Synthesis of dinaphtho[2,1-*d*:1',2'-*g*][1,3,2]dioxaphosphocin 8-sulfides

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In an efficient two step synthesis of substituted 8-aryloxy/arylthio-16*H*-dinaphtho[2,1-*d*:1',2'-*g*][1,3,2] dioxaphosphocin 8-sulfides, dimethylaminopyridine (DMAP) catalyses the preparation of the intermediate monochloride **3** from bis-(2-hydroxy-1-naphthyl)methane (**1**) and thiophosphoryl chloride. Displacement of the chlorine in **3** with substituted sodium phenoxides or thiophenoxides proceeds nearly quantitatively in toluene-tetrahydrofuran at room temperature.

Keywords: phosphorus heterocycles, nucleophilic substitution at P, fused naphthalenes, fused 1,3,2-dioxaphosphocins

Dinaphthodioxaphosphocin 8-oxides/sulfides are the most important class of organophosphorus compounds with many applications: from organic synthesis as reagents, to medicine as drugs and in agriculture as pesticides.[1-5] Many of their derivatives are good analgesics, anti-inflammatories, germicides, antibacterial and antifungal agents.[3-5] Judging from the published research results, there has been an increasing interest in the chemistry of dinaphtho-dioxaphosphocins during the last decade.[6,7] Among them, aryl substituted dinaphthodioxaphosphocins have been extensively investigated and a significant number of procedures for their preparations have been reported.[7] However, only a few methods are reported for the synthesis of dinaphtho-dioxaphosphocin 8-sulfides, and in most cases they were obtained as mixture of compounds with very low yields even under optimum conditions.

A search for a versatile, straightforward and relatively inexpensive procedure for the synthesis of aryl substituted dinaphthodioxaphosphocins has resulted in the development of an efficient procedure for the preparation of the title compounds (**4**). Condensation of bis-(2-hydroxy-1-naphthyl) methane (**1**) and thiophosphoryl chloride (**2**) in equimolar quantities in the presence of triethylamine as a base and DMAP as a catalyst in anhydrous toluene produced 8-chloro-16*H*-dinaphtho[2, 1-*d*:1',2'-*g*][1,3,2]dioxaphosphocin 8-sulfide (**3**) in almost quantitative yield. Subsequently, the monochloride **3** is reacted with sodium phenoxides/ thiophenoxides to obtain the title compounds (**4**) (Scheme 1). Phenols/thiophenols are converted to their respective sodium salts by vigorous stirring with sodium hydride in dry tetrahydrofuran at room temperature.

The advantages of this method over the previously reported procedures are (i) high yields (90–98%), (ii) simple experimental set-up and work-up conditions (iii) low cost reagents and (iv) no direct handling of corrosive phosphorodichloridates and liberated hydrogen chloride.

All compounds **4** exhibited characteristic IR absorptions[8,9] for P=S, P–O–C and P–S–$C_{aromatic}$ groups. In the ^{1}H NMR spectra, dinaphthodioxaphosphocin moieties showed complex multiplets in the region δ 7.32–8.45 for 12 protons. The resonance signal for the bridged methylene protons in all the compounds appeared as two distinct doublets at δ 4.61–4.79 and 5.15–5.24 ($^2J_{H\text{-}H}$ = 15.6–16.4 Hz) indicating their non-equivalence[7] and mutual coupling. Even though coupling between one of the methylene protons and phosphorus, $^5J_{H\text{-}P}$ = 2.9 Hz was reported for dibenzo[*d,g*][1,3,2]dioaxaphos-phocins (A) due to interaction between the electron pair on phosphorus and the axial proton of the bridge CH_2 no such coupling was observed in the H-1 spectra of compounds **4** since the bulky naphthyl groups may force the CH_2 and P=S groups to be far removed from each other to prevent non-bonded interactions (B and C).[7]

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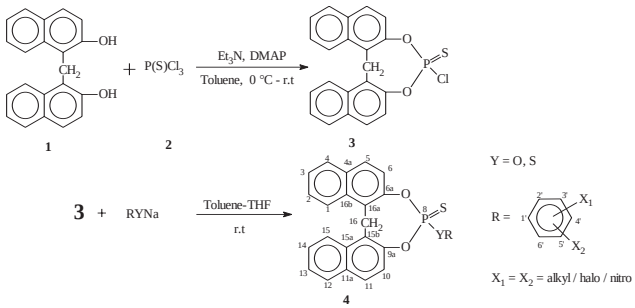


