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Supporting Information

Systematic Ligand Variation to Modulate the Electrochemical Properties of Iron and Manganese Complexes

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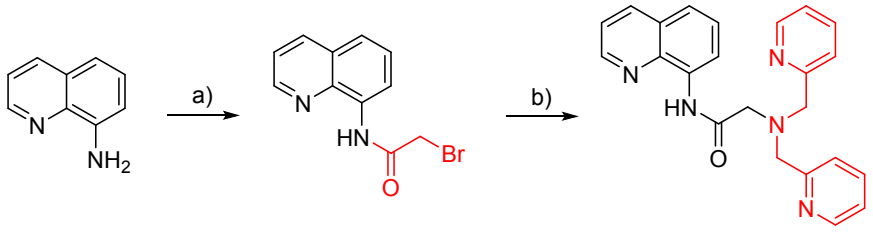
1. Synthetic Procedures and Characterizations

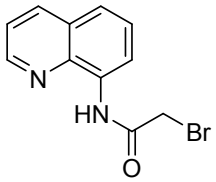
5-chloro-8-nitroquinoline (**6**), 5-methoxy-8-nitroquinoline (**7**) and the H-dpaq^{NO_2} ligand (**5e)** were synthesized according to reported procedures.[1]

1.1. Synthesis of (H-dpaq) (5a)

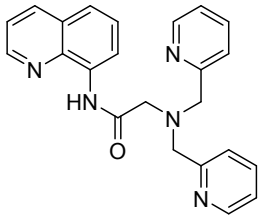


3a **4a** **5a**

Scheme S1. Reaction conditions: a) bromoacetylbromide, Na_2CO_3, MeCN, 0 °C, 20 min; b) bis(2-pyridylmethyl)amine, Na_2CO_3, MeCN, 0 °C to r.t, overnight.



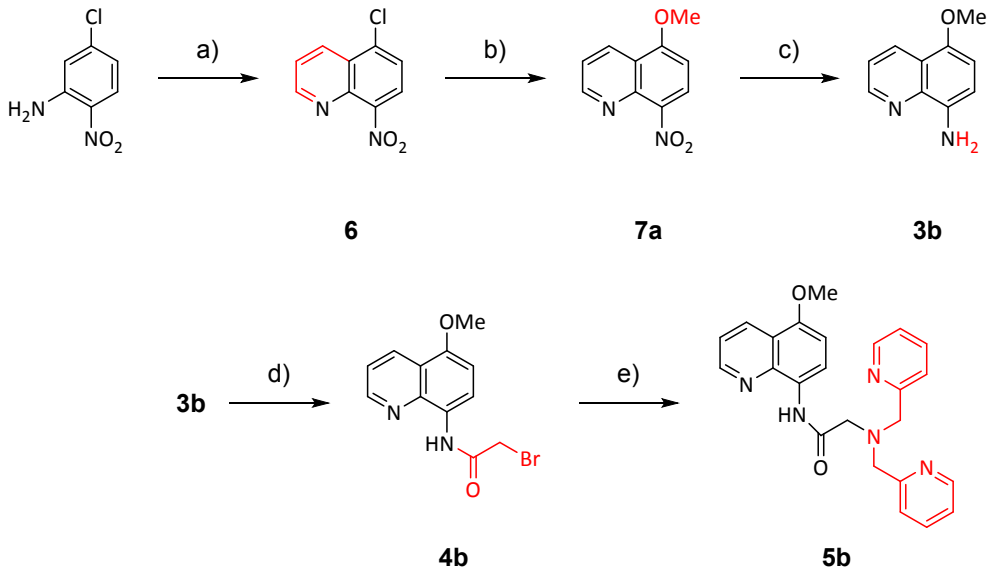
2-Bromo-*N*-(quinolin-8-yl)acetamide (4a). Bromoacetylbromide (146 μL, 1.68 mmol) was slowly added at 0 °C to a mixture of 8-aminoquinoline (**3a**, 200 mg, 1.39 mmol) and sodium carbonate (206 mg, 1.94 mmol) in dry acetonitrile (10 mL). The reaction mixture was stirred at 0 °C for 20 min before the fine dispersed solid was recovered by filtration. The filter cake was washed with acetonitrile (10 mL) and diethylether (10 mL) before drying under high vacuum led to 2-Bromo-*N*-(quinolin-8-yl)acetamide **(4a)** as a light beige solid (318 mg, 1.20 mmol, 86%). The obtained analytical data are consistent with those previously reported in the literature.[1d] **^{1}H-NMR** (400 MHz, CD_3OD, 296 K): δ = 8.88 (dd, *J* = 4.2 Hz, 1.7 Hz, 1H), 8.62 (dd, *J* = 7.7 Hz, 1.3 Hz, 1H), 8.31 (dd, *J* = 8.3 Hz, 1.7 Hz, 1H), 7.66 (dd, *J* = 8.3 Hz, 1.3 Hz, 1H), 7.57 (dd, *J* = 8.2 Hz, 4.1 Hz, 2H), 4.28 (s, 2H). **^{13}C{^{1}H}-NMR** (101 MHz, CD_3OD, 296 K): δ = 167.0, 150.2, 140.0, 137.7, 135.1, 129.6, 127.9, 124.1, 123.2, 118.1, 30.2.



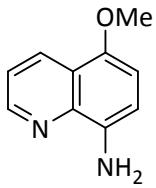
2-(Bis(pyridin-2-ylmethyl)amino)-*N*-(quinolin-8-yl) acetamide (H-dpaq, 5a). Bis(2-pyridylmethyl)amine (162 μL, 0.90 mmol) was slowly added at 0 °C to a mixture of 2-bromo-*N*-(quinolin-8-yl)acetamide (**4a**, 270 mg, 1.02 mmol) and sodium carbonate (111 mg, 1.05 mmol) in acetonitrile (15 mL). The mixture was slowly warmed up to room temperature and stirring was continued overnight. The resulting mixture was filtered over fritted glass to remove excess sodium carbonate. The solution was concentrated to 3 mL leading to the precipitation of a beige solid that was recovered by filtration. The

residue was washed with diethylether (10 mL). Subsequent drying under high vacuum led to **H-dpaq (5a)** as a beige solid (356 mg, 0.929 mmol, 67%). The obtained analytical data are consistent with those previously reported in the literature.[1d] **^{1}H-NMR** (400 MHz, CD_3CN, 296 K): δ = 11.46 (s, 1H), 9.01 (dd, *J* = 1.7 Hz, 2.6 Hz, 1H), 8.65 (dd, *J* = 1.1 Hz, 6.5 Hz, 1H), 8.47 (d, *J* = 4.9 Hz, 2H), 8.31 (dd, *J* = 1.6 Hz, 6.8 Hz, 1H), 7.90 (d, *J* = 7.9 Hz, 2H), 7.70 (td, *J* = 1.7 Hz, 6.0 Hz, 2H), 7.63-7.58 (m, 2H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.18 (dd, *J* = 2.1 Hz, 7.6 Hz, 2H), 3.95 (s, 4H), 3.50 (s, 2H).**^{13}C{^{1}H}-NMR** (101 MHz, CD_3CN, 296 K): δ = 170.4, 159.3, 149.9, 149.8, 139.4, 137.5, 137.3, 135.4, 129.1, 128.0, 124.4, 123.3, 123.0, 122.6, 116.6, 61.7, 60.1.

1.1. Synthesis of (H-dpaq$^{5\text{-OMe}}$) (5b)

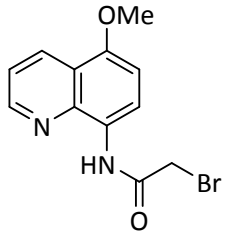


Scheme S2. Reaction conditions: a) glycerol, NaI, H_2SO_4, 150 °C, 2 h ; b) NaOMe, MeOH, reflux, 2 h; c) $SnCl_2 \cdot 2\,H_2O$, EtOH, reflux, 1 h; d) bromoacetylbromide, Na_2CO_3, MeCN, 0 °C, 20 min; e) bis(2-pyridylmethyl)amine, Na_2CO_3, MeCN, 0 °C to r.t., overnight.

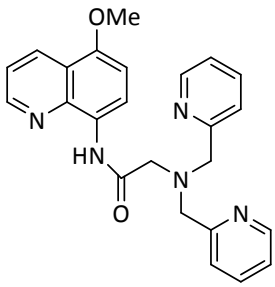


5-Methoxyquinolin-8-amine (3b). The synthesis was performed according to a modified reported procedure.[2] A mixture of 5-methoxy-8-nitroquinoline (**7**, 796 mg, 3.90 mmol) and tin chloride dihydrate (2.65 g, 11.8 mmol) in ethanol (25 mL) was stirred under reflux for one hour. After cooling to room temperature, the solution was diluted with ethyl acetate (15 mL) before an aqueous solution of sodium hydroxide (5 M) was added until pH 11 was reached. The organic phase was separated, washed with brine (3 x 15 mL) and dried over anhydrous sodium sulfate. The volatiles were removed *in vacuo* and drying of the obtained residue under high vacuum led to **5-methoxyquinolin-8-amine (3b)** as a black highly viscous gel (577 mg, 3.31 mmol, 85%). The obtained analytical data are consistent with those previously reported in the literature.[2] **^{1}H-NMR** (400 MHz, $CDCl_3$, 296 K): δ = 8.77 (dd, *J* = 1.8 Hz, 4.2 Hz, 1H), 8.47 (dd, *J* = 1.7 Hz, 8.4 Hz, 1H), 7.33 (dd,

J = 4.2 Hz, 8.5 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.68 (d, *J* = 8.2 Hz, 1H), 4.46 (br s, 2H), 3.88 (s, 3H). **^{13}C-APT-NMR** (101 MHz, $CDCl_3$, 296 K): δ = 148.1, 147.0, 139.1, 137.4, 130.8, 121.1, 120.4, 109.8, 105.4, 55.9.

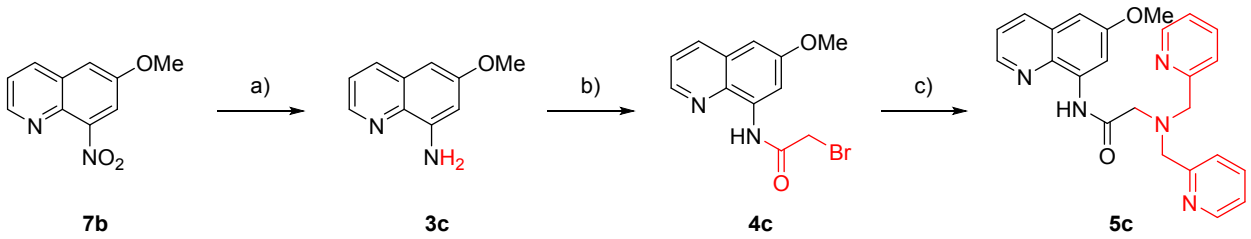


2-Bromo-*N*-(5-methoxyquinolin-8-yl)acetamide (4b). Bromoacetylbromide (290 μL, 3.35 mmol) was slowly added at 0 °C to a mixture of 5-methoxyquinolin-8-amine (**3b**, 485 mg, 2.78 mmol) and sodium carbonate (415 mg, 3.88 mmol) in dry acetonitrile (20 mL). The reaction mixture was stirred at 0 °C for 20 min before the fine dispersed solid was recovered by filtration. The obtained solid was washed with acetonitrile (2 mL). Subsequent drying under high vacuum led to **2-bromo-*N*-(5-methoxyquinolin-8-yl)acetamide (4b)** as a dark brown solid (630 mg, 3,62 mmol, 80%). **^{1}H-NMR** (300 MHz, CD_3CN, 296 K): δ = 9.98 (s, 1H), 8.94 (d, *J* = 8.9 Hz, 1H), 8.89 (dd, *J* = 1.6 Hz, 4.9 Hz, 1H), 8.31 (d, *J* = 8.7 Hz, 1H), 7.73 (dd, *J* = 4.9 Hz, 8.6 Hz, 1H), 7.08 (dd, *J* = 3.7 Hz, 8.7 Hz, 1H), 4.25 (d, *J* = 2.9 Hz, 2H), 3.96 (s, 3H). **^{13}C-APT-NMR** (101 MHz, CD_3OD, 296 K): δ = 152.4, 148.4, 143.2, 132.7, 124.7, 123.2, 122.9, 120.6, 109.8, 104.9, 56.9, 26.2.

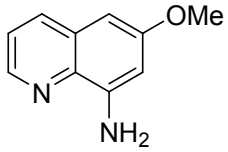


2-(Bis(pyridin-2-ylmethyl)amino)-*N*-(5-methoxyquinolin-8-yl)acetamide (H-dpaq$^{5\text{-OMe}}$, 5b). Bis(2-pyridylmethyl)amine (256 μL, 1.42 mmol) was slowly added at 0 °C to a mixture of 2-bromo-*N*-(5-methoxyquinolin-8-yl)acetamide (**4b**, 437 mg, 1.48 mmol) and sodium carbonate (169 mg, 1.59 mmol) in acetonitrile (23 mL). The mixture was then slowly warmed up to room temperature where it was stirred overnight and subsequently filtered over filter paper to remove excess sodium carbonate. The solvent of the filtrate was removed *in vacuo* and drying under high vacuum led to **2-(bis(pyridin-2-ylmethyl)amino)-*N*-(5-methoxyquinolin-8-yl)acetamide (5b)** as a dark brown liquid (102 mg, 0.247 mmol, 19%). The obtained analytical data are consistent with those previously reported in the literature.[1c] **^{1}H-NMR** (400 MHz, $CDCl_3$, 296 K): δ = 11.36 (s, 1H), 8.93 (dd, *J* = 1.8 Hz, 4.2 Hz, 1H), 8.68 (d, *J* = 8.5 Hz, 1H), 8.61 (dd, *J* = 1.7 Hz, 8.4 Hz, 1H), 8.52 (ddd, *J* = 0.9 Hz, 1.8 Hz, 4.8 Hz, 2H), 7.97 (dt, *J* = 1.2 Hz, 7.9 Hz, 2H), 7.65 (tdd, *J* = 1.8 Hz, 4.3 Hz, 7.7 Hz, 2H), 7.49 (dd, *J* = 4.2 Hz, 8.4 Hz, 1H), 7.20-7.12 (m, 2H), 6.83 (d, *J* = 8.6 Hz, 1H), 4.01 (s, 4H), 3.99 (s, 3H), 3.51 (d, *J* = 1.2 Hz, 2H). **^{13}C-APT-NMR** (101 MHz, $CDCl_3$, 296 K): δ = 169.1, 158.5, 150.5, 149.3, 139.7, 136.7, 136.6, 131.4, 128.0, 123.5, 122.5, 122.1, 120.7, 116.9, 104.6, 61.2, 59.4, 55.9.

