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Oxidative Cycloaddition

Copper Acetate Catalyzed Regioselective Synthesis of Substituted 1,2,3-Triazoles: A Versatile Azide–Alkene Cycloaddition/Oxidation Approach

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Abstract: A copper acetate catalyzed oxidative cycloaddition reaction of benzyl and aryl azides with terminal and internal olefins that contain electron-withdrawing groups (COOR, $CONH_2$, CN, CHO, COR) has been developed. The reaction employs air as the oxidant and does not require any base or additives to afford 1,4-disubstituted and 1,4,5-trisubstituted 1,2,3-triazoles in good to excellent yields with high regioselectivity.

Introduction

1,2,3-Triazoles are a privileged class of heterocyclic compounds with applications in synthetic,[1] medicinal,[2] and materials chemistry.[3] Among them, 1,4-disubstituted and 1,4,5-trisubstituted 1,2,3-triazole derivatives are significant, as they are found in a large number of biologically and pharmaceutically active molecules that have a broad spectrum of properties and act as cannabinoid receptor antagonists as well as anti-influenza, antiepileptic, and anticancer agents (Figure 1).[4]

The copper-catalyzed azide-alkyne cycloaddition (i.e., click reaction) works remarkably well with terminal alkynes[5] to yield 1,4-disubstituted 1,2,3-triazoles. However, the same reaction with internal alkynes[6] for the synthesis of fully substituted 1,2,3-triazoles remains a challenge. Recognized solutions include ruthenium-[7] and iridium-catalyzed[8] cycloaddition reactions of organic azides with internal alkynes. Alternatively, there are reports of a few other oxidative synthetic methods that use organic azides and alkenes as substrates (Scheme 1) such as: (a) a 1,3-dipolar cycloaddition reaction with alkenes that have a leaving group,[9] (b) an organocatalytic cycloaddition reaction with activated keto esters, enones, aldehydes, and nitriles that occurs through enamine intermediates formed in situ,[10] (c) an organocatalytic cycloaddition reaction with alkenes and the loss of two hydrogen atoms,[11] and (d) a copper-catalyzed reaction with olefins that have an electron-deficient carbonyl or nitro group.[12] Although organocatalytic methods [Scheme 1, equations (b) and (c)] offer the common green features of organocatalysis,[13] the approach is restricted in its application because of substrate scope in some cases and long reaction times in others.

In one of the previous copper-catalyzed protocols for the preparation of fully substituted triazoles, Yao[12a] and co-workers used a copper(I) catalyst along with O_2 as the oxidant and *N*,*N*-diisopropylethylamine (DIPEA) as the base to synthesize *N*-benzylated and *N*-alkylated 1,2,3-triazoles with aldehyde, keto, and amide substituents at the 4-position. In the second report, Chen[12b] used expensive $Cu(OTf)_2$ (OTf = trifluoromethanesulfonate) as the catalyst and acetic acid as an additive to synthesize 1,2,3-triazoles with only a nitro substituent at the 4-position. In our ongoing efforts towards the development of new synthetic strategies by using transition-metal catalysts,[14] we investigated whether a more general and economical route that has a wide substrate scope with respect to the organic azide (e.g., benzyl and aryl) and olefin (e.g., ester, amide, nitrile, aldehyde, and keto functional groups) could be developed. Herein, we present a highly regioselective synthesis of 1,4-disubstituted and 1,4,5-trisubstituted 1,2,3-triazoles from olefins

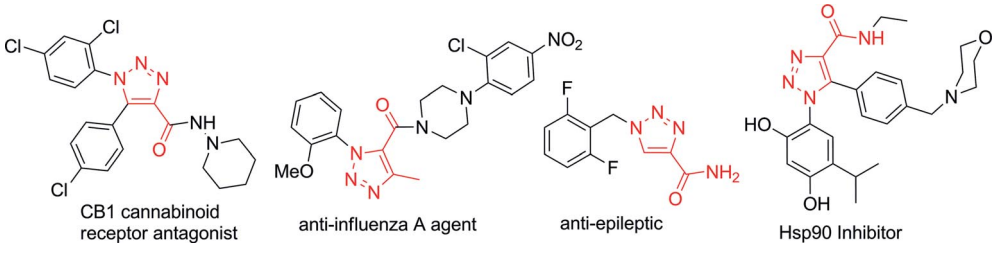

Figure 1. Biologically relevant substituted 1,2,3-triazole derivatives.

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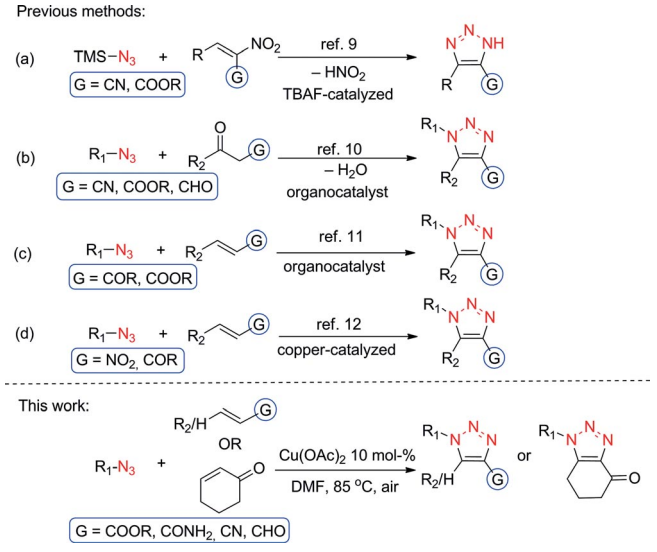


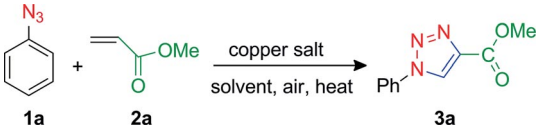
Scheme 1. Synthesis of substituted 1,2,3-triazoles from azides and alkenes (TMS = trimethylsilyl, TBAF = tetra-*n*-butylammonium fluoride, DMF = *N*,*N*-dimethylformamide).

and azides that proceeds through a cycloaddition-oxidation pathway. This developed method provides significant advantages over those reported by Yao and Chen. First, it makes use of inexpensive copper acetate as the catalyst, and second, it is applicable to olefins that contain ester and nitrile functional groups that were previously found inert under the conditions reported by Yao. Finally, this approach does not require any additional base or additive, and the method is suitable for the use of aryl azides as well as cyclic enones as substrates.

