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Graphical Abstract

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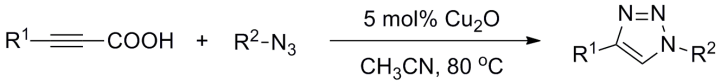

R^1, R^2 = alkyl, aryl

- 38 examples, up to 97% yield
- good functional group tolerance

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Copper-catalyzed decarboxylation/cycloaddition cascade of alkynyl carboxylic acids with azide

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ABSTRACT

A copper-catalyzed decarboxylation/cycloaddition cascade of alkynyl carboxylic acids with azide has been developed. This reaction exhibits good functional group tolerance and wide substrate scope, provides an efficient way to construct 1,4-disubstituted 1,2,3-triazoles.

1. Introduction

1,2,3-Triazoles are well-known highly valuable N-heterocyclic compounds that are ubiquitous in many pharmaceuticals and bioactive molecules.[1] In light of their importance, a number of methods have been developed for the synthesis of 1,2,3-triazoles,[2,3] and among them, the copper(I)-catalyzed 1,3-dipolar cycloaddition of azide and terminal alkyne (CuAAC) is the most prevailing one due to the wide substrate scope, exclusive regioselectivity, very high yields, and mild reaction conditions.[3] Decarboxylative coupling reactions is one of the most powerful methods for the formation of C−C and C−heteroatom bonds.[4,5] Recently, the use of alkynyl carboxylic acids as terminal alkyne surrogates has attracted significant attention because alkynyl carboxylic acids are convenient to synthesize, store, and transport.[6,7] For example, alkynes of low molecular weight are difficult to handle due to their low boiling points. However, the corresponding alkynoic acids, even the most simple propiolic acid, has a very high boiling point and can be easily handled. In this context, copper-catalyzed AAC reactions involving decarboxylation of alkynyl carboxylic acids have been developed. Kolarovič et al. reported an efficient Cu-catalyzed three-component reaction of alkynyl carboxylic acids, aryl iodides, and sodium azide for the formation of 1,2,3-triazoles.[8] Pan, Xu and co-workers developed a novel Cu-catalyzed decarboxylative/cycloaddition reaction for the preparation of 1,4-disubstituted 5-arylselanyl-1,2,3-triazoles from propiolic acids, diselenides and azides.[9] On the basis of our continuing interest in decarboxylative coupling,[10] herein we report a Cu-catalyzed decarboxylation/cycloaddition cascade of alkynyl carboxylic acids with organic azides.

2. Results and discussions

Initially, phenylpropiolic acid (**1a**) and (azidomethyl)trimethylsilane (**2a**) were chosen as the model substrates to optimize reaction conditions for the decarboxylation/cycloaddition cascade. When phenylpropiolic acid was treated with 3.0 equiv of (azidomethyl)trimethylsilane in the presence of 10 mol% of $CuBr_2$ in DMF at 80 °C for 12 h, the reaction proceeded smoothly and afforded the desired 1,4-disubstituted 1,2,3-triazole **3aa** in 10% yield (Table 1, entry 1). Subsequently, various copper catalysts such as CuO, $Cu(OAc)_2$, $CuSO_4·5H_2O$, CuBr, CuCl, Cu_2O and $CuNO_3(PPh_3)_2$ were investigated, and Cu_2O gave the best yield (94%) of **3aa** (Table 1, entries 2–8). Different solvents were investigated, and CH_3CN was proved to be better than the other solvents (Table 1, entries 9–16). Notably, this transformation could occur in H_2O or under solvent free conditions, leading to product in 90% or 91% yield, respectively. The effect of azide stoichiometry and the catalyst loading were also examined, and the results indicate that 5 mol% of catalyst with 1.0 equiv of azide was the best choice (Table 1, entries 17–18). Decreasing the temperature negatively affected the reaction (Table 1, entry 19).

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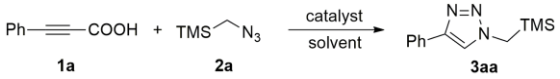
† These authors contributed equally.

Table 1. Optimization of reaction conditions.[a]

