Supporting Information

Rhodium/Copper-Cocatalyzed Coupling-Cyclization of o-Alkenyl Arylisocyanides with Vinyl Azides: One-Pot Synthesis of α-Carbolines

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I. General Information:

All reagents were commercial and were used without further purification. The substrates were prepared according to the previous method reported.\textsuperscript{1,2} Chromatography was carried on flash silica gel (300-400 mesh). All reactions were monitored by TLC, which was performed on percolated aluminum sheets of silica gel 60 (F254). Unless noted, the $^1$H NMR spectra were recorded at 500 MHz, 600 MHz in CDCl$_3$, the $^{13}$C NMR spectra were recorded at 151 MHz in CDCl$_3$ with TMS as internal standard, and the $^{19}$F NMR spectra were recorded at 470 MHz, 565 MHz in CDCl$_3$. All coupling constants ($J$ values) were reported in Hertz (Hz). High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II focus spectrometer (ESI). The compound 3aa was glued on a glass fiber. Data were collected at 293 K using graphite-monochromated Mo K radiation ($\lambda = 0.71073\text{"Å}\$) and IP technique in the range $2.19^\circ < \theta < 27.48^\circ$. Empirical absorption correction was applied. The structures were solved by the direct method and refined by the full-matrix least-squares method on $F^2$ using the SHELXS 97 crystallographic software package. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Hydrogen atoms were located from difference Fourier maps.
II. General Procedure for the Preparation of 3 (3aa as example):

A sealed tube equipped with a magnetic stir bar was charged with 1a (37.4 mg, 0.2 mmol), 2a (58.1 mg, 0.4 mmol), [Rh(COD)Cl]₂ (2.5 mg, 0.005 mmol), CuI (1.9 mg, 0.01 mmol), DPPE (4.1 mg, 0.01 mmol), then toluene (2.0 mL) was added. Subsequently, the reaction mixture was stirred under an oxygen atmosphere (oxygen balloon) at 120 °C for 3.5 h. After the reaction was complete, the solvent was removed under reduced pressure. The crude residue was purified by silica gel column chromatography (EtOAc/petroleum ether = 1/10, V/V) to afford pure product 3aa (42.3 mg, 70%) as a yellow solid.

A gram-scale synthesis of compound 3aa:

An oven-dried vial equipped with a magnetic stir bar was charged with 1a (1.12 g, 6 mmol), 2a (1.74 g, 12 mmol), [Rh(COD)Cl]₂ (73.9 mg, 0.15 mmol), CuI (57.1 mg, 0.3 mmol), DPPE (122.0 mg, 0.3 mmol), and toluene (60.0 mL) was added. Subsequently, the reaction mixture was stirred under an oxygen atmosphere (oxygen balloon) at 120 °C for 4 h. After the reaction was complete, the solvent was removed under reduced pressure. The crude residue was purified by silica gel column chromatography (EtOAc/petroleum ether = 1/10, V/V) to afford pure product 3aa (1.14 g, 62%) as a yellow solid.

Methyl 2-phenyl-9H-pyrido[2,3-b]indole-4-carboxylate (3aa):
Yellow solid, mp: 182 – 183 °C, 42.3 mg, 70% yield. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 11.55 (s, 1H), 8.74 (d, \(J = 8.0\) Hz, 1H), 8.21 – 8.15 (m, 3H), 7.57 – 7.53 (m, 2H), 7.52 – 7.49 (m, 1H), 7.28 (d, \(J = 7.6\) Hz, 1H), 7.22 (t, \(J = 7.6\) Hz, 1H), 6.52 (d, \(J = 8.0\) Hz, 1H), 4.13 (s, 3H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 167.06, 154.06, 153.81, 140.08, 139.38, 132.77, 129.23, 129.14, 127.69, 127.66, 125.80, 120.31, 119.72, 113.76, 113.55, 111.12, 52.66. HRMS(ESI-TOF): [M + H]\(^+\) calculated for C\(_{19}\)H\(_{15}\)N\(_2\)O\(_2\): 303.1128, found: 303.1121.

**Methyl 6-methyl-2-phenyl-9H-pyrido[2,3-b]indole-4-carboxylate (3ba):**

Yellow solid, mp: 191 – 192 °C, 45.6 mg, 72% yield. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 10.70 (s, 1H), 8.56 (s, 1H), 8.17 (d, \(J = 7.3\) Hz, 2H), 8.15 (s, 1H), 7.55 (t, \(J = 7.5\) Hz, 2H), 7.49 (t, \(J = 7.3\) Hz, 1H), 7.18 (d, \(J = 8.2\) Hz, 1H), 6.70 (d, \(J = 8.2\) Hz, 1H), 4.14 (s, 3H), 2.51 (s, 3H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 167.14, 153.84, 139.38, 138.12, 132.58, 129.64, 129.16, 129.10, 129.05, 127.52, 125.60, 119.91, 113.52, 113.30, 110.66, 52.63, 21.72. HRMS(ESI-TOF): [M + H]\(^+\) calculated for C\(_{20}\)H\(_{17}\)N\(_2\)O\(_2\): 317.1285, found: 317.1290.

