Supporting Information

for

Copper-Cascade Catalysis: Synthesis of 3-Functionalized Indoles

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General Considerations

Infrared spectras were obtained on a FTIR spectrometer. $^1$H NMR spectras were recorded on 500 MHz spectrometer. The chemical shifts were reported relative to internal standard TMS (0) in CDCl$_3$ or 2.5 in DMSO-$d_6$. The following abbreviations were used to describe peak patterns where appropriate: b = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants were reported in Hertz (Hz). $^{13}$C NMR were recorded on 125 MHz spectrometer, referred to the internal solvent signals (77.0 ppm for CDCl$_3$ or 40.0 ppm for DMSO-$d_6$). MS and HRMS were obtained using ESI ionization. Melting points were measured with micro melting point apparatus. Sulfonyl azides were prepared according the published methods.$^{1,2}$

General Procedure for the synthesis of 4

To a solution of 2-methyl indole (0.5 mmol), sulfonyl azide (1 mmol) and CuBr (0.05 mmol) in DCM (0.8 mL) in Schlenk tube was added the mixture of alkynes (1 mmol) and pyridine (1 mmol) in DCM (0.8 mL) slowly via syringe. The reaction mixture was stirred at room temperature for 12 h under oxygen. The solution was diluted by DCM (3 mL) and quenched by a mixture of 1N HCl and saturated NH$_4$Cl. The aqueous layer was extracted by DCM and the combined organic layer was washed with NH$_4$Cl (10 mL), brine (10 mL) and dried over anhydrous sodium sulfate. The solvent was removed in vacuum, and the residue was purified by column chromatography on silica gel to give corresponding products. All the compounds were further recrystallized from EA.
Characterization Data for 4

4-methyl-N-(1-(2-methyl-1H-indol-3-yl)-2-oxo-2-phenylethylidene)benzenesulfonamide (4a)

Yellow solid; mp. 227-228 °C; $^1$H NMR (DMSO-$d_6$) δ 12.66 (s, 1H), 7.92-7.90 (m, 3H), 7.73-7.70 (m, 3H), 7.58 (t, $J = 8.0$ Hz, 2H), 7.43-7.39 (m, 3H), 7.22-7.13 (m, 2H), 2.37 (s, 3H), 2.34 (s, 3H) ppm; $^{13}$C NMR (DMSO-$d_6$) δ 197.0, 170.7, 150.5, 143.8, 138.6, 136.1, 135.1, 135.0, 130.2, 129.8, 129.0, 127.1, 126.6, 124.0, 123.4, 121.7, 112.6, 107.9, 21.5, 15.9 ppm; IR (KBr) ν 3270, 3062, 2924, 1675, 1522, 1457, 1284, 1146, 1083, 817, 771, 673 cm$^{-1}$; MS (ESI) m/z 439.2 ([M+Na]$^+$); HRMS (ESI) calcd for C$_{24}$H$_{20}$N$_2$O$_3$S ([M+Na]$^+$), 439.1087; found, 439.1079.

N-(2-(3-chlorophenyl)-1-(2-methyl-1H-indol-3-yl)-2-oxoethylidene)-4-methylbenzenesulfonamide (4b)

Yellow solid; mp. 211-212 °C; $^1$H NMR (CDCl$_3$) δ 9.83 (s, 1H), 7.95-7.90 (m, 2H), 7.78 (d, $J = 8.0$ Hz, 2H), 7.75 (d, $J = 8.0$ Hz, 1H), 7.43 (d, $J = 8.0$ Hz, 1H), 7.25-7.21 (m, 4H), 7.11-7.09 (m, 2H), 2.38 (s, 3H), 2.26 (s, 3H) ppm; $^{13}$C NMR (CDCl$_3$) δ 196.0, 170.0, 149.6, 143.8, 137.7, 136.4, 135.4, 135.3, 134.2, 130.4, 129.6, 128.3,
127.3, 127.1, 126.4, 123.9, 123.5, 122.0, 111.7, 108.6, 21.5, 16.0 ppm; IR (KBr) ν 3277, 3063, 2924, 1684, 1515, 1457, 1257, 1146, 1083, 822, 785, 752 cm⁻¹; MS (ESI) m/z 450.9 ([M+Na]⁺); HRMS (ESI) calcd for C₂₄H₁₉ClN₂O₃S ([M+Na]⁺), 473.0697; found, 473.0685.

\[
\begin{align*}
\text{N-} & \text{(2-(4-methoxyphenyl)-1-(2-methyl-1H-indol-3-yl)-2-oxoethylidene)-4-methylbenzenesulfonamide (4c)} \\
\text{Yellow oil; } & \text{¹H NMR (CDCl₃) } \delta 9.93 \text{ (s, 1H), 8.01 (b, 1H), 7.85-7.82 (m, 4H), 7.24-7.18 (m, 3H), 7.09-7.05 (m, 2H), 6.71 (d, J =8.5 Hz, 2H), 3.67 (s, 3H), 2.36 (s, 3H), 2.22 (s, 3H) ppm; } ^{13} \text{C NMR (CDCl₃) } \delta 195.1, 171.3, 164.4, 149.6, 143.4, 138.2, 135.4, 131.4, 129.4, 128.1, 127.1, 126.6, 123.6, 123.2, 122.1, 114.2, 111.7, 108.8, 55.4, 21.5, 15.6 ppm; \text{ IR (KBr) } \nu 3283, 3053, 2932, 2841, 1671, 1597, 1513, 1457, 1260, 1147, 1084, 820, 787, 673, 556 cm⁻¹; \text{ MS (ESI) } m/z 445.1 ([M-H]⁻); \text{ HRMS (ESI) calcd for C}_{25}H_{22}N_{2}O_{4}S ([M+H]⁺), 447.1373; found, 447.1367.
\end{align*}
\]

\[
\begin{align*}
\text{N-} & \text{(1-(2-methyl-1H-indol-3-yl)-2-oxo-2-phenylethylidene)benzenesulfonamide (4d)} \\
\text{Yellow solid; mp. } 119-120 \text{ °C; } & \text{¹H NMR (CDCl₃) } \delta 9.89 \text{ (s, 1H), 7.97-7.88 (m, 5H),}
\end{align*}
\]
7.51 (t, J = 7.0 Hz, 1H), 7.45-7.42 (m, 3H), 7.29 (t, J = 7.5 Hz, 2H), 7.22-7.20 (m, 1H), 7.09-7.07 (m, 2H), 2.19 (s, 3H) ppm; $^{13}$C NMR (CDCl$_3$) δ 196.9, 171.4, 149.8, 140.9, 135.4, 134.8, 134.4, 132.7, 128.9, 128.8, 127.0, 126.5, 123.8, 123.4, 122.1, 111.7, 108.8, 15.8 ppm; IR (KBr) ν 3273, 3058, 2973, 2927, 1679, 1525, 1458, 1285, 1257, 1147, 1082, 813, 774, 752, 687, 555 cm$^{-1}$; MS (ESI) m/z 403.0 ([M+H]$^+$); HRMS (ESI) calcd for C$_{23}$H$_{18}$N$_2$O$_3$S ([M+Na]$^+$), 425.0930; found, 425.0915.

