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One-pot three component synthesis of 5-allyl-1,2,3-triazoles using copper(I) acetylides†

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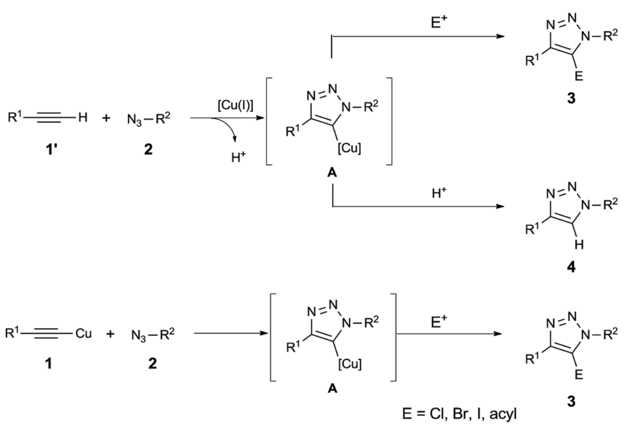
One-pot three-component reactions using copper(I) acetylide, azide, allyl iodide, and NaOH have been developed. The reactions proceed smoothly at room temperature to afford 5-allyl-1,2,3-triazoles, which can be further transformed into a variety of 1,2,3-triazole-fused bi-/tricyclic scaffolds. This method offers the most efficient, convenient, and practical route towards useful polycyclic scaffolds in moderate to excellent yields.

Introduction

1,2,3-Triazoles[1] are very important heterocycles in chemistry and biology.[2] Synthetic molecules containing a 1,2,3-triazole scaffold exhibit diverse biological activities, which have drawn the attention of medicinal chemists in the drug discovery field. Currently, there are several 1,2,3-triazole-containing medicines on the market, and the number of potential pharmaceuticals based on these scaffolds keeps increasing.[3] Beyond the drug market, 1,2,3-triazoles are utilized in a variety of areas including bioconjugation,[4] polymer and materials science,[5] and related areas[6] including supramolecular chemistry,[7] DNA labeling[8] and oligonucleotide synthesis.[9] Such wide applications of 1,2,3-triazoles are due to their facile synthesis through Cu(I)-catalyzed azide–alkyne cycloaddition (CuAAC), so-called 'click chemistry'. Since it was first introduced by Sharpless and co-workers, CuAAC has been rapidly adopted as a universal coupling process. However, in terms of substrate scope, CuAAC is restricted to terminal alkynes, leading to 1,4-disubstituted 1,2,3-triazoles, and the one-pot synthetic methods for the fully substituted 1,2,3-triazoles are still relatively few.[10]

In one-pot three-component reactions used to obtain 5-halo 1,2,3-triazoles, an electrophile X^+ (X = Cl, Br, and I) is added into the CuAAC reaction to trap X^+ with an *in situ* generated 5-copper(I) 1,2,3-triazole intermediate **A** (Scheme 1).[11] However, the result is usually the formation of a mixture of the desired 5-substituted 1,2,3-triazole **3** and the byproduct 1,4-disubstituted 1,2,3-triazole **4**, which is generated from a competitive protonation of the 5-copper(I) 1,2,3-triazole intermediate **A.**[12] This competitive protonation is accelerated by a proton source, provided from the terminal alkyne substrate in the normal CuAAC. Therefore, this problem cannot be avoided in the presence of terminal alkyne substrates or protic polar solvents. Recently, this drawback was smartly overcome by using copper(I) acetylide instead of a terminal alkyne in the halogenation[12] and acylation, by Y. Hu's group.[13]

Copper(I) acetylides are highly crystalline polymeric complexes, $(RC{\equiv}CCu)_n$.[14] They are stable to air, water, acid/base and heat[15] so they can be kept on the shelf for several months without the quality deteriorating. In the absence of exogenous ligands or additives, copper(I) phenylacetylide, $PhC{\equiv}CCu$, is not effective under typical CuAAC conditions:[13] It did not undergo a cycloaddition with azide and did not provide a 1,2,3-triazole product. However, when it was combined with both azide and acyl chloride, it quickly provided 5-acyl-1,2,3-triazoles.[13] The presence of acyl chloride accelerated the cycloaddition of copper(I) phenylacetylide and azide.[13] This intriguing result motivated us to investigate one-pot three-component reactions using copper(I) phenylacetylide. We are particularly interested in 5-allyl-1,2,3-triazoles as precursors for the development of new anticancer agents. However, efficient



Scheme 1 Cu(I)-catalyzed azide–alkyne cycloaddition methods for the synthesis of 5-substituted 1,2,3-triazoles.

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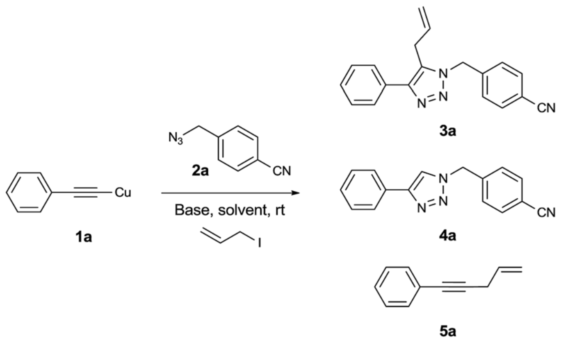
methods for the synthesis of 5-allyl-1,2,3-triazoles are rare.[10a,b] Interestingly, copper(I) acetylide has never been used directly as a substrate for the synthesis of 5-allyl-1,2,3-triazoles, although it is known to be a key intermediate. Herein, we report one-pot three-component reactions for the synthesis of 5-allyl-1,2,3-triazoles from copper(I) acetylides.

Results and discussion

To assess the feasibility of the tandem CuAAC–allylation reaction, we started to investigate one-pot three component reactions in the presence of copper(I) phenylacetylide (**1a**), 4-cyanobenzyl azide (**2a**), allyl iodide, and base (Table 1). In preliminary screening of reaction conditions, we obtained the desired product 5-allyl-1,2,3-triazole **3a** and a byproduct enyne **5a** with 47% and 42% yield respectively after 4 h at room temperature when 1.5 equivalents of cyanobenzyl azide (**2a**), 3 equivalents of allyl iodide, and 2 equivalents of Et_3N were employed (entry 1). The yield of the desired product **3a** increased to 60% and the yield of the byproduct enyne **5a** decreased to 36% when the amount of allyl iodide increased to 4 equivalents (entry 2). The use of Et_3N appeared to decompose the stable polymeric complex with the structure $[(PhC{\equiv}CCu)_2]_n$ into a lower polymeric or a more reactive monomeric structure. As soon as Et_3N was added, the heterogeneous reaction mixture became clear and rapidly yielded both an undesired byproduct as well as the desired product. However, replacing Et_3N with pyridine, quinine, or inorganic bases such as Na_3PO_4, K_3PO_4, Na_2CO_3, K_2CO_3, Cs_2CO_3, NaOH, or KOH did not change the heterogeneity of the reaction. The copper(I) phenylacetylide (**1a**) remained suspended in CH_2Cl_2, which not only slowed reaction progress but also significantly reduced byproduct formation. The reaction using quinine increased the yield of desired product **3a** up to 74%, but interestingly 2% of a protonated byproduct **4a** was isolated instead of the allyl alkyne byproduct **5a** (entry 3). The reaction using pyridine did not significantly increase the yield compared to the reaction of Et_3N. However, the formation of byproducts **4a** and **5a** was not observed (entry 4). Similarly, the reactions using inorganic bases also generated 5-allyl-1,2,3-triazole **3a** as a sole product (entries 5–11). Hydroxide bases (KOH, NaOH: entries 10 and 11) are better than phosphate bases (Na_3PO_4, K_3PO_4: entries 5 and 6) or carbonate bases (Na_2CO_3, K_2CO_3, Cs_2CO_3: entries 7–9) in terms of yield. Among bases used, the best result was obtained with NaOH (84%, entry 10). It appears the use of base is essential for the reaction. Without a base, 5-allyl-1,2,3-triazole **3a** was isolated with only a moderate yield (52%, entry 12). The role of NaOH is not clear, and it is still under investigation. It is also noteworthy that the byproduct 1,4-disubstituted 1,2,3-triazole **4a**, which is generated from a competitive protonation of 5-copper(I) 1,2,3-triazole intermediate **A**, was not detected in reactions using copper(I) phenylacetylide (**1a**) with the exception of quinine.

