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Visible Light-Driven Azidation/Difunctionalization of Vinyl Arenes with Azidobenziodoxole under Copper Catalysis

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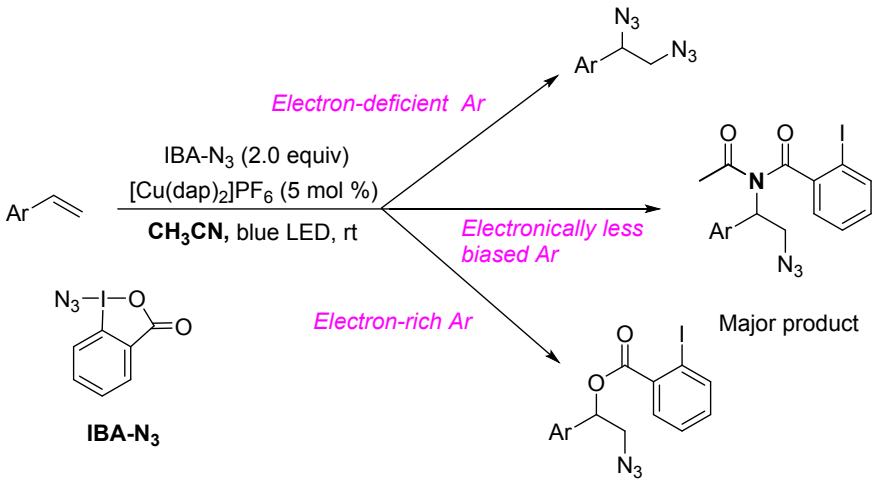
Graphic abstract



Abstract

Visible light-driven azidation of vinyl arenes with azidobenziodoxole as the azidating agent was investigated in acetonitrile by using Cu(I)(phenanthroline)$_2$ complex [Cu(dap)$_2$]PF$_6$ as photocatalyst. The reactions generated three types of difunctionalization products, which correspond to reaction patterns of amido-azidation, benzoyloxy-azidation and diazidation. Electronic nature of the aryl group attached to the olefin moiety was found to play a crucial role in determining the reaction consequence: when the aryl group was electron-rich, the reactions afforded benzoyloxy-azidation products exclusively; for highly electron-deficient vinyl arenes, by contrast, diazidation products were generated in moderate yields. When the aryl group was moderately electron-rich or electron-deficient, on the other hand, a

three-component reaction involving acetonitrile as well as azidobenziodoxole took place to give predominantly amido-azidation products. A plausible mechanism is proposed based on the mechanistic studies to rationalize these results. The reactions of electronically less biased vinyl arenes probably proceed via a redox catalysis pathway, while the electron-rich alkenes are believed to be converted through a radical chain process. The present reactions may be of synthetic usefulness as they provide a new means for the amido-azidation of vinyl arenes.

KEYWORDS: *azidation, azidobenziodoxole, acetonitrile, [Cu(dap)$_2$]PF$_6$, visible light photocatalysis, vinyl arenes*

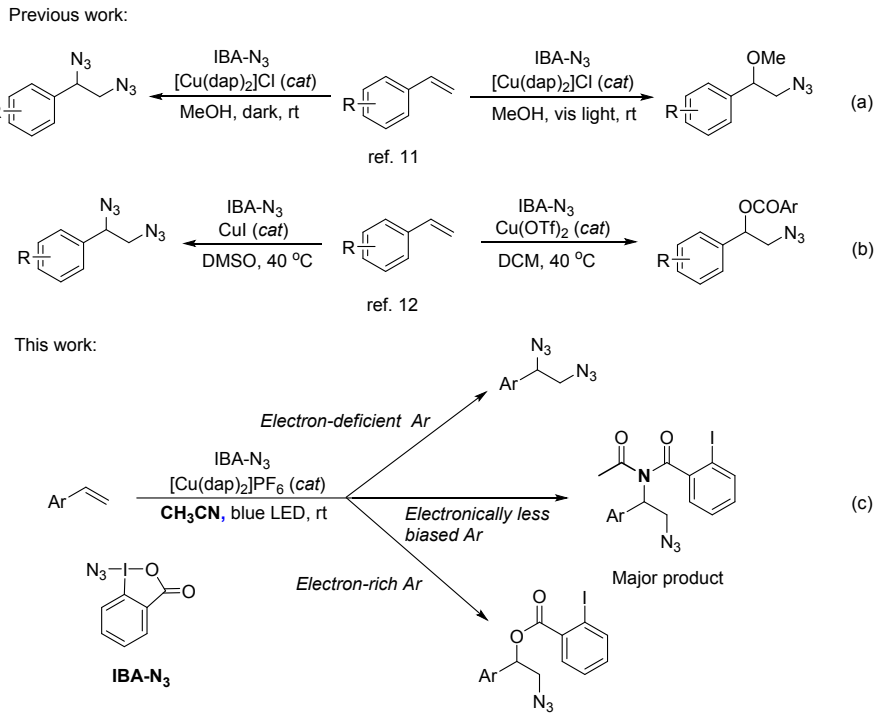
1. INTRODUCTION

Visible light photoredox catalysis has evolved to be a most versatile and powerful tool in organic synthesis during the last decades, with numerous applications being found for it by using ruthenium and iridium-based complexes,[1] or organic dyes as photoccatalyst.[2] Besides ruthenium and iridium complexes, the complexes of earth-abundant first raw transition metals are also capable of initiating radical reactions under visible light irradiation.[3,4] From the view point of practical synthesis, using cheaper earth abundant transition metal catalysts is highly preferable, but their potential usefulness in this aspect has yet to been fully explored.

Alkene azidation/difunctionalization reactions are highly effective for the preparation of densely functionalized azides, which are versatile precursors for the preparation of other nitrogen-containing compounds.[5] Much attention has been paid recently to the development of various types of difunctionalization of alkenes, such as diazidation,[6] amino-azidation,[7] carboazidation,[8] oxy-azidation[9] and sufonyl azidation.[10] In this context, some intriguing results have been reported on copper-catalyzed azidation of activated alkenes. In 2015, Greaney reported that copper complex [Cu(dap)$_2$]Cl (dap = 2,9-bis(4-anisyl)-1,10-phenanthroline) can effectively catalyze the azidation of vinyl arenes with hypervalent iodine reagent 1-azido-1,2-benziodoxole (Zhdankin reagent) as the azidating reagent (Scheme 1, (a)).[11] Notably, they found that when the reaction was performed under visible light irradiation in methanol, methoxy-azidation

products were obtained in high yield. However, when the reactions were carried out in the dark, diazidation products were generated predominantly instead. In the same year, Loh et al. reported a similar copper-catalyzed azidating protocol for the oxy-azidation and diazidation of vinyl arenes ((Scheme 1, (b)).[12] It was found that the catalyst and solvent play a key role on the reaction consequence: Under the catalysis of $Cu(OTf)_2$ in dichloromethane the reactions afforded mainly oxy-azidation products into which an ortho-iodo benzoyloxy was introduced along with the azidyl group. When CuI was used as catalyst and DMSO was used as the solvent, on the other hand, the substrates were converted to diazidation products. Very recently, Rehbein and Reiser et al. managed to convert vinyl arenes to α-azidoketones under the conditions of $[Cu(dap)_2]Cl$-mediated visible light photoredox catalysis by using $TMSN_3$ as azidating reagent and air as oxidant.[13] These studies indicate that azidations of alkenes under copper-catalysis are highly useful for the preparation of functionalized organic azides, and by adjusting the reaction conditions, different functionalities can be being introduced selectively into the products. As a further demonstration of the diversity of this methodology, herein we report that a three-component amido-azidation of vinyl arenes can be realized in acetonitrile with Zhdankin reagent as azidating agent by visible light photoredox catalysis with $[Cu(dap)_2]PF_6$ as catalyst (Scheme 1, (c)). Both acetonitrile and the *ortho*-iodo benzoyloxy group from the Zhdankin reagent can be introduced into products as the amido moiety. Interestingly, the electron nature of the alkenes was found to play a profound effect on the reaction consequence, which was not found in previous reports.[11-13]

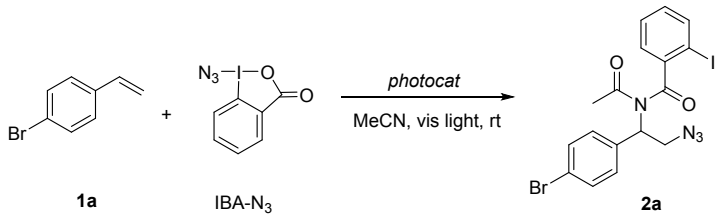
Scheme 1. Copper-Catalyzed Azidation/Difunctionalization of Vinyl Arenes with Zhdankin Reagent



2. RESULTS AND DISCUSSION

On the course of our studies on the azidations of alkenes,[14] we found that when irradiated by visible light (blue LED), *para*-bromostyrene **1a** can be converted to amido-azidation product **2a** in acetonitrile by reacting with Zhdankin reagent under the catalysis of $[Cu(dap)_2]^+$ (Table 1, entries 1 and 2). $[Cu(dap)_2]PF_6$ proved to be more efficient than $[Cu(dap)_2]Cl$ under the current circumstance. By using $[Cu(dap)_2]PF_6$ as the photocatalyst, **2a** can be obtained in 78% yield at a concentration of 0.05 M in CH_3CN with 5 mol % of catalyst loading. The reaction also took place when white LED was used as the light source, but the yield was lower (Table 1, entry 5). When the reaction was conducted in the dark, no **2a** was obtained (Table 1, entry 6); instead, diazidation product **3a** and oxo-azidation product 2-azido-1-(4-bromophenyl)ethan-1-one[13] were generated in yields of 10% and 5%, respectively (Equation 1). Control experiment indicated that the photocatalyst was necessary for complete conversion of **1a** (Table 1, entry 7). Oxygen exhibited a negative effect on the reaction (Table 1, entry 9). As such, when the reaction proceeded in the air, **2a** was generated in only 22% yield, beside which 2-azido-1-(4-bromophenyl)ethan-1-one was obtained in 19% yield.

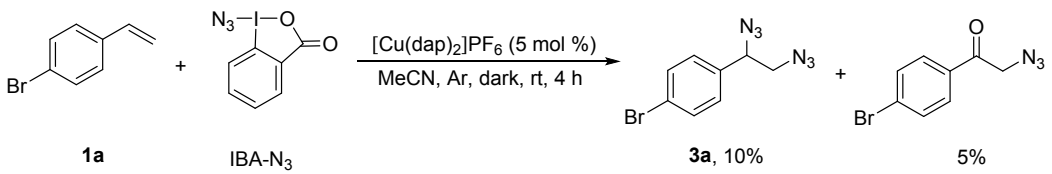
Table 1. Examination of Reaction Conditions[a]



1a IBA-N_3 **2a**

entry	*photocat* (mol %)	IBA-N_3 (equiv)	yield (%)[b]
1	$[Cu(dap)_2]Cl$ (5.0)	2.0	43
2	**$[Cu(dap)_2]PF_6$ (5.0)**	**2.0**	**78**
3	$[Cu(dap)_2]PF_6$ (2.5)	2.0	59
4	$[Cu(dap)_2]PF_6$ (5.0)	1.5	72
5	$[Cu(dap)_2]PF_6$ (5.0)	2.0	54[c]
6	$[Cu(dap)_2]PF_6$ (5.0)	2.0	0[d]
7	--	2.0	7[e]
8	$[Cu(dap)_2]PF_6$ (5.0)	2.0	72[f]
9	$[Cu(dap)_2]PF_6$ (5.0)	2.0	22[g]

[a]The reactions were performed on 0.2 mmol scale in 4.0 mL of acetonitrile (0.05 M) under argon atmosphere with blue LEDs as the light source. Irradiation time was 4 h unless otherwise specified. [b]Isolated yield. [c]With white LED as the light source. [d]Run in dark for 8 h. [e]In the absence of photocatalyst. [f]In 2.0 mL of acetonitrile (0.1 M). [g]Run in the air.