**Methyl 7-methyl-2-phenyl-9H-pyrido[2,3-b]indole-4-carboxylate (3ca):**

Yellow solid, mp: 183 – 184 °C, 44.3 mg, 70% yield. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 11.78 (d, \(J = 4.0\) Hz, 1H), 8.59 (d, \(J = 8.2\) Hz, 1H), 8.20 – 8.15 (m, 2H), 8.12 (s, 1H), 7.56 (t, \(J = 7.2\) Hz, 2H), 7.54 – 7.50 (m, 1H), 7.02 (dd, \(J = 8.2, 1.5\) Hz, 1H), 6.12 (s, 1H), 4.11 (s, 3H), 2.30 (s, 3H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 167.11, 154.01, 153.42, 140.67, 139.76, 138.14, 132.01, 129.22, 128.87, 127.91, 125.47, 121.83, 117.30,

**Methyl 6-methoxy-2-phenyl-9H-pyrido[2,3-b]indole-4-carboxylate (3da):**

Yellow solid, mp: 154 – 155 °C, 41.2 mg, 62% yield. ¹H NMR (600 MHz, CDCl₃) δ 10.85 (s, 1H), 8.35 (d, J = 2.5 Hz, 1H), 8.17 (dd, J = 9.9, 2.6 Hz, 3H), 7.56 – 7.52 (m, 2H), 7.50 (d, J = 7.4 Hz, 1H), 7.00 (dd, J = 8.8, 2.6 Hz, 1H), 6.65 (d, J = 8.8 Hz, 1H), 4.13 (s, 3H), 3.94 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 167.03, 154.08, 154.04, 153.96, 139.36, 134.82, 132.62, 129.13, 129.10, 127.55, 120.16, 117.47, 113.50, 113.46, 111.67, 108.23, 55.94, 52.66. HRMS(ESI-TOF): [M + Na]+ calculated for C₂₀H₁₆N₂NaO₂+: 355.1053, found: 355.1051.

**Methyl 6-chloro-2-phenyl-9H-pyrido[2,3-b]indole-4-carboxylate (3ea):**

Yellow solid, mp. 192 – 193 °C, 43.1 mg, 64% yield. ¹H NMR (600 MHz, CDCl₃) δ 11.51 (s, 1H), 8.77 (d, J = 2.1 Hz, 1H), 8.18 – 8.08 (m, 3H), 7.53 (d, J = 7.8 Hz, 3H), 7.23 (dd, J = 8.6, 2.1 Hz, 1H), 6.40 (d, J = 8.6 Hz, 1H), 4.14 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 166.57, 154.83, 153.93, 139.08, 138.19, 133.10, 129.36, 129.26, 127.79, 127.70, 125.75, 125.53, 120.75, 114.21, 112.75, 112.02, 52.78. HRMS(ESI-TOF): [M + H]+ calculated for C₁₉H₁₄ClN₂O₂+: 337.0738, found: 337.0732.

**Methyl 6-bromo-2-phenyl-9H-pyrido[2,3-b]indole-4-carboxylate (3fa):**
Yellow solid, mp: 192 – 193 °C, 43.5 mg, 57% yield. $^1$H NMR (500 MHz, CDCl$_3$) δ 11.83 (s, 1H), 8.92 (s, 1H), 8.12 (s, 1H), 8.11 – 8.09 (m, 2H), 7.53 (d, $J = 5.0$ Hz, 3H), 7.32 (d, $J = 8.7$ Hz, 1H), 6.21 (d, $J = 8.6$ Hz, 1H), 4.15 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 166.51, 154.80, 153.76, 139.04, 138.51, 133.08, 130.34, 129.35, 129.27, 128.50, 127.73, 121.27, 114.26, 113.18, 112.61, 112.49, 52.78. HRMS(ESI-TOF): [M + H]$^+$ calculated for C$_{19}$H$_{14}$BrN$_2$O$_2$: 381.0233, found: 381.0227.

**Methyl 6,8-difluoro-2-phenyl-9H-pyrido[2,3-b]indole-4-carboxylate (3ga):**

Yellow solid, mp: 197 – 198 °C, 33.8 mg, 50% yield. $^1$H NMR (600 MHz, CDCl$_3$) δ 9.41 (s, 1H), 8.34 (dd, $J = 9.9$, 2.3 Hz, 1H), 8.20 (s, 1H), 8.12 (d, $J = 7.0$ Hz, 2H), 7.51 (t, $J = 7.3$ Hz, 2H), 7.47 – 7.44 (m, 1H), 7.02 – 7.06 (m, 1H), 4.12 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 166.40, 156.64 (dd, $J = 237.07$ Hz, 9.8 Hz), 155.66, 153.52, 147.81 (dd, $J = 247.64$ Hz, 13.6Hz), 138.54, 133.27, 129.52, 128.91, 127.25, 124.47 (d, $J = 15.0$ Hz), 122.33 (d, $J = 6.2$ Hz), 114.20, 112.61, 107.63 (dd, $J = 25.67$ Hz, 4.53 Hz), 102.71 (dd, $J = 29.7$, 19.9 Hz), 52.78. $^{19}$F NMR (470 MHz, CDCl$_3$) δ -119.64 (t, $J = 9.7$ Hz), -131.74 (d, $J = 10.4$ Hz). HRMS(ESI-TOF): [M + H]$^+$ calculated for C$_{19}$H$_{13}$F$_2$N$_2$O$_2$: 339.0940, found: 339.0941.

