

# Generation of 4-Polyfluoroaryl Pyrrolo[1,2-*a*]quinolines via C-H Bond Activation

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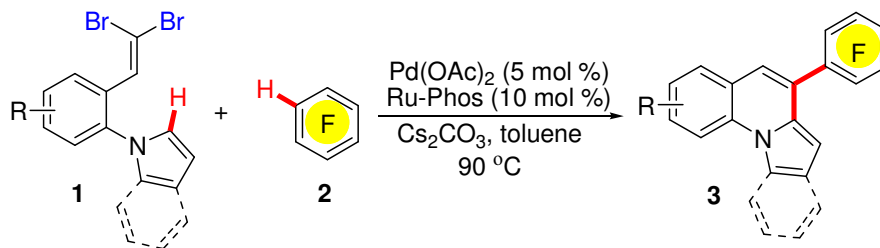
## Supporting Information

1. General experimental methods (S2).
2. General experimental procedure and characterization data (S3-S10).
3. <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectra of compound **3** (S11-S55).

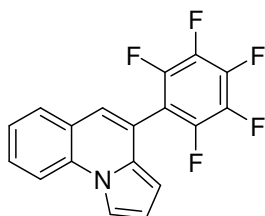
### General experimental methods:

Unless otherwise stated, all commercial reagents were used as received. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63µm, standard grade). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr at 25–35°C. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the  $\delta$  scale.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  on a Bruker DRX-400 spectrometer operating at 400 MHz and 100 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. High resolution mass spectrometry (HRMS) spectra were obtained on a micrOTOF II Instrument.

*General experimental procedure for the palladium-catalyzed reaction of 1-[2-(2,2-dibromoethenyl)phenyl]-1H-pyrrole 1 with polyfluoroarene 2.*

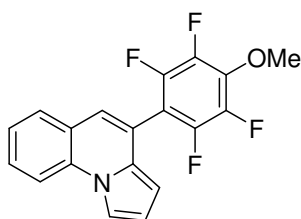


Polyfluoroarene **2** was added to a solution of 1-[2-(2,2-dibromoethenyl)phenyl]-1H-pyrrole **1** (0.4 mmol), Pd(OAc)<sub>2</sub> (5 mol %), Ru-Phos (10 mol %), and Cs<sub>2</sub>CO<sub>3</sub> (3.0 equiv) in toluene (2.0 mL). The mixture was stirred at 90 °C for 12 hours. After completion of the reaction as indicated by TLC, the residue was purified directly by flash chromatography on silica gel to afford products **3**.



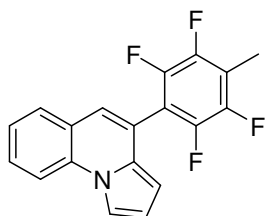
4-(Perfluorophenyl)pyrrolo[1,2-*a*]quinoline (**3a**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.23 (s, 1H), 6.78 (t,  $J = 3.2$  Hz, 1H), 6.99 (s, 1H), 7.32 (t,  $J = 7.3$  Hz, 1H), 7.54 (t,  $J = 7.3$  Hz, 1H), 7.63 (d,  $J = 7.8$  Hz, 1H), 7.86-7.88 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  102.8, 112.8 (m), 112.9, 113.0, 114.2, 117.2, 121.8, 122.9, 123.9, 129.0, 129.1, 129.3, 133.2, 137.7 (dm,  $J_{\text{F}} = 247.5$  Hz), 141.1 (dm,  $J_{\text{F}} = 250.8$  Hz), 144.3 (dm,  $J_{\text{F}} = 247.9$  Hz);  $^{19}\text{F}$  NMR (378 MHz,  $\text{CDCl}_3$ )  $\delta$  -138.9 (s, 2F), -154.1 (d,  $J_{\text{F}} = 23.2$  Hz, 1F), -161.4 (t,  $J_{\text{F}} = 23.2$  Hz, 2F); Elem. Anal. Calcd for  $\text{C}_{18}\text{H}_8\text{F}_5\text{N}$ : C, 64.87; H, 2.42; N, 4.20; Found: C, 64.61; H, 2.28; N, 4.20; HRMS (ESI) calcd for  $\text{C}_{18}\text{H}_8\text{F}_5\text{N}$ : 334.0650 ( $\text{M} + \text{H}^+$ ), found: 334.0663; calcd / found : 0.999996.



