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# Continuous-flow electro-oxidative coupling of sulfides with activated methylene compounds leading to sulfur ylides†

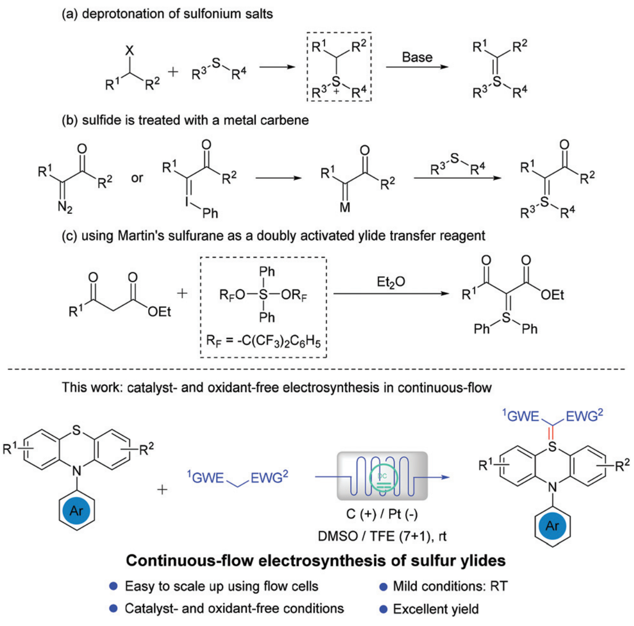
Chengkou Liu,[a] Yang Lin,[a] Chen Cai,[a] Chengcheng Yuan,[a] Zheng Fang[a] and Kai Guo *[a,b]

**An unprecedentedly straightforward electro-oxidative coupling of sulfides with activated methylene compounds to synthesize sulfur ylides has been developed. Good to excellent yields can be obtained under catalyst- and oxidant-free conditions at room temperature. Owing to the use of continuous-flow electrochemical setups, this green, mild and practical electrosynthesis features high efficiency and excellent functional group tolerance and is easy to scale up.**

Sulfur ylides are important precursors in synthetic chemistry for the construction of C–C and C–hetero bonds[1] through epoxidation,[2] aziridination,[3] cyclopropanation,[4] [2,3]-sigmatropic shift,[5] Stevens rearrangement,[6] and allkylation[7] and the synthesis of complex architectures through multi-step cascade cyclizations.[8] Recently, sulfonium and sulfoxonium ylides have been widely used as metal carbene precursors[9] instead of α-diazocarbonyl derivatives,[10] which are hazardous and toxic. Moreover, sulfur ylides have increasingly attracted the interest of medicinal chemists because of their antimicrobial properties.[11]

Traditionally, sulfur ylides are prepared from the deprotonation of sulfonium salts using strong bases (Scheme 1, eqn (a)).[12] In addition, metal carbenes can be transformed into the corresponding sulfur ylides,[13] which are usually prepared from diazo compounds (Scheme 1, eqn (b)). However, a tedious preparation procedure of the activated precursors (diazo compounds) and the use of stoichiometric amounts of metal salts compromise the atom-economy. Most recently, Bayer and co-workers developed a rhodium-catalyzed synthesis of sulfur ylides using phenyliodonium diacetate (PIDA).[14] Rh-Carbenes were formed from iodonium ylide intermediates, which were generated from the active methylene compounds and PIDA (Scheme 1, eqn (b)). Maulide and co-workers found that bis[α,α-bis(trifluoromethyl)benzyloxy]diphenylsulfur (Martin's sulfurane) could be used as an efficient ylide transfer reagent to yield the desired sulfur ylides (Scheme 1, eqn (c)).[15] The relatively costly hypervalent iodine reagent or ylide transfer reagent was required, which led to undesired byproducts and low atom-economy. Thus, it is still desirable to develop more green, economical and efficient methodologies to access sulfur ylides.

