

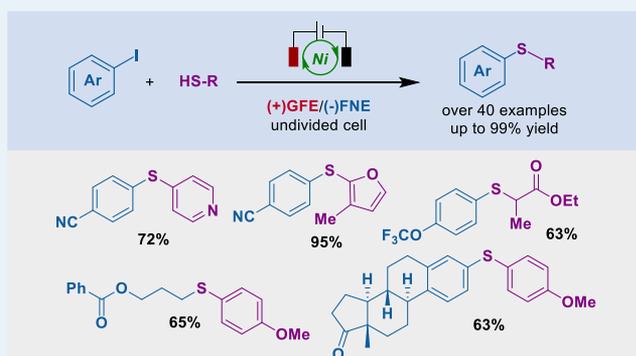
# Electrochemically Promoted Nickel-Catalyzed Carbon–Sulfur Bond Formation

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## Supporting Information

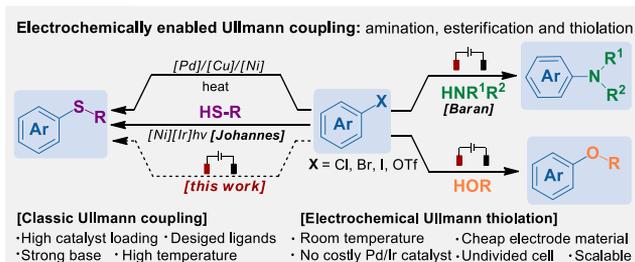
**ABSTRACT:** This work describes a nickel-catalyzed Ullmann-type thiolation of aryl iodides under mild electrochemical conditions. The simple undivided cell with graphene/nickel foam electrode setups offers excellent substrate tolerance, affording aryl and alkyl sulfides in good chemical yields. Furthermore, the mechanism for this electrochemical cross-coupling reaction has been investigated by cyclic voltammetry.



**KEYWORDS:** electrochemistry, nickel, Ullmann coupling, C–S bond, metal catalysis, thiolation, arylation

The classical Ullmann-type coupling reactions have been developed for over a century for C–N, C–O, and C–S bond formations.<sup>1</sup> The scope of the original copper-catalyzed biaryl coupling was limited to electron-deficient aryl halides and requires harsh reaction conditions.<sup>2</sup> Modern variants of the Ullman reaction employing palladium and nickel have widened the substrate scope and rendered conditions milder, although these efforts were plagued by several drawbacks. The cross-coupling of thiols with aryl halides generally rely on the conversion of the thiols to their corresponding thiolates by means of transition-metal catalysis. The strong coordination of thiolates to metals often leads to catalyst deactivation and displays low efficiencies. Thus, Ullmann thiolation is considered more challenging in contrast to amination and etherification, which requires high catalyst loading, specific ligand, excessive heating, and strong base to facilitate this transformation (Scheme 1).<sup>3</sup> Recent development using photoinduced thiol radicals<sup>4</sup> as sulfur source could avoid the problem of catalyst

## Scheme 1. Nickel-Catalyzed Ullmann-Coupling of Thiols with Aryl and Heteroaryl Iodides



**Table 1. Optimization of the Reaction Conditions**

entry	[Ni] catalyst	ligand	solvent	electrolyte	yield <sup>b</sup>
1	NiCl <sub>2</sub>	L1	DMA	LiBr (4 equiv)	9%
2	NiBr <sub>2</sub>	L1	DMA	LiBr (4 equiv)	30%
3	NiI <sub>2</sub>	L1	DMA	LiBr (4 equiv)	76%
4	Ni(acac) <sub>2</sub>	L1	DMA	LiBr (4 equiv)	59%
5	NiCl <sub>2</sub> ·glyme	L1	DMA	LiBr (4 equiv)	91%
6	NiCl <sub>2</sub> ·glyme	L1	DMA	<i>n</i> -Bu <sub>4</sub> NBF <sub>4</sub> (4 equiv)	21%
7	NiCl <sub>2</sub> ·glyme	L2	DMA	LiBr (4 equiv)	87%
8	NiCl <sub>2</sub> ·glyme	L3	DMA	LiBr (4 equiv)	51%
9	NiCl <sub>2</sub> ·glyme	L4	DMA	LiBr (4 equiv)	trace
10	NiCl <sub>2</sub> ·glyme	L5	DMA	LiBr (4 equiv)	trace
11	NiCl <sub>2</sub> ·glyme	L6	DMA	LiBr (4 equiv)	20%
12	NiCl <sub>2</sub> ·glyme	L1	MeCN	LiBr (4 equiv)	21%
13	NiCl <sub>2</sub> ·glyme	L1	DMA	LiBr (1 equiv)	35%

