DOI: 10.1002/adsc.202001436

Advanced Synthesis & Catalysis

Visible Light-Induced [3+2] Cyclization Reactions of Hydrazones with Hypervalent Iodine Diazo Reagents for the Synthesis of 1-Amino-1,2,3-Triazoles

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Manuscript received: November 17, 2020; Revised manuscript received: February 17, 2021;
Version of record online: Februar 25, 2021

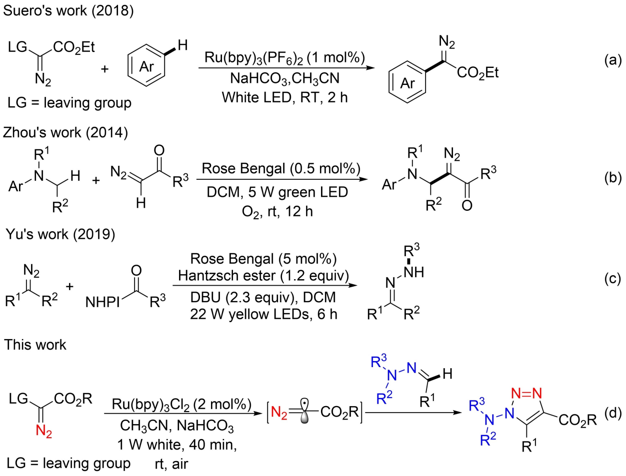
Supporting information for this article is available on the WWW under https://doi.org/10.1002/adsc.202001436

Abstract: In this study, visible-light-induced [3+2] cyclization reactions of hydrazones with hypervalent iodine diazo reagents as diazomethyl radical precursors are reported. Mild reaction conditions, a broad substrate scope, and excellent functional group compatibility were observed. Furthermore, the synthetic utility was demonstrated by gram-scale synthesis and elaboration to several value-added products. This protocol broadens the scope of diazo chemistry, and is applicable to the late-stage functionalization of natural products.

Keywords: [3+2] Cyclization reactions; Hydrazones; Hypervalent iodine diazo reagents; Diazomethyl radical; Visible-light photoredox catalysis

Introduction

Owing to their high and versatile reactivity, diazo compounds are highly valuable building blocks in organic synthesis.[1] For example, diazo compounds have wide-ranging applications as metal carbene precursors,[2] 1,3-dipoles,[3] C nucleophiles,[4] and terminal N electrophiles.[5] In contrast, the utility of the diazo compounds as diazomethyl radical precursors have rarely been studied. Recently, Suero and co-workers have utilized hypervalent iodine(III) reagents[6] by photoredox catalysis to generate diazomethyl radicals (Scheme 1a), which provided an efficient way to site-selective aromatic diazomethylation in aromatic feedstocks and drug molecules. The diazomethyl radical can act as carbyne equivalent to construct a chiral carbon center via an assembly point functionalization. Inspired by these results, and as part of our ongoing research on hydrazones[7] and diazo compounds,[5b–d,8] we proposed that 1-amino-1,2,3-triazoles could be constructed by reacting hydrazones with hypervalent iodine diazo reagents using an aminyl radical-polar crossover strategy.[9]



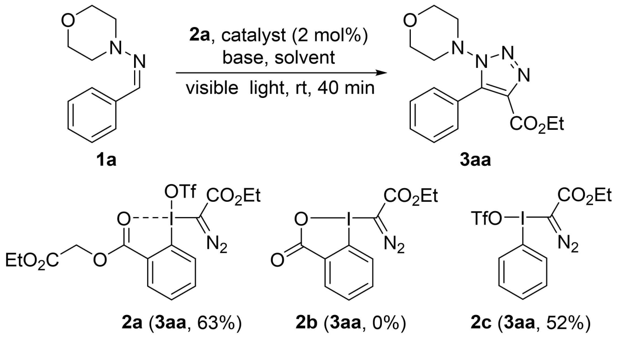
Scheme 1. Representative reactions of the retention of the dinitrogen functionality under light irradiation conditions.