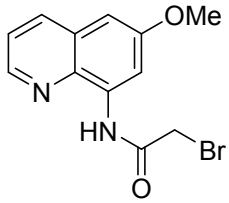
1.2. Synthesis of (H-dpaq$^{6\text{-OMe}}$) (5c)



Scheme S3. Reaction conditions: a) $SnCl_2 \cdot 2\,H_2O$, EtOH, reflux, 1 h; b) bromoacetylbromide, Na_2CO_3, MeCN, 0 °C, 20 min; c) bis(2-pyridylmethyl)amine, Na_2CO_3, MeCN, 0 °C to r.t., overnight.

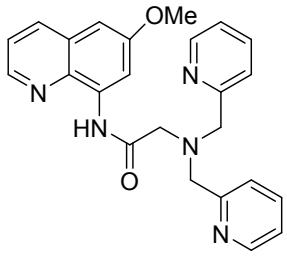


6-Methoxyquinolin-8-amine (3c). The synthesis was performed according to a modified reported procedure.[2] A mixture of 6-methoxy-8-nitroquinoline (**7b**, 1.00 g, 4.91 mmol) and tin chloride dihydrate (3.33 g, 14.8 mmol) in ethanol (20 mL) was stirred under reflux for one hour. After cooling to room temperature, the solution was diluted with ethyl acetate (15 mL) before an aqueous solution of sodium hydroxide (5 M) was added until pH 11 was reached. The organic phase was separated, washed with brine (3 x 15 mL) and dried over anhydrous sodium sulfate. The volatiles were removed *in vacuo* and drying of the obtained residue under high vacuum led to **6-methoxyquinolin-8-amine (3c)** as a black highly viscous gel (656 mg, 3.77 mmol, 77%). The obtained analytical data are consistent with those previously reported in the literature.[2] **^{1}H-NMR** (400 MHz, $CDCl_3$, 296 K): δ = 8.60 (dd, *J* = 1.6 Hz, 4.3 Hz, 1H), 7.96 (dd, *J* = 1.6 Hz, 8.3 Hz, 1H), 7.32 (dd, *J* = 4.3 Hz, 8.3 Hz, 1H), 6.58 (d, *J* = 2.5 Hz, 1H), 6.48 (d, *J* = 2.6 Hz, 1H), 5.01 (br s, 2H), 3.88 (s, 3H). **^{13}C-APT-NMR** (101 MHz, $CDCl_3$, 296 K): δ = 159.4, 145.4, 145.2, 135.5, 130.4, 122.2, 102.2, 95.0, 55.8.



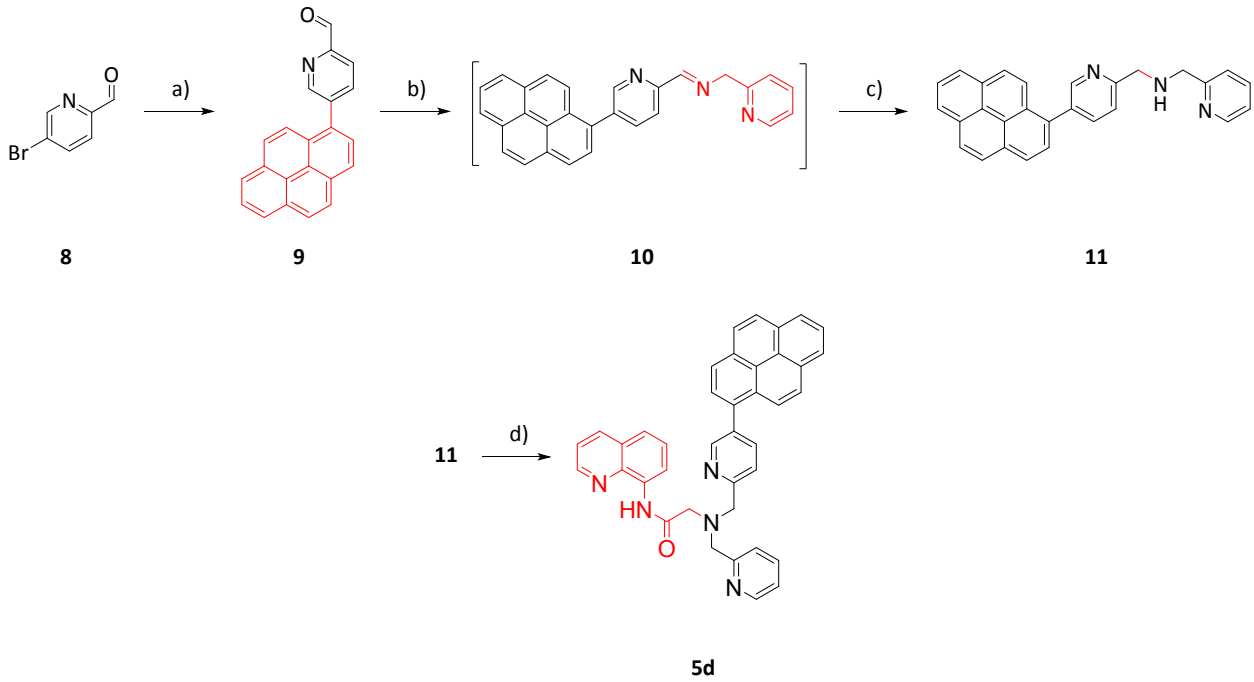
2-Bromo-*N*-(6-methoxyquinolin-8-yl)acetamide (4c). Bromoacetylbromide (290 μL, 3.35 mmol) was slowly added at 0 °C to a mixture of 6-methoxyquinolin-8-amine (**3c**, 485 mg, 2.78 mmol) and sodium carbonate (415 mg, 3.88 mmol) in dry acetonitrile (20 mL). The reaction mixture was stirred at 0 °C for 20 min before the fine dispersed solid was recovered by filtration. The obtained solid was washed with acetonitrile (2 mL). Subsequent drying under high vacuum led to **2-bromo-*N*-(6-methoxyquinolin-8-yl)acetamide (4c)** as a light brown solid (475 mg, 1.61 mmol, 58%). **^{1}H-NMR** (400 MHz, CD_3OD, 296 K): δ = 8.97 (dd, *J* = 8.4 Hz, 1.5 Hz, 1H), 8.93 (dd, *J* = 5.2 Hz, 1.5 Hz, 1H), 7.98 (dd, *J* = 8.5 Hz, 5.2 Hz, 1H), 7.80 (d, *J* = 2.6 Hz, 1H), 7.59 (d, *J* = 2.7 Hz,

1H), 4.24 (s, 2H), 4.03 (s, 3H). **^{13}C-APT-NMR** (101 MHz, CD_3OD, 296 K): 169.1, 161.2, 145.6, 143.7, 140.0, 132.7, 132.0, 132.7, 122.8, 105.9, 57.0, 29.2.

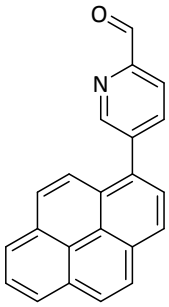


2-(Bis(pyridin-2-ylmethyl)amino)-*N*-(6-methoxyquinolin-8-yl)acetamide (H-dpaq$^{6\text{-OMe}}$, 5c). Bis(2-pyridylmethyl)amine (234 μL, 1.30 mmol) was slowly added at 0 °C to a mixture of 2-bromo-*N*-(6-methoxyquinolin-8-yl)acetamide (**4c**, 387 mg, 1.31 mmol) and sodium carbonate (154 mg, 1.45 mmol) in acetonitrile (25 mL). The mixture was then slowly warmed up to room temperature where it was stirred overnight and subsequently filtered over fritted glass to remove excess sodium carbonate. The solvent of the filtrate was removed *in vacuo* and drying under high vacuum led to **2-(bis(pyridin-2-ylmethyl)amino)-*N*-(6-methoxyquinolin-8-yl)acetamide (5c)** as a dark red liquid (102 mg, 0.247 mmol, 19%).**^{1}H-NMR** (400 MHz, $CDCl_3$, 296 K): δ = 11.47 (s, 1H), 8.71 (dd, *J* = 1.6 Hz, 4.2 Hz, 1H), 8.43 (ddd, *J* = 0.9 Hz, 1.8 Hz, 4.9 Hz, 2H), 8.39 (d, *J* = 2.7 Hz, 1H), 7.99 (dd, *J* = 1.6 Hz, 8.3 Hz, 1H), 7.89 (dt, *J* = 1.1 Hz, 7.9 Hz, 2H), 7.63-7.54 (m, 2H), 7.39 (dd, *J* = 4.2 Hz, 8.3 Hz, 1H), 7.08 (ddd, *J* = 1.2 Hz, 4.9 Hz, 7.5 Hz, 2H), 6.73 (d, *J* = 2.7 Hz, 1H), 3.92 (s, 4H), 3.82 (s, 3H), 3.45 (s, 2H). **^{13}C-APT-NMR** (101 MHz, $CDCl_3$, 296 K): δ = 169.5, 158.3, 158.0, 148.9, 145.5, 136.6, 135.3, 135.1, 134.9, 129.0, 123.3, 122.3, 122.1, 108.8, 99.7, 60.9, 59.2, 55.5. **HRMS (ESI$^+$):** *m/z:* calcd. for $C_{24}H_{23}N_5O_2$ $[M+Na]^+$: 436.17440; found: 436.17435.

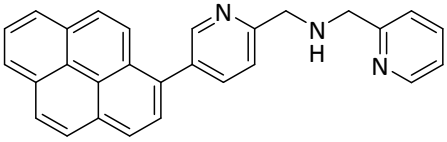
1.3. Synthesis of (H-dpaq^{Pyr}) (5d)



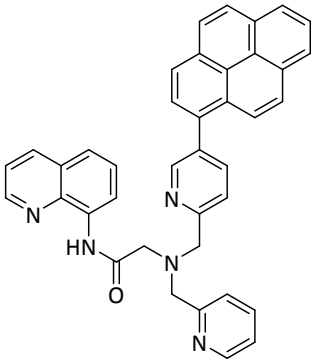
Scheme S4. Reaction conditions: a) pyren-1-ylboronic acid, $Pd(PPh_3)_4$, K_2CO_3, MeCN, 0 °C, 20 min; b) trimethylorthoformate, r.t., 1 h; c) $NaBH_4$, DCM/MeOH, r.t., overnight; d) 2-bromo-*N*-(quinolin-8-yl)acetamide (**4a**), Na_2CO_3, MeCN/DCM, 0 °C to r.t., overnight.



5-(Pyren-1-yl)picolinaldehyde (9). The synthesis was performed according to a modified reported procedure.[3] A mixture of pyren-1-ylboronic acid (0.738 g, 3.00 mmol), 5-bromopicolinaldehyde (**8**, 0.558 g, 3.00 mmol), tetrakis(triphenylphosphine)palladium (0.347 g, 0.300 mmol) and potassium carbonate (1.24 g, 9.00 mmol) in tetrahydrofuran (45 mL) and degassed water (9 mL) was stirred under reflux for 21 h. After that time, the reaction mixture was poured into cold water (50 mL) and was extracted with dichloromethane (3 x 25 mL). The combined organic phases were dried over anhydrous sodium sulfate and the volatiles were removed *in vacuo*. The brownish-yellow residue was purified via column chromatography over silica with a mixture of petrol ether/ethyl acetate (gradient PE/EtOAc 9:1 up to 0:1) as eluent. **5-(Pyren-1-yl)picolinaldehyde (9)** was obtained as a yellow solid (0.640 g, 2.08 mmol, 70%). **^{1}H-NMR** (600 MHz, CD_2Cl_2, 296 K): δ = 10.21 (s, 1H), 9.06 (s, 1H), 8.28 (d, *J* = 7.8 Hz, 1H), 8.26 (d, *J* = 7.8 Hz, 1H), 8.22 (d, *J* = 7.5 Hz, 1H), 8.17-8.12 (m, 4H), 8.11-8.05 (m, 3H), 7.98 (d, *J* = 7.8 Hz, 1H). **^{13}C{^{1}H}-NMR-**(151 MHz, CD_2Cl_2, 296 K): δ = 193.6, 152.0, 151.9, 141.6, 139.1, 132.8, 132.0, 131.8, 131.2 , 129.0, 128.9, 128.6, 127.9, 127.7, 126.8, 126.2, 125.8, 125.3, 125.0, 124.3, 121.6. **HRMS (ESI$^+$):** *m/z:* calcd. for $C_{22}H_{13}NO$ $[M+Na]^+$: 330.08894; found: 330.08841.



