Note

Synthesis of N-(2-Hydroxyaryl)-Benzotriazoles via Metal-Free O-Arylation and N-O Bond Cleavage

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Synthesis of *N*-(2-Hydroxyaryl)-Benzotriazoles *via* Metal-Free *O*-Arylation and N-O Bond Cleavage

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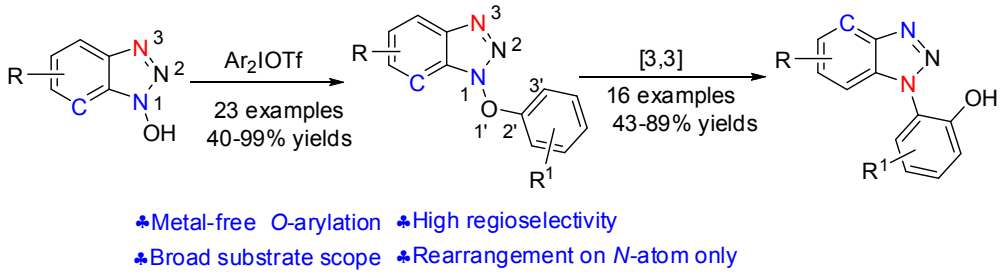


ABSTRACT: A metal-free method for synthesis of *N*-(2-hydroxyaryl)-benzotriazoles *via* *O*-arylation of *N*-hydroxybenzotriazoles with readily available diaryliodonium salts and sequential N−O bonds cleavage under mild conditions has been developed. The [3,3]-rearrangement of N−O bond cleavage could take place on *N*-atom instead of *C*-atom. The reaction was compatible with diverse functional groups and a new type of P, N-ligand was synthesized in three steps.

N-Arylbenzotriazoles are one of the most important classes of *N*-heterocycles in biological, pharmaceutical and medicinal chemistry.[1a] Many these structural motifs possess antiplasmodial, antibacterial, anticancer, and antifungal activities.[1b-e] They are

not only used as useful synthons in organic synthesis,[2] but also served as elegant *N*-ligands in transition-metal catalysis.[3] Thus, development of new methods for construction of the functionalized *N*-arylbenzotriazoles is an important field in organic chemistry. There were many strategies for synthesis of *N*-arylbenzotriazoles with satisfied yields, such as transition-metal catalyzed cross-coupling reaction,[4] palladium catalyzed C−H activation of aryltriazene compounds,[5] or relative transformations.[6] However, there was few efficient methods to prepare *N*-(2-hydroxyaryl)-benzotriazoles, which were also important scaffolds served as potassium channel activator and attracted in biological sciences (Figure 1). Only in 2001, Livi and coworkers demonstrated that *N*-(2-hydroxyphenyl)-benzotriazole can be prepared from anthranilic acid followed by cycloaddition with 2-nitrophenylazide or 2-hydroxyphenylazide in 28% and 54% yields respectively (Scheme 1-1).[7] Although a successful route to synthesize *N*-(2-hydroxyphenyl)-benzotriazole was developed, low yields and only one substrate has been shown. Hence, to explore an efficient strategy to synthesize these compounds is desirable.

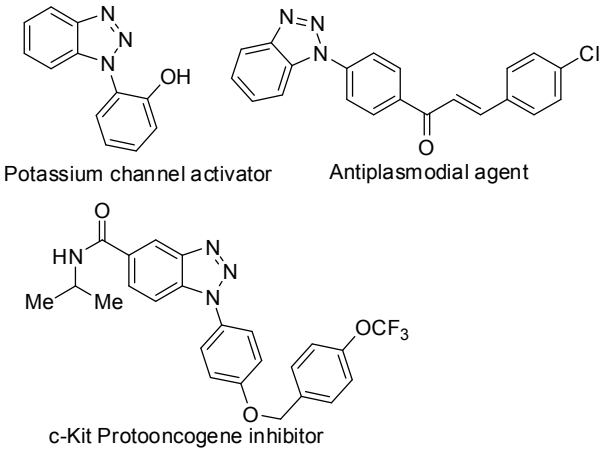
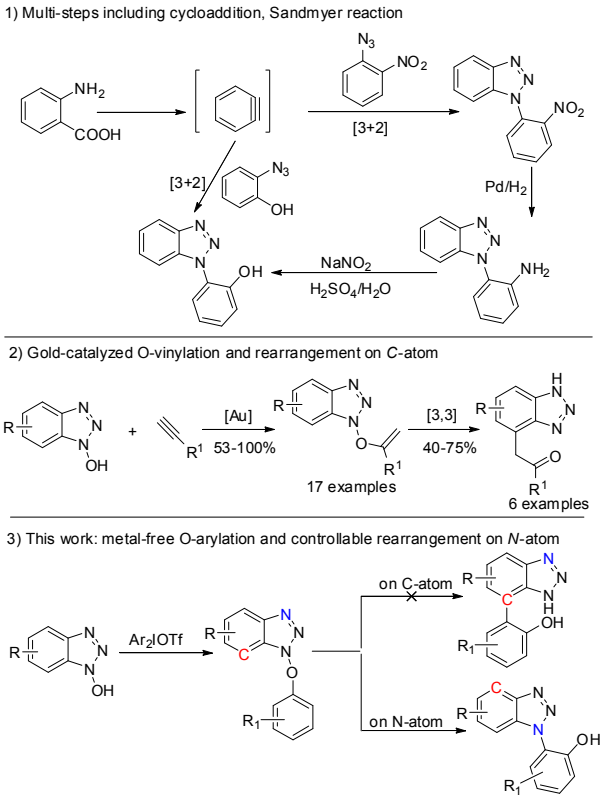


Figure 1. Some examples of biologically active scaffolds.

In the N−O bond system, the rearrangement was always preferably taken place on *C*-atom of aryl ring instead of *N*-atom or gave a mixture.[8] A recent example was reported by Hammond and Xu group in 2013.[8a] The authors developed a gold-catalyzed intermolecular addition of *N*-hydroxybenzotriazoles to terminal alkynes to give vinyl ethers in high yields and excellent regioselectivity, which preferably underwent a [3,3]-sigmatropic rearrangement on *C*-atom to provide highly functionalized benzotriazoles (Scheme 1-2). During the studies of arylation of N−O bonds with diaryliodonium salts in our group,[9,10] we have reported an efficient method to synthesize *N*-aryl benzotriazin-4-ones by *O*-arylation and [3,3]-rearrangement.[9b] The [3,3]-rearrangement of *O*-arylation products only took place on *N*-atom instead of *O*-atom. Continuing to explore the rearrangement of *O*-arylation products in *N*-hydroxybenzotriazoles, we observed that the rearrangement of N−O bond only took place on *N*-atom instead of *C*-atom. Hence, arylation of *N*-hydroxybenzotriazoles to form *O*-arylation products and sequential regioselective [3,3]-rearrangement on *N*-atom will provide diverse useful *N*-(2-hydroxyaryl)-benzotriazoles. Although *O*-arylation product has been obtained by Chan and coworkers *via* copper-mediated cross-coupling of *N*-hydroxybenzotriazole and arylboronic acid, only one example has been shown and no rearrangement product was reported.[11] Herein, we reported a simple, mild, and efficient metal-free strategy to prepare *N*-(2-hydroxyphenyl)-benzotriazoles (Scheme 1-3).

