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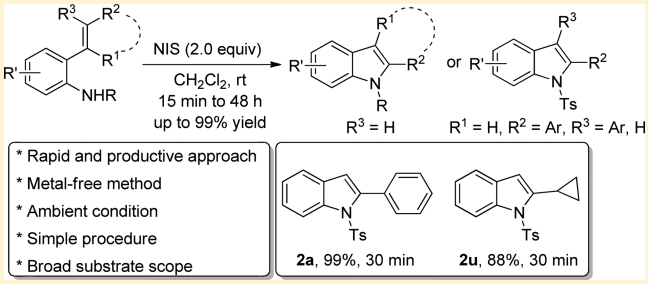
Metal-Free Synthesis of Indole via NIS-Mediated Cascade C−N Bond Formation/Aromatization

Yin-Long Li,[†] Jian Li,[†] Ai-Lun Ma,[†] Ya-Nan Huang,[†] and Jun Deng*[,†,‡]

[†]School of Pharmaceutical Science and Technology, Key Laboratory for Modern Drug Delivery & High-Efficiency, and [‡]Collaborative Innovation Center of Chemical Science and Engineering, Tianjin University, Tianjin 300072, People's Republic of China

Supporting Information

ABSTRACT: A novel rapid synthesis of indoles from *N*-Ts-2-alkenylanilines has been described; the reaction involves a NIS-mediated cascade C−N bond formation/aromatization, and a series of indoles with various functional groups have been synthesized in good to excellent yields under mild conditions without any other additives or catalysts.



INTRODUCTION

Indoles are basic structural elements in a wide range of naturally occurring biologically important compounds and are widely used in chemistry, biology, and material sciences.[1] As a consequence, the development of new and efficient methods to synthesize indoles has attracted great attention from the synthetic community.[2] A diverse array of elegant work has been established, and current research is dominated by transition-metal catalysis with palladium[3] and rhodium.[4] Although transition-metal catalysis has shown comprehensive high efficiency, the metal-free process can circumvent the toxicity issue associated with metal catalysts, which would be a good complement to transition-metal catalysis for meeting the rigorous purity requirements in biological and medicinal research.[5] Considerable progress has been made in metal-free indole synthesis; however, most of them suffer from limitations such as environmental unfriendliness, harsh conditions, and complicated procedures.[6] For example, the Fischer indole synthesis is the pioneer work in this field and has been extensively applied in organic synthesis, but the strong acidic conditions and elevated temperatures might limit the scope.[7] Therefore, the development of a practical and effective metal-free process for indole synthesis is still highly desirable. The intramolecular amination reaction of alkenes is a straightforward approach to indoles and has attracted comprehensive attention.[8] Very recently, Youn reported a 2,3-dichloro-5,6-dicyano-1,4-benzoquinone-mediated metal-free intramolecular C−H amination of *N*-Ts-2-alkenylanilines for the synthesis of indoles at 120 °C (Scheme 1, eq 1).[6a] Under milder conditions, Muñiz achieved rapid and productive synthesis of indoles via modified Koser reagent-mediated intramolecular aminations of 2-vinylanilines, but the methodology has only been used for the monosubstituted terminal alkenes (Scheme 1, eq 2).[6b]

As a common reagent, *N*-haloimides (NCS, NBS, and NIS) have been extensively applied in organic synthesis and have been reported for the synthesis of various heterocyclic compounds.[9] A precedent for NIS-mediated synthesis of indoles via cyclization of 1-(2-aminophenyl)prop-2-yn-1-ols was achieved by Chan (Scheme 1, eq 3).[10b] However, to the best of our knowledge, NIS-mediated indole synthesis from the 2-alkenylanilines without any other additives or catalysts is rarely reported.[10] Therefore, we wish to communicate here our success in achieving the practical and metal-free rapid synthesis of indole under mild conditions via NIS-mediated cascade C−N bond formation/aromatization[11] of *N*-Ts-2-alkenylanilines.

RESULTS AND DISCUSSION

Our initial screening experiments were performed by employing **1a** as the test substrate to assay the best reaction conditions (Table 1). The *N*-haloimides were first evaluated. The results were disappointing (entries 1 and 2, Table 1) when NCS and NBS were used; even the reaction time was extended to 48 h, and the starting material was still not completely consumed. We were surprised to find that NIS (2.0 equiv) was shown to be a very high efficient promoter for this transformation, and the desired indole product **2a** was obtained with 99% yield in 30 min at room temperature (entry 3, Table 1). Compared with NIS, iodine was shown to be less reactive; only 15% yield was afforded, and the reaction time was as long as 2 h (entry 4, Table 1). It must be noted here that 2.0 equiv of NIS is essential for obtaining high yield, and the attempt to reduce the amount of NIS to 1.2 equiv significantly decreased the yield to 56% (entry 6, Table 1). Next, we then turned our attention to evaluate the solvent effect on this reaction; various solvents were examined when using dichloroethane as solvent, and the corresponding indoles were obtained in excellent yields (entry 7, Table 1); however, poor yields were obtained in THF,

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Scheme 1. Metal-Free Indole Synthesis from 2-Alkenylanilines

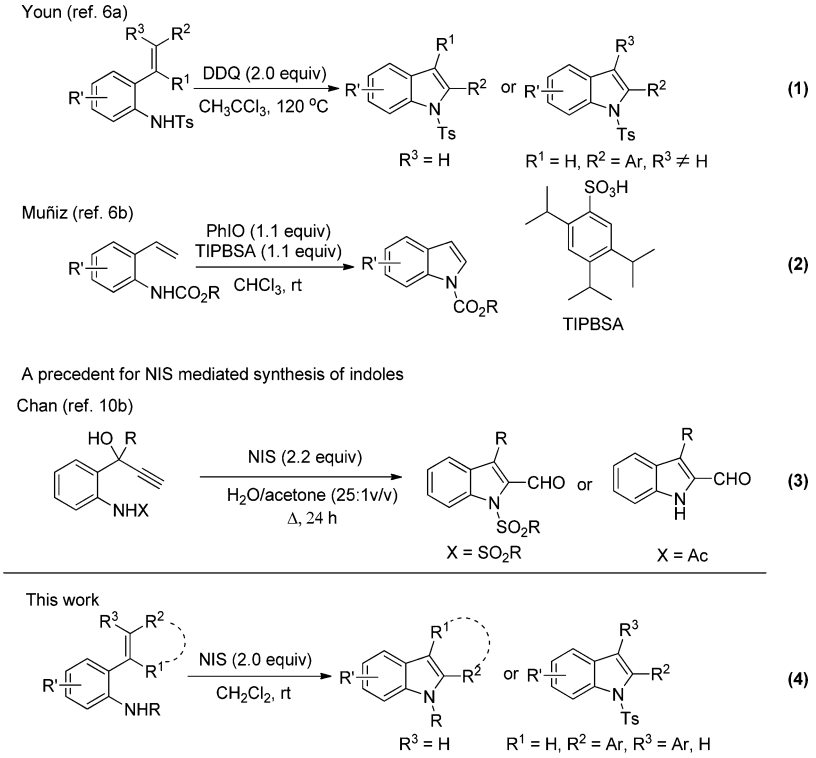
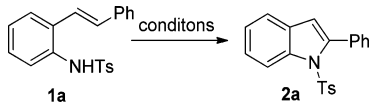


Table 1. Optimization Studies[a]



entry	reagent	solvent	time (h)	yield[b] (%)
1	NCS	CH_2Cl_2	48	23
2	NBS	CH_2Cl_2	48	57
3	NIS	CH_2Cl_2	0.5	99
4	I_2	CH_2Cl_2	2	15
5	Br_2	CH_2Cl_2	12	trace
6[c]	NIS	CH_2Cl_2	10	56
7	NIS	dichloroethane	0.5	95
8	NIS	THF	0.5	65
9	NIS	CH_3CN	0.5	41
10	NIS	DMF	0.5	ND
11	NIS	CCl_4	0.5	ND
12	NIS	1,4-dioxane	0.5	20
13	NIS	EtOAc	0.5	30
14	NIS	EtOH	0.5	trace
15	NIS	acetone	0.5	14
16	NIS	DMSO	0.5	ND
17	NIS	$MeNO_2$	0.5	86

[a]Reaction conditions: **1a** (0.1 mmol), *N*-haloimides (2.0 equiv), solvent (1.0 mL), rt under air. [b]Isolated yield. ND = Not detected. [c]1.2 equiv of NIS was used.

acetonitrile, 1,4-dioxane, and ethyl acetate (entries 8, 9, 12, and 13, Table 1). Other solvents such as DMF and CCl_4 proved to be ineffective for this transformation and resulted in either no reaction or only a trace amount of **2a**. After the discoveries of suitable *N*-haloimide and solvent, the optimal conditions for the synthesis of indole through a NIS-mediated cascade C–N bond formation/aromatization of 2-alkenylanilines were established.

To demonstrate the flexibility of this methodology, the scope of 2-alkenylanilines was studied. First, the substrates with different N-protecting groups on alkenylaniline was explored. As shown in Table 2, the substrates with *N*-Boc can provide the indole product **2b** in moderate yield, and all of the sulfonamide can afford the desired products **2c–f** in good to excellent yields, except for *p*-$NO_2C_6H_4SO_2$, where lower yield was obtained, which was probably caused by the strong electron-withdrawing characteristic of the nitro group. The substrates with N–H, *N*-acetyl, and *N*-Cbz cannot provide the target products (entries 23, 24, and 25). Subsequently, the substrates with various *ortho*-, *para*-, and *meta*-substitution on the phenyl ring at the alkene moiety were tested. The results reveal that there is no major effect on the substitution pattern or steric hindrance of the substituent on the phenyl ring of the substrates; both the electron-donating and electron-withdrawing groups at different positions furnished the corresponding products in good to excellent yields. For example, all three substrates with a methyl group on the phenyl ring provided the desired products **2h–j** in 92–96% yields, but the substrate with strong electron-withdrawing substituents on the phenyl ring showed adverse effects (i.e., NO_2) and only recovered the starting material even when the reaction was run for 48 h. It is noted that the phenyl ring bearing electron-donating groups (*p*-Me, *o*-OMe, and *p*-OMe) gave the desired products **2j**, **2l**, and **2n** in high yields, meanwhile affording the 3-substituted indole products (*p*-Me, 2-/3- = 9.1:1; *o*-OMe, 2-/3- = 1:2; and *p*-OMe, 2-/3- = 1:2.8). These results are consistent with the reported literature and suggest a mechanism involving a 1,2-phenyl migration.[12] However, this method was proven to not be efficient for substrates with mono- and 1,1-disubstituted terminal alkyl substituents, and the 1,1-disubstituted substrate can provide the

