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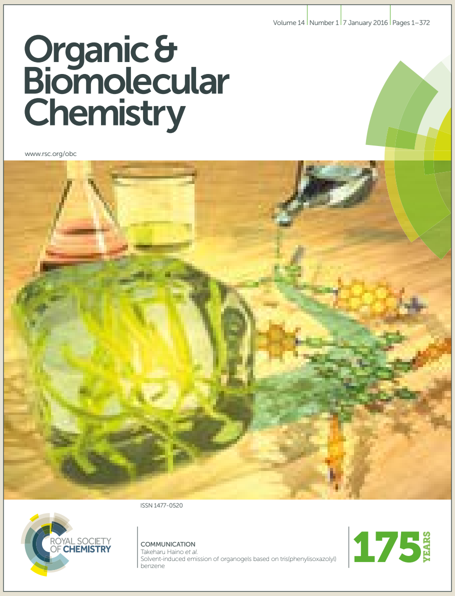
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COMMUNICATION

Copper-Catalyzed Decarboxylative Methylthiolation of Aromatic Carboxylate Salts with DMSO

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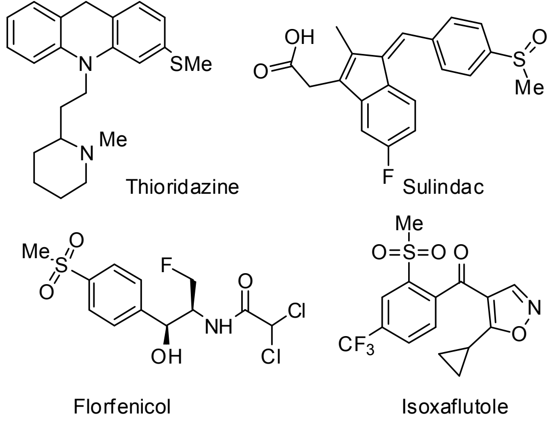
A novel copper-catalyzed decarboxylative methylthiolation of arenecarboxylate salts has been realized using DMSO as the methylthiolation source. Various potassium aryl carboxylates underwent decarboxylative methylthiolation under air to furnish the corresponding aryl methyl thioethers in moderate to excellent yields. The reaction tolerated a wide variety of functional groups. Notably, the synthesis of ethylthioethers was also successfully achieved directly from diethyl sulfoxide under similar reaction conditions.

Aryl methyl thioethers are important structural constituents that are present in many biological and pharmaceutical molecules.[1] In addition, they are versatile intermediates that can be converted into sulfoxides, sulfones (Scheme 1),[2] thiols[3] and arenes,[4] and also find applications in C-C coupling[5] and C-N coupling[6] reactions. Apart from the reduction of sulfoxides,[7] typical methods for the synthesis of aryl methyl thioethers involve the reaction of arylthiols with iodomethane or dimethyl carbonate[8] and directed or heteroatom-facilitated lithiation of aromatic C-H bonds and subsequent electrophilic substitution with dimethyl disulfide.[9] Although transition-metal-catalyzed cross-coupling between aryl halides or aryl boronic acids with sulfenylating reagents such as thiols, sulfonyl chlorides or disulfides have been developed,[10] methylthiolation using this strategy was limited. Thus, the development of a straightforward as well as general method for the preparation of aryl methyl sulfides from readily accessible starting materials is much more challenging and remains to be explored. Dimethyl sulfoxide (DMSO), a cheap and commercially available solvent, has been used as a methylthiolation source in organic synthesis.[11] Along this line, Qing disclosed a CuF_2-$K_2S_2O_8$ mediated methylthiolation of 2-phenylpyridine via pyridine directed C-H activation in 2010 (Eq. 1).[11a] Later in 2011, Cheng developed methylthiolation of aryl halides by using DMSO as the MeS source in the presence of $CuBr/ZnF_2$ and it is interesting to see that the presence of fluoride as a promoter was essential for the process.[11b] Subsequently, Gao described that heteroarenes can directly react with DMSO to construct heteroaryl methyl thioethers by using AgF as catalyst and $Cu(OAc)_2$ as oxidant.[11c]



Scheme 1 Aryl methyl sulfides, sulfoxides and sulfones of pharmaceutical and biological relevance.

