Syntheses of 5-(2-arylazenyl)-1,2,4-triazoles and 2-amino-5-aryl-1,3,4-oxadiazoles

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Dedicated to Charles Rees on the occasion of his 75 th anniversary and 50 years of friendship
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Abstract
Di(benzotriazolyl)methanimine 1 was used for convenient preparation of previously unknown triazoles 11a,b and 15a-d and as a new reagent for the synthesis of oxadiazoles 17a-j.

Keywords: Di(benzotriazolyl)methanimine, triazoles, oxadiazoles, synthesis, hydrazine, hydrazide

Introduction
Di(benzotriazol-1-yl)methanimine 1 is useful for the preparation of carboximidamides 2, guanidines 3,1 triazoles 5,2 and triazinones and triazinthiones 6,3 (Scheme 1). We now extend the reported preparation of 2-amino-5-phenyl-1,3,4-oxadiazole 17a from imine 1 and benzenecarbohydrazide2 to other hydrazides, thus providing a general route to 2-amino-5-aryl-1,3,4-oxadiazoles 17a-j. These compounds, which are antidiabetic,4 antiarthritic and antiinflammatory,5 were previously prepared in high yield from arylhydrazides but this required toxic cyanogen bromide.6-10 We also report the use of 1 for the preparation of novel triazoles 11a,b and 15a-d.
Results and Discussion

By analogy to reactions with amines (Scheme 1), reactions of 1 with hydrazines are expected to give compounds of types 7, 9 and 12. However, after reaction of imine 1 with hydrazine hydrate in THF at 20 °C, we detected only carbohydrazonamide 8'a (isolated yield 41%). Methylhydrazine (from 0.5 to 1.0 equivalent), under similar conditions, formed triazole 11a (isolated yield 57%) probably because intermediate 10a cannot tautomize to give a product with a conjugated structure, and instead eliminates benzotriazole to form the aromatic triazole 11a.
Reactions of imine 1 with 4-methoxyphenylhydrazine in THF at rt for 18 h led to triazole 15a in 86% yield. Analogous reactions of phenylhydrazine, 4-methylphenylhydrazine and 4-bromophenylhydrazine gave mainly products of simple substitution 12b-d, while triazoles 15b-d were detected as minor products. Compound 12b was isolated and purified (yield 85%). However, treatment with t-BuOK (rt, 18 h, 1 eq.) converts intermediates 12b-d quantitatively into triazoles 15b-d (isolated yields 80–85%). The formation of unexpected compounds 15a-d (Scheme 2) suggests condensation of intermediates 12a-d into compounds 13a-d followed by evolution of ammonia to give triazoles 14a-d.

**Table 1. Reactions of imine 1 with compounds RNH-NH**

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<td>2</td>
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<td>(i)</td>
<td>11a</td>
<td>57</td>
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<td>85</td>
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<td>93</td>
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<td>4-tert-Butyl-C₆H₄CO-</td>
<td>(v)</td>
<td>17b</td>
<td>92</td>
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<td>(v)</td>
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<td>(v)</td>
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(i) THF, rt, 24 h; (ii) THF, rt, 4d; (iii) THF, rt, 24 h, t-BuOK; (iv) PhH, refl, 48 h; (v) THF, refl, 3–6 h.
Spontaneous oxidation of hydrazo derivatives 14a-d with atmospheric oxygen afforded deep orange to red colored azo derivatives 15a-d. The ready formation and strong color of these compounds is explained by their highly conjugated planar structure, as confirmed by X-ray analysis for compound 15b. Figure 1 shows a perspective view of the crystal structure of 15b, which has bond lengths and angles similar to those previously reported for a closely related structure. Overall, the molecule is close to planar, with the triazole ring meanplane subtending angles of 10.4, 8.2 and 29.7 ° to the planes of the benzotriazole, phenylazo and phenyl substituents, respectively. As is often the case with planar aromatic compounds, the molecules pack in a herringbone fashion. Spontaneous oxidation of a hydrazo substituent to form a triazole ring was described by Fromm in his preparation of 1-phenyl-5-[(E)-2-phenyldiazenyl]-1,2-dihydro-3H-1,2,4-triazole-3-thione. Azotriazoles similar to compounds 15a-d have been described as dyes.

