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ARTICLE in THE JOURNAL OF ORGANIC CHEMISTRY · SEPTEMBER 2013

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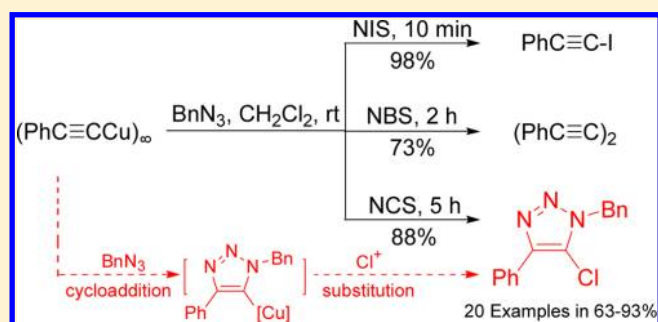
## Tandem Reaction of 1-Copper(I) Alkynes for the Synthesis of 1,4,5-Trisubstituted 5-Chloro-1,2,3-triazoles

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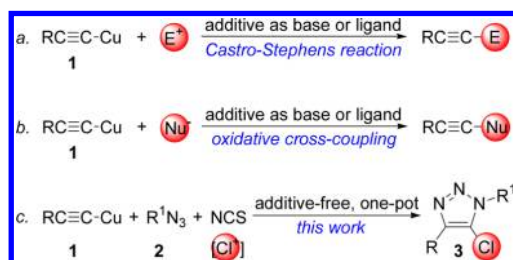
## Supporting Information

**ABSTRACT:** A novel tandem reaction of 1-copper(I) alkynes with azides (cycloaddition) and then NCS (electrophilic substitution) was developed as an efficient method for the synthesis of 1,4,5-trisubstituted 5-chloro-1,2,3-triazoles. The method offers a rare example that a tandem reaction of an organometallic substrate does not involve in the reactivity of the metal–carbon bond in the first step.



The isolated 1-copper(I) alkynes (**1**) are believed to have the polymeric complex structure  $(RC\equiv CCu)_n$ , in which the acetylene bond serves as a ligand without any exogenous ligand.<sup>1</sup> For example, the detailed structures of  $t\text{-BuC}\equiv\text{CCu}$  and  $\text{PhC}\equiv\text{CCu}$  can be drawn as  $(t\text{-BuC}\equiv\text{CCu})_{20}$  and  $(\text{PhC}\equiv\text{CCu})_\infty$ , respectively.<sup>2</sup> Most 1-copper(I) alkynes (**1**) can be simply prepared and isolated as insoluble crystalline solids with extremely chemical stability. Therefore, their structures are poorly understood, and their reactions in organic synthesis are shortly studied to date. As shown in Scheme 1,

Scheme 1



their most important application was in the Castro–Stephens reaction, where the Cu(I)–C bond was substituted by various electrophiles (*a*).<sup>3</sup> Recently, a new application of them was reported by Evano, in which the Cu(I)–C bond was substituted by nucleophiles through an oxidative cross-coupling mechanism (*b*).<sup>4</sup> Herein, we report that 1-copper(I) alkynes (**1**) can also carry out a novel tandem reaction with azides (**2**) (cycloaddition) and then NCS (electrophilic substitution), where the reactivity of Cu(I)–C bond was not involved in the first step to give 1,4,5-trisubstituted 5-chloro-1,2,3-triazoles (**3**) as the final products (*c*).

Recently, 1,4,5-trisubstituted 1,2,3-triazoles were reported to have important applications in organic synthesis, biology, and

material sciences.<sup>5–9</sup> Prominent among them are 1,4,5-trisubstituted 5-halo-1,2,3-triazoles (**3–5**)<sup>6–9</sup> because they can be used as both product and precursor (Figure 1). However,

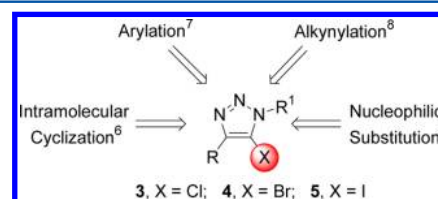
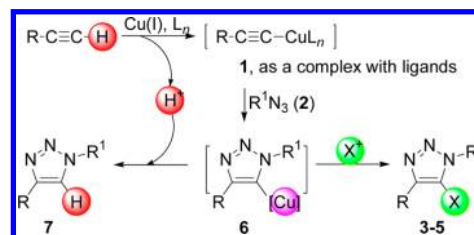


