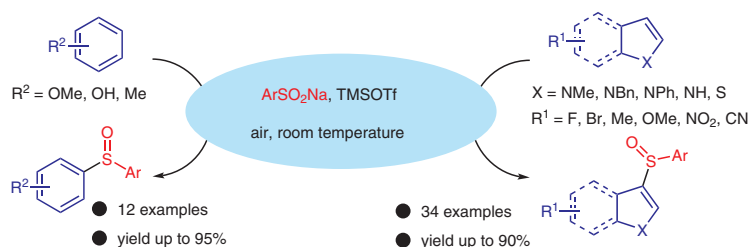


TMSOTf-Promoted Sulfinylation of Electron-Rich Aromatics with Sodium Arylsulfonates

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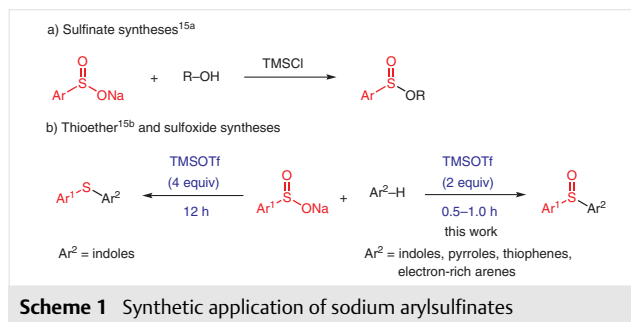
Abstract A new transition-metal-free route for the direct sulfonylation of electron-rich aromatics with sodium arylsulfonates in the presence of TMSOTf is reported. Various electron-rich aromatics, including pyrroles, thiophenes, indoles, and electron-rich arenes, with sodium arylsulfonates are converted into the corresponding sulfoxides in moderate to excellent yields. This protocol possesses many advantages such as readily available and stable starting materials, broad substrate scopes, and transition-metal-free reaction conditions.

Key words sulfonylation, pyrroles, indoles, sulfoxides, sodium arylsulfonates

Sulfoxides are prevalent in important and high-value chemical structures¹ such as the natural products,² pharmaceutically active compounds,³ ligands,⁴ organocatalysis,⁵ and functional materials.⁶ Traditionally, sulfoxides could be prepared by oxidation of sulfides⁷ or nucleophilic substitution of sulfinyl derivatives with organometallic reagents.⁸ In addition, other synthetic approaches to sulfoxides, such as transition-metal-catalyzed arylation of sulfenate anions,⁹ have also been reported.¹⁰ In recent years, direct sulfonylation of electron-rich arenes and heteroarenes has been developed by using sulfinic acids,¹¹ sulfonates,¹² and sulfinamides¹³ as the sulfonylating reagents. Despite these advances, the direct synthesis of the sulfoxides, using easy-to-handle reagents under mild reaction conditions, remains in demand.

On the other hand, sodium arylsulfonates are stable, odorless, and easy-to-handle sulfur compounds, and thus have been widely used as desirable starting materials for the synthesis of organosulfur compounds.^{14,15} We have reported the advantages of using sodium arylsulfonates/TMSCl system with oxygenated nucleophiles for obtaining sulfonates under mild conditions (Scheme 1a).^{15a} Subse-

quently, we reported a TMSOTf-promoted thiolation of indoles with sodium arylsulfonates by in situ overreduction of the new generated, sulfonylated intermediates (Scheme 1b, left).^{15b} We envisioned that the sulfoxide reduction process might be obviated by carefully controlling the reaction conditions, and thus could facilitate a practical sulfoxide synthesis. We report herein the realization of this strategy by shortening the reaction time (i.e., 12 h vs. 0.5–1 h) and simultaneously decreasing the amount of TMSOTf (i.e., 4 equiv vs. 2 equiv), which provide a facile synthetic protocol to sulfoxides from electron-rich arenes and heteroarenes with sodium arylsulfonates (Scheme 1b, right).



