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A NOVEL SYNTHESIS OF 1-ARYL-1*H*-BENZOTRIAZOLES *VIA* OXIDATIVE C-H AMINATION

Zhou Zhou, Qi-Lun Liu, Wen Li, and Yong-Ming Zhu*

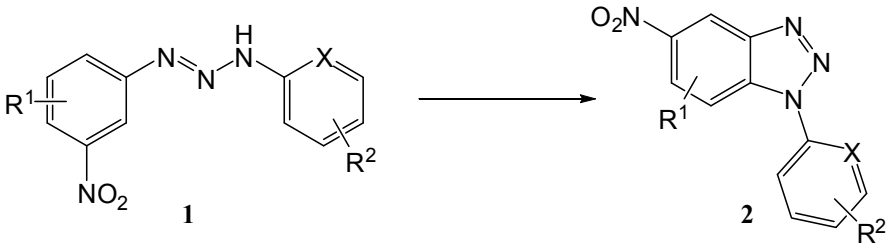
School of Pharmacy, Soochow University, Suzhou, 215123, P. R. China, Phone: +86-512-62880109; Fax: +86-512-67166591; E-mail: zhuyongming@suda.edu.cn

Abstract – A facile, novel and regiospecific protocol for the synthesis of 1-aryl-1*H*-benzotriazoles *via* oxidative C-H amination of corresponding 1,3-diaryltriazenes in DMF in the presence of K_2CO_3 at moderate temperature was developed.

INTRODUCTION

Benzotriazoles are an important class of compounds used in synthetic organic chemistry.[1] They are found to exhibit a broad spectrum of pharmacological activities including antibacterial, antitubercular, anticancer, antidepressant and antifungal activities.[2] Besides, benzotriazoles are widely used as corrosion inhibitor, anti-freeze reagents, UV absorber, anti-fog agents and synthetic auxiliaries.[3]

Inter- and intramolecular C-N bond formation is important in both academic and industrial chemistry, due to the high prevalence of nitrogen-containing biologically active compounds and pharmaceuticals. Particularly, Pd- or Cu-catalyzed amination reactions of aryl halides or pseudohalides have been widely used to construct such compounds, and highly active catalyst systems have been reported.[4,5] In these cases, aryl electrophiles must possess a halide or pseudohalide moiety which limited the application of such reactions. On the other hand, notable advances in C-H functionalization catalyzed by Ru,[6] Rh[7] and Pd[8-10] have been described. Buchwald reported Pd(II)-catalyzed C-H activation/intramolecular amidation for carbazole synthesis in 2005.[8] Moreover, Che disclosed that it was possible to activate sp^3 as well as sp^2 C-H bonds in the presence of $Pd(OAc)_2$, followed by intermolecular amination.[9] Recently, Cu[11] and Pd[12] catalyzed processes for the synthesis of benzotriazoles have been reported, which showed high regiospecificity and wild functional group tolerance. Herein we describe a novel approach to the synthesis of 1-aryl-1*H*-benzotriazoles *via* nitro group participated oxidative C-H amination reactions with easily obtained 1,3-diaryltriazenes compounds as substrates (Scheme 1).