1a IBA-N_3 **3a**, 10% 5%

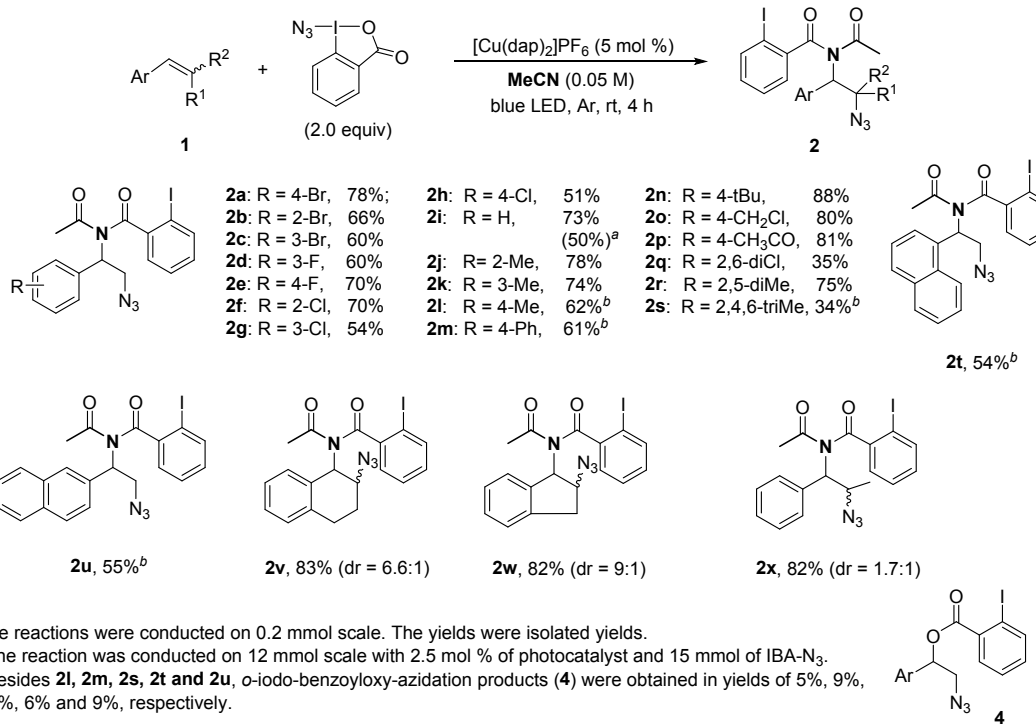
+ recovered **1a** (20%)

Equation 1. Reaction of 1a with IBA-N_3 under Dark

This result is interesting because the transformation has not been revealed in previous reports. Apparently, both the solvent and 2-iodobenzoyloxy moiety from IBA-N_3 were involved in the formation of **2a**. From the synthetic point of view, it is highly desirable to develop new protocols for the amido-azidation of alkenes as this type of reactions would be useful for the preparation of synthetically important 1,2-diamino compounds and their derivatives. In this context, the present reaction might provide a convenient approach toward this goal. To test the scope of the reaction, we applied the optimal conditions (Table 1, entry 2) to variously substituted styrenes and analogous vinyl arenes, and the results are illustrated in Schemes 2 to 5. It can be seen from

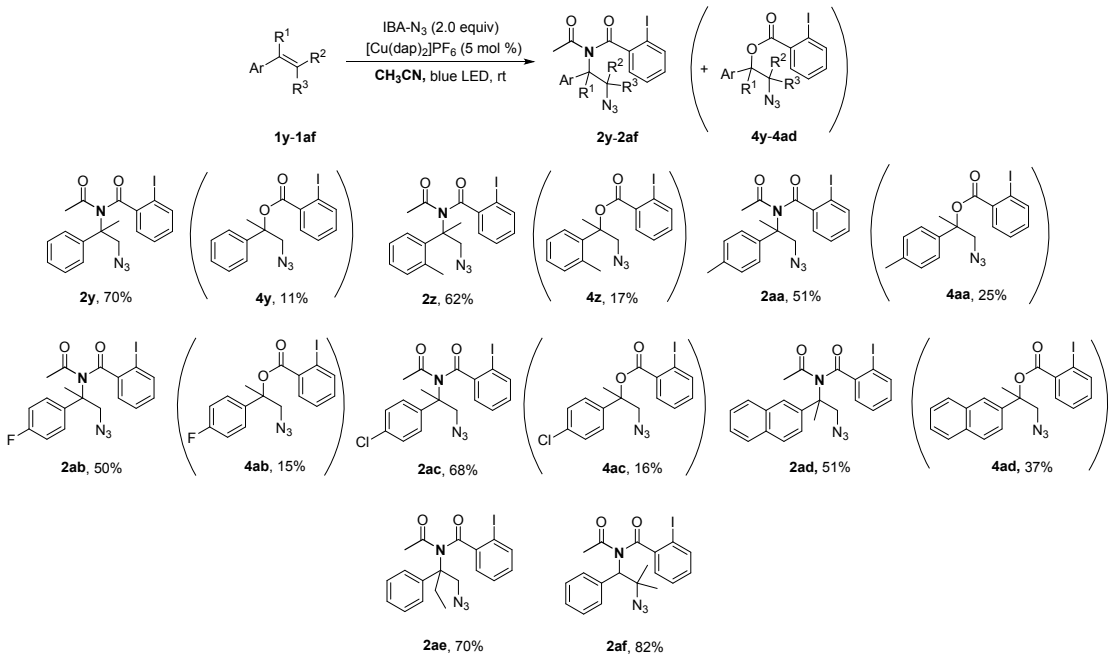
Scheme 2 that halogen-substituted, alkyl-substituted or acetyl-substituted styrenes can be transformed into the amido-azidation products in moderated to good yields. 2-Vinylnaphthalene, 1,2-dihydronaphthalene and 1*H*-indene reacted in the same way. For several tested substrates, benzoyloxy-azidation products were formed as well in varying yields. In case that the vinyl alkenes are of a 1,2-disubstituted pattern, the products were obtained as a mixture of diastereoisomers (**2v**-**2x**). The reactions of trisubstituted vinyl arenes (**2y**-**2af**) also gave mainly amido-azidation products, along with benzoyloxy-azidation products **4** (Scheme 3). The structure of **2ac** was confirmed by X-ray crystallographic analysis (CCDC No. 1878259).

Scheme 2. Scope of Amido-Azidation Reactions of Vinyl Arenes-1



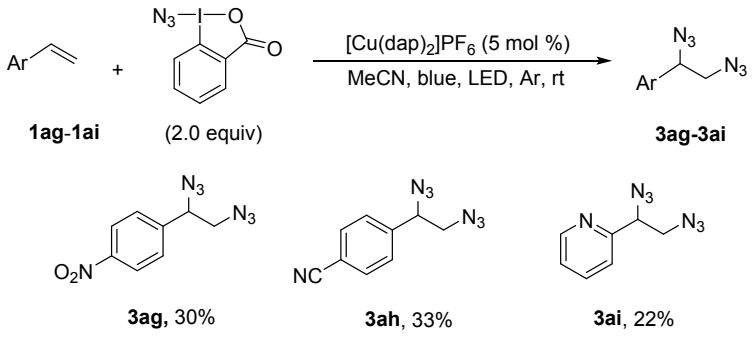
The reactions were conducted on 0.2 mmol scale. The yields were isolated yields.
[a]The reaction was conducted on 12 mmol scale with 2.5 mol % of photocatalyst and 15 mmol of IBA-N_3.
[b]Besides **2l, 2m, 2s, 2t and 2u**, *o*-iodo-benzoyloxy-azidation products (**4**) were obtained in yields of 5%, 9%, 35%, 6% and 9%, respectively.

Scheme 3. Scope of Amido-Azidation Reactions of Vinyl Arenes-2

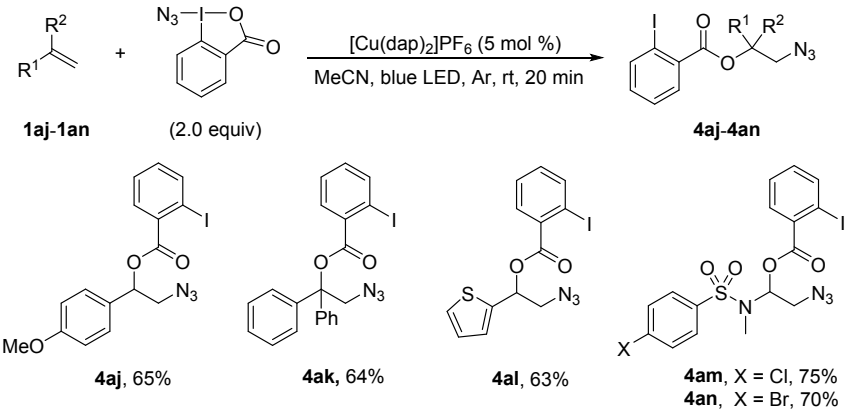


When the standard conditions were applied to 4-nitro and 4-cyano-substituted styrenes, however, no amido-azidation products were obtained. The reactions only delivered diazidation products **3ag** and **3ah** in moderate yields (Scheme 4). The same result was obtained when 2-vinylpyridine was used as the substrate. By contrast, when electron rich 4-methoxy styrene was used as the substrate, the major product became oxy-azidation product **4aj**. The reactions of α-phenyl styrene, 2-vinylthiophene and *N*-vinylbenzenesulfonamides generated the same type of products as well (Scheme 5).

Scheme 4. Reactions of Electron-Deficient Vinyl Arenes

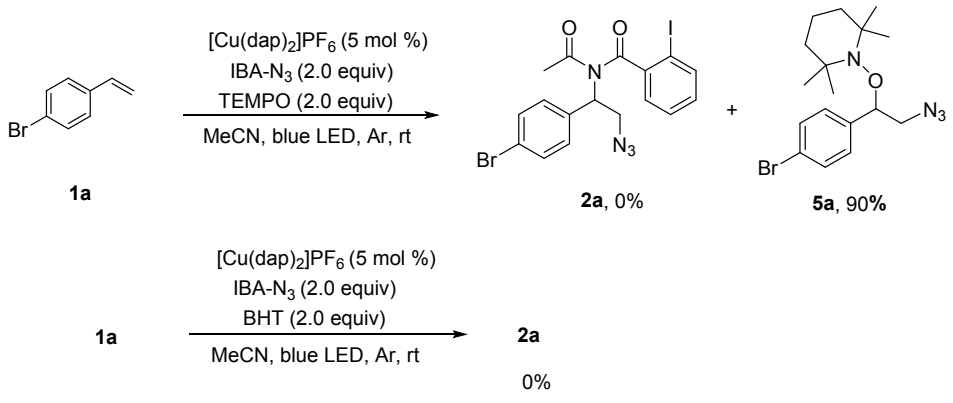


Scheme 5. Reactions of Electron-Rich Olefins

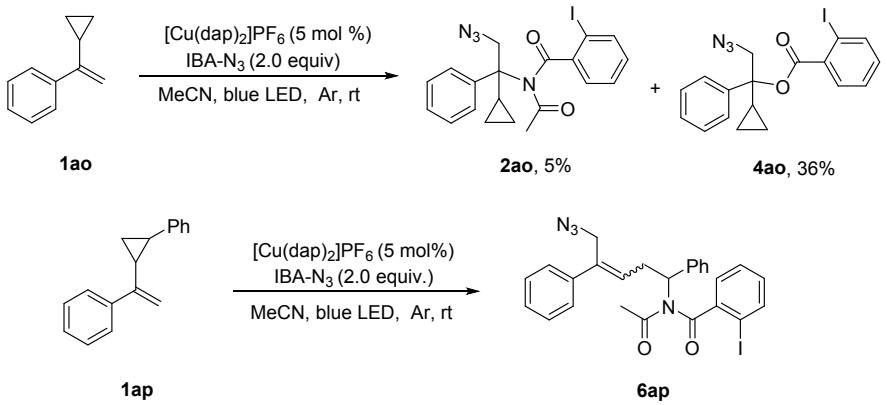


These results demonstrate that the electronic nature of the carbon-carbon double bond exerted a profound effect on the reaction consequence, which was not found in previous reports.[11,12] These three types of products were definitely formed via different pathways. We believe that the reactions were initiated by the single electron reduction of IBA-N_3 by photo-excited $[Cu(dap)_2]^+$, which would generate an azidyl radical. The azidyl radical then adds to olefin moiety to give a carbon radical. This was confirmed by the inhibition experiment with 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) and butylated hydroxytoluene (BHT) (Scheme 6) as well as by radical clock experiments (Scheme 7). In the radical clock experiments, although no ring-opening products were obtained for compound **1ao**, they were generated from compound **1ap** under the standard conditions.

Scheme 6. Inhibition Experiment



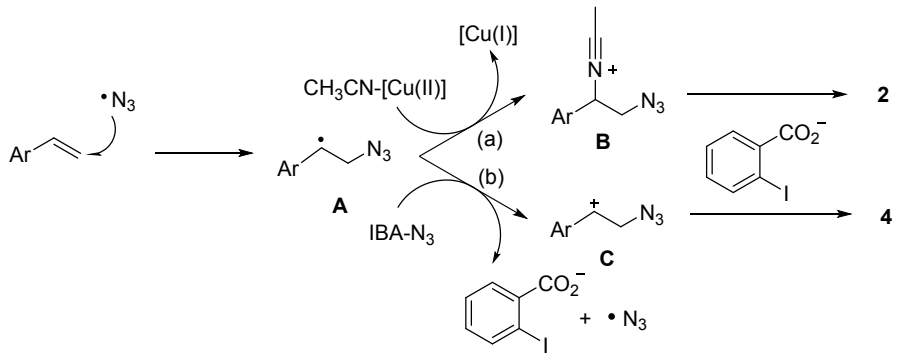
Scheme 7. Radical Clock Experiments



After the carbon radical is formed, the subsequent reactions would lead to different types of products depending on the electronic properties of the aryl group adjacent to the carbon-carbon double bond (Scheme 8). For electron-deficient substrates **1ag-1ai**, this radical would abstract an azidyl group to give diazidation products **3**. Compounds **2**, with an acetonitrile moiety incorporated in their structure, must be generated via intermediacy of a Ritter-type intermediate (**B**) (Scheme 8, (a)), while the formation of compound **4** also indicates the involvement of a carbocation (**C**) (Scheme 8, (b)). In the latter case, **C** probably derives from direct oxidation of carbon radical **A**, which should be favorable for electron rich alkenes. As the reactions of **1aj-1an** did not give amido-azidation products, Carbocation **C** should be in proximity with benzoyloxylate anion, most likely located in the same solvent cage, so that it can be captured by benzoyloxylate anion, rather than reacts with the solvent. If it was the case, IBA-N_3 should act as oxidant for the conversion of **A** to **C**. For the formation of Ritter-type intermediate **B**, on the other hand, a different mechanism should operate, which most likely involves the participation of the copper catalyst. It is well known that Cu(II) can facilely combine with a carbon radical to form a Cu(III) species, which would then undergo C-Nu coupling via reductive elimination. Based on the literature precedents, we assumed that in the present case the Ritter-type intermediate **B** was possibly formed following the same pattern. It is also possible that radical **A** was first oxidized by copper Cu(II) to carbocation **C**, which then coupled with acetonitrile to give **B**.[15] These two mechanisms are difficult to distinguish under current circumstances, but we believe that the former one is more likely based on the

literature reports on analogous transformations.[16] It should be noted that apart from **2**, no Ritter-type products with H_2O as the nucleophile were found under the current circumstances.

