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Synthesis, spectral and antimicrobial activity of [3-(4-chloro-phenoxy)-2,4-diisopropyl)-2,3,4,5-tetrahydro-1H-3λ^5-benzo[e][1,3,2]diazaphosphepin-3-ylidene]-alkyl-amine (Staudinger reaction)

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Abstract: 3-(4-chlorophenoxy)-2,4-diisopropyl-2,3,4,5-tetrahydro-1H-benzo[e][1,3,2]diaza-phosphepine was synthesized starting from 1,2-bis(bromomethyl)benzene by reacting with 2 equimolar isopropyl amine, one equimolar PBr_3 and then one equimolar 4-chlorophenol, respectively. The Staudinger reaction of the diazaphphosphine with a series of alkyl azides gave the corresponding iminophosphoranes. Antibacterial activities of the synthesized iminophosphoranes were screened

Keywords: Iminophosphoranes; 1,2-bis(bromomethyl)benzene; Isopropylamine; phosphorus tribromide; 4-chlorophenol; alkyl azides; antimicrobial activity.

1. Introduction

The reaction of a tertiary phosphine with organic azides to produce an iminophosphorane[1] (phosphinimine) after nitrogen evolution is known as Staudinger reaction[2,3] and it is a versatile tool in organic synthesis.[4,5] In a few instances the primary imination products phosphazides, have been isolated[6-8], or can be trapped via an intramolecular reaction[9] but most such phosphazides lose nitrogen at room temperature or even at lower temperature to give the corresponding imino-phosphoranes in practically quantitative yields.

Isolable phosphazides[10] have been formed in the case of sterically hindered components or the electronic effects of substituents which increase the electron density on phosphorus atom or decrease it on the N-atom of the azides.[11-14] The use of the phosphinimine method in carbohydrate field provides an easy access to various N-containing sugars (carbodiimides, cyclic carbamates, epimines, ureido, guanidine derivatives, etc).[14] In course of the studies on the synthesis and transformation of sugar phosphinimines, recently, a particular interest has been aimed at the

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Staudinger reaction of glycosyl azides bearing an additional functional group at the anomeric carbon. Iminophosphoranes which were found to be excellent reagents in bridging the main group elements with transition elements.[15,16] The versatility of phosphinimines in the synthesis of heterocycles embedded with high-valent transition metals is well documented.[17] Hydrolysis of the Staudinger iminophosphorane is a convenient method for the synthesis of amines.[18] Iminophosphoranes have wide range of applications ,including modification of cell surfaces, protein engineering, specific labeling of nucleic acids, proteomic studies and as a general tool for bioconjugation.[19] In view of the above reports, we herein report the synthesis of novel phosphinimines and their corresponding dimers by Staudinger reaction. Their structures were established by IR, NMR (^{1}H, ^{13}C and ^{31}P NMR) and mass spectral data.

2.Results and Discussion

Synthesis of the title compounds (**9a-g**) was accomplished by the reaction of α,α′-dibromo-*o*-xylene[20] (**1**) with two moles of iso-propylamine (**2**) in the presence of TEA in dry THF at low temperature to form compound **3**. This on further treatment with phosphorus tribromide (**4**) in the presence of TEA in dry THF to form the corresponding phosphoro-bromidite (**5**). This on subsequent reaction with *p*-chlorophenol in the presence of TEA gave compound **7**. This on subsequent reaction with different alkyl azides (**8**) in dry THF at 50-55°C under N_2 atmosphere formed the corresponding iminophosphoranes (**9a-g**) with evolution of nitrogen in 68-75% yield and melted in the range of 143-162°C. Thin layer chromatography was employed to monitor the reaction progress and to determine the purity of the products (1:1,n-hexane:ethyl acetate). All the title compounds (**9a-g**) were readily soluble in polar solvents.

