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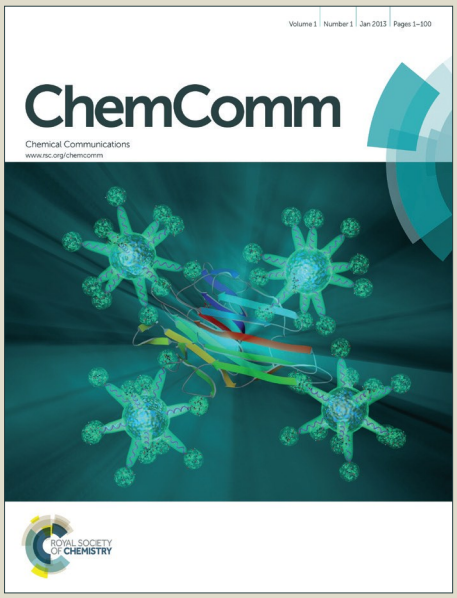

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COMMUNICATION

Aerobic Copper-Catalyzed Decarboxylative Thiolation†

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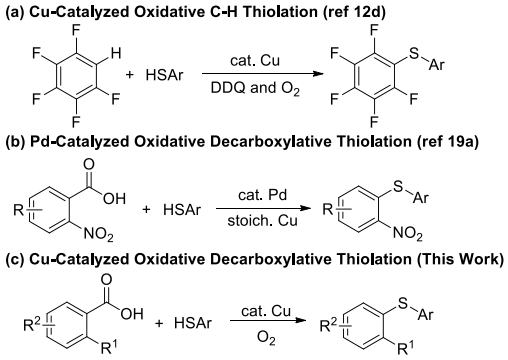
Copper-catalyzed decarboxylative thiolation using molecular oxygen as the sole oxidant was developed. A variety of aromatic carboxylic acids including 2-nitrobenzoic acids, pentafluorobenzoic acid and several heteroaromatic carboxylic acids undergo efficient thiolation to furnish the aryl sulfides in moderate to excellent yields.

Transition-metal-catalyzed cross-coupling reactions have become reliable and efficient methods for the construction of new carbon–heteroatom bonds.[1] The development of cross-coupling reactions to form C–S bonds,[2] however, remains limited when compared to the methods available for C–N and C–O bond formation, despite aryl sulfides having broad pharmaceutical and materials science applications, in addition to their use as intermediates in organic synthesis.[3] In recent decades, the coupling of aryl halides with thiols or disulfides catalyzed by Pd,[4] Cu,[5] Ni,[6] Co,[7] Fe,[8] and other metals[9] have been reported, however, these methods suffer from poor atom- and step-economy and require the separation and disposal of halide-containing byproducts. Copper-catalyzed Chan–Lam-type couplings offer an oxidative route to aryl sulfides, although prefuctionalized organometallic reagents are still needed.[10] Recently, the direct thiolation of arene C-H bonds has been developed as an attractive method to form C–S bonds from unfunctionalized arenes (Scheme 1a). Unfortunately, the activity and selectivity observed in these systems rely on either the use of directing groups,[11] or activated or acidic arene C–H bonds.[12]

Decarboxylative couplings have become attractive alternatives to the use of prefunctionalized organometallic reagents because the benzoic acid coupling partners are widely available, inexpensive and easy to handle and store. Early work in this area, pioneered by Goossen,[13] Myers,[14] and others,[15] mainly focused on the development of C–C bond-forming transformations. Oxidative variants have also been developed and enable coupling of benzoic acids to form C–N,[16] C–O,[17] and C–X bonds.[18] Despite these advances, there are limited examples of the oxidative decarboxylative coupling to form C–S bonds.[19] In existing cases, a Pd catalyst is paired with a Cu or Ag salt to serve as a stoichiometric oxidant and to promote decarboxylation (Scheme 1b). Alternatively, the use of copper-only systems is attractive because noble metals are not needed and benign oxidants, such as O_2, can be employed. The aerobic copper-catalyzed oxidative decarboxylative couplings to form C–C[20] and C–N[15] bonds have been developed, yet the analogous C–S bond forming reactions have not been reported. We report here the first copper-catalyzed decarboxylative thiolation to produce diaryl sulfides using molecular oxygen as the terminal oxidant.



Scheme 1 (a) C-H Thiolation, (b) Pd-Catalyzed, and (c) Cu-Catalyzed Oxidative Decarboxylative Thiolation.