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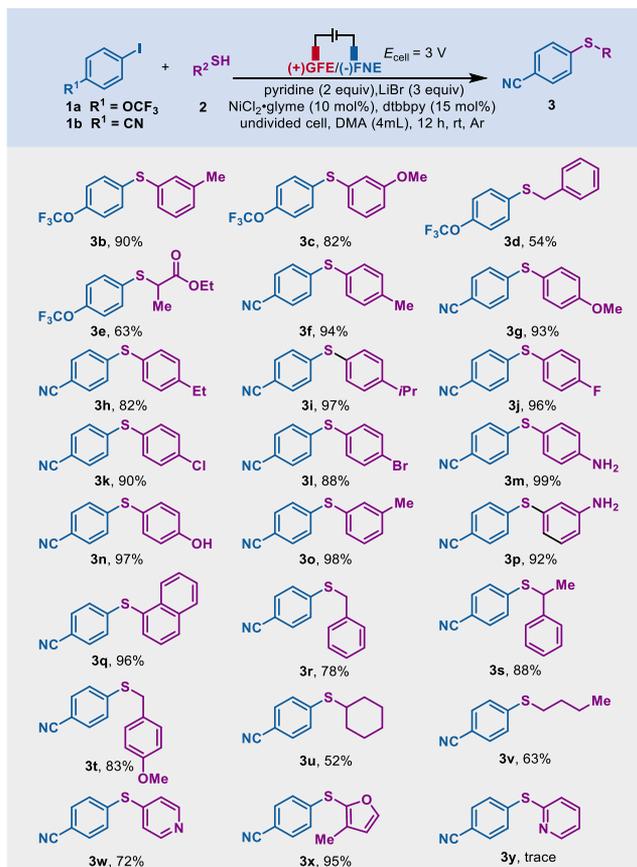
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Table 1. continued

entry	[Ni] catalyst	ligand	solvent	electrolyte	yield <sup>b</sup>
14	NiCl <sub>2</sub> ·glyme	L1	DMA	LiBr (2 equiv)	69%
15	NiCl <sub>2</sub> ·glyme	L1	DMA	LiBr (3 equiv)	96%
16	NiCl <sub>2</sub> ·glyme	L1	DMA	LiBr (4 equiv)	87%
17 <sup>c</sup>	NiCl <sub>2</sub> ·glyme	L1	DMA	LiBr (3 equiv)	99% <sup>d</sup>

<sup>a</sup>Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), solvent (4 mL) under argon atmosphere for 12 h, GFE = graphite felt electrode, FNE = foamed nickel electrode. <sup>b</sup><sup>19</sup>F NMR yield based on **1a**. <sup>c</sup>3 V voltage. <sup>d</sup>92% isolated yield based on **1a**.

Scheme 2. Scope of Thiol Coupling Partner



<sup>a</sup>Reaction conditions: (hetero)aryl iodides (0.20 mmol), thiols (0.40 mmol), [Ni] (0.02 mmol), dtbbpy L1 (0.03 mmol), pyridine (0.4 mmol), DMA (4 mL), LiBr (0.60 mmol). <sup>b</sup>Isolated yield based on iodides.

