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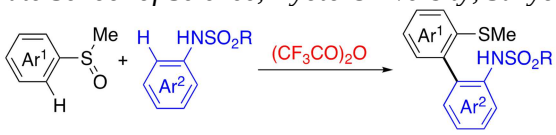

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ABSTRACT

Treatment of aryl sulfoxides and sulfonanilides with trifluoroacetic anhydride resulted in the dehydrative metal-free construction of the corresponding unsymmetrical biaryls. The reaction would proceed via (1) the activation of aryl sulfoxide with the anhydride, (2) interrupted Pummerer reaction of the resulting arylsulfonium with sulfonanilide, (3) [3,3] sigmatropic rearrangement to cleave the transient S–N bond and to form the prospective biaryl C–C bond, and (4) global aromatization. The choice of the amino protecting group is crucial, and only *N*-sulfonylanilines, i.e., sulfonanilides, could participate in the formation of biaryls.

1. Introduction

Biaryls often exist in bioactive molecules[1] and functional materials.[2] Development of new methods for the synthesis of biaryls has thus represented an important challenge in organic synthesis for several decades. After the maturity of the transition-metal-catalyzed approaches[2c, 3] such as cross-coupling, metal-free routes to biaryls have emerged as a new target to explore[4] because the use of heavy metals often poses problems of contamination of products[5] as well as supply risk.

Among such metal-free routes to biaryls, sigmatropic rearrangement of two-heteroatom-tethered intermediate **1** has garnered increasing attention (Scheme 1a).[6-10] Thanks to the rather weak Y–Z bond, the sigmatropic rearrangement takes place to connect the two ring systems with loss of the aromaticity of the two aromatic rings. Global rearomatization of intermediate **2** affords the corresponding disubstituted biaryls **3**. For about a century since the discovery of the benzidine rearrangement,[6a,b] this synthetic trick has been investigated only sporadically for exploring a new variant.[7-9]

In 2016, we discovered that the interrupted Pummerer reaction of aryl sulfoxides with phenols is a good method to generate intermediate **1** (Y = S^+R and Z = O) and that the following charge-accelerated sigmatropic rearrangement[11] ends up with the formation of 2-hydroxy-2'-sulfanylbiaryls.[7a,d,e,12,13] Encouraged by this, we envisioned that this cascade would be also applicable to anilines instead of phenols. Very recently, we have discovered such an extension (Scheme 1b): treatment of a mixture of 3,5-dialkoxyphenyl sulfoxide and anilines with triflic anhydride followed by further treatment with triflic acid promotes a similar cascade (Y = S^+R and Z = NH_2^+ in Scheme 1a) to yield amino- and sulfanyl-substituted biaryls.[9] However, from a synthetic viewpoint, the scope of this reaction is very limited: only 3,5-dialkoxyphenyl sulfoxide was applicable as the sulfoxides. We have thus endeavored to explore different reaction conditions to achieve the use of anilines, which is disclosed herein.

2. Results/Discussion

According to the previous report about the use of phenols[7a], the reaction of benzothienyl sulfoxide (**4a**) with *p*-toluidine (**5a**) was performed in the presence of trifluoroacetic anhydride (TFAA) under various sets of conditions. However, trifluoroacetylation of **5a** always took place predominantly (for instance, Table 1, entry 1). We also examined the reaction of **4a** with **5a** in the presence of triflic anhydride followed by treatment with triflic acid under the previous conditions.[9] Again, trifluoromethanesulfonylation of **5a** took place (entry 2). We thus considered it important to lower the nucleophilicity of **5a** by protecting the amino group with an electron-withdrawing group (Scheme 1c). Several protective groups were examined, and sulfonyl protections were found to show positive effects (entries 3–8). Among them, *p*-anisylsulfonyl-protected **5b** gave the best result (entry 3). Methyl- and *p*-tolylsulfonyl groups are slightly less effective (entries 4 and 5). More electron-donating and sterically demanding 2,4-dimethoxyphenylsulfonyl protection led to the formation of a complex mixture (entry 6). The uses of more electron-withdrawing *p*-cyanophenylsulfonyl and trifluoromethylsulfonyl groups gave complex mixtures (entries 7 and 8). Protections with acyl (entries 9–12) and phosphoryl (entry 13) were completely unreactive, none of the corresponding biaryls were formed at all.

Scheme 1. Sigmatropic Rearrangement of Two-heteroatom-tethered Intermediate Leading to Biaryls

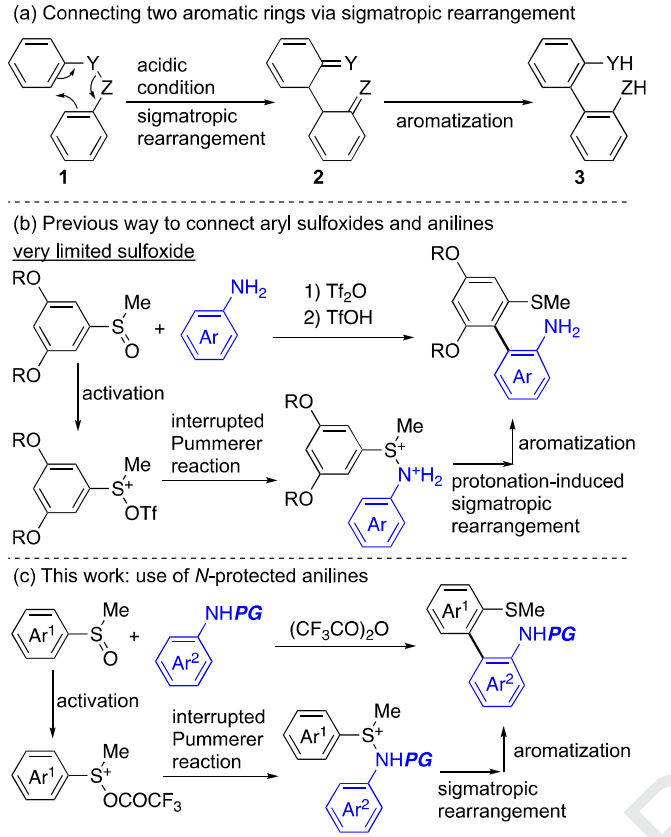
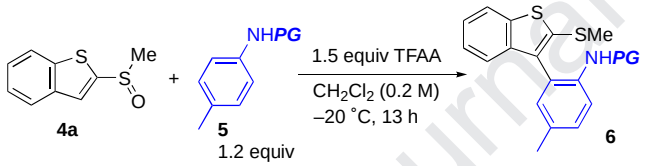


Table 1. Exploring Suitable Protective Group[a]



