有机化学 DOI: 10.6023/cjoc202205026 研究论文
Chinese Journal of Organic Chemistry ARTICLE

碘化钾介导的电催化 *N*-酰基/磺酰基次磺酰胺的合成

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摘要 开发了一种高效、环保的电催化方法合成 *N*-酰基/磺酰基取代的次磺酰胺类化合物. 在单室电解池中, 不同取代基取代的缺电子胺和芳基硫醇反应良好, 以 36%～98%的收率得到 N—S 键偶联产物. 初步的机理研究表明, 该反应可能通过自由基过程进行.

关键词 电合成; N—S 键构建; 次磺酰胺; 交叉偶联放氢反应

Electrochemical Synthesis of *N*-Acyl/Sulfonylsulfenamides Using Potassium Iodide as Mediator

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Abstract An efficient and environmentally friendly electrocatalytic protocol has been developed for synthesizing *N*-acyl/sulfonyl sulfenamides. In an undivided cell, various electron-deficient groups substituted amines and aryl thiols react smoothly to afford the N—S bond formation products in 36%～98% yields. Preliminary mechanistic studies indicate that the reaction may work through a free radical process.

Keywords electrosynthesis; N—S bond formation; sulfenamides; cross coupling hydrogen evolution reaction

1 Introduction

The efficient and clean synthesis of sulfenamide derivatives is significant protocols in organic chemistry, which has been prevalent in the field of biochemistry and pharmacological chemistry, production of fine chemicals, and organic synthesis.[1] Compounds containing N—S bonds have a variety of applications. For example, *N*-((4-chlorophenyl)thio)benzamide and its analogues are plant growth regulators.[2] Tasisulam is an acyl sulfonamide with a unique antitumor dual mechanism of action, involving antiangiogenesis and mitotic inhibition.[3] An orally active gamma secretase inhibitor is studied as a clinical candidate for the treatment of Alzheimer's disease.[4] The sulfenamides such as benfuracarb and furathiocarb are effective pesticides (Figure 1).[5]

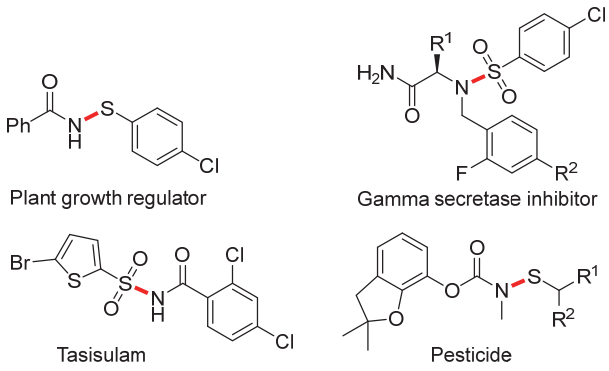

Figure 1 Selected examples of sulfenamides

Generally, the classical methods using the toxicity of chlorinating agents to synthesize sulfenamides involve the

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Received May 18, 2022; revised July 1, 2022; published online July 20, 2022.
Project supported by the National Natural Science Foundation of China (Nos. 21702175, 21961037, 22161044), the Program for Tianshan Innovative Research Team of Xinjiang Uygur Autonomous Region (No. 2021D14011), and the Natural Science Foundation of Xinjiang Uygur Autonomous Region (No. 2020D01C077).
国家自然科学基金(Nos. 21702175, 21961037, 22161044)、新疆维吾尔自治区天山创新团队(No. 2021D14011)、新疆维吾尔自治区自然科学基金(No. 2020D01C077)资助项目.

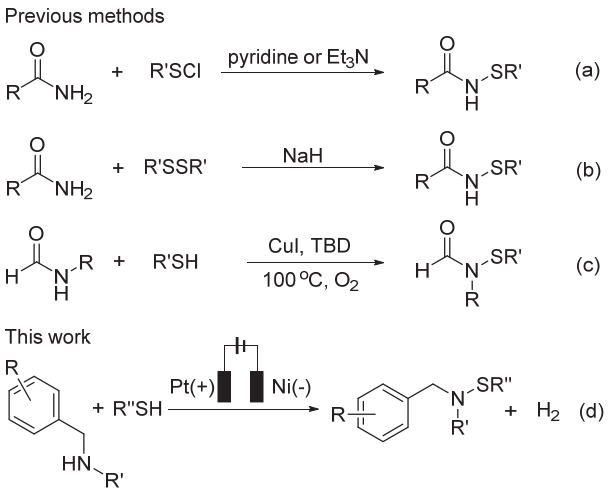
reactions of amides with sulfenyl chlorides (Scheme 1a).[6] Recently, Zhang's group reported the coupling of amides and disulfide in the presence of a large excess amount of NaH to produce *N*-acylsulfenamides (Scheme 1b).[7] The reaction of Cu-catalyzed direct aerobic oxidative cross dehydrogenative coupling (CDC) of amides with thios under O_2 at 100 ℃ has been well developed by Jang (Scheme 1c).[8] The synthesis of electrondeficient sulfenamides has been impeded by the high oxidation susceptibility of sulfur and the low nucleophilicity of amines possessing an electron-withdrawing group during the oxidative coupling reactions. Although some notable achievements have been obtained using these methods, some distinct drawbacks could not be eliminated such as utilization of toxic and sensitive Cl_2 or Br_2, the involvement of transition metal catalysts, prefunctionalization of starting materials, tedious reaction steps, harsh reaction conditions, and limited substrate scope. Therefore, the research on environmentally friendly, efficient and practical synthetic methods of sulfenamide derivatives is of great significance.

In recent years, organic electrochemical synthesis has become a research hotspot because of its green, efficient and mild conditions, especially the electrochemical cross coupling hydrogen evolution reaction has emerged as an ideal alternative to construct X—X (X=N, O, S, P *etc*.) bond.[9] As a kind of good redox mediator, halide salts such as alkali-metal iodides are stable, easy to handle, and inexpensive, and have been frequently used in the field of electrochemistry.[10] However, due to their low solubility in organic solvents, polar solvents and excessive supporting electrolytes are needed in the reaction process, so this limits their application in organic electrosynthesis. Phase-transfer catalysts such as crown ethers and quaternary ammonium or phosphonium salts are known to reduce the Coulombic interactions of halide salts.[11] In our previous work, crown ether was added to the reaction system, which can overcome problems such as poor solubility and low nucleophilicity of potassium bromide in organic solvent.[12]

Driven by our recent success on electrochemical heteroatom-heteroatom bond formation[13] and eco-friendly synthetic chemistry,[14] Herein, we report successful electrochemical anodic cross coupling reaction of amides (formyl/acyl- and sulfonylamides) with various thiols to afford a range of sulfenamides in an undivided cell with the constant current electrolysis (Scheme 1d).