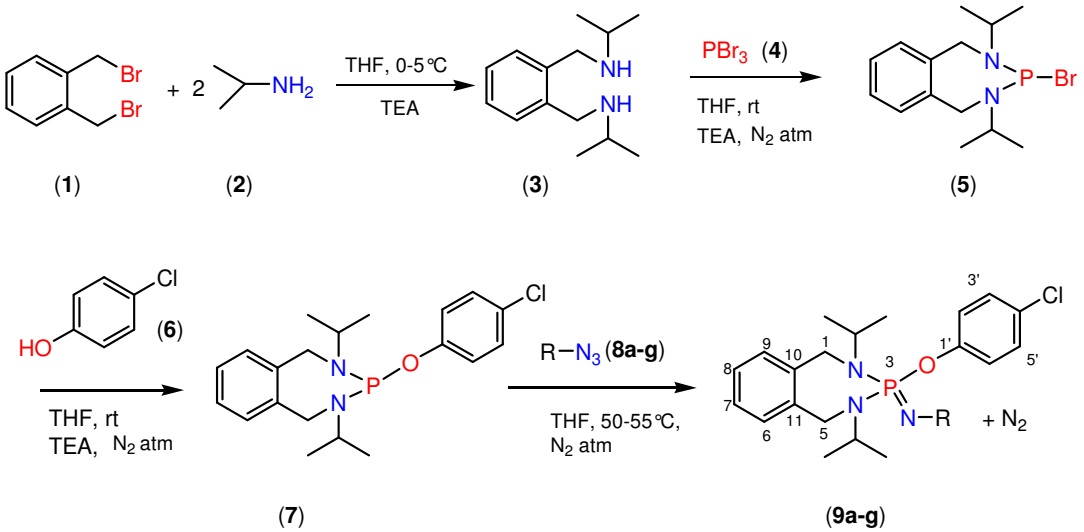
IR absorption bands were observed in the region[16,21-23] 1385 -1375 , 1240-1212 and 1033 - 1019 cm^{-1} for P-N, P=N and N-C respectively.

The aromatic protons of 4-chloro -phenoxy moiety resonated as two different doublets[23] at δ 7.48-7.18 (*J* = 9.2-8.5 Hz,2H, 3′ & 5′-H) and δ 7.32-7.13 (*J* = 8.0-7.5 Hz,2H, 2′ & 6′-H) . The aromatic protons of the title compounds (**9a-g**) resonated as two doublets[18], one at δ 6.76-6.71(*J* = 7.9-7.6 Hz,2H,8&7-H) and another one at δ 6.44-6.41(*J* = 8.2-8.0 Hz,2H,9&6-H). The N-CH of isopropyl moiety and bridged -CH_2 protons gave multiplets due to coupling with adjacent protons at δ 4.90-4.51 and 4.30-3.96 respectively. The –CH_3 protons of isopropyl group resonated as a doublet at δ 1.51-1.15 (*J* = 8.2-7.7 Hz). The protons of the P-$C_{aliphatic}$ moiety of the side chain present in **9a-g** exhibited signals in the expected range.[24]

In the ^{13}C NMR spectral data[24] of **9b, 9e** and **9f** the chemical shifts of the bridged methylene carbons (C-1 and C-5) appeared at δ 55.4- 44.5. The methylidyne and methyl carbons of iso-propylamino group resonated at δ 55.7-55.1 and δ 31.3-30.1. The side chain of the first carbon (P=N-C) resonated as a doublet at δ 57.0-20.3 ($^{2}J_{PNC}$= 10.1-9.7 Hz). In compound **9b** side chain carbon of P=N –CH_2-CH_2-CH_3 gave a doublet at δ 26.5 (*J* = 4.2 Hz) and –CH_2-CH_2-CH_3 at δ 12.3. In compound **9e,** side chain carbon of –CH_2-CH-$(CH_3)_2$ resonated as a doublet at δ 30.1 (*J* = 5.2 Hz). Carbon resonances of the side chain (alkyl groups), upto two carbons of the side chain experienced coupling with phosphorus.[22]

^{31}P NMR chemical shifts[22,23,25,26] of these compounds (**9a-g**) appeared in the expected region 0.14 to -5.65 ppm.

In the FAB mass spectra[27], compounds **9b, 9e** and **9f** exhibited their respective molecular ions at m/z 434 (10.5), 448 (100) and 406 (63.2) respectively.



