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Electrochemical Thiocyanation/Cyclization Cascade to Access Thiocyanato-Containing Benzoxazines

Jianguo Hu [1,2,†], Hao Wan [1,†], Shengchun Wang [3], Hong Yi [3,*] and Aiwen Lei [1,3,*]

[1] National Research Center for Carbohydrate Synthesis, Jiangxi Normal University, Nanchang 330022, China
[2] Academician Workstation, Jiangxi University of Chinese Medicine, Nanchang 330004, China
[3] The Institute for Advanced Studies (IAS), College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China
* Correspondence: hong.yi@whu.edu.cn (H.Y.); aiwenlei@whu.edu.cn (A.L.)
† These authors contributed equally to this work.

Abstract: Due to the importance of SCN-containing heteroarenes, developing novel and green synthetic protocols for the synthesis of SCN-containing compounds has drawn much attention over the last decades. We reported here an electrochemical oxidative cyclization of *ortho*-vinyl aniline to access various SCN-containing benzoxazines. Mild conditions, an extra catalyst-free and oxidant-free system, and good tolerance for air highlight the application potential of this method.

Keywords: electrochemistry; cascade cyclization; thiocyanation; difunctionalization

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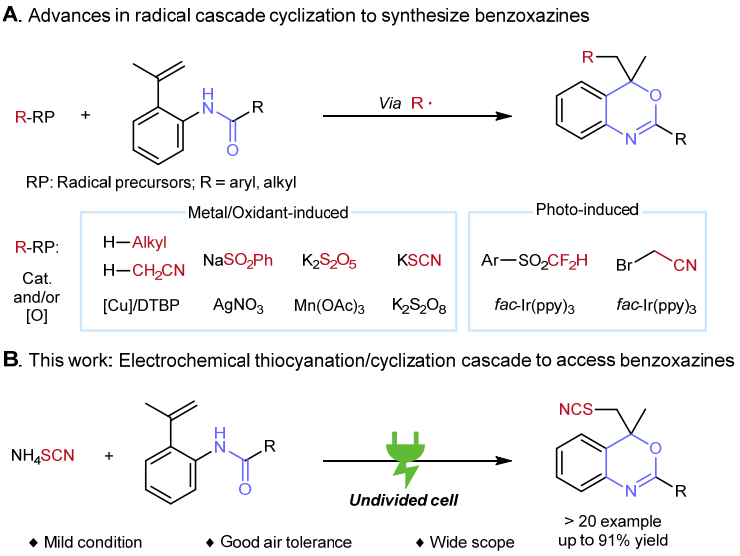
1. Introduction

Due to the unique physiological activities of heteroarenes, heterocyclic compounds are widely present in natural products, pharmaceuticals, pesticides, and materials [1–4]. Among these valuable heterocycles, benzoxazine has also served as a key skeleton in polymers, contributing to their outstanding characteristics [5,6]. Therefore, the construction and modification of benzoxazines have drawn much attention from synthetic chemists and material scientists.

To date, the flourishing development of radical chemistry has provided attractive protocols to access heterocycles via cascade routes [7–13]. Utilizing radicals as functional reagents, the complicated heterocycles could be effectively obtained under mild conditions. In this context, the radical-induced cyclization cascade process is a considerable path for synthesizing benzoxazines (Scheme 1A). Recently, several breakthroughs have been achieved in such processes. In 2015, Ji and co-workers developed a Cu-catalyzed system for cascade cyclization using nitrile as radical precursors [14]. Two years later, Zhao reported a similar catalytic condition in which alkane was used as radical precursors [15]. Additionally, the radical cascade cyclization was also tolerated with *S*-centered radicals. In 2019, Li developed an Ag-induced reaction to obtain benzoxazines in which sulfonyl radicals served as a key [16]. Recently, Liang discovered a $Mn(OAc)_3$-promoted sulfonation-cyclization cascade via the SO_3^- radical [17]. Without the assistance of transition-metal, Guo developed a $K_2S_2O_8$-induced strategy to achieve radical thiocyanooxygenation [18]. Despite of these advances, the heat condition, the use of transition-metal and/or sacrificial oxidant promote the development of alternative methods. Photoredox chemistry provide a mild route to radical cyclization [19,20]. Xiao and colleagues developed an oxytrifluoromethylation of *N*-allylamides to access CF_3-containing oxazolines and benzoxazines with Ru-photocatalysts [21]. In 2016, Fu and co-authors reported a photo-induced oxydifluoromethylation of olefinic amides via a difluoromethyl radical method [22]. Three years later, Sun used bromomethyl cyanides as radical precursors to synthesize 4-cyanoethylated benzoxazines by photo-induction [23]. However, the using of expensive catalysts may limit their further application. Overall, developing a practical and green method with bulk radical precursors is in demand for cascade cyclization to synthesize benzoxazines.



Scheme 1. Recent advances in cyclization cascade to access benzoxazines. (**A**) Advances in radical cascade cyclization. (**B**) Outline of this work: electrochemical thiocyanation/cyclization cascade to access thiocyanato-containing benzoxazines.

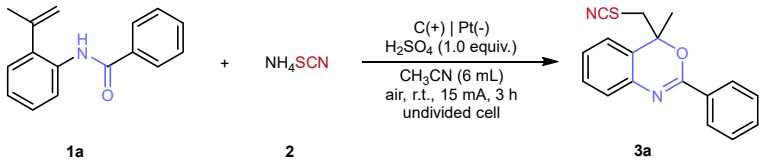
Over the last decade, electrochemical organic synthesis has been regarded as a sustainable technology in which electrons serve as redox reagents [24–27]. Especially, benefiting from diverse derivatizations of the thiocyanic group, electrochemical alkene thiocyanation has undergone vigorous development [28]. For example, the aryl thiocyanate generated by electrochemistry can be effectively transformed to other valuable chemicals, including trifluoromethyl thioether, alkyl thioethers, and tetrazole [29]. Since the wide application of ammonium thiocyanates [30–32], constructing thiocyanato-containing benzoxazines via an *S*-centered radical process is a considerable route [33]. Recently, we have developed an efficient electrochemical method to oxidize the olefinic amides to construct the derivatives of benzoxazines and iminoisobenzofurans [34,35]. Based on these advances, we reported here an electrochemical thiocyanation/cyclization cascade to construct benzoxazine under mild conditions (Scheme 1B). The merit of this method was demonstrated by its extra catalyst-free and oxidant-free conditions. While we were preparing this paper, Huang and coworkers reported a similar work that an electrochemical oxythiocyanation of *ortho*-olefinic amides enables the synthesis of thiocyanated benzoxazines [36].