Scheme 1 Synthetic application of sodium arylsulfonates

Reaction of sodium *p*-toluenesulfonate (**1a**) with *N*-Methylpyrrole (**2a**) was used as a probe for evaluating the reaction conditions (Table 1). Following our previous procedure (2 equiv of TMSCl, CH₂Cl₂, rt),^{15a} reaction of sodium *p*-toluenesulfonate (**1a**) with *N*-Methylpyrrole (**2a**, 1.5 equiv) afforded 2-sulfinylpyrrole **3a** and 3-sulfinylpyrrole **4a** in 6% and 55% yields, respectively (Table 1, entry 1). Subsequently, DMSCl, TIPSCl, TBDMSCl, TMSOTf, BF₃·Et₂O, CF₃SO₃H, *p*-TsOH·H₂O, and AcOH were further investigated for this reaction, and TMSOTf is found to be the most efficient promoter for this reaction (Table 1, entries 1–9). The reaction did not work when it was performed in DMF, DMSO, H₂O (Table 1, entries

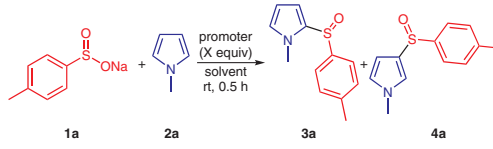
10–12). With the use of MeNO₂, MeCN, THF, 1,4-dioxane, and toluene in comparison to (ClCH₂)₂, lower yields were found (Table 1, entries 13–18). No reaction took place in the absence of TMSOTf (Table 1, entry 19). Further parameters optimization identified the most effective TMSOTf loading as 2.0 equiv (Table 1, entries 13 and 20–24). The reaction was also performed under argon atmosphere, and the same yield was observed (Table 1, entries 13 and 25), which indicated that noble gas atmosphere is not necessary for this reaction.

The optimized sulfonylation reaction conditions proved to be effective for various sodium arylsulfonates **1** and pyrroles/thiophenes **2** (Scheme 2). With the aromatic ring bearing hydrogen atoms, electron-withdrawing and electron-donating groups, sodium arylsulfonates **1** reacted smoothly with *N*-Me-pyrrole (**2a**) in the presence of TMSOTf (2 equiv) in (ClCH₂)₂ at 25 °C to afford sulfoxides **4a–l** in 31–84% yields within 0.5 h. 1-Naphthyl-, 2-naphthyl-, 2-thienyl-, and cyclopropyl-substituted sodium sulfonates reacted with pyrrole **2a** to generate the sulfoxides **4m–p** in 45–77% yields. *N*-Substituted pyrroles with benzyl and phenyl reacted with sodium *p*-toluenesulfonate (**1a**) to afford the sulfoxides **4q** and **4r** in 90% and 89% yields, respectively. Treatment of 1-tosyl-1*H*-pyrrole with sodium arylsulfonate **2a** failed to give the desired sulfoxide **4s**. The reaction of 1*H*-pyrrole and 2,5-dimethyl-1*H*-pyrrole with sodium arylsulfonate **2a** went smoothly to generate the desired sulfoxides **4t** and **4u** in 41% and 36% yields, respectively.

Reaction of 3-ethyl-2,5-dimethyl-1*H*-pyrrole with sodium arylsulfonate **2a** is complex under the standard conditions and the expected sulfoxides **4v** was not observed. Interestingly, treatment of 1-(1-benzyl-1*H*-pyrrol-2-yl)ethan-1-one, an electron-deficient pyrrole, with sodium arylsulfonate **2a** under the standard conditions did not afford the corresponding thermodynamic product 3-sulfinylpyrrole. Instead, kinetic product 2-sulfinylpyrrole **3w** was obtained in 13% yield, whose structure has been determined from the observed different chemical shifts and coupling constant between H_a/H_b (δ_a = 5.54 ppm, δ_b = 5.50 ppm, J_{ab} = J_{ba} = 15.0 Hz, Scheme 2). Ethyl 1-benzyl-2,4-dimethyl-1*H*-pyrrole-3-carboxylate, an electron-deficient pyrrole with its 3-positions possessing substituents, was also investigated, which reacted with sodium arylsulfonate **2a** to generate the overreduction product **5x** in 47% yield. The reaction of thiophene, 3-hexylthiophene with sodium arylsulfonate **2a** went smoothly to afford sulfoxides **4y** and **4z** in 23% and 63% yields, respectively.