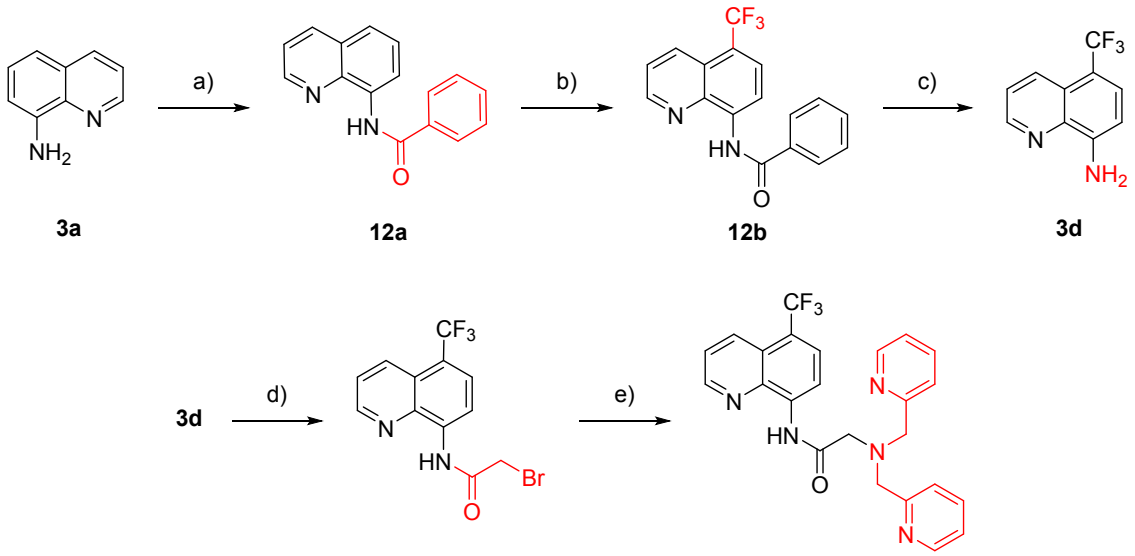
1-(5-(Pyren-1-yl)pyridin-2-yl)-*N*-(pyridin-2-ylmethyl)methanamine (11). The synthesis was performed according to a modified reported procedure.[4] Pyridin-2-ylmethanamine (0.103 mL, 1.00 mmol) was slowly added at room temperature to a solution of 5-(pyren-1-yl)picolinaldehyde (**9**, 0.307 g, 1.00 mmol) in dry trimethylorthoformate (15 mL). After stirring the solution at room temperature for one hour, the solvent was removed under high vacuum. The obtained brownish residue (**10**) was then dissolved in a mixture of dichloromethane (12 mL) and methanol (3 mL), and sodium borohydride (0.078 g, 2.07 mmol) was slowly added to the solution. The resulting mixture was then stirred at room temperature overnight, before being poured into water (20 mL) and adjusting the pH value to 14 by adding an aqueous solution of sodium hydroxide (10 M). The mixture was extracted with diethylether (3 x 20 mL) and the combined organic phases were washed with an aqueous solution of sodium hydroxide (0.5 M, 2 x 20 mL). Subsequently, an aqueous solution of citric acid (1 M, 3 x 20 mL) was added and the pH value was then again adjusted to 14 by addition of an aqueous solution of sodium hydroxide (10 M). The mixture was extracted with dichloromethane (3 x 20 mL). The combined organic phases were dried over anhydrous sodium sulfate and the solvent was removed *in vacuo*. The obtained residue was dried under high vacuum leading to **1-(5-(pyren-1-yl)pyridin-2-yl)-*N*-(pyridin-2-ylmethyl)methanamine (11)** as a yellow oil (0.350 g, 0.876 mmol, 88%). **^{1}H-NMR** (600 MHz, CD_2Cl_2, 296 K): $\delta =$ 8.82 (d, *J* = 2.1 Hz, 1H), 8.58 (d, *J* = 4.8 Hz, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 8.23 (dd, *J* = 6.7 Hz, 0.9 Hz, 1H), 8.19 (d, *J* = 7.4 Hz, 1H), 8.14-8.10 (m, 3H), 8.07-8.02 (m, 2H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.93 (dd, *J* = 2.3 Hz, 5.5 Hz, 1H), 7.69 (td, *J* = 1.9 Hz, 5.9 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.20 (dd, *J* = 4.9 Hz, 2.6 Hz, 1H), 4.12 (s, 2H), 4.08 (s, 2H), 3.06 (br s, 1H). **^{13}C{^{1}H}-NMR** (151 MHz, CD_2Cl_2, 296 K): $\delta =$ 160.0, 158.9, 150.7, 149.6, 138.6, 136.8, 135.4, 134.2, 131.8, 131.4, 131.3, 129.1, 128.3, 128.1, 127.7, 126.6, 125.8, 125.5, 125.3, 125.2, 125.1, 124.9, 122.6, 122.4, 122.2, 55.0, 54.8. **HRMS (ESI$^+$):** *m/z:* calcd. for $C_{28}H_{21}N_3$ $[M+H]^+$: 400.18082; found: 400.18088.



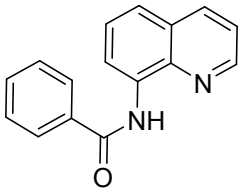
2-(((5-(Pyren-1-yl)pyridin-2-yl)methyl)(pyridin-2-ylmethyl)amino)-*N*-(quinolin-8-yl)acetamide (H-dpaq^{Pyr}, 5d). A solution of 1-(5-(pyren-1-yl)pyridin-2-yl)-*N*-(pyridin-2-ylmethyl)methanamine (**11**, 280 mg, 0.70 mmol) in dry dichloromethane (2 mL) was slowly added at 0 °C to a solution of 2-Bromo-*N*-(quinolin-8-yl)acetamide (**4a**, 199 mg, 0.750 mmol) and sodium carbonate (85 mg, 0.80 mmol) in dry acetonitrile (12 mL). The mixture was then slowly warmed up to room temperature where it was

stirred overnight and subsequently filtered over fritted glass to remove excess sodium carbonate. After removal of the volatiles *in vacuo*, the crude product remained as a dark red oil and was purified via column chromatography over silica with a mixture of ethyl acetate/methanol (gradient: 1:0 up to 9:1) as eluent. **H-dpaq^{Pyr} (5d)** was obtained as a brownish solid (160 mg, 0.274 mmol, 39%). **^{1}H-NMR** (600 MHz, CD_2Cl_2, 296 K): δ = 11.67 (s, 1H), 8.99 (dd, *J* = 1.7 Hz, 2.6 Hz, 1H), 8.80-8.77 (m, 2H), 8.56 (d, *J* = 4.8 Hz, 1H), 8.22 (dd, *J* = 2.9 Hz, 5.0 Hz, 2H), 8.19 (dd, *J* = 1.7 Hz, 6.6 Hz, 1H), 8.17 (dd, *J* = 2.5 Hz, 5.5 Hz, 2H), 8.10 (q, *J* = 3.7 Hz, 8.9 Hz, 2H), 8.05 (d, *J* = 7.9 Hz, 1H), 8.03 (t, *J* = 7.6 Hz, 1H), 8.01 (q, *J* = 9.3 Hz, 5.2 Hz, 2H), 7.92 (dd, *J* = 2.3 Hz, 5.6 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.79 (td, *J* = 1.8 Hz, 5.9 Hz, 1H), 7.57-7.53 (m, 2H), 7.51-7.48 (m, 1H), 7.20 (dd, *J* = 5.0 Hz, 2.5 Hz, 1H), 4.17 (s, 2H), 4.14 (s, 2H), 3.66 (s, 2H). **^{13}C{^{1}H}-NMR** (151 MHz, CD_2Cl_2, 296 K): δ = 169.9, 158.8, 157.6, 150.5, 149.5, 148.7, 139.2, 138.7, 136.9, 136.7, 135.7, 135.0, 134.0, 131.8, 131.4, 131.2, 129.0, 128.6, 128.3, 128.1, 128.0, 127.7, 126.6, 125.8, 125.4, 125.2, 125.1, 125.0, 124.8, 123.9, 123.4, 122.7 , 122.1, 121.0, 116.5, 61.7, 61.4, 60.0. **HRMS (ESI$^+$):** *m/z:* calcd. for $C_{39}H_{29}N_5O$ $[M+H]^+$: 584.24449; found: 584.24445.

1.4. Synthesis of (H-dpaq^{CF3})

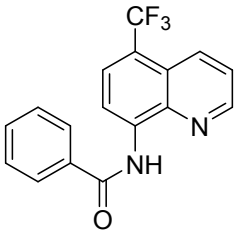


Scheme S5. Reaction conditions: a) benzoylchloride, Et_3N, CH_2Cl_2, r.t, overnight; b) NH_2SO_3H, $PhI(OAc)_2$, $NaSO_2CF_3$, dichloroethane, 50 °C, 24 h; c) HCl, EtOH, 100 °C, 24 h; d) bromoacetylbromide, Na_2CO_3, MeCN, 0 °C, 20 min; e) bis(2-pyridylmethyl)amine, Na_2CO_3, MeCN, 0 °C to r.t., overnight.

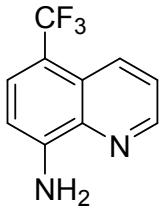


***N*-(quinolin-8-yl)benzamide (12a).** The synthesis was performed according to a modified reported procedure.[5] A solution of benzoylchloride (700 mg, 5.0 mmol),

8-aminoquinoline (**3a**, 665 mg, 4.6 mmol) and triethylamine (0.765 mL, 5.5 mmol) in dry dichloromethane (10 mL) at room temperature was stirred overnight. Subsequently, water (10 mL) was added and the mixture was extracted with dichloromethane (3 x 20 mL). The combined organic phases were washed with water (20 mL) and brine (20 mL) and were dried over anhydrous sodium sulfate before the solvent was removed *in vacuo*. Drying under high vacuum led to ***N*-(quinolin-8-yl)benzamide (12a)** as a brownish-grey solid (985 mg, 3.97 mmol, 86%). The obtained analytical data are consistent with those previously reported in the literature.[6] **^{1}H-NMR** (400 MHz, CD_2Cl_2, 296 K): δ = 10.8 (s, 1H), 8.90 (dd, *J* = 2.0 Hz, 6.8 Hz, 1H), 8.87 (d, *J* = 4.0 Hz, 1H), 8.23 (d, *J* = 8.2 Hz, 1H), 8.08 (d, *J* = 7.6 Hz, 2H), 7.64-7.54 (m, 5H), 7.51 (dd, *J* = 4.3 Hz, 8.3 Hz, 1H). **^{13}C{^{1}H}-NMR** (101 MHz, CD_2Cl_2, 296 K): δ = 165.5, 148.8, 139.1, 136.9, 135.6, 135.1, 132.2, 129.3, 129.2, 128.8, 128.5, 127.7, 127.6, 122.2, 122.1, 116.7.

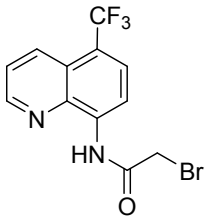


***N*-(5-(Trifluoromethyl)quinolin-8-yl)benzamide (12b).** The synthesis was performed according to a modified reported procedure.[5] A mixture of *N*-(quinolin-8-yl)benzamide (**12a**, 2.48 g, 10.0 mmol), sodium trifluoromethanesulfinate (6.24 g, 20.0 mmol), diacetoxyiodobenzene (6.44 g, 20.0 mmol), sulfamic acid (6.44 g, 20.0 mmol) and dichloroethane (50 mL) was stirred at 50 °C for 24 h. After cooling down to room temperature, the mixture was diluted with dichloromethane (25 mL) and filtered over celite. The filter cake was washed with dichloromethane (3 x 8 mL) and the solvent of the filtrate was removed *in vacuo*. The resulting crude product was purified by column chromatography over silica with a mixture of petrol ether/ethyl acetate (1:1) as eluent. ***N*-(5-(trifluoromethyl)quinolin-8-yl)benzamide (12b)** was obtained as a brownish-grey solid (670.5 mg, 2.12 mmol, 21%). The obtained analytical data are consistent with those previously reported in the literature.[5] **^{1}H-NMR** (400 MHz, CD_2Cl_2, 296 K): δ = 10.9 (s, 1H), 8.99-8.92 (m, 2H), 8.54 (d, *J* = 8.7 Hz, 1H), 8.09 (d, *J* = 7.6 Hz, 2H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.69-7.55 (m, 5H). **^{13}C-APT-NMR** (101 MHz, CD_2Cl_2, 296 K): δ = 165.8, 149.3, 139.0, 138.2, 135.0, 133.5, 132.6, 128.9, 128.0, 127.7, 127.0 (q, *J* = 5.8 Hz), 126.2, 124.7, 123.5, 119.6, 114.2. **^{19}F{^{1}H}-NMR** (377 MHz, CD_2Cl_2, 296 K): δ = -59.0.

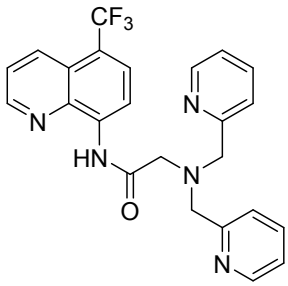


5-(Trifluoromethyl)quinolin-8-amine (3d). The synthesis was performed according to a modified reported procedure.[5] Concentrated hydrochloric acid (5.3 mL) was added to a solution of *N*-(5-(trifluoromethyl)chinolin-8-yl)benzamide (**12b**, 670.5 mg, 2.12 mmol) in ethanol (14 mL). The solution was stirred at 100 °C for 24 h. After that time, the reaction mixture was cooled down to room temperature, concentrated *in vacuo* and an aqueous solution of sodium hydroxide (3 M) was added until the basic pH range was reached. The product was

extracted with dichloromethane (3 x 20 mL) and the combined organic phases were dried over anhydrous sodium sulfate. After removal of the volatiles *in vacuo*, the crude product was further purified via column chromatography on silica with a mixture of dichloromethane/ethyl acetate (gradient: 9:1 up to 1:1) as eluent. **5-(Trifluoromethyl)quinolin-8-amine (3d)** was obtained as a brownish-grey solid (137.9 mg, 0.650 mmol, 31%). The obtained analytical data are consistent with those previously reported in the literature.[5] **^{1}H-NMR** (400 MHz, $CDCl_3$, 296 K): δ = 8.83 (d, *J* = 4.2 Hz, 1H), 8.51 (d, *J* = 8.8 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.58 (dd, *J* = 4.3 Hz, 8.6 Hz, 1H), 6.88 (d, *J* = 8.1 Hz, 1H), 5.84 (br-s, 2H). **^{13}C-APT-NMR** (101 MHz, $CDCl_3$, 296 K): δ = 147.4, 147.2, 133.7, 127.2 (q, J = 5.7 Hz), 126.3, 125.5, 123.6, 122.6, 107.3. **^{19}F{^{1}H}-NMR** (377 MHz, $CDCl_3$, 296 K): δ = -57.9.



