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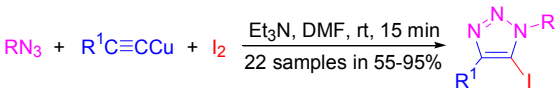

The desired 5-iodo-1,2,3-triazoles were synthesized conveniently without using the pre-made 1-iodoalkynes as substrates.

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ARTICLE TYPE

One-pot three-component synthesis of 1,4,5-trisubstituted 5-iodo-1,2,3-triazoles from 1-copper(I) alkyne, azide and molecular iodine

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Copper(I)-catalyzed cycloaddition of 1-iodoalkyne and azide has proven to be the most efficient method for the synthesis of 1,4,5-trisubstituted 5-iodo-1,2,3-triazoles, but pre-made 1-iodoalkyne is required. We find that the combination of 1-copper(I) alkyne and molecular iodine can well serve as a synthetic equivalent of 1-iodoalkyne. Thus, the desired 5-iodo-1,2,3-triazole can be synthesized by simply mixing this combination and an azide together without the tedious synthesis of the corresponding 1-iodoalkyne.

Introduction

Great progress[1] has been made in application of 1,2,3-triazoles since the discovery of copper(I)-catalyzed cycloaddition of azide (**1**) and terminal alkyne (**2**) (CuAAC).[2] Normal CuAAC reaction produces only 1,4-disubstituted 1,2,3-triazole (**3**). Thus, the importance of 1,4,5-trisubstituted 5-iodo-1,2,3-triazole (**4**) is enhanced recently because its iodine atom can be smoothly converted into various groups to give the corresponding 1,4,5-trisubstituted 1,2,3-triazoles, by which the diversity of structures and properties could be increased (Figure 1).[3-8]

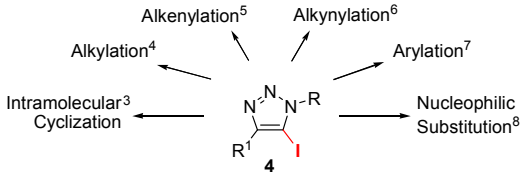
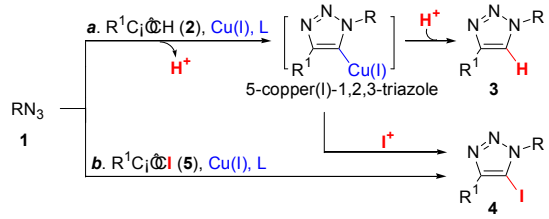


Figure 1 5-Iodo-1,2,3-triazoles (**4**) as versatile substrates.

Investigation showed that two practical methods have been used for the synthesis of 5-iodo-1,2,3-triazoles (**4**) (Scheme 1). Method-*a*[4b,6c,9] is achieved easily by adding an electrophile I^+ into a normal CuAAC reaction to trap the 5-copper(I)-1,2,3-triazole intermediate. But, this method usually gives **4** as a mixture with by-product **3** caused by the competitive substitution of the *in situ* generated electrophile H^+. Method-*b*[4a,7a,7c,10] gives **4** as a single product by using 1-iodoalkyne (**5**) as a substrate under the similar conditions, but pre-made 1-iodoalkynes (**5**) is required.

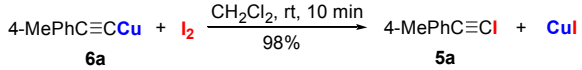


Scheme 1 Two practical methods for the synthesis of **4**.

To date, method-*b* has proven to be the most efficient method for the synthesis of 5-iodo-1,2,3-triazoles (**4**) and a total of five protocols have been reported.[4a,7a,7c,10] In these protocols, the Cu(I)-catalyzed cycloaddition of 1-iodoalkyne and azide proceeds so easily that the synthesis of the substrate 1-iodoalkyne (**5**) has been become a main obstacle. Herein, we would like to report a sixth protocol for the same purpose by using the combination of 1-copper(I) alkyne (**6**) and molecular iodine as a synthetic equivalent of 1-iodoalkyne (**5**). Thus, the desired 5-iodo-1,2,3-triazole (**4**) can be efficiently synthesized by simply mixing this combination and an azide (**1**) together without the tedious synthesis of the corresponding 1-iodoalkyne (**5**).

