Supporting Information

Synthesis of 2-Arylindoles by Rhodium-Catalyzed/Copper-Mediated Annulative Coupling of N-Aryl-2-Aminopyridines and Propargyl Alcohols via Selective C–H/C–C Activation

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I. General remarks

NMR spectra were obtained on a Bruker AV II-400 spectrometer. The $^1$H NMR (400 MHz) chemical shifts were measured relative to CDCl$_3$ as the internal reference (CDCl$_3$: $\delta = 7.26$ ppm) or DMSO-d$_6$ ($\delta = 2.50$, ppm). The $^{13}$C NMR (100 MHz) chemical shifts were given using CDCl$_3$ as the internal standard (CDCl$_3$: $\delta = 77.16$ ppm) or DMSO-d$_6$ ($\delta = 39.52$, ppm). High resolution mass spectra (HR-MS) were obtained with a Shimadzu LCMS-IT-TOF (ESI). Melting points were determined in open glass capillaries and were uncorrected. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. N-aryl-2-aminopyridines and tert-propargyl alcohols were prepared according to the literature procedures.$^{1,2}$ All the solvents mentioned were dried before used.

II. General procedures

1. Representative procedures to access 2-arylindole derivatives

\[
\begin{array}{c}
\text{R}^1 \text{H} \text{N} \text{H} \\
\text{1} \\
\text{H}_2 \text{O} \\
\text{2} \\
\text{[Cp*RhCl}_2 \text{]} (5 \text{ mol%}) \\
\text{Cu(OAc)}_2 (2.5 \text{ equiv}) \\
1,4-dioxane, 12 \text{ h}, N_2 \\
\text{3} \\
\end{array}
\]

A Schlenk tube with a magnetic stir bar was charged with $1$ (0.2 mmol), $2$ (0.6 mmol), [Cp*RhCl$_2$] (6.2 mg, 0.01 mmol), Cu(OAc)$_2$ (100.0 mg, 0.5 mmol) and 1,4-dioxane (1.0 mL). The Schlenk tube was then sealed with a Teflon lined cap and the mixture was heated at 120 °C for 12 hours under N$_2$. The reaction solution was then cooled to ambient temperature, diluted with 5 mL of CH$_2$Cl$_2$, filtered through a celite pad and washed with 10-20 mL of CH$_2$Cl$_2$. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel to provide the desired product 3.

2. A scale-up experiment of $1a$

\[
\begin{array}{c}
\text{R}^1 \text{H} \text{N} \text{H} \\
\text{1a 1.0 mmol 0.184 g} \\
\text{2a 3.0 mmol 0.480 g} \\
\text{[Cp*RhCl}_2 \text{]} (5 \text{ mol%}) \\
\text{Cu(OAc)}_2 (2.5 \text{ equiv}) \\
1,4-dioxane (5.0 mL) \\
12 \text{ h}, N_2 \\
\text{3a 0.68 mmol, 0.193 g} \\
68\% \text{ Yield} \\
\end{array}
\]

A Schlenk tube with a magnetic stir bar was charged with $1a$ (1.0 mmol, 0.184 g), $2a$ (3.0 mmol, 0.480 g), [Cp*RhCl$_2$] (31.0 mg, 0.05 mmol), Cu(OAc)$_2$ (500.0 mg, 2.5 mmol) and 1,4-dioxane (5.0 mL). The Schlenk tube was then sealed with a Teflon lined cap and the mixture was heated at 120 °C for 12 hours under N$_2$. The reaction solution was then cooled to ambient temperature, diluted with 10 mL of CH$_2$Cl$_2$, filtered through a celite pad and washed with 10-20 mL of CH$_2$Cl$_2$. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel to provide the desired product 3a (0.68 mmol, 0.193 g) in 68% yield.

III. Product transformations

1) To a solution of 3a (0.2 mmol) in DMF (1.0 mL), POCl$_3$ (0.3 mmol) was added dropwisely and then the mixture was heated at 50 °C under air overnight. The reaction solution was then cooled to room temperature and purified by column chromatography on silica gel to provide the desired product 4 (70% yield).

2) To a solution of 3a (0.2 mmol) in CHCl$_3$ (3.0 mL), NBS (N-bromosuccinimide) (0.2 mmol) was added portionwisely and then the mixture was heated at r.t. under air for 5 h. The reaction solution was concentrated and purified by column chromatography on silica gel to provide the desired product 5 (85% yield).
3) To a solution of 3a (0.2 mmol) in DMF (2.0 mL), CuI (0.2 mmol) and benzyl cyanide (0.3 mmol) was added and then the mixture was heated at 130 °C under air for 40 h. The reaction solution was then cooled to room temperature, diluted with 5 mL of CH₂Cl₂, filtered through a celite pad and washed with 10-20 mL of CH₂Cl₂. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel to provide the desired product 6 (68% yield).

4) A Schlenk tube with a magnetic stir bar was charged with 3a (0.2 mmol), (4-MeOC₆H₄)₂S (0.1 mmol), KIO₃ (0.02 mmol) and glycerol (1.0 mmol). The Schlenk tube was then sealed with a Teflon lined cap and the mixture was stirred at 100 °C for 6 h under air. The reaction solution was then cooled to room temperature and purified by column chromatography on silica gel to provide the desired product 7 (62% yield).

5) 3bb was obtained in a 45% yield according to the representative procedure. To a solution of 3bb (0.2 mmol) in DCM (1.0 mL), methyl trifluoromethanesulfonate (0.24 mmol) was added dropwisely at 0 °C and the mixture was stirred for 12 h at r.t. The solvent was removed under vacuo. Then, Pd(OH)₂/C (10 wt.%, 19.2 mg), NH₄HCO₃ (2.0 mmol) and MeOH (2.0 mL) were added and the mixture was stirred at 60 °C for 24 h. After cooled to room temperature, the reaction solution was diluted with 5 mL of CH₂Cl₂, filtered through a celite pad and washed with 10-20 mL of CH₂Cl₂. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel to provide the desired product 8 (32% yield).

6) Cleavage of the pyridyl directing group of 3a

To a solution of 3a (0.2 mmol) in DCM (1.0 mL), methyl trifluoromethanesulfonate (0.24 mmol) was added dropwisely at 0 °C and the mixture was stirred for 24 h at r.t. The solvent was removed under vacuo and the residue was dissolved in MeOH (2 mL). Aqueous NaOH solution (2 M, 1.5 mL) was added and the mixture was stirred at 60 °C for 12 h. After being cooled to ambient temperature, the reaction solution was diluted with 5 mL of CH₂Cl₂, filtered through a celite pad and washed with 10-20 mL of CH₂Cl₂. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel to provide the desired product 11 (82% yield).

