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Letter

Regio- and Stereoselective Photoredox-Catalyzed Atom Transfer Radical Addition of Thiosulfonates to Aryl Alkynes

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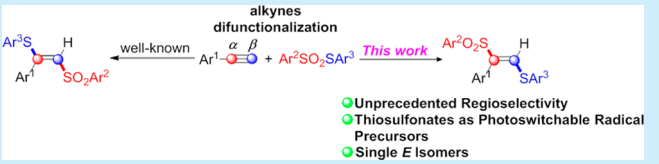
ABSTRACT: Despite extensive investigations, altering the regioselectivity of atom transfer radical addition (ATRA) to alkynes remains a highly desirable yet unachieved challenge. Guided by computational predictions, thiosulfonates were found herein as a tunable radical precursor for thiyl radicals instead of well-recognized sulfonyl radicals. Merging such a finding with ATRA to phenylacetylenes leads to a highly regio- and stereoselective approach to (*E*)-(*β*-arylsulfonylvinyl sulfides. This protocol is feathered by mild conditions, low photocatalyst loading, no transition-metal catalyst required, and broad functional group compatibility. The successful application of our protocol in the late-stage functionalization of bioactive natural product derivatives demonstrates its synthetic utility. Mechanistic studies corroborate the photoredox-catalyzed ATRA pathway and reveal the pivotal role of thiyl radical, to which unprecedented regioselectivity was attributed.



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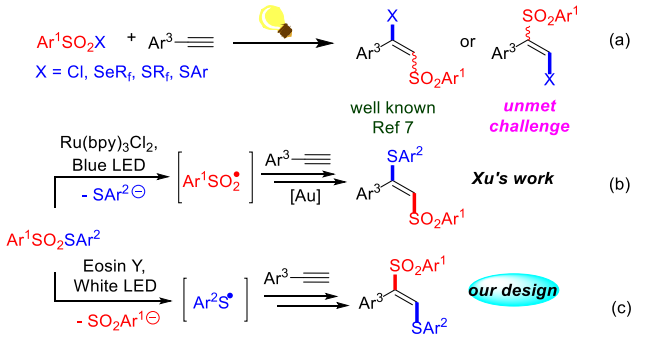
Building on the pioneering work by Kharasch and co-workers,[1] atom transfer radical addition (ATRA) has emerged as one of the most powerful and straightforward methods to install two functional groups across an unsaturated C−C bond in one step.[2] Compared to ATRA of alkenes, the studies on alkynes are overshadowed, probably due to the related issues of stereoselectivity as well as regioselectivity.[3]

Vinyl sulfones, a class of scaffolds of great value in medicinal chemistry[4] and material science,[5] are suitable synthetic targets via a tactic of ATRA to alkynes. In particular, much synthetic effort has been devoted to the development of visible-light photoredox-catalyzed ATRA to alkynes.[6] Nevertheless, challenge of regioselectivity persists, as evidenced by the fact that only *one* type of regioisomeric styrene derivatives bearing a *β*-tosyl group has been reported to date, to the best of our knowledge (Scheme 1a),[7] arising from the overwhelming stability of *α*-aryl alkenyl radical intermediates.

Scheme 1. Representative Photoredox ATRA to Aryl Alkynes



To circumvent the issue of altering regioselectivity of ATRA to alkynes, we envisioned utilizing a radical precursor, which could produce one of the two possible radical intermediates under suitable photoredox conditions, leading to the corresponding regioisomeric addition products, respectively. Under this conjecture, thiosulfonates (RSO_2-SR') have attracted our attention for two major reasons: (1) Thiosulfonates have been widely recognized as a common source of sulfonyl radical.[8] Xu and co-workers reported a gold- and photoredox-co-catalyzed stereoselective ATRA to aryl alkynes with thiosulfonates to deliver (*E*)-(*β*)-arylthiolvinyl sulfones exclusively (Scheme 1b).[7f,h] In this elegant approach, thiosulfonates have been proven as a reliable sulfonyl radical precursor in the presence of $Ru(bpy)_3Cl_2$ as photocatalyst under irradiation of blue LED. (2) Despite the lack of precedence, the generation of thiyl radicals from thiosulfonates is equally feasible from an energetic perspective based on our prediction using density functional theory (see the Supporting Information (SI) for details): single-electron reduction of *S*-(*p*-tolyl)-4-methylbenzenesulfonothioate followed by S−S bond heterolysis was found to favor the formation of thiyl radical ($RS^{\bullet}$) and sulfinate (RSO_2^-) slightly over the formation of sulfonyl radical ($RSO_2^{\bullet}$) and thiolate (RS^-) by 5.1 kcal mol^{-1} in free energy. This computational analysis suggests, under certain conditions, that thiosulfonates could be switched from

