DOI: 10.1002/ejoc.200600201

# New Facile Synthesis of 3,5-Dihydro-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-ones by an Iminophosphorane-Mediated Annulation

**Ju-Zhen Yuan,[a] Bo-Qiao Fu,[a] Ming-Wu Ding,*[a] and Guang-Fu Yang*[a]**

**Keywords:** 3,5-Dihydro-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-one / Iminophosphorane / Carbodiimide / Abnormal aza-Wittig reaction / Synthetic methods / Annulation

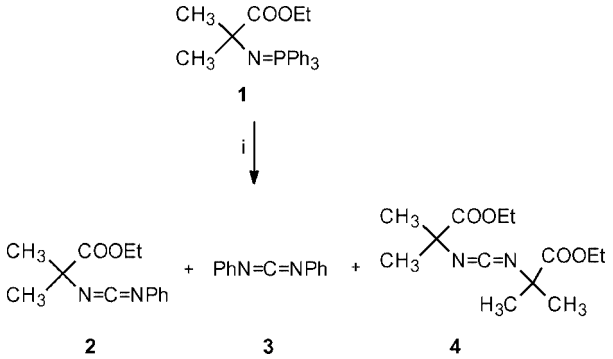
Iminophosphorane **1** reacted with an aromatic isocyanate to unexpectedly give a mixture of carbodiimides **2**, **3** and **4** through both the normal and the abnormal aza-Wittig reactions. 3-Aminoimidazolone **10** was obtained from the reaction of hydrazine hydrate with carbodiimide **2**. Reaction of **10** with triphenyphosphane, hexachloroethane and triethylamine produced iminophosphorane **11** in good yield. A tandem aza-Wittig reaction of iminophosphorane **11** with isocyanate or $CS_2$ generated 3,5-dihydro-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-ones **13** or **15** in satisfactory yield. Carbodiimides **18**, obtained from normal aza-Wittig reactions of vinyl iminophosphorane **17** with aromatic isocyanates, reacted with hydrazine to give 2-arylamino-3-amino-4*H*-imidazol-4-ones **20**. One-pot reactions of 2-arylamino-3-amino-4*H*-imidazol-4-ones **20** with isocyanates (or acyl chlorides), triphenyphosphane, hexachloroethane and triethylamine produced 3,5-dihydro-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-ones **22** (or **23**) in good yields.


## Introduction

Many 4*H*-imidazol-4-ones have shown biological and pharmaceutical activities.[1–3] Some of them exhibited good antibacterial, antifungal and angiotensin II antagonistical activities,[4–6] whereas others appear in a variety of biologically active molecules, particularly in some alkloids in which a common structural unit is a derivatized 2-amino-4*H*-imidazol-4-one moiety.[7,8] The introduction of a triazole ring to the imidazolone system is expected to influence the biological activities significantly. However, useful methods for the synthesis of 3,5-dihydro-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-ones are rare,[9] probably because of the fact that these fused heterocycles, which contain a bridgehead nitrogen atom, are not easily accessible by routine synthetic methods. The aza-Wittig reactions of iminophosphoranes have received increased attention in view of their utility in the synthesis of nitrogen heterocyclic compounds.[10–14] Annelation of ring systems with *N*-heterocycles by means of an aza-Wittig reaction has been widely utilized because of the availability of functionalized iminophosphoranes. Recently we have been interested in the synthesis of quinazolinones, thienopyrimidinones, imidazolones and imidazothiadiazolones by way of the aza-Wittig reaction, with the aim of evaluating their fungicidal activities.[15–21] Here we wish to report a new facile synthesis of previously unreported 3,5-dihydro-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-ones.

## Results and Discussion

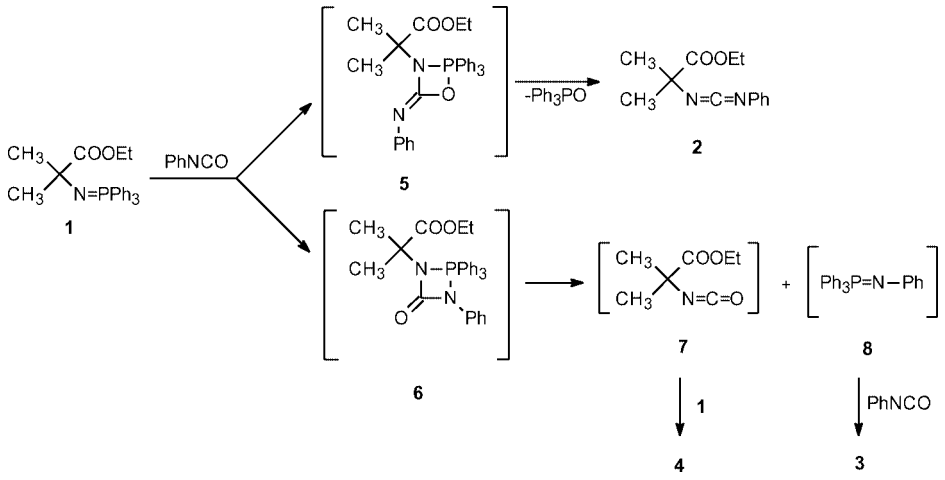
It was reported that iminophosphorane **1** reacted with an aromatic isocyanate to give only carbodiimide **2** by the aza-Wittig reaction.[22] However, we observed that this reaction unexpectedly gave a mixture of carbodiimides **2**, **3** and **4** (Scheme 1). A GC–MS analysis of the reaction mixture revealed the proportions of carbodiimides **2**, **3** and **4** as 45%, 32% and 23%, respectively. Carbodiimides **3** and **4** were probably formed by abnormal aza-Wittig reactions.[23–25]




Scheme 1. Reaction conditions: (i) PhNCO, $CH_2Cl_2$, room temp., 2 h.

The proposed mechanism of the abnormal aza-Wittig reaction, in contrast to the normal aza-Wittig reaction, is out-

[a] Key Laboratory of Pesticide & Chemical Biology, Ministry of Education, College of Chemistry, Central China Normal University,
Wuhan, 430079, P. R. China
E-mail: mwding@mail.ccnu.edu.cn
gfyang@mail.ccnu.edu.cn

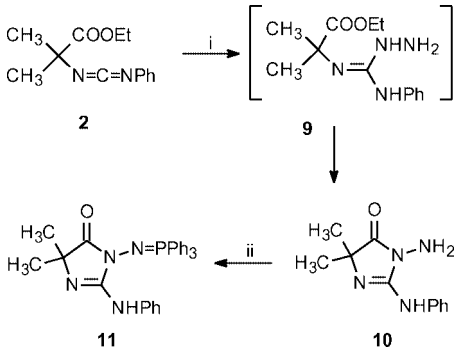



Scheme 2. Proposed mechanism of the abnormal aza-Wittig reaction leading to two different carbodiimides versus that of the normal aza-Wittig reaction.

