Note

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Metal-Free Cascade [4+1] Cyclization Access to 4-Aryl-*NH*-1,2,3-Triazoles from N-Tosylhydrazones and Sodium Azide

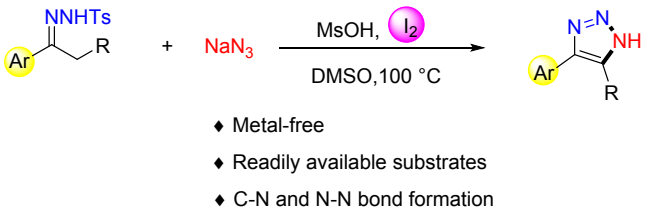
Wen-Ming Shu*,†, Xun-Fang Zhang,† Xiang-Xiang Zhang,† Min Li,† An-Jing Wang,† and An-Xin Wu*,‡

† College of Chemistry and Environmental Engineering, Yangtze University, Jingzhou 434023, P. R. China

‡ Key Laboratory of Pesticide & Chemical Biology, Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, P. R. China

†E-mail: shuwm@yangtzeu.edu.cn.

‡ E-mail: chwuax@mail.ccnu.edu.cn.



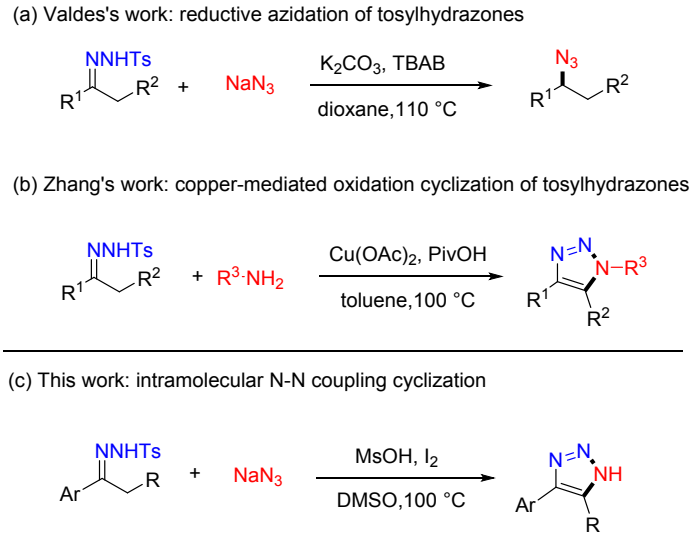
ABSTRACT: A molecular iodine mediated coupling cyclization reaction for the synthesis of 4-aryl-*NH*-1,2,3-triazoles has been developed from N-tosylhydrazones and sodium azide. This metal-free cascade [4+1] cyclization reaction could rapidly synthesize valuable compounds via a sequential C-N and N-N bond formation. Mechanistic studies demostrate that the nitrogen-atoms of the 1,2,3-triazoles are not entirely from sodium azide.

N-Tosylhydrazones are versatile reagents that have wide application in the formation of diverse compounds in organic chemistry.[1] They can facilitate a variety of

useful chemical transformations, including insertion,[2] olefination,[3] alkynylation,[4] cyclization[5] and others.[6] One of the most important conversion approaches is the cross-coupling reaction of *N*-tosylhydrazones, which as masked diazo compounds react with different nucleophiles (C, N, O, S, and P) under metal-free conditions.[2a-c,7] For example, Barluenga and coworkers reported a metal-free reductive coupling reaction of N-tosylhydrazones with sodium azide to obtain primary and secondary alkyl azides (Scheme 1a).[8] Moreover, cyclization reactions involving N-tosylhydrazones have achieved substantial progress in recent years, demonstrating excellent potential advantages for pharmaceuticals and material science.[3e,5f,6b,9] For example, Zhang and coworkers developed a copper-medidated oxidation cyclization reaction for the synthesis of N-substituted 1,2,3-triazoles from N-tosylhydrazones and anilines (Scheme 1b).[10] Metal-free methods that produce N-substituted 1,2,3-triazoles from *N*-tosylhydrazones have also been developed by the Zhang and Ji group.[11] It is worth noting that these synthetic products are N-substituted 1,2,3-triazoles rather than *NH*-1,2,3-triazoles. Thus, developing methods to access N-unsubstituted 1,2,3-triazoles from *N*-tosylhydrazones represents a necessary approach.

NH-1,2,3-Triazoles, an important class of heterocyclic compounds, have widespread applications in pharmaceutical, material, and synthetic fields.[12] Compared to the N-substituted triazoles, the direct synthesis of *NH*-1,2,3-triazoles is fairly challenging, with few methods available.[13] For example, Yang et.al explored a convenient and efficient preparation method for N-unsubstituted 1,2,3-triazoles by 1,3-dipolar cycloaddition of nitroolefins and sodium azide for the synthesis of

Scheme 1. Previous Works and Present Study.

