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Copper-Catalyzed Thioetherification Reactions of Alkyl Halides, Triphenyltin Chloride, and Arylboronic Acids with Nitroarenes in the Presence of Sulfur Sources

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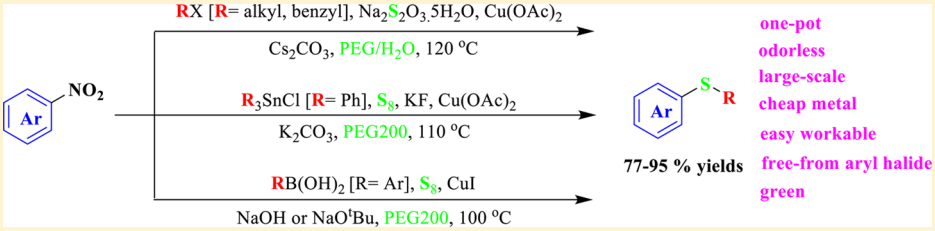
Supporting Information



ABSTRACT: In this article, we report three odorless methods for the thioarylation and thioalkylation of different nitroarenes using alkyl halides (Br, Cl), triphenyltin chloride, and arylboronic acids as the coupling partners. Triphenyltin chloride is capable of delivering all of its phenyl groups to the product. Depending on the reaction, sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$), S_8/KF, and S_8/NaOH systems are found to be effective sources of sulfur in the presence of copper salts. The use of green solvents, inexpensive catalysts, and user-friendly starting materials has made these methods interesting from a green chemistry standpoint.

INTRODUCTION

Sulfides and their derivatives are valuable intermediates in synthetic organic chemistry due to their biological and pharmacological activities.[1−5] Therefore, the search for new methodologies for the synthesis of symmetrical and unsymmetrical sulfides is very important in organic chemistry.[6] The main synthetic method for the preparation of these materials involves the cross-coupling of organic (pseudo)halides with organosulfur nucleophiles in the presence of a suitable catalyst (Scheme 1, path A).[7−12] Transition metals such as palladium,[7] nickel,[8] cobalt,[9] copper,[10] indium,[11] and iron[12] are usually required to drive the reaction forward under mild conditions. Another strategy involves the use of disulfides as the organosulfur sources in the presence of transition-metal complexes of rhodium,[13a,b] copper,[13c,d] and nickel[13e] as the catalysts or under metal-free conditions[13f] (Scheme 1, path B). Arylboronic acids have also been reported to be active as one of the coupling partners in the synthesis of thioethers via cleavage of their C−B bonds catalyzed by copper salts (Scheme 1, path C).[14] The coupling reaction of thiophenol derivatives with nitroarenes in the presence of copper salts is another strategy for the S-arylation of thiophenols (Scheme 1, path D).[15] However, the major drawback of the aforementioned methodologies include the utilization of environmentally unfavorable thiols that can lead to deactivation of the transition-metal catalysts.[16] To overcome this problem, sulfonyl hydrazide have been employed as a thiophenol source, giving the desired unsymmetrical sulfide in good to high yields (Scheme 1, path E).[17] The in situ generation of thiol or thiolate is another interesting modification of this valuable reaction (Scheme 1, paths F−H). Toward this aim, different sulfur sources have been employed such as thiourea,[18] potasium thioacetate,[19] metal sulfides,[20] ethyl xanthogenate,[21] thiocyanate,[22] carbon disulfide,[23] S_8,[24] and $Na_2S_2O_3 \cdot 5H_2O$.[25] Among these, S_8 and $Na_2S_2O_3$ show particular and permissible sources of sulfur for S-arylation due to their low cost and the fact that they are odorless and environmentally benign. However, these procedures still suffer from one or more disadvantages, such as the need for N or P ligands,[19−22,25] elevated reaction temperatures, and/or long reaction times,[20] using toxic, harmful, and volatile organic solvents[20−23] or foul-smelling sulfur sources.[20] Some of these systems are also limited to the synthesis of symmetrical diaryls.[18b,21−24] In addition, there are some other disadvantages associated with the use of aryl halides as the coupling partners, which are generally environmental pollutants. Therefore, there is still great interest in finding new methods and alternative coupling partners for the preparation of unsymmetrical thioethers.

Recently, nitroarenes have been used as a new coupling partner for the S-arylation of thiophenols[15] and sulfinates[26a] and also the synthesis of diaryl ethers via reactions with arylboronic acids.[26b,c] Very recently, we have reported a novel method for one-pot, odorless C−S−C bond formation using arylboronic acid, sulfur powder, and aryl/alkyl halides (Scheme 2a).[27] In

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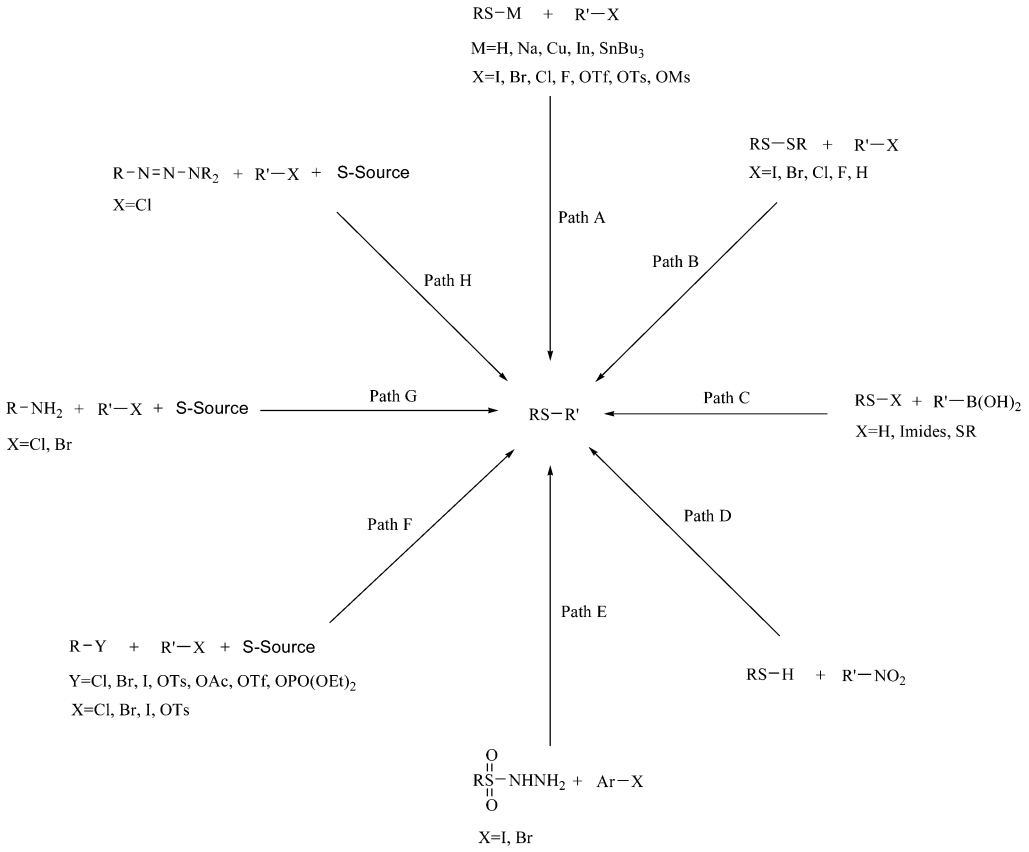
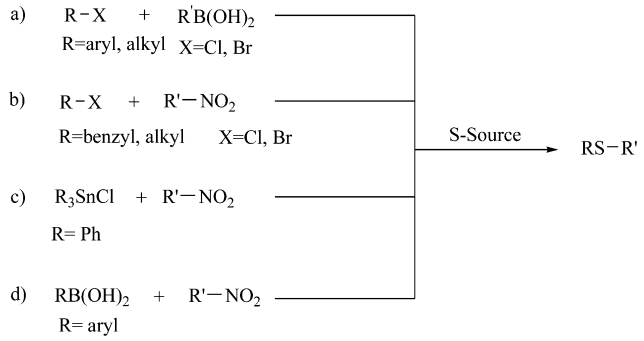
Scheme 1. Different Strategies for the Synthesis of Unsymmetrical Sulfides



Scheme 2. Our (a) Previous and (b−d) Present Strategies toward Unsymmetrical Sulfides



order to expand this method, we became interested in studying the possibility of thioetherification of nitroarenes via processes free from the foul smell of thiols (Scheme 2b−d). To the best of our knowledge, the utilization of nonthiolic procedures for one-pot thioetherification of nitroarenes with alkyl halides, triphenyltin chloride, or arylboronic acids has not been reported.

RESULTS AND DISCUSSION

Initially, the reaction of nitrobenzene with benzyl bromide was investigated in the presence of $Cu(OAc)_2$ as a catalyst. Employing $Na_2S_2O_3·5H_2O$ as a sulfur source and K_2CO_3 as a base in the mixture of PEG200 and water at 100 °C did not result in the desired product, leaving the starting materials intact (Table 1, entry 1). When the reaction temperature was increased to 110 and 120 °C, the desired product was obtained in 58 and 85% yields, respectively (Table 1, entries 2 and 3). Switching the base to Cs_2CO_3 gave the complete conversion of nitrobenzene to the desired product (Table 1, entry 4). Employing Et_3N as an organic base afforded the desired product in only 45% yield as detected by GC (Table 1, entry 5). PEG200 and H_2O were tested as the sole solvents for the reaction, and the desired product was obtained in 77 and 46% yields, respectively (Table 1, entries 6 and 7). DMF/H_2O and dioxane/H_2O mixtures were also tested in this reaction, giving the product in good yields (Table 1, entries 8 and 9). When the amount of $Cu(OAc)_2$ was reduced to 15 mol %, the GC yield dropped to 79% (Table 1, entry 10). CuI and $CuCl_2$ were also effective catalysts for the reaction (Table 1, entries 11 and 12). Other sulfur sources such as the S_8/KF system and thiourea were tested, giving the desired product in low yields (Table 1, entries 13 and 14). Utilizing benzyl mercaptan as a coupling partner (instead of the benzyl bromide/$Na_2S_2O_3·5H_2O$ system) in the reaction gave 65% conversion of nitrobenzene (Table 1, entry 15). The amounts of $Na_2S_2O_3·5H_2O$ and Cs_2CO_3 were also optimized (Table 1, entries 16 and 17). The reaction failed in the absence of a catalyst (Table 1, entry 18).

Under the optimized conditions (Table 1, entry 4), we studied the coupling reaction of various nitroarenes with different alkyl bromides (Table 2). Nitrobenzene reacted with benzyl bromide and benzyl chloride to give the thioether product in excellent yields within 24 and 27 h, respectively (Table 2, entries 1and 2). *n*-Propyl bromide and *n*-hexyl bromide were also active substrates under the reaction conditions, giving high yields of the desired products (Table 2, entries 3 and 4). Nitroarene derivatives, bearing methoxy or methyl as the electron-donating groups, gave the corresponding thioethers in high yields (Table 2, entries 5−10). The reaction of *p*-methoxynitrobenzene with

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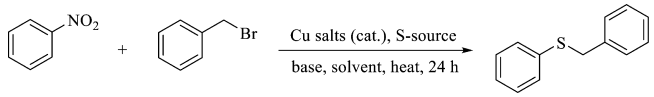
Table 1. Optimization of the Reaction Conditions with Respect to the Effect of Catalysts, Solvent, Base, and Temperature on the Reaction of Nitrobenzene with Benzyl Bromide[a]



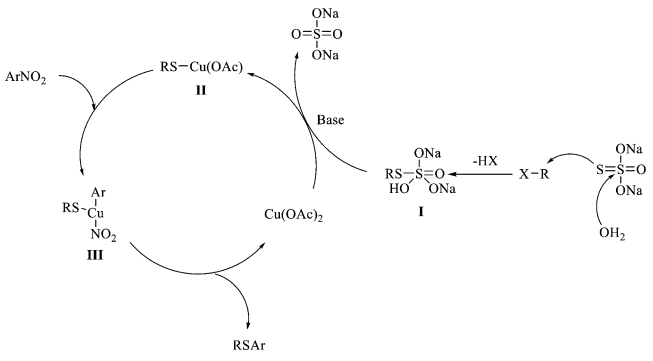
entry	Cu salt	S source	base	solvent	temp (°C)	GC yield (%)
1	$Cu(OAc)_2$	$Na_2S_2O_3{\cdot}5H_2O$	K_2CO_3	PEG200/H_2O	100	
2	$Cu(OAc)_2$	$Na_2S_2O_3{\cdot}5H_2O$	K_2CO_3	PEG200/H_2O	110	58
3	$Cu(OAc)_2$	$Na_2S_2O_3{\cdot}5H_2O$	K_2CO_3	PEG200/H_2O	120	85
4	**$Cu(OAc)_2$**	$Na_2S_2O_3{\cdot}5H_2O$	**Cs_2CO_3**	**PEG200/H_2O**	**120**	**100**
5	$Cu(OAc)_2$	$Na_2S_2O_3{\cdot}5H_2O$	Et_3N	PEG200/H_2O	120	45
6	$Cu(OAc)_2$	$Na_2S_2O_3{\cdot}5H_2O$	Cs_2CO_3	PEG200	120	77
7	$Cu(OAc)_2$	$Na_2S_2O_3{\cdot}5H_2O$	Cs_2CO_3	H_2O	120	46
8	$Cu(OAc)_2$	$Na_2S_2O_3{\cdot}5H_2O$	Cs_2CO_3	DMF/H_2O	120	96
9	$Cu(OAc)_2$	$Na_2S_2O_3{\cdot}5H_2O$	Cs_2CO_3	dioxane/H_2O	120	87
10[b]	$Cu(OAc)_2$	$Na_2S_2O_3{\cdot}5H_2O$	Cs_2CO_3	PEG200/H_2O	120	79
11	CuI	$Na_2S_2O_3{\cdot}5H_2O$	Cs_2CO_3	PEG200/H_2O	120	94
12	$CuCl_2$	$Na_2S_2O_3{\cdot}5H_2O$	Cs_2CO_3	PEG200/H_2O	120	96
13	$Cu(OAc)_2$	S_8/KF	Cs_2CO_3	PEG200	120	21
14	$Cu(OAc)_2$	thiourea	Cs_2CO_3	PEG200	120	56
15[c]	$Cu(OAc)_2$	BnSH	Cs_2CO_3	PEG200	120	65
16[d]	$Cu(OAc)_2$	$Na_2S_2O_3{\cdot}5H_2O$	Cs_2CO_3	PEG200/H_2O	120	86
17[e]	$Cu(OAc)_2$	$Na_2S_2O_3{\cdot}5H_2O$	Cs_2CO_3	PEG200/H_2O	120	72
18		$Na_2S_2O_3{\cdot}5H_2O$	Cs_2CO_3	PEG200/H_2O	120	

[a]Reaction conditions unless stated otherwise: nitrobenzene (1 mmol), benzyl bromide (1.2 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (1.5 mmol), Cu salt (30 mol %), base (3 mmol), and solvent (2 mL). [b]$Cu(OAc)_2$ (15 mol %) was used. [c]No BnBr (reaction time 30 h). [d]$Na_2S_2O_3{\cdot}5H_2O$ (1 mmol) was used. [e]Cs_2CO_3 (1.5 mmol) was used.

cyclohexyl bromide as the secondary alkyl bromide resulted in a 91% yield within a reaction time of 34 h (Table 2, entry 8). It is also observed that the presence of electron-withdrawing groups such as cyano and carbonyl in the nitroarenes increased the reaction rate, regardless of their positions (Table 2, entries 11−17). The reaction of 2-nitropyridine as a heteroaromatic compound with benzyl bromide and benzyl chloride gave the products in excellent yields (Table 2, entries 18 and 19).

The proposed mechanism for the reaction has been depicted in Scheme 3. $Na_2S_2O_3$ reacts with alkyl halide to generate alkyl thiosulfate **I**.[25c] The generated alkyl thiosulfate then reacts with copper acetate to produce intermediate **II**, which adds to nitroarenes, oxidatively producing intermediate **III** via C−N bond cleavage.[15] The desired product is released after reductive elimination, completing the catalytic cycle.

Scheme 3. Proposed Mechanism for the Synthesis of Alkyl/Benzyl Aryl Sulfides through Cross-Coupling Reactions of Nitroarenes with Alkyl/Benzyl Halides using $Na_2S_2O_3{\cdot}5H_2O$ Catalyzed by $Cu(OAc)_2$



Quite recently, Iranpoor and co-workers have developed an efficient method for C−X (X = C, N, S, O) bond formation using triphenyltin chloride as a source of phenyl group.[28] These investigations prompted us to explore the prospects of this novel phenyl group source for other demanding reactions. Encouraged by the above results, $Na_2S_2O_3{\cdot}5H_2O$ was chosen as a sulfur source for the reaction of *p*-methoxynitrobenzene with triphenyltin chloride. Under these conditions, the reaction failed (Table 3, entry 1). Further optimization studies were performed upon this reaction in the presence of the S_8/KF system as a source of sulfur and $Cu(OAc)_2$ as a catalyst. As shown in Table 3, the nature of the base was important, affecting the yield of the desired product (Table 3, entries 2−5). Among the organic and inorganic bases, K_2CO_3 was found to be the most effective base for this reaction (Table 3, entry 5). It was also observed that, using Et_3N as a base in the reaction, diphenyl disulfide was found as only product in PEG200 (Table 3, entry 4). In order to study the effect of the solvents, we have conducted the reaction in PEG200, DMF, dioxane, and CH_3CN (Table 3, entries 5−8). Among the solvents, the most effective were found to be PEG200 and DMF (Table 3, entries 5 and 6). Apart from $Cu(OAc)_2$, CuI and $CuCl_2$ were also active catalysts for the reaction, giving the corresponding phenyl aryl sulfides in high yields (Table 3, entries 9 and 10). In the absence of KF, no product was detected by GC (Table 3, entry 17). Using NaOH instead of KF as a S_8 activator gave a mixture of phenyl aryl sulfide and diphenyl disulfide (Table 3, entry 18). Only 25% of diphenyl sulfide was obtained when triphenyltin chloride was replaced with diphenyl disulfide (Table 3, entry 19).

With optimal conditions in hand (Table 3, entry 4), the generality and the applicability of this method was further examined for the synthesis of phenyl aryl sulfide from the reactions of triphenyltin chloride with structurally diverse nitroarenes. As shown in Table 4, the expected products were

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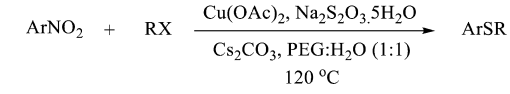
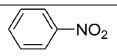
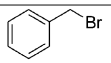
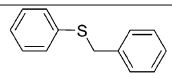
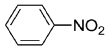
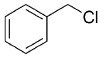
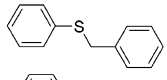
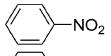
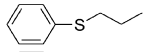
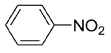
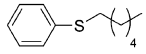
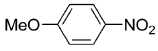
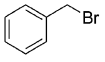
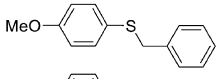
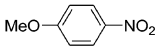
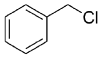
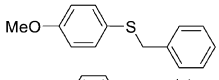
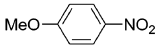
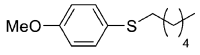
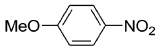
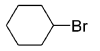
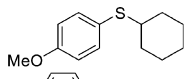
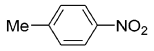
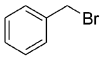
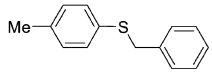
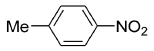
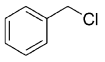
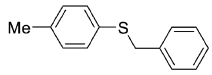
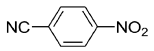
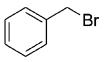
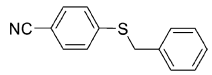
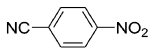
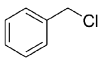
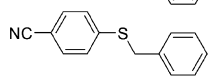
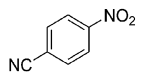
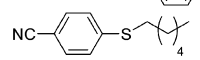
Table 2. Thioetherification of Different Nitroarenes using $Na_2S_2O_3·5H_2O$ and Alkyl/Benzyl Halide Catalyzed by $Cu(OAc)_2$ in PEG/H_2O[a]



Entry	$ArNO_2$	RX	Product	Time (h)	Yield (%)
1				24	96
2				27	92
3[b]				37	89
4				30	95
5				34	86
6				36	87
7				38	89
8				34	91
9				30	81
10				33	84
11				16	81
12				17	84
13				23	88
14				21	88
15				23	79
16				18	84
17				20	82
18				18	89
19				20	90

[a]General procedure: $ArNO_2$ (1 mmol), $Cu(OAc)_2$ (30 mol %), RBr (1.2 mmol), $Na_2S_2O_3·5H_2O$ (1.5 mmol), Cs_2CO_3 (3 mmol), PEG200/H_2O (2 mL). [b]The reaction was carried out in a sealed tube.

