2-Arylhydrazononitriles in heterocyclic synthesis:
a novel route to 1,3-diaryl-1,2,4-triazol-5-amines via a Tiemann rearrangement of arylhydrazonoamidoximes

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Abstract
2-Arylhydrazononitriles react with hydroxylamine hydrochloride in refluxing ethanolic sodium acetate to yield amidoximes that cyclized into 1,2,3-triazol-5-amines or 1,2,4-triazol-5-amines depending on the nature of the substituents on hydrazone linkage. NOE difference experiments could successfully be utilized to distinguish 1,2,3-triazoles from isomeric 1,2,4-triazoles.

Keywords: Enaminonitriles; X-ray crystal structure determination, acetylamino-1,2,3-triazol-5-amines; NOE difference, Boulton-Katritzky rearrangement

Introduction

The chemistry of 2-arylhydrazono-3-substituted nitriles has been extensively investigated in our laboratories in the past.1-3 Our interest in the chemistry of these compounds has recently been revived and we could show that these compounds are excellent precursors to 4-aminopyrazole-5-carboxylic acid derivatives,4,5 interesting precursors to phosphodiesterase inhibitors such as sildenafil citrate (viagra)4,5 as well as 4-acyl-2-substituted-1,2,3-triazolamines, potential precursors to pharmaceutically active triazoloazines; e.g. 1,4-dihydro-5-(2-propoxyphenyl)-7H-1,2,3-triazolo[4,5-d]pyrimidine-7-one (Zaprinast).5,6 In conjunction to our interest in the chemistry of these compounds we report here the results of our work that enabled developing simple, efficient, novel routes to both 1,2,4-triazol-5-amines and 2,4-disubstituted-1,2,3-triazol-5-amines. Derivatives of both ring systems are important both in the dye industry7 and as potential intermediates in pharmaceutical industry.8,9
Results and Discussion

2-Arylhydrazononitriles are readily obtainable via a variety of procedures\textsuperscript{10-13} the simplest is coupling of active methylene nitriles with aromatic diazonium salts.\textsuperscript{11} In this work we could successfully couple active methylene nitriles 1\textsubscript{a-c} with aromatic diazonium salts producing the 2-arylhydrazononitriles 2\textsubscript{a-d}. Benzyl cyanide (3) failed to couple with aromatic diazonium salts under these conditions. As the $\beta$-carbon in enamionitrites has recently been shown by us to be sufficiently electrophilic to couple readily with aromatic diazonium salts,\textsuperscript{14} benzyl cyanide (3) was condensed with triethyl orthoformate and piperidine following a recently published procedure.\textsuperscript{5} The so formed 2-phenyl-3-piperidinoacrylonitrile (4) coupled smoothly with aromatic diazonium salts yielding 2-arylhydrazononitriles 2\textsubscript{e-h}. It is believed that 5 is a non-isolable intermediate as it undergoes ready Japp-Klingemann cleavage\textsuperscript{15} yielding 2\textsubscript{e-h} (Scheme 1).

![Scheme 1](image)

Similar to the reported\textsuperscript{16} formation of amidoximes 6\textsubscript{a-c} on reacting 2\textsubscript{a-c} with hydroxylamine hydrochloride, the arylhydrazononitriles 2\textsubscript{d-h} afforded amidoximes 6\textsubscript{d-h} upon treatment with hydroxyamine hydrochloride under similar conditions. Amidoximes 6\textsubscript{a-c} have been previously cyclized into 1,2,3-triazol-5-amines 7\textsubscript{a-c}, whose structure was supported by X-ray for 7\textsubscript{c}, upon reflux in dimethyl formamide in presence of sodium acetate.\textsuperscript{16} However, in our hands, much better yields of 1,2,3-triazol-5-amines were obtained upon replacing sodium acetate by piperidine (Scheme 2).
Scheme 2