![Figure 1. X-Ray structure of compound 15b.](image)

We also investigated reactions of imine 1 with acyl hydrazides. Similar to methyl hydrazine, acetyl hydrazide readily reacts with imine 1 to give triazole 11b in 42% yield (Scheme 2). In contrast, aryl hydrazides gave oxadiazoles 17a-j in 82–97% yields, independent of the nature of the aryl group (Scheme 2, Table 1). In order to unambiguously confirm the structures of these compounds, an X-ray determination was carried out for compound 17a. Figure 2 shows a perspective view of the molecule, which has the phenyl ring inclined to the plane of the oxadiazole ring at an angle of 12.6 °. The geometry of the oxadiazole ring is similar to that previously observed in other 2-amino-1,3,4-oxadiazoles. The molecules pack in infinite sheets governed by intermolecular hydrogen bonds between each of the amino group hydrogens and oxadiazole nitrogens of adjacent molecules.
Conclusions

In summary we have developed the use of di(benzotriazolyl)methanimine 1 for the convenient preparation of previously unknown triazoles 11a,b and 15a-d and as a new reagent for the synthesis of oxadiazoles 17a-j.

![Figure 2. X-Ray structure of compound 17a.](image)

Experimental Section

General Procedures. Melting points were determined using a capillary melting point apparatus equipped with a digital thermometer and are uncorrected. $^1$H and $^{13}$C NMR spectra were recorded on a 300 MHz NMR spectrometer (300 and 75 MHz respectively) using CDCl$_3$ or DMSO-$d_6$ as solvents with tetramethylsilane as an internal standard. Tetrahydrofuran (THF) was distilled under nitrogen from sodium/benzophenone immediately before use. Column chromatography was conducted with silica gel grade 230–400 mesh. All other reagents were of reagent grade and were used without purification.

$N'$-[Amino(1$H$-1,2,3-benzotriazol-1-yl)methylidene]-1$H$-1,2,3-benzotriazole-1-carboxyhydrazonamide (8). Di(benzotriazol-1yl)methanimine 1 (2g, 7.6 mmol), hydrazine hydrate (191 mg, 3.8 mmol) and THF (30 mL) were stirred at rt for 24 h. The residue obtained after removal of THF was recrystallized from acetone to give 500 mg (41%) of $N'$-[amino(1$H$-benzotriazol-1-yl)methylidene]-1$H$-benzotriazole-1-carbo-hydrazonamide 8, mp 244–245 °C; $^1$H NMR $\delta$ 7.29 (br. s, 4H), 7.58 (t, $J$ = 7.5 Hz, 2H), 7.74 (t, $J$ = 7.4 Hz, 2H), 8.22 (d, $J$ = 8.2 Hz, 2H), 8.61 (d, $J$ = 8.4 Hz, 2H); $^{13}$C NMR $\delta$ 115.5, 119.6, 125.6, 129.5, 130.8, 145.9, 148.8. Anal. Calcd for C$_{14}$H$_{12}$N$_{10}$O$_1$: C, 52.50; H, 3.78; N, 43.73. Found: C, 52.56; H, 3.89; N, 43.83.

