One Pot Hydroamination/[4+3] Cycloaddition: Synthesis towards the Cyclohepta[b]indole Core of Silicine and Ervatamine

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I. General Information
All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on GF254 plates. The silica gel (200-300 meshes) was used for column chromatography, and the distillation range of petro ether was 60-90 °C, ethyl acetate are used for product purification by flash column chromatography. CH₂Cl₂ was dried by distillation over CaH₂. THF was dried by distillation over Na/K alloy. Commercially available reagents and solvents were used without any purification. ¹H and ¹³C NMR spectra were recorded in CDCl₃ solution on Bruker AM-400 MHz or Varian Mercury-600 MHz instruments, and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard. Mass spectra (MS) were measured on spectrometer by direct inlet at 70 eV and signals were given in m/z with relative intensity (%) in brackets. IR spectra were recorded on a Nicolet FT-170SX spectrometer. High-resolution mass spectral analysis (HRMS) data were determined on a Thermo Scientific Orbitrap Elite spectrometer. Melting points were measured on a melting point apparatus and are uncorrected.

II. Experimental Procedures

General Experimental Procedure for the Preparation of 1a-e,¹ To a stirred solution of diisopropylamine (0.21 mL, 1.5 mmol) in anhydrous THF at −78 °C was added n-butyllithium (2.5 M in hexane solution, 0.60 mL, 1.5 mmol) dropwise, and the resulting solution was allowed to stirred at the same temperature for 30 min. The appropriate alkyne (1 mmol) was added in a dropwise manner. The resulting mixture was stirred at the same temperature for 1 h. The corresponding 2-aminobenzaldehyde (0.5 mmol) was dissolved in THF (2 mL) and added to the reaction mixture dropwise and allowed to stir for 1 h at the same temperature. The reaction mixture was slowly warmed up to room temperature and stirred for a further 1 h. Upon completion, the reaction mixture was quenched by adding saturated NH₄Cl (10 mL) and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine (20 mL), dried over Na₂SO₄, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (10% EtOAc/n-hexane) gave the title compound.

N-(2-(1-hydroxy-4-methoxybut-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1a):

Chemical Formula: C₁₉H₁₇NO₄S
Molecular Weight: 345.41

N-(2-(1-hydroxy-4-methoxybut-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1a) was prepared following general procedure as a colorless oil (88.3%). ¹H NMR (400 MHz, CDCl₃) δ 7.86 (s, 1H), 7.68 (d, 2H, J = 8.4 Hz), 7.50 (dd, 1H, J = 7.6, 1.2 Hz), 7.36 (dd, 1H, J = 8.0, 0.8 Hz), 7.27-7.22 (m, 3H), 7.12 (td, 1H, J = 7.6, 1.2 Hz), 5.35 (s, 1H), 4.16 (d, 2H, J = 1.6 Hz), 3.38 (s, 3H), 2.38 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 143.9, 136.7, 135.4, 130.9, 129.7, 129.7, 128.2, 127.2, 125.3, 123.0,
N-(2-(3-cyclopropyl-1-hydroxyprop-2-yn-1-yl)-4-methylphenyl)-4-methylbenzenesulfonamide (1b):

N-(2-(3-cyclopropyl-1-hydroxyprop-2-yn-1-yl)-4-methylphenyl)-4-methylbenzenesulfonamide (1b) was prepared following general procedure as a white solid (96.5%), m.p. 139-140 °C. 1H NMR (400 MHz, CDCl3) δ 7.68 (d, 2H, J = 8.4 Hz), 7.62 (s, 1H), 7.28-7.23 (m, 5H), 7.05 (dd, 1H, J = 8.4, 1.6 Hz), 5.15 (d, 1H, J = 4.0 Hz), 2.40 (s, 3H), 2.30 (s, 3H), 1.34-1.30 (m, 1H), 0.87-0.80 (s, 2H), 0.78-0.75, (m, 2H). 13C NMR (100 MHz, CDCl3) δ 143.7, 136.7, 135.2, 132.4, 132.0, 129.8, 129.6, 128.8, 127.2, 123.5, 92.4, 73.1, 63.0, 21.5, 20.9, 8.3. EI-MS m/z: 65.1 (36.5), 69.1 (15.8), 77.1 (21.4), 91.1 (64.3), 106.1 (14.2), 115.1 (14.7), 127.1 (10.3), 128.1 (10.7), 134.1 (37.8), 139.1 (32.0), 142.1 (11.2), 143.1 (10.1), 144.1 (32.8), 154.1 (22.6), 155.1 (18.9), 157.1 (14.2), 158.1 (12.7), 167.1 (19.4), 172.1 (100), 173.1 (12.9), 182.1 (15.4), 200.1 (52.0). FTIR (neat): 3856, 3842, 3652, 3447, 3272, 2931, 2853, 2346, 2235, 1917, 1736, 1597, 1499, 1491, 1379, 1330, 1265, 1160, 1091, 814, 739, 666 cm⁻¹. HRMS-ESI (m/z): [M+Na]+ calcld 378.1134; found 378.1127.

N-(5-fluoro-2-(1-hydroxy-4-methoxybut-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1c):

N-(5-fluoro-2-(1-hydroxy-4-methoxybut-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1c) was prepared following general procedure as a colorless oil (90.6%). 1H NMR (400 MHz, CDCl3) δ 8.12 (s, 1H), 7.73 (d, 2H, J = 8.0 Hz), 7.41 (td, 1H, J = 6.4, 2.4 Hz), 7.27-7.20 (m, 3H), 6.77 (td, 1H, J = 8.4, 2.8 Hz), 5.32 (d, 1H, J = 5.2 Hz), 4.16 (s, 2H), 3.39 (s, 3H), 2.92 (d, 1H, J = 5.2 Hz), 2.40 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 163.1 (d, J = 247 Hz), 144.2, 137.5, 137.4, 136.5, 129.8, 129.6 (d, J = 9 Hz), 127.2, 111.2 (d, J = 22 Hz), 109.2 (d, J = 27 Hz), 84.6, 83.6, 62.7, 59.8, 58.0, 21.6. EI-MS m/z [M]+: 65.0 (20.3), 75.1 (21.3), 91.1 (100), 147.0 (14.3), 148.0 (13.6), 155.0 (30.5), 175.0 (23.9), 191.0 (12.4), 291.0 (12.7), 304.0 (18.2), 305.0 (32.9), 306.0 (12.3), 317.0 (20.2), 318.0 (17.2), 333.0 (13.7), 335.0 (13.3), 347.0 (24.0), 348.0 (26.2), 349.0 (13.8), 503.0 (17.4). FTIR (neat): 3280, 2931, 2372, 1657, 1613, 1599, 1507, 1408, 1335, 1281, 1168, 1155, 1091, 994, 905, 815, 733, 663, 569, 545 cm⁻¹. HRMS-ESI (m/z): [M+Na]+ calcld 386.0833; found 386.0828.

N-(5-fluoro-2-(1-hydroxy-4,4-dimethylpent-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1d):
N-(5-fluoro-2-(1-hydroxy-4,4-dimethylpent-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1d) was prepared following general procedure as a white solid (81.4%), m.p. 127-128 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.21 (s, 1H), 7.72 (d, 2H, \(J = 8.4\) Hz), 7.41 (dd, 1H, \(J = 8.4, 6.0\) Hz), 7.25 (d, 2H, \(J = 8.0\) Hz), 7.22 (dd, 1H, \(J = 8.0, 2.4\) Hz), 6.75 (td, 1H, \(J = 8.4, 2.8\) Hz), 5.19 (d, 1H, \(J = 4.8\) Hz), 2.52 (t, 1H, \(J = 6.4\) Hz), 2.39 (s, 3H), 1.27 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 162.9 (d, \(J = 235\) Hz), 144.1, 137.4, 136.7, 129.9 (d, \(J = 22\) Hz), 108.9 (d, \(J = 26\) Hz), 98.6, 75.9, 62.7, 30.7, 27.6, 21.5. EI-MS m/z [M]: 65.0 (14.5), 91.1 (54.4), 92.1 (5.9), 155.0 (9.2), 184.0 (4.6), 185.0 (14.4), 186.0 (6.5), 197.0 (5.6), 198.0 (35.1), 199.0 (8.4), 210.0 (9.4), 211.0 (23.7), 212.0 (100), 213.0 (34.1), 214.0 (4.6), 226.0 (53.1), 227.0 (8.3), 258.0 (95.7), 259.0 (17.47), 368.0 (15.14).