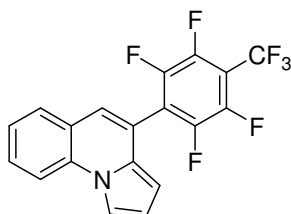
4-(2,3,5,6-Tetrafluoro-4-methoxyphenyl)pyrrolo[1,2-*a*]quinoline (**3b**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.14 (s, 3H), 6.26 (s, 1H), 6.78 (s, 1H), 6.99 (s, 1H), 7.29 (t,  $J = 7.3$  Hz, 1H), 7.50 (t,  $J = 7.3$  Hz, 1H), 7.62 (d,  $J = 7.8$  Hz, 1H), 7.84-7.86 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  62.1, 102.9, 110.9 (t,  $J_{\text{F}} = 19.1$  Hz), 112.7, 112.9, 114.1, 118.0, 121.6, 123.0, 123.8, 128.7, 128.9, 129.6, 133.1, 138.1 (m), 141.1 (dm,  $J_{\text{F}} = 246.0$  Hz), 144.9 (dm,  $J_{\text{F}} = 245.9$  Hz);  $^{19}\text{F}$  NMR (378 MHz,  $\text{CDCl}_3$ )  $\delta$  -140.8 (d,  $J_{\text{F}} = 23.2$  Hz, 2F), -157.5 (d,  $J_{\text{F}} = 23.2$  Hz, 2F); Elem. Anal. Calcd for  $\text{C}_{19}\text{H}_{11}\text{F}_4\text{NO}$ : C, 66.09; H, 3.21; N, 4.06; Found: C, 66.19; H, 2.94; N, 4.02; HRMS (ESI) calcd for  $\text{C}_{19}\text{H}_{11}\text{F}_4\text{NO}$ : 346.0850 ( $\text{M} + \text{H}^+$ ), found: 346.0854; calcd / found : 0.999999.



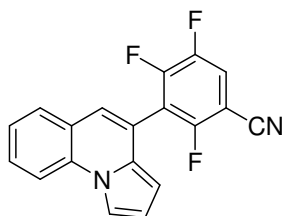
4-(2,3,5,6-Tetrafluoro-4-methylphenyl)pyrrolo[1,2-*a*]quinoline (**3c**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.35 (s, 3H), 6.27 (s, 1H), 6.78 (s, 1H), 7.01 (s, 1H), 7.32 (t,  $J = 7.3$  Hz, 1H), 7.52 (t,  $J = 7.3$  Hz, 1H), 7.64 (d,  $J = 7.3$  Hz, 1H), 7.87-7.89 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  7.07, 102.9, 112.7, 112.9, 114.1, 114.7 (t,  $J_{\text{F}} = 17.2$  Hz), 116.0 (t,  $J_{\text{F}} = 19.1$  Hz), 118.5, 121.5, 123.0, 123.8, 128.7, 129.0, 129.5, 133.2, 144.2 (dm,  $J_{\text{F}} = 256.5$  Hz), 145.2 (dm,  $J_{\text{F}} = 246.0$  Hz);  $^{19}\text{F}$  NMR (378 MHz,  $\text{CDCl}_3$ )  $\delta$  -141.3 (s, 2F), -143.4 (d,  $J_{\text{F}} = 23.2$  Hz, 2F); Elem. Anal. Calcd for  $\text{C}_{19}\text{H}_{11}\text{F}_4\text{N}$  : C, 69.30; H, 3.37; N, 4.25; Found: C, 69.21; H, 3.55; N, 4.33; HRMS (ESI) calcd for  $\text{C}_{19}\text{H}_{11}\text{F}_4\text{N}$ : 330.0900 ( $\text{M} + \text{H}^+$ ), found: 330.0918; calcd / found : 0.999995.