2. Results

2.1. Condition Optimization

Initial condition optimization was examined with *N*-(2-(prop-1-en-2-yl)phenyl)benzamide **1a** as radical acceptor and ammonium thiocyanate **2** as radical precursor (Table 1). After a series of efforts, the optimized condition was established with a carbon rod as the anode, Pt as the cathode, 0.5 M CH_3CN as the solvent, and 1 equivalent H_2SO_4 as the acid. Under a 15 mA electrolysis with 3 h, the desired product **3a** was obtained in 91% isolated yield (entry 1). Without H_2SO_4, this organic transformation was realized in a low yield (entry 2). When trifluoroacetic acid (TFA) was used as the acid, the desired transformation was achieved smoothly in 74% GC yield (entry 3). Using H_2O or 2,2,2-trifluoroethanol (TFE) instead of H_2SO_4, reaction yields obviously decreased (entries 4–5). Moreover, this electrochemical transformation performed worse with other solvents, such as THF, DMSO, and EtOH (entries 6–8). The yields of **3a** were slightly decreased with SS (stainless steel) or Ni plates as the cathode (entries 9–10). Control experiments provide the electrolysis essential for this electrochemical cascade cyclization (entry 11).

Table 1. Condition optimization.



Entry	Variation from the Standard Conditions	Yield (%) [a]
1	None	93 (91 [b])
2	Without H_2SO_4	28
3	TFA instead of H_2SO_4	74
4	H_2O instead of H_2SO_4	28
5	TFE instead of H_2SO_4	10
6	THF instead of MeCN	10
7	DMSO instead of MeCN	28
8	EtOH instead of MeCN	36
9	SS plate instead of Pt plate	70
10	Ni plate instead of Pt plate	59
11	Without electrolysis	N.d.

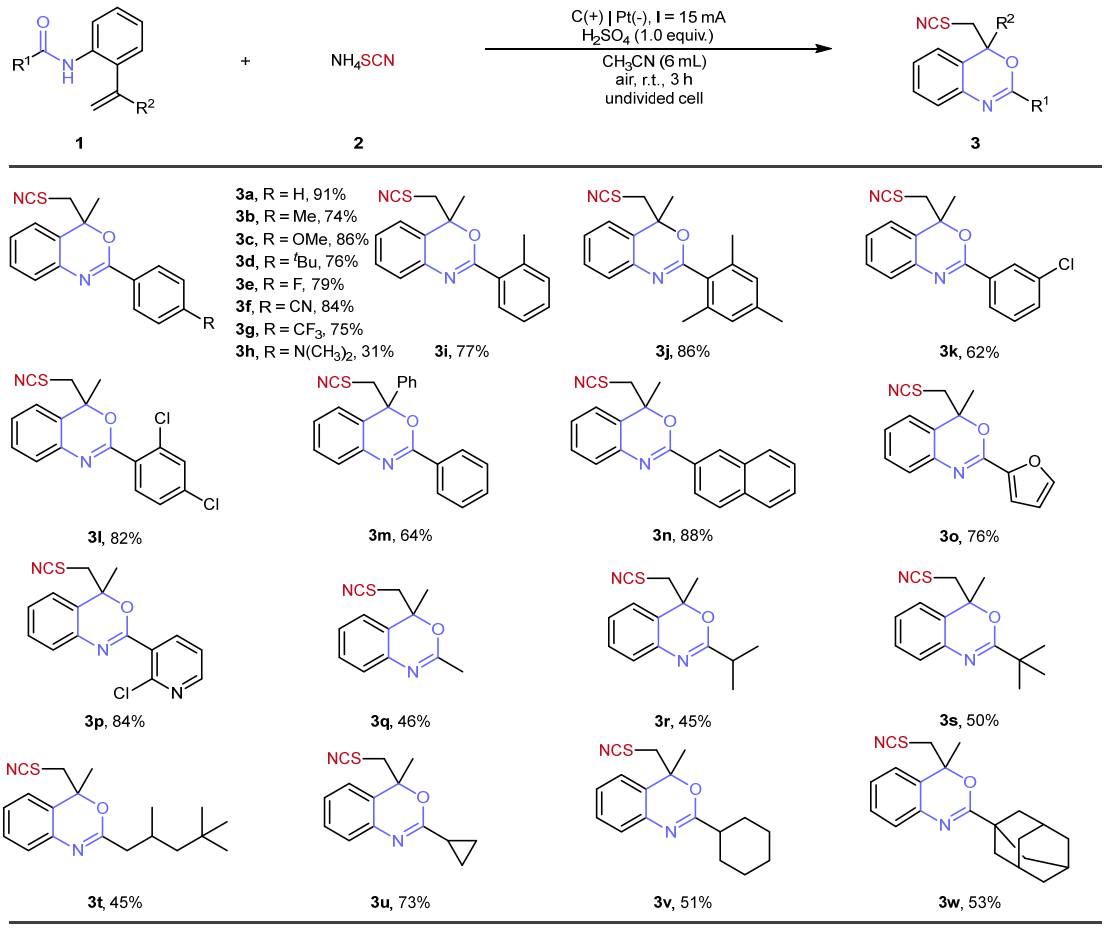
Reaction conditions: carbon rod anode, platinum plate cathode, constant current = 15 mA, **1a** (0.3 mmol), **2** (0.9 mmol), H_2SO_4 (0.3 mmol), CH_3CN (6.0 mL), air, 3 h. [a] Yields of **3a** were determined by gas chromatography (GC) analysis by using biphenyl as the internal standard. [b] Isolated yield. N.d. = not detected.