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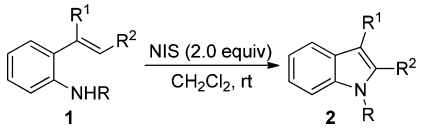
Table 2. Scope of 2-Alkenylanilines[a]



entry	R	R^1	R^2	time (h)	yield[b] (%)
1	Ts	H	Ph (**1a**)	0.5	99 (**2a**)
2	Boc	H	Ph (**1b**)	48	51 (**2b**)
3	Ms	H	Ph (**1c**)	0.5	89 (**2c**)
4	$C_6H_4SO_2$	H	Ph (**1d**)	0.5	85 (**2d**)
5	*p*-$BrC_6H_4SO_2$	H	Ph (**1e**)	0.5	80 (**2e**)
6	*p*-$ClC_6H_4SO_2$	H	Ph (**1f**)	0.5	63 (**2f**)
7	*p*-$NO_2C_6H_4SO_2$	H	Ph (**1g**)	0.5	32 (**2g**)
8	Ts	H	2-MeC_6H_4 (**1h**)	0.5	96 (**2h**)
9	Ts	H	3-MeC_6H_4 (**1i**)	0.5	94 (**2i**)
10	Ts	H	4-MeC_6H_4 (**1j**)	0.25	92 (**2j**)[c]
11	Ts	H	4-*t*Bu-C_6H_4 (**1k**)	0.5	91 (**2k**)
12	Ts	H	2-$MeOC_6H_4$ (**1l**)	0.25	91 (**2l**)[d]
13	Ts	H	3-$MeOC_6H_4$ (**1m**)	0.5	54 (**2m**)
14	Ts	H	4-$MeOC_6H_4$ (**1n**)	0.25	89 (**2n**)[e]
15	Ts	H	4-F-C_6H_4 (**1o**)	0.5	91 (**2o**)
16	Ts	H	4-Cl-C_6H_4 (**1p**)	0.5	92 (**2p**)
17	Ts	H	1-naphthyl (**1q**)	0.25	98 (**2q**)
18	Ts	H	Me (**1r**)	2	32 (**2r**)
19	Ts	H	cyclopropyl (**1s**)	0.5	88 (**2s**)
20	Ts	$(CH_2)_4$ (**1t**)		1	40 (**2t**)
21	Ts	Me	Ph (**1u**)	12	83 (**2u**)
22	Ts	Ph	H (**1v**)	8	21 (**2v**)
23	H	H	Ph (**1w**)	48	ND
24	Cbz	H	Ph (**1x**)	48	ND
25	Ac	H	Ph (**1y**)	48	ND
26[f]	Ts	H	Ph (**1a**)	0.5	94 (**2a**)

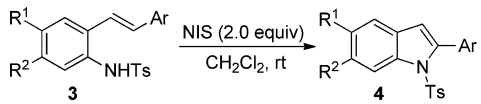
[a]Reaction conditions: **1** (0.1 mmol), NIS (2.0 equiv), CH_2Cl_2 (1.0 mL), rt under air. [b]Isolated yield. [c]Overall yield of 2- and 3-aryl-substituted *N*-Ts-indoles (2-/3- = 9.1:1). [d]Overall yield of 2- and 3-aryl-substituted *N*-Ts-indoles (2-/3- = 1:2). [e]Overall yield of 2- and 3-aryl-substituted *N*-Ts-indoles (2-/3- = 1:2.8). [f]The reaction was performed with 0.5 mmol of **1a**.

product **2v** in 21% yield. To our surprise, the substrate with a cyclopropyl substituent can afford the desired product **2s** in 88% yield. The trisubstituted substrates were also tested and proved to be suitable for this transformation; the fused indole **2t** was obtained in 40% yield and 2,3-substituted indole **2u** in 83% yield.

Next, we explored the substitution pattern of aniline. As shown in Table 3, the reaction exhibited good tolerance to various substituents on the aromatic ring. Whether it is electron-donating or electron-withdrawing, the reaction took place smoothly to provide the desired indoles in 71−92% yields. The fluoro and chloro groups could be tolerated in the reaction conditions to generate the indoles **4d−e** and **4f−g** in good to excellent yields. Moreover, the reaction is not affected by the position of the substituents on the aromatic ring of anilines. The reaction of substrates with trifluoromethyl or ester substitutent could also lead to the desired products **4h−i** in 71 and 76% yields, but with longer reaction time, which is probably due to the electron-withdrawing effect of the substituent group. When more a electron-donating group (e.g., MeO-) was applied, the reaction proceeded at fast rates and could be finished within 30 min to afford the desired product **4c** in 83% yield.

In order to understand the mechanism of this cascade, a C−N bond formation/aromatization process, the *β*,*β*-disubstituted 2-alkenylaniline substrates **5** and **7** were applied under the

Table 3. Scope of 2-Alkenylanilines[a]



entry	substrate	Ar	R^1	R^2	time (h)	yield (%)
1	**3a**	Ph	Me	H	0.5	92 (**4a**)
2	**3b**	Ph	H	Me	0.5	94 (**4b**)
3	**3c**	Ph	MeO	H	0.5	83 (**4c**)
4	**3d**	Ph	F	H	0.5	82 (**4d**)
5	**3e**	Ph	H	F	0.5	90 (**4e**)
6	**3f**	Ph	Cl	H	0.5	86 (**4f**)
7	**3g**	Ph	H	Cl	1.5	89 (**4g**)
8	**3h**	Ph	CF_3	H	12	76 (**4h**)
9	**3i**	Ph	CO_2Et	H	18	71 (**4i**)
10	**3j**	4-MeC_6H_4	Me	H	0.25	89 (**4j**)[b]
11	**3k**	4-MeC_6H_4	CF_3	H	8	95 (**4k**)[c]

[a]Reaction conditions: **3** (0.1 mmol), NIS (2.0 equiv), CH_2Cl_2 (1.0 mL), under air. [b]Overall yield of 2- and 3-aryl-substituted *N*-Ts-indoles (2-/3- = 7.8:1). [c]Overall yield of 2- and 3-aryl-substituted *N*-Ts-indoles (2-/3- = 12:1).

standard reaction conditions (Scheme 2). We hypothesized that the electron-rich aryl group should shift preferentially if the reaction process involved a phenonium ion intermediate.[13] As

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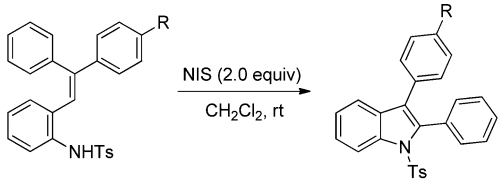
Scheme 2. Trisubstituted Alkene Derivatives Involving a 1,2-Aryl Shift



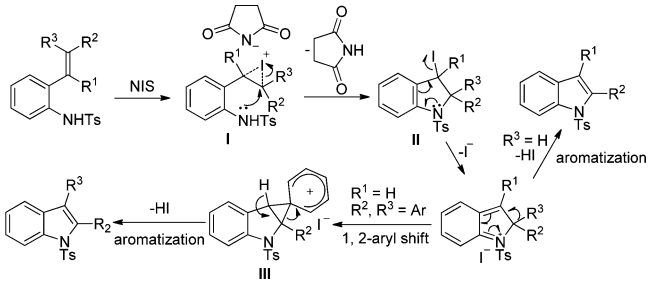
5: R = H
7: R = OMe

6: R = H, 60%, 12 h
8: R = OMe, 44%, 30 min

we anticipated, the result showed that the migration happened and *p*-MeOC$_6$H$_4$ migrated to the 3-position completely. The structure of the product was confirmed by the X-ray structure. However, under the optimized conditions, the β,β-dimethyl-substituted substrate did not afford any product.

On the basis of these findings and the literature reports,[12] a plausible mechanism for the NIS-mediated cascade C−N bond formation/aromatization of *N*-Ts-2-alkenylanilines toward indoles is illustrated in Scheme 3. Initially, NIS reacts with

Scheme 3. Proposed Mechanistic Pathway



the substrate alkene to afford the iodonium ion intermediate **I**, which is subsequently attacked by the amino group to initiate the intramolecular amination, furnishing the indoline **II** followed by the aromatization to form the indole product or undergo 1,2-aryl shift through **III** and then an aromatization to afford the product.

CONCLUSION

In conclusion, an alternative metal-free and simple operation protocol for the rapid synthesis of indoles has been described. With the NIS-mediated cascade C−N bond formation/aromatization reaction of *N*-Ts-2-alkenylanilines under room temperature, a series of indoles with various functional groups have been synthesized in good to excellent yields without any other additives or catalysts. This method could be used by the researchers in the areas of organic and medicinal chemistry. Further investigations on the *N*-haloimide-mediated reaction for the synthesis of other heterocycles are currently underway in our laboratory.

EXPERIMENTAL SECTION

General Information. All reactions were performed in flame-dried glassware. Solvents were distilled prior to use. All commercially available reagents were used as purchased without further purification. Flash column chromatography was performed over silica gel 200−300 mesh. ^{1}H and ^{13}C NMR spectra were obtained on 400 and 600 MHz and 100 and 150 MHz spectrometers, respectively, using $CDCl_3$ with TMS or residual solvent as standard unless otherwise noted. Chemical shift values are given in parts per million and are referenced to the internal standard, TMS (tetramethylsilane). The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet; dd, doublet of doublets; and br s, broad singlet. The coupling constants (J) are reported in hertz (Hz). Infrared spectra were measured on a FT/IR instrument. Melting points were determined with a micromelting point apparatus without corrections. Low-resolution mass spectra were obtained using LS/MSD. High-resolution mass spectrometry (HRMS) was obtained on a Q-TOF microspectrometer.

General Procedure for the Preparation of 2-Styrylaniline Derivatives. The requisite 2-styrylaniline derivatives were prepared following the modified method reported by Youn and co-workers.[6a] To a solution of 2-styrylaniline (0.67 mmol) in CH_2Cl_2 (5.0 mL) were added pyridine (4.0 equiv) and TsCl (1.2 equiv). The mixture was stirred at rt for 4 h. The reaction mixture was quenched by H_2O (5.0 mL), and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography to obtain the corresponding 2-styrylaniline product.

*(E)-4-Methyl-N-(2-styrylphenyl)benzenesulfonamide (**1a**):*[6a] 185 mg, 79% yield, white solid, mp 143−146 °C (lit. 138−141 °C); R_f = 0.50 (20% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.26 (s, 3H), 6.75 (br s, 1H), 6.77 (d, J = 16.2 Hz, 1H), 6.88 (d, J = 16.2 Hz, 1H), 7.12 (d, J = 7.8 Hz, 2H), 7.19−7.37 (m, 8H), 7.48 (d, J = 8.4 Hz, 1H), 7.61 (d, J = 7.8 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.4, 122.7, 126.4, 126.7, 126.9, 127.1, 127.2, 128.0, 128.3, 128.6, 129.6, 132.0, 133.2, 133.3, 136.5, 136.7, 143.9.

*(E)-tert-Butyl (2-styrylphenyl)carbamate (**1b**):*[6a] following the general procedure using $(Boc)_2O$, THF, and Et_3N (2.0 equiv), 158 mg, 80% yield, light yellow solid, mp 127−136 °C (lit. 119−121 °C); R_f = 0.59 (10% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.52 (s, 9H), 6.43 (br s, 1H), 6.97 (d, J = 16.2 Hz, 1H), 7.11 (t, J = 7.2 Hz, 1H), 7.17 (d, J = 16.2 Hz, 1H), 7.25−7.31 (m, 2H), 7.39 (t, J = 7.2 Hz, 2H), 7.49 (d, J = 7.8 Hz, 1H), 7.53 (d, J = 7.2 Hz, 2H), 7.80 (s, 1H).

*(E)-N-(2-Styrylphenyl)methanesulfonamide (**1c**):*[6a] following the general procedure using MsCl as a sulfonylation reagent, 94 mg, 81% yield, white solid, mp 110−113 °C; R_f = 0.31 (20% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.02 (s, 3H), 6.53 (br s, 1H), 7.07 (d, J = 16.2 Hz, 1H), 7.25−7.33 (m, 4H), 7.38 (t, J = 7.2 Hz, 2H), 7.50 (d, J = 7.8 Hz, 1H), 7.54 (d, J = 7.8 Hz, 2H), 7.64 (d, J = 7.8 Hz, 1H).

*(E)-N-(2-Styrylphenyl)benzenesulfonamide (**1d**):*[6a] following the general procedure using benzenesulfonyl chloride as a sulfonylation reagent, 216 mg, 86% yield, white solid, mp 138−141 °C; R_f = 0.50 (20% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.70 (br s, 1H), 6.79 (d, J = 16.2 Hz, 1H), 6.84 (d, J = 16.2 Hz, 1H), 7.22−7.39 (m, 10H), 7.46−7.48 (m, 2H), 7.73 (d, J = 7.8 Hz, 2H).

*(E)-4-Bromo-N-(2-styrylphenyl)benzenesulfonamide (**1e**):* following the general procedure using 4-bromobenzenesulfonyl chloride as a sulfonylation reagent, 177 mg, 64% yield, white solid, mp 148−150 °C; R_f = 0.45 (20% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.76 (d, J = 16.2 Hz, 1H), 6.77 (br s, 1H), 6.86 (d, J = 16.2 Hz, 1H), 7.24−7.34 (m, 8H), 7.44−7.45 (m, 2H), 7.47−7.51 (m, 1H), 7.55 (d, J = 8.4 Hz, 2H); HRMS (ESI) m/z calcd for $C_{20}H_{16}BrNO_2S$ $(M + H)^+$ 414.0163, found 414.0142.