Recently, decarboxylation of carboxylic acids by loss of carbon dioxide (CO_2) has emerged as a useful tool for carbon-carbon and carbon-heteroatom bond formations,[12] because various benzoic acids are widely available, inexpensive and easy to store and handle. The key process of the coupling is that an aryl organometallic species can be generated in situ from aryl carboxylate salts by extrusion of CO_2. Early works in this area by the groups of Gooßen[13], Myers[14], Su[15] and others[16] have shown that aryl carboxylates can undergo a variety of decarboxylative couplings to generate new C-C and C-X bonds. In these existing cases, Pd/Cu and Pd/Ag are the most common bimetallic catalytic systems employed for decarboxylative coupling reactions.[15b,16c-d,17] Typically, they employ a Cu salt or Ag salt to decarboxylate the benzoic acid and a Pd catalyst to enable the cross-coupling. Despite these advances, there are limited examples of decarboxylative coupling to form C-S bonds.[18] For example, Cai in 2014 reported a Pd-catalyzed decarboxylative coupling of *ortho*-nitrobenzoic acids with DMSO to form aryl methyl thioethers (Eq. 2). However, this protocol required more than a stoichiometric amount of CuI in addition to $PdCl_2$ (10 %)

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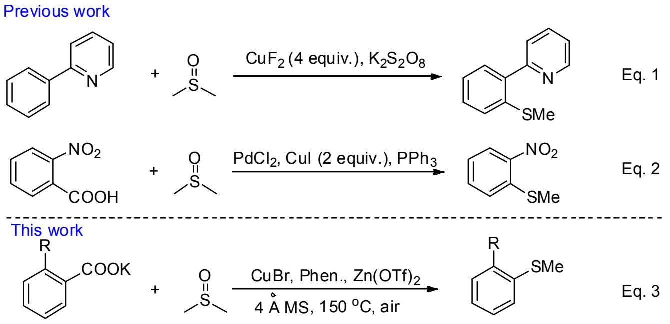
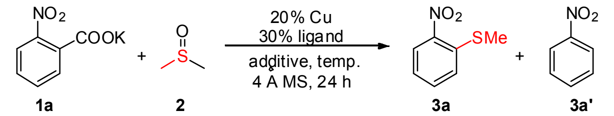
as promoter.[11f] Even though these Pd-catalyzed decarboxylative couplings are quite efficient, the use of an expensive noble metal catalyst such as Pd makes these reactions much less practical. Alternatively, the use of Cu only systems is appealing because copper is considerably cheaper. As a matter of fact, Copper catalyzed or mediated processes for decarboxylation have been gaining more and more attention as evidenced by the recent publications in this area.[16b,16f-j,18c,19] For instance, Gooßen in 2012 developed a decarboxylative etherification of aromatic carboxylic acids by using copper(II) and silver(II) salt as the catalyst.[13c] Later in 2013, they reported a copper-catalyzed *ortho* alkoxylation of aromatic carboxylates with concomitant protodecarboxylation to form arylethers.[13d] In addition to C-O bond formation, copper catalyzed decarboxylative C-N bond formation between aryl carboxylic acids and amines or amides was also demonstrated by Mainolfi using copper(II)-phenanthroline catalyst system.[16f] Very recently, during the preparation of this manuscript, Hoover reported an elegant copper-catalyzed decarboxylative diphenyl thioether synthesis by using thiophenol as the thiolation reagent.[18c] Herein we reported that aryl methyl thioethers can be efficiently synthesized via Cu-catalyzed decarboxylative methylthiolation of aromatic carboxylate salts using DMSO as the methylthiolation source.



Scheme 2 An overview of previous methylthiolation methods vs our approach with DMSO.

