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Electronic Supplementary Information

# PhI(OAc)<sub>2</sub>-mediated dearomative C–N coupling: facile construction of the spiro[indoline-3,2'-pyrrolidine] skeleton

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# **I. General Information**

All the solvents and commercially available reagents were purchased from commercial suppliers. <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra were recorded on a 400 MHz or/and 500 MHz Bruker FT-NMR spectrometers. All chemical shifts are given as  $\delta$  value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). High Resolution Mass (MS) analysis was obtained using on a LC/MSD TOF spectrometer system with Electrospray Ionization (ESI). Melting points were measured on a Mel-Temp apparatus and are uncorrected. IR was recorded on a Bruker Tensor 27 FT-IR spectrometer. Reactions were monitored by thin-layer chromatography (TLC) carried out on commercial silica gel plates (GF254) under UV light. Flash chromatography was performed on silica gel 60 (200–300 mesh).

# **II.** Preparation of Starting Materials

# 2.1 General Procedure for Synthesis of Substrates 1a-1d, 1j-1o, 1q



(i)<sup>1</sup> To a solution of **A** (1.0 equiv) and (2-aminophenyl)-methanol **B1** (2.0 equiv) in DCE was added TFA (30 mol%) at room temperature. The resulting solution was stirred at 50 °C for 12 h. After the reaction was completed (monitored by TLC), the reaction was quenched with saturated aqueous NaHCO<sub>3</sub>, then diluted with CH<sub>2</sub>Cl<sub>2</sub> and washed with brine. The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The residue was purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) to afford the desired product **C**.

(ii)<sup>2</sup> The intermediate **C** (1.0 equiv) was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> and the solution was cooled to 0 °C. Pyridine (1.3 equiv) and benzenesulfonyl chloride (1.2 equiv) were then added dropwise. The reaction mixture was warmed to room temperature and stirred at this temperature for 12 h until TLC analysis showed a complete consumption of the starting material. HCl (1 N) was added and the organic layer was washed with water. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The residue was purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) to afford the desired product **1a-1d**, **1j-1o**, **1q**.

# 2.2 General Procedure for Synthesis of Substrates 1e-1i



(i)<sup>3</sup> The substituted 2-amino-benzoic acid (1.0 equiv) was dissolved in dry THF and the solution was cooled to 0 °C, and then a solution of LiAlH<sub>4</sub> (2.0 equiv) in THF was added dropwise. The resulting mixture was allowed to warm to room temperature and was stirred for 2 h. The mixture was then hydrolyzed by addition of water and 5% NaOH. The resulting suspension was filtered, and the precipitate was washed with ethyl acetate. Then the combined organic collection was evaporated. The residue was purified by flash chromatography (petroleum ether/ethyl acetate = 1/1) to afford the desired product **B** for the next step.

(ii)<sup>1</sup> To a solution of 2-methyl indole (1.0 equiv) and (2-aminophenyl)-methanol **B** (2.0 equiv) in DCE was added TFA (30 mol%) at room temperature. The resulting solution was stirred at 50 °C for 12 h. After the reaction was complete (monitored by TLC), the reaction was quenched with saturated aqueous NaHCO<sub>3</sub>, then diluted with

 $CH_2Cl_2$  and washed with brine. The organic phase was dried over  $Na_2SO_4$ , filtered and concentrated. The residue was purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) to afford the desired product **C**.

(iii)<sup>2</sup> The intermediate **C** (1.0 equiv) was dissolved in dry  $CH_2Cl_2$  and the solution was cooled to 0 °C. Pyridine (1.3 equiv) and benzenesulfonyl chloride (1.2 equiv) were then added dropwise. The reaction mixture was warmed to room temperature and stirred at this temperature for 12 h until TLC analysis showed a complete consumption of the starting material. HCl (1 N) was added and the organic layer was washed with water. The aqueous layer was extracted with  $CH_2Cl_2$ . The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The residue was purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) to afford the desired product **1e-1i**.

#### 2.3 General Procedure for Synthesis of Substrates 1p



 $(i)^4$  A mixture of indole (30 mmol, 3.94 g, 3.0 equiv) and Na<sub>2</sub>CO<sub>3</sub> (20 mmol, 2.12 g, 2.0 equiv) in acetone:water (4:1)stirred 70 °C. was at then 1-bromo-2-(nitromethyl)benzene (10 mmol, 2.16 g, 1.0 equiv) was added and the reaction was stirred for 12 h (monitored by TLC). Upon completion, the mixture was extracted by EtOAc, and washed by water. The combined organic phase was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The residue was purified by flash chromatography (petroleum ether/ethyl acetate = 10/1) to afford the desired product **D** in 46% yield (1.17 g).

(ii)<sup>5</sup> A solution of **D** (3.2 mmol, 0.80 g, 1.0 equiv) in THF:CHCl<sub>3</sub> (1:1, 0.25 M) was

stirred at 0 °C for 5 min. Pyridinium tribromide (3.5 mmol, 1.11 g, 1.1 equiv) was then added portion-wise over 30 minutes. After stirring for 2 h at 0 °C, saturated aqueous sodium sulphite solution was added. Then, saturated aqueous NaHCO<sub>3</sub> solution was added. The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub>, the combined organic fraction was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The residue was purified by flash chromatography (petroleum ether/ethyl acetate = 10/1) to afford the desired product **E** in 89% yield (0.93 g).

(iii)<sup>6</sup> To a solution of **E** (2.8 mmol, 0.93 g, 1.0 equiv) in ethanol (10 mL) was added Fe powder (14 mmol, 0.78 g, 5.0 equiv), and the mixture was cooled to 0 °C, HCl (0.1 N) was added dropwise and the resulting mixture was vigorously stirred at room temperature (monitored by TLC). Upon completion, the mixture was diluted with EtOAc, and filtered through a Celite pad. The filtrate was washed with saturated NaHCO<sub>3</sub> (aq.) and the aqueous phase was back-extracted with EtOAc. The combined organic phases were dried over dry Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuo. The crude material was purified by chromatography over silica gel (petroleum ether/ethyl acetate = 10/1) to afford the desired product **C16** in 60% yield (0.51 g).

(iv)<sup>2</sup> The intermediate **C16** (1 mmol, 0.30 g, 1.0 equiv) was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and the solution was cooled to 0 °C. Pyridine (1.3 mmol, 0.10 g, 1.3 equiv) and benzenesulfonyl chloride (1.2 mmol, 0.21 g, 1.2 equiv) were then added dropwise. The reaction mixture was warmed to room temperature and stirred at this temperature for 12 h until TLC analysis showed a complete consumption of the starting material. HCl (1 N) was added and the organic layer was washed with water. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The residue was purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) to afford the desired product **1p** in 95% yield (0.42 g).

#### 2.4 General Procedure for Synthesis of Substrates 1r



(i)<sup>7</sup> To a solution of 2-methyl-1H-indole (2 mmol, 0.26 g, 1.0 equiv) in DMSO (16 mL) was added 2-aminobenzenethiol (2 mmol, 0.25 g, 1.0 equiv) and NaOH (4 mmol, 0.16 g, 2.0 equiv). The mixture was stirred at 70 °C for 6 h in open air atmosphere. Upon completion, the reaction was allowed to cool down to room temperature. The aqueous layer was extracted with ethyl acetate and water. The combined organic phase was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The residue was purified by flash chromatography (petroleum ether/ethyl acetate = 10/1) to afford the desired product **C18** in 95% yield (0.49 g).