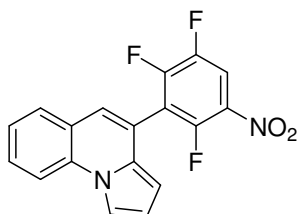
4-(2,3,5,6-Tetrafluoro-4-(trifluoromethyl)phenyl)pyrrolo[1,2-*a*]quinoline (**3d**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.25 (s, 1H), 6.79 (s, 1H), 7.02 (s, 1H), 7.32 (t,  $J = 7.3$  Hz, 1H), 7.54 (t,  $J = 7.3$  Hz, 1H), 7.64 (d,  $J = 7.8$  Hz, 1H), 7.86-7.88 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  102.9, 109.2-109.6 (m), 113.1, 113.2, 116.9, 120.9 (q,  $J_{\text{F}} = 272.7$  Hz), 121.7, 121.9 (q,  $J_{\text{F}} = 27.7$  Hz), 122.6, 124.0, 128.5, 129.2, 129.3, 133.3, 144.3 (dm,  $J_{\text{F}} = 259.3$  Hz), 144.8 (dm,  $J_{\text{F}} = 246.0$  Hz);  $^{19}\text{F}$  NMR (378 MHz,  $\text{CDCl}_3$ )  $\delta$  -56.1 (d,  $J_{\text{F}} = 23.2$  Hz, 3F), -136.8 (s, 2F), -140.0 (s, 2F); Elem. Anal. Calcd for  $\text{C}_{19}\text{H}_8\text{F}_7\text{N}$  : C, 59.54; H, 2.10; N, 3.65; Found: C, 59.65; H, 2.26; N, 3.79; HRMS (ESI) calcd for  $\text{C}_{19}\text{H}_8\text{F}_7\text{N}$ : 384.0618 ( $\text{M} + \text{H}^+$ ), found: 384.0624; calcd / found : 0.999998.



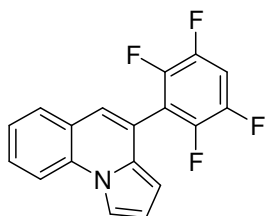
2,4,5-Trifluoro-3-(pyrrolo[1,2-*a*]quinolin-4-yl)benzonitrile (**3e**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.21 (s, 1H), 6.79 (s, 1H), 7.01 (s, 1H), 7.33 (t,  $J = 7.3$  Hz, 1H), 7.49-7.57 (m, 2H), 7.64 (d,  $J = 7.8$  Hz, 1H), 7.87-7.89 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  97.4-97.6 (m), 102.7, 112.2, 113.0, 113.1, 114.2, 116.9, 119.0 (m), 119.8 (d,  $J_{\text{F}} = 21.0$  Hz), 121.7, 122.6, 123.9, 128.7, 129.1, 129.2, 133.2, 147.1 (dm,  $J_{\text{F}} = 249.8$  Hz), 152.1 (dm,  $J_{\text{F}} = 256.5$  Hz), 157.6 (dm,  $J_{\text{F}} = 256.5$  Hz);  $^{19}\text{F}$  NMR (378 MHz,  $\text{CDCl}_3$ )  $\delta$  -107.7 (s, 1F), -121.4 (d,  $J_{\text{F}} = 23.2$  Hz, 1F), -137.0 (s, 1F); Elem. Anal. Calcd for  $\text{C}_{19}\text{H}_9\text{F}_3\text{N}_2$ : C, 70.81; H, 2.81; N, 8.69; Found: C, 70.72; H, 2.97; N, 8.77; HRMS (ESI) calcd for  $\text{C}_{19}\text{H}_9\text{F}_3\text{N}_2$ : 323.0791 ( $\text{M} + \text{H}^+$ ), found: 323.0792; calcd / found : 0.999999.