Results and Discussion

The conditions were examined by using the model reaction between phenyl azide (**1a**) and methyl acrylate (**2a**) with copper acetate in DMF in air at 100 °C. After 12 h, the isolated product was found to be 4-substituted 1,2,3-triazole **3a**. Pleased with the preliminary result, we decided to optimize the reaction results by varying the temperature, solvent, and copper salt. Reaction temperatures in the range 70–110 °C were studied. It was found that an increase in the temperature from 100 to 110 °C afforded a slightly decreased product yield (Table 1, Entries 1 and 2), whereas reducing the temperature to 90 and then 85 °C led to higher conversions (Table 1, Entries 3 and 4). Reducing the temperature further to 80 and 70 °C, however, afforded a decreased yield of **3a** (Table 1, Entries 5 and 6). Therefore, 85 °C was identified as the best temperature for this reaction. Next, the reaction was optimized with regard to the solvent. Tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), dichloromethane (DCM), CH_3CN, C_2H_5OH, H_2O, dioxane and 1,2-dichloroethane (DCE) were tested (Table 1, Entries 7–14) but found to be inferior to DMF, as they gave lower yields of **3a** (30–91 %). A transesterification reaction took place when ethanol was used, and **3b** was formed in 91 % yield instead of the desired product **3a** (Table 1, Entry 11). Next, we screened various copper(I) and copper(II) salts including CuI, CuBr, $Cu(OTf)_2$, CuF_2, $Cu(NO_3)_2$, $CuSO_4$, and $CuBr_2$ (Table 1, Entries 15–21). The lowest yields of 5 and 7 %, respectively, were obtained when $Cu(NO_3)_2$ and $CuBr_2$ were employed (Table 1, Entries 19 and 21). With other copper salts as catalyst, yields were in the range 37–74 % showing $Cu(OAc)_2$ to be the ideal catalyst for this reaction. Further studies involved the catalyst loading, the reduction of which to 5 mol-% lowered the yield of **3a** to 84 % (Table 1, Entry 22). Increasing the catalyst loading to 20 mol-% did not bring about any change, and in the absence of the copper catalyst, no conversion took place (Table 1, Entry 22). Because the reaction was anticipated to proceed through an oxidative process, the procedure was performed under oxygen, but no variation in the yield of **3a** was observed. As expected, **3a** was not formed under inert conditions (Table 1, Entry 23). Thus, the optimized conditions for the triazole formation included the use of 10 mol-% of $Cu(OAc)_2$ in DMF in air at 85 °C for 8 h.

Table 1. Optimization of reaction conditions for the synthesis of 1,4-disubstituted 1,2,3-triazoles.[a]



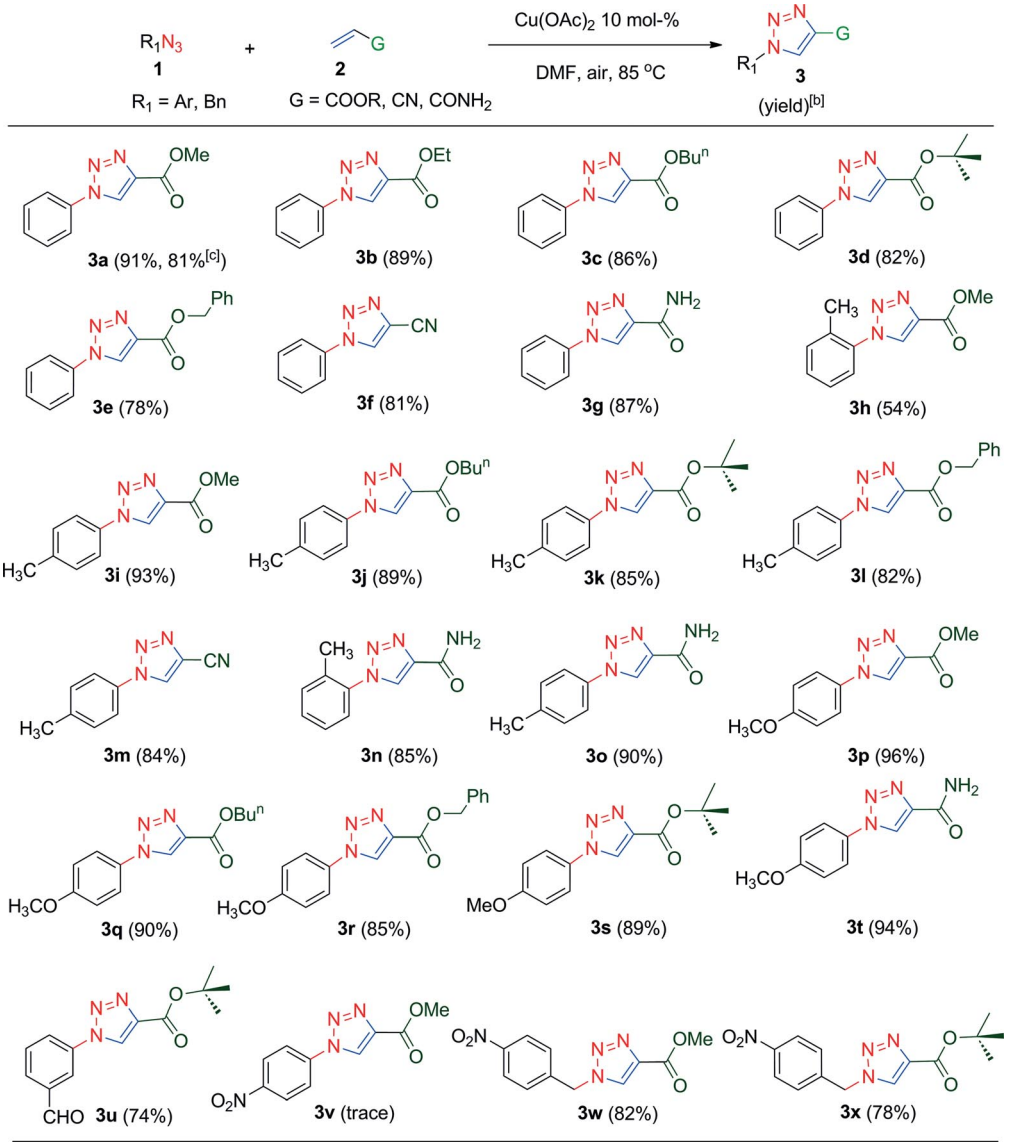
1a **2a** **3a**

Entry	Catalyst [mol-%]	Solvent	Temp. [°C]	Yield[b] [%]
1	$Cu(OAc)_2$	DMF	100	79
2	$Cu(OAc)_2$	DMF	110	76
3	$Cu(OAc)_2$	DMF	90	82
4	$Cu(OAc)_2$	DMF	85	95
5	$Cu(OAc)_2$	DMF	80	92
6	$Cu(OAc)_2$	DMF	70	79
7	$Cu(OAc)_2$	THF	85	73
8	$Cu(OAc)_2$	DMSO	85	82
9	$Cu(OAc)_2$	DCM	85	74
10	$Cu(OAc)_2$	CH_3CN	85	86
11	$Cu(OAc)_2$	C_2H_5OH	85	91[c]
12	$Cu(OAc)_2$	H_2O	85	30
13	$Cu(OAc)_2$	dioxane	85	84
14	$Cu(OAc)_2$	DCE	85	87
15	CuI	DMF	85	74
16	CuBr	DMF	85	45
17	$Cu(OTf)_2$	DMF	85	56
18	CuF_2	DMF	85	74
19	$Cu(NO_3)_2$	DMF	85	5
20	$CuSO_4$	DMF	85	43
21	$CuBr_2$	DMF	85	7
22	$Cu(OAc)_2$	DMF	85	84[d], 95[e], 0[f]
23	$Cu(OAc)_2$	DMF	85	94[g], 0[h]

