Supporting Information

Assembly of 4-Aminoquinolines via Palladium Catalysis: A Mild and Convenient Alternative to S_NAr Methodology

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General Methods. HPLC analysis carried out using PDA detection. Stationary phase: Zorbax SB C18 4.6 mm x 75 mm x 3.5 μ m column. Mobile phase: MeOH/water (water contains 0.1 % TFA). Method conditions: initial hold at either 10 % or 25 % MeOH for 0.5 min, gradient to 100 % over 8 min, then 3 min at 100 % MeOH. All responses fell within the linear range for this instrument; calculations were based on response observing at λ_{max} for the target analyte (**7a**) and internal standard (4,4'-dimethoxybiphenyl) (232 nm and 264 nm respectively). NMR data acquired using a 400 MHz instrument at 298 K and shifts reported relative to respective solvent signals (Cambridge Isotope Labs: <http://www.isotope.com/cil/products/images/nmrchart.pdf>). All reagents and solvents used were obtained from commercial sources and used without any purification. Dioxane, DMF, and PhMe were purchased as anhydrous grade reagents and used as such.

General Procedure A: Bromination of 4-hydroxy-quinolines: To a suspension of the requisite 4-hydroxy-quinoline (36.2 mmol) in DMF (60 mL) at ambient temperature was added slowly phosphorous tribromide (37.3 mmol). (In nearly all cases, the reaction mixture started-out as a suspension and as the full equivalent of phosphorous tribromide was added, went into solution [with exotherm] and reprecipitated. In some cases, additional DMF was added to allow stirring.) The resulting mixture was stirred under N₂ for ½ hour at which point HPLC indicated consumption of the starting material. The mixture was then quenched with ice chips followed by water, and allowed to stir for ½ hour. The reaction mixture was made basic by the addition of solid NaHCO₃ until the pH was >10 (paper) and filtered. The solid was washed with several portion of water and dried in a vac oven (50 °C) for 18 h. In some cases, a solid did not result from these conditions and the product was extracted into EtOAc, which was washed with several

portions of water, dried over Na_2SO_4 , filtered, and concentrated to give the title compound. Unless otherwise noted, no purification was required.

General Procedure B: Palladium Catalyzed Amination of 4-Haloquinolines: This procedure is stated in the Experimental Section of the main paper.

6-Methylsulfanyl-quinolin-4-ol, 2b: A solution of Meldrum's acid (10.8 g, 75.0 mmol) in triethylorthoformate (50 mL) was heated in a sealed tube on a heating block to 145 °C (block temp). After 1 h, the solution was allowed to cool to ~50 °C, and 4-(methylthio)aniline (6.1 mL, 50 mmol) was added drop-wise and the reaction mixture was heated on a heating block to 145 °C (block temp) for ¼ h, then cooled to ambient temperature resulting in a solid. The reaction mixture was diluted with hexane, filtered, and the solids washed with several portions of hexane and dried in a vac oven (50 °C) to give a light brown solid that was slowly added in small portions (~1 gram each) to a 500 mL, 3-neck flask containing Ph_2O (250 mL) pre-heated to 245 °C (internal temperature). **Care must be taken not to perform this addition too rapidly as gasses violently evolve!** Addition time was ~10 min. The internal temperature was kept above 240 °C throughout the addition. After all the solid was added, the mixture was kept at ~250 °C for ~5 min, then allowed to cool to ambient temperature and diluted with hexane, and filtered. The solid was washed with several portions of 30 % Et_2O /hexane and then dried in a vac oven (50 °C) to give a light brown solid (7.3 g). Yield 79 %. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 11.77 (bd, $J = 3.4$ Hz, 1 H), 7.89 - 7.85 (m, 2 H), 7.56 (dd, $J = 2.2, 8.8$ Hz, 1 H), 7.49 (d, $J = 8.8$ Hz, 1 H), 6.03 (d, $J = 7.4$ Hz, 1 H), 2.53 (s, 3 H); ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 175.9, 139.1, 137.8, 132.9, 130.4, 126.3, 120.8, 119.2, 109.7, 15.2; $\text{C}_{10}\text{H}_{10}\text{NOS}$: MH^+ calcd. 192.0478; found 192.0477; HPLC purity @ 254 nm: >99 %.

[1,3]Dioxolo[4,5-g]quinolin-8-ol, 2l was prepared according to the teaching of Ruchelman^{14b}. Yield 74 %. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.58 (d, *J* = 1.4 Hz, 1 H), 7.77 (d, *J* = 7.2 Hz, 1 H), 7.38 (s, 1 H), 7.04 (s, 1 H), 6.12 (s, 2 H), 5.95 (d, *J* = 7.4 Hz, 1 H); ¹³C NMR (101 MHz, DMSO-*d*₆) δ 176.5, 160.9, 155.0, 148.1, 147.2, 131.3, 117.8, 111.8, 111.3, 106.9; C₁₀H₈NO₃: MH⁺ calcd. 190.0499; found 190.0497; HPLC purity @ 254 nm: >98 %.

