Supporting Information

One-step assembly of alkoxypyrroloindolines via iodine-catalyzed alkoxycyclization of indole derivatives

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A. General Information

Chemicals and solvents were purchased from commercial suppliers and used as received unless noted. All products were purified by flash chromatography on silica gel. The chemical yields referred are isolated products. $^1$H NMR and $^{13}$C NMR spectra were recorded on 400 MHz or 600 MHz Bruker spectrometers. Chemical shifts of $^1$H NMR were reported in part per million relative to the CDCl$_3$ residual peak ($\delta$ 7.26). Chemical shifts of $^{13}$C NMR were reported relative to CDCl$_3$ ($\delta$ 77.16). The used abbreviations are as follows: s (singlet), d (doublet), t (triplet), quart. (quartet), quint. (quintet), m (multiplet), br (broad). Multiplets which arise from accidental equality of coupling constants of magnetically non-equivalent protons are marked as virtual (virt.). Melting points were measured on a SGW® X-4B and are not corrected. Reactions were monitored by TLC analysis using silica gel 60 Å F-254 thin layer plates and compounds were visualized with a UV light at 254 nm or 365 nm. Further visualization was achieved by staining with KMnO$_4$ followed by heating on a hot plate. Flash column chromatography was performed on silica gel 60 Å, 10–40 μm.

Substrate 1 were synthesized by following known procedures.$^1$

B. Representative Procedure

A 50 mL round bottom flask was charged with I$_2$ (5.1 mg, 10 mol %), tryptamine substrates 1 (0.2 mmol, 1.0 equiv) and alcohol (12 mL), then TBHP (70% in water, 57.2 μL, 0.4 mmol, 2.0 equiv) was added. The reaction mixture was heated to 65 °C for 3 h before cooled down to room temperature. Saturated aqueous Na$_2$S$_2$O$_3$ (10 mL) solution was slowly introduced and the resulting mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over Na$_2$SO$_4$, filtered, concentrated under reduced pressure and the residue was purified by chromatography on silica gel (eluent: Hexane/EtOAc, 30:1 to 10:1) to afford methoxypyrroloindolene 2. In the case of using pentanol and hexanol, distillation was performed under reduced pressure to recovered the alcohols before chromatography.

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C. Analytical Data of the Alkoxyprroloindoline Products

3a-Methoxy-8-methyl-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole 2a

![2a](image)

Compound 2a was synthesized following the general procedure. A white solid, 50.2 mg, 70% yield.

**m.p.:** 117 – 119 °C.

**TLC:** $R_f = 0.74$ (Hexane/EtOAc = 3:1) [UV, KMnO4].

**$^1$H NMR (400 MHz, CDCl3) $\delta$ 7.84 – 7.72 (m, 2H), 7.40 – 7.28 (m, 2H), 7.21 (virt. td, $J \approx 7.8, 1.3$ Hz, 1H), 7.07 (dd, $J = 7.5, 1.3$ Hz, 1H), 6.71 (virt. td, $J \approx 7.5, 0.8$ Hz, 1H), 6.47 (d, $J = 7.8$ Hz, 1H), 5.36 (s, 1H), 3.56 (ddd, $J = 11.4, 7.7, 2.6$ Hz, 1H), 3.14 – 3.06 (m, 1H), 3.02 (s, 3H), 2.96 (s, 3H), 2.44 (s, 3H), 2.07 (ddd, $J = 12.2, 5.7, 2.6$ Hz, 1H), 1.80 (ddd, $J = 12.3, 11.0, 7.7$ Hz, 1H).

**$^{13}$C NMR (101 MHz, CDCl3) $\delta$ 152.0, 143.8, 136.4, 130.7, 129.9, 127.4, 124.9, 124.0, 117.9, 106.9, 93.9, 86.2, 52.8, 47.6, 38.8, 31.5, 21.7.

**IR (KBr/cm$^{-1}$)** 3041.1, 2946.0, 2828.4, 1609.1, 1491.2, 1465.9, 1347.3, 1160.0, 1091.1, 1021.1, 928.0, 813.1, 748.2, 664.8.

**HRMS (ESI):** C$_{19}$H$_{23}$N$_2$O$_3$S [(M+H)$^+$]: calcd.: 359.1424; found: 359.1433.

3a-Methoxy-4,8-dimethyl-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole 2b

![2b](image)

Compound 2b was synthesized following the general procedure. A white solid, 46.9 mg, 63% yield.

**m.p.:** 139 – 141 °C.

**TLC:** $R_f = 0.73$ (Hexane/EtOAc = 3:1) [UV, KMnO4].

**$^1$H NMR (400 MHz, CDCl3) $\delta$ 7.84 – 7.72 (m, 2H), 7.40 – 7.28 (m, 2H), 7.10 (virt. t, $J \approx 7.7$ Hz, 1H), 6.48 (d, $J = 7.5$ Hz, 1H), 6.30 (d, $J = 7.5$ Hz, 1H), 5.37 (s, 1H), 3.60 – 3.52 (m, 1H), 3.20 (virt. td, $J \approx 10.8, 6.4$ Hz, 1H), 2.99 (s, 3H), 2.92 (s, 3H), 2.44 (s, 3H), 2.20 (s, 3H), 2.18 – 2.12 (m, 1H), 1.91 – 1.79 (m, 1H).

**$^{13}$C NMR (101 MHz, CDCl3) $\delta$ 151.9, 143.8, 136.3, 135.3, 130.5, 129.8, 127.5, 122.0, 120.0, 104.4, 94.9, 86.4, 52.8, 47.5, 38.1, 31.7, 21.7, 17.1.

