SYNTHESIS, SPECTRAL CHARACTERIZATION AND ANTIMICROBIAL ACTIVITY OF 4-α-ARYL AMINO BENZYL DINAPHTHO [2,1-d:1',2'-f][1,3,2] DIOXAPHOSPHEPIN 4-OXIDES

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Abstract: 4-α-Arylamino benzyl dinaphtho [2,1-d:1',2'-f][1,3,2] dioxaphosphepin 4-oxides **4a-j**) were synthesized in excellent yield from three-component one pot reaction of aldehydes, anilines and dinaphtho [2,1-d:1',2'-f][1,3,2] dioxaphosphorobromodite **2** / corresponding hydrogen-phosphite **3** intermediates and characterized by IR, ^{1}H, ^{13}C and ^{31}P NMR spectral data and the title compounds were screened for their antimicrobial activity.

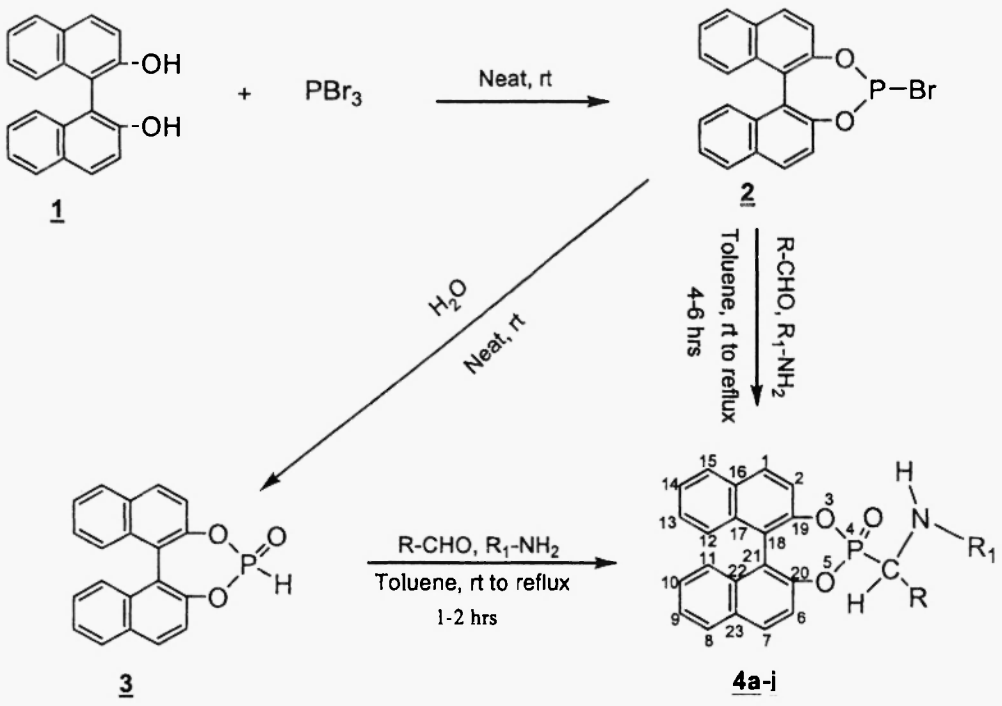
Introduction

Synthesis of α-aminophosphonates has attracted much interest because of their biological activity and structural similarity with α-amino acids (1). They also act as enzyme inhibitors (2), antibiotics and pharmacological agents (3), herbicides (4) and haptens of catalytic antibodies (5). Aminophosphonic acids are also found as constituents in bioactive natural products. In view of this, the title compounds **4a-j** were synthesized and characterized by elemental, ir and nmr (^{1}H, ^{13}C and ^{31}P) and tested for their antibacterial activity.