3-(1$H$-Benzotriazol-1-yl)-1-methyl-1$H$-1,2,4-triazole-5-amine (11a). Compound 1 (1.5 g, 5.7 mmol), methyl hydrazine (150 mg, 3.3 mmol) and THF (50 mL) were stirred at rt for 24 h. The residue obtained after removal of THF was dissolved in DCM and washed with 10% aqueous Na$_2$CO$_3$. The organic layer was dried over MgSO$_4$, filtered, and concentrated in vacuo.
to give 0.35 g (57%) of compound 11a as pink prisms, mp 240–242 °C (decomp.). 1H NMR (DMSO-d6) δ 3.66 (s, 3H), 6.79 (s, 2H), 7.51 (t, J = 7.8 Hz, 1H), 7.68 (t, J = 7.8 Hz, 1H), 8.16 (d, J = 8.7 Hz, 2H); 13C NMR (DMSO-d6) δ 33.8, 112.8, 119.7, 125.2, 129.1, 131.3, 145.2, 151.7, 156.1. Anal. Calcd for C9H9N7: C, 50.23; H, 4.21; N, 45.56. Found: C, 49.84; H, 4.13; N, 45.17.

3-(1H-Benzotriazol-1-yl)-1-acetyl-1H-1,2,4-triazole-5-amine (11b). Compound 1 (1.50 g, 5.7 mmol) and acetohydrazide (0.22 g, 3.0 mmol) were dissolved in dry benzene (40 mL) and heated under reflux for 48 h. After concentration of the reaction mixture, the crude residue was dissolved in CH2Cl2 and washed with 10% aqueous Na2CO3. The organic layer was dried (Na2SO4), filtered and evaporated to yield pure product 11b as white flakes 0.29 g (42%), mp 232–234°C (decomp.). 1H NMR (DMSO-d6) 2.49 (s, 3H), 7.61 (t, J = 7.8 Hz, 1H), 7.80 (t, J = 7.8 Hz, 1H), 8.26 (d, J = 8.2 Hz, 1H), 8.45 (d, J = 8.2 Hz, 1H), 8.81 (br, s, 1H), 9.96 (br, s, 1H); 13C NMR (DMSO-d6) 11.7, 115.8, 120.9, 126.9, 131.2, 131.6, 146.9, 151.1, 160.8, 166.1. Anal. Calcd for C10H9N7O: C, 49.38; H, 3.73; N, 40.31. Found: C, 49.67; H, 3.57; N, 40.54.

1-(4-Methoxyphenyl)-5-((4-methoxyphenyl)diazenyl)-3-(1H-benzotriazol-1-yl)-1,2,4-triazole (15a). Methoxyphenylhydrazine (4.2 mmol, 0.736 g) was added to a suspension of di(benzotriazolyl)methanimines (3.8 mmol, 1 g) in THF (35 mL). The mixture was allowed to react for 4 days. The precipitate formed was filtered off, washed with cold THF, ethyl ether and dried in vacuum to give 1-(4-methoxyphenyl)-5-((4-methoxyphenyl)diazenyl)-3-(1H-benzotriazol-1-yl)-1,2,4-triazole 15a as orange microcrystals in 86% yield, mp 234–235 °C; 1H NMR (CDCl3/TFA) δ 3.93 (s, 3H), 3.96 (s, 3H), 7.01 (d, J = 9.0 Hz, 2H), 7.13 (d, J = 8.9 Hz, 2H), 7.64 (t, J = 7.5 Hz, 1H), 7.76 – 7.81 (m, 3H), 7.92 (d, J = 9.0 Hz, 2H), 8.19 (d, J = 8.5 Hz, 1H), 8.42 (d, J = 8.5 Hz, 1H); 13C NMR (CDCl3/TFA) δ 55.8, 56.0, 112.6, 114.7, 115.2, 118.9, 126.0, 127.4, 127.5, 128.9, 130.9, 131.4, 143.4, 147.2, 153.4, 157.2, 160.5, 166.0. HRMS (FAB) Calcd for C22H18N8O2 (M+1): 427.1631. Found: 427.1605.