*(E)-4-Chloro-N-(2-styrylphenyl)benzenesulfonamide (**1f**):*[6a] following the general procedure using 4-chlorobenzenesulfonyl chloride as a sulfonylation reagent, 198 mg, 80% yield, white solid, mp 129−132 °C; R_f = 0.50 (20% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.57 (br s, 1H), 6.78 (d, J = 16.2 Hz, 1H), 6.83 (d, J = 16.2 Hz, 1H), 7.25−7.36 (m, 10H), 7.49−7.50 (m, 1H), 7.63 (d, J = 8.4 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 122.4, 126.6, 126.8, 126.9, 127.5, 128.3, 128.5, 128.6, 128.7, 129.3, 132.6, 132.7, 133.5, 136.5, 137.8, 139.6.

*(E)-4-Nitro-N-(2-styrylphenyl)benzenesulfonamide (**1g**):*[6a] following the general procedure using 4-nitrobenzenesulfonyl chloride as a sulfonylation reagent, 148 mg, 58% yield, light yellow solid, 184−187 °C; R_f = 0.40 (20% EtOAc/petroleum ether); mp ^{1}H NMR (600

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MHz, $CDCl_3$) δ 6.63 (br s, 1H), 6.72 (d, J = 16.2 Hz, 1H), 6.74 (d, J = 16.2 Hz, 1H), 7.25−7.36 (m, 8H), 7.50−7.51 (m, 1H), 7.85 (d, J = 8.4 Hz, 2H), 8.11 (d, J = 8.4 Hz, 2H).

(E)-4-Methyl-N-(2-(2-methylstyryl)phenyl)benzenevsulfonamide ***(1h)***:[6a] 163 mg, 67% yield, white solid, mp 148−151 °C (lit. 146−151 °C); R_f = 0.40 (20% EtOAc/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 2.32 (s, 3H), 6.69 (br s, 1H), 6.70 (d, J = 16.0 Hz, 1H), 7.01 (d, J = 16.0 Hz, 1H), 7.13−7.29 (m, 8H), 7.36−7.38 (m, 1H), 7.47−7.49 (m, 1H), 7.61 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8, 21.5, 123.9, 125.5, 126.1, 126.6, 126.7, 127.0, 127.2, 128.0, 128.4, 129.7, 130.1, 130.4, 133.3, 133.4, 135.7, 135.8, 136.7, 143.8.

(E)-4-Methyl-N-(2-(3-methylstyryl)phenyl)benzenesulfonamide ***(1i)***:[6a] 170 mg, 70% yield, white solid, mp 116−119 °C (lit. 96−100 °C); R_f = 0.60 (30% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.29 (s, 3H), 2.37 (s, 3H), 6.61 (br s, 1H), 6.71 (d, J = 15.6 Hz, 1H), 6.78 (d, J = 18.0 Hz, 1H), 7.08−7.11 (m, 3H), 7.16 (d, J = 7.8 Hz, 2H),7.20−7.24 (m, 3H), 7.39 (d, J = 7.8 Hz, 1H), 7.45 (d, J = 9.0 Hz, 1H), 7.61 (d, J = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.4, 21.5, 122.3, 123.9, 126.5, 126.6, 127.0, 127.1, 127.2, 128.3, 128.5, 128.9, 129.6, 132.4, 133.1, 133.2, 136.5, 138.1, 143.9.

(E)-4-Methyl-N-(2-(4-methylstyryl)phenyl)benzenesulfonamide ***(1j)***:[6a] 187 mg, 77% yield, white solid, mp 159−162 °C (lit. 159−160 °C); R_f = 0.33 (10% EtOAc/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 3H), 2.35 (s, 3H), 6.62 (br s, 1H), 6.74 (s, 2H), 7.14 (t, J = 12.0 Hz, 4H), 7.19−7.25 (m, 4H), 7.37 (dd, J = 2.0, 8.0, 1H), 7.45 (dd, J = 2.4, 8.0, 1H), 7.60 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 21.4, 121.5, 126.5, 126.6, 126.9, 127.1, 128.2, 129.3, 129.6, 132.3, 133.1, 133.2, 133.9, 136.6, 138.1, 143.9.

(E)-N-(2-(4-(tert-Butyl)styryl)phenyl)-4-methylbenzene-sulfonamide ***(1k)***: 217 mg, 80% yield, white solid, mp 91−94 °C; R_f = 0.26 (10% EtOAc/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (s, 9H), 2.28 (s, 3H), 6.61 (br s, 1H), 6.75 (s, 2H), 7.14−7.25 (m, 6H), 7.33−7.39 (m, 3H), 7.46 (dd, J = 1.2, 6.4 Hz, 1H), 7.62 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 31.3, 34.6, 121.8, 125.5, 126.4, 126.5, 126.6, 126.9, 127.1, 128.2, 129.6, 132.2, 133.20, 133.26, 133.9, 136.6, 143.8, 151.4; mass spectrum (ESI) m/e (% relative intensity) 428.4 (100) $(M + Na)^+$; HRMS (ESI) m/z calcd for $C_{25}H_{27}NO_2S$ $(M + Na)^+$ 428.1660, found 428.1671.

(E)-N-(2-(2-Methoxystyryl)phenyl)-4-methylbenzenesulfonamide ***(1l)***: 152 mg, 60% yield, white solid, mp 163−165 °C; R_f = 0.43 (20% EtOAc/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 3.86 (s, 3H), 6.53 (br s, 1H), 6.80 (d, J = 13.2 Hz, 1H), 6.89 (d, J = 8.4 Hz, 1H), 6.95 (t, J = 7.6 Hz, 1H), 7.12−7.27 (m, 7H), 7.39 (dd, J = 2.4, 8.0, 1H), 7.45 (dd, J = 2.4, 6.8, 1H), 7.61 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 55.5, 110.9, 120.7, 122.9, 125.7, 126.1, 126.8, 127.2, 127.5, 128.1, 129.2, 129.6, 133.2, 133.4, 136.6, 143.9, 156.9; mass spectrum (ESI) m/e (% relative intensity) 401.8 (100) $(M + Na)^+$; HRMS (ESI) m/z calcd for $C_{22}H_{21}NO_3S$ $(M + Na)^+$ 402.1140, found 402.1141.

(E)-N-(2-(3-Methoxystyryl)phenyl)-4-methylbenzenesulfonamide ***(1m)***:[6a] 229 mg, 90% yield, white solid, mp 103−106 °C; R_f = 0.70 (30% EtOAc/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.25 (s, 3H), 3.81 (s, 3H), 6.72 (d, J = 16.0 Hz, 1H), 6.79−6.92 (m, 5H), 7.12 (d, J = 8.4 Hz, 2H), 7.19−7.24 (m, 3H), 7.38 (dd, J = 2.4, 9.2, 1H), 7.46 (dd, J = 2.4, 6.8, 1H), 7.60 (d, J = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 55.3, 111.9, 113.7, 119.4, 123.0, 126.5, 127.0, 127.1, 127.2, 128.4, 129.5, 129.6, 131.9, 133.2, 133.3, 136.5, 138.2, 143.9, 159.8.

(E)-N-(2-(4-Methoxystyryl)phenyl)-4-methylbenzenesulfonamide ***(1n)***:[6a] 229 mg, 90% yield, light yellow solid, mp 122−124 °C (lit. 128−135 °C); R_f = 0.40 (20% EtOAc/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 3H), 3.81 (s, 3H), 6.71 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.8 Hz, 3H), 7.11−7.26 (m, 6H), 7.34−7.36 (m, 1H), 7.43−7.45 (m, 1H), 7.60 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 55.3, 114.0, 120.4, 126.3, 126.5, 126.6, 126.9, 127.1, 127.9, 129.6, 131.6, 131.7, 133.0, 133.5, 133.6, 143.8, 159.6.

(E)-N-(2-(4-Fluorostyryl)phenyl)-4-methylbenzenesulfonamide ***(1o)***: 209 mg, 85% yield, white solid, mp 167−169 °C; R_f = 0.43 (20% EtOAc/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H), 6.74 (d, J = 16.4 Hz, 1H), 6.86 (d, J = 13.2 Hz, 1H), 6.87 (br s, 1H), 6.99 (t, J = 8.4 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 7.20−7.22 (m, 2H), 7.28−7.33 (m, 3H), 7.47 (dd, J = 2.4, 4.8 Hz, 1H), 7.62 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 115.6 (d, J = 21.5 Hz), 122.61, 122.63, 126.4, 126.8, 127.1, 127.2, 128.2 (d, J = 18.0 Hz), 128.4, 129.6, 130.7, 133.0 (d, J = 3.6 Hz), 133.2, 136.5, 143.9, 163.1 (d, J = 70.5 Hz); mass spectrum (ESI) m/e (% relative intensity) 389.8 (100) $(M + Na)^+$; HRMS (ESI) m/z calcd for $C_{21}H_{18}FNO_2S$ $(M + Na)^+$ 390.0940, found 390.0919.

(E)-N-(2-(4-Chlorostyryl)phenyl)-4-methylbenzenesulfonamide ***(1p)***:[6a] 95 mg, 37% yield, white solid, mp 194−197 °C (lit. 195−196 °C); R_f = 0.39 (30% EtOAc/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 6.58 (br s, 1H), 6.75 (d, J = 16.4 Hz, 1H), 6.87 (d, J = 16.4 Hz, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.22−7.25 (m, 4H), 7.28−7.31 (m, 3H), 7.49 (dd, J = 2.0, 4.4 Hz, 1H), 7.61 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 123.4, 126.5, 127.0, 127.1, 127.2, 127.8, 128.6, 128.8, 129.6, 130.6, 133.1, 133.2, 133.7, 135.2, 136.5, 143.9.

(E)-4-Methyl-N-(2-(2-(naphthalen-1-yl)vinyl)phenyl)benzene-sulfonamide ***(1q)***:[6a] 251 mg, 94% yield, light yellow solid, mp 159−161 °C (lit. 143−150 °C); R_f = 0.38 (20% EtOAc/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.17 (s, 3H), 6.74 (br s, 1H), 6.92 (d, J = 16.0 Hz, 1H), 7.08 (d, J = 7.6 Hz, 2H), 7.24−7.28 (m, 2H), 7.36−7.52 (m, 5H), 7.56−7.61 (m, 4H), 7.80 (d, J = 7.2 Hz, 1H), 7.84−7.86 (m, 1H), 8.02−8.04 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 123.4, 123.8, 125.6, 125.9, 126.2, 126.7, 127.1, 127.2, 128.5, 128.60, 128.69, 129.62, 131.2, 133.3, 133.6, 134.2, 136.5, 143.8.

4-Methyl-N-(2-(prop-1-en-1-yl)phenyl)benzenesulfonamide ***(1r)***:[14] 135 mg, 70% yield, Z/E isomer = 3:1, light yellow solid, mp 54−57 °C; R_f = 0.64 (20% EtOAc/petroleum ether). Signals corresponding to (Z)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.50 (dd, J = 7.8, 9.6 Hz, 3H), 2.35 (s, 3H), 5.85−5.96 (m, 1H), 6.64 (br s, 1H), 7.00−7.25 (m, 6H), 7.55 (d, J = 12.0 Hz, 1H), 7.63 (d, J = 12.0 Hz, 2H). Representative signals corresponding to (E)-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.74−1.76 (m, 3H), 2.35 (s, 3H), 5.85−5.96 (m, 1H), 6.13 (br s, 1H), 7.00−7.25 (m, 6H), 7.33 (d, J = 11.4 Hz, 1H), 7.60 (d, J = 12.0 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.2, 18.7, 21.5, 121.2, 124.5, 124.6, 125.3, 126.2, 127.1, 127.2, 127.7, 128.0, 129.0, 129.55, 129.58, 130.0, 131.8, 132.7, 134.2, 136.5, 143.8.

