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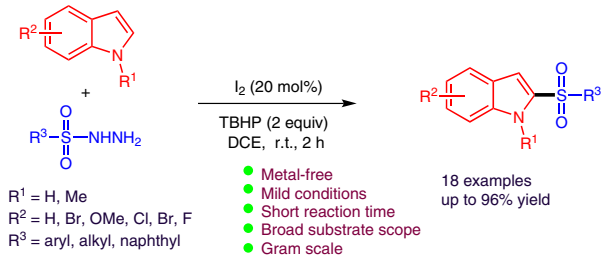
A Sulfonylation Reaction: Direct Synthesis of 2-Sulfonylindoles from Sulfonyl Hydrazides and Indoles

Rajjakfur Rahaman
Pranjit Barman*

Department of Chemistry, National Institute of Technology
Silchar, Silchar-788010, India
barmanpranjit@yahoo.co.in



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Abstract A metal-free synthesis of 2-sulfonylindole derivatives has been developed through a novel TBHP/I_2-mediated coupling of C3/unsubstituted indoles with sulfonyl hydrazides. The reaction utilizes readily available starting materials under mild reaction conditions, providing an alternative and attractive approach to 2-sulfonylindoles with high yields. The developed synthetic procedure is suitable for both N-protected or unprotected indoles.

Key words direct synthesis, sulfonylation, 2-sulfonylindoles, sulfonyl hydrazides, indoles

Organosulfones are important intermediates for pharmaceuticals, agrochemicals, and activating and protecting groups.[1] Indoles represents a prominent structural motif found in naturally occurring compounds and pharmaceutically important agents (Figure 1).[2,3] It has been widely proven that the C2 position of the indole has less priority compared to the C3 position. Hence, the direct C2 functionalization of indole has been more challenging and less studied.

Sulfur-containing group when present in a molecular structure either as a sulfanyl, a sulfenyl, or a sulfonyl, it adds variety to the chemical architecture and also enhances biological activity of the compound.[4]

Particularly, 2-sulfonylindoles affects the inhibition of nucleoside triphosphate hydrolase enzyme, and the sulfonyl group of the 2-sulfonylindoles acts as a temporary functional group which can be removed later by β-elimination.[5]

Generally, indolyl aryl sulfones are synthesized via the oxidation of the corresponding arylthioindoles.[6] During the past few years, alternative methodologies have been developed for the synthesis of 3-arylsulfonyl indoles using aryl

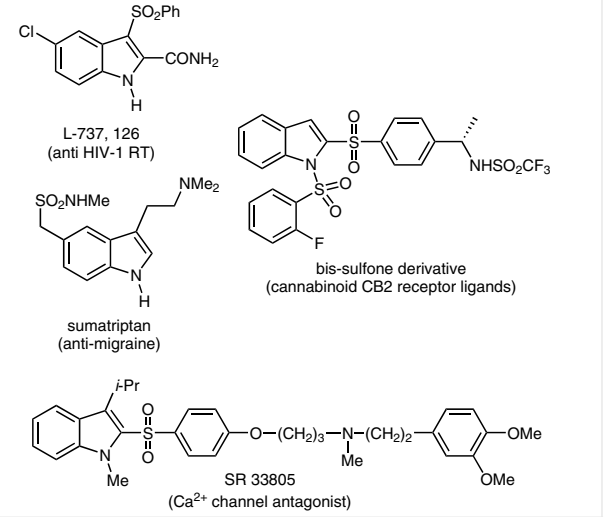


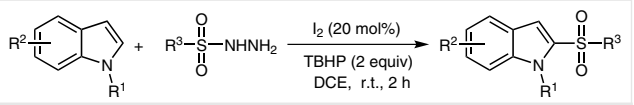
Figure 1 Some biologically active indolyl aryl sulfones

sulfinic acids or aryl sulfonyl halides as sulfonylation reagents.[7] Meanwhile, only a few methods have been developed for 2-arylsulfonyl indoles.[8] However, still the reported methods have some drawbacks such as using nonstable, hazardous, and mutagenic starting materials, difficulty in handling and storage, and the requirements of harsh reaction conditions and prolonged reaction time. Therefore, it is highly desirable to develop an alternative and facile catalytic methodology to construct 2-sulfonylindoles from a synthetic viewpoint.

