Green Chemistry

PAPER

View Article Online
View Journal

Cite this: DOI: 10.1039/c9gc03384j

Metal- and solvent-free direct C–H thiolation of aromatic compounds with sulfonyl chlorides†

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Received 28th September 2019,
Accepted 25th November 2019

DOI: 10.1039/c9gc03384j

rsc.li/greenchem

A simple, efficient and green method for the direct thiolation of aromatic compounds using commercially available sulfonyl chlorides as the sulfur source was developed under metal- and solvent-free conditions. The C–S bond was constructed *via* direct C–H functionalization of diverse aromatic compounds under an oxygen atmosphere. In this process, various diaryl sulfides were synthesized in moderate to excellent yields. This protocol shows a broad substrate scope and good functional group tolerance. Moreover, a gram-scale experiment was also conducted to prove the prospect of this method for the scale-up synthesis of diaryl sulfides. Mechanistic studies indicate that this procedure probably undergoes a radical pathway.

Introduction

Diaryl sulfides are ubiquitous chemical structures that generally exist in natural products, biologically active compounds and functional materials.[1] As crucial building blocks, diaryl sulfides are employed to treat HIV and cancer as well as Parkinson's and Alzheimer's diseases.[2] Given such importance of diaryl sulfides, plenty of significant reactions have been developed for the construction of the C–S bond.[3]

Recently, highly selective and direct functionalization of the C–H bond has attracted great attention in both organic and pharmaceutical fields. The merits of this strategy include its high efficiency, low consumption, and little influence on the environment.[4,5] From the perspective of environmentally friendly and green chemistry, selective oxidative coupling *via* direct functionalization of the C–H bond has proved to be an efficient and economical route for C–S bond formation. In these transformations, various novel and practical sulfenylating or thiolating reagents, such as thiols,[6] disulfides,[7] sodium sulfinates[8] and sulfonyl hydrazides,[9] have been used well. These methods have been powerful tools for the synthesis of diaryl sulfides. Despite the advantages of these reactions, most of them are limited due to the employment of expensive and toxic metals and/or stoichiometric amounts of oxidants (peroxides are commonly used). In the pharmaceutical field, trace metal impurities should be avoided because of the low threshold residual tolerance of metals in drug synthesis. Besides, owing to the increasing attention towards the influence of organic solvents on the environment as well as on the human body, organic reactions in the absence of classical organic solvents have aroused intensive interest of organic researchers.[10] Even though a variety of modern solvents have been extensively explored lately,[11,12] not employing a solvent at all is undoubtedly the best choice. As a consequence, development of solvent-free reactions is important.

As the precursor of sodium sulfinates and sulfonyl hydrazides, sulfonyl chlorides are inexpensive, commercially available and easily accessible to generally serve as sulfonylating agents to construct the C–S bond.[13] Nevertheless, sulfonyl chlorides as sulfenylation sources are relatively less studied.[14] Recently, our group described a series of methodologies for direct thiolation of the C–H bond under metal-free conditions.[15] As our continuing interest in this area, herein, we report a simple and convenient method for the synthesis of diaryl sulfides by direct C–H thiolation of various aromatic compounds with sulfonyl chlorides under metal- and solvent-free conditions (Scheme 1).

Results and discussion

Screening and optimization of the reaction conditions

We started our investigation by choosing 1-methoxynaphthalene (**1a**) and *p*-tolylsulfonyl chloride (**2a**) as the model substrates and using I_2 and diethyl phosphite as the additives. Initially, several iodine additives were examined when the reac-

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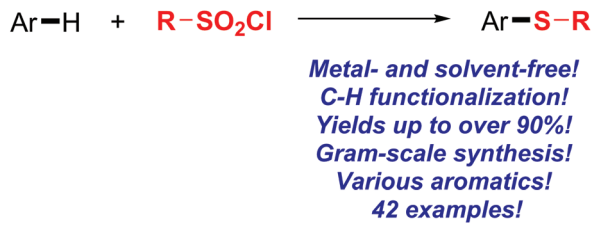
†Electronic supplementary information (ESI) available. See DOI: 10.1039/c9gc03384j



Scheme 1 Metal- and solvent-free direct C–H thiolation of aromatic compounds using sulfonyl chlorides.

