# Synthesis and reactivity of 6-mercapto-6*H*-dibenzo[*c,e*][1,2]-oxaphosphinine 6-sulfide

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**This article is dedicated to Prof. Dr. Rainer Beckert on his 60th birthday.**

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**Abstract**

The synthesis route of the novel 6-mercapto-6*H*-dibenzo[*c,e*][1,2]oxaphosphinine 6-sulfide **4** from 6-chloro-6H-dibenzo[c,e][1,2]oxaphosphinine **1** and its spectroscopic investigation are presented. In addition, reaction of the thiol group with unsaturated functionalities such as acrylates demonstrated that the newly synthesized compound could undergo thiol-ene chemistry. Moreover, modification of the reaction condition led to the formation of the rearrangement product of a thiol-Michael reaction of compound **4** with benzoquinone.

**Keywords:** 6*H*-Dibenzo[*c,e*][1,2]oxaphosphinine, sulfur, phosphorus, rearrangement, thiol-Michael reaction

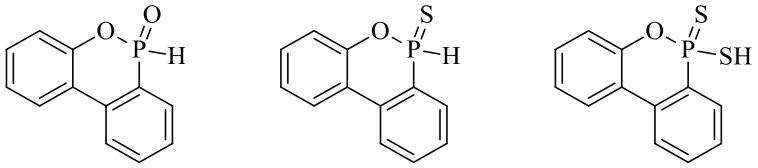
## Introduction

Phosphorus containing molecules have been the subject of an intense research interest since the pioneering work of Michaelis and Arbuzov in the late 19th and early 20th century. [1] The development of the new phosphorus compounds was mainly driven by the discovery of the insecticidal activity of a number of phosphoric acid and phosphonic esters. However, organophosphorus compounds can now be found in a broad spectrum of applications such as agrochemical, catalysis, pharmaceutical and more recently flame retardants.[1-5] Our group is

interested in using the versatility of the phosphorus atom to rationally design organophosphorus compounds that could act as flame retardants.[6-9]

6*H*-dibenzo[*c,e*][1,2]oxaphosphinine 6-oxide (**a**) is a commercially available flame retardant. To broaden its scope of application, novel derivatives of (a) with tailored chemical structures are synthesized in our working group. In an effort to deepen our understanding of the effect of sulfur on the flame retardancy of 6*H*-dibenzo[*c,e*][1,2]oxaphosphinine derivatives in several polymeric materials, the synthesis of 6*H*-dibenzo[*c,e*][1,2]oxaphosphinine 6-sulfide (**b**) and 6-mercapto-6*H*-dibenzo[*c,e*][1,2]oxaphosphinine 6-sulfide **4** were investigated. The synthesis route of (**b**) as the sulfur analogous of (**a**) and its chemical reactivity were previously reported.[10] Hence it will only mentioned as reference for the reactivity of compound **4**. This manuscript will focus on the novel route developed in our laboratory to obtain compound **4** from 6-chloro-6H-dibenzo[c,e][1,2]oxaphosphinine **1**.




(a) (b) (c)

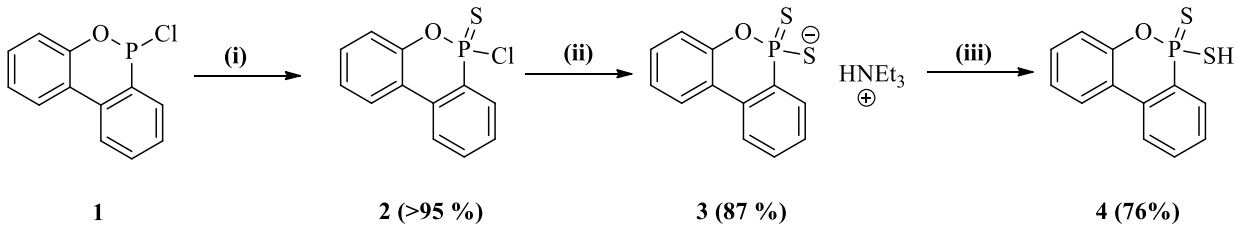
**Figure 1.** Structure of the phosphaphenanthrene derivatives investigated as flame retardants (**a**) 6*H*-dibenzo[*c,e*][1,2]oxaphosphinine 6-oxide, (**b**) 6*H*-dibenzo[c,e][1,2]oxaphosphinine 6-sulfide and (**c**) 6-mercapto-6*H*-dibenzo[*c,e*][1,2]oxaphosphinine 6-sulfide **4.**

## Results and Discussion

To the best of our knowledge the synthesis of compound **4** has never been reported before and reports dealing with the synthesis of phosphonodithioic acids and their reactivity remain scarce. However, Martin *et al*. reported a route to obtain phosphodithioic acid derivatives via reaction of 2-chloro-1,3,2-dithiaphosphospholane with a Grignard reagent followed by exposure to elemental sulphur and subsequent treatment with choline tosylate in presence of a strong base.[11] Similar to Martin *et al*, a trivalent phosphorus molecule P(III) was used as precursor to obtain our target compound. When 6-chloro-*6H*-dibenzo[*c,e*][1,2]oxaphosphinine **1** was heated in dry conditions in the presence of elemental sulfur, 6-chloro-*6H*-dibenzo[*c,e*][1,2]oxaphosphinine 6-sulfide **2** was formed in quantitative yield (Scheme 1). The thionation of the starting material was confirmed using $^{31}$P and $^{1}$H-NMR. The $^{1}$H-NMR spectrum shows the characteristic fingerprint of *6H*-dibenzo[*c*,e][1,2]oxaphosphinine derivatives in the aromatic region while the $^{31}$P-NMR spectrum indicates a change in the oxidation state of the phosphorus atom from P(III) to P(V) with a single peak at 74.5 ppm. This shift is in accordance with the thionation step observed for the synthesis of 6*H*-dibenzo[*c,e*][1,2]oxaphosphinine 6-sulfide.[10] Treatment of a solution of **2** in

toluene with elemental sulfur and triethylamine at 100 °C for 6 h, followed by filtration, several washes with ethanol, toluene and diethyl ether yielded a brown solid. This solid was identified as triethylammonium *6H*-dibenzo[c,e][1,2]oxaphosphinine-6-thiolate 6-sulfide **3** using $^{31}$P and $^{1}$H-NMR. In addition to the characteristic aromatic region, the $^{1}$H-NMR spectrum showed one quartet and one triplet in the aliphatic region, integrating nine and six protons respectively, as well as a broad singlet at 9.61 ppm (one proton) that were attributed to the triethylammonium salt moiety. In addition, the presence of a single peak (99.6 ppm) in the $^{31}$P-NMR spectrum indicated the complete conversion of compound **2** to compound **3**.