Due to their ease of handling, high efficiency, commercial availability, low toxicity, mild reaction conditions, and metal-free features, molecular iodine and its salts have emerged as a promising alternative to catalyse oxidative sulfonylation recently.[9] Numerous methods have demon-

strated impressive advancements of iodine-catalyzed sulfonylation of heteroaromatic compounds and C–C unsaturated bonds.[10]

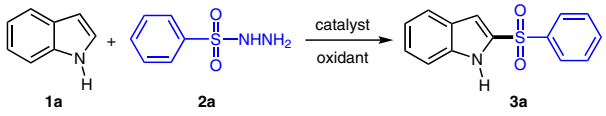
In recent years, arylsulfonyl hydrazides have emerged as excellent synthons for many organic transformations.[11] Depending upon the conditions of reaction they can act as a sulfur electrophiles or nucleophiles.[12,9f] Compared to the other sulfonylating agents sulfonyl hydrazides are much more amenable to handling, because they are readily accessible solids, not sensitive to air and moisture, free of unpleasant odor, exhibit high reactivity, react under relatively mild conditions, and are eco-friendly byproducts (water and N_2). However, to the best of our knowledge, the formation of 2-sulfonylindoles from sulfonyl hydrazides and indoles has not been explored. In our effort to benign protocols, we have continuously tried to endorse the use of nontoxic medium. Therefore, in our approach, we concentrated on the potent combination of a nontoxic medium and transition-metal-free conditions with disulfide or sulfonyl hydrazide species.[13] Herein, we developed an iodine-catalyzed sulfonylation of indoles with sulfonyl hydrazides using DCE as solvent, affording 2-arylsulfonyl indoles in good to excellent yields (Scheme 1).



Scheme 1 Some biologically active indolyl aryl sulfones

In order to achieve optimum reaction conditions, indole (**1a**) and benzenesulfonyl hydrazide (**2a**) were chosen as the model substrates. To our delight, the desired product 2-benzenesulfonylindole (**3a**) was obtained in 50% yield when the reaction was carried out by using I_2 (10 mol%) and TBHP (1 equiv, 70% in water) in 1,2-dichloroethane (DCE) for two hours in an open atmosphere at room temperature (Table 1, entry 5). An increase to 20 mol% of I_2 brought about a reasonable rise in the yield to 70% (Table 1, entry 6). However, further increase in the I_2 concentration did not enhance the yield of the desired product (Table 1, entry 7). Higher yield was observed when **2a** was employed in excess amount (Table 1, entry 8). As illustrated in entries 1–4, different types of iodine-containing catalysts including NIS, KI, NH_4I, and TBAI were examined in the model reaction, and we found that these catalysts hardly facilitate the reaction. Thereafter, we screened the effect of various solvents on the reaction and DCE found to be particularly effective for this transformation. To increase the TBHP loading of 1.5 equivalents improved the yield remarkably, and two equivalents of TBHP were found to be sufficient for a reasonably improved yield of the product (Table 1, entries 10 and 11). Screening a range of oxidants such as H_2O_2, di-*tert*-butyl peroxide (DTBP), $K_2S_2O_8$, and O_2 revealed that other oxidants were ineffective for this transformation (Table 1, entries 13–16). Moreover, there was no product formation observed in the absence of I_2 (Table 1, entry 27), and only a trace amount of the product was obtained without using TBHP in the reaction (Table 1, entry 28).

Table 1 Optimization of the Reaction Conditions[a]



Entry	Catalyst (mol%)	**2a** (equiv)	Solvent	Oxidant (equiv)	Yield (%)[b]
1	NIS (10)	1	DCE	TBHP (1)	40
2	KI (10)	1	DCE	TBHP (1)	30
3	NH_4I (10)	1	DCE	TBHP (1)	37
4	TBAI (10)	1	DCE	TBHP (1)	32
5	I_2 (10)	1	DCE	TBHP (1)	50
6	I_2 (20)	1	DCE	TBHP (1)	70
7	I_2 (30)	1	DCE	TBHP (1)	70
8	I_2 (20)	2	DCE	TBHP (1)	85
9	I_2 (20)	3	DCE	TBHP (1)	85
10	I_2 (20)	2	DCE	TBHP (1.5)	90
11	I_2 (20)	2	DCE	TBHP (2)	92
12	I_2 (20)	2	DCE	TBHP (3)	92
13	I_2 (20)	2	DCE	H_2O_2 (2)	60
14	I_2 (20)	2	DCE	DTBP (2)	70
15	I_2 (20)	2	DCE	$K_2S_2O_8$ (2)	65
16	I_2 (20)	2	DCE	Air (O_2)	15
17	I_2 (20)	2	CH_2Cl_2	TBHP (2)	82
18	I_2 (20)	2	toluene	TBHP (2)	42
19	I_2 (20)	2	MeCN	TBHP (2)	35
20	I_2 (20)	2	MeOH	TBHP (2)	40
21	I_2 (20)	2	H_2O	TBHP (2)	trace
22	I_2 (20)	2	DMSO	TBHP (2)	trace
23	I_2 (20)	2	DMF	TBHP (2)	trace
24	I_2 (20)	2	THF	TBHP (2)	45
25	I_2 (20)	2	1.4-dioxane	TBHP (2)	40
26	I_2 (20)	2	EtOAc	TBHP (2)	30
27	–	2	DCE	TBHP (2)	–[c]
28	I_2 (20)	2	DCE	–	trace

