OL | Organic Letters

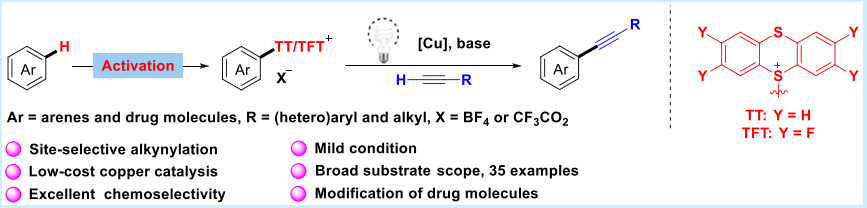
pubs.acs.org/OrgLett Letter

Photoinduced Copper-Catalyzed Site-Selective C(sp^2)−C(sp) Cross-Coupling via Aryl Sulfonium Salts

Lei Liang,* Hong-Ying Niu,* Ren-Long Li, Yao-Fei Wang, Jin-Kai Yan, Chang-Gong Li, and Hai-Ming Guo

Cite This: https://dx.doi.org/10.1021/acs.orglett.0c02364 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information



ABSTRACT: The classical Sonogashira reaction of aryl electrophiles in the presence of Pd catalysts has been well established as a potent method for arylalkyne synthesis. However, the site-selective C(sp^2)−C(sp) cross-coupling strategy using a non-noble-metal catalyst is rare. An efficient alternative approach for the synthesis of arylalkynes via a Cu-catalyzed Sonogashira-type reaction promoted by visible light is described. This method enables site-selective alkynylation from aryl sulfonium salts derived from diverse arenes to a set of arylalkynes with high selectivity and high functional-group compatibility. Moreover, rapid alkynylation of drug molecules is demonstrated.

Arylalkyne motifs are prevalent in the synthesis of pharmaceuticals, macrocycles, molecular organic materials, and natural products.[1] Arylalkynes have been prepared from aryl halides via Sonogashira cross-coupling,[2] and the aryl coupling partners have been subsequently extended to diazonium salts,[3a,b] ammonium salts,[3c] hydrazides,[3d] and carboxylic acids[3e] (Figure 1A). Despite these important successes, a considerable challenge in this field is the site-selective installation of these synthetic linchpins (i.e., halogen, amino, hydrazine, and carboxyl groups) into arenes.[4] Moreover, noble-metal salts as catalysts hamper the practicability of this approach. In fact, because of their low cost and low toxicity, base metals such as Cu and Fe have attracted considerable attention as Sonogashira reaction catalysts over the past decade.[5] In these methods, however, the aryl donor is identified as only aryl halides; late-stage alkynylation of complex organomolecules, in particular, remains elusive. Alternatively, the non-noble-metal-catalyzed site-selective Sonogashira reaction with arenes as inexpensive and readily available feedstocks is of great value but has rarely been explored.

In some recent elegant works, Ritter and co-workers have described the one-step conversion of certain simple arenes into aryl sulfonium salts, which are robust arylating reagents for coupling with a wide range of functional-group precursors.[6] In this method, various functional groups are efficiently incorporated into simple arenes. More importantly, this approach enables the late-stage functionalization of complex molecules and drugs via the aryl sulfonium salts. A related

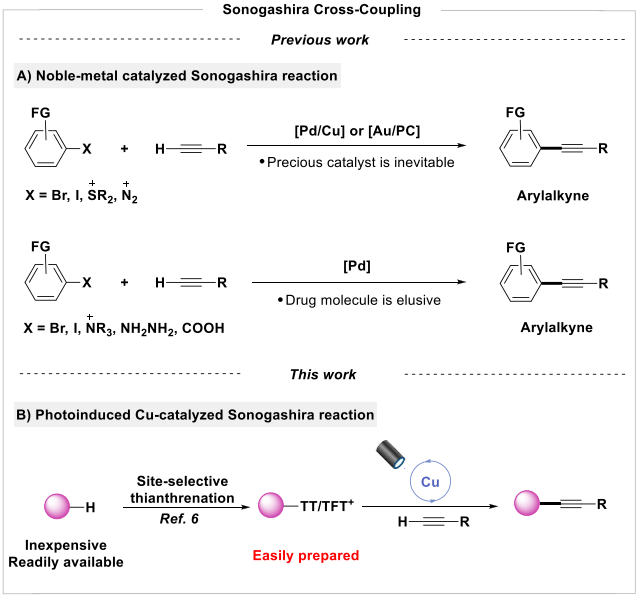


Figure 1. Reaction development.

Received: July 16, 2020

https://dx.doi.org/10.1021/acs.orglett.0c02364
Org. Lett. XXXX, XXX, XXX−XXX

alkynylation reaction with aryl sulfonium salts would complement this strategy and provide an indispensable method for the synthesis of arylalkynes. Notably, the groups of Ritter[4a] and Zhang[7] independently reported the alkynylation of aryl sulfonium salts. However, the use of Pd and heating is inevitable (Figure 1A). We surmised that a method with mild conditions and without Pd as a catalyst would enhance the substrate compatibility and increase the chemoselectivity. Over the past few years, photoredox/Cu cooperative catalysis strategies, which greatly enhance the capability of Cu-catalyzed reactions, have been recognized as an intriguing alternative to cross-coupling reactions.[8] Inspired by these works, we reasoned that aryl sulfonium salts[9] other than aryl halides can be used as versatile electrophiles for dual photoredox/copper-catalyzed C(sp^2)−C(sp) bond formation (Figure 1B). Furthermore, the Cu acetylide complexes, upon coordination of Cu^I salts with acetylenes, will substantially decrease the energy (λ > 350 nm) needed for the photoexcitation and prolong the lifetime (on the order of microseconds) of the excited intermediates,[10] resulting in sufficient reducing ability [$E_{1/2}$ = −1.77 V vs the saturated calomel electrode (SCE)][10c] to reduce the aryl sulfonium ($E_{1/2}$ = −1.05 V vs the SCE).[4b] A proposed reaction pathway is depicted in Figure 2. Initially, the

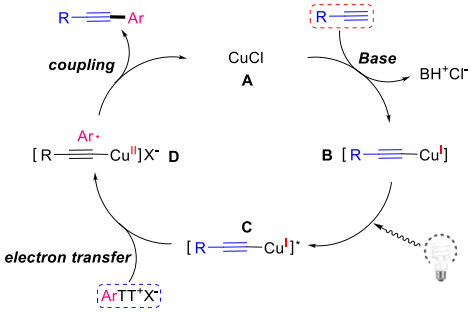


Figure 2. Possible pathways for photoinduced Cu-catalyzed Sonogashira cross-coupling reaction.

coordination of the terminal alkyne to a Cu^I species (**A**) generates Cu acetylide intermediate **B**. The excitation of intermediate **B** generates a photoexcited complex **C**, which reduces the aryl sulfonium salt through a single-electron transfer (SET) process, affording a Cu^{II} complex (**D**). Finally, **D** is expected to undergo reductive elimination to give the arylalkyne and regenerate **A**, closing the catalytic cycle.

The generation of a Cu acetylide intermediate is the key step in this reaction, and related control experiments have been conducted. First, 4-methylphenyl-copper acetylide **2g′** was used as a coupling partner for this reaction (Figure 3A). The desired product **3ag** was obtained in good yield. After that, the

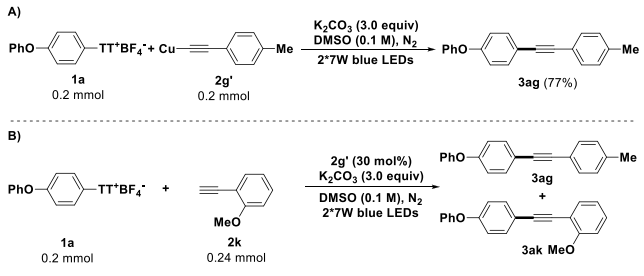
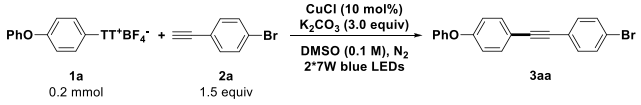


Figure 3. Control experiments.

coupling of aryl sulfonium salt **1a** with alkyne **2k** was investigated by employing **2g′** as the catalyst. Two different products were observed (1:3.5 **3ag**:**3ak**; ratio determined by NMR), which provides better support for an on-cycle copper acetylide species (Figure 3B).