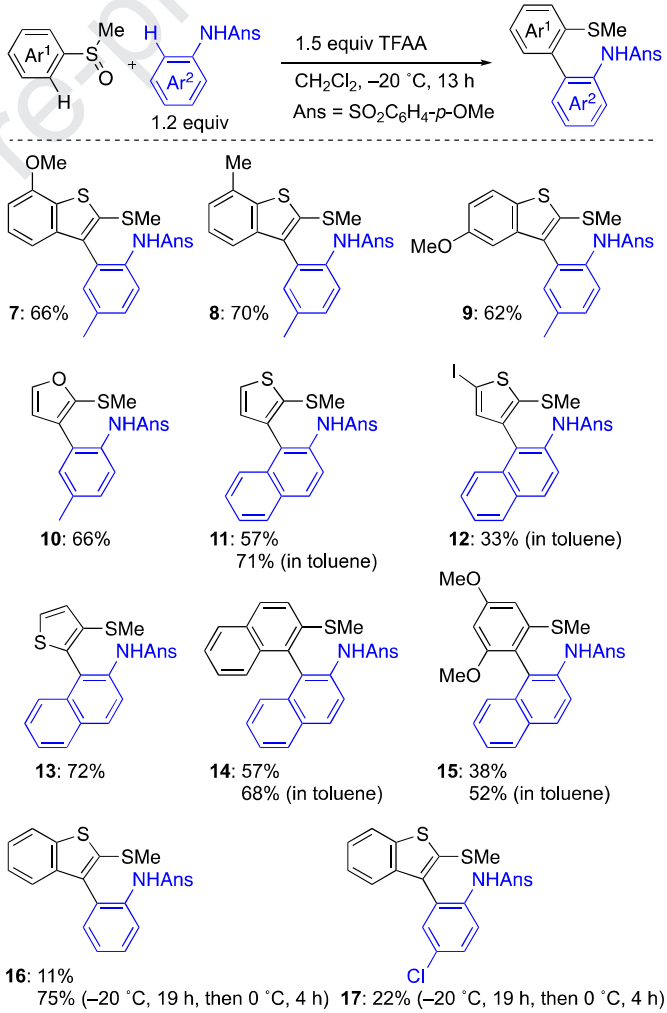
entry	PG	6	NMR yield (%)
1	H (**5a**)	**6a**	0[b,c]
2	H (**5a**)	**6a**	0[d]
3	$SO_2C_6H_4$-*p*-OMe (**5b**)	**6b**	86 (85[e], 85[e,f])
4	SO_2Me (**5c**)	**6c**	69 (72[e])
5	$SO_2C_6H_4$-*p*-Me (**5d**)	**6d**	68 (68[e])
6	$SO_2C_6H_3$-*o*,*p*-$(OMe)_2$ (**5e**)	**6e**	<20[g]
7	$SO_2C_6H_4$-*p*-CN (**5f**)	**6f**	<26[g]
8	SO_2CF_3 (**5g**)	**6g**	<22[g]
9	$COCF_3$ (**5h**)	**6h**	0[h]
10	COMe (**5i**)	**6i**	0[c,h]
11	$CONMe_2$ (**5j**)	**6j**	0[b,c]
12	Fmoc (**5k**)	**6k**	0[h]
13	$PO(OEt)_2$ (**5l**)	**6l**	0[h]

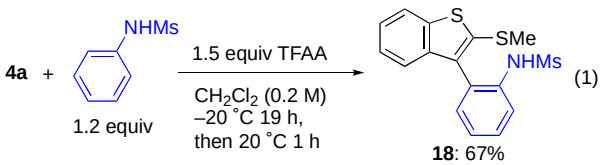
[a]Starting from 0.20 mmol of **4a**. [b]*N*-trifluoroacetylation of **5** occurred. [c]Most of **4a** was recovered. [d]*Under the condtions in Reference 9. N*-trifluoromethanesulfonylation of **5a** occurred. [e]Isolated yield. [f]Starting from 6.0 mmol (1.2 g) of **4a**. [g]Complex product mixture. [h]Most of **5** was recovered.

Employing the *p*-anisylsulfonyl group (Ans) as the best protective group, we surveyed the scope of the reaction (Figure 1). Heteroaromatic sulfoxides underwent the reactions efficiently to yield **7**–**13** in good yields. Carbonaceously aromatic 2-naphthyl sulfoxide and 3,5-dimethoxyphenyl sulfoxide reacted with Ans-protected 2-naphthylamine to yield **14** and **15**, respectively. In the syntheses of **11**, **12**, **14**, and **15**,[14] toluene was the better solvent than dichloromethane while the reason for the solvent effect remains unclear. Unfortunately, indolyl sulfoxides were not suitable for this reaction, being converted to complex mixtures.

Despite the success in using Ans-protected *p*-toluidine and 2-naphthylamine, the reaction proved to be sensitive to substituents on the benzene ring of anilides. For example, the use of *p*-anisylsulfonylaniline instead of **5b**, that is, simply replacing the *p*-methyl group with a hydrogen, had a significantly negative effect on the yield of the desired product **16** (cf. Table 1, entry 3). To overcome the low yield, elevating temperature at the last stage of the reaction from –20 ˚C to 0 ˚C was found to provide the corresponding biaryl **16** in 75% yield.[15] Ans-protected *p*-chloroaniline was far less reactive and converted to **17** in only 22% yield albeit under the improved conditions. Methylsulfonylaniline also reacted under similar temperature control to yield **18** (eq 1). Further investigation is necessary to improve the reaction scope.

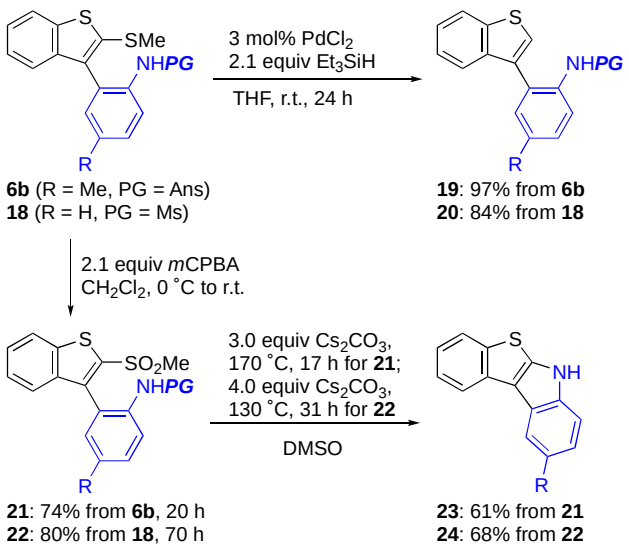
Figure 1. Reaction Scope





Transformations of products **6b** and **18** were explored (Scheme 2). Catalytic removal of the methylsulfanyl group proceeded cleanly under Nakada's conditions[16] to yield **19** and **20**. As another transformation, after oxidation of the sulfanyl moiety of **6b** and **18**, the resulting sulfones **21** and **22** underwent base-mediated S_NAr cyclization to yield benzothienoindoles **23** and **24** with concomitant deprotection.

Scheme 2. Transformations of Products



3. Conclusion

We have developed metal-free, regioselective dehydrative C–H/C–H coupling of aryl sulfoxides with sulfonanilides with the aid of trifluoroacetic anhydride. Anilides have now become available for the synthesis of biaryls by using a sequence of interrupted Pummerer reaction and [3,3] sigmatropic rearrangement, the scope of our strategy being significantly expanded. Interestingly, the reaction was dominated by the protective group of the amino unit, and sulfonyl groups such as *p*-anisylsulfonyl proved to be promising. The products are useful synthetic intermediates. Further expansion of the reaction scope is now in progress in our laboratory.

