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Metal-free synthesis of etherfied 1, 2, 3-triazole idodides through O-H arylation / C-H iodation with diacetoxyiodobenzenes

Yaowen Liu,[a] Jianhua Yang,[a] Xinyuan Ma,[a] Chunmei Han,[a] and Yubo Jiang*[a]

Dedication ((optional))

Abstract: An efficient method for the synthesis of etherfied 1, 2, 3-triazole idodides from 1, 4-disubstituted 1, 2, 3-triazoles under metal free conditions has been developed. In the presence of $ArI(OAc)_2$, a range of 1, 2, 3-triazole substrates bearing hydroxyl group undergo the direct O-H arylation and C-H iodation simultaneously to accomplish the modification of the 1, 2, 3-triazoles. This method provides a concise and efficient pathway to synthesize highly functionalized 1, 2, 3-triazole derivatives in good to excellent yields.

Introduction

1, 2, 3-Triazoles are important five-membered heterocyclic scaffolds, which were widely applied in various fields such as organic synthesis,[1] materials,[2] medicinal chemistry[3] and food additives[4] due to their extensive biological activities. It may display a wide spectrum of biological activities such as anti-HIV,[5] anticancer,[6] antiviral,[7] antifungal,[8] antimicrobial,[9] and antibacterial activities,[10] although the 1, 2, 3-triazole structure was not found in natural products. Numerous compounds bearing this moiety are also well acknowledged for therapeutic effects elucidated in Fig. 1

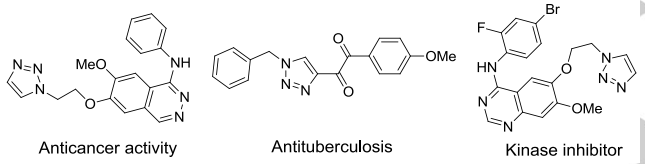

Fig.1. Triazole containing commercial drugs and bioactive molecules.

Owing to these widely applications, the development of facile synthesis and modification of 1, 2, 3-triazole compounds therefore strongly attracted enormous interests. Numerous methods for the preparation of 1, 2, 3-triazole derivatives have been developed in the last decades. Among them, the landmark discovery of the alkyne-azide cycloaddition (AAC) reactions disclosed by Huisgen,[11] Sharpless,[12] and Meldal,[13] respectively, reached unprecedented sophistication and height. Other partners such as activated carbonyl compounds[14] and activated alkenes[15] were also involved for this purpose. However, most traditional methodologies still met some troubles for the target molecules with complicated structures. It is clear that the development of new accesses for various 1, 2, 3-triazoles is highly desirable.[16] In the past few years, Kuang, Shi and Ackermann groups respectively explored various modifications of 2-monosubstituted 1, 2, 3-triazoles including halogenation, arylation, alkoxylation, acylation, and acyloxylation generating corresponding functionalized target molecules.[17] These methods have been proved to have good potential but are mainly limited to the mono-substituted-1, 2, 3-triazoles. Recently, our group explored direct modification of 1, 4-disubstituted 1, 2, 3-triazoles, as a beautiful means for the construction of various 1, 2, 3-triazoles with complicated structures and respectively achieved C-H bond arylation, acylation, and acyloxylation, through the influence of the triazole ring.[18] The aryloxylation process was also acheived by Ullmann C–O coupling, generating a series of etherfied 1, 2, 3-triazoles.[19] With respect to the C-H halogenations, Liu[20] group reported the copper-catalyzed and mediated C–X (X = F, Cl, Br, I) bond formation via direct C–H bond transformation. To the best of our knowledge, there is still no report on the metal-free synthesis of etherfied 1, 2, 3-triazole idodides. Herein, we would like to report a convenient method for metal-free synthesis of etherfied 1, 2, 3-triazole idodides from 1, 4-diaryl 1, 2, 3-triazoles bearing hydroxyl group, in which direct O-H arylation and C-H iodation occurred simultaneously in the presence of $ArI(OAc)_2$.

