Supporting Information

The Impact of Alicyclic Substituents on the Extraction Ability of New Family of 1,10-Phenanthroline-2,9-diamides

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1. Experimental part

1.1 Materials

The list of the studied diamides and their labels (**3a-3h**) are presented in table 1.

All syntheses were performed in argon inert atmosphere. Dichloromethane was purified by distillation over calcium hydride prior to use. Triethylamine was purified by simple distillation, previously held for 12 hours over sodium hydroxide. All the cyclic amines which are liquid under normal conditions were purified by simple or vacuum distillation. Carbazole was previously purified by recrystallization from toluene.

3-Nitrobenzotrifluoride ("F-3") analytical grade was purchased from Rhodia (France) and was used as a solvent in the extraction experiments without further purification.

1.2 Methods

NMR spectra were recorded using standard 5 mm sample tubes on Agilent 400-MR spectrometer with operating frequencies of 400.1 MHz (^{1}H) and 100.6 MHz (^{13}C) and Bruker Avance-600 spectrometer with operating frequencies of 600.1 MHz (^{1}H) and 150.6 MHz (^{13}C). Deuterated solvents $CDCl_3$, THF-d_8, benzene-d_6, acetonitrile-d_3, and DMSO-d_6 for NMR spectra were purchased from commercial sources and used without further purification.

The ROESY spectrum was recorded on the Agilent 400-MR spectrometer using standard ROESYAD pulse sequence with a mixing time 200 msec and an acquisition time 150 msec.

IR spectra were recorded on FTIR spectrometer Nicolet iS5 (Thermo Scientific) using an internal reflectance attachment with diamond optical element – attenuated total reflection (ATR) with 45° angle of incidence. Resolution 4 cm^{-1}, the number of scans is 32.

IR spectra in CCl_4 solutions were recorded in a 0.06 cm cuvette with KBr windows at the concentrations of compounds 0.01 $mol \cdot l^{-1}$ at room temperature. Ultrasonic bath was used to facilitate dissolution of diamides **3f – 3h**.

HRMS ESI - mass spectra were recorded on the MicroTof Bruker Daltonics and Orbitrap Elite instruments.

Single crystals of **1·DMF·H_2O** and **3f** were obtained upon slow isothermal (25ºC) recrystallization of corresponding substances from DMF-ethyl acetate (50/50) mixture, single crystals of **3a** were obtained upon slow adding of n-hexane to a solution of **3a** in ethyl acetate-chloroform (50/50) mixture, and **3b·H_2O** – by recrystallization of **3b** from acetonitrile.

X-ray diffraction experiments for **1·DMF·H_2O** and **3f** were performed on the "Belok"

beamline of the National Research Center "Kurchatov Institute" (Moscow, Russian Federation) using a Rayonix SX165 CCD detector and X-ray radiation with λ = 0.78790 Å and 0.79272 Å for **1·DMF·H$_2$O** and **3f**, respectively. For **3a** and **3b·H$_2$O**, the STOE STADIVARI diffractometer equipped with the fine-focus Cu GeniX 3D radiation source (λ = 1.54186 Å) and a Pilatus 100K detector was used. For **1·DMF·H$_2$O** and **3f**, data reduction procedure was carried out with the *iMOSFLM* program from the CCP4 program set[1], absorption correction was performed with the *SCALA* program[2], whereas for **3a** and **3b·H$_2$O**, the STOE X-AREA program was applied. All structures were determined by direct methods and refined by full-matrix least-squares on F^2 with all non-H atoms given anisotropically. Hydrogen atoms of hydroxy groups and water molecule in **1·DMF·H$_2$O** were located from difference Fourier maps and refined isotropically with U_{iso}(H) = 1.5U_{eq}(O). For **3b·H$_2$O**, we failed to determine the positions of water molecule H atoms, which seem to be disordered. All other H atoms were positioned geometrically and refined as riding at parent C atoms with U_{iso}(H) = 1.5U_{eq}(C) for methyl groups and U_{iso}(H) = 1.2U_{eq}(C) for all other H atoms. For **1·DMF·H$_2$O** and **3f**, all calculations were performed with SHELXTL[3a], whereas for **3a** and **3b·H$_2$O** SHELXT[3b] was used for the structure solution and SHELXL[3a] – for the refinement. Full crystallographic data are deposited in Cambridge Structural Database, deposition numbers 1938798 (**1·DMF·H$_2$O**), 1988714 (**3a**), 1983770 (**3b·H$_2$O**), 1938799 (**3f**). Selected crystal data for the studied compounds are presented below:

1·DMF·H$_2$O: $C_{17}H_{15}Cl_2N_3O_6$, M_r = 428.22, triclinic, *P*-1, *a* = 7.158(1), *b* = 8.352(2), *c* = 15.356(3) Å, α = 81.10(3), β = 82.92(3), γ = 78.62(3)°, *V* = 885.1(3) Å^3, *Z* = 2, d_c = 1.607 g cm^{-3}, μ = 0.538 mm^{-1}, *F*(000) = 440, *T* = 100(2) K, T_{min}/T_{max} = 0.890/0.980, $2\theta_{max}$ = 61.52°, 15682 reflections, 4025 unique (R_{int} = 0.028), R_1 = 0.031 for 3711 reflections with $I > 2\sigma(I)$, wR_2 = 0.089 for all reflections and 268 refined parameters, GoF on F^2 = 1.073.

3a: $C_{22}H_{20}Cl_2N_4O_2$, M_r = 443.32, triclinic, *P*-1, *a* = 7.7488(3), *b* = 10.1002(4), *c* = 13.5780(5) Å, α = 79.974(3), β = 76.276(3), γ = 83.821(3)°, *V* = 1014.12(7) Å^3, *Z* = 2, d_c = 1.452 g cm^{-3}, μ = 3.11 mm^{-1}, *F*(000) = 460, *T* = 293(2) K, T_{min}/T_{max} = 0.672/0.953, $2\theta_{max}$ = 135.95°, 8085 reflections, 3593 unique (R_{int} = 0.023), R_1 = 0.043 for 2581 reflections with $I > 2\sigma(I)$, wR_2 = 0.129 for all reflections and 281 refined parameters, GoF on F^2 = 1.025.

3b·H$_2$O: $C_{24}H_{26}Cl_2N_4O_3$, M_r = 489.39, monoclinic, *C*2/*c*, *a* = 36.3267(15), *b* = 6.8415(2), *c* = 22.1880(11) Å, β = 122.928(3), *V* = 4628.5(4) Å^3, *Z* = 8, d_c = 1.405 g cm^{-3}, μ = 2.81 mm^{-1}, *F*(000) = 2048, *T* = 293(2) K, T_{min}/T_{max} = 0.865/0.972, $2\theta_{max}$ = 135.37°, 26181 reflections, 4179 unique (R_{int} = 0.113), R_1 = 0.036 for 2196 reflections with $I > 2\sigma(I)$, wR_2 = 0.072 for all reflections and 298 refined parameters, GoF on F^2 = 0.846.

3f: $C_{30}H_{20}Cl_2N_4O_2$, M_r = 539.40, triclinic, *P*-1, *a* = 7.2410(14), *b* = 11.680(2), *c* = 14.506(3) Å, α = 103.259(14), β = 95.030(2), γ = 97.662(18)°, *V* = 1174.6(4) Å^3, *Z* = 2, d_c = 1.525 g cm^{-3}, μ = 0.420 mm^{-1}, *F*(000) = 556, *T* = 100(2) K, T_{min}/T_{max} = 0.93/0.97, $2\theta_{max}$ = 61.92°, 18379 reflections, 5233 unique (R_{int} = 0.078), R_1 = 0.059 for 3967 reflections with $I > 2\sigma(I)$, wR_2 = 0.153 for all reflections and 344 refined parameters, GoF on F^2 = 1.021.

Detailed crystallographic data provided here in Chapter 3 (see below, from page S40).

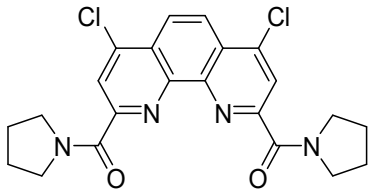
1.3 Synthesis and analytical data

*4,7-dichloro-1,10-phenanthroline-2,9-dicarbonyl chloride **2***

0.35 Mol (118 g) of thoroughly dried dicarboxylic acid **1** was added to 1.4 l of $SOCl_2$ at room temperature and stirring. 100 μl of DMF was added to the resulting suspension and the reaction mixture was stirred for 4 hours at 50ºC. After that, $SOCl_2$ was removed at low pressure (200 Torr), then 250 ml of dry benzene was added to the residue, and then the solvent was distilled off again. Absolute diethyl ether was added to the solid rest. It was washed on a filter with cold ether, after that the product **2** was dried in vacuum to a constant mass. Yield 95%, pale-yellow fibers, T.decomp. > 220°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 2H), 8.52 (s, 2H).

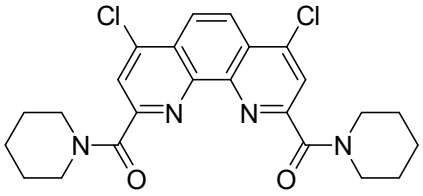
*General method for synthesis of diamides **3a–e***

A solution of the corresponding cyclic amine (50 mmol) in 5 ml of methylene chloride was added at -20ºC under vigorous stirring to a suspension of 10 mmol (3.74 g) of chloride **2** in 25 ml of methylene chloride. Then the reaction mixture was allowed to reach room temperature and stirred overnight. Next, the reaction mixture was diluted with 50 ml of methylene chloride, washed with water (2 × 50 ml), dried over sodium sulfate, and the solvent was distilled off. The residue was treated with hexane, recrystallized from a mixture of chloroform/hexane, obtaining the desired product in the form of a white or slightly colored solid.

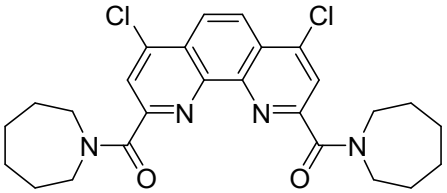


(4,7-Dichloro-9-(pyrrolidin-1-ylcarbonyl)-1,10-phenanthrolin-2-yl)(pyrrolidin-1-yl)-methanone 3a. Yield 82 % (3.64 g), yellowish powder, m.p. 245-247ºC, R_f 0.78 (acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 2H), 8.31 (s, 2H), 4.09 (t, *J* = 6.5 Hz, 4H), 3.74 (t, *J* = 6.5 Hz, 4H), 2.01 – 1.91 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9, 154.3, 145.2, 143.8,

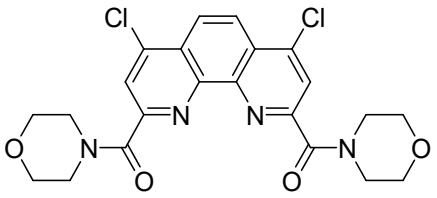
127.5, 124.4, 124.2, 49.2, 47.3, 26.9, 24.2; IR (см$^{-1}$) 3095, 3073, 2968, 2878 (C-H stretching vibrations), 1634, 1622, 1615 (C=O), 1573, 1522, 1449, 1437, 1416 (C=C, C=N); HRMS (ESI-TOF) (*m*/*z*) $[M+H]^+$ calculated for $C_{22}H_{21}Cl_2N_4O_2$ 443.1037, found 443.1034.



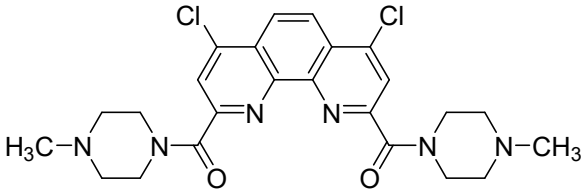
(4,7-Dichloro-9-(piperidin-1-ylcarbonyl)-1,10-phenanthrolin-2-yl)(piperidin-1-yl)-methanone 3b. Yield 81 % (3.82 g), white powder, m.p. 249-251°C, R_f 0.58 (acetone:CH_2Cl_2 1:4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 2H), 8.10 (s, 2H), 3.79 (t, *J* = 5.3 Hz, 4H), 3.72 (t, *J* = 5.3 Hz, 4H), 1.82 – 1.59 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 154.5, 145.3, 143.9, 127.3, 124.3, 124.0, 48.7, 43.9, 26.7, 25.7, 24.7; IR (см$^{-1}$) 3084, 3043, 2938, 2914, 2843 (C-H stretching vibrations), 1634, 1626 (C=O), 1571, 1532, 1456, 1446, 1425 (C=C, C=N); HRMS (ESI-TOF) (*m*/*z*) $[M+H]^+$ calculated for $C_{24}H_{25}Cl_2N_4O_2$ 471.1350, found 471.1335.



Azepan-1-yl(9-(azepan-1-ylcarbonyl)-4,7-dichloro-1,10-phenanthrolin-2-yl)methanone 3c. Yeild 82 % (4.10 g), white powder, m.p. 238-241ºC, R_f 0.53 (acetone:CH_2Cl_2 1:5), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 2H), 8.11 (s, 2H), 3.82 – 3.72 (m, 8H), 1.90 (p, *J* = 5.9 Hz, 4H), 1.78 (p, *J* = 5.9 Hz, 4H), 1.71 – 1.57 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 154.9, 145.4, 143.8, 127.3, 124.1, 124.0, 49.9, 47.4, 29.6, 27.6, 27.3, 27.0; IR (см$^{-1}$) 3037, 2926, 2853 (C-H stretching vibrations), 1634, 1631, 1626 (C=O), 1590, 1530, 1456, 1427 (C=C, C=N); HRMS (ESI-TOF) (*m*/*z*) $[M+H]^+$ calculated for $C_{26}H_{29}Cl_2N_4O_2$ 499.1663, found 499.1662.



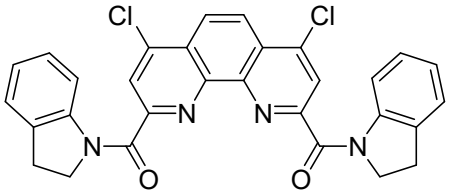
(4,7-dichloro-9-(morpholin-4-ylcarbonyl)-1,10-phenanthrolin-2-yl)(morpholin-4-yl)methanone 3d. Yield 71 % (3.37 g), white powder, m.p. 236-238ºC, R_f 0.75 (acetone:CH_2Cl_2 1:1); ^{1}H NMR (400 MHz, $CDCl_3$), δ 8.41 (s, 2H), 8.21 (s, 2H), 3.98 (t, *J* = 4.8 Hz, 4H), 3.95 – 3.83 (m, 8H), 3.75 (t, *J* = 4.8 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 153.5, 145.1, 144.3, 127.6, 124.9, 124.3, 67.3, 67.0, 48.2, 43.3; IR (см$^{-1}$) 3093, 3026, 2966, 2912, 2852 (C-H stretching vibrations), 1644, 1640, 1634, 1634, 1628, (C=O), 1570, 1528, 1475, 1462, 1444, 1427 (C=C, C=N); HRMS (ESI-TOF) (*m*/*z*) $[M+H]^+$ calculated for $C_{22}H_{21}Cl_2N_4O_4$ 475.0935, found 475.0928.



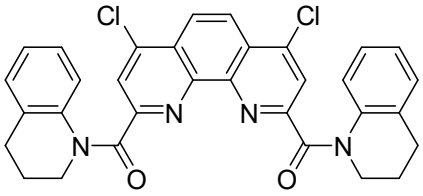
(4,7-dichloro-9-((4-methylpiperazin-1-yl)carbonyl)-1,10-phenanthrolin-2-yl)(4-methylpiperazin-1-yl)methanone 3e. Yield 79 % (3.96 g), white powder, m.p. 235-238ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 2H), 8.17 (s, 2H), 3.98 – 3.87 (m, 8H), 2.55 (t, *J* = 5.0 Hz, 4H), 2.42 (t, *J* = 5.0 Hz, 4H), 2.32 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 153.9, 145.1, 144.1, 127.5, 124.7, 124.2, 55.7, 54.8, 47.5, 46.2, 42.8; IR (см$^{-1}$) 3041, 2973, 2937, 2894, 2860, 2794, 2749 (C-H stretching vibrations), 1635 (C=O), 1531, 1460, 1446, 1425 (C=C, C=N); HRMS (ESI-TOF) (*m*/*z*) $[M+H]^+$ calculated for $C_{24}H_{27}Cl_2N_6O_2$ 501.1568, found 501.1562.

*General method for synthesis of diamides **3f–h***

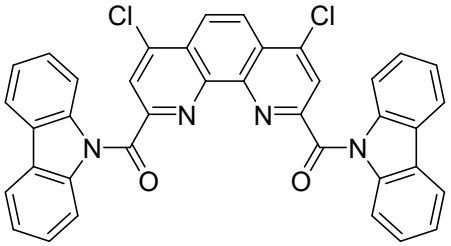
Triethylamine (30 mmol, 3.04 g, 4.20 ml) was added to a suspension of 10 mmol (3.74 g) of chloride **2** in 25 ml of methylene chloride at -20 ºC under vigorous stirring and then the solution of the corresponding secondary amine (22.5 mmol) in 10 ml of methylene chloride was added dropwise. After that, the reaction mixture was stirred at -20 ºC for 1 hour, allowed to reach the room temperature and was additionally stirred for 24 hours. Then it was washed with water (2 × 50 ml), dried over sodium sulfate and the solvent was distilled off. The residue was washed with chloroform, giving the desired product in the form of slightly colored solid.



(4,7-dichloro-9-(2,3-dihydro-1*H*-indol-1-ylcarbonyl)-1,10-phenanthrolin-2-yl)(2,3-dihydro-1*H*-indol-1-yl)methanone 3f. Yield 76 % (4.10 g), yellowish fibers, m.p. 289-290ºC, R_f 0.74 (EtOAc:CH_2Cl_2 1:10); ^{1}H NMR (400 MHz, DMSO-d_6, recorded at 343.15 K) δ 8.56 (s, 2H), 8.39 (s, 2H), 8.20 (bs, 2H), 7.30 (d, J = 7.8 Hz, 2H), 7.22 (bs, 2H), 7.08 (t, J = 7.8 Hz, 2H), 4.52 (bs, 4H), 3.17 – 3.05 (m, 4H); IR (см$^{-1}$) 3109, 3070, 3053, 2971, 2936, 2862 (C-H stretching vibrations), 1634 (C=O), 1597, 1569, 1533, 1481, 1463, 1437, 1403 (C=C, C=N); HRMS (ESI-TOF) (*m*/*z*) $[M+H]^+$ calculated for $C_{30}H_{20}Cl_2N_4O_2$ 539.1045, found 539.1045.



(4,7-dichloro-9-(1,2,3,4-tetrahydroquinolin-1-ylcarbonyl)-1,10-phenanthrolin-2-yl)-(1,2,3,4-tetrahydroquinolin-1-yl)methanone 3g. Yeild 90 % (5.10 g), yellowish powder, m.p. 238-241ºC, R_f 0.59 (EtOAc:CH_2Cl_2 1:2); ^{1}H NMR (400 MHz, C_6D_6) δ 7.96 (s, 2H), 7.84 (s, 2H), 7.62 (bs, 2H), 6.93 – 6.79 (m, 6H), 3.86 – 3.78 (m, 4H), 2.49 (t, J = 6.8 Hz, 4H), 1.70 – 1.62 (m, 4H); ^{13}C NMR (101 MHz, C_6D_6) δ 166.9, 155.5, 145.9, 143.3, 139.7, 131.4, 128.9, 127.2, 126.1, 125.3, 124.9, 124.2, 123.8, 46.2, 27.2, 24.1; IR (см$^{-1}$) 3061, 3042, 2946, 2885, 2843 (C-H stretching vibrations), 1651, 1644, 1640, 1637 (C=O), 1602, 1581, 1571, 1530, 1491, 1450, 1439, 1400 (C=C, C=N); HRMS (ESI-TOF) (*m*/*z*) $[M+H]^+$ calculated for $C_{32}H_{25}Cl_2N_4O_2$ 567.1350, found 567.1349.



9*H*-carbazol-9-yl(9-(9*H*-carbazol-9-ylcarbonyl)-4,7-dichloro-1,10-phenanthrolin-2-yl)methanone 3h. Yield 63 % (4.00 g), white powder, m.p. 389-393ºC; ^{1}H NMR ($CDCl_3$), δ, ppm: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.61 (s, 2H), 8.22 (s, 2H), 7.80 – 7.73 (m, 4H), 7.31 (d, J = 8.5 Hz, 4H), 7.16 (td, J = 7.4, 1.1 Hz, 4H), 7.05 (ddd, J = 8.5, 7.4, 1.1 Hz, 4H);

IR (см$^{-1}$) 3097, 3061 (C-H stretching vibrations), 1674 (C=O), 1527, 1491, 1480, 1444, 1381 (C=C, C=N); HRMS (ESI-TOF) (*m*/*z*) $[M+H]^+$ calculated for $C_{38}H_{21}Cl_2N_4O_2$ 635.1035, found 635.1029.

1.4 Solvent extraction experiments

Solvent extraction experiments were carried out as follows. 0.5 ml of organic solution of the extractant in 3-*nitrobenzotrifluoride* ("F-3") and 0.5 ml of aqueous phase containing nitric acid and radionuclides were mixed in 1.5 ml polypropylene vial. Three sets of aqueous solutions were prepared for extraction experiments. The first one contained trace concentrations of ^{241}Am (≈1500 Bq·ml^{-1}) and ^{152}Eu (≈2500 Bq·ml^{-1}), the second set contained ^{241}Am (≈1500 Bq·ml^{-1}) and ^{244}Cm (≈2000 Bq·ml^{-1}). The third set contained lanthanum and all lanthanides (except promethium) in total concentration 10^{-4} mol·l^{-1}. The phases were stirred for 15 minutes on a vortex shaker at 25±1ºC in an air thermostat. Then samples were centrifuged (5 minutes, 6000 rpm) and aliquots of each phase were taken for determination of radionuclide or lanthanide concentration.

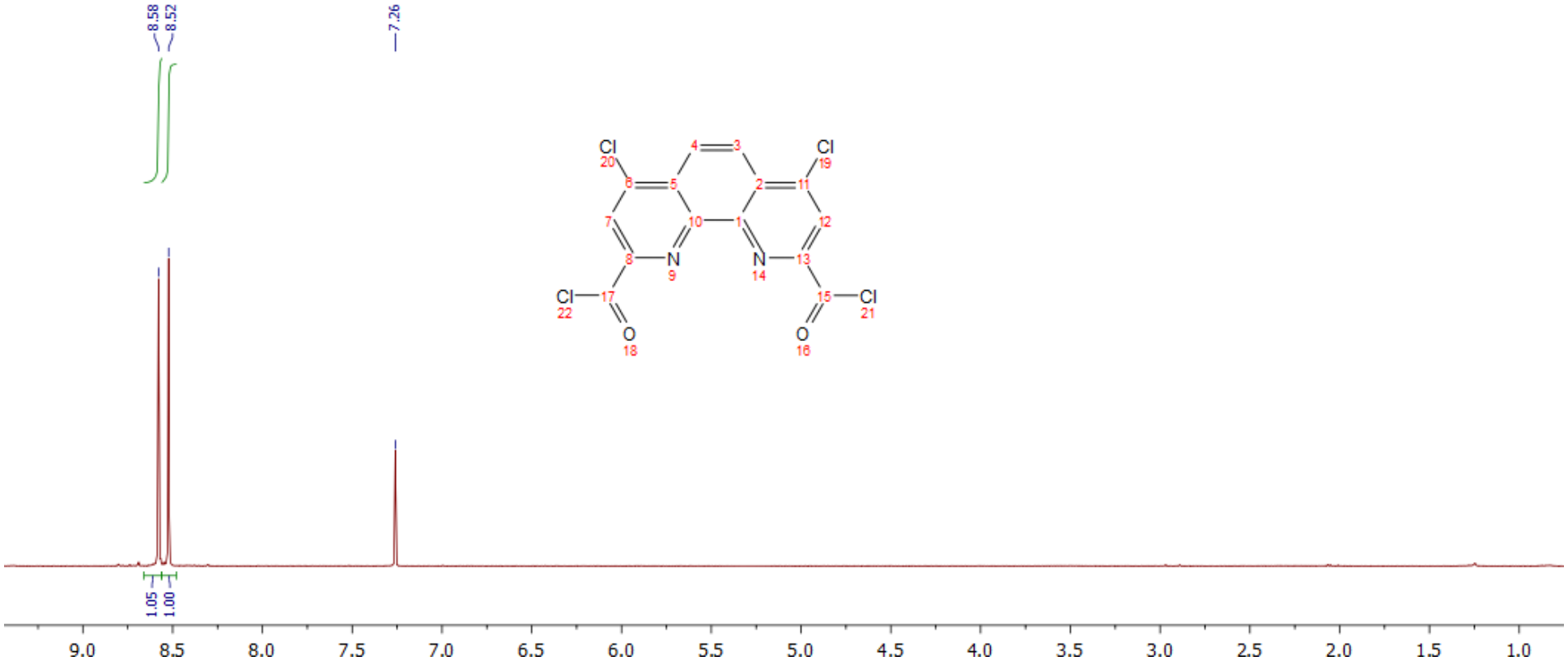
Content of ^{241}Am (E_γ = 59.5 keV) and ^{152}Eu (E_γ = 121.8 keV) was determined by gamma-spectrometry using a high-pure germanium detector GR 3818 (Canberra Ind.) in the first set of experiments. Second set of samples was analyzed by alpha-spectrometry (E_α(^{241}Am) = 5637 keV, E_α(^{244}Cm) = 5901 keV) using an alpha spectrometer Model 7401 with Si detectors (Canberra Ind.). Initial aqueous phase and equilibrium aqueous phases of the third set of samples were analyzed by ICP-OES (Agilent ICP-OES 720).

The distribution ratios (*D*) of metals were calculated for the first set of experiments as the ratio of the counting rate in the organic and aqueous phase. For the second and the third sets of samples activity/concentration in organic phase was calculated as difference between concentrations in initial and equilibrium aqueous phases. The separation factors (*SF*) were calculated as the ratio of the distribution ratios. All extraction experiments were repeated three times. Uncertainties for $0.01 < D < 100$ are about ±10%.

2. NMR, IR and HRMS spectra of synthesized compounds

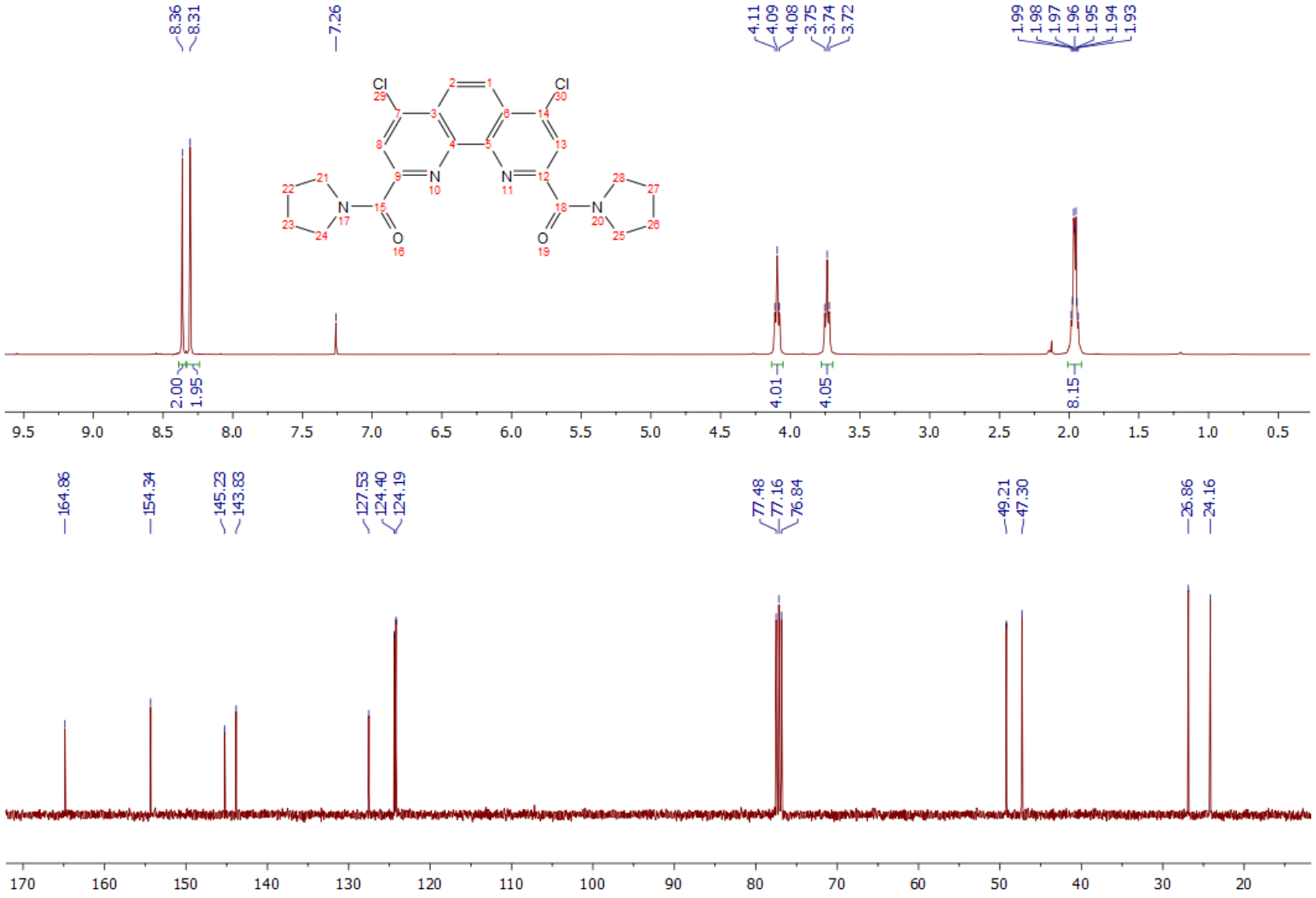
4,7-dichloro-1,10-phenanthroline-2,9-dicarbonyl chloride 2.