To prove the synthetic utility of this synthetic method, gram-scale reaction was carried out under the standard sulfonylation conditions (Scheme 3). The reaction of sodium sulfonate **1a** (30 mmol, 5.34 g) reacted smoothly with pyrrole **2a** (45 mmol) in the presence of TMSOTf (60 mmol) in

Table 1 Optimization of the Reaction Conditions^a



Entry	Promoter (X equiv)	Solvent	Yield of 3a (%) ^b	Yield of 4a (%) ^b
1	TMSCl (2.0)	CH ₂ Cl ₂	6	55
2	DMSCl (2.0)	CH ₂ Cl ₂	4	22
3	TIPSCl (2.0)	CH ₂ Cl ₂	2	20
4	TBDMSCl (2.0)	CH ₂ Cl ₂	3	62
5	TMSOTf (2.0)	CH ₂ Cl ₂	0	76
6	BF ₃ ·Et ₂ O (2.0)	CH ₂ Cl ₂	0	60
7	CF ₃ SO ₃ H (2.0)	CH ₂ Cl ₂	0	66
8	<i>p</i> -TsOH·H ₂ O (2.0)	CH ₂ Cl ₂	0	23
9	AcOH (2.0)	CH ₂ Cl ₂	N.D.	N.D.
10	TMSOTf (2.0)	DMF	N.D.	N.D.
11	TMSOTf (2.0)	DMSO	N.D.	N.D.
12	TMSOTf (2.0)	H ₂ O	N.D.	N.D.
13	TMSOTf (2.0)	(ClCH ₂) ₂	0	88 (83 ^c)
14	TMSOTf (2.0)	MeNO ₂	0	60
15	TMSOTf (2.0)	MeCN	0	81
16	TMSOTf (2.0)	THF	0	74
17	TMSOTf (2.0)	1,4-dioxane	0	50
18	TMSOTf (2.0)	toluene	0	77
19	–	(ClCH ₂) ₂	N.R.	N.R.
20	TMSOTf (0.5)	(ClCH ₂) ₂	6	10
21	TMSOTf (1.0)	(ClCH ₂) ₂	4	38
22	TMSOTf (1.5)	(ClCH ₂) ₂	0	73
23	TMSOTf (3.0)	(ClCH ₂) ₂	0	74
24	TMSOTf (4.0)	(ClCH ₂) ₂	0	64
25 ^d	TMSOTf (2.0)	(ClCH ₂) ₂	0	88

^a General conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), and promoter (0–0.8 mmol) in solvent (1.0 mL) at rt for 0.5 h. DMS = dimethylsilyl; TIPS = triisopropylsilyl; TBDMS = *tert*-butyldimethylsilyl; N.D. = no detection; N.R. = no reaction.