Results and Discussion

Our initial studies focused on the model reaction of 2-(4-(*p*-tolyl)-1*H*-1, 2, 3-triazol-1-yl) phenol **1a** and diacetoxyiodobenzene (DAIB) **2a**. We investigated the effects of catalyst, oxidant, solvent and temperature respectively, as summarized in Table 1. A moderate 61% yield of the product 1-(3-iodo-2-phenoxyphenyl)-4-(*p*-tolyl)-1*H*-1, 2, 3-triazole **3a** was obtained when the reaction was catalyzed by CuCl (0.1 equiv.), using 2 equiv. of $PhI(OAc)_2$ in solvent of PhMe under 120 ˚C for 12h (Table 1, entry 1). The molecular structure of **3a** was unambiguously confirmed by a single crystal X-ray diffraction study (Table 1). Catalyst screening demonstrated that $PdCl_2$ was the best choice, in which a good yield of 65% was obtained (entries 1–7). However, other catalysts such as CuBr, $CuCl_2$, $NiCl_2$, $CoCl_2$, and $AgNO_3$ are not so efficient for this reaction (Table 1, entries 2, 3, 5, 6 and 7). To our delight, a good 67% yield was also reached in the absence of the catalyst (Table 1, entry 8). Next, to gain the ideal yield, the amount of $PhI(OAc)_2$ was examined and it turned out that 3.5 equiv of $PhI(OAc)_2$ could bring a yield of 73% and increasing the amount of DAIB to 4 equiv could not raise the yield evidently (Table 1, entries 9-11). Then, various solvents including CH_3CN, DCE, DMF, and dioxane were also screened, indicating that CH_3CN was the best choice (entries 12–15). Additionally, the yield can not be improved when the reaction temperature was adjusted to lower

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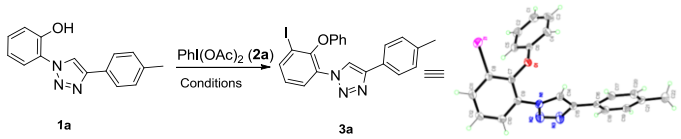
80 ˚C, 100 ˚C or a higher 130 ˚C, respectively (Table 1, entries 16–18). After further optimizations, the best result was obtained using a treatment of 3.5 equiv of DAIB in CH_3CN at 120 ˚C for 12 h, which affording the desired etherfied 1, 2, 3-triazole idodide **3a** in 78% yield (entry 14).

Table 1. Selected optimization of the reaction conditions.[a,b]

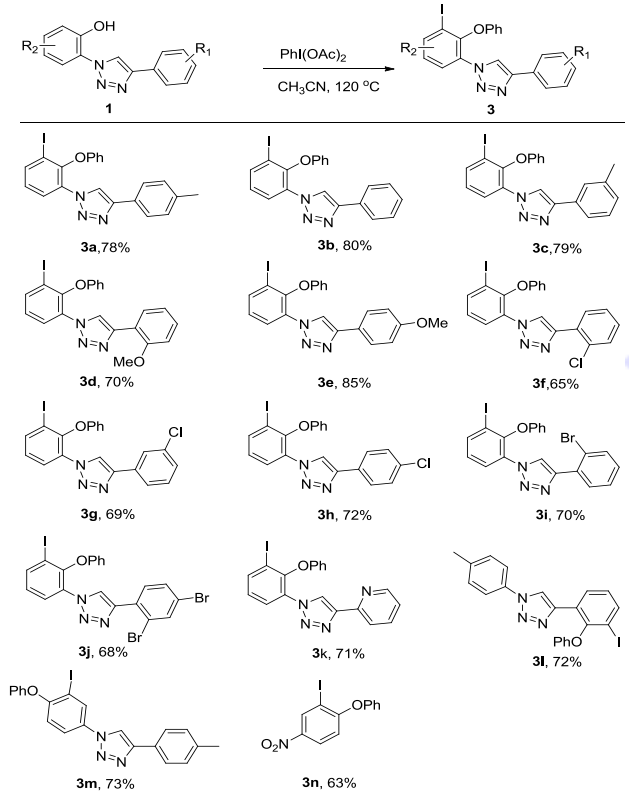


Entry	Catalyst (mol %)	DAIB (Equiv.)	Solvent	Temp. (°C)	Yield [%][b]
1	CuCl (10)	2.0	PhMe	120	61
2	CuBr (10)	2.0	PhMe	120	52
3	$CuCl_2$(10)	2.0	PhMe	120	55
4	$PdCl_2$(10)	2.0	PhMe	120	65
5	$NiCl_2$(10)	2.0	PhMe	120	50
6	$CoCl_2$(10)	2.0	PhMe	120	49
7	$AgNO_3$(10)	2.0	PhMe	120	63
8	--	2.0	PhMe	120	67
9	--	3.0	PhMe	120	69
10	--	3.5	PhMe	120	73
11	--	4.0	PhMe	120	70
12	--	3.5	CH_3CN	120	78
13	--	3.5	DCE	120	63
14	--	3.5	DMF	120	55
15	--	3.5	dioxane	120	59
16	--	3.5	CH_3CN	80	53
17	--	3.5	CH_3CN	100	62
18	--	3.5	CH_3CN	130	75

[a] Reaction conditions unless otherwise noted: 2-(4-(*p*-tolyl)-1*H*-1, 2, 3-triazol-1-yl) phenol **1a** (0.3 mmol) and diacetoxyiodobenzene **2a** (3.5 eq.) were added to solvent (2 mL) and stirred at 120 °C for 12 h. [b] Isolated yield.