Our investigations began during the course of attempting to synthesize Ar-CF_3 via Cu-catalyzed decarboxylative trifluoromethylation between aryl carboxylic acids and Ruppert-Prakash reagent ($TMSCF_3$ as the CF_3 source).[20] Surprisingly, when we treated potassium 2-nitrobenzoate (**1a**) with 2.0 equiv. of $TMSCF_3$ in the presence of 0.2 equiv. of CuBr, 0.3 equiv. of 1, 10-phenanthroline and 4 Å molecular sieves (50 mg/0.3 mmol **1a**) in DMSO under air at 150 °C for 24 h, the methythiolation product **3a** was observed in 46% yield, together with the formation of 52% yield of nitrobenzene **3a'** (Table 1, entry 1). Encouraged by this result, we further investigated other conditions for this reaction. No reaction took place in the absence of additive $TMSCF_3$ showing that an additive is essential for the reaction to proceed (Table 1, entry 2). Replacing $TMSCF_3$ with other additives such as $AgCO_2CF_3$, AgF, $Zn(OAc)_2$ or ZnF_2, gave **3a** either in comparable or lower yields (Table 1, entries 3-6). To our delight, the desired methylthiolation product **3a** was isolated in 85% yield when 2 equiv. of $Zn(OTf)_2$ was added to the reaction mixture (Table 1, entry 7). Examination of other copper salts proved CuBr to be the optimal one while coppers such as Cu_2O, CuI, $Cu(OAc)_2$ and $CuBr_2$ all performed less efficiently (Table 1, entries 8-11). Subsequent evaluation of other ligands such as PPh_3, bpy and *L*-proline afforded **3a** in much lower yields (Table 1, entries 12-14). Running the reaction at temperatures higher or lower than 150 °C actually decreased the yield of **3a** (Table 1, entries 15-16). Furthermore, decreasing the amounts of $Zn(OTf)_2$ to 1 equiv. gave inferior result, providing **3a** in 47% yield (Table 1, entry 17). On the other hand, it was found that the yield of **3a** was decreased to 23% if the reaction was performed under a N_2 atmosphere (Table 1, entry 18). In addition, no reaction took place in the absence of CuBr, implying that the copper catalyst is crucial for this reaction (Table 1, entry 20). It should be mentioned that no desired product **3a** was obtained when 2-nitrobenzoic acid was used in combination with K_2CO_3 or Na_2CO_3 (Table 1, entry 21). Only protodecarboxylation product nitrobenzene **3a'** was observed. Without the molecular sieves, the yield of **3a** also dropped drastically (Table 1, entry 22). Therefore, further substrate screening was carried out using 0.2 equiv. of CuBr, 0.3 equiv. of 1, 10-phenanthroline and 2 equiv. of $Zn(OTf)_2$ in DMSO in the presence of 4 Å molecular sieves at 150 °C under air for 24 h.

Table 1. Screening of the reaction conditions[a]



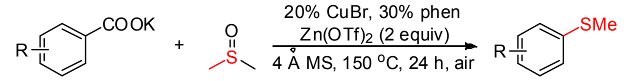
entry	Cu	ligand	additive	temp. (°C)	yield (%) 3a[b]	yield (%) 3a'[b]
1	CuBr	phen	$TMSCF_3$	150	46	52
2[d]	CuBr	phen	-	150	ND	30
3	CuBr	phen	$AgCO_2CF_3$	150	24	63
4	CuBr	phen	AgF	150	<5	86
5	CuBr	phen	$Zn(OAc)_2$	150	35	53
6	CuBr	phen	ZnF_2	150	12	64
7	CuBr	phen	$Zn(OTf)_2$	150	88 (85)[c]	12
8	Cu_2O	phen	$Zn(OTf)_2$	150	35	53
9	CuI	phen	$Zn(OTf)_2$	150	83	13
10	$Cu(OAc)_2$	phen	$Zn(OTf)_2$	150	59	34
11	$CuBr_2$	phen	$Zn(OTf)_2$	150	69	26
12	CuBr	PPh_3	$Zn(OTf)_2$	150	43	52
13	CuBr	bpy	$Zn(OTf)_2$	150	56	42
14	CuBr	L-proline	$Zn(OTf)_2$	150	41	56
15	CuBr	phen	$Zn(OTf)_2$	130	21	34
16	CuBr	phen	$Zn(OTf)_2$	170	71	26
17[e]	CuBr	phen	$Zn(OTf)_2$	150	47	44
18[f]	CuBr	phen	$Zn(OTf)_2$	150	23	70
19[g]	CuBr	-	$Zn(OTf)_2$	150	21	73
20[h]	-	phen	$Zn(OTf)_2$	150	ND	ND
21[i]	CuBr	phen	$Zn(OTf)_2$	150	ND	46
22[j]	CuBr	phen	$Zn(OTf)_2$	150	73	25

[a] *Reaction conditions:* **1a** (0.3 mmol), **2** (2 ml), Cu salt (0.06 mmol), ligand (0.09 mmol), additive (0.6 mmol), 4 Å MS (50 mg), under air for 24 h. [b] GC yield. [c] Isolated yield. [d] No additive was used under the reaction conditions. [e] 1.0 equiv. of $Zn(OTf)_2$ was used. [f] Run at N_2 atmosphere. [g] No ligand was used. [h] No Cu salt was used. [i] 2-nitrobenzoic acid was used instead of **1a**. [j] No 4 Å MS was used.