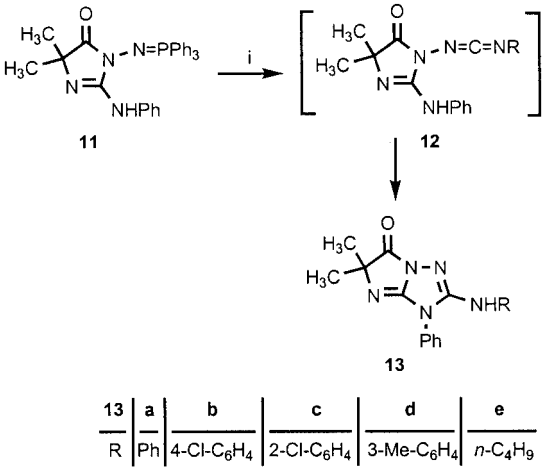
lined in Scheme 2. Both betaines **5** and **6** can be formed upon treatment of iminophosphorane **1** with phenyl isocyanate. Breakdown of betaine **5** involving loss of triphenylphosphane oxide results in carbodiimide **2** as the normal aza-Wittig product. In contrast, betaine **6** can lead to isocyanate group **7** as the abnormal aza-Wittig product with the loss of iminophosphorane **8**. Further reaction of iminophosphorane **1** with **7** or iminophosphorane **8** with PhNCO produced carbodiimide **4** or **3**. The above abnormal aza-Wittig reaction may be a result of the steric hindrance of iminophosphorane **1**. Considering betaine structures **5** and **6**, it is understandable that steric hindrance between bulky dimethyl groups and the phenylimine group in betaine **5** can lead to the preferred formation of betaine **6**. It is noteworthy that only the normal aza-Wittig reaction product was obtained when similar but less sterically hindered iminoposphoranes [such as $RCH(COOEt)N{=}PPh_3$] were used.[26,27]

Carbodiimide **2** was isolated from the reaction mixture by column chromatography and was allowed to react with hydrazine hydrate to give 3-aminoimidazolone **10**. The formation of **10** can be rationalized in terms of an initial nucleophilic addition of hydrazine to give guanidine intermediate **9**, which cyclizes across the strong nucleophilic hydrazine group rather than the phenylamine group to give **10**. Compound **10** was easily converted to novel functionalized iminophosphorane **11** by its reaction with triphenylphosphane, hexachloroethane and triethylamine in good yield (83%, Scheme 3).

When solutions of iminophosphorane **11** in dry dichloromethane were treated with an aromatic isocyanate at room temperature, 2-arylamino-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-ones **13** were isolated as crystalline solids in good yields (81–91%, Scheme 4). Presumably, the conversion of **11** into **13** involves an initial aza-Wittig reaction between iminophosphorane **11** and the isocyanate to give carbodiimide **12** as a highly reactive intermediate, which easily undergoes ring closure across the arylamino group to give **13**.




Scheme 3. Reaction conditions: (i) $NH_2NH_2$, $CH_3CN$, room temp., 2 h; (ii) $Ph_3P$, $C_2Cl_6$, $CH_3CN$, $NEt_3$, room temp., 4–6 h.

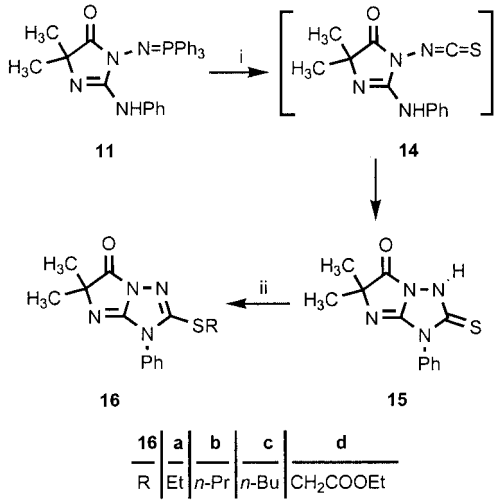



Scheme 4. Reaction conditions: (i) $Ar^1NCO$, $CH_2Cl_2$, room temp., 1–2 h.

Iminophosphorane **11** reacted with $CS_2$ in refluxing dichloromethane to give 2-thioxo-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-one (**15**) in high yield (95%, Scheme 5). The formation of **15** can be viewed as an initial aza-Wittig reaction between iminophosphorane **11** and $CS_2$, which affords in-

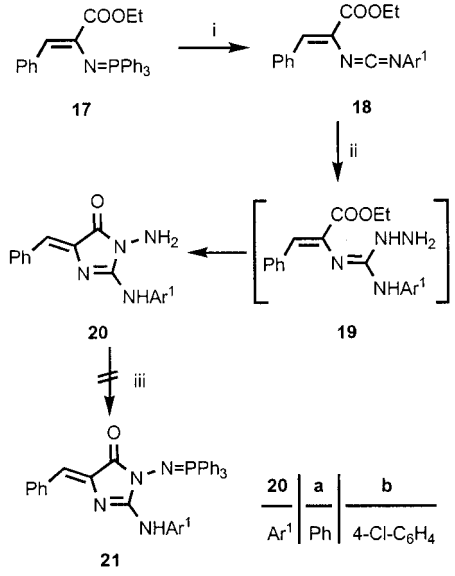
  

termediate isothiocyanate **14** that undergoes cyclization to give **15**. *S*-Alkylation of **15** with an alkyl halide in the presence of solid potassium carbonate gave 2-alkylthio-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-ones **16** in satisfactory yields.



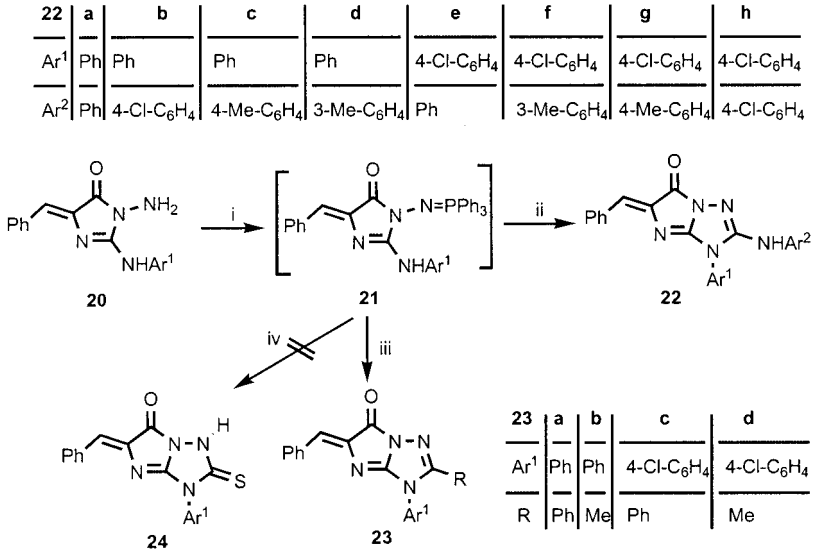

Scheme 5. Reaction conditions: (i) $CS_2$, $CH_2Cl_2$, 40 °C, 3 h; (ii) RX, $CH_3CN$, $K_2CO_3$(s), room temp. or 50–60 °C, 1–4 h.