With the optimal conditions in hand, the scope of 1, 4-disubstituted 1, 2, 3-triazoles **1** was firstly studied. As summarized in Table 2, the reaction of $PhI(OAc)_2$ with various 1, 4-disubstituted 1, 2, 3-triazoles **1** bearing hydroxyl group on *N*-1 aryl or *C*-4 aryl could proceed well and generate the desired products **3** in good to excellent yields (**3a-3n**). The 1, 2, 3-triazole substrates with electron-donating groups (-CH_3, -OMe) on *C*-4 aryl could react well and afford good yields (Table 2, **3a-3e**), and those with an electron-withdrawing group (-Br, -Cl) could also produce the desired compounds in moderate to good yields (Table 2, **3f**-**3j**). The substituent on *C*-4 aryl of 1, 2, 3-triazoles seems to have an obvious effect on the reactions. The substrates with a substituent (-CH_3, -OMe and -Cl) on *meta* or *ortho* position produced only lower yields in comparison with those bearing a group at the *para* position, probably owning to the steric effects (Table 2, **3a** vs. **3c**, **3d** vs. **3e**, **3f** and **3g** vs. **3h**). It should be noted that *C*-4 pyridyl substrate was also tolerated in the system and good yield was also obtained (**3k**). Moreover, when the 1, 2, 3-triazoles has hydroxyl group on *ortho* position of *C*-4 aryl or *para* position of *N*-1 aryl, good yields were achieved (**3l**, **3m**). Additionally, we checked 4-nitrophenol in this system, which could also delivered the desired products in good yield (**3n**).

Table 2. Scope of 1, 4-disubstituted 1, 2, 3-triazoles.[a,b]



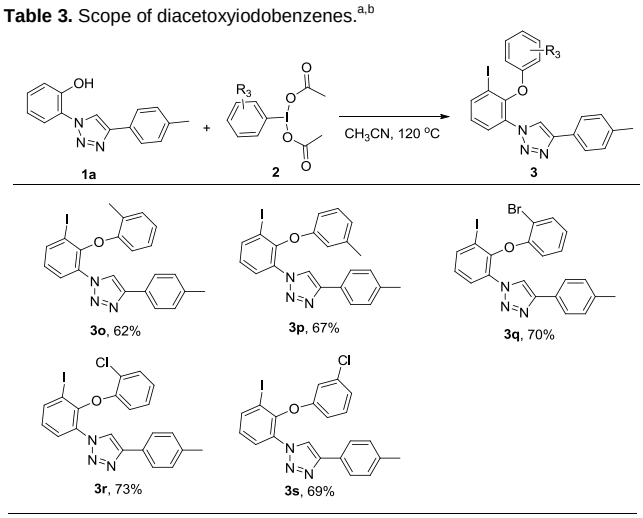
[a] Reaction conditions: 1, 4-disubstituted 1, 2, 3-triazoles **1** (0.3 mmol) and diacetoxyiodobenzenes (1.05 mmol) were added to CH_3CN (2 mL) and stirred at 120 °C for 12 h. [b] Yield of isolated product after column chromatography.

Next, we turned our attention to investigate the scope of the diacetoxyiodobenzenes, which were summarized in Table 3. The reactions of 2-(4-(*p*-tolyl)-1*H*-1, 2, 3-triazol-1-yl) phenol **1a** and various diacetoxyiodobenzenes **2** went smoothly, affording the products in moderate to good yields (Table 3, **3o-3s**). The substrates **2** with an electron-donating group (-Me) are inferior to those bearing an electron-withdrawing group (-Br, -Cl) (**3o and 3p** vs. **3q, 3r and 3s**). Additionally, the steric results of the substituents are closely related to its electronic effect. Electron-donating group on *meta* position are favorable for this transformation (**3p** vs. **3o**), while the electron withdrawing on *meta* position are unfavorable for the reaction (**3r** vs. **3s**).

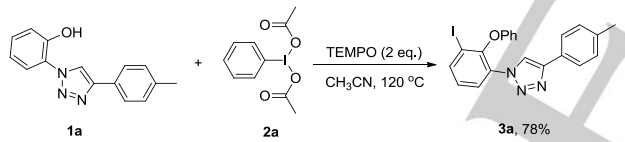
Notably, no product was obtained, when the reaction was conducted with $PhI(OTFA)_2$.

To gain a preliminary mechanistic insight into the reaction, a control experiment was carried out. When 2, 2, 6, 6-tetramethyl-1-piperidiny-loxy (TEMPO), as a radical inhibitor, was added into the reaction under standard conditions, the yield was virtually unaffected (Scheme 1). This result indicates that the reaction is not a radical pathway.