The 1,2,3-triazoles skeleton has been recognised as one of the most privileged structural motifs present in functional materials, ligands, agrochemicals and pharmaceuticals.[10] Among them, 1-amino-1,2,3-triazoles are known to have interesting biological activities and used as α7 nicotinic acetylcholine receptor agonists or dual inhibitors of carbonic anhydrases I/

II.[11] Despite the considerable advances in the [3+2] cycloaddition reaction of either diazo compounds or azides with unsaturated molecules for the synthesis of triazoles, there are just few methodologies to synthesize 1-amino-1,2,3-triazoles.[11] Therefore, the development of general, mild, and efficient synthetic strategies for the 1-amino-1,2,3-triazoles moiety is highly desirable. Until recently, Alcarazo and co-workers have reported the reaction between the α-diazo sulfonium triflates and *N,N*-dialkyl hydrazones to afford 1-(dialkylamino)-1,2,3-triazoles under photoredox catalysis, which further elaborated into mesoionic carbene ligands.[12]

Visible-light-induced photoredox-catalyzed radical cross-coupling reactions are well-established powerful strategies in modern organic synthesis.[13] Recently, with the growth of modern photochemistry, photocatalyzed reactions of diazo compounds have attracted considerable attention. In general, diazo compounds can act as radical acceptors,[14a] carbene[14b–g] and radical precursors,[7a,14h] and nucleophiles[15a] in photocatalytic systems to develop new and valuable chemical transformations. In such transformations, diazo compounds often require N_2 extrusion as a driving force under light irradiation conditions,[16] with few reported examples showing retention of the diazo functionality.[7,15] For example, Zhou and coworkers reported a photocatalytic cross-dehydrogenative coupling reaction of tertiary amines and diazo compounds, affording various β-amino-α-diazocarbonyl compounds (Scheme 1b).[15a] Furthermore, the Yu group developed a visible-light-induced decarboxylative radical cross-coupling of alkyl *N*-hydroxyphthalimide ester with diazoacetates for the synthesis of *N*-alkyl hydrazones (Scheme 1c).[15b] To increase the efficiency of diazo functionality utilization, developing practical methods with high generality for retention of the dinitrogen functionality under visible-light catalysis remains appealing and challenging. Thus, we report the first visible-light-induced [3+2] cyclization reactions of hydrazones with hypervalent iodine diazo reagents as diazomethyl radical precursors to afford 1-amino-1,2,3-triazoles under mild conditions (Scheme 1d).

Table 1. Optimization of reaction conditions.[a,b]



Entry	Catalyst (2 mol%)	Visible light	Yield (%)
1	$[Ru(bpy)_3]Cl_2$	1 W Blue	51
2	$[Ru(bpy)_3]Cl_2$	1 W White	56
3	$[Ru(bpy)_3]Cl_2$	1 W Green	52
4	$[Ru(bpy)_3]Cl_2$	2 W White	46
5	$[Ru(bpy)_3](PF_6)_2$	1 W White	51
6	$Ru(bpy)_3Cl_2{\cdot}H_2O$	1 W White	36
7	Rose Bengal	1 W White	35
8	Eosin Y	1 W White	0
9	$Ir(ppy)_3$	1 W White	11
10	4CzIPN	1 W White	0
11	Mes-Acr$^+$	1 W White	23
12	No	1 W White	0
13	$[Ru(bpy)_3]Cl_2$	No light	0
14[c]	$[Ru(bpy)_3]Cl_2$	1 W White	63
15[d]	$[Ru(bpy)_3]Cl_2$	1 W White	57
16[e]	$[Ru(bpy)_3]Cl_2$	1 W White	38

[a] Reactions were conducted using **1a** (0.2 mmol), **2a** (0.3 mmol), catalyst (2 mol%), and $NaHCO_3$ (0.3 mmol) in CH_3CN (2 mL) at room temperature for 40 min under N_2 atmosphere.

[b] Isolated yield.

[c] Under air.

[d] $Ru(bpy)_3Cl_2$ (1 mol%).

