Synthesis of Dibromodibenzo[*d,g*][1,3,6,2]dioxathiaphosphocin 6-sulfides

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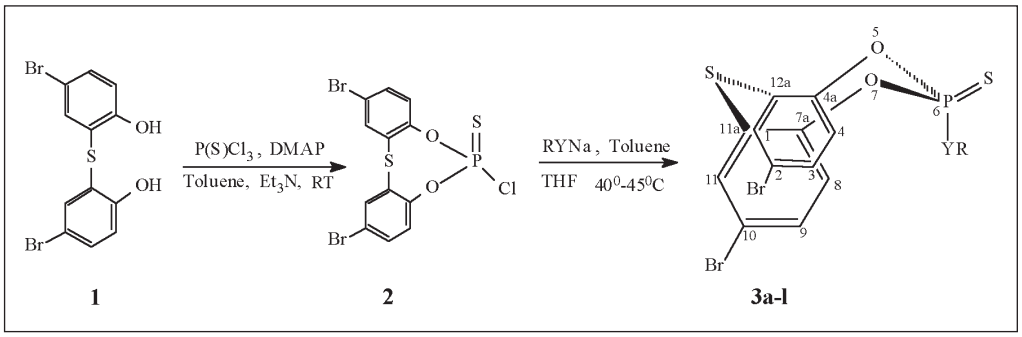

Synthesis of 6-subsituted-2,10-dibromodibenzo[*d,g*][1,3,6,2]dioxathiaphosphocin 6-sulfides (**3a-l**) has been accomplished in a two-step process. Reaction of 5,5'-dibromo-2,2'-dihydroxydiphenyl sulfide **1** and thiophosphoryl chloride in equimolar quantities in the presence of triethylamine as a base and DMAP as a catalyst in anhydrous toluene afforded the intermediate 6-chloro-2,10-dibromodibenzo[*d,g*][1,3,6,2]dioxathiaphosphocin 6-sulfide **2**. Subsequent reaction of the monochloride **2** with sodium phenoxides/ thiophenoxides afforded the title compounds. All the compounds showed moderate activity against bacteria and fungi.

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Introduction.

A large number of organophosphorus esters are potential pesticides some dibenzodioxaphosphocins and dioxathiaphosphocins are antioxidants [1-4] and superior ligands [5]. Synthesis of bulky phenolic phosphate esters was not successful through their phosphorodichloridates [6] due to their explosive nature, moisture and thermal sensitivity. An alternative approach involving a two-step process has been developed for their synthesis. Even though, aryl substituted dibenzo[*d,g*]dioxaphosphocins have been extensively investigated [7] only a few methods were reported for the synthesis of dibenzodioxaphosphocin 6-sulfides, and in most cases they were obtained as mixture of compounds with low yields even under optimum conditions.

Results and Discussion.

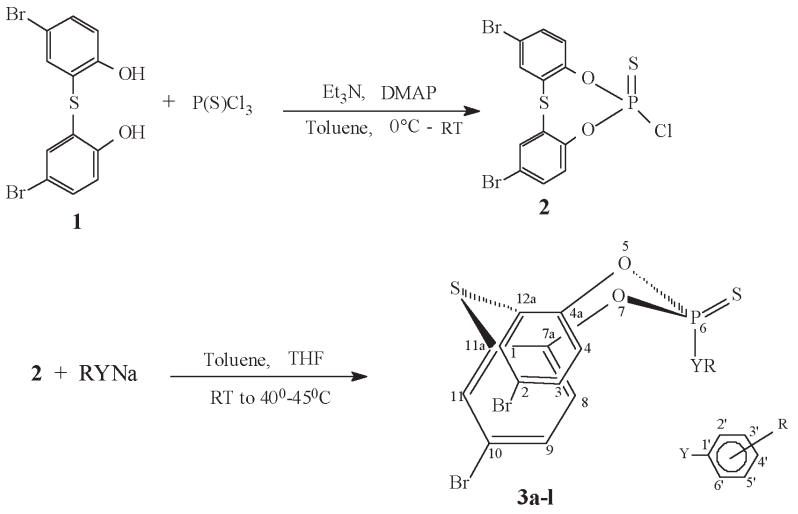
A search for a versatile straight forward and relatively inexpensive procedure for the synthesis of aryl substituted dibenzodioxaphosphocins have resulted in the development of an efficient procedure for the preparation of the title compounds. Compound **1** is converted to the corresponding dioxathiaphosphocin monochloride intermediate **2** by reacting with $PSCl_3$ in toluene in the presence of a base. Triethyl amine, dimethylaminopyridine (DMAP) and sodium hydride are found to be effective bases which drive this reaction to completion. In the second step, the monochloride **2** is reacted with sodium salts of phenols/thiophenols which are obtained by their vigorous stirring with sodium hydride in dry tetrahydrofuran at room temperature, to obtain the title compunds.

