Supporting information

for

Microwave-assisted synthesis of
5,6-dihydroindolo[1,2-a]quinoxaline derivatives by
copper-catalyzed intramolecular N-arylation

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General information

The reagents were purchased from commercial suppliers and used without further purification. All of the microwave-assisted reactions were performed in sealed tubes (capacity 10 mL) under nitrogen atmosphere under microwave heating system (CEM Corp.) at the specified temperature using the standard mode of operation. CH₂Cl₂ used in reactions was reagent grade and distilled from CaH₂. Analytical thin-layer chromatography (TLC) was performed on HSGF 254 (0.15–0.2 mm thickness), visualized by irradiation with UV light (254 nm). Column chromatography was performed using silica gel FCP 200–300. Melting points were measured with a micro melting point apparatus. Nuclear magnetic resonance spectra were recorded on a Brucker AMX-300 or 400 MHz instrument (TMS as IS). Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns were described as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br). Low- and high-resolution mass were measured by the EI method with a Tsou-EI mass spectrometer.

Preparation and characterization data of the materials (1a–1p)

Procedure for the preparation of N-(1H-indol-2-yilmethyl)-2-iodoaniline (1a).

A mixture of 1H-indole-2-carbaldehyde (1 mmol, 145.16 mg, 1.0 equiv) and 2-iodoaniline (1.1 mmol, 240.93 mg, 1.1 equiv) was dissolved in anhydrous dichloromethane (20 mL), trifluoroacetic acid (0.2 mmol, 15 μL, 0.2 equiv) was added under nitrogen, and the resulting mixture was heated to reflux for 4 h. Then the solvent was evaporated, and the residue was dissolved in anhydrous methanol (15 mL), NaBH₄ (4 mmol, 151 mg, 4.0 equiv) was added portionwise. After addition, the mixture was stirred for 30 min and concentrated under vacuum, the reaction mixture was washed with a saturated solution of NH₄Cl, and then extracted with ethyl
acetate. The organic extracts were washed with brine, dried over Na₂SO₄, and concentrated. The residue was purified by flash chromatography (petroleum ether/EtOAc = 16:1 as eluent) to give 1a. White solid (299.4 mg, 86%). Mp 93–95 °C.

\[ ^1H \text{NMR (400 MHz, CDCl}_3 \delta 8.29 (s, 1H), 7.71 (dd, J = 7.8, 1.4 Hz, 1H), 7.62–7.59 (m, 1H), 7.33 (dd, J = 8.0, 0.8 Hz, 1H), 7.21–7.08 (m, 3H), 6.67 (dd, J = 8.2, 1.3 Hz, 1H), 6.57–6.46 (m, 2H), 4.63 (s, 1H), 4.56 (d, J = 4.3 Hz, 2H); } ^13\text{C NMR (126 MHz, CDCl}_3 \delta 147.1, 139.2, 136.1, 129.8, 128.7, 121.9, 120.4, 120.1, 119.9, 111.5, 111.0, 100.4, 85.9, 42.7; } \text{EIMS (m/z, relative intensity): 348 (M}^+\text{, 12), 221 (26), 130 (100), 110 (10); HRMS (EI) calcd for C}_{15}\text{H}_{13}\text{N}_2(M}^+\text{) 348.0123, found: 348.0122.}

Compounds 1b–1p were prepared following the similar procedure carried out for 1a.

N-((5-fluoro-1H-indol-2-ylmethyl)-2-iodoaniline (1b): White solid (307.6 mg, 84%). Mp 80–81 °C. \(^1H\text{NMR (400 MHz, CDCl}_3 \delta 8.24 (s, 1H), 7.69 (dd, J = 7.8, 1.3 Hz, 1H), 7.23–7.11 (m, 3H), 6.88 (td, J = 9.1, 2.5 Hz, 1H), 6.61 (dd, J = 8.2, 1.1 Hz, 1H), 6.53–6.45 (m, 1H), 6.40 (s, 1H), 4.50 (s, 2H); } ^13\text{C NMR (126 MHz, CDCl}_3 \delta 157.1 (d, J_{C-F} = 234.4 Hz), 146.0, 138.2, 137.0, 131.5, 128.8, 128.1 (d, J_{C-F} = 10.3 Hz), 119.1, 110.6 (d, J_{C-F} = 9.8 Hz), 110.5, 109.1 (d, J_{C-F} = 26.2 Hz), 104.2 (d, J_{C-F} = 23.4 Hz), 99.3 (d, J_{C-F} = 4.5 Hz), 84.9, 41.7; } \text{EIMS (m/z, relative intensity): 366 (M}^+\text{, 14), 239 (34), 219 (21), 148 (100); HRMS (EI) calcd for C}_{15}\text{H}_{12}\text{FIN}_2(M}^+\text{) 366.0029, found: 366.0030.}

