ORGANIC CHEMISTRY
FRONTIERS

RESEARCH ARTICLE

View Article Online
View Journal | View Issue

Cite this: *Org. Chem. Front.*, 2025, **12**, 3454

Received 5th February 2025,
Accepted 11th March 2025

DOI: 10.1039/d5qo00248f

rsc.li/frontiers-organic

Electrochemical C(sp^3)–S bond cleavage of thioethers: an approach for simultaneous utilization of carbon- and sulfur-fragments†

Jiawei Huang, Xiaoman Li, Liang Xu * and Yu Wei *

The cleavage and utilization of C–S bonds is a critical challenge in synthetic chemistry, traditionally requiring metal catalysis and disposing of sulfur fragments as wastes. Herein, we report an electrochemical method for the regioselective cleavage of C(sp^3)–S bonds of alkyl aryl thioethers under mild conditions. This electro-oxidative approach generates the corresponding cationic species of both C- and S-fragments after the cleavage of the C–S bonds. Subsequently, these species are captured by O-nucleophiles and converted into aldehydes/ketones and sulfinates. The simultaneous utilization of both C- and S-fragments not only significantly enhances the atom economy but also offers a sustainable alternative to traditional C–S bond cleavage strategies.

Introduction

The construction and cleavage of the carbon–sulfur (C–S) bond, a fundamental structural motif in a vast array of biologically active compounds, pharmaceuticals, agrochemicals, and functional materials, holds a pivotal place in synthetic chemistry.[1–4] To cleave C–S bonds, prefabricated high-valent or charged organosulfur compounds are usually employed.[5,6] For instance, sulfur in the +IV oxidation state can achieve classic Pummerer rearrangement[7] and Mislow–Braverman–Evans rearrangement.[8] In contrast, the direct C–S bond cleavage of thioethers is relatively underdeveloped.

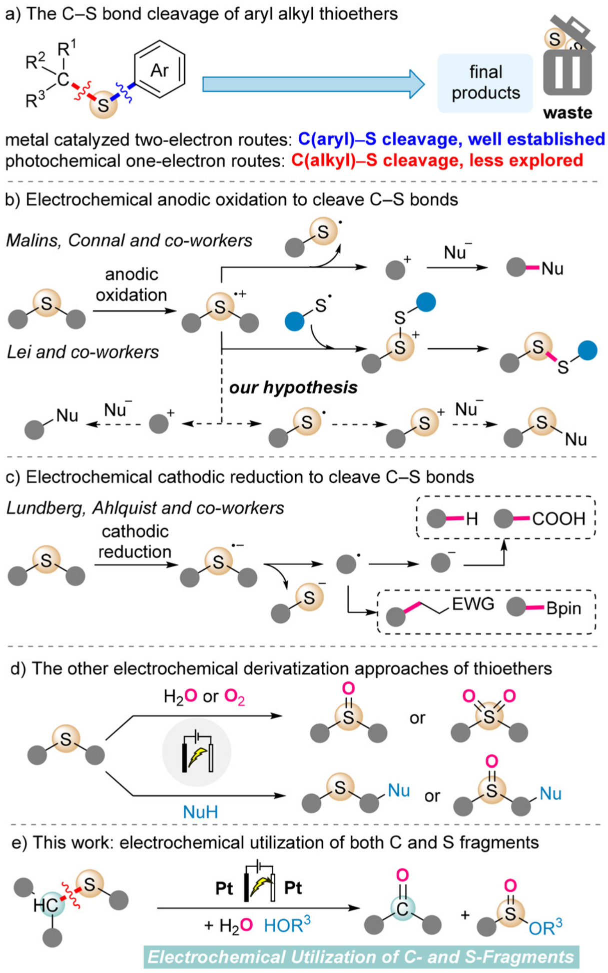
More specifically, to cleave unsymmetrical alkyl aryl thioethers, the well-established transition metal-catalyzed two-electron oxidative addition processes selectively target the C(sp^2)–S bonds,[9–11] and thus offer valuable cross-coupling methods for constructing C(sp^2)–C and C(sp^2)–heteroatom bonds.[12–19] Although less explored, several one-electron protocols have recently been disclosed, inducing the cleavage of C(sp^3)–S bonds regioselectively.[12,20–23] No matter *via* which approach, such transformations usually suffer from the wasteful disposal of sulfur fragments (Scheme 1a), which not only diminishes the atom economy but also squanders potential synthetic opportunities.[24–26] Therefore, the development of more atom-economical strategies for the C–S bond cleavage of thioethers, which allow for the full utilization of C- and S-fragments, is of paramount importance.

The burgeoning growth of electrochemical organic synthesis not only offers sustainable alternatives to conventional synthetic routes but also enables new reactivity and selectivity under mild conditions.[27–31] *Via* utilizing electrons as traceless reagents in redox reactions directly, electrochemical synthesis circumvents the need for stoichiometric chemical oxidants or reductants and thus proceeds with minimal waste.[32–35] In this regard, electrochemical C–S bond activation has also demonstrated significant progress recently, converting thioethers into diverse products.[36,37]

For example, in 2023, the Malins and Connal group[38,39] and the Lei group[40] disclosed two elegant protocols for anodic oxidation induced C–S cleavage of thioethers, independently (Scheme 1b). In both cases, the transformations are believed to be induced by the initially oxidatively formed radical cation species. In the former case, starting from *N*,*S*-acetals, this species decomposes into thiyl radicals and iminium intermediates, which are trapped by *O*-nucleophiles to deliver *N*,*O*-acetals. In the latter case, this species is trapped by another thiyl radical, affording disulfides finally. In the same year, Lundberg, Ahlquist and co-workers disclosed a protocol for electrochemical reductive C–S cleavage of aryl alkyl thioethers (Scheme 1c).[41,42] Alkyl radicals are generated efficiently, which can subsequently be reduced to alkyl anions, thereby participating in a series of desulfurization and functionalization processes. Despite the fruitful achievements, the abovementioned methods make use of either the C- or S-fragment after cleaving the C–S bonds. Therefore, challenges remain in the efficient utilization of both the cleaved C- and S-fragments, necessitating the development of other innovative strategies.

School of Chemistry and Chemical Engineering/State Key Laboratory Incubation Base for Green Processing of Chemical Engineering, Shihezi University, Shihezi, China. E-mail: xuliang4423@shzu.edu.cn, yuweichem@shzu.edu.cn

† Electronic supplementary information (ESI) available. See DOI: **https://doi.org/10.1039/d5qo00248f**



Scheme 1 The approaches to cleave C–S bonds.

