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## FIRST SYNTHESIS OF BENZO[*e*][1,3,2]DIAZAPHOSPHININO[1,6-*c*]- [1,3,2]OXAZAPHOSPHININES

Tarik E. Ali,<sup>a\*</sup> Mohammed A. Assiri,<sup>a,b</sup> and Ibrahim S. Yahia<sup>c</sup>

<sup>a</sup>Department of Chemistry, Faculty of Science, King Khalid University, Abha, Saudi Arabia. <sup>b</sup>Research Center for Advanced Materials Science, King Khalid University, Abha, Saudi Arabia. <sup>c</sup>Department of Physics, Faculty of Science, King Khalid University, Abha, Saudi Arabia

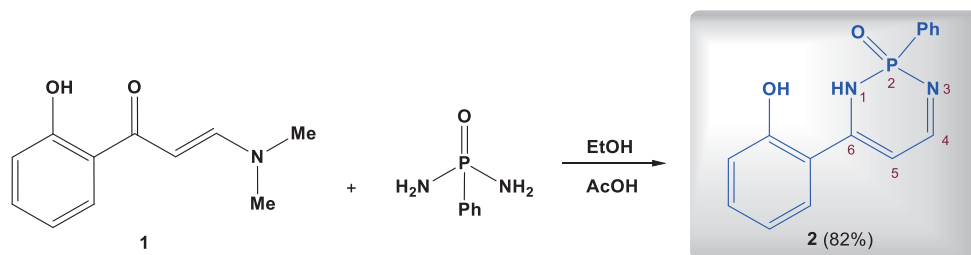
\*E-mail: tarik\_elsayed1975@yahoo.com, tismail@kku.edu.sa

**Abstract** – A series of novel benzo[*e*][1,3,2]diazaphosphinino[1,6-*c*][1,3,2]-oxazaphosphinine derivatives (**3a-f**) were synthesized by cyclization reactions of 6-(2-hydroxyphenyl)-2-phenyl-1*H*-2-oxido-1,3,2-diazaphosphinine (**2**) with some phosphorus dichlorides in the presence of triethylamine in dry dioxane under reflux. The structures of all the synthesized compounds were established by IR, <sup>1</sup>H-, <sup>13</sup>C- and <sup>31</sup>P-NMR spectra as well as by elemental analysis and mass spectral analysis.

The rich chemistry and wide applications of organophosphorus compounds are receiving attraction by the scientists belonging to different scientific disciplines.<sup>1-3</sup> Organophosphorus compounds, which are a wide class of chemical compounds containing organic moieties usually bonded directly to phosphorus or bonded through a heteroatom, such as sulfur, oxygen or nitrogen, are one of the most common chemicals in the human environment. These phosphorus compounds have unique properties and high biological activities such as insecticidal,<sup>4</sup> antimicrobial<sup>5</sup> and anticancer.<sup>6</sup> On the other hand, it is known that 1,3,2-diazaphosphinine ring containing heterocyclic compounds are very interesting biologically active molecules.<sup>7,8</sup> Considering the above facts and our program research on the development of new biologically active heterocyclic organophosphorus compounds,<sup>9-12</sup> we herein reported the synthesis of a novel molecular frame of benzo[*e*][1,3,2]diazaphosphinino[1,6-*c*][1,3,2]oxazaphosphinines.