IV. Mechanistic studies

1. Synthesis of compound 12
A Schlenk tube with a magnetic stir bar was charged with 2a (0.2 mmol), Cu(OAc)$_2$ (40.0 mg, 0.2 mmol) and 1,4-dioxane (1.0 mL). The Schlenk tube was then sealed with a Teflon lined cap and the mixture was heated at 120 °C for 2 hours under N$_2$. The reaction solution was then cooled to ambient temperature, diluted with 5 mL of CH$_2$Cl$_2$, filtered through a celite pad and washed with 10-20 mL of CH$_2$Cl$_2$. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel to provide the desired product 12 in 55% yield.

2. The H/D exchange experiment of 1b

A Schlenk tube with a magnetic stir bar was charged with 1b (0.2 mmol), [Cp*RhCl$_2$]$_2$ (6.2 mg, 0.01 mmol), Cu(OAc)$_2$ (100.0 mg, 0.5 mmol) and 1,4-dioxane (1.0 mL). The Schlenk tube was then sealed with a Teflon lined cap and the mixture was heated at 120 °C for 2 hours under N$_2$. The reaction solution was then cooled to ambient temperature, diluted with 5 mL of CH$_2$Cl$_2$, filtered through a celite pad and washed with 10-20 mL of CH$_2$Cl$_2$. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel to provide [D]$_2$-1b. The deuterium incorporation was calculated from $^1$H-NMR.

3. KIE experiments

A Schlenk tube with a magnetic stir bar was charged with 1b or [D$_6$]-1b (0.2 mmol), 2a (0.6 mmol), [Cp*RhCl$_2$]$_2$ (6.2 mg, 0.01 mmol), Cu(OAc)$_2$ (100.0 mg, 0.5 mmol) and 1,4-dioxane (1.0 mL). The Schlenk tube was then sealed with a Teflon lined cap and the mixture was heated at 120 °C for 2 hours under N$_2$. The reaction solution was then cooled to ambient temperature, diluted with 5 mL of CH$_2$Cl$_2$, filtered through a celite pad and washed with 10-20 mL of CH$_2$Cl$_2$. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel to provide 3b (12 mg) or [D$_4$]-3b (12 mg) and the KIE value was measured to be 1.0.

A Schlenk tube with a magnetic stir bar was charged with 1b (0.1 mmol) and [D$_6$]-1b (0.1 mmol), 2a (0.6 mmol), [Cp*RhCl$_2$]$_2$ (6.2 mg, 0.01 mmol), Cu(OAc)$_2$ (100.0 mg, 0.5 mmol) and 1,4-dioxane (1.0 mL). The Schlenk tube was then sealed with a Teflon lined cap and the mixture was heated at 120 °C for 2 hours under N$_2$. The reaction solution was then cooled to ambient temperature, diluted with 5 mL of CH$_2$Cl$_2$, filtered through a celite pad and washed with 10-20 mL of CH$_2$Cl$_2$. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel to provide a mixture of 3b and [D$_4$]-3b (10 mg) and the KIE value was measured to be 1.1 according to $^1$H-NMR.
4. Catalytic and stoichiometric reactions by using complex 13

A Schlenk tube with a magnetic stir bar was charged with 1b (0.2 mmol), 2a (0.6 mmol), complex 13 (4.4 mg, 0.01 mmol), Cu(OAc)$_2$ (100.0 mg, 0.5 mmol) and 1,4-dioxane (1.0 mL). The Schlenk tube was then sealed with a Teflon lined cap and the mixture was heated at 120 °C for 12 hours under N$_2$. The reaction solution was then cooled to ambient temperature, diluted with 5 mL of CH$_2$Cl$_2$, filtered through a celite pad and washed with 10-20 mL of CH$_2$Cl$_2$. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel to provide 3b in a yield of 65%.

A Schlenk tube with a magnetic stir bar was charged with complex 13 (88 mg, 0.2 mmol), 2a (0.6 mmol), Cu(OAc)$_2$ (100.0 mg, 0.5 mmol) and 1,4-dioxane (1.0 mL). The Schlenk tube was then sealed with a Teflon lined cap and the mixture was heated at 120 °C for 12 hours under N$_2$. The reaction solution was then cooled to ambient temperature, diluted with 5 mL of CH$_2$Cl$_2$, filtered through a celite pad and washed with 10-20 mL of CH$_2$Cl$_2$. The filtrate was collected and concentrated. The residue was purified by column chromatography on silica gel to provide 3b in a yield of 62%.

V. Experimental data for the described substances

5-methyl-2-phenyl-1-(pyridin-2-yl)-1H-indole (3a)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded 3a as a
colorless liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.61 (ddd, $J = 4.9, 1.9, 0.8$ Hz, 1H), 7.61 – 7.54 (m, 2H), 7.47 – 7.41 (m, 1H), 7.28 – 7.22 (m, 5H), 7.17 (ddd, $J = 7.4, 4.9, 1.0$ Hz, 1H), 7.07 – 7.01 (m, 1H), 6.85 (dt, $J = 8.1, 0.9$ Hz, 1H), 6.72 (d, $J = 0.7$ Hz, 1H), 2.45 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.24, 149.15, 139.97, 137.71, 136.96, 132.84, 130.66, 128.98, 128.32, 127.34, 124.60, 121.86, 121.43, 120.29, 111.26, 105.41, 21.47. HRMS (ESI$^+$): calcd for C$_{20}$H$_{17}$N$_2$ [M+H]$^+$ 285.1392, found 285.1396.

2-phenyl-1-(pyridin-2-yl)-1H-indole (3b)
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded 3b as a white solid (mp = 130–131 °C). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.64 (ddd, $J = 4.8, 1.9, 0.7$ Hz, 1H), 7.68 (ddd, $J = 7.1, 6.0, 1.4$ Hz, 2H), 7.64 – 7.58 (m, 1H), 7.29 – 7.19 (m, 8H), 6.89 (d, $J = 8.0$ Hz, 1H), 6.81 (d, $J = 0.4$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.07, 149.19, 139.96, 138.50, 137.76, 132.69, 128.75, 128.71, 128.32, 127.43, 123.02, 122.03, 121.62, 121.36, 120.57, 111.51, 105.62. HRMS (ESI$^+$): calcd for C$_{19}$H$_{15}$N$_2$ [M+H]$^+$ 271.1235, found 271.1238.