(Z)-N-(2-(2-Cyclopropylvinyl)phenyl)-4-methylbenzene-sulfonamide ***(1s)***: 187 mg, 89% yield, light yellow solid, mp 85−88 °C; R_f = 0.57 (10% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.45−0.46 (m, 2H), 0.75−0.77 (m, 2H), 1.26−1.32 (m, 1H), 2.36 (s, 3H), 5.13 (t, J = 12 Hz, 1H), 5.80 (d, J = 10.8 Hz, 1H), 6.79 (br s, 1H), 7.08 (t, J = 7.8 Hz, 1H), 7.17−7.22 (m, 4H), 7.55 (d, J = 7.8 Hz, 1H), 7.62 (d, J = 7.8 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 7.7, 11.0, 21.6, 121.4, 121.5, 124.8, 127.2, 127.8, 129.5, 129.6, 129.9, 134.1, 136.5, 140.9, 143.7; mass spectrum (ESI) m/e (% relative intensity) 336.6 (100) $(M + Na)^+$; HRMS (ESI) m/z calcd for $C_{18}H_{19}NO_2S$ $(M + Na)^+$ 336.1034, found 336.1028.

4-Methyl-N-(2′,3′,4′,5′-tetrahydro-[1,1′-biphenyl]-2-yl)benzene-sulfonamide ***(1t)***: 149 mg, 68% yield, white solid, mp 101−104 °C; R_f = 0.41 (10% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.60−1.67 (m, 6H), 2.08−2.11 (m, 2H), 2.35 (s, 3H), 5.34 (br s, 1H), 6.94−6.96 (m, 2H), 7.03 (t, J = 7.2 Hz, 1H), 7.17−7.20 (m, 3H), 7.58 (d, J = 7.8 Hz, 2H), 7.64 (d, J = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.5, 21.6, 22.8, 25.2, 30.0, 120.9, 124.5, 127.1, 127.6, 128.4, 128.6, 129.5, 130.0, 135.1, 135.8, 136.3, 143.8; HRMS (ESI) m/z calcd for $C_{19}H_{21}NO_2S$ $(M + Na)^+$ 350.1191, found 350.1175.

4-Methyl-N-(2-(1-phenylprop-1-en-2-yl)phenyl)benzene-sulfonamide ***(1u)***: 165 mg, 68% yield (stereochemistry of olefin could not be determined), white solid, mp 63−66 °C; R_f = 0.66 (20% EtOAc/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.74 (s, 3H), 2.23 (s, 3H), 5.95 (s, 1H), 6.89−7.18 (m, 10H), 7.28 (t, J = 7.2 Hz, 1H), 7.51 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.9, 21.5, 119.6, 121.5, 124.9, 127.2, 127.3, 128.0, 128.4, 128.6, 128.9, 129.7, 131.4, 133.0, 134.5, 136.4, 136.6, 137.4, 143.9; mass spectrum (ESI) m/e (% relative intensity) 386.0 (100) $(M + Na)^+$; HRMS (ESI) m/z calcd for $C_{22}H_{21}NO_2S$ $(M + Na)^+$ 386.1191, found 386.1182.

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*4-Methyl-N-(2-(1-phenylvinyl)phenyl)benzenesulfonamide (**1v**):*[6a] 201 mg, 86% yield, white solid, mp 89−91 °C (lit. 90−92 °C); R_f = 0.54 (10% EtOAc/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 3H), 4.88 (d, J = 4.0 Hz, 1H), 5.69 (d, J = 4.0 Hz, 1H), 6.53 (br s, 1H), 7.02 (d, J = 8.8 Hz, 2H), 7.05−7.12 (m, 4H), 7.20−7.34 (m, 4H), 7.44 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 117.1, 121.1, 124.7, 126.3, 127.2, 128.5, 128.81, 128.87, 129.4, 130.4, 133.0, 134.2, 136.0, 138.6, 143.7, 144.9.

*(E)-2-Styrylaniline (**1w**):*[6a] 1.8 g, 63% yield, yellow solid, mp 95−98 °C (lit. 101.5−102.5 °C); R_f = 0.10 (10% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.95 (br s, 2H), 6.72 (d, J = 7.8 Hz, 1H), 6.81 (t, J = 7.8 Hz, 1H), 6.99 (d, J = 16.2 Hz, 1H), 7.09 (t, J = 8.2 Hz, 1H), 7.17 (d, J = 16.2 Hz, 1H), 7.25 (t, J = 7.2 Hz, 1H), 7.34 (t, J = 7.8 Hz, 2H), 7.40 (d, J = 7.8 Hz, 1H), 7.50 (d, J = 7.8 Hz, 2H).

*(E)-N-(2-Styrylphenyl)acetamide (**1x**):*[6a] 121 mg, 67% yield, white solid, mp 140−142 °C (lit. 141−142 °C); R_f = 0.45 (30% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.20 (s, 3H), 6.97 (d, J = 15.6 Hz, 1H), 7.11 (d, J = 16.2 Hz, 1H), 7.19 (t, J = 6.6 Hz, 1H), 7.25−7.31 (m, 3H), 7.37 (t, J = 6.6 Hz, 1H), 7.50 (d, J = 6.6 Hz, 2H), 7.53 (t, J = 7.8 Hz, 1H), 7.78 (d, J = 7.8 Hz, 1H).

*(E)-Benzyl (2-styrylphenyl)carbamate (**1y**):*[6a] 165 mg, 75% yield, yellow solid, mp 93−95 °C; R_f = 0.25 (10% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.23 (s, 2H), 6.72 (br s, 1H), 7.01 (d, J = 16.2 Hz, 1H), 7.16 (d, J = 15.6 Hz, 1H), 7.18 (d, J = 15.0 Hz, 1H), 7.29−7.43(m, 9H), 7.50 (d, J = 7.8 Hz, 2H), 7.54 (d, J = 7.8 Hz, 1H), 7.85 (br s, 1H).

*(E)-4-Methyl-N-(4-methyl-2-styrylphenyl)benzenesulfonamide (**3a**):*[6a] 119 mg, 49% yield, white solid, mp 117−120 °C (lit. 114−120 °C); R_f = 0.30 (10% EtOAc/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 3H), 2.33 (s, 3H), 6.52 (br s, 1H), 6.76−6.77 (m, 2H), 7.05 (dd, J = 1.2, 8.0 Hz, 1H), 7.14 (d, J = 7.6 Hz, 2H), 7.21−7.34 (m, 7H), 7.60 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 21.4, 122.8, 126.6, 126.8, 127.2, 127.5, 127.9, 128.6, 129.2, 129.6, 130.5, 131.5, 133.5, 136.6, 136.8, 137.1, 143.8.

*(E)-4-Methyl-N-(5-methyl-2-styrylphenyl)benzenesulfonamide (**3b**):*[6a] 182 mg, 75% yield, white solid, mp 154−157 °C (lit. 155−157 °C); R_f = 0.45 (20% EtOAc/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.26 (s, 3H), 2.32 (s, 3H), 6.67 (br s, 1H), 6.71 (d, J = 4.8 Hz, 2H), 7.03 (d, J = 7.6 Hz, 1H), 7.14 (d, J = 8.0 Hz, 2H), 7.21 (s, 1H), 7.24−7.30 (m, 5H), 7.37 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 21.4, 122.5, 126.2, 126.5, 127.1, 127.6, 127.8, 128.0, 128.5, 129.6, 130.3, 131.1, 133.0, 136.5, 136.8, 138.6, 143.8.

*(E)-N-(4-Methoxy-2-styrylphenyl)-4-methylbenzenesulfonamide (**3c**):*[6a] 196 mg, 77% yield, white solid, mp 141−145 °C; R_f = 0.40 (20% EtOAc/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.23 (s, 3H), 3.81 (s, 3H), 6.62 (br s, 1H), 6.74 (d, J = 16.0 Hz, 1H), 6.77 (dd, J = 2.8, 8.4 Hz, 1H), 6.84 (d, J = 16.0 Hz, 1H), 7.01 (d, J = 2.8 Hz, 1H), 7.10 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.8 Hz, 1H), 7.24−7.30 (m, 5H), 7.57 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 55.5, 110.7, 113.9, 123.0, 125.9, 126.7, 127.2, 128.0, 128.5, 129.6, 130.2, 131.4, 135.9, 136.5, 136.7, 143.7, 158.8.

*(E)-N-(4-Fluoro-2-styrylphenyl)-4-methylbenzenesulfonamide (**3d**):* 170 mg, 69% yield, white solid, mp 150−153 °C; R_f = 0.57 (20% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.27 (s, 3H), 6.44 (br s, 1H), 6.74 (d, J = 16.2 Hz, 1H), 6.78 (d, J = 16.2 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H); 7.20 (dd, J = 2.4, 9.6 Hz, 1H), 7.27−7.35 (m, 6H), 7.58 (d, J = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.4, 112.4, 115.2 (d, J = 22.5 Hz), 121.8, 126.8, 127.1, 128.4, 128.6, 128.9, 129.7, 130.11, 130.17, 132.8, 136.25, 136.27, 136.4, 144.1; mass spectrum (ESI) m/e (% relative intensity) 389.8 (100) $(M + Na)^+$, HRMS (ESI) m/z calcd for $C_{21}H_{18}FNO_2S$ $(M + Na)^+$ 390.0940, found 390.0921.

*(E)-N-(5-Fluoro-2-styrylphenyl)-4-methylbenzenesulfonamide (**3e**):* 174 mg, 71% yield, light yellow solid, mp 114−117 °C; R_f = 0.50 (20% EtOAc/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 3H), 6.70 (d, J = 16.0 Hz, 1H), 6.78 (d, J = 16.4 Hz, 1H), 6.88 (td, J = 2.4, 8.4 Hz, 1H) 7.06 (br s, 1H), 7.14−7.32 (m, 8H), 7.40 (d, J = 6.0, 8.4 Hz, 1H), 7.66 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 112.4 (d, J = 24.7 Hz), 113.6 (d, J = 21.4 Hz), 121.5, 126.6, 127.1, 128.0 (d, J = 8.9 Hz), 128.2, 128.3, 128.6, 129.8, 132.4 (d, J = 10.6 Hz), 134.7, 136.1, 136.5, 144.2, 163.4 (d, J = 34.7 Hz); mass spectrum (ESI) m/e (% relative intensity) 390.9 (100) $(M + Na)^+$; HRMS (ESI) m/z calcd for $C_{21}H_{18}FNO_2S$ $(M + Na)^+$ 390.0940, found 390.0938.

*(E)-N-(4-Chloro-2-styrylphenyl)-4-methylbenzenesulfonamide (**3f**):*[6a] 203 mg, 79% yield, white solid, mp 143−145 °C; R_f = 0.39 (20% EtOAc/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 3H), 6.75 (s, 3H), 7.13−7.20 (m, 3H), 7.28−7.32 (m, 6H), 7.45 (d, J = 2.4 Hz, 1H), 7.61 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 121.3, 126.2, 126.8, 127.1, 128.2, 128.41, 128.47, 128.6, 129.8, 131.7, 132.9, 133.2, 135.0, 136.20, 136.22, 144.1.

*(E)-N-(5-Chloro-2-styrylphenyl)-4-methylbenzenesulfonamide (**3g**):*[6a] 241 mg, 94% yield, white solid, mp 143−146 °C (lit. 142−145 °C); R_f = 0.48 (20% EtOAc/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H), 6.74−6.77 (m, 2H), 6.96 (s, 1H), 7.16 (dd, J = 1.6, 6.4, Hz, 3H), 7.25−7.32 (m, 5H), 7.39 (d, J = 8.4 Hz, 1H), 7.42 (d, J = 2.0 Hz, 1H), 7.64 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 121.4, 126.1, 126.7, 127.0, 127.1, 127.5, 128.3, 128.6, 129.8, 131.3, 132.7, 133.6, 134.2, 136.1, 136.4, 144.2.