Table 1 Optimization of reaction conditions[a]



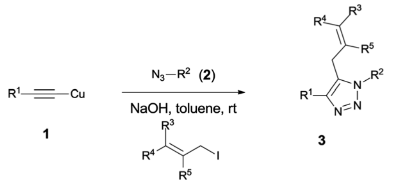
Entry	Base	Solvent	Time (h)	Yield[b] (%) 3a	4a	5a
1[c]	Et_3N	CH_2Cl_2	4	47	0	42
2	Et_3N	CH_2Cl_2	4	60	0	36
3	Quinine	CH_2Cl_2	24	74	2	0
4	Pyridine	CH_2Cl_2	24	63	0	0
5	Na_3PO_4	CH_2Cl_2	24	47	0	0
6	K_3PO_4	CH_2Cl_2	24	45	0	0
7	Na_2CO_3	CH_2Cl_2	24	62	0	0
8	K_2CO_3	CH_2Cl_2	21	71	0	0
9	Cs_2CO_3	CH_2Cl_2	24	67	0	0
10	NaOH	CH_2Cl_2	24	84	0	0
11	KOH	CH_2Cl_2	24	83	0	0
12	—	CH_2Cl_2	24	52	0	0
13	NaOH	Dioxane	24	89	0	0
14	NaOH	THF	24	85	0	0
15	**NaOH**	**Toluene**	**24**	**94**	**0**	**0**
16	NaOH	CH_3CN	24	68	0	0

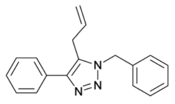
[a] Reaction conditions: **1a** (65.8 mg, 400 μmol), **2a** (94.9 mg, 600 μmol), base (800 μmol), allyl iodide (146 μL, 1.60 mmol), solvent (1 mL). All reactions were carried out under Ar. [b] Isolated yields. [c] 1.20 mmol of allyl iodide was used.

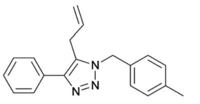
Next, we investigated the solvent effect on the yield of Cu(I)-catalyzed azide–alkyne cycloaddition–allylation reactions of copper(I) acetylides in the presence of NaOH. The reactions were effective in various solvents including CH_2Cl_2, dioxane, THF, toluene, and CH_3CN (entries 13–16). Considering yield of the product, toluene (entry 15) was the best solvent for the reaction. On the basis of Table 1, we chose NaOH as a base and the relatively nonpolar solvent, toluene, for further study.

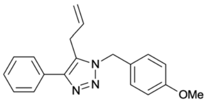
Once we had established optimal reaction conditions, we examined the scope of one-pot three-component reactions (Table 2). We applied the copper(I) acetylide system to various azides in toluene at room temperature. All reactions using copper(I) acetylides in Table 2 smoothly furnished 5-allyl-1,4-disubstituted 1,2,3-triazoles **3b–u** and a trace amount of enyne byproduct **5b–u** at room temperature. As anticipated, the 1,4-disubstituted 1,2,3-triazoles **4**, which are unavoidable in the typical CuAAC reactions, were not detected. First, we explored the reaction scope with benzyl azides. The reaction yields were independent of the electronic nature of azides. Substrates **2c–e** bearing electron-donating substituents and substrates **2f–h** bearing electron-withdrawing substituents underwent the one-pot three-component reactions very smoothly, and provided the corresponding 5-allyl-1,4-disubstituted 1,2,3-triazoles **3c–h** at room temperature, in good to excellent yields (85–97%). The reaction scope was not limited to only benzyl azides, but was

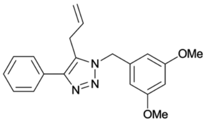
Table 2 Cu(I)-catalyzed azide–alkyne cycloaddition–allylation reactions under optimized conditions[a]

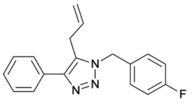


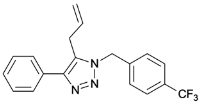

3b (89%, 24 h)

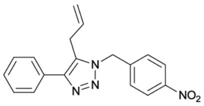

3c (85%, 24 h)

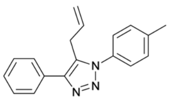

3d (88%, 24 h)

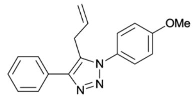

3e (94%, 24 h)

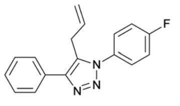

3f (97%, 24 h)

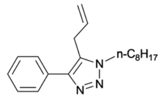

3g (93%, 24 h)

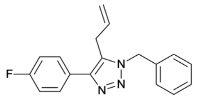

3h (86%, 24 h)

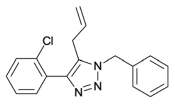

3i (89%, 24 h)

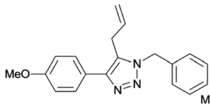

3j (65%, 24 h)

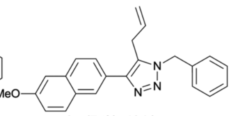

3k (63%, 24 h)

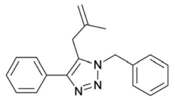

3l (90%, 24 h)

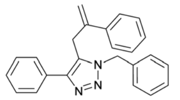

3m (70%, 48 h)

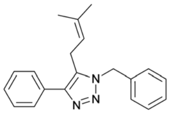

3n (54%, 48 h)

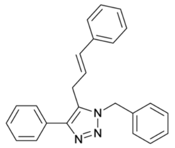

3o (57%, 48 h)

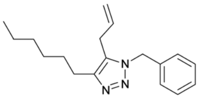

3p (75%, 48 h)


3q (90%, 24 h)


3r (86%, 24 h)

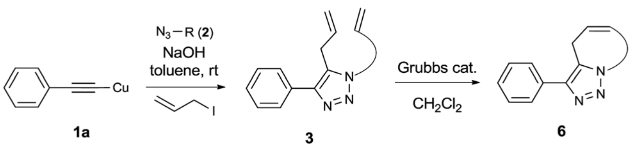

3s (73%, 24 h)

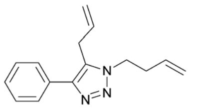
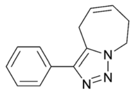
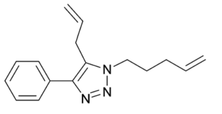
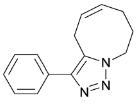
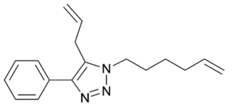
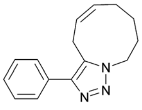
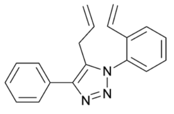
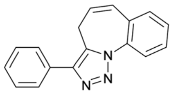
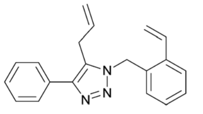
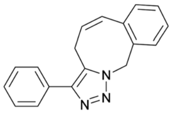

3t (53%, 48 h)


3u (77%, 48 h)

[a] Reaction conditions: **1** (400 μmol), **2** (600 μmol), NaOH (32.0 mg, 800 μmol), allyl iodide (1.60 mmol), toluene (1 mL). All reactions were carried out under Ar.

