BIS(IMINOPHOSPHORANE)-MEDIATED 1,2,4-TRIAZOLO-ANNULATION ON IMIDAZOLE AND BENZIMIDAZOLE RINGS. PREPARATION OF IMIDAZO[1,2-*b*]-1,2,4-TRIAZOLES AND 1,2,4-TRIAZOLO[1,5-*a*]BENZIMIDAZOLES

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This paper is sincerely dedicated to Prof. A. R. Katritzky in celebration of his 65th birthday, with affection and admiration

Abstract- Aza Wittig-type reactions of bis(iminophosphoranes) derived from 1,2-diaminoimidazole and 1,2-diaminobenzimidazole with isocyanates and aroyl chlorides afforded imidazo[1,2-*b*]-1,2,4-triazoles or 1,2,4-triazolo[1,5-*a*]benzimidazoles, respectively.

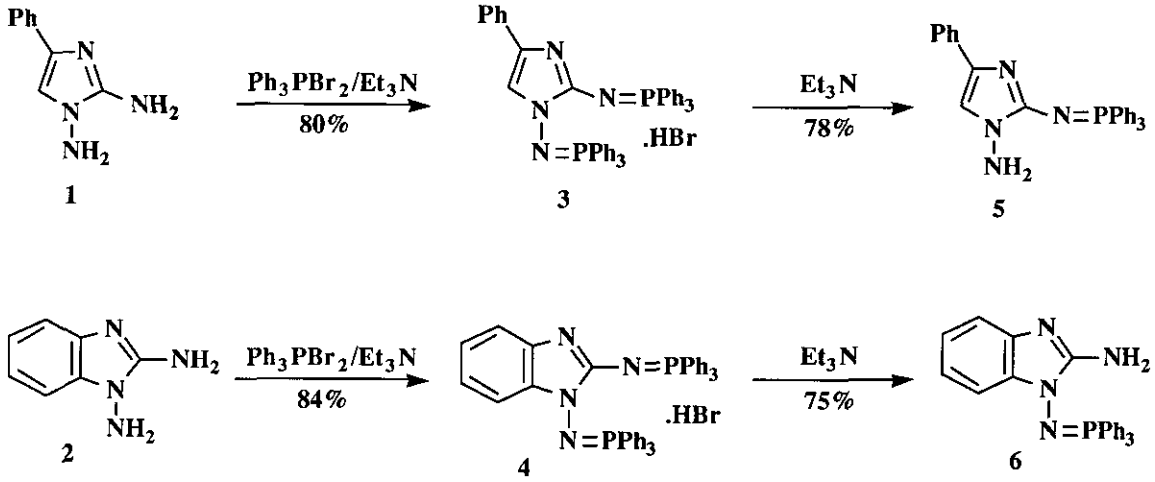
Recent years have witnessed a significant increase in the utilization of bis(iminophosphoranes) as valuable building blocks for the preparation of nitrogen heterocycles.[1] In spite of the important role of *C,C*-bis(iminophosphoranes) in heterocyclic synthesis the chemistry of the *C,N*-bis(iminophosphoranes)[2] has been much less investigated; in fact, while relevant examples involving *C,C*-bis(iminophosphoranes) have been reported,[1] there is only one example describing the synthetic utility of the *C,N*-bis(iminophosphoranes) in the preparation of fused benzotriazepines,[3] to the best of our knowledge.

As a further extention of this methodology, we studied the behaviour in aza Wittig-type reactions of *C,N*-bis(iminophosphoranes) in which one iminophosphorane group is directly linked to a nitrogen atom of an imidazole ring and the other is on a carbon atom of this ring system.

To this end, bis(iminophosphoranes) **(3)** and **(4)** were prepared by treating a benzene solution of 1,2-diamino-

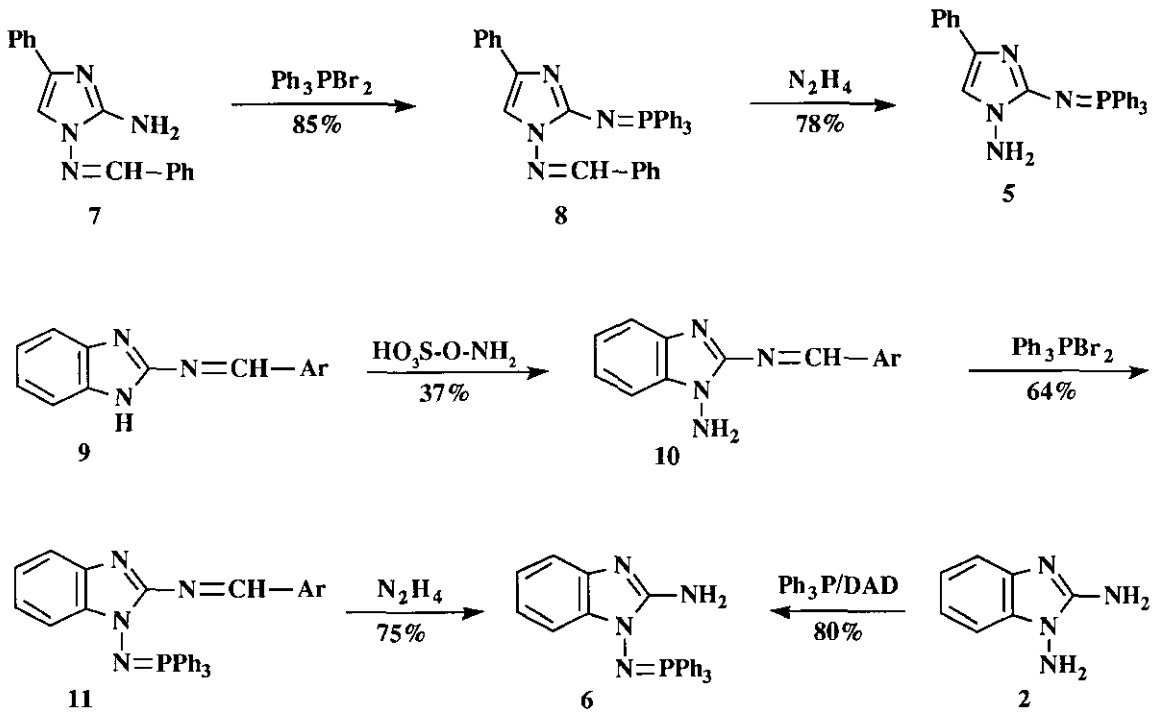
4-phenyl-1*H*-imidazole[4] (**1**) or 1,2-diaminobenzimidazole[5] (**2**) with triphenylphosphine dibromide and triethylamine at reflux temperature. Compounds (**3**) and (**4**) were isolated as bromides; this fact has also been observed in the isolation of the bis(iminophosphorane) derived from the 1,8-diaminonaphthalene.[6]

The ^{31}P nmr spectra of compounds (**3**) and (**4**) clearly indicate the presence of two different signals at δ 12.3-18.1 ppm and δ 21.8-22.1 ppm, respectively; these values are slightly higher than the previously reported values for closely related *C*-heteroaryliminophosphoranes[7] and iminophosphoranes derived from *N*-aminoheterocycles.[3,7] This fact is probably due to the protonation effect.[8] All attempts to deprotonation of bis(iminophosphoranes) (**3**) and (**4**) were unsuccessful; only the action of an excess of aqueous triethylamine provided the *C*-iminophosphorane (**5**) and the *N*-iminophosphorane (**6**) (Scheme 1).



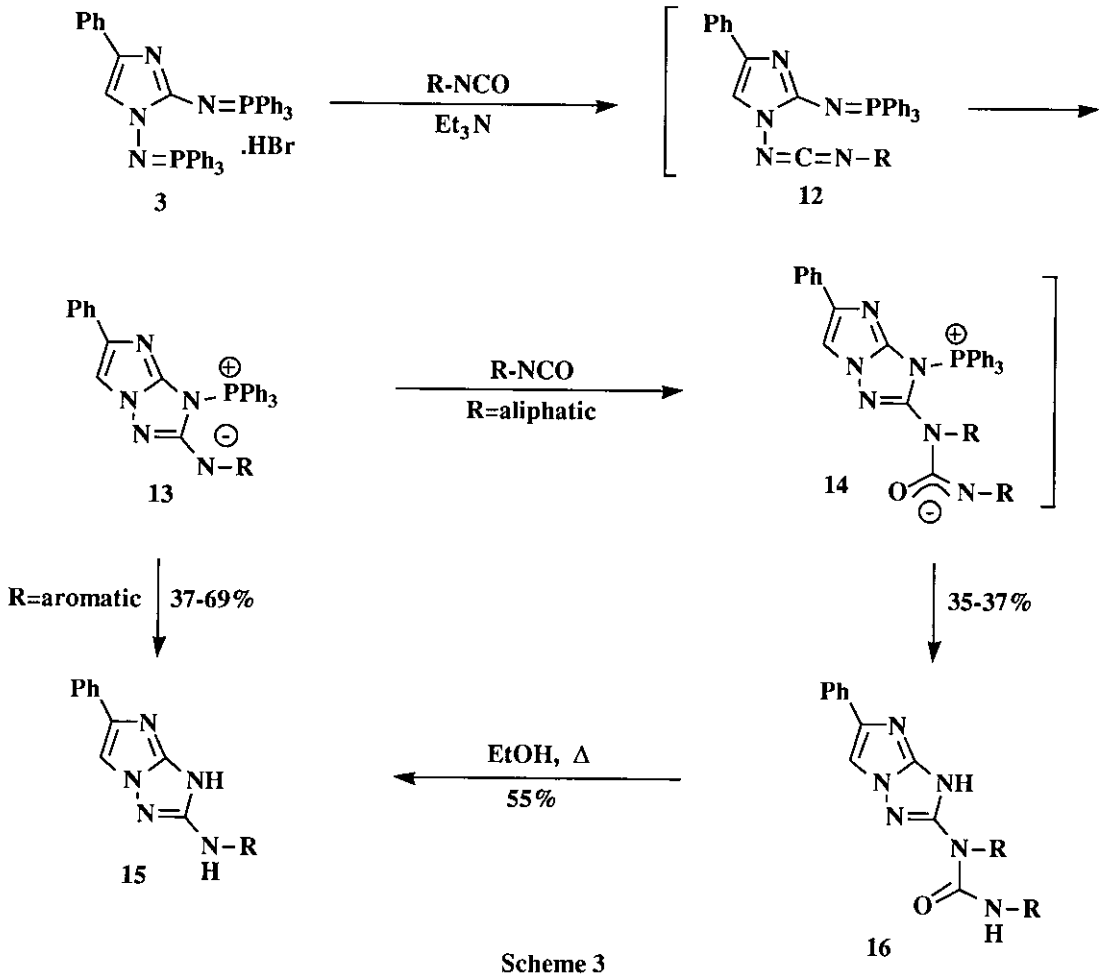
Scheme 1

These compounds have also been obtained by alternative routes. Thus, the *C*-iminophosphorane (**5**) was prepared by a two-step sequence starting from 2-amino-1-benzylidenamino-4-phenyl-1*H*-imidazole[4] (**7**): (a) reaction with triphenylphosphine dibromide and (b) hydrazinolysis. The *N*-iminophosphorane (**6**) was prepared either from 2-(4-methylbenzylidene)aminobenzimidazole (**9**) by: (a) *N*-amination with hydroxylamine-*O* -sulfonic acid, (b) reaction with triphenylphosphine dibromide and (c) hydrazinolysis or from **2** by reaction with triphenylphosphine/diethyl azodicarboxylate system (Scheme 2). The ^{31}P nmr spectra of iminophosphoranes (**5**) and (**6**) only showed one signal, for the compound (**5**) appeared at δ_p 14.9 ppm whereas for compound (**6**) occurred at δ_p 17.0 ppm. Moreover, ^{13}C nmr spectrum for compound (**6**) clearly showed that C-2 and C-7a carbon atoms are coupled with the phosphorous atom.