^{1}H NMR spectra in $CDCl_3$ at 25ºC

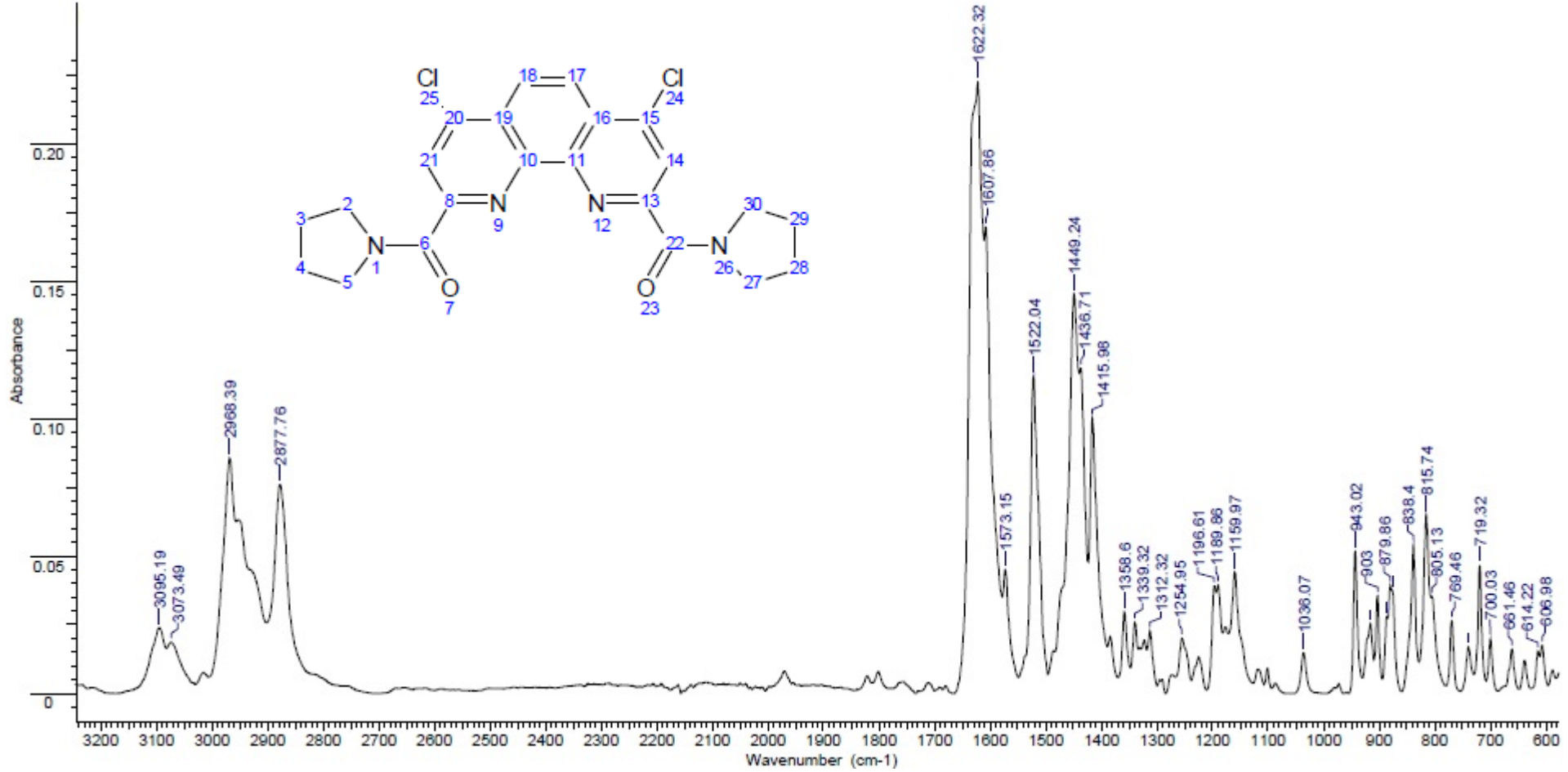


(4,7-dichloro-9-(pyrrolidin-1-ylcarbonyl)-1,10-phenanthrolin-2-yl)(pyrrolidin-1-yl)methanone 3a

^{1}H NMR (above) and ^{13}C NMR (below) spectra in $CDCl_3$ at 25ºC

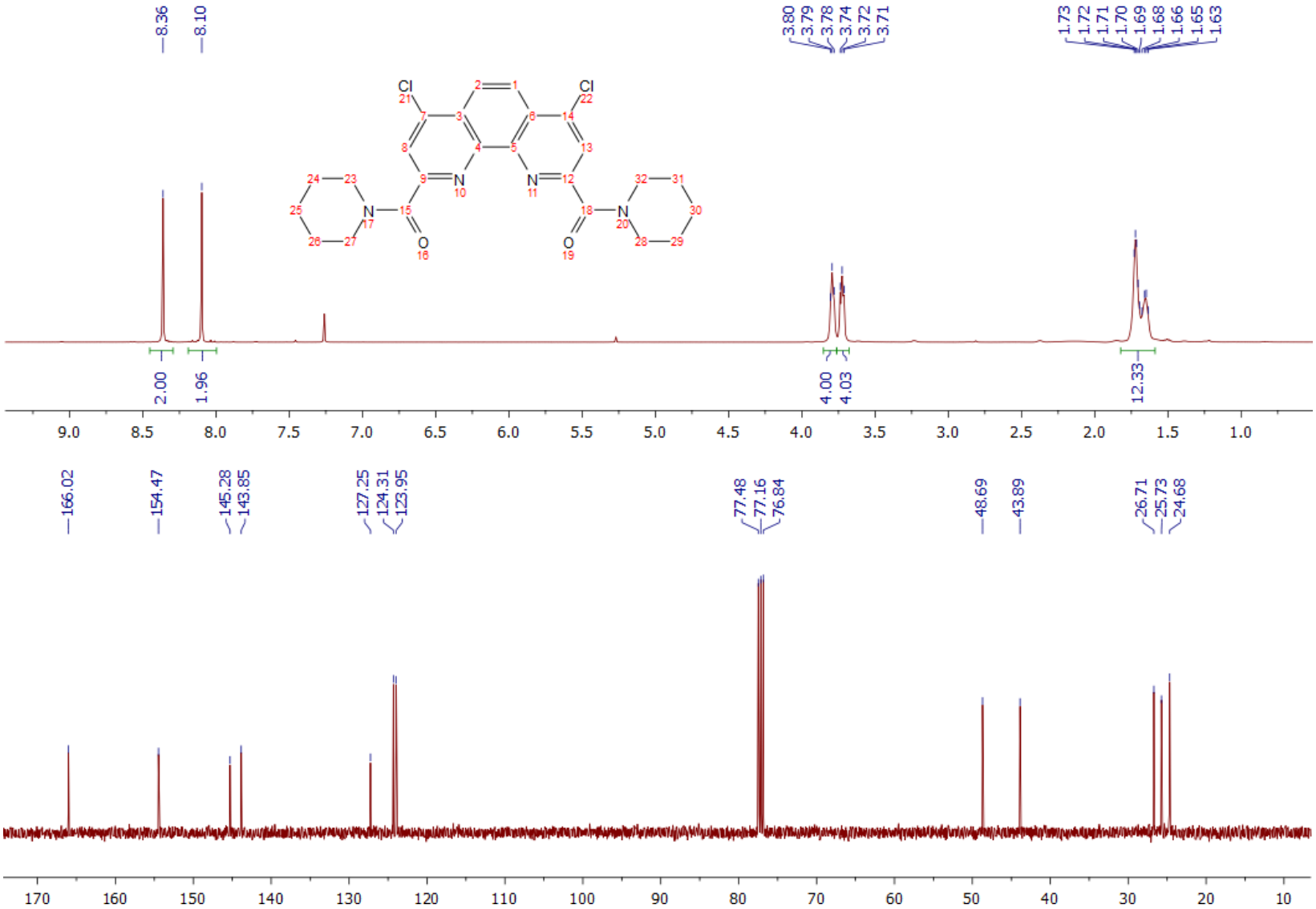


IR spectra at 25ºC

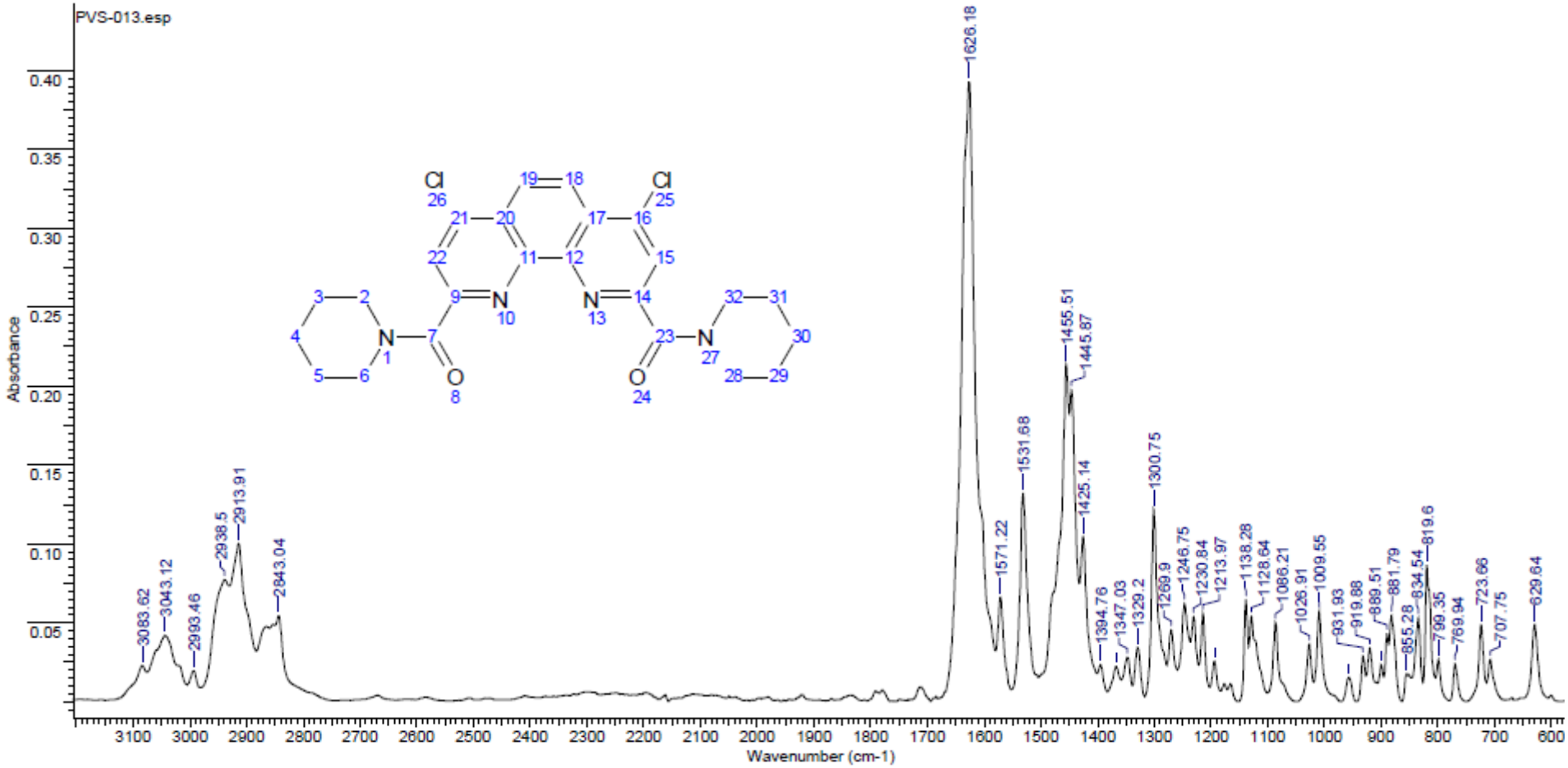


(4,7-dichloro-9-(piperidin-1-ylcarbonyl)-1,10-phenanthrolin-2-yl)(piperidin-1-yl)methanone 3b

^{1}H NMR (above) and ^{13}C NMR (below) spectra in $CDCl_3$ at 25ºC

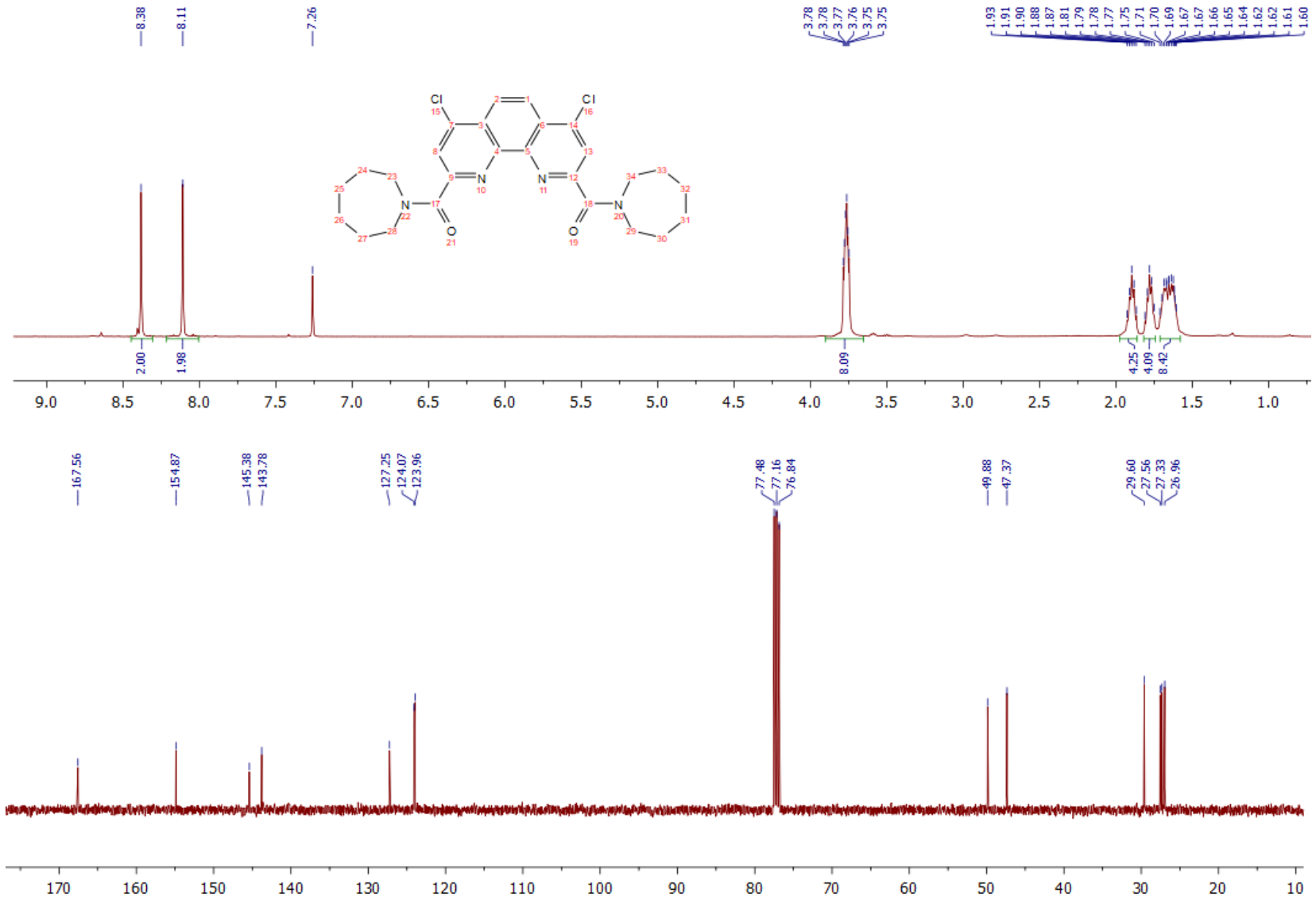


IR spectra at 25ºC

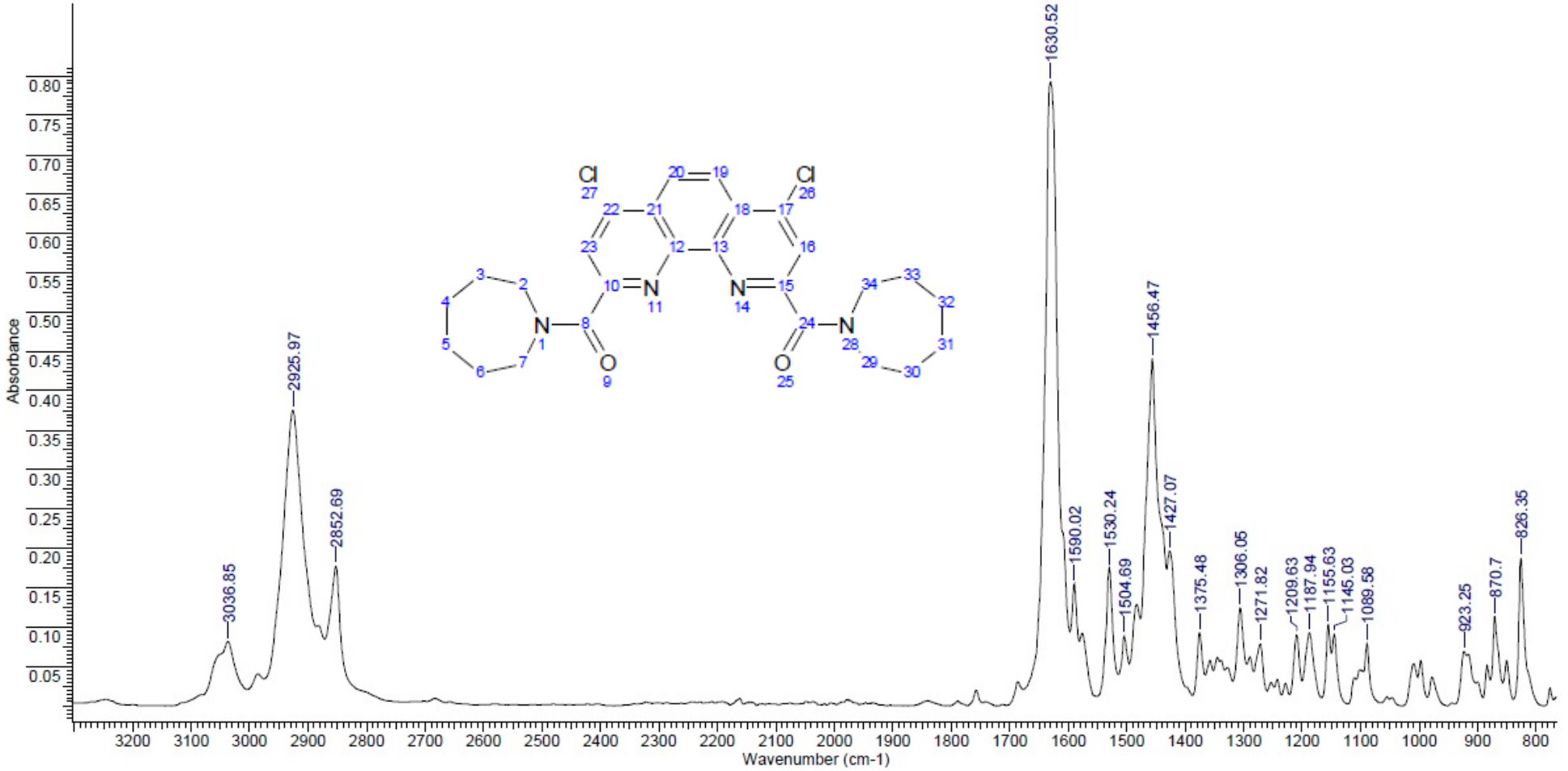


Azepan-1-yl(9-(azepan-1-ylcarbonyl)-4,7-dichloro-1,10-phenanthrolin-2-yl)methanone 3c

^{1}H NMR (above) and ^{3}C NMR [1] (below) spectra in $CDCl_3$ at 25ºC

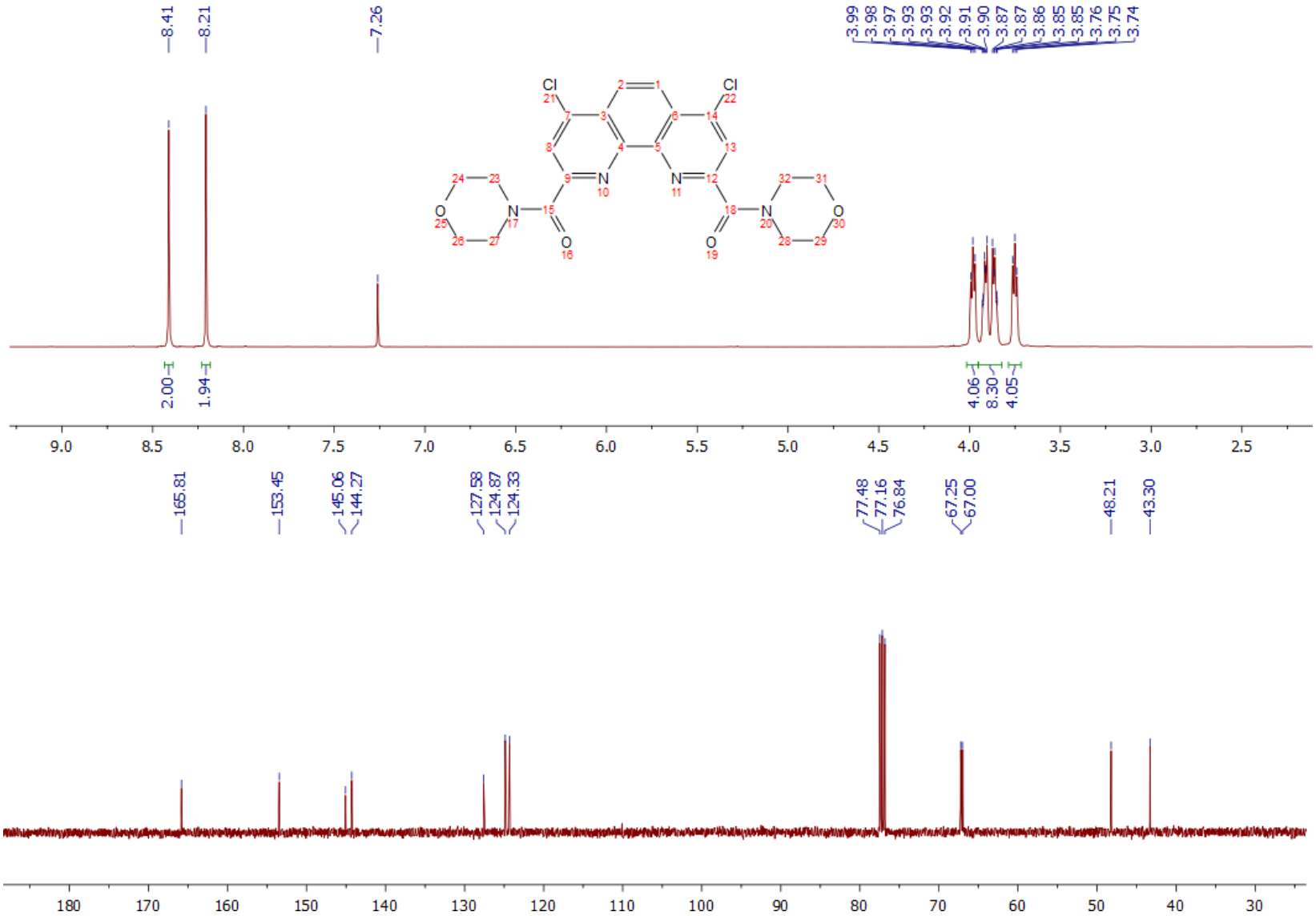


IR spectra at 25ºC

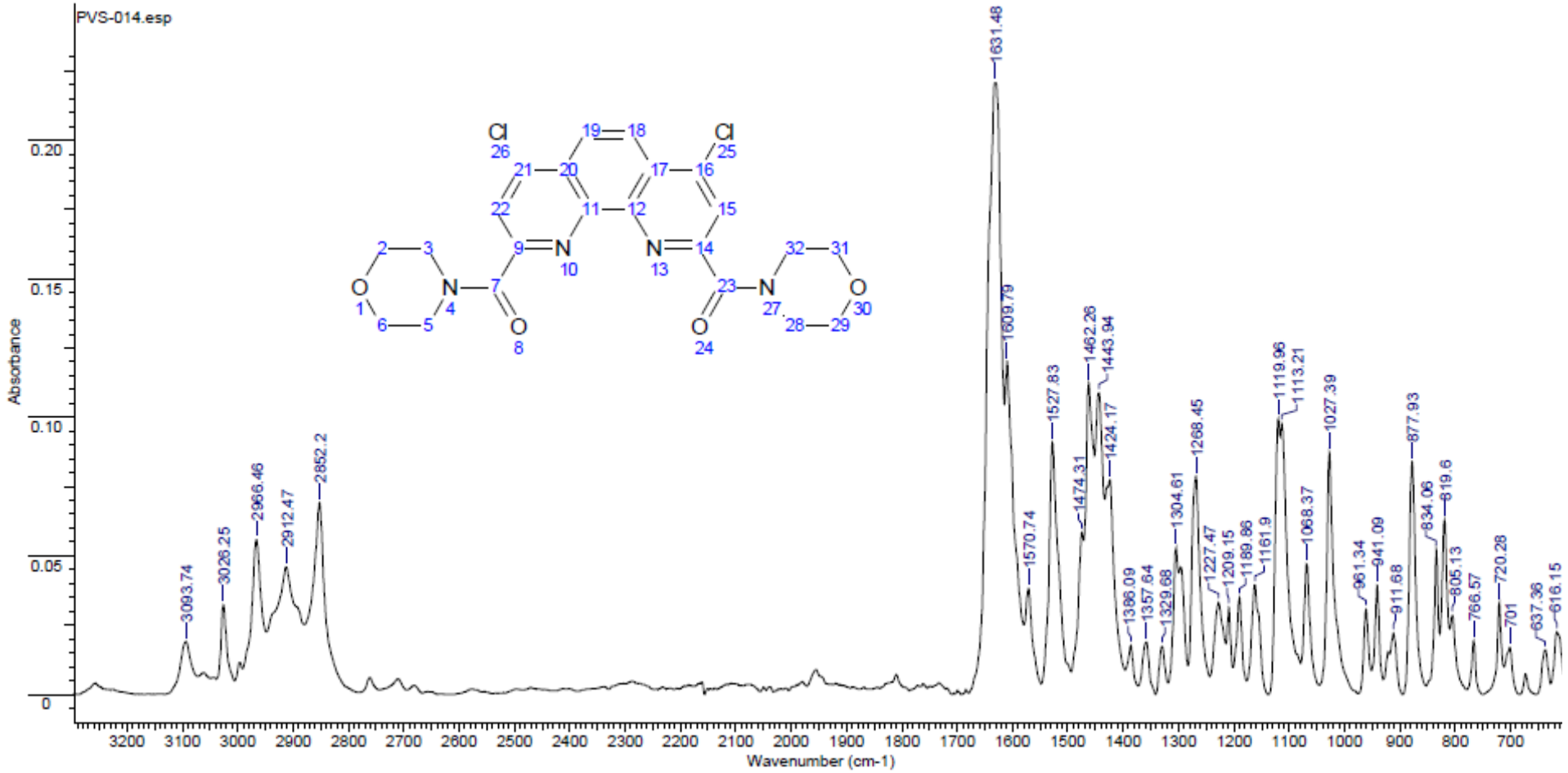


(4,7-Dichloro-9-(morpholin-4-ylcarbonyl)-1,10-phenanthrolin-2-yl)(morpholin-4-yl)methanone 3d