Table 3 Synthesis of fused 1,2,3-triazoles using Cu(I)-catalyzed azide–alkyne cycloaddition–allylation reactions[a] and ring closing metathesis[b]



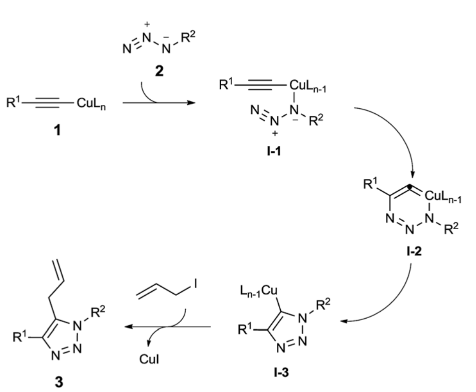
Entry	Yield of **3**[c]	Yield of **6**[c]
1	 **3v** (80%)	 **6v** (79%)
2	 **3w** (75%)	 **6w** (87%)
3	 **3x** (65%)	 **6x** (65%)
4	 **3y** (53%)	 **6y** (92%)[d]
5	 **3z** (55%)	 **6z** (70%)[e]

[a] Reaction conditions: **1a** (65.8 mg, 400 μmol), **2** (600 μmol), NaOH (32.0 mg, 800 μmol), allyl iodide (146 μL, 1.60 mmol), toluene (1 mL). All reactions were carried out under Ar. [b] Reaction conditions: **3** (200 μmol), Grubbs' 1st generation catalyst (5 mol%), CH_2Cl_2 (9.3 mL). [c] Isolated yields. [d] 180 μmol of **3** was used. [e] 150 μmol of **3** and Hoveyda-Grubbs' 2nd generation catalyst (5 mol%) were used.

also compatible with aryl azides **2i–k** and aliphatic azide **2l**. In addition, a variety of copper(I) arylacetylides were also tested. Regardless of the electronic influence of substituents on copper(I) arylacetylides, desired products **3m–p** were obtained in moderate to good yields (54–75%). It is worth noting that this method is not limited to the use of simple allyl iodide. Other various substituted allyl iodides could be used for one-pot three-component reactions, and produced the corresponding 5-allyl-1,4-disubstituted 1,2,3-triazoles **3q–t** with yields in the range of 53–90%. Delightfully, the reaction scope was also expandable to copper(I) alkylacetylide, which afforded 4-alkyl 1,2,3-triazole **3u**.

Finally, we studied further transformations of 5-allyl-1,4-disubstituted 1,2,3-triazoles into various fused polyheterocycles in order to demonstrate the synthetic utility of the 5-allyl-1,4-disubstituted 1,2,3-triazoles as versatile building blocks (Table 3). The alkene-tethered 5-allyl-1,2,3-triazoles **3v–x** were synthesized based on Cu(I)-catalyzed azide–alkyne cycloaddition–allylation reactions of copper(I) acetylides in good yields (entries 1–3, 65–80%) and these were converted into fused 1,2,3-triazoles **6v–x** by ring-closing metathesis reactions, which were effective for the synthesis of 7-, 8- and 9-membered fused 1,2,3-triazoles with good yields (entries 1–3, 65–87%). The transformations were also applicable to substrates bearing styrene-type alkenes **3y** and **3z.** The ring-closing metathesis of **3y** and **3z** proceeded smoothly to afford fused tricyclic 1,2,3-triazoles (entries 4 and 5, 70–92%).

On the basis of previous mechanistic studies[16] and our own observation, we speculate that Cu(I) acetylide **1** coordinates with the azide **2** to form the intermediate **I-1** and following cyclization leads to the metallocycle intermediate **I-2**. The 6-membered Cu(I)-intermediate contracts to the Cu(I)-1,2,3-triazole intermediate **I-3**, which is readily trapped by allyl iodide to yield the desired 5-allyl-1,4-disubstituted 1,2,3-triazole **3** (Scheme 2).



Scheme 2 Plausible mechanism of Cu(I)-mediated one-pot three component synthesis of 5-allyl-1,2,3-triazoles.

Conclusions

In conclusion, we have developed a novel one-pot three component reaction method for the synthesis of 5-allyl-1,4-disubstituted 1,2,3-triazoles from copper(I) acetylides. The 5-allyl-1,4-disubstituted 1,2,3-triazoles were produced *via* 1,3-dipolar cycloaddition followed by *in situ* trapping of the C(sp^2)–Cu intermediate. The byproduct 1,4-disubstituted 1,2,3-triazole **4**, which is generated from a competitive protonation of 5-copper(I) 1,2,3-triazole intermediate **A**, was not isolated. The present method was successfully applied to achieve production of synthetically useful heterocycles. This domino reaction is characterized by mild conditions and no protonated byproduct formation, and allows for the efficient construction of functionalized fused polycyclic 1,2,3-triazoles.

Experimental

General

All reactions were performed in oven-dried glassware fitted with glass stoppers under positive pressure of Ar with magnetic stirring, unless otherwise noted. Air- and moisture-sensitive liquids and solutions were transferred *via* syringe or stainless-steel cannula. TLC was performed on 0.25 mm E. Merck silica gel 60 F_{254} plates and visualized under UV light (254 nm) or by staining with cerium ammonium molybdenate (CAM), potassium permanganate ($KMnO_4$) or *p*-anisaldehyde. Flash chromatography was performed on E. Merck 230–400 mesh silica gel 60. Reagents were purchased from commercial suppliers, and used without further purification unless otherwise noted. Solvents were distilled from proper drying agents (CaH_2 or Na wire) under Ar atmosphere at 760 mmHg. NMR spectra were recorded at 24 °C. Chemical shifts are expressed in ppm relative to TMS (^{1}H, 0 ppm), $CDCl_3$ (^{1}H, 7.26 ppm; ^{13}C, 77.2 ppm), and C_6H_5F (^{19}F, −113.15 ppm); coupling constants are expressed in Hz. High resolution mass spectra (HRMS) were obtained by electrospray ionization (ESI, TOF) or electron ionization (EI, magnetic sector). Infrared spectra were recorded with peaks reported in cm^{-1}.

General procedure for the Cu(I)-catalyzed azide–alkyne cycloaddition–allylation reactions

Copper(I) acetylide (400 μmol) was placed in a 25 mL one-arm roundbottom flask. A solution of azide (600 μmol) in anhydrous toluene (1 mL), allyl iodide (268 mg, 1.60 mmol) and NaOH (32.0 mg, 800 μmol) were sequentially added to the reaction mixture. The resulting suspension was stirred at room temperature for 24 h or 48 h as indicated in Table 1. The mixture was filtered and washed with CH_2Cl_2 (20 mL). To scavenge Cu, polymer-bound ethylenediaminetriacetic acid acetamide (3.0–4.0 mmol g^{-1}, 200 mg) was added to the filtrate, and stirred for 2 h. The polymer was filtered off and the filtrate was concentrated by rotary evaporation. Purification of crude residue by column chromatography yielded **3a–z**. The reaction of **3y** was carried out for 3 days at room temperature.

