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Three-component Coupling Reaction for the Synthesis of Fully Substituted Triazoles: Reactivity Control of Cu-Acetylide toward Alkyl Azides and Diazo Compounds

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Method

Three-component Coupling Reaction for the Synthesis of Fully Substituted Triazoles: Reactivity Control of Cu-Acetylide toward Alkyl Azides and Diazo Compounds

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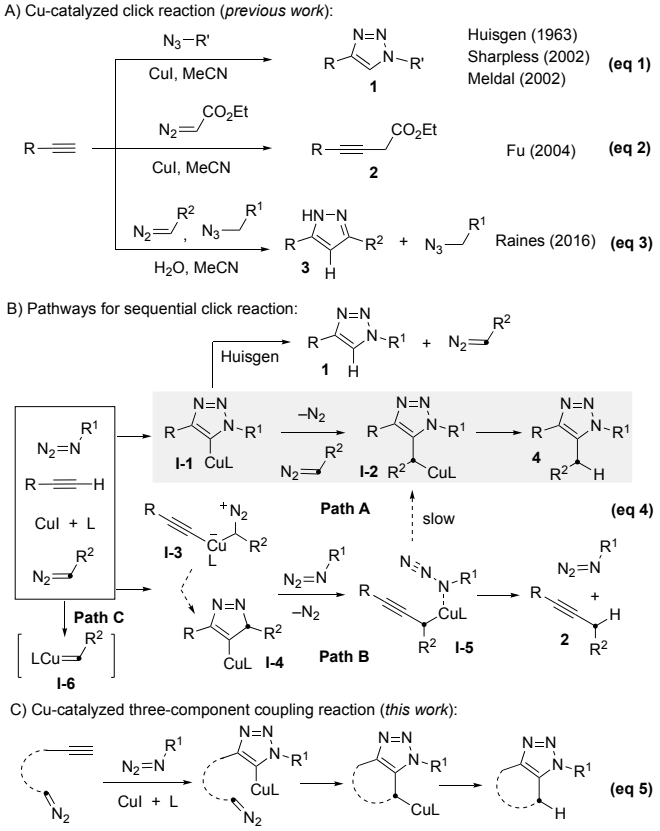
Herein, we reported a Cu-catalyzed three-component coupling reaction of alkynes, azides, and diazo compounds for the synthesis of fully substituted triazoles. The reactivities of alkyl azide and diazo compound toward Cu-acetylide were controlled by the introduction of ligand and stoichiometry of azide and diazo compounds to suppresses the undesired protonation or the alkyne-diazo coupling, maximizing the selectivity for the three-component coupling. Besides, the use of aliphatic alkynes was crucial for achieving high selectivity for the three-component coupling reaction. This method features mild reaction conditions, broad substrate scope, and good functional groups tolerance. A variety of fully substituted triazoles and ring-fused triazoles were synthesized by this method in moderate to good yields.

Introduction

The copper(I)-catalyzed [3+2] cycloaddition between azide and alkyne known as the 'azide-alkyne click reaction' developed by Sharpless[1] and Meldal[2] independently has been drawn great interests because of its capacity to be applied to many fields including chemical biology, medicinal chemistry and material science (Scheme 1, eq 1).[3] While the thermal Huisgen cycloadditions generate a mixture of regioisomers under relatively harsh conditions[4], the corresponding Cu-catalyzed click reactions generate single regioisomeric product under much milder conditions.[3a, 5] In general, Cu-catalyzed azide-alkyne cycloaddition generates 1,4-disubstituted 1,2,3-triazoles **1**, but switching the regioselectivity to form 1,5-disubstituted 1,2,3-triazoles was achieved by using a ruthenium catalyst.[6] Fu reported Cu-catalyzed reaction of alkyne with diazo compound, an isoelectronic structure of an azide, however, provided a formal C–H insertion product **2** rather than a [3+2] cycloaddition product (eq 2).[7] Because of the utility of a [3+2] cycloaddition of diazo compound with alkyne as a tool for copper-free bioconjugation, Raines explored the reactivity and selectivity between azide and diazo compound with alkynes under copper-free conditions.[8] While strained alkynes provided equal mixture of cycloadducts of azide and diazo compound, unstrained electron-deficient alkyne generated D^2-pyrazole **3** selectively along with unreacted azide (eq 3).

On the other hand, the reactivity difference between azide and diazo compounds toward electron-rich alkynes such as Cu-acetylide has not been explored despite the fact that the individual reactions were extensively studied. At this juncture, we envisage that the combined reaction of alkyl azide and diazo compound with alkyne and copper catalyst (eq 4) would provide information about the relative reactivity of these isoelectronic functionalities toward Cu-acetylide. In addition, if the reaction rates of these two competing reactants could be controlled a new sequential reaction could be developed. The reactions to proceed through Path A, Path B and Path C would depend on multiple factors including the structure of azide and diazo compound, their stoichiometry, catalyst loading, and the



Scheme 1. Reactions of Alkyne, Alkyl Azide, and Diazo Compound with Copper Catalyst.

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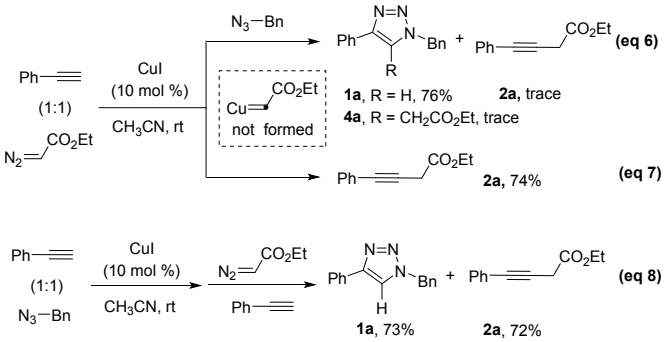
ligand. We predict that in Path A, alkyl azide will outcompete diazo compound to form cycloadduct **I-1** primarily due to its higher Cu-coordinating ability than diazo compound. Once generated, intermediate **I-2** will be protonated to provide triazole **1** or react with diazo compound to generate **I-2**, which upon protonation will give three-component coupled product **4**. However, the competing reaction of diazo compound in Path B will generate adduct **I-3**, which may cyclize to form **I-4** or extrude N_2 to generate **I-5**. Because the Cu-catalyzed coupling of diazo compound with alkyne in eq 2 does not generate pyrazole, **I-3** should disfavor to cyclized to generate **I-4**. Although **I-5** can still undergo [3+2] cycloaddition to form **I-2** the kinetically favored protonation is expected to generate **2** and unreacted azide. To maximize formation **4**, the protonation of **I-1** should be suppressed, which requires high concentration of diazo compound. However, the increased concentration of diazo compound would also increase the possibility of forming Cu-acetylide adduct **I-3** in Path B and Cu-carbenoid **I-6** in Path C as well, which ultimately increases the formation of product **2**. We suspect that the ligand on the Cu-catalyst can modulate the relative rates of these competing pathways and ultimately can maximize the efficiency of forming three-component coupled 1,4,5-trisubstituted **4**. Furthermore, tethering a pair of reactants, for example, alkyne and diazo compound would avoid the problem of undesired protonation at the intermediate stage (eq 5), which would constitute a new strategy for preparing ring-fused triazoles.[9]

Developing efficient methods for preparing 1,4,5-trisubstituted triazoles has drawn significant interest.[6c, 10] One-pot approaches employing a Cu-catalyzed click reaction followed by a C–H arylation sequence were effective,[10l] yet direct trapping of Cu-triazolide intermediate generated from the Cu(I)-catalyzed click reaction has gained popularity.[11] In 2015, Wang reported an efficient direct trapping approach by employing N-tosylhydrazones as a precursor for diazo compounds under relatively harsh conditions.[12] However, due to the high reactivity of diazo compounds in Cu-catalyzed reactions, controlling the sequence and timing of their incorporation at a particular stage of a catalytic cycle is difficult if preformed diazo compounds are employed. This is a general conundrum even when other reactive electrophiles are employed in the direct trapping. To achieve the selectivity for the desired reaction pathway, stoichiometric use of copper catalyst and less reactive trapping agents were needed,[13] which in turn required harsh reaction conditions and long reaction time. Herein, we report sequential incorporation of alkyl azide and diazo compound in click reactions by modulating the reactivities of organocopper intermediates with the associated ligand under mild conditions. Also, relying on tethering of reactants to increase the effective molarity, high pathway-selectivity was achieved to efficiently generate ring-fused triazoles.

Results and Discussion

We commenced our investigation by comparing the reaction of phenyl acetylene and ethyl diazoacetate (EDA) in the

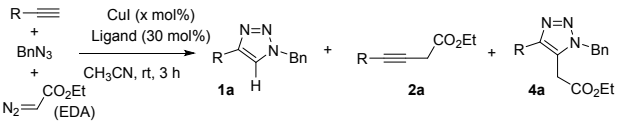


Scheme 2. Control Experiments

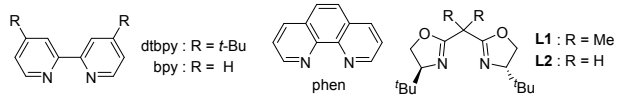
presence and absence of benzyl azide (1:1:1) with CuI (10 mol %) in acetonitrile (Scheme 2). The reaction of phenyl acetylene, EDA and benzyl azide (1:1:1) generated triazole **1a** (76%) and unreacted EDA along with only trace amount of phenylacetylene–EDA coupled product **2a** and sequential coupling product **4a**. On the other hand, the same reaction without benzyl azide under otherwise identical conditions generated product **2a** in 74% yield. To prove the catalytic activity of copper remains the same in both the reactions, a sequential reaction was carried out (eq 8). After complete consumption of benzyl azide (phenyl acetylene: benzyl azide = 1:1), EDA and phenyl acetylene (1:1) was introduced to the reaction mixture. From this reaction, two major products **1a** and **2a** were obtained in 73% and 72% yields, respectively. This result indicates that the copper catalyst to promote the triazole formation in the first step remains to be an active catalyst for the coupling between an alkyne and EDA. At the same time, these results clearly show that EDA and copper catalyst react too slowly to generate a copper carbenoid under the conditions, which provides a solid basis to exclude the formation of Cu-carbenoid **I-6** in Path C from the competing reactions.

