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Electrochemical Direct Thiolation of Lactams with Mercaptans: An Efficient Access to *N*-Acylsulfenamides

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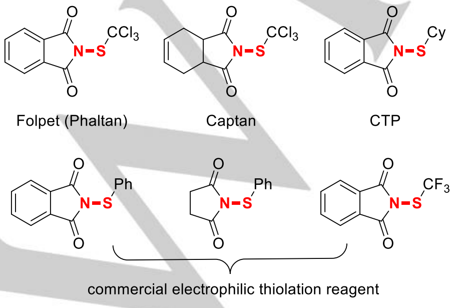
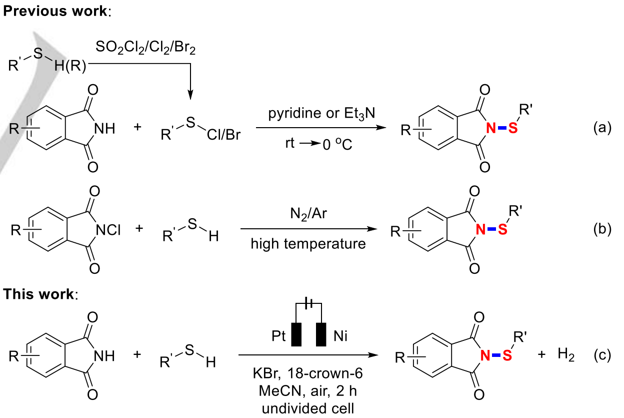
Abstract: An efficient and eco-friendly electrochemical methodology for the oxidative cross coupling hydrogen evolution (CCHE) reactions of lactams with thiols is presented. Various electron deficient *N*-acylsulfenamides are smoothly produced in modest to excellent yields without using any external oxidant. Elementary mechanistic insight supports a possible free radical process and hydrogen is the only side product. This approach provides a safe, convenient, and economical preparation of synthetically important *N*-thiophthalimides in gram scale level.

The selective construction of heteroatom-heteroatom bond, exactly as the formation of carbon-carbon and carbon-heteroatom bond, is one of the core topics in current synthetic organic chemistry.[1] Sulfenamides are a class of important sulfur-containing organic compounds which characterized as the possess of N–S bonds.[2] Among them, *N*-acylsulfenamides as one kind of electron deficient sulfenamides have been prevalent in the field of drug and pesticidal development, fine chemicals production, and organic synthesis. For example, Folpet and Captan have been used as commercial organosulfur pesticides, attribute to their high antifungal activities.[3] *N*-(Cyclohexylthio)phtalimide (CTP) and its analogues are widely employed in rubber industry as anti-scorching agents to accelerate the vulcanization process.[4] Some *N*-thioimides, such as *N*-(phenylthio)phthalimide, 1-(phenylthio)pyrrolidine-2,5-dione, and *N*-(trifluoromethylthio)phthalimide, have been extensively applied as important and commercial available electrophilic thiolation reagents to form organosulfur compounds (Scheme 1).[5]



Scheme 1. Selected and significant *N*-acylsulfenamide compounds.

Generally, traditional methods towards *N*-acylsulfenamides are mainly based on the reaction of lactams with unstable sulfenyl chlorides/bromides under bases at 0 °C or the reaction of *N*-chloro(bromo) lactams with thiols at high temperature (Scheme 2a-b).[6] Recently, Cu- and Co-catalyzed direct aerobic oxidative cross dehydrogenative coupling (CDC) of amides with thios under O_2 at 100 °C have been well developed by Jang and Yang, respectively.[7] Although some remarkable achievements have been obtained using these strategies, some obvious drawbacks can not be eliminated such as the involvement of transition metal catalysts, prefunctionalization of starting materials, tedious reaction steps, harsh reaction conditions, limited substrate scope, and utilization of toxic and sensitive Cl_2 or Br_2. So, the development of clean, robust, environmentally friendly, and practical routes for the synthesis of *N*-acylsulfenamides is still highly desirable.

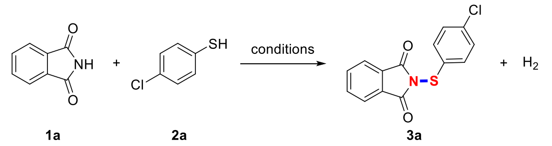


Scheme 2. General methods for thiolation of lactams.