4. Experimental Section

4.1. Instrumentation and Chemicals

^{1}H NMR (600 MHz) and ^{13}C NMR (151 MHz) spectra were recorded on JEOL ECA-600 and JEOL ECZ-600 spectrometers. Chemical shifts (δ) are reported in parts per million relative to residual $CHCl_3$ (^{1}H: δ = 7.26 ppm) and relative to $CDCl_3$ (^{13}C: δ = 77.16 ppm). Column chromatography was carried out on silica gel (Wakosil® C-300), while preparative recycling gel permeation chromatography (GPC) was performed on a JAI LC-9260 II NEXT system using $CHCl_3$ as the eluent. Mass spectra were measured on a Bruker micrOTOF II spectrometer.

Dehydrated THF, DMF, DMSO, CH_2Cl_2, and toluene were purchased from common commercial suppliers and stored under an atmosphere of nitrogen. Anilides **5g**,[17] **5h**,[18] **5i**,[19] **5j**,[20] **5k**,[21] and **5l**[22] were prepared from *p*-toluidine via similar procedures in the previous reports. Aryl sulfoxides 2-(methylsulfinyl)benzothiophene (**4a**),[7a] 2-(methylsulfinyl)naphthalene,[7a] 2-(methylsulfinyl)thiophene,[7a] and 1,3-dimethoxy-5-(methylsulfinyl)benzene[23] were prepared according to the literature.

4.2. Preparation of Substrates

4.2.1. General procedure for oxidation of aryl sulfides to aryl sulfoxides (GP1)

To a solution of an aryl sulfide (0.20 M in CH_2Cl_2), *m*-chloroperbenzoic acid (contains ca. 30% H_2O, 1.1 equiv) was added portionwise at 0 °C. The resulting solution was allowed to warm to room temperature and stirred. Progress of the oxidation was checked by TLC. After completion of the reaction, saturated aqueous $NaHCO_3$ was added to the reaction mixture, and the resulting solution was extracted with EtOAc (20 mL×3). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by chromatography on silica gel to give the corresponding aryl sulfoxide.

4.2.2. Typical procedure for preparation of aryl sulfoxides

The synthesis of 7-methoxy-2-(methylsulfinyl)benzothiophene is representative. A 50-mL round-bottom flask was charged with 7-methoxybenzothiophene (0.80 g, 4.9 mmol, prepared according to the literature[24]) and THF (10 mL). A solution of BuLi (1.6 M in hexane, 3.4 mL, 5.4 mmol) was added dropwise at 0 ºC. The resulting solution was stirred at 0 ºC for 1 h before an addition of dimethyl disulfide (0.45 mL, 5.1 mmol). After the mixture was stirred for 1 h additionally, saturated aqueous $NaHCO_3$ was added. The resulting biphasic solution was extracted with EtOAc (10 mL×3). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to provide 7-methoxy-2-(methylsulfanyl)benzothiophene with some impurities. Subsequent oxidation of the sulfide according to **GP1** provided 7-methoxy-2-(methylsulfinyl)benzothiophene (0.89 g, 3.9 mmol, 80% over two steps) as a brown oil. 7-Methyl-2-(methylsulfinyl)benzothiophene and 5-methoxy-2-(methylsulfinyl)benzothiophene were prepared via the same procedure from 7-methylbenzothiophene and 5-methoxybenzothiophene, respectively.[24]

4.2.3. Preparation of 2-(methylsulfinyl)furan

A 100-mL two-necked flask was charged with furan (1.5 mL, 20 mmol) and THF (20 mL). BuLi (1.6 M in hexane, 12.9 mL, 20 mmol) was added dropwise at 0 ºC. The reaction mixture was allowed to warm to room temperature and stirred for 4 h. Dimethyl disulfide (1.8 mL, 20 mmol) was then added dropwise, and the resulting solution was stirred for 12 h. The reaction was quenched with 6 M aqueous KOH (50 mL), and the resulting biphasic mixture was extracted with EtOAc (30 mL×3). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to provide 2-(methylsulfanyl)furan with some impurities. Subsequent oxidation of the sulfide according to **GP1** provided 2-(methylsulfinyl)furan (1.1 g, 8.6 mmol, 43% over two steps) as a brown oil.

4.2.4. Preparation of 2-iodo-5-(methylsulfinyl)thiophene

A modification of the procedure reported by Procter was used.[25] A 200-mL two-necked flask was charged with 2-iodothiophene (1.0 mL, 10 mmol), DMSO (0.78 mL, 11 mmol), and CH_2Cl_2 (50 mL). Tf_2O (1.8 mL, 11 mmol) was slowly added at –30 ºC. After the solution was stirred for 15 min at –30 ºC, the solution was allowed to warm to room temperature and stirred for an additional 1.5 h. Et_2NH (4.3 mL, 41 mmol) was then added, and the resulting solution was stirred for 6 h. After an addition of H_2O (30 mL), the biphasic solution was extracted with CH_2Cl_2 (30 mL × 3). The combined organic layer was dried over Na_2SO_4, and concentrated under reduced pressure to provide 2-iodo-5-(methylsulfanyl)thiophene with some impurities. Subsequent oxidation of the sulfide according to **GP1** provided 2-iodo-5-

(methylsulfinyl)thiophene (1.25 g, 4.6 mmol, 46% over two steps) as a brown solid.

4.2.5. Preparation of 3-(methylsulfinyl)thiophene

A 100-mL two-necked flask was charged with 3-bromothiophene (1.9 mL, 20 mmol) and hexane (30 mL). BuLi (1.6 M in hexane,13.8 mL, 22 mmol) was added to the mixture dropwise at –40 ºC. After additions of THF (10 mL) and hexane (10 mL), the resulting mixture was allowed to warm to room temperature. After an addition of dimethyl disulfide (2.0 mL, 22 mmol), the resulting mixture was stirred for 12 h before an addition of H_2O (20 mL). The biphasic solution was extracted with CH_2Cl_2 (20 mL×3). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to provide 3-(methylsulfanyl)thiophene with some impurities. Subsequent oxidation of the sulfide according to **GP1** afforded 3-(methylsulfinyl)thiophene (1.0 g, 7.2 mmol, 36% over two steps) as a colorless oil.