Results and Discussion

Many protocols have been reported for the synthesis of 1-iodoalkynes (**5**) from terminal alkynes (**2**). But, only some of them could proceed under mild conditions (without using strong bases or air sensitive reagents) when the special substrates or reagents were employed.[7c,11] Furthermore, since 1-iodoalkynes (**5**) are sensitive to air and light, decompositions are observed during their preparation, purification and storage.[12] In our recent works, 1-iodoalkyne (**5**) was unexpectedly produced from the mixture of 1-Cu(I) alkyne (**6**) and NIS in CH_2Cl_2.[13] As shown in Scheme 2, when we mixed together 1-Cu(I)-2-(4-methyphenyl)ethyne (**6a**) and I_2 in CH_2Cl_2, the desired 1-iodo-2-(4-methyphenyl)ethyne (**5a**) was obtained also in 98% yield within 10 min.

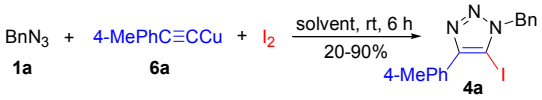


Scheme 2 Preparation of 1-iodoalkyne from 1-Cu(I) alkyne and I_2.

Since this conversion cleanly produced equimolar amounts of **5a** and CuI only, it may be used to synthesize 1-benzyl-4-(4-methylphenyl)-5-iodo-1,2,3-trizole (**4a**) in the presence of benzyl azide (**1a**). As shown in Table 1, this hypothesis was proved and **4a** was obtained in 74% yield after the mixture of **1a**, **6a** and I_2 in

CH_2Cl_2 was stirred for 6 h (entry 1). Many solvents were suitable for this conversion and DMF gave the best results (entry 9).

Table 1 Effect of solvent on the yield of **4a**.[a]

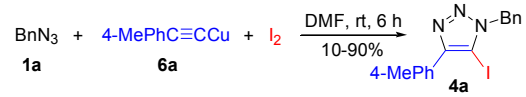


entry	solvent	yield of **4a** (%)[b]
1	CH_2Cl_2	74
2	THF	20
3	$PhCH_3$	25
4	EtOH	43
5	CH_3CN	58
6	CH_3COCH_3	72
7	$ClCH_2CH_2Cl$	75
8	NMP	87
9	DMF	90

[a] The mixture of **1a** (0.75 mmol), **6a** (0.5 mmol) and I_2 (0.5 mmol) in solvent (1 mL) was stirred in a stoppered glass tube. [b] The isolated yields.

Further experiments proved that the yield of **4a** was influenced significantly by the reactant ratios. As shown in Table 2, the yield of **4a** was increased by the increase of the ratio of **1a** (entries 1-4). No comparable changes were observed by using higher ratio of **6a** (entry 5-6). However, the yield of **4a** was decreased sharply by the increase of the ratio of I_2 (entries 7-9). Since 1,4-di(4-methylphenyl)butadiyne [$(4\text{-MePhC}\equiv C)_2$] was separated in these entries, the problem must be caused by the oxidizing property of I_2, by which the *in situ* generated 1-iodoalkyne **5a** underwent a Cu(I)-catalyzed oxidative coupling. The other two popular precursors of I^+, NIS and ICl, were tested also under the similar conditions, but lower yields of **4a** and higher yields of oxidative coupling byproduct were obtained.

Table 2 Effect of the substrate ratio on the yield of **4a**.[a]

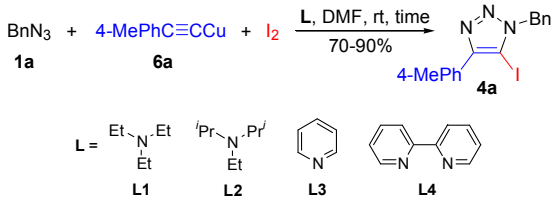


entry	**1a:6a:I_2** (by mole)	yield of **4a** (%)[b]
1	1.0 : 1.0 : 1.0	81
2	1.2 : 1.0 : 1.0	86
3	1.5 : 1.0 : 1.0	90
4	2.0 : 1.0 : 1.0	90
5	1.5 : 1.2 : 1.0	89
6	1.5 : 1.5 : 1.0	88
7	1.5 : 1.0 : 1.2	53
8	1.5 : 1.0 : 1.5	29
9	1.5 : 1.0 : 2.0	10

[a] The mixture (0.5 mmol scale) of **1a**, **6a** and I_2 in DMF (1 mL) was stirred in a stoppered glass tube. [b]The isolated yields.