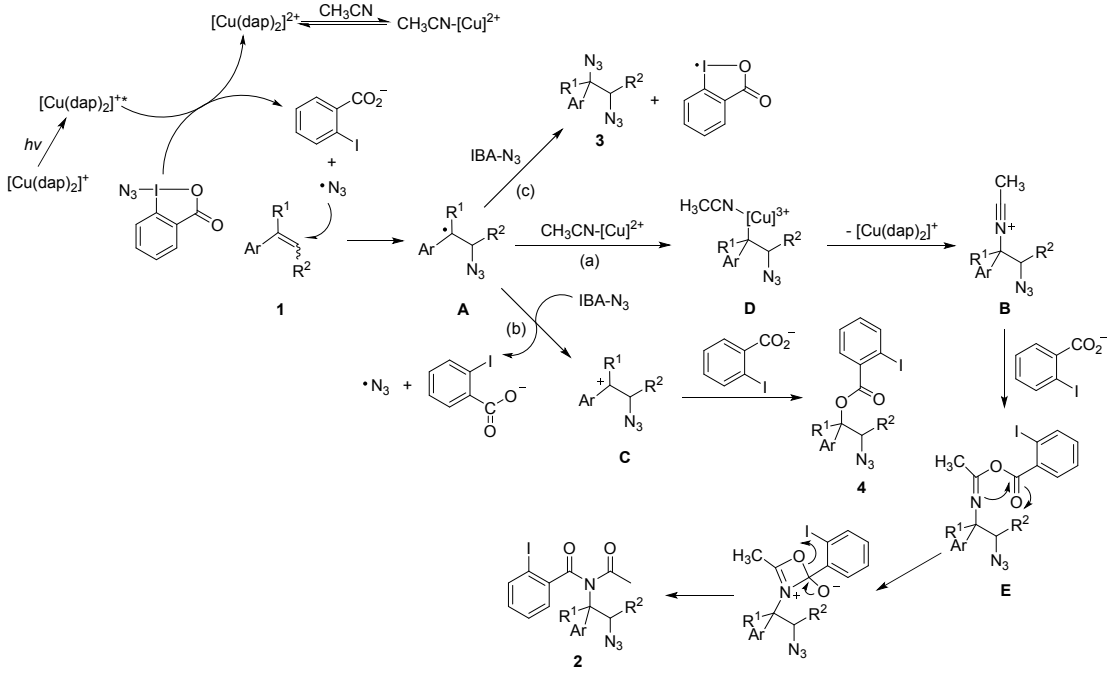
Scheme 8. Possible Pathways for the Formation of 2 and 4



Base on the above analysis, a possible mechanism is proposed to rationalize the present results, which is illustrated in Scheme 9. The reaction is initiated by single electron transfer (SET) between IBA-N_3 and $[Cu(dap)_2^+]$*, which results in the formation of azidyl radical and $[Cu(dap)_2]^{2+}$. The azidyl radical then adds to the carbon-carbon double bond to generate radical **A**. $[Cu(dap)_2]^{2+}$ generated in the SET step binds with acetonitrile to form a complex of CH_3CN-$[Cu]^{2+}$. For electronically less-biased aryl alkenes, intermediate **A** would couples with the CH_3CN-$[Cu]^{2+}$ complex to afford intermediate **D** (path (a)), which then undergoes reductive elimination to give Ritter-type intermediate **B**. The latter is readily captured by *o*-iodo benzoyloxylate anion to give **E**, from which product **2** is formed via rearrangement.

In case that the substrates are electron-rich alkenes, the initially formed radical intermediate **A** is oxidized to the corresponding carbocation **C** by IBA-N_3 (path (b)). **C** then couples with o-iodo benzoyloxylate anion incorporated in the same solvent cage to afford oxy-azidation products **4**. When the vinyl group was attached with a strong electron-withdrawing group, on the other hand, intermediate **A** neither binds with CH_3CN-$[Cu]^{2+}$ species, nor is it further oxidized; it can only abstract an azidyl group from IBA-N_3 to give diazidation products **3** (path (c)).

Scheme 9. Proposed Mechanism



To get more evidence for this mechanism, quantum yield measurements were conducted for the reactions of **1a** and **1aj**.[17] It was anticipated that if IBA-N_3 acted as an oxidant for the oxidative transformation from **A** to **C**, the quantum yield for the reaction should be larger than 1 because the reaction of IBA-N_3 with **A** would result in the formation of the azidyl radical, and thus the oxy-azidation can be effected in a chain process. By contrast, the formation of compounds **2** should involve the copper-mediated redox catalysis, which corresponds to a quantum yield of $\phi \leq 1$. Indeed, the quantum yield for the reaction of **1a** and **1aj** were measured to be 0.17 and 1.15, respectively (The measurement details are presented in Supporting Information), in consistence with the proposed mechanism shown in Scheme 9.

As there are three competitive pathways toward the products from the initially formed radical intermediate **A**, the electronic nature of the aryl group delicately determines which one is more favorable for each substrates. For path (b) toward products **4** to be competitive, a strong electron-donating group is required to render the oxidation of **A** by IBA-N_3 readily occur. This oxidation is much less efficient for less electron-rich substrates, and thus capture of **A** by CH_3CN-$[Cu]^{2+}$ becomes dominant. That highly electron-deficient vinyl arenes cannot be converted to amido-azidation products

indicates that the coupling of CH_3CN-$[Cu]^{2+}$ with **A** is also subjected to the electronic effect.

3. CONCLUSIONS

We have found that the reactions of vinyl arenes with azidobenziodoxole in acetonitrile under the conditions of visible light irradiation with $[Cu(dap)_2]PF_6$ as catalyst can give rise to three types of azidation/difunctionalization products, depending on the electronic nature of the substrates. For alkenes incorporating an electron-rich aryl group, benzoyloxy-azidation products was generated exclusively. When the aryl group attached to the olefin moiety was highly electron-deficient, diazidation products were generated in moderate yields. When the aryl group was less electronically-biased, a three-component reaction involving azidobenziodoxole and the solvent acetonitrile took place, affording mainly amido-azidation product. This crucial impact of substituent's electronic nature on the reaction consequence has not been observed in previous studies. A plausible mechanism is proposed based on mechanistic investigations to rationalize the observed results, where the electronic effect is attributed to its influence on the subsequent reactions of the key carbon radical intermediate formed via addition of azidyl radical to the carbon-carbon double bond. This carbon radical can either couple with the Cu(II) species, or be oxidized by azidobenziodoxole to the corresponding carbocation, or undergo azido transfer with azidobenziodoxole. Besides the mechanistic implications, the present reactions are of potential synthetic usefulness as they provide a new protocol for amido-azidation of vinyl arenes.

EXPERIMENTAL SECTION

General Methods. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-300 MHz spectrometer, a Bruker AM-400 MHz spectrometer or a Bruker AM-600 MHz spectrometer with $CDCl_3$ or DMSO-d_6 as the solvent. In $CDCl_3$, the chemical shifts in ^1H NMR spectra were determined with $Si(CH_3)_4$ as the internal standard (δ = 0.00 ppm); the chemical shifts in ^{13}C NMR spectra were determined based on the chemical

shift of $CDCl_3$ (δ = 77.00 ppm). In DMSO-d_6, the chemical shifts in ^1H NMR and ^{13}C NMR spectra were determined based on the chemical shift of DMSO-d_6 (δ = 2.50 ppm for ^1H NMR spectra and δ = 40.00 ppm for ^{13}C NMR spectra, respectively). The coupling constant(s) (*J* value) are reported in Hz (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet or unresolved, br = broad signal). The high resolution mass spectra (HRMS) were measured on a Bruker micrOTOF QII by ESI. The infrared spectra (FT-IR) were measured on a NEXUS 670 FT-IR spectrometer. Melting points (m.p.) were measured on an XT-4 melting point apparatus and are uncorrected. Single-crystal X-ray analysis was carried on a SuperNova, Eos diffractometer. A UV-visible spectrophotometer with a D_2 lamp was used for the quantum yield measurements. A blue LED apparatus (6 W; peak wavelength: 456.2 nm; half-wave width: 21 nm) equipped with a cooling fan were used as the light source. The reaction vessel is a 15 mL Pyrex glass tube (diameter: 2.0 cm) put at 1.0 cm distance from the light. No filter was used for irradiation. For the gram scale preparation, a common 10 W blue LED ribbon was used as the light source. Flash column chromatography (FCC) was conducted on silica gel (200–300 mesh). Anhydrous acetonitrile were purchased from Energy Chemical and used without further treatment. Other solvents were treated before use following the standard procedures. 1-Azido-1,2-benziodoxole (Zhdankin reagent, IBA-N_3) was prepared according to the reported methods.[18] 2,9-Bis-(4-methoxy-phenyl)-1,10-phenanthroline (dap) and $[Cu(dap)_2]Cl$ was prepared following the reported procedures.[19] $[Cu(dap)_2]PF_6$ was prepared following the reported procedures.[20] **1am** and **1an** were prepared according to literature methods.[21] **1ao** and **1ap** were prepared as reported.[22] All the other materials were obtained from commercial suppliers, and were used without further purification.

General Procedure for the Reaction of 1 with Zhdankin Reagent. Into an oven dried 15 mL Pyrex glass tube equipped with a magnetic stirring bar and a rubber stopper were added $[Cu(dap)_2]PF_6$ (9.9 mg, 0.01 mmol, 5 mol %) and IBA-N_3 (115.6 mg, 0.4 mmol, 2.0 equiv). The tube was evacuated and backfilled with argon for three

times. Then 4 mL of anhydrous acetonitrile was added into the tube with a syringe under argon atmosphere (argon balloon), followed by addition of **1** (0.2 mmol, 1.0 equiv) with a syringe under the same condition. The tube was put at the distance of 1 cm from the blue LED lamps and irradiated under stirring at room temperature (< 28 ^{o}C) for specific time (4 h unless otherwise specified). After the reaction was complete as indicated by TLC, the mixture was diluted with dichloromethane (20 mL). The solution was concentrated under reduced pressure on a rotary evaporator, and the residual was treated with silica gel column chromatography (eluent: petroleum ether (PE)/ethyl acetate (EA) = 20:1 to 10:1 unless otherwise specified) to afford the pure product (s).

Gram-Scale Synthesis of 3i. Into an oven dried 100 mL round-bottom flask equipped with a magnetic stirring bar and a rubber stopper were added $[Cu(dap)_2]PF_6$ (0.289 g, 0.3 mmol, 2.5 mol %) and IBA-N_3 (4.335 g, 15 mmol, 1.25 equiv). The flask was evacuated and backfilled with argon for three times. Then 60 mL of anhydrous acetonitrile was added into the flask with a syringe under argon atmosphere (argon balloon), followed by addition of **1i** (1.25g, 12 mmol) with a syringe. The flask was irradiated by a common 10 W blue LED ribbon (at a distance of 3 cm) under cooling (with an external cooling fan) for 5 h. After the reaction completed as indicated by TLC, the solution was directly concentrated under reduced pressure on a rotary evaporator, and the residual was treated with silica gel column chromatography (eluent: PE/EA = 20:1) to afford the pure product **2i** in 50% yield (2.588 g).

Safety statement: Organic azides are potentially explosive compounds that might decompose dramatically. 1-Azido-1,2-benziodoxole (IBA-N_3) also has its safety concerns.[23] Care should be taken to handle these compounds. However, we haven't experienced a safety problem during our experiments. All organic azides prepared in this work are stable enough to be stored at room temperature at least for a month in the dark.

4-Chloro-*N*-methyl-*N*-vinylbenzenesulfonamide (1am).White solid (on 8.7 mmol scale, 1.872 g, 92%), mp 58–60 ^{o}C, R_f = 0.34 (PE:EA = 10:1). ^{1}H NMR (400 MHz,

$CDCl_3$, δ ppm) 7.73–7.68 (m, 2H), 7.53–7.47 (m, 2H), 6.97 (dd, *J* = 15.6, 9.0 Hz, 1H), 4.39 (dd, *J* = 9.0, 1.5 Hz, 1H), 4.24 (dd, *J* = 15.6, 1.5 Hz, 1H), 2.88 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ ppm) 139.5, 135.9, 133.2, 129.4, 128.3, 94.1, 31.3; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_9H_{11}ClNO_2S]^+$: 232.0194, found: 232.0197.

4-Bromo-*N*-methyl-*N*-vinylbenzenesulfonamide (1an). White solid (on 6.6 mmol scale, 1.635 g, 90%), mp 71–72 °C, R_f = 0.34 (PE:EA = 10:1). ^1H NMR (400 MHz, $CDCl_3$, δ ppm) 7.70–7.59 (m, 4H), 6.96 (dd, *J* = 15.6, 9.0 Hz, 1H), 4.38 (dd, *J* = 9.0, 1.5 Hz, 1H), 4.24 (dd, *J* = 15.7, 1.5 Hz, 1H), 2.88 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ ppm) 136.6, 133.3, 133.4, 128.4, 128.0, 94.1, 31.3; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_9H_{11}BrNO_2S]^+$: 275.9688, found: 275.9690.

***N*-Acetyl-*N*-(2-azido-1-(4-bromophenyl)ethyl)-2-iodobenzamide (2a).** White solid (80 mg, 78%), mp 84–85 °C, R_f = 0.22 (PE:EA = 10:1). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.93 (dd, *J* = 7.9, 3.0 Hz, 1H), 7.47 (dd, *J* = 8.3, 1.9 Hz, 2H), 7.39 (td, *J* = 7.6, 2.5 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.24 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 5.68–5.54 (m, 1H), 4.44 (t, *J* = 10.3 Hz, 1H), 3.97 (dd, *J* = 12.3, 6.1 Hz, 1H), 1.99 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ ppm): 173.6, 172.4, 141.4, 140.7, 135.6, 132.2, 131.7, 129.8, 128.5, 128.3, 122.3, 93.6, 58.9, 51.9, 27.6; FT-IR (KBr, cm^{-1}): 2104, 1714, 1669; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{17}H_{15}BrIN_4O_2]^+$: 512.9418, found 512.9425.

