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TBAI-mediated sulfenylation of arenes with arylsulfonyl hydrazides in DPDME

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ABSTRACT

An efficient TBAI (tetrabutylammonium iodide)-mediated C–H sulfenylation of arenes with arylsulfonyl hydrazides in dipropylene glycol dimethyl ether (DPDME) was described. Various electron-rich arenes were applicable in the reaction, such as naphthylamine, naphthol, aniline, indole, pyrrole, and imidaz o [1,2-a] pyridine. A wide range of the aryl sulfides were obtained with good functional group tolerance. This method features green reaction conditions (odorless and easily available sulfur reagent, recyclable TBAI, and DPDME as solvent), and broad substrate scope. The synthetic potential is demonstrated by gram-scale synthesis and downstream transformations. The mechanism studies show that the reaction is achieved through electrophilic substitution process, and diaryl disulfide may be the main intermediate.

1. Introduction

Aryl sulfides as sulfur-containing organic compounds are indispensable in natural products and bioactive molecules [1], and also have wide applications in a range of fields such as drug development [2], materials science [3], and organic syntheses [4]. In view of the important applications of sulfide compounds and the broad potential application, chemists have developed a series of methods to construct sulfides [5]. Traditionally, transition-metal-catalyzed cross-couplings between C-X/C–H and various sulfur sources have been developed [6]. In spite of some great advantages, some of these processes could suffer from certain drawbacks, including pre-functionalization of reactants, harsh reaction conditions, and toxic metal catalysts [7]. Recently, non-metal-catalyzed or mediated direct sulfenylation of arenes has received considerable attention. Compared with traditional synthetic methods, the metal-free catalysis/participation in C–H functionalization often has the following characteristics: 1) No prior functionalization to prepare organic halides or organometallic reagents; 2) higher atomic economy; 3) shorter synthesis steps; 4) less generated waste [8]. In particular, iodine promotes direct C–H sulfenylation the of arenes for the synthesis of aryl sulfides has been extensively developed [9]. Various sulfur reagents and precursors including thiols, disulfides, sulfonyl chlorides, sulfonyl hydrazines, *N*-(thio) succinicmides, sodium sulfonates, and others have been employed [10–16]. However, these current synthetic methodes suffer from limitations, such as the use of bad odor, air-sensitive thiol substrates, toxic organic solvents, and relatively narrow substrate scopes. Therefore, the development of new sustainable protocols for the synthesis of diverse aryl sulfides in green solvents, such as water or DPDME (dipropylene glycol dimethyl ether), under simple reaction conditions is still highly desirable.

In 2016, Lu et al. reported an I_2/PPh_3-mediated regioselective arylthiolations of aromatic amines, arenols and ketones in an aqueous system, whereby arylsulfenyl radicals in situ generated from odorless sodium arylsulfinates could react with free anilines containing electron-withdrawing groups and complex substrates (estrone and progesterone) (Scheme 1a) [17]. Sinha et al. developed a BSA-iodine cooperative catalyzed C–H sulfenylation of indoles/hydroxyaryls with thiophenols in water. This green cooperative protocol is extendable for sulfenylation of hydroxyaryls with diverse thiols without using any toxic metal catalysts, bases or oxidants (Scheme 1b) [18]. In 2018, Yuan et al. provided a Cobalt-catalyzed aerobic cross-dehydrogenative coupling of arene and thiols. This methodology achieved the C–S bond formation in water with molecular oxygen as the sole oxidant while avoid the use of

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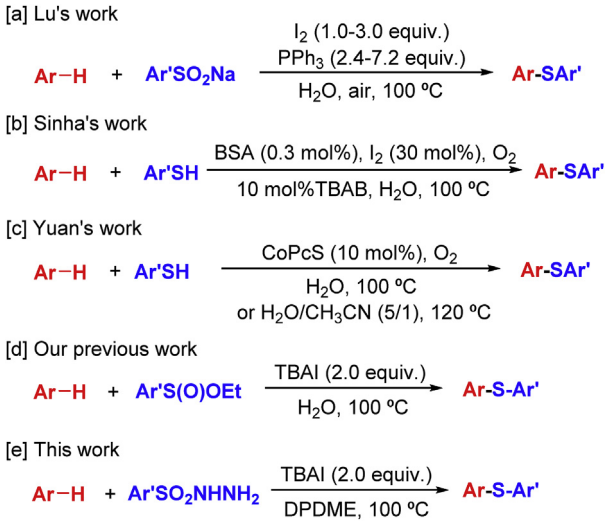


Scheme 1. TBAI-Mediated sulfenylation of arenes.

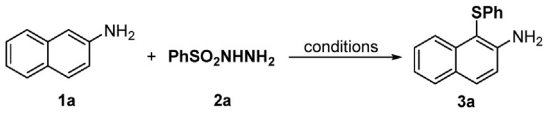
toxic solvents (Scheme 1c) [19]. Recently, we have demonstrated a TBAI-mediated direct sulfenylation of arenes with ethyl arylsulfinates in water, a series of aryl sulfides were obtained in excellent yields. The advantages of this green protocol were simple reaction conditions (metal-free, water as the solvent, in the air), odorless and easily available sulfur reagent, broad substrate scope (Scheme 1d) [20]. As our continuing efforts exploring organosulfur chemistry [21], we report herein an environmentally benign method for the synthesis of aryl sulfides via sulfenylation of arenes with arylsulfonyl hydrazides in DPDME (Scheme 1e). This new method offers some advantages, including a green reaction solvent, a stable and odorless sulfur reagent, simple reaction condition, and recyclable TBAI as promoter. Most importantly, this system has a wider range of substrate than the reported methods.

2. Results and discussion

2.1. Optimization of the reaction conditions

First, we selected β-naphthylamine and *p*-toluenesulfonyl hydrazide as model substrates to optimize the reaction conditions, and the results are shown in Table 1. When the ratio of **1a** and **2a** is 1: 2, the reaction is performed in water at 100 °C for 24 h, and the product 1-(phenylthio)naphthalen-2-amine **3a** is obtained in 45% yield (entry 1). When the ratio of **1a** and **2a** is increased to 1: 3, the yield was increased to 52% (entry 2). To our delight, when 3 equivalents of TBAI were added to the above system, 83% yield could be obtained (entry 3). Also, other phase transfer catalyst (PTC) such as TBAB or TBAC had a good promotion effect on the model reaction, affording the product **3a** in 71% and 68% yields, respectively (entries 4 and 5). However, TBAF as a PTC inhibited the reaction (entry 6). Lowering the reaction temperature was detrimental to the sulfenylation reaction (entry 7). When DPDME a green solvent is used, the reaction could proceed smoothly and provide an excellent yield of 95% (entry 8). Reducing the amount of TBAI could also obtain 90% yield (entry 9). To our delight, when the amount of DPDME was reduced to 0.5 mL, almost quantitative yield of target product **3a** was obtained (entry 10). By shortening the reaction time to 12 h, an excellent yield could still be maintained (entry 11). Based on the above reaction conditions, when the ratio of **1a** and **2a** is 1: 2 or the amount of TBAI was one equivalent, the reaction yield was slightly reduced (entries 12 and 13). Finally, the

Table 1
Optimized reaction conditions[a].



Entry	n (mmol, 1a/2a)	PTC(equiv.)	T (°C)	Solvent (mL)	Yield (%)[b]
1	0.3/0.6	/	100	H_2O (3)	45
2	0.3/0.9	/	100	H_2O (3)	52
3	0.3/0.9	TBAI (3)	100	H_2O (3)	83
4	0.3/0.9	TBAB (3)	100	H_2O (3)	71
5	0.3/0.9	TBAC (3)	100	H_2O (3)	68
6	0.3/0.9	TBAF (3)	100	H_2O (3)	Nr
7	0.3/0.9	TBAI (3)	80	H_2O (3)	69
8	0.3/0.9	TBAI (3)	100	DPDME (3)	95
9	0.3/0.9	TBAI (2)	100	DPDME (3)	90
10	0.3/0.9	TBAI (2)	100	DPDME (0.5)	99
11[c]	0.3/0.9	TBAI (2)	100	DPDME (0.5)	97
12	0.3/0.6	TBAI (2)	100	DPDME (0.5)	92
13	0.3/0.9	TBAI (1)	100	DPDME (0.5)	89

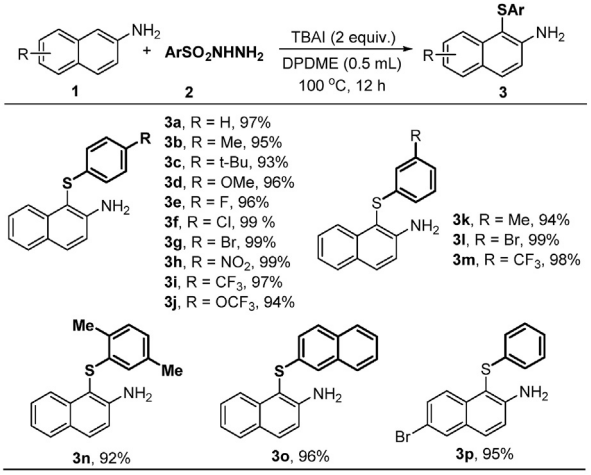
[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.6 or 0.9 mmol), TBAI (0.6 or 0.9 mmol), solvent (3 mL or 0.5 mL), 100 °C, 24 h.
[b] Isolated yield.
[c] 12 h.

optimal reaction conditions are: **1a** (0.3 mmol), **2a** (0.9 mmol), TBAI (0.6 mmol), DPDME (0.5 mL), under air, at 100 °C, for 12 h.