In an attempt to accelerate cyclization, amidoximes 6a-c were refluxed in acetic anhydride. The obtained products could be assigned the oxadiazolylarylhydrazone structure 8a-c or acetylamino-1,2,3-triazoles 9a-c. Structure 9 could be confirmed for these products based on their identity with acetylamino-1,2,3-triazole 9, prepared via acylating 7a-c with acetic anhydride. Interestingly 9a-c could be converted into 7a-c upon reflux in ethanolic sodium ethoxide. To verify whether or not an oxadiazole 8 is formed initially, amidoximes 6 were acylated with acetyl chloride at room temperature, and even under such conditions the only products formed were acetylamino-1,2,3-triazoles 9 (cf. Scheme 2). Thus the intermediacy of oxadiazoles and subsequent Boulton-Katritzky rearrangement, as has recently been assumed, seems least likely. In contrast to the behavior of 6a-c amidoxime 6d cyclized upon reflux in DMF in presence of piperidine to yield the 1,2,4-triazol-5-amine 11d as was established by X-ray crystal structure (cf. Fig. 1).
Figure 1. Crystal structure of 3-(4-nitrophenyl)-1-phenyl-1H-1,2,4-triazol-5-amine (11d).

It is believed that amidoxime 6d in this case has initially undergone a Tiemann rearrangement\textsuperscript{19-24} to yield intermediate 10d that then further cyclized into 11d. It became now clear that we have two competing modes of cyclization that may lead either to 1,2,4-triazole or 1,2,3-triazole amines. It seemed thus mandatory to develop a way to establish, spectroscopically, structure for product of cyclization. An easy way could be achieved through NOE difference experiments. Thus irradiating NH\textsubscript{2} protons in 11d at $\delta$ 6.64 ppm enhanced ortho-aromatic protons at $\delta$ 7.65 ppm while in the 1,2,3-triazole irradiating amino protons did not effect such enhancement.

Compounds 6e-h also cyclized in refluxing DMF, piperidine yielding the 1,2,4-triazol-5-amines 11e-h as indicated from NOE difference experiments (cf. Scheme 3). Conversion of 6 into a 1,2,3-triazole necessitates formation of N-N bond which is an energy demanding process. Aromaticity of the formed 2-substituted-1,2,3-triazole is thus a driving force especially if the substituent can contribute an extra resonance form as in 7a-c (cf. form 7A).

Conclusions

Arylhydrazonoamidoximes are readily obtainable compounds that can be easily cyclized to afford in good yields either 1,2,3-triazolamines or 1,2,4-triazolamines depending on the nature of substituent on the hydrazone carbon. A simple spectroscopic method that allows a reliable structure determination of the cyclization product is also suggested.
Acknowledgements

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Scheme 3

Experimental Section

General Procedures. Melting points were recorded on Gallenkamp apparatus and are uncorrected. Infrared spectra (KBr) were determined on a Perkin-Elmer 2000 FT-IR system. $^1$H NMR was determined on a Bruker DPX 400 MHz superconducting spectrometer in CDCl$_3$ and DMSO-d$_6$ as solvents and using TMS as internal standard. Mass spectra were measured on MS 30 and MS 9 (AEI) spectrometers, with EI 70 eV. Elemental analyses were measured by means of LECO CHNS-932 Elemental Analyzer. Compounds 2a-c, 6a-c and 7a-c were prepared as described in literature.$^{16}$

Crystallographic analysis

The crystals were mounted on a glass fiber. All measurements were performed on an ENRAF NONIUS FR 590. The data were collected at a temperature of 25 °C using the $\omega$ scanning technique to a maximum of a 2θ of 24.108 °. The structure was solved by direct method using SIR 92 and refined by full-matrix least squares. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located geometrically and were refined isotropically.