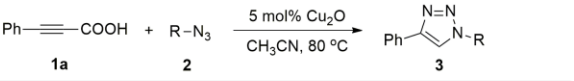


1a 2a 3aa

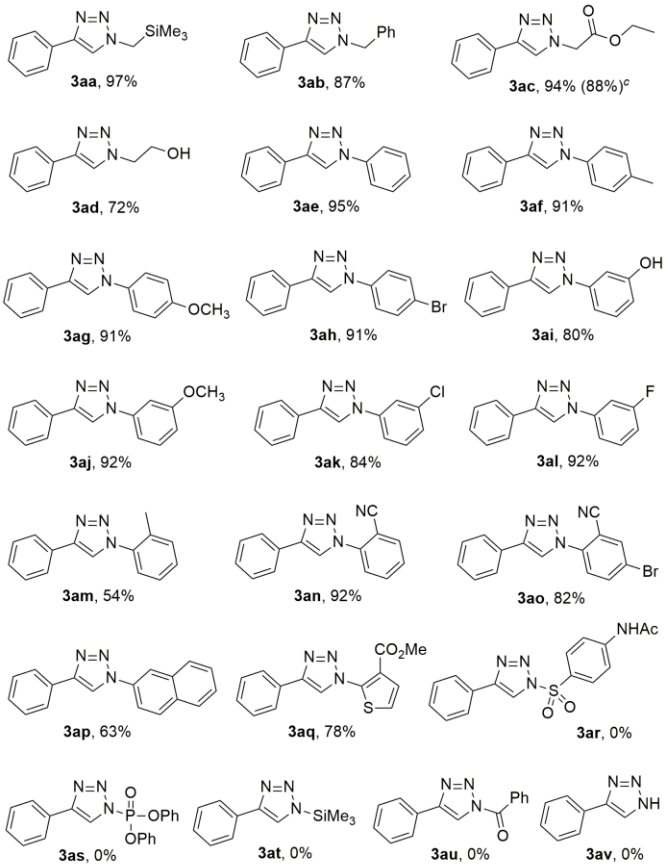
Entry	**2a** (equiv)	Catalyst (equiv)	Solvent	Yield (%)[b]
1	3	$CuBr_2$ (10)	DMF	10
2	3	CuO (10)	DMF	15
3	3	$Cu(OAc)_2$ (10)	DMF	89
4	3	$CuSO_4·5H_2O$ (10)	DMF	85
5	3	CuBr (10)	DMF	84
6	3	CuCl (10)	DMF	80
7	3	Cu_2O (10)	DMF	94
8	3	$CuNO_3(PPh_3)_2$ (10)	DMF	92
9	3	Cu_2O (10)	THF	92
10	3	Cu_2O (10)	Acetone	96
11	3	Cu_2O (10)	DMSO	91
12	3	Cu_2O (10)	DCE	49
13	3	Cu_2O (10)	CH_3CN	97
14	3	Cu_2O (10)	Toluene	92
15	3	Cu_2O (10)	H_2O	91
16	3	Cu_2O (10)	-	90
17	1	Cu_2O (10)	CH_3CN	97
18	1	Cu_2O (5)	CH_3CN	97
19[c]	1	Cu_2O (5)	CH_3CN	94 (93)[d]

[a] Reaction conditions: **1a** (0.30 mmol), **2a** and catalyst in solvent (3 mL) at 80 °C for 12 h under an air atmosphere.
[b] Isolated yield.
[c] 70 °C.
[d] 70 °C, 24 h.

Table 2. Scope of azides.[a,b]



1a 2 3

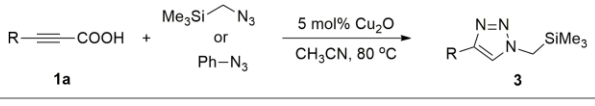


[a] All the reactions were carried out in the presence of 0.30 mmol of **1a**, 1.0 equiv of **2** and 5 mol% Cu_2O in 3.0 mL of CH_3CN at 80 °C under an air atmosphere.
[b] Isolated yield.
[c] The reaction was carried out in the presence of 7.0 mmol of **1a**.

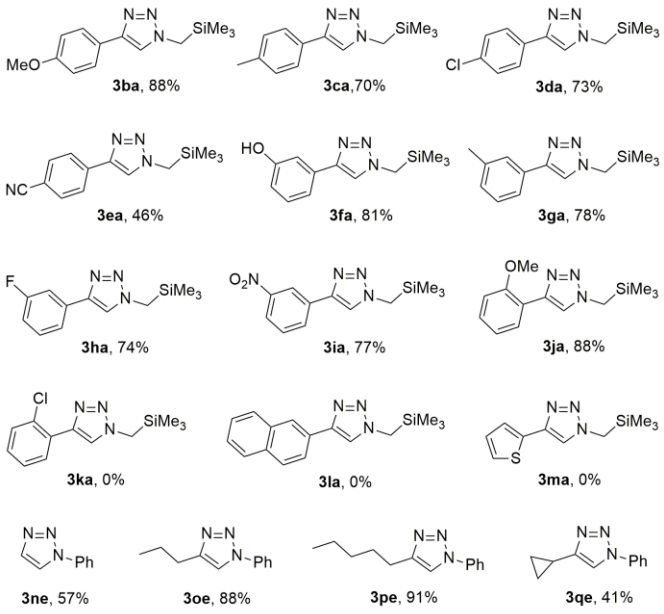
With the optimized reaction conditions, a variety of organic azides were subjected to the optimized conditions to evaluate the scope of the decarboxylation/cycloaddition cascade, and the results are summarized in Table 2. Alkyl azides, such as (azidomethyl)trimethylsilane, benzyl azide, ethyl 2-azidoacetate and 2-azidoethanol, were suitable substrates, affording the desired products **3aa**–**3ad** in satisfactory yields. In addition, this transformation could be readily scaled up with similar efficiency. The reaction of 7.0 mmol of phenylpropiolic acid with ethyl 2-azidoacetate under the standard reaction conditions gave 1.42 g of the desired product **3ac** in 88% yield. Both electron-rich and -poor azidobenzenes could be transferred to the 1,4-disubstituted 1,2,3-triazole **3ae**–**3ao** in moderate to excellent yields, and a series of functional groups, such as methyl, methoxyl, halides, hydroxyl, and nitrile, were compatible with the reaction conditions. Moreover, 2-azidonaphthalene was also compatible with this transformation, albeit in a moderate yield (**3ap**). It was pleasant to find that heterocyclesubstituted azide, methyl 2-azidothiophene-3-carboxylate, provided the corresponding 1,2,3-triazole **3aq** in good yield. However, 4-acetamidobenzenesulfonyl azide, diphenyl phosphorazidate, azidotrimethylsilane, benzoyl azide and sodium azide were not suitable substrates (**3ar**–**3au**).

