JOC The Journal of Organic Chemistry

pubs.acs.org/joc Article

Iodine/DMSO-Promoted Selective Direct Arylthiation of Anilines with Thiols under Metal-Free Conditions

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Cite This: https://dx.doi.org/10.1021/acs.joc.0c02078 Read Online

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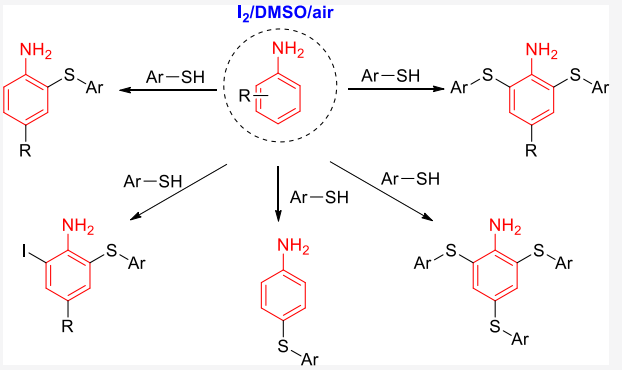
ABSTRACT: An iodine-promoted divergent thiolation of unprotected anilines with thiols for the synthesis of sulfide anilines has been described. The combinational use of I_2 and DMSO played an important role to realize this kind of transformation without the aid of a metal catalyst and strong oxidants. The reaction selectivity was well controlled to provide mono-, bis-, and trisubstituted diaryl sulfide derivatives. More importantly, iodination and sulfenylation can occur simultaneously to provide useful multifunctionalized iodoaniline products. This method afforded an efficient protocol for the construct C−S and C−I bonds from the C−H bond under mild reaction conditions.



INTRODUCTION

Sulfur-containing compounds are crucial for the synthesis of diverse compounds in pharmaceutical drugs, natural products, pesticides, and material science.[1] Among them, diaryl sulfides have attracted much more attention because of their unique biological activity. These compounds have therapeutic potential for the treatment of breast cancer, HIV, diabetes, and inflammatory diseases.[2] In addition, these compounds also act as important synthons for organic synthesis.[3] Therefore, efficient synthetic methods for the construction of various diaryl sulfides have inspired great efforts. During the past several decades, several significant synthetic methods for the construction of diaryl sulfides have been reported. Among these approaches, the transition-metal-catalyzed cross-coupling of thiols, disulfides, or even elemental sulfur with aryl halides and the reaction of organometals such as arylmagnesium compounds and arylboronic acid derivatives with electrophilic arylsulfur reagents are frequently used for the synthesis of diverse diaryl sulfide compounds.[4] However, these methods are susceptible to the need for highly functionalized starting materials, expensive metal catalysts, harsh reaction conditions, and producing a large amount of waste.

Although there are many other alternative methods for the construction of diaryl sulfide derivatives from various starting materials,[5] it is no doubt that the direct arylthiolation of widely present C−H bonds with appropriate thiolating reagents is the most economic and efficient approach.[6] The synthesis of diaryl sulfides via direct C−H sulfenylation under transition-metal-catalyzed or metal-free conditions with diverse sulfur reagents including disulfides,[7] sulfonyl chlorides,[8] sulfinates,[9] sulfonyl hydrazides,[10] and others[11] has attracted considerable attention. In spite of utilities, however, multiple steps are usually indispensable to prepare these highly prefunctionalized sulfenylating reagents. Therefore, the direct oxidative C−H/S−H cross-dehydrogenative couplings (CDCs) of simple and readily available thiols to form C−S bonds can provide an efficient and environmentally benign synthetic approach.[12] In the past several years, some new methods have been developed for the direct oxidative sulfenylation of electron-rich arenes such as phenols,[13] aryl ethers,[14] indole derivatives,[15] or heterocycles[16] under transition-metal-catalyzed or metal-free conditions. Aromatic amines are widely found in drug molecules, pesticides, functional materials, and natural products. Furthermore, because of their active amino groups, these compounds can be easily converted into other nitrogen-containing functional molecules.[17] Therefore, direct functionalization reaction based on aromatic amines has been a hot research field in organic synthesis. Among them, C−S bond formation via C−H sulfenylation of anilines has also attracted considerable interest. Arylsulfonyl hydrazides,[18] arylthiopyrrolidine-2,5-diones,[19] sulfinamides,[20] disulfides,[21] arylsulfonyl chlorides,[22] and thioesters[23] were successfully used as the sulfenylation reagents. Furthermore, Wang and co-workers developed an excellent protocol for direct sulfenylation of substituted anilines with thiols under metal-free conditions.[24]

Received: August 28, 2020

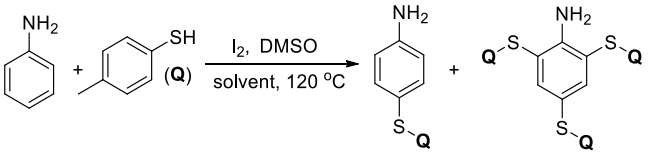
Noël and co-workers reported a one-pot Stadler−Ziegler process to form C−S bonds by employing $Ru(bpy)_3Cl_2·6H_2O$ as a photoredox catalyst.[25] Lei and co-workers communicated a progress on an electrocatalytic oxidant-free dehydrogenative C−H/S−H cross-coupling in a simple undivided cell under constant-current conditions.[26] A catalytic amount of iodine is crucial for this kind of transformation, and the strong oxidant di-*tert*-butyl peroxide is necessary to get a satisfactory reaction yield. Because the reaction tends to occur in the para and ortho positions of the amino group, the selectivity control is critical in this process. In our previous research, we found that combined use of the iodide additive or iodine and DMSO system could provide a mild oxidative reaction condition for selective transformation.[27] We speculate that such a system may also be efficient for the oxidative sulfenylation of anilines with good selectivity and compatible functional groups. As part of our continuing efforts on C−S bond construction under metal-free conditions,[28] herein, we describe metal- and strong oxidant-free direct C−H sulfenylation of anilines with thiols, selectively providing mono-, bis-, and tri-sulfenylation products in reasonable yields. More importantly, iodination and sulfenylation reactions can occur simultaneously to provide very useful multifunctionalized products.

RESULTS AND DISCUSSION

We commenced our investigation using aniline (**1a**) and 4-methylbenzenethiol (**2a**) as the standard substrates to optimize the reaction conditions (Table 1). To our delight, 2,4,6-trisubstituted product **4aa** was generated exclusively in *o*-xylene at 120 °C when I_2 (1 equiv) and DMSO (4 equiv) were used (entry 1). The reaction yield did not increase when other solvents such as toluene, dioxane, and PhCl were used (entries 2−4); however, a better yield could be obtained when *ortho*-dichlorobenzene (*o*-DCB) was used (entry 5). The reaction showed good reactivity under an air atmosphere, and a decline in yield was observed under an O_2 atmosphere (entry 6). Increasing the amount of I_2 or DMSO led to a better yield of the product (entries 7−11). DMSO played a key role in the present thiolation reaction, and no product was observed when the coupling reaction was run in its absence (entry 12). Furthermore, the addition of molecular sieves could further increase the reaction yield to 95% (entry 13). For comparison, when H_2O was added, the reaction yield decreased to 52% (entry 14). It was also interesting to find that 4-substituted product **3aa** was obtained as the major product when excess of aniline was used and N-methyl-2-pyrrolidone (NMP) or DMF was used as a solvent (entries 15 and 16). The reaction yield could be slightly increased by increasing the amount of I_2 or DMSO (entries 17−20). The yield could also be enhanced by adding molecular sieves to give the desired **3aa** in 69% yield (entry 21).

With the optimized reaction conditions in hand, various aryl thiols were investigated for the mono-sulfenylation, and the results are summarized in Scheme 1. The model reaction of **1a** and **2a** afforded **3aa** in 67% isolated yield in the presence of I_2/DMSO using DMF as the solvent. In general, the reaction between aniline (**1a**) and various thiol derivatives bearing methyl and halogens such as F, Cl, and Br on the aromatic ring led to good yields for the desired products. The position of substituents on thiophenol affected the reaction yields significantly (**3aa**, **3ae**, and **3af**). Notably, higher yields could even be achieved when methyl and bromo substituents were presented at the ortho position (**3af** and **3ah**).