Crystal data

C$_{14}$H$_{11}$N$_5$O$_2$, M = 281.275, monoclinic, a = 7.9303 (7), b = 7.3875 (7), c = 23.421 (3) Å, v = 1357.1 (2) (Å)$^3$, $\alpha = \gamma = 90.00$ °, $\beta = 98.483$ (3)', space group: P2$_1$/c, D$_x$ = 1.377 Mg m$^{-3}$
reflection 690 measured, $\theta_{\text{max}} = 24.09^\circ$, oR factor = 0.278. Figure 1 illustrates the structure as determined. Full data can be obtained on request from the CCDC.25

### Synthesis of 2-substituted-2-(2-aryldrazono) acetonitriles (2d-h)

A cold solution of aryldiazonium salts (10 mmol) was prepared by adding a solution of sodium nitrite (1.4 g dissolved in 10 mL water) to cold solution of arylamine hydrochloride (10 mmol of arylamine in 6 mL, 6M HCl) with stirring. The resulting solution of aryldiazonium salts were then added to a cold solution of either enaminoacetonitrile (4) or acetonitrile derivatives (1) in ethanol (50 mL) in the presence of sodium acetate trihydrate (2.8 g, 20 mmol). The mixture was stirred at room temperature for 1 h and the solid product was collected by filtration, washed with water and recrystallized from the appropriate solvent.

**2-(4-Nitrophenyl)-2-(2-phenylhydrazono)acetonitrile (2d).** 1.99g (75%) (green), mp 198 °C [EtOH]; IR (KBr) $\nu = 3240$ (NH), 2208 (CN), 1599 (C=N) cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta = 7.15$-7.46 (m, 5H, Ar-H), 7.95 (d, 2H, $J = 8$ Hz), 8.33 (d, 2H, $J = 8$ Hz), 9.10 (s, 1H, NH); MS, $m/z$ (%) 266 ($M^+$, 80), 239 (10), 91 (100), 77 (40). Anal. Calcd. for C$_{14}$H$_{10}$N$_4$O$_2$: C, 63.15; H, 3.79; N, 21.04. Found: C, 62.99; H, 4.10; N, 20.92.

**2-Phenyl-2-(2-phenylhydrazono)acetonitrile (2e).** 1.55g (70%) (pale yellow), mp 140 °C [MeOH]; IR (KBr) $\nu = 3235$ (NH), 2215 (CN), 1601 (C=N) cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta = 7.06$-7.84 (m, 10H, Ar-H), 8.84 (s, 1H, NH); MS, $m/z$ (%) 221 ($M^+$, 100), 194 (80), 91 (90), 77 (60). Anal. Calcd. for C$_{14}$H$_{11}$N$_3$: C, 76.00; H, 5.01; N, 18.99. Found: C, 75.88; H, 5.12; N, 18.77.

**2-Phenyl-2-[2-(4-methylphenyl)hydrazono]acetonitrile (2f).** 1.69g (72%) (yellow), mp 120 °C [MeOH]; IR (KBr) $\nu = 3252$ (NH), 2207 (CN), 1612 (C=N) cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta = 2.36$ (s, 3H, Ar-CH$_3$), 7.16-7.83 (m, 9H, Ar-H), 8.78 (s, 1H, NH); MS, $m/z$ (%) 235 ($M^+$, 90), 105 (100), 91 (25), 77 (50). Anal. Calcd. for C$_{15}$H$_{13}$N$_3$: C, 76.57; H, 5.57; N, 17.86. Found: C, 76.64; H, 5.72; N, 17.93.

**2-[2-(4-Chlorophenyl)hydrazono]-2-phenyl acetonitrile (2g).** 1.99g (78%) (pale orange), mp 168 °C [EtOH]; IR (KBr) $\nu = 3258$ (NH), 2209 (CN), 1601 (C=N) cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta = 7.21$-7.48 (m, 5H, Ar-H), 7.69 (d, 2H, $J = 8$ Hz), 7.81 (d, 2H, $J = 8$ Hz), 8.79 (s, 1H, NH); MS, $m/z$ (%) 257 ($M^+ + 2$, 40), 256 ($M^+ + 1$, 50), 255 ($M^+$, 100), 125 (90), 111 (20), 77 (15). Anal. Calcd. for C$_{14}$H$_{10}$ClN$_3$: C, 65.76; H, 3.94; N, 16.43. Found: C, 65.57; H, 3.83; N, 16.43.