N-((5-chloro-1H-indol-2-ylmethyl)-2-iodoaniline (1c): White solid (325.2 mg, 85%). Mp 83–84 °C. \(^1H\text{NMR (400 MHz, CDCl}_3 \delta 8.27 (s, 1H), 7.68 (dd, J = 7.8, 1.5 Hz, 1H), 7.52 (d, J = 2.0 Hz, 1H), 7.19–7.05 (m, 3H), 6.59 (dd, J = 8.2, 1.4 Hz, 1H), 6.53–6.44 (m, 1H), 6.38 (s, 1H), 4.61 (s, 1H), 4.50 (d, J = 2.4 Hz, 2H); } ^13\text{C NMR (126 MHz, CDCl}_3 \delta 147.0, 139.2, 137.7, 134.3, 129.81, 129.78, 125.6, 122.1, 120.1, 119.8, 112.0, 111.4, 99.8, 85.9, 77.4, 77.2, 76.9, 42.6; } \text{EIMS (m/z, relative intensity): 384 (M}^+\text{, (Cl}^{37}\text{), 3), 382 (M}^+\text{, (Cl}^{35}\text{), 10), 253 (58), 219 (50), 179 (100), 164 (56); HRMS (EI) calcd for C}_{15}\text{H}_{12}\text{ClN}_2(M}^+\text{) 381.9734, found: 381.9727.}
**N-(5-bromo-1H-indol-2-ylmethyl)-2-iodoaniline (1d):** White solid (354.5 mg, 83%). Mp 87–88 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.31 (s, 1H), 7.71–7.63 (m, 2H), 7.24–7.18 (m, 1H), 7.17–7.09 (m, 2H), 6.59 (dd, \(J = 8.2, 1.4\) Hz, 1H), 6.52–6.45 (m, 1H), 6.40–6.34 (m, 1H), 4.62 (s, 1H), 4.51 (s, 2H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 147.0, 139.2, 137.6, 134.6, 130.5, 129.8, 124.62, 122.8, 122.8, 120.1, 113.2, 112.4, 111.4, 99.7, 85.9, 42.6; EIMS (m/z, relative intensity): 428 (M\(^+\), (Br\(^{81}\), 10), 426 (M\(^+\), (Br\(^{79}\), 10), 301 (Br\(^{81}\), 31), 299 (Br\(^{79}\), 31), 208 (100), 129 (28), 110 (24); HRMS (EI) calcd for C\(_{15}\)H\(_{12}\)BrIN\(_2\) (M\(^+\)) 425.9229, found: 425.9225.

**N-(5-nitro-1H-indol-2-ylmethyl)-2-iodoaniline (1e):** Yellow solid (346.0 mg, 88%). Mp 175–177 °C. \(^1\)H NMR (500 MHz, DMSO) \(\delta\) 11.79 (s, 1H), 8.48 (d, \(J = 2.1\) Hz, 1H), 7.95 (dd, \(J = 9.0, 2.2\) Hz, 1H), 7.65 (dd, \(J = 7.7, 1.1\) Hz, 1H), 7.51 (d, \(J = 9.0\) Hz, 1H), 7.16–7.03 (m, 1H), 6.64 (d, \(J = 8.0\) Hz, 1H), 6.60 (s, 1H), 6.46–6.34 (m, 1H), 5.54 (t, \(J = 5.9\) Hz, 1H), 4.59 (d, \(J = 5.9\) Hz, 2H); \(^{13}\)C NMR (126 MHz, DMSO) \(\delta\) 147.2, 142.1, 140.6, 139.5, 138.9, 129.3, 127.4, 118.7, 116.7, 116.2, 111.5, 111.1, 101.7, 85.0, 40.9; EI MS (m/z, relative intensity): 393 (M\(^+\), 20), 266 (58), 219 (84), 175 (100); HRMS (EI) calcd for C\(_{15}\)H\(_{12}\)IN\(_3\)O (M\(^+\)) 392.9974, found: 392.9963.

**N-(5-methoxy-1H-indol-2-ylmethyl)-2-iodoaniline (1f):** White solid (302.6 mg, 80%). Mp 117–118 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.21 (s, 1H), 7.73 (dd, \(J = 7.8, 1.5\) Hz, 1H), 7.26–7.14 (m, 2H), 7.09 (d, \(J = 2.4\) Hz, 1H), 6.85 (dd, \(J = 8.8, 2.5\) Hz, 1H), 6.68 (dd, \(J = 8.2, 1.4\) Hz, 1H), 6.57–6.47 (m, 1H), 6.43 (s, 1H), 4.64 (s, 1H), 4.55 (s, 2H), 3.88 (s, 3H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 154.4, 147.1, 139.2, 136.8, 131.2, 129.8, 129.2, 119.9, 112.0, 111.7, 111.4, 102.3, 100.2, 85.8, 56.0, 42.8; EIMS (m/z, relative intensity): 378 (M\(^+\), 16), 251 (14), 219 (12), 160 (100); HRMS (EI) calcd for C\(_{16}\)H\(_{15}\)IN\(_3\)O \(\delta\) 378.0229, found: 378.0222.