Table 1. Reaction Optimization[a]



entry	variation from the "standard" conditions	yield (%)
1	none	81
2	no CuCl	0
3	no light	0
4	no K_2CO_3	0
5	MeCN instead of DMSO	32
6	DMF instead of DMSO	25
7	DBU instead of K_2CO_3	43
8	K_3PO_4 instead of K_2CO_3	73
9	CuBr instead of CuCl	65
10	CuI instead of CuCl	72

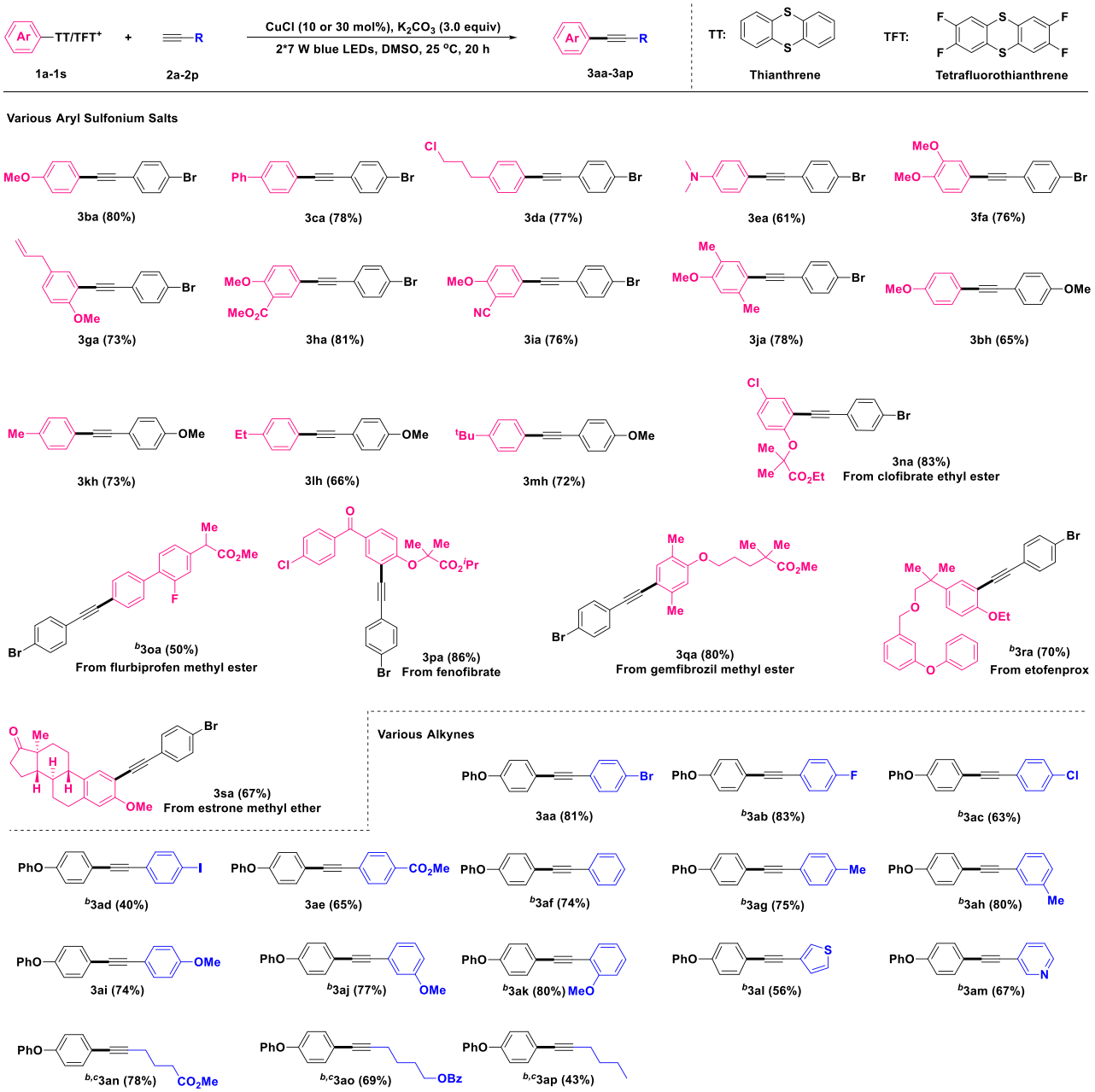
[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), CuCl (10 mol %), and K_2CO_3 (0.6 mmol) in DMSO (2.0 mL) at 25 °C, irradiation with 2 × 7 W blue LED bulbs under N_2 for 20 h. Yields of isolated products.