2-Bromo-*N*-(5-(trifluoromethyl)quinolin-8-yl)acetamide (4d). Bromoacetylbromide (68.2 μL, 0.78 mmol) was slowly added at 0 °C to a solution of 5-(trifluoromethyl)quinolin-8-amine (**3d**, 138 mg, 0.65 mmol) and sodium carbonate (96.2 mg, 0.91 mmol) in dry acetonitrile (10 mL). The reaction mixture was stirred at 0 °C for 20 min before the fine dispersed solid was recovered by filtration. The obtained solid was washed with acetonitrile (3 mL) and diethylether (10 mL), before drying under high vacuum led to 2-Bromo-*N*-(5-(trifluoromethyl)quinolin-8-yl)acetamide **(4d)** as a grey solid (198 mg, 0.59 mmol, 91%). **^{1}H-NMR** (300 MHz, CD_3CN, 296 K): δ = 11.0 (s, 1H), 9.25 (dt, *J* = 8.8 Hz, *J* = 1.5 Hz, 1H), 9.16 (dd, *J* = 5.3 Hz, *J* = 1.5 Hz, 1H), 8.87 (d, *J* = 8.5 Hz, 1H), 8.32 (d, *J* = 8.5 Hz, 1H), 8.22 (dd, *J* = 8.8 Hz, 5.3 Hz, 1H), 4.52 (s, 2H). **^{19}F{^{1}H}-NMR** (377 MHz, CD_2Cl_2, 296 K): δ = -59.2. **HRMS (ESI$^+$):** *m/z:* calcd. for $C_{12}H_9F_3N_2BrO$ $[M+H]^+$: 332.98449; found: 332.98445.



2-(Bis(pyridin-2-ylmethyl)amino)-*N*-(5-(trifluoromethyl)quinolin-8-yl)acetamide (H-dpaq^{CF3}, 5f). Bis(2-pyridylmethyl)amine (103 μL, 0.57 mmol) was slowly added at 0 °C to a mixture of 2-bromo-*N*-(5-(trifluoromethyl)quinolin-8-yl)acetamide (**4d**, 198 mg, 0.60 mmol) and sodium carbonate (68 mg, 0.64 mmol) in dry acetonitrile (9 mL). The mixture was then slowly warmed up to room temperature and stirring was continued overnight. The resulting mixture was filtered over fritted glass to remove excess sodium carbonate. The solvent of the filtrate was removed *in vacuo* and the obtained residue was dried under high vacuum leading to **H-dpaq^{CF3}** (**5f**) as a red solid (75 mg, 0.17 mmol, 26%) which was used without further purification. **^{1}H-NMR** (400 MHz, CD_3CN, 296 K): δ = 11.7 (s, 1H), 9.10 (d, *J* = 4.1 Hz, 1H), 8.68 (d, *J* = 8.2 Hz, 1H), 8.55 (dt, *J* = 1.9 Hz, 8.8 Hz, 1H), 8.47 (d, *J* = 4.7 Hz, 2H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 7.7 Hz, 2H), 7.76 (dd,

J = 4.1 Hz, 8.7 Hz, 1H), 7.68 (dt, *J* = 1.7 Hz, 7.7 Hz, 2H), 7.17 (dd, *J* = 5.4 Hz, 7.0 Hz, 2H), 3.97 (s, 4H), 3.54 (s, 2H). **^{13}C-APT-NMR** (101 MHz, CD_3CN, 296 K): δ = 171.3, 159.3, 150.5, 150.0, 137.5, 129.3, 133.6, 127.6 (q, *J* = 6.0 Hz), 124.5, 123.4, 118.3, 114.3, 61.9, 60.3. **^{19}F{^{1}H}-NMR** (377 MHz, CD_3CN, 296 K): δ = -59.3. **HRMS (ESI$^+$):** *m/z:* calcd. for $C_{24}H_{20}F_3N_5O$ $[M+Na]^+$: 474.15122; found: 474.14902.

2. Supporting Figures

2.1. NMR spectra

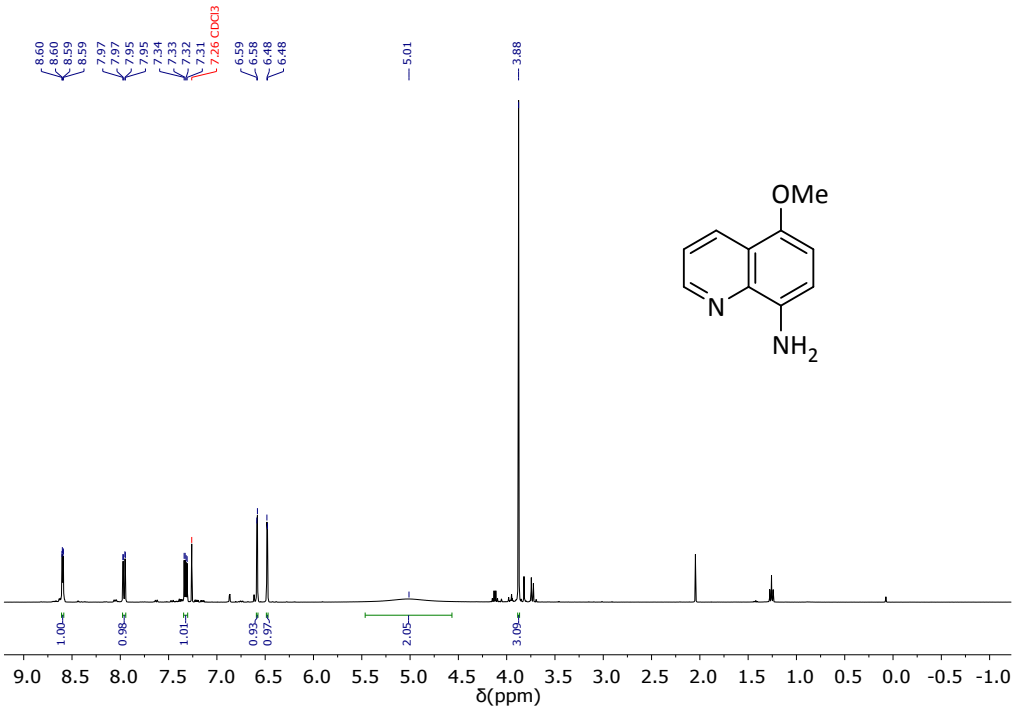


Figure S1. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$, 296 K) of 5-Methoxyquinolin-8-amine (**3b**).

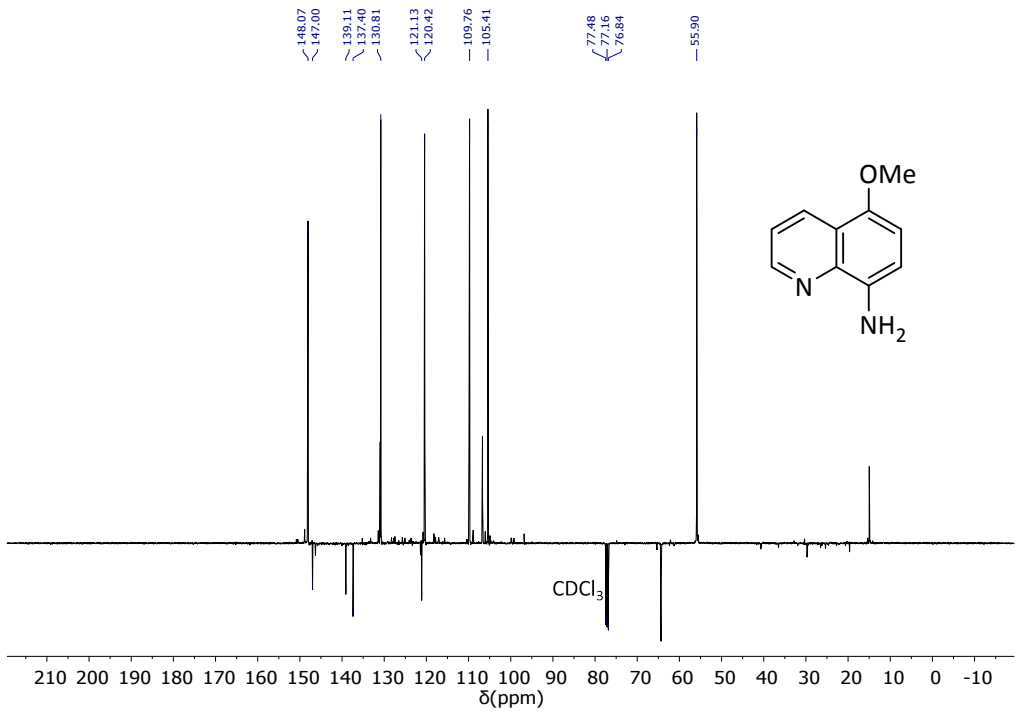


Figure S2. ^{13}C-APT-NMR spectrum (101 MHz, $CDCl_3$, 296 K) of 5-Methoxyquinolin-8-amine (**3b**).

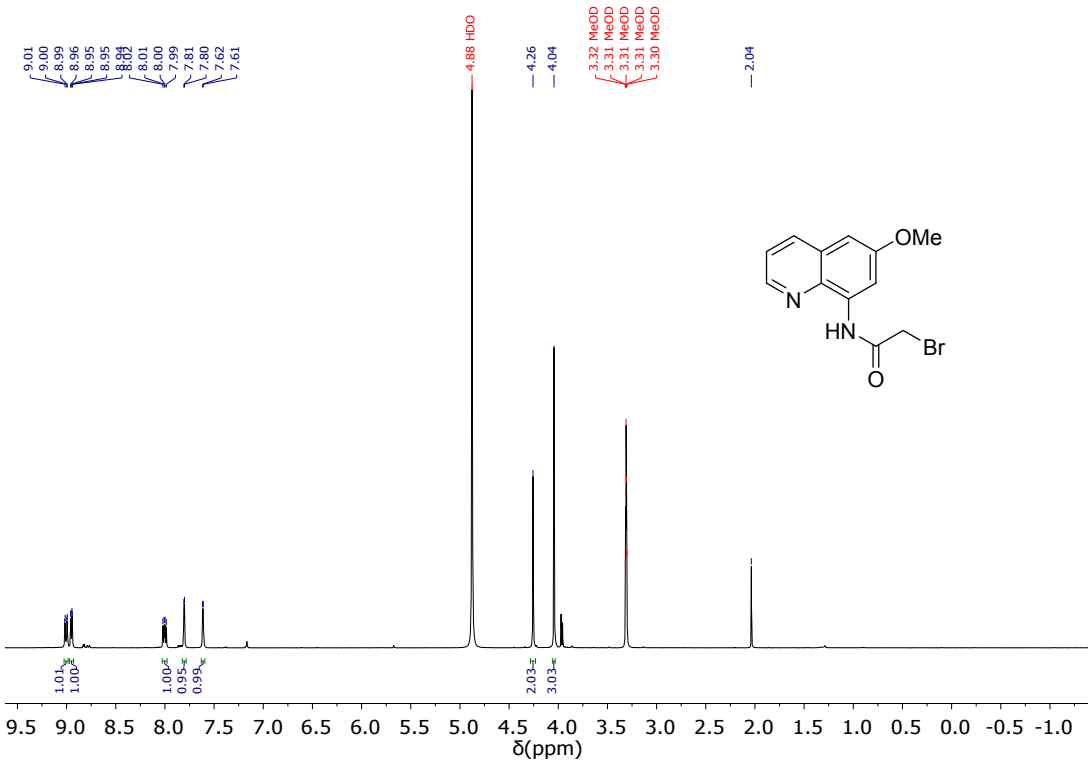


Figure S3. ^{1}H-NMR spectrum (400 MHz, CD_3OD, 296 K) of 2-bromo-*N*-(6-methoxyquinolin-8-yl)acetamide (**4c**).

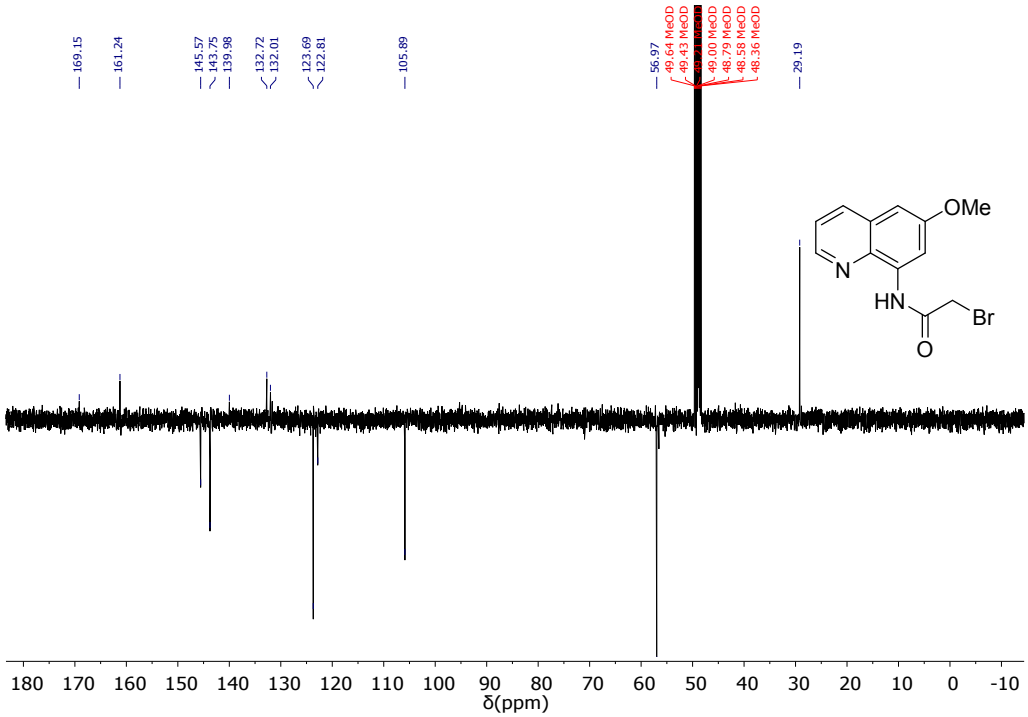


Figure S4. ^{13}C-APT-NMR spectrum (101 MHz, CD_3OD, 296 K) of 2-bromo-*N*-(6-methoxyquinolin-8-yl)acetamide (**4c**).

