Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supplementary Information

For

Transition Metal-Free, Visible-Light Mediated Synthesis of 1,10-Phenanthroline Derived Ligand Systems

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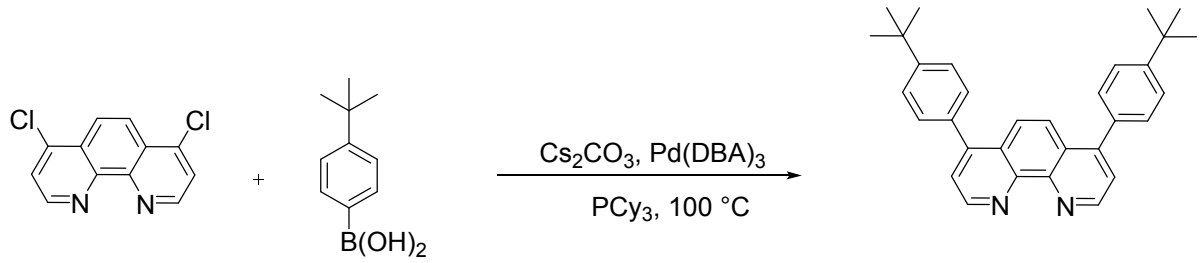
1 Experimental Procedures

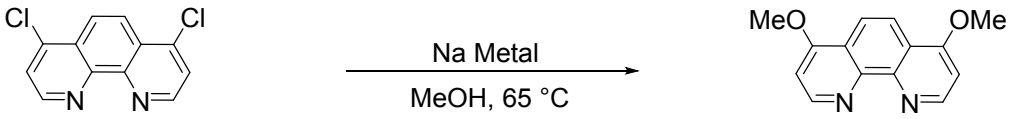
1.1 General Procedures

All reagents were purchased from Alfa-Aesar, Sigma-Aldrich or Fisher Scientific and used as received. Mass spectra were obtained using: a Waters SQD2 (ES), a Shimadzu Axima Confidence (MALDI), a Agilent 6120 Quadrupole LCMS (APCI), or a Thermo EXACTIVE Plus EMR Orbitrap (HRMS) apparatus. Reported mass values fall within ± 10 ppm mass units for electrospray and high resolution mass spectrometry (HRMS). Infrared spectra were recorded on a Thermo Scientific Nicolet iS5 spectrometer. Absorption maxima (ν_{max}) are recorded in wavenumbers (cm^{-1}) with use of the following abbreviations: w, weak; m, medium; s, strong; br, broad. Melting points were recorded on a Sanyo Gallenkamp MPD350 apparatus and readings are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded with B400 Bruker Avance III or B500 Bruker Avance II+ spectrometers. NMR assignments were supported by 2D, ^{1}H-^{1}H COSY and ^{13}C-^{1}H HMQC experiments. Chemical shifts (δ_H) are quoted in parts per million (ppm) to the nearest 0.01 ppm, calibrated to the relevant residual solvent peaks. Coupling constants are reported in Hz. Signal multiplicity is described with the use of the abbreviations: [s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad]. X-Ray crystallography was performed at the University of Manchester by Dr Robin G. Pritchard.

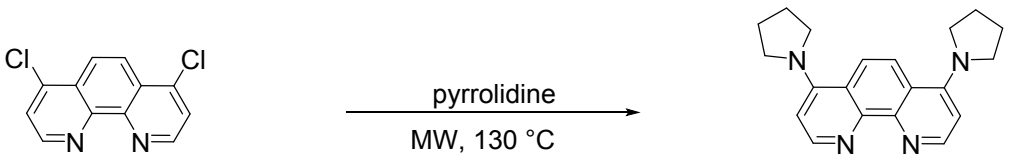
1.2 Synthesis of Substrates for α-C-H Functionalisation



4,7-bis(4-(*t*-butyl)phenyl)-1,10-phenanthroline. A thoroughly degassed suspension of 4,7-dichloro-1,10-phenanthroline (1.00 g, 4.00 mmol), Cs_2CO_3 (4.43 g, 13.6 mmol), 4-*t*-butylphenylboronic acid (2.14 g, 12.0 mmol), $Pd_2(DBA)_3$ (0.18 g, 0.2 mmol, 5 mol %) and PCy_3 (0.13 g, 0.5 mmol, 12 mol %) in dioxane:H_2O (3:1, 30 mL) was heated at 100 °C for 3 h. The resulting suspension was cooled to ambient temperature and diluted with $CHCl_3$ (200 mL). The organics were washed with H_2O (1 x 200 mL), aqueous Na_2CO_3 (saturated solution) (2 x 200 mL), brine (1 x 150 mL), dried over $MgSO_4$ and concentrated *in vacuo* to afford a brown solid. This crude material was recrystallized from MeOH to provide compound **1i** as an orange crystalline solid (1.49 g, 84%). m.p. 109-113 °C; ν_{max} / cm^{-1} 2959, 2900, 1502m; δ_H (500 MHz; $CDCl_3$) 9.23 (2H, d, *J* 4.6, C(2)H and C(9)H), 7.92 (2H, s, C(5)H and C(6)H), 7.60 (2H, d, *J* 4.6, C(3)H and C(8)H), 7.56 (2H, d, *J* 8.4, 2 x Ar-H), 7.49 (2H, d, *J* 8.4, 2 x Ar-H), 1.42 (18H, s, 6 x CH_3); δ_C (125 MHz; $CDCl_3$) 151.6 (Ar-C), 149.7 (C(2) and C(9)), 148.4 (Ar-C), 146.9 (Ar-C), 135.0 (Ar-C), 129.4 (Ar-CH), 126.5 (Ar-C), 125.5 (Ar-CH), 124.1 (C(3) and C(8) or C(5) and C(6)), 123.4 (C(3) and C(8) or C(5) and C(6)), 34.7 (C-$(CH_3)_3$), 31.4 (CH_3); *m/z* (+ES) 445 ($[M+H]^+$, 70 %); HRMS (+ES) calculated for $C_{32}H_{33}N_2$ ($[M+H]^+$): 445.2638, found: 445.2635.



4,7-dimethoxy-1,10-phenanthroline. Anhydrous MeOH (60 mL) was purged with N_2 for 15 minutes before being treated with small portions of sodium metal (0.46 g, 20 mmol). The resulting suspension was left to stir at ambient temperature until complete dissolution was achieved. Compound **1a** (1.00 g, 4.01 mmol) was added and the suspension was heated at reflux for 24 h. Concentration of the resulting yellow solution *in vacuo* to ~15 mL, followed by the addition of H_2O (100 mL) resulted in the formation of a tan precipitate. The suspension was refrigerated overnight, filtered and the filtrate washed with H_2O (3 x 50 mL) and Et_2O (3 x 30 mL), to obtain 4,7-dimethoxy-1,10-phenanthroline **1j** as a white solid (0.86 g, 90 %). m.p. 208-211 °C [Lit.[1] m.p. 209-210 °C]; δ_H (500 MHz; $CDCl_3$) 9.01 (2H, d, *J* 5.4, C(2)H and C(9)H), 8.19 (2H, s, C(5)H and C(6)H), 7.00 (2H, d, *J* 5.4, C(3)H and C(8)H), 4.10 (6H, s, 2 x CH_3); δ_C (125MHz; $CDCl_3$) 162.3 (Ar-C), 151.2 (C(2)H and C(9)H), 146.9 (Ar-C), 121.0 (Ar-C), 119.0 (C(5)H and C(6)H), 102.8 (C(3)H and C(8)H), 55.8 (OCH_3); *m/z* (+ES) 241 ($[M+H]^+$, 100 %). Data consistent with that reported by Buchwald *et al*.[1]

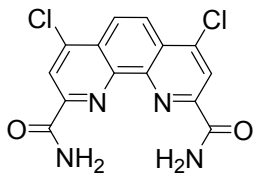


4,7-di(pyrrolidin-1-yl)-1,10-phenanthroline. A stirred suspension of **1a** (0.25 g, 1.0 mmol) in pyrrolidine (1.7 mL) was heated at 130 °C in a microwave reactor for 45 minutes. The reaction mixture was concentrated under *vacuo* and the brown residue washed with a saturated aqueous $NaHCO_3$ solution (3 x 5mL), H_2O (3 x 5mL) and dried under vacuum to afford **1k** as a bright yellow powder (0.30 g, 95 %). m.p. 142-144 °C; ν_{max} / cm^{-1} 2959w, 2949m, 2862w, 1665m, 1619m, 1567s, 1501s; δ_H (500 MHz; D_2O + DCl) 8.32 (2H, d, *J* 7.4 C(2)H and C(9)H), 8.29 (2H, s, C(5)H and C(6)H), 6.92 (2H, d, *J* 7.4 C(3)H and C(8)H), 3.97 (8H, ~br s, 4 x CH_2), 2.13 (8H, ~br s, 4 x CH_2); δ_C (100 MHz; D_2O + DCl) 155.5 (Ar-C), 139.2 (C(2) and (C(9)), 130.7 (Ar-C), 121.4 (C(5) and (C(6)), 118.6 (Ar-C), 104.5 (C(3) and C(8)), 54.0 (CH_2), 25.2 (CH_2); *m/z* (+ES) 319 ($[M+H]^+$, 100 %). HRMS (+HESI) calculated for $C_{20}H_{23}N_4$ ($[M+H]^+$): 319.1917, found: 319.1906. Data consistent with that reported by Ulven *et al*.[2]

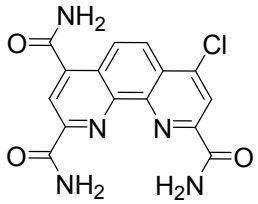
Procedures for Photoredox Mediated α-C-H Functionalisation

General Procedure:

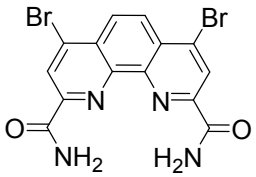
A stirred mixture of the 1,10-phenanthroline derivative (0.10 g, 0.23 – 0.48 mmol, 1.0 eqv.), $(NH_4)_2S_2O_8$ (1.35 – 2.88 mmol, 6.0 eqv.), benzaldehyde (0.46 – 0.96 mmol, 2.0 eqv) and EtOAc: formamide (1:1) (5-10 mL) was placed in an oven dried, 20 mL Teflon sealed vial. The reaction mixture was thoroughly degassed, refilled with N_2, placed in a water bath at 30 °C and irradiated with 2 household compact fluorescent lamps (CFL) (23 W) at a distance of approximately 5 cm for the indicated time. After this period, the mixture was diluted with H_2O (5 mL), filtered and the precipitate washed with H_2O (2 x 5 mL), MeOH (2 x 10 mL) and Et_2O (2 x 10 mL) to afford the target compound.



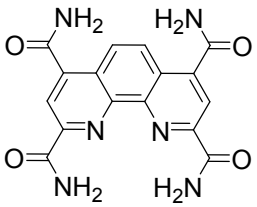
4,7-dichloro-1,10-phenanthroline-2,9-dicarboxamide. According to the general procedure, a mixture of 4,7-dichloro-1,10-phenanthroline (0.10 g, 0.40 mmol), $(NH_4)_2S_2O_8$ (0.55 g, 2.40 mmol) and benzaldehyde (0.09 mL, 0.09 g, 0.80 mmol) in EtOAc: formamide (1:1) (10 mL) was irradiated for 16 h to afford **2a** as a pale tan solid (0.11 g, 82 %). δ_H (500 MHz; DMSO-d_6) 9.00 (2H, br s, N$\underline{H}_2$), 8.56 (2H, s, C(3)$\underline{H}$ and C(8)$\underline{H}$ or C(5)$\underline{H}$ and C(6)$\underline{H}$), 8.52 (2H, s, C(3)$\underline{H}$ and C(8)$\underline{H}$ or C(5)$\underline{H}$ and C(6)$\underline{H}$), 8.05 (2H, br s, N$\underline{H}_2$); δ_C (125 MHz; DMSO-d_6) 164.7 ($\underline{C}ONH_2$), 150.8 (Ar-$\underline{C}$), 145.0 (Ar-$\underline{C}$), 143.2 (Ar-$\underline{C}$), 127.6 (Ar-$\underline{C}$), 124.5 ($\underline{C}$(5)H and $\underline{C}$(6)H or $\underline{C}$(3)H and $\underline{C}$(8)H), 121.7 ($\underline{C}$(5)H and $\underline{C}$(6)H or $\underline{C}$(3)H and $\underline{C}$(8)H); *m/z* (MALDI-dithranol) 335 ([M{$^{35}Cl_2$}+H]$^+$, 100 %), 337 ([M{$^{35}Cl^{37}Cl$}+H]$^+$, 70 %), 339 ([M{$^{37}Cl_2$}+H]$^+$, 20 %). Data consistent with that reported by Edwards *et al*.[3]



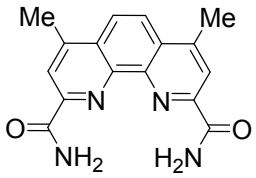
7-chloro-1,10-phenanthroline-2,4,9-tricarboxamide. According to the general procedure, a mixture of 7-chloro-1,10-phenanthroline (0.10 g, 0.47 mmol), $(NH_4)_2S_2O_8$ (0.97 g, 4.23 mmol) and benzaldehyde (0.15 mL, 0.15 g, 1.41 mmol) in EtOAc: formamide (1:1) (10 mL) was irradiated for 48 h. In addition to the general procedure, the resulting yellow solid was further triturated with ice-cold MeOH (2 x 5 mL) to afford target **2b** (0.14 g, 88 %). m.p. 280 °C (decomposed); ν_{max} / cm^{-1} 3429br , 3170br, 1684s (C=O); δ_H (500 MHz; DMSO-d_6) 8.99 (2H, br s, N<u>H</u>$_2$), 8.54 (1H, s, C(3)<u>H</u> or C(8)<u>H</u>), 8.53 (1H, br s, N<u>H</u>), 8.52 (1H, d, *J* 9.5, C(5)<u>H</u> or C(6)<u>H</u>), 8.47 (1H, s, C(3)<u>H</u> or C(8)<u>H</u>), 8.45 (1H, d, *J* 9.5, C(5)<u>H</u> or C(6)<u>H</u>), 8.11 (1H, br s, N<u>H</u>), 8.01 (2H, br s, N<u>H</u>$_2$), δ_C (125 MHz; DMSO-d_6) 168.1 (<u>C</u>ONH$_2$), 165.4 (<u>C</u>ONH$_2$), 165.0 (<u>C</u>ONH$_2$), 150.5 (Ar-<u>C</u>), 150.4 (Ar-<u>C</u>), 145.2 (Ar-<u>C</u>), 144.3 (Ar-<u>C</u>), 144.1 (Ar-<u>C</u>), 143.1 (Ar-<u>C</u>), 127.4 (Ar-<u>C</u>), 126.7 (Ar-<u>C</u>H), 126.5 (Ar-<u>C</u>), 123.6 (Ar-<u>C</u>H), 121.5 (Ar-<u>C</u>H), 119.1 (Ar-C<u>H</u>); *m/z* (+ESI) 366 ([M{^{35}Cl}+Na]$^+$, 100 %), 368 ([M{^{37}Cl}+Na]$^+$; HRMS (+HESI) calculated for $C_{15}H_{10}N_5O_3Na$ ([M+Na]$^+$): 366.0364, found: 366.0351.



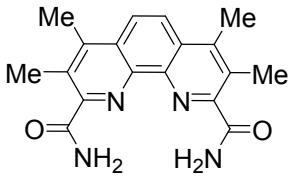
4,7-dibromo-1,10-phenanthroline-2,9-dicarboxamide. According to the general procedure, a mixture of 4,7-dibromo-1,10-phenanthroline (0.10 g, 0.30 mmol), $(NH_4)_2S_2O_8$ (0.41 g, 1.78 mmol) and benzaldehyde (0.06 mL, 0.06 g, 0.60 mmol) in EtOAc: formamide (1:1) (6 mL) was irradiated for 16 h to afford **2c** as a pale tan solid (0.10 g, 78 %). m.p. >300 °C; ν_{max} / cm^{-1} 3438br, 3279br, 3214br, 1692 (C=O); δ_H (500 MHz; DMSO-d_6) 8.97 (2H, br s, N<u>H</u>$_2$), 8.71 (2H, s, C(3)<u>H</u> and C(8)<u>H</u> or C(5)<u>H</u> and C(6)<u>H</u>), 8.47 (2H, s, C(3)<u>H</u> and C(8)<u>H</u> or C(5)<u>H</u> and C(6)<u>H</u>), 8.03 (2H, br s, N<u>H</u>$_2$); δ_C (125 MHz; DMSO-d_6) 164.7 (<u>C</u>ONH$_2$), 150.5 (Ar-<u>C</u>), 144.8 (Ar-<u>C</u>), 134.9 (Ar-<u>C</u>), 129.1 (Ar-<u>C</u>), 127.4 (<u>C</u>(5)H and <u>C</u>(6)H or <u>C</u>(3)H and <u>C</u>(8)H), 125.5 (<u>C</u>(5)H and <u>C</u>(6)H or <u>C</u>(3)H and <u>C</u>(8)H); *m/z* (MALDI-dithranol) 423 ([M{$^{79}Br_2$}+H]$^+$, 50 %), 425 ([M{^{79}Br^{81}Br}+H]$^+$, 100 %), 427 ([M{$^{81}Br_2$}+H]$^+$, 50 %). HRMS (+HESI) calculated for $C_{14}H_9N_4O_2Br_2$ ([M+H]$^+$): 422.9087, found: 422.9086.



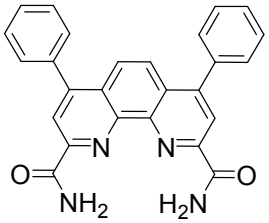
1,10-phenanthroline-2,4,7,9-tetracarboxamide: According to the general procedure, a mixture of 1,10-phenanthroline (0.10 g, 0.55 mmol), $(NH_4)_2S_2O_8$ (1.52 g, 6.66 mmol) and benzaldehyde (0.22 mL, 0.24 g, 2.2 mmol) in EtOAc: formamide (1:1) (10 mL) was irradiated for 16 h. In addition to the general procedure, the resulting yellow solid was further triturated with ice-cold MeOH (2 x 5 mL) to afford target **2d** (0.13 g, 68 %). m.p. >300 °C; ν_{max} / cm^{-1} 3450br, 3338br, 3289br, 3181w, 3068w, 1686 (C=O); 1678 (C=O); δ_H (500 MHz; DMSO-d_6 + DCl) 8.40 (1H, s, C(3)H and C(8)H or C(5)H and C(6)H), 8.34 (2H, s, C(3)H and C(8)H or C(5)H and C(6)H); δ_C (125 MHz; DMSO-d_6 + DCl) 168.4 (CONH$_2$), 165.9 (CONH$_2$), 150.3 (Ar-C), 144.7 (Ar-C), 144.3 (Ar-C), 126.5 (C(5)H and C(6)H or C(3)H and C(8)H), 126.0 (C(5)H and C(6)H or C(3)H and C(8)H), 119.2 (Ar-C); *m/z* (+ESI) 353 ([M+H]$^+$, 100 %). HRMS (+HESI) calculated for $C_{16}H_{12}N_6O_4Na$ ([M+Na]$^+$): 375.0812, found: 375.0797.



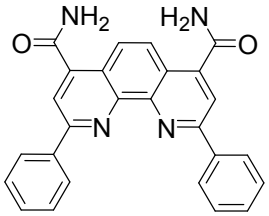
4,7-dimethyl-1,10-phenanthroline-2,9-dicarboxamide. According to the general procedure, a mixture of 4,7-dimethyl-1,10-phenanthroline (0.10 g, 0.48 mmol), $(NH_4)_2S_2O_8$ (0.66 g, 2.88 mmol) and benzaldehyde (0.10 mL, 0.10 g, 0.96 mmol) in EtOAc: formamide (1:1) (10 mL) was irradiated for 20 h to afford **2e** as an off white powder (0.11 g, 75 %). m.p. >300 °C; ν_{max} / cm^{-1} 3430br, 3295br, 1676s (C=O); δ_H (500 MHz; DMSO-d_6) 8.88 (2H, br s, NH$_2$), 8.32 (2H, s, (C(3)H and C(8)H or C(5)H and C(6)H)), 8.30 (2H, s, (C(3)H and C(8)H or C(5)H and C(6)H)), 7.80 (2H, br s, NH$_2$), 2.88 (6H, s, 2 x CH$_3$); δ_C (150 MHz; DMSO-d_6) 165.2 (CONH$_2$), 163.4 (Ar-C), 150.9 (Ar-C), 149.0 (Ar-C), 140.7 (Ar-C), 130.0 (Ar-C), 124.8 (C(3) and C(8) or C(5) and C(6)), 123.5 (C(3) and C(8) or C(5) and C(6)), 19.7 (CH$_3$); *m/z* (APCI) 295 ([M+H]$^+$, 30 %); HRMS (APCI) calculated for $C_{16}H_{15}N_4O_2$ ([M+H]$^+$): 295.1190, found: 295.1191.