Results and discussion

Synthesis of title compounds **4a-j** was accomplished through bisphenolic phorobromodite (6) **2** and corresponding hydrogenphosphite (7,8) **3**. Cyclization of binaphthol **1** with phosphorus tribromide (PBr_3) in presence of solvent and base according to the literature procedure afforded the phosphorobromodite intermediate **2** in very low yield due to the formation of byproducts. But the same reaction with slight excess of PBr_3 under neat conditions yielded the phosphorobromodite **2** in pure form with almost quantitative yield. This simple modification being cost- effective and devoid of side reactions offers the intermediate **2** in the pure form by the removal of the excess PBr_3 under vacuum conditions and it could be used for further reactions. Reaction of **2** with equimolar quantities of aldehydes and anilines in presence of triethylamine in dry toluene under reflux conditions afforded **4** in low yield (75-80 %). Alternatively the title compounds prepared through the hydrogenphosphite intermediate **3** which is obtained by hydrolysis of **2** with water and on drying under vacuum. Reaction of **3** in the same vessel with equimolar quantities of aldehydes and anilines in presence of triethylamine in dry toluene under reflux conditions led to the formation of title compounds **4a-j** in excellent yield (91-95 %). The later procedure is better for it afforded the products **4a-j** with high yields in less time.

Compounds, **4a-j** exhibited characteristic IR absorptions (C-NH), (P=O) and (P-C) bonds (9-11). Aromatic protons resonated at δ 6.70-8.59. N-H proton signal appeared at δ 5.00-6.76. C-H proton gave a doublet at δ 4.46-5.34 (J = 9.9-25.4 Hz) . ^{13}C NMR chemical shifts were interpreted based on comparison with carbon chemical shifts of **3** and related systems (12).The benzyl carbon (P-CH) gave a doublet at δ 51.0-54.28 (J_{PC} = 134.2-147.2 Hz) . ^{31}P NMR signals (13) appeared in the region 23.86-34.01 ppm.



Compd.	R	R_1	Compd.	R	R_1
4a	C_6H_4-Cl (4')	C_6H_4-Br (4")	4f	C_6H_4 (2'-allyl, 3'-OCH_3)	C_6H_4-OCH_3(4")
4b	C_6H_4-Cl (4')	C_6H_4-OCH_3 (4")	4g	C_6H_4-OCH_3 (4')	C_6H_4-Br (4")
4c	C_4H_3S (2')	C_6H_4-Br (4")	4h	C_6H_4-OCH_3 (4')	C_6H_4-OCH_3 (4")
4d	C_4H_3S (2')	C_6H_4-OCH_3 (4")	4i	C_6H_4-$(OCH_3)_2$ (3'&5')	C_6H_4-Br (4")
4e	C_6H_4 (2'-allyl, 3'-OCH_3)	C_6H_4-Br (4")	4j	C_6H_4-$(OCH_3)_2$ (3'&5')	C_6H_4-OCH_3 (4")

Scheme-1

Antimicrobial Activity

Antibacterial Activity

The title 4-α-arylamino benzyl dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin 4-oxides **4a-j** were screened against the growth of *Staphylococcus aureus* (gram +ve) and *Klebsiella pneumoniae* (gram - ve) at concentrations 100, 50 and 25 ppm. Majority of the compounds are highly active against the growth of both *Staphylococcus aureus* and *Klebsiella pneumoniae*. All these results are furnished in Table-1. Penicillin is tested as standard reference compound to compare the activity of these compounds (14)

It is interesting to note that the compounds **4a**, **4b**, **4c**, **4d** and **4g** exhibited very high antibacterial activity.

Compounds **4a**, **4b**, **4c**, **4d** and **4g** exhibited very high activity against *Klebsiella pneumoniae* when compared to the activity of the standard penicillin.

In view of their very strong antibacterial activity, further detailed study on the evaluation of their antibacterial activity is in progress to explore their commercial application.

Antifungal Activity

All compounds **4a-i** were tested for their antifungal activity against the *Pellicularia solmanicolor* (pink disease) and *Macrophomina phaseolina* (dry root rot sunflower and citrus) with three different concentrations (100, 50 and 25 ppm). All these results are presented in Table 1. Most of the compounds showed significant antifungal activity against the growth of both fungi. *Griseofulvin* is used as reference compound to compare the activity of these compounds (15). It is gratifying to note that the compounds **4a**, **4c**, **4d** and **4f** exhibited higher activity than that of the standard *Griseofulvin*, further detailed evaluation of their activity at even lower concentration is in progress. Probably one can find a potential antifungal active compound among them.