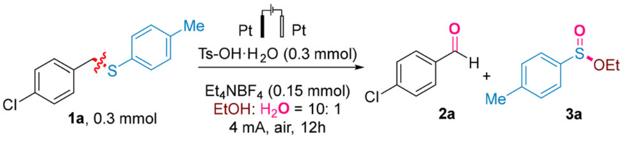
Meanwhile, it is well known that in the electrochemical reactions of thiols, the generated thiyl radicals can be further oxidized to deliver thiyl cations.[43–46] Therefore, it was possible that the C- and S-fragments are both converted into the corresponding cation species, after the C–S cleavage. In this context, it was questioned whether C-cations and S-cations could be trapped by the nucleophiles simultaneously (Scheme 1b), thus affording two products in an atom-economical manner, without wasting any fragment. Despite mechanistic promise, some potential pitfalls should also be contemplated and circumvented. For example, the easily-oxidized thioethers have been demonstrated to undergo diverse electrochemical oxidation reactions with their C–S bonds intact, affording an array of products such as sulfones and sulfoxides (Scheme 1d).[47–52]

Exploiting this logic, we performed proof-of-principle experiments to validate the hypothesis. Herein, the corresponding results were disclosed to showcase the feasibility of this strategy for the first time. Under electrochemical oxidative conditions without sacrificing the electrode, chemical oxidants or metal catalysts, after the regioselective C(sp^3)–S cleavage of aryl alkyl thioethers, the resulting alkyl and arylthiyl motifs would be trapped by O-nucleophiles and converted into aldehydes/ketones and sulfinates (Scheme 1e), respectively.

Results and discussion

To begin with, the reaction parameters were assessed for galvanostatic electrolysis of the benchmark substrate (4-chlorobenzyl)(*p*-tolyl)sulfane **1a**. Following extensive screening (see the ESI† for details), we were pleased to discover that the desired products 4-chlorobenzaldehyde **2a** and ethyl 4-methylbenzenesulfinate **3a** could be obtained with an isolated yield of 86% and 70% under the following conditions (Table 1, entry 1): constant current (I = 4.0 mA) electrolysis for 12 hours using a solvent consisting of EtOH and H_2O (2.0 mL : 0.2 mL), with the additive TsOH·H_2O (*p*-toluenesulfonic acid monohydrate, 0.3 mmol) and the electrolyte Et_4NBF_4 (0.15 mmol). In this regard, while it has been well documented in the literature regarding the electrochemical oxidation of S atoms to afford sulfoxides and sulfones, fortunately, the oxidative cleavage of the C(sp^3)–S bond predominated in this reaction system. Without an electric current, the reaction did not occur (entry 2). When TsOH·H_2O was absent, only a trace amount of the desired products was observed (entry 3). The reaction yield significantly decreased when no additional water was added (entry 4). Replacing TsOH·H_2O with TFA resulted in a decreased yield (entry 5). Changing to other mixed solvents, such as MeCN/H_2O (entry 6), decreased the yield of **2a** and suppressed the formation of **3a**, and generated another byproduct, thiosulfonates (see Scheme 5g). On using graphite electrodes instead of platinum electrodes, the yield of **2a** and **3a** decreased to 45% and 62%, respectively (entry 7). Regulating the current to 6.0 mA was also detrimental to the yields (entry

Table 1 Optimization of reaction conditions[a]