**Methyl 2-phenyl-11H-benzo[f]pyrido[2,3-b]indole-4-carboxylate (3ha):**
Yellow solid, mp: >250 °C, 38.1 mg, 54% yield. $^1$H NMR (600 MHz, DMSO-d$_6$) δ 12.81 (s, 1H), 8.26 (d, $J$ = 7.4 Hz, 2H), 8.09 (d, $J$ = 8.0 Hz, 1H), 8.07 (d, $J$ = 8.8 Hz, 1H), 8.04 (s, 1H), 7.89 (d, $J$ = 8.4 Hz, 1H), 7.81 (d, $J$ = 8.7 Hz, 1H), 7.71 (t, $J$ = 7.6 Hz, 1H), 7.56 (t, $J$ = 7.6 Hz, 2H), 7.51 (d, $J$ = 7.5 Hz, 1H), 7.50 – 7.46 (m, 1H), 4.06 (s, 3H).

$^{13}$C NMR (151 MHz, DMSO-d$_6$) δ 170.19, 151.97, 151.68, 139.14, 138.78, 135.48, 130.04, 129.64, 129.62, 129.41, 129.02, 127.28, 127.20, 124.22, 123.80, 113.78, 112.17, 111.39, 110.34, 53.23.

HRMS(ESI-TOF): [M + Na]$^+$ calculated for C$_{23}$H$_{16}$N$_2$NaO$_2$: 375.1104, found: 375.1098.

2,4-Diphenyl-9H-pyrido[2,3-b]indole (3ia):

Yellow solid, mp: 220 – 222 °C, 46.8 mg, 73% yield. $^1$H NMR (600 MHz, CDCl$_3$) δ 12.29 (s, 1H), 8.17 – 8.11 (m, 2H), 7.68 – 7.63 (m, 2H), 7.52 (d, $J$ = 8.0 Hz, 1H), 7.49 – 7.42 (m, 6H), 7.39 (dd, $J$ = 8.3, 6.1 Hz, 1H), 7.03 (t, $J$ = 7.9 Hz, 1H), 6.85 (t, $J$ = 7.6 Hz, 1H), 6.28 (d, $J$ = 8.1 Hz, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 154.31, 153.45, 146.27, 140.24, 139.52, 139.30, 128.23, 128.85, 128.79, 128.78, 128.70, 127.92, 126.37, 122.32, 120.53, 119.44, 114.45, 112.99, 111.48. HRMS(ESI-TOF): [M + H]$^+$ calculated for C$_{23}$H$_{17}$N$_2$: 321.1386, found: 321.1379.

4-(Perfluorophenyl)-2-phenyl-9H-pyrido[2,3-b]indole (3ja):

Brown solid, mp: 193 – 194 °C, 55.8 mg, 68% yield. $^1$H NMR (600 MHz, CDCl$_3$) δ 11.68 (s, 1H), 8.19 (d, $J$ = 7.3 Hz, 2H), 7.60 – 7.55 (m, 3H), 7.53 (d, $J$ = 7.2 Hz, 1H), 7.28 (d, $J$ = 7.8 Hz, 1H), 7.24 (d, $J$ = 8.4 Hz, 1H), 7.08 (t, $J$ = 7.5 Hz, 1H), 6.61 – 6.55 (m, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 154.54, 152.97, 145.16, 143.50, 139.51,
139.45, 137.21, 129.25, 129.20, 128.91, 127.77, 127.28, 121.07, 120.42, 119.79, 115.03, 114.01, 113.25, 111.67. 19F NMR (470 MHz, CDCl3) δ -139.41 (dd, J = 22.8, 8.3 Hz), -152.71 (t, J = 20.8 Hz), -160.60 (td, J = 22.2, 8.3 Hz). HRMS(ESI-TOF): [M + H]^+ calculated for C23H12F3N2+: 411.0915, found: 411.0921.

2-Phenyl-4-(pyridin-2-yl)-9H-pyrido[2,3-b]indole (3ka):

Brown solid, mp: 192 – 193 °C, 47.6 mg, 74% yield. 1H NMR (600 MHz, CDCl3) δ 12.23 (d, J = 4.8 Hz, 1H), 8.91 (dd, J = 4.8, 1.5 Hz, 1H), 8.23 (dd, J = 7.2, 1.5 Hz, 2H), 7.90 – 7.86 (m, 2H), 7.78 (d, J = 8.9 Hz, 2H), 7.54 – 7.51 (m, 2H), 7.49 – 7.46 (m, 1H), 7.45 – 7.42 (m, 1H), 7.14 (ddd, J = 8.2, 7.1, 1.2 Hz, 1H), 7.01 – 6.97 (m, 1H), 6.42 (d, J = 8.1 Hz, 1H). 13C NMR (151 MHz, CDCl3) δ 157.44, 154.40, 153.68, 150.07, 144.29, 140.07, 139.75, 136.77, 129.14, 128.83, 127.86, 126.65, 124.13, 123.49, 122.99, 120.22, 119.54, 114.05, 112.71, 111.48. HRMS(ESI-TOF): [M + H]^+ calculated for C22H16N3+: 322.1339, found: 322.1342.

Methyl 2-(p-tolyl)-9H-pyrido[2,3-b]indole-4-carboxylate (3ab):

Yellow solid, mp: 193 – 194 °C, 44.3 mg, 70% yield. 1H NMR (600 MHz, CDCl3) δ 11.50 (s, 1H), 8.73 (d, J = 8.0 Hz, 1H), 8.13 (s, 1H), 8.07 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 7.9 Hz, 2H), 7.27 (t, J = 7.3 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 6.54 (d, J = 2.4 Hz, 1H), 4.12 (s, 3H), 2.46 (s, 3H). 13C NMR (151 MHz, CDCl3) δ 167.13, 154.19, 153.78, 140.01, 139.21, 136.60, 132.72, 129.89, 127.56, 127.41, 125.70, 120.23, 119.80,

S7
113.50, 113.23, 111.18, 52.62, 21.34. HRMS(ESI-TOF): [M + H]+ calculated for C_{20}H_{17}N_{2}O_{2}+: 317.1285, found: 317.1293.