Table 1. Screening the Reaction Conditions[a]



1a **2a** **3aa** **4aa**

entry	I_2 (equiv)	DMSO (equiv)	solvent	yield (%)[b] 3aa	yield (%)[b] 4aa
1	1.0	4.0	*o*-xylene	nd	47
2	1.0	4.0	toluene	nd	45
3	1.0	4.0	dioxane	nd	46
4	1.0	4.0	PhCl	nd	53
5	1.0	4.0	*o*-DCB	nd	60
6[c]	1.0	4.0	*o*-DCB	nd	28
7	1.0	6.0	*o*-DCB	nd	65
8	1.0	8.0	*o*-DCB	nd	55
9	1.2	6.0	*o*-DCB	nd	62
10	1.5	6.0	*o*-DCB	nd	68
11	2.0	6.0	*o*-DCB	nd	74
12	1.5	0.0	*o*-DCB	nd	nd
13[d]	**2.0**	**6.0**	***o*-DCB**	**nd**	**95 (90)**[e]
14[f]	2.0	6.0	*o*-DCB	nd	52
15[g]	1.0	4.0	NMP	40	nd
16[g]	1.0	4.0	DMF	42	nd
17[g]	1.0	8.0	DMF	50	nd
18[g]	1.5	4.0	DMF	51	nd
19[g]	2.0	4.0	DMF	50	nd
20[g]	1.5	8.0	DMF	60	nd
21[g,h]	1.5	8.0	DMF	69 (67)[e]	nd

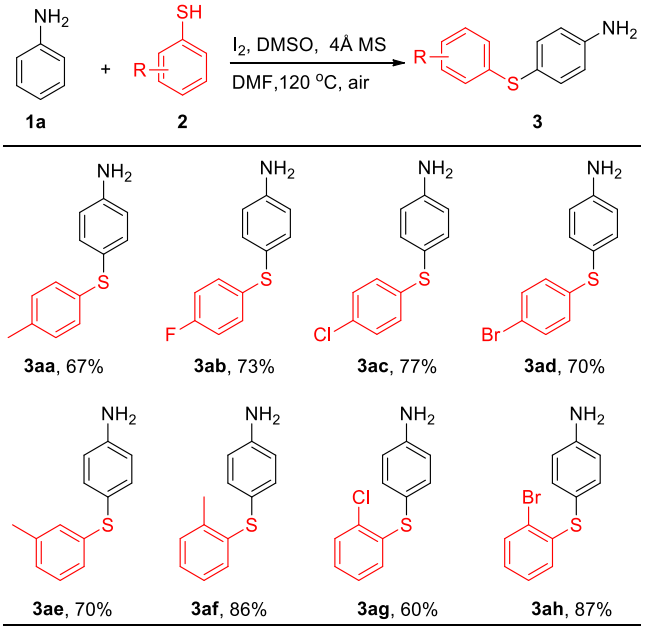
[a]Reaction conditions: **1a** (0.2 mmol), **2a** (1.0 mmol), solvent (1.0 mL), air, 12 h. [b]GC yield based on **1a**. [c]Under O_2. [d]100 mg 4 Å MS. [e]Isolated yield based on **2**. [f]1.5 equiv H_2O. [g]Substrate amounts: **1a** (0.4 mmol), **2a** (0.2 mmol). GC yield based on **2a**. [h]100 mg 4 Å MS.

Subsequently, the substrate scope for the synthesis of trisubstituted products was investigated using different arylthiols under the given reaction conditions. As presented in Scheme 2, a variety of thiols were successfully coupled with aniline (**1a**) to give the corresponding thiolation products in good to high yields under the I_2/DMSO system using *o*-DCB as the solvent. The position of the methyl substituent did not significantly affect the reaction yields, and all of them afforded the desired products in more than 90% yield (**4aa**, **4ae**, and **4af**). Notably, when we used **3aa** instead of **1a**, we also obtained **4aa** in 95%. Halogen functional groups were well accommodated to afford the desired products in reasonable yields. Furthermore, **4ab** was obtained in 97% yield when a fluoro group was presented at the para position. The bromo group located at the ortho position gave a slightly higher yield (**4ad** and **4ah**). Notably, *N*-methylaniline and formanilide could also be involved in this kind of reaction to give the same product **4aa**, both of which lost the functional groups on amine during the reaction.

As noticed by others[24] and us, the easiest place to reach for this kind of arylthiation is the para position of the amino group. Therefore, 4-substituted anilines are always used to prepare ortho arylthiation products. To further explore this method for diaryl sulfide preparation, we investigated several para-substituted anilines for this kind of reaction. To our delight, mono-arylthiation products could be obtained solely

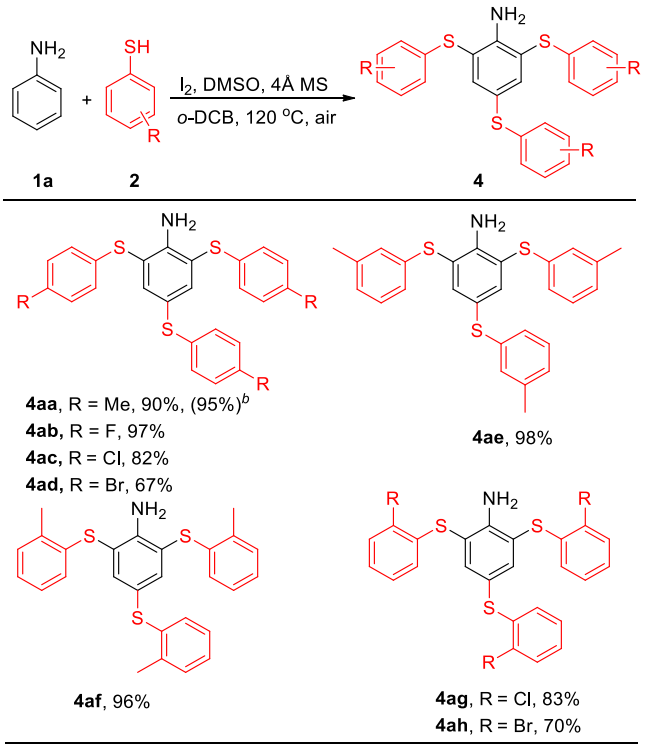
https://dx.doi.org/10.1021/acs.joc.0c02078
J. Org. Chem. XXXX, XXX, XXX−XXX

Scheme 1. Substrate Scope with Respect to the Thiophenols[a]



[a]Reaction conditions: **1a** (0.4 mmol), **2** (0.2 mmol), I_2 (1.5 equiv), DMSO (8 equiv), DMF (1.0 mL), 4 Å MS (100 mg). Air, 12 h. Isolated yield based on **2**.

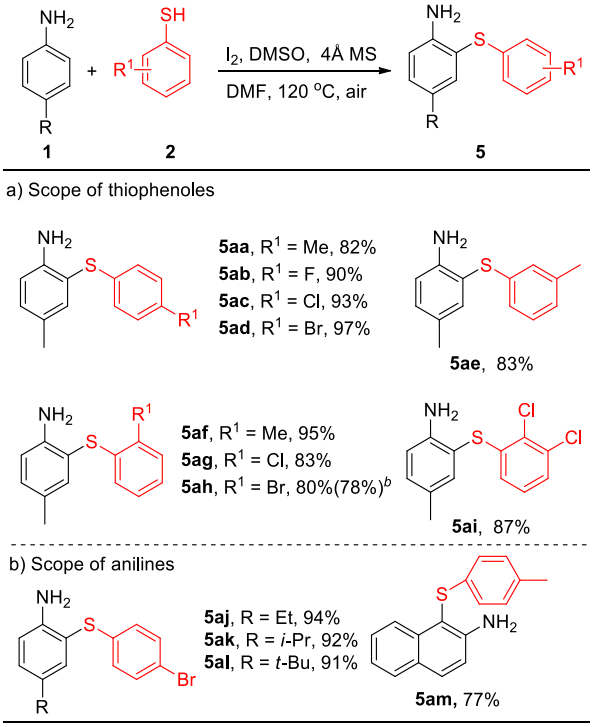
Scheme 2. Substrate Scope with Respect to Anilines[a]



[a]Reaction conditions: **1a** (0.2 mmol), **2** (1.0 mmol), I_2 (2.0 equiv), DMSO (6 equiv), *o*-DCB (1.0 mL), 4 Å MS (100 mg), air, 16 h. Isolated yield based on **1a**. [b]**3aa** instead of **1a** as the substrate.

by using an excess of anilines to give the corresponding products in good to high yields (Scheme 3). For example, when *para*-toluidine was used as the substrate, all thiols with

Scheme 3. Substrate Scope Based on 4-Substituted Anilines[a]



[a]Reaction conditions: **1** (0.4 mmol), **2** (0.2 mmol), I_2 (1.5 equiv), DMSO (8 equiv), DMF (1.0 mL), 4 Å MS (100 mg). Air, 12 h. Yield based on **2**. [b]6 mmol scale.

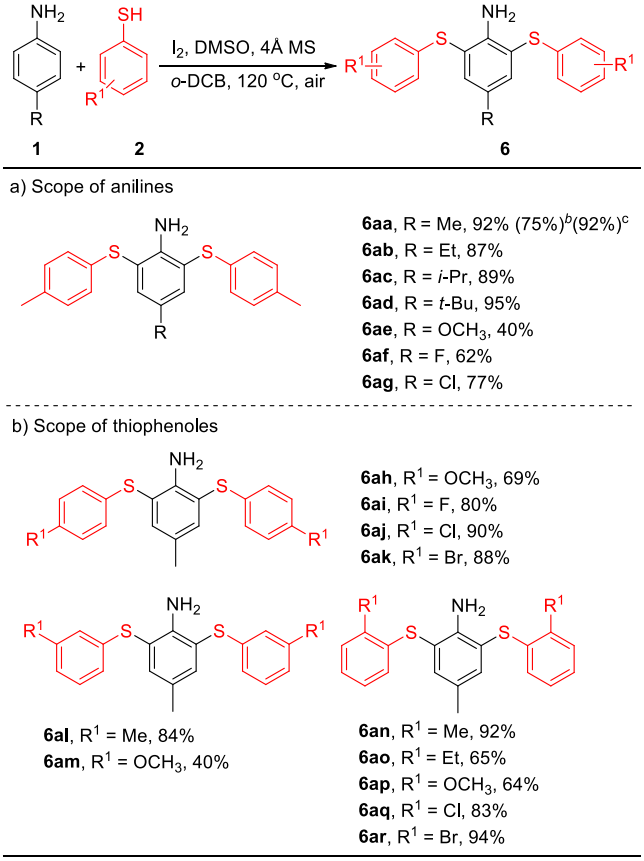
methyl and halogens at the para position could smoothly react to furnish the desired products in excellent yields (**5aa**−**5ad**). A better yield could be achieved when the methyl group was located at the ortho position in aryl thiol. 2,3-Dichlorobenzenethiol could be used for this reaction to afford **5ai** in 87% yield. Notably, other para-substituted anilines could smoothly react with *para*-toluenethiol to give the corresponding products in high yields (**5aj**−**5al**). In addition, we could know that 2-naphthylamine and 4-methylbenzenethiol react with a yield of 77% (**5am**).

