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Copper-Catalyzed C–N Coupling Reactions of Nitrogen-Rich Compounds – Reaction of Iodofurazans with *s*-Tetrazinylamines

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Access to unsymmetrical secondary dihetarylamines through the $Cu(OAc)_2$/2-acetylcyclohexanone catalyzed cross-coupling of *s*-tetrazinylamines with iodofurazans has been developed. The reaction displays good functional group tolerance, involving nitro, azido, and azo groups, which are critical for the construction of energetic materials. Both 3,6-disubstituted and annelated *s*-tetrazines react readily with iodofurazans to furnish the desired products.

Introduction

During the past few years significant advances have been made in the development of energetic, nitrogen-rich heterocycles.[1] As potential candidates for the replacement of common explosives, such as trinitrotoluene (TNT), 1,3,5-trinitro-1,3,5-triazinane (RDX), and 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX), nitrogen-rich compounds form a unique class of energetic materials whose energy is derived, to a large degree, from their very high heats of formation. Azoles (pyrazoles,[2] triazoles,[1c,3] tetrazoles,[1c,4] furazans[5]) and azines (triazines[6] and tetrazines[7]) containing nitro, azo, azoxy, and/or azide substituents are traditional sources of energetic materials. These energetic compounds are attractive because of their higher heats of formation, density, thermal stability, and oxygen balance, but they are also more environmentally acceptable, as a higher percentage of their explosion or burning products is nitrogen gas.

Considerable attention in recent years has been directed toward the synthesis of energetic heterocyclic compounds incorporating two nitrogen-rich rings bonded by an NH bridge. Recently, a few energetic 1,2,4,5-tetrazine compounds, which contain NH-tetrazole[7,8] and NH-furazan[9] moieties as key structural components, were reported (Figure 1). The NH bridge provides increasing solid density by enabling better crystal packing through intra- and intermolecular hydrogen bonding, conferring stability and insensitivity to destructive stimuli.

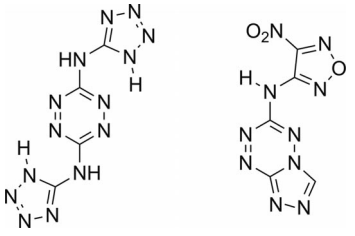

Figure 1. Energetic secondary *s*-tetrazinylamine derivatives.

Given the importance of such scaffolds, we were intrigued by the prospect of an alternative route to their synthesis. Currently, Het-NH-Het bridges are installed through nucleophilic substitution once the heteroaromatic system is already in place. Halogen or 3,5-dimethylpyrazolyl leaving groups at the 3- and/or 6-position(s) of the 1,2,4,5-tetrazine (*s*-tetrazine) ring are displaced by weak nucleophiles such as 5-aminotetrazol[7,8] and 3,4-diaminofurazan.[10] This process requires the employment of strong reagents such as NaH, and these reactions suffer from high reaction temperatures, lengthy reaction times, the formation of byproducts, difficulties in product separation, and the use of strictly anhydrous conditions. The functional group tolerance of these conditions is low, which has led to efforts to identify milder conditions for the construction of the NH bridge.

Furazans (1,2,5-oxadiazoles) are not only "privileged" scaffolds of interest for the preparation of high-energy materials,[5] but they are also widely used in drug-discovery programs.[5e,11] In our continuing investigations of polyfunctionalized aminofurazans,[5a–5d,12] we turned our attention to the investigation of transition-metal-catalyzed C–N couplings for construction of a hybrid with furazan and *s*-tetrazine rings bridged through the NH spacer. Up to now,

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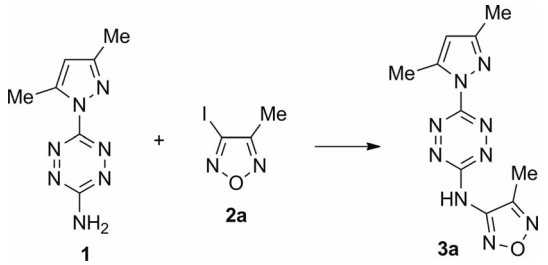
the application of cross-coupling reactions to the synthesis of secondary aminofurazans and aminotetrazines has remained unexplored.