**N-(5-methyl-1H-indol-2-ylmethyl)-2-iodoaniline (1g):** White solid (293.4 mg, 81%). Mp 118–120 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.18 (s, 1H), 7.77 (dd, \(J = 7.8, 1.4\) Hz, 1H), 7.45 (s, 1H), 7.29–7.19 (m, 2H), 7.07 (dd, \(J = 8.2, 1.1\) Hz, 1H), 6.71 (dd, \(J = 8.2, 1.2\) Hz, 1H), 6.62–6.52 (m, 1H), 6.46 (d, \(J = 1.0\) Hz, 1H), 4.67 (s, 1H), 4.56 (d, \(J = 4.7\) Hz, 2H), 2.52 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 146.1, 138.2, 135.1, 133.3,
128.7, 128.3, 127.9, 119.1, 118.8, 110.43, 109.7, 98.8, 84.8, 41.7, 20.6; EIMS (m/z, relative intensity): 362 (M+, 12), 235 (17), 219 (6), 144 (100); HRMS (EI) calcd for C16H15IN2 (M+) 362.0280, found: 362.0289.

N-(5-methyl-1H-indol-2-ylmethyl)-5-chloro-2-idoaniline (1h): White solid (289.6 mg, 73%). Mp 99–101 °C. $^1$H NMR (400 MHz, CDCl3) δ 8.08 (s, 1H), 7.59 (d, J = 8.3 Hz, 1H), 7.41 (d, J = 0.7 Hz, 1H), 7.28–7.21 (m, 1H), 7.04 (dd, J = 8.3, 2.3 Hz, 1H), 6.65 (d, J = 2.3 Hz, 1H), 6.52 (dd, J = 8.3, 2.3 Hz, 1H), 6.43 (d, J = 1.1 Hz, 1H), 4.63 (t, J = 4.9 Hz, 1H), 4.48 (d, J = 5.2 Hz, 2H), 2.47 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 148.0, 139.7, 135.8, 135.1, 134.5, 129.4, 128.8, 123.7, 120.2, 119.6, 111.2, 110.7, 100.6, 82.6, 42.5, 21.6; EIMS (m/z, relative intensity): 398 (M+, (Cl37), 5), 396 (M+, (Cl35), 15), 267 (76), 144 (100); HRMS (EI) calcd for C16H14ClIN2 (M+) 395.9890, found: 395.9891.

N-(1H-indol-2-ylmethyl)-4-trifluoromethyl-2-idoaniline (1i): White solid (308 mg, 74%). Mp 124–126 °C. $^1$H NMR (400 MHz, CDCl3) δ 8.21 (s, 1H), 7.92 (d, J = 1.4 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.40 (dd, J = 8.6, 1.5 Hz, 1H), 7.36–7.33 (m, 1H), 7.21–7.09 (m, 2H), 6.67 (d, J = 8.6 Hz, 1H), 6.50 (d, J = 1.1 Hz, 1H), 4.96 (s, 1H), 4.60 (d, J = 5.2 Hz, 2H); 13C NMR (126 MHz, CDCl3) δ 149.5, 136.2 (q, $J_{C-F}$ = 3.9 Hz), 134.8, 128.5, 127.1 (q, $J_{C-F}$ = 3.8 Hz), 123.7 (q, $J_{C-F}$ = 270.8 Hz), 122.3, 121.3 (q, $J_{C-F}$ = 32.3 Hz), 120.6, 120.3, 111.1, 110.2, 101.1, 84.2, 42.5; EIMS (m/z, relative intensity): 416 (M+, 12), 289 (17), 130 (100); HRMS (EI) calcd for C16H12F3IN2 (M+) 415.9997, found: 415.9984.

N-(1H-indol-2-ylmethyl)-5-chloro-2-idoaniline (1j): White solid (298.5 mg, 78%). Mp 94–96 °C. $^1$H NMR (400 MHz, CDCl3) δ 8.21 (s, 1H), 7.64 (d, J = 7.9 Hz, 1H), 7.61 (d, J = 8.3 Hz, 1H), 7.38 (dd, J = 8.0, 0.8 Hz, 1H), 7.26–7.20 (m, 1H), 7.20–7.14 (m, 1H), 6.67 (d, J = 2.3 Hz, 1H), 6.57–6.51 (m, 2H), 4.67 (s, 1H), 4.52 (d, J = 4.9 Hz, 2H); 13C NMR (101 MHz, CDCl3) δ 148.0, 139.7, 136.2, 135.8, 135.1, 128.5, 122.2, 120.6, 120.2, 119.7, 111.2, 111.1, 101.0, 82.7, 42.5; EIMS (m/z, relative intensity): 384 (M+, (Cl37), 2), 382 (M+, (Cl35), 5), 253 (35), 130 (100), 127 (93); HRMS (EI) calcd for C15H12ClIn2 (M+) 381.9734, found: 381.9732.
N-(1H-indol-2-ylmethyl)-5-fluoro-2-iodoaniline (1k): White solid (293.0 mg, 80%). Mp 101–103 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.23 (s, 1H), 7.67–7.61 (m, 2H), 7.40–7.35 (m, 1H), 7.25–7.14 (m, 2H), 6.53 (dd, J = 2.0, 0.9 Hz, 1H), 6.44 (dd, J = 11.3, 2.8 Hz, 1H), 6.35–6.27 (m, 1H), 4.71 (s, 1H), 4.54 (s, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 164.5 (d, J_{C-F} = 244.9 Hz), 148.5 (d, J_{C-F} = 10.8 Hz), 139.6 (d, J_{C-F} = 9.6 Hz), 136.2, 135.1, 128.6, 122.2, 120.6, 120.2, 111.0, 106.7 (d, J_{C-F} = 22.5 Hz), 101.0, 99.1 (d, J_{C-F} = 27.3 Hz), 78.3, 42.6; EIMS (m/z, relative intensity): 366 (M⁺, 21), 237 (100), 110 (54); HRMS (EI) calcd for C₁₅H₁₂F₂IN₂ (M⁺) 366.0029, found: 366.0020.