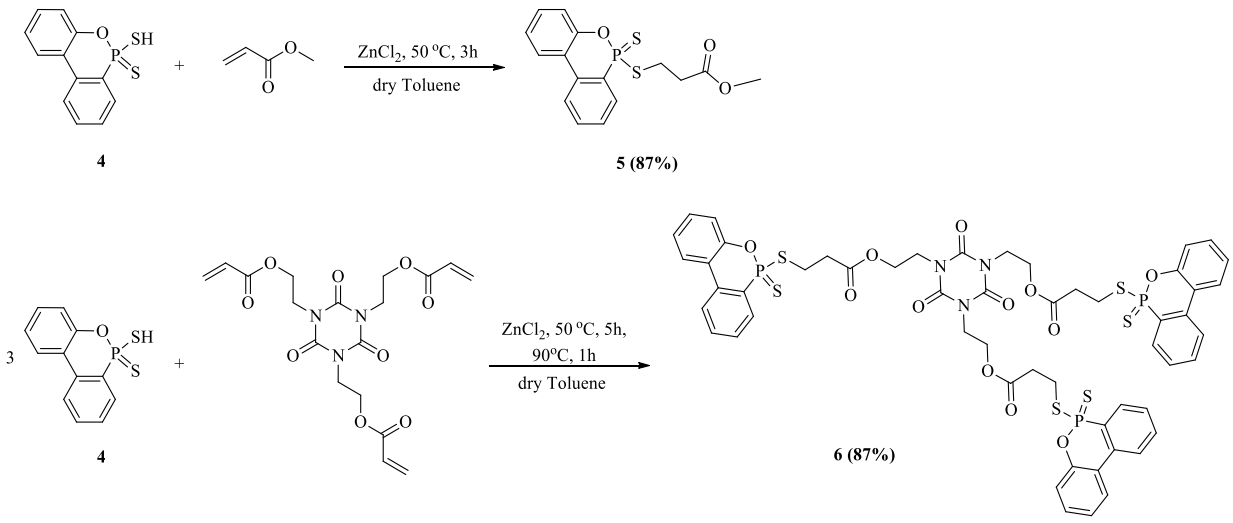



**Scheme 1.** Synthesis route of compound **4**, (i) $S_8$ (1 eq.), 1.5 h at 130°C, 2 h at 150 °C then 1.5 h at 160 °C, (ii) toluene, $Et_3N$ (3 eq.) and $S_8$ (2 eq.) at 95-100 °C for 6 h, (iii) hydrochloric acid, ethanol at 60°C.

Addition of concentrated hydrochloric acid to a warm solution of **3** in ethanol followed by treatment with aqueous sodium chloride yielded, upon cooling, a suspension that was filtered. Subsequent dissolution in hot water followed by a treatment with hydrochloric acid, further filtration and recrystallization from toluene yielded a white solid in high yield (75 %). The combination of NMR spectroscopy and HR-MS of the isolated product enabled the irrevocable assignment of compound **4**. Indeed, the $^{1}$H-NMR spectrum of the white solid showed the characteristic aromatic fingerprint of *6H*-dibenzo[*c*,*e*][1,2]oxaphosphinine derivatives while a singlet at 3.02 ppm indicated the presence of a thiol functionality. In addition, the $^{31}$P-NMR showed a single peak at 78.7 ppm indicating the complete conversion of the triethylammonium salt **3** to the target compound 6-mercapto-6*H*-dibenzo[*c*,*e*][1,2]oxaphosphinine 6-sulfide **4**. This was further confirmed by the HR-MS showing a peak at m/z 263.9836.

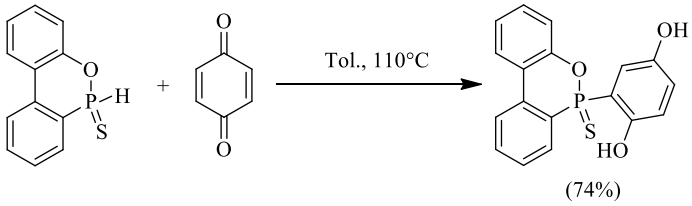
Having successfully synthesized compound **4** *via* a new synthetic route, we investigated its reactivity. The strong acidity of thiol groups eases the formation of the thiolate anions which in turn can act as nucleophiles and react with unsaturated functional groups such as C=C bonds in acrylates. The thiol-ene click reaction has proven to be a versatile tool in organic synthesis.[12-15] In particular, such a strong nucleophilic character has been used in the thiol-Michael reaction which is exploited extensively in synthesis and polymer modification since it leads to thioesters in very high yields.[16,17] Hence, in order to verify the nucleophilicity of compound **4**, it was reacted in the presence of two acrylates as shown in scheme 2.




**Scheme 2.** Thiol-Michael reaction of compound **4** with methyl acrylate (top) and tris[2-(acryloxy)ethyl]isocyanurate (bottom).

An oily solid was isolated from the reaction mixture after heating at 50 °C an equimolar solution of **4** and methyl acrylate in toluene in the presence of $ZnCl_2$ for 3 h. After several washes of the crude product with diethyl ether and pentane, a colorless powder could be filtered off and dried *in vacuo*. The $^{31}$P-NMR spectrum of the obtained powder (compound **5**) showed a singlet at 87.9 ppm indicating that the starting material had fully reacted. The $^{1}$H-NMR spectrum showed the signals characteristic of the *6H*-dibenzo[*c*,*e*][1,2]oxaphosphinine moiety while the aliphatic region showed one singlet and two multiplets, integrating to three, two and two protons respectively, confirming that the hydrothiolation of methyl acrylate was achieved. Similarly, $^{31}$P-NMR of the white solid isolated after the reaction of compound **4** with tris[2-(acryloxy)ethyl]isocyanurate in the presence of $ZnCl_2$ showed the presence of a single peak (87.7 ppm) indicating that the starting material was fully reacted. Confirmation of the hydrothiolation was provided by the $^{1}$H-NMR spectrum that showed four multiplets in the aliphatic region that each integrated to two protons in addition to the eight protons in the aromatic region attributed to the *6H*-dibenzo[*c*,*e*][1,2]oxaphosphinine group.