5-isopropyl-2-phenyl-1-(pyridin-2-yl)-1H-indole (3c)
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded 3c as a light yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.62 (dd, $J = 4.9, 1.4$ Hz, 1H), 8.60 (m, 1H), 7.65 – 7.56 (m, 2H), 7.29 – 7.19 (m, 8H), 6.90 – 6.81 (m, 2H), 6.73 (s, 1H), 3.88 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.24, 152.21, 149.15, 140.15, 137.65, 133.75, 132.78, 129.25, 128.72, 128.35, 127.44, 121.83, 121.44, 112.91, 112.53, 105.56, 102.31, 55.85. HRMS (ESI$^+$): calcd for C$_{22}$H$_{21}$N$_2$O [M+H]$^+$ 313.1705, found 313.1708.

5-methoxy-2-phenyl-1-(pyridin-2-yl)-1H-indole (3d)
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded 3d as a white solid (mp = 91–92 °C). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.50 – 8.42 (m, 1H), 7.65 – 7.56 (m, 2H), 7.29 – 7.26 (m, 5H), 7.23 – 7.17 (m, 1H), 7.12 (d, $J = 2.5$ Hz, 1H), 6.90 – 6.81 (m, 2H), 6.73 (s, 1H), 3.88 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.24, 152.21, 149.15, 140.45, 137.72, 133.75, 132.78, 129.25, 128.72, 128.35, 127.44, 121.83, 121.44, 112.91, 112.53, 105.56, 102.31, 55.85. HRMS (ESI$^+$): calcd for C$_{22}$H$_{21}$N$_2$O [M+H]$^+$ 301.1341, found 301.1345.

2,5-diphenyl-1-(pyridin-2-yl)-1H-indole (3e)
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded 3e as a yellowish solid (mp = 130–131 °C). ^1H NMR (400 MHz, CDCl₃) δ 8.70 – 8.62 (m, 1H), 7.88 (s, 1H), 7.76 (d, J = 8.6 Hz, 1H), 7.68 (d, J = 8.2 Hz, 2H), 7.63 (td, J = 7.8, 2.0 Hz, 1H), 7.48 (ddd, J = 17.6, 9.4, 4.7 Hz, 3H), 7.35 – 7.21 (m, 7H), 6.90 (d, J = 8.0 Hz, 1H), 6.86 (s, 1H). ^13C NMR (100 MHz, CDCl₃) δ 152.00, 149.24, 142.27, 140.61, 138.01, 137.82, 134.83, 132.58, 129.20, 128.76, 128.67, 128.37, 127.55, 126.48, 122.80, 121.93, 121.68, 119.03, 111.82, 105.91. HRMS (ESI⁺): calcd for C₂₅H₁₉N₂ [M+H]^+ 347.1548, found 347.1550.

5-chloro-2-phenyl-1-(pyridin-2-yl)-1H-indole (3f)
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded 3f as a yellowish liquid. ^1H NMR (400 MHz, CDCl₃) δ 8.67 – 8.61 (m, 1H), 7.64 – 7.58 (m, 3H), 7.29 – 7.21 (m, 6H), 7.16 (dd, J = 8.8, 2.1 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 6.73 (s, 1H). ^13C NMR (100 MHz, CDCl₃) δ 151.67, 149.25, 141.20, 137.90, 136.80, 132.16, 129.72, 128.78, 128.41, 127.81, 126.82, 123.15, 121.95, 121.91, 119.90, 112.72, 104.89. HRMS (ESI⁺): calcd for C₁₉H₁₄ClN₂ [M+H]^+ 305.0846, found 305.0849.

5-bromo-2-phenyl-1-(pyridin-2-yl)-1H-indole (3g)
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded 3g as a yellowish liquid. ^1H NMR (400 MHz, CDCl₃) δ 8.64 (dd, J = 4.9, 1.8, 0.7 Hz, 1H), 8.34 (d, J = 1.4 Hz, 1H), 7.89 (dd, J = 7.8, 1.9 Hz, 1H), 7.56 (d, J = 8.8 Hz, 1H), 7.31 – 7.26 (m, 6H), 6.92 (d, J = 8.0 Hz, 1H), 6.73 (s, 1H). ^13C NMR (100 MHz, CDCl₃) δ 151.63, 149.25, 141.07, 137.90, 137.11, 132.12, 130.35, 128.79, 128.41, 127.81, 126.82, 121.95, 119.90, 112.72, 104.76. HRMS (ESI⁺): calcd for C₁₉H₁₄BrN₂ [M+H]^+ 349.0340, found 349.0343; calcd for C₁₉H₁₄BrN₂ [M+H]^+ 351.0320, found 351.0311.

1-(2-phenyl-1-(pyridin-2-yl)-1H-indol-5-yl)ethan-1-one (3h)
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1, v/v) afforded 3h as a yellowish liquid. ^1H NMR (400 MHz, CDCl₃) δ 8.67 (ddd, J = 4.9, 1.8, 0.7 Hz, 1H), 8.34 (d, J = 1.4 Hz, 1H), 7.89 (dd, J = 8.8, 1.7 Hz, 1H), 7.67 (ddd, J = 7.9, 4.3, 2.0 Hz, 2H), 7.31 – 7.26 (m, 6H), 6.92 (d, J = 8.0 Hz, 1H), 6.89 (s, 1H). ^13C NMR (100 MHz, CDCl₃) δ 198.25, 151.34, 149.35, 141.07, 137.90, 137.11, 132.12, 130.35, 128.79, 128.41, 127.81, 126.82, 121.95, 119.90, 112.76, 128.42, 128.22, 127.90, 123.21, 122.54, 122.26, 122.07, 111.40, 106.32, 26.72. HRMS (ESI⁺): calcd for C₂₁H₁₇N₂O [M+H]^+ 313.1341, found 313.1346.

2-phenyl-1-(pyridin-2-yl)-5-(trifluoromethyl)-1H-indole (3i)
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded 3i as a yellowish liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.67 (ddd, J = 4.9, 1.9, 0.8 Hz, 1H), 7.99 – 7.93 (m, 1H), 7.73 (dd, J = 8.7, 0.6 Hz, 1H), 7.66 (ddd, J = 8.0, 7.6, 2.0 Hz, 1H), 7.45 (ddd, J = 8.7, 1.4 Hz, 1H), 7.28 (ddd, J = 4.1, 3.1, 1.6 Hz, 6H), 6.93 – 6.84 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 151.55, 149.51, 141.87, 139.77, 138.17, 132.08, 128.99, 128.60, 128.19, 128.12, 126.65 (q, $^{1}J_{C,F}$ = 271 Hz), 123.93 (q, $^{2}J_{C,F}$ = 31 Hz), 122.38, 122.21, 119.73 (q, $^{3}J_{C,F}$ = 4 Hz), 118.34 (q, $^{3}J_{C,F}$ = 4 Hz), 112.01, 105.81. HRMS (ESI$^+$): calcd for C$_{20}$H$_{14}$F$_{3}$N$_{2}$ [M+H]$^+$ 339.1109, found 339.1113.