Table 3. Scope of diacetoxyiodobenzenes.[a,b]



[a] Reaction conditions: 2-(4-(*p*-tolyl)-1*H*-1, 2, 3-triazol-1-yl) phenol **1a** (0.3 mmol) and diacetoxyiodobenzenes **2** (1.05 mmol) were added to CH_3CN (2 mL) and stirred at 120 °C for 12 h. [b] Yield of isolated product after column chromatography.



Scheme 1. Control Experiment.

Conclusions

In conclusion, we successfully developed a facile and general synthetic rout to obtain etherfied 1, 2, 3-triazole idodides through O-H arylation / C-H iodation with diacetoxyiodobenzenes. The convenient process exhibits good functional group tolerance and provides an efficient access to the 1, 4-disubstituted 1, 2, 3-triazoles bearing both aryloxy and iodo group.

Experimental Section

General synthetic procedure: 1, 4-Disubstituted 1, 2, 3-triazoles **1** (0.3 mmol), diacetoxyiodobenzene **2** (3.5 eq., 1.05 mmol), and CH_3CN (2 mL) were sequentially added to a 15 mL pressure tube. Then the tube was sealed and stirred at 120 °C for 12 h. After consumption of the 1, 4-disubstitued 1, 2, 3-triazoles monitored by TLC analysis, H_2O (15 mL) was added to the mixture and extracted with EtOAc (3 × 25 mL). The combined organic layer was washed with brine (3 × 5 mL), dried with Na_2SO_4, and concentrated under reduced pressure to afford the crude product. Purification by column chromatography on silica gel with EtOAc / PE (1:6) afforded the desired product **3.**

1-(3-iodo-2-phenoxyphenyl)-4-(*p*-tolyl)-1*H*-1, 2, 3-triazole (3a): Yellow solid (106 mg, 78% yield); Mp. 142.0-143.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.17 (s, 1H), 7.99 (ddd, *J* = 13.6, 8.0, 1.4 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.21 (dt, *J* = 14.1, 4.8 Hz, 5H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.74 (d, *J* = 7.9 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.8, 147.9, 146.2, 140.5, 138.2, 131.6, 129.8, 129.5, 127.9, 127.2, 126.2, 125.7, 123.1, 120.5, 115.1, 93.3, 21.3. HRMS (ESI) m/z [M + H$^+$]: calcd for $C_{21}H_{17}IN_3O$: 454.0416, found: 454.0418; IR (KBr): 3437, 3137, 2920, 1588, 1500, 1490, 1390, 1239, 1194, 1031, 872, 814, 742, 509 cm^{-1}.

1-(3-iodo-2-phenoxyphenyl)-4-phenyl-1*H*-1, 2, 3-triazole (3b): Yellow solid (105 mg, 80% yield); Mp. 131.5-133.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.22 (s, 1H), 8.00 (ddd, *J* = 13.9, 8.0, 1.4 Hz, 2H), 7.79 – 7.71 (m, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.21 (dd, *J* = 15.6, 7.7 Hz, 3H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.74 (d, *J* = 7.9 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.8, 147.8, 146.2, 140.5, 131.6, 130.1, 129.8, 128.8, 128.3, 127.9, 126.2, 125.8, 123.1, 120.9, 115.1, 93.3. HRMS (ESI) m/z [M + H$^+$]: calcd for $C_{21}H_{15}IN_3O$: 440.0260, found: 440.0262; IR (KBr): 3440, 3136, 3051, 2924, 2855, 1757, 1671, 1586, 1480, 1442, 1236, 1191, 1070, 1075, 904, 858, 764, 688, 506 cm^{-1}.

1-(3-iodo-2-phenoxyphenyl)-4-(*m*-tolyl)-1*H*-1, 2, 3-triazole (3c): Light yellow oil (107 mg, 79% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.19 (s, 1H), 7.99 (ddd, *J* = 16.6, 8.0, 1.5 Hz, 2H), 7.53 – 7.45 (m, 2H), 7.23 – 7.12 (m, 5H), 6.94 (s, 1H), 6.74 (d, *J* = 7.9 Hz, 2H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.8, 147.9, 140.5, 138.5, 130.1, 129.8, 129.1, 128.7, 128.7, 127.8, 126.5, 125.4, 123.1, 122.9, 120.5, 115.1, 110.8, 93.3, 20.9. HRMS (ESI) m/z [M + H$^+$]: calcd for $C_{21}H_{17}IN_3O$: 454.0416, found: 454.0418; IR (KBr): 3434, 2923, 2857, 1749, 1600, 1534, 1481, 1449, 1377, 1231, 1159, 1035, 858, 786, 749, 693 cm^{-1}.