[a] Reagents and conditions: **1a** (1.0 equiv., 0.17 mmol), **2a** (1.5 equiv., 0.25 mmol), catalyst (10 mol-%, 0.017 mmol), and solvent were heated for 8 h. [b] Yield obtained by HPLC analysis. [c] **3b** was obtained as the product. [d] $Cu(OAc)_2$ (5 mol-%) was employed. [e] $Cu(OAc)_2$ (20 mol-%) was employed. [f] No copper salt was added. [g] Reaction was performed under O_2. [h] Reaction was performed under N_2.

As 1,4-disubstituted triazole derivatives are important precursors to biologically active molecules, the optimized protocol was then applied to their synthesis to explore the scope and generality of the reaction (Table 2). In this regard, we first examined the reaction of aryl and benzyl azides with a variety of electron-deficient terminal olefins. The reaction of phenyl azide

Table 2. Substrate scope of the reaction of azides with electron-deficient terminal olefins.[a]



[a] Reagents and conditions: **1** (1 equiv.), **2** (1.5 equiv.), and $Cu(OAc)_2$ (10 mol-%) in DMF (2.0 mL) was stirred at 85 °C in air. [b] Yield of the isolated product. [c] Reaction was carried out on a gram scale by using **1a** (1.5 g).

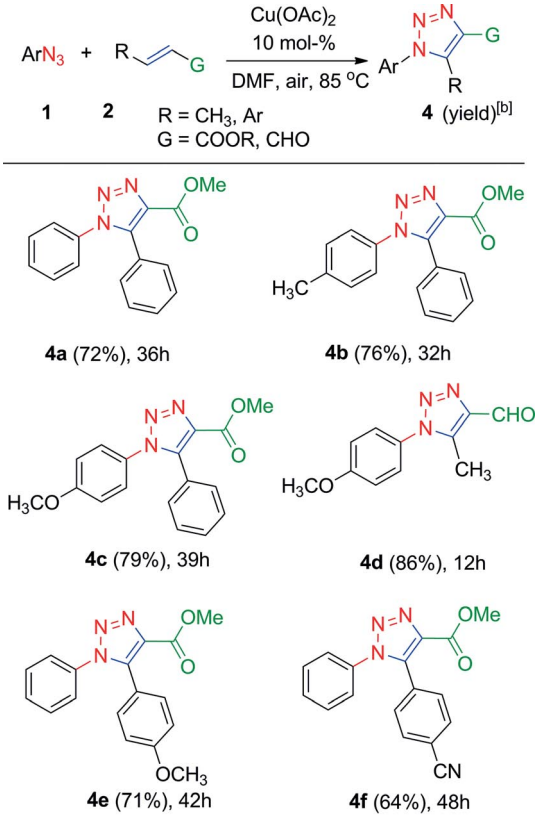
with various esters such as methyl, ethyl, *n*-butyl, pivalyl, and benzyl acrylate provided the corresponding ester-substituted triazole derivatives in good yields (Table 2, compounds **3a**–**3e**). When acrylonitrile and acrylamide were employed as substrates, the reaction afforded the corresponding nitrile- and amide-substituted triazole derivatives in 81 and 87 % yield, respectively (Table 2, compounds **3f** and **3g**). A similar copper-assisted synthesis of nitrile derivatives **3f** and **3m** has not been previously reported.

When the phenyl azide contained an electron-donating methyl or methoxy group at the *ortho* or *para* position of the aromatic ring, the corresponding ester-, amide-, and nitrile-substituted *N*-aryl triazoles were obtained in moderate to high yields (Table 2, compounds **3h**–**3t**). Although the reaction of 2-methylphenyl azide smoothly proceeded with acrylamide to yield **3n** in 85 % yield, the similar reaction with methyl acrylate was more complex, and unidentified side products were obtained, thus giving the desired product **3h** in only 54 % yield. When the phenyl azide contained an electron-deficient formyl group, the yield of the corresponding product **3u** was slightly lower, whereas having a nitro group on the phenyl azide only afforded trace amounts of the desired product **3v**. The reactions of nitro-substituted benzyl azides with methyl and pivalyl acrylate went well, and products **3w** and **3x** were obtained in 82 and 78 % yield, respectively. Yao et al. previously showed that benzyl azides were unable to react with methyl acrylate under their reaction conditions.[12a] However, we successfully isolated the ester derivatives of *N*-benzyltriazoles **3w** and **3x** in moderate yields. Finally, this reaction was possible up to a gram scale, and **3a** was formed in 81 % yield by starting from 1.5 g of **1a**.

To further evaluate the scope of this method for the synthesis of 1,4,5-trisubstituted triazoles, the reaction of azides with

substituted internal olefins was performed under the optimal reaction conditions. To our delight, the desired products (Table 3, compounds **4a**–**4f**) were obtained in moderate yields.

Table 3. Substrate scope for the reaction of azides with electron-deficient internal olefins.[a]



[a] Reagents and conditions: **1** (1.0 equiv.), **2** (1.5 equiv.), and $Cu(OAc)_2$ (10 mol-%) in DMF (2.0 mL) was stirred at 85 °C in air. [b] Yield of isolated product.

