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Synthesis of a new class of 3-methyl-1-substituted-3*H*-1λ^5-benzo [4,5]imidazo[1,2-*c*] [1,3,2]oxazaphosphol-1-one

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Abstract: Synthesis of 3-Methyl-1-substituted-3*H*-1λ^5-benzo [4,5]imidazo[1,2-*c*] [1,3,2] oxazaphosphol-1-one was accomplished by two pathways, firstly, in single step various substituted phosphorodichloridates are treated directly and secondly, through a two step process involving preparation of the monochloride (**2**) and its subsequent reaction with various phenols and amines in dry tetrahydrofuran (THF) in the presence of triethylamine (TEA) at various temperatures from 1-(1H-benzo[d]imidazol-2-yl)ethanol (**1**). All the new compounds were characterized by IR, ^{1}H-, ^{13}C-, ^{31}P-NMR, mass spectral data and elemental analysis.

Keywords: Heterocyclic; Oxazaphosphol-1-one; 1-(1H-benzo[d]imidazol-2-yl)ethanol; Phosphorus oxychloride; Phosphorodichloridates.

Introduction

In recent years heterocyclic systems containing phosphorus atom have considerable attention due to a large variety of interesting pharmacological and biological activities, such as herbicidal [1-3], insecticidal [4], antimicrobial [5] and anticancer properties [6]. Five membered organophosphorus heterocyclic rings have aroused much interest in biological systems. It was found that some of these compounds occur in nucleic acids or are involved as intermediates in a number of biological processes [7]. In addition, various medical and technological applications have been reported [8]. They are known to degrade hydrolytically and enzymatically to limited or non-toxic residues. Due to these reasons they have acquired great attention in synthetic organic chemistry and a number of synthetic methods have been developed during the past two decades. In view of the above observation, new phosphorus heterocyclic systems containing benzoimidazole moiety were synthesized *via* heterocyclization reactions of α, β-bifunctional benzoimidazole with phosphorus reagents.

Results and Discussion

Cyclocondensation of 1-(1*H*-benzo[d]imidazol-2-yl)ethanol (**1**) with phosphorus oxychloride in presence of triethylamine in dry THF at 0-5 °C afforded 1-chloro-3-methyl-3*H*-[1,3,2]oxazaphospholo[3,4-*a*]benzimidazole 1-oxide (**2**), which upon subsequent reaction with various phenols and amines gave 3-Methyl-1-Substituted-3*H*-1λ^5-benzo[4,5]imidazo [1,2-*c*][1,3,2]oxazaphosphol-1-one (**4a-l**) in good yields (Scheme 1). The title compounds are also prepared by condensation of **1** with various aryl phosphorodichloridates **(3a-l)** in the presence of TEA in dry THF directly at 40-50 ºC. The yields of the products obtained by both routes are comparable. Direct condensation of compound **1** with **3a-l** afforded good yields more conveniently than the former method because compound **2** is highly moisture sensitive and difficult to handle. All compounds were purified by recrystallization and were characterized by elemental, IR, ^{1}H, ^{13}C, ^{31}P-NMR, and partly by mass spectral analyses.

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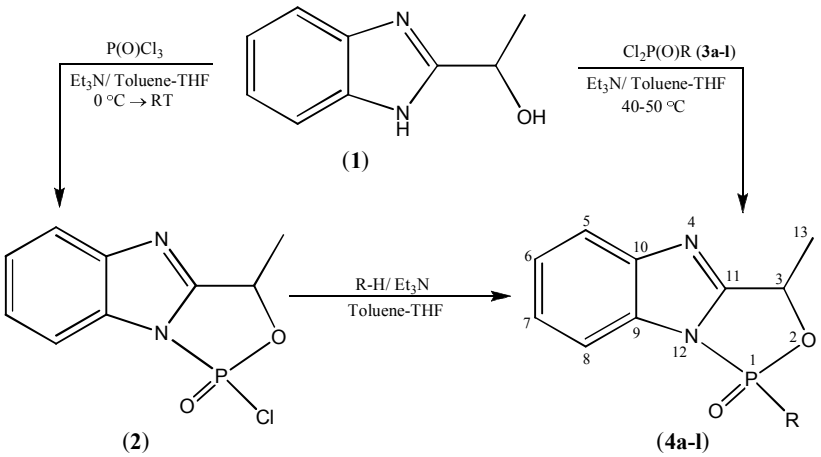