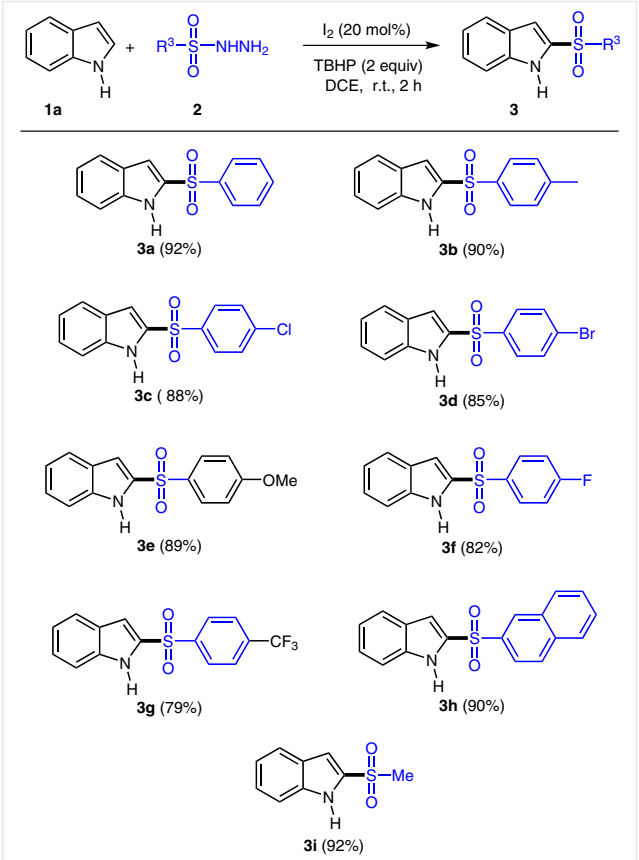
[a] Reaction conditions: **1a** (0.5 mmol), **2a** (1 mmol), catalyst (0.1 mmol, 20 mol%), oxidant (1 mmol), solvent (2 mL), r.t., 2 h under air; NIS = *N*-iodosuccinimide; TBHP = *tert*-butyl hydroperoxide; TBAI = tetrabutylammonium iodide; DTBP = di-*tert*-butyl peroxide.
[b] Isolated yields after column chromatography based on **1a**.
[c] **3a** was not observed (TLC analysis).

After all, the use of I_2 and TBHP were crucial for this reaction, and the optimum reaction conditions for the C2-sulfonylation of indoles were chosen as follows: **1a** (1 equiv),