In recent years there have been significant improvements in the utility of C–N bond-forming reactions. Several published reviews detail the recent progress of Pd[13] and Cu[14] mediated C–N coupling reactions. Typically, the technique is oriented to the synthesis of biologically active pharmaceuticals, natural products, and materials. As a result, these metal-catalyzed cross-coupling reactions usually utilize reactants such as anilines with aryl halides bearing electron-donating groups. Progress has been made in the *N*-arylation of amino heterocycles and in the amination of heterocyclic halides;[15] however, the scope has been quite limited. Reports on similar C–N coupling reactions with the use of electron-poor nitrogen heterocycles or with substrates containing strongly electron-withdrawing substituents on both coupling partners are rare. We were surprised to find that there are few reports on the coupling of hetarylamines and heterocyclic halides when both heterocycles involved contain more than two heteroatoms in the rings. Indeed, perhaps the most notable example is that reported by Guillaumet and co-workers in 2004, where 3-amino-1,2,4-triazine was found to react with chloropyrazine, 2-chloropyrimidine, or 3-bromo-5-nitro-1,2,4-triazole under Pd-catalyzed conditions [10 mol-% $Pd(OAc)_2$ or 4 mol-% $Pd_2(dba)_3$, xantphos as the ligand, K_2CO_3 as the base, and dioxane as the solvent, refluxing under N_2] to furnish the desired secondary amines in good yields.[16] Although the metal-catalyzed formation of C–N bonds is a rapidly expanding area of research, no examples involving the utilization of this methodology for the construction of high-energy compounds are known.

Results and Discussion

As in the case of other metal-catalyzed cross-coupling reactions, the Pd-catalyzed amination protocol has successfully been applied utilizing iodo(het)arenes as excellent substrates. We tested the conditions from Guillaumet and co-workers[16] for the Pd-catalyzed coupling of *s*-tetrazinylamine (**1**)[17] with furazanyl iodide (**2a**).[18] However, these electron-deficient compounds proved to be uniquely challenging coupling partners. Only a trace amount of desired product **3a** was detected after an extended reaction time. A brief survey of other reaction conditions showed that $Pd(OAc)_2$ and $Pd_2(dba)_3$ were ineffective in combination with several different bases (KOH, K_2CO_3, KOAc, K_3PO_4, KO*t*Bu, NaO*t*Bu, and Cs_2CO_3) and solvents (DMF, acetonitrile, DME, toluene, EtOH/toluene; data not shown).

Derivatives of furazan[19] and *s*-tetrazine[20] are known to form coordination compounds with various metal ions. We hypothesized that binding of these heterocycles to the metal center can prevent the catalytic effect of the Pd source.[21] So, to circumvent the problems associated with the formation of this complex, addition of inexpensive copper salts (capable of competitive coordination) could be helpful. Thus, two equivalents of $Cu(OAc)_2$ were added to a mixture of amine **1** and iodide **2a** with $Pd(OAc)_2$ (10 mol-%), xantphos, and Cs_2CO_3 in dimethoxyethane (DME). Fortunately, at 80 °C, coupling did occur (Scheme 1). Secondary amine **3a** was obtained within 12 h, albeit in low yield (11%). Much to our surprise, the same reaction gave a slightly higher yield (19%) when it was done in the absence of $Pd(OAc)_2$.



Scheme 1. Synthesis of *N*-[6-(3,5-dimethyl-1*H*-pyrazol-1-yl)-*s*-tetrazin-3-yl]-4-methylfurazanamine (**3a**).

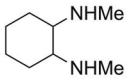
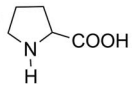
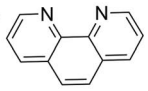
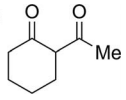
Despite this progress, the low yield and long reaction times are limitations of the method. Recently it has been shown that copper used in C–N bond-formation reactions (Ullmann-type coupling) could be employed with the aid of various ligands, solvents, and additives for the development of catalytic processes.[14] After a screen of copper catalysts, ligands, bases, solvents, reaction temperature, and time, we found that typical nitrogen ligands for copper (Table 1, Entries 1–5) for the arylation of amines or amides did not provide a higher yield or an increase in the rate of coupling amine **1** and iodide **2a**. We also tested other copper salts (Table 1, Entries 6–9). However, only triflate provided slightly better results (Table 1, Entry 9).

