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Aerobic Cross-Dehydrogenative Coupling Reactions for Selective Mono- and Dithiolation of Phenols

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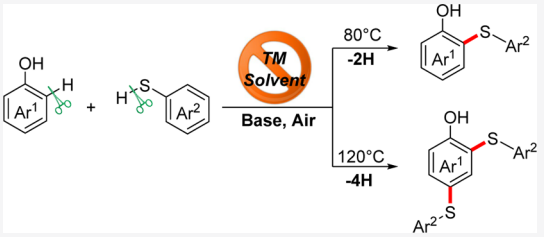
ABSTRACT: A highly efficient strategy for the direct thiolation of phenols under transition metal-free and solvent-free conditions has been developed. These reactions are operationally simple with employing air (molecular oxygen) as an ideal oxidant and can selectively provide mono- and dithiolation products in good to excellent yields under basic conditions. The reaction tolerates a broad range of aryl thiols and arenes and is especially applicable for large-scale synthesis.



INTRODUCTION

The construction of C−S bonds is of great importance in organic synthesis because sulfur moieties are widely found in commercially available drugs, natural products, and fundamental materials.[1] As a consequence, chemists have paid much attention to develop effective methods for their formation. In this context, transition metals catalyzed the cross-coupling of aryl halides, thiols, or disulfides and have been developed as one of the most reliable methods for the construction of C−S bonds.[2] The direct cross-dehydrogenative coupling (CDC) between C−H and S−H is a more attractive strategy for C−S bond formation than the traditional methods as it offers shorter synthetic routes with wide availability of starting materials and atom economical and environmentally benign protocols (Scheme 1).[3] In the past decade, a number of CDC methodologies have been established for C(sp^2)−S bond formation under transition-metal-catalyzed or metal-free conditions (Scheme 1a).[4,5] However, the overwhelming majority of selective mono- and dithiolation of arene reactions with high ortho selectivity that have been reported so far require directing groups (DGs) in the presence of transition-metal catalysts (Scheme 1b).[6] In addition, these transformations are usually performed in toxic organic solvents and require using stoichiometric amounts of chemical oxidants. Therefore, the invention of more safe and efficient protocols for selective mono- and dithiolation of arenes from readily accessible substrates remains a challenging issue.

Performing direct oxidative C−H functionalization under simple and green reaction conditions to achieve high chemoselectivity is always a longstanding goal for organic chemists.[7] From the point of view of sustainable and green chemistry, solvents occupy a strategic place. The reaction performed in green solvents or under solvent-free conditions is greatly desired. On the other hand, in contrast to the traditional chemical oxidants, molecular oxygen, especially air, is considered to be an ideal oxidant due to its abundance and environmental friendliness.[8] What is more, it is so difficult to achieve high chemoselectivity for C−H functionalization without transition-metal catalysts. Therefore, performing such transformations under transition-metal-free and solvent-free conditions and employing air as the oxidant is a dream

Scheme 1. CDC for C(sp^2)−S Bond Formation

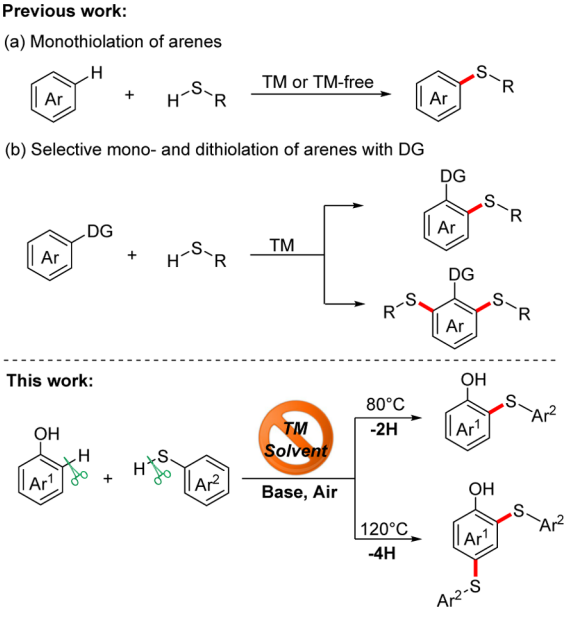


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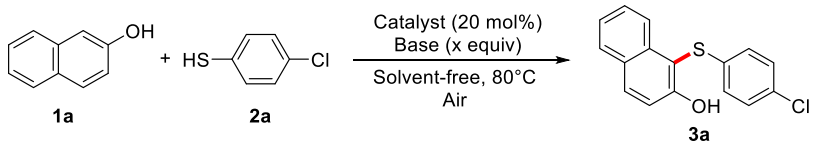
Table 1. Optimization of the Reaction Conditions[a]



1a 2a 3a

entry	catalyst	base (equiv)	time (h)	yield[b] (%)
1	$FeCl_3·6H_2O$	K_2CO_3 (1)	1	85
2	$FeCl_3·6H_2O$		3	
3		K_2CO_3 (1)	3	71
4		Na_2CO_3 (1)	3	41
5		Cs_2CO_3 (1)	3	90
6		K_3PO_4 (1)	3	43
7		KOH (1)	3	70
8		NaOH (1)	3	62
9		***t*BuOK (1)**	**1.5**	**93**
10		*t*BuOLi (1)	3	87
11		DBU (1)	3	
12		*t*BuOK (0.5)	2	77, 95[c]
13		*t*BuOK (0.1)	2	38, 71[c]

[a]Reaction conditions: **1a** (0.6 mmol, 1.0 equiv), **2a** (1.8 mmol, 3.0 equiv), under open air. [b]Yields of isolated products. [c]**1a** (5 mmol, 1.0 equiv), **2a** (7.5 mmol, 1.5 equiv), *t*BuOK (2.5 mmol, 0.5 equiv).

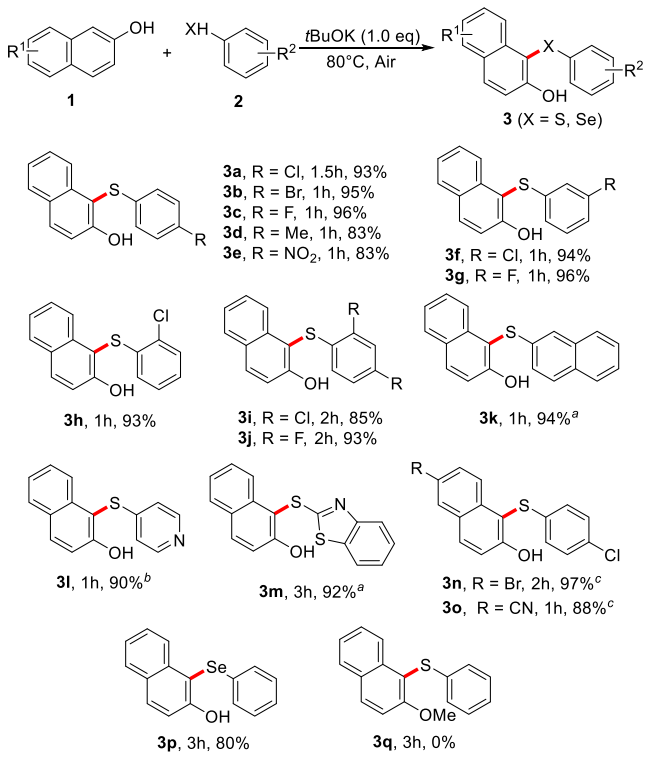
reaction. Here, within our program on sustainable oxidation for C−C and C−heteroatom bond formation,[9] we disclose an unprecedented base-air oxidation system for direct selective thiolation of arenes. This work has made notable achievements that include (1) a free hydroxyl group as a DG to control regioselectivity, (2) controlled temperature for selective mono- and dithiolation, (3) air (molecular oxygen) as the terminal oxidant, (4) performing under transition-metal-free and solvent-free conditions, and (5) readily available for large-scale synthesis.

RESULTS AND DISCUSSION

The thiolation between 2-naphthol (**1a**) and 4-chlorobenzenethiol (**2a**) was selected as model reaction for screening various parameters with air as the oxidant (Table 1). Initial attempts employing $FeCl_3·6H_2O$ as the catalyst and K_2CO_3 as the base under solvent-free conditions at 80 °C afforded monothiolation product **3a** in 85% yield (entry 1). However, $FeCl_3·6H_2O$ could not catalyze this process without any base (entry 2). To our surprise, product **3a** could be obtained in 71% yield in the absence of iron salt under base conditions (entry 3). Although the iron salts could give a higher yield of **3a** in a short time (entry 1 vs 3), we chose to optimize the reaction conditions under base conditions without any transition-metal catalysts. Next, a series of inorganic bases such as Na_2CO_3, Cs_2CO_3, K_3PO_4, KOH, NaOH, *t*BuOK, and *t*BuOLi were evaluated (entries 4−10). They all could drive this reaction, and *t*BuOK delivered desired product **3a** in a good yield up to 93% (entry 9). An organic base named 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was also investigated, but it failed to promote this reaction (entry 11). It was found that an excellent yield of 95% was obtained when the reaction was performed in gram-scale synthesis with 0.5 equiv of *t*BuOK (entry 12). Even when the amount of the base was decreased to 0.1 equiv, the reaction still proceeded smoothly to provide **3a** in 71% yield (entry 13). These results indicate that the present methodology is easily applicable for large-scale synthesis.

With the optimized reaction conditions in hand (Table 1, entry 9), we first investigated the substrate scope of 2-naphthols **1** with a large variety of aryl thiols **2** for the monothiolation reaction (Scheme 2). Overall, the direct thiolation reaction possesses good functional group tolerance on the aromatic ring of thiols, including electron-withdrawing and electron-donating groups at the para, meta, and ortho

Scheme 2. Reaction Scope of Aryl Thiols[a]



[a]Reaction conditions: **1a** (0.6 mmol, 1.0 equiv), **2** (1.8 mmol, 3.0 equiv), and *t*BuOK (1.0 equiv), under open air. Yields of isolated products. [a]DMSO (0.6 mL) was used. [b]At 150 °C. [c]At 120 °C.