N'-Phenyl-1H-1,2,3-benzotriazole-1-carbohydrazonamide (12b). Imine 1 (1.5 g, 5.7 mmol) and phenylhydrazine (0.87 g, 5.7 mmol) were dissolved in dry THF (40 mL) and heated under reflux overnight. After concentration of the reaction mixture, the crude residue was dissolved in DCM and washed with 10% aqueous Na2CO3. The organic layer was dried (Na2SO4), filtered and evaporated to yield 1.22g (85%) of compound 12b as yellow solid; mp 133–135°C (decomp.). 1H NMR (DMSO-d6) δ 5.76 (s, 2H), 6.12 (s, 1H), 6.95 (t, J = 7.3 Hz, 1H), 7.11 (d, J = 7.9 Hz, 2H), 7.30–7.35 (m, 2H), 7.48 (t, J = 7.8 Hz, 1H), 7.63 (t, J = 7.8 Hz, 1H), 8.11 (d, J = 8.5 Hz, 1H), 8.51 (d, J = 8.2 Hz, 1H); 13C NMR (DMSO-d6) δ 112.2, 114.2, 114.7, 115.2, 118.9, 126.0, 127.4, 127.5, 128.9, 130.9, 131.4, 143.4, 147.2, 153.4, 157.2, 160.5, 166.0. Anal. Calcd for C13H12N6: C, 61.89; H, 4.79; N, 33.31. Found: C, 61.65; H, 4.67; N, 32.92.

Ethyl2-[(Z)-amino(1H-1,2,3-benzotriazol-1-yl)methylidene]-1-hydrazine-carboxylate (16k). Compound 1 (1.5 g, 5.7 mmol) and ethyl carbazate (0.59 g, 5.7 mmol) were dissolved in dry THF (50 mL) and heated under reflux for 6 h. After concentration of the reaction mixture, the crude residue was dissolved in DCM and washed with 10% aqueous Na2CO3. The organic layer was dried (Na2SO4), filtered and evaporated to yield 1.40g (99%) of compound 16k as a white solid; mp 163–164°C (decomp.). 1H NMR (DMSO-d6) δ 1.45 (t, J = 7.0 Hz, 3H), 4.35 (q, J = 7.0
Hz, 2H), 7.42 (s, 2H), 7.79 (t, J = 7.7 Hz, 1H), 7.88 (t, J = 7.7 Hz, 1H), 8.34 (d, J = 8.8 Hz, 1H), 8.62 (d, J = 8.2 Hz, 1H), 9.84 (br, s, 1H); $^{13}$C NMR (DMSO-$d_6$) δ 15.6, 61.3, 115.7, 120.3, 126.2, 130.0, 131.4, 142.1, 146.5, 154.9. Anal. Calcd for C$_{10}$H$_{12}$N$_6$O$_2$: C, 48.38; H, 4.87; N, 33.85. Found: C, 48.49; H, 4.84; N, 33.69.

**General procedure for the preparation of 1-aryl-5- (aryldiazenyl)-3-1H-benzotriazol-1-yl-1,2,4-triazoles 15b-d**

The appropriate arylhydrazine (3.8 mmol) was added to a suspension of compound 1 (3.8 mmol, 1 g) in THF (25 mL). The mixture was allowed to react until the disappearance of 1 (TLC control, about 18 h). Then, potassium tert-butoxide (0.43 g, 3.8 mmol) was added into the reaction mixture. After 18 h the solvent was evaporated and the residue was purified by column chromatography (CHCl$_3$ / ethyl ether : 4 / 1) to give compounds 15b-d.

**1-Phenyl-5-(phenyldiazenyl)-3-(1H-benzotriazol-1-yl)-1,2,4-1H-triazole (15b).** Orange microcrystals (82%), mp 218−219 °C; $^1$H NMR (CDCl$_3$) δ 7.48−7.70 (m, 8H), 7.92 (d, J = 8.2 Hz, 2H), 8.06 (d, J = 7.7 Hz, 2H), 8.19 (d, J = 8.4 Hz, 1H), 8.44 (d, J = 8.3 Hz, 1H); $^{13}$C NMR (CDCl$_3$) δ 112.9, 120.1, 124.4, 124.7, 125.1, 129.2, 129.3, 129.4, 131.5, 134.1, 136.4, 146.0, 152.8, 155.6, 157.3. Anal. Calcd for C$_{20}$H$_{14}$N$_8$: C, 65.56; H, 3.85; N, 30.58. Found: C, 65.63; H, 3.68; N, 30.82.