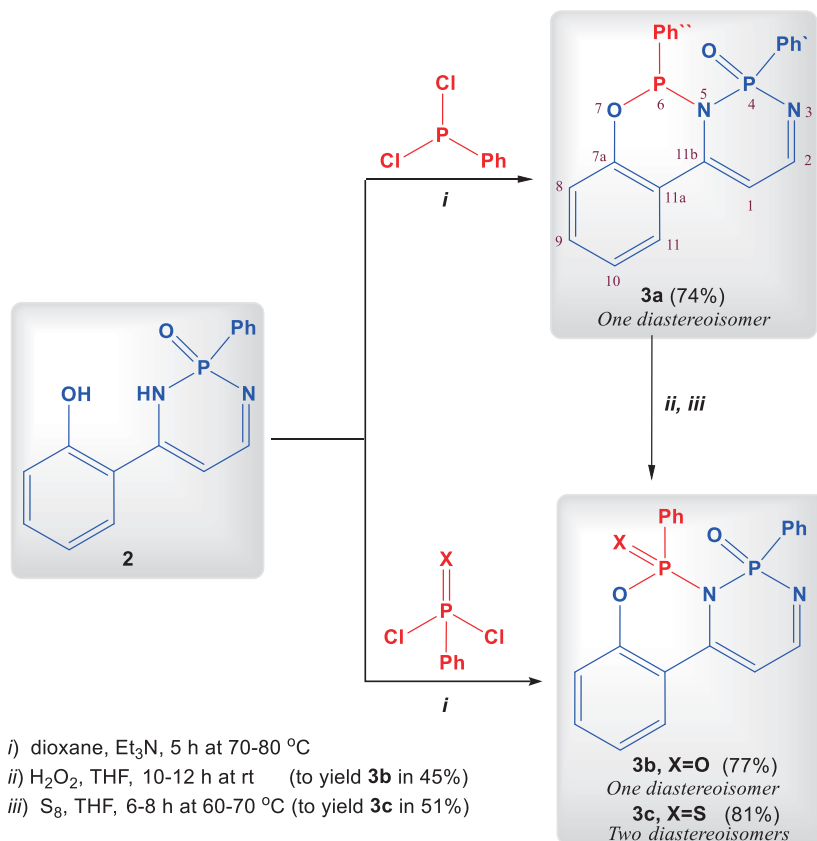
6-(2-Hydroxyphenyl)-2-phenyl-1*H*-2-oxido-1,3,2-diazaphosphinine (**2**), which is the starting material for this work, was obtained from reaction of (*E*)-3-(dimethylamino)-1-(2-hydroxyphenyl)prop-2-en-1-one (**1**)<sup>13</sup> with phenylphosphonic diamide in absolute ethanol containing a few drops of acetic acid (Scheme 1). The IR spectrum of compound **2** recorded the absorption bands for NH and OH groups at 3213 and 3342

$\text{cm}^{-1}$ . Its  $^1\text{H-NMR}$  spectrum displayed the protons  $H-5$  and  $H-4$  of diazaphosphinine ring as two doublets at  $\delta$  5.19 and 7.49 ppm with the same coupling constant  $J=5.2$  Hz, while the NH and OH were showed at  $\delta$  9.89 and 10.03 ppm. Furthermore, its  $^{13}\text{C-NMR}$  spectrum recorded the carbon atoms of diazaphosphinine ring at  $\delta$  71.8 ( $C-5$ ), 151.3 ( $C-6$ ) and 151.9 ( $C-4$ ) ppm. Its  $^{31}\text{P-NMR}$  spectrum exhibited one singlet for one isomer at  $\delta$  27.4 ppm. The mass spectrum of compound **2** showed its molecular ion peak at  $m/e$  284 ( $\text{M}^+$ , 15%).