*(E)-4-Methyl-N-(2-styryl-4-(trifluoromethyl)phenyl)benzenesulfonamide (**3h**):*[6b] 218 mg, 78% yield, white solid, mp 116−118 °C; R_f = 0.38 (20% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.31 (s, 3H), 6.84 (d, J = 15.6 Hz, 1H), 6.86 (d, J = 16.2 Hz, 1H), 7.18−7.19 (m, 3H), 7.29−7.37 (m, 5H), 7.45 (d, J = 5.6 Hz, 1H), 7.54 (d, J = 5.6 Hz, 1H), 7.67 (d, J = 7.8 Hz, 2H), 7.88 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.5, 121.1, 122.9, 123.9, 124.7, 125.0, 126.9, 127.1, 128.4 (d, J = 32.3 Hz), 128.5, 128.7, 129.9, 132.2, 134.3, 130.0, 136.2, 136.5, 144.5.

*(E)-Ethyl 4-(4-methylphenylsulfonamido)-3-styrylbenzoate (**3i**):* 118 mg, 42% yield, white solid, mp 134−137 °C; R_f = 0.45 (20% EtOAc/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38 (t, J = 8.0 Hz, 3H), 2.31 (s, 3H), 4.38 (q, J = 8.0 Hz, 2H), 6.84 (d, J = 16.0 Hz, 1H), 6.90 (d, J = 16.0 Hz, 1H), 7.00 (br s, 1H), 7.19 (d, J = 8.0 Hz, 2H), 7.29−7.39 (m, 5H), 7.51 (d, J = 8.4 Hz, 1H), 7.67 (d, J = 8.4 Hz, 2H), 7.88 (dd, J = 2.0, 8.4 Hz, 1H), 8.11 (d, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 21.5, 61.2, 121.3, 123.5, 126.8, 127.1, 127.9, 128.5, 128.7, 129.4, 129.8, 131.2, 134.0, 136.2, 136.3, 137.4, 144.3, 166.0; mass spectrum (ESI) m/e (% relative intensity) 444.5 (100) $(M + Na)^+$; HRMS (ESI) m/z calcd for $C_{24}H_{23}NO_4S$ $(M + Na)^+$ 444.1246, found 444.1238.

*(E)-4-Methyl-N-(4-methyl-2-(4-methylstyryl)phenyl)benzenesulfonamide (**3j**):* 177 mg, 70% yield, white solid, mp 140−142 °C; R_f = 0.23 (20% EtOAc/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.25 (s, 3H), 2.31 (s, 3H), 2.34 (s, 3H), 6.68 (br s, 1H), 6.72 (d, J = 14.4 Hz, 1H), 6.78 (d, J = 16.4 Hz, 1H), 7.01 (dd, J = 1.2, 8.0 Hz, 1H), 7.11 (dd, J = 2.8, 8.0 Hz, 4H), 7.17−7.23 (m, 3H), 7.27 (s, 1H), 7.60 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 21.3, 21.4, 121.8, 126.6, 126.7, 127.2, 127.4, 129.0, 129.3, 129.6, 130.5, 131.5, 133.6, 134.1, 136.6, 137.0, 137.8, 143.7; mass spectrum (ESI) m/e (% relative intensity) 399.7 (100) $(M + Na)^+$; HRMS (ESI) m/z calcd for $C_{23}H_{23}NO_2S$ $(M + Na)^+$ 400.1347, found 400.1351.

*(E)-4-Methyl-N-(2-(4-methylstyryl)-4-(trifluoromethyl)phenyl)-benzenesulfonamide (**3k**):* 205 mg, 71% yield, white solid, mp 188−191 °C; R_f = 0.18 (10% EtOAc/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3H), 2.37 (s, 3H), 6.77 (d, J = 16.0 Hz, 1H), 6.83 (d, J = 16.0 Hz, 1H), 6.91 (br s, 1H), 7.16 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.25−7.27 (m, 2H), 7.46 (dd, J = 1.6, 8.4 Hz, 1H), 7.55 (d, J = 8.4 Hz, 1H), 7.66 (dd, J = 2.0, 4.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 21.5, 119.9, 123.9, 124.4, 124.8, 125.2, 126.8, 127.1, 128.3, 129.4, 129.9, 132.2, 133.2, 134.5, 136.2 (d, J = 12.0 Hz), 138.8, 144.4; mass spectrum (ESI) m/e (% relative intensity) 454.5 (100) $(M + Na)^+$; HRMS (ESI) m/z calcd for $C_{23}H_{20}F_3NO_2S$ $(M + Na)^+$ 454.1065, found 454.1054.

*N-(2-(2,2-Diphenylvinyl)phenyl)-4-methylbenzenesulfonamide (**5**):*[6a] 228 mg, 80% yield, light yellow solid; R_f = 0.39 (20% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.42 (s, 3H), 6.33 (s, 1H), 6.63 (br s, 1H), 6.79 (d, J = 7.2 Hz, 1H), 6.86−6.91 (m, 3H), 7.07−7.24 (m, 8H), 7.29−7.33 (m, 3H), 7.42 (d, J = 8.4 Hz, 1H), 7.57

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(d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 122.6, 124.0, 125.4, 127.2, 127.9, 128.0, 128.1, 128.2, 128.4, 129.6, 130.3, 130.5, 131.3, 134.1, 136.9, 138.9, 142.3, 143.7, 146.2.

*N-(2-(2-(4-Methoxyphenyl)-2-phenylvinyl)phenyl)-4-methylbenzenesulfonamide (**7**):*[6a] 95 mg, 31% yield, light yellow solid, mp 75−78 °C (lit. 60−66 °C); R_f = 0.50 (20% EtOAc/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 3.77 (s, 3H), 6.23 (s, 1H), 6.43 (s, 1H), 6.72 (d, J = 8.8 Hz, 2H), 6.83−6.95 (m, 4H), 7.09 (dd, J = 1.6, 7.6 Hz, 2H), 7.12−7.25 (m, 5H), 7.32 (d, J = 6.8 Hz, 2H), 7.43 (d, J = 7.6 Hz, 1H), 7.54 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 55.1, 113.9, 120.0, 123.8, 125.4, 127.1, 127.9, 128.1, 128.2, 129.6, 130.5, 130.9, 131.3, 131.6, 133.7, 136.9, 142.6, 143.7, 145.8, 159.3.

General Procedure for the NIS-Mediated Indole Synthsis. To a solution of substrate (0.1 mmol) in CH_2Cl_2 (1.0 mL) was added NIS (45 mg, 0.2 mmol) under air. The resulting mixture was stirred at rt for the reported time, then the mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the corresponding product.

*N-Ts-2-Phenylindole (**2a**):*[6a] reaction time = 30 min; yield = 35 mg, 99%, white solid, mp 145−149 °C (lit. 142−144 °C); R_f = 0.59 (10% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.27 (s, 3H), 6.53 (s, 1H), 7.03 (d, J = 7.8 Hz, 2H), 7.27 (d, J = 8.4 Hz, 3H), 7.35 (t, J = 7.2 Hz, 1H), 7.41−7.44 (m, 4H), 7.49−7.50 (m, 2H), 8.31 (d, J = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.5, 113.6, 116.7, 120.7, 124.3, 124.8, 126.8, 127.5, 128.7, 129.2, 130.3, 130.5, 132.4, 134.6, 138.2, 142.1, 144.5; IR (KBr) cm^{-1} 581, 657, 760, 1168, 1186, 1368, 1451, 1595, 3065; mass spectrum (ESI) m/e (% relative intensity) 370.7 (100) (M + Na)$^+$.

*N-Boc-2-Phenylindole (**2b**):*[6a] reaction time = 48 h; yield = 15 mg, 51%, colorless oil, R_f = 0.79 (10% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.30 (s, 9H), 6.55 (s, 1H), 7.24−7.42 (m, 7H), 7.55 (d, J = 7.8 Hz, 1H), 8.22 (d, J = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 27.5, 83.3, 109.9, 115.2, 120.4, 122.9, 124.3, 127.5, 127.8 128.7, 129.2, 135.0, 137.4, 140.5, 150.2; IR (KBr) cm^{-1} 701, 751, 1134, 1155, 1338, 1361, 1454, 1729, 2353, 2930, 2979.

*N-Ms-2-Phenylindole (**2c**):*[6a] reaction time = 30 min; yield = 24 mg, 89%, white solid, mp 120−124 °C; R_f = 0.38 (10% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.71 (s, 3H), 6.70 (s, 1H), 7.33 (t, J = 7.8 Hz, 1H), 7.38 (t, J = 7.2 Hz, 1H), 7.41−7.42 (m, 3H), 7.54−7.55 (m, 2H), 7.59 (d, J = 7.8 Hz, 1H), 8.12 (d, J = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 39.4, 113.6, 115.8, 121.0, 124.5, 125.1, 127.7, 128.9, 130.1, 130.3, 132.0, 138.0, 142.0; IR (KBr) cm^{-1} 516, 543, 763, 776, 966, 1150, 1178, 1330, 1370, 1450, 2320, 3011.

*N-(Benzenesulfonyl)-2-phenylindole (**2d**):*[6a] reaction time = 30 min; yield = 28 mg, 85%, white solid, mp 99−103 °C (lit. 98−101 °C); R_f = 0.42 (10% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.53 (s, 1H), 7.23 (t, J = 7.8 Hz, 2H), 7.27 (d, J = 7.2 Hz, 1H), 7.34−7.49 (m, 10H), 8.32 (d, J = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 113.7, 116.6, 120.7, 124.4, 124.9, 126.7, 127.5, 128.6, 128.7, 130.3, 130.5, 132.3, 133.5, 137.4, 138.2, 142.1; IR (KBr) cm^{-1} 566, 591, 697, 759, 975, 1049, 1167, 1173, 1187, 1366, 1449, 2378, 3049.

*N-(4-Bromophenylsulfonyl)-2-phenylindole (**2e**):* reaction time = 30 min; yield = 33 mg, 80%, light yellow solid, mp 186−188 °C; R_f = 0.50 (10% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.48 (s, 1H), 7.12 (d, J = 9.0 Hz, 2H), 7.20 (t, J = 7.8 Hz, 1H), 7.27−7.29 (m, 3H), 7.33−7.37 (m, 4H), 7.41 (dd, J = 2.4, 6.6 Hz, 2H), 8.21 (d, J = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 114.2, 116.7, 120.9, 124.7, 125.1, 127.6, 128.2, 128.8, 128.9, 130.2, 130.7, 131.9, 132.1, 136.2, 138.2, 142.0; IR (KBr) cm^{-1} 569, 593, 744, 764, 1052, 1167, 1184, 1372, 1390, 1573, 2378, 2899, 3449; HRMS (ESI) m/z calcd for $C_{20}H_{14}BrNO_2S$ (M + H)$^+$ 412.0008, found 411.9990.

*N-(4-Chlorophenylsulfonyl)-2-phenylindole (**2f**):*[6a] reaction time = 30 min; yield = 23 mg, 63%, white solid, mp 157−159 °C (lit. 152−158 °C); R_f = 0.59 (10% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.56 (s, 1H), 7.21 (d, J = 9.0 Hz, 2H), 7.27 (d, J = 8.4 Hz, 3H), 7.36 (t, J = 7.8 Hz, 1H), 7.42−7.49 (m, 6H), 8.29 (d, J = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 113.1, 115.6, 119.8, 123.6, 124.0, 126.5, 127.1, 127.8, 127.9, 129.2, 129.6, 131.0, 134.6, 137.1, 139.1, 140.9; IR (KBr) cm^{-1} 571, 640, 764, 819, 1051, 1090, 1167, 1184, 1372, 1475, 1584, 2311, 2963, 3062.