Electrosynthesis employs traceless electrons to perform redox reactions obviating the need for an excess of chemical oxidizing and reducing reagents, which leads to low atom-economy, environmental pollution, potential danger and product contamination.[16] In this context, we have been inter-



**Scheme 1** Synthesis of sulfur ylides.

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[a] *College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, Nanjing, 211816 China. E-mail: guok@njtech.edu.cn*

[b] *State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing Tech University, Nanjing, 211816 China*

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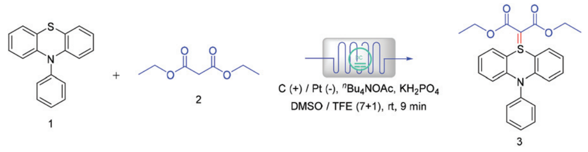
ested in electro-redox reactions, especially the electro-initiation of stable radical or radical-cation intermediates. Recently, we have reported an electrochemical heteroaryl migration using 10-phenyl-10*H*-phenothiazine (PTH) as the efficient redox catalyst *via* an *in situ* generated S-radical-cation intermediate.[17] Thus, we envisioned that the generated S-radical-cations *via* electrooxidation may react with active methylene compounds to give sulfur ylides.

Moreover, several continuous-flow electro-oxidative coupling reactions to construct C–hetero bonds or cyclic compounds were previously reported by us.[18] Compared with traditional batch electrolysis, a larger ratio of the electrode surface to reactor volume and higher heat and mass transfers lead to higher selectivity and productivity.[19] Besides, a less supporting electrolyte is needed and it is easy to scale up. Herein, we report the synthesis of sulfur ylides through unprecedented continuous-flow electro-oxidative coupling of sulfides with active methylene compounds at room temperature under catalyst- and oxidant-free conditions.

The oxidative coupling of PTH with diethyl malonate was chosen as the model reaction to explore the optimal electrolysis conditions in batch (Tables S1–S3†). To our delight, excellent yield (89% isolated yield) was obtained after electrolysis in an undivided cell using a mixed solvent of DMSO/TFE (7 : 1) at a constant current of 10 mA and at 45 °C, with a platinum plate cathode, a carbon cloth anode, $KH_2PO_4$ as a base and $^n$$Bu_4NOAc$ as an electrolyte. No reaction occurred without electric current (Table S1,† entry 12).

Based on the optimized electrolysis conditions in batch, further investigation in a continuous-flow reactor was carried out (Table 1). It was found that a higher constant current led to a decrease of the yield (Table 1, entries 1–3). The isolated yield increased to 81% when the electrolysis time was extended from 2.25 min to 9 min (Table 1, entries 1 and 4–6). Further extending the electrolysis time to 15 min resulted in a dramatic reduction in yield with the formation of a sulfoxide byproduct (Table 1, entry 7). To our delight, the yield was increased to 85% at a higher concentration (0.075 M based on **1**, Table 1, entries 8–10). The further investigation of constant current was carried out (Table 1, entries 11 and 12). A 94% isolated yield was obtained at a constant current of 11 mA (Table 1, entry 12).

**Table 1** Optimization of the electrosynthesis of sulfur ylides in continuous-flow[a]



| Entry | Current (mA) | Residence time (min) | Concentration (based on **1**, M) | Yield[b] (%) |
|---|---|---|---|---|
| 1 | 10 | 2.25 | 0.05 | 69 |
| 2 | 15 | 2.25 | 0.05 | 63 |
| 3 | 20 | 2.25 | 0.05 | 56 |
| 4 | 10 | 3 | 0.05 | 71 |
| 5 | 10 | 4.5 | 0.05 | 77 |
| 6 | 10 | 9 | 0.05 | 81 |
| 7 | 10 | 15 | 0.05 | 63 |
| 8 | 10 | 9 | 0.025 | 69 |
| 9 | 10 | 9 | 0.0375 | 76 |
| 10 | 10 | 9 | 0.075 | 85 |
| 11 | 9 | 9 | 0.075 | 91 |
| 12 | 11 | 9 | 0.075 | 94 |

[a] Reaction conditions: **1** (0.4 mmol), **2** (0.8 mmol), $^n$$Bu_4NOAc$ (0.8 mmol), $KH_2PO_4$ (0.8 mmol), DMSO/TFE (7 mL/1 mL), a C (carbon filled PPS, 5.0 × 4.0 cm) anode, a Pt (SS 316L platinum coated, 5.0 × 4.0 cm) cathode, volume (0.225 mL), residence time, current, rt. [b] Isolated yield.