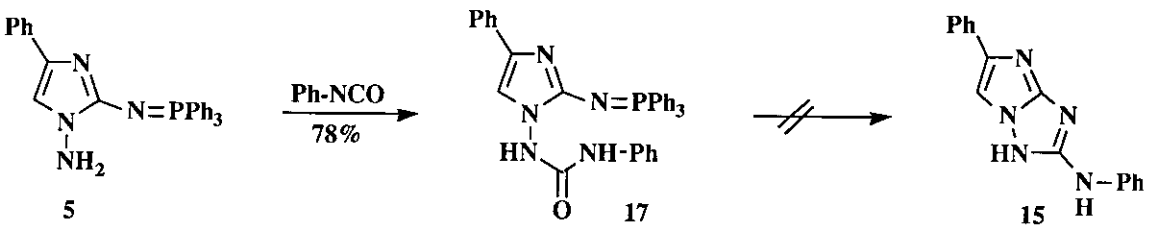
Scheme 2

Bis(iminophosphorane) (**3**) reacted with aromatic isocyanates in dry dichloromethane in the presence of triethylamine at room temperature to afford imidazo[1,2-*b*]-1,2,4-triazoles (**15**) in moderate to good yields. However, the reaction with aliphatic isocyanates under the same reaction conditions provided compounds (**16**) in moderate yields, which were converted into **15a** by heating in ethanol. The formation of imidazo[1,2-*b*]-1,2,4-triazoles (**15**) and (**16**) can be explained by an initial aza Wittig-type reaction between the *N*-iminophosphorane group and one equivalent of the isocyanate to give carbodiimide (**12**), which undergoes cyclization by nucleophilic attack of the nitrogen atom of the *C*-iminophosphorane group on the central carbon atom of the carbodiimide moiety[9] to give a zwitterionic compound (**13**). This compound either undergoes hydrolytic cleavage during the work-up[1e] to give **15** or reacts with a second equivalent of aliphatic isocyanate across the negative nitrogen atom to give **14** , which by hydrolytic cleavage affords **16** (Scheme 3). This mechanism is in accord with our recent results which clearly show that an *N*-iminophosphorane group is more reactive than an *C*-iminophosphorane one in aza Wittig-type reactions with isocyanates.[3]



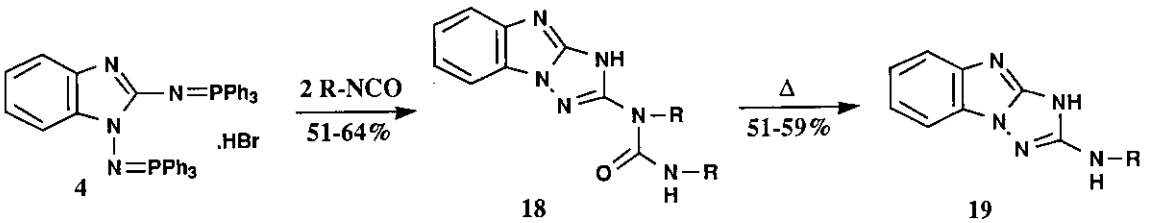
Scheme 3

Support for this mechanism was found for the reaction of *C*-iminophosphorane (**5**) with aromatic isocyanates. For example, the reaction with phenyl isocyanate in benzene at reflux temperature afforded the corresponding urea (**17**) as a crystalline solid in excellent yield. Attempts to cyclize **17** into the corresponding bicyclic compound (**15**) under a variety of reaction conditions failed (Scheme 4).



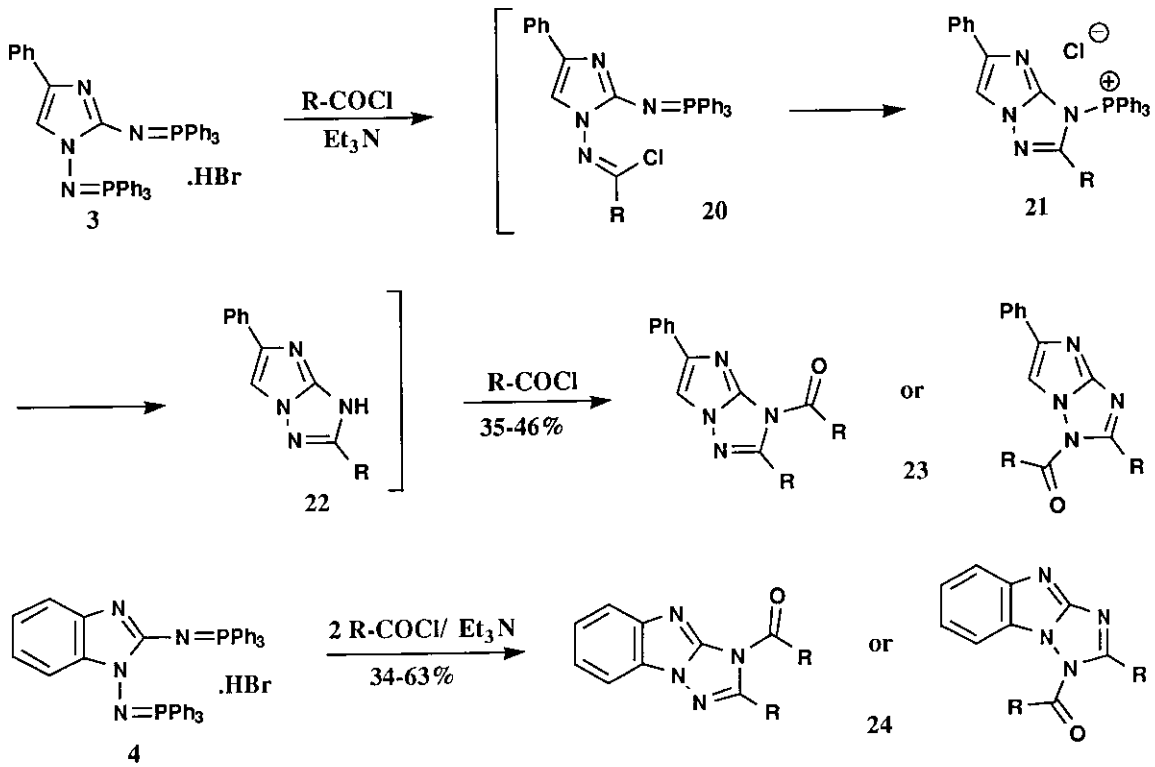
Scheme 4

In analogous reaction sequence, the related bis(iminophosphorane) (**4**) was converted into the bicyclic compounds (**18**) in moderate to good yields by reaction with two equivalents of aliphatic or aromatic isocyanates under the same reaction conditions. These compounds by heating lose one equivalent of isocyanate to give the otherwise not readily available[5,10] 1,2,4-triazolo[1,5-*a*]benzimidazoles (**19**) (Scheme 5).



Scheme 5

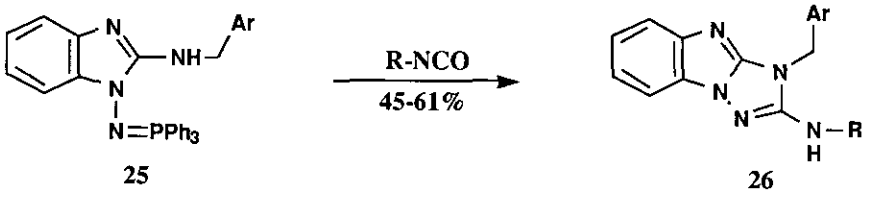
Having established the reactivity of bis(iminophosphoranes) (**3**) and (**4**) in aza Wittig-type reactions with isocyanates, we turned our attention to the behaviour of this sort of bis(iminophosphoranes) towards acyl chlorides. Bis(iminophosphorane) (**3**) reacted with aroyl chlorides in dry dichloromethane in the presence of triethylamine at room temperature to give imidazo[1,2-*b*]-1,2,4-triazoles (**23**) in moderate yields (Scheme 6).



Scheme 6

Presumably, the formation of **23** involves initial formation of the imidoyl chloride (**20**) as an intermediate[11] which clearly undergoes cyclization by nucleophilic attack of the nitrogen atom of the *C*-iminophosphorane portion and subsequent hydrolytic P-N bond cleavage[1a,9] to give **22**., which eventually undergoes acylation on one of the nitrogen atoms of the 1,2,4-triazole ring to give **23** . Attempts to isolate (**22**) using an excess of bis(iminophosphorane) (**3**) failed, the reaction product was found to be **23** albeit in low yield. Similarly, the bis(iminophosphorane) (**4**) was converted into 1,2,4-triazolo[1,5-*a*]benzimidazoles (**24**) by reaction with two equivalents of aroyl chloride under the same reaction conditions.

On the other hand, iminophosphorane (**25**), readily available in almost quantitative yield by reduction with sodium borohydride of the aldiminic carbon-nitrogen double bond of **11** , reacted with isocyanates in dry toluene at reflux temperature to give **26** in moderate to good yields (Scheme 7).



25 **26**

Ar = 4-Me-C_6H_4

Scheme 7

In conclusion, we have developed a simple and highly reliable bis(iminophosphorane)-mediated synthesis of a variety of fused 1,2,4-triazoles with varied substituents at the 1,2,4-triazole ring. These structures are assembled in a simple one-pot procedure, under mild conditions and from readily available starting materials. This 1,2,4-triazolo-annulation reaction significantly expands the scope of the iminophosphorane-methodology for the synthesis of five-membered rings.

EXPERIMENTAL

Melting points were obtained in a Kofler hot-stage apparatus and are uncorrected. Ir spectra were run using NaCl plates on a Nicolet FT-5DX spectrophotometer in Nujol emulsions. ^{1}H Nmr spectra were recorded using a Varian Unity (300 MHz) spectrometer or a Bruker AC-200 (200 MHz) and tetramethylsilane as internal reference. ^{13}C Nmr spectra, were determined on a Varian Unity (75.4 MHz) or a Bruker AC-200 (50.3 MHz) spectrometer. The EI-mass spectra were obtained with a Hewlett-Packard 5993 C spectrometer at 70 eV. Elemental analyses were performed with a Eager 200 instrument.

Preparation of Bis(iminophosphoranes) (3) and (4).

To a solution of triphenylphosphine (2.56 g, 9.8 mmol) in dry benzene (30 ml) a solution of bromine (1.56 g, 9.8 mmol) in the same solvent (20 ml) was added under nitrogen at 0-5°C. The reaction mixture was stirred at this temperature for 1 h and then allowed to warm to room temperature. Then a solution of the corresponding 1,2-diamino compound (**3**) or (**4**) (4.9 mmol) and triethylamine (1.98 g, 19.6 mmol) in dry benzene (20 ml) was added. The resultant solution was stirred at reflux temperature for 24 h. The precipitated solid was filtered, washed with cold ethanol, air-dried, and recrystallized from dichloromethane/n-hexane.

4-Phenyl-1,2-bis(triphenylphosphoranylideneamino)-1*H*-imidazole hydrobromide (3). -Yield: 3.04 g (80%) yellow prisms; mp 228-229°C. Anal. Calcd for $C_{45}H_{36}N_4P_2$.HBr: C, 69.68; H, 4.81; N, 7.22. Found: C, 69.86; H, 4.96; N, 6.97. $\nu_{max.}$ (cm^{-1}) 2679, 1561, 1539, 1456, 1437, 1398, 1036, 721, 692; δ (^1H, 200 MHz) ($CDCl_3$) 7.62 (34H, m), 7.18 (2H, t, J = 7.7 Hz), 7.07 (1H, t, J = 7.2 Hz); δ (^{31}P) 21.83 (N-P), 12.34 (C-P); m/z (%) 434 (2), 419 (38), 418 (19), 301 (12), 276 (88), 262 (25), 198 (11), 185 (15), 184 (16), 183 (100), 152 (21), 122 (25), 115 (7), 108 (29), 107 (25), 77 (38).

1,2-Bis(triphenylphosphoranylideneamino)benzimidazole hydrobromide (4).- Yield: 3.08 g (84%) yellow prisms; mp 196-198°C. Anal. Calcd for $C_{43}H_{34}N_4P_2$.HBr: C, 68.90; H, 4.71; N, 7.47. Found: C, 69.18; H, 4.52; N, 7.20. $\nu_{max.}$ (cm^{-1}) 2748, 2678, 1589, 1514, 1505, 1456, 1439, 1275, 1235, 1184, 1119, 856, 739, 721, 694; δ (^1H, 200 MHz) ($CDCl_3$) 7.46 (34H, m); δ (^{31}P) 22.12 (N-P), 18.14 (C-P); m/z (%) 408 (19), 407 (12), 392 (9), 277 (5), 262 (8), 238 (5), 184 (15), 183 (100), 152 (13), 133 (16), 117 (7), 108 (35), 107 (22), 91 (7), 77 (19).

Preparation of 1-Amino-4-phenyl-2-triphenylphosphoranylideneamino-1*H*-imidazole (5).

Method A.- To a solution of bis(iminophosphorane) (**3**) (0.5 g, 0.6 mmol) in dry benzene (10 ml), triethylamine (0.24 g, 2.4 mmol) was added. The mixture was stirred at room temperature for 24 h. The precipitated ammonium salts were separated by filtration and the filtrate was concentrated to dryness. The residual material was slurried with n-hexane and the formed solid was collected by filtration, dried and recrystallized from ethanol to give **5** (0.17 g, 65%).

Method B.- To a solution of triphenylphosphine (2.17 g, 8.3 mmol) in dry benzene (25 ml), a solution of bromine (1.32 g, 8.3 mmol) in the same solvent (15 ml) was added dropwise under nitrogen at 0-5°C. The resultant mixture was stirred at this temperature for 1 h and then allowed to warm to room temperature. Then a solution of 2-amino-1-bencylideneamino-4-phenyl-1*H*-imidazole (**7**) (2.17 g, 8.3 mmol) and triethylamine (1.67 g, 16.6 mmol) in dry benzene (25 ml) was added. The resultant solution was stirred at reflux temperature for 13 h. The precipitated ammonium salt was separated by filtration and the filtrate was concentrated to dryness. The residue was slurried with n-hexane and then chromatographed over a silica gel column with ethyl acetate as eluent and recrystallized from benzene/n-hexane to afford 2-benzylideneamino-4-phenyl-2-triphenylphosphoranylideneamino-1*H*-imi-

dazole (**8**) (3.69 g, 85%) as yellow prisms, mp 193-194°C. Anal. Calcd for $C_{34}H_{27}N_4P$: C, 78.14; H, 5.21; N, 10.72. Found: C, 78.23; H, 5.15; N, 10.58. $\nu_{max.}$ (cm^{-1}) 1647, 1607, 1566, 1528, 1485, 1449, 1439, 1389, 1346, 1281, 1150, 1113, 1020, 754, 723, 692; δ (^1H, 200 MHz) ($CDCl_3$) 9.05 (1H, s, -CH=N), 7.97 (6H, m), 7.80 (2H, m), 7.68 (2H, d, J = 7.8 Hz), 7.50 (12H, m), 7.30 (2H, t, J = 7.4 Hz), 7.16 (1H, t, J = 7.2 Hz); δ (^{13}C) 149.58 (d, J_{P-C} = 3.1 Hz, C-2), 148.70 (CH=N), 135.42 (q), 134.85 (q), 134.70 (q), 133.10 (d, J_{P-C} = 10.0 Hz), 131.82 (d, J_{P-C} = 2.8 Hz), 129.96, 129.74 (d, J_{P-C} = 102.1 Hz, q), 128.52, 128.29 (d, J_{P-C} = 12.5 Hz), 128.11, 127.53, 125.85, 124.36, 105.04 (C-5); δ (^{31}P) 14.99; m/z (%) 522 (M^+, 3), 419 (6), 418 (13), 303 (5), 262 (24), 185 (14), 184 (18), 183 (100), 158 (4), 157 (5), 152 (13), 133 (5), 117 (5), 108 (50), 107 (19), 105 (23), 104 (39), 103 (55), 102 (4), 77 (45).