The advantages of this method are: (i) high yields (ii) simple experimental setup and work up (iii) low cost reagents and (iv) no direct handling of corrosive phosphorodichloridates and hydrogen chloride [8].

All compounds (**3a-l**) exhibited characteristic ir absorptions [9,10] for P=S, P-O-C and P-S-$C_{aromatic}$ groups. Complex multiplets for the aromatic protons of dibenzodioxathiaphosphocin and 6-aryloxy moieties are observed at δ 6.57-8.16 [11]. The dibenzodioxathiaphosphocin system in **3** showed six ^{13}C chemical shifts [12] for the twelve carbon atoms due to the symmetrical disposition of the two benzene rings on the central dioxathiaphosphocin ring. The carbon atoms of the exocyclic aryloxy function resonated in the expected regions [10]. The ^{31}P NMR signals are observed in the range of 50.17–52.12 ppm for dibenzodioxathiaphosphocin 6-sulfides (**3a-j**). Compounds **3k-l** showed the ^{31}P NMR signals in the downfield region at 86.28 and 84.20 ppm respectively due to the direct attachment of the thiophenoxy group with the pentavalent phosphorus atom [13]. The FAB mass spectrum of **3c** is rationalized in the Scheme 2 as a representative of the series.

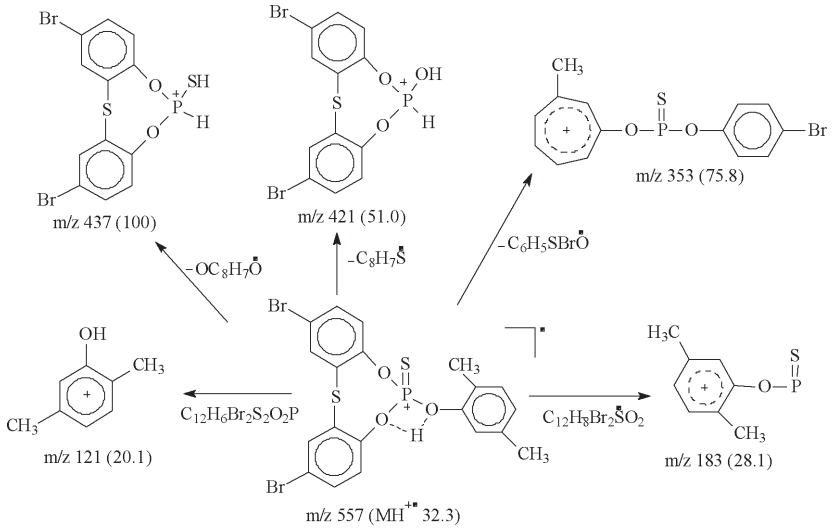
The presence of protonated molecular ion with isotropic peaks for the two bromine atoms in the expected ratio was observed at m/z 557. The observation of ions at m/z 437 and 421 with dibromodibenzodioxathiaphosphocin moiety equivocally confirm the proposed structures.