In addition, a sharp drop in yield was observed when the amount of active methylene compound or electrolyte was reduced, which was similar to the reaction in batch (Table S4†).

Then, the optimized conditions of electrosynthesis of sulfur ylides in both batch and continuous-flow were obtained.

It was noteworthy that compared with the electrolysis yield in batch, the yield using a continuous-flow reactor was boosted to 94% at room temperature (Table 2, entries 1 and 2). However, only trace amounts of the desired sulfur ylide product were detected when the electrolysis was performed in a batch reactor at 25 °C (Table S2,† entry 7). Besides, a higher concentration in batch led to a dramatic reduction in yield (Table S3,† entries 6–8). The reaction in continuous-flow was fully tolerant to higher concentrations, which led to solvent-economy (Table 2, entry 3). Moreover, lower charge was needed in a continuous-flow reactor (Table 2, entry 4).

With the optimized conditions of electrosynthesis of sulfur ylides in continuous-flow being obtained, the versatility of this reaction was probed (Scheme S1,† and Tables 3, 4). Firstly, the coupling of **2** with various sulfides was evaluated (Scheme S1†). Interestingly, the results revealed that the phenothiazine ring and aromatic ring on the linking nitrogen are indispensable in this electrosynthesis of sulfur ylides, probably because of the higher stability of S-radical-cation intermediates. The reaction was furtherly explored by varying the aromatic rings on the linking nitrogen, phenothiazine rings, and the active methylene compounds (Tables 3 and 4). It was found that this electrosynthesis reaction demonstrated broad tolerance toward both electron-donating and electron-withdrawing groups at the phenyl ring A, including H (3), alkyl groups (4–6), halogens (7, 8, 16), phenyl group (9), OMe (10, 17–19), SMe (15), CN (11), $NO_2$ (12), $CF_3$ (13) and $CO_2Et$ (14). In particular, the phenyl ring A bearing highly electron-withdrawing $NO_2$ or highly electron-donating OMe or SMe at the *para* position was converted into the corresponding sulfur

**Table 2** Comparison of optimized conditions of batch and continuous-flow

| Entry | Parameters | Batch | Continuous-flow |
|---|---|---|---|
| 1 | Isolated yield (%) | 89 | 94 |
| 2 | Temperature (°C) | 45 | rt (about 25–27) |
| 3 | Concentration (M, based on **1**) | 0.025 | 0.075 |
| 4 | Charge (F $mol^{-1}$) | 4.67 | 3.65 |

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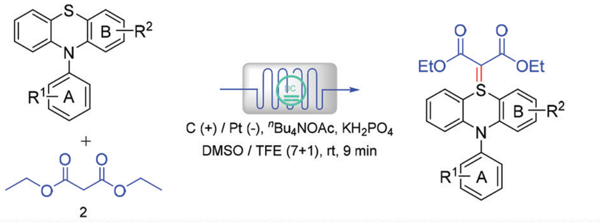
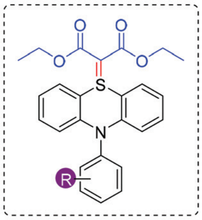
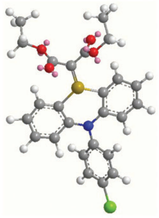
**Table 3** Scope of the sulfides



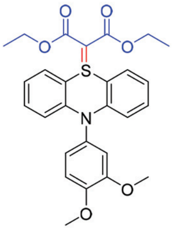


3, R = H, 94%
4, R = 4-Me, 81%
5, R = 4-Et, 77%
6, R = 4-$^i$Pr, 74%
11, R = 4-CN, 87%
12, R = 4-NO$_2$, 76%
13, R = 4-CF$_3$, 89%
14, R = 4-CO$_2$Me, 77%

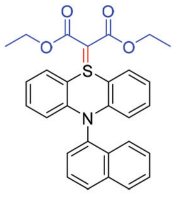
7, R = 4-F, 72%
8, R = 4-Cl, 79%
9, R = 4-Ph, 92%
10, R = 4-OMe, 72%
15, R = 4-SMe, 66%
16, R = 2-Cl, 64%
17, R = 2-OMe, 52%
18, R = 3-OMe, 58%