In recent years, organic electrosynthesis especially the electrochemical cross coupling hydrogen evolution reaction has emerged as an ideal alternative to C–H activation, visible light catalysis, and classical transition metal catalyzed cross coupling reaction.[8,9] Some impressive advances on the construction of X–X (X = N, O, S, P etc.)[10] bonds and synthesis of heterocycles under electrochemical conditions have been developed.[11] With regard to the electrochemical preparation of sulfenamides, some pioneered works have been established via the electrochemical direct N–H/S–H cross coupling. In 2019, Wu group realized the production of sulfinamides following this tactics with secondary amines as N–H source, sulfenamides were demonstrated as reaction intermediates.[12] In the same year, Yang and coworkers developed a practical and scalable electrochemical dehydrogenative coupling of S–H and N–H to sulfenamides under oxidant and metal free conditions.[13] In 1979, Torii reported the electrolytic coupling of imides with disulfides to *N*-acylsulfenamides in mixed supporting electrolytes for 18-22 h.[14] To the best of our knowledge, the synthesis of *N*-acylsulfenamides through the electrocatalytic direct CCHE reactions of lactams and thiols has not been explored. Compared to amines, the nucleophilicity of lactams may hampered its direct cross coupling with thiols.

Driven by the high significance of N-acylsulfenamides and our recent success on electrochemical N–P bond formation[15] and eco-friendly synthetic chemistry,[16] we present herein our recent advance on the build of N–S bond through coupling reactions of lactams and thiols under mild electrosynthetic conditions in an undivided cell with the constant current electrolysis (Scheme 2c).

Table 1. Optimization of the reaction conditions.[a,b]

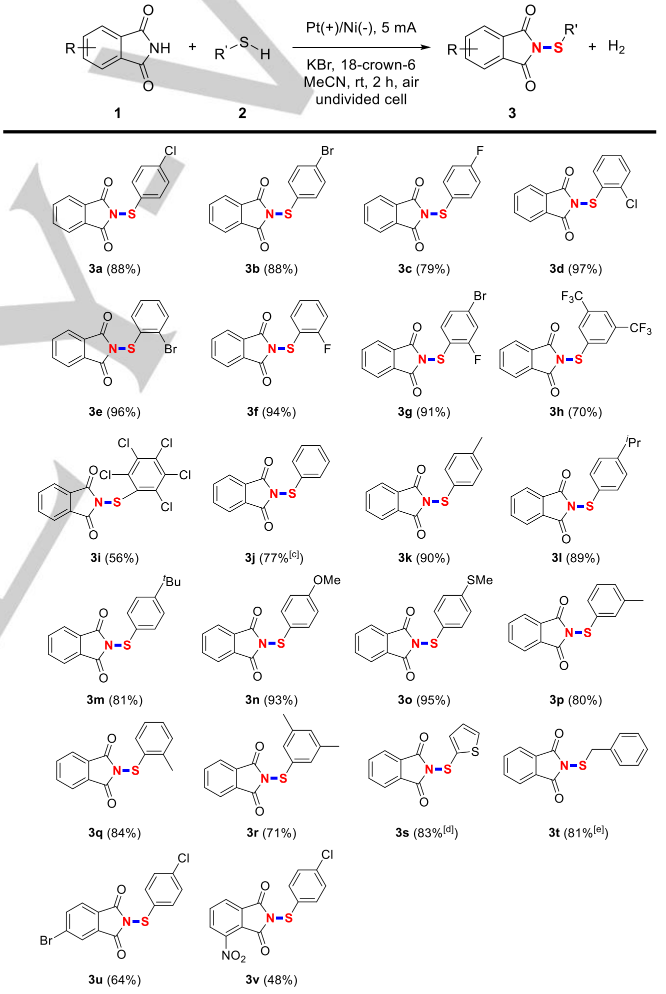


Entry	Electrolyte (eq.)	Solvent	Current (mA)	t (h)	Yield (%)[b]
1	NaBr (1.0)	MeCN	5	2	69
2	KBr (1.0)	MeCN	5	2	79
3	KI (1.0)	MeCN	5	2	32
4	KBr (1.0)	MeCN	0	2	n.d.
5	KBr (0)	MeCN	5	2	n.d.
6[c]	KBr (1.0)	MeCN	5	2	16
7	KBr (1.0)	MeOH	5	2	n.d.
8	KBr (1.0)	CH_2Cl_2	5	2	15
9	KBr (1.0)	DMF	5	2	trace
10	KBr (1.0)	DMSO	5	2	trace
11	KBr (1.5)	MeCN	5	2	68
12	KBr (0.5)	MeCN	5	2	42
13	KBr (1.0)	MeCN	7	2	73
14	KBr (1.0)	MeCN	3	2	53
15	KBr (1.0)	MeCN	5	3	75
16	KBr (1.0)	MeCN	5	1	38
17[d,e]	KBr (1.0)	MeCN	5	2	84
18[d,e,f]	KBr (1.0)	MeCN	5	2	88