Scheme 1



Compd.	YR	Compd.	YR
3a	OC_6H_5	**3g**	$OC_6H_3Cl_2(2¢,4¢)$
3b	$OC_6H_4CH_3(4¢)$	**3h**	$OC_6H_2Cl_3(2¢,4¢,6¢)$
3c	$OC_6H_3(CH_3)_2(2¢,5¢)$	**3i**	$OC_6H_4Br(4¢)$
3d	$OC_6H_4[C(CH_3)_3](4¢)$	**3j**	$OC_6H_4NO_2(4¢)$
3e	$OC_6H_3[C(CH_3)_3](2¢,4¢)$	**3k**	$SC_6H_4Cl(4¢)$
3f	$OC_6H_4Cl(4¢)$	**3l**	$SC_6H_4\ CH_3(4¢)$

Scheme 2



Antimicrobial Activity.

The antimicrobial/fungal activity of **3a-l** were evaluated by food poisoned technique [14] against *Xanthomonas citri* and *Pseudomonas solanauarum*/ *Aspergillus flavus* and *Colletotrichum gloeosporides* respectively at different concentrations 500/1000 ppm. All the compounds exhibited moderate antibacterial/fungal activity (Table 1 & 2).

EXPERIMENTAL

Melting points were determined on a Mel-Temp apparatus and are uncorrected. Elemental analyses are performed by the Central Drug Research Institute, Lucknow, India. ir Spectra are recorded as KBr pellets on a Perkin-Elmer 1430 unit. ^1H, ^{13}C and ^{31}P nmr spectra were recorded on an AMX 400 MHz spectrometer operating at 400 MHz for ^1H, 100 MHz for ^{13}C and 161.9 for ^{31}P in deuteriochloroform. The chemical shifts (δ) are referenced to

Table 1

Antibacterial activity of 6-(Substituted)-2,10-dibromodibenzo-[*d,g*][1,3,6,2]dioxathiaphosphocin 6-Sulfides (**3a-l**)

Compd	*Xanthomonas citri* (%)		*Pseudomonas solanarum* (%)	
	500 ppm	1000 ppm	500 ppm	1000 ppm
3a	7.5 (16.66)	6.0 (33.33)	8.0 (11.11)	6.5 (27.77)
3b	2.3 (74.44)	2.5 (72.22)	3.4 (62.22)	3.4 (62.22)
3c	8.1 (10.00)	8.0 (11.11)	3.6 (60.00)	3.6 (60.00)
3d	3.5 (57.90)	3.3 (63.33)	4.5 (50.00)	4.2 (53.33)
3e	5.6 (37.77)	4.2 (53.33)	5.2 (42.22)	5.1 (43.33)
3f	6.9 (23.33)	6.8 (24.44)	6.3 (30.00)	6.4 (28.88)
3g	4.2 (53.33)	4.5 (50.00)	4.3 (52.22)	4.2 (53.33)
3h	5.5 (38.88)	5.3 (41.11)	6.5 (27.77)	6.3 (30.00)
3i	5.0 (44.44)	4.8 (46.66)	4.8 (46.66)	4.5 (50.00)
3j	5.8 (35.55)	5.4 (40.00)	3.5 (57.90)	3.2 (64.44)
3k	2.4 (73.33)	2.3 (52.5)	3.5 (57.90)	3.3 (63.33)
3l	6.5 (27.77)	6.2 (31.11)	5.5 (38.88)	5.3 (41.11)

*Control of standard (Streptomycin), the bacterial inhibition was recorded as 100%.