To a solution of iminophosphorane (**8**) (2.95 g, 5.6 mmol) in dry ethanol (25 ml), anhydrous hydrazine (1.25 g, 39.2 mmol) was added. The mixture was refluxed at room temperature for 3 h, on cooling the solvent was removed under reduced pressure and the remaining solid was treated with n-hexane, filtered, air-dried and recrystallized from ethanol to give **5** (1.90 g, 78%) as yellow prisms, mp 183-185°C. Anal. Calcd for $C_{27}H_{23}N_4P$: C, 74.64; H, 5.34; N, 12.90. Found: C, 74.53; H, 5.17; N, 12.77. $\nu_{max.}$ (cm^{-1}) 3330, 3183, 1603, 1557, 1523, 1484, 1455, 1438, 1421, 1212, 1185, 1115, 1019, 997, 933, 815, 713, 693; δ (^1H, 200 MHz) ($CDCl_3$) 7.86 (6H, m), 7.45 (11H, m), 7.18 (2H, t, J = 7.5 Hz), 7.01 (1H, t, J = 7.2 Hz), 6.96 (1H, s, H-5), 4.75 (2H, s, NH_2); δ (^{13}C) 150.53 (d, J_{P-C} = 3.8 Hz, C-2), 136.04 (q), 133.05 (d, J_{P-C} = 10.0 Hz), 132.45 (d, J_{P-C} = 0.8 Hz, C-4), 131.79 (d, J_{P-C} = 2.8 Hz), 129.66 (d, J_{P-C} = 101.8 Hz, q), 128.27 (d, J_{P-C} = 12.4 Hz), 127.95, 124.80, 123.72, 111.28 (d, J_{P-C} = 1.4 Hz, C-5); δ (^{31}P) 14.95; m/z (%) 434 (M^+, 4), 433 (14), 276 (7), 262 (65), 185 (14), 184 (18), 183 (100), 152 (13), 135 (12), 132 (10), 119 (58), 116 (29), 108 (50), 107 (20), 91 (38), 77 (18).

Preparation of 2-Amino-1-triphenylphosphoranylideneaminobenzimidazole (6).

Method A.- To a solution of bis(iminophosphorane) (**4**) (0.5 g, 0.7 mmol) in benzene (10 ml), triethylamine (0.24 g, 2.4 mmol) was added. The mixture was stirred at room temperature for 24 h. The precipitated ammonium salt was separated by filtration and the filtrate was concentrated to dryness. The residual material was treated with n-hexane, filtered, air-dried, and recrystallized from ethanol to give **6** (0.21 g, 75%).

Method B.- To a mixture of 1,2-diaminobenzimidazole (**2**) (0.52 g, 3.5 mmol), triphenylphosphine (1.83 g, 7.0 mmol), and tetrahydrofuran (10 ml), a solution of diethyl azodicarboxylate (0.99 g, 7.0 mmol) in tetrahydrofuran (5 ml) was added dropwise. The resultant solution was stirred at room temperature for 12 h, thereafter the solvent was removed under reduced pressure. The residual material was chromatographed over a silica gel column with ethyl acetate/n-hexane (3:1) as eluent and then recrystallized from ethanol to give **6** (1.14 g, 80%).

Method C.- To a solution of 2-(4-methylbenzylidene)amino-1-triphenylphosphoranylideneaminobenzimidazole (**11**) (1.86 g, 3.6 mmmol) in dry ethanol (25 ml), anhydrous hydrazine (1.25 g, 39.2 mmol) was added. The mixture was refluxed for 5 h. After cooling, the solvent was removed under reduced pressure and the residue was washed

with n-hexane, filtered, air-dried, and recrystallized from ethanol to give **6** (1.10 g, 75%) as white prisms, mp 176-178°C. Anal. Calcd for $C_{25}H_{21}N_4P$: C, 73.52; H, 5.18; N, 13.72. Found: C, 73.69; H, 5.01; N, 13.48. $\nu_{max.}$ (cm^{-1}) 3324, 1591, 1483, 1437, 1406, 1300, 1277, 1244, 1182, 1117, 1082, 1005, 851, 743, 723, 693; δ (^1H, 200 MHz) ($CDCl_3$) 7.91 (6H, m), 7.51 (9H, m), 7.34 (1H, m), 7.27 (1H, m), 7.01 (2H, m), 7.01 (2H, m), 4.78 (2H, s, NH_2); δ (^{13}C) 156.37 (d, J_{P-C} = 3.9 Hz, C-2), 139.89 (C-3a), 134.47 (d, J_{P-C} = 1.5 Hz, C-7a), 132.88 (d, J_{P-C} = 10.1 Hz), 132.09 (d, J_{P-C} = 2.8 Hz), 128.96 (d, J_{P-C} = 102.2 Hz, q), 128.49 (d, J_{P-C} = 12.4 Hz), 119.69 (C-6), 118.43 (C-5), 115.75 (C-4), 106.77 (C-7); δ (^{31}P) 17.00; m/z (%) 408 (M^+, 28), 407 (20), 392 (6), 331 (4), 276 (2), 262 (13), 183 (100), 165 (10), 152 (11), 133 (5), 118 (5), 117 (8), 108 (38), 107 (23), 91 (8), 90 (6), 77 (14).

Preparation of 2-(4-Methylbenzylidene)aminobenzimidazole (9).

To a mixture of 2-aminobenzimidazole (2.0 g, 15.0 mmol), 4-tolualdehyde (1.8 g, 15.0 mmol), and ethanol (50 ml) concentrated hydrochloric acid (1 ml) was added. The resultant solution was stirred at reflux temperature for 10 h. On cooling, the solvent was removed under reduced pressure and the residue was washed with n-hexane, filtered, and recrystallized from dichloromethane/n-hexane (1:1) to give **9** (3.32 g, 94%) as yellow prisms, mp 219-221°C. Anal. Calcd for $C_{15}H_{13}N_3$: C, 76.57; H, 5.57; N, 17.86. Found: C, 76.40; H, 5.43; N, 18.06. $\nu_{max.}$ (cm^{-1}) 3364, 1618, 1605, 1570, 1526, 1449, 1427, 1348, 1312, 1287, 1235, 1211, 1042, 814, 748; δ (^1H, 200 MHz) (DMSO-d_6) 12.68 (1H, s, NH), 9.43 (1H, s, CH=N), 7.94 (2H, d, J = 8.0 Hz), 7.51 (2H, m), 7.34 (2H, d, J = 8.0 Hz), 7.17 (2H, m), 2.35 (3H, s, CH_3); δ (^{13}C) 165.14 (CH=N), 155.69 (C-2), 143.17 (q), 138.10 (C-3a= C-7a), 132.60 (q), 129.68, 129.52, 121.67 (C-5= C-6), 119.38 (C-4), 111.52 (C-7), 21.27 (CH_3); m/z (%) 235 (M^+, 33), 234 (100), 220 (4), 144 (2), 143 (3), 119 (5), 118 (40), 117 (24), 104 (4), 103 (13), 102 (6), 91 (34), 90 (28), 89 (11), 77 (22).

Preparation of 1-Amino-2-(4-methylbenzylidene)aminobenzimidazole (10).

To a solution of **9** (2.79 g, 12.0 mmol) in ethanol (5 ml) a solution of potassium hydroxide (2.69 g, 48.0 mmol) in water (15 ml) was added once. To the resultant solution hydroxylamine-*O*-sulfonic acid (1.48 g, 13.0 mmol) was added and the mixture was stirred at room temperature for 24 h. The precipitated solid was collected by filtration, washed with water, air-dried, and recrystallized from ethanol to give **10** (1.11 g, 37%) as yellow prisms, mp 226-228°C. Anal. Calcd for $C_{15}H_{14}N_4$: C, 71.98; H, 5.64; N, 22.38. Found: C, 71.77; H, 5.52; N, 22.20. $\nu_{max.}$ (cm^{-1}) 3412, 1680, 1674, 1642, 1603, 1553, 1456, 1449, 1368, 1286, 1246, 1150, 1113, 889, 822, 754, 735; δ (^1H, 200 MHz) (DMSO-d_6) 9.03 (1H, s, CH=N), 8.02 (2H, d, J = 7.9 Hz), 7.88 (1H, d, J = 7.6 Hz), 7.29 (3H, m), 7.06 (2H, m), 6.93 (2H, s, NH_2), 2.36 (3H, s, CH_3); δ (^{13}C) 154.33 (C-2), 147.77 (CH=N), 142.26 (q), 140.47 (C-3a), 131.50 (q), 129.40 (C-7a), 129.19, 127.87, 122.20 (C-6), 119.02 (C-5), 115.79 (C-4), 110.39 (C-7), 21.08 (CH_3); m/z (%) 250 (M^+, 26), 249 (9), 146 (11), 133 (24), 132 (100), 118 (7), 106 (5), 105 (34), 104 (6), 91 (14), 90 (16), 78 (10), 77 (10).

Preparation of 2-(4-Methylbenzylidene)amino-1-triphenylphosphoranylideneaminobenzimidazole (11).

This compound was prepared according to the procedure described for the preparation of the iminophosphorane (**8**). Compound (**11**) was recrystallized from acetonitrile. Yield: 0.65 g (64%) yellow prisms; mp 224-226°C. Anal. Calcd for $C_{33}H_{27}N_4P$: C, 77.63; H, 5.33; N, 10.97. Found: C, 77.40; H, 5.40; N, 10.83. $\nu_{max.}$ (cm^{-1}) 1620, 1599, 1520, 1460, 1437, 1389, 1319, 1306, 1294, 1265, 1248, 1113, 1059, 1004, 863, 742, 721, 692; δ (^1H, 200 MHz) ($CDCl_3$) 10.17 (1H, s, CH=N), 7.82 (8H, m), 7.44 (10H, m), 7.24 (3H, m), 7.00 (2H, m), 2.37 (3H, s, CH_3); δ (^{13}C) 153.43 (d, J_{P-C} = 2.5 Hz, C-2), 152.06 (CH=N), 140.18 (q), 139.95 (C-3a), 134.37 (d, J_{P-C} = 2.1 Hz, C-7a), 133.02 (d, J_{P-C} = 10.3 Hz), 132.83 (q), 132.17 (d, J_{P-C} = 2.7 Hz), 128.87 (d, J_{P-C} = 102.3 Hz, q), 129.37, 128.53 (d, J_{P-C} = 12.4 Hz), 127.26, 120.87 (C-6), 118.98 (C-5), 115.71 (C-4), 108.21 (C-7), 21.47 (CH_3); ; δ (^{31}P) 17.61; m/z (%) 510 (M^+, 8), 393 (17), 392 (18), 262 (4), 238 (9), 183 (100), 157 (4), 152 (13), 133 (7), 118 (6), 117 (5), 116 (5), 108 (41), 104 (4), 103 (9), 91 (6), 90 (5), 77 (20).

General Procedure for the Preparation of 2-Alkyl(or aryl)amino-5-phenyl-1(or 3)*H*-imidazo-[1,2-*b*]-1,2,4-triazoles (15).

To a solution of bis(iminophosphorane (**3**) (0.75 g, 0.97 mmol) in dry dichloromethane (20 ml), the appropriate aryl isocyanate (0.97 mmol) was added. The reaction mixture was stirred at room temperature for 5 h, then triethylamine (0.20 g, 1.94 mmol) was added. Stirring was continued for additional 2 h. The precipitated white solid was collected by filtration, washed with cold dichloromethane, air-dried, and recrystallized from ethanol to give **15**.

2-Methylamino-5-phenyl-1(or 3)*H*-imidazo[1,2-*b*]-1,2,4-triazole (15a).- Yield: 0.23 g (55%) white prisms; mp 268-269°C. Anal. Calcd for $C_{11}H_{11}N_5$: C, 61.96; H, 5.20; N, 32.84. Found: C, 61.80; H, 4.98; N, 32.63. $\nu_{max.}$ (cm^{-1}) 3443, 3434, 1622, 1572, 1555, 1495, 1412, 1316, 1304, 1181, 1100, 997, 957, 882, 814, 758, 743, 691; δ (^1H, 200 MHz) (DMSO-d_6) 11.98 (1H, s, N_1-H), 7.90 (1H, s, H-6), 7.65 (2H, d, J = 7.7 Hz), 7.37 (2H, t, J = 7.5 Hz), 7.22 (1H, t, J = 7.2 Hz), 5.89 (1H, q, J = 5.0 Hz, N*H*-CH_3), 2.73 (3H, d, J = 5.0 Hz, NH-C*H*$_3$); δ (^{13}C) 167.99 (C-2), 150.26 (C-3a), 130.18 (q), 128.85, 127.02 (C-5), 127.91, 123.54, 103.67 (C-6), 29.45 (CH_3); m/z (%) 213 (M^+, 69), 212 (7), 184 (34), 183 (6), 158 (7), 131 (7), 129 (19), 117 (34), 116 (15), 107 (19), 105 (13), 104 (100), 103 (25), 102 (23), 89 (11), 77 (42), 57 (25), 56 (11).