**IR (KBr/cm$^{-1}$)** 3034.8, 2946.0, 2854.9, 1735.4, 1614.8, 1496.7, 1465.9, 1347.2, 1161.1, 1090.6, 1023.7, 935.1, 809.8, 622.4.
HRMS (ESI): C_{20}H_{24}N_{2}NaO_{3}S [(M+Na)^+]: calcd.: 395.1400; found: 395.1405.

5-Chloro-3a-methoxy-8-methyl-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole 2c

![Chemical structure of 2c]

Compound 2c was synthesized following the general procedure.
A white solid, 53.4 mg, 68% yield.
m.p.: 125 – 127 °C.
TLC: \( R_f = 0.82 \) (Hexane/EtOAc = 3:1) [UV, KMnO₄].

\(^1\)H NMR (400 MHz, CDCl₃) \( \delta \): 7.84 – 7.72 (m, 2H), 7.40 – 7.28 (m, 2H), 7.15 (d, \( J = 8.4 \) Hz, 1H), 7.01 (s, 1H), 6.37 (d, \( J = 8.4 \) Hz, 1H), 5.36 (s, 1H), 3.63 – 3.49 (m, 1H), 3.10 (virt. td, \( J \approx 11.3, 4.8 \) Hz, 1H), 2.99 (s, 3H), 2.97 (s, 3H), 2.44 (s, 3H), 2.03 (dd, \( J = 11.2, 4.8 \) Hz, 1H), 1.78 (virt. td, \( J \approx 11.2, 8.0 \) Hz, 1H).

\(^{13}\)C NMR (101 MHz, CDCl₃) \( \delta \): 150.4, 143.9, 136.1, 130.5, 129.9, 127.4, 126.8, 124.1, 122.5, 107.7, 93.5, 86.3, 53.0, 47.5, 38.7, 31.5, 21.6.

IR (KBr/cm\(^{-1}\)): 3061.3, 2926.5, 1734.1, 1605.3, 1491.2, 1348.1, 1263.2, 1161.3, 1080.0, 1022.3, 933.6, 748.7, 665.2, 574.7, 546.7.

HRMS (ESI): C_{19}H_{21}ClN_{2}NaO_{3}S [(M+Na)^+]: calcd.: 415.0854; found: 415.0856.

5-Fluoro-3a-methoxy-8-methyl-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole 2d

![Chemical structure of 2d]

Compound 2d was synthesized following the general procedure.
A liquid, 44.4 mg, 59% yield.
TLC: \( R_f = 0.77 \) (Hexane/EtOAc = 3:1) [UV, KMnO₄].

\(^1\)H NMR (400 MHz, CDCl₃) \( \delta \): 7.84 – 7.72 (m, 2H), 7.40 – 7.28 (m, 2H), 6.94 – 6.89 (m, 1H), 6.80 (dd, \( J = 8.5, 2.3 \) Hz, 1H), 6.37 (dd, \( J = 8.5, 3.8 \) Hz, 1H), 5.34 (s, 1H), 3.59 – 3.53 (m, 1H), 3.12 (virt. td, \( J \approx 11.0, 5.9 \) Hz, 1H), 2.99 (s, 3H), 2.97 (s, 3H), 2.44 (s, 3H), 2.10 – 1.98 (m, 1H), 1.89 – 1.76 (m, 1H).

\(^{13}\)C NMR (101 MHz, CDCl₃) \( \delta \): 156.5 (d, \( J = 235.5 \) Hz), 148.2, 143.9, 136.2, 129.9, 127.4, 126.3 (d, \( J = 7.8 \) Hz), 117.0 (d, \( J = 23.3 \) Hz), 111.2 (d, \( J = 24.0 \) Hz), 107.4 (d, \( J = 6.9 \) Hz), 93.6, 86.7, 53.0, 47.6, 38.7, 32.2.

IR (KBr/cm\(^{-1}\)): 3062.9, 2928.7, 1735.1, 1497.1, 1373.5, 1243.4, 1161.2, 1125.5, 1024.2, 942.7, 840.6, 745.8, 663.7.

HRMS (ESI): C_{19}H_{21}FN_{2}NaO_{3}S [(M+Na)^+]: calcd.: 399.1149; found: 399.1151.
Compound 2e was synthesized following the general procedure. A white solid, 53.4 mg, 61% yield.

m.p.: 116 – 118 ºC.

TLC: $R_t = 0.74$ (Hexane/EtOAc = 3:1) [UV, KMnO₄].

$^1$H NMR (400 MHz, CDCl₃) δ 7.84 – 7.72 (m, 2H), 7.40 – 7.28 (m, 2H), 7.21 ($\textit{v}t$, $J \approx 7.6$ Hz, 1H), 7.07 (d, $J = 7.2$ Hz, 1H), 6.71 ($\textit{v}t$, $J \approx 7.6$ Hz, 1H), 6.47 (d, $J = 7.2$ Hz, 1H), 5.36 (s, 1H), 3.63 – 3.51 (m, 1H), 3.10 ($\textit{v}t$, $J \approx 12.4$, 5.8 Hz, 1H), 3.02 (s, 3H), 2.96 (s, 3H), 2.44 (s, 3H), 2.07 (dd, $J = 12.4$, 5.8 Hz, 1H), 1.85 – 1.77 (m, 1H).