**2-[2-(4-Nitrophenyl)hydrazono]-2-phenyl acetonitrile (2h).** 2.13g (80%) (pale yellow), mp 214 °C [EtOH]; IR (KBr) $\nu = 3250$ (NH), 2216 (CN), 1598 (C=N) cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta = 7.46$-7.64 (m, 5H, Ar-H), 7.83 (d, 2H, $J = 8$ Hz), 8.23 (d, 2H, $J = 8$ Hz), 11.90 (s, 1H, NH); MS, $m/z$ (%) 266 ($M^+$, 100), 239 (40), 105 (20), 77 (10). Anal. Calcd. for C$_{14}$H$_{10}$N$_4$O$_2$: C, 63.15; H, 3.79; N, 21.04. Found: C, 63.12; H, 3.80; N, 21.11.

### Synthesis of N-hydroxy-2,2-disubstituted-acetamidines (6c-h)

A mixture of 2-aryldrazonocacetonitrile (2) (10 mmol), hydroxylamine hydrochloride (0.69 g, 10 mmol) and sodium acetate anhydrous (3 g) in ethanol (20 mL) was heated under reflux for 3 h. The reaction mixture was poured on water, collected by filtration and recrystallized from the appropriate solvent.
2-[(4-Chlorophenyl)hydrazono]-N-hydroxy-3-oxo-3-phenyl-propionamidine (6c). 2.37g (75%) (yellow), mp 226 °C [H₂O/ EtOH]; IR (KBr) ν = 3488 (OH), 3436, 3276, 3175 (NH₂, NH), 1625 (CO), 1599 (C=N) cm⁻¹; ¹H NMR (CDCl₃) δ = 6.50 (s, 2H, NH₂), 7.01-7.54 (m, 5H, Ar-H), 7.61 (d, 2H, J = 9 Hz), 7.75 (d, 2H, J = 9 Hz), 8.11 (s, 1H, NH), 13.49 (s, 1H, OH); MS, m/z (%) 316 (M⁺, 20), 299 (40), 105 (100), 77 (80).

N-Hydroxy-2-(4-nitrophenyl)-2-(phenylhydrazono)-acetamidine (6d). 1.79g (61%) (red), mp 215 °C [H₂O/ MeOH]; IR (KBr) ν = 3499 (OH), 3381, 3219 (NH₂, NH), 1651, 1609 (2C=N) cm⁻¹; ¹H NMR (CDCl₃) δ = 7.18-8.41 (m, 9H, Ar-H), 10.98 (s, 1H, NH), 12.92 (s, 1H, OH); MS, m/z (%) 284 (20), 239 (30), 91 (90), 77 (55). Anal. Calcd. for C₁₄H₁₃N₅O₃: C, 56.18; H, 4.38; N, 23.40. Found: C, 56.02; H, 4.26; N, 23.62.

N-Hydroxy-2-phenylhydrazono-2-phenyl-acetamidine (6e). 1.77g (70%) (yellow), mp 160 °C [MeOH]; IR (KBr) ν = 3497 (OH), 3381, 3219 (NH₂, NH), 1651, 1609 (2C=N) cm⁻¹; ¹H NMR (CDCl₃) δ = 4.48 (s, 2H, NH₂), 7.01-7.81 (m, 10H, Ar-H), 8.21 (s, 1H, NH), 11.01 (s, 1H, OH); MS, m/z (%) 221 (40), 91 (40), 77 (45). Anal. Calcd. for C₁₄H₁₄N₄O: C, 66.13; H, 5.55; N, 22.03. Found: C, 66.08; H, 5.61; N, 22.12.

N-Hydroxy-2-[(4-methylphenyl)hydrazono]-2-phenyl-acetamidine (6f). 1.88g (70%) (yellow), mp 152 °C [MeOH]; IR (KBr) ν = 3498 (OH), 3392, 3337, 3226 (NH₂, NH), 1650, 1613 (2C=N) cm⁻¹; ¹H NMR (CDCl₃) δ = 2.34 (s, 3H, Ar-CH₃), 6.91-7.58 (m, 9H, Ar-H), 7.66 (s, 1H, NH), 10.68 (s, 1H, OH); MS, m/z (%) 268 (M⁺, 100), 106 (45), 91 (30), 77 (30). Anal. Calcd. for C₁₅H₁₆N₄O: C, 67.15; H, 6.01; N, 20.88. Found: C, 67.08; H, 6.08; N, 20.62.