4-methoxy-N-(1-(2-methyl-1H-indol-3-yl)-2-oxo-2-phenylethylidene)benzenesulfonyl amide (4e)

Yellow solid; mp. 242-243 °C; $^1$H NMR (DMSO-$d_6$) δ 12.6 (s, 1H), 7.90-7.89 (m, 3H), 7.75 (d, J = 8.5 Hz, 2H), 7.72 (t, J = 7.5 Hz, 1H), 7.59 (t, J = 7.5 Hz, 2H), 7.41 (d, J = 8.0 Hz, 1H), 7.20 (t, J = 7.5 Hz, 1H), 7.16-7.11 (m, 3H), 3.83 (s, 3H), 2.32 (s, 3H) ppm; $^{13}$C NMR (DMSO-$d_6$) δ 197.1, 170.3, 163.1, 150.2, 136.1, 135.1, 135.0, 133.0, 129.8, 129.3, 129.0, 126.7, 124.0, 123.4, 121.6, 114.9, 112.5, 107.8, 56.2, 15.8 ppm; IR (KBr) ν 3257, 2928, 2840, 1675, 1595, 1458, 1287, 1260, 1144, 1085, 813, 770, 561 cm$^{-1}$; MS (ESI) m/z 433.2 ([M+H]$^+$); HRMS (ESI) calcd for C$_{24}$H$_{20}$N$_2$O$_4$S ([M+Na]$^+$), 455.1036; found, 455.1032.
4-bromo-N-(1-(2-methyl-1H-indol-3-yl)-2-oxo-2-phenylethylidene)benzenesulfonamide (4f)

Yellow solid; mp. 227-228 °C; $^1$H NMR (CDCl$_3$) $\delta$ 9.86 (s, 1H), 7.99 (b, 1H), 7.89 (d, $J = 6.0$ Hz, 2H), 7.77 (d, $J = 8.5$ Hz, 2H), 7.57 (d, $J = 9.0$ Hz, 2H), 7.46 (t, $J = 7.5$ Hz, 1H), 7.31 (t, $J = 8.0$ Hz, 2H), 7.22-7.20 (m, 1H), 7.12-7.10 (m, 2H), 2.21 (s, 3H) ppm; $^{13}$C NMR (CDCl$_3$) $\delta$ 196.8, 171.6, 150.2, 139.9, 135.4, 134.7, 134.5, 132.1, 129.0, 128.9, 128.6, 127.7, 126.4, 124.0, 123.6, 122.1, 111.7, 109.0, 15.9 ppm; IR (KBr) $\nu$ 3274, 3059, 2970, 1678, 1456, 1258, 1145, 1081, 814, 775, 752, 554 cm$^{-1}$; MS (ESI) m/z 481.1 ([M+H]$^+$); HRMS (ESI) calcd for C$_{23}$H$_{17}$BrN$_2$O$_3$S ([M+Na]$^+$), 503.0035; found, 503.0024.

2-methyl-N-(1-(2-methyl-1H-indol-3-yl)-2-oxo-2-phenylethylidene)benzenesulfonamide (4g)

Pale yellow solid; mp. 204-205 °C; $^1$H NMR (DMSO-$d_6$) $\delta$ 12.70 (s, 1H), 7.88 (m, 3H), 7.71 (t, $J = 7.5$ Hz, 1H), 7.63 (d, $J = 8.0$ Hz, 1H), 7.58-7.52 (m, 3H), 7.42 (d, $J = 8.0$ Hz, 2H), 7.34 (t, $J = 7.5$ Hz, 1H), 7.21 (t, $J = 7.5$ Hz, 1H), 7.16-7.14 (m, 1H), 2.75 (s, 3H), 2.34 (s, 3H) ppm; $^{13}$C NMR (DMSO-$d_6$) $\delta$ 196.5, 171.3, 150.6, 139.8, 137.6,
136.1, 135.0, 134.9, 133.4, 132.8, 129.7, 129.1, 128.0, 126.7, 126.6, 124.1, 123.4, 121.4, 112.6, 108.1, 20.4, 15.9 ppm; IR (KBr) ν 3339, 3060, 2928, 1679, 1524, 1457, 1305, 1260, 1153, 1127, 1062, 813, 760, 690, 548 cm⁻¹; MS (ESI) m/z 417.2 ([M+H]⁺); HRMS (ESI) calcd for C₂₄H₂₀N₂O₃S ([M+Na]⁺), 439.1087; found, 439.1078.

4-bromo-N-(1-(2-methyl-1H-indol-3-yl)-2-oxo-2-p-tolylethylidene)benzenesulfonamide (4h)

Yellow solid; mp. 216-217 °C; ¹H NMR (CDCl₃) δ 9.90 (s, 1H), 7.98 (b, 1H), 7.79-7.76 (m, 4H), 7.58-7.56 (m, 2H), 7.20-7.18 (m, 1H), 7.12-7.06 (m, 4H), 2.23 (s, 3H), 2.21 (s, 3H) ppm; ¹³C NMR (CDCl₃) δ 196.2, 171.8, 150.2, 145.9, 140.1, 135.4, 132.3, 132.1, 129.7, 129.0, 128.6, 127.6, 126.5, 123.9, 123.5, 122.1, 111.8, 109.0, 21.7, 15.8 ppm; IR (KBr) ν 3272, 3059, 2924, 1674, 1603, 1518, 1454, 1311, 1266, 1144, 1082, 1008, 805, 745, 632, 539 cm⁻¹; MS (ESI) m/z 493.3 ([M-H]⁻); HRMS (ESI) calcd for C₂₄H₁₉BrN₂O₃S ([M+Na]⁺), 517.0192; found, 517.0180.

N-(2-(2-bromophenyl)-1-(5-chloro-2-methyl-1H-indol-3-yl)-2-oxoethylidene)-4-m
ethylbenzenesulfonamide (4i)
Yellow solid; mp. 244-245 °C; $^1$H NMR (DMSO-$d_6$) δ 12.80 (s, 1H), 7.90-7.88 (m, 3H), 7.71 (d, $J$ = 7.5 Hz, 2H), 7.62-7.54 (m, 2H), 7.43 (t, $J$ = 8.0 Hz, 3H), 7.24 (d, $J$ = 8.5 Hz, 1H), 2.38 (s, 3H), 2.32 (s, 3H) ppm; $^{13}$C NMR (DMSO-$d_6$) δ 195.0, 169.9, 151.3, 144.1, 138.1, 136.3, 136.2, 135.9, 134.7, 134.5, 132.9, 130.2, 128.9, 128.0, 127.9, 127.2, 124.0, 122.1, 120.1, 114.1, 107.6, 21.5, 15.7 ppm; IR (KBr) ν 3292, 2923, 1581, 1524, 1459, 1287, 1146, 1084, 810, 773, 544 cm$^{-1}$; MS (ESI) m/z 529.0 ([M+H]$^+$); HRMS (ESI) calcd for C$_{24}$H$_{18}$BrClN$_2$O$_3$S ([M+Na]$^+$), 550.9802; found, 550.9798.