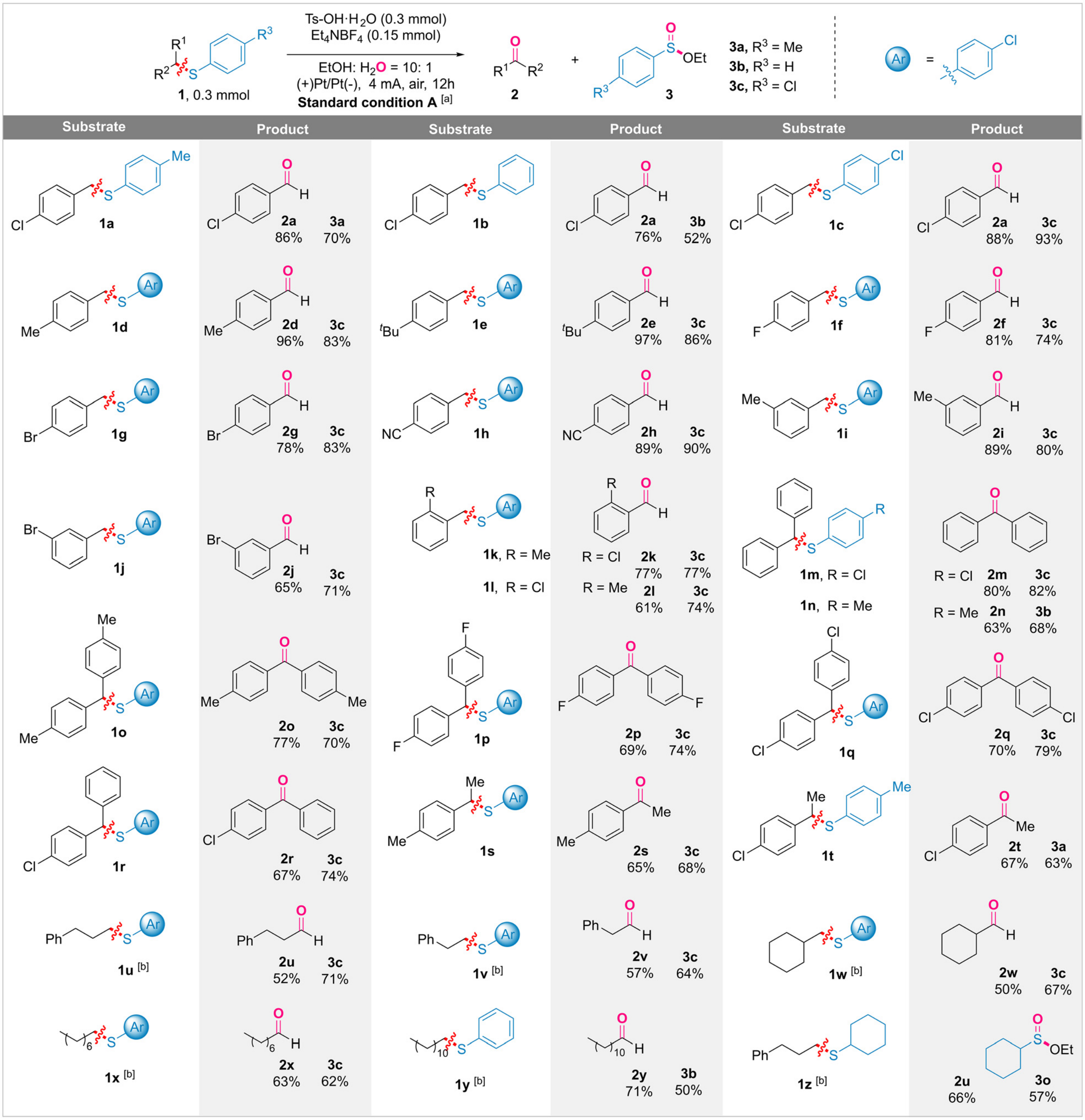


Entry	Variations from the 'standard' conditions	Yield **2a** [a] (%)	Yield **3a** [a] (%)
1	**None**	**86**	**70**
2	Without current	N.D.[b]	N.D.[b]
3	Without TsOH·H_2O	Trace	Trace
4	Without H_2O	39	45
5	TFA instead of TsOH·H_2O	74	67
6	MeCN instead of EtOH	66	N.D.
7	C/C instead of Pt/Pt	45	62
8	6 mA instead of 4 mA	65	53
9	Ar atmosphere	83	83

Standard conditions: **1a** (0.3 mmol), TsOH·H_2O (0.3 mmol), Et_4NBF_4 (0.15 mmol), EtOH (2.0 mL), H_2O (0.2 mL), constant current = 4 mA under air for 12 hours (6.0 F mol^{-1}). [a] Isolated yields. [b] Not detected. TFA = trifluoroacetic acid.

8). The yields of the two products were almost unaffected under an argon atmosphere (entry 9), thereby excluding the possibility of air as the oxygen source or oxidant.

With the optimal reaction conditions in hand, we began to evaluate the scope of the electrochemical C(sp^3)–S bond cleavage of various thioethers, as shown in Scheme 2. First, we examined aryl groups on sulfur and found that the presence of methyl or chlorine at the *para*-position (**1a–1c**) had a minimal effect on the reaction, with all achieving efficient C–S bond cleavage and high yields. Subsequently, the benzyl-substituted aryl groups were investigated, and it was found that a variety of electron-donating (such as methyl and *tert*-butyl) and electron-withdrawing atoms/groups (such as fluorine, chlorine, bromine, and cyano) at the benzyls' *para*-position (**1d–1h**) were well tolerated, affording the corresponding *para*-substituted benzaldehydes and **3a** in moderate to excellent yields. In general, the electronic properties of substituents in these molecules have a limited influence on the isolated yields.



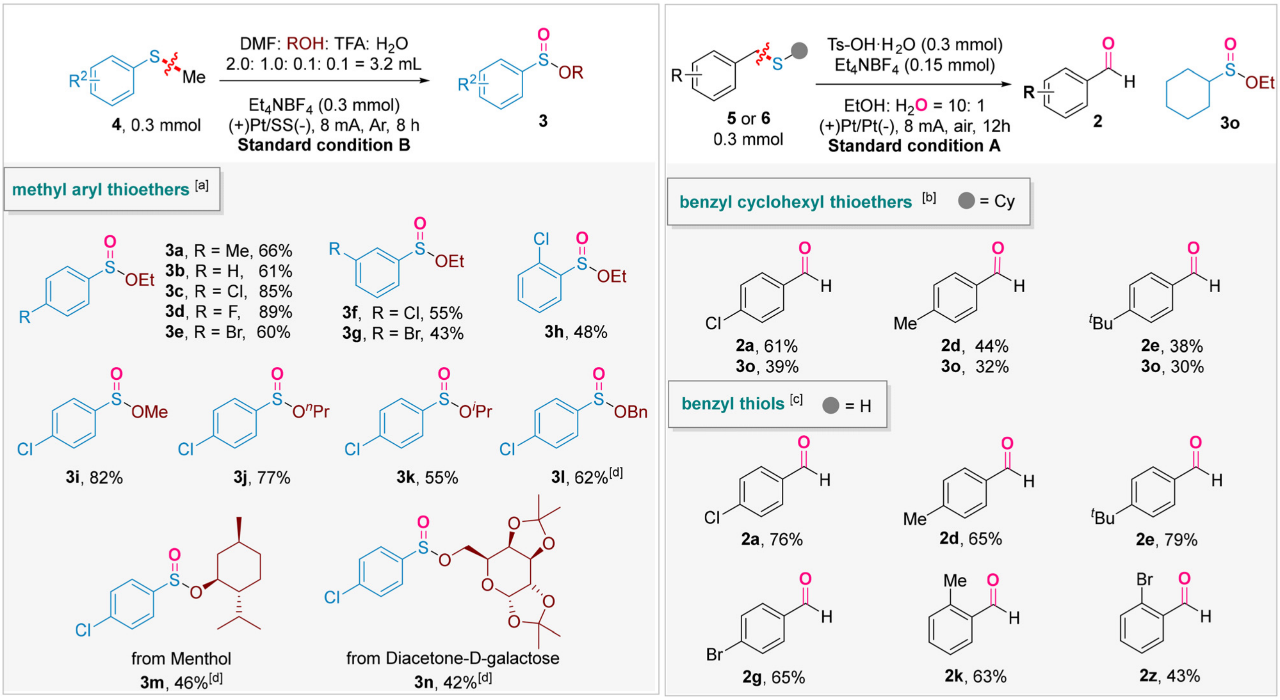
Scheme 2 Substrate scope of alkyl aryl thioethers. [a] Standard conditions A: thioethers (0.3 mmol), TsOH·H_2O (0.3 mmol), Et_4NBF_4 (0.15 mmol), EtOH/H_2O (10/1, 2.2 mL), Pt plate (10 mm × 10 mm × 0.2 mm) as the anode and cathode, constant current = 4 mA under air for 12 hours (6.0 F mol^{-1}), in an undivided cell; [b] standard conditions B: thioethers (0.3 mmol), Et_4NBF_4 (0.3 mmol), DMF/EtOH/TFA/H_2O (2.0/1.0/0.1/0.2, 3.3 mL), Pt plate as the anode and stainless steel plate as the cathode, constant current = 8 mA under Ar for 8 hours (8.0 F mol^{-1}), in an undivided cell.