2.2. Scope and limitations of substrates

Under optimal conditions, we investigated the scope of arylsulfonyl hydrazides for this sulfenylation, and the results were summarized in Table 2. The arylsulfonyl hydrazides with a variety of substituents, such as methyl, *tert*-butyl, methoxy, fluoro, chloro, bromo, nitro, trifluoromethyl, and trifluoromethoxy groups were tolerated to this sulfenylation of naphthalen-2-amine to provide the desired products **3b**–**3m** in excellent yields. The reaction with the sterically congested substrate proceeded very well, affording the desired product **3n** in 92% yield. The substrate with a certain steric hindrance, 2,5-dimethylbenzenesulfonohydrazide, could also

Table 2
Sulfenylation of β-naphthylamine with $ArSO_2NHNH_2$ in DPDME[a].



[a] Reaction conditions: **1** (0.3 mmol), **2** (0.9 mmol), TBAI (0.6 mmol), under air, 100 °C, 12 h; Isolated yield.

react with β-naphthylamine smoothly to give the desired product **3n** with excellent yields. 2-(Ethylsulfonyl)naphthalene performed also quite well in the transformation, and the product **3o** was obtained in 96% yield. The optimal conditions were amenable to the reaction of 6-bromonaphthalen-2-amine, affording the desired product **3p** in 95% yield. It is conceivable that a bromo substituent group should be helpful for further transformation of the product **3p**.

Subsequently, we investigated the sulfenylation reaction of α-naphthylamine with arylsulfonyl hydrazides. The results showed that benzenesulfonyl hydrazide, 4-methylphenylsulfonyl hydrazide, and 4-chlorophenylsulfonyl hydrazide reacted with α-naphthylamine to provide dithioether products **3q**-**3s** with excellent yields. However, 4-nitrophenylsulfonyl hydrazide with a strong electron-withdrawing group as a reactant gave a monothioether product **3t** in 90% yield. It should be noted that when 1 equivalent of benzenesulfonyl hydrazide was used, the monothioether product 4-(phenylthio)naphthalen-1-amine **3u** was also obtained in 58% yield. Table 3.

This excellent reaction system prompted us to investigate the sulfenylation of other aromatic amines as substrates. As shown in Table 4, aniline reacted smoothly with various arylsulfonyl hydrazides to obtain *para*-substituted products **4a**-**4c** in 91–95% yields with the high regioselectivity. In contrast, the reactions of [1,1′-biphenyl]-2-amine with arylsulfonyl hydrazides also proceeded very well, and affording the products **4d**-**4f** in 83–89% yields. The structure of **4d** was further confirmed by single crystal X-ray diffraction (Fig. 1, CCDC: 2,017,288). In addition, we also tried the reaction of diamino substituted substrate such as naphthalene-2,3-diamine, the product 1,4-bis(phenylthio)naphthalene-2,3-diamine **4g** was obtained in 59% yield. Notably, the reaction was compatible with some substituted aniline such as 2-methoxyaniline and 2,5-dimethylaniline, affording the corresponding products **4h** and **4i** in 81% and 99% yields, respectively.

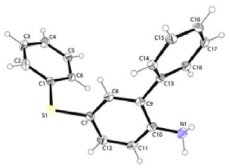
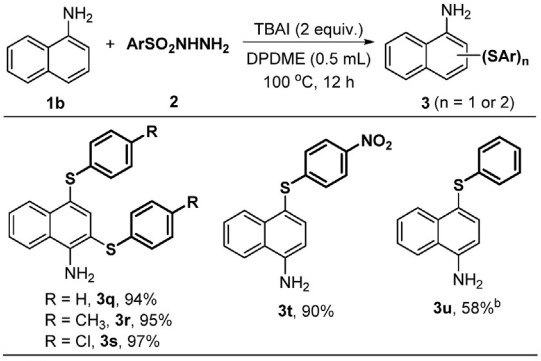


Fig. 1. The crystal structure of compound **4d**.

To further examine the scope and limitations of the sulfenylation, the reactions of various arylsulfonyl hydrazides and 1*H*-indole were tested (Table 5). The results indicated that the substituents from arylsulfonyl hydrazides did not remarkably affect the reaction, and providing the corresponding products **5a**-**5d** with excellent yields. Next, pyrrole and its derivatives were applicable in this reaction, and the 2,5- or 3,4-disulfide substituted products **5e**-**5g** were isolated in 82–90% yields. In addition, the reactivity of imidaz o [1,2-a] pyridine was also examined, the reactions with benzenesulfonohydrazide and 4-methylbenzenesulfonohydrazide worked well, leading to **5h** and **5i** in excellent yields. The reaction with 4-fluorobenzenesulfonohydrazide provided the target product in 58% yield.

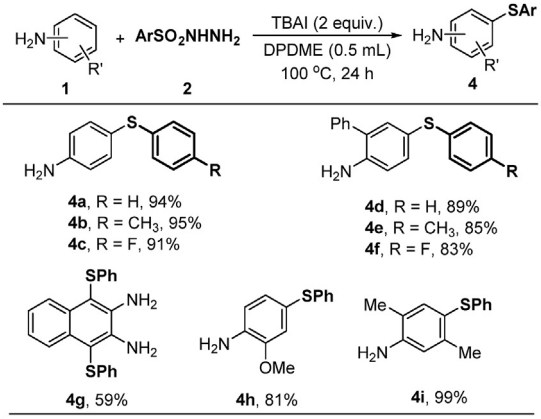
To further expand the substrate scope, we next examined the sulfenylation of naphthalen-2-ol (Table 6). However, we found that the reactions of naphthalen-2-ol with various arylsulfonyl hydrazides could proceed smoothly at 140 °C, and the corresponding products **6a**-**6i** in 43–84% yields. The substrate naphthalene-2-sulfonohydrazide provided the product **6j** in 69% yield. The above results showed that naphthalen-2-ol displayed lower reactivity than β-naphthylamine. In addition, the reactions of naphthalen-1-ol with arylsulfonyl hydrazides was also investigated, and the 2,4-disubstituted aryl sulfides products **6k**-**6m** were obtained in 77–82% yields.

Table 3
Sulfenylation of α-naphthylamine with $ArSO_2NHNH_2$ in DPDME [a]..



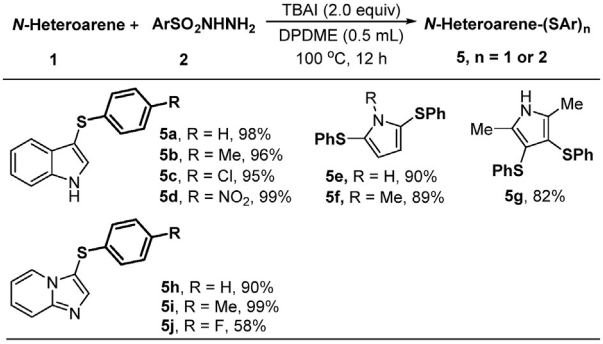
[a] Reaction conditions: **1b** (0.3 mmol), **2** (0.9 mmol), TBAI (0.6 mmol), 100 °C, 12 h; Isolated yield. [b] $PhSO_2NHNH_2$ (0.3 mmol), TBAI (0.3 mmol).

Table 4
Sulfenylation of other aromatic amines with $ArSO_2NHNH_2$ in DPDME [a]..



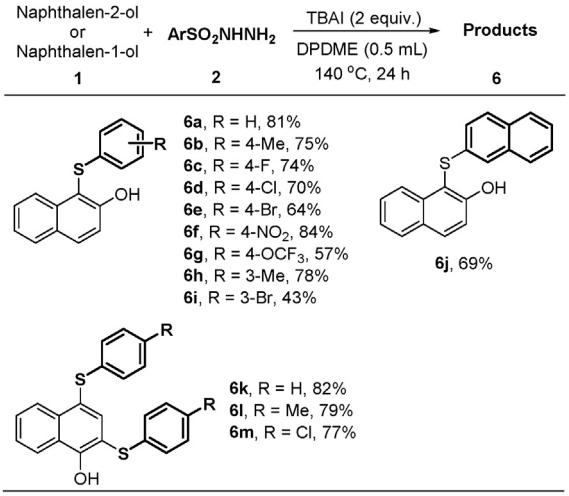
[a] Reaction conditions: **1** (0.3 mmol), **2** (0.9 mmol), TBAI (0.6 mmol), 100 °C, 24 h; Isolated yield.