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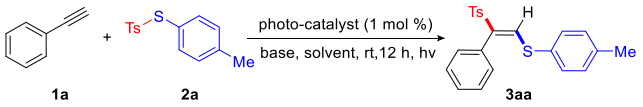
a sulfonyl radical precursor to a thiyl radical precursor and hence achieves the unmet regioselectivity (Scheme 1c) *complementary* to those reported previously.[7f,h] Herein, we report a highly regio- and stereoselective photoredox-catalyzed ATRA to aryl alkynes with thiosulfonates to afford (*E*)-(*β*)-arylsulfonylvinyl sulfides (Scheme 1c). Thiosulfonates were found through mechanistic investigations to exclusively generate thiyl radicals instead of sulfonyl radicals employing Eosin Y as photocatalyst and white LED as light source.

The optimization of reaction conditions commenced by a short survey of three common photocatalysts [$Ru(bpy)_3Cl_2 \cdot 6H_2O$, $Ir(ppy)_3$, and eosin Y] when NaOH served as base in *N*,*N*-dimethylformamide (DMF) under irradiation of green LED (Table 1, entries 1−3). Eosin Y[9] was proven to be

Table 1. Optimization of the Reaction Conditions of Photoredox-Catalyzed ATRA of Phenylacetylene with 2a[a]



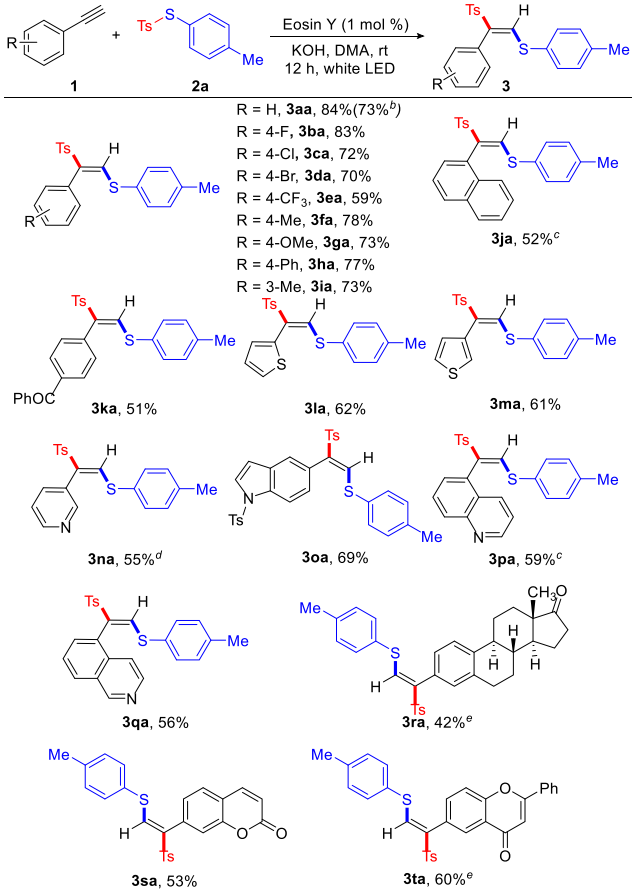
entry	photocatalyst	base	solvent	isolated yield (%)
1	$Ru(bpy)_3Cl_2 \cdot 6H_2O$	NaOH	DMF	21
2	$Ir(ppy)_3$	NaOH	DMF	3
3	Eosin Y	NaOH	DMF	34
4	Eosin Y	$CsOH \cdot H_2O$	DMF	18
5	Eosin Y	KOH	DMF	35
6	Eosin Y	KOH	DMSO	36
7	Eosin Y	KOH	DMA	38
8[b]	Eosin Y	KOH	DMA	53
9[b,c]	Eosin Y	KOH	DMA	84
10[b,c]		KOH	DMA	19
11[b,c]	Eosin Y		DMA	0
12[c,d]	Eosin Y	KOH	DMA	0