1-(3-iodo-2-phenoxyphenyl)-4-(2-methoxyphenyl)-1*H*-1, 2, 3-triazole (3d): Yellow solid (98 mg, 70% yield); Mp. 137.5-138.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.49 (s, 1H), 8.29 (dd, *J* = 7.7, 1.7 Hz, 1H), 8.00 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.31 – 7.27 (m, 1H), 7.21 (ddd, *J* = 8.0, 6.2, 3.0 Hz, 3H), 7.08 – 7.03 (m, 1H), 6.99 (d, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.77 (d, *J* = 7.9 Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.1, 155.7, 146.0, 143.2, 140.2, 132.0, 129.8, 129.0, 127.8, 127.6, 126.2, 124.3, 122.9, 120.9, 118.9, 115.2, 110.8, 93.3, 55.1. HRMS (ESI) m/z [M + H$^+$]: calcd for $C_{21}H_{17}IN_3O_2$: 470.0365, found: 470.0367; IR (KBr): 3414, 3193, 2922, 2853, 1645, 1586, 1442, 1393, 1240, 1189, 1154, 1076, 1021, 861cm^{-1}.

1-(3-iodo-2-phenoxyphenyl)-4-(4-methoxyphenyl)-1*H*-1, 2, 3-triazole (3e): Yellow solid (119 mg, 85% yield); Mp. 140.3-141.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.13 (s, 1H), 8.04 – 7.94 (m, 2H), 7.66 (d, *J* = 8.7 Hz, 2H), 7.20 (td, *J* = 8.2, 4.1 Hz, 3H), 6.96 (dd, *J* = 14.8, 8.0 Hz, 3H), 6.74 (d, *J* = 8.0 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.7, 155.8, 147.7, 146.2, 140.4, 131.7, 129.8, 127.9, 127.1, 126.1, 123.1, 122.7, 120.1, 115.1, 114.2, 93.3, 55.3. HRMS (ESI) m/z [M + H$^+$]: calcd for $C_{21}H_{17}IN_3O_2$: 470.0365, found: 470.0367; IR (KBr): 3446, 3130, 3064, 2923, 2845, 1738, 1603, 1580, 1485, 1467, 1447, 1292, 1242, 1182, 1025, 904, 872, 826, 738, 617, 526 cm^{-1}.

4-(2-chlorophenyl)-1-(3-iodo-2-phenoxyphenyl)-1*H*-1, 2, 3-triazole (3f): Yellow solid (92 mg, 65% yield); Mp. 109.7-110.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.67 (s, 1H), 8.18 (dd, *J* = 7.8, 1.6 Hz, 1H), 8.01 (ddd, *J* = 10.7, 8.1, 1.3 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.35 (dd, *J* = 10.8, 4.3 Hz, 1H), 7.28 – 7.16 (m, 5H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.75 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.8, 146.1, 144.0, 140.6, 131.6, 131.3, 130.2, 129.8, 129.7, 129.1, 128.7, 127.9, 127.0, 126.2, 124.5, 123.04 (s), 115.0, 93.4. HRMS (ESI) m/z [M + H$^+$]: calcd for $C_{20}H_{14}ClIN_3O$: 473.9870, found: 473.9872; IR (KBr): 3436, 3201, 2923, 1640, 1589, 1474, 1440, 1393, 1229, 1190, 1112, 1024, 862, 750 cm^{-1}.

4-(3-chlorophenyl)-1-(3-iodo-2-phenoxyphenyl)-1*H*-1, 2, 3-triazole (3g): Yellow solid (99 mg, 69% yield); Mp. 101.3-102.7 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.21 (s, 1H), 7.99 (ddd, *J* = 19.5, 8.0, 1.3 Hz, 2H), 7.74 (s, 1H), 7.60 (dd, *J* = 6.1, 4.5 Hz, 1H), 7.38 – 7.29 (m, 3H), 7.25 – 7.19 (m, 2H), 7.01 – 6.93 (m, 1H), 6.74 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 155.8, 140.7, 134.8, 131.8, 131.4, 130.1, 129.9, 128.3, 127.9, 127.7, 126.2, 125.8, 123.8, 123.2, 121.3, 115.0, 110.9, 93.3. HRMS (ESI) m/z [M + H$^+$]: calcd for $C_{20}H_{14}ClIN_3O$: 473.9870, found: 473.9872; IR (KBr): 3440, 3165, 3065, 2924, 2855, 1753, 1583, 1476, 1444, 1381, 1230, 1070, 1019, 873, 780, 682, 491cm^{-1}.