Compd.	R
9a	$-CH_2-CH=CH_2$
9b	$-CH_2-CH_2-CH_3$
9c	$-CH(CH_3)_2$
9d	$-CH_2-CH_2-CH_2-CH_3$
9e	$CH_2CH(CH_3)_2$
9f	$-CH_3$
9g	$-CH_2-CH_3$

Scheme-1

Antibacteriala activity; Compounds (**9a-g**) were screened (Table 1) for their antibacterial activity[23] against Gram positive bacteria, *Staphylococcus aureus, Bacillus faecalis* and Gram negative bacteria, *Escherichia coli, Klebsiella pneumoniae* by the disk diffusion method[28] in luriabertani nutrient agar medium at two different concentrations (100, 200 µg/mL) in DMSO. These solutions containing 10^6 cells / mL were added to each Whatmann No.1 (made in UK) filter paper disk (6 mm diameter) and DMSO was used as the control. The freshly prepared agar medium containing bacteria species was loaded to the disks by using micropipette. The plates were incubated at 35°C and examined for zones of inhibition around each disk after 24 hours. The results were compared with the activity of the standard antibiotic *penicillin* (100 µg/mL).

Table-1: Antibacterial activity of compounds **(9a-g)**

Compd.	*Staphylococcus aureus*		*Bacillus faecalis*		*Escherichia coli*		*Klebsiella pneumoniae*	
	100 µg/mL	**200 µg/mL**	**100 µg/mL**	**200 µg/mL**	**100 µg/mL**	**200 µg/mL**	**100 µg/mL**	**200 µg/mL**
9a	7	11	6	10	6	10	6	11
9b	6	12	6	10	7	12	7	11
9c	6	10	6	11	7	10	7	12
9d	6	9	8	12	6	9	7	13
9e	6	11	7	11	9	14	8	13
9f	7	11	7	10	6	10	9	14
9g	6	9	11	14	6	9	8	13
Penicillin[a]	12		11		9		12	

[a] Standard antibacterial compound

The compound **9e** showed equal activity against Gram negative bacteria *Escherichia coli* when compared to that of the standard. The compound **9g** exhibited equal activity against Gram positive bacteria *Bacillus faecalis* when compared to that of *Penicillin*. Other compounds showed moderate activity.

3.Conclusion

We synthesized a series of novel [3-(4-chloro-phenoxy)-2,4-diisopropyl)-2,3,4,5-tetrahydro-1H-3λ^5-benzo[e][1,3,2]diazaphosphepin-3-ylidene]-alkyl-amines by Staudinger reaction in high yields. The advantages are low cost of the starting chemicals, simple experimental procedure and also these compounds exhibited moderate antibacterial activity.

4.Experimental Section

4.1 General

Solvents were used after purifying them by the established procedure, progress of the reaction and purity of the compounds were monitored by thin layer chromatography (TLC) using n-hexane and ethyl acetate (1:1 by volume) as eluting system on silica gel and iodine as visualizing agent. Melting points were determined in open capillary tubes on Melt-temp apparatus, microanalysis was performed at CDRI, Lucknow, India. IR spectra were recorded as KBr pellets on a Nicolet 380 double beam spectrophotometer ($\bar{\nu}$ in cm^{-1}) in Environmental Engineering Lab, S.V.University, Tirupati. ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX 400 MHz spectrometer operating at 400 MHz for ^1H and 100 MHz for ^{13}C, 161.9 MHz for ^{31}P NMR as solutions in DMSO-d_6. The ^1H and ^{13}C chemical shifts were referenced to tetramethyl silane and ^{31}P chemical shifts to 85% H_3PO_4 (*ortho* phosphoric acid). ^1H, ^{13}C and ^{31}P NMR spectral data were obtained from Indian Institute of Science, Bangalore, India. Mass spectra were recorded on a Jeol SX102 DA/600 mass spectrometer using Argon / Xenon (6 KV, 10 mA) as the FAB (fast atom bombardment) gas and also a Shimadzu QP-2000 GC-MS (gas chromatography – mass spectrometry) instrument.