Table 5
Sulfenylation of other aromatic amines with $ArSO_2NHNH_2$ in DPDME [a]..



[a] Reaction conditions: **1** (0.3 mmol), **2** (0.9 mmol), TBAI (0.6 mmol), 100 °C, 12 h; Isolated yield

Table 6
Sulfenylation of naphthol with $ArSO_2NHNH_2$ in DPDME [a]..

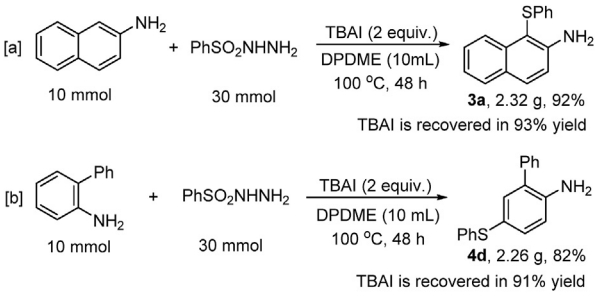


[a] Reaction conditions: **1** (0.3 mmol), **2** (0.9 mmol), TBAI (0.6 mmol), 140 °C, 24 h; Isolated yield.

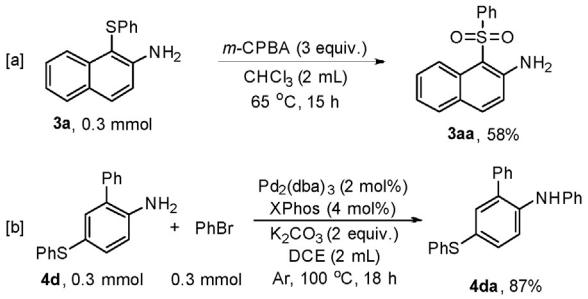
To demonstrate the practicality of this protocol, gram-scale reaction was conducted under standard conditions (Scheme 2). 10 mmol of naphthalen-2-amine reacted with benzenesulfonohydrazide (30 mmol) in 10 mL of DPDMF to give **3a** (2.32 g) in 92% yield (Scheme 2a). The reaction of [1,1′-biphenyl]-2-amine (10 mmol) with benzenesulfonohydrazide (30 mmol) was also performed to provide the product **4d** (2.26 g) in 82% yield (Scheme 2b). It is worth mentioning that after the above two reactions are completed, TBAI could be easily recovered through simple filtration in 93% and 91% yields, respectively.

The multifunctional sulfenylated products allowed many possible further derivations (Scheme 3). For example, oxidation of compound **3a** by *m*-CPBA afforded the product 1-(phenylsulfonyl) naphthalen-2-amine **3aa** in 58% yield (Scheme 3a). Compound **4d** reacted with bromobenzene through C—N coupling in the presence of $Pd_2(dba)_3$/XPhos as catalyst, furnishing the product *N*-phenyl-5-(phenylthio)-[1,1′-biphenyl]-2-amine **4da** in 87% yield (Scheme 3b).

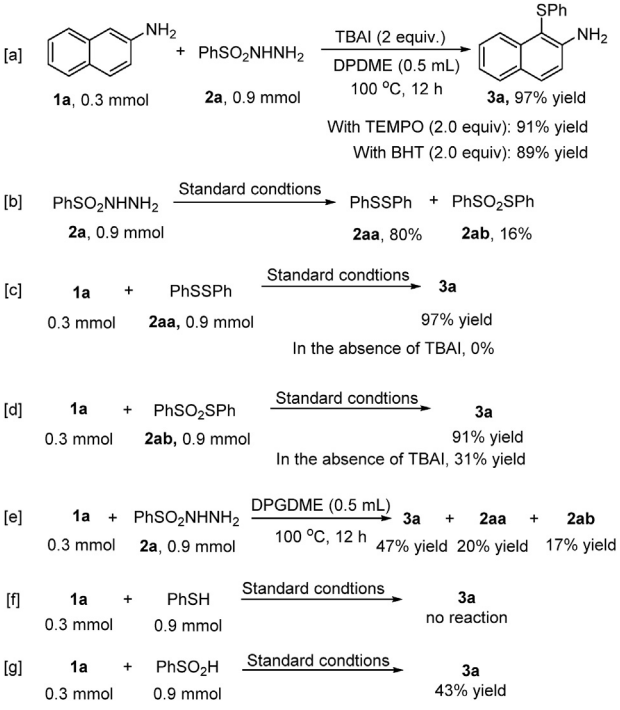
To gain reasonable insight into the reaction mechanism, a series of control experiments were conducted. As Scheme 4 shown, in the presence of TEMPO or BHT, the reaction of naphthalen-2-amine with benzenesulfonohydrazide was not suppressed, and the product **3a** was obtained in 91% and 89% yields, respectively (Scheme 4a). The results showed that the sulfenylation reaction should not be a free radical process. The benzenesulfonohydrazide was treated under standard conditions, affording the products



Scheme 2. Gram-scale synthesis of **3a** and **4d**.

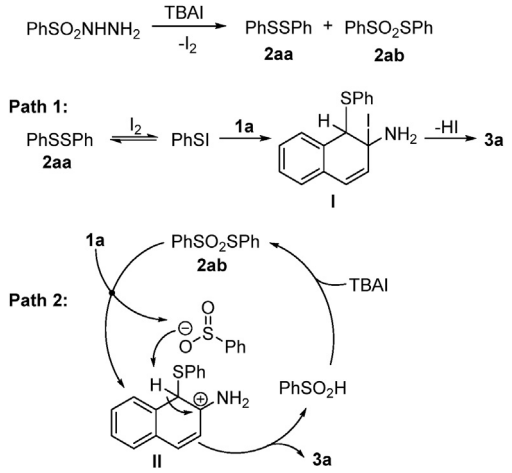


Scheme 3. Chemical transformations of **3a** and **4d**.



Scheme 4. The control experiments.

sulfinothioyldibenzene and S-phenyl benzenesulfonothioate in 80% and 16% yields, respectively (Scheme 4b). This observation implies that sulfinothioyldibenzene and *S*-phenyl benzenesulfonothioate may be important intermediates generated during the reaction. Treatment of naphthalen-2-amine with sulfinothioyldibenzene or S-phenyl benzenesulfonothioate respectively could successfully obtain the desired product **3a** in excellent yields, which further confirms our above speculation (Scheme 4c and 4d). Further, we found that the reaction of 2-naphthylamine and sulfinothioyldibenzene was difficult to proceed in the absence of TBAI (Scheme 4c). This result indicated that TBAI was involved in this sulfenylation reaction. In contrast, the reaction of 2-naphthylamine with diphenyldisulfide in the absence of TBAI can also occur (Scheme 4d). This fact is consistent with the experimental results of the model reaction in the absence of TBAI (Scheme 4e). Using benzenethiol as sulfur to react with **1a**, the desired product **3a** was not obtained (Scheme 4f). This phenomenon indicates that benzenethiol should not be an intermediate in the reaction. When benzenesulfinic acid was treated under the standard conditions, **3a** can be generated in 43% yield (Scheme 4g). This showed that benzenesulfinic acid may be involved in the catalytic cycle of the reaction.



Scheme 5. Proposed reaction mechanism.

Based on above investigation and analysis, a plausible mechanism is outlined in Scheme 5. The reaction is initiated by $PhSO_2NHNH_2$, which can be transformed by TBAI to form the intermediate sulfinothioyldibenzene **2aa** and the intermediate *S*-phenyl benzenesulfonothioate **2 ab**. Next, the sulfenylation of arenes is mainly achieved through the following two routes: (1) **Path 1** (major): Iodothiobenzene formed by the reaction of **2aa** with I_2 undergoes electrophilic substitution with β-naphthylamine to give intermediate **I**. The intermediate **I** loses HI to provide final product **3a**; (2) **Path 2** (minor): the intermediate **2 ab** as an electrophile reacted with **1a** to form the desired product **3a**. The benzenesulfinic acid generated can be converted into **2 ab** in the presence of TBAI. Finally, a sulfenylation cycle was established.

3. Experimental section

3.1. Materials and instruments

Unless otherwise noted, all synthetic steps were performed under air atmosphere using Schlenk tubes. The materials obtained from commercial sources were used without further purification. Melting points were determined with a fusiometer and are not corrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance III HD 400 MHz spectrometer in $CDCl_3$ or DMSO-d_6 solution. All chemical shifts were reported in ppm (δ) relative to the internal standard TMS (0 ppm). High resolution mass spectra (HRMS) were acquired in electrospray ionization (ESI) or atmospheric-pressure chemical ionization (APCI) modes using a TOF mass analyzer.

3.2. General procedure for TBAI-mediated direct sulfenylation of arenes with arylsulfonyl hydrazides

A mixture of arene (0.3 mmol), arylsulfonyl hydrazide (0.6 mmol), TBAI (0.6 mmol), and DPDME (0.5 mL) were added into a Schlenk tube. The solution was stirred and heated to 100 °C for 12 h in air. After completion of the reaction, the mixture was quenched with the saturated solution of NaCl (5 mL) and extracted with CH_2Cl_2 (10 mL × 3). The combined CH_2Cl_2 extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel using PE/EtOAc as the eluent.