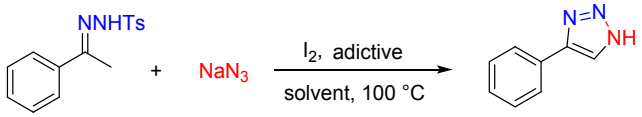


4-aryl-*NH*-1,2,3-triazoles.[15] Additionally, there are other synthetic strategies that use $TMSN_3$ and a one-pot procedure to access *NH*-1,2,3-triazoles.[16] Despite the importance of these reported methods, they still suffer from transition-metal catalyst usage, limited substrate scope, inaccessible starting materials, and harsh reaction conditions.[17] Therefore, the development of a versatile and practical method for the synthesis of *NH*-1,2,3-triazoles under metal-free conditions from simple substrates is still readily needed. Herein, we report a molecular iodine-promoted N–N coupling cyclization of N-tosylhydrazones with sodium azide for the construction of *NH*-1,2,3-triazoles (Scheme 1c).

To establish the optimal reaction conditions, we utilized N-tosylhydrazone **1a** and sodium azide (**2**) as model substrates (Table 1). The desired product 4-phenyl-1*H*-1,2,3-triazole (**3a**) was furnished with a 56% yield when the reaction proceeded in the presence of 0.5 equivalent iodine at 100 °C for 8 h in DMSO (entry 1). Encouraged by these results, we examined the effect of the amount of iodine on

the reaction (entries 1-3). The yield of **3a** increased to 78% when 1.0 equivalent iodine was used (entry 2). Further increasing the amount of iodine was not favorable for this reaction (entry 3). To increase the yield of the desired product **3a**, various additives (TfOH, TsOH, TFA, HCl, H_2SO_4, and MsOH) were also investigated (entries 4-9). The results exhibited that TfOH, H_2SO_4, and MsOH could promote the reaction to varying degrees. MsOH was the most effective additive and increased the product yield to 85% (entry 9). Prolonged reaction time and varied reaction temperature reduced the yield (entries 10-11). Both other azide ($TMSN_3$) and iodine sources (HI, and KI) could not increase the product yield (entries 12-14). We could not obtain the desired product **3a** in the absence of iodine (entry 15). Subsequently, various solvents were screened, and DMSO was the best choice for this reaction. The desired product **3a** was not obtained in other solvents (toluene, DCE, CH_3NO_2, dioxane, and DMF) (entries 16-20).

Table 1. Optimization of the Reaction Conditions[a]



1a **2** **3a**

entry	solvent	I_2 (equiv)	additive	yield[b] (%)
1	DMSO	0.5	-	56[c]
2	DMSO	1.0	-	78[c]
3	DMSO	1.5	-	43[c]
4	DMSO	1.0	HCl	56
5	DMSO	1.0	H_2SO_4	82
6	DMSO	1.0	TFA	72
7	DMSO	1.0	TsOH	71
8	DMSO	1.0	TfOH	83
9	DMSO	1.0	MsOH	85
10	DMSO	1.0	MsOH	75[d]
11	DMSO	1.0	MsOH	82[e]