Compd. **4**	YR	Compd. **4**	YR
a	OC_6H_4-CH_3(2')	**g**	OC_6H_4-F(2')
b	OC_6H_4-CH_3(4')	**h**	OC_6H_4-OCH_3(4')
c	OC_6H_4-Cl(2')	**i**	SC_6H_4-CH_3(4')
d	OC_6H_3-Cl_2(2', 4')	**j**	SC_6H_4-Cl(4')
e	OC_6H_4-NO_2(4')	**k**	SC_6H_4-Br(3')
f	OC_6H_4-$C(CH_3)_3$(4')		

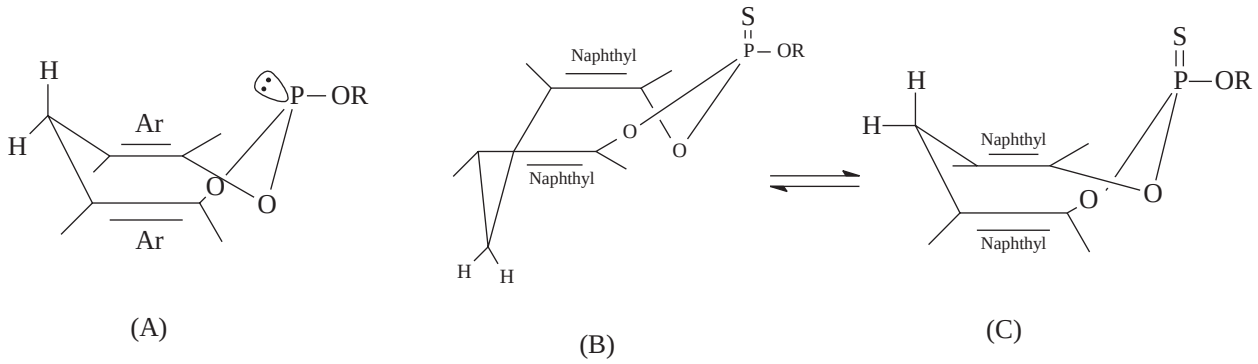
Scheme 1

Similarly, the aromatic and aliphatic methyl protons of 8-substituted moieties exhibited signals in the region δ 7.05–7.35 and δ 1.24–2.45, respectively. The ^{13}C NMR chemical shifts were interpreted based on comparison with carbon chemical shifts of **1** and related system.[6,7,10] The dinaphthodioxaphosphocin system in **4** showed 10 signals from the naphthalene carbon atoms, as expected on account of the symmetry of the system.[7] All these data are provided in experimental section. The ^{31}P NMR signals are observed in the range of –70.5 to –60.7 ppm.[6,7a,b,11] for dinaphtho-dioxaphosphocin 8-sulfides (**4a–k**).

In summary, we have developed a simple and efficient method for the synthesis of dinaphthodioxaphosphocin 8-sulfide derivatives and this method is successful even with phenols substituted with bulky groups. These type of phosphorus heterocycles has potential value as antibacterial and antifungal agents and lubricant additives.

Experimental

All reactions were carried out under anhydrous conditions in nitrogen atmosphere. Melting points were determined with open capillary tubes using a Mel-Temp apparatus. IR spectra (ν_{max} cm^{-1}) were recorded on a SHIMADZU-435/Perkin Elmer 1000 FT IR. NMR spectra were taken on a BRUKER AC 300 spectrometer in $CDCl_3$, operating at 300 MHz for ^{1}H, 75.45 MHz for ^{13}C, and 121.7 MHz for ^{31}P NMR. TMS was used as an internal standard for ^{1}H and ^{13}C and 85% H_3PO_4 was used as an external standard for ^{31}P NMR spectra. The nuclei that are deshielded relative to their respective standards are assigned a positive chemical shift. Coupling constants, *J* are given in Hz. Elemental analyses were performed at the Central Drug Research Institute (CDRI), Lucknow, India. Bis-(2-hydroxy-1-naphthyl)methane (**1**) was prepared according to a reported procedure.[12]



Scheme 2

The purity of materials was assessed by elemental microanalysis, ^{1}H, ^{13}C and ^{31}P NMR and IR spectroscopy. Yields reported correspond to pure products.

