Photoredox Mediated Nickel Catalyzed Cross-Coupling of Thiols With Aryl and Heteroaryl Iodides via Thiyl Radicals

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S *Supporting Information*

ABSTRACT: Ni-catalyzed cross-couplings of aryl, benzyl, and alkyl thiols with aryl and heteroaryl iodides were accomplished in the presence of an Ir-photoredox catalyst. Highly chemoselective C−S cross-coupling was achieved versus competitive C−O and C−N cross-couplings. This C−S cross-coupling method exhibits remarkable functional group tolerance, and the reactions can be carried out in the presence of molecular oxygen. Mechanistic investigations indicated that the reaction proceeded through transient Ni(I)-species and thiyl radicals. Distinct from nickel-catalyzed cross-coupling reactions involving carbon-centered radicals, control experiments and spectroscopic studies suggest that this C−S cross-coupling reaction does not involve a Ni(0)-species.

Scheme 1. Metal-Catalyzed C−O and C−S Cross-Couplings

N ature employs thiyl radicals in a broad range of enzymatic processes including the deoxygenation of ribonucleo-tides.[1] The ease in formation of thiyl radicals from thiols and their exceptional reactivity make them extremely attractive for efficient, and useful radical reactions in organic synthesis.[2] Some notable synthetic applications of thiyl radicals include addition to unsaturated systems,[3] thiol−ene reactions,[4] thiol−yne reactions,[5] radical cyclization reactions,[6] reduction processes,[7] addition−fragmentation reactions,[8a] and H-atom abstraction processes.[8b] Yet, engaging thiyl radicals in transition-metal-catalyzed cross-coupling reactions with aryl halides to construct C−S bonds remains an elusive reaction in organic chemistry.[2]

The high frequency of C−S bonds in drug molecules across many disease types such as cancer, HIV, and Alzheimer's disease necessitates the continued development of C−S bond-forming reactions.[9] Transition-metal-catalyzed C−S cross-coupling re-actions of thiols with aryl halides generally rely on the conversion of the thiols to their corresponding thiolates (Scheme 1a).[10,11] The strong coordination of thiolates to transition-metal catalysts often leads to catalyst deactivation, thus requiring a high catalyst loading, specially designed ligands, and/or a high temperature to facilitate the desired reaction.[10,11] Furthermore, the high temperature and strong base required for these reactions limit functional group tolerance.
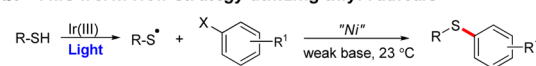
Strategically, we reasoned that the utilization of thiyl radicals,[12a] in lieu of thiolates, may eliminate the problem of catalyst deactivation and deliver a more efficient C−S cross-coupling reaction with the use of simple ancillary ligands. We also envisioned that employing thiyl radicals could provide a highly
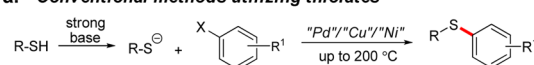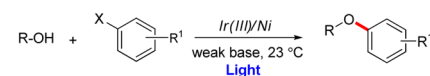
chemoselective reaction that operates at room temperature with broad functional group tolerance.

The combination of a photoredox catalytic cycle with an organometallic cycle has emerged as a powerful tool for cross-coupling reactions.[13] The ability of the photoredox catalyst to modulate transition-metal oxidation states, which allows easy access to elusive reactivity makes the dual-catalytic platform very attractive.[13] We recently undertook a mechanistic investigation into the effect of oxygen on the Ir/Ni dual-catalytic reactions developed by the laboratories of Molander, Doyle, and MacMillan involving C-centered radicals.[13a,b,14] Our investigations of these systems prompted us to consider whether the photoredox mediated dual catalysis could be used as a tool to form thiyl radicals and promote their cross-coupling with aryl halides to form C−S bonds (Scheme 1b). MacMillan et al. recently demonstrated that the Ir/Ni dual-catalytic platform can be extended to carbon−heteroatom cross-coupling by elegantly developing a new C−O cross-coupling method (Scheme 1c).[13d]

Herein, we demonstrate that photogenerated thiyl radicals from various thiols can engage in Ni-catalyzed cross-couplings with aryl and heteroaryl iodides to afford C−S bonds in a highly chemoselective fashion under an Ir/Ni dual-catalytic system.