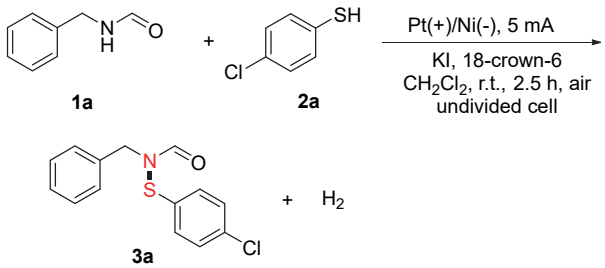
2 Results and discussion

At the outset, *N*-benzylformamide (**1a**) and 4-chlorobenzenethiol (**2a**) were selected as the model substrates to optimize the reaction conditions of the electrochemical dehydrogenative N—S bond coupling. As shown in Table 1, in an undivided cell with a Pt plate as anode and a Ni gauze as cathode, KI as electrolyte and 18-crown-6 as additive were under constant current mode at 5 mA in CH_2Cl_2 at room temperature for 2.5 h. Delightedly, the desired *N*-benzyl-*N*-((4-chlorophenyl)thio)lformamide (**3a**) was



Scheme 1 Synthesis of electron-deficient sulfenamides

Table 1 Optimization of reaction conditions[a]



Entry	Variation from the standard conditions	Yield[b]/%
1	None	98
2	KBr instead of KI	90
3	KCl instead of KI	13
4	NaBr instead of KI	87
5	NaI instead of KI	88
6	TBAI instead of KI	48
7	^{n}Bu$_4$NBF$_4$ instead of KI	n.d.
8	15-Crown-5 instead of 18-crown-6	50
9	Dibenzo-18-crown-6 instead of 18-crown-6	46
10	MeOH instead of CH_2Cl_2	21
11	MeCN instead of CH_2Cl_2	69
12	DMF instead of CH_2Cl_2	70
13	Pt(+)/Pt(−) instead of Pt(+)/Ni(−)	94
14	C(+)/Ni(−) instead of Pt(+)/Ni(−)	72
15	Without 18-crown-6	n.d.
16	Without KI	n.d.
17	Without electric current	n.d.

[a] Standard reaction conditions: **1a** (0.30 mmol), **2a** (0.20 mmol), KI (0.20 mmol), 18-crown-6 (0.20 mmol), CH_2Cl_2 (5.0 mL), Pt plate (10 mm×10 mm×0.1 mm) anode, Ni gauze (10 mm×10 mm×1 mm) cathode, constant current=5 mA, room temperature, 2.5 h, undivided cell, under air. [b] Yield of isolated product. TBAI=tetrabutylammonium iodide. n.d.=not detected.

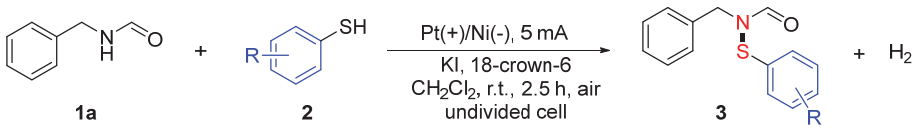
isolated in 98% yield (Table 1, Entry 1). Encouraged by this result, other supporting electrolytes were tested. The results indicated that halogen salts such as KBr, NaBr, NaI, and TBAI could facilitate the reaction smoothly, but the yield of **3a** was not improved (Entries 2～6). While this transfor-

mation did not work in the presence of $^{n}Bu_4NBF_4$ as electrolyte (Entry 7). Furthermore, the yields of product **3a** were dropped to 50% and 46%, when 15-crown-5 and dibenzo-18-crown-6 were used (Entries 8, 9). The use of MeOH, MeCN, and *N*,*N*-dimethylformamide (DMF) as solvent seriously diminished the reaction efficiency, the corresponding product **3a** was isolated in 21%, 69%, and 70%, respectively (Entries 10～12). Afterward, platinum as the cathode was tested, and no improvement in the yield of **3a** could be achieved (Entry 13). Using graphite as the anode material, the yield of product **3a** decreased from 98% to 72% (Entry 14). Decreasing or increasing the constant current both remarkably lowered the formation of the product. Slightly decreasing the reaction time could not improve the yield of **3a**. Blank experiments demonstrated that crown ether, KI, and electricity are all indispensable reaction parameters for this transformation (Entries 15～17).

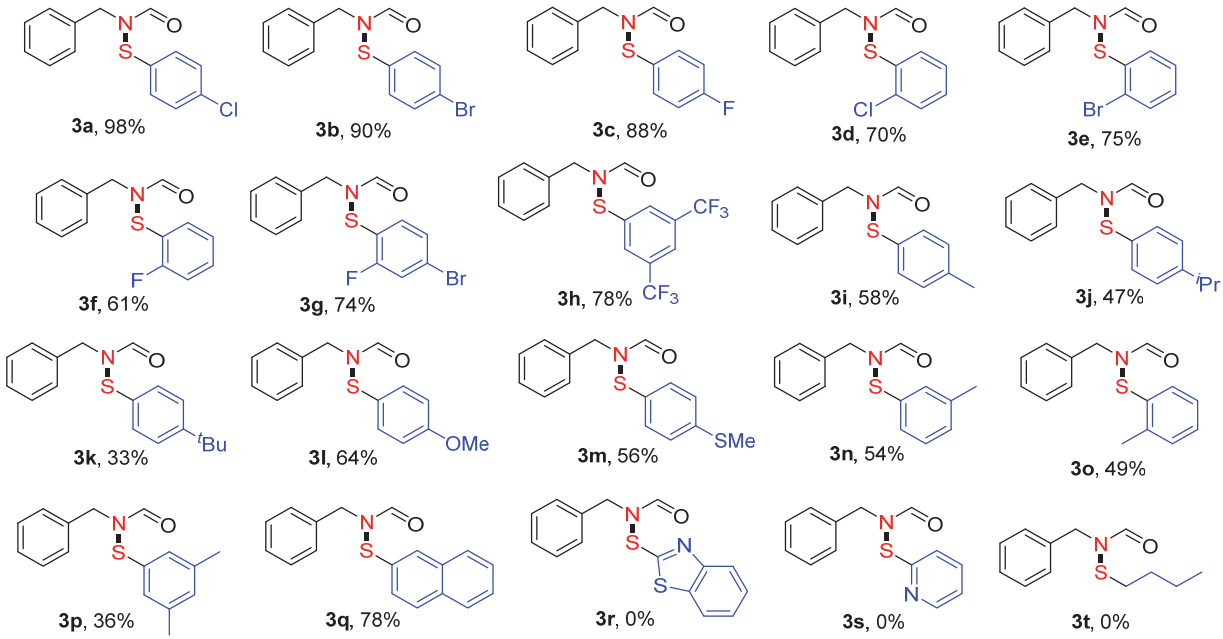
With the optimized conditions in hand, we set to examine the substrate scope of the electrochemical oxidative N—H/S—H cross coupling by using various thiols (Table 2). Firstly, thiols with halide substituents including Cl, Br, and F at the *para*-position of aromatic ring afforded the desired products in high yields (**3a**～**3c**). Changing these halogen atoms to the *ortho*-position of phenyl, the corresponding products **3d**～**3f** were obtained in 70%, 75% and 61% yields. The results confirmed that the steric properties of electron withdrawing groups on aryl mercaptans had negative effects to the electrolysis efficiency. Moreover, two electron deficient groups substituted mercaptans **3g** and **3h** were also tolerated, providing the respective products in 74% and 78% yields. Substrates decorated with electron-donating groups at C-4 position of phenyl ring, such as methyl, *iso*-propyl, *tert*-butyl, methoxy, and methylthio all were suitable for this transformation, albeit with the moderate yields of products **3i**～**3m** (33%～64%). The employment of 3-methyl-, 2-methyl- and 3,5-dimethyl-benzenethiol as starting materials could give comparable yields of the target products **3n**～**3p**, showing that no steric effects for electron rich aryl thiols. In particular, naphthalene-2-thiol also participated in the reaction to afford the coupling product **3q** in 78% yield. Regrettably, heterocyclic- and alkylthiols cannot take part in this reaction (**3r**～**3t**).