[a] Reaction conditions: **1a** (0.4 mmol), **2a** (0.2 mmol), electrolyte, 18-crown-6 (0.1 mmol), solvent (4.0 mL), Pt plate (10 mm x 10 mm x 0.1 mm) anode, Ni gauze (10 mm x 10 mm x 1.0 mm) cathode, the distance between the electrodes (10 mm), constant current, room temperature, undivided cell, 0.1 MPa N_2. [b] Isolated yields. [c] without 18-crown-6. [d] **1a** (0.3 mmol). [e] 18-crown-6 (0.2 mmol). [f] under air.

Initially, the reaction of phthalimide **1a** and 4-chlorobenzenethiol **2a** was selected as the model reaction to screen the optimal electrochemical reaction conditions for the preparation of N–S bond coupling product **3a** (Table 1). The target product was successfully obtained using inexpensive alkali metal salt as electrolytes, among which KBr afforded a satisfactory isolated yield in 79% (entries 1-3). Control experiments revealed the significance of electricity and electrolyte, both of them were indispensable factors to enable this cross coupling reaction (entries 4-5). Crown ethers, which were widely used as chelating agents, played obvious promotion to the electrochemical reaction efficiency, the yield of **3a** decreased dramatically from 79% to 16% in the absence of 18-crown-6 (entry 6). It enabled the high reaction efficiency and was used to simultaneously increase the solubility and nucleophilicity of KBr.[17] Among other tested solvents, only DCM could produce the desired product in a very low yield of 15% (entries 7-10). Increasing or reducing the dosage of KBr both showed negative influence to this reaction (entries 11-12). The yield had little change when the constant current was switched to 7 mA, but it decreased obviously with the lowing of electricity to 3 mA (entries 13-14). The best reaction time was determined as 2 h (entries 15-16). The reaction efficiency was slightly enhanced through the adjustment of the amount of phthalimide **1a** to 1.5 equivalent and the loading of 18-crown-6 to 1.0 equivalent (entry 17). To our delight, this electrolytic reaction proceeded smoothly under air which remarkably simplified the reaction operation, and the yield of the desired product **3a** was raised to 88% (entry 18).

Table 2. Substrate scope for electrochemical thiolation of phthalimides with mercaptans.[a,b]



1 2 3

3a (88%) **3b** (88%) **3c** (79%) **3d** (97%)

3e (96%) **3f** (94%) **3g** (91%) **3h** (70%)

3i (56%) **3j** (77%[c]) **3k** (90%) **3l** (89%)

3m (81%) **3n** (93%) **3o** (95%) **3p** (80%)

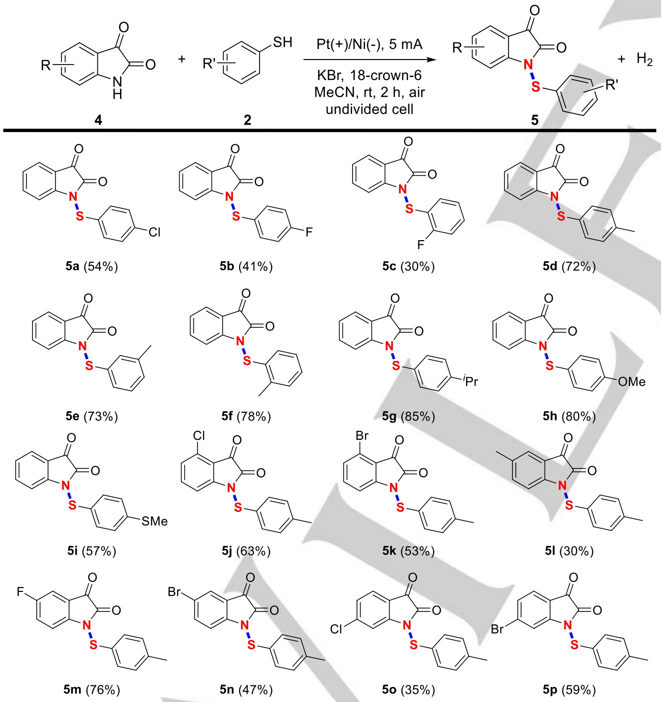
3q (84%) **3r** (71%) **3s** (83%[d]) **3t** (81%[e])