Having seen that the expected product **4a** was not produced efficiently in the reaction with equal amount of azide and diazo compound, we examined reaction conditions employing a bidentate ligand and increased stoichiometry of EDA (Table 1). While the reaction with CuI alone and 1:1:1 ratio of phenyl acetylene, benzyl azide, and EDA provided triazole **1a** as the only isolable product (entry 1), adding 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbpy) to the reaction under otherwise identical conditions provided **1a**, **2a**, and **4a** in a 4.9:0:1 ratio (entry 2). Increasing the catalyst loading to 20 mol% slightly increased **4a** up to 19% (entry 3), and by increasing the amount of EDA, further increase of **4a** and decrease of **1a** was achieved (entry 4). Increasing the stoichiometry of azide increased both the portions of **2a** and **4a** (entry 5) but base additive (K_2CO_3) increased the portion of **1a** with decrement of **4a** (entry 6). With the same stoichiometry, the dtbpy ligand was changed to 2,2'-bipyridine (bpy), which resulted in a decreased ratio of **4a** (entry 7). Reaction with phenanthroline could achieve similar portion of **4a** but the portion of **2a** was significantly decreased (entry 8). Even though Box ligands **L1** and **L2** suppressed the formation of **2a** the portion of protonated product **1a** increased significantly (entries 9 and

Table 1. Optimization of Reaction Conditions[a]



Entry	R	alkyne : azide : EDA	CuI (mol%)	Ligand	Ratio[b] 1a : 2a : 4a	Isolated yield of 4a (%)
1	Ph	1 : 1 : 1	10	none	1 : 0 : 0	N.D.[c]
2	Ph	1 : 1 : 1	10	dtbpy	4.9 : 0 : 1	N.D.
3	Ph	1 : 1 : 1	20	dtbpy	4.2 : 0 : 1	N.D.
4	Ph	1 : 1 : 3	20	dtbpy	7.9 : 1 : 1.2	N.D.
5	Ph	1 : 2 : 3	20	dtbpy	1.3 : 1 : 1.4	N.D.
6[d]	Ph	1 : 2 : 3	20	dtbpy	4.9 : 1 : 2.5	N.D.
7	Ph	1 : 2 : 3	20	bpy	5.4 : 1 : 1.9	N.D.
8	Ph	1 : 2 : 3	20	phen	6.8 : 1 : 4.8	N.D.
9	Ph	1 : 2 : 3	20	**L1**	14 : 1 : 5.2	N.D.
10	Ph	1 : 2 : 3	20	**L2**	5.6 : 1 : 1	N.D.
11	***n*-Bu**	**1 : 2 : 3**	**20**	**dtbpy**	**1 : 0 : 10[b]**	**66**
12	*n*-Bu	1 : 2 : 3	20	bpy	1.9 : 1 : 10	N.D.
13	*n*-Bu	1 : 2 : 3	20	none	10 : 1 : 5.2	N.D.
14	*n*-Bu	1 : 2 : 3	10	none	14 : 1 : 5.0	N.D.

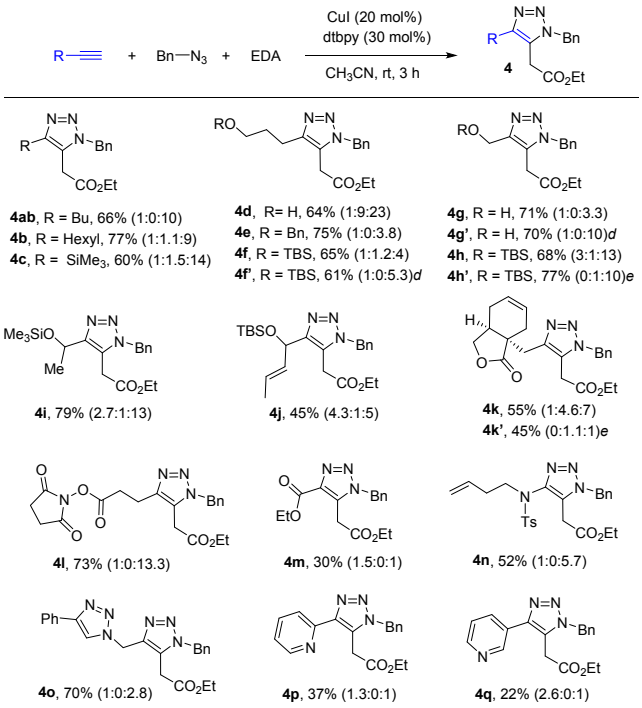


[a]Reaction conditions: alkyne (0.2 mmol, 1.0 eq), azide, ethyl diazoacetate, CuI, ligand (30 mol %) in CH_3CN at rt under N_2 for 3 h. [b]Determined by ^1H NMR of crude mixture. [c]N.D. stands for not determined. [d]With 1 equivalent of K_2CO_3 as additive.

10). At this point, we suspected that the facile protonation in these reactions might be the consequence of the relatively high acidity of phenyl acetylene compared to alkyl acetylenes. Thus, we examined the same condition in entry 5 with 1-hexyne, which provided **4a** as predominant product along with only a small portion of **1a** and **2a** was not observed (entry 11). The same reaction with bpy-ligand provided still provided **4a** as the predominant product but with a compromised ratio (entry 12), and without ligand protonated product **1a** became the major product (entries 13 and 14). These results indicate that the structure of alkyne has a major impact on product distribution.

With these results in hand, we explored the reaction scope by employing a range of structurally different alkynes together with benzyl azide and EDA under the optimized conditions (Table 2). Many functional groups including free hydroxy group (**4d, 4g, 4g'**), alkyl ether (**4e**), silyl ether (**4f**, **4h–4j**) alkene (**4j**, **4k**, **4n**), lactone (**4k**), and sulfonamide and other nitrogen functionality (**4n, 4p, 4q**) are tolerant to the reaction conditions. While alkyl substituted alkynes provided **4ab** and **4b** in good yield and selectivity a bulky trimethtylsilyl substituted alkyne also provided **4c** with similar yield and ratio. Surprisingly, the free hydroxyl groups in **4d, 4g** and **4g'** regardless of the distance from the reaction center did not compromise the yield and ratio of these products. Steric hindrance influences the yield, for example, **4h** containing a silyl ether of a primary alcohol was obtained with higher yield than the secondary alcohol-derived congener **4j**. The role of chelating nitrogen functionality was examined (**4o–4r**). It was found that chelating effect by 2-pyridyl group seems not

Table 2. Impact of the Alkyne Structures on the Yield and Selectivity[a,b,c]

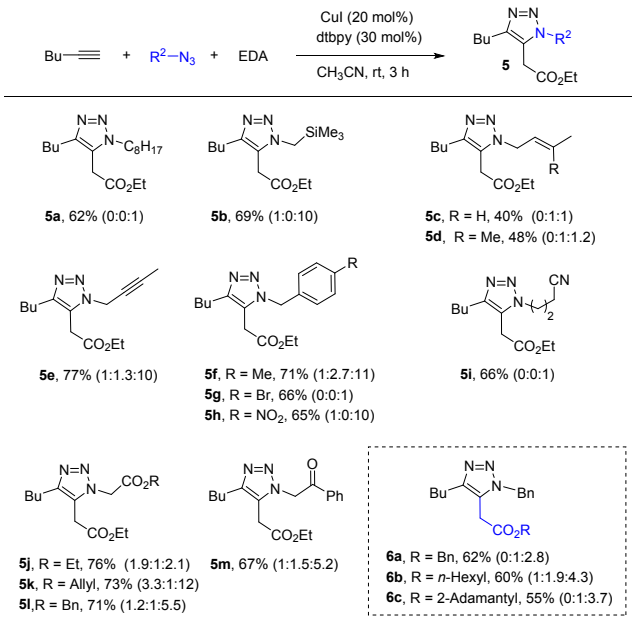


[a]Reaction conditions: alkyne (0.2 mmol, 1.0 eq), azide (2.0 eq), ethyl diazoacetate (3.0 eq), CuI (20 mol %), dtbpy (30 mol %) in CH_3CN at rt under N_2 for 3 h. [b]Isolated yield of 4. [c]Ratios of **1a**:**2a**:**4** before purification are shown in the parenthesis. [d]$C_8H_{17}N_3$ was used instead of N_3Bn. [e]$N_3CH_2SiMe_3$ was used instead of N_3Bn.

involved at the intermediate stage. An *N*-Ts-containing ynamide provided **4n** with slightly lower yield while triazole containing alkyne afforded **4o** in higher yield. Not unexpectedly, electron-withdrawing 2-alkynyl and 3-alkynyl pyridines provided **4p** (37%) and **4q** (22%) in low yield with predominance of protonated products **1p** and **1q**. These results are not surprising because like phenyl acetylene, pyridyl-substituted alkynes are more prone to undergo proton transfer.