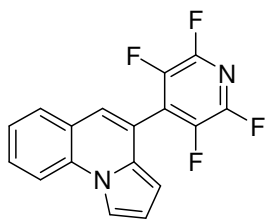
4-(2,3,6-Trifluoro-5-nitrophenyl)pyrrolo[1,2-*a*]quinoline (**3f**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.22 (s, 1H), 6.79 (s, 1H), 7.04 (s, 1H), 7.34 (t,  $J = 7.3$  Hz, 1H), 7.57 (t,  $J = 7.3$  Hz, 1H), 7.66 (d,  $J = 7.8$  Hz, 1H), 7.89-7.91 (m, 2H), 8.05 (q,  $J = 8.3$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  102.7, 113.1, 113.2, 113.8 (d,  $J_{\text{F}} = 22.9$  Hz), 114.3, 116.9, 119.8 (t,  $J_{\text{F}} = 20.9$  Hz), 121.9, 122.7, 124.0, 128.8, 129.2, 129.3, 133.3, 146.0 (dm,  $J_{\text{F}} = 250.7$  Hz), 150.4 (dm,  $J_{\text{F}} = 266.0$  Hz), 152.2 (dm,  $J_{\text{F}} = 251.7$  Hz);  $^{19}\text{F}$  NMR (378 MHz,  $\text{CDCl}_3$ )  $\delta$  -117.3 (s, 1F), -120.8 (d,  $J_{\text{F}} = 23.2$  Hz, 1F), -136.5 (s, 1F); Elem. Anal. Calcd for  $\text{C}_{18}\text{H}_9\text{F}_3\text{N}_2\text{O}_2$ : C, 63.16; H, 2.65; N, 8.18; Found: C, 62.96; H, 2.45; N, 8.24; HRMS (ESI) calcd for  $\text{C}_{18}\text{H}_9\text{F}_3\text{N}_2\text{O}_2$ : 343.0689 ( $\text{M} + \text{H}^+$ ), found: 343.0701; calcd / found : 0.999996.



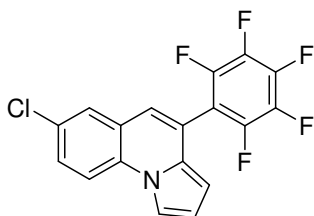
4-(2,3,5,6-Tetrafluorophenyl)pyrrolo[1,2-*a*]quinoline (**3g**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.26 (s, 1H), 6.79 (s, 1H), 7.02 (s, 1H), 7.11-7.16 (m, 1H), 7.32 (t,  $J = 7.3$  Hz, 1H), 7.53 (t,  $J = 7.3$  Hz, 1H), 7.64 (d,  $J = 7.8$  Hz, 1H), 7.87-7.89 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  102.9, 105.7 (t,  $J_{\text{F}} = 21.9$  Hz), 112.8, 113.0, 114.2, 118.2, 118.4 (m), 121.5, 122.9, 123.9, 128.9, 129.1, 129.3, 133.2, 144.3 (dm,  $J_{\text{F}} = 246.9$  Hz), 146.1 (dm,  $J_{\text{F}} = 246.0$  Hz);  $^{19}\text{F}$  NMR (378 MHz,  $\text{CDCl}_3$ )  $\delta$  -138.4 (s, 2F), -139.5 (s, 2F); Elem. Anal. Calcd for  $\text{C}_{18}\text{H}_9\text{F}_4\text{N}$  : C, 68.58; H, 2.88; N, 4.44; Found: C, 68.45; H, 2.67; N, 4.47; HRMS (ESI) calcd for  $\text{C}_{18}\text{H}_9\text{F}_4\text{N}$ : 316.0744 ( $\text{M} + \text{H}^+$ ), found: 316.0752; calcd / found : 0.999997.