With the exception of **4c** and **4e** (both compounds are commercially available), compounds **4a-j** were prepared according to General Procedure A.

4-Bromo-quinoline, 4a. Yield 92 %. ¹H NMR (400 MHz, CDCl₃) δ 8.70 (d, *J* = 4.6 Hz, 1 H), 8.21 (dd, *J* = 1.3, 8.3 Hz, 1 H), 8.13 (d, *J* = 8.3 Hz, 1 H), 7.79 (ddd, *J* = 1.4, 6.9, 8.4 Hz, 1 H), 7.72 (d, *J* = 4.7 Hz, 1 H), 7.67 (ddd, *J* = 1.3, 6.9, 8.2 Hz, 1 H); ¹³C NMR (101 MHz, CDCl₃) δ 150.0, 149.1, 134.3, 130.6, 130.1, 128.1, 128.0, 127.0, 125.2; C₉H₇BrN: MH⁺ calcd. 207.9756; found 207.9756; HPLC purity @ 254 nm: >99 %.

4-Bromo-6-methylsulfanyl-quinoline, 4b. Yield 83 %. ¹H NMR (400 MHz, CDCl₃) δ 8.59 (d, *J* = 4.7 Hz, 1 H), 7.98 (d, *J* = 8.8 Hz, 1 H), 7.87 (d, *J* = 2.1 Hz, 1 H), 7.68 (d, *J* = 4.7 Hz, 1 H), 7.63 (dd, *J* = 2.1, 8.8 Hz, 1 H), 2.65 (s, 3 H); ¹³C NMR (101 MHz, CDCl₃) δ 148.6, 147.1, 139.7, 132.5, 129.9, 129.6, 128.3, 125.5, 120.8, 15.4; C₁₀H₉BrNS: MH⁺ calcd. 253.9634; found 253.9633; HPLC purity @ 254 nm: >99 %.

4-Bromo-6-methoxy-quinoline, 4c. ¹H NMR (400 MHz, CDCl₃) δ 8.49 (d, *J* = 4.7 Hz, 1 H), 7.98 - 7.95 (m, 1 H), 7.61 (d, *J* = 4.7 Hz, 1 H), 7.37 (dd, *J* = 2.9, 8.5 Hz, 1 H), 7.35 (s, 1 H), 3.95 (s, 3 H); ¹³C NMR (101 MHz, CDCl₃) δ 159.2, 147.4, 145.3, 132.6, 131.7, 129.2, 125.5, 123.5, 104.6, 55.9; C₁₀H₉BrNO: MH⁺ calcd. 237.9862; found, 237.9861; HPLC purity @ 254 nm: >99 %.

4-Bromo-7-chloro-quinoline, 4d. Yield 57 %. ^1H NMR (400 MHz, CDCl_3) δ 8.69 (d, J = 4.7 Hz, 1 H), 8.16 (d, J = 9.0 Hz, 1 H), 8.13 (d, J = 2.0 Hz, 1 H), 7.71 (d, J = 4.7 Hz, 1 H), 7.62 (dd, J = 2.1, 9.0 Hz, 1 H); ^{13}C NMR (101 MHz, CDCl_3) δ 151.0, 149.3, 136.7, 134.1, 129.0, 128.9, 128.4, 126.5, 125.4; $\text{C}_9\text{H}_5\text{NBrCl}$: MH^+ calcd. 241.9367; found, 241.9365; HPLC purity @ 254 nm: >99 %.

4,6-Dibromo-quinoline, 4e. ^1H NMR (400 MHz, CDCl_3) δ 8.65 (d, J = 4.7 Hz, 1 H), 8.34 (d, J = 2.2 Hz, 1 H), 7.95 (d, J = 9.0 Hz, 1 H), 7.81 (dd, J = 2.3, 8.9 Hz, 1 H), 7.70 (d, J = 4.7 Hz, 1 H); ^{13}C NMR (101 MHz, CDCl_3) δ 150.0, 147.5, 133.9, 132.7, 131.6, 129.0, 129.0, 125.7, 122.2; $\text{C}_9\text{H}_6\text{NBr}_2$: MH^+ calcd. 285.8861; found, 285.8860; HPLC purity @ 254 nm: >99 %.