4-((5-Allyl-4-phenyl-1*H*-1,2,3-triazol-1-yl)methyl)benzonitrile (3a). TLC: R_f 0.25 (2 : 1 hexane/EtOAc). White solid (113 mg, 94%). Mp = 113–115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68–7.63 (m, 4H), 7.45–7.41 (m, 2H), 7.38–7.34 (m, 1H), 7.28 (d, J = 8.4 Hz, 2H), 5.83 (m, 1H), 5.57 (s, 2H), 5.15 (dd, J = 10.4 Hz, 1.2 Hz, 1H), 4.88 (dd, J = 16.8 Hz, 1.2 Hz, 1H), 3.45 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.2, 140.3, 132.9, 132.1, 131.0, 130.4, 128.9, 128.3, 128.0, 127.3, 118.3, 118.2, 112.6, 51.4, 27.1. HRMS (ESI) *m*/*z* calculated for $C_{19}H_{17}N_4$ [M + H]$^+$ 301.1448, found 301.1451. IR (KBr film): ν 3061, 2229, 1639, 1506, 920, 820, 777, 699 cm^{-1}.

5-Allyl-1-benzyl-4-phenyl-1*H*-1,2,3-triazole (3b). TLC: R_f 0.52 (2 : 1 hexane/EtOAc). Pale yellow liquid (97.9 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70–7.67 (m, 2H), 7.44–7.40 (m, 2H), 7.36–7.30 (m, 4H), 7.20–7.18 (m, 2H), 5.83 (m, 1H), 5.54 (s, 2H), 5.15 (dm, J = 12.0 Hz, 1H), 4.92 (dm, J = 15.2 Hz, 1H), 3.45 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.0, 135.1, 132.4, 131.5, 130.4, 129.1, 128.8, 128.5, 128.0, 127.3, 117.9, 52.1, 27.1. HRMS (ESI) *m*/*z* calculated for $C_{18}H_{18}N_3$ [M + H]$^+$ 276.1495, found 276.1501. IR (KBr film): ν 3063, 3033, 1639, 1608, 1496, 918, 800, 764 cm^{-1}

5-Allyl-1-(4-methylbenzyl)-4-phenyl-1*H*-1,2,3-triazole (3c). TLC: R_f 0.55 (2 : 1 hexane/EtOAc). White solid (97.9 mg, 85%). Mp = 42–44 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69–7.66 (m, 2H), 7.44–7.39 (m, 2H), 7.36–7.31 (m, 1H), 7.14 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 5.84 (m, 1H), 5.49 (s, 2H), 5.17 (dq, J = 10.4 Hz, 2.0 Hz, 1H), 4.93 (dq, J = 17.2 Hz, 2.0 Hz, 1H), 3.45 (m, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.0, 138.3, 132.5, 132.1, 131.5, 130.4, 129.8, 128.8, 128.0, 127.3, 117.9, 52.0, 27.2, 21.3. HRMS (ESI) *m*/*z* calculated for $C_{19}H_{20}N_3$ $[M + H]^+$ 290.1652, found 290.1657. IR (KBr film): ν 3056, 3031, 1639, 1495, 1360, 919, 792, 716 cm^{-1}.

5-Allyl-1-(4-methoxybenzyl)-4-phenyl-1*H*-1,2,3-triazole (3d). TLC: R_f 0.35 (2 : 1 hexane/EtOAc). Pale yellow liquid (107 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68–7.65 (m, 2H), 7.43–7.39 (m, 2H), 7.35–7.31 (m, 1H), 7.15 (dm, J = 9.6 Hz, 2H), 6.86 (dm, J = 9.6 Hz, 2H), 5.84 (m, 1H), 5.46 (s, 2H), 5.16 (dq, J = 10.4 Hz, 2.0 Hz, 1H), 4.92 (dq, J = 16.8 Hz, 2.0 Hz, 1H), 3.78 (s, 3H), 3.46 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 146.0, 132.5, 131.5, 130.3, 128.9, 128.8, 128.0, 127.3, 127.1, 117.8, 114.5, 55.4, 51.7, 27.1. HRMS (ESI) *m*/*z* calculated for $C_{19}H_{20}N_3O$ $[M + H]^+$ 306.1601, found 306.1595. IR (KBr film): ν 3063, 3005, 1639, 1514, 1250, 1032, 921, 825, 715 cm^{-1}

5-Allyl-1-(3,5-dimethoxybenzyl)-4-phenyl-1*H*-1,2,3-triazole (3e). TLC: R_f 0.37 (2 : 1 hexane/EtOAc). White solid (126 mg, 94%). Mp = 80–82 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64–7.61 (m, 2H), 7.38–7.34 (m, 2H), 7.27 (tt, J = 6.4 Hz, 1.2 Hz, 1H), 6.33 (t, J = 2.0 Hz, 1H), 6.27 (d, J = 2.0 Hz, 2H), 5.79 (m, 1H), 5.39 (s, 2H), 5.10 (dq, J = 12.0 Hz, 2.0 Hz, 1H), 4.88 (dq, J = 18.8 Hz, 2.0 Hz, 1H), 3.67 (s, 6H), 3.40 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4, 145.9, 137.3, 132.4, 131.4, 130.5, 128.7, 127.9, 127.2, 117.8, 105.3, 100.0, 55.5, 52.1, 27.1. HRMS (ESI) *m*/*z* calculated for $C_{20}H_{22}N_3O_2$ $[M + H]^+$ 336.1707, found 336.1708. IR (KBr film): ν 3003, 2938, 1598, 1206, 1066, 921, 777 cm^{-1}.

5-Allyl-1-(4-fluorobenzyl)-4-phenyl-1*H*-1,2,3-triazole (3f). TLC: R_f 0.45 (2 : 1 hexane/EtOAc). Pale yellow liquid (114 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68–7.66 (m, 2H), 7.44–7.40 (m, 2H), 7.34 (tt, J = 6.4 Hz, 1.2 Hz, 1H), 7.20 (dd, J = 8.8 Hz, 5.6 Hz, 2H), 7.03 (t, J = 8.8 Hz, 2H), 5.84 (m, 1H), 5.50 (s, 2H), 5.16 (dm, J = 10.0 Hz, 1H), 4.91 (dm, J = 16.4 Hz, 1H), 3.45 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.8 (d, J_{C-F} = 246.0 Hz), 146.1, 132.3, 131.3, 130.9 (d, J_{C-F} = 3.1 Hz), 130.3, 129.3 (d, J_{C-F} = 7.8 Hz), 128.9, 128.1, 127.3, 118.0, 116.1 (d, J_{C-F} = 21.7 Hz), 51.4, 27.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ −113.1. HRMS (ESI) *m*/*z* calculated for $C_{18}H_{17}FN_3$ $[M + H]^+$ 294.1401, found 294.1405. IR (KBr film): ν 3066, 3011, 1640, 1512, 1015, 920, 715, 698 cm^{-1}.

5-Allyl-4-phenyl-1-(4-(trifluoromethyl)benzyl)-1*H*-1,2,3-triazole (3g). TLC: R_f 0.47 (2 : 1 hexane/EtOAc). Light yellow solid (128 mg, 93%). Mp = 63–65 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 8.8 Hz, 2H), 7.59 (d, J = 8.0 Hz, 2H), 7.42 (t, J = 8.0 Hz, 2H), 7.36–7.29 (m, 3H), 5.84 (m, 1H), 5.57 (s, 2H), 5.15 (d, J = 10.0 Hz, 1H), 4.90 (d, J = 17.2 Hz, 1H), 3.45 (dm, J = 3.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.1, 139.1 (q, J_{C-F} = 1.5 Hz), 132.1, 131.2, 130.8 (q, J_{C-F} = 32.5 Hz), 130.5, 128.8, 128.1, 127.6, 127.3, 126.1 (q, J_{C-F} = 3.9 Hz), 124.0 (q, J_{C-F} = 270.9 Hz), 118.0, 51.4, 27.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ −63.1. HRMS (ESI) *m*/*z* calculated for $C_{19}H_{17}N_3F_3$ $[M + H]^+$ 344.1369, found 344.1374. IR (KBr film): ν 3064, 1640, 1496, 1125, 824, 779, 699 cm^{-1}.