3.3. 1-(Phenylthio)naphthalen-2-amine [**3a**] [13a]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 30) as eluent to give the product **3a** as a red solid (73.1 mg, 97%); mp 96.5–99.1 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.06 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 8.8 Hz, 1H), 7.73 (d, J = 7.6 Hz, 1H), 7.37 (t, J = 7.8 Hz, 1H), 7.25–7.14 (m, 2H), 7.06 (t, J = 7.2 Hz, 1H), 6.99 (d, J = 8.0 Hz, 1H), 6.04 (s, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.4, 136.9, 136.3, 131.5, 129.0, 128.4, 127.5, 127.2, 125.6, 124.9, 122.9, 121.5, 118.2, 100.6.

3.4. 1-(p-Tolylthio)naphthalen-2-amine [**3b**] [13a]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 30) as eluent to give the product **3b** as a red solid (72.4 mg, 95%); mp 112.4–117.0 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.06 (d, J = 8.5 Hz, 1H), 7.77 (d, J = 8.8 Hz, 1H), 7.71 (d, J = 7.7 Hz, 1H), 7.37 (td, J = 7.5, 1.3 Hz, 1H), 7.22–7.14 (m, 2H), 7.00 (d, J = 8.1 Hz, 2H), 6.90 (d, J = 8.2 Hz, 2H), 5.99 (s, 2H), 2.18 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.2, 136.3, 134.3, 133.3, 131.4, 129.6, 128.4, 127.4, 127.2, 125.9, 123.0, 121.4, 118.2, 101.4, 39.5, 20.4.

3.5. 1-((4-(tert-Butyl)phenyl)thio)naphthalen-2-amine [**3c**]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 30) as eluent to give the product **3c** as a red solid (85.5 mg, 93%); mp 120.2–122.4 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.08 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 8.9 Hz, 1H), 7.72 (d, J = 7.7 Hz, 1H), 7.37 (td, J = 7.7, 1.2 Hz, 1H), 7.24–7.14 (m, 4H), 6.91 (d, J = 8.5 Hz, 2H), 6.00 (s, 2H), 1.18 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.3, 147.6, 136.4, 133.4, 131.4, 128.4, 127.4, 127.2, 125.9, 125.5, 123.0, 121.4, 118.1, 101.2, 39.5, 34.0, 31.0; HRMS (ESI): m/z calcd for $C_{20}H_{21}NS$ $(M + Na)^+$: 330.1287, found: 330.1281.

3.6. 1-((4-Methoxyphenyl)thio)naphthalen-2-amine [**3d**] [13a]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 30) as eluent to give the product **3d** as a red solid (81.0 mg, 96%); mp 101.8–105.5 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.11 (d, J = 8.5 Hz, 1H), 7.75 (d, J = 8.9 Hz, 1H), 7.71 (d, J = 7.7 Hz, 1H), 7.41–7.36 (m, 1H), 7.16 (d, J = 8.9 Hz, 1H), 6.99 (d, J = 8.9 Hz, 1H), 6.80 (d, J = 8.9 Hz, 1H), 6.01 (s, 1H), 3.65 (s, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.5, 150.0, 136.2, 131.2, 128.4, 128.0, 127.4, 127.3, 127.2, 123.0, 121.4, 118.1, 114.8, 102.6, 55.1, 39.5.

3.7. 1-((4-Fluorophenyl)thio)naphthalen-2-amine [**3e**] [22]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 30) as eluent to give the product **3e** as a red solid (80.0 mg, 99%); mp 90.6–92.8 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.05 (d, J = 8.5 Hz, 1H), 7.78 (d, J = 8.9 Hz, 1H), 7.72 (d, J = 7.7 Hz, 1H), 7.39 (td, J = 8.0 Hz, 1.3 Hz, 1H), 7.21–7.14 (m, 2H), 7.09–6.99 (m, 4H), 6.06 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.6, 159.0, 150.3, 136.2, 132.4, 131.6, 128.5, 127.8, 127.2, 122.8, 121.5, 118.2, 116.1, 115.9, 101.1, 39.5.

3.8. 1-((4-Chlorophenyl)thio)naphthalen-2-amine [**3f**] [13a]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 30) as eluent to give the product **3f** as a red solid (84.8 mg, 99%); mp 123.1–125.8 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.01 (d, J = 8.4 Hz, 1H), 7.79 (d,

J = 8.9 Hz, 1H), 7.72 (d, J = 7.9 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.28–7.11 (m, 4H), 6.97 (d, J = 8.6 Hz, 2H), 6.07 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.5, 136.2, 136.1, 129.5, 128.9, 128.5, 127.6, 127.2, 122.7, 121.5, 118.2, 100.0, 39.5.

3.9. 1-((4-Bromophenyl)thio)naphthalen-2-amine [**3g**] [13a]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 30) as eluent to give the product **3g** as a red solid (97.9 mg, 99%); mp 107.5–109.5 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.00 (d, J = 8.3 Hz, 1H), 7.80 (d, J = 8.9 Hz, 1H), 7.73 (d, J = 7.5 Hz, 1H), 7.40 (td, J = 3.5, 1.5 Hz, 2H), 7.37 (d, J = 2.0 Hz, 1H), 7.23–7.17 (m, 2H), 6.92 (d, J = 2.0 Hz,1H), 6.90 (d, J = 2.0 Hz, 1H), 6.07 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.5, 131.8, 128.5, 127.6, 127.5, 127.2, 122.6, 121.5, 118.2, 117.7, 99.8, 39.5.

3.10. 1-((4-Nitrophenyl)thio)naphthalen-2-amine [**3h**]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 30) as eluent to give the product **3h** as a bright yellow solid (88.0 mg, 99%); mp160–160.5 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.06 (d, J = 9.0 Hz, 2H), 7.91 (d, J = 8.5 Hz, 1H), 7.84 (d, J = 8.9 Hz, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.44–7.33 (td, J = 7.7, 1.2 Hz, 1H), 7.27–7.17 (m, 2H), 7.13 (d, J = 9.0 Hz, 2H), 6.15 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.9, 147.5, 144.6, 136.0, 132.4, 128.6, 127.9, 127.2, 125.5, 124.1, 122.2, 121.8, 118.4, 97.7, 39.5; HRMS (ESI): m/z calcd for $C_{20}H_{21}NS$ $(M + Na)^+$: 297.0692, found: 297.0691.

3.11. 1-((4-(Trifluoromethyl)phenyl)thio)naphthalen-2-amine [**3i**] [13a]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 30) as eluent to give the product **3i** as a red solid (92.7 mg, 97%); mp 120.6–121.9 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.00 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 8.9 Hz, 1H), 7.74 (d, J = 7.7 Hz, 1H), 7.46–7.36 (m, 3H), 7.31 (s, 1H), 7.25–7.11 (m, 3H), 6.12 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.7, 139.1, 136.2, 132.1, 130.0, 129.2, 128.6, 127.8, 127.2, 125.2, 122.5, 121.7, 121.6, 121.5, 118.3, 98.9, 39.5.

3.12. 1-((4-(Trifluoromethoxy)phenyl)thio)naphthalen-2-amine [**3j**]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 30) as eluent to give the product **3j** as a red liquid (94.4 mg, 94%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.04 (d, J = 8.5 Hz, 1H), 7.80 (d, J = 8.9 Hz, 1H), 7.73 (d, J = 7.9 Hz, 1H), 7.39 (t, J = 7.6 Hz, 1H), 7.25–7.20 (m, 2H), 7.20–7.15 (m, 2H), 7.06 (d, J = 8.8 Hz, 2H), 6.10 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.6, 145.8, 136.6, 136.3, 131.9, 128.5, 127.7, 127.3, 127.0, 122.6, 121.9, 121.6, 118.3, 39.5; ^{19}F NMR (376 MHz, DMSO-d_6) δ −57.1; HRMS (ESI): m/z calcd for $C_{17}H_{12}F_3NOS$ $(M + H)^+$: 336.0664, found: 336.0667.

3.13. 1-(m-Tolylthio)naphthalen-2-amine [**3k**] [19]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 30) as eluent to give the product **3k** as a red solid (74.8 mg, 94%); mp 88.8–89.9 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.04 (d, J = 8.5 Hz, 1H), 7.78 (d, J = 8.9 Hz, 1H), 7.72 (d, J = 7.7 Hz, 1H), 7.37 (td, J = 7.7, 1.3 Hz, 1H), 7.22–7.13 (m, 2H), 7.05 (t, J = 7.9 Hz, 1H), 6.92–6.84 (m, 2H), 6.69 (d, J = 7.9 Hz, 1H), 5.99 (s, 2H), 2.16 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.4, 138.2, 136.7, 136.3, 131.5, 128.9, 128.4, 127.4, 127.2, 126.1, 125.8, 122.9, 122.6, 121.4, 118.2, 100.8, 39.5, 21.0.