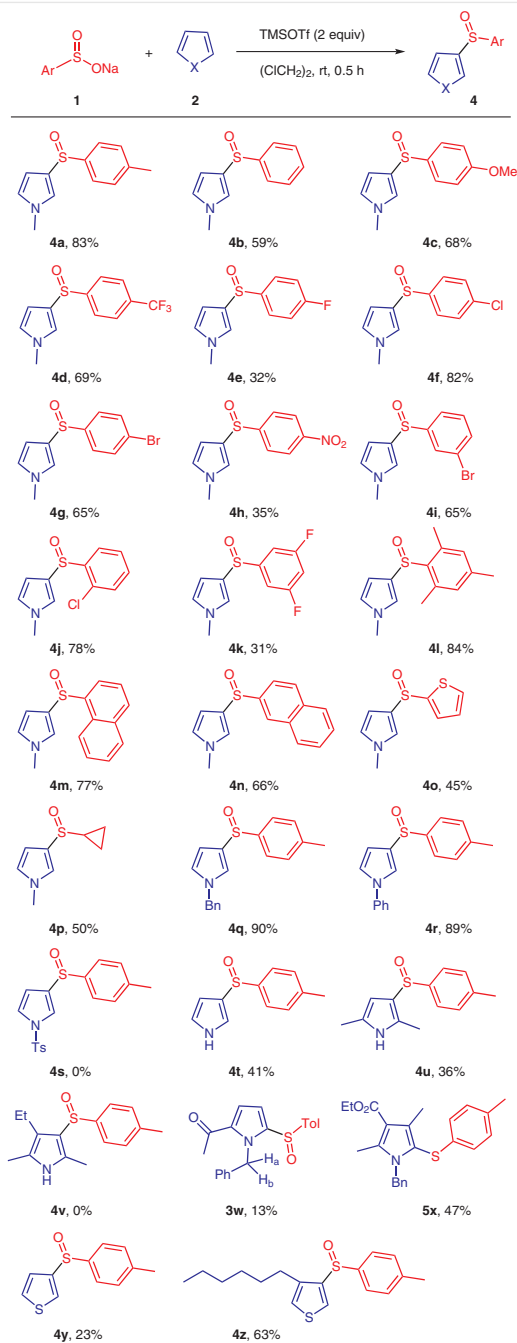
^b The yield was determined by ¹H NMR spectroscopy using 0.2 mmol of CH₂Br₂ as a standard.

^c Isolated yield.

^d Under argon.

(ClCH₂)₂ at 25 °C to afford sulfoxides **4a** (5.32 g) in 81% yield within 0.5 h. This result showed the great potential of this sulfonylation reaction in practical synthesis.

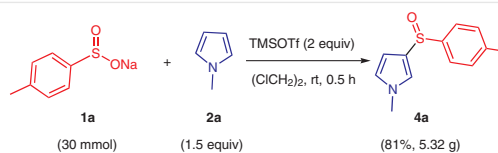
To glean insight into the sulfonylation reaction mechanism, a control experiment was carried out in Scheme 4. By treating of 2-substituted sulfoxide product **3a** in the presence of TMSOTf (2 equiv) in (ClCH₂)₂ at 25 °C, 3-substituted sulfoxide product **4a** was generated in 90% yield. This result



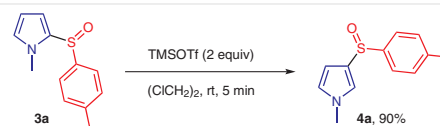
Scheme 2 TMSOTf-promoted sulfonylation of pyrroles/thiophenes **2** with sodium sulfonates **1**. Reagents and conditions: **1** (0.2 mmol), **2** (0.3 mmol), and TMSOTf (0.4 mmol) in (CICH₂)₂ (1.0 mL) at rt for 0.5 h. Isolated yields are given.

indicated that the sulfonylation reaction probably underwent a rearrangement from C2-sulfinylpyrroles **3** to C3-sulfinylpyrroles **4**.

Based on the experimental results and literature reports,^{15,16} the possible reaction pathway for the sulfonyla-



