Supporting information

Efficient synthesis of 4,7-diamino substituted 1,10-phenanthroline-2,9-dicarboxamides

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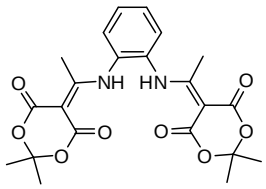
Experimental Procedures

General

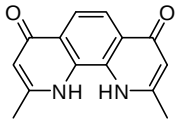
Commercially available chemicals and solvents were used without further purification, unless otherwise stated. DMF was dried and stored over 3 A molecular sieves. Anhydrous 1,4-dioxane was purchased from Sigma-Aldrich and the water content was checked before use. All reactions were conducted under argon using dried glass ware and magnetic stirring. Microwave reactions were performed in an Emrys Creator microwave reactor. Reactions were monitored by TLC (SiO_2-60, F254, Merck) or by HPLC using a Dionex 120 C18 column (5µ, 4.6x150 mm) with 10% acetonitrile in water (0-1 min), 10-100% acetonitrile in water (1-10 min), 100% acetonitrile (11-15 min), both solvents containing 0.05% TFA as modifier, a flow of 1 mL/min and UV detection at 254 and 320 nm. Purification by column chromatography was carried out using silica gel 60 (0.040-0.063 mm, Merck). NMR spectra were recorded on a Bruker Avance III 400 (400 MHz) spectrometer. Chemical shifts are reported in ppm relative to TMS (internal standard, δ 0.00 ppm) or the residual solvent peaks (^{13}C: δ_C $CDCl_3$ 77.16 ppm; DMSO-d_6 39.52 ppm). ESI-HRMS was recorded on a Bruker MicrOTOF-Q II instrument. Purity was determined by HPLC, and confirmed by inspection of ^1H NMR spectra. All compounds were of >95% purity unless otherwise stated.

5,5'-((1,2-Phenylenebis(azanediyl))bis(ethan-1-yl-1-ylidene))bis(2,2-dimethyl-1,3-dioxane-4,6-dione) (4)



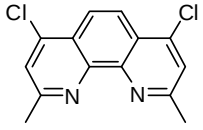
Trimethyl orthoformate (500 mL, 3.83 mol) and Meldrum's acid (20.0 g, 139 mmol) was brought to a gentle reflux for 15 min. The resulting yellow solution was cooled (80 °C) and *o*-phenylenediamine (6.90 g, 63.1 mmol) was added portionwise (exothermic reaction). The resulting mixture was refluxed for 2 h, and left under stirring at rt for 16 h, where a white precipitate formed. The precipitate was filtered off, washed with diethyl ether (4x100 mL) and dried to afford a flaky white solid. Yield: 17.8 g (63%); ^1H NMR (400 MHz, $CDCl_3$) δ 12.77 (s, 2H), 7.50 (dd, *J* = 5.8, 3.6 Hz, 2H), 7.35 (dd, *J* = 5.8, 3.6 Hz, 2H), 2.52 (s, 6H), 1.70 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 167.7, 162.5, 132.5, 129.4, 128.1, 103.3, 87.4, 26.7, 19.7; mp 187-188 °C; ESI-HRMS calcd for $C_{22}H_{24}N_2O_4Na^+$ ($M + Na^+$) 467.1425, found 467.1421.

2,9-Dimethyl-1,10-phenanthroline-4,7(1H,10H)-dione (S1)



Diphenyl ether (500 mL) at 240 °C was added **4** (17.5 g, 38.7 mmol) in small portions, resulting in vigorous gas evolution. The resulting orange solution was brought to reflux for 30 min, and was then allowed to cool to 70 °C, where a dark-brown solid precipitated. The formed precipitate was washed with acetone (2 x 90 mL), hexane (2 x 90 mL) and Et_2O (2 x 90 mL) and dried to afford a fine dark-brown powder. Yield: 8.72 g (94%); ^1H NMR (400 MHz, NaOH in D_2O) δ 7.63 (s, 2H), 6.22 (s, 2H), 2.28 (s, 6H); ^{13}C NMR (101 MHz, NaOH in D_2O) δ 174.5, 155.9, 138.9, 122.9, 117.0, 110.2, 100.0, 21.8; mp >205 °C; ESI-HRMS calcd for $C_{14}H_{11}N_2O_2Na^+$ ($M + Na^+$) 239.0815, found 239.0825.

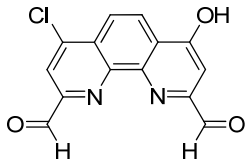
4,7-Dichloro-2,9-dimethyl-1,10-phenanthroline (5)



Phosphoryl chloride (220 mL) under nitrogen was added **S1** (8.50 g, 35.4 mmol) and the resulting solution was stirred at 90 °C for 3½ h. The hot solution was slowly added to a well stirred mixture of ice (700 g) in water (300 mL). After stirring for 15 min, chloroform (200 mL) was added and the resulting two-layer system was carefully brought to pH 13-14 by adding NaOH solution (42.5%, ca. 450 mL). The organic layer was separated and the aqueous layer was extracted four times with 200 mL of chloroform. The combined organic layers were washed with NaOH

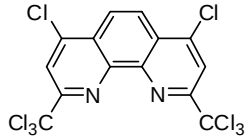
solution (42.5%, 200 mL) and dried over $MgSO_4$. Evaporation of the brown colored solvent afforded **5** as light tan crystals. Yield: 9.50 g (97%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 2H), 7.63 (s, 2H), 2.93 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 146.2, 143.0, 125.2, 124.3, 122.3, 26.0; mp 202 °C; ESI-HRMS calcd for $C_{14}H_{10}Cl_2N_2Na^+$ (M + Na^+) 299.0114, found 299.0107.

4-Chloro-7-hydroxy-1,10-phenanthroline-2,9-dicarbaldehyde (6)



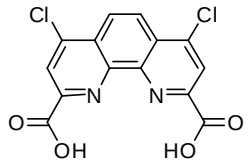
Selenium dioxide (0.208 g, 1.88 mmol) was added to a round-bottom flask containing a solution of **5** (0.100 g, 0.361 mmol) in 1,4-dioxane (6.5 mL) at room temperature. The reaction mixture was heated to 100 °C under stirring for 2 h, during which the color of the mixture changed to black through yellow and red. The solvent was then removed by evaporation to afford a green-black solid (0.31 g). Flash chromatography (MeOH/CH_2Cl_2 9%) on the solid afforded **6** as a yellow powder. Yield: 0,080 g (77%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.75 (s, 1H), 10.32 (s, 1H), 9.95 (s, 1H), 8.57 (d, *J* = 9.1 Hz, 1H), 8.33 (s, 1H), 8.14 (d, *J* = 9.1 Hz, 1H), 7.08 (d, *J* = 1.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.2, 187.4, 179.0, 151.1, 145.4, 140.6, 140.0, 1371, 130.5, 127.2, 126.5, 121.0, 120.2, 119.3; ESI-HRMS calcd for $C_{14}H_8ClN_2O_3^+$: 287.0218, found: 287.0218.

4,7-Dichloro-2,9-bis(trichloromethyl)-1,10-phenanthroline (7)



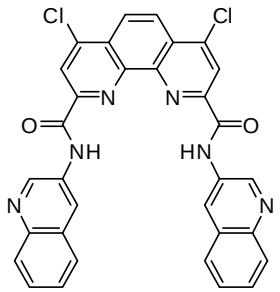
A stirred solution of **5** (9.00 g, 32.5 mmol), *N*-chlorosuccinimide (31.2 g, 234 mmol) and a catalytic amount of benzoyl peroxide (20 mg) in chloroform (700 mL) was refluxed overnight. The reaction mixture was washed with saturated aqueous K_2CO_3 (2 x 200 mL), dried over $MgSO_4$ and concentrated to afford a solid, which was purified by flash-chromatography (2% EtOAc in petroleum ether) to give **7** as white crystals. Yield: 13.5 g (86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 2H), 8.42 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 144.7, 144.3, 127.6, 124.6, 121.3, 97.2; mp 174-175 °C; ESI-HRMS calcd for $C_{14}H_4Cl_8N_2Na^+$ (M + Na^+) 502.7775, found 502.7797.

4,7-Dichloro-1,10-phenanthroline-2,9-dicarboxylic acid (3)



A stirred mixture of **7** (13.00 g, 26.9 mmol) in H_2SO_4 (96%, 16 mL) was heated to 95 °C for 2 h. After cooling, H_2O (50 mL) was slowly added with rapid stirring. The resulting mixture was heated to reflux for 1 h. The mixture was cooled and the formed precipitate was washed with H_2O (5 x 40 mL) and Et_2O (2x30 mL) and dried to afford **3** as a light tan solid. Yield: 9.28 g (97%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.52 (s, 2H), 8.51 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.2, 149.3, 145.8, 143.1, 127.9, 125.0, 124.1; mp >205 °C; ESI-HRMS calcd for $C_{14}H_6Cl_2N_2O_4Na^+$ (M + Na^+) 358.9597, found 358.9580.

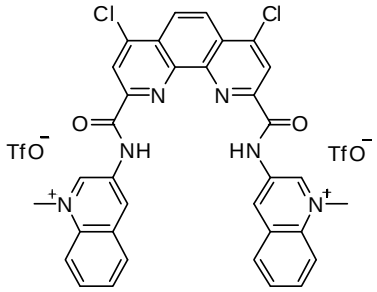
4,7-Dichloro-N^2,N^9-di(quinolin-3-yl)-1,10-phenanthroline-2,9-dicarboxamide (8)



3-Aminoquinoline (423 mg, 2.94 mmol) and HOBt (409 mg, 2.67 mmol) was successively added to a solution of **3** (450 mg, 1.335 mmol) in DMF (50 mL). The mixture was cooled to 0 °C in an ice bath with stirring and added EDC (640 mg, 2.75 mmol). The reaction mixture was then slowly allowed to reach room temperature over 1 hour and stirred at this temperature overnight. The formed precipitate was collected, washed with aqueous $NaHCO_3$ (1%) followed by several Et_2O washings. Drying under reduced pressure gave **8** as a pale yellow solid. Yield:

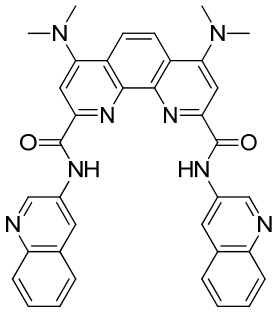
0,613 g (78%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.87 (s, 2H), 9.66 (d, *J* = 2.4 Hz, 2H), 9.13 (d, *J* = 2.4 Hz, 2H), 8.78 (s, 2H), 8.66 (s, 2H), 8.16–8.07 (m, 4H), 7.76 (t, *J* = 7.4 Hz, 2H), 7.68 (t, *J* = 7.4 Hz, 2H); mp >205 °C; ESI-HRMS calcd for $C_{32}H_{18}Cl_2N_6O_2Na^+$ (M + Na^+) 611.0761, found 611.0747.

3,3'-((4,7-Dichloro-1,10-phenanthroline-2,9-dicarbonyl)bis(azanediyl))bis(1-methylquinolin-1-ium) trifluoromethanesulfonate (9·2 TfO^-)



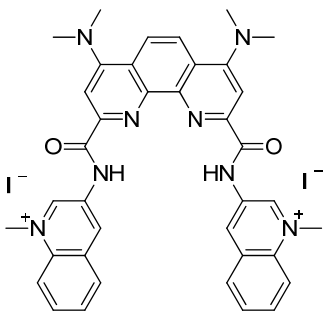
A solution of **8** (67.5 mg, 0.115 mmol) in CH_2Cl_2 (25 mL) was heated to reflux under inert atmosphere. An excess of methyl trifluoromethanesulfonate was added (0.30 mL, 2.72 mmol) and the reaction mixture was stirred for 4 h, after which a yellow compound had precipitated from the yellow mixture. The mixture was evaporated to 8 mL on a rotavap, and the precipitate was isolated by filtration, and washed with CH_2Cl_2 (3 x 1 mL) and Et_2O (3 x 1 mL). Drying under reduced pressure gave the **9** as its triflate salt. Yield: 76.5 mg (73%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.15 (s, 2H), 10.25 (s, 2H), 9.87 (s, 2H), 8.82 (s, 2H), 8.60 (s, 2H), 8.58 (d, *J* = 9.3 Hz, 2H), 8.55 (d, *J* = 8.2 Hz, 2H), 8.28 (t, *J* = 7.8 Hz, 2H), 8.10 (t, *J* = 7.6 Hz, 2H), 4.78 (s, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.5, 149.2, 145.5, 144.8, 144.5, 135.7, 135.0, 134.2, 132.5, 130.4, 130.1, 129.2, 128.8, 125.5, 122.7, 119.2, 46.2; mp >205 °C; ESI-HRMS calcd for $C_{34}H_{24}Cl_2N_6O_2^{2+}$ (M^{2+}) 309.0661, found 309.0654.