Moreover, under the optimal reaction conditions, the products derived from *ortho*- and *meta*-substituted benzylic thioethers were also successfully obtained. Substituents positioned at the *ortho*-positions exhibit good yields (**2k**, 77%; **2l**, 61%) of the corresponding aldehydes. The yields of the corresponding sulfinates **3c** (70%; 74%) were not significantly affected by steric hindrance, demonstrating the robustness of this procedure towards steric effects. Additionally, halides such as Cl and Br were well tolerated in this transformation (**1a–1c**, **1g**, **1j**, and **1l**), leaving ample opportunities for further functionalization of the aldehyde products.

We subsequently evaluated the conversion of α-branched benzyl thioethers as substrates (**1m–1t**) and obtained moderate to good yields of ketone products (63%–80%) and sulfinates (63%–82%). Benzyl thioethers with α-aryls and α-alkyls showed good compatibility with the reaction conditions. The yields of diaryl ketones (**2m–2r**) and alkyl aryl ketones (**2s** and **2t**) were also not significantly affected by the electronic properties of the substituents. It is worth noting that when employing ordinary alkyl phenyl thioethers as substrates, it is likewise possible to selectively cleave the C(sp^3)–S bond, yielding alkyl aldehydes (**2u–2y**) and sulfinates (**3c** and **3b**). Dialkyl sulfides are equally applicable to this system. When cyclohexyl(3-phenylpropyl)sulfane **1z** is introduced into the reaction, the reaction proceeds smoothly. However, we only observe the cleavage of the primary carbon–S bond, resulting in the formation of phenylpropanal **2u** and cyclohexyl sulfinate **3o**, without any evidence of the cleavage of the secondary carbon–S bond.

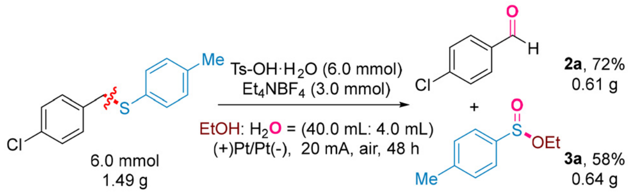
To further explore the applicability of alkyl aryl thioethers in this transformation, a series of methyl aryl thioethers were investigated. As depicted in Scheme 3 (left), in these cases (**4a–4k**), only sulfinates were ultimately obtained. The substituents on the aryl ring of the thioethers had a notable impact on the yields of the products. Substrates bearing electron-withdrawing groups yielded better results compared to those with electron-donating groups (**3a**, 66%; **3c**, 85%). When *ortho*-Cl or *meta*-Cl phenyl thioethers were employed, a noticeable decrease in yield was observed (**3f**, 55%; **3h**, 48%) compared to their *para*-substituted counterparts (**3c**, 85%), indicating that steric hindrance significantly impacts the cleavage of C–S bonds. Additionally, various alcohols were investigated. Primary and secondary alcohols, such as MeOH, ^{n}PrOH, ^{i}PrOH and BnOH, were well tolerated under optimal conditions, affording sulfinates (**3i–3l**) in moderate to good yields. As the nucleophilicity of the alcohol decreased, the yield of the sulfinates gradually declined. Subsequently, we evaluated the applicability of this method to natural products, employing menthol and diacetyl-D-galactose as nucleophilic O-sources. The reactions progressed smoothly, affording the corresponding products **3m** and **3n**, respectively.

Afterward, we began to explore whether the presence of an aromatic group on sulphur was essential for cleaving the



Scheme 3 Substrate scope. Left: methyl aryl thioethers; right: benzyl thioethers/thiols. [a] Standard conditions B: thioethers (0.3 mmol), Et_4NBF_4 (0.3 mmol), DMF/EtOH/TFA/H_2O (2/1/0.1/0.1, 3.2 mL), Pt plate as the anode and stainless steel plate as the cathode, constant current = 8 mA in Ar for 8 h (8.0 F mol^{-1}), in an undivided cell. [b] Standard conditions A: thioethers (0.3 mmol), TsOH·H_2O (0.3 mmol), Et_4NBF_4 (0.15 mmol), EtOH/H_2O (10/1, 2.2 mL), Pt plate (10 mm × 10 mm × 0.2 mm) as the anode and cathode, constant current = 4 mA in air for 12 h (6.0 F mol^{-1}), in an undivided cell. [c] Standard conditions A but constant current = 8 mA (11.9 F mol^{-1}). [d] 5.0 equiv. of alcohol was used.