**Methyl 2-(m-tolyl)-9H-pyrido[2,3-b]indole-4-carboxylate (3ac):**

![Structure of Methyl 2-(m-tolyl)-9H-pyrido[2,3-b]indole-4-carboxylate (3ac)](image)

Yellow solid, mp: 160 – 162 °C, 41.1 mg, 65% yield. ¹H NMR (600 MHz, CDCl₃) δ 11.43 (s, 1H), 8.75 (d, J = 8.0 Hz, 1H), 8.16 (s, 1H), 8.00 (s, 1H), 7.96 (d, J = 7.7 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.23 (t, J = 7.6 Hz, 1H), 6.66 – 6.60 (m, 1H), 4.13 (s, 3H), 2.40 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 167.14, 154.27, 153.76, 140.04, 139.29, 138.93, 132.72, 129.89, 129.12, 128.31, 127.63, 125.73, 124.83, 120.31, 119.75, 113.80, 113.44, 111.08, 52.66, 21.60. HRMS(ESI-TOF): [M + Na]⁺ calculated for C_{20}H_{16}N_{2}NaO_{2}: 339.1104, found: 339.1104.

**Methyl 2-(4-methoxyphenyl)-9H-pyrido[2,3-b]indole-4-carboxylate (3ad):**

![Structure of Methyl 2-(4-methoxyphenyl)-9H-pyrido[2,3-b]indole-4-carboxylate (3ad)](image)

Yellow solid, mp: 174 – 176 °C, 38.5 mg, 58% yield. ¹H NMR (600 MHz, CDCl₃) δ 11.30 (s, 1H), 8.72 (d, J = 8.0 Hz, 1H), 8.15 – 8.08 (m, 3H), 7.32 – 7.28 (m, 1H), 7.24 – 7.20 (m, 1H), 7.06 – 7.02 (m, 2H), 6.70 (d, J = 8.1 Hz, 1H), 4.12 (d, J = 1.3 Hz, 3H), 3.87 (d, J = 1.3 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 167.14, 160.68, 153.85, 153.76, 139.90, 132.73, 131.92, 128.88, 127.37, 125.64, 120.27, 119.88, 114.59, 113.14, 112.85, 111.13, 55.50, 52.60. HRMS(ESI-TOF): [M + Na]⁺ calculated for C_{20}H_{16}N_{2}NaO_{3}: 355.1053, found: 355.1056.
Methyl 2-(4-bromophenyl)-9H-pyrido[2,3-b]indole-4-carboxylate (3a):

Yellow solid, mp: 199 – 200 °C, 41.2 mg, 54% yield. $^1$H NMR (600 MHz, CDCl$_3$) δ 10.16 (s, 1H), 8.78 (d, $J$ = 8.1 Hz, 1H), 8.13 (s, 1H), 8.05 – 7.99 (m, 2H), 7.64 (d, $J$ = 8.5 Hz, 2H), 7.45 (t, $J$ = 7.6 Hz, 1H), 7.29 (t, $J$ = 7.7 Hz, 1H), 7.04 (d, $J$ = 8.1 Hz, 1H), 4.14 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 166.89, 153.43, 152.72, 139.87, 138.06, 132.77, 132.16, 128.89, 128.02, 126.09, 123.61, 120.69, 119.86, 113.66, 113.41, 110.92, 52.72. HRMS(ESI-TOF): [M + H]$^+$ calculated for C$_{19}$H$_{14}$BrN$_2$O$_2$: 381.0233, found: 381.0223.

Methyl 2-(4-chlorophenyl)-9H-pyrido[2,3-b]indole-4-carboxylate (3a):

Yellow solid, mp: 197 – 198 °C, 43.8 mg, 65% yield. $^1$H NMR (600 MHz, CDCl$_3$) δ 10.02 (s, 1H), 8.78 (d, $J$ = 8.1 Hz, 1H), 8.14 (s, 1H), 8.10 (d, $J$ = 8.5 Hz, 2H), 7.49 (d, $J$ = 8.5 Hz, 2H), 7.45 (t, $J$ = 7.6 Hz, 1H), 7.30 (t, $J$ = 7.6 Hz, 1H), 7.08 (d, $J$ = 8.1 Hz, 1H), 4.14 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 166.85, 153.54, 152.59, 139.96, 137.62, 135.29, 132.74, 129.25, 128.70, 127.93, 127.07, 126.04, 120.58, 119.75, 113.70, 113.42, 110.97, 52.69. HRMS(ESI-TOF): [M + H]$^+$ calculated for C$_{19}$H$_{14}$ClN$_2$O$_2$: 337.0738, found: 337.0739.