Having demonstrated the wide scope of alkynes and their structural effect on efficiency and selectivity, we turned our attention to the structural variation of azides (Table 3). In each reaction, 1-hexyne and EDA were employed while the structure of azides was varied. Although it was predicted that more electron-rich azide should be more favorable for increasing the selectivity for Path A over Path B no consistency of their behaviors was observed. For example, crotyl and prenyl azide provided a relatively low yield of **5c** (40%) and **5d** (48%) while 2-butynyl azide afforded 5**e** (77%) in much higher yield. For **5c** and **5d**, only a primary azide adduct was observed although the corresponding adducts of a secondary or a tertiary azide were possible.[14] Benzyl azides with an electron-withdrawing or an electron-donating group at the para position did not show significant differences in forming **5f–5h**. Even a strong electron-withdrawing ester- or a ketone functionality on the a-carbon of azides did not significantly

Table 3. Substrate scopes of Azides and Diazo Compounds[a,b,c]



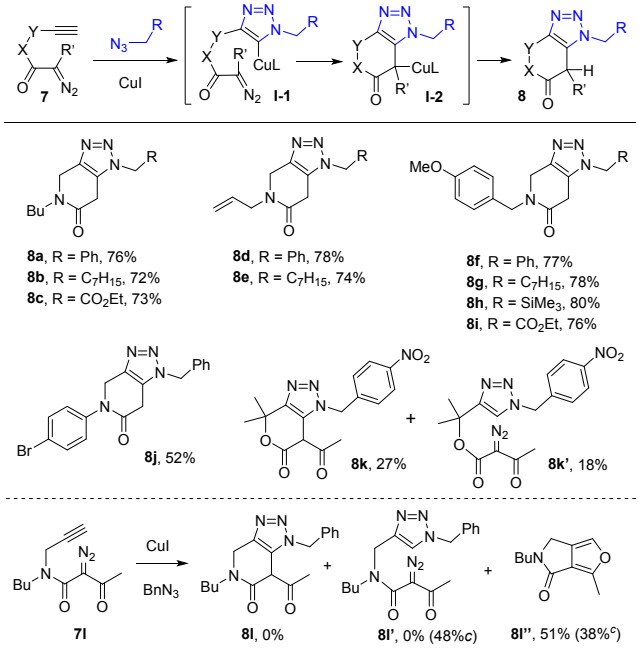
[a]Reaction conditions: 1-hexyne (0.2 mmol, 1.0 eq), azide (2.0 eq), diazo compounds (3.0 eq), CuI (20 mol %), dtbpy (30 mol %) in CH_3CN at rt under N_2 for 3 h. [b]Isolated yield of product **5**. [c]Ratios of **1a**:**2a**:**5** before purification are shown in the parenthesis.

change the yield and selectivity in forming **5j–5m**. The substrate scope of diazo compounds was also examined. Benzyl, and hexyl diazoacetate provided products **6a**, and **6b** in 62, and 60% yield, and even sterically more hindered adamantyl diazoacetate provided **6c** in similar yield (55%).

These results indicate that controlling the reaction pathways by using a ligand has proven effective, however, the competing protonation of the organocopper triazole intermediate is yet to be further improved. We expected that by increasing the effective molarity of diazo compound the competing protonation event could be reduced. To test this hypothesis, alkyne-tethered diazo compounds **7a–7j** were examined (Table 4). To our delight, the expected fused cyclic triazoles **8a–8j** were produced without any protonated product. This suggests that once intermediate **I-1** is generated, the copper moiety has a lesser chance to interact with alkyne **7** for proton exchange rather a more favorable intramolecular interaction of the diazo moiety at the copper center would generate **I-2**. The less reactive diazo compound still can participate in the reaction to generate **8k** in 27% along with a protonated product **8k'** in 18% yield. Surprisingly, diazo amide **7l** did not provide **8l** instead a furan derivative **8l''** was generated exclusively (52%).[15] Under identical reaction conditions with dtbpy as a ligand, protonated product **8l'** was obtained as the major component (48%) along with **8m''** (31%), which demonstrates the crucial role of a ligand for product distribution.

Shown in Scheme 3 is a mechanistic picture of all competing pathways leading to the observed products **1, 2**, and **4**. The initially formed Cu-acetylide **A** reacts mainly with azide to form adduct **B**,[16] which undergoes [3+2] cycloaddition

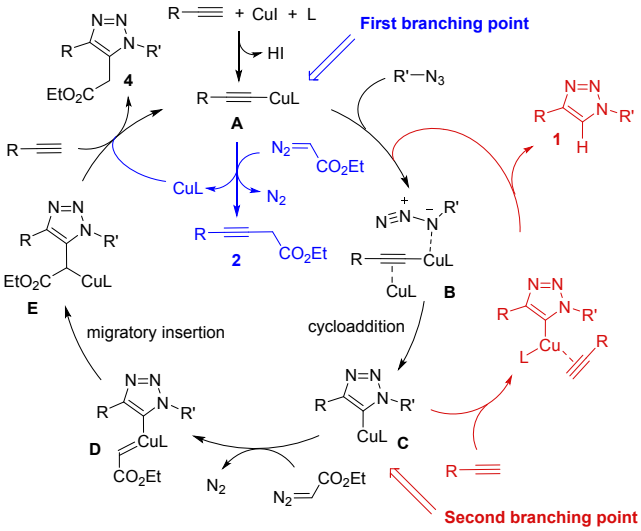
Table 4. Substrate Scope of Alkyne-tethered Diazo Compounds[a,b]



[a]Reaction conditions: alkyne-diazo compound (1.0 eq), benzyl azide (2.0 eq), CuI (20 mol %) in CH_3CN at rt under N_2 for 3 h. [b]Isolated yield. [c]with 30 mol% of dtbpy.

to generate intermediate **C**. At the same time, Cu-acetylide **A** competitively react with EDA to generate minor product **2**. Subsequently, intermediate **C** reacts with EDA to generate Cu-carbenoid **D**, which will lead to intermediate **E**.[17] Intermediate **C** also can interact with an alkyne followed by proton exchange to generate triazole **1** and Cu-acetylide **A**. Finally, alkyne coordination with **E** followed by proton exchange would generate **4** and regenerate Cu-acetylide **A**, which enters a new catalytic cycle.

Based on these mechanisms, we infer that the bidentate ligand provides increased steric hindrance with the bond-



Scheme 3. Proposed Mechanism for the Three Components Coupling Reaction

forming event between **A** and EDA. However, the complexation of strongly coordinating azide at the metal center is not affected, which resulted in improved selectivity. On the other hand, the interaction of a weakly coordinating alkyne with sterically congested **C** will be more severely affected by the ligand than the interaction of more polar EDA. Thus, the minor pathway leading to the formation of **1** is diminished.

Conclusions

We explored the reactivity difference between alkyl azide and diazo compound toward Cu-acetylide in the presence of a nitrigene-based bidentate ligand. Under this condition, alkyl azides are generally more reactive than diazo compounds toward Cu-acetylide to form organocopper triazole intermediate. This vinyl-Cu species is more reactive than Cu-acetylide toward diazo compound, thus selectivity between 3-alkynoate **2** and 1,4,5-trisubstituted-1,2,3-triazoles **4** can be realized. With an appropriate adjustment of a ligand and stoichiometry of azide and diazo compound, the sequence of reaction pathways could be orchestrated to maximize the selectivity of forming **4** over click reaction product **1** and alkyne-diazo coupling product **2**. Besides, the use of aliphatic alkynes could also improve the selectivity significantly for the three-component coupling reaction. In general, under the current reaction condition, the direct formation of Cu-carbenoids from diazo compound and the Cu-catalyst is not involved except for **7l**, which provides **8l"** via a carbenoid pathway. A variety of alkynes and azides could be employed and the electronic factors on these reactants were exploited to control the product distribution, providing fully substituted triazoles.

Experimental Section

I. General Information

All reactions were carried out under an inert nitrogen or argon atmosphere, unless otherwise indicated. Compounds were purchased from Aldrich unless otherwise noted. CH_3CN was purified based on standard procedures. Flash column chromatography was performed using silica gel 60 Å (32-63 mesh) purchased from SiliCycle. Analytical thin-layer chromatography (TLC) was performed on 0.25 mm SiliCycle precoated silica gel 60 (particle size 0.040–0.063 mm). Iodide, $KMnO_4$, UV light (254 nm) and vanillin were used as the TLC stains. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-500 spectrometer. ^1H and ^{13}C chemical shifts were referenced to internal solvent resonances and reported relative to $SiMe_4$; multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Coupling constants, J, are reported in Hz (Hertz). Electrospray ionization (ESI) mass spectra were recorded on a Micromass LCT equipped with a time-of-flight analyzer on a Waters Micromass Q-Tof Ultima in the University of Illinois at Urbana-Champaign. Electron impact (EI) mass spectra were obtained using a Micromass AutoSpecTM.

II. General Procedure for the Three-component Coupling Reaction

1-Hexyne (16 mg, 0.2 mmol), benzyl azide (53.3 mg, 0.4 mmol, 2.0 equiv.) and ethyl diazoacetate (68.7 mg, 0.6 mmol, 3.0 equiv.) were dissolved in dry CH_3CN (1.0 mL), then dtbpy (16.1 mg, 0.06 mmol, 0.3 equiv.) and CuI (7.6 mg, 0.04 mmol, 0.2 equiv.) were added and the reaction mixture was stirred under N_2 atmosphere for 3 h. On completion of the reaction, 1 mL of aq. NH_4Cl and 1 mL of ethyl acetate were added to the reaction mixture and stirred for 5 min. Then reaction mixture was diluted with EtOAc (10 mL) and organic layer was separated and washed with brine. This organic layer dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford the crude material. The crude material was purified by using flash column chromatography to afford product **4ab**.