2.2. Scope of Substrates

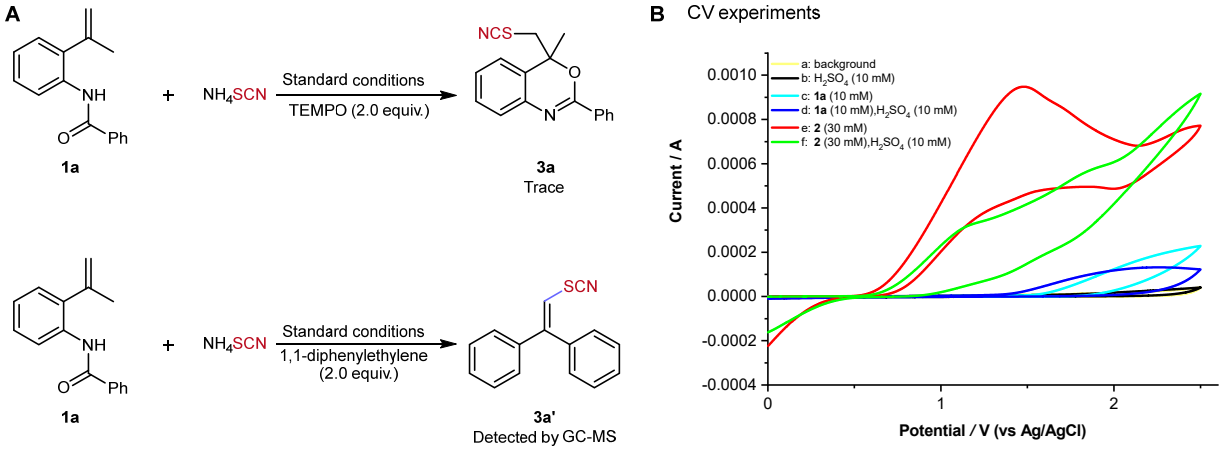
Next, the scope of the substrates was examined (Scheme 2). Various olefinic benzamide derivatives were compatible radical acceptors for achieving the desired transformation. Both electron-donating and electron-withdrawing substitutions on the *para*-position of the phenyl group were well tolerated, producing corresponding products in moderate to high yields (**3a** to **3g**). It is notable that substrates with a redox-sensitive functional groups smoothly completed this electrochemical reaction, for example, *N*-dimethylamino **3h**. Moreover, *ortho*-, *meta*-, and even *multi*-substituted aryl amides were successfully transformed to corresponding products in moderate yields (**3i** to **3l**). In addition, other (hetero)aryl -modified substrates also performed well in this system (**3n** to **3p**). Additionally, this electrochemical cascade cyclization was suitable for stilbene to offer the product in moderate yield (**3m**). Furthermore, a set of alkyl amides realized the desired transformation, forming target products in moderate yields (**3q** to **3w**).

2.3. Mechanistic Studies

Subsequently, radical inhibition experiments were carried out to determine the existence of radical processes (Scheme 3A). With the addition of 2 equivalents 2,2,6,6-tetramethyl-1-piperidinyloxy, the desired transformation was totally inhibited, supporting a radical process involved in this transformation. Moreover, the thiocyanate radical was trapped by 1,1-diphenylethylene under standard conditions. Then, cyclic voltammetry experiments were carried out to investigate the mechanism (Scheme 3B and Supplementary Materials). Without the acid, the oxidation peak of **1a** is not observed. In contrast, the oxidation peak potential of **1a** is detected at 2.27 V in the existence of acid. Notably, the oxidation peak potential of **2** appears at 1.48 V. With the addition of acid, two oxidation peaks of **2** are observed, promoting the secondary oxidation of thiocyanate which is similar to the halogen property {SCN^--$(SCN)_3^-$-$(SCN)_2^-$}. These CV studies disclosed ammonium thiocyanate was preferentially oxidized over **1a**.

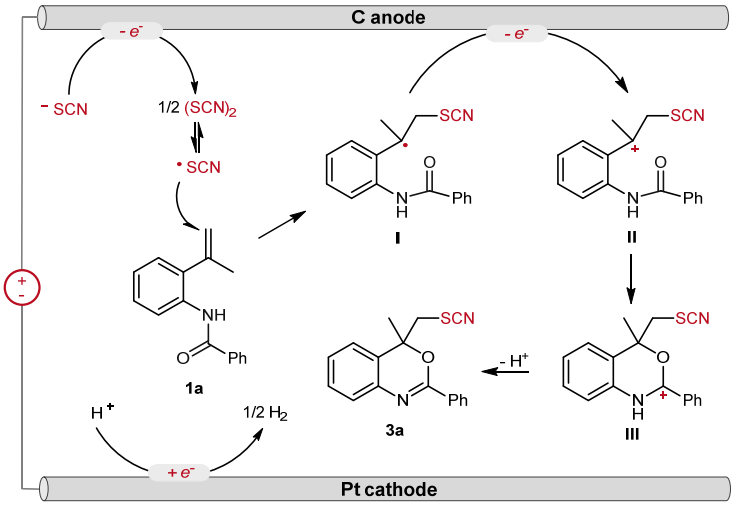


Scheme 2. Scope of substrates. Reaction conditions: carbon rod anode, platinum plate cathode, constant current = 15 mA, **1** (0.3 mmol), **2** (0.9 mmol), H_2SO_4 (0.3 mmol), CH_3CN (6.0 mL), air, 3 h.