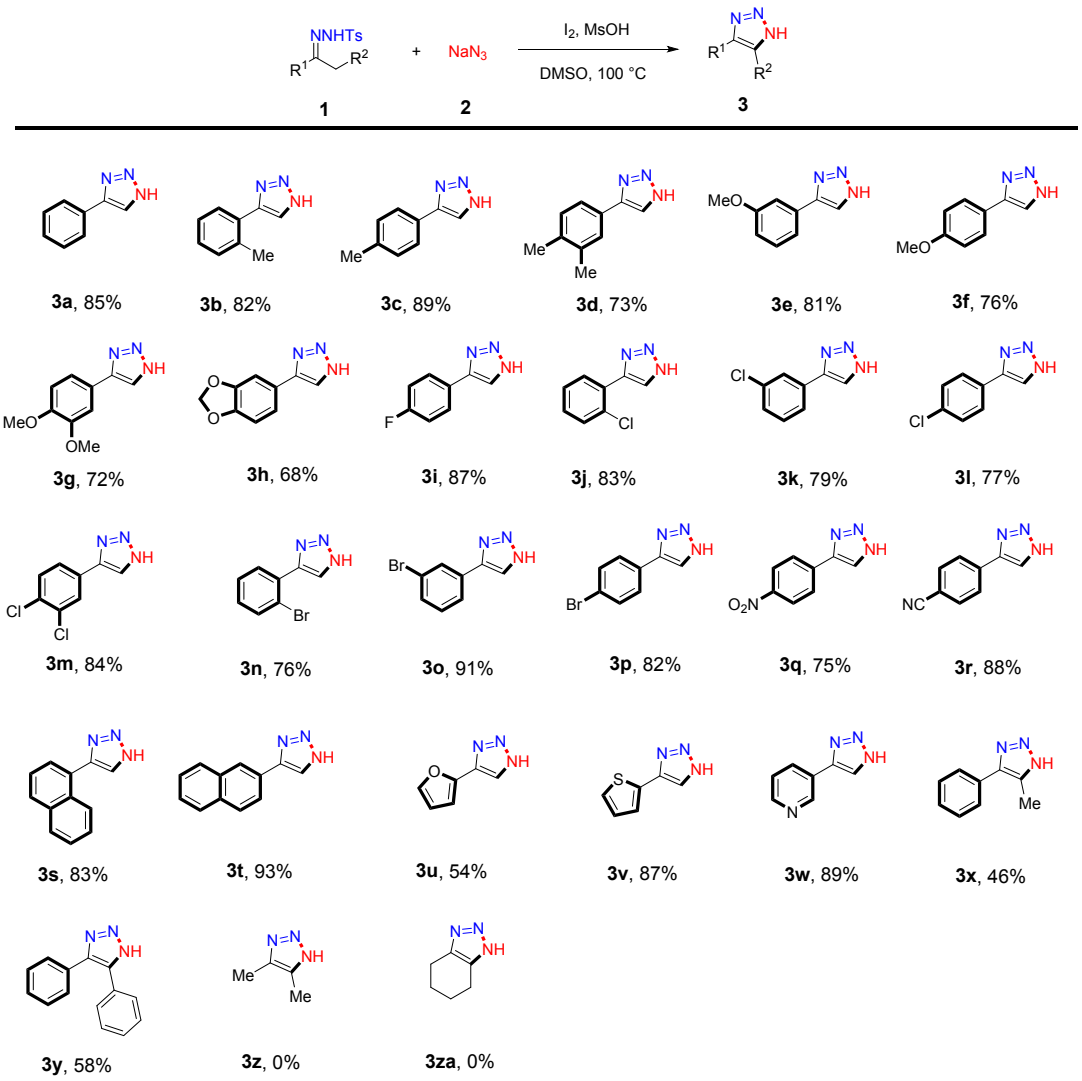
12	DMSO	1.0	MsOH	34[f]
13	DMSO	1.0	MsOH	25[g]
14	DMSO	1.0	MsOH	8[h]
15	DMSO	-	MsOH	0
16	toluene	1.0	MsOH	0
17	DCE	1.0	MsOH	0
18	CH_3NO_2	1.0	MsOH	0
19	dioxane	1.0	MsOH	0
20	DMF	1.0	MsOH	0

[a]Reactions were carried out with **1a** (0.5 mmol, 1.0 equiv), NaN_3 (0.65 mmol, 1.2 equiv), and addictive (0.5 mmol, 1.0 equiv) in DMSO (3 mL) at 100 °C for 3 h. [b]Isalated yield. [c]Reaction time is 8 h. [d]Reaction at 90 °C. [e]Reaction temperature is 110 °C. [f]$TMSN_3$ instead of NaN_3. [g]I_2 replaced by HI. [h]KI as iodine source.

After optimizing the reaction conditions, we explored the substrate scope of N-tosylhydrazones (**3**), as shown in Scheme 2. Notably, the electronic properties of the substituents on the aromatic ring system were shown to have no major influence on the efficiency of this transformation. The N-tosylhydrazones bearing electron-neutral (H), electron-donating (2-Me, 4-Me, 3,4-2Me 3-OMe, 4-OMe, 3,4-2OMe, 3,4-OCH_2O), and electron-withdrawing (4-NO_2, 4-CN) groups attached to the benzene ring transformed smoothly into their corresponding products in good to high yields (**3a**-**3h**, **3q** and **3r**; 68-89%). In addition, the halo-substituted (2-Cl, 3-Cl, 4-Cl, 3,4-2Cl, 2-Br, 3-Br, 4-Br) groups were suitable in this reaction, affording the corresponding products in high yields (76-91%; **3i-3p**). Much to our satisfaction, α-naphthyl and β-naphthyl group substrates were also compatible, giving the expected products in good to excellent yields (**3s-3t**; 83-93%). Furthermore, when the substituents were heterocyclic (2-furyl, 2-thienyl, and 3-pyridyl), the desired products **3u-3w** were obtained in moderate to good yields (54-89%). Moreover, the α-substituted (methyl and phenyl) N-tosylhydrazones could also participate in this

reaction, affording the products **3x-3y** in 46-58% yield. Unfortunately, alkyl and cycloalkyl N-tosylhydrazones were not tolerated in this [4+1] cyclization reaction and we could not obtained the correspounding products (**3z** and **3za**).