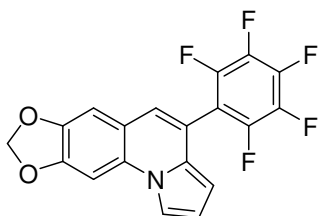
4-(Perfluoropyridin-4-yl)pyrrolo[1,2-*a*]quinoline (**3h**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.29 (s, 1H), 6.84 (s, 1H), 7.10 (s, 1H), 7.25 (s, 1H), 7.39 (t,  $J = 7.3$  Hz, 1H), 7.63 (t,  $J = 7.3$  Hz, 1H), 7.71 (d,  $J = 7.8$  Hz, 1H), 7.93-7.96 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  102.9, 113.2, 113.3, 114.3, 116.7, 121.7, 122.4, 124.1, 127.8, 129.3, 129.6, 130.8 (m), 133.4, 140.0 (dm,  $J_{\text{F}} = 259.0$  Hz), 143.8 (dm,  $J_{\text{F}} = 245.0$  Hz);  $^{19}\text{F}$  NMR (378 MHz,  $\text{CDCl}_3$ )  $\delta$  -89.9 (d,  $J_{\text{F}} = 23.2$  Hz, 2F), -140.0 (s, 2F); Elem. Anal. Calcd for  $\text{C}_{17}\text{H}_8\text{F}_4\text{N}_2$  : C, 64.56; H, 2.55; N, 8.86; Found: C, 64.48; H, 2.21; N, 8.80; HRMS (ESI) calcd for  $\text{C}_{17}\text{H}_8\text{F}_4\text{N}_2$ : 317.0696 ( $\text{M} + \text{H}^+$ ), found: 317.0705; calcd / found : 0.999997.



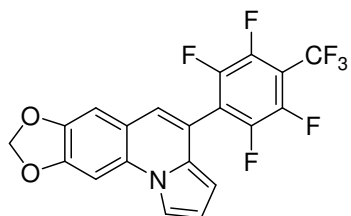
7-Chloro-4-(perfluorophenyl)pyrrolo[1,2-*a*]quinoline (**3i**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.26 (s, 1H), 6.80 (s, 1H), 6.92 (s, 1H), 7.51 (d,  $J = 9.2$  Hz, 1H), 7.64 (s, 1H), 7.83 (d,  $J = 9.2$  Hz, 1H), 7.87 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  103.5, 110.2, 112.1-112.3 (m), 113.3, 113.5, 115.7, 120.6, 122.3, 124.1, 128.1, 128.9, 129.2, 131.7, 137.8 (dm,  $J_{\text{F}} = 252.7$  Hz), 141.2 (dm,  $J_{\text{F}} = 264.1$  Hz), 144.7 (dm,  $J_{\text{F}} = 249.8$  Hz);  $^{19}\text{F}$  NMR (378 MHz,  $\text{CDCl}_3$ )  $\delta$  -138.9 (d,  $J_{\text{F}} = 23.2$  Hz, 2F), -153.5 (t,  $J_{\text{F}} = 23.2$  Hz, 1F), -161.5 (t,  $J_{\text{F}} = 23.2$  Hz, 2F); Elem. Anal. Calcd for  $\text{C}_{18}\text{H}_7\text{ClF}_5\text{N}$ : C, 58.80; H, 1.92; N, 3.81; Found: C, 58.61; H, 2.16; N, 3.72; HRMS (ESI) calcd for  $\text{C}_{18}\text{H}_7\text{ClF}_5\text{N}$ : 368.0260 ( $\text{M} + \text{H}^+$ ), found: 368.0271; calcd / found : 0.999997.