***N*-Acetyl-*N*-(2-azido-1-(2-bromophenyl)ethyl)-2-iodobenzamide (2b).** Colorless liquid (68 mg, 66%), R_f = 0.21 (PE:EA = 10:1). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.91 (d, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.15 (q, *J* = 8.4 Hz, 3H), 5.85 (s, 1H), 4.25 (t, *J* = 11.2 Hz, 1H), 3.95 (dd, *J* = 12.2, 5.7 Hz, 1H), 2.13 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ ppm): 173.7, 172.6, 141.2, 140.5, 133.0, 132.0, 130.5, 129.9, 128.4, 128.2, 127.8, 123.8, 93.4, 59.9, 50.6, 27.3; FT-IR (KBr, cm^{-1}): 2105, 1714, 1672; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{17}H_{15}BrIN_4O_2]^+$: 512.9418, found 512.9413.

***N*-Acetyl-*N*-(2-azido-1-(3-bromophenyl)ethyl)-2-iodobenzamide (2c).** Colorless liquid (62 mg, 60%), R_f = 0.14 (PE:EA = 10:1). ^1H NMR (400 MHz, $CDCl_3$, δ ppm):

7.93 (d, *J* = 7.9 Hz, 1H), 7.56 (s, 1H), 7.46–7.39 (m, 2H), 7.39–7.33 (m, 1H), 7.28–7.21 (m, 2H), 7.21–7.15 (m, 1H), 5.62 (dd, *J* = 9.0, 6.3 Hz, 1H), 4.45 (t, *J* = 10.6 Hz, 1H), 3.98 (dd, *J* = 12.3, 6.0 Hz, 1H), 2.02 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, δ ppm): 173.6, 172.4, 141.3, 140.7, 136.7, 132.2, 131.3, 131.1, 130.1, 128.4, 128.3, 126.5, 122.6, 93.6, 58.7, 51.8, 27.6; FT-IR (KBr, cm^{-1}): 2104, 1713, 1669; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{17}H_{15}BrIN_4O_2]^+$: 512.9418; found: 512.9426.

***N*-Acetyl-*N*-(2-azido-1-(3-fluorophenyl)ethyl)-2-iodobenzamide (2d).** Colorless liquid (54 mg, 60%), R_f = 0.14 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.93 (d, *J* = 7.9 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.31 (dd, *J* = 14.1, 8.1 Hz, 1H), 7.28–7.23 (m, 1H), 7.12–7.23 (m, 3H), 7.03–6.96 (m, 1H), 5.72–5.57 (m, 1H), 4.45 (t, *J* = 10.3 Hz, 1H), 4.00 (dd, *J* = 12.3, 6.0 Hz, 1H), 2.02 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, δ ppm): 173.6, 172.4, 162.7 (d, *J* = 246.0 Hz), 141.4, 140.7, 139.0 (d, *J* = 7.0 Hz), 132.2, 130.1 (d, *J* = 8.0 Hz), 128.5, 128.4, 123.6 (d, *J* = 3.0 Hz), 115.3 (d, *J* = 10.0 Hz), 115.0 (d, *J* = 11.0 Hz), 93.6, 58.9, 52.0, 27.6; ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm) -112.0; FT-IR (KBr, cm^{-1}): 2106, 1713, 1670; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{17}H_{15}FIN_4O_2]^+$: 453.0218, found: 453.0225.

***N*-Acetyl-*N*-(2-azido-1-(4-fluorophenyl)ethyl)-2-iodobenzamide (2e).** Colorless liquid (63 mg, 70%), R_f = 0.20 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.93 (dd, *J* = 7.9, 0.6 Hz, 1H), 7.46–7.39 (m, 2H), 7.37 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.22 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.16 (td, *J* = 7.7, 1.6 Hz, 1H), 7.03 (t, *J* = 8.7 Hz, 2H), 5.64 (dd, *J* = 9.1, 6.4 Hz, 1H), 4.46 (t, *J* = 10.8 Hz, 1H), 3.96 (dd, *J* = 12.3, 6.1 Hz, 1H), 1.99 (s, 3H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, δ ppm): 173.7, 172.5, 162.4 (d, *J* = 246.8 Hz), 141.4, 140.7, 138.6, 132.3, 132.1, 130.1 (d, *J* = 8.2 Hz), 128.4 (d, *J* = 15.0 Hz), 115.5 (d, *J* = 21.0 Hz), 93.6, 58.9, 52.2, 27.7; ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm) -113.3; FT-IR (KBr, cm^{-1}): 2106, 1712, 1678; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{17}H_{15}FIN_4O_2]^+$: 453.0218, found: 453.0210.

***N*-Acetyl-*N*-(2-azido-1-(2-chlorophenyl)ethyl)-2-iodobenzamide (2f).** Colorless liquid (66 mg, 70%), R_f = 0.22 (PE:EA = 10:1). ^{1}H NMR (600 MHz, $CDCl_3$, δ ppm): 7.91 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 7.4 Hz, 1H), 7.37–7.31 (m, 2H), 7.29 (td, *J* =

7.6, 1.2 Hz, 1H), 7.27–7.22 (m, 1H), 7.18 (d, *J* = 6.3 Hz, 1H), 7.14 (td, *J* = 7.7, 1.5 Hz, 1H), 5.95 (s, 1H), 4.30 (t, *J* = 10.2 Hz, 1H), 3.98 (s, 1H), 2.09 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, δ ppm): 173.5, 172.4, 141.4, 140.5, 133.5, 131.9, 130.4, 129.6, 129.6, 128.4, 128.2, 127.1, 93.4, 57.2, 50.7, 27.2; FT-IR (KBr, cm^{-1}): 2105, 1714, 1672; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{17}H_{15}ClIN_4O_2]^+$: 468.9923, found: 468.9929.

***N*-Acetyl-*N*-(2-azido-1-(3-chlorophenyl)ethyl)-2-iodobenzamide (2g).** Colorless liquid (51 mg, 54%), R_f = 0.15 (PE:EA = 10:1). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.93 (d, *J* = 7.9 Hz, 1H), 7.45–7.36 (m, 2H), 7.34–7.23 (m, 4H), 7.18 (td, *J* = 7.8, 1.6 Hz, 1H), 5.63 (dd, *J* = 8.9, 6.4 Hz, 1H), 4.45 (t, *J* = 10.5 Hz, 1H), 3.99 (dd, *J* = 12.3, 6.0 Hz, 1H), 2.02 (s, 3H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, δ ppm): 173.6, 172.4, 141.3, 140.7, 138.5, 134.4, 132.2, 129.8, 128.5, 128.4, 128.3, 128.2, 126.1, 93.6, 58.8, 51.8, 27.7; FT-IR (KBr, cm^{-1}): 2105, 1713, 1669; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $[C_{17}H_{14}ClIN_4O_2Na]^+$: 490.9742, found: 490.9733.

***N*-Acetyl-*N*-(2-azido-1-(4-chlorophenyl)ethyl)-2-iodobenzamide (2h).** Slight yellow solid (48 mg, 51%), mp 86–87 °C, R_f = 0.23 (PE:EA = 10:1). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.94 (d, *J* = 7.9 Hz, 1H), 7.43–7.35 (m, 3H), 7.35–7.29 (m, 2H), 7.24 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.17 (td, *J* = 7.8, 1.4 Hz, 1H), 5.63 (dd, *J* = 9.0, 6.3 Hz, 1H), 4.45 (t, *J* = 10.7 Hz, 1H), 3.97 (dd, *J* = 12.3, 6.1 Hz, 1H), 2.00 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, δ ppm): 173.7, 172.4, 141.4, 140.7, 135.0, 134.2, 132.2, 129.5, 128.7, 128.5, 128.3, 93.6, 58.9, 52.0, 27.7; FT-IR (KBr, cm^{-1}): 2104, 1713, 1669; HRMS (ESI-TOF) m/z: $[M-N_2+Na]^+$ calcd for $[C_{17}H_{14}ClIN_2O_2Na]^+$: 462.9681, found: 462.9679.

***N*-Acetyl-*N*-(2-azido-1-phenylethyl)-2-iodobenzamide (2i).** Slight yellow solid (63 mg, 73%), mp 72–73 °C, R_f = 0.36 (PE:EA = 10:1). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.92 (d, *J* = 7.9 Hz, 1H), 7.44–7.27 (m, 6H), 7.22 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.15 (td, *J* = 7.7, 1.6 Hz, 1H), 5.65 (t, *J* = 8.0 Hz, 1H), 4.49 (t, *J* = 10.9 Hz, 1H), 4.00 (dd, *J* = 12.3, 6.0 Hz, 1H), 2.02 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, δ ppm): 173.8, 172.6, 141.5, 140.6, 136.5, 132.0, 128.6, 128.5, 128.3, 128.2, 127.9, 93.6, 59.5,

52.2, 27.6; FT-IR (KBr, cm^{-1}): 2104, 1713, 1669; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{17}H_{16}IN_4O_2]^+$: 435.0312, found: 435.0319.

***N*-Acetyl-*N*-(2-azido-1-(o-tolyl)ethyl)-2-iodobenzamide (2j).** Colorless liquid (70 mg, 78%), R_f = 0.31 (PE:EA = 10:1). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.91 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.55 (s, 1H), 7.32 (td, *J* = 7.6, 1.0 Hz, 1H), 7.24–7.17 (m, 2H), 7.14 (td, *J* = 7.7, 1.6 Hz, 2H), 7.08 (dd, *J* = 7.6, 1.4 Hz, 1H), 5.89 (s, 1H), 4.41 (s, 1H), 3.86 (s, 1H), 2.31 (s, 3H), 1.96 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ ppm): 174.0, 172.4, 141.6, 140.6, 136.4, 134.5, 131.9, 130.6, 128.6, 128.3, 128.2, 126.3, 93.7, 56.8, 52.0, 27.6, 19.2; FT-IR (KBr, cm^{-1}): 2104, 1714, 1669; HRMS (ESI-TOF) m/z: $[M-N_2+H]^+$ calcd for $[C_{18}H_{18}IN_2O_2]^+$: 421.0407, found: 421.0398.

***N*-Acetyl-*N*-(2-azido-1-(m-tolyl)ethyl)-2-iodobenzamide (2k).** Colorless liquid (66 mg, 74%), R_f = 0.25 (PE:EA = 10:1). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.91 (d, *J* = 7.9 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.17–7.26 (m, 4H), 7.14 (td, *J* = 7.8, 1.5 Hz, 1H), 7.10 (d, *J* = 6.6 Hz, 1H), 5.67–5.54 (m, 1H), 4.47 (t, *J* = 10.9 Hz, 1H), 3.98 (dd, *J* = 12.3, 6.0 Hz, 1H), 2.34 (s, 3H), 2.04 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ ppm): 173.8, 172.6, 141.5, 140.6, 138.1, 136.4, 131.9, 128.9, 128.5, 128.4, 128.4, 128.2, 124.9, 93.6, 59.5, 52.2, 27.6, 21.4; FT-IR (KBr, cm^{-1}): 2104, 1713, 1669; HRMS (ESI-TOF) m/z: $[M-N_2+H]^+$ calcd for $[C_{18}H_{18}IN_2O_2]^+$: 421.0407, found: 421.0398.

***N*-Acetyl-*N*-(2-azido-1-(p-tolyl)ethyl)-2-iodobenzamide (2l).** Colorless liquid (56 mg, 62%), R_f = 0.29 (PE:EA = 10:1). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.95–7.89 (m, 1H), 7.36 (td, *J* = 7.6, 0.9 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.22 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.18–7.12 (m, 3H), 5.68–5.54 (m, 1H), 4.47 (t, *J* = 10.9 Hz, 1H), 3.97 (dd, *J* = 12.3, 6.0 Hz, 1H), 2.32 (s, 3H), 2.02 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ ppm): 173.8, 172.6, 141.6, 140.7, 138.0, 133.5, 132.0, 129.3, 128.5, 128.3, 127.9, 93.7, 59.4, 52.3, 27.7, 21.1; FT-IR (KBr, cm^{-1}): 2104, 1713, 1669; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{18}H_{18}IN_4O_2]^+$: 449.0469, found: 449.0475.

2-Azido-1-(p-tolyl)ethyl 2-iodobenzoate (4l).[12] Colorless liquid (4 mg, 5%), R_f = 0.52 (PE:EA = 10:1). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 8.00 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.90 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.42 (td, *J* = 7.6, 1.2 Hz, 1H), 7.35 (d, *J* = 8.0 Hz,

2H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.16 (td, *J* = 7.7, 1.7 Hz, 1H), 6.11 (dd, *J* = 7.8, 4.3 Hz, 1H), 3.78 (dd, *J* = 13.1, 7.8 Hz, 1H), 3.62 (dd, *J* = 13.1, 4.3 Hz, 1H), 2.35 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, δ ppm): 165.1, 141.5, 138.8, 134.3, 133.7, 132.9, 131.1, 129.4, 127.9, 126.6, 94.3, 75.6, 55.1, 21.2.

***N*-(1-([1,1'-Biphenyl]-4-yl)-2-azidoethyl)-N-acetyl-2-iodobenzamide (2m).** Colorless liquid (62 mg, 61%), R_f = 0.14 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.92 (d, *J* = 7.9 Hz, 1H), 7.63-7.53 (m, 4H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.39–7.30 (m, 2H), 7.27 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.15 (td, *J* = 7.7, 1.6 Hz, 1H), 5.78–5.63 (m, 1H), 4.52 (t, *J* = 10.7 Hz, 1H), 4.03 (dd, *J* = 12.3, 6.0 Hz, 1H), 2.04 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, δ ppm): 173.8, 172.6, 141.5, 141.0, 140.6, 140.3, 135.4, 132.0, 128.7, 128.5, 128.4, 128.3, 127.4, 127.2, 127.0, 93.6, 59.3, 52.2, 27.6; FT-IR (KBr, cm^{-1}): 2104, 1713, 1668; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{23}H_{20}IN_4O_2]^+$: 511.0625, found: 511.0627.

