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Palladium-Catalyzed Direct C2-Biarylation of Indoles

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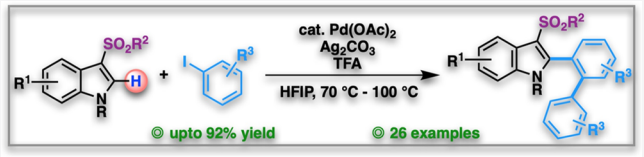
ABSTRACT: Biaryl and indole units are important structural motifs in several bioactive molecules and functional materials. We have accomplished straightforward access to C2-biarylated indole derivatives through palladium-catalyzed C−H activation strategy with a broad range of substrate scope in yields of 24 to 92%. Besides, the UV/visible absorption and fluorescence properties of the ensuing products were explored. The calculated higher dihedral angle and rotational barrier values for the selected C2-biarylated indoles show that these compounds may display atropisomerism at room temperature.



Biaryl compounds are one of the privileged molecules in drug discovery, and 4.3% of known drugs contain a biphenyl framework. Besides, the presence of aromatic substituents in a drug molecule enhances its binding to proteins and influences the interaction between the aromatic and hydrophobic residues. Furthermore, biaryl units are the essential linchpin in ligands for asymmetric catalysis, precursor for organic light-emitting compounds, organic electroluminescent materials, and liquid crystals.[1] Arylated indole and its congeners are a central skeleton in many bioactive molecules. In general, cross-coupling reactions have been historically used to synthesize such skeletons from prefunctionalized indoles.[2] In 2006, C2-arylation of electron-rich heteroarenes using diaryliodonium salts as the arylating reagents in the presence of Pd(II)-catalyst was reported by the Sanford group (Scheme 1a).[3a] Later, Fagnou and co-workers delineated their discovery of palladium-catalyzed oxidative C2-arylation of indoles with arenes in a highly regioselective manner (Scheme 1b).[3b] In 2008, Gaunt et al. demonstrated Cu(II)-catalyzed site-selective C−H arylation of indoles at either C3 or C2-position employing diaryliodonium salts as the arylating source.[3c] In the same year, Larrosa and co-workers described the direct C2-arylation of indoles with iodoarenes using $Pd(OAc)_2$ as the catalyst (Scheme 1c).[3d] A few other reports have been documented for C2-arylation of indoles using aryl boronic acids and aryldiazonium salts as the arylating agents.[4]

Most of the strategies documented for the synthesis of C2-arylated indoles use indoles without C3-substituent. Only limited examples of indoles with C3-substituents,[3a,5] and tryptophan derivatives were evaluated for C2-arylation reaction.[6] The introduction of an aryl group into the C2-position of an *N*-protected-C3-substituted indole is an arduous task, owing to the steric congestion exerted by the substituents present at C3- and *N*1-positions.[5] Besides, the crucial step in the aforementioned reports are electrophilic palladation step, which often demands electron-rich indoles. To the best of our knowledge, the synthetic route to C2-biarylation of indoles

Scheme 1. Palladium-Catalyzed C2-Monoarylation and -Biarylation of Indoles

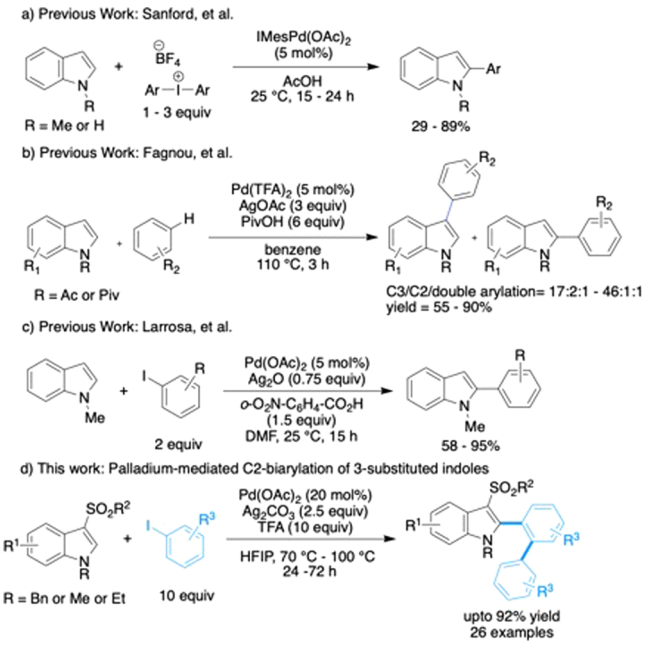


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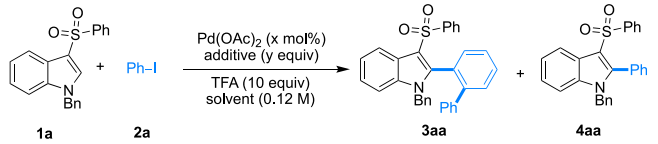
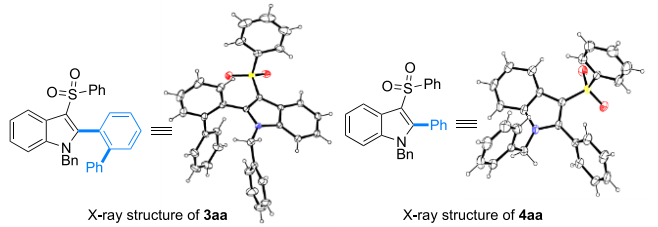
Table 1. Optimization of Reaction Conditions



substrate no.	$Pd(OAc)_2$ (*x* mol %)	additive (*y* equiv)	PhI (equiv)	solvent	temp (°C)	time (h)	**3aa** (%)	**4aa** (%)
1[a]	0.2	Ag_2O (1)	2	DCE	110	48	17	10
2	0.2	AgTFA (1)	2	DCE	110	48	16	trace
3	0.2	Ag_2CO_3 (1)	2	DCE	110	48	35	trace
4	0.2	Ag_2CO_3 (2.5)	10	TFE	110	72	51	nd
5	0.2	Ag_2CO_3 (2.5)	10	HFIP	110	24	64	trace
6	0.2	Ag_2O (2.5)	10	HFIP	110	24	65	nd
7	0.2	AgOTf (2.5)	10	HFIP	110	24	10	44
8[b]	**0.2**	**Ag_2CO_3(2.5)**	**10**	**HFIP**	**70**	**24**	**88**	**nd**
9	0.2	Ag_2CO_3 (2.5)	8	HFIP	70	24	83	nd
10	0.2	Ag_2CO_3 (2.5)	7	HFlP	70	24	79	nd
11	0.2	Ag_2CO_3 (2.5)	5	HFIP	70	24	33	nd
12	0.15	Ag_2CO_3 (2.5)	10	HFIP	70	24	84	nd
13	0.1	Ag_2CO_3 (2.5)	10	HFIP	70	24	80	nd
14	0.05	Ag_2CO_3 (2.5)	10	HFIP	70	24	9	nd
15[c]	0.2		10	HFIP	110	24	trace	trace
16[d]		Ag_2CO_3 (2.5)	10	HFIP	110	24	nd	nd
17[e]	0.2	Ag_2CO_3 (2.5)	10	HFIP	110	24	trace	trace

[a]TFA (1 mL) and DBU (1 equiv) were used. [b]Average isolated yield of four reactions. [c]No Ag_2CO_3. [d]No $Pd(OAc)_2$. [e]No TFA, nd = not detected.



with electron-withdrawing substituents at C3-position has not been documented yet.

Our substrate choice for C−H arylation of indole contains an electron-withdrawing group such as sulfonyl group at C3-position because the existence of sulfonyl moiety in a molecule can improve bioactivity.[7a] Due to the weak coordination ability of sulfone with the transition metal-catalysts, the use of sulfone as the directing group in C−H functionalization reactions has been less-explored in comparison with other sulfur-containing compounds such as sulfides and sulfoxides.[7b,f] In the course of our attempt toward the development of palladium-catalyzed C4-arylation of 3-sulfonylindoles (wherein, the sulfonyl group at the 3-position of indole was expected to act as the directing group),[8] to our surprise, we witnessed C2-biarylation of 3-sulfonylindoles when iodobenzene was employed as the aryl source. The consequent biarylated indole (**3aa**) that has both biaryl and indole units own high synthetic value.[1,9] Thus far, metal-mediated cross-coupling reactions that use prefunctionalized indoles are the common way to construct such C2-biarylated indole derivatives.[9] Hitherto, the realization of C2-biarylated indole derivatives using direct C−H functionalization strategy is an unreported outcome, and we wish to account our new finding in this note.[10]

The reaction between 3-sulfonylated indole (**1a**) with iodobenzene (**2a**, 2 equiv) in the presence of $Pd(OAc)_2$(20 mol %) using DBU (1 equiv) as a base, trifluoroacetic acid[11] (TFA, 1 mL) and silver(I) salts[3d,12] such as Ag_2O (1 equiv) as additives in DCE at 110 °C furnished a mixture of C2-biarylated indole (**3aa**, 17%) along with monoarylated indole (**4aa**, 10%) (Table 1, entry 1). The structures of both **3aa** and **4aa** were unequivocally elucidated by NMR and X-ray analysis.

The use of AgTFA as an additive produced in **3aa** and **4aa** in 16% and trace, respectively (entry 2). However, an additive such as Ag_2CO_3 (1 equiv) rendered **3aa** in 35% yield with a trace amount of **4aa** (entry 3). We screened several catalysts, ligands, additives, and solvents, but none of the combinations could increase the yield of **3aa** (see Supporting Information). Lately, HFIP has been commonly expended as the solvent for C−H functionalization reactions, and it is regarded that the coordinative interaction between HFIP and the metal adds to the electrophilic metalation step.[13] On this basis, the use of TFE and HFIP as the solvent with 10 equiv of **2a** delivered **3aa** in 51% and 64% yields, respectively, along with a trace amount of biphenyl byproduct (entries 4 and 5). Comparable reactivity was observed when Ag_2CO_3 was replaced with Ag_2O (entry 6), whereas, AgOTf diminished the yield of **3aa** to 10% along with 44% of **4aa** (entry 7). Gratifyingly, the high yield of **3aa** was obtained when the reaction was performed at 70 °C (entry 8), and no biphenyl byproduct formation was observed under this optimal reaction conditions. Furthermore, limiting the amount of PhI from 10 to 8, 7, and 5 equiv decreased the yield of **3aa** to 83%, 79%, and 33% respectively (entries 9 to 11). Additionally, reducing the catalytic loading of $Pd(OAc)_2$ to 15 mol % and 10 mol % resulted in slight erosion in the yield of **3aa**, and further, reducing the catalyst loading to 5 mol % significantly reduced the yield to 9% (entries 12 to 14).

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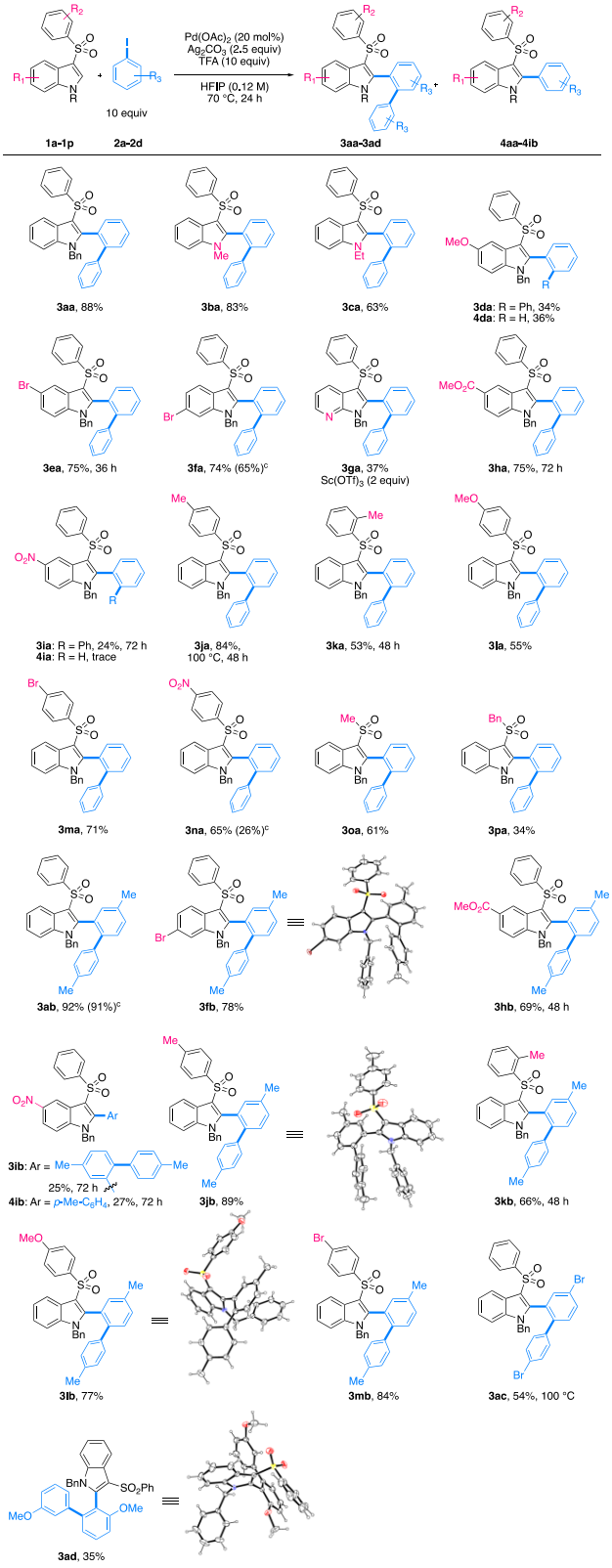
Control reactions in the absence of either Ag_2CO_3 or catalyst resulted in a trace amount of product formation or no reaction, respectively (entries 15 and 16). Furthermore, the reaction without TFA produced only a trace amount of product (entry 17). These results signify that the above-mentioned components are indispensable for the facile C2-biarylation reaction.

With the optimal reaction conditions in hand, next, we explored the substrates scope of various 3-sulfonylated indole derivatives using **2a** as the aryl source (Table 2). 3-phenyl sulfonyl indoles bearing a variety of *N*-alkyl substituents such as benzyl, methyl, and ethyl substituents (**1a**-**1c**) rendered the products **3aa**-**3ca** in 88%, 83%, and 63%, respectively. Sulfonylated indole carrying a methoxy substituent at 5-position (**1d**) furnished a mixture of products **3da** (34%) and **4da** (36%). Indoles (**1e** and **1f**) connected to a halogen substituent at 5- and 6-position afforded the respective products (**3ea** and **3fa**) in good yields. No product formation observed when 3-sulfonylated 7-azaindole derivative (**1g**) was subjected for arylation reaction under the optimized reaction conditions, presumably due to the catalyst arrest caused by the Lewis basic nitrogen present on the indole core. When two equivalents of $Sc(OTf)_3$ was employed as the sacrificial Lewis acid to prevent the catalyst arrest,[14] the required product (**3ga**) was isolated in 37% yield. Besides, the reaction with 3-sulfonylated indole bearing electron-withdrawing group such as an ester functionality at 5-position (**1h**) underwent a facile biarylation reaction to give the analogous product (**3ha**) in 75%, albeit it required an extended reaction time. Whereas the indole carrying a nitro group at the same position (**1i**) gave **3ia** in 24% yield along with a trace amount of **4ia**.