Scheme 3 Gram-scale synthesis

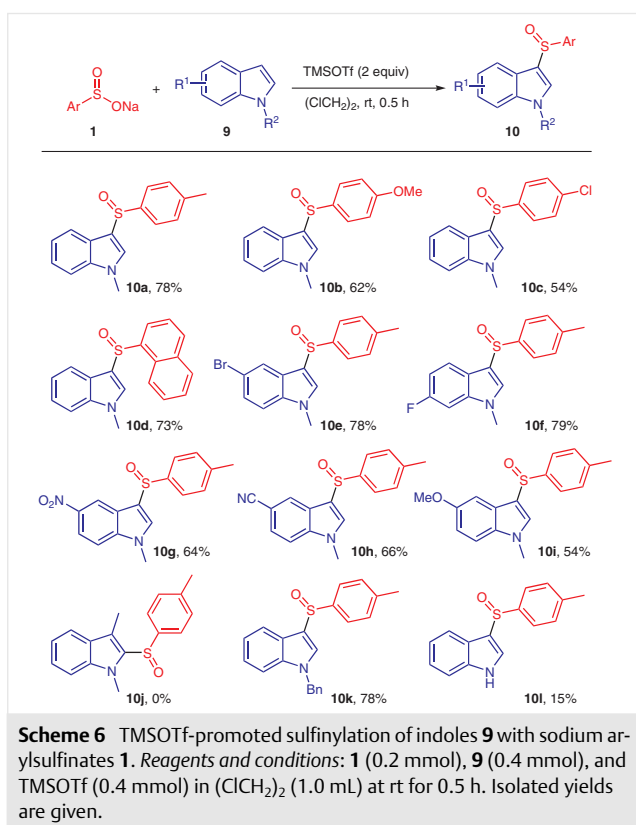
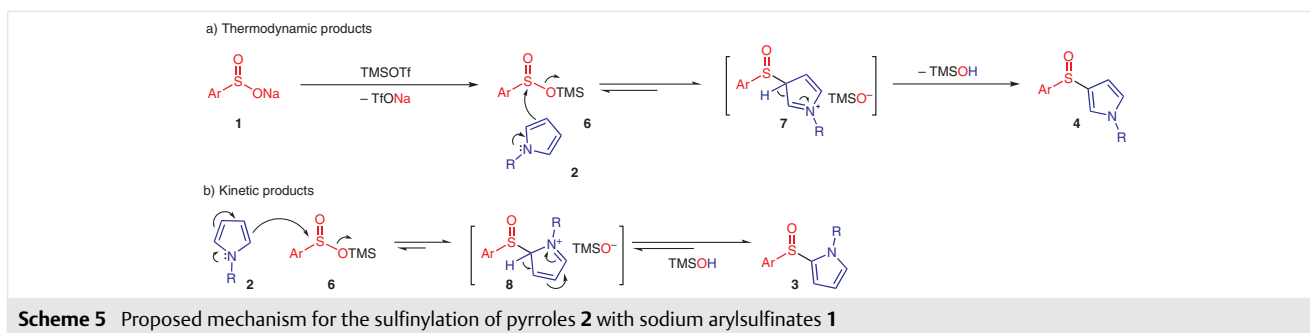


Scheme 4 The control experiment

tion of pyrroles is depicted in Scheme 5. Reaction of sodium arylsulfonates **1** with TMSOTf generated trimethylsilyl sulfonates **6**, which underwent electrophilic substitution reaction with pyrroles **2** at the C3 position to form thermodynamic intermediates **7**. Finally, intermediates **7** were converted into thermodynamic products **4** with the release of TMSOH (Scheme 5, a). On the other hand, electrophilic substitution reaction of trimethylsilyl sulfonates **6** with pyrroles **2** at the C2 position generated kinetic intermediates **8**, which were converted into kinetic products **3** with the release of TMSOH (Scheme 5, b). When electron-rich pyrroles were used as the substrates, thermodynamic products **4** were obtained as the major products under our standard reaction conditions. When electron-deficient pyrroles were used as the substrates, kinetic products, such as 2-sulfinylpyrrole **3w**, or the related overreduction products, such as thioether **5x**, might be obtained.