4,7-Bis(dimethylamino)-N^2,N^9-di(quinolin-3-yl)-1,10-phenanthroline-2,9-dicarboxamide (10)



A sealed vial containing **8** (36.7 mg, 0.127 mmol), DMF (2.0 mL) and NH_3 (24% in H_2O, 0.3 mL) under argon was heated in a microwave reactor to 100 °C for 16 h to give an orange mixture with a yellow precipitate. Dropwise addition of EtOH (4 mL) followed by Et_2O (20 mL) led to the formation of additional precipitate from a light yellow solution. The precipitate was isolated by centrifugation and washed twice with 25% EtOH in Et_2O (4 mL) to afford 38 mg of a yellow powder. The crude product was purified by flash chromatography (MeOH/CH_2Cl_2 1.0-6.0%) to give **10** as a yellow powder. Yield: 31.5 mg (83%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.79 (s, 2H), 9.65 (d, *J* = 1.9 Hz, 2H), 9.08 (s, 2H), 8.16 (s, 2H), 8.09–8.04 (m, 4H), 7.95 (s, 2H), 7.73 (t, *J* = 7.6 Hz, 2H), 7.65 (t, *J* = 7.6 Hz, 2H), 3.22 (s, 12H); ESI-HRMS calcd for $C_{36}H_{31}N_8O_2^+$ (M + H^+) 607.2565, found 607.2576.

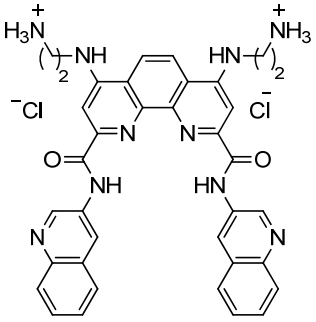
3,3'-((4,7-Bis(dimethylamino)-1,10-phenanthroline-2,9-dicarbonyl)bis(azanediyl))bis(1-methylquinolin-1-ium) iodide (11·2 I^-)



A sealed vial containing a solution of **10** (25.7 mg, 0.042 mmol) and MeI (72 mg, 0.507 mmol) in DMF (1.5 mL) under argon was heated in a microwave reactor to 115 °C for 60 min to give an orange mixture with orange precipitate. Dropwise addition of EtOH (1 mL) followed by addition of Et_2O (6 mL) resulted in the precipitation of a yellow compound from a light yellow mixture. The precipitate was isolated by centrifugation, and was washed twice with 25% EtOH in Et_2O (4 mL) and twice with Et_2O (4 mL). Drying under vacuum afforded the iodide salt of **11** as an orange powder. Yield: 36.0 mg (95%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.07 (s, 2H), 10.27 (s, 2H), 9.83 (s, 2H), 8.53 (d, *J* = 8.0 Hz, 2H), 8.48 (d, *J* = 6.6 Hz, 2H), 8.30–8.20 (m, 2H), 8.18 (s, 2H), 8.11–8.00 (m, 2H), 7.96 (s, 2H), 4.72 (s, 6H), 3.25 (s, 12H); ^{13}C NMR (101

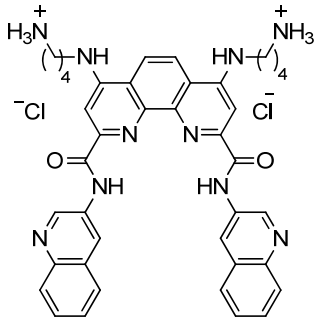
MHz, DMSO-d_6) δ 164.2, 158.6, 147.7, 146.2, 145.7, 135.4, 134.5, 133.8, 132.8, 130.2, 129.9, 129.1, 122.9, 122.5, 119.2, 106.9, 46.3, 43.7; ESI-HRMS calcd for $C_{38}H_{36}N_8O_2^{2+}$ (M^{2+}) 318.1475, found 318.1486.

2,2'-((2,9-Bis(quinolin-3-ylcarbamoyl)-1,10-phenanthroline-4,7-diyl)bis(azanediyl))diethanaminium chloride (12a·2 HCl)



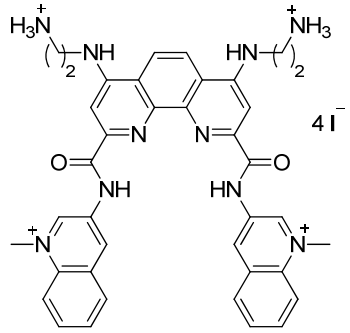
A sealed vial containing **8** (58.9 mg, 0.100 mmol) and ethane-1,2-diamine (2.0 mL, 29.9 mmol) under argon was heated in a microwave reactor to 100 °C for 20 min to give an orange mixture with a precipitate. Dropwise addition of MeCN (6 mL) to the mixture gave additional precipitate. The precipitate was isolated by centrifugation and washed with MeCN (2x5 mL), dried, redissolved in H_2O (1.5 mL) and converted to its HCl-salt by dropwise addition of HCl (1.0 M, aq.) until pH < 1. To the orange mixture was added EtOH (4.5 mL), resulting in a color change to yellow, followed by addition of Et_2O (13 mL). This led to precipitation of a yellow compound which was isolated by centrifugation and washed with Et_2O (3x5 mL). Drying under vacuum afforded the HCl salt of **12a** as a yellow powder. Yield: 66.8 mg (94%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.09 (s, 2H), 9.51 (s, 2H), 9.22 (s, 2H), 9.03 (s, 2H), 8.75 (s, 2H), 8.28 (s, 6H), 8.06 (d, *J* = 8.6 Hz, 4H), 7.80 (s, 2H), 7.76 (t, *J* = 7.6 Hz, 2H), 7.72–7.60 (m, 2H), 3.99–3.87 (m, 4H), 3.33–3.28 (m, 4H); ESI-HRMS calcd. for $C_{40}H_{42}N_{10}O_2^{2+}$ (M^{2+}) 319.1428, found 319.1439.

4,4'-((2,9-Bis(quinolin-3-ylcarbamoyl)-1,10-phenanthroline-4,7-diyl)bis(azanediyl))bis(butan-1-aminium) chloride (12b·2 HCl)



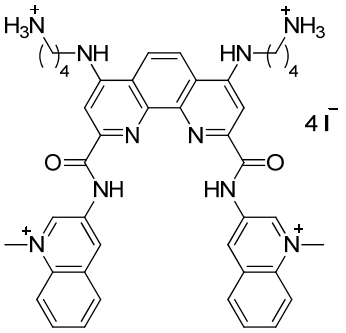
A sealed vial containing **8** (34.9 mg, 0,051 mmol) and butane-1,4-diamine (1.75 mL, 301 eqiv.) under argon was heated to 100 °C for 20 min to give a clear orange mixture. The diamine was removed under reduced pressure, and the resulting orange solid was dissolved in EtOH (2 mL) followed by addition of Et_2O (6 mL). The resulting yellow precipitate was isolated by centrifugation and washed by Et_2O (2 x 3 mL). The precipitate was dissolved in H_2O (1.5 mL) and converted to its HCl salt by dropwise addition of HCl (1.0 M, aq.) until pH < 1. To the now orange mixture, EtOH (1.5 mL) was added dropwise, followed by Et_2O (6.5 mL). The resulting precipitate was isolated by centrifugation and washed with 30% EtOH in Et_2O (7 mL) followed by Et_2O (2 x 3 mL). Drying under vacuum afforded the HCl salt of **12b** as a yellow powder. Yield: 78.4 mg (99%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.15 (s, 2H), 9.55 (s, 2H), 8.97 (s, 2H), 8.55 (s, 2H), 8.13 (s, 6H), 7.94 (d, *J* = 8.3 Hz, 2H), 7.82 (d, *J* = 7.4 Hz, 2H), 7.70 (t, *J* = 7.4 Hz, 2H), 7.64–7.42 (m, 4H), 3.63–3.60 (m, 4H), 3.03–2.83 (m, 4H), 1.99–1.86 (m, 4H), 1.86–1.71 (m, 4H); ESI-HRMS calcd for $C_{40}H_{42}N_{10}O_2^{2+}$ (M^{2+}) 347.1741, found 347.1745.

3,3'-((4,7-Bis((2-ammonioethyl)amino)-1,10-phenanthroline-2,9-dicarbonyl)bis(azanediyl))bis(1-methylquinolin-1-ium) iodide (13a·4 I^-)



A sealed vial containing a solution of **12a**·2HCl (25.9 mg, 0.036 mmol) and MeI (125 mg, 0.881 mmol) in DMF (1.7 mL, dry) under argon was heated to 115 °C for 75 min (50 min + 25 min) to give an orange mixture containing a precipitate. Addition of MeCN (5 mL) followed by Et_2O (6 mL) led to further precipitation, which was isolated by centrifugation. The combined precipitate was washed with Et_2O (4x5 mL) and dried to afford the iodide salt **13a** as an orange powder. Yield: 37.4 mg (87%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.03 (s, 2H), 10.25 (s, 2H), 9.83 (s, 2H), 8.55 (d, *J* = 8.7 Hz, 2H), 8.47 (d, *J* = 8.0 Hz, 2H), 8.41 (s, 2H), 8.25 (t, *J* = 8.0 Hz, 2H), 8.07 (t, *J* = 7.6 Hz, 2H), 7.92 (s, 6H), 7.78 (s, 2H), 7.71 (s, 2H), 4.70 (s, 6H), 3.84–3.70 (m, 4H), 3.31–3.20 (m, 4H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.0, 152.2, 148.1, 145.6, 135.3, 134.3, 133.8, 132.8, 130.2, 129.8, 129.0, 119.8, 119.4, 119.1, 99.4, 46.3, 40.4, 37.5; ESI-HRMS calcd for $C_{38}H_{38}N_{10}O_2^{2+}$ (M^{2+}) 333.1584, found 333.1603.

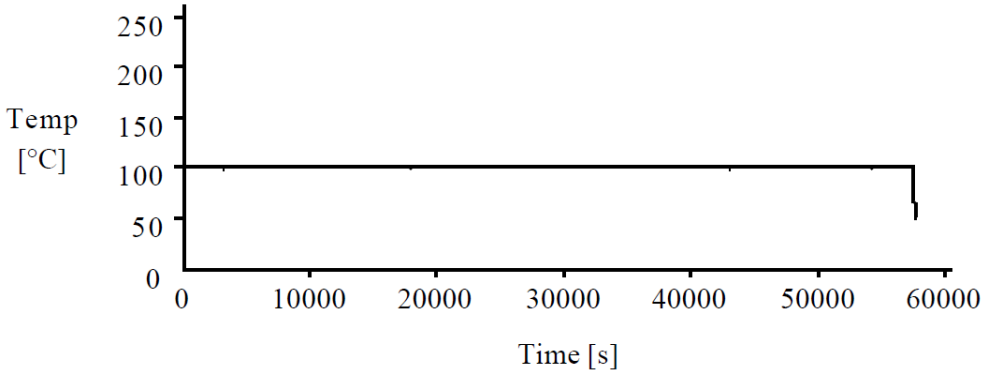
3,3'-((4,7-Bis((4-ammoniobutyl)amino)-1,10-phenanthroline-2,9-dicarbonyl)bis(azanediyl))bis(1-methylquinolin-1-ium) iodide (13b·4 I^-)



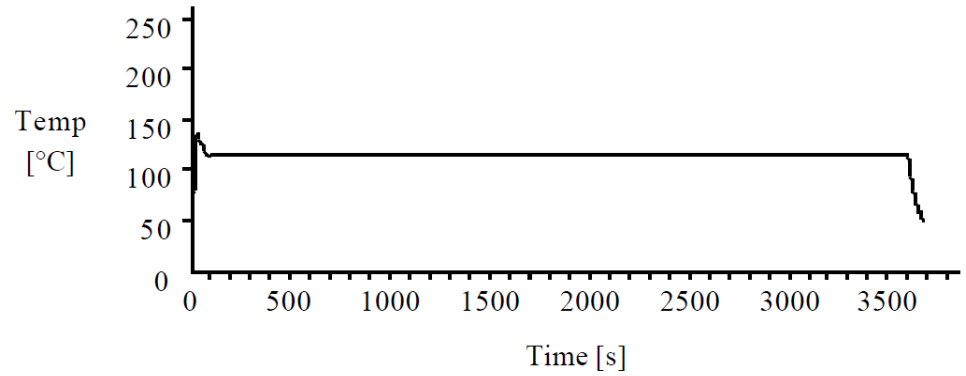
A sealed vial containing a solution of **12b**·2HCl (8.5 mg, 0.059 mmol) and MeI (43 mg, 0,303 mmol, 27.3 eqiv.) in DMF (0.6 mL) under argon was heated in a microwave reactor to 115 °C for 75 min (30 min + 45 min) to give an orange mixture. Dropwise addition of MeCN (9 mL) led to precipitation of a yellow compound, which was washed with MeCN (2x3 mL). Et_2O (30 mL) was added, resulting in further precipitation. The combined precipitate was washed with MeCN in Et_2O (33% v/v, 6 mL) and dried to afford the iodide salt of **13b** as an orange powder. Yield: 13.0 mg (95%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.43 (s, 2H), 10.22 (s, 2H), 9.73 (s, 2H), 8.64 (s, 2H), 8.58–8.49 (m, 4H), 8.46 (d, *J* = 8.0 Hz, 2H), 8.24 (t, *J* = 8.0 Hz, 2H), 8.06 (t, *J* = 7.6 Hz, 2H), 7.93 (s, 6H), 7.64 (s, 2H), 4.72 (s, 6H), 3.66–3.53 (m, 4H), 2.98–2.86 (m, 4H), 1.97–1.80 (m, 4H), 1.80–1.69 (m, 4H); ^{13}C NMR (101 MHz, DMSO-d_6 + 1 drop TFA) δ 163.3, 153.2, 147.1, 145.1, 135.6, 134.5, 134.0, 132.8, 130.4, 129.9, 129.2, 119.5, 119.2, 118.8, 99.8, 46.0, 42.5, 40.4, 38.6, 24.7; ESI-HRMS calcd for $C_{42}H_{46}N_{10}O_2^{2+}$ (M^{2+}) 361.1897, found 361.1916.