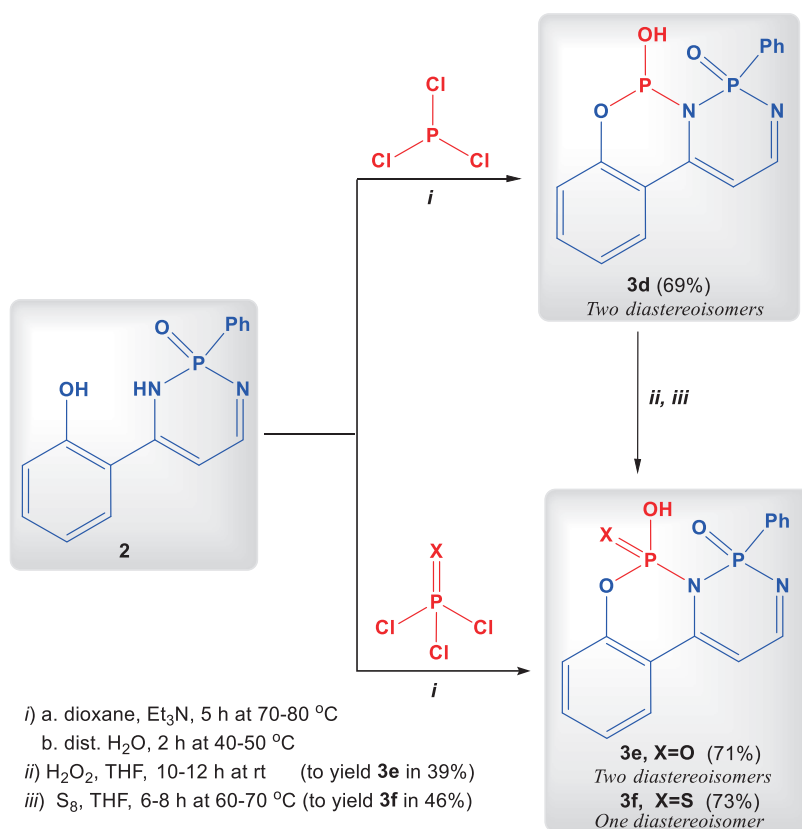
Scheme 1

The presence of two active nucleophilic sites in the starting material **2** provides alternative opportunities in the direction of the reaction with electrophilic phosphorus halides.<sup>14</sup> Its synthetic precursor opens wide opportunities for the use of the diazaphosphinine system in the synthesis of diverse fused phosphorus heterocyclic compounds. Thus, the reaction of compound **2** with triethylamine and phenylphosphorus dichlorides (including P,P-dichlorophenylphosphine, phenylphosphonic dichloride and phenylphosphonothioic dichloride) (Scheme 2) as well as phosphorus chlorides (including phosphorus trichloride, phosphoryl chloride and thiophosphoryl chloride) (Scheme 3) in dry dioxane under reflux led to the formation of benzo[*e*][1,3,2]diazaphosphinino[1,6-*c*][1,3,2]oxazaphosphinines **3a-f** (Schemes 2 and 3). The proposed mechanism involved nucleophilic substitution of the chlorine atom at phosphorus reagents with the OH and NH of compound **2** to form the target fused systems, and released equimolar HCl in form triethylammonium chloride. Moreover, the synthesized products **3b,e** were also obtained by oxidation of compounds **3a** and **3d**, respectively, using hydrogen peroxide in dry tetrahydrofuran in moderate yields (Schemes 2 and 3). Similarly, the synthesized products **3c,f** were obtained by sulfuration of compounds **3a** and **3d**, respectively, using sulfur element in dry tetrahydrofuran in low yields (Schemes 2 and 3). The structure of compounds **3a-f** was deduced from their IR, NMR, MS spectra and elemental analysis. The IR spectra of compounds **3a-f** exhibited absorption bands in the region of 1603–1612 ( $\text{C=N}$ ) and 1211–1239 ( $\text{P=O}$ )  $\text{cm}^{-1}$ . The  $^1\text{H-NMR}$  spectral data of products **3a-f** revealed the total absence of signals specific to the  $\text{NH}_{\text{amidic}}$  and  $\text{OH}_{\text{phenolic}}$  protons of compound **2** which supported the cyclization process. However, the protons  $H-1$  and  $H-2$  were observed as doublets in the region  $\delta$  5.43–5.71 and 7.49–7.64 ppm, respectively, with coupling constants in range 5.6–6.4 Hz.<sup>15,16</sup> Also, the  $^1\text{H-NMR}$  spectra proved the presence of additional signals in the products **3a-c** for the phenyl groups introduced by phenylphosphorus dichlorides.