3u (64%) **3v** (48%)

[a] Reaction conditions: **1** (0.3 mmol), **2** (0.2 mmol), KBr (0.2 mmol), 18-crown-6 (0.2 mmol), MeCN (4.0 mL), Pt plate (10 mm x 10 mm x 0.1 mm) anode, Ni gauze (10 mm x 10 mm x 1.0 mm) cathode, the distance between the electrodes (10 mm), 5 mA, room temperature, 2 h, undivided cell, under air. [b] Isolated yield. [c] Phenyl disulfide (0.1 mmol). [d] 2-Thienyldisulfide (0.1 mmol). [e] Benzyl disulfide (0.1 mmol).

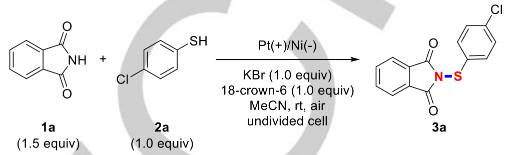
As shown in Table 2, the generality of phthalimides **1** and arylthiols **2** was then primarily explored in the light of the optimized reaction conditions has been established. In principle, a sequence of thiols with different electronic and steric properities were smoothly transformed into their corresponding cross dehydrogenative coupling products under electrochemical conditions in moderate to excellent yields. When monohalogen thiophenols substituted with electron-deficient F, Cl, and Br at C-2 or -4 positions of the phenyl ring were used as starting materials, the desired products were obtained with up to 97% isolated yields (**3a**–**3f**). Polyhalogeno atoms substituted substrates underwent the cross coupling reaction with phthalimide successfully to yield the arylthiolation product **3g** and **3i** in 91 and 56% yields, respectively. The introduction of strong electron withdrawing trifluoromethyl group on the phenyl ring slightly deteriorated the reaction efficiency, a 70% yield of **3h** was obtained. Considering the foul smell of thiophenol, phenyl disulfide was selected to instead of the electroneutral thiophenol and the commercial available electrophilic thionating reagent **3j** was afforded in good yield. Aryl mercaptan with electron-donating groups such as methyl, *iso*-propyl, *tert*-butyl, methoxyl, and methylthio were viable starting materials, furnishing the corresponding products **3k**–**3r** in 71-95% yields. Intriguingly, heteroaromatic and aliphatic disulfide compounds also could be involved in this reaction and generated the direct arylthiolation products **3s** and **3t** in quite good yields. The phthalimides with electron-withdrawing groups underwent this reaction smoothly to assemble their respective coupling products **3s** and **3t**.

Table 3. Substrate scope for electrochemical arylthiolation of isatins with mercaptans.[a,b]



[a] Reaction conditions: **1** (0.3 mmol), **2** (0.2 mmol), KBr (0.2 mmol), 18-crown-6 (0.2 mmol), MeCN (4.0 mL), Pt plate (10 mm x 10 mm x 0.1 mm) anode, Ni gauze (10 mm x 10 mm x 1.0 mm) cathode, the distance between the electrodes (10 mm), 5 mA, room temperature, 2 h, undivided cell, under air.
[b] Isolated yield.