In 2006, Shafir and Buchwald introduced cyclic β-diketone as a supporting ligand, making it possible to carry out highly selective room-temperature, CuI-catalyzed couplings of aryl iodides with aliphatic amines.[22] We tested commercially available 2-acetylcyclohexanone as a ligand for the Cu-catalyzed C–N bond formation in the reaction between **2a** and **1**. Although no coupling occurred at 20 °C under Buchwald's conditions (Table 1, Entry 10), in the presence of K_2CO_3 in DME, desired product **3a** was obtained in 12% yield (Table 1, Entry 11), and at 50 °C in DME the formation of product **3a** was observed in 35% yield (Table 1, Entry 12). A combination of $Cu(OAc)_2$ with potassium carbonate in a mixture of toluene and DME (5:1) provided the best results (Table 1, Entry 17). The product was isolated in 47% yield.

Under the optimized conditions, we explored the substrate scope of this reaction (Table 2). A set of iodofurazans[18] was synthesized and examined. Excellent functional group tolerance was observed. As shown in Table 2, a variety of substituents at the furazan ring allowed formation of the coupling products in moderate yields, irrespective of the sterics and electronics. Gratifyingly, even nitro and azido substituents are compatible with our coupling conditions (Table 2, Entries 5 and 6). Although bis(4-iodoazofurazan-3-yl)diazene (**2h**) coupled with two molecules **1** in 46%

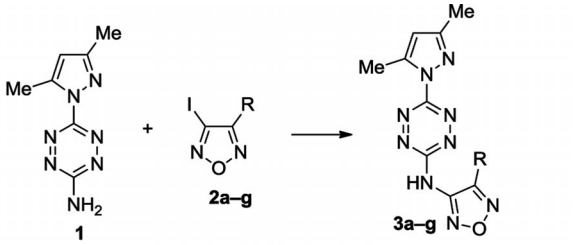
Table 1. Initial optimization coupling reaction compound **1** with **2a**.[a]

Entry	Cu source	Ligand	Solvent	Base	*T* [°C][b]	Time [h][c]	Yield of **3a** [%][d]
1	$Cu(OAc)_2$	L1	toluene	K_2CO_3	60	13	10
2	$Cu(OAc)_2$	L2	toluene	K_2CO_3	60	11	17
3	$Cu(OAc)_2$	L3	toluene	K_2CO_3	60	11	14
4	$Cu(OAc)_2$	L4	toluene	K_2CO_3	60	18	10
5	$Cu(OAc)_2$	L5	toluene	K_2CO_3	60	9	16
6	CuCl	L3	toluene	K_2CO_3	60	15	8
7	CuBr	L3	toluene	K_2CO_3	60	11	13
8	CuI	L3	toluene	K_2CO_3	60	9	18
9	$Cu(OTf)_2$	L3	toluene	K_2CO_3	60	8	23
10[e]	CuI	L6	DMF	Cs_2CO_3	20	24	0[f]
11	CuI	L6	DME	K_2CO_3	20	18	12
12	CuI	L6	DME	K_2CO_3	50	5	35
13	$Cu(OAc)_2$	L6	toluene	K_2CO_3	50	9	27
14	$Cu(OAc)_2$	L6	DME	K_2CO_3	50	4	31
15	$Cu(OTf)_2$	L6	DME	K_2CO_3	50	3.5	26
16	$Cu(OAc)_2$	L6	toluene/DME (4:1)	K_2CO_3	50	4	42
17	$Cu(OAc)_2$	L6	toluene/DME (5:1)	K_2CO_3	50	4	47
18	$Cu(OAc)_2$	L6	toluene/DME (6:1)	K_2CO_3	50	5	38

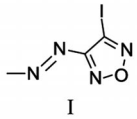
L1 = $(CH_2NHMe)_2$ L2 = $(CH_2NMe_2)_2$ L3 =  L4 =  L5 =  L6 = 

[a] Reaction conditions: Iodofurazan (**2a**, 1.1 mmol), aminotetrazine **1** (1 mmol), Cu source (2.1 mmol), ligand (2 mmol), base (2 mmol), solvent (50–65 mL). [b] At temperature >60 °C, destruction of compound **2a** was observed. [c] Time at which TLC ($CHCl_3$/MeCN, 3:1) indicated complete disappearance of starting iodide **2a**; amine **1** (10 to 25%) can be recovered from the reaction mixture. [d] Yield of isolated product **3a**. [e] Buchwald's conditions.[22] [f] Full destruction of compound **2a** was observed; TLC indicated the presence of starting amine **1** in the reaction mixture.

