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Iodine-Catalyzed C-H Amidation and Imination at 2*α*-Position of 2,3-Disubstituted Indoles with Chloramine Salts

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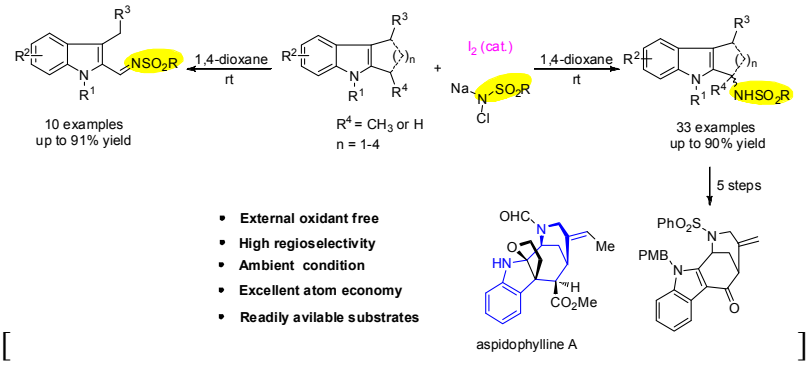
Supporting Information Placeholder



ABSTRACT: A novel iodine-catalyzed amidation and imination at 2*α*-position of 2,3-disubstituted indoles in the presence of chloramine salts with high regioselectivity has been achieved. The protocol is applicable to a wide range of substrates to deliver the corresponding 2*α*-nitrogen-containing indole derivatives. Furthermore, to demonstrate the synthetic value of this established transformation, a concise assembly of the bridged tetracyclic framework of akuammiline alkaloids from the 2*α*-amidated product has been accomplished in five steps.

■ INTRODUCTION

Indoles are among the most privileged structures that are widely found in naturally occurring alkaloids, organic materials, biologically active compounds, and medicinally relevant molecules.[1] Hence, considerable effort has been directed toward the development of efficient methods for their synthesis and functionalization.[2] Meanwhile, The direct functionalization of C-H bonds, which has been studied extensively in recent years, has become a powerful tool in the formation of C-C and C-heteroatom bonds owing to its inherent atom and step economy.[3] Consequently, this approach has attracted growing attention in indole functionalization and many impressive results have been documented.[4] In contrast, the methods for direct C-H bond functionalization of side chains of 2,3-disubstituted indoles are quite limited.[5] For instance, in 2011, Kawasaki and co-workers described an efficient procedure for C-H functionalization at indole 2*α*-position mediated by acyloxythionium species.[5a] Several similar transformations have been achieved *via* an oxidative coupling approach using different oxidants later.[5b-5d] Despite the merits of these methods, most of them suffer from drawbacks such as the relatively narrow scope of substrates and inevitable requirement of stoichiometric external oxidants to regenerate the active catalytic species or yield the reactive intermediates, thus lowering the atom economy and limiting the practical applications. Noticeably, 2*α*-functionalized indoles are not only privileged scaffolds in some bioactive compounds such as anti-HPV agents,[6] NPY receptor antagonists,[7] and PGD_2 receptor antagonists,[8] but also found as the core structures of some indole alkaloids (Figure 1).[9] Therefore, it is of great significance to develop new methods that allow for easy access to these attractive compounds, particularly the 2*α*-nitrogen-containing ones that could serve as key intermediates for the total synthesis of akuammiline alkaloids.[10]

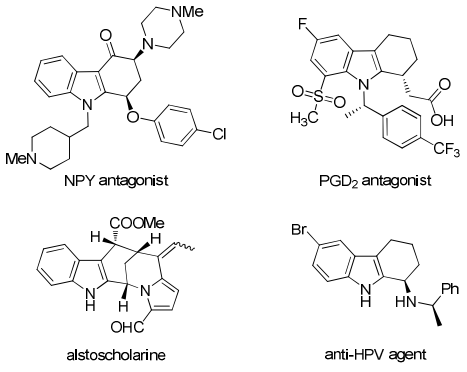
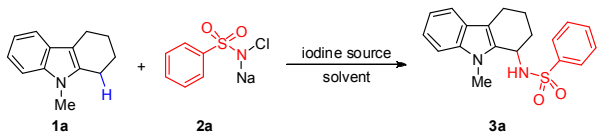


Figure 1. Representative natural products and biologically active molecules with 2*α*-substituted indole motifs.

Table 1. Optimization of Reaction Conditions[a]



Entry	Iodine source	Solvent	Yield [%][b]
1	I_2	CH_3CN	71
2	I_2	THF	68
3	I_2	toluene	44
4	I_2	1,4-dioxane	85
5	I_2	DCM	31
6	I_2	MeOH	28
7	I_2	H_2O	nd
8[c]	I_2	1,4-dioxane	56
9	NaI	1,4-dioxane	12
10	KI	1,4-dioxane	10
11	TBAI	1,4-dioxane	66
12	NIS	1,4-dioxane	81
13	-	1,4-dioxane	nd

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (1.1 mmol), iodine source (10 mol%), solvent (3 mL), room temperature, 9 h. [b] Isolated yield. [c]**2a** (0.6 mmol).

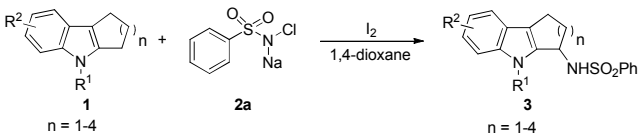
Recently, iodine-based catalytic systems in C-H bond functionalization have been significantly developed featuring the atom economy and the mild and eco-friendly conditions.[11] Furthermore, These protocols are efficient at promoting the synthetically challenging C(sp^3)-H amination.[12] Inspired by the above achievements, and in continuation of our interest in iodine-catalyzed functionalization of indoles,[13] we herein would like to disclose a novel iodine-catalyzed regioselective 2α-amidation and imination of 2,3-disubstituted indoles employing chloramine salts as both oxidants and nitrogen sources.

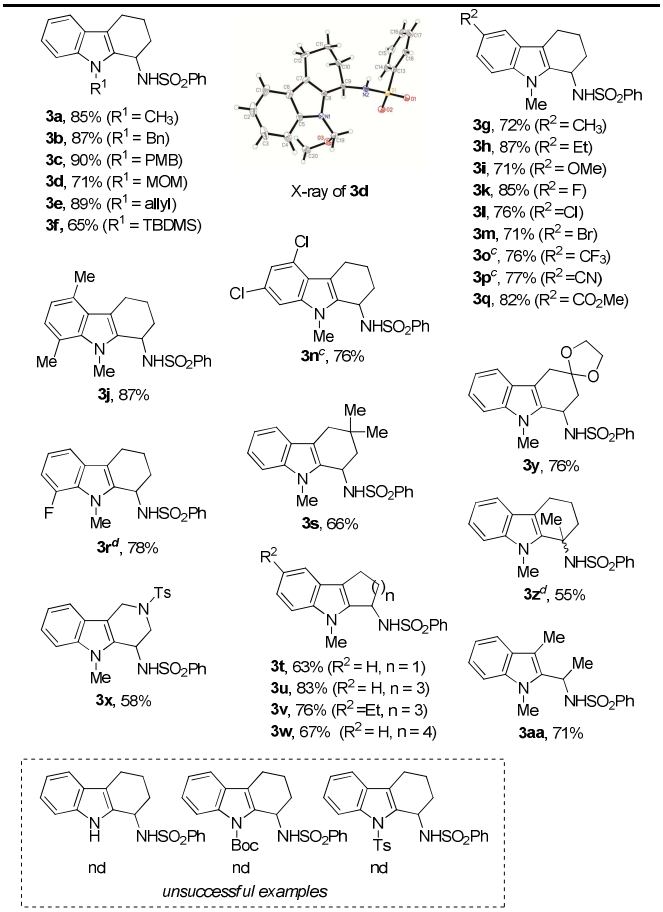
■ RESULTS AND DISCUSSION

Initially, we utilized *N*-methyltetrahydrocarbazole **1a** and chloramine-B **2a** as the model substrates to optimize the reaction conditions (Table 1). Gratifyingly, when the reaction was conducted in the presence of a catalytic amount of molecular iodine in acetonitrile at room temperature for 9 h, the desired compound **3a** was isolated in 71% yield (Table 1, entry 1). Encouraged by this promising result, further screening of the reaction conditions was performed. Among various potential solvents examined, 1, 4-dioxane gave the best result to afford **3a** in 85% yield (entries 2-6), whereas water as solvent did not provide any desired product (entry 7). Decreasing the amount of chloramine-B to 0.6 mmol resulted in a significant reduction in yield (56%, entry 8). Next, several other iodine sources were also tested for their efficiency, but they were found to be inferior to molecular iodine under the given conditions (entries 9-12). Moreover, no target compound was observed in the absence of iodine (entry 13).

With the optimized conditions in hand, we next explored the substrate scope. Initially, a wide range of indole derivatives

Table 2. Scope of 2,3-Disubstituted Indoles[a,b]

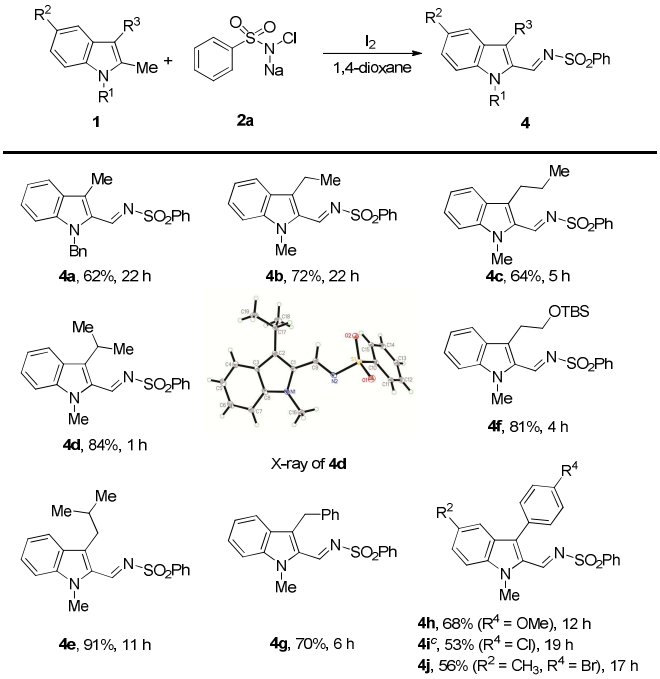




[a]Reaction conditions: **1** (0.5 mmol), chloramine-B (1.1 mmol), I_2 (10 mol%), 1,4-dioxane (3 mL), room temperature, 9 h. [b]Isolated yield. [c]At 50 °C. [d]The reaction time was 17 h.