5-Allyl-1-(4-nitrobenzyl)-4-phenyl-1*H*-1,2,3-triazole (3h). TLC: R_f 0.35 (2 : 1 hexane/EtOAc). Light yellow solid (110 mg, 86%). Mp = 93–95 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (dm, J = 8.8 Hz, 2H), 7.67 (dm, J = 8.8 Hz, 2H), 7.44–7.41 (m, 2H), 7.37–7.33 (m, 3H), 5.84 (m, 1H), 5.61 (s, 2H), 5.14 (dm, J = 12.0 Hz, 1H), 4.89 (dm, J = 17.2 Hz, 1H), 3.47 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.0, 146.2, 142.2, 132.1, 131.0, 130.5, 128.9, 128.3, 128.2, 127.3, 124.3, 118.2, 51.1, 27.1. HRMS (ESI) *m*/*z* calculated for $C_{18}H_{17}N_4O_2$ $[M + H]^+$ 321.1346, found 321.1348. IR (KBr film): ν 3081, 1608, 1520, 1495, 1347, 805, 734 cm^{-1}.

5-Allyl-4-phenyl-1-(*p*-tolyl)-1*H*-1,2,3-triazole (3i). TLC: R_f 0.72 (2 : 1 hexane/EtOAc). White solid (98.3 mg, 89%). Mp = 106–108 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 8.4 Hz, 2H), 7.48–4.37 (m, 5H), 7.33 (d, J = 8.4 Hz, 2H), 5.91 (m, 1H), 5.19 (d, J = 9.6 Hz, 1H), 4.93 (d, J = 17.2 Hz, 1H), 3.57 (dm, J = 4.0 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.4, 140.1, 134.1, 133.4, 131.4, 131.1, 130.1, 128.9, 128.1, 127.3, 125.5, 118.2, 27.7, 21.4. HRMS (ESI) *m*/*z* calculated for $C_{18}H_{18}N_3$ $[M + H]^+$ 276.1495, found 276.1501. IR (KBr film): ν 2919, 1517, 992, 934, 710 cm^{-1}.

5-Allyl-1-(4-methoxyphenyl)-4-phenyl-1*H*-1,2,3-triazole (3j). TLC: R_f 0.37 (3 : 1 hexane/EtOAc). Light brown solid (76.0 mg, 65%). Mp = 97–99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 7.2 Hz, 2H), 7.47–7.34 (m, 5H), 7.03 (d, J = 9.2 Hz, 2H), 5.91 (m, 1H), 5.19 (dd, J = 10.0 Hz, 1.2 Hz, 1H), 4.92 (dd, J = 17.6 Hz, 1.2 Hz, 1H), 3.88 (s, 3H), 3.56 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6, 133.4, 131.4, 129.4, 128.9, 128.8, 128.0, 127.2, 127.1, 118.1, 114.7, 114.6, 55.8, 27.7. HRMS (ESI) *m*/*z* calculated for $C_{18}H_{18}N_3O$ $[M + H]^+$ 292.1444, found 292.1449. IR (KBr film): ν 3081, 1639, 1508, 1260, 1030, 835, 714 cm^{-1}.

5-Allyl-1-(4-fluorophenyl)-4-phenyl-1*H*-1,2,3-triazole (3k). TLC: R_f 0.45 (2 : 1 hexane/EtOAc). Light yellow solid (70.0 mg, 63%). Mp = 121–123 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 7.2 Hz, 2H), 7.54–7.48 (m, 2H), 7.48–7.44 (m, 2H), 7.40–7.36 (m, 1H), 7.24 (t, J = 8.4 Hz, 2H), 5.92 (m, 1H), 5.21 (dd, J = 10.4 Hz, 1.2 Hz, 1H), 4.92 (dd, J = 17.2 Hz, 1.2 Hz, 1H), 3.57 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.3 (d, J_{C-F} = 249.2 Hz), 145.6, 133.2, 132.6 (d, J_{C-F} = 3.1 Hz), 131.2 (d, J_{C-F} = 6.2 Hz), 128.9, 128.3, 127.7 (d, J_{C-F} = 9.3 Hz), 127.3, 126.1, 118.4, 116.7 (d, J_{C-F} = 22.5 Hz), 27.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ −110.9. HRMS (EI) *m*/*z* calculated for $C_{17}H_{14}FN_3$ $[M]^+$ 279.1171, found 279.1172. IR (KBr film): ν 3082, 1514, 1244, 992, 846, 721, 701 cm^{-1}.

5-Allyl-1-octyl-4-phenyl-1*H*-1,2,3-triazole (3l). TLC: R_f 0.65 (2 : 1 hexane/EtOAc). Pale yellow liquid (107 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (dm, J = 8.4 Hz, 2H), 7.42 (tm, J = 8.4 Hz, 2H), 7.35–7.31 (m, 1H), 5.96 (m, 1H), 5.20 (dd, J = 10.4 Hz, 1.2 Hz, 1H), 4.96 (dd, J = 16.8 Hz, 1.2 Hz, 1H), 4.23 (t, J = 7.2 Hz, 2H), 3.58 (m, 2H), 1.92 (quin, J = 7.2 Hz, 2H), 1.40–1.26 (m, 10H), 0.87 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 132.9, 131.7, 129.9, 128.8, 127.9, 127.3, 117.8, 48.3, 31.8, 30.3, 29.3, 29.2, 27.2, 26.8, 22.7, 14.2. HRMS (ESI) *m*/*z* calculated for $C_{19}H_{28}N_3$ $[M + H]^+$ 298.2278, found 298.2278. IR (KBr film): ν 2954, 2926, 1640, 1495, 1361, 765, 698 cm^{-1}.

5-Allyl-1-benzyl-4-(4-fluorophenyl)-1*H*-1,2,3-triazole (3m). TLC: R_f 0.6 (3 : 1 hexane/EtOAc). White solid (81.6 mg, 70%). Mp = 79–81 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (dd, J = 8.8 Hz, 5.6 Hz, 2H), 7.36–7.30 (m, 3H), 7.20–7.18 (m, 2H), 7.11 (t, J = 8.8 Hz, 2H), 5.81 (m, 1H), 5.53 (s, 2H), 5.15 (dd, J = 10.4 Hz, 1.2 Hz, 1H), 4.90 (dd, J = 17.2 Hz, 1.2 Hz, 1H), 3.42 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7 (d, J_{C-F} = 245.3 Hz), 145.2, 135.0, 132.2, 130.2, 129.2, 129.1 (d, J_{C-F} = 8.5 Hz), 128.5, 127.6 (d, J_{C-F} = 3.1 Hz), 127.4, 118.0, 115.8 (d, J_{C-F} = 20.9 Hz), 52.2, 27.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ −110.9. HRMS (ESI) *m*/*z* calculated for $C_{18}H_{17}FN_3$ $[M + H]^+$ 294.1401, found 294.1404. IR (KBr film): ν 3081, 1640, 1510, 1224, 992, 841, 764, 698 cm^{-1}.

5-Allyl-1-benzyl-4-(2-chlorophenyl)-1*H*-1,2,3-triazole (3n). TLC: R_f 0.37 (2 : 1 hexane/EtOAc). Pale yellow liquid (66.7 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47–7.42 (m, 2H), 7.38–7.29 (m, 5H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.65 (m, 1H), 5.58 (s, 2H), 5.05 (dd, *J* = 10.0 Hz, 1.2 Hz, 1H), 4.92 (dd, *J* = 16.8 Hz, 1.2 Hz, 1H), 3.27 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.1, 135.0, 134.1, 132.6, 132.4, 132.2, 130.4, 130.1, 129.8, 129.1, 128.4, 127.2, 126.9, 117.9, 52.3, 27.5. HRMS (EI) *m*/*z* calculated for $C_{18}H_{16}ClN_3$ $[M]^+$ 309.1031, found 309.1033. IR (KBr film): ν 3064, 3032, 1639, 1497, 920, 760, 736, 694 cm^{-1}.