2-([1,1'-Biphenyl]-4-yl)-1-azidopropan-2-yl 2-iodobenzoate (4m).[12] Colorless liquid (8 mg, 9%), R_f = 0.30 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.01 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.93 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.65–7.49 (m, 6H), 7.43 (t, *J* = 7.5 Hz, 3H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.16 (td, *J* = 7.7, 1.7 Hz, 1H), 6.18 (dd, *J* = 7.7, 4.2 Hz, 1H), 3.82 (dd, *J* = 13.1, 7.7 Hz, 1H), 3.68 (dd, *J* = 13.2, 4.3 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, δ ppm): 165.1, 141.8, 141.6, 140.4, 135.6, 134.2, 133.0, 131.2, 128.8, 128.0, 127.5, 127.5, 127.1, 127.0, 94.3, 75.6, 55.1.

***N*-Acetyl-*N*-(2-azido-1-(4-(tert-butyl)phenyl)ethyl)-2-iodobenzamide (2n).** Colorless liquid (86 mg, 88%), R_f = 0.34 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.92 (d, *J* = 7.9 Hz, 1H), 7.39–7.30 (m, 5H), 7.27–7.23 (m, 1H), 7.14 (td, *J* = 7.5, 1.2 Hz, 1H), 5.62 (dd, *J* = 9.3, 6.1 Hz, 1H), 4.49 (t, *J* = 10.9 Hz, 1H), 3.97 (dd, *J* = 12.3, 6.0 Hz, 1H), 2.03 (s, 3H), 1.29 (s, 9H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, δ ppm): 173.8, 172.6, 151.1, 141.6, 140.6, 133.4, 131.2, 128.5, 128.2, 127.6, 125.4, 93.7, 59.3, 52.3, 34.5, 31.2, 27.6; FT-IR (KBr, cm^{-1}): 2104, 1713, 1670; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{21}H_{24}IN_4O_2]^+$: 491.0938, found: 491.0929.

***N*-Acetyl-*N*-(2-azido-1-(4-(chloromethyl)phenyl)ethyl)-2-iodobenzamide (2o).** Colorless liquid (70 mg, 80%), R_f = 0.18 (PE:EA = 10:1). ^{1}H NMR (400 MHz,

$CDCl_3$, δ ppm): 7.92 (dd, *J* = 7.9, 0.6 Hz, 1H), 7.34–7.44 (m, 5H), 7.25 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.16 (td, *J* = 7.7, 1.6 Hz, 1H), 5.65 (dd, *J* = 9.2, 6.2 Hz, 1H), 4.55 (s, 2H), 4.46 (t, *J* = 10.7 Hz, 1H), 3.99 (dd, *J* = 12.3, 6.0 Hz, 1H), 2.01 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ ppm): 173.7, 172.5, 141.4, 140.7, 137.4, 136.8, 132.1, 128.7, 128.5, 128.3, 128.3, 93.6, 59.1, 52.1, 45.6, 27.7; FT-IR (KBr, cm^{-1}): 2105, 1713, 1668; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{18}H_{17}ClIN_4O_2]^+$: 483.0079, found: 483.0076.

***N*-Acetyl-*N*-(1-(4-acetylphenyl)-2-azidoethyl)-2-iodobenzamide (2p).** Colorless liquid (77 mg, 81%), R_f = 0.16 (PE:EA = 5:1), eluent for column chromatography: PE/EA = 10:1 to 3:1. ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.93 (d, *J* = 7.9 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.08 (d, *J* = 8.6 Hz, 2H), 5.65 (dd, *J* = 9.2, 6.1 Hz, 1H), 4.49 (t, *J* = 10.5 Hz, 1H), 3.95 (dd, *J* = 12.4, 6.0 Hz, 1H), 2.29 (s, 3H), 2.00 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ ppm): 173.7, 172.6, 169.2, 150.4, 141.4, 140.7, 134.0, 132.1, 129.4, 128.6, 128.3, 121.7, 93.6, 59.1, 52.1, 27.7, 21.1; FT-IR (KBr, cm^{-1}): 2105, 1760, 1713, 1668; HRMS (ESI-TOF) m/z: $[M-N_2+H]^+$ calcd for $[C_{19}H_{18}IN_2O_3]^+$: 449.0357, found: 449.0366.

***N*-Acetyl-*N*-(2-azido-1-(2,6-dichlorophenyl)ethyl)-2-iodobenzamide (2q).** White solid (35 mg, 35%), mp 137–138 °C, R_f = 0.14 (PE:EA = 10:1). ^1H NMR (600 MHz, $CDCl_3$, δ ppm): 7.92 (d, *J* = 7.9 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.29 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.19–7.14 (m, 2H), 6.14 (s, 1H), 4.54 (dd, *J* = 12.4, 9.5 Hz, 1H), 4.19 (s, 1H), 1.92 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, δ ppm): 173.1, 171.7, 141.6, 140.8, 136.1, 132.1, 131.8, 129.8, 129.6, 129.0, 128.2, 94.0, 58.6, 51.4, 27.7; FT-IR (KBr, cm^{-1}): 2106, 1719, 1674; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{17}H_{14}Cl_2IN_4O_2]^+$:502.9533, found:502.9538.

***N*-Acetyl-*N*-(2-azido-1-(2,5-dimethylphenyl)ethyl)-2-iodobenzamide (2r).** White solid (69 mg, 75%), mp 99–100 °C, R_f = 0.28 (PE:EA = 10:1). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.90 (d, *J* = 7.9 Hz, 1H), 7.31 (t, *J* = 7.1 Hz, 2H), 7.12 (t, *J* = 7.7 Hz, 1H), 7.04 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 2H), 5.82 (s, 1H), 4.39 (t, *J* = 10.5 Hz, 1H), 3.83 (s, 1H), 2.30 (s, 3H), 2.22 (s, 3H), 2.00 (s, 3H); $^{13}C\{^1H\}$ NMR

(100 MHz, $CDCl_3$, δ ppm): 174.1, 172.5, 141.6, 140.5, 135.7, 134.1, 133.2, 132.0, 130.5, 129.1, 129.1, 128.6, 128.2, 93.7, 56.8, 52.1, 27.6, 21.2, 18.8; FT-IR (KBr, cm^{-1}): 2104, 1714, 1670; HRMS (ESI-TOF) m/z: $[M-N_2+Na]^+$ calcd for $[C_{19}H_{20}IN_2O_2Na]^+$: 457.0383, found: 457.0376.

***N*-Acetyl-*N*-(2-azido-1-mesitylethyl)-2-iodobenzamide (2s).** White solid (32 mg, 34%), mp 118–119 °C, R_f = 0.30 (PE:EA = 10:1). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.90 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.13 (td, *J* = 7.7, 1.6 Hz, 1H), 7.08 (s, 1H), 6.79 (s, 2H), 5.64 (s, 1H), 4.55 (dd, *J* = 12.4, 10.9 Hz, 1H), 3.73 (s, 1H), 2.33 (s, 6H), 2.22 (s, 3H), 2.00 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, δ ppm): 174.2, 172.8, 141.5, 140.5, 137.7, 137.1, 132.0, 130.7, 130.1, 129.4, 128.2, 93.7, 59.3, 51.9, 29.6, 27.5, 20.6; FT-IR (KBr, cm^{-1}): 2106, 1715, 1670; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{20}H_{22}IN_4O_2]^+$: 477.0782, found: 477.0786.

2-Azido-1-mesitylethyl 2-iodobenzoate (4s).[12] Colorless liquid (30 mg, 35%), R_f = 0.53 (PE:EA = 10:1). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.98 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.85 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.40 (td, *J* = 7.6, 1.1 Hz, 1H), 7.13 (td, *J* = 7.7, 1.7 Hz, 1H), 6.85 (s, 2H), 6.54 (dd, *J* = 9.4, 4.7 Hz, 1H), 4.02 (dd, *J* = 13.2, 9.3 Hz, 1H), 3.52 (dd, *J* = 13.2, 4.7 Hz, 1H), 2.49 (s, 6H), 2.24 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ ppm): 165.1, 141.5, 138.2, 136.7, 134.3, 132.7, 130.8, 130.2, 129.4, 127.9, 94.3, 73.1, 52.8, 20.8, 20.7.

***N*-Acetyl-*N*-(2-azido-1-(naphthalen-1-yl)ethyl)-2-iodobenzamide (2t).** White solid (52 mg, 54%), mp 164–165 °C, R_f = 0.14 (PE:EA = 10:1). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 8.29 (s, 1H), 7.85 (dd, *J* = 8.1, 1.8 Hz, 2H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 1H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.03 (td, *J* = 7.7, 1.8 Hz, 1H), 6.84 (s, 1H), 6.70 (s, 1H), 4.67 (s, 1H), 4.14 (dd, *J* = 11.8, 5.6 Hz, 1H), 1.84 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, δ ppm): 173.7, 172.5, 141.4, 140.8, 133.7, 132.1, 131.4, 129.3, 129.1, 128.9, 128.2, 127.3, 127.0, 125.8, 124.9, 122.7, 94.1, 55.1, 52.7, 27.7; FT-IR (KBr, cm^{-1}): 2104, 1712, 1668; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{21}H_{18}IN_4O_2]^+$: 485.0469, found: 485.0474.

2-Azido-1-(naphthalen-1-yl)ethyl 2-iodobenzoate (4t).[12] Colorless liquid (5 mg, 6%), R_f = 0.30 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.14 (d, *J* = 8.4 Hz, 1H), 8.03 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.99 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.88 (dd, *J* = 16.8, 8.0 Hz, 2H), 7.71 (d, *J* = 7.1 Hz, 1H), 7.65–7.56 (m, 1H), 7.56–7.42 (m, 3H), 7.19 (td, *J* = 7.7, 1.7 Hz, 1H), 6.97 (dd, *J* = 8.1, 3.7 Hz, 1H), 3.92 (dd, *J* = 13.3, 8.1 Hz, 1H), 3.80 (dd, *J* = 13.3, 3.6 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, δ ppm): 165.2, 141.7, 134.2, 133.8, 133.1, 132.4, 131.3, 130.1, 129.4, 129.2, 128.1, 127.0, 126.1, 125.3, 124.4, 122.5, 94.5, 73.1, 54.9.

***N*-Acetyl-*N*-(2-azido-1-(naphthalen-2-yl)ethyl)-2-iodobenzamide (2u).** Colorless liquid (53 mg, 55%), R_f = 0.14 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.92 (d, *J* = 7.9 Hz, 1H), 7.88–7.77 (m, 4H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.51–7.44 (m, 2H), 7.34 (t, *J* = 7.5 Hz, 1H) 7.23 (d, *J* = 6.6 Hz, 1H), 7.13 (td, *J* = 7.8, 1.5 Hz, 1H), 5.89–5.77 (m, 1H), 4.61 (t, *J* = 10.6 Hz, 1H), 4.10 (dd, *J* = 12.3, 6.0 Hz, 1H), 2.04 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, δ ppm): 173.9, 172.6, 140.6, 128.5, 128.4, 128.3, 128.1, 127.5, 127.3, 126.4, 125.6, 93.6, 59.6, 52.2, 27.7; FT-IR (KBr, cm^{-1}): 2104, 1712, 1668; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{21}H_{18}IN_4O_2]^+$: 485.0469, found: 485.0460.

2-Azido-1-(naphthalen-2-yl)ethyl 2-iodobenzoate (4u).[12] Colorless liquid (8 mg, 9%), R_f = 0.34 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.00 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.96–7.90 (m, 2H), 7.90–7.80 (m, 3H), 7.55 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.52–7.46 (m, 2H), 7.43 (td, *J* = 7.6, 1.2 Hz, 1H), 7.16 (td, *J* = 7.6, 1.7 Hz, 1H), 6.30 (dd, *J* = 7.8, 4.3 Hz, 1H), 3.88 (dd, *J* = 13.1, 7.8 Hz, 1H), 3.71 (dd, *J* = 13.1, 4.3 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, δ ppm): 165.2, 141.6, 134.3, 134.0, 133.4, 133.1, 133.0, 131.2, 128.8, 128.1, 128.0, 127.7, 126.6, 126.5, 126.3, 123.9, 94.3, 75.9, 55.1.

N*-Acetyl-*N*-(2-azido-1,2,3,4-tetrahydronaphthalen-1-yl)-2-iodobenzamide (2v).** Colorless liquid (76 mg, *cis*:*trans* = 6.6:1, 83%), R_f = 0.19 (PE:EA = 10:1). FT-IR (KBr, cm^{-1}): 2102, 1717, 1671; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{19}H_{18}IN_4O_2]^+$: 461.0469, found: 461.0472. ***(cis)-Isomer (major) : ^{1}H NMR (600 MHz, $CDCl_3$, δ ppm): 7.91 (d, *J* = 8.0 Hz, 1H), 7.44 (s, 1H), 7.40 (t, *J* = 7.1 Hz, 1H),

7.28 (d, *J* = 7.3 Hz, 1H), 7.20–7.08 (m, 4H), 6.08 (d, *J* = 6.0 Hz, 1H), 4.11 (s, 1H), 3.15 (d, *J* = 16.7 Hz, 1H), 2.86–2.78 (m, 1H), 2.57 (s, 1H), 2.15–2.08 (m, 1H), 1.89 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, δ ppm): 174.2, 172.0, 142.3, 140.6, 137.0, 132.4, 131.5, 128.8, 128.2, 128.1, 127.6, 127.2, 126.3, 93.9, 60.4, 55.1, 28.1, 27.0, 24.9. **(*trans*)-Isomer (minor) :** ^{1}H NMR (600 MHz, $CDCl_3$, δ ppm): 7.92 (d, *J* = 9.1 Hz, 1H), 7.44 (s, 1H), 7.40 (t, *J* = 7.1 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.20–7.08 (m, 4H), 5.48 (s, 1H), 4.56 (t, *J* = 9.6 Hz, 1H), 3.07 (dd, *J* = 23.4, 10.6 Hz, 1H), 2.89 (d, *J* = 16.9 Hz, 1H), 2.39–2.34 (m, 1H), 2.15–2.08 (m, 1H), 1.89 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, δ ppm): 173.6, 172.0, 141.7, 140.6, 136.0, 134.3, 132.4, 131.6, 128.7, 128.1, 127.0, 126.6, 124.8, 93.9, 61.4, 60.5, 29.6, 28.7, 28.3.