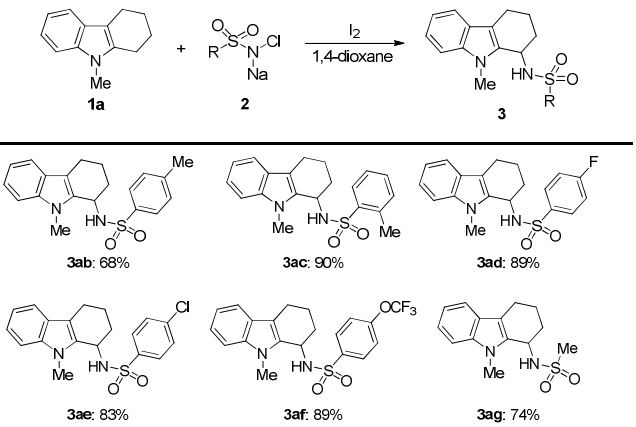
reacted smoothly with chloramine-B **2a**, affording the corresponding products in moderate to excellent yields (Table 2). The introduction of various protecting groups such as methyl, benzyl, PMB, MOM, allyl, and TBDMS for *N*-protection had only marginal influence on performance of the reaction (67-90%, **3a-f**). Among the products, the structure of **3d** was determined by X-ray diffraction of a single crystal.[14] Substrates with both electron-donating and electron-withdrawing groups on the indole core were engaged in this transformation, furnishing the corresponding products in good to excellent yields (**3g-r**). The tolerance of the Br substituent enables further transformation through classical cross-coupling reactions. Notably, the reaction worked well under the standard conditions when cyclic systems of different ring sizes were employed (**3t-w**). Most importantly, more hindered 1-methyl tetrahydrocarbazole derivative **1z** also reacted efficiently with excellent regioselectivity to give the desired 2α-amidated product **3z** in 55% yield. Likewise, the reaction of 2-ethyl-3-methylindole derivative **1aa** proceeded smoothly to give the

Table 3: Scope of 2-Methyl-3-substituted Indoles[a,b]



[a]Reaction conditions: **1** (0.5 mmol), chloramine-B (1.1 mmol), I_2 (10 mol%), 1,4-dioxane (3 mL), room temperature. [b]Isolated yield. [c]At 50 °C.

Table 4: Scope of Chloramine Salts[a,b]

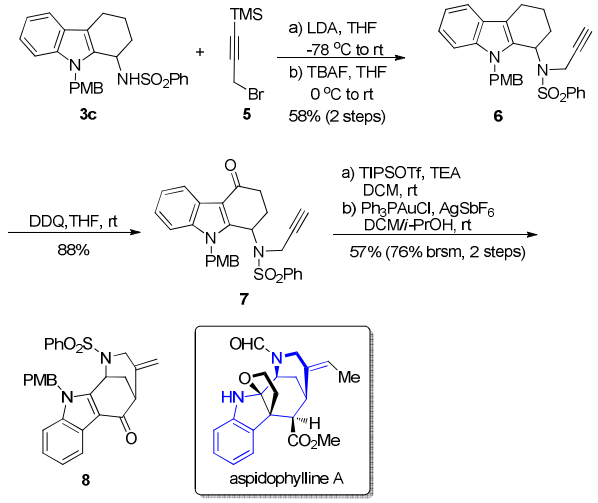


[a]Reaction conditions: **1a** (0.5 mmol), **2** (1.1 mmol), I_2 (10 mol%), 1,4-dioxane (3 mL), room temperature, 9 h. [b]Isolated yield.

desired 2α-amidated product **3aa** in good yield with excellent regioselectivity. These results indicated the regioselectivity might be thermodynamically controlled rather than kinetically.

Interestingly, reaction between chloramine-B and various 2-methyl-3-substituted indoles led to the formation of the corresponding 2α-iminated products instead of amidated ones in moderated to excellent yields (Table 3).[14] It is noteworthy that *N*-EWG-protected aldimines represent a valuable structural motif due to their capacity to serve as versatile building blocks for the synthesis of a wide range of nitrogen-containing compounds.[15]

Scheme 1: Assembly of a Tetracyclic Motif Present in Akuammiline Alkaloids from the Product 3c



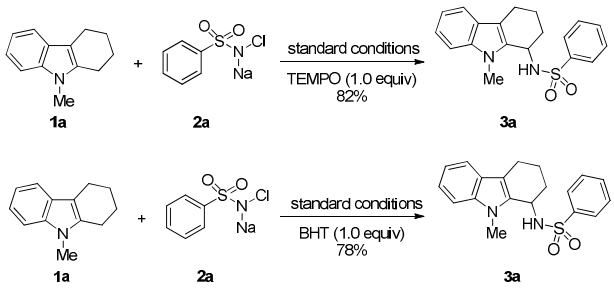
To further explore the potential of our methodology, several other chloramine salts were examined to react with *N*-methyl tetrohydrocarbazole **1a** under the optimized reaction conditions. The reaction proceeded smoothly to deliver the corresponding 2α-amidated products in good to excellent yields (Table 4).

In order to verify the synthetic utility of these C-H amidated products, a concise assembly of the bridged tetracyclic core of akuammiline alkaloids starting from **3c** was performed (Scheme 1). A sequence of *N*-propargylation and desilylation of **3c** afforded compound **6** with good overall efficiency. Treatment of **6** with DDQ furnished ketone **7** in 88% yield, without deprotecting the PMB group. Finally, gold-catalyzed intramolecular cyclization of the silyl enol ether generated from **7** provided the desired 6-*exo*-*dig* cyclization product **8**[10c, 16] in 57% overall yield (76% based on recovered starting material **7**).

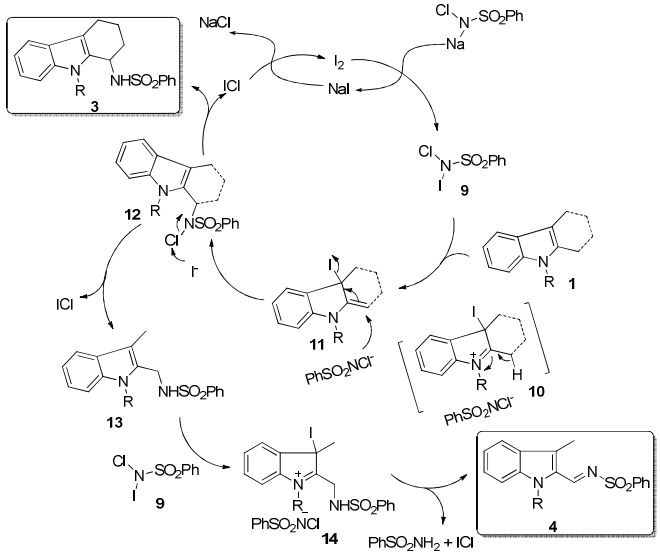
To gain insight into the mechanism of the reaction, the following experiments were carried out. As illustrated in Scheme 2, the reaction was not suppressed when the radical scavenger 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) or 2,6-di-*tert*-butyl-4-methylphenol (BHT) was added under the standard reaction conditions. This means that a radical pathway is not involved in this reaction.

On the basis of these observations and the literature reports,[5b, 17] a plausible mechanism is proposed in Scheme 3. Initially, the interaction of chloramine-B and iodine generates the active species *N*-iodo-chlorobenzenesulfonamide **9**, which subsequently activates the indole moiety **1** to give iminium intermediate **10**. Elimination of a hydrogen atom at the 2α-position provides enamine **11**. Subsequent S_N2'displacement of **11** by the chloramine-B results in the formation of chloramine **12**, which then reacts with iodide ion to give the amidated product **3**. Finally, the resulting iodine monochloride oxidizes NaI to regenerate iodine. As for 2-methyl-3-substituted indoles, the intermediate 2α-amidated indole **13** continues to react with another molecule of **9**, which produces the final iminated product **4** along with the release of benzene sulfonamide and iodine monochloride. The latter then oxidizes NaI to regenerate iodine.

Scheme 2: Radical Scavenger Experiment



Scheme 3: Plausible Reaction Mechanism



■ CONCLUSIONS

In summary, we have developed a general and practical method for iodine-catalyzed regioselective C-H amidation and imination at the 2α-position of 2,3-disubstituted indoles with chloramine salts, which enables the facile and direct construction of various 2α-nitrogen-containing indoles. The reaction features mild and environmentally benign reaction conditions, broad substrate scope, and good functional group compatibility. Furthermore, the products are important synthetic intermediates which have been demonstrated by a concise assembly of the bridged tetracyclic core of akuammiline alkaloids, providing a powerful tool for the total synthesis of natural molecules in this family.

■ EXPERIMENTAL SECTION

General Methods. Unless otherwise noted, all commercial materials and solvents were used without further purification. Commercially available chemicals were obtained from Energy Chemical, TCI, Alfa Aesar and J&K. Thin layer chromatography (TLC) was carried out on GF254 plates (0.25 mm layer thickness) and visualized under UV light (254 nm). The silica gel (200-300 meshes) was used for column chromatography. ^{1}H NMR and ^{13}C NMR were recorded on Agilent 400 MHz spectrometer using TMS as internal standard. Spin multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), td (triplet of doublet), as well as brs (broad). Coupling constants (*J*) are given in hertz (Hz). High resolution mass spectra were obtained on Agilent 6210 ESI/TOF spectrometer.