Scheme 3. Mechanistic studies. (**A**) Radical inhibition experiments. (**B**) CV experiments.

Based on the above results, a plausible mechanism was proposed (Scheme 4). In the anode, the thiocyanate anion was oxidized to form thiocyanate radical, which could react with **1a** to offer *C*-centered radical intermediate **I**. Then, **I** transformed to carbon cation **II** via SET in the anode. Next, the final product **3a** was generated, followed by an intramolecular nucleophilic attack and deprotonation. In the cathode, two protons were reduced to furnish hydrogen.



Scheme 4. Plausible mechanism.

3. Materials and Methods

General procedure for the preparation of substrates: A round-bottom flask was charged with methyltriphenylphosphonium bromide (5.36 g, 15.00 mmol) and dry THF (20.00 mL) under N_2 atmosphere, followed by the addition of potassiumtert-butoxide (1.68 g, 15.00 mmol) at 0 °C. The reaction mixture was allowed to warm to ambient temperature and stir for 0.50 h. Next, 2-aminoacetophenone (**1**–**1**) (1.35 g, 10.00 mmol) was added. The reaction mixture was stirred at room temperature overnight. After completion, the reaction was quenched with saturated $NaHCO_3$ solution and extracted with EtOAc (100.00 mL). The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The reaction mixture was purified via column chromatography to give **1**–**2**. To a solution of **1**–**2** (0.99 g, 7.40 mmol) and Et_3N (1.53 g, 11.10 mmol) in CH_2Cl_2 (15.00 mL) was added the solution of benzoylchloride (1.00 mL, 8.90 mmol) in dichloromethane (5.00 mL) dropwise at 0 °C. After completion, the reaction mixture was purified via column chromatography to give **1a**. Analogues **1a**–**1w** were synthesized by using similar procedures.

General procedure for electrochemical thiocyanation/cyclization cascade: In an oven-dried, undivided three-necked bottle (10 mL) equipped with a stir bar, *N*-(2-(prop-1-en-2-yl)phenyl)benzamide **1a** (0.30 mmol), ammonium thiocyanate **2** (0.90 mmol) was added to the mixture of acetonitrile (6 mL) and sulfuric acid (0.30 mmol). The bottle was equipped with a graphite rod (ϕ 6 mm, about 15 mm immersion depth in solution) as the anode and platinum plate (15 mm × 15 mm × 0.3 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 15 mA under air atmosphere at room temperature for 3 h. After completion of the reaction, as indicated by TLC and GC-MS, the pure product was obtained by flash column chromatography on silica gel.

CV experiments: Cyclic voltammetry experiments were performed in a three-electrode cell connected to a Schlenk line under air at room temperature. The working electrode was a glassy carbon electrode, the counter electrode was a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution, and 6 mL of CH_3CN containing 0.03 M H_2SO_4 was poured into the electrochemical cell in all experiments. The scan rate was 0.1 V/s, ranging from 0 V to 2.5 V. The peak potentials vs. Ag/AgCl were used.

Characterization of products: *4-methyl-2-phenyl-4-(thiocyanatomethyl)-4H-benzo[d*][1,3]*oxazine* (***3a***). White solid was obtained in 91% isolated yield, 79.9 mg, 0.3 mmol scale, R_f = 0.35 (petroleum ether/ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 8.0, 1.7 Hz, 2H), 7.58–7.42 (m, 3H), 7.41–7.33 (m, 2H), 7.29–7.22 (m, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 3.58 (d, *J* = 13.8 Hz, 1H), 3.45 (d, *J* = 13.9 Hz, 1H), 1.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 138.6, 131.8, 131.8, 129.9, 128.3, 127.9, 127.2, 126.3, 125.9, 122.8, 112.2, 78.9, 44.4, 25.8. HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{17}H_{15}N_2OS^+$ 295.0899; found 295.09245.

4-methyl-4-(thiocyanatomethyl)-2-(p-tolyl)-4H-benzo[d][1,3]*oxazine (**3b**).* Colorless oil was obtained in 74% isolated yield, 68.1 mg, 0.3 mmol scale, R_f = 0.35 (petroleum ether/ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11–7.96 (m, 2H), 7.40–7.30 (m, 2H), 7.28–7.19 (m, 3H), 7.11 (dd, *J* = 7.4, 1.2 Hz, 1H), 3.54 (d, *J* = 13.8 Hz, 1H), 3.41 (d, *J* = 13.8 Hz, 1H), 2.40 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 142.3, 138.7, 129.8, 129.0, 128.9, 127.9, 126.9, 126.2, 125.7, 122.8, 112.2, 78.6, 44.2, 25.6, 21.5. HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{18}H_{17}N_2OS^+$ 309.1056; found 309.1062.

2-(4-methoxyphenyl)-4-methyl-4-(thiocyanatomethyl)-4H-benzo[d][1,3]*oxazine (**3c**).* Colorless oil was obtained in 86% isolated yield, 83.8 mg, 0.3 mmol scale, R_f = 0.32 (petroleum ether/ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14–8.07 (m, 2H), 7.38–7.29 (m, 2H), 7.21 (td, *J* = 7.3, 1.7 Hz, 1H), 7.10 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.97–6.91 (m, 2H), 3.84 (s, 3H), 3.55 (d, *J* = 13.8 Hz, 1H), 3.40 (d, J = 13.8 Hz, 1H), 1.87 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 162.5, 155.1, 138.8, 129.72, 129.69, 126.6, 126.1, 125.4, 124.0, 122.7, 113.6, 112.2, 78.5, 55.3, 44.1, 25.4. HRMS (ESI) m/z: [M + H]+ Calcd for $C_{18}H_{17}N_2O_2S^+$ 325.1005; found 325.1013.