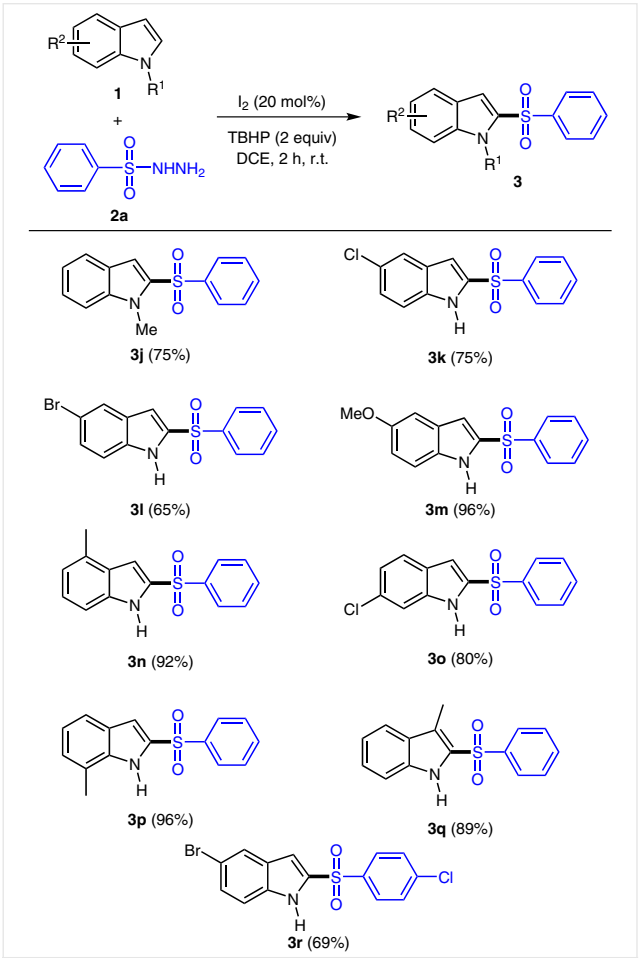
2a (2 equiv), I_2 (20 mol%), TBHP (2 equiv) in DCE at room temperature for two hours (Table 1, entry 11). With the optimized reaction conditions in hand, we next explored the substrate scope and limitations of this new method.

Under the optimized conditions, a range of substituted aryl sulfonyl hydrazides were introduced to react with indole (**1a**) to give 2-arylsulfonyl indoles in good to excellent yields (Scheme 2, 3a–g). Various functional groups such as halogen, methoxy, and methyl could smoothly react with **1a** under the optimized reaction conditions. However, it was observed that sulfonyl hydrazides bearing electron-withdrawing groups deliver the product with high yield. It should be noted that cleavage of the C–halogen bond was not observed. Naphthylsulfonyl hydrazide also reacted with **1a** to give the desired product with high yield without any difficulties (Scheme 2, 3h). To our delight, besides aromatic sulfonyl hydrazides, aliphatic sulfonyl hydrazides were also suitable for this transformation, generating the corresponding products **3i** in excellent yields.

To further extend the applications of the reaction presented here the substrate scope of indoles was investigated under standard conditions. All reactions were performed well and afforded the corresponding 2-sulfonyl indoles in moderate to excellent yields. The electronic effect of the substituents on the indole moiety was also investigated (Scheme 3). Indoles bearing electron-donating groups such as 5-MeO, 4-Me, and 7-Me gave better reactivity and deliver high product yields. Substrate such as 5-O_2N indole did not give the corresponding sulfenylated product.



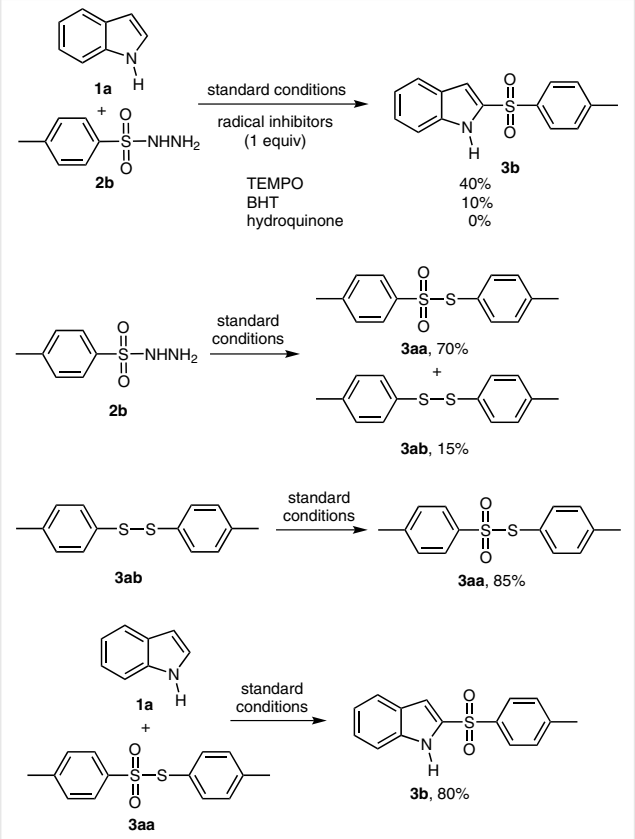
Scheme 2 Sulfonylation of indole (**1a**) with sulfonyl hydrazides. *Reagents and conditions*: **1a** (0.5 mmol), **2** (1.0 mmol), I_2 (0.1 mmol, 20 mol%), TBHP (1.0 mmol), DCE (2 mL), r.t., 2 h; isolated yield based on **1a**.