Next, the substrate scope of *N*-formylamide derivatives was investigated (Table 3). The use of *N*-benzylacetamide, *N*-benzylpropionamide and *N*-benzylbenzamide gave comparable yields of corresponding products **4a**～**4c** in 50%, 62%, and 52%, respectively. Moreover, the *N*-benzyl-acetamide with various substituents on the phenyl ring was compatible with the N—S bond formation reaction, delivering the desired products in good to excellent yields (55%～97%). *N*-Benzylacetamides bearing electron-with-

Table 2 Substrate scope of thiols[a]

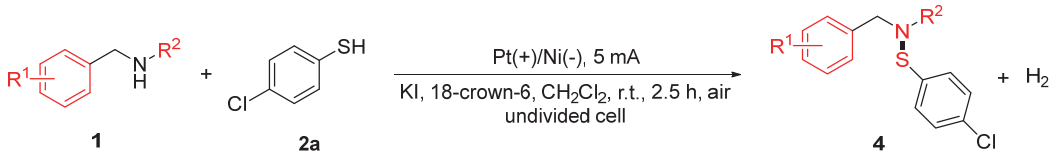


1a 2 3

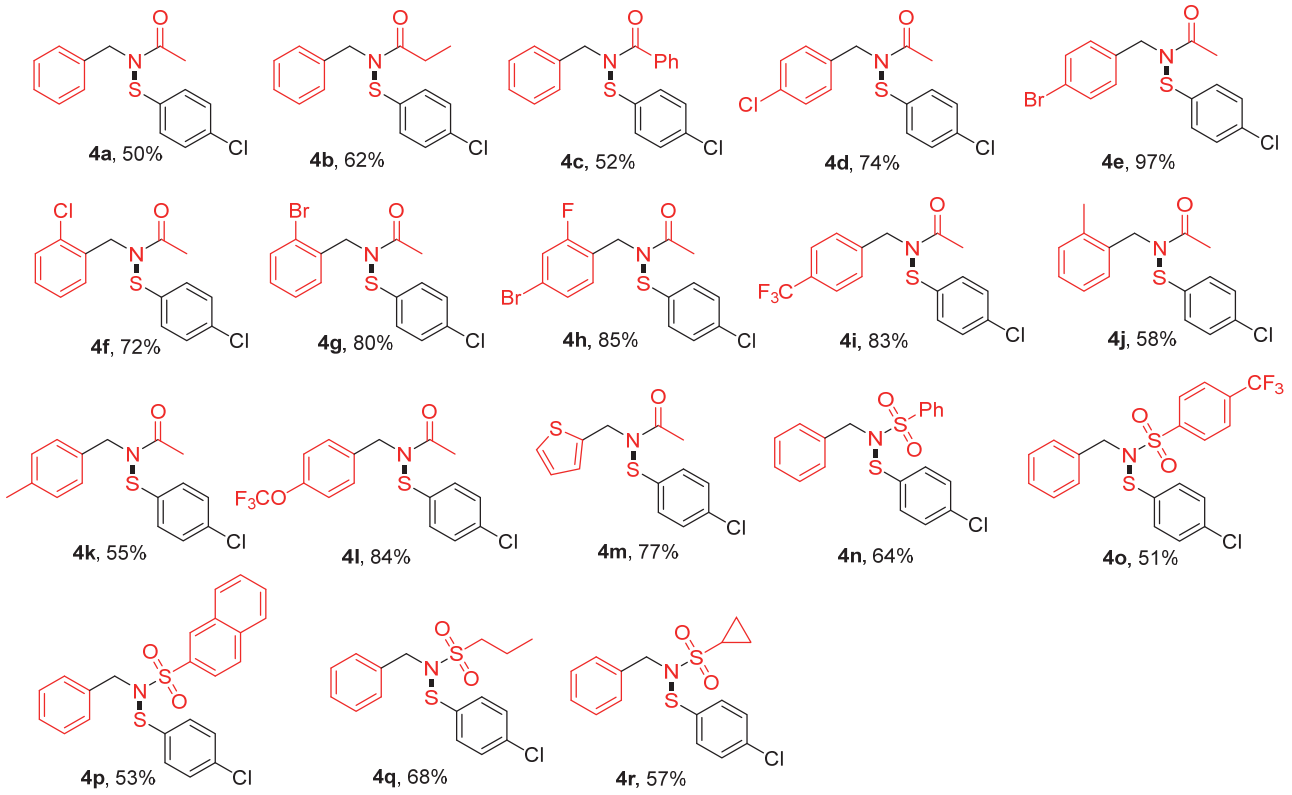


[a] Standard reaction conditions: Pt plate (10 mm×10 mm×0.1 mm) anode, Ni gauze (10 mm×10 mm×1 mm) cathode, constant current=5 mA, **1a** (0.30 mmol), **2a** (0.20 mmol), KI (0.20 mmol), 18-crown-6 (0.20 mmol), CH_2Cl_2 (5.0 mL), room temperature, 2.5 h, undivided cell, under air. Isolated yield.

Table 3 Substrate scope of amides[a]



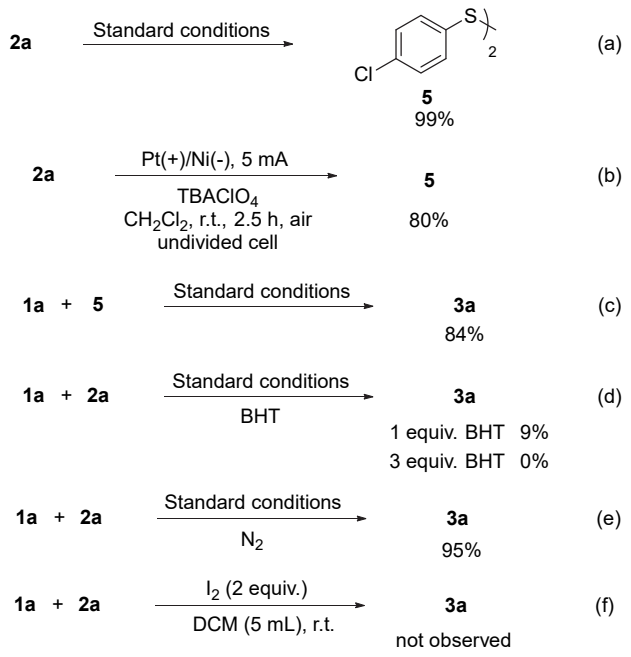
1 2a 4



[a] Standard reaction conditions: Pt plate (10 mm×10 mm×0.1 mm) anode, Ni gauze (10 mm×10 mm×1 mm) cathode, constant current=5 mA, **1a** (0.30 mmol), **2a** (0.20 mmol), KI (0.20 mmol), 18-crown-6 (0.20 mmol), CH_2Cl_2 (5.0 mL), room temperature, 2.5 h, undivided cell, under air. Isolated yield.

drawing groups such as Cl, Br, F, and CF_3 at *para* or *ortho* position resulted in respective products in 72%～97% yields (**4d**～**4i**). The introduction of methyl or trifluoromethoxy on the phenyl ring of *N*-benzylacetamides could be involved in this methodology, producing desired products in moderate to good yields (**4j**～**4l**). *N*-(Thiophen-2-ylmethyl)acetamide also proceeded smoothly with 4-chlorobenzenethiol to afford **4m** in 77% yield. To our delight, under typical conditions of *N*-benzylsulfonamide derivatives were well tolerated in this sulfenylation procedure, a series of N—S bond coupling products were assembled in 51%～68% yields (**4n**～**4r**). Generally, electron-withdrawing groups on the phenyl ring of **1a** were beneficial for the transformation, whereas electron-donating substituents decreased the efficiency. And the benzyl group of substrate **1** is crucial to enable the success of this cross coupling, other electron deficient amides including *N*-phenylformamide and *N*-methylformamide all did work.