III. General Procedure for the Synthesis of Cyclic Triazoles

Diazoamide **S7** (35.8 mg, 0.2 mmol), benzyl azide (53.3 mg, 0.4 mmol, 2.0 equiv.) were dissolved in dry CH_3CN (1.0 mL) and CuI (7.6 mg, 0.04 mmol, 0.2 equiv.) were added, and the reaction mixture was stirred under N_2 atmosphere for 3 h. On completion of the reaction, 1 mL of aq. NH_4Cl and 1 mL of ethyl acetate were added to the reaction mixture and stirred for 5 min. Then reaction mixture was diluted with EtOAc (10 mL) and organic layer was separated and washed with brine. This organic layer dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford the crude material. The crude material was purified by using flash column chromatography to afford product **S8**.

Characterization Data

Ethyl 2-(1-benzyl-4-butyl-1*H*-1,2,3-triazol-5-yl)acetate (4ab)

The compound **4ab** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 5:1 to 1:1). **4ab** was obtained as a yellow oil (40.0 mg, 66% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.8 Hz, 3H), 7.14 (d, *J* = 6.7 Hz, 2H), 5.57 (s, 2H), 4.04 (q, *J* = 7.1 Hz, 2H), 3.44 (s, 2H), 2.61 (t, *J* = 7.7 Hz, 2H), 1.69–1.61 (m, 2H), 1.37–1.32 (m, 2H), 1.18 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.28, 147.35, 134.92, 129.09, 128.46, 127.41, 126.25, 61.75, 52.47, 31.69, 28.96, 24.88, 22.50, 14.13, 13.96; HRMS (ESI) calcd for $C_{17}H_{24}N_3O_2$ $[M + H]^+$ 302.1869, found 302.1865.

Ethyl 2-(1-benzyl-4-hexyl-1*H*-1,2,3-triazol-5-yl)acetate (4b)

The compound **4b** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 2:1). **4b** was obtained as a light-yellow oil (50.8 mg, 77%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.35–7.28 (m, 3H), 7.14 (d, *J* = 6.7 Hz, 2H), 5.56 (s, 2H), 4.03 (q, *J* = 6.9 Hz, 2H), 3.43 (s, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 1.70–1.62 (m, 2H), 1.35–1.24 (m, 8H), 1.18 (t, *J* = 7.0 Hz, 3H), 0.86 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.26, 147.37, 134.91, 129.07, 128.44, 127.38, 126.23, 61.73, 52.46, 31.70, 29.53, 29.09, 28.95, 25.19, 22.66, 14.16, 14.13; HRMS (ESI) calcd for $C_{19}H_{27}N_3O_2$ $[M + H]^+$ 330.2182, found 330.2179.

Ethyl 2-(1-benzyl-4-(trimethylsilyl)-1*H*-1,2,3-triazol-5-yl)acetate (4c)

The compound **4c** was prepared according to the general procedure and was purified by flash column chromatography

(hexane: ethyl acetate = 2:1). **4c** was obtained as a light-yellow oil (37.8 mg, 60% yield). ^{1}H NMR (500 MHz, C_6D_6) δ 7.36 (dd, *J* = 14.5, 7.8 Hz, 3H), 7.19 (d, *J* = 6.8 Hz, 2H), 5.64 (s, 2H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.60 (s, 2H), 1.20 (t, *J* = 7.1 Hz, 3H), 0.36 (s, 9H); ^{13}C NMR (126 MHz, C_6D_6) δ 168.22, 145.84, 135.21, 134.89, 129.01, 128.38, 127.45, 61.72, 51.74, 29.91, 14.07, –0.92; HRMS (ESI) calcd for $C_{16}H_{24}N_3O_2Si$ $[M + H]^+$ 318.1638, found 318.1639.

Ethyl 2-(1-benzyl-4-(3-hydroxypropyl)-1*H*-1,2,3-triazol-5-yl)acetate (4d)

The compound **4d** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 1:1 to acetone). **4d** was obtained as a green oil (38.6 mg, 64% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.29 (m, 3H), 7.14 (d, *J* = 6.8 Hz, 2H), 5.56 (s, 2H), 4.02 (q, *J* = 7.0 Hz, 2H), 3.81–3.58 (m, 2H), 3.51 (s, 2H), 2.80–2.72 (m, 2H), 2.00–1.91 (m, 2H), 1.18 (t, *J* = 7.1 Hz, 3H), 1.12 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.24, 134.51, 129.10, 129.02, 128.45, 127.31, 61.80, 61.43, 52.62, 31.40, 28.92, 21.30, 14.03; HRMS (ESI) calcd for $C_{16}H_{22}N_3O_2$ $[M + H]^+$ 304.1661, found 304.1663.

1-Benzyl-4-(3-(benzyloxy)propyl)-5-(2-(ethylperoxy)-2λ²-ethyl)-1*H*-1,2,3-triazole (4e)

The compound **4e** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 1:1). **4e** was obtained as a yellow oil (59.0 mg, 75% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.24 (m, 8H), 7.14 (d, *J* = 6.3 Hz, 2H), 5.55 (s, 2H), 4.46 (s, 2H), 4.01 (q, *J* = 7.1 Hz, 2H), 3.50 (t, *J* = 6.1 Hz, 2H), 3.43 (s, 2H), 2.74 (t, *J* = 7.4 Hz, 2H), 2.06–1.96 (m, 1H), 1.17 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.27, 146.65, 138.67, 134.85, 129.10, 128.64, 128.49, 128.47, 128.08, 127.82, 127.71, 127.62, 127.41, 126.66, 72.88, 69.32, 61.73, 52.52, 29.28, 28.78, 21.61, 14.13; HRMS (ESI) calcd for $C_{23}H_{28}N_3O_2$ $[M + H]^+$ 394.2131, found 394.2131.

Ethyl 2-(1-benzyl-4-(3-((*tert*-butyldimethylsilyl)oxy)propyl)-1*H*-1,2,3-triazol-5-yl)acetate (4f)

The compound **4f** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 3:1). **4f** was obtained as a yellow oil (54.0 mg, 65% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.28 (m, 3H), 7.13 (d, *J* = 6.4 Hz, 2H), 5.55 (s, 2H), 4.03 (q, *J* = 7.1 Hz, 2H), 3.61 (t, *J* = 5.7 Hz, 2H), 3.46 (s, 2H), 2.70 (t, *J* = 7.5 Hz, 2H), 1.91–1.84 (m, 2H), 1.18 (t, *J* = 7.1 Hz, 3H), 0.87 (s, 9H), 0.01 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.26, 146.85, 134.85, 129.07, 128.45, 127.39, 126.63, 62.06, 61.69, 52.50, 32.39, 28.78, 26.03, 22.20, 21.22, 14.12, –5.21; HRMS (ESI) calcd for $C_{22}H_{36}N_3O_3Si$ $[M + H]^+$ 418.2526, found 413.2518.

Ethyl 2-(4-(3-((*tert*-butyldimethylsilyl)oxy)propyl)-1-octyl-1*H*-1,2,3-triazol-5-yl)acetate (4f')

The compound **4f'** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 1:1). **4f'** was obtained as a yellow oil (40.1 mg, 61% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.21 (t, *J* = 7.4 Hz, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.64 (s, 2H), 3.61 (t, *J* = 6.05 Hz, 4H), 2.70 (t, *J* = 7.5 Hz, 2H), 1.86 (m, 4H), 1.33–1.18 (m, 13H), 0.9–0.82 (m, 12H), 0.02 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.2, 145.8, 126.0, 61.9, 61.6, 48.3, 32.3, 31.7, 29.6, 29.0, 28.7, 26.6, 25.9, 22.5, 21.1, 18.2, 14.0, –5.3; HRMS (ESI) calcd for $C_{23}H_{46}N_3O_3Si$ $[M + H]^+$ 440.3308, found 440.3298.

Ethyl 2-(1-benzyl-4-(hydroxymethyl)-1*H*-1,2,3-triazol-5-yl)acetate (4g)

The compound **4g** was prepared according to the general procedure and was purified by flash column chromatography (ethyl acetate). **4g** was obtained as a brown oil (141.0 mg, 71% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.29 (m, 3H), 7.15 (d, *J* = 6.1 Hz, 2H), 5.57 (s, 2H), 4.77 (s, 2H), 4.03 (q, *J* = 6.8 Hz, 2H), 3.62 (s, 2H), 2.45 (brs, 1H), 1.18 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.39, 146.78, 134.42, 129.18, 128.66, 128.15, 127.43, 62.07, 56.48, 52.59, 28.94, 14.09; HRMS (ESI) calcd for $C_{14}H_{18}N_3O_3$ $[M + H]^+$ 276.1348, found 276.1349.

Ethyl 2-(4-(hydroxymethyl)-1-octyl-1*H*-1,2,3-triazol-5-yl)acetate (4g')

The compound **4g'** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 1:1 to 1:2). **4g'** was obtained as a light-yellow oil (83.0 mg, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.75 (s, 2H), 4.24 (t, *J* = 7.2 Hz, 2H), 4.17 (q, *J* = 7.0 Hz, 2H), 3.78 (s, 2H), 2.81 (s, 1H), 1.90–1.81 (m, 2H), 1.32–1.29 (m, 3H), 1.28–1.21 (m, 10H), 0.86 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.54, 146.41, 127.96, 62.10, 56.33, 48.54, 31.77, 30.04, 29.10, 29.09, 28.98, 26.66, 22.65, 14.14, 14.12; HRMS (ESI) calcd for $C_{15}H_{28}N_3O_3$ $[M + H]^+$ 298.2131, found 298.2129.

Ethyl 2-(1-benzyl-4-(((*tert*-butyldimethylsilyl)oxy)methyl)-1*H*-1,2,3-triazol-5-yl)acetate (4h)

The compound **4h** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 5:1). **4h** was obtained as a yellow oil (59.7 mg, 77% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.82 (s, 2H), 4.14 (q, *J* = 6.9 Hz, 2H), 3.78 (s, 2H), 3.60 (s, 2H), 1.24 (t, *J* = 7.0 Hz, 3H), 0.87 (s, 9H), 0.18 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.51, 144.94, 128.42, 61.60, 58.25, 38.87, 29.02, 25.98, 14.23, –1.70, –5.29; HRMS (ESI) calcd for $C_{20}H_{32}N_3O_3Si$ $[M + H]^+$ 390.2213, found 390.2206.