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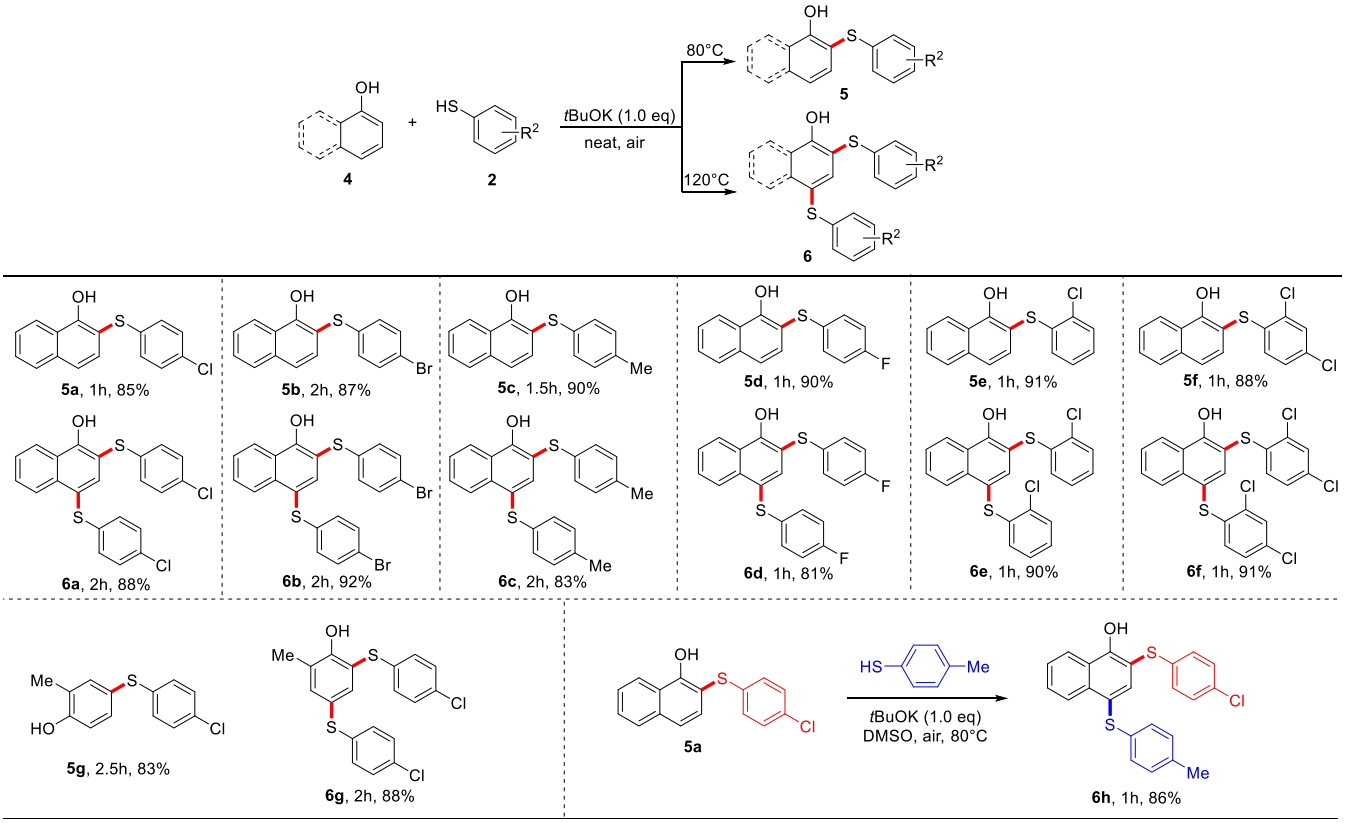
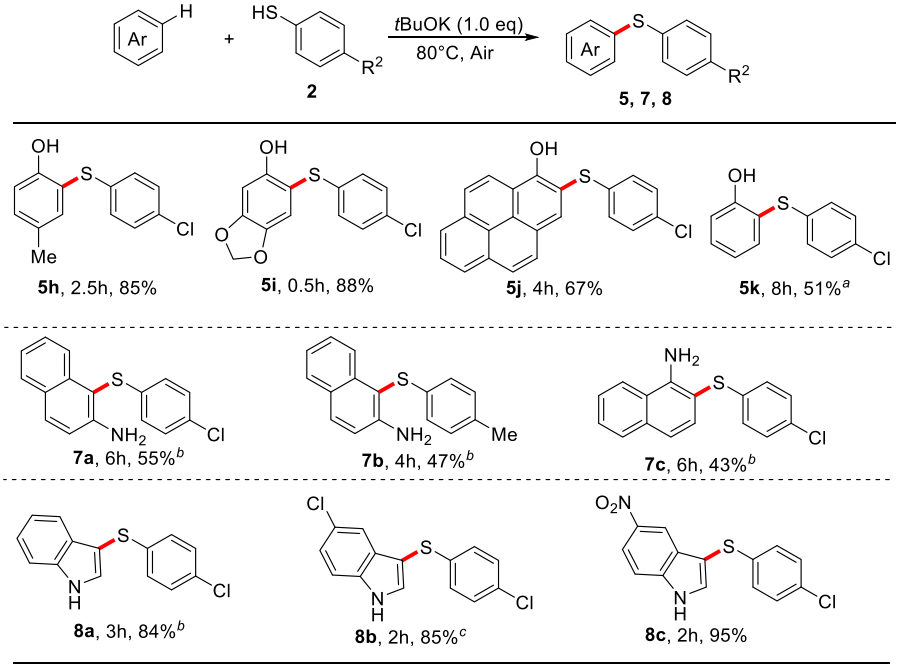
Scheme 3. Selective Synthesis of Mono- and Dithiolated Phenols[a]



[a]Reaction conditions: **4** (0.6 mmol, 1.0 equiv), **2** (1.8 mmol, 3.0 equiv), and *t*BuOK (1.0 equiv), under open air. Yields of isolated products.

Scheme 4. Reaction Scope of Arenes[a]



[a]Reaction conditions: **1** (0.6 mmol, 1.0 equiv), **2** (1.8 mmol, 3.0 equiv), and *t*BuOK (1.0 equiv), under open air. Yields of isolated products. [a]KOH was used instead of *t*BuOK, performed in DMSO (1 mL). [b]At 120 °C. [c]At 150 °C.

positions. They all successfully furnished the thiolation products (**3a**–**h**) in good to excellent yields. There is no obvious steric effect of the ortho position. Remarkably, aryl thiol with disubstituent also smoothly delivered the desired products (**3i** and **3j**). Naphthalene-2-thiol with an extended π-framework was also reactive (**3k**). Additionally, heterocyclic

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thiols, even a strong coordinating pyridine thiol, were well tolerated to afford the thiolated products (**3l** and **3m**) in high yields. The naphthol derivatives were compatible and gave the corresponding products (**3n** and **3o**) in good yields as well. Notably, benzeneselenol could also be coupled with 2-naphthol under the optimized conditions and successfully converted into the desired selenenyl product (**3p**) with a satisfactory yield. It is worth highlighting that the present catalytic system was compatible with various functional groups such as halogens (fluoro, chloro, and bromo), hydroxyl, and cyano, which could be easily further functionalized. However, 2-methoxynaphthalene did not yield the desired product (**3q**). The reason may be that the radical intermediate could be not generated under the present conditions.

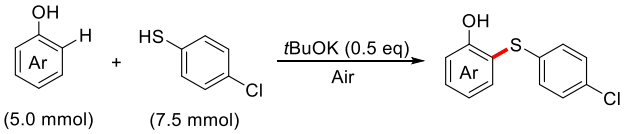
Due to the strong electronic directing effects of the hydroxyl group, the functionalization of phenols often yields a mixture of ortho- and para-substituted products. Next, 1-naphthol was selected as the model substrate to invest the conditions for selective synthesis of substituted phenols. It was found that monothiolation product **5a** could be obtained in 85% yield under the standard conditions. When the temperature was raised to 120 °C, it exclusively afforded dithiolation product **6a** in 88% yield (see Table S2 in the Supporting Information). Next, we evaluated the utility of this method for selective synthesis of mono- and dithiolated phenols. Scheme 3 shows that the reaction between 1-naphthol with a variety of aryl thiols all proceeded smoothly and selectively delivered the corresponding mono- (**5a−f**) and dithiolation products (**6a−f**) in good to excellent yields under 80 or 120 °C. O-cresol as another kind of phenol was also investigated. The mono- and dithiolation products **5g** and **6g** were obtained in 83 and 88% yield, respectively. The dithiolation products could be also prepared in a two-step protocol by introducing two different aryl thiol groups (**6h**). The abovementioned results indicate that base-promoted aerobic CDC reaction for selective synthesis of mono- and dithiolated phenols has been successfully established.

Subsequently, various arenes were tested for the monothiolation under the optimized conditions (Scheme 4). The results are very encouraging. Different kinds of arenes including phenols, naphthylamines, and indoles worked well with this method. A variety of phenols showed high reactivity to afford the corresponding products (**5h−j**), including polyaromatic 1-hydroxypyrene (**5j**). However, naphthylamines showed less reactivity and afforded the desired product in moderate yields (**7a−c**). Indoles even containing a very strong electron-withdrawing nitro group were all well tolerated and provided the corresponding thiolation products (**8a−c**) in good to excellent yields.