tion was performed in acetonitrile at 100 °C under an oxygen atmosphere for 18 hours. Among them, tetramethylammonium iodide (TMAI) showed the best efficiency to give the thiolating product **3aa** in 74% yield (Table 1, entries 1–5). Then, different phosphorus reagents such as di-iso-propyl phosphite, tri-*n*-butyl phosphine and triphenylphosphine were used, which were less efficient (Table 1, entries 6–8). Next, we probed the effect of the solvent on this transformation. When the reaction was carried out in 1,2-dichloroethane or chlorobenzene, lower yields of the desired product were obtained (Table 1, entries 9 and 10). However, strong polar solvents such as *N*,*N*-dimethylformamide and dimethyl sulfoxide were totally negative for this kind of transformation, as no desired product was acquired by TLC and GC-MS methods (Table 1, entries 11 and 12). When the reaction was conducted without any organic solvents, a satisfactory result was achieved (Table 1, entry 13). Upon increasing the amount of **2a** to two equivalents, **3aa** was afforded in an excellent yield (Table 1, entry 14). Lower yields were obtained upon decreasing the reaction temperature or performing the reaction under air (Table 1, entries 15 and 16).

Table 1 Optimization of the reaction conditions[a]

1a **2a** **3aa**

Entry	Additive **1**	Additive **2**	Solvent	Yield[b] (%)
1	I_2	$(EtO)_2P(O)H$	CH_3CN	30
2	KI	$(EtO)_2P(O)H$	CH_3CN	46
3	NH_4I	$(EtO)_2P(O)H$	CH_3CN	52
4	TBAI	$(EtO)_2P(O)H$	CH_3CN	63
5	TMAI	$(EtO)_2P(O)H$	CH_3CN	74
6	TMAI	$(^iPrO)_2P(O)H$	CH_3CN	55
7	TMAI	$^nBu_3P$	CH_3CN	16
8	TMAI	Ph_3P	CH_3CN	68
9	TMAI	$(EtO)_2P(O)H$	DCE	62
10	TMAI	$(EtO)_2P(O)H$	PhCl	65
11	TMAI	$(EtO)_2P(O)H$	DMF	n.d.
12	TMAI	$(EtO)_2P(O)H$	DMSO	n.d.
13	TMAI	$(EtO)_2P(O)H$	Neat	76
14[c]	TMAI	$(EtO)_2P(O)H$	Neat	96
15[c,d]	TMAI	$(EtO)_2P(O)H$	Neat	58
16[c,e]	TMAI	$(EtO)_2P(O)H$	Neat	80

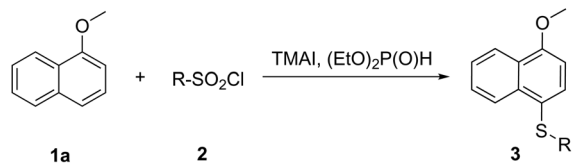
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), additive **1** (0.1 mmol), additive **2** (0.4 mmol), 100 °C, 18 h under O_2, unless otherwise noted. [b] GC yield based on **1a**. [c] **2a** (0.4 mmol). [d] 80 °C. [e] Under air.

Substrate scope and scale-up of the reaction

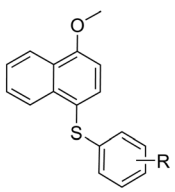
With the optimized reaction conditions in hand, we next set to investigate the scope of this method. As summarised in Table 2, a series of arylsulfonyl chlorides bearing electron-donating groups or electron-withdrawing groups at the *para* position were successfully coupled with 1-methoxynaphthalene (**1a**) to afford the corresponding diaryl sulfides in moderate to excellent yields (Table 2, **3aa–3ai**). Functional groups at the *ortho* or *meta* position of sulfonyl chlorides were also well tolerated under the optimized conditions (Table 2, **3aj–3ap**). Additionally, the reaction of multi- or naphthyl-substituted sulfonyl chlorides, which have large steric hindrance, proceeded smoothly to give the desired products in moderate to high yields (Table 2, **3aq–3at**). It should be noted that the heteroaromatic substrate, 3,5-dimethylisoxazole-4-sulfonyl chloride, was found to react with **1a** and provided aryl–heteroaryl sulfide **3au** in good yield.