N-(1H-indol-2-ylmethyl)-4-methyl-2-iodoaniline (1l): White solid (318.7 mg, 88%). Mp 83–85 °C. ¹H NMR (300 MHz, CDCl₃) δ 8.19 (s, 1H), 7.60 (dd, J = 7.7, 0.5 Hz, 1H), 7.22–7.08 (m, 3H), 7.01 (d, J = 8.2 Hz, 1H), 6.58 (dd, J = 8.2, 2.5 Hz, 1H), 6.44 (d, J = 0.9 Hz, 1H), 4.40 (s, 2H), 3.89 (s, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 146.8, 136.4, 136.0, 130.8, 130.0, 128.5, 123.4, 121.9, 120.4, 120.0, 113.3, 111.0, 101.8, 100.3, 42.3, 26.9; EIMS (m/z, relative intensity): 362 (M⁺, 22), 233 (6), 130 (100); HRMS (EI) calcd for C₁₆H₁₅IN₂ (M⁺) 362.0280, found: 362.0273.

N-(1H-indol-2-ylmethyl)-2-bromoaniline (1m): White solid (247 mg, 82%). Mp 107–108 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.24 (s, 1H), 7.69–7.64 (m, 1H), 7.54 (dd, J = 7.9, 1.5 Hz, 1H), 7.39–7.33 (m, 1H), 7.26–7.16 (m, 3H), 6.77 (dd, J = 8.2, 1.5 Hz, 1H), 6.73–6.66 (m, 1H), 6.54–6.50 (m, 1H), 4.80 (s, 1H), 4.56 (s, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 143.8, 135.1, 135.0, 131.6, 127.8, 127.6, 120.9, 119.4, 119.1, 118.0, 111.1, 110.0, 109.1, 99.3, 41.3; EIMS (m/z, relative intensity): 302 (M⁺, Br₈¹, 9), 300 (M⁺, Br₇⁹, 9), 221 (Br₈¹, 12), 219 (Br₇⁹, 12), 130 (100); HRMS (EI) calcd for C₁₅H₁₃BrN₂ (M⁺) 300.0262, found: 300.0257.

N-(1H-indol-2-ylmethyl)-2-bromo-4-chloroaniline (1n): White solid (241.7 mg, 72%). Mp 135–136 °C. ¹H NMR (300 MHz, CD₃OD) δ 7.46–7.38 (m, 2H), 7.31–7.25 (m, 1H), 7.08–7.00 (m, 2H), 6.98–6.93 (m, 1H), 6.69 (d, J = 8.8 Hz, 1H), 6.31 (s, 1H), 4.51 (s, 2H); ¹³C NMR (101 MHz, MeOD) δ 145.5, 138.1, 137.7, 132.5, 129.8, 129.3,
122.5, 122.1, 120.8, 120.1, 113.6, 111.8, 110.1, 100.6, 42.5; EIMS (m/z, relative intensity): 336 (M⁺, (Br⁺), 6), 334 (M⁺, (Br⁻), 6), 130 (100); HRMS (EI) calcd for C₁₅H₁₂BrClN₂ (M⁺) 333.9872, found: 333.9866.

N-(1H-indol-2-ylmethyl)-2-bromo-4-methylaniline (1o): White solid (261.6 mg, 83%). Mp 132–133 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.26 (s, 1H), 7.63 (d, J = 7.7 Hz, 1H), 7.37–7.28 (m, 2H), 7.24–7.10 (m, 2H), 6.96 (dd, J = 8.2, 1.4 Hz, 1H), 6.65 (d, J = 8.2 Hz, 1H), 6.49 (d, J = 0.9 Hz, 1H), 4.52 (s, 2H), 2.26 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 142.5, 136.4, 136.0, 132.9, 129.3, 128.7, 121.8, 120.4, 120.0, 112.1, 111.0, 100.1, 42.5, 20.2; EIMS (m/z, relative intensity): 316 (M⁺, (Br⁺), 4), 314 (M⁺, (Br⁻), 4), 279 (48), 264 (38), 187 (100), 130 (40); HRMS (EI) calcd for C₁₆H₁₅BrN₂ (M⁺) 314.0419, found: 314.0403.