$^{13}$C NMR (101 MHz, CDCl₃) δ 152.0, 143.8, 136.4, 130.7, 129.9, 127.4, 124.9, 124.0, 117.9, 106.9, 93.9, 86.2, 52.8, 47.6, 38.8, 31.6, 21.6.

IR (KBr/cm⁻¹) 3053.8, 2953.2, 1727.6, 1609.0, 1491.2, 1464.1, 1347.4, 1160.0, 1091.0, 1021.2, 928.0, 813.1, 748.2, 664.8, 572.7, 545.7.

HRMS (ESI): C₁₉H₂₁N₂O₃S \[(M+Na)^+\]: calcd.: 459.0348; found: 459.0351.

HRMS (ESI): C₁₉H₂₁BrN₂NaO₃S \[(M+Na)^+\]: calcd.: 461.0328; found: 461.0331.

Compound 2f was synthesized following the general procedure. A white solid, 45.5 mg, 61% yield.

m.p.: 108 – 110 ºC.

TLC: $R_t = 0.80$ (Hexane/EtOAc = 3:1) [UV, KMnO₄].

$^1$H NMR (400 MHz, CDCl₃) δ 7.79 – 7.77 (m, 2H), 7.35 – 7.33 (m, 2H), 7.02 (dd, $J = 8.0$, 1.0 Hz, 1H), 6.87 (d, $J = 1.0$ Hz, 1H), 6.39 (d, $J = 8.0$ Hz, 1H), 5.32 (s, 1H), 3.58 – 3.52 (m, 1H), 3.16 – 3.06 (m, 1H), 2.99 (s, 3H), 2.96 (s, 3H), 2.44 (s, 3H), 2.25 (s, 3H), 2.06 (ddd, $J = 12.3$, 5.8, 3.2 Hz, 1H), 1.82 (ddd, $J = 12.3$, 10.7, 7.7 Hz, 1H).

$^{13}$C NMR (101 MHz, CDCl₃) δ 150.0, 143.7, 136.4, 131.1, 129.8, 127.4, 127.3, 125.1, 124.5, 107.0, 93.9, 86.6, 52.8, 47.7, 38.6, 32.1, 21.6, 20.8.

IR (KBr/cm⁻¹) 3057.5, 2927.6, 2856.1, 1736.4, 1614.5, 1497.5, 1465.8, 1349.2, 1163.9, 1090.7, 1028.2, 936.0, 806.3, 669.4.

HRMS (ESI): C₂₀H₂₄N₂NaO₃S \[(M+Na)^+\]: calcd.: 395.1400; found: 395.1403.
3a-Methoxy-6,8-dimethyl-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole 2g

![2g](image)

Compound 2g was synthesized following the general procedure. A white solid, 46.9 mg, 63% yield. 

**m.p.:** 103 – 105 °C.

**TLC:** $R_f = 0.70$ (Hexane/EtOAc = 3:1) [UV, KMnO₄].

**¹H NMR (400 MHz, CDCl₃)** δ 7.79 – 7.77 (m, 2H), 7.35 – 7.33 (m, 2H), 7.02 (d, $J = 7.8$ Hz, 1H), 6.87 (s, 1H), 6.39 (d, $J = 8.0$ Hz, 1H), 5.32 (s, 1H), 3.58 – 3.52 (m, 1H), 3.11 (virt. td, $J \approx 11.1, 5.8$ Hz, 1H), 2.99 (s, 3H), 2.96 (s, 3H), 2.44 (s, 3H), 2.25 (s, 3H), 2.09 – 2.04 (m, 1H), 1.89 – 1.76 (m, 1H).

**¹³C NMR (101 MHz, CDCl₃)** δ 150.0, 143.7, 136.4, 131.1, 129.8, 127.4, 127.3, 125.1, 124.5, 107.0, 93.9, 86.6, 52.8, 47.7, 38.6, 32.1, 21.6, 20.8.

**IR (KBr/cm⁻¹)** 3067.9, 2931.5, 2856.9, 1737.9, 1632.0, 1497.4, 1460.7, 1345.6, 1159.8, 1096.1, 1033.2, 935.2, 811.5, 667.8.

**HRMS (ESI):** C₂₀H₂₄N₂NaO₃S [(M+Na)+]: calcd.: 395.1400; found: 395.1400.

3a,5-Dimethoxy-8-methyl-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole 2h

![2h](image)

Compound 2h was synthesized following the general procedure. A white solid, 36.5 mg, 47% yield. 

**m.p.:** 138 – 140 °C.

**TLC:** $R_f = 0.71$ (Hexane/EtOAc = 3:1) [UV, KMnO₄].

**¹H NMR (400 MHz, CDCl₃)** δ 7.79 – 7.77 (m, 2H), 7.35 – 7.33 (m, 2H), 6.79 (dd, $J = 8.6, 2.6$ Hz, 1H), 6.41 (d, $J = 2.6$ Hz, 1H), 5.30 (d, $J = 2.8$ Hz, 1H), 3.74 (s, 3H), 3.58 – 3.52 (m, 1H), 3.55 (ddd, $J = 11.2, 7.7, 3.2$ Hz, 1H), 2.97 (s, 3H), 2.97 (s, 3H), 2.44 (s, 3H), 2.07 (ddd, $J = 11.8, 5.6, 3.0$ Hz, 1H), 1.85 (ddd, $J = 12.4, 10.3, 7.7$ Hz, 1H).

**¹³C NMR (101 MHz, CDCl₃)** δ 153.0, 146.4, 143.8, 136.4, 129.8, 127.5, 126.3, 115.9, 110.4, 109.6, 103.2, 93.5, 81.1, 66.7.