With regards to the scope of the sulfonyl group, a broad range of 3-sulfonylated indoles were studied. The aryl sulfonyl group decorated with electron-donating (**1j**-**1l**), halogen (**1m**), and electron-withdrawing (**1n**) substituents at various position produced the corresponding products (**3ja**-**3na**) in the range of admissible to good yields. Sulfonyl group holding aliphatic substituent such as (3-methylsulfonyl) indole derivative (**1o**) and (3-benzylsulfonyl) indole derivative (**1p**) also worked well and furnished the required products (**3oa** and **3pa**) in 61% and 34% yields, respectively. Next, we explored the scope of aryl iodide source with various 3-sulfonylated indole derivatives under the same reaction conditions. The use of 4-iodotoluene (**2b**) as the aryl source with various 3-sulfonylindoles like (**1a**, **1f**, **1h**, **1j**, **1k**, **1l**, and **1m**) gave the corresponding biarylated indoles (**3ab**, **3fb**, **3hb**, **3jb**, **3kb**, **3lb**, and **3mb**) in the extent of moderate to good yields, whereas in the case of substrate **1i**, a mixture of products (**3ib** and **4ib**) was observed. Interestingly, the reaction between aryl iodide such as 1-bromo-4-iodobenzene (**2c**) and **1a** afforded the respective product (**3ac**) in 54% yield. It is noteworthy that the C−I bond underwent selective coupling reaction in the presence of Pd(II)-catalyst, and the C−Br bond was intact, and it provides an opportunity to postsynthetic modification with the C−Br bond. Moreover, the evaluation of *meta*-substituted aryl iodide such as 3-iodoanisole (**2d**) delivered the associate product (**3ad**) albeit in moderate yield. However, *ortho*-substituted aryl iodides, and aryl iodides having electron-withdrawing substituents are poor substrates for this reaction.

Initially, we thought that C2-biarylation occurs via two successive C−H arylation steps. For example, in path A of Scheme 2; first, the formation of **4lb** is directed by the weak coordination of the sulfonyl group. Then, **4lb** undergoes

Table 2. Substrate Scope of Palladium-Catalyzed C2-Biarylation of Indoles[a,b]



[a]Unless otherwise noted, all reactions were carried out with **1a**−**1p** (1 equiv), **2a**−**2d** (10 equiv), $Pd(OAc)_2$ (20 mol %), Ag_2CO_3 (2.5 equiv), and TFA (10 equiv) in HFIP (0.12 M) at 70 °C for 24 h. [b]Yield of isolated product. [c]$Pd(OAc)_2$ (10 mol %) was employed.

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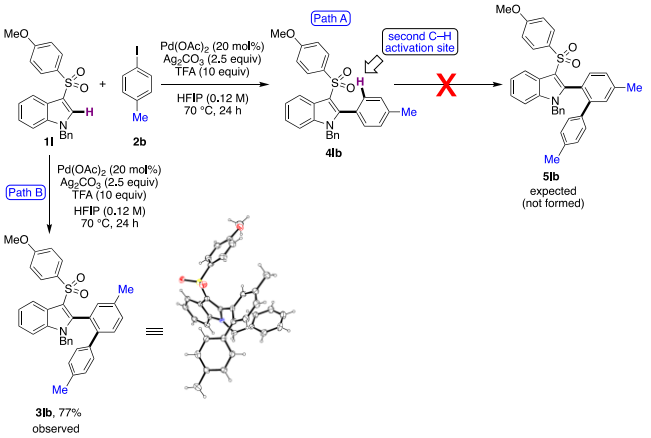
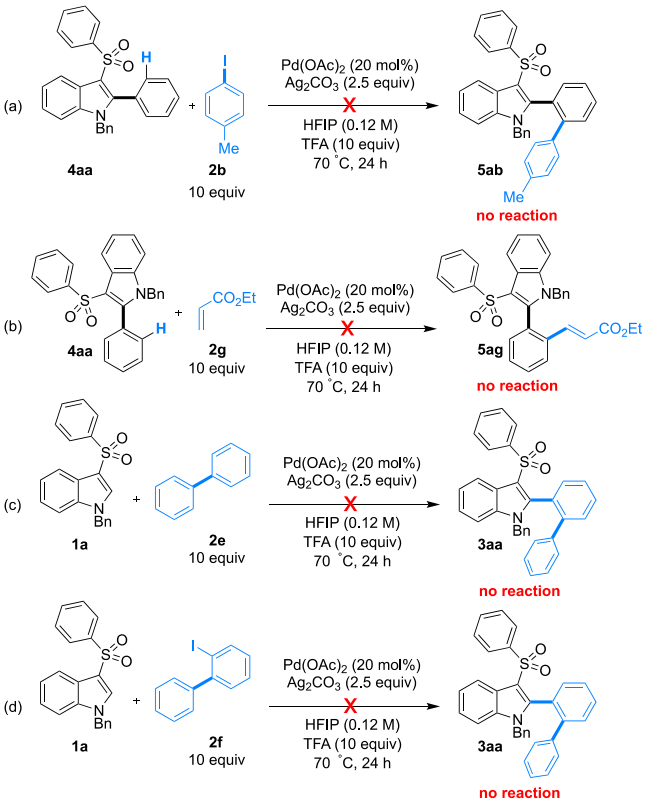
Scheme 2. Structural Analysis of C2-Biarylated Indole Obtained from Substituted Iodoarene and 3-Sulfonylindole



further C−H activation on the aryl ring at the C2-position to form the C2-biarylated product **5lb** (Scheme 2, Path A). However, the single-crystal structure of C2-biarylated compound **3lb** (Scheme 2, Path B) obtained from **1l** and **2b** corroborates that C2-biarylation does not proceed as mentioned in Path A. Also, similar structural pattern was observed in compounds like **3fb**, **3jb**, and **3ad** (Table 2) which were derived from substituted iodoarenes. To understand the precise sequence of reaction mechanism, we performed a few control reactions using **4aa** as the precursor, **2b** and ethyl acrylate (**2g**) as the coupling partner under identical reaction conditions (Scheme 3a and 3b). However, we did not observe the formation of the corresponding C2-biarylated product (**5ab**) or alkenylated product (**5ag**). These results suggest that

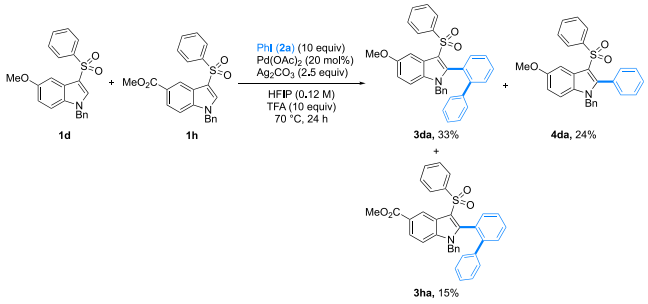
Scheme 3. Control Experiments



C2-biarylation may not proceed via two successive C−H arylation steps. Furthermore, to validate the possibility of oxidative C2-biarylation[3b] of **1a** with biphenyl,[15] a test reaction was set up using biphenyl (**2e**) as the aryl source under the optimized reaction conditions; however, no reaction took place in the aforementioned case (Scheme 3c). Besides, a control reaction was set up using 2-iodobiphenyl (**2f**) and **1a** as the starting precursors to probe whether 2-iodobiphenyl is the competent coupling partner in this reaction. However, no product formation was observed (Scheme 3d).

A competition experiment between the indole bearing an electron-donating group (**1d**) and the indole bearing an electron-withdrawing group (**1h**) furnished the target products **3da** and **3ha** in 33% and 15% yields respectively along with C2-monoaryl product (**4da**) in 24% yield (Scheme 4). This

Scheme 4. Competition Experiment



outcome implies that indole bearing an electron-donating group (**1d**) reacts faster than its counterpart (**1h**), and the rate of the reaction largely depends on the electronic factors of the indole precursor. Therefore, we speculate that the C−H activation takes place via the electrophilic metalation pathway (after coordination of the metal to the sulfonyl group). However, the mechanism for the C2-biarylation step is not fully understood, which requires further studies.

Like rotationally hindered biaryl compounds, the C2-biarylated-3-sulfonylindoles also possess two rotationally hindered biaryl axes. The dihedral angle measured (using X-ray crystal structural analysis) for both biaryl axes of various C2-biarylated-3-sulfonylindoles were either higher or in line with the established dihedral angle of twisted biaryl systems (see Supporting Information).[16] Moreover, the higher rotational energy barrier calculated using theoretical analysis for the selected compounds of C2-biarylated-3-sulfonylindoles (see Supporting Information) shows that these biaryl compounds may display atropisomerism at room temperature.[17]

To explore the synthetic importance of the C2-biarylated-3-sulfonylindoles, we performed a photophysical study[1,9] on selected compounds. We found that the molecules like **3ab**, **3ja**, **3lb**, **3mb**, and **3na** exhibited interesting photophysical properties (See Supporting Information for more details).

To illustrate the practical utility of the present method, we performed a larger scale reaction using **1a** and **2a** as the substrates, and the target product **3aa** was isolated in 82% yield at 90 °C (Scheme 5a).[18a] Next, we focused on *N*-debenzylation of C2-biarylated product (**3aa**) in the presence of KO^{t}Bu in DMSO, and the corresponding debenzylated indole **5aa** was attained in excellent yields (Scheme 5b).[18b]

In summary, we have demonstrated a single-step palladium-promoted synthesis of C2-biarylated-3-sulfonylindoles from 3-

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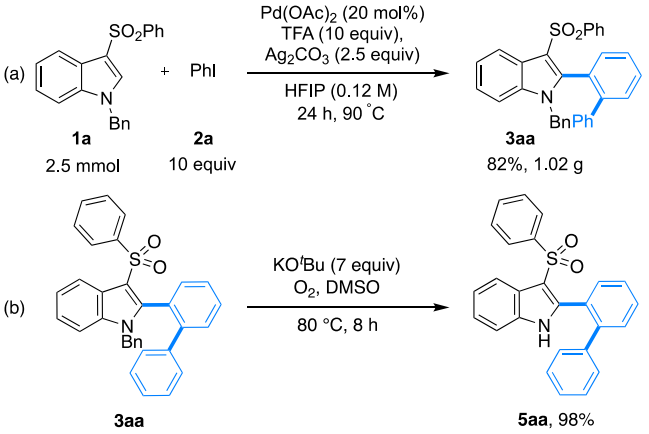
Scheme 5. (a) Large-Scale Experiment. (b) *N*-Debenzylation of 3aa



sulfonylindoles and iodoarenes via a C−H activation strategy. An *N*-benzyl substituent on the C2-biarylated 3-sulfonylindole was readily removed under mild reaction conditions to obtain the respective free indole. We have calculated the rotational energy barrier and the dihedral angle for the selected C2-biarylated indoles. In addition, we have uncovered the interesting UV/visible absorption and fluorescence properties of newly synthesized C2-biarylated-3-sulfonylindoles. Further study to understand the reaction mechanism is currently ongoing in our laboratory.

EXPERIMENTAL SECTION

General Information. All reactions were carried out using standard Schlenk techniques under argon condition. Solvents were obtained from Merck, Alfa Aesar, and Spectrochem. All solvents were dried as per standard purification techniques and then stored under appropriate conditions. HFIP was purchased from TCI and used without any further purification. Iodobenzene and trifluoroacetic acid were purchased from Spectrochem and used without any further purification. Analytical thin-layer chromatography was performed by using aluminum TLC sheets 0.25 mm silica gel 60-F_{254}. Visualization was carried out under UV light. Column chromatography was carried out with silica gel 230−400 mesh (Merck). ^{1}H and ^{13}C{^{1}H} NMRspectra were measured using $CDCl_3$ and DMSO-d_6 as solvents in Bruker 500 MHz NMR instruments. Chemical shifts were set in parts per million (ppm) to 0.0 ppm for TMS or 7.26 ppm for $CDCl_3$ and DMSO-d_6 2.50 ppm. The multiplicities of spectra were denoted by s = singlet, d = doublet, t = triplet, dd = doublet of doublet, td = triplet of doublet, dt = doublet of triplet, q = quartet, m = multiplet, and bs = broad singlet. Coupling constants (J) are reported in hertz (Hz). Mass spectra were measured using Thermo Scientific Q-Exactive HRMS and Xevo G2-XS QTof (Quadrupole Time-of-Flight) Mass Spectrometry. FT-IR spectra were recorded using a Bruker Alpha II spectrometer. CHNS was analyzed by a varioMICRO CHNS instrument. The crystal structure was determined using a Bruker AXS Kappa Apex II ScXRD instrument. Absorption spectra were recorded using a quartz cuvette of 10 mm path length on a Shimadzu UV-3600 vis−NIR spectrometer. Steady-state fluorescence spectra were recorded on Horiba Jobin Yvon Fluorimeter equipped with a thermostat Peltier cell holder in a quartz cuvette of 10 mm path length. Origin 9.0 Pro. Software was used for structure drawing and data analysis.

A. General Procedure for Synthesis of 3-(Phenylthio)-1H-indole Derivatives. Thioether derivatives were prepared following a modified procedure:[19] To a solution of 1*H*-indole (1 equiv) and thiophenol derivatives (1.1 equiv) in ethanol (20 mL) was added a solution of potassium iodide (1.1 equiv) and iodine (1.1 equiv) in 3:1 (v/v) water/ethanol (20 mL) at room temperature under open air. The resulting blackish red reaction mixture was attached with reflux condenser and stirred at 60 °C for 3 days. Then the reaction mixture was cooled to room temperature and diluted with ethyl acetate. The mixture was washed with 5% $Na_2S_2O_3$, water, and brine and then dried over anhydrous Na_2SO_4. The combined organic layer was concentrated under reduced pressure to afford the brown solid. The crude product was purified by column chromatography using ethyl acetate/hexane to afford the desired product.

B. General Procedure for Oxidation of Thioether Derivatives. In a 100 mL two-neck round-bottom flask equipped with a rubber septum and a magnetic bead was placed thioether (1 equiv). To this was added $NaHCO_3$ (0.2 M) aqueous solution with acetone (1:1 by volume), and Oxone (2.5 equiv) was added portionwise. The reaction mixture was stirred at room temperature under open air for 3 days. Excess solvent was removed using rotary evaporator, and then the crude mixture was poured into ice-cold water and extracted with EtOAc. The organic layer was washed with water and brine and dried over anhydrous Na_2SO_4. The combined organic layer was concentrated under reduced pressure to afford the crude sulfonyl derivative. The crude product was isolated by column chromatography using ethyl acetate/hexane to afford the desired product.

C. General Procedure for Protection of Sulfonyl Derivatives. A flame-dried round-bottom (RB) flask equipped with a magnetic stirring bar was charged with sulfonyl derivatives (1 equiv) in DMF, and it was cooled to 0 °C. NaH (2 equiv) was added in portionwise and stirred for 30 min followed by the addition of appropriate alkyl halide (1.1 equiv). The reaction mixture was stirred at 0 °C for 10 min, brought to room temperature, and then further stirred for 3−4 h. The reaction mixture was diluted with water and extracted with EtOAc. The organic layer was washed with water and brine and dried over Na_2SO_4. The combined organic layer was concentrated under reduced pressure and then purified by column chromatography using ethyl acetate/hexane to afford the desired product.