Experimental

Melting points were determined in open capillary tubes and are uncorrected. Elemental analyses were performed at the Central Drug Research Institute, Lucknow, India. IR spectra were recorded as KBr pellets on a Perkin - Elmer, 1430 unit. All NMR spectra were recorded on a AMX - 400 MHz, spectrometer, operating at 400 MHz for ^{1}H, 100 MHz for ^{13}C and 161.9 MHz for ^{31}P. Compounds were dissolved in $CDCl_3$ and the chemical shifts were referenced to TMS (^{1}H & ^{13}C) and 85% H_3PO_4 (^{31}P).

Table-1: Antifungal and Antibacterial Activities of Compounds 4 in Terms of Zone of Inhibition (mm)

Compd.	Bacteria						Fungi					
	Klebsiella pneumoniae			Staphylococcus aureus			*Pellicularia solmanicolor*			*Macrophomina phaseolina*		
	100	50	25	100	50	25	100	50	25	100	50	25
4a	14	8	4	11	8	6	-	-	-	11	6	-
4b	13	8	4	10	8	6	11	8	4	14	9	4
4c	15	12	8	12	9	5	13	9	6	15	10	6
4d	15	12	7	13	10	9	12	10	8	16	9	4
4e	-	-	-	10	8	-	9	5	3	14	11	9
4f	10	5	-	-	-	-	9	5	-	9	-	-
4g	12	8	-	11	8	6	14	10	9	13	12	8
4h	8	5	-	-	-	-	13	9	8	12	10	6
4i	8	4	-	12	10	6	13	9	9	11	9	9
4j	9	4	2	11	9	6	12	8	8	11	8	5
Penicillin	10	6	-	9	5	-						
Griseofulvin							8	5	-	12	9	-

Concentrations expressed in ppm
'-' indicates no activity

Bisphenolic phorobromodite 2 and corresponding hydrogenphosphite 3

To a cold (10-15 °C) solution of slight excess phosphorus tribromide (1.40 g, 0.0052 mol), binaphthol (1, 1.43 g, 0.005 mol) is added portion wise. After the addition, the temperature was slowly raised to room temperature and stirring was continued for an additional one hour. Progress

of the reaction was monitored by thin layer chromatography (TLC) analysis. The excess PBr_3 is removed by distillation in vacuum and the residual product **2** is used for further reactions. (^{31}P: δ 142).

Compound **2** is cooled to 10-15 °C, water (0.09 g, 0.005 mol) is added. After the addition, temperature was slowly raised to room temperature and stirred for an additional one hour. Progress of the reaction was monitored by TLC analysis. Residue of hydrogenphosphite **3** is dried by vacuum suction (^{31}P: δ 1.36) mp 181-182 °C

4-α-(4'-Bromo) phenyl amino (4'-chloro) benzyl dinaphtho [2, 1-d: 1', 2'-f][1, 3, 2] dioxaphosphepin 4-oxide 4a through intermediate 2

The residue of phosphorobromodite **2** was dissolved in dry toluene (20 mL) and kept stirred. 4-chlorobenzaldehyde (0.70 g, 0.005 mol), 4-bromoaniline (0.86 g, 0.005 mol) and a catalytic amount of triethylamine in dry toluene (20 mL) were added at room temperature and the temperature was raised to reflux and stirring was continued for an additional 4-5 hours. Progress of the reaction was monitored by TLC analysis. The solvent was removed under reduced pressure. The residue was purified by column chromatography on 60-120 mesh silica gel using ethyl acetate: hexane (1:2) as an eluent to yield 2.56 g (82%) of **4a**, mp 210-211°C.

4-α-(4'- Bromo) phenyl amino (4'-chloro) benzyl dinaphtho [2,1-d:1',2'-f][1,3,2] dioxaphosphepin 4-oxide 4a through cyclic hydrogen phosphate 3

The residue of hydrogenphosphite **3** was dissolved in dry toluene (20 mL) and kept stirred. 4-chlorobenzaldehyde (0.70 g, 0.005 mol), 4-bromoaniline (0.86 g, 0.005 mol) and a catalytic amount of triethylamine in dry toluene (20 mL) were added at room temperature and the temperature was raised to reflux and stirring was continued for an additional 90-120 min. Progress of the reaction was monitored by TLC analysis. The solvent was removed under reduced pressure. The residue was purified by column chromatography on 60-120 mesh silica gel using ethyl acetate: hexane (1:2) as an eluent to yield 2.91 g (93%) of **4a**, mp 210-211°C. Yield: 93%, mp: 170 - 172°C.