4.2 Synthesis

General procedure for preparation of azides: iso-Butyl azide (8e). In a dry 100 mL round bottomed flask fitted with dropping funnel, calcium chloride tube, sodium azide (0.32 g, 0.005 mole) and 5 mL of dry THF were placed. The reaction mixture was stirred and iso-butyl bromide (0.549 g, 0.005 mole) in 100 mL of dry THF was added at room temperature, when the reaction started, the temperature was increased to 45-50°C. The mixture was cooled to room temperature to get pure iso-butyl azide (**8e**).

General procedure for preparation of 9a-g: [3-(4-chloro-phenoxy)-2,4-diisopropyl)-2,3,4,5-tetrahydro-1H-3λ^5-benzo[e] [1,3,2] diazaphosphepin -3-ylidene]-iso-butyl-amine (9e).α,α′-Dibromo-*o*-xylene (**1**) (1.31 g, 0.005 mole) was treated with two moles of iso-propylamine (**2**) (0.85 g, 0.01 mole) in the presence of triethylamine (0.01 mole) (TEA) in dry tetrahydrofuran (THF), stirred at low temperature (0-5°C) for 3 h. The progress of the reaction was judged by TLC analysis. The reaction mixture was filtered to remove triethylamine hydrobromide to give a solution of **3.**[29] Without further purification to the filtrate of **3**, a solution of phosphorus tribromide (**4**) (0.909 g, 0.005 mole) in 10 mL of dry THF, and triethylamine (0.01 mole) were added and the reaction mixture was stirred for one hour to form the intermediate phosphorobromidite **(5).** The progress of the reaction was judged by TLC analysis. The reaction mixture was filtered under nitrogen atmosphere to remove triethylamine hydrobromide. This on subsequent reaction with *p*-chlorophenol (**6**) (0.059 g, 0.005 mole) in the presence of TEA formed the compound **7.** This on subsequent reaction with iso-butyl azide (**8e**) (0.005 mole) in dry THF at 50-55°C under N_2 atmosphere in 4 hrs yielded the product **9e** with evolution of nitrogen. It was further purified by column chromatography using silica gel (60-120 mesh) as adsorbent and hexane and ethyl acetate (1:1) as an eluent to yield 1.409 g (73%) of **9e**, mp. 155-157°C.

Other compounds **9a-d, 9f** and **9g** were synthesized by adopting the above experimental procedure.

The representative analytical data for

***[3-(4-Chloro-phenoxy)-2,4-diiso-propyl-2,3,4,5-tetra-hydro-1H-3λ^5-benzo[e][1,3,2]diazaphosphepin-3-ylidene]-allylamine* (*9a*):** Pale-yellow solid, Yield: 71%; mp 150-152 °C; Molecular formula: $C_{23}H_{31}N_3POCl$. Elemental analysis: Carbon 63.90_{found} (63.95_{cal}); Hydrogen 7.18_{found} (7.23_{cal}); Nitrogen 9.68_{found} (9.72_{cal}); IR (KBr) ($\nu_{max}cm^{-1}$): 1375 (P-N), 1230 (P=N), 1022 (N-C); ^{1}H-NMR (400 MHz, DMSO-d_6) δ: 7.21 (d, *J*=9.2 H_Z, 2H, 3′ & 5′-H), 7.15 (d, *J*=7.5 H_Z, 2H, 2′ & 6′-H), 6.74 (quasi d, *J*=7.6 H_Z, 2H, 8 & 7-H), 6.44 (quasi d, *J*=8.1 H_Z, 2H,6 & 9-H), 6.05-5.93 (m, 1H, -CH_2-CH=CH_2), 5.30-5.21 (m, 2H, -CH_2-CH=CH_2), 4.75-4.70 (m, 2H,-CH), 4.05-3.98(m,4H, -CH_2), 3.13-3.10 (m, 2H, -CH_2-CH=CH_2), 1.17 (d, *J*=7.8 H_Z, 12H, (-CH_3)$_2$); ^{31}P NMR (161.9 MHz, DMSO-d_6) δ: -1.94.