*N-Ns-2-Phenylindole (**2g**):*[6a] reaction time = 30 min; yield = 12 mg, 32%, light yellow solid, mp 148−151 °C (lit. 140−147 °C); R_f = 0.37 (10% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.60 (s, 1H), 7.30 (t, J = 7.2 Hz, 1H), 7.39 (t, J = 8.4 Hz, 1H), 7.44−7.50 (m, 7H), 7.53 (d, J = 9.0 Hz, 1H), 8.08 (d, J = 9.0 Hz, 2H), 8.29 (d, J = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 114.8, 116.7, 121.1, 123.8, 125.2, 125.4, 127.8, 128.1, 129.1, 130.1, 130.7, 131.7, 138.0, 141.9, 142.2, 150.4; IR (KBr) cm^{-1} 552, 568, 741, 759, 770, 853, 1048, 1173, 1185, 1347, 1381, 1450, 1535, 1608, 2379, 3104.

*N-Ts-2-o-Tolylindole (**2h**):*[6a] reaction time = 30 min; yield = 35 mg, 96%, white solid, mp 98−100 °C (lit. 82−89 °C); R_f = 0.54 (10% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.21 (s, 3H), 2.30 (s, 3H), 6.45 (s, 1H), 7.08−7.10 (m, 3H), 7.21 (t, J = 7.2 Hz, 1H), 7.27 (t, J = 7.8 Hz, 2H), 7.35−7.37 (m, 4H), 7.49 (d, J = 7.2 Hz, 1H), 8.33 (d, J = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 20.5, 21.6, 112.3, 115.7, 120.7, 123.8, 124.6, 124.7, 126.9, 129.1, 129.4, 129.6, 130.1, 130.9, 132.1, 135.6, 137.3, 139.3, 140.3, 144.7; IR (KBr) cm^{-1} 567, 663, 747, 761, 1090, 1177, 1188, 1367, 1450, 1598, 2345, 2921, 3067; mass spectrum (ESI) m/e (% relative intensity) 384.6 (100) (M + Na)$^+$.

*N-Ts-2-m-Tolylindole (**2i**):* reaction time = 30 min; yield = 34 mg, 94%, white solid, mp 130−135 °C; R_f = 0.43 (10% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.27 (s, 3H), 2.41 (s, 3H), 6.52 (s, 1H), 7.03 (d, J = 7.8 Hz, 2H), 7.24−7.31 (m, 7H), 7.33 (t, J = 7.2 Hz, 1H), 7.43 (d, J = 7.2 Hz, 1H), 8.30 (d, J = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.4, 21.6, 113.4, 116.6, 120.7, 124.3, 124.7, 126.8, 127.4, 129.1, 129.4, 130.5, 131.1, 132.3, 134.7, 137.0, 138.2, 142.3, 144.5; IR (KBr) cm^{-1} 541, 570, 582, 656, 760, 1060, 1167, 1183, 1366, 1449, 1595, 1916, 2922, 2955; mass spectrum (ESI) m/e (% relative intensity) 384.3 (100) (M + Na)$^+$; HRMS (ESI) m/z calcd for $C_{22}H_{19}NO_2S$ (M + H)$^+$ 362.1215, found 362.1222.

*N-Ts-2-p-Tolylindole (**2j**) and N-Ts-3-p-Tolylindole (**2j′**):* reaction time = 15 min; yield = 33 mg, 92% (inseparable mixture; **2j**/**2j′** = 9.1:1), white solid, mp 99−104 °C; R_f = 0.46 (10% EtOAc/petroleum ether). Signals corresponding to **2j**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.23 (s, 3H), 2.41 (s, 3H), 6.48 (s, 1H), 7.00 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 7.8 Hz, 3H), 7.27 (d, J = 8.4 Hz, 2H), 7.31 (t, J = 7.8 Hz, 1H), 7.39 (d, J = 7.8 Hz, 3H), 8.30 (d, J = 8.4 Hz, 1H). Signals corresponding to **2j′**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.28 (s, 3H), 2.38 (s, 3H), 7.17 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 7.8 Hz, 3H), 7.66 (s, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.78 (d, J = 8.4 Hz, 2H), 8.05 (d, J = 9.0 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.3, 21.51, 21.55, 113.3, 113.9, 120.5, 120.6, 122.7, 123.5, 124.0, 124.3, 124.6, 124.8, 126.8, 126.9, 127.8, 128.3, 129.2, 129.6, 129.9, 130.2, 130.7, 134.6, 135.5, 137.4, 138.2, 138.8, 142.3, 144.5; IR (KBr) cm^{-1} 574, 661, 757, 813, 1091, 1168, 1368, 1450, 1596, 1910, 2920; mass spectrum (ESI) m/e (% relative intensity) 384.1 (100) (M + Na)$^+$; HRMS (ESI) m/z calcd for $C_{22}H_{19}NO_2S$ (M + H)$^+$ 362.1215, found 362.1217.

*N-Ts-2-p-tert-Butylindole (**2k**):* reaction time = 30 min; yield = 37 mg, 91%, white solid, mp 139−143 °C; R_f = 0.71 (10% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.38 (s, 9H), 2.26 (s, 3H), 6.50 (s, 1H), 7.01 (d, J = 8.4 Hz, 2H), 7.23−7.27 (m, 3H), 7.33 (t, J = 7.8 Hz, 1H), 7.40−7.42 (m, 5H), 8.30 (d, J = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.5, 31.4, 34.7, 113.3, 116.7, 120.6, 124.2, 124.4, 124.6, 126.8, 129.1, 129.4, 130.0, 130.6, 134.6, 138.2, 142.3, 144.4, 151.7; IR (KBr) cm^{-1} 545, 572, 670, 754, 809, 1090, 1121, 1169, 1177, 1367, 1449, 1596, 1917, 2868, 2965; mass spectrum (ESI) m/e (% relative intensity) 404.8 (100) (M + H)$^+$; HRMS (ESI) m/z calcd for $C_{25}H_{25}NO_2S$ (M + H)$^+$ 404.1685, found 404.1674.

*N-Ts-2-(2-Methoxyphenyl)indole (**2l**):* reaction time = 15 min; yield = 11.3 mg, 30% (**2l**/**2l′** = 1:2), white solid, mp 77−80 °C; R_f = 0.50 (10% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.29 (s, 3H), 3.77 (s, 3H), 6.53 (s, 1H), 6.96 (d, J = 8.4 Hz, 1H), 6.99 (t, J = 7.2 Hz, 1H), 7.08 (d, J = 8.4 Hz, 2H), 7.20−7.25 (m, 2H), 7.31 (t, J = 7.8 Hz, 1H), 7.39 (d, J = 7.8 Hz, 2H), 7.43 (t, J = 7.2 Hz, 1H), 7.47 (d, J = 7.8 Hz, 1H), 8.22 (d, J = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.5, 55.4, 110.5, 112.4, 115.6, 119.6, 120.7, 121.8,

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123.5, 124.4, 126.8, 129.2, 130.2, 130.6, 131.8, 135.7, 137.3, 138.0, 144.2, 158.5; IR (KBr) cm^{-1} 544, 572, 661, 751, 1090, 1176, 1188, 1256, 1372, 1447, 1490, 1584, 1597, 2311, 2835, 2932; mass spectrum (ESI) *m/e* (% relative intensity) 378.6 (100) $(M + H)^+$; HRMS (ESI) *m/z* calcd for $C_{22}H_{19}NO_3S$ $(M + Na)^+$ 400.0984, found 400.0975.

*N-Ts-3-(2-Methoxyphenyl)indole (**2l′**):* yield = 22.7 mg, 61%, white solid, mp 72−75 °C; R_f = 0.50 (10% EtOAc/petroleum ether); ^1H NMR (600 MHz, $CDCl_3$) δ 2.31 (s, 3H), 3.82 (s, 3H), 7.01−7.04 (m, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 9.6 Hz, 1H), 7.30−7.35 (m, 2H), 7.49 (dd, *J* = 1.8, 7.2 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.80 (t, *J* = 4.2 Hz, 3H), 8.03 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.5, 55.5, 111.2, 113.6, 119.4, 120.6, 121.1, 121.7, 123.2, 124.4, 125.3, 126.9, 128.8, 129.8, 130.2, 130.6, 134.9, 135.3, 144.8, 156.8; IR (KBr) cm^{-1} 575, 667, 750, 1012, 1135, 1176, 1249, 1361, 1447, 1492, 1594, 1919, 2836, 2938; mass spectrum (ESI) *m/e* (% relative intensity) 400.6 (100) $(M + Na)^+$; HRMS (ESI) *m/z* calcd for $C_{22}H_{19}NO_3S$ $(M + H)^+$ 378.1165, found 378.1147.

*N-Ts-2-(3-Methoxyphenyl)indole (**2m**):*[6a] reaction time = 30 min; yield = 20 mg, 54%, white solid, mp 108−110 °C (lit. 98−104 °C); R_f = 0.46 (10% EtOAc/petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 3H), 3.84 (s, 3H), 6.54 (s, 1H), 6.99 (dd, *J* = 2.0, 8.4 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 3H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.23−7.36 (m, 5H), 7.44 (d, *J* = 7.6 Hz, 1H), 8.31 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 55.3, 113.6, 114.5, 115.9, 116.7, 120.7, 122.8, 124.3, 124.8, 126.8, 128.5, 129.2, 130.5, 133.6, 134.6, 138.3, 141.9, 144.6, 158.7; IR (KBr) cm^{-1} 665, 756, 1038, 1164, 1174, 1224, 1376, 1451, 1591, 2836, 2939; mass spectrum (ESI) *m/e* (% relative intensity) 378.8 (100) $(M + H)^+$.

*N-Ts-2-(4-Methoxyphenyl)indole (**2n**):*[6a] reaction time = 15 min; yield = 8.6 mg, 23% (**2n**/**2n′** = 1:2.8), white solid, mp 135−138 °C (lit. 126−128 °C); R_f = 0.42 (10% EtOAc/petroleum ether); ^1H NMR (600 MHz, $CDCl_3$) δ 2.28 (s, 3H), 3.88 (s, 3H), 6.47 (s, 1H), 6.94 (d, *J* = 12.0 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 7.25−7.27(m, 3H), 7.34 (t, *J* = 8.4 Hz, 1H), 7.42 (d, *J* = 9.0 Hz, 3H), 8.30 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.5, 55.3, 112.8, 112.9, 116.6, 120.4, 124.2, 124.5, 124.7, 126.7, 129.1, 130.6, 131.6, 134.7, 138.1, 140.2, 144.4, 160.0; IR (KBr) cm^{-1} 545, 573, 670, 839, 1066, 1172, 1250, 1366, 1448, 1504, 1613, 2962, 3065; mass spectrum (ESI) *m/e* (% relative intensity) 378.2 (100) $(M + H)^+$.

*N-Ts-3-(4-Methoxyphenyl)indole (**2n′**):* yield = 24.4 mg, 66%, white solid, mp 113−115 °C; R_f = 0.42 (10% EtOAc/petroleum ether); ^1H NMR (600 MHz, $CDCl_3$) δ 2.32 (s, 3H), 3.85 (s, 3H), 6.98 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.27 (t, *J* = 7.8 Hz, 1H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.62 (s, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 8.05 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.5, 55.3, 113.8, 114.3, 120.4, 122.3, 123.4, 123.7, 124.8, 125.4, 126.8, 129.0, 129.5, 129.9, 135.2, 135.5, 144.9, 159.1; IR (KBr) cm^{-1} 570, 665, 711, 748, 837, 1005, 1021, 1089, 1131, 1175, 1250, 1371, 1446, 1507, 1564, 1613, 2353, 2836, 2930, 3444; mass spectrum (ESI) *m/e* (% relative intensity) 400.6 (100) $(M + Na)^+$; HRMS (ESI) *m/z* calcd for $C_{22}H_{19}NO_3S$ $(M + H)^+$ 378.1158, found 378.1133.