Furthermore, the bis-arylthiation product could be selectively obtained by fine-tuning the reaction conditions as shown in Scheme 4. A series of para-substituted anilines were used to react with **2a** to give the corresponding products in good to high yields (**6aa**−**6ad**). At the same time, when we used **5aa** instead of **1a**, we also obtained **6aa** in 92%. However, the much lower yield was obtained when 4-methoxyaniline was used (**6ae**). Notably, halogens such as F and Cl were well tolerated to give the desired product in moderate yields (**6af** and **6ag**). Furthermore, thiols with an electron-donating group reacted smoothly to give products in moderate yields (**6ah**, **6am**, and **6ap**). When alkyls and halogens presented at different positions, they all gave the desired products in good to excellent yields. Notably, **6ar** with an active bromo substituent at the ortho position could be obtained in 94% yield, which provides an opportunity for further conversion.

Interestingly, when we altered the proportion of **1** and **2** under the standard reaction, we were surprised to obtain 2-iodo-4-methyl-6-(*p*-tolylthio)aniline as the new outcome (Scheme 5). We then slightly adjusted the condition of reactions, and we finally got the optimized reaction conditions

https://dx.doi.org/10.1021/acs.joc.0c02078
J. Org. Chem. XXXX, XXX, XXX−XXX

Scheme 4. Substrate Scope with Respect to the Anilines and Thiophenols[a]

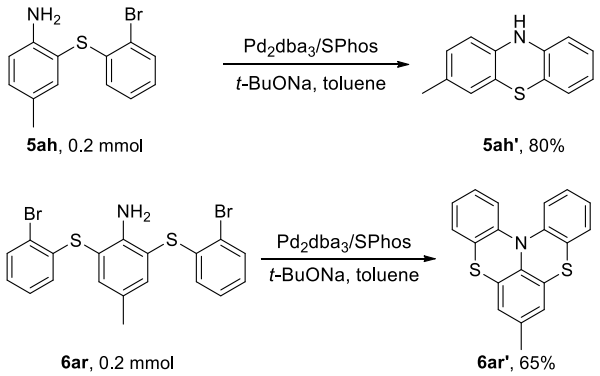


[a]Reaction conditions: **1** (0.2 mmol), **2** (0.5 mmol), I_2 (1.5 equiv), DMSO (4 equiv), *o*-DCB (1.0 mL), 4 Å MS (100 mg), air, 12 h. Isolated yield based on **1**. [b]5 mmol scale. [c]**5aa** instead of **1**.

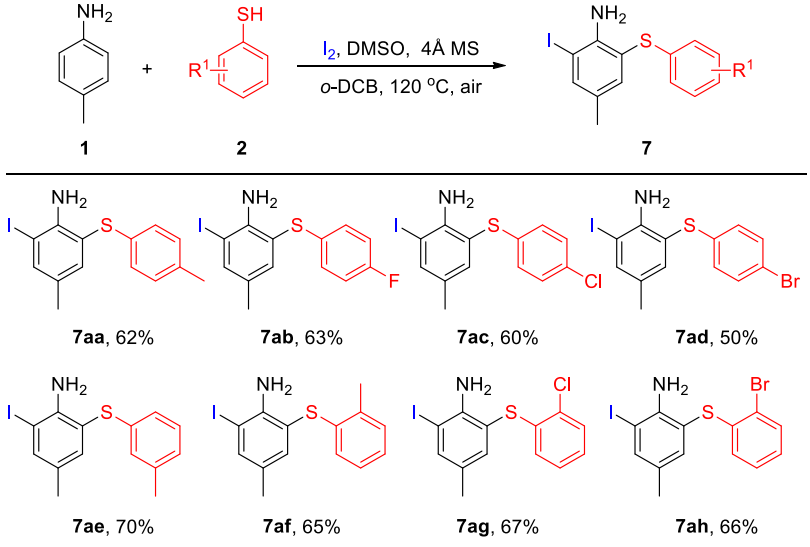
for iodination products: I_2 (2.0 equiv), DMSO (4.0 equiv), and *o*-DCB as the solvent. Under the optimized reaction conditions, **1** was smoothly reacted with several thiols to give the corresponding products in moderate to good yields. More importantly, halogens in thiols were well tolerated to give the desired products with multi-halogen functional groups (**7ab**−**7ad**, **7ag**−**7ah**). No obvious substituent effect was observed when the methyl substituent was located at different positions. This reaction provided an efficient and facile approach to anilines with various functional groups.

As mentioned above, the most advantage of this method is that the reaction conditions are very simple, and no transition-metal catalyst or strong oxidant is needed. Therefore, the reaction has very good functional group stability, which provides a new opportunity for further transformation of the product. We evaluated the transformation of **5ah** and **6ar**, both of which have a reactive bromo group at the ortho position (Scheme 6). When **5ah** and **6ar** were treated with Pd_2dba_3 (2% mmol), SPhos (4% mmol), and *t*-BuONa (2.0 equiv) under an argon atmosphere in NMP (0.6 mL) at 110 °C, both of them smoothly gave the corresponding cyclized products **5ah′** and **6ar′** in 80 and 65% yields, respectively. This method provides a convenient and concise way to synthesize the fused heterocyclic compounds.

Scheme 6. Further Transformation of Products



Scheme 5. Substrate Scope with Respect to Thiophenols[a]



[a]Reaction conditions: **1** (0.4 mmol), **2** (0.2 mmol), I_2 (2.0 equiv), DMSO (4.0 equiv), *o*-DCB (1.0 mL), 4 Å MS (100 mg). Air, 12 h. Yield based on **2**.

https://dx.doi.org/10.1021/acs.joc.0c02078
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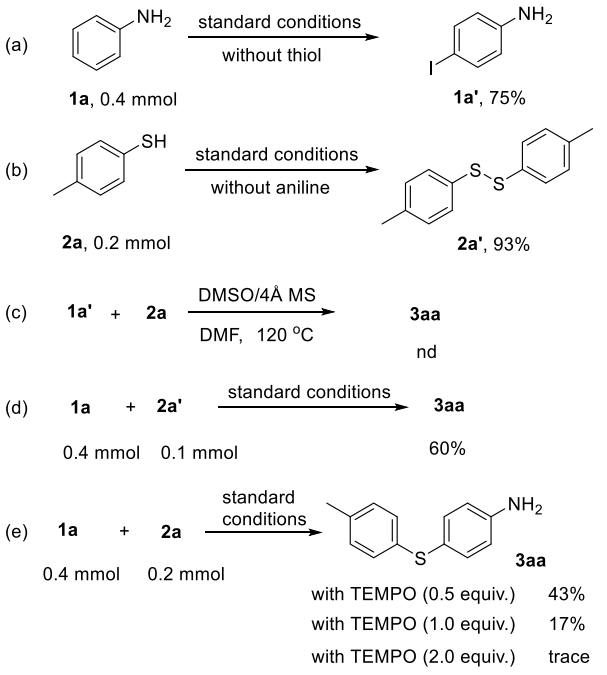
To understand the mechanism of the reaction, several control experiments were performed (Scheme 7). 4-Iodoaniline (**1a′**) was observed when **1a** was treated under the optimized reaction conditions in the absence of the thiol substrate. *p*-Tolyl disulfide (**2a′**) could be obtained in 93% yield from **2a** under standard conditions. However, treatment of **1a′** with **2a** in the absence of I_2 did not yield any desired product, whereas the reaction of **1a** with **2a′** yielded the desired product **3aa** in 60% yield. Hence, disulfides are probably the intermediate products. Meanwhile, 2,2,4,4-tetramethyl-1-piperidinyloxy (TEMPO) was added to the standard reaction conditions, and the reaction was completely inhibited by its 2 equiv. This indicates that a radical pathway was probably involved in this kind of reaction.

Scheme 7. Control Experiments



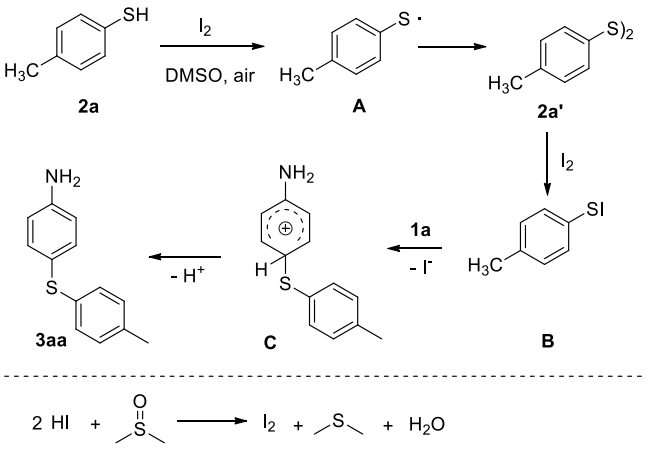
When we probe the substrate scope, we also tried aliphatic thiols, but we did not observe any corresponding products under the standard conditions. These results may be contributed to the high stability of aliphatic disulfide. Besides, electron-deficient anilines also did not work, suggesting an electrophilic sulfuration process in the C−S bond formation.

Based on the above observation and previous literature, a possible reaction mechanism is illustrated in Scheme 8. Initially, the oxidation of the thiol molecule by iodine generates the thiyl radical **A**. Homo-coupling of two thiyl radicals affords the disulfide intermediate **2a′**. The reaction of **2a′** with I_2 forms 2 equiv of electrophilic species *p*-MePhSI (**B**),[29] which attacks aniline to generate intermediate **C**. Finally, deprotonation results in the desired product **3aa**. Similarly, **4aa** can be obtained by repeating these steps. Treatment of HI with DMSO could regenerate the important molecular iodine.