Figure 1. Synthetic applications of 1,4,5-trisubstituted 5-halo-1,2,3-triazoles.

they cannot be prepared by the normal CuAAC reaction (copper-catalyzed azide–alkyne cycloaddition) in which only terminal alkynes are used as substrates and 1,4-disubstituted 1,2,3-triazoles are produced.<sup>1a,10</sup>

Many efforts have been made to develop the methods for the synthesis of 1,4,5-trisubstituted 5-halo-1,2,3-triazoles (**3–5**). As shown in Scheme 2, an early method was to simply add an

Scheme 2



Received: July 26, 2013

Published: September 13, 2013

electrophile  $X^+$  ( $X = \text{Cl}, \text{Br}, \text{and I}$ ) into a normal CuAAC reaction by which the intermediate 5-copper(I) 1,2,3-triazole (**6**)<sup>8a,c,11</sup> was trapped in situ by  $X^+$ . Unfortunately, this method usually gave a mixture containing both the desired product and the byproduct 1,4-disubstituted 1,2,3-triazole (**7**) due to a competitive protonation of  $H^+$ . In some cases, the byproduct **7** was even the major product depending upon the structure of the substrate. This drawback was unavoidable because this  $H^+$  came from the terminal alkyne, which was the required substrate for a normal CuAAC reaction.

To overcome the drawbacks caused by terminal alkynes, 1-bromoalkynes (**8**) were wisely introduced as the substrates (Figure 2).<sup>9b</sup> Under the modified CuAAC conditions, 1,4,5-

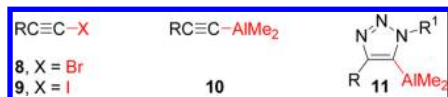
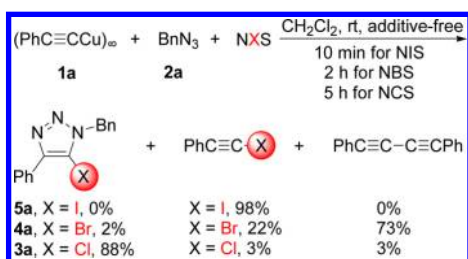


Figure 2. Structures of **8**–**11**.

trisubstituted 5-bromo-1,2,3-triazoles (**4**) were produced smoothly by the cycloaddition of **8** and **2**. Later, 1-iodoalkynes (**9**) were proved to be the most suitable substrates for the synthesis of 1,4,5-trisubstituted 5-iodo-1,2,3-triazoles (**5**).<sup>6,7b,12</sup> Recently, 1-aluminoalkynes (**10**) were reported to be versatile substrates for the synthesis of various 1,4,5-trisubstituted 1,2,3-triazoles including the products **3**–**5**.<sup>13</sup> But, there are two drawbacks to this otherwise efficient method caused by the highly active Al–C bonds in both **10** and its reaction intermediates 5-alumino-1,2,3-triazoles (**11**). First, this method has to be performed under anhydrous conditions because Al–C bonds are sensitive to moisture. Second, the method has to proceed in two steps because these two Al–C bonds do not have chemoselectivity to the electrophile  $X^+$ .

In our recent CuAAC project, 1-copper(I) alkynes (**1**) were used often as substrates and intermediates in the synthesis of 1,4-disubstituted 1,2,3-triazoles.<sup>14</sup> Interestingly, we found that they were perfectly stable to air and moisture but were still never used for the synthesis of 1,4,5-trisubstituted 5-halo-1,2,3-triazoles (**3**–**5**). Thus, we were encouraged to develop an easy method for the synthesis of **3**–**5** by using 1-copper(I) alkynes (**1**) as substrates. Unfortunately, the primary experimental results indicated that only a complicated mixture was produced when the solution of 1-copper(I) phenylethyne (**1a**) and benzyl azide (**2a**) in  $\text{CH}_2\text{Cl}_2$  was treated by NXS ( $X = \text{Cl}, \text{Br}, \text{or I}$ ) in the presence of an additive (as base or ligand), such as  $\text{Et}_3\text{N}$ , DIPEA, pyridine, or 1,10-phenanthroline. However, the same reactions gave a group of interesting results under the additive-free conditions. As shown in Scheme 3, 1-iodophenylethyne was obtained in 98% yield as a single product after **1a**, **2a**, and NIS were mixed together in  $\text{CH}_2\text{Cl}_2$  for 10 min. By

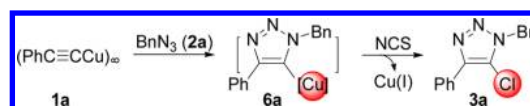
Scheme 3



replacement of NIS with NBS, the same reaction offered a mixture of **4a** (2%), 1-bromophenylethyne (22%) and 1,4-diphenylbutadiyne (73%). To our delight, the desired **3a** was obtained in 88% yield as a major product when NCS served as an electrophile.