**1-(4-Methylphenyl)-5-((4-methylphenyl)diazenyl)-3-(1H-benzotriazol-1-yl)-1,2,4-1H-triazole (15c).** Orange microcrystals (84%), mp 222−224 °C; $^1$H NMR (CDCl$_3$) δ 2.47 (s, 3H), 2.49 (s, 3H), 7.35 (d, J = 8.3 Hz, 2H), 7.40 (d, J = 8.2 Hz, 2H), 7.49 (t, J = 7.5 Hz, 1H), 7.67 (t, J = 7.4 Hz, 1H), 7.79 (d, J = 8.4 Hz, 2H), 7.95 (d, J = 8.3 Hz, 2H), 8.17 (d, J = 8.3 Hz, 1H), 8.43 (d, J = 8.3 Hz, 1H); $^{13}$C NMR (CDCl$_3$) δ 21.2, 21.8, 113.0, 120.12, 124.5, 124.6, 124.7, 125.1, 129.2, 129.3, 129.4, 131.5, 134.1, 136.4, 146.0, 152.8, 155.6, 157.3. Anal. Calcd for C$_{22}$H$_{18}$N$_8$: C, 66.99; H, 4.60. Found: C, 66.95; H, 4.69.

**1-(4-Bromophenyl)-5-((4-bromophenyl)diazenyl)-3-(1H-benzotriazol-1-yl)-1,2,4-1H-triazole (15d).** Orange microcrystals (78%), mp 238−239 °C; $^1$H NMR (CDCl$_3$) δ 7.51 (t, J = 7.5 Hz, 1H), δ 7.66−7.83 (m, 7H), 7.92 (d, J = 8.6 Hz, 2H), 8.19 (d, J = 8.3 Hz, 1H), 8.41 (d, J = 8.3 Hz, 1H); $^{13}$C NMR (CDCl$_3$) δ 112.8, 120.3, 123.6, 125.3, 125.6, 126.1, 129.4, 129.6, 131.4, 132.5, 133.0, 135.3, 146.1, 151.5, 155.8, 157.2. Anal. Calcd for C$_{20}$H$_{12}$Br$_2$N$_8$: C, 45.83; H, 2.31; N, 21.38. Found: C, 45.95; H, 2.11; N, 21.16.

**General procedure for the preparation of 5-aryl-1,3,4-oxadiazol-5-amines 17a-j**

Di(benzotriazolyl)methanimine (1.00 g, 3.8 mmol) and the appropriate arylhydrazide (3.8 mmol) were dissolved in dry THF (40 mL) and heated under reflux for 3−6 h. The precipitate formed after cooling of the reaction mixture to rt was filtered off, washed with cold THF and recrystallized from EtOH or THF (compound 17j) to give the respective 5-aryl-1,3,4-oxadiazol-5-amine 17a-j. Data for compound 17a see.$^2$

**5-[4-(tert-Butyl)phenyl]-1,3,4-oxadiazol-2-ylamine (17b).** White needles (92%), mp 256−258 °C; $^1$H NMR (DMSO-$d_6$) δ 1.29 (s, 9H), 7.22 (s, 2H), 7.54 (d, J = 8.5 Hz, 2H), 7.72 (d, J = 8.4 Hz,
2H); $^{13}$C NMR (DMSO-$d_6$) δ 31.0, 34.8, 121.9, 125.1, 126.2, 153.3, 157.5, 163.9. Anal. Calcd for C$_{12}$H$_{15}$N$_3$O: C, 66.34; H, 6.96; N, 19.34. Found: C, 66.46; H, 7.36; N, 19.33.

