Synthesis and Antimicrobial Activity of Novel Phosphorus Heterocycles with Exocyclic P–C Link

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Several new class of phosphorus heterocyclic compounds containing exocyclic P–C link such as 6-(2'-chloroethyl)/(allyl)/(benzyl)-1,2,4,8,10,11-hexachloro-12H-dibenzo[*d,g*][1,3,2]dioxaphosphocin 6-oxides (5–7), 2-(2''-chloroethyl)/(allyl)-6-(1,1-dimethylethyl)-3-cyclohexyl-3,4-dihydro-2H-1,3,2-benzoxazaphosphorin 2-oxides (9, 10), 2-(2''-chloroethyl)-2,3-dihydro-3-(4'-bromophenyl)-1H-naphth[1,2-*e*][1,3,2]-oxazaphosphorin 2-oxide (12), 2-(2''-chloroethyl)/(allyl)-2,3-dihydro-5-benzoyl-1H-1,3,2-benzodiazaphosphole 2-oxides (14, 15), 4-phenyl-2-(2''-chloroethyl)-1H-1,3,3a,5,6-pentaza-2-phosphapentalene 2-oxide (17) and 4-benzyl-2-(2''-chloroethyl)-1H-1,3,3a,5,6-pentaza-2-phosphapentalene 2-oxide (19) were synthesized by reacting equimolar quantities of corresponding diol (4)/diamines (13, 16, 18), 2-cyclohexylaminomethyl-4-*t*-butylphenol (8) and 1-(4'-bromoanilinomethyl)-2-naphthol (11), with respective phosphonyl dichlorides (1–3) in dry toluene/toluene-tetrahydrofuran/pyridine in the presence of triethylamine at various temperatures. Their structures were established by IR, ¹H-, ¹³C- and ³¹P-NMR spectral data. The mass spectral data were given for compounds 9, 12 and 15. The title compounds were screened for antibacterial activity against *Staphylococcus aureus* and *Escherichia coli* and antifungal activity on *Aspergillus niger* and *Helminthosporium oryzae*. Most of the compounds possess significant activity.

Key words phosphonyl dichloride; hexachlorophene; 1-(4-bromoanilinomethyl)-2-naphthol; 2-cyclohexylaminomethyl-4-*t*-butylphenol; 3,4-diaminobenzophenone; 5-phenyl-1,2-diamino-1,3,4-triazole

In the realm of organophosphorus chemistry, phosphonates are interesting complements, in terms of biological activity.¹⁾ They play an important and useful role as inhibitors of gene expression in mammalian cells²⁾ and as antibiotics.³⁾ They have been also developed to be used as insecticides,³⁾ herbicides,^{3,4)} fungicides^{3,5)} and plant growth regulators.⁴⁾ Recently, they gained importance in the treatment of bone disorders.⁶⁾

Denmark and Hua synthesized exocyclic P–C link compounds as *cis* and *trans* 3-substituted-2-benzyl-6-methyl-1,3,2-oxazaphosphorinane 2-oxides⁷⁾ and 2-allyl-1,3,2-oxazaphospholidine 2-oxides.⁸⁾ In our search for eco/bio-friendly pesticides, we have reported synthesis of several exocyclic P–O and P–NH link dioxaphosphocins,⁹⁾ oxazaphosphorins^{10,11)} and benzodiazaphospholes.¹²⁾ In continuation of our endeavour to develop potential pesticides, a new group of exocyclic P–C link compounds were synthesized.

1,2-Dichloroethane, allyl chloride and benzyl chloride reacted readily with phosphorus trichloride in the presence of aluminium chloride to give complexes, which on treatment with water gave good yields of 2-chloroethyl phosphonyl dichloride (1), allyl phosphonyl dichloride (2) and benzyl phosphonyl dichloride (3) (Chart 1),¹³⁾ respectively. But, vinylchloride did not react in a similar way to yield vinyl phosphonyl dichloride due to its inability to form the com-

plex with aluminium chloride because of extended π -electron delocalisation.