4.2.6. General procedure for preparation of sulfonanilides

A modification of the procedure reported by Nachtsheim was used.[26] The synthesis of **5c** is representative. A Schlenk tube was charged with *p*-toluidine (1.1 g, 10 mmol), pyridine (0.90 mL, 11 mmol), and CH_2Cl_2 (25 mL). Methanesulfonyl chloride (0.85 mL, 11 mmol) was then added portionwise at 0 ºC. The reaction mixture was allowed to warm to room temperature and stirred. After the completion of the reaction was checked by TLC, the reaction was quenched with H_2O (25 mL), and the biphasic solution was extracted with CH_2Cl_2 (25 mL×3). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 3/1) to provide **5c** (1.7 g, 8.9 mmol, 89%) as a white solid. Sulfonanilides **5b**, **5d–f**, 4-methoxy-*N*-phenylbenzenesulfonamide (for **16**), and *N*-(4-chlorophenyl)-4-methoxybenzenesulfonamide (for **17**) were prepared via the same procedure. 2,4-Dimethoxybenzenesulfonyl chloride for the preparation of **5e** was prepared according to the literature.[27]

4.2.7. Preparation of 2-(4-methoxybenzenesulfonyl)aminonaphthalene

A modification of the procedure reported by Guo was used.[28] An oven-dried two-necked flask was charged with CuI (0.29 g, 1.5 mmol), 4-methoxybenzenesulfonamide (6.7 g, 36 mmol), glycine (0.62 g, 6.0 mmol), K_3PO_4 (16 g, 75 mmol), 2-iodonaphthalene (7.6 g, 30 mmol), and DMF (60 mL). The resulting mixture was stirred at 100 ºC for 24 h. The reaction mixture was poured into H_2O (200 mL), and the resulting biphasic solution was extracted with a mixture of EtOAc/hexane (v/v = 1/1, 100 mL×3). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 as an eluent to provide 2-(4-methoxybenzenesulfonyl)aminonaphthalene (4.9 g, 16 mmol, 52%) as a white solid.

4.3. Experimental Procedure

4.3.1. General Procedure for Coupling of Aryl Sulfoxides with Sulfonanilides

The synthesis of **6b** is representative. A Schlenk tube was charged with 2-methylsulfinylbenzothiophene (39.1 mg, 0.20 mmol), sulfonanilide **5b** (66.7 mg, 0.24 mmol), and CH_2Cl_2 (1.0 mL). Trifluoroacetic anhydride (42 μL, 0.30 mmol) was added to the solution in one portion at –20 ºC, and the resulting solution was stirred at the same temperature for 13 h before addition of saturated aqueous $NaHCO_3$. The resulting biphasic solution was extracted with CH_2Cl_2 (2 mL×3). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (hexane/EtOAc = 3/1) to provide **6b** (77.3 mg, 0.17 mmol, 85 %) as a colorless oil.

*4.3.2. Desulfanylation of biaryls (**Scheme 2**)*

A modification of the procedure reported by Nakada was used.[15] The reduction of **18** is representative. A Schlenk tube was charged with biaryl **18** (69.8 mg, 0.20 mmol), $PdCl_2$ (1.1 mg, 3 mol%), and THF (2 mL). After addition of triethylsilane (67 μL, 0.42 mmol), the resulting solution was stirred at room temperature for 24 h. After addition of H_2O (4 mL), the resulting biphasic solution was extracted with CH_2Cl_2 (4 mL×2). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (hexane/ EtOAc = 5/1) to provide **20** (51.0 mg, 0.17 mmol, 84%) as a colorless oil.

*4.3.3. Cyclization of biaryls (**Scheme 2**)*

The reaction of **18** is representative. To a solution of biaryl **18** (698.8 mg, 2.0 mmol) in CH_2Cl_2 (20 mL), *m*-chloroperbenzoic acid (contains ca. 30% H_2O, 1.0 g, 4.2 mmol) was added portionwise at 0 ºC. The resulting solution was allowed to warm to room temperature and stirred for 70 h. Saturated aqueous $NaHCO_3$ was then added, and the aqueous layer was extracted with EtOAc (20 mL×3). The combined organic layer was purified by chromatography on silica gel with CH_2Cl_2 as an eluent to provide the corresponding aryl sulfone **22** (607.9 mg, 1.6 mmol, 80%) as a white solid.

A Schlenk tube was charged with **22** (381.2 mg, 1.0 mmol), Cs_2CO_3 (1.3 g, 4.0 mmol), and DMSO (10 mL). The resulting mixture was stirred at 130 ºC for 31 h and then poured into H_2O (200 mL). The resulting solution was extracted with a mixture of EtOAc/hexane (v/v = 1/1, 100 mL×5). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (hexane/CH_2Cl_2 = 2/1) to provide **24** (151.9 mg, 0.68 mmol, 68%) as a white solid.

4.4. Characterization Data

4.4.1. 7-methoxy-2-(methylsulfinyl)benzothiophene

Brown oil. ^{1}H NMR: δ 7.71 (s, 1H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.9 Hz, 1H), 6.86 (d, *J* = 7.9 Hz, 1H), 4.00 (s, 3H), 2.96 (s, 3H); ^{13}C NMR: δ 154.63, 148.44, 139.90, 130.30, 126.71, 126.27, 117.37, 105.92, 55.92, 44.43; HRMS (APCI-MS, positive) calcd for $C_{10}H_{11}O_2S_2$ $[M+H]^+$: 227.0195, found: 227.0201.

4.4.2. 7-methyl-2-(methylsulfinyl)benzothiophene

Brown oil. ^{1}H NMR: δ 7.74 (s, 1H), 7.69 (d, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 2.97 (s, 3H), 2.58 (s, 3H); ^{13}C NMR: δ 147.55, 141.64, 138.19, 132.60, 126.74, 126.64, 125.80, 122.69, 44.46, 20.35; HRMS (APCI-MS, positive) calcd for $C_{10}H_{11}OS_2$ $[M+H]^+$: 211.0246, found: 211.0243.

4.4.3. 5-methoxy-2-(methylsulfinyl)benzothiophene

Brown solid (m.p. = 106.5–107.9 ºC). ^{1}H NMR: δ 7.74 (d, *J* = 8.2 Hz, 1H), 7.64 (s, 1H), 7.26 (s, 1H), 7.09 (d, *J* = 8.2 Hz, 1H), 3.88 (s, 3H), 2.96 (s, 3H); ^{13}C NMR: δ 158.21, 149.12, 139.45, 133.73, 125.72, 123.69, 117.23, 106.61, 55.74, 44.49; HRMS (APCI-MS, positive) calcd for $C_{10}H_{11}O_2S_2$ $[M+H]^+$: 227.0195, found: 227.0198.

4.4.4. 2-(methylsulfinyl)furan

Brown oil. ^{1}H NMR: δ 7.62 (s, 1H), 6.91 (d, *J* = 3.4 Hz, 1H), 6.49–6.49 (m, 1H), 2.92 (s, 3H); ^{13}C NMR: δ 152.70, 146.83, 115.35, 111.52, 38.63; HRMS (APCI-MS, positive) calcd for $C_5H_7O_2S$ $[M+H]^+$: 131.0161, found: 131.0156.

4.4.5. 2-iodo-5-(methylsulfinyl)thiophene

B Brown solid (m.p. = 82.4–86.8 ºC). ^{1}H NMR ($CDCl_3$): δ 7.25 (d, *J* = 3.4 Hz, 1H), 7.11 (d, *J* = 3.4 Hz, 1H), 2.89 (s, 3H); ^{13}C NMR: δ 152.51, 137.29, 130.74, 80.26, 44.66; HRMS (APCI-MS, positive) calcd for $C_5H_6IOS_2$ $[M+H]^+$: 272.8899, found: 272.8909.