[e] Under O_2. Mes-Acr$^+$ = 9-mesityl-10-methylacridinium perchlorate. 4CzIPN = 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene.

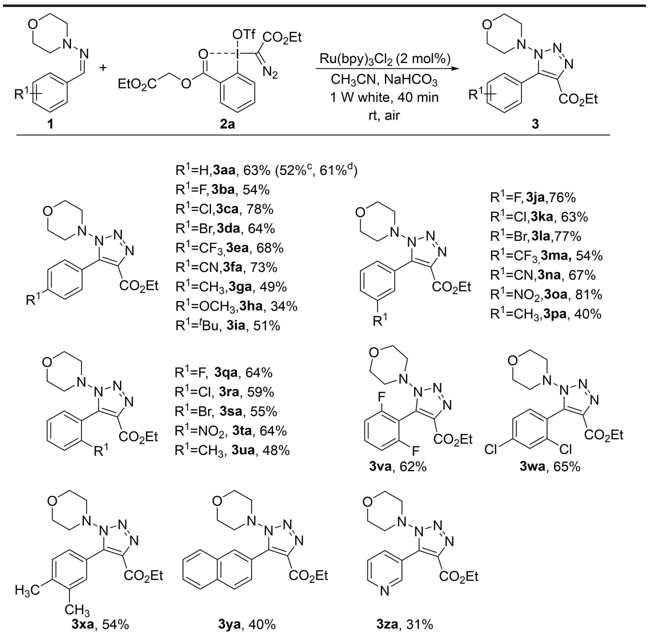
Results and Discussion

Initial investigations were conducted using *N*-morpholino-1-phenylmethanimine (**1a**) and hypervalent iodine diazo reagent **2a** as model substrates under blue LED irradiation (1 W) for 40 min. In the presence of $NaHCO_3$ as base, the reaction catalyzed by $Ru(bpy)_3Cl_2$ (2 mol%) proceeded in acetonitrile at room temperature, and desired 1-amino-1,2,3-triazole **3aa** was obtained in 51% yield (Table 1, entry 1). By changing the light source from blue to white (1 W) LED, the yield of **3aa** increased to 56% (entry 2). Irradiating the reaction by green (1 W) LED resulted in a slightly lower yield (entry 3). When the reaction was performed with white (2 W) LEDs, it was less effective (entry 4). The screening of organometallic photocatalysts, such as $Ru(bpy)_3Cl_2{\cdot}H_2O$, $Ru(bpy)_3(PF_6)_2$, and $Ir(ppy)_3$, and other nonmetallic photocatalysts, such as rose bengal, eosin Y, 4CzIPN, and Mes–Acr$^+$ (entries 6–11), found that $Ru(bpy)_3Cl_2$ exhibited the best catalytic activity regarding the overall reaction outcome (entry 2). The solvent effect was also screened, with common solvents, such as DMF, DCE, THF, DMA, DMSO, and 1,4-dioxane, giving disappointing results (Table S1, entries 1–7). Various bases were also tested, with Na_2CO_3 (54%), NaOH (45%), and AcONa (45%) found to be less effective than $NaHCO_3$, while ^{t}BuOK, $KHCO_3$, K_2CO_3, Na_2HPO_4, and DBU did not afford the target product (Table S1, entries 8–16).

Furthermore, increasing or decreasing base and solvent loadings did not improve the results (Table S1, entries 17–20). Control experiments, conducted by performing the reaction in the dark or in the absence of photocatalyst, failed to provide the desired product, further suggesting that the reaction was photocatalyzed (entries 12 and 13). When the reaction was performed under air, the yield of **3 aa** was improved to 63% (entry 14). Decreasing the $Ru(bpy)_3Cl_2$ loading resulted in a slightly lower yield (entry 15). When the reaction proceeded in O_2, under the optimal conditions, a significant decrease in yield (38%) was observed (entry 16), suggesting that the incremental of the yield is not related with the presence of O_2. Finally, no or poor conversion was observed when **2 a** was replaced by other hypervalent iodine diazo reagents such as **2 b** and **2 c**.