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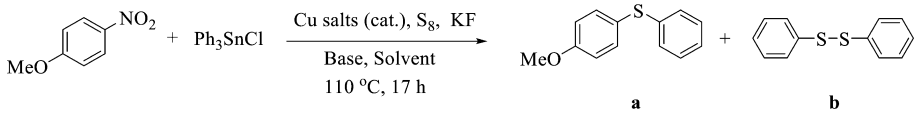
Table 3. Optimization of the Reaction Conditions for the Coupling Reaction of *p*-Methoxynitrobenzene with Triphenyltin Chloride[a]



a b

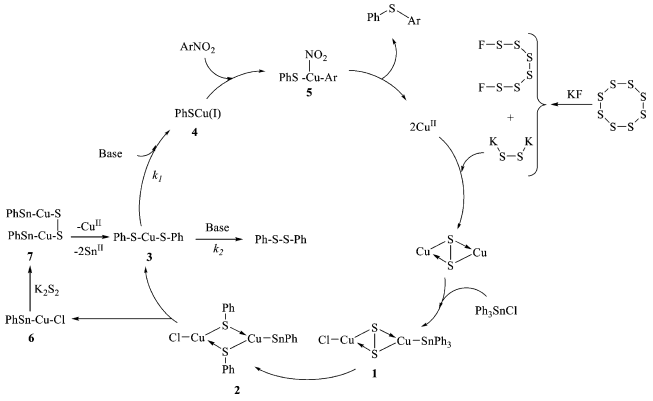
				GC yield (%)	
entry	Cu salt	base	solvent	a	b
1[b]	$Cu(OAc)_2$	K_2CO_3	PEG200		
2	$Cu(OAc)_2$	Cs_2CO_3	PEG200	77	23
3	$Cu(OAc)_2$	NaOH	PEG200	42	55
4	$Cu(OAc)_2$	Et_3N	PEG200		100
5	**$Cu(OAc)_2$**	**K_2CO_3**	**PEG200**	**100**	
6	**$Cu(OAc)_2$**	**K_2CO_3**	**DMF**	**100**	
7	$Cu(OAc)_2$	K_2CO_3	dioxane	68	
8	$Cu(OAc)_2$	K_2CO_3	CH_3CN	67	
9	CuI	K_2CO_3	PEG200	71	
10	$CuCl_2$	K_2CO_3	PEG200	77	
11[c]	$Cu(OAc)_2$	K_2CO_3	PEG200	73	
12[d]	$Cu(OAc)_2$	K_2CO_3	PEG200	73	
13[e]	$Cu(OAc)_2$	K_2CO_3	PEG200	37	
14[f]	$Cu(OAc)_2$	K_2CO_3	PEG200	100	
15[g]	$Cu(OAc)_2$	K_2CO_3	PEG200	89	
16[h]	$Cu(OAc)_2$	K_2CO_3	PEG200	72	
17[i]	$Cu(OAc)_2$	K_2CO_3	PEG200		
18[i]	$Cu(OAc)_2$	NaOH	PEG200	60	21
19[j]	$Cu(OAc)_2$	K_2CO_3	PEG200	25	75

[a]Reaction conditions unless stated otherwise: *p*-methoxynitrobenzene (1 mmol), triphenyltin chloride (0.35 mmol), sulfur (1.5 mmol), Cu salt (25 mol %), KF (3 mmol), base (4 mmol), and solvent (3 mL). [b]The reaction was performed in the presence of $Na_2S_2O_3{\cdot}5H_2O$. [c]$Cu(OAc)_2$ (20 mol %) was employed. [d]KF (2.5 mmol) was used. [e]KF (2 mmol) was used. [f]The reaction was carried out at 120 °C. [g]The reaction was performed at 100 °C. [h]Sulfur (1 mmol) was employed. [i]Without KF. [j]The reaction was performed using diphenyl disulfide instead of Ph_3SnCl for 48 h.

obtained in moderate to high yields. It was shown that nitroarenes with electron-withdrawing groups reacted more quickly than the nitroarenes with electron-releasing groups (Table 4, entries 2–6). Interestingly, *o*-nitrobenzaldehyde as a model for the hindered nitroarenes was also converted to the desired product in good yield (Table 4, entry 6). To investigate the feasibility of applying this method on a preparative scale, the synthesis of phenyl *p*-cyanophenyl sulfide was carried out on a 10 mmol scale of starting materials. The reaction proceeded similarly to the standard laboratory scale (Table 4, entry 4). We also applied this method to the reaction of 2-nitropyridine with triphenyltin chloride, giving 86% yield within 6 h (Table 4, entry 7).

A possible mechanism which agrees with the literature has been given in Scheme 4.[24g,28] K_2S_2 is produced from the reaction of S_8 with KF. Potassium disulfide then reacts with $Cu(OAc)_2$ to generate copper sulfide, which reacts with triphenyltin chloride by oxidative addition to form intermediate **1**. Intermediate **1** transforms into intermediate **2** via phenyl group immigration. The dissociation of the intermediate **2** occurs to form the two intermediates **3** and **6**. We believe that the employed base plays a key role at this stage, determining the reaction pathway by kinetic control. In the presence of K_2CO_3 and nitroarene, transformation of intermediate **3** to intermediate **4** is much quicker than production of disulfide ($k_1 \gg k_2$). Nitroarene reacts with intermediate **4** by oxidative addition to form **5**,[15] which undergoes reductive elimination to afford the desired phenyl aryl sulfide, releasing Cu(II). We observed that, in the absence of nitroarenes, triphenyltin chloride produces diphenyl disulfide in quantitative yield under similar reaction conditions within 24 h.