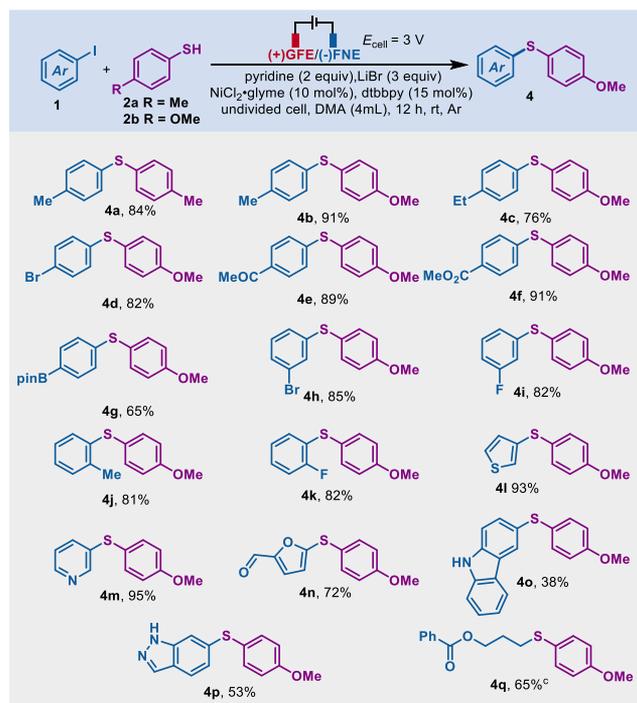
poison, although restricted substrate scope was displayed and heteroaryl thiols were not reported. Presumably, strong oxidizing iridium(III) photocatalyst might interfere with the generation of low-valent nickel species and hindered reductive elimination step.<sup>5</sup>

The advances of electrochemical cross-coupling process have drawn great attention, and many groups have joined this arena. The redox-efficiency, innate scalability and sustainability<sup>6</sup> of such process prompted the investigation of electrochemical dehydrogenative cross-coupling reactions for the C–C,<sup>7</sup> C–O,<sup>8</sup> C–N,<sup>9</sup> and C–S<sup>10</sup> bond formations. However, in a majority of electrochemical dehydrogenative cross-coupling, the substrates were limited to electron-rich (hetero)arenes with regioselective and chemoselective drawbacks.<sup>11</sup> We speculated that an electrochemically enabled Ullmann-type cross-coupling of aryl halides

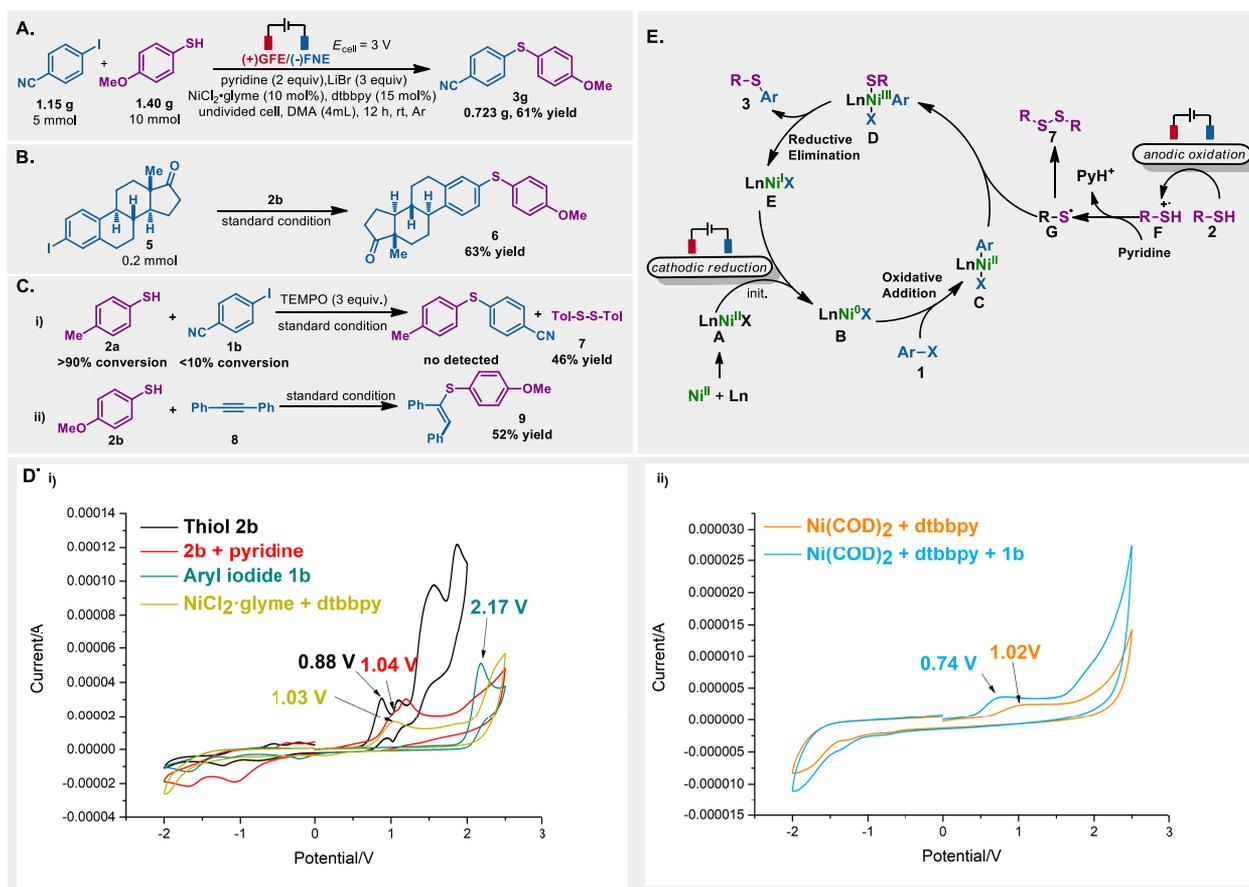
with X–H (X = N, O, S) donors could offer a complementary solution to access synthetically and medicinally useful aryl amines, esters, and thioesters. To our surprise, despite the potential utility of such transformation, only one example of electrochemical Buchwald–Hartwig amination and esterification has been described previously.<sup>12</sup> No electrochemically enabled Ullmann-type thiolation has been reported (Scheme 1). It is noteworthy that a nickel-catalyzed electrochemical C–H amination has also been reported by Lutz Ackermann group recently.<sup>9f</sup>