**Scheme 3.** Reaction of 6H-dibenzo[*c*,*e*][1,2]oxaphosphinine **b** with benzoquinone.Error! Bookmark not defined.

The Michael-like addition of (**a**) with benzoquinone is a well-known reaction applied for manufacture of a commercial flame retardant.[18,19] In a previous study we demonstrated that the replacement of an oxygen atom by a sulfur atom did not prevent the analogous Michael-like addition between **(b)** and benzoquinone (Scheme 3).[10] Thus, the next step of our investigation consisted of reacting compound **4** with benzoquinone. Hence, compound **4** was heated in the presence of benzoquinone and $ZnCl_2$ as a catalyst in a toluene/THF solution at 80°C. After addition of n-pentane, a grey powder precipitated which was dissolved in hot chloroform. Colorless crystals were obtained upon slow cooling of this solution (compound **7**). The $^{31}$P-NMR spectrum of the collected crystals showed that the peak shifted from 78.7 ppm to 73.6 ppm, indicating that a change in the environment of the phosphorus atom had occurred. The $^{1}$H-NMR spectrum confirmed that the addition of compound **4** to benzoquinone occurred as two doublets and one singlet indicative of a 1,2,4-trisubstituted benzene ring were observed in the aromatic region, in addition to the eight protons from the *6H*-dibenzo[*c*,*e*][1,2]oxaphosphinine group. However, the presence of two singlets at 5.45 and 3.46 ppm were in disagreement with the spectrum of the addition product of *6H*-dibenzo[*c*,*e*][1,2]oxaphosphinine 6-sulfide to benzoquinone. Nonetheless, the mass spectrum of the isolated product showed a peak at m/z 371.96 which correspond to the target thiol-Michael reaction product. When the same starting materials were heated in milder conditions without $ZnCl_2$, the $^{31}$P-NMR spectrum of the isolated product (compound **8**) showed a peak at 81.6 ppm. In addition, eventhough the aromatic region also indicated the presence of a 1,2,4-trisubsituted benzene ring besides the eight protons associated with the *6H*-dibenzo[*c*,*e*][1,2]oxaphosphinine group, some noticeable differences were observed in comparison to the $^{1}$H-NMR spectrum of compound **7** (Figure 2). On the other hand, the mass spectrum of the compound **8** also showed a peak corresponding to the target compound at m/z 371.99. This indicated that the two products obtained using different reaction conditions were isomers and that one of them is the rearrangement product of the target molecule.

A single crystal of **8** was successfully isolated by slow evaporation of chloroform. As shown in figure 3, the product formed in the absence of the $ZnCl_2$ catalyst is the target Michael-like addition product. Thus, confirming that compound **4** can be used as a nucleophile. Our attempts to resolve the structure of compound **7** by means of X-ray structure analysis were also successful using crystals of **7** that have been obtained by recrystallization from chloroform. The X-ray structure determination revealed that substance **7** is a rearrangement product of **8** (see figure 4). It can be deducted that the presence of $ZnCl_2$ and the use of moderate heat facilitated the rearrangement of compound **8** to form compound **7** *via* and intramolecular rearrangement (Scheme 5). To confirm this mechanism compound **8** was heated with toluene, THF and a trace of $ZnCl_2$ for 1 h. $^{31}$P-NMR spectroscopy of the obtained solution showed, that the starting material was completely converted into its rearrangement product **7**.

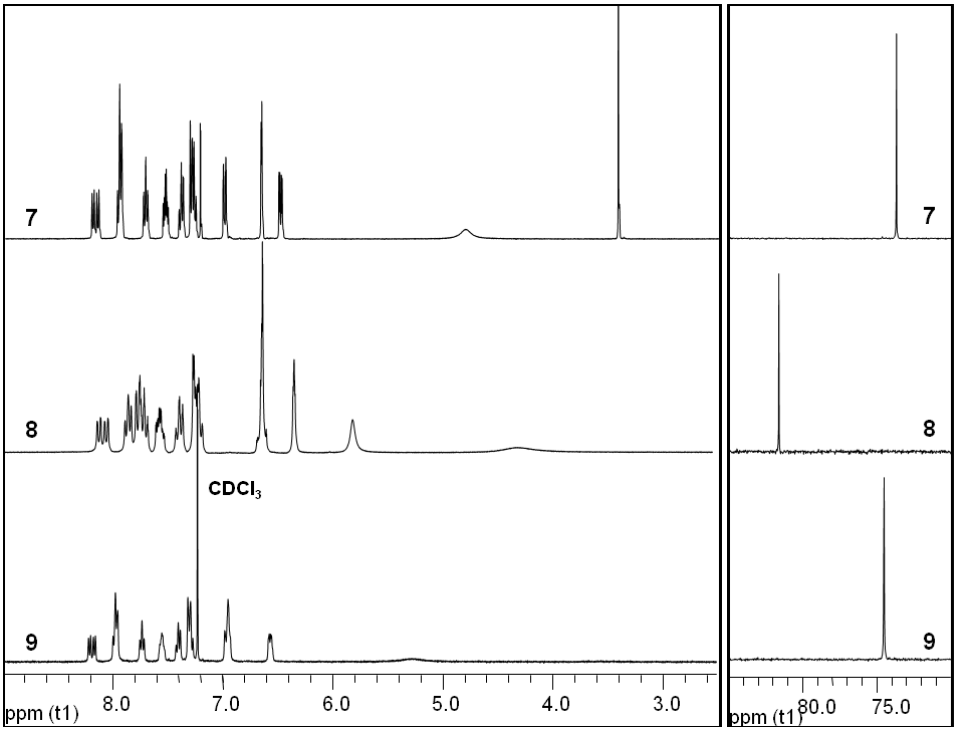
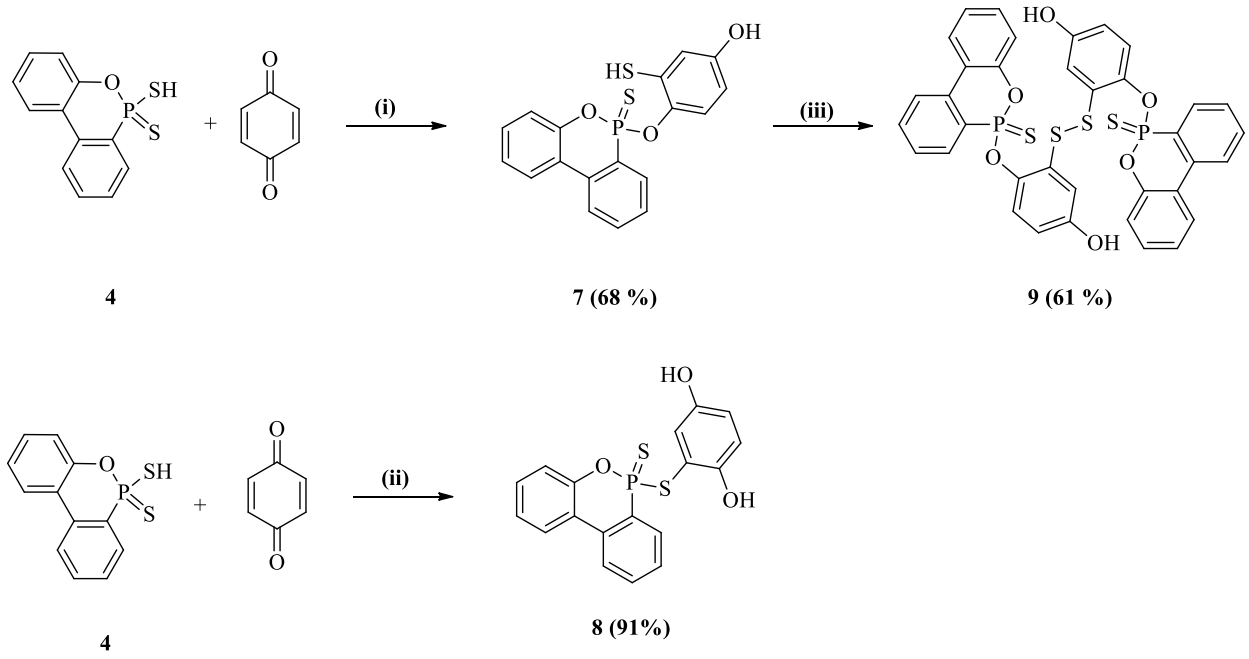