Scheme 4. Proposed Pathway for the Synthesis of Phenyl Aryl Sulfide via C–S Bond Formation Reaction of Triphenyltin Chloride with Nitroarenes using S_8 in the Presence of $Cu(OAc)_2$ as a Catalyst



This shows that, in the absence of nitroarenes, intermediate **4** reverts back to intermediate **3**, from which diphenyl disulfide results. The intermediate **6** reacts with potassium sulfide to give intermediate **7**, which is capable of transferring to intermediate **3**. When Et_3N was used instead of K_2CO_3, intermediate **3** yields diphenyl disulfide exclusively ($k_2 \gg k_1$) even in the presence of nitroarenes, showing the influence of the base upon intermediate **3** (Table 3, entry 3).

In another effort, we studied the reaction of arylboronic acids with nitroarenes to produce unsymmetrical diaryl sulfides. To optimize the reaction conditions, phenylboronic acid and

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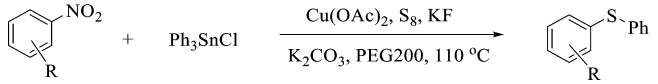
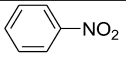
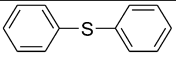
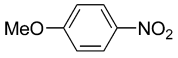
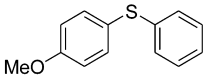
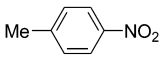
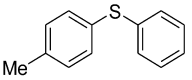
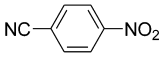
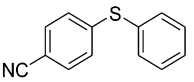
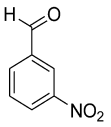
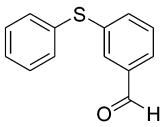
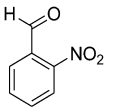
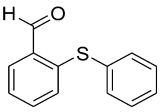
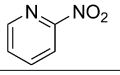
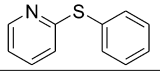
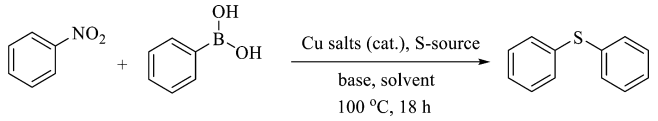
Table 4. Synthesis of Diaryl Sulfides from the Reaction of Nitroarenes with Triphenyltin Chloride Using S_8 Catalyzed by $Cu(OAc)_2$ in PEG200[a]



Entry	$ArNO_2$	Product	Time (h)	Yield (%)
1			11	89
2			17	90
3			15	90
4			7	87 (85)
5			9	95
6			8	80
7			6	86

[a]Standard conditions: nitroarene (1 mmol), triphenyltin chloride (0.35 mmol), sulfur (1.5 mmol), $Cu(OAc)_2$ (25 mol %), KF (3 mmol), K_2CO_3 (4 mmol), and PEG200 (3 mL). A large-scale yield in the last column is shown in parentheses. Conditions: 4-nitrobenzonitrile (10 mmol), $Cu(OAc)_2$ (25 mol %), triphenyltin chloride (3.5 mmol), sulfur (15 mmol), KF (30 mmol), PEG200 (30 mL), and K_2CO_3 (40 mmol)

Table 5. Optimization of the Reaction Conditions for the Reaction of Nitrobenzene with Phenylboronic Acid[a]



entry	Cu salt	S source	base	solvent	GC yield (%)
1	$Cu(OAc)_2$	S_8	K_2CO_3	PEG200	
2	$Cu(OAc)_2$	S_8/KF	K_2CO_3	PEG200	
3	$Cu(OAc)_2$	S_8	Cs_2CO_3	PEG200	8
4	$Cu(OAc)_2$	S_8	NaOH	PEG200	76
5	**CuI**	**S_8**	**NaOH**	**PEG200**	**100**
6[b]	**CuI**	**S_8**	**NaO^{t}Bu**	**PEG200**	**100**
7	CuI	S_8	Et_3N	PEG200	
8	CuI	S_8	DABCO	PEG200	
9[c]	CuI	S_8	NaOH	PEG200	72
10	CuI	S_8	NaOH	DMF	100
11	CuI	S_8		^{n}Bu$_4$NOH (20%)	77
12	CuI	S_8	NaOH	^{n}Bu$_4$NOH (20%)	76
13[d]	CuI	S_8	NaOH	^{n}Bu$_4$NOH (20%)	61
14	CuI	S_8	NaOH	CH_3CN	44
15	CuI	S_8	NaOH	dioxane	51
16	CuI	Na_2S	NaOH	PEG200	78
17	CuI	thiourea	NaOH	PEG200	
18	CuI	$Na_2S_2O_3{\cdot}5H_2O$	NaOH	PEG200	

[a]Reaction conditions unless stated otherwise: nitrobenzene (1 mmol), phenylboronic acid (1.1 mmol), sulfur (1.5 mmol), Cu salt (25 mol %), base (4 mmol) and solvent (2 mL). [b]Reaction time: 20 h. [c]NaOH (3 mmol) was used. [d]The reaction was performed at 120 °C for 24 h.

nitrobenzene were employed as starting materials (Table 5). Inspired by the successful results above, we first conducted the reaction in the presence of $Cu(OAc)_2$, S_8, and K_2CO_3 in PEG200 at 100 °C (Table 5, entry 1). Under these conditions, the reaction failed to produce the desired product. Addition of KF to this mixture was not effective (Table 5, entry 2). Very low

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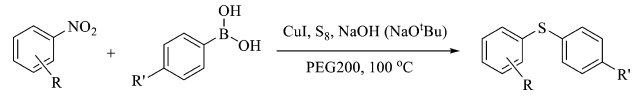
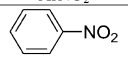
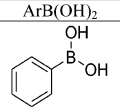
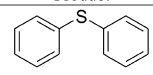
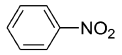
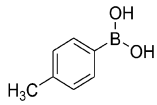
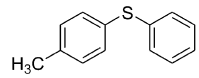
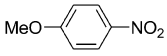
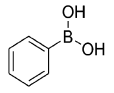
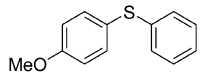
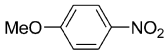
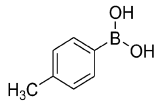
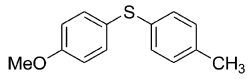
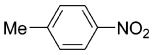
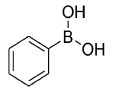
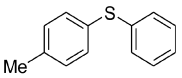
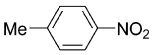
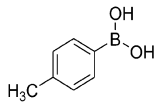
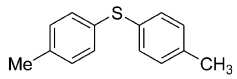
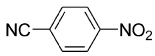
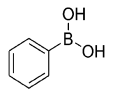
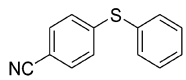
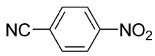
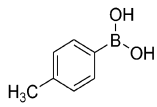
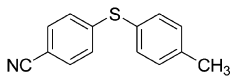
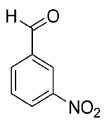
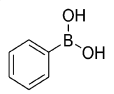
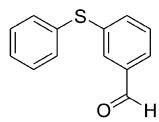
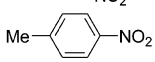
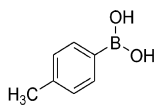
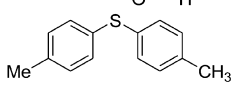
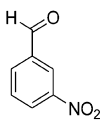
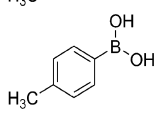
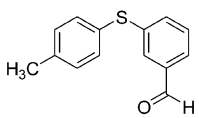
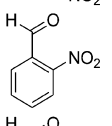
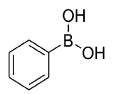
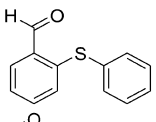
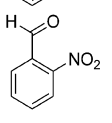
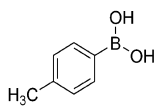
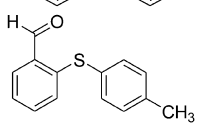
Table 6. C−S Bond Formation of Nitroarenes with Arylboronic Acid for the Synthesis of Unsymmetrical Sulfides using S_8 Catalyzed by CuI[a]