[a]Unless otherwise stated, reactions were carried out with **1a** (0.2 mmol), **2a** (0.1 mmol), photocatalyst (1 mol %), base (0.1 mmol) in solvent (1.0 mL) at room temperature under green LED under an argon atmosphere for 12 h. [b]White LED. [c]**1a** (0.1 mmol), **2a** (0.15 mmol). [d]No light.

superior, affording the desired product **3aa** in 34% yield (Table 1, entry 3). Then two other hydroxide bases ($CsOH \cdot H_2O$ and KOH) were investigated (Table 1, entries 4 and 5), and KOH exhibited slightly better reactivity (Table 1, compare entry 5 to entries 3 and 4). Forging ahead with KOH as base, the yield of **3aa** could be elevated to 38% when *N*,*N*-dimethylacetamide (DMA) served as solvent (Table 1, entry 7). The yield of **3aa** was improved to 53% using white LED instead of green LED as the light source (Table 1, entry 8). Adjusting the limiting agent to **1a** while **2a** was employed in 1.5 equiv resulted in 84% isolated yield of **3aa** (Table 1, entry 9). Additionally, only 19% **3aa** was obtained in the absence of eosin Y (Table 1, entry 10), and no desired product was observed in the absence of either light or base (Table 1, entries 11 and 12), which demonstrated the essential roles of eosin Y, light, and base in the catalytic transformation. Therefore, the optimal conditions for photoredox-catalyzed difunctionalization of alkynes was: **1a** as limiting agent, 1.5 equiv of **2a** as addition partner, 1 mol % of Eosin Y as photocatalyst, 1.0 equiv of KOH as base, under irradiation of white LED light at room temperature for 12 h.

With the optimized conditions in hand, we first investigated the substrate scope of alkynes in photoredox-catalyzed ATRA with **2a** (Scheme 2). The parent phenylacetylene **1a** could react with **2a** to generate **3aa** in 73% yield (1.0 mmol scale),

Scheme 2. Substrate Scope of Aryl Acetylenes in Photoredox-Catalyzed ATRA with 2a[a]



[a]Reaction conditions: **1** (0.1 mmol), **2a** (0.15 mmol), Eosin Y (1 mol %), KOH (0.1 mmol), DMA (1.0 mL), 12 h, white LED under argon. [b]**1** (1.0 mmol), **2a** (1.5 mmol), Eosin Y (1 mol %), KOH (1.0 mmol), DMA (10.0 mL). [c]14 h. [d]Eosin Y (1 mol %), 36 h. [e]**2a** (0.2 mmol), Eosin Y (2 mol %).

demonstrating the synthetic utility of our protocol. Aryl alkynes bearing electron-withdrawing groups, such as *p*-F, -Cl, -Br, and $-CF_3$, were well tolerated by our protocol, affording **3ba**−**3ea** in 59−83% yields. Electron-donating substituents on aryl alkynes (**1f**−**h**) exerted negligible influence on the outcome of the catalysis, providing **3fa**−**3ha** in good yields. *m*-Tolylacetylene was also suitable for the reaction, giving **3ia** in 73% yield. Sterically hindered 1-naphthylacetylene **1j** could be employed as substrate as well, and **3ja** was successfully afforded in slightly diminished yield. The benzoyl group was compatible with the catalytic conditions, furnishing **3ka** in modest yield. Remarkably, this chemistry was also well accommodated by heteroaryl alkynes to generate **3la**−**3qa** with good results, highlighting the expediency and breadth of this protocol. The configuration of **3ma** was unambiguously determined by X-ray crystallography analysis (see the SI for details). Aryl acetylenes derived from commercially available pharmacores, such as estrone (**1r**), coumarin (**1s**), and flavone (**1t**), could be easily introduced with arylsulfonyl and arylthiyl groups under the standard conditions in synthetically useful yields (42−60%). This approach provides a practical tool for