^{1}H NMR (above) and ^{13}C NMR (below) spectra in $CDCl_3$ at 25ºC

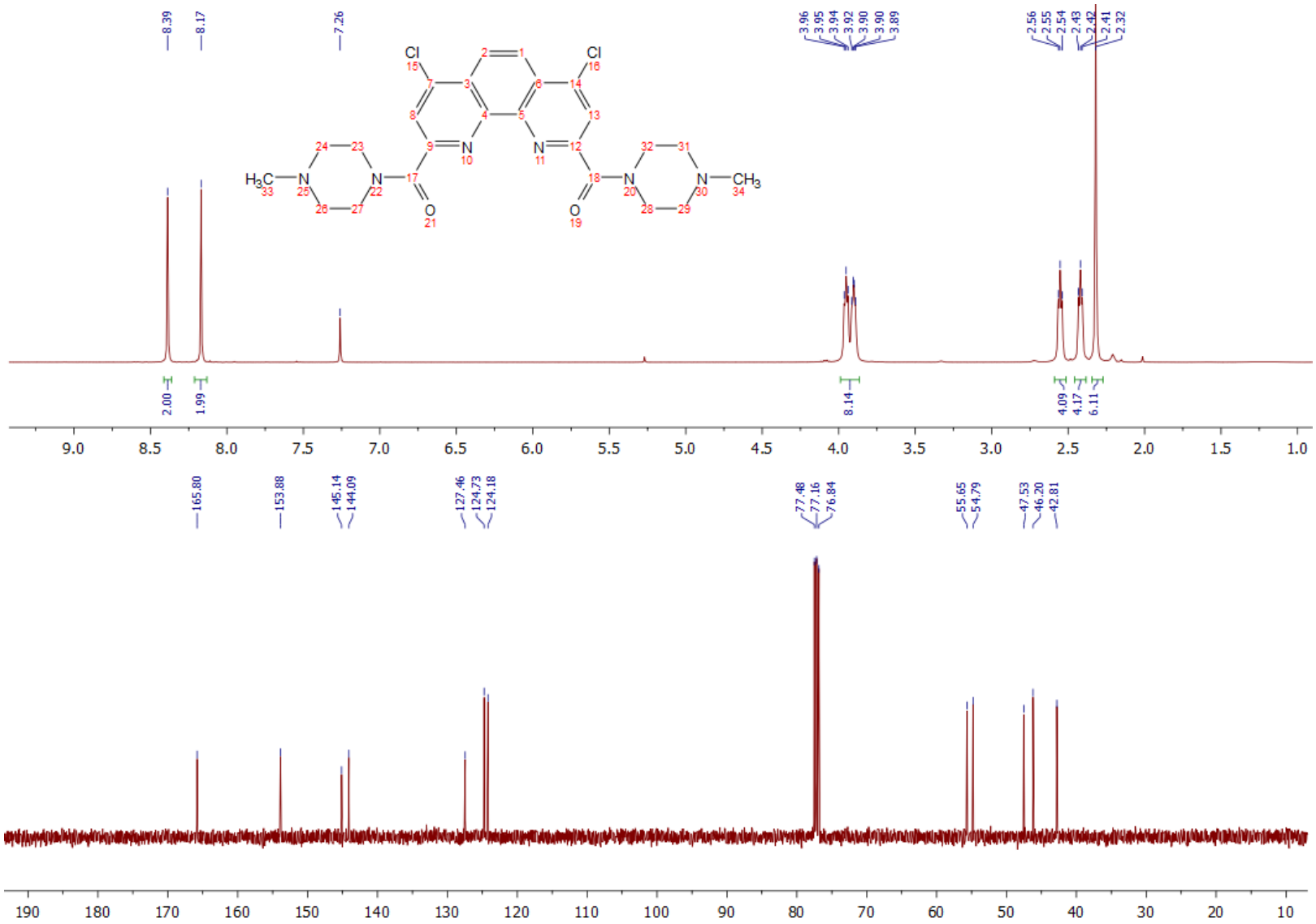


IR spectra at 25ºC

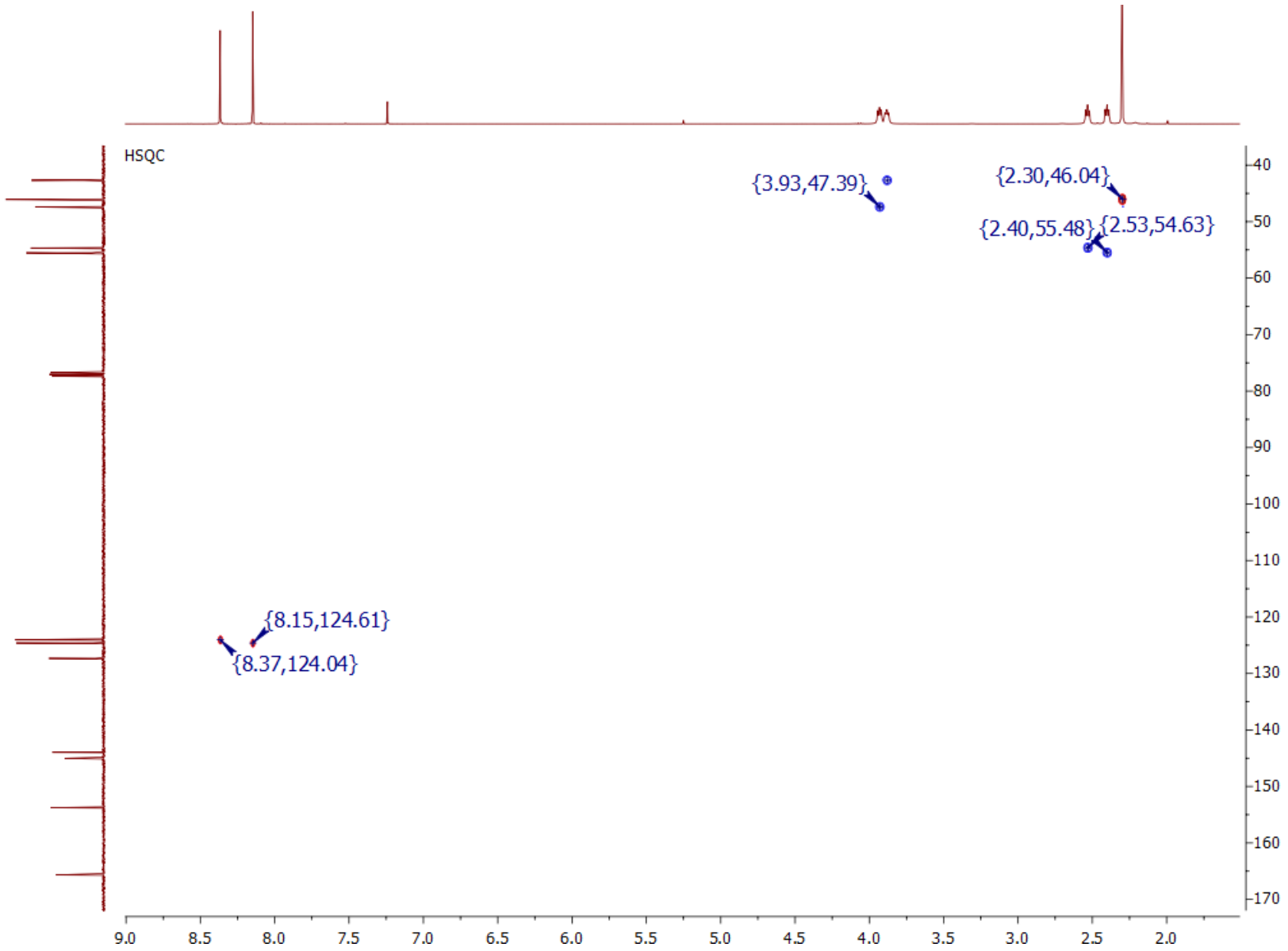


(4,7-Dichloro-9-((4-methylpiperazin-1-yl)carbonyl)-1,10-phenanthrolin-2-yl)(4-methylpiperazin-1-yl)methanone 3e

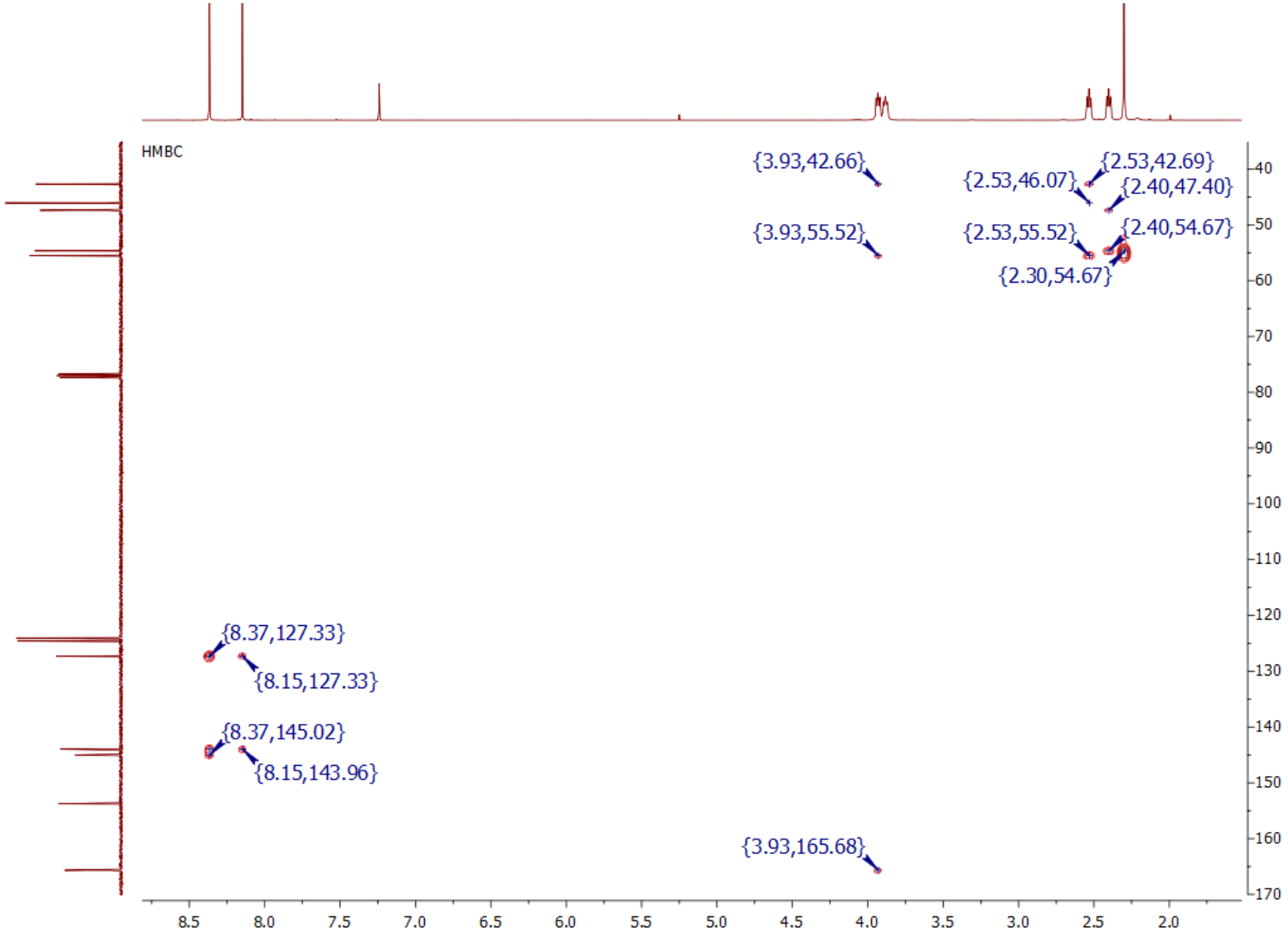
^{1}H NMR (above) and ^{13}C NMR (below) spectra in $CDCl_3$ at 25ºC



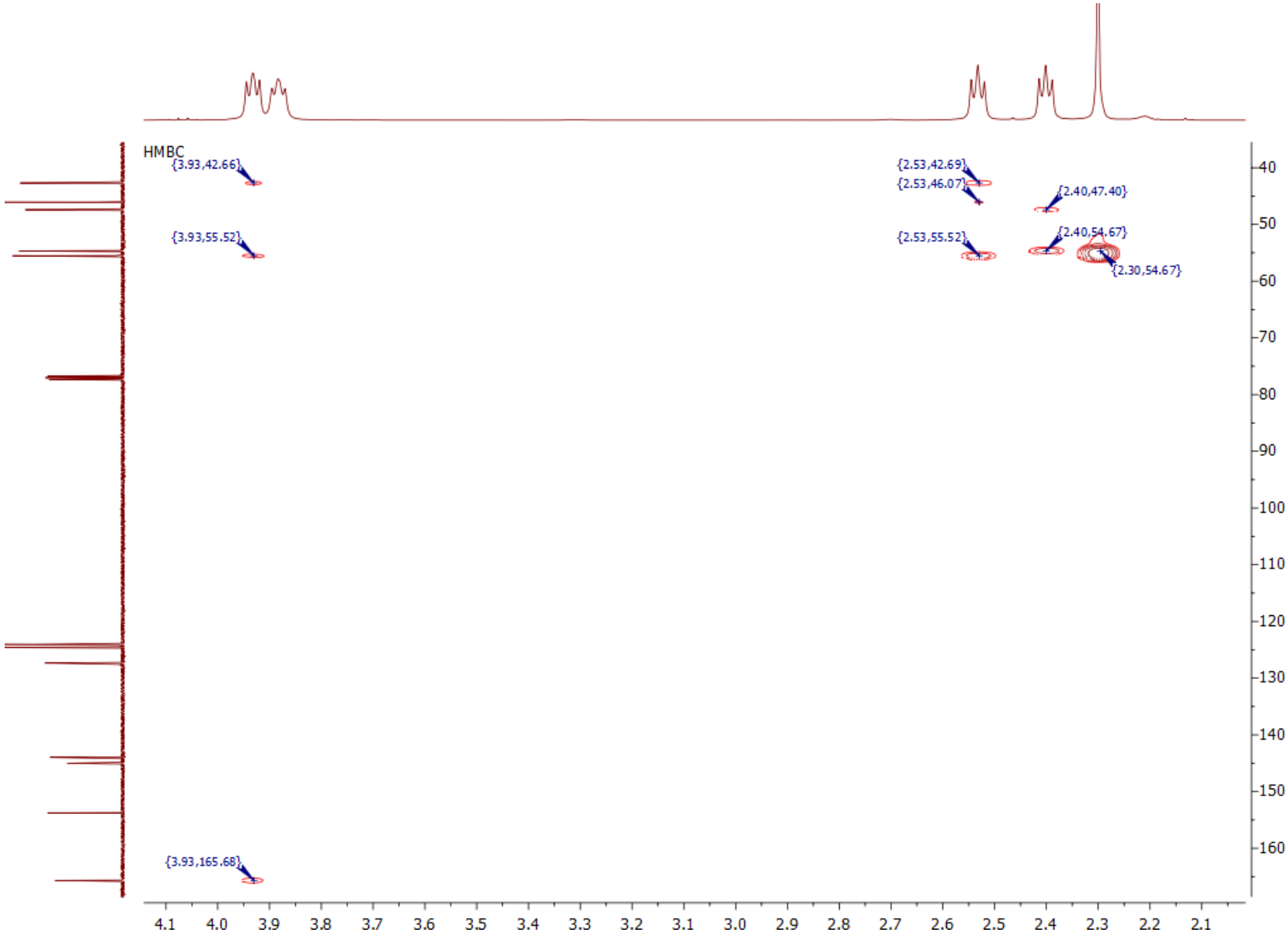
$^{1}H/^{13}C$ HSQC NMR in $CDCl_3$ at 25ºC



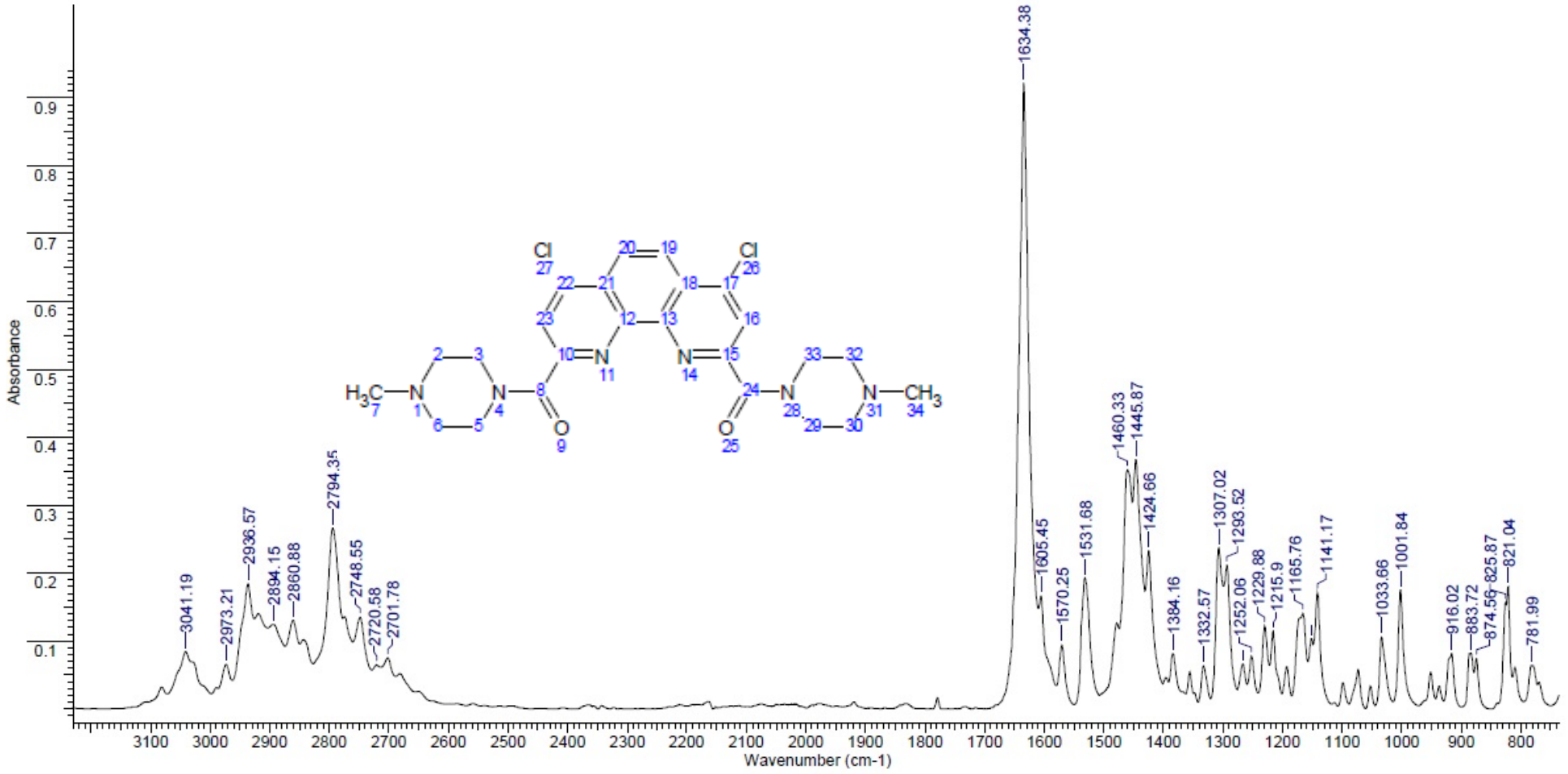
$^{1}H/^{13}C$ HMBC NMR in $CDCl_3$ at 25ºC



$^{1}H/^{13}C$ HMBC NMR in $CDCl_3$ at 25ºC, fragmental view (H-scale region from 4.1 to 2.1 ppm)

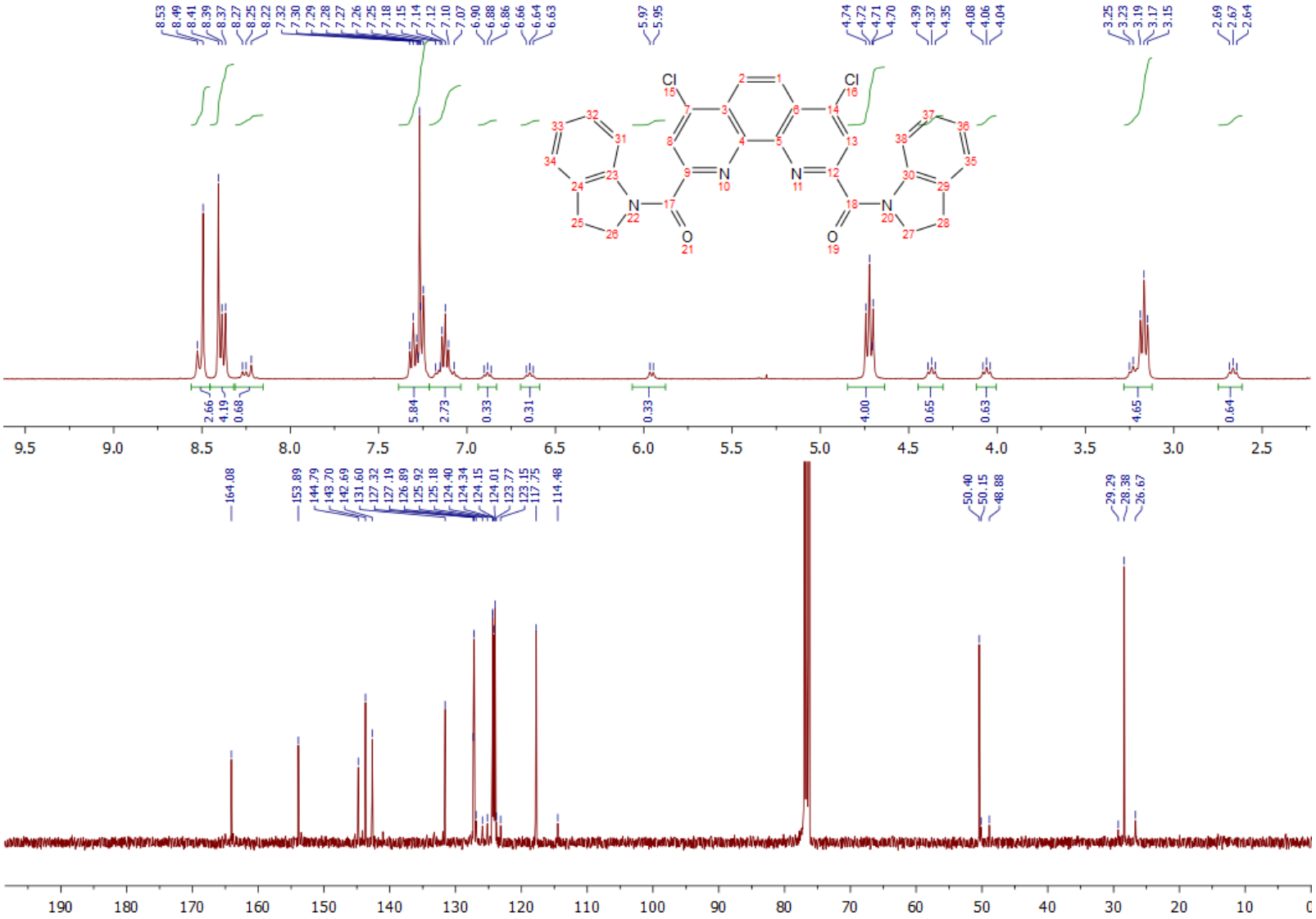


IR spectra at 25ºC

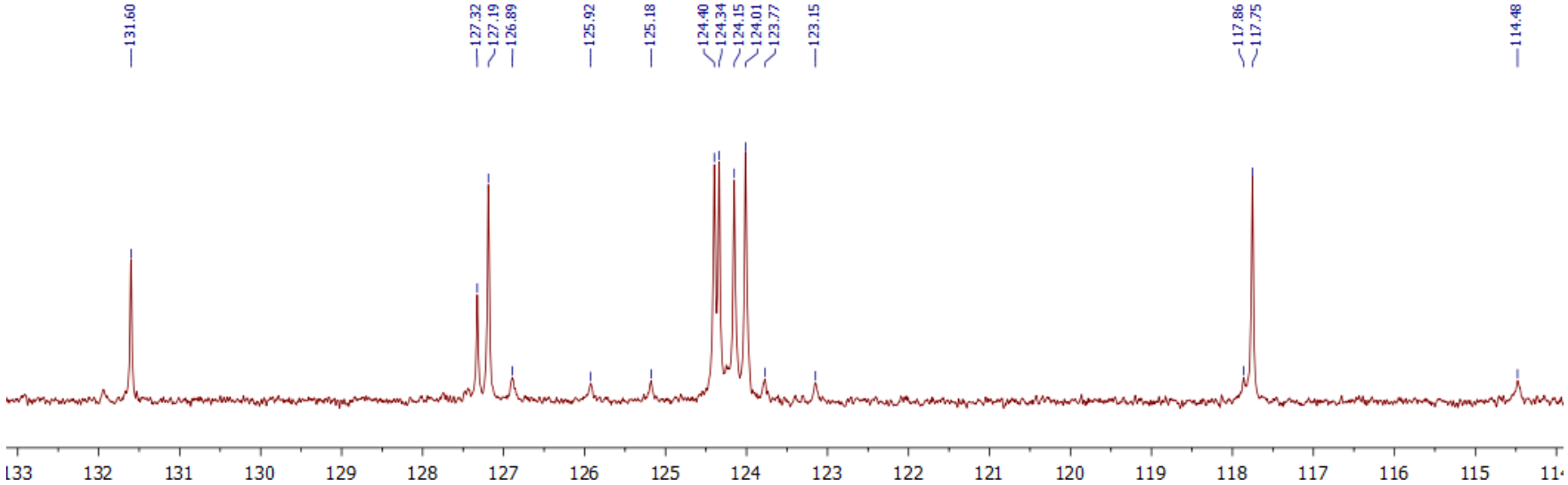


(4,7-Dichloro-9-(2,3-dihydro-1*H*-indol-1-ylcarbonyl)-1,10-phenanthrolin-2-yl)(2,3-dihydro-1*H*-indol-1-yl)methanone 3f

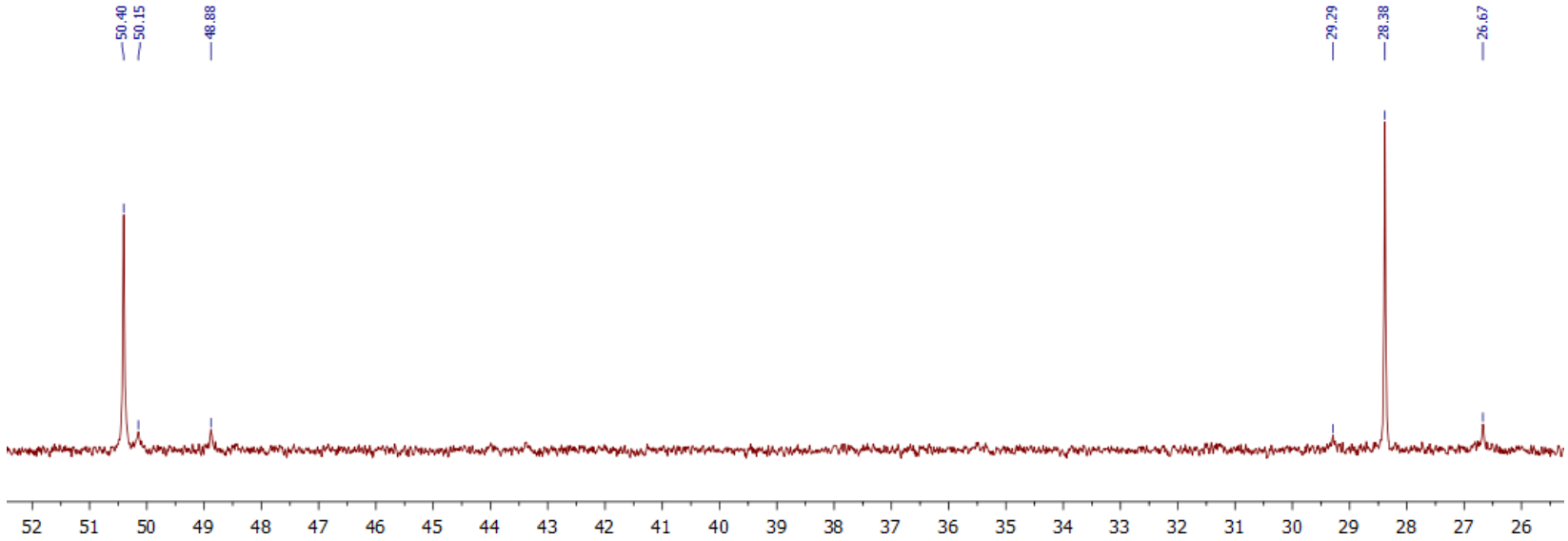
^{1}H NMR (above) and ^{13}C NMR (below) spectra in $CDCl_3$ at 25ºC



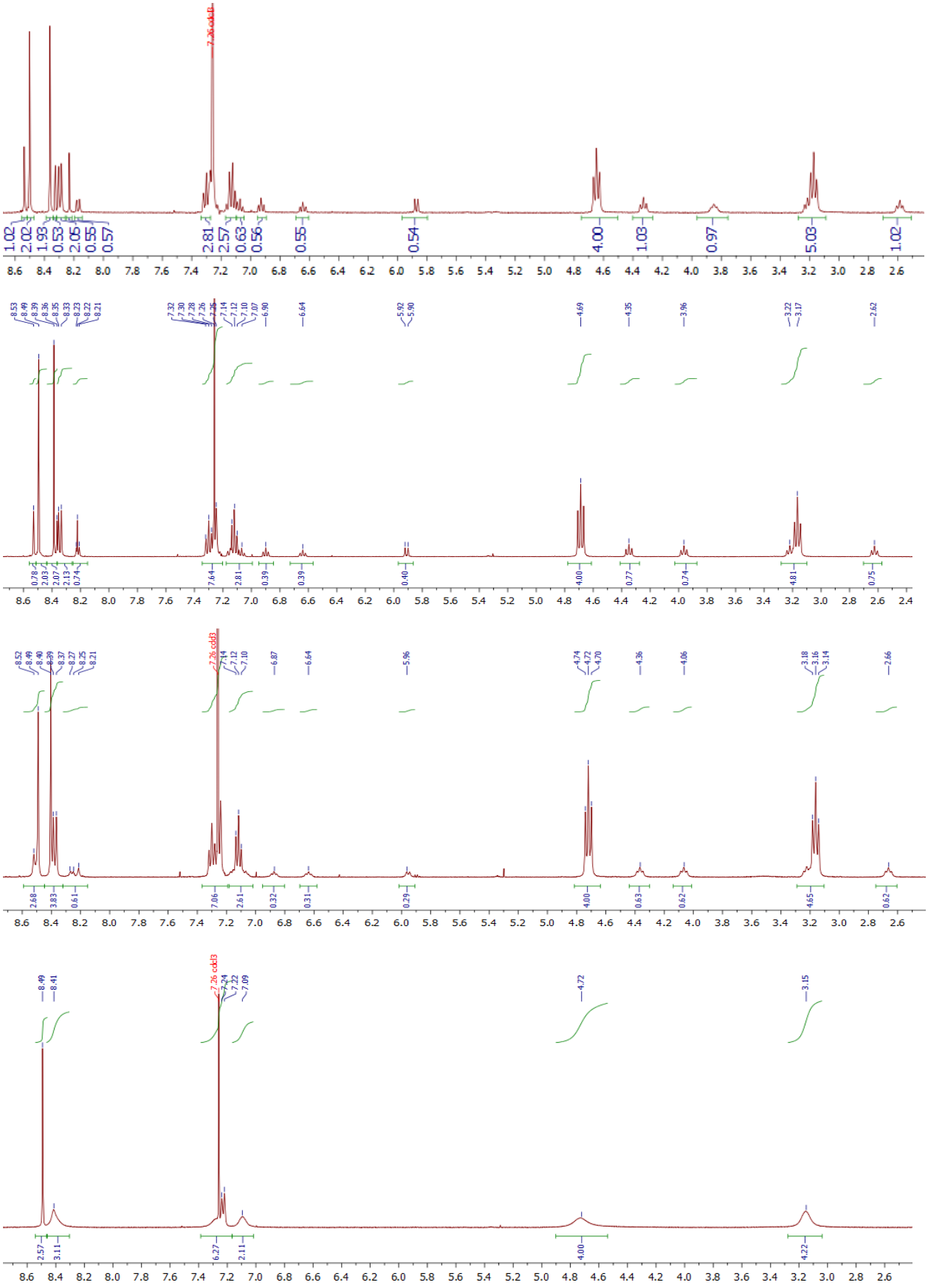
^{13}C NMR spectra in $CDCl_3$ at 25ºC, fragmental view (^{13}C-scale, δ from 114 to 133 ppm)