FTIR (neat): 3467, 3286, 2969, 2928, 2869, 2239, 1704, 1613, 1599, 1506, 1335, 1280.2, 1168, 1154, 1093, 993, 905, 852, 814, 736, 662 cm\(^{-1}\).

HRMS-ESI (m/z): [M+Na]\(^{+}\) calcd 398.1197; found 398.1190.

N-(4-fluoro-2-(1-hydroxy-3-phenylprop-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1e):

N-(4-fluoro-2-(1-hydroxy-3-phenylprop-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1e) was prepared following general procedure as a white solid (73.2%), m.p. 138-139 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.68-7.64 (m, 3H), 7.48 (dd, 2H, \(J = 7.6, 1.2\) Hz), 7.40-7.32 (m, 5H), 7.23 (d, 2H, \(J = 8.4\) Hz), 7.01-6.96 (m, 1H), 5.45 (d, 1H, \(J = 4.8\) Hz), 2.983 (d, 2H, \(J = 5.6\) Hz), 2.396 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 160.4 (d, \(J = 245\) Hz), 144.1, 136.4, 131.8, 130.4, 129.8, 129.1, 128.4, 127.2, 126.4 (d, \(J = 8\) Hz), 121.6, 116.2 (d, \(J = 23\) Hz), 115.4 (d, \(J = 24\) Hz), 88.6, 85.8, 62.4, 21.5. EI-MS m/z [M]: 65.0 (15.3), 83.1 (6.0), 89.1 (5.9), 90.2 (7.4), 91.1 (100), 105.1 (50.2), 110.1 (8.1), 129.1 (10.4), 138.1 (24.6), 139.1 (18.4), 165.1 (7.0), 183.1 (5.8), 211.1 (6.4), 222.1 (11.8), 238.1 (10.1), 239.1 (6.6), 240.1 (29.4). FTIR (neat): 3443, 3275, 3067, 2925, 2854, 2374, 2346, 2232, 1888, 1802, 1597, 1494, 1330, 1185, 1160, 1091, 7588, 691, 666 cm\(^{-1}\). HRMS-ESI (m/z): [M+Na]\(^{+}\) calcd 418.0884; found 418.0876.

N-(2-(3-cyclohexyl-1-hydroxyprop-2-yn-1-yl)-4-fluorophenyl)-4-methylbenzenesulfonamide (1f):

N-(2-(3-cyclohexyl-1-hydroxyprop-2-yn-1-yl)-4-fluorophenyl)-4-methylbenzenesulfonamide (1f) was prepared following general procedure as a white solid (87.1%), m.p. 146-147 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.64 (d, 2H, \(J = 8.4\) Hz), 7.60 (s, 1H), 7.39-7.36 (m, 1H), 7.29-7.24 (m, 5H), 5.05 (d, 1H, \(J = 4.8\) Hz), 2.40 (s, 3H), 2.36 (d, 1H, \(J = 6.4\) Hz), 1.84-1.82 (m, 2H), 1.72-1.69 (m, 2H), 1.53-1.42 (m, 3H), 1.31 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 160.2 (d, \(J = 244\) Hz), 144.0, 136.6, 135.1 (d, \(J = 7\) Hz), 131.0 (d, \(J = 3\) Hz), 129.7, 127.1, 126.1 (d, \(J = 8\) Hz), 115.9 (d, \(J = 23\) Hz), 115.1 (d, \(J = 25\) Hz), 94.2, 77.0, 62.0, 32.3, 29.1, 25.7, 24.8, 21.5. EI-MS m/z [M]-: 55.1 (15.4), 65.1 (11.8), 67.1 (9.1), 77.1 (6.6), 79.1 (7.2), 83.1
N-(2-(1-hydroxy-3-(thiophen-3-yl)prop-2-yn-1-yl)-6-methylphenyl)-4-methylbenzenesulfonamide (1g):

N-(2-(1-hydroxy-3-(thiophen-3-yl)prop-2-yn-1-yl)-6-methylphenyl)-4-methylbenzenesulfonamide (1g) was prepared following general procedure as a white solid (94.8%), m.p. 147-148 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.74 (d, 1H, $J$ = 7.6 Hz), 7.61 (d, 2H, $J$ = 8.4 Hz), 7.48 (dd, 1H, $J$ = 2.8, 0.8 Hz), 7.29-7.26 (m, 5H), 7.16-7.12 (m, 2H), 6.63 (s, 1H), 5.80 (s, 1H), 3.26 (b, 1H), 2.44 (s, 3H), 1.91 (s, 3H) $^1$$^1$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.2, 137.8, 137.3, 136.8, 131.5, 129.9, 129.8, 129.3, 128.4, 128.4, 127.2, 127.1, 125.3, 121.4, 87.8, 82.1, 61.7, 21.6, 18.2. EIMS m/z [M]: 65.0 (14.9), 77.0 (11.6), 83.0 (7.6), 91.1 (27.3), 97.0 (39.1), 111.0 (100), 112.0 (6.7), 113.0 (6.3), 130.1 (8.7), 134.1 (21.2), 135.0 (6.9), 139.1 (5.53), 199.0 (6.4), 224.0 (6.1), 225.0 (5.8), 227.0 (20.2), 240.0 (5.4), 241.0 (7.0), 242.0 (33.0), 243.0 (5.3). FTIR (neat): 3430, 3276, 2925, 2856, 2373, 1597, 1463, 1381, 1325, 1305, 1264, 1184, 1158, 1092, 1026, 909, 787, 736, 665, 627, 568 cm$^{-1}$. HRMS-ESI (m/z): [M+Na]$^+$ calcd 420.0699; found 420.0695.

2,2,3,3,9,9,10,10-octamethyl-5,6-dimethylene-4,8-dioxa-3,9-disilaundecane (4b): 2,2,3,3,9,9,10,10-octamethyl-5,6-dimethylene-4,8-dioxa-3,9-disilaundecane (4b) was prepared according to a literature procedure. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.59 (s, 1H), 5.35 (s, 1H), 4.39 (s, 1H), 4.32 (s, 2H), 1.00 (s, 9H), 0.95 (s, 9H), 0.20 (s, 6H), 0.11 (s, 6H); $^1$$^1$C NMR (100 MHz, CDCl$_3$) $\delta$ 154.0, 143.5, 112.1, 91.9, 62.6, 25.9, 25.8, 18.4, 18.3, -4.7, -5.4. HRMS-ESI (m/z): [M+H]$^+$ calcd 329.2327; found 329.2325.

**General experimental procedure for the one pot hydroamination/[4+3] cycloaddition tandem annulation.** To a stirred solution of compound 1 (0.13 mmol) in anhydrous CH$_2$Cl$_2$ (2 mL) at room temperature was added AgOTf (5 mol%, 6.3 µmol, 1.0 mg), and the resulting solution was allowed to stir at the same temperature for 18 h. As soon as the completion of hydroamination, the appropriate diene (5 eq.) was added in one portion. After carefully dropwise addition of ZnCl$_2$ (1.1 eq., 0.1375 mmol, 1M solution in diethyl ether, 0.14 mL), the resulting mixture was stirred at the same temperature for another 2 h. The reaction mixture was quenched by
saturated NaHCO₃ (10 mL) and extracted with CH₂Cl₂ (3 × 10 mL). The combined organic layer were washed with brine (20 mL), dried over Na₂SO₄, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (1% EtOAc/n-hexane) gave the title compound.

2-(cyclobut-1-en-1-yl)-5-methyl-1-tosyl-1H-indole: A main byproduct of compound 1c under Lewis acid (ZnCl₂) condition.

(Z)-2-(2-methoxyethylidene)-1-tosylindolin-3-ol (2a):

9-(((tert-butyldimethylsilyl)oxy)methyl)-6-(methoxymethyl)-5-tosyl-8-((triisopropylsilyl)oxy)-5,6,7,10-tetrahydrocyclohepta[bl]indole (5a):
9-(((tert-butyldimethylsilyl)oxy)methyl)-6-(methoxymethyl)-5-tosyl-8-((triisopropylsilyl)oxy)-5,6,7,10-tetrahydrocyclohepta[b]indole (5a) was prepared following general procedure as a colorless oil (11%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.17 (dd, 1H, $J$ = 8.4, 0.8 Hz), 7.36 (dd, 1H, $J$ = 6.8, 1.2 Hz), 7.28-7.21 (m, 2H), 7.09 (d, 2H, $J$ = 8.4 Hz), 4.37 (t, 1H, $J$ = 11.6 Hz), 4.34 (d, 1H, $J$ = 11.6 Hz), 4.20 (d, 1H, $J$ = 11.6 Hz), 3.96 (s, 1H), 3.82 (dd, 1H, $J$ = 8.8, 3.2 Hz), 3.52 (t, 1H, $J$ = 9.2 Hz), 3.41-3.25 (m, 5H), 2.78-2.67 (m, 2H), 2.29 (s, 3H), 1.14-1.11 (m, 20H), 0.80 (s, 8H), -0.04 (d, 5H, $J$ = 8.8 Hz).