Microwave temperature–time profiles

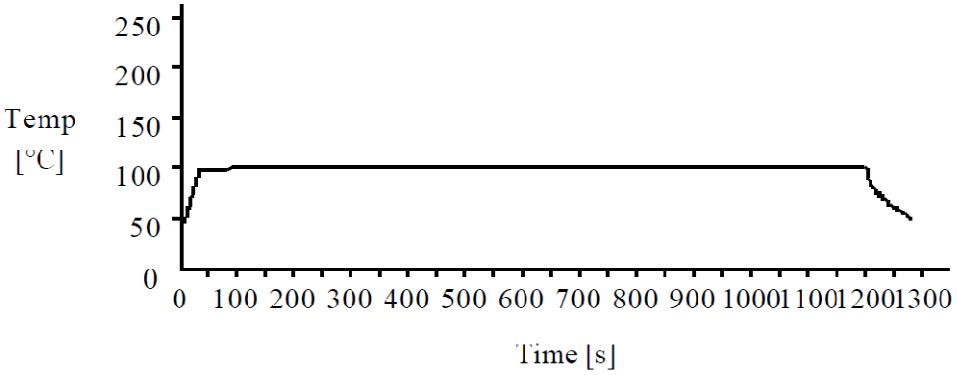
4,7-Bis(dimethylamino)-N^2,N^9-di(quinolin-3-yl)-1,10-phenanthroline-2,9-dicarboxamide (10)
Microwave heating (100 °C, 16h)



3,3'-((4,7-Bis(dimethylamino)-1,10-phenanthroline-2,9-dicarbonyl)bis(azanediyl))bis(1-methylquinolin-1-ium) iodide (11·2 I^-)
Microwave heating (115 °C, 60 min)

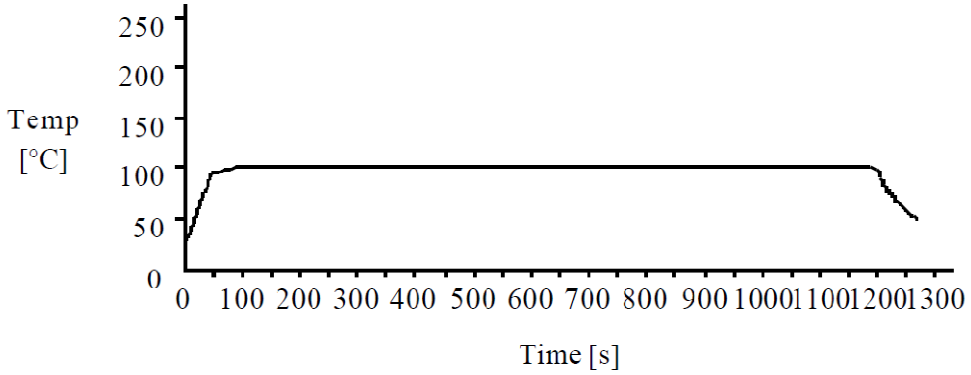


2,2'-((2,9-Bis(quinolin-3-ylcarbamoyl)-1,10-phenanthroline-4,7-diyl)bis(azanediyl))diethanaminium chloride (12a·2 HCl)
Microwave heating (100 °C, 20 min)



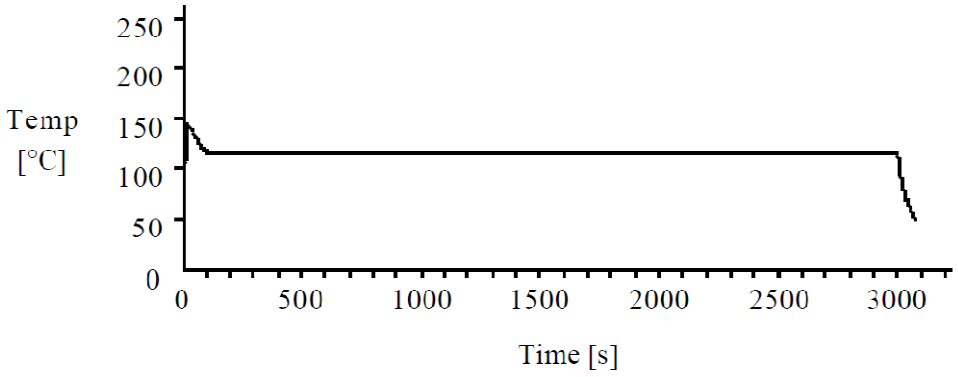
4,4'-((2,9-Bis(quinolin-3-ylcarbamoyl)-1,10-phenanthroline-4,7-diyl)bis(azanediyl))bis(butan-1-aminium) chloride (12b·2 HCl)

Microwave heating (100 °C, 20 min)

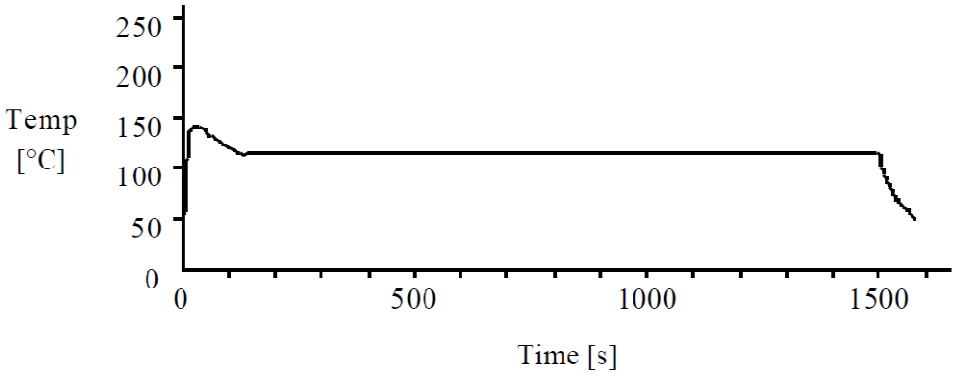


3,3'-((4,7-Bis((2-ammonioethyl)amino)-1,10-phenanthroline-2,9-dicarbonyl)bis(azanediyl))bis(1-methylquinolin-1-ium) iodide (13a·4 I^-)

Microwave heating (115 °C, 50 min)

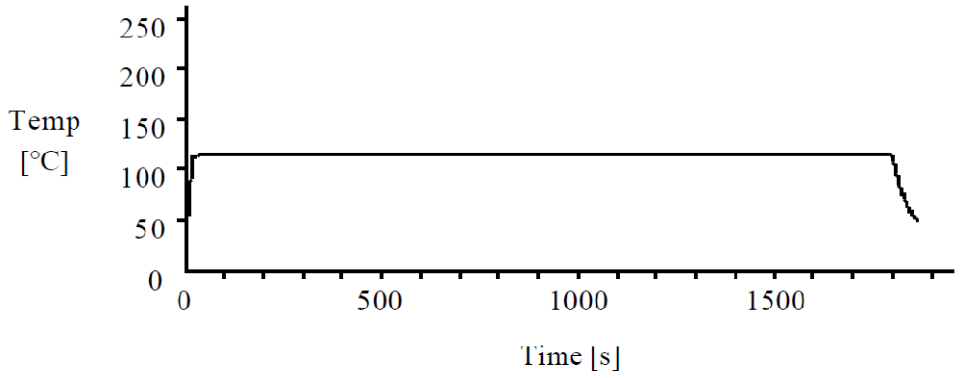


Microwave heating (115 °C, 25 min)

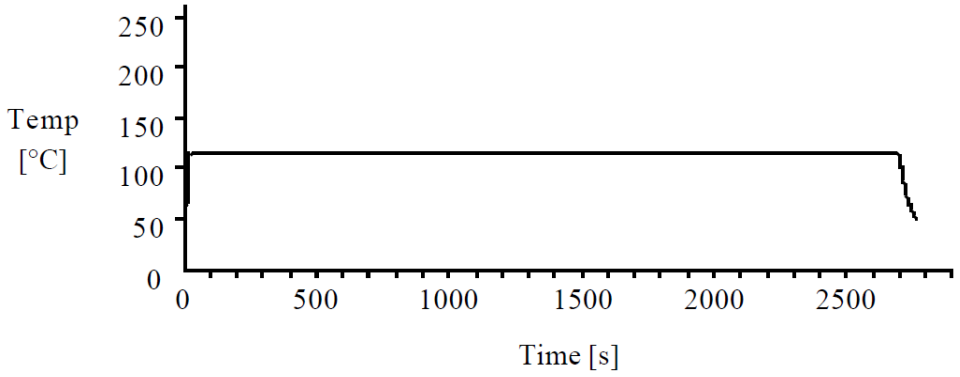


3,3'-((4,7-Bis((4-ammoniobutyl)amino)-1,10-phenanthroline-2,9-dicarbonyl)bis(azanediyl))bis(1-methylquinolin-1-ium) iodide (13b·4 I^-)

Microwave heating (115 °C, 30 min)



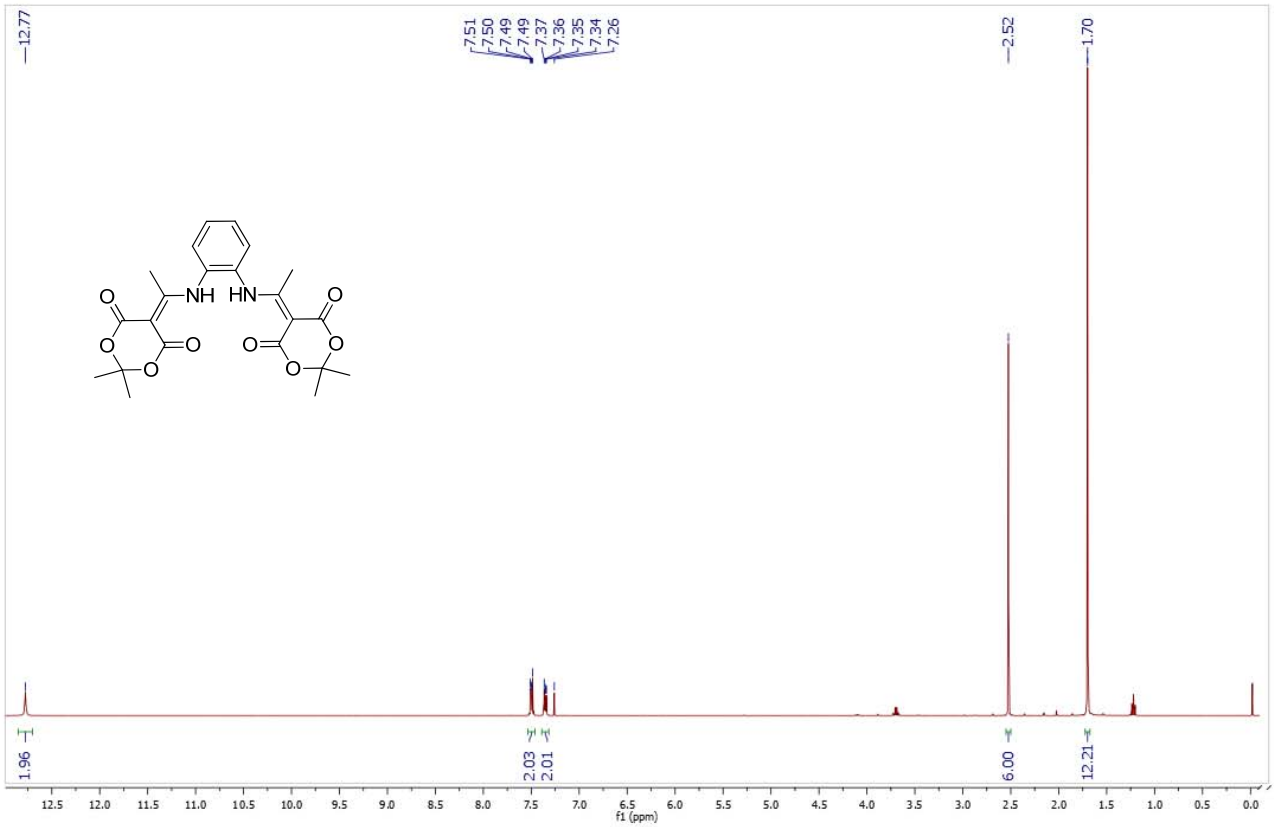
Microwave heating (115 °C, 45 min)