Scheme 3 Substrate scope of various indoles with **2a**. *Reagents and conditions*: **1** (0.5 mmol), **2a** (1.0 mmol), I_2 (0.1 mmol, 20 mol%), TBHP (1.0 mmol), DCE (2 mL), r.t., 2 h; isolated yield.

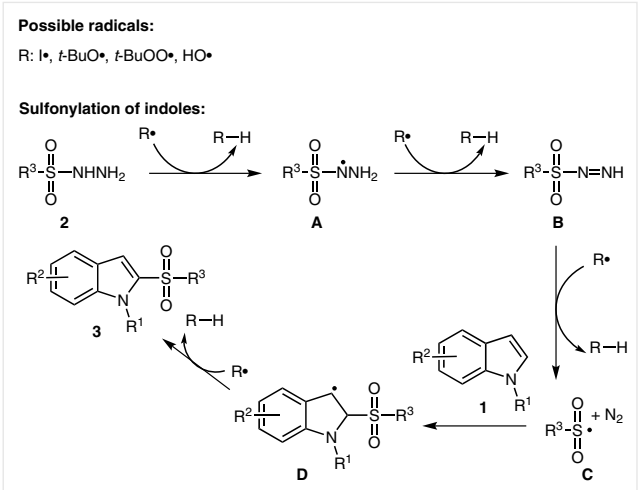
To gather more information, several control experiments were performed to gain an insight into the reaction mechanism (Scheme 4). A reaction of indole **1a** and sulfonyl hydrazides **2b** in the presence of a radical scavenger under the standard conditions resulted in a decrease in product yield. The desired product 2-sulfonylindole **3b** was obtained in 40%, 10%, and 0% yield in the presence of 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO), 2,6-di-*tert*-butyl-4-methylphenol (BHT), and hydroquinone, respectively (Scheme 4). The reaction was suppressed by a radical scavenger and implies that the reaction pathway is likely to involve a radical process. In the absence of indole **1a**, the sulfonyl hydrazide **2b** decompose to form benzenesulfonothio-

ate (**3aa**, 70%) along with a small amount of 1,2-diphenyldisulfane (**3ab**, 15%). Under the optimized conditions **3ab** converted into **3aa**. The intermediate **3aa** was confirmed by the treatment of **1a** with **3aa**, which provided the desired product **3b** in 80% yield (Scheme 5). Since trace amount of product was obtained when the reaction performed without using TBHB (Table 1, entry 28), indicates that I_2 does not react directly with the substrates. Iodine is likely converted into another intermediate in the presence of TBHP prior to reacting with sulfonyl hydrazide or indole.



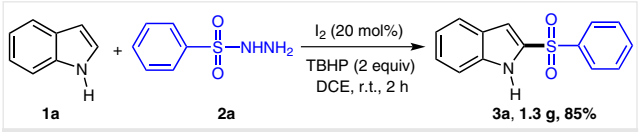
Scheme 4 Control experiments

Based on the aforementioned results, existing literature,[14] and the control experiments a possible mechanism is outlined in Scheme 5. Since the reactions were extremely inactive or did not occur if neither I_2 nor TBHP was employed under the optimized reaction conditions (Table 1, entries 27 and 28), this implies that to lead to the desired 2-sulfonylindoles both I_2 and TBHP did not directly react with the starting materials during the reaction. The transformation is presumed to involve a sulfonyl radical **C**, which is formed by the sequential N–H abstraction by the radicals (I•, *t*-BuO•, *t*-BuOO•, or HO•) generated by the reaction between I_2 and TBHP. The resulting sulfonyl radical could subsequently undergo addition to indole **1**, followed by iodine-catalyzed sulfonylation which afforded 2-sulfonylindole **3**.



Scheme 5 Plausible reaction mechanism

To showcase the practicability of the developed method, the reaction of indole **1a** and sulfonyl hydrazide **2a** was scaled up to 10 mmol, and the desired product **3a** was obtained without any significant loss in yield (1.3 g, 85%, Scheme 6).



Scheme 6 Gram-scale reaction

In conclusion, we have successfully disclosed a facile and efficient method for the synthesis of 2-sulfonylindoles in a highly functional-group compatible manner via I_2/TBHP-mediated reaction of indoles with commercially available sulfonyl hydrazide. The novel method refrains from using expensive metal catalysts and operates efficiently under an open atmosphere at room temperature. The unique method holds significant potential for application to a series of new organic reactions. The synthetic method presented here has many advantages, such as simple operation, short reaction time, inexpensive I_2 catalyst, broad scope of substrate, and excellent yields, and promises to be a greener alternative to earlier methods. Further efforts in this area are in progress in our laboratory.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0036-1588398.