N-Hydroxy-2-[(4-chlorophenyl)hydrazono]-2-phenyl-acetamidine (6g). 1.87g (60%) (yellow), mp 148 °C [H₂O/ MeOH]; IR (KBr) ν = 3499 (OH), 3399, 3274, 3185 (NH₂, NH), 1641, 1599 (2C=N) cm⁻¹; ¹H NMR (CDCl₃) δ = 5.75 (s, 2H, NH₂), 7.16-7.59 (m, 9H, Ar-H), 7.68 (s, 1H, NH), 12.89 (s, 1H, OH); MS, m/z (%) 253 (80), 125 (100), 91 (30), 77 (50). Anal. Calcd. for C₁₄H₁₃ClN₄O: C, 58.24; H, 4.54; N, 19.40. Found: C, 58.27; H, 4.63; N, 19.35.

N-Hydroxy-2-[(4-nitrophenyl)hydrazono]-2-phenyl-acetamidine (6h). 1.79g (60%) (pale yellow), mp 204 °C [H₂O/ MeOH]; IR (KBr) ν = 3495 (OH), 3383, 3270, 3180 (NH₂, NH), 1638, 1601 (2C=N) cm⁻¹; ¹H NMR (CDCl₃) δ = 6.07 (s, 2H, NH₂), 7.38-8.16 (m, 9H, Ar-H), 8.92 (s, 1H, NH), 12.89 (s, 1H, OH); MS, m/z (%) 299 (M⁺, 30), 284 (65), 239 (100), 91 (30), 77 (50). Anal. Calcd. for C₁₄H₁₃N₃O₃: C, 56.18; H, 4.38; N, 23.40. Found: C, 56.12; H, 4.31; N, 23.55.

Synthesis of N-[2,5-disubstituted-2H-1,2,3-triazol-4-yl]acetamide (9a-c)

Method A. Compound (6) (1 mmol) was dissolved in 20 mL acetic acid in the presence of few drops of acetic anhydride. The reaction mixture was refluxed for 4 h and poured into ice-water mixture, extracted with chloroform (3X10 ml). The organic extracts were dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. The residue was purified through preparative thin layer chromatography [eluent: hexane / AcOEt (3:1)]
**Method B.** Compound (6) (1 mmol) was treated with acetyl chloride (0.079 g, 1 mmol) in piperidin (10 mL) and the reaction mixture was stirred for 4 h at room temperature and triturated as in method A.

**N-[2-Phenyl-5-propionyl-2H-1,2,3-triazol-4-yl]acetamide (9a).** 0.18 g (72%) (yellow), mp 176 °C; IR (KBr) $\nu = 3268$ (NH), 1712, 1675 (2CO), 1599 (C=N) cm$^{-1}$; $^1$H NMR (DMSO-d$_6$) $\delta = 1.2$ (t, 3H, $J = 7.5$ Hz), 2.35 (s, 3H, CH$_3$), 2.41 (q, 2H, $J = 7.5$ Hz), 7.21-7.62 (m, 5H, Ar-H), 10.51 (s, 1H, NH); MS, $m/z$ (%) 258 (M$^+$, 100), 229 (60), 201 (50), 77 (35). *Anal. Calcd. for C$_{13}$H$_{14}$N$_4$O$_2$: C, 60.45; H, 5.46; N, 21.69. Found: C, 60.22; H, 5.61; N, 21.72.*

**N-[5-Benzoyl-2-phenyl-2H-1,2,3-triazol-4-yl]acetamide (9b).** 0.21 g (70%) (yellow), mp 196 °C; IR (KBr) $\nu = 3271$ (NH), 1675, 1663 (2CO), 1599 (C=N) cm$^{-1}$; $^1$H NMR (DMSO-d$_6$) $\delta =$ 2.15 (s, 3H, CH$_3$), 7.21-7.82 (m, 10H, Ar-H), 10.71 (s, 1H, NH); MS, $m/z$ (%) 306 (M$^+$, 40), 291 (80), 105 (50), 77 (100). *Anal. Calcd. for C$_{17}$H$_{14}$N$_4$O$_2$: C, 66.66; H, 4.61; N, 18.29. Found: C, 66.52; H, 4.82; N, 18.36.*