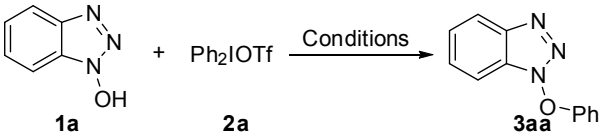


Scheme 1. Strategies for synthesis of *ortho*-(benzotriazol-1-yl)phenols

In order to investigate the rearrangement of *O*-arylation intermediate, the reaction conditions of *O*-arylation were optimized. Firstly, *N*-hydroxybenzotriazole **1a** with diphenyliodonium triflate **2a** was used as model substrates in different solvents, base and temperature (Table 1). The reaction occurred to afford the desired *O*-arylation product **3aa** in 81% yield in DCE (1,2-dichloroethane) when *t*-BuOK was used as base (Table 1, entry 1). The solvents such as MeOH and THF gave inferior results (Table 1, entries 4 and 5). Higher yields were obtained in toluene, MeCN, dioxane, DMF and DMSO (Table 1, entries 2-3 and 6-8). MeCN was chosen as the best solvent for *O*-arylation (Table 1, entry 3). The reaction was effective with *t*-BuOK, KOH, Cs_2CO_3, $NaHCO_3$, and Et_3N (Table 1, entries 9-13), and only 20% yield of **3aa** was observed using pyridine (Table 1, entry 12). When the reaction ran at 40 °C, **3aa** was

obtained in 55% yield and **3aa** was not detected while the reaction temperature was at 80 °C (Table 1, entries 3 and 14-16). Further controlled experiments confirmed that no **3aa** was afforded in the absence of base (Table 1, entry 17). To our delight, when **1a** was enlarged to 2.5 mmol in MeCN, product **3aa** was isolated in 98% yield (Table 1, entry 3). Hence, the optimal conditions were that *t*-BuOK was used as base in MeCN at 25 °C for 18 h.

Table 1. Optimization of reaction conditions.[a]



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

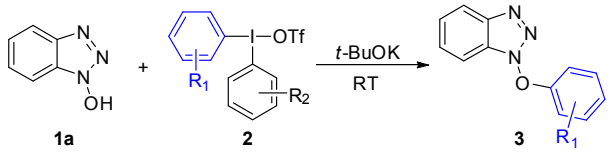
entry	base	solvent	T (°C)	**3aa** %[b]
1	*t*-BuOK	DCE	25	81
2	*t*-BuOK	toluene	25	72
3	*t*-BuOK	MeCN	25	99(98)[c]
4	*t*-BuOK	MeOH	25	12
5	*t*-BuOK	THF	25	54
6	*t*-BuOK	dioxane	25	90
7	*t*-BuOK	DMF	25	96
8	*t*-BuOK	DMSO	25	74
9	KOH	MeCN	25	95
10	Cs_2CO_3	MeCN	25	95
11	$NaHCO_3$	MeCN	25	42
12	pyridine	MeCN	25	20

13	Et_3N	MeCN	25	97
14	*t*-BuOK	MeCN	40	55
15	*t*-BuOK	MeCN	60	20
16	*t*-BuOK	MeCN	80	<5
17	-	MeCN	80	0

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.75 mmol, 1.5 equiv), base (0.75 mmol, 1.5 equiv), solvent (5 mL), 18−24 h; [b] Isolated yields. [c] **1a** was used as 2.5 mmol.

Next, the scope of present protocols was studied for diaryliodonium salts having substituents on the aryl rings. As shown in Table 2, both electron-rich and electron-deficient diaryliodonium salts **2**, with *para*, *meta*, or *ortho*-substituents provided the corresponding products **3aa-3am** in good to excellent yields. The electron-donating groups such as methoxy, methyl gave lower yields of *O*-arylation products (Table 2, entries 2-3), and the major products were the [3,3]-rearrangement products which have been developed as one-pot reaction (see Table 5). When unsymmetrical diaryliodonium salts were tested, the *O*-arylation reaction proceeded smoothly with good chemoselectivity and electron-deficient aryl moieties were preferentially transferred to product **3** (Table 2, entries 9-14).[12] The bromo, chloro, nitro, and ester functional groups were all well tolerated for the iodonium reagents in this transformation.

Table 2. The scope of diaryliodonium salts **2**.[a]



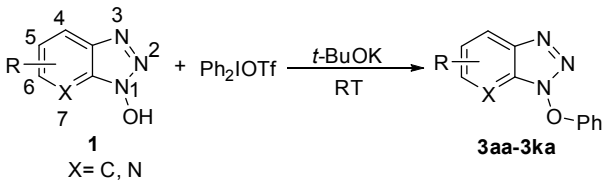
1a **2** **3**

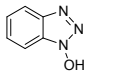
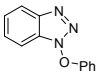
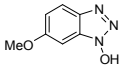
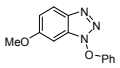
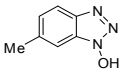
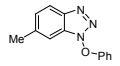
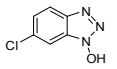
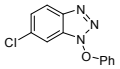
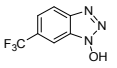
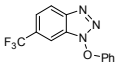
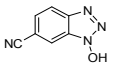
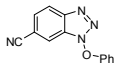
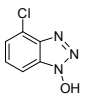
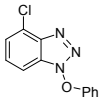
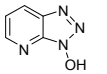
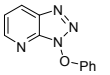
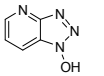
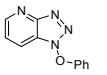
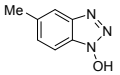
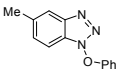
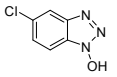
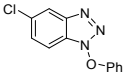
entry	**2**	R^1	R^2	**3**	yield %[b]
1	**2a**	H	H	**3aa**	99
2	**2b**	4-MeO	4-MeO	**3ab**	<5
3	**2c**	4-Me	4-Me	**3ac**	40
4	**2d**	4-Cl	4-Cl	**3ad**	82
5	**2e**	4-F	4-F	**3ae**	57
6	**2f**	3,5-Me_2	3,5-Me_2	**3af**	89
7	**2g**	3-NO_2	3-NO_2	**3ag**	92
8	**2h**	2-Me	2-Me	**3ah**	65
9	**2aa**	H	4-MeO	**3aa**	92
10	**2i**	4-Ph	4-MeO	**3ai**	61
11	**2j**	4-Br	4-MeO	**3aj**	83
12	**2k**	3-Br	4-MeO	**3ak**	81
13	**2l**	2-Br	4-MeO	**3al**	68
14	**2m**	4-CO_2Me	H	**3am**	90

[a] Reaction conditions: **1a** (0.5 mmol), **2** (0.75 mmol, 1.5 equiv), *t*-BuOK (0.75 mmol, 1.5 equiv), MeCN (5 mL), 25 °C, 18−24 h; [b] Isolated yields.

In addition to screening the diaryliodonium salts, a variety of substituted *N*-hydroxybenzotriazoles were examined (Table 3). We found that product **3** was afforded in good to excellent yields when substituted *N*-hydroxybenzotriazoles with both electron-rich groups (Table 3, entries 2-3) and electron-deficient groups were subjected into the optimal conditions (Table 3, entries 4-7). Moreover, *N*-hydroxy-7-azabenzotriazole **1h** and *N*-hydroxy-4-azabenzotriazole **1i** provided desired product **3ha** and **3ia** in 90% yield and 60% yield respectively (Table 3, entries 8 and 9). However, when there were methyl and chloro substituents in 5-position of **1** such as **1j** and **1k**, the yields decreased to moderate (Table 3, entries 10-11).

Table 3. The scope of *N*-hydroxybenzotriazoles **1** [a,b]



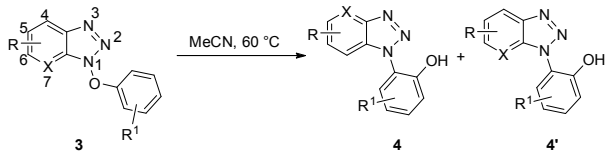
entry		1	3		yield%
1	**1a**			**3aa**	99
2	**1b**			**3ba**	99
3	**1c**			**3ca**	86
4	**1d**			**3da**	81
5	**1e**			**3ea**	74
6	**1f**			**3fa**	62
7	**1g**			**3ga**	50
8	**1h**			**3ha**	90
9	**1i**			**3ia**	60
10	**1j**			**3ja**	36
11	**1k**			**3ka**	43

[a] Reaction conditions: **1** (0.5 mmol), **2a** (0.75 mmol, 1.5 equiv), *t*-BuOK (0.75 mmol, 1.5 equiv), MeCN (5 mL), 25 °C, 18−24 h; [b] Isolated yields.