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(15) **General Procedure for the Synthesis of 2-Sulfonylindoles**
To a mixture of indole **1** (0.5 mmol) with sulfonyl hydrazide **2** (1 mmol), iodine (20 mol%), TBHP (70% in water, 1 mmol) in DCE (2 mL). The resulting reaction mixture was stirred at r.t. for 2 h. Upon completion, distilled deionized H_2O (10 mL) and sat. $Na_2S_2O_3$ (10 mL) were added, and the mixture was extracted with EtOAc (3 × 20 mL). The combined organic layer was washed with sat. brine (20 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuum. The crude product was purified by column chromatography using EtOAc–hexanes (1:5) as eluent to afford the desired 2-sulfonylindole **3**.

(16) See Supporting Information for detailed experimental procedures and characterization data.

2-(Phenylsulfonyl)-1*H*-indole (3a)[8a]
White solid (118.4 mg, 92% yield); mp 159–161 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.81 (br s, 1 H), 8.04 (d, *J* = 7.0 Hz, 2 H), 7.66 (d, *J* = 9.0 Hz, 1 H), 7.50 (d, *J* = 2.5 Hz, 1 H), 7.48 (d, *J* = 8.0 Hz, 1 H), 7.31 (d, *J* = 6.0 Hz, 1 H), 7.21–7.17 (m, 3 H), 7.14 (t, *J* = 7.0 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141, 136.3, 133.5, 130.5, 128.9, 128.5, 124.6, 122.9, 120.7, 119.5, 111.4, 108.9. Anal. Calcd (%) for $C_{14}H_{11}NO_2S$: C, 65.35; H, 4.31; N, 5.44. Found: C, 65.37; H, 4.32; N, 5.45.

2-Tosyl-1*H*-indole (3b)[8a]
White solid (122.1 mg, 90% yield); mp 195–197 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.02 (br s, 1 H), 7.95 (d, *J* = 8.0 Hz, 2 H), 7.65 (d, *J* = 7.5 Hz, 1 H), 7.50 (d, *J* = 2.5 Hz, 1 H), 7.46 (d, *J* = 8.0 Hz, 1 H), 7.30–7.27 (m, 1 H), 7.20 (t, *J* = 7.5 Hz, 1 H), 7.20 (d, *J* = 8.0 Hz, 2 H), 2.33 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.7, 136.3, 135.3, 130.2, 139.3, 128.9, 126.1, 122.8, 120.7, 119.5, 111.3, 108.5, 20.7. Anal. Calcd (%) for $C_{15}H_{13}NO_2S$: C, 66.40; H, 4.83; N, 5.16. Found: C, 66.43; H, 4.81; N, 5.15.

2-[(4-Chlorophenyl)sulfonyl]-1*H*-indole (3c)[8a]
White solid (128.4 mg, 88% yield); mp 146–148 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.82 (br s, 1 H), 7.83 (d, *J* = 9 Hz, 2 H), 7.75 (d, *J* = 8.5 Hz, 2 H), 7.59 (d, *J* = 8.0 Hz, 1 H), 7.49 (d, *J* = 2.5 Hz, 1 H), 7.46 (d, *J* = 8.0 Hz, 1 H), 7.30–7.26 (m, 1 H), 7.20–7.17 (m, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 140, 137.6, 136.3, 130.6, 130.4, 128.6, 126.9, 123.1, 120.9, 119.3, 111.5, 109.1. Anal. Calcd (%) for $C_{14}H_{10}ClNO_2S$: C, 57.63; H, 3.45; N, 4.80. Found: C, 57.65; H, 3.47; N, 4.82.

2-[(4-Bromophenyl)sulfonyl]-1*H*-indole (3d)[8a]
White solid (142.9 mg, 85% yield); mp 191–193 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.87 (br s, 1 H), 7.71 (d, *J* = 8.5 Hz, 2 H), 7.50 (d, *J* = 7.5 Hz, 1 H), 7.42 (d, *J* = 2.5 Hz, 1 H), 7.39 (d, *J* = 7.5 Hz, 1 H), 7.19–7.18 (m, 3 H), 7.12–7.09 (m, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.5, 138.4, 136.3, 131.5, 130.6, 127.2, 123.1, 120.9, 119.3, 118.1, 111.5, 109. Anal. Calcd (%) for $C_{14}H_{10}BrNO_2S$: C, 50.01; H, 3.00; N, 4.17. Found: C, 50.04; H, 3.01; N, 4.15.