Ethyl 2-(4-(((*tert*-butyldimethylsilyl)oxy)methyl)-1-((trimethylsilyl)methyl)-1*H*-1,2,3-triazol-5-yl)acetate (4h')

The compound **4h'** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 1:1). **4h'** was obtained as a yellow oil (59.7 mg, 77% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.83 (s, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 2H), 3.60 (s, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.88 (s, 9H), 0.19 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.4, 144.8, 128.3, 61.5, 58.1, 38.7, 28.9, 25.9, 18.3, 14.1, –1.7, –5.3; HRMS (ESI) calcd for $C_{17}H_{36}N_3O_3Si_2$ $[M + H]^+$ 386.2295, found 386.2286.

Ethyl 2-(1-benzyl-4-(1-hydroxyethyl)-1*H*-1,2,3-triazol-5-yl)acetate (4i')

The compound **4i** was prepared according to the general procedure and converted to **4i'** after purification. **4i'** was purified by flash column chromatography (hexane: ethyl acetate = 1:1). **4i'** was obtained as a light-yellow oil (45.7 mg, 79% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.27 (m, 3H), 7.14 (d, *J* = 6.4 Hz, 2H), 5.54 (s, 2H), 5.08–5.01 (m, 1H), 4.00 (q, *J* = 7.0 Hz, 2H), 3.66 (s, 2H), 2.48 (brs, 1H), 1.62 (d, *J* = 6.4 Hz, 3H),

1.16 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.69, 150.03, 134.52, 129.13, 128.59, 127.41, 126.71, 63.67, 61.96, 52.40, 29.03, 23.31, 14.07; HRMS (ESI) calcd for $C_{15}H_{20}N_3O_3$ [M + H]$^+$ 290.1505, found 290.1506.

Ethyl (*E*)-2-(1-benzyl-4-(1-((*tert*-butyldimethylsilyl)oxy)-3,7-dimethylocta-2,6-dien-1-yl)-1*H*-1,2,3-triazol-5-yl)acetate (4j)

The compound **4j** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 5:1). **4j** was obtained as a mixture of triazole, light-yellow oil (66.3 mg, 45% yield of **4j**). Characteristic data for **4j**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (d, *J* = 6.2 Hz, 2H), 5.49 (s, 2H), 4.08 – 3.98 (m, 2H), 3.75 (d, *J* = 17.4 Hz, 1H), 3.53 (d, *J* = 17.4 Hz, 1H), 1.64 (d, *J* = 6.3 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H), 0.81 (s, 9H), –0.02 (s, 3H), –0.08 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.47, 148.72, 132.65, 129.03, 127.37, 126.36, 125.61, 69.86, 61.51, 52.38, 28.78, 25.90, 17.57, 14.13, –4.83; HRMS (ESI) calcd for $C_{23}H_{36}N_3O_3Si$ [M + H]$^+$ 430.2526, found 430.2517.

Ethyl 2-(1-benzyl-4-(((3aS,7aS)-3-oxo-1,4,7,7a-tetrahydroisobenzofuran-3a(3*H*)-yl)methyl)-1*H*-1,2,3-triazol-5-yl)acetate (4k)

The compound **4k** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 5:1 to 1:1). **4k** was obtained as a light-yellow oil (43.5 mg, 55% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.27 (m, 3H), 7.10 (d, *J* = 7.2 Hz, 2H), 5.85–5.79 (m, 1H), 5.78–5.72 (m, 1H), 5.58 (d, *J* = 15.6 Hz, 1H), 5.41 (d, *J* = 15.6 Hz, 1H), 4.14 (t, *J* = 8.3 Hz, 1H), 4.02 (t, *J* = 7.1 Hz, 2H), 3.85 (t, *J* = 9.4 Hz, 1H), 3.69 (d, *J* = 17.5 Hz, 1H), 3.56 (d, *J* = 17.5 Hz, 1H), 3.05–2.94 (m, 2H), 2.94–2.87 (m, 1H), 2.63–2.53 (m, 1H), 2.35–2.29 (m, 1H), 2.11–2.04 (m, 1H), 2.02–1.92 (m, 1H), 1.17 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.35, 168.40, 142.61, 134.51, 129.07, 128.99, 128.51, 127.41, 125.51, 123.58, 70.44, 61.64, 52.59, 44.70, 34.91, 29.60, 29.55, 28.58, 22.19, 14.08; HRMS (ESI) calcd for $C_{22}H_{26}N_3O_4$ [M + H]$^+$ 396.1923, found 396.1921.

Ethyl 2-(4-(((3aS,7aS)-3-oxo-1,4,7,7a-tetrahydroisobenzofuran-3a(3*H*)-yl)methyl)-1-((trimethylsilyl)methyl)-1*H*-1,2,3-triazol-5-yl)acetate (4k')

The compound **4k'** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 5: 1 to 1:1). **4k'** was obtained as a light-yellow oil (35.2 mg, 45% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.86–5.75 (m, 2H), 4.21–4.10 (m, 3H), 3.97–3.84 (m, 2H), 3.66 (d, *J* = 17.4 Hz, 1H), 3.54 (s, 2H), 3.05–2.91 (m, 3H), 2.63–2.55 (m, 1H), 2.34 (d, *J* = 17.6 Hz, 1H), 2.14–2.06 (m, 1H), 1.98 (d, *J* = 18.1 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.18 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 181.50, 168.77, 141.25, 129.46, 125.52, 123.62, 70.48, 61.68, 44.80, 39.05, 34.82, 29.66, 28.83, 22.18, 14.25, -1.62; HRMS (ESI) calcd for $C_{19}H_{30}N_3O_4Si$ [M + H]$^+$ 392.2006, found 392.1996.

2,5-Dioxopyrrolidin-1-yl 3-(1-benzyl-5-(2-ethoxy-2-oxoethyl)-1*H*-1,2,3-triazol-4-yl)propanoate (4l)

The compound **4l** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 1:1 to 1:2). **4l** was obtained as a yellow oil (60.1 mg, 73% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.9 Hz, 3H), 7.13 (d, *J* = 7.1 Hz, 2H), 5.56 (s, 2H), 4.02 (q, *J* = 7.1 Hz, 2H), 3.50 (s, 2H), 3.12 (t, *J* = 6.9 Hz, 2H), 3.04 (t, *J* = 7.5 Hz, 2H), 2.81 (s, 4H), 1.17 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.99, 168.29, 167.98, 144.26, 134.62, 129.13, 128.52, 127.40, 127.23, 61.86, 52.58, 30.60, 28.83, 25.70, 20.15, 14.12; HRMS (ESI) calcd for $C_{16}H_{20}N_3O_4$ [M – OSu + H]$^+$ 318.1454, found 318.1454.

Ethyl 1-benzyl-5-(2-ethoxy-2-oxoethyl)-1*H*-1,2,3-triazole-4-carboxylate (4m)

The compound **4m** was prepared according to the general procedure and was purified by flash column chromatography (hexanea: ethyl acetate = 3:1 to 1:1). **4m** was obtained as a mixture of triazole, yellow oil (80.0 mg, 30% yield of **4m**). Characteristic data for **4m**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.57 (s, 2H), 4.00 (q, *J* = 7.1 Hz, 2H), 3.90 (s, 2H), 1.12 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.19, 161.29, 140.53, 129.23, 129.09, 128.21, 127.34, 61.75, 54.38, 52.53, 29.24, 13.95; HRMS (ESI) calcd for $C_{16}H_{20}N_3O_4$ [M + H]$^+$ 318.1454, found 318.1454.

Ethyl 2-(1-benzyl-4-((N-(but-3-en-1-yl)-4-methylphenyl)sulfonamido)-1*H*-1,2,3-triazol-5-yl)acetate (4n)

The compound **4n** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 2:1). **4n** was obtained as a yellow oil (48.9 mg, 52% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.39–7.34 (m, 3H), 7.27 (d, *J* = 7.7 Hz, 2H), 7.15 (d, *J* = 6.5 Hz, 2H), 5.62 (s, 2H), 4.94–4.87 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.67 (t, *J* = 7.0 Hz, 2H), 3.61 (s, 2H), 2.41 (s, 3H), 2.15 (q, *J* = 6.6 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.19, 144.12, 143.01, 134.74, 134.50, 134.20, 129.75, 129.25, 128.76, 128.06, 127.44, 119.77, 116.98, 61.77, 53.63, 49.53, 32.62, 28.85, 21.74, 14.20; HRMS (ESI) calcd for $C_{24}H_{29}N_4O_4S$ [M + H]$^+$ 469.1910, found 469.1900.

Ethyl 2-(1-benzyl-4-((4-phenyl-1*H*-1,2,3-triazol-1-yl)methyl)-1*H*-1,2,3-triazol-5-yl)acetate (4o)

The compound **4o** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 1:1 to 1:2). **4o** was obtained as a brown oil (56.3 mg, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.77 (d, *J* = 7.3 Hz, 2H), 7.38 (t, *J* = 7.1 Hz, 2H), 7.32–7.27 (m, 4H), 7.14 (d, *J* = 5.7 Hz, 2H), 5.67 (s, 2H), 5.54 (s, 2H), 3.93 (q, *J* = 6.8 Hz, 2H), 3.64 (s, 2H), 1.08 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.34, 148.24, 140.99, 133.84, 130.45, 129.63, 129.16, 128.84, 128.74, 128.22, 127.46, 125.68, 119.87, 62.00, 52.77, 45.00, 28.62, 13.91; HRMS (ESI) calcd for $C_{22}H_{23}N_6O_2$ [M + H]$^+$ 403.1882, found 403.1875.