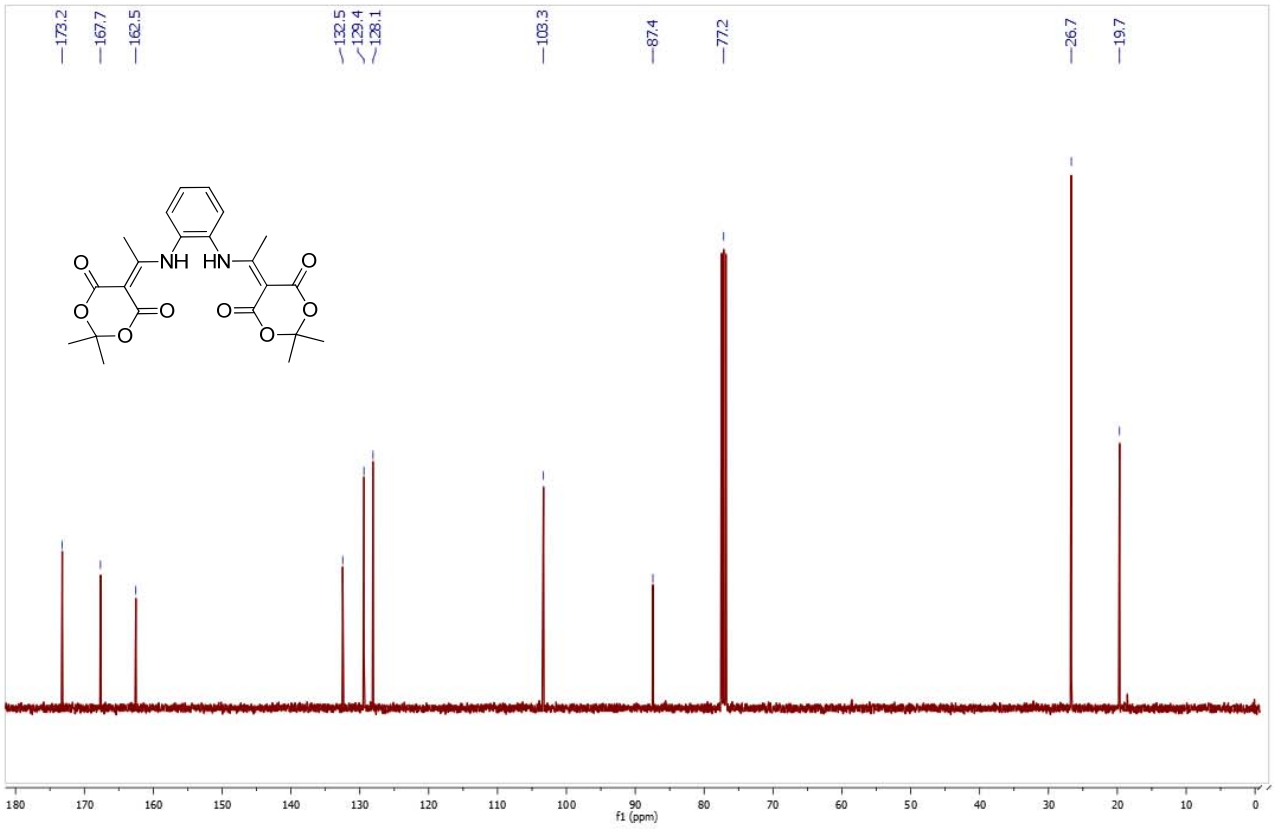


NMR Spectra

5,5'-((1,2-Phenylenebis(azanediyl))bis(ethan-1-yl-1-ylidene))bis(2,2-dimethyl-1,3-dioxane-4,6-dione) (4)

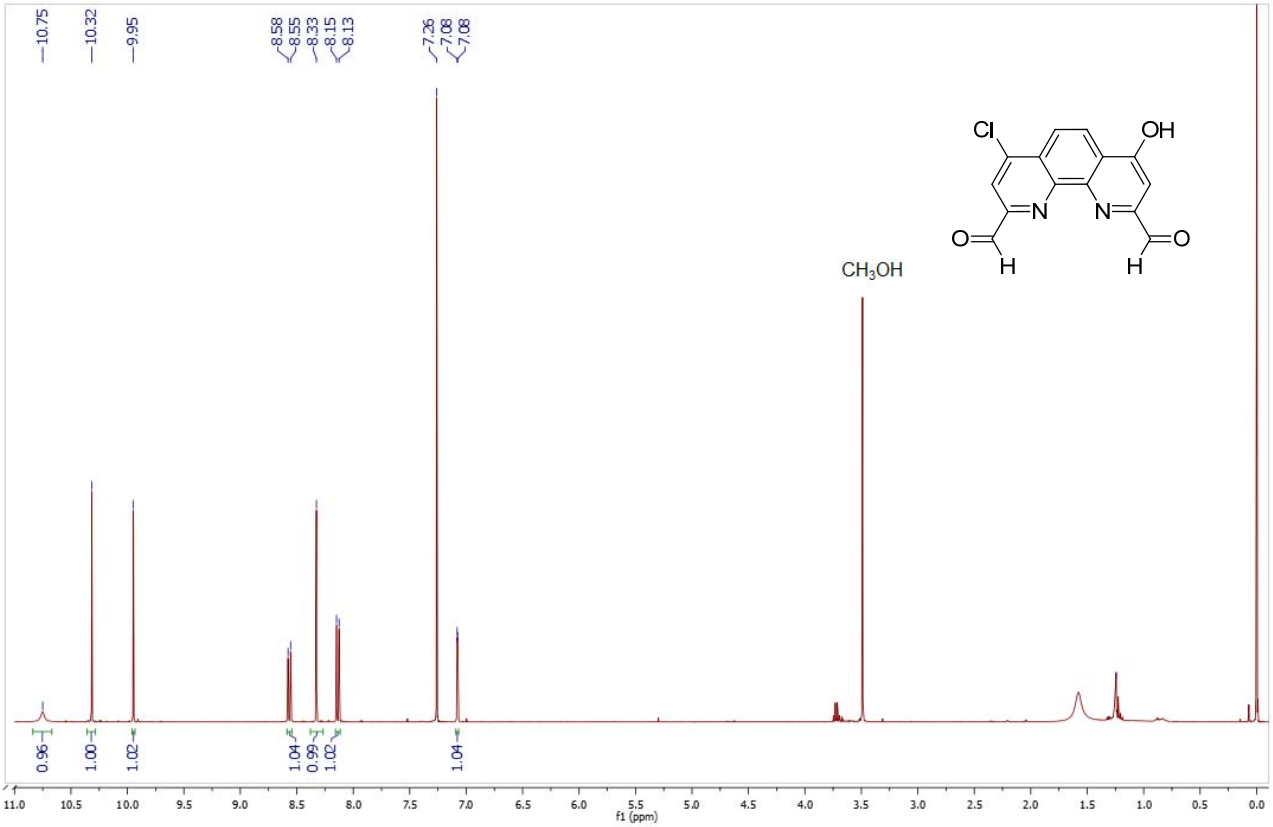
^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (101 MHz, $CDCl_3$)

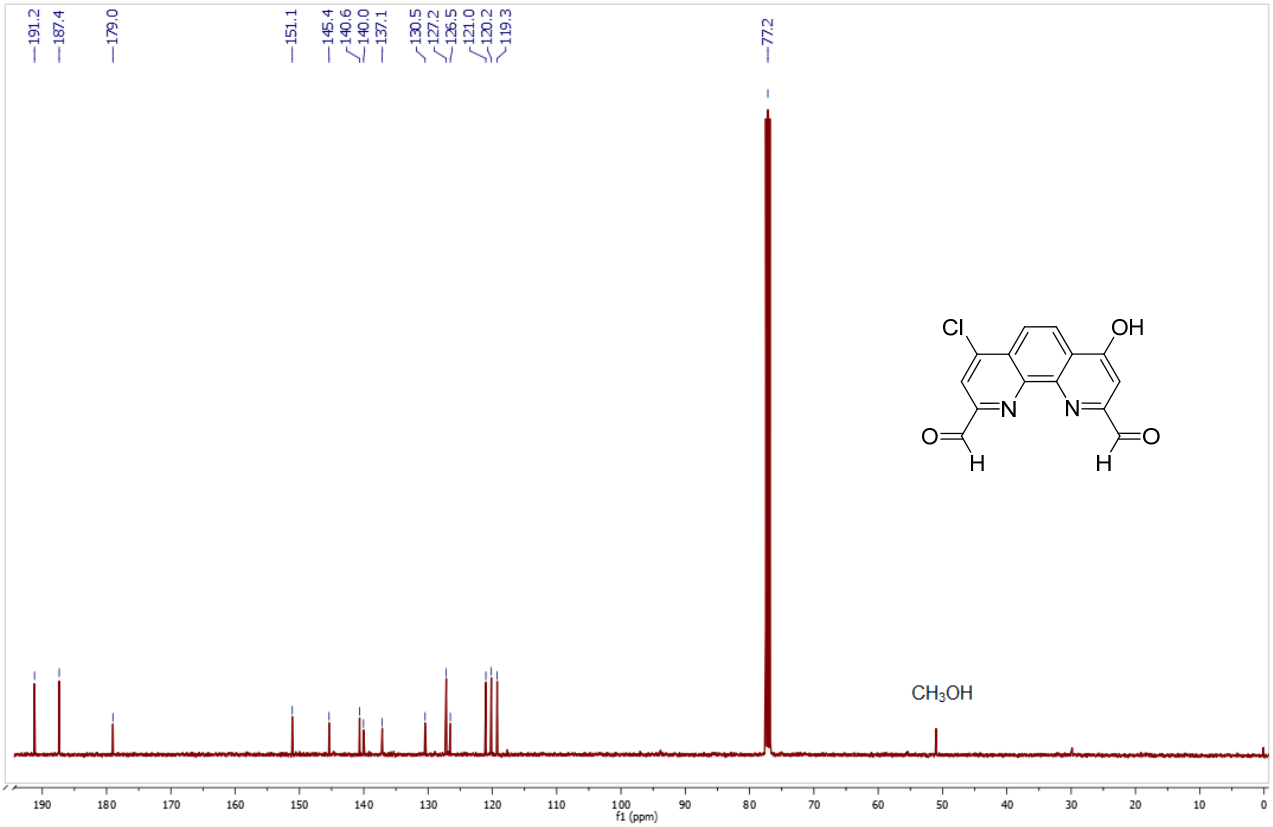




4-Chloro-7-hydroxy-1,10-phenanthroline-2,9-dicarbaldehyde (6)

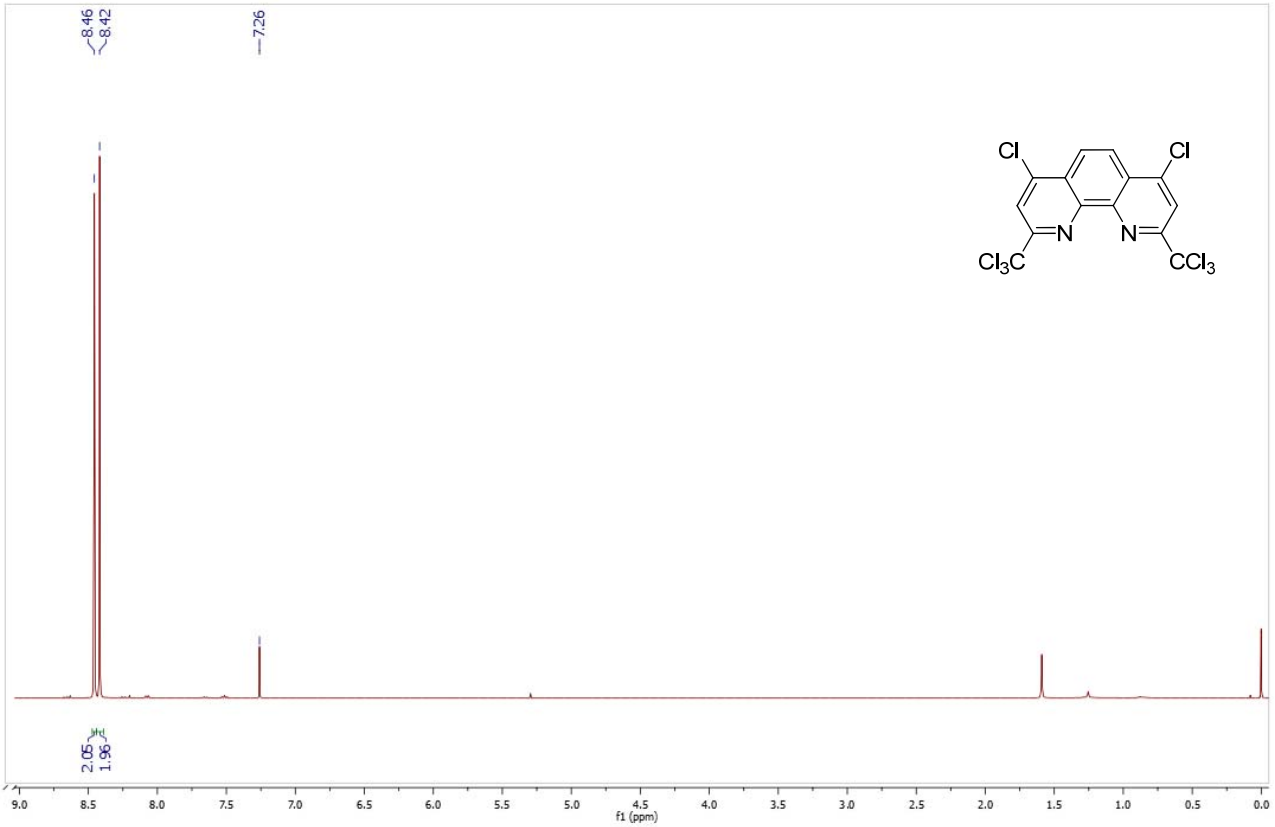
^{1}H NMR (400 MHz, DMSO-d_6); ^{13}C NMR (101 MHz, $CDCl_3$)