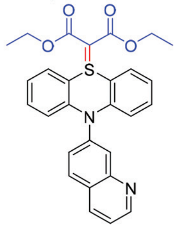
X-ray structure of 8



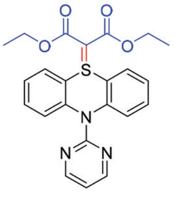
19, 48%



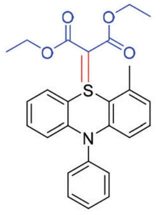
20, 90%



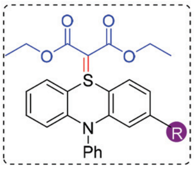
21, 47%



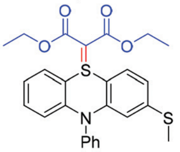
22, 44%



23, 81%



24, R = CH$_3$, 79%
25, R = Cl, 76%
26, R = OMe, 70%
27, R = CF$_3$, 77%



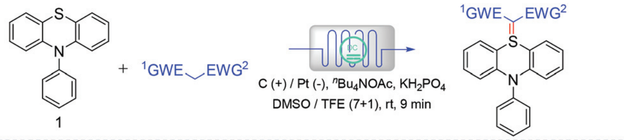
28, 66%

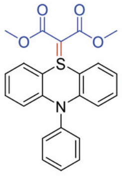
Reaction conditions: sulfide (0.6 mmol), **2** (1.2 mmol), $^n$Bu$_4$NOAc (1.2 mmol), KH$_2$PO$_4$ (1.2 mmol), DMSO/TFE (7 mL/1 mL), a C (carbon filled PPS, 5.0 × 4.0 cm) anode, a Pt (SS 316L platinum coated, 5.0 × 4.0 cm) cathode, volume (0.225 mL), residence time (9 min), total reaction time (320 min), 11 mA, rt, 3.65 F mol$^{-1}$.

ylide in good yield (10, 12). A slightly lower yield was obtained when the A was substituted at the *ortho* or *meta* position (16–18). In addition, this reaction was compatible with substrates with a multisubstituted phenyl ring A (19), naphthalene (20) and a heterocyclic ring such as quinoline (21) and pyrimidine (22).

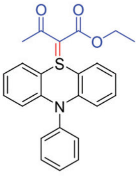
No obvious inhibitory effect on the reactivity was observed by the electronic and steric properties of the B ring (23–28). Even though the B ring was substituted with highly electron-donating OMe or SMe, this electrolysis proceeded smoothly affording good yield (26, 28). Meanwhile, the scope by varying the active methylene compounds was explored (Table 4).

**Table 4** Scope of the active methylene compounds

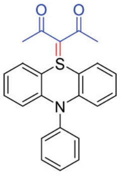




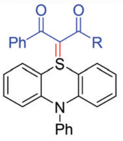
29, 79%



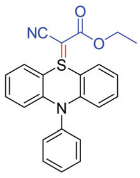
30, 81%



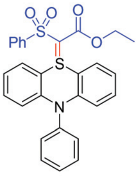
31, 73%



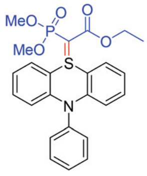
32, R = CH$_3$, 72%
33, R = Ph, 84%
34, R = OEt, 68%



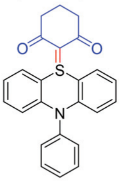
35, 59%



36, 66%



37, 86%



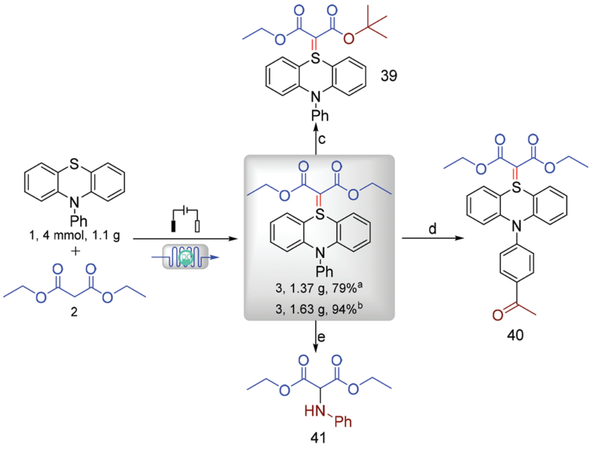
38, 76%

Reaction conditions, see Table 3, isolated yield.