With the *O*-arylation products in hand, the N−O rearrangement reaction was investigated. When various substrates **3** were subjected to MeCN at 60 °C,[13] the desired rearrangement products **4** were obtained in 43-89% yields (Table 4). The results showed that the rearrangement only took place on *N*-atom instead of *C*-atom. The reaction ran smoothly with both electron-donating groups and

electron-withdrawing groups on both aryl rings. The regioselectivity of [3,3]-rearrangement was excellent when R^1 group was 3-NO_2 substituent (Table 4, entry 4). The functional groups were tolerated well, such as bromide, chloride, nitro, and ester groups which will make more potential synthetic applications of *N*-(2-hydroxyaryl)-benzotriazoles. For products **4aa-am**, the [3,3] and [1,3]-rearrangement structures were the same products so that it was hard to determine the selectivity of [3,3] and [1,3]-rearrangement (Table 4, entries 1-7). When there were substituted groups on aryl ring of benzotriazole moiety in **3,** a mixed product of [3,3] and [1,3]-rearrangement on *N*-atom was obtained. The ratio of rearrangement products was depended on the substituted groups (Table 4, entries 9-13). The structure of [3,3] and [1,3]-rearrangement products was determined by 2D NMR spectra of **4ba-ka**. When there was *N*-atom on 7-position in **3ha**, the rearrangement still occurred on N3-atom (Table 4, entry 8). Both electron-donating and electron-withdrawing groups gave [3,3]-rearrangement products as major isomers except for **3ba** with a methoxy group on 6-position providing the [3,3]-rearrangement and [1,3]-rearrangement product as 1:1 ratio (Table 4, entries 9 *vs* 10-13).

Table 4. The thermal rearrangement of *O*-arylation product **3** [a,b]



3 X= C, N **4** [3,3]-product **4'** [1,3]-product

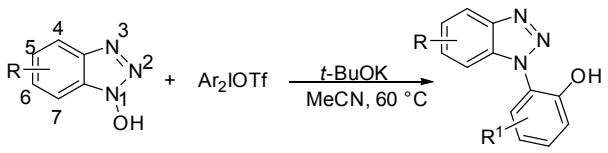
entry	**3**	R	R^1	**4**	yield %
1	**3aa**	H	H	**4aa**	70
2	**3ac**	H	4-Me	**4ac**	52
3	**3af**	H	3,5-Me_2	**4af**	71

4	**3ag**	H	3-NO_2	**4ag**	57 (20:1)[c]
5	**3ah**	H	2-Me	**4ah**	57
6	**3aj**	H	4-Br	**4aj**	57
7	**3am**	H	4-CO_2Me	**4am**	86
8	**3ha**	H	H	**4ha**	61 (20:1)[d]
9	**3ba**	6-OMe	H	**4ba**	85 (1:1)[d]
10	**3da**	6-Cl	H	**4da**	89 (10:1)[d]
11	**3ea**	6-CF_3	H	**4ea**	81 (10:1)[d]
12	**3ja**	5-Me	H	**4ja**	63 (10:1)[d]
13	**3ka**	5-Cl	H	**4ka**	43 (10:1)[d]

[a] Reaction conditions: **3** (0.5 mmol), MeCN (5 mL), 60 °C, 18-24 h; [b] Isolated yields; [c] regioselectivity for [3,3]-rearrangement on aryl ring, >20:1; [d] the ratio of [3,3]-product and [1,3]-product.

During the study of the scope of diaryliodonium salts in Table 2, we found iodonium reagents with electron-donating groups only gave the rearrangement product instead of *O*-arylation product (Table 2, entry 2), which inspired us to develop one-pot reaction to prepare *N*-(2-hydroxyaryl)-benzotriazoles from *N*-hydroxybenzotriazole **1** with iodonium reagent **2**. The results were summarized in Table 5. It showed that the reaction tolerated well for *N*-hydroxybenzotriazoles and diaryliodonium salts. In contrast to Table 4, the ratios of [3,3]- and [1,3]-rearrangement products were the same either by two steps or one-pot reaction (Table 4 *vs* Table 5, **4da** and **4ea**). However, when diaryliodonium salt **2b** was used, the ratio of [3,3]- and [1,3]-rearrangement products turned bad (Table 5, entries 6-8).

Table 5. Synthesis of *N*-(2-hydroxyaryl)-benzotriazole **4** in one-pot reaction [a]

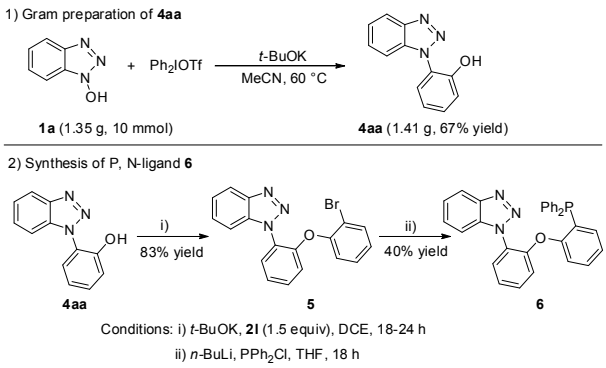


1 (1a, 1d-e) **2 (2a, 2b, 2n)** **4**

entry	**1**	**2**	Ar	**4**	yield %[b]
1	**1a**	**2a**	Ph	**4aa**	69
2	**1a**	**2b**	4-$MeOC_6H_4$	**4ab**	79
3	**1a**	**2n**	4-*t*-BuC_6H_4	**4an**	82
4	**1d**	**2a**	Ph	**4da**	68 (10:1)[c]
5	**1e**	**2a**	Ph	**4ea**	64 (10:1)[c]
6	**1c**	**2b**	4-$MeOC_6H_4$	**4cb**	85 (2.5:1)[c]
7	**1d**	**2b**	4-$MeOC_6H_4$	**4db**	64 (1.4:1)[c]
8	**1f**	**2b**	4-$MeOC_6H_4$	**4fb**	50 (1:1)[c]

[a] Reaction conditions: **1** (0.5 mmol), **2** (0.75 mmol, 1.5 equiv), *t*-BuOK (0.75 mmol, 1.5 equiv), MeCN (5 mL), 60 °C, 18-24 h; [b] Isolated yields; [c] The ratio of [3,3]-rearrangement and [1,3]-rearrangement products.

To better apply this process in synthetic transformations, a gram scale of **1a** was subjected to the optimal conditions, the desired product **4aa** was afforded in 67% yield with 1.41 g (Scheme 2-1). Treatment of **4aa** with iodonium reagent **2l** under *t*-BuOK in DCE at room temperature provided *O*-arylation product **5** in 83% yield, which was easily converted to P, N-ligand **6** in 40% yield. This method will allow further studies on this type of P, N-ligand containing benzotriazole in transition-metal catalysis (Scheme 2-2).[3c,d]



Scheme 2 Application of **4aa**

In summary, we have developed a metal-free strategy to prepare *N*-(2-hydroxyaryl)-benzotriazoles from good to excellent yields under mild conditions. The reaction not only went through *O*-arylation and sequential [3,3]-rearrangement in two steps, but also could run in one-pot reaction in good yields. It was compatible with lots of functional groups as well as *N*-heterocycle substrates. *N*-(2-Hydroxyaryl)-benzotriazoles could be easily converted to a new type of P, N-ligand in two steps.

EXPERIMENTAL SECTION

General Methods. All reactions were performed under an atmosphere of air. Commercially available reagents were used without further purification. The NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on 400 MHz, or 500 MHz instrument with TMS as the internal standard. NMR data are represented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in hertz (Hz), and integration. IR spectra were recorded on FT-IR spectrometer, and only major peaks are reported in cm^{-1}. HRMS were measured in ESI mode and the mass analyzer of the HRMS was TOF. Flash column

chromatography was performed on silica gel (300−400 mesh).