Table 2

Antifungal Activity of 6-(Substituted)-2,10-dibromo-dibenzo[*d,g*][1,3,6,2]dioxathiaphosphocin 6-Sulfides (**3a-l**)

Compd	*Xanthomonas citri* (%)		*Pseudomonas solanarum* (%)	
	500 ppm	1000 ppm	500 ppm	1000 ppm
3a	7.5 (16.66)	7.0 (22.22)	6.5 (27.77)	6.2 (31.11)
3b	4.2 (53.33)	4.0 (55.55)	3.8 (57.77)	3.6 (60.00)
3c	5.8 (35.55)	5.0 (44.44)	5.2 (42.22)	4.8 (46.66)
3d	7.0 (22.22)	5.9 (35.55)	6.8 (24.44)	6.2 (31.11)
3e	7.0 (22.22)	6.8 (24.44)	5.55 (38.33)	5.6 (37.77)
3f	5.4 (40.00)	5.7 (36.66)	5.0 (44.44)	4.5 (50.00)
3g	6.2 (31.11)	6.8 (24.44)	5.6 (37.77)	5.4 (40.00)
3h	7.0 (22.22)	7.2 (20.00)	6.8 (24.44)	6.2 (31.11)
3i	5.0 (44.44)	4.8 (46.66)	4.5 (50.0)	4.2 (53.33)
3j	7.2 (20.00)	7.0 (22.22)	5.0 (44.44)	4.5 (50.00)
3k	4.5 (50.00)	4.3 (52.22)	4.0 (55.55)	3.5 (61.11)
3l	4.0 (55.55)	3.8 (57.77)	3.8 (57.77)	3.0 (66.66)

Control of standard (Mancozeb/Bavistin), the fungus inhibition was recorded as 100%.

TMS (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P). FAB mass spectra are recorded on a JEOL DK, 102/DA/600 system using Argon/Xenon at 6 kV, 10 mA.

5,5¢-Bisbromo-2,2¢-dihydroxydiphenyl sulfide (**1**) was prepared according the reported procedure [14].

6-(2¢,5¢-Dimethylphenoxy)-2,10-dibromodibenzo[*d,g*][1,3,6,2]-dioxathiaphosphocin 6-sulfide (**3c**).

Thiophosphoryl chloride (0.38 g, 0.002 mole) in 25 mL of dry toluene was added dropwise over a period of 20 minutes to a cooled (0 °C) and stirred solution of 5,5¢-dibromo-2,2¢-dihydroxydiphenyl sulfide (**1**, 0.75 g, 0.002 mole) and triethylamine (4.04 g, 0.004 mole) in 40 mL of dry toluene in the presence of a catalytic amount of dimethylaminopyridine (0.3 g, 0.002 mole). After completion of the addition, the reaction mixture was stirred at room temperature for three hours. When TLC indicated completion of the reaction with the formation of the intermediate 6-chloro-2,10-dibromodibenzo[*d,g*][1,3,6,2]dioxathiaphosphocin 6-sulfide (**2**), the reaction mixture was filtered to separate triethylamine hydrochloride and the filtrate was cooled to 0 °C. A suspension of the sodium salt of 2,5-dimethylphenol prepared by vigorous stirring of 2,5-dimethyl phenol (0.07 g 0.06 mmole) and sodium hydride in tetrahydrofuran at room temperature was added to it. After an additional one hour stirring at room temperature, the temperature was raised to 40-45 °C for another two hours. At which time the completion of the reaction was indicated by TLC analyses. The solvent was removed under reduced pressure and the residue after washing with water followed by chilled 2-propanol was recrystallized from 2-propanol to obtain analytically pure compound, 0.80 g (72%), mp 186-187 °C.

6(Phenyl)-2,10-dibromodibenzo[*d,g*][1,3,6,2]dioxathiaphosphocin 6-Sulfide (**3a**).

This compound was obtained in 75 % yield, mp 198-199 °C; ^{31}P NMR: 52.12 ppm; ^{1}H NMR: δ 6.74-8.16 (m, 11H, Ar-H); IR (KBr): ν_{max} 790(P=S), 932, 1188(P-O-$C_{aromatic}$) cm^{-1}.