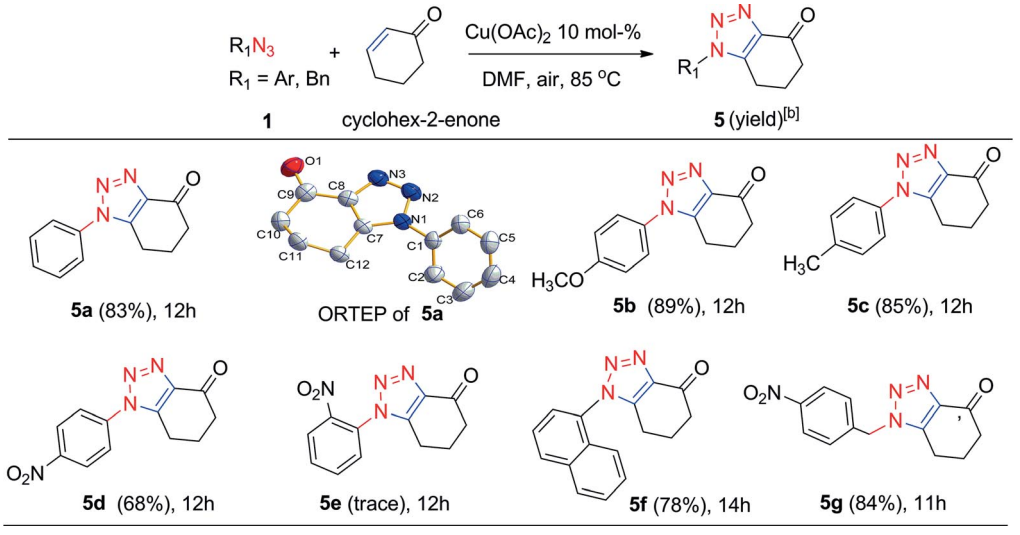
However, the reactions required a longer period of time than those needed for the terminal olefins, and these times varied from 12 to 48 h to produce the corresponding triazoles. This decrease in the rate of the reaction may be attributed to the steric hindrance from the substituents at the β-position to the carbonyl group.

Next, the reaction of azides with cyclic enones was performed as shown in Table 4. We were pleased to find that the reaction went well under the optimized conditions, and the corresponding triazoles (Table 4, compounds **5a**–**5d**, **5f**, and **5g**) were formed in moderate to high yields. The presence of an electron-donating methoxy or methyl group on the phenyl ring of the azide favored the reaction to yield **5b** and **5c** in 89 and 85 % yield, respectively.

When the phenyl azide contained a strong electron-withdrawing nitro group at the *para* position, the yield of the product decreased significantly, and **5d** was obtained in 68 % yield. However, when the nitro substituent occupied the *ortho* position, the effect was more pronounced, and only trace amounts of **5e** were observed. Overall, this protocol has a broad scope and provides a facile route to access new scaffolds such as 1-phenyl-6,7-dihydro-1*H*-benzo[*d*][1,2,3]triazol-4(5*H*)-one (**5a**), the structure of which was identified by X-ray single-crystal analysis.

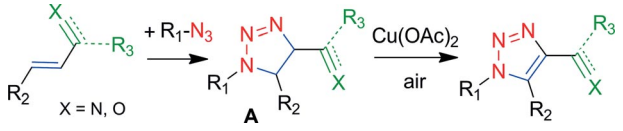
A plausible mechanism for the formation of 1,4-disubstituted and 1,4,5-trisubstituted 1,2,3-triazoles is outlined in Scheme 2. First, quenching studies with (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) were carried out to ascertain whether a free radical was involved in the mechanism. However, the addition of TEMPO did not have any effect on the reaction or the product yield, which suggests that reaction did not follow a radical pathway. We believe that the reaction between the electron-deficient alkene and azide is initiated through a copper acetate assisted stepwise 1,3-dipolar cycloaddition to produce triazoline intermediate **A**, which is further oxidized in presence of a copper catalyst and air to yield the final product. A similar copper/air-assisted oxidative aromatization in heterocyclic molecules

Table 4. Synthesis of 1,4,5-trisubstituted 1,2,3-triazoles from azides and 2-cyclohexen-1-one.[a]



[a] Reagents and conditions: **1** (1.0 equiv.), 2-cyclohexen-1-one (1.5 equiv.), and $Cu(OAc)_2$ (10 mol-%) in DMF (2.0 mL) was stirred at 85 °C in air. [b] Yield of isolated product.

has been previously reported.[15] Air is also rationalized as the oxidant that promotes the regeneration of the Cu^{II} catalyst.[12]



Scheme 2. Plausible mechanism for substituted 1,2,3-triazoles.

Conclusions

In summary, copper acetate has been employed for the first time as an inexpensive and efficient catalyst for the regioselective synthesis of 1,4-disubstituted and 1,4,5-trisubstituted 1,2,3-triazoles. The oxidative dehydrogenative process uses air as the oxidant and does not require any base or additive. This protocol is highly versatile, as it has been applied to both benzyl and aryl azide derivatives as well as a wide range of electron-deficient terminal and internal olefins. Herein, the strategy has been employed as a direct method for the synthesis of 1,2,3-triazoles that contain ester, amide, nitrile, aldehyde, and keto functionalities, which are otherwise difficult to obtain by the direct derivatization of the C-4 and C-5 positions of 1,2,3-triazoles.

Experimental Section

General Methods: All reactions were carried out in the air in an oven-dried round-bottomed flask that was sealed with a septum. All solvents were purchased from Aldrich and Spectrochem and used as received. Copper(II) acetate was purchased from Alfa-Aesar (98 % purity). The aromatic amines and aryl/benzyl bromides were purchased from Aldrich and Merck. Thin layer chromatography was performed on aluminium plates precoated with 60 F254 silica gel, and the compounds were visualized by using either a UV lamp (λ_{max} = 254 nm) or iodine vapors. The products were purified by column chromatography on silica gel (230–400 mesh). The ^1H and ^{13}C NMR spectroscopic data were recorded with a Bruker DPX-300 MHz spectrometer (^1H NMR: 300 and 400 MHz, ^{13}C NMR: 75 and 100 MHz). $CDCl_3$ was used as the NMR solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts (δ) are reported in ppm relative to TMS. The coupling constants (J) are reported in Hz. ESI-MS was performed with a high resolution mass spectrometer by using a quadrupole-TOF mass analyzer. Sodium azide is poisonous and was carefully handled. It should not be inhaled or have direct contact with skin or eyes.

Representative Procedure for the Synthesis of Aryl Azides:[16] Aniline (1 g, 10.75 mmol) was suspended in 17 % hydrochloric acid (65 mL) at room temperature. The solution was cooled to 0 °C by using an ice bath. Then $NaNO_2$ (1.11 g, 16.13 mmol) in water (5 mL) was added in small portions, and the resulting mixture was stirred at 0 °C for 20–30 min. A solution of NaN_3 (1.05 g, 16.13 mmol) in water (10 mL) was added dropwise over 3 min, and the contents were stirred for additional 2 h at room temperature. Upon completion, the reaction mixture was extracted with hexane (3 × 40 mL). The combined organic phases were washed with a saturated $NaHCO_3$ solution (2 × 40 mL) and brine (2 × 40 mL). The organic layer was dried with Na_2SO_4 and evaporated under reduced pressure. The crude residue was purified by column chromatography to give phenyl azide (1.23 g, 96 % yield).