N-(1H-indol-2-ylmethyl)-2-bromo-5-fluoroaniline (1p): White solid (239.4 mg, 75%). Mp 115–116 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.17 (s, 1H), 7.65 (d, J = 7.8 Hz, 1H), 7.46–7.40 (m, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.27–7.21 (m, 1H), 7.21–7.15 (m, 1H), 6.55–6.51 (m, 1H), 6.49 (dd, J = 11.0, 2.8 Hz, 1H), 6.41 (td, J = 8.4, 2.8 Hz, 1H), 4.87 (s, 1H), 4.51 (d, J = 5.3 Hz, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 163.3 (d, J_C–F = 244.2 Hz), 146.1 (d, J_C–F = 11.2 Hz), 136.2, 135.2, 133.1 (d, J_C–F = 10.0 Hz), 128.5, 122.1, 120.5, 120.2, 111.0, 105.5 (d, J_C–F = 23.1 Hz), 104.0, 100.9, 99.5 (d, J_C–F = 27.7 Hz), 42.1; EIMS (m/z, relative intensity): 320 (M⁺, (Br⁺), 7), 318 (M⁺, (Br⁻), 7), 239 (10), 130 (100); HRMS (EI) calcd for C₁₅H₁₂BrFN₂ (M⁺) 318.0168, found: 318.0158.

Preparation and characterization data of of compounds 2

Procedure for the preparation of 5,6-dihydroindolo[1,2-a]quinoxaline (2a).

![Diagram](image)

A high-pressure microwave vessel was loaded with the 1a (0.25 mmol, 1.0 equiv), CuI (0.025 mmol, 4.8 mg, 0.1 equiv), L-proline (0.05 mmol, 5.8 mg, 0.2 equiv), and
K₂CO₃ (0.5 mmol, 69.1 mg, 2.0 equiv) in DMSO (2 mL). The vessel was degassed, refilled with argon, and sealed. The mixture was heated to 90 °C for 45 min under microwave irradiation (fixed power, 30 W). After cooling, the reaction mixture was washed with water, and then extracted with ethyl acetate. The organic extracts were washed with brine, dried over Na₂SO₄, and concentrated. The residue was purified by flash chromatography to give 2a. White solid (92%). Mp 88–89 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, J = 8.1 Hz, 1H), 7.97–7.90 (m, 1H), 7.69 (d, J = 7.8 Hz, 1H), 7.35–7.27 (m, 1H), 7.27–7.21 (m, 1H), 7.10–7.00 (m, 2H), 6.92–6.85 (m, 1H), 6.42 (s, 1H), 4.48 (s, 2H), 4.01 (s, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 138.02, 134.79, 134.06, 129.90, 127.67, 124.06, 122.33, 120.97, 120.91, 120.11, 117.12, 116.13, 111.64, 98.60, 42.16; EIMS (m/z, relative intensity): 220 (M⁺, 32), 218 (100), 190 (20), 190 (14); HRMS (EI) calcd for C₁₅H₁₂N₂ (M⁺) 220.1000, found: 220.0986.

Compounds 2b–2n were prepared following the similar procedure carried out for 2a with the base, temperature and time indicated in Table 2.

9-fluoro-5,6-dihydroindolo[1,2-a]quinoxaline (2b): White solid (56.0 mg, 94%). Mp 78–79 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.86 (dd, J = 9.1, 4.3 Hz, 1H), 7.79 (dd, J = 7.7, 1.6 Hz, 1H), 7.28–7.23 (m, 1H), 7.05–6.93 (m, 3H), 6.85 (dd, J = 7.4, 1.8 Hz, 1H), 6.32 (s, 1H), 4.44 (s, 2H), 3.61 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 157.4 (d, J = 236.2 Hz), 136.9, 135.4, 129.7, 129.6 (d, J = 10.2 Hz), 126.4, 123.3, 119.2, 115.8, 115.2, 111.3 (d, J = 9.5 Hz), 109.2 (d, J = 25.6 Hz), 105.0 (d, J = 23.4 Hz), 97.6 (d, J = 4.2 Hz), 41.2; EIMS (m/z, relative intensity): 238 (M⁺, 30), 236 (100), 208 (18), 118 (13); HRMS (EI) calcd for C₁₅H₁₁FN₂ (M⁺) 238.0906, found: 238.0904.

9-chloro-5,6-dihydroindolo[1,2-a]quinoxaline (2c): White solid (59.2 mg, 93%). Mp 96–97 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, J = 8.9 Hz, 1H), 7.77 (dd, J = 7.7, 1.2 Hz, 1H), 7.56 (d, J = 2.1 Hz, 1H), 7.18 (dd, J = 8.9, 2.1 Hz, 1H), 7.05–6.93 (m, 2H), 6.85 (dd, J = 7.5, 1.5 Hz, 1H), 6.29 (s, 1H), 4.42 (s, 2H), 3.73 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 137.0, 135.1, 131.4, 130.0, 126.2, 125.4, 123.5, 121.4, 119.4, 119.2, 116.0, 115.3, 111.5, 97.2, 41.1; EIMS (m/z, relative intensity): 256 (M⁺, Cl²³), 254 (M⁺, (Cl²³), 84), 252 (100), 218 (26), 190 (23); HRMS (EI) calcd for
C_{15}H_{11}ClN_{2} (M^+) 254.0611, found: 254.0614.