CONCLUSIONS

In summary, we have described a metal- and strong oxidant-free C−S bond formation using anilines and aryl thiols as the starting materials. The combinational use of molecular iodine and DMSO could significantly improve the reaction efficiency and selectivity. Mono-, bis-, and tri-sulfenylation products were selectively formed by fine-tuning the reaction conditions. Synthetically useful functionalities such as halogens were smoothly compatible with the DMSO-based oxidative reaction conditions. Besides, iodination and sulfenylation reactions can occur simultaneously to provide very useful multifunctionalized aniline products. This metal- and strong oxidant-free method provides an efficient and selective alternative access to diaryl sulfides with a free amino group, which may have practical applications in organic and pharmaceutical fields.

Scheme 8. Possible Reaction Mechanism



EXPERIMENTAL SECTION

General Information. All reactions were carried out under an atmosphere of air unless otherwise noted. Column chromatography was performed using silica gel (neutral) (200−300 mesh). ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker-AV (400, 100, and 376 MHz, respectively) instrument internally referenced to tetramethylsilane (TMS) or chloroform signals. Mass spectra were recorded on an Agilent 5975 gas chromatography−mass spectrometry (GC−MS) instrument (EI). High-resolution mass spectra were recorded at Beijing Forestry University. High-resolution mass spectrometry (HRMS) was conducted using electrospray ionization (ESI) or matrix-assisted laser desorption ionization (MALDI) and was performed on an FTMS ICR MS BRUKER 7T. The structures of known compounds were further corroborated by comparing their ^{1}H, ^{13}C, ^{19}F NMR, and MS data with those of the literature. All reagents were obtained from commercial suppliers and used without further purification.

General Procedure for the Synthesis of 3. Aniline (38.0 μL, 0.4 mmol), 4-methylbenzenethiol (25.0 mg, 0.2 mmol), I_2 (75.0 mg, 0.3 mmol), and molecular sieves (100.0 mg) were added to an oven-dried reaction vessel (5 mL). The reaction vessel was sealed, and DMSO (120.0 μL, 1.6 mmol) and DMF (1.0 mL) were added using a syringe. The reaction vessel was stirred in an oil bath at 120 °C for 12 h under an air atmosphere. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (20 mL) and washed with saturated saltwater. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate three times. The combined organic layer was dried over sodium thiosulfate, and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to yield the desired product **3aa** as a yellow liquid (28.9 mg, 67% yield), R_f = 0.50 (petroleum ether/EtOAc = 20:1).

General Procedure for the Synthesis of 4. Aniline (19.0 μL, 0.2 mmol), 4-methylbenzenethiol (124.0 mg, 1.0 mmol), I_2 (100.0 mg, 0.4 mmol), and molecular sieves (100.0 mg) were added to an oven-dried reaction vessel (5 mL). The reaction vessel was sealed, and DMSO (90.0 μL, 1.2 mmol) and *o*-DCB (1.0 mL) were added using a syringe. The reaction vessel was stirred in an oil bath at 120 °C for 12

https://dx.doi.org/10.1021/acs.joc.0c02078
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h under an air atmosphere. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (20 mL) and washed with saturated saltwater. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate three times. The combined organic layer was dried over sodium thiosulfate, and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 150:1) to yield the desired product **4aa** as a yellow solid (82.8 mg, 90% yield), mp 114−116 °C. R_f = 0.60 (petroleum ether/EtOAc = 150:1).

General Procedure for the Synthesis of 5. *p*-Toluidine (43.0 mg, 0.4 mmol), 4-methylbenzenethiol (25.0 mg, 0.2 mmol), I_2 (75.0 mg, 0.3 mmol), and molecular sieves (100.0 mg) were added to an oven-dried reaction vessel (5 mL). The reaction vessel was sealed, and DMSO (120.0 μL, 1.6 mmol) and DMF (1.0 mL) were added using a syringe. The reaction vessel was stirred in an oil bath at 120 °C for 12 h under an air atmosphere. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (20 mL) and washed with saturated saltwater. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate three times. The combined organic layer was dried over sodium thiosulfate, and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1) to yield the desired product **5aa** as a yellow liquid (37.6 mg, 82% yield), R_f = 0.60 (petroleum ether/EtOAc = 50:1).

General Procedure for the Synthesis of 6. *p*-Toluidine (21.5 mg, 0.2 mmol), 4-methylbenzenethiol (63.5 mg, 0.5 mmol), I_2 (75.0 mg, 0.3 mmol), and molecular sieves (100.0 mg) were added to an oven-dried reaction vessel (5 mL). The reaction vessel was sealed, and DMSO (60.0 μL, 0.8 mmol) and *o*-DCB (1.0 mL) were added using a syringe. The reaction vessel was stirred in an oil bath at 120 °C for 12 h under an air atmosphere. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (20 mL) and washed with saturated saltwater. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate three times. The combined organic layer was dried over sodium thiosulfate, and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 150:1) to yield the desired product **6aa** as a light-yellow solid (64.7 mg, 92% yield), mp 102−104 °C. R_f = 0.60 (petroleum ether/EtOAc = 150:1).

Procedure for the Gram-Scale Reaction of 5ah. 2-Bromobenzenethiol (1.2 g, 6 mmol), *p*-toluidine (1.3 g, 12 mmol), I_2 (2.3 g, 9 mmol), and molecular sieves (2.0 g) were added to a round-bottomed flask (50 mL). DMSO (2.4 mL, 40 mmol) and DMF (15 mL) were added using a measuring cylinder. The reaction vessel was stirred in an oil bath at 130 °C for 16 h under an air atmosphere. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (25 mL) and washed with saturated saltwater. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate three times. The combined organic layer was dried over sodium sulfate, and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 50:1) to yield the desired product **5ah** as a yellow liquid (1.38 g, 78% yield). R_f = 0.60 (petroleum ether/EtOAc = 50:1).

Procedure for the Gram-Scale Reaction of 6aa. *p*-Toluidine (547.0 mg, 5 mmol), 4-methylbenzenethiol (1.9 g, 15 mmol), I_2 (1.9 g, 7.5 mmol), and molecular sieves (2.0 g) were added to a round-bottomed flask (50 mL). DMSO (1.2 mL, 20 mmol) and *o*-DCB (15 mL) were added using a measuring cylinder. The reaction vessel was stirred in an oil bath at 130 °C for 18 h under an air atmosphere. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (25 mL) and washed with saturated saltwater. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate three times. The combined organic layer was dried over sodium sulfate, and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 150:1) to yield the desired product **6aa** as a light-yellow solid (1.31 g, 75% yield), mp 102−104 °C. R_f = 0.60 (petroleum ether/EtOAc = 150:1).

*4-(p-Tolylthio)aniline (**3aa**).*[29d] Black liquid (petroleum ether/EtOAc = 20:1); 67% (28.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, *J* = 8.4 Hz, 2H), 7.05 (q, *J* = 8.2 Hz, 4H), 6.65 (d, *J* = 8.4 Hz, 2H), 3.37 (s, 2H), 2.28 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.4, 135.4, 135.3, 129.6, 128.2, 121.8, 115.9, 20.9; HRMS (MALDI) *m*/*z*: $[M]^+$ calcd for $C_{13}H_{13}NS$, 215.0769; found, 215.0765.

*4-((4-Fluorophenyl)thio)aniline (**3ab**).*[29d] Purple-black liquid (petroleum ether/EtOAc = 20:1); 73% (32.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, *J* = 8.6 Hz, 2H), 7.17−7.11 (m, 2H), 6.97−6.89 (m, 2H), 6.67 (d, *J* = 8.2 Hz, 2H), 3.61 (s, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.2 (C−F, $^1J_{C-F}$ = 245.1 Hz), 146.8, 135.4, 134.2 (C−F, $^4J_{C-F}$ = 3.2 Hz), 129.9 (C−F, $^3J_{C-F}$ = 7.9 Hz), 121.4, 116.0, 115.9 (C−F, $^2J_{C-F}$ = 21.9 Hz); ^{19}F NMR (377 MHz, $CDCl_3$): δ −117.10; HRMS (MALDI) *m*/*z*: $[M]^+$ calcd for $C_{12}H_{10}FNS$, 219.0518; found, 219.0514.

*4-((4-Chlorophenyl)thio)aniline (**3ac**).*[29d] Purple-black liquid (petroleum ether/EtOAc = 20:1); 77% (36.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−7.26 (m, 2H), 7.19−7.13 (m, 2H), 7.05−6.99 (m, 2H), 6.70−6.64 (m, 2H), 3.63 (s, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 147.1, 138.4, 136.1, 130.9, 128.8, 128.3, 119.8, 115.9; HRMS (MALDI) *m*/*z*: $[M]^+$ calcd for $C_{12}H_{10}ClNS$, 235.0223; found, 235.0219.

*4-((4-Bromophenyl)thio)aniline (**3ad**).*[29d] Purple liquid (petroleum ether/EtOAc = 20:1); 70% (39.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34−7.28 (m, 4H), 6.97 (d, *J* = 8.6 Hz, 2H), 6.69 (d, *J* = 8.5 Hz, 2H), 3.77 (s, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 147.3, 139.2, 136.2, 131.7, 128.5, 119.0, 118.7, 115.9.