With optimal reaction conditions established, the scope and generality of *N*,*N*-dialkylhydrazones in the [3+2] cyclization reaction were explored (Table 2). Pleasingly, when the reaction was irradiated with sunlight instead of a white LED (1 W), target product **3 aa** was also obtained in 61% yield. Furthermore, various aldehyde hydrazones reacted with **2 a** under the optimized conditions to furnish the corresponding1-amino-1,2,3-triazoles (**3 aa**–**3 za**) in good yields. For example, various *para*-substituted aryl aldehyde hydrazones with halo, trifluoromethyl, and cyano substituents were smoothly converted into corresponding products **3 ba**–**3 fa** in 54%–78% yields. The molecular structure of **3 ca** was unambiguously confirmed using X-ray crystallography (CCDC 2033586).[17] Substrates bearing electron-donating groups (such as methyl, *tert*-butyl, and methoxyl groups) on the aromatic ring were all suitable for photoredox catalysis, affording slightly lower yields (**3 ga**–**3 ia**). From the point of view of the reaction mechanism, hydrazones bearing electron-donating groups at the phenyl ring may decrease the acidity of α-H, which may not facilitate radical addition or deprotonation. *Ortho*- and *meta*-substituted aryl aldehyde hydrazones were also compatible with the reaction conditions, forming target products **3 ka**–**3 ua** in good yields. For disubstituted substrates, the reactions afforded products **3 va**–**3 ya** in 40%–65% yields. In addition to arene aldehydes, a heterocyclic aldehyde was shown to be compatible, affording corresponding product **3 za** in 31% yield. To demonstrate the synthetic applicability of this catalytic system, **3 aa** was synthesized on a 6-mmol scale, affording a 52% isolated yield.

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



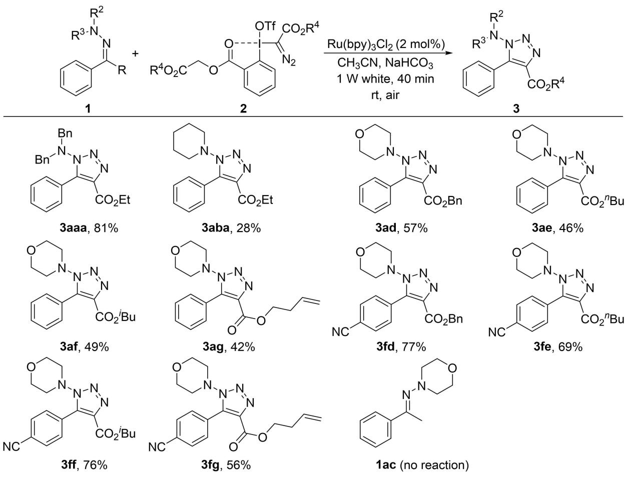
[a] Reactions were conducted using **1** (0.2 mmol), **2a** (0.3 mmol), $Ru(bpy)_3Cl_2$ (2 mol%), and $NaHCO_3$ (0.3 mmol) in CH_3CN (2 mL) at room temperature for 40 min under air.

[b] Isolated yield.

[c] Reaction performed with 6 mmol of **1a**. [d] Under sunlight irradiation.

We next explored the scope of hydrazones and hypervalent iodine diazo reagents under the optimized reaction conditions (Table 3). The results showed that hydrazones **1 aa** and **1 ab** also reacted with **2 a** to produce desired products **3 aaa** and **3 aba**. Notably, diverse substituents, such as benzyl, *n*-butyl, *i*-butyl, and but-3-en-1-yl, were all tolerated by this catalytic system, leading to corresponding products **3 ad**–**3 ag** in acceptable yields. Furthermore, various hypervalent iodine diazo reagents reacted with *para*-cyano-substi-