General procedure for synthesis of *O*-arylation products 3 (Table 2 and **Table 3):** In a 25 mL Schlenk tube was charged with **1** (0.5 mmol) and MeCN (5 mL). *t*-BuOK (0.75 mmol, 1.5 equiv) was added in one portion at room temperature. The mixture was stirred vigorously at room temperature for 5 min. Then, diaryliodonium salts **2** (0.75 mmol, 1.5 equiv) was added in one portion. The reaction mixture was stirred vigorously at room temperature for 18−24 h until the substrate **1** disappeared (monitored by TLC). At this time, the solvent was removed under reduced pressure and the crude product was purified by flash chromatography (the crude residue was dry loaded on silica gel; 1 / 20 − 1 / 5, ethyl acetate / petroleum ether) to provide product **3** as solid.

1-Phenoxy-1H-benzo[1,2,3]triazole (3aa), white solid, 0.104 g, 99% yield. mp: 64−65 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02 (d, J = 8.5 Hz, 1H), 7.45 (d, J = 3.0 Hz, 2H), 7.38−7.35 (m, 1H), 7.28 (t, J = 8.0 Hz, 2H), 7.12 (t, J = 7.5 Hz, 1H), 6.86 (d, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.2, 143.4, 129.9, 128.6, 127.7, 125.2, 124.9, 120.4, 113.9, 108.7; IR (thin film) 3415, 3064, 2876, 1782, 1486, 1376, 1243, 1084, 744, 681 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{12}H_{10}N_3O$ $(M+H)^+$ 212.0824, found 212.0815.

1-(p-Tolyloxy)-1H-benzo[d][1,2,3]triazole (3ac)[11], white solid, 0.045 g, 40% yield. mp: 58−59 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 7.2 Hz, 1H), 7.52 (d, J = 5.0 Hz, 2H), 7.44−7.42 (m, 1H), 7.13 (d, J = 6.4 Hz, 2H), 6.87 (d, J = 7.2 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.3, 143.4, 135.0, 130.3, 128.5, 127.7,

124.8, 120.4, 114.1, 108.7, 20.6; IR (thin film) 3435, 3036, 2923, 1602, 1501, 1374, 1238, 1083, 801, 749 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{13}H_{12}N_3O$ $(M+H)^+$ 226.0980, found 226.0950.

1-(4-Chlorophenoxy)-1H-benzo[d][1,2,3]triazole (3ad), white solid, 0.100 g, 82% yield. mp: 55−56 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 8.11 (d, J = 8.0 Hz, 1H), 7.57−7.50 (m, 2H), 7.47 (t, J = 7.5 Hz, 1H), 7.32 (d, J = 8.5 Hz, 2H), 6.92 (d, J = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.7, 143.4, 130.0, 128.8, 125.1, 120.8, 115.6, 108.5; IR (thin film) 3418, 3069, 1616, 1483, 1373, 1238, 1081, 818, 737 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{12}H_7N_3ClO$ $(M-H)^-$ 244.0278, found 244.0283.

1-(4-Fluorophenoxy)-1H-benzo[d][1,2,3]triazole (3ae), white solid, 0.065 g, 57% yield. mp: 51−52 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 8.10 (d, J = 8.5 Hz, 1H), 7.56−7.55 (m, 2H), 7.47−7.44 (m, 1H), 7.06 (t, J = 8.5 Hz, 2H), 7.00−6.98 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.7 (d, J = 243.2 Hz), 155.1, 143.4, 128.8, 127.5, 125.0, 120.5, 116.7 (d, J = 23.7 Hz), 116.2 (d, J = 8.2 Hz), 108.5; IR (thin film) 3419, 3073, 2977, 1614, 1499, 1378, 1230, 1082, 833, 738 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{12}H_9N_3OF$ $(M+H)^+$ 230.0730, found 230.0722.

1-(3,5-Dimethylphenoxy)-1H-benzo[d][1,2,3]triazole (3af), white solid, 0.106 g, 89% yield. mp: 53−54 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 8.0 Hz, 1H), 7.53 (t, J = 2.4 Hz, 2H), 7.45−7.42 (m, 1H), 6.80 (s, 1H), 6.56 (s, 2H), 2.25 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4, 143.5, 140.1, 128.5, 127.8, 126.9, 124.8, 120.4, 111.7, 108.8, 21.3; IR (thin film) 3416, 3060, 2920, 1781, 1451, 1375, 1278, 1082, 837, 742 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{14}H_{13}N_3ONa$ $(M+Na)^+$ 262.0956, found

262.0945.

1-(3-Nitrophenoxy)-1H-benzo[d][1,2,3]triazole (3ag), yellowish solid, 0.118 g, 92% yield. mp: 105−106 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (d, J = 8.5 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H), 7.83 (s, 1H), 7.62−7.49 (m, 4H), 7.30−7.28 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.3, 149.1, 143.4, 131.0, 129.3, 127.5, 125.4, 120.7, 120.1, 120.0, 109.6, 108.2; IR (thin film) 3423, 3098, 2924, 1727, 1532, 1349, 1276, 1081, 766, 736 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{12}H_7O_3N_4$ $(M-H)^-$ 255.0518, found 255.0525.

1-(o-Tolyloxy)-1H-benzo[d][1,2,3]triazole (3ah), white solid, 0.073 g, 65% yield. mp: 58−59 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02 (d, J = 8.5 Hz, 1H), 7.45−7.44 (m, 2H), 7.37 (t, J = 7.5 Hz, 1H), 7.06 (t, J = 8.5 Hz, 2H), 6.79 (t, J = 8.5 Hz, 2H), 2.24 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.3, 143.4, 135.0, 130.3, 128.5, 127.7, 124.8, 120.4, 114.1, 108.7, 20.6; IR (thin film) 3415, 3063, 2981, 1776, 1486, 1375, 1266, 1083, 835, 743 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{13}H_{10}N_3O$ $(M-H)^-$ 224.0824, found 224.0829.

1-(Biphenyl-4-yloxy)-1H-benzo[d][1,2,3]triazole (3ai), white solid, 0.075 g, 61% yield. mp: 121−122 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (d, J = 8.5 Hz, 1H), 7.49−7.44 (m, 6H), 7.39−7.34 (m, 3H), 7.29 (t, J = 7.0 Hz, 1H), 6.95 (t, J = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.7, 143.4, 139.7, 138.5, 128.8, 128.7, 128.6, 127.7, 127.4, 126.9, 125.0, 120.5, 114.4, 108.7; IR (thin film) 3417, 3065, 2963, 1601, 1484, 1375, 1267, 1083, 754, 695 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{14}N_3O$ $(M+H)^+$ 288.1137, found 288.1127.

1-(4-Bromophenoxy)-1H-benzo[d][1,2,3]triazole (3aj), white solid, 0.119 g, 83% yield. mp: 55−56 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 8.0 Hz, 1H), 7.54−7.51 (m, 2H), 7.49−7.43 (m, 3H), 6.85 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.2, 143.3, 132.9, 128.8, 127.5, 125.1, 120.4, 117.9, 115.9, 108.4; IR (thin film) 3419, 3086, 2960, 1738, 1479, 1370, 1269, 1069, 815, 735 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{12}H_7N_3OBr$ $(M-H)^-$ 287.9772, found 287.9780.

1-(3-Bromophenoxy)-1H-benzo[d][1,2,3]triazole (3ak), yellow solid, 0.117 g, 81% yield. mp: 56−57 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (d, J = 8.5 Hz, 1H), 7.57−7.52 (m, 2H), 7.47−7.44 (m, 1H), 7.34 (d, J = 7.5 Hz, 1H), 7.23−7.19 (m, 1H), 7.15 (s, 1H), 6.88−6.86 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.6, 143.4, 131.1, 128.9, 128.5, 127.6, 125.1, 123.2, 120.6, 117.6, 112.8, 108.5; IR (thin film) 3418, 3072, 1788, 1466, 1372, 1265, 1086, 773, 745 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{12}H_7N_3OBr$ $(M-H)^-$ 287.9772, found 287.9780.