From the outset, a principle concern in the development of such a cross-coupling method was identifying conditions wherein the thiyl radicals can react selectively with a Ni-species. In addition, unlike the Ni-catalyzed cross-couplings involving carbon-centered radicals,[13a,b,14] the oxidation state of Ni that would promote the cross-coupling involving heteroatom radicals was unknown. With these challenges in mind, we evaluated a number of potential Ir-photoredox and Ni catalysts under various conditions in the cross-coupling of 4-methoxybenzyl thiol (**1a**)

(pK_a = 15.4, for benzyl thiol)[15a] and 4-iodotoluene (**2a**). The irradiation of a reaction mixture containing 4-methoxybenzyl thiol (**1a**), 4-iodotoluene (**2a**), Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (**Ir-B**), NiCl$_2$·glyme, dtbbpy (4,4′-di-*tert*-butyl-2,2′-dipyridyl), and pyridine (pK_a = 5.2)[16] in MeCN with blue LEDs for 24 h at room temperature in the presence of O$_2$ gave the C−S cross-coupled product **3a** in excellent conversion (Table 1, entry 1).

Table 1. Ir-Photoredox/Ni Dual-Catalyzed C−S Cross-Coupling: Effect of Reaction Parameters

Ir[dF(CF$_3$)ppy]$_2$(bpy)PF$_6$ (**Ir-A**)　　Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (**Ir-B**)

entry	variation from the standard conditions[a]	yield (%)[b]
1	none	>95
2	no light (dark)	NR[c]
3	no Ir(III)-catalyst	NR
4	no NiCl$_2$·glyme and no dtbbpy	NR
5	no pyridine	<5[d]
6	4-bromotoluene instead of 4-iodotoluene	<5
7	**Ir-A** instead of **Ir-B**	30
8	26 W CF-lamp instead of 34 W blue LEDs	NR
9	**Ir-B** with 34 W green LEDs	NR
10	degassed	>95
11	NiCl$_2$·bpy instead of NiCl$_2$·dtbbpy	>95
12	NiCl$_2$·dppe instead of NiCl$_2$·dtbbpy	70
13	Ni(COD)$_2$ instead of NiCl$_2$·glyme	<5
14	Ni(COD)$_2$ and degassed	<5

[a]Scale of reaction: 0.50 mmol of 4-iodotoluene and 5 mL of 99.8% MeCN (0.10 M). [b]% Conversion was determined by ^{1}H NMR spectroscopy with the aid of an internal standard. [c]NR implies no product was detected by ^{1}H NMR spectroscopy. [d]<5% implies trace product was observed.

A series of control experiments established the importance of light, Ir-catalyst, ligand, Ni-catalyst, and base on the reaction yield (entries 1−5). Though the reaction did not proceed when an aryl bromide was used in place of an aryl iodide (entry 6), the chemoselectivity for aryl iodide over aryl bromide could be advantageous for orthogonal synthesis. In addition to the photoredox catalyst **Ir-B**, the Ir-photoredox catalyst Ir[dF(CF$_3$)-ppy]$_2$(bpy)PF$_6$ (**Ir-A**) also mediated the reaction, *albeit* with lower efficiency (entry 7). We found that the irradiation with blue LEDs is essential for the catalysis, as irradiation with either a white light (26 W CF-lamp) or green LEDs resulted in no reaction (entries 8 and 9). The cross-coupling also proceeded efficiently in the absence of O$_2$ (entry 10). Regarding the competence of other simple bidentate ligands on Ni, the reaction proceeded with good efficiency when either NiCl$_2$·bpy (bpy = 2,2′-bipyridine) or NiCl$_2$·dppe (dppe = 1,2-bis(diphenyl-phosphino)ethane) precatalyst was used (entries 11 and 12). Of significant mechanistic implication and distinct from the Ni-catalyzed cross-coupling reactions involving carbon-centered radicals,[13a,b,14] this cross-coupling reaction does not proceed with a Ni(0)-precatalyst, either in the presence or absence of O$_2$ (entries 13 and 14). Instead, the dimerization of the thiyl radicals to the corresponding disulfide was observed after 24 h. The high efficiency of this C−S cross-coupling reaction in the presence of O$_2$ could also be an indication that a Ni(0)-species is not the active Ni-species in this reaction.[14] Ni(0)-complexes are generally incompatible with O$_2$, and as a result, Ni(0)-catalyzed reactions are generally carried out under anaerobic conditions.[17,18]

