Supporting Information

Gold(I)-Catalyzed Tandem Cyclization Approach to Tetracyclic Indolines

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I. General information

Unless otherwise noted, reagents were obtained commercially and used without further purification. CH$_2$Cl$_2$ was distilled from CaH$_2$ under a nitrogen atmosphere. THF was distilled from sodium-benzophenone under a nitrogen atmosphere. Toluene was distilled from sodium under a nitrogen atmosphere. Thin-layer chromatography (TLC) analysis of reaction mixtures was performed on Dynamicadsorbents silica gel F-254 TLC plates. Flash chromatography was carried out on Zeoprep 60 ECO silica gel. $^1$H and $^{13}$C NMR spectra were recorded with Varian INOVA 400, 500 and Bruker Avance-III 300 spectrometers. Mass spectral and analytical data were obtained via the PE SCIEX/ABI API QSTAR Pulsar i Hybrid LC/MS/MS, Applied Biosystems operated by the Central Analytical Laboratory, University of Colorado at Boulder. Infrared (IR) spectra were recorded on a Thermo Nicolet Avatar 370 FT-IR spectrometer. Melting point (mp) determinations were performed by using a Thomas Hoover capillary melting point apparatus and are uncorrected. High performance liquid chromatography (HPLC) analyses of chiral compounds were performed using a ChiralCel OD column (250 x 4.6 mm) and ChiralPak IA column (250 x 4.6 mm). Compounds were detected by monitoring UV absorbance at 254 nm. Optical rotations were determined on a JASCO 1030 polarimeter at 25 °C. X-Ray crystallographic analysis was carried out by Dr. Joseph Reibenspies at the X-ray Diffraction Laboratory, Texas A & M University.
II. General preparation of alkenylindoles (5a-1 – 5j-1) and characterization data

\[(E)\)-Methyl 2-(3-ethoxy-3-oxoprop-1-enyl)-3-ethyl-1H-indole-1-carboxylate (5a-1):\]\(^{S1}\)

To a solution of the protected indole (1.02 g, 5.0 mmol) in 1, 4-dioxane/AcOH (3:1, v:v, 10.0 mL) was added Pd(OAc)\(_2\) (23 mg, 0.10 mmol), tert-butyl benzoyl peroxide (1.3 g, 6.5 mmol) and ethyl acrylate (2.9 mL, 20.0 mmol). The resulting mixture was heated to 80 °C under N\(_2\) atmosphere for 24 h before it was cooled to RT, diluted with ethyl acetate, and filtered through a pad of celite. The filtrate was washed with saturated aqueous NaHCO\(_3\), dried over anhydrous Na\(_2\)SO\(_4\), and concentrated in vacuo to give a crude oil, which was purified by column chromatography (hexanes/ethyl acetate = 30:1) to afford 5a-1 (1.10 g, 3.6 mmol) as a white solid in 72% yield: m.p. 65–66 ºC; IR (thin film): \(\nu\) 2967, 1740, 1713, 1629, 1455, 1441, 1359, 1176, 1037 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.11 (d, \(J\) = 8.3 Hz, 1H), 8.06 (d, \(J\) = 16.1 Hz, 1H), 7.58 (d, \(J\) = 7.8 Hz, 1H), 7.62 – 7.56 (m, 1H), 7.31–7.27 (m, 1H), 6.11 (d, \(J\) = 16.1 Hz, 1H), 4.29 (q, \(J\) = 7.1 Hz, 2H), 4.05 (s, 3H), 2.84 (q, \(J\) = 7.6 Hz, 2H), 1.36 (t, \(J\) = 7.1 Hz, 3H), 1.31 (t, \(J\) = 7.6 Hz, 3H) ppm; \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 166.92, 152.55, 136.54, 135.87, 131.00, 129.89, 127.31, 126.16, 123.43, 120.49, 119.73, 115.92, 60.84, 54.09, 18.31, 15.21, 14.56 ppm; HRMS (ESI): \(m/z\) Calcd for C\(_{17}\)H\(_{19}\)NNaO\(_4\) \([M+Na]^+\) 324.1206, Found 324.1196.

\[(E)\)-Methyl 2-(3-tert-butoxy-3-oxoprop-1-enyl)-3-methyl-1H-indole-1-carboxylate (5b-1):\]

A colorless oil was obtained in 75% yield by following general procedure. IR (thin film): \(\nu\) 3359, 3053, 2977, 1698, 1626, 1455, 1145, 1065, 1025 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.10 (d, \(J\) = 8.4 Hz, 1H), 8.03 (d, \(J\) = 16.0 Hz, 1H), 7.59 – 7.52 (m, 1H), 7.39 – 7.34 (m, 1H), 7.32 – 7.27 (m, 1H), 6.03 (d, \(J\) = 16.0 Hz, 1H), 4.05 (s, 3H), 2.84 (q, \(J\) = 7.6 Hz, 2H), 1.36 (t, \(J\) = 7.1 Hz, 3H), 1.31 (t, \(J\) = 7.6 Hz, 3H) ppm; \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 166.18, 152.39, 136.19, 134.88, 131.59, 130.70, 126.02, 123.39, 123.23, 120.68, 119.52, 115.71, 80.69, 53.93, 28.38, 10.78 ppm; HRMS (ESI): \(m/z\) Calcd for C\(_{18}\)H\(_{21}\)NNaO\(_4\) \([M+Na]^+\) 338.1362, Found 338.1372.

\[(E)\)-Methyl 2-(3-tert-butoxy-3-oxoprop-1-enyl)-1H-indole-1-carboxylate (5c-1):\]

\[\text{A}\]

colorless oil was obtained in 71% yield by following general procedure. IR (thin film): ν = 2977, 1715, 1625, 1440, 1368, 1160 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.18 (dd, J = 15.8 Hz, 0.9 Hz, 1H), 8.13 (dd, J = 8.5 Hz, 0.9 Hz, 1H), 7.55 (d, J = 7.9 Hz, 1H), 7.35 (dd, J = 8.5 Hz, 1.3 Hz, 1H), 7.30 – 7.26 (m, 1H), 6.97 (s, 1H), 6.34 (d, J = 15.8 Hz, 1H), 4.09 (s, 3H), 1.54 (s, 9H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 165.82, 152.08, 137.31, 134.63, 128.81, 125.66, 123.57, 121.73, 121.10, 115.82, 110.41, 80.55, 53.94, 28.23 ppm; HRMS (ESI): m/z: Calcd for C₁₇H₁₉NNaO₄ [M+Na]^+ 324.1206, Found 324.1192.

(E)-Methyl 2-(3-tert-butoxy-3-oxoprop-1-ynyl)-3-ethyl-5-methoxy-1H-indole-1-carboxylate (5d-1): A white solid was obtained in 78% yield by following general procedure. m.p. 116–118 ºC; IR (thin film): ν = 2971, 2934, 1737, 1705, 1625, 1479, 1366, 1144, 1025 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, J = 8.5 Hz, 1H), 7.96 (d, J = 16.1 Hz, 1H), 7.00 – 6.94 (m, 2H), 6.02 (d, J = 16.1 Hz, 1H), 4.03 (s, 3H), 3.88 (s, 3H), 2.80 (q, J = 7.6 Hz, 2H), 1.55 (s, 9H), 1.30 (t, J = 7.6 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 166.19, 156.29, 152.39, 134.82, 131.74, 131.13, 130.72, 126.61, 122.27, 116.74, 114.55, 101.88, 80.75, 55.84, 53.89, 28.39, 18.28, 15.00 ppm; HRMS (ESI): m/z: Calcd for C₂₀H₂₅NNaO₅ [M+Na]^+ 382.1624, Found 382.1623.

(E)-Tert-butyl 2-(3-butoxy-3-oxoprop-1-ynyl)-3-(2-(1, 3-dioxoisoindolin-2-yl)ethyl)-1H-indole-1-carboxylate (5f-1): A colorless oil was obtained in 73% yield by following general procedure. IR (thin film): ν = 2959, 1771, 1715, 1632, 1455, 1361, 1287, 1166, 1107 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.17 (d, J = 8.3 Hz, 1H), 7.97 (d, J = 16.2 Hz, 1H), 7.89 – 7.83 (m, 2H), 7.75 (d, J = 7.7 Hz, 1H), 7.73 – 7.68 (m, 2H), 7.35 (t, J = 7.3 Hz, 1H), 7.31 – 7.26 (m, 1H), 6.35 (d, J = 16.2 Hz, 1H), 4.25 (t, J = 6.7 Hz, 2H), 4.09 – 3.88 (m, 2H), 3.24 – 3.09 (m, 2H), 1.76 – 1.70 (m, 2H), 1.66 (s, 9H), 1.53 – 1.44 (m, 2H), 0.99 (t, J = 7.4 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 168.09, 166.75, 150.09, 136.58, 135.86, 134.04, 132.35, 132.16, 129.48, 126.02, 123.34, 120.65, 119.77, 119.37, 115.69, 84.72, 64.61, 37.74, 30.90, 28.26, 24.34, 19.29, 13.95 ppm; HRMS (ESI): m/z: Calcd for C₃₀H₃₂N₂NaO₆ [M+Na]^+ 539.2125, Found 539.2172.
(E)-Butyl 3-(3-methyl-1-(4-methylbenzene-sulfonyl)-1H-indol-2-yl)acrylate (5g-1): A colorless oil was obtained in 70% yield by following general procedure. IR (thin film): ν = 2959, 1712, 1450, 1372, 1311, 1175, 1133 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.27 – 8.21 (m, 2H), 7.57 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 7.8 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.30 – 7.26 (m, 1H), 7.13 (d, J = 8.2 Hz, 2H), 6.11 (d, J = 16.1 Hz, 1H), 4.27 (t, J = 6.7 Hz, 2H), 2.30 – 2.32 (m, 6H), 1.75 (dt, J = 14.6 Hz, 6.8 Hz, 2H), 1.52 – 1.43 (m, 2H), 1.00 (t, J = 7.4 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 166.62, 145.00, 137.20, 135.00, 134.64, 131.83, 131.49, 129.74, 126.77, 126.56, 124.15, 123.43, 122.55, 119.93, 115.49, 64.83, 30.88, 21.66, 19.36, 13.94, 11.04 ppm; HRMS (ESI): m/z: Calcd for C₂₃H₂₅NNaO₄S [M+Na]^+ 434.1396, Found 434.1401.

(E)-Butyl 3-(3-ethyl-5-methoxy-1-(4-methylbenzenesulfonyl)-1H-indol-2-yl)acrylate (5h-1): A white solid was obtained in 76% yield by following general procedure. m.p. 146–147 °C; IR (thin film): ν = 2954, 1713, 1630, 1540, 1311, 1176, 1163 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.15 (d, J = 16.1 Hz, 1H), 8.10 (d, J = 9.1 Hz, 1H), 7.50 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 6.98 (dd, J = 9.1 Hz , 2.5 Hz, 1H), 6.85 (d, J = 2.5 Hz, 1H), 6.10 (d, J = 16.1 Hz, 1H), 4.26 (t, J = 6.8 Hz, 2H), 3.84 (s, 3H), 2.71 (q, J = 7.6 Hz, 2H), 2.30 (s, 3H), 1.74 (dt, J = 14.6 Hz, 6.8 Hz, 2H), 1.53 – 1.41 (m, 2H), 1.16 (t, J = 7.6 Hz, 3H), 0.99 (t, J = 7.4 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 166.71, 157.05, 144.89, 134.70, 134.64, 132.28, 131.93, 130.09, 129.74, 126.83, 121.72, 116.92, 115.20, 102.21, 64.93, 55.83, 30.94, 21.74, 19.42, 18.52, 14.66, 14.01 ppm; HRMS (ESI): m/z: Calcd for C₂₅H₂₉NNaO₅S [M+Na]^+ 478.1659, Found 478.1664.

(E)-Butyl 3-(3-(2-(1,3-dioxoisindolin-2-yl)ethyl)-1-(4-methylbenzene-sulfonyl)-1H-indol-2-yl)acrylate (5j-1): A white solid was obtained in 76% yield by following general procedure. m.p. 149–151 °C; IR (thin film): ν = 2959, 2873, 1771, 1713, 1632, 1449, 1174, 1090 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.21 (d, J = 8.4 Hz, 1H), 8.13 (d, J = 16.2 Hz, 1H), 7.87 – 7.78 (m, 2H), 7.75 – 7.69 (m, 2H), 7.67 (d, J = 7.7 Hz, 1H), 7.58 (d, J = 8.4 Hz, 2H), 7.40 – 7.34 (m, 1H), 7.32 – 7.26 (m, 1H), 7.15 (d, J = 8.4 Hz, 2H), 6.38 (d, J = 16.2 Hz, 1H), 4.28 (t, J = 6.8 Hz, 2H), 3.84 – 3.79 (m, 2H), 3.14 – 3.06 (m, 2H), 2.30 – 2.32 (m, 6H), 1.75 (dt, J = 14.6 Hz, 6.8 Hz, 2H), 1.52 – 1.43 (m, 2H), 1.00 (t, J = 7.4 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 166.62, 145.00, 137.20, 135.00, 134.64, 131.83, 131.49, 129.74, 126.77, 126.56, 124.15, 123.43, 122.55, 119.93, 115.49, 64.83, 30.88, 21.66, 19.36, 13.94, 11.04 ppm; HRMS (ESI): m/z: Calcd for C₂₃H₂₅NNaO₄S [M+Na]^+ 434.1396, Found 434.1401.
2.32 (s, 3H), 1.76 (dt, J = 14.6 Hz, 6.8 Hz, 2H), 1.59 – 1.40 (m, 2H), 1.01 (t, J = 7.4 Hz, 3H) ppm; $^{13}$C NMR (101 MHz, CDCl$_3$) δ 168.11, 166.37, 145.16, 137.27, 135.05, 134.21, 133.78, 133.01, 132.14, 130.48, 129.86, 126.87, 126.66, 124.46, 123.49, 123.02, 122.71, 119.89, 115.59, 64.95, 37.42, 30.93, 24.55, 21.78, 19.39, 14.05 ppm; HRMS (ESI): m/z: Calcd for C$_{32}$H$_{30}$N$_2$NaO$_6$S [M+Na]$^+$ 593.1717, Found 593.1733.

(E)-Tert-butyl 2-(3-butoxy-3-oxoprop-1-enyl)-3-methyl-1H-indole-1-carboxylate (5o-1): A white solid was obtained in 72% yield by following general procedure. m.p. 45–46 ºC; IR (thin film): ν = 2959, 2931, 2872, 1731, 1630, 1455, 1354, 1331, 1283, 1145, 1065 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.19 – 8.13 (m, 1H), 8.08 (dd, J = 16.1 Hz, 0.7 Hz, 1H), 7.54 (d, J = 7.8 Hz, 1H), 7.36 (ddd, J = 8.4 Hz, 7.2 Hz, 1.3 Hz, 1H), 7.31 – 7.25 (m, 1H), 6.10 (d, J = 16.1 Hz, 1H), 4.23 (t, J = 6.7 Hz, 2H), 2.39 (s, 3H), 1.78 – 1.67 (m, 2H), 1.67 (s, 9H), 1.52 – 1.38 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H) ppm; $^{13}$C NMR (101 MHz, CDCl$_3$) δ 167.06, 150.36, 136.77, 136.61, 131.41, 130.51, 126.01, 123.04, 120.56, 120.30, 119.50, 115.66, 84.50, 64.62, 30.96, 28.35, 19.38, 13.95, 10.73 ppm; HRMS (ESI): m/z: Calcd for C$_{21}$H$_{27}$NNaO$_4$ [M+Na]$^+$ 380.1832, Found 380.1832.
III. General preparation of alkynylindole substrates 5a-5j (entries 1-10, Table 2) and characterization data

Methyl 2-(3-hydroxypent-4-ynyl)-3-methyl-1H-indole-1-carboxylate (5a, entry 1, Table 2): To a solution of 5a-1 (1.1 g, 3.6 mmol) in anhydrous methanol (10.0 mL) was added 10% Pd/C (110 mg). The resulting mixture was stirred under hydrogen atmosphere (56 psi) for 1 h before it was filtered through a short pad of silica gel to afford 5a-2, which was used for the next step without further purification.