Synthesis of 5, 6, 7, 9, 10, 12, 14, 15, 17 and 19 was achieved by the cyclocondensation of equimolar quantities of hexachlorophene (4), 2-cyclohexylaminomethyl-4-*t*-butylphenol¹⁴⁾ (8), 1-(4-bromoanilinomethyl)-2-naphthol¹⁵⁾ (11), 3,4-diaminobenzophenone (13), 5-phenyl-1,2-diamino-1,3,4-triazole¹⁶⁾ (16) and 3-benzyl-4,5-diamino-1,2,4-triazole¹⁷⁾ (18) with 2-chloroethyl phosphonyl dichloride (1), allyl phosphonyl dichloride (2) and benzyl phosphonyl dichloride (3) in dry toluene/toluene-tetrahydrofuran/pyridine at various temperatures (Chart 2). Purifications of compounds were achieved by filtering off the triethylamine hydrochloride, evaporation of the filtrate, washing of the residue with water and recrystallization of the solid products employing suitable solvents (ethyl acetate-hexane/aqueous 2-propanol). Their structures were established by IR, ¹H-, ¹³C-, ³¹P-NMR and mass spectra.

The bridged methylene protons (12-CH₂) of 5, 6 and 7 showed two distinct doublets in the regions δ 4.36–4.42 and δ 4.81–4.86 due to *geminal* coupling. The expected long-range coupling [*J*_(H,P)] between phosphorus and one of the bridged methylene protons (12-CH₂) was not observed.^{18,19)} The bridged methylene protons (12-CH₂) in certain dibenzodioxaphosphocins, which are largely in the boat–chair conformation, exhibit only *geminal* coupling [*J*_(H,H)] and do not show long-range coupling with phosphorus [*J*_(H,P)].²⁰⁾ The *J*_(H,P) coupling would not be expected for molecules in a boat–chair conformation with the phosphoryl oxygen in a pseudo equatorial position, based upon the through space mechanism for transmission of coupling information, involving the lone pair of electrons of the endocyclic oxygen atoms.²¹⁾ On the same basis, it may be construed that the compounds 5, 6 and 7 may have the boat–chair (BC) confor-

Chart 1

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Chart 2

Fig. 1

mation, which is in rapid conformational equilibrium with either a boat-boat (BB) or a distorted and extended boat-like form²⁰⁾ (Fig. 1).

In compounds **9** and **10** the methylene (C-4) protons of the oxazaphosphorin ring moiety resonated as multiplets²²⁾ at δ 4.00—4.06 and δ 3.97—4.01 as a result of induced coupling with phosphorus. In compound **12**, the C-4 methylene protons gave two multiplets at δ 4.96—5.03 and δ 5.37—5.47 respectively, suggesting that they are magnetically non-equivalent due to their axial and equatorial orientations in the

Fig. 2

six-membered chair conformation of the benzoxazaphosphorin ring¹⁰⁾ (Fig. 2).

Antimicrobial Activity All the compounds **5**, **6**, **7**, **9**,

Table 1. Antimicrobial Activity of **5**, **6**, **7**, **9**, **10**, **12**, **14**, **15**, **17** and **19**

Compd.	Zone of inhibition (mm)							
	Bacteria				Fungi			
	<i>Staphylococcus aureus</i>		<i>Escherichia coli</i>		<i>Aspergillus niger</i>		<i>Helminthosporium oryzae</i>	
	250 ($\mu\text{g}/\text{disc}$)	500 ($\mu\text{g}/\text{disc}$)	250 ($\mu\text{g}/\text{disc}$)	500 ($\mu\text{g}/\text{disc}$)	250 ($\mu\text{g}/\text{disc}$)	500 ($\mu\text{g}/\text{disc}$)	250 ($\mu\text{g}/\text{disc}$)	500 ($\mu\text{g}/\text{disc}$)
5	14	18	16	19	18	26	20	26
6	12	15	12	17	15	24	15	20
7	13	19	10	15	16	22	14	18
9	5	8	4	6	10	16	10	15
10	— ^{a)}	—	—	—	12	18	9	13
12	10	16	8	15	14	20	12	18
14	6	9	4	8	10	15	8	12
15	—	—	—	—	9	14	6	10
17	12	16	8	15	12	16	10	17
19	10	14	12	16	8	12	12	18
Penicillin	22		21					
Streptomycin	27		25					
Griseofulvin					28		28	

a) — indicates no activity.

10, **12**, **14**, **15**, **17** and **19** (Table 1) were screened for their antibacterial activity against *Staphylococcus aureus* and *Escherichia coli* (10^6 cell/ml) by the disc-diffusion method²³⁾ in nutrient agar medium. Various concentrations of synthesized compounds (250, 500 $\mu\text{g}/\text{disc}$) dissolved in dimethylformamide (DMF) were added to each filter disc and DMF was used as control. Plates were incubated at 37 °C and examined for zone of inhibition around each disc after 24 h. The results were compared with standard antibiotics like penicillin and streptomycin (250 $\mu\text{g}/\text{disc}$). Their antifungal activity²⁴⁾ was evaluated against *Aspergillus niger* and *Helminthosporium oryzae* at concentrations of 250 and 500 $\mu\text{g}/\text{disc}$. Griseofulvin was used as reference compound. The fungal cultures were grown on potato dextrose broth at 25 °C for 3 d and finally spore suspension was adjusted to 10^5 spores/ml. Most of the compounds showed significant activity against both bacteria and fungi.