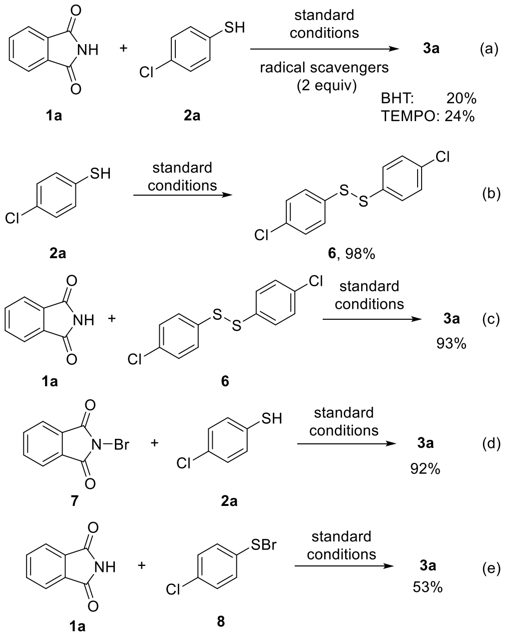
Subsequently, the direct cross dehydrogenative coupling of isatins and aryl mercaptans under this electrochemical strategy was also studied, as illustrated in Table 3. On the whole, the reaction activities of isatins **4** were lower than phthalimides **1**, but a variety of N–S coupling products **5a**–**5p** were also smoothly assembled in satisfactory yields ranging from 30% to 85%. Arylthiols with Cl, F, Me, *iso*-propyl, MeO, and MeS substituents on the aromatic ring were compatible, leading to the desired products in moderate to good yields (**5a**–**5i**). The steric effect of arylthiols had little influence to this reaction (**5d**–**5f**). For substituted isatin derivatives, they were reacted well with various electrical thiol substrates to produce their respective products **5j**–**5p** in moderate to good yields.



2a (mmol)	Pt(+) (mm)	Ni(-) (mm)	*I* (mA)	t (h)	MeCN (mL)	3a (g)	yield of 3a (%)
6	10 x 10 x 0.1	10 x 10 x 1.0	5	24	80	1.48	85
18	20 x 20 x 0.1	20 x 20 x 1.0	25	12	240	4.75	91

Scheme 3. Gram scale reactions.

By slightly adjust partial reaction parameters and keep other conditions unaltered, the model reaction could be easily scaled up to gram scale and kept the similar reaction efficiencies (Scheme 3), which demonstrated that this metholodogy has good practicability, high dependability, and potential amplification manufacturing capability on a much bigger scale.



Scheme 4. Control experiments.

Control experiments were exerted to shed some light on the mechanism of this electrochemical cross coupling reaction. A possible radical process was preliminary demonstrated by the radical trapping experiments employing TEMPO or BHT (Scheme 4a). Under standard conditions, 4-chlorothiophenol **2a** was transformed to disulfide **6** in almost quantative yield (Scheme 4b). Treatment of **1a** with **6** underwent the arylthiolation reaction to produce the product **3a** in 93% yield (Scheme 4c). The intermediates 2-bromoisoindoline-1,3-dione **7** and 4-chlorophenyl hypobromothioite **8** were converted into **3a** in 92% and 53% yields, respectively (Scheme 4d-e). These reaction shows that compounds **6**, **7**, and **8** are possible reaction intermediates for this electrochemical cross coupling reaction.

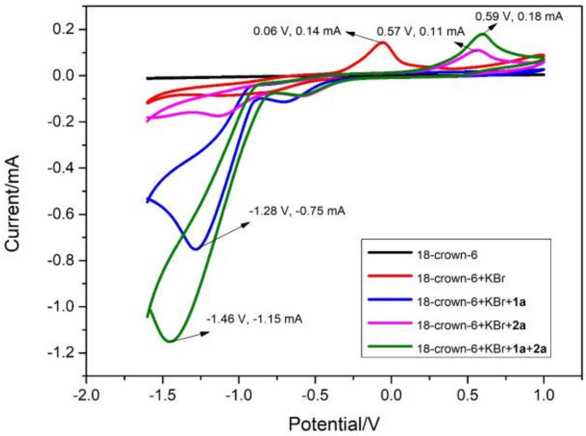
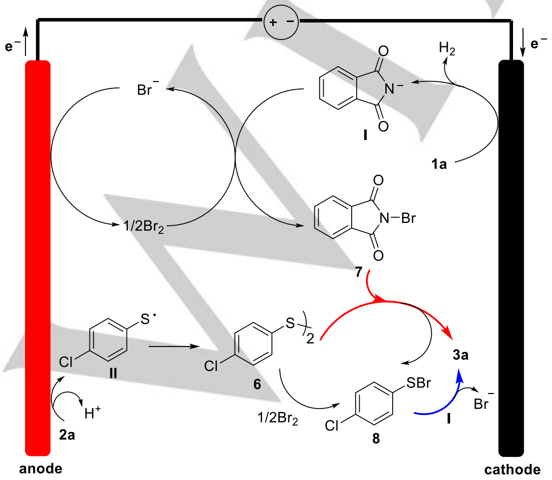


Figure 1. Cyclic voltammetry of **1a**, **2a** and their mixtures in CH_3CN with KBr (0.05 M) and 18-crown-6 (0.05 M) under air. The glassy carbon-disk (R = 5.5 mm, h = 10 mm) was used as the working electrode. The Pt disk (R = 5.5 mm, h = 10 mm) and Ag/AgCl (R = 5.0 mm, h = 10 mm) was used as counter and reference electrode, respectively. The scan rate was 100 mV/s.