5a-2 was dissolved in anhydrous dichloromethane and the solution was cooled to -78 °C before the addition of the solution of DIBAL-H (1.0 M in hexane, 4.3 mL, 4.3 mmol) dropwise. The reaction mixture was stirred for 2 h at -78 °C before it was treated with saturated aqueous solution of Rochelle salt (10.0 mL) at -78 °C. After being stirred for 1 h at RT, the layers were separated. The aqueous layer was extracted with ether, and the combined organic layers were washed with water and brine, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated in vacuo to give 5a-3 as a yellow oil, which was used for the next step without further purification.

A solution of nBuLi (1.6 M in hexanes, 4.5 mL, 7.2 mmol) was added to a solution of trimethylsilylacetylene (1.06 mL, 7.5 mmol) in anhydrous THF (20.0 mL) at -78 °C. The resulting mixture was stirred for 30 min before the addition of the solution of 5a-3 in anhydrous THF (3.0 mL) dropwise. The reaction mixture was stirred for 1 hour at the same temperature before it was quenched with water, and extracted with ethyl acetate. The combined organic layers were washed with water and brine, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated in vacuo to afford a yellow oil, which was then dissolved in anhydrous THF (10.0 mL) and cooled to 0 °C. Tetrabutylammonium fluoride (1.0 M in THF, 3.6 mL, 3.6 mmol) was added dropwise to the above solution, and the resulting mixture was stirred for 10 min at 0 °C. After the reaction was terminated by the addition of water (20.0 mL), the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na$_2$SO$_4$, and concentrated in vacuo to produce a crude oil, which was purified by column chromatography (hexanes/ethyl acetate = 5:1) to afford alkynylindole 5a (616 mg, 2.16 mmol) as a colorless oil in 60% yield over 4 steps:

IR (thin film): $\nu = 3288, 2963, 1731, 1458, 1442, 1360, 1330, 1216, 1136$ cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.05 (dd, $J = 7.1$ Hz, 2.1 Hz, 1H), 7.48 (dd, $J = 6.5$ Hz, 2.5 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.26 – 7.21 (m, 1H), 4.46 (td, $J = 6.1$ Hz, 2.9 Hz, 1H), 4.05 (s, 3H), 3.20 (m, 2H), 2.71 (q, $J = 7.6$ Hz, 2H), 2.53 – 2.49 (d, $J = 4.0$ Hz, 1H), 2.23 (d, $J = 5.5$ Hz, 1H), 2.05 (dt, $J = 10.8$ Hz, 6.6 Hz, 2H), 1.76 (t, $J = 7.6$ Hz, 3H) ppm; $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 152.76, 135.88, 135.40, 130.02, 123.98, 122.97, 122.11, 118.45, 115.95, 84.84, 73.22, 61.78, 53.69, 37.90, 22.28, 17.38, 15.13 ppm; HRMS (ESI): $m/z$: Calcd for...
Methyl 2-(3-hydroxypent-4-ynyl)-3-methyl-1H-indole-1-carboxylate (3, Scheme 1): A colorless oil was obtained in 68% yield by following general procedure. IR (thin film): \(\nu = 3435, 3288, 2955, 2864, 1732, 1459, 1379, 1254, 1221, 1136, 1057\ \text{cm}^{-1}\); \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)) \(\delta 8.06 – 8.02\) (m, 1H), 7.46 – 7.42 (m, 1H), 7.32 – 7.23 (m, 1H), 7.27 – 7.21 (m, 1H), 4.42 (qd, \(J = 6.2\ \text{Hz}, 2.0\ \text{Hz}, 1\text{H})\), 4.05 (s, 3H), 3.25 – 3.20 (m, 2H), 2.50 (d, \(J = 2.0\ \text{Hz}, 1\text{H})\), 2.23 (s, 3H), 2.09 – 2.00 (m, 2H) ppm; \(^{13}\text{C}\) NMR (101 MHz, CDCl\(_3\)) \(\delta 152.60, 135.68, 135.55, 130.83, 123.95, 122.90, 118.21, 115.70, 115.67, 84.92, 73.07, 61.49, 53.56, 37.31, 22.33, 8.73\ ppm; HRMS (ESI): \(m/z\): Calcd for C\(_{16}\)H\(_{17}\)NNaO\(_3\) [M+Na\(^+\)] 294.1101, Found 294.1094.

Methyl 2-(3-hydroxy-5-phenylpent-4-ynyl)-3-methyl-1H-indole-1-carboxylate (5b, entry 2, Table 2): A white solid was obtained in 70% yield by following general procedure. m.p. 91–92 °C; IR (thin film): \(\nu = 3435, 3051, 2954, 2863, 1732, 1459, 1354, 1220, 1135, 756\ \text{cm}^{-1}\); \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)) \(\delta 9.30 – 9.27\) (m, 1H), 8.07 – 8.02 (m, 1H), 7.47 – 7.43 (m, 2H), 7.42 – 7.37 (m, 3H), 7.29 – 7.26 (m, 1H), 7.26 – 7.24 (m, 1H), 4.64 (q, \(J = 6.2\ \text{Hz}, 1\text{H})\), 4.05 (s, 3H), 3.28 (td, \(J = 8.8\ \text{Hz}, 4.0\ \text{Hz}, 2\text{H})\), 2.26 (s, 3H), 2.13 (dd, \(J = 12.0\ \text{Hz}, 8.0\ \text{Hz}, 2\text{H})\) ppm; \(^{13}\text{C}\) NMR (101 MHz, CDCl\(_3\)) \(\delta 152.75, 135.94, 135.70, 131.83, 130.99, 128.56, 128.46, 124.07, 123.00, 122.74, 118.34, 115.83, 115.80, 90.08, 85.15, 62.37, 53.66, 37.66, 22.59, 8.91\ ppm; HRMS (ESI): \(m/z\): Calcd for C\(_{22}\)H\(_{21}\)NNaO\(_3\) [M+Na\(^+\)] 370.1414, Found 370.1426.

Methyl 2-(3-hydroxy-5-phenylpent-4-ynyl)-1H-indole-1-carboxylate (5c, entry 3, Table 2): A colorless oil was obtained in 58% yield by following general procedure. IR (thin film): \(\nu = 3434, 2954, 2853, 1739, 1456, 1332, 1214, 1059\ \text{cm}^{-1}\); \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)) \(\delta 8.07\) (d, \(J = 8.1\ \text{Hz}, 1\text{H})\), 7.47 (d, \(J = 7.1\ \text{Hz}, 1\text{H})\), 7.45 – 7.40 (m, 2H), 7.35 – 7.31 (m, 3H), 7.30 – 7.26 (m, 1H), 7.26 – 7.19 (m, 1H), 6.46 (s, 1H), 4.71 (q, \(J = 6.1\ \text{Hz}, 1\text{H})\), 4.06 (s, 3H), 3.30 – 3.24 (m, 2H), 2.26 – 2.19 (m, 2H), 2.11 (d, \(J = 5.4\ \text{Hz}, 1\text{H})\) ppm; \(^{13}\text{C}\) NMR (101 MHz, CDCl\(_3\)) \(\delta 152.72, 141.09, 136.61, 131.89, 129.56, 128.66,\)
128.50, 123.89, 123.27, 122.68, 120.11, 115.87, 108.66, 89.87, 85.42, 62.44, 53.80, 37.18, 25.86 ppm; HRMS (ESI): m/z: Calcd for C_{21}H_{19}NNaO_3 [M+Na]^+ 356.1257, Found 356.1252.

**Methyl 3-ethyl-2-(3-hydroxy-5-phenylpent-4-ynyl)-5-methoxy-1H-indole-1-carboxylate (5e, entry 5, Table 2):** A colorless oil was obtained in 74% yield by following general procedure. IR (thin film): ν = 3442, 2956, 1731, 1454, 1333, 1221, 1067 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, J = 9.0 Hz, 1H), 7.44 – 7.40 (m, 2H), 7.34 – 7.28 (m, 3H), 6.93 (d, J = 2.6 Hz, 1H), 6.86 (dd, J = 9.0 Hz, 2.6 Hz, 1H), 6.28 (q, J = 7.6 Hz, 2H), 2.68 (q, J = 7.6 Hz, 2H), 2.50 (d, J = 2.1 Hz, 1H), 2.04 (t, J = 8.0 Hz, 2H), 1.21 (t, J = 7.6 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 156.09, 152.61, 136.40, 131.80, 130.96, 130.49, 128.53, 128.44, 122.75, 121.91, 116.73, 111.86, 101.55, 90.07, 85.12, 62.44, 55.88, 53.57, 38.11, 22.57, 17.41, 14.99 ppm; HRMS (ESI): m/z: Calcd for C_{24}H_{25}NNaO₄ [M+Na]^+ 414.1676, Found 414.1667.

**Tert-butyl 3-(2-(1,3-dioxoisindolin-2-yl)ethyl)-2-(3-hydroxypent-4-ynyl)-1H-indole-1-carboxylate (5f, entry 6, Table 2):** A white solid was obtained in 65% yield by
following general procedure. m.p. 140–141 °C; IR (thin film): ν = 3466, 3287, 2930, 2359, 1770, 1457, 1365, 1328, 1161 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.09 – 8.04 (m, 1H), 7.88 – 7.84 (m, 2H), 7.76 – 7.71 (m, 2H), 7.68 (dt, J = 7.9 Hz, 3.1 Hz, 1H), 7.26 – 7.21 (m, 2H), 4.52 – 4.42 (m, 1H), 3.98 – 3.81 (m, 2H), 3.35 – 3.20 (m, 2H), 3.06 (t, J = 8.3 Hz, 2H), 2.91 (d, J = 6.1 Hz, 1H), 2.50 (d, J = 2.1 Hz, 1H), 2.28 – 2.10 (m, 2H), 1.70 (s, 9H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 151.95, 142.71, 141.91, 137.62, 132.89, 129.31, 128.08, 127.96, 126.94, 125.83, 123.79, 121.69, 118.14, 90.00, 82.26, 58.02, 48.51, 33.08, 31.33, 29.91, 28.39, 23.64, 21.61 ppm; HRMS (ESI): m/z: Calcd for C₂₈H₂₉N₂O₅ [M+H]⁺ 473.2086, Found 473.2088.

5-(3-Methyl-1-(4-methylbenzene-sulfonyl)-1H-indol-2-yl)pent-1-yne-3-ol (5g, entry 7, Table 2): A colorless oil was obtained in 72% yield by following general procedure. IR (thin film): ν = 3291, 2924, 1453, 1360, 1232, 1170, 1042 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.0 Hz, 1H), 7.29 – 7.23 (m, 2H), 7.14 (d, J = 8.2 Hz, 2H), 4.43 (m, 1H), 3.17 (td, J = 7.2 Hz, 3.0 Hz, 2H), 2.50 (d, J = 2.1 Hz, 1H), 2.31 (s, 3H), 2.22 – 2.10 (m, 5H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 144.75, 136.84, 135.93, 135.83, 131.60, 129.93, 126.41, 124.53, 123.71, 118.70, 117.98, 115.35, 84.72, 73.30, 61.65, 38.16, 22.20, 21.75, 9.16 ppm; HRMS (ESI): m/z: Calcd for C₂₁H₂₂NO₃S [M+H]⁺ 368.1315, Found 368.1317.

5-(3-Ethyl-5-methoxy-1-(4-methylbenzene-sulfonyl)-1H-indol-2-yl)pent-1-yne-3-ol (5h, entry 8, Table 2): A colorless oil was obtained in 71% yield by following general procedure. IR (thin film): ν = 3289, 2966, 1598, 1447, 1359, 1214, 1175, 1036 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.06 (dd, J = 9.0 Hz, 0.4 Hz, 1H), 7.51 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 6.87 (dd, J = 9.0 Hz, 2.6 Hz, 1H), 6.83 (d, J = 2.2 Hz, 1H), 4.47 (td, J = 6.3 Hz, 2.1 Hz, 1H), 3.83 (s, 3H), 3.22 – 3.04 (m, 2H), 2.60 (m, 2H), 2.51 (d, J = 2.1 Hz, 1H), 2.30 (s, 3H), 2.16 (td, J = 7.8 Hz, 6.4 Hz, 2H), 1.13 (t, J = 7.6 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 156.71, 144.60, 136.47, 135.61, 131.86, 131.62, 129.80, 126.31, 124.48, 116.47, 112.40, 101.85, 84.68, 73.28, 61.73, 55.83, 38.71, 22.28, 21.70, 17.66, 14.77 ppm; HRMS (ESI): m/z: Calcd for C₂₃H₂₅NNaO₄S [M+Na]⁺ 434.1397, Found 434.1400.
5-(3-Ethyl-5-methoxy-1-(4-methylbenzene-sulfonyl)-1H-indol-2-yl)-1-phenylpent-1-yn-3-ol (5i, entry 9, Table 2): A colorless oil was obtained in 77% yield by following general procedure. IR (thin film): \( \nu = 3345, 3027, 2942, 2876, 1603, 1496, 1453, 1046, 747 \text{ cm}^{-1} \); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \): 8.07 (d, \( J = 9.0 \text{ Hz}, 1 \text{H} \)), 7.55 – 7.50 (m, 2H), 7.47 – 7.41 (m, 2H), 7.34 – 7.29 (m, 3H), 7.11 (d, \( J = 8.4 \text{ Hz}, 2 \text{H} \)), 6.87 (dd, \( J = 9.0 \text{ Hz}, 2.6 \text{ Hz}, 1 \text{H} \)), 6.84 – 6.80 (m, 1H), 4.69 (t, \( J = 6.2 \text{ Hz}, 1 \text{H} \)), 3.83 (s, 3H), 3.27 – 3.10 (m, 2H), 2.62 (q, \( J = 7.6 \text{ Hz}, 2 \text{H} \)), 2.30 (s, 3H), 2.28 – 2.16 (m, 2H), 1.17 – 1.10 (m, 3H) ppm; \(^13\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \): 156.73, 144.57, 136.64, 135.75, 131.89, 131.69, 129.81, 128.58, 128.47, 126.35, 124.39, 122.79, 116.50, 112.39, 101.85, 89.87, 85.25, 62.49, 55.84, 38.97, 22.49, 21.72, 17.73, 14.79 ppm; HRMS (ESI): \( m/z \): Calcd for C\(_{29}\)H\(_{28}\)NNaO\(_4\)S \([M+Na]^+\) 510.1509, Found 510.1514.