N*-Acetyl-*N*-(2-azido-2,3-dihydro-1H-inden-1-yl)-2-iodobenzamide (2w).** Colorless liquid (73 mg, *cis*:*trans* = 9:1, 82%), R_f = 0.18 (PE:EA = 10:1). FT-IR (KBr, cm^{-1}): 2106, 1716, 1672; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{18}H_{16}IN_4O_2]^+$: 447.0312, found: 447.0315. ***(cis)-Isomer (major): ^{1}H NMR (600 MHz, $CDCl_3$, δ ppm): 7.91 (d, *J* = 7.9 Hz, 1H), 7.49–7.43 (m, 2H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.27–7.18 (m, 3H), 7.16 (t, *J* = 7.6 Hz, 1H), 5.79 (s, 1H), 4.39 (q, *J* = 8.3 Hz, 1H), 3.54 (dd, *J* = 15.3, 7.8 Hz, 1H), 3.33 (dd, *J* = 15.6, 8.6 Hz, 1H), 2.12 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, δ ppm): 173.5, 172.2, 142.0, 141.4, 140.3, 137.5, 131.7, 128.8, 128.4, 128.4, 127.2, 124.7, 124.1, 93.0, 61.9, 60.4, 37.5, 27.5. **(*trans*)-Isomer (minor) :** ^{1}H NMR (600 MHz, $CDCl_3$, δ ppm): 7.90 (d, *J* = 4.3 Hz, 1H), 7.49–7.43 (m, 2H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.27–7.18 (m, 3H), 7.18–7.15 (m, 1H), 5.41 (s, 1H), 4.84 (q, *J* = 6.9 Hz, 1H), 3.56 (dd, *J* = 15.3, 8.3 Hz, 1H), 2.91 (dd, *J* = 16.1, 6.7 Hz, 1H), 2.35 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, δ ppm): 173.5, 172.2, 142.2, 141.3, 140.2, 138.0, 131.8, 128.2, 127.9, 127.2, 124.9, 124.2, 122.5, 93.0, 68.4, 65.5, 36.8, 27.5.

N*-Acetyl-*N*-(2-azido-1-phenylpropyl)-2-iodobenzamide (2x).[11] *anti-Isomer (2x-1) : White solid (47 mg, 52%), mp. 74–75 °C, R_f = 0.31 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.91 (d, *J* = 7.9 Hz, 1H), 7.52 (d, *J* = 6.9 Hz, 2H), 7.37–7.28 (m, 4H), 7.18 (s, 1H), 7.13 (t, *J* = 7.7 Hz, 1H), 5.36 (d, *J* = 10.8 Hz, 1H), 4.99 (s, 1H), 1.90 (s, 3H), 1.23 (d, *J* = 6.4 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, δ ppm):

173.8, 172.4, 141.6, 140.7, 136.1, 132.0, 129.7, 128.8, 128.4, 128.3, 128.2, 94.0, 65.3, 57.3, 27.7, 18.1; FT-IR (KBr, cm^{-1}): 2114, 1714, 1668; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{18}H_{18}IN_4O_2]^+$: 449.0469, found: 449.0472. ***(syn)-Isomer (2x-2) :*** Colorless liquid (27 mg, 30%), R_f = 0.21 (PE:EA = 10:1). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.90 (d, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 7.0 Hz, 3H), 7.40–7.24 (m, 4H), 7.12 (t, *J* = 7.7 Hz, 1H), 6.80 (d, *J* = 7.2 Hz, 1H), 5.47 (s, 1H), 5.07–4.93 (m, 1H), 1.89 (s, 3H), 1.47 (d, *J* = 6.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ ppm): 173.5, 172.3, 141.5, 140.8, 136.7, 132.2, 129.1, 128.5, 128.4, 128.2, 128.0, 94.0, 63.5, 57.9, 27.4, 17.4; FT-IR (KBr, cm^{-1}): 2123, 2090, 1714, 1669; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{18}H_{18}IN_4O_2]^+$: 449.0469, found: 449.0473.

***N*-Acetyl-*N*-(1-azido-2-phenylpropan-2-yl)-2-iodobenzamide (2y).** Colorless liquid (62 mg, 70%), R_f = 0.16 (PE:EA = 10:1). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.97 (d, *J* = 7.9 Hz, 1H), 7.60 (d, *J* = 7.4 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 7.3 Hz, 1H), 7.20–7.13 (m, 1H), 4.53 (s, 1H), 3.80 (s, 1H), 1.97 (s, 3H), 1.92 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ ppm): 174.4, 171.0, 142.9, 141.3, 140.7, 132.4, 130.1, 128.5, 128.2, 127.4, 125.4, 95.3, 66.9, 59.8, 29.1, 24.7; FT-IR (KBr, cm^{-1}): 2107, 1712, 1671; HRMS (ESI-TOF) m/z: $[M-N_2+H]^+$ calcd for $[C_{18}H_{18}IN_2O_2]^+$: 421.0407, found: 421.0400.

1-Azido-2-phenylpropan-2-yl 2-iodobenzoate (4y).[12] Colorless liquid (9 mg, 11%), R_f = 0.41 (PE:EA = 10:1). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.98 (d, *J* = 7.9 Hz, 1H), 7.86 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.46–7.35 (m, 5H), 7.31 (t, *J* = 7.0 Hz, 1H), 7.15 (td, *J* = 7.7, 1.7 Hz, 1H), 3.84 (d, *J* = 12.8 Hz, 1H), 3.63 (d, *J* = 12.8 Hz, 1H), 2.08 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ ppm): 164.8, 141.3, 141.1, 135.7, 132.6, 130.9, 128.6, 128.0, 128.0, 124.9, 93.8, 84.5, 60.7, 22.4.

***N*-Acetyl-*N*-(1-azido-2-(o-tolyl)propan-2-yl)-2-iodobenzamide (2z).** Colorless liquid (57 mg, 62%), R_f = 0.19 (PE:EA = 10:1). ^1H NMR (600 MHz, $CDCl_3$, δ ppm): 7.94 (d, *J* = 7.9 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 1H), 7.22–7.11 (m, 4H), 4.76 (d, *J* = 10.8 Hz, 1H), 4.12 (d, *J* = 11.9 Hz, 1H), 2.64 (s, 3H), 2.05 (s, 3H), 1.85 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ ppm): 175.7, 170.5, 141.6, 141.1, 139.9, 134.2, 132.9, 132.0, 129.1, 128.1, 127.5, 126.5,

126.1, 95.0, 68.1, 59.4, 29.8, 26.0, 21.1; FT-IR (KBr, cm^{-1}): 2105, 1729, 1668; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{19}H_{20}IN_4O_2]^+$: 463.0625, found: 463.0626.

1-Azido-2-(o-tolyl)propan-2-yl 2-iodobenzoate (4z). Colorless liquid (14 mg, 17%), R_f = 0.37 (PE:EA = 10:1). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 8.00 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.91 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.43 (td, *J* = 7.6, 1.2 Hz, 1H), 7.39–7.34 (m, 1H), 7.27–7.19 (m, 2H), 7.19–7.12 (m, 2H), 4.05 (d, *J* = 12.9 Hz, 1H), 3.53 (d, *J* = 12.8 Hz, 1H), 2.42 (s, 3H), 2.13 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ ppm): 164.1, 141.6, 138.3, 134.7, 134.6, 132.8, 132.7, 131.1, 128.1, 128.0, 126.4, 126.2, 94.2, 85.2, 59.0, 23.4, 22.1; FT-IR (KBr, cm^{-1}): 2103, 1732; HRMS (ESI-TOF) m/z: $[M-N_2+H]^+$ calcd for $[C_{17}H_{17}INO_2]^+$: 394.0298, found: 394.0303.

***N*-Acetyl-*N*-(1-azido-2-(p-tolyl)propan-2-yl)-2-iodobenzamide (2aa).** Colorless liquid (47 mg, 51%), R_f = 0.28 (PE:EA = 10:1). ^1H NMR (600 MHz, $CDCl_3$, δ ppm): 7.97 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.2 Hz, 1H), 7.45–7.36 (m, 3H), 7.20–7.12 (m, 3H), 4.53 (s, 1H), 3.78 (s, 1H), 2.32 (s, 3H), 1.95 (s, 3H), 1.91 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, δ ppm): 174.6, 171.0, 141.3, 140.9, 139.9, 137.0, 132.3, 130.0, 129.3, 128.2, 125.4, 95.2, 66.8, 59.9, 29.1, 21.0; FT-IR (KBr, cm^{-1}): 2106, 1712, 1672; HRMS (ESI-TOF) m/z: $[M-N_2+H]^+$ calcd for $[C_{19}H_{20}IN_2O_2]^+$: 435.0564, found: 435.0568.

1-Azido-2-(p-tolyl)propan-2-yl 2-iodobenzoate (4aa). Colorless liquid (21 mg, 25%), R_f = 0.51 (PE:EA = 10:1). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.99 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.85 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.43 (td, *J* = 7.6, 1.2 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 7.16 (td, *J* = 7.7, 1.8 Hz, 1H), 3.84 (d, *J* = 12.8 Hz, 1H), 3.62 (d, *J* = 12.8 Hz, 1H), 2.34 (s, 3H), 2.07 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ ppm): 164.8, 141.3, 138.1, 137.8, 135.7, 132.6, 130.9, 129.3, 128.0, 124.8, 93.8, 84.5, 60.8, 22.3, 21.0; FT-IR (KBr, cm^{-1}): 2102, 1732; HRMS (ESI-TOF) m/z: $[M-N_2+H]^+$ calcd for $[C_{17}H_{17}INO_2]^+$: 394.0298, found: 394.0304.

N-Acetyl-N-(1-azido-2-(4-fluorophenyl)propan-2-yl)-2-iodobenzamide (2ab). Colorless liquid (47 mg, 50%), R_f = 0.16 (PE:EA = 10:1). ^1H NMR (600 MHz, $CDCl_3$, δ ppm): 7.99 (d, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 7.4 Hz, 1H), 7.51 (dd, *J* = 8.0, 5.2 Hz, 2H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.18 (td, *J* = 7.7, 1.4 Hz, 1H), 7.05 (t, *J* = 8.6

Hz, 2H), 4.48 (s, 1H), 3.76 (s, 1H), 1.96 (s, 3H), 1.92 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, δ ppm): 174.4, 170.8, 161.9 (d, *J* = 245.0 Hz), 141.4, 140.7, 138.8, 132.5, 130.0, 128.3, 127.3 (d, *J* = 7.5 Hz), 115.4 (d, *J* = 21.0 Hz), 95.2, 66.4, 59.9, 29.1, 24.9; ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm) -115.2; FT-IR (KBr, cm^{-1}): 2107, 1712, 1672; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{18}H_{17}FIN_4O_2]^+$: 467.0375, found: 467.0377.

1-Azido-2-(4-fluorophenyl)propan-2-yl 2-iodobenzoate (4ab). Colorless liquid (12 mg, 15%), R_f = 0.38 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.99 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.84 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.48–7.38 (m, 3H), 7.17 (td, *J* = 7.7, 1.7 Hz, 1H), 7.11–7.03 (m, 2H), 3.81 (d, *J* = 12.8 Hz, 1H), 3.63 (d, *J* = 12.8 Hz, 1H), 2.08 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, δ ppm): 164.8, 162.3 (d, *J* = 246.0 Hz), 141.4, 136.9 (d, *J* = 3.0 Hz), 135.4, 132.8, 130.9, 128.0, 126.8 (d, *J* = 8.0 Hz), 115.5 (d, *J* = 21.0 Hz), 93.8, 84.0, 60.7, 22.3; ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm) -114.2; FT-IR (KBr, cm^{-1}): 2105, 1732; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{16}H_{14}FIN_3O_2]^+$: 426.0109, found: 426.0116.

***N*-Acetyl-*N*-(1-azido-2-(4-chlorophenyl)propan-2-yl)-2-iodobenzamide (2ac).** White solid (65 mg, 68%), mp 144–145 °C, R_f = 0.20 (PE:EA = 10:1). ^{1}H NMR (600 MHz, $CDCl_3$, δ ppm): 7.98 (d, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 7.4 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.43 (td, *J* = 7.6, 0.9 Hz, 1H), 7.33 (d, *J* = 8.7 Hz, 2H), 7.18 (td, *J* = 7.7, 1.5 Hz, 1H), 4.45 (s, 1H), 3.78 (s, 1H), 1.92 (s, 6H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, δ ppm): 174.2, 170.7, 141.6, 141.4, 140.6, 133.2, 132.5, 130.0, 128.7, 128.2, 126.9, 95.2, 66.3, 59.7, 29.0; FT-IR (KBr, cm^{-1}): 2107, 1711, 1671; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{18}H_{17}ClIN_4O_2]^+$: 483.0079, found: 483.0084.

1-Azido-2-(4-chlorophenyl)propan-2-yl 2-iodobenzoate (4ac). Colorless liquid (14 mg, 16%), R_f = 0.37 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.99 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.83 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.43 (td, *J* = 7.6, 1.2 Hz, 1H), 7.36 (s, 4H), 7.16 (td, *J* = 7.7, 1.7 Hz, 1H), 3.80 (d, *J* = 12.8 Hz, 1H), 3.64 (d, *J* = 12.8 Hz, 1H), 2.06 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, δ ppm): 164.8, 141.4, 138.1, 139.7, 135.4, 134.0, 132.8, 130.9, 128.8, 128.0, 126.5, 93.8, 83.9, 60.5, 22.3; FT-IR

(KBr, cm^{-1}): 2104, 1732; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $[C_{16}H_{13}ClIN_3O_2Na]^+$: 463.9633, found: 463.9641.