In the early references, the vital role of ligand in Cu(I)-catalyzed cycloaddition of 1-iodoalkynes (**5**) has been reported. For example, Rutjes[14] reported that the mixture of 1-iodoalkyne (**5**), azide (**1**) and CuI failed to give the cycloaddition product in the absence of ligand. But, the similar cycloaddition was reported by Fokin[7c] to give 5-iodo-1,2,3-triazole (**4**) in excellent yields in the presence of 2 equiv of Et_3N. Therefore, four popular ligands **L1-L4** were tested as shown in Table 3. When 2 equiv of Et_3N (**L1**) were added to the reaction, **4a** was obtained in 80% yield within 15 min (entry 2). The similarly efficient result was obtained also when 0.3 equiv of Et_3N (**L1**) was employed (entry 4). The all results in Table 3 indicated that the use of ligand could significantly enhance the reaction rate, but the yield of **4a** was decreased and the coupling product $(4\text{-MePhC}\equiv C)_2$ was only by-product. This may result from the fact that **6a** was activated by dissociating its polymeric structures with Et_3N.[15b-d,17a] Therefore, the activated **6a** underwent two by-reactions to give the by-product: (a) the oxidative coupling between two molecules of **6a**; (b) the Castro−Stephens coupling between **6a** and the *in situ* produced **5a**. Finally, the entry 4 was assigned as our standard conditions.

Table 3 Effects of the ligands **L1-L4** on the reaction.[a]



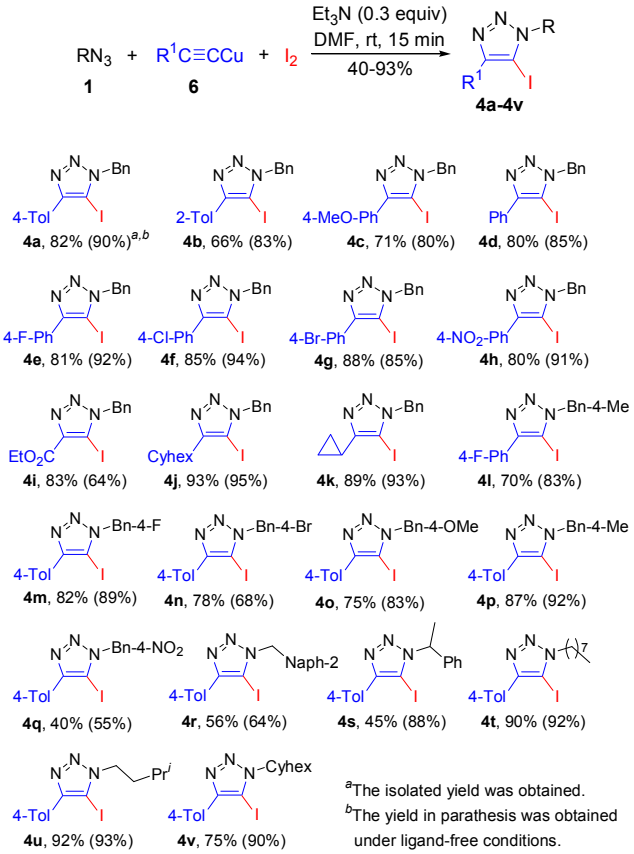
Entry	**L** (equiv)	time	yield of **4a** (%)[b]
1	none	6 h	90
2	**L1** (2.0)	15 min	80
3	**L1** (0.5)	15 min	79
4	**L1** (0.3)	15 min	82
5	**L1** (0.2)	1.5 h	79
6	**L1** (0.1)	4 h	82
7	**L2** (0.3)	15 min	73
8	**L3** (0.3)	1 h	70
9	**L4** (0.3)	4 h	75

[a] The mixture of **1a** (0.75 mmol), **6a** (0.5 mmol) and I_2 (0.5 mmol) in DMF (1 mL) was stirred in a stoppered glass tube. [b] The isolated yields.

