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1,2-Difunctionalization of Acetylene Enabled by Light

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Dedicated to Northwest Normal University on the occasion of its 120th birthday

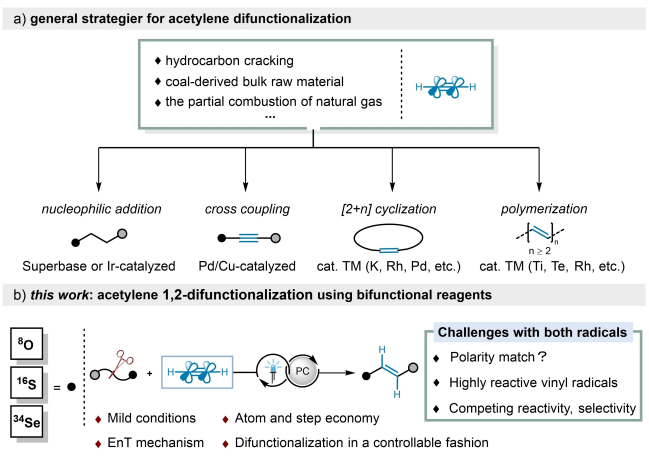
Abstract: Although the direct conversion of gaseous acetylene into value-added liquid commodity chemicals is becoming increasingly attractive, the majority of the established methodologies are focused on cross-coupling, hydro-functionalization, and polymerization. Herein, we describe a 1,2-difunctionalization method that inserts acetylene directly into readily available bifunctional reagents. This method provides access to diverse C2-linked 1,2-bis-heteroatom products in high regio- and stereoselectivity along with opening up previously unexplored synthetic directions. In addition, we demonstrate this method's synthetic potential by converting the obtained products into diverse functionalized molecules and chiral sulfoxide-containing bidentate ligands. Using a combination of experimental and theoretical methods, the mechanism for this insertion reaction was investigated.

Introduction

Acetylene is an abundant, inexpensive, and widely used industrial feedstock. It can be easily obtained through calcium carbide hydrolysis (coal-based), hydrocarbon cracking (petroleum-based), and the partial combustion of natural gas (natural gas-based).[1] Currently, this C2-building block is used to prepare semihydrogenated bulk chemicals, including vinyl acetate, acrylonitrile, acetaldehyde, vinyl chloride monomer (VCM), and propargylic alcohols.[1c] In addition, the iterative 1,2-difunctionalization process serves as a synthetic route for the conjugated polymer-polyacetylene.[2] However, acetylene is not frequently used for the production of fine chemicals. When it is used, the existing techniques are focused on nucleophilic addition,[3] cross-coupling,[4] $[2+n]$ cyclization,[5] and di-/tri-/polymerization[6,7] (Scheme 1a). Despite substantial advances, there is still much to be explored in this domain. For instance, reliable insertion methods for the selective 1,2-difunctionalization of acetylene remain underdeveloped[8] (Scheme 1a), likely due to intrinsic reactivity differences between acetylene and its homologs.[9]

Sulfur, which has diverse oxidation states, is used in many fields including agrochemicals, natural products, functional materials, and biochemistry.[10] For example, approximately 20 % of the top 200 U.S. small-molecule pharmaceuticals are sulfur-containing moieties,[11] and this percentage is growing. Among various organosulfur compounds, a two-carbon unit with a heteroatom on each carbon is frequently found. Bioactive molecules containing this substructural unit often have superior pharmacokinetic features.[10d–g] Furthermore, these types of compounds are important synthetic intermediates and reagents used in many transformations.[12a–b] They are also used in the preparation of materials and polymers.[12c]

As such, the development of efficient methods that expand the available C2-linked 1,2-bis-heteroatom components is of great importance for medicinal and synthetic chemistry. From a retrosynthetic perspective, 1,2-difunctionalization of alkenes and alkynes is an appealing approach for the rapid construction of these components in an atom- and step-economic pathway. Nevertheless, compared to alkene 1,2-difunctionalization[13] alkyne 1,2-difunctionalization is not well studied. This is presumably due to the related issues of regio- and stereoselectivity.[14] Recently, progress has been made in preparing these valuable structural units from alkynes, such as visible-light photo-



Scheme 1. Development of acetylene 1,2-difunctionalization.