***N*-Acetyl-*N*-(1-azido-2-(naphthalen-2-yl)propan-2-yl)-2-iodobenzamide (2ad).** Colorless liquid (51 mg, 51%), R_f = 0.11 (PE:EA = 10:1). ^1H NMR (600 MHz, $CDCl_3$, δ ppm): 7.96 (d, *J* = 7.8 Hz, 1H), 7.90 (s, 1H), 7.85 (t, *J* = 8.9 Hz, 2H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.75–7.71 (m, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.51–7.44 (m, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.3 Hz, 1H), 4.65 (s, 1H), 3.91 (s, 1H), 2.06 (s, 3H), 1.96 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, δ ppm): 174.8, 170.8, 141.3, 140.9, 140.3, 133.1, 132.5, 132.3, 130.0, 128.5, 128.2, 128.2, 127.5, 126.2, 126.1, 124.4, 123.7, 95.2, 67.0, 59.8, 29.2, 25.1; FT-IR (KBr, cm^{-1}): 2106, 1712, 1671; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{22}H_{19}IN_4O_2]^+$: 499.0625, found: 499.0630.

1-Azido-2-(naphthalen-2-yl)propan-2-yl 2-iodobenzoate (4ad). Colorless liquid (34 mg, 37%), R_f = 0.31 (PE:EA = 10:1). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 8.00 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.92–7.79 (m, 5H), 7.55 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.52–7.42 (m, 3H), 7.18 (td, *J* = 7.7, 1.7 Hz, 1H), 3.96 (d, *J* = 12.8 Hz, 1H), 3.71 (d, *J* = 12.8 Hz, 1H), 2.19 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ ppm): 164.9, 141.3, 138.4, 135.6, 133.0, 132.8, 132.3, 132.7, 130.9, 128.5, 128.3, 128.0, 127.6, 126.4, 126.4, 124.3, 122.6, 93.8, 84.6, 60.6, 22.4; FT-IR (KBr, cm^{-1}): 2102, 1731; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{20}H_{17}IN_3O_2]^+$: 458.0360, found: 458.0358.

***N*-Acetyl-*N*-(1-azido-2-phenylbutan-2-yl)-2-iodobenzamide (2ae).** Colorless liquid (65 mg, 70%), R_f = 0.14 (PE:EA = 10:1). ^1H NMR (400 MHz, $CDCl_3$, δ ppm):7.92 (d, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 7.5 Hz, 2H), 7.46 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.37 (td, *J* = 7.8, 3.6 Hz, 3H), 7.26 (t, *J* = 7.3 Hz, 1H), 7.11 (t, *J* = 7.7 Hz, 1H), 4.67 (d, *J* = 11.2 Hz, 1H), 4.22 (d, *J* = 12.2 Hz, 1H), 2.24 (d, *J* = 6.2 Hz, 2H), 2.06 (s, 3H), 0.84 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ ppm): 177.0, 169.0, 142.0, 141.1, 140.9, 131.9, 129.5, 128.3, 128.0, 127.2, 125.9, 94.8, 69.7, 54.4, 30.1, 29.4, 8.8; FT-IR (KBr, cm^{-1}): 2105, 1735, 1668; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $[C_{19}H_{19}IN_4O_2Na]^+$: 485.0445, found: 485.0436.

***N*-Acetyl-*N*-(2-azido-2-methyl-1-phenylpropyl)-2-iodobenzamide (2af).** Colorless liquid (76 mg, 82%), R_f = 0.21 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.89 (d, *J* = 7.9 Hz, 1H), 7.56 (dd, *J* = 6.5, 2.9 Hz, 2H), 7.31–7.22 (m, *J* = 2.9 Hz, 3H), 7.18 (s, 1H), 7.06 (td, *J* = 7.7, 1.3 Hz, 1H), 6.94 (s, 1H), 5.90 (s, 1H), 1.99 (s, 3H), 1.54 (d, *J* = 18.2 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ ppm): 174.5, 172.4, 141.0, 140.8, 135.9, 131.8, 130.7, 128.9, 128.1, 128.1, 127.8, 94.6, 65.4, 64.5, 27.5, 25.8, 25.6; FT-IR (KBr, cm^{-1}): 2107, 1721, 1674; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{19}H_{20}IN_4O_2]^+$: 463.0625, found: 463.0631.

1-(1,2-Diazidoethyl)-4-nitrobenzene (3ag).[12] Slight yellow liquid (14 mg, 30%), R_f = 0.22 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.36–8.22 (m, 2H), 7.64–7.48 (m, 2H), 4.81 (dd, *J* = 7.2, 5.5 Hz, 1H), 3.64–3.42 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ ppm): 148.2, 143.5, 127.9, 124.2, 64.5, 55.8; FT-IR (KBr, cm^{-1}): 2103, 1522, 1349.

4-(1,2-Diazidoethyl)benzonitrile (3ah).[12] Colorless liquid (14 mg, 33%), R_f = 0.16 (PE:EA = 10:1). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.76–7.68 (m, 2H), 7.51–7.44 (m, 2H), 4.74 (dd, *J* = 7.2, 5.5 Hz, 1H), 3.58–3.42 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ ppm): 141.6, 132.8, 127.7, 118.1, 112.9, 64.7, 55.7; FT-IR (KBr,cm^{-1}): 2233, 2106.

2-(1,2-Diazidoethyl)pyridine (3ai).[6a] Colorless liquid (8 mg, 22%), R_f = 0.16 (PE:EA = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.62 (d, *J* = 4.7 Hz, 1H), 7.76 (td, *J* = 7.7, 1.6 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.29 (dd, *J* = 7.6, 4.9 Hz, 1H), 4.72 (dd, *J* = 7.6, 4.8 Hz, 1H), 3.82 (dd, *J* = 12.7, 4.8 Hz, 1H), 3.69 (dd, *J* = 12.7, 7.7 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ ppm): 155.8, 149.8, 137.2, 123.6, 122.0, 65.5, 54.5; FT-IR (KBr, cm^{-1}): 2103, 1590.

2-Azido-1-(4-methoxyphenyl)ethyl 2-iodobenzoate (4aj).[12] Colorless liquid (55 mg, 65%), R_f = 0.31 (PE:EA = 10:1). ^{1}H NMR (600 MHz, $CDCl_3$, δ ppm): 8.00 (d, *J* = 7.9 Hz, 1H), 7.88 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.44–7.38 (m, 3H), 7.16 (t, *J* = 7.7 Hz, 1H), 6.92 (d, *J* = 8.6 Hz, 2H), 6.10 (dd, *J* = 7.7, 4.4 Hz, 1H), 3.80 (s, 3H), 3.79 (dd, *J* = 7.9 Hz, 5.3 Hz, 1H), 3.61 (dd, *J* = 13.1, 4.3 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, δ

ppm): 165.2, 160.0, 141.5, 134.4, 132.9, 131.1, 128.7, 128.2, 127.9, 114.1, 94.2, 75.4, 55.3, 55.1; FT-IR (KBr, cm^{-1}): 2102, 1730.

2-Azido-1,1-diphenylethyl 2-iodobenzoate (4ak). Colorless liquid (60 mg, 64%), R_f = 0.40 (PE:EA = 10:1). ^1H NMR (600 MHz, $CDCl_3$, δ ppm): 7.98 (dd, *J* = 7.8, 3.5 Hz, 1H), 7.93 (s, 1H), 7.49–7.27 (m, 11H), 7.16 (t, *J* = 7.7 Hz, 1H), 4.71 (d, *J* = 5.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ ppm): 164.9, 141.5, 141.3, 135.4, 132.7, 130.7, 128.3, 128.0, 126.4, 93.9, 86.4, 56.7; FT-IR (KBr, cm^{-1}): 2102, 1734; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $[C_{21}H_{16}IN_3NaO_2]^+$: 492.0179, found: 492.0186.

2-Azido-1-(thiophen-2-yl)ethyl 2-iodobenzoate (4al).[12] Colorless liquid (50 mg, 63%), R_f = 0.36 (PE:EA = 10:1). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 8.01 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.88 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.42 (td, *J* = 7.6, 1.2 Hz, 1H), 7.36 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.23 (dd, *J* = 3.6, 1.2 Hz, 1H),7.17 (td, *J* = 7.7, 1.7 Hz, 1H), 7.03 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.45 (dd, *J* = 7.2, 4.6 Hz, 1H), 3.86 (dd, *J* = 13.0, 7.2 Hz, 1H), 3.76 (dd, *J* = 13.1, 4.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, δ ppm): 164.9, 141.5, 138.6, 133.9, 133.0, 131.2, 127.9, 127.2, 126.9, 126.5, 94.3, 71.1, 54.9; FT-IR (KBr, cm^{-1}): 2104, 1732.

2-Azido-1-(4-chloro-N-methylphenylsulfonamido)ethyl 2-iodobenzoate (4am). Colorless liquid (78 mg, 75%), R_f = 0.12 (PE:EA = 10:1), eluent for column chromatography: PE/EA = 10:1 to 3:1. ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.98 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 8.6 Hz, 2H), 7.42–7.30 (m, 4H), 7.17 (td, *J* = 7.9, 2.0 Hz, 1H), 6.83 (t, *J* = 6.6 Hz, 1H), 3.75–3.61 (m, 2H), 3.02 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, δ ppm): 163.9, 141.6, 139.7, 136.5, 133.5, 132.7, 131.0, 129.4, 128.8, 127.8, 94.2, 80.2, 50.6, 30.0; FT-IR (KBr, cm^{-1}): 2108, 1735; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $[C_{16}H_{14}ClIN_4O_4SNa]^+$: 542.9361, found: 542.9360.

2-Azido-1-(4-bromo-N-methylphenylsulfonamido)ethyl 2-iodobenzoate (4an). Colorless liquid (79 mg, 70%), R_f = 0.12 (PE:EA = 10:1), eluent for column chromatography: PE/EA = 10:1 to 3:1. ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.99 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 8.6 Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 2H), 7.39–7.31 (m, 2H), 7.18 (td, *J* = 7.9, 2.5 Hz, 1H), 6.82 (t, *J* = 6.6 Hz, 1H), 3.77–3.63 (m, 2H), 3.02 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, δ ppm): 164.0, 141.7, 139.2, 133.5, 132.9,

132.4, 131.0, 128.9, 128.3, 127.9, 94.2, 80.3, 50.7, 30.2; FT-IR (KBr, cm^{-1}): 2108, 1734; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $[C_{16}H_{14}BrIN_4O_4SNa]^+$: 586.8856, found: 586.8861.

1-(2-Azido-1-(4-bromophenyl)ethoxy)-2,2,6,6-tetramethylpiperidine (5a).[9a] White solid (69 mg, 90%), mp 39–40 °C, R_f = 0.59 (PE:EA = 10:1). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.48 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 4.78 (dd, *J* = 6.5, 4.8 Hz, 1H), 3.70 (dd, *J* = 12.4, 4.6 Hz, 1H), 3.64 (dd, *J* = 12.3, 6.7 Hz, 1H), 1.62–1.23 (m, 9H), 1.18 (s, 3H), 1.02 (s, 3H), 0.69 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, δ ppm): 139.7, 131.3, 129.1, 121.7, 84.3, 60.0, 54.9, 40.3, 34.3, 34.1, 20.2, 17.0; FT-IR (KBr, cm^{-1}): 2103, 1488.

***N*-Acetyl-*N*-(2-azido-1-cyclopropyl-1-phenylethyl)-2-iodobenzamide (2ao).** Colorless liquid (5 mg, 5%), R_f = 0.14 (PE:EA = 10:1). ^1H NMR (600 MHz, $CDCl_3$, δ ppm): 7.97 (d, *J* = 7.9 Hz, 1H), 7.83 (s, 1H), 7.44 (d, *J* = 8.3 Hz, 3H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 7.3 Hz, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 4.88 (s, 1H), 4.16 (d, *J* = 11.5 Hz, 1H), 2.13 (s, 3H), 1.44 (s, 1H), 0.56 (s, 1H), 0.48–0.40 (m, 1H), 0.38–0.30 (m, 1H), 0.14–0.06 (m, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, δ ppm): 175.5, 170.1, 141.2, 140.9, 138.8, 132.1, 130.2, 128.0, 128.0, 127.4, 126.5, 125.5, 95.0, 69.6, 57.6, 29.2, 18.6, 4.7, 2.1; FT-IR (KBr, cm^{-1}): 2105, 1740, 1667; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{20}H_{20}IN_4O_2]^+$: 475.0625, found: 475.0632.

1-Azido-1-cyclopropyl-1-phenylethyl 2-iodobenzoate (4ao). Colorless liquid (32 mg, 36%), R_f = 0.38 (PE:EA = 10:1). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 8.00 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.87 (dt, *J* = 7.8, 1.8 Hz, 1H), 7.47–7.34 (m, 5H), 7.34–7.28 (m, 1H), 7.17 (td, *J* = 7.7, 1.7 Hz, 1H), 4.23 (d, *J* = 12.8 Hz, 1H), 4.14 (d, *J* = 12.8 Hz, 1H), 1.98–1.86 (m, 1H), 0.77–0.66 (m, 1H), 0.65–0.53 (m, 2H), 0.49–0.39 (m, 1H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, δ ppm): 165.1, 141.3, 139.0, 135.7, 132.6, 130.8, 128.2, 128.0, 127.9,125.7, 93.8, 86.7, 56.4, 18.7, 2.9, 2.1; FT-IR (KBr, cm^{-1}): 2101, 1731; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $[C_{18}H_{17}IN_3O_2]^+$: 434.0360, found: 434.0368.