IR (KBr): ν 1224 (P=O), 746 (P-C), 3305 cm^{-1} (C-NH), ^{1}HNMR (400 MHz, $CDCl_3$ / TMS): δ 8.16-6.62(m, 20H), 5.45(brs, 1H, N-H), 5.20(d, *J*=25.4 Hz, 1H, P-CH), ^{13}CNMR (100 MHz, $CDCl_3$/ TMS): δ 138.41, 138.22 (s, 2C, C-1 & 7), 136.29, 136.07 (s, 2C, C-2 & 6), 142.67, 142.46(s, 2C, C-19 & 20), 134.91, 134.61 (s, 2C, C-8 & 15), 133.48, 138.25 (s, 2C, C-9 & 14), 132.96, 132.27(s, 2C, C-10 & 13'), 132.13,132.03(s, 2C, C-11 & 12), 131.91, 130.54 (s, 2C, C-16 & 17), 130.51, 130.19 (s, 2C, C-22 & 23), 130.15, 129.53 (s, 2C, C-18 & 21), 54.20 (d, *J*=147.2 Hz, 1C, P-CH), 134.0(s, 1C, C-1'), 126.8 (s, 2C, C-2' & 6'), 128.1(s, 2C, C-3' & 5'), 130.0(s, 1C, C-4'), 153.8(s, 1C, C-1"), 116.8(s, 2C, C-2" & 6"), 130.1(s, 2C, C-3" & 5"), 128.4(s, 1C, C-4"), ^{31}PNMR (161.9 MHz, $CDCl_3$/ H_3PO_4): δ 33.08, Anal. Calcd. for $C_{33}H_{22}O_3NPClBr$ (626.54): C, 63.20; H, 3.54; N, 2.23., Found C, 63.29; H, 3.61; N, 2.30 %.

Other members of **4** are prepared by adopting the same procedure.

4-α-(4'-Methoxy) phenyl amino (4'-chloro) benzyl dinaphtho [2,1-d:1',2'-f][1,3,2] dioxaphosphepin 4-oxide 4b.

Yield: 95% mp: 121 - 123°C
IR (KBr): ν 1250 (P=O), 717 (P-C), 3306 cm^{-1} (C-NH)

^{1}HNMR (400 MHz, $CDCl_3$ /TMS): δ 8.28-6.14 (m, 20H), 5.00(s, 1H, N-H), 5.34(d, *J*=25.2 Hz, 1H, P-CH), 3.34(s,1H, OCH_3)

^{13}CNMR (100 MHz, $CDCl_3$/ TMS) : δ 140.50,140.43 (s, 2C, C-1 & 7), 140.32, 136.14 (s, 2C, C-2 & 6), 134.99, 133.91(s, 2C, C-19 & 20), 133.88, 133.39(s, 2C, C-8 & 15), 133.23, 132.80(s, 2C, C-9 & 14), 132.67, 132.14(s, 2C, C-10 & 13), 132.12, 132.00(s, 2C, C-11 & 12), 131.01, 130.83(s, 2C, C-116& 17), 130.79, 130.55(s, 2C, C-22 & 23), 130.51, 129.34 (s, 2C, C-18 & 21), 52.4 (d, *J*=135.2 Hz, 1C, P-CH), 132.0(s, 1C, C-1'), 128.4 (s, 2C, C-2' & 6'),126.7 (s, 2C, C-3' & 5'), 131.10(s, 1C, C-4'), 153.4(s, 1C, C-1"), 117.6(s, 2C, C-2" & 6"), 130.54(s, 2C, C-3" & 5"), 133.0(s, 1C, C-4"), 55.2(s, 1C, OCH_3)

^{31}PNMR (161.9 MHz, $CDCl_3$/ H_3PO_4): δ 33.60
Anal. Calcd. for $C_{34}H_{25}O_4NPCl$(577.66): C, 70.64; H, 4.36; N, 2.42.
Found C, 70.71; H, 4.41; N, 2.49 %