The scope of alkynyl carboxylic acids was also examined. As shown in Table 3, phenylglyoxylic acids bearing an electron-donating group (MeO, Me, OH) or an electron-withdrawing group (CN, F, NO_2) at the aryl ring were consistent with the optimized conditions, and the corresponding products **3ba**–**3ja** were obtained in moderate to good yields. However, *ortho*-Cl substituted phenylpropiolic acid, 3-(naphthalen-2-yl)propiolic acid, and thienylpropiolic acid were not suitable substrates (**3ka**-**3ma**). In addition, this transformation is not limited to arylpropiolic acids, alkylpropiolic acids such as propiolic acid, hex-2-ynoic acid, oct-2-ynoic acid, and 3-cyclopropylpropiolic acid also reacted well with azidobenzene, giving the correspondin products **3ne**-**3qe** in moderate to excellent yields.

Table 3. Scope of alkynyl carboxylic acids.[a,b]



1a 3

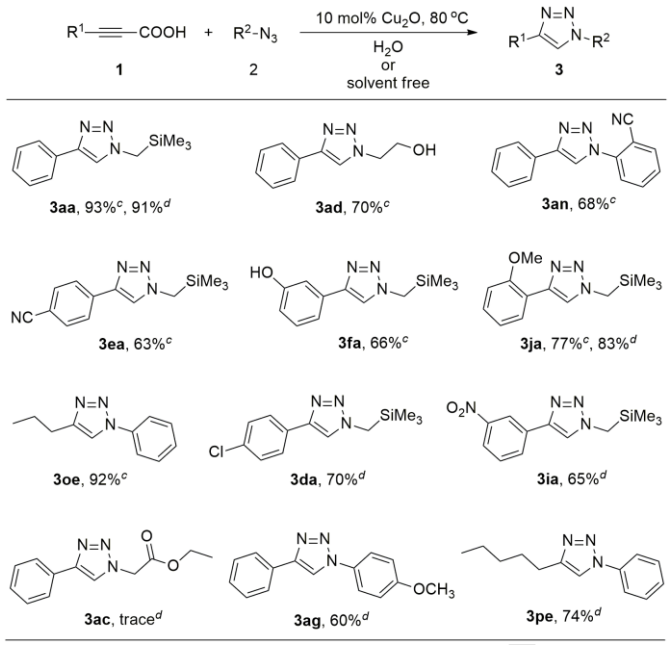


[a] All the reactions were carried out in the presence of 0.30 mmol of **1**, 1.0 equiv of azide and 5 mol% Cu_2O in 3.0 mL of CH_3CN at 80 °C under an air atmosphere.

[b] Isolated yield.

When the solvent, CH_3CN, were replaced by H_2O, the reaction could be achieved. As shown in Table 4, a variety of alkynyl carboxylic acids reacted well with azides, provided the corresponding 1,2,3-triazoles in moderate to excellent yields (**3aa**, **3ad**, **3an**, **3ea**, **3fa**, **3ja**, and **3oe**). This transformation could also occur under solvent free conditions, albeit in moderate yields (**3aa**, **3ja**, **3da**, **3ia**, **3ag**, and **3pe**). However, when phenylpropiolic acid was treated with ethyl 2-azidoacetate under solvent free conditions, only trace amounts of product **3ac** were detected.

Table 4. Synthesis of 1,2,3-triazoles in H_2O or under solvent free conditions.[a]



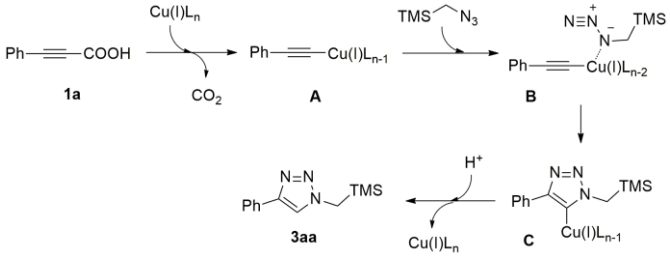
[a] All the reactions were carried out in the presence of 0.30 mmol of **1**, 1.0 equiv of **2** and 10 mol% Cu_2O at 80 °C under an air atmosphere.

[b] Isolated yield.

[c] The reaction was carried out in H_2O (3 mL).

[d] The reaction was carried out under solvent free conditions.

A possible mechanism for this transformation is proposed, as shown in Scheme 1, on the basis of the precedent literature.[3,7] Firstly, the decarboxylation of alkynyl carboxylic acid with the assistance of a copper salt gives the alkynyl copper intermediate **A**. Then the intermediate **A** is subjected to the CuAAC pathway, giving rise to the formation of C-5 cuprate–triazole intermediate **C**. Finally, intermediate **C** was quenched by proton to yield the desired 1,2,3-triazole **3aa**.



Scheme 1. Proposed mechanism.

3. Conclusion

In summary, we have developed a copper-catalyzed decarboxylation/cycloaddition cascade of alkynyl carboxylic acids with azide. It shows a wide substrate scope and good functional group compatibility, thus providing a convenient approach to prepare a variety of 1,4-disubstituted 1,2,3-triazoles. This transformation could also occur in H_2O or under solvent free conditions. Further investigations toward the reaction scope, and applications in organic synthesis are currently ongoing in our laboratory.

4. Experimental Section

4.1. General

^{1}H NMR, ^{13}C NMR and spectra were recorded on Bruker AVANCE III HD 600 (600 MHz for ^{1}H; 151 MHz for ^{13}C) instruments internally referenced to tetramethylsilane (TMS) signal. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. $CDCl_3$, DMSO-d_6, or CD_3OD was used as the NMR solvent in all cases. Mass spectra were mearsured using Thermo LTQ Orbitrap XL spectrometer. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Alkynyl carboxylic acids[11] and organic azides[12] were all prepared following literature procedures. Column chromatography was carried out on silica gel (particle size 200-300 mesh ASTM).