1-(2-Bromophenoxy)-1H-benzo[d][1,2,3]triazole (3al), white solid (0.098 g, 68%). mp: 82−83 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 (d, J = 8.5 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.56−7.53 (m, 1H), 7.46 (t, J = 8.0 Hz, 1H), 7.19 (d, J = 7.5 Hz, 1H), 7.10 (d, J = 7.5 Hz, 1H), 6.71 (d, J = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.5, 143.3, 134.1, 128.9, 128.8, 127.7, 126.6, 125.1, 120.5, 120.4, 115.5, 108.8; IR (thin film) 3418, 3065, 2961, 1781, 1442, 1371, 1266, 1029, 742, 662 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{12}H_7N_3OBr$ $(M-H)^-$ 287.9772, found 287.9779.

Methyl 4-(1H-benzo[d][1,2,3]triazol-1-yloxy)benzoate (3am), white solid, 0.121 g,

90% yield. mp: 123−124 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 8.0 Hz, 1H), 7.98 (d, J = 8.0 Hz, 2H), 7.48−7.39 (m, 3H), 6.88 (d, J = 8.0 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 162.3, 143.4, 131.9, 129.0, 127.6, 127.1, 125.2, 120.6, 113.4, 108.5, 52.2; IR (thin film) 3417, 2950, 1713, 1436, 1386, 1278, 1108, 752, 685 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{14}H_{12}O_3N_3$ $(M+H)^+$ 270.0879, found 270.0866.

6-Methoxy-1-phenoxy-1H-benzo[d][1,2,3]triazole (3ba), white solid, 0.121 g, 99% yield. mp: 72−73 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 8.6 Hz, 1H), 7.29 (t, J = 7.2 Hz, 2H), 7.12 (d, J = 7.2 Hz, 1H), 6.98 (d, J = 8.6 Hz, 1H), 6.98 (d, J = 8.0 Hz, 2H), 6.69 (s ,1H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.9, 159.2, 138.8, 129.9 129.0, 125.0, 121.2, 117.7, 113.7, 88.3, 55.8; IR (thin film) 3428, 3070, 2958, 1721, 1458, 1346, 1230, 1018, 828, 752 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{13}H_{12}O_2N_3$ $(M+H)^+$ 242.0930, found 242.0920.

6-Methyl-1-phenoxy-1H-benzo[d][1,2,3]triazole (3ca), white solid, 0.097 g, 86% yield. mp: 70−71 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J = 8.4 Hz, 1H), 7.28 (t, J = 8.0 Hz, 2H), 7.19−7.15 (m, 2H), 7.11 (t, J = 7.2 Hz, 1H), 6.85 (d, J = 8.0 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 142.1, 139.6, 129.9, 128.1, 127.2, 125.0, 119.8, 113.9, 107.6, 21.8; IR (thin film) 3419, 3055, 2969, 1726, 1480, 1375, 1270, 1069, 812, 754 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{13}H_{12}ON_3$ $(M+H)^+$ 226.0980, found 226.0972.

6-Chloro-1-phenoxy-1H-benzo[d][1,2,3]triazole (3da), white solid, 0.099 g, 81% yield. mp: 76−77 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02 (d, J = 9.0 Hz, 1H), 7.54 (s,

1H), 7.41−7.35 (m, 3H), 7.22 (t, J = 7.5 Hz, 1H), 6.95 (d, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.1, 142.0, 135.3, 130.1, 128.4, 126.3, 125.5, 121.5, 114.1, 108.5; IR (thin film) 3417, 3090, 2943, 1780, 1477, 1370, 1263, 1087, 822, 750 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{12}H_9N_3OCl$ $(M+H)^+$ 246.0433, found 246.0439.

1-Phenoxy-6-(trifluoromethyl)-1H-benzo[d][1,2,3]triazole (3ea), white solid, 0.103 g, 74% yield. mp: 105−106 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.24 (d, J = 9.0 Hz, 1H), 7.87 (s, 1H), 7.69 (d, J = 9.0 Hz, 1H), 7.40 (t, J = 8.0 Hz, 2H), 7.24−7.21 (m, 1H), 6.98 (d, J = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.1, 144.5, 131.4 (q, J = 33.3 Hz), 130.2, 127.2, 125.7, 124.6 (q, J = 270.7 Hz), 121.8 (q, J = 2.7 Hz), 121.7, 114.2, 107.2 (q, J = 4.6 Hz); IR (thin film) 3433, 3102, 2956, 1747, 1486, 1310, 1166, 939, 754, 667 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{13}H_7N_3F_3O$ $(M-H)^-$ 278.0541, found 278.0547.

1-Phenoxy-1H-benzo[d][1,2,3]triazole-6-carbonitrile (3fa), white solid, 0.073 g, 62% yield. mp: 122−123 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, J = 8.4 Hz, 1H), 7.88 (s, 1H), 7.60 (d, J = 8.8 Hz, 1H), 7.34−7.30 (m, 2H), 7.19 (d, J = 8.4 Hz, 1H), 6.91 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0, 144.3, 130.3, 127.7, 127.2, 125.9, 122.0, 117.7, 114.6, 114.2, 112.3; IR (thin film) 3417, 3099, 2978, 1721, 1484, 1375, 1275, 1068, 829, 749 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{13}H_7N_4O$ $(M-H)^-$ 235.0620, found 235.0625.

4-Chloro-1-phenoxy-1H-benzo[d][1,2,3]triazole (3ga), pale yellow solid, 0.062g, 50% yield. mp: 67−68 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (s, 3H), 7.29 (t, J = 7.6 Hz, 2H), 7.18−7.12 (m, 1H), 6.86 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz,

$CDCl_3$): δ 159.1, 140.9, 130.0, 129.5, 129.1, 126.1, 125.5, 124.8, 114.0, 107.4; IR (thin film) 3415, 3071, 2927, 1773, 1484, 1376, 1227, 1091, 778, 747 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{12}H_9ON_3Cl$ $(M+H)^+$ 246.0434, found 246.0425.

3-Phenoxy-3H-[1,2,3]triazolo[4,5-b]pyridine (3ha), white solid, 0.095 g, 90% yield. mp: 84−85 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 8.75 (d, J = 8.0 Hz, 1H), 8.45 (t, J = 8.5 Hz, 1H), 7.46−7.44 (m, 1H), 7.37−7.34 (m, 2H), 7.22 (t, J = 7.5 Hz, 1H), 7.12 (d, J = 8.0 Hz, 2H); ^{13}C NMR (125MHz, $CDCl_3$): δ 159.4, 151.8, 140.0, 135.0, 129.9, 129.4, 125.6, 120.9, 115.1; IR (thin film) 3417, 3066, 2925, 1586, 1482, 1381, 1236, 1018, 775, 750 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{11}H_9N_4O$ $(M+H)^+$ 213.0776, found 213.0770.

1-Phenoxy-1H-[1,2,3]triazolo[4,5-b]pyridine (3ia), yellow solid, 0.064 g, 60% yield. mp: 98−99 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.86 (d, J = 3.6 Hz, 1H), 7.98 (d, J = 7.6 Hz, 1H), 7.55−7.52 (m, 1H), 7.41 (t, J = 8.0 Hz, 2H), 7.26 (t, J = 7.6 Hz, 1H), 6.99 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 154.1, 149.3, 130.1, 125.7, 123.4, 120.3, 117.9, 114.1; IR (thin film) 3432, 2344, 1583, 1482, 1383, 1269, 1153, 754, 684 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{11}H_9N_4O$ $(M+H)^+$ 213.0776, found 213.0767.

5-Methyl-1-phenoxy-1H-benzo[d][1,2,3]triazole (3ja)**,** yellow solid, 0.041 g, 36% yield. mp: 92−93 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.84−7.80 (m, 1H), 7.40−7.34 (m, 4H), 7.18−7.16 (m, 1H), 6.92−6.91 (m, 2H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 144.1, 135.2, 130.8, 130.0, 126.2, 125.1, 119.3, 113.9, 108.2, 21.5; IR (thin film) 3436, 2923, 1586, 1480, 1367, 1238, 1159, 1083, 802, 755 cm^{-1};

HRMS (ESI) *m/z* calcd for $C_{13}H_{12}N_3O$ $(M+H)^+$ 226.0980, found 226.0975.