*3-(Phenylthio)-1H-indole (**1a-Int-1**).*[20] The title compound was prepared as described in general procedure A using indole (17.07 mmol, 1 equiv) as starting material. Yield: 3.5 g, 91%, pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) δ 8.42 (bs, 1H), 7.66 (d, J = 7.9 Hz, 1H), 7.51 (d, J = 2.1 Hz, 1H), 7.47 (d, J = 8.1 Hz, 1H), 7.33−7.29 (m, 1H), 7.22−7.18 (m, 3H), 7.15 (d, J = 7.4 Hz, 2H), 7.09 (t, J = 7.2 Hz, 1H).

*3-(Phenylsulfonyl)-1H-indole (**1a-Int-2**).* The title compound was prepared as described in procedure B using **1a-Int-1** (4.44 mmol, 1 equiv) as starting material. Yield: 960 mg, 84%, off-white solid. Mp: 146.2−154.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 9.34 (bs, 1H), 8.02−8.00 (m, 2H), 7.90−7.88 (m, 1H), 7.85 (d, J = 3.1 Hz, 1H), 7.50−7.42 (m, 3H), 7.40−7.38 (m, 1H), 7.26−7.22 (m, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 143.1, 136.4, 132.8, 130.2, 129.2, 126.8, 124.1, 123.6, 122.7, 119.5, 116.5, 112.5. IR (CH_2Cl_2, cm^{-1}) 3344, 3308, 1588, 1425, 1295, 1147. HRMS (ESI) m/z calcd for $C_{14}H_{11}NO_2S$ [M + H]$^+$; 258.0583, found: 258.0581.

*1-Benzyl-3-(phenylsulfonyl)-1H-indole (**1a**).* The title compound was prepared as described in procedure C using **1a-Int-2** (3.109 mmol, 1 equiv) as starting material. Yield: 640 mg, 59%, off-white solid. Mp: 204.1−214.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.03−8.01 (m, 2H), 7.96−7.92 (m, 1H), 7.82 (s, 1H), 7.51−7.44 (m, 3H), 7.35−7.29 (m, 4H), 7.27−7.23 (m, 2H), 7.14 (d, J = 6.6 Hz, 2H), 5.31 (s, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 143.5. 137.1, 135.2, 133.1, 132.6, 129.3, 129.1, 128.6, 127.4, 126.8, 124.6, 123.9, 122.7, 120.1, 115.8, 111.0, 51.1. IR (CH_2Cl_2, cm^{-1}) 2940, 2870, 1746, 1466, 1151. HRMS (ESI) m/z calcd for $C_{21}H_{17}NO_2S$ [M + H]$^+$; 348.1052, found: 348.1051.

*1-Methyl-3-(phenylsulfonyl)-1H-indole (**1b**).* The title compound was prepared as described in general procedure C using **1a-Int-2** (1.943 mmol, 1 equiv) as starting material. Yield: 452 mg, 86%, off-white solid. Mp: 160.5−165.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.04−8.01 (m, 2H), 7.95 (m, 1H), 7.77 (s, 1H), 7.50−7.43 (m, 3H), 7.35−7.31 (m, 2H), 7.30−7.27 (m, 1H), 3.83 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): 143.7, 137.4, 133.8, 132.5, 129.1, 126.8, 124.4, 123.8, 122.6, 120.0, 115.2, 110.4, 33.8. IR (neat, cm^{-1})

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3082, 2875, 1526, 1310, 1151, 757, 622. HRMS (ESI) m/z calcd for $C_{15}H_{13}NO_2S$ [M + H] $^+$; 272.0739, found: 272.0735.

*1-Ethyl-3-(phenylsulfonyl)-1H-indole (**1c**).* The title compound was prepared as described in general procedure C using **1a-Int-2** (1.943 mmol, 1 equiv) as starting material. Yield: 500 mg, 90%, off-white solid. Mp: 139.4−146.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.03 (d, J = 6.9 Hz, 2H), 7.94 (d, J = 7.7 Hz, 1H), 7.84(s, 1H), 7.49−7.43 (m, 3H), 7.36 (d, J = 8 Hz, 1H), 7.31−7.25 (m, 2H), 4.20 (q, 7.3 Hz, 2H), 1.52 (t, J = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 143.7, 136.6, 132.5, 132.1, 129.1, 126.8, 124.6, 123.6, 122.5, 120.1, 115.2, 110.5, 42.0, 15.1. IR (CH_2Cl_2, cm^{-1}): 3086, 2995, 1522, 1313, 1150, 751. HRMS (ESI) m/z calcd for $C_{16}H_{15}NO_2S$ [M + H]$^+$; 286.0896, found: 286.0892.

*5-Methoxy-3-(phenylthio)-1H-indole (**1d-Int-1**).*[21] The title compound was prepared as described in general procedure A using 5-methoxy indole (6.794 mmol, 1 equiv) as starting material. Yield: 1.5 g, 86%, dark green oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.30 (bs, 1H), 7.35 (d, J = 2.6 Hz, 1H), 7.24 (d, J = 8.7 Hz, 1H), 7.15−7.12 (m, 2H), 7.09−7.07 (m, 2H), 7.05−7.03 (m, 2H), 6.89 (dd, J = 8.8 Hz, 2.4 Hz, 1H), 3.74 (s, 3H).

*5-Methoxy-3-(phenylsulfonyl)-1H-indole (**1d-Int-2**).* The title compound was prepared as described in general procedure B using **1d-Int-1** (1.958 mmol, 1 equiv) as starting material. Yield: 330 mg, 59%, off-white solid. Mp: 151.5−158.4 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 12.15 (s, 1H), 8.11 (d, J = 3 Hz, 1H), 7.98 (dt, J = 6.5 Hz, 1.3 Hz, 2H), 7.61−7.53 (m, 3H), 7.40 (d, J = 8.9 Hz, 1H), 7.20 (d, J = 2.4 Hz, 1H), 6.88 (dd, J = 8.8 Hz, 2.4 Hz, 1H), 3.78 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6): δ (ppm) 155.2, 143.5, 132.6, 131.7, 131.2, 129.3, 126.1, 123.9, 114.1, 113.8, 113.1, 100.2, 55.4. IR (CH_2Cl_2, cm^{-1}): 3352, 3289, 1485, 1292, 1141. HRMS (ESI) m/z calcd for $C_{15}H_{13}NO_3S$ [M + H]$^+$; 288.0688, found: 288.0685.

*1-Benzyl-5-methoxy-3-(phenylsulfonyl)-1H-indole (**1d**).* The title compound was prepared as described in general procedure C using **1d-Int-2** (0.696 mmol, 1 equiv) as starting material. Yield: 235 mg, 89%, pale pink solid. Mp: 184.2−188.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.03−8.0 (m, 2H), 7.76 (s, 1H), 7.52−7.45 (m, 3H), 7.37 (d, J = 2.4 Hz, 1H), 7.35−7.31 (m, 3H), 7.17 (d, J = 9 Hz, 1H), 7.14−7.12 (m, 2H), 6.88 (dd, J = 9 Hz, 2.5 Hz, 1H), 5.28 (s, 2H), 3.85 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 156.3, 143.7, 135.2, 133.2, 132.6, 132.0, 129.2, 129.1, 128.6, 127.3, 126.7, 125.5, 115.0, 114.4, 111.9, 101.4, 56.0, 51.3. IR (CH_2Cl_2, cm^{-1}): 3134, 3048, 1519, 1304, 1229, 1151. HRMS (ESI) m/z calcd for $C_{22}H_{19}NO_3S$ [M + H]$^+$; 378.1158, found: 378.1154.

*5-Bromo-3-(phenylthio)-1H-indole (**1e-Int-1**).*[20] The title compound was prepared as described in general procedure A using 5-Bromo indole (5.1 mmol, 1 equiv) as starting material. Yield: 1.5 g, 97%, pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.43 (bs, 1H), 7.76 (d, J = 1.7 Hz, 1H), 7.49 (d, J = 2.6 Hz, 1H), 7.35 (dd, J = 8.6 Hz, 1.8 Hz, 1H), 7.31 (d, J = 8.5 Hz, 1H), 7.20−7.16 (m, 2H), 7.09−7.07 (m, 3H).

*5-Bromo-3-(phenylsulfonyl)-1H-indole (**1e-Int-2**).* The title compound was prepared as described in general procedure B using **1e-Int-1** (1.644 mmol, 1 equiv) as starting material. Yield: 430 mg, 78%, yellow solid. Mp: 147.3−152.4 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 12.49 (bs, 1H), 8.27 (d, J = 3.0 Hz, 1H), 7.97 (d, J = 7.0 Hz, 2H), 7.88 (s, 1H), 7.62−7.56 (m, 3H), 7.49 (d, J = 8.7 Hz, 1H), 7.38 (dd, J = 8.6 Hz, 1.6 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6): δ (ppm) 143.1, 135.2, 133.1, 132.9, 129.5, 126.2, 126.1, 126.0, 124.8, 120.6, 120.5, 115.1, 114.5, 114.3. IR (CH_2Cl_2, cm^{-1}): 3321, 3296, 3135, 1455, 1420, 1302, 1146, 731, 609. HRMS (ESI) m/z calcd for $C_{14}H_{10}BrNO_2S$ [M]$^+$; 335.9688, found: 335.9687.

*1-Benzyl-5-bromo-3-(phenylsulfonyl)-1H-indole (**1e**).* The title compound was prepared as described in general procedure C using **1e-Int-2** (1.487 mmol, 1 equiv) as starting material. Yield: 530 mg, 83%, white solid. Mp: 147.3−152.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.10 (d, J = 1.8 Hz, 1H), 8.02−7.99 (m, 2H), 7.80 (s, 1H), 7.55−7.47 (m, 3H), 7.35−7.33 (m, 4H), 7.16 (d, J = 8.8 Hz, 1H), 7.13−7.11 (m, 2H), 5.30 (s, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 143.2, 135.7, 134.7, 134.0, 132.9, 129.4, 129.3, 128.8, 127.3, 127.1, 126.8, 126.1, 122.7, 116.4, 115.6, 112.5, 51.4. IR (CH_2Cl_2, cm^{-1}): 3124, 1519, 1314, 1153, 699, 588. HRMS (ESI) m/z calcd for $C_{21}H_{16}BrNO_2S$ [M + 2]$^+$; 428.0130, found: 428.0130.

*6-Bromo-3-(phenylthio)-1H-indole (**1f-Int-1**).*[23] The title compound was prepared as described in general procedure A using 6-Bromo indole (5.1 mmol, 1 equiv) as starting material. Yield: 1.2 g, 77%, white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.41 (bs, 1H), 7.61 (d, J = 1.5 Hz, 1H), 7.47 (d, J = 2.5 Hz, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.26 (dd, J = 8.4 Hz, 1.7 Hz, 1H), 7.18−7.15 (m, 2H), 7.07 (d, J = 8.1 Hz, 3H).

*6-Bromo-3-(phenylsulfonyl)-1H-indole (**1f-Int-2**).* The title compound was prepared as described in general procedure B using **1f-Int-1** (0.986 mmol, 1 equiv) as starting material. Yield: 300 mg, 91%, off-white solid. Mp: 240.2−245.2 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 12.40 (s, 1H), 8.24 (s, 1H), 7.98 (dd, J = 7 Hz, 1.5 Hz, 2H), 7.74 (d, J = 8.5 Hz, 1H), 7.71 (d, J = 1.5 Hz, 1H), 7.64−7.56 (m, 3H), 7.37 (dd, J = 8.5 Hz, 1.7 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6): δ (ppm) 143.1, 137.3, 132.9, 132.6, 129.4, 126.2, 124.8, 122.2, 120.3, 115.9, 115.5, 115.0. IR (CH_2Cl_2, cm^{-1}): 3263, 3227, 1289, 1146, 731, 592. HRMS (ESI) m/z calcd for $C_{14}H_{10}BrNO_2S$ [M]$^+$; 335.9688, found: 335.9687.

*1-Benzyl-6-bromo-3-(phenylsulfonyl)-1H-indole (**1f**).* The title compound was prepared as described in general procedure C using **1f-Int-2** (0.595 mmol, 1 equiv) as starting material. Yield: 150 mg, 59%, off-white solid. Mp: 204.5−211.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.49 (s, 1H), 7.97 (d, J = 7.3 Hz, 2H), 7.90 (s, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.62−7.56 (m, 3H), 7.39−7.29 (m, 6H), 5.53 (s, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 143.2, 137.8, 134.7, 133.5, 132.8, 129.4, 129.2, 128.8, 127.3, 126.8, 126.1, 123.4, 121.4, 117.8, 116.4, 114.0, 51.2. IR (CH_2Cl_2, cm^{-1}): 3129, 3077, 1521, 1313, 1157, 750, 599. HRMS (ESI) m/z calcd for $C_{21}H_{16}BrNO_2S$ [M + 2]$^+$; 428.0130, found: 428.0130.

*3-(Phenylthio)-1H-pyrrolo[2,3-b]pyridine (**1g-Int-1**).*[21] The title compound was prepared as described in procedure A using 7-aza indole (4.23 mmol, 1 equiv) as starting material. Yield: 695 mg, 72%, off-white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 12.10 (bs, 1H), 8.42 (d, J = 4.6 Hz, 1H), 7.97 (d, J = 7.8 Hz, 1H), 7.72 (s, 1H), 7.17 (q, J = 7.5 Hz, 3H), 7.12−7.07 (m, 3H).

*3-(Phenylsulfonyl)-1H-pyrrolo[2,3-b] pyridine (**1g-Int-2**).* The title compound was prepared as described in general procedure B using **1g-Int-1** (1.77 mmol, 1 equiv) as starting material. Yield: 320 mg, 70%, pale violet solid. Mp: 257.9−259.8 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 12.89 (bs, 1H), 8.36 (dd, J = 4.7 Hz, 1.3 Hz, 1H), 8.35 (s, 1H), 8.18 (dd, J = 8.0 Hz, 1.4 Hz, 1H), 8.0 (d, J = 7.8 Hz, 2H), 7.62−7.55 (m, 3H), 7.27 (dd, J = 8.0 Hz, 4.7 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6): δ (ppm) 148.3, 145.0, 143.1, 133.1, 132.2, 129.6, 127.4, 126.4, 118.2, 115.8, 113.8. IR (CH_2Cl_2, cm^{-1}): 3152, 3026, 2938, 1591, 1417, 1310, 1152. HRMS (ESI) m/z calcd for $C_{13}H_{10}N_2O_2S$ [M + H]$^+$; 259.0532, found: 259.0532.

*1-Benzyl-3-(phenylsulfonyl)-1H-pyrrolo[2,3-b]pyridine (**1g**).* The title compound was prepared as described in general procedure C using **1g-Int-2** (0.774 mmol, 1 equiv) as starting material. Yield: 240 mg, 89%, off-white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.43 (d, J = 3.6 Hz, 1H), 8.23 (d, J = 7.8 Hz, 1H), 7.98 (d, 7.4 Hz, 2H), 7.88 (s, 1H), 7.51 (t, J = 7.2 Hz, 1H), 7.46 (t, J = 7.4 Hz, 2H), 7.33 (d, J = 6.8 Hz, 3H), 7.27−7.23 (m, 3H), 5.49 (s, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 147.7, 145.2, 143.1, 135.7, 132.9, 132.5, 129.3, 129.2, 128.5, 128.4, 128.2, 126.8, 118.7, 117.0, 114.7, 48.8. IR (CH_2Cl_2, cm^{-1}): 3137, 3076, 1522, 1312, 1154, 740. HRMS (ESI) m/z calcd for $C_{20}H_{16}N_2O_2S$ [M + H]$^+$; 349.1005, found: 349.1002.