N-(2-(3-bromophenyl)-1-(5-chloro-2-methyl-1H-indol-3-yl)-2-oxoethylidene)-4-methylbenzenesulfonamide (4j)
Yellow oil; $^1$H NMR (CDCl$_3$) δ 10.03 (s, 1H), 8.03-7.99 (m, 2H), 7.79-7.78 (m, 3H), 7.59-7.57 (m, 1H), 7.28 (d, $J$ = 8.0 Hz, 2H), 7.18 (t, $J$ = 7.5 Hz, 1H), 7.13 (d, $J$ = 8.0 Hz, 1H), 7.08-7.06 (m, 1H), 2.40 (s, 3H), 2.18 (s, 3H) ppm; $^{13}$C NMR (CDCl$_3$) δ 195.4, 169.7, 150.4, 144.1, 137.3, 137.2, 136.3, 133.7, 131.2, 130.6, 129.7, 129.3, 127.6, 127.1, 124.3, 123.5, 122.0, 112.7, 108.2, 21.6, 15.7 ppm; IR (KBr) ν 3279, 3063, 2923, 2852, 1689, 1523, 1456, 1350, 1288, 1229, 1148, 1084, 824, 787, 545 cm$^{-1}$; MS (ESI) m/z 528.8 ([M+H]$^+$); HRMS (ESI) calcd for C$_{24}$H$_{18}$BrClN$_2$O$_3$S ([M+Na]$^+$), 550.9802; found, 550.9798.
**N-(2-(4-bromophenyl)-1-(5-chloro-2-methyl-1H-indol-3-yl)-2-oxoethylidene)-4-methylbenzenesulfonamide (4k)**

Yellow oil; $^1$H NMR (CDCl$_3$) $\delta$ 9.84 (s, 1H), 8.02 (br, 1H), 7.80 (d, $J$ = 8.5 Hz, 2H), 7.73 (d, $J$ = 8.0 Hz, 2H), 7.48 (d, $J$ = 8.5 Hz, 2H), 7.29 (d, $J$ = 8.0 Hz, 2H), 7.13 (d, $J$ = 8.5 Hz, 1H), 7.09 (m, 1H), 2.41 (s, 3H), 2.21 (s, 3H) ppm; $^{13}$C NMR (CDCl$_3$) $\delta$ 195.7, 170.0, 149.8, 144.1, 137.3, 133.6, 133.5, 132.4, 130.2, 130.1, 129.7, 129.3, 127.6, 127.2, 124.3, 122.0, 112.5, 108.2, 21.6, 15.7 ppm; IR (KBr) $\nu$ 3275, 2982, 2926, 1732, 1713, 1684, 1584, 1457, 1288, 1244, 1149, 1084, 807, 545 cm$^{-1}$; MS (ESI) m/z 528.9 ([M+H]$^+$); HRMS (ESI) calcd for C$_{24}$H$_{18}$BrClN$_2$O$_3$S ([M+Na]$^+$), 550.9802; found, 550.9798.

**4-bromo-N-(1-(5-chloro-2-methyl-1H-indol-3-yl)-2-oxo-2-phenylethylene)benzenesulfonamide (4l)**

Orange solid; mp. 220-221 °C; $^1$H NMR (CDCl$_3$) $\delta$ 9.65 (s, 1H), 8.05 (b, 1H), 7.87 (d, $J$ =7.5 Hz, 2H), 7.80-7.78 (m, 2H), 7.63-7.61 (m, 2H), 7.51 (t, $J$ =7.5 Hz, 1H), 7.36 (t, $J$ =7.5 Hz, 2H), 7.16-7.09 (m, 2H), 2.20 (s, 3H) ppm; $^{13}$C NMR (CDCl$_3$) $\delta$ 196.3, 171.4, 150.3, 139.6, 134.7, 134.5, 133.6, 132.3, 129.5, 129.1, 128.9, 128.8, 128.1, 127.6, 124.4, 122.1, 112.5, 108.6, 15.7 ppm; IR (KBr) $\nu$ 3282, 3093, 2925, 1677, 1577,
1454, 1350, 1307, 1232, 1147, 1083, 815, 778, 740 cm⁻¹; MS (ESI) m/z 513.5 ([M+H]⁺); HRMS (ESI) calcd for C₂₃H₁₆BrClN₂O₃S ([M+Na]⁺), 536.9646; found, 536.9653.

\[ \text{N-(2-(4-bromophenyl)-1-(5-methoxy-2-methyl-1H-indol-3-yl)-2-oxoethylidene)benzenesulfonamide (4m)} \]

Yellow solid; mp. 165-166 ºC; \(^1\)H NMR (CDCl₃) δ 9.65 (s, 1H), 7.94 (d, \(J = 7.0\) Hz, 2H), 7.79 (d, \(J = 8.0\) Hz, 2H), 7.54-7.45 (m, 6H), 7.09 (d, \(J = 8.5\) Hz, 1H), 6.74-6.72 (m, 1H), 3.65 (s, 3H), 2.21 (s, 3H) ppm; \(^{13}\)C NMR (CDCl₃) δ 195.7, 170.2, 156.7, 149.3, 141.1, 133.6, 132.8, 132.4, 130.3, 129.9, 129.9, 128.9, 127.5, 127.0, 113.4, 112.3, 108.8, 104.8, 55.4, 15.8 cm⁻¹; IR (KBr) ν 3378, 2925, 1680, 1586, 1461, 1303, 1281, 1149, 1084, 815, 554 cm⁻¹; MS (ESI) m/z 511.0 ([M+H]⁺); HRMS (ESI) calcd for C₂₄H₁₉BrN₂O₄S ([M+Na]⁺), 533.0141; found, 533.0127.

\[ \text{N-(1-(2-methyl-1H-indol-3-yl)-2-oxo-2-phenylethylidene)methanesulfonamide (4n)} \]

Yellow solid; mp. 191-192 ºC; \(^1\)H NMR (CDCl₃) δ 9.94 (s, 1H), 8.10 (b, 1H), 7.87 (d, \(J = 8.0\) Hz, 2H), 7.42 (t, \(J = 7.5\) Hz, 1H), 7.29-7.26 (m, 3H), 7.15-7.14 (m, 2H), 3.17
(s, 3H), 2.20 (s, 3H) ppm; $^{13}$C NMR (CDCl$_3$) $\delta$ 196.5, 172.5, 149.8, 135.5, 134.7, 134.5, 128.9, 126.5, 123.9, 123.4, 122.1, 111.8, 108.6, 42.7, 15.6 ppm; IR (KBr) $\nu$ 3361, 3057, 2975, 1675, 1527, 1458, 1291, 1127, 966, 817, 749, 517 cm$^{-1}$; MS (ESI) m/z 339.0 ([M-H]$^-$); HRMS (ESI) calcd for C$_{18}$H$_{16}$N$_2$O$_3$S ([M+Na]$^+$), 363.0774; found, 363.0775.

$\text{N-}(2-(3\text{-bromophenyl})-1-(5\text{-methoxy-2-methyl-1H-indol-3-yl})\text{-2-oxoethylidene})\text{methanesulfonamide (4o)}$

Orange solid; mp. 213-214 °C; $^1$H NMR (DMSO-$d_6$) $\delta$ 12.57 (s, 1H), 8.02 (s, 1H), 7.92 (d, $J$ =8.0 Hz, 1H), 7.87 (d, $J$ =7.5 Hz, 1H), 7.55-7.34 (m, 3H), 6.88-6.86 (m, 1H), 3.73 (s, 3H), 3.18 (s, 3H), 2.33 (s, 3H) ppm; $^{13}$C NMR (DMSO-$d_6$) $\delta$ 195.6, 170.1, 156.5, 150.1, 137.6, 136.9, 132.1, 130.7, 130.6, 128.6, 127.5, 123.0, 113.3, 112.5, 107.3, 105.0, 55.7, 42.8, 16.0 ppm; IR (KBr) $\nu$ 3308, 2928, 1675, 1592, 1468, 1282, 1121, 965, 832, 543 cm$^{-1}$; MS (ESI) m/z 449.0 ([M+H]$^+$); HRMS (ESI) calcd for C$_{19}$H$_{17}$BrN$_2$O$_4$S ([M+Na]$^+$), 470.9985; found, 470.9973.