When vinyl iminophosphorane **17** was used, only carbodiimide **18** was produced by the normal aza-Wittig reaction. Carbodiimides **18** were allowed to react with hydrazine to selectively give 2-arylamino-3-aminoimidazol-4-ones **20** in good yields. Compounds **20** should be easily converted to iminophosphoranes **21** through the reaction with triphenylphosphane, hexachloroethane and triethylamine; however, when triethylamine was added to the mixture of **20**, triphenylphosphane and hexachloroethane in $CH_2Cl_2$ at room temperature, the colour of the reaction mixture quickly turned red, becoming dark gradually, and iminophosphoranes **21** were not obtained because of side reactions (Scheme 6).




Scheme 6. Reaction conditions: (i) $Ar^1NCO$, $CH_2Cl_2$, room temp., 4–6 h; (ii) $NH_2NH_2$, EtOH, room temp., 10 min; (iii) $Ph_3P$, $C_2Cl_6$, $CH_3CN$, $NEt_3$, room temp., 4–6 h.

In order to avoid the side reactions, a one-pot reaction was carried out at room temperature. When triethylamine was added to a mixture of 3-aminoimidazol-4-ones **20**, aromatic isocyanates, triphenyphosphane and hexachloroethane in $CH_2Cl_2$, the colour of the reaction mixture quickly turned red, and 2-arylamino-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-ones **22** were obtained in good overall yields (71–90%) after 1 h reaction. In these cases, iminophosphoranes **21**, generated in situ from **20**, reacted immediately with aromatic isocyanates to give **22** in good yields (Scheme 7). This one-pot reaction method was also successful when acyl chlorides were utilized instead of isocyanates. Thus, 6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-ones **23** were obtained in 57–80% yield from 2-arylamino-3-aminoimidazol-4-ones **20**,




Scheme 7. (i) $Ph_3P$, $C_2Cl_6$, $CH_2Cl_2$, $NEt_3$, room temp.; (ii) $Ar^2NCO$, 1–2 h; (iii) RCOCl, 2–3 h. (iv) $CS_2$, 2 h.

acyl chlorides, triphenylphosphane and hexachloroethane in the presence of triethylamine in dichloromethane at room temperature. Attempts to prepare 2-mercapto-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-ones **24** by the one-pot reaction of 2-arylamino-3-aminoimidazol-4-ones **20** with carbon disulfide, triphenyphosphane, hexachloroethane and triethylamine were unsuccessful. Although iminophosphorane **21** might be produced in this case, the reaction between **21** and $CS_2$ is very slow at room temperature, and the colour of the reaction mixture quickly turned red, becoming dark gradually because of side reactions.

In conclusion, we have demonstrated that the steric iminophosphorane **1** reacts with phenyl isocyanate in normal and abnormal aza-Wittig reactions. A new facile synthesis of 2-substituted 3,5-dihydro-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-ones by way of the aza-Wittig reactions has also been developed. Because of the mild one-pot reaction conditions, good yields, easily accessible starting materials and straightforward product isolation, this method has the potential in the synthesis of many biologically and pharmaceutically active imidazotriazolone derivatives.

## Experimental Section

**General Remarks:** Melting points are uncorrected. MS were measured with a Finnigan Trace MS spectrometer. IR were recorded with a PE-983 infrared spectrometer as KBr pellets. NMR were recorded in $CDCl_3$ or [$D_6$]DMSO with a Varian Mercury 400 spectrometer and resonances relative to TMS. Elementary analyses were taken with a Vario EL III elementary analysis instrument.

***N*-(1-Ethoxycarbonyl-1-methylethyl)iminotriphenylphosphorane (1):** Triphenylphosphane (2.62 g, 10 mmol) in dry $CH_3CN$ (10 mL) was added dropwise to a solution of ethyl 2-azido-2-methylpropionate (1.89 g, 12 mmol) in dry $CH_3CN$ (20 mL) at 60 °C under an argon atmosphere. After the reaction mixture was stirred for 2 h at 80 °C, the solvent was removed under reduced pressure, and the residue was then recrystallized from petroleum ether to give iminophosphorane **1**. White solid (yield 3.41 g, 87%). M.p.: 55–57 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 1.04 (t, $J$ = 7.2 Hz, 3 H, $CH_3$), 1.38 (s, 6 H, $2CH_3$), 3.69 (q, $J$ = 7.2 Hz, 2 H, $CH_2$), 7.38–7.75 (m, 15 H, Ar–H) ppm. MS: *m*/*z* (%) = 391 (78) $[M]^+$, 375 (99), 258 (90), 179 (92), 105 (100), 91 (29). $C_{24}H_{26}NO_2P$ (391.45): calcd. C 73.64, H 6.69, N 3.58; found C 73.58, H 6.60, N 3.67.

***N*-(1-Ethoxycarbonyl-1-methylethyl)-*N*-phenylcarbodiimide (2):** To a solution of iminophosphorane **1** (1.96 g, 5 mmol) in dry dichloromethane (15 mL) was added phenyl isocyanate (0.60 g, 5 mmol) under nitrogen at room temperature. After the reaction mixture was stirred for 2 h at room temperature, the solvent was removed under reduced pressure and ether/petroleum ether (1:2, 20 mL) was added to precipitate triphenylphosphane oxide. The precipitate was filtered, and the solvent was removed to give a mixture of carbodiimides **2** (45%), **3** (32%) and **4** (23%), which was analyzed by GC–MS. Carbodiimides **2**, **3**, and **4** were isolated from the reaction mixture by column chromatography on silica gel in 40%, 24% and 15% yield, respectively.

**Carbodiimide 2:** Light yellow oil. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 1.27 (t, $J$ = 7.2 Hz, 3 H, $CH_3$), 1.58 (s, 6 H, $2CH_3$), 4.22 (q, $J$ = 7.2 Hz, 2 H, $CH_2$), 7.16–7.30 (m, 5 H, Ar–H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 13.9, 27.7 (2 C), 61.4, 61.8, 123.7 (2 C), 124.8, 129.1 (2 C), 136.7, 139.6, 173.4 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 2125 (N=C=N), 1734 (C=O), 1596, 1151 $cm^{-1}$. MS: *m*/*z* (%) = 231 (28) $[M]^+$, 158 (100), 117 (83), 76 (31). $C_{13}H_{16}N_2O_2$ (232.3): calcd. C 67.22, H 6.94, N 12.06; found C 67.48, H 6.79, N 12.12.

**Carbodiimide 3:** Light yellow oil: $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.14–7.19 (m, 6 H, Ar–H), 7.31–7.35 (m, 4 H, Ar–H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 124.1 (4 C), 125.5 (2 C), 129.4 (4 C), 135.2, 138.3 (2 C) ppm. IR (KBr): $\tilde{\nu}$ = 2137 (N=C=N), 1590, 1203 $cm^{-1}$. MS: *m*/*z* (%) = 194 (100) $[M]^+$, 90 (14), 76 (27). $C_{13}H_{10}N_2$ (194.2): calcd. C 80.39, H 5.19, N 14.42; found C 80.31, H 5.33, N 14.25.