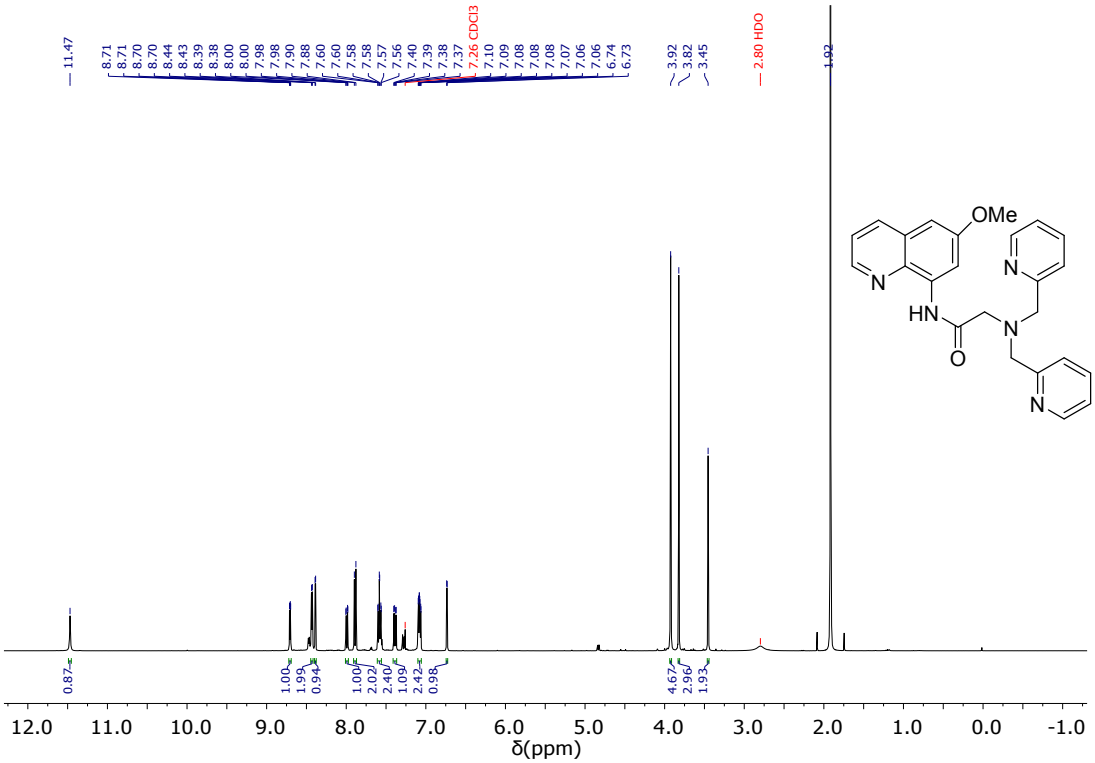


Figure S5. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$, 296 K) of H-dpaq$^{6\text{-OMe}}$ (**5c**).

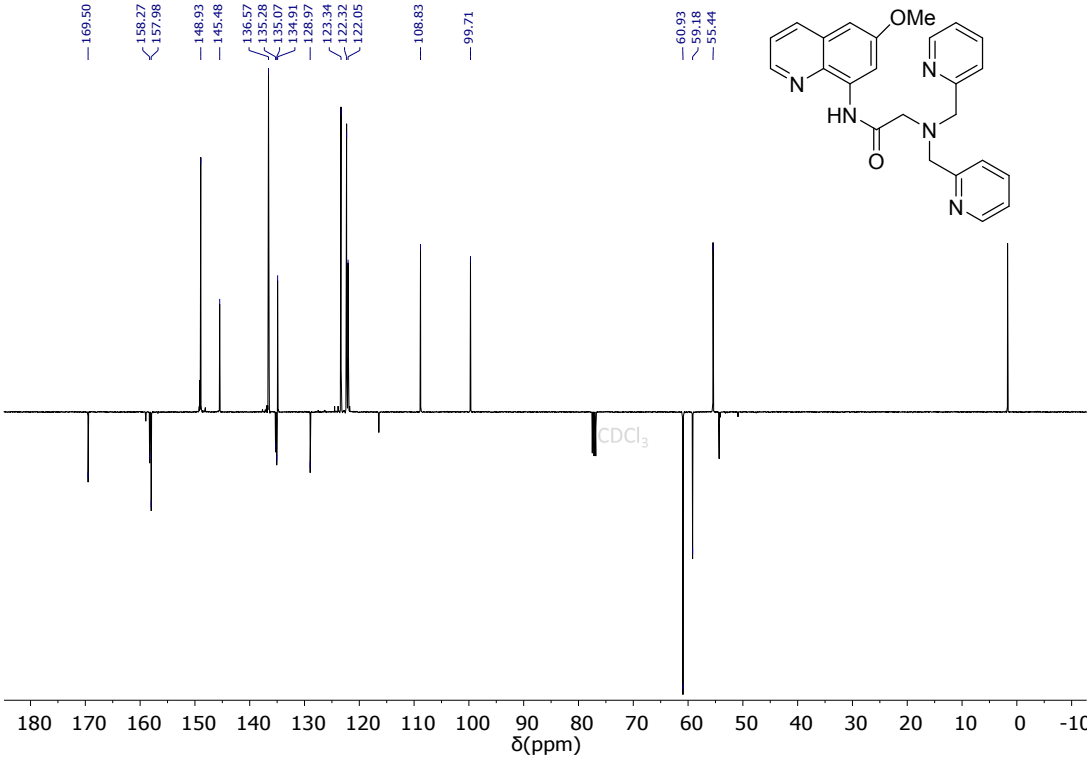


Figure S6. ^{13}C-APT-NMR spectrum (101 MHz, $CDCl_3$, 296 K) of H-dpaq$^{6\text{-OMe}}$ (**5c**).

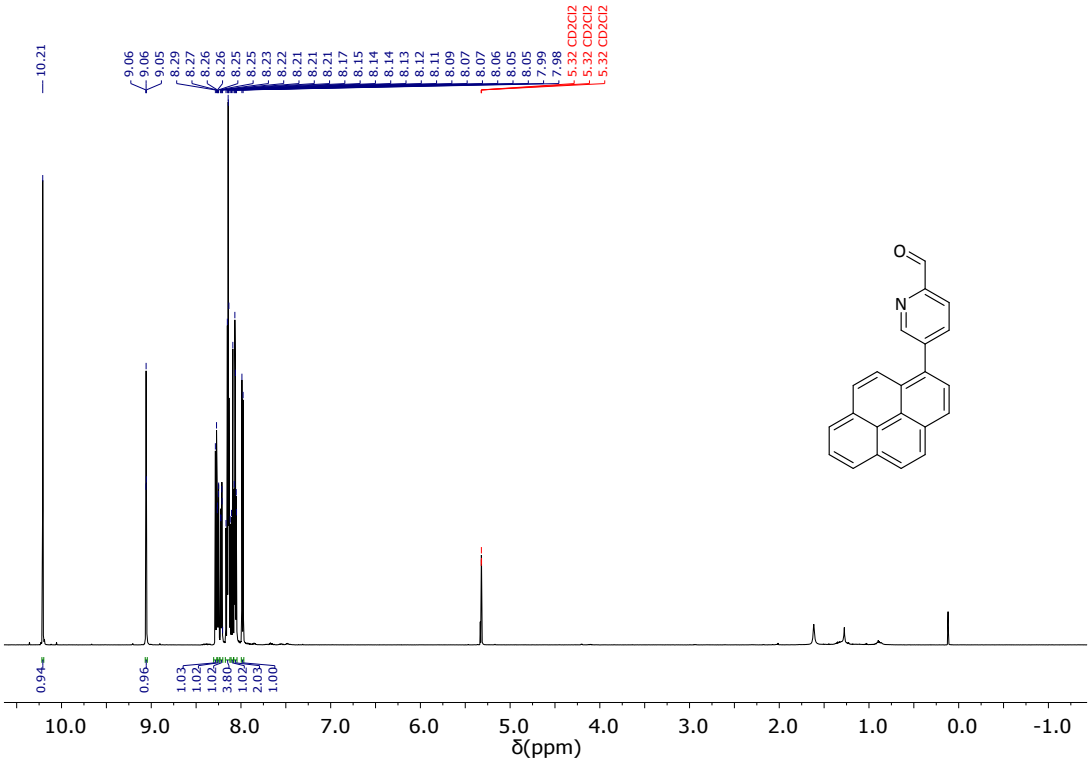


Figure S7. ^{1}H-NMR spectrum (600 MHz, CD_2Cl_2, 296 K) of 5-(pyren-1-yl)picolinaldehyde (**9**).

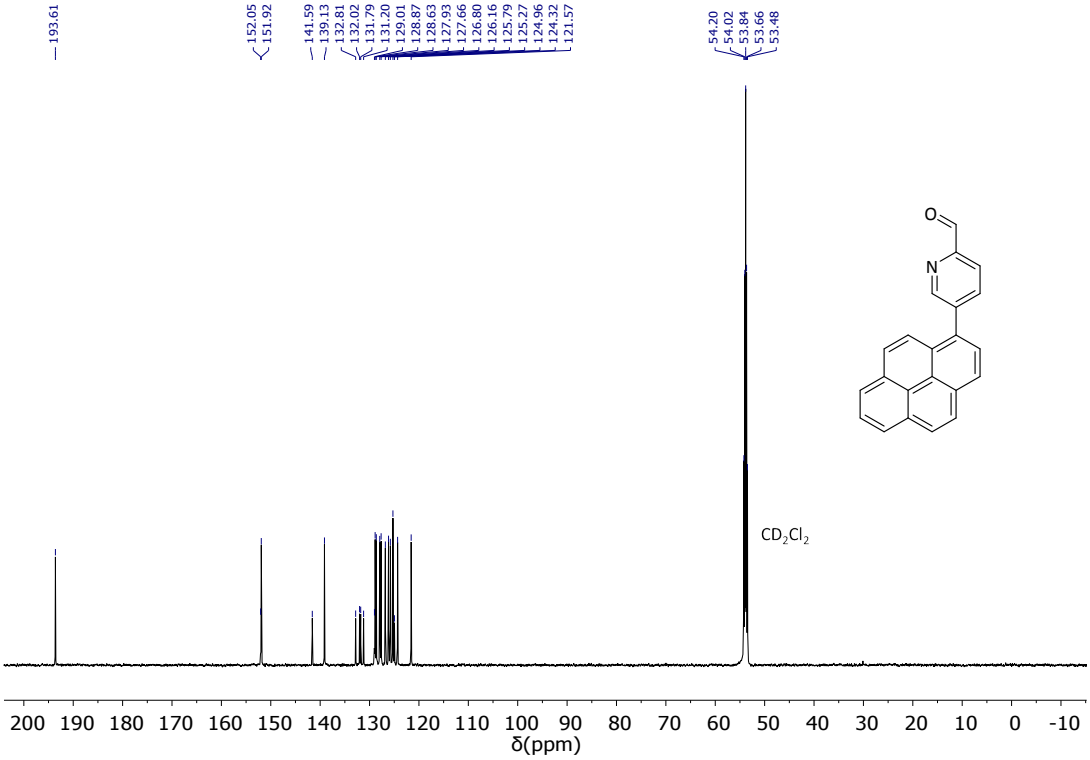


Figure S8. $^{13}C\{^{1}H\}$-NMR spectrum (151 MHz, CD_2Cl_2, 296 K) of 5-(pyren-1-yl)picolinaldehyde (**9**).

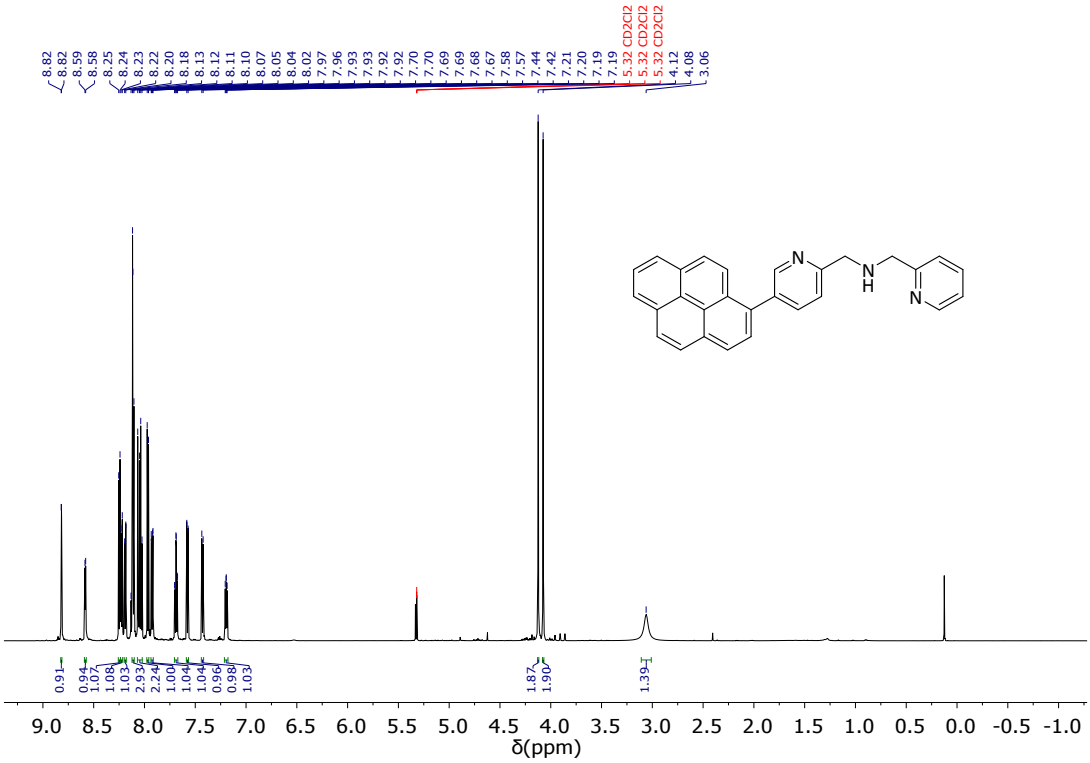


Figure S9. ^{1}H-NMR spectrum (600 MHz, CD_2Cl_2, 296 K) of 1-(5-(pyren-1-yl)pyridin-2-yl)-*N*-(pyridin-2-ylmethyl)methanamine (**11**).