$\text{N-}(1-(1,2\text{-dimethyl-1H-indol-3-yl})\text{-2-oxo-2-phenylethylidene})\text{-4-methylbenzenesul}$
fonamide (4p)
Pale yellow solid; mp. 225-226 °C; $^1$H NMR (CDCl$_3$) $\delta$ 8.00 (d, $J$ = 7.0 Hz, 2H), 7.96-7.95 (b, 1H), 7.83 (d, $J$ = 8.5 Hz, 2H), 7.57 (t, $J$ = 7.5 Hz, 1H), 7.45 (t, $J$ = 8.0 Hz, 2H), 7.26-7.12 (m, 5H), 3.59 (s, 3H), 2.42 (s, 3H), 2.38 (s, 3H) ppm; $^{13}$C NMR (CDCl$_3$) $\delta$ 197.3, 170.5, 148.9, 143.2, 138.2, 137.3, 135.2, 134.1, 129.4, 129.0, 128.9, 127.4, 125.9, 123.5, 123.4, 122.1, 109.7, 108.5, 30.2, 21.5, 13.6 cm$^{-1}$; IR (KBr) $\nu$ 3449, 3060, 2925, 1679, 1504, 1469, 1410, 1302, 1150, 1082, 819, 739, 673, 561, 540 cm$^{-1}$; MS (ESI) m/z 430.9 ([M+H]$^+$); HRMS (ESI) calcd for C$_{25}$H$_{22}$N$_2$O$_3$S ([M+Na]$^+$), 453.1243; found, 453.1233.

4-bromo-N-(1-(2-butyl-1H-indol-3-yl)-2-oxo-2-phenylethylidene)benzenesulfonamide (4q)
Orange oil; $^1$H NMR (DMSO-$d_6$) $\delta$ 12.73 (s, 1H), 7.91 (d, $J$ = 7.0 Hz, 2H), 7.85-7.83 (m, 2H), 7.75-7.58 (m, 6H), 7.42 (d, $J$ = 7.5 Hz, 1H), 7.19 (t, $J$ = 7.0 Hz, 1H), 7.10-7.09 (m, 1H), 2.81 (br, 2H), 1.45-1.30 (m, 2H), 1.13 (br, 2H), 0.73 (t, $J$ = 7.5 Hz, 3H) ppm; $^{13}$C NMR (DMSO-$d_6$) $\delta$ 196.6, 171.0, 155.4, 140.7, 136.4, 135.2, 134.9, 132.9, 129.8, 129.1, 129.0, 127.3, 126.3, 124.0, 123.4, 121.2, 122.9, 107.2, 31.2, 29.0, 22.5, 13.9 cm$^{-1}$; IR (KBr) $\nu$ 3283, 3089, 2957, 2923, 2852, 1678, 1517, 1451, 1148, 1082, 813, 773, 546 cm$^{-1}$; MS (ESI) m/z 522.8 ([M+H]$^+$); HRMS (ESI) calcd for C$_{26}$H$_{23}$BrN$_2$O$_3$S ([M+Na]$^+$), 545.0505; found, 545.0509.

4-methyl-N-(2-oxo-2-phenyl-1-(2-phenyl-1H-indol-3-yl)ethylidene)benzenesulfonamide (4r)

Pale yellow solid; mp. 245-246 °C; $^1$H NMR (DMSO-$d_6$) $\delta$ 12.79 (s, 1H), 8.20 (d, $J$ = 7.5 Hz, 1H), 7.70 (d, $J$ = 8.5 Hz, 2H), 7.56-7.54 (m, 1H), 7.46-7.42 (m, 3H), 7.35-7.26 (m, 7H), 7.13 (t, $J$ = 7.5 Hz, 2H), 7.00 (d, $J$ = 7.5 Hz, 2H), 2.41 (s, 3H) ppm; $^{13}$C NMR (DMSO-$d_6$) $\delta$ 194.8, 171.3, 151.4, 143.8, 138.3, 136.5, 135.0, 134.1, 130.9, 130.1, 129.8, 128.8, 128.5, 127.6, 127.2, 126.6, 124.7, 123.8, 122.7, 112.8, 108.9, 21.4 ppm; IR (KBr) $\nu$ 3392, 3263, 3089, 2975, 2923, 2852, 1678, 1517, 1451, 1148, 1082, 813, 773, 546 cm$^{-1}$; MS (ESI) m/z 478.9 ([M+H]$^+$); HRMS (ESI) calcd for C$_{29}$H$_{22}$N$_2$O$_3$S ([M+Na]$^+$), 501.1243; found, 501.1255.
General Procedure for the synthesis of 5 and 6

![Chemical Structure](image)

To a solution of 2-methyl indole (0.5 mmol), sulfonyl azide (1 mmol) and CuBr (0.05 mmol) in DCM (0.8 mL) in Schlenk tube was added the mixture of alkynes (1 mmol) and pyridine (1 mmol) in DCM (0.8 mL) slowly via syringe. The reaction mixture was stirred at room temperature for 3 h under argon. The solution was diluted by DCM (3 mL) and quenched by a mixture of 1N HCl and saturated NH₄Cl under argon atmosphere. The aqueous layer was extracted by DCM and the combined organic layer was washed with saturated NH₄Cl (10 mL), brine (10 mL) and dried over anhydrous sodium sulfate. The solvent was removed in vacuum, and the residue was purified by column chromatography on silica gel to give corresponding products. All the compounds were further recrystallized from EA.

Characterization Data for 5 and 6

![Chemical Structure](image)

4-methyl-N-(1-(2-methyl-1H-indol-3-yl)-2-phenylethylidene)benzenesulfonamide (5a)
Pale yellow solid; mp. 208-209 °C; ¹H NMR (DMSO-d₆) δ 12.21 (s, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 7.5 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.5 Hz,
1H), 7.25-7.20 (m, 4H), 7.16 (t, \( J = 7.5 \) Hz, 1H), 7.12 (t, \( J = 7.5 \) Hz, 1H), 7.04(t, \( J = 7.5 \) Hz, 1H), 4.84 (s, 2H), 2.50 (s, 3H), 2.39 (s, 3H)ppm; \(^{13}\)C NMR (DMSO-\( d_6 \)) \( \delta \) 176.7, 147.9, 143.0, 140.5, 136.5, 135.7, 129.9, 128.9, 128.5, 127.0, 126.7, 126.6, 123.0, 122.5, 121.8, 112.3, 112.1, 40.9, 21.5, 16.5 ppm; IR (KBr) \( \nu \) 3278, 3056, 2921, 1518, 1461, 1250, 1136, 1076, 1003, 778, 742, 543 cm\(^{-1}\); MS (ESI) m/z 403.2 ([M+H]\(^+\)); HRMS (ESI) calcd for C\(_{24}\)H\(_{22}\)N\(_2\)O\(_2\)S ([M+Na]\(^+\)), 425.1294; found, 425.1285.