5-Phenyl-2-phenylamino-1(or 3)*H*-imidazo[1,2-*b*]-1,2,4-triazole (15b).- Yield: 0.17 g (65%) white prisms; mp 285-286°C. Anal. Calcd for $C_{16}H_{13}N_5$: C, 69.80; H, 4.76; N, 25.44. Found: C, 69.59; H, 4.62; N, 25.21. $\nu_{max.}$ (cm^{-1}) 3268, 3149, 1619, 1606, 1568, 1500, 1484, 1440, 1352, 1299, 1248, 1180, 1016, 974, 882, 750, 707, 687; δ (^1H, 200 MHz) (DMSO-d_6) 12.34 (1H, s, N_1-H), 9.24 (1H, s, NH-Ar), 8.13 (1H, s, H-6), 7.76 (2H, d, J = 7.8 Hz), 7.70 (2H, d, J = 8.3 Hz), 7.46 (2H, t, J = 7.2 Hz), 7.29 (3H, m), 6.84 (1H, t, J = 7.1 Hz); δ (^{13}C) 162.73 (C-2), 149.40

(C-3a), 141.99 (q), 129.82 (q), 128.93, 128.59, 128.04 (C-5), 127.32, 123.85, 119.09, 116.05, 103.78 (C-6); m/z (%) 275 (M^+, 64), 184 (4), 183 (15), 159 (12), 158 (100), 144 (20), 131 (25), 129 (22), 119 (10), 118 (51), 117 (82), 116 (20), 104 (50), 103 (13), 102 (14), 93 (32), 92 (13), 91 (19), 77 (61).

2-(4-Methylphenyl)amino-5-phenyl-1(or 3)*H*-imidazo[1,2-*b*]-1,2,4-triazole (15c).- Yield: 0.18 g (64%) white prisms; mp 301-302°C. Anal. Calcd for $C_{17}H_{15}N_5$: C, 70.57; H, 5.23; N, 20.20. Found: C, 70.45; H, 5.06; N, 19.99. $\nu_{max.}$ (cm^{-1}) 3268, 3149, 1624, 1607, 1564, 1518, 1495, 1483, 1443, 1348, 1298, 1246, 1182, 1017, 974, 909, 860, 837, 804, 712; δ (^1H, 200 MHz) (DMSO-d_6) 12.28 (1H, s, N_1-H), 9.01 (1H, s, NH-Ar), 8.04 (1H, s, H-6), 7.69 (2H, d, J = 7.4 Hz), 7.51 (2H, d, J = 8.4 Hz), 7.41 (2H, t, J = 7.5 Hz), 7.26 (1H, t, J = 7.1 Hz), 7.02 (2H, d, J = 8.4 Hz), 2.20 (3H, s, CH_3); δ (^{13}C) 162.94 (C-2), 149.46 (C-3a), 139.56 (q), 129.87 (q), 129.07, 129.01, 127.98 (C-5), 127.73 (q), 127.38, 123.87, 116.16, 103.81 (C-6), 20.31(CH_3); m/z (%) 289 (M^+, 73), 184 (12), 183 (6), 159 (14), 158 (100), 133 (7), 132 (34), 131 (37), 130 (14), 129 (14), 117 (40), 116 (15), 107 (14), 106 (28), 104 (38), 103 (9), 102 (8), 91 (20), 77 (39).

2-(3-Chlorophenyl)amino-5-phenyl-1(or 3)*H*-imidazo[1,2-*b*]-1,2,4-triazole (15d).- Yield: 0.21 g (69%) white prisms; mp 279-280°C. Anal. Calcd for $C_{16}H_{12}N_5Cl$: C, 62.04; H, 3.90; N, 22.61. Found: C, 61.84; H, 3.78; N, 22.46. $\nu_{max.}$ (cm^{-1}) 3268, 3149, 1618, 1607, 1564, 1497, 1487, 1445, 1336, 1302, 1231, 1179, 1096, 1076, 1022, 928, 912, 872, 835, 775, 714; δ (^1H, 200 MHz) (DMSO-d_6) 12.35 (1H, s, N_1-H), 9.49 (1H, s, NH-Ar), 8.12 (1H, s, H-6), 7.88 (1H, s), 7.70 (2H, d, J = 7.6 Hz), 7.42 (3H, m), 7.24 (2H, m), 6.82 (1H, d, J = 7.3 Hz); δ (^{13}C) 162.12 (C-2), 149.29 (C-3a), 143.38 (q), 133.29 (q), 130.11 (q), 129.71, 128.96, 128.29 (q), 128.29 (C-5), 127.45, 123.88, 118.59, 115.22, 114.64, 103.82 (C-6); m/z (%) 311 (M^++2, 28), 310 (M^++1, 17), 309 (M^+, 80), 274 (12), 184 (10), 183 (35), 159 (13), 158 (99), 157 (11), 153 (7), 152 (23), 144 (11), 137 (14), 131 (28), 129 (43), 128 (11), 127 (35), 117 (100), 116 (31), 111 (19), 104 (74), 103 (19), 102 (22), 91 (11), 77 (39).

2-(4-Chlorophenyl)amino-5-phenyl-1(or 3)*H*-imidazo[1,2-*b*]-1,2,4-triazole (15e).- Yield: 0.11 g (37%) white prisms; mp 306-307°C. Anal. Calcd for $C_{16}H_{12}N_5Cl$: C, 62.04; H, 3.90; N, 22.61. Found: C, 61.96; H, 3.75; N, 22.53. $\nu_{max.}$ (cm^{-1}) 3268, 3138, 1622, 1607, 1564, 1524, 1495, 1483, 1443, 1346, 1296, 1242, 1179, 1094, 1017, 974, 912, 831, 808, 708; δ (^1H, 200 MHz) (DMSO-d_6) 12.31 (1H, s, N_1-H), 9.39 (1H, s, NH-Ar), 8.08 (1H, s, H-6), 7.68 (4H, m), 7.41 (2H, t, J = 7.5 Hz), 7.26 (3H, m); δ (^{13}C) 162.34 (C-2), 149.34 (C-3a), 140.91 (q), 129.74 (q), 128.93, 128.37, 128.20 (C-5), 127.39, 123.88, 122.50 (q), 117.48, 103.77 (C-6); m/z (%) 311 (M^++2, 20), 310 (M^++1, 11), 309 (M^+, 60), 274 (9), 184 (6), 183 (20), 159 (13), 158 (100), 153 (6), 152 (26), 137 (11), 131 (27), 129 (34), 128 (15), 127 (27), 117 (83), 116 (25), 111 (15), 104 (59), 103 (14), 102 (17), 77 (35).

2-(4-Methoxyphenyl)amino-5-phenyl-1(or 3)*H*-imidazo[1,2-*b*]-1,2,4-triazole (15f).- Yield: 0.18 g (62%) white prisms; mp 269-270°C. Anal. Calcd for $C_{17}H_{15}N_5O$: C, 66.87; H, 4.95; N, 22.94. Found: C, 66.73; H, 4.81; N, 22.79. $\nu_{max.}$ (cm^{-1}) 3268, 3149, 1628, 1609, 1576, 1566, 1514, 1486, 1445, 1346, 1298, 1235, 1181, 1044, 1015, 974, 912, 833, 801, 712; δ (^1H, 200 MHz) (DMSO-d_6) 12.23 (1H, s, N_1-H), 8.89 (1H, s, NH-Ar), 8.03 (1H, s, H-

6), 7.68 (2H, d, J = 7.7 Hz), 7.53 (2H, d, J = 8.9 Hz), 7.40 (2H, t, J = 7.5 Hz), 7.26 (1H, t, J = 7.3 Hz), 6.83 (2H, d, J = 9.0 Hz), 3.68 (3H, s, CH_3O); δ (^{13}C) 163.21 (C-2), 152.75 (q), 149.52 (C-3a), 135.64 (q), 129.92 (q), 129.04, 127.89 (C-5), 127.38, 123.86, 117.43, 114.07, 103.84 (C-6), 55.29 (CH_3O); m/z (%) 305 (M^+, 100), 290 (28), 184 (11), 183 (53), 159 (12), 158 (79), 148 (25), 147 (8), 133 (38), 131 (25), 129 (17), 123 (11), 122 (49), 117 (76), 116 (19), 108 (23), 104 (47), 103 (18), 102 (11), 77 (36).

General Procedure for the Preparation of 2-(*N*-Alkylcarbamoyl)alkylamino-5-phenyl-1(or 3)*H*-imidazo-[1,2-*b*]-1,2,4-triazoles (16).

To a solution of bis(iminophosphorane) (**3**) (0.75 g, 0.97 mmol) in dry dichoromethane (15 ml), the appropriate alkyl isocyanate (1.94 mmol) was added. The reaction mixture was stirred at room temperature for 10 h, then triethylamine (0.20 g, 1.94 mmol) was added and stirring was continued for additional 5 h. The solvent was removed under reduced pressure and the oil material was chromatographed over a silica gel column with ethyl acetate/n-hexane (1:1) as eluent to give **16** which were recrystallized from dichloromethane/n-hexane.

2-(*N*-Methylcarbamoyl)methylamino-5-phenyl-1(or 3)*H*-imidazo[1,2-*b*]-1,2,4-triazole (16a).- Yield: 0.09 g (37%) white prisms; mp 260-262°C. Anal. Calcd for $C_{13}H_{14}N_6O$: C, 57.77; H, 5.22; N, 31.09. Found: C, 57.89; H, 5.03; N, 32.90. $\nu_{max.}$ (cm^{-1}) 3368, 3314, 1723, 1634, 1607, 1573, 1526, 1462, 1414, 1335, 1225, 833, 747, 718, 691; δ (^1H, 200 MHz) (DMSO-d_6) 7.79 (1H, q, J = 3.8 Hz, CH_3-N*H*-CO), 7.74 (2H, d, J = 7.3 Hz), 7.53 (1H, s, H-6), 7.40 (2H, d, J = 7.5 Hz), 7.22 (1H, t, J = 7.3 Hz), 6.94 (1H, q, J = 4.9 Hz, N*H*-CH_3), 3.02 (6H, t, J = 4.6 Hz, 2xCH_3); δ (^{13}C) 153.93 (C-3a), 150.23 (C-2), 140.30 (C=O), 140.07 (C-5), 134.35 (q), 128.49, 126.60, 124.44, 104.42 (C-6), 28.73 (CH_3-NH), 26.67 (*C*H_3-NH-CO); m/z (%) 270 (M^+, 16), 214 (13), 213 (100), 212 (9), 184 (18), 158 (8), 117 (5), 116 (4), 104 (10), 103 (10), 102 (4), 77 (4), 58 (13), 57 (3).

2-(*N*-Benzylcarbamoyl)benzylamino-5-phenyl-1(or 3)*H*-imidazo[1,2-*b*]-1,2,4-triazole (16b).- Yield: 0.14 g (35%) white prisms; mp 131-133°C. Anal. Calcd for $C_{25}H_{22}N_6O$: C, 71.07; H, 5.25; N, 19.89. Found: C, 70.90; H, 5.11; N, 19.67. $\nu_{max.}$ (cm^{-1}) 3362, 3298, 1717, 1626, 1605, 1589, 1573, 1553, 1516, 1456, 1364, 1335, 1304, 1217, 1028, 822, 746, 725, 712, 696; δ (^1H, 200 MHz) (DMSO-d_6) 8.46 (1H, t, J = 5.9 Hz, -CH_2-N*H*-CO), 7.70 (2H, d, J = 7.7 Hz), 7.41 (1H, s, H-6), 7.25 (15H, m), 4.58 (2H, d, J = 5.9 Hz, -CH_2-), 4.50 (2H, d, J = 5.9 Hz, -CH_2-); δ (^{13}C) 152.96 (C-3a), 149.74 (C-2), 140.17 (C=O), 140.15 (C-5), 137.17 (q), 137.08 (q), 134.26, 128.70, 128.64, 128.44, 127.64, 127.54, 127.24, 126.58, 124.42, 104.48 (C-6), 46.30 (-CH_2-NH), 43.91 (-*C*H_2-NH-CO). A tertiary carbon atom is not observed; m/z (%) 290 (4), 289 (M^+-RNCO, 18), 185 (14), 184 (77), 183 (11), 159 (11), 131 (8), 129 (10), 117 (20), 116 (17), 106 (46), 104 (40), 102 (17), 91 (100), 77 (26).

Preparation of 4-Phenyl-1-(*N*-phenylcarbamoyl)-2-triphenylphosphoranylideneamino-1*H*-imidazole (17).