2-(4-(tert-butyl)phenyl)-4-methyl-4-(thiocyanatomethyl)-4H-benzo[d][1,3]*oxazine (**3d**).* White solid was obtained in 76% isolated yield, 79.8 mg, 0.5 mmol scale, Rf = 0.39 (petroleum ether/ethyl acetate = 10:1). 1H NMR (400 MHz, CDCl3) δ 8.12–8.05 (m, 2H), 7.53–7.45 (m, 2H), 7.41–7.33 (m, 2H), 7.29–7.21 (m, 1H), 7.14 (dd, J = 7.6, 1.3 Hz, 1H), 3.59 (d, J = 13.7 Hz, 1H), 3.45 (d, J = 13.8 Hz, 1H), 1.91 (s, 3H), 1.35 (s, 9H). 13C NMR (101 MHz, CDCl3) δ 155.4, 138.8, 129.9, 129.0, 127.8, 127.0, 126.4, 125.83, 125.79, 125.4, 122.8, 112.3, 78.7, 44.3, 34.9, 31.1, 25.7. HRMS (ESI) *m*/*z*: [M + H]+ Calcd for $C_{21}H_{23}N_2OS^+$ 351.1525; found 351.1547.

2-(4-fluorophenyl)-4-methyl-4-(thiocyanatomethyl)-4H-benzo[d][1,3]*oxazine (**3e**).* White solid was obtained in 79% isolated yield, 73.7 mg, 0.3 mmol scale, Rf = 0.30 (petroleum ether/ethyl acetate = 10:1). 1H NMR (400 MHz, CDCl3) δ 8.22–8.12 (m, 2H), 7.40–7.30 (m, 2H), 7.24 (td, J = 7.4, 1.7 Hz, 1H), 7.17–7.08 (m, 3H), 3.56 (d, J = 13.9 Hz, 1H), 3.42 (d, J = 14.0 Hz, 1H), 1.89 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 166.2, 163.7, 154.3, 138.4, 130.2, 130.1, 129.9, 127.89, 127.86, 127.2, 126.1, 125.8, 122.8, 115.5, 115.3, 112.1, 79.0, 44.3, 25.8. 19F NMR (376 MHz, CDCl3) δ −107.52. HRMS (ESI) *m*/*z*: [M + H]+ Calcd for $C_{17}H_{14}FN_2OS^+$ 313.0803; found 313.0805.

4-(4-methyl-4-(thiocyanatomethyl)-4H-benzo[d][1,3]*oxazin-2-yl)benzonitrile (**3f**).* White solid was obtained in 84% isolated yield, 79.7 mg, 0.3 mmol scale, R_f = 0.20 (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33–8.23 (m, 2H), 7.77–7.69 (m, 2H), 7.45–7.34 (m, 2H), 7.34–7.25 (m, 1H), 7.14 (dd, *J* = 7.6, 1.4 Hz, 1H), 3.58 (d, *J* = 14.1 Hz, 1H), 3.46 (d, *J* = 14.1 Hz, 1H), 1.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2, 137.8, 135.8, 131.9, 130.0, 128.2, 128.0, 126.2, 126.0, 122.8, 118.3, 114.6, 111.8, 79.6, 44.4, 26.2. HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{18}H_{14}FN_3OS^+$ 320.0852; found 320.0863.

4-methyl-4-(thiocyanatomethyl)-2-(4-(trifluoromethyl)phenyl)-4H-benzo[d][1,3]*oxazine (**3g**).* White solid was obtained in 75% isolated yield, 81.3 mg, 0.3 mmol scale, R_f = 0.21 (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.43–7.34 (m, 2H), 7.32–7.25 (m, 1H), 7.13 (dd, *J* = 7.6, 1.3 Hz, 1H), 3.57 (d, *J* = 14.0 Hz, 1H), 3.45 (d, *J* = 14.0 Hz, 1H), 1.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 138.1, 135.1 (d, *J* = 1.5 Hz), 133.0 (q, *J* = 32.7 Hz), 130.0, 128.2, 127.8, 126.1 (d, *J* = 1.8 Hz), 125.2 (q, *J* = 3.8 Hz),125.1, 123.8 (q, *J* = 273.7 Hz) 122.9, 112.0, 79.4, 44.4, 26.1. ^{19}F NMR (376 MHz, CDCl3) δ -62.76. HRMS (ESI) *m*/*z*: [M + H]+ Calcd for $C_{18}H_{14}F_3N_2OS^+$ 363.0772; found 363.0773.

4-(4-(isothiocyanatomethyl)-4-methyl-4H-benzo[d][1,3]*oxazin-2-yl)-N,N-dimethylaniline (**3h**).* White solid was obtained in 31% isolated yield, 31.3 mg, 0.3 mmol scale, Rf = 0.39 (petroleum ether/ethyl acetate = 10:1). 1H NMR (400 MHz, CDCl3) δ 8.40 (d, J = 2.0 Hz, 1H), 8.11 (dd, J = 8.4, 2.0 Hz, 1H), 7.44–7.33 (m, 2H), 7.28–7.22 (m, 3H), 7.13 (dd, J = 7.4, 1.2 Hz, 1H), 3.58 (d, J = 13.9 Hz, 1H), 3.45 (d, J = 13.9 Hz, 1H), 2.78 (s, 6H), 1.92 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 154.2, 153.8, 138.4, 130.0, 129.1, 128.9, 128.0, 127.4, 126.2, 126.0, 122.9, 122.8, 120.6, 112.1, 111.1, 78.8, 44.4, 44.3, 25.9. HRMS (ESI) m/z: [M + H]+ Calcd for $C_{19}H_{20}N_3OS^+$ 395.0095; found 395.1007.