Our investigation of the copper-catalyzed decarboxylative thiolation began with 2-nitrobenzoic acid (**1a**) and thiophenol (**2a**) as coupling partners (Table 1). The initial conditions employing a $Cu(OAc)_2$/1,10-phenanthroline precatalyst and 1 atm O_2 as the oxidant in DMSO at 140°C for 24 h gave 83% yield of the desired product **3a** (entry 1). Decreasing the copper loading from 30 mol% to 10 mol% had no effect on the yield (entry 2). Both Cu^{I} and Cu^{II} salts are effective catalysts and there is no significant dependence on the counteranions

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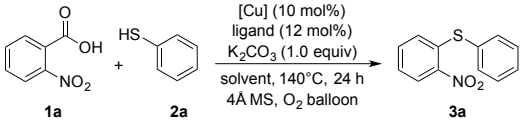
†Electronic Supplementary Information (ESI) available: Experimental procedures, details on reaction development, characterization data for starting materials and reaction products and ^{1}H and ^{13}C NMR spectra. See DOI: 10.1039/x0xx00000x

Table 1 Optimization of Reaction Conditions for the Copper-Catalyzed Decarboxylative Thiolation[a]



1a 2a 3a

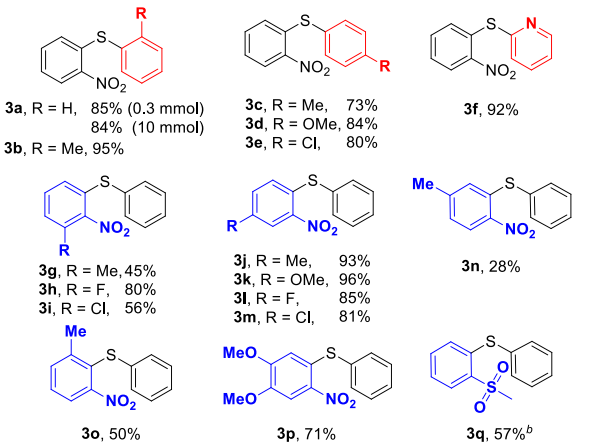
entry	[Cu]	ligand	solvent	yield **3a** (%)[b]
1[c]	$Cu(OAc)_2$	phen	DMSO	83
2	$Cu(OAc)_2$	phen	DMSO	82
3	$CuBr_2$	phen	DMSO	80
4	$CuCl_2$	phen	DMSO	79
5	$Cu_2(OH)_2CO_3$	phen	DMSO	85
6	CuBr	phen	DMSO	86
7	CuCl	phen	DMSO	75
8	CuOAc	phen	DMSO	85
9	Cu_2O	phen	DMSO	81
10	**CuI**	**phen**	**DMSO**	**88 (85)[d]**
11	CuI	phen	DMF	71
12	CuI	phen	NMP	66
13	CuI	phen	*p*-xylene	14
14	CuI	phen	anisole	27
15	–	phen	DMSO	0
16	CuI	–	DMSO	18
17	CuI	bipy	DMSO	37
18	CuI	PPh_3	DMSO	20
19[e]	CuI	phen	DMSO	6
20[f]	CuI	phen	DMSO	3
21[g]	CuI	phen	DMSO	66
22[h]	CuI	phen	DMSO	83

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.6 mmol) and 4Å molecular sieves (500 mg) in a solvent (5 mL). [b]1H NMR yield with 1,3,5-trimethoxybenzene as an internal standard. [c]$Cu(OAc)_2$ (30 mol%), phen (40 mol%). [d]Isolated yield in parenthesis. [e]Without K_2CO_3. [f]at 110 °C. [g]Air balloon. [h]CuI (5 mol%), phen (6 mol%).

employed (entries 3 to 10). CuI was chosen for further study due to the low cost and high efficiency of this precatalyst (entry 10). The choice of solvent plays a critical role in the formation of the desired product with polar aprotic solvents (DMSO, DMF, and NMP, entries 10-12) providing the product in moderate to good yields, and nonpolar solvents (*p*-xylene and anisole, entries 13 and 14) leading to large amounts of nitrobenzene formed by competitive protodecarboxylation. Control experiments confirmed that both copper (entry 15) and 1,10-phenanthroline (entry 16) are required for effective formation of the coupling product. The use of 2,2'-bipyridine or triphenylphosphine in place of phen resulted in decreased yields (entries 17 and 18). Excluding base or conducting the reaction at a lower temperature resulted in very poor yields

Table 2 Scope of Thiols for the Copper-Catalyzed Decarboxylative Thiolation of Benzoic Acids[a]

1 2 3



[a]Isolated yields. [b]at 160 °C. General reaction conditions: 1 (0.3 mmol), 2 (0.6 mmol) and 500 mg 4Å MS in 5 mL of DMSO.