Compound	R	Compound	R
4a	OC_6H_5	**4g**	OC_6H_4-Cl(4′)
4b	OC_6H_4-CH_3(3′)	**4h**	OC_6H_3-$(Cl)_2$(2′,6′)
4c	OC_6H_4-CH_3(4′)	**4i**	OC_6H_4-Br(4′)
4d	OC_6H_3-$(CH_3)_2$(2′,5′)	**4j**	$N(CH_2CH_2Cl)_2$
4e	OC_6H_3-$(CH_3)_2$(2′,6′)	**4k**	$N(CH_2CH_2)_2O$
4f	OC_6H_4-Cl(2′)	**4l**	$N(CH_2CH_2)_2CH_2$

Scheme 1.

Product yields and elemental analysis, IR, ^{1}H, ^{13}C and ^{31}P-NMR data of **4a–l** are given and the data agreed with the proposed chemical structures. Compounds **4a-l** exhibited characteristic IR stretching frequencies in the regions 1198-1250, 1165-1187 and 963-998 cm^{-1} for P=O, C-O and P-O respectively [9].

In ^{1}H-NMR spectra [10] the aromatic protons in the compounds **4a-l** gave as multiplet in the region δ 6.93-7.66. The benzylic proton resonated as a quartet at δ 4.98-5.52. The methyl groups of the title compounds resonated as a singlet in the region δ 2.21-2.63 and the remaining all protons are resonated at their corresponding regions. The ^{13}C-NMR spectra for **3a-f** and **3j-l** showed carbon chemical shifts in the expected region. The ^{31}P-NMR resonates as a two distinguishable singlets at δ 2.89 and 3.27 and -10.62 to -0.13. The mass spectra of compounds **3a, 3b, 3e & 3f** showed their respective molecular ion peaks in the expected m/z mass values.

Experimental

The melting points were determined in open capillary tubes on a Mel-Temp apparatus and were uncorrected. The IR spectra (ν_{max}, cm^{-1}) were recorded as KBr pellets on Perkin Elmer 1000 unit. The ^{1}H, ^{13}C and ^{31}P-NMR spectra were recorded on a Varian AMX 400 MHz NMR spectrometer operating at 400 MHz for ^{1}H, 100.57 MHz for ^{13}C and 161.7 MHz for ^{31}P-NMR. All the compounds were dissolved in DMSO-d_6 and chemical shifts were referenced to TMS (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P). Microanalyses data were obtained from Central Drug Research Institute (CDRI), Lucknow, India.

Typical General Procedure for 3-methyl-1-phenoxy-3H-1λ^5-benzo[4,5]imidazo[1,2-c][1,3,2]oxazaphosphol-1-one **(4a)**:

(a) To a stirred solution of **1** (0.324 g, 0.002 mol) and triethylamine (0.404 g, 0.004 mol) in dry toluene (20 mL) and dry THF (15 mL) was added dropwise a solution phenyl phosphorodichloridate, **3a**, (0.422 g, 0.002 mol) in dry THF (15 mL) at 0 °C. After addition, the temperature was maintained between 30-40 °C, and the progress of the reaction was monitored by TLC. The crude products obtained as residues after removing the solvent by rotaevaporator were purified by repeatedly washing with water to remove any residual triethylamine hydrochloride and then with cold methanol to remove the unreacted starting materials and other impurities. The crude compound (**4a**) was further purified by flash chromatography on silica gel, using ethyl acetate**:** hexane (1**:**3) as eluent and recrystallized from aqueous ethanol to get pure **4a**, 0.408 g, (68 %), mp: 195-197 °C.