4-methyl-4-(thiocyanatomethyl)-2-(o-tolyl)-4H-benzo[d][1,3]*oxazine (**3i**).* Colorless oil was obtained in 77% isolated yield, 70.5 mg, 0.3 mmol scale, Rf = 0.35 (petroleum ether/ethyl

acetate = 10:1). 1H NMR (400 MHz, CDCl3) δ 7.86–7.80 (m, 1H), 7.41–7.30 (m, 3H), 7.30–7.22 (m, 3H), 7.12 (dd, J = 7.7, 1.4 Hz, 1H), 3.60 (d, J = 13.7 Hz, 1H), 3.47 (d, J = 13.7 Hz, 1H), 2.65 (s, 3H), 1.88 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 156.8, 138.4, 138.3, 131.6, 131.5, 130.6, 129.8, 129.5, 127.3, 125.8, 125.7, 125.4, 122.8, 112.0, 79.2, 44.4, 26.4, 21.8. HRMS (ESI) *m*/*z*: [M + H]+ Calcd for $C_{18}H_{17}N_2OS^+$ 309.1056; found 309.1071.

2-mesityl-4-methyl-4-(thiocyanatomethyl)-4H-benzo[d][1,3]*oxazine (**3j**).* White solid was obtained in 86% isolated yield, 86.3 mg, 0.3 mmol scale, Rf = 0.36 (petroleum ether/ethyl acetate = 10:1). 1H NMR (400 MHz, CDCl3) δ 7.40–7.33 (m, 1H), 7.31–7.25 (m, 2H), 7.11 (dd, J = 8.0, 1.4 Hz, 1H), 6.89 (s, 2H), 3.69 (d, J = 13.7 Hz, 1H), 3.48 (d, J = 13.6 Hz, 1H), 2.36 (s, 6H), 2.28 (s, 3H), 1.85 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 157.4, 139.1, 137.8, 135.7, 130.5, 129.9, 128.3, 127.5, 125.9, 124.6, 123.0, 111.9, 79.8, 45.2, 28.4, 21.1, 19.5. HRMS (ESI) *m*/*z*: [M + H]+ Calcd for $C_{20}H_{21}N_2OS^+$ 337.1369; found 337.1380.

2-(3-chlorophenyl)-4-methyl-4-(thiocyanatomethyl)-4H-benzo[d][1,3]*oxazine (**3k**).* White solid was obtained in 62% isolated yield, 60.7 mg, 0.3 mmol scale, Rf = 0.35 (petroleum ether/ethyl acetate = 10:1). 1H NMR (400 MHz, CDCl3) δ 8.06 (t, J = 1.9 Hz, 1H), 7.99–7.94 (m, 1H), 7.43–7.37 (m, 1H), 7.34–7.24 (m, 3H), 7.22–7.16 (m, 1H), 7.05 (dd, J = 7.6, 1.4 Hz, 1H), 3.48 (d, J = 13.9 Hz, 1H), 3.36 (d, J = 13.9 Hz, 1H), 1.82 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 153.9, 138.2, 134.4, 133.6, 131.7, 129.9, 129.6, 127.8, 127.6, 126.1, 126.0, 125.8, 122.8, 111.9, 79.3, 44.4, 26.0. HRMS (ESI) *m*/*z*: [M + H]+ Calcd for $C_{17}H_{14}ClN_2OS^+$ 329.0510; found 329.0519.

2-(2,4-dichlorophenyl)-4-methyl-4-(thiocyanatomethyl)-4H-benzo[d][1,3]*oxazine (**3l**).* White solid was obtained in 82% isolated yield, 88.4 mg, 0.3 mmol scale, Rf = 0.29 (petroleum ether/ethyl acetate = 10:1). 1H NMR (400 MHz, CDCl3) δ 7.68 (d, J = 8.4 Hz, 1H), 7.38 (d, J = 2.1 Hz, 1H), 7.31 (ddd, J = 8.5, 7.2, 1.4 Hz, 1H), 7.27–7.19 (m, 3H), 7.04 (dd, J = 7.6, 1.4 Hz, 1H), 3.54 (d, J = 13.9 Hz, 1H), 3.43 (d, J = 13.9 Hz, 1H), 1.82 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 154.8, 137.9, 137.0, 133.9, 132.2, 130.5, 130.3, 130.0, 128.0, 127.1, 126.0, 125.3, 123.0, 111.9, 80.5, 44.6, 26.8. HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{17}H_{13}N_2Cl_2OS^+$ 363.0120; found 363.0129.

2,4-diphenyl-4-(thiocyanatomethyl)-4H-benzo[d][1,3]*oxazine (**3m**).* Colorless oil was obtained in 64% isolated yield, 68.4 mg, 0.3 mmol scale, R_f = 0.27 (petroleum ether/ethyl acetate = 5:1). ^{1}H NMR (400 MHz, CDCl3) δ 8.30–8.21 (m, 2H), 7.54–7.43 (m, 3H), 7.42–7.37 (m, 2H), 7.36–7.24 (m, 6H), 7.20–7.14 (m, 1H), 4.05–3.88 (m, 2H). 13C NMR (101 MHz, CDCl3) δ 155.4, 140.0, 139.5, 131.8, 131.6, 130.1, 129.0, 128.8, 128.4, 127.9, 126.9, 126.1, 125.6, 124.7, 124.0, 112.1, 82.3, 43.6. HRMS (ESI) *m*/*z*: [M + H]+ Calcd for $C_{22}H_{17}N_2OS^+$ 357.1056; found 357.1084.

4-methyl-2-(naphthalen-2-yl)-4-(thiocyanatomethyl)-4H-benzo[d][1,3]*oxazine (**3n**).* Colorless oil was obtained in 88% isolated yield, 90.3 mg, 0.3 mmol scale, Rf = 0.31 (petroleum ether/ethyl acetate = 5:1). 1H NMR (400 MHz, CDCl3) δ 8.63 (d, J = 1.7 Hz, 1H), 8.26 (dd, J = 8.7, 1.8 Hz, 1H), 7.98–7.94 (m, 1H), 7.90–7.81 (m, 2H), 7.58–7.47 (m, 2H), 7.42–7.34 (m, 2H), 7.27–7.19 (m, 1H), 7.12–7.07 (m, 1H), 3.55 (d, J = 13.9 Hz, 1H), 3.42 (d, J = 13.9 Hz, 1H), 1.91 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 155.3, 138.6, 134.9, 132.6, 129.8, 129.04, 129.02, 128.6, 128.0, 127.7, 127.2, 126.5, 126.3, 125.8, 124.3, 122.8, 112.2, 78.9, 44.2, 25.7. HRMS (ESI) *m*/*z*: [M + H]+ Calcd for $C_{21}H_{17}N_2OS^+$ 345.1056; found 345.1060.