To demonstrate the practicality of this unique thiolation reaction, we also conducted the gram-scale synthesis of **5i** and **8a** (Scheme 5a). The results are very encouraging. When we decreased the base loading and substrate ratio to 0.5 equiv and 1:1.5, respectively, all the thiolation products could be isolated in higher yields. Then, several derivatization experiments were carried out. Compound **3a** could be oxidized by treatment with oxone in different solvents, affording corresponding sulfoxide (**9**) and sulfone (**10**) in 86 and 92% yield, respectively. Alternatively, the hydroxyl group of **3a** could be easily transformed to the methoxy group (**11**). Furthermore, trifluoromethanesulfonate (**12**) could be obtained in a near quantitative yield from **3a**.

Scheme 5. Gram-Scale Synthesis and Synthetic Manipulations[a]

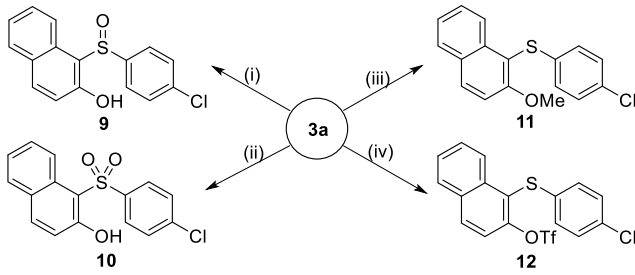
(a) Gram-scale synthesis



(5.0 mmol) (7.5 mmol)

Product	Yield of gram-scale synthesis	Yield of 0.6 mmol-scale synthesis
5i	93% (1.31 g)	88%
8a	97% (1.26 g)	84%

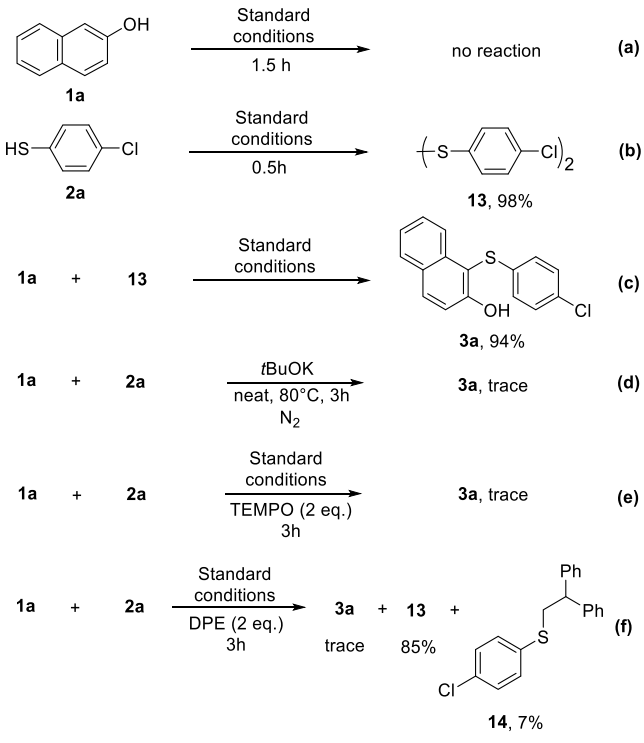
(b) Synthetic manipulations



[a]Conditions: (i) oxone (0.6 equiv) and ethanol, 60 °C, 2h, 86% yield. (ii) Oxone (1.5 equiv) and ethanol/H_2O (1:1), 60 °C, 3h, 92% yield. (iii) CH_3I (1.5 equiv), K_2CO_3 (2.0 equiv), and DMF, r.t., 98% yield. (iv) Tf_2O (1.5 equiv), pyridine (2.0 equiv), and DCM, 0 °C to r.t., 98% yield.

To gain an understanding of the reaction mechanism, some control experiments were carried out (Scheme 6). First, we performed the homocoupling of **1a** and **2a** under the standard conditions(Scheme 6a,b). Only **2a** afforded corresponding coupling product **13**. Next, treatment of **1a** with homocoupling

Scheme 6. Control Experiments



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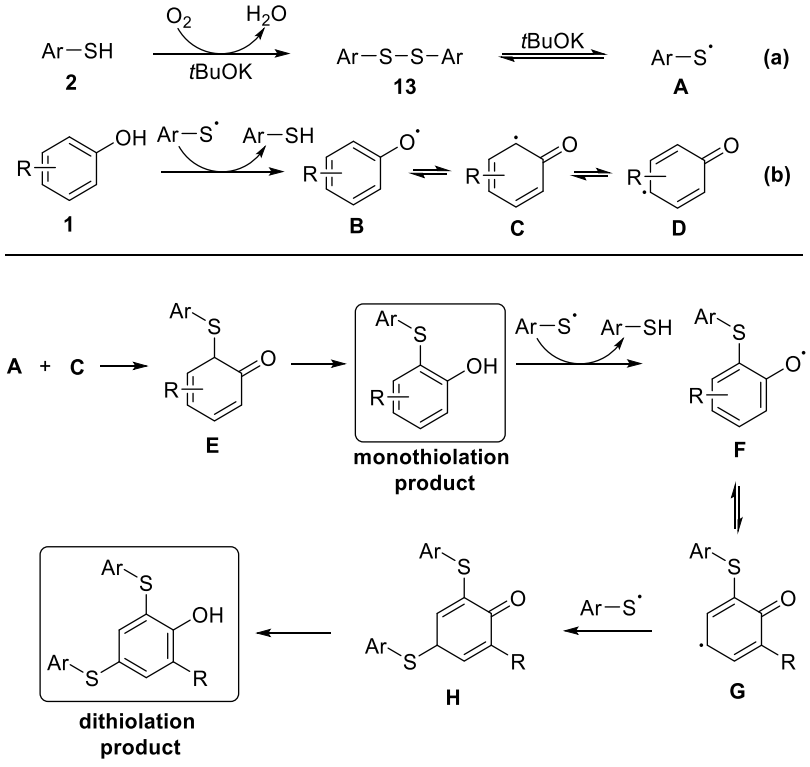
Scheme 7. Proposed Reaction Mechanism



product **13** delivered thiolation product **3a** in 94% yield (Scheme 6c). The abovementioned results indicate that intermediate **13** may be involved in the reaction. When the reaction was performed under N_2, the coupling of **1a** with **2a** did not proceed, which implies the importance of air (molecular oxygen; Scheme 6d). Moreover, the reaction was completely inhibited in the presence of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy; Scheme 6e) or DPE (1,1-diphenylethylene; Scheme 6f), thus indicating that a radical process may be involved. The isolation of product **14** suggests that intermediate **A** (see Scheme 7) may be generated in the reaction.

On the basis of the preliminary experimental results, a tentative mechanism is depicted in Scheme 7. Initially, aryl thiol **2** undergoes homocoupling reaction to form intermediate **13**, which could be transformed to radical **A** under basic conditions (Scheme 7a). Subsequently, **A** abstracts a hydrogen atom from phenol to form **2** and the radicals **B**, **C**, and **D**. Next, **A** couples with **C** to furnish the desired monothiolation product, which could be further oxidized to give radical **F**. Then, **G** of resonance **F** easily couples with radical **A** to afford the dithiolation product through intermediate **H**. Naphthylamines and indoles undergo a similar transformation.

CONCLUSIONS

In summary, we have developed selective CDC reaction for the synthesis of mono- and dithiolation arenes under basic conditions without using any transition-metal catalysts and solvents. Environmentally friendly air (molecular oxygen) was employed as an ideal oxidant. This method is featured with simple and green reaction conditions, broad substrate scope, and good functional group tolerance, providing a practical protocol for synthetic chemistry and industrial manufacturing.

EXPERIMENTAL SECTION

General Information. All reagents including the starting materials (arenes and thiols) are commercially available (purchased from Sigma-Aldrich, TCI, and Alfa Aesar) and were used without further purification. The melting points were determined with an X-4 apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer with DMSO-d_6 as the solvent. The chemical shifts are reported relative to tetramethyl silane (TMS) as the internal standard. The ^{1}H NMR data are reported as the chemical shift in parts per million, multiplicity (s, singlet; d, doublet; t, triplet; and m, multiplet), coupling constant in hertz, and number of protons. High-resolution mass spectrometry (HRMS) spectra were obtained on an IonSpec Fourier-transform ion cyclotron resonance mass spectrometer with electrospray ionization (ESI) resource.

General Procedure for the Preparation of Compounds 3, 5, 7, and 8. In a 10 mL reaction vial, equipped with a magnetic stirring bar, arenes (0.6 mmol), aromatic thiols (1.8 mmol), and *t*-BuOK (0.6 mmol, 67.3 mg) were added. Then, the vial was placed in a preheated metal block at 80 °C in the presence of ambient air. The formation of the monothiolation products was monitored by TLC. After completion of the reaction, the mixture was cooled to 50 °C and diluted with ethyl acetate (5.0 mL) and then quenched with cold water (15 mL) and extracted with ethyl acetate (2 × 20 mL). After drying with anhydrous Na_2SO_4, the organic layer was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (200−300 mesh) using petroleum/ethyl acetate (20/1−10/1) as eluent to afford the desired monothiolation products.

*1-((4-Chlorophenyl)thio)naphthalen-2-ol (**3a**).*[4c] The title compound was isolated by column chromatography (eluent: petroleum ether) as a white solid in 93% yield (160.0 mg). mp 180−181 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.39 (s, 1H, OH), 8.17 (d, 1H, ArH, J = 8.8 Hz), 7.98 (d, 1H, ArH, J = 8.8 Hz), 7.89 (d, 1H, ArH, J = 8 Hz), 7.50 (t, 1H, ArH, J = 7.8 Hz), 7.38−7.33 (m, 2H, ArH), 7.25 (d, 2H, ArH, J = 8.4 Hz), 6.94 (d, 2H, ArH, J = 8.4 Hz). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 158.9, 137.3, 136.1, 132.8, 129.8, 129.3, 129.0, 128.2, 127.7, 124.2, 123.8, 118.9, 107.4.