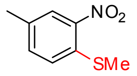
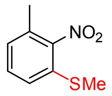
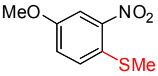
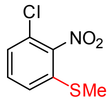
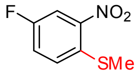
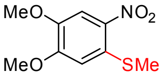
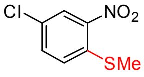
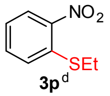
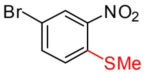
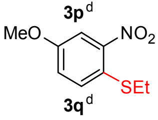
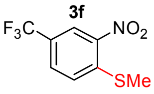
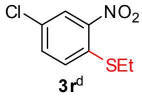
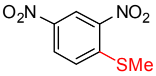
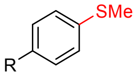
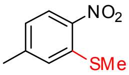
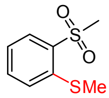
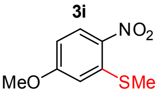
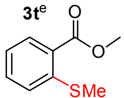
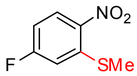
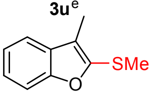
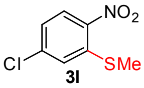
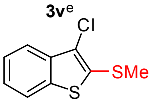
With the optimized conditions in hand, we next set out to explore the scope and limitation of our reaction and the results are summarized in Table 2. As shown in Table 2, a wide range of methylthiolation products could be synthesized via this protocol in yields ranging from 41 to 85%. Functional groups such as methyl, methoxy, fluoro, chloro, bromo, nitro as well as trifluoromethyl groups were well tolerated on the phenyl ring of the aryl carboxylates. Potassium 2-nitrobenzoates bearing substituents at the C4 or C5 positions all furnished the desired products in moderate to good yields (Table 2, entries **3b**-**3l**). From the table, we can see that the reaction slightly favors electron-rich substituents at the C4 position (**3b**-**3c**, 80-81% yields) and electron-withdrawing substituents at the C5 position (**3k**-**3l**, 72-75% yields). On the other hand, potassium 4-nitro-2-nitrobenzoate, which has two strong electron-withdrawing nitro groups on the phenyl ring, only gave the desired decarboxylative coupling product **3h** in 41% yield and the reaction temperature has to be increased to 170 °C (Table 2, entry **3h**). Additionally, C3 substituted substrates could also participate in the methylthiolation, giving the desired products **3m** and **3n** in 61% and 54% yields (Table 2, entries **3m** and **3n**), respectively. The disubstituted potassium 4, 5-dimethoxylbenzoate was also applicable for this transformation, affording the methylthiolative product **3o** in 83% yield (Table 2, entry **3o**). Moreover, ethylthioethers also could be successfully obtained directly using diethyl sulfoxide as the solvent in 60-67% yields (Table 2, entries **3p**-**3r**). Unfortunately, besides potassium *para*-methoxy benzoate, the reaction of potassium benzoate also met with failure when they were subjected to our method, showing that electron density on the phenyl ring is critical for the reaction to be successful (Table 2, entry **3s**). Subsequently, we explored other potassium benzoate derivatives with electron-withdrawing substituents in this reaction. Surprisingly, attempts to use potassium *meta*- and *para*-nitrobenzoate as coupling partners failed under the standard conditions, indicating the position of the electron withdrawing group is important for the reaction to proceed (not shown in Table 2, please see the SI). Pleasingly, the reactions of potassium 2-methylsulfonyl benzoate and potassium 2-(methoxycarbonyl)benzoate delivered the desired product **3t** and **3u** in moderate yields at a slightly elevated temperature (Table 2, entries **3t** and **3u**), whereas potassium 2-trifluoromethylbenzoate, potassium 2-cyanobenzoate, potassium 2-acetyl benzoate as well as potassium 2-fluorobenzoate all failed (not shown in Table 2, please see the SI), suggesting the possibility of replacing the nitro group with other electron-withdrawing groups. Furthermore, potassium heteroarene carboxylates such as benzofuran- and benzothiophene-derived carboxylates were also viable substrates, giving **3v** and **3w** in 54% and 51% yields, respectively (Table 2, entries **3v** and **3w**).