Anal. Calcd. for $C_{18}H_{11}O_3Br_2S_2P$: C 40.68, H 2.05. Found: C 40.77, H 2.09%.

6(MethylPhenoxy)-2,10-dibromodibenzo[*d,g*][1,3,6,2]dioxathiaphosphocin 6-Sulfide (**3b**).

This compound was obtained in 68 % yield, mp 182-183 °C; ^{31}P NMR: 52.10 ppm; ^{13}C NMR: δ 138.2 (s, 2C, C-1 and C-11), 134.0 (s, 2C, C-2 and C-10), 126.4 (s, 2C, C-3 and C-9), 119.2 (s, 2C. C-4 and C-8), 150.8 (s, 2C, C-4a and 7a), 126.0 (s, 2C, C-11a and C-12a), 149.0 (d, *J*=7.2 Hz, C-1'), 120.2 (C-2'), 126.4 (C-3'), 133.0 (C-4'), 129.0 (C-5'), 120.2 (C-6'), 20.9 (CH_3); ^{1}H NMR: δ 6.72-7.90 (m,10H, Ar-H), 2.37 (s, 3H, CH_3); IR (KBr): ν_{max} 794(P=S), 930, 1187(P-O-$C_{aromatic}$) cm^{-1}; FAB Mass: 547(MH+4, 8.7), 545(MH+2, 15.6), 543($MH^{+\Sigma}$, 8.1), 513(8.1), 481(63.4), 513(8.1), 437(24.3), 405(10.8), 313(25.6), 233(14.8), 154(63.4), 107(52.6), 90(74.2), 55(100).

Anal. Calcd. for $C_{19}H_{13}O_3Br_2S_2P$: C 41.88, H 2.36. Found: C 41.93, H 2.40%.

6(2,5-DimethylPhenoxy)-2,10-dibromodibenzo[*d,g*][1,3,6,2]-dioxathiaphosphocin 6-Sulfide (**3c**).

This compound was obtained in 72 % yield, mp 160-161 °C; ^{31}P NMR: 51.47 ppm; ^{13}C NMR: δ 138.8 (s, 2C, C-1 and C-11), 134.4 (s, 2C, C-2 and C-10), 126.8 (s, 2C, C-3 and C-9), 119.0 (s, 2C, C-4 and C-8), 151.3 (s, 2C, C-4a and C-7a), 125.2 (s, 2C, C-

11a and C-12a), 149.1 (C-1'), 131.3 (C-2'), 125.2 (C-3'), 126.8 (C-4'), 137.1 (C-5'), 119.2 (C-6'), 15.6 (2'-CH_3), 20.9 (5'-CH_3); ^{1}H NMR: δ 6.90-7.86 (m, 10H, Ar-H), 2.31 (d, *J*= 7.2 Hz, 6H); IR (KBr): ν_{max} 797(P=S), 932, 1186(P-O-$C_{aromatic}$) cm^{-1}; FAB Mass: 561(MH+4, 30.9), 559(MH+2, 57.6), 557($MH^{+\Sigma}$, 32.3), 496(25.2), 437(100), 421(51.0), 405(29.5), 358(20.0), 337(18.5), 305(53.5), 250(42.1), 183(28.1), 154(36.5), 136(36.5), 121(20.1), 91(21.0).

Anal. Calcd. for $C_{20}H_{15}O_3Br_2S_2P$: C 43.00, H 2.66. Found: C 43.03, H 2.70%.

6(4-*tert*-Butylphenoxy)-2,10-dibromodibenzo[*d,g*][1,3,6,2]-dioxathiaphosphocin 6-Sulfide (**3d**).