- i*) dioxane, Et<sub>3</sub>N, 5 h at 70-80 °C  
*ii*) H<sub>2</sub>O<sub>2</sub>, THF, 10-12 h at rt (to yield **3b** in 45%)  
*iii*) S<sub>8</sub>, THF, 6-8 h at 60-70 °C (to yield **3c** in 51%)

**Scheme 2**



- i*) a. dioxane, Et<sub>3</sub>N, 5 h at 70-80 °C  
       b. dist. H<sub>2</sub>O, 2 h at 40-50 °C  
*ii*) H<sub>2</sub>O<sub>2</sub>, THF, 10-12 h at rt (to yield **3e** in 39%)  
*iii*) S<sub>8</sub>, THF, 6-8 h at 60-70 °C (to yield **3f** in 46%)

**Scheme 3**

The  $^{13}\text{C}$ -NMR spectra of compounds **3a-c** exhibited signals attributable to the additional carbon atoms of phenyl groups, besides of three characteristic signals for carbon atoms of diazaphosphinine moieties at  $\delta$  73.1–77.1 (*C*-1), 146.8–149.8 (*C*-11a) and 150.3–153.3 (*C*-2) ppm, in compounds **3a-f**. In the novel products, two new chiral centers were generated at the two phosphorus atoms, then four diastereoisomers ( $\text{S}_\text{P}\text{S}_\text{P}$ ,  $\text{R}_\text{P}\text{R}_\text{P}$ ,  $\text{S}_\text{P}\text{R}_\text{P}$ ,  $\text{R}_\text{P}\text{S}_\text{P}$ ) might be found in the products **3a-f**.<sup>17</sup> We failed to obtain suitable crystals to conduct X-ray crystallography to confirm these suggestions. Also, the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra did not help to discover these diastereoisomers. The  $^{31}\text{P}$ -NMR spectrum was the only tool that supported the presence of one or more diastereoisomers. The  $^{31}\text{P}$ -NMR spectra of products **3a,b,f** showed only one peak for each phosphorus atom.<sup>18</sup> Moreover, the  $^{31}\text{P}$ -NMR spectra for products **3c,d,e** displayed two peaks for each phosphorus atom with a smaller shift difference value  $\delta = 0.2\text{--}0.5$  ppm. The ratio of the intensities of **3c,d,e** was approximately 46:54, 45:55, 47:53 by the integration of suitable signals, respectively. These results revealed the presence of one isomer in the products **3a,b,f** and merely two isomers in the products **3c,d,e**. Unfortunately, owing to the close values of  $R_f$  of diastereoisomers, it appeared to be impossible to isolate them by column chromatography or recrystallization.

In summary, construction of novel fused phosphorus heterocyclic systems such as benzo[*e*][1,3,2]-diazaphosphinino[1,6-*c*][1,3,2]oxazaphosphinines were achieved *via* reaction of 6-(2-hydroxyphenyl)-2-phenyl-1*H*-2-oxido-1,3,2-diazaphosphinine with some phosphorus dichloride and trichloride in good yields.

## EXPERIMENTAL

The melting points were determined in an open capillary tube on a digital Stuart SMP-3 apparatus. Infrared spectra were measured on FT-IR (Nicolet IS10) spectrophotometer using KBr disks and Perkin-Elmer 293 spectrophotometer using KBr disks.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were measured on Gemini-300BB spectrometer (400 and 100 MHz), using  $\text{DMSO-}d_6$  as a solvent and TMS ( $\delta$ ) as an internal standard.  $^{31}\text{P}$ -NMR spectra were measured on a Bruker (162 MHz) spectrophotometer using  $\text{DMSO-}d_6$  as a solvent, TMS as an internal standard and 85%  $\text{H}_3\text{PO}_4$  as an external reference. Mass spectra were recorded on a Gas Chromatographic GCMSqp 1000 ex Shimadzu instrument at 70 eV and direct probe controller inlet part to single quadrupole mass analyzer in (Thermo Scientific GCMS). Elemental microanalysis was performed on Perkin-Elmer 2400II at the Chemical War department, Ministry of Defense. The purity of the synthesized compounds was checked by thin layer chromatography (TLC) and elemental microanalysis.