9-bromo-5,6-dihydroindolo[1,2-a]quinoxaline (2d): White solid (70.3 mg, 94%).
Mp 128–129 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.84 (d, $J = 8.9$ Hz, 1H), 7.82–7.79 (m, 1H), 7.76 (d, $J = 2.0$ Hz, 1H), 7.35 (dd, $J = 8.8$, 2.0 Hz, 1H), 7.08–6.99 (m, 2H), 6.89 (dd, $J = 7.5$, 1.7 Hz, 1H), 6.33 (s, 1H), 4.47 (s, 2H), 3.73 (s, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 137.0, 135.0, 131.7, 130.6, 126.2, 124.0, 123.5, 122.5, 119.3, 116.1, 115.3, 113.0, 112.0, 97.1, 41.1; EIMS (m/z, relative intensity): 300 (M$^+$, (Br$^8$), 100), 298 (M$^+$, (Br$^7$), 100), 217 (42), 190 (29), 110 (22); HRMS (EI) calcd for C$_{15}$H$_{11}$BrN$_2$ (M$^+$) 298.0106, found: 298.0102.

9-nitro-5,6-dihydroindolo[1,2-a]quinoxaline (2e): Yellow solid (64.3 mg, 97%).
Mp 181–182 °C. $^1$H NMR (500 MHz, DMSO) δ 8.56 (d, $J = 1.6$ Hz, 1H), 8.13 (d, $J = 9.2$ Hz, 1H), 8.03 (dd, $J = 9.1$, 1.8 Hz, 1H), 7.89 (d, $J = 7.9$ Hz, 1H), 7.11–7.02 (m, 1H), 6.98 (d, $J = 7.6$ Hz, 1H), 6.94–6.84 (m, 1H), 6.69 (s, 1H), 6.28 (s, 1H), 4.38 (s, 2H); $^{13}$C NMR (126 MHz, DMSO) δ 141.4, 139.7, 139.2, 135.8, 129.0, 125.6, 125.2, 118.8, 117.33, 117.27, 117.2, 116.2, 111.8, 100.2, 40.6; EIMS (m/z, relative intensity): 265 (M$^+$, 100), 233 (22), 218 (80), 190 (16); HRMS (EI) calcd for C$_{15}$H$_{11}$N$_3$O$_2$ (M$^+$) 265.0851, found: 265.0845.

9-methoxy-5,6-dihydroindolo[1,2-a]quinoxaline (2f): White solid (56.3 mg, 90%).
Mp 109–110 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.88–7.80 (m, 2H), 7.10 (d, $J = 2.5$ Hz, 1H), 7.02–6.97 (m, 2H), 6.90 (dd, $J = 9.0$, 2.6 Hz, 1H), 6.86–6.82 (m, 1H), 6.30 (s, 1H), 4.44 (s, 2H), 3.88 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 154.8, 137.8, 135.3, 130.7, 129.3, 127.7, 123.9, 120.1, 116.6, 116.0, 112.4, 111.6, 103.2, 98.4, 55.9, 42.2; EIMS (m/z, relative intensity): 250 (M$^+$, 4), 248 (100), 218 (14), 205 (81); HRMS (EI) calcd for C$_{16}$H$_{14}$N$_2$O (M$^+$) 250.1106, found: 250.1101.

9-methyl-5,6-dihydroindolo[1,2-a]quinoxaline (2g): White solid (53.3 mg, 91%).
Mp 90–91 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.86 (d, $J = 8.5$ Hz, 2H), 7.44 (d, $J = 9.2$ Hz, 1H), 7.09 (d, $J = 8.5$ Hz, 1H), 7.06–6.95 (m, 2H), 6.90–6.82 (m, 1H), 6.30 (s, 1H), 4.46 (s, 2H), 3.73 (s, 1H), 2.48 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 137.9, 134.7, 132.5, 130.2, 127.8, 123.9, 123.8, 120.8, 120.1, 116.9, 116.1, 111.4, 98.2, 42.2,
21.5; EIMS (m/z, relative intensity): 234 (M+, 28), 232 (100), 218 (8), 116 (15); HRMS (EI) calcd for C_{16}H_{14}N_{2} (M+) 234.1157, found: 234.1139.

3-chloro-9-methyl-5,6-dihydroindolo[1,2-a]quinoxaline (2h): White solid (61.8 mg, 92%). Mp 118–120 °C. \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.78 (d, \( J = 8.5 \) Hz, 1H), 7.74 (d, \( J = 8.6 \) Hz, 1H), 7.43 (s, 1H), 7.10 (dd, \( J = 8.5, 1.6 \) Hz, 1H), 6.94 (dd, \( J = 8.6, 2.3 \) Hz, 1H), 6.80 (d, \( J = 2.3 \) Hz, 1H), 6.30 (s, 1H), 4.42 (s, 2H), 3.99 (s, 1H), 2.49 (s, 3H); \( ^{13}C \) NMR (126 MHz, CDCl\(_3\)) \( \delta \) 138.8, 134.0, 132.3, 130.5, 130.2, 128.6, 126.2, 124.0, 120.9, 119.6, 117.5, 115.7, 111.2, 98.6, 41.9, 21.4; EIMS (m/z, relative intensity): 270 (M+\(^+\), (Cl\(^{37}\)), 22), 268 (M+\(^+\), (Cl\(^{35}\)), 69), 267 (100), 252 (7), 232 (10); HRMS (EI) calcd for C_{16}H_{13}ClN_{2} (M+) 268.0767, found: 268.0757.