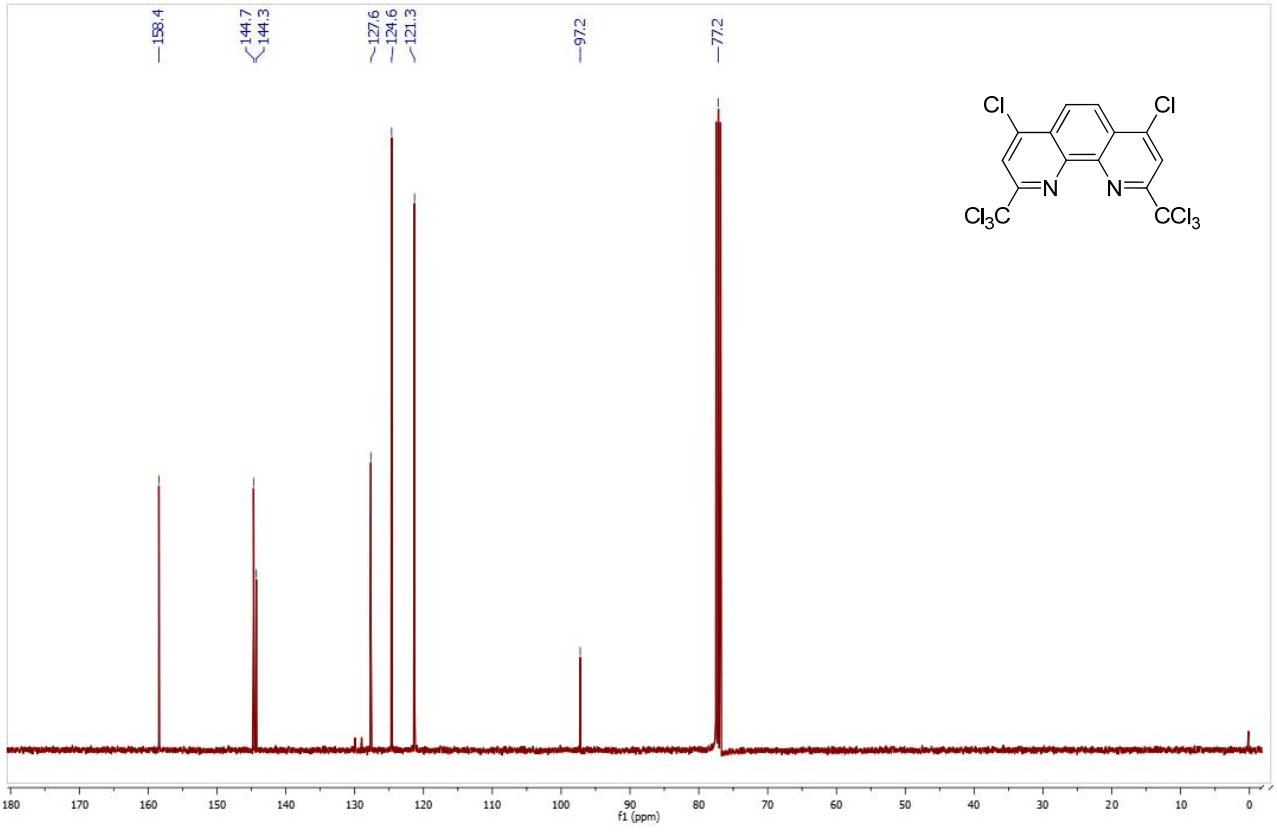




4,7-Dichloro-2,9-bis(trichloromethyl)-1,10-phenanthroline (7)

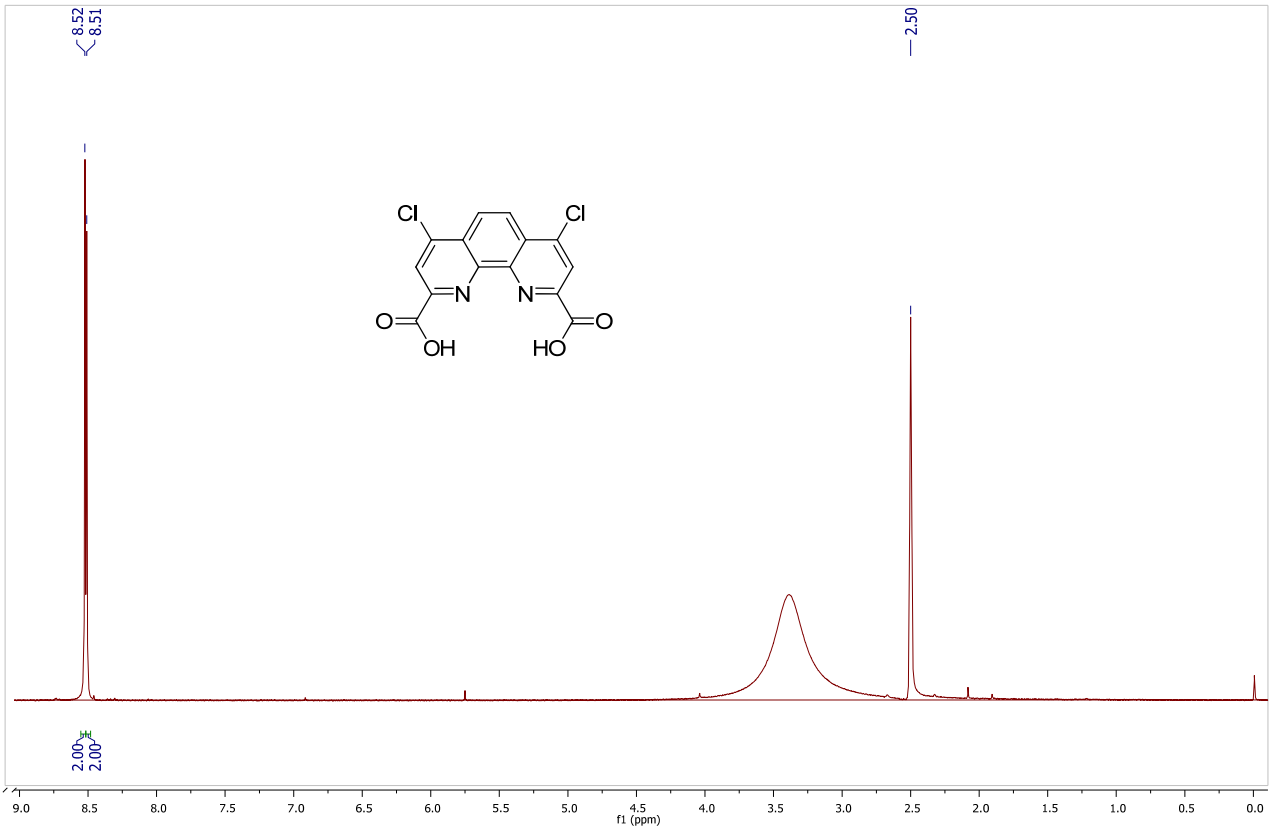
^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (101 MHz, $CDCl_3$)

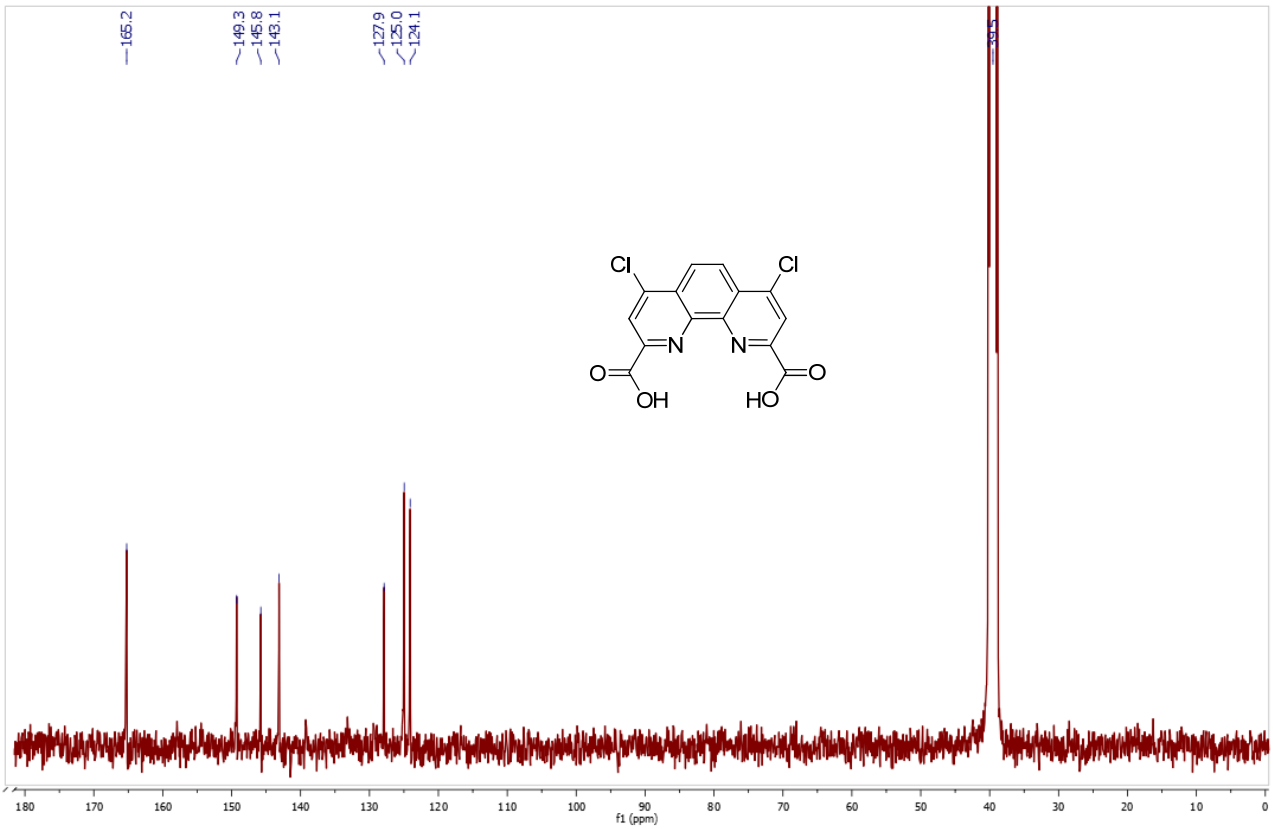




4,7-Dichloro-1,10-phenanthroline-2,9-dicarboxylic acid (3)

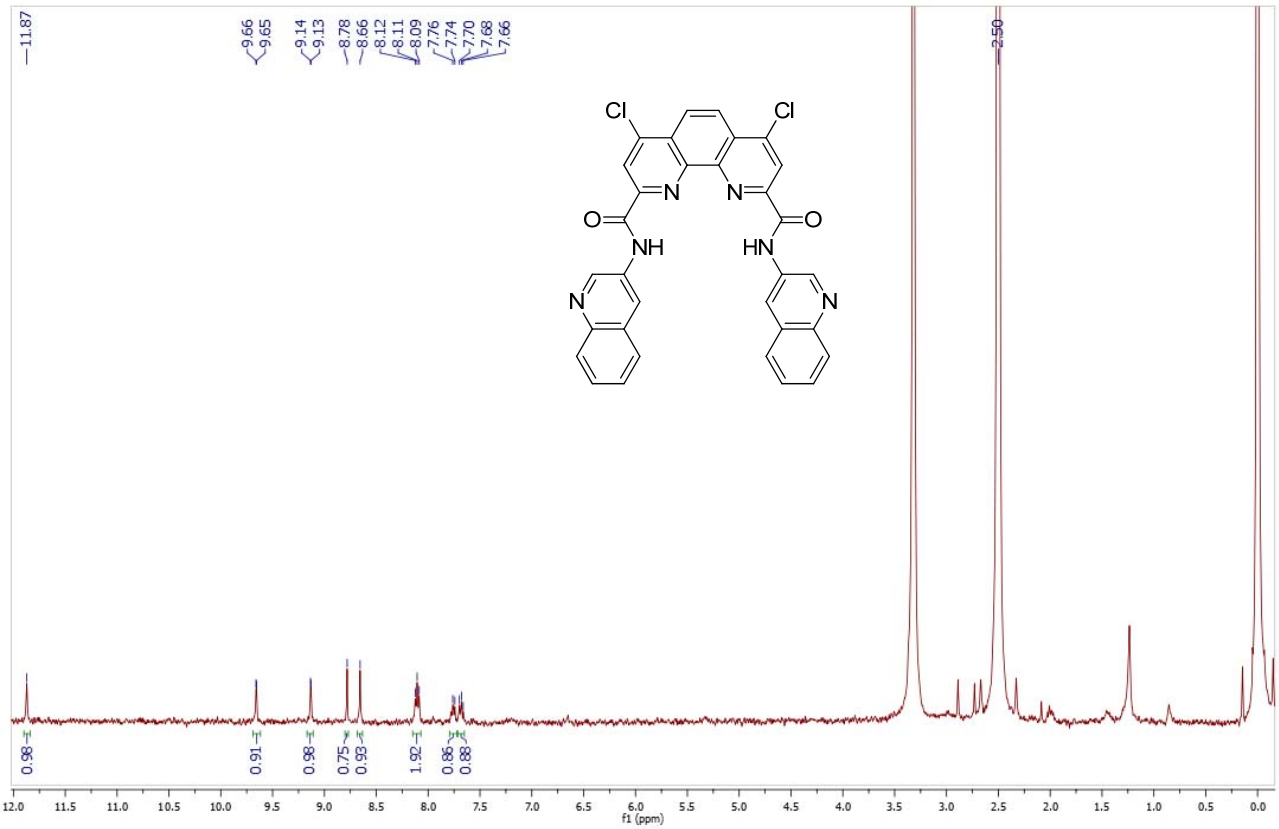
^{1}H NMR (400 MHz, DMSO-d_6); ^{13}C NMR (101 MHz, DMSO-d_6)