Ethyl 2-(1-benzyl-4-(pyridin-2-yl)-1*H*-1,2,3-triazol-5-yl)acetate (4p)

The compound **4p** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 1:1). **4p** was obtained as light-yellow solid (24.9 mg, 37% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.0 Hz, 1H), 8.22 (d, *J* = 7.9 Hz, 1H), 7.74 (t, *J* = 7.7 Hz, 1H), 7.36–7.28 (m, 3H), 7.20 (d, *J* = 7.0 Hz, 2H), 7.17–7.13 (m, 1H), 5.62 (s, 2H), 4.22 (s, 2H), 4.03 (q, *J* = 7.1 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.71, 151.59, 148.96, 144.96, 136.68, 134.56, 129.43, 129.14, 128.57, 127.42, 122.33,

120.95, 61.43, 52.42, 30.02, 14.15; HRMS (ESI) calcd for $C_{18}H_{19}N_4O_2$ $[M + H]^+$ 323.1508, found 323.1505.

Ethyl 2-(1-benzyl-4-(pyridin-3-yl)-1*H*-1,2,3-triazol-5-yl)acetate (4q)

The compound **4q** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 1:5). **4q** was obtained as a mixture of triazole, light-yellow solid (43.2 mg, 22% yield of **4q**). Characteristic data for **4q**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 5.4 Hz, 1H), 7.21 (d, *J* = 6.7 Hz, 2H), 5.66 (s, 2H), 4.06 (q, *J* = 6.9 Hz, 2H), 3.66 (s, 2H), 1.18 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.76, 148.99, 146.80, 145.69, 144.22, 134.17, 128.97, 128.18, 127.46, 62.14, 52.72, 29.54, 14.05; HRMS (ESI) calcd for $C_{18}H_{19}N_4O_2$ $[M + H]^+$ 323.1508, found 323.1505.

Ethyl 2-(4-butyl-1-octyl-1*H*-1,2,3-triazol-5-yl)acetate (5a): The compound **5a** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 2:1). **5a** was obtained as a light-yellow oil (40.0 mg, 62% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.22 (t, *J* = 7.3 Hz, 2H), 4.15 (q, *J* = 6.9 Hz, 2H), 3.61 (s, 2H), 2.62 (t, *J* = 7.5 Hz, 2H), 1.90–1.82 (m, 2H), 1.68–1.60 (m, 2H), 1.39–1.21 (m, *J* = 24.9, 13.9, 7.0 Hz, 20H), 0.91 (t, *J* = 7.2 Hz, 3H), 0.86 (t, *J* = 6.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.43, 146.45, 125.80, 61.83, 48.49, 31.83, 31.69, 30.12, 29.18, 29.06, 26.77, 24.89, 22.71, 22.52, 14.17, 13.96; HRMS (ESI) calcd for $C_{18}H_{34}N_3O$ $[M + H]^+$ 324.2651, found 324.2648.

Ethyl 2-(4-butyl-1-((trimethylsilyl)methyl)-1*H*-1,2,3-triazol-5-yl)acetate (5b)

The compound **5b** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 5:1 to 1:1). **5b** was obtained as a light-yellow oil (41.0 mg, 69% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.11 (q, *J* = 7.1 Hz, 2H), 3.57 (s, 2H), 3.56 (s, 2H), 2.56 (t, *J* = 7.6 Hz, 2H), 1.61 (q, *J* =7.3 Hz, 2H), 1.31 (m, 2H), 1.20 (t, *J* = 7.1 Hz, 3H), 0.87 (t, *J* = 7.3 Hz, 3H), 0.14 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.3, 145.6, 126.4, 61.5, 38.8, 31.4, 29.0, 24.8, 22.3, 14.0, 13.8, –1.7; HRMS (ESI) calcd for $C_{14}H_{28}N_3O_2Si$ $[M + H]^+$ 298.1951, found 298.1953.

Ethyl 2-(1-(but-2-en-1-yl)-4-butyl-1*H*-1,2,3-triazol-5-yl)acetate (5c)

The compound **5c** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 1:1 to 2:1). **5c** was obtained as a light-yellow oil (21.5 mg, 40% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.70–5.60 (m, 1H), 5.60–5.50 (m, 1H), 4.88 (d, *J* = 5.5 Hz, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.61 (s, 2H), 2.60 (t, *J* = 7.7 Hz, 2H), 1.68 (d, *J* = 5.7 Hz, 3H), 1.65–1.59 (m, 2H), 1.36–1.31 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.41, 146.92, 130.71, 129.37, 124.56, 123.69, 61.72, 50.73, 31.70, 28.93, 24.81, 22.47, 17.72, 14.18, 13.93; HRMS (ESI) calcd for $C_{14}H_{24}N_3O_2$ $[M + H]^+$ 266.1869, found 266.1872.

Ethyl 2-(4-butyl-1-(3-methylbut-2-en-1-yl)-1*H*-1,2,3-triazol-5-yl)acetate (5d)

The compound **5d** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 2:1). **5d** was obtained as a light-yellow oil (26.9 mg, 48% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.27 (t, *J* = 6.1 Hz, 1H), 4.96 (d, *J* = 6.7 Hz, 2H), 4.15 (t, *J* = 7.0 Hz, 2H), 3.60 (s, 2H), 2.61 (t, *J* = 7.7 Hz, 2H), 1.79 (s, 3H), 1.75 (s, 3H), 1.68–1.61 (m, 2H), 1.38–1.33 (m, 2H), 1.25 (t, *J* = 7.0 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.53, 146.95, 138.05, 125.81, 118.12, 61.76, 47.15, 31.77, 28.91, 25.77, 24.89, 22.54, 18.21, 14.23, 13.99; HRMS (ESI) calcd for $C_{15}H_{26}N_3O_2$ $[M + H]^+$ 280.2025, found 280.2020.

Ethyl 2-(1-(but-2-yn-1-yl)-4-butyl-1*H*-1,2,3-triazol-5-yl)acetate (5e)

The compound **5e** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 2:1). **5e** was obtained as a yellow oil (40.5 mg, 77% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.13 (s, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 2H), 2.62 (t, *J* = 7.6 Hz, 2H), 1.82 (s, 3H), 1.68–1.62 (m, 2H), 1.37–1.33 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.50, 147.16, 126.18, 83.03, 71.27, 61.84, 39.16, 31.71, 28.99, 24.84, 22.50, 14.24, 13.97, 3.67; HRMS (ESI) calcd for $C_{14}H_{22}N_3O_2$ $[M + H]^+$ 264.1712, found 264.1712.

Ethyl 2-(4-butyl-1-(4-methylbenzyl)-1*H*-1,2,3-triazol-5-yl)acetate (5f)

The compound **5f** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 5:1 to 1:1). **5f** was obtained as a yellow oil (44.7 mg, 71% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (d, *J* = 7.4 Hz, 2H), 7.04 (d, *J* = 7.4 Hz, 2H), 5.52 (s, 2H), 4.05 (q, *J* = 6.9 Hz, 2H), 3.43 (s, 2H), 2.60 (t, *J* = 7.5 Hz, 2H), 2.31 (s, 3H), 1.68–1.60 (m, 2H), 1.35–1.31 (m, 2H), 1.19 (t, *J* = 7.0 Hz, 3H), 0.90 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.33, 147.30, 138.28, 131.85, 129.73, 127.43, 126.17, 61.72, 52.33, 31.69, 28.94, 24.86, 22.49, 21.21, 14.12, 13.95; HRMS (ESI) calcd for $C_{18}H_{26}N_3O_2$ $[M + H]^+$ 316.2025, found 316.2024.

Ethyl 2-(1-(4-bromobenzyl)-4-butyl-1*H*-1,2,3-triazol-5-yl)acetate (5g)

The compound **5g** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 3:1 to 1:1). **5g** was obtained as a light-yellow oil (50.4 mg, 66% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 8.1 Hz, 2H), 5.50 (s, 2H), 4.03 (q, *J* = 7.1 Hz, 2H), 3.43 (s, 2H), 2.61 (t, *J* = 7.5 Hz, 2H), 1.69–1.58 (m, 2H), 1.37–1.30 (m, 2H), 1.18 (t, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.12, 147.49, 133.87, 132.21, 129.13, 126.24, 122.55, 61.84, 51.76, 31.62, 28.91, 24.82, 22.45, 14.09, 13.91; HRMS (ESI) calcd for $C_{17}H_{23}N_3O_2Br$ $[M + H]^+$ 380.0974, found 380.0963.

Ethyl 2-(4-butyl-1-(4-nitrobenzyl)-1*H*-1,2,3-triazol-5-yl)acetate (5h)

The compound **5h** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 1:1). **5h** was obtained as a light-yellow oil (45.1 mg, 65% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 5.66 (s, 2H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.47 (s, 2H), 2.63 (t, *J* = 7.7 Hz, 2H), 1.70–1.62 (m, 2H), 1.39–1.31 (m, 2H), 1.18 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.04, 148.02, 147.54, 142.08, 128.26, 126.38, 124.27, 61.99, 51.41, 31.61, 31.55,

28.94, 24.83, 22.46, 14.12, 13.92; HRMS (ESI) calcd for $C_{17}H_{23}N_4O_4$[M + H]$^+$ 347.1719, found 347.1716.