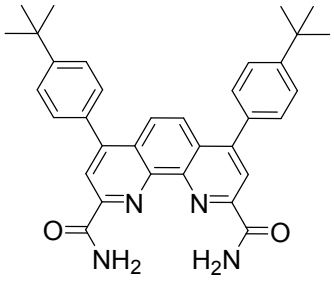
3,4,7,8-tetramethyl-1,10-phenanthroline-2,9-dicarboxamide. According to the general procedure, a mixture of 3,4,7,8-tetramethyl-1,10-phenanthroline (0.10 g, 0.42 mmol), $(NH_4)_2S_2O_8$ (0.58 g, 2.54 mmol) and benzaldehyde (0.09 mL, 0.09 g, 0.85 mmol) in EtOAc: formamide (1:1) (10 mL) was irradiated for 48 h to afford **2f** as an off white powder (0.82 g, 62 %). m.p. >300 °C; ν_{max} / cm^{-1} 3353, 3188, 1657s (C=O); δ_H (500 MHz; DMSO-d_6) 8.22 (2H, s, (C(5)H and C(6)H), 8.22 (2H, br s, NH_2), 7.71 (2H, br s, NH_2), 2.71 (6H, s, 2 x CH_3), 2.59 (6H, s, 2 x CH_3); δ_C (125 MHz; DMSO-d_6) 169.9 ($CONH_2$), 153.0 (Ar-C), 143.7 (Ar-C), 142.2 (Ar-C), 128.5 (Ar-C), 127.1 (Ar-C), 123.2 (C(5)H and C(6)H), 15.5 (CH_3), 14.6 (CH_3); *m/z* (APCI) 323 ($[M+H]^+$, 100 %); HRMS (APCI) calculated for $C_{18}H_{18}N_4O_2$ ($[M+H]^+$): 323.1503, found: 323.1500.



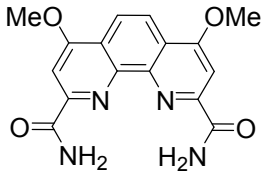
4,7-diphenyl-1,10-phenanthroline-2,9-dicarboxamide. According to the general procedure, a mixture of 4,7-diphenyl-1,10-phenanthroline (0.10 g, 0.30 mmol), $(NH_4)_2S_2O_8$ (0.41 g, 1.81 mmol) and benzaldehyde (0.06 mL, 0.06 g, 0.60 mmol) in EtOAc: formamide (1:1) (10 mL) was irradiated for 20 h to afford **2g** as an off white solid (0.09 g, 75 %). m.p. 215-217 °C; δ_H (500 MHz; DMSO-d_6) 9.05 (2H, br s, NH_2), 8.35 (2H, s, C(3)H and C(8)H or C(5)H and C(6)H), 8.01 (2H, s, C(3)H and C(8)H or C(5)H and C(6)H), 7.97 (2H, br s, NH_2), 7.64 (10H, m, Ar-H); δ_C (125 MHz; DMSO-d_6) 166.5 ($CONH_2$), 150.2 (Ar-C), 149.8 (Ar-C), 145.5 (Ar-C), 137.5 (Ar-C), 130.1 (Ar-CH), 129.5 (Ar-CH), 129.4 (Ar-CH), 127.9 (Ar-C), 125.7 (C(5)H and C(6)H or C(3)H and C(8)H)), 121.8 (C(5)H and C(6)H or C(3)H and C(8)H)); *m/z* (APCI) 441 ($[M+Na]^+$, 15 %), 419 ($[M+H]^+$, 100 %). Data consistent with that reported by Edwards *et al*.[3]



2,9-diphenyl-1,10-phenanthroline-4,7-dicarboxamide. According to the general procedure, a mixture of 2,9-diphenyl-1,10-phenanthroline (0.10 g, 0.30 mmol), $(NH_4)_2S_2O_8$ (0.41 g, 1.80 mmol) and benzaldehyde (0.06 mL, 0.06 g, 0.60 mmol) in EtOAc: formamide (1:1) (8 mL) was irradiated for 24 h. In addition to the general procedure, the resulting solid was further triturated with ice-cold MeOH (2 x 5 mL) to afford target **2h** as a bright yellow solid (0.10 g, 81 %). m.p. 180-183 °C; ν_{max} / cm^{-1} 3311br (N-H), 3175br (N-H), 1663m (C=O), 1599m (C=C); δ_H (500 MHz; DMSO-d_6) 8.56 (4H, d, *J* 7.4, Ar-H), 8.45 (2H, br s, NH_2), 8.43 (2H, s, C(3)H and C(8)H or C(5)H and C(6)H), 8.28 (2H, s, C(3)H and C(8)H or C(5)H and C(6)H), 8.05 (2H, br s, NH_2), 7.67 (4H, d, *J* 7.4, Ar-H), 7.58 (2H, d, *J* 7.4, Ar-H); δ_C (125 MHz; DMSO-d_6) 168.6 ($CONH_2$), 155.22 (Ar-C), 147.8 (Ar-C), 143.6 (Ar-C), 138.4 (Ar-C), 130.0 (Ar-CH), 129.1 (Ar-CH), 127.4 (Ar-CH), 123.9 (C(5)H and C(6)H or C(3)H and C(8)H), 123.8 (Ar-C), 117.9 (C(5)H and C(6)H or C(3)H and C(8)H); *m/z* (+ES) 419 ($[M+H]^+$, 100 %); HRMS (+HESI) calculated for $C_{26}H_{19}O_2N_4$ ($[M+H]^+$): 419.1503, found: 419.1494.



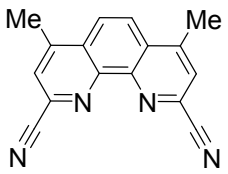
4,7-bis(4-(*t*-butyl)phenyl)-1,10-phenanthroline-2,9-dicarboxamide. According to the general procedure, a mixture of 4,7-bis(4-(tert-butyl)phenyl)-1,10-phenanthroline (0.10 g, 0.23 mmol), $(NH_4)_2S_2O_8$ (0.31 g, 1.35 mmol) and benzaldehyde (0.05 mL, 0.50 g, 0.46 mmol) in EtOAc: formamide (1:1) (5 mL) was irradiated for 48 h to afford **2i** as a white powder (0.08 g, 65 %). m.p. >300 °C; ν_{max} / cm^{-1} 3377, 2958, 1686 (C=O); δ_H (500 MHz; $CDCl_3$) 8.58 (2H, s, (C(3)H and C(8)H or C(5)H and C(6)H)), 8.57 (2H, d, *J* 4.3, NH_2), 8.09 (2H, s, (C(3)H and C(8)H or C(5)H and C(6)H)), 7.60 (4H, d, *J* 8.3, 4 x Ar-CH), 7.53 (4H, d, *J* 8.3, 4 x Ar-CH), 5.83 (2H, d, *J* 4.3, NH_2), 1.44 (18H, s, 6 x CH_3); δ_C (125 MHz; $CDCl_3$) 166.8 ($CONH_2$), 152.2 (Ar-C), 150.5 (Ar-C), 148.7 (Ar-C), 134.2 (Ar-C), 129.5 (Ar-CH), 128.6 (Ar-C), 125.7 (Ar-CH), 125.6 (C(3) and C(8) or C(5) and C(6)), 125.1 (Ar-C), 122.0 (C(3) and C(8) or C(5) and C(6)), 34.8 (C-$(CH_3)_3$), 31.3 (CH_3); *m/z* (APCI) 531 ($[M+H]^+$, 100 %); HRMS (APCI) calculated for $C_{34}H_{35}N_4O_2$ ($[M+H]^+$): 531.2755, found: 531.2753.



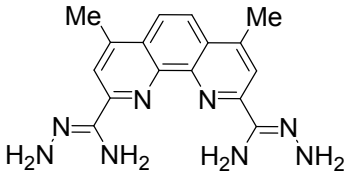
4,7-dimethoxy-1,10-phenanthroline-2,9-dicarboxamide. According to the general procedure, a mixture of 4,7-dimethoxy-1,10-phenanthroline (0.10 g, 0.42 mmol), $(NH_4)_2S_2O_8$ (0.57 g, 2.50 mmol) and benzaldehyde (0.08 mL, 0.08 g, 0.83 mmol) in EtOAc: formamide (1:1) (10 mL) was irradiated for 48 h to afford **2j** as a white powder (0.07 g, 53 %). δ_H (500 MHz; DMSO-d_6) 8.88 (2H, br s, N<u>H</u>$_2$), 8.25 (2H, s, C(3)<u>H</u> and C(8)<u>H</u> or C(5)<u>H</u> and C(6)<u>H</u>), 7.94 (2H, s, C(3)<u>H</u> and C(8)<u>H</u> or C(5)<u>H</u> and C(6)<u>H</u>), 7.82 (2H, br s, N<u>H</u>$_2$), 4.19 (6H, s, 2 x OC<u>H</u>$_3$); δ_C (125 MHz; DMSO-d_6) 166.1 (<u>C</u>ONH$_2$), 163.0 (Ar-<u>C</u>), 151.7 (Ar-<u>C</u>), 144.8 (Ar-<u>C</u>), 121.6 (<u>C</u>(5)H and <u>C</u>(6)H or <u>C</u>(3)H and <u>C</u>(8)H), 120.1 (<u>C</u>(5)H and <u>C</u>(6)H or <u>C</u>(3)H and <u>C</u>(8)H), 101.1 (Ar-<u>C</u>), 56.6 (<u>C</u>OCH$_3$); *m/z* (APCI) 328 ([M+H]$^+$, 100 %). Data consistent with that reported by Edwards *et al*.[3]

1.3.1 Synthesis of $CyMe_4$-BTPhen Ligands

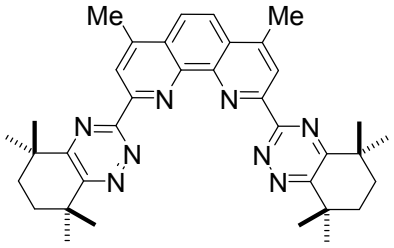
1.3.1.1 Synthesis of 4,7-dimethyl-$CyMe_4$-BTPhen



4,7-dimethyl-1,10-phenanthroline-2,9-dicarbonitrile. To DMF (14 mL) under a N_2 atmosphere was added oxalyl chloride (0.38 mL, 0.56 g, 4.44 mmol) at 0 °C with stirring. A white precipitate formed immediately which was accompanied by gas evolution. Once gas evolution had stopped, a suspension of bis-amide **2e** (0.45 g, 1.53 mmol) in DMF (10 mL) was added. The resulting mixture was left to stir for 5 h at 0 °C. Pyridine (0.55 mL, 0.55 g, 6.90 mmol) was added and the mixture left to stir for a further 30 min before being neutralised with a saturated solution of aqueous K_2CO_3 (12 mL), forming a precipitate. Precipitation was further encouraged through the addition of H_2O (25 mL). The precipitate was filtered, washed with H_2O (3 x 15 mL) and Et_2O (3 x 15 mL). The solid was dried *in vacuo* over silica to yield **3a** as a light tan powder (0.30 g, 77 %). m.p. >300 °C; ν_{max} / cm^{-1} 3037m, 2232w (C≡N), 1614m, 1565s, 1548s; δ_H (500 MHz; DMSO-d_6) 8.35 (2H, s, C(3)H and C(8)H or C(5)H and C(6)H), 8.27 (2H, s, C(3)H and C(8)H or C(5)H and C(6)H), 2.85 (6H, s, 2 x CH_3); δ_C (125 MHz; DMSO-d_6) 148.0 (Ar-C), 144.9 (Ar-C), 132.5 (Ar-C), 129.6 (Ar-C), 127.9 (C(5)H and C(6)H) or C(4)H and C(8)H), 125.2 (C(5)H and C(6)H) or C(4)H and C(8)H), 117.7 (C≡N), 18.5 (CH_3); *m/z* (APCI) 259 ($[M+H]^+$, 100 %); HRMS (+ES) calculated for $C_{16}H_{11}N_4$ ($[M+H]^+$): 259.0965, found: 259.0968.

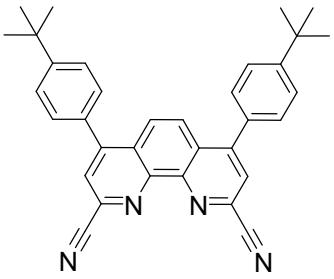


(2Z,9Z)-4,7-dimethyl-1,10-phenanthroline-2,9-bis(carbohydrazonamide). A suspension of **3a** (0.20 g, 0.78 mmol) in EtOH (8.5 mL) was treated with hydrazine hydrate (6.5 mL, 50-60 %). The suspension was left to stir for 72 h at ambient temperature, before being concentrated *in vacuo*. The precipitate was washed with H_2O (2 x 10 mL), Et_2O (3 x 40 mL) and dried *in vacuo* to yield compound **4a** as a bright yellow solid (0.18 g, 72 %). m.p. 250 °C (decomposed); ν_{max} / cm^{-1} 3324br (N-H), 3189br (N-H), 1617s, 1576s, 1543s; δ_H (500 MHz; DMSO-d_6) 8.14 (2H, s, C(3)H and C(8)H or C(5)H and C(6)H), 8.09 (2H, s, C(3)H and C(8)H or C(5)H and C(6)H), 6.07 (4H, br s, 2 x NH_2), 5.59 (4H, br s, 2 x NH_2), 2.76 (6H, s, 2 x CH_3); δ_C (125 MHz; DMSO) 150.7 (C=NNH_2), 144.8 (Ar-C), 143.7 (Ar-C), 143.5 (Ar-C), 127.4 (Ar-C), 121.9 (C(5)H and C(6)H or C(3)H and C(8)H), 119.3 (C(5)H and C(6)H or C(3)H and C(8)H), 18.9 (CH_3); *m/z* (+ES) 323 ([M+H]$^+$, 100 %); HRMS (APCI) calculated for $C_{16}H_{19}N_8$ ([M+H]$^+$): 323.1727, found: 323.1712.

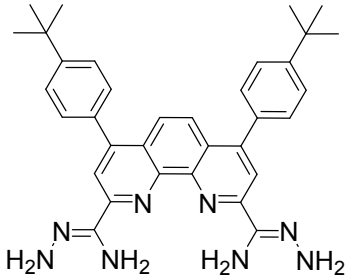


4,7-dimethyl-2,9-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[e][1,2,4]triazin-3-yl)-1,10-phenanthroline. A stirred suspension of **4a** (0.15 g, 0.47 mmol) and 3,3,6,6-tetramethylcyclohexane-1,2-dione **5a** (0.174 g, 1.02 mmol) in EtOH (6.0 mL) was heated at reflux for 5 h. After this time, the yellow suspension was allowed to cool to ambient temperature and taken to dryness *in vacuo*. The resulting yellow solid was triturated with cold Et_2O (3 x 20 mL) to give the desired bis-triazinyl-1,10-phenanthroline **6a** (0.20 g, 71 %) as a bright yellow solid. m.p. 185-188 °C; ν_{max} / cm^{-1} 3517br (N-H), 2960s, 2928s, 2862s, 1622m, 1577m; δ_H (500 MHz; $CDCl_3$) 8.73 (2H, s, C(3)H and C(8)H), 8.19 (2H, s, C(5)H and C(6)H), 2.95 (6H, s, 2 x CH_3), 1.91 (8H, s, 4 x CH_2), 1.60 (12H, s, 4 x CH_3), 1.56 (12H, s, 4 x CH_3); δ_C (125 MHz; $CDCl_3$) 164.9 (Ar-C), 163.0 (Ar-C), 161.7 (Ar-C), 153.3 (Ar-C), 146.6 (Ar-C), 145.4 (Ar-C), 128.9 (Ar-C), 124.2 (C(3)H and C(8)H), 123.1 (C(5)H and C(6)H), 37.5 (quat C), 36.5 (quat C), 33.7 (CH_2), 29.8 (CH_3), 29.3 (CH_3), 19.5 (CH_3); *m/z* (+ES) 587 ([M+H]$^+$, 100 %); HRMS (APCI) calculated for $C_{36}H_{43}N_8$ ([M+H]$^+$): 587.3605, found: 587.3582.

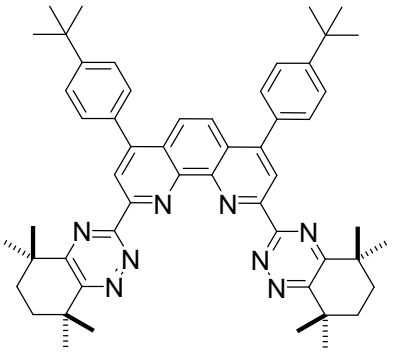
1.3.1.2 Synthesis of 4,7-di-(4'-*t*-Bu-Phenyl)-CyMe$_4$-BTPhen



4,7-bis(4-(*tert*-butyl)phenyl)-1,10-phenanthroline-2,9-dicarbonitrile. To DMF (11 mL) under a N_2 atmosphere was added oxalyl chloride (0.24 mL, 0.35 g, 1.36 mmol) at 0 ^oC with stirring. A white precipitate formed immediately which was accompanied by gas evolution. Once evolution of gas had stopped, a suspension of bis-amide **2i** (0.5 g, 0.94 mmol) in DMF (6 mL) was added. The resulting mixture was left to stir for 6 h at 0 ^oC. Pyridine (0.34 mL, 0.35 g, 4.24 mmol) was added and the mixture left to stir for a further 30 min before being neutralised with a saturated solution of aqueous K_2CO_3 (15 mL), forming a precipitate. Precipitation was further encouraged through the addition of H_2O (30 mL). The precipitate was filtered and washed with H_2O (3 x 20 mL). The solid was dried *in vacuo* to yield **3b** as a pink powder (0.39 g, 85 %). m.p. >300 °C; ν_{max} / cm^{-1} 2960m, 2902w, 2865w, 1611m (C≡N); δ_H (500 MHz; $CDCl_3$) 8.10 (2H, s, (C(3)H and C(8)H or C(5)H and C(6)H)), 7.99 (2H, s, (C(3)H and C(8)H or C(5)H and C(6)H)), 7.61 (4H, d, *J* 8.2, 4 x Ar-CH), 7.47 (4H, d, *J* 8.2, 4 x Ar-CH), 1.42 (18H, s, 6 x CH_3); δ_C (125 MHz; $CDCl_3$) 153.1 (Ar-C), 150.7 (Ar-C), 146.6 (Ar-C), 133.8 (Ar-C), 132.6 (Ar-C), 129.4 (Ar-CH), 128.4 (Ar-C), 127.5 (C(3) and C(8) or C(5) and C(6)), 126.5 (C(3) and C(8) or C(5) and C(6)), 126.1 (Ar-CH), 117.3 (C≡N), 34.9 (C-$(CH_3)_3$), 31.3 (CH_3); *m/z* (+ES) 495 ($[M+H]^+$, 100 %); HRMS (APCI) calculated for $C_{34}H_{31}N_4$ ($[M+H]^+$): 495.2543, found: 495.2550.