4.4.6. 3-(methylsulfinyl)thiophene

Brown oil. ^{1}H NMR: δ 7.77–7.78 (m, 1H), 7.50–7.52 (m, 1H), 7.27–7.29 (m, 1H), 2.81 (s, 3H); ^{13}C NMR: δ 144.89, 128.67, 125.60, 122.76, 43.06; HRMS (APCI-MS, positive) calcd for $C_5H_7OS_2$ $[M+H]^+$: 146.9933, found: 146.9934.

*4.4.7. 4-methoxy-N-(4-methylphenyl)benzenesulfonamide (**5b**)*

White solid (m.p. = 96.0–97.3 ºC). ^{1}H NMR: δ 7.69 (d, *J* = 8.9 Hz, 2H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.96 (d, *J* = 8.2 Hz, 2H), 6.88 (d, *J* = 8.9 Hz, 2H), 6.84 (br, 1H), 3.82 (s, 3H), 2.26 (s, 3H); ^{13}C NMR: δ 163.15, 135.42, 133.99, 130.77, 129.96, 129.57, 122.40, 114.25, 55.69, 20.97; HRMS (APCI-MS, positive) calcd for $C_{14}H_{15}NO_3S$ $[M]^+$: 277.0767 found: 277.0774.

*4.4.8. 2,4-dimethoxy-N-(4-methylphenyl)benzenesulfonamide (**5e**)*

White solid (m.p. = 130.2–131.6 ºC). ^{1}H NMR: δ 7.70 (d, *J* = 8.9 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 2H), 6.94 (d, *J* = 8.2 Hz, 2H), 6.81 (br, 1H), 6.47 (d, *J* = 2.7 Hz, 1H), 6.43 (dd, *J* = 8.9, 2.7 Hz, 1H), 4.00 (s, 3H), 3.80 (s, 3H), 2.23 (s, 3H); ^{13}C NMR: δ 165.04, 157.73, 135.08, 134.40, 132.84, 129.83, 121.82, 118.75, 104.56, 99.50, 56.47, 55.78, 20.92; HRMS (APCI-MS, positive) calcd for $C_{15}H_{17}NO_4S$ $[M]^+$: 307.0873, found: 307.0869.

*4.4.9. 4-cyano-N-(4-methylphenyl)benzenesulfonamide (**5f**)*

Yellow solid (m.p. = 151.7–153.1 ºC). ^{1}H NMR: δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.94 (d, *J* = 8.2 Hz, 2H), 6.79 (br, 1H), 2.29 (s, 3H); ^{13}C NMR: δ 143.15, 136.57, 132.92, 132.76, 130.25, 128.00, 122.95, 117.38, 116.67, 20.99; HRMS (APCI-MS, positive) calcd for $C_{14}H_{12}N_2O_2S$ $[M]^+$: 272.0614, found: 272.0627.

4.4.10. 4-methoxy-N-(naphthalen-2-yl)benzenesulfonamide

White solid (m.p. = 121.1–124.1 ºC). ^{1}H NMR: δ 7.76 (d, *J* = 7.5 Hz, 1H), 7.71–7.74 (m, 4H), 7.52 (d, *J* = 2.1 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.21 (dd, *J* = 8.9, 2.1 Hz, 1H), 6.85 (d, *J* = 9.6 Hz, 2H), 6.70 (br, 1H), 3.79 (s, 3H); ^{13}C NMR: δ 163.27, 134.35, 133.77, 131.14, 130.58, 129.58, 129.48, 127.75, 127.63, 126.78, 125.56, 121.11, 118.33, 114.38, 55.65; HRMS (APCI-MS, positive) calcd for $C_{17}H_{16}NO_3S$ $[M+H]^+$: 314.0845, found: 314.0838.

4.4.11. 4-methoxy-N-phenylbenzenesulfonamide

White solid (m.p. = 105.9–106.9 ºC). ^{1}H NMR: δ 7.70 (d, *J* = 8.9 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 2H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 7.5 Hz, 2H), 6.88 (d, *J* = 8.9 Hz, 2H), 6.69 (br, 1H), 3.82 (s, 3H); ^{13}C NMR: δ 163.26, 136.70, 130.74, 129.57, 129.46, 125.50, 121.81, 114.31, 55.71; HRMS (APCI-MS, positive) calcd for $C_{13}H_{14}NO_3S$ $[M+H]^+$: 264.0689, found: 264.0686.

4.4.12. N-(4-chlorophenyl)-4-methoxybenzenesulfonamide

White solid (m.p. = 94.6–95.9 ºC). ^{1}H NMR: δ 7.72 (d, *J* = 8.9 Hz, 2H), 7.30 (s, 1H), 7.18 (d, *J* = 8.9 Hz, 2H), 7.03 (d, *J* = 8.9 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR: δ 163.40, 135.38, 130.89, 130.17, 129.57, 129.51, 122.95, 114.45, 55.73; HRMS (APCI-MS, positive) calcd for $C_{13}H_{12}{}^{35}ClNO_3S$ [M]: 297.0221, found: 297.0223.

*4.4.13. 4-methoxy-N-(4-methyl-2-(2-(methylsulfanyl)benzothiophen-3-yl)phenyl)benzenesulfonamide (**6b**)*

Colorless oil (77.3 mg, 0.17 mmol, 85%). ^{1}H NMR: δ 7.73 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.23–7.30 (m, 4H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.96 (s, 1H), 6.77 (s, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 6.47 (d, *J* = 9.7 Hz, 2H), 3.69 (s, 3H), 2.48 (s, 3H), 2.33 (s, 3H); ^{13}C NMR: δ 162.61, 139.74, 139.36, 136.57, 135.51, 131.90, 131.72, 131.65, 130.62, 130.29, 128.88, 126.95, 124.70, 124.35, 124.14, 122.18, 121.63, 113.78, 55.34, 20.97, 19.03; HRMS (APCI-MS, positive) calcd for $C_{23}H_{22}NO_3S_3$ $[M+H]^+$: 456.0756, found: 456.0751.

*4.4.14. N-(4-methyl-2-(2-(methylsulfanyl)benzothiophen-3-yl)phenyl)methanesulfonamide (**6c**)*

White solid (52.5 mg, 0.15 mmol, 72%, m.p. = 114.0–115.3 ºC). ^{1}H NMR: δ 7.82 (d, *J* = 7.5 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.29–7.36 (m, 3H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.12 (s, 1H), 6.28 (s, 1H), 2.69 (s, 3H), 2.55 (s, 3H), 2.39 (s, 3H); ^{13}C NMR: δ 139.71, 139.61, 138.12, 135.63, 132.57, 132.15, 130.84, 130.71, 126.33, 125.39, 124.80, 122.30, 121.76 (one of these aromatic signals contains overlapping), 39.23, 20.96, 18.96; HRMS (APCI-MS, positive) calcd for $C_{17}H_{17}NO_2S_3$ $[M]^+$: 363.0416, found: 363.0426.