4-(4-chlorophenyl)-1-(3-iodo-2-phenoxyphenyl)-1*H*-1, 2, 3-triazole (3h): Yellow solid (103 mg, 72% yield); Mp. 149.1-150.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.19 (s, 1H), 7.99 (ddd, *J* = 23.4, 8.0, 1.3 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.21 (dd, *J* = 16.0, 7.9 Hz, 3H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.73 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.8, 146.8, 146.2, 140.7, 134.1, 131.5, 129.9, 129.0, 128.6, 127.9, 126.9, 126.1, 123.1, 120.9, 115.0, 93.3. HRMS (ESI) m/z [M + H$^+$]: calcd for $C_{20}H_{14}ClIN_3O$: 473.9870, found: 473.9872; IR (KBr): 3434, 3136, 2920, 2854, 1652, 1589, 1478, 1458, 1390, 1240, 1190, 1158, 1090, 1030, 904, 871, 828, 742, 512 cm^{-1}.

4-(2-bromophenyl)-1-(3-iodo-2-phenoxyphenyl)-1*H*-1, 2, 3-triazole (3i): Yellow solid (108 mg, 70% yield); Mp. 99.6-100.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.71 (s, 1H), 8.03 (d, *J* = 17.2 Hz, 2H), 7.77 – 7.52 (m, 2H), 7.41 (d, *J* = 35.3 Hz, 2H), 7.22 (dd, *J* = 20.5, 13.0 Hz, 3H), 6.98 (s, 1H), 6.76 (d, *J* = 7.1 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 155.9, 140.6, 134.5, 131.8, 130.8, 130.5, 129.8, 129.4, 128.8, 128.5, 127.8, 127.6, 126.2, 124.3, 123.1, 121.2, 115.2, 93.4. HRMS (ESI) m/z [M + H$^+$]: calcd for $C_{20}H_{14}BrIN_3O$: 517.9365, found: 517.9367; IR (KBr): 3441, 3200, 2924, 2856, 1745, 1667, 1586, 1533, 1474, 1443, 1396, 1304, 1228, 1195, 1158, 1021, 970, 915, 864, 750, 689, 642, 489, 440 cm^{-1}.

4-(2, 4-dibromophenyl)-1-(3-iodo-2-phenoxyphenyl)-1*H*-1, 2, 3-triazole (3j): Yellow solid (121 mg, 68% yield); Mp. 124.1-125.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.73 (s, 1H), 8.24 (s, 1H), 8.01 (dd, *J* = 18.6, 7.6 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 1H), 7.35 – 7.09 (m, 4H), 6.99 (s, 1H), 6.75 (d, *J* = 7.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 140.8, 139.9, 136.9, 134.8, 133.1, 132.3, 129.9, 129.8, 128.0, 127.9, 126.2, 126.1, 124.6, 123.9, 123.1, 121.6, 115.2, 93.4. HRMS (ESI) m/z [M + H$^+$]: calcd for $C_{20}H_{13}Br_2IN_3O$: 597.8450, found: 597.8452; IR (KBr): 3438, 2922, 2856, 1737, 1637, 1586, 1448, 1379, 1332, 1155, 1079, 1031, 874, 788, 748, 446 cm^{-1}.

4-cyclopropyl-1-(3-iodo-2-phenoxyphenyl)-1*H*-1, 2, 3-triazole (3k): Yellow solid (93 mg, 71% yield); Mp. 139.1-140.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.60 (s, 1H), 8.57 (d, *J* = 3.5 Hz, 1H), 8.10 (d, *J* = 7.8 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.74 (t, *J* = 7.7 Hz, 1H), 7.18 (dt, *J* = 17.7, 7.9 Hz, 4H), 6.93 (t, *J* = 7.3 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 155.9, 149.7, 149.4, 146.9, 140.8, 136.7, 131.6, 129.7, 127.7, 126.4, 123.5, 122.9, 122.8 120.3, 115.3, 110.8, 93.2. HRMS (ESI) m/z [M + H$^+$]: calcd for $C_{19}H_{14}IN_4O$: 441.0212, found: 441.0214; IR (KBr): 3366, 3177, 3053, 2922, 2854, 1746, 1588, 1471, 1232, 1020, 863, 757, 496 cm^{-1}.