General procedure for the synthesis of 3. A 25 mL round bottom flask with a magneton was charged with 2,3-disubstituted indole **1** (0.5 mmol), chloramine salt **2** (1.1 mmol), and 1,4-dioxane (3 mL) under air at room temperature, and then I_2 (13 mg, 0.05 mmol) was added. The mixture was stirred vigorously for 9 h. After that, the reaction mixture was filtered. The filtrate was concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent afforded the desired product **3**.

General procedure for the synthesis of 4. A 25 mL round bottom flask with a magneton was charged with 2-methyl-3-substituted indole **1** (0.5 mmol), chloramine-B **2a** (0.24 g, 1.1 mmol), and 1, 4-dioxane (3 mL) under air at room temperature, and then I_2 (13 mg, 0.05 mmol) was added. The mixture was vigorously stirred and monitored by thin layer chromatography. After completion, the reaction mixture was filtered. The filtrate was concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent afforded the desired product **4**.

Procedures for the synthesis of bridged tetracycle 8. Alkyne 6: To a stirred solution of benzenesulfonamide **3c** (0.60 g, 1.35 mmol) in dry THF (18 mL) were added dropwise LDA (1.35 mL, 2.70 mmol, 2.0 M in THF) at -78 °C. The reaction mixture was stirred at that temperature for 30 min and then warmed up to 0 °C. TMS-propargylbromide **5** (0.45 mL, 2.76 mmol) and (n-Bu)$_4$NI (0.51 mg, 1.35 mmol) were added. The reaction mixture was warmed to room temperature and stirred for further 12 h. After completion, the resultant mixture was quenched with saturated NH_4Cl (30 mL), extracted with ethyl acetate (3 x 30 mL), dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The obtained brown oil was dissolved in dry THF (3 mL), and then cooled to 0 ^{o}C. To the stirred solution was added dropwise TBAF (2 mL, 2.0 mmol, 1 M in THF). The resultant mixture was warmed to room temperature and stirred for 30 min before it was quenched with brine (10 mL). The resultant mixture was extracted with ethyl acetate (3 x 10 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography with EtOAc/petroleum ether (1:6) to give the alkyne **6** (0.383g, 58%, 2 steps) as a colorless oil which was solidified on standing.

Ketone 7: To the stirred solution of alkyne **6** (99 mg, 0.20 mmol) in THF/water (11 mL, 10:1) was added DDQ (93 mg, 0.41 mmol) at 0 °C. The resultant mixture was allowed to warm to room temperature and stirred at that temperature for 3 h before it was quenched with saturated aq. $NaHCO_3$ (10 mL) and extracted with EtOAc (3 × 15 mL). The combined organic phases were washed with brine (10 mL) and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent under vacuum, the residue was subjected to flash column chromatography for purification using EtOAc/petroleum ether (1:2) as eluent to give the ketone **7** (90 mg, 88%) as a brown solid.

Terminal alkene 8: To a stirred solution of ketone **7** (0.10 g, 0.20 mmol) in dry CH_2Cl_2 (10 mL) were sequentially added Et_3N (0.11 mL, 0.80 mmol) and TIPSOTf (0.22 mL, 0.80 mmol) at room temperature. The reaction mixture was stirred

at that temperature for 2 h. The resultant mixture was concentrated under vacuum, and the residue was purified by flash column chromatography with EtOAc/petroleum ether (1:5) to give the silyl enol ether (0.121 g, 92%) as a brown oil. The oil was then dissolved in dry CH_2Cl_2 (5 mL). To the stirred solution were sequentially added *i*-PrOH (0.38 mL), 4 Å molecular sieves (0.2 g), Ph_3PAuCl (5 mg, 5 mol%), $AgSbF_6$ (4 mg, 5 mol%), and 2,4,6-tri-*tert*-butylpyrimidine (5 mg, 10 mol%) at room temperature. The resultant mixture was allowed to stir at that temperature for 13 h. After that, the resultant mixture was directly subjected to flash column chromatography for purification using EtOAc/petroleum ether (1:3) as eluent to give the cyclization product **8** (59 mg, 57%, 76% brsm, 2 steps) as a white solid and ketone **7** (25 mg) was recovered.

Characterization Data of Products. *N-(9-methyl-2,3,4,9-tetrahydro-1H-carbazol-1-yl)benzenesulfonamide (**3a**):* White solid, 144 mg, 85% yield, m.p. 231.2-232.8 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.14 (dd, *J* = 8.2, 2.6 Hz, 1H), 7.98 – 7.79 (m, 2H), 7.64 (tdd, *J* = 9.5, 4.9, 2.2 Hz, 3H), 7.37 (ddd, *J* = 22.7, 8.2, 2.5 Hz, 2H), 7.19 – 7.05 (m, 1H), 6.97 (td, *J* = 7.4, 2.4 Hz, 1H), 4.68 (dd, *J* = 8.2, 3.5 Hz, 1H), 3.44 (s, 3H), 2.73 – 2.56 (m, 1H), 2.45 – 2.33 (m, 1H), 1.89 – 1.71 (m, 1H), 1.67 – 1.50 (m, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 142.9, 137.2, 133.0, 132.9, 129.7, 126.8, 126.2, 122.1, 118.9, 118.6, 111.9, 109.7, 45.6, 30.2, 29.2, 20.8, 17.8. HRMS-ESI (m/z): calcd for $C_{19}H_{21}N_2O_2S$ $[M + H]^+$: 341.1318, found 341.1317.

*N-(9-benzyl-2,3,4,9-tetrahydro-1H-carbazol-1-yl)benzenesulfonamide (**3b**):* White solid, 182 mg, 87% yield, m.p. 216.1-218.0 □. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.7 Hz, 2H), 7.66 – 7.38 (m, 4H), 7.29 – 7.04 (m, 6H), 6.89 – 6.72 (m, 2H), 5.17 (d, *J* = 2.8 Hz, 2H), 4.78 (d, *J* = 8.6 Hz, 1H), 4.66 (d, *J* = 8.4 Hz, 1H), 2.96 – 2.77 (m, 1H), 2.61 (dd, *J* = 10.6, 4.9 Hz, 1H), 1.93 – 1.64 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 137.9, 137.1, 132.7, 131.5, 129.2, 128.6, 127.1, 126.9, 126.4, 125.9, 122.7, 119.4, 118.8, 113.6, 109.9, 46.1, 45.8, 30.1, 20.7, 17.7. HRMS-ESI (m/z): calcd for $C_{25}H_{25}N_2O_2S$ $[M + H]^+$: 417.1631, found 417.1637.

*N-(9-(4-methoxybenzyl)-2,3,4,9-tetrahydro-1H-carbazol-1-yl)benzenesulfonamide (**3c**):* White solid, 202 mg, 90% yield, m.p. 137.7-140.1 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.29 (d, *J* = 8.7 Hz, 1H), 7.97 – 7.81 (m, 2H), 7.71 – 7.52 (m, 3H), 7.49 – 7.37 (m, 1H), 7.32 – 7.21 (m, 1H), 7.05 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 6.99 – 6.88 (m, 3H), 6.80 (d, *J* = 8.7 Hz, 2H), 5.33 (d, *J* = 16.4 Hz, 1H), 5.10 (d, *J* = 16.4 Hz, 1H), 4.69 – 4.54 (m, 1H), 3.68 (s, 3H), 2.79 – 2.62 (m, 1H), 2.48 – 2.36 (m, 1H), 1.84 (dd, *J* = 14.5, 8.3 Hz, 1H), 1.64 – 1.47 (m, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.7, 142.9, 136.8, 132.9, 132.7, 130.7, 129.7, 128.1, 126.7, 126.6, 122.3, 119.2, 118.8, 114.2, 112.5, 110.6, 55.4, 45.9, 45.3, 29.8, 20.8, 17.6. HRMS-ESI (m/z): calcd for $C_{26}H_{27}N_2O_3S$ $[M + H]^+$: 447.1737, found 447.1738.

*N-(9-(methoxymethyl)-2,3,4,9-tetrahydro-1H-carbazol-1-yl)benzenesulfonamide (**3d**):* White solid, 135 mg, 71% yield, m.p. 146.6-148.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dt, *J* = 6.9, 1.5 Hz, 2H), 7.67 – 7.60 (m, 1H), 7.55 (ddt, *J* = 8.6, 7.1, 1.5 Hz, 2H), 7.47 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.43 – 7.34 (m, 1H), 7.29 – 7.18 (m, 1H), 7.12 (ddt, *J* = 8.5, 7.1, 1.3 Hz, 1H), 5.35 – 5.05 (m, 3H), 4.81 – 4.73 (m, 1H), 3.24 (s, 3H), 2.83 – 2.70 (m, 1H), 2.60 – 2.43 (m, 1H), 2.02 – 1.87 (m, 1H), 1.84 – 1.64 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 137.6, 132.8, 131.4, 129.2, 127.1, 126.8, 123.1, 120.1, 118.9, 115.4, 109.6, 73.3, 56.0, 46.1, 29.8, 20.6, 17.8. HRMS-ESI (m/z): calcd for $C_{20}H_{22}N_2NaO_3S$ $[M + Na]^+$: 393.1243, found 393.1241.

*N-(9-allyl-2,3,4,9-tetrahydro-1H-carbazol-1-yl)benzenesulfonamide (**3e**):* Brown solid, 162 mg, 89% yield, m.p. 116.0-118.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.90 (m, 2H), 7.71 – 7.41 (m, 4H), 7.21 (d, *J* = 5.7 Hz, 2H), 7.08 (ddd, *J* = 7.9, 5.9, 2.0 Hz, 1H), 5.89 – 5.72 (m, 1H), 5.15 – 5.00 (m, 1H), 4.78 – 4.45 (m, 5H), 2.80 (dd, *J* = 15.7, 3.6 Hz, 1H), 2.56 (ddd, *J* = 16.3, 11.1, 6.5 Hz, 1H), 1.90 – 1.66 (m, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 142.9, 136.7, 134.9, 132.9, 132.5, 129.8, 126.7, 126.4, 122.2, 119.1, 118.8, 116.4, 112.3, 110.3, 45.7, 45.0, 29.9, 20.8, 17.8. HRMS-ESI (m/z): calcd for $C_{21}H_{23}N_2O_2S$ $[M + H]^+$: 367.1475, found 367.1476.