In summary, we have reported an effective and simple route for the synthesis of novel compounds with exocyclic P–C linkage and proved that dibenzodioxaphosphocin ring system exist preferentially in boat–chair conformation.

Experimental

Melting points determined on a Mel-Temp apparatus were uncorrected. IR spectra were recorded in KBr pellets on a Perkin–Elmer 1430 unit. The ^1H -, ^{13}C - and ^{31}P -NMR spectra were taken on AMX 400 MHz spectrometer operating at 400 MHz for ^1H , 100 MHz for ^{13}C and 161.9 MHz for ^{31}P . Compounds were referenced from TMS (^1H and ^{13}C , δ or ppm). All ^{31}P -NMR data were taken on similar solutions and referenced to 85% H_3PO_4 (^{31}P , δ or ppm). Mass spectral data were recorded for **12** on GC-MS at 70 eV, with a direct inlet system. General procedures for the preparations of **5**, **6**, **7**, **9**, **10**, **12**, **14**, **15**, **17** and **19** are illustrated with the synthesis of **5**.

Hexachlorophene (**4**), 3,4-diaminobenzophenone (**13**) were procured from Aldrich Chemical Company, Inc, U.S.A. and were used without further purification. **8**, **11**, **16** and **18** compounds were prepared according to the reported procedures.

Synthesis of 6-(2'-Chloroethyl)-1,2,4,8,10,11-hexachloro-12H-dibenzo[d,g][1,3,2]dioxaphosphocin 6-Oxide (5) 2-Chloroethyl phosphonyl dichloride (**1**, 0.36 g, 2 mmol) in dry toluene (20 ml) was added to the stirred solution of hexachlorophene (**4**, 0.812 g, 2 mmol) and triethylamine (0.404 g, 4 mmol) in dry toluene (40 ml) over a period of twenty minutes at 0 °C. The reaction mixture was slowly heated to 50–55 °C and stirring was continued

for 5 h. The progress of the reaction was monitored by thin layer chromatography (TLC) in the 1 : 4 mixture of ethyl acetate and hexane as mobile solvent. The reaction mixture was filtered to separate triethylamine hydrochloride and the solvent in the filtrate was removed off under reduced pressure. The crude cyclized product after washing with water and drying was recrystallized from ethyl acetate–hexane to obtain pure **5**. Yield 0.67 g (65%), mp 150–152 °C. *Anal.* Calcd for $\text{C}_{15}\text{H}_8\text{Cl}_6\text{O}_3\text{P}$; C, 34.96; H, 1.56. Found: C, 34.82; H, 1.68. IR (KBr) cm^{-1} : 1280 (P=O), 736 (P–C). ^{31}P -NMR (CDCl_3) δ : 22.0. ^1H -NMR (CDCl_3) δ : 7.55 (s, 2H, C-3, 9-H, Ar-H), [4.86 (d, $J=15.9$ Hz, 1H, Ha), 4.36 (d, $J=15.9$ Hz, 1H, Hb): bridged CH_2], 3.98–4.05 (m, 2H, CH_2Cl), 2.82–2.91 (m, 2H, P– CH_2). ^{13}C -NMR (CDCl_3) δ : 133.2 (s, 2C, C-1, 11), 131.6 (s, 2C, C-2, 10), 130.4 (d, $J=3.2$ Hz, 2C, C-3, 9), 125.0 (d, $J=6$ Hz, 2C, C-4, 8), 146.1 (d, $J=10.5$ Hz, 2C, C-4a, 7a), 129.4 (s, 2C, C-11a, 12a), 29.7 (s, 1C, C-12, bridged CH_2), 32.7 (d, $J_{\text{PC}}=132.8$ Hz, 1C, C-1', P– CH_2), 36.3 (s, 1C, C-2', CH_2Cl).

This procedure was used for the preparation of **6**, **7**, **9**, **10**, **12**, **14**, **15**, **17** and **19** compounds. The physical and spectroscopic data²⁵⁾ of all the compounds are given below.