4-(3-iodo-2-phenoxyphenyl)-1-(*p*-tolyl)-1*H*-1, 2, 3-triazole (3l): Yellow solid (97 mg, 72% yield); Mp. 174.3-175.7 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.49 (dd, *J* = 7.8, 1.5 Hz, 1H), 8.14 (s, 1H), 7.90 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.27 (dt, *J* = 7.3, 3.7 Hz, 4H), 7.16 (t, *J* = 7.9 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 2H), 2.40 (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.9, 150.0, 142.3, 139.8, 138.9, 128.8, 127.7, 126.3, 122.5, 121.5, 120.4, 115.0, 111.9, 92.6, 21.1. HRMS (ESI) m/z [M + H$^+$]: calcd for $C_{21}H_{17}IN_3O$: 454.0416, found: 454.0418; IR (KBr): 3423, 3141, 3041, 2923, 2855, 1728, 1594, 1518, 1483, 1440, 1331, 1293, 1235, 1160, 1117, 1076, 1041, 874, 815, 779, 717, 688, 524 cm^{-1}.

1-(3-iodo-4-phenoxyphenyl)-4-(*p*-tolyl)-1*H*-1, 2, 3-triazole (3m): Yellow solid (99 mg, 73% yield); Mp. 98.2-99.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.09 (s, 1H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.44 – 7.37 (m, 3H), 7.27 (dd, *J* = 8.8, 4.8 Hz, 4H), 7.06 (dd, *J* = 8.6, 0.9 Hz, 2H), 6.99 (dd, *J* = 8.3, 1.3 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.4, 156.1, 147.6, 141.9, 138.3, 130.1, 129.9, 129.6, 127.3, 125.8, 124.4, 122.6, 121.3, 119.5, 119.0, 89.8, 21.3. HRMS (ESI) m/z [M + H$^+$]: calcd for $C_{21}H_{17}IN_3O$: 454.0416, found: 454.0418; IR (KBr): 3421, 2922, 2854, 1644, 1573, 1474, 1386, 1247, 1198, 1036, 897, 789, 694, 520 cm^{-1}.

2-iodo-4-nitro-1-phenoxybenzene (3n): Yellow solid (65 mg, 63% yield); Mp. 54.6-54.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.73 (d, *J* = 2.7 Hz, 1H), 8.11 (dd, *J* = 9.1, 2.7 Hz, 1H), 7.44 (tt, *J* = 4.2, 2.2 Hz, 2H), 7.34 – 7.23 (m, 1H), 7.15 – 7.04 (m, 2H), 6.74 (d, *J* = 9.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.5, 154.6, 142.9, 135.4, 130.3, 125.7, 125.2, 120.3,

115.1, 85.9. HRMS (ESI) m/z [M + H$^+$]: calcd for $C_{12}H_9IN_3O$: 341.9627, found: 341.9629; IR (KBr): 3834, 3759, 3096, 2931, 2851, 2634, 2448, 2355, 2068, 1898, 1791, 1694, 1656, 1584, 1488, 1343, 1258, 1181, 1115, 1026, 896, 813, 750, 684, 497 cm^{-1}.

1-(3-iodo-2-(*o*-tolyloxy)phenyl)-4-(*p*-tolyl)-1*H*-1, 2, 3-triazole (3o): Yellow solid (86 mg, 62% yield); Mp. 116.4-117.6 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.07 (s, 1H), 8.03 – 7.94 (m, 2H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 4H), 6.95 (s, 1H), 6.25 (d, *J* = 8.0 Hz, 1H), 2.40 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* = 154.0, 140.6, 138.2, 131.4, 129.5, 127.7, 127.3, 127.0, 126.3, 125.6, 125.4, 124.5, 122.8, 120.5, 120.2, 112.2, 110.8, 93.2, 21.3, 21.2. HRMS (ESI) m/z [M + H$^+$]: calcd for $C_{22}H_{19}IN_3O$: 468.0573, found: 468.0575; IR (KBr): 3416, 3142, 2921, 2855, 1749, 1648, 1577, 1479, 1577, 1479, 1446, 1375, 1228, 1176, 1109, 1031, 872, 815, 753, 515 cm^{-1}.

1-(3-iodo-2-(*m*-tolyloxy)phenyl)-4-(*p*-tolyl)-1*H*-1, 2, 3-triazole (3p): Yellow solid (93 mg, 67% yield); Mp. 135.1-136.8 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* = 8.17 (s, 1H), 7.99 (ddd, *J* = 9.4, 8.1, 1.5 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.45 (s, 1H), 7.23 (s, 2H), 7.21 (s, 2H), 6.95 (s, 1H), 6.77 (d, *J* = 7.5 Hz, 1H), 2.37 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* = 149.7, 147.8, 139.2, 138.9, 138.2, 129.8, 129.7, 129.3, 127.9, 127.6, 126.61, 125.9, 125.8, 122.7, 120.2, 119.5, 119.4, 117.0, 21.4, 21.3. HRMS (ESI) m/z [M + H$^+$]: calcd for $C_{22}H_{19}IN_3O$: 468.0573, found: 468.0575; IR (KBr): 3390, 3178, 2922, 2855, 1750, 1648, 1615, 1576, 1451, 1376, 1231, 1137, 1028, 932, 863, 813, 799, 773, 756, 689, 541, 515 cm^{-1}.