The generation of thiyl radicals from thiol (**1a**) in the presence of the photoredox catalyst **Ir-B** was experimentally supported by trapping the thiyl radicals with olefin (**4**) to give thioether (**5**) in good yield (Figure 1a).[12]
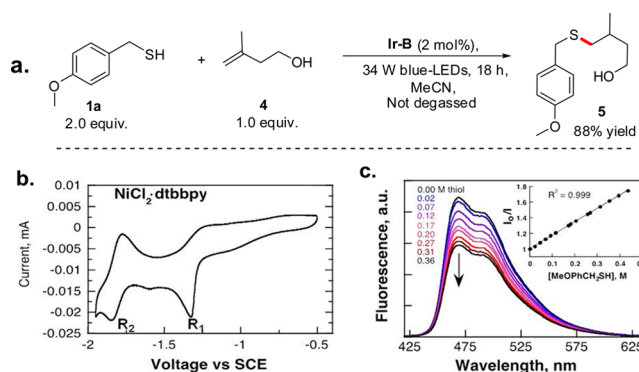

Figure 1. (a) Trapping of the thiyl radicals with an olefin. (b) The CV of NiCl$_2$·dtbbpy. (c) Steady-state emission quenching of *Ir^{III} with thiol (**1a**); (Inset) Stern-Volmer analysis of the results

In order to rationalize the dependence of this cross-coupling reaction on the oxidation state of the Ni-precatalyst, we carried out electrochemical studies of NiCl$_2$·dtbbpy in MeCN. The cyclic voltammetry (CV) of NiCl$_2$·dtbbpy showed an irreversible two-electron reduction peak (**R$_1$**) corresponding to the Ni^{II}/Ni^0 couple at −1.34 V versus saturated calomel electrode (SCE) in MeCN (Figure 1b). This reduction potential (**R$_1$**) is similar to that reported for NiCl$_2$·bpy ($E_{1/2}^{red}$ [Ni^{II}/Ni^0] = −1.36 V versus SCE in DMF).[19] The quasi-reversible reduction peak observed at **R$_2$** ($E_{1/2}^{red}$ = −1.88 V) can be ascribed to the Ni^0/Ni$^{0•−}$ couple.[19] Since the Ni^{II}/Ni^0 couple reduction potentials of NiCl$_2$·dtbbpy and NiCl$_2$·bpy complexes fall within the margin of error of the reduction potential of the reductant **Ir^{II}** (**Ir-B**, $E_{1/2}^{red}$ [Ir^{III}/Ir^{II}] = −1.37 V versus SCE in MeCN),[20] it is difficult to accurately ascertain the thermodynamic favorability of their reduction to Ni(0)-species. However, the fact that a reaction that does not proceed with a Ni(0)-species, proceeds with NiCl$_2$·dppe ($E_{1/2}^{red}$ [Ni^{II}/Ni^I] = −0.88 V and [Ni^I/Ni^0] = −1.41 V versus SCE in DMF/THF),[21] which thermodynamically and kinetically should be easily reduced to its Ni(I) oxidation state by **Ir^{II}**, supports that a Ni(I)-species is the active Ni-species in this reaction. Therefore, we hypothesize that the reduction of the Ni(II)-complexes to their corresponding Ni(I)-species by **Ir^{II}** is thermodynamically and kinetically facile.

Finally, time-resolved emission spectroscopy showed that the excited state lifetime of 2.25 μs for *Ir^{III} (the excited state of **Ir-B**) as measured by its emission at 500 nm remains unchanged in the presence of 0.2 M pyridine (Supporting Information). From the steady-state emission quenching experiment, a bimolecular rate constant of 7.6×10^5 M^{-1} s^{-1} was obtained for the quenching reaction between *Ir^{III} and 4-methoxybenzyl thiol (**1a**). These experiments confirmed that the thiol (**1a**) quenches the emission of *Ir^{III} (Figure 1c), and the Stern−Volmer analysis gave an excellent linear regression (Figure 1c, inset).

Based on these mechanistic data, a proposed mechanism for the dual catalysis is depicted in Figure 2. Visible-light irradiation of the heteroleptic Ir^{III}-photocatalyst (**Ir-B**) generates a long-
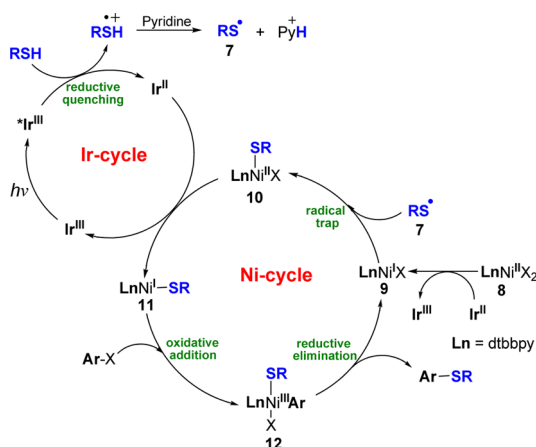
Figure 2. Proposed mechanism for the C−S cross-coupling.