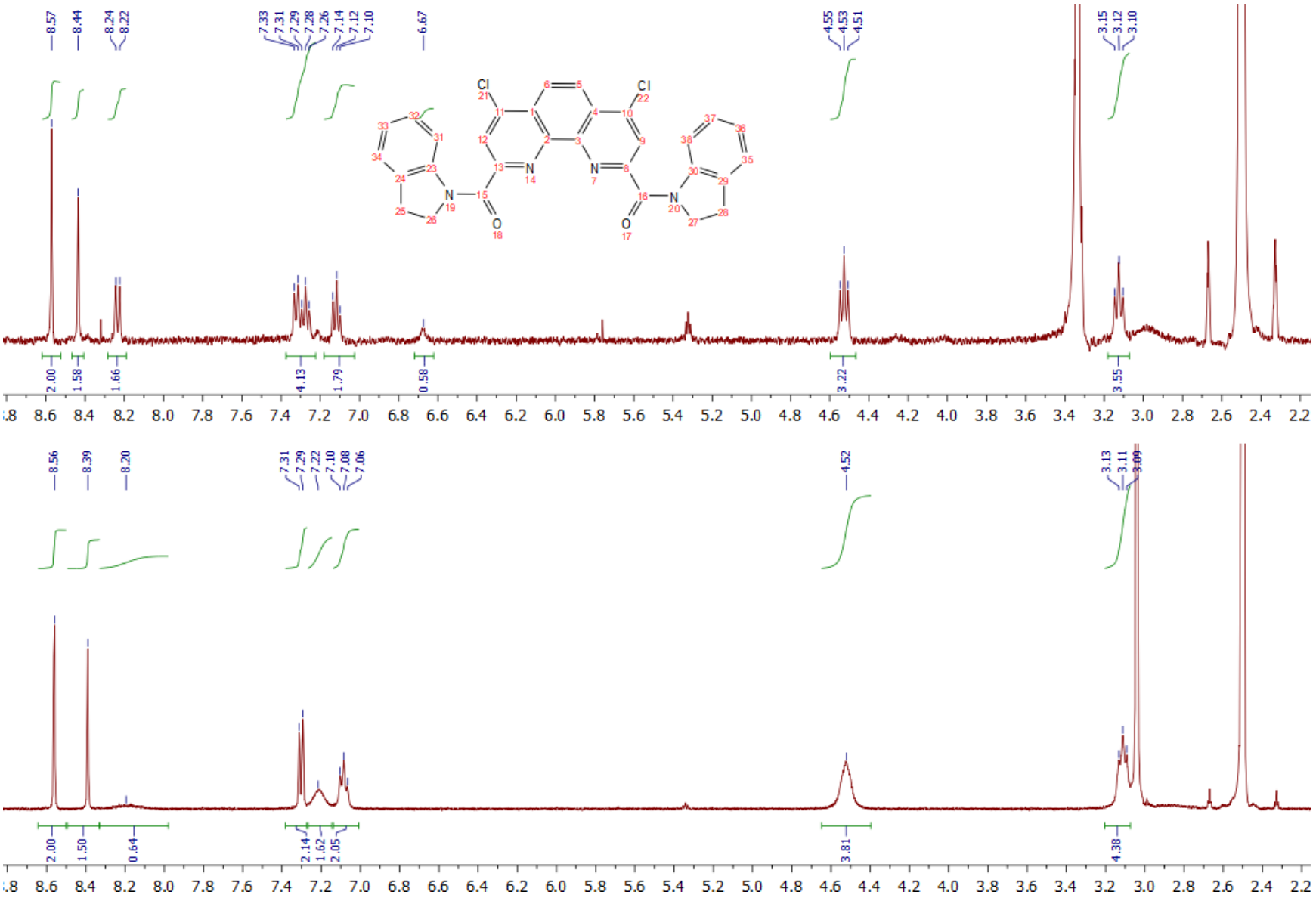
^{13}C NMR spectra in $CDCl_3$ at 25ºC, fragmental view (^{13}C-scale, δ from 26 to 52 ppm)



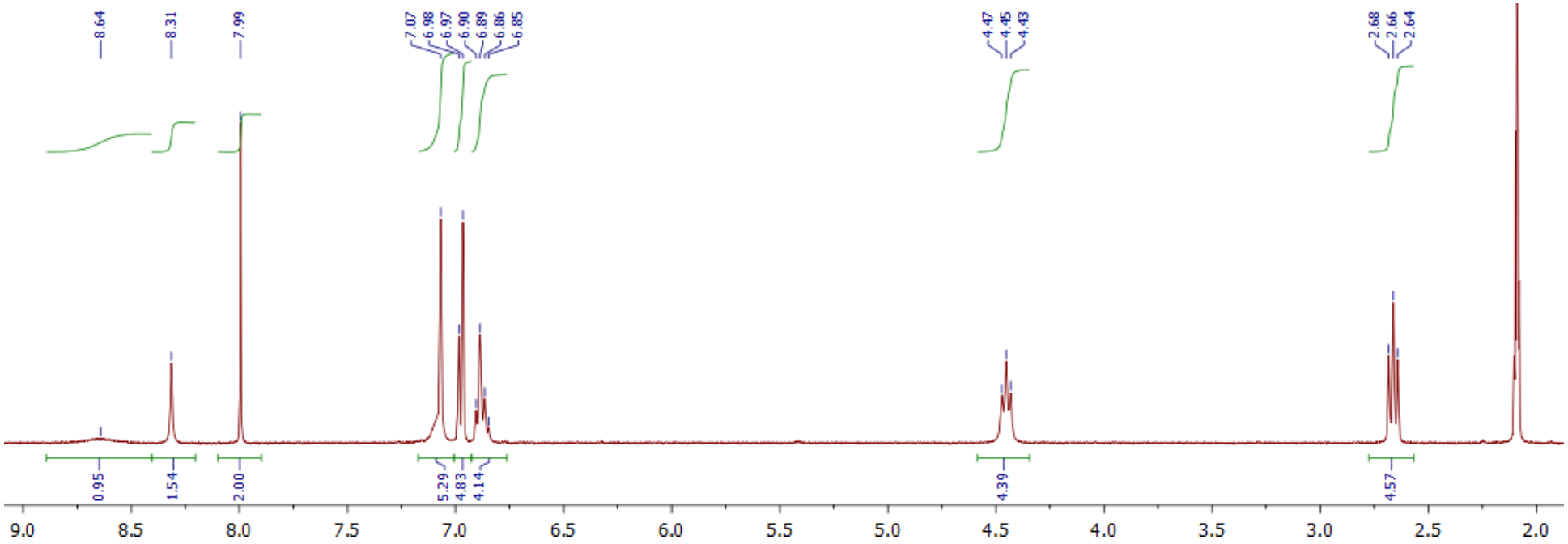
^{1}H NMR spectra in $CDCl_3$ at -30ºC, 0ºC, 25ºC and 55ºC (from top to bottom)



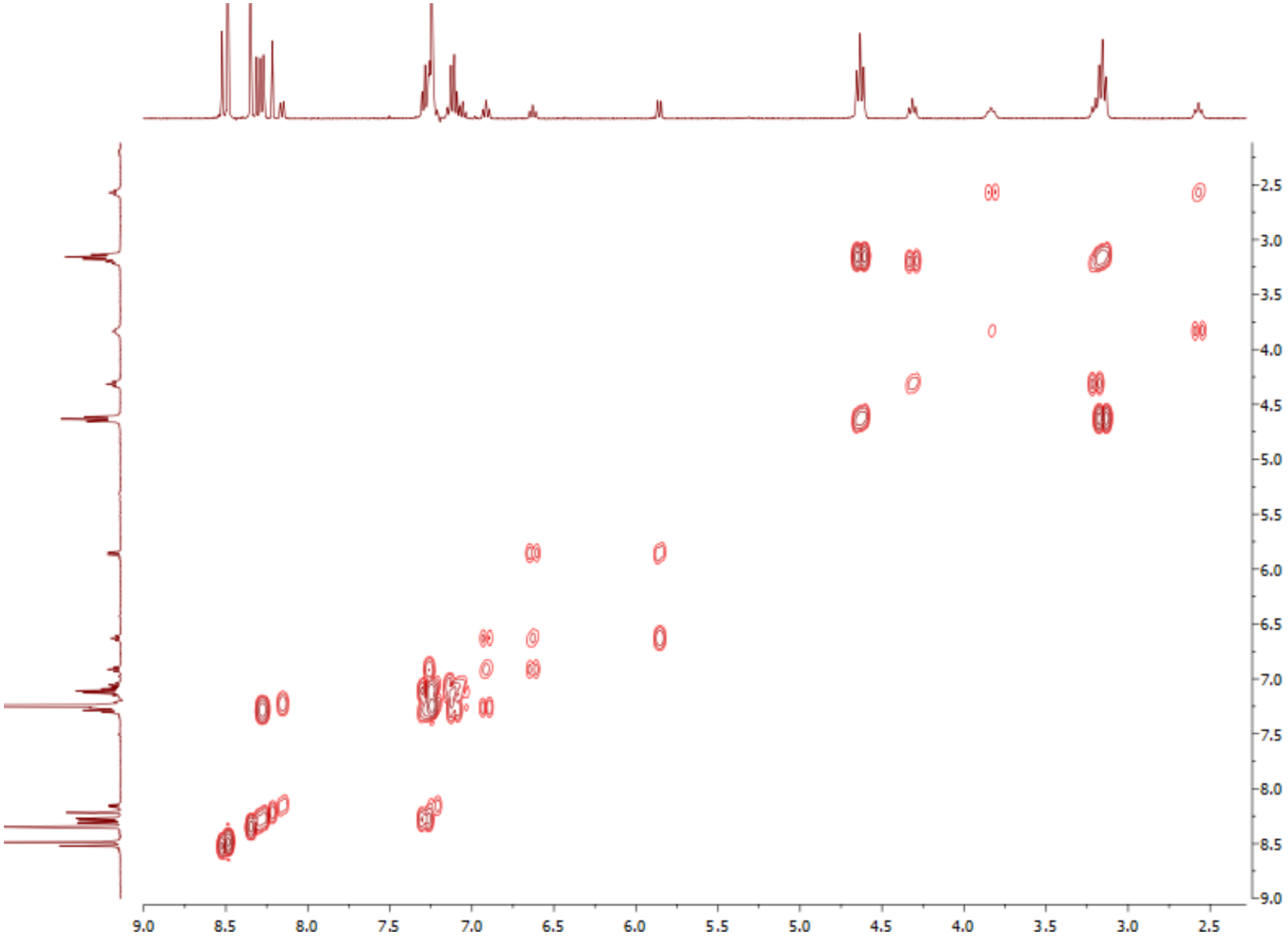
^{1}H NMR spectra in DMSO-d_6 at 25ºC (above) and 55ºC (below)



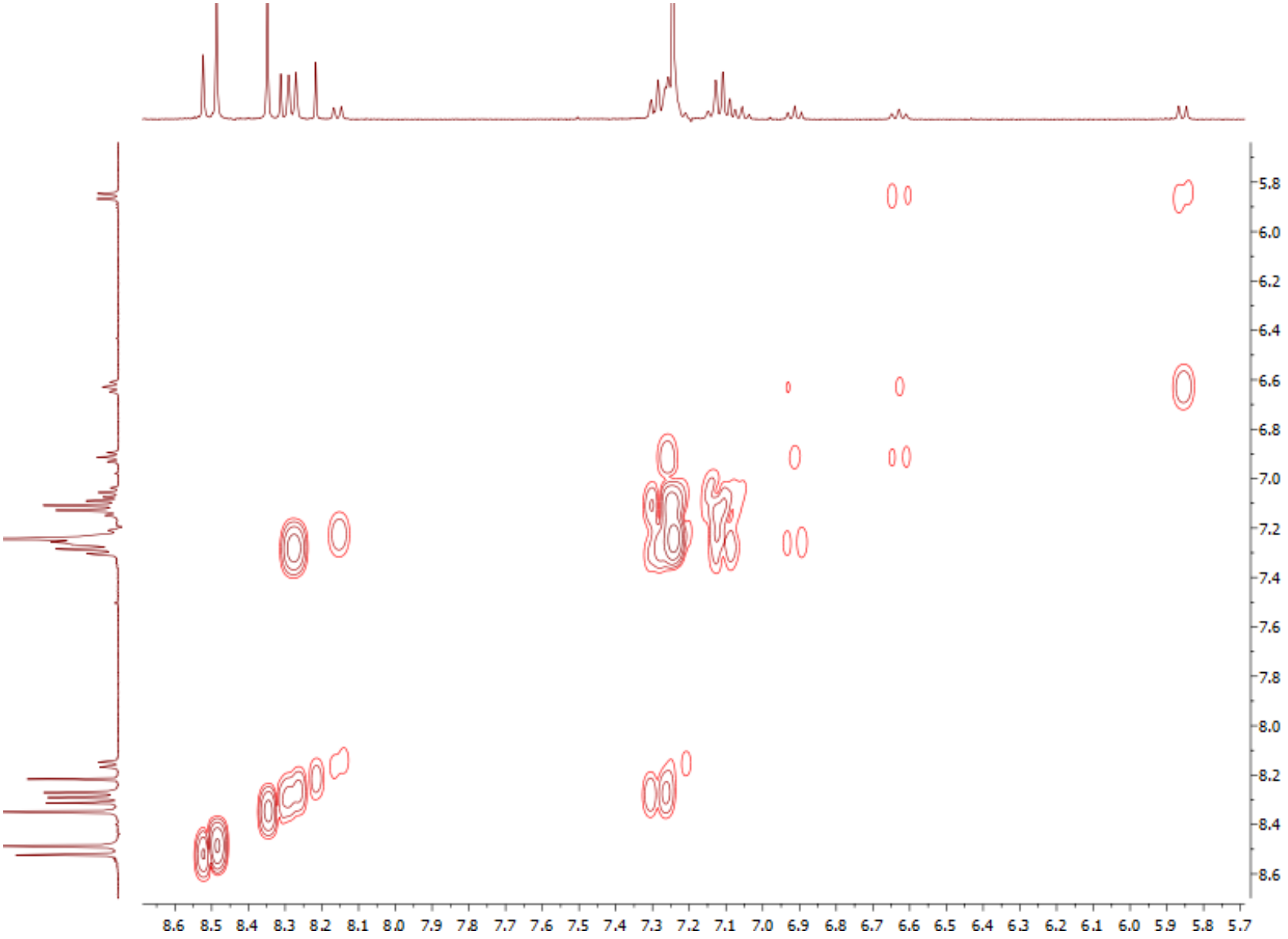
^{1}H NMR spectra in toluene-d_8 at 55ºC



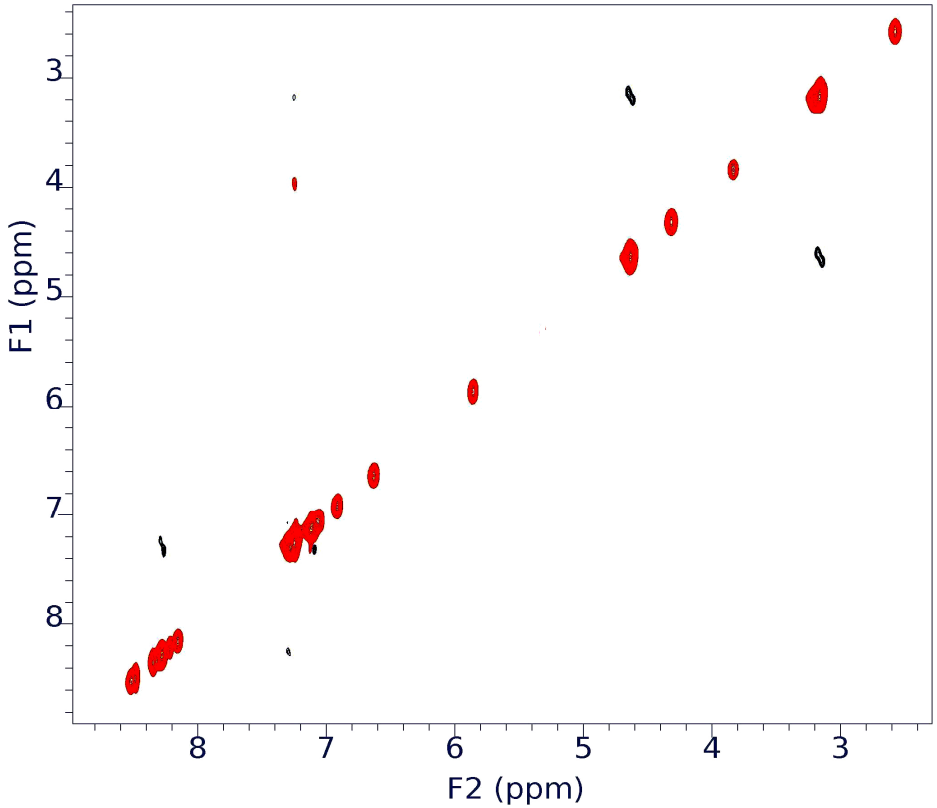
COSY $^{1}H/^{1}H$ NMR spectra in $CDCl_3$ at -30ºC (general view)

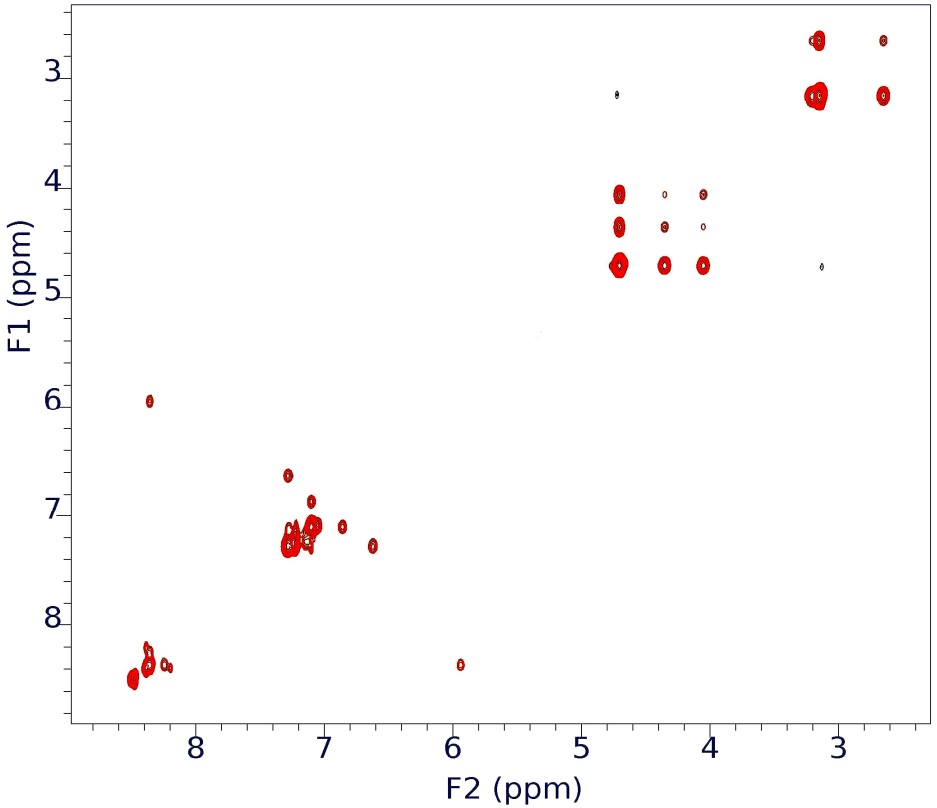


COSY $^{1}H/^{1}H$ NMR spectra in $CDCl_3$ at -30ºC (fragmental view)

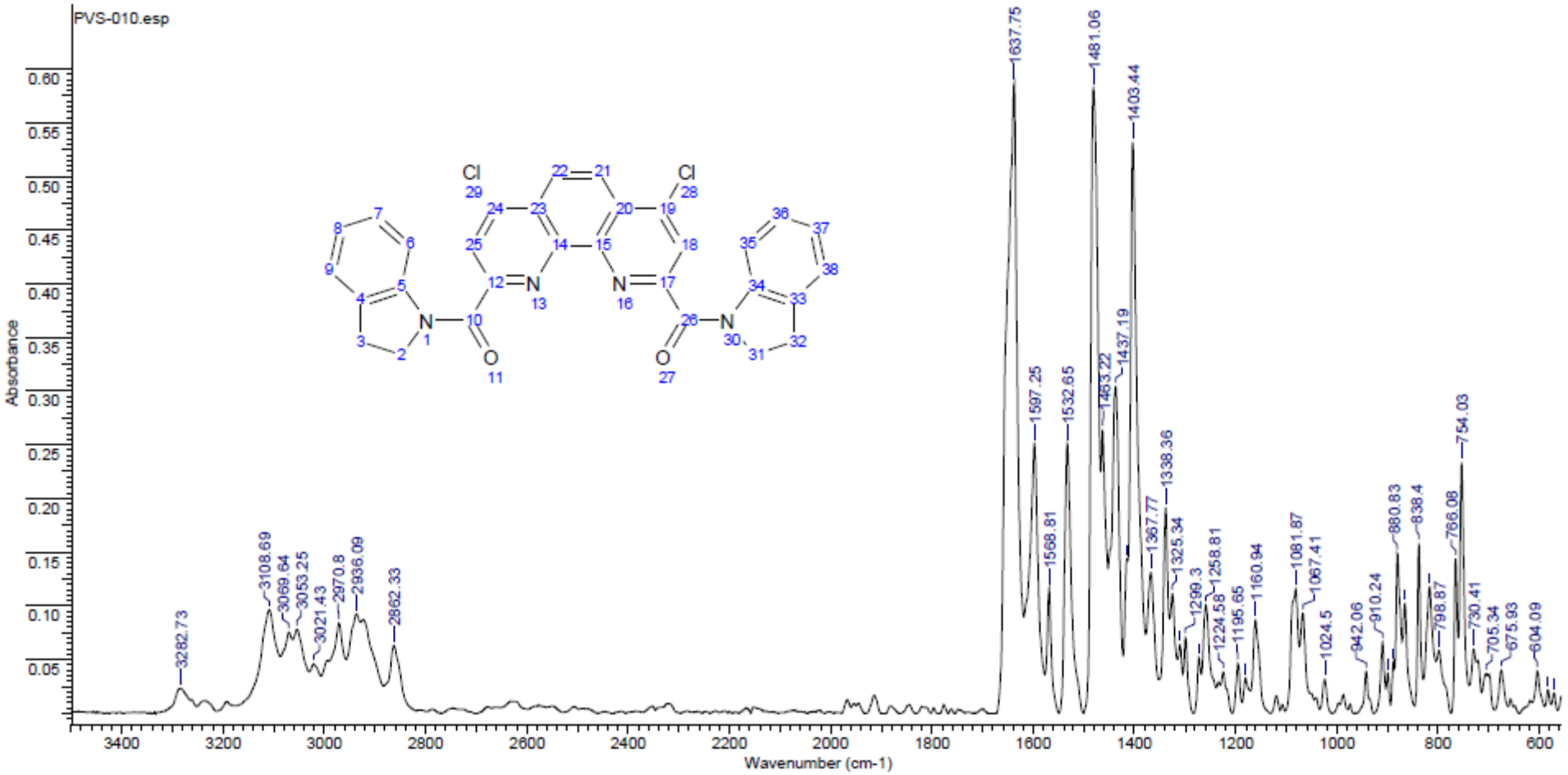


ROESY $^{1}H/^{1}H$ NMR spectra in $CDCl_3$ at -30ºC (left) and 25 ºC (right)