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*1-(4-Bromo-phenylsulfanyl)-naphthalen-2-ol (**3b**).*[10] The title compound was isolated by column chromatography (eluent: petroleum ether) as a pale yellow solid in 95% yield (188.8 mg). mp 118−119 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.41 (s, 1H, OH), 8.18 (d, 1H, ArH, J = 8.4 Hz), 7.98 (d, 1H, ArH, J = 9.0 Hz), 7.89 (d, 1H, ArH, J = 8.0 Hz), 7.52−7.48 (m, 1H, ArH), 7.39−7.34 (m, 4H, ArH), 6.90 (d, 2H, ArH, J = 8.6 Hz). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 158.9, 138.0, 136.1, 132.9, 132.2, 129.1, 129.0, 128.3, 128.1, 124.3, 123.8, 119.0, 118.0, 107.4.

*1-(4-Fluoro-phenylsulfanyl)-naphthalen-2-ol (**3c**).*[11] The title compound was isolated by column chromatography (eluent: petroleum ether) as a white solid in 96% yield (155.5 mg). mp 116−118 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.33 (s, 1H, OH), 8.24 (d, 1H, ArH, J = 8.0 Hz), 7.97 (d, 1H, ArH, J = 8.0 Hz), 7.88 (d, 1H, ArH, J = 8.0 Hz), 7.52−7.49 (m, 1H, ArH), 7.37−7.34 (m, 2H, ArH), 7.08−7.00 (m, 4H, ArH). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 160.6 (d, J_{CF} = 240.4 Hz), 158.8, 136.2, 133.6, 132.7, 129.0, 128.5, 128.1, 124.4, 123.7, 119.0, 116.6, 116.3, 108.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ −116.2.

*1-p-Tolylsulfanyl-naphthalen-2-ol (**3d**).*[4c] The title compound was isolated by column chromatography (eluent: petroleum ether) as a pale yellow solid in 83% yield (132.7 mg). mp 76−78 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.24 (s, 1H, OH), 8.23 (d, 1H, ArH, J = 8.0 Hz), 7.93 (d, 1H, ArH, J = 8.0 Hz), 7.85 (d, 1H, ArH, J = 8.0 Hz), 7.47 (t, 1H, ArH, J = 8.0 Hz), 7.37−7.31 (m, 2H, ArH), 6.98 (d, 2H, ArH, J = 8.0 Hz), 6.88 (d, 2H, ArH, J = 8.0 Hz), 2.17 (s, 3H, CH). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 158.8, 136.3, 134.7, 134.6, 132.4, 130.5, 130.3, 129.1, 129.0, 128.6, 128.0, 126.6, 124.6, 123.7, 119.0, 108.7, 20.9.

*1-((4-Nitrophenyl)thio)naphthalen-2-ol (**3e**).*[11] The title compound was isolated by column chromatography (eluent: petroleum ether: ethyl acetate = 8:1) as a yellow solid in 83% yield (148.1 mg). mp 125−127 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.67 (s, 1H, OH), 8.12 (d, 1H, ArH, J = 8.4 Hz), 8.06 (d, 3H, ArH, J = 8.8 Hz), 7.93 (d, 1H, ArH, J = 8.0 Hz), 7.52 (t, 1H, ArH, J = 7.5 Hz), 7.45−7.34 (m, 2H, ArH), 7.12 (d, 2H, ArH, J = 8.8 Hz). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 159.2, 148.7, 144.8, 135.9, 133.5, 129.2, 129.1, 128.5, 125.8, 124.5, 124.0, 123.9, 119.0, 105.6.

*1-(3-Chloro-phenylsulfanyl)-naphthalen-2-ol (**3f**).* The title compound was isolated by column chromatography (eluent: petroleum ether) as a white solid in 94% yield (161.8 mg). mp 115−117 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.47 (s, 1H, OH), 8.20 (d, 1H, ArH, J = 8.0 Hz), 8.00 (d, 1H, ArH, J = 12.0 Hz), 7.89 (d, 1H, ArH, J = 8.0 Hz), 7.50 (t, 1H, ArH, J = 8.0 Hz), 7.40−7.34 (m, 2H, ArH), 7.20 (t, 1H, ArH, J = 8.0 Hz), 7.11 (d, 1H, ArH, J = 8.0 Hz), 6.94 (d, 2H, ArH, J = 12.0 Hz). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 159.1, 140.9, 136.2, 134.1, 133.1, 131.0, 129.1, 128.3, 125.2, 125.1, 124.7, 124.2, 123.9, 119.0, 107.0. HRMS (ESI) m/z: calcd for $C_{16}H_{11}ClNaOS$ ([M + Na]$^+$), 309.0111; found, 309.0109.

*1-(3-Fluoro-phenylsulfanyl)-naphthalen-2-ol (**3g**).*[10] The title compound was isolated by column chromatography (eluent: petroleum ether) as a yellow sticky liquid in 96% yield (155.7 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.52 (s, 1H, OH), 8.22 (d, 1H, ArH, J = 8.4 Hz), 8.03 (d, 1H, ArH, J = 9.2 Hz), 7.92 (d, 1H, ArH, J = 8.0 Hz), 7.55−7.50 (m, 1H, ArH), 7.43−7.36 (m, 2H, ArH), 7.28−7.22 (m, 1H, ArH), 6.93−6.89 (m, 1H, ArH), 6.84−6.82 (m, 1H, ArH), 6.74−6.71 (m, 1H, ArH). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 162.9 (d, J_{CF} = 243.8 Hz), 159.1, 141.1, 136.2, 133.1, 129.1, 128.3, 124.3, 123.8, 122.0, 119.0, 112.6, 112.2, 107.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ −111.4.

*1-(2-Chloro-phenylsulfanyl)-naphthalen-2-ol (**3h**).*[10] The title compound was isolated by column chromatography (eluent: petroleum ether) as a yellow liquid in 93% yield (160.0 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.55 (s, 1H, OH), 8.12 (d, 1H, ArH, J = 8.0 Hz), 8.01 (d, 1H, ArH, J = 8.0 Hz), 7.89 (d, 1H, ArH, J = 8.0 Hz), 7.50−7.41 (m, 3H, ArH), 7.35 (t, 1H, ArH, J = 8.0 Hz), 7.07−7.03 (m, 1H, ArH), 7.01−6.97 (m, 1H, ArH), 6.33−6.31 (m, 1H, ArH). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 159.4, 137.3, 136.2, 133.2, 130.1, 129.9, 129.2, 129.1, 128.3, 127.9, 126.2, 126.1 124.1, 123.9, 119.1, 106.1.

*1-(2,4-Dichloro-phenylsulfanyl)-naphthalen-2-ol (**3i**).* The title compound was isolated by column chromatography (eluent: petroleum ether) as a pale yellow liquid in 85% yield (163.8 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.62 (s, 1H, OH), 8.05 (t, 2H, ArH, J = 9.2 Hz), 7.92 (d, 1H, ArH, J = 8.0 Hz), 7.66 (d, 1H, ArH, J = 2.4 Hz), 7.53−7.49 (m, 1H, ArH), 7.40−7.36 (m, 2H, ArH), 7.13 (dd, 1H, ArH, J = 8.8 Hz), 6.27 (d, 1H, ArH, J = 8.4 Hz). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 159.4, 136.4, 136.0, 133.5, 130.7, 129.9, 129.3, 129.2, 128.5, 128.2, 127.2, 124.0, 123.9, 119.0, 105.5. HRMS (ESI) m/z: calcd for $C_{16}H_{11}Cl_2OS$ ([M + H]$^+$), 320.9902; found, 320.9904.

*1-((2,4-Difluorophenyl)thio)naphthalen-2-ol (**3j**).* The title compound was isolated by column chromatography (eluent: petroleum ether) as a yellow sticky liquid in 93% yield (160.9 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.56 (s, 1H, OH), 8.25 (d, 1H, ArH, J = 8.4 Hz), 8.01 (d, 1H, ArH, J = 9.2 Hz), 7.90 (d, 1H, ArH, J = 8.0 Hz), 7.56−7.51 (m, 1H, ArH), 7.41−7.30 (m, 3H, ArH), 6.91−6.86 (m, 1H, ArH), 6.62−6.56 (m, 1H, ArH). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 159.3, 136.2, 133.0, 129.1, 128.3, 124.1, 123.8, 120.9, 120.7, 119.0, 112.7, 112.5, 105.9, 105.0, 104.7, 104.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ −107.5, −111.8. HRMS (ESI) m/z: calcd for $C_{16}H_{11}F_2OS$ ([M + H]$^+$), 289.0493; found, 289.0494.

*1-(Naphthalen-2-ylsulfanyl)-naphthalen-2-ol (**3k**).*[4c] The title compound was isolated by column chromatography (eluent: petroleum ether) as a white solid in 94% yield (170.6 mg). mp 87−88 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.45 (s, 1H, OH), 8.31 (d, 1H, ArH, J = 8.8 Hz), 8.02 (d, 1H, ArH, J = 8.8 Hz), 7.90 (d, 1H, ArH, J = 8.0 Hz), 7.79−7.73 (m, 2H, ArH), 7.62−7.60 (m, 1H, ArH), 7.50−7.33 (m, 6H, ArH), 7.20 (dd, 1H, ArH, J_1 = 2.0 Hz, J_2 = 8.8 Hz). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 159.1, 136.4, 136.0, 133.8, 132.8, 131.3, 129.2, 129.1, 128.9, 128.1, 128.0, 127.0, 125.7, 125.2, 124.6, 123.8, 123.6, 119.1, 108.0.