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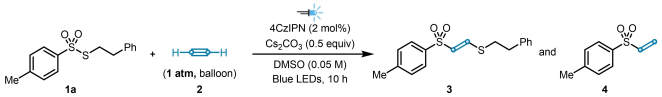
redox catalysis,[15] TBHP/FeX_3-mediated sulfonylation,[16] and ultraviolet light irradiation.[17] Although these approaches are used to create C2-linked molecular architectures, there are some drawbacks. The use of peroxide at elevated temperatures, the need for complex UV irradiation devices, and the significant amounts of waste produced constrain their wide use. Furthermore, existing approaches are limited to using electronically biased alkynes, which stabilize preferred intermediates, to control the product configuration.[18] Therefore, the development of an alternative method to efficiently synthesize the C2-linked molecular architecture directly from acetylene under mild conditions is still needed. Drawing inspiration from the photocatalyzed insertion reaction,[19] we envisioned a bifunctional reagent that could produce two different heteroradicals at an equal rate by energy transfer (EnT)-mediated sigma-bond homolysis. At this point, acetylene captures one of the resultant radicals, producing a vinyl radical intermediate which then quickly couples with the other heteroatom-radical. This prevents acetylene from taking part in hydrofunctionalization or polymerization side reactions. This strategy, if successful, circumvents the drawbacks and unlocks a general and practical insertion strategy for the 1,2-difunctionalization of acetylene. However, using acetylene in the radical protocol has potential pitfalls: First, diffusion-controlled reactions between free radicals result in mixtures of homodimers and cross-coupled products when both radicals have equal lifetimes and are created at the same rate.[20,21] Second, the vinyl radical intermediate generated in situ, is a highly reactive σ radical. The σ radicals tend to undergo undesired "boomerang" radical addition reactions.[3a,22] Therefore the desired radical-radical coupling must meet a kinetic phenomenon (called the persistent radical effect (PRE).[23] Third, the vinyl radicals have two configurations (*Z* and *E*). The *Z*/*E* isomerization is very facile, due to its very low inversion barrier.[24] Finally, acetylene's lack of substituents renders it distinct from its homologs. It may polymerize under an open-shell system to form the undesired linear and cyclic oligomers.[25]

In this article, we describe the photocatalyzed, highly regio- and stereoselective, one-pot 1,2-difunctionalization of acetylene with easily accessible bifunctional reagents to provide a variety of 1,2-bis-heteroatom-capped alkenyl scaffolds. The method was applied to the late-stage functionalization of natural products and pharmaceuticals to install C2-linked 1,2-bis-heteroatom components. This method was also used to create, synthetically valuable chiral sulfoxide-containing bidentate ligand libraries. Experimental and computational mechanistic studies show that the regioselectivity stems from the large reactivity difference between the two different S-centered radical species and the thermodynamic properties of the products.

Results and Discussion

With this hypothesis in mind, we selected an array of potential bifunctional reagents **1a**–**1f** (see Supporting Information) as representative EnT-activated substrates to evaluate the proposed 1,2-difunctionalization reaction. After systematically optimizing the reaction parameters, the optimized reaction conditions were determined to be 4CzIPN as the photocatalyst, Cs_2CO_3 as the Brønsted base additive (to inhibit the undesired side reactions), bifunctional reagent **1a** as the radical precursor, and DMSO as the solvent, taking place at ambient temperature under an atmospheric pressure of acetylene with irradiation from blue light-emitting diodes (LEDs) (see Supporting Information for details). Under the optimized reaction conditions, thiosulfonate **1a** and acetylene **2** gave β-(sulfur)vinyl sulfones **3a** in 62% isolated yield with >98:1 E/Z ratio (Table 1, entry 1). When using other solvents such as CH_3CN, THF, and ethylacetate instead of DMSO, the yield of the sulfur-sulfonylation product **3a** was significantly decreased (entry 2). Adding

Table 1: Optimization of the Reaction Conditions.[a]



Entry	Deviation from standard conditions	Yield of 3[b]	Yield of 4[b]
1	none	65 (62)[c]	n.d.
2	Other solvents instead of DMSO	6–50	5–13
3	No base	49	23
4	$MesAcr^+ClO_4^-$ instead of 4CzIPN	n.d.	n.d.
5	Eosin Y or $Ru(bpy)_3Cl_2$ instead of 4CzIPN	<20%	n.d.
6	Thioxanthone instead of 4CzIPN	34	trace
7	Benzophenone instead of 4CzIPN	28	12
8	$[Ir(bpy)_2(dtbbpy)][PF_6]$ instead of 4CzIPN	49	n.d.
9	No light (dark, 26 h)	n.d.	n.d.
10	No 4CzIPN	trace	trace
11	Acetylene/air ≈4/1 instead of acetylene	32	trace
12	$DMSO/H_2O$ = 10/1 instead of DMSO	63	n.d.

[a] Standard reaction conditions: **1a** (0.1 mmol), 4CzIPN (2 mol%), and Cs_2CO_3 (0.5 equiv) in DMSO (0.05 M) were irradiated with blue light-emitting diodes (λ_{max} = 425 nm) at room temperature with an acetylene balloon (its size was roughly 10 cm in diameter) for 10 h. [b] Yield of the crude product by ^1H NMR using 1,3,5-trimethoxylbenzene as the internal standard. [c] Isolated yield is shown in parentheses.

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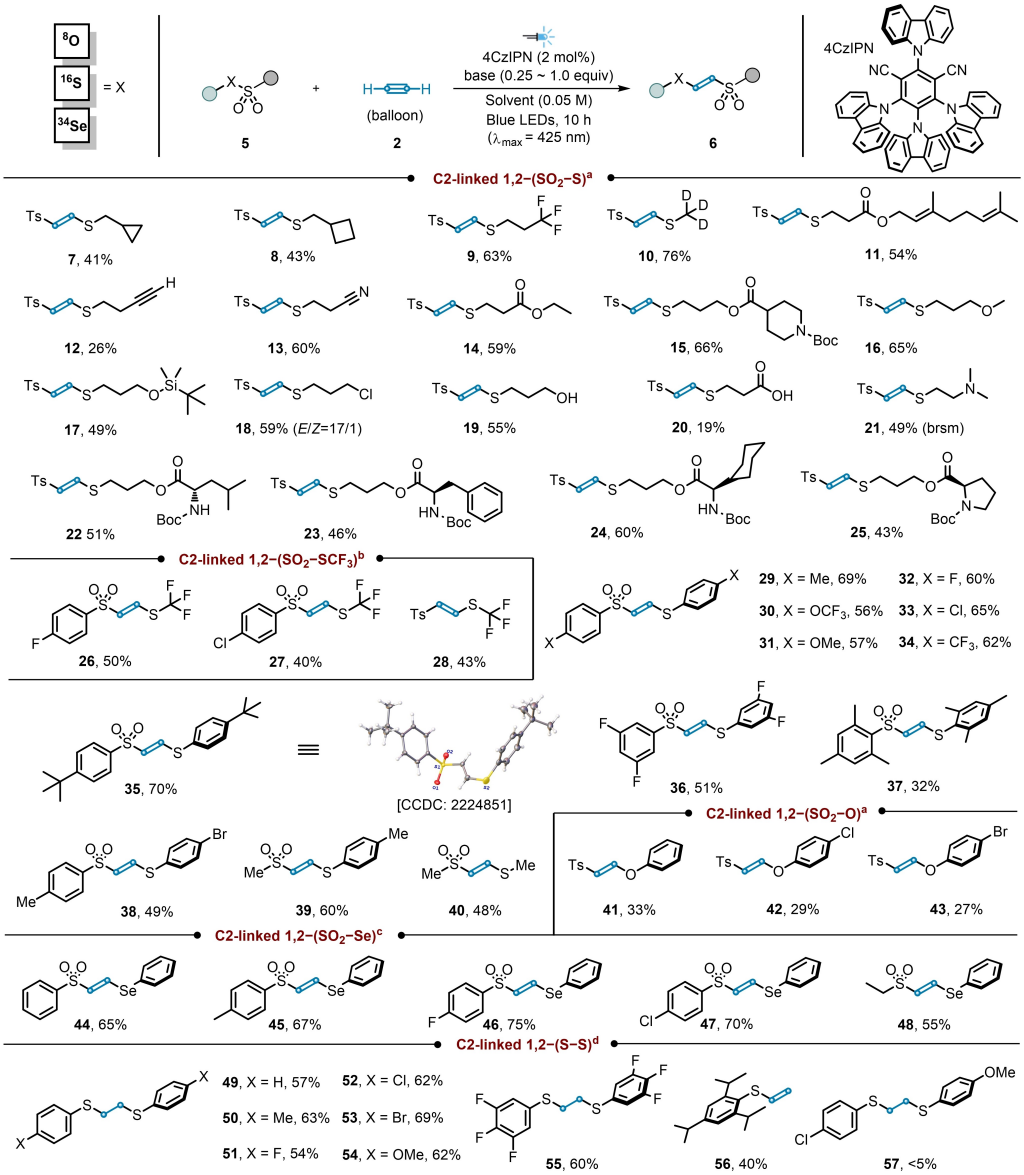
other bases, K_2CO_3 and Li_2CO_3, provided lower yields. Omitting Cs_2CO_3 slightly decreased the yield and a small amount of vinyl sulfone **4** was produced by the H-atom abstraction process (entry 3). These results indicate that the H-atom transfer process can be easily suppressed by the base trapping the proton,[26] without impacting the radical-coupling process. However, changing the photocatalyst to $MesAcr^+ClO_4^-$, eosin Y, or $Ru(bpy)_3Cl_2$ lowered the yield to less than 20% (entries 4 and 5). It's worth noting that benzophenone irradiated at 365 nm or thioxanthone irradiated at 405 nm could provide product **3a** in 34% and 28% yield, respectively (entries 6 and 7). In addition, the more chemically robust Ir^{III} complex was a suitable catalyst, albeit with a slightly diminished yield of product **3** (entry 8). This result suggests that an ET reaction from the excited photocatalyst to the bifunctional reagent **1a** is a possible path. In addition, control experiments revealed that visible light, photocatalyst, anaerobic, and acetylene atmosphere were all essential for the high efficiency of this transformation (entries 9–11). Notably, the presence of water had no noticeable effect on the reaction (entry 12).