(ii)<sup>2</sup> The intermediate **C18** (1 mmol, 0.25 g, 1.0 equiv) was dissolved in dry  $CH_2Cl_2$  (5 mL) and the solution was cooled to 0 °C. Pyridine (1.3 mmol, 0.10 g, 1.3 equiv) and benzenesulfonyl chloride (1.2 mmol, 0.21 g, 1.2 equiv) were then added dropwise. The reaction mixture was warmed to room temperature and stirred at this temperature for 12 h until TLC analysis showed a complete consumption of the starting material. HCl (1 N) was added and the organic layer was washed with water. The aqueous layer was extracted with  $CH_2Cl_2$ . The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The residue was purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) to afford the desired product **1r** in 88% yield (0.35 g).

#### 2.5 General Procedure for Synthesis of Substrates 1s



(i)<sup>8</sup> A mixture of phenyl hydrazine (12 mmol, 1.30 g, 1.2 equiv) and 6-chloro-2-hexanone (10 mmol, 1.35 g, 1.0 equiv) in EtOH (40 mL) was heated at 80 °C for 24 h. The mixture was purified by trituration from  $CH_2Cl_2/Et_2O$  afford the desired product **C19** in 20% yield (0.45 g).

(ii)<sup>2</sup> The intermediate **C19** (2 mmol, 0.45 g, 1.0 equiv) was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> and the solution was cooled to 0 °C. Triethylamine (4 mmol, 0.41 g, 2 equiv) and benzenesulfonyl chloride (2.4 mmol, 0.42 g, 1.2 equiv) were then added dropwise. The reaction mixture was warmed to room temperature and stirred at this temperature for 12 h until TLC analysis showed a complete consumption of the starting material. HCl (1 N) was added and the organic layer was washed with water. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The residue was purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) to afford the desired product **1s** in 84% yield (0.55 g).

The compound 1t was prepared by following literature 9.

# **III. General Procedures**

#### 3.1 General Procedure for the Synthesis of the Spirocyclic Indolenines



To a solution of 1 (0.1 mmol, 1.0 equiv) in HFIP (1 mL) was added PIDA (0.12 mmol,

1.2 equiv). The mixture was stirred for 0.5 h at room temperature in open air atmosphere. Upon completion, it was concentrated under reduced pressure. The residue was purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) to afford the desired product **2**.

#### 3.2 Synthesis of 2a in 1.5 mmol scale



To a solution of **1a** (1.5 mmol, 0.59 g, 1.0 equiv) in HFIP (6 mL) was added PIDA (1.8 mmol, 0.58 g, 1.2 equiv). The mixture was stirred at room temperature for 1 h in open air atmosphere. Upon completion, it was concentrated under reduced pressure. The residue was purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) to afford the product **2a** (0.51 g) as yellowish solid in 87% yield.

### 3.3 Procedure for the Synthesis of the compound 3



To a solution of **2a** (0.05 mmol, 19.0 mg, 1.0 equiv) in dry DCM (1 mL) was added TMSCN (0.25 mmol, 32.0  $\mu$ L) and AlCl<sub>3</sub> (0.025 mmol, 3.3 mg, 0.5 equiv), the mixture was vigorously stirred at room temperature for 4 h and monitored by TLC. Upon completion, the mixture was quenched with by H<sub>2</sub>O at 0 °C, the organic layer was separated and dried over dry Na<sub>2</sub>SO<sub>4</sub>, then concentrated in vacuo. The crude material was purified by chromatography over silica gel (petroleum ether/ethyl acetate = 5/1) to afford the desired product as a white solid.

#### 3.4 Procedure for the Synthesis of the compound 4



To a solution of 2p (0.1 mmol, 44.0 mg, 1.0 equiv) in dry DCM (1 mL) was added TFA (0.5 mmol, 37.0 µL, 5.0 equiv), the mixture was vigorously stirred at room temperature for 12 h and monitored by TLC. Upon completion, the reaction was quenched with saturated aqueous NaHCO<sub>3</sub>, then diluted with DCM and was washed with brine. The organic phases were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The residue was purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) to afford the desired product as a white solid.

# **IV Characterization Data**



**4-Methyl-***N***-(2-((2-methyl-1***H***-indol-3-yl)methyl)phenyl)benzenesulfonamide (1a)** Yellow solid, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.92 (br, s, 1H), 7.37-7.33 (m, 3H), 7.28-7.27 (m, 1H), 7.19-7.14 (m, 2H), 7.11-7.05 (m, 4H), 6.94-6.89 (m, 2H), 6.69 (br, s, 1H), 3.77 (s, 2H), 2.36 (s, 3H), 2.34 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  143.75, 136.79, 135.69, 135.63, 132.39, 132.06, 130.52, 129.63, 128.33, 127.51, 127.21, 125.55, 122.77, 121.74, 119.75, 118.60, 110.51, 107.47, 27.97, 21.65, 11.83; HRMS (ESI) calcd for C<sub>23</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 391.1475, found 391.1475.



*N*-(2-((2-methyl-1*H*-indol-3-yl)methyl)phenyl)methanesulfonamide (1b)

Yellow solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.95 (br, s, 1H), 7.46-7.40 (m, 2H), 7.28-7.24 (m, 2 H), 7.19-7.15 (m, 1H), 7.13-7.07 (m, 2H), 6.95-6.92 (m, 1H), 6.50 (br, s, 1H), 4.10 (s, 2H), 2.52 (s, 3H), 2.46 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  136.14, 135.73, 132.00, 131.58, 131.28, 128.22, 127.99, 125.47, 121.91, 121.21, 119.89, 118.65, 110.63, 107.69, 39.20, 28.70, 11.87; HRMS (ESI) calcd for C<sub>17</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 315.1162, found 315.1164.



**4-Chloro-***N***-(2-((2-methyl-1***H***-indol-3-yl)methyl)phenyl)benzenesulfonamide (1c)** Yellow solid, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.94 (br, s, 1H), 7.33-7.31 (m, 3H), 7.29-7.28 (m, 1H), 7.25-7.24 (m, 1H), 7.22-7.21 (m, 2H), 7.19-7.16 (m, 1H), 7.14-7.08 (m, 2H), 6.94-6.93 (m, 2H), 6.80 (br, s, 1H), 3.82 (s, 2H), 2.35 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  139.45, 138.04, 135.71, 135.39, 132.10, 132.03, 130.85, 129.26, 128.56, 128.24, 127.68, 125.69, 122.12, 121.91, 119.94, 118.57, 110.59, 107.34, 28.22, 11.82; HRMS (ESI) calcd for C<sub>22</sub>H<sub>20</sub>ClN<sub>2</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 411.0929, found 411.0939.



#### *N*-(2-((2-methyl-1*H*-indol-3-yl)methyl)phenyl)benzenesulfonamide (1d)

Yellow solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.92 (br, s, 1H), 7.50-7.46 (m, 3H), 7.34-7.27 (m, 4H), 7.22-7.20 (m, 1H), 7.18-7.14 (m, 1H), 7.13-7.06 (m, 2H), 6.96-6.90 (m, 2H), 6.72 (br, s, 1H), 3.77 (s, 2H), 2.33 (s, 3H); <sup>13</sup>C NMR (125 MHz,

CDCl<sub>3</sub>):  $\delta$  139.76, 135.71, 135.57, 132.91, 132.47, 132.08, 130.66, 129.03, 128.33, 127.57, 127.19, 125.66, 122.77, 121.82, 119.82, 118.61, 110.54, 107.47, 28.07, 11.86; HRMS (ESI) calcd for C<sub>22</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 377.1318, found 377.1327.