This compound was obtained in 74 % Yield, mp 186-187 °C; ^{31}P NMR: 51.84 ppm; ^{13}C NMR: δ 138.9 (s, 2C, C-1 and C-11), 134.5 (s, 2C, C-2 and C-10), 126.6 (s, 2C, C-3 and C-9), 119.2 (s, 2C. C-4 and C-8), 153.8 (s, 2C, C-4a and C-7a), 126.3 (s, 2C, C-11a and C-12a), 153.8 (d, *J*=7.1 Hz, C-1'), 120.3 (C-2'), 126.3 (C-3'), 134.2 (C-4'), 125.3 (C-5'), 117.1 (C-6'), 35.0(4'-*tert*-C), 31.8(3CH_3); ^{1}H NMR: δ 6.57-7.85 (m, 9H, Ar-H), 1.26 (s, 9H, C(CH_3)); IR(KBr): ν_{max} 770(P=S), 924, 1180(P-O-$C_{aromatic}$) cm^{-1}.

Anal. Calcd. for $C_{22}H_{19}O_3Br_2S_2P$: C 45.02, H 3.21. Found: C 45.06, H 3.26%.

6(2,4Di-*tert*-butylphenoxy)-2,10-dibromodibenzo[*d,g*][1,3,6,2]-dioxathiaphos-phocin 6-Sulfide (**3e**).

This compound was obtained in 78 % yield, mp 170-171 °C; ^{31}P NMR: 50.17 ppm; ^{13}C NMR: δ 138.4 (s, 2C, C-1 and C-11), 134.5 (s, 2C, C-2 and C-10), 126.0 (s, 2C, C-3 and C-9), 119.6 (s, 2C, C-4 and C-8), 152.0(s, 2C, C-4a and C-7a), 125.0 (s, 2C, C-11a and C-12a), 148.0 (C-1'), 132.0 (C-2'), 128.4 (C-3'), 133.8 (C-4'), 125.0 (C-5'), 117.0 (C-6'), 34.5 (2'-*tert*-C), 29.7 (3CH_3), 35.6 (4'-*tert*-C), 31.6(3CH_3); ^{1}H NMR: δ 6.90-7.86 (m, 8H, Ar-H), 1.29 [s, 9H, 2'-C(CH_3)], 1.40 [s, 9H, 4'-C(CH_3)]; IR(KBr): ν_{max} 782(P=S), 938, 1176(P-O-$C_{aromatic}$) cm^{-1}.

Anal. Calcd. for $C_{26}H_{27}O_3Br_2S_2P$: C 48.58, H 4.19. Found: C 48.61, H 4.23%.

6(4-Chlorophenoxy)-2,10-dibromodibenzo[*d,g*][1,3,6,2]-dioxathiaphosphocin 6-Sulfide (**3f**).

This compound was obtained in 69% yield, mp 150-151 °C; ^{31}P NMR: 51.40 ppm; ^{1}H NMR: δ 6.80-7.96(m,10H, Ar-H); IR(KBr): ν_{max} 796(P=S), 928, 1186(P-O-$C_{aromatic}$) cm^{-1}.

Anal. Calcd. for $C_{18}H_{10}O_3Br_2S_2PCl$: C 38.24, H 1.74. Found: C 38.28, H 1.78%.

6(2,4-Dichlorophenoxy)-2,10-dibromodibenzo[*d,g*][1,3,6,2]-dioxathiaphosphocin 6-Sulfide (**3g**).

This compound was obtained in 72 % yield, mp 173-174 °C; ^{31}P NMR: 51.70 ppm; ^{1}H NMR: δ 6.94-7.65(m,8H, Ar-H); IR(KBr): ν_{max} 794(P=S), 936, 1160(P-O-$C_{aromatic}$) cm^{-1}.

Anal. Calcd. for $C_{18}H_9O_3Br_2S_2PCl_2$: C 36.04, H 1.47. Found: C 36.08, H 1.51%

6(2,4,6-Trichlorophenoxy)-2,10-dibromodibenzo[*d,g*][1,3,6,2]-dioxathiaphosphocin 6-Sulfide (**3h**).