**N-[5-Benzoyl-2-(4-chlorophenyl)-2H-1,2,3-triazol-4-yl]acetamide (9c).** 0.255 g (75%) (yellow), mp 226 °C; IR (KBr) $\nu = 3280$ (NH), 1689, 1671 (2CO), 1596 (C=N) cm$^{-1}$; $^1$H NMR (DMSO-d$_6$) $\delta =$ 2.05 (s, 3H, CH$_3$), 7.56-7.73 (m, 5H, Ar-H), 8.00 (d, 2H, $J = 9$ Hz), 8.04 (d, 2H, $J = 9$ Hz), 10.83 (s, 1H, NH); $^{13}$C NMR (DMSO-d$_6$) $\delta =$ 23.81 (CH$_3$), 121.39, 129.68, 130.73, 130.92, 133.67, 134.68, 137.28, 138.44, 145.83 (Ar-Cs), 137.85, 138.05, 138.81, 138.94, 139.15, 148.42, 156.86, 157.59; MS, $m/z$ (%) 340 (M$^+$, 50), 325 (100), 105 (80), 77 (100). *Anal. Calcd. for C$_{17}$H$_{13}$ClN$_4$O$_2$: C, 59.92; H, 3.85; N, 16.44. Found: C, 59.62; H, 3.82; N, 16.46.*

**Synthesis of 1,3-disubstituted-1H-[1,2,4]triazol-5-amines (11d-h)**

A solution of 6 (1 mmol) in DMF (20 mL) in presence of piperidin (2 mL) was refluxed for 4 h. The solid product was collected by filtration and recrystallized from appropriate solvent.

**3-(4-Nitrophenyl)-1-phenyl-1H-[1,2,4]triazol-5-amine (11d).** 0.195 g (68%) (pale brown), mp 204 °C [EtOH]; IR (KBr) $\nu =$ 3465, 3332 (NH$_2$), 1597 (C=N) cm$^{-1}$; $^1$H NMR (DMSO-d$_6$) $\delta =$ 6.74 (s, 2H, NH$_2$), 7.42-7.65 (m, 5H, Ar-H), 8.17 (d, 2H, $J = 8$ Hz), 8.31 (d, 2H, $J = 8$ Hz), 8.04 (d, 2H, $J = 9$ Hz), 10.83 (s, 1H, NH); $^{13}$C NMR (DMSO-d$_6$) $\delta =$ 125.11, 127.51, 128.64, 129.90, 130.57, 137.95, 138.46, 145.83 (Ar-Cs), 168.15, 187.04 (2C=O); MS, $m/z$ (%) 281 (M$^+$, 100), 239 (50), 91 (90), 77 (25). *Anal. Calcd. for C$_{14}$H$_{11}$N$_5$O$_2$: C, 59.78; H, 3.94; N, 24.90. Found: C, 59.61; H, 3.88; N, 24.90.*

**1,3-Diphenyl-1H-[1,2,4]triazol-5-amine (11e).** 0.165 g (70%) (dark yellow), mp 175 °C [EtOH]; IR (KBr) $\nu =$ 3430, 3302 (NH$_2$), 1608 (C=N) cm$^{-1}$; $^1$H NMR (DMSO-d$_6$) $\delta =$ 5.71 (s, 2H, NH$_2$), 7.11-7.93 (m, 10H, Ar-H); $^{13}$C NMR (DMSO-d$_6$) $\delta =$ 124.81, 125.11, 125.64, 126.42, 127.07, 129.45, 130.16, 141.22, 150.46, 152.51; MS, $m/z$ (%) 236 (M$^+$, 100), 194 (40), 77 (25). *Anal. Calcd. for C$_{14}$H$_{12}$N$_4$: C, 71.17; H, 3.94; N, 24.90. Found: C, 59.61; H, 3.88; N, 24.85.*