2-phenyl-1-(pyridin-2-yl)-1H-indole-5-carbonitrile (3j)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded 3j as a white solid (mp = 155-156 °C). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.70 – 8.63 (m, 1H), 8.01 (d, J = 1.0 Hz, 1H), 7.73 – 7.63 (m, 2H), 7.45 (dd, J = 8.6, 1.6 Hz, 1H), 7.33 – 7.28 (m, 4H), 7.26 (t, J = 2.9 Hz, 2H), 6.88 (d, J = 8.0 Hz, 1H), 6.84 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 150.00, 148.42, 141.31, 138.82, 137.16, 130.48, 127.86, 127.52, 127.42, 127.26, 124.86, 124.81, 121.55, 121.13, 119.50, 111.51, 104.22, 103.37. HRMS (ESI$^+$): calcd for C$_{20}$H$_{14}$N$_{3}$ [M+H]$^+$ 296.1188, found 296.1190.

5-fluoro-2-phenyl-1-(pyridin-2-yl)-1H-indole (3k)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded 3k as a colorless liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.64 (dd, J = 4.9, 1.8 Hz, 1H), 7.62 (ddd, J = 14.3, 6.6, 3.2 Hz, 2H), 7.32 – 7.21 (m, 7H), 6.96 (td, J = 9.1, 2.5 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 6.75 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.90 (d, $^{1}J_{C,F}$ = 235 Hz), 152.02, 149.35, 141.58, 137.99, 135.12, 132.49, 129.25 (d, $^{2}J_{C,F}$ = 10 Hz), 128.91, 128.54, 127.88, 122.09, 121.91, 112.64 (d, $^{3}J_{C,F}$ = 10 Hz), 111.24 (d, $^{3}J_{C,F}$ = 26 Hz), 105.55 (d, $^{3}J_{C,F}$ = 23 Hz), 105.53 (d, $^{3}J_{C,F}$ = 4 Hz). HRMS (ESI$^+$): calcd for C$_{20}$H$_{14}$FN$_{2}$ [M+H]$^+$ 289.1141, found 289.1143.

6-methyl-2-phenyl-1-(pyridin-2-yl)-1H-indole (3l)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded 3l as a white solid (mp = 144–145 °C). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.65 (dd, J = 4.9, 1.3 Hz, 1H), 7.60 (td, J = 7.7, 2.0 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.48 (s, 1H), 7.27 – 7.18 (m, 6H), 7.03 (d, J = 8.0 Hz, 1H), 6.86 (d, J = 8.0 Hz, 1H), 6.76 (s, 1H), 2.45 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.20, 149.16, 139.36, 138.92, 137.75, 133.02, 132.83, 128.62, 128.29, 127.23, 126.52, 123.05, 122.09, 121.51, 120.21, 111.39, 105.56, 21.98. HRMS (ESI$^+$): calcd for C$_{20}$H$_{14}$N$_{2}$ [M+H]$^+$ 285.1392, found 285.1393.
6-chloro-2-phenyl-1-(pyridin-2-yl)-1H-indole (3m)
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded 3m as a yellowish liquid. 1H NMR (400 MHz, CDCl3) δ 8.70 – 8.61 (m, 1H), 7.72 – 7.68 (m, 1H), 7.61 (ddd, J = 9.4, 7.8, 1.9 Hz, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.30 – 7.21 (m, 6H), 7.16 (dd, J = 8.4, 1.8 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 6.76 (s, 1H). 13C NMR (100 MHz, CDCl3) δ 150.53, 148.26, 139.60, 137.71, 136.89, 131.16, 127.77, 127.66, 127.36, 126.67, 126.18, 120.96, 120.90, 120.87, 120.31, 110.69, 104.33. HRMS (ESI+): calcd for C19H14ClN2 [M+H]+ 305.0846, found 305.0849.

5,6-dimethyl-2-phenyl-1-(pyridin-2-yl)-1H-indole (3n)
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded 3n as a white solid (mp = 105–106 °C). 1H NMR (400 MHz, CDCl3) δ 8.63 (dd, J = 4.9, 1.8 Hz, 1H), 7.59 (td, J = 7.8, 1.9 Hz, 1H), 7.48 (s, 1H), 7.41 (s, 1H), 7.27 – 7.17 (m, 6H), 6.85 (d, J = 8.0 Hz, 1H), 6.70 (s, 1H), 2.35 (d, J = 5.6 Hz, 6H). 13C NMR (100 MHz, CDCl3) δ 152.40, 149.12, 139.12, 137.66, 137.58, 132.98, 132.21, 130.01, 128.58, 128.26, 127.12, 127.04, 121.90, 121.30, 120.67, 111.83, 105.32, 20.66, 20.08. HRMS (ESI+): calcd for C21H19N2 [M+H]+ 299.1548, found 299.1549.

5,6-dichloro-2-phenyl-1-(pyridin-2-yl)-1H-indole (3o)
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded 3o as a yellowish solid (mp = 144–145 °C). 1H NMR (400 MHz, CDCl3) δ 8.70 – 8.64 (m, 1H), 7.83 (s, 1H), 7.72 (s, 1H), 7.66 – 7.60 (m, 1H), 7.32 – 7.23 (m, 6H), 6.82 (d, J = 8.0 Hz, 1H), 6.71 (d, J = 0.5 Hz, 1H). 13C NMR (100 MHz, CDCl3) δ 151.29, 149.35, 141.77, 138.03, 137.10, 131.77, 130.76, 128.49, 128.28, 128.05, 126.65, 125.17, 122.14, 121.81, 121.34, 113.38, 104.65. HRMS (ESI+): calcd for C19H13Cl2N2 [M+H]+ 339.0456, found 339.0460.

7-methyl-2-phenyl-1-(pyridin-2-yl)-1H-indole (3p)
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded 3p as a colorless liquid. 1H NMR (400 MHz, CDCl3) δ 8.70 – 8.60 (m, 1H), 7.62 (td, J = 7.7, 1.9 Hz, 1H), 7.54 (t, J = 8.2 Hz, 1H), 7.34 – 7.29 (m, 1H), 7.28 – 7.18 (m, 5H), 7.08 (t, J = 7.7 Hz, 2H), 6.94 (d, J = 7.1 Hz, 1H), 6.75 (s, 1H), 1.91 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 153.55, 148.66, 141.65, 137.54, 137.40, 132.75, 129.18, 128.97, 128.02, 127.32, 125.31, 125.11, 123.34, 121.81, 120.82, 118.62, 104.23, 19.54. HRMS (ESI+): calcd for C20H17N2 [M+H]+ 285.1392, found 285.1395.
5-methyl-1-(pyridin-2-yl)-2-(o-toly)-1H-indole (3q)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded 3q as a white solid (mp = 149–150 °C). 1H NMR (400 MHz, CDCl3) δ 8.58 – 8.53 (m, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.30 (d, J = 7.4 Hz, 1H), 7.24 – 7.06 (m, 5H), 6.68 (dd, J = 8.1, 0.9 Hz, 1H), 6.58 (s, 1H), 2.47 (s, 3H), 2.04 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 152.04, 148.82, 138.97, 137.42, 137.37, 135.53, 132.91, 131.02, 130.58, 130.16, 128.86, 128.19, 125.58, 124.37, 120.80, 120.26, 120.06, 111.73, 105.91, 21.44, 20.17. HRMS (ESI+): calcd for C21H19N2 [M+H]+ 299.1548, found 299.1549.