EI-MS m/z [M]-: 57.1 (4.9), 59.1 (83.3), 60.1 (6.9), 61.1 (7.2), 73.1 (78.4), 74.1 (8.0), 75.1 (100), 76.0 (36.5), 89.1 (13.2), 91.1 (18.4), 101.1 (7.4), 115.1 (35.5), 129.1 (5.2), 133.1 (9.5), 157.2 (5.9), 180.1 (8.2), 192.0 (6.4), 208.1 (7.0), 236.1 (5.6), 254.1 (6.6), 322.2 (9.4), 365.2 (5.6), 411.3 (11.5), 522.2 (8.3), 652.3 (4.6). FTIR (neat): 3368, 3066, 2954, 2926, 2855, 2713, 2373, 2346, 1738, 1675, 1598, 1510, 1459, 1376, 1262, 1176, 1151, 1118, 1092, 1053, 837, 742, 680 cm$^{-1}$. HRMS-ESI (m/z): [M+H]$^+$ calcd 698.3725; found 698.3718.

8-((tert-butyldimethylsilyl)oxy)-9-(((tert-butyldimethylsilyl)oxy)methyl)-6-(methoxymethyl)-5-tosyl-5,6,7,10-tetrahydrocyclohepta[b]indole (5b):

8-((tert-butyldimethylsilyl)oxy)-9-(((tert-butyldimethylsilyl)oxy)methyl)-6-(methoxymethyl)-5-tosyl-5,6,7,10-tetrahydrocyclohepta[b]indole (5b) was prepared following general procedure as a colorless oil (less than 3%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.19 (d, 1H, $J$ = 7.6 Hz), 7.49 (d, 2H, $J$ = 8.4 Hz), 3.79 (dd, 1H, $J$ = 7.2, 1.2 Hz), 7.26-7.24 (m, 3H), 7.11 (d, 2H, $J$ = 8.0 Hz), 4.32 (d, 1H, $J$ = 12.0 Hz), 4.18 (d, 1H, $J$ = 11.6 Hz), 3.94 (s, 1H), 3.86 (dd, 1H, $J$ = 8.8, 3.2 Hz), 3.48 (t, 1H, $J$ = 9.2 Hz), 3.43-3.28 (m, 5H), 2.70 (d, 2H, $J$ = 5.6 Hz), 2.40-2.31 (m, 4H), 0.98 (s, 9H), 0.81 (s, 9H), 0.17 (d, 6H, $J$ = 11.6 Hz), 0.01 (d, 4H, $J$ = 3.6 Hz), -0.04 (s, 3H). No $^{13}$C NMR data collected because of product unstable in deuterated solvent. EI-MS m/z [M]-: 65.1 (15.2), 73.1 (63.8), 75.0 (63.9), 77.1 (10.7), 89.1 (28.9), 91.1 (87.0), 119.1 (10.9), 127.1 (10.2), 154.1 (24.9), 155.1 (37.5), 156.1 (10.3), 167.1 (17.5), 168.1 (11.5), 180.1 (56.3), 181.1 (21.6), 194.0 (11.2), 208.0 (14.9), 209.0 (12.6), 222.1 (14.3), 254.1 (100), 255.1 (18.2), 284.1 (32.4), 297.1 (9.7), 328.1 (9.9), 329.1 (52.5), 330.2 (16.9), 364.1 (20.9), 478.1 (17.2), 484.2 (13.9). FTIR (neat): 3678, 3652, 3394, 3060, 2954, 2928, 2854, 2373, 2346, 1921, 1798, 1701, 1598, 1454, 1371, 1255, 1189, 1172, 1152, 1112, 1094, 836, 577 cm$^{-1}$. HRMS-ESI (m/z): [M+H]$^+$ calcd 656.3256; found 656.3248.

6-(methoxymethyl)-9-methylene-5-tosyl-6,7,9,10-tetrahydrocyclohepta[b]indol-8(5H)-one (5c):

6-(methoxymethyl)-9-methylene-5-tosyl-6,7,9,10-tetrahydrocyclohepta[b]indol-8(5H)-one (5c) was prepared following general procedure as a light yellow oil (53 % from 4a, 69 % from 4b).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.20 (d, 1H, $J$ = 7.6 Hz), 7.45 (d, 2H, $J$ = 8.0 Hz), 7.42 (d, 1H, $J$ = 1.2 Hz), 7.36-7.28 (m, 2H), 7.13 (d, 2H, $J$ = 8.4 Hz), 5.99 (s, 1H), 5.30 (d, 1H, $J$ = 1.2 Hz), 4.23-4.22 (m,
1H), 3.93-
3.83 (m, 2H), 3.73-3.61 (m, 2H), 3.08-3.04 (m, 1H), 2.31 (s, 3H), 1.59 (s, 3H).

13C NMR (100 MHz, CDCl3) δ: 200.3, 144.9, 144.8, 137.2, 135.1, 134.7, 130.4, 129.7, 126.1, 125.2, 124.0, 122.2, 121.0, 118.0, 116.2, 75.7, 58.7, 42.0, 37.3, 28.4, 21.5. EI-MS m/z [M]-: 65.1 (13.1), 77.1 (92.6), 89.1 (12.7), 115.1 (12.7), 128.1 (12.7), 144.4 (42.8), 151.1 (42.8), 167.1 (7.2), 168.1 (4.7), 179.0 (4.3), 180.1 (52.1), 181.1 (18.3), 194.1 (12.3), 200.1 (4.7), 208.1 (12.5), 209.1 (12.5), 221.2 (12.1), 254.1 (100), 255.1 (21.3), 336.1 (6.5), 364.1 (21.3), 365.1 (5.1).

FTIR (neat): 3427, 3307, 3067, 3047, 2962, 2926, 2865, 2739, 2587, 2373, 2345, 2306, 2251, 1913, 1719, 1598, 1453, 1364, 1213, 1191, 1171, 1154, 1122, 1091, 754, 733, 682, 665, 581, 545 cm\(^{-1}\). HRMS-ESI (m/z): [M+H]+ calcd 410.1784; found 410.1780.

6-(methoxymethyl)-8-methyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[b]indole (3a):

6-(methoxymethyl)-8-methyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[b]indole (3a) was prepared following general procedure as a colorless oil (88%). 1H NMR (400 MHz, CDCl3) δ: 8.20 (d, 1H, \(J = 8.4 \) Hz), 7.52 (d, 2H, \(J = 8.0 \) Hz), 7.33-7.20 (m, 3H), 7.13 (d, 2H, \(J = 8.4 \) Hz), 5.65 (t, 1H, \(J = 4.4 \) Hz), 4.07 (dd, 1H, \(J = 9.6, 4.4 \) Hz), 3.73 (dd, 1H, \(J = 9.2, 4.0 \) Hz), 3.51-3.45 (m, 1H), 3.38 (s, 3H), 3.36-3.30 (m, 2H), 2.52 (d, 2H, \(J = 4.8 \) Hz), 2.30 (s, 3H), 1.82 (s, 3H); 13C NMR (100 MHz, CDCl3) δ: 144.4, 137.2, 136.7, 136.4, 136.0, 131.1, 129.6, 126.2, 124.4, 123.5, 121.4, 120.3, 117.9, 115.6, 73.7, 58.3, 35.9, 32.4, 26.4, 23.8, 21.5. EI-MS m/z [M]-: 65.1 (29.8), 77.1 (10.6), 89.1 (10.9), 91.1 (92.6), 115.1 (13.0), 128.1 (11.6), 130.1 (10.5), 151.2 (11.2), 155.1 (18.9), 167.1 (22.9), 168.1 (11.5), 180.1 (36.5), 192.1 (10.6), 193.1 (23.5), 194.1 (94.5), 195.1 (33.9), 208.1 (54.5), 240.2 (100), 241.2 (15.4). FTIR (neat): 3427, 3307, 3067, 3047, 2962, 2926, 2827, 2739, 2587, 2373, 2345, 2306, 2251, 1913, 1719, 1598, 1453, 1364, 1213, 1191, 1171, 1154, 1122, 1091, 754, 733, 682, 665, 581, 545 cm\(^{-1}\). HRMS-ESI (m/z): [M+H]+ calcd 396.1628; found 396.1623.

