,4″), 3.49 (2H, sept, $J=6.9$ Hz, Me_2CH-7′,7″), 7.65 (2H, brd s, H-2′,2″), 7.79 (4H, s, H-3,4,5,6), 8.43 (2H, dd, $J=11.2$, 2.0 Hz, H-6′,6″), 8.52 (2H, d, $J=11.2$ Hz, H-5′,5″), 8.53 (2H, d, $J=2.0$ Hz, H-8′,8″) and 8.77 (2H, brd s, HC^+-α_1,α_2); The 125 MHz ^{13}C NMR (CD_3CN) spectrum was assigned as follows using the 2D NMR (HMQC and HMBC) techniques: δ 173.7 (C-7′,7″), 162.8 (C-8a′,8a″), 158.7 (C-4′,4″), 153.2 (C-3a′,3a″), 151.9 (C-5′,5″), 147.5 (HC^+-α_1,α_2), 147.2 (C-1′,1″), 145.7 (C-6′,6″), 143.2 (C-3′,3″), 141.3 (C-2′,2″), 140.2 (C-8′,8″), 137.9 (C-1,2), 134.1 (C-3,6), 132.3 (C-4,5), 40.5 (Me_2CH-7′,7″), 29.6 (Me-4′,4″), 23.7 ($(CH_3)_2CH$-7′,7″) and 13.8 (Me-1′,1″).
6. Compound **6** was prepared by the following procedure: To a solution of guaiazulene (**1**) (100 mg, 0.50 mmol) in methanol (1.5 mL) as added a solution of benzaldehyde (80 μL, 0.77 mmol) in methanol (0.5 mL) containing hexafluorophosphoric acid (60% aqueous solution, 0.2 mL). The mixture was stirred at 25°C for 1.5 h under aerobic conditions, giving a precipitation of a reddish-orange solid of **6**, which was centrifuged at 2.5 krpm for 1 min. The crude product thus obtained was carefully washed with diethyl ether, and was recrystallized from acetonitrile–diethyl ether (1:4, vol/vol) (several times) to provide stable single crystals (208 mg, 0.48 mmol, 96% yield) suitable for X-ray crystallographic analysis.
7. A total of 4447 reflections with $2\theta_{max}=55.0°$ were collected on a Rigaku AFC-5R automated four-circle diffractometer with graphite–monochromated Mo-Kα radiation ($\lambda=0.71069$ Å, rotating anode: 50 kV, 180 mA) at 296 K. The structure was solved by direct methods (SIR-97) and expanded using Fourier techniques (DIRDIF-94). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on F^2. All calculations were performed using the teXsan crystallographic software package. The deposition number is CCDC: 191407. Crystallographic data for **2**: $C_{38}H_{40}F_{12}P_2$ (FW = 786.66), dark red prism (crystal size, 0.20×0.20×0.30 mm), monoclinic, *Cc* (#9), $a=8.899(4)$, $b=17.077(5)$, $c=24.842(4)$ Å, $\beta=91.17(3)°$, $V=3774(2)$ Å^3, $Z=4$, $D_{calcd}=1.384$ g/cm^3, μ(Mo-Kα) = 2.01 cm^{-1}, scan width = (0.79+0.30 tan θ)°, scan mode = ω, scan rate = 8.0°/min, measured reflections = 4447, observed reflections = 4021, no. of parameters = 470, $R_1=0.074$, $wR_2=0.217$. Goodness of Fit indicator = 1.58.
8. A total 4869 reflections with $2\theta_{max}=55.1°$ were collected on a Rigaku AFC-5R automated four-circle diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda=0.71069$ Å, rotating anode: 50 kV, 180 mA) at 296 K. The structure was solved by direct methods (SIR-97) and expanded using Fourier techniques (DIRDIF-94). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on F^2. All calculations were performed using the teXsan crystallographic software package. The deposition number is CCDC: 192216. Crystallographic data for **6**: $C_{22}H_{23}F_6P$

(FW = 432.39), reddish-orange block (crystal size, 0.60× 0.60×0.50 mm), triclinic, *P*-1 (#2), $a = 10.217(1)$, $b = 13.980(2)$, $c = 7.865(1)$ Å, $\alpha = 93.56(1)$, $\beta = 110.422(10)$, $\gamma = 72.22(1)°$, $V = 1001.3(2)$ Å^3, $Z = 2$, $D_{calcd} = 1.434$ g/cm^3, μ(Mo-Kα) = 1.97 cm^{-1}, scan width = (1.31+0.30 tan θ)°, scan mode = ω–2θ, scan rate = 16.0°/min, measured reflections = 4869, observed reflections = 4607, no. of parameters = 262, $R_1 = 0.071$, $wR_2 = 0.243$. Goodness of Fit indicator = 2.21.

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10. Recently the isolated yield of compound **7** has increased to 30% by careful chromatographic purification.
11. Compound **10**: $R_f = 0.67$ on silica-gel TLC (AcOEt/hexane = 1/1, vol/vol); blue prisms (from CH_2Cl_2/hexane = 1/5, vol/vol), mp 202°C; found: C, 91.17; H, 8.37%. Calcd for $C_{38}H_{42}$: C, 91.51; H, 8.49%.; exact EI-MS (70 eV), found: *m*/*z* 498.3320; calcd for $C_{38}H_{42}$: M^+, *m*/*z* 498.3286; UV–vis λ_{max} (CH_2Cl_2) nm (log ε), 247 (4.72), 294 (4.99), 354 (4.13), 371 (4.06) and 624 (3.00); 500 MHz ^{1}H NMR (CD_2Cl_2), δ 1.35 (12H, d, $J = 6.9$ Hz, ($C\mathbf{H}_3$)$_2$CH-7′,7″), 2.60 (6H, s, Me-1′,1″), 2.84 (6H, s, Me-4′,4″), 3.03 (2H, sept, $J = 6.9$ Hz, $Me_2C\mathbf{H}$-7′,7″), 4.56 (4H, s, H_2C-1,4), 6.80 (2H, d, $J = 10.6$ Hz, H-5′,5″), 6.92 (4H, s, H-2,3,5,6), 7.26 (2H, dd, $J = 10.6$, 2.0 Hz, H-6′,6″), 7.38 (2H, s, H-2′,2″) and 8.09 (2H, d, $J = 2.0$ Hz, H-8′,8″); 125 MHz ^{13}C NMR (CD_2Cl_2), δ 145.4 (C-4′,4″), 141.1 (C-2′,2″), 140.7 (C-1,4), 138.9 (C-7′,7″), 137.9 (C-8a′,8a″), 134.7 (C-6′,6″), 133.3 (C-8′,8″), 133.0 (C-3a′,3a″), 128.4 (C-2,3,5,6), 126.1 (C-5′,5″), 126.0 (C-3′,3″), 124.2 (C-1′,1″), 37.7 ($Me_2\mathbf{C}$H-7′,7″), 36.7 (H_2C-1,4), 26.5 (Me-4′,4″), 24.4 (($\mathbf{C}H_3$)$_2$CH-7′,7″) and 12.6 (Me-1′,1″).