1,3-Dicarbonyl compounds including malonic esters (3–29), keto esters (30, 34), and diketones (31–33, 38) exhibited excellent reaction compatibility and furnished the desired products in good to excellent yields. Remarkably, cyclic diketone was also a viable substrate (38). Besides, cyanoacetate (35), phenylsulfonylacetic acid ester (36) and phosphonate ester (37) underwent electro-oxidative coupling to afford the corresponding sulfur ylides smoothly.

Furthermore, we performed gram-scale experiments in batch and continuous-flow (Table 5). A slight reduction in yield was observed when the reaction was applied on a decagram scale in batch (from 89% to 79%). In contrast, a stable

**Table 5** Gram-scale synthesis in batch and continuous-flow and derivatization of α-carbonyl sulfonium ylide **3**



$^a$ Gram-scale synthesis in batch. $^b$ Gram-scale synthesis in continuous-flow. $^c$ *t*-BuOH, KOH, 80 °C, 58%. $^d$ AlCl$_3$, AcCl, 43%. $^e$ Aniline, Cu(OAc)$_2$, 37%.

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and excellent yield was obtained using a continuous-flow reactor. Next, further derivatizations of **3** were carried out *via* transesterification and acetylation to give the corresponding ester (39) and aryl methyl ketone (40). In addition, the α-tertiary amino ester (41) was generated from the protonation–amination of α-carbonyl sulfonium ylide 3.

Intrigued by the efficient continuous-flow electrosynthesis of sulfur ylides, a series of mechanistic studies were conducted to unravel its reaction mechanism (Scheme 2 and Fig. 1). The results of the H/D exchange experiments provided strong support for the existence of the fast cleavage of the C–H bond of activated methylene compounds (Scheme 2a). A minor KIE (kinetic isotope effect, $k_H/k_D \approx 1.36$) further substantiated the conclusion above and revealed that the C–H cleavage of activated methylene compounds was not the rate-determining step (Scheme 2b). At the same time, this electro-oxidative coupling reaction was probed by voltammetric analysis (Fig. 1). An obvious oxidation peak of **1** was observed at 1.16 V (Fig. 1a, blue and green lines).

While diethyl malonate **2** revealed no redox activity (Fig. 1a, pink and indigo lines), which revealed that **1** was possible to be oxidized firstly to give the corresponding radical-cation intermediate. Nevertheless, the oxidation peak of **1** disappeared with the generation of a new oxidation peak at 1.49 V in the presence of **2** and base. Compared with substrate **1**, the oxidation potential of the new peak was shifted to a less positive potential. This indicated that the existence of the inter-reaction between **1** and **2**, which affected the electro-oxidative process of **1**. This result was similar to the proton-coupled electron transfer process.[20]

The oxidation potentials of TEMPO and BHT were higher than the oxidation potential of **1** (TEMPO: 1.68 V, Fig. 1b, blue line; BHT: 2.10 V, pink line), which indicated that TEMPO and BHT were possible not to interfere with the oxidation of **1**. Moreover, no desired product was detected when a radical scavenger TEMPO or BHT was introduced (Scheme 2c). The above results further substantiated the existence of a radical-cation intermediate. Moreover, a radical cation signal ($g$ = 2.00737, $A_N$ = 13.18 G, $A_H$ = 10.27 G) was observed in the electron paramagnetic resonance (EPR) spectrum (Fig. 2).

On the basis of the mechanistic studies and previous reports,[17,21] a plausible catalytic cycle of electro-synthesizing sulfur ylides was proposed (Scheme 3). The stable radical-cation intermediate **1-1** was generated *via* single electron oxidation at the anode, which reacted with the enol intermediate **2-1** to give the radical intermediate **1-2**. Further oxidation of **1-2** at the anode led to the generation of cation intermediate **1-3**. Finally, the deprotonation of **1-3** delivered the desired product.