3.14. 1-((3-Bromophenyl)thio)naphthalen-2-amine [**3l**]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 30) as eluent to give the product **3l** as a red liquid (98.0 mg, 99%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.00 (d, J = 8.6 Hz, 1H), 7.81 (d, J = 8.8 Hz, 1H), 7.73 (d, J = 7.7 Hz, 1H), 7.39 (td, J = 7.9, 1.3 Hz, 1H), 7.26 (dq, J = 7.9, 0.9 Hz, 1H), 7.23–7.12 (m, 3H), 7.07 (t, J = 1.8 Hz, 1H), 6.98 (dq, J = 7.9, 1.0 Hz, 1H), 6.10 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.6, 140.0, 136.1, 132.0, 130.9, 128.5, 127.7, 127.7, 127.4, 127.2, 122.6, 122.2, 121.6, 118.2, 99.3, 39.5; HRMS (ESI): m/z calcd for $C_{16}H_{12}BrNS$ $(M + Na)^+$: 351.9766, found: 351.9772.

3.15. 1-((3-(Trifluoromethyl)phenyl)thio)naphthalen-2-amine [**3m**]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 30) as eluent to give the product **3m** as a red liquid (93.9 mg, 98%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.02 (d, J = 8.5 Hz, 1H), 7.82 (d, J = 8.9 Hz, 1H), 7.74 (d, J = 7.8 Hz, 1H), 7.39 (dd, J = 10.0, 7.1 Hz, 2H), 7.33 (s, 1H), 7.27–7.14 (m, 1H), 6.14 (s, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.7, 139.1, 136.2, 132.1, 130.0, 129.7, 129.1, 128.5, 127.7, 127.2, 125.2, 122.5, 121.7, 121.6, 121.5, 118.3, 99.0, 39.5; HRMS (ESI): m/z calcd for $C_{17}H_{21}F_3NS$ $(M + H)^+$: 320.0715, found: 320.0718.

3.16. 1-((2,5-Dimethylphenyl)thio)naphthalen-2-amine [**3n**] [13a]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 30) as eluent to give the product **3n** as a red solid (71.0 mg, 92%); mp 62.7–65.1 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.99 (d, J = 8.5 Hz, 1H), 7.80 (d, J = 8.9 Hz, 1H), 7.73 (d, J = 7.7 Hz, 1H), 7.37 (td, J = 7.7, 1.3 Hz, 1H), 7.22 (d, J = 8.9 Hz, 1H), 7.18 (td, J = 7.4, 1.1 Hz, 1H), 7.08 (d, J = 7.6 Hz, 1H), 6.78 (d, J = 8.3 Hz, 1H), 6.18 (s, 1H), 5.96 (s, 2H), 2.45 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.5, 136.4, 135.4, 135.2, 131.5, 130.0, 128.4, 127.4, 127.3, 125.3, 124.0, 123.0, 121.5, 118.2, 100.0, 39.5, 20.7, 19.2.

3.17. 1-(Naphthalen-2-ylthio)naphthalen-2-amine [**3o**]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 30) as eluent to give the product **3o** as a red solid (86.6 mg, 96%); mp 120.7–122.3 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.10 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.9 Hz, 1H), 7.76 (t, J = 8.2 Hz, 3H), 7.66–7.57 (d, J = 7.9 Hz, 1H), 7.46 (s, 1H), 7.43–7.33 (m, 3H), 7.26 (d, J = 8.9 Hz, 1H), 7.17 (td, J = 8.8, 4.2 Hz, 2H), 6.09 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.5, 136.3, 134.7, 133.3, 131.7, 130.9, 128.5, 128.5, 127.6, 127.5, 127.3, 126.6, 125.2, 124.5, 123.0, 122.9, 121.5, 118.3, 100.5, 39.5; HRMS (ESI): m/z calcd for $C_{20}H_{15}NS$ $(M + H)^+$: 302.0998, found: 302.0995.

3.18. 6-Bromo-1-(phenylthio)naphthalen-2-amine [**3p**]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 30) as eluent to give the product **3p** as a reddish solid (93.9 mg, 95%); mp 122.4–123.0 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.96 (dd, J = 12.0, 5.5 Hz, 1H), 7.77 (d, J = 8.9 Hz, 1H), 7.48 (dd, J = 9.0, 2.1 Hz, 1H), 7.28–7.15 (m, dd, J = 17,5, 8.4 Hz, 3H), 7.08 (tt, J = 7.7, 1,1 Hz, 1H), 7.02–6.86 (m, 2H), 6.15 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.9, 136.5, 135.1, 130.7, 130.2, 130.1, 129.1, 128.4, 125.6, 125.3, 125.1, 119.4, 114.0, 100.6,

39.5; HRMS (ESI): *m/z* calcd for $C_{16}H_{12}BrNS$ $(M + H)^+$: 329.9947, found: 329.9951.

3.19. 2,4-Bis(phenylthio)naphthalen-1-amine [**3q**]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 30) as eluent to give the product **3q** as a white solid (107.8 mg, 94%); mp 100–101 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 9.3 Hz, 1H), 7.97 (s, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.54–7.42 (m, 2H), 7.2–7.15 (t, J = 7.5 Hz, 2H), 7.1–7.06 (m, 5H), 7.03 (t, J = 7.5 Hz, 3H), 5.20 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 143.5, 139.2, 136.6, 136.1, 129.2, 128.9, 128.3, 127.2, 126.6, 126.5, 126.0, 125.7, 125.1, 123.9, 122.0, 117.3, 108.1, 77.2; HRMS (ESI): *m/z* calcd for $C_{22}H_{17}NS_2$ $(M + H)^+$: 360.0877, found: 360.0870.

3.20. 2,4-Bis(p-tolylthio)naphthalen-1-amine [**3r**]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 30) as eluent to give the product **3r** as a white solid (110.4 mg, 95%); mp 101–102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 9.0 Hz, 1H), 7.93 (s, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.51–7.46 (t, J = 6.8 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 7.05–6.97 (m, 4H), 6.95 (t, J = 6.5 Hz, 4H), 5.14 (s, 2H), 2.24 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.3, 142.8, 135.8, 135.7, 135.4, 135.0, 132.9, 130.0, 129.7, 128.1, 127.2, 127.0, 125.9, 123.9, 122.0, 118.0, 109.0, 77.2, 21.0, 21.0; HRMS (ESI): *m/z* calcd for $C_{24}H_{21}NS_2$ $(M + Na)^+$: 410.1007, found: 410.1004.

3.21. 2,4-Bis((4-chlorophenyl)thio)naphthalen-1-amine [**3s**]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 30) as eluent to give the product **3r** as a white solid (124.6 mg, 97%); mp 98–99 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 8.7 Hz, 1H), 7.92 (s, 1H), 7.81 (d, J = 8.9 Hz, 1H), 7.58–7.47 (m, 2H), 7.15 (d, J = 8.6 Hz, 2H), 7.09 (d, J = 8.6 Hz, 2H), 7.00 (d, J = 8.7 Hz, 2H), 6.93 (d, J = 8.6 Hz, 2H), 5.24 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0, 143.2, 137.7, 135.9, 135.1, 131.7, 131.0, 129.3, 129.0, 128.6, 127.9, 127.8, 127.0, 126.2, 123.9, 122.1, 117.0, 107.6, 77.2; HRMS (ESI): *m/z* calcd for $C_{22}H_{15}Cl_2NS_2$ $(M + H)^+$: 428.0098, found: 428.0093.

3.22. 4-((4-Nitrophenyl)thio)naphthalen-1-amine [**3t**]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 10) as eluent to give the product **3t** as a yellow liquid (79.9 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.9 Hz, 2H), 7.90–7.78 (m, 2H), 7.63–7.49 (m, 2H), 7.45 (d, J = 8.5 Hz, 1H), 7.31 (d, J = 8.5 Hz, 1H), 7.11 (d, J = 8.9 Hz, 2H), 5.01 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 146.4, 145.4, 135.6, 133.2, 128.9, 127.8, 125.9, 125.6, 124.2, 123.2, 121.7, 119.2, 105.0, 77.2; HRMS (ESI): *m/z* calcd for $C_{16}H_{12}N_2O_2S$ $(M + H)^+$: 297.0694, found: 297.0690.

3.23. 4-(Phenylthio)naphthalen-1-amine [**3u**] [23]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 8) as eluent to give the product **3u** as a red liquid (43.7 mg, 58%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (t, J = 9.7 Hz, 2H), 7.52 (m, 3H), 7.28 (d, J = 8.5 Hz, 1H), 7.21 (t, J = 7.5 Hz, 2H), 7.13–7.06 (m, 3H), 5.06 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 137.2, 135.2, 133.8, 129.1, 128.8, 127.1, 126.5, 125.5, 123.3, 121.7, 118.7, 77.2.