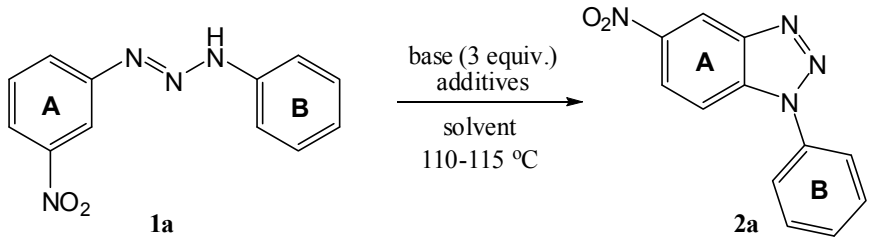


Scheme 1

RESULTS AND DISCUSSION

Our investigation began by examining the conversion of 1-(3-nitrophenyl)-3-phenyltriaz-1-ene (**1a**) into the corresponding benzotriazole (**2a**). Firstly, **1a**, which was easily obtained according to the reported protocol,[13] $Pd(OAc)_2$ and oxidant in DMF was reacted under N_2. Unfortunately, no desired cyclized product was obtained probably due to the instability of **1a** under our utilized reaction conditions (entries 1 and 2). In the light of kinetic and mechanistic studies of the decomposition of triazenes[14] base was applied in the following study of the cyclization process. Replacement of chemical oxidant with oxygen gave an isolated 77% yield of desired product though the catalyst $Pd(OAc)_2$ was removed (entry 4). This result promoted us to further optimize this annulation chemistry, and the results were summarized in Table1.

Table 1. Optimization of reaction condition[a]



Entry	Solvent	Base	Additives	Yield(%) [b]
1	DMF	---	10% $Pd(OAc)_2$ 1equiv $Cu(OAc)_2$	-[c]
2	DMF	---	10% $Pd(OAc)_2$ 1equiv $PhI(OAc)_2$	-[c]
3	DMF	K_2CO_3	10% $Pd(OAc)_2$	75
4	DMF	K_2CO_3	-	77
5	DMF	K_2CO_3	-	78[c]
6	DMSO	K_2CO_3	-	76

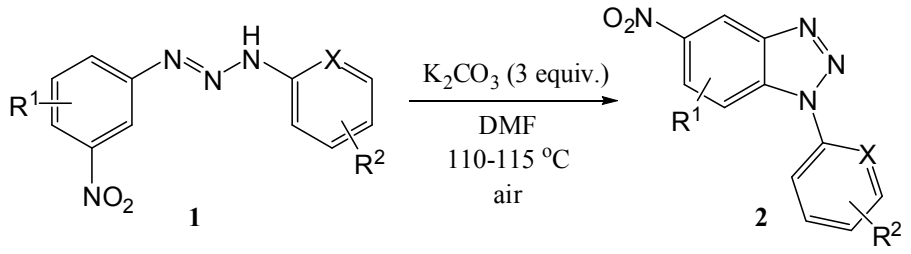
7	toluene	K_2CO_3	-	N.R.[d]
8	1,4-dioxane	K_2CO_3	-	N.R.
9	DMF	Cs_2CO_3	-	46
10	DMF	K_3PO_4	-	43
11	DMF	Na_2CO_3	-	75
12	DMF	TEA	-	N.R.
13	DMF	-	-	N.R.

[a] Reaction condition: A solution of **1a** (0.5 mmol) and base (1.5 mmol) in 5 mL anhydrous solvent was heated under air at 110-115 °C and monitored by TLC. [b] Isolated yield by FC on silica gel. [c] Under N_2. [d] N. R.= no reaction.

As shown in Table 1, while a nitro group was attached meta to triazene in A ring, almost equal yield was obtained in the absence of $Pd(OAc)_2$ (entries 3 and 4). While the reaction was carried out under nitrogen, we also obtained almost the same isolated yield of **2a** (entry 5). DMF was the best solvent compared with other solvents used in our experiment (entries 4-8). Base was indispensable in the present protocol and the best yield was obtained with K_2CO_3 (entries 4, 9-13). Thus the optimal cyclization reaction was carried out in DMF at 110-115 °C under air in the presence of K_2CO_3.

On the basis of the above results, the scope of the reaction was explored with different substrates. As shown in Table 2, the reaction condition was of quite general character and tolerant of a wide range of functionalities. Best yield was obtained while R^1 was H, R^2 was 4-F, followed by R_2 was 3-CO_2Et, and 3-CF_3 (entries 4, 13 and 10). As can be seen from entries 5 and 8, steric hindrance led to slightly lower yields and prolonged reaction time. The substituents on the two aromatic rings had different effects on the yields (entries 2, 3, 14 and 15). Both electron-donating and electron-withdrawing substituents on A ring decreased the yields drastically due to steric hindrance, which possibly obstruct the conversion of the conjugation system by affecting the coplanarity of nitro group and A ring (entries 14-16). The plausible mechanism was shown in Scheme 2, the reaction possibly proceeded *via* a vicarious nucleophilic substitution.[15] The oxidation process possibly proceeds *via* abstraction the leaving H by O_2 in a radical manner, recombination of the radical with hydroperoxide radical, and elimination of hydroperoxide anion by electron donation from the anionic nitro group. Electron-donating and electron-withdrawing groups on the other aromatic ring had no significant effects on the yields (entries 1-4, 6, 7, 10-13).