**Figure 2**. Left: $^{1}$H-NMR spectrum of compound **7** (top), compound **8** (middle) and compound **9** (bottom) ($CDCl_3$); Right: $^{31}$P-NMR spectrum of compound **7** (top), compound **8** (middle) and compound **9** (bottom), ($CDCl_3$).

Compound **7** has been subjected to an oxidative dimerization according to scheme 4. A solution of **7** was treated with iodine in the presence of triethylamine and ethanol, whereby a solid precipitated, which was filtered off and then stirred with diluted aqueous hydrochloric acid and chloroform. After separation of the organic layer and evaporation of the solvent compound **9** was obtained as a white solid. The $^{31}$P-NMR spectrum of compound **9** shows a single peak at 74.5 ppm, indicating that **7** reacted completely in an oxidative environment. As expected, no significant difference was observed in the aromatic region of $^{1}$H-NMR spectrum between compound **7** and compound **9** (see figure 2). However, the singlet at 3.46 ppm was not present in the $^{1}$H-NMR spectrum of compound **9**. This indicated that the thiol groups formed a disulfide bridge in compound **9** during the oxidation reaction.




**Scheme 4.** Reaction of compound 4 with benzoquinone (i) $ZnCl_2$, Toluene/ THF, 80°C for 45 min, (ii) Toluene, 45-47°C for 20 min, (iii) iodine / triethylamine for 3 h, ethanol.

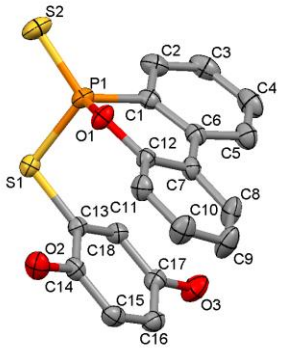



**Figure 3.** View of the molecular structure of compound **8** in the crystal, H atoms and solvent molecules omitted due to reasons of clarity. Selected bond lengths [Å] and angles [°]: P1-S1 1.77795 (15), P1- S2 2.1109 (6), P1-O1 1.7870 (17), P1-C1 1.9121 (6), S1-C13 1.3948 (18); O1-P1-C1 102.75 (7), O1-P1-S2 112.95 (5), C1-P1-S2 119.06 (6), O1-P1-S1 106.97 (5), C1-P1-S1107.56 (5), S2-P1-S1 106.91 (3).

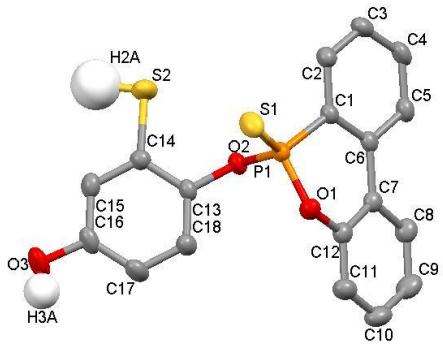
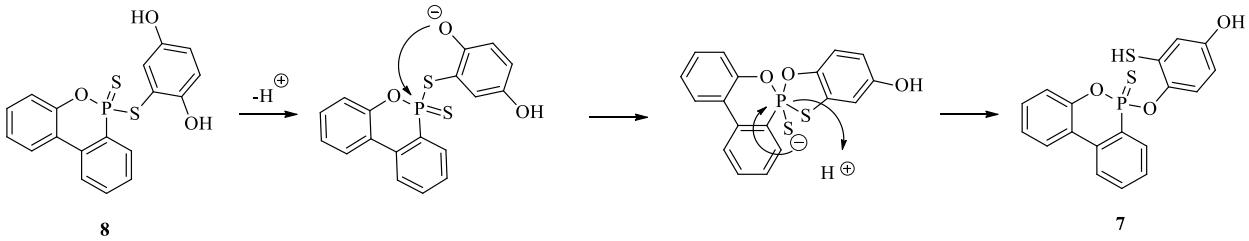



**Figure 4.** View of the molecular structure of compound **7** in the crystal, H atoms and solvent molecules omitted due to reasons of clarity. Selected bond lengths [**Å**] and angles [°]: P1-S1 1.9176 (8), P1-C1 1.769 (2), P1-O1 1.5924 (16), P1-O2 1.6049 (16), O2-C13 1.408 (2), C14-S2 1.765 (2), C16-O3 1.367 (3); O1-P1-O2 104.64 (9), O1-P1-C1 103.74 (9), O2-P1-C1 (99.99 (9), O1-P1-S1 110.15 (7), O2-P1-S1 116.17 (7), C1-P1-S1120.34 (8).




**8** **7**

**Scheme 5.** Suggested mechanism for the rearrangement of compound **8** into compound **7**.

## Conclusions

In summary, we have developed a new synthetic route for the formation of 6-mercapto-6*H*-dibenzo[*c*,*e*][1,2]oxaphosphinine 6-sulfide **4** from 6-chloro-6H-dibenzo[*c*,*e*][1,2]oxaphosphinine **1**. The relative ease of synthesis of compound **4** combined with its interesting reactivity makes it an attractive molecule for a wide variety of chemical investigations not limited to the field of flame retardancy.