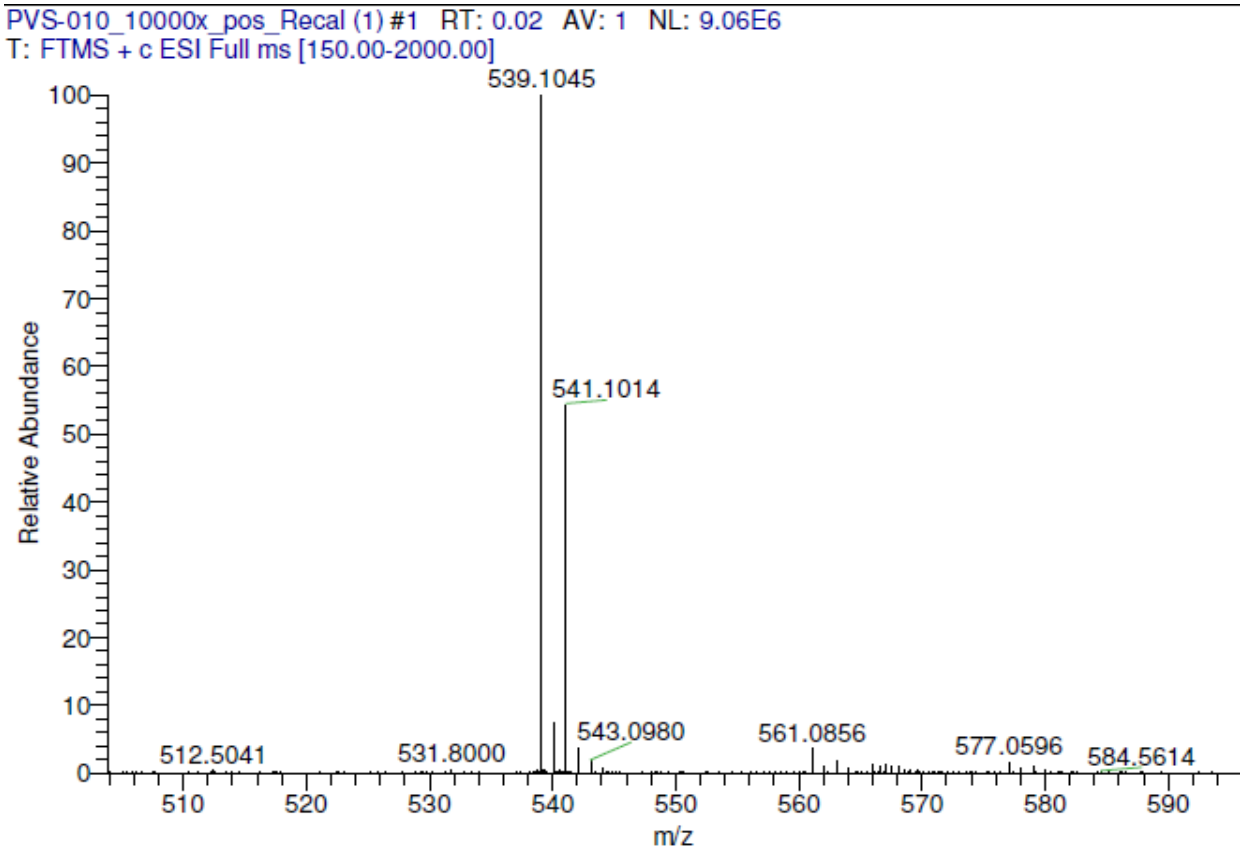




IR spectra at 25 ºC

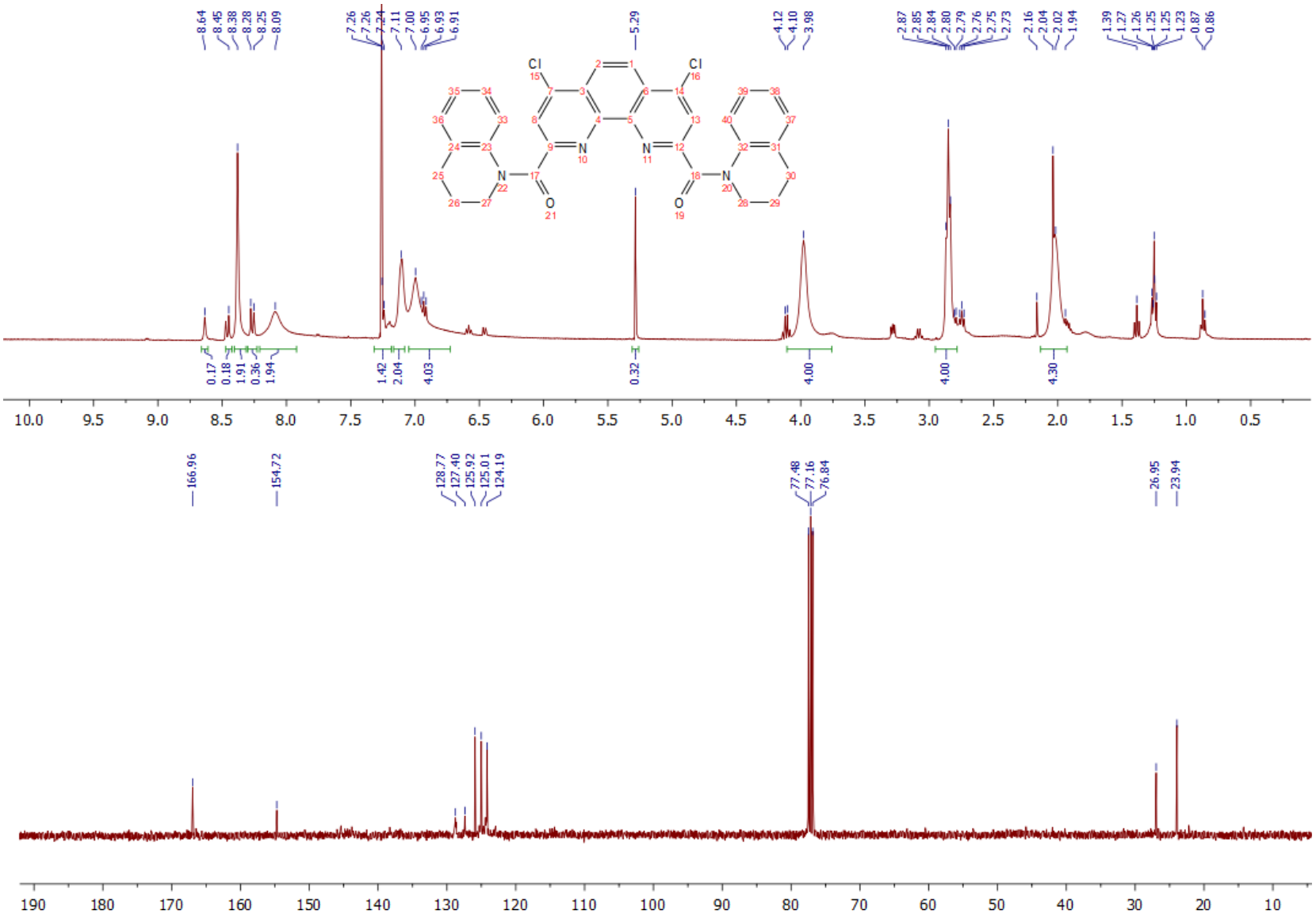


HRMS spectra

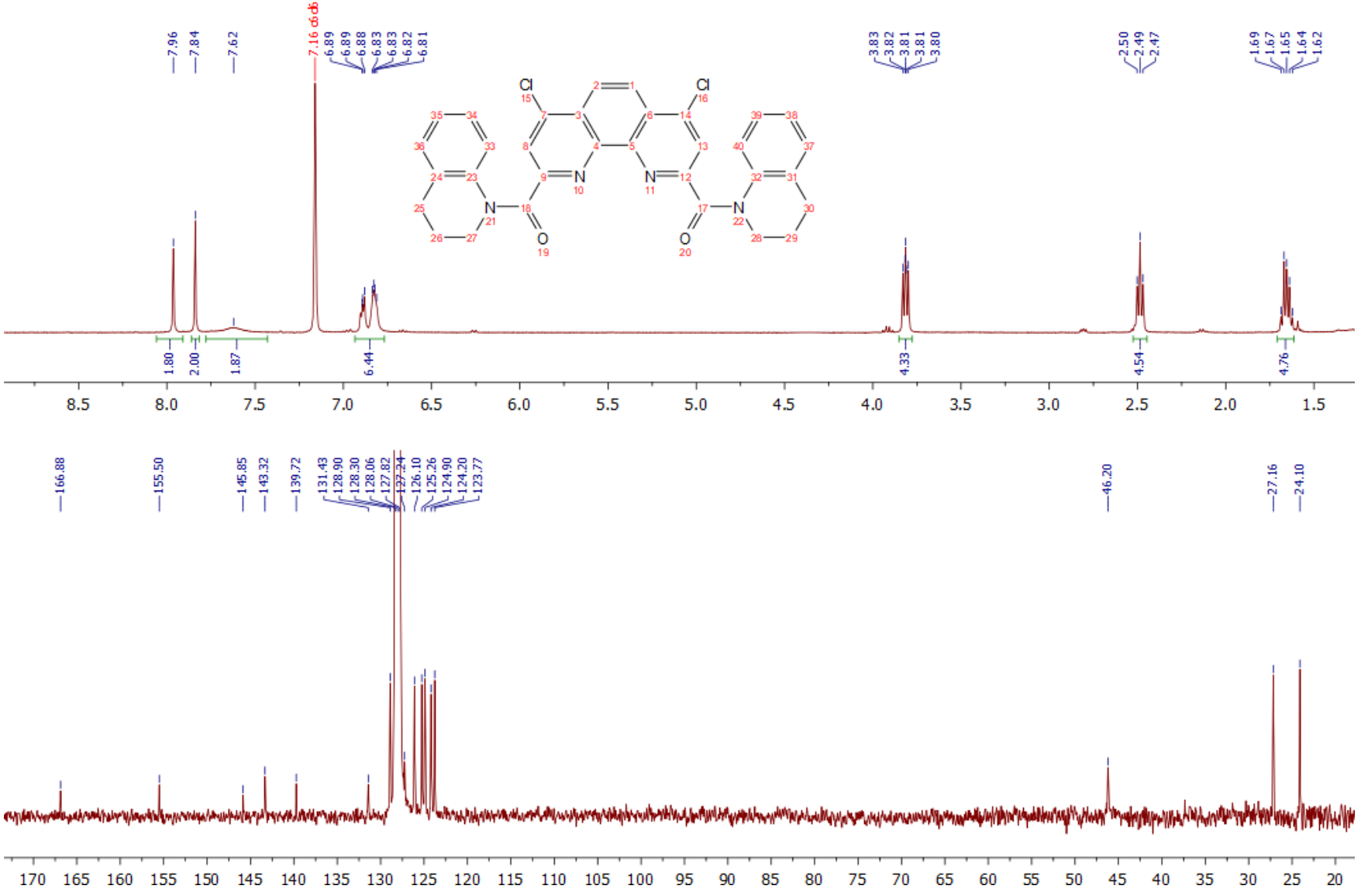


4(4,7-Dichloro-9-(1,2,3,4-tetrahydroquinolin-1-ylcarbonyl)-1,10-phenanthrolin-2-yl)(1,2,3,4-tetrahydroquinolin-1-yl)methanone 3g

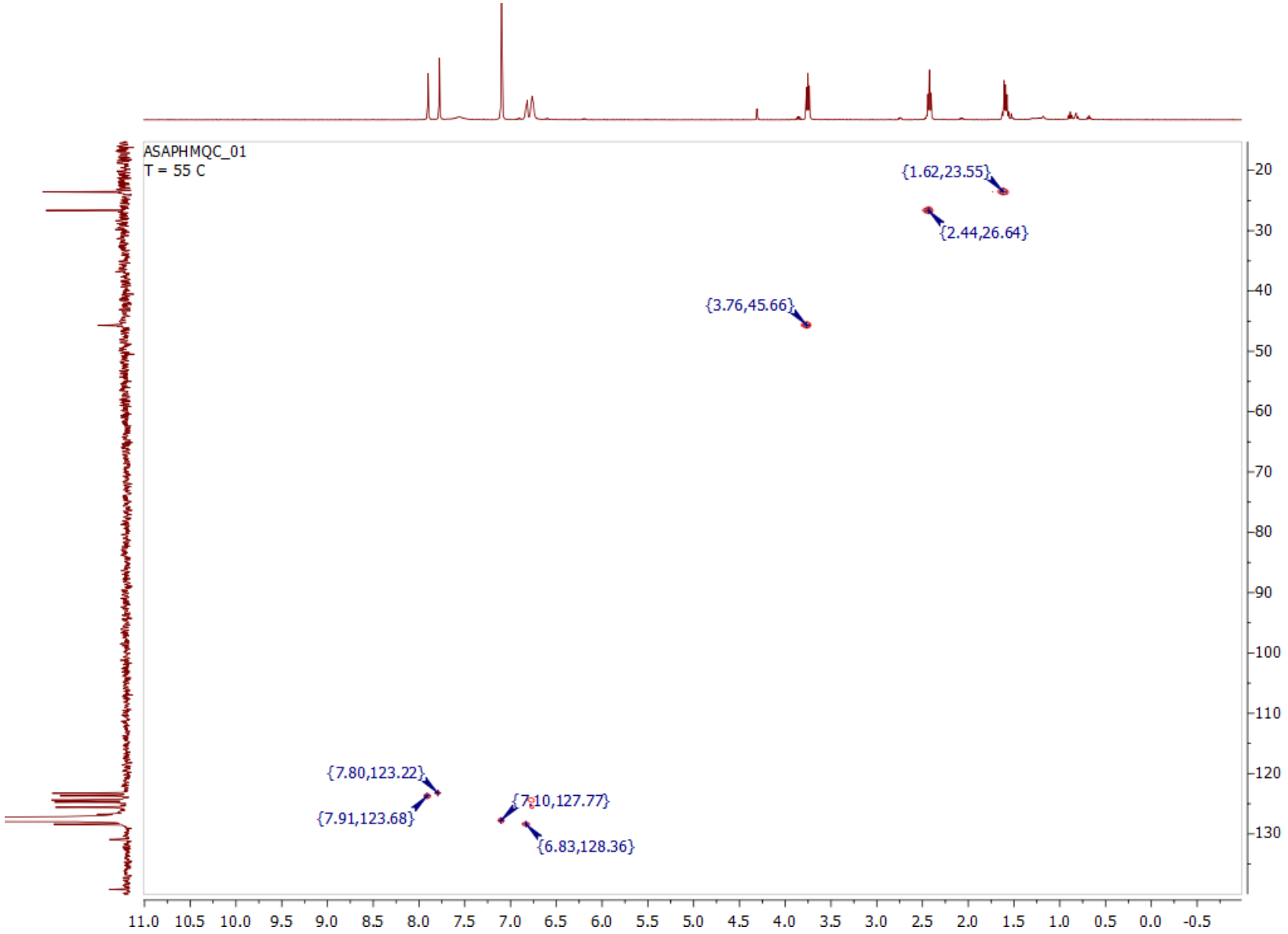
^{1}H NMR (above) and ^{13}C NMR (below) spectra in $CDCl_3$ at 25 ºC



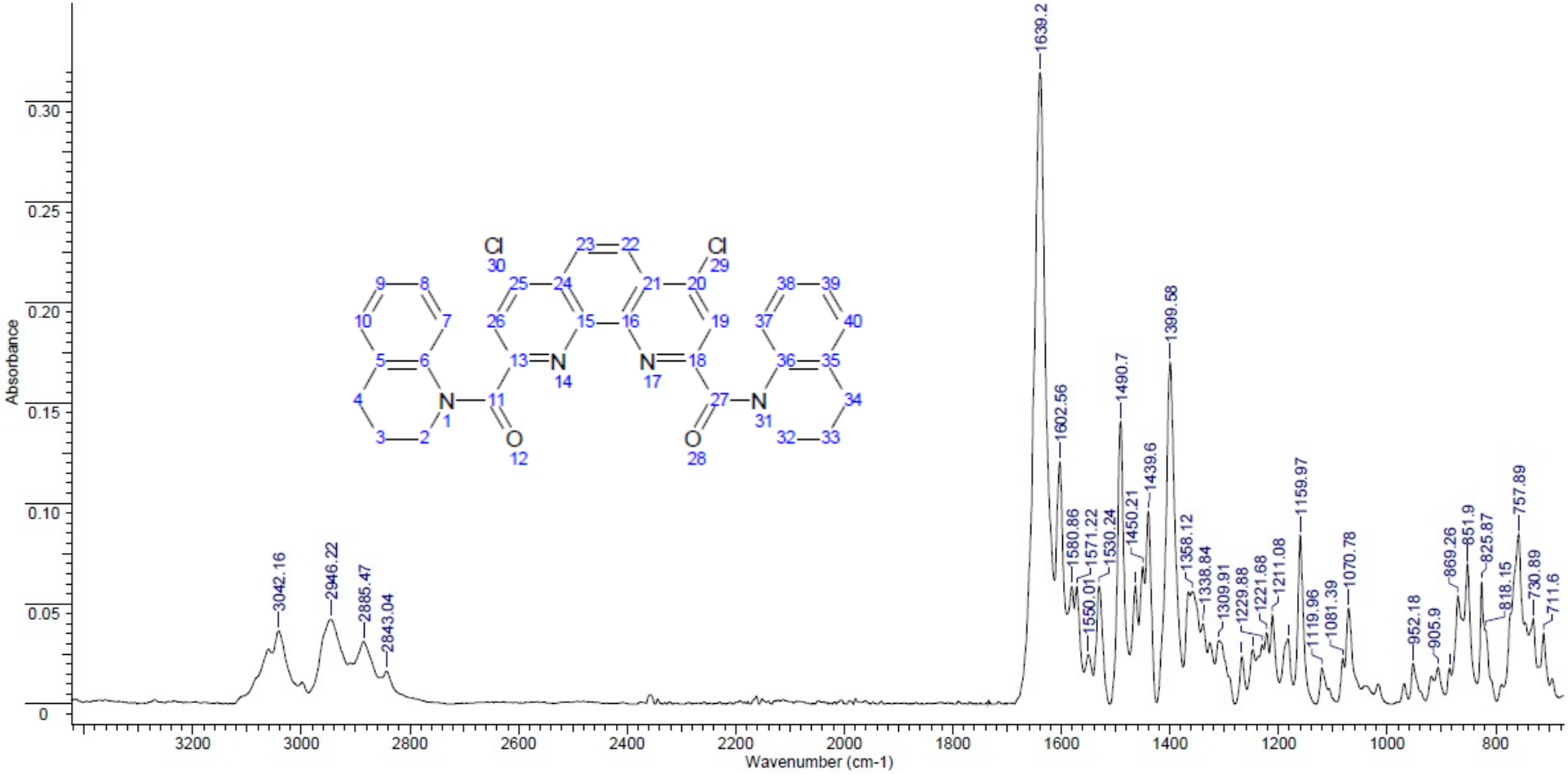
^{1}H NMR (above) and ^{13}C NMR (below) spectra in C_6D_6 at 55ºC



$^{1}H/^{13}C$ ASAPHMQC NMR spectra in C_6D_6 at 55ºC

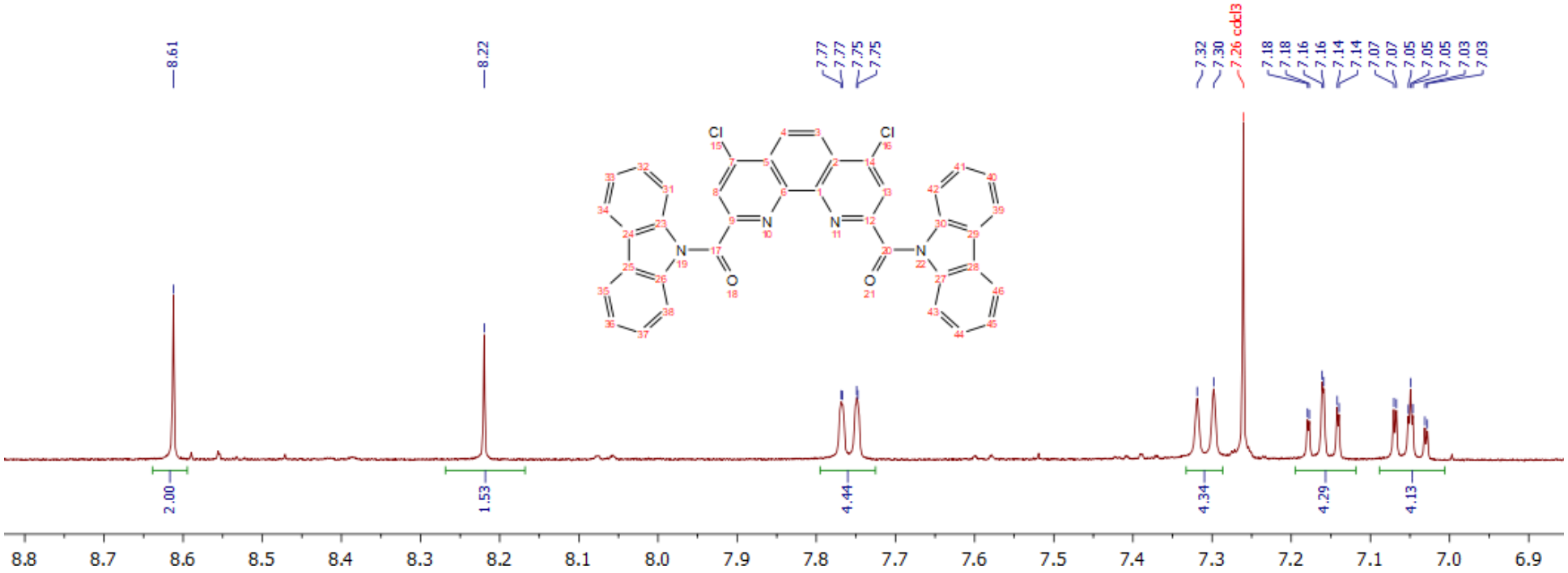


IR spectra at 25ºC

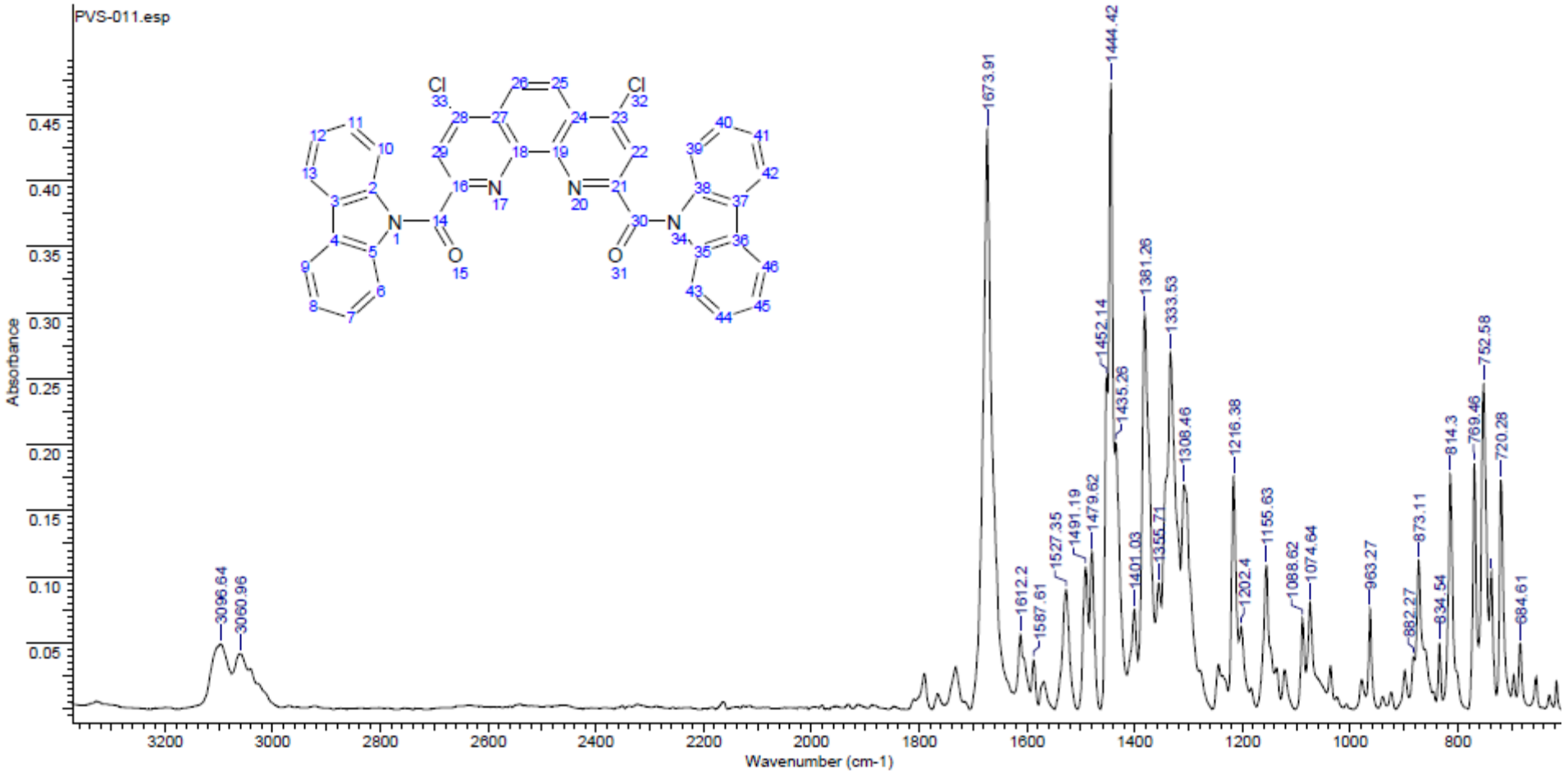


9*H*-Carbazol-9-yl(9-(9*H*-carbazol-9-ylcarbonyl)-4,7-dichloro-1,10-phenanthrolin-2-yl)methanone 3h

^{1}H NMR spectra in $CDCl_3$ at 55ºC, fragmental view (H-scale from 8.8 to 6.9 ppm)



IR spectra at 25ºC



HRMS spectra

Display Report

Analysis Info

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Sample Name	/MUSE PVS-011	Instrument / Ser#	micrOTOF 10248
Comment	C38H20Cl2N4O2 mH 635.1036 clb added CH3CN		

Acquisition Parameter

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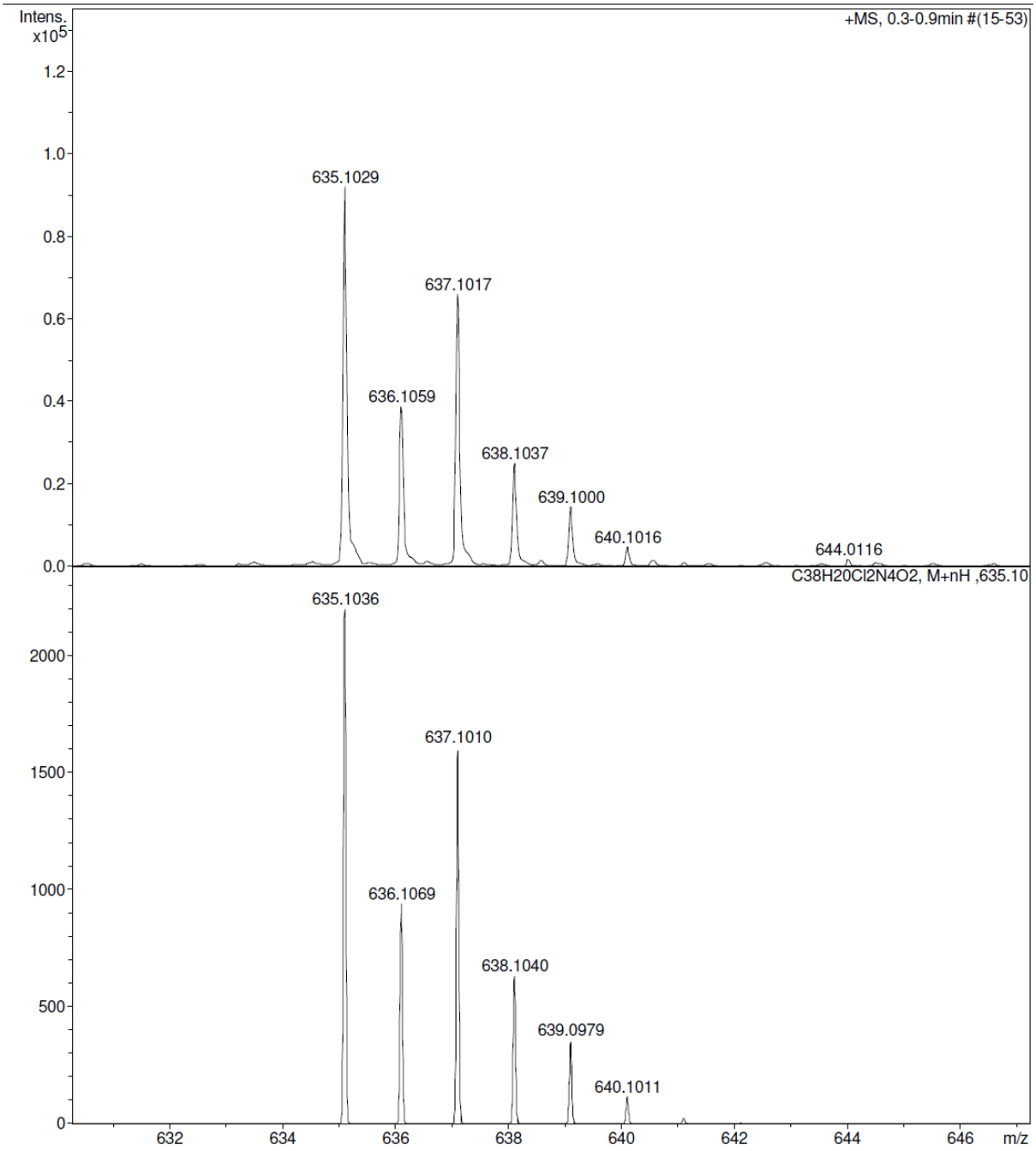
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Bruker Compass DataAnalysis 4.0 printed: 11.07.2019 11:53:33 Page 1 of 1

3. Extraction testing data

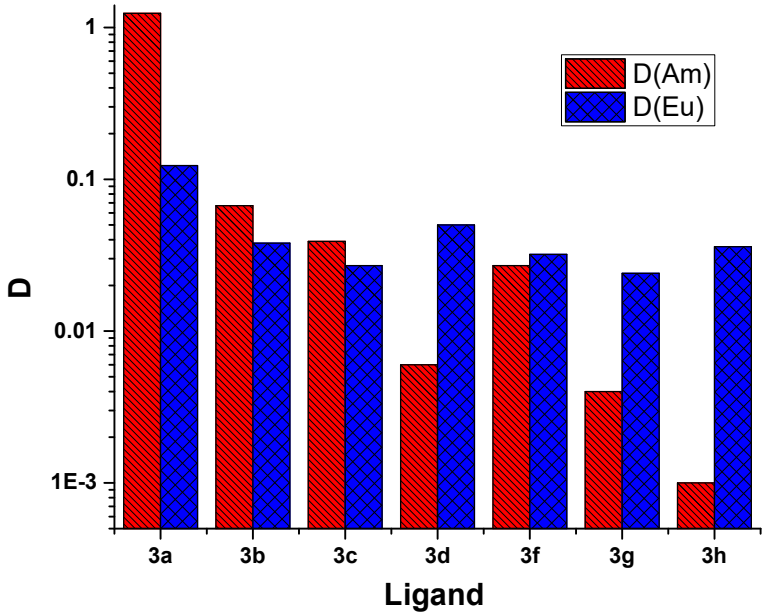


Figure S1 The distribution ratios (*D*) of Am^{3+} and Eu^{3+} for extraction from 3 mol·l^{-1} nitric acid. The organic phase is saturated solutions of ligands in "F-3".

Solvation numbers for 3a

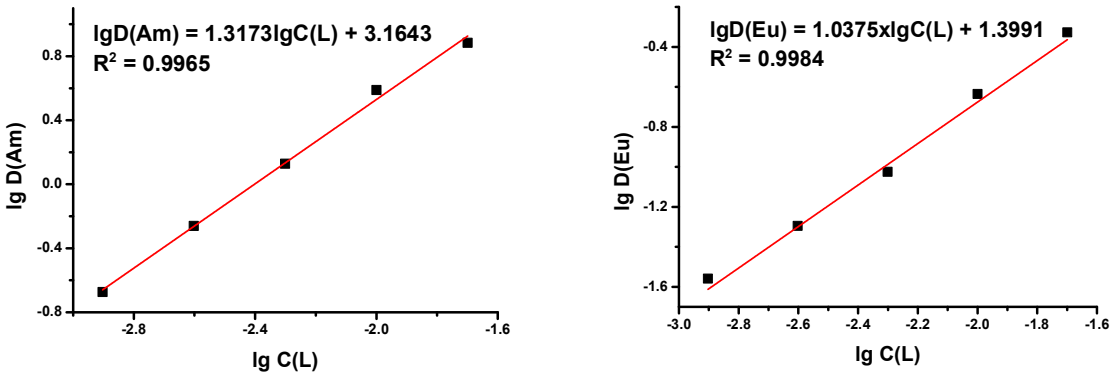


Figure S2. lgD(Am)-lgC(L) and lgD(Eu)-lgC(L) dependences for **3a** ligand. Aqueous phase – 5 mol·l^{-1} nitric acid

Table S1. The distribution ratios (*D*) of $Am^{3+}$and Eu^{3+} depending on the concentration of the ligand **3a** in "F-3" during extraction from 5 mol·l^{-1} HNO_3.

3a, M	$D(Am^{3+})$	$D(Eu^{3+})$
0.015	7.66	0.47
0.01	3.88	0.23
0.005	1.34	0.09
0.0025	0.55	0.05
0.00125	0.21	0.03

4. X-ray analysis data

4,7-dichloro-1,10-phenanthroline-2,9-dicarboxylic acid 1.

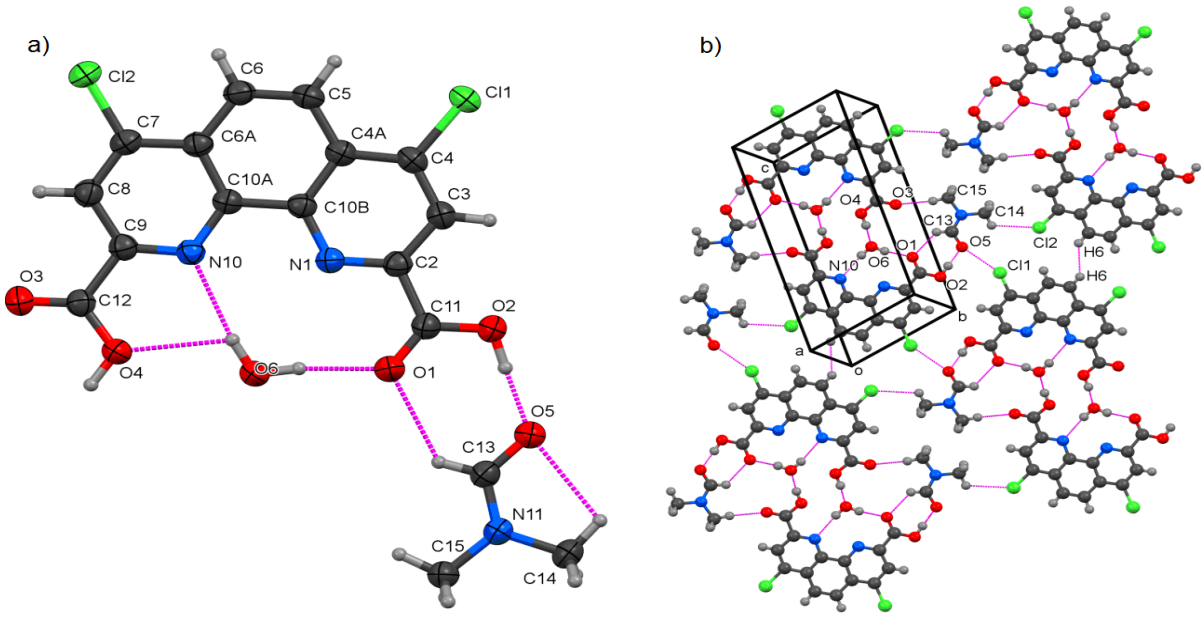


Figure S3. Asymmetric part of crystal structure of **1·DMF·H₂O** (*a*) and packing diagram showing the layer structure (*b*). Thermal ellipsoids are drawn at the 70% probability level.