Entry	$ArNO_2$	$ArB(OH)_2$	Product	Time(h)	Yield (%)[b]
1				18	84
2				24	80
3				28	75
4				36	80
5				24	77
6				31	76
7				9	90
8				11	89
9[c]				12	85
6				31	76
10[c]				14	81
11[c]				11	79
12[c]				13	78
13[c]				9	85
14[c]				11	90

[a]Conditions: nitroarene (1 mmol), arylboronic acid (1.1 mmol), CuI (25 mol %), sulfur (1.5 mmol), NaOH (4 mmol), PEG200 (2 mL), 110 °C. [b]Yield after column chromatographic separation. [c]The reaction was carried out in the presence of NaO^{t}Bu as base.

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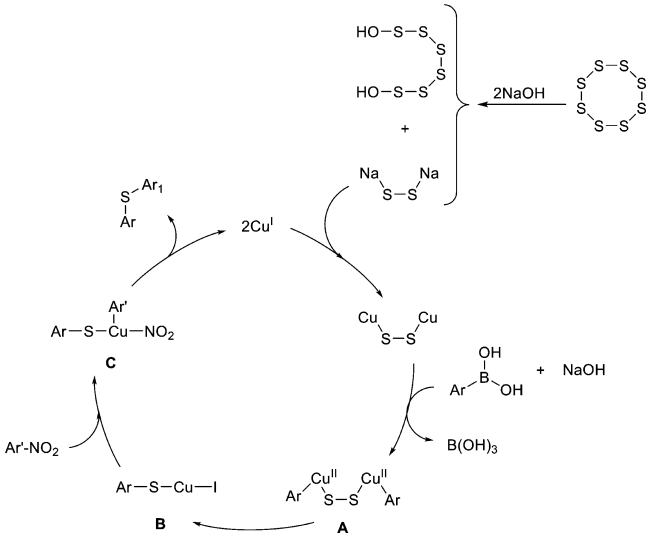
conversion of nitrobenzene was observed by changing the base to Cs_2CO_3 (Table 5, entry 3). Using NaOH as a base in this reaction resulted in a drastic enhancement in the yield of the desired product (Table 5, entry 5). PEG200 and DMF were found to be effective solvents for this reaction (Table 5, entries 5 and 10). Changing the catalyst to CuI had a good effect on the efficiency of the reaction (Table 5, entries 5 and 6). NaO^{t}Bu was also a suitable base for this reaction (Table 5, entry 6). While organic bases such as Et_3N and DABCO were not effective (Table 5, entries 7 and 8), a 20% aqueous solution of ^{n}Bu$_4$NOH showed moderate efficiency (Table 5, entries 11−13). Acetonitrile and dioxane were not suitable solvents (Table 5, entries 14 and 15). Whereas Na_2S was an active sulfur source, giving the desired product in excellent yield, other sources such as thiourea and $Na_2S_2O_3{\cdot}5H_2O$ failed to react (Table 5, entries 16 and 18).

Under the optimized conditions, reactions of various nitroarenes with arylboronic acids were studied to afford a diverse range of unsymmetrical diaryl sulfides (Table 6). The reactions proceeded well, and the corresponding sulfides were obtained in yields of between 75 and 90%. Nitroarenes with electron-donating groups (Table 6, entries 2−6) and electron-withdrawing groups (Table 6, entries 7−12) gave the corresponding thioethers in good yields. Impressively, irrespective of the position of substituents on nitroarenes, excellent yields of aryl sulfides were obtained (Table 6, entries 9−12). Generally, nitroarenes with electron-withdrawing groups showed reactivity much greater than those having electron-donating groups (Table 6, entries 2−12). Likewise, arylboronic acids containing electron-donating groups showed less reactivity (entries 1−12).

In order to gain insight into the reaction, we subjected phenylboronic acid to the standard reaction conditions in the absence of nitroarenes (Table 5, entry 5). After 24 h, 56% diphenyl disulfide was detected by GC. However, in the absence of phenylboronic acid, the reaction of nitrobenzene did not result in any product, showing that the organosulfur nucleophile might result from arylboronic acids rather than nitroarenes. On the basis of these observations and also our previously reported results,[28] a plausible reaction pathway for the reaction of arylboronic acid with nitroarenes in the presence of S_8 is presented in Scheme 5. It is hypothesized that S_8 reacts with NaOH or NaO^{t}Bu to produce sodium disulfide.[24g] The stable copper disulfide is formed from the reaction of sodium disulfide with CuI. Copper disulfide reacts with the arylboronic acid via an oxidative-addition reaction to give intermediate **A**, which converts to intermediate **B**. The intermediate **B** reacts with nitroarenes via C−N bond cleavage to provide the key intermediate **C**. The desired product may result from reductive elimination of the key intermediate **C**.

Scheme 5. Proposed Mechanism for the Synthesis of Diaryl Sulfide by the Reaction of Nitroarenes and Arylboronic Acid using S_8 in the Presence of CuI



prepare structurally diverse alkyl/benzyl aryl sulfides and diaryl sulfides.

EXPERIMENTAL SECTION

General Remarks. All of the reactions were carried out in screw-capped tubes. All materials were obtained from commercial sources and used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded on 400 MHz ^{1}H (100MHz ^{13}C) or 250 MHz ^{1}H (62 MHz ^{13}C) spectrometers at ambient temperature with $CDCl_3$ as a solvent.

General Procedure for the Synthesis of Alkyl Aryl Sulfides using Alkyl/Benzyl Halides and Nitroarenes. A one-necked flask was charged with $Cu(OAc)_2$ (50 mg, 0.3 mmol), cesium carbonate (978 mg, 3 mmol), $Na_2S_2O_3{\cdot}5H_2O$ (373 mg, 1.5 mmol), alkyl/benzyl halide (1.2 mmol), nitroarene (1 mmol), and PEG200/H_2O (2 mL, 1/1). The mixture was stirred at 120 °C for the appropriate reaction time (Table 2). The reaction mixture was cooled to room temperature. Water (4 mL) was added to the reaction mixture, and organics were extracted with EtOAc (3 × 5 mL). Evaporation of the solvent followed by purification on silica gel (*n*-hexane/EtOAc) provided the corresponding alkyl/benzyl aryl sulfide in 79−96% yield.