*4.4.15. 4-methyl-N-(4-methyl-2-(2-(methylsulfanyl)benzothiophen-3-yl)phenyl)benzenesulfonamide (**6d**)*

Colorless oil (59.8 mg, 0.14 mmol, 68%). ^{1}H NMR: δ 7.74 (d, *J* = 8.2 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.25–7.30 (m, 4H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.97 (s, 1H), 6.83 (m, 3H), 6.73 (d, *J* = 8.2 Hz, 1H), 2.50 (s, 3H), 2.34 (s, 3H), 2.20 (s, 3H); ^{13}C NMR: δ 143.20, 139.74, 139.43, 136.60, 136.11, 135.54, 131.86, 131.77, 131.70, 130.33, 129.31, 126.91, 126.85, 124.70, 124.34, 124.09, 122.27, 121.73, 21.60, 21.00, 19.08; HRMS (APCI-MS, positive) calcd for $C_{23}H_{21}NO_2S_3$ $[M]^+$: 439.0729, found: 439.0742.

*4.4.16. 4-methoxy-N-(2-(6-methoxy-2-(methylsulfanyl)benzothiophen-3-yl)-4-methylphenyl)benzenesulfonamide (**7**)*

White solid (64.1 mg, 0.13 mmol, 66%, m.p. = 155.0–160.7 ºC). ^{1}H NMR: δ 7.68 (d, *J* = 8.2 Hz, 1H), 7.30 (d, *J* = 8.9 Hz, 2H), 7.22 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.07 (t, *J* = 7.9 Hz, 1H), 6.95 (d, *J* = 2.1 Hz, 1H), 6.71–6.73 (m, 2H), 6.51 (d, *J* = 8.9 Hz, 2H), 6.40 (d, *J* = 7.9 Hz, 1H), 4.03 (s, 3H), 3.72 (s, 3H), 2.49 (s, 3H), 2.32 (s, 3H); ^{13}C NMR: δ 162.59, 153.74, 141.40, 137.27, 135.50, 131.93, 131.82, 130.83, 130.29, 128.95, 127.93, 127.15, 126.14, 124.17, 114.96, 113.83, 104.46 (one of these aromatic signals contains overlapping), 55.95, 55.39, 21.02, 19.07; HRMS (APCI-MS, positive) calcd for $C_{24}H_{23}NO_4S_3$ $[M]^+$: 485.0784, found: 485.0782.

*4.4.17. 4-methoxy-N-(4-methyl-2-(7-methyl-2-(methylsulfanyl)benzothiophen-3-yl)phenyl)benzenesulfonamide (**8**)*

Colorless oil (65.7 mg, 0.14 mmol, 70%). ^{1}H NMR: δ 7.68 (d, *J* = 8.2 Hz, 1H), 7.29 (d, *J* = 9.6 Hz, 2H), 7.22 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 1.4 Hz, 1H), 6.73 (s, 1H), 6.60 (d, *J* = 7.5 Hz, 1H), 6.48 (d, *J* = 9.6 Hz, 2H), 3.70 (s, 3H), 2.55 (s, 3H), 2.49 (s, 3H), 2.32 (s, 3H); ^{13}C NMR: δ 162.61, 139.61, 139.58, 136.25, 135.39, 132.45, 131.97, 131.79, 131.25, 130.74, 130.26, 128.95, 127.14, 125.23,

124.77, 123.84, 119.96, 113.78, 55.37, 21.00, 20.22, 19.18; HRMS (APCI-MS, positive) calcd for $C_{24}H_{23}NO_3S_3$ $[M]^+$: 469.0835, found: 469.0838.

*4.4.18. 4-methoxy-N-(2-(5-methoxy-2-(methylsulfanyl)benzothiophen-3-yl)-4-methylphenyl)benzenesulfonamide (**9**)*

Colorless oil (60.2 mg, 0.12 mmol, 62%). ^{1}H NMR: δ 7.68 (d, *J* = 8.2 Hz, 1H), 7.58 (d, *J* = 8.9 Hz, 1H), 7.25 (d, *J* = 9.6 Hz, 2H), 7.22 (dd, *J* = 8.2, 1.4 Hz, 1H), 6.95 (d, *J* = 1.4 Hz, 1H), 6.89 (dd, *J* = 8.9, 2.1 Hz, 1H), 6.80 (s, 1H), 6.44 (d, *J* = 9.6 Hz, 2H), 6.15 (d, *J* = 2.1 Hz, 1H), 3.69 (s, 3H), 3.65 (s, 3H), 2.46 (s, 3H), 2.31 (s, 3H); ^{13}C NMR: δ 162.61, 157.70, 141.01, 137.62, 135.72, 131.79, 131.54, 131.28, 130.65, 130.32, 128.95, 127.31, 124.67, 122.30, 113.87, 113.68, 104.92 (one of these aromatic signals contains overlapping), 55.41, 55.31, 21.01, 18.95; HRMS (APCI-MS, positive) calcd for $C_{24}H_{23}NO_4S_3$ $[M]^+$: 485.0784, found: 485.0781.

*4.4.19. 4-methoxy-N-(4-methyl-2-(2-(methylsulfanyl)furan-3-yl)phenyl)benzenesulfonamide (**10**)*

Brown oil (51.4 mg, 0.13 mmol, 66%). ^{1}H NMR: δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 2.1 Hz, 1H), 7.07 (d, *J* = 8.2 Hz, 1H), 7.05–7.00 (br, 1H), 6.98 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 2H), 6.46–6.47 (m, 2H), 3.80 (s, 3H), 2.44 (s, 3H), 2.38 (s, 3H); ^{13}C NMR: δ 163.21, 154.80, 147.11, 134.78, 132.27, 131.56, 130.73, 130.58, 129.64, 120.97, 120.07, 115.57, 114.32, 110.88, 55.67, 21.44, 18.71; HRMS (APCI-MS, positive) calcd for $C_{19}H_{19}NO_4S_2$ $[M]^+$: 389.0750, found: 389.0757.

*4.4.20. 4-methoxy-N-(1-(2-(methylsulfanyl)thiophen-3-yl)naphthalen-2-yl)benzenesulfonamide (**11**)*

The reaction was performed in toluene. Colorless oil (62.7 mg, 0.14 mmol, 71%). ^{1}H NMR: δ 7.98 (d, *J* = 8.9 Hz, 1H), 7.88 (d, *J* = 8.9 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 8.9 Hz, 2H), 7.41 (t, *J* = 8.2 Hz, 1H), 7.33–7.36 (m, 2H), 7.20 (d, *J* = 8.2 Hz, 1H), 6.81 (d, *J* = 8.9 Hz, 2H), 6.66 (s, 1H), 6.24 (d, *J* = 5.5 Hz, 1H), 3.79 (s, 3H), 2.22 (s, 3H); ^{13}C NMR: δ 163.22, 136.71, 135.96, 132.96, 132.58, 131.17, 130.93, 130.42, 129.65, 129.43, 128.23, 127.35, 126.91, 125.60, 125.42, 123.01, 120.63, 114.23, 55.70, 20.56; HRMS (APCI-MS, positive) calcd for $C_{22}H_{19}NO_3S_3$ $[M]^+$: 441.0522, found: 441.0516.