Methyl 2-(2-chlorophenyl)-9H-pyrido[2,3-b]indole-4-carboxylate (3a):
Yellow solid, mp: 194 – 195 °C, 45.8 mg, 68% yield. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 12.01 (s, 1H), 8.79 (dd, $J = 7.9$, 1.3 Hz, 1H), 8.05 (s, 1H), 7.77 (dd, $J = 7.5$, 1.7 Hz, 1H), 7.64 (dd, $J = 8.1$, 1.2 Hz, 1H), 7.48 (td, $J = 7.8$, 1.7 Hz, 1H), 7.41 (td, $J = 7.5$, 1.3 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.25 – 7.22 (m, 1H), 6.30 (d, $J = 8.1$ Hz, 1H), 4.11 (s, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 166.91, 153.42, 152.52, 140.32, 139.03, 133.05, 132.07, 131.96, 130.50, 129.92, 127.86, 127.42, 125.98, 120.30, 119.46, 117.13, 113.98, 111.00, 52.67. HRMS(ESI-TOF): [M + H]$^+$ calculated for C$_{19}$H$_{14}$ClN$_2$O$_2$: 337.0738, found: 337.0730.

Methyl 2-(3-chlorophenyl)-9H-pyrido[2,3-b]indole-4-carboxylate (3ah):

Yellow solid, mp: 168 – 170 °C, 48.5 mg, 72% yield. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 10.84 (s, 1H), 8.65 (d, $J = 8.0$ Hz, 1H), 7.99 (m, 1H), 7.95 (d, $J = 1.0$ Hz, 1H), 7.87 (dt, $J = 7.5$, 1.5 Hz, 1H), 7.33 (d, $J = 8.0$ Hz, 1H), 7.30 (t, $J = 7.7$ Hz, 1H), 7.25 (d, $J = 8.0$ Hz, 1H), 7.15 (t, $J = 7.6$ Hz, 1H), 6.64 (d, $J = 8.1$ Hz, 1H), 4.02 (d, $J = 1.3$ Hz, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 166.76, 153.51, 152.13, 140.96, 140.06, 135.15, 132.66, 130.33, 128.99, 128.02, 127.54, 126.08, 125.55, 120.53, 119.65, 114.03, 113.59, 110.95, 52.69. HRMS(ESI-TOF): [M + Na]$^+$ calculated for C$_{19}$H$_{13}$ClN$_2$NaO$_2$: 359.0558, found: 359.0551.

Methyl 2-(4-fluorophenyl)-9H-pyrido[2,3-b]indole-4-carboxylate (3ai):

Yellow solid, mp: 166 – 169 °C, 42.9 mg, 67% yield. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 10.91 (s, 1H), 8.75 (d, $J = 8.1$ Hz, 1H), 8.16 – 8.11 (m, 2H), 8.09 (d, $J = 1.0$ Hz, 1H), 7.37 (td, $J = 7.6$, 7.0, 1.2 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.20 (t, $J = 8.6$ Hz, 2H), 6.80 –
6.76 (m, 1H), 4.13 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 166.93, 164.43, 162.78, 153.25 (d, $J = 102.68$ Hz), 139.91, 135.39 (d, $J = 3.02$), 132.79, 129.30 (d, $J = 9.06$ Hz), 127.82, 125.95, 120.52, 119.77, 116.06 (d, $J = 21.14$), 113.42 (d, $J = 4.53$), 110.92, 77.25, 52.69. 

$^{19}$F NMR (471 MHz, CDCl$_3$) δ -112.53 – -112.59 (m). HRMS(ESI-TOF): [M + Na]$^+$ calculated for $C_{19}H_{13}FN_2NaO_2$: 343.0853, found: 343.0856.

**Methyl 2-(3-fluorophenyl)-9H-pyrido[2,3-b]indole-4-carboxylate (3aj):**

![Chemical structure of 3aj]

Yellow solid, mp: 164 – 165 °C, 41.6 mg, 65% yield. $^1$H NMR (600 MHz, CDCl$_3$) δ 10.97 (s, 1H), 8.75 (d, $J = 7.8$ Hz, 1H), 8.08 (s, 1H), 7.90 (d, $J = 8.2$ Hz, 1H), 7.83 (d, $J = 10.0$ Hz, 1H), 7.45 (q, $J = 7.7$ Hz, 1H), 7.34 (t, $J = 7.6$ Hz, 1H), 7.23 (d, $J = 8.0$ Hz, 1H), 7.16 (t, $J = 8.3$ Hz, 1H), 6.73 (d, $J = 8.0$ Hz, 1H), 4.11 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 166.81, 163.45 (d, $J = 246.13$), 153.54, 152.35 (d, $J = 3.12$ Hz), 141.50 (d, $J = 7.55$ Hz), 140.09, 132.71, 130.64 (d, $J = 7.55$), 127.99, 126.06, 123.09 (d, $J = 3.02$), 120.52, 119.68, 115.90 (d, $J = 21.14$ Hz), 114.40 (d, $J = 24.16$ Hz), 114.02, 113.64, 110.92, 52.68. $^{19}$F NMR (470 MHz, CDCl$_3$) δ -112.20 (q, $J = 8.4$ Hz). HRMS(ESI-TOF): [M + Na]$^+$ calculated for $C_{19}H_{13}FN_2NaO_2$: 343.0853, found: 343.0854.