2-(2-(2-(3-Hydroxypent-4-ynyl)-1-(4-methylbenzene-sulfonyl)-1H-indol-3-yl)ethyl)-isoindoline-1,3-dione (5j, entry 10, Table 2): A colorless oil was obtained in 69% yield by following general procedure. IR (thin film): \( \nu = 3349, 2963, 1713, 1596, 1447, 1358, 1218, 1180 \text{ cm}^{-1} \); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \): 8.19 – 8.15 (m, 1H), 7.89 – 7.78 (m, 2H), 7.77 – 7.70 (m, 2H), 7.65 – 7.60 (m, 1H), 7.57 (d, \( J = 8.0 \text{ Hz}, 2 \text{H} \)), 7.33 – 7.23 (m, 2H), 7.16 (d, \( J = 8.0 \text{ Hz}, 2 \text{H} \)), 4.50 (tdd, \( J = 6.8 \text{ Hz}, 4.6 \text{ Hz}, 2.1 \text{ Hz}, 1 \text{H} \)), 3.88 – 3.78 (m, 2H), 3.31 – 3.13 (m, 2H), 3.03 – 2.97 (m, 2H), 2.53 (d, \( J = 2.1 \text{ Hz}, 1 \text{H} \)), 2.33 (s, 3H), 2.28 – 2.11 (m, 2H) ppm; \(^13\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \): 168.46, 144.89, 137.56, 136.85, 131.98, 134.33, 132.19, 130.28, 130.02, 126.45, 124.73, 123.97, 123.58, 118.81, 118.01, 115.36, 84.71, 73.26, 61.53, 39.00, 37.77, 29.92, 23.89, 22.21, 21.79 ppm; HRMS (ESI): \( m/z \): Calcd for C\(_{30}\)H\(_{27}\)N\(_2\)O\(_5\)S \([M+H]^+\) 527.1635, Found 527.1637.
IV. General preparation of alkynylindoles containing nitrogen nucleophiles 5k-5n (entries 11-14, Table 2) and characterization data

Methyl 2-(3-azido-5-(trimethylsilyl)pent-4-ynyl)-3-ethyl-5-methoxy-1H-indole-1-carboxylate (5k-2): A solution of alcohol 5d-4 (1.94 g, 5.0 mmol) in anhydrous dichloromethane (10.0 mL) was cooled to -20 °C before triethylamine (1.70 mL, 12.0 mmol) was added dropwise. The mixture was stirred at -20 °C for 10 min; then tosyl chloride (0.47 mL, 6.0 mmol) was added over a period of 10 min. The resulting mixture was stirred at 0 °C for 2 h before quenched with saturated aqueous NaHCO₃ (10.0 mL) and extracted with CH₂Cl₂. The combined organic extracts were dried over anhydrous Na₂SO₄ and filtered through a pad of celite, and the solvent was removed in vacuo to yield crude 5k-1.

A mixture of 5k-1 and sodium azide (0.98 g, 15.0 mmol) in anhydrous DMF (20.0 mL) was stirred at RT for 12 h. After removal of DMF in vacuo, water was added to the reaction solution and the mixture was extracted with ethyl acetate. The combined extracts were dried over anhydrous Na₂SO₄ and concentrated in vacuo to give a crude oil, which was purified by column chromatography (hexanes/ethyl acetate = 20:1) to afford azide 5k-2 (1.24 g, 3.0 mmol) as a yellowish oil in 60% yield (2 steps): IR (thin film): ν = 2961, 2106, 1732, 1478, 1442, 1363, 1262, 1217, 1131, 845 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.95 (d, J = 9.0 Hz, 1H), 6.93 (d, J = 2.6 Hz, 1H), 6.87 (dd, J = 9.0 Hz, 2.6 Hz, 1H), 4.18 – 4.12 (m, 1H), 4.03 (s, 3H), 3.87 (s, 3H), 3.21 – 3.08 (m, 2H), 2.68 (q, J = 7.6 Hz, 2H), 2.00 (q, J = 7.4 Hz, 2H), 1.22 (t, J = 7.6 Hz, 3H), 0.22 (s, 9H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 156.13, 152.39, 135.55, 130.83, 130.52, 122.11, 116.73, 112.03, 112.01, 101.56, 100.48, 92.73, 55.88, 55.86, 53.53, 53.24, 35.51, 23.13, 17.38, 15.00, 0.05 ppm; HRMS (ESI): m/z: Calcd for C₂₁H₂₉Na₂NaO₃Si [M+Na]⁺ 435.1823, Found 435.1840.

2-(3-Azido-5-(trimethylsilyl)pent-4-ynyl)-3-ethyl-5-methoxy-1-tosyl-1H-indole(5m-2): A yellowish oil was obtained in 56% yield by following general procedure. IR (thin film): ν = 2964, 2106, 1599, 1475, 1362, 1216, 1035, 744 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, J = 9.0 Hz, 1H), 7.48 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 6.85 (dd, J = 9.0 Hz, 2.6 Hz, 1H), 6.81 (d, J = 2.4 Hz, 1H), 4.12 (t, J = 6.7 Hz, 1H), 3.81 (s, 3H), 3.14 – 2.99 (m, 2H), 2.58 (q, J = 7.6 Hz, 2H), 2.29 (s, 3H), 2.15 – 2.05 (m, 2H), 1.11 (t, J = 7.6 Hz, 3H), 0.20 (s, 9H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 156.75, 144.59, 135.87, 135.67, 131.77, 131.66, 129.80, 126.33, 124.68, 116.51, 112.53, 112.01, 101.87, 100.37.
92.70, 55.83, 55.81, 53.16, 36.26, 29.90, 23.03, 21.72, 17.68, 14.78, 0.07 ppm; HRMS (ESI): \( m/z \) Calcd for C\(_{26}\)H\(_{32}\)N\(_4\)NaO\(_3\)Si \([M+Na]^+\) 531.1857, Found 531.1843.

**Methyl 3-ethyl-5-methoxy-2-(3-(methoxycarbonylamino)pent-4-ynyl)-1H-indole-1-carboxylate (5k, entry 11, Table 2):** To the solution of the azide 5k-2 in anhydrous THF (10.0 mL) at RT was added triphenylphosphine (0.87 g, 3.3 mmol) and water (0.54 mL, 30.0 mmol). The resulting mixture was heated to 55 °C for 1.5 h before it was cooled to RT and concentrated in vacuo. The residue 5k-3 was then dissolved in anhydrous dichloromethane (10.0 mL) and cooled to 0 °C. To the cooled solution triethylamine (1.65 mL, 6.0 mmol) was added followed by the addition of methyl chloroformate (0.25 mL, 3.2 mmol). The resulting solution was stirred at RT for 3 h before quenched with saturated aqueous NaHCO\(_3\). The layers were separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na\(_2\)SO\(_4\), and the solvents were removed in vacuo to give the crude 5k-4, which was used for the next step without further purification.

Tetrabutylammonium fluoride (1.0 M in THF, 3.0 mL, 3.0 mmol) was added to a solution of 5k-4 in THF at 0 °C, and the resulting mixture was stirred for 10 min at 0 °C. After the reaction was terminated by the addition of water, the organic layer was extracted with ethyl acetate. The combined organic parts were washed with brine, dried over anhydrous Na\(_2\)SO\(_4\), and concentrated in vacuo to give a crude oil, which was purified by column chromatography (hexanes/ethyl acetate = 3:1) to afford propargyl carbamate 5k (715 mg, 1.92 mmol) as a colorless oil in 64% yield over 3 steps: IR (thin film): \( \nu = \) 3295, 2964, 1731, 1723, 1522, 1475, 1361, 1242 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 7.95 \) (d, \( J = 9.0 \) Hz, 1H), 6.94 (d, \( J = 2.5 \) Hz, 1H), 6.88 (dd, \( J = 9.0 \) Hz, 2.5 Hz, 1H), 5.25-5.15 (br, 1H), 4.60-4.50 (br, 1H), 4.05 (s, 3H), 3.88 (s, 3H), 3.72 (s, 3H), 3.17 – 3.04 (m, 2H), 2.67 (q, \( J = 7.6 \) Hz, 2H), 2.37 (d, \( J = 2.3 \) Hz, 1H), 2.04 – 1.94 (m, 2H), 1.22 (t, \( J = 7.6 \) Hz, 3H) ppm; \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta = 156.38, 156.13, 152.48, 135.86, 130.89, 130.43, 121.89, 116.75, 111.98, 101.55, 83.23, 77.43, 71.58, 55.90, 55.88, 53.60, 52.53, 43.31, 35.78, 23.10, 17.40, 15.07 ppm; HRMS (ESI): \( m/z \) Calcd for C\(_{22}\)H\(_{25}\)N\(_5\)O\(_5\) [M+H]\(^+\) 373.1758, Found 373.1759.
Methyl 3-ethyl-5-methoxy-2-(3-(4-methylphenylsulfonamido)pent-4-ynyl)-1H-indole-1-carboxylate (5l, entry 12, Table 2): A colorless oil was obtained in 69% yield by following general procedure. IR (thin film): \( \nu = 3274, 2961, 2929, 1731, 1607, 1478, 1442, 1332, 1161, 1090 \text{ cm}^{-1} \); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 7.92 (d, J = 9.0 \text{ Hz}, 1\text{H}), 7.77 (d, J = 6.4 \text{ Hz}, 2\text{H}), 7.27 (d, J = 6.4 \text{ Hz}, 2\text{H}), 6.92 (d, J = 2.6 \text{ Hz}, 1\text{H}), 6.86 (dd, J = 9.0 \text{ Hz}, 2.6 \text{ Hz}, 1\text{H}), 5.09 (d, J = 8.2 \text{ Hz}, 1\text{H}), 4.15 (qd, J = 6.7 \text{ Hz}, 2.3 \text{ Hz}, 1\text{H}), 4.02 (s, 3\text{H}), 3.87 (s, 3\text{H}), 3.17 – 3.00 (m, 2\text{H}), 2.62 (q, J = 7.6 \text{ Hz}, 2\text{H}), 2.41 (s, 3\text{H}), 2.15 (d, J = 2.3 \text{ Hz}, 1\text{H}), 1.99 – 1.96 (m, 2\text{H}), 1.17 (t, J = 7.6 \text{ Hz}, 3\text{H}) \text{ ppm}; \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta = 156.07, 152.39, 143.60, 137.36, 135.45, 130.77, 130.39, 129.62, 127.49, 121.97, 116.71, 111.99, 101.52, 81.86, 72.88, 55.85, 53.63, 45.38, 36.45, 22.87, 21.68, 17.32, 15.00 \text{ ppm}; \text{HRMS (ESI): } m/z: \text{ Calcd for C}_{25}\text{H}_{28}\text{N}_{2}\text{NaO}_{5}\text{S} [\text{M+Na}^+] 491.1611, \text{ Found 491.1614.}

Methyl 5-(3-ethyl-5-methoxy-1-(4-methylbenzene-sulfoyl)-1H-indol-2-yl)pent-1-ynylcarbamate (5m, entry 13, Table 2): A colorless oil was obtained in 52% yield by following general procedure. IR (thin film): \( \nu = 3294, 2965, 1723, 1599, 1520, 1475, 1360, 1246, 1163, 1047 \text{ cm}^{-1} \); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta = 8.05 (d, J = 9.0 \text{ Hz}, 1\text{H}), 7.49 (d, J = 8.0 \text{ Hz}, 2\text{H}), 7.13 (d, J = 8.0 \text{ Hz}, 2\text{H}), 6.87 (d, J = 9.0 \text{ Hz}, 2.5 \text{ Hz}, 1\text{H}), 6.83 (d, J = 2.5 \text{ Hz}, 1\text{H}), 5.18 (d, J = 7.2 \text{ Hz}, 1\text{H}), 4.55 – 4.45 (br, 1\text{H}), 3.83 (s, 3\text{H}), 3.72 (s, 3\text{H}), 3.10 – 2.96 (m, 2\text{H}), 2.57 (q, J = 7.6 \text{ Hz}, 2\text{H}), 2.34 (d, J = 2.3 \text{ Hz}, 1\text{H}), 2.31 (s, 3\text{H}), 2.19 – 2.06 (m, 2\text{H}), 1.12 (t, J = 7.6 \text{ Hz}, 3\text{H}) \text{ ppm}; \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta = 156.74, 156.50, 144.64, 143.98, 135.74, 131.72, 131.63, 129.84, 126.29, 124.36, 116.39, 112.54, 101.88, 83.18, 71.57, 55.82, 52.55, 43.24, 36.61, 23.11, 21.69, 17.68, 14.81 \text{ ppm}; \text{HRMS (ESI): } m/z: \text{ Calcd for C}_{25}\text{H}_{28}\text{N}_{2}\text{NaO}_{5}\text{S} [\text{M+Na}^+] 491.1611, \text{ Found 491.1599.}

Methyl 3-ethyl-5-methoxy-2-(3-(2-nitrophenylsulfonamido)pent-4-ynyl)-1H-indole-1-carboxylate (5n, entry 14, Table 2): A colorless oil was obtained in 65% yield by following general procedure. IR (thin film): \( \nu = 3286, 2962, 2932, 1728, 1608, 1541, 1478, 1363, 1170, 1132 \text{ cm}^{-1} \); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 8.24 – 8.15 (m, 1\text{H}), 7.95 – 7.92 (m, 2\text{H}), 7.78 – 7.70 (m, 2\text{H}), 6.94 (d, J = 2.3 \text{ Hz}, 1\text{H}), 6.89 (dd, J = 9.0 \text{ Hz}, 2.6 \text{ Hz}, 1\text{H}), 5.96 – 5.85 (br, 1\text{H}), 4.35 – 4.24 (br, 1\text{H}), 4.06 (s, 3\text{H}), 3.89 (s, 3\text{H}), 3.29 – 3.08 (m, 2\text{H}), 2.67 (q, J = 7.6 \text{ Hz}, 2\text{H}), 2.11 – 2.02 (m, 3\text{H}), 1.21 (t, J = 7.6 \text{ Hz}, 3\text{H}) \text{ ppm; } \(^{13}\)C
NMR (101 MHz, CDCl$_3$) $\delta$ 156.06, 152.33, 147.92, 135.16, 134.18, 133.84, 132.91, 131.66, 130.72, 130.37, 125.50, 122.08, 116.71, 112.07, 112.04, 101.48, 80.97, 73.40, 55.80, 53.65, 46.09, 36.26, 22.95, 17.34, 15.04 ppm; HRMS (ESI): $m/z$: Calcd for C$_{24}$H$_{26}$N$_3$O$_7$ [M+H]$^+$ 500.1486, Found 500.1473.
V. General procedure of gold(I)-catalyzed tandem cyclization reaction (Table 2)

\[
\begin{align*}
\text{Ph}_3\text{PAuCl} (2.5 \text{ mg, 0.005 mmol}) & \quad \text{to} \\
\text{AgSbF}_6 (1.7 \text{ mg, 0.005 mmol}) & \quad \text{in anhydrous dichloromethane (0.50 mL)}
\end{align*}
\]

at RT. The resulting catalyst solution was then added to a solution of substrate \(5a\) (28.5 mg, 0.10 mmol) in anhydrous dichloromethane (0.50 mL) dropwise at RT. The resulting mixture was kept stirring at RT until TLC showed that there was no starting material \(5a\) left (about 1 h). The reaction mixture was then filtered through a short pad of silica gel. The filtrate was concentrated in vacuo, and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to afford tetracyclic indoline \(6a\) (entry 1, Table 2, 23.7 mg, 0.083 mmol) as a colorless oil in 83% yield: IR (thin film): \(\nu = 2957, 2923, 1720, 1458, 1442, 1360, 1242, 1132 \text{ cm}^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.79 (d, J = 7.6 \text{ Hz}, 1\text{H}), 7.26 - 7.21 (m, 2\text{H}), 7.07 (td, J = 7.5 \text{ Hz}, 1.0 \text{ Hz}, 1\text{H}), 5.10 (d, J = 0.7 \text{ Hz}, 1\text{H}), 5.01 (s, 1\text{H}), 4.59 (d, J = 6.1 \text{ Hz}, 1\text{H}), 3.91 (s, 3\text{H}), 3.06 - 3.03 (m, 1\text{H}), 2.27 (tdd, J = 12.4 \text{ Hz}, 6.1 \text{ Hz}, 1\text{H}), 2.10 (ddd, J = 12.4 \text{ Hz}, 9.0 \text{ Hz}, 3.5 \text{ Hz}, 1\text{H}), 1.90 (dq, J = 15.2 \text{ Hz}, 7.6 \text{ Hz}, 1\text{H}), 1.79 (ddd, J = 12.2 \text{ Hz}, 9.1 \text{ Hz}, 5.5 \text{ Hz}, 1\text{H}), 1.72 - 1.60 (m, 1\text{H}), 0.60 (t, J = 7.4 \text{ Hz}, 3\text{H}) \text{ ppm}; \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 157.21, 154.02, 133.34, 128.04, 123.93, 123.29, 115.94, 105.62, 102.47, 77.15, 60.11, 53.09, 33.23, 30.82, 29.93, 23.54, 8.90 \text{ ppm}; \text{HRMS (ESI): } m/z \text{: Calcd for } C_{17}H_{20}NO_3 [M+H]^+ 286.1437, \text{ Found 286.1443.}
\]