Table 2. Synthesis of *N*-[6-(3,5-dimethyl-1*H*-pyrazol-1-yl)-*s*-tetrazin-3-yl]-4-*R*-furazanamines **3a**–**g**.[a]



1 **2a–g** **3a–g**

Entry	Furazan	R	Product	Yield [%]
1	**2a**	Me	**3a**	47
2	**2b**	OMe	**3b**	54
3	**2c**	NH_2	**3c**	12[b]
4	**2d**	Ph	**3d**	61
5	**2e**	N_3	**3e**	58
6	**2f**	NO_2	**3f**	48
7[c]	**2g**		**3g**	46
8	**2h**	I	**3h**	0
9	**2i**	NHAc	**3i**	0

[a] Reaction conditions: Iodofurazan **2a**–**i** (1.1 mmol), aminotetrazine **1** (1 mmol), $Cu(OAc)_2$ (2.1 mmol), 2-acetylcyclohexanone (2 mmol), K_2CO_3 (2 mmol), toluene/DME (5:1, 50 mL), 50 °C, 4 h. [b] Complicated reaction mixture was formed; silica gel chromatography gave secondary amine **3c** as the sole isolable product. [c] Two equivalents of aminotetrazine **1** and 80 mL of the solvent were used; both iodine atoms in compound **2g** were displaced by aminotetrazine moieties.

yield, all efforts to couple 3,4-diiodofurazan **2h** (R = I) failed (Table 2, Entry 8). Attempts to couple Ac protected amine **2i** were disappointing (Table 2, Entry 9); an intractable mixture of products was obtained, and isolation of desired product **3i** was unsuccessful.

The structures of secondary amines **3a**–**f** and **3g** are supported by IR, ^1H NMR, and ^{13}C NMR spectroscopy, and, where possible, ^{14}N and ^{15}N NMR spectroscopy and elemental analysis. Single crystals of solvated compound **3e** suitable for X-ray crystal structure determination were obtained from a DMSO solution. X-ray crystal structures of the solvate are shown in Figure 2.[23] Structural details are given in the Supporting Information. Compounds **3a**–**h** are red or brown crystals that are stable at room temperature and are not hygroscopic.

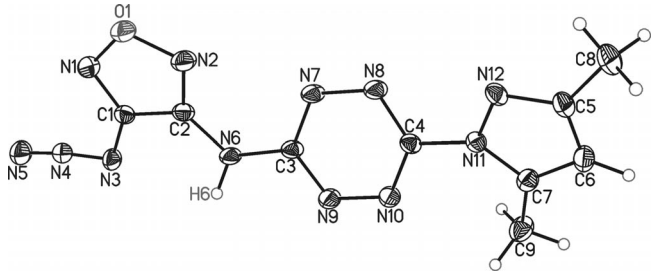
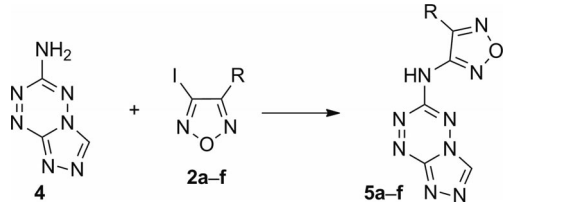


Figure 2. ORTEP view (thermal displacement ellipsoids drawn at 50% probability) of compound **3e**.

The method can be extended to the similar functionalization of [1,2,4]triazolo[4,3-*b*][1,2,4,5]tetrazin-3-amine **4**[24]

(Table 3). A variety of substituted iodofurazans **2a**–**f** undergo coupling with compound **4** to provide products **5a**–**f** in good yields.

Table 3. Synthesis of secondary amines **5a**–**f** from compound **4**.[a]



Entry	Furazan	R	Product	Yield [%]
1	**2a**	Me	**5a**	52
2	**2b**	OMe	**5b**	55
3	**2c**	NH_2	**5c**	18[b]
4	**2d**	Ph	**5d**	57
5	**2e**	N_3	**5e**	54
6	**2f**	NO_2	**5f**	43

[a] Reaction conditions: Iodofurazan **2a**–**f** (1.1 mmol), aminotetrazine **4** (1 mmol), $Cu(OAc)_2$ (2.1 mmol), 2-acetylcyclohexanone (2 mmol), K_2CO_3 (2 mmol), toluene/DME (5:1, 50 mL), 50 °C, 4 h. [b] Complicated reaction mixture was formed; silica gel chromatography gave secondary amine **5c** as the sole isolable product.