5-Chloro-1-phenoxy-1H-benzo[d][1,2,3]triazole (3ka), yellow solid, 0.053 g, 43% yield. mp: 77−78 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (s, 1H), 7.51−7.47 (m, 2H), 7.37 (t, J = 7.0 Hz, 2H), 7.22 (t, J = 7.0 Hz, 1H), 6.94 (d, J = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 144.0, 131.0, 130.1, 129.7, 126.5, 125.5, 119.8, 114.0, 109.7; IR (thin film) 3433, 2925, 1585, 1477, 1373, 1261, 1151, 799, 744 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{12}H_9N_3OCl$ $(M+H)^+$ 246.0434, found 246.0430.

General procedure for synthesis of rearrangement products 4 from 3 (Table 4): In a 25 mL Schlenk tube was charged with **3** (0.5 mmol) and MeCN (5 mL). The reaction mixture was stirred vigorously at 60 °C for 18−24 h until the substrate **3** disappeared (monitored by TLC). At this time, the solvent was removed under reduced pressure and the crude product was purified by flash chromatography (the crude residue was dry loaded on silica gel; 1 / 10 − 1 / 1, ethyl acetate / petroleum ether) to provide product **4** as solid.

2-(1H-Benzo[d][1,2,3]triazol-1-yl)phenol (4aa), white solid, 0.073 g, 70% yield. mp: 205−206 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.39 (s, 1H), 8.14 (d, J = 8.5 Hz, 1H), 7.58−7.55 (m, 1H), 7.50−7.44 (m, 4H), 7.18 (d, J = 7.0 Hz, 1H), 7.07−7.03 (m, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 152.4, 145.4, 134.0, 131.6, 128.5, 128.2, 124.5, 123.7, 120.0, 119.6, 117.5, 112.0; IR (thin film) 3424, 3074, 2966, 1601, 1463, 1277, 1099, 1011, 785, 742 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{12}H_8N_3O$ $(M-H)^-$ 210.0667, found 210.0672.

2-(1H-Benzo[d][1,2,3]triazol-1-yl)-4-methylphenol (4ac), white solid, 0.059 g, 52%

yield. mp: 196−197 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.11 (brs, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.58 (t, J = 7.6 Hz, 1H), 7.47−7.43 (m, 2H), 7.30−7.25 (m, 2H), 7.08 (d, J = 8.4 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 149.9, 145.4, 134.0, 132.0, 129.1, 129.1, 128.5, 128.2, 124.4, 123.3, 119.6, 117.3, 112.1, 20.2; IR (thin film) 3668, 3426, 2977, 1617, 1395, 1247, 1062, 888, 734 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{13}H_{11}N_3ONa$ $(M+Na)^+$ 248.0800, found 248.0791.

2-(1H-Benzo[d][1,2,3]triazol-1-yl)-4,6-dimethylphenol (4af), white solid, 0.085 g, 71% yield. mp: 85−86 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.4 Hz, 1H), 7.40 (t, J = 8.0 Hz, 1H), 7.26−7.22 (m, 2H), 6.80 (s, 1H), 6.69 (s, 1H), 2.31 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.2, 145.1, 141.7, 136.5, 133.9, 128.1, 124.4, 123.5, 119.8, 119.4, 115.8, 110.2, 21.4, 17.4; IR (thin film) 3098, 2922, 1597, 1452, 1320, 1273, 1106, 1055, 839, 746 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{14}H_{14}N_3O$ $(M+H)^+$ 240.1137, found 240.1129.

2-(1H-Benzo[d][1,2,3]triazol-1-yl)-5-nitrophenol (4ag), white solid, 0.073 g, 57% yield. mp: 241−242 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.49 (s, 1H), 8.19 (d, J = 8.4 Hz, 1H), 7.75−7.68 (m, 2H), 7.64 (t, J = 7.6 Hz, 1H), 7.57 (s, 1H), 7.55−7.48 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 155.0, 147.6, 145.3, 134.3, 132.4, 129.0, 124.9, 122.6, 119.9, 116.0, 115.7, 111.5; IR (thin film) 3666, 3405, 2978, 1611, 1532, 1366, 1254, 1066, 811, 741 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{12}H_9N_4O_3$ $(M+H)^+$ 257.0675, found 257.0665.

2-(1H-Benzo[d][1,2,3]triazol-1-yl)-6-methylphenol (4ah), white solid, 0.064 g, 57% yield. mp: 179−180 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.23 (s, 1H), 8.15 (d, J =

8.5 Hz, 1H), 7.57−7.54 (m, 1H), 7.47−7.44 (m, 2H), 7.38 (d, J = 7.5 Hz, 1H), 7.28 (d, J = 7.5 Hz, 1H), 7.00 (d, J = 7.5 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 150.4, 145.5, 134.2, 132.6, 128.2, 127.8, 125.9, 124.6, 124.4, 120.2, 119.7, 111.8, 17.0; IR (thin film) 3417, 2975, 2693, 1592, 1478, 1357, 1219, 1065, 785, 738 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{13}H_{12}N_3O$ $(M+H)^+$ 226.0980, found 226.0972.

2-(1H-Benzo[d][1,2,3]triazol-1-yl)-4-bromophenol (4aj), white solid, 0.082 g, 57% yield. mp: 227−229 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.76 (s, 1H), 8.16 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 2.4 Hz, 1H), 7.66−7.63 (m, 1H), 7.58 (d, J = 6.8 Hz, 1H), 7.52−7.47 (m, 2H), 7.15 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.0, 145.4, 134.2, 133.9, 130.8, 128.5, 125.0, 124.6, 119.7, 119.4, 112.0, 110.2; IR (thin film) 3660, 3080, 2964, 1721, 1593, 1498, 1393, 1280，1075，742 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{12}H_8N_3OBrNa$ $(M+Na)^+$ 311.9748, found 311.9732.

Methyl 3-(1H-benzo[d][1,2,3]triazol-1-yl)-4-hydroxybenzoate (4am), white solid 0.115 g, 86% yield. mp: 241−242 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.47 (s, 1H), 8.17 (d, J = 8.0 Hz, 1H), 8.08−8.06 (m, 2H), 7.61−7.57 (m, 1H), 7.53−7.46 (m, 2H), 7.30 (t, J = 8.4 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.7, 156.8, 145.4, 133.9, 132.8, 129.8, 128.5, 124.7, 123.8, 121.5, 119.8, 117.7, 112.0, 52.5; IR (thin film) 3422, 2975, 2615, 1725, 1610, 1432, 1278, 1050, 881, 754 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{14}H_{12}N_3O_3$ $(M+H)^+$ 270.0879, found 270.0870.

2-(1H-[1,2,3]Triazolo[4,5-b]pyridin-1-yl)phenol (4ha), white solid, 0.065 g, 61% yield. mp: 220−221 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.52 (s, 1H), 8.78 (d, J =

3.6 Hz, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.64 (dd, J = 8.4 Hz, 4.0 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.20 (d, J = 8.0 Hz, 1H), 7.09 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 157.0, 152.0, 148.7, 131.8, 128.2, 126.5, 123.6, 123.4, 121.7, 120.2, 117.5; IR (thin film) 3409, 3097, 2967, 2735, 1598, 1516, 1464, 1280, 1094, 1005, 785, 749 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{11}H_9N_4O$ $(M+H)^+$ 213.0776, found 213.0768.

2-(5-Methoxy-1H-benzo[d][1,2,3]triazol-1-yl)phenol (4ba), white solid, 0.102 g, 85% yield. mp: 190−191 °C; (*Major isomer*) ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.35 (s, 1H), 8.00 (d, J = 8.8 Hz, 1H), 7.54 (d, J = 1.6 Hz, 1H), 7.48−7.42 (m, 2H), 7.37 (d, J = 8.8 Hz, 1H), 7.20−7.15 (m, 1H), 7.06−7.02 (m, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 157.2, 152.1, 146.4, 140.6, 131.4, 128.3, 123.8, 120.3, 120.0, 117.5, 112.7, 92.1, 56.2; (*Minor isomer*) ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.35 (s, 1H), 7.48−7.42 (m, 2H), 7.48 (s, 1H), 7.20−7.15 (m, 2H), 7.06−7.02 (m, 1H), 6.78 (d, J = 1.6 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.1, 152.4, 146.4, 135.3, 129.5, 128.4, 123.8, 120.4, 120.0, 117.6, 116.6, 98.9, 56.2; IR (thin film) 3442, 2378, 1607, 1518, 1453, 1383, 1274, 1213, 1035, 784, 737 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{13}H_{12}N_3O_2$ $(M+H)^+$ 242.0930, found 242.0920.