Representative Procedure for Synthesis of Benzyl Azides:[17] A solution of sodium azide (453.6 mg, 6.98 mmol) in water (5 mL) was slowly added to a solution of *p*-nitrobenzyl bromide (1 g, 4.65 mmol) in acetone (50 mL) at 0 °C. The progress of the reaction was monitored by TLC analysis, and after 16 h, the reaction reached completion. The mixture was extracted with ethyl acetate, and the organic layer was concentrated under reduced pressure. The crude residue was purified by column chromatography to give *p*-nitrobenzyl azide (786.9 mg, 95 % yield).

Representative Procedure for the Preparation of the Cinnamates:[18] A mixture of bromobenzene (1 g, 6.37 mmol), methyl acrylate (764.4 mg, 7.64 mmol), potassium carbonate (1.32 g, 9.56 mmol), palladium acetate (28.5 mg, 0.13 mmol), and triphenylphosphine (66.8 mg, 0.25 mmol) was heated under a reflux condenser at 130 °C for 24 h. The progress of the reaction was monitored by TLC analysis. Upon completion of the reaction, the mixture was extracted with ethyl acetate and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (hexane/EtOAc, 90:10) to give methyl cinnamate (976.9 mg, 94 % yield).

Procedure for the Preparation of Triazoles (3a–3x, 4a–4f, and 5a–5g): An oven-dried round-bottomed flask was charged with the aryl or phenyl azide (100 mg, 0.84 mmol), $Cu(OAc)_2$ (15 mg, 0.084 mmol), and the acrylate/α,β-unsaturated cyclohexenone (1.5 equiv.) in *N*,*N*-dimethylformamide (2 mL). The flask was sealed with a septum, and the contents were stirred and heated in a preheated oil bath at 85 °C for 6–39 h. The mixture was cooled to room temperature and diluted with ethyl acetate. The resulting mixture was then extracted with ethyl acetate (2 × 10 mL), and the combined organic layers were dried with anhydrous Na_2SO_4 and concentrate under vacuum. The residue was purified over a column of silica gel (ethyl acetate/hexane eluent) to give the pure triazole.

Procedure for Quenching the Reaction with TEMPO: To examine the mechanistic route of the reaction, TEMPO (131 mg, 0.84 mmol) was added to a mixture of **1a** (100 mg, 0.84 mmol), **2a** (108 mg, 1.26 mmol), and $Cu(OAc)_2$ (15 mg, 0.084 mmol) in DMF (2 mL). The contents were stirred at 85 °C for 8 h. However, the reaction was not quenched by the addition of the TEMPO, and product **3a** was isolated (155 mg, 91 % yield).

Methyl 1-Phenyl-1*H*-1,2,3-triazole-4-carboxylate (3a): White solid (155.2 mg, 91 % yield). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.58 (s, 1 H), 7.77 (d, J = 6.9 Hz, 2 H), 7.55–7.49 (m, 3 H), 3.98 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.9, 140.5, 136.3, 129.9, 129.5, 125.6, 120.7, 52.2 ppm. MS (ESI): m/z = 226 $[M + Na]^+$. HRMS: calcd. for $C_{10}H_9N_3NaO_2^+$ $[M + Na]^+$ 226.0586; found 226.0581.

Ethyl 1-Phenyl-1*H*-1,2,3-triazole-4-carboxylate (3b): White solid (162.3 mg, 89 % yield). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.54 (s, 1 H), 7.77 (d, J = 6 Hz, 2 H), 7.58–7.49 (m, 3 H), 4.46 (q, J = 9 Hz, 2 H), 1.44 (t, J = 15 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.6, 140.8, 136.4, 129.9, 129.5, 125.5, 120.8, 61.4, 14.3 ppm. MS (ESI): m/z = 218 $[M + H]^+$. HRMS: calcd. for $C_{11}H_{12}N_3O_2^+$ $[M + H]^+$ 218.0924; found 218.0918.

Butyl 1-Phenyl-1*H*-1,2,3-triazole-4-carboxylate (3c): White solid (177.1 mg, 86 % yield). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.44 (s, 1 H), 7.71–7.67 (m, 2 H), 7.50–7.20 (m, 2 H), 4.33 (t, J = 6.9 Hz, 2 H), 1.77–1.67 (m, 2 H), 1.44–1.37 (m, 2 H), 0.90 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.7, 140.9, 136.4, 129.9, 129.5, 125.5, 120.8, 65.3, 30.7, 19.1, 14.1, 13.7 ppm. MS (ESI): m/z = 246 $[M + H]^+$. HRMS: calcd. for $C_{13}H_{16}N_3O_2^+$ $[M + H]^+$ 246.1237; found 246.1233.

***tert*-Butyl 1-Phenyl-1*H*-1,2,3-triazole-4-carboxylate (3d):** White solid (168.8 mg, 82 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.44 (s, 1 H), 7.74 (d, J = 7.5 Hz, 2 H), 7.56–7.48 (m, 3 H), 1.63 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.8, 142.1, 136.5, 129.9, 129.4, 125.2, 120.8, 82.5, 28.0 ppm. MS (ESI): m/z = 246 $[M + H]^+$. HRMS: calcd. for $C_{13}H_{16}N_3O_2^+$ $[M + H]^+$ 246.1237; found 246.1230.

Benzyl 1-Phenyl-1*H*-1,2,3-triazole-4-carboxylate (3e): White solid (182.8 mg, 78 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.50 (s, 1 H), 7.74 (d, J = 8.1 Hz, 2 H), 7.57–7.47 (m, 5 H), 7.41–7.35 (m, 3 H), 5.44 (s, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.4, 140.5, 136.4, 135.4, 129.9, 129.6, 128.7, 128.6, 128.5, 125.7, 120.9, 67.0 ppm. MS (ESI): m/z = 280 $[M + H]^+$. HRMS: calcd. for $C_{16}H_{14}N_3O_2^+$ $[M + H]^+$ 280.1080; found 280.1071.

1-Phenyl-1*H*-1,2,3-triazole-4-carbonitrile (3f): White solid (115.7 mg, 81 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.49 (s, 1 H), 7.75 (d, J = 6.9 Hz, 2 H), 7.63–7.56 (m, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.8, 130.2, 129.5, 127.6, 122.1, 121.0, 111.2 ppm. MS (ESI): m/z = 171 $[M + H]^+$. HRMS: calcd. for $C_9H_7N_4^+$ $[M + H]^+$ 171.0665; found 171.0658.

1-Phenyl-1*H*-1,2,3-triazole-4-carboxamide (3g): White solid (137.4 mg, 87 % yield). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.25 (s, 1 H), 8.00–7.95 (m, 3 H), 7.62–7.64 (m, 3 H), 7.64–7.54 (m, 3 H), 7.52–7.54 (m, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 161.8, 144.3, 136.8, 130.4, 129.6, 125.3, 12.9 ppm. MS (ESI): m/z = 189 $[M + H]^+$. HRMS: calcd. for $C_9H_9N_4O^+$ $[M + H]^+$ 189.0770; found 189.0762.