**IR (KBr/cm⁻¹)** 3362.6, 2924.1, 2853.2, 1738.4, 1620.2, 1499.2, 1346.5, 1249.8, 1160.5, 1102.7, 1027.0, 934.9, 814.3, 703.4.
6-Fluoro-3a-methoxy-8-methyl-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole 2i

Compound 2i was synthesized following the general procedure.

A white solid, 48.2 mg, 64% yield.

m.p.: 109 – 111 °C.

TLC: R<sub>f</sub> = 0.79 (Hexane/EtOAc = 3:1) [UV, KMnO<sub>4</sub>].

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.79 – 7.77 (m, 2H), 7.35 – 7.33 (m, 2H), 7.01 – 6.93 (m, 1H), 6.36 (virt. t, J ≈ 8.6 Hz, 1H), 6.14 (d, J = 10.1 Hz, 1H), 5.38 (s, 1H), 3.63 – 3.50 (m, 1H), 3.08 (td, J = 11.6, 5.5 Hz, 1H), 2.99 (s, 3H), 2.96 (s, 3H), 2.44 (s, 3H), 2.09 – 1.96 (m, 1H), 1.83 – 1.69 (m, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.6 (d, J = 244.8 Hz), 153.6 (d, J = 12.0 Hz), 143.9, 136.3, 129.9, 127.4, 125.0 (d, J = 12.0 Hz), 120.4, 104.0 (d, J = 25.1 Hz), 94.5 (d, J = 25.1 Hz), 93.4, 86.5, 52.7, 47.5, 38.7, 31.2, 21.6.

IR (KBr/cm<sup>-1</sup>) 3063.8, 2929.8, 1600.3, 1457.2, 1345.7, 1163.2, 1095.6, 1024.3, 942.7, 840.6, 705.8, 665.7.

HRMS (ESI): C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>NaO<sub>4</sub>S [(M+Na<sup>+</sup>)]: calcd.: 411.1349; found: 411.1351.

6-Chloro-3a-methoxy-8-methyl-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole 2j

Compound 2j was synthesized following the general procedure.

A white solid, 47.9 mg, 61% yield.

m.p.: 105 – 107 °C.

TLC: R<sub>f</sub> = 0.76 (Hexane/EtOAc = 3:1) [UV, KMnO<sub>4</sub>].

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.79 – 7.77 (m, 2H), 7.35 – 7.33 (m, 2H), 6.66 (d, J = 7.7 Hz, 1H), 6.42 (s, 1H), 5.37 (s, 1H), 3.62 – 3.50 (m, 1H), 3.08 (virt. td, J ≈ 11.6, 5.7 Hz, 1H), 2.99 (s, 3H), 2.96 (s, 3H), 2.44 (s, 3H), 2.09 – 1.94 (m, 1H), 1.84 – 1.70 (m, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.9, 143.9, 136.6, 136.2, 129.9, 127.4, 124.9, 124.9, 123.5, 117.6, 106.9, 93.4, 86.2, 52.8, 47.5, 38.7, 31.2, 21.6.

IR (KBr/cm<sup>-1</sup>) 3063.5, 2927.9, 1735.3, 1493.4, 1427.9, 1300.7, 1203.8, 1114.1, 1023.3, 981.1, 877.4, 809.2, 752.3, 665.5, 593.3, 575.2.

HRMS (ESI): C<sub>19</sub>H<sub>21</sub>ClN<sub>2</sub>NaO<sub>3</sub>S [(M+Na<sup>+</sup>)]: calcd.: 415.0854; found: 415.0855.
3a-Methoxy-7,8-dimethyl-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole 2k

\[
\begin{align*}
\text{O} & \quad \text{N} \\
\text{N} & \quad \text{Ts} \\
\text{Me} & \quad \text{H} \\
\end{align*}
\]

Compound 2k was synthesized following the general procedure. A white solid, 44.7 mg, 60% yield.

m.p.: 77 – 79 °C.

TLC: Rf = 0.81 (Hexane/EtOAc = 3:1) [UV, KMnO4].

\(^1\text{H} \text{ NMR} \) (400 MHz, CDCl\(_3\)) \(\delta 7.79 – 7.77 \) (m, 2H), \(7.35 – 7.33 \) (m, 2H), 6.97 (virt. dt, \(J \cong 7.6, 2.1, 0.81 \) Hz, 2H), 6.77 (virt. t, \(J \cong 7.6 \) Hz, 1H), 5.20 (s, 1H), 3.62 – 3.56 (m, 1H), 3.14 (s, 3H), 2.99 (s, 3H), 2.95 – 2.82 (m, 1H), 2.41 (s, 3H), 2.20 (d, \(J = 4.6 \) Hz, 3H), 2.19 – 2.15 (m, 2H).

\(^{13}\text{C} \text{ NMR} \) (101 MHz, CDCl\(_3\)) \(\delta 151.4, 143.3, 137.2, 133.4, 129.5, 127.4, 127.4, 122.0, 121.9, 120.7, 93.5, 88.8, 53.0, 46.6, 38.5, 38.3, 21.6, 18.9.

IR (KBr/cm\(^{-1}\)) 3057.9, 2988.3, 2854.7, 1755.8, 1613.3, 1498.7, 1384.9, 1212.5, 1092.3, 1025.4, 937.9, 812.2, 669.8.

HRMS (ESI): C\(_{20}\)H\(_{25}\)N\(_2\)O\(_3\)S \([\text{M+H}]^+\): calcd.: 373.1580; found: 373.1581.