**Tetracyclic indoline 4 (Scheme 1):** A white solid was obtained in 83% yield by following general procedure. m.p. 105–106 °C; IR (thin film): \(\nu = 2956, 2924, 1720, 1479, 1440, 1361, 1240, 1101 \text{ cm}^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.76 (d, J = 8.2 \text{ Hz}, 1\text{H}), 7.26 (d, J = 7.5 \text{ Hz}, 1\text{H}), 7.19 (td, J = 8.2 \text{ Hz}, 1.3 \text{ Hz}, 1\text{H}), 7.02 (t, J = 7.5 \text{ Hz}, 1\text{H}), 5.10 (s, 1\text{H}), 5.00 (s, 1\text{H}), 4.57 (t, J = 11.8 \text{ Hz}, 1\text{H}), 3.89 (s, 3\text{H}), 2.99 (td, J = 12.1 \text{ Hz}, 5.0 \text{ Hz}, 1\text{H}), 2.23 (tdd, J = 12.4 \text{ Hz}, 6.1 \text{ Hz}, 3.6 \text{ Hz}, 1\text{H}), 2.09 (ddd, J = 12.4 \text{ Hz}, 9.0 \text{ Hz}, 3.6 \text{ Hz}, 1\text{H}), 1.76 (ddd, J = 12.3 \text{ Hz}, 9.0 \text{ Hz}, 5.4 \text{ Hz}, 1\text{H}), 1.31 (s, 3\text{H}) \text{ ppm}; \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 156.91, 154.36, 141.66, 136.09, 127.94, 123.96, 122.88, 116.20, 106.05, 102.42, 77.28, 56.86, 53.11, 30.62, 26.25, 23.40 \text{ ppm}; \text{HRMS (ESI): } m/z \text{: Calcd for } C_{16}H_{17}NNaO_3 [M+Na]^+ 294.1101, \text{ Found 294.1090.
Tetracyclic indoline 6b (entry 2, Table 2): A colorless oil was obtained in 65% yield by following general procedure. IR (thin film): ν = 3581, 2923, 1715, 1463, 1360, 1236 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, J = 8.2 Hz, 1H), 7.44 – 7.33 (m, 5H), 7.15 – 7.08 (m, 1H), 6.79 (td, J = 7.5 Hz, 1.0, 1H), 6.59 (dd, J = 7.6 Hz, 0.9 Hz, 1H), 5.96 (d, J = 4.9 Hz, 1H), 4.55 (dd, J = 6.3 Hz, 5.0 Hz, 1H), 3.93 (s, 3H), 3.38 – 3.29 (m, 1H), 2.52 – 2.37 (m, 1H), 2.37 – 2.29 (m, 1H), 2.04 (ddd, J = 11.7 Hz, 9.2 Hz, 2.7 Hz, 1H), 1.48 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 154.37, 143.06, 139.55, 134.45, 129.07, 128.09, 128.36, 128.09, 126.66, 124.34, 115.48, 102.66, 72.79, 52.52, 33.82, 30.02, 26.17, 23.24 ppm; HRMS (ESI): m/z: Calcd for C₂₂H₂₁NNaO₃ [M+Na]⁺ 370.1414, Found 370.1409.

Tetracyclic indoline 6c (entry 3, Table 2): A colorless oil was obtained in 67% yield by following general procedure. IR (thin film): ν = 3608, 3583, 2924, 1714, 1477, 1358, 1259 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.78 (d, J = 7.6 Hz, 1H), 7.55 – 7.46 (m, 2H), 7.45 – 7.36 (m, 3H), 7.14 (t, J = 7.9 Hz, 1H), 6.75 (td, J = 7.9 Hz, 5.0 Hz, 1H), 6.50 (d, J = 7.5 Hz, 1H), 6.41 (dd, J = 4.7 Hz, 1.9 Hz, 1H), 4.74 – 4.61 (m, 1H), 4.11 – 4.14 (m, 1H), 3.94 (s, 3H), 3.42 (t, J = 11.9 Hz, 1H), 2.37 (ddd, J = 11.5 Hz, 7.0 Hz, 4.4 Hz, 1H), 2.12 (td, J = 9.2 Hz, 4.6 Hz, 1H), 2.00 (dt, J = 12.6 Hz, 8.4 Hz, 1H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 154.28, 142.97, 139.46, 134.36, 130.91, 129.48, 128.98, 128.36, 128.00, 126.57, 124.25, 123.19, 115.39, 99.91, 72.70, 52.43, 33.73, 29.93, 14.30 ppm; HRMS (ESI): m/z: Calcd for C₂₁H₁₉NNaO₃ [M+Na]⁺ 356.1257, Found 356.1250.

Tetracyclic indoline 6d (entry 4, Table 2): A colorless oil was obtained in 85% yield by following general procedure. IR (thin film): ν = 2964, 1720, 1484, 1367, 1114, 1087, 1025, 1065 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.66 (d, J = 8.9 Hz, 1H), 7.42 – 7.28 (m, 5H), 6.67 (dd, J = 8.9 Hz, 2.7 Hz, 1H), 6.18 (d, J = 2.7 Hz, 1H), 5.94 (d, J = 5.0 Hz, 1H), 4.53 – 4.49 (m, 1H), 3.90 (s, 3H), 3.56 (s, 3H), 3.36 (t, J = 10.7 Hz, 1H), 2.41 – 2.29 (m, 3H), 2.03 (dt, J = 11.5 Hz, 7.1 Hz, 2H), 1.95 (dt, J = 15.9 Hz, 7.9 Hz, 1H), 1.89 (dd, J = 14.1 Hz, 7.5 Hz, 1H), 0.54 (t, J = 7.4 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 157.12, 156.57, 153.92, 136.74, 134.82, 116.49, 112.24, 110.00, 109.97, 105.87, 102.49, 102.45, 77.10, 60.16, 55.87, 52.96, 33.11, 30.79, 23.59, 8.88 ppm; HRMS (ESI): m/z:
Calcd for C_{18}H_{21}NNaO_4 [M+Na]^+ 338.1362, Found 338.1353.

**Tetracyclic indoline 6e (entry 5, Table 2):** A colorless oil was obtained in 75% yield by following general procedure. IR (thin film): ν = 2925, 1713, 1481, 1362, 1272, 1100, 1045 cm^{-1}; ^1H NMR (500 MHz, CDCl_3) δ 7.66 (d, J = 8.2 Hz, 1H), 7.42 – 7.28 (m, 5H), 6.67 (dd, J = 8.2 Hz, 2.7 Hz, 1H), 6.18 (t, J = 2.7 Hz, 1H), 5.94 (d, J = 5.0 Hz, 1H), 4.53 – 4.49 (m, 1H), 3.90 (s, 3H), 3.56 (s, 3H), 3.36 (t, J = 10.7 Hz, 1H), 2.41 – 2.29 (m, 2H), 2.03 (dt, J = 11.5 Hz, 7.1 Hz, 1H), 1.95 (dt, J = 15.9 Hz, 7.9 Hz, 1H), 1.89 (dd, J = 14.1 Hz, 7.5 Hz, 1H), 0.54 (t, J = 7.4 Hz, 3H) ppm; ^13C NMR (101 MHz, CDCl_3) δ 154.99, 154.20, 141.31, 140.55, 136.66, 132.98, 130.78, 127.98, 115.88, 112.67, 110.84, 102.73, 71.23, 56.60, 55.63, 52.86, 33.38, 31.41, 30.00, 23.31, 9.42 ppm; HRMS (ESI): m/z: Calcd for C_{24}H_{26}NO_4 [M+H]^+ 392.1856, Found 392.1854.

**Tetracyclic indoline 6f (entry 6, Table 2):** A white solid was obtained in 84% yield by following general procedure. m.p. 165–167 ºC; IR (thin film): ν = 2978, 1772, 1713, 1475, 1458, 1360, 1163, 1094, 1025 cm^{-1}; ^1H NMR (400 MHz, CDCl_3) δ 7.80 – 7.76 (m, 3H), 7.72 – 7.65 (m, 2H), 7.36 (dd, J = 7.5 Hz, 1.0 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.11 (td, J = 8.0 Hz, 2.6 Hz, 1H), 5.10 (s, 1H), 5.01 (s, 1H), 4.59 (d, J = 6.0 Hz, 1H), 3.45 (td, J = 12.9 Hz, 4.1 Hz, 1H), 3.20 (td, J = 12.6 Hz, 5.5 Hz, 1H), 3.10 (ddd, J = 13.5 Hz, 12.1 Hz, 5.2 Hz, 1H), 2.44 (ddd, J = 12.4 Hz, 9.0 Hz, 3.4 Hz, 1H), 2.34 – 2.19 (m, 1H), 1.99 – 1.87 (m, 1H), 1.79 (ddd, J = 12.3 Hz, 9.1 Hz, 5.6 Hz, 1H), 1.63 (s, 9H) ppm; ^13C NMR (101 MHz, CDCl_3) δ 168.11, 156.65, 152.32, 143.06, 134.14, 132.18, 132.03, 128.47, 124.12, 123.32, 123.24, 116.26, 105.51, 102.78, 82.85, 58.44, 38.39, 33.93, 30.86, 29.90, 28.59, 23.63 ppm; HRMS (ESI): m/z: Calcd for C_{28}H_{29}N_2O_5 [M+H]^+ 473.2071, Found 473.2086.

**Tetracyclic indoline 6g (entry 7, Table 2):** A colorless oil was obtained in 85% yield by following general procedure. IR (thin film): ν = 2924, 1475, 1458, 1360, 1163, 1094, 1025 cm^{-1}; ^1H NMR (500 MHz, CDCl_3) δ 7.95 – 7.89 (m, 2H), 7.54 (d, J = 8.2 Hz, 1H), 7.24 – 7.21 (m, 2H), 7.18 – 7.14 (m, 1H), 7.05 – 6.99 (m, 1H), 5.07 (s, 1H), 4.98 (s, 1H),
4.56 (d, J = 6.0 Hz, 1H), 3.04 – 2.93 (m, 1H), 2.36 (s, 3H), 2.20 (ddd, J = 15.7 Hz, 8.9 Hz, 3.6 Hz, 2H), 1.78 – 1.70 (m, 1H), 1.23 (s, 3H) ppm; $^{13}$C NMR (101 MHz, CDCl$_3$) δ 156.36, 144.26, 141.37, 136.65, 136.15, 129.64, 128.08, 127.97, 124.22, 123.29, 114.95, 107.58, 102.61, 77.34, 57.66, 30.39, 25.55, 24.05, 21.79 ppm; HRMS (ESI): m/z: Calcd for C$_{21}$H$_{22}$NO$_3$S [M+H]$^+$ 368.1315, Found 368.1318.

Tetra cyclic indoline 6h (entry 8, Table 2): A colorless oil was obtained in 88% yield by following general procedure. IR (thin film): ν = 2934, 1475, 1456, 1359, 1162, 1099, 1027 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.95 – 7.90 (m, 2H), 7.43 (d, J = 8.9 Hz, 1H), 7.25 – 7.21 (m, 2H), 6.75 (d, J = 2.6 Hz, 1H), 6.70 (dd, J = 8.9 Hz, 2.7 Hz, 1H), 5.02 (s, 1H), 4.95 (s, 1H), 4.53 (d, J = 5.8 Hz, 1H), 3.74 (s, 3H), 3.06 – 2.93 (m, 1H), 2.36 (s, 3H), 2.25 – 2.17 (m, 2H), 1.83 (dq, J = 15.2 Hz, 7.6 Hz, 1H), 1.77 – 1.70 (m, 1H), 1.67 – 1.58 (m, 1H), 0.66 (t, J = 7.5 Hz, 3H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) δ 156.63, 156.55, 144.06, 136.83, 136.34, 134.70, 129.56, 129.55, 129.53, 128.20, 128.19, 128.17, 114.71, 112.34, 110.63, 107.49, 102.62, 77.29, 60.95, 55.88, 32.82, 30.41, 24.28, 21.76, 8.74 ppm; HRMS (ESI): m/z: Calcd for C$_{23}$H$_{25}$NNaO$_4$S [M+Na]$^+$ 434.1397, Found 434.1402.

Tetra cyclic indoline 6i (entry 9, Table 2): A colorless oil was obtained in 64% yield by following general procedure. IR (thin film): ν = 2941, 1472, 1456, 1364, 1160, 1099 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.95 – 8.02 (m, 2H), 7.53 (d, J = 8.1 Hz, 1H), 7.41 – 7.25 (m, 5H), 6.67 (dd, J = 8.1 Hz, 2.5 Hz, 1H), 6.15 (t, J = 2.5 Hz, 1H), 5.92 (d, J = 5.0 Hz, 1H), 4.52 – 4.43 (m, 1H), 3.56 (s, 3H), 3.36 (t, J = 10.8 Hz, 1H), 2.42 – 2.26 (m, 2H), 2.23 (s, 3H), 2.04 (dt, J = 11.5 Hz, 7.2 Hz, 2H), 1.95 (dt, J = 15.9 Hz, 7.6 Hz, 1H), 1.89 (dd, J = 14.2 Hz, 7.6 Hz, 1H), 0.54 (t, J = 7.4 Hz, 3H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$) δ 155.92, 141.24, 140.48, 136.59, 132.91, 130.71, 127.82, 127.61, 126.51, 124.23, 115.81, 112.60, 110.77, 102.66, 71.16, 56.53, 55.56, 52.79, 33.31, 31.34, 29.93, 23.24, 21.78, 9.35 ppm; HRMS (ESI): m/z: Calcd for C$_{29}$H$_{29}$NNaO$_4$S [M+Na]$^+$ 510.1509, Found 510.1503.

Tetra cyclic indoline 6j (entry 10, Table 2): A colorless oil was obtained in 82% yield
by following general procedure. IR (thin film): \( \nu = 2924, 1772, 1713, 1458, 1399, 1365, 1164, 1090, 1038 \text{ cm}^{-1} \); \(^1\text{H} \text{ NMR (400 MHz, CDCl}_3) \delta 7.98 (d, \text{J} = 8.4 \text{ Hz}, 2\text{H}), 7.79 (m, 2\text{H}), 7.69 (m, 2\text{H}), 7.57 (d, \text{J} = 8.2 \text{ Hz}, 1\text{H}), 7.32 (dd, \text{J} = 7.5 \text{ Hz}, 0.9 \text{ Hz}, 1\text{H}), 7.26 – 7.20 (m, 1\text{H}), 7.11 (td, \text{J} = 7.5 \text{ Hz}, 1.0 \text{ Hz}, 1\text{H}), 5.06 (s, 1\text{H}), 4.98 (s, 1\text{H}), 4.57 (d, \text{J} = 5.9 \text{ Hz}, 1\text{H}), 3.57 – 3.45 (m, 1\text{H}), 3.15 (dd, \text{J} = 12.9 \text{ Hz}, 5.7 \text{ Hz}, 1\text{H}), 2.60 (td, \text{J} = 9.2 \text{ Hz}, 4.5 \text{ Hz}, 1\text{H}), 2.35 – 2.26 (m, 4\text{H}), 2.17 (td, \text{J} = 13.1 \text{ Hz}, 4.9 \text{ Hz}, 1\text{H}), 1.98 – 1.89 (m, 1\text{H}), 1.84 – 1.73 (m, 1\text{H}) \text{ ppm}; \(^{13}\text{C} \text{ NMR (101 MHz, CDCl}_3) \delta 168.03, 155.80, 144.36, 142.27, 136.50, 134.17, 132.20, 131.89, 129.68, 128.67, 128.32, 124.62, 123.79, 123.37, 114.50, 106.94, 103.14, 59.44, 38.29, 33.61, 30.51, 29.93, 24.28, 21.77 ppm; HRMS (ESI): \text{m/z:} \text{Calcd for C}_{30}\text{H}_{27}\text{N}_{2}\text{O}_5\text{S [M+H]}^+ 527.1635, \text{Found 527.1636}. 