2-(5-Chloro-1H-benzo[d][1,2,3]triazol-1-yl)phenol (4da), white solid, 0.109 g, 89% yield. mp: 218−219 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.47 (s, 1H), 8.30 (s, 1H), 7.61−7.58 (m, 1H), 7.53−7.46 (m, 3H), 7.19 (d, J = 8.4 Hz, 1H), 7.08 (t, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.2, 146.0, 132.9, 131.8, 129.1, 128.8, 128.4, 123.3, 120.1, 119.0, 117.5, 113.8; IR (thin film) 3434, 3083, 2972, 2738, 1601,

1464, 1276, 1122, 936, 802, 740 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{12}H_9N_3OCl$ $(M+H)^+$ 246.0434, found 246.0424.

2-(5-(Trifluoromethyl)-1H-benzo[d][1,2,3]triazol-1-yl)phenol (4ea), white solid, 0.112 g, 81% yield. mp: 223−224 °C; ^1H NMR (500 MHz, DMSO-d_6): δ 10.54 (s, 1H), 8.68 (s, 1H), 7.89 (d, J = 8.5 Hz, 1H), 7.73 (d, J = 8.5 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.21 (d, J = 8.5 Hz, 1H), 7.10 (d, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 152.3, 144.6, 135.6, 132.0, 128.5, 125.8 (q, J = 270.7 Hz), 125.3 (q, J = 31.8 Hz), 124.7 (q, J = 2.8 Hz), 123.1, 120.2, 118.3 (q, J = 4.6 Hz), 117.5, 113.8; IR (thin film) 3432, 3086, 2962, 2736, 1599, 1463, 1333, 1221, 1133, 825, 754 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{13}H_9N_3OF_3$ $(M+H)^+$ 280.0698, found 280.0689.

2-(6-Methyl-1H-benzo[d][1,2,3]triazol-1-yl)phenol (4ja), yellowish solid, 0.071g, 63% yield. mp: 189−190 °C; ^1H NMR (500 MHz, DMSO-d_6): δ 10.36 (s, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.47−744 (m, 2H), 7.28 (d, J = 8.5 Hz, 1H), 7.24 (s, 1H), 7.18 (d, J = 8.5 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 152.5, 144.0, 138.4, 134.5, 131.5, 128.5, 126.6, 123.8, 120.0, 119.2, 117.5, 110.9, 21.8; IR (thin film) 3386, 3066, 2927, 2724, 1601, 1513, 1458, 1276, 1111,797, 741 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{13}H_{12}N_3O$ $(M+H)^+$ 226.0980, found 226.0974.

2-(6-Chloro-1H-benzo[d][1,2,3]triazol-1-yl)phenol (4ka), yellowish solid, 0.052 g, 43% yield. mp: 215−216 °C; ^1H NMR (400 MHz, DMSO-d_6): δ 10.46 (s, 1H), 8.20 (d, J = 8.8 Hz, 1H), 7.57 (s, 1H), 7.53−7.45 (m, 3H), 7.19 (d, J = 8.0 Hz, 1H), 7.08 (t, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.1, 144.1, 134.5, 133.2, 131.7,

128.3, 125.3, 123.3, 121.3, 120.1, 117.6, 111.8; IR (thin film) 3429, 3072, 2926, 2734, 1603, 1515, 1463, 1272, 1101, 803, 744 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{12}H_9N_3OCl$ $(M+H)^+$ 246.0434, found 246.0431.

General procedure for one-pot reaction for synthesis of rearrangement products 4 (Table 5): In a 25 mL Schlenk tube was charged with **1** (0.5 mmol) and MeCN (5 mL). *t*-BuOK (0.75 mmol, 1.5 equiv) was added in one portion at room temperature. The mixture was stirred vigorously at room temperature for 5 min. Then, diaryliodonium salts **2** (0.75 mmol, 1.5 equiv) was added in one portion. The reaction mixture was stirred vigorously at 60 °C for 18−24 h until the substrate **1** disappeared (monitored by TLC). At this time, the solvent was removed under reduced pressure and the crude product was purified by flash chromatography (the crude residue was dry loaded on silica gel; 1 / 10 − 1 / 2, ethyl acetate / petroleum ether) to provide product **4** as solid.

2-(1H-Benzo[d][1,2,3]triazol-1-yl)-4-methoxyphenol (4ab), yellow solid, 0.095 g, 79% yield. mp: 163−164 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.84 (s, 1H), 8.16 (d, J = 8.0 Hz, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.50−7.43 (m, 2H), 7.11−7.08 (m, 3H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.7, 146.0, 145.3, 133.9, 128.2, 124.5, 123.7, 119.6, 118.2, 117.7, 113.0, 112.1, 56.2; IR (thin film) 3442, 2378, 1607, 1518, 1453, 1383, 1274, 1213, 1035, 784, 737 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{13}H_{12}N_3O_2$ $(M+H)^+$ 242.0930, found 242.0922.

2-(1H-Benzo[d][1,2,3]triazol-1-yl)-4-tert-butylphenol (4an), yellowish solid, 0.109 g, 82% yield. mp: 156−157 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.18 (s, 1H), 8.15

(d, J = 8.0 Hz, 1H), 7.58−7.45 (m, 5H), 7.14 (d, J = 8.8 Hz, 1H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 149.8, 145.4, 142.6, 134.0, 128.3, 128.1, 124.8, 124.4, 123.1, 119.6, 117.1, 112.2, 34.3, 31.6; IR (thin film) 3042, 2962, 2783, 2621, 1739, 1609, 1512, 1265, 1109, 830, 738 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{16}H_{18}N_3O$ $(M+H)^+$ 268.1450, found 268.1441.

4-Methoxy-2-(5-methyl-1H-benzo[d][1,2,3]triazol-1-yl)phenol (4cb), white solid, 0.108 g, 85% yield. mp: 164−165 °C; (*major isomer*) ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.83 (s, 1H), 7.89 (s, 1H), 7.39 (s, 2H), 7.10-7.05 (m, 3H), 3.74 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.7, 145.9, 145.8, 134.0, 132.5, 130.5, 130.2, 123.9, 118.2, 117.5, 112.9, 111.8, 56.2, 21.4; (*minor isomer*) ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.80 (s, 1H), 8.00 (d, J = 7.2 Hz, 1H), 7.29-7.26 (m, 2H), 7.10-7.05 (m, 3H), 3.75 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.7, 146.1, 144.0, 138.4, 134.4, 126.6, 123.8, 119.1, 118.3, 117.6, 113.1, 111.0, 56.2, 21.8; IR (thin film) 3431, 2962, 2767, 1604, 1516, 1460, 1280, 1210, 1040, 887, 786 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{14}H_{13}N_3O_2Na$ $(M+Na)^+$ 278.0905, found 278.0894.

2-(5-Chloro-1H-benzo[d][1,2,3]triazol-1-yl)-4-methoxyphenol (4db), white solid, 0.088 g, 64% yield. mp: 209−210 °C; (*major isomer*) ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.95 (s, 1H), 8.30 (s, 1H),7.59 (s, 1H), 7.55 (d, J = 9.0 Hz, 1H), 7.13−7.12 (m, 1H), 7.10−7.08 (s, 2H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.7, 145.8, 145.7, 132.8, 128.8, 125.4, 123.3, 119.0, 118.3, 118.0, 113.9, 112.9, 56.2; (*minor isomer*) ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.95 (s, 1H), 8.20 (d, J = 9.0 Hz, 1H), 7.61 (s, 1H), 7.51 (dd, J = 9.0 Hz, 1.0 Hz, 1H), 7.13−7.12 (m, 1H), 7.10−7.08 (s, 2H), 3.75

(s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.8, 146.0, 144.1, 133.3, 129.1, 125.4, 123.3, 121.3, 118.3, 118.0, 113.9, 111.9, 56.2; IR (thin film) 3010, 2771, 1609, 1517, 1467, 1272, 1212, 1038, 804 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{13}H_{11}N_3O_2Cl$ $(M+H)^+$ 276.0540, found 276.0531.