## Experimental Section

**General.** Unless stated otherwise, solvents and chemicals were obtained from commercial sources and used without further purification. NMR spectra were recorded with a Varian INOVA-400 (400 MHz). Chemical shifts are reported as δ values relative to the solvent peak. All $^{31}$P-NMR spectra are measured proton decoupled. All $^{13}$C-NMR spectra were measured proton decoupled and phosphorus coupled. $^{1}$H-NMR spectra were measured phosphorus coupled.

Melting points are uncorrected and measured with a Büchi B-545. High resolution mass spectrometry (HR-MS) analyses were performed on a MicroMass GCT (time of flight (TOF); electron ionization (EI), 70 eV). IR spectra were recorded with a Varian 660-IR (FT-IR).

**Triethylammonium 6*H*-dibenzo[*c*,*e*][1,2]oxaphosphinine-6-thiolate 6-sulfide (3): Compound 1** (50.0 g, 0.214 mol) was charged in a thoroughly dried three-neck round bottom flask fitted with a thermometer, a condenser and an argon inlet. Compound **1** was then molten under an Ar atmosphere using an oil bath at 80 °C. Elemental sulphur (6.89 g, 0.215 mol) was added to the fully molten compound **1.** The reaction mixture was then heated at 130 °C for 1.5 h. The temperature of the oil bath was then raised and maintained at 150 °C for 2 h. Finally, the temperature of the oil bath was raised and maintained at 160 °C for another 1.5 h. $^{31}$P-NMR analysis of the molten reaction mixture showed that compound **1** was fully consumed and that the intermediate **2** was formed ($\delta$ = 74.5 ppm ($CDCl_3$)). The heat source was then removed and the reaction mixture allowed cooling down. Once the temperature of the reaction mixture reached 80 °C, dry toluene (150 ml) was added and the mixture was stir until full dissolution of **2**. After complete dissolution of **2** in toluene, triethylamine (66.0 g, 0.652 mol) was added, shortly followed by the addition of elemental sulphur (14.0 g, 0.475 mol). The reaction mixture was then heated under Argon atmosphere using an oil bath at 95-100°C for 6 h. The reaction mixture gradually darkened as the reaction was progressing. Once the reaction was completed, the heat source was removed and the dark brown reaction mixture was cooled to room temperature. The precipitate formed during the reaction was filtered off and washed with toluene to yield a brown powder which still contained traces of triethylaminonium chloride salt. Ethanol (300 ml) was added to the isolated brown powder, the suspension was stirred at room temperature for 15 min and filtered. This step was repeated until no trace triethylamonium chloride salt was observed. Finally toluene (200 ml) was added to the isolated brown powder and the viscous solution was stirred at 80 °C for 30 min. The suspension was filtered, the powder washed with diethyl ether to yield the target compound as a light powder which was then dried *in vacuo* (68.0 g, 0.186 mol, 87 %) mp 137-139 °C; $^{31}$P NMR ($CDCl_3$) $\delta$ = 99.6 ppm; $^{1}$H-NMR ($CDCl_3$) $\delta$ = 9.62 (s, 1H), 8.05 (dd, *J* = 16.7 Hz, *J*= 7.1 Hz, 1H), 7.84 (d, *J* = 9.9 Hz, 2H), 7.72 (t, *J* = 6.4 Hz, 1H), 7.46-7.36 (m, 2H), 7.31-7.25 (m, 1H), 7.18-7.10 (m, 2H), 3.17 (t, *J* = 7.0 Hz, 6H), 1.31 ppm (t, *J* = 7.3 Hz, 9H); $^{13}$C-NMR ($CDCl_3$) $\delta$ = 150.9 (d, *J* = 10.3 Hz, 1C), 138.7 (d, *J* = 103.4 Hz, 1C), 132.1 (d, *J* = 5.5 Hz, 1C), 130.1 (d, *J* = 2.7 Hz, 1C), 129.3 (s, 1C), 128.3 (d, *J* = 13.8 Hz, 1C), 127.9 (d, *J* = 14.6 Hz, 1C), 124.9 (d, *J* = 1.4 Hz, 1C), 124.6 (d, *J* = 12.8 Hz, 1C), 123.4 (s, 1C), 123.2 (s, 1C), 120.7 (d, *J* = 5.3 Hz, 1C), 46.0 (s, 3C), 8.5 ppm (s, 3C); IR $\nu$ 2976 (s), 2942 (s), 2671(m), 1471 (vs), 1425 (s), 1209 (vs), 1161 (m), 1112(vs), 1067 (w), 1040 (m), 875 (s), 780, 673 $cm^{-1}$; HR-MS calc for [$C_{18}H_{24}NOPS_2$] 263.9832 found 263.9850.

**6-Mercapto-6*H*-dibenzo[*c*,*e*][1,2]oxaphosphinine 6-sulfide (4):** compound **3** (22.5g, 61.1 mmol) and ethanol (150 ml) were charged in a three-neck round bottom flask fitted with a condenser and a thermometer and heated using an oil bath at 85 °C under Ar atmosphere. Once

the solid was dissolved, a solution of concentrated hydrochloric acid (80 ml) was dropped in over a 5 min period and allowed to stir for another 5 min. An aqueous NaCl solution (70g in 350 mL) was added while stirring. The resulting suspension was then cooled to 50 °C and filtered. The collected solid was suspended in $H_2O$ (500 mL) and heated at 70 °C for 30 min. NaCl was then added to the filtrate under stirring and concentrated HCl (100 ml) was added. The formed white solid was filtered and washed with cold water. The resulting white powder was dried *in vacuo*. The crude product was recrystallized from toluene to yield the target molecule **4** as white crystals (12.2g, 46.2 mmol, 76%) mp 128-130°C; $^{31}$P NMR ($CDCl_3$) δ = 78.7 ppm; $^{1}$H-NMR ($CDCl_3$) δ = 8.13 (dd, *J* = 17.4 Hz, *J* = 8.5 Hz, 1H), 7.94-7.86 (m, 2H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.55 (dt, *J* = 6.5 Hz, J = 3.8 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.36-7.26 (m, 2H), 3.13 (s, 1H); $^{13}$C-NMR ($CDCl_3$) δ = 149.2 (d, *J* = 12.8 Hz, 1C), 133.5 (s, 1C), 130.9 (s, 1C), 130.3 (d, *J* = 109.8 Hz, 1C), 130.1 (d, *J* = 14.9 Hz, 1C), 128.9 (d, *J* = 16.5 Hz), 125.5 (d, *J* = 1.5 Hz, 1C), 125.3 (d, *J* = 1.7 Hz, 1C), 123.8 (d, *J* = 10.7 Hz, 1C), 122.9 (d, *J* = 13.7 Hz, 1C), 120.9 ppm (d, *J* = 6.4 Hz, 1C); IR ν 3067, 2367, 1555, 1468, 1442, 1192, 1111, □□917,□□895 (vs), 747 (vs), 700, 660, 536 (vs) $cm^{-1}$; HR-MS $[C_{12}H_9OS_2P]^+$ calc. 263.9832, found 263.9836.