2-(furan-2-yl)-4-methyl-4-(thiocyanatomethyl)-4H-benzo[d][1,3]*oxazine (**3o**).* Yellow oil was obtained in 76% isolated yield, 64.8 mg, 0.3 mmol scale, Rf = 0.22 (petroleum ether/ethyl acetate = 5:1). 1H NMR (400 MHz, CDCl3) δ 7.62 (dd, J = 1.7, 0.8 Hz, 1H), 7.42–7.33 (m, 2H), 7.27–7.21 (m, 1H), 7.15 (dd, J = 3.5, 0.8 Hz, 1H), 7.14–7.09 (m, 1H), 6.54 (dd, J = 3.5, 1.8 Hz, 1H), 3.58 (d, J = 14.0 Hz, 1H), 3.39 (d, J = 13.9 Hz, 1H), 1.89 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 148.2, 145.9, 145.7, 137.9, 129.9, 127.2, 126.2, 125.8, 122.8, 115.5, 112.0, 111.9, 78.8, 43.9, 25.5. HRMS (ESI) *m*/*z*: [M + H]+ Calcd for $C_{15}H_{13}N_2O_2S^+$ 285.0692; found 285.0721.

2-(2-chloropyridin-3-yl)-4-methyl-4-(thiocyanatomethyl)-4H-benzo[d][1,3]*oxazine (**3p**).* White solid was obtained in 84% isolated yield, 82.9 mg, 0.3 mmol scale, Rf = 0.21 (petroleum ether/ethyl acetate = 5:1). 1H NMR (400 MHz, CDCl3) δ 8.49 (dd, J = 4.8, 2.0 Hz, 1H), 8.17 (dd, J = 7.6, 2.0 Hz, 1H), 7.45–7.30 (m, 4H), 7.14 (dd, J = 7.9, 1.3 Hz, 1H), 3.65 (d, J = 14.0 Hz, 1H), 3.55 (d, J = 14.0 Hz, 1H), 1.94 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 154.2, 150.8, 149.3,

140.0, 137.7, 130.0, 128.8, 128.2, 126.0, 125.2, 123.1, 122.2, 111.8, 80.8, 44.7, 27.1. HRMS (ESI) *m*/*z*: [M + H]+ Calcd for $C_{16}H_{13}N_3ClOS^+$ 330.0462; found 330.0471.

2,4-dimethyl-4-(thiocyanatomethyl)-4H-benzo[d][1,3]*oxazine (**3q**).* Colorless oil was obtained in 46% isolated yield, 32.1 mg, 0.3 mmol scale, Rf = 0.32 (petroleum ether/ethyl acetate = 5:1). 1H NMR (400 MHz, CDCl3) δ 7.32 (td, J = 7.6, 1.5 Hz, 1H), 7.25–7.13 (m, 2H), 7.03 (dd, J = 7.7, 1.4 Hz, 1H), 3.48 (d, J = 13.9 Hz, 1H), 3.27 (d, J = 14.0 Hz, 1H), 2.19 (s, 3H), 1.80 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 159.0, 138.0, 129.8, 127.0, 125.3, 125.0, 122.8, 112.2, 78.7, 45.0, 26.5, 21.4. HRMS (ESI) *m*/*z*: [M + H]+ Calcd for $C_{12}H_{13}N_2OS^+$ 233.0743; found 233.0743.

2-isopropyl-4-methyl-4-(thiocyanatomethyl)-4H-benzo[d][1,3]*oxazine (**3r**).* Colorless oil was obtained in 66% isolated yield, 51.5 mg, 0.3 mmol scale, Rf = 0.33 (petroleum ether/ethyl acetate = 2:1). 1H NMR (400 MHz, CDCl3) δ 7.39–7.34 (td, J = 7.6, 1.5 Hz, 1H), 7.32–7.24 (m, 2H), 7.06 (dd, J = 7.6, 1.5 Hz, 1H), 3.63–3.42 (m, 2H), 1.86 (s, 6H), 1.83 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 158.8, 137.0, 130.0, 128.2, 126.2, 125.4, 122.9, 111.8, 111.6, 80.6, 55.5, 44.2, 26.7, 26.6. HRMS (ESI) *m*/*z*: [M + H]+ Calcd for $C_{14}H_{16}N_2OS^+$ 260.1055; found 260.1056.

2-(tert-butyl)-4-methyl-4-(thiocyanatomethyl)-4H-benzo[d][1,3]*oxazine (**3s**).* Colorless oil was obtained in 50% isolated yield, 41.2 mg, 0.3 mmol scale, Rf = 0.35 (petroleum ether/ethyl acetate =10:1). 1H NMR (400 MHz, CDCl3) δ 7.32 (t, J = 7.3 Hz, 1H), 7.21 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 8.1 Hz, 1H), 3.53 (d, J = 13.6 Hz, 1H), 3.42 (d, J = 13.7 Hz, 1H), 1.74 (s, 3H), 1.28 (s, 9H). 13C NMR (101 MHz, CDCl3) δ 166.3, 138.3, 129.6, 126.8, 125.6, 125.5, 122.5, 112.3, 78.0, 44.1, 37.2, 27.4, 26.0. HRMS (ESI) *m*/*z*: [M + H]+ Calcd for $C_{15}H_{18}N_2OS^+$ 275.1212; found 275.1213.