6-(methoxymethyl)-8,9-dimethyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[b]indole (3b):

6-(methoxymethyl)-8,9-dimethyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[b]indole (3b) was prepared following general procedure as a colorless oil (97%). 1H NMR (400 MHz, CDCl3) δ: 8.16 (dd, 1H, \(J = 8.4, 1.2 \) Hz), 7.44 (d, 2H, \(J = 8.4 \) Hz), 7.34 (dd, 1H, \(J = 8.4, 2.0 \) Hz), 7.27-7.19 (m, 2H), 7.07 (d, 2H, \(J = 8.0 \) Hz), 3.94-3.88 (m, 2H), 3.40 (s, 3H), 3.37-3.30 (m, 2H), 3.20 (d, 1H, \(J = 17.2 \) Hz), 2.67-2.58 (m, 2H), 2.27 (s, 3H), 1.82 (s, 3H), 1.75 (s, 3H); 13C NMR (100 MHz, CDCl3) δ: 8.16 (dd, 1H, \(J = 8.4, 1.2 \) Hz), 7.44 (d, 2H, \(J = 8.4 \) Hz), 7.34 (dd, 1H, \(J = 8.4, 2.0 \) Hz), 7.27-7.19 (m, 2H), 7.07 (d, 2H, \(J = 8.0 \) Hz), 3.94-3.88 (m, 2H), 3.40 (s, 3H), 3.37-3.30 (m, 2H), 3.20 (d, 1H, \(J = 17.2 \) Hz), 2.67-2.58 (m, 2H), 2.27 (s, 3H), 1.82 (s, 3H), 1.75 (s, 3H); 13C NMR (100 MHz, CDCl3) δ: 144.3, 137.2, 136.7, 136.0, 131.1, 129.6, 126.2, 124.4, 123.5, 121.4, 120.3, 117.9, 115.6, 73.7, 58.3, 35.9, 32.4, 26.4, 23.8, 21.5. EI-MS m/z [M]-: 65.1 (29.8), 77.1 (10.6), 89.1 (10.9), 91.1 (92.6), 115.1 (13.0), 128.1 (11.6), 130.1 (10.5), 152.1 (11.2), 155.1 (18.9), 167.1 (22.9), 168.1 (11.5), 180.1 (36.5), 192.1 (10.6), 193.1 (23.5), 194.1 (94.5), 195.1 (33.9), 208.1 (54.5), 240.2 (100), 241.2 (15.4). FTIR (neat): 3427, 3307, 3067, 3047, 2962, 2926, 2827, 2739, 2587, 2373, 2345, 2306, 2251, 1913, 1719, 1598, 1453, 1364, 1213, 1191, 1171, 1154, 1122, 1091, 754, 733, 682, 665, 581, 545 cm\(^{-1}\). HRMS-ESI (m/z): [M+H]+ calcd 410.1784; found 410.1780.
6-cyclopropyl-2,8,9-trimethyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[b]indole (3c):

6-cyclopropyl-2,8,9-trimethyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[b]indole (3c) was prepared following general procedure as a light yellow oil (63%). \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.00 (d, 1H, \(J = 8.4\) Hz), 7.33 (d, 2H, \(J = 8.4\) Hz), 7.08-7.03 (m, 4H), 3.29-3.25 (m, 1H), 3.24 (s, 1H), 2.61 (d, 1H, \(J = 14.0\) Hz), 2.39 (s, 3H), 2.31 (s, 1H), 2.27 (s, 3H), 1.85 (s, 3H), 1.75 (s, 1H), 1.70-1.67 (m, 1H), 1.00-0.84 (m, 3H), 0.51-0.31 (m, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 143.9, 141.7, 135.3, 134.7, 133.5, 132.7, 129.1, 128.7, 128.1, 126.3, 125.3, 121.2, 117.9, 116.6, 38.5, 38.1, 30.8, 22.2, 21.5, 21.5, 21.4, 21.2, 16.9, 4.2; El-MS m/z [M]-: 65.0 (20.5), 91.1 (44.8), 133.1 (12.2), 180.0 (12.2), 181.0 (13.3), 194.0 (33.3), 195.0 (15.8), 196.0 (25.3), 207.0 (12.9), 208.0 (44.8), 209.105 (14.7), 220.0 (17.5), 221.0 (13.7), 222.1 (38.3), 234.0 (20.3), 235.1 (12.2), 248.1 (16.9), 264.1 (100), 265.1 (24.1), 419.1 (33.1). FTIR (neat): 3425, 2924, 2863, 2732, 2257, 1720, 1598, 1493, 1368, 1306, 1262, 1205, 1175, 1136, 1090, 1045, 1020, 957, 909, 810, 733, 703, 672, 651, 607, 572, 547 cm\(^{-1}\). HRMS-ESI (m/z): [M+H]\(^+\) calcd 420.1992; found 420.1987.

3-fluoro-6-(methoxymethyl)-8-methyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[b]indole (3d):

3-fluoro-6-(methoxymethyl)-8-methyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[b]indole (3d) was prepared following general procedure as a colorless oil (71%). \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.96 (dd, 1H, \(J = 10.8, 2.0\) Hz), 7.55 (d, 2H, \(J = 8.4\) Hz), 7.26-7.21 (m, 1H), 7.17 (d, 2H, \(J = 8.4\) Hz), 6.98 (td, 1H, \(J = 8.8, 2.0\) Hz), 5.64 (t, 1H, \(J = 4.4\) Hz), 4.04-4.01 (m, 1H), 3.72-3.69 (m, 1H), 3.49-3.44 (m, 1H), 3.38 (s, 3H), 3.29-3.28 (m, 2H), 2.50 (d, 2H, \(J = 4.0\) Hz), 2.33 (s, 3H), 1.82 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 160.8 (d, \(J = 239\) Hz), 144.7, 137.5 (d, \(J = 4\) Hz), 136.8, 136.5 (d, \(J = 12\) Hz), 135.8, 129.8, 127.3, 126.2, 121.1, 119.8, 118.6 (d, 1H, \(J = 10\) Hz), 111.6 (d, 1H, \(J = 24\) Hz), 103.1 (d, 1H, \(J = 29\) Hz), 73.6, 58.4, 35.9, 32.4, 26.4, 23.8, 21.5. El-MS m/z [M]-: 65.0 (20.5), 91.1 (44.8), 133.1 (12.2), 180.0 (12.2), 181.0 (13.3), 194.0 (33.3), 195.0 (15.8), 196.0 (25.3), 207.0 (12.9), 208.0 (44.8), 209.105 (14.7), 220.0 (17.5), 221.0 (13.7), 222.1 (38.3), 234.0 (20.3), 235.1 (12.2), 248.1 (16.9), 264.1 (100), 265.1 (24.1), 419.1 (33.1). FTIR (neat): 3344, 3114, 3053, 2955, 2926, 2854, 2721, 2371, 2345, 1871, 1799, 1737, 1612, 1598, 1486, 1461, 1376, 1267, 1191, 1174, 1138, 1123, 1092, 741, 585 cm\(^{-1}\). HRMS-ESI (m/z): [M+H]\(^+\) calcd 414.1534; found 414.1527.

3-fluoro-6-(methoxymethyl)-8,9-dimethyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[b]indole (3e):