General Procedure for the Synthesis of Phenyl Aryl Sulfides using Triphenyltin Chloride and Nitroarenes. A one-necked flask was charged with $Cu(OAc)_2$ (50 mg, 0.25 mmol), potassium carbonate (552 mg, 4.0 mmol), S_8 (46 mg, 1.5 mmol), KF (180 mg, 3 mmol), nitroarene (1 mmol), triphenyltin chloride (0.35 mmol), and PEG200 (3 mL). The mixture was magnetically stirred and heated at 110 °C for the appropriate reaction time (Table 4). After completion of the reaction, the reaction mixture was cooled to room temperature and H_2O (4 mL) was added. The product was extracted with EtOAc (3 × 4 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification by column chromatography on silica gel (*n*-hexane/EtOAc) gave the desired phenyl aryl sulfides in 80−95% yields.

General Procedure for the Synthesis of Unsymmetrical Diaryl Sulfides using Arylboronic Acids and Nitroarenes. A one-necked flask was charged with CuI (50 mg, 0.25 mmol), sodium hydroxide (160 mg, 4.0 mmol), S_8 (47 mg, 1.5 mmol), nitroarene (1 mmol), arylboronic acid (1.1 mmol), and PEG200 (2 mL). The mixture was magnetically stirred and heated at 100 °C for the appropriate reaction time (Table 6). After completion of the reaction, the reaction mixture was cooled to room temperature. Water (4 mL) was added, and the product was extracted with EtOAc (3 × 4 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification by column chromatography on silica gel (*n*-hexane/EtOAc) gave the desired diaryl sulfides in 75−90% yields.

CONCLUSIONS

In summary, we have developed efficient methodologies for the synthesis of unsymmetrical diaryl sulfides via cross-coupling reactions of triphenyltin chloride or arylboronic acid as thiolating agents with nitroarenes as the effective starting materials using S_8 as a sulfur surrogate and Cu salts as catalysts. Moreover, thioarylation reactions were performed using $Na_2S_2O_3{\cdot}5H_2O$ as a sulfur source in the copper-catalyzed reaction of nitroarenes with alkyl/benzyl halides. Important features of these procedures are as follows: (1) relief from foul-smelling thiols, making the methods easier and more practical; (2) use of commercially available, inexpensive, easy-to-handle and chemically stable sulfur sources, starting materials, and catalysts; (3) the ability to

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Benzyl phenyl sulfide (Table 2, entry 1):[25c] white solid, 192 mg (96% yield); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 4.02 (s, 2 H), 7.12−7.23 (m, 10 H); $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 39.14, 126.55, 127.51, 128.40, 128.83, 129.20, 129.89, 136.91, 137.75.

Butyl phenyl sulfide (Table 2, entry 3):[25f] colorless oil, 107 mg (89% yield); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 0.82 (t, J = 7.5 Hz, 3 H), 1.31−1.37 (m, 2 H), 1.39−1.57 (m, 2 H), 2.87 (t, J = 7.2 Hz, 3 H), 7.01−7.26 (m, 5 H); $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 13.68, 21.99, 31.24, 33.24, 125.62, 128.81, 128.91, 137.08.

Hexyl phenyl sulfide (Table 2, entry 4):[25f] colorless oil, 184 mg (95% yield); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 0.96 (t, J = 7.2 Hz, 3 H), 1.45−1.54 (m, 6 H), 1.69−1.74 (m, 2 H), 3.02 (t, J = 7.2 Hz, 2 H), 7.11−7.35 (m, 5 H); $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 14.02, 22.53, 28.47, 28.59, 31.32, 31.97, 120.85, 123.96, 126.00, 131.23.

Benzyl p-methoxyphenyl sulfide (Table 2, entry 5):[25c] white solid, 198 mg (86% yield); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 3.65 (s, 3 H), 3.93 (s, 2 H), 6.69−6.71 (m, 2 H), 7.09−7.17 (m, 7 H); $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 40.1, 54.2, 113.3, 125.0, 125.9, 127.3, 127.8, 132.9, 137.0, 158.1.

Hexyl p-methoxyphenyl sulfide (Table 2, entry 7):[25f] colorless oil, 199 mg (89% yield); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 0.96 (t, J = 7.2 Hz, 3 H), 1.46−1.60 (m, 6 H), 1.68−1.78 (m, 2 H), 2.89 (t, J = 7.2 Hz, 2 H), 3.79 (s, 3 H), 6.80−6.95 (d, J = 7.5 Hz, 2 H), 7.36−7.45 (d, J = 7.5 Hz, 2 H); $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 14.10, 22.76, 28.48, 31.33, 31.88, 55.26, 114.25, 124.95, 135.58, 159.29.

Cyclohexyl p-methoxyphenyl sulfide (Table 2, entry 8):[25c] white solid, 198 mg (91% yield); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 1.20−1.38 (m, 6 H), 1.74 (m, 2 H), 1.91−1.94 (m, 2 H), 2.85−2.92 (m, 1 H), 3.79 (s, 3 H), 6.83 (d, J = 6.2 Hz, 2 H), 7.38 (d, J = 6.2 Hz, 2 H); $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 26.10, 33.36, 47.88, 55.26, 114.25, 124.95, 135.58, 159.29.

Benzyl p-tolyl sulfide (Table 2, entry 9):[25c] white solid, 173 mg (81% yield); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 2.19 (s, 3 H), 3.94 (s, 2 H), 6.93−7.08 (m, 2 H), 7.10−7.22 (m, 7 H); $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 21.16, 39.79, 127.16, 128.51, 128.92, 129.10, 129.70, 130.71, 132.57, 136.58.

Benzyl p-cyanophenyl sulfide (Table 2, entry 11):[25c] white solid, 198 mg (84% yield); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 4.32 (s, 2 H), 7.11−7.95 (m, 9 H); $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 35.35, 108.44, 118.81, 127.75, 127.98, 128.79, 132.24, 136.70, 142.99.

Hexyl p-cyanophenyl sulfide (Table 2, entry 13):[25f] white solid, 193 mg (88% yield); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 0.97 (t, J = 6.5 Hz, 3 H), 1.45−1.54 (m, 6 H), 1.69−1.74 (m, 2 H), 3.03 (t, J = 6.5 Hz, 2 H), 7.61−7.90 (m, 4 H); $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 14.10, 22.59, 28.32, 28.53, 31.47, 31.90, 109.32, 115.23, 127.97, 130.05, 140.85.