We investigated the Sonogashira reaction of aryl sulfonium salt **1a** with 1-Br-4-ethynylbenzene **2a** in the presence of a Cu salt as a catalyst under blue light-emitting diode (LED) irradiation. The optimal reaction conditions were determined (Scheme 1; see Tables S1−S7). The desired arylalkyne **3aa** was obtained in good yield under the standard conditions [81% (Table 1, entry 1)]. Control reactions established that the Cu catalyst, base, and light were all essential for the coupling (Table 1, entries 2−4). When dimethyl sulfoxide (DMSO) was replaced with other solvents, the desired product was obtained in lower yields (Table 1, entries 5 and 6; see Table S2). K_2CO_3 was identified as the best base among those investigated (Table 1, entries 7 and 8; see Table S3). Among various Cu salts, CuCl was the best choice (Table 1, entries 9−11; see Table S4). We considered that the ligand may affect the activity of the Cu acetylate complexes and therefore screened different commercially available ligands. The corresponding results show that the use of ligands had little effect on the reaction; only the use of a Cu catalyst (CuCl; no ligand co-additive) as the catalyst was a better choice (see Table S5).

With the optimized reaction conditions in hand, we explored a wider variety of aryl sulfonium salts (Scheme 1, **1b**−**1s**) as the electrophiles. The use of aryl sulfonium salts instead of aryl halides as electrophiles rendered the current Sonogashira coupling method amenable to diverse arenes. Functional groups such as halogen (**3da**), allyl (**3ga**), ester (**3ha**), and cyano (**3ia**) were all tolerated well. Monosubstituted aryl sulfonium salts (**1b**−**1e**) underwent the cross-coupling reaction with 1-Br-4-ethynylbenzene **2a** to give the desired products in good yields. In addition, challenging substrates that bear two or three functional groups on their aromatic rings (**1f**−**1j**) were also suitable substrates. The corresponding products were obtained in moderate to good yields (**3fa**−**3ja**). Highly symmetrical alkynes are an important set of building

https://dx.doi.org/10.1021/acs.orglett.0c02364
Org. Lett. XXXX, XXX, XXX−XXX

Scheme 1. Substrate Scope for C(sp^2)-C(sp) Cross-Coupling[a]



[a]Reaction conditions: **1a−1s** (0.2 mmol), **2a−2m** (0.3 mmol), CuCl (10 mol %), and K_2CO_3 (0.6 mmol) in DMSO (2.0 mL) at 25 °C, irradiation with 2 × 7 W blue LED bulbs under N_2 for 20 h. Yields of isolated products. [b]CuCl (30 mol %). [c]With 0.4 mmol of terminal alkyne (**2n−2p**).

blocks in organic synthesis. 1-Ethynyl-4-methoxybenzene **2h** was selected as an alkyne coupling partner to react with 4-methoxy aryl sulfonium salt **1b**, and 1,2-bis(4-methoxyphenyl) ethyne **3bh** was obtained with ease. 4-Alkyl aryl sulfonium salts were also obtained in good yields (**3kh−3mh**). The protocol could also be extended to the late-stage alkynylation of drugs (**3na−3sa**), which was difficult to accomplish otherwise, demonstrating the potential of this work for the rapid modification of pharmaceuticals.