### Synthesis of 6-(2-hydroxyphenyl)-2-phenyl-1*H*-2-oxido-1,3,2-diazaphosphinine (**2**)

A mixture of compound **1** (1.91 g, 10 mmol) and phenylphosphonic diamide (1.56 g, 10 mmol) in absolute EtOH (50 mL) containing a few drops of glacial acetic acid, was heated under reflux for 6 h.

After cooling, the formed precipitate was filtered off and crystallized from EtOH to give the product **2** as canary yellow solid in 82% yield; mp 152–153 °C. IR (KBr), ( $\nu$  max,  $\text{cm}^{-1}$ ): 3342 (br, OH), 3213 (NH), 1616 (C=N), 1585 (C=C), 1218 (P=O).  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ ): 5.19 (d, 1H,  $J=5.2$  Hz, H-5), 6.75–7.33 (m, 9H, Ar-H), 7.49 (d, 1H,  $J=5.2$  Hz, H-4), 9.89 (br, 1H, NH), 10.03 (br, 1H, OH).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{DMSO-}d_6$ ): 71.8 (C-5), 109.8 (C-1<sub>phenol</sub>), 116.6 (C-3<sub>phenol</sub>), 119.6 (C-5<sub>phenol</sub>), 122.4 (C-6<sub>phenol</sub>), 129.1 (C-4<sub>phenol</sub>), 129.4 (C-3',5'<sub>phenyl</sub>), 133.7 (C-2',6'<sub>phenyl</sub>), 134.3 (d,  $J=117$  Hz, C-1'<sub>phenyl</sub>), 135.2 (C-4'<sub>phenyl</sub>), 151.3 (C-6), 151.9 (C-4), 156.5 (C-2<sub>phenol</sub>).  $^{31}\text{P-NMR}$  (162 MHz,  $\text{DMSO-}d_6$ ): 27.4 ppm. MS ( $m/z$ , I%): 284 ( $\text{M}^+$ , 15%). Anal. Calcd for  $\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_2\text{P}$  (284.26): C, 63.38%; H, 4.61%; N, 9.85%. Found: C, 63.15%; H, 4.39%; N, 9.68%.

### General procedure for reaction of compound **2** with phenylphosphorus dichlorides: Synthesis of the products **3a-c**.

A solution of phosphorus reagent (including each P,P-dichlorophenylphosphine, phenylphosphonic dichloride and phenylphosphonothioic dichloride) (5 mmol) in dry dioxane (5 mL) was added to a solution of compound **2** (0.71 g, 5 mmol) in dry dioxane (30 mL) in the presence of triethylamine (1.4 mL, 10 mmol) as a catalyst, under stirring for 15 min at 10 °C then heated under reflux for 5 h at 70–80 °C. The formed inorganic salt was removed. The solutions were concentrated to their half volumes and left to cool. The formed solids were filtered off, washed with water and crystallized from diluted EtOH.