8-(4′-Methylphenoxy)-16H-dinaphtho[2,1-d:1′,2′-g][1,3,2] dioxaphosphocin 8-sulfide (**4b**) (*typical procedure for compounds* **4**): Thiophosphoryl chloride (**2**, 1.69 g, 0.01 mol) in dry toluene (20 ml) was added dropwise to a cold (0 °C) and stirred solution of bis-(2-hydroxy-1-naphthyl)methane (**1**, 3.0 g, 0.01 mol) and triethylamine (2.02 g, 0.02 mol) in dry toluene (40 ml) in the presence of a catalytic amount of dimethylaminopyridine (DMAP) (0.03 gm, 0.25 mmol). After completion of the addition, the reaction mixture was stirred at room temperature for 1 hour. Progress of the reaction was monitored by thin layer chromatography. When TLC indicated completion of the reaction with the formation of the monochloride 8-chloro-16*H*-dinaphtho[2,1-*d*:1',2'-*g*][1,3,2]dioxa-phosphocin 8-sulfide (**3**), the reaction mixture was filtered to separate triethylamine hydrochloride and the filtrate was cooled to 0 °C. A solution of the sodium salt of 4-methylphenol, prepared by vigorous stirring of 4-methylphenol (1.08 g, 0.01 mol) and sodium hydride in tetrahydrofuran at room temperature was added. After an additional 1 h stirring at room temperature, when completion of the reaction was indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was washed with water followed by chilled isopropanol and recrystallized from isopropanol to obtain pure compound **4b**.

8-(2′-Methylphenoxy)-16H-dinaphtho(2,1-d:1′,2′-g][1,3,2] dioxaphosphocin 8-sulfide (**4a**): Yield 92%, m.p. 142–144 °C (from isopropanol). IR (KBr): ν_{max} 742 (P=S), 908, 1216 cm^{-1} (P–O–$C_{aromatic}$). ^{1}H NMR: δ_H 7.49–8.23 (m, 12H, Ar-H), 7.18–7.35 (m, 4H, OAr-H), 5.24 (d, *J* = 16.1 Hz, 16 Ha), 4.74 (d, *J* = 16.4 Hz, 16 Hb), 2.40 (s, 3H, 2'-CH_3). ^{13}C NMR: δ_C 127.3 (s, 2C, C-1, 15), 125.8 (s, 2C, C-2, 14), 125.4 (s, 2C, C-3, 13), 129.4 (s, 2C, C-4, 12), 129.1 (s, 2C, C-5, 11), 120.4 (d, 2C, *J* = 4.8 Hz, C-6, 10), 148.6 (d, 2C, *J* = 13.7 Hz, C-6a, 9a), 124.4 (d, 2C, *J* = 6.6 Hz, C-15b, 16a), 132.2 (s, 2C, C-15a, 16b), 132.6 (s, 2C, C-4a, 11a), 148.7 (s, 1C, C-1'), 129.4 (s, 1C, C-2'), 131.6 (s, 1C, C-3'), 125.4 (s, 1C, C-4'), 127.6 (s, 1C, C-5'), 123.4 (s, 1C, C-6'), 24.3 (s, 1C, C-16), 17.2 (s, 1C, 2'-$\underline{C}H_3$). ^{31}P NMR (121.7 MHz, $CDCl_3$/85% H_3PO_4): δ_P 61.5 ppm. Anal. Calcd for $C_{28}H_{21}O_3PS$ (478.51): C, 71.78; H, 4.52. Found: C, 71.53, H, 4.42 %.