4-bromo-N-(1-(2-methyl-1H-indol-3-yl)-2-phenylethylidene)benzenesulfonamide (5b)

Pale yellow solid; mp. 198-199 °C; \(^1\)H NMR (DMSO-\( d_6 \)) \( \delta \) 12.31 (s, 1H), 7.90 (m, 3H), 7.80 (d, \( J = 8.0 \) Hz, 2H), 7.36 (d, \( J = 8.0 \) Hz, 1H), 7.25 (t, \( J = 7.0 \) Hz, 2H), 7.21-7.13 (m, 4H), 7.06 (t, \( J = 7.5 \) Hz, 1H), 4.84 (s, 2H), 2.51 (s, 3H) ppm; \(^{13}\)C NMR (DMSO-\( d_6 \)) \( \delta \) 177.2, 148.7, 142.6, 136.3, 135.8, 132.6, 128.9, 128.5, 126.9, 126.7, 126.6, 123.2, 122.8, 121.8, 112.4, 112.2, 41.1, 16.6 ppm; IR (KBr) \( \nu \) 3297, 3060, 3027, 1578, 1460, 1270, 1141, 1082, 1009, 790, 744, 539 cm\(^{-1}\); MS (ESI) m/z 466.9 ([M+H]\(^+\)); HRMS (ESI) calcd for C\(_{23}\)H\(_{19}\)BrN\(_2\)O\(_2\)S ([M+Na]\(^+\)), 489.0243; found, 489.0237.
$N$-(1-(2-methyl-1$H$-indol-3-yl)-2-phenylethylidene)benzenesulfonamide (5c)

Pale yellow solid; mp. 175-176 °C; $^1$H NMR (DMSO-$d_6$) $\delta$ 12.24 (s, 1H), 7.96 (d, $J$ = 7.5 Hz, 2H), 7.88 (d, $J$ = 8.0 Hz, 1H), 7.67-7.60 (m, 3H), 7.35 (d, $J$ = 8.0 Hz, 1H), 7.27-7.22 (m, 4H), 7.17 (t, $J$ = 7.0 Hz, 1H), 7.13 (t, $J$ = 7.5 Hz, 1H), 7.03 (t, $J$ = 8.0 Hz, 1H), 4.86 (s, 2H), 2.50 (s, 3H) ppm; $^{13}$C NMR (DMSO-$d_6$) $\delta$ 176.9, 148.2, 143.3, 136.5, 135.7, 132.8, 129.6, 128.9, 128.6, 127.0, 126.7, 126.6 123.1, 122.6, 121.8, 112.4, 112.1, 41.1, 16.5 ppm; IR (KBr) v 3318, 3059, 1526, 1486, 1459, 1282, 1257, 1141, 789, 750, 585, 529 cm$^{-1}$; MS (ESI) m/z 389.0 ([M+H]$^+$); HRMS (ESI) calcd for C$_{23}$H$_{20}$N$_2$O$_2$S ([M+Na]$^+$), 411.1138; found, 411.1131.

4-methoxy-$N$-(1-(2-methyl-1$H$-indol-3-yl)-2-phenylethylidene)benzenesulfonamide (5d)

Pale yellow solid; mp. 201-202 °C; $^1$H NMR (DMSO-$d_6$) $\delta$ 12.19 (s, 1H), 7.92-7.87 (m, 3H), 7.34 (d, $J$ = 8.0 Hz, 1H), 7.25 (t, $J$=7.5 Hz, 2H), 7.21-7.10 (m, 6H), 7.05 (t, $J$ = 8.0 Hz, 1H), 4.83 (s, 2H), 3.84 (s, 3H), 2.50 (s, 3H) ppm; $^{13}$C NMR (DMSO-$d_6$) $\delta$ 176.4, 162.5, 137.7, 136.5, 135.7, 135.2, 128.9, 128.5, 127.0, 126.7, 123.0, 122.5, 121.9, 114.7, 112.3, 112.0, 56.1, 40.7, 16.4 ppm; IR (KBr) v 3281, 3063, 2963, 2967, 1596, 1582, 1515, 1498, 1460, 1258, 1139, 1082, 809, 778, 548 cm$^{-1}$, MS (ESI) m/z 419.0 ([M+H]$^+$); HRMS (ESI) calcd for C$_{24}$H$_{22}$N$_2$O$_3$S ([M+Na]$^+$), 441.1243; found, 441.1232.
N-(1-(2-methyl-1\textit{H}-indol-3-yl)-2-phenylethylidene)methanesulfonamide (5e)

Pale yellow solid; mp. 205-206 °C; \(^1\)H NMR (DMSO-\textit{d}_6) \(\delta\) 12.14 (s, 1H), 8.09 (d, \(J = 8.0\) Hz, 1H), 7.37-7.36 (m, 1H), 7.26-7.22 (m, 4H), 7.18-7.13 (m, 3H), 4.76 (s, 2H), 3.25 (s, 3H), 2.58 (s, 3H) ppm; \(^{13}\)C NMR (DMSO-\textit{d}_6) \(\delta\) 176.5, 147.2, 136.5, 135.7, 128.8, 128.7, 126.7, 122.9, 122.4, 122.0, 112.0, 111.8, 43.9, 41.3, 16.5 ppm; IR (KBr) \(\nu\) 3263, 3029, 2936, 1541, 1520, 1462, 1269, 1104, 810, 743, 501 cm\(^{-1}\); MS (ESI) m/z 327.1 ([M+H]\(^+\)); HRMS (ESI) calcd for C\(_{18}\)H\(_{18}\)N\(_2\)O\(_2\)S ([M+Na]\(^+\)), 349.0981; found, 349.0973.

4-bromo-N-(1-(5-methoxy-2-methyl-1\textit{H}-indol-3-yl)-2-phenylethylidene)benzenesulfonamide (5f)