2-(trifluoromethyl)-5,6-dihydroindolo[1,2-a]quinoxaline (2i): White solid (69.2 mg, 96%). Mp 98–100 °C. \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.10 (d, \( J = 1.3 \) Hz, 1H), 7.93 (dd, \( J = 8.4, 0.6 \) Hz, 1H), 7.65 (d, \( J = 7.5 \) Hz, 1H), 7.36–7.29 (m, 1H), 7.28–7.19 (m, 2H), 6.86 (d, \( J = 8.2 \) Hz, 1H), 6.40 (d, \( J = 0.8 \) Hz, 1H), 4.51 (s, 2H), 3.57 (s, 1H); \( ^{13}C \) NMR (126 MHz, CDCl\(_3\)) \( \delta \) 140.7, 134.0, 133.8, 130.1, 127.1, 124.7(q, \( J_{C-F} = 269 \) Hz), 123.0, 121.7 (q, \( J_{C-F} = 33 \) Hz), 121.5, 121.2, 121.1 (q, \( J_{C-F} = 3.9 \) Hz), 115.5, 113.9 (q, \( J_{C-F} = 3.8 \) Hz), 111.5, 99.5, 41.7; EIMS (m/z, relative intensity): 288 (M+\(^+\), 3), 144 (8), 130 (100); HRMS (EI) calcd for C_{16}H_{11}F_{3}N_{2} (M+) 288.0874, found: 288.0868.

3-chloro-5,6-dihydroindolo[1,2-a]quinoxaline (2j): White solid (60.5 mg, 95%). Mp 104–105 °C. \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.90 (d, \( J = 8.3 \) Hz, 1H), 7.77 (d, \( J = 8.6 \) Hz, 1H), 7.65 (dd, \( J = 7.8, 0.6 \) Hz, 1H), 7.32–7.25 (m, 1H), 7.24–7.18 (m, 1H), 6.94 (dd, \( J = 8.6, 2.3 \) Hz, 1H), 6.81 (d, \( J = 2.3 \) Hz, 1H), 6.38 (s, 1H), 4.43 (s, 2H), 3.95 (s, 1H); \( ^{13}C \) NMR (126 MHz, CDCl\(_3\)) \( \delta \) 139.0, 134.1, 133.9, 129.9, 128.9, 126.1, 122.6, 121.2, 121.1, 119.7, 117.8, 115.8, 111.5, 99.0, 41.9; EIMS (m/z, relative intensity): 256 (M+\(^+\), (Cl\(^{37}\)), 20), 254 (M+\(^+\), (Cl\(^{35}\)), 72), 252 (100), 218 (22), 190 (24); HRMS (EI) calcd for C_{15}H_{11}ClN_{2} (M+) 254.0611, found: 254.0609.

3-fluoro-5,6-dihydroindolo[1,2-a]quinoxaline (2k): White solid (54.2 mg, 91%). Mp 87–88 °C. \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.86 (dd, \( J = 8.3, 0.6 \) Hz, 1H), 7.76–
7.69 (m, 1H), 7.60 (dd, J = 7.8, 0.5 Hz, 1H), 7.26–7.19 (m, 1H), 7.19–7.13 (m, 1H), 6.62 (td, J = 8.6, 2.8 Hz, 1H), 6.48 (dd, J = 9.5, 2.8 Hz, 1H), 6.32 (d, J = 0.7 Hz, 1H), 4.35 (s, 2H), 3.79 (s, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 158.3 (d, $J_{C-F}$ = 241.9 Hz), 138.4 (d, $J_{C-F}$ = 10.1 Hz), 133.1, 132.9, 128.7, 122.8, 121.4, 120.0, 119.9, 116.7 (d, $J_{C-F}$ = 9.7 Hz), 110.3, 105.0 (d, $J_{C-F}$ = 22.8 Hz), 102.2 (d, $J_{C-F}$ = 25.9 Hz), 97.6, 40.9; EIMS (m/z, relative intensity): 238 (M$^+$, 54), 237 (100), 208 (14), 119 (13); HRMS (EI) calcd for C$_{15}$H$_{11}$FN$_2$ (M$^+$) 238.0906, found: 238.0897.

2-methyl-5,6-dihydroindolo[1,2-a]quinoxaline (2l): White solid (51.5 mg, 88%). Mp 79–81 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.00 (d, J = 8.3 Hz, 1H), 7.72 (d, J = 0.7 Hz, 1H), 7.65 (d, J = 7.8 Hz, 1H), 7.32–7.26 (m, 1H), 7.23–7.18 (m, 1H), 6.85 (dd, J = 7.9, 0.9 Hz, 1H), 6.79–6.75 (m, 1H), 6.38 (s, 1H), 4.42 (s, 2H), 3.53 (s, 1H), 2.42 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 134.6, 134.0, 133.0, 128.9, 128.7, 126.7, 123.5, 121.2, 120.0, 119.8, 116.8, 115.1, 110.7, 97.5, 41.4, 20.3; EIMS (m/z, relative intensity): 234 (M$^+$, 57), 233(100), 218 (14), 116 (16); HRMS (EI) calcd for C$_{16}$H$_{14}$N$_2$ (M$^+$) 234.1157, found: 234.1141.