**Carbodiimide 4:** Light yellow oil. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 1.28 (t, $J$ = 7.2 Hz, 6 H, $2CH_3$), 1.54 (s, 12 H, $4CH_3$), 4.20 (q, $J$ = 7.2 Hz, 4 H, $2CH_2$) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 14.0 (2 C), 27.4 (4 C), 60.6 (2 C), 61.4 (2 C), 137.8, 173.5 (2 C=O) ppm. IR (KBr): $\tilde{\nu}$ = 2146 (N=C=N), 1743 (C=O), 1385, 1151 $cm^{-1}$. MS: *m*/*z* (%) = 270 (4) $[M]^+$, 242 (8), 227 (9), 197 (86), 168 (81), 114 (83), 55 (100). $C_{13}H_{22}N_2O_4$ (270.3): calcd. C 57.76, H 8.20, N 10.36; found C 57.68, H 8.23, N 10.18.

**3-Amino-5,5-dimethyl-2-phenylamino-4*H*-imidazol-4-one (10):** To the solution of carbodiimide **2** (1.16 g, 5 mmol) prepared above in $CH_3CN$ (15 mL) was added hydrazine hydrate (0.29 g, 5 mmol, 85%) in $CH_3CN$ (5 mL). The mixture was stirred for 1 h at room temperature, and the solvent was removed under reduced pressure. The residue was recrystallized from ether and petroleum ether (1:2) to give **10**. White solid (yield 0.92 g, 84%). M.p.: 114–116 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 1.45 (s, 6 H, 2 $CH_3$), 4.19 (s, 2 H, $NH_2$), 7.06 (s, 1 H, N–H), 7.33–7.67 (m, 5 H, Ar–H) ppm. MS: *m*/*z* (%) = 218 (92) $[M]^+$, 202 (29), 190 (22), 175 (100), 118 (44), 76 (28). $C_{11}H_{14}N_4O$ (218.3): calcd. C 60.53, H 6.47, N 25.67; found C 60.72, H 6.40, N 25.53.

***N*-(5,5-Dimethyl-2-phenylamino-4*H*-imidazol-4-on-3-yl)iminotriphenylphosphorane (11):** To a mixture of **10** (1.74 g, 8 mmol), $PPh_3$ (3.14 g, 12 mmol) and $C_2Cl_6$ (2.84 g, 12 mmol) in dry $CH_3CN$ (20 mL) was added dropwise $NEt_3$ (2.42 g, 24 mmol) at room temperature. After stirring for 5 h, the precipitate was filtered, washed quickly with cold water and dried to give iminophosphorane **11**. White solid (yield 3.17 g, 83%). M.p.: 224–226 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 1.10 (s, 6 H, 2 $CH_3$), 7.02 (s, 1 H, N–H), 7.27–7.85 (m, 20 H, Ar–H) ppm. MS: *m*/*z* (%) = 478 (91) $[M]^+$, 463 (31), 435 (19), 319 (38), 262 (100), 183 (62), 76 (53). $C_{29}H_{27}N_4OP$ (478.5): calcd. C 72.79, H 5.69, N 11.71; found C 72.86, H 5.45, N 11.95.

**2-Amino-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-ones (13):** To a solution of iminophosphorane **11** (0.48 g, 1 mmol) in dry $CH_2Cl_2$ (10 mL) was added isocyanate (1 mmol) at room temperature. After stirring for 1–2 h, the solvent was removed under reduced pressure and the residue was recrystallized from dichloromethane and petroleum ether to give **13**. Isocyanate used for **13a**: phenyl isocyanate; **13b**: 4-chlorophenyl isocyanate; **13c**: 2-chlorophenyl isocyanate; **13d**: 3-methylphenyl isocyanate; **13e**: *n*-butyl isocyanate.

**3,5-Dihydro-5,5-dimethyl-3-phenyl-2-phenylamino-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-one (13a):** White solid (yield 0.27 g, 85%). M.p.: 186–187 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 1.48 (s, 6 H, 2 $CH_3$), 6.38 (s, 1 H, N–H), 7.10–7.67 (m, 10 H, Ar–H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 24.7 (2 C), 75.5, 118.8, 123.8, 126.5, 128.4 (2 C), 129.2, 131.0, 132.0 (2 C), 151.8, 154.3, 174.8 (C=O) ppm. MS: *m*/*z* (%) = 319 (11) $[M]^+$, 291 (55), 277 (100), 250 (48), 198 (15), 76 (49). $C_{18}H_{17}N_5O$ (319.4): calcd. C 67.70, H 5.37, N 21.93; found C 67.57, H 5.24, N 21.98.

**2-(4-Chlorophenylamino)-3,5-dihydro-5,5-dimethyl-3-phenyl-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-one (13b):** White solid (yield 0.32 g,

91%). M.p.: 252–253 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 1.50 (s, 6 H, 2 $CH_3$), 6.19 (s, 1 H, N–H), 7.27–7.68 (m, 9 H, Ar–H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 24.6 (2 C), 75.6, 120.0 (2 C), 126.6 (2 C), 129.0, 129.3 (2 C), 130.0, 130.2, 131.1 (2 C), 135.3, 151.5, 154.1, 174.7 (C=O) ppm. MS: *m*/*z* (%) = 353 (8) $[M]^+$, 325 (85), 283 (100), 234 (48), 76 (61). $C_{18}H_{16}ClN_5O$ (353.8): calcd. C 61.11, H 4.56, N 19.79; found C 61.18, H 4.47, N 19.71.

**2-(2-Chlorophenylamino)-3,5-dihydro-5,5-dimethyl-3-phenyl-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-one (13c):** White solid (yield 0.29 g, 83%). M.p.: 253–254 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 1.51 (s, 6 H, 2 $CH_3$), 7.00–7.69 (m, 9 H, Ar–H), 8.41 (s, 1 H, N–H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 24.6 (2 C), 75.7, 119.7, 121.6, 124.0, 126.2 (2 C), 128.3, 128.9, 129.9, 130.2, 131.0 (2 C), 133.4, 151.1, 153.9, 174.8 (C=O) ppm. MS: *m*/*z* (%) = 353 (23) $[M]^+$, 325 (100), 284 (67), 76 (21). $C_{18}H_{16}ClN_5O$ (353.8): calcd. C 61.11, H 4.56, N 19.79; found C 61.25, H 4.74, N 19.95.