To further study the reaction mechanism, several control experiments were carried out (Scheme 2). 4-Chlorothiophenol **2a** was transformed to disulfide **5** in almost quantative yield under standard conditions (Scheme 2a). Even in the absence of KI, 80% disulfide **5** was also obtained with a supporting electrolyte without iodine (Scheme 2b). Treatment of **1a** with **5** underwent the arylthiolation reaction to produce the target product **3a** in 83% yield (Scheme 2c). These results show that compound **5** is a possible reaction intermediate for this electrochemical cross coupling reaction. When 3.0 equiv. of butylated hydroxytoluene (BHT) was employed, the desired product **3a** was not detected, which indicated the possible production of free radicals during the reaction (Scheme 2d). The model reaction was performed in a nitrogen atmosphere to obtain the target product **3a** at 95% yield (Scheme 2e), indicating that the reaction occurred through the oxidation of the electrode not the dioxygen oxidation. When the reaction of **1a** with **2a** was performed at 2 equiv. of I_2, the desired product **3a** was not obtained (Scheme 2f), which indicates that I_2 does not participate in the reaction, but rather the oxidation of iodine anions to iodine radicals to indirectly oxidized the reaction substrate to cause the reaction.



Scheme 2 Mechanistic studies

Furthermore, electron paramagnetic resonance (EPR) experiments were performed to detect the possible radical intermediate with the addition of a free radical spin-trapping agent 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO). When DMPO was added to the stoichiometric reaction of KI under constant current conditions, an EPR signal was identified. This showed that a iodine free radical may be involved in this process (Figure 2a). The formation of a nitrogen radical was observed when DMPO was added to the mixture of KI and **1a** (Figure 2b).

The cyclic voltammetry (CV) experiments were conducted to find the redox potential of the reactants and their mixtures (Figure 3). The result demonstrated that 18-crown-6 did not participate the redox process. The potassium iodide had an oxidant peak at 0.04 V, it indicated that iodine ion could be oxidized at the anode. An oxidation peak of **1a** in dichloromethane was observed at 0.57 V. At the same time, oxidation peak of **2a** could also be observed at 0.59 V. When **1a** and **2a** were added simultaneously, a remarkable increase in the catalytic current which reflects the chemical interaction between these two compounds. The redox properties of *N*-benzylformamide (**1a**) and 4-chlorobenzenethiol (**2a**) in different electrolyte were also investigated. Using $^{n}Bu_4NClO_4$ as the electrolyte, the cyclic voltammograms showed irreversible oxidation waves for *N*-benzylformamide (**1a**) at 0.65 V, comparing with KI as electrolyte, the voltage was increased by 0.07 V. However, when $^{n}Bu_4NClO_4$ was replaced with KI, no oxidation peak was observed for 4-chlorobenzenethiol (**2a**).

Based on the observation mentioned above and literature reports, a proposed mechanism of this electro-oxidative N—H/S—H cross coupling reaction is depicted in Scheme 3. Firstly, 18-crown-6 coordinates with potassium ion and

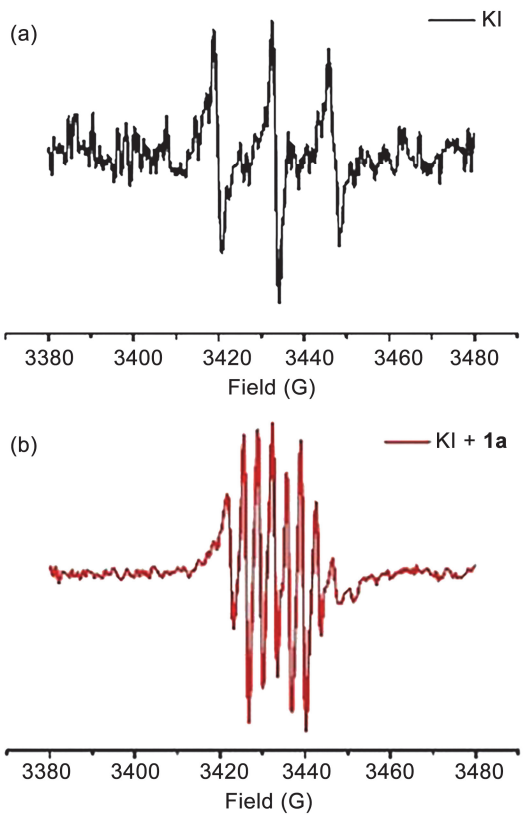


Figure 2 (a) EPR measurement of a solution of KI and 18-crown-6 in CH_2Cl_2 in the presence of DMPO under constant-current conditions for 10 min; (b) EPR measurement of **1a** under the same reaction conditions

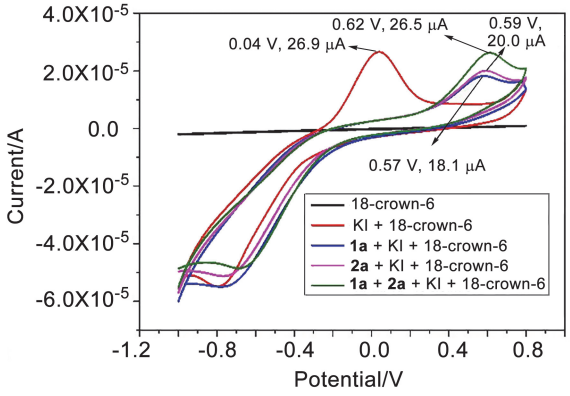
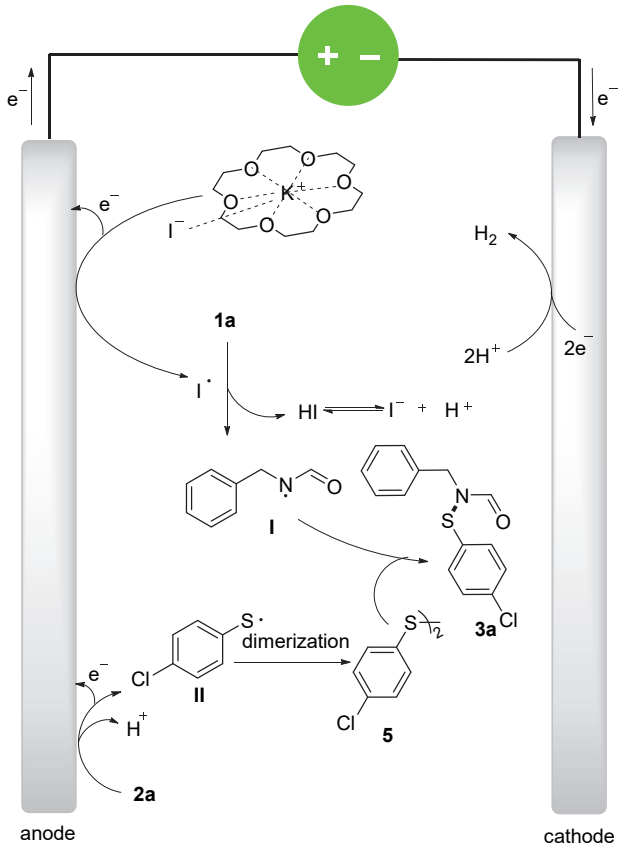


Figure 3 Cyclic voltammetry of **1a** and **2a** in CH_2Cl_2 with KI (0.04 mol/L) and 18-crown-6 (0.04 mol/L) under air

The glassy carbon-disk (R=5.5 mm, h=10 mm) was used as the working electrode. The Pt disk (R=5.5 mm, h=10 mm) and Ag/AgCl (R=5.0 mm, h = 10 mm) was used as counter and reference electrode, respectively. The scan rate was 100 mV/s.

releases iodine ion which is oxidized at the anode to generate iodine radical.[11] The iodine radical react with **1a** to generate amide free radical intermediate **I** and one molecule of hydrogen iodide. Meanwhile, 4-chlorothiophen **2a** can also be oxidized at the anode through single-electron-transfer (SET) oxidation to yield the sulfur radical **II**, which undergoes rapid dimerization to yield the disulfide **5**. The



Scheme 3 Proposed mechanism

generated amide free radical intermediate **I** can undergo the either direct coupling with sulfur radical or disulfide to furnish the desired product **3a**. At the same time, concomitant cathodic reduction proton could release hydrogen gas at the cathode.