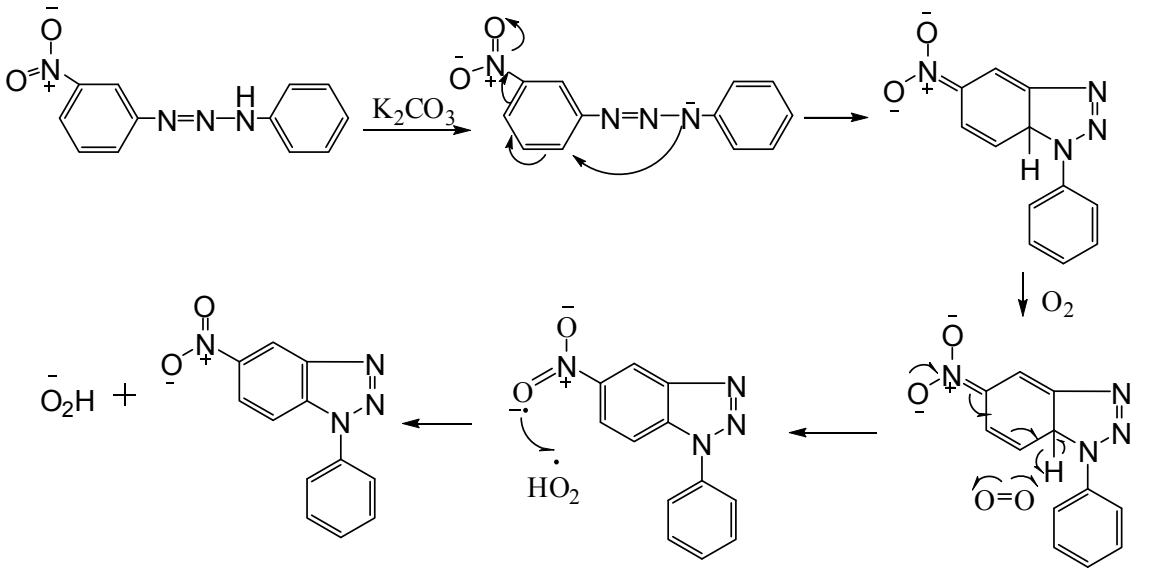
Table 2. Cyclization of Triazenes[a]



Entry	Substrates	R^1	R^2	Products	t(h)	Yield[%][b]
1	**1a**	H	H	**2a**	9	77
2	**1b**	H	4-Me	**2b**	9	74
3	**1c**	H	4-OMe	**2c**	9	72
4	**1d**	H	4-F	**2d**	8	87
5	**1e**	H	2-Me	**2e**	40	55
6	**1f**	H	4-Cl	**2f**	24	73
7	**1g**	H	3-CF_3	**2g**	11	80
8	**1h**	H	2-Me, 5-Cl	**2h**	40	59
9	**1i**	H	H, (X=N[c])	**2i**	11	67
10	**1j**	H	3-NO_2	**2j**	36	79
11	**1k**	H	3-SO_2Ph	**2k**	40	77
12	**1l**	H	3-CN	**2l**	24	65
13	**1m**	H	3-CO_2Me	**2m**	24	81
14	**1n**	4-Me	H	**2n**	24	23
15	**1o**	4-OMe	H	**2o**	13	33
16	**1p**	4-Cl	H	**2p**	24	Trace

[a] Reaction condition: **1** (0.5 mmol), K_2CO_3 (1.5 mmol), DMF (5 mL). [b] Isolated yield by FC. [c] For entry 9, X=N, for others, X=C.