So far, we successfully developed a one-pot three-component method for the synthesis of 1,4,5-trisubsituted 5-iodo-1,2,3-triazoles. In fact, this similar ideal has been attempted by Fokin,[7c] but it failed possibly because the catalytically active complex was disrupted either through oxidation of the metal or displacement/destruction of the ligand. However, there were no such problems in our method for three possible reasons. (a) Molecular iodine (a weak electrophile with the lowest oxidizability) was used as the resource of I^+ because 1-Cu(I) alkyne (**6**) has strong nucleophilicity. (b) A clean metathesis between 1-Cu(I) alkyne (**6**) and I_2 occurred without use of any additive and formation of any waster, in which the quantitatively formed 1-iodoalkyne (**5**) and CuI are the essential substrate and catalyst, respectively. (c) The *in situ* formed stoichiometric amount of Cu(I) was used as a catalyst, by which the catalytic cycle of Cu(I) was unnecessary.

Thus, the success of our method is mainly due to the use of 1-Cu(I) alkyne (**6**) as a substrate. It is well known that most 1-Cu(I)-alkyne (**6**) can be easily prepared as yellow crystals within 1 h[15,16d,17b] and can be stored in air for years without notable decomposition.[15-17] Therefore, it is synthetically convenient and valuable to use the combination of 1-Cu(I)-alkyne (**6**) and I_2 as a synthetic equivalent of 1-iodoalkyne (**5**), by which no needs of preparation, purification and storage of 1-iodoalkyne (**5**).

Finally, the scope of substrates and products were tested to generalize this method. As shown in Scheme 3, two yields obtained from two different procedures were reported for each product to meet the different needs. Most products were synthesized in good to excellent yields by both procedures. Compared with the procedure with ligand, the ligand-free procedure gave the higher yields, but the longer reaction time was required. The product **4q** was obtained in the lowest yield may be caused by its poor solubility. It quickly crystallized from DMF once it formed even though the double amounts of DMF were used, by which some of unreacted 1-Cu(I)-alkynes (**6h**) were wrapped.



Scheme 3 The scope of the method.

Conclusions

A "one-pot" three-component method for the synthesis of 1,4,5-trisubsituted 5-iodo-1,2,3-triazoles was developed from 1-Cu(I) alkyne, azide and I_2. In this method, the combination of 1-Cu(I) alkyne and I_2 is well served as a synthetic equivalent of 1-iodoalkyne without need of tedious preparation, purification and storage of 1-iodoalkyne.

Experimental

General information

All melting points were determined on a Yanaco melting point apparatus and were uncorrected. IR spectra were recorded as KBr pellets on a Nicolet FT-IR 5DX spectrometer. All spectra of ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded on a JEOL JNM-ECA 400 spectrometer in $CDCl_3$ (otherwise as indicated). TMS was used as an internal reference and J values are given in Hz. HRMS were obtained on a Bruker micrOTOF-Q II spectrometer. Copper(I) alkynes **6a-6k** were prepared by reported procedure in literature.[15,16d,17b]

A typical procedure for the preparation of 1-benzyl-4-(4-methylphenyl)-5-iodo-1,2,3-triazole (4a). Procedure A with a ligand: To a stirred suspension of 1-copper(I)-2-(4-methylphenyl)ethyne (**6a**, 89.4 mg, 0.5 mmol) in DMF (1 mL) in a glass tube was added BnN_3 (**1a**, 99.9 mg, 0.75 mmol), I_2 (126.9 mg, 0.5 mmol) and Et_3N (15.2 mg, 0.15 mmol) successively at room temperature. After 15 min, the resultant mixture was subjected to a fresh column chromatography [silica gel, 10% EtOAc in petroleum ether (60−90 °C)] to give 153 mg (82%) of product **4a** as a white solid.