*1-(Pyridin-4-ylsulfanyl)-naphthalen-2-ol (**3l**).* The title compound was isolated by column chromatography (eluent: petroleum ether) as a yellow liquid in 90% yield (136.8 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.60 (s, 1H, OH), 8.25 (dd, 2H, ArH, J_1 = 1.4 Hz, J_2 = 4.8 Hz), 8.10 (d, 1H, ArH, J = 8.0 Hz), 8.03 (d, 1H, ArH, J = 8.0 Hz), 7.92 (d, 1H, ArH, J = 8.0 Hz), 7.53−7.49 (m, 1H, ArH), 7.40−7.36 (m, 2H, ArH), 6.86 (dd, 2H, ArH, J_1 = 1.6 Hz, J_2 = 4.6 Hz). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 159.2, 149.7, 149.5, 136.0, 133.4, 129.2, 129.1, 128.5, 124.0, 120.3, 119.0, 104.9. HRMS (ESI) m/z: calcd for $C_{15}H_{12}NOS$ ([M + H]$^+$), 254.0634; found, 254.0647.

*1-(Benzothiazol-2-ylsulfanyl)-naphthalen-2-ol (**3m**).*[4c] The title compound was isolated by column chromatography (eluent: petroleum ether) as a gray solid in 92% yield (170.8 mg). mp 156−158 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.99 (s, 1H, OH), 8.24 (d, 1H, ArH, J = 8.4 Hz), 8.09 (d, 1H, ArH, J = 8.4 Hz), 7.94 (d, 1H, ArH, J = 8.0 Hz), 7.83−7.77 (m, 2H, ArH), 7.56 (t, 1H, ArH, J = 7.6 Hz), 7.41 (d, 3H, ArH, J = 7.6 Hz), 7.26 (t, 1H, ArH, J = 7.2 Hz). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 105.7, 118.6, 120.9, 121.5, 123.2, 123.6, 123.9, 126.1, 128.3, 128.6, 128.7, 133.9, 134.7, 135.4, 153.8, 159.1, 170.4.

*6-Bromo-1-(4-chloro-phenylsulfanyl)-naphthalen-2-ol (**3n**).*[12] The title compound was isolated by column chromatography (eluent: petroleum ether) as a white solid in 97% yield (212.8 mg). mp 198−201 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.63 (s, 1H, OH), 8.17 (d, 1H, ArH, J = 2.0 Hz), 8.10 (d, 1H, ArH, J = 8.8 Hz), 7.98 (d, 1H, ArH, J = 8.8 Hz), 7.62 (dd, 1H, ArH, J_1 = 2.0 Hz, J_2 = 9.0 Hz), 7.39 (d, 1H, ArH, J = 8.8 Hz), 7.26 (d, 2H, ArH, J = 8.4 Hz), 6.94 (d, 2H, ArH, J = 8.4 Hz). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 164.1, 141.7, 139.7, 136.8, 135.8, 135.5, 135.1, 134.7, 134.6, 134.3, 134.1, 132.6, 131.5, 125.0, 121.5, 112.7.

*5-(4-Chloro-phenylsulfanyl)-6-hydroxy-naphthalene-2-carbonitrile (**3o**).* The title compound was isolated by column chromatography (eluent: petroleum ether) as a white solid in 88% yield (164.6 mg). mp 157−159 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.13 (s, 1H, OH), 8.54 (d, 1H, ArH, J = 1.4 Hz), 8.30 (d, 1H, ArH, J = 8.8 Hz), 8.13 (d, 1H, ArH, J = 9.2 Hz), 7.78 (dd, 1H, ArH, J_1 = 1.6 Hz, J_2 = 8.8 Hz), 7.50 (d, 1H, ArH, J = 9.2 Hz), 7.27 (d, 2H, ArH, J = 8.4 Hz), 6.96 (d, 2H, ArH, J = 8.8 Hz). ^{13}C{^{1}H} NMR (100 MHz,

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DMSO-d_6): δ 161.2, 137.7, 136.1, 134.8, 133.1, 129.7, 129.0, 128.3, 127.6, 127.4, 125.2, 120.3, 119.2, 107.9, 105.5. HRMS (ESI) *m*/*z*: calcd for $C_{17}H_{11}ClNOS$ ([M + H]$^+$), 312.0244; found, 312.0248.

*1-Phenylselanyl-naphthalen-2-ol (**3p**).*[13] The title compound was isolated by column chromatography (eluent: petroleum ether) as a white solid in 80% yield (143.6 mg). mp 78−79 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.25 (s, 1H, OH), 8.25 (d, 1H, ArH, *J* = 8.4 Hz), 7.94 (d, 1H, ArH, *J* = 8.8 Hz), 7.85 (d, 1H, ArH, *J* = 8.0 Hz), 7.48−7.44 (m, 1H, ArH), 7.37−7.31 (m, 2H, ArH), 7.17−7.08 (m, 5H, ArH). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 157.7, 136.1, 132.8, 132.0, 129.2, 128.6, 128.5, 127.5, 126.4, 125.6, 123.1, 118.1, 107.5.

*2-(4-Chloro-phenylsulfanyl)-naphthalen-1-ol (**5a**).*[14] The title compound was isolated by column chromatography (eluent: petroleum ether) as a colorless liquid in 85% yield (146.2 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.02 (s, 1H, OH), 8.27 (d, 1H, ArH, *J* = 8.0 Hz), 7.89 (d, 1H, ArH, *J* = 7.6 Hz), 7.61−7.54 (m, 2H, ArH), 7.46 (d, 1H, ArH, *J* = 8.4 Hz), 7.39 (d, 1H, ArH, *J* = 8.4 Hz), 7.35 d, 2H, ArH, *J* = 8.8 Hz), 7.11 (d, 2H, ArH, *J* = 8.8 Hz). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 154.5, 136.2, 134.8, 131.9, 130.3, 129.0, 128.8, 127.6, 127.4, 125.7, 125.1, 122.6, 120.3, 110.3.

*2-(4-Bromo-phenylsulfanyl)-naphthalen-1-ol (**5b**).* The title compound was isolated by column chromatography (eluent: petroleum ether) as a white solid in 87% yield (172.9 mg). mp 72−74 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.05 (s, 1H, OH), 8.30 (d, 1H, ArH, *J* = 7.6 Hz), 7.93−7.91 (m, 1H, ArH), 7.63−7.56 (m, 2H, ArH), 7.51−7.48 (m, 3H, ArH), 7.42 (d, 1H, ArH, *J* = 8.4 Hz), 7.07 (d, 2H, ArH, *J* = 8.4 Hz). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 155.1, 137.4, 135.3, 132.5, 132.4, 129.5, 128.1, 127.9, 126.2, 125.6, 123.1, 120.8, 119.0, 110.5. HRMS (ESI) *m*/*z*: calcd for $C_{16}H_{12}BrOS$ ([M + H]$^+$), 330.9787; found, 330.9793.

*2-p-Tolylsulfanyl-naphthalen-1-ol (**5c**).*[14] The title compound was isolated by column chromatography (eluent: petroleum ether) as a pink solid in 90% yield (143.9 mg). mp 180−181 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.85 (s, 1H, OH), 8.25−8.22 (m, 1H, ArH), 7.86−7.84 (m, 1H, ArH), 7.56−7.51 (m, 2H, ArH), 7.41 (d, 1H, ArH, *J* = 8.8 Hz), 7.30 (d, 1H, ArH, *J* = 8.4 Hz), 7.13−7.08 (m, 4H, ArH), 2.25 (s, 3H, CH). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 153.9, 136.2, 134.8, 133.3, 131.6, 130.3, 129.1, 128.1, 127.5, 126.1, 125.5, 122.9, 120.6, 112.9, 20.98.

*2-(4-Fluoro-phenylsulfanyl)-naphthalen-1-ol (**5d**).*[14] The title compound was isolated by column chromatography (eluent: petroleum ether) as a colorless liquid in 90% yield (145.9 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.95 (s, 1H, OH), 8.27−8.25 (m, 1H, ArH), 7.88−7.86 (m, 1H, ArH), 7.58−7.53 (m, 2H, ArH), 7.44 (d, 1H, ArH, *J* = 8.8 Hz), 7.35 (d, 1H, ArH, *J* = 8.4 Hz), 7.25−7.21 (m, 2H, ArH), 7.19−7.14 (m, 2H, ArH). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 162.6, 160.1, 154.2, 135.0, 132.6, 132.5, 131.8, 130.9, 130.8, 128.1, 127.7, 126.2, 125.5, 123.0, 120.7, 116.8, 116.6, 112.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ −111.4.

*2-(2-Chloro-phenylsulfanyl)-naphthalen-1-ol (**5e**).* The title compound was isolated by column chromatography (eluent: petroleum ether) as a colorless liquid in 91% yield (156.6 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.12 (s, 1H, OH), 8.31 (d, 1H, ArH, *J* = 8.0 Hz), 7.92 (d, 1H, ArH, *J* = 7.6 Hz), 7.64−7.55 (m, 2H, ArH), 7.51−7.49 (m, 2H, ArH), 7.39 (d, 1H, ArH, *J* = 8.4 Hz), 7.18−7.13 (m, 2H, ArH), 6.60−6.57 (m, 1H, ArH). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 156.0, 137.0, 135.6, 132.9, 130.5, 130.0, 128.2, 128.2, 128.1, 127.2, 127.0, 126.3, 125.7, 123.2, 121.1, 108.8. HRMS (ESI) *m*/*z*: calcd for $C_{16}H_{12}ClOS$ ([M + H]$^+$), 287.0292; found, 287.0293.