In conclusion, a novel pathway for the synthesis of 1-aryl-1*H*-benzotriazoles *via* nitro group participated oxidative C-H amination under relatively mild condition has been developed. The synthetic strategy, with readily available substituted 1,3-diaryltriazenes as starting materials, provides regiospecifically and atom-economically corresponding 1-aryl-1*H*-benzotriazoles in good yields.



Scheme 2. Plausible mechanism

EXPERIMENTAL

General

DMF and DMSO were dried over CaH_2, toluene and 1,4-dioxane were dried over Na and distilled. Flash chromatography (FC): silica gel (SiO_2; 300-400 mesh) from Qingdao Ocean Chemicals, P. R. China. TLC: Silica-gel GF254 plates. Melting points were determined without correction on an XT5 digital melting-point apparatus purchased from Beijing Keyi Elec-opti Instrument Factory. ^{1}H NMR and ^{13}C NMR spectra were obtained from a solution in $CDCl_3$ or DMSO-d_6 with tetramethylsilane (TMS) as internal standard using Varian Inova 400/101 MHz (^{1}H/^{13}C) or 300/75 MHz (^{1}H/^{13}C) spectrometer, δ in parts per million (ppm), and J in hertz (Hz). IR data were recorded on Varian 1000 FT-IR using KBr tablets, wavenumbers in cm^{-1}. HRMS analyses were carried out using a time-of-flight mass spectrometry (TOFMS) or Saturan2200 (ESI) instrument.

General procedure for the synthesis of benzotriazoles (2):

A mixture of **1** (0.5 mmol), K_2CO_3 (1.5 mmol) and DMF (5 mL) in a flask filled with a magnetic stirring bar under air was stirred at 110-115 °C. The process of the reaction was monitored by TLC using *n*-hexane/EtOAc or $CHCl_3$/*n*-hexane. After the reaction mixture was cooled to room temperature and 30 mL EtOAc was added. The organic layer was washed with water and brine, dried over anhydrous Na_2SO_4. After removing the solvent, the residue was purified by FC on silica gal eluting with *n*-henane/EtOAc or $CHCl_3$/*n*-hexane to give **2**.

5-Nitro-1-phenyl-1*H*-benzo[*d*][1,2,3]triazole (2a): Pale yellow crystals (EtOAc/*n*-hexane), mp 171-172 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (t, J = 7.39 Hz, 1H), 7.69 (t, J = 7.78 Hz, 1H), 7.78 (d, J =

8.30 Hz, 1H), 7.86 (d, *J* = 9.10 Hz, 1H), 8.45-8.49 (m, 1H), 9.10 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 111.13, 117.62, 123.22, 123.36, 129.79, 130.30, 135.05, 136.06, 145.00, 145.67. IR (KBr): 3100, 1614, 1523, 1458, 1069, 801, 740, 690. HRMS (EI) calcd for $C_{13}H_{10}N_4O_2$ [M^+]: 240.0647, found: 240.0647.

5-Nitro-1-*p*-tolyl-1*H*-benzo[*d*][1,2,3]triazole (2b): Pale yellow crystals (EtOAc/*n*-hexane), mp 173.5-174.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.51 (s, 1H), 7.47 (d, *J* = 7.52 Hz, 1H), 7.64 (d, *J* = 7.97 Hz, 1H), 7.81 (d, *J* = 9.10 Hz, 1H), 8.45 (d, *J* = 8.98 Hz, 1H), 9.09 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.38, 111.13, 117.53, 123.10, 123.18, 130.78, 133.55, 135.12, 144.90, 140.12. IR (KBr): 3019, 2926, 1616, 1524, 1352, 1075, 1055, 814, 799, 736. HRMS (EI) calcd for $C_{13}H_{10}N_4O_2$ [M^+]: 254.0804, found: 254.0804.