**Methyl 2-(4-cyanophenyl)-9H-pyrido[2,3-b]indole-4-carboxylate (3ak):**

![Chemical structure of 3ak]

Yellow solid, mp: 168 – 169 °C, 34.0 mg, 52% yield. $^1$H NMR (500 MHz, DMSO-$d_6$) δ 12.38 (s, 1H), 8.63 (d, $J = 8.1$ Hz, 1H), 8.38 (d, $J = 8.3$ Hz, 2H), 8.24 (s, 1H), 7.99 (d, $J = 8.3$ Hz, 2H), 7.57 (d, $J = 5.9$ Hz, 2H), 7.28 (td, $J = 7.1$, 6.1, 2.1 Hz, 1H), 4.08
(s, 3H). $^{13}$C NMR (151 MHz, DMSO-$d_6$) $\delta$ 166.89, 153.48, 150.88, 143.06, 141.26, 133.26, 132.71, 128.71, 127.85, 125.97, 120.51, 119.27, 119.16, 113.30, 112.98, 111.87, 111.78, 53.27. HRMS(ESI-TOF): [M + H]$^+$ calculated for C$_{20}$H$_{14}$N$_3$O$_2$: 328.1081, found: 328.1089.

Methyl 2-(4-(trifluoromethyl)phenyl)-9H-pyrido[2,3-b]indole-4-carboxylate (3al):

\[
\text{MeO}_2\text{C} \quad \text{CF}_3
\]

Green solid, mp: 173 – 175 °C, 37.0 mg, 50% yield. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 10.95 (s, 1H), 8.76 (d, $J$ = 8.0 Hz, 1H), 8.16 (d, $J$ = 8.0 Hz, 2H), 8.09 (s, 1H), 7.73 (d, $J$ = 8.1 Hz, 2H), 7.32 (s, 1H), 7.25 (s, 1H), 6.60 (d, $J$ = 8.0 Hz, 1H), 4.12 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 166.70, 153.57, 152.08, 142.54, 140.07, 132.75, 130.85 (d, $J$ = 33.22 Hz), 128.12, 127.79, 126.18, 126 (d, $J$ = 3.02 Hz), 124.17 (d, $J$ = 271.8 Hz), 120.69, 119.59, 114.28, 113.84, 110.93, 52.72. $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ -62.54 (s). HRMS(ESI-TOF): [M + H]$^+$ calculated for C$_{20}$H$_{14}$F$_3$N$_2$O$_2$: 371.1002, found: 371.0976.

Methyl 2-(naphthalen-2-yl)-9H-pyrido[2,3-b]indole-4-carboxylate (3am):

\[
\text{MeO}_2\text{C} \quad \text{Me}
\]

Yellow solid, mp: 175 – 177 °C, 45.8 mg, 65% yield. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 10.24 (s, 1H), 8.77 (d, $J$ = 7.9 Hz, 1H), 8.62 (d, $J$ = 1.8 Hz, 1H), 8.30 (d, $J$ = 9.9 Hz, 2H), 7.99 – 7.94 (m, 2H), 7.92 – 7.89 (m, 1H), 7.53 (ddd, $J$ = 6.6, 3.9, 1.8 Hz, 2H), 7.29 (t, $J$ = 7.5 Hz, 1H), 7.26 – 7.23 (m, 1H), 6.95 (s, 1H), 4.15 (s, 3H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 167.09, 153.93, 153.58, 139.86, 136.49, 133.68, 133.63, 132.72, 128.77, 127.73, 126.85, 126.71, 126.48, 125.93, 124.90, 120.51, 119.94, 113.97,
113.37, 110.95, 52.66. HRMS(ESI-TOF): [M + H]$^+$ calculated for C$_{23}$H$_{17}$N$_2$O$_2$$^+$: 353.1285, found: 353.1285.

**Methyl 2-benzyl-9$H$-pyrido[2,3-\textit{b}]indole-4-carboxylate (3an):**

![Image](image)

Yellow solid, mp: 160 – 161 °C, 31.6 mg, 50% yield. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 9.30 (s, 1H), 8.74 (d, $J = 8.1$ Hz, 1H), 7.59 (s, 1H), 7.49 (t, $J = 7.5$ Hz, 1H), 7.44 (d, $J = 8.0$ Hz, 1H), 7.31 (d, $J = 4.3$ Hz, 4H), 7.28 (d, $J = 7.6$ Hz, 1H), 7.23 (dd, $J = 8.6, 4.3$ Hz, 1H), 4.34 (s, 2H), 4.06 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 167.06, 157.53, 153.05, 139.48, 139.26, 132.56, 129.06, 128.66, 127.63, 126.51, 125.89, 120.55, 120.08, 115.97, 112.47, 110.75, 52.53, 44.53. HRMS(ESI-TOF): [M + H]$^+$ calculated for C$_{20}$H$_{17}$N$_2$O$_2$$^+$: 317.1285, found: 317.1287.

**Methyl 2-(phenoxymethyl)-9$H$-pyrido[2,3-\textit{b}]indole-4-carboxylate (3ao):**

![Image](image)

White solid, mp: 185 °C, 26.6 mg, 40% yield. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 9.45 (s, 1H), 8.80 (d, $J = 8.1$, 1.0 Hz, 1H), 7.94 (s, 1H), 7.54 – 7.50 (m, 2H), 7.33 – 7.29 (m, 3H), 7.07 – 7.04 (m, 2H), 6.99 (td, $J = 7.3, 1.0$ Hz, 1H), 5.36 (s, 2H), 4.10 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 166.86, 158.48, 153.38, 152.84, 139.57, 132.72, 129.56, 128.09, 126.21, 121.30, 120.73, 119.92, 114.97, 114.27, 114.07, 110.87, 70.77, 52.65. HRMS(ESI-TOF): [M + Na]$^+$ calculated for C$_{20}$H$_{16}$N$_2$NaO$_3$$^+$: 355.1053, found: 355.1045.