**4,6-Diphenyl-4-oxido-6H-benzo[e][1,3,2]diazaphosphinino[1,6-c][1,3,2]oxazaphosphinine (3a):** Pale yellow solid in 74% yield; mp 188–190 °C. IR (KBr), ( $\nu$  max,  $\text{cm}^{-1}$ ): 1612 (C=N), 1587 (C=C), 1211 (P=O).  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ ): 5.49 (d, 1H,  $J=6.4$  Hz, H-1), 6.88–7.51 (m, 14H, Ar-H), 7.63 (d, 1H,  $J=6.4$  Hz, H-2).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{DMSO-}d_6$ ): 73.8 (C-1), 110.3 (C-11a), 113.3 (C-8), 119.2 (C-10), 122.1 (C-11), 126.4 (C-2'',6''<sub>phenyl</sub>), 128.1 (C-3'',5''<sub>phenyl</sub>), 128.8 (C-9), 128.9 (C-3',5'<sub>phenyl</sub>), 129.4 (C-4''<sub>phenyl</sub>), 133.9 (C-2',6'<sub>phenyl</sub>), 135.2 (d,  $J=118$  Hz, C-1'<sub>phenyl</sub>), 135.4 (C-4'<sub>phenyl</sub>), 139.2 (d,  $J=124$  Hz, C-1''<sub>phenyl</sub>), 149.0 (C-11b), 151.6 (C-2), 152.6 (C-7a).  $^{31}\text{P-NMR}$  (162 MHz,  $\text{DMSO-}d_6$ ): 32.6 and 26.1 ppm. MS ( $m/z$ , I%): 390 ( $\text{M}^+$ , 18%). Anal. Calcd for  $\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_2\text{P}_2$  (390.32): C, 64.62%; H, 4.13%; N, 7.18%. Found: C, 64.35%; H, 3.98%; N, 6.92%.

**4,6-Dioxido-4,6-diphenylbenzo[e][1,3,2]diazaphosphinino[1,6-c][1,3,2]oxazaphosphinine (3b):** Yellow solid in 77% yield; mp 198–200 °C. IR (KBr), ( $\nu$  max,  $\text{cm}^{-1}$ ): 1603 (C=N), 1591 (C=C), 1222, 1234 (P=O).  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ ): 5.53 (d, 1H,  $J=6.0$  Hz, H-1), 7.21–7.37 (m, 14H, Ar-H), 7.62 (d, 1H,  $J=6.0$  Hz, H-2).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{DMSO-}d_6$ ): 73.1 (C-1), 110.6 (C-11a), 113.8 (C-8), 119.7 (C-10), 122.5 (C-11), 128.3 (C-3'',5''<sub>phenyl</sub>), 128.4 (C-9), 129.2 (C-3',5'<sub>phenyl</sub>), 130.5 (C-2'',6''<sub>phenyl</sub>), 132.1 (C-4''<sub>phenyl</sub>), 133.6 (C-2',6'<sub>phenyl</sub>), 134.3 (d,  $J=116$  Hz, C-1'<sub>phenyl</sub>), 136.1 (C-4'<sub>phenyl</sub>), 136.4 (d,  $J=118$  Hz, C-1''<sub>phenyl</sub>), 148.5 (C-11b), 152.3 (C-2), 153.9 (C-7a).  $^{31}\text{P-NMR}$  (162 MHz,  $\text{DMSO-}d_6$ ): 34.6 and 31.2 ppm. MS ( $m/z$ , I%): 406 ( $\text{M}^+$ , 11%). Anal. Calcd for  $\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_3\text{P}_2$  (406.32): C, 62.08%; H,

3.97%; N, 6.89%. Found: C, 61.86%; H, 3.71%; N, 6.62%.