Procedure B without a ligand: To a stirred suspension of copper(I)-2-(4-methylphenyl)ethyne (**6a**, 89.4 mg, 0.5 mmol) in DMF (1 mL) in a glass tube was added BnN_3 (**1a**, 99.9 mg, 0.75 mmol) and I_2 (126.9 mg, 0.5 mmol) successively at room temperature. After 6 h [the end-point was indicated by the fact that the *in situ* generated (4-methylphenyl)ethynyl iodide (**5a**) was exhausted], the resultant mixture was subjected to a fresh column chromatography [silica gel, 10% EtOAc in petroleum ether (60−90 °C)] to give 167 mg (90%) of product **4a** as a white solid, mp 110−112 °C (lit.[7c] 119−120 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.2 Hz, 2H), 7.38−7.29 (m, 5H), 7.26 (d, J = 7.8 Hz, 2H), 5.66 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 138.5, 134.3, 129.2 (2C), 128.8 (2C), 128.4, 127.8 (2C), 127.3 (3C), 76.1, 54.3, 21.3.

The products **4b-4v** were prepared similarly by this procedure.

1-Benzyl-4-(2-methylphenyl)-5-iodo-1,2,3-triazole (4b). Light yellow solid (124 mg, 66%), mp 108−110 °C. IR ν 3028, 2950, 2856, 1607, 1502, 1458, 1217 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.29 (m, 8H), 7.25−7.22 (m, 1H), 5.66 (s, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 137.7, 134.4, 130.6, 130.5, 129.8, 129.2, 129.0 (2C), 128.6, 127.9 (2C), 125.5, 79.7, 54.4, 20.3. HRMS (ESI-TOF) (m/z): calcd for $C_{16}H_{14}IN_3$, $[M + H]^+$ 376.0305; found 376.0293.

1-Benzyl-4-(4-methoxyphenyl)-5-iodo-1,2,3-triazole (4c). White solid (139 mg, 71%), mp 116−118 °C (lit.[18] 114−115 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 7.3 Hz, 2H), 7.36−7.29 (m, 5H), 6.98 (d, J = 7.4 Hz, 2H), 5.65 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 150.1, 134.4, 128.8 (2C), 128.7 (2C), 128.4, 127.8 (2C), 122.7, 113.9 (2C), 75.6, 55.3, 54.3.

1-Benzyl-4-phenyl-5-iodo-1,2,3-triazole (4d). White solid (144 mg, 80%), mp 136−138 °C (lit.[8a] 138.7−140.3 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.8 Hz, 2H), 7.45−7.30 (m, 8H), 5.67 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 134.3, 130.2, 128.9 (2C), 128.6, 128.5 (2C), 128.4, 127.8 (2C), 127.4 (2C), 76.4, 54.3.

1-Benzyl-4-(4-fluorophenyl)-5-iodo-1,2,3-triazole (4e). White solid (154 mg, 81%), mp 142−143 °C (lit.[8a] 150.8−152.0 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93−7.90 (m, 2H), 7.39−7.30

(m, 5H), 7.16-7.12 (m, 2H), 5.66 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9 (d, J_{CF} = 247.9 Hz), 149.4, 134.2, 129.3 (d, J_{CF} = 8.6 Hz, 2C), 128.9 (2C), 128.5, 127.8 (2C), 126.3, 115.5 (d, J_{CF} = 21.0 Hz, 2C), 76.2, 54.4.

1-Benzyl-4-(4-chlorophenyl)-5-iodo-1,2,3-triazole (4f). White solid (168 mg, 85%), mp 135−137 °C (lit.[7b] no melting point was reported). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.7 Hz, 2H), 7.42 (d, J = 8.7 Hz, 2H), 7.39−7.30 (m, 5H), 5.66 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 134.5, 134.1, 128.9 (2C), 128.8 (2C), 128.7, 128.6 (2C), 128.5, 127.8 (2C), 76.4, 54.4.