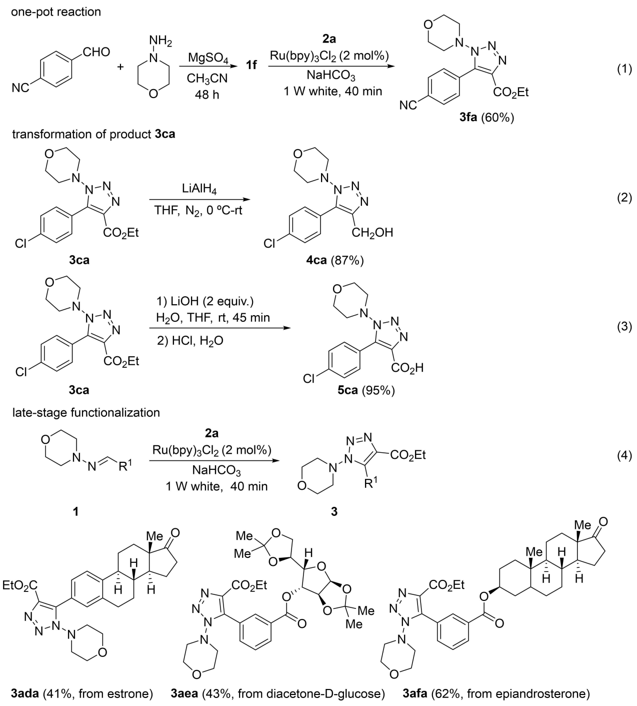
Table 3. Scope of hydrazones and hypervalent iodine diazo reagents.[a,b]



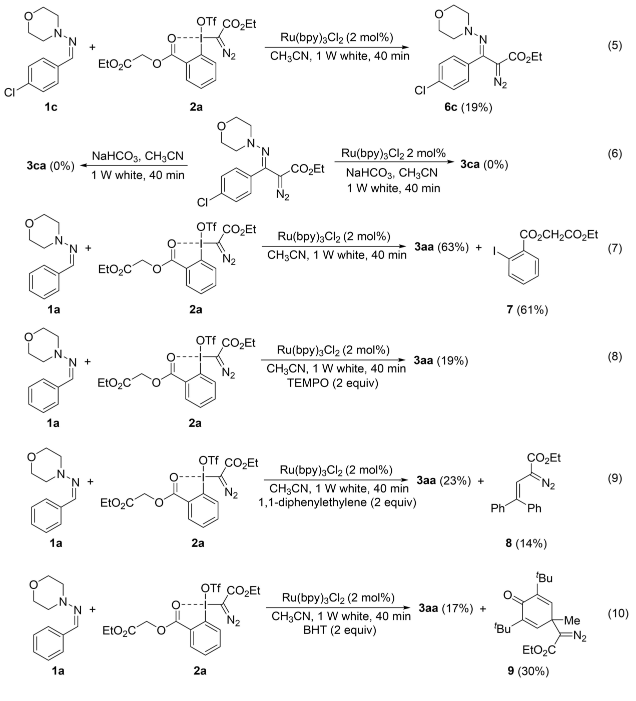
[a] Reactions were conducted using **1** (0.2 mmol), **2** (0.3 mmol), $Ru(bpy)_3Cl_2$ (2 mol%), and $NaHCO_3$ (0.3 mmol) in CH_3CN (2 mL) at room temperature for 40 min under air.

[b] Isolated yield.

tuted aryl aldehyde hydrazones with a highly reactive profile, affording the target products in 56%–77% yields (**3 fd–3 fg**). As for ketone-derived hydrazone **1 ac**, the reaction did not take place under the standard conditions.



Scheme 2. Demonstration of synthetic utility.



Scheme 3. Mechanistic investigations.