4a: Anal. Calcd for: $C_{15}H_{13}N_2O_3P$: C, 60.00; H, 4.36; N, 9.33. Found: C, 60.06; H, 4.40; N, 9.41; IR (KBr, cm^{-1}): 1250 (-P=O), 1187 (O-C), 977 (P-O); ^{1}H- NMR (400 MHz, DMSO-d_6, δ/ ppm): 5.52 (1H, q, -H(3)), 7.23-7.66 (9H, m, Ar-H), 2.13 (3H, d, $^3J_{HH}$ = 8.6 Hz, -CH_3(13)); ^{13}C-NMR (100 MHz, DMSO-d_6, δ/ ppm): 65.7 (C_3), 132.5 (C_5), 131.7 (C_6), 131.2 (C_7), 130.6 (C_8), 135.5 (C_9), 133.7 (C_{10}), 155.0 (C_{11}), 22.0 (C_{13}), 154.4 ($C_{1'}$), 123.1 ($C_{2'}$ & $C_{6'}$), 128.1 ($C_{3'}$ & $C_{5'}$), 124.5 ($C_{4'}$); ^{31}P-NMR (161.7 MHz, DMSO-d_6, δ/ ppm): -1.24, -3.49; MS (*m/z*, (relative aboundance), %): 300 ($M^{+\cdot}$), 229 (M-H, 100), 274 (40), 256 (17), 245 (42), 207 (25), 150 (37).

1-(4-bromophenoxy)-3-methyl-3H-1λ^5-benzo[4,5]imidazo[1,2-c][1,3,2]oxazaphosphol-1-one **(4i)**:

(b) To a cold (0 °C) and stirred solution of 1-(1H-benzo[d]imidazol-2-yl)ethanol, **1**, (0.324 g, 0.002 mol) and triethylamine (0.404 g, 0.004 mol) in dry toluene (20 mL) and dry THF (15 mL) was added dropwise a solution of phosphorus oxychloride (0.3 g, 0.002 mol) in dry toluene (10 mL). After completion of addition, the reaction mixture was stirred at 40-50 °C for 30 min; the progress of the reaction was monitored by TLC (ethyl acetate**:** hexane, 1**:**3). After completion of the reaction triethylamine hydrochloride was sucked off. To the filtrate a solution of 4-bromo phenol, **3i**, (0.35 g, 0.002 mol) and triethylamine (0.404 g, 0.004 mol) in dry toluene (20 mL) was added and the progress of the reaction was monitored by TLC. Triethylamine hydrochloride was filtered off; the solvent was removed by rotaevaporator and purified by repeatedly washing with water to remove any residual triethylamine hydrochloride and then with cold methanol to remove the unreacted starting materials and other impurities. The crude compound **4i** was further purified by flash chromatography on silica gel, using ethyl acetate: hexane (1:3) as eluent and recrystallized from 2-propanol to obtain pure **4i**, 0.493 g, (65 %), mp: 128-130 °C.

4i: Anal. Calcd for: $C_{15}H_{12}BrN_2O_3P$: C, 47.52; H, 3.19; N, 7.39. Found: C, 47.59; H, 3.11; N, 7.46; IR (KBr, cm^{-1}): 1223 (-P=O), 1171 (O-C), 998 (P-O); ^{1}H- NMR (400 MHz, DMSO-d_6, δ/ ppm): 5.42 (1H, q, -H(3)), 7.08-7.26 (8H, m, Ar-H), 2.14 (3H, d, $^3J_{HH}$ = 8.5 Hz, -CH_3(13)); ^{31}P-NMR (161.7 MHz, DMSO-d_6, δ/ ppm): 2.89; MS (*m/z*, (relative aboundance), %): 378 ($M^{+\cdot}$, 25), 380 (M+2, 12), 363 (43), 352 (58), 351 (53), 355 (42), 354 (35), 326 (42), 325 (51), 262 (37), 260 (25), 207 (100), 180 (36), 154 (25), 144 (82), 129 (35), 117 (23).

All the titled compounds were prepared by the above same two procedures.