1-Benzyl-4-(4-bromophenyl)-5-iodo-1,2,3-triazole (4g). White solid (194 mg, 88%), mp 136−138 °C (lit.[7b] no melting point was reported). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.7 Hz, 2H), 7.58 (d, J = 8.7 Hz, 2H), 7.39−7.30 (m, 5H), 5.66 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 134.1, 131.7 (2C), 129.1, 128.9 (2C), 128.8 (2C), 128.5, 127.8 (2C), 127.7, 76.4, 54.4.

1-Benzyl-4-(4-nitrophenyl)-5-iodo-1,2,3-triazole (4h). Yellow solid (162 mg, 80%), mp 126−128 °C. IR ν 3042, 1595, 1514, 1451, 1340 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 9.2 Hz, 2H), 8.20 (d, J = 9.2 Hz, 2H), 7.40−7.32 (m, 5H), 5.70 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 147.5, 136.5, 133.8, 129.0 (2C), 128.7, 127.8 (2C), 127.7 (2C), 123.8 (2C), 77.7, 54.6. HRMS (ESI-TOF) (*m/z*): calcd for $C_{15}H_{11}IN_4O_2$, $[M + H]^+$ 407.0000; found 407.0002.

1-Benzyl-5-iodo-1,2,3-triazole-4-carboxylic acid ethyl ester (4i). White solid (148 mg, 83%), mp 141−143 °C (lit.[10] no melting point was reported). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.33 (m, 3H), 7.28−7.26 (m, 2H), 5.67 (s, 2H), 4.44 (q, J = 7.3 Hz, 2H), 1.43 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 142.2, 133.5, 128.9 (2C), 128.7, 127.8 (2C), 84.6, 61.5, 54.4, 14.2.

1-Benzyl-4-cyclohexyl-5-iodo-1,2,3-triazole (4j). Light yellow solid (171 mg, 93%), mp 104−106 °C. IR ν 3032, 2929, 2848, 1608, 1492, 1442, 1215 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.30 (m, 3H), 7.28−7.23 (m, 2H), 5.56 (s, 2H), 2.64−2.56 (m, 1H), 1.86−1.81 (m, 4H), 1.75−1.67 (m, 3H), 1.41−1.26 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 134.6, 128.8 (2C), 128.3, 127.7 (2C), 76.9, 53.9, 36.0, 31.9 (2C), 26.4 (2C), 25.8. HRMS (ESI-TOF) (*m/z*): calcd for $C_{15}H_{18}IN_3$, $[M + H]^+$ 368.0618; found 368.0613.

1-Benzyl-4-cyclopropyl-5-iodo-1,2,3-triazole (4k). Light yellow solid (145 mg, 89%), mp 103−105 °C (lit.[7c] 114−116 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.30 (m, 3H), 7.29−7.24 (m, 2H), 5.54 (s, 2H), 1.80−1.74 (m, 1H), 1.06−1.02 (m, 2H), 1.00−0.94 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 134.5, 128.8 (2C), 128.3, 127.7 (2C), 77.6, 54.0, 7.5 (2C), 7.2.

1-(4-Methylbenzyl)-4-(4-fluorophenyl)-5-iodo-1,2,3-triazole (4l). Light yellow solid (138 mg, 70%), mp 170−172 °C. IR ν 3029, 2924, 2852, 1604, 1530, 1472, 1229 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92−7.89 (m, 2H), 7.23−7.11 (m, 6H), 5.62 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (d, J_{CF} = 247.0 Hz), 149.4, 138.4, 131.2, 129.5 (2C), 129.3 (d, J_{CF} = 8.6 Hz, 2C), 127.8 (2C), 126.4, 115.5 (d, J_{CF} = 21.0 Hz, 2C), 76.1, 54.2, 21.1. HRMS (ESI-TOF) (*m/z*): calcd for $C_{16}H_{13}FIN_3$, $[M + H]^+$ 394.0211; found 394.0207.