***[3-(4-Chloro-phenoxy)-2,4-diiso-propyl-2,3,4,5-tetra-hydro-1H-3λ^5-benzo[e][1,3,2]diazaphosphepin-3-ylidene]-propyl-amine* (*9b*):** Pale-yellow solid, Yield: 70%; mp 145-147 °C; Molecular formula: $C_{23}H_{33}N_3POCl$. Elemental analysis: Carbon 63.58_{found} (63.65_{cal}); Hydrogen 7.62_{found} (7.66_{cal}); Nitrogen 9.63_{found} (9.68_{cal}); IR (KBr) ($\nu_{max}cm^{-1}$): 1381 (P-N), 1240 (P=N), 1033 (N-C); ^{1}H-NMR (400 MHz, DMSO-d_6) δ: 7.25 (d, *J* = 9.1 H_Z, 2H, 3′ & 5′-H), 7.18 (d, *J*=7.6 H_Z, 2H, 2′ & 6′-H), 6.75 (quasi d, *J*=7.8 H_Z, 2H,8 & 7-H), 6.42 (quasi d, *J*=8.0 H_Z, 2H,6 & 9-H), 4.78-4.73 (m, 2H,-CH), 4.04-3.97(m,4H,-CH_2), 2.42-2.27 (m, 2H, -CH_2-CH_2-CH_3), 1.30-1.25 (m, 2H, -CH_2-CH_2-CH_3), 1.16 (d, *J*=7.9 H_Z, 12H, (-CH_3)$_2$), 0.98 (t,

J=6.9Hz, 3H, -CH_2-CH_2-$\underline{CH_3}$) ; ^{13}NMR (100 MHz, DMSO-d_6) δ: 156.2(C-1′),131.2 (C-3′ & C-5′), 129.2 (C-10 & C-11), 128.2 (C-6 & C-9), 126.3 (C-4′), 122.2 (C-7 & C-8), 116.3 (C-2′ & C-6′), 55.7 (-$\underline{CH}$-$(CH_3)_2$), 54.8 (d, $^2J_{PNC}$=9.7 Hz.,$\underline{CH_2}$-CH_2-CH_3), 44.5(-CH_2), 30.3 (-CH-$\underline{CH_3}$)$_2$), 26.5 (d, *J*=4.2 Hz, -CH_2-$\underline{CH_2}$-CH_3), 12.3 (-CH_2-CH_2-$\underline{CH_3}$); ^{31}P NMR (161.9 MHz, DMSOd_6) δ: 0.14; MS:m/z (%)= 434(10.5,$M^{+\bullet}$), 393(54.2), 329(85.3), 231(100), 203(58.3), 162(78.3), 105(92.1), 83(45.2).

***[3-(4-Chloro-phenoxy)-2,4-diiso-propyl-2,3,4,5-tetra-hydro-1H-3λ^5-benzo[e][1,3,2]diazaphosphepin-3-ylidene]-iso-propylamine*(*9c*)**: Pale-yellow solid, Yield: 68%; mp 143-145 ^oC; Molecular formula: $C_{23}H_{33}N_3POCl$. Elemental analysis: Carbon 63.59_{found} (63.65_{cal}); Hydrogen 7.60_{found} (7.66_{cal}); Nitrogen 9.63_{found} (9.68_{cal}); IR (KBr) ($\nu_{max}cm^{-1}$): 1376 (P-N), 1235 (P=N), 1027 (N-C); ^{1}H-NMR (400 MHz, DMSO-d_6) δ: 7.28 (d, *J*=9.0 H_Z, 2H, 3′ & 5′-H), 7.20 (d, *J*=8.0 H_Z, 2H, 2′ & 6′-H), 6.73 (quasi d, *J*=7.9 H_Z, 2H,8 & 7-H), 6.43 (quasi d, *J*=8.4 H_Z, 2H,6 & 9-H), 4.81-4.75 (m, 2H,-CH), 4.04-3.98 (m,4H,-CH_2), 2.19-2.15 (-$\underline{CH}$-$(CH_3)_2$, m, H), 1.57 (d, *J* = 7.8 Hz, 6H, -CH-($\underline{CH_3}$)$_2$) 1.18 (d, *J*=8.0 H_Z, 12H, (-CH_3)$_2$); ^{31}P NMR (161.9 MHz, DMSO-d_6) δ: -5.65.