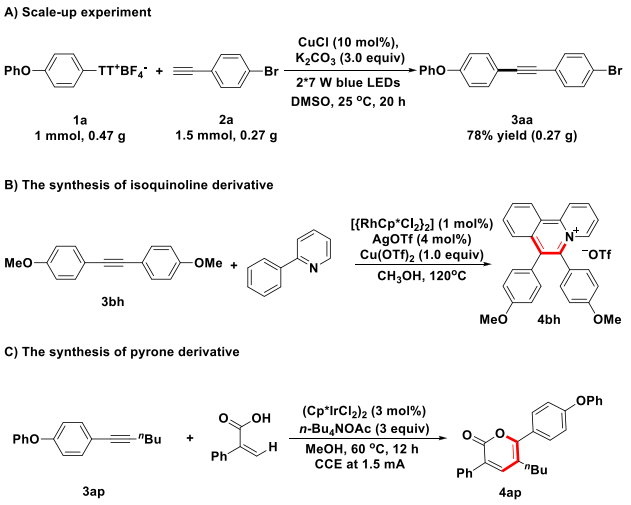
Subsequently, the coupling of 4-phenoxy aryl sulfonium salt **1a** with a series of terminal alkynes was evaluated, and the results were summarized in Scheme 1. Cu acetylide was regarded as the key catalyst of this reaction according to the possible pathways described in Figure 2. During the experiment, we found that changing the alkyne affected the activity of the Cu acetylide intermediate such that the aryl sulfonium salt could not be completely converted in some cases. Fortunately, this problem was solved well by simply increasing the amount of CuCl to 30%. The reactions with phenyl-substituted acetylenes containing diverse electronic properties at the *para* position (**2a−2g**) furnished the corresponding arylalkynes in moderate to good yields (40−83%). Notably, 1-Br-4-ethynylbenzene and 1-I-4-ethynylbenzene (**2a** and **2d**, respectively), which are incompatible with the conventional approach, proceeded well in this coupling, demonstrating its excellent chemoselectivity. The yields of the desired products were maintained when the methoxy group was present at the *meta* or *ortho* position of the phenyl (**3aj** or **3ak**, respectively).

https://dx.doi.org/10.1021/acs.orglett.0c02364
Org. Lett. XXXX, XXX, XXX−XXX

To our delight, the coupling was successful for terminal alkynes with other groups such as thiophene, pyridine, alkyl, and substituted alkyl groups (**2l**–**2p**).

To further explore the prospective use of this methodology, we carried out the scale-up synthesis of arylalkynes. As shown in Scheme 2A, **3aa** was obtained in 78% yield when 1.0 mmol

Scheme 2. Scale-up and Transformations



aryl sulfonium salt **1a** was treated with 1-Br-4-ethynylbenzene **2a** in the presence of 10 mol % CuCl and 3.0 equiv of K_2CO_3. Arylalkynes make up an important class of building blocks in organic synthesis.[11] We therefore examined the applications of arylalkynes in macrocyclic construction. Isoquinolinium salt **4bh** was obtained in 70% yield by treatment of arylalkyne **3bh** with 2-phenylpyridine through oxidative C–H activation and annulation (Scheme 2B). Next, α-pyrone derivative **4ap** was delivered in 78% yield via Ir-catalyzed electrochemical vinylic C–H annulation of 2-phenylacrylic acid with arylalkyne **3ap** (Scheme 2C).

In summary, the photoinduced site-selective Cu-catalyzed Sonogashira coupling of aryl sulfonium salts with terminal alkynes was demonstrated. This coupling method enables rapid transformation of readily available arenes into arylalkynes, which are important building blocks in synthetic chemistry. The successful alkynylation of arenes, many of which contain sensitive functional groups (e.g., alkene, ester, cyano, or heterocyclic groups), underscores the high chemoselectivity and functional-group tolerance of this method. Moreover, the site-selective alkynylation of drug molecules was realized. This work substantially expands the scope of the metal-catalyzed $C(sp^2)$–$C(sp)$ coupling reaction and provides a facile synthesis strategy for the construction of diversely functionalized arylalkynes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c02364.