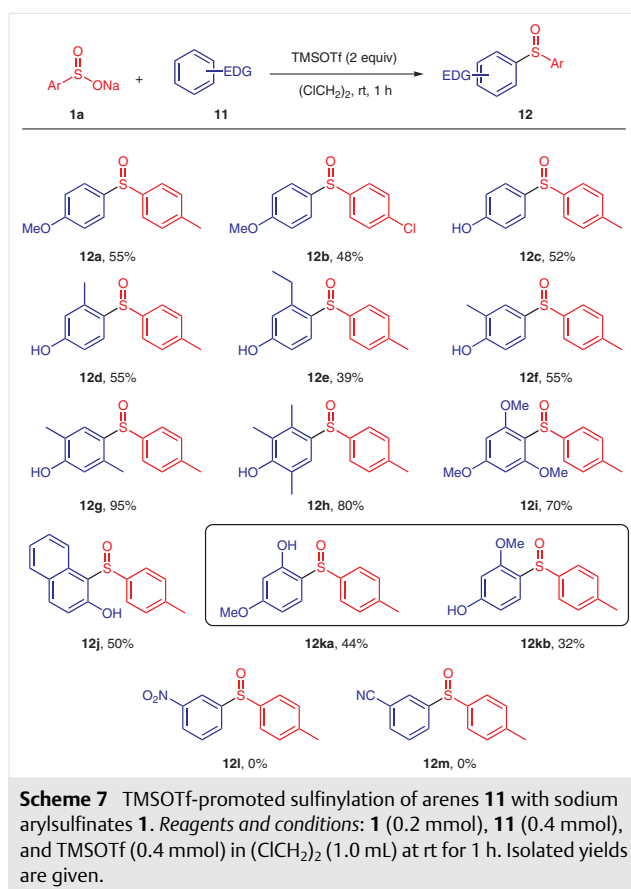
Sulfonylation of indoles **9** with sodium arylsulfonates **1** were subsequently investigated (Scheme 6). With the aromatic ring bearing electron-withdrawing or electron-donating groups (Cl, Me, MeO), sodium sulfonates **1** reacted smoothly with *N*-methylindole (**9a**) in the presence of TMSOTf (2 equiv) in (CICH₂)₂ at 25 °C to afford sulfoxides **10a–c** in 54–78% yields within 0.5 h. Sodium naphthalene-1-sulfonate reacted well with indole **9a** to afford sulfoxide **10d** in 73% yield. A wide variety of indoles with substituent groups such as halogen, nitro, cyano, and methoxy reacted smoothly with sodium *p*-toluenesulfonate (**1a**) to afford sulfoxides **10e–i** in 54–79% yields. Unfortunately, treatment of 1,3-dimethyl-1*H*-indole with sodium arylsulfonate **2a** failed to provide the desired sulfoxide **10j**. *N*-Substituted indole with benzyl and *N*-unsubstituted indole reacted with sodium *p*-toluenesulfonate (**1a**) to generate sulfoxides **10k** and **10l** in 78% and 15% yields, respectively.

The feasibility of this sulfoxide synthesis was also explored by using various arenes **11** as the substrates (Scheme 7). Arenes **11** bearing electron-donating groups (EDG) such as OMe, OH, and Me reacted with sodium arylsulfonates **1** in the presence of TMSOTf (2 equiv) in (CICH₂)₂ at 25 °C to afford sulfoxides **12a–i** in 39–95% yields within 1 h.



Naphthalen-2-ol reacted well with sodium *p*-toluenesulfonate (**1a**) to afford the desired sulfoxide **12j** in 50% yield. Treatment of 3-methoxyphenol with sodium arylsulfonate **1a** afforded the two sulfoxide isomers **12ka** and **12kb** in 44% and 32% yields, respectively. Treatment of nitrobenzene and cyanobenzene with sodium sulfinate **2a** under the standard conditions failed to give the desired sulfoxides **12l** and **12m**; meanwhile, the starting material nitrobenzene and cyanobenzene were recovered in 89% and 86% yields, respectively.

In summary, we have developed a facile sulfoxides synthesis via the TMSOTf-promoted sulfonylation of electron-rich aromatics, including pyrroles, thiophenes, indoles, and electron-rich arenes, with sodium arylsulfonates under



transition-metal-free conditions.¹⁷ A wide variety of sulfoxides were obtained with moderate to excellent yields. These reactions could take place under mild conditions without the need for using transition-metal catalysts, which offers attractive industrial application prospects.

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Supporting Information

Supporting information for this article is available online at <https://doi.org/10.1055/s-0039-1691563>.