5-methyl-1-(pyridin-2-yl)-2-(m-toly)-1H-indole (3r)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded 3r as a white solid (mp = 106–107 °C). 1H NMR (400 MHz, CDCl3) δ 8.62 (dd, J = 4.9, 1.2 Hz, 1H), 7.59 (ddd, J = 8.4, 7.0, 3.1 Hz, 2H), 7.44 (s, 1H), 7.16 (ddd, J = 20.2, 11.3, 6.2 Hz, 3H), 7.08 – 7.02 (m, 2H), 6.98 (d, J = 7.6 Hz, 1H), 6.87 (d, J = 8.0 Hz, 1H), 6.71 (s, 1H), 2.46 (s, 3H), 2.28 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 152.31, 149.07, 140.13, 137.95, 137.61, 136.91, 129.34, 128.98, 128.10, 128.08, 125.83, 124.47, 121.86, 121.34, 120.21, 111.21, 105.24, 21.42, 21.41. HRMS (ESI+): calcd for C21H19N2 [M+H]+ 299.1548, found 299.1551.

5-methyl-1-(pyridin-2-yl)-2-(p-toly)-1H-indole (3s)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded 3s as a yellowish liquid. 1H NMR (400 MHz, CDCl3) δ 8.65 – 8.61 (m, 1H), 7.65 – 7.54 (m, 2H), 7.43 (s, 1H), 7.22 – 7.18 (m, 1H), 7.16 (d, J = 8.1 Hz, 2H), 7.08 – 7.01 (m, 3H), 6.86 (d, J = 8.0 Hz, 1H), 6.69 (s, 1H), 2.45 (s, 3H), 2.32 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 152.34, 149.08, 140.06, 137.65, 137.17, 136.86, 130.56, 129.92, 129.02, 128.55, 124.36, 121.88, 121.34, 120.13, 111.18, 109.99, 104.91, 21.42, 21.21. HRMS (ESI+): calcd for C21H19N2 [M+H]+ 299.1548, found 299.1549.

2-[[1,1'-biphenyl]-4-yl]-5-methyl-1-(pyridin-2-yl)-1H-indole (3t)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded 3t as a yellowish solid (mp = 155–156 °C). 1H NMR (400 MHz, CDCl3) δ 8.67 – 8.61 (m, 1H), 7.64 (td, J = 7.7, 1.9 Hz, 1H), 7.58 (d, J = 8.0 Hz, 3H), 7.51 (d, J = 8.3 Hz, 2H), 7.47 – 7.39 (m, 3H), 7.35 – 7.30 (m, 3H), 7.24 – 7.19 (m, 1H), 7.05 (d, J = 8.4 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 6.78 (s, 1H), 2.47 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 152.26, 149.21, 140.41, 139.92, 139.60, 137.83, 137.08, 131.73, 130.71, 129.00, 128.96, 128.80, 127.41,
2-(4-methoxyphenyl)-5-methyl-1-(pyridin-2-yl)-1H-indole (3u)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded 3u as a white solid (mp = 101–102 °C). ¹H NMR (400 MHz, CDCl₃) δ 8.63 (ddd, J = 4.9, 1.9, 0.7 Hz, 1H), 7.59 (ddd, J = 13.0, 9.5, 5.2 Hz, 2H), 7.42 (s, 1H), 7.22 – 7.15 (m, 3H), 7.02 (ddd, J = 8.5, 1.4 Hz, 1H), 6.85 (d, J = 8.1 Hz, 1H), 6.80 (d, J = 8.8 Hz, 2H), 6.65 (d, J = 0.5 Hz, 1H), 3.79 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 158.95, 152.30, 149.07, 139.82, 137.67, 136.72, 130.54, 129.11, 129.03, 125.33, 124.21, 121.89, 121.35, 120.02, 113.78, 111.12, 104.42, 55.22, 21.43. HRMS (ESI⁺): calcd for C₂₆H₂₁N₂O [M+H]⁺ 361.1705, found 361.1710.

2-(4-fluorophenyl)-5-methyl-1-(pyridin-2-yl)-1H-indole (3v)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded 3v as a colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 8.61 (ddd, J = 4.9, 1.9, 0.8 Hz, 1H), 7.67 – 7.60 (m, 1H), 7.55 (d, J = 8.4 Hz, 1H), 7.45 – 7.42 (m, 1H), 7.24 – 7.19 (m, 3H), 7.05 (dd, J = 8.5, 1.4 Hz, 1H), 7.00 – 6.93 (m, 2H), 6.88 (dt, J = 8.0, 0.8 Hz, 1H), 6.69 (d, J = 0.5 Hz, 1H), 2.46 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.26 (d, Jₐ₋ₓ = 246 Hz), 152.15, 149.38, 139.03, 137.95, 136.95, 130.88, 130.43 (d, Jₐ₋ₓ = 8 Hz), 129.13 (d, Jₐ₋ₓ = 3 Hz), 128.97, 124.77, 121.91, 121.69, 120.38, 115.50 (d, Jₐ₋ₓ = 21 Hz), 111.26, 105.37, 21.56. HRMS (ESI⁺): calcd for C₂₀H₁₆F₂O₂ [M+H]⁺ 303.1298, found 303.1302.