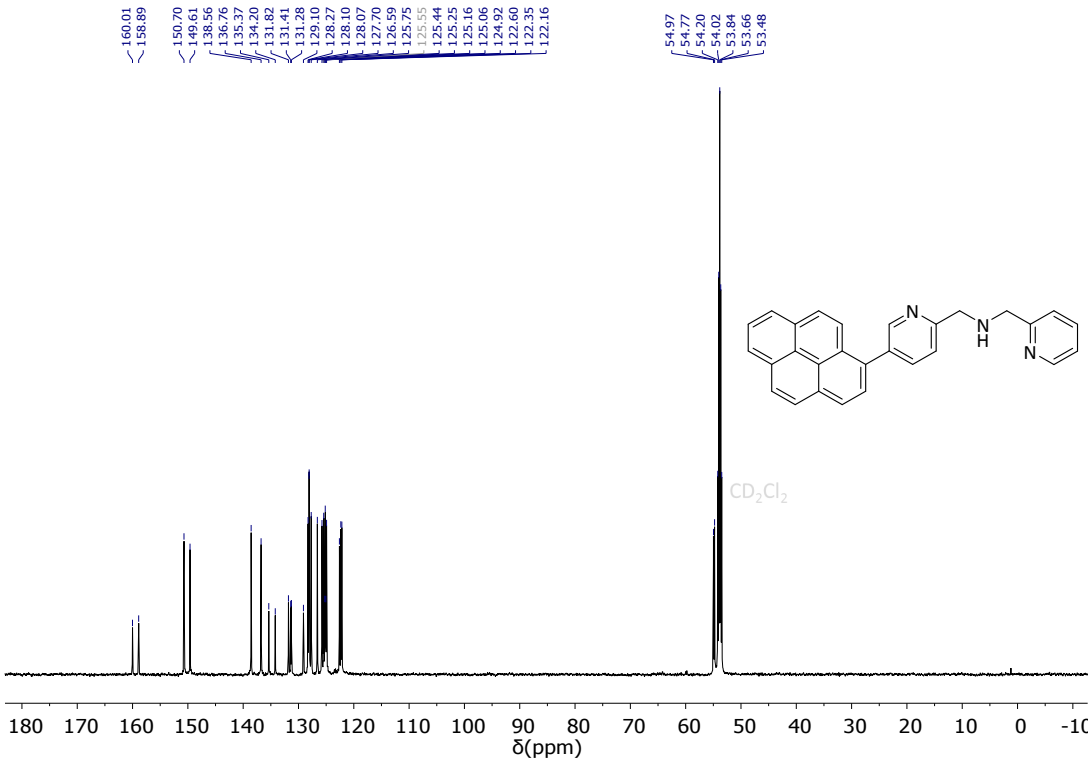


Figure S10. $^{13}C\{^{1}H\}$-NMR spectrum (151 MHz, CD_2Cl_2, 296 K) of 1-(5-(pyren-1-yl)pyridin-2-yl)-*N*-(pyridin-2-ylmethyl)methanamine (**11**).

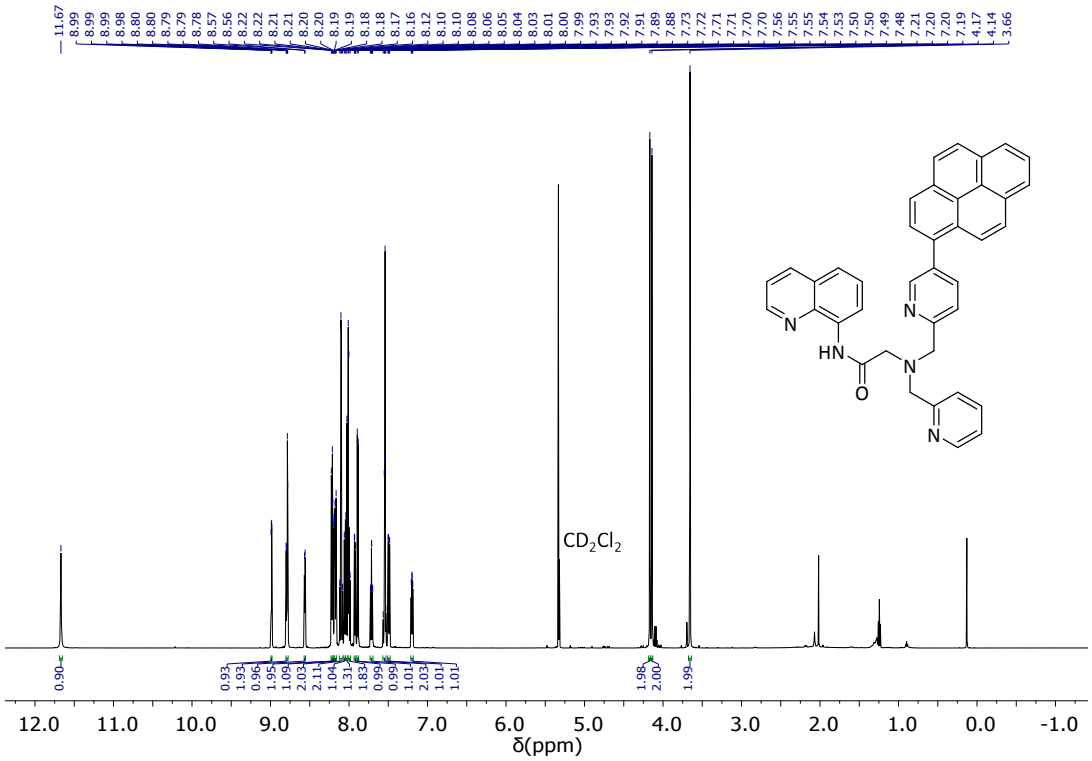


Figure S11. ^{1}H-NMR spectrum (600 MHz, CD_2Cl_2, 296 K) of H-dpaq^{Pyr} (**5d**).

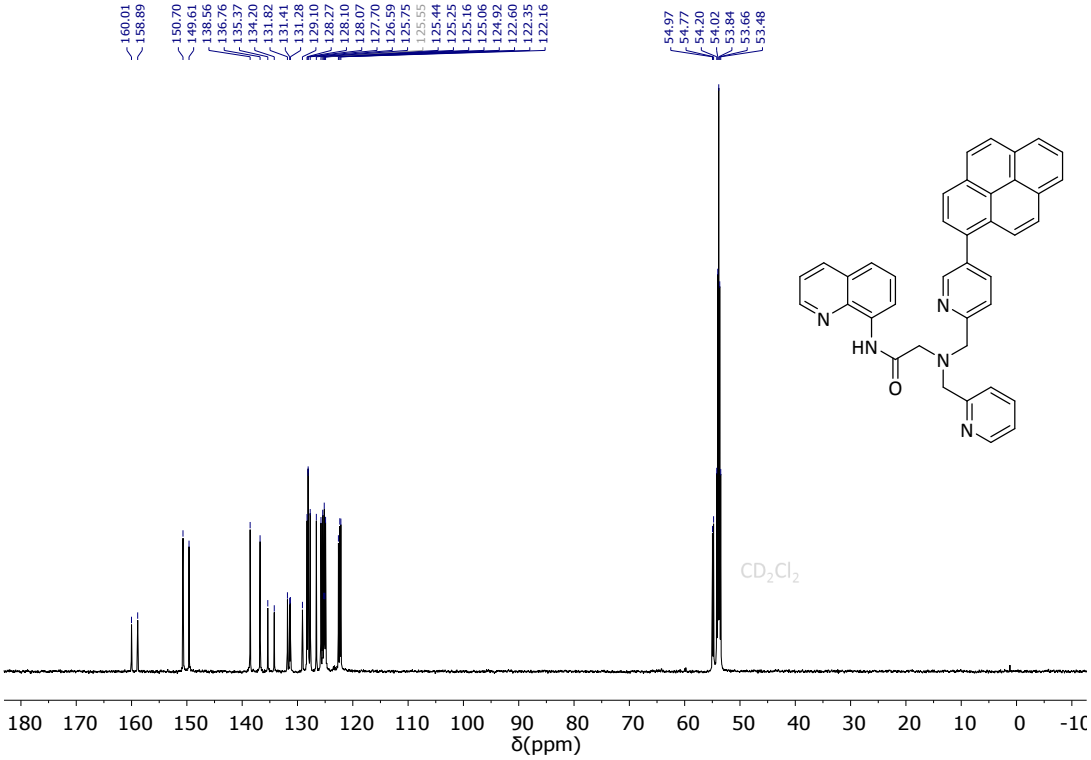


Figure S12. $^{13}C\{^{1}H\}$-NMR spectrum (151 MHz, CD_2Cl_2, 296 K) of H-dpaq^{Pyr} (**5d**).

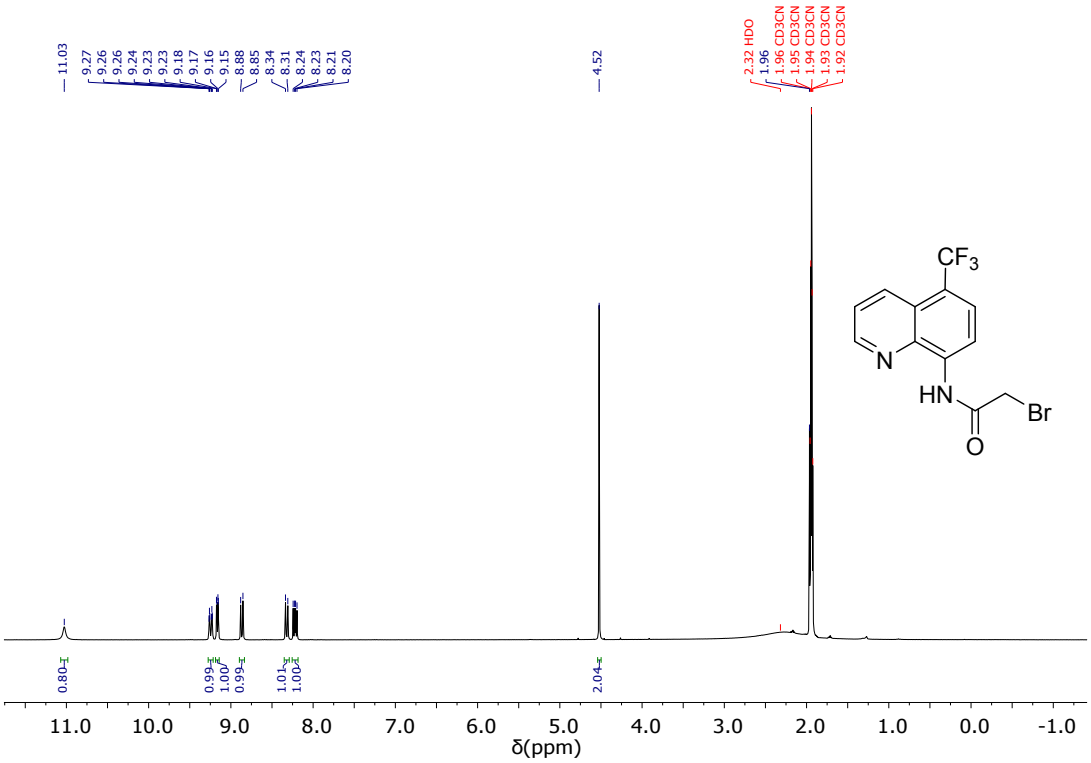


Figure S13. ^{1}H-NMR spectrum (300 MHz, CD_3CN, 296 K) of 2-Bromo-*N*-(5-(trifluoromethyl)quinolin-8-yl)acetamide (**4d**).

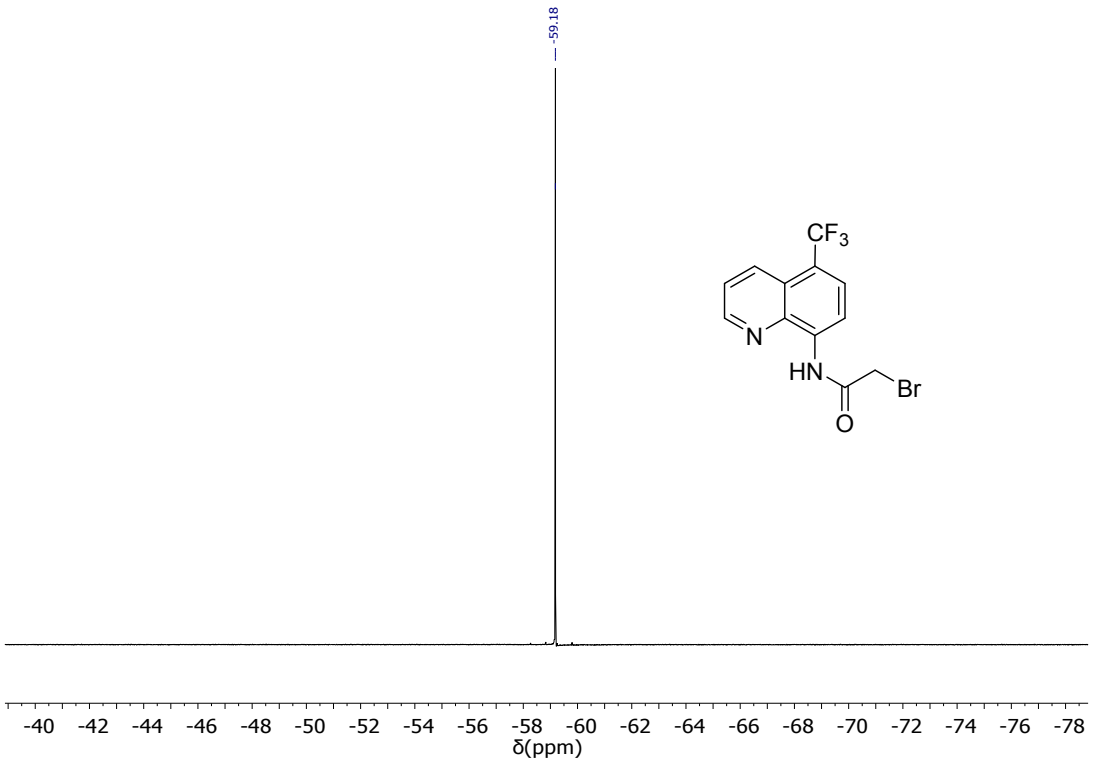


Figure S14. $^{19}F\{^{1}H\}$-NMR spectrum (377 MHz, CD_3CN, 296 K) of 2-Bromo-*N*-(5-(trifluoromethyl)quinolin-8-yl)acetamide (**4d**).