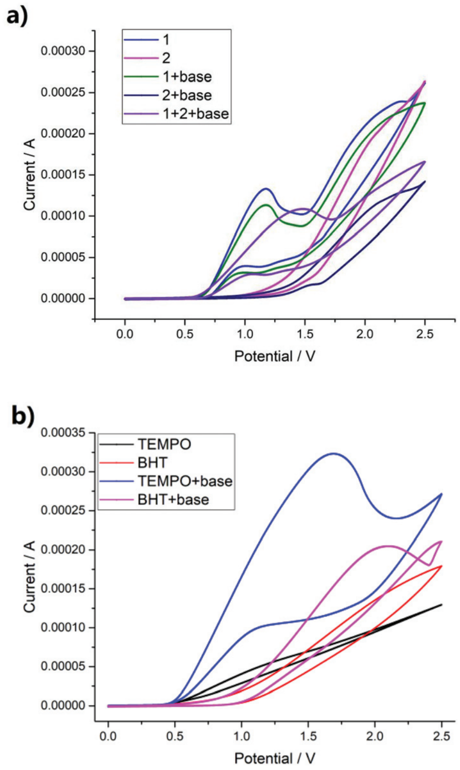
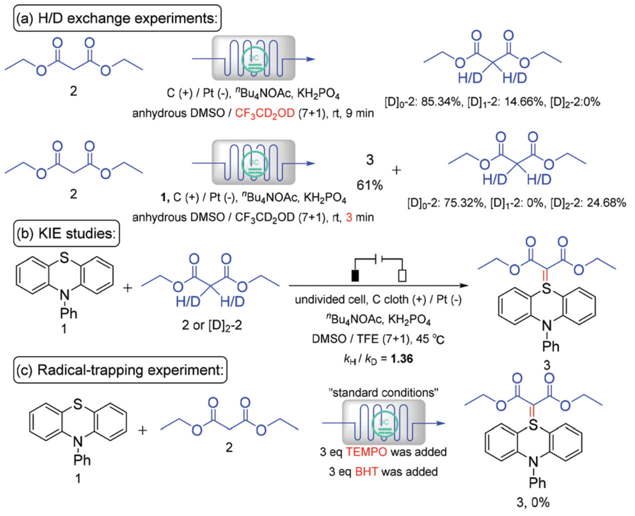


**Fig. 1** Cyclic voltammetry. (a) cyclic voltammetry of reactants; (b) cyclic voltammetry of additives.



**Scheme 2** Key mechanistic findings.

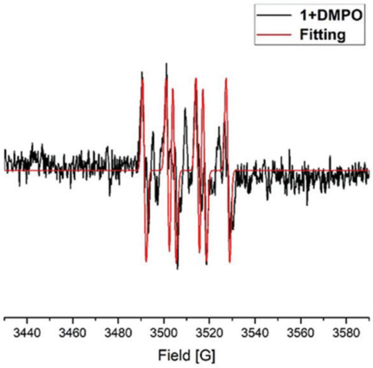


**Fig. 2** The electron paramagnetic resonance spectrum of **1**.

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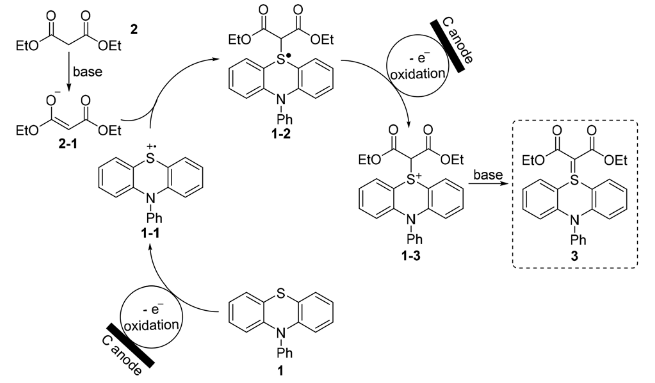

Scheme 3 Proposed mechanism for electro-synthesizing sulfur ylides.

## Conclusions

In summary, we have developed an unprecedented ambient temperature electro-oxidative coupling of sulfides with active methylene compounds to give sulfur ylides in a continuous-flow reactor under catalyst- and oxidant-free conditions. Owing to the use of continuous-flow equipment, this method features mild and green reaction conditions, high efficiency and a broad substrate scope and is easy to scale up, which shows tremendous application potential in industrial chemistry. Furthermore, the products generated with phenothiazine scaffolds are used as potential organic catalysts in photoredox reactions and electrosynthesis.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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