The results in Scheme 3 clearly indicate that the reaction products strongly depend upon the properties of NXS. For example, NIS is a strong electrophile, and therefore, it undergoes a fast electrophilic substitution with **1a** to yield 1-iodophenylethyne as a unique product. However, NBS as a moderate electrophile reacts slowly with **1a** to initially yield some 1-bromophenylethyne. Then, the produced 1-bromophenylethyne further reacts with unreacted **1a** to form 1,4-diphenylbutadiyne as a major product by the Castro–Stephens reaction. However, the conditional experiments showed that the electrophilic substitution between **1a** and NCS proceeded very slowly under the same conditions (<10% of **1a** was consumed in 5 h) because NCS was the weakest electrophile compared to NIS and NBS. Thus, a CuAAC reaction between **1a** and **2a** occurs preferentially to give **6a** as an intermediate because the “click reaction” has a high thermodynamic driving force (Scheme 4).<sup>15</sup> The intermediate **6a** is then trapped by

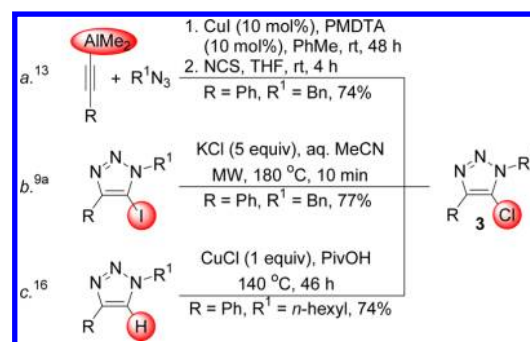
Scheme 4



NCS to give **3a**. This result indicates that the Cu(I)–C bond of **1a** has much lower reactivity than that of **6a** because **1a** is a polymeric complex. This result also offers a rare example whereby a tandem reaction of an organometallic substrate does not involve in the reactivity of the metal–carbon bond in the first step.

To further confirm the hypothesized pathway in Scheme 4, the cycloaddition of 1-chlorophenylethyne ( $\text{PhC}\equiv\text{CCl}$ ) and **2a** was tested in the presence of 1 equiv of  $\text{CuCl}$  ( $\text{CH}_2\text{Cl}_2$ , rt, 5 h). As was expected, no desired product **3a** was obtained, and  $\text{PhC}\equiv\text{CCl}$  was confirmed to not be an intermediate in the conversion of **1a** to **3a**. Thus far, we discovered a novel tandem reaction method for the synthesis of 1,4,5-trisubstituted 5-chloro-1,2,3-triazoles (**3**). Since the synthesis of **3** was the most difficult task among the isomers **3**–**5** and there were only three chemoselective procedures (*a–c*, Scheme 5)<sup>9a,13,16</sup> for this purpose in the literature to date, this mild and convenient tandem reaction method may be a valuable addition.

Scheme 5



Since product **3a** was produced under extremely simple conditions, only the solvent needs to be optimized. As shown in Table 1, the solvents have a significant effect on the yield of **3a**,

**Table 1. Effect of Solvent on the Reaction<sup>a</sup>**

entry	solvent	conc of <b>1a</b> (mmol/mL)	yield of <b>3a</b> <sup>b</sup> (%)
1	MeOH	0.5/1	32
2	MeCN	0.5/1	53
3	toluene	0.5/1	57
4	THF	0.5/1	70
5	CHCl <sub>3</sub>	0.5/1	76
6	ClCH <sub>2</sub> CH <sub>2</sub> Cl	0.5/1	84
7	CH <sub>2</sub> Cl <sub>2</sub>	<b>0.5/1</b>	<b>88</b>
8	CH <sub>2</sub> Cl <sub>2</sub>	0.5/2	83
9	CH <sub>2</sub> Cl <sub>2</sub>	0.5/4	85

<sup>a</sup>The mixture of **1a** (0.5 mmol), **2a** (0.6 mmol), and NCS (0.6 mmol) in solvent was stirred in a stoppered tube at room temperature for 5 h.