*Methyl 3-(Phenylthio)-1H-indole-5-carboxylate (**1h-Int-1**).*[20] The title compound was prepared as described in general procedure A using methylindole-5-carboxylate (2.854 mmol, 1 equiv) as starting material. Yield: 700 mg, 86%, white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.81 (bs, 1H), 8.39 (s, 1H), 7.98 (dd, J = 8.6 Hz, 1.1 Hz, 1H), 7.55 (d, J = 2.4 Hz, 1H), 7.45 (d, J = 8.6 Hz, 1H), 7.17 (t, J = 7.6 Hz, 2H), 7.10−7.05 (m, 3H), 3.90 (s, 3H).

*Methyl 3-(Phenylsulfonyl)-1H-indole-5-carboxylate (**1h-Int-2**).* The title compound was prepared as described in general procedure B using **1h-Int-1** (1.765 mmol, 1 equiv) as starting material. Yield:

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500 mg, 90%, off-white solid. Mp: 201.9−205.3 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 12.65 (bs, 1H), 8.45 (d, J = 1.1 Hz, 1H), 8.37 (d, J = 1.8 Hz, 1H), 7.97−7.95 (m, 2H), 7.86 (dd, J = 8.6 Hz, 1.6 Hz, 1H), 7.62−7.58 (m, 4H), 3. 87 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6): δ (ppm) 166.6, 143.2, 139.0, 133.9, 133.0, 129.6, 126.1, 124.1, 123.4, 122.9, 120.7, 115.7, 113.2, 52.1. IR (CH_2Cl_2, cm^{-1}): 3357, 3277, 1700, 1309, 1148. HRMS (ESI) m/z calcd for $C_{16}H_{13}NO_4S$ [M + H]$^+$; 316.0638, found: 316.0633.

*Methyl 1-Benzyl-3-(phenylsulfonyl)-1H-indole-5 carboxylate (**1h**).* The title compound was prepared as described in general procedure C using **1h-Int-2** (0.634 mmol, 1 equiv) as starting material. Yield: 200 mg, 78%, white solid. Mp: 209.9−213.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.68 (d, J = 1 Hz, 1H), 8.04 (td, J = 6.8 Hz, 1.2 Hz, 2H), 7.96 (dd, J = 8.7 Hz, 1.6 Hz, 1H), 7.87 (s, 1H), 7.54−7.46 (m, 3H), 7.35−7.33 (m, 4H), 7.15−7.13 (m, 2H), 5.34 (s, 2H), 3.94 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 167.3, 143.2, 139.4, 134.7, 134.5, 134.4, 132.9, 129.4, 129.3, 128.8, 127.4, 126.9, 125.3, 124.9, 124.2, 122.7, 117.5, 110.8, 52.3, 51.4. IR (CH_2Cl_2, cm^{-1}): 3075, 2967, 1725, 1320, 1254, 1154. HRMS (ESI) m/z calcd for $C_{23}H_{19}NO_4S$ [M + H]$^+$; 406.1107, found: 406.1100.

*5-Nitro-3-(phenylthio)-1H-indole (**1i-Int-1**).*[20] The title compound was prepared as described in general procedure A using 5-nitroindole (6.167 mmol, 1 equiv) as starting material. Yield: 1.4 g, 84%, pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 8.90 (bs, 1H), 8.57 (d, J = 2.1 Hz, 1H), 8.17 (dd, J = 9.0 Hz, 2.2 Hz, 1H), 7.66 (d, J = 2.5 Hz, 1H), 7.51 (d, J = 8.9 Hz, 1H), 7.21−7.18 (m, 2H), 7.13−7.10 (m, 3H).

*5-Nitro-3-(phenylsulfonyl)-1H-indole (**1i-Int-2**).* The title compound was prepared as described in general procedure B using **1i-Int-1** (3.699 mmol, 1 equiv) as starting material. Yield: 700 mg, 63%, pink solid. Mp: 241.1−242.8 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 12.94 (bs, 1H), 8.64 (d, J = 2.2 Hz, 1H), 8.52 (s, 1H), 8.12 (dd, J = 9.0 Hz, 2.2 Hz, 1H), 8.02−8.00 (m, 2H), 7.71 (d, J = 9 Hz, 1H), 7.64−7.57 (m, 3H). ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) 142.8, 142.7, 139.5, 135.7, 133.2, 129.7, 126.3, 122.6, 118.6, 116.9, 115.0, 114.0. IR (CH_2Cl_2, cm^{-1}): 3113, 2872, 1526, 1340, 1144. HRMS (ESI) m/z calcd for $C_{14}H_{10}N_2O_4S$ [M + H]$^+$; 303.0434, found: 303.0432.

*1-Benzyl-5-nitro-3-(phenylsulfonyl)-1H-indole (**1i**).* The title compound was prepared as described in general procedure C using **1i-Int-2** (0.992 mmol, 1 equiv) as starting material. Yield: 250 mg, 64%, yellow solid. Mp: 208−210.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.84 (d, J = 2.1 Hz, 1H), 8.12 (dd, J = 9.1 Hz, 2.2 Hz, 1H), 8.03 (t, J = 7.8 Hz, 2H), 7.97 (s, 1H), 7.57−7.49 (m, 3H), 7.39−7.35 (m, 4H), 7.16−7.14 (m, 2H), 5.38 (s, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 143.9, 142.6, 139.7, 135.9, 134.1, 133.3, 129.5, 129.1, 127.4, 127.0, 124.0, 119.4, 118.8, 117.1, 111.4, 51.7. IR (CH_2Cl_2, cm^{-1}): 3128, 3074, 1528, 1343, 1153, 737. HRMS (ESI) m/z calcd for $C_{21}H_{16}N_2O_4S$ [M + H]$^+$; 393.0903, found: 393.0903.

*3-(p-Tolylthio)-1H-indole (**1j-Int-1**).*[21] The title compound was prepared as described in general procedure **A** using indole (4.268 mmol, 1 equiv) as starting material. Yield: 500 mg, 49%, white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.38 (bs, 1H), 7.62 (d, J = 7.9 Hz, 1H), 7.48 (d, J = 2.6 Hz, 1H), 7.43 (d, J = 8.1 Hz, 1H), 7.28−7.24 (m, 1H), 7.16 (t, J = 7.5 Hz, 1H), 7.03 (d, J = 6.4 Hz, 2H), 6.98 (d, J = 8.1 Hz, 2H), 2.25 (s, 3H).

*3-Tosyl-1H-indole (**1j-Int-2**).* The title compound was prepared as described in general procedure B using **1j-Int-1** (0.794 mmol, 1 equiv) as starting material. Yield: 200 mg, 93%, white solid. Mp: 172.5−178.7 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 12.23 (bs, 1H), 8.16 (s, 1H), 7.85 (d, J = 8.2 Hz, 2H), 7.76 (d, J = 7.8 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.25−7.17 (m, 2H), 2.30 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6): δ (ppm) 143.1, 140.6, 136.4, 131.3, 129.7, 126.3, 123.1, 121.7, 118.6, 115.0, 112.8, 20.9. IR (CH_2Cl_2, cm^{-1}): 3341, 3307, 1604, 1425, 1294, 1146, 687. HRMS (ESI) m/z calcd for $C_{15}H_{13}NO_2S$ [M + H]$^+$; 272.0739, found: 272.0736.

*1-Benzyl-3-tosyl-1H-indole (**1j**).* The title compound was prepared as described in general procedure C using **1j-Int-2** (0.626 mmol, 1 equiv) as starting material. Yield: 190 mg, 84%, off-white solid. Mp: 175.5−181.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.93−7.90 (m, 3H), 7.80 (s, 1H), 7.35−7.28 (m, 4H), 7.26−7.23 (m, 4H), 7.15−7.14 (m, 2H), 5.31 (s, 2H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 143.4, 140.6, 137.1, 135.3, 132.9, 129.8, 129.2, 128.5, 127.3, 126.9, 124.6, 123.9, 122.6, 120.1, 116.3, 110.9, 51.1, 21.6. IR (CH_2Cl_2, cm^{-1}): 3130, 3078, 1523, 1151, 746, 679. HRMS (ESI) m/z calcd for $C_{22}H_{19}NO_2S$ [M + H]$^+$; 362.1209, found: 362.1203.

*3-(o-Tolylthio)-1H-indole (**1k-Int-1**).*[22] The title compound was prepared as described in general procedure **A** using indole (4.268 mmol, 1 equiv) as starting material. Yield: 580 mg, 57%, white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.38 (bs, 1H), 7.60 (d, J = 7.9 Hz, 1H), 7.45 (d, J = 9.5 Hz, 2H), 7.29 (t, J = 8.1 Hz, 1H), 7.19−7.14 (m, 2H), 6.99 (t, J = 7.1 Hz, 1H), 6.91 (t, J = 7.3 Hz, 1H), 6.74 (d, J = 7.8 Hz, 1H), 2.51 (s, 3H).

*3-(o-Tolylsulfonyl)-1H-indole (**1k-Int-2**).* The title compound was prepared as described in general procedure B using **1k-Int-1** (0.418 mmol, 1 equiv) as starting material. Yield: 112 mg, 99%, off-white solid. Mp: 189.3−193.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 9.45 (bs, 1H), 8.26 (d, J = 7.7 Hz, 1H), 7.86 (d, J = 3 Hz, 1H), 7.69 (d, J = 7.9 Hz, 1H), 7.43−7.35 (m, 3H), 7.24−7.15 (m, 3H), 2.54 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 140.4, 137.7, 136.4, 133.2, 132.8, 130.7, 128.7, 126.5, 124.1, 123.5, 122.5, 119.3, 115.7, 112.4, 20.1. IR (CH_2Cl_2, cm^{-1}): 3380, 3313, 1295, 1146, 687, 584. HRMS (ESI) m/z calcd for $C_{15}H_{13}NO_2S$ [M + H]$^+$; 272.0739, found: 272.0737.

*1-Benzyl-3-(o-tolylsulfonyl)-1H-indole (**1k**).* The title compound was prepared as described in general procedure C using **1k-Int-2** (0.368 mmol, 1 equiv) as starting material. Yield: 117 mg, 88%, off-white solid. Mp: 175.9−183.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.27 (dd, J = 7.7 Hz, 1.2 Hz, 1H), 7.87 (s, 1H), 7.72 (d, J = 7.9 Hz, 1H), 7.41 (td, J = 7.4 Hz, 1.4 Hz, 1H), 7.37 (d, J = 7.4 Hz, 1H), 7.35−7.30 (m, 4H), 7.25−7.22 (m, 1H), 7.20−7.15 (m, 4H), 5.35 (s, 2H), 2.54 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 140.7, 137.6, 137.0, 135.4, 133.7, 133.0, 132.7, 129.3, 128.8, 128.6, 127.3, 126.5, 124.6, 123.9, 122.6, 120.0, 115.1, 110.9, 51.1, 20.1. IR (CH_2Cl_2, cm^{-1}): 3074, 2940, 1522, 1309, 1158. HRMS (ESI) m/z calcd for $C_{22}H_{19}NO_2S$ [M + H]$^+$; 362.1209, found: 362.1203.

*3-((4-Methoxyphenyl)thio)-1H-indole (**1l-Int-1**).*[21] The title compound was prepared as described in general procedure A using indole (4.268 mmol, 1 equiv) as starting material. Yield: 350 mg, 32%, off-white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.31 (s, 1H), 7.62 (d, J = 7.9 Hz, 1H), 7.43 (d, J = 2.5 Hz, 1H), 7.39 (d, J = 8.1 Hz, 1H), 7.25−7.22 (m, 1H), 7.16−7.12 (m, 3H), 6.73 (d, J = 8.8 Hz, 2H), 3.72 (s, 3H).

*3-((4-Methoxyphenyl)sulfonyl)-1H-indole (**1l-Int-2**).* The title compound was prepared as described in general procedure B using **1l-Int-1** (0.783 mmol, 1 equiv) as starting material. Yield: 167 mg, 74%, off-white solid. Mp: 154.6−162.8 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 9.41 (bs, 1H), 7.94 (dt, J = 8.9 Hz, 2.9 Hz, 2H), 7.88−7.85 (m, 1H), 7.81 (d, J = 3.0 Hz, 1H), 7.40−7.37 (m, 1H), 7.25−7.20 (m, 2H), 6.90 (dt, J = 8.9 Hz, 2.8 Hz, 2H), 3.79 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6): δ (ppm) 163.0, 136.5, 134.8, 129.8, 129.0, 124.0, 123.4, 122.5, 119.4, 117.1, 114.4, 112.5, 55.7. IR (CH_2Cl_2, cm^{-1}): 3340, 1602, 1506, 1267, 1142. HRMS (ESI) m/z calcd for $C_{15}H_{13}NO_3S$ [M + H]$^+$; 288.0688, found: 288.0684.

*1-Benzyl-3-((4-methoxyphenyl)sulfonyl)-1H-indole (**1l**).* The title compound was prepared as described in general procedure C using **1l-Int-2** (0.348 mmol, 1 equiv) as starting material. Yield: 125 mg, 95%, pink solid. Mp: 168.1−178.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.99 (d, J = 8.0 Hz, 2H), 7.94−7.93 (m, 1H), 7.83 (s, 1H), 7.38−7.31 (m, 4H), 7.29−7.26 (m, 2H), 7.17 (d, J = 6.7 Hz, 2H), 6.95 (d, J = 9.5 Hz, 2H), 5.33 (s, 2H), 3.83 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 162.9, 137.0, 135.3, 135.2, 132.7, 129.2, 129.0, 128.5, 127.3, 124.4, 123.8, 122.5, 120.0, 116.6, 114.3, 110.9, 55.7, 51.0. IR (CH_2Cl_2, cm^{-1}): 3131, 2949, 2853, 1602, 1521, 1265, 1147, 744. HRMS (ESI) m/z calcd for $C_{22}H_{19}NO_3S$ [M + H]$^+$; 378.1158, found: 378.1157.

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*3-((4-Bromophenyl)thio)-1H-indole (**1m-Int-1**).*[22] The title compound was prepared as described in general procedure A using indole (8.536 mmol, 1 equiv) as starting material. Yield: 320 mg, 12%, off-white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.41 (bs, 1H), 7.56 (d, J = 7.9 Hz, 1H), 7.47 (d, J = 2.6 Hz, 1H), 7.43 (d, J = 8.2 Hz, 1H), 7.29−7.24 (m, 3H), 7.17 (t, J = 7.5 Hz, 1H), 6.95 (d, J = 8.6 Hz, 2H).

*3-((4-Bromophenyl)sulfonyl)-1H-indole (**1m-Int-2**).* The title compound was prepared as described in general procedure B using **1m-Int-1** (0.986 mmol, 1 equiv) as starting material. Yield: 280 mg, 84%, off-white solid. Mp: 187.0−188.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 12.34 (bs, 1H), 8.21 (d, J = 3.1 Hz, 1H), 7.89 (dd, J = 6.8 Hz, 1.7 Hz, 2H), 7.76 (d, J = 8.5 Hz, 3H), 7.51 (d, J = 8 Hz, 1H), 7.27−7.19 (m, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 142.7, 136.5, 132.5, 132.0, 128.3, 126.6, 123.3, 123.0, 122.0, 118.5, 114.0, 113.0. IR (CH_2Cl_2, cm^{-1}): 3326, 3136, 1713, 1581, 1425, 1147, 749. HRMS (ESI) m/z calcd for $C_{14}H_{10}BrNO_2S$ [M + 2]$^+$; 337.9660, found: 337.9660.