*N-Ts-2-(4-Fluorophenyl)indole (**2o**):*[15] reaction time = 30 min; yield = 33 mg, 91%, white solid, mp 134−137 °C; R_f = 0.62 (10% EtOAc/petroleum ether); ^1H NMR (600 MHz, $CDCl_3$) δ 2.27 (s, 3H), 6.51 (s, 1H), 7.04 (d, *J* = 7.8 Hz, 2H), 7.10 (t, *J* = 8.4 Hz, 2H), 7.24−7.27 (m, 3H), 7.35 (td, *J* = 1.2, 8,4 Hz, 1H), 7.42−7.46 (m, 3H), 8.31 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.5, 113.6, 114.5 (d, *J* = 21.6 Hz), 116.6, 120.7, 124.4, 124.9, 126.7, 128.4 (d, *J* = 3.2 Hz), 129.2, 130.4, 132.1 (d, *J* = 8.3 Hz), 134.6, 138.2, 140.9, 144.7, 163.9 (d, *J* = 240 Hz); IR (KBr) cm^{-1} 572, 662, 761, 827, 844, 1170, 1187, 1367, 1501, 1596, 1905, 2321, 2921, 3067; mass spectrum (ESI) *m/e* (% relative intensity) 388.2 (100) $(M + Na)^+$.

*N-Ts-2-(4-Chlorophenyl)indole (**2p**):*[6a] reaction time = 30 min; yield = 35 mg, 92%, light yellow solid, mp 138−141 °C (lit. 133−135 °C); R_f = 0.61 (10% EtOAc/petroleum ether); ^1H NMR (600 MHz, $CDCl_3$) δ 2.24 (s, 3H), 6.51 (s, 1H), 7.01 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 9.0 Hz, 3H), 7.32−7.37 (m, 3H), 7.41 (d, *J* = 8.4 Hz, 3H), 8.28 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 20.4, 113.0, 115.6, 119.7, 123.4, 124.0, 125.6, 126.7, 128.2, 129.3, 129.8, 130.4, 133.3, 133.7, 137.2, 139.7, 143.6; IR (KBr) cm^{-1} 563, 569, 659, 754, 807, 822, 1047, 1089, 1168, 1367, 1449, 1487, 1595, 2353, 2377, 2963; mass spectrum (ESI) *m/e* (% relative intensity) 382.6 (100) $(M + H)^+$.

*N-Ts-2-(1-Naphthyl)indole (**2q**):*[6a] reaction time = 15 min; yield = 39 mg, 98%, white solid, mp 139−143 °C (lit. 138−142 °C); R_f = 0.45 (10% EtOAc/petroleum ether); ^1H NMR (600 MHz, $CDCl_3$) δ 2.25 (s, 3H), 6.65 (s, 1H), 6.96 (d, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.40−7.46 (m, 3H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.64 (d, *J* = 9.0 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 8.40 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.5, 113.7, 115.8, 120.8, 123.9, 124.4, 124.8, 125.8, 126.1, 126.2, 126.9, 128.0, 129.2, 129.3, 129.5, 129.9, 130.1, 133.1, 133.4, 135.3, 137.6, 138.8, 144.6; IR (KBr) cm^{-1} 569, 581, 802, 1175, 1372, 1449, 1597, 2353, 3049, 3443; mass spectrum (ESI) *m/e* (% relative intensity) 420.4 (100) $(M + Na)^+$.

*N-Ts-2-Methylindole (**2r**):*[16] reaction time = 2 h; yield = 9 mg, 32%, light yellow oil; R_f = 0.45 (10% EtOAc/petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3H), 2.59 (s, 3H), 6.33 (s, 1H), 7.17−7.27 (m, 4H), 7.40 (d, *J* = 4.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 8.16 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 15.7, 21.5, 109.5, 114.5, 119.9, 123.3, 123.7, 126.3, 129.6, 129.8, 136.3, 137.0, 137.3, 144.6; IR (KBr) cm^{-1} 544, 584, 691, 747, 811, 1053, 1151, 1188, 1240, 1368, 1443, 1453, 1597, 2928, 2964; mass spectrum (ESI) *m/e* (% relative intensity) 308.6 (100) $(M + Na)^+$.

*N-Ts-2-Cyclopropylindole (**2s**):*[17] reaction time = 30 min; yield = 27 mg, 88%, light yellow oil; R_f = 0.43 (5% EtOAc/petroleum ether); ^1H NMR (600 MHz, $CDCl_3$) δ 0.50 (d, *J* = 6.0 Hz, 2H), 0.88 (d, *J* = 7.8 Hz, 2H), 2.25 (s, 3H), 2.33−2.38 (m, 1H), 6.09 (s, 1H), 7.09−7.12 (m, 3H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 8.13 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 7.34, 8.39, 20.5, 104.9, 113.4, 119.1, 122.3, 122.8, 125.5, 128.2, 128.6, 135.5, 136.3, 143.0, 143.5; IR (KBr) cm^{-1} 543, 571, 658, 689, 747, 810, 1023, 1078, 1146, 1173, 1368, 1452, 1915, 2309, 3011, 3068; mass spectrum (ESI) *m/e* (% relative intensity) 334.7 (100) $(M + Na)^+$.

*N-Ts-1,2,3,4-Tetrahydrocarbazole (**2t**):*[18] reaction time = 60 min; yield = 13 mg, 40%, light yellow solid, mp 119−123 °C (lit. 116−118 °C); R_f = 0.56 (10% EtOAc/petroleum ether); ^1H NMR (600 MHz, $CDCl_3$) δ 1.75−1.79 (m, 2H), 1.84−1.88 (m, 2H), 2.32 (s, 3H), 2.56−2.58 (m, 2H), 2.98−3.01 (m, 2H), 7.18 (t, *J* = 8.4 Hz, 2H), 7.22 (dd, *J* = 0.6, 7.2 Hz, 1H), 7.24−7.25 (m, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 8.15 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.1, 21.5, 22.0, 23.2, 24.6, 114.3, 117.9, 118.5, 123.1, 123.8, 126.3, 129.7, 130.3, 135.3, 136.2, 136.3, 144.4; IR (KBr) cm^{-1} 541, 575, 585, 665, 1088, 1132, 1165, 1179, 1365, 1453, 1597, 2925, 2953; mass spectrum (ESI) *m/e* (% relative intensity) 348.8 (100) $(M + Na)^+$.

*N-Ts-3-Methyl-2-phenylindole (**2u**):*[18] reaction time = 12 h; yield = 30 mg, 83%, light yellow solid, mp 145−148 °C (lit. 152−157 °C); R_f = 0.52 (10% EtOAc/petroleum ether); ^1H NMR (400 MHz, $CDCl_3$) δ 2.03 (s, 3H), 2.28 (s, 3H), 7.02 (d, *J* = 8.0 Hz, 2H), 7.27−7.31 (m, 3H), 7.33−7.37 (m, 3H), 7.40−7.44 (m, 4H), 8.33 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 9.5, 21.5, 116.2, 119.0, 123.9, 124.9, 126.8, 127.3, 127.4, 128.3, 129.2, 131.3, 131.5, 131.8, 135.1, 136.7, 137.2, 142.1; IR (KBr) cm^{-1} 571, 665, 704, 750, 954, 1120, 1174, 1189, 1371, 1453, 1597, 2924, 3055; mass spectrum (ESI) *m/e* (% relative intensity) 384.8 (100) $(M + Na)^+$.

*N-Ts-3-Phenylindole (**2v**):*[6a] reaction time = 8 h; yield = 7 mg, 21%, light yellow solid; R_f = 0.46 (10% EtOAc/petroleum ether); ^1H NMR (600 MHz, $CDCl_3$) δ 2.33 (s, 3H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 9.6 Hz, 2H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.60 (d, *J* = 7.2 Hz, 2H), 7.69 (s, 1H), 7.78 (d, *J* = 7.2 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 2H), 8.06 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 20.3, 112.5, 119.1, 121.6, 122.2, 122.6, 123.5, 125.5, 126.2, 126.5, 127.5, 127.9, 128.6, 131.7, 133.8, 134.1, 143.7; IR (KBr) cm^{-1} 579, 670, 747, 815, 1012, 1088, 1135, 1177, 1362, 1447, 1595, 1725, 2311, 2926, 3415; mass spectrum (ESI) *m/e* (% relative intensity) 370.9 (100) $(M + Na)^+$.

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*N-Ts-5-Methyl-2-phenylindole (**4a**):*[6a] reaction time = 30 min; yield = 33 mg, 92%, white solid, mp 111−113 °C (lit. 114−115 °C); R_f = 0.50 (10% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.27 (s, 3H), 2.40 (s, 1H), 6.46 (s, 1H), 7.03 (d, J = 7.8 Hz, 2H), 7.16 (d, J = 9.0 Hz, 1H), 7.21 (s, 1H), 7.25 (d, J = 8.4 Hz, 2H), 7.40−7.42 (m, 3H), 7.48−7.50 (m, 2H), 8.17 (d, J = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.2, 21.5, 113.6, 116.4, 120.7, 126.2, 126.8, 127.4, 128.5, 129.1, 130.2, 130.8, 132.5, 133.9, 134.5, 136.5, 142.2, 144.4; IR (KBr) cm^{-1} 545, 587, 695, 761, 805, 1049, 1172, 1374, 1462, 1600, 2379, 2919, 3431; mass spectrum (ESI) m/e (% relative intensity) 384.7 (100) (M + Na)$^+$.

*N-Ts-6-Methyl-2-phenylindole (**4b**):*[6a] reaction time = 30 min; yield = 34 mg, 94%, white solid, mp 178−180 °C (lit. 145−152 °C); R_f = 0.69 (10% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.27 (s, 3H), 2.51 (s, 3H), 6.47 (s, 1H), 7.03 (d, J = 7.8 Hz, 2H), 7.08 (d, J = 7.8 Hz, 1H), 7.25 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 7.8 Hz, 1H), 7.39−7.40 (m, 3H), 7.46−7.47 (m, 2H), 8.12 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.5, 22.1, 113.6, 116.8, 120.2, 125.7, 126.7, 127.4, 128.3, 128.5, 129.1, 130.2, 132.6, 134.7, 134.9, 138.7, 141.4, 144.4; IR (KBr) cm^{-1} 576, 672, 696, 763, 838, 1054, 1163, 1368, 1444, 1597, 2916, 3069; mass spectrum (ESI) m/e (% relative intensity) 384.9(100) (M + Na)$^+$.

*N-Ts-5-Methoxy-2-phenylindole (**4c**):*[6a] reaction time = 30 min; yield = 31 mg, 83%, white solid, mp 123−125 °C; R_f = 0.48 (10% EtOAc/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 3H), 3.81(s, 3H), 6.46 (s, 1H), 6.87 (d, J = 2.4 Hz, 1H), 6.95 (dd, J = 2.4, 8.8 Hz, 1H), 7.02 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 7.40−7.41 (m, 1H), 7.42 (d, J = 6.0 Hz, 2H), 7.50 (dd, J = 2.4, 4.0 Hz, 2H), 8.19 (d, J = 8.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.5, 55.5, 103.1, 113.4, 113.9, 117.7, 126.8, 127.5, 128.6, 129.1, 130.2, 131.7, 132.4, 132.8, 134.3, 143.1, 144.4, 157.1; IR (KBr) cm^{-1} 547, 593, 760, 858, 1028, 1148, 1173, 1187, 1223, 1366, 1434, 1468, 1610, 2839, 2995; mass spectrum (ESI) m/e (% relative intensity) 378.8 (100) (M + H)$^+$.

*N-Ts-5-Fluoro-2-phenylindole (**4d**):*[15] reaction time = 30 min; yield = 30 mg, 82%, light yellow solid, mp 112−115 °C (lit. 110−112 °C); R_f = 0.57 (10% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.29 (s, 3H), 6.49 (s, 1H), 7.04 (d, J = 7.8 Hz, 2H), 7.08 (d, J = 9.0 Hz, 2H), 7.24 (d, J = 7.8 Hz, 2H), 7.42−7.44 (m, 3H), 7.24 (d, J = 7.2 Hz, 2H), 8.31 (dd, J = 4.2, 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.5, 106.3 (d, J = 24.0 Hz), 112.6 (d, J = 25.5 Hz), 113.3 (d, J = 3.0 Hz), 119.1 (d, J = 9.0 Hz), 126.8, 127.6, 128.9, 129.2, 130.3, 131.6, 132.0, 134.3, 134.5, 143.9, 144.7, 160.9 (d, J = 90.0 Hz); IR (KBr) cm^{-1} 544, 589, 657, 763, 807, 1055, 1130, 1174, 1379, 1460, 1598, 1724, 2378, 2926, 3053; mass spectrum (ESI) m/e (% relative intensity) 366.2 (100) (M + H)$^+$.