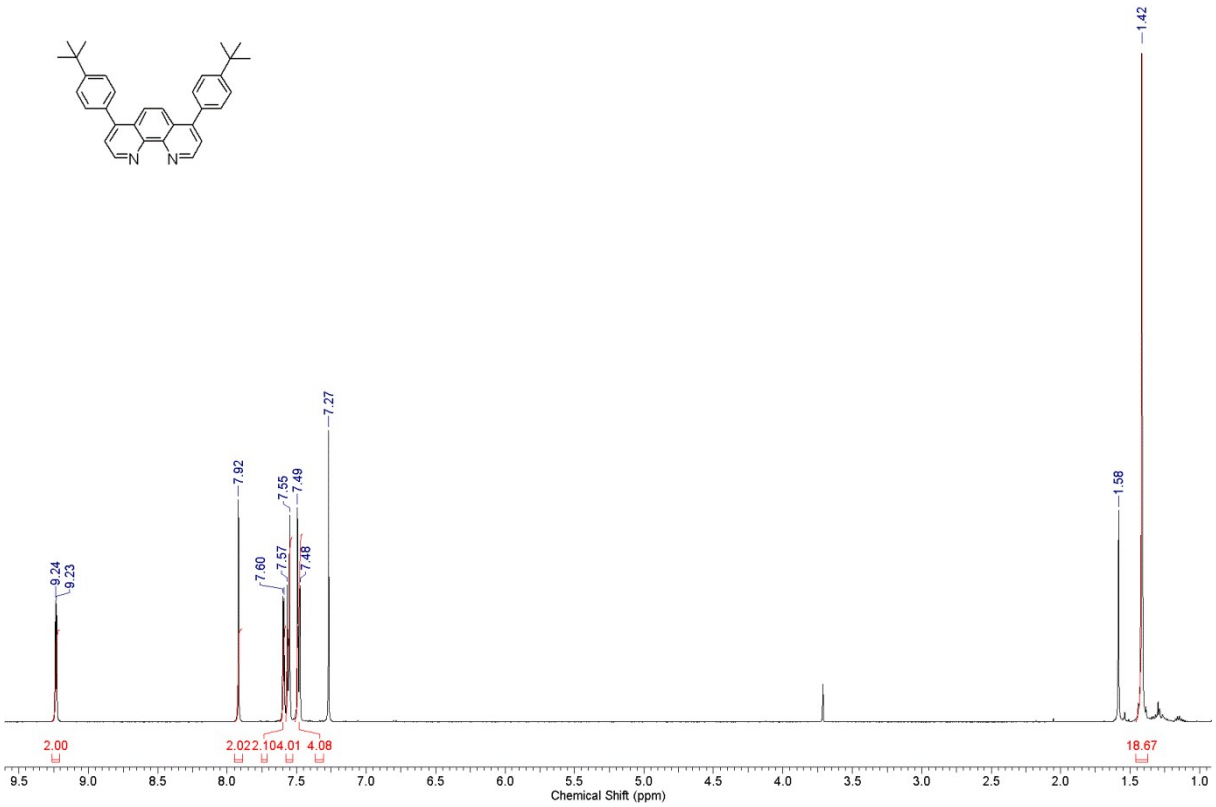
(2Z,9Z)-4,7-bis(4-(*t*-butyl)phenyl)-1,10-phenanthroline-2,9-bis(carbohydrazonamide). A suspension of **3b** (0.20 g, 0.40 mmol) in EtOH (3.5 mL) was treated with hydrazine hydrate (3.5 mL, 50-60 %). The suspension was left to stir for 72 h at ambient temperature, before being concentrated *in vacuo*. The yellow precipitate was washed with H_2O (2 x 30 mL), Et_2O (2 x 10 mL) and dried *in vacuo* to yield compound **4b** as a bright yellow solid (0.21 g, 95 %). m.p. 260 °C (decomposed); ν_{max} / cm^{-1} 3339br (N-H), 3181br (N-H), 2955m, 2901w, 2866w, 1680m, 1613m, 1540s; δ_H (500 MHz; $CDCl_3$) 8.34 (2H, s, C(3)H and C(8)H or C(5)H and C(6)H), 7.91 (2H, s, C(3)H and C(8)H or C(5)H and C(6)H), 7.53 (4H, d, *J* 7.8, 4 x Ar-CH), 7.49 (4H, d, *J* 7.8, 4 x Ar-CH), 5.70 (4H, br s, 2 x NH_2), 4.76 (4H, br s, 2 x NH_2), 1.40 (18H, s, 6 x CH_3); δ_C (125 MHz; $CDCl_3$) 151.6 (C=NNH_2), 149.9 (Ar-C), 148.9 (Ar-C), 145.0 (Ar-C), 135.0 (Ar-C), 129.5 (Ar-CH), 127.1 (Ar-C), 125.4 (Ar-CH), 124.2 (C(5)H and C(6)H or C(3)H and C(8)H), 119.7 (C(5)H and C(6)H or C(3)H and C(8)H), 34.7 (C-$(CH_3)_3$), 31.3 (CH_3); *m/z* (+HESI) 559 ($[M+H]^+$, 100 %); HRMS (+HESI) calculated for $C_{34}H_{39}N_8$ ($[M+H]^+$): 559.3292, found: 559.3292.

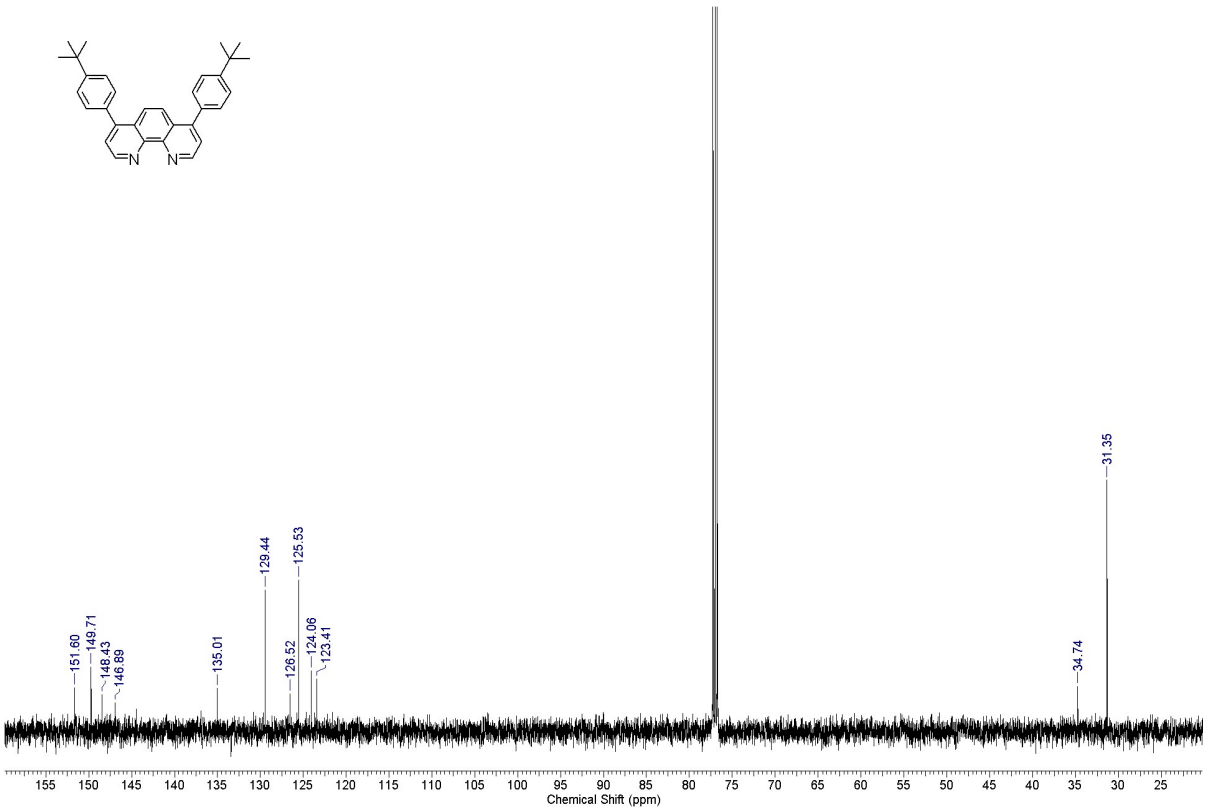


4,7-bis(4-(*t*-butyl)phenyl)-2,9-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo-[e][1,2,4]triazin-3-yl)-1,10-phenanthroline. A stirred suspension of **4b** (0.40 g, 0.72 mmol) and 3,3,6,6-tetramethylcyclohexane-1,2-dione **5a** (0.266 g, 1.58 mmol) in EtOH (9.0 mL) was heated at reflux for 5 h. After this time, the yellow suspension was allowed to cool to ambient temperature and taken to dryness *in vacuo*. The resulting yellow solid was triturated with cold MeOH (3 x 25 mL) to give the desired BTPhen **6b** (0.40 g, 68 %) as a bright yellow solid. m.p. >300 °C; ν_{max} / cm^{-1} 3621br (N-H), 2956m, 2932m, 2866w, 1521s; δ_H (500 MHz; $CDCl_3$) 8.79 (2H, s, C(3)H and C(8)H or C(5)H and C(6)H), 8.05 (2H, s, C(3)H and C(8)H or C(5)H and C(6)H), 7.59 (8H, s, 8 x Ar-CH), 1.91 (8H, s, 4 x CH_2), 1.58 (12H, s, 4 x CH_3), 1.55 (12H, s, 4 x CH_3), 1.43 (18H, s, 6 x CH_3); δ_C (125 MHz; $CDCl_3$) 164.8 (Ar-C), 163.0 (Ar-C), 161.8 (Ar-C), 153.3 (Ar-C), 151.8 (Ar-C), 149.6 (Ar-C), 147.3 (Ar-C), 135.0 (Ar-C), 129.6 (Ar-CH), 127.6 (Ar-C), 125.6 (Ar-CH), 125.1 (C(3)H and C(8)H or C(5)H and C(6)H)), 123.8 (C(3)H and C(8)H or C(5)H and C(6)H), 37.5 (quat C), 36.6 (quat C), 34.8 (C-$(CH_3)_3$), 33.8 (CH_2), 33.7 (CH_2), 31.4 (CH_3), 29.8 (CH_3), 29.3 (CH_3); *m/z* (MALDI-dithranol) 845 ($[M+Na]^+$, 100 %); HRMS (+HESI) calculated for $C_{54}H_{63}N_8$ ($[M+H]^+$): 823.5170, found: 823.5176.