*1-Benzyl-3-((4-bromophenyl)sulfonyl)-1H-indole (**1m**).* The title compound was prepared as described in general procedure C using **1m-Int-2** (0.654 mmol, 1 equiv) as starting material. Yield: 250 mg, 90%, off-white solid. Mp: 180.7−185.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.92−7.89 (m, 1H), 7.87 (dt, J = 8.6 Hz, 2.4 Hz, 2H), 7.80 (s, 1H), 7.59 (dt, J = 8.6 Hz, 2.4 Hz, 2H), 7.36−7.31 (m, 4H), 7.29−7.26 (m, 2H), 7.16−7.14 (m, 2H), 5.32 (s, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 142.6, 137.1, 135.1, 133.2, 132.4, 129.3, 128.7, 128.4, 127.6, 127.4, 124.5, 124.1, 122.9, 119.9, 115.4, 111.1, 51.2. IR (CH_2Cl_2, cm^{-1}): 3126, 3082, 1521, 1318, 1152, 748. HRMS (ESI) m/z calcd for $C_{21}H_{16}BrNO_2S$ [M + 2]$^+$; 428.0130, found: 428.0130.

*3-((4-Nitrophenyl)thio)-1H-indole (**1n-Int-1**).*[19] The title compound was prepared as described in general procedure A using indole (8.536 mmol, 1 equiv) as starting material. Yield: 2.23 g, 97%, yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.62 (bs, 1H), 8.0 (dt, J = 9 Hz, 2.6 Hz, 2H), 7.55−7.50 (m, 3H), 7.32 (t, J = 7.6 Hz, 1H), 7.20 (t, J = 7.5 Hz, 1H), 7.13 (dt, J = 9 Hz, 2.6 Hz, 2H).

*5-Nitro-3-(phenylsulfonyl)-1H-indole (**1n-Int-2**).* The title compound was prepared as described in general procedure B using **1n-Int-1** (3.699 mmol, 1 equiv) as starting material. Yield: 700 mg, 63%, off-white solid. Mp: 241.1−242.8 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm): δ (ppm) 12.46 (bs, 1H), 8.35 (d, J = 8.8 Hz, 2H), 8.30 (d, J = 3.1 Hz, 1H), 8.22 (d, J = 8.8 Hz, 2H), 7.79 (d, J = 7.7 Hz, 1H), 7.52 (d, J = 7.9 Hz, 1H), 7.28−7.22 (m, 2H). ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) 149.7, 148.6, 136.5, 132.8, 127.8, 124.8, 123.5, 123.1, 122.2, 118.4, 113.1, 113.0. HRMS (ESI) m/z calcd for $C_{14}H_{10}N_2O_4S$ [M + H]$^+$; 303.0434, found: 303.0432.

*1-Benzyl-3-((4-nitrophenyl)sulfonyl)-1H-indole (**1n**).* The title compound was prepared as described in general procedure C using **1n-Int-2** (1.654 mmol, 1 equiv) as starting material. Yield: 619 mg, 95%, yellow solid. Mp: 145.4−150.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.29 (dt, J = 8.9 Hz, 2.2 Hz, 2H), 8.18 (dt, J = 8.9 Hz, 2.2 Hz, 2H), 7.95−7.92 (m, 1H), 7.84 (s, 1H), 7.38−7.34 (m, 4H), 7.33−7.30 (m, 2H), 7.17−7.15 (m, 2H), 5.34 (s, 2H): ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 150.0, 149.2, 137.2, 134.8, 133.9, 129.4, 128.8, 128.1, 127.4, 124.5, 124.4, 123.3, 119.7, 114.2, 111.3, 51.3. IR (CH_2Cl_2, cm^{-1}): 3126, 3052, 2873, 1536, 1356, 1156, 746. HRMS (ESI) m/z calcd for $C_{21}H_{16}N_2O_4S$ [M + H]$^+$; 393.0903, found: 393.0902.

*3-(Methylsulfonyl)-1H-indole (**1o-Int-2**).* The title compound was prepared as described in the reported procedure[24] with indole (4.268 mmol, 1 equiv) as starting material. Yield: 350 mg, 42%, off-white solid. Mp: 161.8−164 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 9.06 (bs, 1H), 7.93 (d, J = 7.3 Hz, 1H), 7.80 (d, J = 1.8 Hz, 1H)7.48 (d, J = 7.5 Hz, 1H), 7.35−7.30 (m, 2H), 3.18 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 136.3, 129.8, 124.3, 123.7, 122.8, 119.4, 116.5, 112.4, 45.5. IR (CH_2Cl_2, cm^{-1}): 3143.7, 1424.9, 1298, 1130, 759.3. HRMS (ESI) m/z calcd for $C_9H_9NO_2S$ [M + H]$^+$; 196.0426, found: 196.0426.

*1-Benzyl-3-(methylsulfonyl)-1H-indole (**1o**).* The title compound was prepared as described in general procedure C using **1o-Int-1** (1.536 mmol, 1 equiv) as starting material. Yield: 290 mg, 66%, off-white solid. Mp: 132.0−136.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.97−7.94 (m, 1H), 7.74 (s, 1H), 7.40−7.32 (m, 6H), 7.18 (d, J = 7 Hz, 2H), 5.34 (s, 2H), 3.17 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 137.0, 135.2, 132.9, 129.3, 128.6, 127.5, 124.6, 124.0, 122.8, 119.8, 115.3, 111.1, 51.1, 45.6. IR (CH_2Cl_2, cm^{-1}): 3129, 3052, 2940, 1525, 1306, 1142, 757. HRMS (ESI) m/z calcd for $C_{16}H_{15}NO_2S$ [M + H]$^+$; 286.0896, found: 286.0891.

*3-(Benzylthio)-1H-indole (**1p-Int-1**).*[25] The title compound was prepared as described in general procedure A using indole (8.536 mmol, 1 equiv) as starting material. Yield: 1.3 g, 64%, off-white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.93 (bs, 1H), 7.68 (d, J = 7.4 Hz, 1H), 7.22−7.13 (m, 6H), 7.04−7.02 (m, 2H), 6.83 (d, J = 2.5 Hz, 1H).

*3-(Benzylsulfonyl)-1H-indole (**1p-Int-2**).* The title compound was prepared as described in general procedure B using **1p-Int-1** (3.51 mmol, 1 equiv) as starting material. Yield: 700 mg, 73%, off-white solid. Mp: 153.8−156.2 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 12.14 (bs, 1H), 7.75 (d, J = 3.0 Hz, 1H), 7.59 (d, J = 8 Hz, 1H), 7.52 (d, J = 8.2 Hz, 1H), 7.29−7.21 (m, 4H), 7.15 (t, J = 7.6 Hz, 1H), 7.09 (d, J = 7.0 Hz, 2H), 4.54 (s, 2H). ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6): δ (ppm) 136.1, 132.1, 130.8, 129.6, 128.1, 124.0, 123.0, 121.5, 118.9, 112.7, 112.2, 62.2. IR (CH_2Cl_2, cm^{-1}): 3356, 3321, 1516, 1299, 1117. HRMS (ESI) m/z calcd for $C_{15}H_{13}NO_2S$ [M + H]$^+$; 272.0735, found: 272.0734.

*1-Benzyl-3-(benzylsulfonyl)-1H-indole (**1p**).* The title compound was prepared as described in general procedure C using **1p-Int-2** (1.842 mmol, 1 equiv) as starting material. Yield: 650 mg, 97%, off-white solid. Mp: 161.1−162.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.78 (d, J = 7.1 Hz, 1.5 Hz, 1H), 7.33−7.30 (m, 4H), 7.29−7.23 (m, 4H), 7.17 (t, J = 7.6 Hz, 2H), 7.05−7.02 (m, 4H), 5.23 (s, 2H), 4.40 (s, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 136.7, 135.3, 134.4, 130.8, 129.5, 129.2, 128.5, 127.2, 125.1, 123.9, 122.8, 120.0, 111.8, 110.9, 63.2, 51.0. IR (CH_2Cl_2, cm^{-1}): 3051, 2935, 1523, 1311. HRMS (ESI) m/z calcd for $C_{22}H_{19}NO_2S$ [M + H]$^+$; 362.1203, found: 362.1201.

D. General Experimental Procedure for C2-Biarylation of Indole Derivatives. To a 15 mL flame-dried sealed tube equipped with a magnetic stir bar were added indole derivatives (30 mg, 1 equiv), and then, the tube was evacuated and refilled with argon. To this were added $Pd(OAc)_2$ (20 mol %), Ag_2CO_3 (2.5 equiv), aryl iodide (10 equiv), HFIP (0.12 M), and TFA (10 equiv). Then, the reaction mixture was stirred at 70 °C in preheated oil bath for 24 h. The resulting mixture was cooled to room temperature, quenched with saturated $NaHCO_3$(5 mL), and diluted with EtOAc (5 mL). The crude mixture was washed with brine solution (10 mL), extracted with ethyl acetate (3 × 5 mL), and dried over anhydrous Na_2SO_4. The combined organic layer was evaporated under reduced pressure, and the crude product was purified by column chromatography using ethyl acetate/hexane.

*2-([1,1′-Biphenyl]-2-yl)-1-benzyl-3-(phenylsulfonyl)-1H-indole (**3aa**).* The title compound was prepared as described in general procedure D using **1a** (0.086 mmol, 1 equiv) and iodobenzene (**2a**, 0.86 mmol) as starting materials and purified by column chromatography using 10% ethyl acetate/hexane. Yield: 38 mg, 88%, white solid. Mp: 129.2−135.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.38 (d, J = 8.1 Hz, 1H), 7.74 (d, J = 8 Hz, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.50 (d, J = 7.7 Hz, 1H), 7.44 (t, J = 6.9 Hz, 1H), 7.36 (t, J = 7.3 Hz, 3H),7.31−7.27 (m, 2H), 7.15−7.02 (m, 7H), 6.96−6.92 (m, 3H), 6.58 (d, J = 7.5 Hz, 2H), 4.70 (d, J = 16.3 Hz, 1H), 4.56 (d, J = 16.3 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 144.2, 144.1, 142.2, 139.9, 135.8, 135.4, 133.5, 132.6, 130.7, 130.4, 130.2, 128.9, 128.7, 128.5, 127.6, 127.4, 127.1, 126.9, 126.4, 125.7, 123.5, 122.8, 120.8, 114.5, 111.3, 47.9. IR (CH_2Cl_2, cm^{-1}): 3078,1461, 1328, 1152, 748. HRMS (ESI) m/z calcd for $C_{33}H_{25}NO_2S$ [M + H]$^+$; 500.1678, found: 500.1678.

*2-([1,1′-Biphenyl]-2-yl)-1-methyl-3-(phenylsulfonyl)-1H-indole (**3ba**).* The title compound was prepared as described in general procedure D using **1b** (0.11 mmol, 1 equiv) and iodobenzene (**2a**, 1.1 mmol) as starting materials and purified by column chromatography

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using 20% ethyl acetate/hexane. Yield: 39 mg, 83%, white solid. Mp: 178.2−161.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.35 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 7.3 Hz, 2H), 7.63−7.60 (m, 1H), 7.53−7.51 (m, 1H), 7.47−7.40 (m, 2H), 7.36−7.31 (m, 4H), 7.26 (t, J = 8.0 Hz, 1H), 7.12 (d, J = 8.2 Hz, 1H), 7.08 (t, J = 7.3 Hz, 1H), 7.02 (t, J = 7.4 Hz, 2H), 6.88 (d, J = 7.2 Hz, 2H), 3.01 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 144.2, 144.1, 142.5, 140.0, 135.8, 133.1, 132.5, 130.6, 130.0, 128.9, 128.5, 128.4, 127.3, 127.2, 126.9, 126.7, 125.4, 123.4, 122. 7, 120. 7, 113. 5, 110.0, 30.7. IR (CH_2Cl_2, cm^{-1}): 3076, 2942, 1469, 1310, 1153. HRMS (ESI) m/z calcd for $C_{27}H_{21}NO_2S$ [M + H]$^+$; 424.1365, found: 424.1363.

*2-([1,1′-Biphenyl]-2-yl)-1-ethyl-3-(phenylsulfonyl)-1H-indole (**3ca**).* The title compound was prepared as described in general procedure D using **1c** (0.105 mmol, 1 equiv) and iodobenzene (**2a**, 1.05 mmol) as starting materials and purified by column chromatography using 20% ethyl acetate/hexane. Yield: 29 mg, 63%, white solid. Mp: 182.4−194.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.37 (d, J = 7.9 Hz, 1H), 7.74−7.72 (m, 2H), 7.62 (td, J = 8.7 Hz, 1.15 Hz, 1 H), 7.54 (d, J = 7.7 Hz, 1H), 7. 43 (td, J = 8.6 Hz, 1.2 Hz, 2H), 7.36−7.31 (m, 3H), 7.28−7.27 (m, 2H), 7.20 (d, J = 8.1 Hz, 1H), 7.12−7.01 (m, 5H), 3.56 (q, J = 14.5 Hz, 2 H), 0.87 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 143.7, 136.6, 132.5, 132.1, 129.1, 126.8, 124.6, 123.6, 122.5, 120.1, 115.2, 110.5, 42.0, 15.1. IR (CH_2Cl_2, cm^{-1}): 3076, 2992, 2946, 1309, 1151. HRMS (ESI) m/z calcd for $C_{28}H_{23}NO_2S$ [M + H]$^+$; 438.1522, found: 438.1522.

*2-([1,1′-Biphenyl]-2-yl)-1-benzyl-5-methoxy-3-(phenylsulfonyl)-1H-indole (**3da**).* The title compound was prepared as described in general procedure D using **1d** (0.08 mmol, 1 equiv) and iodobenzene (**2a**, 0.80 mmol) as starting materials and purified by column chromatography using 15−20% ethyl acetate/hexane. Yield: 14.3 mg, 34%, white solid. Mp: 201.4−204.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.86 (d, J = 2.4 Hz, 1H), 7.72 (d, J = 8.3 Hz, 2H), 7.57 (td, J = 8.95 Hz, 1.4 Hz, 1H), 7.49−7.43 (m, 2H), 7−37−7.34 (m, 3H), 7.29 (dd, J = 7.6 Hz, 1.2 Hz, 1H), 7.14−7.02 (m, 7H), 6.89−6.88 (m, 2H), 6.81 (d, J = 8.9 Hz, 1H), 6.77 (dd, J = 8.9 Hz, 2.4 Hz, 1H), 6.57 (d, J = 6.8 Hz, 2H), 4.66 (d, J = 16.3 Hz, 1H), 4.48 (d, J = 16.3 Hz, 1H), 3.92 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 156.2, 144.2, 144.1, 142.2, 139.9, 135.8, 133.6, 132.6, 130.6, 130.3, 130.1, 128.9, 128.7, 128.5, 127.6, 127.4, 127.1, 126.9, 126.8, 126.5, 126.3, 114.1, 113.9, 112.2, 102.0, 56.0, 48.0. IR (CH_2Cl_2, cm^{-1}): 3075, 2944, 2849, 1460, 1296, 1150, 732, 598. HRMS (ESI) m/z calcd for $C_{34}H_{27}NO_3S$ [M + H]$^+$; 530.1784, found: 530.1781.