With the optimal reaction conditions in hand, the scope of this reaction was systematically investigated using different thiosulfonates. As shown in Scheme 2, a wide range of thio/oxy/seleno-sulfonates **5**, which contained various functional groups, were successfully transformed into diversely



Scheme 2. Substrate scope for 1,2-thio/seleno/oxy-sulfonylation and C2-linked 1,2-bisthioether of acetylene. [a] DMSO (dimethyl sulfoxide), thiosulfonate (0.25 mmol), Cs_2CO_3 (0.5 equiv), 4CzIPN (5.0 μmol, 2.0 mol%). [b] DMC (dimethyl carbonate), trifluoromethylsulfonate (0.25 mmol), $MesAcr^+ClO_4^-$ (5.0 μmol, 2.0 mol%). [c] CH_3CN, 4CzIPN (5.0 μmol, 2.0 mol%), Selenosulfonates (0.25 mmol, 1.0 equiv), pyridine (0.25 mmol, 1.0 equiv). [d] DMC (dimethyl carbonate), disulfide (0.25 mmol), Hantzsch ester (1.0 equiv). Boc = *tert*-butoxymethyl, Ts = 4-toluenesulfonyl. A balloon was filled with acetylene gas until its size was roughly 20 cm in diameter.

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functionalized vinylsulfones **6** libraries with moderate yields and excellent trans-regioselectivity. Although S-alkyl arenethiosulfonates are recognized as challenging substrates in visible-light organic photocatalysis,[13a] we were pleased to find that this type of bifunctional reagent was compatible with our conditions. Unsymmetrical S-alkyl arenethiosulfonates, with cyclopropane, cyclobutene, trifluoromethyl, and methyl-d_3 units, provided the thiosulfonyl difunctionalization products (**7**–**10**). Interestingly, a bifunctional reagent tethered to a trisubstituted olefin was also an amenable substrate (**11**). This indicates that acetylene is more reactive than the tri-substituted olefin in current reaction conditions. To evaluate the selectivity of this transformation, we investigated substrates with the alkynyl or nitrile on the aliphatic chain and found that both gave the desired products (**12** and **13**), although the alkynyl (**12**) in a substantially lower yield probable due to the competing addition reaction. To our delight, several commonly encountered organic functionalities like ester (**14** and **15**), ether (**16** and **17**), and –Cl (**18**), along with unprotected hydroxyl (**19**) and unprotected carboxylic acid (**20**) were compatible substrates. The corresponding 1,2-difunctionalization products could provide versatile synthetic handles for further functionalization. Noteworthy is that a simple tertiary amine also undergoes this insertion reaction (**21** based on recovered starting materials), indicating that reductive quenching is not the main process in our system.[27] The good compatibility was further evidenced by the late-stage alkenylation of complex chiral structures containing protected amino acids, such as L-leucine (**22**), L-phenylalanine (**23**), L-cyclohexylglycine (**24**) and L-proline (**25**). These alkenylations all could take place with no erosion of enantiomeric excess. To better understand this insertion reaction, several other terminal and internal alkynes were used under the optimized reaction conditions. No insertion products were observed when acetylene was replaced by 1,2-diphenylethyne, but-2-yne-1,4-diol, or hept-6-yn-1-ol. However, 1-ethyl-4-ethynylbenzene provided the insertion product, in a relatively lower yield. These results suggest that this reaction might be sensitive to the electronic nature and steric factors of the alkynes (see Supporting Information). The trifluoromethylthio moiety is a highly sought structural motif owing to its intrinsic properties, including its high lipophilicity.[15a] Accordingly, we next switched our attention to the trifluoromethylthiosulfonylation of acetylene. Fortunately, *para*-F, *para*-Cl, and *para*-methyl $ArSO_2SCF_3$ were suitable substrates, delivering the desired products (**26**–**28**) under modified conditions. After the investigation of unsymmetrical S-alkyl arenethiosulfonates, we then turned our attention to symmetrical S-aryl arenethiosulfonates. As shown in Scheme 2, the electronic perturbation of the system did not hamper reactivity (**29**–**36**). The configuration of (**35**) was further confirmed by its X-ray structure. However, the reaction was hampered by *ortho* substituents on the aryl motif (**37**), as the conversion and yield decreased with increased steric bulk of the substituent. In addition, unsymmetrical S-aryl arenethiosulfonates (**38**), S-aryl alkanethiosulfonates (**39**), and even symmetrical S-alkyl alkanethiosulfonates (**40**) were compatible with the current 1,2-difunctionalization reaction. To our delight, we were able to successfully extend this insertion reaction to oxygen and selenium, obtaining the corresponding seleno/oxosulfonylation products. O-aryl tosylates containing the unsubstitued, or substituted (4-Cl, or 4-Br) phenol motifs, easily undergo this insertion reaction to give the desired alkenylation products (**41**–**43**). Existing synthetic strategies for accessing β-(seleno)vinyl sulfone compounds are frequently limited to activated alkynes under metal-catalyzed reactions or yield mixtures of regio- and stereoisomeric products.[14a] However, this 1,2-difunctionalization method chemo- and regioselectivity produces the β-(seleno)vinyl sulfone frameworks (**44**–**48**). Symmetrical C2-linker (S–S) molecules have been employed as unique ligands for the palladium-catalyzed allylic C–H functionalization process.[28a] Thus, we reasoned that if a suitable H-atom transfer agent was used, this protocol could be extended to assemble C2-linked bidentate-ligand skeletons using readily available disulfides as the bifunctional reagent. After the systematic screening of various reaction parameters, the optimal reaction conditions were established as visible-light irradiation and Hantzsch ester as the HAT reagent in a solution of DMC at ambient temperature. As shown at the bottom of Scheme 2, a wide range of disulfides reacted well with acetylene under the newly established conditions to provide C2-inserted scaffolds (**49**–**55**). While polar chemistry can be used to synthesize such scaffolds, they need to use unpleasant-smelling thiophenols.[28] The sterically bulky 1,2-bis(2,4,6-triisopropylphenyl)disulfane could also react with acetylene, but delivering (2,4,6-triisopropylphenyl)(vinyl)sulfane (**56**), which is routinely utilized in organic synthesis, paving the way for versatile follow-up transformations. Unfortunately, when an unsymmetrical disulfide was subject to these insertion conditions, the corresponding insertion product (**57**) was not obtained, probably due to the difference in the selectivity and reactivity of the thiol radicals formed. Eventually, to investigate the effect of pressure on the reaction efficiency and product yield, a simple positive-pressure reaction device was designed. Interestingly, the positive-pressure photoreactor did not improve the reaction yield, but it did shorten the completion time (see Supporting Information).