***[3-(4-Chloro-phenoxy)-2,4-diiso-propyl-2,3,4,5-tetra-hydro-1H-3λ^5-benzo[e][1,3,2]diazaphosphepin-3-ylidene]-butyl-amine* (*9d*)**: Pale-yellow solid, Yield: 69%; mp 151-153 ^oC; Molecular formula: $C_{24}H_{35}N_3POCl$. Elemental analysis: Carbon 64.26_{found} (64.34_{cal}); Hydrogen 7.83_{found} (7.87_{cal}); Nitrogen 9.30_{found} (9.37_{cal}); IR (KBr) ($\nu_{max}cm^{-1}$): 1373 (P-N), 1232 (P=N), 1029 (N-C); ^{1}H-NMR (400 MHz, DMSO-d_6) δ: 7.30 (d, *J*=8.9 H_Z, 2H, 3′ & 5′-H), 7.21 (d,*J*=7.9 H_Z, 2H, 2′ & 6′-H), 6.71 (quasi d, *J*=7.8 H_Z, 2H,8 & 7-H), 6.43 (quasi d, *J*=8.3 H_Z, 2H,6 & 9-H), 4.79-4.73 (m, 2H,-CH), 4.02-3.99(m,4H,-CH_2), 2.23-2.20 (-$\underline{CH_2}$-CH_2-CH_2-CH_3, m, 2H), 1.51-1.45 (-CH_2-$\underline{CH_2}$-CH_2-CH_3, m, 2H), 1.20 (d, *J*=7.7 H_Z, 12H, (-CH_3)$_2$), 1.20-1.17 (-CH_2-CH_2-$\underline{CH_2}$-CH_3, m, 2H), 0.98(t, *J*=7.0 Hz, 3H, -CH_2-CH_2-CH_2-$\underline{CH_3}$); ^{31}P NMR (161.9 MHz, DMSO-d_6) δ: -0.21.

***[3-(4-Chloro-phenoxy)-2,4-diiso-propyl-2,3,4,5-tetra-hydro-1H-3λ^5-benzo[e][1,3,2]diazaphosphepin-3-ylidene]-iso-butylamine* (*9e*)**: Pale-yellow solid, Yield: 73%; mp 155-157 ^oC; Molecular formula: $C_{24}H_{35}N_3POCl$. Elemental analysis: Carbon 64.25_{found} (64.34_{cal}); Hydrogen 7.82_{found} (7.87_{cal}); Nitrogen 9.31_{found} (9.37_{cal}); IR (KBr) ($\nu_{max}cm^{-1}$): 1384 (P-N), 1212 (P=N), 1019 (N-C); ^{1}H-NMR (400 MHz, DMSO-d_6) δ: 7.42 (d, *J*=8.6 H_Z, 2H, 3′ & 5′-H), 7.15 (d, *J*=8.0 H_Z, 2H, 2′ & 6′-H), 6.72 (quasi d, *J*=7.8 H_Z, 2H,8 & 7-H), 6.41 (quasi d, *J*=8.2 H_Z, 2H,6 & 9-H), 4.73-4.60 (m, 2H,-CH), 4.03-3.96 (m,4H,-CH_2), 3.31-3.14 (-CH_2-$\underline{CH}$-$(CH_3)_2$, m, 1H), 2.70-2.58 (-$\underline{CH_2}$-CH-$(CH_3)_2$, m, 2H), 1.15 (d, *J*=7.8 H_Z, 12H, (-CH_3)$_2$), 0.80(-CH_2-CH-($\underline{CH_3}$)$_2$, d, *J*=5.8 Hz, 6H); ^{13}C-NMR (100 MHz, DMSO-d_6) δ: 155.5(C-1′),130.3 (C-3′ & C-5′), 128.5 (C-10 & C-11), 128.3 (C-6 & C-9), 126.2 (C-4′), 122.1 (C-7 & C-8), 116.3 (C-2′ & C-6′),57.0 (-$\underline{CH_2}$-CH-$(CH_3)_2$), 55.1 (-$\underline{CH}$-$(CH_3)_2$), 45.4(-CH_2), 31.3 (-CH-($\underline{CH_3}$)$_2$), 29.1 (d, *J*=5.2 Hz, -CH_2-$\underline{CH}$-$(CH_3)_2$), 20.1 (-CH_2-CH-($\underline{CH_3}$)$_2$); ^{31}P NMR (161.9 MHz, DMSO-d_6) δ: 3.21;MS:m/z(%)=448(100,$M^{+\bullet}$),406(25.8),353(15.5)289(32.7),230(34.4),189(18.9).