1-(4-Fluorobenzyl)-4-(4-methylphenyl)-5-iodo-1,2,3-triazole (4m). Light yellow solid (161 mg, 82%), mp 128−130 °C. IR ν 3036, 2918, 2860, 1605, 1506, 1471, 1222 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.2 Hz, 2H), 7.33−7.25 (m, 4H), 7.06-7.01 (m, 2H), 5.62 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (d, J_{CF} = 245.7 Hz), 150.3, 138.6, 130.1 (d, J_{CF} = 3.8 Hz), 129.8 (d, J_{CF} = 8.4 Hz, 2C), 129.2 (2C), 127.3 (2C), 127.2, 115.9 (d, J_{CF} = 22.1 Hz, 2C), 75.9, 53.6, 21.3. HRMS (ESI-TOF) (*m/z*): calcd for $C_{16}H_{13}FIN_3$, $[M + H]^+$ 394.0211; found 394.0206.

1-(4-Bromobenzyl)-4-(4-methylphenyl)-5-iodo-1,2,3-triazole (4n). Light yellow solid (177 mg, 78%), mp 157−159 °C. IR ν 3027, 2935, 2856, 1584, 1478, 1228 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 7.8 Hz, 2H), 7.48 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.2 Hz, 2H), 7.18 (d, J = 8.2 Hz, 2H), 5.60 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 138.6, 133.3, 132.1 (2C), 129.5 (2C), 129.2 (2C), 127.3 (2C), 127.1, 122.6, 76.0, 53.7, 21.3. HRMS (ESI-TOF) (*m/z*): calculated for $C_{16}H_{13}BrIN_3$, $[M + H]^+$ 453.9410; found 453.9408.

1-(4-Methoxylbenzyl)-4-(4-methylphenyl)-5-iodo-1,2,3-triazole (4o). White solid (152 mg, 75%), mp 121−123 °C. IR ν 3015, 2929, 2840, 1610, 1510, 1442, 1245 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 7.4 Hz, 2H), 7.29−7.24 (m, 4H), 6.86 (d, J = 7.8 Hz, 2H), 5.57 (s, 2H), 3.78 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 150.2, 138.4, 129.4 (2C), 129.1 (2C), 127.3, 127.2 (2C), 126.4, 114.2 (2C), 75.8, 55.2, 53.9, 21.3. HRMS (ESI-TOF) (*m/z*): calculated for $C_{17}H_{16}IN_3O$, $[M + H]^+$ 406.0411; found 406.0403.

1-(4-Methylbenzyl)-4-(4-methylphenyl)-5-iodo-1,2,3-triazole (4p). Light yellow solid (169 mg, 87%), mp 116−118 °C. IR ν 3026, 2917, 2860, 1615, 1510, 1472, 1222 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.2 Hz, 2H), 7.26-7.14 (m, 6H), 5.61 (s, 2H), 2.39 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 138.4, 138.3, 131.3, 129.5 (2C), 129.2 (2C), 127.8 (2C), 127.3, 127.2 (2C), 76.0, 54.1, 21.3, 21.1. HRMS (ESI-TOF) (*m/z*): calcd for $C_{17}H_{16}IN_3$, $[M + H]^+$ 390.0462; found 390.0463.

1-(4-Nitrobenzyl)-4-(4-methylphenyl)-5-iodo-1,2,3-triazole (4q). Light yellow solid (84 mg, 40%), mp 190−192 °C. IR ν 3020, 2920, 2860, 1607, 1535, 1346, 1224 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.26 (d, J = 8.7 Hz, 2H), 7.80 (d, J = 8.2 Hz, 2H), 7.46 (d, J = 8.7 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 5.91 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 150.2, 148.1, 143.8, 138.8, 130.1 (2C), 129.4 (2C), 128.4, 127.7 (2C), 124.9 (2C), 82.6, 53.7, 21.8. HRMS (ESI-TOF) (*m/z*): calcd for $C_{16}H_{13}IN_4O_2$, $[M + H]^+$ 421.0156; found 421.0152.