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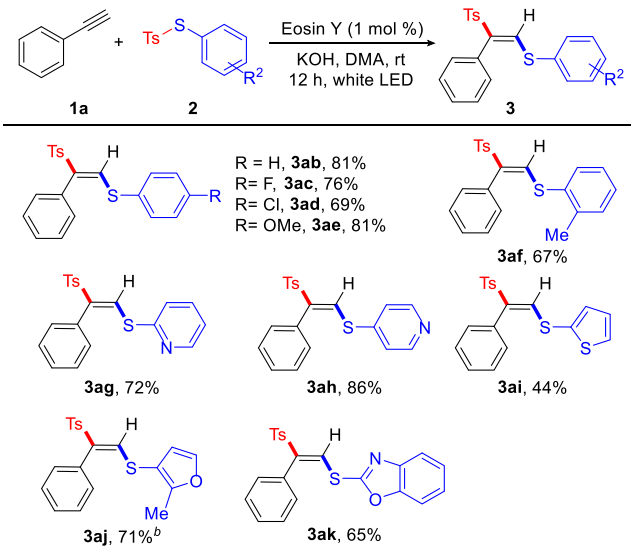
the late-stage modification of bioactive natural products and drugs.

We next turned our attention to the substrate generality of *S*-aryl thiosulfonates **2** in photocatalyzed ATRA with **1a** (Scheme 3). Substrates possessing the electron-withdrawing

Scheme 3. Substrate Scope of *S*-Aryl-4-Methylbenzenesulfonothioates in Photoredox-Catalyzed ATRA with 1a[a]

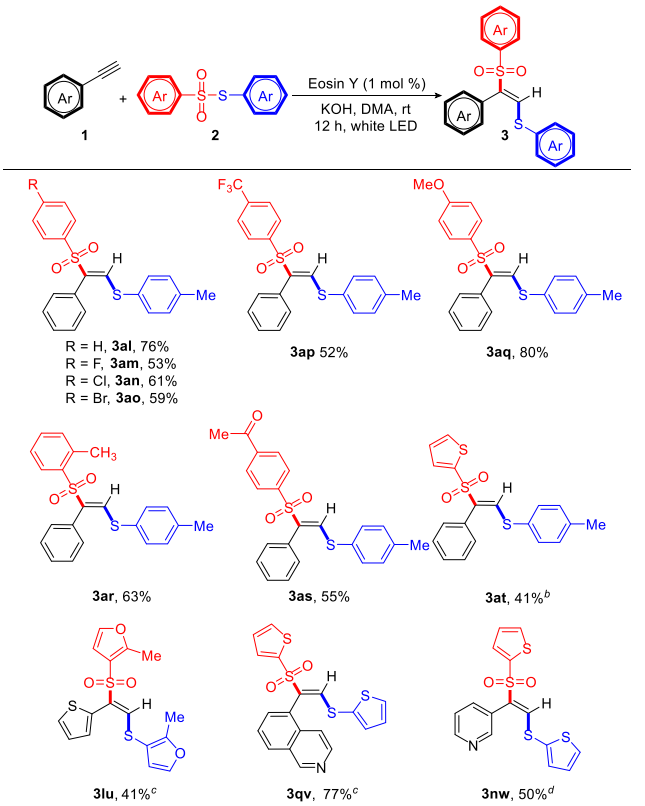


[a]Reaction conditions: **1a** (0.1 mmol), **2** (0.15 mmol), Eosin Y (1 mol %), KOH (0.1 mmol), DMA (1.0 mL), 12 h, white LED under argon. [b]**2j** (0.2 mmol), Eosin Y (2 mol %).