(entries 19 and 20). Changing the oxidant to air furnished 3a in moderate yields (entry 21). Further decreasing the catalyst loading slightly decreased the yield (entry 22). Thus, the following optimized reaction conditions were identified: CuI (10 mol%), phen (12 mol%) and K_2CO_3 (1.0 eq.) in DMSO at 140°C with 1 atm O_2 as the oxidant.

With the optimized reaction conditions in hand, the scope of thiophenol coupling partners was explored (Table 2). Thiophenols bearing both electron-donating and -withdrawing substituents all reacted smoothly to afford the corresponding aryl sulfides in high yields (**3a-e**), and no effect of steric hindrance on the yield was observed (**3b**). Although the heteroaromatic pyridine-2-thiol also performed well (**3f**), alkyl thiols are not compatible with this Cu-catalyzed protocol (Scheme S1a). It was worth noting that preparative-scale reaction (10 mmol, **3a**) proceeded well, indicating the feasibility of this method for practical synthesis. Subsequently, the scope of the benzoic acid coupling partners was explored. C3 or C4 substituted 2-nitrobenzoic acids all delivered the desired products in moderate to good yields (**3g-m**). The reaction favors electron-withdrawing substituents at the C3 position (**3h**) and electron-donating substituents at the C4 position (**3j** and **3k**). When 5-methyl-2-nitrobenzoic acid was used, a low yield of the desired product **3n** was obtained due to partial oxidation of the C-5 methyl group (Scheme S1b). However, a methyl substituent is tolerated when located at the C3, C4, and C6 positions of 2-nitrobenzoic acid (**3g**, **3j** and **3o**). The disubstituted 2-nitrobenzoic acid was also viable for this transformation, affording the corresponding thioether in 71% yield (**3p**). The 2-chloro-4-nitrobenzoic acid was an ineffective substrate for this methodology (Scheme S1c), indicative of the importance of the nitro group in the *ortho*

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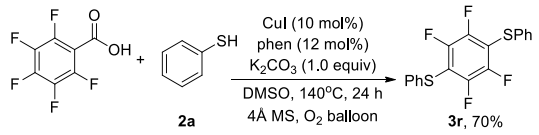
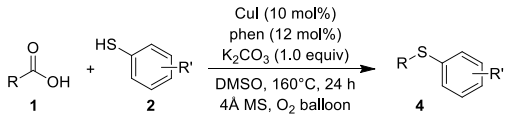
Scheme 2 Decarboxylative Thiolation/S_NAr of Pentafluorobenzoic Acid.

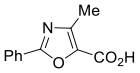
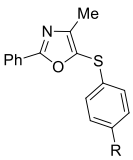
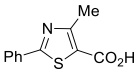
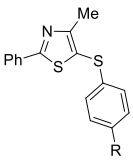
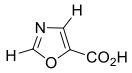
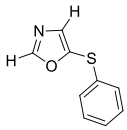
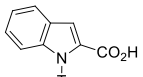
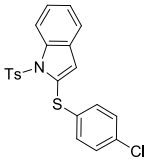
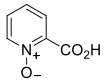
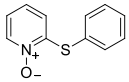


position.[21] This key result also eliminated the possibility of a tandem prodecarboxylation/C–H thiolation reaction pathway.[22] The 2-methylsulfonyl benzoic acid participated well In the reaction (**3q**), suggesting the possibility of replacing the *ortho*-nitro group with other eletron-withdrawing and chelating substituents.

Because polyfluorobenzoic acids are efficient coupling partners in other Cu catalyzed decarboxylative cross-coupling reactions,[14a] pentafluorobenzoic acid was tested under our reaction conditions. To our delight, a highly symmetric dithiolated product (**3r**) was obtained in good yield (Scheme 2) through decarboxylative thiolation/nucleophilic aromatic substitution.[23] In contrast, 2,3,4,5-tetrafluorobenzoic acid formed the S_NAr/decarboxylative protonation product as the major product (Scheme S1d), suggesting the importance of the *ortho*-difluoro substituents in the coupling step.