3a-Methoxy-8-methyl-1-(methylsulfonyl)-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole 2l

\[
\begin{align*}
\text{O} & \quad \text{N} \\
\text{N} & \quad \text{Ms} \\
\text{Me} & \quad \text{H} \\
\end{align*}
\]

Compound 2l was synthesized following the general procedure. A liquid, 40.7 mg, 72% yield.

TLC: Rf = 0.27 (Hexane/EtOAc = 3:1) [UV, KMnO4].

\(^1\text{H} \text{ NMR} \) (400 MHz, CDCl\(_3\)) \(\delta 7.27 \) (virt. t, \(J \cong 7.8 \) Hz, 1H), 7.18 (d, \(J = 7.9 \) Hz, 1H), 6.81 (virt. t, \(J \cong 7.9 \) Hz, 1H), 6.54 (d, \(J = 7.8 \) Hz, 1H), 5.26 (s, 1H), 3.72 (virt. t, \(J \cong 8.7 \) Hz, 1H), 3.18 – 3.11 (m, 1H), 3.07 (s, 3H), 3.00 (s, 3H), 2.95 – 2.39 (m, 1H), 2.35 (dd, \(J = 11.4, 5.0 \) Hz, 1H).

\(^{13}\text{C} \text{ NMR} \) (101 MHz, CDCl\(_3\)) \(\delta 152.3, 130.9, 125.3, 124.3, 118.7, 107.8, 94.2, 86.5, 53.1, 47.2, 39.2, 38.5, 33.1.

IR (KBr/cm\(^{-1}\)) 3363.4, 3195.4, 2927.7, 2829.7, 1736.8, 1609.2, 1490.9, 1465.0, 1337.3, 1203.1, 1153.9, 1105.5, 1024.8, 929.6, 875.5, 815.1, 755.8.

3a-Methoxy-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole 2m

![Chemical structure of 2m](image)

Compound 2m was synthesized following the general procedure. A white solid, 33.1 mg, 48% yield.

**m.p.:** 121 – 123 °C.

**TLC:** $R_t = 0.66$ (Hexane/EtOAc = 3:1) [UV, KMnO$_4$].

**$^1$H NMR** (400 MHz, CDCl$_3$) $\delta$ 7.79 – 7.77 (m, 2H), 7.35 – 7.33 (m, 2H), 7.18 (dd, $J = 15.8$, 7.6 Hz, 2H), 6.81 (virt. t, $J \approx 7.4$ Hz, 1H), 6.66 (d, $J = 7.4$ Hz, 1H), 5.21 (s, 1H), 4.95 (s, 1H), 3.47 – 3.34 (m, 1H), 3.21 (dd, $J = 15.9$, 9.4 Hz, 1H), 3.01 (s, 3H), 2.44 (s, 3H), 2.35 – 2.25 (m, 1H), 2.24 – 2.13 (m, 1H).

**$^{13}$C NMR** (101 MHz, CDCl$_3$) $\delta$ 150.5, 143.9, 135.5, 130.7, 129.9, 127.4, 125.1, 124.5, 119.5, 110.3, 94.2, 80.1, 52.6, 46.9, 37.4, 21.6.

**IR (KBr/cm$^{-1}$)** 3400.1, 3369.1, 3053.5, 2951.6, 2923.8, 2854.1, 1737.3, 1609.4, 1468.2, 1335.6, 1201.7, 1159.2, 1092.1, 1055.4, 937.9, 812.3, 751.4, 662.5.

**HRMS (ESI):** C$_{18}$H$_{21}$N$_2$O$_3$S [(M+H)$^+$]: calcd.: 345.1267; found: 345.1280.

8-Benzyl-3a-methoxy-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole 2n

![Chemical structure of 2n](image)

Compound 2n was synthesized following the general procedure. A liquid, 78.2 mg, 90% yield.

**TLC:** $R_t = 0.79$ (Hexane/EtOAc = 3:1) [UV, KMnO$_4$].

**$^1$H NMR** (400 MHz, CDCl$_3$) $\delta$ 7.79 – 7.77 (m, 2H), 7.35 – 7.33 (m, 2H), 7.30 (d, $J = 7.3$ Hz, 4H), 7.16 (virt. t, $J \approx 7.6$ Hz, 1H), 7.08 (d, $J = 7.2$ Hz, 1H), 6.72 (virt. t, $J \approx 7.2$ Hz, 1H), 6.47 (d, $J = 7.9$ Hz, 1H), 5.55 (s, 1H), 4.79 – 4.62 (m, 2H), 3.73 – 3.56 (m, 1H), 3.18 (virt. td, $J \approx 11.8$, 5.4 Hz, 1H), 2.83 (s, 3H), 2.43 (s, 3H), 2.08 (virt. dt, $J \approx 11.8$, 5.4 Hz, 1H), 1.87 – 1.70 (m, 1H).

**$^{13}$C NMR** (101 MHz, CDCl$_3$) $\delta$ 151.3, 143.8, 138.3, 136.5, 130.7, 129.9, 128.6, 127.7, 127.4, 127.2, 124.8, 124.4, 117.9, 107.2, 94.2, 84.5, 52.8, 48.2, 47.4, 39.6, 21.7.

**IR (KBr/cm$^{-1}$)** 3394.6, 3030.3, 2925.3, 2853.5, 1733.7, 1607.1, 1489.8, 1452.7, 1349.3, 1297.4, 1160.7, 1091.1, 928.1, 813.0, 738.5, 664.7.