Tetracyclic indoline 6k (entry 11, Table 2): A colorless oil was obtained in 78% yield by following general procedure. IR (thin film): \( \nu = 3095, 1720, 1442, 1432, 1261, 1105, 1129 \text{ cm}^{-1} \); \(^1\text{H} \text{ NMR (400 MHz, CDCl}_3) \delta 7.74 (d, \text{J} = 8.3 \text{ Hz}, 1\text{H}), 6.92 (d, \text{J} = 2.6 \text{ Hz}, 1\text{H}), 6.79 (dd, \text{J} = 8.3 \text{ Hz}, 2.6 \text{ Hz}, 1\text{H}), 5.95 – 6.45 (br, 1\text{H}), 5.27 (s, 1\text{H}), 5.16 (s, 1\text{H}), 4.75 – 4.83 (br, 1\text{H}), 3.90 (s, 3\text{H}), 3.81 (s, 3\text{H}), 3.69 (s, 3\text{H}), 3.00 – 2.85 (m, 1\text{H}), 2.01-2.04 (m, 1\text{H}), 1.82 (t, \text{J} = 7.4 \text{ Hz}, 2\text{H}), 0.78 (t, \text{J} = 7.4 \text{ Hz}, 3\text{H}) \text{ ppm}; \(^{13}\text{C} \text{ NMR (101 MHz, CDCl}_3) \delta 156.65, 155.93, 153.08, 146.44, 144.36, 135.08, 134.42, 116.23, 111.87, 108.23, 105.31, 55.85, 53.32, 53.04, 52.46, 48.78, 35.19, 32.60, 29.91, 8.59 ppm; HRMS (ESI): \text{m/z:} \text{Calcd for C}_{20}\text{H}_{25}\text{N}_{2}\text{O}_5 \text{[M+H]}^+ 373.1758, \text{Found 373.1752}. 

Tetracyclic indoline 6l (entry 12, Table 2): A colorless oil was obtained in 75% yield by following general procedure. IR (thin film): \( \nu = 3274, 2923, 1713, 1481.71, 1275, 1158, 1093, 1035 \text{ cm}^{-1} \); \(^1\text{H} \text{ NMR (400 MHz, CDCl}_3) \delta 7.66 (m, 3\text{H}), 7.28 – 7.21 (m, 2\text{H}), 6.74 (dd, \text{J} = 8.9 \text{ Hz}, 2.7 \text{ Hz}, 1\text{H}), 6.70 (d, \text{J} = 2.6 \text{ Hz}, 1\text{H}), 5.92 (s, 1\text{H}), 5.20 (s, 1\text{H}), 5.10 (d, \text{J} = 1.2 \text{ Hz}, 1\text{H}), 4.59 (d, \text{J} = 9.0 \text{ Hz}, 1\text{H}), 4.33 (dd, \text{J} = 15.1 \text{ Hz}, 6.2 \text{ Hz}, 1\text{H}), 3.88 (s, 3\text{H}), 3.78 (s, 3\text{H}), 2.65 (ddd, \text{J} = 17.1 \text{ Hz}, 6.4 \text{ Hz}, 3.2 \text{ Hz}, 1\text{H}), 2.41 (s, 3\text{H}), 2.14 (dt, \text{J} = 17.1 \text{ Hz}, 6.0 \text{ Hz}, 1\text{H}), 1.79 – 1.68 (m, 1\text{H}), 1.66 – 1.57 (m, 1\text{H}), 0.62 (q, \text{J} = 7.1 \text{ Hz}, 3\text{H}) \text{ ppm}; \(^{13}\text{C} \text{ NMR (101 MHz, CDCl}_3) \delta 155.99, 153.01, 145.45, 144.24, 143.58, 138.12, 134.81, 134.53, 129.84, 127.23, 116.14, 111.99, 111.49, 111.5, 105.17, 60.63, 55.86, 53.06, 52.67, 52.04, 35.90, 32.74, 29.92, 29.59, 21.77, 21.29, 14.42, 8.60 ppm; HRMS (ESI): \text{m/z:} \text{Calcd for C}_{25}\text{H}_{29}\text{N}_{2}\text{O}_5 \text{S [M+H]}^+ 469.1792, \text{Found 469.1778}. 

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Tetracyclic indoline 6m (entry 13, Table 2): A white solid was obtained in 79% yield by following general procedure. m.p. 129–130 °C; IR (thin film): ν = 2924, 1724, 1525, 1476, 1363, 1252, 1171, 1088, 1037 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.79 (d, J = 8.8 Hz, 1H), 7.59 (d, J = 8.3 Hz, 2H), 7.51 – 7.44 (m, 1H), 7.19 (d, J = 8.1 Hz, 1H), 6.80– 6.82 (m, 2H), 6.01 (dd, J = 5.3 Hz, 3.3 Hz, 1H), 5.11 (s, 1H), 5.05 (s, 1H), 4.70 – 4.53 (m, 1H), 3.79 (s, 3H), 3.68 (s, 3H), 2.85 (dd, J = 17.7 Hz, 7.2 Hz, 3.3 Hz, 1H), 2.35 (s, 3H), 2.11 (dt, J = 17.7 Hz, 6.0 Hz, 1H), 1.35 – 1.27 (m, 1H), 0.60 – 0.53 (m, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 156.70, 156.56, 145.58, 144.80, 144.61, 135.49, 134.76, 134.63, 129.63, 129.39, 127.46, 116.93, 112.72, 112.05, 108.84, 108.27, 55.83, 54.01, 52.46, 48.54, 34.26, 32.71, 29.93, 21.77, 8.28 ppm; HRMS (ESI): m/z: Calcd for C₂₅H₂₈N₂NaO₅S [M+Na]⁺ 491.1611, Found 491.1598.

Tetracyclic indoline 6n (entry 14, Table 2): A colorless oil was obtained in 70% yield by following general procedure. IR (thin film): ν = 2923, 2852, 1714, 1539, 148, 1363, 1275, 1165 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.05 (dd, J = 7.8 Hz, 1.4 Hz, 1H), 7.70 (td, J = 9.5 Hz, 1H), 5.79 (d, J = 9.5 Hz, 1H), 5.32 (s, 1H), 5.18 (s, 1H), 4.55 (dt, J = 9.2 Hz, 4.5 Hz, 1H), 3.92 (s, 3H), 3.74 (s, 3H), 2.65 (dd, J = 16.6 Hz, 4.9 Hz, 3.1 Hz, 1H), 2.44 (ddd, J = 16.6 Hz, 7.1 Hz, 4.4 Hz, 1H), 1.71 (dq, J = 14.7 Hz, 7.3 Hz, 2H), 1.61 – 1.44 (m, 1H), 0.66 (t, J = 7.3 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 155.70, 152.94, 147.44, 145.25, 144.76, 135.02, 134.98, 134.63, 133.32, 132.56, 131.25, 125.67, 115.99, 113.80, 110.85, 109.87, 104.89, 60.63, 55.60, 54.88, 53.16, 51.46, 38.10, 29.93, 14.42, 8.91 ppm; HRMS (ESI): m/z: Calcd for C₂₄H₂₆N₃O₇S [M+H]⁺ 500.1486, Found 500.1481.

Tetracyclic indoline 6o (Scheme 2): A colorless oil was obtained in 80% yield by following general procedure. The ee of 6o was determined as 81% by chiral HPLC analysis (ChiralPak IA column, hexanes/iPrOH = 98:2, 0.50 mL/min, t₁ for major isomer is 9.7 min, for minor isomer is 15.1 min). [α]D = −26.5 cm³ g⁻¹ dm⁻¹ (c = 1.43 g cm⁻³ in EtOAc). IR (thin film): ν = 2975, 1715., 1478, 1461, 1366, 1317, 1246, 1164, 1100, 750 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.73 (d, J = 8.0 Hz, 1H), 7.28 – 7.26 (m, 1H), 7.20 – 7.18 (m, 1H), 7.14 (d, J = 8.0 Hz, 1H), 7.08 – 7.00 (m, 1H), 6.98 (d, J = 8.0 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 6.83 (dd, J = 7.1 Hz, 1H), 6.75 (dd, J = 7.1 Hz, 1H), 6.68 (dd, J = 7.1 Hz, 1H), 6.64 – 6.56 (m, 2H), 6.43 (d, J = 9.5 Hz, 1H), 5.59 (d, J = 9.5 Hz, 1H), 5.22 (s, 1H), 5.05 (s, 1H), 4.73 – 4.54 (m, 1H), 3.90 (s, 3H), 3.78 (s, 3H), 2.64 (dddd, J = 16.6 Hz, 16.6 Hz, 4.4 Hz, 3.3 Hz, 1H), 2.39 (s, 3H), 2.36 (s, 3H), 1.74 (dq, J = 14.7 Hz, 7.3 Hz, 2H), 1.62 – 1.44 (m, 1H), 0.66 (t, J = 7.3 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 156.70, 156.56, 145.58, 144.80, 144.61, 135.49, 134.76, 134.63, 129.63, 129.39, 127.46, 116.93, 112.72, 112.05, 108.84, 108.27, 55.83, 54.01, 52.46, 48.54, 34.26, 32.71, 29.93, 21.77, 8.28 ppm; HRMS (ESI): m/z: Calcd for C₂₃H₂₈N₂NaO₅S [M+Na]⁺ 491.1611, Found 491.1598.
(td, $J = 8.2$ Hz, 1.3 Hz, 1H), 7.02 (td, $J = 7.5$ Hz, 1.3 Hz, 1H), 5.11 (s, 1H), 5.01 (s, 1H), 4.59 (d, $J = 6.0$ Hz, 1H), 3.06 (td, $J = 15.5$ Hz, 5.0 Hz, 1H), 2.24 (tdd, $J = 12.4$ Hz, 6.1 Hz, 3.6 Hz, 1H), 2.17 – 2.02 (m, 1H), 1.76 (ddd, $J = 12.1$ Hz, 9.0 Hz, 5.4 Hz, 1H), 1.62 (s, 9H), 1.33 (s, 3H) ppm; $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 157.27, 152.75, 142.05, 136.12, 127.81, 123.55, 122.86, 116.23, 106.25, 102.17, 82.59, 77.13, 56.67, 30.68, 28.59, 26.17, 23.33 ppm; HRMS (ESI): $m/z$: Calcd for C$_{19}$H$_{24}$NO$_3$ [M+H]$^+$ 314.1751, Found 314.1748.
VI. Preparation of enantioenriched alkylnylindole substrate 5o and characterization data

*Tert*-butyl 3-methyl-2-(3-oxo-5-(trimethylsilyl)pent-4-ynyl)-1H-indole-1-carboxylate (5o-2): PDC (376 mg, 1.0 mmol) was added to a stirred mixture of the alcohol 5o-1 (193 mg, 0.50 mmol) and activated 4 Å molecular sieves (400 mg) in anhydrous dichloromethane (5.0 ml). The resulting mixture was stirred for 5 h; then it was diluted with diethyl ether (15.0 mL). The resulting suspension was filtrated through a pad of silica gel. The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (hexanes/ethyl acetate=20:1) to provide 5o-2 (163 mg, 0.43 mmol) as a colorless oil in 85% yield: IR (thin film): ν = 3050, 2975, 2150, 1731, 1681, 1456, 1332, 1252, 1135, 847 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.08 (d, J = 7.6 Hz, 1H), 7.43 (dd, J = 7.7 Hz, 1.1 Hz, 1H), 7.27 – 7.20 (m, 2H), 3.36 – 3.33 (m, 2H), 2.95 – 2.90 (m, 2H), 2.21 (s, 3H), 1.68 (s, 9H), 0.21 (s, 9H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 186.94, 150.55, 135.93, 134.61, 130.63, 123.96, 122.62, 118.30, 115.72, 115.69, 115.22, 102.04, 98.29, 83.84, 45.50, 28.41, 21.53, 8.86, -0.66 ppm; HRMS (ESI): m/z: Calcd for C₂₂H₂₉LiNO₃Si [M+Li]⁺ 390.2072, Found 390.2084.

(S)-*Tert*-butyl 2-(3-hydroxy-5-(trimethylsilyl)pent-4-ynyl)-3-methyl-1H-indole-1-carboxylate (5o-3)⁵²: Ketone 5o-2 (163 mg, 0.43 mmol) (azeotropically dried with toluene under an inert atmosphere) was treated with catalyst a (108 µL, 0.20 M in toluene, 0.022 mmol). The toluene was removed in vacuo before anhydrous dichloromethane (1.0 mL) was added. The resulting solution was then cooled to -78 ºC. A solution of catecholborane (0.52 mmol, 54 µL) in anhydrous dichloromethane (200 µL) was then added dropwise over 10 min. The reaction mixture was stirred at -78 ºC for 5 h before quenched with MeOH (1.0 mL). The mixture was then warmed to RT, diluted with diethyl ether, washed with saturated aqueous NaHCO₃ until the aqueous layer was colorless. The organic phase was further washed with brine, dried over anhydrous Na₂SO₄, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexanes/ethyl acetate=10:1) to provide 5o-1 (124 mg, 0.33 mmol) as a


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colorless oil in 75% yield: IR (thin film): ν = 3442, 3279, 1732, 1452, 1350, 1343, 1235 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.13 – 7.94 (m, 1H), 7.44 – 7.39 (m, 1H), 7.25 – 7.19 (m, 2H), 4.38 (t, J = 6.3 Hz, 1H), 3.21 (t, J = 7.3 Hz, 2H), 2.22 (s, 3H), 2.12 – 1.96 (m, 2H), 1.69 (s, 9H), 0.16 (s, 9H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 150.89, 136.10, 135.87, 130.83, 123.80, 122.63, 118.24, 115.78, 115.14, 106.81, 89.69, 83.95, 62.29, 37.81, 29.92, 28.50, 22.53, 8.89, 0.06 ppm; HRMS (ESI): m/z: Calcd for C₂₂H₃₂NO₅Si [M+H]⁺ 386.2146, Found 386.2139.