**3,5-Dihydro-5,5-dimethyl-2-(3-methylphenylamino)-3-phenyl-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-one (13d):** White solid (yield 0.29 g, 87%). M.p.: 250–251 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 1.48 (s, 6 H, 2 $CH_3$), 2.34 (s, 3 H, $CH_3$), 6.08 (s, 1 H, N–H), 6.91–7.65 (m, 9 H, Ar–H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 21.5, 24.7 (2 C), 75.5, 115.9, 119.2, 124.8, 126.6 (2 C), 129.2, 130.2 (2 C), 131.1 (2 C), 136.5, 139.4, 151.1, 153.9, 174.8 (C=O) ppm. MS: *m*/*z* (%) = 333 (9) $[M]^+$, 305 (100), 264 (78), 214 (21). $C_{19}H_{19}N_5O$ (333.4): calcd. C 68.45, H 5.74, N 21.01; found C 68.53, H 5.57, N 21.25.

**2-(*n*-Butylamino)-3,5-dihydro-5,5-dimethyl-3-phenyl-6*H*-imidazo-[1,2-*b*]-1,2,4-triazol-6-one (13e):** White solid (yield 0.24 g, 81%). M.p.: 217–218 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 0.93 (t, *J* = 7.2 Hz, 3 H, $CH_3$), 1.28–1.64 (m, 4 H, $CH_2CH_2$), 1.45 (s, 6 H, 2 $CH_3$), 3.33–3.38 (m, 2 H, $NCH_2$), 4.13 (s, 1 H, N–H), 7.45–7.59 (m, 5 H, Ar–H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 13.6, 19.9, 24.6 (2 C), 31.1, 42.5, 75.2, 125.9 (2 C), 129.4, 130.7 (3 C), 155.1, 155.4, 174.5 (C=O) ppm. MS: *m*/*z* (%) = 299 (99) $[M]^+$, 271 (100), 256 (45), 214 (87), 159 (41). $C_{16}H_{21}N_5O$ (299.4): calcd. C 64.19, H 7.07, N 23.39; found C 64.13, H 7.17, N 23.21.

**2-Thioxo-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-one (15):** To a solution of iminophosphorane **11** (4.78 g, 10 mmol) in dry dichloromethane (15 mL) was added excess $CS_2$ (10 mL) under nitrogen at room temperature. After the reaction mixture was heated at reflux for 3 h, the precipitated solid was collected by filtration to give **15**. White solid (yield 2.47 g, 95%). M.p.: 240–241 °C. $^1$H NMR ($CDCl_3$/TFA, 400 MHz): $\delta$ = 1.72 (s, 6 H, 2 $CH_3$), 7.44–7.74 (m, 5 H, Ar–H) ppm. MS: *m*/*z* (%) = 260 (4) $[M]^+$, 230 (100), 189 (21), 140 (28), 77 (22). $C_{12}H_{12}N_4OS$ (260.3): calcd. C 55.37, H 4.65, N 21.52; found C 55.18, H 4.69, N 21.65.

**2-Alkylthio-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-one (16):** A mixture of **15** (0.26 g, 1 mmol), alkyl halide (1.2 mmol) and solid potassium carbonate (0.28 g, 2 mmol) in $CH_3CN$ (10 mL) was stirred for 1–4 h at room temperature or 50–60 °C and filtered; the filtrate was condensed, and the residue was recrystallized from dichloromethane/petroleum ether to give **16**. Alkyl halide and reaction conditions used for: **16a**: ethyl iodide, room temp.; **16b**: *n*-propyl bromide, 50 °C; **16c**: *n*-butyl bromide, 60 °C; **16d**: ethyl bromoacetate, room temp.

**3,5-Dihydro-5,5-dimethyl-2-ethylthio-3-phenyl-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-one (16a):** White solid (yield 0.24 g, 83%). M.p.: 114–115 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 1.45 (t, *J* = 7.2 Hz, 3 H, $CH_3$), 1.50 (s, 6 H, 2 $CH_3$), 3.24 (q, *J* = 7.2 Hz, 2 H, $SCH_2$), 7.44–7.55 (m, 5 H, Ar–H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 14.1, 24.6 (2 C), 26.1, 76.3, 125.7 (2 C), 129.4, 130.1 (2 C), 130.3, 155.9, 159.2, 174.3 (C=O) ppm. MS: *m*/*z* (%) = 288 (14) $[M]^+$, 260 (89), 217 (67), 183 (88), 77 (100). $C_{14}H_{16}N_4OS$ (288.4): calcd. C 58.31, H 5.59, N 19.43; found C 58.15, H 5.45, N 19.47.

**3,5-Dihydro-5,5-dimethyl-3-phenyl-2-propylthio-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-one (16b):** White solid (yield 0.27 g, 88%). M.p.: 111–112 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 1.04 (t, *J* = 7.2 Hz, 3 H, $CH_3$), 1.50 (s, 6 H, 2 $CH_3$), 1.78–1.84 (m, 2 H, $CH_2$), 3.20 (t, *J* = 7.2 Hz, 2 H, $SCH_2$), 7.46–7.54 (m, 5 H, Ar–H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 13.2, 22.1, 24.6 (2 C), 33.5, 76.4, 125.7 (2 C), 129.3, 130.1 (2 C), 130.4, 156.0, 159.4, 174.4 (C=O) ppm. MS: *m*/*z* (%) = 302 (17) $[M]^+$, 273 (53), 231 (100), 189 (31), 76 (61). $C_{15}H_{18}N_4OS$ (302.4): calcd. C 59.58, H 6.00, N 18.53; found C 59.64, H 5.86, N 18.44.

**2-Butylthio-3,5-dihydro-5,5-dimethyl-3-phenyl-2-butylthio-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-one (16c):** White solid (yield 0.26 g, 82%). M.p.: 114–116 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 0.92 (t, *J* = 7.6 Hz, 3 H, $CH_3$), 1.51 (s, 6 H, 2 $CH_3$), 1.40–1.79 (m, 4 H, $CH_2CH_2$), 3.23 (t, *J* = 7.2 Hz, 2 H, $SCH_2$), 7.44–7.56 (m, 5 H, Ar–H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 13.5, 21.8, 24.6 (2 C), 31.2, 32.3, 76.3, 125.7 (2 C), 129.4, 130.1 (2 C), 130.3, 156.0, 159.5, 174.3 (C=O) ppm. MS: *m*/*z* (%) = 316 (10) $[M]^+$, 292 (31), 230 (100), 182 (57), 76 (34). $C_{16}H_{20}N_4OS$ (316.4): calcd. C 60.73, H 6.37, N 17.71; found C 60.62, H 6.34, N 17.76.

**3,5-Dihydro-5,5-dimethyl-2-ethoxycarbonylmethylthio-3-phenyl-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-one (16d):** White solid (yield 0.29 g, 85%). M.p.: 109–110 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 1.32 (t, *J* = 7.2 Hz, 3 H, $CH_3$), 1.48 (s, 6 H, 2$CH_3$), 4.04 (s, 2 H, $SCH_2$), 4.26 (q, *J* = 7.2 Hz, 2 H, $OCH_2$), 7.46–7.54 (m, 5 H, Ar-H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 14.0, 24.9 (2), 34.6, 61.9, 76.4, 125.5 (2), 129.5, 130.1 (2), 130.4, 158.6, 159.4, 174.4 (C=O) ppm. MS: *m*/*z* (%) = 346 (12) $[M]^+$, 318 (100), 294 (19), 245 (26). $C_{16}H_{18}N_4O_3S$ (346.4): calcd. C 55.48, H 5.24, N 16.17; found C 55.64, H 5.36, N 16.01.