Methyl 1-(*o*-Tolyl)-1*H*-1,2,3-triazole-4-carboxylate (3h): Yellow solid (88.1 mg, 54 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.28 (s, 1 H), 7.45–7.35 (m, 4 H), 4.01 (s, 3 H), 2.23 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.9, 140.0, 135.9, 133.7, 131.7, 130.5, 128.9, 127.1, 125.9, 52.3, 17.8 ppm. MS (ESI): m/z = 240 $[M + Na]^+$. HRMS: calcd. for $C_{11}H_{11}N_3NaO_2^+$ $[M + Na]^+$ 240.0743; found 240.0747.

Methyl 1-(*p*-Tolyl)-1*H*-1,2,3-triazole-4-carboxylate (3i): White solid (151.7 mg, 93 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.49 (s, 1 H), 7.64 (d, J = 6.3 Hz, 2 H), 7.36 (d, J = 6 Hz, 2 H), 4.01 (s, 3 H), 2.46 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.1, 139.4, 138.8, 133.0, 129.4, 124.5, 119.7, 51.3, 28.7 ppm. MS (ESI): m/z = 218 $[M + H]^+$. HRMS: calcd. for $C_{11}H_{12}N_3O_2^+$ $[M + H]^+$ 218.0924; found 218.0917.

Butyl 1-(*p*-Tolyl)-1*H*-1,2,3-triazole-4-carboxylate (3j): White solid (173.3 mg, 89 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.38 (s, 1 H), 7.55 (d, J = 8.1 Hz, 2 H), 7.26 (d, J = 8.1 Hz, 2 H), 4.32 (t, J = 6.9 Hz, 2 H), 2.36 (s, 3 H), 1.74–1.66 (m, 2 H), 1.43–1.36 (m, 2 H), 0.90 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.8, 140.7, 139.7, 134.1, 130.8, 125.4, 120.7, 65.2, 30.7, 29.7, 21.1, 19.1, 13.7 ppm. MS (ESI): m/z = 260 $[M + H]^+$. HRMS: calcd. for $C_{14}H_{18}N_3O_2^+$ $[M + H]^+$ 260.1393; found 260.1386.

***tert*-Butyl 1-(*p*-Tolyl)-1*H*-1,2,3-triazole-4-carboxylate (3k):** White solid (165.5 mg, 85 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.38 (s, 1 H), 7.62 (d, J = 8.1 Hz, 2 H), 7.33 (d, J = 8.1 Hz, 2 H), 2.43 (s, 3 H), 1.63 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.9, 142.0, 139.6, 134.2, 130.4, 125.1, 120.7, 82.4, 28.3, 22.0 ppm. MS (ESI): m/z = 260 $[M + H]^+$. HRMS: calcd. for $C_{14}H_{18}N_3O_2^+$ $[M + H]^+$ 260.1393; found 260.1388.

Benzyl 1-(*p*-Tolyl)-1*H*-1,2,3-triazole-4-carboxylate (3l): White solid (180.6 mg, 82 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.48 (s, 1 H), 7.61 (d, J = 8.4 Hz, 3 H), 7.48–7.28 (m, 6 H), 5.42 (s, 2 H), 2.42 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.5, 140.3, 139.8, 135.5, 134.0, 130.4, 128.6, 128.6, 128.5, 125.7, 120.7, 66.9, 21.1 ppm. MS (ESI): m/z = 260 $[M + H]^+$. HRMS: calcd. for $C_{17}H_{16}N_3O_2^+$ $[M + H]^+$ 294.1237; found 294.1229.

1-(*p*-Tolyl)-1*H*-1,2,3-triazole-4-carbonitrile (3m): White solid (116.2 mg, 84 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.38 (s, 1 H), 7.60 (d, J = 7.2 Hz, 2 H), 7.38 (d, J = 7.8 Hz, 2 H), 2.46 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.6, 133.5, 130.5, 127.4, 121.7, 120.8, 111.1, 21.0 ppm. MS (ESI): m/z = 185 $[M + H]^+$. HRMS: calcd. for $C_{10}H_9N_4^+$ $[M + H]^+$ 185.0821; found 185.0814.

1-(*o*-Tolyl)-1*H*-1,2,3-triazole-4-carboxamide (3n): White solid (129.0 mg, 85 % yield). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.89 (s, 1 H), 8.00 (s, 1 H), 7.61 (s, 1 H), 7.47–7.40 (m, 4 H), 2.15 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.4, 143.6, 133.1, 131.3, 130.1, 128.1, 127.0, 126.1, 17.3 ppm. MS (ESI): m/z = 225 $[M + H]^+$. HRMS: calcd. for $C_{10}H_{10}N_4NaO^+$ $[M + H]^+$ 225.0747; found 225.0736.

1-(*p*-Tolyl)-1*H*-1,2,3-triazole-4-carboxamide (3o): White solid (136.6 mg, 90 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.18 (s, 1 H), 7.98 (s, 1 H), 7.83 (d, J = 10.1 Hz, 2 H), 7.59 (s, 1 H), 7.41 (d, J = 8.7 Hz, 2 H), 2.39 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.6, 144.3, 139.3, 134.2, 130.7, 125.1, 120.8 ppm. MS (ESI): m/z = 225 $[M + H]^+$. HRMS: calcd. for $C_{10}H_{10}N_4NaO^+$ $[M + H]^+$ 225.0747; found 225.0736.

Methyl 1-(4-Methoxyphenyl)-1*H*-1,2,3-triazole-4-carboxylate (3p): White solid (150.1 mg, 96 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.45 (s, 1 H), 7.67 (d, J = 8.7 Hz, 2 H), 7.06 (d, J = 9 Hz, 2 H), 4.02 (s, 3 H), 3.90 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.2, 160.4, 140.4, 129.7, 125.6, 122.5, 115.0, 55.7, 52.3 ppm. MS (ESI): m/z = 234 $[M + H]^+$. HRMS: calcd. for $C_{11}H_{12}N_3O_3^+$ $[M + H]^+$ 234.0873; found 234.0867.

Butyl 1-(4-Methoxyphenyl)-1*H*-1,2,3-triazole-4-carboxylate (3q): White solid (166.1 mg, 90 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.34 (s, 1 H), 7.54 (d, J = 8.7 Hz, 3 H), 6.96 (d, J = 9 Hz, 2 H), 4.32 (t, J = 6.6 Hz, 2 H), 3.79 (s, 3 H), 1.70 (q, J = 7.2 Hz, 3 H), 1.40 (q, J = 7.5 Hz, 2 H), 0.90 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.8, 160.4, 140.6, 129.7, 125.5, 122.5, 114.9, 65.3, 55.7, 30.7, 19.2, 13.7 ppm. MS (ESI): m/z = 276 $[M + H]^+$. HRMS: calcd. for $C_{14}H_{18}N_3O_3^+$ $[M + H]^+$ 276.1342; found 276.1335.