Next, we conducted cyclic voltammetry (CV) experiments to find the redox potentials of the reactants and their mixtures (Figure 1). The potassium bromide had an oxidant peak at 0.06 V (red curve), it indicated that bromide ion could be oxidized at anode. A reduction peak of **1a** in acetonitrile was observed at -1.28 V (blue curve), it suggested that **1a** was reduced at cathode. At the same time, an oxidation peak of **2a** could be observe at 0.57 V (pink curve). When **1a** and **2a** were added together (green curve), a remarkable increase in the catalytic current and the new oxidation peak at 0.59 V were observed, reflecting the chemical interaction between these two compounds.



Scheme 5. Proposed mechanism.

According to our research findings mentioned above and relevant reports,[14,18] a plausible mechanism is proposed as shown in Scheme 5. Bromide anion is firstly oxidized at anode to Br_2, which reacts with nitrogen anion intermediate **I** generated through the cathodic reduction of **1a** to form the intermediate **7**. In the meanwhile, **2a** is reduced to sulfur radical intermediate **II**, which dimerizes to the disulfide **6**. The interaction of **6** with Br_2 could produce the intermediate **8**. Subsequently, one way is the cross coupling of **7** with **6** to deliver the target product **3** (red arrow). Another way is the nucleophilic attack of **8** by the intermediate **I** (blue arrow). H_2 is releasd as the byproduct through the reduction of proton at cathode.

In conclusion, we have reported a practical and ideal electrocatalytic method for the construction of electron deficient *N*-acylsulfenamides via direct N–H/S–H cross coupling hydrogen evolution reaction which avoids the use of preactivation substrates and noxious chlorine gas or liquid bromine. The advantages of this protocol including commercial available raw materials, mild reaction conditions, broad substrate scope, good compatibility of functional groups, and handy operation. Notably, gram scale reactions indicate good economics and efficiency for large scale production of the commercialized and widely used *N*-(arylthio)phthalimides and their analogues.

Experimental Section

General Procedure for the Synthesis of 3a: Under air, a mixture of isoindoline-1,3-dione **1a** (44 mg, 0.3 mmol), 4-chlorobenzenethiol **2a** (29 mg, 0.2 mmol), KBr (24 mg, 0.2 mmol), 18-crown-6 (53 mg, 0.2 mmol) and MeCN (4.0 mL) were added in an oven-dried undivided bottle (10 mL). The bottle was equipped with Pt plate (10 mm x 10 mm x 0.1 mm) as anode and Ni gauze (10 mm x 10 mm x 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 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 ºC)/EtOAc = 10:1, v/v) to afford the desired product **3a** as a white solid (51 mg, 88% yield).

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Keywords: lactams • mercaptans • thiolation • *N*-acylsulfenamides • N–S bonds

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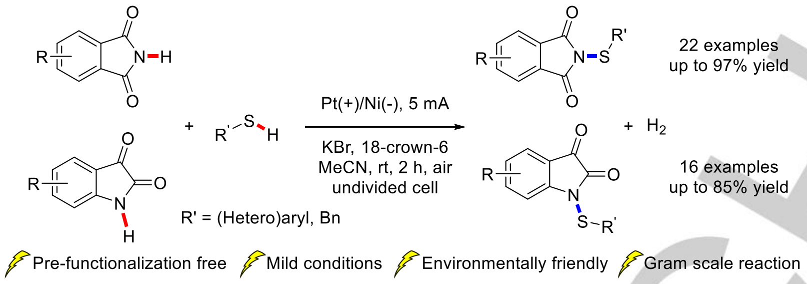

A variety of *N*-acylsulfenamides are produced by the electrochemical enabled cross coupling of readily available feedstocks under standard conditions. This protocol is practical and has wide substrate scope with good reaction efficiency (38 examples, up to 97% yield). A possible free radical mechanism is preliminarily demonstrated.