**HRMS (ESI):** C$_{25}$H$_{27}$N$_2$O$_3$S [(M+H)$^+$]: calcd.: 435.1737; found: 435.1739.

---

S10
8-Benzyl-3a-ethoxy-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole 2o

\[
\begin{aligned}
&\text{O} \\
&\text{N} \\
&\text{H} \\
&\text{Ts} \\
&\text{Bn} \\
\end{aligned}
\]

2o

Compound 2o was synthesized following the general procedure.

A white solid, 70.0 mg, 78% yield.

\text{m.p.:} 127 – 129 °C.

\text{TLC:} R_f = 0.60 (Hexane/EtOAc = 3:1) [UV, KMnO_4].

\text{^1H NMR (400 MHz, CDCl}_3\delta 7.79 – 7.77 (m, 2H), 7.35 – 7.33 (m, 2H), 7.30 (\text{virt. t}, J \approx 7.9 \text{ Hz, 4H}), 7.26 (s, 1H), 7.13 (\text{virt. t}, J \approx 7.7 \text{ Hz, 1H}), 7.07 (d, J = 7.3 \text{ Hz, 1H}), 6.69 (\text{virt. t}, J \approx 7.2 \text{ Hz, 1H}), 6.45 (d, J = 7.9 \text{ Hz, 1H}), 5.54 (s, 1H), 4.68 (s, 2H), 3.69 – 3.58 (m, 1H), 3.18 (\text{virt. td}, J \approx 11.6, 5.5 \text{ Hz, 1H}), 3.05 – 2.98 (m, 1H), 2.89 – 2.77 (m, 1H), 2.43 (s, 3H), 2.10 – 2.04 (m, 1H), 1.82 – 1.74 (m, 1H), 0.94 (\text{virt. t}, J \approx 6.5 \text{ Hz, 3H}).

\text{^13C NMR (101 MHz, CDCl}_3\delta 151.0, 143.8, 138.3, 136.5, 130.5, 129.8, 128.6, 127.7, 127.5, 127.2, 125.7, 124.2, 117.9, 107.2, 93.7, 85.0, 60.7, 48.2, 47.3, 39.9, 21.6, 15.5.

\text{IR (KBr/cm}^{-1}\text{)} 3393.9, 3030.1, 2956.4, 2924.1, 2853.9, 1737.3, 1606.8, 1489.2, 1451.4, 1349.6, 1161.1, 1073.6, 937.8, 813.1, 737.8, 664.5.

\text{HRMS (ESI):} C_{26}H_{28}N_2NaO_3S \ [(\text{M+Na})^+]: \text{calcd.: 471.1713; found: 471.1716.}

8-Benzyl-3a-isopropoxy-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole 2p

\[
\begin{aligned}
&\text{O} \\
&\text{N} \\
&\text{H} \\
&\text{Ts} \\
&\text{Bn} \\
\end{aligned}
\]

2p

Compound 2p was synthesized following the general procedure.

A pink liquid, 49.1 mg, 53% yield.

\text{TLC:} R_f = 0.59 (Hexane/EtOAc = 3:1) [UV, KMnO_4].

\text{^1H NMR (400 MHz, CDCl}_3\delta 7.79 – 7.77 (m, 2H), 7.35 – 7.33 (m, 2H), 7.34 – 7.26 (m, 5H), 7.19 – 7.09 (m, 2H), 6.69 (\text{virt. t}, J \approx 7.3 \text{ Hz, 1H}), 6.50 (d, J = 8.1 \text{ Hz, 1H}), 5.47 (s, 1H), 4.69 (dd, J = 41.5, 16.2 Hz, 2H), 3.62 (dd, J = 12.2, 7.7 Hz, 1H), 3.22 – 3.15 (m, 1H), 3.06 (\text{virt. td}, J \approx 12.5, 5.1 \text{ Hz, 1H}), 2.43 (s, 3H), 2.05 (dd, J = 12.0, 4.7 Hz, 1H), 1.73 – 1.67 (m, 1H), 0.86 – 0.77 (m, 3H).
$^{13}$C NMR (101 MHz, CDCl$_3$) δ 151.4, 143.8, 138.4, 136.7, 130.6, 129.6, 127.8, 127.4, 126.4, 124.9, 117.7, 107.0, 93.5, 85.4, 67.7, 47.9, 46.9, 40.3, 24.3, 23.8, 21.7.

IR (KBr/cm$^{-1}$) 3030.0, 2960.2, 2925.3, 1729.4, 1604.2, 1488.4, 1460.8, 1346.0, 1308.6, 1246.6, 1159.9, 1054.8, 946.9, 813.2, 747.8, 699.9.

HRMS (ESI): C$_{27}$H$_{30}$N$_2$NaO$_4$S [(M+Na)$^+$]: calcd.: 485.1869; found: 485.1872.

8-Benzyl-3a-butoxy-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole 2q

Compound 2q was synthesized following the general procedure.

A yellow liquid, 66.7 mg, 70% yield.

TLC: $R_f = 0.61$ (Hexane/EtOAc = 3:1) [UV, KMnO$_4$].