Phenyl isocyanate (0.27 g, 2.3 mmol) was added to a solution of iminophosphorane (**5**) (1.0 g, 2.3 mmol)in dry

toluene (15 ml). The resultant solution was stirred at reflux temperature for 3 h. After cooling, the solvent was removed under reduced pressure and the residue was treated with n-hexane. The solid formed was filtered, air-dried, and recrystallized from ethanol to give **17** (0.99 g, 78%) as white prisms, mp 196-197°C. Anal. Calcd for $C_{34}H_{28}N_5OP$: C, 73.77; H, 5.10; N, 12.65. Found: C, 73.46; H, 4.91; N, 12.39. $\nu_{max.}$ (cm^{-1}) 3381, 1733, 1603, 1563, 1547, 1520, 1501, 1485, 1458, 1439, 1343, 1316, 1229, 1181, 1115, 1044, 756, 723, 692; δ (^1H, 200 MHz) (DMSO-d_6) *9.18 (1H, s, NH), 9.08 (1H, s, NH), 7.87 (6H, m), 7.52 (13H, m), 7.26 (4H, m), 7.01 (2H, m)*; δ (^{13}C) 150.30 (C=O), 150.94 (d, J_{P-C} = 4.5 Hz, C-2), 139.58 (q), 135.64 (q), 132.79 (d, J_{P-C} = 10.1 Hz), 132.12 (d, J_{P-C} = 1.3 Hz), 129.82 (d, J_{P-C} = 103.8 Hz, q), 129.81, 128.76, 128.44 (d, J_{P-C} = 12.3 Hz), 128.15, 125.05, 123.47, 118.74, 113.08; δ (^{31}P) 15.98; m/z (%) 434 (8), 303 (26), 262 (21), 184 (19), 183 (100), 152 (46), 119 (69), 116 (23), 108 (79), 107 (28), 92 (22), 77 (43).

General Procedure for the Preparation of 2-[*N*-Alkyl(or aryl)carbamoyl]alkyl(or aryl)amino-1(or 3)*H*-1,2,4-triazolo[1,5-*a*]benzimidazoles (18).

To a solution of bis(iminophosphorane **(4)** (1.50 g, 2.0 mmol) in dry dichoromethane (15 ml), the appropriate isocyanate (2.0 mmol) was added. The reaction mixture was stirred at room temperature for 10 h. Then, Triethylamine (0.20 g, 2.0 mmol) was added and the stirring was continued for additional 5 h. The solvent was removed under reduced pressure and the residual material was either recrystallized from ethanol (for aromatic isocyanates) or chromatographed over a silica gel column with ethyl acetate/n-hexane (1:1) as eluent (for aliphatic isocyanates) to give **18**.

2-(*N*-Methylcarbamoyl)methylamino-1(or 3)*H*-1,2,4-triazolo[1,5-*a*]benzimidazole (18a).- Yield: 0.26 g (53%) white prisms; mp 176-178°C. Anal. Calcd for $C_{11}H_{12}N_6O$: C, 54.09; H, 4.95; N, 34.41. Found: C, 53.98; H, 5.13; N, 34.22. $\nu_{max.}$ (cm^{-1}) 3341, 3290, 1719, 1619, 1586, 1559, 1514, 1454, 1443, 1435, 1406, 1312, 1288, 1275, 1236, 1188, 1177, 1123, 963, 748, 725, 700; δ (^1H, 200 MHz) ($CDCl_3$) 8.36 (1H, m, H-8), 7.55 (1H, m, H-5), 7.29 (2H, m), 4.53 (1H, q, J = 5.1 Hz, N*H*-CH_3), 3.04 (6H, m, 2xCH_3); δ (^{13}C) 167.42 (C-2), 150.08 (C-3a), 149.94 (C=O), 130.76 (C-4a), 125.35 (C-8a), 123.93 (C-7), 123.54 (C-6), 116.46 (C-5), 109.17 (C-8), 29.97 (CH_3-NH), 26.88 (*C*H_3-NH-CO); m/z (%) 244 (M^+, 17), 188 (12), 187 (100), 186 (19), 159 (13), 158 (43), 157 (3), 144 (5), 133 (8), 132 (18), 131 (15), 118 (8), 117 (8), 105 (9), 104 (16), 102 (11), 90 (20), 77 (14), 58 (18), 57 (6).

2-(*N*-Benzylcarbamoyl)benzylamino-1(or 3)*H*-1,2,4-triazolo[1,5-*a*]benzimidazole (18b).- Yield: 0.41 g (51%) white prisms; mp 151-153°C. Anal. Calcd for $C_{23}H_{20}N_6O$: C, 69.68; H, 5.08; N, 21.20. Found: C, 69.57; H, 5.01; N, 21.45. $\nu_{max.}$ (cm^{-1}) 3347, 3268, 1726, 1715, 1615, 1589, 1557, 1501, 1476, 1456, 1433, 1345, 1310, 1279, 1236, 986, 963, 747, 727, 700; δ (^1H, 200 MHz) (DMSO-d_6) 8.18 (2H, m), 7.36 (14H, m), 4.60 (2H, d, J = 5.8 Hz, -*C*H_2-NH-CO), 4.42 (2H, d, J = 6.3 Hz, -C*H*$_2$-NH); δ (^{13}C) 166.70 (C-2), 149.86 (C=O), 149.13 (C-3a), 140.14 (q), 138.27 (q), 130.46 (C-4a), 128.55, 128.13, 127.33, 127.29, 127.22, 126.62, 125.06 (C-8a), 124.06 (C-7), 123.21 (C-6),

115.82 (C-5), 109.08 (C-8), 45.97 (-CH_2-NH), 43.43 (-CH_2-NH-CO); m/z (%) 396 (M^+, 5), 264 (6), 263 (32), 262 (10), 159 (10), 158 (40), 144 (2), 134 (5), 133 (24), 132 (12), 131 (6), 117 (5), 106 (27), 105 (11), 104 (10), 91 (100), 90 (11), 77 (9).

2-(*N*-Phenylcarbamoyl)phenylamino-1(or 3)*H*-1,2,4-triazolo[1,5-*a*]benzimidazole (18c).- Yield: 0.42 g (58%) white prisms; mp 335-336°C. Anal. Calcd for $C_{21}H_{16}N_6O$: C, 68.47; H, 4.38; N, 22.81. Found: C, 68.33; H, 4.26; N, 23.03. $\nu_{max.}$ (cm^{-1}) 3330, 3290, 1725, 1625, 1608, 1585, 1563, 1500, 1472, 1455, 1381, 1325, 1308, 1291, 1257, 1014, 889, 747, 685; δ (^1H, 200 MHz) (DMSO-d_6) 9.37 (1H, s, NH), 8.66 (1H, s, NH-CO), 7.66 (3H, m), 7.47 (3H, m), 7.25 (6H, m), 6.91 (2H, m); δ (^{13}C) 163.14 (C-2), 152.55 (C=O), 152.07 (C-3a), 141.58 (q), 139.70 (q), 132.90 (C-4a), 128.77, 128.65, 124.42 (C-8a), 122.33 (C-7), 121.82 (C-6), 119.51, 118.22, 116.26, 112.47 (C-5), 109.03 (C-8); m/z (%) 368 (M^+, 1), 250 (18), 249 (100), 209 (3), 158 (9), 144 (6), 133 (7),.132 (80), 119 (79), 118 (17), 117 (5), 105 (18), 104 (8), 92 (12), 91 (49), 90 (22), 77 (28).

2-[*N*-(4-Methylphenyl)carbamoyl](4-methylphenyl)amino-1(or 3)*H*-1,2,4-triazolo[1,5-*a*]benzimidazole (18d).- Yield: 0.51 g (64%) white prisms; mp 330-331°C. Anal. Calcd for $C_{23}H_{20}N_6O$: C, 69.68; H, 5.08; N, 21.20. Found: C, 69.50; H, 5.32; N, 21.45. $\nu_{max.}$ (cm^{-1}) 3314, 3287, 1723, 1624, 1617, 1605, 1584, 1566, 1520, 1507, 1472, 1453, 1393, 1323, 1304, 1291, 1258, 1188, 1123, 1011, 808, 741; δ (^1H, 200 MHz) (DMSO-d_6) 9.22 (1H, s, NH), 8.49 (1H, s, NH-CO), 7.61 (3H, m), 7.45 (1H, m), 7.34 (2H, d, J = 8.3 Hz), 7.22 (2H, m), 7.07 (4H, m), 2.22 (6H, s, 2xCH_3); δ (^{13}C) 163.35 (C-2), 152.65 (C=O), 152.11 (C-3a), 139.18 (q), 137.24 (q), 132.89 (C-4a), 130.50 (q), 129.12, 129.04, 128.05 (q), 124.46 (C-8a), 122.19 (C-7), 121.12 (C-6), 118.25, 116.34, 112.41 (C-5), 108.95 (C-8), 20.29 (CH_3); m/z (%) 396 (M^+, 1), 264 (4), 263 (21), 262 (3), 158 (3), 134 (9), 133 (100), 132 (75), 131 (5), 105 (19), 104 (28), 91 (15), 90 (6), 77 (15).

2-[*N*-(4-Chlorophenyl)carbamoyl](4-chlorophenyl)amino-1(or 3)*H*-1,2,4-triazolo[1,5-*a*]benzimidazole (18e).- Yield: 0.49 g (56%) white prisms; mp 341-343°C. Anal. Calcd for $C_{21}H_{14}N_6OCl_2$: C, 57.68; H, 3.23; N, 19.22. Found: C, 57.43; H, 3.09; N, 18.98. $\nu_{max.}$ (cm^{-1}) 3324, 3279, 1725, 1622, 1609, 1582, 1574, 1568, 1557, 1497, 1472, 1453, 1308, 1289, 1250, 1194, 1090, 1009, 824, 747, 696; δ (^1H, 200 MHz) (DMSO-d_6) 9.62 (1H, s, NH), 8.91 (1H, s, NH-CO), 7.70 (3H, m), 7.50 (3H, m), 7.30 (6H, m); δ (^{13}C) 162.74 (C-2), 152.31 (C=O), 151.90 (C-3a), 140.50 (q), 138.53 (q), 132.86 (C-4a), 128.56, 128.42, 125.48 (q), 124.31 (C-8a), 122.88 (q), 122.40 (C-7), 121.19 (C-6), 119.79, 117.65, 112.48 (C-5), 109.05 (C-8); m/z (%) 285 (32), 284 (19), 283 (M^+-ArNCO, 100), 248 (14), 158 (11), 154 (4), 153 (7), 133 (9), 132 (87), 127 (8), 126 (10), 125 (8), 117 (5), 111 (9), 105 (21), 104 (8), 90 (29), 77 (4).

2-[*N*-(4-Methoxyphenyl)carbamoyl](4-methoxyphenyl)amino-1(or 3)*H*-1,2,4-triazolo[1,5-*a*]benzimidazole (18f).- Yield: 0.52 g (60%) white prisms; mp 308-309°C. Anal. Calcd for $C_{23}H_{20}N_6O_3$: C, 64.48; H, 4.71; N, 19.61. Found: C, 64.66; H, 4.89; N, 19.40. $\nu_{max.}$ (cm^{-1}) 3330, 3290, 1721, 1630, 1615, 1584, 1574, 1572, 1518, 1474, 1456, 1391, 1319, 1304, 1246, 1181, 1044, 1009, 839, 822, 808, 748, 707; δ (^1H, 200 MHz) (DMSO-d_6) 9.12 (1H, s, NH),

8.36 (1H, s, NH-CO), 7.59 (3H, m), 7.44 (1H, m), 7.33 (2H, d, J = 8.0 Hz), 7.24 (2H, m), 6.86 (4H, m), 3.69 (6H, s, 2xCH_3O); δ (^{13}C) 163.52 (C-2), 154.34 (q), 152.95 (C=O), 152.89 (q), 152.11 (C-3a), 135.13 (q), 132.91 (q), 132.83 (C-4a), 124.43 (C-8a), 122.13 (C-7), 121.12 (C-6), 119.92, 117.57, 114.00, 113.95, 112.38 (C-5), 108.86 (C-8), 55.33 (CH_3O); m/z (%) 280 (18), 279 (M^+-ArNCO, 100), 265 (14), 264 (81), 158 (18), 157 (29), 148 (8), 144 (8), 133 (24), 132 (56), 122 (7), 118 (6), 117 (6), 108 (10), 106 (4), 104 (8), 90 (25), 77 (8).

General Procedure for the Preparation of 2-Alkyl(or aryl)amino-1*H*-1,2,4-triazolo[1,5-*a*]benzimidazoles (19).

A solution of compound **(18)** (2.0 mmol) in ethanol (15 ml) was refluxed with stirring for 24 h. After cooling, the solvent was removed under reduced pressure and the residue was recrystallized from ethanol to give **19**.

2-Methylamino-1*H*-1,2,4-triazolo[1,5-*a*]benzimidazole (19a).- Yield: 0.20 g (52%) white prisms; mp 288-290°C. Anal. Calcd for $C_9H_9N_5$: C, 57.74; H, 4.85; N, 37.41. Found: C, 57.62; H, 4.66; N, 37.59. $\nu_{max.}$ (cm^{-1}) 3285, 3200, 1634, 1624, 1497, 1483, 1456, 1395, 1329, 1229, 1173, 1109, 1036, 1009, 986, 845, 747, 733; δ (^1H, 200 MHz) (DMSO-d_6) 11.42 (1H, s, N_1-H), 7.04 (1H, m, H-8), 6.92 (1H, m, H-5), 6.71 (2H, m, H-6, H-7), 5.60 (1H, q, J = 4.2 Hz, N*H*-CH_3), 2.40 (3H, d, J = 4.2 Hz, CH_3-NH); δ (^{13}C) 168.32 (C-2), 152.87 (C-3a), 132.49 (C-4a), 124.52 (C-8a), 121.23 (C-7), 120.56 (C-6), 111.95 (C-5), 108.26 (C-8), 29.28 (CH_3); m/z (%) 187 (M^+, 100), 186 (24), 159 (18), 158 (82), 157 (11), 145 (8), 144 (10), 133 (9), 132 (14), 131 (12), 118 (5), 117 (7), 105 (5), 104 (6), 90 (13), 55 (4).