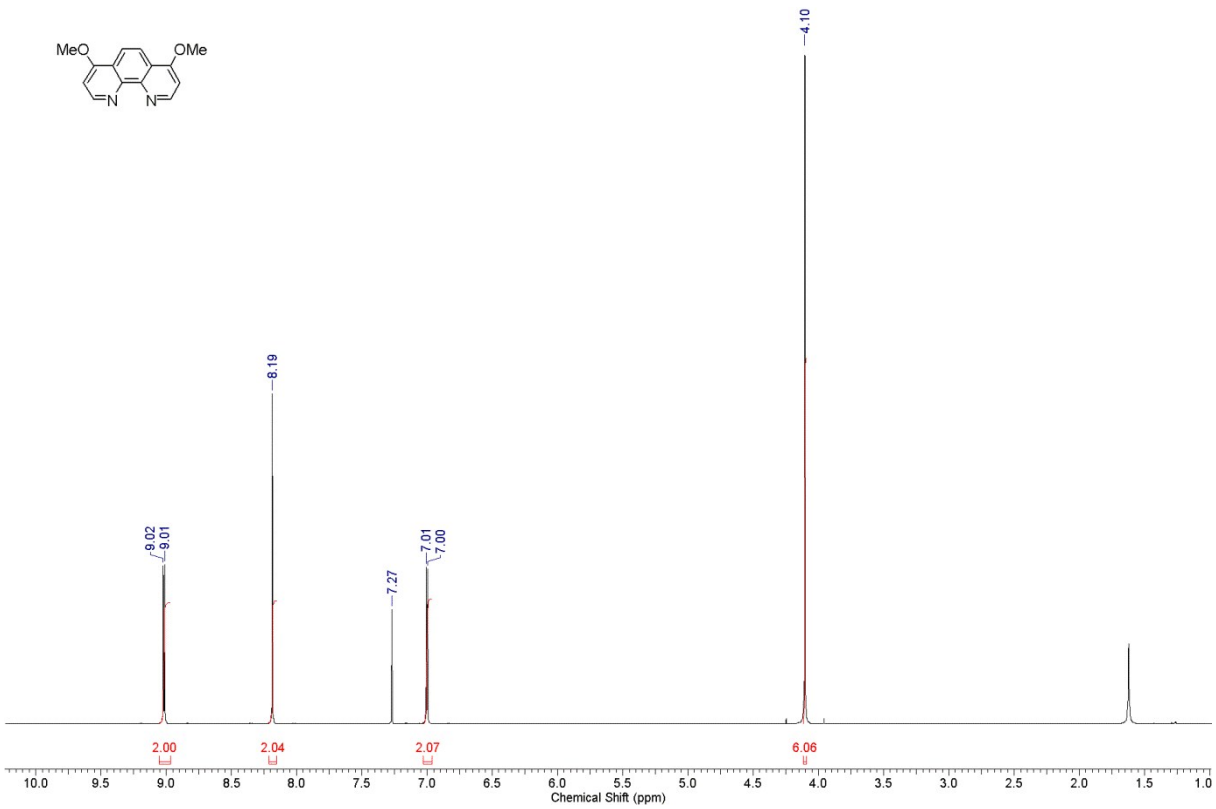
2 Key ^{1}H and ^{13}C NMR Spectra

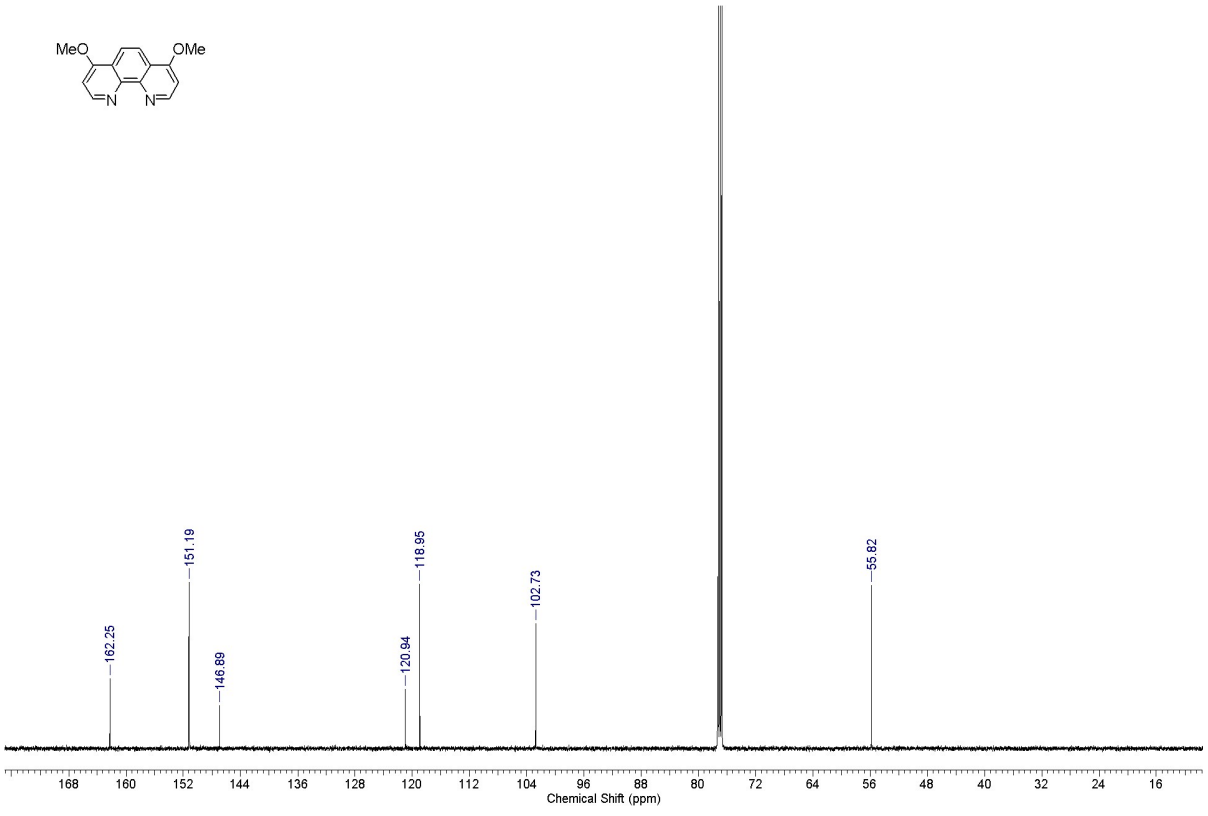
^{1}H and ^{13}C NMR Spectrum of 1i



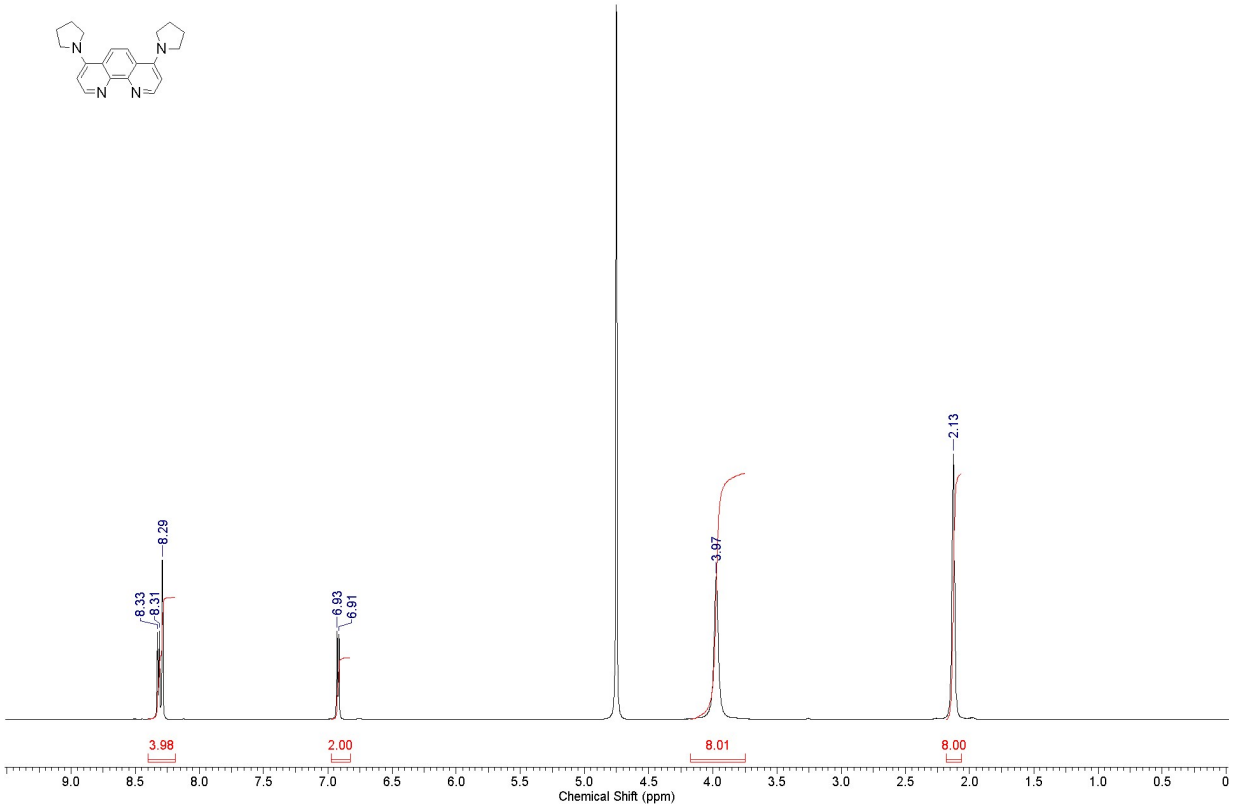


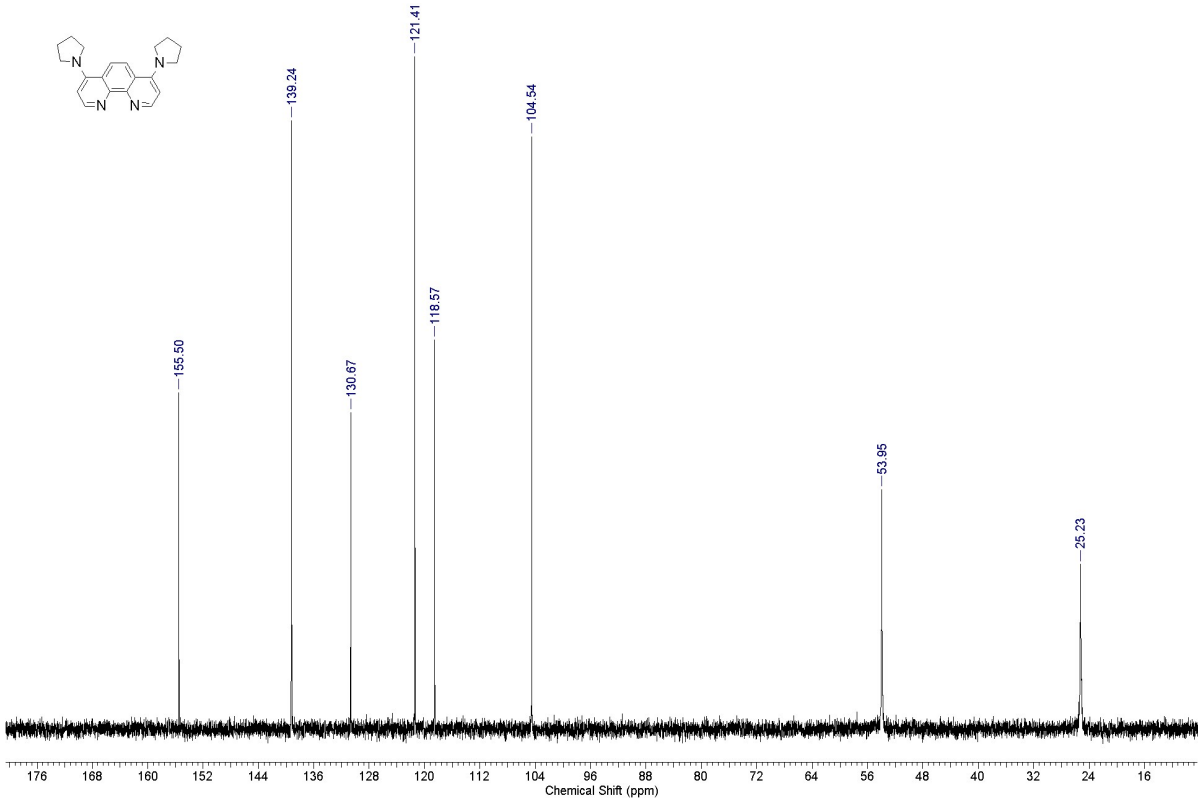
^{1}H NMR and ^{13}C NMR Spectrum of 1j



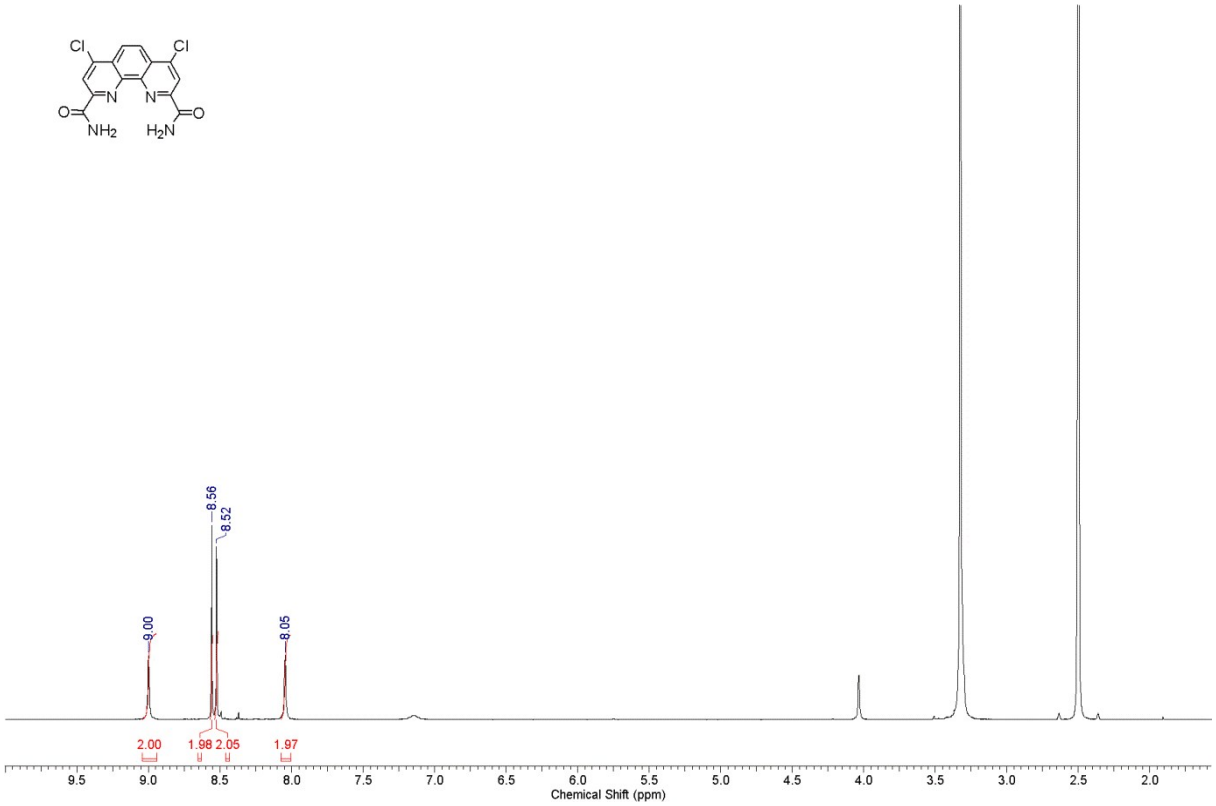


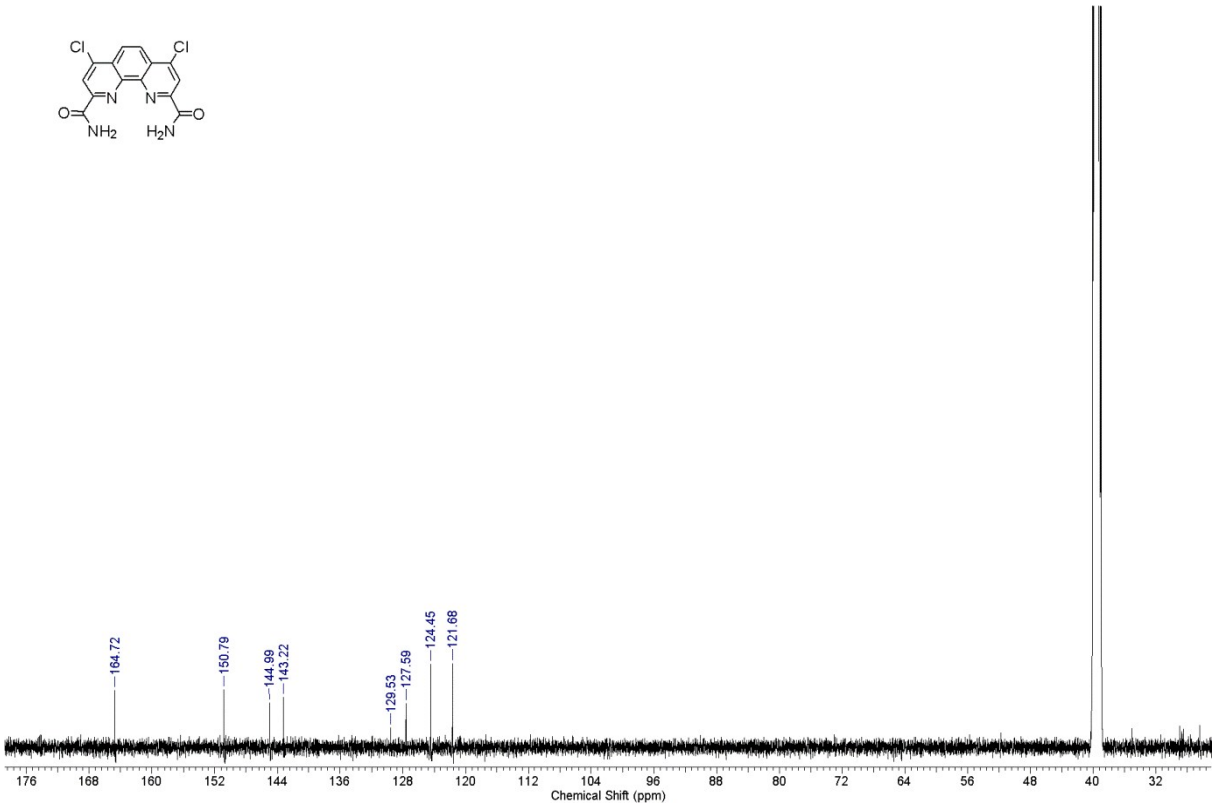
^{1}H and ^{13}C NMR Spectrum of 1k



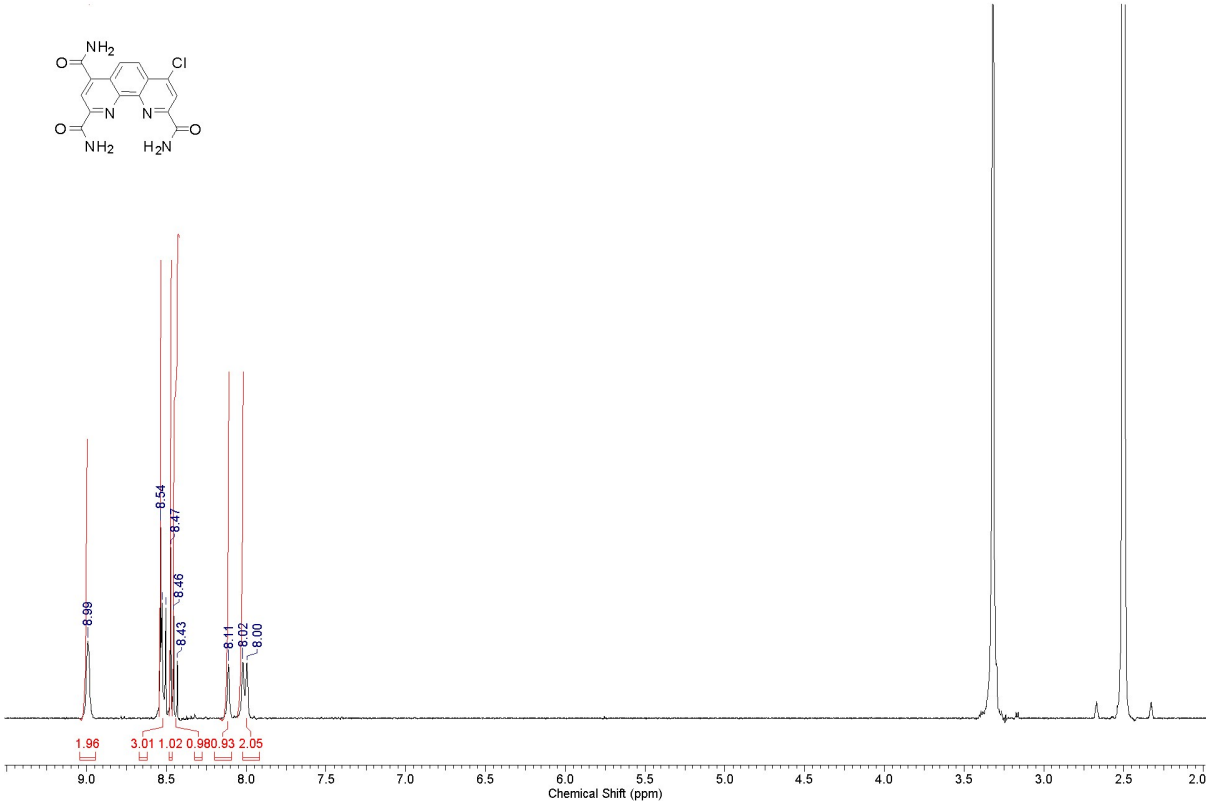


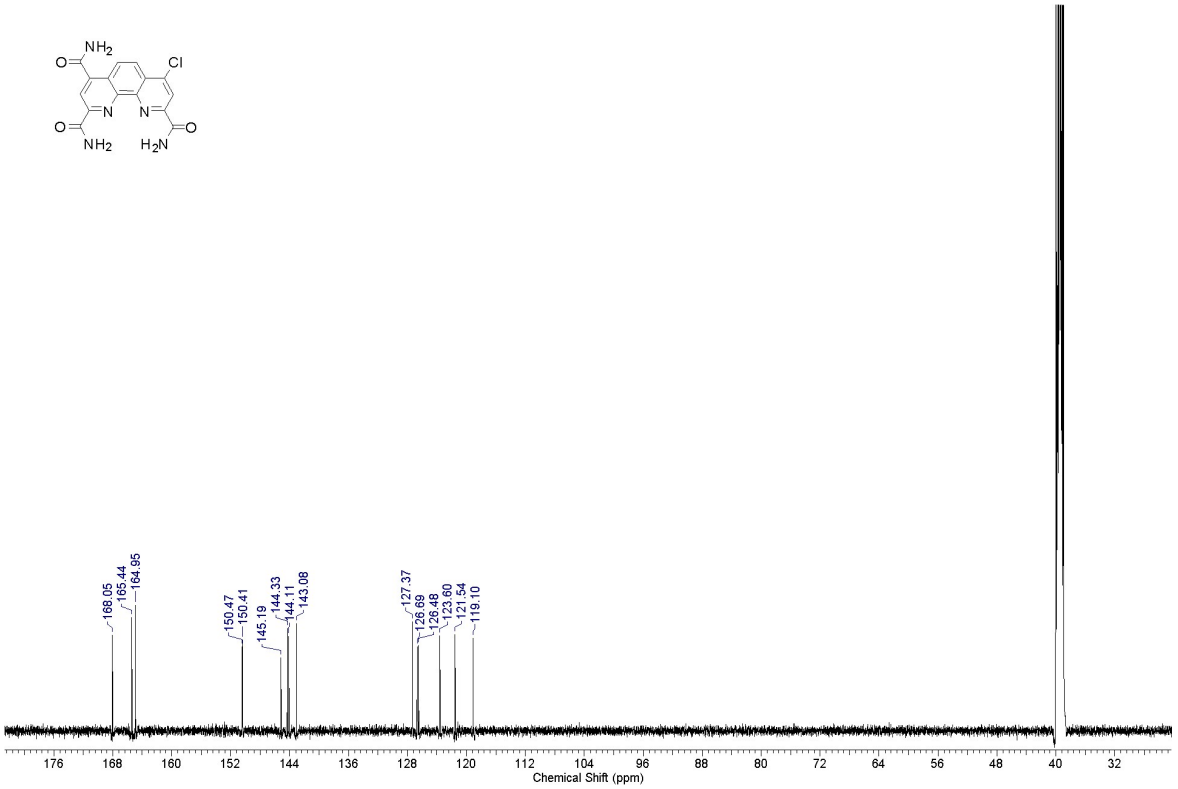
^{1}H and ^{13}C NMR Spectrum of 2a



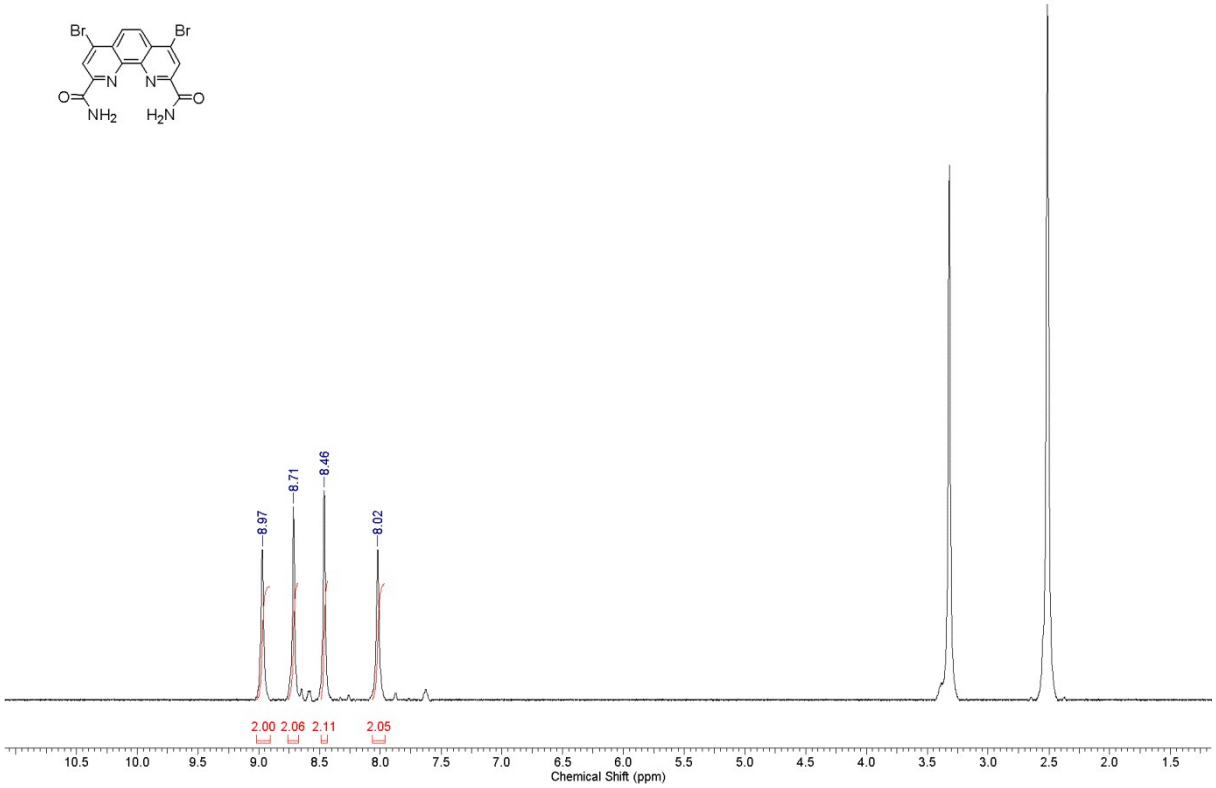


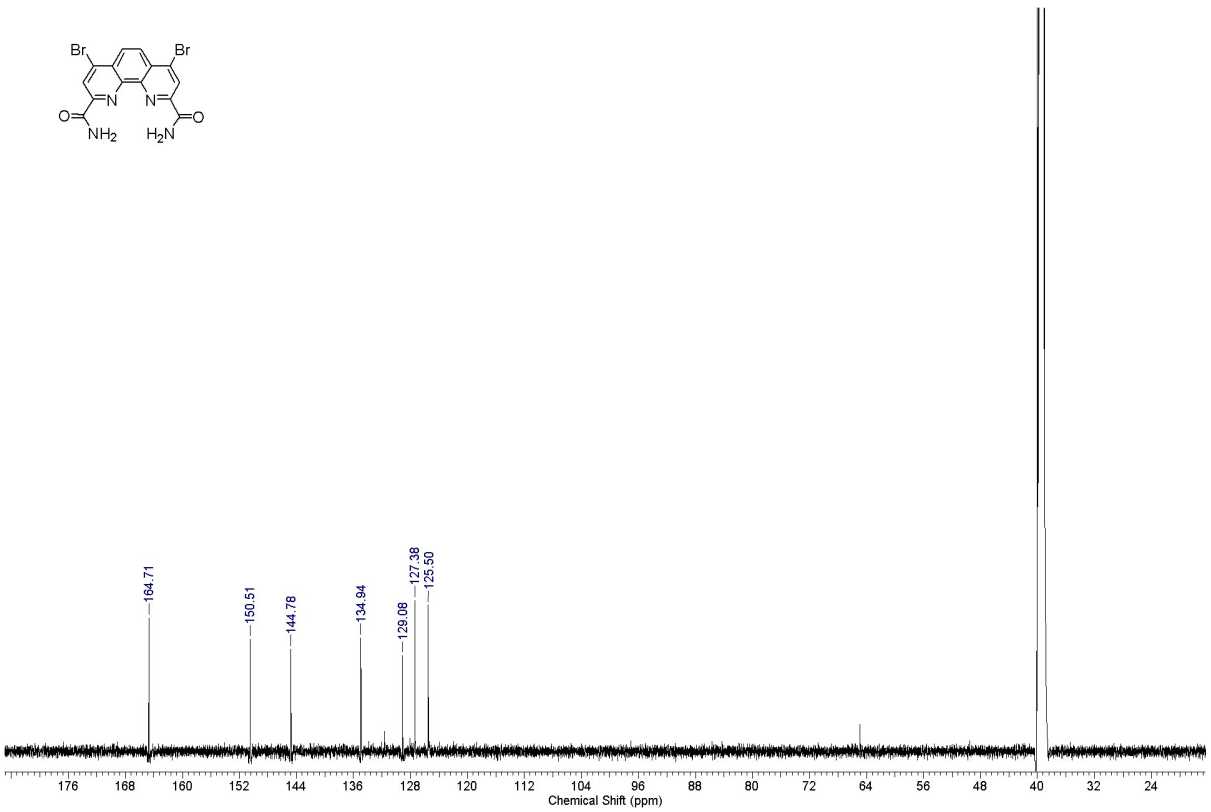
^{1}H and ^{13}C NMR Spectrum of 2b



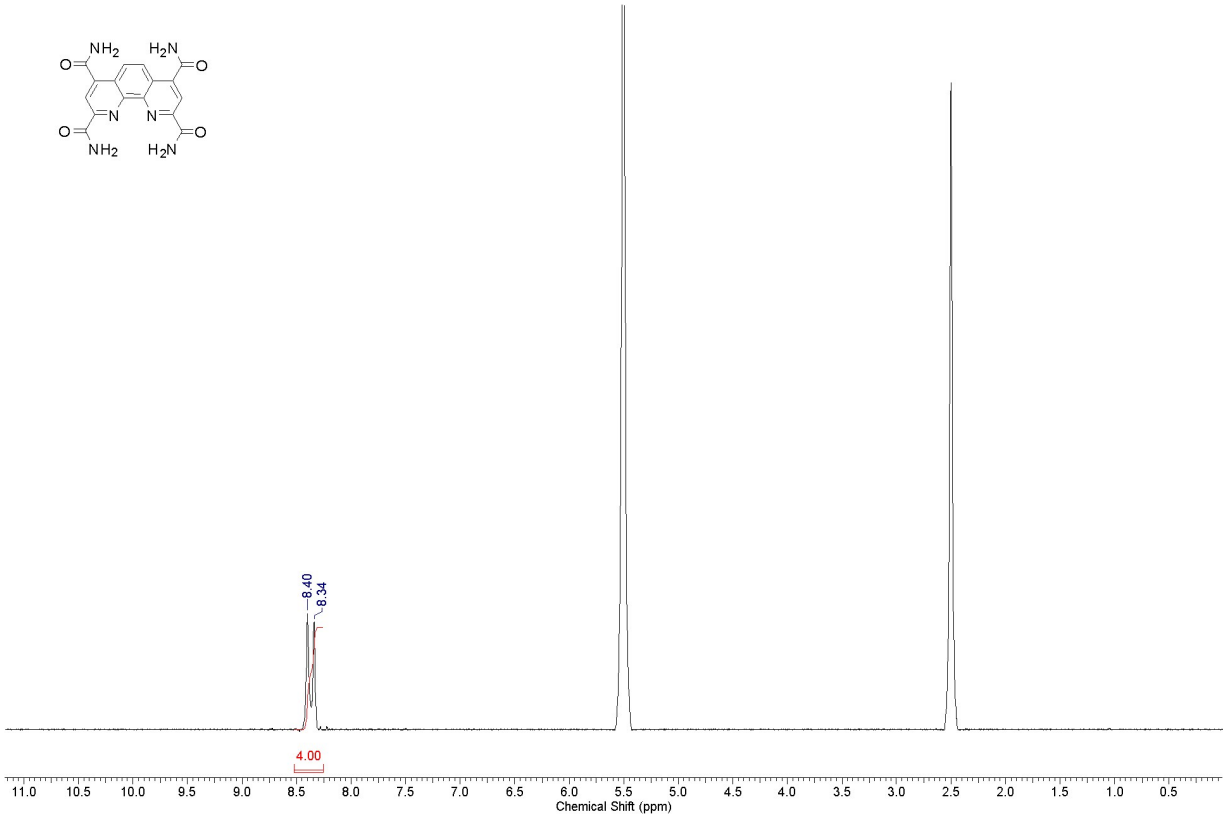


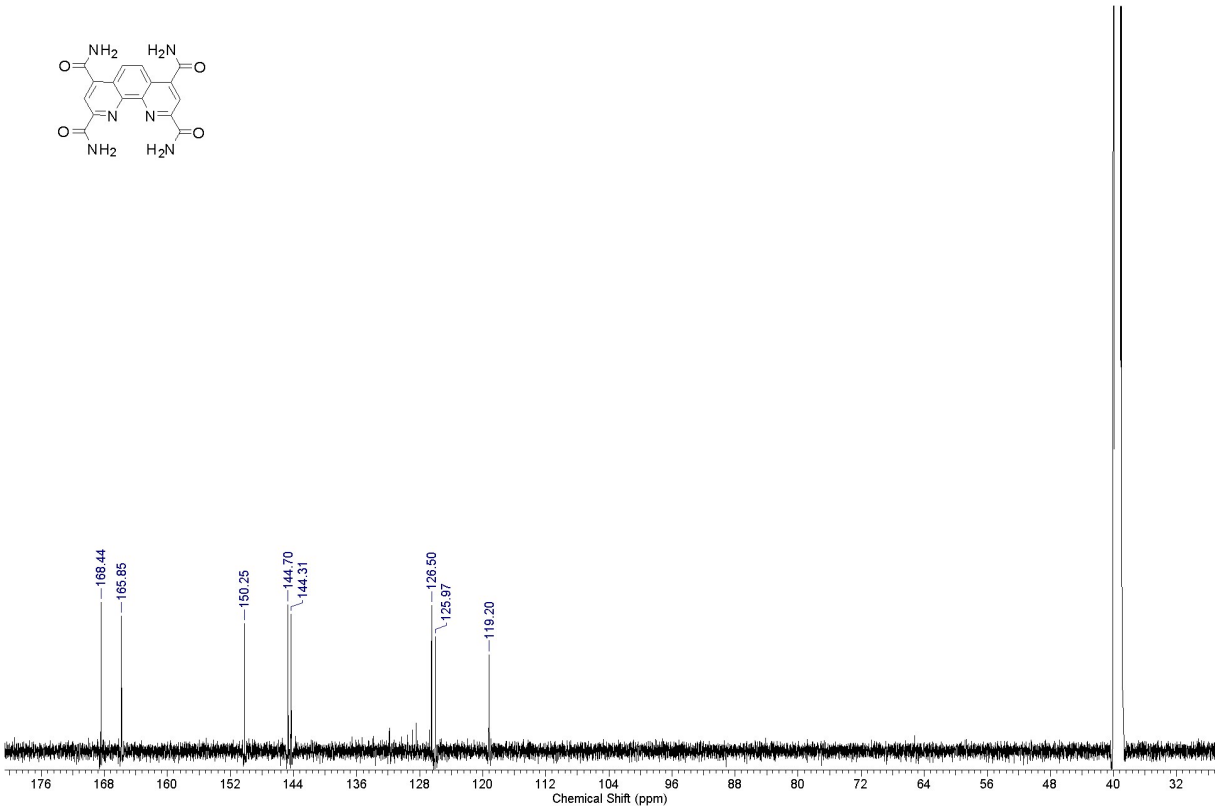
^{1}H and ^{13}C NMR Spectrum of 2c