All secondary amines **5a**–**f** were isolated and fully characterized by elemental analysis and IR, ^{1}H NMR, ^{13}C NMR, and ^{15}N NMR spectroscopy. The crystal of azide **5e** was grown through the slow cooling of a solution in *i*PrOH/H_2O and characterized by X-ray crystallography.[25] General view of compound **5e** is depicted in Figure 3, whereas the structural details are given in the Supporting Information.

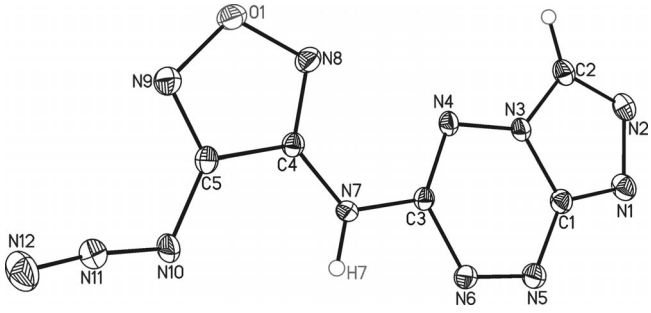


Figure 3. ORTEP view (thermal displacement ellipsoids drawn at 50% probability) of compound **5e**.

Conclusions

In conclusion, a robust method for the Cu-catalyzed coupling of a variety of furazanyl iodides with *s*-tetrazinylamines has been reported. This protocol represents the only current method by which electron-deficient nitrogen-rich heterocyclic iodides can be coupled to electron-deficient nitrogen-rich heterocyclic amines. This C–N bond-forming reaction made use of catalytic $Cu(OAc)_2$ and the ligand 2-acetylcyclohexanone. These conditions tolerated a wide degree of functionality including nitro, azido, and azo groups. This new methodology should find wide applications in many areas associated not only with energetic compounds, but with drug discovery and materials chemistry as well. We are currently working to expand the scope of this methodology and to apply it to the construction of nitrogen-rich frameworks containing others nitrogen heterocyclic building blocks.

Experimental Section

General. Infrared spectra were determined in KBr pellets with a Perkin–Elmer Model 577 spectrometer. Mass spectra were recorded with a Varian MAT-311A instrument. ^{1}H NMR, ^{13}C NMR, ^{15}N NMR, and ^{14}N NMR (external standard: CH_3NO_2) spectra were recorded at 300.13, 75.47, 50.7, and 21.68 MHz, respectively. The chemical shift values (δ) are expressed relative to the chemical shift of the solvent or to an external standard without correction nitromethane (^{14}N and ^{15}N). Analytical TLC was performed by using commercially precoated silica gel plates (Silufol UV_{254}), and visualization was effected with short-wavelength UV light. Melting points were determined with Gallenkamp melting point apparatus.

Typical Experimental Procedure: To a solution of 2-acetylcyclohexanone (0.28 g, 2.0 mmol) and copper acetate (0.36 g, 2.1 mmol) in anhydrous toluene/DME (5:1, 25 mL) was added a solution of 3-iodo-4-*R*-furazan **2a**–**h** (1.1 mmol) and *s*-tetrazin-3-amine **1** or **4** (1.0 mmol) in the same solvent (25 mL). Then, potassium carbonate (0.27 g, 2.0 mmol) was added to the reaction mixture, which was stirred at 50 °C for 4 h. The dark brown solution was evaporated in vacuo to leave a solid. This residue was suspended in H_2O (30 mL), and the pH of the solution was adjusted to ca. 3 by the dropwise addition of 0.1 N HCl. A red or yellow solid separated from the solution. The crude product was purified by crystallization from *i*PrOH/H_2O to give **3** or **5**.

***N*-[6-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-1,2,4,5-tetrazin-3-yl]-4-methylfurazan-3-amine (3a):** Red solid, m.p. 165–167 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 2.24 (s, 3 H), 2.41 (s, 3 H), 2.50 (s, 3 H), 6.25 (s, 1 H), 11.77 (br. s, 1 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 8.3, 12.9, 13.3, 109.8, 142.2, 148.0, 150.5, 151.3, 157.9, 160.0 ppm. IR (KBr): $\tilde{\nu}$ = 3592, 3240, 3048, 1616, 1600, 1576, 1484, 1424, 1272, 1224, 1080, 1040, 980, 944, 880, 812 cm^{-1}. MS: *m*/*z* = 273 [M]$^+$, 243, 121, 96. $C_{10}H_{11}N_9O{\cdot}H_2O$ (291.27): calcd. C41. 24, H 4.50, N 43.28; found C 41.33, H 4.54, N 43.23.