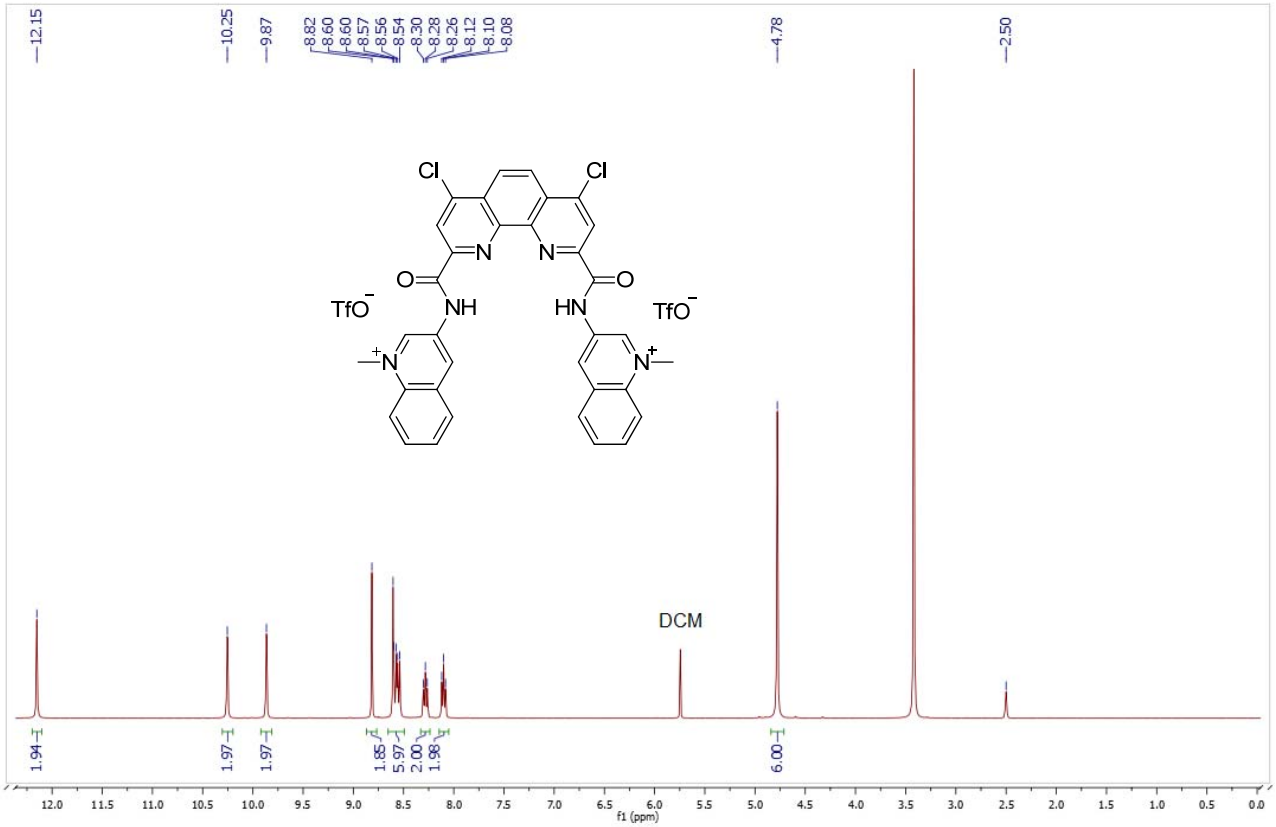
4,7-Dichloro-N^2,N^9-di(quinolin-3-yl)-1,10-phenanthroline-2,9-dicarboxamide (8)

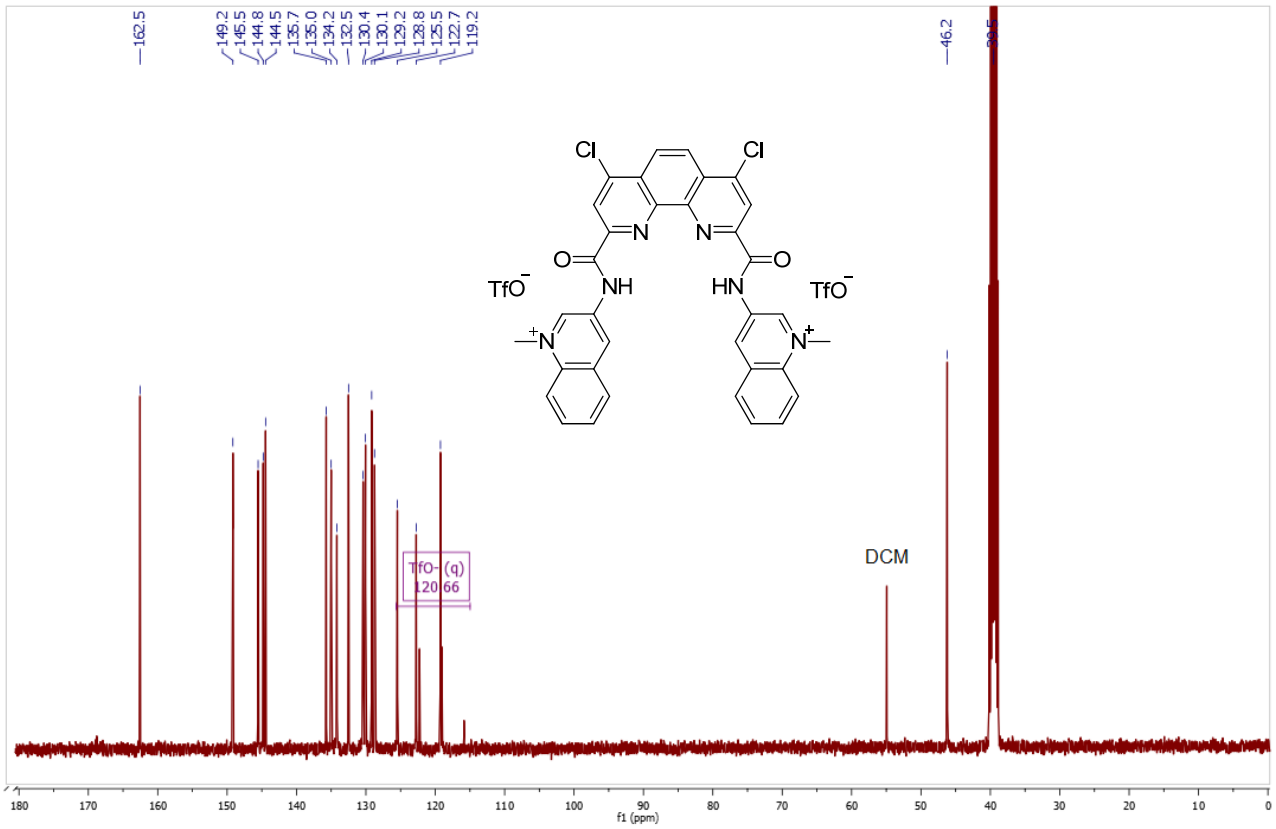
^{1}H NMR (400 MHz, DMSO-d_6)



3,3'-((4,7-Dichloro-1,10-phenanthroline-2,9-dicarbonyl)bis(azanediyl))bis(1-methylquinolin-1-ium) trifluoromethanesulfonate (9·2 TfO^-)

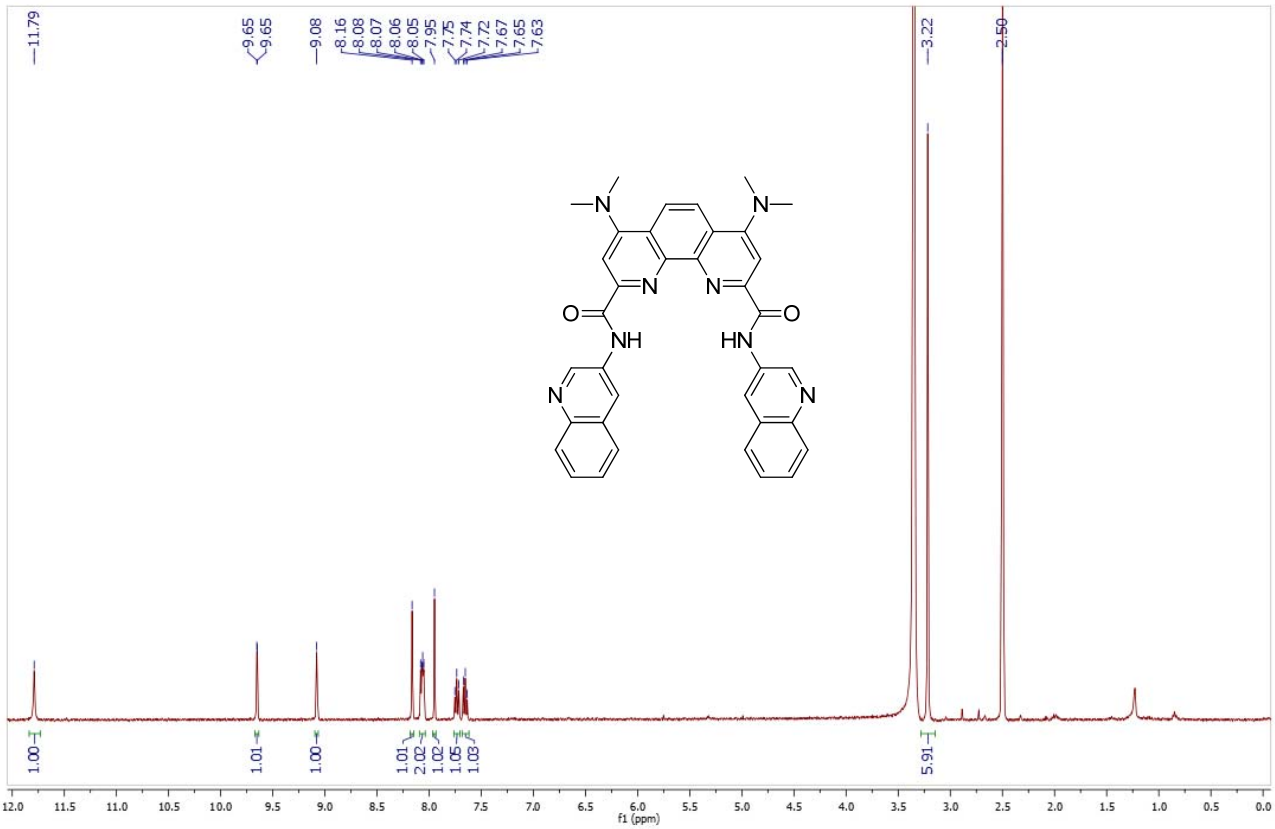
^1H NMR (400 MHz, DMSO-d_6); ^{13}C NMR (101 MHz, DMSO-d_6)





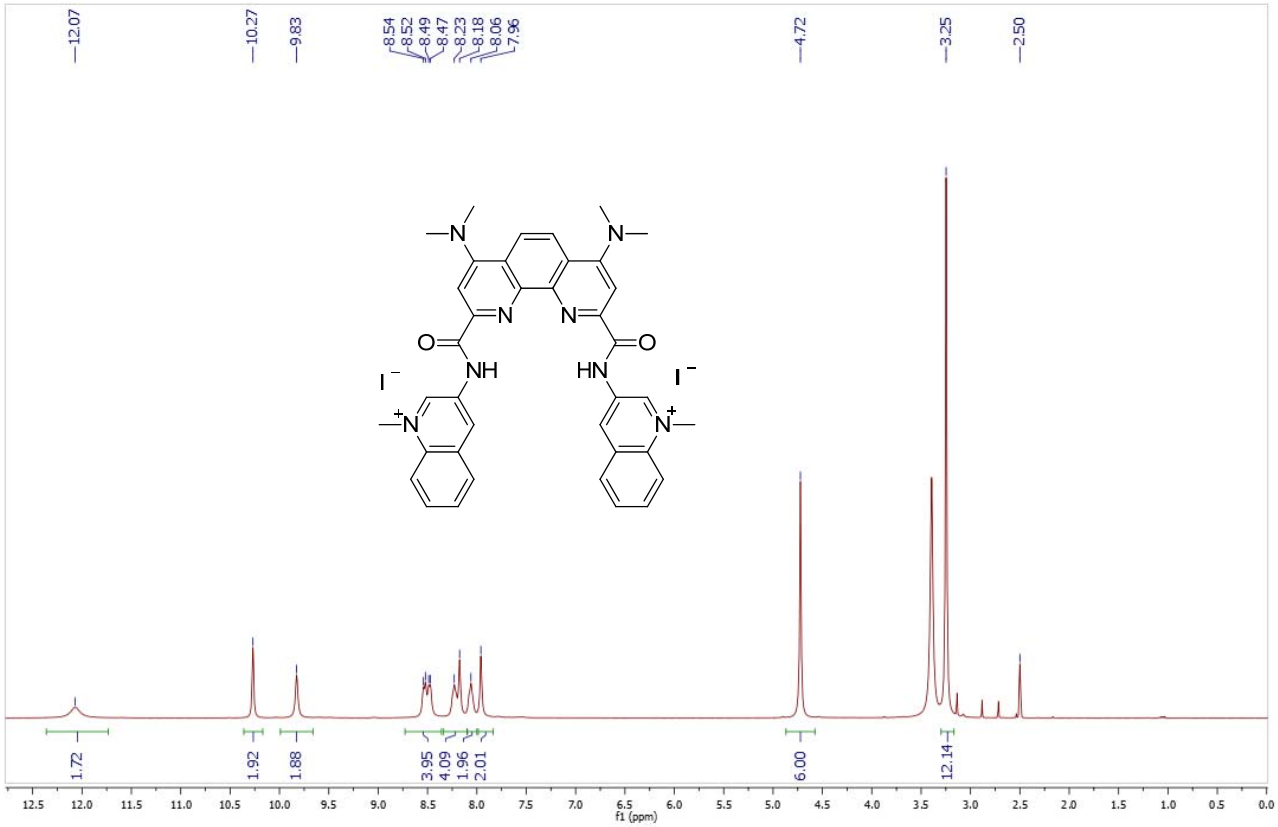
4,7-Bis(dimethylamino)-*N*^{2},*N*^{9}-di(quinolin-3-yl)-1,10-phenanthroline-2,9-dicarboxamide (10)