1-(2-Hydroxy-5-methoxyphenyl)-1H-benzo[d][1,2,3]triazole-5-carbonitrile (4fb), yellowish solid, 0.066 g, 50% yield. mp: 237−239 °C; (*one isomer*) ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.98 (s, 1H), 8.38 (d, J = 8.4 Hz, 1H), 8.20 (s, 1H), 7.93 (d, J = 8.8 Hz, 1H), 7.17 (s, 1H), 7.11 (s, 2H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.7, 145.9, 145.8, 135.6, 130.6, 127.0, 121.4, 118.7, 118.4, 118.3, 114.0, 112.9, 107.2, 56.2; (*the other isomer*) ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.99 (s, 1H), 8.70 (s, 1H), 8.09 (d, J = 8.0 Hz, 1H), 7.84−7.82 (m, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.17 (s, 2H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.7, 146.6, 144.6, 135.6, 133.3, 126.5, 123.0, 122.9, 119.2, 118.9, 118.7, 112.9, 110.6, 56.2; IR (thin film) 3663, 3413, 2977, 2228, 1608, 1515, 1392, 1212, 1050, 886, 815 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{14}H_{11}N_4O_2$ $(M+H)^+$ 267.0882, found 267.0873.

General procedure for synthesis of 5: In a 25 mL Schlenk tube was charged with **4aa** (0.5 mmol) and MeCN (5 mL). *t*-BuOK (0.75 mmol, 1.5 equiv) was added in one portion at room temperature. The mixture was stirred vigorously at room temperature for 5 min. Then, diaryliodonium salts **2l** (0.75 mmol, 1.5 equiv) was added in one portion. The reaction mixture was stirred vigorously at room temperature for 18 h until the substrate **4aa** disappeared (monitored by TLC). At this time, the solvent was removed under reduced pressure and the crude product was purified by flash

chromatography (the crude residue was dry loaded on silica gel; 1 / 20 − 1 / 5, ethyl acetate / petroleum ether) to provide product **5** as solid.

1-(2-(2-Bromophenoxy)phenyl)-1H-benzo[d][1,2,3]triazole (5), light yellow oil, 0.151 g, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 8.4 Hz, 1H), 7.65 (d, J = 8.4 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.42−7.35 (m, 3H), 7.30 (t, J = 8.0 Hz, 1H), 7.23−7.19 (m, 1H), 7.10 (t, J = 7.6 Hz, 1H), 6.87−6.81 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0, 150.7, 145.5, 133.9, 133.7, 130.8, 128.7, 128.5, 127.7, 126.8, 125.8, 123.9, 123.8, 120.7, 119.6, 118.0, 114.7, 111.5; IR (thin film) 3065, 2856, 1586, 1460, 1252, 1116, 1049, 749 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{13}N_3OBr$ $(M+H)^+$ 366.0242, found 366.0220.

General procedure for synthesis of 6: In a 25 mL Schlenk tube was charged with **5** (0.5 mmol) and THF (5 mL) under N_2 atmosphere. The mixture was stirred vigorously at −78 °C for 2 min. *n*-BuLi (0.75 mmol, 1.6 M in hexane, 1.5 equiv) was added slowly. After completion, the mixture was kept at −78 °C for 1 h. Then, PPh_2Cl (0.5 mmol, 1.0 equiv) was dropped to the mixture slowly. The reaction mixture was stirred vigorously for 2 h and then moved to room temperature for 1 h until **5** was disappeared (monitored by TLC). At this time, quenched by water (10 mL) and exacted with ether (3 × 10 mL). The organic layers were combined, washed with brine (10 mL), dried over Na_2SO_4, and filtered. Then, the solvent was removed under reduced pressure and the crude product was purified by flash chromatography (the crude residue was dry loaded on silica gel; 1 / 50 − 1 / 10, ethyl acetate / petroleum ether) to provide product **6** as solid.

1-(2-(2-(Diphenylphosphino)phenoxy)phenyl)-1H-benzo[d][1,2,3]triazole (6), white solid, 0.094 g, 40% yield. mp: 187−188 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 8.5 Hz, 1H), 7.39 (d, J = 7.5 Hz, 1H), 7.28−7.21 (m, 5H), 7.18−7.15 (m, 5H), 7.12 (t, J = 7.5 Hz, 4H), 7.02 (t, J = 7.5 Hz, 1H), 6.93−6.90 (m, 2H), 6.80−6.78 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.9, 157.8, 151.3, 145.4, 135.8 (d, J_{C-P} = 10.0 Hz), 134.3, 133.8, 133.6, 133.5, 133.4, 133.3, 130.6 (d, J_{C-P} = 4.8 Hz), 129.6 (d, J_{C-P} = 4.0 Hz), 128.5, 128.4, 128.3, 128.2, 127.5, 127.2, 124.7, 123.7, 123.6, 119.4, 119.0, 118.7, 111.4 (d, J_{C-P} = 2.7 Hz); IR (thin film) 3447, 3061, 1586, 1502, 1435, 1242, 1080, 748, 696 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{30}H_{23}N_3OP$ $(M+H)^+$ 472.1579, found 472.1606.

General procedure for Synthesis of *N*-hydroxybenzotriazoles 1: In a 100 mL round-bottle flask was charged with *o*-chloronitrobenzene derivatives (11.655 mmol) and EtOH (40 mL). Then, hydrazine hydrate (116.6 mmol, 10 equiv) was added at room temperature. The mixture was stirred vigorously under refluxing for 20 h and then cooled to room temperature. EtOH was evaporated under reduced pressure from the reaction mixture. Cold MeOH (20 mL) was added to the residue and the mixture was acidified with conc. HCl. This addition induced precipitation of a solid. The solid was collected by filtration and washed with amount of cold MeOH to provide *N*-hydroxy benzotriazoles **1** as solid.

N-hydroxy benzotriazole **1a**, **1d**, **1e**, **1h**, **1j** and **1k** were purchased from Sigma-Aldrich. **1b**,[14] **1c**,[8a] **1f**,[8a] **1g**[15] and **1i**[16] were prepared as the literatures, and spectra data matched literature values.

General procedure for synthesis of diaryliodonium salts 2: Aryl boronic acid (10 mmol, 1.0 equiv) and CH_2Cl_2 (40 mL) were combined in a dried round-bottom flask. The mixture was cooled to 0 °C for 5 min, BF_3•OEt_2 (1.12 mL, 1.10 equiv) was added, and the mixture was stirred for 10 min. A solution of 2-(diacetoxyiodo)arene (1.05 equiv) in CH_2Cl_2 (20 mL) was added slowly for 10-15 min and stirred for additional 10 min. The mixture was warmed to room temperature and stirred for 1 h. The reaction was cooled to 0 °C again and TfOH (1.67 mL, 1.1 equiv) was dropped into the mixture. Then, the mixture was stirred for 10 min at 0 °C and warmed to room temperature for additional 10 min. At this time, the solvent was removed under reduced pressure and the residual ran through a short silica gel column (about 5 cm) with 5% of MeOH in CH_2Cl_2 quickly. The mixture was concentrated under vacuum and Et_2O (100 mL) was added to the residual to form a white solid. Filtrated and obtained the diaryliodonium salts **2** as white solid.

All diaryliodonium salts **2** are reported before and their spectra data matched literature values: **2a**, **c**[17], **2b**, **2d-e, 2h** and **2n**[18], **2g**[19], **2i**[20], **2j**[21], **2k**[22], **2f**[23].

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Spectra of compounds **3aa-3am**, **3ba-3ka**, **4**, **5**, and **6** (PDF)

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Notes

The authors declare no competing financial interest.

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