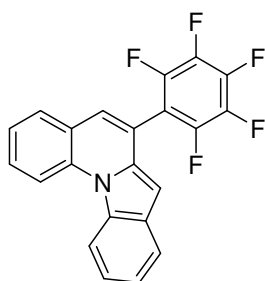
4-(Perfluorophenyl)-[1,3]dioxolo[4,5-*g*]pyrrolo[1,2-*a*]quinoline (**3j**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.06 (s, 2H), 6.18 (s, 1H), 6.78 (s, 1H), 6.89 (s, 1H), 7.02 (s, 1H), 7.34 (s, 1H), 7.70 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  95.1, 101.6, 101.8, 106.6, 111.9, 111.4-111.6 (m), 113.0, 114.9, 117.3, 121.5, 129.2 (d,  $J_{\text{F}} = 4.7$  Hz), 137.7 (dm,  $J_{\text{F}} = 252.7$  Hz), 140.9 (dm,  $J_{\text{F}} = 257.4$  Hz), 144.7 (dm,  $J_{\text{F}} = 248.8$  Hz), 144.8, 149.3;  $^{19}\text{F}$  NMR (378 MHz,  $\text{CDCl}_3$ )  $\delta$  -138.9 (d,  $J_{\text{F}} = 23.2$  Hz, 2F), -154.4 (d,  $J_{\text{F}} = 23.2$  Hz, 1F), -161.6 (s, 2F); Elem. Anal. Calcd for  $\text{C}_{19}\text{H}_8\text{F}_5\text{NO}_2$ : C, 60.49; H, 2.14; N, 3.71; Found: C, 60.26; H, 2.03; N, 3.92; HRMS (ESI) calcd for  $\text{C}_{19}\text{H}_8\text{F}_5\text{NO}_2$ : 378.0548 ( $\text{M} + \text{H}^+$ ), found: 378.0565; calcd / found : 0.999995.



4-(2,3,5,6-Tetrafluoro-4-(trifluoromethyl)phenyl)-[1,3]dioxolo[4,5-g]pyrrolo[1,2-a]quinoline (**3k**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.08 (s, 2H), 6.21 (s, 1H), 6.80 (s, 1H), 6.93 (s, 1H), 7.04 (s, 1H), 7.36 (s, 1H), 7.72 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  95.1, 101.7, 101.9, 106.7, 108.9-109.7 (m), 112.1, 113.2, 114.6, 117.1, 120.9 (q,  $J_{\text{F}} = 271.7$  Hz), 121.5, 122.0 (q,  $J_{\text{F}} = 18.1$  Hz), 128.5, 129.5, 144.2 (dm,  $J_{\text{F}} = 256.5$  Hz), 144.8 (dm,  $J_{\text{F}} = 244.1$  Hz), 144.9, 149.7;  $^{19}\text{F}$  NMR (378 MHz,  $\text{CDCl}_3$ )  $\delta$  -56.0 (d,  $J_{\text{F}} = 23.2$  Hz, 3F), -136.9 (s, 2F), 140.1 (s, 2F); Elem. Anal. Calcd for  $\text{C}_{20}\text{H}_8\text{F}_7\text{NO}_2$  : C, 56.22; H, 1.89; N, 3.28; Found: C, 56.28; H, 1.87; N, 3.35; HRMS (ESI) calcd for  $\text{C}_{20}\text{H}_8\text{F}_7\text{NO}_2$ : 428.0516 ( $\text{M} + \text{H}^+$ ), found: 428.0520; calcd / found : 0.999999.