*1-Benzyl-5-methoxy-2-phenyl-3-(phenylsulfonyl)-1H-indole (**4da**).* The title compound was prepared as described in general procedure D using **1d** (0.08 mmol, 1 equiv) and iodobenzene (**2a**, 0.80 mmol) as starting materials and purified by column chromatography using 15−20% ethyl acetate/hexane. Yield: 13 mg, 36%, white solid. Mp: 151.8−156.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.84 (d, J = 2.4 Hz, 1H), 7.62−7.60 (m, 2H), 7.48−7.40 (m, 2H), 7.38−7.35 (m, 2H), 7.32−7.29 (m, 2H), 7.22−7.19 (m, 5H), 7.09 (d, J = 8.9 Hz, 1H), 6.89 (dd, J = 8.9 Hz, 2.5 Hz, 1H), 6.83−6.82 (m, 2H), 5.06 (s, 2H), 3.94 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 156.4, 144.7, 144.2, 136.3, 132.3, 131.0, 130.7, 129.9, 129.0, 128.9, 128.7, 128.2, 127.8, 126.6, 126.2, 126.1, 114.4, 113.5, 112.0, 102.2, 56.0, 48.0. IR (CH_2Cl_2, cm^{-1}): 3077, 2951, 2849, 1454, 1296, 1149. HRMS (ESI) m/z calcd for $C_{28}H_{23}NO_3S$ [M + H]$^+$; 454.1471, found: 454.1466.

*2-([1,1′-Biphenyl]-2-yl)-1-benzyl-5-bromo-3-(phenylsulfonyl)-1H-indole (**3ea**).* The title compound was prepared as described in general procedure D using **1e** (0.070 mmol, 1 equiv) and iodobenzene (**2a**, 0.70 mmol) as starting materials with extended reaction time (36 h) and purified by column chromatography using 10−15% ethyl acetate/hexane. Yield: 30.5 mg, 75%, white solid. Mp: 130.3−133.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.59 (s, 1H), 7.71 (d, J = 7.8 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.50−7.45 (m, 2H), 7.39−7.36 (m, 3H), 7.31 (d, J = 7.6 Hz, 1H), 7.22 (d, J = 8.7 Hz, 1H), 7.14−7.02 (m, 6H), 6.84−6.78 (m, 3H), 6.55 (d, J = 7.2 Hz, 2H), 4.67 (d, J = 16.2 Hz, 1H), 4.47 (d, J = 16.3 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 145.1, 143.6, 142.1, 139.6, 135.3, 134.0, 133.5, 132.8, 130.9, 130.2, 129.0, 128.8, 128.5, 127.8, 127.5, 127.2, 127.1, 127.0, 126.7, 126.5, 126.3, 123.4, 116.5, 114.3, 112.8, 48.0. IR (CH_2Cl_2, cm^{-1}): 3078, 2940, 1458, 1393, 1320, 1151, 743, 591. HRMS (ESI) m/z calcd for $C_{33}H_{24}BrNO_2S$ [M]$^+$; 578.0783, found: 578.0768.

*2-([1,1′-Biphenyl]-2-yl)-1-benzyl-6-bromo-3-(phenylsulfonyl)-1H-indole (**3fa**).* The title compound was prepared as described in general procedure D using **1f** (0.070 mmol, 1 equiv) and iodobenzene (**2a**, 0.70 mmol) as starting materials and purified by column chromatography using 15−20% ethyl acetate/hexane. Yield: 30.2 mg, 74%, white solid. Mp: 101.1−109.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.29 (d, J = 8.6 Hz, 1H), 7.71−7.69 (m, 2H), 7.59 (td, J = 7.6 Hz, 1.4 Hz, 1H), 7.50 (dd, J = 7.8 Hz, 0.9 Hz, 1H), 7.46 (tt, J = 7.5 Hz, 1.2 Hz, 1H), 7.41−7.35 (m, 4H), 7.29 (dd, J = 7.6 Hz, 1.1 Hz, 1H), 7.15−7.08 (m, 5H), 7.06−7.03 (m, 2H), 6.85 (d, J = 7.4 Hz, 2H) 6.57 (d, J = 1.4 Hz, 2H), 4.66 (d, J = 16.3, 1H), 4.48 (d, J = 16.3 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 144.7, 143.7, 142.1, 139.7, 137.6, 136.2, 135.2, 133.5, 132.8, 130.9, 130.4, 130.2, 129.0, 128.8, 128.5, 127.8, 127.6, 127.0, 126.9, 126.5, 126.3, 126.1, 124.6, 122.2, 117.2, 115.0, 114.1, 47.9. IR (CH_2Cl_2, cm^{-1}): 3076, 2938, 1456, 1151, 740, 696, 601. HRMS (ESI) m/z calcd for $C_{33}H_{24}BrNO_2S$ [M + 2]$^+$; 580.0742, found: 580.0743.

*2-([1,1′-Biphenyl]-2-yl)-1-benzyl-3-(phenylsulfonyl)-1H-pyrrolo-[2,3-b]pyridine (**3ga**).* The title compound was prepared by following a modified general procedure D: A 10 mL flame-dried RB flask was equipped with **1g** (0.0861 mmol, 1 equiv), and the flask was evacuated and refilled with argon. To this were added $Sc(OTf)_3$ (0.172 mmol, 2 equiv) and HFIP (0.4 mL), and the mixture was stirred for 30 min at room temperature. Then the reaction mixture was transferred to a sealed tube containing $Pd(OAc)_2$ (0.017 mmol, 20 mol %), Ag_2CO_3 (0.215 mmol, 2.5 equiv), iodobenzene (0.86 mmol, 10 equiv), and HFIP (0.3 mL). TFA was added to this combined mixture (0.86 mmol, 10 equiv), and then the reaction mixture was stirred at 70 °C in a preheated oil bath for 24 h. The resulting mixture was cooled to room temperature, quenched with saturated $NaHCO_3$(5 mL), and diluted with EtOAc (5 mL). The crude mixture was washed with brine solution (10 mL), extracted with ethyl acetate (3 × 5 mL), and dried over anhydrous Na_2SO_4. The combined organic layer was evaporated under reduced pressure, and the crude product was purified by column chromatography using 20−30% ethyl acetate/hexane. Yield: 16.1 mg, 37%, white solid. Mp: 200−210.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.10 (dd, J = 4.7 Hz, 1.5 Hz, 1H), 8.00 (dd, J = 7.9 Hz, 1.5 Hz, 1H), 7.94 (d, J = 7.8 Hz, 2H), 7.55−7.53 (m, 1H), 7.52−7.48 (m, 4H), 7.38 (s, 1H), 7.32 (d, J = 7.6 Hz, 2H), 7.11−7.09 (m, 4 H), 7.04−7.01 (m, 6H), 5.43 (s, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 147.1, 144.1, 143.5, 140.3, 132.8, 131.8, 130.3, 130.1 129.2, 128.7, 128.5, 128.1, 127.7, 127.2, 126.8, 118.2, 116.2, 114.1, 43.3. IR (CH_2Cl_2, cm^{-1}): 3072, 2937, 1521, 1399, 1316, 1156. HRMS (ESI) m/z calcd for $C_{32}H_{24}N_2O_2S$ [M + H]$^+$; 501.1631, found: 501.1627.

*Methyl 2-([1,1′-Biphenyl]-2-yl)-1-benzyl-3-(phenylsulfonyl)-1H-indole-5-carboxylate (**3ha**).* The title compound was prepared as described in general procedure D using **1h** (0.074 mmol, 1 equiv) and iodobenzene (**2a**, 0.74 mmol) as starting materials with an extended reaction time (72 h) and purified by column chromatography using 15−20% ethyl acetate/hexane. Yield: 31 mg, 75%, white solid. Mp: 122.3−124.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 9.13 (d, J = 1.3 Hz, 1H), 7.85 (dd, J = 8.7 Hz, 1.6 Hz, 1H), 7.75 (d, J = 7.9 Hz, 2H), 7.61 (td, J = 7.6 Hz, 1.3 Hz, 1H), 7.51 (d, J = 7.7 Hz, 1H), 7.46 (t, J = 7.1 Hz, 1H), 7.41−7.36 (m, 3H), 7.31 (dd, J = 7.6 Hz, 1.1 Hz, 1H), 7.14−7.06 (m, 4H), 7.02 (t, J = 7.7 Hz, 2H), 6.98 (d, J = 8.7 Hz, 1H), 6.86 (d, J = 7.8 Hz, 2H), 6.56 (d, J = 7.1 Hz, 2H), 4.69 (d, J = 16.3 Hz, 1H), 4.54 (d, J = 16.3 Hz, 1H), 3.96 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 167.7, 145.7, 143.6, 142.1, 139.6, 137.8, 137.3, 135.3, 133.5, 132.9, 130.9, 130.2, 129.0, 128.8, 128.6, 128.5, 127.8, 127.6, 127.1, 126.5, 126.3, 125.2, 125.0, 123.4, 115.9, 111.2, 52.2, 48.0. IR (CH_2Cl_2, cm^{-1}): 3078, 2968, 1723, 1321, 1246, 1151. HRMS (ESI) m/z calcd for $C_{35}H_{27}NO_4S$ [M + H]$^+$; 558.1733, found: 558.1727.

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*2-([1,1′-Biphenyl]-2-yl)-1-benzyl-5-nitro-3-(phenylsulfonyl)-1H-indole (**3ia**).* The title compound was prepared as described in general procedure D using **1i** (0.076 mmol, 1 equiv) and iodobenzene (**2a**, 0.76 mmol) as starting materials with an extended reaction time (72 h) and purified by column chromatography using 15−20% ethyl acetate/hexane. Yield: 10 mg, 24%, white solid. Mp: 140.6−145.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 9.34 (d, J = 2.2 Hz, 1H), 8.02 (dd, J = 9.1 Hz, 2.2 Hz, 1H), 7.74−7.72 (m, 2H), 7.64 (td, J = 7.6 Hz, 1.3 Hz, 1H), 7.55−7.52 (m, 1H), 7.49 (tt, J = 7.4 Hz, 1.1 Hz, 1H), 7.45−7.35 (m, 4H), 7.17−7.09 (m, 4H), 7.04 (t, J = 7.7 Hz, 2H), 6.99 (d, J = 9.1 Hz, 1H), 6.82−6.80 (m, 2H), 6.56 (d, J = 7.1 Hz, 2H), 4.72 (d, J = 16.2 Hz, 1H), 4.51 (d, J = 16.3 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 147.3, 144.0, 143.0, 142.1, 139.4, 138.0, 137.6, 137.4, 134.8, 133.5, 133.2, 131.3, 130.4, 129.2, 129.0, 128.6, 128.5, 128.1, 127.8, 127.6, 127.2, 126.3, 125.9, 125.1, 119.1, 118.0, 117.2, 111.6, 48.4. IR (CH_2Cl_2, cm^{-1}): 3081, 2943, 1530, 1343, 1153. HRMS (ESI) m/z calcd for $C_{33}H_{24}N_2O_4S$ [M + H]$^+$; 545.1529, found: 545.1529.

*2-([1,1′-Biphenyl]-2-yl)-1-benzyl-3-tosyl-1H-indole (**3ja**).* The title compound was prepared as described in general procedure D using **1j** (0.083 mmol, 1 equiv) and iodobenzene (**2a**, 0.83 mmol) as starting materials at 100 °C with an extended reaction time (48 h) and purified by column chromatography using 15−20% ethyl acetate/hexane. Yield: 36 mg, 84%, white solid. Mp: 153.4−155.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.37 (d, J = 8.1 Hz, 1H), 7.65 (d, J = 8.1 Hz, 2H), 7.58 (td, J = 7.6 Hz, 1.1 Hz, 1H), 7.51 (d, J = 7.5 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.29 (t, J = 7.4 Hz, 2H), 7.17−7.04 (m, 9H), 6.98−6.94 (m, 3H), 6.58 (d, J = 7.3 Hz, 2H), 4.71 (d, J = 16.3 Hz, 1H), 4.58 (d, J = 16.3 Hz, 1H), 2.33 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 144.0, 143.3, 142.2, 141.3, 139.9, 135.8, 135.4, 133.4, 130.6, 130.2, 129.5, 128.8, 128.7, 128.4, 127.5, 127.4, 127.2, 127.0, 126.9, 126.4, 125.7, 123.4, 122.6, 120.8, 114.8, 111.3, 47.8, 21.6. IR (CH_2Cl_2, cm^{-1}): 3072, 2937, 1462, 1149. HRMS (ESI) m/z calcd for $C_{34}H_{27}NO_2S$ [M + H]$^+$; 514.1835, found: 514.1833.

*2-([1,1′-Biphenyl]-2-yl)-1-benzyl-3-(o-tolylsulfonyl)-1H-indole (**3ka**).* The title compound was prepared as described in general procedure D using **1k** (0.083 mmol, 1 equiv) and iodobenzene (**2a**, 0.83 mmol) as starting materials with an extended reaction time (48 h) and purified by column chromatography using 15−20% ethyl acetate/hexane. Yield: 22.5 mg, 53%, white solid. Mp: 144.5−145.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.40 (d, J = 8.1 Hz, 1H), 7.50 (td, J = 7.6 Hz, 1.4 Hz, 1H), 7.44 (d, J = 7.5 Hz, 1H), 7.39 (d, J = 7.3 Hz, 1H), 7.30−7.27 (m, 2H), 7.23 (td, J = 7.6 Hz, 1.2 Hz, 1H), 7.18 (d, J = 7.7 Hz, 2H), 7.16−7.09 (m, 5H), 7.06−7.00 (m, 4H), 6.86 (d, J = 7.7 Hz, 2H), 6.60 (d, J = 7.3 Hz, 2H), 4.69 (d, J = 16.5 Hz, 1H), 4.56 (d, J = 16.3 Hz, 1H), 2.55 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 144.0, 142.2, 141.7, 139.8, 138.1, 135.9, 135.0, 133.9, 132.6, 132.3, 130.5, 130.0, 128.8, 128.7, 128.5, 128.4, 127.6, 127.4, 126.9, 126.6, 126.5, 126.3, 125.9, 123.4, 122.7, 121.3, 113.7, 111.3, 47.8, 20.5. IR (CH_2Cl_2, cm^{-1}): 3074, 2947, 1462, 1307, 1154, 746, 702. HRMS (ESI) m/z calcd for $C_{34}H_{27}NO_2S$ [M + H]$^+$; 514.1835, found: 514.1835.

*2-([1,1′-Biphenyl]-2-yl)-1-benzyl-3-((4-methoxyphenyl) sulfonyl)-1H-indole (**3la**).* The title compound was prepared as described in general procedure D using **1l** (0.080 mmol, 1 equiv) and iodobenzene (**2a**, 0.80 mmol) as starting materials and purified by column chromatography using 15−20% ethyl acetate/hexane. Yield: 23.2 mg, 55%, white solid. Mp: 183.5−186.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.36 (d, J = 8.1, 1H), 7.69 (d, J = 8.9 Hz, 2H), 7.58 (td, J = 7.6 Hz, 1.3 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.36 (td, J = 7.5 Hz, 1.2 Hz, 1H), 7.28 (t, J = 7.6 Hz, 2H), 7.15−7.05 (m, 7H), 7.00 (d, J = 7.9 Hz, 2H), 6.95 (d, J = 8.3 Hz, 1H), 6.83 (d, J = 8.9 Hz, 2H), 6.58 (d, J = 7.0 Hz, 2H), 4.71 (d, J = 16.3 Hz, 1H), 4.58 (d, J = 16.3 Hz, 1H), 3.78 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 162.9, 143.7, 142.2, 140.0, 136.2, 135.9, 135.4, 133.5, 130.6, 130.2, 129.1, 128.8, 128.7, 128.5, 127.5, 127.4, 127.3, 126.9, 126.4, 125.6, 123.4, 122.6, 120.8, 115.2, 114.1, 111.3, 55.7, 47.8. IR (CH_2Cl_2, cm^{-1}), 30778, 2951, 2856, 1602, 1462, 1327, 1265, 1145. HRMS (ESI) m/z calcd for $C_{34}H_{27}NO_3S$ [M + H]$^+$; 530.1784, found: 530.1790.