*4-(m-Tolylthio)aniline (**3ae**).*[29d] Light-pink liquid (petroleum ether/EtOAc = 20:1); 70% (30.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34−7.28 (m, 4H), 6.97 (d, *J* = 8.6 Hz, 2H), 6.69 (d, *J* = 8.5 Hz, 2H), 3.77 (s, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.7, 139.2, 138.6, 135.9, 128.6, 127.9, 126.2, 124.4, 120.7, 115.9, 21.3; HRMS (MALDI) *m*/*z*: $[M]^+$ calcd for $C_{13}H_{13}NS$, 215.0769; found, 215.0767.

*4-(o-Tolylthio)aniline (**3af**).*[29d] Light-pink liquid (petroleum ether/EtOAc = 20:1); 86% (37.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26−7.22 (m, 2H), 7.16−7.11 (m, 1H), 7.07−6.98 (m, 2H), 6.93−6.85 (m, 1H), 6.67 (d, *J* = 8.5 Hz, 2H), 3.62 (s, 2H), 2.37 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.7, 138.3, 135.9, 135.6, 123.0, 127.6, 126.3, 125.3, 120.4, 116.0, 20.1.

*4-((2-Chlorophenyl)thio)aniline (**3ag**).*[29d] Purple liquid (petroleum ether/EtOAc = 20:1); 60% (28.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37−7.27 (m, 3H), 7.06−6.97 (m, 2H), 6.75−6.66 (m, 3H), 3.80 (s, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 147.7, 139.6, 137.2, 130.3, 129.2, 126.9, 126.8, 125.5, 117.7, 116.0; HRMS (MALDI) *m*/*z*: $[M]^+$ calcd for $C_{12}H_{10}ClNS$, 235.0223; found, 235.0221.

*4-((2-Bromophenyl)thio)aniline (**3ah**).* Purple liquid (petroleum ether/EtOAc = 20:1); 87% (48.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50−7.45 (m, 1H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.10−7.04 (m, 1H), 6.95−6.89 (m, 1H), 6.71 (d, *J* = 8.5 Hz, 2H), 6.68−6.63 (m, 1H), 3.84 (s, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 147.8, 141.6, 137.3, 132.5, 127.5, 126.8, 125.7, 120.0, 118.2, 116.0; HRMS (MALDI) *m*/*z*: $[M]^+$ calcd for $C_{12}H_{10}BrNS$, 278.9717; found, 278.9713.

*2,4,6-Tris(p-tolylthio)aniline (**4aa**).* Colorless solid (petroleum ether/EtOAc = 150:1); 90% (82.6 mg); mp 114−116 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (s, 2H), 7.12−7.09 (m, 2H), 7.06 (s, 2H), 7.02 (t, *J* = 8.4 Hz, 8H), 5.03 (s, 2H), 2.30 (s, 3H), 2.29 (s, 6H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 149.7, 142.9, 136.1, 136.0, 134.3, 131.7, 129.9, 129.8, 128.9, 127.5, 121.6, 116.9, 21.0, 21.0; HRMS (MALDI) *m*/*z*: $[M]^+$ calcd for $C_{27}H_{25}NS_3$, 459.1150; found, 459.1149.

*2,4,6-Tris((4-fluorophenyl)thio)aniline (**4ab**).* Yellow solid (petroleum ether/EtOAc = 150:1); 97% (91.2 mg); mp 89−91 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (s, 2H), 7.21−7.17 (m, 2H), 7.12−7.06 (m, 4H), 6.95 (t, *J* = 8.4 Hz, 6H), 4.91 (s, 2H); ^{13}C {^{1}H} NMR

https://dx.doi.org/10.1021/acs.joc.0c02078
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(100 MHz, $CDCl_3$): δ 161.71 (C−F, $^1J_{C-F}$ = 246.6 Hz), 161.64 (C−F, $^1J_{C-F}$ = 246.6 Hz), 149.48, 142.41, 132.56 (C−F, $^4J_{C-F}$ = 3.3 Hz), 131.17 (C−F, $^3J_{C-F}$ = 8.0 Hz), 130.04 (C−F, $^4J_{C-F}$ = 3.3 Hz), 129.58 (C−F, $^3J_{C-F}$ = 8.0 Hz), 122.12, 117.30, 116.35 (C−F, $^2J_{C-F}$ = 22.2 Hz), 116.17 (C−F, $^2J_{C-F}$ = 22.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −115.40, −115.45; HRMS (MALDI) *m/z*: $[M]^+$ calcd for $C_{24}H_{16}F_3NS_3$, 471.0397; found, 471.0396.

2,4,6-Tris((4-chlorophenyl)thio)aniline (**4ac**). Yellow solid (petroleum ether/EtOAc = 150:1); 82% (85.4 mg); mp 113−115 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (s, 2H), 7.22 (d, *J* = 8.6 Hz, 6H), 7.10 (d, *J* = 8.6 Hz, 2H), 7.02 (d, *J* = 8.6 Hz, 4H), 4.87 (s, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 150.4, 144.2, 136.6, 133.7, 132.2, 132.0, 129.4, 129.3, 129.1, 128.3, 120.7, 116.2; HRMS (MALDI) *m/z*: $[M]^+$ calcd for $C_{24}H_{16}Cl_3NS_3$, 518.9511; found, 518.9515.

2,4,6-Tris((4-bromophenyl)thio)aniline (**4ad**). Yellow solid (petroleum ether/EtOAc = 150:1); 67% (87.6 mg); mp 122−124 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (s, 2H), 7.36 (d, *J* = 8.5 Hz, 6H), 7.02 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 4H), 5.08 (s, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 150.5, 144.5, 137.4, 134.4, 132.2, 132.0, 129.6, 128.5, 120.5, 120.0, 119.9, 116.0; HRMS (MALDI) *m/z*: $[M]^+$ calcd for $C_{24}H_{16}Br_3NS_3$, 652.7975; found, 652.7977.

2,4,6-Tris(m-tolylthio)aniline (**4ae**). Yellow liquid (petroleum ether/EtOAc = 150:1); 98% (90.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 1.3 Hz, 2H), 7.11 (t, *J* = 7.6 Hz, 3H), 6.98−6.85 (m, 9H), 5.12 (s, 2H), 2.26 (s, 9H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 150.7, 144.7, 138.9, 138.7, 138.3, 135.2, 128.9, 128.8, 128.3, 127.4, 126.9, 126.6, 124.8, 123.9, 120.3, 116.1, 21.4, 21.3; HRMS (MALDI) *m/z*: $[M]^+$ calcd for $C_{27}H_{25}NS_3$, 459.1150; found, 459.1162.

2,4,6-Tris(o-tolylthio)aniline (**4af**). Yellow solid (petroleum ether/EtOAc = 150:1); 96% (88.1 mg); mp 114−116 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (s, 2H), 7.14 (t, *J* = 6.5 Hz, 3H), 7.10−7.03 (m, 6H), 7.00 (d, *J* = 6.0 Hz, 1H), 6.80 (d, *J* = 6.9 Hz, 2H), 4.85 (s, 2H), 2.37 (s, 6H), 2.34 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 149.9, 143.0, 136.9, 136.7, 136.0, 134.2, 130.4, 130.2, 128.6, 126.6, 126.5, 126.2, 126.1, 126.0, 121.0, 116.2, 20.2, 20.1; HRMS (MALDI) *m/z*: $[M]^+$ calcd for $C_{27}H_{25}NS_3$, 459.1150; found, 459.1167.

2,4,6-Tris((2-chlorophenyl)thio)aniline (**4ag**). Yellow solid (petroleum ether/EtOAc = 150:1); 83% (86.5 mg); mp 133−135 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (s, 2H), 7.37−7.31 (m, 3H), 7.14−7.08 (m, 6H), 6.91−6.86 (m, 1H), 6.77−6.72 (m, 2H), 5.21 (s, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 151.8, 146.2, 137.9, 134.4, 131.9, 131.6, 129.8, 129.7, 128.0, 127.3, 127.1, 126.9, 126.9, 126.6, 118.9, 115.1; HRMS (MALDI) *m/z*: $[M]^+$ calcd for $C_{24}H_{16}Cl_3NS_3$, 518.9511; found, 518.9515.

2,4,6-Tris((2-bromophenyl)thio)aniline (**4ah**). Yellow solid (petroleum ether/EtOAc = 150:1); 70% (91.6 mg); mp 114−116 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (s, 2H), 7.52 (t, *J* = 8.4 Hz, 3H), 7.18−7.13 (m, 3H), 7.05−6.97 (m, 3H), 6.86 (d, *J* = 7.9 Hz, 1H), 6.73 (d, *J* = 7.9 Hz, 2H), 5.20 (s, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 151.6, 146.3, 139.9, 136.4, 133.1, 133.0, 127.9, 127.9, 127.7, 127.1, 126.8, 126.7, 121.6, 121.4, 119.4, 115.7; HRMS (MALDI) *m/z*: $[M]^+$ calcd for $C_{24}H_{16}Br_3NS_3$, 652.7975; found, 652.7977.

4-Methyl-2-(p-tolylthio)aniline (**5aa**).[29d] Yellow solid (petroleum ether/EtOAc = 50:1); 82% (37.6 mg); mp 74−76 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (s, 1H), 7.06−6.97 (m, 5H), 6.70 (d, *J* = 8.1 Hz, 1H), 3.93 (s, 2H), 2.27 (s, 3H), 2.23 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.0, 137.1, 135.3, 133.1, 131.6, 129.7, 128.1, 126.9, 115.5, 115.2, 20.9, 20.1; HRMS (MALDI) *m/z*: $[M]^+$ calcd for $C_{14}H_{15}NS$, 229.0925; found, 229.0924.