The high compatibility of the insertion reaction encouraged us to investigate its practicality for late-stage functionalization (Scheme 3). Five non-steroidal drugs that reduce the signs and symptoms of pain and inflammation (loxoprofen, ibuprofen, fenbufen, isoxepac, and oxaprozin) were compatible with the current insertion method, affording products (**58**–**62**). Estrone, a well-known estrogen used to treat perimenopausal and postmenopausal symptoms, gives the desired insertion product (**63**). The S-containing vinyl moiety could be introduced to three anti-arthritic medications (**64**–**66**) using the current 1,2-difunctionalization reaction conditions. In addition, sulbactam (**67**) used to treat infections, febuxostat (**68**) used to manage chronic hyperuricemia, and gemfibrozil (**69**) used to reduce coronary heart disease risk, were all found to be compatible with this insertion reaction.

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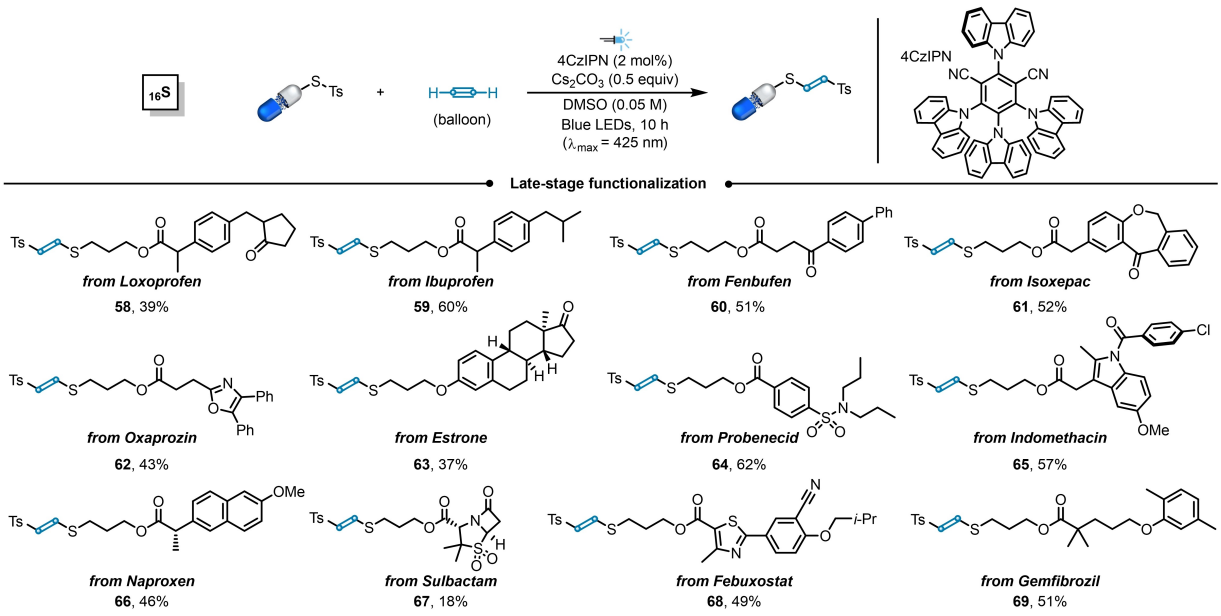
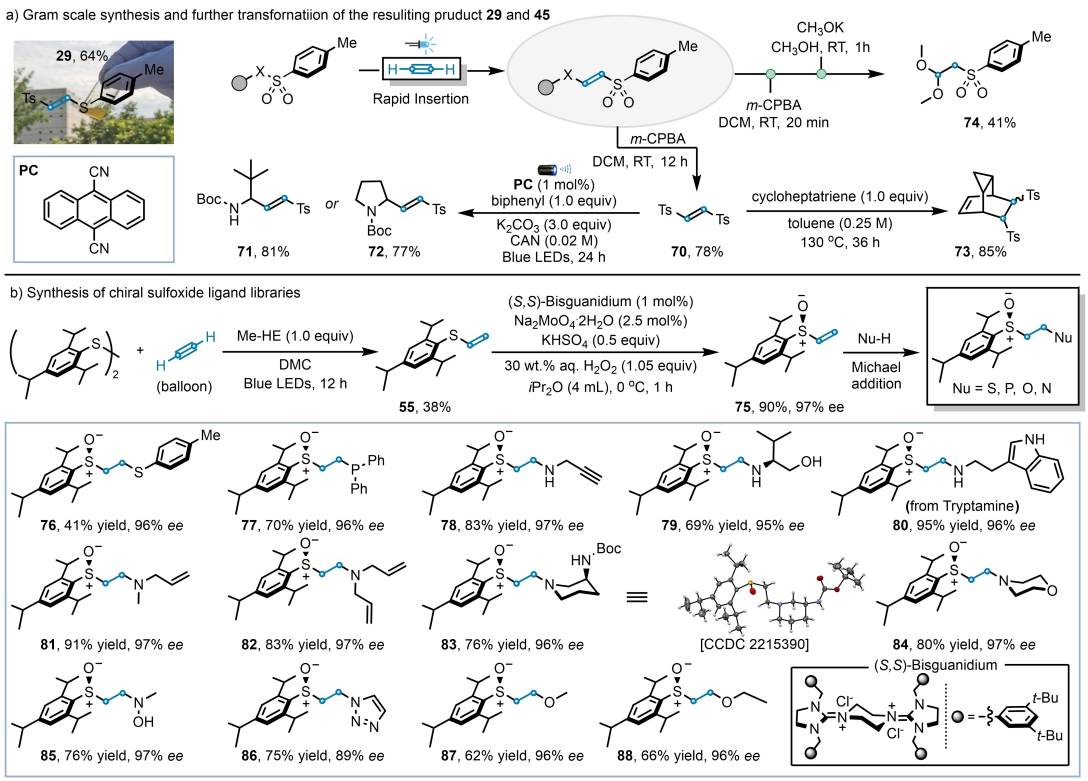


Scheme 3. Applications in Late-Stage Functionalization. Reaction conditions: DMSO (dimethyl sulfoxide), thiosulfonate (0.25 mmol), Cs_2CO_3 (0.5 equiv), 4CzIPN (5.0 μmol, 2.0 mol%), and a balloon were filled with acetylene gas until its size was roughly 20 cm in diameter.