This compound was obtained in 74 % yield, mp 164-165 °C; ^{31}P NMR: 50.48 ppm; ^{1}H NMR: δ 7.00-7.85(m,7H, Ar-H); IR(KBr): ν_{max} 797(P=S), 930, 1180(P-O-$C_{aromatic}$) cm^{-1}.

Anal. Calcd. for $C_{18}H_8O_3Br_2S_2PCl_3$: C 34.08, H 1.22. Found: C 34.12, H 1.27%.

6(4-Bromophenoxy)-2,10-dibromodibenzo[*d,g*][1,3,6,2]-dioxathiaphosphocin 6-Sulfide (**3i**).

This compound was obtained in 82 % yield, mp 148-149 °C; ^{31}P NMR: 51.52 ppm; ^{13}C NMR: δ 138.9 (s, 2C, C-1 and C-11), 134.6 (s, 2C, C-2 and C-10), 128.1 (s, 2C, C-3 and C-9), 119.4 (s, 2C, C-4 and C-8), 151.2 (s, 2C, C-4a and C-7a), 125.1 (s, 2C, C-11a and C-12a), 149.4 (C-1'), 119.4 (C-2'), 125.1 (C-3'), 134.6 (C-4'), 128.0 (C-5'), 119.4 (C-6'); ^{1}H NMR: δ 6.94-8.00 (m, 10H, Ar-H); IR(KBr): ν_{max} 705(P=S), 942, 1191(P-O-$C_{aromatic}$) cm^{-1}; FAB Mass: 613(MH+6, 23.5), 611(MH+4, 69.2), 609(MH+2, 55.4), 607($MH^{+\Sigma}$, 19.4), 509(13.8), 437(66.4), 405(11.0), 374(11.0), 307(80.3), 289(80.3), 257(19.3),178(29.0), 154(100), 136(88.6), 107(74.7), 89(49.8).

Anal. Calcd. for $C_{18}H_{10}O_3Br_3S_2P$: C 35.44, H 1.61. Found: C 35.49, H 1.65%.

6(4-Nitrophenoxy)-2,10-dibromodibenzo[*d,g*][1,3,6,2]dioxathi-aphosphocin 6-Sulfide (**3j**).

This compound was obtained in 70 %, mp 158-159 °C; ^{31}P NMR: 50.70 ppm; ^{1}H NMR: δ 6.80-7.94 (m, 10H, Ar-H); IR(KBr): ν_{max} 774(P=S), 920, 1180(P-O-$C_{aromatic}$) cm^{-1}

Anal. Calcd. for $C_{18}H_{10}NO_5Br_2S_2P$: C 37.34, H 1.71. Found: C 37.38, H 1.75%.

6(4-Chlorothiophenoxy)-2,10-dibromodibenzo[*d,g*][1,3,6,2]-dioxathiaphosphocin 6-Sulfide (**3k**).

This compound was obtained in 64 % yield, mp 202-203 °C; ^{31}P NMR: 86.28 ppm; ^{1}H NMR: δ 6.84-8.04(m,10H, Ar-H); IR(KBr): ν_{max} 797(P=S), 594, 518(P-S-$C_{aromatic}$) cm^{-1}.

Anal. Calcd. for $C_{18}H_{10}O_2Br_2S_3PCl$: C 37.19, H 1.68. Found: C 37.23, H 1.73%.

6(4-Methylthiophenoxy)-2,10-dibromodibenzo[*d,g*][1,3,6,2]-dioxathiaphosphocin 6-sulfide (**3l**).

This compound was obtained in 68 % yield, mp 176-177 °C; ^{31}P NMR: 84.20 ppm; ^{1}H NMR: δ 6.82-7.90 (m, 10H, Ar-H), 2.32 (s, 3H, CH_3); IR(KBr): ν_{max} 762(P=S), 582, 527(P-S-$C_{aromatic}$) cm^{-1}.

Anal. Calcd. for $C_{19}H_{13}O_2Br_2S_3P$: C 40.68, H 2.29. Found: C 40.73, H 2.33%.

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