2-(4-chlorophenyl)-5-methyl-1-(pyridin-2-yl)-1H-indole (3w)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded 3w as a yellowish solid (mp = 111–112 °C). ¹H NMR (400 MHz, CDCl₃) δ 8.61 (ddd, J = 4.9, 1.9, 0.8 Hz, 1H), 7.68 – 7.60 (m, 1H), 7.54 (d, J = 8.4 Hz, 1H), 7.46 – 7.40 (m, 1H), 7.24 – 7.16 (m, 5H), 7.05 (dd, J = 8.5, 1.3 Hz, 1H), 6.90 (dt, J = 8.0, 0.8 Hz, 1H), 6.72 (d, J = 0.6 Hz, 1H), 2.46 (d, J = 5.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 152.00, 149.35, 138.74, 137.96, 137.07, 133.31, 131.39, 130.86, 129.81, 128.86, 128.58, 124.90, 121.80, 121.68, 120.40, 111.18, 105.70, 21.45. HRMS (ESI⁺): calcd for C₂₀H₁₅ClO₂ [M+H]⁺ 319.1002, found 319.1005.

methyl 4-(5-methyl-1-(pyridin-2-yl)-1H-indol-2-yl)benzoate (3x)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded 3x as a colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 8.61 (ddd, J = 4.9, 2.0, 0.8 Hz, 1H), 7.97 – 7.88 (m, 2H), 7.65 (ddd,
$J = 8.0$, 7.5, 2.0 Hz, 1H), 7.55 (d, $J = 8.4$ Hz, 1H), 7.50 – 7.44 (m, 1H), 7.34 – 7.30 (m, 2H), 7.23 (ddd, $J = 7.5$, 4.9, 1.0 Hz, 1H), 7.10 – 7.04 (m, 1H), 6.93 (dt, $J = 8.0$, 0.9 Hz, 1H), 6.83 (d, $J = 0.7$ Hz, 1H), 3.90 (s, 3H), 2.46 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.83, 151.91, 149.36, 138.74, 137.98, 137.34, 137.28, 130.94, 129.57, 128.77, 128.55, 128.27, 125.26, 121.73, 120.56, 116.11, 106.71, 52.15, 21.42. HRMS (ESI$^+$): calcd for C$_{22}$H$_{19}$N$_2$O $[M+H]^+$ 343.1447, found 343.1448.

![1-4-(5-methyl-1-(pyridin-2-yl)-1H-indol-2-yl)phenyl]ethan-1-one (3y)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded 3y as a colorless liquid. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.64 – 8.59 (m, 1H), 7.85 (d, $J = 8.2$ Hz, 2H), 7.68 (td, $J = 7.7$, 2.0 Hz, 1H), 7.55 (d, $J = 8.5$ Hz, 1H), 7.47 (d, $J = 0.7$ Hz, 1H), 7.34 (d, $J = 8.2$ Hz, 2H), 7.26 – 7.22 (m, 1H), 7.08 (dd, $J = 8.5$, 1.6 Hz, 1H), 6.96 (d, $J = 8.0$ Hz, 1H), 6.85 (s, 1H), 2.58 (s, 3H), 2.47 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 197.61, 151.91, 149.40, 138.64, 138.03, 137.44, 135.44, 130.99, 129.92, 128.76, 128.38, 125.35, 121.77, 121.72, 120.58, 111.15, 106.87, 26.61, 21.42. HRMS (ESI$^+$): calcd for C$_{22}$H$_{19}$N$_2$O $[M+H]^+$ 327.1497, found 327.1500.

![4-(5-methyl-1-(pyridin-2-yl)-1H-indol-2-yl)benzonitrile (3z)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1, v/v) afforded 3z as a white solid (mp = 104–105 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.64 – 8.55 (m, 1H), 7.73 (td, $J = 7.7$, 1.9 Hz, 1H), 7.53 (dd, $J = 11.2$, 4.5 Hz, 3H), 7.47 (s, 1H), 7.35 – 7.31 (m, 2H), 7.30 – 7.26 (m, 1H), 7.09 (dd, $J = 8.5$, 1.5 Hz, 1H), 7.01 (d, $J = 8.0$ Hz, 1H), 6.84 (s, 1H), 2.46 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 151.62, 149.55, 138.20, 137.82, 137.50, 137.36, 132.06, 131.18, 128.70, 128.63, 125.69, 121.99, 121.56, 120.74, 118.84, 111.08, 110.43, 107.37, 21.40. HRMS (ESI$^+$): calcd for C$_{22}$H$_{19}$N$_3$ $[M+H]^+$ 310.1344, found 310.1349.

![5-methyl-2-(naphthalen-1-yl)-1-(pyridin-2-yl)-1H-indole (3aa)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded 3aa as a yellowish solid (mp = 125–126 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.50 (dd, $J = 4.9$, 1.2 Hz, 1H), 8.01 (d, $J = 8.3$ Hz, 1H), 7.82 – 7.77 (m, 3H), 7.51 (s, 1H), 7.44 – 7.39 (m, 3H), 7.34 (ddd, $J = 8.3$, 6.8, 1.4 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.12 (dd, $J = 8.5$, 1.4 Hz, 1H), 6.98 (ddd, $J = 7.4$, 4.9, 0.9 Hz, 1H), 6.78 (s, 1H), 6.62 (d, $J = 8.1$ Hz, 1H), 2.50 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 151.96, 148.75, 137.61, 137.37, 135.92, 133.49, 132.15, 130.77, 130.71, 128.91, 128.87, 128.46, 128.08, 126.40, 126.00, 125.90, 125.08, 124.63, 120.88, 120.35, 120.18, 111.71, 107.35, 21.47. HRMS (ESI$^+$): calcd for C$_{26}$H$_{18}$N$_2$ $[M+H]^+$ 335.1548, found 335.1549.
5-methyl-2-(naphthalen-2-yl)-1-(pyridin-2-yl)-1H-indole (3ab)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded 3ab as a yellowish solid (mp = 129–130 °C). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.63 (ddd, \(J = 4.9, 1.9, 0.7\) Hz, 1H), 7.81 – 7.68 (m, 4H), 7.63 (d, \(J = 8.4\) Hz, 1H), 7.59 – 7.52 (m, 1H), 7.45 (ddd, \(J = 5.9, 4.5, 1.9\) Hz, 3H), 7.31 (dd, \(J = 8.5, 1.8\) Hz, 1H), 7.18 (ddd, \(J = 7.4, 4.9, 1.0\) Hz, 1H), 7.07 (dd, \(J = 8.5, 1.4\) Hz, 1H), 6.89 (d, \(J = 8.1\) Hz, 1H), 2.47 (s, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 152.28, 149.18, 139.93, 137.79, 137.10, 133.24, 132.44, 130.74, 130.33, 129.04, 127.78, 127.64, 127.50, 126.62, 126.32, 126.15, 124.72, 121.85, 121.42, 120.31, 111.29, 105.93, 21.46.

HRMS (ESI\(^+\)): calcd for C\(_{24}\)H\(_{19}\)N\(_2\) [M+H]\(^+\) 335.1548, found 335.1551.