*2-([1,1′-Biphenyl]-2-yl)-1-benzyl-3-((4-bromophenyl) sulfonyl)-1H-indole (**3ma**).* The title compound was prepared as described in general procedure D using **1m** (0.070 mmol, 1 equiv) and iodobenzene (**2a**, 0.70 mmol) as starting materials and purified by column chromatography using 15−20% ethyl acetate/hexane. Yield: 29 mg, 71%, white solid. Mp: 195.2−211.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.31 (d, J = 8.1 Hz, 1H), 7.60−7.57 (m, 3H), 7.53−7.49 (m, 3H), 7.36 (td, J = 7.5 Hz, 1.2 Hz, 1H), 7.30 (t, J = 7.4 Hz, 1H), 7.20 (dd, J = 7.7 Hz, 1.1 Hz, 1H), 7.18−7.13 (m, 3H), 7.12−7.06 (m, 5H), 7.01−6.98 (m, 3H), 6.60 (d, J = 6.9 Hz, 2H), 4.75 (d, J = 16.2 Hz, 1H), 4.64 (d, J = 16.3 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 144.5, 143.2, 142.3, 139.8, 135.6, 135.5, 133.0, 132.2, 130.7, 130.3, 128.7, 128.5, 128.4, 127.6, 127.5, 127.1, 127.0, 126.4, 125.6, 123.7, 122.9, 120.6, 113.8, 111.5, 48.0. IR (CH_2Cl_2, cm^{-1}): 3075, 3047, 2943, 1394, 1330, 1150, 744. HRMS (ESI) m/z calcd for $C_{33}H_{24}BrNO_2S$ [M + 2]$^+$; 580.0742, found: 580.0765.

*2-([1,1′-Biphenyl]-2-yl)-1-benzyl-3-((4-nitrophenyl)sulfonyl)-1H-indole (**3na**).* The title compound was prepared as described in general procedure D using **1n** (0.076 mmol, 1 equiv) and iodobenzene (**2a**, 0.76 mmol) as starting materials and purified by column chromatography using 15−20% ethyl acetate/hexane. Yield: 26.9 mg, 65%, yellow solid. Mp: 109−111.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.29 (d, J = 8.1 Hz, 1H), 8.18 (d, J = 8.8 Hz, 2H), 7.86 (d, J = 8.7 Hz, 2H), 7.62 (t, J = 7.5 Hz, 1H), 7.54 (d, J = 7.7 Hz, 1H), 7.39−7.32 (m, 2H), 7.22−7.10 (m, 6H), 7.09−7.03 (m, 3H), 6.97 (d, J = 7.4 Hz, 2H), 6.62 (d, J = 7.2 Hz, 2H), 4.78 (d, J = 16.3 Hz, 1H), 4.69 (d, J = 16.3 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 149.9, 149.6, 145.2, 142.2, 139.7, 135.7, 135.4, 132.7, 131.0, 130.5, 128.8, 128.6, 128.0, 127.8, 127.7, 127.1, 126.8, 126.4, 125.5, 124.2, 124.1, 123.3, 120.4, 112.6, 111.7, 48.1. IR (CH_2Cl_2, cm^{-1}): 3117, 3076, 1536, 1354, 1152, 744. HRMS (ESI) m/z calcd for $C_{33}H_{24}N_2O_4S$ [M + H]$^+$; 545.1529, found: 545.1512.

*2-([1,1′-Biphenyl]-2-yl)-1-benzyl-3-(methylsulfonyl)-1H-indole (**3oa**).* The title compound was prepared as described in general procedure D using **1o** (0.105 mmol, 1 equiv) and iodobenzene (**2a**, 1.05 mmol) as starting materials and purified by column chromatography using 10−15% ethyl acetate/hexane. Yield: 28 mg, 61%, white solid. Mp: 121.2−124.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.00 (d, J = 8.0 Hz, 1H), 7.57−7.52 (m, 2H), 7.34 (td, J = 8.5 Hz, 1.6 Hz, 1H), 7.31−7.26 (m, 2H), 7.24−7.21 (m, 1H), 7.20−7.15 (m, 9H), 6.77−6.76 (m, 2H), 5.01 (s, 2H), 2.66 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 143.9, 142.4, 140.4, 137.6, 135.9, 135.8, 131.9, 130.5, 130.4, 129.0, 128.9, 128.5, 127.8, 127.5, 127.2, 126.5, 125.2, 123.8, 122.7, 120.1, 113.2, 111.5, 48.0, 44.8. IR (CH_2Cl_2, cm^{-1}): 3075, 2941, 1462, 1308, 1140, 738, 703. HRMS (ESI) m/z calcd for $C_{28}H_{23}NO_2S$ [M + H]$^+$; 438.1522, found: 438.1521.

*2-([1,1′-Biphenyl]-2-yl)-1-benzyl-3-(benzylsulfonyl)-1H-indole (**3pa**).* The title compound was prepared as described in general procedure D using **1p** (0.083 mmol, 1 equiv) and iodobenzene (**2a**, 0.83 mmol) as starting materials and purified by column chromatography using 10−15% ethyl acetate/hexane. Yield: 14.6 mg, 34%, white solid. Mp: 219.3−222.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.74 (d, J = 7.7 Hz, 1H), 7.47−7.42 (m, 2H), 7.34 (t, J = 7.4 Hz, 1H), 7.26−7.23 (m, 3H), 7.21−7.15 (m, 9H), 7.09−7.05 (m, 2H), 7.01 (d, J = 7.2 Hz, 2H), 6.69 (d, J = 6.7 Hz, 2H), 6.16 (d, J = 7.5 Hz, 1H), 4.86 (s, 2H) 4.24 (d, J = 13.6 Hz, 1H), 4.08 (d, J = 13.6 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ (ppm) 145.1, 142.4, 140.4, 136.1, 135.6, 131.4, 131.3, 130.2, 130.0, 129.5, 129.0, 128.7, 128.6, 128.5, 127.7, 127.5, 127.4, 126.7, 126.3, 125.6, 123.6, 122.6, 120.1, 111.3, 110.7, 62.9, 47.8. IR (CH_2Cl_2, cm^{-1}): 2936, 2879, 1463, 131, 1120, 747. HRMS (ESI) m/z calcd for $C_{34}H_{27}NO_2S$ [M + H]$^+$; 514.1835, found: 514.1835.

*1-Benzyl-2-(4,4′-dimethyl-[1,1′-biphenyl]-2-yl)-3-(phenylsulfonyl)-1H-indole (**3ab**).* The title compound was prepared as described in general procedure D using **1a** (0.086 mmol, 1 equiv) and 4-iodotoluene (**2b**, 0.86 mmol) as starting materials and purified by column chromatography using 15−20% ethyl acetate/Hexane. Yield: 42 mg, 92%, white solid. Mp: 189.7−193.9 °C. ^{1}H NMR (500 MHz,

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$CDCl_3$): δ (ppm) 8.42 (d, J = 8.1 Hz, 1H), 7.76 (d, J = 8 Hz, 2H), 7.47 (t, J = 7.4 Hz, 1H), 7.39−7.34 (m, 4H), 7.32−7.29 (m, 1H), 7.16−7.09 (m, 2H), 7.07−7.04 (m, 2H), 6.96 (d, J = 8.3 Hz, 1H), 6.89−6.82 (m, 5H), 6.55 (d, J = 7.3 Hz, 2H), 4.70 (d, J = 16.3 Hz, 1H), 4.62 (d, J = 16.3 Hz, 1H), 2.29 (s, 3H), 2.22 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ (ppm) 144.8, 144.3, 139.3, 137.0, 136.8, 136.2, 135.9, 135.4, 133.8, 132.5, 131.3, 130.0, 129.2, 128.8, 128.6, 128.5, 127.4, 126.9, 126.8, 126.4, 125.8, 123.4, 122.7, 120.8, 114.2, 111.4, 47.9, 21.1, 21.0. IR (CH_2Cl_2, cm^{-1}): 3075, 2937, 1459, 1328, 1151. HRMS (ESI) m/z calcd for $C_{35}H_{29}NO_2S$ $[M + H]^+$; 528.1991, found: 528.1989.

*1-Benzyl-6-bromo-2-(4,4′-dimethyl-[1,1′-biphenyl]-2-yl)-3-(phenylsulfonyl)-1H-indole (**3fb**).* The title compound was prepared as described in general procedure D using **1f** (0.070 mmol, 1 equiv) and 4-iodotoluene (**2b**, 0.70 mmol) as starting materials and purified by column chromatography using 15−20% ethyl acetate/hexane. Yield: 33.5 mg, 78%, white solid. Mp: 221.5−234.8 °C. ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.31 (d, J = 8.6 Hz, 1H), 7.71 (d, J = 7.8 Hz, 2H), 7.47 (t, J = 7.4 Hz, 1H), 7.42−7.36 (m, 5H), 7.15−7.12 (m, 2H), 7.10−7.07 (m, 2H), 6.88 (s, 1H), 6.85 (d, J = 8.1 Hz, 2H), 6.79 (d, J = 8.1 Hz, 2H), 6.54 (d, J = 7.2 Hz, 2H), 4.64 (d, J = 16.3 Hz, 1H), 4.52 (d, J = 16.3 Hz, 1H), 2.29 (s, 3H), 2.24 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ (ppm) 145.3, 143.9, 139.2, 137.0, 136.8, 136.4, 136.2, 135.3, 133.9, 132.7, 131.6, 130.0, 129.3, 128.9, 128.7, 128.4, 127.7, 127.0, 126.4, 126.3, 126.0, 124.7, 122.2, 117.0, 114.6, 114.2, 48.0, 21.2, 21.0. IR (CH_2Cl_2, cm^{-1}): 3047, 2968, 2936, 1152. HRMS (ESI) m/z calcd for $C_{35}H_{28}BrNO_2S$ $[M + 2]^+$; 608.1096, found: 608.1076.

*Methyl 1-Benzyl-2-(4,4′-dimethyl-[1,1′-biphenyl]-2-yl)-3-(phenylsulfonyl)-1H-indole-5-carboxylate (**3hb**).* The title compound was prepared as described in general procedure D using **1h** (0.074 mmol, 1 equiv) and 4-iodotoluene (**2b**, 0.74 mmol) as starting materials with an extended reaction time (48 h) and purified by column chromatography using 15−20% ethyl acetate/hexane. Yield: 30 mg, 69%, white solid. Mp: 205.2−208.1 °C. ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 9.15 (d, J = 1.3 Hz, 1H), 7.86 (dd, J = 8.7 Hz, 1.6 Hz, 1H), 7.76 (d, J = 8.3 Hz, 2H), 7.48 (tt, J = 7.4 Hz, 1.1 Hz, 1H), 7.40−7.37 (m, 4H), 7.13−7.10 (m, 1H), 7.08−7.05 (m, 2H), 6.98 (d, J = 8.7 Hz, 1H), 6.90 (s, 1H), 6.82 (s, 4H), 6.53 (d, J = 7.3 Hz, 2H), 4.69 (d, J = 16.3 Hz, 1H), 4.60 (d, J = 16.3 Hz, 1H), 3.96 (s, 3H), 2.30 (s, 3H), 2.22 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ (ppm) 167.7, 146.3, 143.8, 139.2, 137.8, 137.0, 136.7, 136.4, 135.4, 133.8, 132.8, 131.6, 130.1, 129.3, 128.9, 128.6, 128.5, 127.6, 127.1, 126.4, 126.3, 125.3, 124.9, 124.8, 123.3, 115.6, 111.2, 52.2, 48.11, 21.1, 21.0. IR (CH_2Cl_2, cm^{-1}): 3043, 2964, 1723, 1320, 1245, 1151. HRMS (ESI) m/z calcd for $C_{37}H_{31}NO_4S$ $[M + H]^+$; 586.2046, found: 586.2046.

*1-Benzyl-2-(4,4′-dimethyl-[1,1′-biphenyl]-2-yl)-5-nitro-3-(phenylsulfonyl)-1H-indole (**3ib**).* The title compound was prepared as described in general procedure D using **1i** (0.076 mmol, 1 equiv) and 4-iodotoluene (**2b**, 0.76 mmol) as starting materials with an extended reaction time (72 h) and purified by column chromatography using 15−20% ethyl acetate/hexane. Yield: 11 mg, 25%, off-white solid. Mp: 229−238.4 °C. ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 9.36 (s, 1H), 8.02 (d, J = 9.0 Hz, 1H), 7.74 (d, J = 7.7 Hz, 2H), 7.51 (t, J = 7.4 Hz, 1H), 7.42−7.40 (m, 4H), 7.16−7.07 (m, 3H), 7.00 (d, J = 9.0 Hz, 1H), 6.94 (s, 1H), 6.83 (d, J = 7.7 Hz, 2H), 6.76 (d, J = 7.6 Hz, 2H), 6.52 (d, J = 7.5 Hz, 2H), 4.71 (d, J = 16.2 Hz, 1H), 4.57 (d, J = 16.3 Hz, 1H), 2.33 (s, 3H), 2.22 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ (ppm) 147.9, 144.0, 143.3, 139.2, 138.0, 137.3, 136.7, 136.5, 134.9, 133.8, 133.1, 132.0, 130.2, 129.4, 129.1, 128.8, 128.4, 127.9, 127.3, 126.4, 125.7, 125.2, 118.9, 117.9, 116.9, 111.7, 48.4, 21.1, 21.06. IR (CH_2Cl_2, cm^{-1}): 2937, 2870, 1527, 1340, 1153. HRMS (ESI) m/z calcd for $C_{35}H_{28}N_2O_4S$ $[M + H]^+$; 573.1843, found: 573.1840.

*1-Benzyl-5-nitro-3-(phenylsulfonyl)-2-(p-tolyl)-1H-indole (**4ib**).* The title compound was prepared as described in general procedure D using **1i** (0.076 mmol, 1 equiv) and 4-iodotoluene (**2b**, 0.76 mmol) as starting materials with an extended reaction time (72 h) and purified by column chromatography using 15−25% ethyl acetate/hexane. Yield: 10 mg, 27%, off-white solid. Mp: 217.1−221.3 °C. ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 9.28 (d, J = 2.1 Hz, 1H), 8.25 (dd, J = 9.1 Hz, 2.2 Hz, 1H), 7.78 (s, 1H), 7.64 (d, J = 9.1 Hz, 1H), 7.55 (d, J = 7.9 Hz, 2H), 7.46−7.33 (m, 7H), 7.29−7.22 (m, 4H), 5.24 (d, J = 14.3 Hz, 1H), 4.81 (d, J = 14.3 Hz, 1H), 2.51 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ (ppm) 144.9, 143.8, 143.4, 138.6, 137.4, 136.8, 135.9, 135.8, 134.3, 132.7, 131.9, 131.3, 129.7, 129.5, 129.4, 128.7, 128.4, 127.2, 126.5, 125.9, 119.1, 118.7, 115.1, 109.7, 47.6, 21.2. IR (neat, cm^{-1}): 3046, 2938, 1527, 1342, 1151. Elemental analysis calculated (%): C 69.69, H 4.60, N 5.81, S 6.64; found: C 64.37, H 4.05, N 5.20, S 5.81. QTof (ESI) m/z calcd for $C_{28}H_{22}N_2O_4S$ $[M-H]^+$; 481.1228, found: 481.1212.