*N*-(4-chloro-2-((2-methyl-1*H*-indol-3-yl)methyl)phenyl)benzenesulfonamide (1e) Yellow solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.96 (br, s, 1H), 7.52-7.46 (m, 3H), 7.34-7.30 (m, 2H), 7.28-7.25 (m, 2H), 7.16-7.09 (m, 3H), 6.94-6.93 (m, 2H), 6.73 (br, s, 1H) , 3.71 (s, 2H), 2.29 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  139.44, 135.68, 134.72, 134.07, 133.15, 132.35, 131.20, 130.30, 129.17, 128.08, 127.53, 127.15, 124.20, 121.91, 119.95, 118.36, 110.66, 106.60, 27.79, 11.82; HRMS (ESI) calcd for C<sub>22</sub>H<sub>20</sub>ClN<sub>2</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 411.0929, found 411.0928.



*N*-(3-chloro-2-((2-methyl-1*H*-indol-3-yl)methyl)phenyl)benzenesulfonamide (1f) Yellow solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.99 (br, s, 1H), 7.46-7.43 (m, 1H), 7.33-7.31 (m, 2H), 7.29-7.21 (m, 5H), 7.14-7.07 (m, 2H), 7.02-7.00 (m, 2H), 6.95-6.91 (m, 1H), 4.03 (s, 2H), 2.38 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  139.29, 137.99, 135.73, 135.03, 133.07, 132.11, 129.03, 129.01, 128.08, 127.84, 127.04, 126.18, 122.13, 120.16, 119.87, 118.56, 110.64, 106.49, 24.69, 11.80; HRMS (ESI) calcd for C<sub>22</sub>H<sub>20</sub>ClN<sub>2</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 411.0929, found 411.0939.



*N*-(5-methoxy-2-((2-methyl-1*H*-indol-3-yl)methyl)phenyl)benzenesulfonamide (1g) Yellow solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.93 (br, s, 1H), 7.48-7.42 (m, 3H), 7.29-7.27 (m, 3H), 7.12-7.09 (m, 2H), 6.96-6.89 (m, 3H), 6.78 (br, s, 1H), 6.61 (dd, *J* = 8.4 Hz, 2.6 Hz, 1H), 3.72 (s, 3H), 3.71 (s, 2H), 2.34 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  159.02, 139.61, 136.43, 135.74, 132.92, 131.94, 131.28, 129.01, 128.33, 127.20, 123.75, 121.81, 119.81, 118.72, 111.19, 110.52, 107.71, 107.68, 55.48, 27.39, 11.84; HRMS (ESI) calcd for C<sub>23</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub>S<sup>+</sup> [M+H]<sup>+</sup> 407.1424, found 407.1429.



*N*-(4-methyl-2-((2-methyl-1*H*-indol-3-yl)methyl)phenyl)benzenesulfonamide (1h) Yellow solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.91 (br, s, 1H), 7.58-7.51 (m, 3H), 7.40-7.36 (m, 2H), 7.25-7.24 (m, 1H), 7.10-7.06 (m, 1H), 6.96-6.90 (m, 2H), 6.82 (s, 1H), 6.69 (s, 1H), 6.42 (br, s, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.62 (s, 2H), 2.27 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 147.84, 147.34, 139.82, 135.63, 132.95, 131.90, 129.05, 128.33, 127.61, 127.36, 126.93, 121.66, 119.67, 118.52, 113.41, 110.50, 109.22, 107.88, 56.22, 56.08, 27.37, 11.19.



*N*-(2-methyl-6-((2-methyl-1*H*-indol-3-yl)methyl)phenyl)benzenesulfonamide (1i) Yellow solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.80 (br, s, 1H), 7.78-7.76 (m, 2H), 7.60-7.58 (m, 1H), 7.50-7.46 (m, 2H), 7.25-7.23 (m, 1H), 7.09-6.91 (m, 6H), 6.13 (br, s, 1H), 3.85 (s, 2H), 2.25 (s, 3H), 2.02 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  140.89, 140.43, 137.75, 135.52, 133.04, 132.77, 132.24, 129.41, 129.19, 128.71, 128.31, 127.96, 127.47, 121.27, 119.42, 118.60, 110.28, 108.91, 27.64, 18.69, 11.99; HRMS (ESI) calcd for C<sub>22</sub>H<sub>21</sub>ClN<sub>2</sub>O<sub>2</sub>S<sup>-</sup> [M-H]<sup>-</sup> 389.1324, found 389.1342.



*N*-(2-((5-fluoro-2-methyl-1*H*-indol-3-yl)methyl)phenyl)benzenesulfonamide (1j) Yellow solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.93 (br, s, 1H), 7.53-7.50 (m, 3H), 7.36-7.33 (m, 3H), 7.19-7.15 (m, 3H), 7.11-7.07 (m, 1H), 6.86-6.81 (m, 1H), 6.61 (br, s, 1H), 6.50 (dd, J = 9.6 Hz, 2.0 Hz, 1H), 3.71 (s, 2H), 2.33 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 157.90 (d, J = 232.9 Hz), 139.71, 135.38, 134.08, 133.11, 132.34, 132.09, 130.48, 129.09, 127.74, 127.17, 126.00, 123.30, 111.04 (d, J = 9.6 Hz), 109.88 (d, J = 26.1 Hz), 107.72, 103.78 (d, J = 23.8 Hz), 27.89, 11.99; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>): δ -124.25 (s, 1F); HRMS (ESI) calcd for C<sub>22</sub>H<sub>20</sub>FN<sub>2</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 395.1224, found 395.1242.



*N*-(2-((6-fluoro-2-methyl-1*H*-indol-3-yl)methyl)phenyl)benzenesulfonamide (1k) Yellow solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.92 (br, s, 1H), 7.52-7.48 (m, 3H), 7.34-7.30 (m, 3H), 7.25-7.20 (m, 2H), 7.10-7.06 (m, 1H), 6.95 (dd, *J* = 9.5 Hz, 2.2 Hz, 1H), 6.81-6.78 (m, 1H), 6.68-6.62 (m, 2H), 3.75 (s, 2H), 2.32 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  159.84 (d, *J* = 235.8 Hz ), 139.69, 135.70, 135.60, 135.50, 132.99, 132.32, 130.59, 129.04, 127.70, 127.15, 125.77, 124.82, 122.87, 119.30 (d, *J* = 10.0 Hz), 108.26 (d, J = 23.9 Hz), 107.55, 97.09 (d, J = 26.0 Hz), 28.22, 12.04; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>):  $\delta$  -121.53 (s, 1F); HRMS (ESI) calcd for C<sub>22</sub>H<sub>20</sub>FN<sub>2</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 395.1224, found 395.1231.