4-α-(4'-Bromo) phenyl amino 2'-thiophenemethyl dinaphtho [2,1-d:1',2'-f][1,3,2] dioxaphosphepin 4-oxide 4c.
Yield: 91% mp: 150 - 152°C
IR (KBr): ν 1239 (P=O), 749 (P-C), 3316 cm^{-1} (C-NH)
^{1}HNMR (400 MHz, $CDCl_3$ /TMS): δ 8.14-6.42(m, 19H), 5.79(s, 1H, N-H), 5.19(s, 1H, P-CH)
^{31}PNMR (161.9 MHz, $CDCl_3$/ H_3PO_4): δ 33.28
Anal. Calcd. for $C_{31}H_{21}O_3NPBrS$(598.139): C, 62.20; H, 3.53; N, 2.34.
Found C, 62.28; H, 3.61; N, 2.42%

4-α-(4'-Methoxy) phenyl amino 2'-thiophenemethyl dinaphtho [2,1-d:1',2'-f][1,3,2] dioxaphosphepin 4-oxide 4d.
Yield: 92% mp: 176 - 178°C
IR (KBr): ν 1239 (P=O), 749 (P-C), 3316 cm^{-1} (C-NH)
^{1}HNMR (400 MHz, $CDCl_3$ /TMS): δ 8.16-6.59(m, 19H), 5.83(s, 1H, N-H), 5.34(d, *J*=25.4 Hz, 1H, P-CH), 3.46(s, 3H, OCH_3)
^{31}PNMR (161.9 MHz, $CDCl_3$/ H_3PO_4): δ 33.28
Anal. Calcd. for $C_{32}H_{24}O_4NPS$(549.26): C, 69.91; H, 4.40; N, 2.55.
Found C, 70.01; H, 4.48; N, 2.49 %

4-α-(4'-Bromo) phenyl amino (2'-allyl, 3'-methoxy) benzyl dinaphtho [2,1-d:1',2'-f][1,3,2] dioxaphosphepin 4-oxide 4e.
Yield: 93% mp: 189 - 191°C
IR (KBr): ν 1239 (P=O), 749 (P-C), 3316 cm^{-1} (C-NH)
^{1}HNMR (400 MHz, $CDCl_3$ /TMS): δ 8.30-6.69(m, 19H), 6.70(d, *J*=8.8 Hz, 1H, N-H), 4.46(d, *J*=9.9 Hz, 1H, P-CH), 2.54-2.48(m, 2H, Ar-CH_2-CH=CH_2), 5.27-5.18(m, 2H, Ar-CH_2-CH=CH_2), 4.98-5.00(m, 1H, Ar-CH_2-CH=CH_2), 3.37(s, 3H, OCH_3).
^{13}CNMR (100 MHz, $CDCl_3$/ TMS): δ 140.90, 140.87 (s, 2C, C-1 & 7), 140.67, 140.63 (s, 2C, C-2 & 6), 139.93, 139.87(s, 2C, C-19 & 20), 139.83, 139.76(s, 2C, C-8 & 15), 133.72, 132.69(s, 2C, C-9 & 14), 132.54, 132.38(s, 2C, C-10 & 13), 132.22, 132.08(s, 2C, C-11 & 12), 131.22, 129.50(s, 2C, C-16 & 17), 129.34, 129.18(s, 2C, C-22 & 23), 128.97, 128.58 (s, 2C, C-18 & 121), 54.1 (d, *J*=139.2 Hz, 1C, P-CH), 132.2(s, 1C, C-1'), 127.4 (s, 2C, C-2' & 6'),126.7 (s, 2C, C-3' & 5'), 131.10(s, 1C, C-4'), 55.26(s, 1C, OCH_3), 131.3 (d, *J*= 60.0 Hz, C-1, Ar-CH_2-CH=CH_2), 130.3

(Ar-CH_2-CH=CH_2), 117.5 (d, J = 14 Hz, Ar-CH_2-CH=CH_2), 153.8(s, 1C, C-1"), 117.2(s, 2C, C-2" & 6"), 131.54(s, 2C, C-3" & 5"), 137.2(s, 1C, C-4")
^{31}PNMR (161.9 MHz, $CDCl_3$/ H_3PO_4): δ 33.28
Anal. Calcd. for $C_{37}H_{29}O_4NPBr$(662.15): C, 67.06; H, 4.41; N, 2.11.
Found C, 66.98; H, 4.46; N, 2.22 %