**2-Arylamino-3-amino-4*H*-imidazol-4-ones 20:** To a solution of vinyliminophosphorane **17**[21] (2.25 g, 5 mmol) in dry dichloromethane (15 mL) was added aromatic isocyanate (5 mmol) under nitrogen at room temperature. After the reaction mixture was stirred for 4–6 h, the solvent was removed under reduced pressure, and ether/petroleum ether (1:2, 20 mL) was added to precipitate triphenylphosphane oxide. The precipitate was filtered, and the solvent was removed to give carbodiimides **18**, which were used directly without further purification. To the solution of **18** prepared above in EtOH (15 mL) was added hydrazine hydrate (0.35 g, 6 mmol, 85%) in EtOH (5 mL). The mixture was stirred for 10 min at room temperature and filtered to give 2-arylamino-3-amino-4*H*-imidazol-4-ones **20**. Isocyanate used for: **20a**: phenyl isocyanate; **20b**: 4-chlorophenyl isocyanate.

**3-Amino-3,5-dihydro-2-phenylamino-5-phenylmethylene-4*H*-imidazol-4-one (20a):** Yellow solid (yield 1.06 g, 76%). M.p.: 191–193 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 4.23 (s, 2 H, $NH_2$), 6.88 (s, 1 H, =CH), 7.14–8.14 (m, 11 H, Ar–H and N–H) ppm. IR (KBr): $\tilde{\nu}$ = 3340, 3322 (N–H), 1702 (C=O), 1660 (C=C), 1599, 1156 $cm^{-1}$. MS: *m*/*z* (%) = 278 (98) $[M]^+$, 263 (19), 249 (22), 219 (37), 116 (100). $C_{16}H_{14}N_4O$ (278.3): calcd. C 69.05, H 5.07, N 20.13; found C 69.30, H 5.01, N 20.26.

**3-Amino-2-(4-chlorophenylamino)-3,5-dihydro-5-phenylmethylene-4*H*-imidazol-4-one (20b):** Yellow solid (yield 1.16 g, 74%). M.p.: 245–246 °C. $^1$H NMR ([$D_6$]DMSO, 400 MHz): $\delta$ = 5.34 (s, 2 H, $NH_2$), 6.66 (s, 1 H, =CH), 7.30–8.14 (m, 9 H, Ar–H), 9.63 (s, 1 H, N–H) ppm. IR (KBr): $\tilde{\nu}$ = 3330, 3302 (N–H), 1728 (C=O), 1660 (C=C), 1596, 1154 $cm^{-1}$. MS: *m*/*z* (%) = 314 (30), 312 (88) $[M]^+$, 297 (21), 253 (18), 218 (13), 168 (68), 116 (100). $C_{16}H_{13}ClN_4O$

(312.8): calcd. C 61.45, H 4.19, N 17.91; found C 61.69, H 4.06, N 17.94.

**2-Arylamino-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-ones 22:** To a mixture of imidazolone **20** (3 mmol), $Ar^2NCO$ (3 mmol), $PPh_3$ (1.05 g, 4 mmol) and $C_2Cl_6$ (0.95 g, 4 mmol) in dry $CH_2Cl_2$ (15 mL) was added dropwise $NEt_3$ (0.81 g, 8 mmol) at room temperature. The colour of the reaction mixture quickly turned red. After the solution was stirred for 1–2 h the solvent was removed under reduced pressure, and the residue was recrystallized from EtOH to give 2-arylamino-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-ones **22**. Starting material and isocyanate used for: **22a**: **20a** and phenyl isocyanate; **22b**: **20a** and 4-chlorophenyl isocyanate; **22c**: **20a** and 4-methylphenyl isocyanate; **22d**: **20a** and 3-methylphenyl isocyanate; **22e**: **20b** and phenyl isocyanate; **22f**: **20b** and 3-methylphenyl isocyanate; **22g**: **20b** and 4-methylphenyl isocyanate; **22h**: **20b** and 4-chlorophenyl isocyanate.

**3,5-Dihydro-3-phenyl-2-phenylamino-5-phenylmethylene-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-one (22a):** Yellow crystals (yield 0.81 g, 71%). M.p.: 241–242 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 6.13 (s, 1 H, N–H), 7.09–8.03 (m, 16 H, Ar–H and =CH) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 119.2, 120.2, 122.2, 123.6, 124.2, 128.1 (2 C), 128.7 (3 C), 129.2 (3 C), 130.3 (2 C), 130.9, 131.2 (2 C), 132.4 (2 C), 143.8, 153.6, 159.8 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3358 (N–H), 1713 (C=O), 1658 (C=C), 1580, 1100 cm$^{-1}$. MS: *m*/*z* (%) = 379 (1) $[M]^+$, 351 (3), 233 (7), 116 (85), 77 (100). $C_{23}H_{17}N_5O$ (379.4): calcd. C 72.81, H 4.52, N 18.46; found C 72.89, H 4.44, N 18.61.

**2-(4-Chlorophenylamino)-3,5-dihydro-3-phenyl-5-phenylmethylene-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-one (22b):** Yellow crystals (yield 1.03 g, 83%). M.p.: >300 °C. $^1$H NMR ([D$_6$]DMSO, 400 MHz): $\delta$ = 6.89 (s, 1 H, =CH), 7.35–8.04 (m, 14 H, Ar–H), 9.18 (s, 1 H, N–H) ppm. IR (KBr): $\tilde{\nu}$ = 3355 (N–H), 1708 (C=O), 111 (C–H), 222 (N–H), 1661 (C=C), 1580, 1109 cm$^{-1}$. MS: *m*/*z* (%) = 415 (12), 413 (32) $[M]^+$, 385 (38), 356 (7), 233 (14), 152 (45), 116 (100). $C_{23}H_{16}ClN_5O$ (413.9): calcd. C 66.75, H 3.90, N 16.92; found C 66.70, H 3.81, N 16.95.

**3,5-Dihydro-2-(4-methylphenylamino)-3-phenyl-5-phenylmethylene-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-one (22c):** Yellow crystals (yield 0.93 g, 79%). M.p.: 270–271 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 2.31 (s, 3 H, $CH_3$), 6.08 (s, 1 H, N–H), 7.11–8.02 (m, 15 H, Ar–H and =CH) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 20.9, 119.0, 120.2, 122.3, 123.6, 124.1, 128.0 (2 C), 128.9 (3 C), 129.5 (2 C), 130.4 (2 C), 130.9, 131.4 (2 C), 132.3 (2 C), 143.8, 153.8, 159.8 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3362 (N–H), 1711 (C=O), 1659 (C=C), 1582, 1104 cm$^{-1}$. MS: *m*/*z* (%) = 393 (4) $[M]^+$, 365 (10), 336 (5), 233 (8), 116 (100). $C_{24}H_{19}N_5O$ (393.4): calcd. C 73.27, H 4.87, N 17.80; found C 73.46, H 4.95, N 17.55.