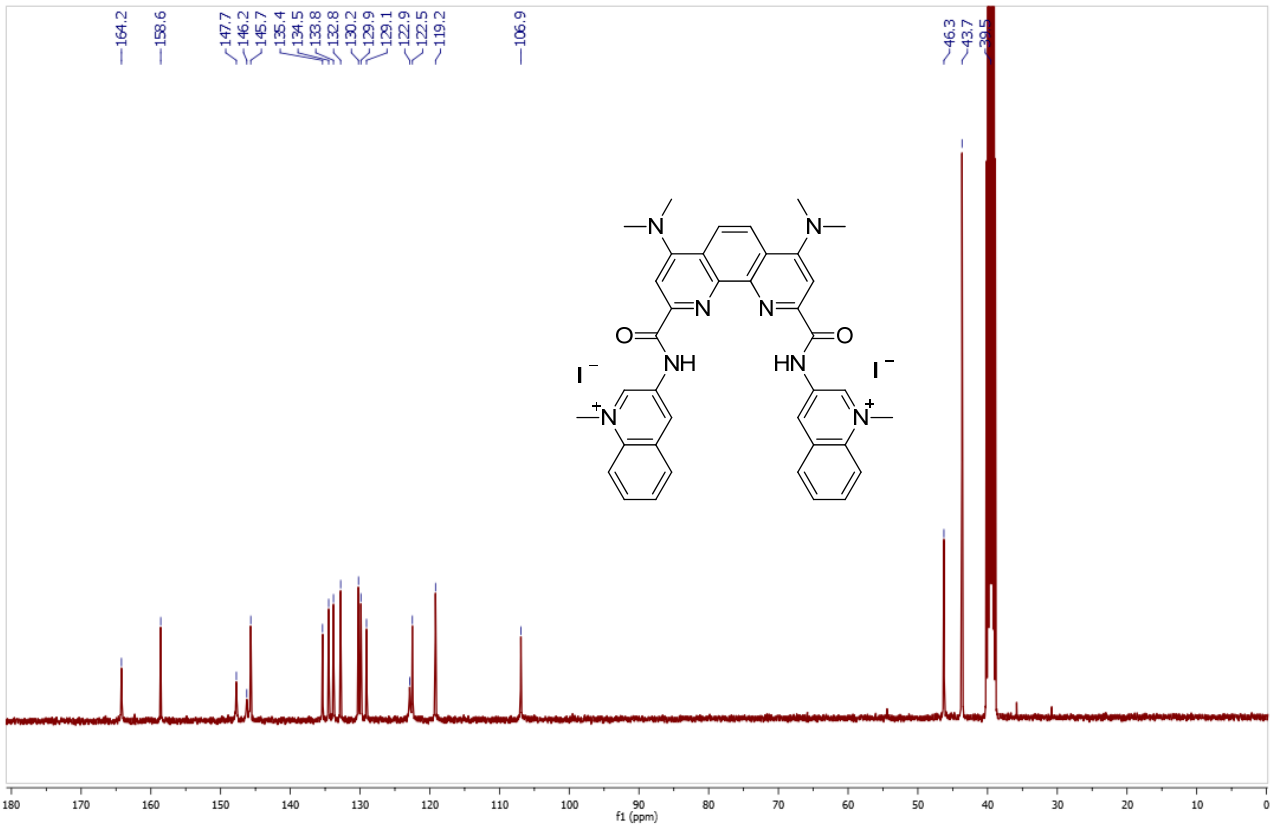
^{1}H NMR (400 MHz, DMSO-d_6)



3,3'-((4,7-Bis(dimethylamino)-1,10-phenanthroline-2,9-dicarbonyl)bis(azanediyl))bis(1-methylquinolin-1-ium) iodide (11)

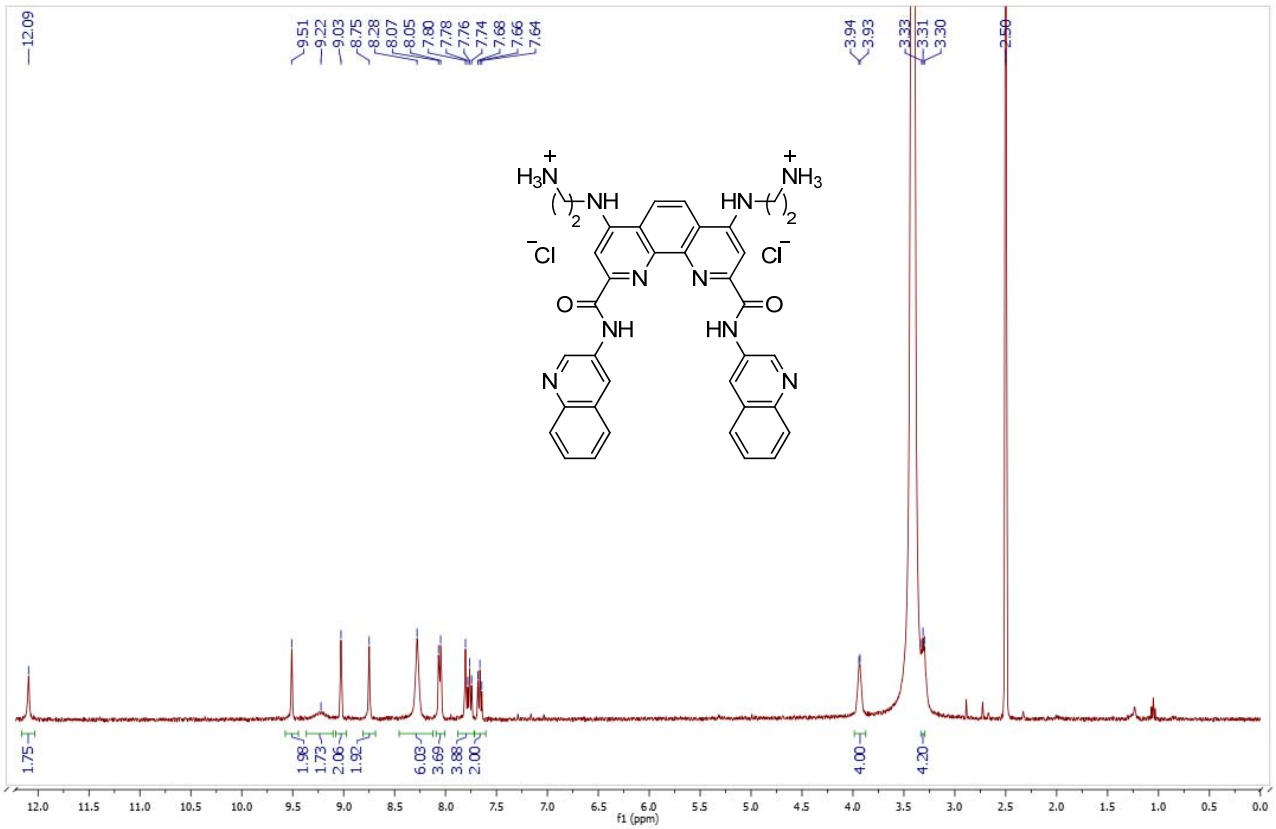
^{1}H NMR (400 MHz, DMSO-d_6); ^{13}C NMR (101 MHz, DMSO-d_6)

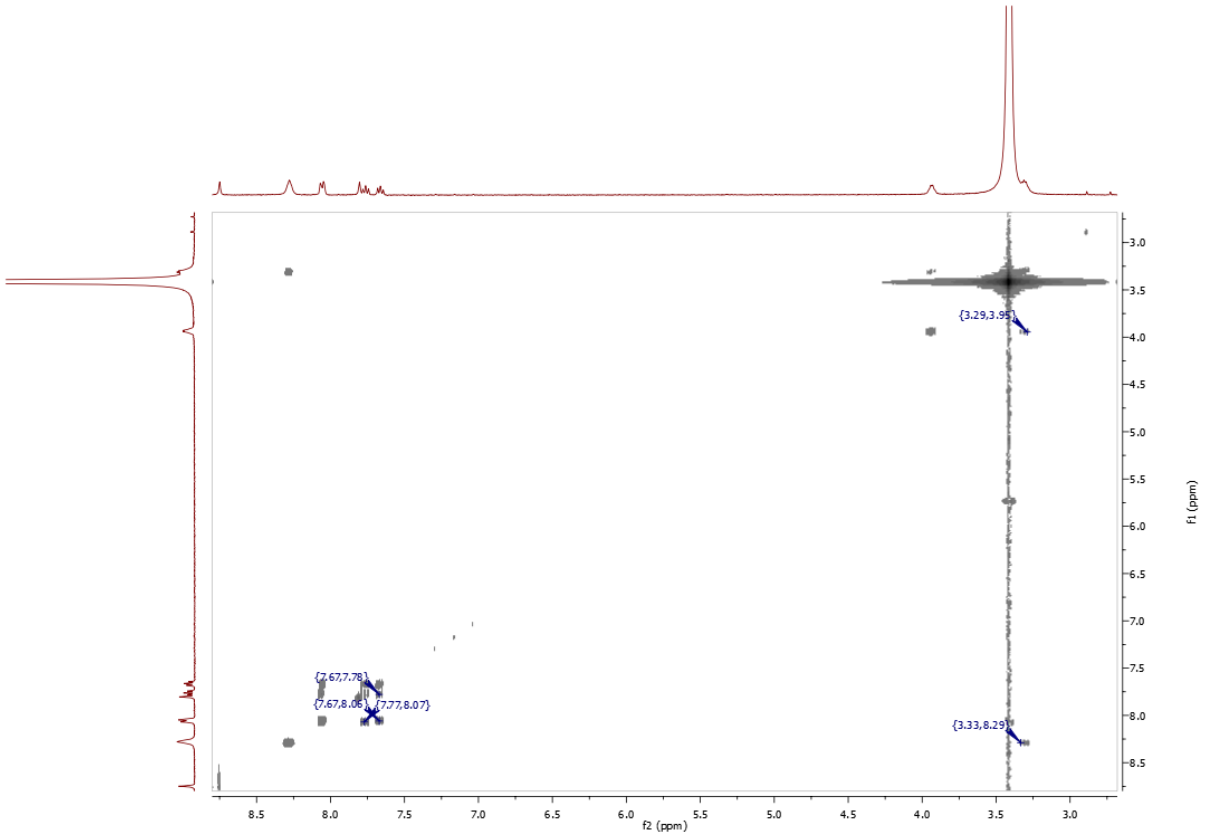




2,2'-((2,9-Bis(quinolin-3-ylcarbamoyl)-1,10-phenanthroline-4,7-diyl)bis(azanediyl))diethanaminium chloride (12a)