2-Benzylamino-1*H*-1,2,4-triazolo[1,5-*a*]benzimidazole (19b).- Yield: 0.26 g (52%) white prisms; mp 257-258°C. Anal. Calcd for $C_{15}H_{13}N_5$: C, 68.43; H, 4.98; N, 26.60. Found: C, 68.50; H, 4.81; N, 26.41. $\nu_{max.}$ (cm^{-1}) 3273, 3200, 1634, 1621, 1589, 1580, 1495, 1456, 1445, 1364, 1314, 1231, 1171, 1040, 1009, 847, 748, 731, 696; δ (^1H, 200 MHz) (DMSO-d_6) 12.02 (1H, s, N_1-H), 7.39 (9H, m), 6.88 (1H, t, J = 6.1 Hz, N*H*-CH_2-), 4.44 (2H, d, J = 6.1 Hz, -CH_2-NH); δ (^{13}C) 167.65 (C-2), 152.92 (C-3a), 140.74 (q), 132.57 (C-4a), 128.00, 127.07, 126.37, 124.49 (C-8a), 121.59 (C-7), 120.85 (C-6), 112.18 (C-5), 108.51 (C-8), 46.03 (CH_2); m/z (%) 263 (M^+, 47), 262 (9), 234 (4), 186 (16), 172 (10), 160 (5), 159 (18), 157 (4), 133 (21), 132 (7), 131 (7), 118 (7), 117 (9), 116 (6), 106 (38), 105 (11), 104 (10), 102 (9), 91 (100), 90 (24), 77 (11).

2-Phenylamino-1*H*-1,2,4-triazolo[1,5-*a*]benzimidazole (19c).- Yield: 0.26 g (53%) white prisms; mp 332-333°C. Anal. Calcd for $C_{14}H_{11}N_5$: C, 67.46; H, 4.45; N, 28.09. Found: C, 67.25; H, 4.29; N, 27.84. $\nu_{max.}$ (cm^{-1}) 3268, 3202, 1632, 1609, 1600, 1574, 1568, 1493, 1474, 1456, 1368, 1298, 1235, 1175, 1042, 893, 837, 741, 694; δ (^1H, 200 MHz) (DMSO-d_6) 12.16 (1H, s, N_1-H), 9.42 (1H, s, NH), 7.72 (2H, d, J = 8.2 Hz), 7.69 (1H, m, H-8), 7.47 (1H, m, H-5),7.27 (4H, m), 6.84 (1H, t, J = 7.2 Hz); δ (^{13}C) 163.15 (C-2), 152.08 (C-3a), 141.60 (q), 132.90 (C-4a), 128.66, 124.42 (C-8a), 122.31 (C-7), 121.18 (C-6), 119.51, 116.27, 112.47 (C-5), 109.02 (C-8); m/z (%) 249 (M^+, 100), 248 (9), 208 (8), 158 (5), 157 (2), 132 (32), 124 (7), 118 (8), 105 (9), 91 (5), 90 (9), 77 (9).

2-(4-Methylphenyl)amino-1*H*-1,2,4-triazolo[1,5-*a*]benzimidazole (19d).- Yield: 0.31 g (59%) white prisms; mp 331-332°C. Anal. Calcd for $C_{15}H_{13}N_5$: C, 68.43; H, 4.98; N, 26.60. Found: C, 68.50; H, 4.78; N, 26.78. $\nu_{max.}$ (cm^{-1}) 3270,3200, 1630, 1622, 1617, 1601, 1568, 1559, 1520, 1472, 1454, 1360, 1336, 1296, 1237, 1171, 1044, 1013, 907, 816, 743; δ (^1H, 200 MHz) (DMSO-d_6) 12.24 (1H, s, N_1-H), 9.33 (1H, s, NH), 7.67 (3H, m), 7.51 (1H, m, H-5), 7.28 (2H, m),7.13 (2H, d, J = 7.8 Hz), 2.28 (3H, s, CH_3); δ (^{13}C) 163.38 (C-2), 152.14 (C-3a), 139.20 (q), 132.92 (C-4a), 129.09, 128.10 (q), 124.49 (C-8a), 122.23 (C-7), 121.16 (C-6), 116.38, 112.45 (C-5), 108.98 (C-8), 20.31 (CH_3); m/z (%) 263 (M^+, 100), 262 (18), 248 (2), 222 (4), 158 (9), 132 (51), 131 (11), 117 (3), 116 (4), 106 (8), 105 (18), 104 (10), 91 (16), 90 (17), 77 (21).

2-(4-Chlorophenyl)amino-1*H*-1,2,4-triazolo[1,5-*a*]benzimidazole (19e).- Yield: 0.29 g (51%) white prisms; mp 335-336°C. Anal. Calcd for $C_{14}H_{10}N_5Cl$: C, 59.27; H, 3.55; N, 24.68. Found: C, 59.14; H, 3.36; N, 24.44. $\nu_{max.}$ (cm^{-1}) 3268, 3187, 1624, 1605, 1566, 1559, 1495, 1472, 1454, 1362, 1335, 1296, 1235, 1173, 1098, 1042, 1013, 905, 847, 824, 741; δ (^1H, 200 MHz) (DMSO-d_6) 12.24 (1H, s, N_1-H), 9.64 (1H, s, NH), 7.76 (2H, d, J = 8.9 Hz), 7.70 (1H, m, H-8), 7.52 (1H, m, H-5),7.36 (2H, d, J = 8.9 Hz), 7.29 (2H, m); δ (^{13}C) 162.78 (C-2), 152.03 (C-3a), 140.53 (q), 132.89 (C-4a), 128.48, 124.35 (C-8a), 122.94 (q), 122.44 (C-7), 121.24 (C-6), 117.70, 112.54 (C-5), 109.10 (C-8); m/z (%) 285 (M^++2, 33), 283 (M^+, 100), 282 (6), 248 (16), 207 (4), 158 (7), 157 (2), 152 (6), 125 (3), 132 (32), 111 (4), 105 (7), 90 (10).

2-(4-Methoxyphenyl)amino-1*H*-1,2,4-triazolo[1,5-*a*]benzimidazole (19f).- Yield: 0.31 g (57%) white prisms; mp 293-294°C. Anal. Calcd for $C_{15}H_{13}N_5O$: C, 64.51; H, 4.69; N, 25.07. Found: C, 64.77; H, 4.48; N, 25.25. $\nu_{max.}$ (cm^{-1}) 3252, 3117, 1630, 1622, 1607, 1570, 1559, 1516, 1491, 1476, 1456, 1337, 1282, 1260, 1237, 1179, 1117, 1046, 1036, 1019, 912, 851, 831, 793, 739, 710; δ (^1H, 200 MHz) (DMSO-d_6) 12.15 (1H, s, N_1-H), 9.11 (1H, s, NH), 7.62 (3H, m), 7.44 (1H, m, H-5),7.23 (2H, m), 6.88 (2H, d, J = 8.4 Hz), 3.70 (3H, s, CH_3O); δ (^{13}C) 163.57 (C-2), 152.94 (q), 152.15 (C-3a), 135.17 (q), 132.86 (C-4a), 124.47 (C-8a), 122.14 (C-7), 121.14 (C-6), 117.64, 114.04, 112.40 (C-5), 108.88 (C-8), 55.19 (CH_3O); m/z (%) 279 (M^+, 100), 278 (5), 265 (11), 264 (61), 158 (4), 157 (6), 148 (2), 133 (6), 132 (18), 122 (2), 105 (6), 90 (6).

General Procedure for the Preparation of 1(or 3)-Acyl-2-aryl-5-phenyl-1(or 3)*H*-imidazo[1,2-*b*]-1,2,4-triazoles (23) and 2-Aryl-1(or 3)-aroyl-1(or 3)*H*-1,2,4-triazolo[1,5-*a*]benzimidazoles (24).

To a solution of bis(iminophosphorane) (**3**) or (**4**) (1.0 mmol) in dry dichloromethane (20 ml), the appropriate acyl chloride (2 mmol) was added. The mixture was stirred at room temperature for 10 h. Then, triethylamine (0.4 g, 2.0 mmol) was added and the stirring was continued at this temperature for additional 5 h. The solvent was removed under reduced pressure and the residue was washed with ethanol, filtered, air-dried, and recrystallized from ethanol (compounds (**23**)) or acetonitrile (compounds (**24**)).

1(or 3)-Benzoyl-2,5-diphenyl-1(or 3)*H*-imidazo[1,2-*b*]-1,2,4-triazole (23a).- Yield: 0.13 g (38%) white prisms;

mp 177-179°C. Anal. Calcd for $C_{23}H_{16}N_4O$: C, 75.81; H, 4.43; N, 15.37. Found: C, 75.67; H, 4.25; N, 15.11. $\nu_{max.}$ (cm^{-1}) 1711, 1617, 1601, 1549, 1449, 1427, 1336, 1289, 1273, 1215, 1123, 1115, 930, 829, 760, 694; δ (^1H, 200 MHz) ($CDCl_3$) 8.01 (4H, m), 7.67 (1H, t, J = 7.3 Hz), 7.45 (11H, m); δ (^{13}C) 165.56 (C-2), 165.03 (C=O), 151.73 (C-3a), 134.43, 133.19 (q), 131.30 (q), 131.25 (q), 131.07, 129.32, 128.90 (C-5), 128.81, 128.62, 128.39, 128.39, 127.79, 126.47, 109.39 (C-6); m/z (%) 364 (M^+, 30), 260 (10), 259 (8), 129 (6), 106 (8), 105 (100), 104 (3), 103 (5), 102 (4), 77 (29).

1(or 3)-(4-Methylbenzoyl)-2-(4-methylphenyl)-5-phenyl-1(or 3)*H*-imidazo[1,2-*b*]-1,2,4-triazole (23b).- Yield: 0.17 g (44%) white prisms; mp 226-228°C. Anal. Calcd for $C_{25}H_{20}N_4O$: C, 76.51; H, 5.14; N, 14.28. Found: C, 76.36; H, 5.02; N, 14.46. $\nu_{max.}$ (cm^{-1}) 1703, 1609, 1576, 1553, 1460, 1429, 1330, 1271, 1182, 1119, 1109, 1020, 972, 828, 735, 698; δ (^1H, 200 MHz) (DMSO-d_6) 8.35 (1H, s, H-6), 8.09 (2H, d, J = 8.1 Hz), 7.92 (2H, d, J = 7.8 Hz), 7.52 (7H, m), 7.35 (2H, d, J = 8.1 Hz), 2.57 (3H, s, CH_3), 2.45 (3H, s, CH_3); δ (^{13}C) 165.13 (C-2), 163.65 (C=O), 151.39 (C-3a), 145.28 (q), 138.67 (q), 132.34 (q), 130.92, 129.01, 128.99, 128.87 (C-5), 128.43 (q), 128.39 (q), 128.24, 128.16, 127.42, 125.73, 110.04 (C-6), 21.17 (CH_3), 20.71 (CH_3); m/z (%) 392 (M^+, 6), 129 (3), 119 (100), 117 (2), 116 (4), 103 (2), 102 (3), 91 (34), 89 (5), 77 (4).

1(or 3)-(4-Bromobenzoyl)-2-(4-bromophenyl)-5-phenyl-1(or 3)*H*-imidazo[1,2-*b*]-1,2,4-triazole (23c).- Yield: 0.17 g (35%) white prisms; mp 258-259°C. Anal. Calcd for $C_{23}H_{14}N_4OBr_2$: C, 52.90; H, 2.70; N, 10.73. Found: C, 53.15; H, 2.88; N, 10.60. $\nu_{max.}$ (cm^{-1}) 1711, 1605, 1584, 1574, 1545, 1460, 1449, 1427, 1334, 1265, 1179, 1107, 1067, 1011, 922, 841, 750, 729; δ (^1H, 200 MHz) ($CDCl_3$/CF_3COOH) 8.01 (4H, m), 7.67 (1H, t, J = 7.3 Hz), 7.45 (11H, m); δ (^{13}C) 172.87 (q), 155.15 (q), 140.46 (q), 136.06 (q), 133.06 (q), 133.26, 132.38, 132.02, 131.00, 130.59 (q), 129.80, 128.45, 128.35 (q), 127.02 (q), 126.03, 122.63 (q), 105.35 (C-6). A quaternary carbon atom is not observed; m/z (%) 524 (M^++2, 4), 522 (M^+, 4), 186 (7), 185 (99), 184 (8), 183 (100), 157 (28), 155 (28), 129 (14), 116 (5), 104 (11), 103 (6), 102 (18), 102 (18), 77 (17), 76 (23).