Under the optimized reaction conditions, we further examined other aromatic compounds such as ethers and phenols (Table 3). The reaction of 2-naphthol with *p*-tolsulfonyl chloride (**2a**) gave the corresponding thiolating product in a high yield. Interestingly, the same results were obtained upon employing 1-bromo-2-naphthol and 2-tetralone as the substrates (Table 3, **4aa**). 2-Methoxynaphthalene and 2-ethoxynaphthalene also successfully coupled with **2a** to afford **4ab**

Table 2 Reaction of 1-methoxynaphthalene with sulfonyl chlorides[a]

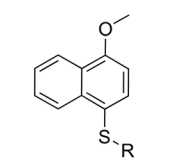


1a **2** **3**

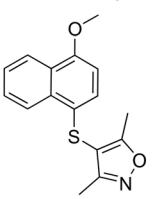


R = 4-Me, **3aa**, 90%
R = H, **3ab**, 82%
R = 4-^{t}Bu, **3ac**, 81%
R = 4-OMe, **3ad**, 91%
R = 4-CF_3, **3ae**, 72%
R = 4-F, **3af**, 84%
R = 4-Br, **3ag**, 73%
R = 4-I, **3ah**, 70%
R = 4-NO_2, **3ai**, 48%

R = 3-F, **3aj**, 67%
R = 3-CN, **3ak**, 65%
R = 3-SO_2Me, **3al**, 48%
R = 2-Me, **3am**, 91%
R = 2-OCF_3, **3an**, 46%
R = 2-F, **3ao**, 83%
R = 2-NO_2, **3ap**, 21%
R = 2,4-Cl_2, **3aq**, 84%
R = 2,4,6-Me_3, **3ar**, 42%



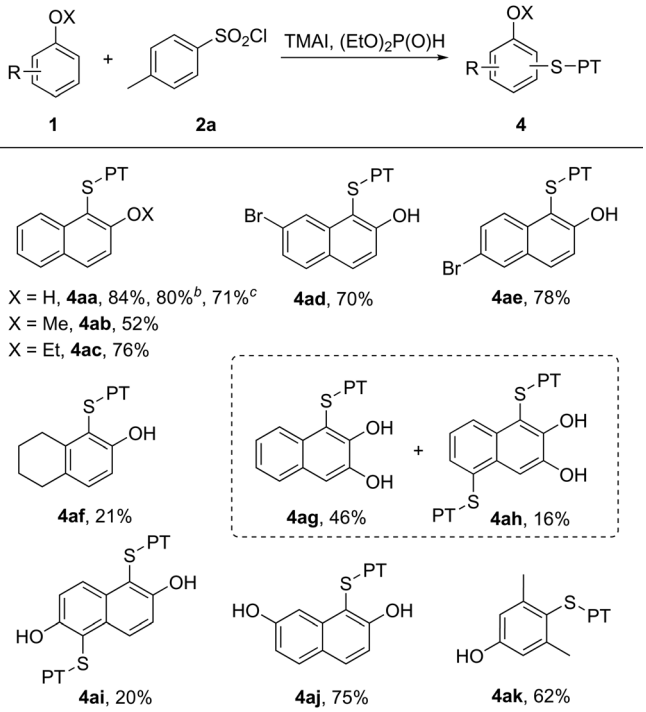
R = 1-naphthyl, **3as**, 53%
R = 2-naphthyl, **3at**, 82%



3au, 77%

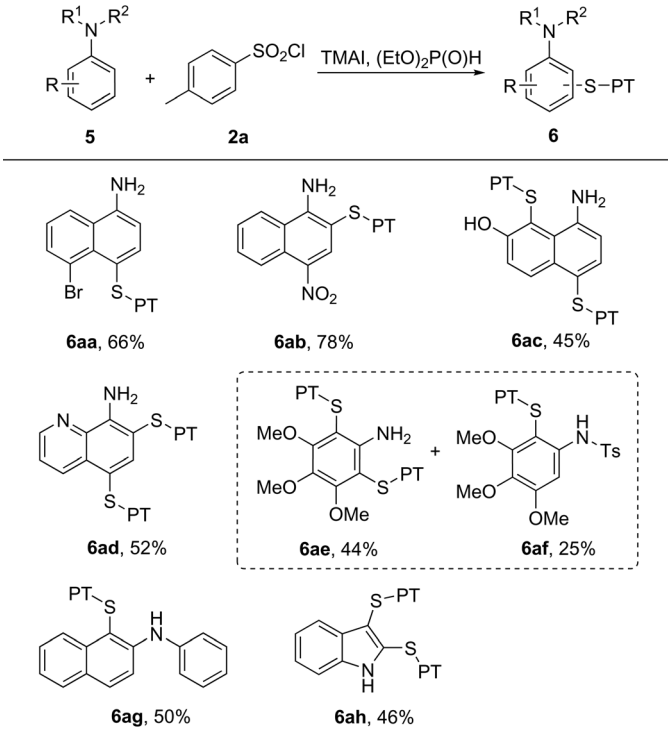
[a] Reaction conditions: **1** (0.2 mmol), **2a** (0.4 mmol), TMAI (0.1 mmol), $(EtO)_2P(O)H$ (0.4 mmol), 100 °C, O_2, 18 h. Isolated yield based on **1**.