Benzyl m-formylphenyl sulfide (Table 2, entry 14):[6c] yellow oil, 201 mg (88% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 4.18 (s, 2 H), 7.40−7.47 (m, 4 H), 7.78−7.86 (m, 4 H), 8.05 (s, 1 H), 9.99 (s, 1 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 39.46, 123.39, 127.01, 128.40, 128.59, 129.02, 129.77, 130.65, 132.38, 137.33, 138.01, 190.76.

Benzyl o-formylphenyl sulfide (Table 2, entry 16):[6c] brown oil, 191 mg (84% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 4.17 (s, 2 H), 7.22−7.38 (m, 5 H), 7.47−7.55 (m, 3 H), 7.84−7.86 (m, 1 H), 10.29 (s, 1 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 38.84, 126.13, 127.59, 127.94, 128.72, 129.14, 129.78, 131.77, 134.06, 136.21, 141.12, 191.53.

Benzyl 2-pyridyl sulfide (Table 2, entry 18):[17a] yellow oil, 179 mg (89% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 4.50 (s, 2 H), 7.02 (d, J = 4.8 Hz, 1 H), 7.19−7.51 (m, 7 H), 8.51 (d, J = 4.8 Hz, 1 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 34.46, 119.64, 122.12, 127.14, 128.54, 129.02, 136.01, 138.02, 149.44, 158.85.

Diphenyl sulfide (Table 4, entry 1):[23d] colorless liquid, 165 mg (89% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 7.26−7.40 (m, 10 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 127.12, 129.27, 131.11, 135.86.

Phenyl p-methoxyphenyl sulfide (Table 4, entry 2):[20a] yellow oil, 194 mg (90% yield); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 4.25 (s, 3 H), 7.11−7.35 (m, 9 H); $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 55.34, 116.40, 126.81, 127.48, 128.53, 129.47, 137.40, 138.22, 158.29.

Phenyl p-tolyl sulfide (Table 4, entry 3):[23a] yellow oil, 180 mg (90% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 2.30 (s, 3 H), 7.14−7.43 (m, 9 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 21.30, 126.11, 127.10, 127.72, 129.13, 129.49, 131.08, 133.68, 137.06.

Phenyl p-cyanophenyl sulfide (Table 4, entry 4):[7m] colorless oil, 183 mg (87% yield); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 6.95−7.06 (m, 5 H), 7.31−7.91 (m, 4 H); $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 108.68, 118.81, 127.31, 129.42, 129.95, 130.81, 132.38, 132.85, 134.50, 145.72.

Phenyl m-formylphenyl sulfide (Table 4, entry 5):[7m] colorless oil, 203 mg (95% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 7.36−7.63 (m, 6 H), 7.72−7.84 (m, 2 H), 8.04 (s, 1 H), 9.96 (s, 1 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 128.19, 128.4, 129.61, 130.66, 132.37, 133.66, 135.33, 136.17, 137.26, 138.01, 190.76.

Phenyl o-formylphenyl sulfide (Table 4, entry 6):[7m] colorless oil, 171 mg (80% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 7.12−7.14 (m, 1 H), 7.29−7.48 (m, 7 H), 7.90−7.92 (m, 1 H), 10.42 (s, 1 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 126.32, 128.48, 129.75, 130.37, 131.97, 133.21, 133.35, 133.75, 134.11, 141.61, 191.60.

Phenyl 2-pyridyl sulfide (Table 4, entry 7):[17a] colorless oil, 161 mg (88% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 6.86 (d, J = 4.8 Hz, 1 H), 6.94−6.97 (m, 1 H), 7.38−7.40 (m, 4 H), 7.54−7.58 (m, 2 H), 8.40 (d, J = 4.8 Hz, 1 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 119.96, 121.36, 129.14, 129.68, 131.01, 134.94, 136.80, 149.52, 161.46.

p-Methoxyphenyl p-tolyl sulfide (Table 6, entry 4):[15] yellow oil, 184 mg (80% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 2.36 (s, 3 H), 3.85 (s, 3 H), 6.92 (d, J = 8.4 Hz, 2 H), 7.12 (d, J = 7.6 Hz, 2 H), 7.19 (d, J = 8.4 Hz, 2 H), 7.42 (d, J = 7.6 Hz, 2 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 21.06, 55.39, 114.92, 125.65, 129.40, 129.84, 134.43, 136.15, 159.50.

Di-p-tolyl sulfide (Table 6, entry 6):[23d] white solid, 163 mg (76% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 2.25 (s, 6 H), 7.08 (d, J = 8 Hz, 4 H), 7.32 (d, J = 8 Hz, 4 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 21.09, 128.52, 129.81, 131.11, 137.46.

p-Cyanophenyl p-tolyl sulfide (Table 6, entry 8):[15] white solid, 200 mg (89% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 2.44 (s, 3 H), 7.14 (d, J = 8.4 Hz, 2 H), 7.28 (d, J = 8.4 Hz, 2 H) 7.44−7.49, (m, 4 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 21.36, 108.28, 118.96, 126.77, 130.79, 132.31, 133.44, 134.99, 140.00, 146.64.

m-Formylphenyl p-tolyl sulfide (Table 6, entry 10):[7l] colorless oil, 184 mg (81% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 2.41 (s, 3 H), 7.21−7.29 (m, 2 H), 7.38−7.49 (m, 2 H), 7.67−7.72 (m, 1 H), 7.77−7.85 (m, 3 H), 9.95 (s, 1 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 21.26, 127.15, 128.41, 129.48, 130.49, 132.38, 133.50, 134.24, 137.05, 138.01, 139.98, 191.77.

o-Formylphenyl p-tolyl sulfide (Table 6, entry 12):[7l] colorless oil, 177 mg (78% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 2.42 (s, 3 H), 7.04−7.06 (m, 1 H), 7.24−7.26 (m, 2 H), 7.30−7.33 (m, 2 H), 7.38−7.41 (m, 2 H), 7.87−7.89 (m, 1 H), 10.40 (s, 1 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 21.29, 125.68, 128.94, 129.28, 130.61, 132.28, 133.18, 133.97, 134.06, 139.05, 142.86, 191.54.

2-Pyridyl p-tolyl sulfide (Table 6, entry 14):[17a] colorless oil, 190 mg (90% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 2.36 (s, 3 H), 6.80 (d, J = 4.8 Hz, 1 H) 6.92−6−97 (m, 1 H), 7.20−7.29 (m, 2

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H),7.37−7.39 (m, 1 H), 7.41−7.43 (m, 1 H), 7.49−7.53 (m, 1 H), 8.38 (d, J = 4.8 Hz, 1 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS) δ (ppm) 21.34, 119.65, 120.86, 127.65, 130.51, 135.22, 136.68, 139.49, 149.42, 162.15.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01248.

^1H and $^{13}C\{^1H\}$ NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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