*2-(2,4-Dichloro-phenylsulfanyl)-naphthalen-1-ol (**5f**).* The title compound was isolated by column chromatography (eluent: petroleum ether) as a colorless liquid in 88% yield (169.6 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.19 (s, 1H, OH), 8.31 (d, 1H, ArH, *J* = 8.0 Hz), 7.92 (d, 1H, ArH, *J* = 7.2 Hz), 7.67−7.56 (m, 3H, ArH), 7.51 (d, 1H, ArH, *J* = 8.8 Hz), 7.40 (d, 1H, ArH, *J* = 8.4 Hz), 7.26−7.23 (m, 1H, ArH), 6.57 (d, 1H, ArH, *J* = 8.8 Hz). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 156.1, 136.5, 135.8, 132.8, 131.1, 130.5, 129.4, 128.4, 128.2, 128.2, 126.3, 125.7, 123.3, 121.2, 108.3. HRMS (ESI) *m*/*z*: calcd for $C_{16}H_{11}Cl_2OS$ ([M + H]$^+$), 320.9902; found, 320.9902.

*4-(4-Chloro-phenylsulfanyl)-2-methyl-phenol (**5g**).* The title compound was isolated by column chromatography (eluent: petroleum ether) as a colorless liquid in 83% yield (124.8 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.87 (s, 1H, OH), 7.32 (d, 2H, ArH, *J* = 8.4 Hz), 7.25 (s, 1H, ArH), 7.18 (dd, 1H, ArH, J_1 = 2.4 Hz, J_2 = 8.4 Hz), 7.05 (d, 2H, ArH, *J* = 8.4 Hz), 6.87 (d, 1H, ArH, *J* = 8.4 Hz), 2.12 (s, 3H, CH). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 157.3, 138.8, 137.5, 134.1, 130.4, 129.5, 128.7, 126.4, 119.6, 116.4, 16.3. HRMS (ESI) *m*/*z*: calcd for $C_{13}H_{10}ClOS$ ([M − H]$^-$), 249.0146; found, 249.0144.

*2-(4-Chloro-phenylsulfanyl)-4-methyl-phenol (**5h**).*[14] The title compound was isolated by column chromatography (eluent: petroleum ether) as a colorless liquid in 85% yield (127.8 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.77 (s, 1H, OH), 7.35 (d, 2H, ArH, *J* = 8.4 Hz), 7.11 (d, 2H, ArH, *J* = 8.8 Hz), 7.06 (d, 2H, ArH, *J* = 7.6 Hz), 6.86 (d, 1H, ArH, *J* = 7.6 Hz), 2.17 (s, 3H, CH). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 155.1, 135.7, 134.7, 131.0, 130.3, 129.4, 128.9, 128.6, 117.0, 115.9, 19.8.

*6-(4-Chloro-phenylsulfanyl)-benzo[1,3]dioxol-5-ol (**5i**).* The title compound was isolated by column chromatography (eluent: petroleum ether) as a white solid in 88% yield (148.2 mg). mp 109−111 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.75 (s, 1H, OH), 7.31 (d, 2H, ArH, *J* = 8.8 Hz), 7.03 (d, 2H, ArH, *J* = 8.4 Hz), 6.90 (s, 1H, ArH), 6.61 (s, 1H, ArH), 6.00 (s, 2H, CH). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 154.7, 150.2, 140.9, 137.8, 130.1, 129.3, 128.2, 114.8, 106.3, 102.0, 98.6. HRMS (ESI) *m*/*z*: calcd for $C_{13}H_9ClO_3S$ (M^+), 279.9961; found, 279.9962.

*2-(4-Chloro-phenylsulfanyl)-pyren-1-ol (**5j**).* The title compound was isolated by column chromatography (eluent: petroleum ether) as a yellow liquid in 67% yield (145.1 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.41 (s, 1H, OH), 8.43 (d, 1H, ArH, *J* = 9.2 Hz), 8.26 (s, 1H, ArH), 8.22−8.15 (m, 3H, ArH), 8.06−7.95 (m, 3H, ArH), 7.39 (d, 2H, ArH, *J* = 8.8 Hz), 7.21 (d, 2H, ArH, *J* = 8.8 Hz). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 152.0, 135.9, 131.8, 131.6, 131.4, 131.1, 130.4, 130.0, 129.7, 127.4, 127.3, 127.2, 126.1, 125.5, 125.3, 125.2, 124.8, 122.1, 120.0, 117.9. HRMS (ESI) *m*/*z*: calcd for $C_{22}H_{14}ClOS$ ([M + H]$^+$), 361.0448; found, 361.0451.

*2-((4-Chlorophenyl)thio)phenol (**5k**).*[15] The title compound was isolated by column chromatography (eluent: petroleum ether) as a colorless liquid in 51% yield (72.4 mg). ^{1}H NMR (400 MHz, chloroform-*d*): δ 7.51 (dd, 1H, ArH, J_1 = 7.7, J_2 = 1.6 Hz), 7.41−7.35 (m, 1H, ArH), 7.23−7.17 (m, 2H, ArH), 7.07 (dd, 1H, ArH, J_1 = 8.2, J_2 = 1.1 Hz), 7.02−6.98 (m, 2H, ArH), 6.98−6.93 (m, 1H, ArH), 6.43 (s, 1H, OH). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.18, 136.83, 134.45, 132.57, 132.15, 129.32, 128.12, 121.46, 115.93, 115.75.

General Procedure for the Preparation of Compounds 6a−g. In a 10 mL reaction vial, equipped with a magnetic stirring bar, arenes (0.6 mmol), aromatic thiols (1.8 mmol), and *t*-BuOK (0.6 mmol, 67.3 mg) were added. Then, the vial was placed in a preheated metal block at 120 °C in the presence of ambient air. The formation of the dithiolation products was monitored by TLC. After completion of the reaction, the mixture was cooled to 50 °C and diluted with ethyl acetate (5.0 mL) and then quenched with cold water (15 mL) and extracted with ethyl acetate (2 × 20 mL). After drying with anhydrous Na_2SO_4, the organic layer was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (200−300 mesh) using petroleum/ethyl acetate (20/1−10/1) as the eluent to afford desired dithiolation products.

*2,4-Bis-(4-chloro-phenylsulfanyl)-naphthalen-1-ol (**6a**).*[16] The title compound was isolated by column chromatography (eluent: petroleum ether) as a white solid in 88% yield (226.7 mg). mp 141−142 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.70 (s, 1H, OH), 8.40 (d, 1H, ArH, *J* = 8.4 Hz), 8.18 (d, 1H, ArH, *J* = 7.2 Hz), 7.77 (s, 1H, ArH), 7.64 (d, 2H, ArH, *J* = 3.2 Hz), 7.37 (d, 2H, ArH, *J* = 8.0 Hz), 7.28 (d, 2H, ArH, *J* = 8.0 Hz), 7.18 (d, 2H, ArH, *J* = 8.0 Hz), 7.03 (d, 2H, ArH, *J* = 8.0 Hz). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 157.2, 141.3, 137.1, 136.0, 135.3, 131.2, 130.8, 129.8, 129.7, 129.6, 129.3, 128.8, 127.0, 126.8, 125.8, 124.2, 119.4, 111.7.

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*2,4-Bis-(4-bromo-phenylsulfanyl)-naphthalen-1-ol (**6b**).* The title compound was isolated by column chromatography (eluent: petroleum ether) as a yellow solid in 92% yield (286.1 mg). mp 161−164 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.72 (s, 1H, OH), 8.39−8.37 (m, 1H, ArH), 8.18−8.15 (m, 1H, ArH), 7.76 (s, 1H, ArH), 7.67−7.63 (m, 2H, ArH), 7.49 (d, 2H, ArH, J = 8.8 Hz), 7.41 (d, 2H, ArH, J = 8.4 Hz), 7.09 (d, 2H, ArH, J = 8.8 Hz), 6.95 (d, 2H, ArH, J = 8.8 Hz). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 157.3, 141.5, 137.7, 136.7, 135.4, 132.5, 129.9, 129.4, 129.0, 127.1, 126.7, 125.8, 124.2, 119.4, 119.1, 119.0, 111.4. HRMS (ESI) m/z: calcd for $C_{22}H_{13}Br_2OS_2$ ([M − H]$^-$), 514.8780; found, 514.8783.

*2,4-Bis-p-tolylsulfanyl-naphthalen-1-ol (**6c**).* The title compound was isolated by column chromatography (eluent: petroleum ether) as a white solid in 83% yield (193.5 mg). mp 102−104 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.40 (s, 1H, OH), 8.34−8.30 (m, 1H, ArH), 8.19−8.16 (m, 1H, ArH), 7.62−7.57 (m, 2H, ArH), 7.54 (s, 1H, ArH), 7.13 (s, 4H, ArH), 7.03 (d, 2H, ArH, J = 8.4 Hz), 6.95 (d, 2H, ArH, J = 8.0 Hz), 2.26 (s, 3H, CH), 2.20 (s, 3H, CH). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 155.2, 139.0, 136.7, 135.9, 134.6, 133.8, 132.4, 130.5, 130.4, 129.7, 128.6, 128.2, 126.8, 126.6, 125.8, 123.8, 120.8, 114.0, 21.0, 20.9. HRMS (ESI) m/z: calcd for $C_{24}H_{21}OS_2$ ([M + H]$^+$), 389.1028; found, 389.1024.

*2,4-Bis-(4-fluoro-phenylsulfanyl)-naphthalen-1-ol (**6d**).* The title compound was isolated by column chromatography (eluent: petroleum ether) as a white solid in 81% yield (192.7 mg). mp 108−109 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.54 (s, 1H, OH), 8.36−8.33 (m, 1H, ArH), 8.20−8.18 (m, 1H, ArH), 7.66−7.55 (m, 3H, ArH), 7.30−7.26 (m, 2H, ArH), 7.21−7.16 (m, 2H, ArH), 7.12−7.07 (m, 4H, ArH). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 161.6 (d, J_{CF} = 242.6 Hz), 161.2 (d, J_{CF} = 242.1 Hz), 155.6, 139.1, 134.6, 132.7, 131.6, 130.3, 128.9, 126.9, 126.6, 125.6, 123.9, 120.8, 117.0, 116.8, 113.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ −115.2, −116.6. HRMS (ESI) m/z: calcd for $C_{22}H_{14}F_2OS_2$ (M$^+$), 396.0454; found, 396.0452.