*1-Benzyl-2-(4,4′-dimethyl-[1,1′-biphenyl]-2-yl)-3-tosyl-1H-indole (**3jb**).* The title compound was prepared as described in general procedure D using **1j** (0.083 mmol, 1 equiv) and 4-iodotoluene (**2b**, 0.83 mmol) as starting materials and purified by column chromatography using 15−20% ethyl acetate/hexane. Yield: 40 mg, 89%, white solid. Mp: 211.3-218.1 °C. ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.39 (d, J = 8.1 Hz, 1H), 7.66 (d, J = 8.2 Hz, 2H), 7.38−7.33 (m, 2H), 7.29 (t, J = 7.5, 1H), 7.18−7.15 (m, 2H), 7.13−7.09 (m, 2H), 7.07−7.04 (m, 2H), 6.96−6.92 (m, 3H), 6.84 (d J = 8.2 Hz, 3H), 6.54 (d, J = 7.3 Hz, 2H), 4.70 (d, J = 16.2 Hz, 1H), 4.63 (d, J = 16.3 Hz, 1H), 2.35 (s, 3H), 2.29 (s, 3H), 2.23 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ (ppm) 144.6, 143.2, 141.6, 139.3, 137.0, 136.8, 136.2, 135.9, 135.4, 133.8, 131.3, 130.0, 129.4, 129.2, 128.7, 128.5, 127.3, 127.0, 126.4, 125.8, 123.3, 122.5, 120.8, 114.5, 111.3, 47.9, 21.6, 21.1, 21.0. IR (CH_2Cl_2, cm^{-1}): 3044, 2934, 1462, 1329, 1150, 819, 747, 584. HRMS (ESI) m/z calcd for $C_{36}H_{31}NO_2S$ $[M + H]^+$; 542.2148, found: 542.2148.

*1-Benzyl-2-(4,4′-dimethyl-[1,1′-biphenyl]-2-yl)-3-(o-tolylsulfonyl)-1H-indole (**3kb**).* The title compound was prepared as described in general procedure D using **1k** (0.083 mmol, 1 equiv) and 4-iodotoluene (**2b**, 0.83 mmol) as starting materials with extended reaction time (48 h) and purified by column chromatography using 15−20% ethyl acetate/Hexane. Yield: 29.5 mg, 66%, white solid. Mp: 149.5−152.3 °C. ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.45 (d, J = 8.1 Hz, 1H), 7.50 (d, J = 7.9 Hz, 1H), 7.33−7.25 (m, 4H), 7.20 (d, J = 7.5 Hz, 1H), 7.16−7.03 (m, 5H), 6.98 (d, J = 8.3 Hz, 1H), 6.85 (s, 4H), 6.68 (s, 1H), 6.56 (d, J = 6.9 Hz, 2H), 4.68 (d, J = 16.3 Hz, 1H), 4.60 (d, J = 16.3 Hz, 1H), 2.55 (s, 3H), 2.23 (s, 3H), 2.16 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ (ppm) 144.6, 142.1, 139.4, 138.1, 137.4, 136.9, 136.8, 136.2, 136.0, 135.0, 134.1, 132.5, 132.2, 131.2, 129.9, 129.1, 128.9, 128.6, 128.5, 127.4, 126.6, 126.4, 126.3, 125.8, 123.2, 122.6, 121.3, 113.5, 111.3, 47.9, 21.1, 21.08, 20.5. IR (CH_2Cl_2, cm^{-1}): 3069, 2939, 1461, 1306, 1154, 743. HRMS (ESI) m/z calcd for $C_{36}H_{31}NO_2S$ $[M + H]^+$; 542.2148, found: 542.2130.

*1-Benzyl-2-(4,4′-dimethyl-[1,1′-biphenyl]-2-yl)-3-((4-methoxyphenyl)sulfonyl)-1H-indole (**3lb**).* The title compound was prepared as described in general procedure D using **1l** (0.0795 mmol, 1 equiv) and 4-iodotoluene (**2b**, 0.79 mmol) as starting materials and purified by column chromatography using 15−20% ethyl acetate/hexane. Yield: 34.2 mg, 77%, white solid. Mp: 197.8−200.3 °C. ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.38 (d, J = 8.1 Hz, 1H), 7.69 (dt, J = 5.0 Hz, 2.8 Hz, 2H), 7.38−7.32 (m, 2H), 7.29 (t, J = 7.3 Hz, 1H), 7.15−7.09 (m, 2H), 7.07−7.04 (m, 2H), 6.96−6.94 (m, 3H), 6.87−6.83 (m, 5H), 6.55 (d, J = 7.25 Hz, 2H), 4.66 (q, J = 16.3 Hz, 2H), 3.80 (s, 3H), 2.30 (s, 3H), 2.23 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ (ppm) 162.8, 144.3, 139.4, 137.1, 136.8, 136.4, 136.2, 136.0, 135.4, 133.8, 131.3, 130.0, 129.2, 129.1, 128.7, 128.5, 127.4, 127.1, 126.5, 125.7, 123.3, 122.5, 120.8, 115.0, 114.0, 111.3, 55.7, 47.9, 21.1, 21.0. IR (CH_2Cl_2, cm^{-1}): 3044, 2935, 2857, 1603, 1145. HRMS (ESI) m/z calcd for $C_{36}H_{31}NO_3S$ $[M + H]^+$; 558.2097, found: 558.2095.

*1-Benzyl-3-((4-bromophenyl)sulfonyl)-2-(4,4′-dimethyl-[1,1′-biphenyl]-2-yl)-1H-indole (**3mb**).* The title compound was prepared as described in general procedure D using **1m** (0.070 mmol, 1 equiv) and 4-iodotoluene (**2b**, 0.70 mmol) as starting materials and purified by column chromatography using 15−20% ethyl acetate/hexane. Yield: 36 mg, 84%, white solid. Mp: 227.7−242.1 °C. ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.34 (d, J = 8.1 Hz, 1H), 7.60 (dt, J = 8.6 Hz,

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2.2 Hz, 2H), 7.50 (dt, J = 8.6 Hz, 2.2 Hz, 2H), 7.40 (d, J = 7.8 Hz, 1H), 7.35 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.31 (t, J = 7.6 Hz, 1H), 7.18−7.12 (m, 2H), 7.10−7.06 (m, 2H), 7.01 (d, J = 8.3 Hz, 1H), 6.93 (d, J = 8.1 Hz, 2H), 6.87 (d, J = 8.0 Hz, 2H), 6.80 (s, 1H), 6.57 (d, J = 7.2 Hz, 2H), 4.72 (q, J = 16.3 Hz, 2H), 2.29 (s, 3H), 2.24 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ (ppm) 145.0, 143.4, 139.4, 137.0, 136.9, 136.3, 135.7, 135.5, 133.4, 132.0, 131.4, 130.2, 129.3, 128.6, 128.5, 127.5, 127.4, 126.8, 126.5, 125.7, 123.6, 122.8, 120.6, 113.5, 111.5, 48.0, 21.2, 21.0. IR (CH_2Cl_2, cm^{-1}): 3070, 2939, 2878, 1331, 1149, 746. HRMS (ESI) m/z calcd for $C_{35}H_{28}BrNO_2S$ $[M + 2]^+$; 608.1096, found: 608.1076.

*1-Benzyl-2-(4,4′-dibromo-[1,1′-biphenyl]-2-yl)-3-(phenylsulfonyl)-1H-indole (**3ac**).* The title compound was prepared as described in general procedure D using **1a** (0.0863 mmol, 1 equiv) and 1-bromo-4-iodobenzene (**2c**, 0.863 mmol) as starting materials at 100 °C and purified by column chromatography using 15−20% ethyl acetate/hexane. Yield: 30.8 mg, 54%, white solid. Mp: 229.2−235.9 °C. ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.40 (d, J = 8.1 Hz, 1H), 7.82 (d, J = 7.5 Hz, 2H), 7.69 (dd, J = 8.2 Hz, 1.9 Hz, 1H), 7.54 (t, J = 7.3 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.36−7.32 (m, 2H), 7.22−7.17 (m, 3H), 7.14 (d, J = 7.3 Hz, 1H), 7.09 (t, J = 7.5 Hz, 2H), 7.03−7.00 (m, 4H), 6.47 (d, J = 7.4 Hz, 2H), 4.72 (dd, J = 16.5 Hz, 6.4 Hz, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ (ppm) 144.1, 141.8, 140.3, 137.7, 135.7, 135.2, 135.1, 133.8, 132.9, 131.9, 131.6, 130.4, 129.4, 129.2, 128.8, 127.6, 126.8, 126.0, 125.4, 124.1, 123.2, 122.4, 121.1, 120.8, 115.4, 111.5, 48.1. IR (CH_2Cl_2, cm^{-1}): 3071, 2937, 2864, 1462, 1152, 735, 599. HRMS (ESI) m/z calcd for $C_{33}H_{23}Br_2NO_2S$ $[M + Na]^+$; 679.9688, found: 679.9683.

*1-Benzyl-2-(3,3′-dimethoxy-[1,1′-biphenyl]-2-yl)-3-(phenylsulfonyl)-1H-indole (**3ad**).* The title compound was prepared as described in general procedure D using **1a** (0.0863 mmol, 1 equiv) and 3-iodoanisole (**2d**, 0.863 mmol) as starting materials and purified by column chromatography using 15−20% ethyl acetate/hexane. Yield: 17 mg, 35%, white solid. Mp: 196.9−201.5 °C. ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.20 (d, J = 8.1 Hz, 1H), 7.85 (d, J = 8.1 Hz, 2H), 7.51−7.44 (m, 2H), 7.39 (t, J = 7.4 Hz, 2H), 7.26−7.23 (m, 1H), 7.14−7.06 (m, 7H), 7.02 (d, J = 8.2 Hz, 1H), 6.89 (d, J = 7.5 Hz, 1H), 6.78 (d, J = 8.3 Hz, 1H), 6.72−6.69 (m, 3H), 4.73 (dd, J = 16.2 Hz, 4.8 Hz, 2H), 3.51 (s, 3H), 3.16 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ (ppm) 159.4, 158.0, 144.3, 144.1, 141.3, 141.1, 136.0, 132.1, 131.5, 129.2, 128.6, 128.5, 127.4, 126.8, 126.0, 123.1, 122.5, 122.4, 121.4, 120.3, 116.9, 114.8, 114.3, 113.4, 111.3, 109.3, 55.5, 54.6, 48.0. IR (CH_2Cl_2, cm^{-1}): 3072, 2955, 2849, 1268, 1149. HRMS (ESI) m/z calcd for $C_{35}H_{29}NO_4S$ $[M + H]^+$; 560.1890, found: 560.1887.

*E. Large-Scale Reaction for the Synthesis of 2-([1,1′-Biphenyl]-2-yl)-1-benzyl-3-(phenylsulfonyl)-1H-indole (**3aa**).* To a 250 mL flame-dried sealed tube equipped with a magnetic stir bar were added **1a** (2.5 mmol, 868.5 mg, 1 equiv), and then the tube was evacuated and refilled with argon. To this were added $Pd(OAc)_2$ (0.5 mmol, 112.2 mg, 20 mol %), Ag_2CO_3 (6.25 mmol, 1.72 g, 2.5 equiv), iodobenzene (25 mmol, 2.77 mL, 10 equiv), HFIP (15 mL), and TFA (25 mmol, 1.87 mL 10 equiv). Then the reaction mixture was stirred at 90 °C in preheated oil bath for 24 h. The resulting mixture was cooled to room temperature, quenched with saturated $NaHCO_3$(20 mL), and diluted with EtOAc (25 mL). The crude mixture was washed with brine solution (50 mL), extracted with ethyl acetate (3 × 20 mL), and dried over anhydrous Na_2SO_4. The combined organic layer was evaporated under reduced pressure, and the crude product was purified by column chromatography using ethyl acetate/hexane (10−15%). Yield: 1.02 g, 82%, off-white solid. Mp: 129.2−135.4 °C. ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.38 (d, J = 8.1 Hz, 1H), 7.74 (d, J = 8 Hz, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.50 (d, J = 7.7 Hz, 1H), 7.44 (t, J = 6.9 Hz, 1H), 7.36 (t, J = 7.3 Hz, 3H),7.31−7.27 (m, 2H), 7.15−7.02 (m, 7H), 6.96−6.92 (m, 3H), 6.58 (d, J = 7.5 Hz, 2H), 4.70 (d, J = 16.3 Hz, 1H), 4.56 (d, J = 16.3 Hz, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ (ppm) 144.2, 144.1, 142.2, 139.9, 135.8, 135.4, 133.5, 132.6, 130.7, 130.4, 130.2, 128.9, 128.7, 128.5, 127.6, 127.4, 127.1, 126.9, 126.4, 125.7, 123.5, 122.8, 120.8, 114.5, 111.3, 47.9. IR (CH_2Cl_2, cm^{-1}): 3078,1461, 1328, 1152, 748. HRMS (ESI) m/z calcd for $C_{33}H_{25}NO_2S$ $[M + H]^+$; 500.1678, found: 500.1678.

F. Deprotection of N-Benzyl Group.[18b] To a flame-dried two-neck RB flask equipped with a magnetic stirring bar were added **3aa** (0.40 mmol, 1 equiv) and KO^{t}Bu (2.8 mmol, 7 equiv) in DMSO (5 mL), and then the reaction mixture was heated at 80 °C for 8 h under oxygen atmosphere (1 atm). The resulting mixture was cooled to room temperature, quenched with 0.1 M HCl (10 mL), and diluted with ethyl (acetate (10 mL). The reaction mixture was extracted with ethyl acetate (10 mL × 5), washed with water (10 mL) and brine solution (10 mL), and then dried over anhydrous $NaSO_4$. The combined organic layer was evaporated under reduced pressure, and the crude product was purified by column chromatography using 20−30% ethyl acetate/hexane to afford **5aa**. Yield: 161 mg, 98%, white solid. Mp: 191.6−198.8 °C. ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.30 (d, J = 8.1 Hz, 1H), 7.94 (bs, 1H), 7.74 (d, J = 8 Hz, 2H), 7.64 (d, J = 6.6 Hz, 1H), 7.57 (td, J = 7.6 Hz, 1.2 Hz, 1H), 7.47−7.43 (m, 3H), 7.35 (t, J = 7.7 Hz, 2H), 7.29 (t, J = 7.6 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 7.13−7.09 (m, 2H), 7.04 (t, J = 7.5 Hz, 2H), 6.82 (d, J = 7.9 Hz, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ (ppm) 144.1, 142.2, 141.7, 139.9, 134.4, 133.4, 132.6, 130.4, 130.3, 128.9, 128.7, 128.5, 128.2, 127.4, 126.9, 126.7, 125.4, 123.9, 122.6, 120.9, 114.4, 111.2. IR (CH_2Cl_2, cm^{-1}): 3305, 3079, 2938, 1688, 1543, 1457, 1410, 1310, 1143, 730. HRMS (ESI) m/z calcd for $C_{26}H_{19}NO_2S$ $[M + H]^+$; 410.1209, found: 410.1205.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c01123.

General experimental procedures, characterization, X-ray crystal structure data, and copies of the ^1H and ^{13}CNMR spectra of all new compounds (PDF)

Accession Codes

CCDC 2068424, 2068426−2068428, and 2068430−2068431 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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