lived excited state *$\mathbf{Ir^{III}}$ (2.25 μs). A single electron transfer (SET) oxidation of the thiol ($E_{1/2}^{ox}$ = +0.83 V versus SCE in MeCN for benzyl thiol),[12a,15] by the oxidizing photoexcited *$\mathbf{Ir^{III}}$ ($E_{1/2}^{red}$ [*$\mathrm{Ir^{III}/Ir^{II}}$] = +1.21 V versus SCE in MeCN),[20] produces both the thiol radical cation (**6**) and $\mathbf{Ir^{II}}$. Deprotonation of the highly acidic radical cation (pK_a = 2.4 for benzyl thiol radical cation)[15] by pyridine produces a thiyl radical (**7**). An SET reduction of the NiCl$_2$·dtbbpy (**8**) by $\mathbf{Ir^{II}}$ delivers a Ni^I-halide (**9**). At this juncture, a thiyl radical (**7**) rapidly intercepts the Ni^I-halide (**9**) to form a Ni^{II}-species (**10**), which is reduced by $\mathbf{Ir^{II}}$ to a Ni^I−sulfide complex (**11**) while concomitantly regenerating the $\mathbf{Ir^{III}}$. Oxidative addition of an aryl iodide to the Ni^I−sulfide complex (**11**) delivers a Ni^{III}-complex (**12**), which undergoes a facile reductive elimination process[18] to forge the C−S cross-coupled product and reproduces a Ni^I-halide complex (**9**). We believe, in addition to being the base, pyridine also stabilizes the coordinatively unsaturated Ni^I-halide (**9**) and Ni^I-sulfide (**11**) complexes (see the Supporting Information for the effects of other bases and more CV studies). The preference for aryl iodide may be attributed to the inability of the Ni^I-sulfide (**11**) to oxidatively add to the stronger aryl bromide bond or the proclivity toward concerted oxidative addition.[10d,22]

With the optimized conditions in hand, we explored the scope of this C−S cross-coupling protocol. As envisioned, the scope of the aryl iodide is very broad under these mild conditions (Table 2). A range of *ortho*-substituted aryl iodides bearing amino, methoxy, fluoro, and methyl groups engaged in the cross-couplings to forge C−S bonds in good yields (**3b**–**3e**). However, *ortho,ortho*-dimethyliodobenzene failed to cross-couple (**3f**), likely due to increased steric hindrance. Aryl iodides containing functional groups for orthogonal transformations such as organoboronate (**3g**), carboxylic acid (**3h**), primary amine (**3i**), aldehyde (**3j**), ketone (**3k**), bromide (**3l**), nitrile (**3m**), and dimethyl (**3n**) all coupled with complete chemoselectivity and high efficiencies to give products in good to excellent yields. Heteroaromatic iodides, which are common building blocks in the preparation of bioactive compounds, such as indole (**3o**), protected pyrazole (**3p** vs **3q**), pyridine (**3r**), pyrimidine (**3s**), and thiophene (**3t**), are all effective electrophiles in this protocol.