1-(2-Naphthylmethyl)-4-(4-methylphenyl)-5-iodo-1,2,3-triazole (4r). White solid (119 mg, 56%), mp 154−156 °C. IR ν 3049, 2922, 2860, 1726, 1507, 1437, 1227 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85−7.78 (m, 5H), 7.73 (s, 1H), 7.50−7.46 (m, 2H), 7.41 (d, J = 8.2 Hz, 1H), 7.25 (d, J = 7.8 Hz, 2H), 5.80 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 138.5

(2C), 133.1, 133.0, 131.7, 129.2, 128.8, 127.9, 127.7, 127.3 (3C), 127.1, 126.5, 126.4, 125.1, 76.1, 54.5, 21.3. HRMS (ESI-TOF) (*m/z*): calcd for $C_{20}H_{16}IN_3$, $[M + H]^+$ 426.0462; found 426.0458.

1-(α-Methylbenzyl)-4-(4-methylphenyl)-5-iodo-1,2,3-triazole (4s). White solid (88 mg, 45%), mp 144−146 °C. IR *v* 3023, 2994, 2931, 2861, 1611, 1480, 1448, 1217 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 7.8 Hz, 2H), 7.36−7.29 (m, 5H), 7.26−7.24 (m, 2H), 5.78 (q, J = 7.2 Hz, 1H), 2.38 (s, 3H), 2.10 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 140.2, 138.4, 129.1 (2C), 128.8 (2C), 128.2, 127.5 (2C), 127.4, 126.6 (2C), 76.6, 61.4, 22.3, 21.3. HRMS (ESI-TOF) (*m/z*): calcd for $C_{17}H_{16}IN_3$, $[M + H]^+$ 390.0462; found 390.0466.

1-(Oct-1-yl)-4-(4-methylphenyl)-5-iodo-1,2,3-triazole (4t). Light yellow solid (179 mg, 90%), mp 72−74 °C. IR *v* 3038, 2920, 2856, 1641, 1510, 1460, 1225 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 7.8 Hz, 2H), 7.27 (d, J = 7.8 Hz, 2H), 4.42 (t, J = 7.3 Hz, 2H), 2.40 (s, 3H), 1.98−1.91 (m, 2H), 1.38−1.28 (m, 10H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 138.3, 129.2 (2C), 127.5, 127.3 (2C), 75.8, 50.9, 31.7, 29.9, 29.0, 28.9, 26.4, 22.6, 21.3, 14.0. HRMS (ESI-TOF) (*m/z*): calcd for $C_{17}H_{24}IN_3$, $[M + H]^+$ 398.1088; found 398.1085.

1-(3-Methylbut-1-yl)-4-(4-methylphenyl)-5-iodo-1,2,3-triazole (4u). White solid (163 mg, 92%), mp 83−85 °C. IR *v* 3035, 2950, 2920, 2861, 1641, 1514, 1460, 1255 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 7.8 Hz, 2H), 7.27 (d, J = 7.8 Hz, 2H), 4.44 (t, J = 7.8 Hz, 2H), 2.40 (s, 3H), 1.84 (q, J = 6.9 Hz, 2H), 1.73−1.66 (m, 1H), 1.01 (d, J = 8.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 138.3, 129.2, 127.5 (2C), 127.3 (2C), 76.7, 49.4, 38.6, 25.6, 22.3 (2C), 21.3. HRMS (ESI-TOF) (*m/z*): calcd for $C_{14}H_{18}IN_3$, $[M + H]^+$ 356.0618; found 356.0616.

1-Cycylohexyl-4-(4-methylphenyl)-5-iodo-1,2,3-triazole (4v). Light yellow solid (138 mg, 75%), mp 156−158 °C. IR *v* 3035, 2923, 2853, 1611, 1510, 1450, 1225 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 7.8 Hz, 2H), 7.26 (d, J = 7.8 Hz, 2H), 4.41−4.34 (m, 1H), 2.39 (s, 3H), 2.12−1.95 (m, 6H), 1.79−1.76(m, 1H), 1.52−1.26 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 138.2, 129.1 (2C), 127.6, 127.5 (2C), 75.8, 61.1, 32.7 (2C), 25.4 (2C), 25.0, 21.3. HRMS (ESI-TOF) (*m/z*): calcd for $C_{15}H_{18}IN_3$, $[M + H]^+$ 368.0618; found 368.0618.

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Notes and references

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