*4.4.21. N-(1-(5-iodo-2-(methylsulfanyl)thiophen-3-yl)naphthalen-2-yl)-4-methoxybenzenesulfonamide (**12**)*

The reaction was performed in toluene. White solid (37.5 mg, 0.07 mmol, 33%, m.p. = 186.2–188.0 ºC). ^{1}H NMR: δ 8.00 (d, *J* = 8.9 Hz, 1H), 7.91 (d, *J* = 8.9 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.47 (d, *J* = 8.9 Hz, 2H), 7.43 (t, *J* = 8.2 Hz, 1H), 7.37 (t, *J* = 8.2 Hz, 1H), 7.20 (d, *J* = 8.2 Hz, 1H), 6.86 (d, *J* = 8.9 Hz, 2H), 6.57 (s, 1H), 6.04 (s, 1H), 3.84 (s, 3H), 2.20 (s, 3H); ^{13}C NMR: δ 163.21, 141.50, 139.75, 138.20, 132.68, 132.46, 131.46, 130.71, 130.00, 129.28, 128.33, 127.11, 125.73, 125.46, 122.74, 122.06, 114.42, 73.87, 55.76, 20.61; HRMS (APCI-MS, positive) calcd for $C_{22}H_{18}INO_3S_3$ $[M]^+$: 566.9488, found: 566.9474.

*4.4.22. 4-methoxy-N-(1-(3-(methylsulfanyl)thiophen-2-yl)naphthalen-2-yl)benzenesulfonamide (**13**)*

Colorless oil (63.6 mg, 0.14 mmol, 72%). ^{1}H NMR: δ 8.01 (d, *J* = 8.9 Hz, 1H), 7.89 (d, *J* = 8.9 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 9.4 Hz, 2H), 7.52 (d, *J* = 5.5 Hz, 1H), 7.36–7.41 (m, 2H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.16 (d, *J* = 5.5 Hz, 1H), 6.84 (d, *J* = 9.4 Hz, 2H), 6.82 (s, 1H), 3.78 (s, 3H), 2.25 (s, 3H); ^{13}C NMR: δ 163.34, 135.49, 134.32, 133.79, 130.86, 130.75, 130.71, 129.60, 128.93, 128.69, 128.17, 128.15, 127.28, 125.47, 125.34, 119.11, 118.31, 114.28, 55.67, 17.47; HRMS (APCI-MS, positive) calcd for $C_{22}H_{19}NO_3S_3$ $[M]^+$: 441.0522, found: 441.0526.

*4.4.23. 4-methoxy-N-(2'-(methylsulfanyl)-[1,1'-binaphthalen]-2-yl)benzenesulfonamide (**14**)*

The reaction was performed in toluene. White solid (66.0 mg, 0.14 mmol, 68%, m.p. = 190.5–191.9 ºC, using toluene as solvent). ^{1}H NMR: δ 8.19 (d, *J* = 8.9 Hz, 1H), 7.98–8.01 (m, 2H), 7.86–7.88 (m, 2H), 7.53 (d, *J* = 8.9 Hz, 1H), 7.44 (d, *J* = 8.9 Hz, 2H), 7.35–7.38 (m, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 8.2 Hz, 1H), 6.64 (d, *J* = 8.9 Hz, 2H), 6.47 (d, *J* = 8.2 Hz, 1H), 6.41 (s, 1H), 3.78 (s, 3H), 2.38 (s, 3H); ^{13}C NMR: δ 163.09, 138.03, 133.05, 132.86, 132.66, 131.18, 131.05, 130.05, 129.94, 129.31, 128.24, 128.19, 127.47, 127.32, 127.13, 125.37, 125.28, 125.22, 124.34, 123.11, 122.36, 119.22, 114.03 (one of these aromatic signals contains overlapping), 55.54, 15.32; HRMS (APCI-MS, positive) calcd for $C_{28}H_{23}NO_3S_2$ $[M]^+$: 485.1114, found: 485.1119.

*4.4.24. N-(1-(2,4-dimethoxy-6-(methylsulfanyl)phenyl)naphthalen-2-yl)-4-methoxybenzenesulfonamide (**15**)*

Colorless oil (51.5 mg, 0.10 mmol, 52%, using toluene as solvent). ^{1}H NMR: δ 8.01 (d, *J* = 8.9 Hz, 1H), 7.84 (d, *J* = 8.9 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 8.9 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 8.9 Hz, 1H), 6.81 (d, *J* = 8.9 Hz, 2H), 6.54 (s, 1H), 6.43 (d, *J* = 2.1 Hz, 1H), 6.35 (d, *J* = 2.1 Hz, 1H), 3.94 (s, 3H), 3.77 (s, 3H), 3.44 (s, 3H), 2.18 (s, 3H); ^{13}C NMR: δ 163.07, 161.85, 158.89, 142.90, 133.35, 133.00, 131.58, 130.88, 129.64, 129.43, 128.19, 126.71, 125.14, 124.90, 121.38, 118.56, 113.97, 111.87, 101.89, 94.81, 55.78, 55.61 (2C), 15.19; HRMS (APCI-MS, positive) calcd for $C_{26}H_{25}NO_5S_2$ $[M]^+$: 495.1169, found: 495.1172.

*4.4.25. 4-methoxy-N-(2-(2-(methylsulfanyl)benzothiophen-3-yl)phenyl)benzenesulfonamide (**16**)*

White solid (65.7 mg, 0.15 mmol, 75%, m.p. = 161.0–168.8 ºC). ^{1}H NMR: δ 7.82 (d, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 8.9 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.15 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.77 (br, 1H), 6.73 (d, *J* = 7.5 Hz, 1H), 6.54 (d, *J* = 8.9 Hz, 2H), 3.72 (s, 3H), 2.48 (s, 3H); ^{13}C NMR: δ 162.79, 139.65, 139.45, 137.20, 134.69, 131.45, 131.38, 130.56, 129.59, 129.01, 126.51, 125.46, 124.82, 124.48, 123.15, 122.12, 121.75, 113.88, 55.42, 19.11; HRMS (APCI-MS, positive) calcd for $C_{22}H_{19}NO_3S_3$ [M]: 441.0522, found: 441.0519.

*4.4.26. N-(4-chloro-2-(2-(methylsulfanyl)benzothiophen-3-yl)phenyl)-4-methoxybenzenesulfonamide (**17**)*

Colorless oil (21.0 mg, 0.04 mmol, 22%). ^{1}H NMR: δ 7.77 (d, *J* = 8.9 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.40 (dd, *J* = 8.9, 2.7 Hz, 1H), 7.32 (d, *J* = 8.9 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 2.7 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.72–6.73 (m, 2H), 6.54 (d, *J* = 8.9 Hz, 2H), 3.73 (s, 3H), 2.51 (s, 3H); ^{13}C NMR: δ 163.01, 139.43, 139.33, 138.17, 133.52, 131.17, 130.88, 130.41, 129.80, 129.66, 129.07, 128.27, 125.08, 124.66, 124.59, 121.88, 121.86, 114.04, 55.48, 19.13; HRMS (APCI-MS, positive) calcd for $C_{22}H_{18}{}^{35}ClNO_3S_3$ [M]: 475.0132, found: 475.0134.

