Efficient Route to Unknown Quinolino[2,3-c]cinnolines; Synthesis of Neocryptolepines

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SUPPORTING DATA

A. Procedures.....	2
B. ¹ H NMR Spectra.....	25
C. ¹³ C NMR Spectra.....	59
D. DEPT 135 ¹³ C NMR Spectra.....	87
E. Mass Spectra.....	90
F. Infrared Spectra.....	106
G. X-Ray Crystallography.....	128
H. List of Compounds (including melting points).....	137

A. Procedures

1a

2-Aminobenzaldehyde (1a): The title product is prepared according to a literature procedure.⁵⁹ In a three-necked round bottom flask is successively added ferrous sulfate heptahydrate (105.00 g, 380.0 mmol), water (175.00 mL), concentrated hydrochloric acid (12 *N*, 0.50 mL) and *o*-nitobenzaldehyde (6.00 g, 40.0 mmol). The reaction is stirred with heating. When the temperature of the reaction mixture reaches 90 °C, ammonium hydroxides (25.00 mL) is added in one portion, and at two-minute intervals, three portions (10.00 mL) of ammonium hydroxide are added. The mixture is steam distilled immediately to yield the title product as white crystals (3.10 g, 65%) m.p. 37-38 °C (Lit. 38-39°C).⁵⁹ ¹H NMR (300 MHz, CDCl₃): δ 9.87 (s, 1H), 7.49 (d.d, $J_1 = 7.8$ Hz, $J_2 = 1.5$ Hz, 1H), 7.32-7.26 (m, 1H), 6.78-6.73 (m, 1H), 6.65 (d, $J = 8.4$ Hz, 1H), 6.12 (b, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 194.1, 149.9, 135.8, 135.2, 118.8, 116.4, 116.0.

1b

2-Amino-5-chlorobenzaldehyde (1b): The title product is prepared according to a literature procedure.⁶⁰ Iron powder (0.94 g, 16.8 mmol) and concentrated

hydrochloric acid (12 N, 0.20 mL) are added to a solution of 5-chloro-2-nitrobenzaldehyde (1.00 g, 5.4 mmol) in ethanol: acetic acid: water (2:2:1, 25.00 mL). The reaction mixture is refluxed for 15 minutes and is then stirred at room temperature for 40 minutes. The insoluble material is filtered, and the filtrate is extracted with diethylether. The organic layer is washed with Na₂CO₃ (25.00 mL × 3), brine (25.00 mL × 3), and water (25.00 mL × 3). The organic layer is dried over anhydrous MgSO₄ and is evaporated *in vacuo*. Recrystallizations from hexane gave the title product as yellow needles (0.58 g, 70%) m.p. 73-74 °C (Lit. 73.5-74.5 °C).⁶¹ ¹H NMR (300 MHz, CDCl₃): δ 9.81 (s, 1H), 7.45 (d, *J* = 2.4 Hz, 1H), 7.28-7.26 (m, 1H), 6.62 (d, *J* = 8.7 Hz, 1H), 6.14 (b, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 192.9, 148.3, 135.3, 134.3, 120.8, 119.3, 117.7.

1c

2-Amino-3,5-dibromobenzaldehyde (1c): title product is prepared according to a literature procedure.⁶² 2-Aminobenzaldehyde **1a** (1.00g, 8.26 mmol) dissolved in ethanol (50.00mL), and the solution stirred at 20°C, while bromine (2.91g, 18.2 mmol) dissolved in water (75.00 mL) and KBr (8.93g) was added drop wise during 10 min. The suspension of yellow product was then stirred for 1hr. After addition of excess of NaHCO₃, the mixture was chilled, and the title product was collected by filtration. Crystallization from ethanol gave yellow needles. m.p. 137-139 °C (Lit. 136-139°C).⁶²

^1H NMR (300 MHz, CDCl_3): δ 9.76 (s, 1H), 7.72 (d, $J = 2.1$ Hz, 1H), 7.59 (d, $J = 2.4$ Hz, 1H), 6.70 (b, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 192.0, 145.9, 139.8, 137.1, 120.1, 110.8, 106.7.

1d

2-Amino-4,5-dimethoxybenzaldehyde (1d): The title product is prepared according to a literature procedure.⁶⁰ Iron powder (0.82 g, 14.2 mmol) and concentrated hydrochloric acid (12 N, 0.20 mL) are added to a solution of 4,5-dimethoxy-2-nitrobenzaldehyde (1.00 g, 4.7 mmol) in ethanol: acetic acid: water (2:2:1, 25.00 mL). The reaction mixture is refluxed for 15 minutes and is then stirred at room temperature for 40 minutes. The insoluble material is filtered, and the filtrate is extracted with diethylether. The organic layer is washed with Na_2CO_3 (25.00 mL $\times$ 3), brine (25.00 mL $\times$ 3), and water (25.00 mL $\times$ 3). The organic layer is dried over anhydrous MgSO_4 and is evaporated *in vacuo*. The crude solid is purified by flash chromatography (hexane: ethylacetate, 3:1) to yield the title product as yellow oil (0.30 g, 35%) m.p. 83-85°C (Lit. 84-86°C).⁶³ ^1H NMR (300 MHz, CDCl_3): δ 9.69 (s, 1H), 6.88 (s, 1H), 6.12 (s, 1H), 6.09 (b, 2H), 3.89 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 191.5, 156.1, 147.2, 141.0, 115.8, 111.3, 98.4, 56.5, 56.0.

3a

3-(2-Nitrophenyl)quinolin-2-amine (3a): Pyrrolidine (0.50 mL) is added to a solution of 2-aminobenzaldehyde **1a** (1.00 g, 8.3 mmol) and 2-nitrobenzylcyanide **2a** (1.34 g, 8.3 mmol) in methanol (10.00 mL). A solution of methanolic KOH (5%, 0.50 mL) is added to the reaction mixture which is heated to reflux for 2 hours. Upon cooling, the precipitate is filtered and is washed with cold methanol to afford the title product as yellow needles (1.60 g, 73%) m.p. 205-207 °C. ¹H NMR (300 MHz, CDCl₃): δ 8.09 (dd, *J*₁ = 8.1 Hz, *J*₂ = 1.2 Hz, 1H), 7.75-7.70 (m, 3H), 7.64-7.56 (m, 3H), 7.51 (dd, *J*₁ = 7.5 Hz, *J*₂ = 1.5 Hz, 1H), 7.28 (dd, *J*₁ = 8.1 Hz, *J*₂ = 1.2 Hz, 1H), 4.58 (b, 2H). ¹H NMR (300 MHz, DMSO-*d*₆): δ 8.18 (dd, *J*₁ = 8.1 Hz, *J*₂ = 1.2 Hz, 1H), 7.85 (dt, *J*₁ = 7.5 Hz, *J*₂ = 1.5 Hz, 1H), 7.78 (s, 1H), 7.72 (dt, *J*₁ = 7.8 Hz, *J*₂ = 1.5 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.57-7.52 (m, 3H), 7.23-7.18 (m, 1H), 5.90 (b, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 154.4, 149.3, 147.6, 136.5, 133.4, 132.7, 132.0, 130.1, 129.6, 127.5, 126.1, 124.8, 123.7, 123.2, 121.1. IR (KBr, cm⁻¹): ν_{max} 3458, 3438 (b, NH₂); 1520, 1346 (s, NO₂). HRMS: *m/z* calculated for C₁₅H₁₁N₃O₂ 265.08513, found [M]⁺ 265.14708.

3b

3-(5-Methyl-2-nitrophenyl)quinolin-2-amine (3b): Pyrrolidine (0.20 mL) is added to a solution of 2-aminobenzaldehyde **1a** (0.38 g, 3.1 mmol) and 5-methyl-2-nitrobenzylcyanide **2b** (0.55 g, 3.1 mmol) in methanol (10.00 mL). A solution of methanolic KOH (5%, 0.50 mL) is added to the reaction mixture which is heated to reflux for 2 hours. Upon cooling, the precipitate is filtered and is washed with cold methanol to afford the title product as yellow crystals (0.65 g, 73%) m.p. 201-203 °C. ¹H NMR (300 MHz, CDCl₃): δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.71 (dd, *J*₁ = 8.4 Hz, *J*₂ = 0.6 Hz, 1H), 7.69 (s, 1H), 7.63-7.57 (m, 2H), 7.40 (qd, *J*₁ = 8.1 Hz, *J*₂ = 2.4 Hz, *J*₃ = 0.6 Hz, 1H), 7.31-7.27 (m, 2H), 4.65 (b, 2H), 2.50 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 154.5, 147.4, 146.7, 145.1, 136.2, 133.2, 132.1, 130.2, 130.0, 127.5, 126.0, 125.1, 123.7, 123.1, 121.8, 21.5. IR (KBr, cm⁻¹): ν_{max} 3450, 3315 (br, NH₂); 1516, 1350 (s, NO₂). HRMS: *m/z* calculated for C₁₆H₁₃N₃O₂ 279.10078, found [M]⁺ 279.23297.

3c

6-Chloro-3-(2-nitrophenyl)quinolin-2-amine (3c): Pyrrolidine (0.20 mL) is added to a solution of 2-amino-5-chlorobenzaldehyde **1b** (1.00 g, 6.4 mmol) and 2-

nitrobenzylcyanide **2a** (1.10 g, 6.4 mmol) in methanol (10.00 mL). A solution of methanolic KOH (5%, 0.50 mL) is added to the reaction mixture which is heated to reflux for 30 minutes. Upon cooling, the precipitate is filtered and is washed with cold methanol to afford the title product as orange solid (1.34 g, 70%) m.p. 255-257°C. ¹H NMR (300 MHz, CDCl₃): δ 8.14 (dd, *J*₁ = 8.4 Hz, *J*₂ = 1.2 Hz, 1H), 7.70 (dt, *J*₁ = 7.2 Hz, *J*₂ = 1.2 Hz, 1H), 7.69-7.63 (m, 3H), 7.60 (d, *J* = 2.4 Hz, 1H), 7.55 (d, *J* = 2.4 Hz, 1H), 7.52-7.49 (m, 1H), 4.63 (b, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 155.4, 148.8, 143.6, 136.0, 135.6, 133.9, 132.5, 130.9, 130.2, 129.3, 125.3, 125.2, 123.1, 121.8, 115.1. IR (KBr, cm⁻¹): ν_{max} 3450, 3350 (br, NH₂); 1520, 1350 (s, NO₂). GC-MS (CH₃CN): *m/z* calculated for C₁₅H₁₀N₃O₂Cl 299.0, found [M]⁺ 299.0, *t*_R = 26.15 min.

3d

6,8-Dibromo-3-(2-nitrophenyl)quinolin-2-amine (3d): Pyrrolidine (0.20 mL) is added to a solution of 2-amino-3,5-dibromobenzaldehyde **1c** (1.00 g, 3.6 mmol) and 2-nitrobenzylcyanide **2a** (0.60 g, 3.6 mmol) in methanol (10.00 mL). A solution of methanolic KOH (5%, 0.50 mL) is added to the reaction mixture which is heated to reflux for 2 hours. Upon cooling, the precipitate is filtered and is washed with copious amounts of cold methanol to afford the title product as yellow solid. If precipitation is not realized, the reaction mixture is dried under reduced pressure and the crude solid is recrystallized using dichloromethane: hexane to yield the title product as deep yellow solid (1.00 g, 66%) m.p. 142-144°C. ¹H NMR (300 MHz, CDCl₃): δ 7.93 (dd, *J*₁ = 8.1

Hz, $J_2 = 1.2$ Hz, 1H), 7.78 (d, $J = 2.1$ Hz, 1H), 7.77 (dt, $J_1 = 7.5$ Hz, $J_2 = 1.2$ Hz, 1H), 7.71 (d, $J = 2.4$ Hz, 1H), 7.66 (dt, $J_1 = 7.5$ Hz, $J_2 = 1.5$ Hz, 1H), 7.59 (s, 1H), 7.48 (dd, $J_1 = 7.5$ Hz, $J_2 = 1.5$ Hz, 1H), 4.9 (b, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 155.4, 148.8, 143.6, 136.0, 135.7, 133.9, 132.5, 130.9, 130.2, 129.3, 125.3, 125.2, 123.1, 121.8, 115.1. IR (KBr, cm^{-1}): ν_{max} 3434 (br, NH_2); 1588, 1336 (s, NO_2). GC-MS (CH_3CN): m/z calculated for $\text{C}_{15}\text{H}_9\text{N}_3\text{O}_2\text{Br}_2$ 422.9, found $[\text{M}]^+$ 422.9, $t_R = 31.99$ min.

3e

6,7-Dimethoxy-3-(2-nitrophenyl)quinolin-2-amine (3e): Pyrrolidine (0.20 mL) is added to a solution of 2-amino-4,5-dimethoxybenzaldehyde **1d** (0.50 g, 2.7 mmol) and 2-nitrobenzylcyanide **2a** (0.45 g, 2.7 mmol) in methanol (10.00 mL). A solution of methanolic KOH (5%, 0.50 mL) is added to the reaction mixture which is heated to reflux for 2 hours. Upon cooling, the reaction mixture is dried under reduced pressure, and the resulting crude solid is purified using column chromatography to yield the title product as yellow oil (0.35, 40%). m.p. 206-208°C. ^1H NMR (300 MHz, CDCl_3): δ 8.05 (dd, $J_1 = 8.1$ Hz, $J_2 = 1.2$ Hz, 1H), 7.70 (dt, $J_1 = 7.5$ Hz, $J_2 = 1.2$ Hz, 1H), 7.58 (dt, $J_1 = 8.1$ Hz, $J_2 = 1.5$ Hz, 1H), 7.57 (s, 1H), 7.48 (dd, $J_1 = 7.5$ Hz, $J_2 = 1.5$ Hz, 1H), 7.11 (s, 1H), 6.89 (s, 1H), 5.05 (b, 2H), 3.98 (s, 3H), 3.92 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 153.4, 152.8, 149.4, 147.2, 144.1, 135.2, 133.4, 132.8, 132.2, 129.4, 124.8, 118.4, 118.2, 105.9, 105.8, 56.1, 56.0. IR (KBr, cm^{-1}): ν_{max} 3436, 3358 (br,

NH₂); 1531, 1342 (s, NO₂). GC-MS (CH₃CN): *m/z* calculated for C₁₇H₁₅N₃O₄ 325.1, found [M]⁺ 325.1, *t_R* = 28.99 min.

4a

Quinolino[2,3-*c*]cinnoline 5-oxide (4a): 3-(2-Nitrophenyl)quinolin-2-amine

3a (1.00 g, 3.7 mmol) is dissolved in a warm solution of methanolic KOH (10.00 mL). The mixture is stirred with heating to reflux for 10 minutes. Upon cooling, the precipitate is filtered and is washed with cold methanol to yield the title product as yellow solid (0.88 g, 95%) decomp. 275 °C. ¹H NMR (300 MHz, CDCl₃): δ 9.19 (s, 1H), 8.83 (d, *J* = 8.4 Hz, 1H), 8.62 (d, *J* = 8.1 Hz, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 8.02 (t, 1H), 7.87 (q, 1H), 7.69 (t, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 151.3, 149.9, 137.8, 133.3, 131.8, 130.7, 130.5, 130.1, 127.9, 127.6, 127.1, 122.9, 122.6, 113.0. IR (KBr, cm⁻¹): ν_{max} 1323 (m, N-O). HRMS: *m/z* calculated mass for C₁₅H₉N₃O 247.07456, found [M+H]⁺ 248.08177.

4b

2-Methylquinolino[2,3-*c*]cinnoline 5-oxide (4b): 3-(5-Methyl-2-

nitrophenyl)quinolin-2-amine **3b** (0.50 g, 1.8 mmol) is dissolved in a warm solution of

methanolic KOH (10.00 mL). The mixture is stirred with heating to reflux for 10 minutes. Upon cooling, the precipitate is filtered and washed with cold methanol to yield the title product as yellow solid (0.45 g, 95%) decomp. 277 °C. ¹H NMR (300 MHz, CDCl₃): δ 9.20 (s, 1H), 8.73 (d, *J* = 8.7 Hz, 1H), 8.40 (s, 1H), 8.35 (d, *J* = 8.7 Hz, 1H), 8.09 (d, *J* = 8.7 Hz, 1H), 7.92-7.89 (m, 1H), 7.72-7.66 (m, 2H), 5.34 (b, 2H), 2.71 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 151.5, 149.8, 144.6, 136.1, 131.9, 131.6, 130.6, 130.1, 127.8, 127.7, 127.5, 127.1, 122.7, 122.2, 113.0, 22.1. IR (KBr, cm⁻¹): ν_{max} 1323 (m, N-O). HRMS: *m/z* calculated mass for C₁₆H₁₁N₃O 261.09021, found [M+H]⁺ 262.09739.

4c

10-Chloroquinolino[2,3-*c*]cinnoline 5-oxide (4c): 6-Chloro-3-(2-nitrophenyl)quinolin-2-amine **3c** (0.50 g, 1.7 mmol) is dissolved in a warm solution of methanolic KOH (10.00 mL). The mixture is stirred with heating to reflux for 10 minutes. Upon cooling, the precipitate is filtered and is washed with cold methanol to yield the title product as yellow solid (0.45 g, 95%). m.p. > 300°C. ¹H NMR (300 MHz, CDCl₃-trifluoroacetic acid): δ 9.75 (s, 1H), 8.74 (t, *J* = 8.1, 2H), 8.50 (d, *J* = 9.3 Hz, 1H), 8.34 (d, *J* = 1.8 Hz, 1H), 8.26 (t, 1H), 8.16-8.08 (m, 2H). ¹³C NMR (75 MHz, CDCl₃- trifluoroacetic acid): δ 160.4, 159.9, 146.5, 138.6, 138.5, 136.7, 136.1, 133.4, 127.6, 127.4, 125.5, 123.3, 123.1, 114.5, 112.8. IR (KBr, cm⁻¹): ν_{max} 1338 (m, N-O). MS: *m/z* calculated for C₁₅H₈N₃OCl 281.0, found [M+H]⁺ 282.1.

4d

8,10-Dibromoquinolino[2,3-c]cinnoline 5-oxide (4d): 6,8-Dibromo-3-(2-nitrophenyl)quinolin-2-amine **3d** (0.50 g, 1.2 mmol) is dissolved in a warm solution of methanolic KOH (10.00 mL). The mixture is stirred with heating to reflux for 20 minutes. Upon cooling, the precipitate is filtered and washed with cold methanol to yield the title product as yellow solid (0.45 g, 95%). m.p. > 300°C. ^1H NMR (300 MHz, DMSO- d_6 , 90 °C): 9.79 (s, 1H), 8.92 (dd, $J_1 = 8.1$ Hz, $J_2 = 0.9$ Hz, 1H), 8.73 (dd, $J_1 = 8.4$ Hz, $J_2 = 0.9$ Hz, 1H), 8.55 (d, $J = 2.1$ Hz, 1H), 8.46 (d, $J = 2.1$ Hz, 1H), 8.24-8.18 (m, 1H), 8.08-8.05 (m, 1H). ^1H NMR (300 MHz, CDCl₃-trifluoroacetic acid): 10.02(s, 1H), 8.82 (dt, $J_1 = 7.5$ Hz, $J_2 = 0.9$ Hz, 2H), 8.66(d, $J = 1.8$, 1H), 8.64(d, $J = 1.8$, 1H), 8.35 (dt, $J_1 = 8.1$ Hz, $J_2 = 0.9$ Hz, 1H), 8.19 (dt, $J_1 = 8.4$ Hz, $J_2 = 1.2$ Hz, 1H). ^{13}C NMR (75 MHz, CDCl₃-trifluoroacetic acid): 144.2, 142.0, 137.3, 134.6, 131.6, 128.2, 125.1, 124.7, 123.9, 123.2, 119.9, 115.8, 114.5, 112.3, 108.6. IR (KBr, cm⁻¹): ν_{max} 1335 (m, N-O). MS: m/z calculated for C₁₅H₇N₃OBr₂ 404.9, found [M+H]⁺ 405.8.

4e

9,10-Dimethoxyquinolino[2,3-*c*]cinnoline 5-oxide (4e): 6,7-Dimethoxy-3-(2-nitrophenyl)quinolin-2-amine **3e** (0.25 g, 7.7 mmol) is dissolved in a warm solution of methanolic KOH (10.00 mL). The mixture is stirred with heating to reflux for 20 minutes. Upon cooling, the precipitate is filtered and washed with cold methanol to yield the title product as yellow solid (0.22 g, 95%). Decomp. 277-279°C. ^1H NMR (300 MHz, CDCl_3): δ 8.88 (s, 1H), 8.79 (d, $J = 8.4$ Hz, 1H), 8.49 (d, $J = 8.4$ Hz, 1H), 7.95 (t, 1H), 7.79 (t, 1H), 7.49 (s, 1H), 7.19 (s, 1H), 4.11 (s, 3H), 4.08 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 154.9, 151.5, 150.0, 147.9, 137.3, 132.9, 129.8, 127.8, 127.6, 123.8, 122.8, 122.2, 111.3, 107.3, 104.0, 56.4, 56.3. IR (KBr, cm^{-1}): ν_{max} 1344 (m, N-O). MS: m/z calculated for $\text{C}_{17}\text{H}_{13}\text{N}_3\text{O}_3$ 307.1, found $[\text{M}+\text{H}]^+$ 308.1.

5a

Quinolino[2,3-*c*]cinnoline (5a): Zinc dust (2.35 g, 36.4 mmol) is added to a solution of quinolino[2,3-*c*]cinnoline 5-oxide **4a** (0.50 g, 2.0 mmol) in hot glacial acetic acid (5.00 mL). The reaction mixture is heated to reflux for 10 minutes. Upon cooling,

the insoluble material is filtered, and the filtrate is neutralized with aqueous KOH solution. The mixture was extracted with dichloromethane (25.00 mL $\times$ 3) and was washed with water (25.00 mL $\times$ 3). The organic layer was dried over anhydrous MgSO₄, and was evaporated *in vacuo*. The crude solid was purified using column chromatography (hexane: ethyl acetate; 1:2) to afford the title product as a yellow solid (0.32 g, 70 %) m.p. 285-287 °C. ¹H NMR (300 MHz, CDCl₃): δ 9.43 (s, 1H), 8.86-8.83 (m, 1H), 8.69-8.66 (m, 1H), 8.53 (dd, J_1 = 8.7 Hz, J_2 = 0.9 Hz, 1H), 8.18 (dd, J_1 = 7.8 Hz, J_2 = 0.6 Hz, 1H), 8.01-7.92 (m, 3H), 7.79-7.75 (m, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 151.4, 149.2, 143.7, 132.5, 132.1, 131.9, 131.6, 130.7, 129.9, 129.0, 128.9, 127.8, 121.5, 120.1, 113.7. HRMS: m/z calculated mass for C₁₅H₉N₃ 231.07965, found [M+H]⁺ 232.08693.

5b

2-Methylquinolino[2,3-c]cinnoline (5b): Zinc dust (0.05 g, 0.7 mmol) is added to a solution of 2-methylquinolino[2,3-c]cinnoline 5-oxide **4b** (0.01 g, 0.04 mmol) in hot glacial acetic acid (10.00 mL). The reaction mixture is heated to reflux for 10 minutes. Upon cooling, the insoluble material is filtered, and the filtrate is neutralized with aqueous KOH solution. The mixture was extracted with dichloromethane (25.00 mL $\times$ 3) and was washed with water (25.00 mL $\times$ 3). The organic layer was dried over anhydrous MgSO₄, and was evaporated *in vacuo* to afford

the title product as a yellow solid (0.10 g, 53 %). Decomp. 252-254°C. ^1H NMR (300 MHz, CDCl_3): δ 9.38 (s, 1H), 8.66 (d, $J = 8.4$ Hz, 1H), 8.47, (d, $J = 8.7$ Hz, 1H), 8.40 (s, 1H), 8.09 (d, $J = 8.4$ Hz, 1H), 7.91-7.85 (m, 1H), 7.73-7.68 (m, 2H), 2.67 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 150.6, 148.2, 142.7, 141.7, 130.9, 130.8, 130.5, 130.4, 129.8, 127.9, 127.8, 126.7, 120.1, 119.2, 112.8, 28.7. MS: m/z calculated for $\text{C}_{16}\text{H}_{11}\text{N}_3$ 245.3, found $[\text{M}+\text{H}]^+$ 246.1.

5c

10-Chloroquinolino[2,3-*c*]cinnoline (5c): Zinc dust (2.00 g, 30.6 mmol) is added to a solution of 10-chloroquinolino[2,3-*c*]cinnoline 5-oxide **4c** (0.50 g, 1.7 mmol) in hot glacial acetic acid (5.00 mL). The reaction mixture is heated to reflux for 10 minutes. Upon cooling, the insoluble material is filtered, and the filtrate is neutralized with aqueous KOH solution. The mixture was extracted with dichloromethane (25.00 mL $\times$ 3) and was washed with water (25.00 mL $\times$ 3). The organic layer was dried over anhydrous MgSO_4 , and was evaporated *in vacuo* to afford the title product as a yellow solid (0.33 g, 70 %). m.p. 285-287°C. ^1H NMR (300 MHz, CDCl_3): δ 9.42 (s, 1H), 8.92-8.89 (m, 1H), 8.74-8.71 (m, 1H), 8.53 (d, $J = 4.3$ Hz, 1H), 8.19 (d, $J = 2.4$ Hz, 1H), 8.08-8.02 (m, 2H), 7.90 (dd, $J_1 = 9.3$ Hz, $J_2 = 2.4$ Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3): δ 151.4, 147.6, 143.9, 135.2, 132.9, 132.8, 132.4, 132.3, 131.0, 130.4, 129.4, 126.1, 121.7, 119.8, 114.6. MS: m/z calculated for $\text{C}_{15}\text{H}_8\text{N}_3\text{Cl}$ 265.0, found $[\text{M}+\text{H}]^+$ 266.1.

5d

5e

8,10-Dibromoquinolino[2,3-*c*]cinnoline (5d) and 10-Dibromoquinolino[2,3-*c*]cinnoline (5e): Zinc dust (0.60 g, 9.0 mmol) is added to a solution of 8,10-dibromoquinolino[2,3-*c*]cinnoline 5-oxide **4d** (0.22 g, 0.5 mmol) in hot glacial acetic acid (20.00 mL). The reaction mixture which turns red in color is heated to reflux for 20 minutes. Upon cooling, the insoluble material is filtered and washed with hot acetic acid. The filtrate is neutralized with aqueous KOH solution. The mixture is extracted with dichloromethane (25.00 mL $\times$ 3) and is washed with water (25.00 mL $\times$ 3). The organic layer is dried over anhydrous MgSO₄ and is evaporated *in vacuo*. The crude solid is purified using column chromatography (dichloromethane) to afford **5d** as a yellow solid (0.08 g, 38%). m.p. >300°C. ¹H NMR (300 MHz, CDCl₃): δ 9.36 (s, 1H), 8.89-8.86 (m, 1H), 8.65-8.62 (m, 1H), 8.35 (d, *J* = 2.1 Hz, 1H), 8.27 (d, *J* = 1.8 Hz, 1H), 8.01-7.98 (m, 2H). MS: *m/z* calculated for C₁₅H₇N₃Br₂ 388.9, found [M+H]⁺ 389.5 . And **5e** as well (0.10 g, 59%). m.p. >300°C. ¹H NMR (300 MHz, CDCl₃): δ 9.40 (s, 1H), 8.93-8.89 (m, 1H), 8.72-8.68 (m, 1H), 8.44 (d, *J* = 9.3 Hz, 1H), 8.37 (dt, *J*₁ = 8.4 Hz, *J*₂ = 2.1 Hz, 1H), 8.07-8.00 (m, 3H). MS: *m/z* calculated for C₁₅H₁₂N₃Br 309.0-311.03, found [M+H]⁺ 310.1-312.1).

5f

9,10-Dimethoxyquinolino[2,3-*c*]cinnoline (5f): Zinc dust (0.76 g, 11.0 mmol) is added to a solution of 9,10-dimethoxyquinolino[2,3-*c*]cinnoline 5-oxide **4e** (0.20 g, 0.7 mmol) in hot glacial acetic acid (10.00 mL). The reaction mixture is heated to reflux for 10 minutes. Upon cooling, the insoluble material is filtered, and the filtrate is neutralized with aqueous KOH solution. The mixture was extracted with dichloromethane (25.00 mL $\times$ 3) and was washed with water (25.00 mL $\times$ 3). The organic layer was dried over anhydrous MgSO₄, and was evaporated *in vacuo* to afford the title product as a yellow solid (0.10 g, 53 %). Decomp. 267-269°C. ¹H NMR (300 MHz, CDCl₃): δ 9.10 (s, 1H), 8.77-8.74 (m, 1H), 8.56-8.53 (m, 1H), 7.89-7.83 (m, 2H), 7.66 (s, 1H), 7.20 (s, 1H), 4.07 (s, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 154.0, 151.5, 150.2, 146.5, 142.9, 131.0, 130.8, 128.1, 127.1, 125.3, 120.2, 119.6, 111.6, 106.4, 102.5, 55.5, 55.4. MS: m/z calculated for C₁₇H₁₃N₃O₂ 292.3, found [M]⁺ 292.1.

6a

3-(2-Aminophenyl)quinolin-2-amine (6a): Zinc dust (2.21 g, 34.0 mmol) is added to a solution of 3-(2-nitrophenyl)quinolin-2-amine **3a** (0.50 g, 1.9 mmol) in hot glacial acetic acid (5.00 mL). The reaction mixture is heated to reflux for 10 minutes. Upon cooling, the insoluble material is filtered, and the filtrate is neutralized with aqueous KOH solution. The mixture is extracted with dichloromethane (25.00 mL $\times$ 3) and is washed with water (25.00 mL $\times$ 3). The organic layer is dried over anhydrous MgSO₄ and is evaporated *in vacuo* to afford the title product as a yellow solid (0.20 g, 45 %). m.p. 133-135°C. ¹H NMR (300 MHz, CDCl₃): δ 7.85 (s, 1H), 7.72-7.56 (m, 3H), 7.28-7.24 (m, 1H), 7.15 (dd, $J_1 = 7.5$ Hz, $J_2 = 1.5$ Hz, 1H), 6.88 (d, $J = 7.5$ Hz, 1H), 6.82 (d, $J = 8.1$ Hz, 1H), 4.98 (b, 2H), 3.72 (b, 2H). ¹³C NMR (75 MHz, CDCl₃): δ 155.4, 147.4, 144.2, 138.6, 131.0, 129.8, 129.7, 127.5, 125.6, 124.0, 122.8, 122.1, 122.0, 119.1, 115.9. IR (KBr, cm⁻¹): $\nu_{\max}$ 3443-3415 (s, N-H), 3358-3330 (s, N-H). HRMS: m/z calculated mass for C₁₅H₁₃N₃ 235.11095, found [M+H]⁺ 236.07181.

6b

3-(2-Aminophenyl)-6-chloroquinolin-2-amine (6b): Zinc dust (2.21 g, 34.0 mmol) is added to a solution of 6-chloro-3-(2-nitrophenyl)quinolin-2-amine **3c** (0.50 g, 1.9 mmol) in hot glacial acetic acid (5.00 mL). The reaction mixture is heated to reflux for 10 minutes. Upon cooling, the insoluble material is filtered, and the filtrate is neutralized with aqueous KOH solution. The mixture is extracted with dichloromethane (25.00 mL $\times$ 3) and is washed with water (25.00 mL $\times$ 3). The organic layer is dried

over anhydrous MgSO_4 and is evaporated *in vacuo*. The crude solid is purified using column chromatography (hexane: ethylacetate) to afford the title product as a yellow solid (0.20 g, 45 %) m.p. 128-130 °C. ^1H NMR (300 MHz, CDCl_3): δ 7.67 (s, 1H), 7.54-7.50 (m, 2H), 7.42 (dd, $J_1 = 9$ Hz, $J_2 = 2.4$ Hz, 1H), 7.22 (dt, $J_1 = 7.8$ Hz, $J_2 = 1.5$ Hz, 1H), 7.09 (dd, $J_1 = 7.5$ Hz, $J_2 = 1.2$ Hz, 1H), 6.83 (dd, $J_1 = 7.5$ Hz, $J_2 = 0.9$ Hz, 1H), 6.81-6.77 (m, 1H), 5.26 (b, 2H), 3.70 (b, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 155.6, 145.9, 144.1, 137.5, 130.9, 130.4, 130.0, 127.9, 127.2, 126.2, 124.6, 123.0, 121.6, 119.1, 116.0. IR (KBr, cm^{-1}): ν_{max} 3397-3291 (s, N-H), 3119-3015 (s, N-H).. GC-MS (CH_3CN): m/z calculated for $\text{C}_{15}\text{H}_{12}\text{N}_3\text{Cl}$ 269.1, found $[\text{M}]^+$ 269.0, $t_{\text{R}} = 25.36$ min.

6c

3-(2-Aminophenyl)-6,8-dibromoquinolin-2-amine (6c): (A) Zinc dust (0.04 g, 0.6 mmol) is added to a solution of 6,8-dibromo-3-(2-nitrophenyl)quinolin-2-amine **3d** (0.25 g, 0.6 mmol) in hot glacial acetic acid (7.00 mL). The reaction mixture is stirred at room temperature overnight. The insoluble material is filtered and the filtrate is neutralized with aqueous KOH solution. The crude solid obtained is filtered and purified using column chromatography (Hexane: Ethyl acetate) to afford the title product as a yellow solid (0.10 g, 43%). (B) a mixture of 6,8-dibromo-3-(2-nitrophenyl)quinolin-2-amine **3d** (0.22 g, 0.5 mmol) and 10% Pd/C (60 mg) in ethanol (20mL) was hydrogenated at 40 psi overnight. The resulting suspension was filtered and

washed with ethanol to afford the title product as a yellow solid (0.11g, 55%). m.p. 201-203°C. ^1H NMR (300 MHz, CDCl_3): δ 7.96 (d, $J = 2.1$ Hz, 1H), 7.73 (s, 1H), 7.71 (d, $J = 2.4$ Hz, 1H), 7.29-7.24 (m, 1H), 7.11 (dd, $J_1 = 7.8$ Hz, $J_2 = 1.5$ Hz, 1H), 6.87 (dt, $J_1 = 7.5$ Hz, $J_2 = 1.2$ Hz, 1H), 6.83 (dd, $J_1 = 8.1$ Hz, $J_2 = 0.9$ Hz, 1H), 5.19 (b, 2H), 3.77 (b, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 156.4, 144.1, 143.5, 137.9, 135.5, 130.9, 130.2, 129.3, 125.6, 123.8, 121.4, 120.9, 119.1, 116.1, 114.6. IR (KBr, cm^{-1}): ν_{max} 3458-3419 (s, N-H), 3341-3203 (s, N-H). GC-MS (CH_3CN): m/z calculated for $\text{C}_{15}\text{H}_{11}\text{N}_3\text{Br}_2$ 392.9, found $[\text{M}-\text{H}]^+$ 391.9.

6d

3-(2-Aminophenyl)-6-bromoquinolin-2-amine (6d) : Zinc dust (0.70 g, 10.8 mmol) is added to a solution of 6,8-dibromo-3-(2-nitrophenyl)quinolin-2-amine **3d** (0.25 g, 0.6 mmol) in hot glacial acetic acid (10.00 mL). The reaction mixture is heated to reflux for 10 minutes. Upon cooling, the insoluble material is filtered, and the filtrate is neutralized with aqueous KOH solution. The mixture is extracted with dichloromethane (25.00 mL $\times$ 3) and is washed with water (25.00 mL $\times$ 3). The organic layer is dried over anhydrous MgSO_4 and is evaporated *in vacuo*. The crude solid is purified using column chromatography (hexane: ethylacetate) to afford the title product as a yellow solid. m.p. 186-188°C. ^1H NMR (300 MHz, CDCl_3): δ 7.19 (s, 1H), 7.18 (s, 1H), 7.08-6.98 (m, 2H), 6.69 (dt, $J_1 = 8.4$ Hz, $J_2 = 1.5$ Hz, 1H), 6.55 (dd, $J_1 = 7.5$ Hz, J_2

= 1.5 Hz, 1H), 6.33-6.25 (m, 2H), 4.95 (b, 2H), 3.29 (b, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 155.8, 145.1, 144.2, 137.9, 133.2, 130.9, 130.1, 129.5, 126.4, 124.9, 123.3, 121.0, 119.1, 116.1, 115.8. IR (KBr, cm^{-1}): ν_{max} 3389-3298 (s, N-H), 3121-3064 (s, N-H). MS: m/z calculated for $\text{C}_{15}\text{H}_{12}\text{N}_3\text{Br}$ 314.1, found $[\text{M}]^+$ 314.0.

6e

3-(2-Amino-5-methylphenyl)-quinolin-2-amine (6e): Zinc dust (0.13 g, 2.0 mmol) is added to a solution of 3-(5-methyl-2-nitrophenyl)quinolin-2-amine **3b** (0.03 g, 0.1 mmol) in hot glacial acetic acid (5.00 mL). The reaction mixture is heated to reflux for 10 minutes. Upon cooling, the insoluble material is filtered, and the filtrate is neutralized with aqueous KOH solution. The mixture is extracted with dichloromethane (25.00 mL $\times$ 3) and is washed with water (25.00 mL $\times$ 3). The organic layer is dried over anhydrous MgSO_4 and is evaporated *in vacuo* to afford the title product as a yellow solid (0.20 g, 45 %). m.p. 175-177°C. ^1H NMR (300 MHz, CDCl_3): δ 7.75 (s, 1H), 7.62 (d, J = 8.4 Hz, 1H) 7.55 (d, J = 8.1 Hz, 1H), 7.49 (dt, J_1 = 6.9 Hz, J_2 = 1.2 Hz, 1H), 7.22-7.17 (m, 1H), 6.97 (dd, J_1 = 8.1 Hz, J_2 = 2.1 Hz, 1H), 6.89 (d, J = 1.5 Hz, 1H), 6.66 (d, J = 8.1 Hz, 1H), 4.95 (b, 2H), 3.51 (b, 2H), 2.21 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 154.4, 146.2, 140.6, 137.5, 130.3, 129.3, 128.8, 127.3, 126.5, 124.5, 123.0, 121.8, 121.2, 121.1, 115.1, 19.4. IR (KBr, cm^{-1}): ν_{max} 3461-3443 (s, N-H), 3361-3343 (s, N-H). MS: m/z calculated for $\text{C}_{16}\text{H}_{15}\text{N}_3$ 250.3, found $[\text{M}]^+$ 250.2.

7a

6H-Indolo[2,3-*b*]quinoline (7a): In a water/ice bath, conc. HCl (2.00 mL) is added drop wise to a solution of 3-(2-Aminophenyl)quinolin-2-amine **6a** (0.60 g, 2.5 mmol), NaNO₂ (0.22 g, 3.2 mmol), in H₂O (1.00 mL) and methanol (5.00 mL). Upon stirring for 2 hours at room temperature, the mixture is made basic using aqueous KOH solution. The crude solid obtained is filtered and purified using column chromatography (hexanes: ethyl acetate; 4:1) to afford the title product as a yellow solid (0.30g, 54%). m.p. >300°C. ¹H NMR (300 MHz, DMSO-*d*₆): δ 11.70 (s, 1H), 9.06 (s, 1H), 8.27 (d, *J* = 7.5 Hz, 1H), 8.11 (d, *J* = 7.2, 1H), 7.98 (d, *J* = 8.7 Hz, 1H), 7.75-7.69 (m, 1H), 7.52-7.46 (m, 3H), 7.29-7.24 (m, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 162.6, 155.9, 146.0, 129.6, 129.3, 129.1, 128.5, 128.2, 126.1, 125.1, 123.5, 122.2, 121.7, 117.7, 112.1. IR (KBr, cm⁻¹): ν_{max} 3141, 1615, 1462, 1406, 1231. MS: *m/z* calculated for C₁₅H₁₀N₂ 218.3, found [M+H]⁺ 219.5.

7b

2-Chloro-6H-indolo[2,3-*b*]quinoline (7b): In a water/ice bath, conc. HCl (2.00 mL) is added dropwise to a solution of 3-(2-aminophenyl)-6-chloroquinolin-2-

amine **6b** (0.20 g, 0.7 mmol), NaNO₂ (0.08 g, 1.0 mmol), in H₂O (1.00 mL) and methanol (5.00 mL). Upon stirring for 2 hours at room temperature, the mixture is made basic using aqueous KOH solution. The crude solid obtained is filtered and is purified using column chromatography (hexanes: ethyl acetate; 4:1) to afford the title product as a white solid (0.10 g, 55%). m.p. >300°C. ¹H NMR (300 MHz, DMSO-*d*₆): δ 11.74 (s, 1H), 9.01 (s, 1H), 8.25 (d, *J* = 7.5 Hz, 1H), 8.20 (d, *J* = 2.4 Hz, 1H), 8.14 (s, 1H), 7.97 (d, *J* = 9.3 Hz, 1H), 7.70 (dd, *J*₁ = 9 Hz, *J*₂ = 2.4 Hz, 1H), 7.56-7.51 (m, 2H). ¹H NMR (300 MHz, CDCl₃): 8.16 (s, 1H), 7.83 (s, 1H) 7.80 (d, *J* = 1.8, 1H), 7.64-7.55 (m, 3H), 5.63 (b, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 155.3, 146.2, 145.1, 135.1, 131.7, 131.6, 130.6, 130.0, 129.5, 129.4, 129.3, 129.2, 127.9, 126.4, 125.3. IR (KBr, cm⁻¹): ν_{max} 3122, 1658, 1621, 1488, 1450, 1074. MS: *m/z* calculated for C₁₅H₉N₂Cl 252.3, found [M-H]⁻ 251.3.

7c

2,4-dibromo-6H-indolo[2,3-*b*]quinoline (7c): In a water/ice bath, conc. HCl (2.00 mL) is added dropwise to a solution of 6,8-Dibromo-3-(2-nitrophenyl)quinolin-2-amine **6c** (0.20 g, 0.5 mmol), NaNO₂ (0.05 g, 0.7 mmol), in H₂O (1.00 mL) and methanol (5.00 mL). Upon stirring for 2 hours at room temperature, the mixture is made basic using aqueous KOH solution. The crude solid obtained is filtered and is purified using column chromatography (hexanes: ethyl acetate; 4:1) to afford the title product as

a yellow solid (0.15 g, 79%). m.p. >300°C. ^1H NMR (300 MHz, CDCl_3): δ 10.70 (s, 1H), 8.35 (s, 1H), 8.08 (d, $J = 8.4$ Hz, 1H), 8.07 (d, $J = 4.8$ Hz, 1H), 7.99 (d, $J = 1.2$ Hz, 1H), 7.84 (d, $J = 3$ Hz, 1H), 7.69 (t, 1H), 7.45 (t, 1H). ^{13}C NMR (75 MHz, CDCl_3): δ 144.2, 142.2, 136.7, 135.6, 132.8, 129.7, 129.6, 126.2, 125.5, 121.8, 121.7, 121.4, 119.8, 118.6, 111.7. MS: m/z calculated for $\text{C}_{15}\text{H}_8\text{N}_2\text{Br}_2$ 375.9, found $[\text{M}+\text{H}]^+$ 377.0.

8a

Neocryptolepine (8a): title product is prepared according to a literature procedure.⁶⁴ Dimethyl sulfate (13.00 mg, 0.1mmol) is added to a solution of 6*H*-Indolo[2,3-*b*]quinoline **7a** (23.00 mg, 0.1mmol) in acetonitrile (5.00mL) and refluxed for 6 hours. The organic layer is then washed with an aqueous solution of K_2CO_3 (5.00 mL $\times$ 3), then dried over anhydrous MgSO_4 and is evaporated *in vacuo*. The crude solid is purified by chromatography (16.8 mg, 70%). m.p. 103-105°C (Lit. 102°C).³² ^1H NMR (300 MHz, CDCl_3): δ 8.48 (s, 1H), 8.15 (dd, $J_1 = 8.1$ Hz, $J_2 = 1.2$ Hz, 1H), 7.93 (dd, $J_1 = 7.8$ Hz, $J_2 = 1.5$ Hz, 1H), 7.79-7.73 (m, 2H), 7.70 (dd, $J_1 = 7.8$ Hz, $J_2 = 0.9$ Hz, 1H), 7.52 (dd, $J_1 = 7.8$ Hz, $J_2 = 0.9$ Hz, 1H), 7.40 (dd, $J_1 = 7.8$ Hz, $J_2 = 0.9$ Hz, 1H), 7.22 (dd, $J_1 = 7.5$ Hz, $J_2 = 0.9$ Hz, 1H), 4.32 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ 157.8, 155.6, 137.0, 130.2, 129.8, 129.3, 128.2, 127.9, 124.0, 121.8, 120.9, 120.8, 119.9, 117.6, 114.0, 32.2. MS: m/z calculated for $\text{C}_{16}\text{H}_{12}\text{N}_2$ 232.1, found $[\text{M}+\text{H}]^+$ 233.2.

2-Chloroneocryptolepine (8b): title product is prepared according to a literature procedure.⁶⁴ Dimethyl sulfate (10.00 mg, 0.1mmol) is added to a solution of 2-Chloro-6*H*-Indolo[2,3-*b*]quinoline **7b** (25.00 mg, 0.1mmol) in acetonitrile (10.00mL) and refluxed for 6 hours. The organic layer is then washed with an aqueous solution of K₂CO₃ (5.00 mL × 3), then dried over anhydrous MgSO₄ and is evaporated *in vacuo*. The crude solid is purified by chromatography (19 mg, 73%). m.p. 168-170°C (Lit. 167.4°C).³² ¹H NMR (300 MHz, CDCl₃): δ 8.40 (s, 1H), 8.15 (dd, *J*₁ = 9 Hz, *J*₂ = 2.4 Hz, 1H), 7.90 (d, *J* = 1.2 Hz, 1H), 7.73 (dd, *J*₁ = 7.5 Hz, *J*₂ = 0.9 Hz, 1H), 7.67-7.66 (m, 2H), 7.48 (dd, *J*₁ = 7.5 Hz, *J*₂ = 1.2 Hz, 1H), 7.18 (dd, *J*₁ = 7.5 Hz, *J*₂ = 0.9 Hz, 1H), 4.32 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 156.6, 155.4, 135.2, 130.7, 129.9, 129.0, 128.9, 127.2, 126.4, 123.8, 121.7, 121.2, 119.8, 117.8, 115.6, 33.1. MS: *m/z* calculated for C₁₆H₁₂N₂ 266.1, found [M+H]⁺ 267.1.

SPECTROSCOPIC DATA

B. ^1H NMR Spectra

Figure 1 ^1H NMR for 2-aminobenzaldehyde **1a** in CDCl₃.

Figure 2: ¹H NMR for 2-amino-5-chlorobenzaldehyde 1b in CDCl₃

Figure 3: ¹H NMR for 2-amino-3,5-dibromobenzaldehyde **1c** in CDCl₃.

Figure 4: ^1H NMR for 2-amino-4,5-dimethoxybenzaldehyde 1d in CDCl_3 .

Figure 5: ¹H NMR for 3-(2-nitrophenyl)quinolin-2-amine 3a in CDCl₃.

Figure 6: ¹H NMR for 3-(2-nitrophenyl)quinolin-2-amine 3a in DMSO-*d*₆.

Figure 7: ¹H NMR for 3-(5-methyl-2-nitrophenyl)quinolin-2-amine 3b in CDCl₃.

Figure 8: ¹H NMR for 6-chloro-3-(2-nitrophenyl)quinolin-2-amine 3c in CDCl₃.

Figure 9: ^1H NMR for 6,8-dibromo-3-(2-nitrophenyl)quinolin-2-amine 3d in CDCl_3 .

Figure 10: ¹H NMR for 6,7-dimethoxy-3-(2-nitrophenyl)quinolin-2-amine 3e in CDCl₃.

Figure 11: ¹H NMR for quinolino[2,3-c]cinnoline 5-oxide **4a** in CDCl₃.

Figure 12: ¹H NMR for 2-methylquinolino[2,3-c]cinnoline 5-oxide 4b in CDCl₃.

Figure 13: ¹H NMR for 10-chloroquinolino[2,3-c]cinnoline 5-oxide **4c** in CDCl₃-Trifluoroacetic acid.

Figure 14: ¹H NMR for 8,10-dibromoquinolino[2,3-*c*]cinnoline 5-oxide 4d in DMSO-*d*₆, 90 °C.

Figure 15: ¹H NMR for 8,10-dibromoquinolino[2,3-*c*]cinnoline 5-oxide 4d in CDCl₃-Trifluoroacetic acid

Figure 16: ¹H NMR for 9,10-dimethoxyquinolino[2,3-c]cinnoline 5-oxide **4e** in CDCl₃.

Figure 17: ¹H NMR for quinolino[2,3-*c*]cinnoline 5a in CDCl₃.

Figure 18: ¹H NMR for 2-methylquinolino[2,3-c]cinnoline 5b in CDCl₃.

Figure 19: ¹H NMR for 10-chloroquinolino[2,3-c]cinnoline **5c** in CDCl₃.

Figure 21: ¹H NMR for 10-bromoquinolino[2,3-*c*]cinnoline 5e in CDCl₃.

Figure 22: ¹H NMR for 9,10-dimethoxyquinolino[2,3-*c*]cinnoline 5f in CDCl₃.

Figure 23: ¹H NMR for 3-(2-aminophenyl)quinolin-2-amine 6a in CDCl₃

Figure 24: ^1H NMR for 3-((2-aminophenyl)quinoline-2-amine **6a** in $\text{CDCl}_3 + \text{D}_2\text{O}$

Figure 25: ¹H NMR for 3-(2-aminophenyl)-6-chloroquinolin-2-amine 6b in CDCl₃.

Figure 26: ¹H NMR for 3-(2-aminophenyl)-6,8-dibromoquinolin-2-amine 6c in CDCl₃.

Figure 27: ^1H NMR for 3-(2-aminophenyl)-8-dibromoquinolin-2-amine 6d in CDCl_3 .

Figure 28: ¹H NMR for 3-(2-Amino-5-methyl-phenyl)-quinolin-2-amine 6e in CDCl₃

Figure 29: ^1H NMR for 6*H*-indolo[2,3-*b*]quinoline 7a in $\text{DMSO-}d_6$.

Figure 30: ¹H NMR for 2-Chloro-6*H*-indolo[2,3-*b*]quinoline 7b in CDCl₃.

Figure 31: ¹H NMR for 2-Chloro-6H-indolo[2,3-b]quinoline 7b in DMSO.

Figure 32: ¹H NMR for 2,4-Dibromo-6H-indolo[2,3-b]quinoline **7c** in CDCl₃.

Figure 33: ¹H NMR for Neocryptolepine 8a in CDCl₃.

Figure 34: ¹H NMR for 2-Chloroneocryptolepine 8b in CDCl₃.

C. ^{13}C NMR Spectra

Figure 35: ^{13}C NMR for 2-aminobenzaldehyde 1a in CDCl_3 .

Figure 36: ¹³C NMR for 2-amino-5-chlorobenzaldehyde **1b** in CDCl₃.

Figure 37: ¹³C NMR for 2-amino-3,5-dibromobenzaldehyde **1c** in CDCl₃.

Figure 38: ¹³C NMR for 2-amino-4,5-dimethoxybenzaldehyde **1d** in CDCl₃.

Figure 39: ¹³C NMR for 3-(2-nitrophenyl)quinolin-2-amine 3a in CDCl₃.

Figure 40: ¹³C NMR for 3-(5-methyl-2-nitrophenyl)quinolin-2-amine 3b in CDCl₃.

Figure 41: ¹³C NMR for 6-chloro-3-(2-nitrophenyl)quinolin-2-amine **3c** in CDCl₃.

Figure 42: ¹³C NMR for 6,8-dibromo-3-(2-nitrophenyl)quinolin-2-amine 3d in CDCl₃.

Figure 43: ¹³C NMR for 6,7-dimethoxy-3-(2-nitrophenyl)quinolin-2-amine **3e** in CDCl₃.

Figure 44: ¹³C NMR for quinolino[2,3-*c*]cinoline 5-oxide 4a in CDCl₃.

Figure 45: ¹³C NMR for 2-methylquinolino[2,3-c]cinnoline 5-oxide **4b** in CDCl₃.

Figure 46: ^{13}C NMR for 10-chloroquinolino[2,3-*c*]cinnoline 5-oxide 4c in CDCl_3 + trifluoroacetic acid.

Figure 47: ¹³C NMR for 8,10-dibromoquinolino[2,3-*c*]cinnoline 5-oxide 4d in CDCl₃.

Figure 48: ¹³C NMR for 9,10-dimethoxyquinolino[2,3-*c*]cinnoline 5-oxide 4e in CDCl₃.

Figure 49: ¹³C NMR for quinolino[2,3-*c*]cinnoline 5a in CDCl₃.

Figure 50: ¹³C NMR for 2-methylquinolino[2,3-c]cinnoline 5b in CDCl₃.

Figure S1: ¹³C NMR for 10-chloroquinolino[2,3-c]cinnoline 5c in CDCl₃.

Figure S2: ¹³C NMR for 9,10-dimethoxyquinolino[2,3-*c*]cinnoline **5f** in CDCl₃.

155.43
 147.36
 144.16
 138.60
 130.99
 129.85
 129.75
 127.52
 125.59
 123.99
 122.83
 122.10
 121.98
 119.05
 115.91

Figure S3: ^{13}C NMR for 3-(2-aminophenyl)quinolin-2-amine 6a in CDCl_3 .

Figure 54: ¹³C NMR for 3-(2-aminophenyl)-6-chloroquinolin-2-amine 6b in CDCl₃.

Figure S5: ¹³C NMR for 3-(2-aminophenyl)-6,8-dibromoquinolin-2-amine **6c** in CDCl₃.

Figure S6: ¹³C NMR for 3-(2-aminophenyl)- 8-bromoquinolin-2-amine 6d in CDCl₃.

Figure S7: ¹³C NMR for 3-(2-Amino-5-methyl-phenyl)-quinolin-2-amine **6e** in CDCl₃.

Figure 59: ¹³C NMR for 6H-indolo[2,3-b]quinoline **7a** in CDCl₃.

Figure 60: ¹³C NMR for 2-Chloro-6*H*-indolo[2,3-*b*]quinoline 7b in CDCl₃.

Figure 61: ¹³C NMR for 2,4-Dibromo-6*H*-indolo[2,3-*b*]quinoline **7c** in CDCl₃.

Figure 62: ¹³C NMR for Neocryptolepine 8a in CDCl₃.

Figure 63: ¹³C NMR for 2-Chloroneocryptolepine 8b in CDCl₃.

D. DEPT 135 ^{13}C NMR

Figure 64: DEPT 135 ^{13}C NMR for 3-(2-nitrophenyl)quinolin-2-amine **3a** in CDCl_3 .

Figure 65: DEPT 135 ^{13}C NMR for quinolino[2,3-c]cinnoline 5-oxide **4a** in CDCl_3 .

137.89
133.20
130.89
130.12
129.50
126.45
119.14
116.09

6e

Figure 66: DEPT ¹³⁵ ¹³C NMR for 3-(2-Aminophenyl)-6-bromoquinolin-2-amine **6d** in CDCl₃.

E. Mass Spectra

3a

Figure 67: HR-MS for 3-(2-Nitrophenyl)quinolin-2-amine 3a

3b

Figure 68: HR-MS for 3-(5-methyl-2-nitrophenyl)quinolin-2-amine 3b.

RT: 0.00 - 30.99

05-07-2009-RMB-29 #1167 RT: 26.15 AV: 1 NL: 3.27E6
T: + e Full ms [50.00-600.00]

Figure 69: GC-MS for 6-chloro-3-(2-nitrophenyl)quinolin-2-amine **3c**.

3c

RT: 0.00 - 46.01

07-21-2009-RMB-26 #1498 RT: 32.00 AV: 1 NL: 2.58E3
T: + c Full ms [50.00-600.00]

Figure 70: GC-MS for 6,8-Dibromo-3-(2-nitrophenyl)quinolin-2-amine **3d**.

RT: 0.00 - 31.01

07-20-2009-RMB-63 #1325 RT: 28.77 AV: 1 NL: 2.52E3
T: + e Full ms [50.00-600.00]

Figure 71: GC-MS for 6,7-Dimethoxy-3-(2-nitrophenyl)quinolin-2-amine **3e**.

3e

4a

Figure 72: HR-MS for Quinolino[2,3-*c*]cinnoline 5-oxide 4a.

4b

Figure 73: HR-MS for 2-Methylquinolino[2,3-*c*]cinnoline 5-oxide 4b.

4c

Figure 74: MS for 10-Chloroquinolino[2,3-*c*]cinnoline 5-oxide **4c**.

4d

Figure 75: MS for 8,10-Dibromoquinolino[2,3-*c*]cinnoline 5-oxide **4d**.

Figure 76: MS for 9,10-Dimethoxyquinolino[2,3-*c*]cinnoline 5-oxide **4e**.

Figure 77: HR-MS for Quinolino[2,3-*c*]cinnoline **5a**.

5b

Figure 78: MS for 2-Methylquinolino[2,3-*c*]cinnoline 5b.

5c

Figure 79: MS for 10-Chloroquinolino[2,3-*c*]cinnoline 5c.

Figure 80: MS for 8,10-Dibromoquinolino[2,3-*c*]cinnoline **5d**.

Figure 81: MS for 10-Bromoquinolino[2,3-*c*]cinnoline **5e**.

5f

Figure 82: MS for 9,10-Dimethoxyquinolino[2,3-c]cinnoline 5f.

6a

Figure 83: HR-MS for 3-(2-Aminophenyl)quinolin-2-amine 6a.

RT: 0.00 - 31.01

07-20-2009-RMB-50 #1142 RT: 25.34 AV: 1 NL: 1.82E5
T: + e Full ms [50.00-800.00]

Figure 84: GC-MS for 3-(2-aminophenyl)-6-chloroquinolin-2-amine **6b**.

RT: 0.00 - 31.01

08-06-2009--RMB-58 #1406 RT: 30.28 AV: 1 NL: 5.82E3
T: + c Full ms [50.00-600.00]

Figure 85: GC-MS for 3-(2-aminophenyl)-6,8-dibromoquinolin-2-amine **6c**.

6c

6d

Figure 86: MS for 3-(2-aminophenyl)-6-bromoquinolin-2-amine 6d.

6e

Figure 87: MS for 3-(2-Amino-5-methylphenyl)-quinolin-2-amine 6e.

Figure 88: MS for 6*H*-Indolo[2,3-*b*]quinoline 7a

Figure 89: MS for 2-Chloro-6*H*-indolo[2,3-*b*]quinoline 7b

Figure 90: MS for 2,4-Dibromo-6H-indolo[2,3-b]quinoline 7c

Figure 91: MS for Neocryptolepine 8a.

Figure 92: MS for 2-Chloroneocryptolepine 8b.

F. Infrared Spectra

Figure 93: IR for 3-(2-nitrophenyl)quinolin-2-amine 3a

Figure 94: IR for 3-(5-Methyl-2-nitrophenyl)quinolin-2-amine **3b**

Figure 95: IR for 6-Chloro-3-(2-nitrophenyl)quinolin-2-amine **3c**

Figure 96: IR for 6,8-Dibromo-3-(2-nitrophenyl)quinolin-2-amine **3d**

Figure 97: IR for Quinolono[2,3-c]cinnoline 5-oxide **4a**

Figure 98: IR for 2-Methylquinolino[2,3-c]cinnoline 5-oxide **4b**

Figure 99: IR for 10-Chloroquinolino[2,3-c]cinnoline 5-oxide **4c**

Figure 100: IR for 8,10-Dibromoquinolino[2,3-c]cinnoline 5-oxide **4d**

Figure 101: IR for 9,10-Dimethoxyquinolino[2,3-*c*]cinnoline 5-oxide **4e**

Figure 102: IR for Quinolino[2,3-*c*]cinnoline 5a

Figure 103: IR for 2-Methylquinolino[2,3-c]cinnoline 5b

Figure 104: IR for 10-Chloroquinolino[2,3-c]cinnoline 5c

Figure 105: IR for 8,10-Dibromoquinolino[2,3-c]cinnoline 5d

Figure 106: IR for 10-Bromoquinolino[2,3-*c*]cinnoline **5e**

Figure 107: IR for 9,10-Dimethoxyquinolino[2,3-*c*]cinnoline **5f**

Figure 108: IR for 3-(2-Aminophenyl)quinolin-2-amine **6a**

Figure 109: IR for 3-(2-Aminophenyl)-6-chloroquinolin-2-amine 6b

Figure 110: IR for 3-(2-Aminophenyl)-6,8-dibromoquinolin-2-amine **6c**

Figure 111: IR for 3-(2-Aminophenyl)-6-bromoquinolin-2-amine **6d**

Figure 112: IR for 3-(2-Amino-5-methyl-phenyl)-quinolin-2-ylamine **6e**

Figure 113: IR for 6H-indolo[2,3-b]quinoline 7a.

Figure 114: IR for 2-Chloro-6*H*-indolo[2,3-*b*]quinoline 7b.

G. X-Ray Crystallography

6,8-Dibromo-3-(2-nitrophenyl)quinolin-2-amine **3d**

Experimental

A concentrated solution of **3d** was placed into a 5mm OD tube and layered with hot methanol, then sealed and left to slowly cool down and evaporate. After few days, crystals of a suitable size and quality were formed.

A light yellow block with approximate orthogonal dimensions 0.28 x 0.10 x 0.07mm³ was placed and optically centered on the Bruker APEXII⁶⁵ CCD diffractometer at −183°C. The initial unit cell was indexed using a least-squares analysis of a random set of reflections collected from three series of 0.3° wide ω -scans, 10 seconds per frame, and 30 frames per series that were well distributed in reciprocal space. Four ω -scan data frame series were collected [MoK α] with 0.3° wide scans, 30 seconds per frame at varying ϕ angles.

Structural determination and Refinement:

The crystal to detector distance was 5.23cm, thus providing a complete sphere of data to $2\theta_{\max}=61.05^\circ$. A total of 19586 reflections were collected and corrected for Lorentz and polarization effects and absorption using face indexing and Blessing's

method as incorporated into the program SADABS^{66,67,70} with 4481 unique. All crystallographic calculations were performed on a Personal computer (PC) with a Pentium 3.20GHz processor and 4GB of extended memory. The SHELXTL⁶⁸ program package was implemented to determine the probable space group and set up the initial files. System symmetry, systematic absences and intensity statistics indicated the centrosymmetric monoclinic space group P2₁/c (no. 14). The structure was determined by direct methods with the successful location of nearly all of the non-hydrogen atoms of the molecule using the program XS^{69,70}. The structure was refined with XL^{69,70}. The 19586 data collected were merged based upon identical indices yielding 15752 data [R(int)=0.0175] that were further truncated to 2 θ_{max} =55.0° and merged during least-squares refinement to 12165 unique data [R(int)=0.0250]. A single least-squares difference-Fourier cycle was required to locate the remaining hydrogen atoms. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were allowed to refine freely (xyzU) during the final convergence stage. The final structure was refined to convergence with R(F)=2.42%, wR(F²)=4.33%, GOF=1.052 for all 3288 unique reflections [R(F)=1.86%, wR(F²)=4.22% for those 2910 data with Fo > 4 σ (Fo)]. The final difference-Fourier map was featureless indicating that the structure is both correct and complete. An empirical correction for extinction was also attempted but found to be negative and therefore not applied.

Crystal data and structure refinement

Empirical formula

C₁₅ H₉ Br₂ N₃ O₂

Formula weight	423.07	
Temperature	90(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2 ₁ /c	
Unit cell dimensions	a = 4.8819(2) Å	α = 90°.
	b = 16.5176(6) Å	β =
	94.664(1)°.	
	c = 17.7871(6) Å	γ = 90°.
Volume	1429.55(9) Å ³	
Z	4	
Density (calculated)	1.966 Mg/m ³	
Absorption coefficient	5.681 mm ⁻¹	
F(000)	824	
Crystal size	0.28 x 0.10 x 0.07 mm ³	
Crystal color and habit	Yellow Plate	
Diffractometer	Bruker APEX-II CCD	
Theta range for data collection	2.47 to 27.50°.	
Index ranges	-6 ≤ h ≤ 6	
	-21 ≤ k ≤ 21	
	-23 ≤ l ≤ 23	
Reflections collected	12165	
Independent reflections	3288 [R(int) = 0.0250]	
Observed reflections (I > 2σ(I))	2910	
Completeness to theta = 27.50°	99.9 %	

Absorption correction	Numerical
Max. and min. transmission	0.6919 and 0.2944
Solution method	SHELXS-97 (Sheldrick, 2008)
Refinement method	SHELXL-97 (Sheldrick, 2008) Full-matrix least-squares on F ²
Data / restraints / parameters	3288 / 0 / 235
Goodness-of-fit on F ²	1.052
Final R indices [I>2sigma(I)]	R1 = 0.0186, wR2 = 0.0422
R indices (all data)	R1 = 0.0242, wR2 = 0.0433
Largest diff. peak and hole	0.407 and -0.466 e.Å ⁻³

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å² $\times 10^3$) for 3d. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	6255(1)	6195(1)	5965(1)	17(1)
C(1)	5581(4)	6912(1)	5144(1)	13(1)
C(1A)	3477(3)	6747(1)	4564(1)	12(1)
C(2)	7196(4)	7593(1)	5142(1)	14(1)
Br(3)	8921(1)	9110(1)	4584(1)	16(1)
C(3)	6759(4)	8152(1)	4553(1)	14(1)
	x	y	z	U(eq)
C(4)	4796(4)	8030(1)	3973(1)	14(1)
C(4A)	3167(3)	7326(1)	3973(1)	12(1)
C(5)	1246(4)	7145(1)	3354(1)	13(1)
C(6)	-221(3)	6443(1)	3340(1)	12(1)

C(7)	8(4)	5942(1)	4011(1)	12(1)
N(7)	1854(3)	6076(1)	4589(1)	12(1)
C(8)	-1967(3)	6232(1)	2644(1)	13(1)
N(8)	-1708(3)	5305(1)	4047(1)	15(1)
C(9)	-3774(4)	6817(1)	2322(1)	14(1)
C(10)	-5434(4)	6673(1)	1664(1)	17(1)
C(11)	-5330(4)	5931(1)	1304(1)	18(1)
C(12)	-3547(4)	5338(1)	1598(1)	16(1)
C(13)	-1895(4)	5497(1)	2253(1)	13(1)
N(13)	84(3)	4857(1)	2504(1)	15(1)
O(13)	2314(2)	5060(1)	2814(1)	18(1)
O(14)	-578(3)	4150(1)	2372(1)	26(1)

Bond lengths [Å] and angles [°] for 3d

Br(1)-C(1)	1.8887(18)	N(8)-H(8A)	0.84(2)
C(1)-C(2)	1.375(3)	N(8)-H(8B)	0.84(2)
C(1)-C(1A)	1.421(2)	C(9)-C(10)	1.389(3)
C(1A)-N(7)	1.366(2)	C(9)-H(9)	0.92(2)
C(1A)-C(4A)	1.421(2)	C(10)-C(11)	1.387(3)
C(2)-C(3)	1.400(3)	C(10)-H(10)	0.96(2)
C(2)-H(2)	0.94(2)	C(11)-C(12)	1.384(3)
Br(3)-C(3)	1.9002(18)	C(11)-H(11)	0.91(2)
C(3)-C(4)	1.365(2)	C(12)-C(13)	1.386(2)

C(4)-C(4A)	1.408(3)	C(12)-H(12)	0.93(2)
C(4)-H(4)	0.91(2)	C(13)-N(13)	1.477(2)
C(4A)-C(5)	1.419(2)	N(13)-O(13)	1.227(2)
C(5)-C(6)	1.362(3)	N(13)-O(14)	1.229(2)
C(5)-H(5)	0.95(2)	C(2)-C(1)-C(1A)	122.37(17)
C(6)-C(7)	1.449(2)	C(2)-C(1)-Br(1)	116.86(13)
C(6)-C(8)	1.487(2)	C(1A)-C(1)-Br(1)	120.77(14)
C(7)-N(7)	1.329(2)	N(7)-C(1A)-C(4A)	122.89(15)
C(7)-N(8)	1.351(2)	N(7)-C(1A)-C(1)	121.25(16)
C(8)-C(9)	1.399(3)	C(4A)-C(1A)-C(1)	115.85(16)
C(8)-C(13)	1.400(3)	C(1)-C(2)-C(3)	119.30(16)
C(1)-C(2)-H(2)	121.6(13)	C(9)-C(8)-C(13)	115.80(16)
C(3)-C(2)-H(2)	119.1(13)	C(9)-C(8)-C(6)	118.58(16)
C(4)-C(3)-C(2)	121.56(17)	C(13)-C(8)-C(6)	125.56(16)
C(4)-C(3)-Br(3)	119.96(14)	C(7)-N(8)-H(8A)	120.5(16)
C(2)-C(3)-Br(3)	118.46(13)	C(7)-N(8)-H(8B)	118.4(16)
C(3)-C(4)-C(4A)	118.94(17)	H(8A)-N(8)-H(8B)	118(2)
C(3)-C(4)-H(4)	122.0(13)	C(10)-C(9)-C(8)	122.17(18)
C(4A)-C(4)-H(4)	119.0(13)	C(10)-C(9)-H(9)	119.3(13)
C(4)-C(4A)-C(5)	120.79(17)	C(8)-C(9)-H(9)	118.5(13)
C(4)-C(4A)-C(1A)	121.95(16)	C(11)-C(10)-C(9)	119.99(18)
C(5)-C(4A)-C(1A)	117.15(16)	C(11)-C(10)-H(10)	121.8(13)
C(6)-C(5)-C(4A)	120.48(17)	C(9)-C(10)-H(10)	118.2(13)

C(6)-C(5)-H(5)	120.3(12)	C(12)-C(11)-C(10)	119.71(17)
C(4A)-C(5)-H(5)	119.1(12)	C(12)-C(11)-H(11)	117.6(14)
C(5)-C(6)-C(7)	117.78(16)	C(10)-C(11)-H(11)	122.6(14)
C(5)-C(6)-C(8)	118.70(16)	C(11)-C(12)-C(13)	119.30(18)
C(7)-C(6)-C(8)	123.52(16)	C(11)-C(12)-H(12)	122.1(12)
N(7)-C(7)-N(8)	118.53(16)	C(13)-C(12)-H(12)	118.5(12)
N(7)-C(7)-C(6)	122.94(16)	C(12)-C(13)-C(8)	123.00(17)
N(8)-C(7)-C(6)	118.53(16)	C(12)-C(13)-N(13)	116.09(16)
C(7)-N(7)-C(1A)	117.97(15)	C(8)-C(13)-N(13)	120.84(15)
O(13)-N(13)-O(14)	123.80(16)	O(14)-N(13)-C(13)	117.85(15)
O(13)-N(13)-C(13)	118.32(15)		

Symmetry transformations used to generate equivalent atoms:

Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 3d. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Br(1)	21(1)	14(1)	15(1)	4(1)	-5(1)	-4(1)
C(1)	17(1)	11(1)	12(1)	0(1)	1(1)	2(1)
C(1A)	14(1)	10(1)	12(1)	-2(1)	2(1)	1(1)
C(2)	14(1)	14(1)	14(1)	-2(1)	0(1)	0(1)
Br(3)	17(1)	11(1)	18(1)	0(1)	-1(1)	-4(1)
C(3)	14(1)	10(1)	17(1)	-3(1)	3(1)	-2(1)
C(4)	16(1)	11(1)	13(1)	1(1)	2(1)	1(1)

C(4A)	12(1)	12(1)	14(1)	-2(1)	2(1)	1(1)
C(5)	16(1)	12(1)	12(1)	1(1)	2(1)	1(1)
C(6)	12(1)	12(1)	12(1)	-1(1)	1(1)	0(1)
C(7)	14(1)	11(1)	12(1)	-2(1)	3(1)	0(1)
N(7)	13(1)	12(1)	12(1)	-1(1)	0(1)	-1(1)
C(8)	13(1)	15(1)	12(1)	2(1)	3(1)	-4(1)
N(8)	16(1)	15(1)	13(1)	3(1)	-2(1)	-4(1)
C(9)	16(1)	14(1)	13(1)	0(1)	2(1)	-1(1)
C(10)	16(1)	19(1)	15(1)	4(1)	0(1)	1(1)
C(11)	19(1)	21(1)	13(1)	1(1)	-1(1)	-4(1)
C(12)	22(1)	14(1)	13(1)	-2(1)	2(1)	-4(1)
<hr/>						
	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
<hr/>						
C(13)	14(1)	12(1)	13(1)	2(1)	2(1)	-2(1)
N(13)	22(1)	13(1)	12(1)	0(1)	3(1)	0(1)
O(13)	14(1)	21(1)	19(1)	2(1)	1(1)	1(1)
O(14)	40(1)	11(1)	27(1)	-2(1)	-7(1)	1(1)

Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 3d

	x	y	z	U(eq)
<hr/>				
H(2)	8620(40)	7687(13)	5521(12)	15(5)
H(4)	4530(40)	8385(13)	3582(12)	14(5)
H(5)	1070(40)	7506(12)	2935(11)	10(5)

H(8A)	-1670(50)	5016(15)	4435(13)	23(6)
H(8B)	-3140(50)	5294(14)	3753(13)	23(6)
H(9)	-3860(40)	7309(14)	2556(12)	14(5)
H(10)	-6640(40)	7099(13)	1472(12)	17(5)
H(11)	-6380(40)	5814(13)	874(13)	18(6)
H(12)	-3390(40)	4836(13)	1366(11)	8(5)

Hydrogen bonds for 3d [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(8)-H(8A)...N(7)#1	0.84(2)	2.51(3)	3.335(2)	168(2)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z+1

H. List of Compounds

Number	Name	Structure	Melting Point (°C)
3a	3-(2-Nitrophenyl)quinolin-2-amine		205.0 – 207.0
3b	3-(5-Methyl-2-nitrophenyl)quinolin-2-amine		201.0 – 203.0
3c	6-Chloro-3-(2-nitrophenyl)quinolin-2-amine		255.0 – 257.0
3d	6,8-Dibromo-3-(2-nitrophenyl)quinolin-2-amine		142.0 – 144.0
3e	6,7-Dimethoxy-3-(2-nitrophenyl)quinolin-2-amine		206.0 – 208.0
4a	Quinolino[2,3- <i>c</i>]cinnoline 5-oxide		Decomp. 275

4b	2-Methylquinolino[2,3- <i>c</i>]cinnoline 5-oxide		Decomp. 277
4c	10-Chloroquinolino[2,3- <i>c</i>]cinnoline 5-oxide		>300
4d	8,10-Dibromoquinolino[2,3- <i>c</i>]cinnoline 5-oxide		>300
4e	9,10-Dimethoxyquinolino[2,3- <i>c</i>]cinnoline 5-oxide		Decomp. 278
5a	Quinolino[2,3- <i>c</i>]cinnoline		285.0 – 287.0
5b	2-Methylquinolino[2,3- <i>c</i>]cinnoline		Decomp. 253
5c	10-Chloroquinolino[2,3- <i>c</i>]cinnoline		285.0 – 287.0

5d	8,10-Dibromoquinolino[2,3-c]cinnoline		>300
5d'	10-Bromoquinolino[2,3-c]cinnoline		>300
5e	9,10-Dimethoxyquinolino[2,3-c]cinnoline		Decomp. 268
6a	3-(2-Aminophenyl)quinolin-2-amine		133.0 – 135.0
6b	3-(2-Amino-5-methylphenyl)-quinolin-2-amine		175.0 – 177.0
6c	3-(2-Aminophenyl)-6-chloroquinolin-2-amine		128.0 – 130.0
6d	3-(2-Aminophenyl)-6,8-dibromoquinolin-2-amine		201.0 – 203.0

6d'	3-(2-Aminophenyl)-8-bromoquinolin-2-amine		186.0 -188.0
7a	6 <i>H</i> -Indolo[2,3- <i>b</i>]quinoline		>300
7b	2-Chloro-6 <i>H</i> -indolo[2,3- <i>b</i>]quinoline		>300
7c	2,4-Dibromo-6 <i>H</i> -indolo[2,3- <i>b</i>]quinoline		>300
8a	Neocryptolepine		103.0-105.0
8b	2-Chloroneocryptolepine		168.0 – 170.0