*N-(9-(tert-butyldimethylsilyl)-2,3,4,9-tetrahydro-1H-carbazol-1-yl)benzenesulfonamide (**3f**):* Brown solid, 147 mg, 65% yield, m.p. 68.6-71.3 °C,. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dq, *J* = 7.1, 1.2 Hz, 2H), 7.62 – 7.52 (m, 2H), 7.53 – 7.44 (m, 2H), 7.40 (dq, *J* = 7.7, 1.1 Hz, 1H), 7.21 – 7.11 (m, 1H), 7.12 – 7.03 (m, 1H), 5.04 (dd, *J* = 5.9, 3.0 Hz, 1H), 4.57 (dd, *J* = 5.9, 2.5 Hz, 1H), 2.81 – 2.70 (m, 1H), 2.55 (ddd, *J* = 16.4, 11.2, 7.2 Hz, 1H), 2.11 – 2.00 (m, 1H), 1.67 – 1.53 (m, 1H), 1.49 – 1.35 (m, 2H), 0.88 (d, *J* = 1.1 Hz, 9H), 0.81 (dd, *J* = 12.3, 1.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 142.3, 136.7, 132.4, 129.8, 129.0, 126.5, 122.4, 119.7, 118.3, 117.4, 115.0, 49.2, 28.7, 27.1, 20.8, 20.7, 15.6, -0.4, -0.7. HRMS-ESI (m/z): calcd for $C_{24}H_{33}N_2O_2S$ Si $[M + H]^+$: 441.2027, found 441.2030.

*N-(6,9-dimethyl-2,3,4,9-tetrahydro-1H-carbazol-1-yl)benzenesulfonamide (**3g**):* Brown solid, 128 mg, 72% yield, m.p. 212.0-214.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.90 (m, 2H), 7.71 – 7.44 (m, 3H), 7.26 (dd, *J* = 2.2, 1.2 Hz, 1H), 7.13 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 4.85 – 4.60 (m, 2H), 3.48 (t, *J* = 1.2 Hz, 3H), 2.85 – 2.70 (m, 1H), 2.57 – 2.36 (m, 4H), 1.89 – 1.60 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 135.8, 132.8, 131.6, 129.3, 128.3, 126.9, 126.2, 124.0, 118.4, 112.3, 108.8, 46.1, 30.2, 29.1, 21.4, 20.6, 18.0. HRMS-ESI (m/z): calcd for $C_{20}H_{23}O_2N_2S$ $[M + H]^+$: 355.1475, found 355.1476.

*N-(6-ethyl-9-methyl-2,3,4,9-tetrahydro-1H-carbazol-1-yl)benzenesulfonamide (**3h**)*: Brown solid, 160 mg, 87% yield, m.p. 157.6-159.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.93 (m, 2H), 7.67 – 7.59 (m, 1H), 7.56 (dd, *J* = 8.4, 6.6 Hz, 2H), 7.31 (dd, *J* = 6.1, 3.0 Hz, 1H), 7.02 – 6.96 (m, 2H), 4.79 (d, *J* = 8.5 Hz, 1H), 4.68 (d, *J* = 8.5 Hz, 1H), 3.76 (s, 3H), 3.15 – 3.00 (m, 2H), 2.83 – 2.71 (m, 1H), 2.60 – 2.43 (m, 1H), 1.86 – 1.62 (m, 4H), 1.37 – 1.27 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 135.4, 132.8, 132.1, 129.3, 127.9, 127.3, 126.9, 123.9, 119.3, 116.6, 113.3, 46.2, 32.0, 30.2, 25.9, 20.6, 17.7, 16.8. HRMS-ESI (m/z): calcd for $C_{21}H_{25}N_2O_2S$ $[M + H]^+$: 369.1631, found 369.1636.

*N-(6-methoxy-9-methyl-2,3,4,9-tetrahydro-1H-carbazol-1-yl)benzenesulfonamide (**3i**)*: White solid, 132 mg, 71% yield, m.p. 174.7-175.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (ddd, *J* = 8.7, 3.2, 1.5 Hz, 2H), 7.70 – 7.48 (m, 3H), 7.13 (dd, *J* = 8.8, 3.3 Hz, 1H), 6.89 (ddt, *J* = 10.2, 3.7, 1.9 Hz, 2H), 4.77 (t, *J* = 4.2 Hz, 2H), 3.84 (s, 3H), 3.47 (s, 3H), 2.73 (dd, *J* = 15.3, 3.6 Hz, 1H), 2.57 – 2.41 (m, 1H), 1.89 – 1.64 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 141.7, 132.7, 132.7, 132.2, 129.2, 126.9, 126.2, 112.5, 112.3, 109.8, 100.7, 56.0, 46.1, 30.2, 29.2, 20.7, 18.0. HRMS-ESI (m/z): calcd for $C_{20}H_{23}N_2O_3S$ $[M + H]^+$: 371.1424, found 371.1429.

*N-(5,8,9-trimethyl-2,3,4,9-tetrahydro-1H-carbazol-1-yl)benzenesulfonamide (**3j**)*: Yellow solid, 161 mg, 87% yield, m.p.

150.0-150.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 7.2, 1.8 Hz, 2H), 7.70 – 7.48 (m, 3H), 6.76 (d, *J* = 7.2 Hz, 1H), 6.64 (d, *J* = 7.2 Hz, 1H), 4.80 – 4.54 (m, 2H), 3.76 (s, 3H), 3.17 – 3.03 (m, 1H), 2.85 – 2.72 (m, 1H), 2.68 (s, 3H), 2.57 (s, 3H), 1.86 – 1.72 (m, 2H), 1.69 – 1.60 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 143.1, 136.0, 132.9, 132.7, 129.7, 128.3, 126.7, 126.0, 124.9, 120.4, 118.7, 112.6, 45.7, 32.1, 29.3, 23.5, 20.3, 20.1, 17.8. HRMS-ESI (m/z): calcd for $C_{21}H_{25}N_2O_2S$ $[M + H]^+$: 369.1631, found 369.1637.

N-(6-fluoro-9-methyl-2,3,4,9-tetrahydro-1H-carbazol-1-yl) benzenesulfonamide ***(3k)***: Brown solid, 155 mg, 85% yield, m.p. 218.6-220.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 7.86 (m, 2H), 7.69 – 7.47 (m, 3H), 7.13 (ddd, *J* = 19.7, 9.2, 3.4 Hz, 2H), 6.96 (td, *J* = 9.1, 2.5 Hz, 1H), 4.91 – 4.60 (m, 2H), 3.53 (s, 3H), 2.80 – 2.65 (m, 1H), 2.58 – 2.40 (m, 1H), 1.87 – 1.60 (m, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.2 (d, *J* = 231.7 Hz), 142.9, 135.0, 133.9, 132.9, 129.7, 126.8, 126.2 (d, *J* = 9.8 Hz), 112.0 (d, *J* = 4.8 Hz), 110.8 (d, *J* = 9.7 Hz), 110.0 (d, *J* = 25.9 Hz), 103.5 (d, *J* = 23.0 Hz), 45.6, 30.1, 29.5, 20.7, 17.7. HRMS-ESI (m/z): calcd for $C_{19}H_{20}FN_2O_2S$ $[M + H]^+$: 359.1224, found 359.1221.

N-(6-chloro-9-methyl-2,3,4,9-tetrahydro-1H-carbazol-1-yl) benzenesulfonamide ***(3l)***: Brown solid, 144 mg, 76% yield, m.p. 210.0-212.6 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.15 (ddd, *J* = 8.3, 3.8, 2.4 Hz, 1H), 8.02 – 7.84 (m, 2H), 7.73 – 7.57 (m, 3H), 7.45 (dd, *J* = 3.9, 1.9 Hz, 1H), 7.43 – 7.31 (m, 1H), 7.11 (ddd, *J* = 8.8, 4.0, 1.9 Hz, 1H), 4.68 (dd, *J* = 8.1, 4.0 Hz, 1H), 3.45 (s, 3H), 2.65 (dq, *J* = 15.6, 3.3 Hz, 1H), 2.37 (dd, *J* = 15.6, 11.3 Hz, 1H), 1.79 (d, *J* = 10.5 Hz, 1H), 1.64 – 1.48 (m, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 142.9, 135.7, 134.8, 132.9, 129.7, 127.2, 126.8, 123.6, 121.9, 118.0, 111.8, 111.4, 45.5, 30.1, 29.5, 20.6, 17.7. HRMS-ESI (m/z): calcd for $C_{19}H_{20}ClN_2O_2S$ $[M + H]^+$: 375.0929, found 375.0931.

N-(6-bromo-9-methyl-2,3,4,9-tetrahydro-1H-carbazol-1-yl) benzenesulfonamide ***(3m)***: Brown solid, 150 mg, 71% yield, m.p. 210.4-210.7 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.15 (d, *J* = 8.1 Hz, 1H), 7.90 (dt, *J* = 8.0, 1.4 Hz, 2H), 7.72 – 7.53 (m, 4H), 7.35 (d, *J* = 8.7 Hz, 1H), 7.22 (dt, *J* = 8.7, 1.5 Hz, 1H), 4.68 (dt, *J* = 7.8, 3.5 Hz, 1H), 3.45 (d, *J* = 1.2 Hz, 3H), 2.73 – 2.57 (m, 1H), 2.37 (ddd, *J* = 15.8, 10.9, 5.1 Hz, 1H), 1.78 (q, *J* = 7.8, 5.4 Hz, 1H), 1.58 (q, *J* = 7.8, 6.2 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 142.8, 135.9, 134.6, 132.9, 129.7, 127.9, 126.8, 124.4, 121.0, 111.9, 111.7, 111.5, 45.5, 30.1, 29.4, 20.6, 17.7. HRMS-ESI (m/z): calcd for $C_{19}H_{19}BrN_2NaO_2S$ $[M + Na]^+$: 441.0243, found 441.0247.