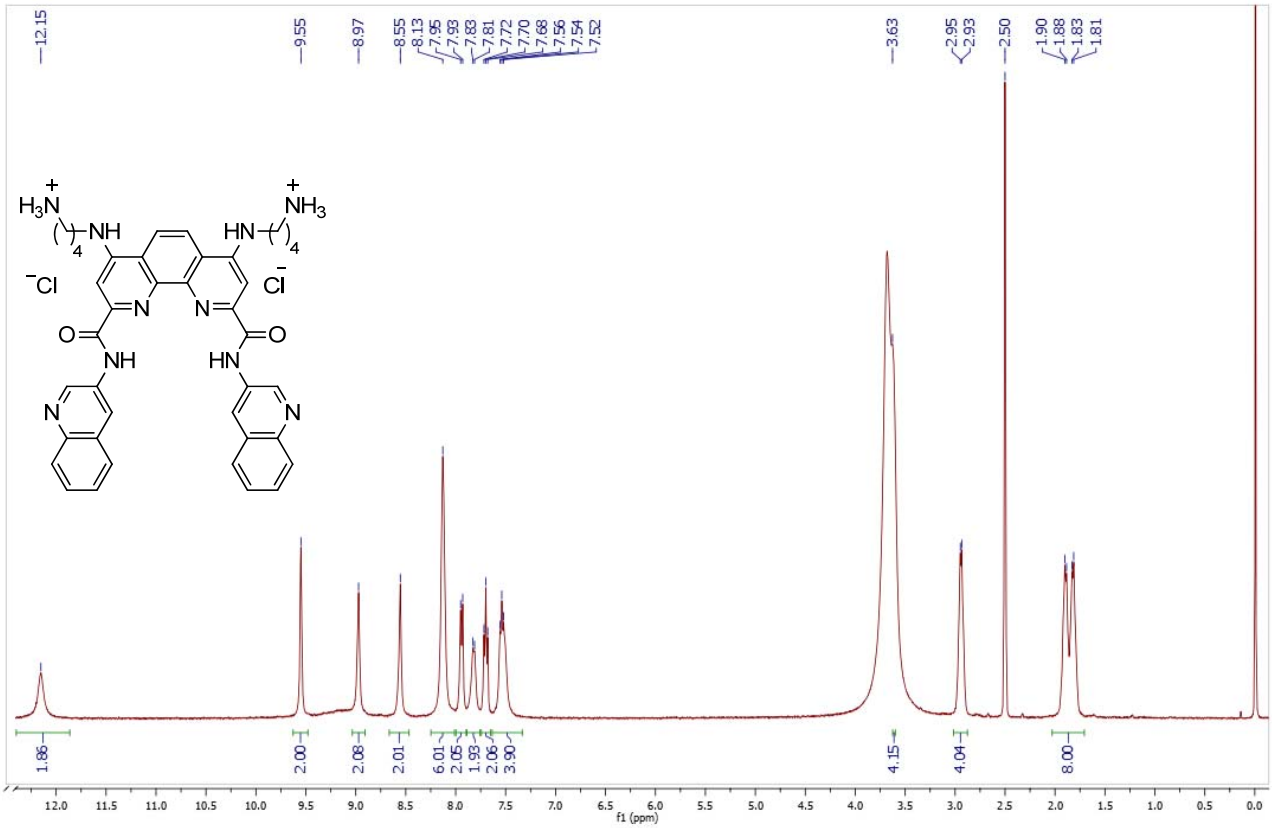
^{1}H NMR (400 MHz, DMSO-d_6); ^{1}H COSY NMR (400 MHz; 400 MHz, DMSO-d_6)

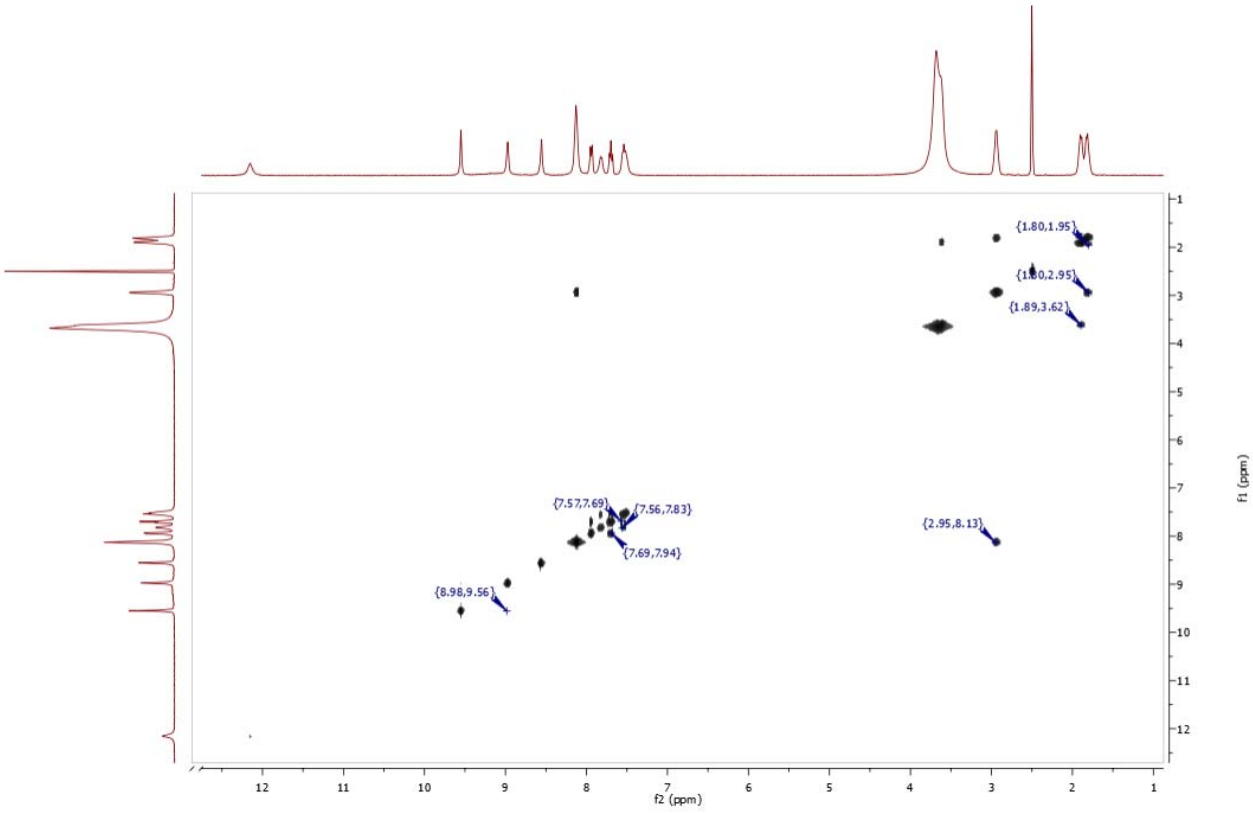




4,4'-((2,9-Bis(quinolin-3-ylcarbamoyl)-1,10-phenanthroline-4,7-diyl)bis(azanediyl))bis(butan-1-aminium) chloride (12b)

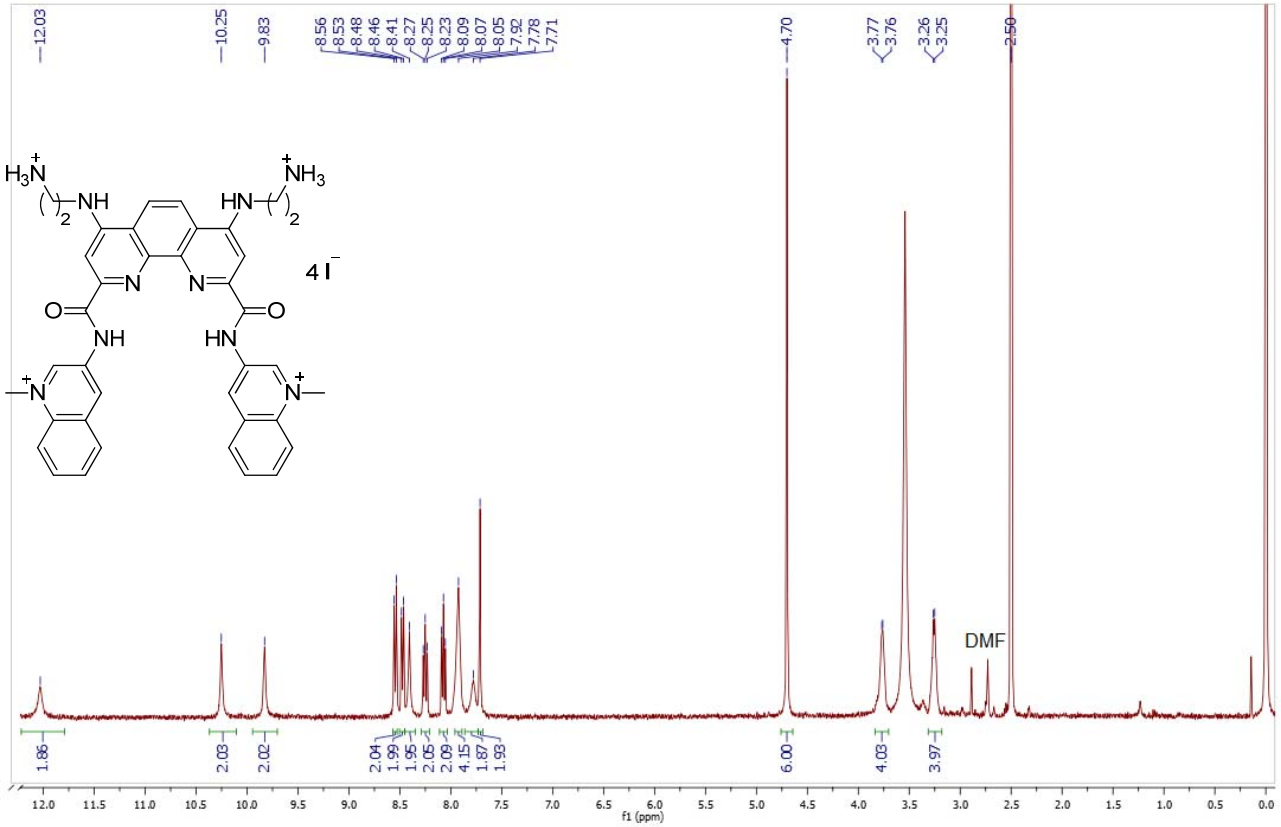
^{1}H NMR (400 MHz, DMSO-d_6); ^{1}H COSY NMR (400 MHz; 400 MHz, DMSO-d_6)

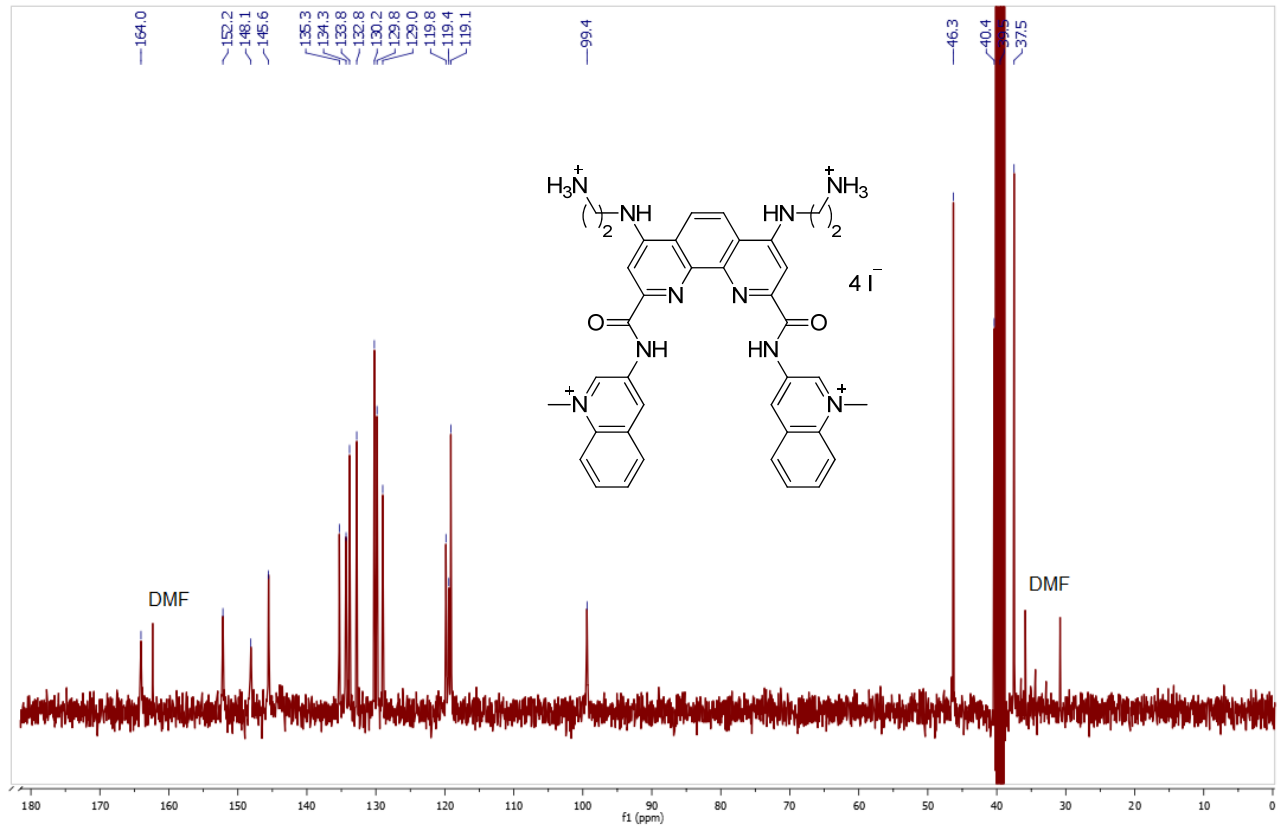




3,3'-((4,7-Bis((2-ammonioethyl)amino)-1,10-phenanthroline-2,9-dicarbonyl)bis(azanediyl))bis(1-methylquinolin-1-ium) iodide (13a)

^{1}H NMR (400 MHz, DMSO-d_6); ^{13}C NMR (101 MHz, DMSO-d_6)





3,3'-((4,7-Bis((4-ammoniobutyl)amino)-1,10-phenanthroline-2,9-dicarbonyl)bis(azanediyl))bis(1-methylquinolin-1-ium) iodide (13b)

^{1}H NMR (400 MHz, DMSO-d_6); ^{13}C NMR (101 MHz, DMSO-d_6, TFA)