**3,5-Dihydro-2-(3-methylphenylamino)-3-phenyl-5-phenylmethylene-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-one (22d):** Yellow crystals (yield 0.99 g, 84%). M.p.: 240–241 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 2.36 (s, 3 H, $CH_3$), 6.06 (s, 1 H, N–H), 6.92–8.03 (m, 15 H, Ar–H and =CH) ppm. IR (KBr): $\tilde{\nu}$ = 3391 (N–H), 1704 (C=O), 1658 (C=C), 1581, 1107 cm$^{-1}$. MS: *m*/*z* (%) = 393 (96) $[M]^+$, 364 (89), 336 (29), 233 (63), 116 (100). $C_{24}H_{19}N_5O$ (393.4): calcd. C 73.27, H 4.87, N 17.80; found C 73.32, H 4.79, N 17.83.

**3-(4-Chlorophenyl)-3,5-dihydro-2-phenylamino-5-phenylmethylene-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-one (22e):** Yellow crystals (yield 1.00 g, 81%). M.p.: >300 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 6.14 (s, 1 H, N–H), 7.12–8.02 (m, 15 H, Ar–H and =CH) ppm. IR (KBr): $\tilde{\nu}$ = 3305 (N–H), 1710 (C=O), 1655 (C=C), 1589, 1101 cm$^{-1}$. MS: *m*/*z* (%) = 415 (28), 413 (83) $[M]^+$, 385 (70), 356 (30), 232 (78), 204 (61), 116 (100). $C_{23}H_{16}ClN_5O$ (413.9): calcd. C 66.75, H 3.90, N 16.92; found C 66.71, H 3.98, N 16.75.

**3-(4-Chlorophenyl)-3,5-dihydro-2-(3-methylphenylamino)-5-phenylmethylene-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-one (22f):** Yellow crystals (yield 1.10 g, 86%). M.p.: >300 °C. $^1$H NMR ([D$_6$]DMSO, 400 MHz): $\delta$ = 2.30 (s, 3 H, $CH_3$), 6.88–8.04 (m, 14 H, Ar–H and =CH), 8.93 (s, 1 H, N–H) ppm. IR (KBr): $\tilde{\nu}$ = 3406 (N–H), 1714 (C=O), 1661 (C=C), 1589, 1095 cm$^{-1}$. MS: *m*/*z* (%) = 429 (28), 427 (82) $[M]^+$, 399 (71), 370 (39), 232 (75), 116 (100). $C_{24}H_{18}ClN_5O$ (427.9): calcd. C 67.37, H 4.24, N 16.37; found C 67.45, H 4.17, N 16.20.

**3-(4-Chlorophenyl)-3,5-dihydro-2-(4-methylphenylamino)-5-phenylmethylene-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-one (22g):** Yellow crystals (yield 0.94 g, 73%). M.p.: >300 °C. $^1$H NMR ([D$_6$]DMSO, 400 MHz): $\delta$ = 2.27 (s, 3 H, $CH_3$), 6.88 (s, 1 H, =CH), 7.12–8.02 (m, 13 H, Ar–H), 8.91 (s, 1 H, N–H) ppm. IR (KBr): $\tilde{\nu}$ = 3437 (N–H), 1699 (C=O), 1658 (C=C), 1591, 1093 cm$^{-1}$. MS: *m*/*z* (%) = 429 (10), 427 (27) $[M]^+$, 399 (28), 370 (13), 116 (100). $C_{24}H_{18}ClN_5O$ (427.9): calcd. C 67.37, H 4.24, N 16.37; found C 67.30, H 4.11, N 16.44.

**3-(4-Chlorophenyl)-2-(4-chlorophenylamino)-3,5-dihydro-5-phenylmethylene-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-one (22h):** Yellow crystals (yield 1.21 g, 90%). M.p.: >300 °C. $^1$H NMR ([D$_6$]DMSO, 400 MHz): $\delta$ = 6.90 (s, 1 H, =CH), 7.36–8.04 (m, 13 H, Ar–H), 9.17 (s, 1 H, N–H) ppm. IR (KBr): $\tilde{\nu}$ = 3255 (N–H), 1702 (C=O), 1659 (C=C), 1587, 1092 cm$^{-1}$. MS: *m*/*z* (%) = 447 (75) $[M]^+$, 419 (68), 390 (17), 232 (64), 116 (100). $C_{23}H_{15}Cl_2N_5O$ (448.3): calcd. C 61.62, H 3.37, N 15.62; found C 61.48, H 3.21, N 15.85.

**2-Substituted 6*H*-Imidazo[1,2-*b*]-1,2,4-triazol-6-ones 23:** To a mixture of imidazolone **20** (3 mmol), RCOCl (3 mmol), $PPh_3$ (1.05 g, 4 mmol) and $C_2Cl_6$ (0.95 g, 4 mmol) in dry $CH_2Cl_2$ (15 mL) was added dropwise $NEt_3$ (1.11 g, 11 mmol) at room temperature. The colour of the reaction mixture turned red. After the solution was stirred for 2–3 h the solvent was removed under reduced pressure, and the residue was recrystallized from EtOH to give 6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-ones **23**. Starting material and acyl chloride used for: **23a**: **20a** and benzoyl chloride; **23b**: **20a** and acetyl chloride; **23c**: **20b** and benzoyl chloride; **23d**: **20b** and acetyl chloride.

**3,5-Dihydro-2,3-diphenyl-5-phenylmethylene-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-one (23a):** Yellow crystals (yield 0.86 g, 79%). M.p.: 247–249 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.17 (s, 1 H, =CH), 7.34–8.08 (m, 15 H, Ar–H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 123.0, 124.9, 127.3 (2 C), 128.6 (4 C), 128.7 (4 C), 129.4, 129.5, 129.8 (2 C), 131.4 (2 C), 132.4, 143.3, 155.4, 160.6 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 1739 (C=O), 1652 (C=C), 1581, 1095 cm$^{-1}$. MS: *m*/*z* (%) = 364 (42) $[M]^+$, 335 (45), 232 (11), 116 (31). $C_{23}H_{16}N_4O$ (364.4): calcd. C 75.81, H 4.43, N 15.37; found C 75.64, H 4.57, N 15.21.

**3,5-Dihydro-2-methyl-3-phenyl-5-phenylmethylene-6*H*-imidazo-[1,2-*b*]-1,2,4-triazol-6-one (23b):** Yellow crystals (yield 0.57 g, 57%). M.p.: 243–244 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 2.35 (s, 3 H, $CH_3$), 7.13 (s, 1 H, =CH), 7.29–8.04 (m, 10 H, Ar–H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 12.2, 122.6, 126.7 (2 C), 128.6 (2 C), 129.3, 129.6, 130.0 (2 C), 131.2, 131.3 (2 C), 131.6, 134.2, 143.5, 155.3, 160.3 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 1728 (C=O), 1657 (C=C), 1580, 1102 cm$^{-1}$. MS: *m*/*z* (%) = 302 (100) $[M]^+$, 273 (80), 232 (29), 205 (8), 117 (41). $C_{18}H_{14}N_4O$ (302.3): calcd. C 71.51, H 4.67, N 18.53; found C 71.68, H 4.72, N 18.47.