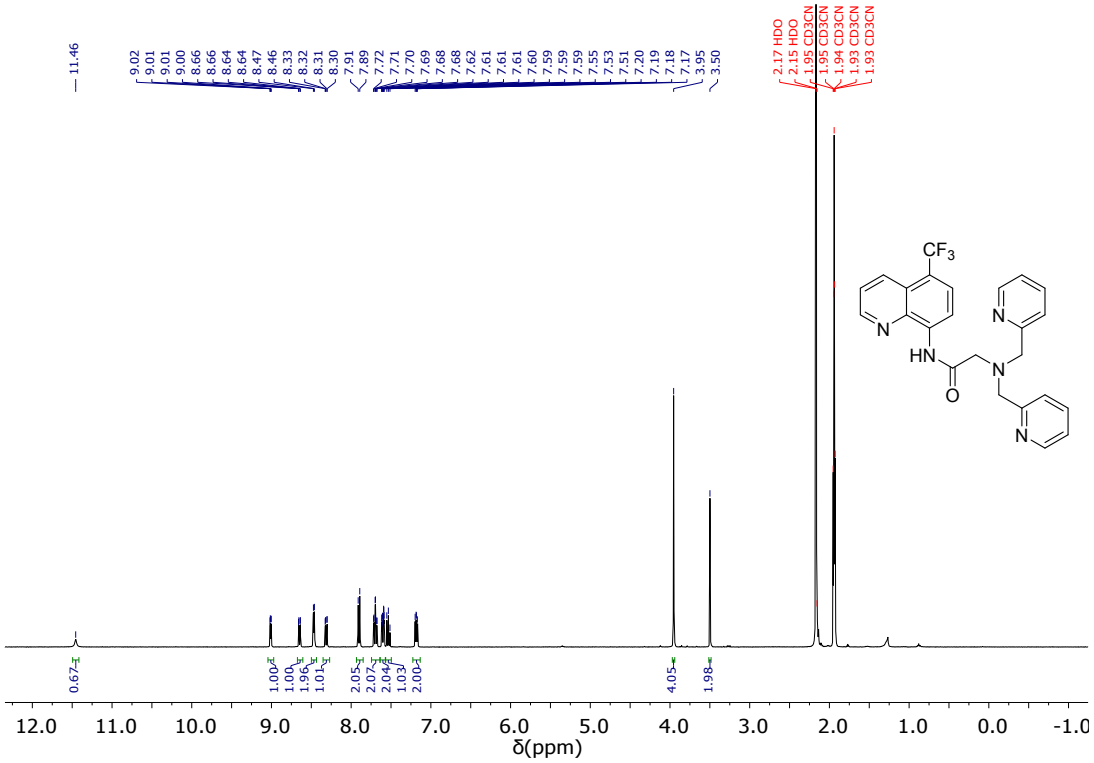


Figure S15. ^{1}H-NMR spectrum (400 MHz, CD_3CN, 296 K) of H-dpaq^{CF3} (**5f**).

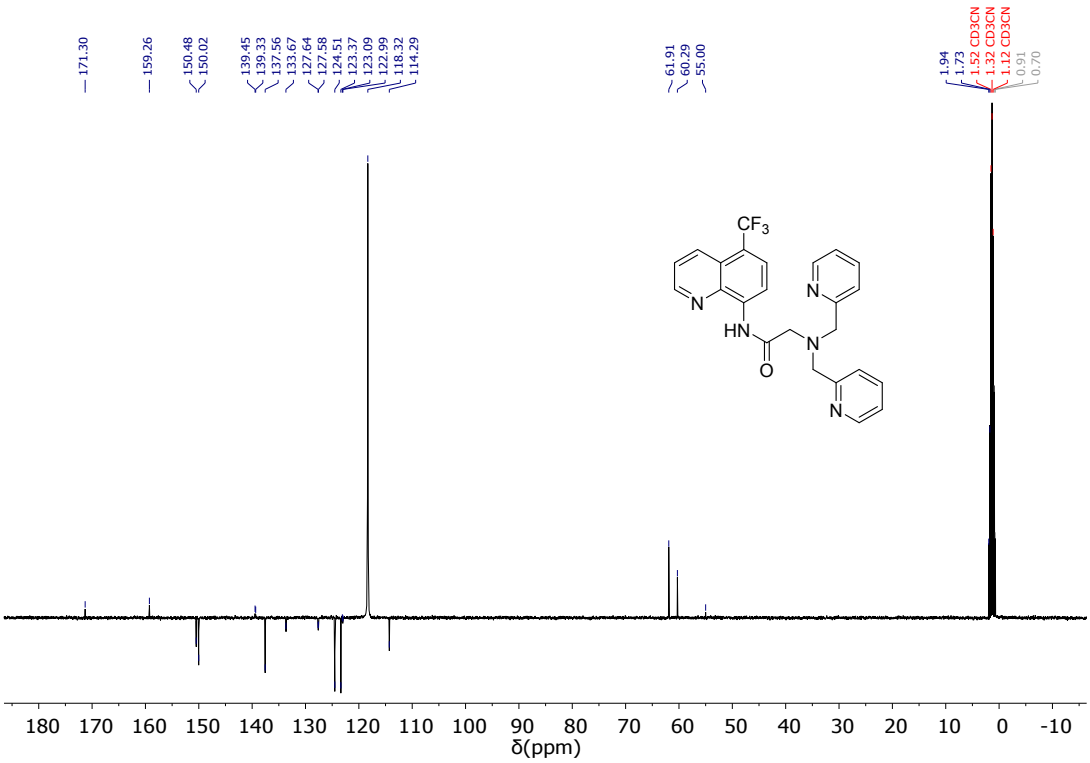


Figure S16. ^{13}C-APT-NMR spectrum (101 MHz, CD_3CN, 296 K) of H-dpaq^{CF3} (**5f**).

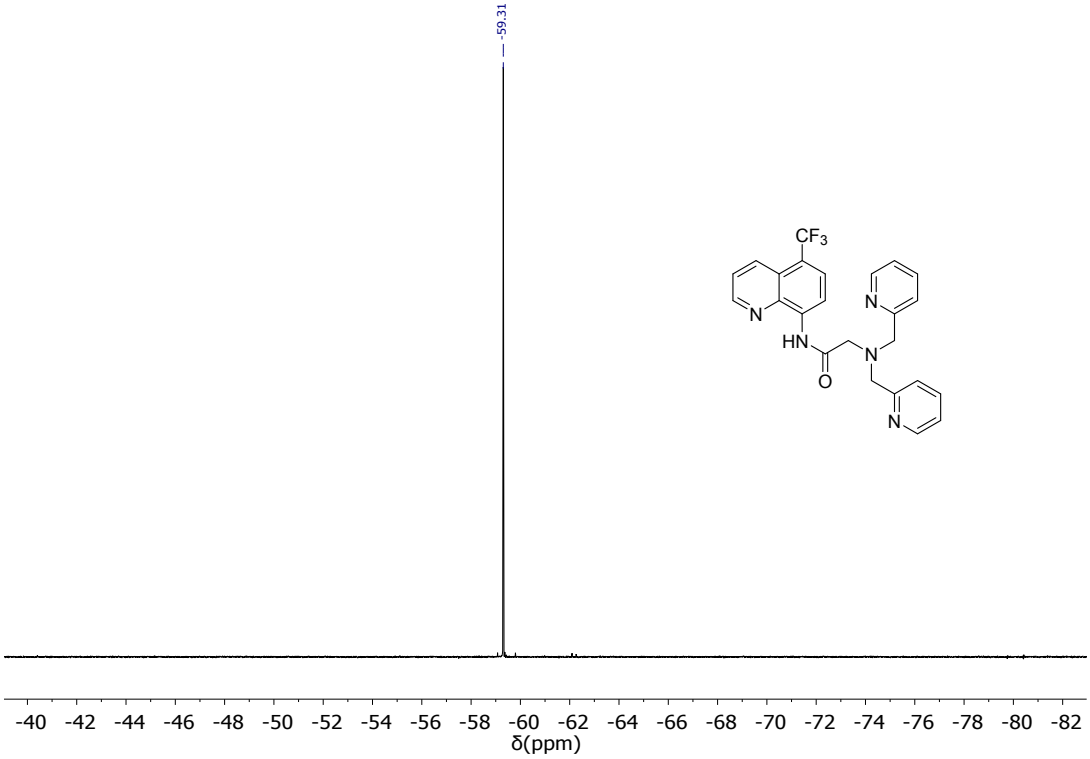


Figure S17. ^{19}F{^{1}H}-NMR spectrum (377 MHz, CD_3CN, 296 K) of H-dpaq^{CF3} (**5f**).

2.2. Electrochemistry

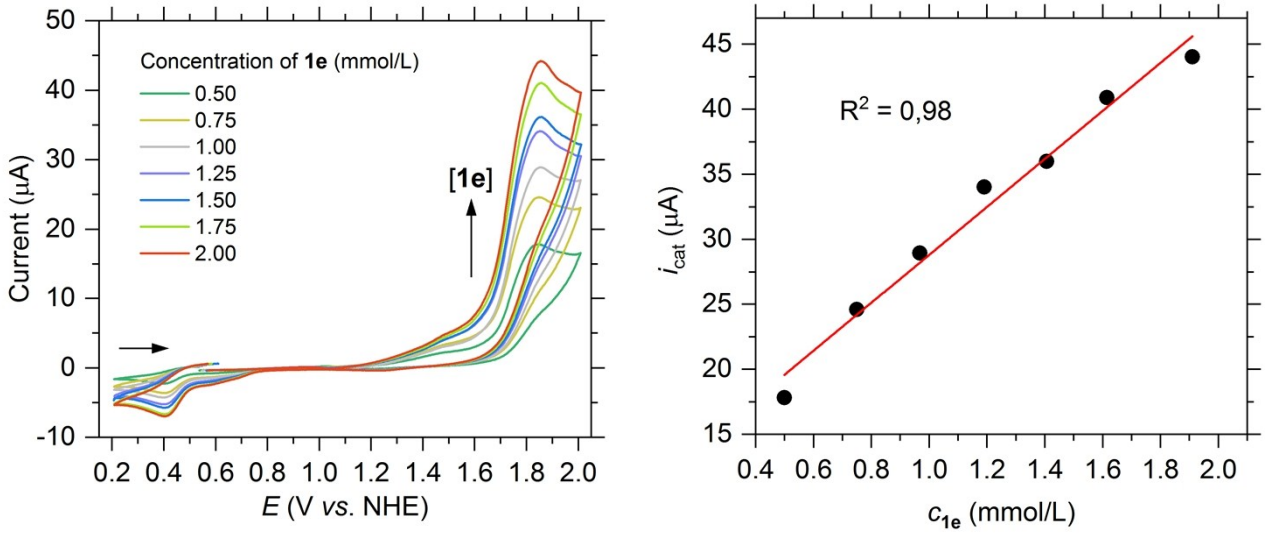


Figure S18. Left: CV of $[Fe(dpaq^{5\text{-}NO_2})](ClO_4)_2$ (**1e**) with increasing concentration (0.50 – 2.00 mM) in PC (3.2 vol% H_2O (1.85 M), 200 mM $LiClO_4$) at a scan rate of 75 mV/s with subtracted background. Right: Plot of i_{cat} *vs*. the concentration of **1e**.

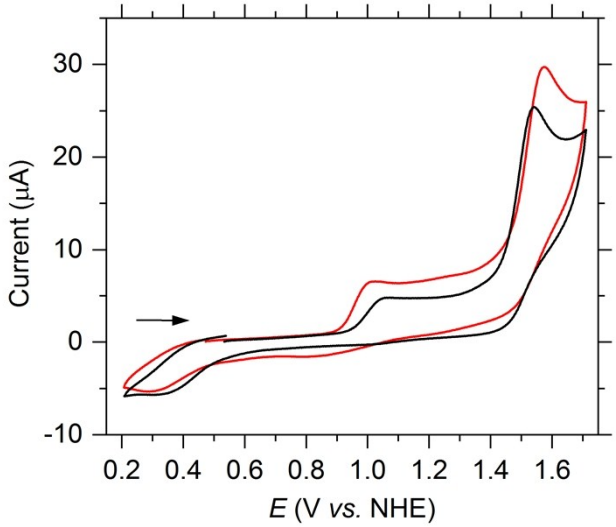


Figure S19. CV of $[Fe(dpaq^{5\text{-}H})(H_2O)](ClO_4)_2$ (**1a**, red) and $[Fe(dpaq^{6\text{-}OMe})(H_2O)](ClO_4)_2$ (**1c**, black) (both 1.0 mM) in PC (3.2 vol% H_2O (1.85 M), 200 mM $LiClO_4$) at a scan rate of 75 mV/s.

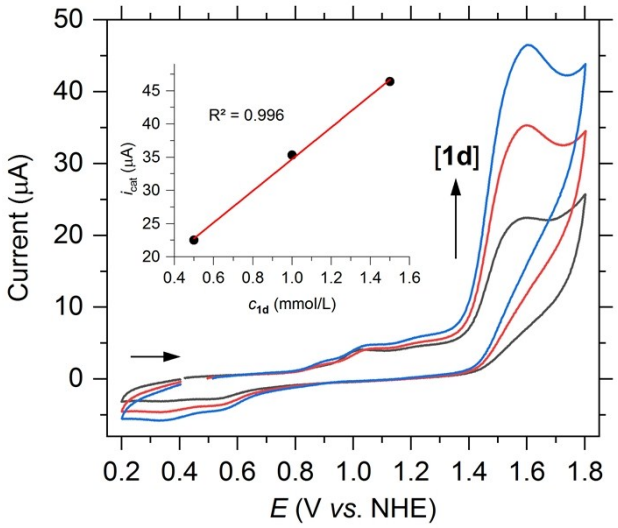


Figure S20. CV of [Fe(dpaq^{Pyr})]$(ClO_4)_2$ (**1d**) with increasing concentration from 0.5 mM (black), 1.0 mM (red) up to 1.5 mM (blue) in PC (3.2 vol% H_2O (1.85 M), 200 mM $LiClO_4$) at a scan rate of 75 mV/s.