4.2. General procedures for copper-catalyzed decarboxylation/cycloaddition cascade of alkynyl carboxylic acids with azide

In a Schlenk tube, alkynyl carboxylic acid **1** (0.3 mmol), azide **2** (0.3 mmol), Cu_2O (0.015 mmol), and CH_3CN (3 mL) were added. The mixture was allowed to stir at 80 °C for 12 hours. After substrate was consumed, the reaction mixture was cooled to room temperature and concentrated in vacuum, then purified by flash chromatography on silica gel with petroleum ether/ethyl acetate as the eluent to afford the corresponding product **3**.

*4.2.1. 4-phenyl-1-((trimethylsilyl)methyl)-1H-1,2,3-triazole (**3aa**)*

This compound was prepared by the general procedures. Purified by column chromatography (petroleum ether : ethyl acetate = 6 : 1). Yield = 97%. White solid, mp 85–88 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (dd, J = 7.5, 0.7 Hz, 2H), 7.63 (s, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.33–7.30 (m, 1H), 3.99–3.92 (m, 2H), 0.18 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.5, 130.8, 128.8, 127.9, 125.6, 120.2, 42.1, -2.4. IR (film) υ_{max}: 3133, 2956, 1947, 1670, 1609, 1463, 1437, 1250, 851, 765, 693 cm^{-1}. HRMS calc. for $C_{12}H_{17}N_3Si$ $(M+H)^+$, 232.1265; found, 232.1263.

*4.2.2. 1-benzyl-4-phenyl-1H-1,2,3-triazole (**3ab**)*

This compound was prepared by the general procedures. Purified by column chromatography (petroleum ether : ethyl acetate = 6 : 1). Yield = 87%. White solid, mp 128–133 °C.^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82–7.75 (m, 2H), 7.66 (s, 1H), 7.45–7.33 (m, 5H), 7.31 (t, J = 7.4 Hz, 3H), 5.56 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.2, 134.6, 130.5, 129.1, 128.8, 128.7, 128.1, 128.0, 125.6, 119.5, 54.2. IR (film) υ_{max}: 3446, 3142, 1645, 1607, 1552, 1494, 1452, 1208, 1046, 768, 729, 695 cm^{-1}. HRMS calc. for $C_{15}H_{13}N_3$ $(M+H)^+$, 236.1182; found, 236.1181.

*4.2.3. ethyl 2-(4-phenyl-1H-1,2,3-triazol-1-yl)acetate (**3ac**)*

This compound was prepared by the general procedures. Purified by column chromatography (petroleum ether : ethyl acetate = 3 : 1). Yield = 88%. White solid, mp 95–97 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.84 (dd, J = 8.2, 1.1 Hz, 2H), 7.43 (dd, J

= 10.7, 4.6 Hz, 2H), 7.37–7.30 (m, 1H), 5.20 (s, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.2, 148.2, 130.3, 128.8, 128.2, 125.7, 120.9, 62.4, 50.9, 14.0. IR (film) υ_{max}: 3488, 3135, 3007, 2947, 1754, 1648, 1465, 1373, 1220, 1016, 768, 693 cm^{-1}. HRMS calc. for $C_{12}H_{13}N_3O_2$ $(M+H)^+$, 232.1081; found, 232.1082.

*4.2.4. 2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethan-1-ol (**3ad**)*

This compound was prepared by the general procedures. Purified by column chromatography (petroleum ether : ethyl acetate = 3 : 1). Yield = 72%. White solid, mp 85–87 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.61 (d, *J* = 7.3 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 4.45 (d, *J* = 4.0 Hz, 2H), 4.34–4.14 (m, 1H), 4.10 (d, *J* = 3.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.2, 130.0, 128.7, 128.1, 125.4, 121.0, 61.0, 53.0. IR (film) υ_{max}: 3309, 3132, 2927, 2879, 1660, 1578, 1463, 1215, 1078, 1039, 762, 696 cm^{-1}. HRMS calc. for $C_{10}H_{11}N_3O$ $(M+H)^+$, 190.0975; found, 190.0972

*4.2.5. 1,4-diphenyl-1H-1,2,3-triazole (**3ae**)*

This compound was prepared by the general procedures. Purified by column chromatography (petroleum ether : ethyl acetate = 8 : 1). Yield = 95%. White solid, mp 241–243 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.96–7.85 (m, 2H), 7.80 (d, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 7.9 Hz, 2H), 7.50–7.41 (m, 3H), 7.37 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.4, 137.0, 130.2, 129.8, 128.9, 128.8, 128.4, 125.8, 120.5, 117.6. IR (film) υ_{max}: 3445, 3120, 1652, 1597, 1503, 1459, 1415, 1231, 1040, 758, 691 cm^{-1}. HRMS calc. for $C_{14}H_{11}N_3$ $(M+H)^+$, 222.1026; found, 222.1027.

*4.2.6. 4-phenyl-1-(p-tolyl)-1H-1,2,3-triazole (**3af**)*

This compound was prepared by the general procedures. Purified by column chromatography (petroleum ether : ethyl acetate = 6 : 1). Yield = 91%. White solid, mp 174–176 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.90 (dd, *J* = 8.1, 1.0 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.2, 138.8, 134.7, 130.3, 130.2, 128.8, 128.3, 125.8, 120.4, 117.6, 21.1. IR (film) υ_{max}: 3439, 2130, 1643, 1518, 1401, 1230, 1116, 1042, 816, 761, 693 cm^{-1}. HRMS calc. for $C_{15}H_{13}N_3$ $(M+H)^+$, 236.1182; found, 236.1180.