In order to gain some information on the reaction mechanism, a series of control experiments were conducted under the optimized conditions. Because the fact that DMSO can decompose to yield methanethiol and dimethyl disulfide when heated has been reported,[21,11d,11n] we wondered whether our reaction goes through this process or not. When we conducted the reaction of **1a** with 10 equiv of dimethyl disulfide in DMF, the desired methylthioether product could be isolated in 77% yield, indicating that the disulfide may serve as an intermediate in the reaction (Scheme 3, Eq. 4). To further confirm that SMe- indeed migrates from DMSO, we carried out the reaction with DMSO-d_6 as the solvent, and completely deuterated product **3a-d$_3$** was observed by ^{1}H NMR analysis (Scheme 3, Eq. 5). Moreover, when we added MeSSMe into the reaction mixture using DMSO-d_6 as the solvent, both **3a** and **3a-d$_3$** were obtained in a ratio of 2:1. The fact that **3a** was the major product suggested that dimethyl disulfide may serve as an advanced intermediate in our reaction (Scheme 3, Eq. 6). On the other hand, the reaction of **1a** with dimethyl disulfide went smoothly to afford the desired methylthioether product **3a** in good yield in the absence of $Zn(OTf)_2$ (Scheme 3, Eq. 7). In addition, when one equiv. of radical scavenger, TEMPO or BHT, was employed in the reaction mixture, the reaction could be performed without loss of the yield. This result suggested that the reaction may not involve a radical process.

Table 2. Scope of copper-catalyzed decarboxylative methylthiolation of substituted aromatic carboxylate salts[a]



1b-1v **2** **3b-3v**

Product	Yield (%)[b]	Product	Yield (%)[b]
 **3b**	81	 **3m**	61
 **3c**	80	 **3n**	54
 **3d**	78	 **3o**	83
 **3e**	71	 **3p**[d]	67
 **3f**	67	 **3q**[d]	65
 **3g**	73	 **3r**[d]	60
 **3h**[c]	41	 **3s** (R = H, OMe)	ND
 **3i**	71	 **3t**[e]	45
 **3j**	67	 **3u**[e]	67
 **3k**	72	 **3v**[e]	54
 **3l**	75	 **3w**[e]	51

[a] *Reaction conditions*: **1** (0.3 mmol), **2** (2 ml), CuBr (0.06 mmol), phen (0.09 mmol), $Zn(OTf)_2$ (0.6 mmol), 4 Å MS (50 mg), under air for 24 h. [b] Isolated yield. [c] Run at 170 °C for 48 h. [d] Diethyl sulfoxide (2 ml) was used instead of DMSO. [e] Run at 170 °C for 36 h.

A gram-scale reaction was carried out to demonstrate the scalability of this reaction. Employing potassium 2-nitrobenzoate as substrate, the desired the methythiolation product was obtained in 86% yield under the standard conditions (Scheme 4).