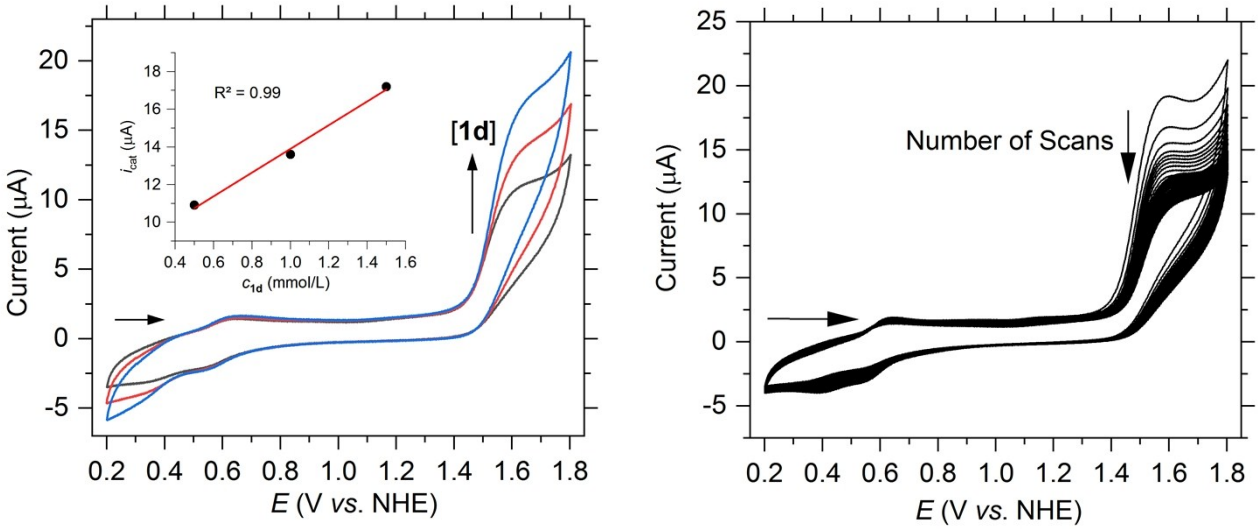


Figure S21. Left: CV after 50 scans of [Fe(dpaq^{Pyr})]$(ClO_4)_2$ (**1d**) with increasing concentration from 0.5 mM (black), 1.0 mM (red) up to 1.5 mM (blue) in PC (3.2 vol% H_2O (1.85 M), 200 mM $LiClO_4$) at a scan rate of 75 mV/s. Right: 50 successive CVs of **1d** (0.5 mM) in PC (3.2 vol% H_2O (1.85 M), 200 mM $LiClO_4$) at a scan rate of 75 mV/s.

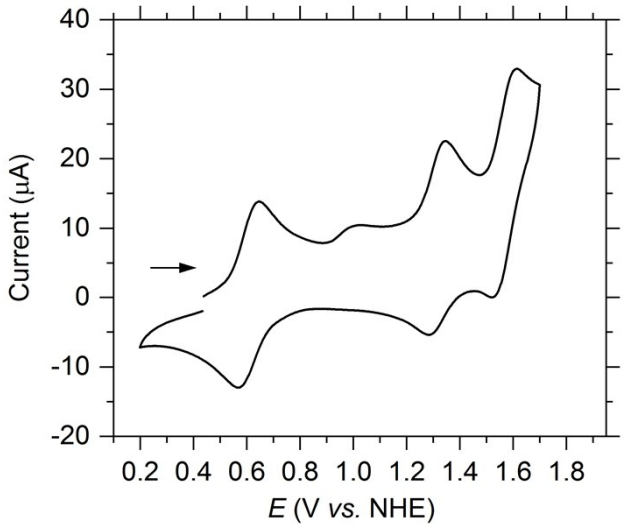


Figure S22. CV of [Mn(dpaq^{H})]ClO_4 (**2a**, 1.0 mM) in acetonitrile with 100 mM (n-Bu)$_4$N(ClO_4) at a scan rate of 300 mV/s.

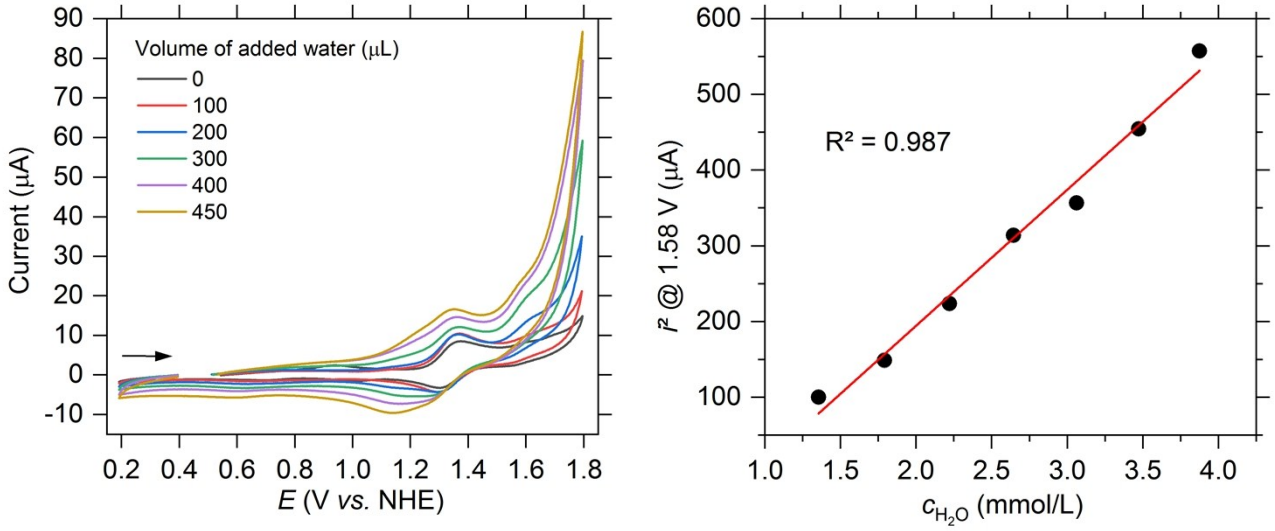


Figure S23. Left: CV of [Mn(dpaq^{H})]ClO_4 (**2a**, 1.0 mM) in acetonitrile with 100 mM (n-Bu)$_4$N(ClO_4) and an increasing amount of water at a scan rate of 50 mV/s. Right: Plot of i_{cat}^2 *vs*. the concentration of water.

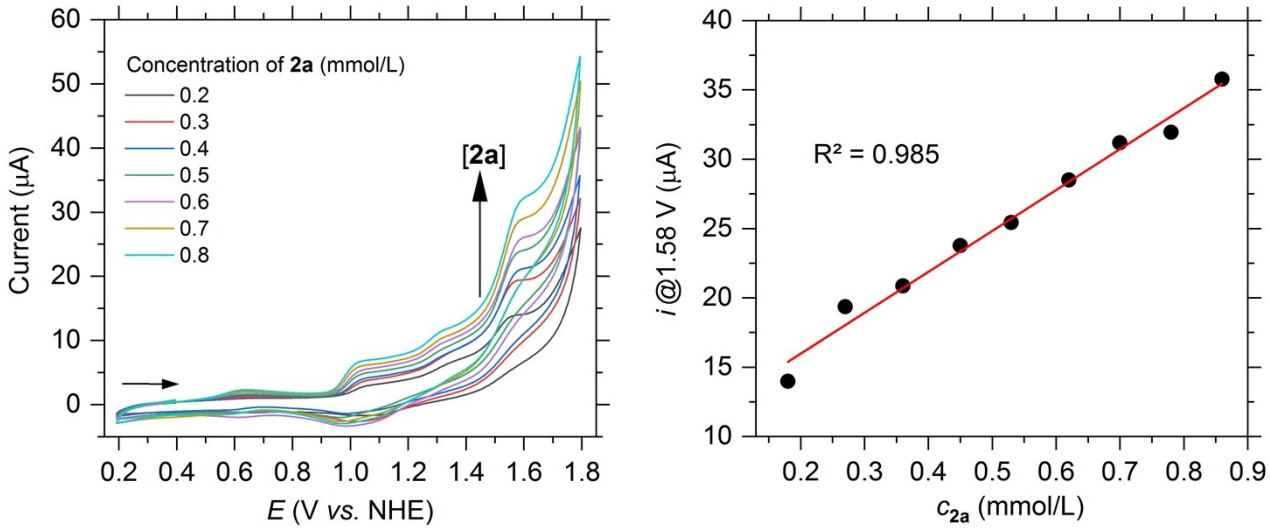


Figure S24. Left: CV of [Mn(dpaq^{H})]ClO_4 (**2a**) with increasing concentration in acetonitrile with 100 mM (n-Bu)$_4$N(ClO_4) and 7 vol% water (4.05 M) at a scan rate of 50 mV/s. Right: Plot of i_{cat} *vs*. the concentration of **2a**.

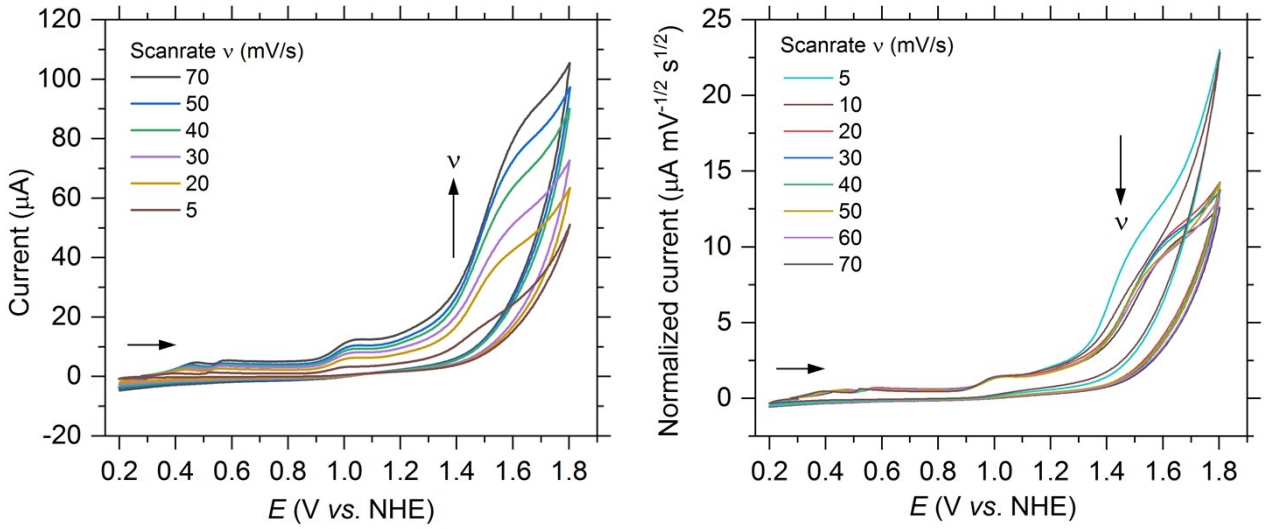


Figure S25. Left: CV of [Mn(dpaq^{H})]ClO_4 (**2a**, 1.0 mM) in borate buffer (0.2 M, pH 8) with increasing scan rate. Right: Normalized current ($i/\nu^{0.5}$) *vs*. potential.

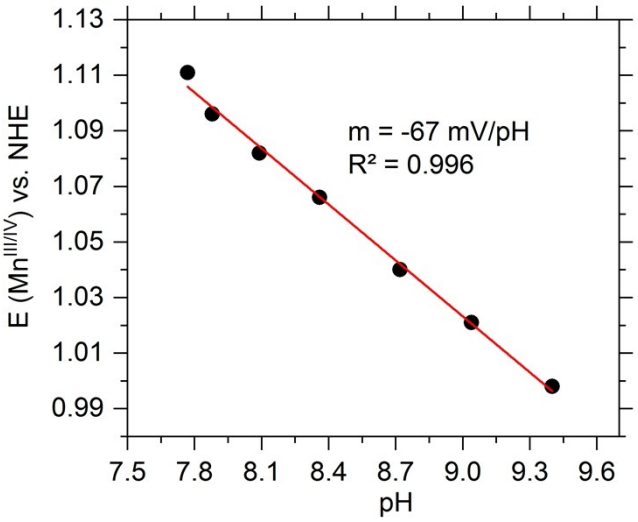


Figure S26. Pourbaix diagram for Mn^{III}-OH/Mn^{IV}=O (1.0 mM) of **2a** in a borate buffer (0.2 M).

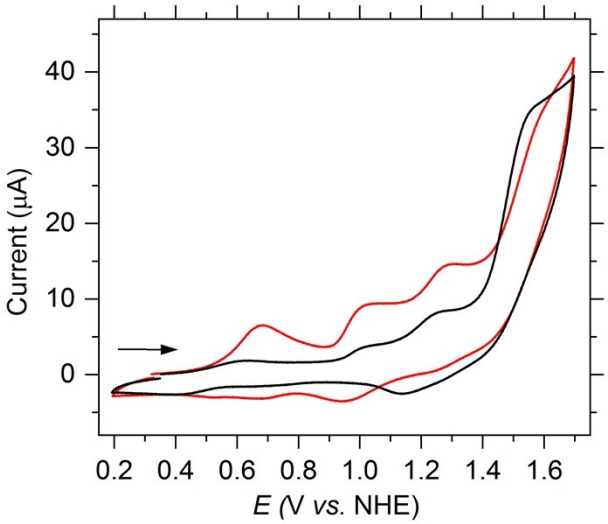


Figure S27. CV of $[Mn(dpaq^{H})]ClO_4$ (**2a**, red) and of $[Mn(dpaq^{Pyr})]ClO_4$ (**2d**, black) (both 1.0 mM) in PC (3.2 vol% H_2O (1.85 M), 200 mM $LiClO_4$) at a scan rate of 75 mV/s.

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