5-Allyl-1-benzyl-4-(4-methoxyphenyl)-1*H*-1,2,3-triazole (3o). TLC: R_f 0.37 (3 : 1 hexane/EtOAc). Pale yellow liquid (70.0 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.8 Hz, 2H), 7.36–7.30 (m, 3H), 7.20–7.18 (m, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 5.82 (m, 1H), 5.52 (s, 2H), 5.13 (dd, *J* = 12.0 Hz, 1.6 Hz, 1H), 4.91 (dd, *J* = 17.2 Hz, 1.6 Hz, 1H), 3.83 (s, 3H), 3.42 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 145.9, 135.3, 132.5, 129.8, 129.1, 128.6, 128.4, 127.3, 124.1, 117.8, 114.3, 55.5, 52.2, 27.2. HRMS (ESI) *m*/*z* calculated for $C_{19}H_{20}N_3O$ $[M + H]^+$ 306.1601, found 306.1604. IR (KBr film): ν 2932, 1616, 1508, 1251, 1015, 836, 727, 696 cm^{-1}.

5-Allyl-1-benzyl-4-(6-methoxynaphthalen-2-yl)-1*H*-1,2,3-triazole (3p). TLC: R_f 0.37 (2 : 1 hexane/EtOAc). Light yellow solid (106 mg, 75%). Mp = 113–115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 0.8 Hz, 1H), 7.83 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.38–7.31 (m, 3H), 7.23–7.21 (m, 2H), 7.17–7.14 (m, 2H), 5.87 (m, 1H), 5.57 (s, 2H), 5.18 (dd, *J* = 10.4 Hz, 1.2 Hz, 1H), 4.98 (dd, *J* = 17.2 Hz, 1.2 Hz, 1H), 3.93 (s, 3H), 3.52 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.1, 146.2, 135.2, 134.2, 132.5, 130.4, 129.9, 129.2, 129.1, 128.5, 127.4 (2C), 126.8, 126.1, 126.0, 119.3, 118.0, 105.8, 55.5, 52.2, 27.3. HRMS (EI) *m*/*z* calculated for $C_{23}H_{21}N_3O$ 355.1687, found 355.1685. IR (KBr film): ν 2936, 2840, 1634, 1600, 1263, 1029, 726, 695 cm^{-1}.

1-Benzyl-5-(2-methylallyl)-4-phenyl-1*H*-1,2,3-triazole (3q). TLC: R_f 0.73 (2 : 1 hexane/EtOAc). Light yellow solid (104 mg, 90%). Mp = 56–58 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.39–7.28 (m, 4H), 7.19 (dd, *J* = 7.6, 1.6 Hz, 2H), 5.51 (s, 2H), 4.90 (t, *J* = 1.2 Hz, 1H), 4.44 (s, 1H), 3.32 (s, 2H), 1.77 (d, *J* = 0.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.1, 140.3, 135.0, 131.4, 130.6, 128.9, 128.7, 128.3, 127.8, 127.2, 127.1, 112.8, 52.0, 30.9, 22.9. HRMS (ESI) *m*/*z* calculated for $C_{19}H_{20}N_3$ $[M + H]^+$ 290.1652, found 290.1654. IR (KBr film): ν 3063, 3031, 1605, 1496, 1251, 890, 770, 729 cm^{-1}.

1-Benzyl-4-phenyl-5-(2-phenylallyl)-1*H*-1,2,3-triazole (3r). TLC: R_f 0.54 (2 : 1 hexane/EtOAc). Colorless liquid (120 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (dt, *J* = 7.2, 1.6 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 2H), 7.37–7.28 (m, 9H), 7.22–7.13 (m, 2H), 5.52 (s, 2H), 5.47 (t, *J* = 1.6 Hz, 1H), 4.65 (t, *J* = 2.0 Hz, 1H), 3.82 (t, *J* = 2.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 142.6, 139.7, 134.9, 131.2, 130.3, 129.0, 128.8, 128.6, 128.4, 128.3, 128.0, 127.4, 127.1, 125.7, 114.3, 52.2, 28.5. HRMS (ESI) *m*/*z* calculated for $C_{24}H_{22}N_3$ $[M + H]^+$ 352.1808, found 352.1807. IR (KBr film): ν 3058, 3032, 1954, 1628 cm^{-1}.

1-Benzyl-5-(3-methylbut-2-en-1-yl)-4-phenyl-1*H*-1,2,3-triazole (3s). TLC: R_f 0.37 (2 : 1 hexane/EtOAc). White solid (89.0 mg, 73%). Mp = 86–88 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.38–7.28 (m, 4H), 7.16 (d, *J* = 6.4 Hz, 2H), 5.54 (s, 2H), 4.93 (m, 1H), 3.41 (d, *J* = 6.4 Hz, 2H), 1.65 (d, *J* = 1.6 Hz, 3H), 1.62 (d, *J* = 0.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.1, 135.2, 135.1, 132.6, 131.6, 128.9, 128.6, 128.1, 127.7, 127.4, 127.0, 118.5, 52.0, 25.5, 22.3, 18.1. HRMS (ESI) *m*/*z* calculated for $C_{20}H_{22}N_3$ $[M + H]^+$ 304.1808, found 304.1811. IR (KBr film): ν 3025, 1654, 1602, 1494, 1249, 968, 728, 708 cm^{-1}.

1-Benzyl-5-cinnamyl-4-phenyl-1*H*-1,2,3-triazole (3t). TLC: R_f 0.51 (2 : 1 hexane/EtOAc). White solid (74.5 mg, 53%). Mp = 100–102 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 7.2 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.38–7.26 (m, 6H), 7.25–7.18 (m, 5H), 6.21 (d, *J* = 16.0 Hz, 1H), 6.12 (dt, *J* = 16.0, 5.2 Hz, 1H), 5.58 (s, 2H), 3.61 (dd, *J* = 5.2, 1.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.9, 136.3, 135.0, 132.5, 131.3, 130.5, 129.0, 128.7, 128.6, 128.3, 129.9, 127.8, 127.3, 127.2, 126.2, 123.6, 52.2, 26.3. HRMS (ESI) *m*/*z* calculated for $C_{24}H_{21}N_3$ $[M + H]^+$ 352.1808, found 352.1812. IR (KBr film): ν 3082, 3025, 1955, 1654, 727 cm^{-1}.

5-Allyl-1-benzyl-4-hexyl-1*H*-1,2,3-triazole (3u). TLC: R_f 0.54 (2 : 1 hexane/EtOAc). Colorless oil (87.2 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.27 (m, 3H), 7.12 (dd, *J* = 8.0 Hz, 2.0 Hz, 2H), 5.72–5.58 (m, 1H), 5.46 (s, 2H), 5.07 (dq, *J* = 10.4 Hz, 1.6 Hz, 1H), 4.89 (dq, *J* = 16.8 Hz, 1.6 Hz, 1H), 3.22 (dt, *J* = 5.6 Hz, 1.6 Hz, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 1.66 (quintet, *J* = 6.4 Hz, 2H), 1.41–1.22 (m, 6H), 0.87 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 144.8, 136.1, 133.3, 130.4, 128.6, 127.8, 127.2, 116.7, 50.6, 30.9, 28.9, 28.2, 25.9, 24.2, 22.0, 13.8. HRMS (ESI) *m*/*z* calculated for $C_{18}H_{25}N_3$ $[M + H]^+$ 284.2121, found 284.2127. IR (KBr film): ν 3065, 3033, 2928, 1640, 1456, 992, 729 cm^{-1}.