1-(4-Methoxyphenyl)-5-nitro-1*H*-benzo[*d*][1,2,3]triazole (2c): Pale yellow crystals ($CHCl_3$/*n*-hexane), mp 251-252 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.93 (s, 3H), 7.16 (d, *J* = 8.95 Hz, 2H), 7.66 (d, *J* = 8.92 Hz, 1H), 7.77 (d, *J* = 9.22 Hz, 2H), 8.44 (dd, *J* = 9.13, 1.87 Hz, 1H), 9.09 (s, 1H). ^{13}C NMR (75 MHz, DMSO -d_6): δ 55.64, 112.05, 115.20, 116.70, 123.06, 125.14, 128.36, 134.97, 144.52, 144.56, 160.01. IR (KBr): 3107, 3182, 2982, 1614, 1521, 1351, 822, 802, 739. HRMS (EI) calcd for $C_{13}H_{10}N_4O_3$ [M^+]: 270.0750, found: 270.0753.

1-(4-Fluorophenyl)-5-nitro-1*H*-benzo[*d*][1,2,3]triazole (2d): Pale yellow crystals (EtOAc/*n*-hexane), mp 190.5-191.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (t, *J* = 8.40 Hz, 1H), 7.74-7.80 (m, 2H), 7.82 (d, *J* = 9.13 Hz, 1H), 8.07 (d, *J* = 9.09 Hz, 1H), 8.47 (dd, *J* = 9.08, 1.65 Hz, 1H), 9.07 (d, *J* = 1.52 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 163.90, 160.62, 144.71, 144.64, 134.91, 131.96, 126.04, 125.92, 123.35, 117.29, 116.98, 116.88, 112.21. IR (KBr): 3107, 3070, 1603, 1526, 1525, 1352, 1231, 841, 742. HRMS (EI) calcd for $C_{12}H_7FN_4O_2$ [M^+]: 258.0553, found: 258.0556.

5-Nitro-1-*o*-tolyl-1*H*-benzo[*d*][1,2,3]triazole (2e): Pale brown crystals (EtOAc/*n*-hexane), mp 113.5-114.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.14 (s, 3H), 7.41 (d, *J* = 7.63 Hz, 1H), 7.44-7.59 (m, 4H), 8.42 (d, *J* = 8.96 Hz, 1H), 9.10 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.84, 110.88, 117.55, 123.27, 126.85, 127.45, 130.93, 132.08, 134.29, 135.26, 136.54, 144.78, 144.97. IR (KBr):3107, 3090, 2926, 1616, 1605, 1518, 1466, 1348, 1071, 1032, 804, 762. HRMS (EI) calcd for $C_{13}H_{10}N_4O_2$ [M^+]: 254.0804, found: 254.0802.

1-(4-Chlorophenyl)-5-nitro-1*H*-benzo[*d*][1,2,3]triazole (2f): Pale yellow crystals (EtOAc/*n*-hexane), mp 218.5-219.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.83 Hz, 2H), 7.74 (d, *J* = 8.82 Hz, 2H), 7.82 (d, *J* = 9.13 Hz, 1H), 8.49 (dd, *J* = 9.13, 1.93 Hz, 1H), 9.11 (d, *J* = 1.39 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 110.87, 1117.83, 123.69, 124.40, 130.60, 134.59, 134.92, 135.81, 145.16, 145.80. IR (KBr): 3109, 1616, 1522, 1499, 1347, 1098, 1040, 827, 802, 741. HRMS (EI) calcd for $C_{12}H_7ClN_4O_2$ [M^+]: 274.0258, found: 274.0260.

5-Nitro-1-(3-(trifluoromethyl)phenyl)-1*H*-benzo[*d*][1,2,3]triazole (2g): Pale yellow crystals (EtOAc/*n*-hexane), mp 109.5-110.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (m, 3H), 8.03 (d, *J* = 6.94 Hz, 1H), 8.09 (s, 1H), 8.52 (d, *J* = 9.05 Hz, 1H), 9.12 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 110.77, 117.91, 120.07, 120.11, 120.15, 120.18, 121.95, 123.98, 124.66, 126.19, 126.40, 126.44, 126.47, 126.50, 131.19, 132.57, 132.90, 133.23, 133.58, 134.82, 136.64, 145.27, 145.92. IR (KBr): 3096, 1616, 1541, 1462, 1354, 1327, 1116, 903, 807, 739, 696. HRMS (EI) calcd for $C_{13}H_7F_3N_4O_2$ [M^+]: 308.0521, found: 308.0515.