<sup>b</sup>Isolated yields.

and MeOH gave the lowest yield (entry 1). Interestingly, halo-containing solvents, such as CHCl<sub>3</sub>, ClCH<sub>2</sub>CH<sub>2</sub>Cl, and CH<sub>2</sub>Cl<sub>2</sub> (entries 5–7), were all good solvents, and CH<sub>2</sub>Cl<sub>2</sub> gave the best results (entry 7). The reaction concentrations did not have a comparable effect on the reaction (entries 7–9). Finally, the entry 7 was assigned as our standard conditions.

As shown in Scheme 6, this novel method was general and efficient for the molecular diversity. Under the standard conditions, 1-copper(I) alkynes (**1**), azides (**2**) and NCS

reacted smoothly to give the corresponding 1,4,5-trisubstituted 5-chloro-1,2,3-triazoles (**3a–t**) in satisfactory yields. By fixing 1-copper(I) phenylethyne (**1a**), all tested azides were suitable substrates (see: the products **3a–i**) and the azides bearing bulky groups gave relatively low yields (see: the products **3e** and **3h**). By fixing benzyl azide (**2a**), no apparent difference was observed for all tested 1-copper(I) alkynes, no matter which electron-donating groups (see: the products **3j–k**) or electron-withdrawing-groups (see: the product **3l**) are on the arylethyne.

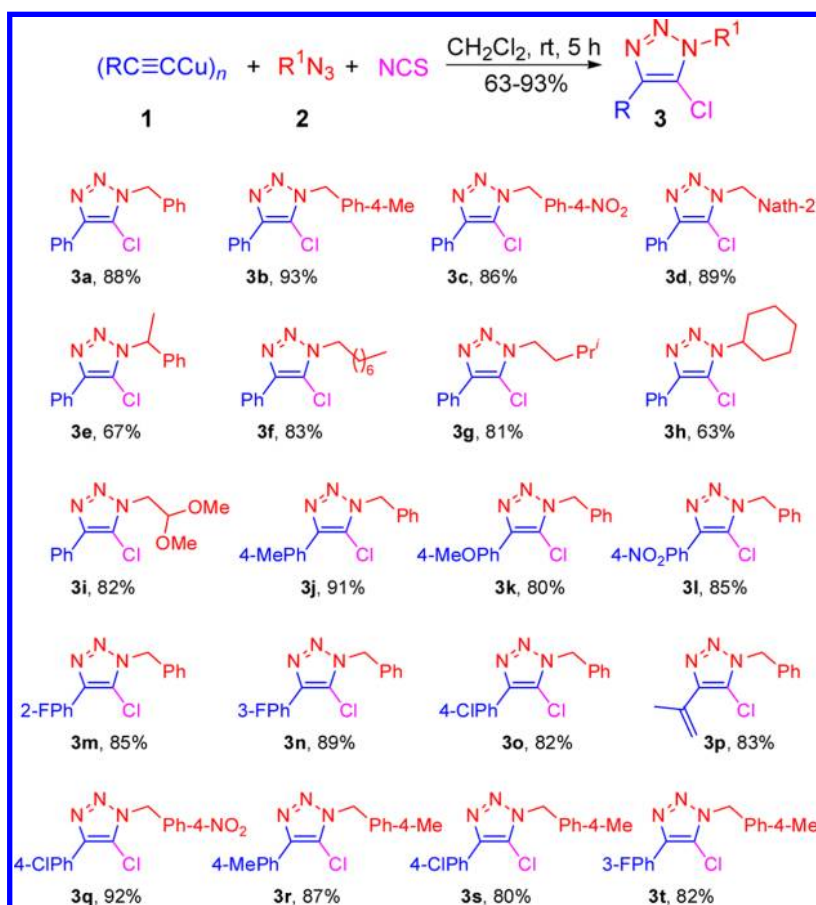
In conclusion, a novel tandem reaction method was established for the preparation of 1,4,5-trisubstituted 5-chloro-1,2,3-triazoles by directly using the isolated 1-copper(I) alkynes as substrates. The method shows noteworthy importance because it proceeds under mild conditions and its products are expected to have important medicinal properties.

## EXPERIMENTAL SECTION

The <sup>1</sup>H NMR (300 MHz) and <sup>13</sup>C NMR (75 MHz) spectra were recorded in CDCl<sub>3</sub>. TMS was used as an internal reference, and *J* values are given in hertz. 1-Copper(I) alkynes (**1**) were prepared according to the procedure reported in ref 3c.