3 Conclusions

In conclusion, we have reported a KI-mediated electrochemical coupling of electron-deficient amines (*N*-formyl/acyl- and sulfonylamides) and thiols to afford *N*-formyl/acyl/sulfonylsulfenamides in moderate to excellent yields without over-oxidation of sulfur. The advantages of this protocol include mild reaction conditions, broad substrate scope, good compatibility of functional groups, and handy operation. A possible reaction mechanism is proposed on the basis of control experiments and electron paramagnetic resonance spectroscopy studies.

4 Experimental section

4.1 General experimental information

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Inova-400 (400 and 100 MHz, respectively) spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.00 or $CDCl_3$ [δ (^{1}H NMR), 7.26; δ (^{13}C NMR) 77.16]. The HRMS analysis was obtained on an Agilent 6540 UHD Q-TOF mass spectrometer. The melting point was recorded on BÜCHI (M-560) and uncorrected. Analytical thin layer chromatography (TLC) was performed on 0.25 mm silica gel 60 F254 plates and viewed by UV light (254 nm). Column chromatographic purification was performed using 200～300 mesh silica gel. Electrochemical reactions were performed on a DC Power Supply (GPD-2303S). H_2 detection experiment was conducted on an ES20B-H2 gas detector (Shenzhen Eyesky Technology Co., Ltd). Cyclic voltammetry (CV) was carried out on a CHI660E electrochemical workstation (CH Instruments, Ins).

4.2 General procedure for the synthesis of **3a**

Under air, a mixture of *N*-benzylformamide (**1a**, 41 mg, 0.3 mmol), 4-chlorobenzenethiol **2a** (29 mg, 0.2 mmol), KI (33 mg, 0.2 mmol), 18-crown-6 (53 mg, 0.2 mmol) and CH_2Cl_2 (5.0 mL) were added in an oven-dried undivided bottle (10 mL). The bottle was equipped with Pt plate (10 mm×10 mm×0.1 mm) as anode and Ni gauze (10 mm×10 mm×1.0 mm) as cathode. The distance between the electrodes was 10 mm. The resulting mixture was stirred and electrolyzed at a constant current of 5 mA at ambient temperature for 2.5 h. When the reaction was finished, the resulting mixture was evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography [eluent: petroleum ether (60～90 ℃)/EtOAc, V∶V=6∶1] to afford the desired product **3a** as a colorless oily liquid (54 mg, 98% yield).

N-Benzyl-*N*-((4-chlorophenyl)thio)formamide (**3a**):[15] Eluent: petroleum ether (60～90 ℃)/EtOAc, V∶V=6∶1. 54.4 mg, 98% yield. Colorless oily liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.54 (s, 1H), 7.27～7.26 (m, 5H), 7.25～7.22 (m, 2H), 7.09～7.05 (m, 2H), 4.67 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 168.3, 136.0, 135.00, 134.0, 129.5, 129.0, 128.6, 128.0, 127.6, 50.9.

N-Benzyl-*N*-((4-bromophenyl)thio)formamide (**3b**): Eluent: petroleum ether (60～90 ℃)/EtOAc, V∶V=6∶1. 58 mg, 90% yield. Pale yellow oily liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.55 (s, 1H), 7.45～7.41 (m, 2H), 7.30～7.27 (m, 3H), 7.26～7.24 (m, 2H), 7.04～7.00 (m, 2H), 4.69 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 168.3, 136.0, 135.8, 132.5, 129.1, 128.7, 128.1, 127.6, 121.9, 51.0. HRMS (ESI) calcd for $C_{14}H_{13}BrNOS$ $[M+H]^+$ 321.9896, found 321.9895.

N-Benzyl-*N*-((4-fluorophenyl)thio)formamide (**3c**): Eluent: petroleum ether (60～90 ℃)/EtOAc, V∶V=6∶1. 46 mg, 88% yield. Colorless oily liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.61 (s, 1H), 7.28～7.25 (m, 3H), 7.24～7.20 (m, 4H), 7.03～6.98 (m, 2H), 4.66 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 168.3, 162.9 (d, J=248.0 Hz), 136.2, 131.3 (d, J=3.0 Hz), 130.4 (d, J=9.0 Hz), 129.0, 128.7, 128.0, 116.6 (d, J=22.0 Hz), 50.9. HRMS (ESI) calcd for $C_{14}H_{12}FKNOS$ $[M+K]^+$ 300.0255, found 300.0253.

N-Benzyl-*N*-((2-chlorophenyl)thio)formamide (**3d**): Eluent: petroleum ether (60～90 ℃)/EtOAc, V∶V=6∶1. 38.9 mg, 70% yield. Pale yellow oily liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.46 (s, 1H), 7.32～7.28 (m, 6H), 7.20 (dd, J=7.6, 1.4 Hz, 1H), 7.16 (dd, J=7.6, 1.7 Hz, 1H),

6.95 (dd, J=7.8, 1.6 Hz, 1H), 4.73 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 168.7, 136.4, 136.1, 130.1, 129.1, 129.0, 128.7, 128.1, 127.9, 127.6, 124.6, 51.2. HRMS (ESI) calcd for $C_{14}H_{13}ClNOS$ $[M+H]^+$ 278.0401, found 278.0397.

N-Benzyl-*N*-((2-bromophenyl)thio)formamide (**3e**): Eluent: petroleum ether (60～90 ℃)/EtOAc, V∶V=6∶1. 48.33 mg, 75% yield. Colorless oily liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.44 (s, 1H), 7.49 (dd, J=7.9, 1.2 Hz, 1H), 7.33～7.30 (m, 4H), 7.29～7.26 (m, 2H), 7.07 (td, J=7.9, 1.6 Hz, 1H), 6.89 (dd, J=8.0, 1.5 Hz, 1H), 4.74 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 168.7, 138.4, 136.1, 133.2, 129.1, 128.7, 128.2, 128.2, 127.8, 124.1, 117.4, 51.3. HRMS (ESI) calcd for $C_{14}H_{13}BrNOS$ $[M+H]^+$ 321.9896, found 321.9896.

N-Benzyl-*N*-((2-fluorophenyl)thio)formamide (**3f**): Eluent: petroleum ether (60～90 ℃)/EtOAc, V∶V=6∶1. 31.9 mg, 61% yield. Colorless oily liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.61 (d, J=1.5 Hz, 1H), 7.32～7.28 (m, 1H), 7.27～7.25 (m, 5H), 7.23～7.18 (m, 1H), 7.10～7.04 (m, 2H), 4.67 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 168.7 (d, J=2.0 Hz), 160.5 (d, J=246.0 Hz), 136.2, 131.1, 131.0, 130.9 (d, J=1 Hz), 128.8 (d, J=37.0 Hz), 128.0, 124.9 (d, J=4.0 Hz), 123.2 (d, J=17 Hz), 116.4 (d, J=21 Hz), 51.0. HRMS (ESI) calcd for $C_{14}H_{13}FNOS$ $[M+H]^+$ 262.0696, found 262.0694.