1-(5-Chloro-2-methylphenyl)-5-nitro-1*H*-benzo[*d*][1,2,3]triazole (2h): Pale brown crystals ($CHCl_3$/*n*-hexane), mp 176.8-177.8 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.12 (s, 3H), 7.41-7.57 (m, 4H), 8.46 (dd, *J* = 9.06, 1.91 Hz, 1H), 9.12 (d, *J* = 1.76 Hz, 1H). ^{13}C NMR (101 MHz, CDCl3): δ 17.53, 110.68, 117.72, 123.65, 126.95, 131.06, 132.78, 133.16, 133.85, 135.09, 136.31, 144.86, 145.15. IR (KBr): 3086, 1616, 1531, 1497, 1354, 1045, 901, 824, 800, 739. HRMS (EI) calcd for $C_{13}H_9ClN_4O_2$ [M^+]: 288.0414, found: 288.0415.

5-Nitro-1-(pyridin-2-yl)-1*H*-benzo[*d*][1,2,3]triazole (2i): White crystals ($CHCl_3$/*n*-hexane), mp 212.5-213.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 7.40, 4.92 Hz, 1H), 8.02 (dt, *J* = 8.27, 7.94, 1.80 Hz, 1H), 8.35 (d, *J* = 8.30 Hz, 1H), 8.50 (dd, *J* = 9.17, 2.08 Hz, 1H), 8.66 (d, *J* = 4.84 Hz, 1H), 8.86 (d, *J* = 9.17 Hz, 1H),9.07 (d, *J* = 1.90 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 114.68, 115.89, 116.97, 123.42, 123.71, 134.28, 139.46, 145.34, 146.06, 148.70, 151.08. IR (KBr): 3069, 1611, 1589, 1522, 1483, 1445, 1356, 1042, 926, 804, 781, 737. HRMS (EI) calcd for $C_{11}H_7N_5O_2$ [M^+]: 241.0600, found: 241.0600.

5-Nitro-1-(3-nitrophenyl)-1*H*-benzo[*d*][1,2,3]triazole (2j): Pale yellow crystals (EtOAc/*n*-hexane), mp 182-183 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.03 (t, *J* = 8.18 Hz, 1H), 8.23 (d, *J* = 9.16 Hz, 1H), 8.41 (dd, *J* = 8.05, 1.12 Hz, 1H), 8.45-8.55 (m, 2H), 8.71 (t, *J* = 1.91 Hz, 1H), 9.20 (d, *J* = 1.58 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 112.42, 117.06, 118.47, 123.80, 124.18, 129.65, 131.85, 134.93, 136.33, 144.90, 145.02, 148.64. IR (KBr): 3104, 1616, 1531, 1354, 1043, 804, 737, 677. LCMS (ESI) calcd for $C_{12}H_8N_5O_4$ [M^++H]: 286.0571, found: 286.0572.

5-Nitro-1-(3-(phenylsulfonyl)phenyl)-1*H*-benzo[*d*][1,2,3]triazole (2k): Pale yellow crystals (EtOAc/*n*-hexane), mp 224-224.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62-7.79 (m, 3H), 7.98 (t, *J* = 8.00 Hz, 1H), 8.11 (t, *J* = 8.56 Hz, 3H), 8.25 (dd, *J* = 15.74, 8.02 Hz, 2H), 8.46-8.55 (m, 2H), 9.21 (d, *J* = 1.12 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6): δ112.30, 116.92, 122.00, 123.64, 127.70, 128.16, 129.91, 131.99, 134.18, 134.79, 136.43, 140.29, 143.04, 144.82, 144.97. IR (KBr): 3084, 3071, 1618, 1595, 1530, 1491, 1447, 1348, 1321, 1306, 1155, 911, 816, 739, 687. HRMS (ESI) calcd for $C_{18}H_{13}N_4O_4S$ [M^++H]: 381.0652, found: 381.0667.