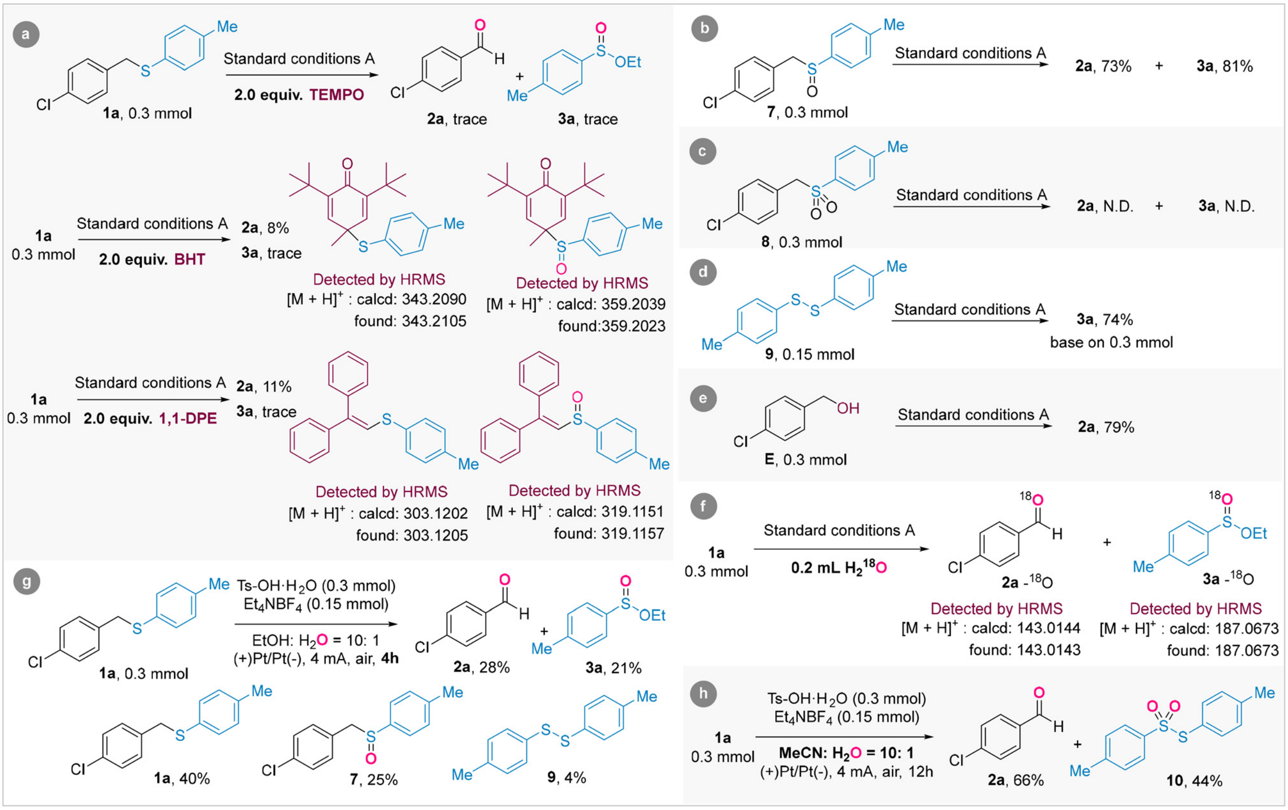
C(sp^3)–S bond (Scheme 3, right). Starting from cyclohexyl benzyl thioethers as the initial raw material, the reaction can still proceed smoothly, generating the corresponding aryl aldehydes with moderate yields (38%–61%), indicating that there is regional selectivity in the cleavage of the C(sp^3)–S bond, proving that the phenyl group on the sulfur is not essential. At the same time, we can also obtain cyclohexyl sulfinate **3o**. Subsequently, under optimized conditions, regardless of whether the substituent's nature is electron-donating or electron-withdrawing, the C–S bond can be cleaved with moderate yields *via* benzyl thiols to afford the corresponding aryl aldehydes. *ortho*-Substituted benzyl thiols also performed well, affording aldehydes **2k** and **2z** in 63% and 43% yields, respectively.



Scheme 4 Gram-scale cleavage of the C–S bond.

To verify the practicality and scalability of the electrochemical cleavage of C(sp^3)–S bonds, we conducted a gram-scale experiment. We attempted the electrochemical oxidative cleavage of 6.0 mmol (1.49 g) of thioether **1a**. As shown in Scheme 4, by simply scaling up the amount of each reagent and maintaining a constant current of 20 mA for 48 hours, we were able to obtain **2a** (0.62 g) with a yield of 72% and **3a** (0.64 g) with a yield of 58%.

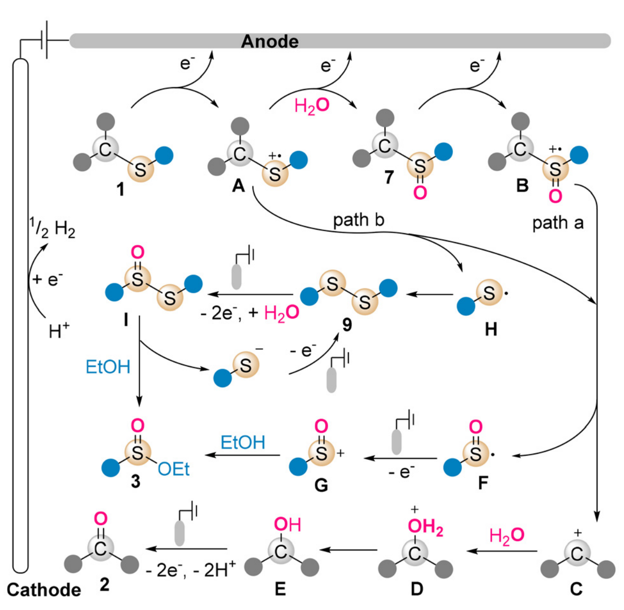
In order to further illustrate the reaction mechanism, the following control experiments (Scheme 5) were performed. First, radical trapping experiments were conducted to explore the reaction mechanism (Scheme 5a). Under standard conditions, radical scavengers such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), butylated hydroxytoluene (BHT), and 1,1-diphenylethylene (1,1-DPE) all exerted inhibitory effects on the formation of **2a** and **3a**. Furthermore, HRMS analysis identified the capture products of sulfide radicals **H** and sulfone radicals **F**, suggesting that both types of radicals are likely generated and involved in the reaction mechanism. To further delve into the details of this transformation, intermediate experiments were also conducted (Scheme 5b). Under standard conditions, compound **7** was utilized to afford **2a** in a yield of 73% and **3a** in a yield of 81%, indicating that **7** might be a crucial intermediate in this chemical transformation. Then, when sulfone **8** (Scheme 5c), instead of thioethers, was treated under



Scheme 5 Mechanistic studies. (a) Radical trapping experiment. (b) Intermediate experiments. (c) Intermediate experiments. (d) Intermediate experiments. (e) Intermediate experiments. (f) ^{18}O Labelling experiments. (g) Monitoring the reaction in the middle stage. (h) Control experiment without nucleophiles.

the optimized conditions, no desired products could be obtained, excluding the possibility of sulfone as the critical intermediate. Disulfide may be a key intermediate in the reaction, so we attempted to treat disulfide **9** under standard condition A. The reaction proceeded smoothly, affording sulfinate **3a** in a yield of 74% (Scheme 5d). Alcohols might be another key intermediate in the reaction process. Therefore, we attempted to treat benzyl alcohol **E** under standard conditions (Scheme 5e). The reaction proceeded smoothly, affording **2a** with a 79% yield. Next, conducting ^{18}O labelling experiments with ^{18}O-water resulted in the formation of ^{18}O-containing **2a** and **3a** (Scheme 5f), indicating that the two merged oxygen atoms of these two products originated from H_2O. This conclusion was also reinforced by the efficient reaction in the absence of air (O_2), as shown in Table 1 (entry 9). Subsequently, to gain a deeper insight into the intermediates during the reaction process, we analysed the components of the reaction mixture after 4 hours of reaction (Scheme 5g). It was found that in addition to the reactants and products, sulfoxide **7** and disulfide **9** could also be isolated. Finally, we wanted to know what will happen when the reaction does not contain O-nucleophiles. When we changed the solvent from ethanol to acetonitrile, the reaction still proceeded, but no generation of compound **3a** was observed. Instead, thiosulfonates **10** were obtained (Scheme 5h). We hypothesized that this might be due to the overoxidation of disulfides generated during the reaction under electrooxidative conditions.[53,54]