3-fluoro-6-(methoxymethyl)-8,9-dimethyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[b]indole (3e) was prepared following general procedure as a colorless oil (79%). \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.92 (dd, 1H, \(J = 10.4, 2.0\) Hz), 7.47 (d, 2H, \(J = 8.4\) Hz), 7.29-7.24 (m, 1H), 7.12 (d, 2H, \(J = 8.4\) Hz), 6.97 (td, 1H, \(J = 8.8, 2.4\) Hz), 3.91-3.85 (m, 2H), 3.41 (s, 3H), 3.39-3.29 (m, 2H), 3.15 (d, 1H, \(J = 17.2\) Hz).
6-(tert-butyl)-3-fluoro-8-methyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[b]indole (3f): 6-(tert-butyl)-3-fluoro-8-methyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[b]indole (3f) was prepared following general procedure as a colorless oil (45%). 1H NMR (400 MHz, CDCl3) δ 7.69 (d, 2H, J = 8.4 Hz), 7.36 (dd, 1H, J = 10.8, 2.4 Hz), 7.22 (d, 2H, J = 8.0 Hz), 6.96 (dd, 1H, J = 7.6, 6.0 Hz), 6.64 (td, 1H, J = 8.4, 2.4, 2.0 Hz), 5.53 (s, 1H), 3.58-3.55 (m, 1H), 3.00 (dd, 1H, J = 15.2, 5.6 Hz), 2.70 (d, 1H, J = 12.4 Hz), 2.43-2.38 (m, 4H), 2.18 (dd, 1H, J = 15.2, 5.2, 4.4 Hz), 1.86 (s, 3H), 1.63 (s, 3H), 1.57 (s, 3H), 0.85 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 162.7 (d, J = 247 Hz), 143.6 (d, J = 12 Hz), 143.4, 138.1, 135.7, 132.5, 131.6, 129.3 (d, J = 3 Hz), 129.0, 127.0, 124.0 (d, J = 10 Hz), 120.9, 108.8 (d, J = 23 Hz), 101.2 (d, J = 29 Hz), 78.9, 76.7, 49.7, 35.1, 33.6, 23.7, 22.9, 22.6, 21.5, 17.8. EI-MS m/z [M]-: 65.1 (21.3), 67.1 (9.6), 69.1 (9.4), 91.1 (66.8), 133.1 (8.1), 148.1 (27.4), 155.1 (8.5), 172.1 (11.7), 185.1 (15.7), 186.1 (26.5), 187.1 (19.9), 198.1 (8.0), 201.1 (15.0), 201.1 (9.9), 202.1 (100), 203.1 (15.0), 212.1 (9.6), 228.1 (8.1), 270.2 (13.3), 357.2 (63.6), 358.2 (15.08). FTIR (neat): 3405, 3034, 2925, 2857, 2730, 2588, 2370, 2346, 2258, 1878, 1800, 1599, 1491, 1454, 1432, 1356, 1274, 1259, 1162.5, 1109, 1092, 734, 706, 667, 584, 547 cm⁻¹. HRMS-ESI (m/z): [M+Na]⁺ calcd 448.1717; found 448.1710.

2-fluoro-8,9-dimethyl-6-phenyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[b]indole (3g): 4,8,9-trimethyl-6-(thiophen-3-yl)-5-tosyl-5,6,7,10-tetrahydrocyclohepta[b]indole (3g) was prepared following general procedure as a light yellow oil (29%). 1H NMR (400 MHz, CDCl3) δ 8.07 (dd, 1H, J = 9.2, 4.8 Hz), 7.17-7.09 (m, 6H), 7.02-6.94 (m, 5H), 5.10 (t, 1H, J = 3.2 Hz), 3.54 (d, 1H, J = 17.6 Hz), 3.25 (d, 1H, J = 17.2 Hz), 3.05 (d, 1H, J = 14.0 Hz), 2.48-2.43 (m, 2H), 2.28 (s, 3H), 1.76 (s, 3H), 1.10 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 159.8 (d, J = 238 Hz), 143.9, 143.0, 139.8, 135.9, 132.1, 129.6, 129.3, 128.5, 127.8, 126.3, 125.9, 116.2 (d, J = 9 Hz), 119 (d, J = 25 Hz), 103.8 (d, J = 24 Hz), 42.1, 41.6, 30.2, 21.4, 20.9, 20.7. EI-MS m/z [M]-: 65.1 (20.0), 91.1 (100), 200.0 (13.7), 212.0 (15.6), 226.0 (11.8), 235.0 (21.7), 236.0 (15.5), 248.0 (16.7), 262.0 (24.5), 272.0 (13.6), 273.0 (8.9), 274.0 (17.4), 288.0 (29.3), 289.1 (20.6), 302.0 (13.9), 303.1 (19.0), 304.1 (83.7), 305.1 (19.2), 459.0 (35.5), 460.0 (10.3). FTIR (neat): 3762, 3335, 3064, 3031, 2926, 2860, 2374, 1598, 1493,
1464, 1453, 1372, 1266, 1175, 1156, 1117, 1090, 1033, 963, 898, 856, 808, 701, 668, 576, 543, 492 cm⁻¹. HRMS-ESI (m/z): [M+H]⁺ calcd 460.1741; found 460.1737.

6-cyclohexyl-2-fluoro-8,9-dimethyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[b]indole (3h):

6-cyclohexyl-2-fluoro-8,9-dimethyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[b]indole (3h) was prepared following general procedure as a colorless oil (56%). ¹H NMR (400 MHz, CDCl₃) δ 8.09 (dd, 1H, J = 8.8, 4.4 Hz), 7.30 (d, 2H, J = 8.4 Hz), 7.04 (d, 2H, J = 8.0 Hz), 6.97-6.92 (m, 2H), 3.51 (t, 1H, J = 5.2 Hz), 3.43 (d, 1H, J = 18.0 Hz), 2.83 (d, 1H, J = 18.0 Hz), 2.60 (dd, 1H, J = 14.4, 10.4 Hz), 2.29 (s, 3H), 2.13 (d, 2H, J = 12.0 Hz), 1.78 (s, 3H), 1.75-1.64 (m, 2H), 1.55 (s, 5H), 1.37-1.29 (m, 2H), 1.17-1.13 (m, 2H), 1.06-1.03 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 160.4 (d, J = 240 Hz), 144.2, 143.4, 134.3, 133.7 (d, J = 9 Hz), 133.1, 130.0, 129.0, 127.7, 126.2, 123.8 (d, J = 3 Hz), 117.8 (d, J = 9 Hz), 111.4 (d, J = 25 Hz), 103.5 (d, J = 24 Hz), 42.8, 41.4, 33.1, 31.3, 30.6, 29.7, 28.7, 26.6, 21.5, 20.7, 14.1. EI-MS m/z [M]-: 55.0 (62.6), 56.1 (34.4), 57.0 (33.6), 59.0 (18.9), 64.0 (18.0), 65.0 (23.0), 67.0 (20.3), 69.1 (100), 70.1 (25.4), 71.1 (18.6), 73.1 (20.9), 77.1 (22.5), 85.1 (28.1), 91.0 (57.0), 92.1 (17.8), 98.1 (28.1), 99.1 (25.2), 108.1 (21.3), 112.1 (18.5), 126.0 (18.7). FTIR (neat): 3333, 2926, 2855, 2373, 1799, 1703, 1597, 1546, 1457, 1376, 1298, 1262, 1174, 1121, 1090, 906, 809, 733, 658, 571 cm⁻¹. HRMS-ESI (m/z): [M+H]⁺ calcd 466.2211; found 466.2206.

4,8,9-trimethyl-6-(thiophen-3-yl)-5-tosyl-5,6,7,10-tetrahydrocyclohepta[b]indole (3i):

4,8,9-trimethyl-6-(thiophen-3-yl)-5-tosyl-5,6,7,10-tetrahydrocyclohepta[b]indole (3i) was prepared following general procedure as a light yellow oil (43%). ¹H NMR (400 MHz, CDCl₃) δ 7.20-7.13 (m, 2H), 7.09 (dd, 2H, J = 7.6, 2.4 Hz), 7.05(d, 2H, J = 8.0 Hz), 6.95 (d, 2H, J = 8.0 Hz), 6.87 (dd, 1H, J = 2.4, 0.8 Hz), 6.83 (dd, 1H, J = 4.8, 1.6 Hz), 4.91 (dd, 1H, J = 8.4, 1.6 Hz), 3.32 (s, 3H), 2.88 (d, 1H, J = 16.8 Hz), 2.67 (dd, 1H, J = 13.6, 11.4 Hz), 2.57 (s, 3H), 2.49 (dd, 1H, J = 14.0, 4.0, 3.6 Hz), 2.294 (s, 3H), 1.580 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 145.2, 143.6, 141.9, 139.2, 135.8, 133.1, 131.8, 130.2, 128.8, 128.4, 128.4, 127.7, 127.2, 126.5, 125.0, 124.5, 121.2, 115.6, 41.0, 38.7, 29.5, 21.5, 21.4, 20.6, 19.8. EI-MS m/z [M]-: 65.1 (35.6), 91.1 (84.7), 97.1 (100), 111.1 (30.4), 115.1 (10.7), 175.1 (12.4), 194.1 (13.2), 196.1 (21.2), 207.1 (9.8), 208.1 (21.2), 209.1 (13.5), 222.2 (50.9), 223.1 (14.9), 264.1 (27.7), 276.1 (16.8), 290.2 (21.4), 291.1 (12.7), 305.2 (13.1), 306.2 (78.6), 307.2 (27.5), 461.2 (9.6). FTIR (neat): 3371, 3103, 3048, 2980, 2931, 2858, 2733, 2585, 2524, 2372, 2345, 2304, 2249, 1915, 1848, 1721, 1597, 1451, 1413, 1366, 1265, 1190, 1168, 1087, 896, 809, 776, 739, 704, 693, 675, 575, 543 cm⁻¹. HRMS-ESI (m/z): [M+H]⁺ calcd 462.1556; found 462.1549.

6-(methoxymethyl)-5-tosyl-5,6,7,10-tetrahydro-7,10-ethanocyclohepta[b]indole (3j):
6-(methoxymethyl)-5-tosyl-5,6,7,10-tetrahydro-7,10-ethanocyclohepta[b]indole (3j) was prepared following general procedure as a colorless oil (72%). 1H NMR (400 MHz, CDCl$_3$) $\delta$ 8.17 (dd, 1H, $J = 6.8, 1.6$ Hz), 7.43 (d, 2H, $J = 8.4$ Hz), 7.35 (d, 1H, $J = 6.8$ Hz), 7.34-7.20 (m, 2H), 7.08 (d, 2H, $J = 8.0$ Hz), 6.49 (t, 1H, $J = 8.0$ Hz), 6.07 (t, 1H, $J = 8.0$ Hz), 3.99 (dd, 1H, $J = 9.2, 3.6$ Hz), 3.83-3.79 (m, 1H), 3.47 (d, 1H, $J = 2.0$ Hz), 3.45 (s, 3H), 3.39-3.34 (m, 1H), 3.21-3.16 (m, 1H), 2.28 (s, 3H), 1.94-1.86 (m, 1H) 1.79-1.64 (m, 2H), 1.58-1.50 (m, 1H), 0.89-0.84 (m, 1H); 13C NMR (100 MHz, CDCl$_3$) $\delta$ 144.4, 137.3, 136.6, 134.6, 134.6, 130.6, 130.0, 129.3, 126.9, 126.2, 124.3, 123.9, 117.7, 116.5, 73.4, 58.6, 46.1, 31.2, 31.0, 29.1, 23.3, 21.5. EI-MS m/z [M]-: 65.0 (16.8), 91.1 (35.9), 151.0 (6.2), 152.1 (12.5), 178.0 (13.5), 179.0 (100), 180.0 (30.3), 191.0 (6.4), 204.0 (12.0), 205.0 (7.4), 206.0 (21.4), 207.0 (8.0), 220.1 (6.4), 224.0 (7.3), 334.0 (86.5), 335.0 (18.8), 362.0 (50.1), 363.0 (11.7), 407.0 (17.3). FTIR (neat): 3038, 2934, 2865, 2826, 1638, 1597, 1493, 1475, 1451, 1365, 1306, 1293, 1271, 1232, 1187, 1168, 1148, 1116, 1089, 1025, 978, 968, 942, 900, 868, 832, 768, 726, 705, 676, 652, 577, 548 cm$^{-1}$. HRMS-ESI (m/z): [M+H]$^+$ calcd 408.1628; found 408.1623.

6-cyclopropyl-2-methyl-5-tosyl-5,6,7,10-tetrahydro-7,10-ethanocyclohepta[b]indole (3k): 6-cyclopropyl-2-methyl-5-tosyl-5,6,7,10-tetrahydro-7,10-ethanocyclohepta[b]indole (3k) was prepared following general procedure as a light yellow oil (56%). 1H NMR (400 MHz, CDCl$_3$) $\delta$ 8.00 (d, 1H, $J = 8.4$ Hz), 7.36 (d, 2H, $J = 8.4$ Hz), 7.11 (s, 1H), 7.08-7.03 (m, 3H), 6.47 (t, 1H, $J = 8.4$ Hz), 6.18 (t, 1H, $J = 8.4$ Hz), 3.43-3.05 (m, 1H), 3.14-3.11 (m, 1H), 3.03-2.98 (m, 1H), 2.40 (s, 3H), 2.29 (s, 3H), 1.94-1.90 (m, 1H), 1.76-1.73 (m, 2H), 1.15-1.11 (m, 1H), 0.91-0.84 (m, 2H), 0.51-0.49 (m, 2H), 0.42-0.40 (m, 1H). 13C NMR (100 MHz, CDCl$_3$) $\delta$ 143.9, 139.5, 136.2, 135.5, 133.8, 133.7, 131.7, 128.8, 127.1, 126.4, 125.3, 117.8, 117.1, 48.4, 35.8, 30.7, 29.3, 23.6, 21.5, 21.3, 16.7, 6.0, 3.7. EI-MS m/z [M]-: 91.1 (59.3), 144.1 (17.0), 167.0 (28.3), 168.0 (28.5), 181.1 (18.3), 182.0 (100), 183.0 (65.2), 184.1 (15.0), 193.0 (20.1), 194.0 (23.0), 218.0 (17.2), 220.0 (30.9), 221.0 (14.8), 232.0 (17.6), 234.1 (46.5), 262.1 (38.3), 338.0 (56.6), 339.0 (18.3), 342.1 (17.1), 417.1 (32.4). FTIR (neat): 3334, 3013, 2928, 2864, 2374, 2256, 1639, 1597, 1462, 1436, 1291, 1271, 1232, 1187, 1168, 1148, 1116, 1089, 1025, 978, 968, 942, 900, 868, 832, 768, 726, 705, 676, 652, 577, 545 cm$^{-1}$. HRMS-ESI (m/z): [M+H]$^+$ calcd 418.1835; found 418.1829.

3-fluoro-6-(methoxymethyl)-5-tosyl-5,6,7,10-tetrahydro-7,10-ethanocyclohepta[b]indole (3l): 3-fluoro-6-(methoxymethyl)-5-tosyl-5,6,7,10-tetrahydro-7,10-ethanocyclohepta[b]indole (3l) was prepared following general procedure as a colorless oil (67%). 1H NMR (400 MHz, CDCl$_3$) $\delta$ 7.91 (dd, 1H, $J = 8.0, 2.0$ Hz), 7.45 (d, 2H, $J = 8.4$ Hz), 7.26 (dd, 1H, $J = 8.4, 5.6$ Hz), 7.12 (d, 2H, $J = 8.0$ Hz), 6.98 (td, 1H, $J = 7.2, 2.4$ Hz), 6.49 (t, 1H, $J = 8.0$ Hz), 6.07 (t, 1H, $J = 8.0$ Hz), 3.97 (dd, 1H, $J = 7.2, 3.6$ Hz), 3.78-3.75 (m, 1H), 3.43 (s, 3H), 3.42-3.34 (m, 2H), 3.18-3.17 (m, 1H), 2.31 (s, 3H), 1.92-1.88 (m, 1H), 1.76-1.63 (m, 2H), 1.56-1.50 (m, 1H). 13C NMR (100 MHz, CDCl$_3$) $\delta$ 160.8 (d, $J = 240$ Hz), 144.7, 137.5 (d, $J = 12$ Hz),
136.4, 134.8 (d, J = 4 Hz), 134.5, 130.1, 129.4, 126.8, 126.4, 126.2, 118.3 (d, J = 9 Hz), 112.0 (d, J = 24 Hz), 104.0 (d, J = 29 Hz), 73.3, 58.6, 46.1, 31.2, 31.1, 29.2, 23.2, 21.5. EI-MS m/z [M]: 65.1 (8.4), 91.1 (31.2), 155.0 (10.1), 170.0 (5.0), 196.0 (6.1), 197.0 (56.0), 198.0 (17.7), 222.0 (6.1), 223.0 (5.1), 224.0 (18.5), 225.0 (6.4), 238.0 (8.2), 270.1 (7.1), 352.0 (100), 353.0 (20.5), 354.0 (7.4), 380.0 (51.9), 381.0 (12.3), 425.0 (16.1), 426.0 (5.0). FTIR (neat): 3338, 3113, 3048, 2934, 2865, 2374, 1892, 1596, 1582, 1480, 1459, 1397, 1364, 1267, 1237, 1185, 1166, 1128, 1113, 1084, 979, 908, 825, 806, 722, 701, 657, 586, 547 cm⁻¹. HRMS-ESI (m/z): [M+H]⁺ calcd 426.1534; found 426.1528.