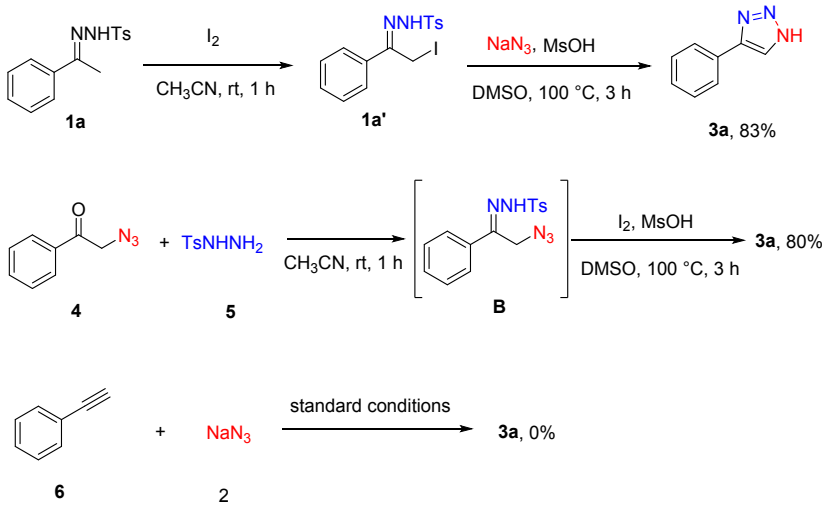
Scheme 2. Scope of N-tosylhydrazones[a]



[a] Reactions were performed with **1** (1.0 mmol, 1.0 equiv), **2** (1.2 mmol, 1.2 equiv), I_2 (1.0 mmol, 1.0 equiv), and MsOH (1.0 mmol, 1.0 equiv) in DMSO (5 mL) at 100 °C for 3 h. Isolated products.

To gain insight into the reaction process, a series of control experiments were performed (Scheme 3). The α-iodo N-tosylhydrazone **1a′** was obtained by the reaction of N-tosylhydrazone (**1a**) with iodine in CH_3CN at room temperature for 1 h.[5f] Later, the reaction between **1a′** and sodium azide in DMSO at 100 °C for 3 h in the presence of MsOH proceeded smoothly to give the target product **3a** in 83% yield. Moreover, 2-azido-1-phenylethan-1-one (**4**) reacted with p-toluenesulfonyl hydrazide (**5**) leading to α-azido N-tosylhydrazone **B**, which could be transformed into product **3a** in 80% yield under standard conditions. Furthermore, the desired product **3a** was not afforded when using ethynylbenzene **6** as a substrate. These results indicate that compounds **1a′** and **B** are probably intermediates for this reaction and that ethynylbenzene **6** cannot serve as an intermediate.

Scheme 3. Control Experiments[a]

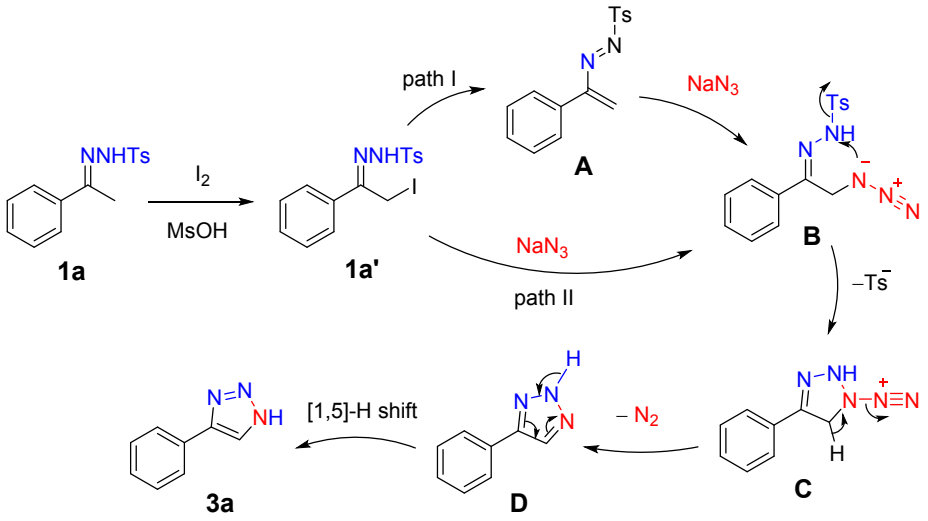


[a]Isolated yields.