*4.2.7. 1-(4-methoxyphenyl)-4-phenyl-1H-1,2,3-triazole (**3ag**)*

This compound was prepared by the general procedures. Purified by column chromatography (petroleum ether : ethyl acetate = 5 : 1). Yield = 91%. White solid, mp 166–169 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.92–7.86 (m, 2H), 7.70–7.64 (m, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 8.9 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.8, 148.1, 130.4, 130.3, 128.8, 128.3, 125.7, 122.1, 117.8, 114.7, 55.6. IR (film) υ_{max}: 3450, 3120, 2961, 1649, 1551, 1457, 1238, 1036, 827, 766, 694, cm^{-1}. HRMS calc. for $C_{15}H_{13}N_3O$ $(M+H)^+$, 252.1131; found, 252.1130.

*4.2.8. 1-(4-bromophenyl)-4-phenyl-1H-1,2,3-triazole (**3ah**)*

This compound was prepared by the general procedures. Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). Yield = 91%. White solid, mp 165–167 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.40 (s, 1H), 8.23 (d, *J* = 1.7 Hz, 1H), 8.06–8.00 (m, 1H), 7.95 (d, *J* = 7.8 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 8.1 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 147.6, 135.8, 132.9, 130.1, 129.1, 128.4, 125.3, 121.9, 121.4, 119.7. IR (film) υ_{max}: 3441, 3096, 1648, 1583, 1559, 1507, 1460, 1226, 1040, 765, 695 cm^{-1}. HRMS calc. for $C_{14}H_{10}BrN_3$ $(M+H)^+$, 300.0131; found, 300.0128.

*4.2.9. 3-(4-phenyl-1H-1,2,3-triazol-1-yl)phenol (**3ai**)*

This compound was prepared by the general procedures. Purified by column chromatography (petroleum ether : ethyl acetate = 2 : 1). Yield = 80%. White solid, mp 214–217 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.15 (s, 1H), 9.27 (s, 1H), 7.96 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.51 (dd, *J* = 10.7, 4.8 Hz, 2H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.41–7.35 (m, 3H), 6.92 (ddd, *J* = 8.1, 2.3, 0.9 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 158.6, 147.2, 137.6, 130.8, 130.3, 129.0, 128.2, 125.4, 119.6, 115.7, 110.4, 107.0. IR (film) υ_{max}: 3144, 1615, 1601, 1556, 1511, 1330, 1275, 1106, 765, 711, 693 cm^{-1}. HRMS calc. for $C_{15}H_{13}N_3O$ $(M+H)^+$, 238.0975; found, 238.0976.

*4.2.10. 1-(3-methoxyphenyl)-4-phenyl-1H-1,2,3-triazole (**3aj**)*

This compound was prepared by the general procedures. Purified by column chromatography (petroleum ether : ethyl acetate = 6 : 1). Yield = 92%. White solid, mp 111–113 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.90 (d, *J* = 8.1 Hz, 2H), 7.43 (dd, *J* = 9.9, 4.5 Hz, 2H), 7.40 (ddd, *J* = 9.9, 5.8, 1.7 Hz, 2H), 7.37 – 7.32 (m, 1H), 7.29 (dd, *J* = 7.9, 0.8 Hz, 1H), 6.98–6.93 (m, 1H), 3.88–3.84 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.5, 148.2, 137.9, 130.4, 130.1, 128.8, 128.3, 125.7, 117.6, 114.5, 112.2, 106.2, 55.5. IR (film) υ_{max}: 3443, 3126, 3010, 1652, 1605, 1478, 1264, 1040, 848, 765, 690 cm^{-1}. HRMS calc. for $C_{15}H_{13}N_3O$ $(M+H)^+$, 252.1131; found, 252.1131.

*4.2.11. 1-(3-chlorophenyl)-4-phenyl-1H-1,2,3-triazole (**3ak**)*

This compound was prepared by the general procedures. Purified by column chromatography (petroleum ether : ethyl acetate = 5 : 1). Yield = 84%. White solid, mp 167–170 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.93–7.88 (m, 2H), 7.85 (t, *J* = 1.9 Hz, 1H), 7.72 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.51–7.42 (m, 4H), 7.39 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.6, 137.9, 135.6, 130.9, 129.9, 129.0, 128.8, 128.6, 125.9, 120.7, 118.4, 117.4. IR (film) υ_{max}: 3444, 3098, 1651, 1590, 1480, 1453, 1286, 1157, 791, 765, 695 cm^{-1}. HRMS calc. for $C_{14}H_{10}ClN_3$ $(M+H)^+$, 256.0636; found, 256.0635.

*4.2.12. 1-(3-fluorophenyl)-4-phenyl-1H-1,2,3-triazole (**3al**)*

This compound was prepared by the general procedures. Purified by column chromatography (petroleum ether : ethyl acetate = 2 : 1). Yield = 92%. White solid, mp 185–187 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.91 (dd, *J* = 5.1, 3.2 Hz, 2H), 7.63–7.56 (m, 2H), 7.55–7.50 (m, 1H), 7.47 (dd, *J* = 10.5, 4.8 Hz, 2H), 7.42–7.35 (m, 1H), 7.21–7.12 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.1 (d, J_{C-F} = 248.7 Hz), 148.6, 138.2 (d, J_{C-F} = 9.9 Hz), 131.2 (d, J_{C-F} = 9.1 Hz), 129.9, 129.0, 128.6, 125.9, 117.4, 115.8 (d, J_{C-F} = 3.3 Hz), 115.7 (d, J_{C-F} = 21.1 Hz), 108.2 (d, J_{C-F} = 26.2 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -109.62. IR (film) υ_{max}: 3446, 3121, 1649, 1607, 1501, 1450, 1232, 916, 763, 694 cm^{-1}. HRMS calc. for $C_{14}H_{10}FN_3$ $(M+H)^+$, 240.0932; found, 240.0931.