5-Allyl-1-(but-3-en-1-yl)-4-phenyl-1*H*-1,2,3-triazole (3v). TLC: R_f 0.55 (2 : 1 hexane/EtOAc). Pale yellow liquid (76.8 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 6.8 Hz, 2H), 7.42 (t, *J* = 6.8 Hz, 2H), 7.33 (tt, *J* = 6.8 Hz, 1.2 Hz, 1H), 5.97 (m, 1H), 5.78 (m, 1H), 5.21 (dq, *J* = 10.0 Hz, 0.8 Hz, 1H), 5.14–5.08 (m, 2H), 4.94 (dq, *J* = 17.2 Hz, 0.8 Hz, 1H), 4.29 (t, *J* = 7.2 Hz, 2H), 3.58 (m, 2H), 2.70 (q, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 133.5, 132.8, 131.6, 130.1, 128.8, 127.9, 127.3, 118.2, 117.9, 47.5, 34.4, 27.2. HRMS (ESI) *m*/*z* calculated for $C_{15}H_{18}N_3$ $[M + H]^+$ 240.1495, found 240.1502. IR (KBr film): ν 3080, 1640, 1495, 918, 766, 699 cm^{-1}.

5-Allyl-1-(pent-4-en-1-yl)-4-phenyl-1*H*-1,2,3-triazole (3w). TLC: R_f 0.70 (2 : 1 hexane/EtOAc). Pale yellow liquid (77.7 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 7.2 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 5.95 (m, 1H), 5.79 (m, 1H), 5.20 (d, *J* = 10.0 Hz, 1H), 5.07 (d, *J* = 10.0 Hz, 1H), 5.03 (d, *J* = 17.2 Hz, 1H), 4.95 (d, *J* = 17.2 Hz, 1H), 4.23 (t, *J* = 7.2 Hz, 2H), 3.57 (m, 2H), 2.14 (q, *J* = 7.2 Hz, 2H), 2.04 (quin, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 136.8, 132.8, 131.6, 130.0, 128.7, 127.8, 127.2, 117.8, 116.1, 47.4, 30.7, 29.1, 27.1. HRMS (ESI) *m*/*z* calculated for $C_{16}H_{20}N_3$ $[M + H]^+$ 254.1652, found 254.1660. IR (KBr film): ν 3079, 2979, 1640, 1495, 916, 765, 700 cm^{-1}.

5-Allyl-1-(hex-5-en-1-yl)-4-phenyl-1*H*-1,2,3-triazole (3x). TLC: R_f 0.65 (2 : 1 hexane/EtOAc). Pale yellow liquid (69.5 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68–7.65 (m, 2H), 7.43–7.39 (m, 2H), 7.34–7.31 (m, 1H), 5.95 (m, 1H), 5.76 (m, 1H), 5.20 (dd, J = 10.0 Hz, 0.8 Hz, 1H), 5.04–4.98 (m, 2H), 4.94 (dd, J = 8.8 Hz, 0.8 Hz, 1H), 4.23 (t, J = 7.6 Hz, 2H), 3.57 (m, 2H), 2.10 (q, J = 7.6 Hz, 2H), 1.94 (quin, J = 7.6 Hz, 2H), 1.47 (quin, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 138.0, 132.8, 131.6, 129.9, 128.8, 127.8, 127.3, 117.8, 115.3, 48.0, 33.2, 29.5, 27.1, 25.9. HRMS (ESI) *m*/*z* calculated for $C_{17}H_{22}N_3$ $[M + H]^+$ 268.1808, found 268.1814. IR (KBr film): ν 3079, 2978, 1640, 1495, 914, 769, 698 cm^{-1}.

5-Allyl-4-phenyl-1-(2-vinylphenyl)-1*H*-1,2,3-triazole (3y). TLC: R_f 0.6 (2 : 1 hexane/EtOAc). Light yellow solid (60.8 mg, 53%). Mp = 81–83 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 7.6 Hz, 2H), 7.74 (d, J = 8.0 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.44–7.36 (m, 2H), 7.31 (d, J = 7.6 Hz, 1H), 6.18 (dd, 17.6 Hz, 11.2 Hz, 1H), 5.73 (d, J = 17.6 Hz, 1H), 5.72–5.65 (m, 1H), 5.27 (d, J = 10.8 Hz, 1H), 5.02 (d, J = 10.0 Hz, 1H), 4.81 (d, J = 16.4 Hz, 1H), 3.43 (d, J = 5.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 135.5, 133.7, 132.8, 132.3, 131.3, 130.9, 130.7, 128.9, 128.5, 128.1, 127.2 (2C), 126.4, 118.2, 117.9, 27.5. HRMS (ESI) *m*/*z* calculated for $C_{19}H_{18}N_3$ $[M + H]^+$ 288.1495, found 288.1492. IR (KBr film): ν 3063, 2964, 1640, 1494, 991, 769, 698 cm^{-1}.

5-Allyl-4-phenyl-1-(2-vinylbenzyl)-1*H*-1,2,3-triazole (3z). TLC: R_f 0.35 (6 : 1 hexane/EtOAc). Light brown liquid (66.6 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 6.8 Hz, 2H), 7.50 (d, J = 8.0 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.6 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.20 (t, J = 7.6 Hz, 1H), 7.03 (dd, J = 16.8 Hz, 10.8 Hz, 1H), 6.81 (d, J = 7.6 Hz, 1H), 5.80 (m, 1H), 5.67 (dd, J = 17.2 Hz, 0.8 Hz, 1H), 5.63 (s, 2H), 5.42 (dd, J = 12.0 Hz, 0.8 Hz, 1H), 5.13 (d, J = 10.4 Hz, 1H), 4.88 (d, J = 17.2 Hz, 1H), 3.41 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.0, 136.7, 133.4, 132.3, 132.1, 131.4, 130.7, 128.9, 128.6, 128.4, 128.0, 127.5, 127.3, 126.8, 118.2, 117.8, 49.8, 27.1. HRMS (ESI) *m*/*z* calculated for $C_{20}H_{20}N_3$ $[M + H]^+$ 302.1652, found 302.1646. IR (KBr film): ν 3062, 3033, 1639, 1608, 1495, 919, 771, 699 cm^{-1}.

Experimental procedure for ring closing metathesis

Synthesis of 3-phenyl-7,8-dihydro-4*H*-[1,2,3]triazolo[1,5-α]azepine (6v). The diene **3v** (47.9 mg, 200 μmol) was dissolved in anhydrous CH_2Cl_2 (6 mL). A solution of Grubbs' 1st generation catalyst (8.2 mg, 10.0 μmol) in anhydrous CH_2Cl_2 (3.3 mL) was added to the reaction mixture *via* a cannula, and stirred at room temperature for 19 h. Upon completion of the reaction, the solvent was removed *in vacuo*. The residue was purified by column chromatography to afford **6v** as a pale green liquid (33.3 mg, 79%). TLC: R_f 0.3 (2 : 1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J = 7.2 Hz, 2H), 7.44 (t, J = 7.2 Hz, 2H), 7.35 (t, J = 7.2 Hz, 1H), 5.75–5.73 (m, 2H), 4.71 (t, J = 6.0 Hz, 2H), 3.70–3.69 (m, 2H), 2.55–2.52 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.7, 133.2, 131.5, 129.0, 128.8, 127.9, 127.8, 123.2, 47.9, 27.9, 25.5. HRMS (ESI) *m*/*z* calculated for $C_{13}H_{14}N_3$ $[M + H]^+$ 212.1182, found 212.1185. IR (KBr film): ν 3058, 1660, 1624, 1498, 772, 699 cm^{-1}.