**(S)-Tert-butyl 2-(3-hydroxypent-4-ynyl)-3-methyl-1H-indole-1-carboxylate (5o, Scheme 2):** The TMS group was removed by following general procedure, and 5o was obtained as a colorless oil in 95% yield: The ee of 5o was determined as 81% by chiral HPLC analysis (ChiralCel OD column, hexanes/iPrOH = 97:3, 0.75 mL/min, tₘ for major isomer is 16.4 min, for minor isomer is 18.5 min). [α]₂₀° = –25.3 cm⁻³ g⁻¹ dm⁻¹ (c = 1.50 g cm⁻³ in EtOAc). IR (thin film): ν = 3435, 3289, 1732, 1459, 1354, 1333, 1221, 1136 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.05 – 8.00 (m, 1H), 7.45 – 7.41 (m, 1H), 7.25 – 7.20 (m, 2H), 4.42-4.35 (m, 1H), 3.22 (t, J = 7.2 Hz, 2H), 2.48 (d, J = 2.1 Hz, 1H), 2.34 (d, J = 5.9 Hz, 1H), 2.23 (s, 3H), 2.09-2.02 (m, 2H), 1.69 (s, 9H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ150.91, 135.93, 135.83, 130.80, 123.83, 122.65, 118.26, 115.77, 115.23, 85.01, 84.02, 73.13, 61.59, 37.70, 28.48, 22.38, 8.87 ppm; HRMS (ESI): m/z: Calcd for C₁₉H₂₃NNaO₃ [M+Na]⁺ 336.1570, Found 336.1578.
VII. Unexpected gold(I)-catalyzed reactions and characterization data

**Methyl 2-(3-hydroxydodec-4-ynyl)-3-methyl-1H-indole-1-carboxylate (5p):** A colorless oil was obtained in 86% yield by following general procedure. IR (thin film): \( \nu = 3446, 2929, 2857, 2359, 1735, 1458, 1353, 1220, 1139 \text{ cm}^{-1} \); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta 8.07 – 8.01 \text{ (m, 1H)}, 7.48 – 7.40 \text{ (m, 1H)}, 7.29 – 7.21 \text{ (m, 2H)}, 4.36 \text{ (m 1H)}, 4.04 \text{ (s, 3H)}, 3.26 – 3.15 \text{ (m, 2H)}, 2.23 \text{ (s, 3H)}, 2.21 – 2.17 \text{ (m, 2H)}, 2.01 – 1.95 \text{ (m, 2H)}, 1.52 – 1.45 \text{ (m, 2H)}, 1.42 – 1.34 \text{ (m, 2H)}, 1.32 – 1.22 \text{ (m, 4H)}, 0.88 \text{ (t, } J = 7.0 \text{ Hz, 3H)} \text{ ppm}; \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta 152.71, 136.17, 135.71, 131.01, 124.00, 122.97, 118.30, 115.77, 115.66, 85.96, 81.15, 53.61, 38.00, 31.53, 28.82, 28.76, 22.74, 22.60, 18.90, 14.27, 8.86 \text{ ppm}; HRMS (ESI): \( m/z \): Calcd for C\(_{22}\)H\(_{29}\)NNaO\(_3\) [M+Na\(^+\)] 378.2040, Found 378.2035.

**(E)-Methyl 3-methyl-2-(5-oxoundec-3- enyl)-1H-indole-1-carboxylate (6p):** A colorless oil was obtained in 75% yield by following general procedure. IR (thin film): \( \nu = 2924, 2852, 1736, 1458, 1355, 1220, 1134 \text{ cm}^{-1} \); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta 8.07 – 8.00 \text{ (m, 1H)}, 7.48 – 7.42 \text{ (m, 1H)}, 7.33 – 7.20 \text{ (m, 2H)}, 6.87 \text{ (dt, } J = 15.8 \text{ Hz, 7.0 Hz, 1H)}, 6.12 \text{ (dt, } J = 15.9 \text{ Hz, 1.5 Hz, 1H)}, 4.05 \text{ (s, 3H)}, 3.22 – 3.16 \text{ (m, 2H)}, 2.57 – 2.52 \text{ (m, 2H)}, 2.52 – 2.47 \text{ (m, 2H)}, 2.19 \text{ (s, 3H)}, 1.33 – 1.23 \text{ (m, 8H)}, 0.93 – 0.82 \text{ (m, 3H)} \text{ ppm}; \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta 201.08, 152.65, 146.00, 135.63, 135.44, 131.01, 130.88, 124.23, 123.08, 118.47, 115.84, 115.80, 53.68, 40.33, 31.84, 29.93, 29.21, 25.79, 24.43, 22.74, 14.29, 9.01 \text{ ppm}; HRMS (ESI): \( m/z \): Calcd for C\(_{22}\)H\(_{30}\)NO\(_3\) [M+H\(^+\)] 356.2220, Found 356.2221.

**Methyl 2-(3-acetamidopent-4-ynyl)-3-ethyl-5-methoxy-1H-indole-1-carboxylate (5q):** A colorless oil was obtained in 62% yield by following general procedure. IR (thin film): \( \nu = 3282, 2962, 1731, 1651, 1538, 1364, 1133, 1089 \text{ cm}^{-1} \); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta 7.91 \text{ (d, } J = 9.0 \text{ Hz, 1H)}, 6.92 \text{ (d, } J = 2.6 \text{ Hz, 1H)}, 6.86 \text{ (dd, } J = 9.0 \text{ Hz, 2.6 Hz, 1H)}, 6.17 – 6.10 \text{ (br, 1H)}, 4.82 – 4.75 \text{ (m, 1H)}, 4.03 \text{ (s, 3H)}, 3.87 \text{ (s, 3H)}, 3.20 – 3.03 \text{ (m, 2H)}, 2.66 \text{ (q, } J = 7.6 \text{ Hz, 2H)}, 2.32 \text{ (d, } J = 2.3 \text{ Hz, 1H)}, 2.02 \text{ (s, 3H)}, 2.00 – 1.90 \text{ (m, 2H)}, 1.21 \text{ (t, } J = 7.6 \text{ Hz, 3H)} \text{ ppm}; \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta 169.57, 156.13, 152.53, 135.96, 130.88, 130.32, 121.89, 116.74, 111.98, 101.51, 83.16, 71.26, 55.87, 53.58, 41.29, 35.38, 23.34, 23.04, 17.38, 15.07 \text{ ppm}; HRMS (ESI): \( m/z \): Calcd for C\(_{20}\)H\(_{24}\)N\(_2\)O\(_4\) [M+Na\(^+\)] 379.1628, Found 379.1632.
Methyl 3-ethyl-5-methoxy-2-(2-(2-methyl-5-methylene-4,5-dihydrooxazol-4-yl)ethyl)-1H-indole-1-carboxylate (6q): A colorless oil was obtained in 88% yield by following general procedure. IR (thin film) ν = 3012, 1732, 1677, 1478, 1440, 1386, 1263, 1216, 1130 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.97 (dd, J = 9.0 Hz, 0.4 Hz, 1H), 6.92 (d, J = 2.3 Hz, 1H), 6.86 (dd, J = 9.0 Hz, 2.6 Hz, 1H), 4.69 (t, J = 2.8 Hz, 1H), 4.59 – 4.51 (m, 1H), 4.23 (t, J = 2.8 Hz, 1H), 4.02 (s, 3H), 3.86 (s, 3H), 3.15 – 3.11 (m, 2H), 2.77 – 2.56 (m, 2H), 2.11 (d, J = 1.6 Hz, 3H), 2.08 – 1.97 (m, 1H), 1.85 – 1.70 (m, 1H), 1.20 (t, J = 7.6 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 163.08, 163.00, 156.11, 152.46, 136.68, 130.99, 130.63, 121.70, 116.71, 116.65, 111.86, 111.81, 101.57, 101.50, 83.56, 68.01, 55.95, 55.90, 53.52, 53.49, 36.59, 22.95, 17.41, 15.05, 14.29 ppm; HRMS (ESI): m/z: Calcd for C₂₀H₂₅N₂O₄ [M+H]+ 357.1809, Found 357.1808.
VIII. General preparation of alkynyindoles 7a-7h (entries 1-8, Table 3) and characterization data

\[ \text{Tert-butyl 2-(but-3-ynyl)-3-(2-(1,3-dioxoisindolin-2-yl)ethyl)-1H-indole-1-carboxylate (7a-1):} \]

To a solution of aldehyde 5f-3 (4.46 g, 10 mmol) in anhydrous MeOH (20 mL) was added a solution of Ohira-Bestmann Reagent (4.80 g, 25 mmol) in MeOH (5 mL) and K₂CO₃ (4.15 g, 30 mmol) at 0 °C. The resulting mixture was stirred at RT for 3 h before quenched with an aqueous solution of NH₄Cl. The aqueous phase was extracted with ethyl acetate, and the combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo to give an oil. Purification by column chromatography (hexanes/ethyl acetate = 3:1) afforded alkyne 7a-1 (3.76 g, 8.5 mmol) as a white solid in 85% yield: m.p. 183–184 °C. IR (thin film): \( \nu = 3305, 2930, 1769, 1712, 1457, 1363, 1165, 1107 \text{ cm}^{-1};^{1H} \text{NMR (400 MHz, CDCl}_3\text{)} \delta 8.13 – 8.07 (m, 1H), 7.89 – 7.82 (m, 2H), 7.73 – 7.68 (m, 3H), 7.26 – 7.20 (m, 2H), 3.96 – 3.85 (m, 2H), 3.32 (t, \( J = 7.3 \text{ Hz, } 2H \)), 3.17 – 3.04 (m, 2H), 84.19, 83.70, 69.59, 38.09, 28.43, 26.25, 23.78, 19.62 ppm; \text{HRMS (ESI): } m/z: \text{Calcd for C}_{27}H_{26}N_{2}O_{4}[M+Na]^+ 465.1785, \text{Found 465.1779.}

\[ \text{Tert-butyl 2-(but-3-ynyl)-3-(2-(tert-butoxycarbonylamino)ethyl)-1H-indole-1-carboxylate (7a, entry 1, Table 3):} \]

To a solution of 7a-1 (3.76 g, 8.5 mmol) in absolute EtOH (20 mL) was added anhydrous hydrazine (3.0 mL, 85 mmol). The resulting mixture was heated to 60 °C for 1 h before it was cooled to RT, filtered through a pad of celite. The filtrate was concentrated in vacuo to give 7a-2 as colorless oil, which was used in the next step without purification.

To a solution of 7a-2 in anhydrous dichloromethane was added triethylamine (2.4 mL, 17.0 mmol) and Boc₂O (2.3 g, 10.2 mmol) at 0 °C. The resulting mixture was stirred at RT for 3 h before an aqueous solution of NH₄Cl was added. The aqueous phase was extracted with ethyl acetate, and the combined organic layers were washed with brine,
dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated *in vacuo* to give an oil. Purification by column chromatography (hexanes/ethyl acetate = 5:1) afforded alkyne 7a (2.84 g, 6.9 mmol) as a colorless oil in 81% yield over 2 steps: IR (thin film): $\nu = 2976$, 2927, 1725, 1367, 1164, 1133 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.10 (d, $J = 7.9$ Hz, 1H), 7.51 (d, $J = 7.6$ Hz, 1H), 7.32 – 7.18 (m, 2H), 4.70 – 4.50 (br, 1H), 3.38 (d, $J = 5.8$ Hz, 2H), 3.24 (t, $J = 7.6$ Hz, 1H), 1.69 (s, 9H), 1.44 (s, 9H) ppm; $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 156.04, 150.51, 136.15, 136.05, 129.75, 124.20, 122.85, 118.62, 117.11, 115.91, 84.17, 83.75, 79.42, 69.49, 40.74, 28.61, 28.42, 26.25, 24.99, 19.62 ppm; HRMS (ESI): m/z: Calcd for C$_{24}$H$_{33}$N$_2$O$_4$ [M+H$^+$] $^+$ 413.2435, Found 413.2441.

**Tert-butyl 3-(2-(tert-butoxycarbonylamino)ethyl)-2-(4-phenylbut-3-ynyl)-1H-indole-1-carboxylate (7b, entry 2, Table 3):** A solution of alkyne 7a (144 mg, 0.35 mmol) and iodosobenzene (195 mg, 0.53 mmol) in THF (2 mL) was frozen with liquid nitrogen and thoroughly degassed under high vacuum. Pd(PPh$_3$)$_2$Cl$_2$ (28 mg, 0.04 mmol) was added and the resulting suspension was degassed in the same way. Freshly purified copper(I) iodide (16 mg, 0.08 mmol) was added and degassing was repeated. Previously degassed triethylamine (0.5 mL, 3.5 mmol) was added and the mixture was heated at 70 °C for 2 h. The reaction was allowed to cool to RT, saturated aqueous NaHCO$_3$ was added and the mixture was extracted with ethyl acetate. The combined extracts were dried over anhydrous Na$_2$SO$_4$ and concentrated *in vacuo* to give brown foam, which was purified by column chromatography (hexanes/ethyl acetate = 10:1) to afford 7b (140 mg, 0.29 mmol) as a colorless oil in 84% yield: IR (thin film): $\nu = 2974$, 2928, 1708, 1476, 1382, 1172 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.13 (d, $J = 8.0$ Hz, 1H), 7.52 (d, $J = 7.4$ Hz, 1H), 7.37 – 7.29 (m, 2H), 7.27 – 7.16 (m, 5H), 4.68 – 4.45 (br, 1H), 3.50 – 3.27 (m, 4H), 2.97 (t, $J = 6.8$ Hz, 2H), 2.75 (t, $J = 7.4$ Hz, 2H), 1.71 (s, 9H), 1.44 (s, 9H) ppm; $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 156.05, 150.57, 136.28, 136.20, 131.65, 129.81, 128.39, 127.82, 124.18, 123.89, 122.86, 118.58, 117.13, 115.92, 89.43, 84.17, 81.65, 79.40, 40.75, 28.60, 28.44, 26.51, 24.97, 20.67 ppm; HRMS (ESI): Calcd for C$_{30}$H$_{36}$N$_2$NaO$_4$ [M+Na$^+$] $^+$ 511.2567, Found 511.2559.

**Tert-butyl 2-(but-3-ynyl)-3-(2-(4-methylphenylsulfonamido)ethyl)-1H-indole-1-carboxylate (7c, entry 3, Table 3):** A colorless oil was obtained in 88% yield by following general procedure. IR (thin film): $\nu = 3291$, 2927, 1727, 1457, 1325, 1158 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.08 (d, $J = 8.3$ Hz, 1H), 7.65 (d, $J = 8.2$ Hz, 2H), 7.34 (d, $J = 7.7$
Tert-butyl 2-(but-3-ynyl)-3-(2-(2-nitrophenylsulfonamido)ethyl)-1H-indole-1-carboxylate (7d, entry 4, Table 3): A colorless oil was obtained in 80% yield by following general procedure. IR (thin film): $\nu$ = 3294, 2927, 1726, 1540, 1457, 1394, 1164 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.01 (d, $J = 8.3$ Hz, 1H), 7.98 – 7.93 (m, 1H), 7.73 – 7.69 (m, 1H), 7.58 (pd, $J = 7.5$ Hz, 1.7 Hz, 2H), 7.32 (d, $J = 7.8$ Hz, 1H), 7.24 – 7.18 (m, 1H), 7.16 – 7.09 (m, 1H), 5.38 (t, $J = 5.8$ Hz, 1H), 3.42 (dd, $J = 13.1$ Hz, 7.1 Hz, 2H), 3.18 (t, $J = 7.2$ Hz, 2H), 2.98 (t, $J = 7.2$ Hz, 2H), 2.48 (td, $J = 7.2$ Hz, 2.6 Hz, 2H), 1.91 (t, $J = 2.6$ Hz, 1H), 1.68 (s, 9H) ppm; $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 150.27, 147.65, 136.14, 136.05, 129.81, 124.32, 122.97, 118.52, 117.12, 116.01, 110.84, 84.46, 83.58, 69.60, 43.77, 29.90, 28.41, 26.15, 25.12, 19.54 ppm; HRMS (ESI): m/z: Calcd for C$_{26}$H$_{30}$N$_2$NaO$_4$S [M+Na]$^+$ 489.1819, Found 489.1800.