4-methyl-4-(thiocyanatomethyl)-2-(2,4,4-trimethylpentyl)-4H-benzo[d][1,3]*oxazine (**3t**).* Colorless oil was obtained in 45% isolated yield, 44.6 mg, 0.3 mmol scale, Rf = 0.35 (petroleum ether/ethyl acetate = 10:1). 1H NMR (400 MHz, CDCl3) δ 7.35–7.29 (m, 1H), 7.23–7.17 (m, 2H), 7.06–7.01 (m, 1H), 3.52 (dd, J = 13.8, 8.3 Hz, 1H), 3.34 (t, J = 14.1 Hz, 1H), 2.52–2.34 (m, 1H), 2.30–2.16 (m, 1H), 2.15–2.06 (m, 1H), 1.79 (d, J = 6.5 Hz, 3H), 1.39–1.28 (m, 1H), 1.20–1.09 (m, 1H), 1.04 (dd, J = 6.6, 3.4 Hz, 3H), 0.92 (d, J = 4.8 Hz, 9H). 13C NMR (101 MHz, CDCl3) δ 160.8 (d, J = 5.8 Hz), 138.0 (d, J = 5.3 Hz), 129.8 (d, J = 4.0 Hz), 126.8 (d, J = 3.6 Hz), 125.5 (d, J = 6.3 Hz), 125.2, 122.7 (d, J = 10.6 Hz), 112.1 (d, J = 1.8 Hz), 78.4 (d, J = 3.9 Hz), 50.5 (d, J = 25.3 Hz), 44.7 (dd, J = 39.5, 19.6 Hz), 31.0 (d, J = 2.9 Hz), 30.0, 27.5 (d, J = 10.3 Hz), 26.8, 26.5, 22.5 (d, J = 19.5 Hz). HRMS (ESI) *m*/*z*: [M + H]+ Calcd for $C_{19}H_{27}N_2OS^+$ 331.1839; found 331.1843.

2-cyclopropyl-4-methyl-4-(thiocyanatomethyl)-4H-benzo[d][1,3]*oxazine (**3u**).* Colorless oil was obtained in 73% isolated yield, 56.6 mg, 0.3 mmol scale, Rf = 0.22 (petroleum ether/ethyl acetate = 5:1). 1H NMR (400 MHz, CDCl3) δ 7.33–7.27 (td, J = 7.6, 1.4 Hz, 1H), 7.21–7.12 (m, 2H), 7.02 (dd, J = 7.9, 1.3 Hz, 1H), 3.48 (d, J = 13.8 Hz, 1H), 3.32 (d, J = 13.9 Hz, 1H), 1.80–1.67 (m, 4H), 1.16–1.04 (m, 2H), 0.97–0.85 (m, 2H). 13C NMR (101 MHz, CDCl3) δ 162.0, 138.4, 129.7, 126.3, 125.6, 124.6, 122.6, 112.1, 78.4, 44.2, 25.8, 14.4, 7.4, 6.9. HRMS (ESI) *m*/*z*: [M + H]+ Calcd for $C_{14}H_{15}N_2OS^+$ 259.0900; found 259.0906.

2-cyclohexyl-4-methyl-4-(thiocyanatomethyl)-4H-benzo[d][1,3]*oxazine (**3v**).* White solid was obtained in 51% isolated yield, 45.5 mg by 1H NMR, 0.3 mmol scale, Rf = 0.39 (petroleum ether/ethyl acetate = 5:1). 1H NMR (400 MHz, CDCl3) δ 7.35–7.29 (m, 1H), 7.23–7.17 (m, 2H), 7.07–7.02 (m, 1H), 3.51 (d, J = 13.7 Hz, 1H), 3.36 (d, J = 13.7 Hz, 1H), 2.42–2.29 (m, 1H), 2.00–1.91 (m, 2H), 1.87–1.78 (m, 2H), 1.76 (s, 3H), 1.74–1.65 (m, 1H), 1.57–1.45 (m, 2H), 1.38–1.19 (m, 3H). 13C NMR (101 MHz, CDCl3) δ 164.3, 138.2, 129.8, 126.8, 125.7, 125.2, 122.7, 112.2, 78.1, 44.5, 43.6, 26.1, 25.7, 25.7, 25.6. HRMS (ESI) *m*/*z*: [M + H]+ Calcd for $C_{17}H_{21}N_2OS^+$ 301.1369; found 301.1379.

2-(adamantan-1-yl)-4-methyl-4-(thiocyanatomethyl)-4H-benzo[d][1,3]*oxazine (**3w**).* Colorless oil was obtained in 53% isolated yield, 46.7 mg, 0.3 mmol scale, Rf = 0.44 (petroleum ether/ethyl acetate = 5:1). 1H NMR (400 MHz, CDCl3) δ 7.34–7.29 (m, 1H), 7.23–7.17 (m, 2H), 7.04 (dd, J = 7.6, 1.4 Hz, 1H), 3.51 (d, J = 13.6 Hz, 1H), 3.40 (d, J = 13.6 Hz, 1H), 2.11–2.02 (m, 3H), 1.95 (d, J = 2.9 Hz, 6H), 1.74 (d, J = 2.7 Hz, 9H). 13C NMR (101 MHz, CDCl3) δ 165.9, 138.5, 129.6, 126.7, 125.9, 125.5, 122.6, 112.4, 77.8, 44.2, 39.03, 38.98, 36.5, 28.0, 25.9. *HRMS (ESI) m/z*: [M + H]+ Calcd for $C_{21}H_{25}N_2OS^+$ 353.1682; found 3531694.

4. Conclusions

We have developed an electrochemical method to produce various benzoxazines under extra catalyst-free and oxidant-free conditions. The good functional group tolerance, excellent performance under air, and scalability demonstrated the application potential of this method. We believe this method not only provides a synthetic route towards thiocyanato-containing benzoxazines but also has a potential to inspire other electrochemical thiocyanations.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal13030631/s1, Figure S1: cyclic voltammetry experiments; NMR spectra [37].

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