Based on the above experimental results, a possible reaction mechanism is proposed as shown in Scheme 4 (with **3a** as an example). Initially, α-iodination of

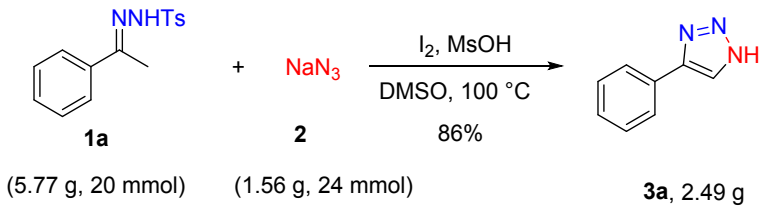
N-tosylhydrazone **1a** generates intermediate **1a′** in the presence of I_2.[11b] Next, two possible approaches were proposed for the conversion from **1a′** to intermediate **B**. Elimination of HI from **1a′** gives the intermediate 1-tosyl-2-vinyldiazene **A**,[10a] which undergoes an aza-Michael addition with NaN_3 to obtain the intermediate **B** (path I). Direct nucleophilic substitution of NaN_3 onto intermediate **1a′** is another possible route for the formation of intermediate **B** (path II). Subsequently, the intermediate **B** could be smoothly cyclized to intermediate **C** by formation of an N-N bond. Finally, the intermediate **C** produced to the intermediate **D** with the elimination of nitrogen, which is converted to the final product **3a** via a [1,5]-H shift.

Scheme 4. A Possible Mechanism



To demonstrate the potential applications for organic synthesis, the reaction of tosylhydrazone **1a** and NaN_3 was performed on a gram scale (Scheme 5). Gratifyingly, the reaction carried out very well, and the phenyl-1*H*-1,2,3-triazole **3a** was furnished in 86% yield.

Scheme 5. Gram Scale Experiment



CONCLUSION

In summary, we developed a molecular iodine-promoted [4+1] cyclization of N-tosylhydrazones with sodium azide for the synthesis of 4-aryl-*NH*-1,2,3-triazole derivatives. This metal-free strategy could rapidly synthesize valuable compounds via sequential C–N and N–N bond formation in a single step. Further studies on this method for the synthesis of other bioactive compounds and applications are in progress in our laboratory.

EXPERIMENTAL SECTION

General Information. N-tosylhydrazones **1** were prepared according to the literature procedure.[18] Other substrates and reagents were commercial and used without further purification. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200-300 mesh). ^{1}H NMR spectra were determined at 25 °C on a Varian Mercury 400 or 600 MHz spectrometer. ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on 100/150 MHz. Chemical shifts are given in ppm relative to the internal standard of tetramethylsilane (TMS). HRMS were obtained on an Thermo Scientific LTQ Orbitrap XL equipped with an atmospheric-pressure chemical ionization (APCI) source or electrospray ionization (ESI) source. The X-ray crystal-structure determinations were obtained on a Bruker APEX DUO CCD system.

General Procedure for the Synthesis of 3a-3y (3a as example). The mixture of

N-tosylhydrazone **1a** (288.4 mg, 1.0 mmol), sodium azide (78.0 mg, 1.2 mmol), iodine (253.8 mg, 1.0 mmol), and methylsulphonic acid (96.1 mg, 1.0 mmol) was added in DMSO (5 mL), and the resulting mixture was stirred at 100 °C for 3 h. After the reaction completed, and then added 100 mL water to the mixture, extracted with EtOAc three times (3 × 100 mL). Dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc = 30/1) to afford the desired product **3a**.

4-phenyl-1H-1,2,3-triazole (**3a**):[15a,19]

Yield 85% (123.4 mg); white solid; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 15.06 (s, 1H), 8.30 (s, 1H), 7.92–7.91 (m, 2H), 7.48 (s, 2H), 7.38 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 146.3, 130.9, 129.0, 128.3, 125.7, 119.5; ITMS (ESI, LCQ-fleet): m/z $[M+H]^+$ $C_8H_8N_3$: 145.92 (100), 146.91 (13.6).

4-(o-tolyl)-1H-1,2,3-triazole (**3b**):[21]

Yield 82% (130.5 mg); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 13.22 (s, 1H), 7.84 (s, 1H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.28 – 7.20 (m, 2H), 7.20 – 7.14 (m, 1H), 2.38 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 144.6, 135.8, 130.8, 129.4, 129.0, 128.6, 128.5, 126.0, 20.8; HRMS (ESI, LTQ-Orbitrap): m/z $[M+H]^+$ calcd for $C_9H_{10}N_3$: 160.0869, found: 160.0862.