6-(Allyl)-1,2,4,8,10,11-hexachloro-12H-dibenzo[d,g][1,3,2]dioxaphosphocin 6-Oxide (6) Yield: 0.55 g (56%); mp 106–108 °C. *Anal.* Calcd for $\text{C}_{16}\text{H}_9\text{Cl}_6\text{O}_3\text{P}$; C, 38.98; H, 1.84. Found: C, 38.79; H, 1.56. IR (KBr) cm^{-1} : 1234 (P=O), 737 (P–C). ^{31}P -NMR ($\text{DMSO}-d_6$) δ : 24.51. ^1H -NMR ($\text{DMSO}-d_6$) δ : 7.75 (s, 2H, C-3, 9-H, Ar-H), [4.81 (d, $J=16.2$ Hz, 1H, Ha), 4.39 (d, $J=16.2$ Hz, 1H, Hb); bridged CH_2], 2.58–2.87 (m, 2H, P– CH_2), 5.73–5.87 (m, 1H, CH), 5.12 (d, $J_{\text{trans}}=16.7$ Hz, CH_2), 5.04 (d, $J_{\text{cis}}=9.8$ Hz, CH_2), 7.59 and 7.60 (2d, $J_{\text{gem}}=2.7$, 2.4 Hz, CH_2). ^{13}C -NMR ($\text{DMSO}-d_6$) δ : 134.3 (C-1, 11), 130.6 (C-2, 10), 129.4 (C-3, 9), 126.2 (C-4, 8), 151.5 (C-4a, 7a), 128.7 (C-11a, 12a), 33.9 (C-12, bridged CH_2), 31.3 (d, $J_{\text{PC}}=160.0$ Hz, C-1', P– CH_2), 134.3 (C-2'), 117.5 (d, $J_{\text{PC}}=14$ Hz, C-3').

6-(Benzyl)-1,2,4,8,10,11-hexachloro-12H-dibenzo[d,g][1,3,2]dioxaphosphocin 6-Oxide (7) Yield: 0.55 g (51%); mp 152–154 °C. *Anal.* Calcd for $\text{C}_{20}\text{H}_{11}\text{Cl}_6\text{O}_3\text{P}$; C, 44.23; H, 2.04. Found: C, 44.45; H, 2.19. IR (KBr) cm^{-1} : 1287 (P=O), 730 (P–C). ^{31}P -NMR ($\text{DMSO}-d_6$) δ : 23.94. ^1H -NMR ($\text{DMSO}-d_6$) δ : 7.60 (s, 2H, C-3, 9-H), [4.84 (d, $J=16.0$ Hz, 1H, Ha), 4.42 (d, $J=16.0$ Hz, 1H, Hb); bridged CH_2], 7.21–7.74 (m, 5H, Ar-H), 3.21 (d, $J_{\text{PH}}=20.2$ Hz, P– CH_2). ^{13}C -NMR ($\text{DMSO}-d_6$) δ : 134.3 (C-1, 11), 131.0 (C-2, 10), 129.7 (C-3, 9), 125.8 (C-4, 8), 151.6 (C-4a, 7a), 128.7 (C-11a, 12a), 29.7 (C-12, bridged CH_2), 31.3 (d, $J_{\text{PC}}=162.9$ Hz, C-1', P– CH_2), 134.3 (C-2'), 128.6 (C-3', 7'), 127.7 (C-4', 6'), 126.3 (C-5').

2-(2'-Chloroethyl)-6-(1,1-dimethylethyl)-3-cyclohexyl-3,4-dihydro-2H-1,3,2-benzoxazaphosphorin 2-Oxide (9) Yield: 0.46g (62%); mp 203–205 °C. *Anal.* Calcd for $\text{C}_{19}\text{H}_{29}\text{NPO}_3\text{Cl}$; C, 61.68; H, 7.90; N, 3.78. Found: C, 61.82; H, 7.73; N, 3.86. IR (KBr) cm^{-1} : 1262 (P=O), 742 (P–C). ^{31}P -NMR (CDCl_3) δ : 16.00. ^1H -NMR (CDCl_3) δ : 6.85–7.48 (m, 3H, Ar-H), 4.00–4.06 (m, 2H, 4- CH_2), 1.26 (s, 9H, *t*-butyl-H), 1.45–1.78 (m, 11H, Cyclohexyl-H), 3.79–3.85 (m, 2H, CH_2Cl), 2.51–2.68 (m, 2H, P– CH_2). ^{13}C -NMR (CDCl_3) δ : 43.6 (C-4), 123.8 (C-5), 147.1 (C-6), 126.3 (C-7),