***N*-[6-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-1,2,4,5-tetrazin-3-yl]-4-methoxyfurazan-3-amine (3b):** Orange solid, m.p. 200–202 °C (dec.). ^{1}H NMR ([D$_6$]DMSO): δ = 2.24 (s, 3 H), 2.51 (s, 3 H), 4.12 (s, 3 H), 6.24 (s, 1 H), 11.88 (br. s, 1 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 12.9, 13.3, 59.7, 109.8, 142.2, 142.8, 151.3, 158.0, 159.8, 160.5 ppm. ^{15}N NMR ([D$_6$]DMSO): δ = 12.19, –9.09, –14.54, –25.97, –78.02, –173.93, –298.27 ppm. IR (KBr): $\tilde{\nu}$ = 2944, 1617, 1573, 1491, 1434, 1302, 1085, 995, 959, 857, 813, 557 cm^{-1}. $C_{10}H_{11}N_9O_2$ (289.25): calcd. C 41.52, H 3.83, N 43.58; found C 41.57, H 3.89, N 43.50.

***N*-[6-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-1,2,4,5-tetrazin-3-yl]-4-aminofurazan-3-amine (3c):** Red solid, m.p. 214–217 °C (mp 87–89 °C[10]). ^{1}H NMR ([D$_6$]DMSO): δ = 2.44 (s, 3 H); 2.49 (s, 3 H), 3.47 (s, 2 H), 6.24 (s, 1 H), 11.43 (br. s, 1 H) ppm. ^{13}C NMR ([D$_6$]-DMSO): δ = 13.0, 13.5, 109.8, 142.2, 143.5, 151.4, 152.5, 158.0, 160.1 ppm. ^{15}N NMR ([D$_6$]DMSO): δ = 7.17, –9.44, –18.34, –29.36, –78.63, –174.30, –299.57 ppm. IR (KBr): $\tilde{\nu}$ = 3476, 3330, 3224, 2992, 2936, 2848, 1648, 1604, 1560, 1492, 1452, 1436, 1320, 1260, 1080, 1048, 1024, 948, 832, 804 cm^{-1}. MS: *m*/*z* = 274 [M]$^+$,

241, 121, 96. $C_9H_{10}N_{10}O{\cdot}H_2O$ (292.26): calcd. C 36.99, H 4.14, N 47.93; found C 37.07, H 4.19, N 47.85.

***N*-[6-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-1,2,4,5-tetrazin-3-yl]-4-phenylfurazan-3-amine (3d):** Red solid, m.p. 197–198 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 2.22 (s, 3 H), 2.41 (s, 3 H), 6.19 (s, 1 H), 7.50 (br. s, 3 H), 7.80 (br. s, 2 H), 11.74 (br. s, 1 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 12.8, 13.2, 109.7, 124.7, 127.6, 129.1, 130.8, 142.1, 149.5, 150.7, 151.3, 157.9, 160.5 ppm. IR (KBr): $\tilde{\nu}$ = 2928, 1582, 1483, 1449, 1420, 1262, 1083, 1063, 1047, 1027, 976, 878, 810, 770, 727, 701 cm^{-1}. MS: *m*/*z* = 335 [M]$^+$, 305, 121, 96. $C_{15}H_{13}N_9O$ (335.32): calcd. C 53.73, H 3.91, N 37.59; found C 53.81, H 3.95, N 37.49.

***N*-[6-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-1,2,4,5-tetrazin-3-yl]-4-azidofurazan-3-amine (3e):** Red solid, m.p. 150–156 °C (dec.). ^{1}H NMR ([D$_6$]DMSO): δ = 2.25 (s, 3 H), 2.50 (s, 3 H), 6.27 (s, 1 H), 12.00 (br. s, 1 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 13.5, 13.8, 110.4, 142.8, 145.5, 149.8, 152.0, 158.6, 160.3 ppm. ^{14}N NMR ([D$_6$]-DMSO): δ = –142.7 ppm. IR (KBr): $\tilde{\nu}$ = 3516, 3398, 2144, 1600, 1484, 1424, 1288, 1260, 1076, 1024, 988, 972, 952, 832, 812, 760 cm^{-1}. MS: *m*/*z* = 300 [M]$^+$, 276, 216, 122, 106, 101, 97, 95. $C_9H_8N_{12}O{\cdot}H_2O$ (318.25): calcd. C 33.97, H 3.17, N 52.81; found C 34.07, H 3.21, N 52.78.