groups, such as 4-F (**2c**) and 4-Cl (**2d**), furnished **3ac** and **3ad** in 76% and 69% yield, respectively. *S*-Aryl thiosulfonates with electron-donating groups, exemplified by **2e**, were well tolerated, giving **3ae** in 81% yield. The sterically demanding 2-tolylthiosulfonates **2f** reacted with **1a** smoothly under the optimal conditions to afford **3af** in 67% yield. It is noteworthy that *S*-heteroaryl thiosulfonates bearing 2-pyridinyl (**2g**), 4-pyridinyl (**2h**), 2-thienyl (**2i**), 2-methyl-3-furanyl (**2j**), and 2-benzoxazole (**2k**) moieties could be successfully employed as addition substrates to prepare the corresponding products in yields ranging from 44% to 86%.

Furthermore, the substrate scope of a variety of arylsulfonyl methyl thiosulfonates **2** in ATRA with phenylacetylene (**1a**) was examined (Scheme 4). The parent phenylsulfonyl thiosulfonates (**2l**) reacted smoothly with **1a** to provide **3al** in 76% yield. Substrates bearing the electron-withdrawing 4-F (**2m**), 4-Cl (**2n**), 4-Br (**2o**), or 4-CF_3(**2p**) groups furnished the corresponding products (**3am**−**3ap**) in 52−61% yields. Electron-donating 4-OMe on arylsulfonyl thiosulfonate was well suited for the catalytic transformation, giving **3aq** in 80% yield. Sterically hindered 2-tolylsulfonyl thiosulfonates (**1r**) underwent addition reaction with **1a** to give **3ar** in 63% yield. *S*-(*p*-Tolyl)-4-acetylbenzenesulfonothioate (**2s**) could also be successfully utilized under our standard conditions. To our delight, heteroarylsulfonyl thiosulfonate **3t** bearing a 2-thienyl moiety could afford **3at** via this route, albeit in lower yield (41%). Our photoredox-catalyzed addition protocol could be successfully applied to the synthesis of trisubstituted alkenes bearing heteroaryl, heteroaryl thiyl and heteroaryl sulfonyl groups (**3lu**, **3qv**, and **3nw**), a class of compounds which are

Scheme 4. Substrate Scope of *S*-*p*-Tolylarylsulfonothioates in Photoredox-Catalyzed ATRA with 1a and Synthetic Application of Trisubstituted Alkenes with Three Heteroaryl Moieties[a]



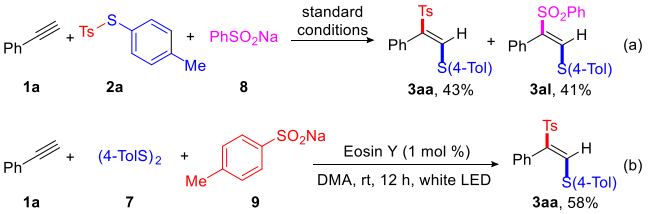
[a]Reaction conditions: **1a** (0.1 mmol), **2** (0.15 mmol), eosin Y (1 mol %), KOH (0.1 mmol), DMA (1.0 mL), 12 h, white LED under argon. [b]**2t** (0.2 mmol), Eosin Y (2 mol %). [c]**2u** or **2v** (0.2 mmol). [d]Eosin Y (2 mol %).

challenging to prepare previously as evidenced by lack of precedence in literature.

To probe the rationale of the unexpected regioselectivity, a series of mechanistic experiments have been performed. First, we observed that this addition process required continuous visible-light irradiation based on the results of light "on−off" experiment (see the SI for details), which indicates that the present reaction proceeds likely through a photoredox catalytic process rather than a radical-chain pathway.[10]

When sodium benzensulfinate (**8**) was subjected to the standard reactions with **1a** and **2a**, both the desired products **3aa** derived from **1a** and **2a** and the crossover product **3al** from **1a**, **2a**, and **8** were obtained in similar yields (Scheme 5a), indicating the character of sulfonyl group is indeed an *anion* instead of a *radical*. Following this hypothesis, disulfides