**4,6-Diphenyl-4-oxido-6-sulfido-6 $\lambda^5$ -benzo[e][1,3,2]diazaphosphinino[1,6-c][1,3,2]oxazaphosphinine**

**(3c):** Pale orange solid in 81% yield; mp 214–215 °C. IR (KBr), ( $\nu$  max,  $\text{cm}^{-1}$ ): 1610 (C=N), 1593 (C=C), 1231 (P=O), 732 (P=S).  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ ): 5.71 (d, 1H,  $J=5.6$  Hz, H-1), 6.96–7.41 (m, 14H, Ar-H), 7.64 (d, 1H,  $J=5.6$  Hz, H-2).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{DMSO-}d_6$ ): 75.2 (C-1), 111.3 (C-11a), 115.6 (C-8), 121.9 (C-10), 123.2 (C-11), 129.2 (C-9), 129.4 (C-3',5' phenyl), 129.6 (C-3'',5'' phenyl), 130.8 (C-2'',6'' phenyl), 132.2 (C-2',6' phenyl), 133.8 (C-4' phenyl), 134.2 (C-4 phenyl), 136.1 (d,  $J=120$  Hz, C-1' phenyl), 138.3 (d,  $J=121$  Hz, C-1'' phenyl), 149.1 (C-11b), 154.2 (C-2), 156.2 (C-7a).  $^{31}\text{P-NMR}$  (162 MHz,  $\text{DMSO-}d_6$ ): 31.6, 31.9 and 38.4, 38.6 ppm. MS ( $m/z$ , I%): 422 ( $\text{M}^+$ , 8%). Anal. Calcd for  $\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_2\text{P}_2\text{S}$  (422.39): C, 59.72%; H, 3.82%; N, 6.63%; S, 7.59%. Found: C, 59.53%; H, 3.56%; N, 6.35%; S, 7.38%.

**General procedure for reaction of compound 2 with phosphorus chlorides: Synthesis of the products 3d-f.**

A solution of phosphorus reagent (including each phosphorus trichloride, phosphoryl chloride and thiophosphoryl chloride) (5 mmol) in dry dioxane (5 mL) was added to a solution of compound 2 (0.71 g, 5 mmol) in dry dioxane (30 mL) in the presence of triethylamine (1.4 mL, 10 mmol) as a catalyst, under stirring for 15 min at 10 °C then heated under reflux for 5 h at 70–80 °C. The formed inorganic salt was removed. The solutions were concentrated to their half volumes and left to cool. The obtained oily mixtures dissolved in distilled water (30 mL) and stirred at 40–50 °C for 2 h. After cooling, all the crude products were filtered off, washed with water, and crystallized from diluted MeOH.

**6-Hydroxy-4-oxido-4-phenyl-6H-benzo[e][1,3,2]diazaphosphinino[1,6-c][1,3,2]oxazaphosphinine (3d):**

Yellow solid in 69% yield; mp 169–171 °C. IR (KBr), ( $\nu$  max,  $\text{cm}^{-1}$ ): 3402 (br, OH), 1605 (C=N), 1588 (C=C), 1226 (P=O).  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ ): 3.71 (br, 1H, OH), 5.43 (d, 1H,  $J=5.6$  Hz, H-1), 6.81–6.94 (m, 2H, Ar-H), 7.13–7.36 (m, 7H, Ar-H), 7.53 (d, 1H,  $J=5.6$  Hz, H-2).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{DMSO-}d_6$ ): 74.2 (C-1), 111.2 (C-11a), 113.9 (C-8), 119.5 (C-10), 122.7 (C-11), 127.9 (C-9), 128.9 (C-3',5' phenyl), 132.6 (C-2',6' phenyl), 133.6 (d,  $J=119$  Hz, C-1' phenyl), 135.1 (C-4' phenyl), 147.9 (C-11b), 153.1 (C-2), 154.2 (C-7a).  $^{31}\text{P-NMR}$  (162 MHz,  $\text{DMSO-}d_6$ ): 32.5, 32.9 and 12.6, 12.2 ppm. MS ( $m/z$ , I%): 330 ( $\text{M}^+$ , 10%). Anal. Calcd for  $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_3\text{P}_2$  (330.22): C, 54.56%; H, 3.66%; N, 8.48%. Found: C, 54.21%; H, 3.48%; N, 8.24%.

**4,6-Dioxido-6-hydroxy-4-phenylbenzo[e][1,3,2]diazaphosphinino[1,6-c][1,3,2]oxazaphosphinine (3e):**

Yellow solid in 71% yield; mp 192–194 °C. IR (KBr), ( $\nu$  max,  $\text{cm}^{-1}$ ): 3411 (br, OH), 1610 (C=N), 1591 (C=C), 1226, 1239 (P=O).  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ ): 4.11 (br, 1H, OH), 5.48 (d, 1H,  $J=5.6$  Hz, H-1), 7.18–7.41 (m, 9H, Ar-H), 7.49 (d, 1H,  $J=5.6$  Hz, H-2).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{DMSO-}d_6$ ): 75.7 (C-1), 109.8 (C-11a), 114.1 (C-8), 120.1 (C-10), 122.9 (C-11), 128.3 (C-3',5' phenyl), 128.6 (C-9),