The proposition of Ullmann thiolation protocol under electrochemical conditions might be realized through careful redox manipulation of the nickel catalyst as each electrochemical process seamlessly combines concurrent anodic oxidations with cathodic reductions.<sup>13</sup> Thus, various oxidation states of nickel complexes could coexist in harmony under electrolytic conditions and precisely initiated and ceased by fine-tuning of the cell voltage.<sup>14</sup> The use of an undivided cell is rare and challenging in this situation.<sup>15</sup> Graphene/nickel foam electrodes were chosen in order to enhance the charge exchange.<sup>16</sup> Thus, we carried out electrolysis experiments with a survey of nickel catalysts using *p*-toluene thiol and *p*-iodobenzene in LiBr/DMA solution (Table 1). These studies reveal that nickel salt and ligand is able to promote the desired cross-coupling sequence. NiCl<sub>2</sub>, NiBr<sub>2</sub>, and NiI<sub>2</sub> could afford the thiolation product in low to moderate yields (entries 1–3). We next tested Bu<sub>4</sub>NBF<sub>4</sub> as electrolyte, but just 21% yield was afforded (entry 6). A series of ligands were screened (entries 7–10). Good to excellent yields were achieved with sterically hindered groups at para position of the dipyrindyl ligands (entries 5 and 7). Poor conversions were observed using L4–L6 (entries 9–11). Other solvent such as MeCN provided a very poor result.

Scheme 3. Scope of (Hetero)aryl Iodide Coupling Partner



<sup>a</sup>Reaction conditions: (hetero)aryl iodides (0.2 mmol), thiols (0.4 mmol), [Ni] (0.02 mmol), dtbbpy (0.03 mmol), pyridine (0.4 mmol), DMA (4 mL), LiBr (0.60 mmol). <sup>b</sup>Isolated yield based on iodides. <sup>c</sup>Made from alkyl bromide.



**Figure 1.** (A) Gram scale of the reaction; (B) Further elaboration; (C) Radical trapping experiments; (D) Cyclic voltammetry studies; (E) Proposed reaction mechanism.

The ratio of the added electrolyte has a significant influence on the yields (entries 13–16). The highest isolated yield was achieved with 3 equiv of LiBr at  $E_{\text{cell}} = 3\text{ V}$  (entry 17). Under the optimized conditions, various thiols **2** reacted smoothly with aryl iodides **1a** and **1b** to provide sulfides a range of substituted aryls (**3a**, **3c**, **3f–3q**) in good to excellent yields (Scheme 2). Notably, alkyl (**3d**, **3r–3v**), heteroaryls (**3w** and **3x**), and ester (**3e**) bearing thiols, which have proven to be challenging substrates using other cross-coupling procedures, also underwent highly selective reactions under the present conditions.