8-(4′-Methylphenoxy)-16H-dinaphtho(2,1-d:1′,2′-g][1,3,2] dioxaphosphocin 8-sulfide (**4b**): yield 93%, m.p. 138–140 °C (from isopropanol). IR (KBr): ν_{max} 740 (P=S), 913, 1211 cm^{-1} (P–O–$C_{aromatic}$). ^{1}H NMR: δ_H 7.32–8.28 (m, 12H, Ar-H), 7.21–7.25 (m, 4H -OAr-H), 5.24 (d, *J* = 16.2 Hz,16 Ha), 4.73 (d, *J* = 16.2 Hz, 16 Hb), 2.37 (s, 3H, 4'-CH_3). ^{13}C NMR: δ_C 128.9 (s, 2C, C-1, 15), 125.4 (s, 2C, C-2, 14), 124.3 (s, 2C, C-3, 13), 129.3 (s, 2C, C-4, 12), 129.0 (s, 2C, C-5, 11), 120.3 (d, 2C, *J* = 4.6 Hz, C-6, 10), 148.5 (d, 2C, *J* = 12.2 Hz, C-6a, 9a), 123.3 (s, 2C, C-15b, 16a), 132.2 (s, 2C, C-15a, 16b), 132.4 (s, 2C, C-4a, 11a), 148.4 (s, 1C, C-1'), 120.8 (s, 2C, C-2', 6'), 130.2 (s, 2C, C-3', 5'), 135.4 (s, 1C, C-4'), 24.2 (s, 1C, C-16), 20.8 (s, 1C, 4'-$\underline{C}H_3$). ^{31}P NMR: δ_P 70.5 ppm. Anal. Calcd for $C_{28}H_{21}O_3PS$ (468.51): C, 71.78; H, 4.52. Found: C, 71.48; H, 4.39 %.

8-(2′-Chlorophenoxy)-16H-dinaphtho(2,1-d:1′,2′-g][1,3,2] dioxaphosphocin 8-sulfide (**4c**): yield: 89%, m.p. 152–154 °C (from isopropanol). IR (KBr): ν_{max} 739 (P=S), 918, 1251 cm^{-1} (P–O–$C_{aromatic}$). ^{1}H NMR: δ 7.47–8.26 (m, 12H, Ar-H), 7.23–7.33 (m, 4H, OAr-H), 5.22 (d, *J* = 16.2 Hz, 16 Ha), 4.65 (d, *J* = 16.2 Hz, 16 Hb). ^{13}C NMR: δ_C 125.8 (s, 2C, C-1, 15), 124.4 (s, 2C, C-2, 14), 124.3 (s, 2C, C-3, 13), 129.1 (s, 2C, C-4, 12), 127.6 (s, 2C, C-5, 11), 120.4 (s, 2C, C-6, 10), 148.5 (d, 2C, *J* = 13.4 Hz, C-6a, 9a), 123.4 (s, 2C, C-15b, 16a), 132.2 (d, 2C, *J* = 1.9 Hz, C-15a, 16b), 132.5 (s, 2C, C-4a, 11a), 148.7 (s, 1C, C-1'), 129.4 (d, 1C, *J* = 1.2 Hz, C-2'), 127.5 (s, 1C, C-3'), 124.4 (s, 1C, C-4'), 124.3 (s, 1C, C-5'), 120.5 (s, 1C, C-6'), 24.3 (s, 1C, C-16'). ^{31}P NMR: δ_P 61.5 ppm. Anal. Calcd. for $C_{27}H_{18}ClO_3PS$ (488.93): C, 66.33; H, 3.71. Found: C, 65.98; H, 3.63 %.

8-(2′,4′-Dichlorophenoxy)-16H-dinaphtho(2,1-d:1′,2′-g] [1,3,2] dioxaphosphocin 8-sulfide (**4d**): yield 93%, m.p. 180–182 °C (from isopropanol). IR (KBr): ν_{max} 740 (P=S), 914, 1188 cm^{-1} (P–O–$C_{aromatic}$). ^{1}H NMR: δ_H 7.47–8.26 (m, 12H, Ar-H), 7.23–7.33 (m, 3H, OAr-H), 5.21 (d, *J* = 16.2 Hz, 16 Ha), 4.63 (d, *J* = 16.2 Hz, 16 Hb). ^{13}C NMR: δ_C 125.8 (s, 2C, C-1, 15), 124.4 (s, 2C, C-2, 14), 123.4 (s, 2C, C-3, 13), 129.3 (d, 2C, *J* = 1.2 Hz, C-4, 12), 129.1 (s, 2C, C-5, 11), 120.4 (d, 2C, *J* = 4.9 Hz, C-6, 10), 148.6 (d, 2C, *J* = 13.3 Hz, C-6a, 9a), 132.5 (s, 2C, C-15a, 16b), 132.2 (d, 1C, *J* = 1.9 Hz, C-2'), 124.3 (s, 1C, C-3'), 129.4 (s, 1C, C-4'), 127.5 (s, 1C, C-5'), 24.3 (s, 1C, C-16). ^{31}P NMR: δ_P 61.5 ppm. Anal. Calcd for $C_{27}H_{17}Cl_2O_3PS$ (523.42): C, 61.96; H, 3.27. Found: C, 61.65; H, 3.19%.