Benzyl 1-(4-Methoxyphenyl)-1*H*-1,2,3-triazole-4-carboxylate (3r): White solid (176.2 mg, 85 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.48 (s, 1 H), 7.65 (d, J = 8.4 Hz, 3 H), 7.48–7.30 (m, 6 H), 5.42 (s, 2 H), 2.42 (s, 2 H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 160.5, 140.3, 139.8, 135.5, 134.0, 130.4, 128.6, 128.6, 128.5, 125.7, 120.7, 66.9, 21.2 ppm. MS (ESI): m/z = 310 $[M + H]^+$. HRMS: calcd. for $C_{17}H_{16}N_3O_3^+$ $[M + H]^+$ 310.1186; found 310.1178.

***tert*-Butyl 1-(4-Methoxyphenyl)-1*H*-1,2,3-triazole-4-carboxylate (3s):** White solid (164.2 mg, 89 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.33 (s, 1 H), 7.64 (d, J = 8.7 Hz, 2 H), 7.03 (d, J = 8.4 Hz, 2 H), 3.87 (s, 3 H), 1.63 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.3, 159.9, 141.9, 129.9, 125.2, 122.5, 114.9, 82.4, 55.7, 28.2 ppm. MS (ESI): m/z = 276 $[M + H]^+$. HRMS: calcd. for $C_{14}H_{18}N_3O_3^+$ $[M + H]^+$ 276.1342; found 276.1337.

1-(4-Methoxyphenyl)-1*H*-1,2,3-triazole-4-carboxamide (3t): White solid (137.5 mg, 94 % yield). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.11 (s, 1 H), 7.95 (s, 1 H), 7.84 (d, J = 9 Hz, 1 H), 7.56 (s, 1 H), 7.12 (d, J = 7.12 Hz, 1 H), 3.82 (s, 3 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 161.3, 159.5, 143.6, 129.6, 124.6, 122.1, 114.8, 55.5 ppm. MS (ESI): m/z = 219 $[M + H]^+$. HRMS: calcd. for $C_{10}H_{11}N_4O_2^+$ $[M + H]^+$ 219.0876; found 219.0869.

***tert*-Butyl 1-(3-Formylphenyl)-1*H*-1,2,3-triazole-4-carboxylate (3u):** White solid (137.4 mg, 74 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.12 (s, 1 H), 8.54 (s, 1 H), 8.27 (d, J = 0.6 Hz, 1 H), 8.13 (d, J = 6.6 Hz, 2 H), 8.02 (d, J = 7.5 Hz, 2 H), 7.78 (t, J = 7.5 Hz, 1 H), 1.40 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.5, 159.5, 142.5,

137.8, 137.7, 130.9, 130.6, 126.2, 125.1, 120.5, 82.9, 28.3 ppm. MS (ESI): *m/z* = 276 $[M + H]^+$. HRMS: calcd. for $C_{14}H_{16}N_3O_3^+$ $[M + H]^+$ 276.1186; found 276.1189.

Methyl 1-(4-Nitrobenzyl)-1*H*-1,2,3-triazole-4-carboxylate (3w): Yellow solid (120.6 mg, 82 % yield). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.27 (d, *J* = 8.7 Hz, 2 H), 8.11 (s, 1 H), 7.46, (d, *J* = 8.4 Hz, 2 H), 5.73 (s, 2 H), 3.97 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.8, 148.4, 140.6, 128.8, 127.6, 124.5, 113.5, 53.4, 52.4 ppm. MS (ESI): *m/z* = 263 $[M + H]^+$. HRMS: calcd. for $C_{11}H_{11}N_4O_4^+$ $[M + H]^+$ 263.0774; found 263.0768.

***tert*-Butyl 1-(4-Nitrobenzyl)-1*H*-1,2,3-triazole-4-carboxylate (3x):** Yellow solid (133.2 mg, 78 % yield). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.20 (d, *J* = 8.7 Hz, 2 H), 8.03 (s, 1 H), 7.42, (d, *J* = 8.4 Hz, 2 H), 5.70 (s, 2 H), 1.5 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.7, 148.3, 142.4, 141.2, 128.9, 127.5, 124.5, 82.8, 53.4, 28.3 ppm. MS (ESI): *m/z* = 305 $[M + H]^+$. HRMS: calcd. for $C_{14}H_{17}N_4O_4^+$ $[M + H]^+$ 305.1244; found 305.1238.

Methyl 1,5-Diphenyl-1*H*-1,2,3-triazole-4-carboxylate (4a): White solid (185.2 mg, 72 % yield). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.36 (m, 6 H), 7.31–7.26 (m, 4 H), 3.90 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.4, 141.0, 136.6, 135.8, 130.2, 130.0, 129.6, 129.3, 128.4, 125.6, 125.2, 52.1 ppm. MS (ESI): *m/z* = 280 $[M + H]^+$. HRMS: calcd. for $C_{16}H_{14}N_3O_2^+$ $[M + H]^+$ 280.1080; found 280.1071.

Methyl 5-Phenyl-1-(*p*-tolyl)-1*H*-1,2,3-triazole-4-carboxylate (4b): White solid (167.4 mg, 76 % yield). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.37–7.34 (m, 3 H), 7.32 (s, 1 H), 7.28–7.18 (m, 5 H), 3.93 (s, 3 H), 1.97 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.6, 142.2, 135.9, 135.1, 134.8, 131.3, 130.5, 129.9, 128.2, 127.8, 126.8, 125.2, 52.2, 17.5 ppm. MS (ESI): *m/z* = 294 $[M + H]^+$. HRMS: calcd. for $C_{17}H_{16}N_3O_2^+$ $[M + H]^+$ 294.1237; found 294.1231.

Methyl 1-(4-Methoxyphenyl)-5-phenyl-1*H*-1,2,3-triazole-4-carboxylate (4c): White solid (163.8 mg, 79 % yield). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.40 (m, 4 H), 7.31–7.30 (m, 2 H), 7.22–7.20 (m, 3 H), 3.93 (s, 3 H), 2.39 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.5, 140.2, 136.0, 130.2, 130.1, 129.5, 129.3, 129.1, 128.4, 125.3, 122.5, 52.1, 21.4 ppm. MS (ESI): *m/z* = 294 $[M + H]^+$. HRMS: calcd. for $C_{17}H_{16}N_3O_2^+$ $[M + H]^+$ 294.1237; found 294.1231.