The molecule of **1** is closely planar, with the mean deviation of non-hydrogen atoms from the least-squared plane of 0.096(1) Å, and adopts in the crystal a *trans-cis* conformation (Fig. 4*a*). Data on bond lengths, flat and dihedral angles and intermolecular contacts in this structure are given in ESI (Table S4).

In the crystal of **1·H₂O·DMF**, the molecules are linked by O–H···O and O–H···N hydrogen bonds into hexamers **(1)₂(H₂O)₂(DMF)₂** and further by Cl···O, Cl···H and H···H contacts – into flat layers parallel to the (2 1 -1) plane (Fig. 4*b*). These layers are joined by π-π interactions, with the interplanar distance of 3.252(1) Å and the shortest intermolecular contact involving phenanthroline carbon atoms C4···C5 (1-*x*, 1-*y*, -*z*) of 3.406(2) Å. In contrast to three other structures presented in this work, in crystals of **1·H₂O·DMF**, the phenanthroline fragments do not exhibit stacking. They are interlaced with DMF molecules of neighboring layers.

Table S2. Crystal data and structure refinement for **1·DMF·H_2O**

Identification code	**1·DMF·H_2O**	
Empirical formula	C17 H15 Cl2 N3 O6	
Formula weight	428.22	
Temperature	100(2) K	
Wavelength	0.7879 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 7.1583(14) Å	α = 81.10(3)°.
	b = 8.3520(17) Å	β = 82.92(3)°.
	c = 15.356(3) Å	γ = 78.62(3)°.
Volume	885.1(3) $Å^3$	
Z	2	
Density (calculated)	1.607 Mg/m^3	
Absorption coefficient	0.538 mm^{-1}	
F(000)	440	
Crystal size	0.20 x 0.10 x 0.03 mm^3	
Theta range for data collection	1.495 to 30.758°.	
Index ranges	-9<=h<=9, -10<=k<=10, -19<=l<=19	
Reflections collected	15682	
Independent reflections	4025 [R(int) = 0.0281]	
Completeness to theta = 28.212°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.980 and 0.890	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4025 / 4 / 268	
Goodness-of-fit on F^2	1.073	
Final R indices [for 3711 rflns with I>2σ(I)]	R1 = 0.0313, wR2 = 0.0871	
R indices (all data)	R1 = 0.0335, wR2 = 0.0888	
Extinction coefficient	0.041(4)	
Largest diff. peak and hole	0.297 and -0.241 e·$Å^{-3}$	

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **1·DMF·H_2O**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
Cl(1)	1854(1)	5842(1)	-767(1)	26(1)
Cl(2)	6463(1)	-1793(1)	1981(1)	30(1)
O(1)	1395(2)	8576(1)	2859(1)	36(1)
O(2)	535(1)	9952(1)	1565(1)	28(1)
O(3)	6935(1)	687(1)	4889(1)	31(1)
O(4)	5182(1)	3232(1)	4748(1)	29(1)
N(1)	2753(2)	5792(1)	2093(1)	23(1)
C(2)	1908(2)	7128(2)	1604(1)	24(1)
C(3)	1610(2)	7200(2)	714(1)	24(1)
C(4)	2205(2)	5788(2)	330(1)	24(1)
C(4A)	3083(2)	4319(2)	819(1)	23(1)
C(5)	3678(2)	2799(2)	463(1)	26(1)
C(6)	4516(2)	1434(2)	963(1)	26(1)
C(6A)	4859(2)	1464(2)	1856(1)	23(1)
C(7)	5751(2)	70(2)	2396(1)	25(1)
C(8)	6066(2)	168(2)	3243(1)	26(1)
C(9)	5481(2)	1703(2)	3552(1)	24(1)
N(10)	4618(1)	3054(1)	3081(1)	22(1)
C(10A)	4302(2)	2939(2)	2242(1)	22(1)
C(10B)	3349(2)	4408(2)	1710(1)	22(1)
C(11)	1253(2)	8631(2)	2072(1)	25(1)
C(12)	5936(2)	1818(2)	4475(1)	24(1)
O(5)	-301(1)	2356(1)	2426(1)	28(1)
N(11)	-216(2)	3298(1)	3726(1)	25(1)
C(13)	143(2)	2141(2)	3204(1)	26(1)
C(14)	-1175(2)	4964(2)	3428(1)	30(1)
C(15)	415(2)	2974(2)	4614(1)	30(1)
O(6)	6218(2)	3706(1)	6163(1)	41(1)

Table S4. Bond lengths [Å] and angles [°] for **1·DMF·H_2O**.

Cl(1)-C(4)	1.7269(13)	C(6A)-C(10A)	1.4159(17)
Cl(2)-C(7)	1.7328(14)	C(7)-C(8)	1.3643(18)
O(1)-C(11)	1.2175(16)	C(8)-C(9)	1.4043(18)
O(2)-C(11)	1.3024(16)	C(8)-H(8)	0.9500
O(2)-H(2)	0.92(2)	C(9)-N(10)	1.3273(17)
O(3)-C(12)	1.2114(17)	C(9)-C(12)	1.5139(18)
O(4)-C(12)	1.3063(16)	N(10)-C(10A)	1.3549(16)
O(4)-H(4)	0.91(2)	C(10A)-C(10B)	1.4618(18)
N(1)-C(2)	1.3276(17)	O(5)-C(13)	1.2516(16)
N(1)-C(10B)	1.3489(17)	N(11)-C(13)	1.3165(17)
C(2)-C(3)	1.3994(17)	N(11)-C(14)	1.4569(17)
C(2)-C(11)	1.5088(17)	N(11)-C(15)	1.4569(17)
C(3)-C(4)	1.3690(19)	C(13)-H(13)	0.9500
C(3)-H(3)	0.9500	C(14)-H(14A)	0.9800
C(4)-C(4A)	1.4110(18)	C(14)-H(14B)	0.9800
C(4A)-C(10B)	1.4186(17)	C(14)-H(14C)	0.9800
C(4A)-C(5)	1.4275(18)	C(15)-H(15A)	0.9800
C(5)-C(6)	1.350(2)	C(15)-H(15B)	0.9800
C(5)-H(5)	0.9500	C(15)-H(15C)	0.9800
C(6)-C(6A)	1.4273(18)	O(6)-H(6A)	0.89(2)
C(6)-H(6)	0.9500	O(6)-H(6B)	0.88(2)
C(6A)-C(7)	1.4104(18)		

C(11)-O(2)-H(2)	109.4(13)
C(12)-O(4)-H(4)	112.1(12)
C(2)-N(1)-C(10B)	117.83(11)
N(1)-C(2)-C(3)	124.32(12)
N(1)-C(2)-C(11)	115.39(11)
C(3)-C(2)-C(11)	120.29(11)
C(4)-C(3)-C(2)	117.56(12)
C(4)-C(3)-H(3)	121.2
C(2)-C(3)-H(3)	121.2
C(3)-C(4)-C(4A)	120.88(12)
C(3)-C(4)-Cl(1)	118.49(10)
C(4A)-C(4)-Cl(1)	120.62(10)
C(4)-C(4A)-C(10B)	116.41(12)
C(4)-C(4A)-C(5)	123.36(12)
C(10B)-C(4A)-C(5)	120.22(12)
C(6)-C(5)-C(4A)	120.64(12)
C(6)-C(5)-H(5)	119.7

C(4A)-C(5)-H(5)	119.7
C(5)-C(6)-C(6A)	121.46(12)
C(5)-C(6)-H(6)	119.3
C(6A)-C(6)-H(6)	119.3
C(7)-C(6A)-C(10A)	116.52(11)
C(7)-C(6A)-C(6)	123.20(12)
C(10A)-C(6A)-C(6)	120.28(12)
C(8)-C(7)-C(6A)	120.93(12)
C(8)-C(7)-Cl(2)	119.37(10)
C(6A)-C(7)-Cl(2)	119.70(10)
C(7)-C(8)-C(9)	117.61(12)
C(7)-C(8)-H(8)	121.2
C(9)-C(8)-H(8)	121.2
N(10)-C(9)-C(8)	124.37(12)
N(10)-C(9)-C(12)	118.51(11)
C(8)-C(9)-C(12)	117.08(11)
C(9)-N(10)-C(10A)	117.48(11)
N(10)-C(10A)-C(6A)	123.08(12)
N(10)-C(10A)-C(10B)	118.57(11)
C(6A)-C(10A)-C(10B)	118.34(11)
N(1)-C(10B)-C(4A)	122.97(12)
N(1)-C(10B)-C(10A)	118.03(11)
C(4A)-C(10B)-C(10A)	119.00(11)
O(1)-C(11)-O(2)	124.22(12)
O(1)-C(11)-C(2)	121.54(12)
O(2)-C(11)-C(2)	114.24(11)
O(3)-C(12)-O(4)	125.47(12)
O(3)-C(12)-C(9)	121.15(12)
O(4)-C(12)-C(9)	113.37(11)
C(13)-N(11)-C(14)	121.56(12)
C(13)-N(11)-C(15)	120.97(11)
C(14)-N(11)-C(15)	117.41(11)
O(5)-C(13)-N(11)	124.03(12)
O(5)-C(13)-H(13)	118.0
N(11)-C(13)-H(13)	118.0
N(11)-C(14)-H(14A)	109.5
N(11)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
N(11)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
N(11)-C(15)-H(15A)	109.5

N(11)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
N(11)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
H(6A)-O(6)-H(6B)	111(2)

Table S5. Anisotropic displacement parameters ($Å^2$ x 10^3) for **1·DMF·H_2O**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	29(1)	30(1)	20(1)	-3(1)	-5(1)	-6(1)
Cl(2)	37(1)	21(1)	31(1)	-7(1)	-5(1)	-2(1)
O(1)	51(1)	27(1)	27(1)	-7(1)	-12(1)	6(1)
O(2)	36(1)	22(1)	26(1)	-3(1)	-7(1)	-1(1)
O(3)	37(1)	27(1)	29(1)	-2(1)	-11(1)	0(1)
O(4)	35(1)	27(1)	25(1)	-7(1)	-9(1)	2(1)
N(1)	24(1)	23(1)	23(1)	-4(1)	-3(1)	-3(1)
C(2)	23(1)	24(1)	24(1)	-4(1)	-3(1)	-4(1)
C(3)	24(1)	25(1)	23(1)	-1(1)	-4(1)	-4(1)
C(4)	23(1)	29(1)	20(1)	-2(1)	-3(1)	-6(1)
C(4A)	21(1)	26(1)	23(1)	-4(1)	-1(1)	-5(1)
C(5)	29(1)	29(1)	22(1)	-6(1)	-2(1)	-6(1)
C(6)	29(1)	24(1)	25(1)	-7(1)	-1(1)	-5(1)
C(6A)	24(1)	24(1)	23(1)	-4(1)	-1(1)	-5(1)
C(7)	26(1)	22(1)	27(1)	-5(1)	-1(1)	-4(1)
C(8)	28(1)	23(1)	27(1)	-2(1)	-4(1)	-3(1)
C(9)	23(1)	24(1)	24(1)	-3(1)	-3(1)	-4(1)
N(10)	22(1)	23(1)	22(1)	-3(1)	-3(1)	-3(1)
C(10A)	22(1)	23(1)	22(1)	-4(1)	-2(1)	-5(1)
C(10B)	21(1)	23(1)	22(1)	-4(1)	-2(1)	-4(1)
C(11)	26(1)	23(1)	26(1)	-3(1)	-5(1)	-2(1)
C(12)	24(1)	24(1)	24(1)	-2(1)	-3(1)	-5(1)
O(5)	34(1)	26(1)	25(1)	-4(1)	-5(1)	-2(1)
N(11)	26(1)	22(1)	26(1)	-4(1)	-3(1)	-1(1)
C(13)	26(1)	23(1)	27(1)	-4(1)	-3(1)	-2(1)
C(14)	33(1)	22(1)	33(1)	-4(1)	-4(1)	0(1)
C(15)	33(1)	29(1)	28(1)	-7(1)	-7(1)	0(1)
O(6)	59(1)	31(1)	31(1)	-12(1)	-22(1)	12(1)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **1·DMF·H_2O**.

Atom	x	y	z	U(iso)
H(2)	290(30)	10835(18)	1877(12)	43
H(4)	5540(30)	3310(20)	5286(8)	44
H(3)	1016	8192	388	29
H(5)	3483	2747	-132	31
H(6)	4886	431	715	31
H(8)	6661	-769	3610	31
H(13)	779	1077	3432	31
H(14A)	-289	5732	3403	45
H(14B)	-2295	5277	3844	45
H(14C)	-1586	5007	2838	45
H(15A)	1002	1810	4740	45
H(15B)	-688	3231	5047	45
H(15C)	1354	3665	4651	45
H(6A)	6970(30)	3010(20)	6526(12)	61
H(6B)	5930(30)	4693(16)	6337(14)	61

Table S7. Torsion angles [°] for **1·DMF·H_2O**.

C(10B)-N(1)-C(2)-C(3)	-0.62(18)
C(10B)-N(1)-C(2)-C(11)	179.32(10)
N(1)-C(2)-C(3)-C(4)	1.07(19)
C(11)-C(2)-C(3)-C(4)	-178.87(11)
C(2)-C(3)-C(4)-C(4A)	0.11(18)
C(2)-C(3)-C(4)-Cl(1)	179.96(9)
C(3)-C(4)-C(4A)-C(10B)	-1.55(17)
Cl(1)-C(4)-C(4A)-C(10B)	178.60(9)
C(3)-C(4)-C(4A)-C(5)	177.99(11)
Cl(1)-C(4)-C(4A)-C(5)	-1.87(17)
C(4)-C(4A)-C(5)-C(6)	179.81(12)
C(10B)-C(4A)-C(5)-C(6)	-0.68(19)
C(9)-N(10)-C(10A)-C(6A)	-0.49(17)
C(9)-N(10)-C(10A)-C(10B)	179.80(11)
C(7)-C(6A)-C(10A)-N(10)	1.12(18)
C(6)-C(6A)-C(10A)-N(10)	-178.79(11)
C(7)-C(6A)-C(10A)-C(10B)	-179.16(11)
C(6)-C(6A)-C(10A)-C(10B)	0.93(17)
C(2)-N(1)-C(10B)-C(4A)	-1.02(18)
C(2)-N(1)-C(10B)-C(10A)	179.24(11)
C(4)-C(4A)-C(10B)-N(1)	2.06(17)
C(5)-C(4A)-C(10B)-N(1)	-177.49(11)
C(4)-C(4A)-C(10B)-C(10A)	-178.19(10)
C(5)-C(4A)-C(10B)-C(10A)	2.26(17)
N(10)-C(10A)-C(10B)-N(1)	-2.87(17)
C(6A)-C(10A)-C(10B)-N(1)	177.40(10)
C(4A)-C(5)-C(6)-C(6A)	-0.8(2)
C(5)-C(6)-C(6A)-C(7)	-179.23(12)
C(5)-C(6)-C(6A)-C(10A)	0.68(19)
C(10A)-C(6A)-C(7)-C(8)	-0.68(18)
C(6)-C(6A)-C(7)-C(8)	179.22(12)
C(10A)-C(6A)-C(7)-Cl(2)	179.48(9)
C(6)-C(6A)-C(7)-Cl(2)	-0.61(17)
C(6A)-C(7)-C(8)-C(9)	-0.31(19)
Cl(2)-C(7)-C(8)-C(9)	179.53(9)
C(7)-C(8)-C(9)-N(10)	1.03(19)
C(7)-C(8)-C(9)-C(12)	-176.74(11)
C(8)-C(9)-N(10)-C(10A)	-0.64(18)
C(12)-C(9)-N(10)-C(10A)	177.11(10)
N(10)-C(10A)-C(10B)-C(4A)	177.37(10)
C(6A)-C(10A)-C(10B)-C(4A)	-2.35(17)
N(1)-C(2)-C(11)-O(1)	-4.26(18)
C(3)-C(2)-C(11)-O(1)	175.68(12)
N(1)-C(2)-C(11)-O(2)	176.00(11)
C(3)-C(2)-C(11)-O(2)	-4.06(17)
N(10)-C(9)-C(12)-O(3)	-170.34(12)
C(8)-C(9)-C(12)-O(3)	7.57(18)
N(10)-C(9)-C(12)-O(4)	8.52(16)
C(8)-C(9)-C(12)-O(4)	-173.57(11)
C(14)-N(11)-C(13)-O(5)	-0.4(2)
C(15)-N(11)-C(13)-O(5)	-177.43(12)

Table S8. Hydrogen bonds for **1·DMF·H_2O** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2)...O(5)#1	0.92(2)	1.59(2)	2.5086(15)	175.6(19)
O(4)-H(4)...O(6)	0.91(2)	1.59(2)	2.4919(15)	171.4(19)
C(13)-H(13)...O(1)#2	0.95	2.33	3.0445(18)	131.2
C(15)-H(15A)...O(3)#3	0.98	2.34	3.298(2)	165.4
O(6)-H(6A)...O(1)#4	0.89(2)	1.81(2)	2.6964(18)	172(2)
O(6)-H(6B)...O(4)#4	0.88(2)	2.30(2)	2.7802(17)	113.9(17)
O(6)-H(6B)...N(10)#4	0.88(2)	2.15(2)	3.0316(17)	172(2)

Symmetry transformations used to generate equivalent atoms:

#1 x, y+1, z #2 x, y-1, z #3 -x+1, -y, -z+1 #4 -x+1, -y+1, -z+1

1,10-phenantroline-4,7-dichloro-2,9-diylbis(pyrrolidin-1-yl-methanone) 3a

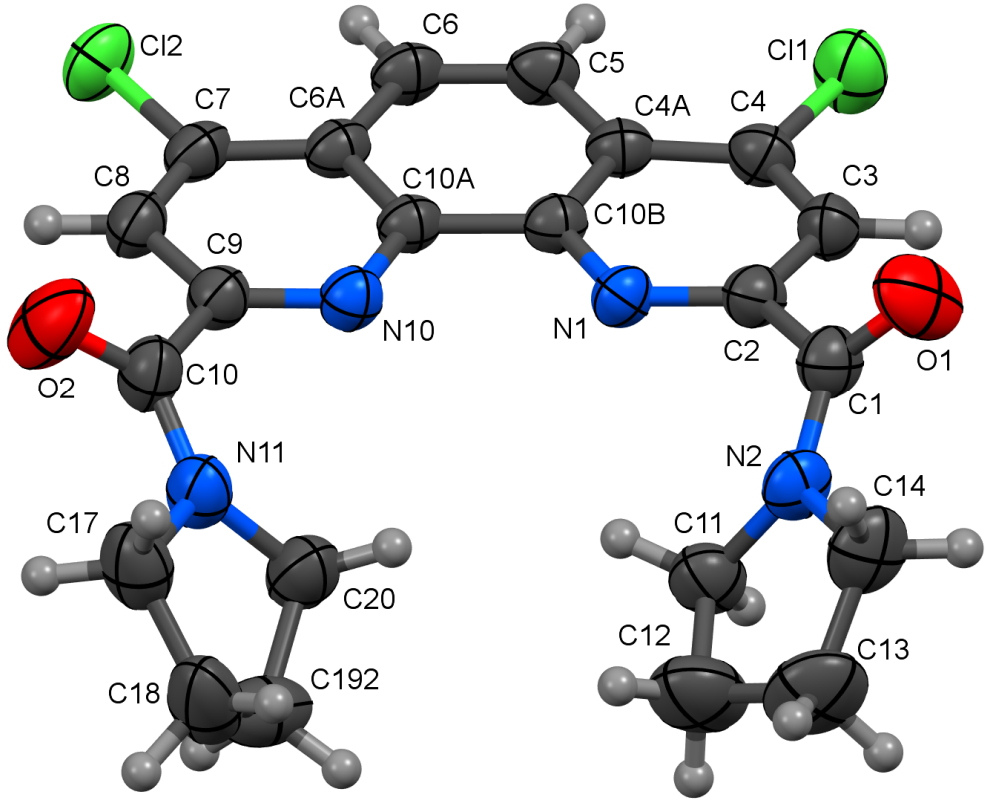


Table S9. Crystal data and structure refinement for **3a.**

Identification code	**3a**
Empirical formula	C22 H20 Cl2 N4 O2
Formula weight	443.32
Temperature	293(2) K
Wavelength	1.54186 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 7.7488(3) Å α = 79.974(3)°
	b = 10.1002(4) Å β = 76.276(3)°
	c = 13.5780(5) Å γ = 83.821(3)°
Volume	1014.12(7) $Å^3$
Z, Calculated density	2, 1.452 Mg/m^3
Absorption coefficient	3.110 mm^{-1}
F(000)	460
Crystal size	0.22 x 0.18 x 0.02 mm
Theta range for data collection	4.456 to 67.977°
Limiting indices	-4<=h<=9, -9<=k<=12, -16<=l<=16
Reflections collected / unique	8085 / 3593 [R(int) = 0.0232]
Completeness to theta = 67.686°	97.2 %
Absorption correction	Multi-scan

Max. and min. transmission	0.953 and 0.672
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3593 / 0 / 281
Goodness-of-fit on F^2	1.025
Final R indices [I>2sigma(I)]	R1 = 0.0432, wR2 = 0.1222
R indices (all data)	R1 = 0.0603, wR2 = 0.1295
Extinction coefficient	n/a
Largest diff. peak and hole	0.306 and -0.295 e·$Å^{-3}$

Table S10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **3a.** U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Cl(1)	1025(1)	9026(1)	5934(1)	70(1)
Cl(2)	3076(1)	2109(1)	4436(1)	60(1)
N(1)	4006(2)	5707(2)	7680(1)	41(1)
N(2)	5645(3)	6753(2)	9114(2)	50(1)
N(10)	4822(2)	3232(2)	7112(2)	43(1)
N(11)	7470(3)	1310(2)	7851(2)	54(1)
O(1)	2842(3)	7632(3)	9555(2)	82(1)
O(2)	5727(3)	-203(2)	7639(2)	87(1)
C(2)	3620(3)	6913(2)	7955(2)	43(1)
C(3)	2687(3)	7969(3)	7437(2)	48(1)
C(4)	2140(3)	7732(2)	6609(2)	46(1)
C(4A)	2465(3)	6453(2)	6286(2)	42(1)
C(5)	1913(3)	6120(3)	5441(2)	48(1)
C(6)	2308(3)	4888(3)	5158(2)	47(1)
C(6A)	3288(3)	3864(2)	5710(2)	41(1)
C(7)	3725(3)	2557(3)	5463(2)	46(1)
C(8)	4656(3)	1617(3)	6031(2)	48(1)
C(9)	5194(3)	2016(2)	6841(2)	45(1)
C(10A)	3866(3)	4141(2)	6554(2)	39(1)
C(10B)	3440(3)	5471(2)	6861(2)	39(1)
C(1)	4036(3)	7132(3)	8940(2)	49(1)
C(10)	6169(4)	955(3)	7482(2)	54(1)
C(11)	7239(3)	6334(3)	8376(2)	61(1)
C(12)	8571(5)	5904(5)	9021(3)	94(1)
C(13)	8041(5)	6577(4)	9915(3)	90(1)
C(14)	6068(4)	6932(3)	10080(2)	68(1)
C(17)	8400(4)	302(3)	8502(3)	70(1)
C(18)	9914(5)	1015(4)	8636(4)	92(1)
C(191)	9660(30)	2590(20)	8171(15)	61(4)
C(192)	10121(10)	2111(12)	7844(8)	75(2)
C(20)	8315(4)	2587(3)	7610(3)	68(1)

Table S11. Bond lengths [Å] and angles [°] for **3a**.

Cl(1)-C(4)	1.735(2)	C(4A)-C(10B)	1.418(3)
Cl(2)-C(7)	1.734(2)	C(4A)-C(5)	1.419(3)
N(1)-C(2)	1.319(3)	C(5)-C(6)	1.349(4)
N(1)-C(10B)	1.353(3)	C(6)-C(6A)	1.429(3)
N(2)-C(1)	1.328(3)	C(6A)-C(7)	1.404(3)
N(2)-C(11)	1.468(3)	C(6A)-C(10A)	1.405(3)
N(2)-C(14)	1.469(3)	C(7)-C(8)	1.370(4)
N(10)-C(9)	1.326(3)	C(8)-C(9)	1.397(3)
N(10)-C(10A)	1.357(3)	C(9)-C(10)	1.513(3)
N(11)-C(10)	1.332(3)	C(10A)-C(10B)	1.456(3)
N(11)-C(20)	1.461(4)	C(11)-C(12)	1.490(4)
N(11)-C(17)	1.473(3)	C(12)-C(13)	1.448(5)
O(1)-C(1)	1.220(3)	C(13)-C(14)	1.505(5)
O(2)-C(10)	1.223(3)	C(17)-C(18)	1.502(5)
C(2)-C(3)	1.404(3)	C(18)-C(192)	1.396(8)
C(2)-C(1)	1.504(3)	C(18)-C(191)	1.61(2)
C(3)-C(4)	1.357(3)	C(191)-C(20)	1.43(1)
C(4)-C(4A)	1.414(3)	C(192)-C(20)	1.518(8)
C(2)-N(1)-C(10B)	118.0(2)	N(10)-C(9)-C(8)	124.3(2)
C(1)-N(2)-C(11)	127.2(2)	N(10)-C(9)-C(10)	118.5(2)
C(1)-N(2)-C(14)	120.4(2)	C(8)-C(9)-C(10)	117.2(2)
C(11)-N(2)-C(14)	111.7(2)	N(10)-C(10A)-C(6A)	123.6(2)
C(9)-N(10)-C(10A)	117.1(2)	N(10)-C(10A)-C(10B)	117.1(2)
C(10)-N(11)-C(20)	128.7(2)	C(6A)-C(10A)-C(10B)	119.3(2)
C(10)-N(11)-C(17)	120.1(2)	N(1)-C(10B)-C(4A)	123.4(2)
C(20)-N(11)-C(17)	110.8(2)	N(1)-C(10B)-C(10A)	118.0(2)
N(1)-C(2)-C(3)	123.7(2)	C(4A)-C(10B)-C(10A)	118.6(2)
N(1)-C(2)-C(1)	118.3(2)	O(1)-C(1)-N(2)	123.1(2)
C(3)-C(2)-C(1)	117.7(2)	O(1)-C(1)-C(2)	117.4(2)
C(4)-C(3)-C(2)	118.1(2)	N(2)-C(1)-C(2)	119.5(2)
C(3)-C(4)-C(4A)	121.2(2)	O(2)-C(10)-N(11)	122.5(2)
C(3)-C(4)-Cl(1)	119.3(2)	O(2)-C(10)-C(9)	118.2(2)
C(4A)-C(4)-Cl(1)	119.5(2)	N(11)-C(10)-C(9)	119.3(2)
C(4)-C(4A)-C(10B)	115.6(2)	N(2)-C(11)-C(12)	103.2(2)
C(4)-C(4A)-C(5)	124.6(2)	C(13)-C(12)-C(11)	107.9(3)
C(10B)-C(4A)-C(5)	119.8(2)	C(12)-C(13)-C(14)	107.5(2)
C(6)-C(5)-C(4A)	121.5(2)	N(2)-C(14)-C(13)	103.9(3)
C(5)-C(6)-C(6A)	120.9(2)	N(11)-C(17)-C(18)	104.6(3)
C(7)-C(6A)-C(10A)	116.4(2)	C(192)-C(18)-C(17)	105.2(4)

C(7)-C(6A)-C(6)	123.7(2)	C(17)-C(18)-C(191)	108.5(6)
C(10A)-C(6A)-C(6)	119.9(2)	C(20)-C(191)-C(18)	102.3(11)
C(8)-C(7)-C(6A)	120.8(2)	C(18)-C(192)-C(20)	108.8(5)
C(8)-C(7)-Cl(2)	119.0(2)	C(191)-C(20)-N(11)	112.1(8)
C(6A)-C(7)-Cl(2)	120.2(2)	N(11)-C(20)-C(192)	100.2(4)
C(7)-C(8)-C(9)	117.7(2)		

Table S12. Anisotropic displacement parameters ($Å^2$ x 10^3) for **3a.**
The anisotropic displacement factor exponent takes the form:
$-2\cdot\pi^2[\ h^2\cdot a^{*2}\cdot U11 + ... + 2\cdot h\cdot k\cdot a^*\cdot b^*\cdot U12\ ]$

	U11	U22	U33	U23	U13	U12
Cl(1)	86(1)	54(1)	81(1)	-11(1)	-48(1)	13(1)
Cl(2)	74(1)	67(1)	53(1)	-23(1)	-25(1)	-12(1)
N(1)	44(1)	47(1)	37(1)	-12(1)	-14(1)	-3(1)
N(2)	58(1)	57(1)	40(1)	-14(1)	-21(1)	-3(1)
N(10)	47(1)	44(1)	41(1)	-7(1)	-15(1)	-4(1)
N(11)	64(1)	45(1)	61(1)	-10(1)	-29(1)	4(1)
O(1)	69(1)	125(2)	58(1)	-48(1)	-11(1)	12(1)
O(2)	109(2)	49(1)	119(2)	6(1)	-62(2)	-19(1)
C(2)	41(1)	51(1)	40(1)	-12(1)	-9(1)	-2(1)
C(3)	49(1)	46(1)	52(2)	-15(1)	-16(1)	2(1)
C(4)	45(1)	46(1)	50(1)	-5(1)	-18(1)	1(1)
C(4A)	39(1)	47(1)	41(1)	-5(1)	-13(1)	-4(1)
C(5)	48(1)	57(2)	45(1)	-6(1)	-22(1)	-1(1)
C(6)	47(1)	59(2)	40(1)	-10(1)	-18(1)	-7(1)
C(6A)	40(1)	50(1)	37(1)	-10(1)	-10(1)	-8(1)
C(7)	45(1)	53(1)	44(1)	-14(1)	-11(1)	-14(1)
C(8)	53(1)	45(1)	52(2)	-15(1)	-13(1)	-8(1)
C(9)	48(1)	43(1)	48(1)	-9(1)	-14(1)	-5(1)
C(10A)	38(1)	46(1)	35(1)	-7(1)	-10(1)	-6(1)
C(10B)	38(1)	45(1)	33(1)	-7(1)	-9(1)	-4(1)
C(1)	55(1)	55(2)	40(1)	-14(1)	-11(1)	-4(1)
C(10)	67(2)	42(1)	58(2)	-9(1)	-24(1)	-2(1)
C(11)	57(2)	75(2)	60(2)	-21(1)	-25(1)	5(1)
C(12)	71(2)	125(3)	99(3)	-30(2)	-44(2)	9(2)
C(13)	95(2)	111(3)	82(2)	-9(2)	-59(2)	-8(2)
C(14)	90(2)	78(2)	46(2)	-16(1)	-32(1)	-8(2)
C(17)	84(2)	59(2)	74(2)	-13(2)	-37(2)	19(2)
C(18)	92(2)	85(2)	121(3)	-48(2)	-63(2)	33(2)
C(191)	53(7)	95(12)	40(8)	-23(6)	-10(6)	-5(7)
C(192)	57(3)	111(6)	62(5)	-17(4)	-12(3)	-21(3)
C(20)	69(2)	59(2)	86(2)	-16(2)	-36(2)	-4(1)

Table S13. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **3a.**

	x	y	z	U(eq)
H(3)	2451	8807	7654	57
H(5)	1262	6767	5073	58
H(6)	1939	4703	4595	56
H(8)	4920	743	5883	58
H(11A)	7636	7078	7840	74
H(11B)	7015	5594	8065	74
H(12A)	8610	4935	9228	112
H(12B)	9746	6149	8635	112
H(13A)	8675	7386	9807	108
H(13B)	8313	5987	10512	108
H(14A)	5418	6336	10655	81
H(14B)	5782	7856	10204	81
H(17A)	8841	-483	8169	85
H(17B)	7613	17	9159	85
H(181)	11039	624	8280	110
H(182)	9922	920	9358	110
H(183)	9634	1317	9299	110
H(184)	10994	423	8582	110
H(191)	9266	3137	8712	73
H(192)	10754	2909	7723	73
H(193)	10933	1847	7237	90
H(194)	10616	2836	8048	90
H(201)	8844	2758	6881	81
H(202)	7416	3311	7770	81
H(203)	7679	3230	8046	81
H(204)	8417	2982	6896	81

Table S14. Torsion angles [°] for **3a**.