8-(4′-Nitrophenoxy)-16H-dinaphtho(2,1-d:1′,2′-g][1,3,2] dioxaphosphocin 8-sulfide (**4e**): yield 88%, m.p. 188–190 °C (from isopropanol-dichloromethane). IR (KBr): ν_{max} 743 (P=S), 906, 1234 cm^{-1} (P–O–$C_{aromatic}$). ^{1}H NMR: δ_H 7.43–8.27 (m, 12H, Ar-H), 7.26–7.33 (m, 4H, OAr-H), 5.22 (d, *J* = 16.1 Hz, 16 Ha), 4.64 (d, *J* = 16.0 Hz, 16 Hb). ^{13}C NMR: δ_C 126.1 (s, 2C, C-1, 15), 125.9 (s, 2C, C-2, 14), 125.4 (s, 2C, C-3, 13), 129.2 (s, 2C, C-4, 12), 127.7 (s, 2C, C-5, 11), 120.5 (d, 2C, *J* = 4.6 Hz, C-6, 10), 148.7 (d, 2C, *J* = 13.8 Hz, C-6a, 9a), 121.4 (d, 2C, *J* = 4.5 Hz, C-15b, 16a), 132.3 (s, 2C, C-15a, 16b), 132.6 (s, 2C, C-4a, 11a), 124.5 (d, 2C, *J* = 7.6 Hz, C-2', 6'), 123.5 (s, 2C, C-3', 5'), 143.9 (s, 1C, C-4'), 24.4 (s, 1C, C-16). ^{31}P NMR: δ_P 68.6 ppm. Anal. Calcd for $C_{27}H_{18}NO_5PS$ (499.48): C, 64.93; H, 3.63. Found: C, 65.03; H, 3.55 %.

8-(4′-t-Butylphenoxy)-16H-dinaphtho(2,1-d:1′,2′-g][1,3,2] dioxaphosphocin 8-sulfide (**4f**): yield 91%, m.p. 156–158 °C (from isopropanol). IR (KBr): ν_{max} 728 (P=S), 908, 1207 cm^{-1} (P–O–$C_{aromatic}$). ^{1}H NMR: δ_H 7.41–8.19 (m, 12H, Ar-H), 7.17–7.27 (m, 4H, OAr-H), 5.15 (d, *J* = 16.0 Hz, 16 Ha), 4.61 (d, *J* = 16.2 Hz, 16 Hb), 1.24 (s, 9H, $C(CH_3)_3$). ^{13}C NMR: δ_C 127.1 (s, 2C, C-1, 15), 126.2 (s, 2C, C-2, 14), 121.0 (s, 2C, C-3, 13), 129.8 (d, 2C, *J* = 1.2 Hz, C-4, 12), 129.6 (s, 2C, C-5, 11), 120.9 (d, 2C, *J* = 3.6 Hz, C-6, 10), 149.1 (d, 2C, *J* = 13.7 Hz, C-6a, 9a), 132.7 (d, 2C, *J* = 2.0 Hz, C-15a, 16b), 133.0 (s, 2C, C-4a, 11a), 148.8 (s, 1C, C-1'), 119 (d, 2C, *J* = 4.6 Hz, C-2', 6'), 127.0 (s, 2C, C-3', 5'), 143.0 (s, 1C, C-4'), 24.8 (s, 1C, C-16), 35.0 (s, 1C, C-4'-*t*-$\underline{C}(CH_3)_3$), 31.8 (s, 3C, C-4'-t-C($\underline{C}H_3)_3$). ^{31}P NMR: δ_P 66.1 ppm. Anal. Calcd for $C_{31}H_{27}O_3PS$ (510.59): C, 72.92; H, 5.33. Found: C, 73.05; H, 5.22 %.