To further demonstrate the synthetic utility of this protocol and the target products, we conducted a one-pot reaction of 4-cyanobenzaldehyde and morpholin-4-amine in CH_3CN for 48 h, which led to in situ generation of aldehyde hydrazone **1 f** in the presence of $MgSO_4$. Subsequent addition of $Ru(bpy)_3Cl_2$, **2 a**, and $NaHCO_3$ allowed the reaction to proceed smoothly under the optimized conditions, with product **3 fa** isolated in 60% yield (Scheme 2, eq 1). Furthermore, product **3 ca** was readily reduced to alcohol **4 ca** by $LiAlH_4$ in THF under mild conditions (Scheme 2, eq 2). The hydrolysis of **3 ca** provided convenient access to corresponding acid **5 ca** in excellent yield by simple treatment with aqueous LiOH and acid (Scheme 2, eq 3). Notably, this methodology can be utilized for the late-stage functionalization of natural product derivatives. For example, aldehyde hydrazones of estrone, diacetone-*D*-glucose, and epiandrosterone (**1 ad**, **1 ae**, and **1 af**) were synthesized and applied to this transformation under the optimized reaction conditions. Desired 1-amino-1,2,3-triazoles **3 ada**, **3 aea**, and **3 afa** were obtained in 41%, 43%, and 62% yield, respectively (Scheme 2, eq 4).

To gain insight into the reaction mechanism, various control experiments were performed (Scheme 3, eqs. 5–10). As reported by Alcarazo's group, the reaction mechanism suggests that α-diazo hydrazone ultimately tautomerize to the corresponding 1,2,3-triazole.[12] First, we investigated whether the α-diazo hydrazone was a key intermediate in this visible-light-induced [3 + 2] cyclization reaction.[18] Therefore, aldehyde hydrazone **1 c** was reacted with diazo compound **2 a** in the absence of base under the optimized conditions, with α-diazo hydrazone **6 c** isolated in 19% yield (Scheme 3, eq 5). Furthermore, when α-diazo hydrazone **6 c** was used as a starting material under the standard visible-light-induced [3 + 2] cyclization reaction conditions or in the presence of base, desired product **3 ca** was not obtained (Scheme 3, eq 6). These results indicated that the aminyl radical-polar mechanism was critical for visible-light-induced photoredox catalysis of a single-electron transfer (SET) process. Furthermore, *o*-iodobenzoate **7** was isolated in 61% yield under the standard reaction conditions (Scheme 3, eq 7). When a stoichiometric amount of radical scavengers 2,2,6,6-tetramethyl-1-piperidinoxyl (TEMPO), 1,1-diphenylethylene, or 2,6-di-*tert*-butyl-4-methylphenol (BHT) was added under the optimized conditions, the reaction gave dramatically lower yields (Scheme 3, eqs. 8–10). Corresponding radical trapping adducts **8** and **9** were also isolated in 14% and 30% yields, respectively. The molecular structure of **9** was unambiguously confirmed using X-ray crystallography (CCDC 2055775).[17] Stern-Volmer fluorescence quenching experiments indicated that **2 a** efficiently quenched the $*[Ru(bpy)_3]^{2+}$ excited state (Figure 1).

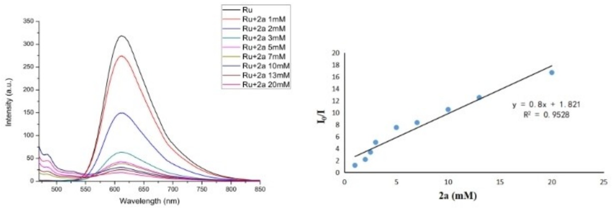
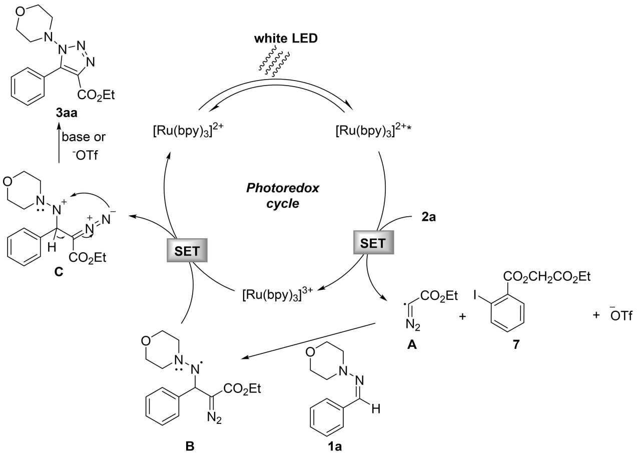


Figure 1. Stern-Volmer experiments on reagent **2 a**.