**Typical Procedure for the Preparation of 1-Benzyl-4-phenyl-5-chloro-1,2,3-triazole (3a).** To a suspension of 1-copper(I) phenylethyne (**1a**, 82 mg, 0.5 mmol) and benzyl azide (**2a**, 80 mg, 0.6 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) was added NCS (80 mg, 0.6 mmol). The resultant mixture was stirred at room temperature for 5 h and then passed through column chromatography [silica gel, 10% EtOAc in petroleum ether (60–90 °C)] to give 119 mg (88%) of product **3a** as a white solid: mp 60–62 °C (lit.<sup>13</sup> mp 58–60 °C); IR (KBr)  $\nu$

**Scheme 6**





3063, 3035, 2952, 1606  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  7.97–7.91 (m, 2H), 7.45–7.26 (m, 8H), 5.52 (s, 2H);  $^{13}\text{C}$  NMR  $\delta$  141.8, 133.7, 129.2, 128.8 (2C), 128.6 (2C), 128.5, 128.4, 127.7 (2C), 126.2 (2C), 121.6, 51.9; HRMS (ESI-TOF)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{12}\text{ClN}_3$   $[\text{M} + \text{H}]^+$  270.0793, found 270.0792.

A similar procedure was used for the preparation of products **3b–t**.

**1-(4-Methylbenzyl)-4-phenyl-5-chloro-1,2,3-triazole (3b):** white solid; 132 mg (93%); mp 83–85  $^{\circ}\text{C}$ ; IR (KBr)  $\nu$  3028, 2984, 1611  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  7.96 (d,  $J$  = 7.92 Hz, 2H), 7.44–7.31 (m, 3H), 7.21–7.12 (m, 4H), 5.49 (s, 2H), 2.30 (s, 3H);  $^{13}\text{C}$  NMR  $\delta$  141.8, 138.4, 130.8, 129.5 (2C), 129.2, 128.5 (2C), 128.4, 127.7 (2C), 126.2 (2C), 121.5, 51.8, 21.0; HRMS (ESI-TOF)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{14}\text{ClN}_3$   $[\text{M} + \text{H}]^+$  284.0949, found 284.0950.

**1-(4-Nitrobenzyl)-4-phenyl-5-chloro-1,2,3-triazole (3c):** white solid; 135 mg (86%); mp 123–125  $^{\circ}\text{C}$ ; IR (KBr)  $\nu$  3079, 2953, 2851, 1606  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  8.24–8.14 (m, 2H), 7.99–7.90 (m, 2H), 7.52–7.33 (m, 5H), 5.67 (s, 2H);  $^{13}\text{C}$  NMR  $\delta$  147.9, 142.1, 140.6, 128.8, 128.7 (3C), 128.5 (2C), 126.1 (2C), 124.1 (2C), 121.7, 50.9; HRMS (ESI-TOF)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{11}\text{ClN}_4\text{O}_2$   $[\text{M} + \text{H}]^+$  315.0643, found 315.0642.

**1-(2-Naphthylmethyl)-4-phenyl-5-chloro-1,2,3-triazole (3d):** white solid; 142 mg (89%); mp 95–97  $^{\circ}\text{C}$ ; IR (KBr)  $\nu$  3055, 1601  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  7.98–7.96 (m, 2H), 7.82–7.74 (m, 4H), 7.50–7.32 (m, 6H), 5.69 (s, 2H);  $^{13}\text{C}$  NMR  $\delta$  142.0, 133.0 (2C), 131.1, 129.2, 128.9, 128.6 (2C), 128.5, 127.9, 127.7, 127.0, 126.5 (2C), 126.2 (2C), 125.0, 121.7, 52.2; HRMS (ESI-TOF)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{14}\text{ClN}_3$   $[\text{M} + \text{H}]^+$  320.0949, found 320.0951.

**1-(1-Ethylbenzyl)-4-phenyl-5-chloro-1,2,3-triazole (3e):** white solid; 95 mg (67%); mp 88–90  $^{\circ}\text{C}$ ; IR (KBr)  $\nu$  3063, 3032, 2990, 1607  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  7.98–7.95 (m, 2H), 7.47–7.24 (m, 8H), 5.71 (q,  $J$  = 6.87 Hz, 1H), 2.07 (d,  $J$  = 6.87 Hz, 3H);  $^{13}\text{C}$  NMR  $\delta$  141.8, 139.5, 129.3, 128.8 (2C), 128.5 (2C), 128.3, 128.2, 126.3 (4C), 121.4, 58.9, 21.3; HRMS (ESI-TOF)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{14}\text{ClN}_3$   $[\text{M} + \text{H}]^+$  284.0949, found 284.0948.