*N*-(2-((5-chloro-2-methyl-1*H*-indol-3-yl)methyl)phenyl)benzenesulfonamide (11) Yellow solid, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.95 (br, s, 1H), 7.56-7.54 (m, 3H), 7.39-7.34 (m, 3H), 7.18-7.16 (m, 2H), 7.10-7.09 (m, 2H), 7.05-7.04 (m, 1H), 6.83 (s, 1H), 6.56 (br, s, 1H), 3.69 (s, 2H), 2.28 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$ 139.70, 135.21, 133.96, 133.86, 133.22, 132.59, 130.32, 129.47, 129.17, 127.73, 127.16, 126.18, 125.45, 123.73, 121.99, 118.01, 111.50, 107.32, 27.54, 11.92; HRMS (ESI) calcd for C<sub>22</sub>H<sub>20</sub>ClN<sub>2</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 411.0929, found 411.0924.



*N*-(2-((2,5-dimethyl-1*H*-indol-3-yl)methyl)phenyl)benzenesulfonamide (1m) Yellow solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.84 (br, s, 1H), 7.52-7.47 (m, 3H), 7.38-7.30 (m, 3H), 7.19-7.15 (m, 3H), 7.10-7.06 (m, 1H), 6.95-6.93 (m, 1H), 6.78-6.76 (m, 2H), 3.72 (s, 2H), 2.31 (s, 3H), 2.26 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 139.79, 135.50, 133.94, 132.90, 132.59, 132.31, 130.56, 129.00, 128.93, 128.55, 127.47, 127.18, 125.64, 123.27, 122.83, 118.19, 110.24, 106.81, 27.91, 21.60, 11.87; HRMS (ESI) calcd for  $C_{23}H_{23}N_2O_2S^+$  [M+H]<sup>+</sup> 391.1475, found 391.1476.



#### *N*-(2-((5-methoxy-2-methyl-1*H*-indol-3-yl)methyl)phenyl)benzenesulfonamide

(**1n**) Yellow solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.84 (br, s, 1H), 7.49-7.45 (m, 3H), 7.32-7.28 (m, 3H), 7.24-7.22 (m, 1H), 7.17-7.14 (m, 2H), 7.10-7.06 (m, 1H), 6.76-6.73 (m, 2H), 6.41 (d, J = 2.3 Hz, 1H), 3.75 (s, 2H), 3.61 (s, 3H), 2.29 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  154.17, 139.68, 135.65, 132.95, 132.91, 132.33, 130.73, 130.68, 128.99, 128.76, 127.57, 127.16, 125.52, 122.55, 111.40, 111.19, 107.04, 101.12, 55.84, 28.24, 11.95; HRMS (ESI) calcd for C<sub>23</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub>S<sup>+</sup> [M+H]<sup>+</sup> 407.1424, found 407.1419.



*N*-(2-((4-fluoro-5-methoxy-2-methyl-1*H*-indol-3-yl)methyl)phenyl)benzenesulfon amide (10)

Yellow solid, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.87 (br, s, 1H), 7.62-7.60 (m, 2H), 7.51-7.48 (m, 1H), 7.38-7.32 (m, 3H), 7.11-7.10 (m, 1H), 7.03-7.02 (m, 2H), 6.94-6.93 (m, 1H), 6.86-6.83 (m, 1H), 6.72 (br, s, 1H), 3.86 (s, 3H), 3.83 (s, 2H), 2.15 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  146.23 (d, J = 243.8 Hz), 140.50 (d, J = 9.8Hz), 139.77, 134.66, 134.15, 133.77, 133.02 (d, J = 10.4 Hz), 132.93, 130.47, 129.04, 127.26, 127.18, 126.06, 123.61, 118.23 (d, J = 16.9 Hz), 111.70, 106.58, 105.69 (d, J = 4.1 Hz), 58.99, 27.62, 11.81; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>):  $\delta$  -146.37 (s, 1F); HRMS (ESI) calcd for C<sub>23</sub>H<sub>22</sub>FN<sub>2</sub>O<sub>3</sub>S<sup>+</sup> [M+H]<sup>+</sup> 425.1330, found 425.1330.



#### *N*-(2-((2-bromo-1*H*-indol-3-yl)methyl)phenyl)benzenesulfonamide (1p)

Yellow solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.21 (br, s, 1H), 7.61-7.59 (m, 2H), 7.50-7.46 (m, 1H), 7.41-7.39 (m, 1H), 7.34-7.30 (m, 2H), 7.28-7.27 (m, 1H), 7.20-7.07 (m, 4H), 6.99-6.91 (m, 2H), 6.58 (br, s, 1H), 3.76 (s, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  139.56, 136.55, 135.00, 133.00, 132.11, 130.69, 129.03, 127.77, 127.42, 127.25, 126.10, 123.87, 122.88, 120.50, 118.75, 111.73, 110.78, 108.90, 28.26; HRMS (ESI) calcd for C<sub>22</sub>H<sub>18</sub>BrN<sub>2</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 441.0267, found 441.0243.



### *N*-(2-((2-phenyl-1*H*-indol-3-yl)methyl)phenyl)benzenesulfonamide (1q)

Yellow solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.28 (br, s, 1H), 7.50-7.37 (m, 8H), 7.24-7.15 (m, 7H), 7.09-7.06 (m, 1H), 6.93-6.86 (m, 2H), 6.52 (br, s, 1H), 3.86 (s, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  140.00, 136.85, 136.16, 135.72, 133.14, 133.09, 132.65, 130.81, 129.75, 129.37, 129.28, 129.02, 128.97, 128.06 127.48, 126.33, 124.01, 123.36, 120.61, 120.31, 111.63, 109.08, 28.81; HRMS (ESI) calcd for C<sub>27</sub>H<sub>23</sub>FN<sub>2</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 439.1475, found 439.1471.



#### *N*-(2-((2-methyl-1*H*-indol-3-yl)thio)phenyl)benzenesulfonamide (1r)

Yellow solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.28 (br, s, 1H), 7.76-7.74 (m, 2H),

7.58-7.54 (m, 2H), 7.43-7.39 (m, 2H), 7.34-7.32 (m, 1H), 7.28-7.17 (m, 3H), 7.13-7.07 (m, 2H), 6.91-6.90 (m, 2H), 2.45 (s, 3H);  $^{13}$ C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$ 140.71, 139.47, 135.55, 134.64, 133.09, 129.80, 129.74, 129.59, 129.06, 127.56, 127.10, 125.74, 122.62, 122.44, 121.05, 118.71, 110.92, 98.31, 12.27; HRMS (ESI) calcd for C<sub>21</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> 395.0882, found 395.0889.



# *N*-(3-(2-methyl-1*H*-indol-3-yl)propyl)benzenesulfonamide (1s)

Yellow solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.77-7.76 (m, 3H), 7.56-7.52 (m, 1H), 7.47-7.43 (m, 2H), 7.35-7.33 (m, 1H), 7.24-7.23 (m, 1H), 7.11-7.07 (m, 1H), 7.04-7.01 (m, 1H), 4.48 (br, s, 1H), 2.99-2.94 (m, 2H), 2.66 (t, *J* = 7.2 Hz, 2H), 2.29 (s, 3H), 1.80-1.73 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  140.01, 135.41, 132.66, 131.31, 129.19, 128.46, 127.12, 121.17, 119.33, 117.88, 110.44, 43.25, 30.18, 21.33, 11.73; HRMS (ESI) calcd for C<sub>18</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub>S<sup>-</sup> [M-H]<sup>-</sup> 327.1167, found 327.1178.