**Methyl 3-((6-sulfido-6*H*-dibenzo[*c*,*e*][1,2]oxaphosphinin-6-yl)thio)propanoate (5)**: compound **4** (6.61 g, 25.0 mmol), $ZnCl_2$ (0.17 g, 1.25 mmol) and dry toluene (50 ml) were charged into a three-neck round bottom flask fitted with a condenser and a magnetic stirrer. The mixture was heated at 50 °C under Ar atmosphere using an oil bath and a solution of methylacrylate (2.69 g, 31.2 mmol) in toluene (10 ml) was added dropwise over 20 min. Once the addition was completed, the reaction mixture was heated for a further 3 h and 50 °C. The precipitated zinc by product was removed by filtration. The solvent was then removed in vacuo to yield an oily substance. After trituration with a hot mixture of diethyl ether (25 ml) and pentane (25 ml) under Ar atmosphere, a white solid was formed. The suspension was then cooled to – 20°C and the solid was filtered off to yield the target compound as a white powder (7.6 g, 21.6 mmol, 87 %) mp 75-82°C; $^{31}$P NMR ($CDCl_3$) δ = 87.9 ppm; $^{1}$H-NMR ($CDCl_3$) δ = 8.03 (dd, *J* = 16.6 Hz, *J* = 7.5 Hz, 1H), 7.89 (d, *J* = 7.5 Hz, 1H), 7.86 (d, *J* = 5.7 Hz, 1H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.55 (dt, *J* = 7.3 Hz, *J* = 3.5 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.31-7.25 9m, 1H), 7.20 (d, *J* = 7.9 Hz, 1H), 3.65 (s, 3H), 3.49-3.09 (m, 2H), 2.88-2.66 ppm (m, 2H); $^{13}$C-NMR ($CDCl_3$) δ = 171.4 (s, 1C), 149.3 (d, *J* = 11.9 Hz, 1C), 134.8 (d, *J* = 5.5 Hz, 1C), 133.5 (d, *J* = 2.7 Hz, 1C), 130.8 (s, 1C), 130.6 (s, 1C), 128.7 (d, *J* = 15.6 Hz, 1C), 127.1 (s, 1C), 125.1 (d, *J* = 7.7 Hz, 1C), 123.8 (d, *J* = 10.5 Hz, 1C), 123.1 (s, 1C), 122,9 (s, 1C), 120.6 (d, *J* = 6.4 Hz, 1C), 51.7 (s, 1C), 35.2 (d, *J* = 3.5 Hz, 1C), 27.3 ppm (d, *J* = 3.6 Hz, 1C); IR ν 3066 , 2998, 2948, 1756 (vs), 1592, 1584, 1472 (s), 1447 (s), 1436 (s), 1365 (vs), 1277, 1226 (vs), 1186 (vs), 1152, 1149 vs), 1043(m), 918 (w), 898 (vs), 826 (m) $cm^{-1}$; HR-MS calc. for $[C_{16}H_{15}O_3PS_2]^+$ 350.0200 ,found 350.0239.

**(2,4,6-Trioxo-1,3,5-triazinane-1,3,5-triyl)tris(ethane-2,1-diyl) tris(3-((6-sulfido-6*H*-dibenzo[*c*,*e*][1,2]oxaphosphinin-6-yl)thio)propanoate) (6)**: compound **4** (4.73 g, 18.0 mmol),

$ZnCl_2$ (0.05 g, 0.37 mmol) and abs. toluene (50 ml) were charged into a three-neck round bottom flask fitted with a condenser and a magnetic stirrer. The mixture was heated at 50 °C under Ar atmosphere using an oil bath and a solution a tris[2-(acryloxy)ethyl]isocyanurate (2.54 g, 6.0 mmol) in toluene (15 ml) was added dropwise over 90 min. Once the addition was completed, the reaction mixture was heated for a further 5 h and 50 °C. The temperature was then raised to 90 °C for 1 h. Further $ZnCl_2$ (0.03 g, 0.22 mmol) was added and the reaction mixture was refluxed until complete consumption of the acrylate could be observed *via* NMR spectroscopy. The precipitated zinc by product was removed by filtration. The solution was then concentrated *in vacuo* to yield the target compound as a white powder (6.34 g, 5.22 mmol, 87 %); m.p. 80-120°C; $^{31}$P NMR ($CDCl_3$) δ = 87.7 ppm; $^{1}$H-NMR ($CDCl_3$) δ = 7.94 (dd, *J* = 16.6 Hz, *J* = 7.6 Hz, 3H), 7.81 (d, *J* = 7.3 Hz, 3H), 7.79 (d, *J* = 5.4 Hz, 3H), 7.61 (t, *J* = .5 Hz, 3H), 7.45 (dt, *J* = 7.3 Hz, *J* = 3.5 Hz, 3H), 7.31 (t, *J* = 7.8 Hz, 3H), 7.23-7.17 (m, 3H), 7.11 (d, *J* = 7.9 Hz, 3H), 4.26-4.11 (m, 6H), 4.03 (d, *J* = 4.6 Hz, 6H), 3.29-2.98 (m, 6H), 2.75-2.52 ppm (m, 6H); $^{13}$C-NMR ($CDCl_3$) δ = 170.8 (s, 3C), 149.2 (d, *J* = 12.2 Hz, 3C), 148.7 (s, 3C), 134.7 (d, *J* = 5.5 Hz, 3C), 133.6 (d, *J* = 2.6 Hz, 3C), 130.8 (s, 3C), 130.7 (s,3C), 128.8 (d, *J* = 15.8 Hz, 3C), 127.8 (d, *J* = 109.5 Hz, 3C), 125.2 (d, *J* = 5.9 Hz, 3C), 123.8 (d, *J* = 10.1 Hz, 3C), 123.0 (s, 3C), 122.8 (s, 3C), 120.5 (d, *J* = 6.3 Hz, 3C), 61.3 (s, 3C), 41.8 (s, 3C), 35.3 (s, 3C), 35.2 (s, 3C), 27.1 (s, 3C), 27.1 ppm (s, 3C); IR ν 3470, 3062, 2963, 1738 (s), 1694 (vs), 1457 (vs), 1238, 1191(s), 1113 (s), 895, 786, 760 $cm^{-1}$. Calc. (%) for $C_{54}H_{48}P_3S_6N_3O_{12}$: C, 53.33; H, 3.98; N, 3.48; P, 7.64; S, 15.82. Found (%): C, 53.03; H, 3.91; N, 3.33; P, 7.36; S, 16.09.