N-(5,7-dichloro-9-methyl-2,3,4,9-tetrahydro-1H-carbazol-1 -yl)benzenesulfonamide ***(3n)***: Pale yellow solid, 157 mg, 76% yield, m. p. 235.3-237.5 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.18 (d, *J* = 8.2 Hz, 1H), 7.94 – 7.84 (m, 2H), 7.73 – 7.58 (m, 3H), 7.53 (d, *J* = 1.6 Hz, 1H), 7.05 (d, *J* = 1.6 Hz, 1H), 4.68 (dd, *J* = 8.0, 3.9 Hz, 1H), 3.46 (s, 3H), 3.08 – 2.93 (m, 1H), 2.61 (ddd, *J* = 16.4, 11.0, 5.5 Hz, 1H), 1.76 (dd, *J* = 12.2, 6.9 Hz, 1H), 1.53 (dt, *J* = 10.4, 3.6 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 142.8, 138.4, 135.5, 133.0, 130.0, 126.8, 126.5, 126.0, 122.0, 119.3, 112.0, 109.3, 45.4, 30.0, 29.3, 22.6, 17.6. HRMS-ESI (m/z): calcd for $C_{19}H_{18}O_2N_2Cl_2NaS$ $[M + Na]^+$: 431.0358, found 431.0359.

N-(9-methyl-6-(trifluoromethyl)-2,3,4,9-tetrahydro-1H-carbazol-1-yl)benzenesulfonamide ***(3o)***: White solid, 154 mg, 76% yield, m.p. 182.4-184.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.90 (m, 2H), 7.75 (s, 1H), 7.61 (dd, *J* = 7.3, 1.7 Hz, 1H), 7.54 (ddd, *J* = 8.8, 6.7, 1.7 Hz, 2H), 7.44 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.30 (d, *J* = 8.8 Hz, 1H), 4.97 – 4.72 (m, 2H), 3.58 (s, 3H), 2.78 (dt, *J* = 15.9, 2.6 Hz, 1H), 2.54 (td, *J* = 10.4, 4.9 Hz, 1H), 1.90 – 1.63 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 138.6, 133.6, 132.9, 129.3, 126.8, 125.4, 124.0(q, *J* = 269.5 Hz), 121.3 (q, *J* = 31.8 Hz), 119.0 (q, *J* = 3.5 Hz), 116.4 (q, *J* = 4.2 Hz), 113.9, 109.3, 45.9, 29.9, 29.4, 20.4, 17.8. HRMS-ESI (m/z): calcd for $C_{20}H_{20}O_2N_2F_3S$ $[M + H]^+$: 409.1192, found 409.1194.

N-(6-cyano-9-methyl-2,3,4,9-tetrahydro-1H-carbazol-1-yl)-benzenesulfonamide ***(3p)***: White solid, 143 mg, 77% yield, m.p. 275.3-277.7 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.16 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 1.5 Hz, 1H), 7.91 – 7.82 (m, 2H), 7.63 (tt, *J* = 8.9, 6.1 Hz, 3H), 7.54 (d, *J* = 8.6 Hz, 1H), 7.45 (dd, *J* = 8.5, 1.6 Hz, 1H), 4.70 (dd, *J* = 8.0, 3.9 Hz, 1H), 3.49 (s, 3H), 2.78 – 2.63 (m, 1H), 2.43 – 2.31 (m, 1H), 1.82 – 1.71 (m, 1H), 1.58 (q, *J* = 7.7 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 142.7, 138.7, 135.8, 133.0, 129.8, 126.8, 126.0, 124.8, 124.4, 121.2, 113.3, 111.1, 100.8, 45.4, 30.0, 29.6, 20.5, 17.5. HRMS-ESI (m/z): calcd for $C_{20}H_{20}O_2N_3S$ $[M + H]^+$: 366.1271, found 366.1273.

Methyl 9-methyl-1-(phenylsulfonamido)-2,3,4,9-tetrahydro-1H-carbazole-6-carboxylate ***(3q)***: Pale yellow solid, 164 mg, 82% yield, m.p. 199.3-200.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 1.7 Hz, 1H), 8.01 – 7.92 (m, 2H), 7.89 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.71 – 7.49 (m, 3H), 7.23 (d, *J* = 8.8 Hz, 1H), 4.95 – 4.74 (m, 2H), 3.91 (s, 3H), 3.58 (s, 3H), 2.80 (dt, *J* = 16.3, 3.1 Hz, 1H), 2.54 (ddd, *J* = 16.0, 10.4, 5.2 Hz, 1H), 1.89 – 1.63 (m, 4H). ^{13}C NMR (101 MHz, cdcl$_3$) δ 168.2, 141.6, 139.8, 133.2, 132.8, 129.3, 126.8, 125.6, 123.6, 121.7, 120.8, 114.5, 108.6, 51.8, 45.9, 30.0, 29.4, 20.5, 17.8. HRMS-ESI (m/z): calcd for $C_{21}H_{23}O_4N_2S$ $[M + H]^+$: 399.1373, found 399.1373.

N-(8-fluoro-9-methyl-2,3,4,9-tetrahydro-1H-carbazol-1-yl)-benzenesulfonamide ***(3r)***: White solid, 140 mg, 78% yield, m.p. 184.3-185.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dt, *J* = 8.5, 1.3 Hz, 2H), 7.65 – 7.56 (m, 1H), 7.52 (ddd, *J* = 8.5, 6.7, 1.4 Hz, 2H), 7.17 (d, *J* = 7.7 Hz, 1H), 6.91 (tdd, *J* = 7.9, 4.5, 1.3 Hz, 1H), 6.87 – 6.78 (m, 1H), 4.80 (d, *J* = 8.7 Hz, 1H), 4.72 (q, *J* = 4.9, 3.9 Hz, 1H), 3.66 (s, 3H), 2.73 (dd, *J* = 16.6, 4.5 Hz, 1H), 2.49 (td, *J* = 10.1, 5.0 Hz, 1H), 1.93 – 1.53 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1 (d, *J* = 243.9 Hz), 141.5, 132.8, 132.8, 130.0 (d, *J* = 5.7 Hz), 129.3, 126.8, 125.1 (d, *J* = 8.9 Hz), 119.1 (d, *J* = 6.5 Hz), 114.4 (d, *J* = 3.4 Hz), 113.7 (d, *J* = 1.7 Hz), 108.1 (d, *J* = 18.3 Hz), 45.7, 31.6 (d, *J* = 6.4 Hz), 30.1, 20.7, 17.6. HRMS-ESI (m/z): calcd for $C_{19}H_{20}FN_2O_2S$ $[M + H]^+$: 359.1224, found 359.1227.

N-(3,3,9-trimethyl-2,3,4,9-tetrahydro-1H-carbazol-1-yl)benzenesulfonamide ***(3s)***: White solid, 121 mg, 66% yield, m.p. 223.3-226.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 7.90 (m, 2H), 7.68 – 7.62 (m, 1H), 7.58 (ddd, *J* = 8.5, 6.5, 1.6 Hz, 2H), 7.44 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.28 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.22 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 7.08 (ddd, *J* = 7.9, 6.8, 1.2 Hz, 1H), 4.84 (dt, *J* = 11.5, 6.0 Hz, 1H), 4.57 (d, *J* = 9.9 Hz, 1H), 3.71 (s, 3H), 2.61 – 2.37 (m, 2H), 1.61 (dd, *J* = 13.6, 6.0 Hz, 1H), 1.36 (dd, *J* = 13.6, 6.1 Hz, 1H), 0.97 (s, 3H), 0.88 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 142.9, 138.0, 133.0, 131.6, 129.7, 126.8, 126.5, 121.9, 118.9, 118.5, 111.2, 109.7, 47.0, 44.5, 34.9, 31.7, 30.5, 30.4, 26.5. HRMS-ESI (m/z): calcd for $C_{21}H_{25}O_2N_2S$ $[M + H]^+$: 369.1631, found 369.1634.

N-(4-methyl-1,2,3,4-tetrahydrocyclopenta[b]indol-3-yl)benzenesulfonamide ***(3t)***: White solid, 106 mg, 63% yield, m.p. 180.6-181.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.88 (m,

2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.27–7.26 (m, 2H), 7.12 – 7.05 (m, 1H), 5.03 (t, *J* = 8.5 Hz, 1H), 4.67 (d, *J* = 9.9 Hz, 1H), 3.61 (s, 3H), 2.84 (t, *J* = 8.6 Hz, 1H), 2.73 – 2.52 (m, 2H), 1.96 (t, *J* = 10.0 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 143.1, 142.2, 142.1, 132.9, 129.7, 127.0, 123.4, 121.5, 119.31, 119.30, 119.1, 110.5, 52.2, 37.3, 30.3, 22.7. HRMS-ESI (m/z): calcd for $C_{18}H_{19}N_2O_2S$ $[M + H]^+$: 327.1162, found 327.1166.

*N-(5-methyl-5,6,7,8,9,10-hexahydrocyclohepta[b]indol-6-yl)benzenesulfonamide (**3u**)*: White solid, 180 mg, 83% yield, m.p. 140.7-141.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dt, *J* = 8.3, 1.2 Hz, 2H), 7.56 – 7.34 (m, 4H), 7.24 – 7.13 (m, 2H), 7.11 – 6.99 (m, 1H), 4.96 (td, *J* = 6.7, 6.1, 3.4 Hz, 1H), 4.78 (d, *J* = 7.2 Hz, 1H), 3.46 (s, 3H), 2.93 (ddd, *J* = 15.7, 6.6, 2.4 Hz, 1H), 2.64 (ddd, *J* = 15.5, 11.3, 2.6 Hz, 1H), 2.19 – 2.06 (m, 1H), 1.99 – 1.71 (m, 4H), 1.65 – 1.57 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 136.0, 135.0, 132.5, 128.9, 127.0, 126.7, 122.1, 119.0, 118.5, 115.6, 109.2, 49.4, 31.8, 29.2, 28.1, 24.0, 23.5. HRMS-ESI (m/z): calcd for $C_{20}H_{23}N_2O_2S$ $[M + H]^+$: 355.1475, found 355.1478.