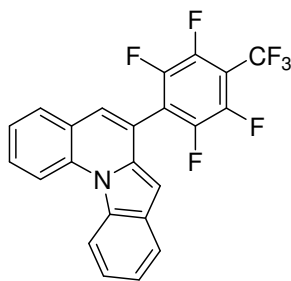


6-(Perfluorophenyl)indolo[1,2-a]quinoline (**3l**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.49 (s, 1H), 7.13 (s, 1H), 7.31 (t,  $J = 7.8$  Hz, 1H), 7.36 (t,  $J = 7.3$  Hz, 1H), 7.43 (t,  $J = 7.3$  Hz, 1H), 7.61-7.65 (m, 2H), 7.79 (d,  $J = 7.8$  Hz, 1H), 8.45 (d,  $J = 8.3$  Hz, 1H), 8.57 (d,  $J = 8.7$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  97.1, 112.1-112.6 (m), 114.3, 115.4, 117.5, 121.4, 122.2, 122.4, 123.1, 126.9, 129.4, 129.9, 133.3, 134.5, 136.6, 137.8 (dm,  $J_{\text{F}} = 246.9$  Hz), 141.2 (dm,  $J_{\text{F}} = 257.4$  Hz), 144.9 (dm,  $J_{\text{F}} = 248.9$  Hz);  $^{19}\text{F}$  NMR (378 MHz,  $\text{CDCl}_3$ )  $\delta$  -138.8 (d,  $J_{\text{F}} = 23.2$  Hz, 2F), -153.5 (t,  $J_{\text{F}} = 23.2$  Hz, 1F), -161.0 (t,  $J_{\text{F}} = 23.2$  Hz, 2F); Elem. Anal. Calcd for  $\text{C}_{22}\text{H}_{10}\text{F}_5\text{N}$  : C, 68.93; H, 2.63; N, 3.65; Found: C, 68.97; H, 2.62; N, 3.53; HRMS (ESI) calcd for  $\text{C}_{22}\text{H}_{10}\text{F}_5\text{N}$ : 384.0806 ( $\text{M} + \text{H}^+$ ), found: 384.0809; calcd / found :

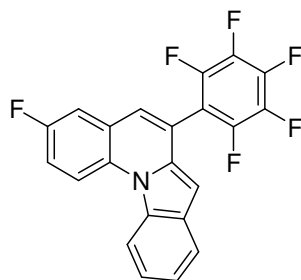


0.999999.



6-(2,3,5,6-Tetrafluoro-4-(trifluoromethyl)phenyl)indolo[1,2-*a*]quinoline (**3m**)

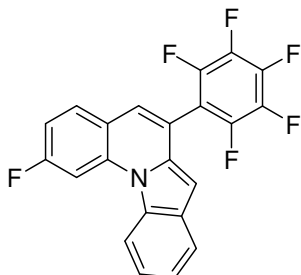
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.51 (s, 1H), 7.14 (s, 1H), 7.30 (t,  $J = 7.3$  Hz, 1H), 7.36 (t,  $J = 7.3$  Hz, 1H), 7.43 (t,  $J = 7.3$  Hz, 1H), 7.61-7.65 (m, 2H), 7.79 (d,  $J = 7.8$  Hz, 1H), 8.43 (d,  $J = 8.3$  Hz, 1H), 8.55 (d,  $J = 8.7$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  97.2, 109.5-110.0 (m), 114.3, 115.4, 117.2, 120.8 (q,  $J_{\text{F}} = 277.6$  Hz), 121.4, 121.5 (q,  $J_{\text{F}} = 27.6$  Hz), 122.3, 122.6, 122.9, 123.2, 126.8, 129.6, 129.8, 130.2, 133.3, 133.7, 136.8, 144.4 (dm,  $J_{\text{F}} = 257.4$  Hz), 144.9 (dm,  $J_{\text{F}} = 247.9$  Hz);  $^{19}\text{F}$  NMR (378 MHz,  $\text{CDCl}_3$ )  $\delta$  -56.0 (d,  $J_{\text{F}} = 23.2$  Hz, 3F), -136.7 (s, 2F), -139.6 (s, 2F); Elem. Anal. Calcd for  $\text{C}_{23}\text{H}_{10}\text{F}_7\text{N}$  : C, 63.75; H, 2.33; N, 3.23; Found: C, 63.84; H, 2.09; N, 3.34; HRMS (ESI) calcd for  $\text{C}_{23}\text{H}_{10}\text{F}_7\text{N}$ : 434.0774 ( $\text{M} + \text{H}^+$ ), found: 434.0774; calcd / found : 1.000000.