Experimental procedures, synthesis of the starting materials, and compound characterization data (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Lei Liang – *School of Chemistry and Chemical Engineering, Henan Institute of Science and Technology, Xinxiang, Henan 453003, China*; orcid.org/0000-0002-4945-122X; Email: skyliang1126@hist.edu.cn

Hong-Ying Niu – *School of Chemistry and Chemical Engineering, Henan Institute of Science and Technology, Xinxiang, Henan 453003, China*; Email: niuhy_@163.com

Authors

Ren-Long Li – *School of Chemistry and Chemical Engineering, Henan Institute of Science and Technology, Xinxiang, Henan 453003, China*

Yao-Fei Wang – *School of Chemistry and Chemical Engineering, Henan Institute of Science and Technology, Xinxiang, Henan 453003, China*

Jin-Kai Yan – *School of Chemistry and Chemical Engineering, Henan Institute of Science and Technology, Xinxiang, Henan 453003, China*

Chang-Gong Li – *School of Chemistry and Chemical Engineering, Henan Institute of Science and Technology, Xinxiang, Henan 453003, China*

Hai-Ming Guo – *School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, China*; orcid.org/0000-0003-0629-4524

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.0c02364

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors are grateful for the financial support from the National Natural Science Foundation of China (U1604283 and 51903073).

■ REFERENCES

(1) (a) Diederich, F.; Stang, P. J.; Tykwinski, R. R., Eds. *Acetylene Chemistry*; Wiley-VCH: Weinheim, Germany, 2005. (b) Wang, D.; Gao, S. Sonogashira coupling in natural product synthesis. *Org. Chem. Front.* **2014**, *1*, 556. (c) Xie, J.; Bogliotti, N. Synthesis and Application of Carbohydrate-Derived Macrocyclic Compounds. *Chem. Rev.* **2014**, *114*, 7678. (d) Mphahlele, M. J.; Maluleka, M. M. Advances in Metal-Catalyzed Cross-Coupling Reactions of Halogenated Quinazolinones and Their Quinazoline Derivatives. *Molecules* **2014**, *19*, 17435. (e) Karak, M.; Barbosa, L. C. A.; Hargaden, G. C. Recent mechanistic developments and next generation catalysts for the Sonogashira coupling reaction. *RSC Adv.* **2014**, *4*, 53442. (f) Bagley, M. C.; Dale, J. W.; Merritt, E. A.; Xiong, X. Thiopeptide Antibiotics. *Chem. Rev.* **2005**, *105*, 685.

(2) Chinchilla, R.; Nájera, C. The Sonogashira Reaction: A Booming Methodology in Synthetic Organic Chemistry. *Chem. Rev.* **2007**, *107*, 874.

(3) (a) Tlahuext-Aca, A.; Hopkinson, M. N.; Sahoo, B.; Glorius, F. Dual Gold/Photoredox-Catalyzed C(sp)-H Arylation of Terminal Alkynes with Diazonium Salts. *Chem. Sci.* **2016**, *7*, 89. (b) Fabrizi, G.; Goggiamani, A.; Sferrazza, A.; Cacchi, S. Sonogashira Cross-Coupling of Arenediazonium Salts. *Angew. Chem., Int. Ed.* **2010**, *49*, 4067. (c) Chen, Q.; Gao, F.; Tang, H.; Yao, M.; Zhao, Q.; Shi, Y.; Dang, Y.; Cao, C. Sonogashira Cross-Coupling of Aryltrimethylammonium Salts. *ACS Catal.* **2019**, *9*, 3730. (d) Zhao, Y.; Song, Q. Palladium-catalyzed aerobic oxidative cross-coupling of arylhydrazines with terminal alkynes. *Chem. Commun.* **2015**, *51*, 13272. (e) Jiang, Q.; Li,

H.; Zhang, X.; Xu, B.; Su, W. Pd-Catalyzed Decarboxylative Sonogashira Reaction via Decarboxylative Bromination. *Org. Lett.* **2018**, *20*, 2424.

(4) (a) Berger, F.; Plutschack, M. B.; Riegger, J.; Yu, W.; Speicher, S.; Ho, M.; Frank, N. C.; Ritter, T. Site-selective and versatile aromatic C−H functionalization by thianthrenation. *Nature* **2019**, *567*, 223. (b) Reduction potential of aryl sulfonium salt **1b**: $E_{1/2}$ = −1.05 V (see page S12 of the Supporting Information).

(5) (a) Shanmugam, M.; Sagadevan, A.; Charpe, V. P.; Pampana, V. K. K.; Hwang, K. C. Cu_2O Nanocrystals-Catalyzed Photoredox Sonogashira Coupling of Terminal Alkynes and Arylhalides Enhanced by CO_2. *ChemSusChem* **2020**, *13*, 287. (b) Monnier, F.; Turtaut, F.; Duroure, L.; Taillefer, M. Copper-Catalyzed Sonogashira-Type Reactions Under Mild Palladium-Free Conditions. *Org. Lett.* **2008**, *10*, 3203. (c) Carril, M.; Correa, A.; Bolm, C. Iron-Catalyzed Sonogashira Reactions. *Angew. Chem., Int. Ed.* **2008**, *47*, 4862.