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.79 – 7.77 (m, 2H), 7.41 – 7.34 (m, 2H), 7.32 – 7.27 (m, 4H), 7.26 – 7.23 (m, 1H), 7.14 (virt. td, $J \approx 8.0$, 1.3 Hz, 1H), 7.10 – 7.02 (m, 1H), 6.69 (virt. td, $J \approx 8.3$, 1.3 Hz, 1H), 6.47 (d, $J = 8.0$ Hz, 1H), 5.48 (s, 1H), 4.73 – 4.64 (m, 2H), 3.67 – 3.61 (m, 1H), 3.18 (virt. td, $J \approx 11.9$, 5.6 Hz, 1H), 2.93 (virt. dt, $J \approx 8.8$, 6.5 Hz, 1H), 2.70 (virt. dt, $J \approx 8.8$, 6.5 Hz, 1H), 2.43 (s, 3H), 2.12 – 2.06 (m, 2H), 1.75 (virt. td, $J \approx 11.9$, 7.8 Hz, 1H), 1.31 – 1.20 (m, 3H), 1.18 – 1.08 (m, 2H), 0.80 (t, $J = 7.3$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 151.1, 143.7, 138.3, 136.5, 130.5, 129.8, 128.6, 127.7, 127.4, 127.2, 125.7, 124.3, 117.8, 107.1, 93.6, 84.8, 65.0, 48.1, 47.4, 39.8, 32.0, 21.6, 19.3, 13.9.

IR (KBr/cm$^{-1}$) 3391.8, 3030.4, 2956.9, 2925.9, 2869.3, 1607.3, 1489.6, 1462.0, 1349.9, 1161.5, 1088.0, 1048.7, 934.3, 813.0, 738.1, 664.2.

HRMS (ESI): C$_{28}$H$_{33}$N$_2$O$_3$S [(M+H)$^+$]: calcd.: 477.2206; found: 477.2214.

8-benzyl-3a-(hexyloxy)-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole 2r

Compound 2r was synthesized following the general procedure.

A yellow liquid, 67.6 mg, 67% yield.

TLC: $R_f = 0.63$ (Hexane/EtOAc = 3:1) [UV, KMnO$_4$].

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.79 – 7.77 (m, 2H), 7.41 – 7.35 (m, 2H), 7.34 – 7.27 (m, 4H), 7.26 – 7.23 (m, 1H), 7.14 (virt. td, $J = 7.9$, 1.3 Hz, 1H), 7.10 – 7.02 (m, 1H), 6.70 (td, $J = 7.9$, 1.3 Hz, 1H), 6.47 (d, $J = 8.0$ Hz, 1H), 5.49 (s, 1H), 4.73 – 4.64 (m, 2H), 3.67 – 3.61 (m, 1H), 3.18 (virt. td, $J \approx 11.9$, 5.6 Hz, 1H), 2.92 (virt. dt, $J \approx 8.8$, 6.4 Hz, 1H), 2.70 (dt, $J = 8.8$, 6.7 Hz, 1H), 2.43 (s, 3H), 2.10 – 2.04 (m, 1H), 1.79 – 1.71 (m, 1H), 1.31 – 1.24 (m, 4H), 1.19 – 1.06 (m, 4H), 0.88 (t, $J = 7.2$ Hz, 3H).
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 151.1, 143.7, 138.3, 136.5, 130.5, 129.8, 128.6, 127.7, 127.4, 127.2, 125.7, 124.3, 117.8, 107.1, 93.6, 84.8, 65.4, 48.1, 47.3, 39.8, 31.7, 29.9, 25.8, 22.7, 21.6, 14.2.

IR (KBr/cm$^{-1}$) 3059.1, 3030.5, 2927.1, 2857.7, 1739.4, 1607.6, 1489.7, 1462.0, 1350.7, 1161.7, 1090.1, 937.3, 812.7, 739.5, 664.2.

HRMS (ESI): C$_{30}$H$_{36}$N$_2$NaO$_3$S [(M+Na)$^+$]: calcd.: 527.2339; found: 527.2340.

8-benzyl-3a-methoxy-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indole 4

Compound 4 was synthesized following the general procedure. A white solid, 36.6 mg, 65% yield.

m.p.: 72 – 74 °C.

TLC: $R_f$ = 0.88 (Hexane/EtOAc = 3:1) [UV, KMnO$_4$].

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 – 7.28 (m, 4H), 7.26 – 7.20 (m, 2H), 7.14 (virt. t, $J \approx$ 7.5 Hz, 1H), 6.75 (t, $J = 7.5$ Hz, 1H), 6.41 (d, $J = 7.9$ Hz, 1H), 5.43 (s, 1H), 4.58 – 4.44 (m, 2H), 4.05 (virt. t, $J \approx$ 7.9 Hz, 1H), 3.68 – 3.60 (m, 1H), 3.09 (s, 3H), 2.47 (virt. td, $J \approx$ 11.6, 7.7 Hz, 1H), 2.30 (dd, $J = 11.8, 4.2$ Hz, 1H).$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 151.6, 138.2, 130.3, 128.6, 127.4, 127.2, 126.2, 124.7, 117.9, 106.2, 98.6, 93.6, 66.9, 53.2, 48.6, 41.0.

IR (KBr/cm$^{-1}$) 3029.3, 2932.9, 2870.9, 1735.5, 1607.8, 1490.3, 1458.8, 1358.8, 1316.8, 1130.9, 1112.4, 1057.4, 944.8, 742.8, 699.3.

HRMS (ESI): C$_{18}$H$_{20}$NO$_2$ [(M+H)$^+$]: calcd.: 282.1489; found: 282.1491.

8-Benzyl-3a-methoxy-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indol-2-one 6

Compound 6 was synthesized following the general procedure. A liquid, 20.1 mg, 34% yield.

TLC: $R_f$ = 0.83 (Hexane/EtOAc = 3:1) [UV, KMnO$_4$].