*N-(2-ethyl-5-methyl-5,6,7,8,9,10-hexahydrocyclohepta[b]-indol-6-yl)benzenesulfonamide (**3v**)*: Yellow solid, 148 mg, 76% yield, m.p. 170.1-172.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.79 (m, 2H), 7.64 – 7.48 (m, 1H), 7.48 – 7.36 (m, 2H), 7.31 (dt, *J* = 7.5, 1.1 Hz, 1H), 7.08 – 6.91 (m, 2H), 4.97 (t, *J* = 6.5 Hz, 1H), 4.74 (d, *J* = 7.3 Hz, 1H), 3.71 (s, 3H), 3.03 (q, *J* = 7.5 Hz, 2H), 2.93 – 2.82 (m, 1H), 2.68-2.58 (m, 1H), 2.17 – 2.07 (m, 1H), 1.94 – 1.70 (m, 4H), 1.60 (dd, *J* = 5.7, 2.9 Hz, 1H), 1.31 (td, *J* = 7.5, 0.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 135.5, 134.3, 132.5, 128.9, 128.0, 127.5, 126.8, 123.8, 119.2, 116.5, 116.2, 49.5, 32.0, 31.6, 27.9, 26.2, 23.8, 23.3, 16.7. HRMS-ESI (m/z): calcd for $C_{22}H_{26}N_2NaO_2S$ $[M + Na]^+$: 405.1607, found 405.1609.

*N-(5-methyl-6,7,8,9,10,11-hexahydro-5H-cycloocta[b]indol-6-yl)benzenesulfonamide (**3w**)*: Pale yellow solid, 123 mg, 67% yield, m.p. 170.8-172.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 8.5, 2.2 Hz, 2H), 7.50 – 7.37 (m, 2H), 7.34 – 7.24 (m, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.07 (ddt, *J* = 7.7, 3.9, 1.6 Hz, 1H), 5.17 – 5.03 (m, 1H), 5.02 – 4.87 (m, 1H), 3.56 (s, 3H), 3.10 – 2.88 (m, 1H), 2.77 – 2.61 (m, 1H), 2.11 (d, *J* = 11.7 Hz, 1H), 1.90 (ddd, *J* = 14.0, 6.8, 3.5 Hz, 1H), 1.76 – 1.65(m, 1H), 1.62-1.43 (m, 3H), 1.31 – 1.08 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 136.9, 132.5, 132.5, 128.7, 126.8, 126.8, 121.6, 118.8, 118.2, 113.4, 108.8, 50.3, 34.8, 30.1, 29.4, 25.6, 23.2, 22.2. HRMS-ESI (m/z): calcd for $C_{21}H_{25}O_2N_2S$ $[M + H]^+$: 369.1631, found 369.1631.

*N-(5-methyl-2-tosyl-2,3,4,5-tetrahydro-1H-pyrido[4,3-b]indol-4-yl)benzenesulfonamide (**3x**)*: White solid, 143 mg, 58% yield, m.p. 112.9-114.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 7.98 (m, 2H), 7.74 – 7.68 (m, 1H), 7.65 (ddd, *J* = 8.5, 6.4, 1.5 Hz, 2H), 7.57 – 7.49 (m, 2H), 7.40 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.32 – 7.28 (m, 3H), 7.27 – 7.23 (m, 1H), 7.10 (ddd, *J* = 8.0, 6.8, 1.4 Hz, 1H), 5.27 (dd, *J* = 10.1, 1.8 Hz, 1H), 4.83 (d, *J* = 13.7 Hz, 1H), 4.75 (d, *J* = 10.2 Hz, 1H), 3.78-3.66 (m, 4H), 3.47 (d, *J* = 12.4 Hz, 1H), 2.58 (dt, *J* = 12.4, 2.0 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 144.1, 142.0, 137.4, 133.4, 133.1, 130.5, 130.3, 129.8, 127.8, 127.1, 123.9, 122.6, 119.6, 118.7, 110.1, 107.6, 50.5, 45.6, 43.2, 29.1, 21.4. HRMS-ESI (m/z): calcd for $C_{25}H_{26}O_4N_3S_2$ $[M + H]^+$: 496.1359, found 496.1360.

*N-(9-methyl-1,2,4,9-tetrahydrospiro[carbazole-3,2'-[1,3]dioxolan]-1-yl)benzenesulfonamide (**3y**)*: White solid, 152 mg, 76% yield, m.p. 249.3-250.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dt, *J* = 8.6, 1.5 Hz, 2H), 7.68 – 7.61 (m, 1H), 7.57 (ddd, *J* = 8.7, 6.6, 1.7 Hz, 2H), 7.47 – 7.41 (m, 1H), 7.33 – 7.26 (m, 1H), 7.25 – 7.19 (m, 1H), 7.09 (ddt, *J* = 7.9, 6.8, 1.1 Hz, 1H), 5.83 – 5.71 (m, 1H), 4.98 (dd, *J* = 10.5, 4.8 Hz, 1H), 4.02 (ddd, *J* = 7.4, 5.4, 1.8 Hz, 1H), 3.89 (td, *J* = 6.6, 5.7, 1.8 Hz, 2H), 3.74 – 3.55 (m, 4H), 3.07 – 2.78 (m, 2H), 2.02 (ddd, *J* = 13.9, 5.0, 1.7 Hz, 1H), 1.61 (dd, *J* = 13.9, 2.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 138.0, 132.8, 130.8, 129.3, 127.0, 125.7, 122.5, 119.2, 118.5, 109.3, 109.3, 109.1, 64.6, 64.5, 46.8, 36.4, 32.1, 29.5. HRMS-ESI (m/z): calcd for $C_{21}H_{23}N_2O_4S$ $[M + H]^+$: 399.1373, found 399.1373.

*N-(1,9-dimethyl-2,3,4,9-tetrahydro-1H-carbazol-1-yl)benzenesulfonamide (**3z**)*: White solid, 97 mg, 55% yield, m.p.165.8-168.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.78 (m, 2H), 7.61 – 7.38 (m, 4H), 7.28 – 7.15 (m, 2H), 7.13 – 7.01 (m, 1H), 4.87 (s, 1H), 3.64 (s, 3H), 2.74 – 2.56 (m, 2H), 2.36 – 2.20 (m, 1H), 1.93 – 1.64 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 137.6, 135.4, 132.5, 128.9, 127.0, 125.9, 122.4, 119.2, 118.8, 112.4, 108.9, 56.7, 40.4, 31.4, 25.7, 21.4, 20.4. HRMS-ESI (m/z): calcd for $C_{20}H_{23}N_2O_2S$ $[M + H]^+$: 355.1475, found 355.1473.

*N-(1-(1,3-dimethyl-1H-indol-2-yl)ethyl)benzenesulfonamide (**3aa**)*: White solid, 116 mg, 71% yield, m.p. 114.8-117.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dq, *J* = 8.5, 1.3 Hz, 2H), 7.44 – 7.35 (m, 1H), 7.31 – 7.24 (m, 1H), 7.20 – 7.13 (m, 1H), 7.12 – 7.00 (m, 4H), 5.16 (d, *J* = 4.7 Hz, 1H), 5.03 – 4.93 (m, 1H), 3.50 (s, 3H), 2.16 (s, 3H), 1.61 (dt, *J* = 7.2, 1.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.6, 136.7, 133.2, 132.1, 128.3, 127.7, 126.6, 121.8, 118.9, 118.6, 108.7, 108.6, 45.8, 30.3, 21.1, 8.8. HRMS-ESI (m/z): calcd for $C_{18}H_{21}O_2N_2S$ $[M + H]^+$: 329.1318, found 329.1318.

*4-methyl-N-(9-methyl-2,3,4,9-tetrahydro-1H-carbazol-1-yl)benzenesulfonamide (**3ab**)*: Brown solid, 120 mg, 68% yield, m.p. 186.1-186.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dt, *J* = 8.3, 1.9 Hz, 2H), 7.54 – 7.42 (m, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.25 (dtt, *J* = 7.9, 3.0, 1.5 Hz, 2H), 7.08 (ddd, *J* = 8.0, 6.5, 1.7 Hz, 1H), 4.78 (dd, *J* = 8.6, 3.0 Hz, 1H), 4.69 (dd, *J* = 8.7, 3.7 Hz, 1H), 3.55 (s, 3H), 2.86 – 2.73 (m, 1H), 2.60 – 2.43 (m, 4H), 1.86 – 1.64 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 138.8, 137.3, 131.8, 129.8, 126.9, 126.1, 122.3, 119.0, 118.7, 112.8, 109.1, 46.0, 30.1, 29.1, 21.6, 20.6, 18.0. HRMS-ESI (m/z): calcd for $C_{20}H_{23}N_2O_2S$ $[M + H]^+$: 355.1475, found 355.1479.

*2-methyl-N-(9-methyl-2,3,4,9-tetrahydro-1H-carbazol-1-yl)benzenesulfonamide (**3ac**)*: Brown solid, 160 mg, 90% yield, m.p. 208.5-210.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.02 (m, 1H), 7.61 – 7.44 (m, 2H), 7.42 – 7.31 (m, 2H), 7.30 – 7.17 (m, 2H), 7.09 (ddd, *J* = 7.9, 6.5, 1.4 Hz, 1H), 4.84 – 4.70 (m, 2H), 3.55 (s, 3H), 2.87 – 2.74 (m, 1H), 2.64 (s, 3H), 2.54 (dt, *J* = 10.4, 4.2 Hz, 1H), 1.92 – 1.62 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.5, 137.3, 136.8, 132.9, 132.6, 131.7, 129.2, 126.4, 126.0, 122.4, 119.1, 118.7, 112.8, 109.1, 45.9, 30.1, 29.0, 20.6, 20.3, 18.1. HRMS-ESI (m/z): calcd for $C_{20}H_{23}N_2O_2S$ $[M + H]^+$: 355.1475, found 355.1477.