Table 3 Substrate scope[a]



[a] Reaction conditions: **1** (0.2 mmol), **2a** (0.4 mmol), TMAI (0.1 mmol), $(EtO)_2P(O)H$ (0.4 mmol), 100 °C, O_2, 18 h. Isolated yield based on **1**. PT = *p*-Tol. [b] 2-Tetralone as the substrate. [c] 1-Bromo-2-naphthol as the substrate.

Table 4 Substrate scope[a]



[a] Reaction conditions: **5** (0.2 mmol), **2a** (0.4 mmol), TMAI (0.1 mmol), $(EtO)_2P(O)H$ (0.4 mmol), 100 °C, O_2, 18 h. Isolated yield based on **5**. PT = *p*-Tol; Ts = *p*-tolsulfonyl.

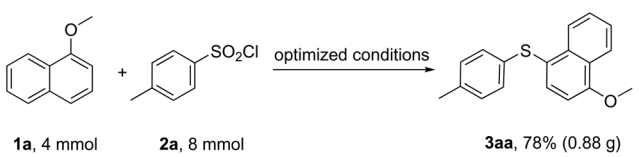
and **4ac** in 52% and 76% yields, respectively. When 2-naphthol containing a bromo group at the C-6 or C-7 site was subjected to this reaction system, sulfenylating products were achieved in good yields without the cleavage of the C–Br bond (Table 3, **4ad**–**4ae**). Notably, 5,6,7,8-tetrahydro-2-naphthol was also compatible with this kind of transformation, even though the yield of the reaction decreased obviously (Table 3, **4af**). It is interesting to note that when dihydroxyl naphthalenes were used in this reaction, some of them generated dithiolating products (Table 3, **4ag**–**4aj**). To our delight, when we tested this protocol with 3,5-dimethylphenol, the reaction proceeded well to afford the target compound **4ak** in a moderate yield.

Apart from the above-mentioned substrates, the reaction of aromatic amines also proceeded smoothly under optimal conditions, and the results are illustrated in Table 4. Various 1-naphthylamine derivatives were successfully coupled with *p*-tolsulfonyl chloride (**2a**) to afford aryl sulfides in moderate to good yields (Table 4, **6aa**–**6ad**). The reaction of trimethoxy-substituted aniline with **2a** led to the formation of a disulfenylation compound along with the formation of *N*-sulfonylated products (Table 4, **6ae**–**6af**). When *N*-phenyl-2-naphthylamine was subjected to this transformation, **6ag** was obtained in a yield of 50%. Subsequently, indole, a versatile building block in organic and pharmaceutical chemistry, was also compatible with this method to provide the dithiolation product **6ah** at the C-2 and C-3 positions.

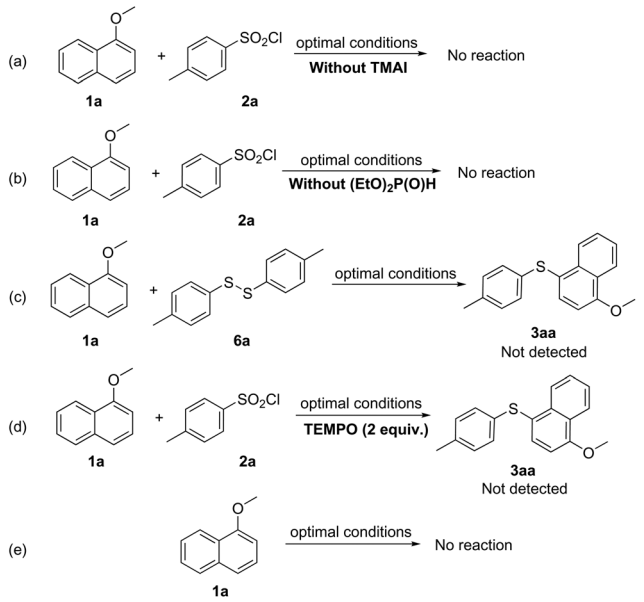
Encouraged by this convenient and effective approach for the direct synthesis of aryl sulfides, a gram-scale experiment was executed to testify the potential of this protocol. As shown in Scheme 2, we conducted the reaction of 1-methoxynaphthalene (**1a**, 4 mmol) with *p*-tolsulfonyl chloride (**2a**, 8 mmol) under the optimized conditions to afford the corresponding diaryl sulfide **3aa** in good yield, proving the prospect of this method for the scale-up synthesis of diaryl sulfides.