4-(p-tolyl)-1H-1,2,3-triazole (**3c**):[15a,19a]

Yield 89% (141.7 mg); white solid; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 15.13 (s, 1H), 8.31 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 2.34 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 145.9, 137.6, 129.6, 129.2, 127.8, 125.6, 20.9; ITMS (ESI, LCQ-fleet): m/z $[M+H]^+$ $C_9H_{10}N_3$: 159.98 (100), 160.95 (8.71).

4-(3,4-dimethylphenyl)-1H-1,2,3-triazole (**3d**):

Yield 73% (126.4 mg); white solid; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 15.14 (s, 1H), 8.30 (s, 1H), 7.71 (s, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.35–6.96 (m, 1H), 2.28 (s,

3H), 2.24 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ (ppm) 146.3, 136.9, 136.4, 130.1, 128.1, 126.8, 123.2, 19.5, 19.2; HRMS (ESI, LTQ-Orbitrap): m/z $[M+H]^+$ calcd for $C_{10}H_{12}N_3$: 174.1026, found: 174.1023.

4-(3-methoxyphenyl)-1H-1,2,3-triazole (**3e**):[19a,20]

Yield 81% (141.9 mg); yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 13.97 (s, 1H), 7.99 (s, 1H), 7.52–7.35 (m, 2H), 7.32 (t, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 3.83 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 160.0, 146.4, 130.8, 130.0, 128.5, 118.5, 114.6, 111.3, 55.3; HRMS (ESI, LTQ-Orbitrap): m/z $[M+H]^+$ calcd for $C_9H_{10}N_3O$: 176.0818, found: 176.0819.

4-(4-methoxyphenyl)-1H-1,2,3-triazole (**3f**):[15a,19]

Yield 76% (133.2 mg); white solid; ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 15.02 (s, 1H), 8.25 (s, 1H), 7.82 (d, J = 8.8 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ (ppm) 159.3, 146.1, 129.9, 127.0, 123.1, 114.4, 55.2; ITMS (ESI, LCQ-fleet): m/z $[M+H]^+$ $C_9H_{10}N_3O$: 175.95 (100), 176.96 (10.66).

4-(3,4-dimethoxyphenyl)-1H-1,2,3-triazole (**3g**):[20-21]

Yield 72% (147.7 mg); white solid; ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 14.93 (s, 1H), 8.24 (s, 1H), 7.47 (s, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 3.86 (s, 3H), 3.81 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ (ppm) 149.1, 146.3, 130.2, 123.5, 118.2, 112.1, 109.3, 55.6, 55.5; ITMS (ESI, LCQ-fleet): m/z $[M+H]^+$ $C_{10}H_{12}N_3O_2$: 206.02 (100), 207.08 (25.02), 207.83 (7.81).

4-(benzo[d][1,3]dioxol-5-yl)-1H-1,2,3-triazole (**3h**):[19a]

Yield 68% (128.7 mg); white solid; ^1H NMR (400 MHz, DMSO-d6): δ (ppm) 15.11 (s, 1H), 8.28 (s, 1H), 7.47–7.44 (m, 1H), 7.43–7.41 (m, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.10 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ (ppm) 147.9, 147.3, 145.6, 128.5, 124.5, 119.4, 108.8, 106.1, 101.3; HRMS (ESI, LTQ-Orbitrap): m/z $[M+H]^+$ calcd for $C_9H_8N_3O_2$: 190.0611, found 190.0615.

4-(4-fluorophenyl)-1H-1,2,3-triazole (**3i**):[15a,21]

Yield 87% (142.0 mg); white solid; ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 15.29 (s, 1H), 8.41 (s, 1H), 8.01–7.98 (m, 2H), 7.35 (t, *J* = 8.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (100

MHz, DMSO-d_6): δ (ppm) 162.1 (d, J_{CF} = 243.4 Hz), 144.8, 129.9, 127.7 (d, J_{CF} = 8.1 Hz), 115.9 (d, J_{CF} = 21.6 Hz) ; ITMS (ESI, LCQ-fleet): m/z $[M+H]^+$ $C_8H_7FN_3$: 163.92 (100), 164.92 (9.46).

4-(2-chlorophenyl)-1H-1,2,3-triazole (**3j**):[15a, 19b]

Yield 83% (149.1 mg); white solid; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 15.41 (s, 1H), 8.39 (s, 1H), 7.98 (s, 1H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.52–7.37 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ (ppm) 143.0, 133.1, 130.9, 130.2, 129.6, 129.4, 127.5, 122.8; HRMS (ESI, LTQ-Orbitrap): m/z $[M+H]^+$ calcd for $C_8H_7ClN_3$: 180.0323, found: 180.0329.