**6-(4-Hydroxy-2-mercaptophenoxy)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-sulfide (7):** A mixture of compound **4** (4.96 g, 18.75 mmol) and $ZnCl_2$ (0.1g, 0.73 mmol) in 60 mL dry toluene was heated using an oil bath at 80 °C under Ar atmosphere. While stirring, a solution of benzoquinone (2.03 g, 18.75 mmol) in tetrahydrofuran (30 mL) was added dropwise over 15 min. The reaction mixture was maintained at 80 °C for 45 min after the addition of the benzoquinone solution was complete. Then, after removal of the heat source, the reaction mixture was allowed to cool to room temperature. The solution was then concentrated *in vacuo* to ca. 40 mL and n-pentane (30 mL) was added. A small amount of a tar-like impurity was removed by decantation to give a colorless solution. Then, further n-pentane (200 mL) was added over 20 min while stirring. A viscous liquid separated slowly solidifying. The solid was isolated by decantation and filtration and then it was dried *in vacuo* to yield a pale yellow powder (7.3 g). The crude product was dissolved in chloroform (120 mL) under Ar atmosphere. After the solution had been cooled to room temperature, colorless crystals of **7** were obtained which were suitable for X-ray structure determination. The crystals were isolated by filtration and the filtrate was concentrated to give a second fraction of **7.** The collected crystals were dried *in vacuo* at 100°C to yield pure **7** as a white powder (4.76 g, 12.7 mmol, 68 %); m.p. 128-131°C; $^{31}$P NMR ($CDCl_3$) δ = 73.6 ppm; $^{1}$H-NMR ($CDCl_3$) δ = 8.20 (dd, *J* = 17.4 Hz, *J* = 8.6 Hz, 1H), 7.97 (t, *J* = 7.6 Hz, 2H), 7.73 (t, *J* = 7.9 Hz, 1H), 7.55 (dt, *J* = 7.5 Hz, *J* = 3.8 Hz, 1H), 7.40 (t, *J* = 7.4 Hz), 7.29 (q, *J* = 6.9 Hz), 7.03 (dd, *J* = 7.3 Hz, *J* = 1.8 Hz, 1H), 6.69 (d, *J* = 2.2 Hz, 1 H),

6.52 (dd, *J* = 8.7 Hz, *J* = 2.9 Hz, 1H), 5.45 (s, 1H), 3.46 ppm (s, 1H); $^{13}$C-NMR ($CDCl_3$) δ = 152.6 (s, 1C), 150.0 (s, 1C), 140.7 (d, *J* = 9.9 Hz, 1C), 134.7 (d, *J* = 5.3 Hz, 1C). 133.7 (d, *J* = 2.7 Hz, 1C), 131.6 (d, *J* = 15.4 Hz, 1C), 130.6 (s, 1C), 128.7 (d, *J* = 19.4 Hz, 1C), 128.2 (d, *J* = 14.2 Hz, 1C), 126.0 (d, *J* = 143.6 Hz, 1C), 125.9 (d, *J* = 5.5 Hz, 1C), 125.2 (d, *J* = 1.3 Hz, 1C), 125.1 (d, *J* = 6.0 Hz, 1C), 123.8 (d, *J* = 10.9 Hz, 1C), 122.6 (d, *J* = 12.0 Hz, 1C), 122.3 (d, *J* = 3.7 Hz, 1C), 120.1 (d, *J* = 6.4 Hz, 1C), 116.7 (d, *J* = 1.4 Hz, 1C), 113.2 ppm(d, *J* = 1.8 Hz, 1C);IR ν 3400 (br), 1575, 1557, 1484 (vs), 1432, 1280, 1180 (vs), 1151, 1113, 923 (vs), 888 (vs), 774, 753, 724 cm$^{-1}$; HR-MS calc for $[C_{18}H_{13}O_3PS_2]^+$ 372.0044, found 372.0077.

**6-((2,5-Dihydroxyphenyl)thio)-6*H*-dibenzo[*c*,*e*][1,2]oxaphosphinine 6-sulfide (8)**: Under Ar atmosphere, a warm solution of benzoquinone (1.62 g, 15.00 mmol) in dry toluene (25 ml) was slowly added to a warm (35-40 °C) solution of **4** (3.90 g, 15.0 mmol) in dry toluene (40 ml). A few minutes after the start of the addition, the formation of the solid was observed in the reaction vessel. The reaction mixture was further heated at 45-47°C. 20 min after in the addition of the benzoquinone solution was completed. The suspension was then cooled using an ice-bath and the precipitate was filtered off and dried *in vacuo*. The product was isolated as a gray powder (5.11g, 13.7 mmol, 91 %). m.p. 55°C (decomposes); $^{31}$P NMR ($CDCl_3$) δ = 81.6 ppm; $^1$H-NMR ($CDCl_3$) δ = 8.01 (dd, *J* = 16.4 Hz, *J* = 6.5 Hz, 1H), 7.79 (t, *J* = 7.4 Hz, 1H), 7.71-7.61 (m, 2H), 7.49 (dt, *J* = 7 Hz, J = 3.8 Hz, 1H), 7.32 (t, *J* = 8.1 Hz, 1H), 7.19-7.11 (m, 2H), 6.55 (s, 2H), 6.26 (s, 1H), 5.72 (s, 1H), 4.08 (s, 1H);$^{13}$C-NMR ($CDCl_3$) δ = 155.1 (s, 1C), 149.6 (d, *J* = 12.2 Hz, 1C), 139.2 (d, *J* = 9.8 Hz, 1C), 134.7 (s, 1C), 134.5 (d, *J* = 5.2 Hz, 1C), 131.4 (s, 1C), 131.4 (d, *J* = 15.2 Hz, 1C), 129.3 (d, *J* = 16.6 Hz, 1C), 126.9 (d, *J* = 5.0 Hz, 1C), 126.4 (s, 1C), 125.9 (s, 1C), 125.7 (d, *J* = 133.4 Hz, 1C), 124.9 (d, *J* = 10.5 Hz, 1C), 122.5 (d, *J* = 12.0 Hz, 1C), 122.3 (d, *J* = 3.8 Hz, 1C), 120.4 (d, *J* = 6.2 Hz, 1C), 116.8 (s, 1C), 113.3 (s, 1C); IR ν 2361, 2337, 1698, 1467(vs), 1444 (s), 1326, 1217 (s), 1191 (s), 1112, 922 (vs), 818, 788, 749, 666 cm$^{-1}$.