To showcase the robustness of this insertion reaction, product **29** was readily prepared at 5 mmol scales with a yield (64%) comparable to the 0.25 mmol scale (69% yield) (Scheme 4a left). To further demonstrate the potential synthetic applications of this method, the resulting alkenyl insertion products were transformed into diverse valuable building blocks. As shown in Scheme 4a right, treatment of **29** with *m*-CPBA afforded electrophilic intermediate **70**



Scheme 4. Synthetic Application. [a] Gram scale synthesis and further transformation of the resulting products **29** and **45**. [b] Based on the resultant product **55**, chiral sulfoxide ligand libraries were synthesized.

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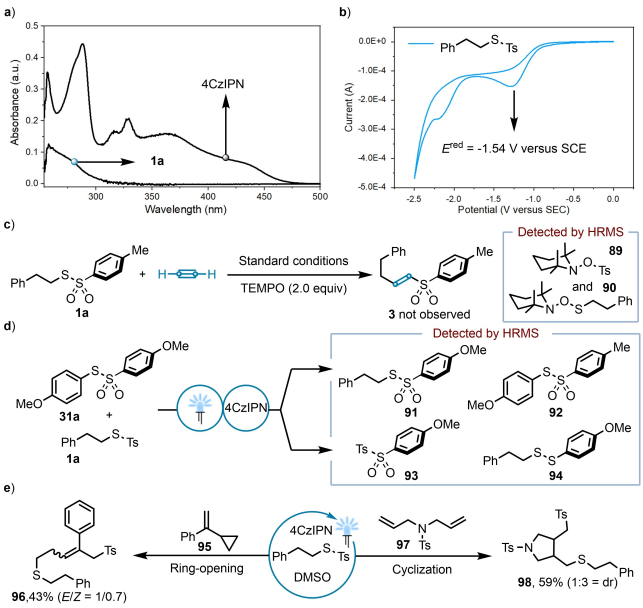
bearing a lower LUMO, which could be further functionalizated. Such as decarboxylative alkenylation with *N*-Boc-L-*tert*-leucine or *N*-Boc-D-prolin to deliver adducts **71** and **72**, respectively, or a Diels–Alder cycloaddition with 1,3,5-cycloheptatriene to give tricyclic product **73**.[29a–b] The product **45** was converted in two steps into the corresponding β-acetal sulfone derivative **74** in 41 % yield.[29c] Furthermore, chiral sulfoxides are well-known as powerful chiral auxiliaries with high to excellent asymmetric inductions.[30] To access them, we first carried out a large-scale (5 mmol) synthesis of(2,4,6- triisopropylphenyl)(vinyl)sulfane **55** without a dramatic reduction in yield.