Mechanistic investigations

In order to obtain more information on the reaction mechanism, several control experiments were carried out. When the model reaction was performed in the absence of TMAI, no reaction occurred (Scheme 3a). The same result was obtained when the reaction was carried out without $(EtO)_2P(O)H$ (Scheme 3b). The reaction of 1,2-di-*p*-tolyldisulfane with **1a** did not afford the desired product **3aa** (Scheme 3c). Furthermore, under standard conditions, the use of 2,2,4,4-tetramethyl-1-



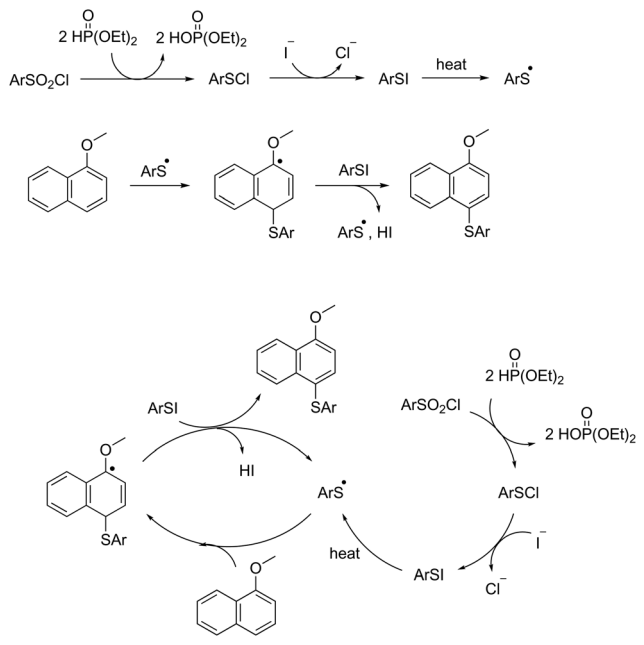
Scheme 2 Gram-scale experiment.



Scheme 3 Control experiments.

piperidinyloxy (TEMPO), a radical scavenger, overtly suppressed the formation of **3aa** (Scheme 3d), indicating that this transformation probably undergoes a radical procedure. When **1a** was employed without the addition of **2a** under optimal conditions, the homocoupling product of **1a** was not observed by TLC and GC-MS methods (Scheme 3e).

Based on the above results and previous reports,[8a–c,g,14c] a plausible reaction mechanism is proposed, as shown in Scheme 4. Firstly, the reduction of arylsulfonyl chloride generates ArSCl with the assistance of diethyl phosphite or other reductive reagents. Then, ArSCl is attacked by iodide anions to yield ArSI. Subsequently, an ArS radical intermediate is produced by the homolysis of ArSI under heating. Finally, this key radical is added to an arene to give an arene–SAr radical intermediate, which is coupled with ArSI to afford the desired diaryl sulfide accompanied by the formation of the ArS radical and HI.



Scheme 4 Proposed mechanism.

Conclusions

In summary, we have described a metal- and solvent-free methodology for the direct C–H thiolation of aromatic compounds using readily available arylsulfonyl chlorides as the thiolating reagents. The C–S bond was constructed *via* direct C–H functionalization of various aromatic compounds under an oxygen atmosphere. The reaction shows a broad substrate scope and good functional group tolerance. This method provides a simple, green and economical route for the synthesis of versatile diaryl sulfides. Mechanistic investigations indicate that a radical pathway might be involved in this transformation.

Experimental

General procedure for the synthesis of 3aa

p-Tolsulfonyl chloride (0.4 mmol, if solid) and TMAI (0.1 mmol) were added to an oven-dried reaction vessel equipped with a magnetic stirring bar. Then the vessel was purged with oxygen three times, and *p*-tolsulfonyl chloride (0.4 mmol, if liquid), 1-methoxynaphthalene (0.2 mmol) and $(EtO)_2P(O)H$ (0.4 mmol) were added by using a syringe. The vessel was sealed and stirred at 100 °C for 18 hours. After the completion of the reaction, the reaction mixture was diluted with ethyl acetate and washed with saturated sodium thiosulfate solution. The organic layer was concentrated under reduced pressure to yield the crude product, which was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 50 : 1) to give the desired product **3aa** in 90% yield as a yellow oil.

For full experimental data, see the ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21801076), Hunan Provincial Natural Science Foundation of China (2019JJ50415), the Scientific Research Program of Huaihua (2018N2204) and Hunan University of Medicine.

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