N-Benzyl-*N*-((4-bromo-2-fluorophenyl)thio)formamide (**3g**): Eluent: petroleum ether (60～90 ℃)/EtOAc, V∶V=6∶1. 50.4 mg, 74% yield. Colorless oily liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.59 (d, J=1.6 Hz, 1H), 7.27～7.23 (m, 5H), 7.22～7.18 (m, 2H), 7.02 (t, J=8.0 Hz, 1H), 4.66 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 168.4, 160.1 (d, J=251.0 Hz), 136.0, 131.1, 131.9, 128.8 (d, J=36.0 Hz), 128.2 (d, J=4.0 Hz), 128.1, 123.8 (d, J=9.0 Hz), 122.6 (d, J=17.0 Hz), 120.0 (d, J=25.0 Hz), 51.1. HRMS (ESI) calcd for $C_{14}H_{12}BrFNOS$ $[M+H]^+$ 339.9802, found 339.9804.

N-Benzyl-*N*-((3,5-bis(trifluoromethyl)phenyl)thio)formamide (**3h**): Eluent: petroleum ether (60～90 ℃)/EtOAc, V∶V=6∶1. 59.2 mg, 78% yield. Colorless oily liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.55 (s, 1H), 7.64 (s, 1H), 7.40 (s, 2H), 7.28～7.26 (m, 2H), 7.24～7.21 (m, 3H), 4.79 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 168.1, 138.3 (d, J=576.0 Hz), 132.7 (q, J=34.0 Hz), 129.4, 128.8, 128.5, 124.3 (d, J=3.0 Hz), 124.2, 121.4, 121.1 (d, J=4.0 Hz), 52.1. HRMS (ESI) calcd for $C_{16}H_{11}F_6N$ NaOS $[M+Na]^+$ 402.0358, found 402.0358.

N-Benzyl-*N*-(*p*-tolylthio)formamide (**3i**): Eluent: petroleum ether (60～90 ℃)/EtOAc, V∶V=6∶1. 29.9 mg, 58% yield. Colorless yellow oily liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.59 (s, 1H), 7.31～7.27 (m, 3H), 7.26～7.24 (m, 2H), 7.14 (s, 4H), 4.65 (s, 2H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 168.5, 138.8, 136.4, 132.6, 130.2, 129.0, 128.6, 127.9, 127.9, 50.6, 21.3. HRMS (ESI) calcd for $C_{15}H_{16}NOS$ $[M+H]^+$ 258.0947, found 258.0947.

N-Benzyl-*N*-((4-isopropylphenyl)thio)formamide (**3j**): Eluent: petroleum ether (60～90 ℃)/EtOAc, V∶V=6∶1. 26.8 mg, 47% yield. Colorless yellow oily liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.59 (s, 1H), 7.29～7.24 (m, 5H), 7.20～7.15 (m, 4H), 4.66 (s, 2H), 2.92～2.85 (m, 1H), 1.24 (s, 3H), 1.22 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 168.6, 149.7, 136.5, 133.0, 129.0, 128.6, 127.9, 127.9, 127.6, 50.7, 34.0, 24.0. HRMS (ESI) calcd for $C_{17}H_{20}NOS$ $[M+H]^+$ 286.1260, found 286.1258.

N-Benzyl-*N*-((4-(*tert*-butyl)phenyl)thio)formamide (**3k**): Eluent: petroleum ether (60～90 ℃)/EtOAc, V∶V=6∶1. 19.8 mg, 33% yield. White solid, m.p. 104.1～105.1 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.59 (s, 1H), 7.36～7.32 (m, 2H), 7.28～7.23 (m, 5H), 7.18～7.15 (m, 2H), 4.67 (s, 2H), 1.30 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 168.6, 151.9, 136.5, 132.7, 129.0, 128.6, 127.9, 127.4, 126.5, 50.7, 34.8, 31.3. HRMS (ESI) calcd for $C_{18}H_{22}NOS$ $[M+H]^+$ 300.1417, found 300.1415.

N-Benzyl-*N*-((4-methoxyphenyl)thio)formamide (**3l**): Eluent: petroleum ether (60～90 ℃)/ EtOAc, V∶V=6∶1. 35.0 mg, 64% yield. Colorless yellow oily liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.66 (s, 1H), 7.32～7.28 (m, 5H), 7.26～7.23 (m, 2H), 6.88～6.84 (m, 2H), 4.62 (s, 2H), 3.81 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 168.3, 160.9, 136.5, 132.9, 128.9, 128.6, 127.8, 126.1, 115.0, 55.6, 50.3. HRMS (ESI) calcd for $C_{15}H_{16}NO_2S$ $[M+H]^+$ 274.0896, found 274.0890.

N-Benzyl-*N*-((4-(methylthio)phenyl)thio)formamide (**3m**): Eluent: petroleum ether (60～90 ℃)/EtOAc, V∶V=6∶1. 32.4 mg, 56% yield. Colorless yellow oily liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.59 (s, 1H), 7.29～7.23 (m, 5H), 7.19～7.14 (m, 4H), 4.65 (s, 2H), 2.47 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 168.3, 140.0, 136.3, 132.1, 129.0, 128.6, 128.6, 127.9, 127.1, 50.6, 15.7. HRMS (ESI) calcd for $C_{15}H_{15}NNaOS_2$ $[M+Na]^+$ 312.0487, found 312.0486.

N-Benzyl-*N*-(*m*-tolylthio)formamide (**3n**): Eluent: petroleum ether (60～90 ℃)/EtOAc, V∶V=6∶1. 27.8 mg, 54% yield. Colorless yellow oily liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.56 (s, 1H), 7.30～7.25 (m, 5H), 7.20 (d, J=7.7 Hz, 1H), 7.06 (d, J=7.5 Hz, 1H), 6.99 (d, J=7.8 Hz, 1H), 6.95 (s, 1H), 4.69 (s, 2H), 2.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 168.7, 139.5, 136.4, 136.3, 129.3, 129.1, 128.8, 128.6, 128.0, 126.7, 123.3, 50.9, 21.5. HRMS (ESI) calcd for $C_{15}H_{16}NOS$ $[M+H]^+$ 258.0947, found 258.0947.

N-Benzyl-*N*-(*o*-tolylthio)formamide (**3o**): Eluent: petroleum ether (60～90 ℃)/EtOAc, V∶V=6∶1. 25.2 mg, 49% yield. Colorless yellow oily liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.52 (s, 1H), 7.32～7.29 (m, 5H), 7.20～7.17 (m, 3H), 7.06 (d, J=7.0 Hz, 1H), 4.71 (s, 2H), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 168.8, 136.4, 135.7, 134.4, 130.9, 128.9, 128.7, 128.0, 127.3, 127.0, 124.5, 50.8, 19.2. HRMS (ESI) calcd for $C_{15}H_{16}NOS$ $[M+H]^+$ 258.0947, found 258.0947.

N-Benzyl-*N*-((3,5-dimethylphenyl)thio)formamide (**3p**): Eluent: petroleum ether (60～90 ℃)/EtOAc, V∶V=6∶1. 19.5 mg, 36% yield. Colorless yellow oily liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.54 (s, 1H), 7.29～7.25 (m, 5H),

6.86 (s, 1H), 6.76 (s, 2H), 4.68 (s, 2H), 2.26 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 168.7, 139.3, 136.5, 136.1, 129.8, 129.1, 128.6, 127.9, 123.7, 50.9, 21.3. HRMS (ESI) calcd for $C_{16}H_{18}NOS$ $[M+H]^+$ 272.1104, found 272.1100.

N-Benzyl-*N*-(naphthalen-2-ylthio)formamide (**3q**): Eluent: petroleum ether (60～90 ℃)/EtOAc, *V*∶*V*=6∶1. 45.8 mg, 78% yield. White solid, m.p. 118.2～119.8 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.63 (s, 1H), 7.80～7.70 (m, 3H), 7.58 (s, 1H), 7.51～7.45 (m, 2H), 7.29～7.27 (m, 4H), 7.25～7.22 (m, 2H), 4.73 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 168.6, 136.3, 133.7, 133.5, 132.7, 129.4, 129.1, 128.6, 128.0, 127.9, 127.6, 127.2, 126.7, 125.0, 123.5, 50.9. HRMS (ESI) calcd for $C_{18}H_{16}NOS$ $[M+H]^+$ 294.0947, found 294.0943.