**Methyl 2-hexyl-9$H$-pyrido[2,3-\textit{b}]indole-4-carboxylate (3ap):**

S13
White solid, mp: 158 – 159 °C, 26.7 mg, 43% yield. $^1$H NMR (600 MHz, CDCl$_3$) δ 10.47 (s, 1H), 8.76 (d, $J$ = 8.1 Hz, 1H), 7.60 (s, 1H), 7.54 – 7.48 (m, 2H), 7.30 (td, $J$ = 7.5, 6.9, 1.4 Hz, 1H), 4.11 (s, 3H), 3.07 – 3.03 (m, 2H), 1.85 (m, 2H), 1.42 (q, $J$ = 7.2 Hz, 2H), 1.31 (m, 4H), 0.86 (t, $J$ = 7.0 Hz, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 167.25, 159.31, 153.36, 139.43, 132.33, 127.37, 125.76, 120.35, 120.14, 115.29, 112.31, 110.78, 52.53, 38.45, 31.71, 30.35, 29.14, 22.58, 14.06. HRMS(ESI-TOF): [M + Na]$^+$ calculated for C$_{19}$H$_{22}$N$_2$NaO$_2$: 333.1573, found: 333.1572.

Methyl 2-(cyclohex-1-en-1-yl)-9H-pyrido[2,3-b]indole-4-carboxylate (3aq):

Yellow solid, mp: 147 – 148 °C, 38.0 mg, 62% yield. $^1$H NMR (600 MHz, CDCl$_3$) δ 11.17 (s, 1H), 8.73 (d, $J$ = 8.1 Hz, 1H), 7.84 (d, $J$ = 1.5 Hz, 1H), 7.46 (t, $J$ = 7.5 Hz, 1H), 7.42 (d, $J$ = 8.1 Hz, 1H), 7.29 – 7.23 (m, 1H), 6.95 (q, $J$ = 2.0 Hz, 1H), 4.11 (d, $J$ = 1.5 Hz, 3H), 2.72 (q, $J$ = 5.6, 4.4 Hz, 2H), 2.33 – 2.28 (m, 2H), 1.91 – 1.85 (m, 2H), 1.75 (t, $J$ = 6.0 Hz, 2H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 167.31, 155.73, 153.25, 139.99, 136.30, 132.34, 129.86, 127.40, 125.73, 120.23, 120.04, 112.94, 112.21, 111.02, 52.55, 26.61, 26.17, 22.96, 22.14. HRMS(ESI-TOF): [M + Na]$^+$ calculated for C$_{19}$H$_{18}$N$_2$NaO$_2$: 329.1260, found: 329.1268.

Reference:


III. General Procedure for the Preparation of 5aa:

\[
\begin{align*}
\text{1a} & \quad \text{CO}_2\text{Me} & + & \text{N}_3 & \quad \text{Ph} \quad \text{1H} \\
\text{2a} & \quad \text{NC} & & \text{N} & \quad \text{Ph} \\
& & & \text{[Rh(COD)Cl]}_2 (2.5 \text{ mol\%}) & \text{rt} \\
& & & \text{DPPE (5 mol\%)} & \\
& & & \text{toluene} & \\
\end{align*}
\]

An oven-dried vial equipped with a magnetic stir bar was charged with 1a (37.4 mg, 0.2 mmol), 2a (58.1 mg, 0.4 mmol), [Rh(COD)Cl]₂ (2.5 mg, 0.005 mmol), DPPE (4.0 mg, 0.01 mmol), and toluene (2.0 mL) were added. The reaction was then stirred at room temperature for 3.5 h until arylisocyanide disappeared, the solvent was removed under reduced pressure. The crude residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/15, V/V) to afford pure product 5aa (29.2 mg, 48%) as a yellow liquid.

\textit{(E)-Methyl 3-2-(((1-phenylvinyl)imino)methylene)amino)phenyl}acrylate (5aa):

Yellow liquid. \(^1\)H NMR (600 MHz, CDCl₃) \(\delta\) 8.10 (d, \(J = 16.1\) Hz, 1H), 7.64 – 7.59 (m, 2H), 7.55 (dd, \(J = 7.9, 1.5\) Hz, 1H), 7.39 – 7.32 (m, 3H), 7.30 (td, \(J = 7.7, 1.5\) Hz, 1H), 7.20 (dd, \(J = 8.0, 1.2\) Hz, 1H), 7.16 – 7.12 (m, 1H), 6.48 (d, \(J = 16.1\) Hz, 1H), 5.38 (s, 1H), 5.19 (s, 1H), 3.80 (s, 3H). \(^{13}\)C NMR (151 MHz, CDCl₃) \(\delta\) 167.35, 141.80, 140.34, 138.25, 138.40, 132.69, 131.09, 128.94, 128.62, 128.60, 127.53, 125.69, 125.60, 125.54, 119.21, 106.30, 51.75. HRMS(ESI-TOF): [M + Na]\(^+\) calculated for C\(_{19}\)H\(_{16}\)N\(_2\)NaO\(_2\): 327.1104, found: 327.1094.
IV. General Procedure for the Preparation of 4aa:

A Schlenck tube charged with 1a (37.4 mg, 0.2 mmol), 2a (58.1 mg, 0.4 mmol), [Rh(COD)Cl]₂ (2.5 mg, 0.005 mmol), CuI (1.9 mg, 0.01 mmol), DPPE (4.1 mg, 0.01 mmol) and a magnetic stir bar was evacuated three times under high vacuum and backfilled with N₂. Then toluene (2.0 mL) was added under N₂ atmosphere via syringe and the reaction mixture was heated and stirred for 2.5 h at 120 °C. After the reaction was complete, the solvent was removed under reduced pressure. The crude residue was purified by silica gel column chromatography to afford the mixture of product 4aa and 3aa in 69% yield (According to ¹H NMR of mixture 4aa and 3aa, 4aa: 3aa = 11: 1).