Ethyl 2-(4-butyl-1-(3-cyanopropyl)-1*H*-1,2,3-triazol-5-yl)acetate (5i)

The compound **5i** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 1:1 to 0:1). **5i** was obtained as a light-yellow oil (36.7 mg, 66% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.35 (t, *J* = 6.4 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.65 (s, 2H), 2.61 (t, *J* = 7.5 Hz, 2H), 2.47 (t, *J* = 6.9 Hz, 2H), 2.38–2.32 (m, 2H), 1.67–1.59 (m, 2H), 1.38–1.31 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.34, 146.70, 126.46, 118.70, 62.06, 46.25, 31.59, 28.80, 25.39, 24.76, 22.41, 14.82, 14.17, 13.89; HRMS (ESI) calcd for $C_{14}H_{23}N_4O_2$[M + H]$^+$ 279.1821, found 279.1824.

Diethyl 2,2'-(4-butyl-1*H*-1,2,3-triazole-1,5-diyl)diacetate (5j)

The compound **5j** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 5: 1 to 1:1). **5j** was obtained as a mixture of triazole, light-yellow oil (45.0 mg, 76% yield of **5j**). Characteristic data for **5j**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.17 (s, 2H), 4.26–4.18 (m, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.63 (s, 2H), 2.63 (t, *J* = 7.6 Hz, 2H), 1.67–1.59 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.33, 127.10; HRMS (ESI) calcd for $C_{14}H_{24}N_3O_4$ [M + H]$^+$ 298.1767, found 298.1764.

Allyl 2-(4-butyl-5-(2-ethoxy-2-oxoethyl)-1*H*-1,2,3-triazol-1-yl)acetate (5k)

The compound **5k** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 3:1 to 1:1). **5k** was obtained as a mixture of triazole**,** yellow oil (45.2 mg, 73% yield of **5k**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.91–5.83 (m, *J* = 7.4, 5.7, 3.8 Hz, 1H), 5.33–5.25 (m, 2H), 5.23 (s, 2H), 4.65 (d, *J* = 5.4 Hz, 2H), 4.13 (q, *J* = 7.0 Hz, 2H), 3.64 (s, 2H), 2.64 (t, *J* = 7.5 Hz, 2H), 1.69–1.61 (m, 2H), 1.36–1.31 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.40, 166.49, 146.86, 131.04, 127.12, 122.03, 119.70, 119.61, 66.74, 61.95, 49.66, 31.65, 29.01, 24.81, 22.38, 14.14, 13.92; HRMS (ESI) calcd for $C_{15}H_{24}N_3O_4$ [M + H]$^+$ 310.1767, found 310.1766.

Benzyl 2-(4-butyl-5-(2-ethoxy-2-oxoethyl)-1*H*-1,2,3-triazol-1-yl)acetate (5l)

The compound **5l** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 1:1). **5l** was obtained as a mixture triazole, yellow oil (50.8 mg, 71% yield of **5l**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.33 (m, 3H), 7.32–7.29 (m, 2H), 5.24 (s, 2H), 5.19 (s, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.61 (s, 2H), 2.64 (t, *J* = 7.6 Hz, 2H), 1.68–1.61 (m, 2H), 1.38–1.32 (m, *J* = 14.8, 6.8 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.35, 166.62, 146.83, 134.70, 128.79, 128.50, 127.12, 122.04, 67.92, 61.90, 50.82, 49.70, 31.64, 28.95, 24.78, 22.35, 13.91; HRMS (ESI) calcd for $C_{19}H_{26}N_3O_4$ [M + H]$^+$ 360.1923, found 360.1917.

Ethyl 2-(4-butyl-1-(2-oxo-2-phenylethyl)-1*H*-1,2,3-triazol-5-yl)acetate (5m)

The compound **5m** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 1:1). **5m** was obtained as a light-yellow oil (44.1 mg, 67% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.66 (t, *J* = 7.3 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 5.94 (s, 2H), 4.11 (q, *J* = 7.6 Hz, 2H), 3.61 (s, 2H), 2.68 (t, *J* = 7.6 Hz, 2H), 1.74–1.65 (m, 2H), 1.43–1.33 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H), 0.93 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.06, 168.74, 146.87, 134.63, 134.22, 129.25, 128.33, 127.67, 61.90, 54.72, 31.73, 29.19, 24.90, 22.46, 14.13, 13.98; HRMS (ESI) calcd for $C_{18}H_{24}N_3O_3$[M + H]$^+$ 330.1818, found 330.1817.

Benzyl 2-(1-benzyl-4-butyl-1*H*-1,2,3-triazol-5-yl)acetate (6a)

The compound **6a** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 2:1). **6a** was obtained as a light-yellow oil (45.0 mg, 62% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.34 (m, 3H), 7.30–7.28 (m, 3H), 7.27–7.24 (m, 2H), 7.11–7.05 (m, 2H), 5.52 (s, 2H), 5.02 (s, 2H), 3.47 (s, 2H), 2.59 (t, *J* = 7.5 Hz, 2H), 1.65–1.57 (m, 2H), 1.35–1.26 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.10, 147.43, 135.14, 134.78, 129.10, 128.81, 128.53, 128.48, 127.42, 126.05, 67.49, 52.53, 31.66, 28.93, 24.86, 22.50, 13.93; HRMS (ESI) calcd for $C_{22}H_{26}N_3O_2$ [M + H]$^+$ 364.2025, found 364.2019.

Hexyl 2-(1-benzyl-4-butyl-1*H*-1,2,3-triazol-5-yl)acetate (6b)

The compound **6b** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 3:1). **6b** was obtained as a light-yellow oil (42.5 mg, 60% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.28 (m, 3H), 7.14 (d, *J* = 7.0 Hz, 2H), 5.56 (s, 2H), 3.97 (t, *J* = 6.7 Hz, 2H), 3.44 (s, 2H), 2.61 (t, *J* = 7.6 Hz, 2H), 1.69–1.59 (m, 2H), 1.57–1.49 (m, 2H), 1.35–1.24 (m, 8H), 0.93–0.89 (m, 3H), 0.89–0.86 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.36, 147.30, 134.91, 129.09, 128.45, 127.40, 126.25, 65.93, 52.45, 31.69, 31.44, 30.75, 28.95, 28.47, 25.56, 24.88, 22.61, 22.52, 14.08, 13.95; HRMS (ESI) calcd for $C_{21}H_{32}N_3O_2$ [M + H]$^+$ 358.2495, found 358.2485.

(1*R*,3*S*,5*r*,7*r*)-Adamantan-2-yl 2-(1-benzyl-4-butyl-1*H*-1,2,3-triazol-5-yl)acetate (6c)

The compound **6c** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 3:1). **6c** was obtained as a light-yellow oil (45.0 mg, 55% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.28 (m, 3H), 7.15 (d, *J* = 6.8 Hz, 2H), 5.58 (s, 2H), 4.86 (s, 1H), 3.47 (s, 2H), 2.63 (t, *J* = 7.6 Hz, 2H), 1.90–1.87 (m, 2H), 1.85–1.80 (m, *J* = 7.9 Hz, 4H), 1.80–1.72 (m, 6H), 1.68–1.62 (m, 2H), 1.54–1.48 (m, 2H), 1.38–1.32 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.71, 147.22, 134.91, 129.11, 128.46, 127.41, 126.48, 78.89, 52.44, 37.29, 36.33, 31.85, 31.78, 29.39, 27.11, 26.93, 24.93, 13.94; HRMS (ESI) calcd for $C_{25}H_{34}N_3O_2$ [M + H]$^+$ 408.2651, found 408.2641.

Allyl 2-(1-benzyl-4-butyl-1*H*-1,2,3-triazol-5-yl)acetate (6d)

The compound **6d** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 3:1). **6d** was obtained as a light-yellow oil (45.1 mg, 73% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.29 (m, *J* = 7.2 Hz, 3H), 7.14 (d, *J* = 6.1 Hz, 2H), 5.85–5.76 (m, 1H), 5.57 (s, 2H), 5.25 (d, *J* = 6.0 Hz, 1H), 5.23 (s, 1H), 4.47 (d, *J* = 5.4 Hz, 2H), 3.47 (s, 2H), 2.62 (t, *J* = 7.6 Hz, 2H), 1.70–1.62 (m, 2H), 1.39–1.30 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz,

$CDCl_3$) δ 167.96, 147.45, 134.87, 131.40, 129.27, 129.13, 128.50, 127.44, 126.07, 119.33, 66.32, 52.53, 31.69, 28.88, 24.90, 22.53, 13.97; HRMS (ESI) calcd for $C_{18}H_{24}N_3O_2$ $[M + H]^+$ 314.1868, found 314.1864.

1-Benzyl-5-butyl-1,4,5,7-tetrahydro-6*H*-[1,2,3]triazolo[4,5-*c*]pyridin-6-one (8a)

The compound **8a** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 1:1). **8a** was obtained as a light-yellow oil (43.2 mg, 76% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 (m, 3H), 7.22 (m, 2H), 5.46 (s, 2H), 4.57 (t, *J* = 2.7 Hz, 2H), 3.47 (m, 2H), 3.37 (t, *J* = 2.6 Hz, 2H), 1.57 (m, 2H), 1.33 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.9, 137.3, 133.7, 129.2, 128.9, 127.8, 110.2, 52.6, 48.0, 45.4, 28.9, 28.3, 20.1, 13.8; HRMS (ESI) calcd for $C_{16}H_{21}N_4O$ $[M + H]^+$ 285.1710, found 285.1711.

5-Butyl-1-octyl-1,4,5,7-tetrahydro-6*H*-[1,2,3]triazolo[4,5-*c*]pyridin-6-one (8b)

The compound **8b** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 1:1). **8b** was obtained as a light-yellow oil (44.1 mg, 72% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 4.60 (s, 2H), 4.22 (t, *J* = 7.1 Hz, 2H), 3.61 (s, 2H), 3.53 (m, 2H), 1.86 (m, 2H), 1.61 (m, 2H), 1.31 (m, 12H), 0.94 (t, *J* = 7.3 Hz, 3H), 0.86 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.0, 136.6, 127.5, 48.4, 48.0, 45.4, 31.6, 29.8, 29.0, 28.9, 28.3, 26.5, 22.5, 20.1, 14.0, 13.8; HRMS (ESI) calcd for $C_{17}H_{31}N_4O$ $[M + H]^+$ 307.2492, found 307.2501.