*4.2.13. 4-phenyl-1-(o-tolyl)-1H-1,2,3-triazole (**3am**)*

This compound was prepared by the general procedures. Purified by column chromatography (petroleum ether : ethyl acetate = 7 : 1). Yield = 54%. White solid, mp 199–201 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.92 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.48–7.44 (m, 2H), 7.44–7.41 (m, 1H), 7.40–7.33 (m, 4H), 2.27 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.5, 136.4, 133.7, 131.5, 130.3, 129.9, 128.9, 128.3, 126.8, 125.9, 125.7, 121.1, 17.9. IR (film) υ_{max}: 3442, 3123, 2924, 1638, 1465, 1408, 1233, 1039, 761, 694

cm^{-1}. HRMS calc. for $C_{15}H_{13}N_3$ $(M+H)^+$, 236.1182; found, 236.1182.

*4.2.14. 2-(4-phenyl-1H-1,2,3-triazol-1-yl)benzonitrile (**3an**)*

This compound was prepared by the general procedures. Purified by column chromatography (petroleum ether : ethyl acetate = 2 : 1). Yield = 92%. White solid, mp 168–174 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.97–7.94 (m, 1H), 7.93 (dd, *J* = 5.1, 3.2 Hz, 2H), 7.88 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.82 (td, *J* = 7.9, 1.5 Hz, 1H), 7.61 (td, *J* = 7.7, 1.1 Hz, 1H), 7.48 (dd, *J* = 10.5, 4.8 Hz, 2H), 7.42–7.36 (m, 1H).^{13}C NMR (151 MHz, $CDCl_3$) δ 148.7, 138.6, 134.5, 134.4, 129.7, 129.5, 129.0, 128.8, 126.1, 125.3, 119.8, 115.8, 106.3. IR (film) υ_{max}: 3433, 3131, 2232, 1646, 1601, 1509, 1450, 1231, 1033, 768, 689 cm^{-1}. HRMS calc. for $C_{15}H_{10}N_4$ $(M+H)^+$, 247.0978; found, 249.0979.

*4.2.15. 5-bromo-2-(4-phenyl-1H-1,2,3-triazol-1-yl)benzonitrile (**3ao**)*

This compound was prepared by the general procedures. Purified by column chromatography (petroleum ether : ethyl acetate = 3 : 1). Yield = 82%. White solid, mp 199–203 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.00 (d, *J* = 2.1 Hz, 1H), 7.96–7.90 (m, 3H), 7.87 (d, *J* = 8.7 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.9, 137.7, 137.5, 136.7, 129.4, 129.0, 128.9, 126.4, 126.1, 122.9, 119.5, 114.6, 107.5. IR (film) υ_{max}: 3441, 3116, 2235, 1631, 1503, 1477, 1390, 1228, 1031, 834, 767, 694 cm^{-1}. HRMS calc. for $C_{15}H_9BrN_4$ $(M+H)^+$, 325.0083; found, 325.0084.

*4.2.16. 1-(naphthalen-2-yl)-4-phenyl-1H-1,2,3-triazole (**3ap**)*

This compound was prepared by the general procedures. Purified by column chromatography (petroleum ether : ethyl acetate = 5 : 1). Yield = 63%. White solid, mp 199–201 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.24 (s, 1H), 8.04 (d, *J* = 8.7 Hz, 1H), 8.01–7.84 (m, 5H), 7.65–7.53 (m, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.5, 134.4, 133.2, 132.9, 130.2, 130.1, 128.9, 128.5, 128.3, 128.0, 127.5, 127.0, 125.9, 118.9, 118.4, 117.7. IR (film) υ_{max}: 3440, 3121, 1643, 1600, 1480, 1445, 1255, 1090, 819, 763, 740, 692 cm^{-1}. HRMS calc. for $C_{18}H_{13}N_3$ $(M+H)^+$, 272.1182; found, 272.1182.

*4.2.17. methyl 2-(4-phenyl-1H-1,2,3-triazol-1-yl)thiophene-3-carboxylate (**3aq**)*

This compound was prepared by the general procedures. Purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1). Yield = 78%. White solid, mp 147–149 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.92 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.63–7.59 (m, 1H), 7.59–7.55 (m, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.37 – 7.32 (m, 1H), 3.85 (t, *J* = 1.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.6, 146.9, 138.3, 131.0, 130.1, 128.8, 128.2, 126.4, 125.8, 122.3, 121.3, 52.5. IR (film) υ_{max}: 3402, 3111, 1708, 1560, 1473, 1437, 1314, 1190, 796, 780, 695 cm^{-1}. HRMS calc. for $C_{14}H_{11}N_3O_2S$ $(M+H)^+$, 286.0645; found, 286.0643.

*4.2.18. 4-(4-methoxyphenyl)-1-((trimethylsilyl)methyl)-1H-1,2,3-triazole (**3ba**)*

This compound was prepared by the general procedures. Purified by column chromatography (petroleum ether : ethyl acetate = 6 : 1). Yield = 88%. White solid, mp 106–108 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.8 Hz, 2H), 7.55 (s, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.93 (s, 2H), 3.84 (s, 3H), 0.17 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.4, 147.3, 126.8, 123.5, 119.4, 114.1, 55.3, 42.0, -2.5. IR (film) υ_{max}: 3132, 2955, 1615, 1558, 1498, 1409, 1249, 1030, 837, 799, 702 cm^{-1}. HRMS calc. for $C_{13}H_{19}N_3OSi$ $(M+H)^+$, 262.1370; found, 262.1367.