**Rearrangement of compound 8 to 7:** Under Ar atmosphere, compound 8 (0.74 g, 2.00 mmol) and $ZnCl_2$ (0.01 g) were stirred in a mixture of toluene and THF (10 mL / 5 mL) for 1 h. After evaporation of the solvents, compound **7** was obtained in nearly quantitative yield and a purity of approx. 97%; $^{31}$P NMR ($CDCl_3$) δ = 73.6 ppm.

**6,6'-((Disulfanediylbis(4-hydroxy-2,1-phenylene))bis(oxy))bis(6*H*-dibenzo[*c*,*e*][1,2] oxaphosphinine 6-sulfide) (9)**: Compound **7** (1.12 g, 30.00 mmol) was dissolved in 25 mL ethanol under Ar and triethylamine (0.40 g, 40 mmol) was added. While stirring, a solution of iodine (0.40 g, 31.00 mmol) in ethanol (30 ml) was added dropwise over 15 min at room temperature. The formation of a solid was observed in the reaction vessel. The reaction mixture was further stirred for 3 h at room temperature. The precipitate was filtered off with a glass frit, rinsed with diethyl ether and dried. The obtained solid was stirred with chloroform (30 mL), water (50 mL) and hydrochloric acid (0.5 mL) at room temperature for 1 h. Afterwards, the mixture was filtered through a glass frit and the aqueous layer was removed. The chloroformic

solution was treated with diluted hydrochloric acid again. The aqueous layer was removed and the solution was dried over sodium sulphate. Then, the solvent was distilled off *in vacuo* to yield pure **9** as a white solid (0.68 g, 9.15 mmol, 61 %); $^{31}$P NMR ($CDCl_3$) δ = 74.5 ppm; $^{1}$H-NMR ($CDCl_3$) δ = 8.19 (dd, *J* = 17.7 Hz, *J* = 7.7 Hz, 1H), 7.97 (t, *J* = 8.40 Hz, 2H), 7.75 (t, *J* = 7.55 Hz, 1H), 7.58 (dt, *J* = 7.63 Hz, *J* = 3.3 Hz, 1H), 7.43 (t, *J* = 7.48 Hz), 7.29 (t, *J* = 9.27 Hz, 2H), 6.96 (d, *J* = 12.2 Hz, 2H), 6.56 (dd, *J* = 8.50 Hz, *J* = 3.37 Hz, 1H), 5.3 (s, broad, 1H), $^{13}$C-NMR ($CDCl_3$) δ = 153.6 (d, *J* = 1.8 Hz, 2 C), 149.8 (d, *J* = 12.0 Hz, 2 C), 140.4 (d, *J* = 10.1, 2 C), 134.8 (d, *J* = 5.5 Hz, 2 C), 133.8 (d, *J* = 2.8 Hz, 2 C), 131.5 (d, *J* = 15.6 Hz, 2 C), 130.6 (s, 2 C), 129.6 (t, *J* = 5.0 Hz, 2 C), 128.5 (d, *J* = 16.5 Hz, 2 C), 126.9 (s, 2 C), 125.2 (d, *J* = 10.1 Hz, 2 C), 124.6 (s, 2 C), 122.8 (s, 2 C), 122.6 (t, *J* = 3.7 Hz, 2 C), 120.2 (d, *J* = 6.4 Hz, 2 C), 114.6 (t, *J* = 2.7 Hz, 2 C), 113.9 (d, *J* = 8.3 Hz, 2 C); IR ν 3550 (br), 2963, 2361, 2340, 1474, 1261 (s), 1098 (br), 917, 798. 753 $cm^{-1}$.

**Crystallography**

Crystal structure analyses were conducted on a Bruker Apex II Quazar diffractometer with Mo-$K_\alpha$ (λ=0.71073, graphite monochromator) at 200 K. A Lorentz and Polarisation correction was applied. Experimental absorption correction was done with SADABS, structure solution and refinement was performed with SHELX 97. XPMA and Mercury 2.2 were used for visualisation.

Complete crystallographic data of compounds **7** and **8** have been deposited with the Cambridge Crystallographic Data Centre (deposition numbers CCDC 865377 and 865378). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033, e-mail: deposit@ccdc.cam.ac.uk).

Structural details for **7**: Reflections collected: 34314, independent reflections: 8645 [R(int) = 0.0264], formula $C_{18}H_{13}O_3PS_2$ , MM per molecule 372.39 g/mol, T = 200(2) K, triclinic; unit cell dimensions: a = 9.9881 (5) Å, b = 13.6065 (7) Å , c = 14.9264 (8) Å, α = 69.149 (10) °, β = 82.172 (10)°, γ = 83.516 (10)°, V = 1873.47 (17) $Å^3$, density (calc.) = 1.532 $g/cm^3$, Absorption coefficient = 0.600 $mm^{-1}$, F(000) = 884, goodness-of-fit on $F^2$ = 1.040, crystal size = 0.04 x 0.12 x 0.52 $mm^3$, index ranges -13 <= h <= 13, -18 <= k <= 18, -19 <= l <= 19, completeness: 90.2 %, $R_1$ (I>2σ) = 0.0465, $wR_2$ = 0.1184 (all data), largest difference peak and hole: 1.364 and -1.118 e $Å^3$.

Structural details for **8**: Reflections collected: 15315, independent reflections: 3803 [R(int) = 0.0172], formula $C_{18}H_{13}O_3PS_2$, MM per molecule 372.31 g/mol, T = 200(2) K, monoclinic, unit cell dimensions: a = 12.4404 (9) Å, b = 11.4289 (9) Å; c = 12.5640 (10) Å, α = 90°, β = 114.5190 (10)°, γ = 90°, V = 1625.3 (2) $Å^3$, density (calc.) = 1.555 $g/cm^3$, Absorption coefficient = 0.437 $mm^{-1}$, F(000) = 784, goodness-of-fit on $F^2$= 1.046, crystal size = 0.55 x 0.50 x 0.45 $mm^3$, index ranges -16 <= h <= 16, -15 <= k <= 15, -16 <= l <= 16; completeness: 92.8 %, $R_1$ (I>2σ) = 0.0324, $wR_2$ = 0.0859 (all data), largest difference peak and hole: 0.814 and -0.320 e $Å^3$.

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