Pale yellow solid; mp. 215-216 °C; \(^1\)H NMR (DMSO-\textit{d}_6) \(\delta\) 12.18 (s, 1H), 7.91 (d, \(J = 8.0\) Hz, 2H), 7.82 (d, \(J = 8.0\) Hz, 2H), 7.32-7.28 (m, 3H), 7.24-7.20 (m, 4H), 6.74 (d, \(J = 7.5\) Hz, 1H), 4.82 (s, 2H), 3.42 (s, 3H), 2.47 (s, 3H) ppm; \(^{13}\)C NMR (DMSO-\textit{d}_6) \(\delta\) 176.5, 156.0, 148.6, 142.9, 136.3, 132.6, 130.3, 129.0, 128.8, 128.5, 127.9, 126.8, 126.5, 112.8, 112.4, 104.4, 55.1, 41.3, 16.5 ppm; IR (KBr) \(\nu\) 3281, 3029, 2936, 1541, 1520, 1462, 1269, 1104, 810, 743, 501 cm\(^{-1}\); MS (ESI) m/z 495.2 ([M-H]\(^-\)); HRMS (ESI) calcd for C\(_{24}\)H\(_{21}\)BrN\(_2\)O\(_3\)S ([M+Na]\(^+\)), 519.0348; found, 519.0340.
N-(2-(4-bromophenyl)-1-(5-methoxy-2-methyl-1H-indol-3-yl)ethylidene)-4-methylbenzenesulfonamide (5g)
Pale yellow solid; mp. 204-205 °C; $^1$H NMR (DMSO-$d_6$) $\delta$ 12.14 (s, 1H), 7.86 (d, $J$ = 8.0 Hz, 2H), 7.49 (d, $J$ = 8.0 Hz, 2H), 7.40 (d, $J$ = 8.0 Hz, 2H), 7.36 (d, $J$ = 1.5 Hz, 1H), 7.23 (d, $J$ = 8.5 Hz, 1H), 7.18 (d, $J$ = 8.0 Hz, 2H), 6.74 (dd, $J_1$ = 9.0 Hz, $J_2$ = 2.5 Hz, 1H), 4.77 (s, 2H), 3.41 (s, 3H), 2.47 (s, 3H), 2.39 (s, 3H) ppm; $^{13}$C NMR (DMSO-$d_6$) $\delta$ 175.3, 156.0, 148.1, 143.0, 140.7, 136.0, 131.8, 130.7, 130.3, 129.9, 127.9, 126.7, 119.9, 112.7, 112.7, 112.1, 104.4, 55.1, 40.5, 21.4, 16.5 ppm; IR (KBr) $\nu$ 3290, 2957, 1592, 1513, 1473, 1279, 1142, 828, 768, 542 cm$^{-1}$; MS (ESI) m/z 509.3 ([M-H]$^-$); HRMS (ESI) calcd for C$_{25}$H$_{23}$BrN$_2$O$_3$S ([M+Na]$^+$), 533.0505; found, 533.0489.

N-(1-(5-chloro-2-methyl-1H-indol-3-yl)-2-phenylethylidene)benzenesulfonamide (5h)
Pale yellow solid; mp. 177-178 °C; $^1$H NMR (DMSO-$d_6$) $\delta$ 12.36 (s, 1H), 7.99 (d, $J$ = 7.0 Hz, 2H), 7.89 (d, $J$ = 2.0 Hz, 1H), 7.71-7.63 (m, 3H), 7.34 (d, $J$ = 9.0 Hz, 1H), 7.29 (t, $J$ = 7.5 Hz, 2H), 7.23-7.18 (m, 3H), 7.15 (dd, $J_1$ = 8.5 Hz, $J_2$ = 2.0 Hz, 1H),
4.83 (s, 2H), 2.48 (s, 3H) ppm; $^{13}$C NMR (DMSO-$d_6$) $\delta$ 176.5, 149.2, 143.1, 136.2, 134.2, 133.0, 129.6, 129.0, 128.5, 128.3, 127.3, 126.8, 126.6, 123.1, 121.6, 113.5, 111.9, 41.1, 16.2 ppm; IR (KBr) $\nu$ 3309, 3063, 3027, 1578, 1521, 1458, 1356, 1284, 1143, 1082, 793, 751, 727, 589, 533 cm$^{-1}$; MS (ESI) m/z 422.7 ([M+H$^+$]); HRMS (ESI) calcd for C$_{23}$H$_{19}$Cl$_2$N$_2$O$_2$S ([M+Na$^+$]), 445.0748; found, 445.0746.

$\text{N-}(1-\text{(5-chloro-2-methyl-1H-indol-3-yl)}-2-(\text{3-chlorophenyl})\text{ethylidene})\text{methanesulfonamide (5i)}$

Pale yellow solid; mp. 188-189 °C; $^1$H NMR (DMSO-$d_6$) $\delta$ 12.36 (s, 1H), 8.08 (s, 1H), 7.38 (d, $J = 8.5$ Hz, 1H), 7.32-7.24 (m, 3H), 7.20-7.16 (m, 2H), 4.75 (s, 2H), 3.28 (s, 3H), 2.57 (s, 3H) ppm; $^{13}$C NMR (DMSO-$d_6$) $\delta$ 175.5, 148.6, 138.8, 134.2, 133.5, 130.8, 128.4, 128.1, 127.3, 127.2, 126.9, 123.0, 121.3, 113.6, 111.2, 43.8, 40.7, 16.5 ppm; IR (KBr) $\nu$ 3246, 1531, 1476, 1462, 1440, 1271, 1115, 1004, 959, 815, 497 cm$^{-1}$; MS (ESI) m/z 417.6 ([M+Na$^+$]); HRMS (ESI) calcd for C$_{18}$H$_{16}$Cl$_2$N$_2$O$_2$S ([M+Na$^+$]), 417.0202; found, 417.0209.

$\text{N-}(2-\text{(3-bromophenyl)-1(2-methyl-1H-indol-3-yl)ethylidene)-4-methylbenzenesulfonamide}$
fonamide (5j)
Pale yellow solid; mp. 204-205 °C; $^1$H NMR (DMSO-$d_6$) $\delta$ 12.31 (s, 1H), 7.90 (d, $J = 8.0$ Hz, 1H), 7.82 (d, $J = 8.0$ Hz, 2H), 7.39-7.35 (m, 5H), 7.24-7.21 (m, 2H), 7.15 (t, $J = 8.0$ Hz, 1H), 7.07 (t, $J = 7.5$ Hz, 1H), 4.84 (s, 2H), 2.52 (s, 3H), 2.38 (s, 3H) ppm; $^{13}$C NMR (DMSO-$d_6$) $\delta$ 175.8, 148.4, 143.2, 140.3, 139.2, 135.8, 131.1, 131.1, 130.0, 129.7, 127.6, 126.9, 126.8, 123.2, 122.8, 122.2, 121.8, 112.2, 21.5, 16.6 ppm; IR (KBr) $\nu$ 3360, 3264, 3200, 2920, 1518, 1460, 1305, 1218, 119.9, 112.2, 21.5, 16.5 ppm; MS (ESI) m/z 481.2 ([M+H$^+$]); HRMS (ESI) calcd for C$_{24}$H$_{21}$BrN$_2$O$_2$S ([M+Na$^+$]), 503.0399; found, 503.0398.

\[ \text{N-(2-(4-bromophenyl)-1-(2-methyl-1H-indol-3-yl)ethyldiene)-4-methylbenzenesulfonylamine (5k)} \]
Pale yellow solid; mp. 211-212 °C; $^1$H NMR (DMSO-$d_6$) $\delta$ 12.27 (s, 1H), 7.86 (d, $J = 8.0$ Hz, 1H), 7.82 (d, $J = 8.0$ Hz, 2H), 7.45 (d, $J = 8.5$ Hz, 2H), 7.40 (d, $J = 8.0$ Hz, 2H), 7.35 (d, $J = 7.5$ Hz, 1H), 7.15-7.12 (m, 3H), 7.05 (t, $J = 7.5$ Hz, 1H), 4.79 (s, 2H), 2.50 (s, 3H), 2.40 (s, 3H) ppm; $^{13}$C NMR (DMSO-$d_6$) $\delta$ 176.1, 148.2, 143.1, 140.4, 135.9, 135.7, 131.8, 130.7, 129.9, 126.9, 126.7, 123.1, 122.6, 121.8, 119.9, 112.2, 21.5, 16.5 ppm; IR (KBr) $\nu$ 3360, 3264, 3065, 2920, 1518, 1460, 1305, 1261, 1157, 1138, 1077, 1007, 814, 777, 540 cm$^{-1}$; MS (ESI) m/z 481.2 ([M+H$^+$]); HRMS (ESI) calcd for C$_{24}$H$_{21}$BrN$_2$O$_2$S ([M+Na$^+$]), 503.0399; found, 503.0398.
**N-(1-(1,2-dimethyl-1\textit{H}-indol-3-yl)-2-phenylethylidene)-4-methylbenzenesulphonamide (5l)**