2-chloro-5,6-dihydroindolo[1,2-a]quinoxaline (2n): White solid (53.5 mg, 84%). Mp 90–91 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.91 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 2.2 Hz, 1H), 7.62 (d, J = 7.7 Hz, 1H), 7.31–7.26 (m, 1H), 7.23–7.14 (m, 1H), 6.97 (dd, J = 8.4, 2.2 Hz, 1H), 6.78 (d, J = 8.4 Hz, 1H), 6.38 (d, J = 0.7 Hz, 1H), 4.46 (s, 2H), 3.47 (s, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 136.5, 134.3, 134.0, 130.0, 128.3, 124.7, 123.7, 122.8, 121.4, 121.2, 117.2, 116.8, 111.5, 99.3, 42.1; EIMS (m/z, relative intensity): 256 (M$^+$, (Cl$^{37}$), 18), 254 (M$^+$, (Cl$^{35}$), 62), 190 (18), 126 (12); HRMS (EI) calcd for C$_{13}$H$_{11}$ClN$_2$ (M$^+$) 254.0611, found: 254.0600.
$^1$H and $^{13}$C NMR spectra

$N$-$(1H$-indol-2-ylmethyl)$-2$-iodoaniline (1a)
N-(5-fluoro-1H-indol-2-ylmethyl)-2-iodoaniline (1b)

Chemical Formula: C_{17}H_{15}FN_{2}
Exact Mass: 366.0029
9-fluoro-5,6-dihydroindolo[1,2-α]quinoxaline (2b)
$N$-(5-chloro-$1H$-indol-2-ylmethyl)-2-idoaniline (1c)
9-chloro-5,6-dihydroindolo[1,2-α]quinoxaline (2c)

Chemical Formula: C_{21}H_{16}ClN_{2}
Exact Mass: 254.0811
$N$-(5-bromo-$1H$-indol-2-ylmethyl)-2-iodoaniline (1d)
9-bromo-5,6-dihydroindolo[1,2-α]quinoxaline (2d)
N-(5-nitro-1H-indol-2-ylmethyl)-2-iodoaniline (1e)

Chemical Formula: C_{29}H_{26}N_{2}O_{2}
Exact Mass: 392.9974
9-nitro-5,6-dihydroindolo[1,2-α]quinoxaline (2e)
N-(5-methoxy-1H-indol-2-ylmethyl)-2-iodoaniline (1f)

Chemical Formula: C_{25}H_{22}N_{2}O
Exact Mass: 378.0229
9-methoxy-5,6-dihydroindolo[1,2-α]quinoxaline (2f)
$N$-(5-methyl-$1H$-indol-2-ylmethyl)-2-idoaniline (1g)
9-methyl-5,6-dihydroindolo[1,2-a]quinoxaline (2g)

Chemical Formula: C_{14}H_{14}N_{2}
Exact Mass: 234.1157

[Diagram of chemical structure]

Chemical Formula: C_{14}H_{14}N_{2}
Exact Mass: 234.1157
N-(5-methyl-1H-indol-2-ylmethyl)-5-chloro-2-iodoaniline (1h)
3-chloro-9-methyl-5,6-dihydroindolo[1,2-a]quinoxaline (2h)
$N$-(1$H$-indol-2-ylmethyl)-4-trifluoromethyl-2-iodoaniline (1i)
2-(trifluoromethyl)-5,6-dihydroindolo[1,2-\(\alpha\)]quinoxaline (2i)
N-(1H-indol-2-ylmethyl)-5-chloro-2-idoaniline (1j)

Chemical Formula: C_{12}H_{11}ClN_{2}
Exact Mass: 381.9734
3-chloro-5,6-dihydroindolo[1,2-α]quinoxaline (2j)

Chemical Formula: C_{19}H_{18}ClN_2
Exact Mass: 254.0611
N-(1H-indol-2-ylmethyl)-5-fluoro-2-iodoaniline (1k)
3-fluoro-5,6-dihydroindolo[1,2-α]quinoxaline (2k)
$N$-(1H-indol-2-ylmethyl)-4-methyl-2-iodoaniline (II)
2-methyl-5,6-dihydroindolo[1,2-α]quinoxaline (2l)
N-(1H-indol-2-ylmethyl)-2-bromoaniline (1m)

Chemical Formula: C_{18}H_{19}BrN_{2}

Exact Mass: 300.0262
$N-(1\text{H}-\text{indol}-2\text{-ylmethyl})-2\text{-bromo-4-chloroaniline}$ (1n)

Chemical Formula: $C_{29}H_{27}BrCIN_2$

Exact Mass: 333.9872
2-chloro-5,6-dihydroindolo[1,2-α]quinoxaline (2n)
$N$-(1$H$-indol-2-ylmethyl)-2-bromo-4-methylaniline (1o)
$N$-(1H-indol-2-ylmethyl)-2-bromo-5-fluoroaniline (1p)

Chemical Formula: $C_{20}H_{16}BrF_2N_2$  
Exact Mass: 318.0168