Ethyl 2-(5-butyl-6-oxo-4,5,6,7-tetrahydro-1*H*-[1,2,3]triazolo[4,5-*c*]pyridin-1-yl)acetate (8c)

The compound **8c** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 1:1). **8c** was obtained as a light-yellow oil (40.1 mg, 73% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 5.06 (s, 2H), 4.61 (s, 2H), 4.26 (q, *J* = 7.0 Hz, 2H), 3.59 (s, 2H), 3.52 (m, 2H), 1.61 (m, 2H), 1.36 (td, *J* = 14.9, 7.4 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 163.8, 137.2, 129.1, 62.6, 49.1, 48.0, 45.3, 28.9, 28.1, 20.1, 14.1, 13.8; HRMS (ESI) calcd for $C_{13}H_{21}N_4O_3$ $[M + H]^+$ 281.1608, found 281.1609.

5-Allyl-1-benzyl-1,4,5,7-tetrahydro-6*H*-[1,2,3]triazolo[4,5-*c*]pyridin-6-one (8d)

The compound **8d** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 1:1). **8d** was obtained as a light-yellow oil (41.9 mg, 78% yield). ^1H NMR (500 MHz, $CDCl_3$) d 7.35 (m, 3H), 7.22 (m, 2H), 5.77 (tdd, *J* = 16.6, 10.8, 6.1 Hz, 1H), 5.48 (s, 2H), 5.22 (m, 2H), 4.55 (t, *J* = 2.8 Hz, 2H), 4.12 (d, *J* = 6.1 Hz, 2H), 3.40 (t, *J* = 2.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.9, 137.3, 133.6, 131.6, 129.3, 128.9, 127.8, 127.7, 118.6, 52.6, 50.3, 44.8, 28.3; HRMS (ESI) calcd for $C_{15}H_{17}N_4O$ $[M + H]^+$ 269.1397, found 269.1400.

5-Allyl-1-octyl-1,4,5,7-tetrahydro-6*H*-[1,2,3]triazolo[4,5-*c*]pyridin-6-one (8e)

The compound **8e** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 1:1). **8e** was obtained as a light-yellow oil (42.9 mg, 74% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 5.85–5.73 (m, 1H), 5.23 (m, 2H), 4.56 (s, 2H), 4.22 (t, *J* = 7.1 Hz, 2H), 4.15 (d, *J* = 6.0 Hz, 2H), 3.63 (s, 2H), 1.85 (m, 2H), 1.26 (m, 10H), 0.85 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.0, 136.6, 131.6, 127.3, 118.6, 50.3, 48.4, 44.9, 31.7, 29.8, 29.0, 28.9, 28.3, 26.5, 22.5, 14.0; HRMS (ESI) calcd for $C_{16}H_{27}N_4O$ $[M + H]^+$ 291.2179, found 291.2188.

1-Benzyl-5-(4-methoxybenzyl)-1,4,5,7-tetrahydro-6*H*-[1,2,3]triazolo[4,5-*c*]pyridin-6-one (8f)

The compound **8f** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 1:1). **8f** was obtained as a light-yellow oil (53.6 mg, 77% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 7.35 (m, 3H), 7.23 (m, 4H), 6.84 (d, *J* = 7.3 Hz, 2H), 5.46 (s, 2H), 4.64 (s, 2H), 4.49 (s, 2H), 3.77 (s, 3H), 3.43 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.1, 159.3, 137.2, 133.6, 130.1, 129.8, 129.2, 129.1, 129.1, 128.9, 128.9, 128.1, 128.0, 127.8, 127.6, 114.1, 55.3, 52.6, 50.5, 44.6, 28.4; HRMS (ESI) calcd for $C_{20}H_{21}N_4O_2$ $[M + H]^+$ 349.1659, found 349.1662.

5-(4-Methoxybenzyl)-1-octyl-1,4,5,7-tetrahydro-6*H*-[1,2,3]triazolo[4,5-*c*]pyridin-6-one (8g)

The compound **8g** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 1:1). **8g** was obtained as a light-yellow oil (57.8 mg, 78% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 4.69 (s, 2H), 4.51 (s, 2H), 4.22 (t, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 3.67 (s, 2H), 1.85 (m, 2H), 1.33–1.21 (m, 10H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.2, 159.3, 136.6, 129.9, 128.1, 127.2, 114.1, 55.3, 50.5, 48.4, 44.7, 31.7, 29.8, 29.0, 28.9, 28.4, 26.5, 22.6, 14.0; HRMS (ESI) calcd for $C_{21}H_{31}N_4O_2$ $[M + H]^+$ 371.2442, found 371.2444.

5-(4-Methoxybenzyl)-1-((trimethylsilyl)methyl)-1,4,5,7-tetrahydro-6H-[1,2,3]triazolo[4,5-*c*]pyridin-6-one (8h)

The compound **8h** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 1:1). **8h** was obtained as a light-yellow oil (55.1 mg, 80% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 4.69 (s, 2H), 4.51 (t, *J* = 2.7 Hz, 2H), 3.79 (s, 3H), 3.62 (m, 4H), 0.17 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.5, 159.3, 136.1, 129.9, 128.2, 127.6, 114.1, 55.3, 50.5, 44.9, 39.3, 28.5, –2.0; HRMS (ESI) calcd for $C_{17}H_{25}N_4O_2Si$ $[M + H]^+$ 345.1741, found 345.1746.

Ethyl 2-(5-(4-methoxybenzyl)-6-oxo-4,5,6,7-tetrahydro-1*H*-[1,2,3]triazolo[4,5-*c*]pyridin-1-yl)acetate (8i)

The compound **8i** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 1:1). **8i** was obtained as a light-yellow oil (52.5 mg, 76% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 5.06 (s, 2H), 4.69 (s, 2H), 4.52 (s, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 3H), 3.67 (s, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 164.0, 159.3, 137.1, 129.8, 128.8, 128.1, 114.2, 62.6, 55.3, 50.5, 49.1, 44.6, 28.2, 14.1; HRMS (ESI) calcd for $C_{17}H_{21}N_4O_4$ $[M + H]^+$ 345.1557, found 345.1558.

1-Benzyl-5-(4-bromophenyl)-1,4,5,7-tetrahydro-6*H*-[1,2,3]triazolo[4,5-*c*]pyridin-6-one (8j)

The compound **8j** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 1:1). **8j** was obtained as a light-yellow oil (39.7 mg, 52% yield). ^{1}H NMR (500 MHz, $CDCl_3$) d 7.58 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 6.6 Hz, 2H), 7.27 (d, *J* = 6.6 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 5.53 (s, 2H), 4.89 (s, 2H), 3.56 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.7, 141.2, 137.2, 133.5, 132.9, 129.3, 129.1, 129.0, 128.4, 127.8, 127.6, 121.6, 52.7, 49.1, 28.8; HRMS (ESI) calcd for $C_{18}H_{16}BrN_4O$ $[M + H]^+$ 383.0502, found 383.0512.

7-Acetyl-4,4-dimethyl-1-(4-nitrobenzyl)-4,7-dihydropyrano[3,4-d][1,2,3]triazol-6(1*H*)-one (8k)

The compound **8k** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 1:1 to 1:3). **8k** was obtained as a light-yellow oil (18.6 mg, 27% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H), 5.91 (s, 1H), 4.99 (s, 2H), 2.40 (s, 3H), 2.08 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.89, 164.40, 159.49, 147.52, 144.65, 128.60, 124.05, 117.33, 48.49, 28.15, 27.66, 20.93; HRMS (ESI) calcd for $C_{16}H_{17}N_2O_5$ $[M - N_2 + H]^+$ 317.1137, found 317.1135.

***N*-((1-Benzyl-1*H*-1,2,3-triazol-4-yl)methyl)-*N*-butyl-2-diazo-3-oxobutanamide (8l')**

The compound **8l'** was prepared according to the general procedure with 30 mol % of dtbpy as additive and was purified by flash column chromatography (hexane: ethyl acetate = 2:1 to 1:1). **8l'** was obtained as a light-yellow oil (34.0 mg, 48%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.36–7.31 (m, 3H), 7.24 (d, *J* = 6.1 Hz, 2H), 5.49 (s, 2H), 4.57 (s, 2H), 3.29 (t, *J* = 7.5 Hz, 2H), 2.27 (s, 3H), 1.60–1.52 (m, 2H), 1.29–1.20 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.22, 144.14, 134.65, 129.20, 128.86, 128.08, 123.29, 54.30, 48.45, 42.42, 29.84, 27.29, 20.03, 13.75; HRMS (ESI) calcd for $C_{18}H_{23}N_6O_2$ $[M + H]^+$ 355.1882, found 355.1874.

5-Butyl-3-methyl-5,6-dihydro-4*H*-furo[3,4-*c*]pyrrol-4-one (8l'')

The compound **8l''** was prepared according to the general procedure and was purified by flash column chromatography (hexane: ethyl acetate = 2:1). **8l''** was obtained as a light-yellow oil (20.0 mg, 52%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (s, 1H), 4.21 (s, 2H), 3.45 (t, *J* = 7.3 Hz, 2H), 2.47 (s, 3H), 1.61–1.52 (m, 2H), 1.39–1.30 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.03, 148.04, 131.18, 129.79, 126.60, 125.52, 44.30, 42.51, 30.30, 20.15, 13.90, 12.83; HRMS (ESI) calcd for $C_{11}H_{16}NO_2$ $[M + H]^+$ 194.1181, found 194.1182.

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