It was asymmetrically oxidized to the chiral sulfoxide **75** in excellent yields and enantioselectivities with the aid of Tan's bisguanidinium-catalyzed sulfoxidation.[31] Subsequently, a variety of chiral sulfoxide-containing bidentate ligands, (Scheme 4b), were prepared by adding a variety of nucleophiles to the chiral Michael acceptor **75**. Thiol, phosphine, amines (primary and secondary), hydroxylamine, triazole, and alcohols were used as efficient nucleophiles to assemble the chiral ligand library **76–87**. These products contain the CH_2–CH_2 unit with various C–S, C–P, C–N, and C–O bonds. In all these transformations, the enantioselectivities could be well maintained. Furthermore, the absolute configuration of **83** was determined by single-crystal X-ray analysis.[32] These unique chiral skeletons may find applications in future asymmetric catalysis.[30c]

Having evaluated the scope of these photocatalyzed insertion reactions, we carried out mechanistic and computational studies to gain more information about the proposed mechanism. Initially, we investigated the radical generation process. UV/Vis absorption spectroscopy indicated that near the excitation wavelength the photocatalyst, 4CzIPN, is the only light-absorbing species in the reaction mixture (λ_{max} = 450 nm, Scheme 5a). This result rules out the possibility of **1a** or acetylene being directly excited under typical reaction conditions. In addition, fluorescence quenching studies demonstrated **1a** undergoes appreciable bimolecular quenching only with the photocatalyst 4CzIPN (See Supporting Information). When combined with the earlier result that, the alkenylation product **3** yields correlated with the intrinsic triplet energy of the photocatalyst but were unrelated to their redox characteristics, these results hint that an energy transfer process is likely to be operating. Meanwhile, cyclic voltammetry analysis of **1a** found E^{red} = −1.54 V (versus saturated calomel electrode, SCE) in CH_3CN, which excludes the single electron transfer process from *4CzIPN ($*E^{red}$ = −1.04 V). It should be noted that radical initiators, such as azobisisobutyronitrile (AIBN), dibenzoyl peroxide (BPO), and even simple heating, all failed to initiate the reaction, whereas direct ultraviolet-light irradiation could provide **3** in low yield (See Supporting Information for details). These findings suggest that a radical route generated by energy transfer was feasible. To this end, we performed a radical scrambling experiment to investigate the presence of S-centered radical intermediates in the reaction. The reaction was suppressed when (2,2,6,6-tetramethylpiperidin-1-yl)oxyl TEMPO was added, and the observation of TEMPO-adducts (**89** and **90**) by high-



Scheme 5. Investigation of the mechanism. [a] UV/Vis absorption spectroscopy of the reaction components. [b] Cyclic voltammetry studies. [c] TEMPO Experiment. [d] Cross-coupling Reaction. [e] Radical clock experiments.

resolution mass spectrometry (HRMS) suggest the involvement of two different S-centered radical species in this transformation. Moreover, the acetylene-free radical crossover experiment afforded four potential crossover products (**91–94**) that were detected by HRMS, presumably through the uncatalyzed recombination of the free thiol and sulfuryl radicals (Scheme 5d). "Radical clock" experiments with substrates **95** and **97** produced the desired 5-exo-trig cyclization product **98**, and the cyclopropane ring-opening product **96** bolstered the presence of radical intermediates even further (Scheme 5b).