*2,4-Bis-(2-chloro-phenylsulfanyl)-naphthalen-1-ol (**6e**).* The title compound was isolated by column chromatography (eluent: petroleum ether) as a colorless liquid in 90% yield (231.9 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.88 (s, 1H, OH), 8.44−8.41 (m, 1H, ArH), 8.13−8.11 (m, 1H, ArH), 7.77 (s, 1H, ArH), 7.70−7.66 (m, 2H, ArH), 7.52−7.47 (m, 2H, ArH), 7.23−7.17 (m, 2H, ArH), 7.14−7.06 (m, 2H, ArH), 6.76−6.73 (m, 1H, ArH), 6.47 (dd, 1H, ArH, J_1 = 1.6 Hz, J_2 = 7.6 Hz). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 158.6, 142.6, 137.3, 136.2, 135.9, 130.9, 130.2, 130.0, 129.8, 128.4, 128.3, 127.8, 127.5, 127.4, 127.2, 126.9, 125.7, 124.4, 117.8, 109.8. HRMS (ESI) m/z: calcd for $C_{22}H_{14}Cl_2OS_2$ (M$^+$), 427.9863; found, 427.9843.

*2,4-Bis-(2,4-dichloro-phenylsulfanyl)-naphthalen-1-ol (**6f**).* The title compound was isolated by column chromatography (eluent: petroleum ether) as a colorless liquid in 91% yield (272.1 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.01 (s, 1H, OH), 8.46−8.44 (m, 1H, ArH), 8.11−8.09 (m, 1H, ArH), 7.83 (s, 1H, ArH), 7.73−7.63 (m, 4H, ArH), 7.27 (dd, 1H, ArH, J_1 = 2.0 Hz, J_2 = 8.8 Hz), 7.14 (dd, 1H, ArH, J_1 = 2.0 Hz, J_2 = 8.8 Hz), 6.73 (d, 1H, ArH, J = 8.4 Hz), 6.55 (d, 1H, ArH, J = 8.8 Hz). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 159.0, 142.8, 136.7, 135.9, 135.8, 131.5, 130.9, 130.8, 130.7, 130.0, 129.5, 129.4, 128.7, 128.5, 128.4, 127.2, 127.0, 125.6, 124.5, 117.4, 109.2. HRMS (ESI) m/z: calcd for $C_{22}H_{12}Cl_4OS_2$ (M$^+$), 495.9084; found, 495.9075.

*2,4-Bis((4-chlorophenyl)thio)-6-methylphenol (**6g**).* The title compound was isolated by column chromatography (eluent: petroleum ether) as a colorless liquid in 88% yield (207.7 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.53 (s, 1H, OH), 7.40−7.37 (m, 2H, ArH), 7.36−7.32 (m, 2H, ArH), 7.30 (dd, 1H, ArH, J_1 = 0.8 Hz, J_2 = 2.3 Hz), 7.22−7.18 (m, 2H, ArH), 7.14−7.06 (m, 3H, ArH), 2.22 (s, 3H, CH). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 155.9, 137.1, 136.9, 136.5, 134.6, 131.9, 131.4, 131.2, 129.9, 129.7, 129.6, 128.0, 122.5, 121.6, 17.1. HRMS (ESI) m/z: calcd for $C_{19}H_{15}Cl_2OS_2$ ([M + H]$^+$), 392.9936; found, 392.9939.

Procedure for the Preparation of Compound 6h. In a 10 mL reaction vial, equipped with a magnetic stirring bar, **4a** (0.6 mmol, 172.1 mg), 4-methylbenzenethiol (1.8 mmol, 223.6 mg), and *t*-BuOK (0.6 mmol, 67.3 mg) were added. Then, the vial was placed in a preheated metal block at 80 °C in the presence of ambient air. The formation of the dithiolation product was monitored by TLC. After completion of the reaction, the mixture was cooled to 50 °C and diluted with ethyl acetate (5.0 mL) and then quenched with cold water (15 mL) and extracted with ethyl acetate (2 × 20 mL). After drying with anhydrous Na_2SO_4, the organic layer was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (200−300 mesh) using petroleum/ethyl acetate (20/1−10/1) as the eluent to afford desired dithiolation product 6h as a colorless liquid in 86% yield (211.1 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.52 (s, 1H, OH), 8.40−8.31 (m, 1H, ArH), 8.27−8.16 (m, 1H, ArH), 7.66−7.59 (m, 3H, ArH), 7.40−7.30 (m, 2H, ArH), 7.16 (d, 2H, ArH, J = 8.6 Hz), 7.08−6.95 (m, 4H, ArH), 2.21 (s, 3H, CH). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 155.8, 139.1, 135.5, 135.4, 134.5, 133.1, 130.7, 129.9, 129.4, 129.1, 128.5, 127.9, 126.4, 126.1, 125.3, 123.5, 120.8, 111.3, 20.4. HRMS (ESI) m/z: calcd for $C_{23}H_{17}ClOS_2$ (M$^+$), 408.0409; found, 408.0401.

*1-(4-Chloro-phenylsulfanyl)-naphthalen-2-ylamine (**7a**).*[4c] The title compound was isolated by column chromatography (eluent: petroleum ether) as a brown liquid in 55% yield (94.3 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.98 (d, 1H, ArH, J = 8.4 Hz), 7.79 (d, 1H, ArH, J = 8.8 Hz), 7.73 (d, 1H, ArH, J = 8.0 Hz), 7.41−7.36 (m, 1H, ArH), 7.26 (d, 2H, ArH, J = 8.4 Hz), 7.20−7.17 (m, 2H, ArH), 6.95 (d, 2H, ArH, J = 8.6 Hz), 6.07 (s, 2H, NH). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 151.0, 136.6, 132.3, 129.9, 129.4, 129.0, 128.1, 127.7, 123.1, 122.0, 118.7, 100.4.

*1-p-Tolylsulfanyl-naphthalen-2-ylamine (**7b**).*[4c] The title compound was isolated by column chromatography (eluent: petroleum ether) as a yellow liquid in 47% yield (74.8 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.05 (d, 1H, ArH, J = 8.4 Hz), 7.79 (d, 1H, ArH, J = 8.8 Hz), 7.74 (d, 1H, ArH, J = 8.0 Hz), 7.40 (t, 1H, ArH, J = 7.2 Hz), 7.21−7.17 (m, 2H, ArH), 7.03 (d, 2H, ArH, J = 7.6 Hz), 6.89 (d, 2H, ArH, J = 7.2 Hz), 6.01 (s, 2H, NH), 2.21 (s, 3H, CH). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 150.7, 134.8, 133.8, 131.9, 130.1, 128.9, 127.9, 127.7, 126.4, 123.4, 121.9, 118.6, 20.9.

*2-(4-Chloro-phenylsulfanyl)-naphthalen-1-ylamine (**7c**).*[17] The title compound was isolated by column chromatography (eluent: petroleum ether) as a brown liquid in 43% yield (73.7 mg). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.80 (d, 1H, ArH, J = 7.8 Hz), 7.55−7.51 (m, 2H, ArH), 7.49−7.44 (m, 1H, ArH), 7.38 (d, 1H, ArH, J = 8.4 Hz), 7.33−7.29 (m, 2H, ArH), 7.15 (d, 1H, ArH, J = 8.4 Hz), 7.05−7.01 (m, 2H, ArH), 6.21 (s, 2H, NH). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 148.0, 136.8, 135.4, 134.0, 130.2, 129.4, 128.5, 128.4, 128.1, 127.7, 125.3, 123.7, 123.0, 116.8, 104.4. HRMS (ESI) m/z: calcd for $C_{16}H_{13}ClNS$ ([M + H]$^+$), 286.0452; found, 286.0465.

*3-((4-Chlorophenyl)thio)-1H-indole (**8a**).*[18] The title compound was isolated by column chromatography (eluent: petroleum ether/ethyl acetate = 4:1) as a white solid in 84% yield (130.9 mg). mp 116−118 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.75 (s, 1H, NH), 7.79 (d, 1H, CH, J = 2.4 Hz), 7.50 (d, 1H, ArH, J = 8.0 Hz), 7.38 (d, 1H, ArH, J = 8.0 Hz), 7.26 (d, 2H, ArH, J = 8.6 Hz), 7.20 (t, 1H, ArH, J = 6.0 Hz), 7.08 (t, 1H, ArH, J = 7.0 Hz), 7.01 (d, 2H, ArH, J = 8.8 Hz). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 138.9, 137.2, 133.1, 129.7, 129.2, 128.8, 127.3, 122.7, 120.7, 118.6, 112.9, 99.1.

*5-Chloro-3-(4-chloro-phenylsulfanyl)-1H-indole (**8b**).*[5c] The title compound was isolated by column chromatography (eluent: petroleum ether/ethyl acetate = 4:1) as a white solid in 85% yield (150.0 mg). mp 132−134 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.97 (s, 1H, NH), 7.90 (d, 1H, ArH, J = 2.8 Hz), 7.52 (d, 1H, ArH, J = 8.6 Hz), 7.33 (d, 1H, ArH, J = 1.8 Hz), 7.29 (d, 2H, ArH, J = 8.6 Hz), 7.21 (dd, 1H, ArH, J_1 = 2.0 Hz, J_2 = 8.6 Hz), 7.01 (d, 2H, ArH, J = 8.6 Hz). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 137.8, 135.3, 134.5, 129.7, 129.6, 128.9, 127.0, 125.1, 122.4, 117.1, 114.2, 98.6.