N-Benzyl-*N*-((4-chlorophenyl)thio)acetamide (**4a**): Eluent: petroleum ether (60～90 ℃)/EtOAc, *V*∶*V*=6∶1. 29.2 mg, 50% yield. Colorless yellow oily liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.32～7.29 (m, 5H), 7.28～7.25 (m, 2H), 6.97 (d, *J*=8.5 Hz, 2H), 4.79 (s, 2H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 176.3, 137.2, 136.2, 132.6, 129.7, 129.0, 128.6, 127.9, 124.5, 54.2, 22.0. HRMS (ESI) calcd for $C_{15}H_{15}ClNOS$ $[M+H]^+$ 292.0557, found 292.0554.

N-Benzyl-*N*-((4-chlorophenyl)thio)propionamide (**4b**): Eluent: petroleum ether (60～90 ℃)/EtOAc, *V*∶*V*=6∶1. 37.9 mg, 62% yield. Colorless yellow oily liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.30～7.25 (m, 7H), 6.95 (d, *J*=8.4 Hz, 2H), 4.81 (s, 2H), 2.70 (q, *J*=7.3 Hz, 2H), 1.14 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 179.3, 137.3, 136.4, 132.4, 129.6, 129.0, 128.6, 127.9, 124.3, 54.4, 26.7, 9.8. HRMS (ESI) calcd for $C_{16}H_{17}ClNOS$ $[M+H]^+$ 306.0714, found 306.0713.

N-Benzyl-*N*-((4-chlorophenyl)thio)benzamide (**4c**)[15]: Know compound. [Eluent: petroleum ether (60～90 ℃)/EtOAc, *V*∶*V*=6∶1. 36.8 mg, 52% yield. White solid, m.p. 136.5～136.9 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.50～7.47 (m, 2H), 7.43～7.37 (m, 2H), 7.36～7.31 (m, 6H), 7.27～7.25 (m, 2H), 6.98～6.95 (m, 2H), 4.67 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 176.3, 137.0, 136.0, 135.0, 133.1, 130.6, 129.6, 128.9, 128.7, 128.1, 128.0, 127.6, 126.2, 54.6.

N-(4-Chlorobenzyl)-*N*-((4-chlorophenyl)thio)acetamide (**4d**): Eluent: petroleum ether (60～90 ℃)/EtOAc, *V*∶*V*=6∶1. 48.3 mg, 74% yield. Colorless yellow oily liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.33～7.30 (m, 2H), 7.28～7.23 (m, 4H), 6.99 (d, *J*=8.6 Hz, 2H), 4.75 (s, 2H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 176.2, 135.8, 135.7, 133.8, 132.8, 130.4, 129.7, 128.7, 124.6, 53.6, 21.9. HRMS (ESI) calcd for $C_{15}H_{14}Cl_2NOS$ $[M+H]^+$ 326.0168, found 326.0167.

N-(4-Bromobenzyl)-*N*-((4-chlorophenyl)thio)acetamide (**4e**): Eluent: petroleum ether (60～90 ℃)/EtOAc, *V*∶*V*=6∶1. 71.9 mg, 97% yield. Colorless yellow oily liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.43～7.40 (m, 2H), 7.33～7.29 (m, 2H), 7.18 (d, *J*=8.3 Hz, 2H), 6.99 (d, *J*=8.5 Hz, 2H), 4.73 (s, 2H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 176.3, 136.2, 135.8, 132.9, 131.8, 130.8, 129.8, 124.6, 122.0, 53.7, 21.9. HRMS (ESI) calcd for $C_{15}H_{14}BrClNOS$ $[M+H]^+$ 369.9663, found 369.9659.

N-(2-Chlorobenzyl)-*N*-((4-chlorophenyl)thio)acetamide (**4f**): Eluent: petroleum ether (60～90 ℃)/EtOAc, *V*∶*V*=6∶1. 47.0 mg, 72% yield. Colorless yellow oily liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.33～7.330 (m, 3H), 7.22～7.20 (m, 3H), 7.04 (d, *J*=8.3 Hz, 2H), 4.96 (s, 2H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 176.4, 136.0, 134.4, 134.1, 132.9, 130.0, 129.7, 129.1, 127.0, 125.1, 51.4, 21.9. HRMS (ESI) calcd for $C_{15}H_{14}Cl_2NOS$ $[M+H]^+$ 326.0168, found 326.0165.

N-(2-Bromobenzyl)-*N*-((4-chlorophenyl)thio)acetamide (**4g**): Eluent: petroleum ether (60～90 ℃)/EtOAc, *V*∶*V*=6∶1. 59.3 mg, 80% yield. Colorless yellow oily liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.50 (d, *J*=8.0 Hz, 1H), 7.31～7.25 (m, 3H), 7.17～7.12 (m, 2H), 7.04 (d, *J*=8.3 Hz, 2H), 4.94 (s, 2H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 176.4, 136.0, 135.9, 133.0, 132.9, 129.9, 129.7, 129.3, 127.6, 125.1, 124.1, 53.7, 21.9. HRMS (ESI) calcd for $C_{15}H_{14}BrClNOS$ $[M+H]^+$ 369.9663, found 369.9661.

N-(4-Bromo-2-fluorobenzyl)-*N*-((4-chlorophenyl)thio)-acetamide (**4h**): Eluent: petroleum ether (60～90 ℃)/EtOAc, *V*∶*V*=6∶1. 66.1 mg, 85% yield. Colorless yellow oily liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.33～7.30 (m, 2H), 7.24～7.16 (m, 3H), 7.02 (d, *J*=8.5 Hz, 2H), 4.82 (s, 2H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 176.3, 161.0 (d, *J*=250.0 Hz), 135.7, 133.1, 132.1 (d, *J*=5.0 Hz), 129.7, 127.6 (d, *J*=4.0 Hz), 125.2, 123.4 (d, *J*=15.0 Hz), 122.1 (d, *J*=10.0 Hz), 119.2 (d, *J*=25.0 Hz), 47.3, 21.9. HRMS (ESI) calcd for $C_{15}H_{13}BrClFNOS$ $[M+H]^+$ 387.9568, found 387.9565.

N-((4-Chlorophenyl)thio)-*N*-(4-(trifluoromethyl)benzyl)acetamide (**4i**): Eluent: petroleum ether (60～90 ℃)/EtOAc, *V*∶*V*=6∶1. 59.7 mg, 83% yield. Colorless yellow oily liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.55 (d, *J*=8.1 Hz, 2H), 7.41 (d, *J*=8.0 Hz, 2H), 7.33～7.29 (m, 2H), 7.00 (d, *J*=8.6 Hz, 2H), 4.84 (s, 2H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 176.3, 141.1, 135.6, 132.6, 133.1, 130.2 (d, *J*=29.0 Hz), 125.6 (q, *J*=4.0 Hz), 124.8, 122.8, 54.0, 21.9. HRMS (ESI) calcd for $C_{16}H_{14}ClF_3NOS$ $[M+H]^+$ 360.0431, found 360.0430.