*4.2.19. 4-(p-tolyl)-1-((trimethylsilyl)methyl)-1H-1,2,3-triazole (**3ca**)*

This compound was prepared by the general procedures. Purified by column chromatography (petroleum ether : ethyl acetate = 7 : 1). Yield = 70%. White solid, mp 110–112 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.59 (s, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 3.90 (s, 2H), 2.35 (s, 3H), 0.15 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.2, 137.5, 129.2, 127.8, 125.3, 119.8, 41.8, 21.1, -2.6. IR (film) υ_{max}: 3442, 3136, 2954, 1909, 1659, 1558, 1453, 1250, 1216, 852, 702 cm^{-1}. HRMS calc. for $C_{13}H_{19}N_3Si$ $(M+H)^+$, 246.1421; found, 246.1421.

*4.2.20. 4-(4-chlorophenyl)-1-((trimethylsilyl)methyl)-1H-1,2,3-triazole (**3da**)*

This compound was prepared by the general procedures. Purified by column chromatography (petroleum ether : ethyl acetate = 5 : 1). Yield = 73%. White solid, mp 108–110 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.6 Hz, 2H), 7.62 (s, 1H), 7.39 (d, *J* = 8.6 Hz, 2H), 3.95 (s, 2H), 0.18 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.4, 133.6, 129.3, 129.0, 126.8, 120.2, 42.1, -2.5. IR (film) υ_{max}: 3448, 2957, 1654, 1482, 1401, 1245, 1089, 974, 838, 516 cm^{-1}. HRMS calc. for $C_{12}H_{16}ClN_3Si$ $(M+H)^+$, 266.0875; found, 266.0874.

*4.2.21. 4-(1-((trimethylsilyl)methyl)-1H-1,2,3-triazol-4-yl)benzonitrile (**3ea**)*

This compound was prepared by the general procedures. Purified by column chromatography (petroleum ether : ethyl acetate = 2 : 1). Yield = 46%. White solid, mp 146–149 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00–7.90 (m, 2H), 7.81 (s, 1H), 7.69 (dd, *J* = 8.2, 2.1 Hz, 2H), 3.99 (s, 2H), 0.19 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.4, 135.1, 132.5, 125.8, 121.4, 118.7, 110.9, 42.1, -2.6. IR (film) υ_{max}: 3426, 3124, 2956, 2219, 1665, 1615, 1405, 1299, 1237, 845, 701 cm^{-1}. HRMS calc. for $C_{13}H_{16}N_4Si$ $(M+H)^+$, 257.1217; found, 257.1215.

*4.2.22. 3-(1-((trimethylsilyl)methyl)-1H-1,2,3-triazol-4-yl)phenol (**3fa**)*

This compound was prepared by the general procedures. Purified by column chromatography (petroleum ether : ethyl acetate = 3 : 1). Yield = 81%. White solid, mp 136–140 °C. ^{1}H NMR (600 MHz, CD_3OD) δ 8.45 (s, 1H), 7.33 (t, *J* = 7.9 Hz, 1H), 7.29–7.21 (m, 2H), 6.89 (ddd, *J* = 8.1, 2.4, 0.9 Hz, 1H), 4.20 (s, 2H), 0.21 (s, 9H). ^{13}C NMR (151 MHz, MeOD) δ 159.5, 146.8, 131.5, 129.8, 124.7, 118.2, 117.8, 113.9, 44.4, -2.7. IR (film) υ_{max}: 3028, 2954, 1696, 1622, 1588, 1472, 1414, 1371, 1281, 846, 783 cm^{-1}. HRMS calc. for $C_{12}H_{17}N_3OSi$ $(M+H)^+$, 248.1214; found, 248.1210.

*4.2.23. 4-(m-tolyl)-1-((trimethylsilyl)methyl)-1H-1,2,3-triazole (**3ga**)*

This compound was prepared by the general procedures. Purified by column chromatography (petroleum ether : ethyl acetate = 7 : 1). Yield = 78%. White solid, mp 78–80 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.62 (s, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 3.93 (s, 2H), 2.38 (s, 3H), 0.16 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.4, 138.3, 130.6, 128.59, 128.57, 126.1, 122.6, 120.1, 41.9, 21.3, -2.6. IR (film) υ_{max}: 3445, 2955, 1616, 1558, 1493, 1249, 1221, 842, 794, 699 cm^{-1}. HRMS calc. for $C_{13}H_{19}N_3Si$ $(M+H)^+$, 246.1421; found, 246.1418.

*4.2.24. 4-(3-fluorophenyl)-1-((trimethylsilyl)methyl)-1H-1,2,3-triazole (**3ha**)*

This compound was prepared by the general procedures. Purified by column chromatography (petroleum ether : ethyl acetate = 6 :

1). Yield = 74%. White solid, mp 107–111 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.61–7.57 (m, 1H), 7.55 (ddd, *J* = 10.0, 2.4, 1.6 Hz, 1H), 7.38 (td, *J* = 8.0, 6.0 Hz, 1H), 7.04–6.97 (m, 1H), 3.96 (s, 2H), 0.18 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.1 (d, J_{C-F} = 245.4 Hz), 146.4 (d, J_{C-F} = 2.7 Hz), 133.0 (d, J_{C-F} = 8.5 Hz), 130.3 (d, J_{C-F} = 8.5 Hz), 121.1 (d, J_{C-F} = 2.8 Hz), 120.5 , 114.7 (d, J_{C-F} = 21.2 Hz), 112.5 (d, J_{C-F} = 22.9 Hz), 42.1, -2.5. ^{19}F NMR (565 MHz, $CDCl_3$) δ -112.81. IR (film) υ_{max}: 3135, 2958, 1621, 1588, 1444, 1251, 1225, 1000, 851, 784 cm^{-1}. HRMS calc. for $C_{12}H_{16}FN_3Si$ $(M+H)^+$, 250.1170; found, 250.1168.