4-(3-chlorophenyl)-1H-1,2,3-triazole (**3k**):[19a]

Yield 79% (141.9 mg); white solid; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 15.33 (s, 1H), 8.51 (s, 1H), 8.04–7.94 (m, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ (ppm) 144.5, 133.8, 132.6, 130.9, 127.9, 125.2, 124.1; ITMS (ESI, LCQ-fleet): m/z $[M+H]^+$ $C_8H_7ClN_3$: 179.91 (100), 180.97 (11.72), 181.99 (34.50), 183.0 (4.80).

4-(4-chlorophenyl)-1H-1,2,3-triazole (**3l**):[15a,19b]

Yield 77% (138.3 mg); white solid; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 15.41 (s, 1H), 8.46 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ (ppm) 144.67, 132.8, 129.4, 129.0, 127.3; ITMS (ESI, LCQ-fleet): m/z $[M+H]^+$ $C_8H_7ClN_3$: 179.94 (100), 180.92 (11.81), 181.88 (34.50), 182.98 (4.67).

4-(3,4-dichlorophenyl)-1H-1,2,3-triazole (**3m**):

Yield 84% (179.8 mg); white solid; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 15.45 (s, 1H), 8.53 (s, 1H), 8.20–8.13 (m, 1H), 7.94–7.88 (m, 1H), 7.69 (d, *J* = 8.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ (ppm) 143.7, 131.9, 131.2, 131.0, 130.5, 127.1, 125.5; HRMS (ESI, LTQ-Orbitrap): m/z $[M+H]^+$ calcd for $C_8H_6Cl_2N_3$: 213.9933, found 213.9932.

4-(2-bromophenyl)-1H-1,2,3-triazole (**3n**):[20, 21]

Yield 76% (170.3 mg); yellow solid; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 15.40 (s, 1H), 8.38 (s, 1H), 7.85 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 7.6 Hz,

1H), 7.35 (t, *J* = 7.6 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6): δ (ppm) 144.5, 133.5, 131.5, 131.0, 130.0, 128.0, 121.2; HRMS (ESI, LTQ-Orbitrap): m/z $[M+H]^+$ calcd for $C_8H_7BrN_3$: 223.9818, found: 223.9819.

4-(3-bromophenyl)-1H-1,2,3-triazole (**3o**):[21]

Yield 91% (203.9 mg); yellow solid; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 15.27 (s, 1H), 8.45 (s, 1H), 8.17 (s, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6): δ (ppm) 144.9, 133.1, 131.1, 130.8, 128.1, 124.5, 122.4, 120.4; ITMS (ESI, LCQ-fleet): m/z $[M+H]^+$ $C_8H_7BrN_3$: 223.92 (99.99), 224.99 (11.58), 225.90 (100), 227.01 (9.87).

4-(4-bromophenyl)-1H-1,2,3-triazole (**3p**):[15a]

Yield 82% (183.7 mg); yellow solid; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 15.36 (s, 1H), 8.45 (s, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.72–7.65 (m, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6): δ (ppm) 144.7, 131.9, 129.8, 127.8, 127.6, 121.2; ITMS (ESI, LCQ-fleet): m/z $[M+H]^+$ $C_8H_7BrN_3$: 223.89 (100), 225.00 (12.67), 225.88 (97.56), 226.99 (10.77).

4-(4-nitrophenyl)-1H-1,2,3-triazole (**3q**):[19]

Yield 75% (142.6 mg); yellow solid; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 15.39 (s, 1H), 8.65 (s, 1H), 8.33 (d, *J* = 8.8 Hz, 2H), 8.17 (d, *J* = 8.8 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6): δ (ppm) 146.8, 143.9, 137.1, 126.4, 124.4; HRMS (ESI, LTQ-Orbitrap): m/z $[M+H]^+$ calcd for $C_8H_7N_4O_2$: 191.0564, found: 191.0560.

4-(1H-1,2,3-triazol-4-yl)benzonitrile (**3r**):[15a]

Yield 88% (149.8 mg); white solid; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 15.31 (s, 1H), 8.60 (s, 1H), 8.13 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 8.4 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6): δ (ppm) 144.3, 135.1, 132.9, 127.7, 126.2, 118.9, 110.4; ITMS (ESI, LCQ-fleet): m/z $[M+H]^+$ $C_9H_7N_4$: 171.02 (100), 102.04 (9.12).