118.2 (d, $J=7.1$ Hz), 147.6 (d, $J=7.4$ Hz, C-9), 124.5 (s, 1C, C-10), 34.7 (C-11), 31.9 (C-12), 55.6 (C-1'), 32.1 (C-2', 6'), 25.8 (C-3', 5'), 25.2 (C-4'), 31.4 (d, $J_{PC}=145.1$ Hz, C-1'', P-CH₂), 36.3 (C-2'', CH₂Cl). EI-MS m/z (%): 347 (13, M⁺), 291 (30), 262 (65), 245 (37), 219 (40), 164 (56), 147 (38), 91 (31), 56 (100).

2-(Allyl)-6-(1,1-dimethylethyl)-3-cyclohexyl-3,4-dihydro-2H-1,3,2-benzoxazaphosphorin 2-Oxide (10) Yield: 0.41 g (58%); mp 186–188 °C. *Anal.* Calcd for C₂₀H₃₀NPO₂: C, 68.26; H, 8.95; N, 3.98. Found: C, 68.49; H, 8.26; N, 3.98. IR (KBr) cm⁻¹: 1224 (P=O), 736 (P-C). ³¹P-NMR (DMSO-*d*₆) δ : 18.48. ¹H-NMR (DMSO-*d*₆) δ : 7.02–7.42 (m, 5H, Ar-H + olefinic-H), 1.13 (s, 9H, *t*-butyl-H), 1.60–2.10 (m, 11H, Cyclohexyl-H), 3.97–4.01 (m, 2H, 4-CH₂), 3.62–3.90 (m, 2H, P-CH₂), 5.04–5.93 (m, 1H, CH), 5.09 (d, $J_{trans}=17.6$ Hz, 2H, CH₂), 5.92 (d, $J_{cis}=9.5$ Hz, 2H, CH₂). ¹³C-NMR (DMSO-*d*₆) δ : 42.9 (C-4), 124.4 (C-5), 149.3 (C-6), 126.9 (C-7), 117.7 (C-8), 145.7 (C-9), 122.7 (C-10), 34.4 (C-11), 33.1 (C-12), 55.4 (C-1'), 33.9 (C-2', 6'), 24.8 (C-3', 5'), 24.0 (C-4'), 31.3 (d, $J_{PC}=156.2$ Hz, C-1'', P-CH₂), 132.4 (C-2''), 116.7 (d, $J_{PC}=13.3$ Hz, C-3'').

2-(2''-Chloroethyl)-2,3-dihydro-3-(4'-bromophenyl)-1H-naphth[1,2-*e*][1,3,2]oxazaphosphorin 2-Oxide (12) Yield: 0.59 g (68%); mp 235–237 °C. *Anal.* Calcd for C₁₉H₁₆NPO₂ClBr: C, 52.26; H, 3.69; N, 3.20. Found: C, 52.08; H, 3.54; N, 3.09. IR (KBr) cm⁻¹: 1217 (P=O), 744 (P-C). ³¹P-NMR (CDCl₃) δ : 18.94. ¹H-NMR (CDCl₃) δ : 7.13–7.78 (m, 10H, Ar-H), [5.37–5.47 (m, Ha), 4.96–5.03 (m, Hb); 4-CH₂], 4.23–4.28 (m, 2H, CH₂Cl), 2.67–2.75 (m, 2H, P-CH₂). ¹³C-NMR (CDCl₃) δ : 51.4 (C-4), 130.7 (C-5), 121.9 (C-6), 129.6 (C-7), 129.0 (C-8), 127.5 (C-9), 119.0 (C-10), 149.6 (C-11), 114.5 (C-12), 132.8 (C-13), 128.5 (C-14), 147.1 (C-1'), 118.7 (C-2', 6'), 132.5 (C-3', 5'), 112.2 (C-4'), 32.4 (d, $J_{PC}=131.9$ Hz, C-1'', P-CH₂), 36.7 (C-2'', CH₂Cl). GC-MS m/z (%): 437 [27, (M⁺+2)], 435 (19, (M⁺)), 372 (28.5), 326 (13.3), 325 (11.4), 309 (65), 293 (9), 230 (65), 184 (19), 173 (21), 171 (19), 156 (18), 144 (28), 128 (60), 83 (100).