4-α-(4^1-Methoxy) phenyl amino (2^1-allyl, 3^1-methoxy) benzyl dinaphtho [2,1-d:1',2'-f][1,3,2] dioxaphosphepin 4-oxide 4f.
Yield: 93% mp: 180 - 182°C
IR (KBr): ν 1265(P=O), 741 (P-C), 3321 cm^{-1} (C-NH)
^{1}HNMR (400 MHz, $CDCl_3$ /TMS): δ 8.24-6.62(m, 19H), 6.70(d, J = 8.8 Hz, 1H, N-H), 5.23(d, J=9.9 Hz, 1H, P-CH), 2.51-2.49(m, 2H, Ar-CH_2-CH=CH_2), 5.20-5.24(m, 2H, Ar-CH_2-CH=CH_2), 4.99-5.09(m, 1H, Ar-CH_2-CH=CH_2), 3.38, 3.29(s, 6H, 2(OCH_3).
^{31}PNMR (161.9 MHz, $CDCl_3$/ H_3PO_4): δ 33.44
Anal. Calcd. for $C_{38}H_{32}O_5NP$ (613.27): C, 74.36; H, 5.26; N, 2.28.
Found C, 74.41; H, 5.30; N, 2 35 %

4-α-(4^1-Bromo) phenyl amino (4^1-methoxy) benzyl dinaphtho [2,1-d:1',2'-f][1,3,2] dioxaphosphepin 4-oxide 4g.
Yield: 94% mp: 195 - 196°C
IR (KBr): ν 1239 (P=O), 749 (P-C), 3316 cm^{-1} (C-NH)
^{1}HNMR (400 MHz, $CDCl_3$ /TMS): δ 8.59-6.74(m, 20H), 6.76(d, J=8.7 Hz, 1H, N-H), 5.00(d, J=24.4 Hz, 1H, P-CH), 3.66(s, 3H, OCH_3).
^{13}CNMR (100 MHz, $CDCl_3$/ TMS): δ 152.84, 147.33 (s, 2C, C-1 & 7), 145.41, 138.00 (s, 2C, C-2 & 6), 137.31, 133.72(s, 2C, C-19 & 20), 131.84, 131.12 (s, 2C, C-8 & 15), 130.86, 130.12 (s, 2C, C-9 & 14), 128.95,128.61(s, 2C, C-10 & 13), 127.10,126.94(s, 2C, C-11 & 12), 126.19, 124.41 (s, 2C, C-16 & 17), 123.85, 121.57 (s, 2C, C-22 & 23), 120.61, 120.20 (s, 2C, C-18 & 21), 65.80 (d, J=131.5 Hz, 1C, P-CH), 137.40(s, 1C, C-1'), 119.69 (s, 2C, C-2' & 6'), 117.94(s, 2C, C-3' & 5'), 116.71(s, 1C, C-4'), 55.3(s, 1C, OCH_3), 160.85(s, 1C, C-1"), 115.68(s, 2C, C-2" & 6"), 127.27(s, 2C, C-3" & 5"), 128.37(s, 1C, C-4")
^{31}PNMR (161.9 MHz, $CDCl_3$/ H_3PO_4): δ 33.28
Anal. Calcd. for $C_{34}H_{25}O_4PNBr$(622.11): C, 65.59; H, 4.05; N, 2.25.
Found C, 65.63; H, 4.00; N, 2.32%

4-α-(4^1-Methoxy) phenyl amino (4^1-methoxy) benzyl dinaphtho [2,1-d:1',2'-f][1,3,2] dioxaphosphepin 4-oxide 4h.
Yield: 93% mp: 201 - 203°C
IR (KBr): ν 1268 (P=O), 754 (P-C), 3425 cm^{-1} (C-NH)
^{1}HNMR (400 MHz, $CDCl_3$ /TMS): δ 7.99-6.21(m, 20H), 6.13(d, J=8.8 Hz, 1H, N-H), 4.94(d, J = 25.5 Hz, 1H, P-CH), 3.83, 3.76(s, 6H, 2(OCH_3)).
^{13}CNMR (100 MHz, $CDCl_3$/ TMS) : δ 151.95, 147.41 (s, 2C, C-1 & 7), 138.12, 133.42 (s, 2C, C-2 & 6), 133.79, 139.42(s, 2C, C-19 & 20), 129.55, 128.81 (s, 2C, C-8 & 15), 128.70, 128.16 (s, 2C, C-9 & 14), 128.04, 126.37(s, 2C, C-10 & 13), 125.11,124.77(s, 2C, C-11 & 12), 124.25, 122.82 (s, 2C, C-16 & 17), 122.48, 120.60 (s, 2C, C-22 & 23), 120.33, 118.75 (s, 2C, C-18 & 21), 55.05 (d, J=114.2 Hz, 1C, P-CH), 130.28(s, 1C, C-1'), 115.25 (s, 2C, C-2' & 6'), 114.72(s, 2C, C-3' & 5'), 114.19(s, 1C, C-4'), 51.10(s, 2C, 2-OCH_3), 158.76(s, 1C, C-1"), 113.91(s, 2C, C-2" & 6"), 112.27(s, 2C, C-3" & 5"), 152.89(s, 1C, C-4")