Scheme 5. Crossover Experiments



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7 and 9 were utilized together as addition partners in place of 2a, and the desired product 3aa was successfully afforded in 58% yield (Scheme 5b). To gain more insight into the catalytic mechanism, 2,2,6,6-tetramethylpiperidinooxy (TEMPO) as a radical scavenger was subjected to our standard conditions. As we expected, the reaction was significantly inhibited; in addition, thiyl radical was trapped by TEMPO to yield the products 10 (see the SI for details).[11] Moreover, introduction of 1 equiv of 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) into the standard catalytic reaction between 1a and 2a resulted in the isolation of radical trapped complex 11, which was identified by electron paramagnetic resonance spectroscopy (EPR)[12] and HRMS analysis (see the SI for details). These results collectively led to the conclusion that thiyl radicals generated from thiosulfonates are indeed the key intermediate in our photoredox-catalyzed addition reactions. The Stern−Volmer experiment of eosin Y by 1a and 2a (see the SI for details) clearly indicates that the excited state of eosin Y was quenched by 2a, whereas 1a exhibited no quenching effect at all.

Based on the aforementioned results, a plausible mechanism is illustrated (Figure 1). Photocatalytic cycle begins with

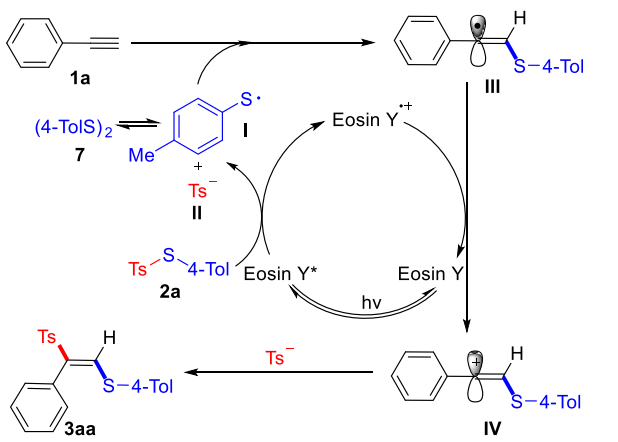

Figure 1. Proposed mechanism of photoredox-catalyzed ATRA reactions of alkynes with thiosulfonates.

oxidative quenching of the excited-state eosin Y*[13] by thiosulfonates 2a to yield the thiyl radical **I** and Ts anion **II**. The thiyl radical **I**[14] is added to phenylacetylene to afford the α-alkenyl carbon radical (**III**), which is then single-electron oxidized by eosin $Y^{\bullet+}$ to deliver the benzyl alkenyl cation **IV**, and regenerate the ground-state Eosin Y to close up the photocatalytic cycle at the same time. Finally, the target product 3aa was produced from the nucleophilic attack of Ts anion (**II**) to alkenyl cation **III**. The role of base in our protocol is believed to enhance the absorbance of eosin Y via an acid−base interaction.[15]

In conclusion, we have developed a photoredox-catalyzed ATRA reaction to aryl alkynes with thiosulfonates to prepare (*E*)-(β)-arylsulfonylvinyl sulfides in excellent regio- and stereoselectivity. Our protocol features mild reaction conditions, various functional groups, low catalyst loading, and no transition-metal catalyst. To demonstrate its synthetic utility, this ATRA method was successfully applied in the late-stage functionalization of bioactive natural product derivatives. The mechanistic studies support a photoredox-catalyzed pathway. In the presence of eosin Y under irradiation of white LED, thiosulfonates were developed to be a competent precursor for thiyl radicals instead of well-recognized sulfonyl radicals, leading to the unprecedented regioselectivity of our protocol. This work not only offers a facile access to (*E*)-(β)-sulfonylvinyl sulfides but also provides a basis for the photoswitchable radical formation in other contexts.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01982.

Detailed experimental procedures, characterization data, and NMR spectra of new compounds (PDF)

Accession Codes

CCDC 1948420 contains the supplementary crystallographic data (**3ma**) for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

T.J. designed and supervised the project. Z.P. and H.Z. performed the experiments. H.Y. conducted the computational studies. T.J. and Z.P. analyzed the results and wrote the paper.

Notes

The authors declare no competing financial interest.

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X-ray crystallography analysis, and EPR fitting data, respectively.

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