C(10B)-N(1)-C(2)-C(3)	-1.2(3)	C(6A)-C(10A)-C(10B)-N(1)	179.6(2)
C(10B)-N(1)-C(2)-C(1)	172.4(2)	N(10)-C(10A)-C(10B)-C(4A)	179.1(2)
N(1)-C(2)-C(3)-C(4)	0.5(4)	C(6A)-C(10A)-C(10B)-C(4A)	-0.7(3)
C(1)-C(2)-C(3)-C(4)	-173.1(2)	C(11)-N(2)-C(1)-O(1)	-170.1(3)
C(2)-C(3)-C(4)-C(4A)	1.2(4)	C(14)-N(2)-C(1)-O(1)	-0.4(4)
C(2)-C(3)-C(4)-Cl(1)	-178.6(2)	C(11)-N(2)-C(1)-C(2)	11.5(4)
C(3)-C(4)-C(4A)-C(10B)	-2.0(3)	C(14)-N(2)-C(1)-C(2)	-178.8(2)
Cl(1)-C(4)-C(4A)-C(10B)	177.8(2)	N(1)-C(2)-C(1)-O(1)	-128.5(3)
C(3)-C(4)-C(4A)-C(5)	179.0(2)	C(3)-C(2)-C(1)-O(1)	45.4(3)
Cl(1)-C(4)-C(4A)-C(5)	-1.2(3)	N(1)-C(2)-C(1)-N(2)	49.9(3)
C(4)-C(4A)-C(5)-C(6)	178.2(2)	C(3)-C(2)-C(1)-N(2)	-136.1(2)
C(10B)-C(4A)-C(5)-C(6)	-0.7(4)	C(20)-N(11)-C(10)-O(2)	170.2(3)
C(4A)-C(5)-C(6)-C(6A)	0.7(4)	C(17)-N(11)-C(10)-O(2)	-1.9(4)
C(5)-C(6)-C(6A)-C(7)	179.2(2)	C(20)-N(11)-C(10)-C(9)	-9.7(4)
C(5)-C(6)-C(6A)-C(10A)	-0.7(3)	C(17)-N(11)-C(10)-C(9)	178.2(2)
C(10A)-C(6A)-C(7)-C(8)	0.5(3)	N(10)-C(9)-C(10)-O(2)	141.1(3)
C(6)-C(6A)-C(7)-C(8)	-179.4(2)	C(8)-C(9)-C(10)-O(2)	-35.4(4)
C(10A)-C(6A)-C(7)-Cl(2)	-180.0(2)	N(10)-C(9)-C(10)-N(11)	-39.1(3)
C(6)-C(6A)-C(7)-Cl(2)	0.1(3)	C(8)-C(9)-C(10)-N(11)	144.5(2)
C(6A)-C(7)-C(8)-C(9)	-1.8(3)	C(1)-N(2)-C(11)-C(12)	-174.7(3)
Cl(2)-C(7)-C(8)-C(9)	178.6(2)	C(14)-N(2)-C(11)-C(12)	14.8(3)
C(10A)-N(10)-C(9)-C(8)	-0.5(3)	N(2)-C(11)-C(12)-C(13)	-23.5(4)
C(10A)-N(10)-C(9)-C(10)	-176.7(2)	C(11)-C(12)-C(13)-C(14)	23.9(4)
C(7)-C(8)-C(9)-N(10)	1.9(4)	C(1)-N(2)-C(14)-C(13)	-172.1(3)
C(7)-C(8)-C(9)-C(10)	178.1(2)	C(11)-N(2)-C(14)-C(13)	-0.9(3)
C(9)-N(10)-C(10A)-C(6A)	-1.0(3)	C(12)-C(13)-C(14)-N(2)	-14.1(4)
C(9)-N(10)-C(10A)-C(10B)	179.2(2)	C(10)-N(11)-C(17)-C(18)	172.1(3)
C(7)-C(6A)-C(10A)-N(10)	1.0(3)	C(20)-N(11)-C(17)-C(18)	-1.3(3)
C(6)-C(6A)-C(10A)-N(10)	-179.1(2)	N(11)-C(17)-C(18)-C(192)	-18.7(7)
C(7)-C(6A)-C(10A)-C(10B)	-179.3(2)	N(11)-C(17)-C(18)-C(191)	8.7(10)
C(6)-C(6A)-C(10A)-C(10B)	0.6(3)	C(17)-C(18)-C(191)-C(20)	-12.9(15)
C(2)-N(1)-C(10B)-C(4A)	0.2(3)	C(17)-C(18)-C(192)-C(20)	31.9(10)
C(2)-N(1)-C(10B)-C(10A)	179.9(2)	C(18)-C(191)-C(20)-N(11)	12.3(16)
C(4)-C(4A)-C(10B)-N(1)	1.3(3)	C(10)-N(11)-C(20)-C(191)	179.6(11)
C(5)-C(4A)-C(10B)-N(1)	-179.6(2)	C(17)-N(11)-C(20)-C(191)	-7.7(12)
C(4)-C(4A)-C(10B)-C(10A)	-178.3(2)	C(10)-N(11)-C(20)-C(192)	-153.9(5)
C(5)-C(4A)-C(10B)-C(10A)	0.7(3)	C(17)-N(11)-C(20)-C(192)	18.8(6)
N(10)-C(10A)-C(10B)-N(1)	-0.6(3)	C(18)-C(192)-C(20)-N(11)	-31.6(9)

Table S15. Hydrogen bonds for **3a** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(11)-H(11B)...N(1)	0.97	2.50	3.041(3)	115.5
C(18)-H(183)...O(1)#1	0.97	2.44	3.243(5)	140.1
C(191)-H(191)...O(1)#1	0.97	2.57	3.22(2)	124.0
C(20)-H(202)...N(10)	0.97	2.40	2.923(3)	113.4

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+2

1,10-phenantroline-4,7-dichloro-2,9-diylbis(piperidin-1-yl-methanone) 3b

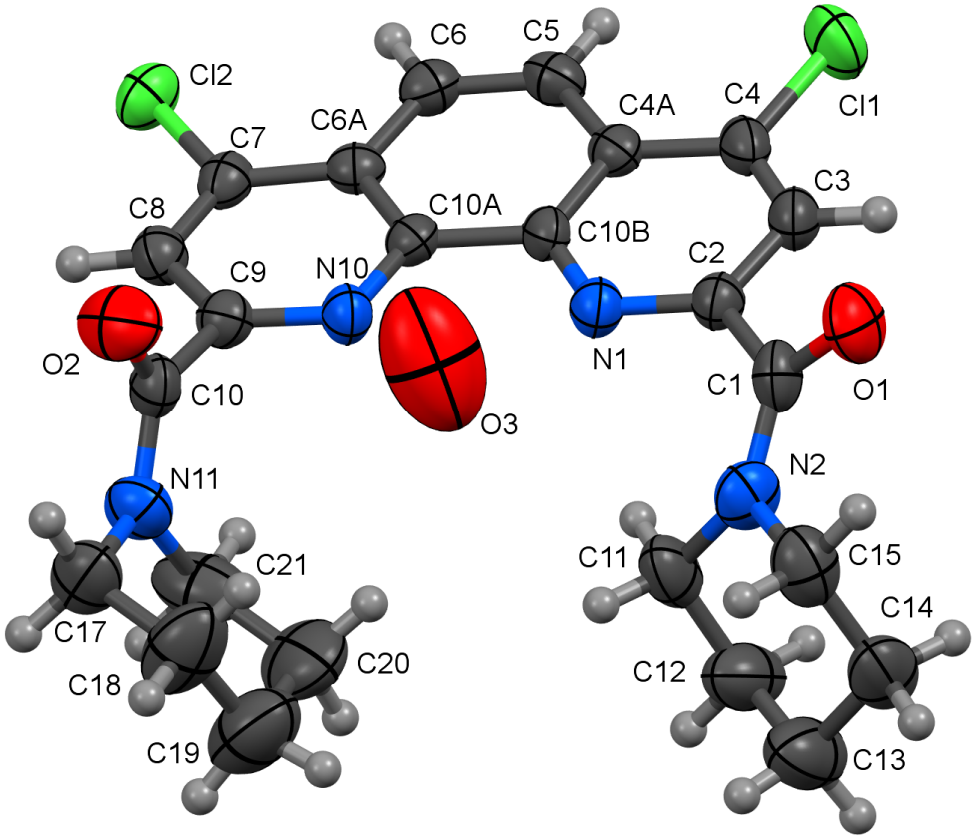


Table S16. Crystal data and structure refinement for **3b·H_2O.**

Identification code	3b
Empirical formula	$C_{24}H_{26}Cl_2N_4O_3$
Formula weight	489.39
Temperature	292(2) K
Wavelength	1.54186 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 36.3267(15) Å α = 90°
	b = 6.8415(2) Å β = 122.928(3)°
	c = 22.1880(11) Å γ = 90°
Volume	4628.5(4) $Å^3$
Z, Calculated density	8, 1.405 Mg/m^3
Absorption coefficient	2.810 mm^{-1}
F(000)	2048
Crystal size	0.12 x 0.10 x 0.02 mm
Theta range for data collection	3.998 to 67.731°
Limiting indices	-43<=h<=43, -4<=k<=8, -24<=l<=26
Reflections collected / unique	26181 / 4179 [R(int) = 0.1129]
Completeness to theta = 67.686°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.972 and 0.805
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4179 / 0 / 298

Goodness-of-fit on F^2	0.846
Final R indices [I>2sigma(I)]	R1 = 0.0362, wR2 = 0.0591
R indices (all data)	R1 = 0.0992, wR2 = 0.0721
Extinction coefficient	n/a
Largest diff. peak and hole	0.138 and -0.154 e/Å^{-3}

Table S17. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **3b·H_2O.** U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Cl(1)	1863(1)	5596(1)	3851(1)	67(1)
Cl(2)	2220(1)	5750(1)	814(1)	52(1)
O(1)	3520(1)	4399(3)	5939(1)	64(1)
O(2)	3944(1)	3082(3)	2818(1)	78(1)
O(3)	4013(1)	3332(5)	4453(2)	161(1)
N(1)	3216(1)	5624(3)	4235(1)	42(1)
N(10)	3340(1)	5415(3)	3138(1)	41(1)
N(2)	3895(1)	6663(3)	5735(1)	55(1)
N(11)	4157(1)	6245(3)	3013(1)	56(1)
C(2)	3155(1)	5658(3)	4770(1)	40(1)
C(3)	2740(1)	5624(3)	4668(1)	45(1)
C(4)	2382(1)	5642(3)	3999(1)	45(1)
C(4A)	2422(1)	5677(3)	3397(1)	38(1)
C(5)	2059(1)	5764(3)	2662(1)	45(1)
C(6)	2122(1)	5767(3)	2114(1)	43(1)
C(6A)	2558(1)	5669(3)	2256(1)	37(1)
C(7)	2644(1)	5648(3)	1705(1)	40(1)
C(8)	3066(1)	5485(3)	1878(1)	43(1)
C(9)	3399(1)	5352(3)	2600(1)	42(1)
C(10A)	2921(1)	5589(3)	2967(1)	38(1)
C(10B)	2857(1)	5628(3)	3561(1)	37(1)
C(1)	3541(1)	5553(4)	5524(1)	47(1)
C(11)	3937(1)	8236(4)	5326(1)	65(1)
C(12)	4011(1)	10199(5)	5686(2)	82(1)
C(13)	4399(1)	10116(5)	6451(2)	94(1)
C(14)	4349(1)	8469(5)	6860(1)	76(1)
C(15)	4270(1)	6515(4)	6470(1)	68(1)
C(10)	3864(1)	4818(4)	2821(1)	44(1)
C(17)	4617(1)	5771(5)	3312(1)	70(1)
C(18)	4884(1)	6081(5)	4100(2)	96(1)
C(19)	4833(1)	8106(6)	4294(2)	107(1)
C(20)	4355(1)	8625(5)	3961(2)	101(1)
C(21)	4094(1)	8239(4)	3163(2)	84(1)

Table S18. Bond lengths [Å] and angles [°] for **3b·H_2O.**

Cl(1)-C(4)	1.729(2)	C(4A)-C(10B)	1.415(3)
Cl(2)-C(7)	1.724(2)	C(4A)-C(5)	1.436(3)
O(1)-C(1)	1.245(3)	C(5)-C(6)	1.356(3)
O(2)-C(10)	1.222(3)	C(6)-C(6A)	1.439(3)
N(1)-C(2)	1.321(3)	C(6A)-C(10A)	1.403(3)
N(1)-C(10B)	1.348(3)	C(6A)-C(7)	1.417(3)
N(10)-C(9)	1.325(3)	C(7)-C(8)	1.368(3)
N(10)-C(10A)	1.359(3)	C(8)-C(9)	1.391(3)
N(2)-C(1)	1.341(3)	C(9)-C(10)	1.526(3)
N(2)-C(15)	1.453(3)	C(10A)-C(10B)	1.458(3)
N(2)-C(11)	1.468(3)	C(11)-C(12)	1.510(4)
N(11)-C(10)	1.332(3)	C(12)-C(13)	1.508(4)
N(11)-C(21)	1.452(3)	C(13)-C(14)	1.518(4)
N(11)-C(17)	1.460(3)	C(14)-C(15)	1.532(4)
C(2)-C(3)	1.398(3)	C(17)-C(18)	1.483(4)
C(2)-C(1)	1.489(3)	C(18)-C(19)	1.492(4)
C(3)-C(4)	1.340(3)	C(19)-C(20)	1.514(5)
C(4)-C(4A)	1.421(3)	C(20)-C(21)	1.511(4)
C(2)-N(1)-C(10B)	117.6(2)	C(7)-C(8)-C(9)	118.0(2)
C(9)-N(10)-C(10A)	117.3(2)	N(10)-C(9)-C(8)	124.7(2)
C(1)-N(2)-C(15)	119.3(2)	N(10)-C(9)-C(10)	114.5(2)
C(1)-N(2)-C(11)	127.0(2)	C(8)-C(9)-C(10)	120.3(2)
C(15)-N(2)-C(11)	113.3(2)	N(10)-C(10A)-C(6A)	122.8(2)
C(10)-N(11)-C(21)	124.3(2)	N(10)-C(10A)-C(10B)	117.1(2)
C(10)-N(11)-C(17)	120.0(2)	C(6A)-C(10A)-C(10B)	120.1(2)
C(21)-N(11)-C(17)	112.9(2)	N(1)-C(10B)-C(4A)	123.9(2)
N(1)-C(2)-C(3)	123.1(2)	N(1)-C(10B)-C(10A)	117.9(2)
N(1)-C(2)-C(1)	119.6(2)	C(4A)-C(10B)-C(10A)	118.2(2)
C(3)-C(2)-C(1)	117.1(2)	O(1)-C(1)-N(2)	122.2(2)
C(4)-C(3)-C(2)	119.5(2)	O(1)-C(1)-C(2)	117.5(2)
C(3)-C(4)-C(4A)	120.5(2)	N(2)-C(1)-C(2)	120.2(2)
C(3)-C(4)-Cl(1)	120.8(2)	N(2)-C(11)-C(12)	112.0(2)
C(4A)-C(4)-Cl(1)	118.7(2)	C(13)-C(12)-C(11)	110.6(3)
C(10B)-C(4A)-C(4)	115.4(2)	C(12)-C(13)-C(14)	111.0(2)
C(10B)-C(4A)-C(5)	120.1(2)	C(13)-C(14)-C(15)	110.9(2)
C(4)-C(4A)-C(5)	124.6(2)	N(2)-C(15)-C(14)	110.3(2)
C(6)-C(5)-C(4A)	121.3(2)	O(2)-C(10)-N(11)	124.4(2)
C(5)-C(6)-C(6A)	120.5(2)	O(2)-C(10)-C(9)	116.9(2)
C(10A)-C(6A)-C(7)	117.3(2)	N(11)-C(10)-C(9)	118.7(2)
C(10A)-C(6A)-C(6)	119.8(2)	N(11)-C(17)-C(18)	111.0(2)
C(7)-C(6A)-C(6)	123.0(2)	C(17)-C(18)-C(19)	111.7(3)
C(8)-C(7)-C(6A)	119.8(2)	C(18)-C(19)-C(20)	111.6(3)
C(8)-C(7)-Cl(2)	119.4(2)	C(21)-C(20)-C(19)	110.6(3)
C(6A)-C(7)-Cl(2)	120.7(2)	N(11)-C(21)-C(20)	110.9(3)

Table S19. Anisotropic displacement parameters ($Å^2$ x 10^3) for **3b·H_2O.** The anisotropic displacement factor exponent takes the form:
$-2\cdot\pi^2[\ h^2\cdot a^{*2}\cdot U11 + ... + 2\cdot h\cdot k\cdot a^*\cdot b^*\cdot U12\ ]$

	U11	U22	U33	U23	U13	U12
Cl(1)	54(1)	92(1)	75(1)	-4(1)	47(1)	-4(1)
Cl(2)	56(1)	56(1)	37(1)	-2(1)	20(1)	1(1)
O(1)	74(1)	74(1)	49(1)	16(1)	38(1)	5(1)
O(2)	69(1)	58(1)	116(2)	-16(1)	56(1)	6(1)
O(3)	130(2)	223(3)	141(2)	85(2)	80(2)	75(2)
N(1)	44(1)	45(1)	39(1)	-2(1)	25(1)	1(1)
N(10)	41(1)	47(1)	39(1)	-3(1)	26(1)	1(1)
N(2)	47(1)	70(2)	37(1)	4(1)	15(1)	2(1)
N(11)	41(1)	65(2)	63(2)	-6(1)	28(1)	-2(1)
C(2)	44(1)	41(1)	36(1)	-1(1)	24(1)	-1(1)
C(3)	54(2)	49(2)	43(2)	-3(1)	32(1)	-1(1)
C(4)	56(2)	41(1)	55(2)	-7(1)	41(1)	-5(1)
C(4A)	41(1)	33(1)	47(1)	-6(1)	27(1)	-2(1)
C(5)	39(1)	41(1)	57(2)	0(1)	28(1)	-2(1)
C(6)	45(1)	38(1)	41(1)	-2(1)	20(1)	-3(1)
C(6A)	39(1)	30(1)	41(1)	-1(1)	21(1)	-2(1)
C(7)	51(1)	32(1)	38(1)	0(1)	25(1)	0(1)
C(8)	49(2)	43(2)	44(2)	1(1)	29(1)	-1(1)
C(9)	42(1)	41(1)	46(2)	-3(1)	25(1)	0(1)
C(10A)	41(1)	33(1)	40(1)	-7(1)	23(1)	-4(1)
C(10B)	43(1)	36(1)	42(1)	-7(1)	29(1)	-2(1)
C(1)	56(2)	54(2)	40(1)	5(1)	32(1)	8(1)
C(11)	61(2)	92(2)	47(2)	7(2)	32(2)	-12(2)
C(12)	86(2)	87(2)	61(2)	-3(2)	32(2)	-32(2)
C(13)	106(3)	106(3)	68(2)	-6(2)	45(2)	-43(2)
C(14)	55(2)	119(3)	44(2)	-8(2)	20(2)	-19(2)
C(15)	58(2)	86(2)	59(2)	12(2)	32(2)	9(1)
C(10)	45(2)	52(2)	43(2)	-4(1)	28(1)	4(1)
C(17)	45(2)	94(2)	72(2)	-15(2)	31(2)	0(2)
C(18)	63(2)	127(3)	68(2)	-23(2)	17(2)	10(2)
C(19)	87(3)	121(3)	94(3)	-41(2)	36(2)	-10(2)
C(20)	122(3)	70(2)	130(3)	-40(2)	81(3)	-14(2)
C(21)	69(2)	48(2)	137(3)	7(2)	57(2)	1(1)

Table S20. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **3b·H_2O.**

	x	y	z	U(eq)
H(3)	2712	5589	5061	54
H(5)	1774	5820	2561	53
H(6)	1882	5834	1643	52
H(8)	3128	5464	1522	52
H(111)	3672	8292	4848	78
H(112)	4180	7949	5275	78
H(121)	4063	11178	5423	98
H(122)	3751	10575	5678	98
H(131)	4426	11350	6687	113
H(132)	4665	9917	6456	113
H(141)	4104	8749	6907	91
H(142)	4612	8379	7338	91
H(151)	4529	6159	6470	81
H(152)	4217	5501	6719	81
H(171)	4729	6588	3089	85
H(172)	4641	4418	3208	85
H(181)	5191	5847	4281	115
H(182)	4795	5150	4328	115
H(191)	4964	9026	4131	129
H(192)	4987	8214	4813	129
H(201)	4236	7855	4184	121
H(202)	4330	9995	4048	121
H(211)	3785	8462	2966	101
H(212)	4187	9140	2932	101

Table S21. Torsion angles [°] for **3b·H_2O.**

C(10B)-N(1)-C(2)-C(3)	2.4(3)	N(10)-C(10A)-C(10B)-N(1)	4.5(3)
C(10B)-N(1)-C(2)-C(1)	176.9(2)	C(6A)-C(10A)-C(10B)-N(1)	-177.5(2)
N(1)-C(2)-C(3)-C(4)	-2.9(4)	N(10)-C(10A)-C(10B)-C(4A)	-175.9(2)
C(1)-C(2)-C(3)-C(4)	-177.6(2)	C(6A)-C(10A)-C(10B)-C(4A)	2.2(3)
C(2)-C(3)-C(4)-C(4A)	0.6(4)	C(15)-N(2)-C(1)-O(1)	0.4(4)
C(2)-C(3)-C(4)-Cl(1)	179.9(2)	C(11)-N(2)-C(1)-O(1)	-171.8(2)
C(3)-C(4)-C(4A)-C(10B)	1.9(3)	C(15)-N(2)-C(1)-C(2)	-179.1(2)
Cl(1)-C(4)-C(4A)-C(10B)	-177.4(2)	C(11)-N(2)-C(1)-C(2)	8.7(4)
C(3)-C(4)-C(4A)-C(5)	-177.8(2)	N(1)-C(2)-C(1)-O(1)	-133.6(2)
Cl(1)-C(4)-C(4A)-C(5)	2.9(3)	C(3)-C(2)-C(1)-O(1)	41.2(3)
C(10B)-C(4A)-C(5)-C(6)	1.2(3)	N(1)-C(2)-C(1)-N(2)	45.9(3)
C(4)-C(4A)-C(5)-C(6)	-179.1(2)	C(3)-C(2)-C(1)-N(2)	-139.3(2)
C(4A)-C(5)-C(6)-C(6A)	0.4(3)	C(1)-N(2)-C(11)-C(12)	116.0(3)
C(5)-C(6)-C(6A)-C(10A)	-0.6(3)	C(15)-N(2)-C(11)-C(12)	-56.5(3)
C(5)-C(6)-C(6A)-C(7)	179.3(2)	N(2)-C(11)-C(12)-C(13)	54.2(3)
C(10A)-C(6A)-C(7)-C(8)	2.2(3)	C(11)-C(12)-C(13)-C(14)	-53.9(4)
C(6)-C(6A)-C(7)-C(8)	-177.8(2)	C(12)-C(13)-C(14)-C(15)	54.7(4)
C(10A)-C(6A)-C(7)-Cl(2)	-179.8(2)	C(1)-N(2)-C(15)-C(14)	-116.9(3)
C(6)-C(6A)-C(7)-Cl(2)	0.3(3)	C(11)-N(2)-C(15)-C(14)	56.3(3)
C(6A)-C(7)-C(8)-C(9)	-0.2(3)	C(13)-C(14)-C(15)-N(2)	-55.1(3)
Cl(2)-C(7)-C(8)-C(9)	-178.3(2)	C(21)-N(11)-C(10)-O(2)	-166.3(3)
C(10A)-N(10)-C(9)-C(8)	1.2(3)	C(17)-N(11)-C(10)-O(2)	-6.5(4)
C(10A)-N(10)-C(9)-C(10)	-170.3(2)	C(21)-N(11)-C(10)-C(9)	12.4(4)
C(7)-C(8)-C(9)-N(10)	-1.6(4)	C(17)-N(11)-C(10)-C(9)	172.3(2)
C(7)-C(8)-C(9)-C(10)	169.4(2)	N(10)-C(9)-C(10)-O(2)	90.1(3)
C(9)-N(10)-C(10A)-C(6A)	1.0(3)	C(8)-C(9)-C(10)-O(2)	-81.8(3)
C(9)-N(10)-C(10A)-C(10B)	179.1(2)	N(10)-C(9)-C(10)-N(11)	-88.7(3)
C(7)-C(6A)-C(10A)-N(10)	-2.7(3)	C(8)-C(9)-C(10)-N(11)	99.3(3)
C(6)-C(6A)-C(10A)-N(10)	177.3(2)	C(10)-N(11)-C(17)-C(18)	-104.3(3)
C(7)-C(6A)-C(10A)-C(10B)	179.3(2)	C(21)-N(11)-C(17)-C(18)	57.7(3)
C(6)-C(6A)-C(10A)-C(10B)	-0.7(3)	N(11)-C(17)-C(18)-C(19)	-54.9(4)
C(2)-N(1)-C(10B)-C(4A)	0.4(3)	C(17)-C(18)-C(19)-C(20)	53.2(4)
C(2)-N(1)-C(10B)-C(10A)	-179.9(2)	C(18)-C(19)-C(20)-C(21)	-52.2(4)
C(4)-C(4A)-C(10B)-N(1)	-2.5(3)	C(10)-N(11)-C(21)-C(20)	103.8(3)
C(5)-C(4A)-C(10B)-N(1)	177.2(2)	C(17)-N(11)-C(21)-C(20)	-57.3(3)
C(4)-C(4A)-C(10B)-C(10A)	177.9(2)	C(19)-C(20)-C(21)-N(11)	53.8(4)
C(5)-C(4A)-C(10B)-C(10A)	-2.4(3)		

Table S22. Hydrogen bonds for **3b·H_2O** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(8)-H(8)...O(1)#1	0.93	2.39	3.287(3)	161.5
C(11)-H(111)...N(1)	0.97	2.34	3.003(3)	125.0
C(12)-H(121)...O(3)#2	0.97	2.53	3.477(4)	164.5
C(14)-H(141)...Cl(1)#3	0.97	2.99	3.836(3)	146.6

Symmetry transformations used to generate equivalent atoms:
#1 x,-y+1,z-1/2 #2 x,y+1,z #3 -x+1/2,-y+3/2,-z+1

(4,7-dichloro-9-(2,3-dihydro-1*H*-indol-1-ylcarbonyl)-1,10-phenanthrolin-2-yl)(2,3-dihydro-1*H*-indol-1-yl)methanone 3f

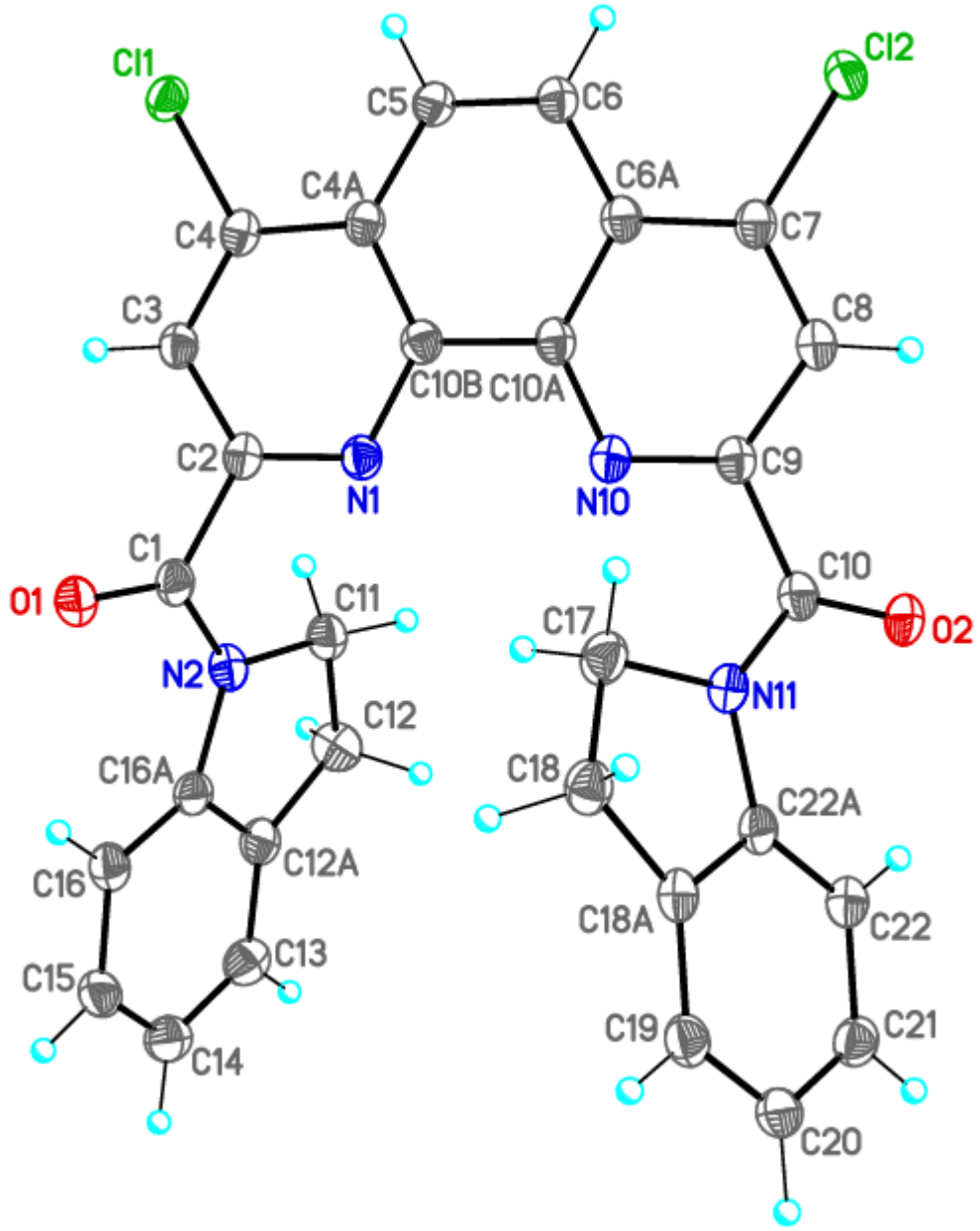


Table S23. Crystal data and structure refinement for **3f**.