Synthesis of 3-phenyl-4,7,8,9-tetrahydro-[1,2,3]triazolo[1,5-α]azocine (6w). The diene **3w** (50.7 mg, 200 μmol) was dissolved in anhydrous CH_2Cl_2 (6 mL). A solution of Grubbs' 1st generation catalyst (8.2 mg, 10.0 μmol) in anhydrous CH_2Cl_2 (3.3 mL) was added to the reaction mixture *via* a cannula. The reaction mixture was stirred at room temperature for overnight, and was brought to reflux for 6 h. Upon completion of the reaction, the solvent was removed *in vacuo*. The residue was purified by column chromatography to afford **6w** as pale yellow liquid (39.0 mg, 87%). TLC: R_f 0.35 (2 : 1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 7.6 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.6 Hz, 1H), 5.79–5.67 (m, 2H), 4.53 (t, J = 5.2 Hz, 2H), 3.64 (d, J = 4.8 Hz, 2H), 1.90–1.82 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4, 132.9, 131.7, 128.8, 128.4, 127.9, 127.8, 127.1, 47.2, 27.2, 24.4, 23.1. HRMS (ESI) *m*/*z* calculated for $C_{14}H_{16}N_3$ $[M + H]^+$ 226.1339, found 226.1336. IR (KBr film): ν 2929, 1665, 1626, 1447, 733, 698 cm^{-1}.

Synthesis of (*Z*)-3-phenyl-7,8,9,10-tetrahydro-4*H*-[1,2,3]triazolo[1,5-α]azonine (6x) and (*E*)-1,10-bis(5-allyl-4-phenyl-1*H*-1,2,3-triazol-1-yl)dec-5-ene (6x′). The diene **3x** (53.5 mg, 200 μmol) was dissolved in anhydrous CH_2Cl_2 (6 mL). A solution of Grubbs' 1st generation catalyst (8.2 mg, 10.0 μmol) in anhydrous CH_2Cl_2 (3.3 mL) was added to the reaction mixture *via* a cannula. The reaction mixture was brought to reflux for 8 h. Upon completion of the reaction, the solvent was removed *in vacuo*. The residue was purified by column chromatography to afford **6x** as a white solid (31.0 mg, 65%) and a dimer **6x′** as colorless liquid (8.0 mg, 8%). **6x:** TLC: R_f 0.2 (2 : 1 hexane/EtOAc). Mp = 201–203 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 7.6 Hz, 2H), 7.45 (t, J = 7.6 Hz, 2H), 7.36 (t, J = 7.6 Hz, 1H), 5.81 (m, 1H), 5.66 (m, 1H), 4.51 (t, J = 6.0 Hz, 2H), 3.61 (d, J = 7.6 Hz, 2H), 2.35–2.30 (m, 2H), 2.01 (quin, J = 6.4 Hz, 2H), 1.67–1.61 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.2, 131.7, 131.5, 131.0, 128.9, 128.0, 127.6, 126.3, 45.8, 25.9, 25.1, 23.0, 21.9. HRMS (ESI) *m*/*z* calculated for $C_{15}H_{18}N_3$ $[M + H]^+$ 240.1495, found 240.1498. IR (KBr film): ν 2959, 2932, 1491, 733, 720, 697 cm^{-1}.

6x′: TLC: R_f 0.17 (2 : 1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 7.2 Hz, 4H), 7.42 (t, J = 7.2 Hz, 4H), 7.34 (t, J = 7.2 Hz, 2H), 6.00–5.91 (m, 2H), 5.39–5.35 (m, 2H), 5.21 (d, J = 10.4 Hz, 2H), 4.95 (d, J = 17.2 Hz, 2H), 4.25–4.22 (m, 4H), 3.59–3.57 (m, 4H), 2.09–2.01 (m, 4H), 1.96–1.89 (m, 4H), 1.43 (quin, J = 7.6 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.2, 132.8, 131.4, 130.3, 130.1, 128.9, 128.0, 127.4, 117.9, 48.2, 32.0, 29.6, 27.2, 26.6. HRMS (ESI) *m*/*z* calculated for $C_{33}H_{39}N_6$ $[M + H]^+$ 507.3231, found 507.3232. IR (KBr film): ν 2925, 1660, 1600, 1495, 917, 770, 698 cm^{-1}.

Synthesis of 3-phenyl-4*H*-benzo[*f*][1,2,3]triazolo[1,5-α]azepine (6y). The diene **3y** (52.0 mg, 180 μmol) was dissolved in anhydrous CH_2Cl_2 (6 mL). A solution of Grubbs' 1st generation catalyst (8.2 mg, 10.0 μmol) in anhydrous CH_2Cl_2 (3.3 mL) was added to the reaction mixture *via* a cannula. The reaction mixture was stirred at room temperature for 8 h. Upon completion of the reaction, the solvent was removed *in vacuo*. The residue was purified by column chromatography to afford **6y** as a white solid (43.0 mg, 92%). TLC: R_f 0.37 (6 : 1 hexane/

EtOAc). Mp = 96–98 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (dd, J = 7.6 Hz, 1.2 Hz, 1H), 7.71 (d, J = 7.6 Hz, 2H), 7.50–7.41 (m, 4H), 7.41–7.36 (m, 2H), 6.65 (d, J = 10.4 Hz, 1H), 6.18 (m, 1H), 3.51 (d, J = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2, 135.0, 134.9, 130.9, 130.8, 130.2, 129.0, 128.8, 128.7, 128.2, 128.1, 127.9, 127.6, 124.0, 21.2. HRMS (ESI) m/z calculated for $C_{17}H_{14}N_3$ $[M + H]^+$ 260.1182, found 260.1179. IR (KBr film): ν 2919, 1700, 1600, 1491, 992, 772, 699 cm^{-1}.

Synthesis of (*Z*)-3-phenyl-4,11-dihydrobenzo[*f*][1,2,3]triazolo[1,5-α]azocine (6z). The diene **3z** (47.0 mg, 150 μmol) was dissolved in anhydrous CH_2Cl_2 (6 mL). A solution of Hoveyda-Grubbs' 2nd generation catalyst (5.0 mg, 7.9 μmol) in anhydrous CH_2Cl_2 (3.3 mL) was added to the reaction mixture *via* a cannula. The reaction mixture was stirred at room temperature for 4 h. Upon completion of the reaction, the solvent was removed *in vacuo*. The residue was purified by column chromatography to afford **6z** as a pale green solid (29.5 mg, 72%). TLC: R_f 0.27 (6 : 1 hexane/EtOAc). Mp = 159–161 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58–7.54 (m, 3H), 7.45–7.38 (m, 3H), 7.37–7.35 (m, 2H), 7.30 (d, J = 8.4 Hz, 1H), 7.08 (d, J = 10.4 Hz, 1H), 6.03 (dt, J = 10.4 Hz, 7.6 Hz, 1H), 5.49 (s, 2H), 3.30 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 139.2, 134.0, 131.5, 131.3, 130.9, 129.3, 128.8, 128.7, 128.6, 128.2, 128.0, 127.7, 126.2, 53.4, 22.6. HRMS (ESI) m/z calculated for $C_{18}H_{16}N_3$ $[M + H]^+$ 274.1339, found 274.1336. IR (KBr film): ν 3025, 2360, 1494, 995, 754, 735, 699 cm^{-1}.

Conflicts of interest

There are no conflicts to declare.

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