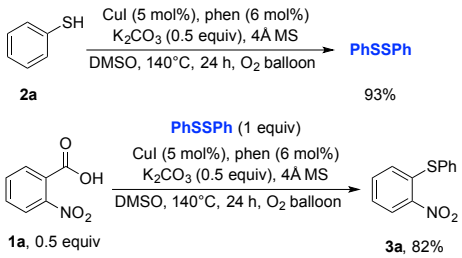
Table 3 Scope of Heteroaromatic Carboxylic Acids for the Copper-Catalyzed Decarboxylative Thiolation[a]



Entry	1	Product	Yield of 4[b]
1 2 3			**4a**, R = H, 59% **4b**, R = OMe, 62% **4c**, R = Cl, 69%
4 5 6			**4d**, R = H, 63% **4e**, R = OMe, 70% **4f**, R = Cl, 60%
7			**4g**, 36%[c]
8			**4h**, 68%[d]
9			**4i**, 45%[c,e]

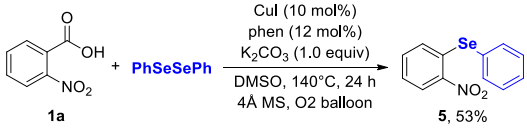
[a]Reaction conditions: **1** (0.3 mmol), **2** (0.9 mmol) and 500 mg 4Å MS in 5 mL of DMSO. [b]Isolated yields. [c]**1** (0.9 mmol), **2** (0.3 mmol). [d]at 110°C. [e]at 140°C.

Next, we were intrigued by the possibility of employing heteroaromatic carboxylic acids in our current methodology. There are few systems that catalyze the decarboxylative couplings of heteroaromatic acids[24] and to the best of our knowledge, there are no examples of such a transformation catalyzed by first-row transitional-metals. In addition, the heteroaryl sulfides are attractive targets because they are common scaffolds in pharmaceutical agents used to treat inflammation,[3a] cancer,[25a] HIV,[25b] Alzheimer's disease and Parkinson's disease.[25c] We began our exploration of heteroaromatic carboxylic acids with oxazole-5-carboxylic acid (Table 3, entres 1-3), and were pleased to find that the corresponding heteroaryl sulfide **4a** was obtained in moderate yield under slightly modified conditions. No obvious electronic effect on the thiophenol coupling partner was observed (**4b, 4c**). Similarly, the substituted thiozole-5-carboxylic acid delivered the thiolation products in synthetically useful yields (entries 4-6). The simple oxazole-5-carboxylic acid also underwent decarboxylative thiolaion to yield **4g**, albeit in slightly lower yield (entry 7). The formation of **4g** as the only thiolation product indicated the chemoselectivity achieved from decarboxylative coupling; complementary to the 2-substituted products that would arise from dehydrogenative thiolation.[26] The *N*-protected indole 2-carboxylic acid (entry 8) and picolinic acid *N*-oxide (entry 9) could also be employed in this reaction, highlighting the broad scope of this protocol.



To obtain insights into the reaction pathway, preliminary mechanistic studies were performed. The inclusion of radical scavengers such as TEMPO and 9,10-dihydroanthracene had no significant effect on the yield of **3a** (Table S1) suggesting a radical pathway to be unlikely. Monitoring the reaction of 2-nitrobenzoic acid (**1a)** with thiophenol (**2a)** by GC-MS revealed the presence of phenyl disulfide during and after the reaction. Control experiments showed that in the absence of **1a** phenyl disulfide (PhSSPh) was formed in good yield (93%, eq 1). Furthermore, the reaction of **1a** with PhSSPh generated the coupling product **3a** in good yield (82%, eq 2), suggesting that the coupling reaction likely proceeds through the disulfide.[27] Inspired by the efficient coupling of disulfides, we explored

Scheme 3 The Synthesis of Diaryl Selenide by Copper-Catalyzed Oxidative Decarboxylative Coupling



diselenides as possible coupling partners.[2] To our delight, diphenyl diselenide led to the desired cross-coupling product **5** in moderate yield (Scheme 3).

In conclusion, we have disclosed the first example of a copper-catalyzed decarboxylative thiolation of benzoic acids under aerobic conditions. The broad scope of heteroaromatic carboxylic acids tolerated by this catalyst system is unprecedented for oxidative decarboxylative coupling reactions catalyzed by first-row transition-metals. We have identified the disulfide to be a key intermediate, yet the nature of the active catalyst remains unclear. Full mechanistic studies are underway to reveal the detailed reaction pathway.

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21 Similar limitations have been observed in other Cu (see ref. 16, 18c and 20), Pd (see ref. 13a), and Ni (K. Yang, P. Wang, C. Zhang, A. Kadi, H.-K. Fun, Y. Zhang, H. Lu, *Eur. J. Org. Chem.*, 2014, 7586.) catalysed decarboxylative cross-couplings.

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