***N*-[6-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-1,2,4,5-tetrazin-3-yl]-4-nitrofurazan-3-amine (3f):** Pink solid, m.p. 188–190 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 2.25 (s, 3 H), 2.52 (s, 3 H), 6.28 (s, 1 H), 12.42 (br. s, 1 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 13.2, 13.5, 110.3, 142.6, 145.5, 151.9, 155.7, 158.4, 159.2 ppm. ^{14}N NMR ([D$_6$]DMSO): δ = –33.4 ($\Delta\nu$1/2 = 191 Hz, NO_2) ppm. IR (KBr): $\tilde{\nu}$ = 3400–3300, 2928, 1604, 1576, 1540, 1480, 1424, 1372, 1348, 1076, 1052, 1028, 976 cm^{-1}. MS: *m*/*z* = 304 [M]$^+$, 257, 241, 163, 121, 106, 95. $C_9H_8N_{10}O_3$ (304.23): calcd. C 35.53, H 2.65, N 46.04; found C 35.59, H 2.68, N 45.95.

4,4′-Azobis{3-[6-(3,5-dimethyl-1*H*-pyrazol-1-yl)[1,2,4,5]tetrazin-3-yl]-furazan-3-amine} 3g: Orange solid, m.p. 260–261 °C (m.p. 260–261 °C[9]).

***N*-([1,2,4]Triazolo[4,3-*b*][1,2,4,5]tetrazin-3-yl)-4-methylfurazan-3-amine (5a):** Yellow solid, m.p. 237–238 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 2.46 (s, 3 H), 9.69 (s, 1 H), 12.07 (br. s, 1 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 8.2, 137.1, 147.5, 149.9, 150.1, 152.8 ppm. IR (KBr): $\tilde{\nu}$ = 3504, 3384, 3120, 2800, 1616, 1596, 1560, 1500, 1472, 1440, 1388, 1272, 1240, 1156, 1048, 1008, 968, 884, 816, 744, 660 cm^{-1}. MS: *m*/*z* = 219 [M]$^+$, 189, 163, 137, 124. $C_6H_5N_9O$ (219.16): calcd. C 32.88, H 2.30, N 57.52; found C 32.97, H 2.33, N 57.45.

***N*-([1,2,4]Triazolo[4,3-*b*][1,2,4,5]tetrazin-3-yl)-4-methoxyfurazan-3-amine (5b):** Yellow solid, m.p. 231 °C (dec.). ^{1}H NMR ([D$_6$]DMSO): δ = 4.14 (s, 3 H), 9.71 (s, 1 H), 12.20 (br. s, 1 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 159.9, 152.3, 149.9, 142.4, 137.2, 59.9 ppm. ^{15}N NMR ([D$_6$]DMSO): δ = 57.34, 31.62, 10.38, –16.11, –38.08, –57.87, –154.75, –176.84, –295.57 ppm. IR (KBr): $\tilde{\nu}$ = 3156, 2790, 1610, 1550, 1460, 1405, 1376, 1260, 1212, 1150, 1027, 966, 831, 747, 657 cm^{-1}. $C_6H_5N_9O_2$ (235.16): calcd. C 30.64, H 2.14, N 53.61; found C 30.70, H 2.16, N 53.54.

***N*-([1,2,4]Triazolo[4,3-*b*][1,2,4,5]tetrazin-3-yl)-4-aminofurazan-3-amine (5c):** Yellow solid, m.p. 275–278 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 6.30 (s, 2 H), 9.66 (s, 2 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 137.1, 142.8, 149.9, 151.5, 152.6 ppm. IR (KBr): $\tilde{\nu}$ = 3344, 3220, 3124, 2816, 1636, 1608, 1560, 1472, 1440, 1408, 1388, 1344, 1292, 1264, 1232, 1160, 1048, 1020, 968, 836, 744, 660 cm^{-1}. MS: *m*/*z* = 220 [M]$^+$, 190, 163, 137, 124. $C_5H_4N_{10}O$ (220.15): calcd. C 27.28, H 1.83, N 63.62; found C 27.35, H 1.90, N 63.58.