*N-Ts-6-Fluoro-2-phenylindole (**4e**):* reaction time = 30 min; yield = 33 mg, 90%, white solid, mp 103−105 °C; R_f = 0.61 (10% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.21 (s, 3H), 6.41 (s, 1H), 6.94 (td, J = 2.4, 8.4 Hz, 1H), 6.98 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 7.29 (dd, J = 4.5, 8.4 Hz, 1H), 7.33 (t, J = 8.4 Hz, 3H), 7.38 (t, J = 7.8 Hz, 2H), 7.97 (dd, J = 1.8, 10.2 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.5, 104.1 (d, J = 12.0 Hz), 112.6 (d, J = 24.0 Hz), 121.3 (d, J = 9.0 Hz), 126.7, 126.8, 127.5, 128.7, 129.3, 130.3, 132.1, 134.5, 138.4 (d, J = 12.0 Hz), 142.4 (d, J = 4.5 Hz), 144.8, 160.1, 161.6; IR (KBr) cm^{-1} 543, 580, 763, 836, 1048, 1178, 1379, 1477, 1592, 2321, 2353, 3057; mass spectrum (ESI) m/e (% relative intensity) 366.5 (100) (M + H)$^+$; HRMS (ESI) m/z calcd for $C_{21}H_{16}FNO_2S$ (M + Na)$^+$ 388.0777, found 388.0752.

*N-Ts-5-Chloro-2-phenylindole (**4f**):*[6a] reaction time = 30 min; yield = 33 mg, 86%, white solid, mp 142−145 °C (lit. 136−137 °C); R_f = 0.61 (10% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.28 (s, 3H), 6.46 (s, 1H), 7.03 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 7.8 Hz, 2H), 7.29 (d, J = 9.0 Hz, 1H), 7.40−7.44 (m, 4H), 7.47 (d, J = 7.2 Hz, 2H), 8.23 (d, J = 9.0 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.5, 112.6, 117.7, 120.3, 124.9, 126.7, 127.5, 128.9, 129.3, 130.0, 130.3, 131.7, 131.8, 134.4, 134.6, 143.6, 144.9; IR (KBr) cm^{-1} 543, 686, 763, 809, 1051, 1165, 1178, 1188, 1377, 1446, 2321, 2377, 2922, 3055, 3102; mass spectrum (ESI) m/e (% relative intensity) 382.7 (100) (M + H)$^+$.

*N-Ts-6-Chloro-2-phenylindole (**4g**):*[6a] reaction time = 90 min; yield = 34 mg, 89%, white solid, mp 145−148 °C (lit. 140−144 °C); R_f = 0.57 (10% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.29 (s, 3H), 6.48 (s, 1H), 7.06 (d, J = 8.4 Hz, 2H), 7.24−7,26 (m, 3H), 7.35 (d, J = 8.4 Hz, 1H), 7.40−7.45 (m, 5H), 8.34 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.5, 112.8, 121.3, 124.9, 126.8, 127.5, 127.5, 128.90, 128.94, 129.4, 130.4, 130.6, 131.8, 134.5, 138.6, 142.6, 144.9; IR (KBr) cm^{-1} 573, 658, 762, 838, 1053, 1166, 1177, 1190, 1380, 1456, 1599, 2919, 3061; mass spectrum (ESI) m/e (% relative intensity) 382.4 (100) (M + H)$^+$.

*N-Ts-2-Phenyl-5-(trifluoromethyl)indole (**4h**):*[6a] reaction time = 12 h; yield = 32 mg, 76%, white solid, mp 123−125 °C (lit. 120−124 °C); R_f = 0.67 (20% EtOAc/petroleum ether); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.30 (s, 3H), 6.58 (s, 1H), 7.07 (d, J = 7.8 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 7.41−7.47 (m, 5H), 7.60 (d, J = 8.4 Hz, 1H), 7.74 (s, 1H), 8.42 (d, J = 9.0 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.5, 112.6, 116.7, 118.1 (q, J = 3.0 Hz), 121.3 (q, J = 4.5 Hz), 125.4 (q, J = 270.0 Hz), 126.6 (q, J = 31.5 Hz), 126.8, 127.5, 129.1, 129.5, 130.0, 130.5, 131.6, 134.6, 139.6, 143.6, 145.1; IR (KBr) cm^{-1} 592, 654, 761, 1051, 1060, 1115, 1166, 1177, 1190, 1335, 1379, 1448, 2377, 3050; mass spectrum (ESI) m/e (% relative intensity) 438.7 (100) (M + Na)$^+$.

*N-Ts-2-Phenyl-5-ethoxycarbonylindole (**4i**):* reaction time = 18 h; yield = 30 mg, 71%, white solid, mp 163−165 °C; R_f = 0.64 (20% EtOAc/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (t, J = 6.4 Hz, 3H), 2.20 (s, 3H), 4.32 (q, J = 6.4 Hz, 2H), 6.51 (s, 1H), 6.97 (t, J = 8.0 Hz, 2H), 7.16−7.19 (m, 2H), 7.34−7.41 (m, 5H), 7.97 (dd, J = 1.6, 8.8 Hz, 1H), 8.09 (d, J = 1.2 Hz, 1H), 8.28 (d, J = 8.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 14.4, 21.5, 61.0, 113.3, 116.1, 122.7, 125.8, 126.6, 126.7, 127.6, 128.9, 129.3, 130.1, 130.4, 131.8, 134.6, 140.7, 143.2, 144.9, 166.7; IR (KBr) cm^{-1} 587, 659, 764, 813, 1089, 1177, 1189, 1251, 1307, 1445, 1714, 2377, 2979; mass spectrum (ESI) m/e (% relative intensity) 442.9 (100) (M + Na)$^+$; HRMS (ESI) m/z calcd for $C_{24}H_{21}NO_4S$ (M + Na)$^+$ 442.1083, found 442.1062.

*N-Ts-5-Methyl-2-p-tolylindole (**4j**) and N-Ts-5-Methyl-3-p-tolylindole (**4j′**):* reaction time = 15 min; yield = 33 mg, 89% (inseparable mixture; **4j**/**4j′** = 7.8:1), white solid, mp 143−145 °C; R_f = 0.50 (10% EtOAc/petroleum ether). Signals corresponding to **4j**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.26 (s, 3H), 2.39 (s, 3H), 2.42 (s, 3H), 6.42 (s, 1H), 7.01 (d, J = 7.8 Hz, 2H), 7.13 (d, J = 8.4 Hz, 1H), 7.18 (s, 1H), 7.21−7.27 (m, 4H), 7.39 (d, J = 7.8 Hz, 2H), 8.16 (d, J = 8.4 Hz, 1H). Signals corresponding to **4j′**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.30 (s, 3H), 2.40 (s, 3H), 7.47 (d, J = 7.8 Hz, 3H), 7.52 (s, 1H), 7.60 (s, 1H), 7.77 (d, J = 8.4 Hz,, 2H), 7.92 (d, J = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.3, 21.4, 21.5, 113.3, 116.4, 120.5, 126.0, 126.82, 126.85, 127.8, 128.2, 129.1, 129.6, 129.7, 129.9, 130.1, 130.9, 133.9, 134.5, 136.4, 138.5, 142.4, 144.3; IR (KBr) cm^{-1}545, 573, 664, 814, 1059, 1174, 1366, 1461, 1597, 1714, 2311, 2920; mass spectrum (ESI) m/e (% relative intensity) 376.9 (100) (M + H)$^+$; HRMS (ESI) m/z calcd for $C_{23}H_{21}NO_2S$ (M + Na)$^+$ 398.1191, found 398.1157.

*N-Ts-5-Trifluoromethyl-2-p-tolylindole (**4k**) and N-Ts-5-Trifluoromethyl-3-p-tolylindole (**4k′**):* reaction time = 8 h; yield = 41 mg, 95% (inseparable mixture; **4k**/**4k′** = 12:1), white solid; R_f = 0.65 (10% EtOAc/petroleum ether). Signals corresponding to **4k**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.30 (s, 3H), 2.44 (s, 3H), 6.55 (s, 1H), 7.06 (d, J = 7.8 Hz, 2H), 7.23−7.27 (m, 4H), 7.36 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 9.0 Hz, 1H), 7.72 (s, 1H), 8.41 (d, J = 9.0 Hz, 1H). Signals corresponding to **4k′**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.35 (s, 3H), 2.42 (s, 3H), 7.45 (d, J = 7.8 Hz, 2H), 7.74 (s, 1H), 7.81 (d, J = 8.4 Hz, 2H), 8.01 (s, 1H), 8.14 (d, J = 9.0 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.4, 21.5 112.5, 116.9, 118.0 (q, J = 3.75 Hz), 121.2 (q, J = 3.3 Hz), 123.6, 125.4, 126.3, 126.5, 126.8, 126.9, 127.8, 128.3, 128.7, 129.4, 129.8, 130.1, 130.3, 134.6, 139.1, 139.5, 143.8, 145.0; IR (KBr) cm^{-1} 549, 667, 813, 1063, 1123, 1165, 1179, 1337, 1373, 1448, 1507, 1595, 2376, 2920; mass spectrum (ESI) m/e (% relative intensity) 452.0 (100) (M + Na)$^+$; HRMS (ESI) m/z calcd for $C_{23}H_{18}F_3NO_2S$ (M + H)$^+$ 430.1089, found 430.1040.

*N-Ts-2,3-Diphenylindole (**6**):*[6a] reaction time = 12 h; yield = 25 mg, 60%, white solid, mp 167−170 °C (lit. 173−174 °C); R_f = 0.29 (10% EtOAc/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (s,

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3H), 7.09 (t, J = 5.2 Hz, 4H), 7.18−7.30 (m, 9H), 7.34 (d, J = 6.4 Hz, 2H), 7.41 (t, J = 7.2 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H), 8.41 (d, J = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.5, 116.2, 119.9, 124.1, 124.7, 125.1, 126.9, 127.2, 128.1, 128.4, 129.3, 129.8, 130.4, 130.9, 132.1, 132.6, 135.3, 136.8, 137.2, 144.6; IR (KBr) cm^{-1} 576, 666, 701, 751, 1086, 1178, 1382, 1448, 1508, 2377, 3056; mass spectrum (ESI) m/e (% relative intensity) 424.7 (100) $(M + H)^+$.

*N-Ts-3-(4-Methoxyphenyl)-2-phenylindole (**8**):*[6a] reaction time = 30 min; yield = 20 mg, 44%, white solid; R_f = 0.43 (10% EtOAc/petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 3.75 (s, 3H), 6.77 (d, J = 6.8 Hz, 2H), 7.01 (d, J = 8.8 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 7.23−7.34 (m, 8H), 7.40 (td, J = 1.2, 8.4 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 8.40 (d, J = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 21.5, 55.2, 113.7, 116.2, 120.0, 124.1, 124.4, 124.8, 125.1, 126.9, 127.3, 128.4, 129.2, 130.6, 130.9, 131.1, 132.1, 135.3, 136.4, 137.2, 144.5, 158.5; IR (KBr) cm^{-1} 572, 665, 801, 1024, 1093, 1175, 1262, 1375, 1511, 2311, 2926, 2963; mass spectrum (ESI) m/e (% relative intensity) 476.7 (100) $(M + Na)^+$.

■ ASSOCIATED CONTENT

Supporting Information

Copies of NMR and IR spectra for all substrates and products and X-ray structural file of compound **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jdeng@tju.edu.cn.

Notes

The authors declare no competing financial interest.

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