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- (17) **General Procedure for the Preparation of Sulfoxides 4**
The mixture of sodium arylsulfinate (0.2 mmol, 1.0 equiv), pyrrole/thiophenes (0.3 mmol, 1.5 equiv), and TMSOTf (0.4 mmol, 2.0 equiv) in (ClCH₂)₂ (1.0 mL) was stirred at 25 °C for 0.5 h. After completion of the reaction, water (5 mL) and dichloromethane (10 mL) were added. The two layers were separated, and the aqueous phase was extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed by brine, dried over anhydrous Na₂SO₄, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (ethyl acetate–petroleum ether = 1:1) to afford the desired sulfoxides **4**.
Compound **4a**: white solid, mp 84–86 °C; 36.3 mg, 83% yield. ¹H NMR (400 MHz, CDCl₃): δ = 7.53 (d, *J* = 8.2 Hz, 2 H), 7.27 (d, *J* = 8.0 Hz, 2 H), 6.95 (t, *J* = 2.0 Hz, 1 H), 6.58 (t, *J* = 2.5 Hz, 1 H), 6.16 (dd, *J* = 3.0, 1.7 Hz, 1 H), 3.64 (s, 3 H), 2.39 (s, 3 H). ¹³C NMR (100

MHz, CDCl₃): δ = 141.9, 140.3, 129.3, 126.8, 124.5, 124.3, 123.9, 107.4, 36.4, 21.2. Data are in accordance to those previously reported.^{13a}

General Procedure for the Preparation of Sulfoxides 10

The mixture of sodium arylsulfinate (0.2 mmol, 1.0 equiv), indole (0.4 mmol, 2.0 equiv), and TMSOTf (0.4 mmol, 2.0 equiv) in (ClCH₂)₂ (1.0 mL) was stirred at 25 °C for 0.5 h. After completion of the reaction, water (5 mL) and dichloromethane (10 mL) were added. The two layers were separated, and the aqueous phase was extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed by brine, dried over anhydrous Na₂SO₄, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (ethyl acetate–petroleum ether = 1:1) to afford the desired sulfoxides **10**.

Compound **10a**: white solid, mp 138–139 °C; 42.0 mg, 78% yield. ¹H NMR (400 MHz, CDCl₃): δ = 7.62 (d, *J* = 8.2 Hz, 2 H), 7.48 (d, *J* = 8.7 Hz, 2 H), 7.34–7.24 (m, 4 H), 7.12–7.08 (m, 1 H), 3.79 (s, 3 H), 2.40 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ = 140.9, 140.3, 137.6, 132.5, 129.5, 124.8, 124.3, 123.2, 121.3, 119.8, 116.5, 110.0, 33.2, 21.2. Data are in accordance to those previously reported.^{13a}

General Procedure for the Preparation of Sulfoxides 12

The mixture of sodium arylsulfinate (0.2 mmol, 1.0 equiv), arene (0.4 mmol, 2.0 equiv), and TMSOTf (0.4 mmol, 2.0 equiv) in (ClCH₂)₂ (1.0 mL) was stirred at 25 °C for 1 h. After completion of the reaction, water (5 mL) and dichloromethane (10 mL) were added. The two layers were separated, and the aqueous phase was extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed by brine, dried over anhydrous Na₂SO₄, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (ethyl acetate–petroleum ether = 1:1) to afford the desired sulfoxides **12**.

Compound **12a**: colorless oil, 27.0 mg, 55% yield. ¹H NMR (400 MHz, CDCl₃): δ = 7.55 (d, *J* = 8.8 Hz, 2 H), 7.49 (d, *J* = 8.1 Hz, 2 H), 7.25 (d, *J* = 7.3 Hz, 2 H), 6.95 (d, *J* = 8.8 Hz, 2 H), 3.81 (s, 3 H), 2.36 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ = 161.8, 142.5, 141.2, 136.9, 129.8, 127.0, 124.7, 114.7, 55.4, 21.3. Data are in accordance to those previously reported.^{11a}