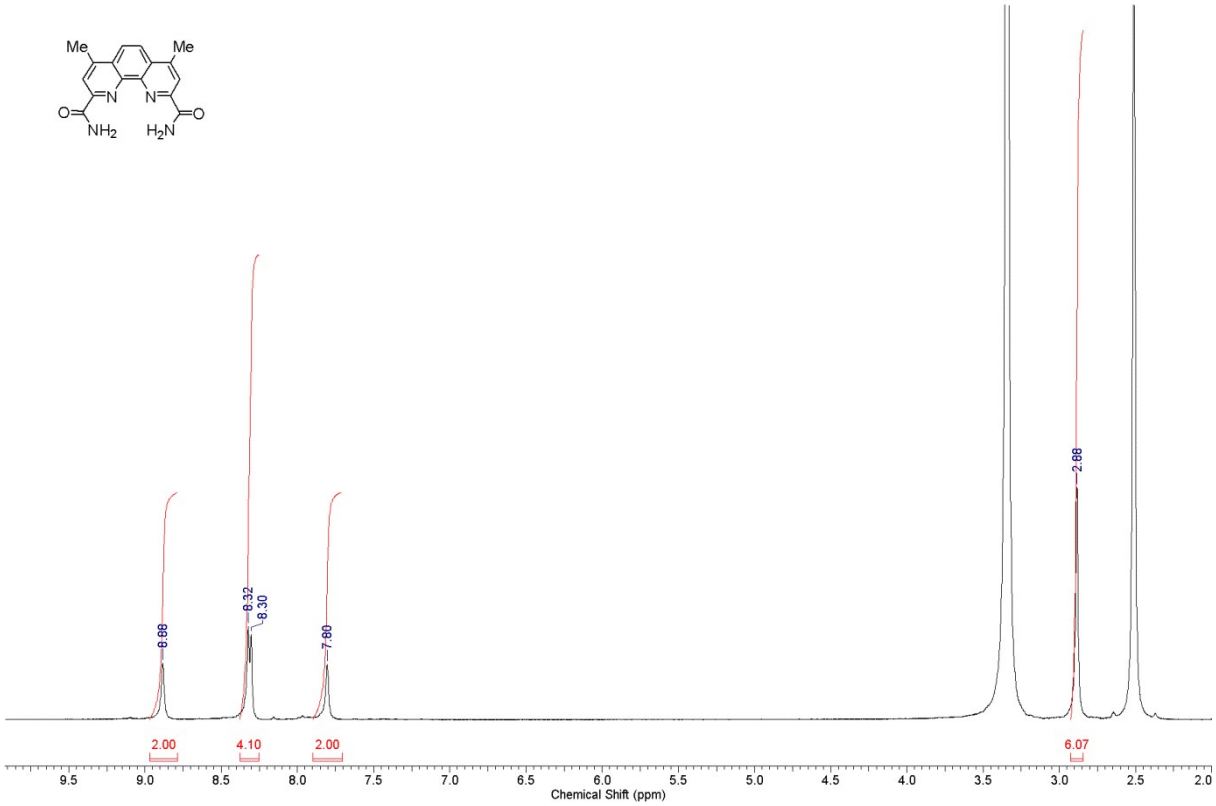


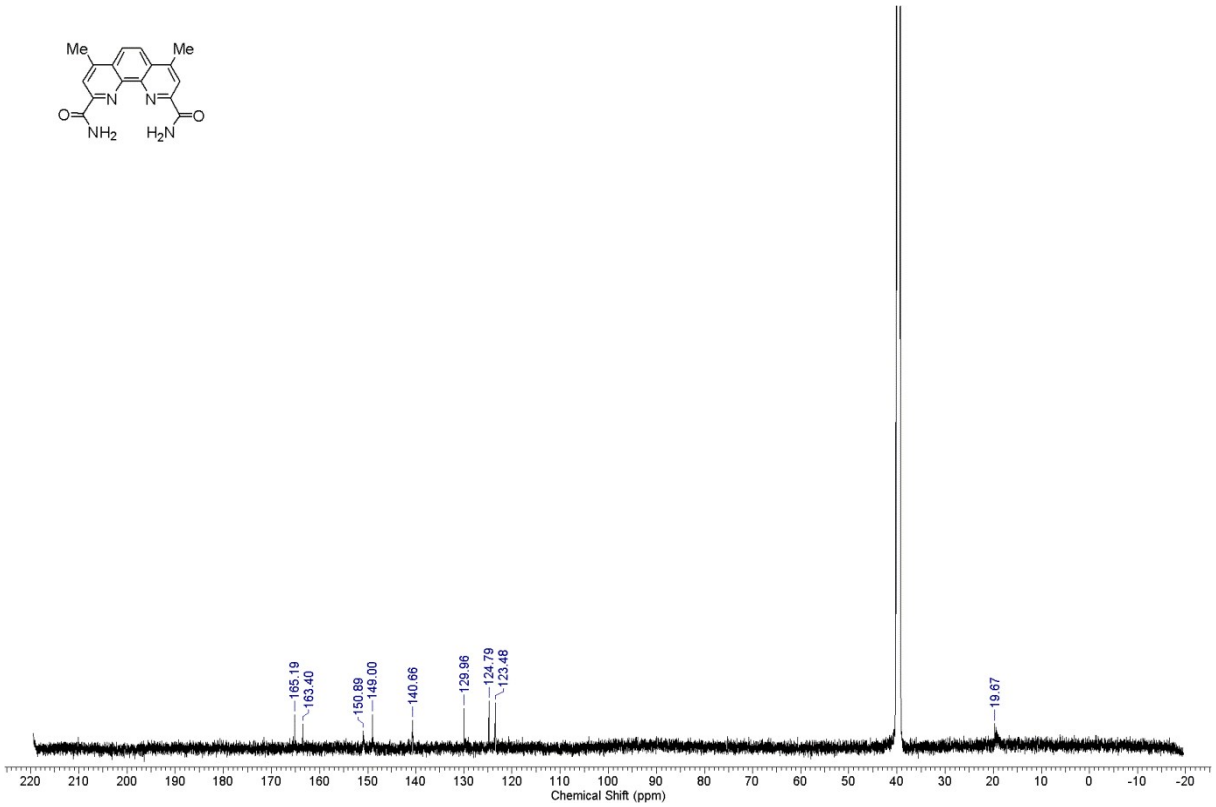
^{1}H and ^{13}C NMR Spectrum of 2d



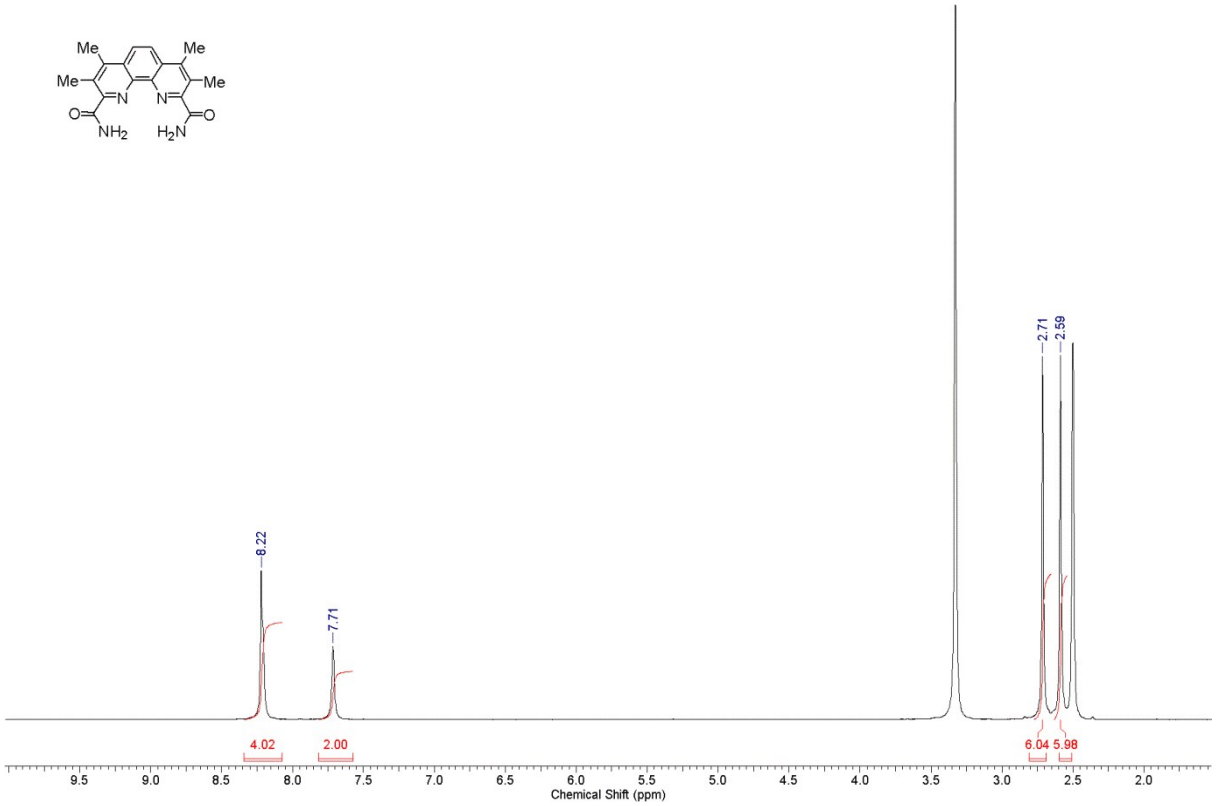


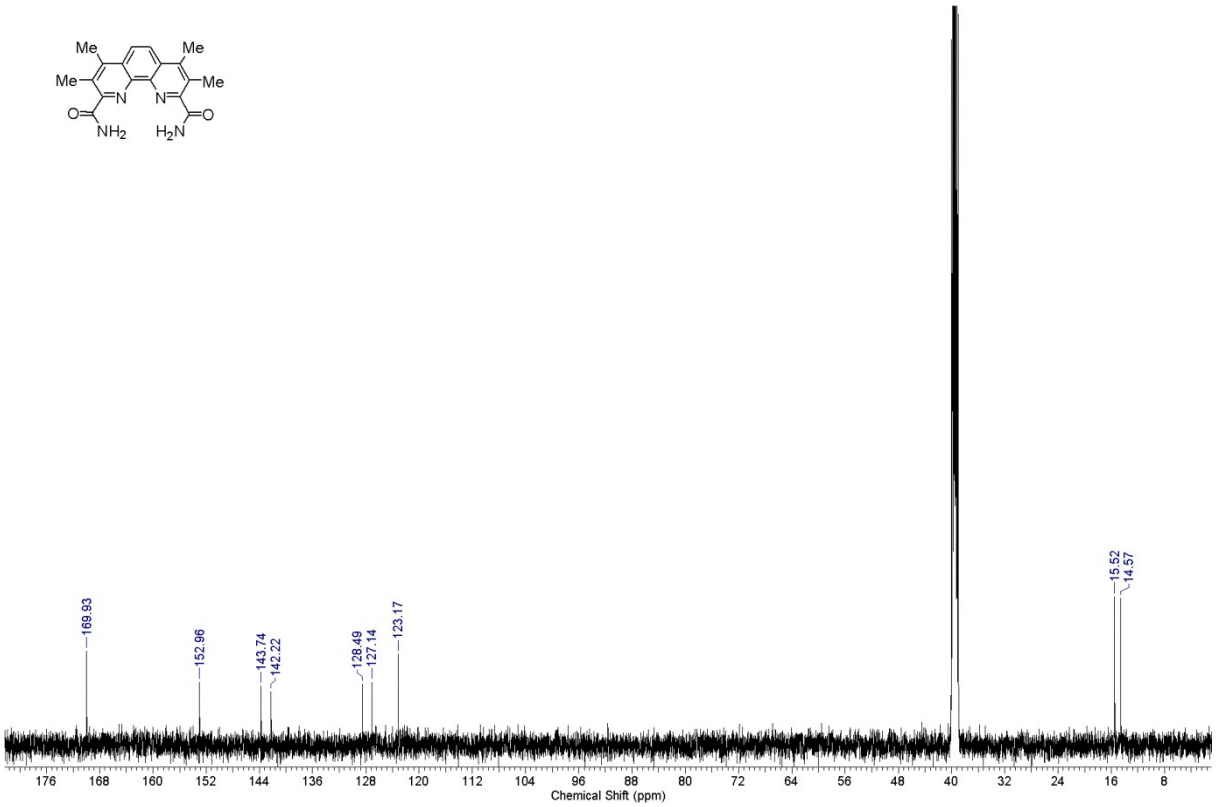
^{1}H and ^{13}C NMR Spectrum of 2e



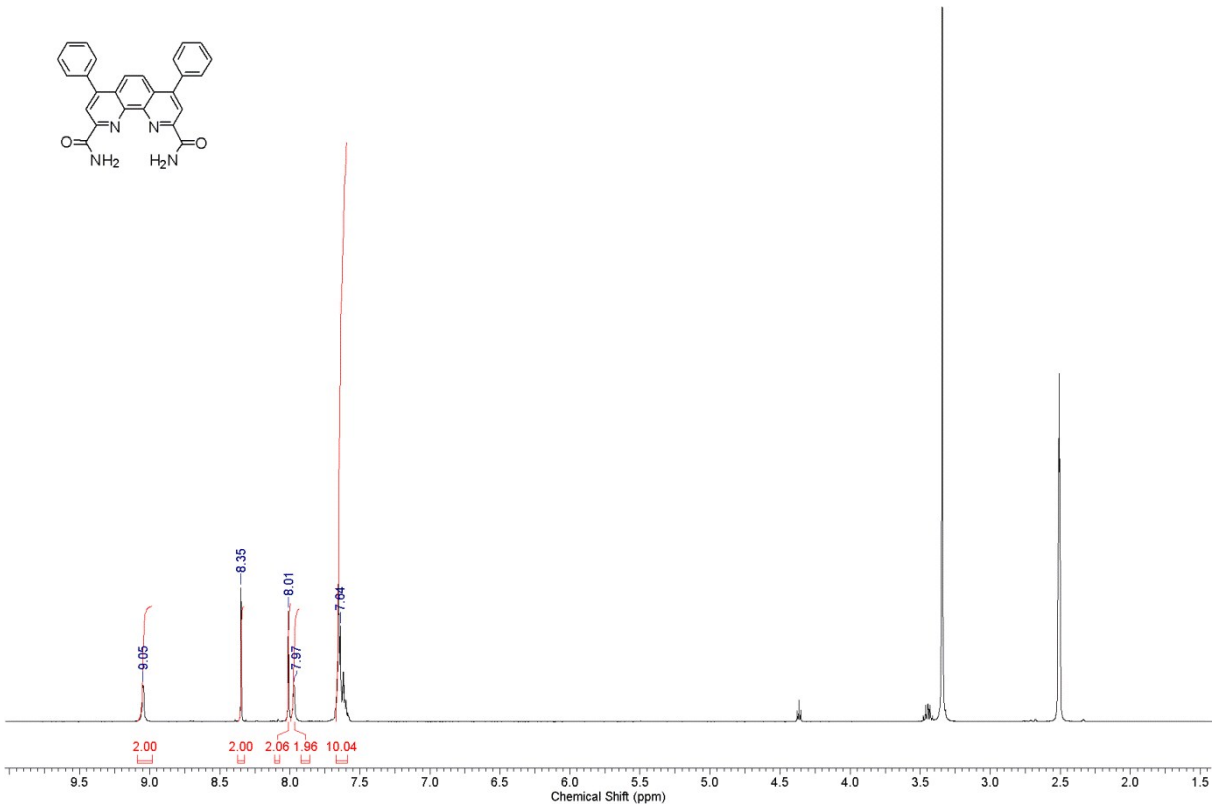


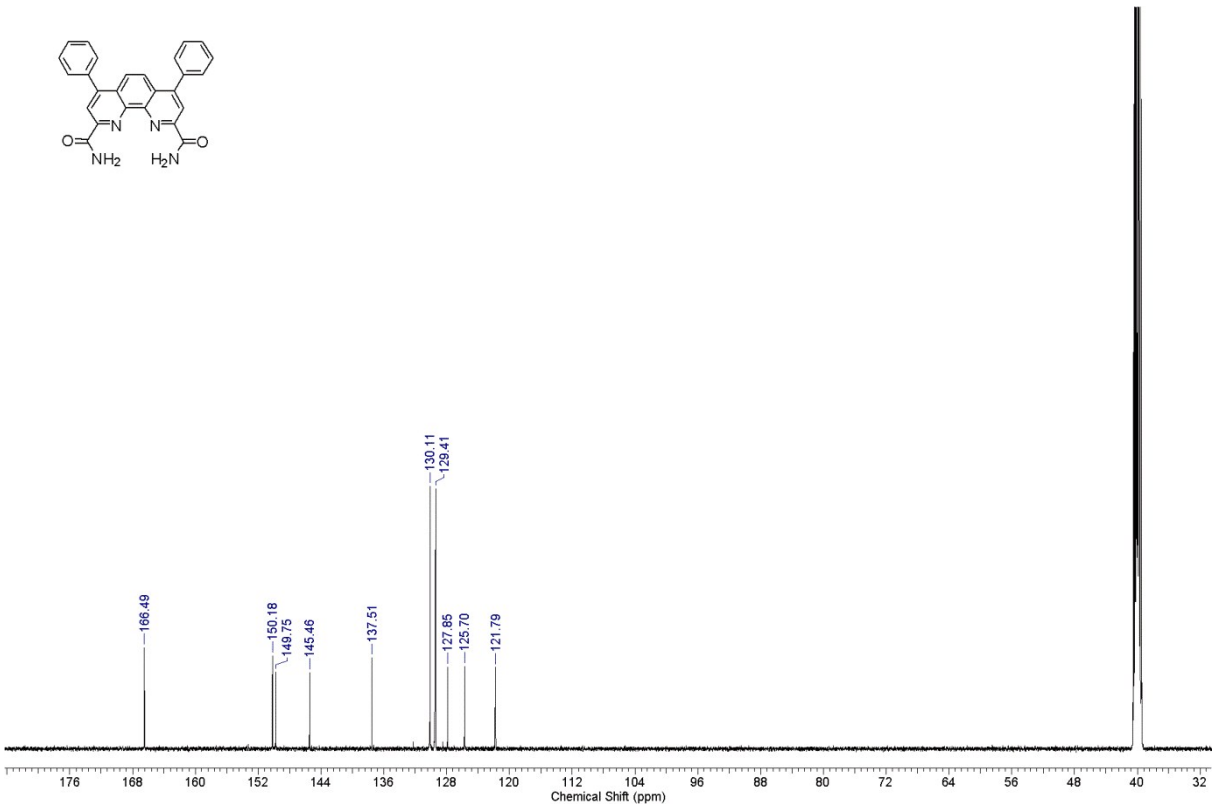
^{1}H and ^{13}C NMR Spectrum of 2f



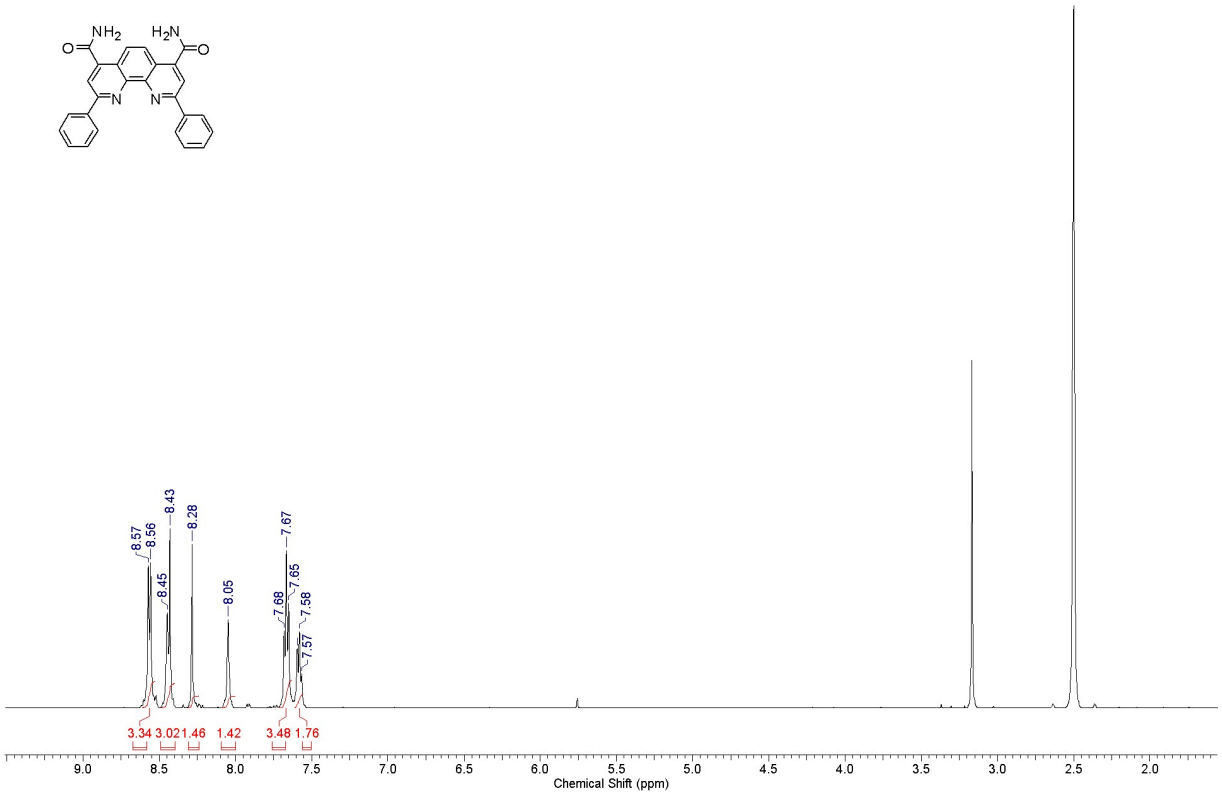


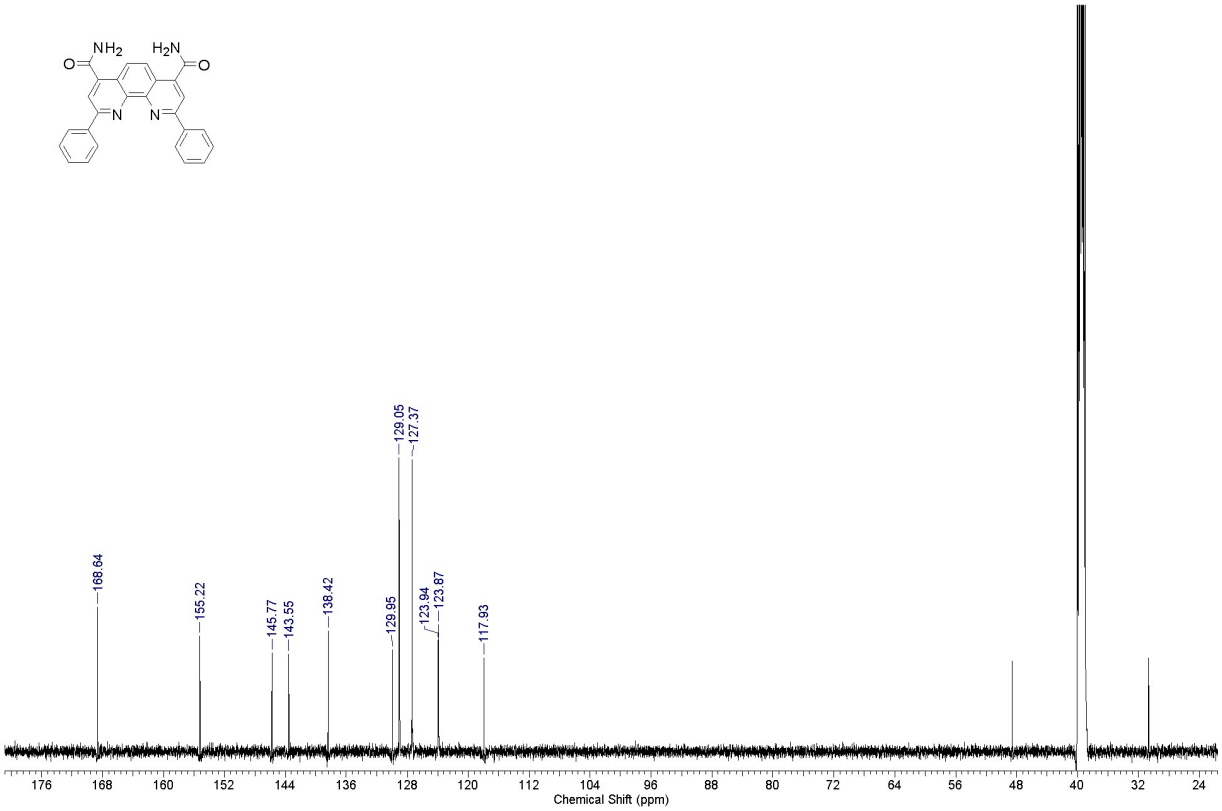
^{1}H and ^{13}C NMR Spectrum of 2g



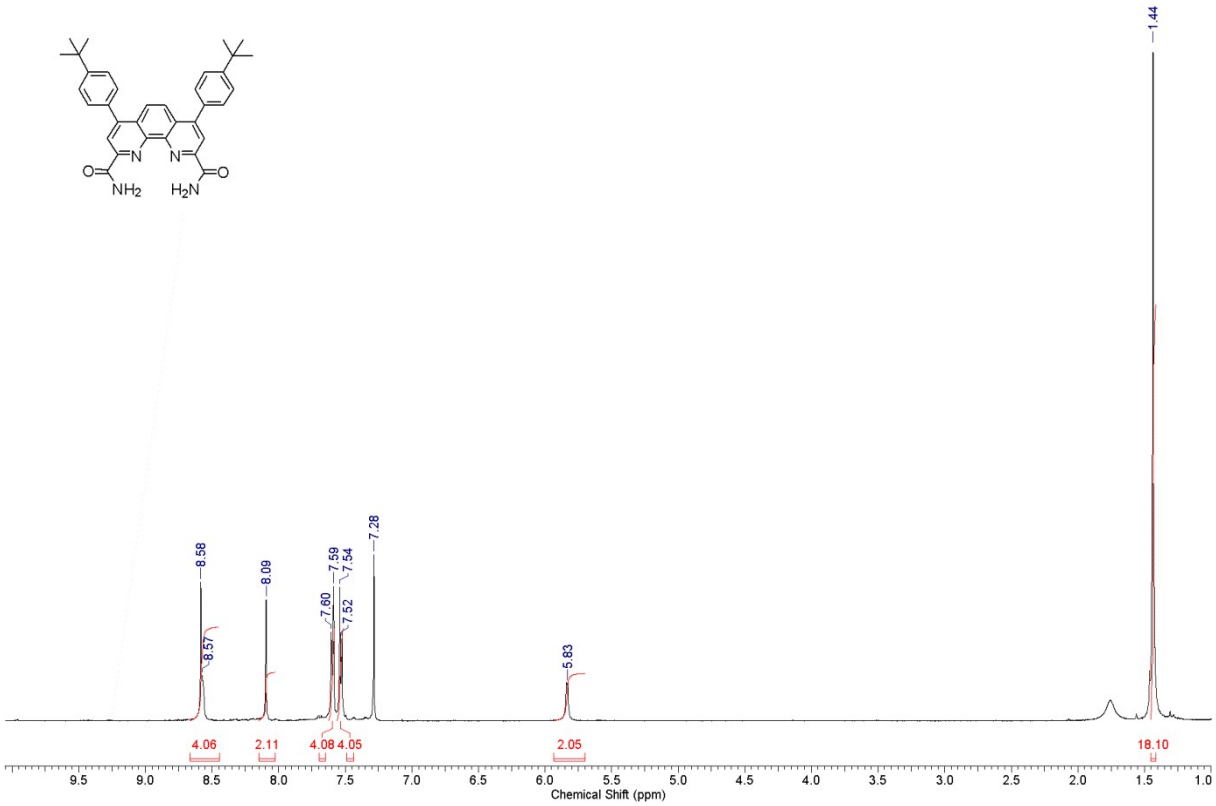


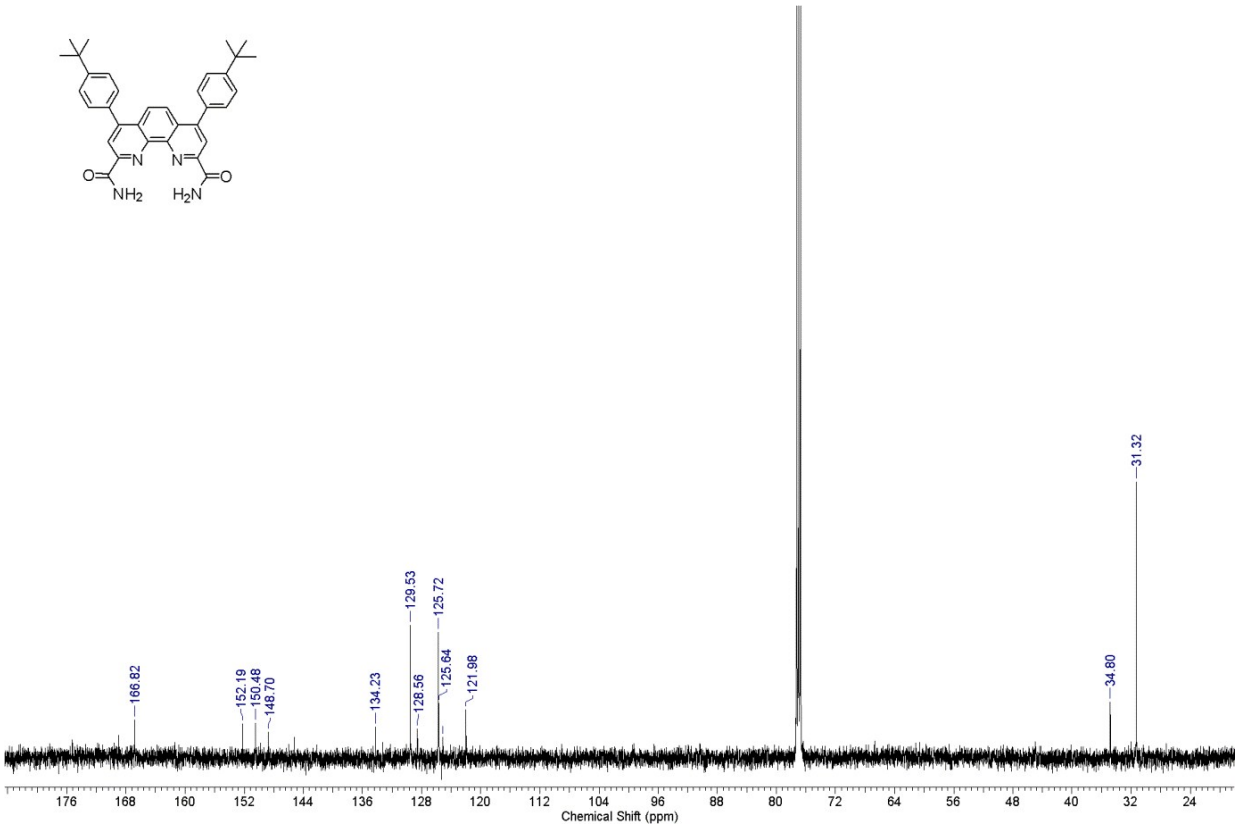
^{1}H and ^{13}C NMR Spectrum of 2h



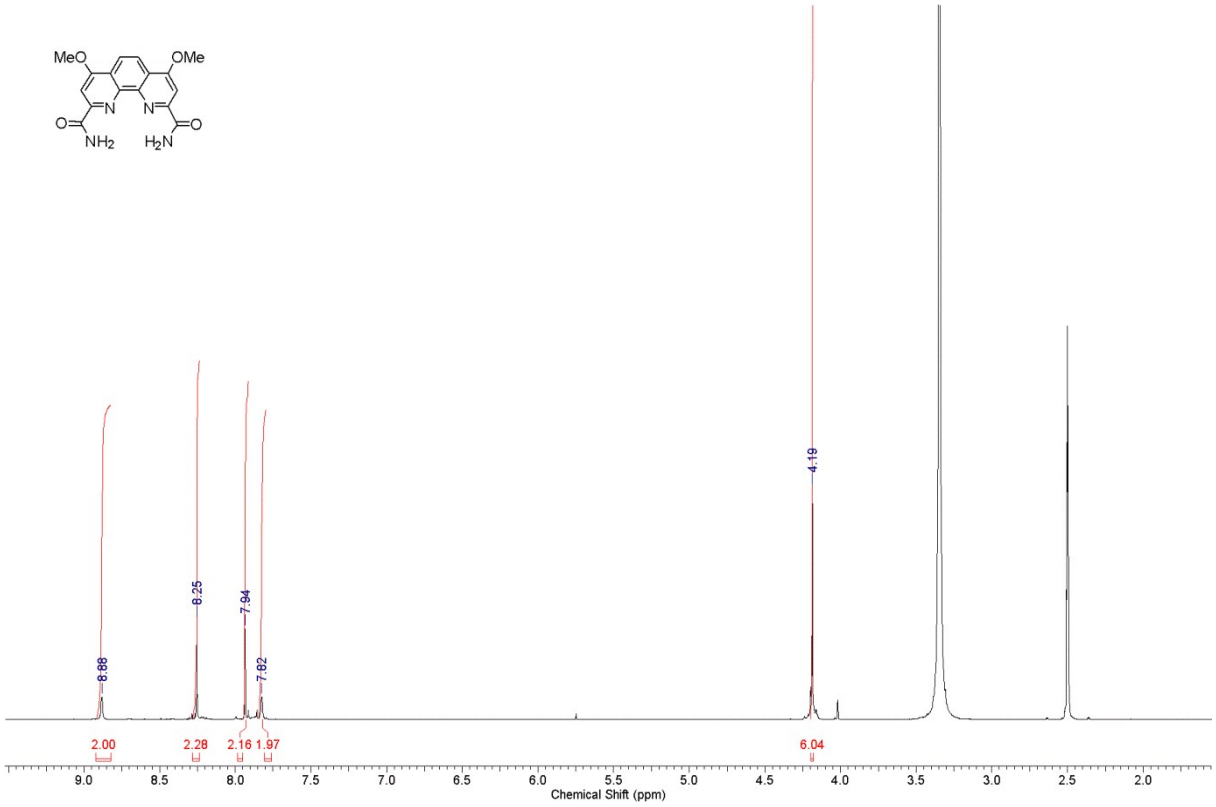


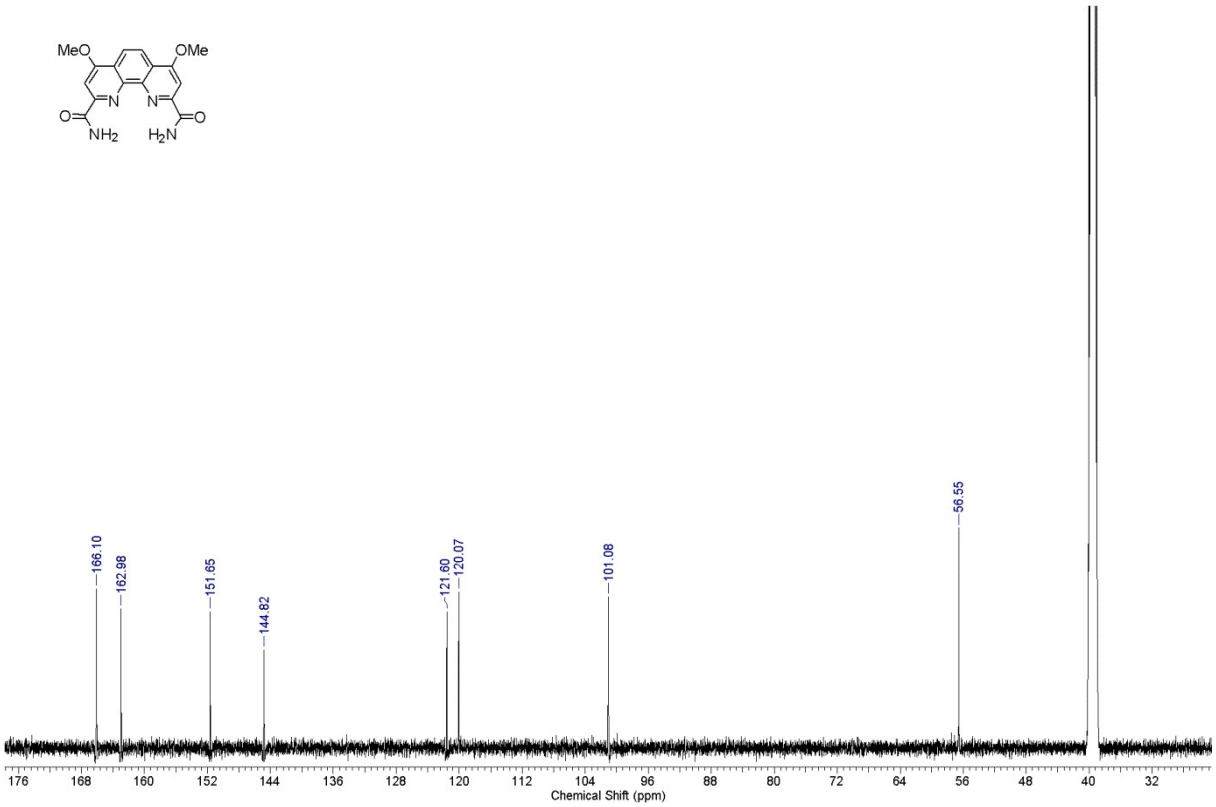
^{1}H and ^{13}C NMR Spectrum of 2i