1-(2-(2-bromophenoxy)-3-iodophenyl)-4-(*p*-tolyl)-1*H*-1, 2, 3-triazole (3q): Yellow solid (111 mg, 70% yield); Mp. 165.8-166.4 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) *δ* = 8.44 (s, 1H), 8.03 (dd, *J* = 7.9, 2.6 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.56 – 7.45 (m, 1H), 7.25 (d, *J* = 3.8 Hz, 3H), 7.02 (t, *J* = 7.8 Hz, 1H), 6.82 (t, *J* = 7.1 Hz, 1H), 6.31 (d, *J* = 7.4 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) *δ* = 151.7, 149.0, 143.2, 140.2, 133.8, 129.5, 128.6, 128.3, 127.1, 126.0, 125.7, 124.2, 120.5, 119.5, 113.6, 110.8, 99.6, 92.9, 21.3. HRMS (ESI) m/z [M + H$^+$]: calcd for $C_{21}H_{16}BrIN_3O$: 531.9521, found: 531.9523; IR (KBr): 3387, 3164, 3079, 2920, 2854, 1764, 1648, 1578, 1459, 1236, 1020, 873, 742, 658, 511 cm^{-1}.

1-(2-(2-chlorophenoxy)-3-iodophenyl)-4-(*p*-tolyl)-1*H*-1, 2, 3-triazole (3r): Yellow solid (106 mg, 73% yield); Mp. 152.2-153.5 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* = 8.41 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.34 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.27 – 7.20 (m, 3H), 6.93 (dtd, *J* = 36.7, 7.6, 1.5 Hz, 2H), 6.34 (dd, *J* = 8.2, 1.3 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* = 150.8, 148.1, 145.3, 140.3, 138.2, 131.1, 130.8, 129.5, 128.3, 127.9, 127.2, 126.1, 125.7, 123.8, 121.9, 120.4, 113.9, 92.9, 21.3. HRMS (ESI) m/z [M + H$^+$]: calcd for $C_{21}H_{16}ClIN_3O$: 488.0027, found: 488.0029; IR (KBr): 3430, 3149, 2922, 1643, 1583, 1475, 1390, 1241, 1029, 876, 816, 748, 512 cm^{-1}.

1-(2-(3-chlorophenoxy)-3-iodophenyl)-4-(*p*-tolyl)-1*H*-1, 2, 3-triazole (3s): Yellow solid (101 mg, 69% yield); Mp. 137.5-138.4 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* = 8.14 (s, 1H), 8.02 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.20 (m, 3H), 7.11 (t, *J* = 8.2 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.79 (t, *J* = 2.1 Hz, 1H), 6.60 (dd, *J* = 8.3, 2.4 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* = 145.8, 140.6, 138.4, 135.3, 130.6, 129.5, 128.3, 127.1, 126.4, 126.4, 125.7, 123.5, 120.4, 118.9, 115.9, 113.3, 104.9, 89.5, 21.3. HRMS (ESI) m/z [M + H$^+$]: calcd for $C_{21}H_{16}ClIN_3O$: 488.0027, found: 488.0029; IR (KBr): 3392, 3169, 3060, 2922, 2854, 1745, 1647, 1587, 1471, 1440, 1274, 1232, 1193, 1079, 1017, 904, 872, 769, 722, 673, 509, 442 cm^{-1}.

CCDC 1553558 (for 3a), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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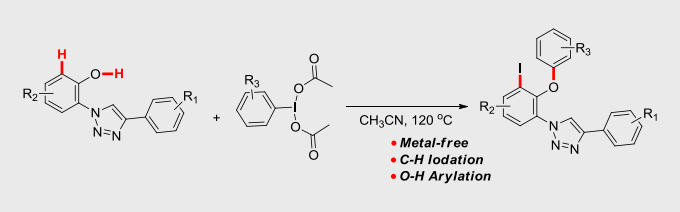

A method for the synthesis of etherfied 1, 2, 3-triazole idodides from 1, 4-disubstituted 1, 2, 3-triazoles under metal free conditions has been developed. In the presence of ArI(OAc)$_2$, a range of 1, 2, 3-triazole substrates bearing hydroxyl group undergo the direct O-H arylation and C-H iodation simultaneously and was modified in good to excellent yields.

* Functionalized triazoles

*Key Topic** **O-H Arylation • C-H Iodation • 1, 4-Disubstituted 1, 2, 3-triazoles • Metal-free**

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Metal-free synthesis of etherfied 1, 2, 3-triazole idodides through O-H arylation / C-H iodation with diacetoxyiodobenzenes