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.61 (d, $J = 7.6$ Hz, 1H), 7.30 – 7.22 (m, 4H), 7.21 – 7.07 (m, 5H), 5.26 (s, 2H), 3.77 (s, 2H), 3.69 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 172.5, 137.5, 136.6, 128.8, 128.0, 127.7, 127.2, 126.9, 122.1, 119.5, 119.2, 109.8, 107.6, 52.0, 50.1, 31.2.

IR (KBr/cm$^{-1}$) 3029.8, 2952.2, 2925.0, 1737.5, 1613.8, 1466.3, 1356.6, 1334.3, 1255.7, 1160.6, 1012.7, 740.6, 700.8.

HRMS (ESI): C$_{18}$H$_{17}$NNaO$_3$ [(M+Na)$^+$]: calcd.: 318.1101; found: 318.1104.
D. Scale-up Reaction and Synthesis of CPC-1

A 500 mL round bottom flask was charged with I₂ (114.3 mg, 10 mol %), substrate 1 (4.5 mmol, 1.49 g, 1.0 equiv) and methanol (250 mL), then TBHP (70% in water, 1.16 mL, 9.0 mmol, 2.0 equiv) was slowly added. The reaction mixture was heat to reflux for 3 h before cooled down to room temperature. Saturated aqueous Na₂S₂O₃ (100 mL) solution was slowly introduced and the resulting mixture was extracted with EtOAc (3 × 100 mL). The combined organic layers were dried over Na₂SO₄, filtered, concentrated under reduced pressure and the residue was purified by chromatography on silica gel (eluent: Hexane/EtOAc, 30:1 to 10:1) to afford adduct 2a (1.19 g, 74%).

To a solution of compound 2a (1.19 g, 3.30 mmol) in anhydrous MeOH (200 mL) was added activated Mg (3.96 g, 165 mmol). Then the reaction mixture was vigorously stirred at ambient temperature for 24 h and then filtered over celite. The filtrate was concentrated in vacuum to give intermediate 7 in quantitative yield. This intermediate was dissolved in MeOH (40 mL) was added formaldehyde (37% water solution, 0.43 mL) at 0 ℃. The reaction mixture was stirred for 5 h at room temperature. Then, NaBH₃CN (621.7 mg, 9.9 mmol) was added and the reaction was stirred for 2 h at room temperature. Then the reaction mixture was quenched with H₂O (50 mL), and extracted with EtOAc. The organic layers were combined and dried over Na₂SO₄, filtered, concentrated in vacuum. The residue was purified by chromatography on silica gel (eluent: Hexane/EtOAc, 20:1 to 5:1) to afford CPC-1 as an oil (0.59 g, 82%).

**TLC:** $R_f = 0.24$ (DCM/MeOH = 20:1) [UV, KMnO₄].

**¹H NMR** (600 MHz, CDCl₃) δ 7.24 – 7.16 (m, 2H), 6.74 (virt. td, $J \approx$ 7.4, 1.0 Hz, 1H), 6.45 (d, $J$ = 7.9 Hz, 1H), 4.84 (s, 1H), 3.24 – 3.15 (m, 1H), 3.11 (s, 3H), 2.92 (s, 3H), 2.84 – 2.76 (m, 1H), 2.63 – 2.60 (m, 1H), 2.58 (s, 3H), 2.20 – 2.16 (m, 1H).

**¹³C NMR** (101 MHz, CDCl₃) δ 153.11, 129.80, 127.98, 124.10, 118.04, 107.87, 94.03, 91.71, 52.52, 52.45, 39.29, 38.60, 36.32.

The spectra data are matched with those reported².

---

E. X-Ray crystallographic analysis of 2a

Table 1 Crystal data and structure refinement for T.

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Radiation MoKα (λ = 0.71073)
2Θ range for data collection: 2.124 to 52.466
Index ranges: -23 ≤ h ≤ 21, -9 ≤ k ≤ 9, -15 ≤ l ≤ 10
Reflections collected: 13043
Independent reflections: 3282 [Rint = 0.0634, Rsigma = 0.0777]
Data/restraints/parameters: 3282/0/310
Goodness-of-fit on F2: 1.018
Final R indexes [I>=2σ (I)]: R1 = 0.0799, wR2 = 0.1827
Final R indexes [all data]: R1 = 0.1509, wR2 = 0.2228
Largest diff. peak/hole / e Å⁻³: 1.35/-0.32

F. Mechanistic study

A 50 mL round bottom flask was charged with I₂ (5.1 mg, 10 mol %), tryptamine 1a (0.2 mmol, 65.6 mg, 1.0 equiv) and MeOH (12 mL), then TBHP (70% in water, 57.2 μL, 0.4 mmol, 2.0 equiv) and TEMPO (0.2 mmol, 31.2 mg) was added. The reaction mixture was heat to reflux for 3 h before cooled down to room temperature. Saturated aqueous Na₂S₂O₃ (10 mL) solution was slowly introduced and the resulting mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over Na₂SO₄, filtered, concentrated under reduced pressure and the residue was purified by chromatography on silica gel (eluent: Hexane/EtOAc, 30:1 to 10:1) to afford methoxypyridoindolenine 2a (48.8 mg, 68% yield)

When TEMPO (1.0 mmol, 156 mg) was used by following the same protocol described above, the product 2a was isolated in 65% yield (46.5 mg). These outcomes rule out the possibility of a radical process.
G. $^1$H and $^{13}$C NMR spectra data of all products