**1-Octyl-4-phenyl-5-chloro-1,2,3-triazole (3f):** yellow oil; 121 mg (83%); IR (KBr)  $\nu$  3062, 3033, 2956, 2855, 1608  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  8.00–7.96 (m, 2H), 7.48–7.26 (m, 3H), 4.35 (t,  $J$  = 7.20 Hz, 2H), 1.98–1.91 (m, 2H), 1.34–1.27 (m, 10H), 0.88 (t,  $J$  = 7.20 Hz, 3H);  $^{13}\text{C}$  NMR  $\delta$  141.5, 129.4, 128.6 (2C), 128.3, 126.2 (2C), 121.3, 48.4, 31.6, 29.3, 29.0, 28.9, 26.3, 22.5, 14.0; HRMS (ESI-TOF)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{22}\text{ClN}_3$   $[\text{M} + \text{H}]^+$  292.1575, found 292.1577.

**1-(3-Methylbutyl)-4-phenyl-5-chloro-1,2,3-triazole (3g):** yellow oil; 101 mg (81%); IR (KBr)  $\nu$  3062, 2958, 2871, 1608  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  7.99–7.96 (m, 2H), 7.48–7.33 (m, 3H), 4.36 (t,  $J$  = 7.56 Hz, 2H), 1.86–1.78 (m, 2H), 1.70–1.61 (m, 1H), 0.99 (d,  $J$  = 6.51 Hz, 6H);  $^{13}\text{C}$  NMR  $\delta$  141.5, 129.3, 128.5 (2C), 128.3, 126.2 (2C), 121.2, 46.7, 37.9, 25.4, 22.1 (2C); HRMS (ESI-TOF)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{16}\text{ClN}_3$   $[\text{M} + \text{H}]^+$  250.1106, found 250.1107.

**1-Cyclohexyl-4-phenyl-5-chloro-1,2,3-triazole (3h):** green solid; 82 mg (63%); mp 100–102  $^{\circ}\text{C}$ ; IR (KBr)  $\nu$  3074, 2931, 2855, 1611  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  7.99–7.93 (m, 2H), 7.48–7.34 (m, 3H), 4.41–4.31 (m, 1H), 2.14–1.95 (m, 6H), 1.79–1.74 (m, 1H), 1.51–1.26 (m, 3H);  $^{13}\text{C}$  NMR  $\delta$  141.4, 129.6, 128.6 (2C), 128.3, 126.4 (2C), 120.6, 58.6, 32.3 (2C), 25.3 (2C), 25.0; HRMS (ESI-TOF)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{16}\text{ClN}_3$   $[\text{M} + \text{H}]^+$  262.1106, found 262.1104.

**1-(2,2-Dimethoxyethyl)-4-phenyl-5-chloro-1,2,3-triazole (3i):** colorless oil; 110 mg (82%); IR (KBr)  $\nu$  3061, 3029, 2959, 2836, 1608  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  8.00–7.97 (m, 2H), 7.48–7.27 (m, 3H), 4.87 (t,  $J$  = 5.52 Hz, 1H), 4.46 (d,  $J$  = 5.52 Hz, 2H), 3.40 (s, 6H);  $^{13}\text{C}$  NMR  $\delta$  141.3, 129.2, 128.5 (2C), 128.3, 126.2 (2C), 122.3, 101.8, 54.5 (2C), 49.2; HRMS (ESI-TOF)  $m/z$  calcd for  $\text{C}_{12}\text{H}_{14}\text{ClN}_3\text{O}_2$   $[\text{M} + \text{H}]^+$  268.0847, found 268.0848.

**1-Benzyl-4-(4-methylphenyl)-5-chloro-1,2,3-triazole (3j):** white solid; 129 mg (91%); mp 76–78  $^{\circ}\text{C}$ ; IR (KBr)  $\nu$  3065, 2951, 2871, 1645  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  7.84 (d,  $J$  = 8.25 Hz, 2H), 7.34–7.18 (m, 7H), 5.49 (s, 2H), 2.34 (s, 3H);  $^{13}\text{C}$  NMR  $\delta$  141.9, 138.2, 133.8, 129.2 (2C), 128.8 (2C), 128.4, 127.6 (2C), 126.3, 126.0 (2C), 121.1, 51.8, 21.1; HRMS (ESI-TOF)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{14}\text{ClN}_3$   $[\text{M} + \text{H}]^+$  284.0949, found 284.0947.