The scope of the aryl iodide coupling partner was also explored. Using conditions identical to those employed in Scheme 2, a range of aryl iodides **1** underwent radical thiolation with *p*-methyl or methoxyl thiophenol to provide sulfides **4** (Scheme 3). Aryls bearing ketone (**4e**), ester (**4f**), and borane (**4g**) functionalities were tolerated in this electrochemically enabled radical process. Heteroarenes including thiophene (**4l**), pyridine (**4m**), furan (**4n**), carbazole (**4o**), and benzopyrazole pyridine (**4m**), furan (**4n**), carbazole (**4o**), and benzopyrazole (**4p**) substituted iodides also furnished the corresponding products in high efficiency. Notably, linear ester could also be well-adopted in this nickel-catalytic system (**4q**).

Further elaboration of this electrochemical coupling sequence is presented in Figure 1. The scalability of this reaction was demonstrated through the cross-coupling of *p*-iodobenzonitrile and 4-methoxybenzenethiol on gram scale under the standard conditions with 100 mL undivided cell setup (Figure 1A). Electrochemical cross-coupling can also derivatize thiol motifs in bioactive molecules such as iodinated estrone **5**, affording **6**

in 63% yield (Figure 1B). In the radical-scavenging experiment, by adding 3 equiv of TEMPO, the cross-coupling product was completely suppressed, and the homocoupling product **7** was observed (Figure C-i). Further trapping of thiol radical with diphenylacetylene **8** under the same conditions furnished the thiolated olefin **9** in 52% yield, which verified the radical pathway of this process (Figure C-ii). No evidence indicated the presence of bromine radicals in the reaction mixture (see Supporting Information). Therefore, it is likely that thiols are directly oxidized to thiol radicals at the anode. To elucidate the reaction mechanism, cyclic voltammetry experiments were performed at the concentration of  $10^{-4}\text{ M}$  in MeCN with  $n\text{-Bu}_4\text{NPF}_6$  as electrolyte (0.2 M) using glassy carbon working electrode, Pt wire counter electrode, and SCE reference electrode with scan rate at  $0.2\text{ V}\cdot\text{s}^{-1}$ . First, we compared the redox potentials of all the possible reactive intermediates. As shown in Figure 1D-i, iodide **1b** and Ni(II) catalyst displayed relatively high oxidative potentials (2.17 and 1.03 V vs SCE, respectively). Thiol **2b** exhibited multiple irreversible oxidative waves from 0.88 V vs SCE. By adding pyridine to **2b**, only one oxidative wave showed at 1.04 V, indicating that pyridine could stabilize the oxidation process of thiols. These anodic events substantiated the initiation of catalytic cycle was more likely to be oxidation of **2b** to its radical **G** in assistance of base. In a separate voltammetric study, we measured the redox potentials of nickel complex species (Figure 1D-ii). An oxidative wave at 1.21 V was observed with the preformed Ni(0)-L, which shifted to 0.74 V on the addition of iodide **1b** to the Ni(0) complex. These events strongly suggested that Ni(0) was the actual reactive

species and oxidative insertion of aryl iodide resulted in the formation of Ni(II) intermediate. Based on the above evidence, a plausible mechanism for this Ni-catalytic electrochemical thiolation is proposed. As illustrated in Figure 1E, a single electron transfer (SET) oxidation of the thiol on anode produces the thiol radical cation F. Proton abstraction of F by pyridine affords a thiol radical G with aryl disulfide 7. Meanwhile, a cathodic reduction of NiCl<sub>2</sub>·dtbbpy A delivers a Ni(0)-X B followed by oxidative addition of aryl halide 1 to generate Ar-Ni(II)-X species C, which traps the thiol radical G to deliver a Ni(III)-complex D. Finally, reductive elimination of D furnishes the cross-coupled product 3 with Ni(I)-X complex E followed by cathodic reduction to regenerate Ni(0)-X B.

In summary, a robust electrochemistry facilitated nickel-catalyzed C-S cross-coupling protocol has been developed. The protocol affords both aryl and alkyl thiols with a wide array of functionalized aryl and heteroaryl iodides under mild conditions. The anodic and cathodic processes synergistically harness radical-mediated nickel species of different oxidation states in an undivided cell unit. Further study on Ullmann-type thiolation is underway in our laboratory.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.8b04633.

Synthetic procedures and characterization data (PDF)

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All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

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