6-cyclohexyl-2-fluoro-5-tosyl-5,6,7,10-tetrahydro-7,10-ethanocyclohepta[b]indole (3m):

6-cyclohexyl-2-fluoro-5-tosyl-5,6,7,10-tetrahydro-7,10-ethanocyclohepta[b]indole (3m) was prepared following general procedure as a light yellow oil (41%). ¹H NMR (400 MHz, CDCl₃) δ 8.09 (dd, 2H, J = 9.6, 4.8 Hz), 7.36 (d, 2H, J = 8.0 Hz), 7.07 (d, 2H, J = 8.0 Hz), 6.99-6.93 (m, 2H), 6.38 (t, 1H, J = 8.0 Hz), 6.09 (t, 1H, J = 8.0 Hz), 3.56 (t, 1H, J = 4.8 Hz), 3.30-3.28 (m, 1H), 3.02 (q, 1H, J = 7.2 Hz), 2.30 (m, 4H), 1.84-1.78 (m, 2H), 1.70-1.60 (m, 2H), 1.56-1.55 (m, 3H), 1.43-1.05 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 142.6 (d, J = 370 Hz), 135.1, 133.9, 133.7, 132.7, 132.3, 129.2, 129.0, 128.7, 126.7, 126.3, 118.4 (d, J = 9Hz), 111.4 (d, J = 24 Hz), 103.6 (d, J = 24 Hz), 51.8, 43.8, 32.3, 32.1, 31.6, 30.0, 29.4, 27.4, 27.4, 26.9, 25.1, 21.5. EI-MS m/z [M⁻]: 71.1 (28.6), 73.1 (41.2), 85.2 (27.5), 89.1 (17.8), 97.1 (38.1), 105.1 (26.2), 113.1 (17.8), 117.2 (34.8), 125.1 (18.0), 135.1 (39.3), 149.1 (28.1), 172.1 (25.2), 185.1 (41.4), 186.1 (43.8), 198.1 (25.0), 201.1 (22.4), 202.1 (23.9), 303.1 (69.6), 353.1 (100), 385.2 (18.4), 463.3 (46.7). FTIR (neat): 3039, 2930, 2854, 2666, 2590, 2258, 1912, 1796, 1638, 1597, 1493, 1465, 1363, 1307, 1263, 1175, 1149, 1137, 1089, 1063, 992, 909, 840, 810, 731, 670, 611, 569, 544, 506, 429 cm⁻¹. HRMS-ESI (m/z): [M+H]⁺ calcd 464.2054; found 464.2050.

4-methyl-6-(thiophen-3-yl)-5-tosyl-5,6,7,10-tetrahydro-7,10-ethanocyclohepta[b]indole (3n):

4-methyl-6-(thiophen-3-yl)-5-tosyl-5,6,7,10-tetrahydro-7,10-ethanocyclohepta[b]indole (3n) was prepared following general procedure as a light yellow oil (40%). ¹H NMR (400 MHz, CDCl₃) δ 7.28-7.20 (m, 2H), 7.17-7.13 (m, 4H), 7.05 (d, 2H, J = 8.0 Hz), 6.79-6.77 (m, 2H), 6.39 (t, 1H, J = 8.0 Hz), 5.68 (t, 1H, J = 8.0 Hz), 4.90 (d, 1H, J = 4.8 Hz), 3.41 (t, 1H, J = 3.6 Hz), 2.96 (q, 1H, J = 6.8 Hz), 2.61 (s, 3H), 2.35 (s, 3H), 1.89-1.82 (m, 1H), 1.78-1.66 (m, 2H), 1.55-1.51 (m, 1H), 0.92-0.86 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 143.9, 143.1, 139.6, 139.0, 135.8, 134.4, 134.1, 131.2, 130.4, 130.1, 128.7, 128.3, 126.2, 125.0, 123.9, 121.6, 115.5, 47.5, 38.9, 30.4, 29.0, 24.4, 21.7, 21.5. EI-MS m/z [M⁻]: 65.0 (14.8), 79.0 (6.5), 91.0 (40.1), 97.0 (45.5), 123.0 (13.2), 165.0 (7.1), 194.0 (11.4), 207.0 (7.2), 220.0 (13.4), 224.0 (9.7), 226.0 (6.3), 256.0 (6.6), 274.0 (10.9), 275.0 (6.3), 276.0 (49.5), 277.0 (10.0), 303.0 (25.4), 304.0 (100), 305.0 (22.9), 459.0 (11.7). FTIR (neat): 3394, 3042, 2934, 2864, 2254, 1917, 1596, 1493, 1452, 1412, 1365, 1305, 1291, 1262, 1233, 1189, 1167, 1112, 1089, 1061, 987, 909, 572, 837, 812, 775, 759, 773, 642, 578, 562, 528 cm⁻¹. HRMS-ESI (m/z): [M+H]⁺ calcd 460.1399;
3-fluoro-6-(methoxymethyl)-5-tosyl-5,6,7,10-tetrahydro-7,10-methanocyclohepta[b]indole (3o): 3-fluoro-6-(methoxymethyl)-5-tosyl-5,6,7,10-tetrahydro-7,10-methanocyclohepta[b]indole (3o) was prepared following general procedure as a colorless oil (65%). 1H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80 (dd, 1H, $J$ = 10.0, 1.0 Hz), 7.31 (d, 2H, $J$ = 8.4 Hz), 7.28-7.22 (m, 1H), 7.07 (t, 2H, $J$ = 8.8 Hz), 6.97-6.92 (m, 1H), 6.33-6.29 (m, 1H), 5.88-5.85 (m, 1H), 4.28 (dd, 1H, $J$ = 9.2, 2.8 Hz), 3.57 (t, 1H, $J$ = 9.6 Hz), 3.47 (s, 3H), 3.43-3.40 (m, 1H), 3.30-3.29 (m, 1H), 2.28 (s, 3H), 2.01-1.94 (m, 2H). Major isomer of 3o 13C NMR (100 MHz, CDCl$_3$) $\delta$ 160.6 (d, $J$ = 239 Hz), 144.5, 142.5, 139.5, 134.4, 133.0, 131.4, 130.7, 129.6, 129.4 (d, $J$ = 3 Hz), 126.3, 118.4 (d, $J$ = 9 Hz), 112.0 (d, $J$ = 24 Hz), 103.7 (d, $J$ = 29 Hz), 75.8, 58.8, 40.8, 39.9, 36.9, 36.1, 21.5. EI-MS m/z [M$^{-}$]: 69.1 (9.9), 91.1 (43.4), 155.0 (33.5), 184.0 (16.3), 185.0 (15.4), 196.0 (8.1), 198.0 (12.0), 209.0 (11.1), 210.0 (34.5), 211.0 (19.9), 212.0 (9.6), 222.0 (8.0), 224.1 (26.1), 225.1 (6.3), 256.1 (18.8), 366.0 (100), 367.0 (22.0), 368.0 (8.9), 411.0 (35.4), 412.1 (7.9). FTIR (neat): 3366, 3054, 2952, 2927, 2865, 2589, 2370, 1795, 1613, 1596, 1482, 1448, 1427, 1366, 1265, 1232, 1186, 1169, 1113, 1088, 1031, 980, 917, 864, 825, 809, 738, 708, 666, 585, 548 cm$^{-1}$. HRMS-ESI (m/z): [M+H]$^{+}$ calcd 412.1377; found 412.1371.
III. Determination of Relative Configuration of Products.

1D NOE (CDCl$_3$) spectrum of endo-3j, 600 MHz

1D NOE (CDCl$_3$) spectrum of endo-3k, 600 MHz
1D NOE (CDCl$_3$) spectrum of endo-3I, 600 MHz

X-Ray Diffraction Analysis of Arylation Product endo-3o.
The crystallographic data of endo-3o were summarized in the following table.

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CIF file of endo-3o can be obtained from the Cambridge Crystallographic Data Centre using deposition number CCDC 1001592. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk].