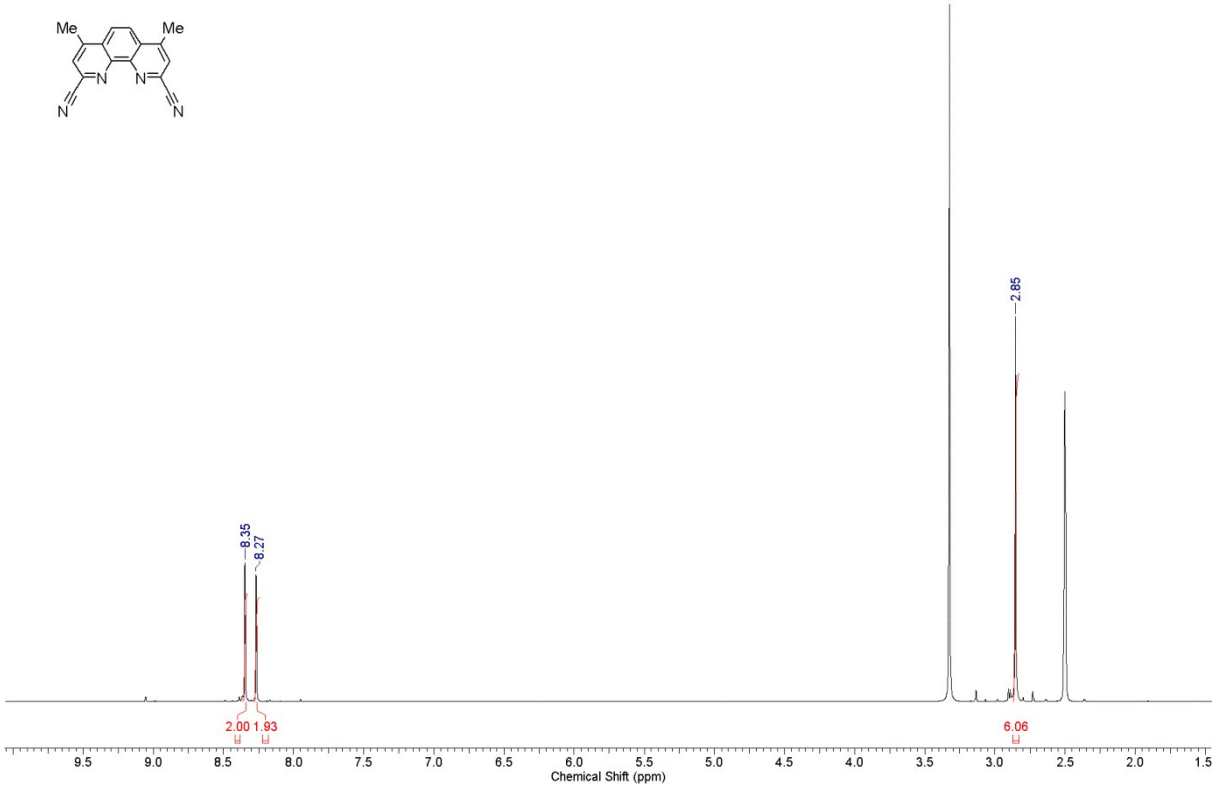


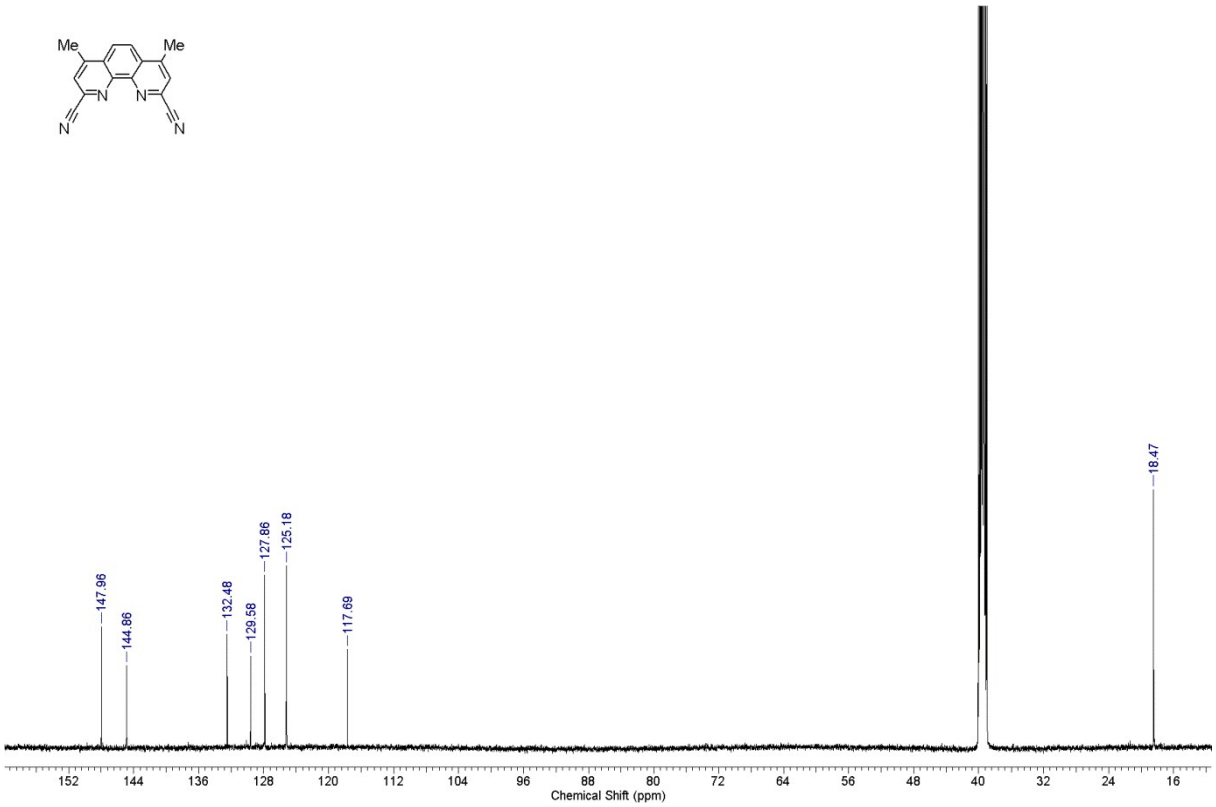
^{1}H and ^{13}C NMR Spectrum of 2j



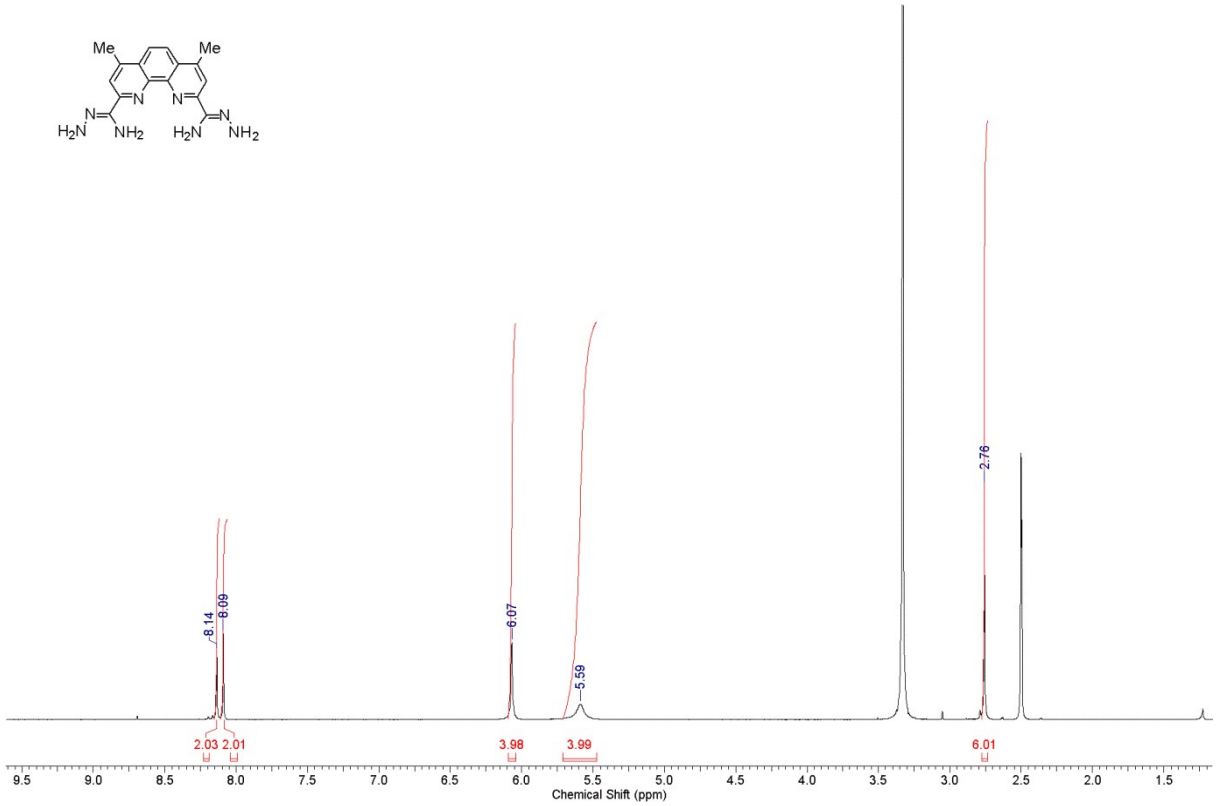


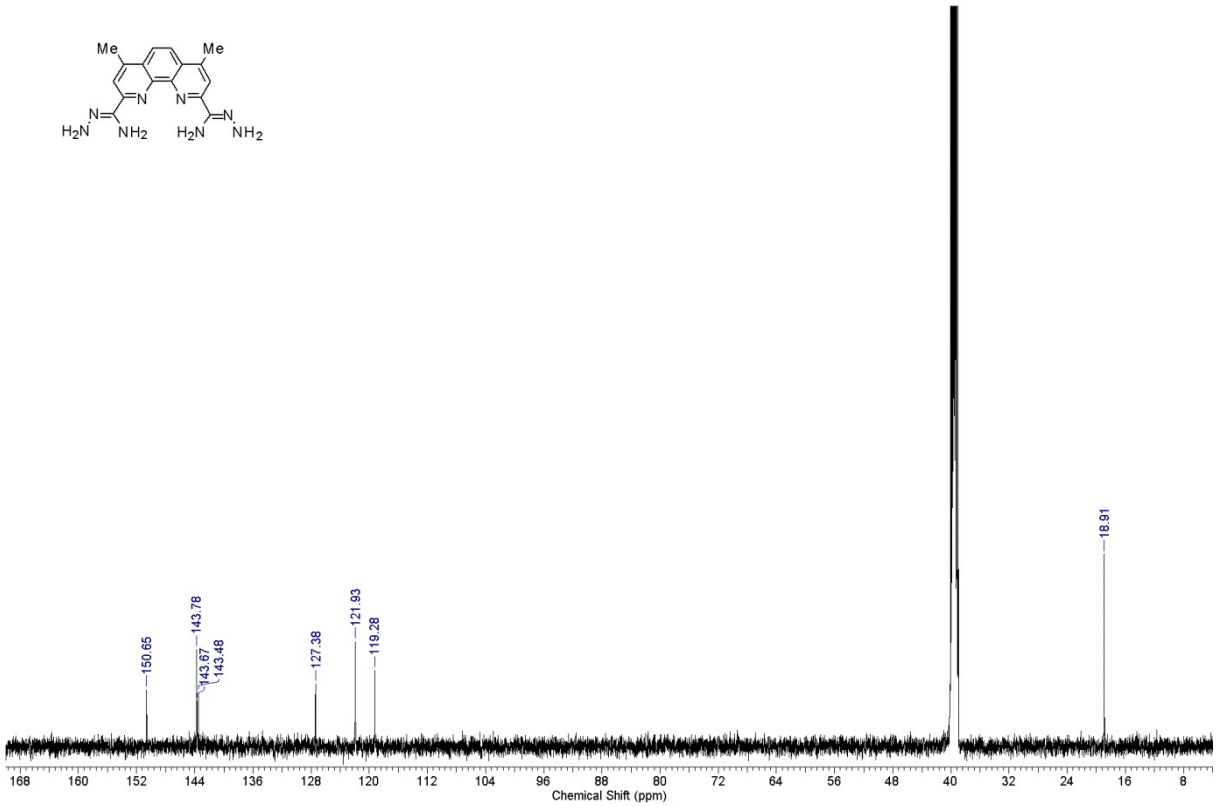
^{1}H and ^{13}C NMR Spectrum of 3a



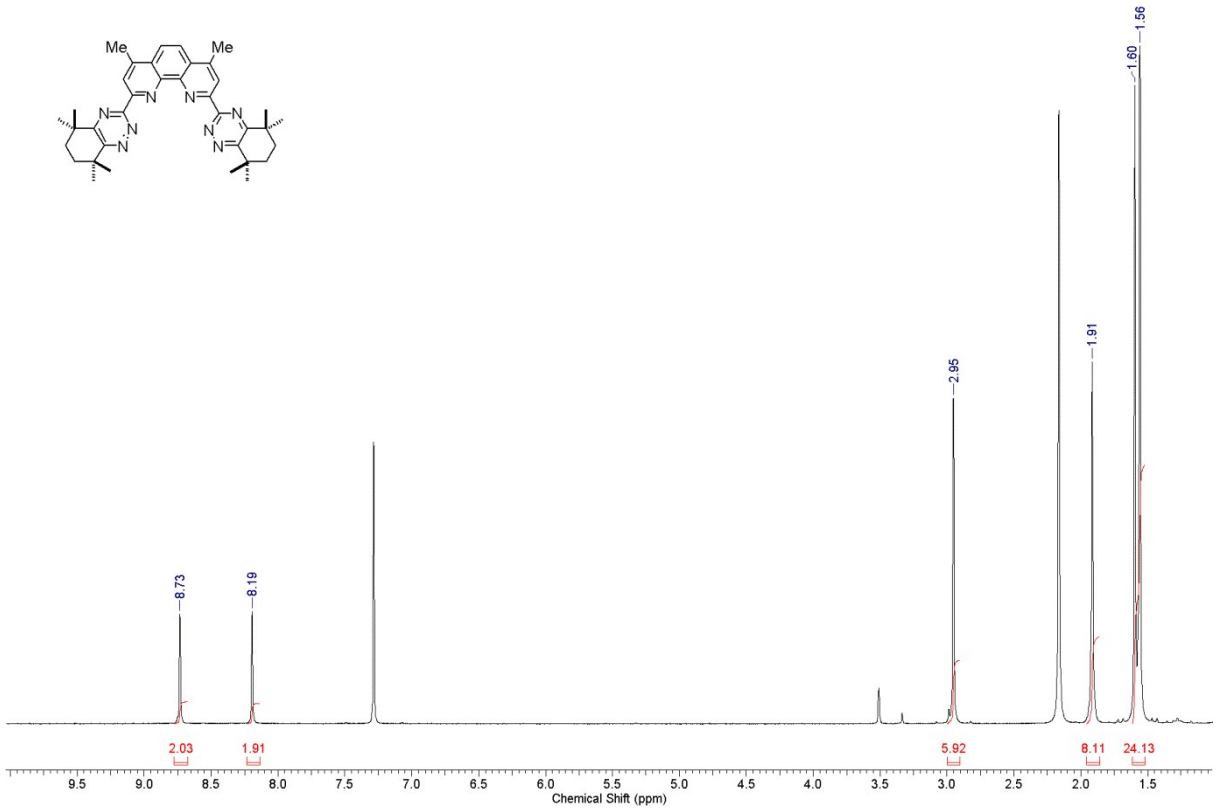


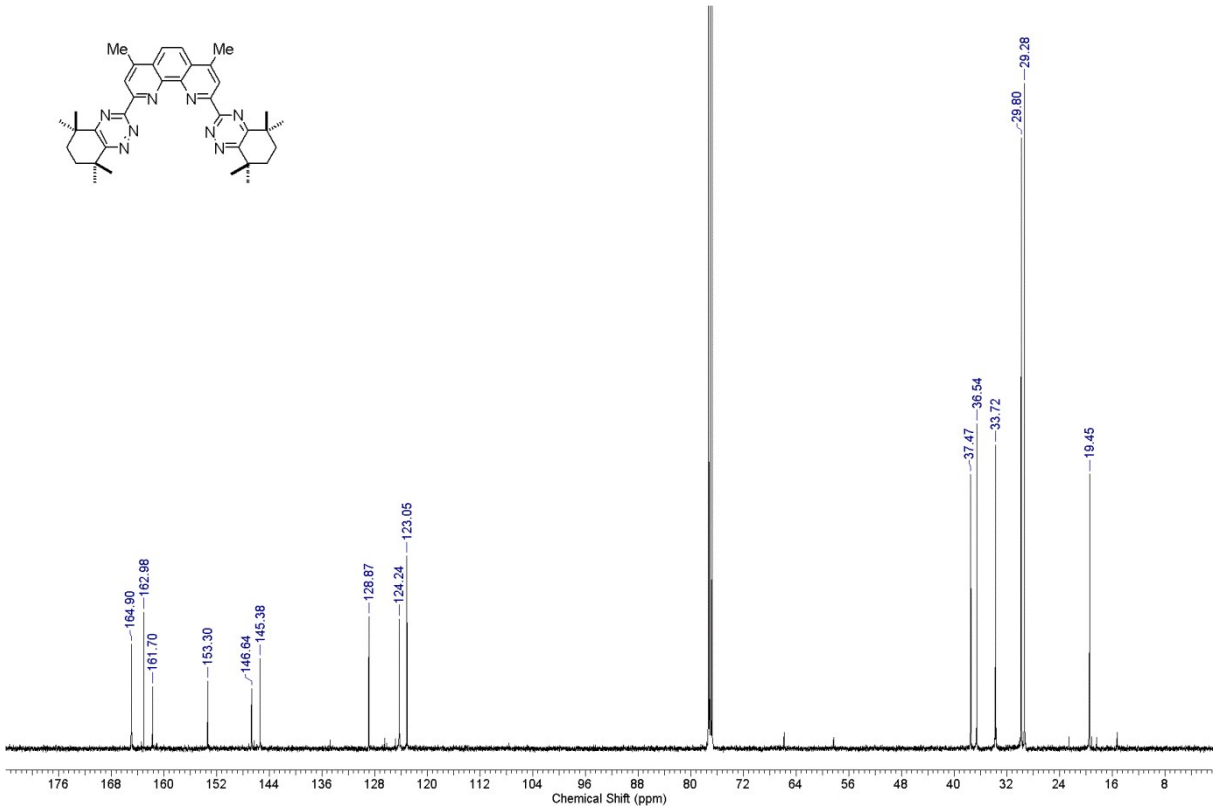
^{1}H and ^{13}C NMR Spectrum of 4a



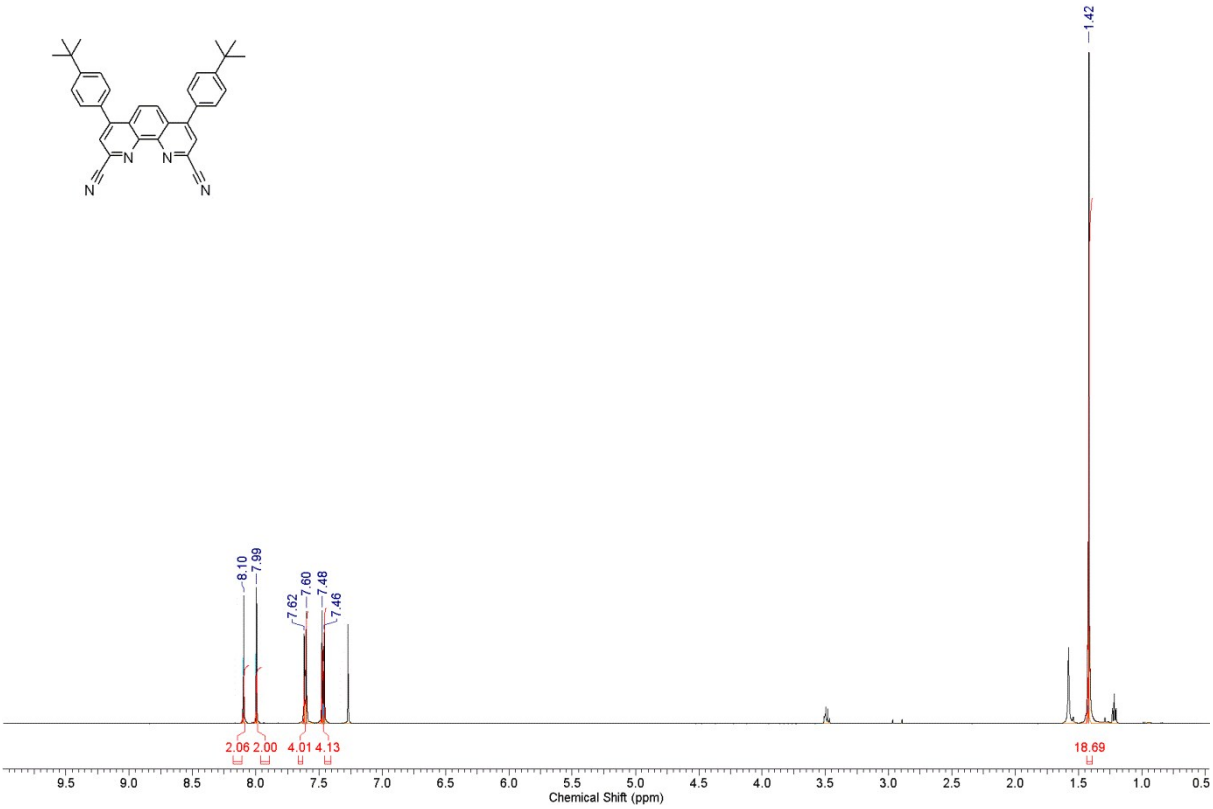


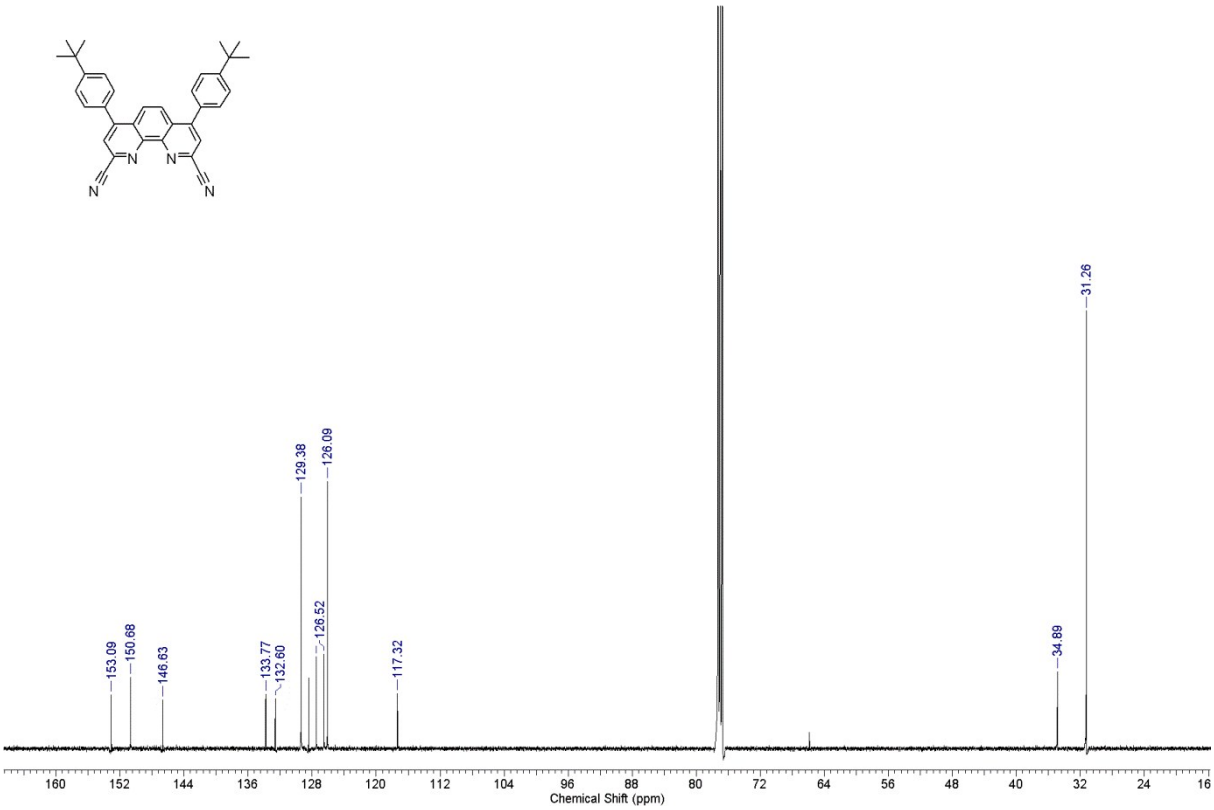
^{1}H and ^{13}C NMR Spectrum of 6a



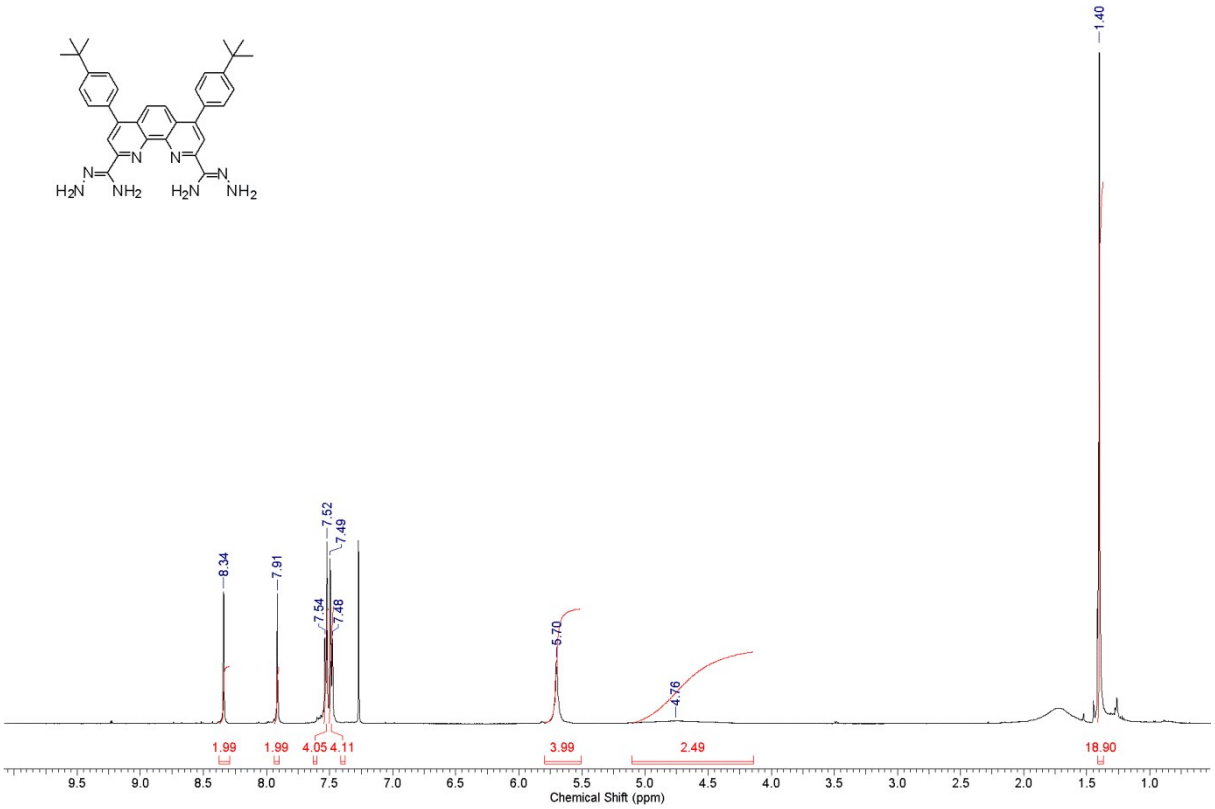


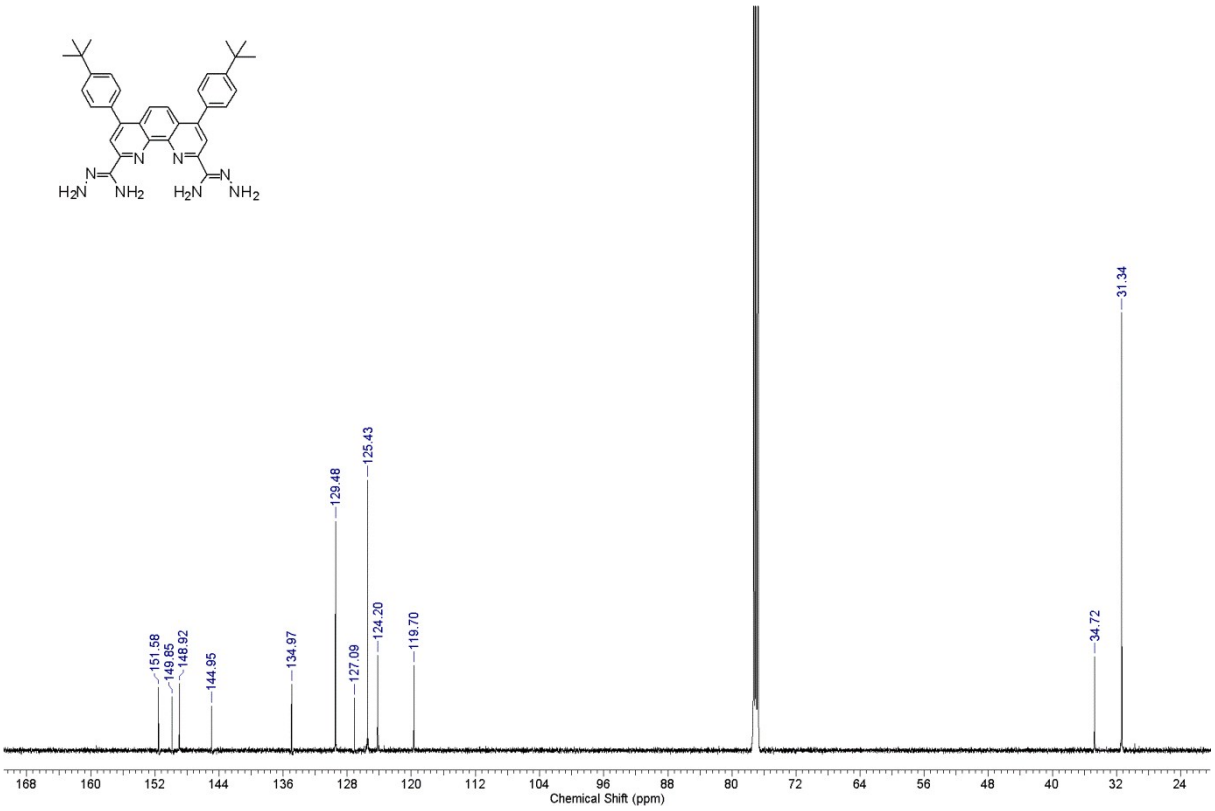
^{1}H and ^{13}C NMR Spectrum of 3b



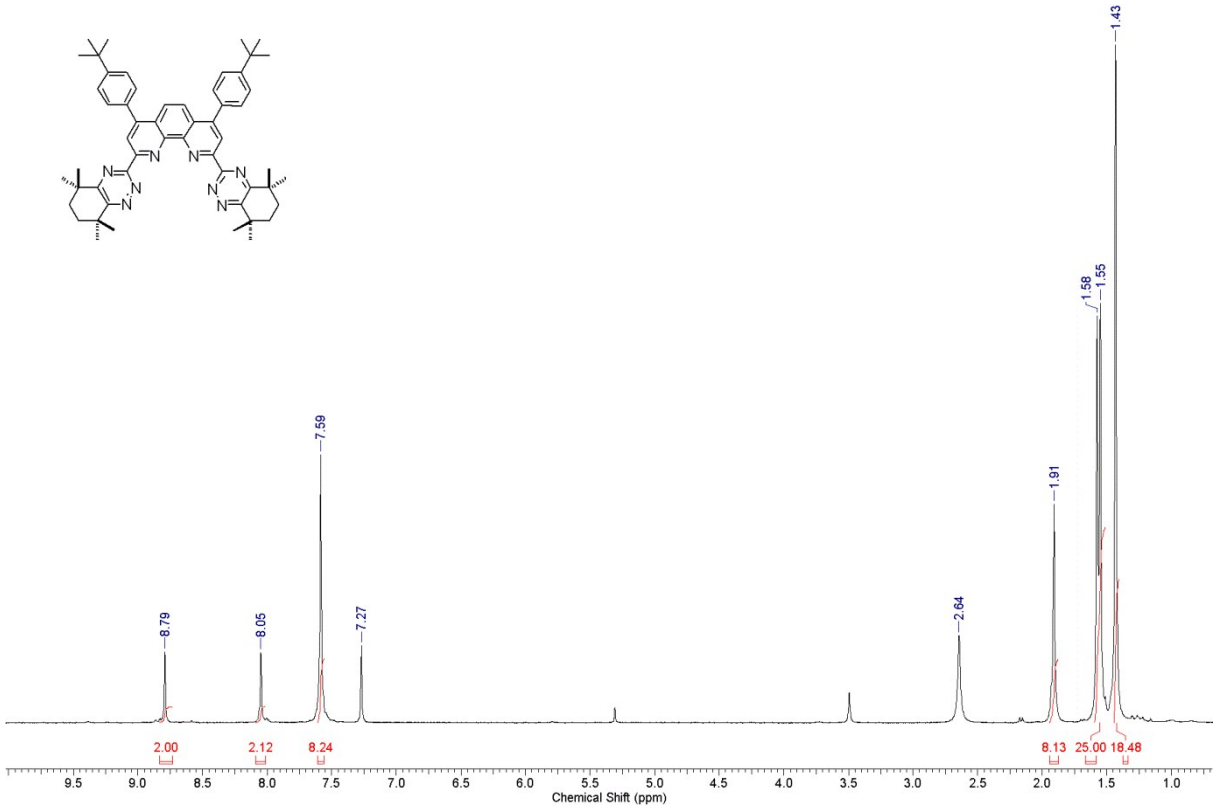


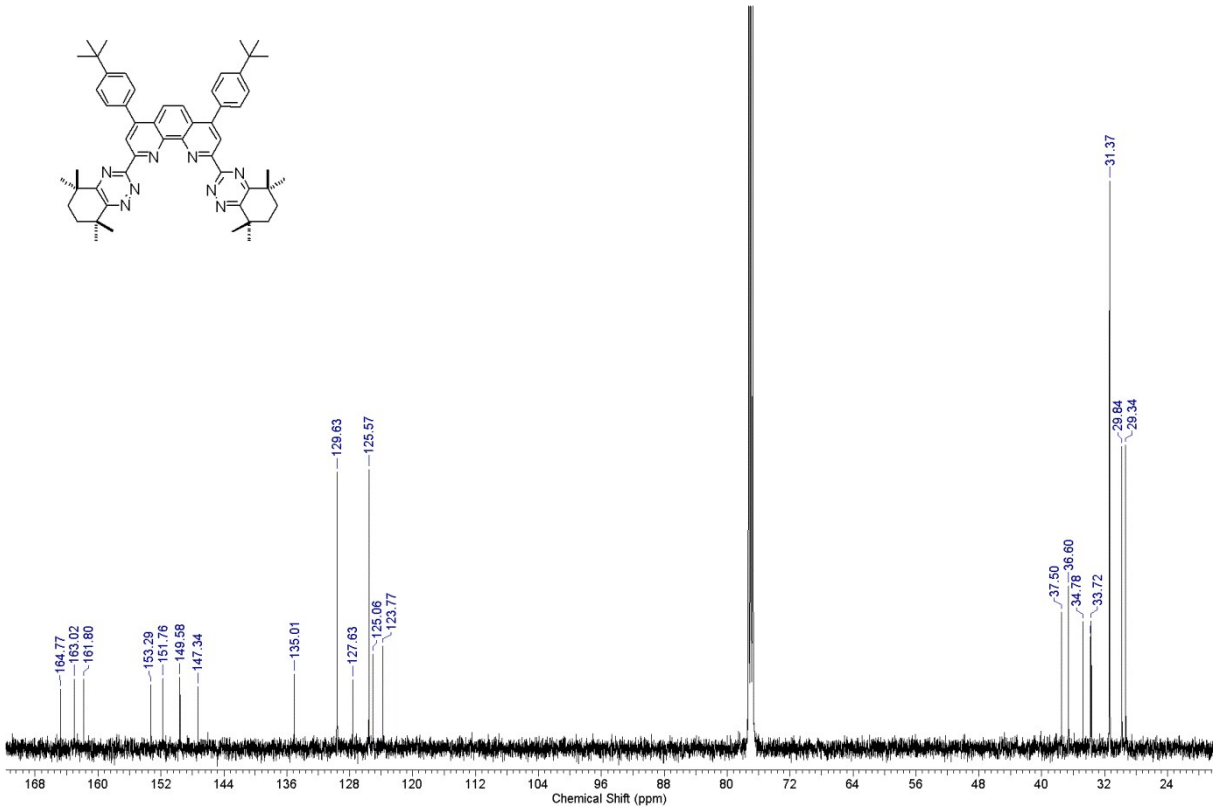
^{1}H and ^{13}C NMR Spectrum of 4b





^{1}H and ^{13}C NMR Spectrum of 6b