5-methyl-2-(phenanthren-9-yl)-1-(pyridin-2-yl)-1H-indole (3ac)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded 3ac as a yellowish solid (mp = 175–176 °C). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.65 (dd, \(J = 8.2, 3.7\) Hz, 2H), 8.47 (ddd, \(J = 4.9, 1.9, 0.7\) Hz, 1H), 7.95 (dd, \(J = 8.2, 0.9\) Hz, 1H), 7.82 (dd, \(J = 9.6, 5.4\) Hz, 3H), 7.65 (ddd, \(J = 8.4, 7.0, 1.4\) Hz, 1H), 7.61 – 7.49 (m, 3H), 7.39 (ddd, \(J = 8.2, 7.0, 1.1\) Hz, 1H), 7.23 – 7.18 (m, 1H), 7.13 (dd, \(J = 8.5, 1.5\) Hz, 1H), 6.91 (ddd, \(J = 7.4, 4.9, 0.9\) Hz, 1H), 6.83 (s, 1H), 6.76 (d, \(J = 8.1\) Hz, 1H), 2.51 (s, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 151.99, 148.74, 137.85, 137.85, 137.54, 135.92, 131.19, 131.01, 130.74, 130.04, 128.08, 127.78, 127.61, 127.50, 126.62, 126.32, 126.15, 124.72, 121.85, 121.42, 120.31, 111.29, 105.93, 107.40, 21.49.

HRMS (ESI\(^+\)): calcd for C\(_{28}\)H\(_{21}\)N\(_2\) [M+H]\(^+\) 385.1705, found 385.1708.

5-methyl-2-(pyren-1-yl)-1-(pyridin-2-yl)-1H-indole (3ad)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded 3ad as a yellowish solid (mp = 183–184 °C). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.50 (s, 1H), 8.31 (d, \(J = 9.2\) Hz, 1H), 8.02 (ddd, \(J = 29.2, 26.2, 13.0\) Hz, 8H), 7.84 (d, \(J = 14.5\) Hz, 1H), 7.55 (s, 1H), 7.14 (s, 2H), 6.91 (s, 2H), 6.60 – 6.53 (m, 1H), 2.52 (s, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 151.98, 148.82, 137.99, 137.40, 136.15, 131.29, 130.98, 130.87, 130.85, 129.73, 129.05, 128.70, 127.98, 127.90, 127.82, 127.31, 126.10, 125.30, 125.18, 125.16, 124.75, 124.58, 124.38, 120.86, 120.60, 120.23, 111.77, 108.09, 21.51.

HRMS (ESI\(^+\)): calcd for C\(_{30}\)H\(_{21}\)N\(_2\) [M+H]\(^+\) 409.1705, found 409.1709.
2-(3,5-dimethylphenyl)-5-methyl-1-(pyridin-2-yl)-1H-indole (3ae)
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded 3ae as a colorless liquid. \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \): 8.59 (m, 1H), 7.63 – 7.56 (m, 2H), 7.43 (s, 1H), 7.19 (ddd, \( J = 7.4, 4.9, 0.9 \) Hz, 1H), 7.03 (ddd, \( J = 8.4, 1.6 \) Hz, 1H), 6.87 (dd, \( J = 5.4, 2.6 \) Hz, 4H), 6.70 (s, 1H), 2.46 (s, 3H), 2.21 (s, 6H). \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) \( \delta \): 152.37, 149.01, 140.27, 137.73, 137.55, 136.87, 132.60, 130.53, 129.05, 128.99, 126.52, 124.38, 121.89, 121.28, 120.17, 111.21, 105.12, 21.43, 21.27. HRMS (ESI\(^+\)): calcd for C\(_{22}\)H\(_{21}\)N\(_2\) [M+H]\(^+\) 313.1705, found 313.1710.

![Image of 2-(3,5-dimethylphenyl)-5-methyl-1-(pyridin-2-yl)-1H-indole (3ae)](image)

5-methyl-1-(pyridin-2-yl)-2-(thiophen-2-yl)-1H-indole (3af)
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded 3af as a colorless liquid. \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \): 8.69 – 8.63 (m, 1H), 7.77 – 7.68 (m, 1H), 7.45 – 7.36 (m, 2H), 7.32 – 7.20 (m, 2H), 7.14 – 7.00 (m, 2H), 6.92 (td, \( J = 4.8, 2.2 \) Hz, 1H), 6.80 – 6.71 (m, 2H), 2.45 (s, 3H). \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) \( \delta \): 151.70, 149.33, 137.96, 136.99, 134.50, 133.17, 130.67, 128.59, 127.28, 126.41, 125.60, 124.77, 122.30, 122.21, 120.18, 110.84, 105.30, 21.43. HRMS (ESI\(^+\)): calcd for C\(_{18}\)H\(_{13}\)N\(_2\)S [M+H]\(^+\) 291.0956, found 291.0959.

![Image of 5-methyl-1-(pyridin-2-yl)-2-(thiophen-2-yl)-1H-indole (3af)](image)

5-methyl-2-phenyl-1-(pyridin-2-yl)-1H-indole-3-carbaldehyde (4)
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded 4 as a white solid (mp = 175–176 °C). \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \): 8.85 (s, 1H), 8.62 (dd, \( J = 4.9, 1.2 \) Hz, 1H), 8.30 (s, 1H), 7.66 (td, \( J = 7.8, 1.9 \) Hz, 1H), 7.43 – 7.33 (m, 6H), 7.29 (ddd, \( J = 7.5, 4.9, 0.9 \) Hz, 1H), 7.16 (ddd, \( J = 8.5, 1.5 \) Hz, 1H), 6.91 (d, \( J = 8.0 \) Hz, 1H), 2.52 (s, 3H). \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) \( \delta \): 187.68, 150.35, 149.84, 149.53, 138.15, 135.74, 133.68, 131.04, 129.37, 128.93, 128.40, 126.24, 125.59, 122.92, 122.22, 121.86, 116.59, 111.09, 21.50. HRMS (ESI\(^+\)): calcd for C\(_{21}\)H\(_{17}\)N\(_2\)O [M+H]\(^+\) 313.1341, found 313.1342.