IV. NMR Spectra of Compounds

1a $^1$H NMR, 400 MHz, CDCl$_3$

![NMR Spectrum of 1a in CDCl$_3$](image1)

Chemical Formula: C$_{19}$H$_{19}$NO$_2$S
Molecular Weight: 345.41

1a $^{13}$C NMR, 100 MHz, CDCl$_3$

![NMR Spectrum of 1a in CDCl$_3$](image2)
Chemical Formula: C_{12}H_{11}NO_3S
Molecular Weight: 345.41

1b \(^1\)H NMR, 400 MHz, CDCl\(_3\)

Chemical Formula: C_{12}H_{11}NO_3S
Molecular Weight: 355.45

1b \(^{13}\)C NMR, 100 MHz, CDCl\(_3\)
Chemical Formula: C_{20}H_{18}NO_{3}S
Molecular Weight: 355.45

1c $^1H$ NMR, 400 MHz, CDCl$_3$

Chemical Formula: C_{14}H_{13}FNO_{3}S
Molecular Weight: 363.40

1c $^{13}$C NMR, 100 MHz, CDCl$_3$
$\text{H NMR, 400 MHz, CDCl}_3$

Chemical Formula: $\text{C}_{10}\text{H}_9\text{FNO}_2\text{S}$
Molecular Weight: 363.40

$\text{C NMR, 100 MHz, CDCl}_3$

Chemical Formula: $\text{C}_{23}\text{H}_{23}\text{FNO}_2\text{S}$
Molecular Weight: 375.46

$\text{H NMR, 400 MHz, CDCl}_3$

$\text{C NMR, 100 MHz, CDCl}_3$
Chemical Formula: C_{22}H_{18}FNO_{3}S
Molecular Weight: 395.45

Chemical Formula: C_{23}H_{22}FNO_{3}S
Molecular Weight: 375.46

1e $^1$H NMR, 400 MHz, CDCl$_3$

1e $^{13}$C NMR, 100 MHz, CDCl$_3$
Chemical Formula: C_{23}H_{19}FNO_{2}S
Molecular Weight: 401.49

1f \^1H NMR, 400 MHz, CDCl\textsubscript{3}

Chemical Formula: C_{23}H_{19}FNO_{2}S
Molecular Weight: 395.45

1f \^13C NMR, 100 MHz, CDCl\textsubscript{3}
Chemical Formula: C_{21}H_{16}FNO_3S
Molecular Weight: 401.49

1g H NMR, 400 MHz, CDCl_3

Chemical Formula: C_{21}H_{14}NO_3S_2
Molecular Weight: 397.51

1g C NMR, 100 MHz, CDCl_3
**Chemical Formula:** C_{21}H_{18}NO_{2}S_{2}

**Molecular Weight:** 397.51

**4b** $^{1}$H NMR, 400 MHz, CDCl$_3$

**Chemical Formula:** C_{17}H_{20}O_{2}S_{2}

**Molecular Weight:** 328.64

**4b** $^{13}$C NMR, 100 MHz, CDCl$_3$
$2a$ $^1$H NMR, 400 MHz, CDCl$_3$

Chemical Formula: C$_{17}$H$_{20}$O$_2$Si$_2$
Molecular Weight: 328.64

$2a$ $^{13}$C NMR, 100 MHz, CDCl$_3$

Chemical Formula: C$_{18}$H$_{23}$NO$_2$S
Molecular Weight: 345.41
2-(cyclobut-1-en-1-yl)-5-methyl-1-tosyl-1H-indole $^1$H NMR, 400 MHz, CDCl$_3$  

Chemical Formula: C$_{18}$H$_{17}$NO$_2$S  
Molecular Weight: 345.41

2-(cyclobut-1-en-1-yl)-5-methyl-1-tosyl-1H-indole $^{13}$C NMR, 100 MHz, CDCl$_3$  

Chemical Formula: C$_{18}$H$_{17}$NO$_2$S  
Molecular Weight: 337.44
Chemical Formula: C_{20}H_{13}NO_2S
Molecular Weight: 337.44
5a COSY NMR, 400 MHz, CDCl₃

Chemical Formula: C₁₉H₁₇NO₃S₂
Molecular Weight: 698.11

5c ¹H NMR, 400 MHz, CDCl₃

Chemical Formula: C₁₉H₁₅NO₃S
Molecular Weight: 409.4980

5c ¹³C NMR, 100 MHz, CDCl₃
Chemical Formula: C_{23}H_{23}NO_{4}S
Molecular Weight: 409.4980

$\text{Sc}^{13}C$ NMR, 100 MHz, CDCl$_3$

Chemical Formula: C_{23}H_{23}NO_{4}S
Molecular Weight: 409.4980
5c COSY NMR, 400 MHz, CDCl₃

5b ¹H NMR, 400 MHz, CDCl₃

Chemical Formula: C₅H₅NO₅S₂
Molecular Weight: 656.0350

3a ¹H NMR, 400 MHz, CDCl₃
Chemical Formula: C_{33}H_{33}NO_{3}S
Molecular Weight: 395.51

3a C-13 NMR, 100 MHz, CDCl₃

Chemical Formula: C_{33}H_{33}NO_{3}S
Molecular Weight: 395.51

3a COSY NMR, 400 MHz, CDCl₃
Chemical Formula: C_{20}H_{27}NO_{3}S
Molecular Weight: 395.51

3b $^1$H NMR, 400 MHz, CDCl$_3$

Chemical Formula: C_{20}H_{27}NO_{3}S
Molecular Weight: 409.54

3b $^{13}$C NMR, 100 MHz, CDCl$_3$
$\text{H NMR, 400 MHz, CDCl}_3$

Chemical Formula: $C_{34}H_{28}NO_3S$
Molecular Weight: 409.54

$3c \ ^1H \text{ NMR, 400 MHz, CDCl}_3$

Chemical Formula: $C_{33}H_{29}NO_3S$
Molecular Weight: 419.58
$^{13}$C NMR, 100 MHz, CDCl$_3$

Chemical Formula: C$_{29}$H$_{34}$NO$_3$S
Molecular Weight: 419.58

$^1$H NMR, 400 MHz, CDCl$_3$

Chemical Formula: C$_{27}$H$_{32}$FNO$_3$S
Molecular Weight: 413.50
Chemical Formula: C_{28}H_{28}FNO_2S
Molecular Weight: 427.53

3f $^1$H NMR, 400 MHz, CDCl$_3$

Chemical Formula: C_{26}H_{28}FNO_2S
Molecular Weight: 425.50

3f $^{13}$C NMR, 100 MHz, CDCl$_3$
$\text{F}$

Chemical Formula: C$_{39}$H$_{39}$FNO$_2$S
Molecular Weight: 425.56

$\text{H NMR, 400 MHz, CDCl}_3$

$3g$ $^1$H NMR, 400 MHz, CDCl$_3$

Chemical Formula: C$_{39}$H$_{39}$FNO$_2$S
Molecular Weight: 459.57
$3g$ $^{13}$C NMR, 100 MHz, CDCl$_3$

Chemical Formula: C$_{20}$H$_{12}$FNO$_2$S
Molecular Weight: 459.57

$3h$ $^1$H NMR, 400 MHz, CDCl$_3$

Chemical Formula: C$_{20}$H$_{12}$FNO$_2$S
Molecular Weight: 465.62
3h $^{13}$C NMR, 100 MHz, CDCl$_3$

Chemical Formula: C$_{29}$H$_{27}$FNO$_2$S
Molecular Weight: 465.62

3i $^1$H NMR, 400 MHz, CDCl$_3$

Chemical Formula: C$_{29}$H$_{27}$NO$_2$S$_2$
Molecular Weight: 481.84
$3i^{13}$C NMR, 100 MHz, CDCl$_3$

Chemical Formula: C$_{29}$H$_{22}$NO$_3$S$_2$
Molecular Weight: 461.64

$3j$ $^1$H NMR, 400 MHz, CDCl$_3$

Chemical Formula: C$_{29}$H$_{22}$NO$_3$S
Molecular Weight: 407.53
Chemical Formula: C_{18}H_{18}NO_{2}S
Molecular Weight: 407.53

3j^{13}C NMR, 100 MHz, CDCl₃

Chemical Formula: C_{20}H_{22}NO_{2}S
Molecular Weight: 407.53

3j COSY NMR, 100 MHz, CDCl₃

3k $^1$H NMR, 400 MHz, CDCl₃
Chemical Formula: C_{29}H_{27}NO_{2}S
Molecular Weight: 417.56

\[ \text{Chemical Formula: C}_{29}\text{H}_{27}\text{NO}_{2}\text{S} \]
\[ \text{Molecular Weight: 417.56} \]
$^{1}H$ NMR, 400 MHz, CDCl$_3$ (part A)

Chemical Formula: C$_{24}$H$_{11}$FNO$_2$S
Molecular Weight: 463.61

$^{1}H$ NMR, 400 MHz, CDCl$_3$ (part B)

Chemical Formula: C$_{28}$H$_{13}$FNO$_2$S
Molecular Weight: 483.61
$^{13}$C NMR, 100 MHz, CDCl$_3$

Chemical Formula: C$_{29}$H$_{29}$FNO$_2$S
Molecular Weight: 463.61

$^1$H NMR, 400 MHz, CDCl$_3$

Chemical Formula: C$_{29}$H$_{29}$NO$_2$S$_2$
Molecular Weight: 456.62
Chemical Formula: C_{23}H_{23}NO_{8}S
Molecular Weight: 411.49
Chemical Formula: C_{29}H_{32}FNO_{3}S
Molecular Weight: 411.49