Based on the above results and literature reports,[7,10] a reaction mechanism was proposed, as shown in Scheme 4. Initially, photoredox catalyst $[Ru(bpy)_3]^{2+}$ is photoexcited to the $*[Ru(bpy)_3]^{2+}$ excited state ($E_{1/2}(Ru^{III}/*Ru^{II}) = -0.81$ V vs. SCE in CH_3CN).[13] Single-electron reduction of reagent **2 a** (reduction potential, $E_{red} = 0.95$ V vs. SCE in CH_3CN) gives diazomethyl radical **A**[7] and strong oxidant $[Ru(bpy)_3]^{3+}$. The SET process was confirmed by fluorescence-quenching experiments (Figure 1). Diazomethyl radical **A** then directly attacks the C=N bond to deliver aminyl radical intermediate **B**, which undergoes single-electron oxidation by $[Ru(bpy)_3]^{3+}$ to form amino-cation intermediate **C** and regenerates $[Ru(bpy)_3]^{2+}$, completing the catalytic cycle. Finally, intramolecular cyclization affords the corresponding 1-amino-1,2,3-triazoles in the presence of base.

Conclusion

The synthesis of 1-amino-1,2,3-triazoles using hypervalent iodine diazo reagents as diazomethyl radical precursors under photoredox catalysis has been reported for the first time. This [3+2] cyclization reaction is distinguished by mild reaction conditions, a broad substrate scope, and excellent functional-group compatibility. Furthermore, the 1-amino-1,2,3-triazoles products underwent further transformations, demonstrating that this method is applicable to the late-stage functionalization of natural products. Preliminary mechanistic studies were conducted and a plausible catalytic cycle was proposed.



Scheme 4. Plausible reaction mechanism.

Experimental Section

General Information

Experimental All chemicals were obtained from commercial sources and were used as received unless otherwise noted. ^1H, ^{13}C and ^{19}F NMR spectra were recorded using $CDCl_3$ or DMSO as a solvent on a 400 MHz spectrometer at 298 K. The chemical shift is given in dimensionless δ values and is frequency referenced relative to TMS in ^1H and ^{13}C NMR spectroscopy. High-resolution mass spectra (HRMS) were obtained on an Agilent Q-TOF 6224 spectrometer. The intensity data were recorded on a Bruker D8 QUEST with Mo-Kα radiation ($\lambda = 0.71073$ Å). The crystal structure was solved by means of direct methods and refined by employing full-matrix least squares on F^2 (*SHELXTL-2014*). The photocatalytic reactions were performed on WATTCAS Parallel Light Reactor (WP-TEC-1020HSL) with 1 W LED. Column chromatography was performed on silica gel (300–400 mesh) using ethyl acetate (EA)/petroleum ether (PE).

General Procedure for the Preparation of 3 (3 aa as Example)

A solution of **1 a** (0.2 mmol), **2 a** (0.3 mmol), $Ru(bpy)_3Cl_2$ (2 mol%, 2.6 mg), and $NaHCO_3$ (0.3 mmol, 25.2 mg) in CH_3CN (2.0 mL) was stirred at room temperature with 1 W white LED for 40 min under air atmosphere. After the reaction was complete (monitored by TLC), the solvent was removed under reduced pressure. The crude residue was purified by silica gel column chromatography (EtOAc/petroleum ether = 1:5, V/V) to afford pure product **3 aa**.

Acknowledgements

We acknowledge financial support from the National Natural Science Foundation of China (21702087, and 21801105), the LiaoNing Revitalization Talents Program (XLYC1907010 and XLYC1902085), the Research Project Fund of Liaoning Provincial Department of Education (L2020033), and talent Scientific Research Fund of Liaoning Shihua University (2016XJJ-078 and 2016XJJ-079).

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