**1-Benzyl-4-(4-methoxyphenyl)-5-chloro-1,2,3-triazole (3k):** white solid; 120 mg (80%); mp 61–62  $^{\circ}\text{C}$ ; IR (KBr)  $\nu$  3063, 3033, 2940, 2836, 1612  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  7.91–7.87 (m, 2H), 7.37–7.24 (m, 5H), 6.99–6.94 (m, 2H), 5.52 (s, 2H), 3.81 (s, 3H);  $^{13}\text{C}$  NMR  $\delta$  159.7, 141.8, 133.8, 128.8 (2C), 128.5, 127.7 (2C), 127.5 (2C), 121.8, 120.7, 114.0 (2C), 55.2, 51.9; HRMS (ESI-TOF)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{14}\text{ClN}_3\text{O}$   $[\text{M} + \text{H}]^+$  300.0898, found 300.0901.

**1-Benzyl-4-(4-nitrophenyl)-5-chloro-1,2,3-triazole (3l):** yellow solid; 134 mg (85%); mp 130–132  $^{\circ}\text{C}$ ; IR (KBr)  $\nu$  3033, 1599  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  8.30 (d,  $J$  = 8.25 Hz, 2H), 8.18 (d,  $J$  = 8.25 Hz, 2H), 7.40–7.32 (m, 5H), 5.61 (s, 2H);  $^{13}\text{C}$  NMR  $\delta$  147.4, 139.9, 135.5, 133.3, 129.1 (2C), 128.8, 127.9 (2C), 126.6 (2C), 124.0 (2C), 123.2, 52.3; HRMS (ESI-TOF)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{11}\text{ClN}_4\text{O}_2$   $[\text{M} + \text{H}]^+$  315.0643, found 315.0644.

**1-Benzyl-4-(2-fluorophenyl)-5-chloro-1,2,3-triazole (3m):** colorless oil; 122 mg (85%); IR (KBr)  $\nu$  3066, 3034, 2951, 2855, 1582  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  7.70–7.64 (m, 1H), 7.41–7.28 (m, 6H), 7.24–7.12 (m, 2H), 5.56 (s, 2H);  $^{13}\text{C}$  NMR  $\delta$  159.5 (d,  $J$  = 249.0 Hz), 138.7, 133.7, 130.7 (d,  $J$  = 2.9 Hz, 2C), 128.9 (2C), 128.5, 127.8 (2C), 124.2 (d,  $J$  = 2.8 Hz), 124.0, 117.1 (d,  $J$  = 14.3 Hz), 115.9 (d,  $J$  = 21.5 Hz), 52.1; HRMS (ESI-TOF)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{11}\text{ClFN}_3$   $[\text{M} + \text{H}]^+$  288.0698, found 288.0700.

**1-Benzyl-4-(3-fluorophenyl)-5-chloro-1,2,3-triazole (3n):** white solid; 128 mg (89%); mp 64–66  $^{\circ}\text{C}$ ; IR (KBr)  $\nu$  3079, 3035, 2925, 1617  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  7.77–7.67 (m, 2H), 7.43–7.24 (m, 6H), 7.08–7.01 (m, 1H), 5.56 (s, 2H);  $^{13}\text{C}$  NMR  $\delta$  162.8 (d,  $J$  = 243.8 Hz), 140.8, 133.6, 131.3 (d,  $J$  = 8.6 Hz), 130.3 (d,  $J$  = 7.9 Hz), 128.9 (2C), 128.6, 127.8 (2C), 122.0, 121.7, 115.3 (d,  $J$  = 20.8 Hz), 113.1 (d,  $J$  = 23.0 Hz), 52.1; HRMS (ESI-TOF)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{11}\text{ClFN}_3$   $[\text{M} + \text{H}]^+$  288.0698, found 288.0701.

**1-Benzyl-4-(4-chlorophenyl)-5-chloro-1,2,3-triazole (3o):** white solid; 125 mg (82%); mp 124–126  $^{\circ}\text{C}$ ; IR (KBr)  $\nu$  3066, 3034, 2933, 1603  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  7.92–7.89 (m, 2H), 7.42–7.31 (m, 7H), 5.56 (s, 2H);  $^{13}\text{C}$  NMR  $\delta$  141.0, 134.4, 133.6, 129.0 (2C), 128.9 (2C), 128.7, 127.8 (3C), 127.5 (2C), 121.7, 52.1; HRMS (ESI-TOF)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{11}\text{Cl}_2\text{N}_3$   $[\text{M} + \text{H}]^+$  304.0403, found 304.0402.