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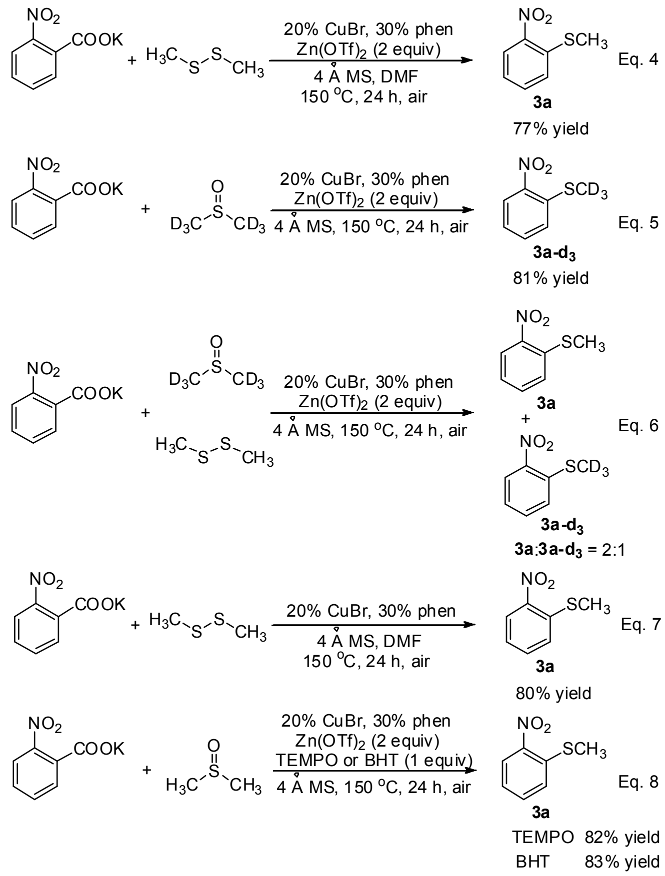
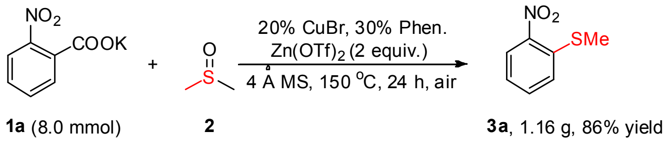
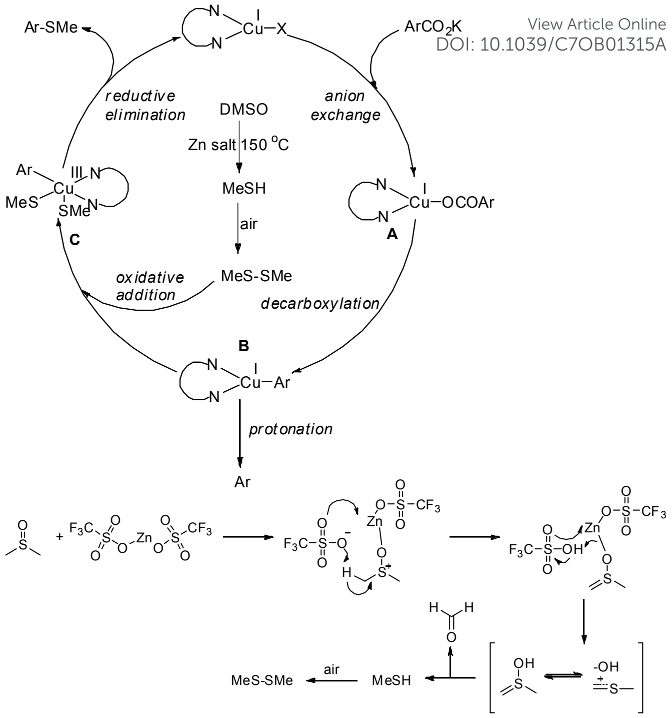


Scheme 3 Control Experiments.



Scheme 4 Gram-scale reaction.

Based on the reported literatures[21,11d,11n] and the evidence above, a plausible mechanism for the copper catalyzed methylthiolation of aromatic carboxylate salts with DMSO is proposed and depicted in Scheme 5. First, a Cu(I) benzoate species **A** is formed from the catalyst and benzoate by anion exchange, which subsequently undergoes decarboxylation to form the aryl-Cu(I) species **B**. Next **B** will react with dimethyl disulfide which itself is generated in situ from DMSO to afford the copper complex **C** via oxidative addition. Finally reductive elimination of the Cu(III)-complex **C** furnishes the desired product **3** and Cu(I) enters back into the catalytic cycle. It has been reported that the addition of Zn salt can facilitate the formation of MeSSMe from DMSO under air (Scheme 5, bottom half).[11d]



Scheme 5 Plausible Mechanism.

In summary, we have demonstrated a novel synthesis of aryl methyl thioethers via copper-catalyzed decarboxylative methylthiolation of arenecarboxylate salts using DMSO as the methylthiolation source. Simple copper salt CuBr was used as the catalyst and 1, 10-phenanthroline was utilized as ligand. In order to achieve good yields, it was found that the reaction was critically dependent on the addition of two equiv. of $Zn(OTf)_2$ as additive and the reaction is run under air. The reaction tolerated a wide variety of functional groups and various aryl methyl thioethers were efficiently synthesized in 41-85% yield. Furthermore, the synthesis of ethylthioethers was also successfully achieved directly from diethyl sulfoxide under the reaction conditions. Further studies on the clarification of the reaction mechanism and applications to other substrates are underway and the results will be reported in due course.

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A novel copper-catalyzed decarboxylative methylthiolation of arenecarboxylate salts has been realized using DMSO as the methylthiolation source.