Spectral data of title compounds 4b-l:

3-methyl-1-(3-methylphenoxy)-3H-1λ^5-benzo[4,5]imidazo[1,2-c][1,3,2]oxazaphosphol-1-one **(4b)**:

Yield: 58 %; mp: 215-217 °C; Anal. Calcd for: $C_{16}H_{15}N_2O_3P$: C, 61.15; H, 4.81; N, 8.91. Found: C, 61.20; H, 4.89; N, 8.97; IR (KBr, cm^{-1}): 1198 (-P=O), 1165 (O-C), 975 (P-O); ^{1}H- NMR (400 MHz, DMSO-d_6, δ/ ppm): 5.32 (1H, q, -H(3)), 7.01-7.66 (8H, m, Ar-H), 2.13 (3H, d, $^3J_{HH}$ = 8.4 Hz, -CH_3(13)), 2.62 (3H, s, -CH_3 (3')); ^{13}C-NMR (100 MHz, DMSO-d_6, δ/ ppm): 67.2 (C_3), 130.4 (C_5), 130.2 (C_6), 129.0 (C_7), 128.7 (C_8), 136.9 (C_9), 135.6 (C_{10}), 155.3 (C_{11}), 21.3 (C_{13}), 153.8 ($C_{1'}$), 120.2 ($C_{2'}$), 139.5 ($C_{3'}$), 124.1 ($C_{4'}$), 129.8 ($C_{5'}$), 120.2 ($C_{6'}$), 21.9 (Ar-CH_3(3')); ^{31}P-NMR (161.7 MHz, DMSO-d_6, δ/ ppm): -0.31, -1.44; MS (*m/z*, (relative aboundance), %): 314 ($M^{+\cdot}$, 21), 299 (87), 286 (24), 271 (25), 261 (28), 209 (40), 123 (35), 91 (100), 76 (24).

3-methyl-1-(4-methylphenoxy)-3H-1λ^5-benzo[4,5]imidazo[1,2-c][1,3,2]oxazaphosphol-1-one **(4c)**:

Yield: 52 %; mp: 231-233 °C; Anal. Calcd for: $C_{16}H_{15}N_2O_3P$: C, 61.15; H, 4.81; N, 8.91. Found: C, 61.23; H, 4.87; N, 8.98; IR (KBr, cm^{-1}): 1232 (-P=O), 1178 (O-C), 978 (P-O); ^{1}H- NMR (400 MHz, DMSO-d_6, δ/ ppm): 4.98 (1H, q, -H(3)), 6.94-7.56 (8H, m, Ar-

H), 2.17 (3H, d, $^3J_{HH}$ = 8.3 Hz, -CH_3(13)), 2.63 (3H, s, -CH_3 (4')); ^{13}C-NMR (100 MHz, DMSO-d_6, δ/ ppm): 66.6 (C_3), 131.4 (C_5), 131.0 (C_6), 130.8 (C_7), 130.4 (C_8), 136.3 (C_9), 132.2 (C_{10}), 154.6 (C_{11}), 20.7 (C_{13}), 149.6 ($C_{1'}$), 119.7 ($C_{2'}$), 130.2 ($C_{3'}$), 135.7 ($C_{4'}$), 130.2 ($C_{5'}$), 119.7 ($C_{6'}$), 21.4 (Ar-CH_3(4')); ^{31}P-NMR (161.7 MHz, DMSO-d_6, δ/ ppm): -0.41, -1.22.

1-(2,5-dimethylphenoxy)-3-methyl-3H-1λ^5-benzo[4,5]imidazo[1,2-c][1,3,2] oxazaphosphol-1-one **(4d)**:

Yield: 60 %; mp: 280-282 °C; Anal. Calcd for: $C_{17}H_{17}N_2O_3P$: C, 62.19; H, 5.22; N, 8.53. Found: C, 61.28; H, 5.29; N, 8.57; IR (KBr, cm^{-1}): 1222 (-P=O), 1175 (O-C), 971 (P-O); ^{1}H- NMR (400 MHz, DMSO-d_6, δ/ ppm): 5.46 (1H, q, -H(3)), 6.92-7.21 (7H, m, Ar-H), 2.05 (3H, d, $^3J_{HH}$ = 8.4 Hz, -CH_3(13)), 2.24 (3H, s, -CH_3 (2')), 2.33 (3H, s, -CH_3 (5')); ^{13}C-NMR (100 MHz, DMSO-d_6, δ/ ppm): 64.4 (C_3), 132.5 (C_5), 131.6 (C_6), 129.6 (C_7), 129.0 (C_8), 136.8 (C_9), 134.6 (C_{10}), 155.9 (C_{11}), 20.7 (C_{13}), 153.0 ($C_{1'}$), 130.5 ($C_{2'}$), 135.2 ($C_{3'}$), 131.0 ($C_{4'}$), 138.0 ($C_{5'}$), 128.2 ($C_{6'}$), 16.7 (Ar-CH_3(2')), 21.5 (Ar-CH_3(5')); ^{31}P-NMR (161.7 MHz, DMSO-d_6, δ/ ppm): -1.43, -1.48; MS (*m/z*, (relative aboundance), %): 328 ($M^{+\cdot}$, 25), 327 (48), 313 (75), 310 (41), 275 (50), 207 (75), 180 (37), 144 (100), 117 (42), 109 (32), 91 (23).

1-(2,6-dimethylphenoxy)-3-methyl-3H-1λ^5-benzo[4,5]imidazo[1,2-c][1,3,2] oxazaphosphol-1-one **(4e)**:

Yield: 59 %; mp: 193-195 °C; Anal. Calcd for: $C_{17}H_{17}N_2O_3P$: C, 62.19; H, 5.22; N, 8.53. Found: C, 61.27; H, 5.15; N, 8.59; IR (KBr, cm^{-1}): 1215 (-P=O), 1172 (O-C), 963 (P-O); ^{1}H- NMR (400 MHz, DMSO-d_6, δ/ ppm): 5.49 (1H, q, -H(3)), 6.93-7.21 (7H, m, Ar-H), 2.10 (3H, d, $^3J_{HH}$ = 8.4 Hz, -CH_3(13)), 2.21 (6H, s, 2×-CH_3 (2' & 6')); ^{13}C-NMR (100 MHz, DMSO-d_6, δ/ ppm): 64.5 (C_3), 132.5 (C_5), 131.7 (C_6), 129.6 (C_7), 129.1 (C_8), 136.8 (C_9), 134.6 (C_{10}), 155.9 (C_{11}), 20.7 (C_{13}), 153.0 ($C_{1'}$), 127.5 ($C_{2'}$), 131.2 ($C_{3'}$), 126.2 ($C_{4'}$), 131.2 ($C_{5'}$), 127.5 ($C_{6'}$), 23.7 (Ar-CH_3(2' & 6')); ^{31}P-NMR (161.7 MHz, DMSO-d_6, δ/ ppm): -8.21, -9.56; MS (*m/z*, (relative aboundance), %): 328 ($M^{+\cdot}$, 27), 313 (24), 302 (25), 276 (46), 212 (12), 207 (100), 122 (35), 105 (12).

1-(2-chlorophenoxy)-3-methyl-3H-1λ^5-benzo[4,5]imidazo[1,2-c][1,3,2]oxazaphosphol-1-one **(4f)**:

Yield: 62 %; mp: 90-92 °C; Anal. Calcd for: $C_{15}H_{12}ClN_2O_3P$: C, 53.83; H, 3.61; N, 8.37. Found: C, 53.88; H, 3.67; N, 8.45; IR (KBr, cm^{-1}): 1220 (-P=O), 1168 (O-C), 974 (P-O); ^{1}H- NMR (400 MHz, DMSO-d_6, δ/ ppm): 5.31 (1H, q, -H(3)), 7.07-7.29 (8H, m, Ar-H), 2.09 (3H, d, $^3J_{HH}$ = 8.3 Hz, -CH_3(13)); ^{13}C-NMR (100 MHz, DMSO-d_6, δ/ ppm): 64.4 (C_3), 132.3 (C_5), 130.8 (C_6), 129.8 (C_7), 129.7 (C_8), 136.2 (C_9), 134.4 (C_{10}), 154.6 (C_{11}), 20.9 (C_{13}), 150.0 ($C_{1'}$), 125.1 ($C_{2'}$), 130.5 ($C_{3'}$), 125.9 ($C_{4'}$), 123.9 ($C_{5'}$), 125.1 ($C_{6'}$); ^{31}P-NMR (161.7 MHz, DMSO-d_6, δ/ ppm): 3.27; MS (*m/z*, (relative aboundance), %): 334.7 ($M^{+\cdot}$, 23), 319 (22), 308(32), 299 (46), 282 (100), 218 (45), 207 (39), 144 (29), 128 (35), 76 (78).