3-(5-Nitro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)benzonitrile (2l): Pale yellow crystals (EtOAc/*n*-hexane), mp 219-220 °C. ^{1}H NMR (300 MHz, DMSO-d_6): 7.94 (t, *J* = 8.00 Hz, 1H), 8.16-8.10 (m, 1H), 8.28 (t, *J* =

7.70 Hz, 2H), 8.45-8.51 (m, 2H), 9.19 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): 112.61, 113.17, 116.95, 117.75, 123.61, 126.76, 128.29, 131.59, 133.34, 134.72, 136.22, 144.88, 144.96. IR (KBr): 3093, 2235, 1616, 1582, 1497, 1450, 1352, 1043, 802, 741, 685. HRMS (ESI) calcd for $C_{13}H_8N_5O_2$ [M^++H]: 266.0673, found: 266.0657.

Ethyl 3-(5-nitro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)benzoate (2m): Pale yellow crystals (EtOAc/*n*-hexane), mp 142.5-143.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.45 (t, *J* = 7.12 Hz, 3H), 4.47 (q, *J* = 7.12, 7.09 Hz, 2H), 7.78 (t, *J* = 7.91 Hz, 1H), 7.88 (d, *J* = 9.12 Hz, 1H), 7.98-8.05 (m, 1H), 8.27 (d, *J* = 7.81 Hz, 1H), 8.50 (dd, *J* = 9.11, 1.93 Hz, 1H), 8.45 (s, 1H), 9.11 (d, *J* = 1.84 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.43, 61.95, 110.98, 117.76, 123.72, 123.84, 127.29, 130.56, 130.51, 132.87, 134.95, 136.33, 145.15, 145.82, 165.16. IR (KBr): 3105, 2988, 1724, 1607, 1587, 1532, 1458, 1354, 1292, 1049, 802, 750, 739. HRMS (ESI) calcd for $C_{15}H_{13}N_4O_4$ [M^++H]: 313.0931, found: 313.0929.

6-Methyl-5-nitro-1-phenyl-1*H*-benzo[*d*][1,2,3]triazole (2n): Pale yellow crystals (EtOAc/*n*-hexane), mp 183-184 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.76 (s, 3H), 7.58 (t, *J* = 7.37 Hz, 1H), 7.70-7.64 (m, 3H), 7.76 (d, *J* = 8.02 Hz, 2H), 8.82 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.66, 112.92, 118.12, 123.21, 129.61, 130.27, 130.42, 133.95, 136.25, 144.25, 147.05. IR (KBr): 3065, 2926, 2855, 1624, 1595, 1524, 1501, 1462, 1435, 1351, 1285, 1055, 889, 856, 789, 764, 696. HRMS (ESI) calcd for $C_{13}H_{11}N_4O_2$ [M^++H]: 255.0877, found: 256.0877.

6-Methoxy-5-nitro-1-phenyl-1*H*-benzo[*d*][1,2,3]triazole (2o): Pale yellow crystals ($CHCl_3$/*n*-hexane), mp 183-184 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.02 (s, 3H), 7.15 (s, 1H), 7.59 (t, *J* = 7.29 Hz, 1H), 7.68 (t, *J* = 7.68 Hz, 2H), 7.73 (d, *J* = 7.74 Hz, 2H), 8.58 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 57.49, 93.86, 116.70, 123.31, 129.39, 130.26, 133.69, 152.11. IR (KBr): 3100, 2968, 2930, 1626, 1595, 1532, 1483, 1433, 1350, 1269, 899, 793, 762, 691. HRMS (ESI) calcd for $C_{13}H_{11}N_4O_2$ [M^++H]: 271.0826, found: 271.0828.

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