3 Solvent Extraction Studies

3.1 General Procedure for Extraction Experiments

A 500 µL aliquot of **6a** (2 mM) and **6b** (2 mM) in 1-octanol was contacted with a 500 µL aliquot of 0.1M – 3M HNO_3 in a 2 mL glass vial. The aqueous phase was spiked with ^{241}Am(III) and ^{152}Eu(III) (1 kBq/mL). The resulting biphasic system was shaken at T = 20 ± 1 °C on an orbital shaker at 2500/min for 120 hours.[+] The phases were centrifugally separated and 300 µL of each phase was analysed using a Packard Cobra Auto Gamma 5003 spectrometer.

^{241}Am(III) and ^{152}Eu(III) distribution ratios, $D_{Am(III)}$ and $D_{Eu(III)}$, were calculated from the ratio of organic to aqueous phase metal ion concentrations which are proportional to the respective gamma count rates per volume:

$D_{M(III)} = [M(III)_{org}]/[M(III)_{aq}]$.

[+] To ensure that equilibrium was attained.

4 X-ray Crystallographic Structure of Eu(III) Complex

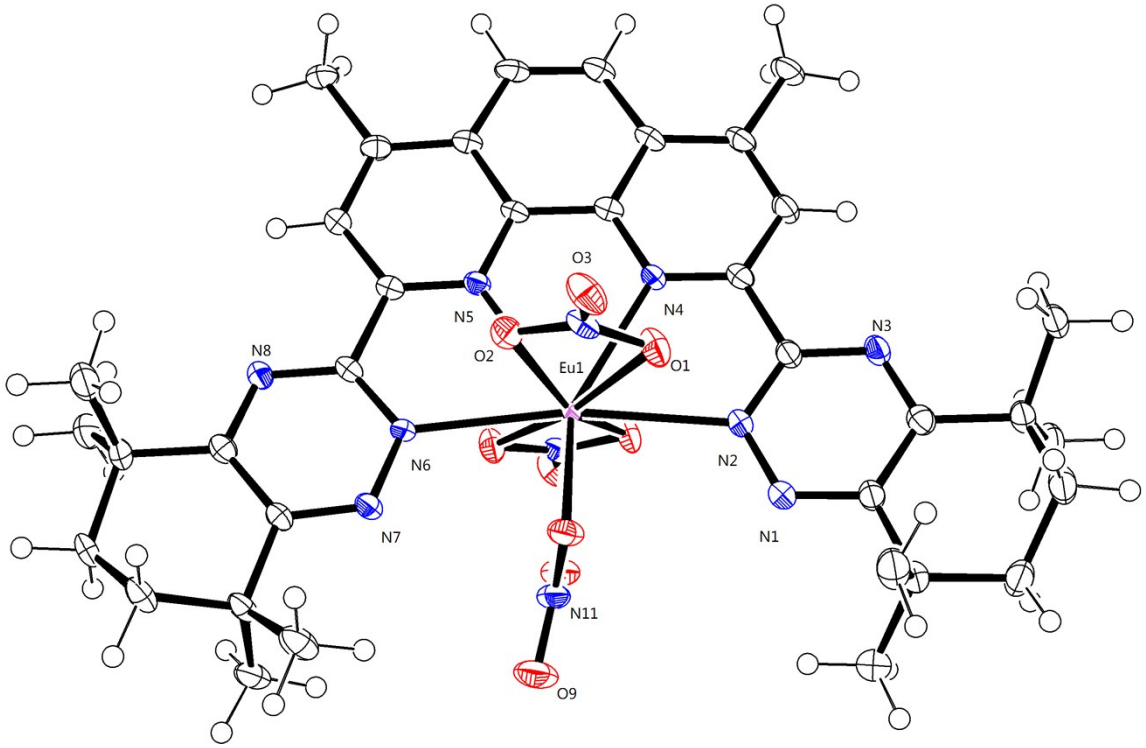


Fig. S1. X-ray crystallographic structure of 4,7-Me-CyMe$_4$-BTPhen–Eu(NO$_3$)$_3$ complex (*c*-*c* conformer). Thermal ellipsoids are shown at 50 % probability. Additional solvent molecules are omitted for clarity.

References

[1] R. A. Altman, S. L. Buchwald, *Org. Lett.* **2006**, *8*, 2779–2782.

[2] J. Engel-Andreasen, B. Shimpukade, T. Ulven, *Green Chem.* **2013**, *15*, 336.

[3] A. C. Edwards, C. Wagner, A. Geist, N. A. Burton, C. A. Sharrad, R. W. Adams, R. G. Pritchard, P. J. Panak, R. C. Whitehead, L. M. Harwood, *Dalt. Trans.* **2016**.