*4.4.27. N-(2-(2-(methylsulfanyl)benzothiophen-3-yl)phenyl)methanesulfonamide (**18**)*

The reaction was performed at –20 ˚C for 19 h and then at 20 ˚C for 1 h. White solid (46.8 mg, 0.13 mmol, 67%, m.p. = 133.8–139.9 ºC). ^{1}H NMR: δ 7.82 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J*

= 8.2 Hz, 1H), 7.48–7.51 (m, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.30–7.33 (m, 3H), 7.22 (d, *J* = 7.5 Hz, 1H), 6.35 (s, 1H), 2.78 (s, 3H), 2.55 (s, 3H); ^{13}C NMR: δ 139.71, 139.63, 138.49, 135.33, 131.88, 130.67, 130.07, 125.75, 125.43, 125.41, 124.88, 122.31, 121.78, 121.14, 39.43, 19.04; HRMS (APCI-MS, positive) calcd for $C_{16}H_{15}NO_2S_3$ $[M]^+$: 349.0259, found: 349.0267.

*4.4.28. N-(2-(benzothiophen-3-yl)-4-methylphenyl)-4-methoxybenzenesulfonamide (**19**)*

White solid (197.5 mg, 0.48 mmol, 97%, m.p. = 182.3–183.7 ºC). ^{1}H NMR: δ 7.90 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.35–7.39 (m, 3H), 7.21–7.26 (m, 2H), 7.09 (d, *J* = 7.5 Hz, 1H), 6.99 (s, 1H), 6.87 (s, 1H), 6.71 (d, *J* = 8.9 Hz, 2H), 6.43 (s, 1H), 3.80 (s, 3H), 2.33 (s, 3H); ^{13}C NMR: δ 163.04, 140.24, 138.17, 135.10, 132.78, 132.39, 131.56, 130.64, 130.02, 129.26, 127.61, 125.11, 125.04, 124.84, 122.98, 122.66, 122.57, 114.03, 55.64, 20.93; HRMS (APCI-MS, positive) calcd for $C_{22}H_{19}NO_3S_2$ $[M]^+$: 409.0801, found: 409.0804.

*4.4.29. N-(2-(benzothiophen-3-yl)phenyl)methanesulfonamide (**20**)*

Colorless oil (51.0 mg, 0.17 mmol, 84%). ^{1}H NMR: δ 7.95 (d, *J* = 8.2 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.41–7.48 (m, 4H), 7.34–7.39 (m, 2H), 7.26 (t, *J* = 7.5 Hz, 1H), 6.39 (s, 1H), 2.81 (s, 3H); ^{13}C NMR: δ 140.58, 138.10, 135.38, 132.61, 131.63, 129.74, 126.51, 126.03, 125.37, 125.10, 124.97, 123.29, 122.50, 120.08, 39.64; HRMS (APCI-MS, positive) calcd for $C_{15}H_{14}NO_2S_2$ $[M+H]^+$: 304.0460, found: 304.0468.

*4.4.30. N-(4-methyl-2-(2-(methylsulfonyl)benzothiophen-3-yl)phenyl)-4-methoxybenzenesulfonamide (**21**)*

Yellow solid (312.2 mg, 0.64 mmol, 74%, m.p. = 186.0–187.3 ºC). ^{1}H NMR: δ 7.85 (d, *J* = 8.2 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.29–7.33 (m, 3H), 7.18 (t, *J* = 7.5 Hz, 1H), 6.93 (s, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.43 (d, *J* = 8.9 Hz, 2H), 3.70 (s, 3H), 2.88 (s, 3H), 2.35 (s, 3H); ^{13}C NMR: δ 162.32, 140.07, 140.01, 138.42, 137.83, 136.34, 132.60, 131.75, 131.52, 131.04, 128.65, 127.84, 127.34, 127.00, 125.70, 125.47, 122.30, 113.74, 55.35, 44.40, 21.01; HRMS (APCI-MS, positive) calcd for $C_{23}H_{21}NO_5S_3$ $[M]^+$: 487.0576, found: 487.0582.

*4.4.31. N-(2-(2-(methylsulfonyl)benzothiophen-3-yl)phenyl)methanesulfonamide (**22**)*

White solid (607.9 mg, 1.59 mmol, 80%, m.p. = 233.7–234.9 ºC). ^{1}H NMR: δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.9 Hz, 1H), 7.56–7.61 (m, 2H), 7.45 (t, *J* = 7.9 Hz, 1H), 7.32–7.36 (m, 2H), 7.25 (d, *J* = 7.5 Hz, 1H), 6.48 (s, 1H), 3.01 (s, 3H), 2.85 (s, 3H); ^{13}C NMR: δ 140.59, 139.77, 139.70, 137.24, 136.42, 131.18, 130.69, 128.72, 126.40, 125.20, 125.08, 124.05, 123.12, 121.74, 45.00, 40.25; HRMS (APCI-MS, positive) calcd for $C_{16}H_{16}NO_4S_3$ $[M+H]^+$: 382.0236, found: 382.0233.

*4.4.32. 9-methyl-6H-benzo[4,5]thieno[2,3]indole (**23**)*

Yellow solid (72.7 mg, 0.30 mmol, 61%, m.p. =151.3–154.7 ºC). ^{1}H NMR: δ 8.11 (d, *J* = 8.2 Hz, 2H), 7.83 (s, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 2.57 (s, 3H); ^{13}C NMR: δ 140.21, 139.66, 138.57, 132.89, 130.04, 125.15, 123.69, 123.53, 123.01, 122.35, 120.73, 118.84, 118.77, 111.12, 21.71; HRMS (APCI-MS, positive) calcd for $C_{15}H_{11}NS$ $[M]^+$: 237.0607, found: 237.0608.

*4.4.33. 6H-benzo[4,5]thieno[2,3]indole (**24**)*

White solid (151.9 mg, 0.68 mmol, 68%, m.p. = 152.1–152.9 ºC).^{1}H NMR: δ 8.36 (br, 1H), 8.12 (d, *J* = 7.5 Hz, 1H), 8.03–8.05 (m, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.44–7.46 (m, 1H), 7.28–7.33 (m, 3H); ^{13}C NMR: δ 141.37, 140.06, 138.59, 132.81, 125.19, 123.71, 122.85, 122.49, 122.18, 120.78, 120.69, 119.19, 118.85, 111.47; HRMS (APCI-MS, positive) calcd for $C_{14}H_{10}NS$ $[M+H]^+$: 224.0528, found: 224.0533.

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14. Simple methyl phenyl sulfoxide, instead of 3,5-dimethoxyphenyl sulfoxide, was converted to the corresponding biaryl in less than 10% yield.
15. The slow formation of **16** provided a chance to observe a putative S–N-bonded sulfonium intermediate that should be formed from **4a** and *p*-anisylsulfonylaniline at –20 ˚C. For details, see Supplementary Material.
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Supplementary Material

Supplementary data to this article can be found online at

Declaration of interests

☒ 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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: