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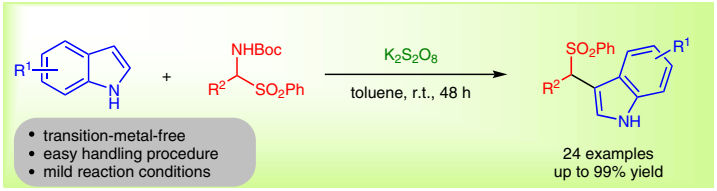
$K_2S_2O_8$-Activated Friedel–Crafts Type Alkylation of Indoles with α-Amido Sulfones

Xiaoyan Wu
Lu Xue
Shilong Luo
Shiqi Jia
Jun Ao
Wenling Qin*

Innovative Drug Research Centre, School of Pharmaceutical Sciences, Chongqing University, No.55 Daxuecheng, South Rd., Shapingba, Chongqing 401331, P. R. of China
wenling.qin@cqu.edu.cn



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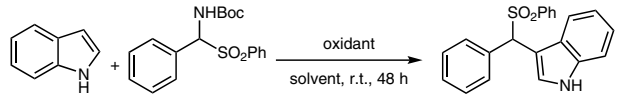
Abstract A $K_2S_2O_8$-activated regioselective alkylation of α-amido sulfones at the C-3 position of indoles is reported. The protocol developed herein provides an alternative new strategy to the previous approach by using Lewis acid, clay, and resin as catalyst for this Friedel–Crafts type alkylation of indoles with α-amido sulfones. The formed product bears a versatile transformable sulfone group and an amino group. The reaction condition is tolerant to a wide range of substrates, including a series of indoles with electron-withdrawing and electron-donating groups at different positions. Moreover, a variety of α-substituted phenylamido sulfones and some α-aliphatic amido sulfones also give the desired products in modest yield. Furthermore, a preliminary mechanism study was performed and the plausible reaction mechanism is discussed.

Key words $K_2S_2O_8$, indole alkylation, α-amido sulfone, Friedel–Crafts reaction

Substitution of indoles is an evergreen attractive topic for organic chemists due to the versatile biological and pharmaceutical interests of indole derivatives.[1] Electron enrichment of the indole ring makes it a good counterpart of various nucleophiles, and the studies focused on this field are abundant and fruitful.[2] Moreover, the alkylation at C-3 position of indole ring has been extensively studied due to the pharmaceutical applications of the corresponding adducts.[3] Various reagents have been utilized for the alkylation at C-3 position of indole ring. Recently, *N*-acyliminium ions derived from α-amido sulfones have been used as the objects of several nucleophilic addition protocols. The formation of *N*-acyliminium ions ordinarily occurs in an acidic ambient and our interest was directed towards their applications on indole ring addition reactions. According to literature reports, α-amido sulfones have been utilized in either symmetric or asymmetric alkylation of indoles to produce 3-amido- or 3-sulfonyl-substituted indoles, which bear a broad scope for further transformation.[4] Up to the present, some efficient and practical procedures have been developed for the C-3 alkylation of indoles. Among these procedures, Lewis acids, such as $InBr_3$,[5] $B(C_6F_5)_3$,[6] $Yb(OTf)_3$,[7] and $FeCl_3{\cdot}6H_2O$[8] catalyzed Friedel–Crafts reactions of α-amido sulfones with indoles for the synthesis of 3-substituted indoles were well investigated. Meanwhile, clay, represented by Montmorillonite K-10, had been demonstrated to be an efficient catalyst for this type of reaction.[9] Moreover, Kadam and co-workers reported that ion-exchange resin Amberlyst-15 could also catalyze this Friedel–Crafts type reaction.[10]

Apart from the catalyst scavenge for the efficiency of the addition reaction of α-amido sulfones to indole ring, the regioselectivity caused by different additives was investigated by Blay.[11] The results indicated that the basic additives led to the formation of N-substituted adducts, whereas the acidic one led to the C-3 alkylated products. This interesting result inspired us to envisage that other catalysts (or additives) might also be used as efficient additives for this reaction. Hence, we turned our attention to gather the approaches for the activation of the C-3 position of indoles and started to search for activation approaches. Besides the Lewis acids and other interesting reagents, catalysts for oxidative activation of the C-3 position of indoles was also disclosed by several groups.[12] Among them, $K_2S_2O_8$ had been demonstrated as an efficient reagent for activation of the C-3 position of the indole ring, which usually contains a radical involved mechanism. Nevertheless, to the best of our knowledge, no investigations on $K_2S_2O_8$-activated alkylation of indoles with α-amido sulfones have been reported.

Table 1 Screening of the Reaction Conditions[a]



1a **2a** **3aa**

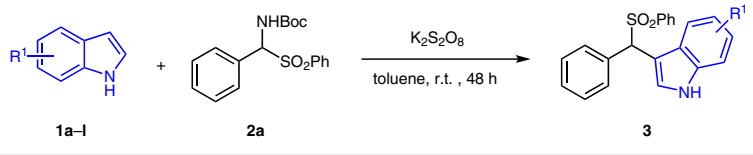
Entries	Solvent	Oxidant	Yield (%)[b]
1	toluene	$K_2S_2O_8$	84
2	toluene	Oxone	69
3	toluene	*m*-CPBA	41
4	toluene	H_2O_2	51
5	toluene	MnO_2	27
6	toluene	I_2	26
7	CH_2Cl_2	$K_2S_2O_8$	79
8	MeCN	$K_2S_2O_8$	51
9	THF	$K_2S_2O_8$	61
10	DMF	$K_2S_2O_8$	61
11	H_2O	$K_2S_2O_8$	4

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), oxidant (0.4 mmol) in solvent (1.2 mL) at r.t. for 48 h, unless otherwise specified.
[b] Isolated yield.

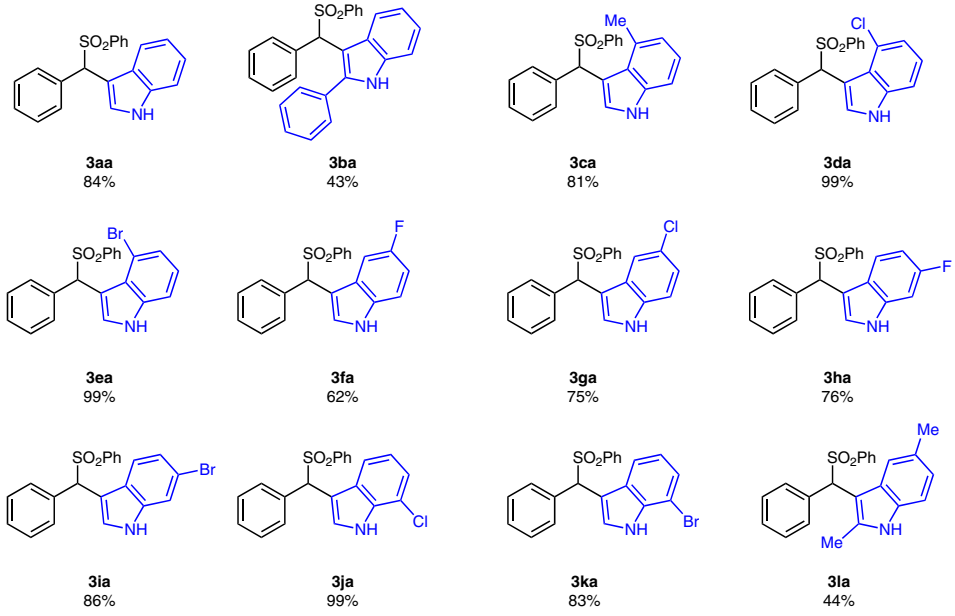
We initiated our exploration by investigating oxidants for indole alkylation reaction with α-amido sulfone. $K_2S_2O_8$ was demonstrated to be the best oxidative activator for this reaction and gave only C-3 alkylated products (Table 1, entry 1). Oxone gave a modest yield for the same reaction (entry 2). Nevertheless, other oxidants displayed poor performance for the reaction and none of them led to the formation of N-substituted adducts. Encouraged by this result, the influence of solvents was investigated for this indole C-3 alkylation reaction with α-amido sulfones by using $K_2S_2O_8$ as the activator.

As shown in Table 1, toluene as solvent gave the best yield at room temperature (Table 1, entry 1). Dichloromethane as reaction solvent gave a slightly lower yield than toluene (entry 7). Acetonitrile, THF, and DMF as the solvents resulted in a modest yield (entries 8–10). However, water as the solvent gave only a trace amount of the desired product (entry 11).

With the optimal reaction condition in our hand, the substrate scope of this $K_2S_2O_8$-activated indole C-3 alkylation reaction with α-amido sulfones was investigated. A series of substituted indoles were evaluated first, indoles bearing electron-withdrawing and electron-donating groups gave the desired C-3 alkylation products bearing sulfone substitutions in good yields (Scheme 1). No obvious



1a–l **2a** **3**

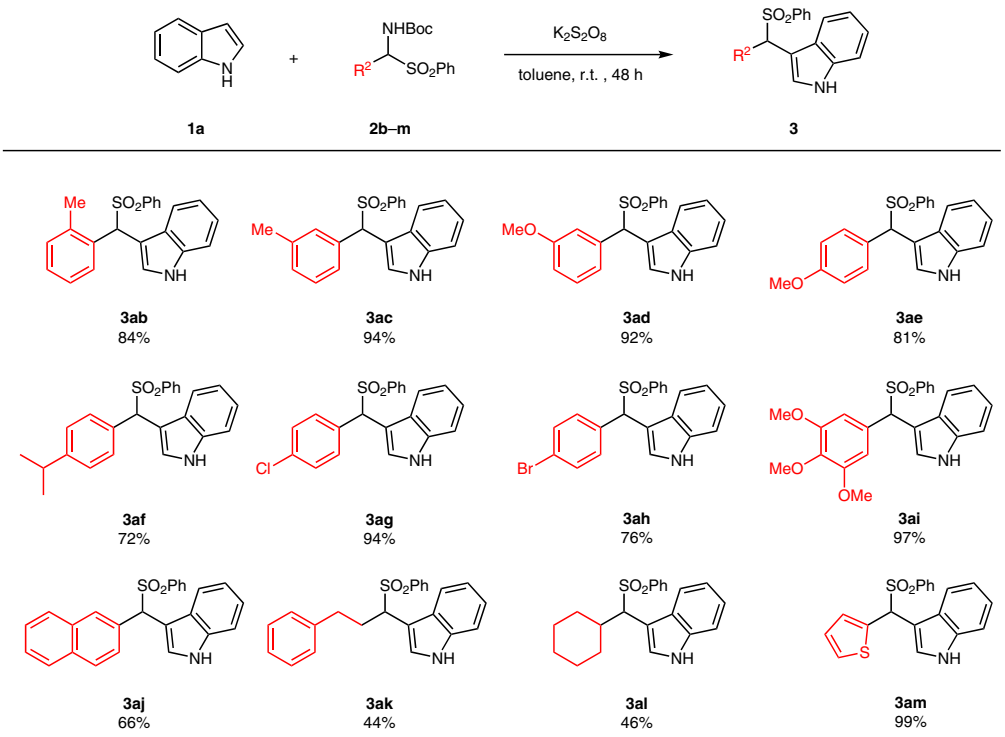


3aa 84% **3ba** 43% **3ca** 81% **3da** 99%

3ea 99% **3fa** 62% **3ga** 75% **3ha** 76%

3ia 86% **3ja** 99% **3ka** 83% **3la** 44%

Scheme 1 Scope of indoles. *Reagents and conditions*: indoles **1a–l** (0.2 mmol), α-amido sulfone **2a** (0.2 mmol), $K_2S_2O_8$ (0.4 mmol) in solvent (1.2 mL) at r.t. for 48 h, unless otherwise specified.



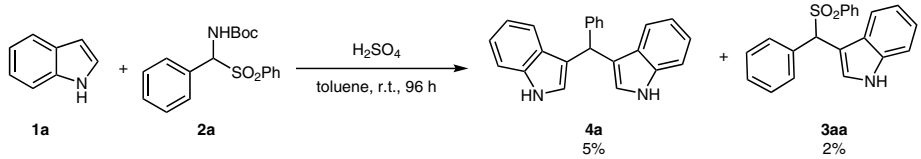
Scheme 2 Scope of α-amido sulfones. *Reagents and conditions*: indoles **1a** (0.2 mmol), α-amido sulfone **2b–m** (0.2 mmol), $K_2S_2O_8$ (0.4 mmol) in solvent (1.2 mL) at r.t. for 48 h, unless otherwise specified.

pattern was found in the relationships between the nature of substitution on indoles and the reaction yields. The substitution on different positions of indole ring influenced the reaction yield. This regio-effect was manifested by products **3ba** and **3la**, in which a substitution at C-2 position caused a sterically hindered circumstance and led to a relatively lower yield.

Furthermore, the scope of α-amido sulfones was investigated. First, different substitutions on the α-substituted phenylamido sulfones were well tolerant to our reaction conditions, including electron-withdrawing and -donating groups. Moreover, the substitution position did not influence the reaction performance. α-Aliphatic-substituted amido sulfones **3ak**, **3al** gave the desired C-3 adducts in a lower yield because the electron-donating nature of aliphatic groups decreased the transformation ability of α-amido sulfones into the corresponding acyliminium forms (Scheme 2). The reaction with *N*-carbobenzyloxy (*N*-Cbz)-protected α-amido sulfone afforded the desired alkylation product **3aa** in 51% yield, while with the corresponding benzamide and *p*-toluenesulfonamide, no Friedel–Crafts alkylation product was observed.

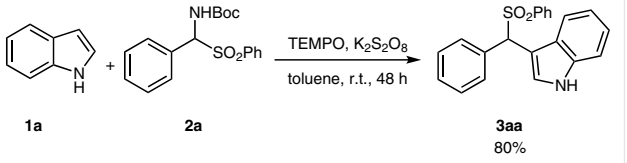
After the substrate scope had been investigated, some control experiments were performed to get an insight into the reaction mechanism. It is known that $K_2S_2O_8$ has the potential to hydrolysis and give acidic products,[13a] meanwhile presence of this acid is sufficient for the alkylation of indoles with α-amido sulfones. So first a control experiment was performed in which sulfuric acid was used as additive for the reaction as shown in Scheme 3. The C-3 alkylated product **3aa** and side product **4a** were obtained in a very low yield even after 96 hours. It indicated that the role of $K_2S_2O_8$ in this indole alkylation reaction was not merely as a source of acid, but also serves as an additive to accelerate the reaction.

Inspired by the control experiments and the work of $K_2S_2O_8$-mediated aerobic oxysulfonylation of olefins by Chawla et al.[12b] a mechanism involving a radical intermedi-



Scheme 3 Control experiment. *Reagents and conditions*: **1a** (0.2 mmol), **2a** (0.2 mmol), H_2SO_4 (0.4 mmol) in toluene (1.2 mL) at r.t. for 96 h.

ate is proposed. To prove this deduction, a radical trapping experiment was performed. As shown in Scheme 4, under the optimized reaction conditions and using TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) as a radical scavenger, the indole C-3 alkylation product **3aa** was detected, indicating that radical was not involved in the reaction.



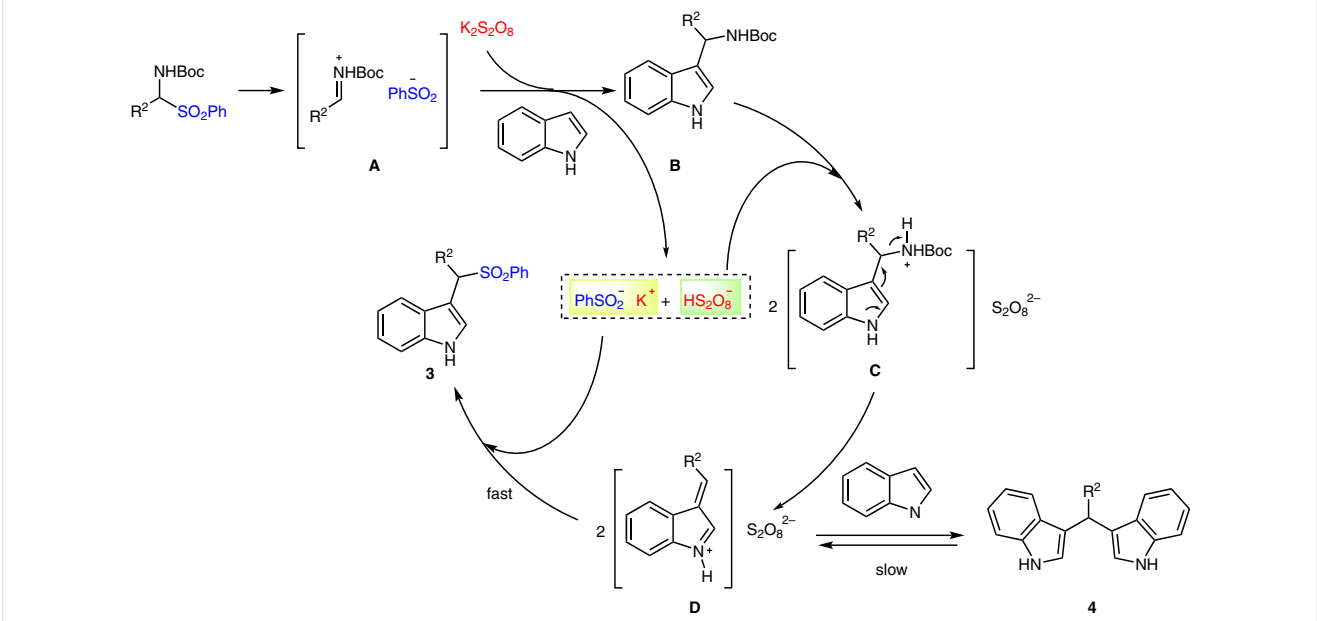
Scheme 4 Radical trapping experiment of the $K_2S_2O_8$-activated alkylation of α-amido sulfones with indoles. *Reagents and conditions*: **1a** (0.2 mmol), **2a** (0.2 mmol), TEMPO (0.05 mmol), $K_2S_2O_8$ (0.4 mmol) in toluene (1.2 mL) at r.t. for 48 h.

Based on the above experimental results and literature reports,[13] a plausible reaction mechanism for the $K_2S_2O_8$-activated alkylation of indoles by α-amido sulfones is depicted in Scheme 5. First, the acyliminium benzenesulfinate **A** was formed under the reaction conditions, and then after the deprotonation and addition to indole ring gives the indole carbamate **B**, potassium benzenesulfinate, and $HS_2O_8^-$ in the presence of $K_2S_2O_8$.

Intermediate **B** is then converted into **D** through **C** in the presence of $HS_2O_8^-$. Along with the addition of previously generated one molecule of benzenesulfinic acid potassium salt into **D**, the final product **3** is formed. Notably, intermediate **D**, the 3-alkeneindole, may undergo an alkylation with another equivalent of indole to give the side product **4**, which can be isolated in some cases from the reaction system. The presence of $K_2S_2O_8$ resulted in the formation of potassium benzenesulfinate and accelerates its reaction with intermediate **D**. Furthermore, we have performed the reaction by using intermediate **B** as the starting material, to react with α-amido sulfone and potassium benzenesulfinate in the presence of $K_2S_2O_8$. The target product was successfully formed while the yields (36% and 20%, respectively) decreased compared to the original procedure (84%).

In conclusion, we have developed a $K_2S_2O_8$-activated C-3 alkylation of indoles by α-amido sulfones. This method provides an alternative new strategy to the previous approach by using Lewis acid, clay, and resin as catalyst. In particular, this protocol can be performed at ambient temperature and allows gentle reaction conditions, meanwhile with excellent regioselectivity at C-3 of indole ring. Particularly, α-aliphatic amido sulfones are suitable substrates for this reaction. The product bears a versatile transformable sulfone group and amino group. The reaction conditions showed the high tolerance to a wide range of indoles and α-amido sulfones. A radical trapping experiment revealed that this $K_2S_2O_8$-activated alkylation at C-3 of indole by α-amido sulfones did not involve a radical process. Further investigations to elucidate the detailed mechanism and synthetic applications of this efficient and practical protocol are currently underway in our laboratory.

All reagents were obtained from Adamas, Accela, or Acros and used without further purification, unless otherwise noted. The products were purified by column chromatography with Huanghai Silica Gel 50–75 μm, ultrapure silica gel. ^{1}H NMR and ^{13}C NMR spectra were re-



Scheme 5 Plausible mechanism of $K_2S_2O_8$-activated alkylation of α-amido sulfones with indoles

corded in DMSO-d_6 or $CDCl_3$ on an Agilent 400MR DD2 (400 MHz) spectrometer. The chemical shifts were reported in ppm relative to Me_4Si as an internal standard. High-resolution mass spectra (HRMS) were performed on Bruker solarix 7.0T spectrometer. Melting points were determined on a micro melting point apparatus in open capillaries and are uncorrected. All reactions were carried out under N_2 atmosphere in oven-dried glassware with magnetic stirring.

$K_2S_2O_8$-Activated Friedel–Crafts Type Alkylation of Indoles with α-Amido Sulfones; General Procedure

To a 10 mL flame-dried Schlenk tube equipped with a stirring bar, indole **1** (0.2 mmol), α-amido-sulfone **2** (0.2 mmol), and $K_2S_2O_8$ (108.1 mg, 0.4 mmol) were added. Toluene (1.2 mL) was injected into the tube at r.t. After stirring for 48 h, the mixture was purified by silica gel chromatography to afford the desired product **3**.

3-[Phenyl(phenylsulfonyl)methyl]-1*H*-indole (3aa)

Pink powder; yield: 58.4 mg (84%); mp 177.5–179.5 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.32 (s, 1 H), 7.72 (d, *J* = 7.9 Hz, 3 H), 7.69–7.59 (m, 3 H), 7.53 (t, *J* = 7.3 Hz, 1 H), 7.42 (t, *J* = 7.6 Hz, 2 H), 7.37–7.26 (m, 4 H), 7.06 (t, *J* = 7.5 Hz, 1 H), 6.95 (t, *J* = 7.4 Hz, 1 H), 6.27 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 138.57, 135.30, 133.94, 133.33, 130.20, 128.63, 128.34, 128.12, 126.92, 125.41, 121.47, 118.90, 118.61, 111.48, 106.28, 66.46.

HRMS (ESI): *m*/*z* calcd for $[C_{21}H_{17}NO_2SNa, M + Na]^+$: 370.08722; found: 370.08717.

2-Phenyl-3-[phenyl(phenylsulfonyl)methyl]-1*H*-indole (3ba)

White crystals; yield: 36.4 mg (43%); mp 219.2–219.9 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.58 (s, 1 H), 8.14 (d, *J* = 7.6 Hz, 1 H), 7.63 (d, *J* = 6.7 Hz, 2 H), 7.58 (t, *J* = 7.2 Hz, 1 H), 7.52–7.43 (m, 3 H), 7.43–7.24 (m, 8 H), 7.17 (pent, *J* = 6.8 Hz, 2 H), 7.06 (d, *J* = 5.4 Hz, 2 H), 5.75 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 139.82, 138.24, 136.19, 133.62, 133.27, 131.05, 129.75, 128.80, 128.68, 128.60, 128.35, 127.72, 126.14, 122.30, 121.89, 119.75, 111.58, 103.00, 69.55.

HRMS (ESI): *m*/*z* calcd for $[C_{27}H_{21}NO_2SNa, M + Na]^+$: 446.11852; found: 446.11841.

4-Methyl-3-[phenyl(phenylsulfonyl)methyl]-1*H*-indole (3ca)

Brown power; yield: 58.6 mg (81%); mp 174.5–175.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (s, 1 H), 8.00 (d, *J* = 2.5 Hz, 1 H), 7.68 (d, *J* = 7.6 Hz, 2 H), 7.49 (t, *J* = 7.4 Hz, 1 H), 7.43–7.31 (m, 4 H), 7.29–7.25 (m, 3 H), 7.17 (d, *J* = 8.2 Hz, 1 H), 7.00 (t, *J* = 7.6 Hz, 1 H), 6.75 (d, *J* = 7.1 Hz, 1 H), 6.14 (s, 1 H), 2.57 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.53, 135.66, 133.60, 133.33, 130.50, 129.38, 128.84, 128.65, 128.44, 125.37, 124.83, 122.29, 122.11, 109.70, 107.42, 69.58, 20.80.

HRMS (ESI): *m*/*z* calcd for $[C_{22}H_{19}NO_2SNa, M + Na]^+$: 384.10287; found: 384.10290.

4-Chloro-3-[phenyl(phenylsulfonyl)methyl]-1*H*-indole (3da)

White crystals; yield: 75.6 mg (99%); mp 156.5–158.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.93 (s, 1 H), 7.99–7.94 (m, 1 H), 7.68 (d, *J* = 7.9 Hz, 2 H), 7.52–7.40 (m, 3 H), 7.35 (t, *J* = 7.5 Hz, 2 H), 7.25 (s, 3 H), 7.14 (d, *J* = 6.9 Hz, 1 H), 6.98–6.90 (m, 2 H), 6.78 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.23, 136.79, 133.54, 133.37, 130.40, 128.81, 128.63, 128.38, 126.05, 125.08, 123.16, 122.72, 121.39, 110.59, 106.84, 67.62.

HRMS (ESI): *m*/*z* calcd for $[C_{21}H_{16}ClNO_2SNa, M + Na]^+$: 404.04824; found: 404.04816.

4-Bromo-3-[phenyl(phenylsulfonyl)methyl]-1*H*-indole (3ea)

White crystals; yield: 84.4 mg (99%); mp 161.0–162.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.04 (s, 1 H), 7.97 (d, *J* = 2.2 Hz, 1 H), 7.70 (d, *J* = 7.8 Hz, 2 H), 7.52–7.41 (m, 3 H), 7.35 (t, *J* = 7.6 Hz, 2 H), 7.29–7.20 (m, 3 H), 7.18–7.09 (m, 2 H), 7.02 (s, 1 H), 6.84 (t, *J* = 7.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.20, 136.68, 133.43, 133.38, 130.43, 128.78, 128.65, 128.37, 126.57, 124.86, 124.14, 122.98, 112.85, 111.27, 106.87, 66.74.

HRMS (ESI): *m*/*z* calcd for $[C_{21}H_{16}BrNO_2SNa, M + Na]^+$: 447.99773; found: 447.99768.

5-Fluoro-3-[phenyl(phenylsulfonyl)methyl]-1*H*-indole (3fa)

Pink powder; yield: 45.3 mg (62%); mp 188.6–189.6 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.45 (s, 1 H), 7.81 (d, *J* = 2.4 Hz, 1 H), 7.71 (d, *J* = 7.6 Hz, 2 H), 7.64 (d, *J* = 6.3 Hz, 2 H), 7.55 (t, *J* = 7.4 Hz, 1 H), 7.49 (dd, *J* = 10.3, 2.2 Hz, 1 H), 7.43 (t, *J* = 7.7 Hz, 2 H), 7.37–7.25 (m, 4 H), 6.91 (td, *J* = 9.2, 2.3 Hz, 1 H), 6.29 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 158.13, 155.83, 138.45, 133.81, 133.39, 131.94, 130.15, 128.65, 128.38, 128.20, 127.54, 127.50, 127.39, 112.59, 112.50, 109.85, 109.58, 106.64, 106.60, 103.61, 103.37, 66.15.

HRMS (ESI): *m*/*z* calcd for $[C_{21}H_{16}FNO_2SNa, M + Na]^+$: 388.07779; found: 388.07783.

5-Chloro-3-[phenyl(phenylsulfonyl)methyl]-1*H*-indole (3ga)

Pink powder; yield: 57.3 mg (75%); mp 171.1–172.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (s, 1 H), 7.70 (s, 1 H), 7.63 (d, *J* = 6.8 Hz, 2 H), 7.50 (t, *J* = 6.0 Hz, 1 H), 7.47–7.39 (m, 2 H), 7.39–7.31 (m, 3 H), 7.30–7.22 (m, 3 H), 7.18 (d, *J* = 8.5 Hz, 1 H), 7.05 (d, *J* = 8.3 Hz, 1 H), 5.60 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.90, 133.78, 133.56, 132.99, 129.96, 128.93, 128.70, 128.65, 128.57, 128.07, 126.23, 125.85, 122.81, 117.64, 112.50, 106.71, 68.86.

HRMS (ESI): *m*/*z* calcd for $[C_{21}H_{16}ClNO_2SNa, M + Na]^+$: 404.04824; found: 404.04830.

6-Fluoro-3-[phenyl(phenylsulfonyl)methyl]-1*H*-indole (3ha)

Pink powder; yield: 55.5 mg (76%); mp 161.1–162.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (s, 1 H), 7.67 (d, *J* = 2.3 Hz, 1 H), 7.63 (d, *J* = 7.5 Hz, 2 H), 7.50 (t, *J* = 7.5 Hz, 1 H), 7.46–7.42 (m, 2 H), 7.34 (t, *J* = 7.9 Hz, 3 H), 7.30–7.26 (m, 3 H), 6.98 (dd, *J* = 9.4, 2.0 Hz, 1 H), 6.84–6.78 (m, 1 H), 5.64 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 160.05, 157.71, 138.44, 135.22, 135.09, 133.77, 133.40, 130.17, 128.67, 128.37, 128.19, 126.18, 126.15, 123.76, 119.91, 119.80, 107.64, 107.39, 106.61, 97.56, 97.31, 66.24.

HRMS (ESI): *m*/*z* calcd for $[C_{21}H_{16}FNO_2SNa, M + Na]^+$: 388.07779; found: 388.07776.

6-Bromo-3-[phenyl(phenylsulfonyl)methyl]-1*H*-indole (3ia)

Pink powder; yield: 73.3 mg (86%); mp 174.5–176.5 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.48 (s, 1 H), 7.78 (d, *J* = 2.4 Hz, 1 H), 7.72 (d, *J* = 7.5 Hz, 2 H), 7.68–7.59 (m, 3 H), 7.58–7.52 (m, 2 H), 7.43 (t, *J* = 7.7 Hz, 2 H), 7.35–7.25 (m, 3 H), 7.10 (dd, *J* = 8.5, 1.5 Hz, 1 H), 6.32 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 138.38, 136.20, 133.67, 133.43, 130.17, 128.68, 128.37, 128.21, 126.65, 126.02, 121.84, 120.58, 114.23, 114.10, 106.74, 66.12.

HRMS (ESI): *m*/*z* calcd for [$C_{21}H_{16}BrNO_2SNa$, M + Na]$^+$: 447.99773; found: 447.99769.

7-Chloro-3-[phenyl(phenylsulfonyl)methyl]-1*H*-indole (3ja)

Red powder; yield: 75.6 mg (99%); mp 161.5–163.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.71 (s, 1 H), 7.79 (d, *J* = 2.4 Hz, 1 H), 7.64 (d, *J* = 7.7 Hz, 2 H), 7.50–7.40 (m, 3 H), 7.35–7.29 (m, 3 H), 7.29–7.21 (m, 3 H), 7.12 (d, *J* = 7.6 Hz, 1 H), 6.95 (t, *J* = 7.8 Hz, 1 H), 5.66 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.94, 133.43, 132.93, 132.73, 130.01, 128.89, 128.65, 128.59, 128.50, 128.35, 125.47, 121.84, 120.83, 117.05, 116.73, 108.40, 68.95.

HRMS (ESI): *m*/*z* calcd for [$C_{21}H_{16}ClNO_2SNa$, M + Na]$^+$: 404.04824; found: 404.04831.

7-Bromo-3-[phenyl(phenylsulfonyl)methyl]-1*H*-indole (3ka)

Pink crystals; yield: 70.8 mg (83%); mp 167.8–168.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.62 (s, 1 H), 7.81 (s, 1 H), 7.64 (d, *J* = 7.7 Hz, 2 H), 7.51–7.39 (m, 3 H), 7.39–7.20 (m, 7 H), 6.91 (t, *J* = 7.8 Hz, 1 H), 5.65 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.96, 134.15, 133.44, 132.91, 130.02, 128.91, 128.66, 128.60, 128.51, 128.05, 125.37, 124.86, 121.24, 117.67, 108.63, 104.80, 68.97.

HRMS (ESI): *m*/*z* calcd for [$C_{21}H_{16}BrNO_2SNa$, M + Na]$^+$: 447.99773; found: 447.99770.

2,5-Dimethyl-3-[phenyl(phenylsulfonyl)methyl]-1*H*-indole (3la)

Light yellow powder; yield: 33.0 mg (44%); mp 179.6–181.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (s, 1 H), 7.76 (d, *J* = 6.7 Hz, 2 H), 7.54 (d, *J* = 7.7 Hz, 2 H), 7.49 (s, 1 H), 7.43 (t, *J* = 7.4 Hz, 1 H), 7.35–7.28 (m, 3 H), 7.24 (d, *J* = 7.7 Hz, 2 H), 7.06 (d, *J* = 8.2 Hz, 1 H), 6.91 (d, *J* = 8.1 Hz, 1 H), 5.63 (s, 1 H), 2.38 (s, 3 H), 1.99 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.91, 135.44, 133.29, 133.08, 132.92, 129.89, 129.16, 128.62, 128.38, 128.28, 128.09, 127.43, 123.05, 120.52, 109.89, 103.46, 69.59, 21.66, 11.98.

HRMS (ESI): *m*/*z* calcd for [$C_{23}H_{21}NO_2SNa$, M + Na]$^+$: 398.11852; found: 398.11849.

3-[(Phenylsulfonyl)(*o*-tolyl)methyl]-1*H*-indole (3ab)

Brown powder; yield: 60.7 mg (84%); mp 150.2–152.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.62 (s, 1 H), 7.95 (d, *J* = 7.6 Hz, 1 H), 7.69 (d, *J* = 2.3 Hz, 1 H), 7.65 (d, *J* = 7.5 Hz, 2 H), 7.47 (t, *J* = 7.4 Hz, 1 H), 7.36–7.26 (m, 4 H), 7.26–7.20 (m, 1 H), 7.16 (t, *J* = 7.0 Hz, 1 H), 7.11 (t, *J* = 7.5 Hz, 1 H), 7.05–6.99 (m, 2 H), 6.04 (s, 1 H), 2.17 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.66, 136.94, 135.36, 133.37, 132.01, 130.33, 129.65, 128.88, 128.55, 128.40, 127.09, 126.38, 125.19, 122.33, 119.96, 117.84, 111.44, 107.49, 63.71, 19.62.

HRMS (ESI): *m*/*z* calcd for [$C_{22}H_{19}NO_2SNa$, M + Na]$^+$: 384.10287, found: 384.10282.

3-[(Phenylsulfonyl)(*m*-tolyl)methyl]-1*H*-indole (3ac)

White crystals; yield: 68.0 mg (94%); mp 149.9–151.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51 (s, 1 H), 7.68 (d, *J* = 2.5 Hz, 1 H), 7.64 (d, *J* = 7.3 Hz, 2 H), 7.45 (t, *J* = 7.4 Hz, 1 H), 7.38 (d, *J* = 8.0 Hz, 1 H), 7.34–7.23 (m, 5 H), 7.18–7.10 (m, 2 H), 7.10–7.05 (m, 1 H), 7.02 (t, *J* = 7.5 Hz, 1 H), 5.66 (s, 1 H), 2.25 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.25, 138.08, 135.41, 133.26, 133.03, 130.80, 129.30, 128.93, 128.48, 128.30, 127.15, 126.96, 124.85, 122.36, 119.95, 118.10, 111.37, 107.13, 68.98, 21.33.

HRMS (ESI): *m*/*z* calcd for [$C_{22}H_{19}NO_2SNa$, M + Na]$^+$: 384.10287; found: 384.10280.

3-[(3-Methoxyphenyl)(phenylsulfonyl)methyl]-1*H*-indole (3ad)

Red powder; yield: 69.5 mg (92%); mp 83.0–85.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.74 (s, 1 H), 7.63 (d, *J* = 7.7 Hz, 2 H), 7.53 (s, 1 H), 7.43 (d, *J* = 7.8 Hz, 1 H), 7.36 (t, *J* = 7.3 Hz, 1 H), 7.27–7.16 (m, 3 H), 7.13 (t, *J* = 7.9 Hz, 1 H), 7.10–6.96 (m, 4 H), 6.78 (d, *J* = 7.9 Hz, 1 H), 5.70 (s, 1 H), 3.62 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.30, 137.93, 135.39, 134.57, 133.28, 129.33, 128.74, 128.46, 126.79, 125.08, 122.42, 122.15, 119.77, 117.95, 115.70, 113.94, 111.55, 106.35, 68.94, 55.06.

HRMS (ESI): *m*/*z* calcd for [$C_{22}H_{19}NO_3SNa$, M + Na]$^+$: 400.09778; found: 400.09781.

3-[(4-Methoxyphenyl)(phenylsulfonyl)methyl]-1*H*-indole (3ae)

Pink powder; yield: 61.1 mg (81%); mp 73.5–75.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.70 (s, 1 H), 7.52 (d, *J* = 7.7 Hz, 2 H), 7.46 (s, 1 H), 7.35–7.22 (m, 4 H), 7.19–7.06 (m, 3 H), 6.96 (t, *J* = 7.4 Hz, 1 H), 6.89 (t, *J* = 7.3 Hz, 1 H), 6.64 (d, *J* = 7.6 Hz, 2 H), 5.58 (s, 1 H), 3.58 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.61, 138.07, 135.43, 133.20, 131.28, 128.74, 128.46, 126.81, 124.94, 122.13, 119.73, 118.04, 113.75, 111.52, 106.75, 68.38, 55.10.

HRMS (ESI): *m*/*z* calcd for [$C_{22}H_{19}NO_3SNa$, M + Na]$^+$: 400.09778; found: 400.09775.

3-[(4-Isopropylphenyl)(phenylsulfonyl)methyl]-1*H*-indole (3af)

Light yellow crystals; yield: 56.1 mg (72%); mp 172.5–174.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49 (s, 1 H), 7.70 (d, *J* = 2.1 Hz, 1 H), 7.63 (d, *J* = 7.8 Hz, 2 H), 7.47–7.36 (m, 4 H), 7.32–7.22 (m, 3 H), 7.16–7.07 (m, 3 H), 7.02 (t, *J* = 7.5 Hz, 1 H), 5.67 (s, 1 H), 2.91–2.79 (m, 1 H), 1.19 (d, *J* = 6.8 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.35, 138.34, 135.40, 133.20, 130.33, 130.06, 128.90, 128.44, 126.98, 126.54, 124.80, 122.37, 119.95, 118.20, 111.33, 107.37, 68.75, 33.73, 23.83.

HRMS (ESI): *m*/*z* calcd for [$C_{24}H_{23}NO_2SNa$, M + Na]$^+$: 412.13417; found: 412.13420.

3-[(4-Chlorophenyl)(phenylsulfonyl)methyl]-1*H*-indole (3ag)

Pink powder; yield: 71.8 mg (94%); mp 97.5–99.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (s, 1 H), 7.68–7.60 (m, 3 H), 7.47 (t, *J* = 7.4 Hz, 1 H), 7.42–7.25 (m, 6 H), 7.25–7.19 (m, 2 H), 7.13 (t, *J* = 7.5 Hz, 1 H), 7.03 (t, *J* = 7.5 Hz, 1 H), 5.68 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.95, 135.46, 134.64, 133.54, 131.77, 131.39, 128.87, 128.69, 128.64, 126.75, 124.80, 122.56, 120.12, 118.05, 111.49, 106.66, 68.27.

HRMS (ESI): *m*/*z* calcd for $[C_{21}H_{16}ClNO_2SNa, M + Na]^+$: 404.04824; found: 404.04821.

3-[(4-Bromophenyl)(phenylsulfonyl)methyl]-1*H*-indole (3ah)

Pink powder; yield: 64.8 mg (76%); mp 170.9–172.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (s, 1 H), 7.68–7.62 (m, 3 H), 7.49 (t, *J* = 7.4 Hz, 1 H), 7.42–7.27 (m, 8 H), 7.14 (t, *J* = 7.5 Hz, 1 H), 7.03 (t, *J* = 7.5 Hz, 1 H), 5.66 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.98, 135.45, 133.55, 132.30, 131.69, 131.62, 128.89, 128.70, 126.75, 124.74, 122.91, 122.62, 120.17, 118.09, 111.44, 106.75, 68.32.

HRMS (ESI): *m*/*z* calcd for $[C_{21}H_{16}BrNO_2SNa, M + Na]^+$: 447.99773; found: 447.99770.

3-[(Phenylsulfonyl)(3,4,5-trimethoxyphenyl)methyl]-1*H*-indole (3ai)

Light yellow powder; yield: 84.9 mg (97%); mp 85.0–87.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.03 (s, 1 H), 7.64 (d, *J* = 7.1 Hz, 3 H), 7.51–7.39 (m, 2 H), 7.27 (dd, *J* = 14.0, 7.6 Hz, 3 H), 7.09 (t, *J* = 7.4 Hz, 1 H), 7.02 (t, *J* = 7.4 Hz, 1 H), 6.68 (s, 2 H), 5.67 (s, 1 H), 3.78 (s, 3 H), 3.68 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.75, 137.91, 137.91, 135.51, 133.23, 128.76, 128.70, 128.43, 126.72, 124.94, 122.18, 119.74, 118.11, 111.48, 107.26, 106.36, 69.18, 60.64, 55.87.

HRMS (ESI): *m*/*z* calcd for $[C_{24}H_{23}NO_5SNa, M + Na]^+$: 460.11891; found: 460.11893.

3-[Naphthalen-2-yl(phenylsulfonyl)methyl]-1*H*-indole (3aj)

Brown powder; yield: 52.5 mg (66%); mp 165.4–166.0 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.33 (s, 1 H), 8.49 (d, *J* = 8.4 Hz, 1 H), 8.23 (d, *J* = 7.3 Hz, 1 H), 7.86 (dd, *J* = 14.7, 7.8 Hz, 4 H), 7.76 (d, *J* = 2.4 Hz, 1 H), 7.62–7.42 (m, 5 H), 7.40–7.31 (m, 3 H), 7.08–7.02 (m, 2 H), 6.92 (t, *J* = 7.5 Hz, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 138.79, 135.45, 133.35, 133.23, 131.46, 130.13, 128.73, 128.62, 128.58, 128.52, 127.94, 126.76, 126.55, 126.17, 125.66, 125.16, 123.29, 121.49, 119.03, 118.57, 111.58, 106.92, 61.48.

HRMS (ESI): *m*/*z* calcd for $[C_{25}H_{19}NO_2SNa, M + Na]^+$: 420.10287; found: 420.10284.

3-[3-Phenyl-1-(phenylsulfonyl)propyl]-1*H*-indole (3ak)

Light yellow powder; yield: 33.0 mg (44%); mp 49.0–51.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.55 (s, 1 H), 7.50 (d, *J* = 7.5 Hz, 2 H), 7.41 (t, *J* = 7.4 Hz, 1 H), 7.31–7.14 (m, 7 H), 7.11 (t, *J* = 7.5 Hz, 1 H), 7.05–6.93 (m, 4 H), 4.38 (d, *J* = 11.0 Hz, 1 H), 2.83–2.64 (m, 2 H), 2.58–2.40 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.21, 137.38, 135.85, 133.19, 128.88, 128.45, 128.43, 128.41, 126.97, 126.17, 125.17, 122.27, 120.02, 118.76, 111.36, 106.52, 63.35, 32.61, 29.44.

HRMS (ESI): *m*/*z* calcd for $[C_{23}H_{21}NO_2SNa, M + Na]^+$: 398.11852; found: 398.11849.

3-[Cyclohexyl(phenylsulfonyl)methyl]-1*H*-indole (3al)

Light yellow powder; yield: 32.5 mg (46%); mp 152.5–153.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (s, 1 H), 7.53 (d, *J* = 7.6 Hz, 2 H), 7.41–7.21 (m, 4 H), 7.16 (t, *J* = 7.6 Hz, 2 H), 7.08 (t, *J* = 7.5 Hz, 1 H), 6.95 (t, *J* = 7.3 Hz, 1 H), 4.38 (d, *J* = 5.2 Hz, 1 H), 2.78–2.63 (m, 1 H), 2.19–1.98 (m, 2 H), 1.79–1.65 (m, 2 H), 1.60 (d, *J* = 12.5 Hz, 1 H), 1.34 (dq, *J* = 26.0, 12.6 Hz, 2 H), 1.23–0.95 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.38, 135.16, 132.68, 128.21, 128.15, 127.70, 125.50, 122.06, 119.80, 118.07, 111.09, 106.07, 68.38, 38.00, 32.37, 29.77, 26.22, 25.97, 25.87.

HRMS (ESI): *m*/*z* calcd for $[C_{21}H_{23}NO_2SNa, M + Na]^+$: 376.13417; found: 376.13412.

3-[(Phenylsulfonyl)(thiophen-2-yl)methyl]-1*H*-indole (3am)

Pink solid; yield: 70.0 mg (99%); mp 86.5–88.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.96 (s, 1 H), 7.60 (d, *J* = 7.6 Hz, 2 H), 7.50–7.37 (m, 3 H), 7.34–7.20 (m, 5 H), 7.11 (t, *J* = 7.4 Hz, 1 H), 7.06–7.00 (m, 1 H), 5.83 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.82, 135.54, 133.29, 128.78, 128.62, 128.46, 126.74, 126.08, 125.75, 125.54, 122.22, 119.90, 118.42, 111.48, 106.54, 64.72.

HRMS (ESI): *m*/*z* calcd for $[C_{19}H_{15}NO_2S_2Na, M + Na]^+$: 376.04364; found: 376.04360.

3,3′-(Phenylmethylene)bis(1*H*-indole) (4a) (Scheme 3)

Red powder; yield: 3.2 mg (5%); mp 94.5–96.4 °C.

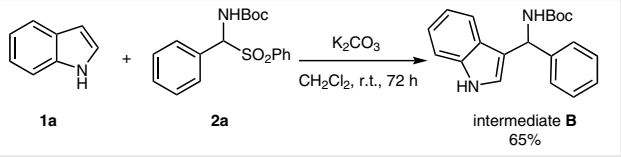
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (s, 2 H), 7.35 (d, *J* = 7.9 Hz, 2 H), 7.30 (d, *J* = 7.1 Hz, 2 H), 7.27–7.20 (m, 4 H), 7.18 (d, *J* = 7.2 Hz, 1 H), 7.13 (t, *J* = 7.6 Hz, 2 H), 6.97 (t, *J* = 7.5 Hz, 2 H), 6.48 (s, 2 H), 5.83 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.95, 136.54, 128.65, 128.17, 126.96, 126.08, 123.59, 121.83, 119.84, 119.49, 119.14, 111.03, 40.09.

HRMS (ESI): *m*/*z* calcd for $[C_{24}H_{26}N_2O_3SNa, M + Na]^+$: 445.15563; found: 445.15523.

tert-Butyl [(1*H*-Indol-3-yl)(phenyl)methyl]carbamate (Intermediate B)

Intermediate **B** was prepared following the literature procedure (Scheme 6).[11]



Scheme 6 Preparation of intermediate **B**

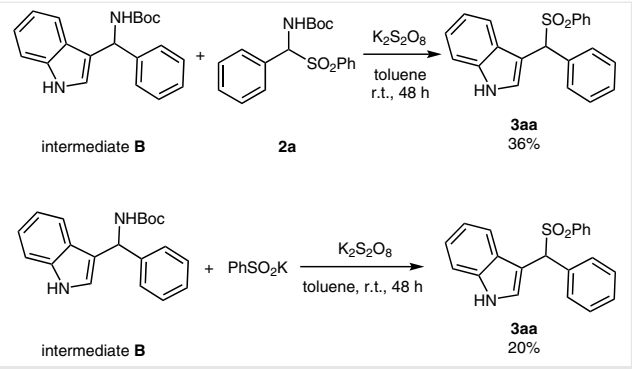
To a 25 mL flame-dried Schlenk flask equipped with a stirring bar were added indole **1a** (117.2 mg, 1.0 mmol), α-amido sulfone **2a** (347.4 mg, 1.0 mmol), and K_2CO_3 (414.6 mg, 3.0 mmol). CH_2Cl_2 (12 mL) was injected into the flask at r.t. After stirring for 72 hours, the mixture was purified by silica gel chromatography to afford the product **B**; red powder; yield: 209.6 mg (65%); mp 136.2–138.0 C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (s, 1 H), 7.49 (d, *J* = 7.6 Hz, 1 H), 7.36 (d, *J* = 7.2 Hz, 2 H), 7.31 (t, *J* = 7.2 Hz, 3 H), 7.28–7.22 (m, 1 H), 7.17 (t, *J* = 7.5 Hz, 1 H), 7.07 (t, *J* = 7.5 Hz, 1 H), 6.63 (s, 1 H), 6.27–6.10 (m, 1 H), 5.25 (s, 1 H), 1.45 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.27, 142.00, 136.64, 128.31, 127.04, 126.77, 125.83, 123.30, 122.30, 119.68, 119.29, 117.63, 111.34, 79.56, 51.67, 28.38.

3-[Phenyl(phenylsulfonyl)methyl]-1*H*-indole (3aa)

Intermediate **B** reacted with α-amido sulfone **2a** and potassium benzenesulfinate as shown in Scheme 7.



Scheme 7 Reactions of intermediate **B**

With α-Amido Sulfone: To a 10 mL flame-dried Schlenk tube equipped with a stirring bar were added intermediate **B** (64.5 mg, 0.2 mmol), α-amido sulfone **2a** (69.5 mg, 0.2 mmol), and $K_2S_2O_8$ (108.1 mg, 0.4 mmol). Toluene (1.2 mL) was injected into the tube at r.t. After stirring for 48 h, the mixture was purified by silica gel chromatography to afford the product **3aa**; yield: 25.0 mg (36%).

With Potassium Benzenesulfinate: To a 10 mL flame-dried Schlenk tube equipped with a stirring bar were added intermediate **B** (64.5 mg, 0.2 mmol), potassium benzenesulfinate (36.1 mg, 0.2 mmol), and $K_2S_2O_8$ (108.1 mg, 0.4 mmol). Toluene (1.2 mL) was injected into the tube at r.t. After stirring for 48 h, the mixture was purified by silica gel chromatography to afford the product **3aa**; yield: 13.9 mg (20%).

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