3.24. 4-(Phenylthio)aniline [**4a**] [24]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 10) as eluent to give the product **4a** as an orange solid (57.3 mg, 94%); mp 83.4–84.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.28 (dt, J = 8.6, 2.8 Hz, 2H), 7.24–7.19 (t, J = 7.5 Hz, 2H), 7.17–7.07 (m, 3H), 6.72–6.64 (dt, J = 4.3, 2.4 Hz, 2H), 3.79 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 139.8, 136.2, 128.9, 127.4, 125.4, 120.6, 116.0, 77.2.

3.25. 4-(p-Tolylthio)aniline [**4b**] [25]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 10) as eluent to give the product **4b** as a yellow liquid (61.4 mg, 95%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (dt, J = 6.5, 2.3 Hz, 2H), 7.07 (d, J = 8.3 Hz, 2H), 7.02 (d, J = 8.2 Hz, 2H), 6.68–6.53 (dt, J = 8.6, 2.3 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 135.4, 129.7, 128.2, 121.6, 115.9, 77.2, 21.0.

3.26. 4-((4-Fluorophenyl)thio)aniline [**4c**] [25]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 10) as eluent to give the product **4c** as an orange liquid (59.8 mg, 91%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.25 (dt, J = 8.5, 2.4 Hz, 2H), 7.14 (tt, J = 8.7, 2.4 Hz, 2H), 6.98–6.89 (dt, J = 8.6, 2.4 Hz, 2H), 6.71–6.64 (m, 2H), 3.82 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 160.2, 146.8, 135.5, 134.3, 130.1, 130.0, 121.6, 116.1, 115.9, 77.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ −117.1.

3.27. 5-(Phenylthio)-[1,1′-biphenyl]-2-amine [**4d**]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 30) as eluent to give the product **4d** as a white solid (74.1 mg, 89%), mp 83.4–84.5 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.27–7.21 (t, J = 7.7 Hz, 2H), 7.18 (d, J = 2.0 Hz, 1H), 7.17 (d, J = 2.1 Hz, 1H), 7.12–7.06 (tt, J = 7.7, 1.3 Hz, 1H), 7.01 (dd, J = 8.0, 1.6 Hz, 2H), 6.64–6.59 (dt, J = 8.6, 2.4 Hz, 2H), 5.52 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 146.3, 139.5, 138.5, 136.7, 135.1, 129.0, 128.9, 128.5, 127.1, 126.7, 126.5, 125.2, 116.4, 116.3, 39.5; HRMS (APCI): *m/z* calcd for $C_{18}H_{15}NS$ $(M + H)^+$: 278.0998, found: 278.0995.

3.28. 5-(p-Tolylthio)-[1,1′-biphenyl]-2-amine [**4e**]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 30) as eluent to give the product **4e** as a yellow liquid (74.1 mg, 85%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 4.4 Hz, 4H), 7.36 (q, J = 4.5 Hz, 1H), 7.31–7.25 (m, 2H), 7.15 (d, J = 8.1 Hz, 2H), 7.06 (d, J = 8.3 Hz, 2H), 6.76 (d, J = 8.1 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 138.6, 136.1, 135.7, 135.4, 134.3, 129.8, 129.1, 129.0, 128.6, 127.6, 122.3, 116.6, 77.2, 21.1. HRMS (APCI): *m/z* calcd for $C_{19}H_{17}NS$ $(M + H)^+$: 292.1155, found: 292.1149.

3.29. 5-((4-Fluorophenyl)thio)-[1,1′-biphenyl]-2-amine [**4f**]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 10) as eluent to give the product **4f** as a brown liquid (73.4 mg, 83%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.40 (m, 4H), 7.38–7.32 (m, 1H), 7.28–7.23 (m, 2H), 7.22–7.16 (m, 2H), 6.98–6.88 (m, 2H), 6.73 (d, J = 8.1 Hz, 1H), 3.87 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 160.2, 144.1, 138.5, 136.2, 134.4, 134.2 (d, J = 3.2 Hz), 130.2, 129.1, 129.0, 128.6, 127.7, 121.7,

116.5, 116.2, 115.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ −116.9. HRMS (ESI): m/z calcd for $C_{18}H_{14}FNS$ $(M + H)^+$: 296.0904, found: 296.0901.

3.30. 1,4-Bis(phenylthio)naphthalene-2,3-diamine [**4g**]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 30) as eluent to give the product **4g** as a white solid (66.2 mg, 59%), mp 110–112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (dd, J = 6.3, 3.3 Hz, 1H), 7.34 (dd, J = 6.4, 3.3 Hz, 1H), 7.20 (t, J = 7.5 Hz, 1H), 7.10 (dd, J = 16.3, 7.8 Hz, 2H), 4.68 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.7, 136.3, 131.1, 129.2, 126.3, 125.5, 125.2, 124.9, 110.8, 77.2; HRMS (ESI): m/z calcd for $C_{22}H_{18}N_2S_2$ $(M + H)^+$: 375.0986, found: 375.0980.

3.31. 2-Methoxy-4-(phenylthio)aniline [**4h**] [25]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 10) as eluent to give the product **4h** as a gray liquid (56.2 mg, 81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.18 (m, 2H), 7.15–7.07 (m, 3H), 7.01 (dd, J = 8.0, 1.9 Hz, 1H), 6.96 (d, J = 1.8 Hz, 1H), 6.71 (d, J = 8.0 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 139.9, 137.1, 128.9, 128.4, 125.2, 116.8, 115.2, 77.2, 55.7.

3.32. 2,5-Dimethyl-4-(phenylthio)aniline [**4i**] [26]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 10) as eluent to give the product **4i** as a gray liquid (68.4 mg, 99%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 1H), 7.20–7.14 (m, 2H), 7.08–7.02 (tt, J = 7.4, 1.4 Hz, 1H), 7.01–6.97 (m, 2H), 6.62 (s, 1H), 3.72 (s, 2H), 2.26 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.9, 141.7, 139.8, 138.9, 128.9, 126.0, 124.7, 120.9, 118.7, 117.1, 77.2, 20.5, 16.8.

3.33. 3-(Phenylthio)-1H-indole [**5a**] [21d]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 10) as eluent to give the product **5a** as a white solid (67.6 mg, 98%), mp 121.3–122.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.46–7.38 (m, 2H), 7.29–7.22 (m, 1H), 7.15 (td, J = 7.8, 3.2 Hz, 3H), 7.10 (d, J = 6.8 Hz, 2H), 7.04 (t, J = 7.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3, 136.6, 130.8, 129.2, 128.8, 126.0, 124.9, 123.2, 121.0, 119.8, 111.7, 102.9.

3.34. 3-(p-Tolylthio)-1H-indole [**5b**] [21d]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 10) as eluent to give the product **5b** as a white solid (68.7 mg, 96%), mp 137.6–138.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 2.0 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.28–7.23 (m, 2H), 7.18–7.13 (m, 1H), 7.03 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 8.0 Hz, 2H), 2.24 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.6, 135.6, 134.8, 130.5, 129.6, 129.2, 126.4, 123.1, 121.0, 119.8, 111.6, 103.7, 21.0.

3.35. 3-((4-Chlorophenyl)sulfinyl)-1H-indole [**5c**] [21d]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 10) as eluent to give the product **5c** as a white solid (74.1 mg, 95%), mp 137.6–138.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 2.8 Hz, 1H), 7.44 (d, J = 8.4 Hz, 1H), 7.30–7.25 (m, 1H), 7.20–7.14 (m, 1H), 7.11 (d, J = 8.4 Hz, 2H), 7.01 (d, J = 8.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.9, 136.6, 130.8, 130.7, 128.9, 127.2, 123.3, 121.2, 119.6, 111.8, 102.6.

3.36. 3-((4-Nitrophenyl)thio)-1H-indole [**5d**] [21d]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 10) as eluent to give the product **5d** as a yellow solid (80.1 mg, 99%), mp 121.2–121.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.02–7.96 (m, 2H), 7.58–7.45 (m, 3H), 7.36–7.26 (m, 1H), 7.23–7.15 (m, 1H), 7.15–7.08 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 145.0, 136.7, 131.4, 128.5, 125.2, 124.0, 123.6, 121.5, 119.3, 112.1, 100.2.

3.37. 2,5-Bis(phenylthio)-1H-pyrrole [**5e**] [21d]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 100) as eluent to give the product **5e** as a light gray liquid (77.1 mg, 92%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.21 (s, 1H), 7.31 (s, 1H), 7.30 (s, 2H), 7.28 (s, 1H), 7.15 (t, J = 7.4 Hz, 2H), 7.05 (d, J = 1.2 Hz, 2H), 7.03 (d, J = 1.0 Hz, 2H), 6.58 (d, J = 2.4 Hz, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 138.5, 129.1, 125.7, 125.6, 119.5, 119.2, 39.5.

3.38. 1-Methyl-2,5-bis(phenylthio)-1H-pyrrole [**5f**]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 100) as eluent to give the product **5f** as a colourless liquid (77.7 mg, 88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, J = 12.5, 4.8 Hz, 1H), 7.12 (t, J = 7.4 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H), 6.69 (s, 1H), 3.50 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1, 129.2, 125.9, 125.7, 122.2, 119.5, 77.2, 31.5; HRMS (ESI): m/z calcd for $C_{17}H_{15}NS_2$ $(M + H)^+$: 298.0719, found: 298.0724.