In addition, we investigated a diverse set of thiols to further highlight the versatility of this method (Table 3). We found that a wide range of thiols are effective coupling partners including thiophenols (**13a** and **13b**) as well as simple and functionalized alkyl thiols (**13c** and **13d**). Interestingly, *N*-Boc-cysteine undergoes only the C−S cross-coupling reaction without any
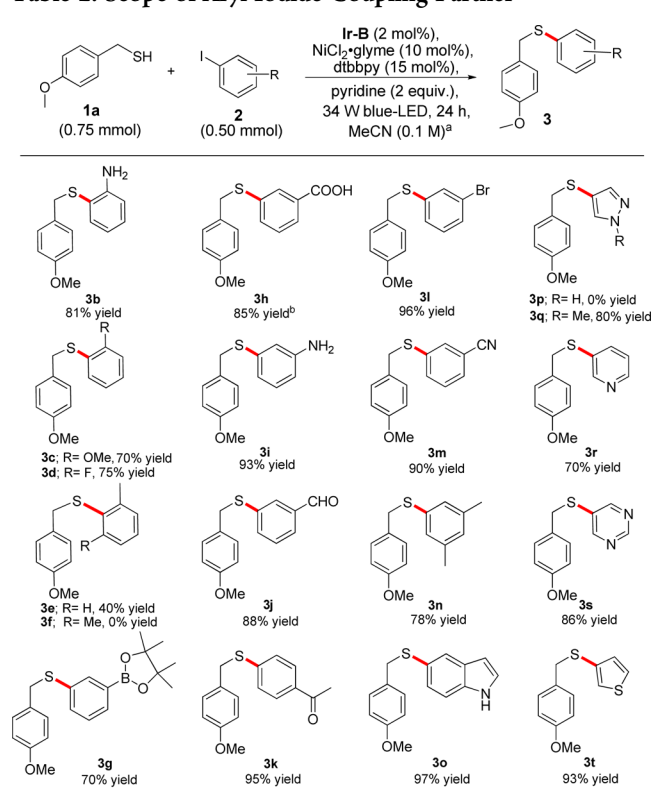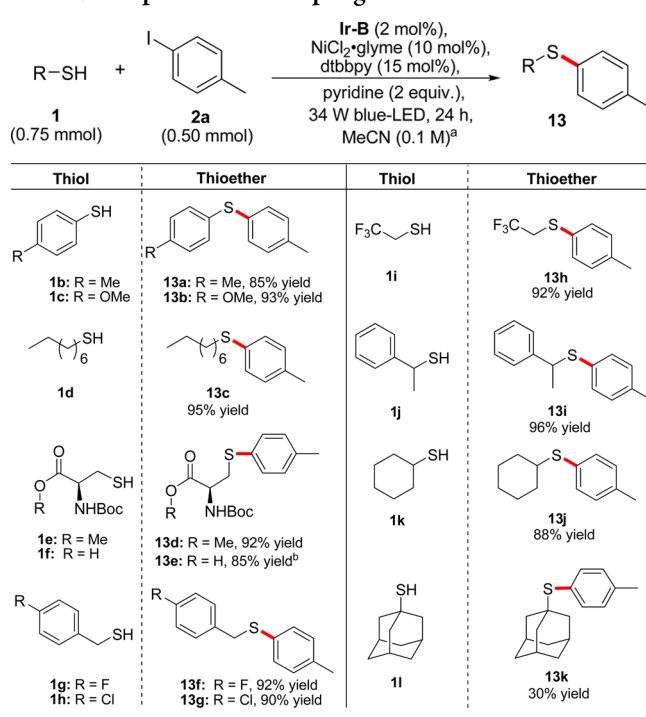
Table 2. Scope of Aryl Iodide Coupling Partner

**Table 3. Scope of Thiol Coupling Partner**

decarboxylative C−C bond formation[13b,14] to give **13e** in good yield. Thiols bearing β-electron-deficient groups are also competent substrates in this transformation (**13f**, **13g**, and **13h**). Notably, secondary and tertiary thiols also gave the desired thioethers in good to moderate yields (**13i**, **13j**, and **13k**).

A reaction mixture containing a 1:1 ratio of 4-methoxybenzyl alcohol and 4-methoxybenzyl thiol as competitive nucleophiles in the presence of 4-iodotoluene (**2a**) gave exclusively the C−S

cross-coupled product with no C−O bond formation[13d] (see Supporting Information). Futhermore, consistent with the effects of radical stability, a secondary thiol (**1j**) gave twice as much cross-coupled product (**13i:13m** = 2:1) in a competition reaction with a primary thiol (**1m**) (Scheme 2). It is noteworthy that MacMillan's C−O coupling method operates under a unique set of conditions and a different mechanism.[13d]

Scheme 2. Primary and Secondary Thiols Competition Reaction
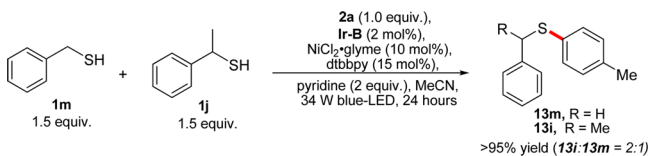
In conclusion, we have developed a mild, highly chemoselective, and robust photoinduced Ni-catalyzed method for the cross-coupling of aryl, benzyl, and alkyl thiols with a wide array of functionalized aryl and heteroaryl iodides. To the best of our knowledge, this study is the first method that allows thiyl radicals or any heteroatom radical to engage in a transition-metal catalyzed cross-coupling reactions with iodoarenes. The ability of the catalytic system to operate with high efficiency in the presence of molecular oxygen further enhances the practical utility of this method. Control experiments and spectroscopic studies indicated that this reaction does not involve a Ni(0)-species but is catalyzed by a transient Ni(I)-species. With this method, we have expanded on the utilities of thiyl radicals and developed a versatile C−S cross-coupling method that should find widespread application in organic synthesis.

■ ASSOCIATED CONTENT

ⓢ Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b11244.

> Additional experimental and electrochemical studies; Experimental procedures; characterization data and spectra for all new compounds (PDF)

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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