*N*-(2-((1*H*-indol-3-yl)methyl)phenyl)-4-methylbenzenesulfonamide (1t) Yellowish solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.11 (br, s, 1H), 7.44-7.42 (m, 3H), 7.37-7.35 (m, 1H), 7.25-7.15 (m, 4H), 7.13-7.11 (m, 3H), 7.05-7.02 (m, 1H), 6.79-6.78 (m, 1H), 6.68 (br, s, 1H), 3.71 (s, 2H), 2.38 (s, 3H).



# 2-Methyl-1'-tosylspiro[indole-3,2'-indoline] (2a)

Yellowish solid, 34.8 mg, yield: 89%; M.p. 138-143 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.78 (d, J = 8.2 Hz, 1H), 7.52 (d, J = 7.7 Hz, 1H), 7.33-7.30 (m, 1H), 7.28-7.24 (m, 3H), 7.19 (d, J = 7.4 Hz, 1H), 7.06-7.03 (m, 1H), 7.00-6.98 (m, 2H), 6.69-6.65 (m, 1H), 6.37 (d, J = 7.4 Hz, 1H), 3.46 (d, J = 16.1 Hz, 1H), 3.03 (d, J = 16.1 Hz, 1H), 2.46 (s, 3H), 2.32 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  182.52, 153.05, 143.84, 142.56, 137.62, 136.23, 129.44, 129.16, 128.37, 127.71, 127.28, 125.50, 125.30, 123.04, 121.73, 120.60, 113.70, 79.89, 39.14, 21.43, 15.71; IR (KBr) 3115.7, 2919.5, 2851.2, 1596.3, 1587.1, 1493.5, 1474.9, 1383.4, 1354.4, 1170.6, 1111.6, 1090.6, 965.8, 777.1 cm<sup>-1</sup>; HRMS (ESI) calcd for C<sub>23</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 389.1318, found 389.1316.



# 2-Methyl-1'-(methylsulfonyl)spiro[indole-3,2'-indoline] (2b)

Yellowish solid, 25.6 mg, yield: 82%; M.p. 196-200 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.57 (d, J = 7.7 Hz, 1H), 7.45-7.43 (m, 1H), 7.41-7.37 (m, 1H), 7.34-7.27 (m, 2H), 7.11-7.08 (m, 3H), 3.53 (d, J = 16.0 Hz, 1H), 3.08 (d, J = 16.0 Hz, 1H), 2.74 (s, 3H), 2.46 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  182.51, 153.75, 142.39, 138.09, 130.52, 128.79, 127.86, 125.99, 125.75, 123.49, 121.62, 121.16, 113.03, 80.24, 38.94, 38.87, 15.67; IR (KBr) 3016.4, 2989.3, 2917.2, 2849.5, 1646.5, 1588.3, 1475.7, 1461.3, 1350.8, 1247.8, 1161.3, 1114.2, 960.1, 766.0 cm<sup>-1</sup>; HRMS (ESI) calcd for C<sub>17</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 313.1005, found 313.0982.



# 1'-((4-Chlorophenyl)sulfonyl)-2-methylspiro[indole-3,2'-indoline] (2c)

Yellowish solid, 35.2 mg, yield: 86%; M.p. 172-176 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.83 (d, J = 8.2 Hz, 1H), 7.52 (d, J = 7.6 Hz, 1H), 7.36-7.25 (m, 4H), 7.22-7.21 (m, 1H), 7.16-7.14 (m, 2H), 7.10-7.06 (m, 1H), 6.70-6.66 (m, 1H), 6.32 (d, J = 7.4 Hz, 1H), 3.49 (d, J = 16.0 Hz, 1H), 3.03 (d, J = 16.0 Hz, 1H), 2.48 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  182.32, 153.54, 142.42, 139.69, 137.76, 137.37, 129.85, 128.96, 128.69, 128.66, 128.00, 125.87, 125.49, 123.62, 121.71, 120.96, 113.82, 80.04, 39.14, 15.93; IR (KBr) 3059.1, 2919.0, 2850.5, 1612.6, 1586.1, 1475.8, 1460.1, 1385.3, 1357.6, 1241.0, 1221.0, 1171.9, 1112.0, 1087.3, 1006.1, 967.4, 755.0 cm<sup>-1</sup>; HRMS (ESI) calcd for C<sub>22</sub>H<sub>18</sub>ClN<sub>2</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 409.0772, found 409.0754.



# 2-Methyl-1'-(phenylsulfonyl)spiro[indole-3,2'-indoline] (2d)

Yellowish solid, 36.3 mg, yield: 97%; M.p. 112-115 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.83 (d, J = 8.2 Hz, 1H), 7.52 (d, J = 7.6 Hz, 1H), 7.44-7.40 (m, 1H), 7.37-7.32 (m, 3H), 7.27-7.18 (m, 4H), 7.08-7.04 (m, 1H), 6.65-6.61 (m, 1H), 6.32 (d, J = 7.4 Hz, 1H), 3.47 (d, J = 16.1 Hz, 1H), 3.04 (d, J = 16.1 Hz, 1H), 2.47 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  182.47, 153.36, 142.61, 139.34, 137.55, 132.99, 129.63, 128.73, 128.56, 127.90, 127.27, 125.71, 125.54, 123.32, 121.77, 120.79, 113.87, 79.96, 39.21, 15.86; IR (KBr) 3058.1, 2920.0, 2852.0, 1587.0, 1459.5, 1384.2, 1355.5, 1170.3, 1113.8, 1088.4, 965.3, 753.3 cm<sup>-1</sup>; HRMS (ESI) calcd for C<sub>22</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 375.1162, found 375.1153.



## 5'-Chloro-2-methyl-1'-(phenylsulfonyl)spiro[indole-3,2'-indoline] (2e)

Yellowish solid, 40.2 mg, yield: 98%; M.p. 158-160 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.76 (d, J = 8.7 Hz, 1H), 7.52 (d, J = 7.6 Hz, 1H), 7.46-7.42 (m, 1H), 7.33-7.18 (m, 7H), 6.65-6.61 (m, 1H), 6.30 (d, J = 7.3 Hz, 1H), 3.44 (d, J = 16.3 Hz, 1H), 3.02 (d, J = 16.3 Hz, 1H), 2.45 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  181.84, 153.41, 141.43, 139.15, 137.16, 133.20, 129.87, 129.84, 129.83, 128.61, 128.56, 127.23, 125.85, 125.64, 121.75, 120.93, 114.73, 80.17, 38.88, 15.83; IR (KBr) 3090.1, 3068.6, 2920.5, 2850.8, 1597.0, 1468.6, 1384.2, 1350.9, 1167.4, 1088.9, 1050.1, 819.1, 598.3 cm<sup>-1</sup>; HRMS (ESI) calcd for C<sub>22</sub>H<sub>18</sub>ClN<sub>2</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 409.0772, found 409.0751.