***N*-([1,2,4]Triazolo[4,3-*b*][1,2,4,5]tetrazin-3-yl)-4-phenylfurazan-3-amine (5d):** Yellow solid, m.p. 240–242 °C. ^{1}H NMR ([D$_6$]DMSO): δ = 7.54 (br. s, 3 H), 7.84 (d, *J* = 7.7 Hz, 2 H), 9.60 (s, 1 H), 12.02 (br. s, 1 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 124.3, 128.1, 129.3, 131.0, 136.9, 149.1, 150.0, 150.6, 153.4 ppm. IR (KBr): $\tilde{\nu}$ = 3476, 3144, 1592, 1556, 1476, 1380, 1324, 1268, 1228, 1032, 980, 964, 876, 824, 772, 696, 656 cm^{-1}. MS: *m*/*z* = 281 [M]$^+$, 251, 136, 124. $C_{11}H_7N_9O$ (281.23): calcd. C 46.98, H 2.51, N 44.82; found C 47.05, H 2.54, N 44.77.

***N*-([1,2,4]Triazolo[4,3-*b*][1,2,4,5]tetrazin-3-yl)-4-azidofurazan-3-amine (5e):** Yellow solid, m.p. 194–195 °C (dec.). ^{1}H NMR ([D$_6$]-DMSO): δ = 9.71 (s, 1 H), 12.29 (br. s, 1 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 137.3, 144.6, 148.6, 150.0, 152.3 ppm. ^{14}N NMR ([D$_6$]DMSO): δ = –149.18 ppm. ^{15}N NMR ([D$_6$]DMSO): δ = 57.56, 30.48, 13.22, 5.84, –37.56, –57.49, –141.32, –142.69, –154.18, –176.93, –225.88, –300.53 ppm. IR (KBr): $\tilde{\nu}$ = 3412, 3216, 3168, 2152, 1604, 1560, 1512, 1416, 1400, 1264, 1232, 1144, 1028, 956, 840, 748, 676 cm^{-1}. MS: *m*/*z* = 246 [M]$^+$, 217, 204, 136, 124. $C_5H_2N_{12}O$ (246.15): calcd. C 24.40, H 0.82, N 68.28; found C 24.44, H 0.87, N 68.21.

***N*-([1,2,4]Triazolo[4,3-*b*][1,2,4,5]tetrazin-3-yl)-4-nitrofurazan-3-amine (5f):** Yellow solid, m.p. 235–236 °C (dec.). ^{1}H NMR ([D$_6$]-DMSO): δ = 9.81 (s, 1 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 137.3, 145.2, 149.9, 151.5, 154.9 ppm. ^{14}N NMR ([D$_6$]DMSO): δ = –33.26 ($\Delta\nu$1/2 = 183 Hz, NO_2) ppm. IR (KBr): $\tilde{\nu}$ = 3364, 3160, 3144, 1604, 1572, 1536, 1452, 1392, 1348, 1324, 1220, 1188, 1148, 1140, 1052, 1028, 988, 960 cm^{-1}. MS: *m*/*z* = 250 [M]$^+$, 219, 204, 187, 146, 101. $C_5H_2N_{10}O_3$ (250.14): calcd. C 24.01, H 0.81, N 56.00; found C 24.09, H 0.85, N 55.93.

Supporting Information (see footnote on the first page of this article): Description of crystal structure of compounds **3e** and **5e**.

Acknowledgments

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[23] Crystallographic data for compound **3e**: $C_9H_8N_{12}O\cdot 0.5(C_2H_6SO)$ at 100 K are orthorhombic, space group *Pbca*: a = 26.892(2) Å, b = 6.5401(4) Å, c = 16.3668(11) Å, V = 2878.6(3) Å^3, Z = 8, M = 339.34, $d_{calcd.}$ = 1.566 g cm^{-3}, μ = 0.187 mm^{-1}, $F(000)$= 1400, wR_2 = 0.1088, GOF = 1.012 for 4969 independent reflections (R_{int} = 0.0427) with $2\theta < 62°$, R_1 = 0.0395 for 3718 reflections with $I > 2\sigma(I)$. CCDC-832211 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[25] Crystallographic data for compound **5e**: $C_5H_2N_{12}O\cdot H_2O$ at 100 K are monoclinic, space group $P2_1/n$: a = 6.6755(8) Å, b = 15.310(2) Å, c = 10.2794(12) Å, β = 104.234(2)° V = 1018.3(2) Å^3, Z = 4, M = 264.20, $d_{calcd.}$ = 1.723 g cm^{-3}, μ = 0.141 mm^{-1}, $F(000)$= 536, wR_2 = 0.1160, GOF = 1.032 for 3517 independent reflections (R_{int} = 0.0550) with $2\theta < 62°$, R_1 = 0.0471 for 2428 reflections with $I > 2\sigma(I)$. CCDC-832212 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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