Methyl 2-phenyl-4,9-dihydro-3H-pyrido[2,3-b]indole-4-carboxylate (4aa):

Yellow solid. ¹H NMR (600 MHz, CDCl₃) δ 9.88 (s, 1H), 8.07 (dd, J = 7.9, 1.6 Hz, 2H), 7.58 (d, J = 7.8 Hz, 1H), 7.50 – 7.45 (m, 3H), 7.12 – 7.07 (m, 1H), 7.05 – 6.99 (m, 1H), 6.77 (d, J = 8.1 Hz, 1H), 4.21 (dd, J = 9.6, 4.4 Hz, 1H), 3.70 – 3.73 (m, 1H), 3.66 (s, 3H), 3.07 – 3.12 (m, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 173.52, 165.88, 142.52, 138.51, 134.60, 130.84, 128.87, 127.20, 125.32, 122.00, 120.38, 119.17, 111.59, 93.94, 52.25, 35.60, 28.97. HRMS(ESI-TOF): [M + H]⁺ calculated for C₁₉H₁₇N₂O₂⁺: 305.1285, found: 305.1286.
V. General Procedure from 5aa to 4aa:

A Schlenck tube charged with 5aa (60.9 mg, 0.2 mmol), CuI (1.9 mg, 0.01 mmol), and a magnetic stir bar was evacuated three times under high vacuum and backfilled with N₂. Then toluene (2.0 mL) was added under N₂ atmosphere via syringe and the reaction mixture was heated and stirred for 1.5 h at 120 °C. After the reaction was complete, the solvent was removed under reduced pressure. The crude residue was purified by silica gel column chromatography to afford the mixture of product 4aa and 3aa in 79% yield (According to ¹H NMR of mixture 4aa and 3aa, 4aa : 3aa = 6: 1).
VI. General Procedure from 4aa to 3aa:

An oven-dried vial equipped with a magnetic stir bar was charged with the mixture 4aa (48.7 mg, 0.16 mmol) and 3aa (12.2 mg, 0.04 mmol) under an O₂ atmosphere, then toluene (2.0 mL) was added. The reaction was stirred at 120 °C for 1.5 h. After completion of the reaction (monitored by TLC), the solvent was removed under reduced pressure with rotary evaporator. The crude residue was purified by silica gel column chromatography (EtOAc/petroleum ether = 1:10, V/V) to afford pure product 3aa generated from 4aa (41.1 mg, 85%) as a yellow solid.
VII. Copies of $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR Spectra of Compounds 3-5:

**Figure 1.** $^1$H NMR, $^{13}$C NMR spectra of compound 3aa
Figure 2. $^1$H NMR, $^{13}$C NMR spectra of compound 3ba
Figure 3. $^1$H NMR, $^{13}$C NMR spectra of compound 3ca
Figure 4. $^1$H NMR, $^{13}$C NMR spectra of compound 3da
Figure 5. $^1$H NMR, $^{13}$C NMR spectra of compound 3ea
Figure 6. $^1$H NMR, $^{13}$C NMR spectra of compound 3fa
Figure 7. $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra of compound 3ga
Figure 8. $^1$H NMR, $^{13}$C NMR spectra of compound 3ha
Figure 9. $^1$H NMR, $^{13}$C NMR spectra of compound 3ia
Figure 10. $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra of compound 3ja
Figure 11. $^1$H NMR, $^{13}$C NMR spectra of compound 3ka
Figure 12. $^1$H NMR, $^{13}$C NMR spectra of compound 3ab
Figure 13. $^1$H NMR, $^{13}$C NMR spectra of compound 3ac
Figure 14. $^1$H NMR, $^{13}$C NMR spectra of compound 3ad
Figure 15. $^1$H NMR, $^{13}$C NMR spectra of compound 3ae
Figure 16. $^1$H NMR, $^{13}$C NMR spectra of compound 3af
Figure 17. \(^1\)H NMR, \(^{13}\)C NMR spectra of compound 3ag
Figure 18. $^1$H NMR, $^{13}$C NMR spectra of compound 3ah
Figure 19. $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra of compound 3ai
Figure 20. $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra of compound 3aJ
**Figure 21.** $^1$H NMR, $^{13}$C NMR spectra of compound 3ak
Figure 22. $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra of compound 3al
Figure 23. $^1$H NMR, $^{13}$C NMR spectra of compound 3am
Figure 24. $^1$H NMR, $^{13}$C NMR spectra of compound 3an
Figure 25. $^1$H NMR, $^{13}$C NMR spectra of compound 3ao.
Figure 26. $^1$H NMR, $^{13}$C NMR spectra of compound 3ap
Figure 27. $^1$H NMR, $^{13}$C NMR spectra of compound 3aq
Figure 28. $^1$H NMR, $^{13}$C NMR spectra of compound 4aa
Figure 29. $^1$H NMR, $^{13}$C NMR spectra of compound 5aa