8-(2′- Fluorophenoxy)-16H-dinaphtho(2,1-d:1′,2′-g][1,3,2]dioxa-phosphocin 8-sulfide (**4g**): yield 95%, m.p. 190–192 °C (isopropanol-dichloromethane). IR (KBr): ν_{max} 745 (P=S), 920, 1228 cm^{-1} (P–O–$C_{aromatic}$). ^{1}H NMR: δ_H 7.49–8.45 (m, 12H, Ar-H), 7.05–7.32 (m, 4H, OAr-H), 5.21 (d, *J* = 16.4 Hz, 16 Ha), 4.74 (d, *J* = 16.0 Hz, 16 Hb). ^{13}C NMR: δ 127.9 (s, 2C, C-1, 15), 127.6 (s, 2C, C-2, 14), 126.4 (s, 2C, C-3, 13), 129.1 (s, 2C, C-4, 12), 128.2 (s, 2C, C-5, 11), 120.4 (s, 2C, *J* = 4.8 Hz, C-6, 10), 148.6 (d, 2C, *J* = 13.4 Hz, C-6a, 9a), 123.5 (s, 2C, C-15b, 16a), 132.9 (s, 2C, C-15a, 16b), 136.1 (s, 2C, C-4a, 11a), 150.1 (s, 1C, C-1'), 129.4 (d, 1C, *J* = 1.5 Hz, C-2'), 125.8 (s, 1C, C-3'), 126.9 (s, 1C, C-4'), 124.4 (d, 1C, *J* = 4.6 Hz, C-6'), 24.3 (s, 1C, C-16). ^{31}P NMR: δ_P 63.4 ppm. Anal. Calcd for $C_{27}H_{18}FO_3PS$ (472.48): C, 68.46; H, 3.84. Found: C, 68.43; H, 3.75.

8-(4′-Methoxyphenoxy)-16H-dinaphtho(2,1-d:1′,2′-g][1,3,2] dioxaphosphocin 8-sulfide (**4h**): yield 96%, m.p. 210 °C (dec.). IR (KBr): ν_{max} 747 (P=S), 918, 1230 cm^{-1} (P–O–$C_{aromatic}$). ^{1}H NMR:

δ_H 7.39–8.22 (m, 12H, Ar-H), 7.12–7.25 (m, 4H, OAr-H), 5.15 (d, *J* = 16.0 Hz, 16 Ha), 4.72 (d, *J* = 16.1 Hz, 16 Hb), 3.69 (s, 3H, 4'-OCH_3). ^{13}C NMR: δ_C 127.9 (s, 2C, C-1, 15), 126.5 (s, 2C, C-2, 14), 124.7 (s, 2C, C-3, 13), 128.4 (s, 2C, C-4, 12), 128.1 (s, 2C, C-5, 11), 119.7 (d, 2C, *J* = 4.4 Hz, C-6, 10), 147.8 (d, 2C, *J* = 11.1 Hz, C-6a, 9a), 122.4 (d, 2C, *J* = 3.2 Hz, C-15b, 16a), 147.7 (s, 1C, C-1'), 121.0 (d, 2C, *J* = 4.6 Hz, C-2', 6'), 123.4 (s, 2C, C-3', 5'), 130.9 (s, 1C, C-4'), 23.3 (s, 1C, C-16), 54.5 (s, 1C, 4'-O<u>C</u>H_3). ^{31}P NMR: δ_P 66.0 ppm. Anal. Calcd for $C_{28}H_{21}O_4PS$ (484.51): C, 69.41; H, 4.37. Found: C, 69.33; H, 4.29 %.