#### 4'-Chloro-2-methyl-1'-(phenylsulfonyl)spiro[indole-3,2'-indoline] (2f)

Yellowish solid, 39.0 mg, yield: 95%; M.p. 170-174 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.73 (d, J = 6.5 Hz, 1H), 7.53 (d, J = 6.0 Hz, 1H), 7.46-7.43 (m, 1H), 7.36-7.34 (m, 2H), 7.31-7.27 (m, 2H), 7.24-7.20 (m, 2H), 7.06 (d, J = 6.4 Hz, 1H), 6.69-6.66 (m, 1H), 6.36 (d, J = 5.8 Hz, 1H), 3.43 (d, J = 13.5 Hz, 1H), 3.13 (d, J = 13.5 Hz, 1H), 2.46 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  182.15, 153.49, 143.92, 139.29, 137.39, 133.24, 131.63, 130.09, 129.86, 128.84, 127.23, 126.47, 125.71, 123.36, 121.92, 120.95, 112.01, 79.64, 38.51, 15.75; IR (KBr) 3065.1, 2922.5, 2850.1, 1590.9, 1477.4, 1383.1, 1356.2, 1239.9, 1165.9, 1087.1, 1048.4, 972.2, 753.2 cm<sup>-1</sup>; HRMS (ESI) calcd for C<sub>22</sub>H<sub>18</sub>ClN<sub>2</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 409.0772, found 409.0767.



#### 6'-Methoxy-2-methyl-1'-(phenylsulfonyl)spiro[indole-3,2'-indoline] (2g)

Yellowish solid, 31.5 mg, yield: 78%; M.p. 122-124 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.51 (d, J = 7.5 Hz, 1H), 7.45-7.41 (m, 2H), 7.37-7.35 (m, 2H), 7.25-7.19 (m, 3H), 7.07 (d, J = 8.2 Hz, 1H), 6.65-6.59 (m, 2H), 6.34 (d, J = 7.3 Hz, 1H), 3.89 (s, 3H), 3.39 (d, J = 15.8 Hz, 1H), 2.97 (d, J = 15.8 Hz, 1H), 2.46 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  182.36, 160.56, 153.49, 143.88, 139.49, 137.66, 133.01, 129.61, 128.76, 127.37, 125.88, 125.52, 121.83, 120.79, 119.71, 108.47, 101.22, 80.79, 55.91, 38.57, 15.89; IR (KBr) 3068.8, 2921.3, 2850.1, 1611.1, 1587.4, 1498.4, 1444.2, 1384.3, 1356.9, 1287.2, 1168.7, 1085.0, 687.9 cm<sup>-1</sup>; HRMS (ESI) calcd for C<sub>23</sub>H<sub>21</sub>N<sub>2</sub>O<sub>3</sub>S + [M+H]<sup>+</sup> 405.1267, found 405.1257.



#### 2,5',6'-Trimethyl-1'-(phenylsulfonyl)spiro[indole-3,2'-indoline] (2h)

Yellowish solid, 32.0 mg, yield: 80%; M.p. 200-204 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.53-7.50 (m, 2H), 7.44-7.41 (m, 1H), 7.34-7.32 (m, 2H), 7.27-7.18 (m, 3H), 6.74 (s, 1H), 6.61-6.58 (m, 1H), 6.30 (d, *J* = 7.2 Hz, 1H), 4.01 (s, 3H), 3.86 (s, 3H), 3.40 (d, *J* = 15.7 Hz, 1H), 2.96 (d, *J* = 15.7 Hz, 1H), 2.46 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  182.33, 153.41, 149.48, 145.79, 139.57, 137.43, 136.12, 132.89, 129.56, 128.74, 127.19, 125.50, 121.78, 120.72, 118.67, 109.27, 99.49, 80.35, 56.62, 39.15, 15.88; IR (KBr) 3091.5, 2961.5, 2935.7, 2837.5, 1585.7, 1503.5, 1446.0, 1384.3, 1353.8, 1224.9, 1188.8, 1167.4, 1088.5, 1009.0, 719.9 cm<sup>-1</sup>.



# 2,7'-Dimethyl-1'-(phenylsulfonyl)spiro[indole-3,2'-indoline] (2i)

Yellowish solid, 24.9 mg, yield: 64%; M.p. 103-108 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.67-7.64 (m, 2H), 7.56 (d, J = 7.4 Hz, 1H), 7.44-7.40 (m, 1H), 7.33-7.24 (m, 4H), 7.14-7.11 (m, 2H), 7.07-7.06 (m, 2H), 3.55 (d, J = 16.3 Hz, 1H), 3.14 (d, J = 16.3 Hz, 1H), 2.30 (s, 3H), 2.18 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  182.39, 153.82, 141.35, 141.22, 137.43, 132.80, 132.37, 132.13, 130.06, 128.90, 128.34, 126.85, 125.83, 125.27, 124.57, 123.05, 120.33, 81.42, 39.12, 21.06, 16.49; IR (KBr) 3063.0, 2956.4, 2923.3, 2852.5, 1589.1, 1460.2, 1447.3, 1384.2, 1333.6, 1160.7, 1092.3, 754.3 cm<sup>-1</sup>; HRMS (ESI) calcd for C<sub>23</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 389.1318, found 389.1296.



#### 5-Fluoro-2-methyl-1'-(phenylsulfonyl)spiro[indole-3,2'-indoline] (2j)

Yellowish, 38.5 mg, yield: 98%; M.p. 129-133 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 7.86 (d, J = 8.2 Hz, 1H), 7.50-7.44 (m, 2H), 7.41-7.40 (m, 2H), 7.37-7.33 (m, 1H), 7.25-7.20 (m, 3H), 7.10-7.06 (m, 1H), 6.96-6.91 (m, 1H), 5.95 (dd, J = 7.6 Hz, 2.3 Hz, 1H), 3.47 (d, J = 16.1 Hz, 1H), 3.01 (d, J = 16.1 Hz, 1H), 2.45 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  182.44 (d, J = 3.6 Hz), 160.81 (d, J = 244.4 Hz), 149.35, 142.45, 139.30, 139.01 (d, J = 8.6 Hz), 133.41, 128.76, 127.50, 127.12, 125.80, 123.56, 121.45 (d, J = 8.7 Hz), 116.16 (d, J = 23.4 Hz), 113.96, 109.78 (d, J = 25.2 Hz), 80.03, 39.09, 15.87; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>):  $\delta$  -117.30 (s, 1F); IR (KBr) 3080.2, 2920.8, 2850.7, 1588.6, 1477.3, 1383.3, 1359.5, 1256.4, 1169.1, 1088.4, 759.4 cm<sup>-1</sup>; HRMS (ESI) calcd for C<sub>22</sub>H<sub>18</sub>FN<sub>2</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 393.1068, found 393.1059.



#### 6-Fluoro-2-methyl-1'-(phenylsulfonyl)spiro[indole-3,2'-indoline] (2k)

Yellowish solid, 39.0 mg, yield: 99%; M.p. 116-120 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.84 (d, J = 8.2 Hz, 1H), 7.48-7.44 (m, 1H), 7.41-7.39 (m, 2H), 7.36-7.32 (m, 1H), 7.27-7.20 (m, 4H), 7.09-7.05 (m, 1H), 6.34-6.29 (m, 1H), 6.25-6.22 (m, 1H), 3.46 (d, J = 16.1 Hz, 1H), 3.02 (d, J = 16.1 Hz, 1H), 2.47 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  184.87, 163.94 (d, J = 245.2 Hz), 155.17 (d, J = 11.2 Hz), 142.46, 139.39, 133.29 (d, J = 2.9 Hz), 133.19, 128.82, 128.69, 127.57, 127.15, 125.74, 123.47, 122.38 (d, J = 9.8 Hz), 113.91, 111.90 (d, J = 23.2 Hz), 108.70 (d, J = 24.2 Hz), 79.43, 39.18, 16.05; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>):  $\delta$  -111.47 (s, 1F); IR (KBr) 3067.5, 2921.5, 2851.7, 1594.6, 1475.8, 1354.9, 1244.8, 1179.2, 1165.6, 764.2 cm<sup>-1</sup>; HRMS (ESI) calcd for C<sub>22</sub>H<sub>18</sub>FN<sub>2</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 393.1068, found 393.1062.