5-(4-Aminophenyl)-1,3,4-oxadiazol-2-amine (17c). White prisms (82%), mp 254–255 °C (lit. 6 273–274 °C); $^1$H NMR (DMSO-$d_6$) δ 5.73 (s, 2H), 6.66 (d, $J = 8.5$ Hz, 2H), 7.01 (s, 2H), 7.48 (d, $J = 8.5$ Hz, 2H); $^{13}$C NMR (DMSO-$d_6$) δ 11.5, 113.8, 126.7, 151.1, 158.4, 163.0. Anal. Calcd for C$_8$H$_8$N$_4$O: C, 54.54; H, 4.58; N, 31.80. Found: C, 54.36; H, 4.40; N, 31.67.

5-(2-Aminophenyl)-1,3,4-oxadiazol-2-amine (17d). White microcrystals (92%), mp 184–186 °C; $^1$H NMR (DMSO-$d_6$) δ 6.58 (s, 2H), 6.64 (t, $J = 7.5$ Hz, 1H), 6.85 (d, $J = 8.2$ Hz, 1H), 7.17 (t, $J = 7.3$ Hz, 1H), 7.22 (s, 2H), 7.45 (d, $J = 8.0$ Hz, 1H); $^{13}$C NMR (DMSO-$d_6$) δ 105.5, 115.5, 115.6, 126.2, 130.9, 146.8, 158.1, 162.5. Anal. Calcd for C$_8$H$_8$N$_4$O: C, 54.54; H, 4.58; N, 31.80. Found: C, 54.88; H, 4.61; N, 31.78.

4-(5-Amino-1,3,4-oxadiazol-2-yl)phenol (17e). White needles (93%), mp 276–278 °C (lit. 7 274–276 °C); $^1$H NMR (DMSO-$d_6$) δ 6.90 (d, $J = 8.5$ Hz, 2H), 7.11 (s, 2H), 7.63 (d, $J = 8.5$ Hz, 2H); $^{13}$C NMR (DMSO-$d_6$) δ 116.3, 116.9, 127.8, 158.5, 160.3, 164.2. Anal. Calcd for C$_8$H$_7$N$_3$O$_2$: C, 54.24; H, 3.98; N, 23.72. Found: C, 53.96; H, 3.84; N, 23.56.

5-(4-Nitrophenyl)-1,3,4-oxadiazol-2-amine (17f). Yellow needles (97%), mp 255–257 °C (lit. 8 270 °C); $^1$H NMR (DMSO-$d_6$) δ 7.57 (s, 2H), 8.03 (d, $J = 8.8$ Hz, 2H), 8.37 (d, $J = 8.8$ Hz, 2H); $^{13}$C NMR (DMSO-$d_6$) δ 124.8, 126.1, 130.0, 148.1, 156.2, 164.8. Anal. Calcd for C$_8$H$_6$N$_4$O$_3$: C, 46.61; H, 2.93; N, 27.18. Found: C, 46.52; H, 2.63; N, 27.00.

5-(3-Nitrophenyl)-1,3,4-oxadiazol-2-amine (17g). Yellow needles (96%), mp 251–253 °C (lit. 8 262 °C); $^1$H NMR (DMSO-$d_6$) δ 7.47 (s, 2H), 7.83 (t, $J = 7.9$ Hz, 1H), 8.20 (d, $J = 7.1$ Hz, 1H), 8.33 (d, $J = 7.8$ Hz, 1H), 8.46 (s, 1H); $^{13}$C NMR (DMSO-$d_6$) δ 119.5, 124.8, 125.9, 131.1, 131.3, 148.4, 155.9, 164.5. Anal. Calcd for C$_8$H$_6$N$_4$O$_3$: C, 46.61; H, 2.93; N, 27.18. Found: C, 46.51; H, 2.83; N, 27.00.

5-(4-Chlorophenyl)-1,3,4-oxadiazol-2-amine (17h). White microcrystals (96%), mp 231–233 °C (lit. 8 274 °C); $^1$H NMR (DMSO-$d_6$) δ 7.36 (s, 2H), 7.61 (d, $J = 8.5$ Hz, 2H), 7.81 (d, $J = 8.5$ Hz, 2H); $^{13}$C NMR (DMSO-$d_6$) δ 123.4, 126.9, 129.5, 135.0, 156.7, 164.2. Anal. Calcd for C$_8$H$_6$ClN$_3$O: C, 49.12; H, 3.09; N, 21.48. Found: C, 49.16; H, 2.83; N, 21.47.