1(or 3)-(4-Chlorobenzoyl)-2-(4-Chlorophenyl)-5-phenyl-1(or 3)*H*-imidazo[1,2-*b*]-1,2,4-triazole (23d).- Yield: 0.19 g (46%) white prisms; mp 243-244°C. Anal. Calcd for $C_{23}H_{14}N_4OCl_2$: C, 63.76; H, 3.26; N, 12.93. Found: C, 63.61; H, 3.18; N, 12.80. $\nu_{max.}$ (cm^{-1}) 1715, 1605, 1588, 1578, 1547, 1487, 1456, 1447, 1427, 1404, 1333, 1265, 1209, 1179, 1111, 1090, 1017, 924, 878, 847, 729, 696; δ (^1H, 200 MHz) (DMSO-d_6) 8.22 (1H, s, H-6), 8.04 (2H, d, J = 8.5 Hz), 7.93 (2H, d, J = 8.5 Hz), 7.76 (2H, d, J = 7.4 Hz), 7.44 (7H, m); δ (^{13}C) 166.45 (C-2), 162.38 (C=O), 151.61 (q), 137.81 (q), 133.42 (q), 131.29 (q), 131.12, 129.64 (q), 129.35 (C-5), 128.99, 128.69, 128.69, 128.10 (q), 127.48 (q), 124.44, 103.54 (C-6). A quaternary carbon atom is not observed; m/z (%) 434(M^++2, 3), 432 (M^+, 9), 293 (1), 141 (32), 139 (100), 137 (2), 129 (3), 116 (10), 113 (17), 111 (21), 104 (2), 77 (4), 75 (6).

1(or 3)-(4-Methoxybenzoyl)-2-(4-methoxyphenyl)-5-phenyl-1(or 3)*H*-imidazo[1,2-*b*]-1,2,4-triazole (23e).- Yield: 0.13 g (39%) white prisms; mp 227-229°C. Anal. Calcd for $C_{25}H_{20}N_4O_3$: C, 70.34; H, 4.75; N, 13.20. Found: C, 70.47; H, 4.60; N, 13.10. $\nu_{max.}$ (cm^{-1}) 1701, 1607, 1580, 1555, 1534, 1470, 1456, 1429, 1339, 1252, 1175, 1117,

1105, 1036, 924, 843, 747, 698; δ (^{1}H, 200 MHz) ($CDCl_3$/CF_3COOH) 7.91 (2H, d, J = 8.7 Hz), 7.74 (2H, d, J = 8.7 Hz), 7.65 (1H, s, H-6), 7.35 (5H, m), 6.98 (2H, d, J = 8.7 Hz), 6.82 (2H, d, J = 8.7 Hz), 3.84 (3H, s, CH_3O), 3.82 (3H, s, CH_3O); δ (^{13}C) 165.69 (C-2), 162.87 (C=O), 162.50 (q), 159.62 (q), 144.69 (q), 134.95 (q), 133.57, 129.94 (q), 128.95, 128.95, 128.43, 126.68 (C-5), 121.38 (q), 118.10 (q), 114.69, 114.54, 108.40 (C-6), 55.63 (CH_3O), 55.40 (CH_3O); m/z (%) 424 (M^+, 18), 290 (7), 289 (12), 186 (8), 135 (100), 133 (4), 129 (3), 107 (7), 103 (3), 92 (8), 77 (9).

1(or 3)-Benzoyl-2-phenyl-1(or 3)*H*-1,2,4-triazolo[1,5-*a*]benzimidazole (24a).- Yield: 0.13 g (39%) white prisms; mp 215-216°C. Anal. Calcd for $C_{21}H_{14}N_4O$: C, 74.54; H, 4.17; N, 16.56. Found: C, 74.43; H, 4.05; N, 16.78. $\nu_{max.}$ (cm^{-1}) 1700, 1605, 1597, 1557, 1520, 1495, 1472, 1456, 1449, 1429, 1390, 1316, 1271, 1221, 1186, 1157, 1109, 1073, 1026, 968, 943, 858, 779, 756, 698; δ (^{1}H, 200 MHz) ($CDCl_3$/CF_3COOH) 8.10 (1H, dd, J = 7.5, 1.8 Hz), 7.91 (5H, m), 7.73 (1H, d, J = 7.4 Hz), 7.50 (7H, m); δ (^{13}C) 166.22 (C-2), 164.78 (C=O), 151.59 (C-3a), 133.99 (q), 132.70 (C-4a), 131.56 (q), 130.28 (q), 129.92, 129.70 (q), 128.68, 128.53, 126.82, 125.91 (C-7), 125.65 (C-6), 125.18 (C-8a), 117.38 (C-5), 111.05 (C-8); m/z (%) 338 (M^+, 4), 130 (2), 106 (8), 105 (100), 104 (1), 103 (3), 102 (8), 77 (32).

1(or 3)-(4-Methylbenzoyl)-2-(4-methylphenyl)-1(or 3)*H*-1,2,4-triazolo[1,5-*a*]benzimidazole (24b).- Yield: 0.18 g (48%) white prisms; mp 237-238°C. Anal. Calcd for $C_{23}H_{18}N_4O$: C, 75.39; H, 4.95; N, 15.29. Found: C, 75.14; H, 4.77; N, 15.10. $\nu_{max.}$ (cm^{-1}) 1699, 1615, 1601, 1559, 1534, 1495, 1472, 1456, 1429, 1395, 1316, 1271, 1225, 1186, 1179, 1107, 1076, 1022, 966, 941, 868, 822, 789, 756, 721; δ (^{1}H, 200 MHz) ($CDCl_3$) 8.31 (1H, d, J = 6.9 Hz), 7.90 (4H, m), 7.81 (1H, d, J = 6.9 Hz), 7.37 (4H, m), 7.19 (2H, d, J = 7.6 Hz), 2.51 (3H, s, CH_3), 2.36 (3H, s, CH_3); δ (^{13}C) 166.46 (C-2), 165.49 (C=O), 152.52 (C-3a), 144.45 (q), 139.63 (q), 133.03 (C-4a), 131.94 (q), 130.38, 129.14, 128.77, 128.27 (q), 126.55, 125.67 (C-8a), 125.18 (C-7), 125.14 (C-6), 117.74 (C-5), 110.58 (C-8), 21.86 (CH_3), 21.40 (CH_3) m/z (%) 366 (M^+, 17), 247 (2), 130 (7), 120 (9), 119 (100), 117 (6), 116 (9), 103 (3), 102 (30), 91 (48), 90 (10), 89 (11), 76 (5).

1(or 3)-(4-Bromobenzoyl)-2-(4-bromophenyl)-1(or 3)*H*-1,2,4-triazolo[1,5-*a*]benzimidazole (24c).- Yield: 0.17 g (34%) white prisms; mp 314-315°C. Anal. Calcd for $C_{21}H_{12}N_4OBr_2$: C, 50.84; H, 2.44; N, 11.29. Found: C, 50.67; H, 2.26; N, 11.16. $\nu_{max.}$ (cm^{-1}) 1703, 1595, 1578, 1555, 1514, 1489, 1470, 1449, 1424, 1389, 1312, 1109, 1074, 1007, 829, 766, 747; δ (^{1}H, 200 MHz) ($CDCl_3$/CF_3COOH) 8.08 (1H, d, J = 7.7 Hz), 7.96 (2H, d, J = 8.6 Hz), 7.73 (7H, m), 7.56 (1H, m), 7.35 (1H, d, J = 8.4 Hz); δ (^{13}C) 164.42 (C-2), 158.39 (C=O), 145.97 (C-3a), 133.11, 132.98, 131.61 (C-4a), 131.47 (q), 131.35, 128.79, 128.47 (q), 128.08 (C-7), 128.03 (q), 127.40 (C-6), 124.35 (q), 123.37 (C-8a), 116.42 (C-5), 112.66 (C-8); m/z (%) 498 (M^++2, 3), 496 (M^+, 3), 186 (7), 185 (100), 184 (7), 183 (99), 181 (2), 157 (23), 155 (28), 130 (8), 104 (13), 103 (5), 102 (47), 76 (24).

1(or 3)-(4-Chlorobenzoyl)-2-(4-chlorophenyl)-1(or 3)*H*-1,2,4-triazolo[1,5-*a*]benzimidazole (24d).- Yield: 0.19 g (46%) white prisms; mp 309-310°C. Anal. Calcd for $C_{21}H_{12}N_4OCl_2$: C, 61.93; H, 2.97; N, 13.76. Found: C,

62.08; H, 2.16; N, 13.51. $\nu_{max.}$ (cm^{-1}) 1705, 1620, 1595, 1582, 1559, 1518, 1489, 1472, 1456, 1427, 1381, 1309, 1267, 1221, 1186, 1090, 1071, 1017, 939, 862, 837, 758; δ (^1H, 200 MHz) (DMSO-d_6) 8.15 (2H, d, J = 8.2 Hz), 7.97 (2H, d, J = 7.9 Hz), 7.86 (1H, d, J = 7.4 Hz), 7.44 (7H, m); δ (^{13}C) 166.37 (C-2), 163.15 (C=O), 153.96 (C-3a), 137.77 (q), 134.12 (q), 133.84 (C-4a), 131.07, 130.66 (q), 129.56 (q), 128.74, 128.65, 127.72, 124.05 (C-7), 123.66 (C-8a), 121.32 (C-6), 112.96 (C-5), 110.41 (C-8); m/z (%) 408 (M^++2, 3), 406 (M^+, 9), 141 (33), 140 (8), 139 (100), 137 (3), 130 (2), 113 (10), 111 (30), 103 (2), 102 (16), 75 (14).

1(or 3)-(4-Methoxybenzoyl)-2-(4-methoxyphenyl)-1(or 3)*H*-1,2,4-triazolo[1,5-*a*]benzimidazole (24e).- Yield: 0.25 g (63%) white prisms; mp 217-218°C. Anal. Calcd for $C_{23}H_{18}N_4O_3$: C, 69.34; H, 4.55; N, 14.06. Found: C, 69.53; H, 4.78; N, 13.78. $\nu_{max.}$ (cm^{-1}) 1690, 1607, 1588, 1561, 1534, 1516, 1495, 1474, 1447, 1426, 1389, 1310, 1268, 1250, 1192, 1177, 1111, 1073, 1032, 964, 871, 841, 791, 721, 619; δ (^1H, 200 MHz) ($CDCl_3$/CF_3COOH) 8.10 (1H, m), 7.92 (4H, m), 7.81 (1H, m), 7.43 (2H, m), 7.00 (2H, d, J = 9.0 Hz), 6.90 (2H, d, J = 8.8 Hz), 3.92 (3H, s, CH_3O), 3.81 (3H, s, CH_3O); δ (^{13}C) 165.30 (C-2), 164.65 (C=O), 164.49 (q), 161.30 (q), 151.68 (C-3a), 132.96 (C-4a), 132.48 (q), 128.47, 125.56 (C-7), 125.26 (C-6), 123.50 (C-8a), 122.44 (q), 117.30, 114.12, 113.87 (C-5), 110.88 (C-8), 55.57 (CH_3O), 55.29 (CH_3O); m/z (%) 398 (M^+, 21), 264 (2), 263 (3), 136 (9), 135 (100), 133 (2), 130 (2), 107 (3), 103 (1), 102 (7), 92 (5), 77 (3).

1(or 3)-Cinnamoyl-2-styryl-1(or 3)*H*-1,2,4-triazolo[1,5-*a*]benzimidazole (24f).- Yield: 0.19 g (48%) white prisms; mp 198-199°C. Anal. Calcd for $C_{25}H_{18}N_4O$: C, 76.91; H, 4.65; N, 14.35. Found: C, 76.68; H, 4.78; N, 14.06. $\nu_{max.}$ (cm^{-1}) 1701, 1624, 1597, 1526, 1456, 1443, 1356, 1327, 1285, 1275, 1260, 1194, 1142, 1109, 964, 758, 739, 698; δ (^1H, 200 MHz) ($CDCl_3$) 8.53 (1H, m), 8.46 (1H, d, J = 15.6 Hz), 8.03 (1H, d, J = 15.6 Hz), 7.69 (4H, m), 7.55 (2H, d, J = 6.7 Hz), 7.37 (8H, m), 7.11 (2H, d, J = 15.6 Hz); δ (^{13}C) 164.95 (C-2), 162.87 (C=O), 151.79 (C-3a), 147.87, 136.11 (q), 135.20, 134.40 (q), 132.41 (C-4a), 131.00, 128.96, 128.92, 128.70, 128.60, 127.09, 125.45 (C-7), 125.30 (C-8a), 125.22 (C-6a), 118.28 (C-5), 117.90, 117.55, 110.28 (C-8); m/z (%) 390 (M^+, 2), 267 (7), 259 (5), 132 (10), 131 (100), 129 (3), 128 (4), 104 (5), 103 (36), 102 (13), 101 (2), 77 (17).

Preparation of 2-(4-Methylbenzyl)amino-1-triphenylphosphoranylideneaminobenzimidazole (25).

To a mixture of iminophosphorane (**11**) (1.86 g, 3.6 mmol), dry tetrahydrofuran (20 ml), methanol (10 ml), sodium borohydride (0.41 g, 10.9 mmol) was added. The resultant solution was refluxed and stirred for 4 h. After cooling, separated solid was washed with water (2x10 ml), n-hexane (2x15 ml), air-dried, and recrystallized from ethanol to give **25** (1.83 g, 99%) as white prisms; mp 221-222°C. Anal. Calcd for $C_{33}H_{29}N_4P$: C, 77.33; H, 5.70; N, 10.93. Found: C, 77.20; H, 5.61; N, 11.05. $\nu_{max.}$ (cm^{-1}) 3202, 1620, 1591, 1522, 1458, 1437, 1368, 1306, 1275, 1115, 1078, 1005, 912, 801, 735, 721, 692; δ (^1H, 200 MHz) (DMSO-d_6) 7.87 (6H, m, J_{P-H} = 12.3 Hz, J = 7.3, 1.5 Hz), 7.61 (9H, m), 7.30 (2H, d, J = 7.9 Hz), 7.06 (3H, m), 6.97 (1H, s, H-5), 6.79 (2H, m), 6.31 (1H, t, J = 5.2 Hz, NH), 4.33 (2H, d, J = 5.2 Hz, CH_2), 2.30 (3H, s, CH_3); δ (^{13}C) 155.83 (C-2), 139.57 (C-3a), 136.21 (q), 134.98 (q), 134.03 (d,

J_{P-C} = 1.5 Hz, C-7a), 132.72 (d, J_{P-C} = 10.1 Hz), 132.39 (d, J_{P-C} = 1.9 Hz), 129.11, 128.74 (d, J_{P-C} = 101.6 Hz, q), 128.74 (d, J_{P-C} = 11.3 Hz), 128.62, 119.32 (C-6), 118.02 (C-5), 114.94 (C-4), 106.95 (C-7), 53.86 (CH_2), 20.71 (CH_3); δ (^{31}P) 19.62; m/z (%) 512 (M^+, 4), 408 (7), 407 (27), 392 (9), 262 (6), 183 (100), 152 (11), 133 (5), 118 (9), 117 (54), 108 (51), 107 (19), 105 (52), 91 (74), 77 (19).