***[3-(4-Chloro-phenoxy)-2,4-diiso-propyl-2,3,4,5-tetra-hydro-1H-3λ^5-benzo[e][1,3,2]diazaphosphepin-3-ylidene]-methyl-amine* (*9f*)**: Pale-yellow solid, Yield: 74%; mp 160-162 ^oC; Molecular formula: $C_{21}H_{29}N_3POCl$. Elemental analysis: Carbon 62.10_{found} (62.14_{cal}); Hydrogen 7.17_{found} (7.20_{cal}); Nitrogen10.30_{found} (10.35_{cal}); IR (KBr) ($\nu_{max}cm^{-1}$): 1385 (P-N), 1227 (P=N), 1021 (N-C); ^{1}H-NMR (400 MHz, DMSO-d_6) δ: 7.38 (d, *J*=8.5 H_Z, 2H, 3′ & 5′-H), 7.22 (d, *J*=7.8 H_Z, 2H, 2′ & 6′-H), 6.71 (quasi d, *J*=7.6 H_Z, 2H,8 & 7-H), 6.43 (quasi d, *J*=8.1 H_Z, 2H,6 & 9-H), 4.81-4.73 (m, 2H,-CH), 4.04-3.98(m,4H,-CH_2), 1.21(-CH_3, s, 3H) 1.19 (d, *J*=7.9 H_Z, 12H, (-CH_3)$_2$); ^{13}C-NMR (100 MHz, DMSO-d_6) δ: 156.3 (C-1′), 131.9 (C-3′ & C-5′),

128.9 (C-10 & C-11), 128.6 (C-6 & C-9), 126.5 (C-4′),122.5 (C-7 & C-8), 116.8 (C-2′ & C-6′), 55.5 (-CH-$(CH_3)_2$), 45.3(-CH_2), 30.5 (-CH-(CH_3)$_2$, 20.3 (d,[2] J_{PNC}=9.9Hz, CH_3); ^{31}P NMR (161.9 MHz, DMSOd_6) δ: 0.19;MS:m/z(%)=406 (63.2, $M^{+\bullet}$), 370 (15.7) 301 (40.3), 249 (22.8), 237 (68.4), 146 (66.6), 116 (47.3),100 (100).

***[3-(4-Chloro-phenoxy)-2,4-diiso-propyl-2,3,4,5-tetra-hydro-1H-3λ^5-benzo[e][1,3,2]diazaphosphepin-3-ylidene]-ethyl-amine* (*9g*):** Pale-yellow solid, Yield: 75%; mp 158-160 ^oC; Molecular formula: $C_{22}H_{31}N_3POCl$. Elemental analysis: Carbon 62.85_{found} (62.92_{cal}); Hydrogen 7.40_{found} (7.44_{cal}); Nitrogen 9.94_{found} (10.00_{cal}); IR (KBr) ($\nu_{max}cm^{-1}$): 1383 (P-N), 1233 (P=N), 1029 (N-C); ^{1}H-NMR (400 MHz, DMSO-d_6) δ: 7.40 (d, *J*=8.8 H_Z, 2H, 3′ & 5′-H), 7.32 (d, *J*=7.6 H_Z, 2H, 2′ & 6′-H), 6.73 (quasi d, *J*=7.8 H_Z, 2H,8 & 7-H), 6.42 (quasi d, *J*=8.0 H_Z, 2H,6 & 9-H), 4.90-4.85 (m, 2H,-CH), 4.02-3.96 (m,4H,-CH_2), 2.09-2.00 (-CH_2-CH_3, m, 2H), 1.23(-CH_2-CH_3, t, *J*=6.8 Hz, 3H) 1.18 (d, *J*=8.0 H_Z, 12H, (-CH_3)$_2$); ^{31}P NMR (161.9 MHz, DMSO-d_6) δ: 0.15.

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