Based on the above mechanistic results and the previous report,[40,55–58] two plausible mechanisms are proposed, as shown in Scheme 6. In the first pathway (path a), thioether **1** undergoes single electron oxidation at the anode, yielding a sulphur radical cation intermediate **A**. Then, in the presence of water, sulfoxide intermediate **7** is generated, which is further oxidized at the anode to form sulfoxide radical cation **B**. This intermediate **B** subsequently undergoes cleavage to form a carbocation **C** and a sulfoxide radical **F**. Afterwards, the carbocation combines with water to form **D**, which undergoes deprotonation to generate benzyl alcohol intermediate **E**. The following loss of electrons and protons at the anode will lead to carbonyl compound **2**. Meanwhile, sulfoxide radical **F** undergoes anodic oxidation to generate sulfoxide cation **G**, followed by nucleophilic attack by alcohol to yield sulfinates **3**. Alternatively, *via* another pathway (path b), sulphur radical cation intermediate **A** directly cleaves to form sulphur radical **H** and carbocation **C**. Subsequently, the homo-coupling of **H** generates disulfide **9**, which subsequently undergoes electrooxidation to form thiosulfinates **I**. Finally, the nucleophilic attack of **I** by ethanol yields sulfinates **3**.



Scheme 6 Proposed mechanism.

Conclusions

In summary, this work presents a method for the cleavage of $C(sp^3)$–S bonds of thioethers under electrochemical conditions. This approach is characterized by high chemoselectivity, regioselectivity, and atom economy, leading to aldehydes/ketones and sulfinates simultaneously. Compared to traditional methods employing transition metal catalysis for C–S bond cleavage, this method exhibits higher regioselectivity toward $C(sp^3)$–S bond cleavage. Moreover, this represents the first example of simultaneous utilization of S- and C-fragments after the cleavage of thioethers under electrochemical conditions. The increased atom economy will not only enhance the sustainability of this transformation but also open up new ample chemical space for derivatization of thioethers.

Author contributions

J. Huang: conceptualisation, supervision, writing, and editing. X. Li: investigation, review and editing. Y. Wei and L. Xu: review and editing. All authors discussed the experimental results and commented on the manuscript.

Data availability

All relevant data are within the manuscript and the ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We are thankful for the financial support from the National Natural Science Foundation of China (22061036) and Shihezi University (no. 2023ZD077).

References

1 C. Bauchart-Thevret, B. Stoll and D. G. Burrin, Intestinal metabolism of sulfur amino acids, *Nat. Prod. Rep.*, 2009, **22**, 175–187.

2 Y. Liao, M. Wang and X. Jiang, Sulfur-containing peptides: Synthesis and application in the discovery of potential drug candidates, *Curr. Opin. Chem. Biol.*, 2023, **75**, 102336–102345.

3 N. Wang, P. Saidhareddy and X. Jiang, Construction of sulfur-containing moieties in the total synthesis of natural products, *Nat. Prod. Rep.*, 2020, **37**, 246–275.

4 Q. Yu, L. Bai and X. Jiang, Disulfide Click Reaction for Stapling of S–terminal Peptides, *Angew. Chem., Int. Ed.*, 2023, **62**, e202314379.

5 D. Kaiser, I. Klose, R. Oost, J. Neuhaus and N. Maulide, Bond-Forming and -Breaking Reactions at Sulfur(IV): Sulfoxides, Sulfonium Salts, Sulfur Ylides, and Sulfinate Salts, *Chem. Rev.*, 2019, **119**, 8701–8780.

6 S. A. Vizer, E. S. Sycheva, A. A. A. Al Quntar, N. B. Kurmankulov, K. B. Yerzhanov and V. M. Dembitsky, Propargylic Sulfides: Synthesis, Properties, and Application, *Chem. Rev.*, 2014, **115**, 1475–1502.

7 L. H. S. Smith, S. C. Coote, H. F. Sneddon and D. J. Procter, Beyond the Pummerer Reaction: Recent Developments in Thionium Ion Chemistry, *Angew. Chem., Int. Ed.*, 2010, **49**, 5832–5844.

8 I. Colomer, M. Velado, R. Fernández de la Pradilla and A. Viso, From Allylic Sulfoxides to Allylic Sulfenates: Fifty Years of a Never-Ending [2,3]-Sigmatropic Rearrangement, *Chem. Rev.*, 2017, **117**, 14201–14243.

9 S. Huang, M. Wang and X. Jiang, Ni-catalyzed C–S bond construction and cleavage, *Chem. Soc. Rev.*, 2022, **51**, 8351–8377.

10 J. Lou, Q. Wang, P. Wu, H. Wang, Y.-G. Zhou and Z. Yu, Transition-metal mediated carbon–sulfur bond activation and transformations: an update, *Chem. Soc. Rev.*, 2020, **49**, 4307–4359.

11 L. Wang, W. He and Z. Yu, Transition-metal mediated carbon–sulfur bond activation and transformations, *Chem. Soc. Rev.*, 2013, **42**, 599–621.

12 S. Chen, X. Guo, H. Hou, S. Geng, Z. Liu, Y. He, X. S. Xue and Z. Feng, Thioethers as Dichotomous Electrophiles for Site–Selective Silylation via C–S Bond Cleavage, *Angew. Chem., Int. Ed.*, 2023, **62**, e202303470.

13 M. Tobisu, Y. Masuya, K. Baba and N. Chatani, Palladium (II)-catalyzed synthesis of dibenzothiophene derivatives via the cleavage of carbon–sulfur and carbon–hydrogen bonds, *Chem. Sci.*, 2016, **7**, 2587–2591.

14 T. Yanagi, R. J. Somerville, K. Nogi, R. Martin and H. Yorimitsu, Ni-Catalyzed Carboxylation of C(sp^2)–S Bonds with CO2: Evidence for the Multifaceted Role of Zn, *ACS Catal.*, 2020, **10**, 2117–2123.