131.7 (C-2',6' phenyl), 132.6 (d,  $J=120$  Hz, C-1' phenyl), 133.3 (C-4' phenyl), 146.8 (C-11b), 153.3 (C-2), 154.6 (C-7a).  $^{31}\text{P}$ -NMR (162 MHz, DMSO- $d_6$ ): 33.1, 33.4 and 14.8, 15.1 ppm. MS ( $m/z$ , I%): 346 ( $\text{M}^+$ , 18%). Anal. Calcd for  $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_4\text{P}_2$  (346.22): C, 52.02%; H, 3.49%; N, 8.09%. Found: C, 51.83%; H, 3.21%; N, 7.75%.

**6-Hydroxy-4-oxido-4-phenyl-6-sulfido-6 $\lambda^5$ -benzo[e][1,3,2]diazaphosphinino[1,6-c][1,3,2]oxazaphosphinine (3f):** Pale orange solid in 73% yield; mp 199–201 °C. IR (KBr), ( $\nu$  max,  $\text{cm}^{-1}$ ): 3395 (br, OH), 1612 (C=N), 1589 (C=C), 1224 (P=O), 728 (P=S).  $^1\text{H}$ -NMR (400 MHz, DMSO- $d_6$ ): 3.93 (br, 1H, OH), 5.63 (d, 1H,  $J=6.0$  Hz, H-1), 6.88–7.18 (m, 2H, Ar-H), 7.22–7.37 (m, 7H, Ar-H), 7.52 (d, 1H,  $J=6.0$  Hz, H-2).  $^{13}\text{C}$ -NMR (100 MHz, DMSO- $d_6$ ): 77.1 (C-1), 110.2 (C-11a), 115.1 (C-8), 120.9 (C-10), 123.8 (C-11), 128.8 (C-9), 129.1 (C-3',5' phenyl), 132.1 (C-2',6' phenyl), 133.8 (C-4' phenyl), 136.1 (d,  $J=119$  Hz, C-1' phenyl), 149.8 (C-11b), 150.3 (C-2), 154.1 (C-7a).  $^{31}\text{P}$ -NMR (162 MHz, DMSO- $d_6$ ): 30.8 and 13.3 ppm. MS ( $m/z$ , I%): 362 ( $\text{M}^+$ , 13%). Anal. Calcd for  $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_3\text{P}_2\text{S}$  (362.29): C, 49.73%; H, 3.34%; N, 7.73%; S, 8.85%. Found: C, 49.54%; H, 3.11%; N, 7.52%; S, 8.51%.

**General procedure for oxidation of compounds 3a and 3d with hydrogen peroxide: Synthesis of the products 3b and 3e.**

A solution of each compound of **3a** and **3d** (2 mmol) in THF (15 mL) and aqueous hydrogen peroxide (30%, 0.25 mL) was stirred for 10-12 h at room temperature. The reaction mixtures were concentrated to their half volumes, and then add  $\text{Et}_2\text{O}$  (20 mL). The isolated precipitates **3b** and **3e**, respectively, in 45 and 39% yields, were filtered off, dried and crystallized from the proper solvent.

**General procedure for sulfuration of compounds 3a and 3d with sulfur element: Synthesis of the products 3c and 3f.**

A solution of each compound of **3a** and **3d** (2 mmol) in THF (15 mL) and sulfur element (3 mmol) was heated under reflux for at 6-8 h room at 60-70 °C. The reaction mixtures were concentrated to their half volumes. When the reaction mixtures were cooled, they deposited pale orange solids **3c** and **3f** which were filtered off, washed with benzene and crystallized from the proper solvent.

## ACKNOWLEDGEMENT

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