Tert-butyl 3-(2-acetamidoethyl)-2-(but-3-ynyl)-1H-indole-1-carboxylate (7e, entry 5, Table 3): A colorless oil was obtained in 74% yield by following general procedure. IR (thin film): $\nu$ = 3290, 2922, 2851, 1726, 1650, 1457, 1341, 1163 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.10 (d, $J = 7.4$ Hz, 1H), 7.56 – 7.51 (m, 1H), 7.33 – 7.26 (m, 1H), 7.26 – 7.20 (m, 1H), 5.65 – 5.56 (br, 1H), 3.52 (q, $J = 6.8$ Hz, 2H), 3.25 (t, $J = 7.3$ Hz, 2H), 2.94 (t, $J = 7.0$ Hz, 2H), 2.54 (td, $J = 7.3$ Hz, 2.6 Hz, 2H), 1.96 (t, $J = 2.6$ Hz, 1H), 1.93 (s, 3H), 1.70 (s, 9H) ppm; $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 170.35, 150.52, 136.14, 136.05, 129.81, 124.32, 122.97, 118.52, 117.12, 116.01, 110.84, 84.31, 83.70, 69.90, 39.95, 28.45, 26.16, 24.46, 23.58, 19.63 ppm; HRMS (ESI): m/z: Calcd for C$_{21}$H$_{26}$N$_2$NaO$_3$ [M+Na]$^+$ 377.1835, Found 377.1817.
(E)-Butyl 3-(3-(2-(tert-butoxycarbonylamino)ethyl)-1H-indol-2-yl)acrylate (7f-2): A colorless oil was obtained in 60% yield by following general procedure. IR (thin film): \( \nu = 3339, 2961, 1693, 1613, 1513, 1455, 1251, 1171, 1069, 739 \text{ cm}^{-1} \); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.50 – 8.35 (br, 1H), 7.75 (d, \( J = 15.9 \text{ Hz}, 1\)H), 7.64 (d, \( J = 8.0 \text{ Hz}, 1\)H), 7.33 (d, \( J = 8.2 \text{ Hz}, 1\)H), 7.29 – 7.24 (m, 2H), 7.11 (t, \( J = 7.5 \text{ Hz}, 1\)H), 6.20 (d, \( J = 15.9 \text{ Hz}, 1\)H), 4.65 – 4.52 (br, 1H), 4.22 (t, \( J = 6.6 \text{ Hz}, 2\)H), 3.43 – 3.35 (m, 2H), 3.10 – 3.06 (m, 2H), 1.86 – 1.55 (m, 2H), 1.51 – 1.40 (m, 9H), 0.97 (t, \( J = 7.3 \text{ Hz}, 3\)H) ppm; \(^13\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 167.63, 156.13, 137.76, 132.06, 130.90, 128.48, 125.10, 120.14, 119.63, 114.97, 111.37, 79.40, 64.69, 41.66, 30.92, 28.57, 28.29, 25.03, 19.32, 19.22, 13.92 ppm; HRMS (ESI): Calcd for C\(_{22}\)H\(_{31}\)N\(_2\)O\(_4\) [M+H]\(^+\) 387.2278, Found 387.2289.

Tert-butyl 2-(2-(3-oxopropyl)-1H-indol-3-yl)ethylcarbamate (7f-4): A colorless oil was obtained in 82% yield by following general procedure. IR (thin film): \( \nu = 3402, 3055, 2976, 2931, 2772, 1689, 1513, 1462, 1366, 1169, 741 \text{ cm}^{-1} \); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 9.88 (s, 1H), 8.40 – 8.31 (br, 1H), 7.50 (d, \( J = 7.9 \text{ Hz}, 1\)H), 7.30 (d, \( J = 7.8 \text{ Hz}, 1\)H), 7.19 – 7.12 (m, 1H), 7.10 – 7.02 (m, 1H), 4.60 – 4.50 (br, 1H), 3.37 (dd, \( J = 12.6 \text{ Hz}, 6.2 \text{ Hz}, 2\)H), 3.12 – 2.97 (m, 2H), 2.94 – 2.86 (m, 4H), 1.43 (s, 9H) ppm; \(^13\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 202.34, 202.31, 156.13, 135.48, 134.99, 128.11, 121.43, 119.21, 118.20, 110.73, 108.43, 79.19, 44.27, 41.22, 28.50, 24.74, 18.08 ppm; HRMS (ESI): Calcd for C\(_{18}\)H\(_{25}\)N\(_2\)O\(_3\) [M+H]\(^+\) 317.1860, Found 317.1867.

Tert-butyl 2-(2-(but-3-ynyl)-1H-indol-3-yl)ethylcarbamate (7f, entry 6, Table 3): A colorless oil was obtained in 87% yield by following general procedure. IR (thin film): \( \nu = 3403, 3303, 2975, 2931, 2772, 1689, 1511, 1462, 1250, 1166 \text{ cm}^{-1} \); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.30 (s, 1H), 7.53 (d, \( J = 7.8 \text{ Hz}, 1\)H), 7.32 (d, \( J = 7.9 \text{ Hz}, 1\)H), 7.20 – 7.13 (m, 1H), 7.09 (t, \( J = 7.5 \text{ Hz}, 1\)H), 4.70 – 4.56 (br, 1H), 3.38 (d, \( J = 6.4 \text{ Hz}, 2\)H), 3.12 – 2.97 (m, 2H), 2.94 – 2.86 (m, 4H), 1.43 (s, 9H) ppm; \(^13\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 156.14, 135.67, 135.00, 128.18, 121.77, 119.52, 118.54, 110.79, 109.19, 84.10, 79.29, 70.31, 41.20, 28.63, 25.00, 24.81,
19.47 ppm; HRMS (ESI): Calcd for C_{19}H_{25}N_{2}O_{2} [M+H]^+ 313.1911, Found 313.1911.

**N-(2-(2-(But-3-ynyl)-1H-indol-3-yl)ethyl)acetamide (7h, entry 7, Table 3):** A colorless oil was obtained in 84 % yield by following general procedure. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.46 – 8.31 (br, 1H), 7.52 (d, \(J = 7.7\) Hz, 1H), 7.33 (d, \(J = 7.9\) Hz, 1H), 7.17 (t, \(J = 7.2\) Hz, 1H), 7.10 (t, \(J = 7.4\) Hz, 1H), 5.75 – 5.62 (br, 1H), 3.53 (dd, \(J = 12.9\) Hz, 6.4 Hz, 2H), 3.04 – 2.87 (m, 4H), 2.55 (td, \(J = 6.9\) Hz, 2.6 Hz, 2H), 2.11 (t, \(J = 2.5\) Hz, 1H), 1.93 (s, 3H) ppm; \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 171.13, 135.67, 135.02, 128.22, 121.94, 119.75, 118.33, 110.95, 108.95, 83.99, 70.48, 40.61, 29.92, 24.93, 24.18, 23.37, 19.46 ppm; HRMS (ESI): m/z: Calcd for C_{16}H_{19}N_{2}O \[M+H\]^+ 255.1492, Found 255.1480.

**Butyl 3-(3-(2-(1,3-dioxoisindolin-2-yl)ethyl)-1-methyl-1H-indol-2-yl)propanoate (7h-2):** To a solution of ester 5f-2 (1.56 g, 3.0 mmol) in anhydrous dichloromethane (10 mL) was added trifluoroacetic acid (2.3 mL, 30.0 mmol). The resulting mixture was stirred at RT for 2 h before the solvents were removed in vacuo to give an oil, which was dissolved in anhydrous DMF (10 mL) and cooled to -50 °C. A solution of NaHMDS (2.0 M in THF, 1.6 mL, 3.2 mmol) was added to the above solution. After 30 min, iodomethane (0.37 mL, 6.0 mmol) was added in one portion and the resulting mixture was slowly warmed to RT and stirred for 2 h before it was quenched with water, and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na\(_2\)SO\(_4\), and concentrated in vacuo to afford a yellow oil, which was purified by column chromatography (hexanes/ethyl acetate = 10:1) to afford N-methyl indole 7h-2 (1.23 g, 2.85 mmol) as a colorless oil in 95% yield over 2 steps: IR (thin film): \(\nu\) = 2957, 1770, 1712, 1470, 1396, 1258, 1171, 1024 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.95 – 7.86 (m, 2H), 7.77 – 7.76 (m, 3H), 7.31 (d, \(J = 5.8\) Hz, 1H), 7.25 – 7.20 (m, 1H), 7.16 – 7.11 (m, 1H), 4.15 (t, \(J = 6.7\) Hz, 2H), 4.00 – 3.88 (m, 2H), 3.76 (s, 3H), 3.28 – 3.20 (m, 2H), 3.20 – 3.12 (m, 2H), 2.77 – 2.63 (m, 2H), 1.64 (dt, \(J = 14.6\) Hz, 7.0 Hz, 2H), 1.46 – 1.34 (m, 2H), 0.99 – 0.92 (m, 3H) ppm; \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 172.61, 168.48, 136.99, 135.98, 134.03, 132.40, 127.66, 123.33, 121.39, 119.42, 118.54, 109.04, 108.14, 64.85, 38.91, 34.75, 30.78, 29.92, 29.87, 24.02, 20.03, 19.29, 13.91 ppm; HRMS (ESI): m/z: Calcd for C_{26}H_{38}N_{2}NaO_{4} [M+Na]^+ 455.1914, Found 455.1934.
4-Methyl-N-(2-(1-methyl-2-(3-oxopropyl)-1H-indol-3-yl)ethyl)benzenesulfonamide (7h-4): To a solution of 7h-2 (1.23 g, 2.85 mmol) in absolute EtOH (5 mL) was added anhydrous hydrazine (1.0 mL, 28.5 mmol). The resulting mixture was heated to 60 °C for 1 h before it was cooled to RT, filtered through a pad of celite. The filtrate was concentrated in vacuo to give amine 7h-3 as a crude oil, which was used in the next step without purification.

To a solution of 7h-3 in anhydrous dichloromethane was added triethylamine (0.8 mL, 5.7 mmol) and TsCl (0.77 g, 3.42 mmol) at 0 °C. The resulting mixture was stirred at RT for 10 h before quenched with an aqueous solution of NH₄Cl. The aqueous phase was extracted with ethyl acetate, and the combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo to give an oil, which was purified by column chromatography (hexanes/ethyl acetate=5:1) to afford sulfonamide 7h-4 (1.05 g, 2.3 mmol) as a colorless oil in 81% yield over 2 steps: IR (thin film): ν = 3290, 2958, 2872, 1731, 1471, 1330, 1160 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 7.9 Hz, 1H), 7.23 (d, J = 6.6 Hz, 2H), 7.21 – 7.15 (m, 2H), 7.07 – 7.00 (m, 1H), 4.45 (t, J = 6.2 Hz, 1H), 4.07 (t, J = 6.7 Hz, 2H), 3.67 (s, 3H), 3.21 (q, J = 6.7 Hz, 2H), 3.08 – 3.03 (m, 2H), 2.95 (t, J = 6.8 Hz, 2H), 2.56 – 2.50 (m, 2H), 2.40 (s, 3H), 1.62 – 1.53 (m, 2H), 1.32 (dt, J = 14.7 Hz, 7.5 Hz, 2H), 0.90 (t, J = 7.4 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 172.44, 143.12, 136.91, 136.13, 129.72, 129.57, 127.14, 127.03, 121.30, 119.21, 118.06, 109.00, 107.36, 64.73, 43.58, 34.39, 30.59, 29.73, 29.67, 24.97, 21.53, 21.50, 19.74, 19.11, 13.75 ppm; HRMS (ESI): m/z: Calcd for C₂₅H₃₃N₂O₄S [M+Na]⁺ 457.2156, Found 457.2144.

N-(2-(2-(But-3-ynyl)-1-methyl-1H-indol-3-yl)ethyl)-4-methylbenzenesulfonamide (7h, entry 8, Table 3): Ester 7h-4 (1.05 g, 2.3 mmol) was dissolved in anhydrous dichloromethane and the solution was cooled to -78 °C before the addition of the solution of DIBAL-H (1.0 M in hexane, 2.76 mL, 2.76 mmol) dropwise. The reaction mixture was stirred for 1 h at -78 °C before it was treated with saturated aqueous solution of Rochelle salt (5.0 mL) at -78 °C. After being stirred at RT for 1 h, the layers were separated. The aqueous layer was extracted with ether, and the combined organic layers were washed with water and brine, dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo to produce aldehyde 7h-5 as a yellow oil, which was used for the next step without further purification.
To a solution of aldehyde 7h-5 in anhydrous MeOH (5 mL) was added a solution of Ohira-Bestmann Reagent (1.03 g, 5.75 mmol) in MeOH (5 mL) and K$_2$CO$_3$ (0.96 g, 6.9 mmol) at 0 °C. The resulting mixture was stirred at RT for 3 h before quenched with an aqueous solution of NH$_4$Cl. The aqueous phase was extracted with ethyl acetate, and the combined organic layers were washed with brine, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated in vacuo to give an oil, which was purified by column chromatography (hexanes/ethyl acetate = 5:1) to afford alkyne 7h (0.70 g, 1.8 mmol) as a white solid in 80% yield over 2 steps: m.p. 160–161 °C. IR (thin film): ν = 3287, 2924, 1471, 1324.49, 1158, 1093 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.65 – 7.59 (m, 2H), 7.37 – 7.32 (m, 1H), 7.27 – 7.20 (m, 3H), 7.17 (ddd, $J = 8.2$ Hz, 7.0 Hz, 1.1 Hz, 1H), 7.02 (ddd, $J = 8.0$ Hz, 7.0 Hz, 1.1 Hz, 1H), 4.35 (t, $J = 6.1$ Hz, 1H), 3.68 (s, 3H), 3.23 (q, $J = 6.7$ Hz, 2H), 3.02 – 2.91 (m, 4H), 2.48 – 2.34 (m, 5H), 1.96 (t, $J = 2.7$ Hz, 1H) ppm; $^{13}$C NMR (101 MHz, CDCl$_3$) δ 143.41, 137.04, 136.90, 136.28, 129.78, 127.19, 127.16, 121.54, 119.39, 118.25, 109.20, 107.59, 82.96, 69.98, 43.63, 30.05, 30.00, 25.18, 23.64, 21.70, 21.67, 19.60 ppm; HRMS (ESI): m/z: Calcd for C$_{22}$H$_{24}$N$_2$NaO$_2$S [M+Na]$^+$ 403.1450 , Found 403.1461.
IX. Gold(I)-catalyzed tandem cyclization studies for the synthesis of akuammilines (Table 3)

The catalyst solution was first prepared by addition of Ph$_3$PAuCl (2.5 mg, 0.005 mmol) to a suspension of AgSbF$_6$ (1.7 mg, 0.005 mmol) in anhydrous toluene (0.50 mL) at RT. The suspension was stirred for 20 min at RT under Argon atmosphere. The resulting catalyst solution was then added to a solution of substrate 7a (41.2 mg, 0.10 mmol) in anhydrous toluene (0.50 mL) dropwise at RT. The resulting mixture was heated at 60 °C until TLC showed that there was no starting material 7a left (about 1-2 h). The reaction mixture was cooled to RT, filtered through a short pad of silica gel. The filtrate was concentrated in vacuo, and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford 8a (entry 1, Table 3, 23.7 mg, 0.083 mmol) as a colorless oil in 75% yield: IR (thin film): $\nu = 2973, 2927, 1708, 1477, 1376, 1172, 1144$ cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.68 (s, 1H), 7.23 – 7.12 (m, 2H), 7.00 (t, $J = 7.3$ Hz, 1H), 5.74 – 5.70 (m, 1H), 5.60 (d, $J = 10.0$ Hz, 1H), 3.53 (t, $J = 9.1$ Hz, 2H), 3.00 (dt, $J = 17.3$ Hz, 8.7 Hz, 1H), 2.25 (dd, $J = 13.1$ Hz, 5.9 Hz, 2H), 2.16 – 2.11 (m, 1H), 2.07 – 1.97 (m, 2H), 1.57 (s, 9H), 1.45 (s, 9H) ppm; $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 142.29, 134.20, 128.15, 128.12, 126.40, 123.17, 122.27, 118.03, 117.95, 117.88, 117.81, 117.61, 87.70, 81.31, 76.75, 56.61, 56.57, 46.27, 33.93, 29.91, 29.58, 29.54, 29.41, 28.76, 28.63, 28.50, 27.99, 27.93, 27.88, 23.21, 22.91 ppm; HRMS (ESI): $m/z$: Calcd for C$_{24}$H$_{32}$N$_2$NaO$_4$ [M+Na]$^+$ 435.2254, Found 435.2266.