Orange solid; mp. 171-172 °C; \(^1\)H NMR (DMSO-\(d_6\)) \(\delta\) 7.89 (d, \(J = 8.0\) Hz, 1H), 7.84 (d, \(J = 8.5\) Hz, 2H), 7.49 (d, \(J = 8.0\) Hz, 1H), 7.40 (d, \(J = 8.0\) Hz, 2H), 7.23-7.07 (m, 7H), 4.90 (s, 2H), 3.67 (s, 3H), 2.53 (s, 3H), 2.39 (s, 3H) ppm; \(^{13}\)C NMR (DMSO-\(d_6\)) \(\delta\) 176.9, 148.1, 143.1, 140.4, 137.4, 136.6, 130.0, 128.9, 128.6, 126.7, 126.0, 122.9, 122.8, 121.4, 112.2, 111.1, 41.4, 30.5, 21.4, 14.0 ppm; IR (KBr) \(v\) 3449, 3030, 2924, 1513, 1470, 1410, 1379, 1144, 1085, 738, 542 cm\(^{-1}\); MS (ESI) m/z 417.7 ([M+H]\(^+\)); HRMS (ESI) calcd for C\(_{25}\)H\(_{24}\)N\(_2\)O\(_2\)S ([M+Na]\(^+\)), 439.1451; found, 439.1442.

**\((Z)-N-(2-(2-bromophenyl)-1-(2-methyl-1\textit{H}-indol-3-yl)vinyl)-4-methylbenzenesulphonamide (6a)\)**

Pale yellow solid; mp. 173-174 °C; \(^1\)H NMR (DMSO-\(d_6\)) \(\delta\) 11.00 (s, 1H), 9.68 (s, 1H), 7.68 (d, \(J = 8.0\) Hz, 2H), 7.47 (d, \(J = 8.0\) Hz, 1H), 7.40 (d, \(J = 8.0\) Hz, 2H), 7.20 (d, \(J = 8.0\) Hz, 1H), 7.02 (d, \(J = 7.5\) Hz, 1H), 6.96 (t, \(J = 7.5\) Hz, 1H), 6.88-6.82 (m, 2H), 6.78 (t, \(J = 8.0\) Hz, 1H), 6.53-6.52 (m, 1H), 6.32 (s, 1H), 2.39 (s, 3H), 1.78 (s, 3H) ppm; \(^{13}\)C NMR (DMSO-\(d_6\)) \(\delta\) 143.4, 137.9, 137.8, 136.0, 135.6, 133.0, 132.6, 129.9, 129.7, 127.8, 127.7, 127.4, 127.2, 123.7, 120.9, 119.4, 118.9, 115.8, 111.0, 106.6, 21.5,
(Z)-N-(2-(2-bromophenyl)-1-(5-chloro-2-methyl-1H-indol-3-yl)vinyl)-4-methylbenzenesulfonamide (6b)

Pale yellow solid; mp. 208-209 °C; $^1$H NMR (DMSO-$d_6$) $\delta$ 11.19 (s, 1H), 9.74 (s, 1H), 7.62 (d, $J = 8.0$ Hz, 2H), 7.50 (d, $J = 7.5$ Hz, 1H), 7.37 (d, $J = 8.0$ Hz, 2H), 7.19 (d, $J = 8.5$ Hz, 1H), 6.95-6.89 (m, 2H), 6.82 (t, $J = 7.5$ Hz, 1H), 6.77 (m, 1H), 6.51 (t, $J = 7.5$ Hz, 1H), 6.42 (s, 1H), 2.39 (s, 3H), 1.79 (s, 3H) ppm; $^{13}$C NMR (DMSO-$d_6$) $\delta$ 143.6, 138.0, 137.6, 137.5, 134.0, 132.6, 132.3, 130.0, 129.7, 129.0, 128.1, 127.4, 127.3, 124.1, 123.7, 120.8, 117.9, 116.7, 112.4, 106.4, 21.5, 12.3 ppm; IR (KBr) $\nu$ 3314, 3220, 2920, 1630, 1467, 1441, 1301, 1155, 1072, 803, 753, 708, 684 cm$^{-1}$; MS (ESI) m/z 515.1 ([M+H]$^+$); HRMS (ESI) calcd for C$_{24}$H$_{20}$BrClN$_2$O$_2$S ([M+Na]$^+$), 537.0010; found, 537.0018.
Pale yellow solid; mp. 155-156 °C; $^1$H NMR (DMSO-$d_6$) δ 10.88 (s, 1H), 9.65 (s, 1H), 7.63 (d, $J = 8.0$ Hz, 2H), 7.48-7.46 (m, 1H), 7.37 (d, $J = 8.0$ Hz, 2H), 7.05 (d, $J = 8.5$ Hz, 1H), 6.88-6.85 (m, 1H), 6.79 (t, $J = 7.5$ Hz, 1H), 6.59-6.57 (m, 1H), 6.55-6.53 (m, 1H), 6.33 (t, $J = 2.5$ Hz, 1H), 6.29 (s, 1H), 3.54 (s, 3H), 2.38 (s, 3H), 1.93 (s, 3H) ppm; $^{13}$C NMR (DMSO-$d_6$) δ 153.7, 143.4, 138.0, 137.6, 137.0, 133.1, 132.5, 130.4, 129.9, 128.0, 127.8, 127.4, 127.2, 123.6, 115.3, 111.5, 110.6, 106.4, 100.8, 55.3, 21.4, 12.6 ppm; IR (KBr) ν 3394, 3328, 3228, 2924, 1625, 1484, 1451, 1163, 1063, 806, 675, 550 cm$^{-1}$; MS (ESI) m/z 511.0 ([M+H$^+$]); HRMS (ESI) calcd for C$_{25}$H$_{23}$BrN$_2$O$_3$S ([M+Na$^+$]), 533.0505; found, 533.0508.

**General Procedure for the synthesis of 7.**

![General Procedure for the synthesis of 7.](image)

To a mixture of 6a (0.3 mmol), CuI (0.03 mmol, 0.1 equiv), 1,10-phenanathroline (0.06 mmol, 0.2 equiv), and Cs$_2$CO$_3$(0.6 mmol, 2.0 equiv) was added DMF (4 mL). The reaction mixture was heated at 80 °C for 16 h under argon. The reaction was diluted with EA and washed with H$_2$O and saturated NaCl solution. The organic layer was dried over MgSO$_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel.