(6) (a) Li, J.; Chen, J.; Sang, R.; Ham, W.-S.; Plutschack, M. B.; Berger, F.; Chabbra, S.; Schnegg, A.; Genicot, C.; Ritter, T. Photoredox catalysis with aryl sulfonium salts enables site-selective late-stage fluorination. *Nat. Chem.* **2020**, *12*, 56. (b) Xu, P.; Zhao, D.; Berger, F.; Hamad, A.; Rickmeier, J.; Petzold, R.; Kondratiuk, M.; Bohdan, K.; Ritter, T. Site-Selective Late-Stage Aromatic [^{18}F] Fluorination via Aryl Sulfonium Salts. *Angew. Chem., Int. Ed.* **2020**, *59*, 1956. (c) Alvarez, E. M.; Plutschack, M. B.; Berger, F.; Ritter, T. Site-Selective C−H Functionalization−Sulfination Sequence to Access Aryl Sulfonamides. *Org. Lett.* **2020**, *22*, 4593. (d) Sang, R.; Korkis, S. E.; Su, W.; Ye, F.; Engl, P. S.; Berger, F.; Ritter, T. Site-selective C-H oxygenation via Aryl Sulfonium Salts. *Angew. Chem., Int. Ed.* **2019**, *58*, 16161. (e) Ye, F.; Berger, F.; Jia, H.; Ford, J.; Wortman, A.; Börgel, J.; Genicot, C.; Ritter, T. Aryl Sulfonium Salts for Site-Selective Late-Stage Trifluoromethylation. *Angew. Chem., Int. Ed.* **2019**, *58*, 14615. (f) Engl, P. S.; Häring, A. P.; Berger, F.; Berger, G.; Pérez-Bitrián, A.; Ritter, T. C-N Cross-Couplings for Site-Selective Late-Stage Diversification via Aryl Sulfonium Salts. *J. Am. Chem. Soc.* **2019**, *141*, 13346.

(7) Tian, Z.-Y.; Wang, S.-M.; Jia, S.-J.; Song, H.-X.; Zhang, C.-P. Sonogashira Reaction Using Arylsulfonium Salts as Cross-Coupling Partners. *Org. Lett.* **2017**, *19*, 5454.

(8) (a) Hazra, A.; Lee, M. T.; Chiu, J. F.; Lalic, G. Photoinduced Copper-Catalyzed Coupling of Terminal Alkynes and Alkyl Iodides. *Angew. Chem., Int. Ed.* **2018**, *57*, 5492. (b) Mao, R.; Frey, A.; Balon, J.; Hu, X. Decarboxylative C(sp^3)-N cross-coupling via synergetic photoredox and copper catalysis. *Nat. Catal.* **2018**, *1*, 120. (c) 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. (d) Ratani, T. S.; Bachman, S.; Fu, G. C.; Peters, J. C. Photoinduced, Copper-Catalyzed Carbon-Carbon Bond Formation with Alkyl Electrophiles: Cyanation of Unactivated Secondary Alkyl Chlorides at Room Temperature. *J. Am. Chem. Soc.* **2015**, *137*, 13902. (e) Sagadevan, A.; Hwang, K. C. Photo-Induced Sonogashira C-C Coupling Reaction Catalyzed by Simple Copper(I) Chloride Salt at Room Temperature. *Adv. Synth. Catal.* **2012**, *354*, 3421.