15 S. Yang, X. Yu and M. Szostak, Divergent Acyl and Decarbonylative Liebeskind–Srogl Cross-Coupling of Thioesters by Cu-Cofactor and Pd–NHC (NHC = N-Heterocyclic Carbene) Catalysis, *ACS Catal.*, 2023, **13**, 1848–1855.

16 M. Zhang, B. B. Zhang, Q. Lin, Z. Jiang, J. Zhang, Y. Li, S. Pei, X. Han, H. Xiong, X. Liang, Y. Lin, Z. Wei, F. Zhang, X. Zhang, Z. X. Wang, Q. Shi and H. Huang, An Efficient Direct Arylation Polycondensation via C–S Bond Cleavage, *Angew. Chem., Int. Ed.*, 2023, **62**, e202306307.

17 Y.-H. Lu, C. Wu, J.-C. Hou, Z.-L. Wu, M.-H. Zhou, X.-J. Huang and W.-M. He, Ferrocene-Mediated Photocatalytic Annulation of N-Sulfonyl Ketimines on a Polycrystalline WSe2 Semiconductor Photocatalyst, *ACS Catal.*, 2023, **13**, 13071–13076.

18 H.-T. Ji, K.-L. Wang, W.-T. Ouyang, Q.-X. Luo, H.-X. Li and W.-M. He, Photoinduced, additive- and photosensitizer-free multi-component synthesis of naphthoselenazol-2-amines with air in water, *Green Chem.*, 2023, **25**, 7983–7987.

19 Z. Zhang, X. Fang, A. Aili, S. Wang, J. Tang, W. Lin, L. Xie, J. Chen and K. Sun, Cascade Radical Trifluoromethylthiolation/Cyclization of Dienes To Access SCF_3-Containing Medium-Sized Heterocycles, *Org. Lett.*, 2023, **25**, 4598–4602.

20 Z. Lian, B. N. Bhawal, P. Yu and B. Morandi, Palladium-catalyzed carbon-sulfur or carbon-phosphorus bond metathesis by reversible arylation, *Science*, 2017, **356**, 1059–1063.

21 Y. Wang, L. F. Deng, X. Zhang, Z. D. Mou and D. Niu, A Radical Approach to Making Unnatural Amino Acids: Conversion of C–S Bonds in Cysteine Derivatives into C–C Bonds, *Angew. Chem., Int. Ed.*, 2020, **60**, 2155–2159.

22 B. Hong, K. C. C. Aganda and A. Lee, Oxidative C–S Bond Cleavage of Benzyl Thiols Enabled by Visible-Light-Mediated Silver(II) Complexes, *Org. Lett.*, 2020, **22**, 4395–4399.

23 L. Wei, W. Bai, Z. Hu, Z. Yang and L. Xu, Visible light-induced metal-free chemoselective oxidative cleavage of benzyl C–heteroatom (N, S, Se) bonds utilizing organoboron photocatalysts, *Chem. Commun.*, 2023, **59**, 13344–13347.

24 T. Delcaillau, A. Bismuto, Z. Lian and B. Morandi, Nickel–Catalyzed Inter– and Intramolecular Aryl Thioether Metathesis by Reversible Arylation, *Angew. Chem., Int. Ed.*, 2019, **59**, 2110–2114.

25 T. Delcaillau, A. Woenckhaus-Alvarez and B. Morandi, Nickel-Catalyzed Cyanation of Aryl Thioethers, *Org. Lett.*, 2021, **23**, 7018–7022.

26 V. Hirschbeck, P. H. Gehrtz and I. Fleischer, Metal–Catalyzed Synthesis and Use of Thioesters: Recent Developments, *Chem. – Eur. J.*, 2018, **24**, 7092–7107.

27 N. Neerathilingam, M. B. Reddy and R. Anandhan, Regioselective Synthesis of 2° Amides Using Visible-Light-Induced Photoredox-Catalyzed Nonaqueous Oxidative C–N Cleavage of N,N-Dibenzylanilines, *J. Org. Chem.*, 2021, **86**, 15117–15127.

28 D. Shao, Y. Wu, S. Hu, W. Gao, Y. Du, X. Jia, S. Liu, M. Zhou and J. Chen, Decoupled Photoelectrochemical Cerium-Catalyzed Oxydichlorination of Alkynes: Slow Releasing of Chloride Ions and Chlorine Radicals, *ACS Sustainable Chem. Eng.*, 2022, **10**, 10294–10302.

29 K. Sun, J. Lei, Y. Liu, B. Liu and N. Chen, Electrochemically Enabled Intramolecular and Intermolecular Annulations of Alkynes, *Adv. Synth. Catal.*, 2020, **362**, 3709–3726.

30 H.-T. Tang, Y.-Z. Pan and Y.-M. Pan, Research progress in electrochemical/photochemical utilization of methanol as a C1 source, *Green Chem.*, 2023, **25**, 8313–8327.

31 K. Sun, F. Xiao, B. Yu and W.-M. He, Photo-/electrocatalytic functionalization of quinoxalin-2(1H)-ones, *Chin. J. Catal.*, 2021, **42**, 1921–1943.

32 H.-Y. Zhou, H.-T. Tang and W.-M. He, The future of organic electrochemistry current transfer, *Chin. J. Catal.*, 2023, **46**, 4–10.

33 A. Wiebe, T. Gieshoff, S. Möhle, E. Rodrigo, M. Zirbes and S. R. Waldvogel, Electrifying Organic Synthesis, *Angew. Chem., Int. Ed.*, 2018, **57**, 5594–5619.

34 S. Möhle, M. Zirbes, E. Rodrigo, T. Gieshoff, A. Wiebe and S. R. Waldvogel, Modern Electrochemical Aspects for the Synthesis of Value–Added Organic Products, *Angew. Chem., Int. Ed.*, 2018, **57**, 6018–6041.

35 Y. Yuan and A. Lei, Electrochemical Oxidative Cross-Coupling with Hydrogen Evolution Reactions, *Acc. Chem. Res.*, 2019, **52**, 3309–3324.

36 N. Amri and T. Wirth, Recent Advances in the Electrochemical Synthesis of Organosulfur Compounds, *Chem. Rec.*, 2021, **21**, 2526–2537.