*3-(4-Chloro-phenylsulfanyl)-5-nitro-1H-indole (**8c**).* The title compound was isolated by column chromatography (eluent: petroleum ether/ethyl acetate = 4:1) as a yellow solid in 95% yield (173.7 mg). mp 191−193 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.47 (s, 1H, NH), 8.25 (d, 1H, ArH, J = 2.2 Hz), 8.14 (s, 1H, ArH),

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8.10 (dd, 1H, ArH, J_1 = 2.2 Hz, J_2 = 9.0 Hz), 7.71 (d, 1H, ArH, J = 9.0 Hz), 7.30 (d, 2H, ArH, J = 8.6 Hz), 7.01 (d, 2H, ArH, J = 8.0 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 141.6, 140.0, 137.2, 136.8, 129.9, 129.0, 127.9, 127.3, 117.7, 114.7, 113.3, 102.1. HRMS (ESI) m/z: calcd for $C_{14}H_9ClN_2O_2S$ (M^+), 304.0073; found, 304.0073.

Product Transformation Processes for Compounds 9−12. *1-((4-Chlorophenyl)sulfinyl)naphthalen-2-ol (**9**).* In a 25 mL reaction flask, equipped with a magnetic stirring bar, **3a** (1.0 mmol, 286.8 mg) and oxone (0.6 mmol, 368.9 mg) were added to ethanol (5.0 mL). After the resulting mixture was stirred at 60 °C (oil bath) for 2 h, the mixture was cooled to room temperature and water (5 mL) was added. Then, the mixture was extracted with ethyl acetate (2 × 20 mL). After drying with anhydrous Na_2SO_4, the organic layer was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (200−300 mesh) using petroleum/ethyl acetate (20/1) as the eluent to afford pure product **9** as a white solid (260.4 mg, 86% yield). mp 191−193 °C. ^1H NMR (400 MHz, DMSO-d_6): δ 11.25 (s, 1H, OH), 8.38 (d, 1H, ArH, J = 8.5 Hz), 7.99 (d, 1H, ArH, J = 9.0 Hz), 7.86 (d, 1H, ArH, J = 7.9 Hz), 7.65−7.54 (m, 4H, ArH), 7.41 (t, 1H, ArH, J = 7.7 Hz), 7.33 (t, 1H, ArH, J = 7.5 Hz), 7.26 (d, 1H, ArH, J = 9.0 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO): δ 157.1, 144.6, 135.2, 135.1, 129.7, 129.4, 128.9, 128.0, 126.4, 124.2, 122.4, 118.9, 118.3, 99.9. HRMS (ESI) m/z: calcd for $C_{16}H_{12}ClO_2S$ ($[M + H]^+$), 303.0241; found, 303.0239.

*1-((4-Chlorophenyl)sulfonyl)naphthalen-2-ol (**10**).*[19] In a 25 mL reaction flask, equipped with a magnetic stirring bar, **3a** (1.0 mmol, 286.8 mg) and oxone (1.5 mmol, 922.1 mg) were added to mixed solvent of ethanol and water (1:1, 5.0 mL). After the resulting mixture was stirred at 60 °C (oil bath) for 3 h, the mixture was cooled to room temperature and water (5 mL) was added. Then, the mixture was extracted with ethyl acetate (2 × 20 mL). After drying with anhydrous Na_2SO_4, the organic layer was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (200−300 mesh) using petroleum/ethyl acetate (20/1) as the eluent to afford pure product **10** as a white solid (293.3 mg, 92% yield). mp 119−121 °C. ^1H NMR (400 MHz, DMSO-d_6): δ 11.35 (s, 1H, OH), 9.06 (d, 1H, ArH, J = 8.8 Hz), 8.13 (d, 1H, ArH, J = 9.0 Hz), 8.01−7.89 (m, 3H, ArH), 7.69−7.61 (m, 3H, ArH), 7.45 (t, 1H, ArH, J = 7.6 Hz), 7.20 (d, 1H, ArH, J = 9.0 Hz).$^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 157.9, 142.5, 138.4, 137.7, 130.7, 129.6, 129.5, 129.2, 129.1, 128.4, 126.4, 124.3, 122.8, 119.4, 115.5.

*(4-Chlorophenyl)(2-methoxynaphthalen-1-yl)sulfane (**11**).*[20] In a 5 mL reaction flask, equipped with a magnetic stirring bar, **3a** (0.5 mmol, 143.4 mg) and K_2CO_3 (1.0 mmol, 138.2 mg) were added to dry DMF (2.0 mL) under argon. Then, CH_3I (46.7 μL, 0.75 mmol) was added dropwise with a syringe. After stirring at room temperature for 3 h, the mixture was quenched with water (5 mL) and extracted with ethyl acetate (2 × 20 mL). After drying with anhydrous Na_2SO_4, the organic layer was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (200−300 mesh) using petroleum/ethyl acetate (10/1) as the eluent to afford pure product **11** as a white solid (147.4 mg, 98%). mp 112−113 °C. ^1H NMR (400 MHz, DMSO-d_6): δ 8.26 (d, 1H, ArH, J = 8.5 Hz), 8.19 (d, 1H, ArH, J = 9.1 Hz), 7.98 (d, 1H, ArH, J = 8.3 Hz), 7.63 (d, 1H, ArH, J = 9.1 Hz), 7.59−7.51 (m, 1H, ArH), 7.48−7.39 (m, 1H, ArH), 7.29−7.20 (m, 2H, ArH), 6.98−6.89 (m, 2H, ArH), 3.94 (s, 3H, CH). $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6): δ 159.7, 137.2, 135.7, 133.2, 129.8, 129.6, 129.3, 129.1, 128.5, 127.8, 124.6, 124.5, 114.5, 110.9, 57.1.

*1-((4-Chlorophenyl)thio)naphthalen-2-yl Trifluoromethanesulfonate (**12**).* In a 5 mL reaction flask, equipped with a magnetic stirring bar, **3a** (0.5 mmol, 143.4 mg) and pyridine (80.7 μL, 1 mmol) were added to dry CH_2Cl_2 (1.0 mL) under argon at 0 °C. Then, trifluoromethanesulfonic anhydride (125 μL, 0.75 mmol) was added dropwise to the mixture at 0 °C. After complete addition, the mixture was warmed to room temperature and stirred for 2 h. The mixture was then quenched with water (5 mL) and extracted with ethyl acetate (2 × 20 mL). After drying with anhydrous Na_2SO_4, the organic layer was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (200−300 mesh) using petroleum/ethyl acetate (10/1) as the eluent to afford pure product **12** as wax in 98% yield (205.2 mg). ^1H NMR (400 MHz, DMSO-d_6): δ 8.44−8.34 (m, 2H, ArH), 8.24−8.16 (m, 1H, ArH), 7.81−7.69 (m, 3H, ArH), 7.37−7.29 (m, 2H, ArH), 7.12−7.03 (m, 2H, ArH). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO): δ 150.0, 134.5, 134.4, 133.4, 131.6, 129.8, 129.8, 129.6, 129.2, 128.3, 126.4, 122.4, 120.3, 117.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ −73.5 (d, J = 11.3 Hz). HRMS (ESI) m/z: calcd for $C_{17}H_{11}ClF_3O_3S_2$ ($[M + H]^+$), 418.9785; found, 418.9790.

Procedure for the Control Experiment [Scheme 6b, 1,2-Bis(4-chlorophenyl)disulfane (13)].[5c] In a 10 mL reaction flask, equipped with a magnetic stirring bar, 4-chlorobenzenethiol (1.8 mmol, 260.3 mg) and *t*-BuOK (0.6 mmol, 67.3 mg) were added. Then, the vial was placed in a preheated metal block and stirred at 80 °C in the presence of ambient air. After the reaction had reached completion (monitored by TLC), cold water (15 mL) was added. The mixture was extracted with ethyl acetate (2 × 20 mL). After drying with anhydrous Na_2SO_4, the organic layer was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (200−300 mesh) using petroleum/ethyl acetate (20/1−10/1) as the eluent to afford pure 1,2-bis(4-chlorophenyl)disulfane **13** in 98% yield (253.3 mg) as a light yellow solid. mp 69−71 °C. ^1H NMR (400 MHz, DMSO-d_6): δ 7.61−7.46 (m, 8H, ArH). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 134.5, 132.5, 129.4, 129.1.

Procedure for the Control Experiment [Scheme 6f, (4-Chlorophenyl)(2,2-diphenylethyl)sulfane (14)].[21] In a 10 mL reaction flask, equipped with a magnetic stirring bar, 2-naphthol (0.6 mmol, 86.5 mg), 4-chlorobenzenethiol (1.8 mmol, 260.3 mg), 1,1-diphenylethylene (1.2 mmol, 216.2 mg), and *t*-BuOK (0.6 mmol, 67.3 mg) were added. Then, the vial was placed in a preheated metal block at 80 °C in the presence of ambient air. After completion of the reaction (monitored by TLC), cold water (15 mL) was added. After drying with anhydrous Na_2SO_4, the mixture was extracted with ethyl acetate (2 × 20 mL). The organic layer was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (200−300 mesh) using petroleum/ethyl acetate (20/1−9/1) as the eluent to provide **13** and **14** in 85% (219.7 mg) yield and 7% (40.9 mg, yield based on 4-chlorobenzenethiol) yield, respectively. ^1H NMR (400 MHz, DMSO-d_6): δ 7.39−7.33 (m, 7H, ArH), 7.32−7.23 (m, 5H, ArH), 7.19 (t, 2H, ArH, J = 7.1 Hz), 4.18 (t, 1H, CH, J = 8.0 Hz), 3.73 (d, 2H, CH, J = 8.0 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 143.3, 135.5, 130.2, 129.7, 128.9, 128.4, 127.7, 126.5, 49.8, 37.4.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00898.

Optimization details, control experiments, and ^1H, ^{13}C, and ^{19}F NMR spectra of all products (PDF)

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Notes

The authors declare no competing financial interest.

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