3.39. 2,5-Dimethyl-3,4-bis(phenylthio)-1H-pyrrole [**5g**] [21d]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 100) as eluent to give the product **5g** as a white solid (76.6 mg, 82%), mp 89.7–91.5 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.59 (s, 1H), 7.14 (t, J = 7.7 Hz, 4H), 7.04–6.97 (tt, J = 7.4, 1.3 Hz, 2H), 6.89 (dd, J = 8.4, 1.1 Hz, 4H), 2.22 (s, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 139.7, 133.4, 128.6, 124.8, 124.2, 107.5, 39.5, 11.6; HRMS (ESI): m/z calcd for $C_{18}H_{17}NS_2$ $(M + Na)^+$: 334.0695, found: 334.0700.

3.40. 3-(Phenylthio)imidaz o [1,2-a] pyridine [**5h**] [27]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 5) as eluent to give the product **5h** as a white solid (61.1 mg, 90%); mp 97–99 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dt, J = 6.8, 1.1 Hz, 1H), 7.99 (s, 1H), 7.71 (dt, J = 9.1, 1.0 Hz, 1H), 7.31 (m, 1H), 7.23–7.17 (m, 2H), 7.15–7.10 (m, 1H), 6.99 (dd, J = 7.1, 1.4 Hz, 2H), 6.87 (td, J = 6.8, 1.0 Hz, 1H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 142.5, 135.3, 129.4, 126.3, 126.2, 126.1, 124.4, 118.2, 113.3, 110.7, 77.2.

3.41. 3-(p-Tolylthio)imidaz o [1,2-a]pyridine e[**5i**] [27]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 5) as eluent to give the product **5i** as a white solid (71.7 mg, 99%); mp 100–102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dt, J = 6.8, 1.1 Hz, 1H), 7.98 (s, 1H), 7.69 (dt, J = 9.0, 1.0 Hz, 1H), 7.27 (td, J = 6.9, 1.3 Hz, 1H), 7.00 (d, J = 8.1 Hz, 2H), 6.96–6.89 (m, 2H), 6.84 (td, J = 6.8, 1.0 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 142.1, 136.3, 131.4, 130.0, 126.6, 125.9, 124.3, 118.1, 113.1, 111.3, 77.2, 20.9.

3.42. 3-((4-Fluorophenyl)thio)imidazo [1,2-a]pyridine [5j] [28]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 5) as eluent to give the product **5j** as a yellow liquid (42.0 mg, 58%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (t, J = 5.6 Hz, 1H), 7.98 (d, J = 5.5 Hz, 1H), 7.70 (dd, J = 8.6, 4.9 Hz, 1H), 7.39–7.22 (m, 1H), 7.02 (q, J = 7.0, 5.3 Hz, 2H), 6.91 (m, 3H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 160.5, 148.1, 142.4, 130.1 (d, J = 3.2 Hz), 128.6, 128.5, 126.2, 124.2, 118.3, 116.7, 116.4, 113.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ −115.7.

3.43. 1-(Phenylthio)naphthalen-2-ol [6a] [13a]

The crude mixture was purified via column chromatography using ethyl acetate as eluent to give the product **6a** as a yellow solid (61.3 mg, 81%); mp 65–67 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.3 Hz, 1H), 7.92 (d, J = 8.8 Hz, 1H), 7.83 (d, J = 7.7 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.37 (m, 2H), 7.17 (d, J = 8.5 Hz, 3H), 7.15–7.08 (m, 1H), 7.04 (d, J = 6.6 Hz, 2H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 135.6, 135.5, 133.0, 132.8, 129.6, 129.2, 128.7, 128.0, 126.5, 126.0, 124.8, 124.0, 117.0, 108.2, 77.2.

3.44. 1-(p-Tolylthio)naphthalen-2-ol [6b] [13a]

The crude mixture was purified via column chromatography using ethyl acetate as eluent to give the product **6b** as a yellow solid (59.8 mg, 75%); mp 77–79 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 8.5 Hz, 1H), 7.90 (d, J = 8.9 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.50 (t, J = 7.1 Hz, 1H), 7.40–7.32 (m, 2H), 7.23 (s, 1H), 6.98 (q, J = 8.4 Hz, 4H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 136.0, 135.6, 132.8, 131.9, 130.1, 129.6, 128.7, 128.0, 126.8, 124.9, 123.9, 117.0, 108.8, 77.2, 21.0.

3.45. 1-((4-Fluorophenyl)thio)naphthalen-2-ol [6c] [29]

The crude mixture was purified via column chromatography using ethyl acetate as eluent to give the product **6c** as a yellow solid (60.0 mg, 74%); mp 63–65 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.5 Hz, 1H), 7.92 (d, J = 8.9 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.55–7.47 (td, J = 7.7, 1.1 Hz, 1H), 7.43–7.32 (m, 2H), 7.20 (s, 1H), 7.06–6.99 (m, 2H), 6.94–6.85 (m, 2H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 157.1, 135.4, 133.1, 130.5, 129.7, 128.9, 128.5, 128.4, 128.2, 124.6, 124.1, 117.0, 116.6, 116.3, 108.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ −116.2.

3.46. 1-((4-Chlorophenyl)thio)naphthalen-2-ol [6d] [13a]

The crude mixture was purified via column chromatography using ethyl acetate as eluent to give the product **6d** as a yellow solid (60.1 mg, 70%); mp 85–87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.9 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.55–7.47 (td, J = 7.7, 1.1 Hz, 1H), 7.43–7.32 (m, 2H), 7.17–7.09 (m, 3H), 6.99–6.90 (m, 2H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 135.3, 134.1, 133.3, 132.0, 129.7, 129.4, 128.8, 128.3, 127.8, 127.8, 124.6, 124.1, 117.1, 107.7, 77.2.

3.47. 1-((4-Bromophenyl)thio)naphthalen-2-ol [6e] [13a]

The crude mixture was purified via column chromatography using ethyl acetate as eluent to give the product **6e** as a yellowe solid (63.5 mg, 64%); mp 103–105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.9 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.57–7.47 (m, 1H), 7.42–7.37 (m, 1H), 7.35 (d, J = 8.9 Hz, 1H), 7.33–7.24 (dt, J = 8.6, 2.3 Hz, 2H), 7.10 (s, 1H), 6.93–6.85 (dt, J = 8.6, 2.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 135.3, 134.8, 133.3, 132.3, 129.6, 128.8, 128.3, 128.0, 124.6, 124.1, 119.8, 117.1, 107.6, 77.2.

3.48. 1-((4-Nitrophenyl)thio)naphthalen-2-ol [6f] [13a]

The crude mixture was purified via column chromatography using ethyl acetate as eluent to give the product **6f** as a yellow solid (74.9 mg, 84%); mp 119–121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.6 Hz, 1H), 8.00 (m, 3H), 7.86 (d, J = 8.0 Hz, 1H), 7.56–7.49 (m, 1H), 7.42 (t, J = 7.0 Hz, 1H), 7.37 (d, J = 9.0 Hz, 1H), 7.08 (d, J = 9.0 Hz, 2H), 6.90 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 145.9, 145.2, 135.0, 134.0, 129.7, 129.0, 128.6, 126.1, 124.5, 124.4, 124.1, 117.3, 105.7.

3.49. 1-((4-Nitrophenyl)thio)naphthalen-2-ol [6g] [30]

The crude mixture was purified via column chromatography using ethyl acetate as eluent to give the product **6g** as a yellow solid (57.1 mg, 57%); mp 51–53 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.9 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.52 (t, J = 8.2 Hz, 1H), 7.40 (t, J = 8.0 Hz, 1H), 7.35 (d, J = 8.9 Hz, 1H), 7.10 (s, 1H), 7.03 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 147.4, 135.2, 134.1, 133.2, 129.6, 128.7, 128.2, 127.5, 124.4, 124.1, 121.9, 117.0, 107.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ −58.1.

3.50. 1-(m-Tolylthio)naphthalen-2-ol [6h] [19]

The crude mixture was purified via column chromatography using ethyl acetate as eluent to give the product **6h** as a yellow solid (62.2 mg, 78%); mp 87–89 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 8.5 Hz, 1H), 7.92 (d, J = 8.9 Hz, 1H), 7.84 (d, J = 8.1 Hz, 1H), 7.52 (td, J = 7.6, 7.0, 1.2 Hz, 1H), 7.43–7.34 (m, 2H), 7.22 (s, 1H), 7.07 (t, J = 7.9 Hz, 1H), 6.95 (s, 2H), 6.82 (d, J = 7.9 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 139.2, 135.6, 135.2, 132.9, 129.6, 129.2, 128.7, 128.0, 127.1, 127.0, 124.9, 123.6, 117.0, 108.3, 77.2, 21.5.