Identification code	**3f**	
Empirical formula	C30 H20 Cl2 N4 O2	
Formula weight	539.40	
Temperature	100(2) K	
Wavelength	0.79272 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 7.2410(14) Å	α = 103.259(14)°.
	b = 11.680(2) Å	β = 95.030(2)°.
	c = 14.506(3) Å	γ = 97.662(18)°.
Volume	1174.6(4) Å^3	

Z	2
Density (calculated)	1.525 Mg/m^3
Absorption coefficient	0.420 mm^{-1}
F(000)	556
Crystal size	0.15 x 0.05 x 0.05 mm^3
Theta range for data collection	1.621 to 30.956°.
Index ranges	-9<=h<=9, -15<=k<=15, -18<=l<=17
Reflections collected	18379
Independent reflections	5233 [R(int) = 0.0782]
Completeness to theta = 28.401°	97.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.970 and 0.930
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5233 / 0 / 344
Goodness-of-fit on F^2	1.021
Final R indices [for 3967 rflns with I>2σ(I)]	R1 = 0.0593, wR2 = 0.1400
R indices (all data)	R1 = 0.0796, wR2 = 0.1531
Extinction coefficient	0.0017(2)
Largest diff. peak and hole	0.556 and -0.591 e.$Å^{-3}$

Table S24. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **3f**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
Cl(1)	8479(1)	1751(1)	4525(1)	28(1)
Cl(2)	6572(1)	7792(1)	7018(1)	29(1)
O(1)	10198(3)	3311(2)	1305(1)	32(1)
O(2)	4792(3)	9134(2)	3699(1)	30(1)
N(1)	7817(3)	4637(2)	2970(2)	26(1)
N(2)	7145(3)	3479(2)	892(2)	28(1)
C(1)	8616(4)	3437(2)	1515(2)	26(1)
C(2)	8271(3)	3601(2)	2546(2)	26(1)
C(3)	8543(4)	2696(2)	3010(2)	26(1)
C(4)	8290(3)	2888(2)	3948(2)	26(1)
C(4A)	7872(3)	3989(2)	4459(2)	24(1)
C(5)	7711(3)	4278(2)	5457(2)	26(1)
C(6)	7339(3)	5365(2)	5908(2)	26(1)
C(6A)	7090(3)	6245(2)	5385(2)	24(1)
C(7)	6674(3)	7390(2)	5804(2)	25(1)
C(8)	6371(3)	8185(2)	5264(2)	26(1)
C(9)	6574(3)	7833(2)	4288(2)	25(1)
N(10)	6993(3)	6789(2)	3859(2)	25(1)
C(10A)	7216(3)	5999(2)	4394(2)	25(1)
C(10B)	7652(3)	4835(2)	3914(2)	25(1)
C(10)	6221(4)	8663(2)	3657(2)	25(1)
N(11)	7509(3)	8814(2)	3055(2)	26(1)
C(11)	5170(4)	3430(3)	1118(2)	31(1)
C(12)	3971(4)	3276(3)	170(2)	37(1)
C(12A)	5367(4)	3439(2)	-511(2)	30(1)
C(13)	5087(4)	3531(2)	-1444(2)	33(1)
C(14)	6624(4)	3704(2)	-1935(2)	35(1)
C(15)	8424(4)	3780(2)	-1488(2)	33(1)
C(16)	8742(4)	3668(2)	-555(2)	31(1)
C(16A)	7194(4)	3513(2)	-75(2)	27(1)
C(17)	9368(4)	8404(3)	3084(2)	32(1)
C(18)	10530(4)	9148(2)	2526(2)	30(1)
C(18A)	9052(4)	9594(2)	1963(2)	27(1)
C(19)	9212(4)	10137(2)	1216(2)	30(1)
C(20)	7629(4)	10504(2)	827(2)	31(1)
C(21)	5934(4)	10328(2)	1189(2)	30(1)
C(22)	5750(4)	9786(2)	1939(2)	28(1)
C(22A)	7334(4)	9414(2)	2317(2)	26(1)

Table S25. Bond lengths [Å] and angles [°] for **3f**.

Cl(1)-C(4)	1.738(3)	C(11)-C(12)	1.522(4)
Cl(2)-C(7)	1.726(3)	C(11)-H(11A)	0.9900
O(1)-C(1)	1.230(3)	C(11)-H(11B)	0.9900
O(2)-C(10)	1.235(3)	C(12)-C(12A)	1.498(4)
N(1)-C(2)	1.323(3)	C(12)-H(12A)	0.9900
N(1)-C(10B)	1.354(3)	C(12)-H(12B)	0.9900
N(2)-C(1)	1.349(4)	C(12A)-C(13)	1.381(4)
N(2)-C(16A)	1.416(4)	C(12A)-C(16A)	1.399(4)
N(2)-C(11)	1.492(3)	C(13)-C(14)	1.390(4)
C(1)-C(2)	1.510(4)	C(13)-H(13)	0.9500
C(2)-C(3)	1.402(4)	C(14)-C(15)	1.386(4)
C(3)-C(4)	1.360(4)	C(14)-H(14)	0.9500
C(3)-H(3)	0.9500	C(15)-C(16)	1.392(4)
C(4)-C(4A)	1.415(3)	C(15)-H(15)	0.9500
C(4A)-C(10B)	1.416(4)	C(16)-C(16A)	1.383(4)
C(4A)-C(5)	1.428(4)	C(16)-H(16)	0.9500
C(5)-C(6)	1.362(4)	C(17)-C(18)	1.537(4)
C(5)-H(5)	0.9500	C(17)-H(17A)	0.9900
C(6)-C(6A)	1.431(4)	C(17)-H(17B)	0.9900
C(6)-H(6)	0.9500	C(18)-C(18A)	1.508(4)
C(6A)-C(10A)	1.414(4)	C(18)-H(18A)	0.9900
C(6A)-C(7)	1.419(3)	C(18)-H(18B)	0.9900
C(7)-C(8)	1.372(4)	C(18A)-C(19)	1.381(4)
C(8)-C(9)	1.408(4)	C(18A)-C(22A)	1.395(4)
C(8)-H(8)	0.9500	C(19)-C(20)	1.395(4)
C(9)-N(10)	1.322(3)	C(19)-H(19)	0.9500
C(9)-C(10)	1.508(4)	C(20)-C(21)	1.385(4)
N(10)-C(10A)	1.352(3)	C(20)-H(20)	0.9500
C(10A)-C(10B)	1.466(3)	C(21)-C(22)	1.386(4)
C(10)-N(11)	1.354(3)	C(21)-H(21)	0.9500
N(11)-C(22A)	1.414(3)	C(22)-C(22A)	1.392(4)
N(11)-C(17)	1.488(3)	C(22)-H(22)	0.9500

C(2)-N(1)-C(10B)	117.4(2)
C(1)-N(2)-C(16A)	126.4(2)
C(1)-N(2)-C(11)	124.0(2)
C(16A)-N(2)-C(11)	109.5(2)
O(1)-C(1)-N(2)	124.7(3)
O(1)-C(1)-C(2)	118.9(2)
N(2)-C(1)-C(2)	116.4(2)
N(1)-C(2)-C(3)	124.0(2)
N(1)-C(2)-C(1)	116.7(2)
C(3)-C(2)-C(1)	119.3(2)
C(4)-C(3)-C(2)	117.9(2)
C(4)-C(3)-H(3)	121.0
C(2)-C(3)-H(3)	121.0
C(3)-C(4)-C(4A)	121.3(2)
C(3)-C(4)-Cl(1)	119.10(19)
C(4A)-C(4)-Cl(1)	119.5(2)
C(4)-C(4A)-C(10B)	115.3(2)
C(4)-C(4A)-C(5)	124.3(2)
C(10B)-C(4A)-C(5)	120.5(2)
C(6)-C(5)-C(4A)	121.2(2)
C(6)-C(5)-H(5)	119.4
C(4A)-C(5)-H(5)	119.4
C(5)-C(6)-C(6A)	120.3(2)
C(5)-C(6)-H(6)	119.9
C(6A)-C(6)-H(6)	119.9
C(10A)-C(6A)-C(7)	115.9(2)
C(10A)-C(6A)-C(6)	120.7(2)
C(7)-C(6A)-C(6)	123.4(2)
C(8)-C(7)-C(6A)	121.2(2)
C(8)-C(7)-Cl(2)	119.5(2)
C(6A)-C(7)-Cl(2)	119.3(2)
C(7)-C(8)-C(9)	117.0(2)
C(7)-C(8)-H(8)	121.5
C(9)-C(8)-H(8)	121.5
N(10)-C(9)-C(8)	124.7(2)
N(10)-C(9)-C(10)	116.1(2)
C(8)-C(9)-C(10)	119.2(2)
C(9)-N(10)-C(10A)	117.6(2)
N(10)-C(10A)-C(6A)	123.6(2)
N(10)-C(10A)-C(10B)	117.5(2)
C(6A)-C(10A)-C(10B)	118.9(2)
N(1)-C(10B)-C(4A)	123.9(2)

N(1)-C(10B)-C(10A)	117.6(2)
C(4A)-C(10B)-C(10A)	118.5(2)
O(2)-C(10)-N(11)	124.3(2)
O(2)-C(10)-C(9)	119.4(2)
N(11)-C(10)-C(9)	116.3(2)
C(10)-N(11)-C(22A)	125.7(2)
C(10)-N(11)-C(17)	125.3(2)
C(22A)-N(11)-C(17)	108.9(2)
N(2)-C(11)-C(12)	105.5(2)
N(2)-C(11)-H(11A)	110.6
C(12)-C(11)-H(11A)	110.6
N(2)-C(11)-H(11B)	110.6
C(12)-C(11)-H(11B)	110.6
H(11A)-C(11)-H(11B)	108.8
C(12A)-C(12)-C(11)	104.2(2)
C(12A)-C(12)-H(12A)	110.9
C(11)-C(12)-H(12A)	110.9
C(12A)-C(12)-H(12B)	110.9
C(11)-C(12)-H(12B)	110.9
H(12A)-C(12)-H(12B)	108.9
C(13)-C(12A)-C(16A)	119.5(3)
C(13)-C(12A)-C(12)	130.0(3)
C(16A)-C(12A)-C(12)	110.5(2)
C(12A)-C(13)-C(14)	119.6(3)
C(12A)-C(13)-H(13)	120.2
C(14)-C(13)-H(13)	120.2
C(15)-C(14)-C(13)	119.9(3)
C(15)-C(14)-H(14)	120.0
C(13)-C(14)-H(14)	120.0
C(14)-C(15)-C(16)	121.6(3)
C(14)-C(15)-H(15)	119.2
C(16)-C(15)-H(15)	119.2
C(16A)-C(16)-C(15)	117.5(3)
C(16A)-C(16)-H(16)	121.2
C(15)-C(16)-H(16)	121.2
C(16)-C(16A)-C(12A)	121.8(3)
C(16)-C(16A)-N(2)	128.6(3)
C(12A)-C(16A)-N(2)	109.5(2)
N(11)-C(17)-C(18)	104.6(2)
N(11)-C(17)-H(17A)	110.8
C(18)-C(17)-H(17A)	110.8
N(11)-C(17)-H(17B)	110.8

C(18)-C(17)-H(17B)	110.8
H(17A)-C(17)-H(17B)	108.9
C(18A)-C(18)-C(17)	103.0(2)
C(18A)-C(18)-H(18A)	111.2
C(17)-C(18)-H(18A)	111.2
C(18A)-C(18)-H(18B)	111.2
C(17)-C(18)-H(18B)	111.2
H(18A)-C(18)-H(18B)	109.1
C(19)-C(18A)-C(22A)	120.4(2)
C(19)-C(18A)-C(18)	129.6(2)
C(22A)-C(18A)-C(18)	110.0(2)
C(18A)-C(19)-C(20)	118.7(3)
C(18A)-C(19)-H(19)	120.6
C(20)-C(19)-H(19)	120.6
C(21)-C(20)-C(19)	120.3(3)
C(21)-C(20)-H(20)	119.8
C(19)-C(20)-H(20)	119.8
C(20)-C(21)-C(22)	121.7(3)
C(20)-C(21)-H(21)	119.2
C(22)-C(21)-H(21)	119.2
C(21)-C(22)-C(22A)	117.5(3)
C(21)-C(22)-H(22)	121.2
C(22A)-C(22)-H(22)	121.2
C(22)-C(22A)-C(18A)	121.3(2)
C(22)-C(22A)-N(11)	128.8(2)
C(18A)-C(22A)-N(11)	109.9(2)

Table S26. Anisotropic displacement parameters ($Å^2$ x 10^3) for **3f**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	32(1)	23(1)	31(1)	7(1)	3(1)	8(1)
Cl(2)	33(1)	27(1)	26(1)	2(1)	7(1)	8(1)
O(1)	31(1)	35(1)	33(1)	7(1)	7(1)	12(1)
O(2)	28(1)	30(1)	35(1)	7(1)	7(1)	13(1)
N(1)	26(1)	24(1)	25(1)	3(1)	2(1)	6(1)
N(2)	27(1)	29(1)	30(1)	4(1)	7(1)	9(1)
C(1)	29(1)	20(1)	30(1)	3(1)	6(1)	6(1)
C(2)	24(1)	24(1)	29(1)	4(1)	3(1)	6(1)
C(3)	27(1)	24(1)	28(1)	3(1)	3(1)	7(1)
C(4)	22(1)	25(1)	31(2)	6(1)	3(1)	6(1)
C(4A)	20(1)	23(1)	28(1)	4(1)	2(1)	4(1)
C(5)	24(1)	26(1)	27(1)	6(1)	3(1)	5(1)
C(6)	24(1)	26(1)	27(1)	5(1)	4(1)	6(1)
C(6A)	21(1)	24(1)	27(1)	4(1)	3(1)	3(1)
C(7)	22(1)	24(1)	29(1)	4(1)	3(1)	4(1)
C(8)	24(1)	22(1)	29(1)	2(1)	5(1)	5(1)
C(9)	22(1)	24(1)	27(1)	3(1)	3(1)	5(1)
N(10)	24(1)	22(1)	28(1)	4(1)	2(1)	5(1)
C(10A)	21(1)	24(1)	27(1)	2(1)	3(1)	4(1)
C(10B)	21(1)	27(1)	26(1)	6(1)	3(1)	4(1)
C(10)	24(1)	23(1)	26(1)	1(1)	3(1)	5(1)
N(11)	26(1)	22(1)	29(1)	4(1)	4(1)	7(1)
C(11)	27(1)	33(1)	33(2)	7(1)	7(1)	9(1)
C(12)	30(1)	41(2)	36(2)	7(1)	1(1)	1(1)
C(12A)	34(1)	20(1)	32(2)	2(1)	4(1)	5(1)
C(13)	37(2)	26(1)	34(2)	5(1)	-2(1)	3(1)
C(14)	49(2)	25(1)	29(2)	4(1)	3(1)	6(1)
C(15)	42(2)	28(1)	31(2)	5(1)	12(1)	9(1)
C(16)	33(1)	29(1)	31(2)	4(1)	6(1)	10(1)
C(16A)	36(1)	19(1)	26(1)	2(1)	3(1)	7(1)
C(17)	26(1)	35(1)	40(2)	13(1)	7(1)	12(1)
C(18)	25(1)	30(1)	37(2)	8(1)	7(1)	6(1)
C(18A)	27(1)	22(1)	30(1)	1(1)	5(1)	7(1)
C(19)	33(1)	25(1)	30(2)	3(1)	8(1)	6(1)
C(20)	42(2)	25(1)	26(1)	3(1)	6(1)	7(1)
C(21)	35(1)	25(1)	29(2)	4(1)	1(1)	8(1)
C(22)	27(1)	25(1)	30(1)	3(1)	3(1)	7(1)
C(22A)	29(1)	20(1)	27(1)	1(1)	5(1)	6(1)

Table S27. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **3f**.

Atom	x	y	z	U(iso)
H(3)	8894	1972	2679	32
H(5)	7867	3701	5812	31
H(6)	7244	5540	6574	31
H(8)	6040	8939	5537	31
H(11A)	5016	4174	1573	37
H(11B)	4814	2750	1402	37
H(12A)	3204	2473	-34	44
H(12B)	3126	3881	215	44
H(13)	3851	3476	-1748	40
H(14)	6441	3769	-2577	42
H(15)	9466	3913	-1826	40
H(16)	9976	3696	-259	37
H(17A)	9237	7543	2777	39
H(17B)	9963	8551	3750	39
H(18A)	11396	9818	2964	36
H(18B)	11265	8651	2098	36
H(19)	10379	10258	972	35
H(20)	7713	10876	312	37
H(21)	4871	10585	916	36
H(22)	4585	9673	2187	34

Table S28. Torsion angles [°] for **3f**.

C(16A)-N(2)-C(1)-O(1)	-7.1(4)
C(11)-N(2)-C(1)-O(1)	169.5(2)
C(16A)-N(2)-C(1)-C(2)	170.7(2)
C(11)-N(2)-C(1)-C(2)	-12.7(4)
C(10B)-N(1)-C(2)-C(3)	1.6(4)
C(10B)-N(1)-C(2)-C(1)	-174.8(2)
O(1)-C(1)-C(2)-N(1)	115.4(3)
N(2)-C(1)-C(2)-N(1)	-62.6(3)
O(1)-C(1)-C(2)-C(3)	-61.2(3)
N(2)-C(1)-C(2)-C(3)	120.9(3)
N(1)-C(2)-C(3)-C(4)	1.3(4)
C(1)-C(2)-C(3)-C(4)	177.6(2)
C(2)-C(3)-C(4)-C(4A)	-3.6(4)
C(2)-C(3)-C(4)-Cl(1)	176.23(19)
C(3)-C(4)-C(4A)-C(10B)	2.9(4)
Cl(1)-C(4)-C(4A)-C(10B)	-176.89(18)
C(3)-C(4)-C(4A)-C(5)	-175.7(2)
Cl(1)-C(4)-C(4A)-C(5)	4.5(4)
C(4)-C(4A)-C(5)-C(6)	178.8(2)
C(10B)-C(4A)-C(5)-C(6)	0.2(4)
C(4A)-C(5)-C(6)-C(6A)	0.3(4)
C(5)-C(6)-C(6A)-C(10A)	0.3(4)
C(5)-C(6)-C(6A)-C(7)	179.1(2)
C(10A)-C(6A)-C(7)-C(8)	1.6(4)
C(6)-C(6A)-C(7)-C(8)	-177.3(2)
C(10A)-C(6A)-C(7)-Cl(2)	-177.78(18)
C(6)-C(6A)-C(7)-Cl(2)	3.4(3)
C(6A)-C(7)-C(8)-C(9)	-2.7(4)
Cl(2)-C(7)-C(8)-C(9)	176.63(19)
C(7)-C(8)-C(9)-N(10)	1.4(4)
C(7)-C(8)-C(9)-C(10)	178.9(2)
C(8)-C(9)-N(10)-C(10A)	1.1(4)
C(10)-C(9)-N(10)-C(10A)	-176.4(2)
C(9)-N(10)-C(10A)-C(6A)	-2.3(4)
C(9)-N(10)-C(10A)-C(10B)	179.1(2)
C(7)-C(6A)-C(10A)-N(10)	1.1(4)
C(6)-C(6A)-C(10A)-N(10)	179.9(2)
C(7)-C(6A)-C(10A)-C(10B)	179.6(2)
C(6)-C(6A)-C(10A)-C(10B)	-1.5(4)
C(2)-N(1)-C(10B)-C(4A)	-2.3(4)

C(2)-N(1)-C(10B)-C(10A)	177.8(2)
C(4)-C(4A)-C(10B)-N(1)	0.1(4)
C(5)-C(4A)-C(10B)-N(1)	178.8(2)
C(4)-C(4A)-C(10B)-C(10A)	180.0(2)
C(5)-C(4A)-C(10B)-C(10A)	-1.3(4)
N(10)-C(10A)-C(10B)-N(1)	0.5(3)
C(6A)-C(10A)-C(10B)-N(1)	-178.2(2)
N(10)-C(10A)-C(10B)-C(4A)	-179.4(2)
C(6A)-C(10A)-C(10B)-C(4A)	2.0(4)
N(10)-C(9)-C(10)-O(2)	130.1(3)
C(8)-C(9)-C(10)-O(2)	-47.5(4)
N(10)-C(9)-C(10)-N(11)	-48.2(3)
C(8)-C(9)-C(10)-N(11)	134.1(2)
O(2)-C(10)-N(11)-C(22A)	-7.5(4)
C(9)-C(10)-N(11)-C(22A)	170.8(2)
O(2)-C(10)-N(11)-C(17)	170.7(3)
C(9)-C(10)-N(11)-C(17)	-11.1(4)
C(1)-N(2)-C(11)-C(12)	-170.0(2)
C(16A)-N(2)-C(11)-C(12)	7.1(3)
N(2)-C(11)-C(12)-C(12A)	-8.6(3)
C(11)-C(12)-C(12A)-C(13)	-171.7(3)
C(11)-C(12)-C(12A)-C(16A)	7.5(3)
C(16A)-C(12A)-C(13)-C(14)	-0.4(4)
C(12)-C(12A)-C(13)-C(14)	178.8(3)
C(12A)-C(13)-C(14)-C(15)	0.1(4)
C(13)-C(14)-C(15)-C(16)	1.1(4)
C(14)-C(15)-C(16)-C(16A)	-2.0(4)
C(15)-C(16)-C(16A)-C(12A)	1.7(4)
C(15)-C(16)-C(16A)-N(2)	-174.1(2)
C(13)-C(12A)-C(16A)-C(16)	-0.6(4)
C(12)-C(12A)-C(16A)-C(16)	-179.9(2)
C(13)-C(12A)-C(16A)-N(2)	176.0(2)
C(12)-C(12A)-C(16A)-N(2)	-3.3(3)
C(1)-N(2)-C(16A)-C(16)	-9.3(4)
C(11)-N(2)-C(16A)-C(16)	173.7(3)
C(1)-N(2)-C(16A)-C(12A)	174.5(2)
C(11)-N(2)-C(16A)-C(12A)	-2.5(3)
C(10)-N(11)-C(17)-C(18)	-160.7(2)
C(22A)-N(11)-C(17)-C(18)	17.7(3)
N(11)-C(17)-C(18)-C(18A)	-18.4(3)
C(17)-C(18)-C(18A)-C(19)	-167.8(3)
C(17)-C(18)-C(18A)-C(22A)	13.7(3)

C(22A)-C(18A)-C(19)-C(20)	0.2(4)
C(18)-C(18A)-C(19)-C(20)	-178.1(3)
C(18A)-C(19)-C(20)-C(21)	0.2(4)
C(19)-C(20)-C(21)-C(22)	-0.2(4)
C(20)-C(21)-C(22)-C(22A)	-0.4(4)
C(21)-C(22)-C(22A)-C(18A)	0.9(4)
C(21)-C(22)-C(22A)-N(11)	-178.0(2)
C(19)-C(18A)-C(22A)-C(22)	-0.8(4)
C(18)-C(18A)-C(22A)-C(22)	177.8(2)
C(19)-C(18A)-C(22A)-N(11)	178.2(2)
C(18)-C(18A)-C(22A)-N(11)	-3.1(3)
C(10)-N(11)-C(22A)-C(22)	-12.2(4)
C(17)-N(11)-C(22A)-C(22)	169.4(3)
C(10)-N(11)-C(22A)-C(18A)	168.8(2)
C(17)-N(11)-C(22A)-C(18A)	-9.5(3)

Table S29. Hydrogen bonds for **3f** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(8)-H(8)...O(2)#1	0.95	2.45	3.397(3)	177.7
C(11)-H(11B)...Cl(2)#2	0.99	2.75	3.580(3)	141.9
C(16)-H(16)...O(1)	0.95	2.41	2.949(4)	115.9
C(17)-H(17B)...Cl(1)#3	0.99	2.77	3.729(3)	163.4
C(18)-H(18A)...Cl(2)#4	0.99	2.97	3.780(3)	139.7
C(22)-H(22)...O(2)	0.95	2.42	2.939(3)	114.5

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+2,-z+1 #2 -x+1,-y+1,-z+1 #3 -x+2,-y+1,-z+1

#4 -x+2,-y+2,-z+1

Table S30. Selected bond lengths and angles in crystal structures of **1·DMF·H_2O**, **3a**, **3b·H_2O** and **3f**.

Atoms	Bond (Å) / angle (°)	Atoms	Angle (°)
1·DMF·H_2O			
C11–O1	1.218(2)	N1–C2–C11–O1	-4.3(2)
C11–O2	1.302(2)	N1–C2–C11–O2	176.0(1)
C12–O3	1.211(2)	N10–C9–C12–O4	8.52(2)
C12–O4	1.306(2)	N10–C9–C12–O3	-170.3(1)
3a			
C1–O1	1.220(3)	C2–C1–N2–C11	11.5(3)
C1–N2	1.328(3)	O1–C1–C2–C3	45.4(3)
C10–O2	1.223(3)	N2–C1–C2–N1	49.9(3)
C10–N11	1.333(3)	C9–C10–N11–C20	-9.7(3)
C11–N2–C14	111.7(2)	O2–C10–N11–C17	-2.0(3)
C17–N11–C20	110.8(2)	N10–C9–C10–N11	-39.1(3)
O1–C1–N2–C14	-0.3(3)	C8–C9–C10–O2	-35.4(3)
3b·H_2O			
C1–O1	1.245(3)	C2–C1–N2–C11	8.7(4)
C1–N2	1.341(3)	O1–C1–C2–C3	41.2(3)
C10–O2	1.222(3)	N2–C1–C2–N1	45.9(3)
C10–N11	1.332(3)	C9–C10–N11–C21	12.4(4)
C11–N2–C15	113.3(2)	O2–C10–N11–C17	-6.5(4)
C17–N11–C21	112.9(2)	N10–C9–C10–N11	-88.7(3)
O1–C1–N2–C15	0.4(4)	C8–C9–C10–O2	-81.8(3)
3f			
C1–O1	1.230(3)	C2–C1–N2–C11	-12.7(4)
C1–N2	1.349(4)	N2–C1–C2–N1	-62.6(3)
C10–O2	1.235(3)	O1–C1–C2–C3	-61.2(3)
C10–N11	1.354(3)	O2–C10–N11–C22A	-7.5(4)
C11–N2–C16A	109.5(2)	C9–C10–N11–C17	-11.1(4)
C17–N11–C22A	108.9(2)	N10–C9–C10–N11	-48.2(4)
O1–C1–N2–C16A	-7.1(4)	C8–C9–C10–O2	-47.5(3)

Appendix A.

Table S31. ^{13}C NMR chemical shifts for C=O carbon atoms and absorption maxima of the band of valence vibrations of C(O) groups in the IR spectra of compounds **3a-c** and **3f-g** in crystalline state and solutions.

Compound	NMR ^{13}C ($CDCl_3$), $\delta_{\underline{C}=O}$, ppm	$\nu_{C=O\ max}$ in solid, cm^{-1}	$\nu_{C=O\ max}$ in CCl_4, cm^{-1}
3a	164.9	1622	1634
3b	166.0	1627	1638
3c	167.6	1631	1636
3f	164.6	1639	1649
3g	166.9	1638	1647
3h	N/A	1674	1674

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