Tetracyclic indoline 8b (entry 2, Table 3): A colorless oil was obtained in 84% yield by following general procedure. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.28 – 7.21 (m, 3H), 7.14 – 7.05 (m, 1H), 6.97 – 6.92 (m, 2H), 6.69 (t, $J = 7.3$ Hz, 1H), 6.20 (d, $J = 6.7$ Hz, 1H), 5.60 (d, $J = 3.9$ Hz, 1H), 3.82 – 3.78 (m, 1H), 3.65 – 3.55 (m, 1H), 2.92 – 2.82 (m, 1H), 2.47 (dd, $J = 12.3$ Hz, 6.1 Hz, 2H), 2.35 (td, $J = 12.0$ Hz, 8.3 Hz, 1H), 2.26 (d, $J = 18.5$ Hz, 1H), 1.92 – 1.83 (m, 1H), 1.63 (s, 9H), 1.43 (s, 9H) ppm; $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 141.76, 141.17, 139.40, 131.52, 130.41, 129.94, 129.65, 128.10, 127.74, 126.98, 124.67, 122.36, 118.14, 110.31, 88.28, 81.30, 46.12, 33.21, 30.04, 28.89, 28.75, 24.00 ppm; HRMS (ESI): $m/z$: Calcd for C$_{30}$H$_{36}$N$_2$NaO$_4$ [M+Na]$^+$ 511.2567, Found 511.2577.
Tetracyclic indoline 8c (entry 3, Table 3): A colorless oil was obtained in 81% yield by following general procedure. IR (thin film): ν = 2924, 1697, 1477, 1365, 1161, 1098, 1043 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 7.50 (d, J = 8.3 Hz, 2H), 7.20 (d, J = 7.7 Hz, 1H), 7.11 (d, J = 8.0 Hz, 2H), 7.09 – 7.04 (m, 1H), 6.98 (td, J = 7.8 Hz, 1.5 Hz, 1H), 6.93 (dt, J = 7.4 Hz, 3.7 Hz, 1H), 5.70 – 5.62 (m, 1H), 5.49 (dt, J = 9.9 Hz, 1.9 Hz, 1H), 3.83 – 3.71 (m, 2H), 2.92 (dd, J = 16.2 Hz, 10.2 Hz, 1H), 2.26 – 2.15 (m, 1H), 2.15 – 2.08 (m, 2H), 2.01 – 1.87 (m, 1H), 1.61 (s, 9H) ppm; \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) δ 142.70, 141.90, 137.62, 132.88, 129.29, 128.07, 127.96, 127.03, 126.94, 125.83, 123.79, 121.69, 118.14, 89.99, 82.26, 58.02, 48.55, 48.49, 31.40, 31.36, 31.30, 29.91, 28.38, 23.63, 21.60 ppm; HRMS (ESI): m/z: Calcd for C\(_{26}\)H\(_{30}\)N\(_2\)NaO\(_4\)S [M+Na]\(^+\) 489.1819, Found 489.1823.

Tetracyclic indoline 8d (entry 4, Table 3): A colorless oil was obtained in 88% yield by following general procedure. IR (thin film): ν = 2925, 1711, 1544, 1366, 1164, 1035 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 7.91 (s, 1H), 7.62 (dd, J = 11.4 Hz, 3.8 Hz, 1H), 7.60 – 7.49 (m, 3H), 7.20 (ddd, J = 7.3 Hz, 4.3 Hz, 2.8 Hz, 2H), 7.07 (t, J = 7.4 Hz, 1H), 5.70 – 5.65 (m, 1H), 5.55 (d, J = 10.0 Hz, 1H), 3.93 – 3.82 (m, 1H), 3.66 (d, J = 13.8 Hz, 1H), 3.14 (m, 1H), 2.46 (dd, J = 12.7 Hz, 5.7 Hz, 1H), 2.24 (td, J = 12.1 Hz, 8.2 Hz, 1H), 2.11 – 2.07 (m, 2H), 1.95 – 1.86 (m, 1H), 1.56 (s, 9H) ppm; \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) δ 151.97, 148.34, 141.89, 135.06, 133.19, 133.11, 131.74, 131.15, 128.67, 128.35, 125.74, 124.12, 122.29, 117.99, 90.61, 82.65, 58.54, 49.55, 32.80, 31.80, 29.91, 28.38, 28.26, 23.41, 22.87, 14.35 ppm; HRMS (ESI): m/z: Calcd for C\(_{25}\)H\(_{27}\)N\(_3\)NaO\(_6\)S [M+Na]\(^+\) 520.1513, Found 520.1517.

Tetracyclic indoline 8e (entry 5, Table 3): A colorless oil was obtained in 80% yield by following general procedure. IR (thin film): ν = 2927, 1698, 1664, 1477, 1404, 1364, 1167 cm\(^{-1}\); \(^1\)H NMR (400 MHz, C\(_6\)D\(_6\), 60°C) δ 8.41 – 8.11 (m, 1H), 7.10 – 7.01 (m, 1H), 6.92 – 6.79 (m, 2H), 5.55 – 5.41 (m, 1H), 5.36 (d, J = 10.1 Hz, 1H), 3.69 (d, J = 14.3 Hz, 1H), 2.80 – 2.56 (m, 2H), 2.34 (t, J = 14.4 Hz, 1H), 1.87 (dd, J = 12.3 Hz, 7.4 Hz, 2H), 1.63 – 1.52 (m, 12H) ppm; \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) δ 169.31, 143.17, 134.44, 134.30, 132.88, 132.20, 129.50, 129.39, 128.61, 128.34, 128.02, 126.41, 124.88, 124.63, 123.06, 122.37, 122.10, 119.44, 117.47, 88.15, 81.56, 55.88, 47.23, 46.05, 33.84, 31.68, 29.92, 29.20, 28.47, 28.13, 27.68, 24.71, 23.39, 23.25, 22.67 ppm; HRMS (ESI): m/z:
Calcd for C_{21}H_{26}N_{2}O_{3} [M+Na]^+ 377.1835, Found 377.1846.

Tetracyclic indoline 8f (entry 6, Table 3): A colorless oil was obtained in 87% yield by following general procedure. IR (thin film): \( \nu = 3377, 2972, 2927, 1681, 1609, 1365, 1254, 1169, 951 \text{ cm}^{-1} \); \(^1\)H NMR (400 MHz, Toluene-d\textsubscript{8}, 95°C) \( \delta = 6.90 – 6.82 \) (m, 2H), 6.62 (d, \( J = 7.4 \) Hz, 1H), 6.35 (d, \( J = 7.6 \) Hz, 1H), 5.58 – 5.45 (m, 3H), 3.37 (s, 1H), 3.37 (t, \( J = 8.2 \) Hz, 1H), 3.10 – 3.02 (m, 1H), 2.80 – 2.68 (br, 1H), 2.23 (dd, \( J = 16.3 \) Hz, 11.1 Hz, 9H) ppm; \(^{13}\)C NMR (101 MHz, CD\textsubscript{3}OD) \( \delta = \) 155.72, 155.68, 150.35, 149.86, 133.85, 133.59, 131.21, 131.20, 129.33, 126.66, 126.58, 124.05, 123.95, 123.92, 120.21, 120.19, 111.14, 111.02, 87.28, 86.91, 82.09, 80.97, 58.22, 57.08, 47.43, 47.38, 47.28, 35.33, 34.89, 30.28, 30.25, 29.30, 29.26, 29.03, 28.90, 23.78 ppm; HRMS (ESI): \( m/z \): Calcd for C\textsubscript{19}H\textsubscript{25}N\textsubscript{2}O\textsubscript{2} [M+H]^+ 313.1911, Found 313.1917.

Tetracyclic indoline 8g (entry 7, Table 3): A colorless oil was obtained in 83% yield by following general procedure. IR (thin film): \( \nu = 3387, 2924, 1660, 1457, 1401, 1311, 1127 \) cm\textsuperscript{-1}; \(^1\)H NMR (500 MHz, CDCl\textsubscript{3}) \( \delta = 7.16 – 7.03 \) (m, 2H), 6.75 (dd, \( J = 7.4 \) Hz, 6.5 Hz, 1H), 6.62 (d, \( J = 7.7 \) Hz, 1H), 5.79 (s, 1H), 5.76 – 5.59 (m, 2H), 3.59 (t, \( J = 8.5 \) Hz, 1H), 3.29 – 3.17 (m, 1H), 2.92 (dd, \( J = 13.6 \) Hz, 3.2 Hz, 1H), 2.45 (dd, \( J = 12.7 \) Hz, 5.5 Hz, 1H), 2.41 – 2.26 (m, 2H), 2.23 – 2.11 (m, 1H), 1.97 (s, 3H), 1.78 – 1.67 (m, 1H) ppm; \(^{13}\)C NMR (101 MHz, CDCl\textsubscript{3}) \( \delta = 170.56, 149.24, 131.90, 129.60, 128.58, 126.37, 123.04, 119.17, 110.61, 87.38, 55.46, 47.58, 34.49, 29.92, 27.70, 27.66, 23.91, 22.87 ppm; HRMS (ESI): \( m/z \): Calcd for C\textsubscript{16}H\textsubscript{19}N\textsubscript{2}O \[M+H]^+ 255.1492 , Found 255.1483.

Tetracyclic indoline 8h (entry 8, Table 3): A colorless oil was obtained in 86% yield by following general procedure. IR (thin film): \( \nu = 2923, 1605, 1491, 1332, 1153, 1094, 920 \) cm\textsuperscript{-1}; \(^1\)H NMR (500 MHz, CDCl\textsubscript{3}) \( \delta = 7.63 – 7.59 \) (m, 2H), 7.19 (d, \( J = 8.0 \) Hz, 2H), 7.12 (td, \( J = 7.7 \) Hz, 1.3Hz, 1H), 7.02 (dd, \( J = 7.2 \) Hz, 0.9 Hz, 1H), 6.69 (td, \( J = 7.4 \) Hz, 0.9 Hz, 1H), 6.36 (d, \( J = 7.8 \) Hz, 1H), 5.73 – 5.61 (m, 2H), 3.49 (td, \( J = 7.7 \) Hz, 3.8 Hz, 1H), 3.15 (d, \( J = 6.5 \) Hz, 1H), 3.01 (s, 3H), 3.00 – 2.92 (m, 1H), 2.38 (s, 3H), 2.36 – 2.29 (m, 1H), 2.10 – 1.95 (m, 4H) ppm; \(^{13}\)C NMR (101 MHz, CDCl\textsubscript{3}) \( \delta = 149.45, 142.89, 138.22, 131.22, 129.54, 129.49, 128.80, 127.02, 125.28, 122.00, 118.05, 106.57, 93.71, 57.62, 48.10, 34.80, 29.73, 29.70, 28.18, 22.65, 21.64, 21.62 ppm; HRMS (ESI): \( m/z \): Calcd for
C$_{22}$H$_{24}$N$_2$NaO$_2$S [M+H]$^+$ 403.1450, Found 403.1464.

To a solution of the substrate 8f (31 mg, 0.1 mmol) in anhydrous dichloromethane (0.5 mL) was added pyridine (40 μL, 0.5 mmol) and a solution of triphosgene (89 mg, 0.3 mmol) in dichloromethane (0.2 mL) at -10 °C. The reaction was slowly warmed to RT and stirred for 30 min. MeOH (40 μL, 1 mmol) was added to the above solution and the reaction was stirred for another 2h before the solvents were removed in vacuo to give a crude oil, which was purified by column chromatography (petroleum ether/ethyl acetate=10:1) to produce 9 (29.6 mg, 0.08 mmol) as a colorless oil in 80% yield: IR (thin film): ν = 2927, 1708, 1479, 1378, 1242, 1169, 752 cm$^{-1}$; $^1$H NMR (400 MHz, C$_6$D$_6$, 60 °C) δ 8.16 (d, $J$ = 7.6 Hz, 1H), 7.12 – 7.05 (m, 1H), 6.97 – 6.83 (m, 2H), 5.59 – 5.51 (m, 1H), 5.47 (d, $J$ = 10.0 Hz, 1H), 3.64 (s, 3H), 3.50 – 3.47 (m, 1H), 3.18 – 2.98 (m, 2H), 2.42 – 2.35 (m, 1H), 2.15 – 1.95 (m, 1H), 2.06 – 1.96 (m, 1H), 1.90 – 1.78 (m, 1H), 1.74 – 1.63 (m, 1H), 1.42 (s, 9H) ppm; $^{13}$C NMR (101 MHz, C$_6$D$_6$,60 °C) δ 154.54, 153.76, 142.55, 135.21, 129.01, 128.89, 128.27, 127.04, 123.63, 122.61, 117.82, 89.34, 79.72, 56.92, 52.35, 52.29, 47.13, 35.35, 28.94, 28.73, 23.53 ppm; HRMS (ESI): m/z: Caled for C$_{21}$H$_{27}$N$_2$O$_4$ [M+H]$^+$ 371.1965 , Found 371.1958.
Parameter Value (f2, f1)

Title yxl-i-315-NOESY

Comment yxl-i-315, NOESY, 500ms mix

Solvent CDCl3

Temperature 295.1

Number of Scans 16

Acquisition Date 2009-10-02T07:38:29

Spectrometer Frequency (300.13, 300.13)

Spectral Width (2564.1, 2564.1)

Lowest Frequency (-24.3, -25.8)

Nucleus (1H, 1H)

Acquired Size (1024, 256)

Spectral Size (1024, 1024)
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**Diagram:**

The diagram illustrates a spectral peak at 4.75 ppm with a chemical structure labeled with various atoms and bonds. The structure includes various functional groups and rings, indicative of a complex molecular compound.

**Chemical Structure:**

- **Atoms:** C, H, N, O, Me, MeO.
- **Rings:** Multiple aromatic and heterocyclic rings.
- **Functional Groups:** MeO, N, H.
The image appears to be a chemical structure with peaks labeled on an NMR spectrum. The chemical is identified as 5HT3. The peaks are labeled with their corresponding ppm values.
Parameter Value (f2, f1)
1 Title yxl-iii-me-ts-au, gHSQC
2 Solvent CDCl3
3 Acquisition Date 2009-12-23T21:49:23
4 Number of Scans 2
5 Spectrometer Frequency (300.13, 75.47)
6 Spectral Width (2427.2, 14012.2)
7 Lowest Frequency (27.9, -1701.6)
8 Nucleus (1H, 13C)
9 Acquired Size (512, 400)
10 Spectral Size (1024, 2048)
Parameter Value (f2, f1)

1. Title yxl-iii-me-ts-au, gHSQC
2. Solvent CDCl3
3. Acquisition Date 2009-12-23T21:49:23
4. Number of Scans 2
5. Spectrometer Frequency (300.13, 75.47)
6. Spectral Width (2427.2, 14012.2)
7. Lowest Frequency (27.9, -1701.6)
8. Nucleus (1H, 13C)
9. Acquired Size (512, 400)
10. Spectral Size (1024, 2048)
Comparison between spectrum of Overmann's intermediate and our synthetic intermediate.
Comparison between spectrum of Overmann's intermediate and our synthetic intermediate.