2-((4-Fluorophenyl)thio)-4-methylaniline (**5ab**).[30] Colorless liquid (petroleum ether/EtOAc = 50:1); 90% (42.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (s, 1H), 7.11−7.00 (m, 3H), 6.96−6.87 (m, 2H), 6.71 (d, *J* = 8.1 Hz, 1H), 3.95 (s, 2H), 2.23 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.2 (C−F, $^1J_{C-F}$ = 244.9 Hz), 146.1, 137.1, 131.9 (C−F, $^4J_{C-F}$ = 4.5 Hz), 128.6 (C−F, $^3J_{C-F}$ = 7.8 Hz), 128.2, 116.0 (C−F, $^2J_{C-F}$ = 22.1 Hz), 115.6, 114.7, 20.2; ^{19}F NMR (376 MHz, $CDCl_3$): δ −117.2; HRMS (MALDI) *m/z*: $[M]^+$ calcd for $C_{13}H_{12}FNS$, 233.0675; found, 233.0674.

2-((4-Chlorophenyl)thio)-4-methylaniline (**5ac**).[31] Yellow liquid (petroleum ether/EtOAc = 50:1); 93% (46.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (s, 1H), 7.20−7.14 (m, 2H), 7.09−7.03 (m, 1H), 7.03−6.95 (m, 2H), 6.72 (d, *J* = 8.1 Hz, 1H), 4.13 (s, 2H), 2.24 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.3, 137.4, 135.6, 132.2, 131.1, 129.0, 128.2, 127.6, 115.6, 113.7, 20.2; HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{13}H_{13}ClNS$, 250.0452; found, 250.0441.

2-((4-Bromophenyl)thio)-4-methylaniline (**5ad**). Yellow liquid (petroleum ether/EtOAc = 50:1); 97% (57.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 8.5 Hz, 2H), 7.25 (s, 1H), 7.08−7.02 (m, 1H), 6.93 (d, *J* = 8.5 Hz, 2H), 6.72 (d, *J* = 8.1 Hz, 1H), 3.99 (s, 2H), 2.24 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.3, 137.4, 136.3, 132.2, 131.9, 128.2, 127.8, 118.9, 115.6, 113.5, 20.2; HRMS (MALDI) *m/z*: $[M]^+$ calcd for $C_{13}H_{12}BrNS$, 292.9874; found, 292.9875.

4-Methyl-2-(m-tolylthio)aniline (**5ae**).[24] Colorless liquid (petroleum ether/EtOAc = 50:1); 83% (38.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (s, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.06−7.02 (m, 1H), 6.92 (d, *J* = 9.6 Hz, 2H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.72 (d, *J* = 8.1 Hz, 1H), 3.81 (s, 2H), 2.26 (s, 3H), 2.24 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.2, 138.8, 137.4, 136.6, 131.8, 128.8, 128.1, 127.1, 126.3, 123.5, 115.5, 114.5, 21.4, 20.2.

4-Methyl-2-(o-tolylthio)aniline (**5af**).[24] Colorless solid (petroleum ether/EtOAc = 50:1); 95% (43.5 mg); mp 75−77 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (s, 1H), 7.16−7.12 (m, 1H), 7.08−6.98 (m, 3H), 6.76−6.68 (m, 2H), 3.93 (s, 2H), 2.41 (s, 3H), 2.24 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.2, 137.3, 135.8, 135.1, 131.7, 130.1, 128.4, 126.5, 125.3, 125.1, 115.5, 114.0, 20.2, 20.0.

2-((2-Chlorophenyl)thio)-4-methylaniline (**5ag**). Yellow solid (petroleum ether/EtOAc = 50:1); 85% (42.2 mg); mp 81−83 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37−7.30 (m, 1H), 7.27 (s, 1H), 7.12−7.07 (m, 1H), 7.07−7.00 (m, 2H), 6.75 (d, *J* = 8.2 Hz, 1H), 6.66−6.60 (m, 1H), 3.94 (s, 2H), 2.25 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.8, 137.9, 136.1, 132.5, 130.8, 129.4, 128.4, 127.1, 126.2, 125.9, 115.6, 112.4, 20.2; HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{13}H_{13}ClNS$, 250.0452; found, 250.0442.

2-((2-Bromophenyl)thio)-4-methylaniline (**5ah**).[32] Light-yellow solid (petroleum ether/EtOAc = 50:1); 80% (47.1 mg); mp 82−84 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 7.9 Hz, 1H), 7.28 (s, 1H), 7.09 (t, *J* = 7.5 Hz, 2H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 3.87 (s, 2H), 2.25 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.7, 138.1, 137.8, 132.7, 132.6, 128.4, 127.7, 126.2, 126.1, 120.5, 115.6, 113.0, 20.2.

2-((2,3-Dichlorophenyl)thio)-4-methylaniline (**5ai**). White solid (petroleum ether/EtOAc = 50:1); 87% (49.5 mg); mp 120−122 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, *J* = 2.4 Hz, 1H), 7.21−7.16 (m, 1H), 7.14−7.08 (m, 1H), 6.97 (t, *J* = 8.0 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 6.54−6.48 (m, 1H), 3.99 (s, 2H), 2.25 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.7, 139.0, 137.8, 133.2, 132.9, 128.5, 127.3, 126.4, 124.0, 115.7, 112.1, 20.2; HRMS (MALDI) *m/z*: $[M]^+$ calcd for $C_{13}H_{11}Cl_2NS$, 282.9989; found, 282.9990.

2-((4-Bromophenyl)thio)-4-ethylaniline (**5aj**). Yellow liquid (petroleum ether/EtOAc = 50:1); 94% (57.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34−7.29 (m, 2H), 7.27 (d, *J* = 1.9 Hz, 1H), 7.11−7.06 (m, 1H), 6.95−6.89 (m, 2H), 6.74 (d, *J* = 8.2 Hz, 1H), 4.03 (s, 2H), 2.54 (q, *J* = 7.6 Hz, 2H), 1.19 (t, *J* = 7.6 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.5, 136.3, 134.9, 131.9, 131.1, 127.7, 118.8, 115.6, 113.4, 27.7, 15.7; HRMS (MALDI) *m/z*: $[M]^+$ calcd for $C_{14}H_{14}BrNS$, 307.0030; found, 307.0026.

2-((4-Bromophenyl)thio)-4-isopropylaniline (**5ak**). Wine-red solid (petroleum ether/EtOAc = 50:1); 92% (59.3 mg); mp 54−56 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (s, 1H), 7.32−7.28 (m, 2H), 7.15−7.11 (m, 1H), 6.92 (d, *J* = 8.6 Hz, 2H), 6.75 (d, *J* = 8.2 Hz, 1H), 4.04 (s, 2H), 2.87−2.74 (m, 1H), 1.22 (s, 3H), 1.20 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.5, 139.7, 136.3, 135.0, 131.9, 129.7, 127.7, 118.8, 115.6, 113.4, 33.0, 24.1; HRMS (MALDI) *m/z*: $[M]^+$ calcd for $C_{15}H_{16}BrNS$, 321.0187; found, 321.0182.

2-((4-Bromophenyl)thio)-4-(tert-butyl)aniline (**5al**). Yellow liquid (petroleum ether/EtOAc = 50:1); 91% (61.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 2.3 Hz, 1H), 7.35−7.27 (m, 3H), 6.92

https://dx.doi.org/10.1021/acs.joc.0c02078
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(d, J = 8.5 Hz, 2H), 6.76 (d, J = 8.4 Hz, 1H), 4.02 (s, 2H), 1.28 (s, 9H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.2, 142.0, 136.4, 134.0, 131.9, 128.7, 127.6, 118.8, 115.3, 113.0, 34.0, 31.4; HRMS (MALDI) m/z: $[M]^+$ calcd for $C_{16}H_{18}BrNS$, 335.0343; found, 335.0347.

*1-((4-Bromophenyl)thio)naphthalen-2-amine (**5am**).*[24] Black liquid (petroleum ether/EtOAc = 10:1); 77% (40.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, J = 8.5 Hz, 1H), 7.75 (m, J = 12.1, 8.5 Hz, 2H), 7.45 (m, J = 11.3, 4.1 Hz, 1H), 7.30−7.26 (m, 1H), 7.07 (d, J = 8.8 Hz, 1H), 6.97 (q, J = 8.4 Hz, 4H), 4.42 (s, 2H), 2.26 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 148.2, 136.6, 134.8, 133.1, 131.6, 129.7, 128.4, 128.3, 127.7, 126.0, 124.3, 122.5, 117.6, 105.2, 20.8; HRMS (ESI) $[M + H]^+$ m/z calcd for $C_{17}H_{16}NS$, 266.0998; found, 266.1002.

*4-Methyl-2,6-bis(p-tolylthio)aniline (**6aa**).* Light-yellow solid (petroleum ether/EtOAc = 150:1); 92% (64.7 mg); mp 102−104 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (s, 2H), 7.02 (q, J = 8.3 Hz, 8H), 4.79 (s, 2H), 2.28 (s, 6H), 2.22 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 148.0, 138.9, 135.6, 132.6, 129.8, 127.3, 127.0, 115.6, 20.9, 20; HRMS (MALDI) m/z: $[M]^+$ calcd for $C_{21}H_{21}NS_2$, 351.1115; found, 351.1111.

*4-Ethyl-2,6-bis(p-tolylthio)aniline (**6ab**).* Yellow solid (petroleum ether/EtOAc = 150:1); 87% (63.6 mg); mp 86−88 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (s, 2H), 7.01 (q, J = 8.2 Hz, 8H), 4.79 (s, 2H), 2.52 (q, J = 7.5 Hz, 2H), 2.28 (s, 6H), 1.18 (t, J = 7.6 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 148.3, 137.9, 135.5, 133.9, 132.6, 129.8, 126.9, 115.5, 27.5, 20.9, 15.6; HRMS (MALDI) m/z: $[M]^+$ calcd for $C_{22}H_{23}NS_2$, 365.1272; found, 365.1266.