8-(4′-Methylthiophenoxy)-16H-dinaphtho(2,1-d:1′,2′-g][1,3,2] dioxaphosphocin 8-sulfide (**4i**): yield 94%, m.p. 130–140 °C (isopropanol). IR (KBr): ν_{max} 752 (P=S), 584, 520 cm^{-1} (P–S–$C_{aromatic}$). ^{1}H NMR: δ_H 7.38–8.26 (m, 12H, Ar-H), 7.22–7.33 (m, 4H, OAr-H), 5.22 (d, *J* = 16.2 Hz, 16 Ha), 4.65 (d, *J* = 15.9 Hz, 16 Hb), 2.45 (s, 3H, 4'-CH_3). ^{13}C NMR: δ_C 126.7 (s, 2C, C-1, 15), 125.8 (s, 2C, C-2, 14), 129.1 (s, 2C, C-4, 12), 127.5 (s, 2C, C-5, 10), 120.4 (d, 2C, *J* = 4.9 Hz, C-6, 10), 148.6 (d, 2C, *J* = 13.5 Hz, C-6a, 9a), 120.6 (d, 2C, *J* = 5.1 Hz, C-15b, 16a), 132.2 (s, 2C, C-15a, 16b), 132.5 (s, 2C, C-4a, 11a), 131.0 (s, 1C, C-1'), 127 (d, 2C, J = 6.6 Hz, C-2', 6'), 123.4 (s, 2C, C-3', 5'), 129.4 (s, 1C, C-4'), 24.3 (s, 1C, C-16), 24.2 (s, 1C, 4'-<u>C</u>H_3). ^{31}P NMR: δ_P 60.5 ppm. Anal. Calcd for $C_{28}H_{21}O_2PS_2$ (484.58): C, 69.40; H, 4.37. Found: C, 69.22; H, 4.26%.

8-(4′-Chlorothiophenoxy)-16H-dinaphtho(2,1-d:1′,2′-g][1,3,2] dioxaphosphocin 8-sulfide (**4j**): Yield 91%, m.p. 142–143 °C (isopropanol-dichloromethane). IR (KBr): ν_{max} 754 (P=S), 582, 527cm^{-1} (P–S–$C_{aromatic}$). ^{1}H NMR: δ_H 7.47–8.25 (m, 12H, Ar-H), 7.23–7.32 (m, 4H, OAr-H), 5.21 (d, *J* = 16.1 Hz, 16 Ha), 4.64 (d, *J* = 15.6 Hz, 16 Hb). ^{13}C NMR: δ_C 126.1 (s, 2C, C-1, 15), 129.4 (s, 2C, C-4, 12), 127.9 (s, 2C, C-5, 11), 120.7 (d, 2C, *J* = 3.5 Hz, C-6, 10), 148.9 (d, 2C, *J* = 10.3 Hz, C-6a, 9a), 132.5 (s, 2C, C-15a, 16b), 132.8 (s, 2C, C-4a, 11a), 124.6 (d, 2C, *J* = 5.7 Hz, C-2', 6'), 123.7 (s, 2C, C-3', 5'), 129.7 (s, 1C, C-4'), 24.6 (s, 1C, C-16). ^{31}P NMR: δ_P 62.8 ppm. Anal. Calcd for $C_{27}H_{18}Cl_2O_2PS_2$ (504.99): C, 64.22; H, 3.59. Found: C, 64.03; H, 3.51 %.

8-(2′-Bromophenoxy)-16H-dinaphtho(2,1-d:1′,2′-g][1,3,2] dioxaphosphocin 8-sulfide (**4k**): yield 92%, m.p. 165–168 °C (isopropanol-dichloromethane). IR (KBr): ν_{max} 748 (P=S), 940, 1232 cm^{-1} (P–O–$C_{aromatic}$). ^{1}H NMR: δ_H 7.45–8.29 (m, 12H, Ar-H), 7.20–7.28 (m, 4H, OAr-H), 5.24 (d, *J* = 16.0 Hz, 16 Ha), 4.79 (d, *J* = 16.1 Hz, 16 Hb). ^{13}C NMR: δ_C 127.4 (s, 2C, C-1, 15), 125.5 (s, 2C, C-2, 14), 124.4 (s, 2C, C-3, 13), 129.2 (d, 2C, *J* = 4.5 Hz, C-4, 12), 127.6 (s, 2C, C-5, 11), 120.6 (d, 2C, *J* = 4.5 Hz, C-6, 10), 148.8 (d, 2C, *J* = 10.9 Hz, C-6a, 9a), 123.6 (s, 2C, C-15b, 16a), 132.1 (s, 2C, C-15a, 16b), 132.6 (s, 2C, C-4a, 11a), 149.7 (s, 1C, C-1'), 129.1 (s, 1C, C-3'), 123.5 (s, 1C, C-4'), 124.3 (d, 1C, *J* = 5.5 Hz, C-6'), 24.3 (s, 1C, C-16). ^{31}P NMR: δ_P 60.7 ppm. Anal. Calcd for $C_{27}H_{18}BrO_2PS_2$ (549.45): C, 59.02; H, 3.30. Found C, 58.93, H, 3.19%.