1-(4-Methoxyphenyl)-5-methyl-1*H*-1,2,3-triazole-4-carbaldehyde (4d): White solid (125.2 mg, 86 % yield). ^1H NMR (300 MHz, $CDCl_3$): δ = 10.28 (s, 1 H), 7.39 (d, *J* = 9 Hz, 2 H), 7.09 (d, *J* = 9 Hz, 2 H), 3.91 (s, 3 H), 2.60 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 186.5, 160.9, 143.8, 137.7, 127.7, 126.6, 114.9, 55.7, 9.7 ppm. MS (ESI): *m/z* = 218 $[M + H]^+$. HRMS: calcd. for $C_{11}H_{12}N_3O_2^+$ $[M + H]^+$ 218.0924; found 218.0918.

Methyl 5-(4-Methoxyphenyl)-1-phenyl-1*H*-1,2,3-triazole-4-carboxylate (4e): White solid (184.3 mg, 71 % yield). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.38 (m, 4 H), 7.30–7.26 (m, 2 H), 7.24–7.22 (m, 2 H), 7.24–7.22 (m, 2 H), 6.89 (d, *J* = 8.4 Hz, 2 H), 3.92 (s, 3 H), 3.82 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.6, 160.8, 140.9, 131.7, 130.2, 130.0, 129.5, 129.3, 128.4, 125.3, 114.0, 55.3, 52.1 ppm. MS (ESI): *m/z* = 310 $[M + H]^+$. HRMS: calcd. for $C_{17}H_{16}N_3O_3^+$ $[M + H]^+$ 310.1186; found 310.1188.

Methyl 5-(4-Cyanophenyl)-1-phenyl-1*H*-1,2,3-triazole-4-carboxylate (4f): White solid (163.5 mg, 64 % yield). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 8.4 Hz, 2 H), 7.47–7.42 (m, 4 H), 7.28 (s, 3 H), 3.39 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.1, 139.1, 137.1, 135.3, 132.1, 131.1, 130.4, 130.1, 129.7, 125.2, 117.8, 114.0, 52.3 ppm. MS (ESI): *m/z* = 305 $[M + H]^+$. HRMS: calcd. for $C_{17}H_{13}N_4O_2^+$ $[M + H]^+$ 305.1033; found 305.1037.

1-Phenyl-6,7-dihydro-1*H*-benzo[*d*][1,2,3]triazol-4(5*H*)-one (5a): White solid (148.5 mg, 83 % yield). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.81–7.56 (m, 5 H), 3.05 (t, *J* = 6 Hz, 3 H), 2.83–2.62 (m, 2 H), 2.24 (t, *J* = 6 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.4, 144.6, 142.3, 135.6, 129.8, 129.8, 123.5, 38.2, 23.1, 21.7 ppm. MS (ESI): *m/z* = 236 $[M + Na]^+$. HRMS: calcd. for $C_{12}H_{11}N_3NaO^+$ $[M + Na]^+$ 236.0794; found 236.0798.

1-(4-Methoxyphenyl)-6,7-dihydro-1*H*-benzo[*d*][1,2,3]triazol-4(5*H*)-one (5b): White solid (145.1 mg, 89 % yield). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 9 Hz, 2 H), 7.07 (d, *J* = 8.7 Hz, 2 H), 3.90 (s, 3 H), 3.00 (t, *J* = 6.3 Hz, 2 H), 2.67 (t, *J* = 6.3 Hz, 2 H), 2.30–2.21 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.2, 160.5, 144.3, 142.1, 128.5, 114.9, 55.7, 38.2, 29.8, 23.2, 21.6 ppm. MS (ESI): *m/z* = 244 $[M + H]^+$. HRMS: calcd. for $C_{13}H_{14}N_3O_2^+$ $[M + H]^+$ 244.1080; found 244.1073.

1-(*p*-Tolyl)-6,7-dihydro-1*H*-benzo[*d*][1,2,3]triazol-4(5*H*)-one (5c): White solid (145 mg, 85 % yield). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 8.4 Hz, 2 H), 7.39 (d, *J* = 8.4 Hz, 2 H), 3.03 (t, *J* = 6 Hz, 2 H), 2.69 (t, *J* = 6 Hz, 2 H), 2.48 (s, 3 H), 2.31–2.24 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.1, 144.2, 142.4, 140.1, 133.2, 130.4, 123.3, 38.3, 23.2, 21.7, 21.2 ppm. MS (ESI): *m/z* = 228 $[M + H]^+$. HRMS: calcd. for $C_{13}H_{14}N_3O^+$ $[M + H]^+$ 228.1131; found 228.1124.

1-(4-Nitrophenyl)-6,7-dihydro-1*H*-benzo[*d*][1,2,3]triazol-4(5*H*)-one (5d): Pale yellow solid (107 mg, 68 % yield). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.47 (d, *J* = 9.0 Hz, 2 H), 7.86 (d, *J* = 8.7 Hz, 2 H), 3.15 (t, *J* = 6.0 Hz, 2 H), 2.71 (t, *J* = 6 Hz, 2 H), 2.36–2.30 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.6, 147.9, 144.3, 142.9, 140.4, 125.4, 123.7, 38.1, 23.1, 22.2 ppm. MS (ESI): *m/z* = 281 $[M + Na]^+$. HRMS: calcd. for $C_{12}H_{10}N_4NaO_3^+$ $[M + Na]^+$ 281.0645; found 281.0648.

1-(Naphthalen-1-yl)-6,7-dihydro-1*H*-benzo[*d*][1,2,3]triazol-4(5*H*)-one (5f): Brown solid (121 mg, 78 % yield). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 8.4 Hz, 2 H), 8.01 (d, *J* = 8.4 Hz, 1 H), 7.67–7.53 (m, 2 H), 7.32–7.28 (m, 1 H), 2.78–2.68 (m, 4 H), 2.27–2.19 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.2, 147.0, 141.7, 134.2, 131.4, 131.2, 128.9, 128.6, 128.3, 127.4, 125.1, 124.7, 121.6, 38.4, 23.0, 20.7 ppm. MS (ESI): *m/z* = 264 $[M + H]^+$. HRMS: calcd. for $C_{16}H_{14}N_3O^+$ $[M + H]^+$ 264.1132; found 264.1131.

1-(4-Nitrobenzyl)-6,7-dihydro-1*H*-benzo[*d*][1,2,3]triazol-4(5*H*)-one (5g): Yellow solid (128 mg, 84 % yield). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.27 (d, *J* = 8.7 Hz, 2 H), 8.11 (s, 1 H), 7.46, (d, *J* = 8.4 Hz, 2 H), 5.73 (s, 2 H), 3.97 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.1, 148.3, 144.9, 142.6, 140.9, 128.6, 124.6, 51.4, 38.2, 29.8, 22.9, 20.3 ppm. MS (ESI): *m/z* = 273 $[M + H]^+$. HRMS: calcd. for $C_{13}H_{13}N_4O_3^+$ $[M + H]^+$ 273.0982; found 273.0975.

CCDC 1416103 (for **5a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Supporting Information (see footnote on the first page of this article): Full experimental details and crystallographic data (Figure S1 and Table S1).

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