2-[(4-Methoxyphenyl)sulfonyl]-1*H*-indole (3e)[8a]
White solid (127.9 mg, 89% yield); mp 186–187 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.81 (br s, 1 H), 7.9 (d, *J* = 8.5 Hz, 2 H), 7.42 (d, *J* = 2.5 Hz, 1 H), 7.31 (d, *J* = 8.5 Hz, 1 H), 7.09 (d, *J* = 7.5 Hz, 2 H), 7.06–7.03 (m, 2 H), 6.91 (d, *J* = 8.5 Hz, 1 H), 3.77 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.9, 136.4, 135, 131.2, 129.8, 128.5, 125.5, 124.5, 115, 113.4, 112.3, 108.6, 55.6. Anal. Calcd (%) for $C_{15}H_{13}NO_3S$: C, 62.70; H, 4.56; N, 4.87. Found: C, 62.72; H, 4.55; N, 4.89.

2-[(4-Fluorophenyl)sulfonyl]-1*H*-indole (3f)[8a]
White solid (112.9 mg, 82% yield); mp 155–157 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.95 (br s, 1 H), 8.03 (d, *J* = 8.5 Hz, 2 H), 7.57–7.52 (m, 3 H), 7.36 (t, *J* = 7.0 Hz, 1 H), 7.24 (t, *J* = 7.5 Hz, 1 H), 7.16 (d, *J* = 9 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166 (d, *J* = 251.6 Hz), 136.4 (d, *J* = 3 Hz), 135, 130 (d, *J* = 9.6 Hz), 128.3, 124.9, 123.4, 121.3, 119.1, 116.3 (d, *J* = 22.6 Hz), 111.8, 109. Anal. Calcd (%) for $C_{14}H_{10}FNO_2S$: C, 61.08; H, 3.66; N, 5.09. Found: C, 61.05; H, 3.67; N, 5.06.

2-(Naphthalen-2-ylsulfonyl)-1*H*-indole (3h)[8a]
White solid (138.3 mg 90% yield); mp 156–158 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.05 (br s, 1 H), 8.46 (s, 1 H), 7.96–7.93 (m, 2 H), 7.72 (d, *J* = 8.0 Hz, 1 H), 7.65–7.61 (m, 2 H), 7.48–7.45 (m, 2 H), 7.38–7.33 (m, 2 H), 7.29–7.25 (m, 2 H), 7.16–7.13 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.5, 136.4, 133.6, 131.2, 130.5, 128.9, 128.1, 127.5, 126.8, 126.2, 124.9, 124.6, 123.3, 122.9, 120.8, 119.5, 111.4, 108.6. Anal. Calcd (%) for $C_{18}H_{13}NO_2S$: C, 70.34; H, 4.26; N, 4.56. Found: C, 70.31; H, 4.23; N, 4.57.

2-(Methylsulfonyl)-1*H*-indole (3i)[8a]
White solid (89.8 mg, 92% yield); mp 184–186 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.01 (br s, 1 H), 7.65 (d, *J* = 7.5 Hz, 1 H), 7.43 (d, *J* = 8.0 Hz, 1 H), 7.29–7.25 (m, 1 H), 7.22–7.16 (m, 2 H), 3.25 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 136.4, 133.3, 126.9, 126.2, 122.9, 121, 111.6, 108.2, 45.2. Anal. Calcd (%) for $C_9H_9NO_2S$: C, 55.37; H, 4.65; N, 7.17. Found: C, 55.40; H, 4.63; N, 7.15.

5-Methoxy-2-(phenylsulfonyl)-1*H*-indole (3m)[8a]
White solid (137.9 mg, 96% yield); mp 135–137 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.01 (br s, 1 H), 8.02 (d, *J* = 8.0 Hz, 2 H), 7.57–7.51 (m, 3 H), 7.36 (d, *J* = 7.6 Hz, 1 H), 7.22 (s, 1 H), 7.16–7.12 (m, 2 H), 3.81 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155, 140.9, 134.1, 133.5, 132.6, 129.8, 128.1, 127.7, 117.6, 112.3, 109, 102.3, 55.5. Anal. Calcd (%) for $C_{15}H_{13}NO_3S$: C, 62.70; H, 4.56; N, 4.87. Found: C, 62.67; H, 4.57; N, 4.85.