**1,3-Diphenyl-1H-[1,2,4]triazol-5-amine (11f).** 0.165 g (70%) (dark yellow), mp 175 °C [MeOH]; IR (KBr) $\nu =$ 3450, 3317 (NH$_2$), 1599 (C=N) cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta =$ 5.71 (s, 2H, NH$_2$), 7.61-8.31 (m, 10H, Ar-H); $^{13}$C NMR (CDCl$_3$) $\delta =$ 124.81, 125.11, 125.64, 126.42, 127.07, 129.45, 130.16, 141.22, 150.46, 152.51; MS, $m/z$ (%) 236 (M$^+$, 100), 194 (40), 77 (25). *Anal. Calcd. for C$_{14}$H$_{12}$N$_4$: C, 71.17; H, 3.94; N, 24.90. Found: C, 59.61; H, 3.88; N, 24.85.*

**1-(4-Methylphenyl)-3-phenyl-1H-[1,2,4]triazol-5-amine (11g).** 0.175 g (70%) (yellow), mp 160 °C [MeOH]; IR (KBr) $\nu =$ 3455, 3317 (NH$_2$), 1599 (C=N) cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta =$ 2.3 (s, 3H, Ar-CH$_3$), 5.81 (s, 2H, NH$_2$), 7.11-7.93 (m, 9H, Ar-H); $^{13}$C NMR (CDCl$_3$) $\delta =$ 26.61, 123.81, 124.15, 124.54, 124.92, 125.51, 125.92, 131.27, 133.82, 143.16, 151.53; MS, $m/z$ (%) 250 (M$^+$, 100).
100), 208 (60), 91 (40), 77 (25). Anal. Calcd. for C₁₅H₁₄N₄: C, 71.98; H, 5.64; N, 22.38. Found: C, 71.90; H, 5.41; N, 22.50.

1-(4-Chlorophenyl)-3-phenyl-1H-[1,2,4]triazol-5-amine (11g). 0.19 g (70%) (orange), mp 148 °C; IR (KBr) ν = 3446, 3327 (NH₂), 1599 (C=N) cm⁻¹; ¹H NMR (CDCl₃) δ = 5.84 (s, 2H, NH₂), 7.16 (d, 2H, J = 8 Hz), 7.21-7.53 (m, 5H, Ar-H), 7.59 (d, 2H, J = 8 Hz); ¹³C NMR (CDCl₃) δ = 124.18, 125.82, 127.14, 127.95, 130.18, 135.45, 136.28, 145.11, 154.22, 156.12; MS, m/z (%) 272 (M⁺+2, 50), 270 (M⁺, 20), 228 (60), 125 (100), 77 (25). Anal. Calcd. for C₁₄H₁₁ClN₄: C, 62.11; H, 4.10; N, 20.70. Found: C, 61.99; H, 4.01; N, 20.60.

1-(4-Nitrophenyl)-3-phenyl-1H-[1,2,4]triazol-5-amine (11h). 0.20 g (70%) (dark yellow), mp 182 °C; IR (KBr) υ = 3447, 3387 (NH₂), 1598 (C=N) cm⁻¹; ¹H NMR (CDCl₃) δ = 5.75 (s, 2H, NH₂), 7.45-8.05 (m, 5H, Ar-H), 8.07 (d, 2H, J = 8 Hz), 8.47 (d, 2H, J = 8 Hz); ¹³C NMR (CDCl₃) δ = 126.45, 126.70, 127.64, 129.56, 129.93, 130.54, 138.05, 144.21, 145.16, 153.50; MS, m/z (%) 281 (M⁺, 30), 239 (40), 77 (100). Anal. Calcd. for C₁₄H₁₁N₅O₂: C, 59.78; H, 3.94; N, 24.90. Found: C, 59.90; H, 4.01; N, 24.71.

References

25. Crystal data for 11d (ref. CCDC 619484) can be obtained on request from the director, Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EW, UK