#### 5-Chloro-2-methyl-1'-(phenylsulfonyl)spiro[indole-3,2'-indoline] (2l)

Yellowish solid, 37.6 mg, yield: 92%; M.p. 170-175 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.86 (d, J = 8.2 Hz, 1H), 7.51-7.49 (m, 1H), 7.42 (d, J = 8.2 Hz, 1H), 7.37-7.33 (m, 3H), 7.25-7.19 (m, 4H), 7.09-7.05 (m, 1H), 6.14 (d, J = 1.8 Hz, 1H), 3.46 (d, J = 16.1Hz, 1H), 3.00 (d, J = 16.1 Hz, 1H), 2.47 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$ 183.14, 151.99, 142.42, 139.08, 138.92, 133.59, 131.20, 129.80, 128.78, 128.72, 127.45, 127.01, 125.81, 123.57, 122.50, 121.62, 113.95, 79.87, 38.99, 15.87; IR (KBr) 3112.2, 3065.3, 2921.4, 2852.7, 1594.0, 1478.0, 1458.8, 1446.1, 1384.5, 1353.9, 1241.6, 1165.4, 1114.0, 1087.4, 968.2, 751.5 cm<sup>-1</sup>; HRMS (ESI) calcd for C<sub>22</sub>H<sub>18</sub>ClN<sub>2</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 409.0772, found 409.0776.



#### 2,5-Dimethyl-1'-(phenylsulfonyl)spiro[indole-3,2'-indoline] (2m)

Yellowish solid, 34.6 mg, yield: 89%; M.p. 129-134 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.81 (d, J = 8.2 Hz, 1H), 7.44-7.33 (m, 5H), 7.20-7.16 (m, 3H), 7.09-7.02 (m, 2H), 6.00 (s, 1H), 3.46 (d, J = 16.1 Hz, 1H), 3.00 (d, J = 16.1 Hz, 1H), 2.46 (s, 3H), 1.89 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  181.52, 151.27, 142.68, 139.54, 137.40, 135.15, 132.85, 130.20, 128.55, 128.42, 128.01, 127.33, 125.72, 123.30, 122.82, 120.30, 113.89, 79.75, 39.15, 20.85, 14.75; IR (KBr) 3067.0, 2920.3, 2852.2, 1594.8, 1477.6, 1460.5, 1357.6, 1231.5, 1168.3, 1114.6, 1088.3, 689.5 cm<sup>-1</sup>; HRMS (ESI) calcd for C<sub>23</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 389.1318, found 389.1301.



# 5-Methoxy-2-methyl-1'-(phenylsulfonyl)spiro[indole-3,2'-indoline] (2n)

Yellowish solid, 32.4 mg, yield: 80%; M.p. 140-144 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.85 (d, J = 8.2 Hz, 1H), 7.44-7.38 (m, 4H), 7.35-7.31 (m, 1H), 7.24-7.19 (m, 3H), 7.08-7.04 (m, 1H), 6.76 (dd, J = 8.4 Hz, 2.3 Hz, 1H), 5.81 (d, J = 2.2 Hz, 1H), 3.46 (d, J = 16.1 Hz, 1H), 3.40 (s, 3H), 3.02 (d, J = 16.1 Hz, 1H), 2.43 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  180.32, 157.85, 146.96, 142.61, 139.57, 138.71, 132.97, 128.57, 127.87, 127.35, 125.76, 123.34, 121.10, 114.55, 113.89, 108.17, 79.99, 55.39, 39.27, 15.73; IR (KBr) 3067.3, 2960.4, 2920.1, 2839.0, 1596.4, 1475.9, 1383.9, 1354.8, 1286.4, 1179.6, 1163.7, 1112.9, 1025.9, 826.4, 756.8 cm<sup>-1</sup>; HRMS (ESI) calcd for C<sub>23</sub>H<sub>21</sub>N<sub>2</sub>O<sub>3</sub>S<sup>+</sup> [M+H]<sup>+</sup> 405.1267, found 405.1259.



**4-Fluoro-5-methoxy-2-methyl-1'-(phenylsulfonyl)spiro[indole-3,2'-indoline] (20)** Yellowish solid, 36.3 mg, yield: 86%; M.p. 120-124 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.82 (d, *J* = 8.2 Hz, 1H), 7.47-7.42 (m, 3H), 7.33-7.29 (m, 1H), 7.24-7.20 (m, 3H), 7.18-7.16 (m, 1H), 7.06-7.02 (m, 1H), 6.84-6.80 (m, 1H), 3.71 (s, 3H), 3.43 (d, *J* = 16.3 Hz, 1H), 3.19 (d, *J* = 16.3 Hz, 1H), 2.42 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$ 181.19, 148.78 (d, *J* = 253.3 Hz), 147.77, 146.42 (d, *J* = 10.6 Hz), 142.31, 138.66, 133.13, 128.48, 128.44, 127.91, 127.17, 125.17, 124.14 (d, *J* = 13.6 Hz), 123.35, 115.90 (d, *J* = 3.2 Hz), 114.13, 113.66, 79.63 (d, *J* = 3.3 Hz), 56.75, 37.81, 15.37; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>):  $\delta$  -135.03 (s, 1F); IR (KBr) 3066.5, 2996.1, 2916.1, 2841.5, 1596.2, 1498.1, 1461.7, 1353.8, 1262.6, 1164.0, 1113.5, 1086.3, 1061.4, 823.2, 754.9 cm<sup>-1</sup>; HRMS (ESI) calcd for C<sub>23</sub>H<sub>20</sub>FN<sub>2</sub>O<sub>3</sub>S<sup>+</sup> [M+H]<sup>+</sup> 423.1173, found 423.1180.



2-Bromo-1'-(phenylsulfonyl)spiro[indole-3,2'-indoline] (2p)

Yellowish solid, 43.0 mg, yield: 98%; M.p. 135-140 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.73 (d, J = 8.2 Hz, 1H), 7.57 (d, J = 7.8 Hz, 1H), 7.49-7.47 (m, 3H), 7.34-7.28 (m, 4H), 7.22-7.20 (m, 1H), 7.09-7.05 (m, 1H), 6.84-6.80 (m, 1H), 6.54 (d, J = 7.4 Hz, 1H), 3.63 (d, J = 16.3 Hz, 1H), 3.15 (d, J = 16.3 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  166.35, 152.60, 142.17, 139.56, 137.74, 133.33, 130.05, 128.92, 128.67, 127.40, 127.17, 126.60, 125.59, 123.46, 122.24, 121.34, 113.73, 81.71, 39.91; IR (KBr) 3018.0, 2949.6, 1600.7, 1462.0, 1384.7, 1357.8, 1334.2, 1235.6, 1161.4, 1089.0, 902.1, 587.2 cm<sup>-1</sup>; HRMS (ESI) calcd for C<sub>21</sub>H<sub>16</sub>BrN<sub>2</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 439.0110, found 439.0111.