4-Bromo-7-nitro-quinoline, 4f. Yield 40 % after SiO_2 gel chromatography (75 % yield as a mixture with 4g). Eluent: 0.9 % THF/(hexane: CH_2Cl_2 [1:1]) in a step gradient to 4 %. ^1H NMR (400 MHz, CDCl_3) δ 9.03 (d, J = 2.0 Hz, 1 H), 8.85 (d, J = 4.6 Hz, 1 H), 8.43 (dd, J = 2.1, 9.3 Hz, 1 H), 8.39 (dd, J = 0.6, 9.0 Hz, 1 H), 7.90 (d, J = 4.6 Hz, 1 H); ^{13}C NMR (101 MHz, CDCl_3) δ 152.1, 148.5, 147.9, 133.9, 130.95, 128.9, 127.7, 126.0, 121.0; $\text{C}_9\text{H}_6\text{BrN}_2\text{O}_2$: MH^+ calcd. 252.9607; found, 252.9605; HPLC purity @ 254 nm: >99 %.

4-Bromo-5-nitro-quinoline, 4g. Yield 35 % after SiO_2 gel chromatography (75 % yield as a mixture with 4f). Eluent: 0.9 % THF/(hexane: CH_2Cl_2 [1:1]) in a step gradient to 4 %. ^1H NMR (400 MHz, CDCl_3) δ 8.77 (d, J = 4.7 Hz, 1 H), 8.35 (dd, J = 1.8, 8.0 Hz, 1 H), 7.88 (d, J = 4.7 Hz, 1 H), 7.85 - 7.78 (m, 2 H); ^{13}C NMR (101 MHz, CDCl_3) δ 151.0, 149.5, 147.9, 134.5, 129.4, 128.7, 128.0, 123.8, 119.4; $\text{C}_9\text{H}_5\text{N}_2\text{O}_2\text{Br}$: MH^+ calcd. 252.9607; found, 252.9606; HPLC purity @ 254 nm: >99 %.

4-Bromo-quinoline-6-carbonitrile, 4h. Yield 78 %. ^1H NMR (CD_3OD) δ 8.82 (d, J = 4.8 Hz, 1 H), 8.70 (d, J = 1.8 Hz, 1 H), 8.22 (d, J = 8.9 Hz, 1 H), 8.06 (dd, J = 1.8, 8.8 Hz, 1 H),

8.02 (d, $J = 4.8$ Hz, 1 H); ^{13}C NMR (CDCl_3) δ 152.9, 150.1, 134.7, 133.6, 131.9, 131.3, 127.9, 126.9, 118.5, 112.0; $\text{C}_{10}\text{H}_6\text{BrN}_2$ MH^+ calcd. 232.9709; found, 232.9707; HPLC purity @ 254 nm: >99 %.

4-Bromo-quinoline-6-carboxylic acid methyl ester, 4i. Yield >99 %. ^1H NMR (400 MHz, CDCl_3) δ 8.95 (d, $J = 1.7$ Hz, 1 H), 8.77 (d, $J = 4.69$ Hz, 1 H), 8.36 (dd, $J = 1.8, 8.8$ Hz, 1 H), 8.16 (d, $J = 8.7$ Hz, 1 H), 7.78 (d, $J = 4.7$ Hz, 1 H), 4.04 (s, 3 H); ^{13}C NMR (101 MHz, CDCl_3) δ 166.4, 152.0, 150.9, 135.6, 130.5, 130.1, 130.0, 129.5, 127.5, 126.0, 52.9; $\text{C}_{11}\text{H}_9\text{BrNO}_2$: MH^+ calcd. 267.9791; found, 267.9789; HPLC purity @ 254 nm: >99 %.

4-Bromo-6,8-difluoro-quinoline, 4j. Yield 59 %. ^1H NMR (400 MHz, CDCl_3) δ 8.70 (d, $J = 4.6$ Hz, 1 H), 7.81 (d, $J = 4.6$ Hz, 1 H), 7.69 (ddd, $J = 1.7, 2.7, 9.2$ Hz, 1 H), 7.32 (ddd, $J = 2.7, 8.6, 11.4$ Hz, 1 H); ^{13}C NMR (101 MHz, CDCl_3) δ 160.5 (dd, $J = 11.9, 250.3$ Hz), 158.9 (dd, $J = 13.5, 262.0$ Hz), 149.3 (dd, $J = 1.5, 2.7$ Hz), 136.9 (dd, $J = 1.5, 12.0$ Hz), 133.4 (dd, $J = 5.1, 6.0$ Hz), 129.8 (dd, $J = 2.1, 11.4$ Hz), 127.1, 106.9 (dd, $J = 4.6, 24.4$ Hz), 106.4 (dd, $J = 22.5, 29.5$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -107.0 (q, $J = 8.8$ Hz, 1 F), -117.8 (ddd, $J = 2.0, 8.6, 10.0$ Hz 1 F); $\text{C}_9\text{H}_5\text{NBrF}_2$: MH^+ calcd. 243.9568; found, 243.9566; HPLC purity @ 254 nm: >97 %.

4-Bromo-6-7-dimethoxy-quinoline, 4k. Yield 40 %. ^1H NMR (400 MHz, CDCl_3) δ 8.48 (d, $J = 4.8$ Hz, 1 H), 7.56 (d, $J = 4.8$ Hz, 1 H), 7.42 (d, $J = 9.3$ Hz, 1 H), 7.37 (s, 1 H), 4.08 (s, 3 H), 4.06 (s, 3 H); ^{13}C NMR (101 MHz, CDCl_3) δ 153.1, 151.0, 147.7, 146.1, 131.9, 123.6, 123.4, 108.3, 104.5, 56.4, 56.3; $\text{C}_{11}\text{H}_{11}\text{NO}_2\text{Br}$: MH^+ calcd. 267.9968; found, 267.9966; HPLC purity @ 254 nm: >99 %.

8-bromo-[1,3]dioxolo[4,5-g]quinoline, 4l. Yield 46 %. ^1H NMR (CDCl_3) δ 8.44 (d, $J = 4.8$ Hz, 1 H), 7.52 (d, $J = 4.8$ Hz, 1 H), 7.46 (s, 1 H), 7.34 (s, 1 H), 6.13 (s, 2 H); ^{13}C NMR

(CD₃OD) δ 153.7, 151.4, 148.5, 148.2, 134.0, 126.7, 125.1, 105.8, 104.4, 103.1; C₁₀H₇NO₂Br: MH⁺ calcd. 251.9655; found 251.9652; HPLC purity @ 254 nm: >99 %.

Compounds **7a-f**, **7h-k**, **10-12**, **14**, and **16** were prepared by General Procedure B. The reported yield represents the average of at least two runs.

N¹,N¹-Diethyl-N⁴-quinolin-4-yl-pentane-1,4-diamine, 7a. Yield 88 %. ¹H NMR (400 MHz, CDCl₃) δ 8.54 (d, *J* = 5.4 Hz, 1 H), 7.97 (dd, *J* = 0.8, 8.5 Hz, 1 H), 7.73 (d, *J* = 8.5 Hz, 1 H), 7.61 (ddd, *J* = 1.1, 6.9, 8.2 Hz, 1 H), 7.40 (ddd, *J* = 1.2, 6.8, 8.2 Hz, 1 H), 6.44 (d, *J* = 5.3 Hz, 1 H), 5.13 (d, *J* = 7.3 Hz, 1 H), 3.78 - 3.68 (m, 1 H), 2.52 (q, *J* = 7.2 Hz, 4 H), 2.44 (t, *J* = 7.0 Hz, 2 H), 1.78 - 1.56 (m, 4 H), 1.32 (d, *J* = 6.4 Hz, 3 H), 1.01 (t, *J* = 7.2 Hz, 6 H); ¹³C NMR (101 MHz, CDCl₃) δ 150.9, 149.1, 148.6, 129.7, 128.8, 124.2, 119.7, 118.9, 98.9, 52.6, 48.2, 46.8, 34.5, 23.8, 20.2, 11.5; C₁₈H₂₈N₃: MH⁺ calcd. 286.2278; found 286.2275; HPLC purity @ 254 nm: >99 %.

N¹,N¹-Diethyl-N⁴-(6-methylsulfanyl-quinolin-4-yl)-pentane-1,4-diamine, 7b. Yield 63 %. ¹H NMR (400 MHz, CD₃OD) δ 8.27 (d, *J* = 5.7 Hz, 1 H), 8.01 (d, *J* = 2.0 Hz, 1 H), 7.71 (d, *J* = 8.9 Hz, 1 H), 7.55 (dd, *J* = 2.1, 8.9 Hz, 1 H), 6.54 (d, *J* = 5.6 Hz, 1 H), 3.88 - 3.79 (m, 1 H), 2.61 (s, 3 H), 2.54 (q, *J* = 7.1 Hz, 4 H), 2.49 (t, *J* = 7.6 Hz, 2 H), 1.81 - 1.72 (m, 1 H), 1.68 - 1.59 (m, 3 H), 1.34 (d, *J* = 6.5 Hz, 3 H), 1.01 (t, *J* = 7.2 Hz, 6 H); ¹³C NMR (101 MHz, CD₃OD) δ 151.4, 150.7, 147.5, 136.6, 130.4, 129.4, 121.0, 119.5, 100.1, 53.8, 49.5 (measured using HSQC), 47.9, 35.3, 24.3, 20.6, 16.5, 11.3; C₁₉H₃₀N₃S: MH⁺ calcd. 332.2155; found, 332.2151; HPLC purity @ 254 nm: >99 %.

N¹,N¹-Diethyl-N⁴-(6-methoxy-quinolin-4-yl)-pentane-1,4-diamine, 7c. Yield 78 %. ¹H NMR (400 MHz, CD₃OD) δ 8.22 (dd, *J* = 0.6, 5.6 Hz, 1 H), 7.71 (d, *J* = 9.1 Hz, 1 H), 7.52 (d, *J* = 2.8 Hz, 1 H), 7.28 (dd, *J* = 2.5, 9.1 Hz, 1 H), 6.52 (d, *J* = 5.6 Hz, 1 H), 3.95 (s, 3 H), 3.88 -

3.81 (m, 1 H), 2.54 (q, $J = 7.1$ Hz, 4 H), 2.50 (t, $J = 7.4$ Hz, 2 H), 1.82 - 1.73 (m, 1 H), 1.68 - 1.58 (m, 3 H), 1.35 (d, $J = 6.4$ Hz, 3 H) 1.01 (t, $J = 7.1$ Hz, 6 H); ^{13}C NMR (101 MHz, CD_3OD) δ 158.5, 151.4, 149.1, 144.8, 130.4, 122.3, 121.1, 101.6, 99.6, 56.4, 55.0, 53.8, 47.8, 35.4, 24.3, 20.7, 11.3; $\text{C}_{19}\text{H}_{30}\text{N}_3\text{O}$: MH^+ calcd. 316.2383; found, 316.2379; HPLC purity @ 254 nm: >99 %.

N^4 -(7-Chloro-quinolin-4-yl)- N^1,N^1 -diethyl-pentane-1,4-diamine, 7d. Yield 74 %. ^1H NMR (400 MHz, CDCl_3) δ 8.50 (d, $J = 5.4$ Hz, 1 H), 7.92 (d, $J = 2.1$ Hz, 1 H), 7.63 (d, $J = 8.9$ Hz, 1 H), 7.33 (dd, $J = 2.1, 8.9$ Hz, 1 H), 6.40 (d, $J = 5.7$ Hz, 1 H), 5.20 (d, $J = 7.4$ Hz, 1 H), 3.73 - 3.66 (m, 1 H), 2.50 (q, $J = 7.4$ Hz, 4 H), 2.43 (t, $J = 7.0$ Hz, 2 H), 1.76 - 1.54 (m, 4 H), 1.30 (d, $J = 6.7$ Hz, 3 H), 0.99 (t, $J = 7.1$ Hz, 6 H); ^{13}C NMR (101 MHz, CD_3OD) δ 152.6, 152.3, 150.2, 136.5, 127.8, 126.0, 124.6, 119.0, 100.1, 55.0, 53.8, 48.0, 36.0, 24.3, 20.8, 11.3; $\text{C}_{18}\text{H}_{27}\text{N}_3\text{Cl}$: MH^+ calcd. 320.1888; found, 320.1884; HPLC purity @ 254 nm: >99 %.

N^4 -(6-Bromo-quinolin-4-yl)- N^1,N^1 -diethyl-pentane-1,4-diamine, 7e. Yield 58 %. ^1H NMR (CD_3OD) δ 8.46 (d, $J = .1.9$ Hz, 1 H), 8.34 (d, $J = 6.1$ Hz, 1 H), 7.73-7.68 (m, 2 H), 6.57 (d, $J = 5.9$ Hz, 1 H), 3.86-3.78 (m, 1 H), 2.53 (q, $J = 7.5$ Hz, 4 H), 2.49 (d, $J = 8.0$, 1 H), 2.47 (d, $J = 6.9$ Hz, 1 H), 1.76-1.59 (m, 4 H), 1.32 (d, $J = 6.7$ Hz, 3 H), 1.01 (t, $J = 6.7$ Hz, 6 H); ^{13}C NMR (CD_3OD) δ 151.9, 151.6, 148.1, 133.9, 131.0, 125.5, 121.9, 119.0, 100.3, 55.0, 49.6, 47.9, 35.30, 24.3, 20.5, 11.3; $\text{C}_{18}\text{H}_{27}\text{N}_3\text{Br}$: MH^+ calcd. 364.1383; found, 364.1379; HPLC purity @ 254 nm: >93. %.

N^1,N^1 -Diethyl- N^4 -(7-nitro-quinolin-4-yl)-pentane-1,4-diamine, 7f. Yield 32 %. ^1H NMR (CDCl_3) δ 8.81 (d, $J = 2.5$ Hz, 1 H), 8.63 (d, $J = 5.5$ Hz, 1 H), 8.13 (dd, $J = 2.4, 9.1$ Hz, 1 H), 7.85 (dd, $J = 2.0, 9.2$ Hz, 1 H), 6.54 (d, $J = 5.6$ Hz, 1 H), 3.75-3.68 (m, 1 H), 2.52 (q, $J = 7.2$ Hz, 2 H), 2.53 (q, $J = 7.2$ Hz, 2 H), 2.44 (t, $J = 7.0$ Hz, 2 H), 1.77-1.58 (m, 4 H), 1.32 (d, $J = 6.4$

Hz, 3 H), 1.00 (t, $J = 7.5$ Hz, 6 H); ^{13}C NMR (101 MHz, CD_3OD) δ 153.9, 152.2, 149.7, 148.8, 125.0, 124.7, 124.0, 118.5, 101.7, 53.7, 49.9, 47.9, 35.2, 24.2, 20.4, 11.3; $\text{C}_{18}\text{H}_{27}\text{N}_4\text{O}_2$: MH^+ calcd. 331.2129; found, 331.2126; HPLC purity @ 254 nm: >96 %.

4-(4-Diethylamino-1-methyl-butylamino)-quinoline-6-carbonitrile, 7h. Yield 51 %. ^1H NMR (CD_3OD) δ 8.77 (d, $J = 1.8$ Hz, 1 H), 8.43 (d, $J = 5.8$ Hz, 1 H), 7.87 (dd, $J = 1.1, 8.6$ Hz, 1 H), 7.82 (dd, $J = 1.7, 8.5$ Hz, 1 H), 6.66 (d, $J = 5.9$ Hz, 1 H), 3.90 - 3.82 (m, 1 H), 2.54 (q, $J = 7.0$ Hz, 4 H), 2.51 - 2.47 (m, 1 H), 1.80-1.55 (m, 4 H), 1.34 (d, $J = 6.3$ Hz, 3 H), 1.01 (t, $J = 7.3$ Hz, 6 H); ^{13}C NMR (101 MHz, CD_3OD) δ 154.1, 152.5, 151.0, 131.5, 130.6, 130.0, 120.2, 120.4, 108.5, 101.1, 55.0, 49.9, 47.9, 35.2, 24.3, 20.4, 11.4; $\text{C}_{19}\text{H}_{27}\text{N}_4$: MH^+ calcd. 311.2230; found, 311.2229; HPLC purity @ 254 nm: >99 %.

4-(4-Diethylamino-1-methyl-butylamino)-quinoline-6-carboxylic acid methyl ester, 7i. Yield 75 %. ^1H NMR (400 MHz, CD_3OD) δ 8.98 (d, $J = 1.9$ Hz, 1 H), 8.39 (d, $J = 5.7$ Hz, 1 H), 8.17 (dd, $J = 2.0, 8.9$ Hz, 1 H), 7.82 (d, $J = 8.8$ Hz, 1 H), 6.62 (d, $J = 6.0$ Hz, 1H), 3.98 (s, 3 H), 3.91 - 3.84 (m, 1 H), 2.55 (q, $J = 7.1$ Hz, 4 H), 2.51 (t, $J = 7.8$ Hz, 2 H), 1.84 - 1.75 (m, 1 H), 1.70 - 1.58 (m, 3 H), 1.35 (d, $J = 6.4$ Hz, 3 H), 1.01 (t, $J = 7.3$ Hz, 6 H); ^{13}C NMR (101 MHz, CD_3OD) δ 168.4, 153.40, 153.38, 151.8, 130.1, 129.3, 127.0, 126.2, 119.8, 100.4, 53.8, 52.9, 47.9, 35.2, 24.3, 20.5, 11.3; $\text{C}_{20}\text{H}_{30}\text{N}_3\text{O}_2$: MH^+ calcd. 344.2333; found, 344.2328; HPLC purity @ 254 nm: >99 %.

N^4 -(6,8-Difluoro-quinolin-4-yl)- N^1, N^1 -diethyl-pentane-1,4-diamine, 7j. Yield 74 %. ^1H NMR (CD_3OD) δ 8.35 (d, $J = 5.6$ Hz, 1 H), 7.83 (ddd, $J = 1.7, 2.7, 10.7$ Hz, 1 H), 7.32 (ddd, $J = 2.6, 8.7, 11.1$ Hz, 1 H), 6.64 (d, $J = 5.8$ Hz, 1 H), 3.87-3.80 (m, 1 H), 2.55 (q, $J = 7.4$, 4 H), 2.51 (d, $J = 7.8$ Hz, 1 H), 2.49 (d, $J = 7.0$ Hz, 1 H), 1.77-1.58 (m, 4 H), 1.29 (d, $J = 6.3$ Hz, 3 H), .98 (t, $J = 7.5$ Hz, 6 H); ^{13}C NMR (101 MHz, CD_3OD) δ 159.9 (dd, $J = 13.2, 255.4$ Hz),

159.8 (dd, $J = 12.1, 243.8$ Hz), 151.6 (dd, $J = 3.4, 4.6$ Hz), 151.1 (dd, $J = 1.1, 2.0$ Hz), 137.0 (dd, $J = 2.0, 12.0$ Hz), 122.0 (dd, $J = 4.0, 10.2$ Hz), 105.6 (dd, $J = 23.0, 29.5$ Hz), 102.7 (dd, $J = 4.9, 23.5$ Hz), 100.8, 53.7, 49.7, 47.9, 35.2, 24.2, 20.5, 11.3; ^{19}F NMR (CD_3OD) δ -120.8 (ddd, $J = 1.9, 6.6, 11$ Hz, 1 H), -115.4 (ddd, $J = 6.5, 8.5, 10.5$ Hz, 1 H); $\text{C}_{18}\text{H}_{26}\text{N}_3\text{F}_2$: MH^+ calcd. 332.2089; found, 332.2085; HPLC purity @ 254 nm: >99 %.

N^4 -(6,7-Dimethoxy-quinolin-4-yl)- N^1,N^1 -diethyl-pentane-1,4-diamine, 7k. Yield 79 %. ^1H NMR (CD_3OD) δ 8.18 (d, $J = 5.6$ Hz, 1 H), 7.50 (s, 1 H), 7.17 (s, 1 H), 6.46 (d, $J = 5.8$ Hz, 1 H), 3.98 (s, 3 H), 3.95 (s, 3 H), 3.86-3.79 (m, 1 H), 2.54 (q, $J = 7.2$ Hz, 4 H), 2.48 – 2.44 (m, 2 H), 1.78-1.68 (m, 1 H), 1.66-1.55 (m, 3 H), 1.34 (d, $J = 6.8$ Hz, 3 H), 1.01 (t, $J = 7.2$ Hz, 6 H); ^{13}C NMR (101 MHz, CD_3OD) δ 153.6, 151.3, 149.8, 149.2, 146.1, 114.7, 108.1, 102.0, 99.1, 56.9, 56.4, 53.8, 49.4, 47.8, 35.5, 24.3, 20.8, 11.3; $\text{C}_{20}\text{H}_{32}\text{O}_2\text{N}_3$: MH^+ calcd. 346.2489; found, 346.2486; HPLC purity @ 254 nm: >99 %.

N' -(6-Bromo-quinolin-4-yl)- N,N -diethyl-propane-1,3-diamine, 10e. Yield 65 %. ^1H NMR (CD_3OD) δ 8.36 (d, $J = 5.6$ Hz, 1 H), 8.28 – 8.27 (m, 1 H), 7.73-7.68 (m, 2 H), 6.51 (d, $J = 6.1$ Hz, 1 H), 3.38 (t, $J = 6.8$ Hz, 2 H), 2.65 (d, $J = 7.0$ Hz, 1 H), 2.63 (d, $J = 5.0$ Hz, 1 H), 2.61 (q, $J = 7.1$ Hz, 4 H), 1.92 (p, $J = 6.9$ Hz, 2 H), 1.08 (t, $J = 7.1$ Hz, 6 H); ^{13}C NMR (CD_3OD) δ 152.0, 147.8, 133.8, 131.1, 125.3, 121.8, 119.1, 100.0, 55.0, 52.5, 48.0, 43.4, 25.9, 11.7; $\text{C}_{16}\text{H}_{23}\text{N}_3\text{Br}$: MH^+ calcd. 336.1070; found, 336.1067; HPLC purity @ 254 nm: >89. %.

N,N -Diethyl- N' -(7-nitro-quinolin-4-yl)-propane-1,3-diamine, 10f. Yield 74 %. ^1H NMR (CD_3OD) δ 8.61 (d, $J = 2.3$ Hz, 1 H), 8.48 (d, $J = 5.7$ Hz, 1 H), 8.24 (d, $J = 9.3$ Hz, 1 H), 8.14 (dd, $J = 2.4, 9.3$ Hz, 1 H), 6.65 (d, $J = 5.2$ Hz, 1 H), 3.41 (t, $J = 6.8$ Hz, 2 H), 2.67 (d, $J = 7.1$ Hz, 1 H), 2.65 (d, $J = 5.8$ Hz, 1 H), 2.62 (q, $J = 7.1$, 4 H), 1.98-1.91 (m, 2 H), 1.04 (t, $J = 7.1$ Hz, 6 H); ^{13}C NMR (CD_3OD) δ 153.9, 152.7, 149.7, 148.7, 124.8, 124.8, 123.9, 118.6, 101.5,

52.1, 48.0, 43.2, 26.0, 11.6; $C_{16}H_{23}N_4O_2$: MH^+ calcd. 303.1816; found, 303.1812; HPLC purity @ 254 nm: >97 %.

4-(3-Diethylamino-propylamino)-quinoline-6-carbonitrile, 10h. Yield 85 %. 1H NMR (CD_3OD) δ 8.60 (d, J = 1.7 Hz, 1 H), 8.46 (d, J = 5.7 Hz, 1 H), 7.89 (d, J = 8.7 Hz, 1 H), 7.83 (dd, J = 1.6, 8.7 Hz, 1 H), 6.63 (d, J = 5.9 Hz, 1 H), 3.43 (t, J = 6.7 Hz, 2 H), 2.66 (d, J = 7.3 Hz, 1 H), 2.65 (d, J = 5.1 Hz, 1 H), 2.63 (q, J = 7.4 Hz, 4 H), 1.98-1.91 (m, 2 H), 1.08 (t, J = 7.0, 6 H); ^{13}C NMR (101 MHz, CD_3OD) δ 154.2, 153.0, 150.8, 131.5, 130.6, 129.6, 120.01, 120.04, 108.7, 100.8, 52.2, 48.0, 43.2, 26.0, 11.6; $C_{17}H_{23}N_4$: MH^+ calcd. 283.1917; found, 283.1915; HPLC purity @ 254 nm: >99 %.

***N*-(2,2-Dimethyl-1,3-dioxolan-4-ylmethyl)-*N*-quinolin-4-yl-hydrazine, 12.** Yield 85 %. 1H NMR (CD_3OD) δ 8.19 (d, J = 5.7 Hz, 1 H), 7.43 (s, 1 H), 7.11 (s, 1 H), 6.54 (d, J = 5.6 Hz, 1 H), 6.09 (s, 2 H), 4.47 – 4.41 (m, 1 H), 4.14 (dd, J = 6.4, 8.4 Hz, 1 H), 3.82 (dd, J = 6.1, 8.5 Hz, 1 H), 3.52 (dd, J = 5.6, 13.8 Hz, 1 H), 3.47 (dd, J = 5.6, 13.9 Hz, 1 H), 1.42 (s, 3 H), 1.35 (s, 3 H); ^{13}C NMR (CD_3OD) δ 152.3, 152.1, 149.1, 148.5, 147.1, 115.8, 110.9, 105.4, 103.4, 99.5, 98.3, 75.7, 68.6, 46.8, 27.4, 25.8; $C_{15}H_{18}N_2O_2$: MH^+ calcd. 301.1194; found, 301.1199; HPLC purity @ 254 nm: >99 %.

Dimethyl-[3-(*N*-quinolin-4-yl-hydrazino)-propyl]-amine, 14. Yield 85 %. 1H NMR (CD_3OD) δ 8.17 (d, J = 5.8 Hz, 1 H), 7.40 (s, 1 H), 7.09 (s, 1 H), 6.44 (d, J = 5.7 Hz, 1 H), 6.08 (s, 2 H), 3.37 (t, J = 6.9 Hz, 2 H), 2.49 (d, J = 7.1, 1 H), 2.47 (d, J = 7.5 Hz, 1 H), 2.29 (s, 6 H), 1.91 (q, J = 7.1 Hz, 2 H); ^{13}C NMR (CD_3OD) δ 152.3, 152.0, 149.2, 148.4, 147.0, 115.8, 105.4, 103.4, 99.1, 98.4, 58.7, 45.7, 42.6, 27.3; $C_{15}H_{19}N_3O_2$: MH^+ calcd. 274.1550; found, 274.1547; HPLC purity @ 254 nm: >99 %.

4-Morpholin-4-yl-quinoline, 16. Yield 86 %. ^1H NMR (CD_3OD) δ 8.64 (d, $J = 5.2$ Hz, 1 H), 8.12 (d, $J = 8.7$ Hz, 1 H), 7.96 (d, $J = 8.7$ Hz, 1 H), 7.73 – 7.69 (m, 1 H), 7.58 – 7.54 (m, 1 H), 7.02 (d, $J = 5.2$ Hz, 1 H), 3.98 – 3.96 (m, 4 H), 3.27 – 3.25 (m, 4 H); ^{13}C NMR (CD_3OD) δ 159.3, 151.8, 150.2, 130.9, 129.7, 127.0, 125.3, 124.7, 110.0, 68.1, 54.0; $\text{C}_{13}\text{H}_{15}\text{N}_2\text{O}$: MH^+ calcd. 215.1179; found, 215.1179; HPLC purity @ 254 nm: >98 %.

Phenyl-quinolin-4-yl-amine, 17. Yield 77 %. ^1H NMR (CD_3OD) δ 8.37 (d, $J = 5.6$ Hz, 1 H), 8.30 (ddd, $J = 0.7, 1.3, 8.6$ Hz, 1 H), 7.89 (ddd, $J = 0.7, 1.3, 8.6$ Hz, 1 H), 7.71 (ddd, $J = 1.3, 6.9, 9.9$ Hz, 1 H), 7.54 (ddd, $J = 1.3, 6.9, 9.9$ Hz, 1 H), 7.46-7.37 (m, 6 H), 7.23 – 7.19 (m, 1 H), 6.93 (d, $J = 5.5$ Hz, 1 H); ^{13}C NMR (CDCl_3) δ 151.2, 149.4, 147.6, 140.1, 130.5, 129.9, 129.6, 125.6, 124.9, 122.8, 119.9, 119.7, 102.5; $\text{C}_{15}\text{H}_{13}\text{N}_2$: MH^+ calcd. 221.1073; found, 221.1071; HPLC purity @ 254 nm: >96 %.