Unlike substituted alkenes, acetylene is a symmetrical molecule possessing two beginning routes to produce the corresponding vinyl radical intermediate. To gain insights into the reaction path and *Z*/*E*-regioselectivity, we turned to dispersion-corrected density functional theory (DFT) calculations, using **1a** as the model substrate. DFT calculations revealed that a radical addition of the thiol radical to acetylene **2** occurs via **TS1**, affording the vinyl radical **II**, while the sulfonyl radical added to acetylene **2** would produce another vinyl radical **III**. Transition state **TS1** is more stable than **TS2** by 3.5 kcal mol^{-1} in Gibbs free energy, which suggests the reaction pathway initiated by the thiol radical is preferred. Then a radical-radical cross-coupling between vinyl radical **II** and the sulfonyl radical would generate the thermally stable *trans* configuration **3** via the minimum energy crossing point (**MECP-1**). Furthermore, the *Z*-configured product **3′** was found to be 3.2 kcal mol^{-1} less stable than the *E*-configuration product **3** due to an increased unstable resonance relationship between the two vicinal substituents. Altogether, the computed reaction pathways are consistent with the observed selectivity, side products, and radical scrambling results. These experimental

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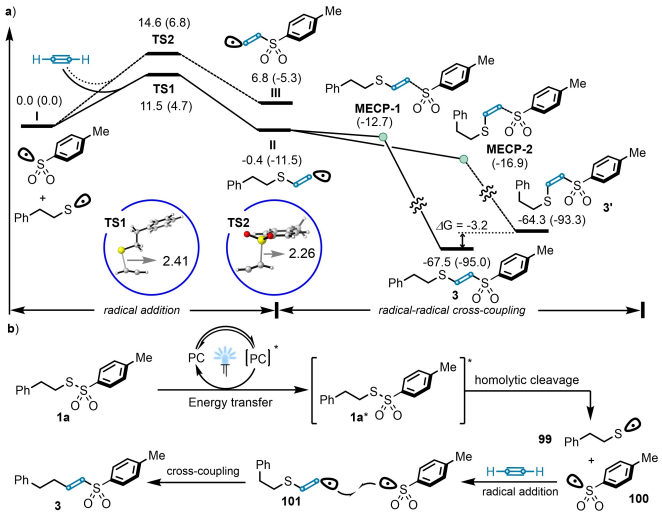
and theoretical results, lead to the proposed reaction mechanism shown in Scheme 6b. Photoexcitation of the organic PC yields the excited state species PC*, which undergoes ET with **1a** to provide the excited state **1a***. Next, **1a*** undergoes a smooth S–S bond cleavage, resulting in a thiol radical **99** and a sulfuryl radical **100**. Subsequent addition of the thiol radical **99** to the acetylenes C≡C leads to the vinyl radical intermediate **101**, in which the newly formed bond length is nearly 2.41 Å. Finally, selective radical-radical cross-coupling between sulfuryl radical **100** and vinyl radical **101** (both of which are σ-radicals) affords the final product **3**. The last step is kinetically feasible based on the persistent radical effect.[21c,23]

Conclusion

In conclusion, we report a general method for the 1,2-difunctionalization of acetylene using a photocatalyzed insertion process. This method, inserts acetylene directly into readily available bifunctional reagents, selectively forming two different C–X bonds. This 1,2-difunctionalization method, done under mild conditions, uses acetylene to access a variety of C2-linked functional structures, with a previously unattainable scope and functional-group tolerance. Applications for the functionalization of natural products and drug molecules are also demonstrated. The resulting S-containing vinyl frameworks are important and versatile scaffolds in synthetic chemistry. The scaffolds can be easily transformed into diverse functionalized molecules and chiral sulfoxide-containing bidentate ligand libraries. Mechanistic studies and DFT calculations provide detailed insight into the reaction mechanism. We hope that this approach will address a long-standing unsolved problem posed by acetylene chemistry and inspire organic chemists to develop more general modes of synthesis for the value-added functionalization of the feedstock acetylene.



Scheme 6. Density functional theory calculations and proposed reaction mechanism. [**a**] Free energy profile for the model reaction calculated at the M06-2X/def2TZVPP-SMD(DMSO)//B3LYP-D3(BJ)/def2SVP-SMD-(DMSO) level of theory. All distances are given in angstroms (Å), and all energies $\Delta G(\Delta E_{ele})$ are shown in kcal mol^{-1}. [**b**] Proposed reaction mechanism for the 1,2-difunctionalization of acetylene.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interests.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: Acetylene · 1,2-Difunctionalization · Olefins · Photochemistry · Radical Chemistry

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[32] Deposition Numbers 2224851 (for **35**) and 2215390 (for **83**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Research Articles

Photocatalysis

S. Lü, Z. Wang, X. Gao, K. Chen,*
S. Zhu* ——— **e202300268**

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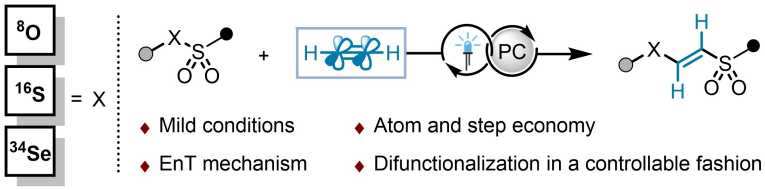

Reported is the regio- and stereoselective light-enabled installation of two distinct sulfides into acetylene. The resulting S-containing vinyl frameworks are important and versatile scaffolds that can be easily transformed into diverse functionalized molecules and chiral sulfoxide-containing bidentate ligands. Experimental and theoretical data on the mechanism are reported.

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