37 Z. Ye, X. Zhang, W. Ma and F. Zhang, Advances in S–N bond formation via electrochemistry: a green route utilizing diverse sulfur and nitrogen sources, *Green Chem.*, 2023, **25**, 2524–2540.

38 D. K. P. Veedu, L. A. Connal and L. R. Malins, Tunable Electrochemical Peptide Modifications: Unlocking New Levels of Orthogonality for Side–Chain Functionalization, *Angew. Chem., Int. Ed.*, 2022, **62**, e202215470.

39 D. K. P. Veedu, L. A. Connal and L. R. Malins, Fine-Tuning Electroauxiliary-Mediated Peptide Modifications Using Second-Generation Electroactive Amino Acids, *Org. Lett.*, 2023, **25**, 3633–3638.

40 Y. Li, H. Wang, Z. Wang, H. Alhumade, Z. Huang and A. Lei, Electrochemical radical-mediated selective C(sp^3)–S bond activation, *Chem. Sci.*, 2023, **14**, 372–378.

41 J. Kuzmin and H. Lundberg, Metal-free Electrochemical Desulfurative Borylation of Thioethers, *ChemRxiv*, 2024, preprint, DOI: **10.26434/chemrxiv-2024-9r9hl**.

42 J. Kuzmin, J. Röckl, N. Schwarz, J. Djossou, G. Ahumada, M. Ahlquist and H. Lundberg, Electroreductive Desulfurative Transformations with Thioethers as Alkyl Radical Precursors**, *Angew. Chem., Int. Ed.*, 2023, **62**, e202304272.

43 X. Li, J. Huang, L. Xu, J. Liu and Y. Wei, Electrochemical Oxidative Dehydrogenative Coupling of Sulfoximines to Construct N–sulfenyl and N–phosphinyl Sulfoximines, *Adv. Synth. Catal.*, 2023, **365**, 4647–4653.

44 X.-B. Zhu, Y. Yu, Y. Yuan and K.-Y. Ye, Electrochemical multicomponent reaction toward vicinal sulfenyltetrazolation of unactivated alkenes, *Org. Chem. Front.*, 2023, **10**, 5064–5069.

45 Y. Yu, Y. Jiang, S. Wu, Z. Shi, J. Wu, Y. Yuan and K. Ye, Electrochemistry enabled selective vicinal fluorosulfenylation and fluorosulfoxidation of alkenes, *Chin. Chem. Lett.*, 2022, **33**, 2009–2014.

46 F. Zhang, Y. Wang, Y. Wang and Y. Pan, Electrochemical Deoxygenative Thiolation of Preactivated Alcohols and Ketones, *Org. Lett.*, 2021, **23**, 7524–7528.

47 Z.-H. Fu, H.-D. Tian, S.-F. Ni, J. S. Wright, M. Li, L.-R. Wen and L.-B. Zhang, Scalable selective electrochemical oxidation of sulfides to sulfoxides, *Green Chem.*, 2022, **24**, 4772–4777.

48 L. Ma, H. Zhou, M. Xu, P. Hao, X. Kong and H. Duan, Integrating hydrogen production with anodic selective oxidation of sulfides over a CoFe layered double hydroxide electrode, *Chem. Sci.*, 2021, **12**, 938–945.

49 H. Wang, M. Yu, P. Zhang, H. Wan, H. Cong and A. Lei, Electrochemical dual-oxidation strategy enables access to α-chlorosulfoxides from sulfides, *Sci. Bull.*, 2022, **67**, 79–84.

50 H. Wang, M. He, Y. Li, H. Zhang, D. Yang, M. Nagasaka, Z. Lv, Z. Guan, Y. Cao, F. Gong, Z. Zhou, J. Zhu, S. Samanta, A. D. Chowdhury and A. Lei, Electrochemical Oxidation Enables Regioselective and Scalable α-C(sp^3)-H Acyloxylation of Sulfides, *J. Am. Chem. Soc.*, 2021, **143**, 3628–3637.

51 D. Yang, Z. Guan, Y. Peng, S. Zhu, P. Wang, Z. Huang, H. Alhumade, D. Gu, H. Yi and A. Lei, Electrochemical oxidative difunctionalization of diazo compounds with two different nucleophiles, *Nat. Commun.*, 2023, **14**, 1476–1483.

52 M. Klein and S. R. Waldvogel, Anodic Dehydrogenative Cyanamidation of Thioethers: Simple and Sustainable Synthesis of N–Cyanosulfilimines, *Angew. Chem., Int. Ed.*, 2021, **60**, 23197–23201.

53 J. Strehl and G. Hilt, Synthesis of Symmetrical and Unsymmetrical Thiosulfonates from Disulfides through Electrochemically Induced Disulfide Bond Metathesis and Site–Selective Oxidation, *Eur. J. Org. Chem.*, 2021, e202101007.

54 Z. Yang, Y. Shi, Z. Zhan, H. Zhang, H. Xing, R. Lu, Y. Zhang, M. Guan and Y. Wu, Sustainable Electrocatalytic Oxidant–Free Syntheses of Thiosulfonates from Thiols, *ChemElectroChem*, 2018, **5**, 3619–3623.

55 T. Del Giacco, O. Lanzalunga, A. Lapi, M. Mazzonna and P. Mencarelli, Photosensitized Oxidation of Aryl Benzyl Sulfoxides. Evidence for Nucleophilic Assistance to the C–S Bond Cleavage of Aryl Benzyl Sulfoxide Radical Cations, *J. Org. Chem.*, 2015, **80**, 2310–2318.

56 J. Xu, Z. Wu, H. Wan, G. Deng, B. Lu, A. K. Eckhardt, P. R. Schreiner, T. Trabelsi, J. S. Francisco and X. Zeng, Phenylsulfinyl Radical: Gas-Phase Generation, Photoisomerization, and Oxidation, *J. Am. Chem. Soc.*, 2018, **140**, 9972–9978.

57 C. Ai, H. Shen, D. Song, Y. Li, X. Yi, Z. Wang, F. Ling and W. Zhong, Metal- and oxidant-free electrochemical synthesis of sulfinic esters from thiols and alcohols, *Green Chem.*, 2019, **21**, 5528–5531.

58 S. Guo, Y. Li, Q.-H. Li and K. Zheng, Electrochemical desulfurative formation of C–N bonds through selective activation of inert C(sp^3)–S bonds, *Chem. Commun.*, 2024, **60**, 2501–2504.