1-(4-chlorophenoxy)-3-methyl-3H-1λ^5-benzo[4,5]imidazo[1,2-c][1,3,2]oxazaphosphol-1-one **(4g)**:

Yield: 50 %; mp: 96-98 °C; Anal. Calcd for: $C_{15}H_{12}ClN_2O_3P$: C, 53.83; H, 3.61; N, 8.37. Found: C, 53.88; H, 3.69; N, 8.42; IR (KBr, cm^{-1}): 1218 (-P=O), 1166 (O-C), 971 (P-O); ^{1}H- NMR (400 MHz, DMSO-d_6, δ/ ppm): 5.40 (1H, q, -H(3)), 7.09-7.30 (8H, m, Ar-H), 2.07 (3H, d, $^3J_{HH}$ = 8.3 Hz, -CH_3(13)); ^{31}P-NMR (161.7 MHz, DMSO-d_6, δ/ ppm): -9.65, -10.62; MS (*m/z*, (relative aboundance), %): 334 ($M^{+\cdot}$, 20), 336 (M+2, 8), 319 (40), 307 (32), 291 (32), 281 (58), 223 (45), 207 (90), 180 (28), 144 (100), 129 (42), 117 (32), 76 (28).

1-(2,6-dichlorophenoxy)-3-methyl-3H-1λ^5-benzo[4,5]imidazo[1,2-c][1,3,2] oxazaphosphol-1-one **(4h)**: Yield:

53 %; mp: 115-117 °C; Anal. Calcd for: $C_{15}H_{11}Cl_2N_2O_3P$: C, 48.81; H, 3.00; N, 7.59. Found: C, 48.86; H, 2.92; N, 7.65; IR (KBr, cm^{-1}): 1225 (-P=O), 1168 (O-C), 981 (P-O); ^{1}H- NMR (400 MHz, DMSO-d_6, δ/ ppm): 5.47 (1H, q, -H(3)), 7.12-7.34 (7H, m, Ar-H), 2.06 (3H, d, $^3J_{HH}$ = 8.3 Hz, -CH_3(13)); ^{31}P-NMR (161.7 MHz, DMSO-d_6, δ/ ppm): -6.24, -6.98; MS (*m/z*, (relative aboundance), %): 368.7 ($M^{+\cdot}$, 19), 342 (21), 341 (22), 325 (32), 315 (32), 250 (15), 223 (45), 207 (82), 161 (52), 144 (100), 116 (31), 91 (22), 76 (20).

1-[di(2-chloroethyl)amino]-3-methyl-3H-1λ^5-benzo[4,5]imidazo[1,2-c][1,3,2] oxazaphosphol-1-one **(4j)**:

Yield: 57 %; mp: 188-190 °C; Anal. Calcd for: $C_{13}H_{16}Cl_2N_3O_2P$: C, 44.85; H, 4.63; N, 12.07. Found: C, 42.76; H, 4.38; N, 11.48; IR (KBr, cm^{-1}): 1216 (-P=O), 1173 (O-C), 983 (P-O); ^{1}H- NMR (400 MHz, DMSO-d_6, δ/ ppm): 5.33 (1H, q, -H(3)), 7.14-7.36 (8H, m, Ar-H), 2.03 (3H, d, $^3J_{HH}$ = 8.3 Hz, -CH_3(13)), 4.14-