![Image of 5-methyl-2-phenyl-1-(pyridin-2-yl)-1H-indole-3-carbaldehyde (4)](image)

3-bromo-5-methyl-2-phenyl-1-(pyridin-2-yl)-1H-indole (5)
Purification by column chromatography on silica gel (petroleum ether/dichloromethane = 5/1, v/v) afforded 5 as a white solid (mp = 134–135 °C). \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \): 8.57 (ddd, \( J = 4.9, 1.9, 0.7 \) Hz, 1H), 7.58 (d, \( J = 8.5 \) Hz, 1H), 7.56 – 7.51 (m, 1H), 7.46 – 7.43 (m, 1H), 7.39 – 7.28 (m, 5H), 7.16 (ddd, \( J = 7.4, 4.9, 1.0 \) Hz, 1H), 7.11 (dd, \( J = 8.5, 1.3 \) Hz, 1H), 6.76 (dt, \( J = 8.1, 0.8 \) Hz, 1H), 2.50 (s, 3H). \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) \( \delta \): 152.89, 149.84, 149.53, 138.05, 135.74, 133.68, 131.04, 129.37, 128.93, 128.40, 126.24, 125.59, 122.92, 122.22, 121.86, 116.59, 111.09, 21.50. HRMS (ESI\(^+\)): calcd for C\(_{20}\)H\(_{16}\)BrN\(_2\) [M+H]\(^+\) 363.0497, found 363.0499.
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded 6 as a white solid (mp = 142–143 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.64 (ddd, $J = 4.9, 1.8, 0.7$ Hz, 1H), 7.67 (td, $J = 7.8, 1.9$ Hz, 1H), 7.63 – 7.59 (m, 1H), 7.46 (d, $J = 8.5$ Hz, 1H), 7.40 – 7.29 (m, 6H), 7.15 (dd, $J = 8.5, 1.2$ Hz, 1H), 6.91 (d, $J = 8.0$ Hz, 1H), 2.50 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.47, 149.63, 146.38, 138.38, 135.35, 133.09, 129.63, 129.46, 129.06, 128.94, 128.79, 128.41, 127.99, 127.21, 126.49, 123.10, 122.23, 119.21, 119.14, 111.93, 88.14, 21.47.

HRMS (ESI$^+$): calcd for C$_{21}$H$_{16}$N$_3$ [M+H]$^+$ 310.1344, found 310.1349.

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded 7 as a white solid (mp = 177–178 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.60 (dd, $J = 4.9, 1.2$ Hz, 1H), 7.62 – 7.53 (m, 2H), 7.47 (d, $J = 0.7$ Hz, 1H), 7.30 – 7.25 (m, 5H), 7.20 (ddd, $J = 7.4, 4.9, 0.9$ Hz, 1H), 7.12 – 7.04 (m, 3H), 6.82 (d, $J = 8.1$ Hz, 1H), 6.75 – 6.70 (m, 2H), 3.72 (s, 3H), 2.43 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.58, 151.73, 149.14, 143.62, 137.80, 135.88, 131.62, 130.85, 130.73, 130.46, 129.62, 128.16, 128.08, 127.98, 125.57, 121.94, 121.84, 119.54, 114.52, 111.48, 104.92, 55.33, 21.51.

HRMS (ESI$^+$): calcd for C$_{27}$H$_{23}$N$_2$O$_3$ [M+H]$^+$ 423.1531, found 423.1534.

N-(2-(1H-indol-2-yl)phenyl)acetamide (3bb)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1, v/v) afforded 3bb as a colorless liquid. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.57 (d, $J = 3.7$ Hz, 1H), 8.13 (d, $J = 8.2$ Hz, 1H), 7.70 (dd, $J = 11.1, 9.6$ Hz, 3H), 7.60 (td, $J = 7.8, 1.8$ Hz, 1H), 7.37 – 7.27 (m, 3H), 7.25 (s, 1H), 7.21 (ddd, $J = 7.5, 4.9, 0.9$ Hz, 1H), 7.08 (t, $J = 7.3$ Hz, 1H), 6.85 (d, $J = 8.0$ Hz, 1H), 6.75 (s, 1H), 1.98 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.33, 151.25, 149.05, 138.21, 137.75, 136.35, 135.61, 131.23, 129.52, 128.49, 123.96, 123.48, 122.95, 122.15, 121.70, 121.62, 120.78, 120.60, 111.84, 106.88, 24.70.

HRMS (ESI$^+$): calcd for C$_{21}$H$_{18}$N$_2$O [M+H]$^+$ 328.1450, found 328.1456.

N-(2-(1H-indol-2-yl)phenyl)acetamide (8)
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1, v/v) afforded 8 as a white solid (mp = 131–132 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.55 (s, 1H), 8.31 (d, $J$ = 8.2 Hz, 1H), 7.85 (s, 1H), 7.68 (d, $J$ = 7.9 Hz, 1H), 7.44 (t, $J$ = 8.3 Hz, 2H), 7.40 – 7.34 (m, 1H), 7.28 – 7.24 (m, 1H), 7.22 – 7.15 (m, 2H), 6.65 (s, 1H), 2.10 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.88, 136.63, 135.33, 134.13, 129.34, 129.23, 128.70, 124.49, 123.41, 122.79, 121.86, 120.73, 120.53, 111.18, 102.44, 24.78. HRMS (ESI$^+$): calcd for C$_{16}$H$_{13}$N$_2$O [M+H]$^+$ 251.1184, found 251.1180.

5-methyl-2-phenyl-1H-indole (11)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1, v/v) afforded 11 as a brown solid (mp = 216–217 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.24 (s, 1H), 7.64 (dd, $J$ = 8.3, 1.1 Hz, 2H), 7.46 – 7.39 (m, 3H), 7.33 – 7.26 (m, 2H), 7.02 (dd, $J$ = 8.3, 1.4 Hz, 1H), 6.75 (dd, $J$ = 2.1, 0.8 Hz, 1H), 2.45 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 136.91, 134.13, 131.49, 128.52, 128.44, 127.95, 126.54, 124.03, 122.95, 119.27, 109.51, 98.51, 20.44. HRMS (ESI$^+$): calcd for C$_{15}$H$_{14}$N [M+H]$^+$ 208.1126, found 208.1129.

1,4-diphenylbuta-1,3-diyne (12)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1, v/v) afforded 11 as a white solid (mp = 85–86 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.57 – 7.50 (m, 4H), 7.40 – 7.31 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 132.52, 129.23, 128.46, 121.80, 81.56, 73.91. GC-MS: m/z = 202. Its characterization is in accordance with the literature (J. Org. Chem. 2019, 84, 4413).

Compound 13

13 was recrystallized from dichloromethane as a reddish brown solid (mp = 285–286 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 10.15 (s, 1H), 8.77 (s, 1H), 7.50 (ddd, $J$ = 8.7, 7.2, 1.8 Hz, 1H), 7.37 (t, $J$ = 7.9 Hz, 2H), 7.24 (s, 1H), 7.11 (t, $J$ = 7.4 Hz, 2H), 6.79 – 6.71 (m, 1H), 1.56 (s, 15H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.53, 151.94, 138.83, 138.19, 128.70, 122.78, 119.70, 114.59, 109.20, 98.96, 93.56, 93.47, 7.93. HRMS (ESI$^+$): calcd for C$_{21}$H$_{26}$ClN$_2$NaRh [M+Na]$^+$ 465.0581, found 465.0585.

VII. References

VIII. Copies of $^1$H and $^{13}$C spectra

![Chemical structure of 3a](image)