*4-fluoro-N-(9-methyl-2,3,4,9-tetrahydro-1H-carbazol-1-yl)benzenesulfonamide (**3ad**)*: White solid, 159 mg, 89% yield, m.p. 183.1-184.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.1 Hz, 1H), 8.07 – 7.90 (m, 2H), 7.61 – 7.28 (m, 4H), 7.13 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 6.99 (ddd, *J* = 7.9, 7.0, 1.0 Hz, 1H), 4.71 (dt, *J* = 7.4, 3.4 Hz, 1H), 3.47 (s, 3H), 2.69 (ddd, *J* = 15.7, 5.4, 2.2 Hz, 1H), 2.49 – 2.32 (m, 1H), 1.93 – 1.76 (m,

1H), 1.64 (q, *J* = 6.8, 5.6 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 151.0 (d, *J* = 152.8 Hz), 139.5, 137.3, 132.9, 129.9, 129.8, 126.2, 122.1, 118.8 (d, *J* = 22.1 Hz), 116.9 (d, *J* = 22.7 Hz), 112.0, 109.7, 45.7, 30.3, 29.3, 20.8, 17.8. HRMS-ESI (m/z): calcd for $C_{19}H_{19}FN_2NaO_2S$ $[M + Na]^+$: 381.1043, found 381.1036.

*4-chloro-N-(9-methyl-2,3,4,9-tetrahydro-1H-carbazol-1-yl) benzenesulfonamide (**3ae**)*: Pale brown solid, 155 mg, 83% yield, m.p. 169.9-172.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.48 (dd, *J* = 14.4, 8.1 Hz, 3H), 7.31 – 7.16 (m, 2H), 7.12 – 6.96 (m, 1H), 4.87 – 4.66 (m, 2H), 3.56 (s, 3H), 2.87 – 2.67 (m, 1H), 2.53 (ddd, *J* = 15.6, 10.2, 4.7 Hz, 1H), 1.86 – 1.59 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 139.2, 137.3, 131.3, 129.5, 128.3, 126.0, 122.5, 119.1, 118.7, 112.9, 109.1, 46.2, 30.2, 29.2, 20.6, 17.9. HRMS-ESI (m/z): calcd for $C_{19}H_{20}ClN_2O_2S$ $[M + H]^+$: 375.0929, found 375.0925.

*N-(9-methyl-2,3,4,9-tetrahydro-1H-carbazol-1-yl)-4-(trifluoromethoxy)benzenesulfonamide (**3af**)*: White solid, 189 mg, 89% yield, m.p. 150.8-152.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.54 – 7.44 (m, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.29 – 7.20 (m, 2H), 7.11 (ddd, *J* = 8.1, 5.4, 2.6 Hz, 1H), 4.98 (d, *J* = 8.5 Hz, 1H), 4.81 (d, *J* = 8.7 Hz, 1H), 3.54 (s, 3H), 2.81 (dd, *J* = 15.4, 4.3 Hz, 1H), 2.57 (dd, *J* = 15.1, 9.4 Hz, 1H), 1.88 – 1.62 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 140.2, 137.4, 131.3, 129.0, 126.0, 122.6, 121.1, 119.2, 118.7, 113.1, 109.1, 46.2, 30.3, 29.1, 20.6, 17.9. HRMS-ESI (m/z): calcd for $C_{20}H_{20}F_3N_2O_3S$ $[M + H]^+$: 425.1147, found 425.1141.

*N-(9-methyl-2,3,4,9-tetrahydro-1H-carbazol-1-yl)methanesulfonamide (**3ag**)*: Pale yellow solid, 103 mg, 74% yield, m.p. 118.0-118.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.9 Hz, 1H), 7.25 (dt, *J* = 14.6, 8.1 Hz, 2H), 7.15 – 6.99 (m, 1H), 4.89 (dt, *J* = 7.8, 3.5 Hz, 1H), 4.60 (d, *J* = 8.6 Hz, 1H), 3.72 (s, 3H), 3.04 (s, 3H), 2.84 (ddd, *J* = 16.0, 5.6, 2.4 Hz, 1H), 2.61 (ddd, *J* = 16.1, 11.0, 5.6 Hz, 1H), 2.28 – 2.09 (m, 1H), 2.08 – 1.92 (m, 2H), 1.82 (dddd, *J* = 13.4, 10.8, 5.3, 3.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.3, 131.7, 126.0, 122.4, 119.1, 118.7, 112.7, 109.1, 45.9, 43.0, 31.3, 29.4, 20.7, 18.1. HRMS-ESI (m/z): calcd for $C_{14}H_{19}N_2O2S$ $[M + H]^+$: 279.1162, found 279.1157.

*(E)-N-((1-benzyl-3-methyl-1H-indol-2-yl)methylene)benzenesulfonamide (**4a**)*: Pale yellow solid, 120 mg, 62% yield, m.p. 146.5-148.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (d, *J* = 1.2 Hz, 1H), 7.75 (dt, *J* = 8.5, 1.3 Hz, 2H), 7.69 (dt, *J* = 8.1, 1.2 Hz, 1H), 7.52 (td, *J* = 7.4, 1.3 Hz, 1H), 7.39 (td, *J* = 7.5, 6.8, 1.2 Hz, 3H), 7.33 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.20 – 7.12 (m, 1H), 7.12 – 7.00 (m, 3H), 6.86 (dd, *J* = 6.9, 1.6 Hz, 2H), 5.80 (s, 2H), 2.63 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 141.6, 139.4, 137.7, 132.8, 131.2, 128.9, 128.7, 128.4, 127.8, 127.4, 127.3, 127.0, 126.3, 121.5, 120.7, 110.7, 48.2, 9.6. HRMS-ESI (m/z): calcd for $C_{23}H_{21}N_2O_2S$ $[M + H]^+$: 389.1318, found 389.1319.

*(E)-N-((3-ethyl-1-methyl-1H-indol-2-yl)methylene)benzenesulfonamide (**4b**)*: Pale green solid, 118 mg, 72% yield, m.p. 113.9-116.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (d, *J* = 3.0 Hz, 1H), 8.09 – 7.93 (m, 2H), 7.69 (dd, *J* = 8.1, 3.1 Hz, 1H), 7.65 – 7.52 (m, 3H), 7.42 (dt, *J* = 7.4, 4.9 Hz, 1H), 7.31 (dd, *J* = 8.5, 3.1 Hz, 1H), 7.18 – 7.08 (m, 1H), 4.04 (s, 3H), 3.24 – 2.91 (m, 2H), 1.42 – 1.18 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 141.7, 139.4, 137.0, 133.1, 129.1, 128.3, 127.5, 127.3, 126.1, 121.4, 120.4, 110.4, 32.4, 17.9, 17.0. HRMS-ESI (m/z): calcd for $C_{18}H_{19}N_2O_2S$ $[M + H]^+$: 327.1162, found 327.1165.

*(E)-N-((1-methyl-3-propyl-1H-indol-2-yl)methylene)benzenesulfonamide (**4c**)***:** Yellow solid, 110 mg, 64% yield, m.p. 112.8-115.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 8.04 – 7.96 (m, 2H), 7.66 (dt, *J* = 8.4, 1.0 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.53 (ddd, *J* = 8.3, 6.8, 1.2 Hz, 2H), 7.40 (ddd, *J* = 8.1, 6.8, 1.1 Hz, 1H), 7.29 (d, *J* = 8.7 Hz, 1H), 7.11 (ddd, *J* = 7.7, 6.9, 0.9 Hz, 1H), 4.03 (s, 3H), 2.99 (t, *J* = 7.5 Hz, 2H), 1.69 (q, *J* = 7.4 Hz, 2H), 0.99 – 0.90 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 141.7, 139.4, 135.3, 133.1, 129.1, 128.2, 128.0, 127.5, 126.6, 121.5, 120.4, 110.4, 32.4, 26.4, 25.3, 14.0. HRMS-ESI (m/z): calcd for $C_{19}H_{21}N_2O_2S$ $[M + H]^+$: 341.1318, found 341.1323.

*(E)-N-((3-isopropyl-1-methyl-1H-indol-2-yl)methylene)benzenesulfonamide (**4d**)*: Brown solid, 146 mg, 84% yield, m.p. 133.2-134.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.27 (d, *J* = 1.5 Hz, 1H), 8.09 – 7.96 (m, 2H), 7.85 (d, *J* = 8.3 Hz, 1H), 7.68 – 7.50 (m, 3H), 7.44 – 7.36 (m, 1H), 7.32 (d, *J* = 8.6 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 4.04 (s, 3H), 3.72 – 3.45 (m, 1H), 1.52 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 142.1, 140.9, 139.4, 133.1, 129.1, 127.9, 127.5, 126.7, 124.9, 123.0, 120.2, 110.6, 32.6, 26.4, 23.9. HRMS-ESI (m/z): calcd for $C_{19}H_{21}N_2O_2S$ $[M + H]^+$: 341.1318, found 341.1314.

*(E)-N-((3-isobutyl-1-methyl-1H-indol-2-yl)methylene)benzenesulfonamide (**4e**)*: Brown solid, 162 mg, 91% yield, m.p. 143.3-144.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (s, 1H), 8.04 – 7.97 (m, 2H), 7.70 – 7.58 (m, 2H), 7.55 (ddt, *J* = 8.4, 6.7, 1.3 Hz, 2H), 7.41 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.31 (dq, *J* = 8.6, 1.2 Hz, 1H), 7.12 (ddd, *J* = 8.0, 6.8, 1.0 Hz, 1H), 4.05 (s, 3H), 2.89 (d, *J* = 7.2 Hz, 2H), 1.94 (dt, *J* = 13.5, 6.7 Hz, 1H), 0.94 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 141.6, 139.3, 134.3, 133.1, 129.1, 128.4, 128.2, 127.6, 127.0, 121.7, 120.4, 110.3, 33.5, 32.5, 31.0, 22.7. HRMS-ESI (m/z): calcd for $C_{20}H_{23}N_2O_2S$ $[M + H]^+$: 355.1475, found 355.1469.