4.40 (4H, m, NCH_2), 3.32-3.76 (4H, m, CH_2Cl); ^{13}C-NMR (100 MHz, DMSO-d_6, δ/ ppm): 62.1 (C_3), 134.2 (C_5), 128.7 (C_6), 127.6 (C_7), 127.8 (C_8), 135.1 (C_9), 134.4 (C_{10}), 155.4 (C_{11}), 22.1 (C_{13}), 48.3 (NCH_2), 39.8 (CH_2Cl); ^{31}P-NMR (161.7 MHz, DMSO-d_6, δ/ ppm): -0.13, -1.23; MS (*m/z*, (relative aboundance), %): 347 ($M^{+\cdot}$, 21), 332 (38), 329(25), 320 (36), 312 (48), 298 (31), 294 (81), 285 (100), 284 (82), 270 (95), 268 (75), 241 (68), 236 (82), 223 (76), 208 (100), 144 (52).

3-methyl-1-morpholino-3H-1λ^5-benzo[4,5]imidazo[1,2-c][1,3,2]oxazaphosphol-1-one **(4k)**:
Yield: 59 %; mp: 178-180 °C; Anal. Calcd for: $C_{13}H_{16}N_3O_3P$: C, 53.24; H, 5.50; N, 14.33. Found: C, 53.21; H, 5.46; N, 14.34; IR (KBr, cm^{-1}): 1218 (-P=O), 1175 (O-C), 986 (P-O); ^{1}H- NMR (400 MHz, DMSO-d_6, δ/ ppm): 5.31 (1H, q, -H(3)), 7.16-7.39 (4H, m, Ar-H), 2.04 (3H, d, $^3J_{HH}$ = 8.2 Hz, -CH_3(13)), 4.16-4.45 (4H, m, NCH_2), 3.46-3.97 (4H, m, CH_2O); ^{13}C-NMR (100 MHz, DMSO-d_6, δ/ ppm): 62.3 (C_3), 134.7 (C_5), 127.2 (C_6), 126.8 (C_7), 127.8 (C_8), 134.8 (C_9), 134.9 (C_{10}), 154.9 (C_{11}), 21.2 (C_{13}), 43.2 (NCH_2), 56.9 (CH_2O); ^{31}P-NMR (161.7 MHz, DMSO-d_6, δ/ ppm): -1.28, -3.78; MS (*m/z*, (relative aboundance), %): 293 ($M^{+\cdot}$, 13), 278 (32), 266 (22), 265 (34), 263 (40), 250 (37), 240 (35), 208 (100),144 (46), 76 (48).

3-methyl-1-piperidino-3H-1λ^5-benzo[4,5]imidazo[1,2-c][1,3,2]oxazaphosphol-1-one **(4l)**:
Yield: 58 %; mp: 185-187 °C; Anal. Calcd for: $C_{14}H_{18}N_3O_2P$: C, 57.73; H, 6.23; N, 14.43. Found: C, 57.74; H, 6.21; N, 14.40; IR (KBr, cm^{-1}): 1221 (-P=O), 1176 (O-C), 991 (P-O); ^{1}H- NMR (400 MHz, DMSO-d_6, δ/ ppm): 5.33 (1H, q, -H(3)), 7.12-7.35 (4H, m, Ar-H), 2.05 (3H, d, $^3J_{HH}$ = 8.2 Hz, -CH_3(13)), 4.15-4.41 (4H, m, NCH_2), 1.82-1.89 (4H, m, CH_2CH_2), 1.02-1.07 (2H, m, CH_2CH_2); ^{13}C-NMR (100 MHz, DMSO-d_6, δ/ ppm): 62.3 (C_3), 134.8 (C_5), 126.9 (C_6), 127.2 (C_7), 127.4 (C_8), 135.8 (C_9), 135.1 (C_{10}), 154.9 (C_{11}), 21.9 (C_{13}), 49.5 (NCH_2), 24.8 (3×CH_2); ^{31}P-NMR (161.7 MHz, DMSO-d_6, δ/ ppm): -1.28, -3.78; MS (*m/z*, (relative aboundance), %): 291 ($M^{+\cdot}$, 15), 276 (21), 264 (26), 263 (100), 248 (53), 238 (32), 236 (30), 220 (28), 208 (78), 207 (65), 144 (48), 117 (31), 76 (28).

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