^{31}PNMR (161.9 MHz, $CDCl_3$/ H_3PO_4): δ 23.86
Anal. Calcd. for $C_{35}H_{28}O_5NP$ (573.23): C, 73.27; H, 4.92; N, 2.44.
Found C, 73.34; H, 4.86; N, 2.52 %

4-α-(4^1-Bromo) phenyl amino (3^1, 5^{1}dimethoxy) benzyl dinaphtho [2,1-d:1',2'-f][1,3,2] dioxaphosphepin 4-oxide 4i.
Yield: 94% mp: 162 - 164°C
IR (KBr): ν 1260 (P=O), 746 (P-C), 3405 cm^{-1} (C-NH)
^{1}HNMR (400 MHz, $CDCl_3$ /TMS): δ 8.27-6.72(m, 19H), 5.41(brs, 1H, N-H), 5.10(d, *J*=25.1 Hz, 1H, P-CH), 3.40(s, 6H, $(OCH_3)_2$).
^{13}CNMR (100 MHz, $CDCl_3$/ TMS): δ 137.41, 137.25 (s, 2C, C-1 & 7), 136.12, 136.07 (s, 2C, C-2 & 6), 147.01, 149.03 (s, 2C, C-19 & 20), 133.91, 133.71 (s, 2C, C-8 & 15), 133.48, 138.25 (s, 2C, C-9 & 14), 132.96, 132.27(s, 2C, C-10 & 13), 132.13, 132.03(s, 2C, C-11 & 12), 131.91, 130.54 (s, 2C, C-16 & 17), 130.92 (s, 2C, C-22 & 23), 129.12, 129.14 (s, 2C, C-18 & 21), 53.20 (d, *J*=139.4 Hz, 1C, P-CH), 132.20(s, 1C, C-1'), 127.08 (s, 2C, C-2' & 6'), 126.10(s, 2C, C-3' & 5'), 126.70(s, 1C, C-4'), 153.8(s, 1C, C-1"), 117.8(s, 2C, C-2" & 6"), 156.10(s, 2C, C-3" & 5"), 119.0(s, 1C, C-4"), 51.02(s, 2C, $(OCH_3)_2$)
^{31}PNMR (161.9 MHz, $CDCl_3$/ H_3PO_4): δ 33.16
Anal. Calcd. for $C_{35}H_{27}O_5NPBr$(652.13): C, 64.40; H, 4.17; N, 2.15.
Found C, 64.32; H, 4.21; N, 2.11%

4-α-(4^1-Methoxy) phenyl amino (3^1,5^{1}dimethoxy) benzyl dinaphtho [2,1-d:1',2'-f][1,3,2] dioxaphosphepin 4-oxide 4j.
Yield: 93% mp: 131 - 133°C
IR (KBr): ν 1261 (P=O), 729 (P-C), 3327 cm^{-1} (C-NH)
^{1}HNMR (400 MHz, $CDCl_3$ /TMS): δ 8.31-6.72(m, 19H), 5.25(brs, 1H, N-H), 4.90(d, *J*=20.4 Hz, 1H, P-CH), 3.31(s, 3H, OCH_3), 3.43(s, 6H, $(OCH_3)_2$).
^{31}PNMR (161.9 MHz, $CDCl_3$/ H_3PO_4): δ 30.22
Anal. Calcd. for $C_{36}H_{30}O_6NP$ (603.25): C, 71.61; H, 5.01; N, 2.32.
Found C, 71.69; H, 4.91; N, 2.28 %

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