4-(naphthalen-1-yl)-1H-1,2,3-triazole (**3s**):[22]

Yield 83% (162.0 mg); white solid; 1H NMR (400 MHz, DMSO-d_6): δ (ppm) 15.46 (s, 1H), 8.65 (s, 1H), 8.38 (s, 1H), 8.02 (t, J = 7.6 Hz, 2H), 7.87 (d, J = 6.4 Hz, 1H), 7.65–7.58 (m, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6): δ (ppm) 145.7, 133.7, 130.5, 128.8, 128.5, 128.1, 127.2, 126.8, 126.2, 125.6; ITMS (ESI, LCQ-fleet): m/z

$[M+H]^+$ $C_{12}H_{10}N_3$: 195.98 (100), 197.03 (32.36), 198.77 (12.45).

4-(naphthalen-2-yl)-1H-1,2,3-triazole (**3t**):[19b,21]

Yield 93% (181.5 mg); white solid; 1H NMR (400 MHz, DMSO-d_6): δ (ppm) 15.39 (s, 1H), 8.59 (s, 1H), 8.36 (s, 1H), 8.02 (t, J = 7.6 Hz, 2H), 7.83 (d, J = 6.4 Hz, 1H), 7.73–7.37 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ (ppm) 145.7, 133.6, 130.5, 128.8, 128.5, 128.0, 127.2, 126.8, 126.2, 125.6, 125.5; ITMS (ESI, LCQ-fleet): m/z $[M+H]^+$ $C_{12}H_{10}N_3$: 196.01 (100), 196.97 (17.58), 198.81 (23.13).

4-(furan-2-yl)-1H-1,2,3-triazole (**3u**):[15a,19b,21]

Yield 54% (73.0 mg); brown solid; 1H NMR (400 MHz, DMSO-d_6): δ (ppm) 15.14 (s, 1H), 8.14 (s, 1H), 7.79 (s, 1H), 6.93–6.80 (m, 1H), 6.65–6.63 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ (ppm) 146.0, 143.0, 138.9, 130.2, 111.7, 107.2; ITMS (ESI, LCQ-fleet): m/z $[M+H]^+$ $C_6H_6N_3O$: 135.88 (100), 136.95 (10.48).

4-(thiophen-2-yl)-1H-1,2,3-triazole (**3v**):[15a,21]

Yield 87% (131.5 mg); brown solid; 1H NMR (400 MHz, DMSO-d_6): δ (ppm) 14.96 (s, 1H), 8.15 (s, 1H), 8.13 (d, J = 8.0 Hz, 2H), 7.60–7.43 (m, 2H), 7.16–7.13 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ (ppm) 141.6, 132.7, 130.3, 127.9, 125.8, 125.0; ITMS (ESI, LCQ-fleet): m/z $[M+H]^+$ $C_6H_6N_3S$: 151.91 (100), 152.84 (12.50).

3-(1H-1,2,3-triazol-4-yl)pyridine (**3w**):[23]

Yield 89% (130.1 mg); white solid; ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 15.23 (s, 1H), 9.12 (s, 1H), 8.59 (s, 1H), 8.41 (s, 1H), 8.27 (d, J = 8.0 Hz, 1H), 7.54–7.50 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ (ppm) 149.3, 146.8, 133.0, 131.3, 126.5, 124.1, 120.3; ITMS (ESI, LCQ-fleet): m/z $[M+H]^+$ $C_7H_7N_4$: 223.89 (100), 225.00 (12.67).

5-methyl-4-phenyl-1H-1,2,3-triazole (**3x**):[14b,15a,22]

Yield 46% (73.2 mg); white solid; 1H NMR (400 MHz, DMSO-d_6): δ (ppm) 14.69 (s, 1H), 7.80–7.71 (m, 2H), 7.48 (s, 2H), 7.40–7.35 (m, 1H), 2.46 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ (ppm) 131.4, 128.7, 127.7, 127.1, 126.8, 126.2, 11.5; ITMS (ESI, LCQ-fleet): m/z $[M+H]^+$ $C_9H_{10}N_3$: 159.95 (100),160.92 (24.77).

4,5-diphenyl-1H-1,2,3-triazole (**3y**):[14b,15a]

Yield 58% (128.3 mg); white solid; 1H NMR (400 MHz, DMSO-d_6): δ (ppm)

15.22 (s, 1H), 7.54 (s, 4H), 7.41 (s, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6): δ (ppm) 143.2, 131.2, 128.6, 128.2, 128.0; HRMS (ESI, LTQ-Orbitrap) m/z $[M+H]^+$ calcd for $C_{14}H_{12}N_3$: 222.1026, found 222.1029.

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra of compounds **3a-3y**. This material is available free of charge via the Internet at http://pubs.acs.org.

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