(9) (a) Aukland, M. H.; Šiaučiulis, M.; West, A.; Perry, G. J. P.; Procter, D. J. Metal-free photoredox-catalysed formal C−H/C−H coupling of arenes enabled by interrupted Pummerer activation. *Nat. Catal.* **2020**, *3*, 163. (b) Wu, J.; Wang, Z.; Chen, X.-Y.; Wu, Y.; Wang, D.; Peng, Q.; Wang, P. Para-selective borylation of monosubstituted benzenes using a transient mediator. *Sci. China: Chem.* **2020**, *63*, 336. (c) Varga, B.; Gonda, Z.; Tóth, B. L.; Kotschy, A.; Novák, Z. A Ni−Ir Dual Photocatalytic Liebeskind Coupling of Sulfonium Salts for the Synthesis of 2-Benzylpyrrolidines. *Eur. J. Org. Chem.* **2020**, *2020*, 1466. (d) Huang, C.; Feng, J.; Ma, R.; Fang, S.; Lu, T.; Tang, W.; Du, D.; Gao, J. Redox-Neutral Borylation of Aryl Sulfonium Salts via C−S Activation Enabled by Light. *Org. Lett.* **2019**, *21*, 9688. (e) Otsuka, S.; Nogi, K.; Rovis, T.; Yorimitsu, H. Photoredox-Catalyzed Alkenylation of Benzylsulfonium Salts. *Chem. - Asian J.* **2019**, *14*, 532. (f) Donck, S.; Baroudi, A.; Fensterbank, L.; Goddard, J.-P.; Ollivier, C. Visible-Light Photocatalytic Reduction of Sulfonium Salts as a Source of Aryl Radicals. *Adv. Synth. Catal.* **2013**, *355*, 1477. (g) Péter, Á.; Perry, G. J. P.; Procter, D. J. Radical C−C Bond Formation using Sulfonium Salts and Light. *Adv. Synth. Catal.* **2020**, *362*, 2135. (h) Kozhushkov, S. I.; Alcarazo, M. Synthetic Applications of Sulfonium Salts. *Eur. J. Inorg. Chem.* **2020**, *2020*, 2486. (i) Otsuka, S.; Nogi, K.; Yorimitsu, H. C−S Bond Activation. *Top. Curr. Chem.* **2018**, *376*, 13. (j) Fensterbank, L.; Goddard, J.-P.; Malacria, M.; Ollivier, C. Homolytic Reduction of Onium Salts. *Chimia* **2012**, *66*, 425. (k) Kaiser, D.; Klose, I.; Oost, R.; Neuhaus, J.; Maulide, N. Bond-Forming and -Breaking Reactions at Sulfur(IV): Sulfoxides, Sulfonium Salts, Sulfur Ylides, and Sulfinate Salts. *Chem. Rev.* **2019**, *119*, 8701.

(10) (a) Yam, V. W. W.; Lee, W.-K.; Lai, T. F. Synthesis, spectroscopy, and electrochemistry of trinuclear copper(I) acetylides. X-ray crystal structure of $[Cu_3(\mu\text{-}Ph_2PCH_2PPh_2)_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}C^tBu)(\mu_3\text{-}Cl)]PF_6$. *Organometallics* **1993**, *12*, 2383. (b) Yam, V. W. W.; Lee, W.-K.; Cheung, K. K.; Lee, H.-K.; Leung, W.-P. Photophysics and photochemical reactivities of organocopper(I) complexes. Crystal structure of $[Cu_2(PPh_2Me)_4(\mu,\eta^1\text{-}C{\equiv}CPh)_2]$. *J. Chem. Soc., Dalton Trans.* **1996**, 2889. (c) Yam, V. W.-W.; Kam-Wing Lo, K.; Man-Chung Wong, K. Luminescent polynuclear metal acetylides. *J. Organomet. Chem.* **1999**, *578*, 3.

(11) (a) Yang, Q.-L.; Xing, Y.-K.; Wang, X.-Y.; Ma, H.-X.; Weng, X.-J.; Yang, X.; Guo, H.-M.; Mei, T.-S. Electrochemistry-Enabled Ir-Catalyzed Vinylic C-H Functionalizztion. *J. Am. Chem. Soc.* **2019**, *141*, 18970. (b) Zhang, G.; Yang, L.; Wang, Y.; Xie, Y.; Huang, H. An efficient Rh/O2 catalytic system for oxidative C-H activation/annulation: evidence for Rh(I) to Rh(III) oxidation by molecular oxygen. *J. Am. Chem. Soc.* **2013**, *135*, 8850.

https://dx.doi.org/10.1021/acs.orglett.0c02364
Org. Lett. XXXX, XXX, XXX−XXX