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References

1 A.D.F. Toy and E.N. Walsh, *Phosphorus Chemistry in Everyday Living;* 2nd edn., American Chemical Society: Washington, 1987.
2 J.I.G. Cadogan, *Organophosphorus Reagents in Organic Synthesis;* Academic Press: London, 1979.
3 M. Eto and R. Engel, *Handbook of Organophosphorus Chemistry;* Marcel Dekker, Inc., New York, 1992**.**
4 (a) K.A. O'Leary and J.W. Tracy, *Exp. Parasitol.* 1991**, 72,** 355; (b) J.D. Spivak and L.D. Steinhuebel, *J. Heterocycl. Chem.* 1984**, 21,** 1285.
5 (a) B. Iorga, F. Eymery and P. Savignac, *Synthesis* 1999, **207**; (b) S.C. Fields, *Tetrahedron* 1999**, 55**, 12 237; (c) A.P. Bouteille, L. Lamande, L. Lopez, L. Cazaux and J. Bellan, *Tetrahedron*, 1998**, 54**, 3817.
6 (a) B.S. Reddy, K. Anuradha, C.D. Reddy, N.J. Kumar, M. Krishnaiah and K.D. Berlin, *Heteroatom Chemistry* 1995**, 6**, 5, 485; (b) K.A. Kumar, C.S. Reddy and C.D. Reddy, *Ind. J. Chem.*, 2003, **42,** 2589.
7 (a) C.D. Reddy, R.S.N. Reddy, M.S. Reddy, M. Krishnaiah, K.D. Berlin and P. Sunthankar, *Phosphorus, Sulfur and Silicon* 1991**, 62**, 1.; (b) C.D. Reddy, R.S. Reddy, C.N. Raju, M. Elmasri, K.D. Berlin and S. Subramanian, *Magn. Reson. Chem.* 1991**, 29**, 1140; (c) C.D. Reddy, K.D. Berlin, R.S. Reddy, C.N. Raju, M. Elmasri and S. Subramanian, *Phosphorus, Sulfur and Silicon* 1993**, 81**, 61; (d) P.A. Odorisio, S.D. Pastor, J.D. Spivack, L. Steinhubel and R.K. Rodebaugh, *Phosphorus and Sulfur*, 1983, **15**, 9; (e) S. Mani Naidu, M. Krishnaiah and K. Sivakumar, *Acta Cryst*. 1996**, C52**, 1556.
8 (a) L.C. Thomas, *The Interpretation of the Infrared Spectra of Organophosphorus Compounds;* Heyden, London, 1974; (b) A.C. Chapman and R. Harper, *Chem. Ind.* (London), 1962**,** 985.
9 R.M. Silverstein and F.X. Webster, *Spectrometric Identification of Organic Compounds*, 6th edn., John Wiley, Sons, Inc.; New York, 1998.
10 G.W. Buchanan, D.A. Ross and J.B. Stothers, *J. Am. Chem. Soc.* 1966**, 88**, 4301; (b) D.M. Grant and B.V. Cheney, *J. Am. Chem. Soc*. 1967**, 89**, 5315.
11 D.G. Gorenstein, *Phosphorus-31 NMR, Principles and Applications;* Academic Press, Inc.: Florida, 1984**,** 12.
12 Y. Ogata and A. Kowasaki, *Tetrahedron* 1969**, 25**, 2589.