N-((4-Chlorophenyl)thio)-*N*-(2-methylbenzyl)acetamide (**4j**): Eluent: petroleum ether (60～90 ℃)/EtOAc, *V*∶*V*=6∶1. 35.5 mg, 58% yield. Colorless yellow oily liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.31～7.28 (m, 2H), 7.17～7.11 (m, 4H), 6.98 (d, *J*=8.3, 2H), 4.83 (s, 2H), 2.41 (s, 3H), 2.26 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 176.4, 136.8, 136.2, 134.9, 132.7, 130.5, 129.7, 129.3, 127.9, 126.1, 124.7, 50.9, 22.1, 19.4. HRMS (ESI) calcd for $C_{16}H_{17}ClNOS$ $[M+H]^+$ 306.0714, found 306.0712.

N-((4-Chlorophenyl)thio)-*N*-(4-methylbenzyl)acetamide (**4k**): Eluent: petroleum ether (60～90 ℃)/EtOAc, *V*∶*V*=6∶1. 33.6 mg, 55% yield. Colorless yellow oily liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.31～7.27 (m, 2H), 7.19 (d, *J*=7.9 Hz, 2H), 7.10 (d, *J*=8.0 Hz, 2H), 6.98 (d, *J*=8.5 Hz, 2H), 4.75 (s, 2H), 2.36 (s, 3H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 176.3, 137.7, 136.3, 134.2, 132.6,

129.7, 129.3, 129.0, 124.5, 53.9, 22.0, 21.3. HRMS (ESI) calcd for $C_{16}H_{17}ClNOS$ $[M+H]^+$ 306.0714, found 306.0712.

N-((4-Chlorophenyl)thio)-*N*-(4-(trifluoromethoxy)benzyl)acetamide (**4l**): Eluent: petroleum ether (60～90 ℃)/EtOAc, *V*∶*V*=6∶1. 63.1 mg, 84% yield. Colorless yellow oily liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 7.34 (d, *J*=8.6 Hz, 2H), 7.30～7.27 (m, 2H), 7.13 (d, *J*=7.9 Hz, 2H), 6.97 (d, *J*=8.6 Hz, 2H), 4.79 (s, 2H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 176.3, 149.0 (q, *J*=2.0 Hz), 135.9 (d, *J*=11.0 Hz), 132.9, 130.5, 129.7, 124.6, 121.8, 121.1, 119.3, 53.8, 21.9. HRMS (ESI) calcd for $C_{16}H_{14}ClF_3NO_2S$ $[M+H]^+$ 376.0380, found 376.0377.

N-((4-Chlorophenyl)thio)-*N*-(thiophen-2-ylmethyl)acetamide (**4m**): Eluent: petroleum ether (60～90 ℃)/EtOAc, *V*∶*V*=6∶1. 45.9 mg, 77% yield. Colorless yellow oily liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 7.30～7.27 (m, 2H), 7.23 (dd, *J*=5.1, 1.0 Hz, 1H), 7.01 (d, *J*=3.4 Hz, 1H), 6.97 (d, *J*=8.5 Hz, 2H), 6.91 (dd, *J*=5.1, 3.5 Hz, 1H), 4.93 (s, 2H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 175.9, 139.0, 136.2, 132.6, 129.6, 128.0, 126.7, 126.2, 124.4, 49.4, 21.9. HRMS (ESI) calcd for $C_{13}H_{13}ClNOS_2$ $[M+H]^+$ 298.0122, found 298.0119.

N-Benzyl-*N*-((4-chlorophenyl)thio)benzenesulfonamide (**4n**): Eluent: petroleum ether (60～90 ℃)/EtOAc, *V*∶*V*=6∶1. 49.9 mg, 64% yield. White solid, m.p. 92～94 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 7.91～7.88 (m, 2H), 7.63～7.59 (m, 1H), 7.53～7.49 (m, 2H), 7.25～7.21 (m, 5H), 7.16～7.09 (m, 4H), 4.64 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 139.0, 135.4, 135.0, 134.1, 133.4, 129.6, 129.4, 129.2, 129.0, 128.6, 128.4, 127.9, 58.0. HRMS (ESI) calcd for $C_{19}H_{17}ClNO_2S_2$ $[M+H]^+$ 390.0384; found 390.0379.

N-Benzyl-*N*-((4-chlorophenyl)thio)-4-(trifluoromethyl)-benzenesulfonamide (**4o**): Eluent: petroleum ether (60～90 ℃)/EtOAc, *V*∶*V*=6∶1. 46.71 mg, 51% yield. White solid, m.p. 89～92 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 7.96 (d, *J*=8.7 Hz, 2H), 7.73 (d, *J*=8.3 Hz, 2H), 7.27～7.22 (m, 5H), 7.18～7.12 (m, 4H), 4.68 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 142.5, 137.8, 137.0, 134.9 (d, *J*=33.3 Hz), 134.7 (d, *J*=58.6 Hz), 134.7, 129.8, 129.6, 129.1, 128.6, 128.5 (d, *J*=27.3 Hz), 126.3 (q, *J*=4.0 Hz), 124.6, 58.5. HRMS (ESI) calcd for $C_{20}H_{16}ClF_3NO_2S_2$ $[M+H]^+$ 458.0258; found 458.0239.

N-Benzyl-*N*-((4-chlorophenyl)thio)naphthalene-2-sulfonamide (**4p**): Eluent: petroleum ether (60～90 ℃)/EtOAc, *V*∶*V*=6∶1. 46.54 mg, 53% yield. White solid, m.p. 110～111 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 8.43 (s, 1 H), 7.92 (t, *J*=7.8 Hz, 3H), 7.83 (dd, *J*=8.7, 1.8 Hz, 1H), 7.68～7.59 (m, 2H), 7.27～7.19 (m, 6H), 7.12 (s, 3H), 4.69 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 135.8, 135.4, 135.1, 135.0, 134.1, 132.1, 129.6, 129.6, 129.5, 129.5, 129.5, 129.2, 129.0, 128.5, 128.4, 128.0, 127.8, 122.8, 58.1. HRMS (ESI) calcd for $C_{23}H_{19}ClNO_2S_2$ $[M+H]^+$ 440.0540; found 440.0531.

N-Benzyl-*N*-((4-chlorophenyl)thio)propane-1-sulfonamide (**4q**): Eluent: petroleum ether (60～90 ℃)/EtOAc, *V*∶*V*=6∶1. 48 mg, 68% yield. White solid, m.p. 89～90 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 7.38～7.36 (m, 2H), 7.31～7.29 (m, 3H), 7.25～7.19 (m, 4H), 4.69 (s, 2H), 3.05～3.01 (m, 2H), 1.85～1.76 (m, 2H), 1.00 (t, *J*=7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 135.9, 135.0, 134.2, 129.5, 129.1, 129.0, 128.7, 128.5, 58.1, 54.4, 17.2, 13.1. HRMS (ESI) calcd for $C_{16}H_{19}ClNO_2S_2$ $[M+H]^+$ 356.0540, found 356.0532.

N-Benzyl-*N*-((4-chlorophenyl)thio)cyclopropanesulfonamide (**4r**): Eluent: petroleum ether (60～90 ℃)/EtOAc, *V*∶*V*=6∶1. 36.4 mg, 57% yield. White solid, m.p. 84.2～85.2 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 7.39～7.37 (m, 2H), 7.31～7.29 (m, 3H), 7.24～7.19 (m, 4H), 4.71 (s, 2H), 2.43～2.37 (m, 1H), 1.29～1.25 (m, 2H), 0.99～0.93 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 136.1, 135.4, 133.9, 129.3, 129.1, 128.7, 128.6, 128.5, 58.2, 30.5, 6.0. HRMS (ESI) calcd for $C_{16}H_{17}ClNO_2S_2$ $[M+H]^+$ 354.0384, found 354.0378.

Supporting Information The ^{1}H NMR and ^{13}C NMR spectra of all products. The HRMS of new products **3b**～**3p** and **4a**～**4r**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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