3.51. 1-((3-Bromophenyl)thio)naphthalen-2-ol [6i]

The crude mixture was purified via column chromatography using ethyl acetate as eluent to give the product **6i** as a white solid (42.6 mg, 43%); mp 55–56 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.5 Hz, 1H), 7.94 (d, J = 8.9 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.52 (td, J = 7.7, 1.2 Hz, 1H), 7.40 (td, J = 7.5, 1.0 Hz, 1H), 7.35 (d, J = 8.9 Hz, 1H), 7.27–7.19 (m, 2H), 7.07 (s, 1H), 7.02 (t, J = 7.9 Hz, 1H), 6.89 (dq, J = 7.9, 1.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 137.9, 135.3, 133.4, 130.6, 129.7, 129.2, 129.0, 128.8, 128.3, 124.9, 124.6, 124.2, 123.3, 117.1, 107.1, 77.2; HRMS (ESI): m/z calcd for $C_{16}H_{11}BrOS$ $(M + H)^+$: 330.9789, found: 330.9782.

3.52. 1-(Naphthalen-2-ylthio)naphthalen-2-ol [6j]

The crude mixture was purified via column chromatography using ethyl acetate as eluent to give the product **6j** as a white solid (62.2 mg, 69%); mp 91–93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 8.5 Hz, 1H), 7.92 (d, J = 8.9 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 9.3 Hz, 1H), 7.64 (d, J = 8.7 Hz, 1H), 7.54 (d, J = 9.4 Hz, 1H), 7.46 (td, J = 7.6, 7.0, 1.2 Hz, 1H), 7.41 (d, J = 1.5 Hz, 1H), 7.40–7.32 (m, 4H), 7.22 (d, J = 5.2 Hz, 1H), 7.17 (dd, J = 8.7, 1.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 135.6, 133.8, 133.1, 132.9, 131.9, 129.7, 129.0, 128.7, 128.1, 127.8, 127.2, 126.8, 125.8, 124.8, 124.7, 124.0, 117.1, 108.2.

3.53. 2,4-Bis(phenylthio)naphthalen-1-ol [6k] [30]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 10) as eluent to give the product **6k** as a bright yellow solid (89.7 mg, 82%), mp 98–100 °C;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (dt, J = 7.6, 3.2 Hz, 2H), 7.97 (s, 1H), 7.63–7.53 (m, 2H), 7.38 (s, 1H), 7.27–7.21 (m, 2H), 7.20–7.16 (m, 2H), 7.16–7.13 (m, 2H), 7.13–7.04 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 141.2, 138.4, 136.5, 135.6, 129.4, 129.1, 129.0, 127.2, 127.0, 126.5, 126.3, 125.5, 124.8, 123.9, 121.3, 109.7.

3.54. 2,4-Bis(p-tolylthio)naphthalen-1-ol [**6l**]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 10) as eluent to give the product **6l** as a bright yellow solid (92.1 mg, 79%), mp 95–97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41–8.31 (m, 2H), 7.91 (s, 1H), 7.58 (p, J = 6.7 Hz, 2H), 7.37 (s, 1H), 7.06 (s, 4H), 7.01 (s, 4H), 2.30 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 140.4, 136.6, 136.2, 135.6, 134.5, 132.0, 130.2, 129.8, 128.9, 127.8, 127.7, 124.8, 123.8, 122.1, 110.4, 21.1; HRMS (APCI): m/z calcd for $C_{24}H_{20}OS_2$ $(M - H)^+$: 287.0881, found: 287.0884.

3.55. 2,4-Bis((4-chlorophenyl)thio)naphthalen-1-ol [**6m**]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 10) as eluent to give the product **6m** as a bright yellow solid (98.4 mg, 77%), mp 89–91 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (dd, J = 6.9, 2.4 Hz, 1H), 8.28 (dd, J = 7.1, 2.2 Hz, 1H), 7.90 (s, 1H), 7.60 (dt, J = 8.7, 2.2 Hz, 2H), 7.31 (dt, J = 8.7, 2.4 Hz, 1H), 7.25–7.17 (dt, J = 8.7, 2.4 Hz, 2H), 7.17–7.09 (dt, J = 8.7, 2.4 Hz, 2H), 7.07–7.01 (m, 2H), 7.01–6.91 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 140.89, 136.9, 136.3, 134.1, 132.7, 131.5, 129.6, 129.5, 129.2, 128.6, 128.3, 126.8, 126.2, 125.0, 124.1, 121.2, 109.4.

3.56. General procedure for gram-scale synthetic experiment of [**3a**] and [**4d**]

A mixture of naphthalen-2-amine or [1,1′-biphenyl]-2-amine (10 mmol), benzenesulfonohydrazide (30 mmol), TBAI (2 equiv.), and DPDMF (10 mL) were added into a Schlenk tube. The solution was stirred and heated to 100 °C for 48 h in air. After completion of the reaction, the mixture was cooled to room temperature, and the insoluble TBAI was filtered and washed with ethyl acetate (10 mL × 3). Subsequently, the TBAI were recoverd in 93% and 91% yields, respectively. The filtrate was concentrated in vacuum, and the crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 10) as eluent to afford the final product **3a** and **4d** in 92% (2.32 g) and 82% (2.26 g) yields, respectively.

3.57. Typical procedure for the synthesis of [**3aa**]

To a 25 mL tube were added **3a** (0.3 mmol), and *m*-CPBA (0.9 mmol) in 2 mL of $CHCl_3$. The reaction vessel was allowed to stir at 65 °C for 15 h. After completion of the reaction, the mixture was quenched with the saturated solution of NaCl (5 mL) and extracted with dichloromethane (3 × 10 mL). The organic phase was dried over Na_2SO_4 and concentrated in vacuum, and the crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 5) as eluent to afford the final product 1-(phenylsulfonyl)naphthalen-2-amine **3aa** in 58% yield.

3.58. 1-(Phenylsulfonyl)naphthalen-2-amine [**3aa**]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 5) as eluent to give the product **3aa** as a red solid (48.2 mg, 58%), mp 88–89 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.31 (dd, J = 8.7, 1.0 Hz, 1H), 8.00–7.87 (m, 2H), 7.82 (d, J = 9.0 Hz, 1H), 7.67 (dd, J = 7.9, 1.2 Hz, 1H), 7.64–7.59 (tt, J = 7.3, 1.8 Hz, 1H), 7.59–7.53 (m, 2H), 7.38 (m, 3H), 7.23–7.15 (m, 1H), 7.10 (d, J = 9.1 Hz, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 145.0, 143.4, 135.8, 133.2, 130.5, 129.4, 129.0, 128.3, 126.6, 125.5, 122.3, 121.9, 120.5, 105.3; HRMS (APCI): m/z calcd for $C_{16}H_{13}NO_2S$ $(M + H)^+$: 284.0742, found: 284.0736.

3.59. Typical procedure for the synthesis of [**4da**]

To a 25 mL tube were added **4d** (0.3 mmol), bromobenzene (0.3 mmol), $Pd_2(dba)_3$ (2 mol%), XPhos (4%), and K_2CO_3 (0.6 mmol) in 2 mL of DCE. The reaction vessel was allowed to stir at 100 °C for 18 h under argon atmosphere. After completion of the reaction, the mixture was quenched with the saturated solution of NaCl (5 mL) and extracted with dichloromethane (3 × 10 mL). The organic phase was dried over Na_2SO_4 and concentrated in vacuum. The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 10) as eluent to give the final product *N*-phenyl-5-(phenylthio)-[1,1′-biphenyl]-2-amine **4da** in 87% yield.

3.60. N-phenyl-5-(phenylthio)-[1,1′-biphenyl]-2-amine [**4da**]

The crude mixture was purified via column chromatography using ethyl acetate/petroleum ether (1 : 10) as eluent to give the product **4da** as a red liquid (61.5 mg, 87%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 3.9 Hz, 4H), 7.40 (d, J = 9.4 Hz, 2H), 7.36 (s, 2H), 7.33–7.27 (m, 6H), 7.22–7.14 (m, 1H), 7.10 (d, J = 7.8 Hz, 2H), 7.01 (t, J = 7.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 140.9, 138.6, 138.2, 136.3, 134.0, 131.7, 129.5, 129.4, 129.2, 129.1, 128.5, 128.0, 125.9, 123.9, 122.2, 119.5, 116.9; HRMS (APCI): m/z calcd for $C_{24}H_{19}NS$ $(M + H)^+$: 354.1313, found: 354.1306.

4. Conclusions

In summary, we have developed an efficient TBAI-mediated sulfenylation of arenes with arylsulfonyl hydrazides. DPDME was identified as excellent green solvent that are crucial for the electrophilic substitution process. A series of aryl sulfides was obtained in moderate to excellent yields. The reaction exhibited green reaction condition (recyclable TBAI and DPDME as solvent), broad substrate scope, and good functional group compatibility. The potential application is exemplified by gram-scale synthesis and further transformations. The mechanism studies show that diaryl disulfide may be the main intermediate.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2020.131646.

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