![2'-methyl-1-tosyl-2,3'-bi(1'H-indole) (7a) (image)
Pale yellow solid; mp. 91-92°C. $^1$H NMR (CDCl$_3$) $\delta$ 8.38 (d, $J$ = 8.5 Hz, 1H), 8.15 (s, 1H), 7.47 (d, $J$ = 7.5 Hz, 1H), 7.35 (t, $J$ = 7.5, 1H), 7.31-7.26 (m, 2H), 7.17 (d, $J$ = 8.5 Hz, 2H), 7.14-7.11 (m, 2H), 6.99 (t, $J$ = 7.5, 1H), 6.86 (d, $J$ = 8.0 Hz, 2H), 6.57 (s, 1H), 2.39 (s, 3H), 2.22 (s, 3H) ppm; $^{13}$C NMR (CDCl$_3$) $\delta$ 144.2, 138.0, 136.7, 134.9, 134.7, 130.8, 129.3, 129.1, 126.8, 124.1, 123.8, 121.3, 120.2, 120.0, 118.7, 116.3, 113.3, 110.3, 104.8, 21.4, 13.1 ppm; IR (KBr) v 3402, 3056, 2922, 2854, 1598, 1456, 1172, 1090, 1055, 747, 675, 578 cm$^{-1}$; MS (ESI) m/z 401.3 ([M+H]$^+$); HRMS (ESI) calcd for C$_{24}$H$_{20}$N$_2$O$_2$S ([M+Na]$^+$), 423.1138; found, 423.1134.

5'-chloro-2'-methyl-1-tosyl-2,3'-bi(1'H-indole) (7b)

Pale yellow solid; mp. 205-206°C. $^1$H NMR (CDCl$_3$) $\delta$ 8.40 (dd, $J_2$ = 0.5 Hz, $J_2$ = 8.5 Hz, 1H), 8.23 (s, 1H), 7.51 (d, $J$ = 7.5 Hz, 1H), 7.35 (m, 1H), 7.32-7.31 (m, 1H), 7.19 (d, $J$ = 8.5 Hz, 1H), 7.07 (d, $J$ = 8.0 Hz, 2H), 7.05-7.03 (m, 1H), 6.86 (d, $J$ = 7.5, 2H), 6.73 (d, $J$ = 2.0 Hz, 1H), 6.57 (s, 1H), 2.42 (s, 3H), 2.26 (s, 3H) ppm; $^{13}$C NMR (CDCl$_3$) $\delta$ 144.6, 138.6, 138.1, 135.0, 133.6, 132.9, 130.4, 130.3, 129.1, 126.7, 125.8, 124.4, 123.9, 121.4, 120.4, 117.9, 116.2, 113.5, 111.2, 104.3, 21.5, 13.2 ppm; IR (KBr) v 3404, 3057, 2922, 1597, 1467, 1452, 1364, 1224, 1173, 812, 733 cm$^{-1}$; MS (ESI) m/z 435.0 ([M+H]$^+$); HRMS (ESI) calcd for C$_{24}$H$_{19}$ClN$_2$O$_2$S ([M+Na]$^+$), 457.0748; found, 457.0759.
**5'-methoxy-2'-methyl-1-tosyl-2,3'-bi(1'H-indole) (7c)**

Yellow oil; \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 8.40 (d, \(J = 8.05\) Hz, 1H), 8.08 (s, 1H), 7.51 (d, \(J = 7.5\) Hz, 1H), 7.38-7.35 (m, 1H), 7.31-7.29 (m, 1H), 7.19-7.15 (m, 3H), 6.86 (d, \(J = 8.0\) Hz, 2H), 6.77-6.75 (m, 1H), 6.57 (s, 1H), 6.04 (d, \(J = 2.0\) Hz, 1H), 3.65 (s, 3H), 2.37 (s, 3H), 2.27 (s, 3H) ppm; \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 154.4, 144.2, 138.0, 137.6, 135.2, 134.7, 130.6, 129.9, 129.5, 129.0, 126.9, 124.2, 123.7, 120.2, 116.2, 113.0, 111.2, 111.0, 104.5, 100.3, 55.5, 21.3, 13.1 ppm; IR (KBr) \(\nu\) 3409, 1633, 1485, 1453, 1254, 1175, 909, 812, 799, 676 cm\(^{-1}\); MS (ESI) m/z 431.1 ([M+H]\(^+\)); HRMS (ESI) calcd for C\(_{25}\)H\(_{22}\)N\(_2\)O\(_3\)S ([M+Na]\(^+\)), 453.1243; found, 453.1252.

**General procedure for the synthesis of 8**

To a solution of 4a (0.25 mmol) in dry THF was slowly added \(n\)-BuLi in hexane (120 \(\mu\)L, 0.3 mmol) at -78 °C under Ar. And the reaction mixture was stirred at this temperature for 2h, then warmed to room temperature for 1h. The solution was diluted with DCM (3 mL) and quenched by saturated NH\(_4\)Cl under argon atmosphere. The aqueous layer was extracted by DCM and the combined organic layer was washed with saturated NH\(_4\)Cl (10 mL), brine (10 mL) and dried over anhydrous sodium sulfate. The solvent was removed in vacuum, and the residue was purified by column chromatography on silica gel and further recrystallized from EA.
N-(2-hydroxy-4-methyl-2-phenyl-2,3-dihydrocyclopenta[b]indol-1(4H)-ylidene)-4-methylbenzenesulfonamide (8)

Yellow solid; mp. 219-220 °C; $^1$H NMR (DMSO-$d_6$) $\delta$ 8.49 (d, $J$ = 7.5 Hz, 1H), 7.71 (d, $J$ =8.5 Hz, 2H), 7.65 (d, $J$ = 8.5, 1H), 7.42-7.24 (m, 9H), 6.47 (s, 1H), 3.85 (s, 3H), 3.64 (d, $J$ = 18.5, 1H), 3.48 (d, $J$ =18.0 Hz, 1H), 2.36 (s, 3H) ppm; $^{13}$C NMR (DMSO-$d_6$) $\delta$ 177.2, 166.9, 145.4, 144.2, 142.5, 140.9, 129.6, 128.4, 127.6, 126.5, 125.5, 124.4, 123.3, 122.9, 113.7, 111.7, 88.3, 40.8, 31.9, 21.4 ppm; IR (KBr) v 3543, 3453, 3058, 2950, 1597, 1526, 1451, 1412, 1282, 1147, 1084, 856, 824, 754, 576 cm$^{-1}$; MS (ESI) m/z 431.4 ([M+H]$^+$); HRMS (ESI) calcd for C$_{25}$H$_{22}$N$_2$O$_3$S ([M+Na]$^+$), 453.1243; found, 453.1232.

References and Notes
2. Caution: Although the mixture of sulfonyl azides is the safest of a group of diazo compounds, one should keep in mind the inherent instability, shock sensitivity, and explosive power of azides. All users should exercise appropriate caution.
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4d in CDCl$_3$
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4e in DMSO-\(d_6\)
4g in DMSO-$d_6$
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4h in CDCl₃
4i in DMSO-d₆
4j in CDCl₃
$4o$ in DMSO-$d_6$
4r in DMSO-\textsubscript{d\textsubscript{6}}
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5b in DMSO-$d_6$
5e in DMSO-\textit{d}_6
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51 in DMSO-d$_6$
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$\text{Br}$

$\text{Cl}$

$\text{SO}_2\text{O}$

$\text{NH}$

$\text{H}$

$\text{6b in DMSO-d}_6$
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Ts-N

7a in CDCl₃
8 in DMSO-\textit{d}_6
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8 in DMSO-\textit{d}_6