# 2-Phenyl-1'-(phenylsulfonyl)spiro[indole-3,2'-indoline] (2q)

Yellowish solid, 33.1 mg, yield: 76%; M.p. 239-241 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.20 (d, J = 8.2 Hz, 2H), 7.90 (d, J = 8.2 Hz, 1H), 7.69 (d, J = 7.7 Hz, 1H), 7.47-7.29 (m, 8H), 7.24-7.22 (m, 1H), 7.17-7.10 (m, 3H), 6.69-6.65 (m, 1H), 6.42 (d, J = 7.3 Hz, 1H), 3.78 (d, J = 16.4 Hz, 1H), 3.15 (d, J = 16.4 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  177.52, 152.64, 142.16, 139.54, 139.44, 132.88, 131.65, 131.35, 129.68, 128.93, 128.66, 128.61, 127.90, 127.33, 126.14, 123.44, 121.69, 121.13, 114.08, 78.78, 40.99; IR (KBr) 3057.3, 2921.4, 2849.8, 1646.2, 1596.1, 1537.2, 1459.6, 1384.7, 1357.8, 1264.9, 1238.0, 1161.7, 974.2, 772.7 cm<sup>-1</sup>; HRMS (ESI) calcd for C<sub>27</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 437.1318, found 437.1315.



2'-Methyl-3-(phenylsulfonyl)-3H-spiro[benzo[d]thiazole-2,3'-indole] (2r)

Yellowish solid, 25.0 mg, yield: 64%; M.p. 146-150 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.82 (d, J = 8.2 Hz, 1H), 7.54-7.47 (m, 4H), 7.35-7.30 (m, 3H), 7.20-7.15 (m, 2H), 7.06-7.02 (m, 1H), 6.87-6.83 (m, 1H), 6.80-6.78 (m, 1H), 2.55 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  180.27, 152.49, 139.34, 138.55, 136.84, 133.67, 130.74, 129.03, 127.48, 126.23, 125.98, 125.73, 124.12, 123.58, 123.12, 121.20, 114.94, 83.07, 15.59; IR (KBr) 3067.7, 2920.5, 2850.1, 1587.4, 1461.7, 1384.2, 1362.4, 1226.3, 1170.0, 1108.0, 1087.3, 981.2, 754.4 cm<sup>-1</sup>; HRMS (ESI) calcd for C<sub>21</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> 393.0726, found 393.0716.



# 2-Methyl-1'-(phenylsulfonyl)spiro[indole-3,2'-pyrrolidine] (2s)

Yellowish solid, 10.4 mg, yield: 32%; M.p. 127-130 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.51-7.49 (m, 1H), 7.46-7.42 (m, 1H), 7.28-7.23 (m, 5H), 6.76-6.72 (m, 1H), 6.42-6.41 (m, 1H), 4.04-3.98 (m, 1H), 3.75-3.69 (m, 1H), 2.44 (s, 3H), 2.36-2.29 (m, 1H), 2.26-2.20 (m, 2H), 1.90-1.84 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  183.71, 153.43, 138.92, 138.05, 132.43, 129.17, 128.64, 127.45, 125.18, 122.12, 120.77, 77.69, 49.83, 37.39, 23.72, 15.98; IR (KBr) 3061.3, 3007.3, 2975.8, 2893.4, 2850.8, 1614.4, 1480.9, 1377.8, 1182.0, 1127.0, 1102.6, 723.7 cm<sup>-1</sup>; HRMS (ESI) calcd for C<sub>18</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 327.1162, found 327.1157.



# 1'-tosylspiro[indole-3,2'-indoline] (2t)

Yellowish solid, 28.3 mg, yield: 76%; M.p. 148-152 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.22 (s, 1H), 7.78-7.76 (m, 1H), 7.61-7.59 (m, 1H), 7.34-7.29 (m, 4H), 7.20-7.18 (m, 1H), 7.06-7.00 (m, 3H), 6.82-6.78 (m, 1H), 6.56-6.54 (m, 1H), 3.64 (d, *J* = 16.0 Hz, 1H), 2.97 (d, *J* = 16.0 Hz, 1H), 2.32 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  172.63, 153.48, 144.10, 142.54, 137.39, 135.90, 129.61, 129.44, 128.48, 128.16, 127.31, 126.71, 125.73, 123.21, 121.92, 121.53, 113.89, 79.67, 37.01, 21.60; IR (KBr) 3144.1, 3066.5, 2957.1, 2924.2, 1698.9, 1641.2, 1597.9, 1517.6, 1460.0, 1356.9, 1167.2, 1090.0, 753.4, 544.2 cm<sup>-1</sup>; HRMS (ESI) calcd for C<sub>18</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup> 375.1162, found 375.1184.



#### 2-Methyl-1'-(phenylsulfonyl)-2,3'-spirobi[indoline]-2-carbonitrile (3)

White solid, 17.0 mg, yield: 82%; M.p. 135-137 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.83 (d, J = 8.4 Hz, 1H), 7.30-7.24 (m, 3H), 7.11-7.02 (m, 5H), 6.91 (d, J = 8.0 Hz, 1H), 6.69-6.65 (m, 1H), 6.57-6.55 (m, 1H), 4.56 (br, s, 1H), 3.93 (d, J = 17.6 Hz, 1H), 3.80 (d, J = 17.6 Hz, 1H), 2.34 (s, 3H), 1.85 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  150.55, 143.82, 142.13, 137.63, 131.27, 129.22, 128.75, 127.61, 127.17, 126.94, 125.69, 124.61, 124.21, 122.43, 121.17, 115.16, 113.49, 80.39, 70.17, 42.01, 21.64, 21.22; IR (KBr) 3357.1, 3048.9, 2922.5, 2852.3, 2228.1, 1598.4, 1480.0, 1462.7, 1375.4, 1357.0, 1337.0, 1169.2, 1111.6, 1089.3, 1018.9, 965.0, 754.6 cm<sup>-1</sup>; HRMS (ESI) calcd for C<sub>24</sub>H<sub>20</sub>N<sub>3</sub>O<sub>2</sub>S<sup>-</sup> [M-H]<sup>-</sup> 414.1276, found 414.1256.



#### 1'-(Phenylsulfonyl)-2,3'-spirobi[indolin]-2-one (4)

White solid, 33.2 mg, yield: 88%; M.p. 158-162 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.75 (br, s, 1H), 7.88-7.86 (m, 2H), 7.52-7.49 (m, 1H), 7.42-7.34 (m, 3H), 7.22-7.16 (m, 3H), 7.02-6.99 (m, 1H), 6.93-6.92 (m, 1H), 6.83-6.75 (m, 2H), 3.77 (d, J = 15.8 Hz, 1H), 3.22 (d, J = 15.8 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  177.95, 141.72, 139.88, 139.53, 133.29, 130.51, 129.95, 129.01, 128.26, 127.95, 127.38, 125.38, 123.27, 123.05, 122.95, 112.68, 111.05, 71.41, 42.28; IR (KBr) 3363.4, 3066.2, 2926.2, 1731.2, 1619.8, 1475.0, 1384.8, 1358.0, 1334.7, 1235.7, 1166.0, 1115.9, 1089.4, 979.9, 750.9 cm<sup>-1</sup>; HRMS (ESI) calcd for C<sub>21</sub>H<sub>15</sub>N<sub>2</sub>O<sub>3</sub>S<sup>-</sup> [M-H]<sup>-</sup> 375.0803, found 375.0823.

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# VI. Copies of <sup>1</sup>H and <sup>13</sup>C NMR Spectra







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