2-(2''-Chloroethyl)-2,3-dihydro-5-benzoyl-1H-1,3,2-benzodiazaphosphole 2-Oxide (14) Yield: 0.33 g (52%); mp 158–160 °C (d). *Anal.* Calcd for C₁₅H₁₄N₂PO₂Cl: C, 56.17; H, 4.39; N, 8.73. Found : C, 56.28; H, 4.52; N, 8.61. IR (KBr) cm⁻¹: 1260 (P=O), 797 (P-C), 3352 (P-NH), 1621 (C=O). ³¹P-NMR (DMSO-*d*₆) δ : 21.22. ¹H-NMR (DMSO-*d*₆) δ : 7.07 (s, 4-H), 6.55 (d, $J=7.8$ Hz, 6-H), 6.90 (d, $J=8.1$ Hz, 7-H), 7.48–7.59 (m, 5H, benzoyl-H), 3.67–3.72 (m, 2H, CH₂Cl), 2.68–2.76 (m, 2H, P-CH₂).

2-(Allyl)-2,3-dihydro-5-benzoyl-1H-1,3,2-benzodiazaphosphole 2-Oxide (15) Yield: 0.36 g (60%); mp 149–151 °C. *Anal.* Calcd for C₁₆H₁₅N₂PO₂: C, 64.42; H, 5.06; N, 9.39. Found: C, 64.54; H, 5.26; N, 9.27. IR (KBr) cm⁻¹: 1262 (P=O), 1604 (C=O), 3356 (P-NH), 728 (P-C). ³¹P-NMR (DMSO-*d*₆) δ : 24.37. ¹H-NMR (DMSO-*d*₆) δ : 6.93 (s, 4-H), 6.72 (d, $J=7.9$ Hz, 6-H), 7.00 (d, $J=7.2$ Hz, 7-H), 7.18–7.59 (m, 7H, benzoyl-H + olefinic-H), 9.08 (br s, 2H, NH), 3.66–3.87 (m, 2H, P-CH₂), 5.29–5.89 (m, 1H, CH), 5.26 (d, $J_{trans}=18$ Hz, CH₂), 5.64 (d, $J_{cis}=11.6$ Hz, CH₂). EI-MS m/z (%): 298 (35, M⁺), 241 (20), 212 (7), 136 (100), 107 (50), 105 (30).

4-(Phenyl)-2-(2''-chloroethyl)-1H-1,3,3a,5,6-pentaza-2-phosphapentalene 2-Oxide (17) Yield: 0.25 g (44%); mp 238–240 °C. *Anal.* Calcd for C₁₀H₁₁N₅POCl: C, 42.34; H, 3.90; N, 24.68. Found: C, 42.18; H, 3.69; N, 24.45. IR (KBr) cm⁻¹: 1205 (P=O), 782 (P-C), 3363 (P-NH). ³¹P-NMR (DMSO-*d*₆) δ : 24.17. ¹H-NMR (DMSO-*d*₆) δ : 7.17–7.79 (m, 5H, Ar-H), 13.83 (d, $J=24.7$ Hz, N-NH), 9.11 (s, P-NH), 2.02–2.30 (m, 2H, P-CH₂), 3.09–3.73 (m, 2H, CH₂Cl). ¹³C-NMR (DMSO-*d*₆) δ : 157.4 (C-4, C=N), 157.7 (C-6a, C=N), 144.9 (C-1'), 125.6 (C-2', 6), 129.0 (C-3', 5'), 129.8 (C-4'), 29.6 (d, $J_{PC}=133.4$ Hz, C-1'', P-CH₂), 45.8 (C-2'', CH₂Cl).

4-(Benzyl)-2-(2''-chloroethyl)-1H-1,3,3a,5,6-pentaza-2-phosphapentalene 2-Oxide (19) Yield: 0.22 g (42%); mp 206–208 °C. *Anal.* Calcd for C₁₁H₁₃N₅POCl: C, 44.38; H, 4.40; N, 23.52. Found: C, 44.52; H, 4.27; N, 23.63. IR (KBr) cm⁻¹: 1258 (P=O), 3210 (P-NH), 803 (P-C). ³¹P-NMR (DMSO-*d*₆) δ : 22.33. ¹H-NMR (DMSO-*d*₆) δ : 7.01–7.36 (m, 4H, Ar-H),

4.63 (s, 2H, 1'-CH₂), 10.19 (d, $J=24.3$ Hz, N-NH), 6.30 (s, 1H, P-NH), 2.14–2.29 (m, 2H, P-CH₂), 3.68–4.06 (m, 2H, CH₂Cl).

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