**1-Benzyl-4-isopropenyl-5-chloro-1,2,3-triazole (3p):** colorless oil; 97 mg (83%); IR (KBr)  $\nu$  3065, 3034, 2980, 2953, 1635  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  7.37–7.26 (m, 5H), 5.70 (s, 1H), 5.49 (s, 2H), 5.24 (s, 1H), 2.23 (s, 3H);  $^{13}\text{C}$  NMR  $\delta$  142.6, 133.8, 133.3, 128.8 (2C), 128.4, 127.7 (2C), 121.5, 114.5, 51.8, 21.1; HRMS (ESI-TOF)  $m/z$  calcd for  $\text{C}_{12}\text{H}_{12}\text{ClN}_3$   $[\text{M} + \text{H}]^+$  234.0793, found 234.0795.

**1-(4-Nitrobenzyl)-4-(4-chlorophenyl)-5-chloro-1,2,3-triazole (3q):** yellow solid; 161 mg (92%); mp 134–136  $^{\circ}\text{C}$ ; IR (KBr)  $\nu$  2925, 2852, 1603  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  8.23 (d,  $J$  = 8.94 Hz, 2H), 7.96–7.88 (m, 2H), 7.53–7.40 (m, 4H), 5.68 (s, 2H);  $^{13}\text{C}$  NMR  $\delta$  148.0, 141.2, 140.4, 134.6, 128.9 (2C), 128.6 (2C), 127.4 (2C), 127.3, 124.2 (2C), 121.8, 51.1; HRMS (ESI-TOF)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{10}\text{Cl}_2\text{N}_4\text{O}_2$   $[\text{M} + \text{H}]^+$  349.0254, found 349.0253.

**1-(4-Methylbenzyl)-4-(4-methylphenyl)-5-chloro-1,2,3-triazole (3r):** white solid; 130 mg (87%); mp 52–54  $^{\circ}\text{C}$ ; IR (KBr)  $\nu$  3023, 2920, 2856, 1649  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  7.84 (d,  $J$  = 8.25 Hz, 2H), 7.24–7.08 (m, 6H), 5.47 (s, 2H), 2.35 (s, 3H), 2.30 (s, 3H);  $^{13}\text{C}$  NMR  $\delta$  141.9, 138.3, 138.2, 130.8, 129.5 (2C), 129.2 (2C), 127.7 (2C), 126.4, 126.1 (2C), 121.1, 51.7, 21.2, 21.0; HRMS (ESI-TOF)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{16}\text{ClN}_3$   $[\text{M} + \text{H}]^+$  298.1106, found 298.1107.

**1-(4-Methylbenzyl)-4-(4-chlorophenyl)-5-chloro-1,2,3-triazole (3s):** white solid; 127 mg (80%); mp 83–85  $^{\circ}\text{C}$ ; IR (KBr)  $\nu$  3025, 2920, 1608  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  7.93–7.87 (m, 2H), 7.42–7.37 (m, 2H), 7.23–7.13 (m, 4H), 5.50 (s, 2H), 2.32 (s, 3H);  $^{13}\text{C}$  NMR  $\delta$  140.9, 138.5, 134.3, 130.6, 129.6 (2C), 128.8 (2C), 127.8 (2C), 127.4 (2C), 124.9, 121.6, 51.9, 21.1; HRMS (ESI-TOF)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{13}\text{Cl}_2\text{N}_3$   $[\text{M} + \text{H}]^+$  318.0559, found 318.0561.

**1-(4-Methylbenzyl)-4-(3-fluorophenyl)-5-chloro-1,2,3-triazole (3t):** white solid; 124 mg (82%); mp 98–100  $^{\circ}\text{C}$ ; IR (KBr)  $\nu$  3026, 2956, 2855, 1617  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  7.77–7.67 (m, 2H), 7.43–7.36 (m, 1H), 7.25–7.14 (m, 4H), 7.08–7.02 (m, 1H), 5.52 (s, 2H), 2.33 (s, 3H);  $^{13}\text{C}$  NMR  $\delta$  162.9 (d,  $J$  = 243.8 Hz), 140.8, 138.6, 131.4 (d,  $J$  = 8.6 Hz), 130.6, 130.3 (d,  $J$  = 8.6 Hz), 129.6 (2C), 127.8 (2C),

121.9, 121.8, 115.3 (d,  $J = 21.5$  Hz), 113.1 (d,  $J = 23.7$  Hz), 52.0, 21.1; HRMS (ESI-TOF)  $m/z$  calcd for  $C_{16}H_{13}ClFN_3$  [ $M + H$ ] $^+$  302.0855, found 302.0856.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

$^1H$  and  $^{13}C$  NMR spectra for products 3a–t. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported by the National Natural Scientific Foundation of China (21072112 and 21221062).

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