*4-Isopropyl-2,6-bis(p-tolylthio)aniline (**6ac**).* Deep-yellow solid (petroleum ether/EtOAc = 150:1); 89% (67.5 mg); mp 68−70 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (s, 2H), 7.03 (d, J = 8.1 Hz, 4H), 6.98 (d, J = 8.3 Hz, 4H), 4.78 (s, 2H), 2.88−2.64 (m, 1H), 2.27 (s, 6H), 1.20 (d, J = 6.9 Hz, 6H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 148.4, 138.6, 136.6, 135.4, 132.6, 129.8, 126.8, 115.3, 32.9, 24.0, 20.9; HRMS (MALDI) m/z: $[M]^+$ calcd for $C_{23}H_{25}NS_2$, 379.1428; found, 379.1422.

*4-(tert-Butyl)-2,6-bis(p-tolylthio)aniline (**6ad**).* Light-yellow liquid (petroleum ether/EtOAc = 150:1); 95% (74.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (s, 2H), 7.04 (d, J = 8.1 Hz, 4H), 6.98 (d, J = 8.2 Hz, 4H), 4.77 (s, 2H), 2.28 (s, 6H), 1.27 (s, 9H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 148.1, 141.0, 135.8, 135.4, 132.6, 129.8, 126.7, 115.0, 34.0, 31.4, 20.9; HRMS (MALDI) m/z: $[M]^+$ calcd for $C_{24}H_{27}NS_2$, 393.1585; found, 393.1582.

*4-Methoxy-2,6-bis(p-tolylthio)aniline (**6ae**).* Bright-yellow liquid (petroleum ether/EtOAc = 150:1); 40% (29.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (s, 2H), 7.06 (d, J = 6.7 Hz, 8H), 3.72 (s, 3H), 2.29 (s, 6H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 151.4, 144.5, 143.4, 136.1, 131.9, 129.9, 127.8, 122.9, 117.7, 55.9, 21.0; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{22}NOS_2$, 368.1137; found, 368.1122.

*4-Fluoro-2,6-bis(p-tolylthio)aniline (**6af**).* Wine-red solid (petroleum ether/EtOAc = 150:1); 62% (44.1 mg); mp 53−55 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (d, J = 8.2 Hz, 2H), 7.07 (s, 8H), 4.70 (s, 2H), 2.30 (s, 6H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.1 (C−F, $^1J_{C-F}$ = 240.5 Hz), 145.59 (C−F, $^4J_{C-F}$ = 2.1 Hz), 136.6, 131.1, 130.0, 128.4, 122.84 (C−F, $^2J_{C-F}$ = 22.7 Hz), 117.77 (C−F, $^3J_{C-F}$ = 7.9 Hz), 20.98; ^{19}F NMR (376 MHz, $CDCl_3$): δ −126.1; HRMS (MALDI) m/z: $[M]^+$ calcd for $C_{20}H_{18}FNS_2$, 355.0865; found, 355.0859.

*4-Chloro-2,6-bis(p-tolylthio)aniline (**6ag**).* Light-yellow solid (petroleum ether/EtOAc = 150:1); 77% (57.2 mg); mp 112−114 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (s, 2H), 7.10−7.02 (m, 8H), 4.90 (s, 2H), 2.30 (s, 6H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 148.2, 136.5, 136.5, 131.2, 130.0, 128.0, 121.4, 117.7, 21.0; HRMS (MALDI) m/z: $[M]^+$ calcd for $C_{20}H_{18}ClNS_2$, 371.0569; found, 371.0563.

*2,6-Bis((4-methoxyphenyl)thio)-4-methylaniline (**6ah**).* Light-yellow liquid (petroleum ether/EtOAc = 150:1); 69% (59.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (s, 2H), 7.11 (d, J = 8.8 Hz, 4H), 6.79 (d, J = 8.8 Hz, 4H), 4.78 (s, 2H), 3.75 (s, 6H), 2.18 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.4, 147.0, 137.5, 129.8, 127.31, 126.4, 117.2, 114.7, 55.3, 20.0; HRMS (MALDI) m/z: $[M]^+$ calcd for $C_{21}H_{21}NO_2S_2$, 383.1014; found, 383.1012.

*2,6-Bis((4-fluorophenyl)thio)-4-methylaniline (**6ai**).* Dark-red liquid (petroleum ether/EtOAc = 150:1); 80% (57.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (s, 2H), 7.07 (m, J = 8.7, 5.1 Hz, 4H), 6.93 (t, J = 8.6 Hz, 4H), 4.80 (s, 2H), 2.22 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.3 (C−F, $^1J_{C-F}$ = 245.6 Hz), 147.9, 139.1, 131.1 (C−F, $^4J_{C-F}$ = 3.2 Hz), 128.82 (C−F, $^3J_{C-F}$ = 7.9 Hz), 127.6, 116.1 (C−F, $^2J_{C-F}$ = 22.1 Hz), 115.7, 20.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ −116.5. HRMS (MALDI) m/z: $[M]^+$ calcd for 359.0614; found, 359.0618.

*2,6-Bis((4-chlorophenyl)thio)-4-methylaniline (**6aj**).* White solid (petroleum ether/EtOAc = 150:1); 90% (70.6 mg); mp 92−94 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (s, 2H), 7.22−7.16 (m, 4H), 7.03−6.96 (m, 4H), 4.76 (s, 2H), 2.24 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 148.3, 139.8, 134.8, 131.6, 129.1, 127.8, 127.7, 114.6, 20.0; HRMS (MALDI) m/z: $[M]^+$ calcd for $C_{19}H_{15}Cl_2NS_2$, 391.0023; found, 391.0019.

*2,6-Bis((4-bromophenyl)thio)-4-methylaniline (**6ak**).* White solid (petroleum ether/EtOAc = 150:1); 88% (84.7 mg); mp 94−96 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (s, 2H), 7.33 (d, J = 8.0 Hz, 4H), 6.93 (d, J = 7.9 Hz, 4H), 4.74 (s, 2H), 2.24 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 148.4, 139.9, 135.5, 132.0, 128.0, 127.7, 119.3, 114.4, 20.0; HRMS (MALDI) m/z: $[M]^+$ calcd for $C_{19}H_{15}Br_2NS_2$, 480.8992; found, 480.9004.

*4-Methyl-2,6-bis(m-tolylthio)aniline (**6al**).* Bright-yellow liquid (petroleum ether/EtOAc = 150:1); 84% (59.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (s, 2H), 7.10 (t, J = 7.8 Hz, 2H), 6.92 (d, J = 7.3 Hz, 4H), 6.86 (d, J = 7.9 Hz, 2H), 4.81 (s, 2H), 2.26 (s, 6H), 2.24 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 148.6, 139.5, 138.8, 136.1, 128.9, 127.3, 127.1, 126.5, 123.5, 114.8, 21.4, 20.0; HRMS (MALDI) m/z: $[M]^+$ calcd for $C_{21}H_{21}NS_2$, 351.1115; found, 351.1111.

*2,6-Bis((3-methoxyphenyl)thio)-4-methylaniline (**6am**).* Light-yellow liquid (petroleum ether/EtOAc = 150:1); 40% (30.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (s, 2H), 7.13 (t, J = 8.0 Hz, 2H), 6.70−6.59 (m, 6H), 4.72 (s, 2H), 3.71 (s, 6H), 2.23 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.0, 148.7, 139.9, 137.8, 129.8, 127.4, 118.6, 114.5, 111.9, 111.1, 55.1, 20.0; HRMS (MALDI) m/z: $[M]^+$ calcd for $C_{21}H_{21}NO_2S_2$, 383.1014; found, 383.1015.

*4-Methyl-2,6-bis(o-tolylthio)aniline (**6an**).* Light-yellow solid (petroleum ether/EtOAc = 150:1); 92% (64.6 mg); mp 113−115 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (s, 2H), 7.16−7.13 (m, 2H), 7.07−7.00 (m, 4H), 6.79−6.71 (m, 2H), 4.72 (s, 2H), 2.40 (s, 6H), 2.23 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 148.4, 139.2, 135.4, 135.2, 130.2, 127.7, 126.5, 125.5, 125.4, 114.5, 20.0; HRMS (ESI) $[M + H]^+$ m/z calcd for $C_{21}H_{22}NS_2$, 352.1188; found, 352.1175.

*2,6-Bis((2-ethylphenyl)thio)-4-methylaniline (**6ao**).* Light-yellow solid (petroleum ether/EtOAc = 150:1); 85% (64.5 mg); mp 53−55 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (s, 2H), 7.17 (d, J = 7.4 Hz, 2H), 7.09 (t, J = 7.4 Hz, 2H), 7.02 (t, J = 7.5 Hz, 2H), 6.76 (d, J = 7.8 Hz, 2H), 4.69 (s, 2H), 2.80 (q, J = 7.5 Hz, 4H), 2.23 (s, 3H), 1.29 (t, J = 7.5 Hz, 6H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 148.4, 141.3, 139.2, 134.6, 128.5, 127.7, 126.5, 125.9, 125.7, 114.8, 26.6, 20.0, 14.2; HRMS (MALDI) m/z: $[M]^+$ calcd for $C_{23}H_{25}NS_2$, 379.1428; found, 379.1427.