4-Methyl-2-(phenylsulfonyl)-1*H*-indole (3n)[8a]
White solid (124.8 mg, 92% yield); mp 166–169 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.01 (br s, 1 H), 7.96 (d, *J* = 8.4 Hz, 2 H), 7.50–7.45 (m, 3 H), 7.32–7.27 (m, 3 H), 6.96 (d, *J* = 7.2 Hz, 1 H), 2.51 (s, 3 H). Anal. Calcd (%) for $C_{15}H_{13}NO_2S$: C, 66.40; H, 4.83; N, 5.16. Found: C, 66.38; H, 4.80; N, 5.17.

6-Chloro-2-(phenylsulfonyl)-1*H*-indole (3o)[8a]
White solid (116.7 mg, 80% yield); mp 181–183 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.01 (br s, 1 H), 8.01 (d, *J* = 8.5 Hz, 2 H), 7.55–7.49 (m, 4 H), 7.24 (d, *J* = 7.5 Hz, 1 H), 7.09–7.06 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.9, 136.4, 133.9, 129.7, 128.2, 125.9, 124.8, 123.3, 121.2, 119, 111.7, 109. Anal. Calcd (%) for $C_{14}H_{10}ClNO_2S$: C, 57.63; H, 3.45; N, 4.80. Found: C, 57.61; H, 3.47; N, 4.78.

7-Methyl-2-(phenylsulfonyl)-1*H*-indole (3p)[1]
White solid (130.2 mg, 96% yield); mp 171–173 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.97 (br s, 1 H), 7.98 (d, *J* = 8.0 Hz, 2 H), 7.61–7.53 (m, 4 H), 7.20 (s, 1 H), 7.13–7.07 (m, 2 H), 2.50 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.1, 136.2, 134.2, 131.8, 130.2, 129.4, 129, 126.2, 122.9, 120.7, 119.6, 111, 19.7. Anal. Calcd (%) for $C_{15}H_{13}NO_2S$: C, 66.40; H, 4.83; N, 5.16. Found: C, 66.37; H, 4.81; N, 5.15.

3-Methyl-2-(phenylsulfonyl)-1*H*-indole (3q)[8d]
White solid (120.7 mg 89% yield); mp 168–169 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.87 (br s, 1 H), 7.99 (d, *J* = 7.6 Hz, 2 H), 7.60–7.49 (m, 4 H), 7.43–7.40 (t, *J* = 7.6 Hz, 2 H), 7.18–7.15 (t, *J* = 7.6 Hz, 1 H), 2.53 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.5,

136.2, 133.5, 129.4, 128.2, 127, 126.1, 122.2, 120.5, 119.6, 112.1, 111.4, 8.8. Anal. Calcd (%) for $C_{15}H_{13}NO_2S$: C, 66.40; H, 4.83; N, 5.16. Found: C, 66.42; H, 4.80; N, 5.13.

5-Bromo-2-[(4-chlorophenyl)sulfonyl]-1*H*-indole (3r)[8b]

Brown solid (127.8 mg, 69% yield); mp 183–186 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.85 (br s, 1 H), 8.02 (d, *J* = 7.0 Hz, 2 H), 7.81 (s, 1 H), 7.59 (d, *J* = 7.0 Hz, 2 H), 7.46 (d, *J* = 7.0 Hz, 1 H), 7.43 (d, *J* = 7.5, 1 H), 7.14 (d, *J* = 2.0 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.1, 140, 137.4, 136.3, 131, 130, 129.2, 129, 126.4, 115.8, 114.3, 108.5. Anal. Calcd (%) for $C_{14}H_9BrClNO_2S$: C, 45.37; H, 2.45; N, 3.78. Found: C, 45.39; H, 2.44; N, 3.75.

S-*p*-Tolyl-4-methylbenzenesulfonothioate (3aa)[9f]

White solid (194.9 mg 70% yield); mp 91–93 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 7.0 Hz, 2 H), 7.22–7.16 (m, 4 H), 7.14 (d, *J* = 7.0 Hz, 2 H), 2.36 (s, 3 H), 2.32 (s, 3 H).

1,2-Di-*p*-tolyldisulfane (3ab)[9f]

White solid (36.8, mg 15% yield); mp 45–48 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 8.0 Hz, 4 H), 7.12 (d, *J* = 8.0 Hz, 2 H), 2.35 (s, 6 H).