**3-(4-Chlorophenyl)-3,5-dihydro-2-phenyl-5-phenylmethylene-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-one (23c):** Yellow crystals (yield 0.96 g, 80%). M.p.: >300 °C. $^1$H NMR ([D$_6$]DMSO, 400 MHz): $\delta$

= 7.03 (s, 1 H, =CH), 7.39–8.11 (m, 14 H, Ar–H) ppm. IR (KBr): $\tilde{\nu}$ = 1723 (C=O), 1653 (C=C), 1587, 1092 $cm^{-1}$. MS: *m/z* (%) = 400 (30), 398 (88) $[M]^+$, 370 (68), 335 (12), 266 (70), 151 (100). $C_{23}H_{15}ClN_4O$ (398.9): calcd. C 69.26, H 3.79, N 14.05; found C 69.32, H 3.64, N 14.11.

**3-(4-Chlorophenyl)-3,5-Dihydro-2-methyl-5-phenylmethylene-6*H*-imidazo[1,2-*b*]-1,2,4-triazol-6-one (23d):** Yellow crystals (yield 0.71 g, 72%). M.p.: 242–244 °C. $^1H$ NMR ([$D_6$]DMSO, 400 MHz): $\delta$ = 2.50 (s, 3 H, $CH_3$), 6.96 (s, 1 H, =CH), 7.33–8.07 (m, 9 H, Ar–H) ppm. IR (KBr): $\tilde{\nu}$ = 1725 (C=O), 1655 (C=C), 1584, 1094 $cm^{-1}$. MS: *m/z* (%) = 338 (5), 336 (14) $[M]^+$, 308 (23), 266 (19), 232 (8), 151 (51), 116 (100). $C_{18}H_{13}ClN_4O$ (336.8): calcd. C 64.20, H 3.89, N 16.64; found C 64.28, H 3.96, N 16.47.

## Acknowledgments

We gratefully acknowledge financial support of this work by the Natural Science Foundation of Hubei Province for outstanding youth (2006ABB016) and the Natural Science Foundation of China (20102001).

[1] T. S. Sulkowski, D. P. Strike, H. M. Elockdah; US 5599829, **1997** [*Chem. Abstr.* **1997**, *126*, 195251h].
[2] B. L. Pilkington, S. E. Russell, A. J. Whittle, W. R. Mound, M. D. Turnbull, A. M. Kozakiewicz, W. G. Whittingham; GB 2329180, **1999** [*Chem. Abstr.* **1999**, *131*, 44817z].
[3] A. I. Khodair, H. I. El-Subbagh, A. M. Al-Obaid, *Phosphorus Sulfur Silicon Relat. Elem.* **1998**, *140*, 159–181.
[4] K. Kiec-Kononowicz, E. Szymanska, M. Motyl, W. Holzer, A. Bialecka, A. Kasprowicz, *Pharmazie* **1998**, *53*, 680–684.
[5] S. D. Trivedi, H. T. Kubawat, H. H. Parekh, *J. Indian Chem. Soc.* **2002**, *79*, 282–283.
[6] T. Okazaki, K. Kikuchi, T. Watanable, A. Suga, M. Shibasaki, A. Fujimori, O. Inagaki, I. Yanagisawa, *Chem. Pharm. Bull.* **1998**, *46*, 777–781.
[7] A. Loukaci, M. Guyot, A. Chiaroni, C. Riche, *J. Nat. Prod.* **1998**, *61*, 519–522.
[8] H. Sato, M. Tsuda, K. Watanabe, J. Kobayashi, *Tetrahedron* **1998**, *54*, 8687–8690.
[9] P. J. Garratt, S. N. Thorn, R. Wrigglesworth, *Tetrahedron* **1993**, *49*, 165–176.
[10] F. Palacios, C. Alonso, M. Rodriguez, E. Martinez de Marigorta, G. Rubiales, *Eur. J. Org. Chem.* **2005**, 1795–1804.
[11] P. N. D. Singh, R. F. Klima, S. Muthukrishnan, R. S. Murthy, J. Sankaranarayanan, H. M. Stahlecker, B. Patel, A. D. Gudmundsdottir, *Tetrahedron Lett.* **2005**, *46*, 4213–4217.
[12] C. E. Hoesl, A. Nefzi, R. A. Houghten, *Tetrahedron Lett.* **2003**, *44*, 3705–3708.
[13] E. Bellur, H. Goerls, P. Langer, *J. Org. Chem.* **2005**, *70*, 4751–4761.
[14] S. Brase, C. Gil, K. Knepper, V. Zimmermann, *Angew. Chem. Int. Ed.* **2005**, *44*, 5188–5240.
[15] M. W. Ding, S. Z. Xu, J. F. Zhao, *J. Org. Chem.* **2004**, *69*, 8366–8371.
[16] M. W. Ding, Y. F. Chen, N. Y. Huang, *Eur. J. Org. Chem.* **2004**, 3872–3878.
[17] J. F. Zhao, C. Xie, S. Z. Xu, M. W. Ding, W. J. Xiao, *Org. Biomol. Chem.* **2006**, *4*, 130–134.
[18] M. W. Ding, S. J. Yang, J. Zhu, *Synthesis* **2004**, 75–79.
[19] M. W. Ding, B. Q. Fu, L. Cheng, *Synthesis* **2004**, 1067–1071.
[20] J. F. Zhao, C. Xie, M. W. Ding, H. W. He, *Chem. Lett.* **2005**, *34*, 1022–1023.
[21] M. W. Ding, Y. Sun, S. J. Yang, X. P. Liu, Z. J. Liu, *Synth. Commun.* **2003**, *33*, 1651–1658.
[22] M. Watanabe, H. Okada, T. Teshima, M. Noguchi, A. Kakehi, *Tetrahedron* **1996**, *52*, 2827–2838.
[23] M. Nitta, D. Ohtsuki, Y. Mitsumoto, S. Naya, *Tetrahedron* **2005**, *61*, 6073–6081.
[24] C. E. Hoesl, A. Nefzi, R. A. Houghten, *Tetrahedron Lett.* **2003**, *44*, 3705–3708.
[25] L. Bruche, L. Garanti, G. Zecchi, *J. Chem. Soc., Perkin Trans. 1* **1986**, 2177.
[26] M. W. Ding, H. Y. Tu, Z. J. Liu, *Synth. Commun.* **1997**, *27*, 3657–3662.
[27] M. Heras, M. Ventura, A. Linden, J. Villalgordo, *Tetrahedron* **2001**, *57*, 4371–4388.

Received: March 7, 2006
Published Online: July 19, 2006