3-Fluoro-6-(perfluorophenyl)indolo[1,2-*a*]quinoline (**3n**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.51 (s, 1H), 7.05 (s, 1H), 7.31-7.38 (m, 3H), 7.43 (t,  $J = 7.3$  Hz, 1H), 7.79 (d,  $J = 7.3$  Hz, 1H), 8.35 (d,  $J = 8.3$  Hz, 1H), 8.49-8.51 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  97.5, 112.1-112.2 (m), 113.8, 114.6 (d,  $J_{\text{F}} = 22.9$  Hz), 116.6, 116.7, 116.9, 119.0, 121.6, 122.3, 122.8, 124.6 (d,  $J_{\text{F}} = 8.6$  Hz), 125.7, 129.6, 133.1, 134.1, 137.8 (dm,  $J_{\text{F}} = 246.9$  Hz), 141.3 (dm,  $J_{\text{F}} = 254.6$  Hz), 144.8 (dm,  $J_{\text{F}} = 247.9$  Hz), 158.0 (d,  $J_{\text{F}} = 242.2$  Hz);  $^{19}\text{F}$  NMR (378 MHz,  $\text{CDCl}_3$ )  $\delta$  -119.2(s, 1F),

-138.7 (d,  $J_F = 23.2$  Hz, 2F), -153.1 (d,  $J_F = 23.2$  Hz, 1F), -160.8 (t,  $J_F = 23.2$  Hz, 2F);  
Elem. Anal. Calcd for  $C_{22}H_9F_6N$  : C, 65.84; H, 2.26; N, 3.49; Found: C, 65.92; H,  
2.17; N, 3.72; HRMS (ESI) calcd for  $C_{22}H_9F_6N$ : 402.0712 ( $M + H^+$ ), found: 402.0718;  
calcd / found : 0.999998.



2-Fluoro-6-(perfluorophenyl)indolo[1,2-*a*]quinoline (**3o**)

$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  6.50 (s, 1H), 7.08-7.13 (m, 2H), 7.41 (t,  $J = 7.3$  Hz, 1H), 7.48 (t,  $J = 7.3$  Hz, 1H), 7.66 (t,  $J = 7.3$  Hz, 1H), 7.80 (d,  $J = 7.8$  Hz, 1H), 8.31 (d,  $J = 11.4$  Hz, 1H), 8.39 (d,  $J = 8.7$  Hz, 1H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  97.5, 103.0 (d,  $J_F = 27.6$  Hz), 110.8 (d,  $J_F = 22.9$  Hz), 112.0-112.2 (m), 114.0, 116.7, 119.7, 121.5, 122.7 (d,  $J_F = 10.5$  Hz), 126.1, 130.0, 131.0 (d,  $J_F = 10.5$  Hz), 133.2, 134.3, 137.6 (d,  $J_F = 13.5$  Hz), 138.2 (dm,  $J_F = 254.6$  Hz), 141.3 (dm,  $J_F = 255.8$  Hz), 144.9 (dm,  $J_F = 249.8$  Hz), 163.4 (d,  $J_F = 247.9$  Hz);  $^{19}F$  NMR (378 MHz,  $CDCl_3$ )  $\delta$  -107.2 (s, 1F), -138.8 (s, 2F), -153.4 (s, 1F), -161.0 (t,  $J_F = 23.2$  Hz, 2F); Elem. Anal. Calcd for  $C_{22}H_9F_6N$  : C, 65.84; H, 2.26; N, 3.49; Found: C, 65.76; H, 2.17; N, 3.35; HRMS (ESI) calcd for  $C_{22}H_9F_6N$ : 402.0712 ( $M + H^+$ ), found: 402.0719; calcd / found : 0.999998.