*2,6-Bis((2-methoxyphenyl)thio)-4-methylaniline (**6ap**).* White solid (petroleum ether/EtOAc = 50:1); 64% (49.0 mg); mp 141−142 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (s, 2H), 7.11 (t, J = 7.7 Hz, 2H), 6.87−6.78 (m, 4H), 6.69 (d, J = 7.6 Hz, 2H), 4.87 (s, 2H), 3.91 (s, 6H), 2.23 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.7, 149.4, 140.0, 127.4, 126.4, 124.5, 121.2, 113.5, 110.3, 55.8, 20.0; HRMS (MALDI) m/z: $[M]^+$ calcd for $C_{21}H_{21}NO_2S_2$, 383.1014; found, 383.1015.

*2,6-Bis((2-chlorophenyl)thio)-4-methylaniline (**6aq**).* White solid (petroleum ether/EtOAc = 150:1); 83% (65.1 mg); mp 120−122 °C;

https://dx.doi.org/10.1021/acs.joc.0c02078
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^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (s, 2H), 7.36−7.31 (m, 2H), 7.09−7.03 (m, 4H), 6.70−6.65 (m, 2H), 4.80 (s, 2H), 2.26 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 149.2, 140.6, 135.4, 131.2, 129.6, 127.9, 127.1, 126.3, 113.3, 20.0; HRMS (MALDI) m/z: $[M]^+$ calcd for $C_{19}H_{15}Cl_2NS_2$, 391.0023; found, 391.0019.

*2,6-Bis((2-bromophenyl)thio)-4-methylaniline (**6ar**).* White solid (petroleum ether/EtOAc = 150:1); 94% (90.4 mg); mp 137−139 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55−7.48 (m, 2H), 7.44 (s, 2H), 7.16−7.08 (m, 2H), 7.02−6.95 (m, 2H), 6.67−6.61 (m, 2H), 4.80 (s, 2H), 2.27 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 149.1, 140.6, 137.3, 132.9, 128.0, 127.7, 126.5, 126.3, 121.0, 113.9, 20.0; HRMS (MALDI) m/z: $[M]^+$ calcd for $C_{19}H_{15}Br_2NS_2$, 480.8992; found, 480.9004.

*2-Iodo-4-methyl-6-(p-tolylthio)aniline (**7aa**).* Yellow liquid (petroleum ether/EtOAc = 100:1); 62% (44.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 1.2 Hz, 1H), 7.24 (d, J = 1.5 Hz, 1H), 7.07−7.00 (m, 4H), 4.42 (s, 2H), 2.28 (s, 3H), 2.19 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.2, 140.9, 137.5, 135.9, 132.3, 129.9, 129.2, 127.4, 115.1, 83.9, 20.9, 19.6; HRMS (MALDI) m/z: $[M]^+$ calcd for $C_{14}H_{14}INS$, 354.9892; found, 354.9892.

*2-((4-Fluorophenyl)thio)-6-iodo-4-methylaniline (**7ab**).* Yellow liquid (petroleum ether/EtOAc = 100:1); 63% (45.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56−7.52 (m, 1H), 7.24 (d, J = 1.2 Hz, 1H), 7.11−7.06 (m, 2H), 6.98−6.91 (m, 2H), 4.39 (s, 2H), 2.20 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.4 (C−F, $^1J_{C-F}$ = 245.7 Hz), 146.1, 141.2, 137.6, 131.0 (C−F, $^4J_{C-F}$ = 3.2 Hz), 129.4, 129.0 (C−F, $^3J_{C-F}$ = 7.9 Hz), 116.2 (C−F, $^2J_{C-F}$ = 22.1 Hz), 114.7, 83.9, 19.6; ^{19}F NMR (377 MHz, $CDCl_3$): δ −116.34; HRMS (MALDI) m/z: $[M]^+$ calcd for $C_{13}H_{11}FINS$, 358.9641; found, 358.9641.

*2-((4-Chlorophenyl)thio)-6-iodo-4-methylaniline (**7ac**).* Yellow liquid (petroleum ether/EtOAc = 100:1); 60% (45.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 1.3 Hz, 1H), 7.25 (d, J = 1.3 Hz, 1H), 7.21−7.17 (m, 2H), 7.02−6.98 (m, 2H), 4.59 (s, 2H), 2.20 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.34, 141.6, 137.9, 134.7, 131.6, 129.4, 129.2, 127.9, 113.5, 83.9, 19.6; HRMS (MALDI) m/z: $[M]^+$ calcd for $C_{13}H_{11}ClINS$, 374.9345; found, 374.9346.

*2-((4-Bromophenyl)thio)-6-iodo-4-methylaniline (**7ad**).* Yellow liquid (petroleum ether/EtOAc = 100:1); 50% (42.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 1.1 Hz, 1H), 7.33 (d, J = 8.5 Hz, 2H), 7.25 (d, J = 1.0 Hz, 1H), 6.93 (d, J = 8.5 Hz, 2H), 4.60 (s, 2H), 2.20 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.4, 141.6, 137.9, 135.4, 132.1, 129.4, 128.1, 119.4, 113.3, 83.9, 19.6; HRMS (MALDI) m/z: $[M]^+$ calcd for $C_{13}H_{11}BrINS$, 418.8840; found, 418.8842.

*2-Iodo-4-methyl-6-(m-tolylthio)aniline (**7ae**).* Yellow liquid (petroleum ether/EtOAc = 100:1); 70% (49.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, J = 1.3 Hz, 1H), 7.26 (d, J = 1.3 Hz, 1H), 7.12 (t, J = 7.9 Hz, 1H), 6.95 (d, J = 6.5 Hz, 2H), 6.86 (d, J = 7.9 Hz, 1H), 4.31 (s, 2H), 2.28 (s, 3H), 2.20 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.4, 141.2, 138.9, 137.9, 135.8, 129.2, 129.0, 127.4, 126.8, 123.9, 114.3, 83.8, 21.4, 19.7; HRMS (ESI) $[M + H]^+$ m/z calcd for $C_{14}H_{15}INS$, 355.9964; found, 355.9969.

*2-Iodo-4-methyl-6-(o-tolylthio)aniline (**7af**).* Yellow liquid (petroleum ether/EtOAc = 100:1); 65% (46.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 1.3 Hz, 1H), 7.20 (d, J = 1.3 Hz, 1H), 7.18−7.14 (m, 1H), 7.09−7.00 (m, 2H), 6.74−6.70 (m, 1H), 4.22 (s, 2H), 2.40 (s, 3H), 2.19 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.3, 141.1, 137.7, 135.4, 135.0, 130.2, 129.4, 126.7, 125.8, 125.6, 113.8, 83.8, 20.0, 19.7; HRMS (MALDI) m/z: $[M]^+$ calcd for $C_{14}H_{14}INS$, 354.9892; found, 354.9892.

*2-((2-Chlorophenyl)thio)-6-iodo-4-methylaniline (**7ag**).* Yellow liquid (petroleum ether/EtOAc = 100:1); 67% (50.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J = 1.4 Hz, 1H), 7.36−7.32 (m, 1H), 7.27 (d, J = 1.3 Hz, 1H), 7.09−7.04 (m, 2H), 6.66−6.61 (m, 1H), 4.54 (s, 2H), 2.22 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.9, 142.0, 138.5, 135.4, 131.0, 129.6, 129.5, 127.3, 126.4, 126.3, 112.1, 83.8, 19.6; HRMS (MALDI) m/z: $[M]^+$ calcd for $C_{13}H_{11}ClINS$, 374.9345; found, 374.9346.

*2-((2-Bromophenyl)thio)-6-iodo-4-methylaniline (**7ah**).* Yellow liquid (petroleum ether/EtOAc = 100:1); 66% (55.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J = 1.7 Hz, 1H), 7.52 (m, J = 7.9, 1.1 Hz, 1H), 7.27 (d, J = 1.3 Hz, 1H), 7.14−7.09 (m, 1H), 6.98 (m, J = 7.7, 1.5 Hz, 1H), 6.60 (m, J = 8.0, 1.4 Hz, 1H), 4.31 (s, 2H), 2.22 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.8, 142.0, 138.4, 137.3, 132.8, 129.5, 127.9, 126.5, 126.3, 120.7, 112.6, 83.8, 19.6; HRMS (MALDI) m/z: $[M]^+$ calcd for $C_{13}H_{11}BrINS$, 418.8840; found, 418.8842.

*3-Methyl-10H-phenothiazine (**5ah'**, CAS: 3939-47-7).*[33,34] ^{1}H NMR (400 MHz, DMSO): δ 8.45 (s, 1H), 6.95 (t, J = 7.6 Hz, 1H), 6.88 (d, J = 7.5 Hz, 1H), 6.77 (d, J = 7.9 Hz, 1H), 6.70 (d, J = 12.2 Hz, 2H), 6.65 (d, J = 7.9 Hz, 1H), 6.57 (d, J = 8.0 Hz, 1H), 2.11 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, DMSO): δ 142.8, 140.0, 131.1, 128.4, 127.9, 126.9, 126.68, 121.9, 116.7, 116.6, 114.7, 20.4.

*7-Methylbenzo[5,6][1,4]thiazino[2,3,4-kl]phenothiazine (**6ar'**).*[33,34] White solid (petroleum ether/EtOAc = 100:1); 65% (41.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21−7.14 (m, 4H), 7.09 (t, J = 7.2 Hz, 2H), 7.01 (t, J = 7.4 Hz, 2H), 6.79 (s, 2H), 2.20 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 142.7, 136.8, 134.7, 127.9, 127.3, 126.9, 126.0, 125.4, 124.4, 120.4, 20.4; HRMS (MALDI) m/z: $[M]^+$ calcd for $C_{19}H_{13}NS_2$, 319.0489; found, 319.0492.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02078.

Full characterization data and copies of NMR spectral data (PDF)

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■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (21871226 and 21572194) and the China Postdoctoral Science Foundation (2018M632976 and 2019T120709).

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https://dx.doi.org/10.1021/acs.joc.0c02078
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