General Procedure for the Preparation of 2-Alkyl(or aryl)amino-3-(4-methylbenzyl)-3*H*-1,2,4-triazolo-[1,5-*a*]benzimidazoles (26).

To a solution of iminophosphorane (**25**) (0.4 g, 0.78 mmol) in dry toluene (15 ml), the appropriate isocyanate (0.78 mmol) was added. The reaction mixture was refluxed for 35 h. After cooling, the separated solid was collected by filtration washed with cold toluene (2x5 ml), air-dried, and recrystallized from toluene to give **26.**

2-Benzylamino-3-(4-methylbenzyl)-3*H*-1,2,4-triazolo[1,5-*a*]benzimidazole (26a).- Yield: 0.17 g (61%) white prisms; mp 211-212°C. Anal. Calcd for $C_{23}H_{21}N_5$: C, 75.18; H, 5.76; N, 19.06. Found: C, 75.01; H, 5.98; N, 19.26. $\nu_{max.}$ (cm^{-1}) 3395, 1647, 1620, 1584, 1563, 1505, 1478, 1402, 1381, 1362, 1306, 1240, 1221, 1040, 806, 752, 735, 698; δ (^1H, 200 MHz) (DMSO-d_6) 8.86 (1H, t, J = 4.9 Hz, NH), 7.37 (6H, m), 7.04 (7H, m),5.42 (2H, s, N_3-CH_2-Ar), 4.66 (2H, d, J = 4.9 Hz, NH-CH_2-Ph), 2.19 (3H, s, CH_3); δ (^{13}C) 165.47 (C-2), 160.83 (C-3a), 145.72 (C-4a), 138.44 (q), 137.76 (q), 131.12 (q), 129.19, 128.34, 128.19 (C-8a), 128.02, 127.66, 127.22, 121.10 (C-7), 118.83 (C-6), 118.03 (C-5), 108.07 (C-8), 52.72 (N_3-CH_2-Ar), 46.02 (NH-CH_2-Ph), 20.61 (CH_3); m/z (%) 367 (M^+, 8), 365 (3), 263 (8), 262 (7), 159 (20), 158 (23), 157 (3), 118 (7), 117 (7), 106 (20), 105 (100), 104 (9), 103 (10), 91 (74), 77 (16).

3-(4-Methylbenzyl)-2-phenylamino-3*H*-1,2,4-triazolo[1,5-*a*]benzimidazole (26b).- Yield: 0.13 g (47%) white prisms; mp 257-258°C. Anal. Calcd for $C_{22}H_{19}N_5$: C, 74.77; H, 5.42; N, 19.82. Found: C, 74.60; H, 5.31; N, 19.55. $\nu_{max.}$ (cm^{-1}) 3202, 1630, 1617, 1605, 1572, 1512, 1499, 1476, 1408, 1381, 810, 752, 735, 692; δ (^1H, 200 MHz) (DMSO-d_6) 10.36 (1H, s, NH), 7.77 (2H, d, J = 8.0 Hz), 7.55 (1H, d, J = 7.4 Hz, H-8), 7.45 (3H, m), 7.15 (7H, m), 5.59 (2H, s, CH_2), 2.17 (3H, s, CH_3); δ (^{13}C) 161.65 (C-2), 159.73 (C-3a), 145.50 (C-4a), 138.53 (q), 137.90 (q), 130.90 (q), 129.33, 128.98, 127.79, 127.64 (C-8a), 123.20, 121.40 (C-7), 119.20, 119.20 (C-6), 118.43 (C-5), 108.43 (C-8), 53.35 (CH_2), 20.56 (CH_3); m/z (%) 353 (M^+, 13), 249 (9), 248 (3), 132 (4), 118 (15), 117 (3), 106 (7), 105 (100), 104 (5), 103 (10), 102 (6), 91 (7), 77 (18).

3-(4-Methylbenzyl)-2-(4-methylphenyl)amino-3*H*-1,2,4-triazolo[1,5-*a*]benzimidazole (26c).- Yield: 0.13 g (47%) white prisms; mp 262-263°C. Anal. Calcd for $C_{23}H_{21}N_5$: C, 75.18; H, 5.06; N, 19.06. Found: C, 75.37; H, 5.59; N, 18.82. $\nu_{max.}$ (cm^{-1}) 3254, 1634, 1613, 1572, 1549, 1508, 1476, 1381, 1339, 1248, 1121, 810, 756, 733; δ (^1H, 200 MHz) (DMSO-d_6) 10.29 (1H, s, NH), 7.65 (2H, d, J = 8.2 Hz), 7.56 (1H, d, J = 7.4 Hz, H-8), 7.45 (1H, d, J = 7.6 Hz, H-5), 7.21 (2H, d, J = 8.3 Hz), 7.08 (6H, m), 5.57 (2H, s, CH_2), 2.29 (3H, s, CH_3), 2.16 (3H, s, CH_3); δ (^{13}C) 161.91 (C-2), 159.92 (C-3a), 145.55 (C-4a), 137.89 (q), 135.97 (q), 132.30 (q), 130.91 (q), 129.37, 129.32,

127.84, 127.73 (C-8a), 121.35 (C-7), 119.31, 119.19 (C-6), 118.39 (C-5), 108.37 (C-8), 53.41 (CH_2), 20.57 (CH_3), 20.36 (CH_3); m/z (%) 367 (M^+, 7), 263 (8), 262 (2), 248 (4), 235 (7), 133 (6), 132 (15), 131 (8), 118 (11), 117 (9), 116 (5), 107 (6), 105 (100), 104 (9), 103 (12), 91 (26), 77 (23).

2-(4-Fluorophenyl)amino-3-(4-methylbenzyl)-3*H*-1,2,4-triazolo[1,5-*a*]benzimidazole (26d).- Yield: 0.13 g (45%) white prisms; mp 265-266°C. Anal. Calcd for $C_{22}H_{18}N_5F$: C, 71.14; H, 4.88; N, 18.86. Found: C, 71.02; H, 4.61; N, 18.62. $\nu_{max.}$ (cm^{-1}) 3218, 1622, 1595, 1578, 1549, 1516, 1505, 1478, 1431, 1381, 1337, 1219, 831, 812, 795, 756, 735; δ (^1H, 200 MHz) (DMSO-d_6) 10.37 (1H, s, NH), 7.80 (2H, dd, J = 8.9 Hz, J_{F-H} = 4.8 Hz), 7.54 (1H, d, J = 7.5 Hz, H-8), 7.46 (1H, d, J = 7.6 Hz, H-5), 7.15 (8H, m), 5.58 (2H, s, CH_2), 2.17 (3H, s, CH_3); δ (^{13}C) 161.74 (C-2), 159.71 (C-3a), 158.12 (d, J_{F-C} = 240.1 Hz, q), 145.48 (C-4a), 137.92 (q), 135.92 (q), 130.92 (q), 129.34, 127.80, 127.67 (C-8a), 121.41 (C-7), 121.12 (d, J_{F-C} = 8.0 Hz), 119.25 (C-6), 118.41 (C-5), 115.58 (d, J_{F-C} = 22.4 Hz), 108.42 (C-8), 53.34 (CH_2), 20.56 (CH_3); m/z (%) 371 (M^+, 12), 267 (5), 136 (3), 132 (3), 121 (4), 117 (3), 106 (9), 105 (100), 103 (6), 102 (4), 95 (4), 91 (3), 77 (9).

3-(4-Methylbenzyl)-2-(4-methoxyphenyl)amino-3*H*-1,2,4-triazolo[1,5-*a*]benzimidazole (26e).- Yield: 0.13 g (45%) white prisms; mp 238-239°C. Anal. Calcd for $C_{23}H_{21}N_5O$: C, 72.04; H, 5.52; N, 18.26. Found: C, 71.85; H, 5.36; N, 18.01. $\nu_{max.}$ (cm^{-1}) 3252, 1617, 1576, 1546, 1512, 1478, 1339, 1238, 1040, 831, 756, 737; δ (^1H, 200 MHz) (DMSO-d_6) 10.25 (1H, s, NH), 7.66 (2H, d, J = 9.0 Hz), 7.54 (1H, d, J = 7.3 Hz, H-8), 7.44 (1H, d, J = 7.6 Hz, H-5), 7.11 (6H, m), 6.99 (2H, d, J = 9.0 Hz), 5.54 (2H, s, CH_2), 3.75 (3H, s, CH_3O), 2.17 (3H, s, CH_3); δ (^{13}C) 162.31 (C-2), 160.12 (C-3a), 155.53 (q), 145.58 (C-4a), 137.94 (q), 131.51 (q), 130.96 (q), 129.35, 127.93, 127.84 (C-8a), 121.36 (C-7), 121.17, 119.20 (C-6), 118.36 (C-5), 114.23, 108.35 (C-8), 55.26 (CH_3O), 53.45 (CH_2), 20.61 (CH_3); m/z (%) 383 (M^+, 5), 279 (18), 264 (15), 225 (5), 211 (5), 210 (6), 159 (4), 158 (6), 157 (9), 139 (7), 133 (4), 132 (24), 123 (13), 122 (6), 119 (11), 118 (21), 106 (12), 105 (100), 104 (7), 103 (10), 102 (7), 91 (14), 77 (17).

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REFERENCES

1. (a) P. Molina, A. Arques, A. Alías, and M. V. Vinader, *Tetrahedron Lett.*, 1991, **32**, 4401; (b) P. Molina, M. Alajarín, and A. Vidal, *Tetrahedron Lett.*, 1991, **32**, 5379; (c) P. Molina, M. Alajarín, and A. Vidal, *J. Chem.*

Soc., Chem. Commun., 1992, 295; (d) P. Molina, M. Alajarín, and A. Vidal, *J. Org. Chem.*, 1992, **57**, 6703; (e) P. Molina, A. Arques, A. Alías, M.C. Foces-Foces, and A. L. Llamas-Saiz, *J. Chem. Soc., Chem. Commun.*, 1992, 424; (f) P. Molina, M. Alajarín, and A. Vidal, *J. Org. Chem.*, 1993, **58**, 1687.

2. We denote as *C,C*-bis(iminophosphoranes) those compounds which both iminophosphorane groups are placed either on an aromatic, a heteroaromatic, or an unsaturated carbon-carbon side chain. In *C,N*-bis(imino phosphoranes) one iminophosphorane group is directly linked to aromatic, heteroaromatic or unsaturated carbon-carbon side chain while the other is on a nitrogen atom belonging to a heteroaromatic ring.
3. (a)P. Molina, A. Arques, and A. Alías, *Tetrahedron Lett.*, 1991, **32**, 2979; (b) P. Molina, A. Arques, A. Alías, M. V. Vinader, M. C. Foces-Foces, and F. Hernandez-Cano, *Tetrahedron*, 1992, **48**, 3091.
4. H. Beyer, A. Hetzheim, H. Honeck, D. Ling, and T. Pyl, *Chem. Ber.*, 1968, **101**, 3151.
5. R. I. F. Ho, and A. R. Day, *J. Org. Chem.*, 1973, **38**, 3084.
6. A. L. Llamas-Saiz, C. Foces-Foces, J. Elguero, P. Molina, M. Alajarín, and A. Vidal, *J. Chem. Soc., Perkin Trans 1*, 1991, 1667.
7. P. Molina, M. Alajarín, M. J. Pérez de Vega, and A. López, *Heterocycles*, 1989, **29**, 1607.
8. A. L. Llamas-Saiz, C. Foces-Foces, J. Elguero, F. Aguilar-Parrilla, H. H. Limbach, P. Molina, M. Alajarín, A. Vidal, R. M. Claramunt, and C. López, *J. Chem. Soc., Perkin Trans 2*, submitted.
9. P. Molina, A. Arques, and A. Alías, *J. Org. Chem.*, 1993, **58**, 5264.
10. (a)Y. Tamura, Y. Hayashi, J-H. Kim, and M. Ikeda, *Chem. Pharm. Bull.*, 1979, **27**, 2521; (b) T. A. Kuz'menko, V. V. Kuz'menko, A. F. Pozharskii, and A. M. Simonov, *Khim. Geterotsikl. Soedin.*, 1988, **8**, 1070; (c) T. A. Kuz'menko, V. V. Kuz'menko, A. F. Pozharskii, and N. A. Klynev, *Khim. Geterotsikl. Soedin.*, 1988, **9**, 1226.
11. E. Zbiral and E. Bauer, *Phosphorus*, 1972, **2**, 35.

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