5-(2-Chlorophenyl)-1,3,4-oxadiazol-2-amine (17i). Yellow needles (95%), mp 164–166 °C (lit. 9 166 °C); $^1$H NMR (DMSO-$d_6$) δ 7.34 (s, 2H), 7.47–7.56 (m, 2H), 7.63 (d, $J = 7.7$ Hz, 1H), 7.81 (d, $J = 7.0$ Hz, 1H); $^{13}$C NMR (DMSO-$d_6$) δ 123.6, 127.8, 130.4, 131.08, 131.11, 132.0, 155.4, 164.3. Anal. Calcd for C$_8$H$_6$ClN$_3$O: C, 49.12; H, 3.09; N, 21.48. Found: C, 48.87; H, 2.73; N, 21.24.

5-(4-Pyridinyl)-1,3,4-oxadiazol-2-amine (17j). White needles (97%), mp 232–234 °C (THF) (lit. 10 262 °C); $^1$H NMR (DMSO-$d_6$) δ 7.57 (s, 2H), 7.72 (d, $J = 4.7$ Hz, 2H), 8.74 (d, $J = 4.7$ Hz, 2H); $^{13}$C NMR (DMSO-$d_6$) δ 119.6, 132.0, 151.6, 156.6, 165.4. Anal. Calcd for C$_7$H$_6$N$_4$O: C, 51.85; H, 3.73; N, 34.55. Found: C, 51.51; H, 3.49; N, 34.40.
X-ray crystallography
Data were collected with a Siemens SMART CCD area detector, using graphite monochromatized MoKα radiation (\(\lambda = 0.71073\) Å). The structures were solved by direct methods using SHELXS\(^{15}\) and refined on F\(^2\), using all data, by full-matrix least-squares procedures using SHELXL.\(^{16}\) Hydrogen atoms were included in calculated positions, with isotropic displacement parameters 1.2 times the isotropic equivalent of their carrier atoms.

**Crystal data for 15b.** \(\text{C}_{20}\text{H}_{14}\text{N}_{8}\), MW 366.39, monoclinic, \(P2_1/n\), \(a = 12.686(3)\) Å, \(b = 8.366(2)\) Å, \(c = 17.310(5)\) Å, \(\beta = 108.152(3)\) °, \(V = 1745.8(8)\) Å\(^3\), \(Z = 4\), \(T = -105\) °C, \(F(000) = 760\), \(\mu (\text{MoK}\alpha) = 0.091\) mm\(^{-1}\), \(D_{\text{calc}} = 1.394\) g.cm\(^{-3}\), \(\theta_{\text{max}} 53^\circ\) (CCD area detector, 98% completeness), \(wR(F^2) = 0.0922\) (all 3537 data), \(R = 0.0346\) (3031 data with \(I > 2\sigma(I)\).

**Crystal data for 17a.** \(\text{C}_8\text{H}_7\text{N}_3\text{O}\), MW 161.17, monoclinic, \(P2_1/n\), \(a = 11.290(6)\) Å, \(b = 5.983(3)\) Å, \(c = 11.654(6)\) Å, \(\beta = 98.892(7)\) °, \(V = 777.6(7)\) Å\(^3\), \(Z = 4\), \(T = -100\) °C, \(F(000) = 336\), \(\mu (\text{MoK}\alpha) = 0.097\) mm\(^{-1}\), \(D_{\text{calc}} = 1.377\) g.cm\(^{-3}\), \(\theta_{\text{max}} 53^\circ\) (CCD area detector, 97% completeness), \(wR(F^2) = 0.1320\) (all 1563 data), \(R = 0.0461\) (1270 data with \(I > 2\sigma(I)\).

**References**