ASSOCIATED CONTENT

Description of the light source, details of mechanistic studies, copies of ^{1}H NMR and ^{13}C NMR spectra, X-ray crystal data (CIF) for compound **2ac**, this material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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References

1. For reviews, see: (a) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. Visible Light Photoredox Catalysis with Transition Mental Complex: Applications in Organic Synthesis. *Chem. Rev.* **2013**, *113*, 5322−5363. (b) Shaw, M. H.; Twilton, J.; MacMillan, D. W. C. Photoredox Catalysis in Organic Chemistry. *J. Org. Chem.* **2016**, *81*, 6898−6926.
2. For a review, see: Romero, N. A.; Nicewicz, D. A. Organic Photoredox Catalysis. *Chem. Rev.* **2016**, *116*, 10075−10166.
3. Reiser, O. Shining Light on Copper: Unique Opportunities for Visible-Light-Catalyzed Atom Transfer Radical Addition Reactions and Related Processes. *Acc. Chem. Res.* **2016**, *49*, 1990−1996.
4. Larsen, C. B.; Wenger, O. S. Photoredox Catalysis with Metal Complexes Made from Earth-Abundant Elements. *Chem. Eur. J.* **2018**, *24*, 2039−2058.
5. For reviews, see: (a) Wu, K.; Liang, Y.; Jiao, N. Azidation in the Difunctionalization of Olefins. *Molecules* **2016**, *21*, 352−372. (b) Goswami, M.;

de Bruin, B. Metal-Catalysed Azidation of Organic Molecules. *Eur. J. Org. Chem.* **2017**, *2017*, 1152–1176.

6. For latest examples, see: (a) Fu, N.; Sauer, G. S.; Saha, A.; Loo, A.; Lin, S. Metal-Catalyzed Electrochemical Diazidation of Alkenes. *Science* **2017**, *357*, 575–579. (b) Peng, H.; Yuan, Z.; Chen, P.; Liu, G. Palladium-Catalyzed Intermolecular Oxidative Diazidation of Alkenes. *Chin. J. Chem.* **201**7, *35*, 876–880. (c) Zhou, H.; Jian, W.; Qian, B.; Ye, C.; Li, D.; Zhou, J.; Bao, H. Copper-Catalyzed Ligand-Free Diazidation of Olefins with $TMSN_3$ in CH_3CN or in H_2O. *Org. Lett.* **2017**, *19*, 6120–6123. (d) Sauer, G. S.; Lin, S. An Electrocatalytic Approach to the Radical Difunctionalization of Alkenes. *ACS Catal.* **2018**, *8*, 5175–5187. (e) Shen, S.-J.; Zhu, C.-L.; Lu, D.-F.; Xu, H. Iron-Catalyzed Direct Olefin Diazidation via Peroxyester Activation Promoted by Nitrogen-Based Ligands. *ACS Catal.* **2018**, *8*, 4473–4482. (f) Reddy, T. R.; Rao, D. S.; Kashyap, S. Visible-Light Activated Metal Catalyst-Free Vicinal Diazidation of Olefins with Sulfonium Iodate(I) Species. *Chem. Commun.* **2019**, *55*, 2833–2836. (g) Siu, J. C.; Parry, J. B.; Lin, S. Aminoxyl-Catalyzed Electrochemical Diazidation of Alkenes Mediated by a Metastable Charge-Transfer Complex. *J. Am. Chem. Soc.* **2019**, *141*, 2825–2831. (h) Wu, J.; Dou, Y.; Guillot, R.; Kouklovsky, C.; Vincent, G. Electrochemical Dearomative 2,3-Difunctionalization of Indoles. *J. Am. Chem. Soc.* **2019**, *141*, 2832–2837.

7. For latest examples, see: (a) Shen, K.; Wang, Q. Copper-Catalyzed Alkene Aminoazidation as a Rapid Entry to 1,2-Diamines and Installation of an Azide Reporter onto Azahetereocycles. *J. Am. Chem. Soc.* **2017**, *139*, 13110–13116. (b) Davies, J.; Sheikh, N. S.; Leonori, D. Photoredox Imino Functionalizations of Olefins. *Angew. Chem. Int. Ed.* **2017**, *56*, 13361–13365. (c) Wang, F.-L.; Dong, X.-Y.; Lin, J.-S.; Zeng, Y.; Jiao,G.-Y.; Gu, Q.-S.; Guo, X.-Q.; Ma, C.-L.; Liu, X.-Y. Catalytic Asymmetric Radical Diamination of Alkenes. *Chem.* **2017**, *3*, 979–990.

8. For latest examples, see: (a) Liu, Z.; Liu, Z.-Q. An Intermolecular Azidoheteroarylation of Simple Alkenes via Free-Radical Multicomponent

Cascade Reactions. *Org. Lett.* **2017**, *19*, 5649−5652. (b) Bunescu, A.; Ha, T. M.; Wang, Q.; Zhu, J. Copper-Catalyzed Three-Component Carboazidation of Alkenes with Acetonitrile and Sodium Azide. *Angew. Chem. Int. Ed.* **2017**, *56*, 10555−10558. (c) Zhao, D.; Kang, K.; Wan, W.; Jiang, H.; Deng, H.; Chen, Y.; Hao, J. Manganese-Mediated/-Catalyzed Oxidative Carboazidation of Acrylamides. *Org. Chem. Front.* **2017**, *4*, 1555−1560. (d) Zhang, R.; Yu, H.; Li, Z.; Yan, Q.; Li, P.; Wu, J.; Qi, J.; Jiang, M.; Sun, L. Iron-Mediated Azidomethylation or Azidotrideuteromethylation of Active Alkenes with Azidotrimethylsilane and Dimethyl Sulfoxide. *Adv. Synth. Catal.* **2018**, *360*, 1384−1388. (e) Zhang, Y.-X.; Jin, R.-X.; Yin, H.; Li, Y.; Wang, X.-S. Copper-Catalyzed Dichloromethylazidation of Alkenes Using $BrCCl_2H$ as a Stoichiometric Dichloromethylating Reagent. *Org. Lett.* **2018**, *20*, 7283−7287. (f) Li, W.-Y.; Wu, C.-S.; Wang, Z.; Luo, Y. Fe-Catalyzed Three-Component Carboazidation of Alkenes with Alkanes and Trimethylsilyl Azide. *Chem. Commun.* **2018**, *54*, 11013−11016. (g) Zhang, L.; Liu, S.; Zhao, Z.; Su, H.; Hao, J.; Wang, Y. (Salen)Mn(III)-Catalyzed Chemoselective Acylazidation of Olefins. *Chem. Sci.* **2018**, *9*, 6085−6090. (h) Yang, B.; Ren, X.; Shen, X.; Li, T.; Lu, Z. Visible Light-Promoted Three-Component Carboazidation of Unactivated Alkenes with $TMSN_3$ and Acrylonitrile. *Chin. J. Chem.* **2018**, *36*, 1017−1023.

9. For latest examples, see: (a) Zhang, B.; Studer, A. Stereoselective Radical Azidooxygenation of Alkenes. *Org. Lett.* **2013**, *15*, 4548−4551. (b) Alazet, S.; Le Vaillant, F.; Nicolai, S.; Courant, T.; Waser, J. Divergent Access to (1,1) and (1,2)-Azidolactones from Alkenes using Hypervalent Iodine Reagents. *Chem. Eur. J.* **2017**, *23*, 9501−9504. (c) Yang, B.; Lu, Z. Visible-Light-Promoted Metal-Free Aerobic Hydroxyazidation of Alkenes. *ACS Catal.* **2017**, *7*, 8362−8365. (d) Cong, F.; Wei, Y.; Tang, P. Combining Photoredox and Silver Catalysis for Azidotrifluoromethoxylation of Styrenes. *Chem. Commun.* **2018**, *54*, 4473−4476. (e) Wei, W.; Cui, H.; Yue, H.; Yang, D. Visible-Light-Enabled Oxyazidation of Alkenes Leading to α-Azidoketones in Air. *Green Chem.* **2018**, *20*, 3197−3202.

10. Xiong, Y.; Sun, Y.; Zhang, G. Copper-Catalyzed Synthesis of β-Azido Sulfonates or Fluorinated Alkanes: Divergent Reactivity of Sodium Sulfinates. *Org. Lett.* **2018**, *20*, 6250−6254.
11. Fumagalli, G.; Rabet, P. T. G.; Boyd, S.; Greaney, M. F. Three-Component Azidation of Styrene-Type Double Bonds: Light-Switchable Behavior of a Copper Photoredox Catalyst. *Angew. Chem. Int. Ed.* **2015**, *54*, 11481−11484.
12. Lu, M.-Z.; Wang, C.-Q.; Loh, T.-P. Copper-Catalyzed Vicinal Oxyazidation and Diazidation of Styrenes under Mild Conditions: Access to Alkyl Azides. *Org. Lett.* **2015**, *17*, 6110−6113.
13. Hossain, A.; Vidyasagar, A.; Eichinger, C.; Lankes, C.; Phan, J.; Rehbein, J.; Reiser, O. Visible-Light-Accelerated Copper(II)-Catalyzed Regio- and Chemoselective Oxo-Azidation of Vinyl Arenes. *Angew. Chem. Int. Ed.* **2018**, *57*, 8288−8292.
14. (a) Ma, H.; Li, D.; Yu, W. Synthesis of Quinoxaline Derivatives via Tandem Oxidative Azidation/Cyclization Reaction of *N*-Arylenamines. *Org. Lett.* **2016**, *18*, 868−871. (b) Yang, T.; Zhu, H.; Yu, W. Copper-Catalyzed Radical Reactions of 2-Azido-*N*-arylacrylamides with 1-(Trifluoromethyl)-1,2-benziodoxole and 1-Azidyl-1,2-benziodoxole. *Org. Biomol. Chem.* **2016**, *14*, 3376−3384. (c) Ma, H.; Zhang, X.; Chen, L.; Yu, W. A Domino Azidation/C–H Amination Approach toward Trifluoromethyl Substituted Imidazoles. *J. Org. Chem.* **2017**, *82*, 11841−11847. (d) Li, D.; Ma, H.; Li, Y.; Yu, W. Visible Light-Promoted Tandem Azidation/Cyclization of N-arylenamines towards Quinoxalines. *J. Photochem. Photobio. A: Chem.* **2018**, *355*, 382−388. (e) Wang, J.-J.; Yu, W. Anti-Markovnikov Hydroazidation of Alkenes by Visible-Light Photoredox Catalysis. *Chem. Eur. J.* **2019**, *25*, 3510−3514.
15. (a) Yasu, Y.; Koike, T.; Akita, M. Intermolecular Aminotrifluoromethylation of Alkenes by Visible-Light-Driven Photoredox Catalysis. *Org. Lett.* **2013**, *15*, 2136−2139. (b) Fumagalli, G.; Boyd, S.; Greaney, M. F. Oxyarylation and Aminoarylation of Styrenes Using Photoredox Catalysis. *Org. Lett.* **2013**, *15*, 4398−4401.

16. Wang, F.; Chen, P.; Liu, G. Copper-Catalyzed Radical Relay for Asymmetric Radical Transformations. *Acc. Chem. Res.* **2018**, *51*, 2036–2046.
17. (a) Cismesia, M. A.; Yoon, T. P. Characterizing Chain Processes in Visible Light Photoredox Catalysis. *Chem. Sci.* **2015**, *6*, 5426–5434. (b) Luis-Barrera, J.; Laina-Martin, V.; Rigotti, T.; Peccati, F.; Solans-Monfort, X.; Sodupe, M.; Mas-Balleste, R.; Liras, M.; Aleman, J. Visible-Light Photocatalytic Intramolecular Cyclopropane Ring Expansion. *Angew. Chem., Int. Ed.* **2017**, *56*, 7826–7830. (c) Klauck, F. J. R.; James, M. J.; Glorius, F. Deaminative Strategy for the Visible-Light-Mediated Generation of Alkyl Radicals. *Angew. Chem. Int. Ed.* **2017**, *56*, 12336–12339. (d) Ham,W. S.; Hillenbrand, J.; Jacq, J.; Genicot, C.; Ritter, T. Divergent Late-Stage (Hetero)aryl C-H Amination by the Pyridinium Radical Cation. *Angew. Chem. Int. Ed.* **2019**, *58*, 532–536.
18. Vita, V. M.; Waser, J. Azidation of β-Keto Esters and Silyl Enol Ethers with a Benziodoxole Reagent. *Org. Lett.* **2013**, *15*, 3246–3249.
19. Pirtsch, M.; Paria, S.; Matsuno, T.; Isobe, H.; Reiser, O. $[Cu(dap)_2]Cl$ As an Efficient Visible-Light-Driven Photoredox Catalyst in Carbon-Carbon Bond-Forming Reactions. *Chem. Eur. J.* **2012**, *18*, 7336–7340.
20. Cetin, M. M.; Hodson, R. T.; Hart, C. R.; Cordes, D. B.; Findlater, M.; Casadonte, D. J., Jr.; Cozzolino, A. F.; Mayer, M. F. Characterization and Photocatalytic Behavior of 2,9-Di(Aryl)-1,10-Phenanthroline Copper(I) Complexes. *Dalton Transactions* **2017**, *46*, 6553–6569.
21. (a) Laha, J. K.; Sharma, S.; Dayal, N. Palladium-Catalyzed Regio- and Chemo-selective Reactions of 2-Bromobenzyl Bromides: Expanding the Scope for the Synthesis of Biaryls Fused to a Seven−Membered Sultam. *Eur. J. Org. Chem.* **2015**, 7885–7891. (b) Sperger, C. A.; Tungen, J. E.; Fiksdahl, A. Gold(I)-Catalyzed Reactions of Propargyl Esters with Vinyl Derivatives. *Eur. J. Org. Chem.* **2011**, *2011*, 3719–3722.
22. Chen, C.; Shen, X.; Chen, J.; Hong, X.; Lu, Z. Iron-Catalyzed Hydroboration of Vinylcyclopropanes. *Org. Lett.* **2017**, *19*, 5422–5425.

23. Alazet, S.; Preindl, J.; Simonet-Davin, R.; Nicolai, S.; Nanchen, A.; Meyer, T.; Waser, J. Cyclic Hypervalent Iodine Reagents for Azidation: Safer Reagents and Photoredox-Catalyzed Ring Expansion. *J. Org. Chem.* **2018**, *83*, 12334−12356.