*4.2.25. 4-(3-nitrophenyl)-1-((trimethylsilyl)methyl)-1H-1,2,3-triazole (**3ia**)*

This compound was prepared by the general procedures. Purified by column chromatography (petroleum ether : ethyl acetate = 3 : 1). Yield = 77%. White solid, mp 136–139 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.64–8.57 (m, 1H), 8.28–8.21 (m, 1H), 8.16 (ddd, *J* = 8.2, 2.2, 0.9 Hz, 1H), 7.82 (s, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 4.01 (s, 2H), 0.20 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.5, 145.2, 132.6, 131.3, 129.8, 122.4, 121.1, 120.2, 42.3, -2.5. IR (film) υ_{max}: 3124, 3094, 2960, 2918, 1669, 1525, 1460, 1348, 1251, 847, 758 cm^{-1}. HRMS calc. for $C_{12}H_{16}N_4O_2Si$ $(M+H)^+$, 277.1115; found, 277.1112.

*4.2.26. 4-(2-methoxyphenyl)-1-((trimethylsilyl)methyl)-1H-1,2,3-triazole (**3ja**)*

This compound was prepared by the general procedures. Purified by column chromatography (petroleum ether : ethyl acetate = 7 : 1). Yield = 88%. White solid, mp 62–63 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.92 (s, 1H), 7.32–7.27 (m, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 8.3 Hz, 1H), 3.94 (s, 2H), 3.92 (s, 3H), 0.17 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.4, 142.7, 128.6, 127.4, 123.8, 120.9, 119.6, 110.7, 55.3, 41.7, -2.5. IR (film) υ_{max}: 2961, 2911, 2842, 1605, 1546, 1489, 1442, 1249, 1023, 856, 761 cm^{-1}. HRMS calc. for $C_{13}H_{19}N_3OSi$ $(M+H)^+$, 262.1370; found, 262.1369.

*4.2.27. 1-phenyl-1H-1,2,3-triazole (**3ne**)*

This compound was prepared by the general procedures. Purified by column chromatography (petroleum ether : ethyl acetate = 6 : 1). Yield = 57%. White solid, mp 49–53 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 1.0 Hz, 1H), 7.85 (d, *J* = 2.9 Hz, 1H), 7.75 (dd, *J* = 5.7, 2.3 Hz, 2H), 7.53 (dd, *J* = 9.8, 5.5 Hz, 2H), 7.48–7.42 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.9, 134.4, 129.7, 128.7, 121.7, 120.6. IR (film) υ_{max}: 3147, 2921, 1595, 1502, 1319, 1229, 1096, 1036, 762, 686 cm^{-1}. HRMS calc. for $C_8H_7N_3$ $(M+H)^+$, 146.0713; found, 146.0711.

*4.2.28. 1-phenyl-4-propyl-1H-1,2,3-triazole (**3oe**)*

This compound was prepared by the general procedures. Purified by column chromatography (petroleum ether : ethyl acetate = 7 : 1). Yield = 88%. White turbid liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81–7.65 (m, 3H), 7.50 (t, *J* = 7.9 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 2.78 (t, *J* = 7.6 Hz, 2H), 1.81–1.72 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.9, 137.2, 129.6, 128.3, 120.3, 118.8, 27.6, 22.6, 13.7. IR (film) υ_{max}: 3134, 2958, 1599, 1556, 1506, 1464, 1228, 1047, 987, 756, 687 cm^{-1}. HRMS calc. for $C_{11}H_{13}N_3$ $(M+H)^+$, 188.1182; found, 188.1178.

*4.2.29. 4-pentyl-1-phenyl-1H-1,2,3-triazole (**3pe**)*

This compound was prepared by the general procedures. Purified by column chromatography (petroleum ether : ethyl acetate = 7 : 1). Yield = 91%. White solid, mp 41–43 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (ddd, *J* = 4.2, 3.5, 2.4 Hz, 3H), 7.54–7.45 (m, 2H), 7.44–7.36 (m, 1H), 2.82–2.74 (m, 2H), 1.79–1.68 (m, 2H), 1.41–1.34 (m, 4H), 0.91 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.1, 137.2, 129.6, 128.3, 120.3, 118.7, 31.4, 29.0, 25.6, 22.4, 13.9. IR (film) υ_{max}: 3139, 2957, 2932, 1599, 1502, 1464, 1343, 1228, 1043, 756, 690 cm^{-1}. HRMS calc. for $C_{13}H_{17}N_3$ $(M+H)^+$, 216.1495; found, 216.1491.

*4.2.30. 4-cyclopropyl-1-phenyl-1H-1,2,3-triazole (**3qe**)*

This compound was prepared by the general procedures. Purified by column chromatography (petroleum ether : ethyl acetate = 5 : 1). Yield = 41%. White solid, mp 75–78 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 9.2, 1.4 Hz, 3H), 7.49 (t, *J* = 7.9 Hz, 2H), 7.43–7.38 (m, 1H), 2.07–1.98 (m, 1H), 1.03–0.98 (m, 2H), 0.95–0.91 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.9, 137.1, 129.6, 128.4, 120.3, 117.8, 7.8, 6.6. IR (film) υ_{max}: 3495, 3137, 1636, 1568, 1502, 1462, 1231, 1051, 757, 692 cm^{-1}. HRMS calc. for $C_{11}H_{11}N_3$ $(M+H)^+$, 186.1026; found, 186.1025.

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