*(E)-N-((3-(2-((tert-butyldimethylsilyl)oxy)ethyl)-1-methyl-1 H-indol-2-yl)methylene)benzenesulfonamide (**4f**)*: Yellow solid, 185 mg, 81% yield, m.p. 105.9-107.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 – 9.11 (m, 1H), 8.09 – 7.97 (m, 2H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.64 – 7.57 (m, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 8.6 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 4.06 (s, 3H), 3.83 (t, *J* = 6.6 Hz, 2H), 3.25 (t, *J* = 6.6 Hz, 2H), 0.79 (s, 9H), 0 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 141.5, 139.5, 133.0, 131.4, 129.0, 128.8, 128.1, 127.5, 126.8, 121.4, 120.5, 110.3, 63.7, 32.5, 28.2, 25.9, 18.3, -5.5. HRMS-ESI (m/z): calcd for $C_{24}H_{33}N_2O_3SSi$ $[M + H]^+$: 457.1976, found 457.1977.

*(E)-N-((3-benzyl-1-methyl-1H-indol-2-yl)methylene)benzenesulfonamide (**4g**)*: Yellow solid, 137 mg, 70% yield, m.p. 185.4-187.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (d, *J* = 1.0 Hz, 1H), 7.91 (dt, *J* = 8.3, 1.2 Hz, 2H), 7.65 – 7.54 (m, 2H), 7.50 (ddd, *J* = 8.3, 6.7, 1.2 Hz, 2H), 7.44 – 7.37 (m, 1H), 7.31 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.25 – 7.13 (m, 5H), 7.10 (ddt, *J* = 8.0, 6.8, 1.1 Hz, 1H), 4.40 (s, 2H), 4.05 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 141.6, 140.0, 139.1, 133.1, 132.2, 129.1, 128.6, 128.2, 128.2, 128.2, 127.6, 126.7, 126.4, 121.7, 120.9, 110.4, 32.4, 30.3. HRMS-ESI (m/z): calcd for $C_{23}H_{21}N_2O_2S$ $[M + H]^+$: 389.1318, found 389.1322.

*(E)-N-((3-(4-methoxyphenyl)-1-methyl-1H-indol-2-yl)methylene)benzenesulfonamide (**4h**)*: Yellow solid, 137 mg, 68% yield, m.p. 136.0-137.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ

8.95 (s, 1H), 8.00 – 7.92 (m, 2H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.58 (d, *J* = 7.3 Hz, 1H), 7.52 (dd, *J* = 8.4, 6.7 Hz, 2H), 7.49 – 7.42 (m, 1H), 7.39 – 7.31 (m, 3H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 8.5 Hz, 2H), 4.13 (s, 3H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 159.8, 141.5, 139.2, 135.1, 133.1, 131.8, 129.1, 128.4, 127.8, 127.6, 126.1, 124.1, 122.3, 121.3, 114.5, 110.4, 55.4, 32.7. HRMS-ESI (m/z): calcd for $C_{23}H_{21}N_2O_3S$ $[M + H]^+$: 405.1267, found 405.1261.

*(E)-N-((3-(4-chlorophenyl)-1-methyl-1H-indol-2-yl)methylene)benzenesulfonamide (**4i**)*: Yellow solid, 164 mg, 80% yield, m.p. 185.3-187.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 7.99 – 7.92 (m, 2H), 7.62 (dd, *J* = 16.3, 7.7 Hz, 2H), 7.57 – 7.43 (m, 5H), 7.37 (dd, *J* = 19.2, 8.3 Hz, 3H), 7.18 (t, *J* = 7.5 Hz, 1H), 4.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 141.3, 138.8, 134.5, 133.3, 133.3, 131.8, 130.3, 129.2, 129.1, 128.5, 127.8, 127.7, 125.9, 121.8, 121.7, 110.5, 32.8. HRMS-ESI (m/z): calcd for $C_{22}H_{18}ClN_2O_2S$ $[M + H]^+$: 409.0772, found 409.0779.

*(E)-N-((3-(4-bromophenyl)-1,5-dimethyl-1H-indol-2-yl)methylene)benzenesulfonamide (**4j**)*: Yellow solid, 133 mg, 56% yield, m.p. 164.6-166.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (d, *J* = 1.0 Hz, 1H), 8.11 – 7.91 (m, 2H), 7.68 – 7.63 (m, 2H), 7.62 – 7.58 (m, 1H), 7.57 – 7.48 (m, 2H), 7.40 (q, *J* = 1.2 Hz, 1H), 7.33 – 7.27 (m, 4H), 4.13 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 140.0, 138.9, 133.2, 132.7, 132.1, 132.1, 131.3, 131.0, 130.7, 129.1, 127.7, 127.6, 126.0, 122.6, 120.7, 110.3, 32.9, 21.4. HRMS-ESI (m/z): calcd for $C_{23}H_{20}BrN_2O_2S$ $[M + H]^+$: 467.0429, found 467.0422.

*N-(9-(4-methoxybenzyl)-2,3,4,9-tetrahydro-1H-carbazol-1-yl)-N-(prop-2-yn-1-yl)benzenesulfonamide (**6**)*: White solid, m.p. 114.2-114.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dt, *J* = 8.4, 1.1 Hz, 2H), 7.61 – 7.52 (m, 2H), 7.51 – 7.42 (m, 2H), 7.28 – 7.15 (m, 2H), 7.15 – 7.07 (m, 1H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.80 – 6.74 (m, 2H), 5.46 – 5.34 (m, 2H), 5.28 (d, *J* = 16.9 Hz, 1H), 3.82 (dt, *J* = 18.6, 1.7 Hz, 1H), 3.75 (d, *J* = 0.8 Hz, 3H), 3.54 (ddd, *J* = 18.6, 2.5, 0.9 Hz, 1H), 2.84 (dt, *J* = 15.9, 5.2 Hz, 1H), 2.65 (ddd, *J* = 15.2, 8.4, 6.2 Hz, 1H), 2.09 – 1.98 (m, 1H), 1.98 – 1.87 (m, 2H), 1.84 – 1.65 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 140.9, 137.8, 132.8, 130.0, 129.1, 128.8, 128.0, 127.3, 126.5, 122.8, 119.3, 118.7, 116.7, 113.8, 110.1, 79.5, 72.7, 55.2, 51.4, 45.8, 33.8, 29.3, 20.8, 20.5. HRMS-ESI (m/z): calcd for $C_{29}H_{29}N_2O_3S$ $[M + H]^+$: 485.1893, found 485.1888.

*N-(9-(4-methoxybenzyl)-4-oxo-2,3,4,9-tetrahydro-1H-carbazol-1-yl)-N-(prop-2-yn-1-yl)benzenesulfonamide (**7**)*: Brown solid, m.p. 168.6-171.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 – 8.20 (m, 1H), 7.96 (ddd, *J* = 8.5, 2.7, 1.3 Hz, 2H), 7.69 – 7.57 (m, 1H), 7.50 (tq, *J* = 7.2, 1.5 Hz, 2H), 7.34 – 7.17 (m, 3H), 6.97 – 6.86 (m, 2H), 6.80 (dd, *J* = 8.9, 2.3 Hz, 2H), 5.61 – 5.51 (m, 1H), 5.42 (dd, *J* = 6.0, 2.0 Hz, 2H), 4.06 – 3.94 (m, 1H), 3.80 – 3.72 (m, 3H), 3.67 – 3.56 (m, 1H), 2.96 (dddd, *J* = 17.5, 11.5, 5.8, 2.2 Hz, 1H), 2.50 – 2.35 (m, 1H), 2.26 – 2.07 (m, 2H), 2.08 – 1.98 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.1, 159.0, 143.1, 140.0, 137.9, 133.3, 129.0, 128.0, 127.9, 127.2, 124.7, 124.2, 123.2, 122.3, 116.3, 114.2, 110.6, 78.4, 73.6, 55.2, 49.5, 46.4, 34.8, 34.4, 28.1. HRMS-ESI (m/z): calcd for $C_{29}H_{27}N_2O_4S$ $[M + H]^+$: 499.1686, found 499.1681.

*(1S,5S)-11-(4-methoxybenzyl)-4-methylene-2-(phenylsulfonyl)-2,3,4,5-tetrahydro-1H-1,5-methanoazocino[3,4-b]indol-6-(11H)-one (**8**)*: White solid, m.p. 97.6-100.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.17 (m, 1H), 7.89 – 7.78 (m, 2H), 7.58 (dt, *J* = 6.5, 1.7 Hz, 1H), 7.50 (tt, *J* = 6.1, 1.5 Hz, 2H), 7.42 – 7.35 (m, 1H), 7.34 – 7.27 (m, 2H), 7.12 – 7.01 (m, 2H), 6.84 (dt, *J* = 8.7, 1.8 Hz, 2H), 5.61 (d, *J* = 16.3 Hz, 1H), 5.46 (d, *J* = 16.5 Hz, 1H), 5.38 (s, 1H), 4.99 (s, 1H), 4.87 (d, *J* = 2.2 Hz, 1H), 4.23 (d, *J* = 16.4 Hz, 1H), 3.77 (t, *J* = 1.9 Hz, 4H), 3.18 (s, 1H), 2.28 – 2.17 (m, 1H), 1.72 – 1.59 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.1, 159.2, 144.7, 140.2, 137.7, 137.6, 133.1, 129.4, 128.4, 127.6, 127.2, 124.6, 123.9, 123.3, 122.2, 114.4, 114.4, 114.1, 110.7, 55.3, 51.4, 46.5, 46.2, 45.4, 33.2. HRMS-ESI (m/z): calcd for $C_{29}H_{27}N_2O_4S$ $[M + H]^+$: 499.1686, found 499.1683.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.
Single Crystal Data for **3d**
Single Crystal Data for **4d**
Copies of ^{1}H and ^{13}C NMR spectra for all products (PDF)
CIF data for **3d** (CIF)
CIF data for **4d** (CIF)

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Notes

The authors declare no competing financial interest.

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