

# Supporting Information

## **Spin-Crossover Tuning in Synergistic Luminescent Fe(II) Coordination Compounds via Topochemical [4+4] Photocycloaddition of an Anthracene-Based Ligand**

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## Experimental Protocols

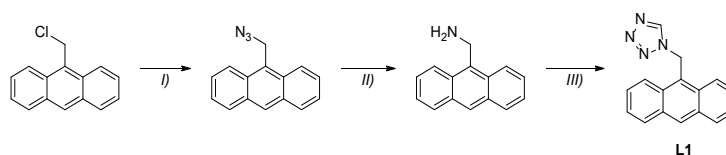
All syntheses were performed with dried glassware, anhydrous and degassed solvents, and under an atmosphere of argon. Reaction monitoring was performed by TLC, if not otherwise noted. Anthracen-9-ylmethanamine was synthesized according to a literature protocol<sup>1</sup>, all other starting materials were commercially purchased and used without further purifications if not stated otherwise. Irradiation experiments were conducted with an LX500 controller (OmniCure® spot curing system) and a 365 nm LED through quartz glass resulting in a light intensity of approx.  $7 \cdot 10^5 \mu\text{W}/\text{cm}^2$ . The light intensity was measured with an Ocean Optics 200+ device and the SpectraSuit.

### NMR Measurements

NMR measurements were performed in dry, deuterated solvents on a Bruker Avance UltraShield 400 MHz or a 600 MHz spectrometer. The recorded <sup>1</sup>H and <sup>13</sup>C spectra were referenced internally to residual proton signals, respectively, to the solvent resonances and reported relative to TMS.

### HR-MS Measurements

HR-MS measurements were performed in 10 μM solutions of CH<sub>3</sub>CN/H<sub>2</sub>O mixtures. The experimental setup consists of an Agilent G7167B multi sampler, an Agilent G7120A binary pump with a degasser, an Agilent G7116B oven, and an Agilent 6545 Q-TOF mass spectrometer equipped with a dual AJS and Multimode ion source (Agilent Technologies, Palo Alto, United States).



**Scheme 1.** Synthesis of **L1**, reagents and conditions: *i*) NaN<sub>3</sub>, DMF, 50 °C, 2 h, quant.; *ii*) Ph<sub>3</sub>P, H<sub>2</sub>O, THF, 0 °C to rt, o.n., 94.9 %; *iii*) NaN<sub>3</sub>, triethyl orthoformate, acetic acid, 65 °C, o.n., 25.7 %.

### Synthesis of 1-(anthracen-9-ylmethyl)-1H-tetrazole (**L1**)

For the following synthesis a modified literature protocol was used.<sup>2</sup>

Anthracen-9-ylmethanamine (1.77 g, 8.54 mmol, 1.00 equiv.) and NaN<sub>3</sub> (0.837 g, 12.8 mmol, 1.50 equiv.) were added to a mixture of triethyl orthoformate (2.00 g, 13.2 mmol, 1.55 equiv.) and glacial acetic acid (70.8 mL). After the reaction mixture was stirred at 65 °C over night, it was cooled to room temperature, diluted with CH<sub>2</sub>Cl<sub>2</sub> (150 mL) and poured into water (150 mL). The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 100 mL) and the combined organic phases were washed with water (1 x 100 mL). Then the organic phases were dried over MgSO<sub>4</sub> and concentrated in *vacuo* to yield an orange-yellow solid. The crude product was purified by column chromatography (approx. 400 g silica gel; mobile phase: CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>3</sub>CN = 40:1; R<sub>F</sub> = 0.33) to yield 0.576 g (25.7 %) of **L1** as off-white solid. <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ = 9.56 (s, 1H), 8.73 (s, 1H), 8.57 (d, J = 8.9 Hz, 2H), 8.15 (d, J = 8.5 Hz, 2H), 7.70 – 7.62 (m, 2H), 7.61 – 7.52 (m, 2H), 6.75 ppm (s, 2H). <sup>13</sup>C{<sup>1</sup>H}-NMR (151 MHz, DMSO-*d*<sub>6</sub>): δ = 143.8, 16, 131.0, 130.4, 129.5, 129.2, 127.3, 125.5, 124.5, 123.8, 43.8 ppm. HR-MS ESI (+) *m/z* calc. for C<sub>16</sub>H<sub>12</sub>N<sub>4</sub> [M+H]<sup>+</sup>: 261.1134, not detected. Observed fragment: C<sub>15</sub>H<sub>11</sub> [M-tetrazole]<sup>+</sup>, *m/z* calc. 191.0861, found: 191.085

### [4+4] Photocycloaddition of **L1** in Solution (Synthesis of **L2**)

A solution of **L1** (200 mg, 0.762 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was irradiated with 365 nm LED light at room temperature for 6 h. A precipitation formed which was separated from the solution and the crude product was washed with diethyl ether (4 x 12 mL) to yield 188 mg (94.7 %) of **L2** as white solid. <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ = 8.37 (s, 2H), 7.15 (d, J = 7.4 Hz, 4H), 6.90 – 6.70 (m, 12H), 6.00 (s, 4H), 4.31 ppm (s, 2H). <sup>13</sup>C{<sup>1</sup>H}-NMR (151 MHz, DMSO-*d*<sub>6</sub>): δ = 143.9, 141.8, 140.9, 128.1, 126.0, 125.7, 125.3, 59.1, 55.4, 50.3 ppm. HR-MS ESI (+) *m/z* calc. for C<sub>32</sub>H<sub>24</sub>N<sub>8</sub> [M+H]<sup>+</sup>: 521.2202, found: 521.2210.

#### [4+4] Photocycloaddition of L1 in Solid State (Synthesis of L2)

A solid-state powder sample of L1 (20.0 mg, 0.0762 mmol) was irradiated with 365 nm LED light at room temperature for 8 h. Every 30 min the powder was homogenized. The conversion rate (<sup>1</sup>H-NMR) reached a plateau after 3 h at 50 %. Due to the successful synthesis of L2 in solution, the product was not isolated.

The [4+4] photocycloaddition is quantitatively reversible by heating L2 in DMSO to 150 °C for 10 min. The solid powder of L2 is thermally stable until 175 °C.

#### Synthesis of Coordination Compound 1

Fe(ClO<sub>4</sub>)<sub>2</sub>•6H<sub>2</sub>O (17.3 mg, 0.0477 mmol, 1.00 equiv.) and a spatula tip of ascorbic acid were mixed in in CH<sub>3</sub>CN (1 mL), filtrated and added to a mixture of L1 (49.7 mg, 0.191 mmol, 4.00 equiv.) and CH<sub>3</sub>CN (2 mL). After the reaction mixture was stirred at 40 °C over night, it was cooled to room temperature, two thirds of the solvent were evaporated and diethyl ether (12 mL) was added to precipitate the yellowish crude product. The precipitation was separated from the yellow supernatant, washed with diethyl ether (3 x 6 mL) and dried in high vacuum to yield 39.0 mg (59.3 %) of 1 as off-white solid.

#### Synthesis of Coordination Compound 2 via Complexation of L1 and L2

Fe(ClO<sub>4</sub>)<sub>2</sub>•6H<sub>2</sub>O (17.3 mg, 0.0477 mmol, 1.00 equiv.) and a spatula tip of ascorbic acid were mixed in in CH<sub>3</sub>CN (1 mL), filtrated and added to a mixture of L1 (24.8 mg, 0.0953 mmol, 2.00 equiv.), L2 (24.8 mg, 0.0477 mmol, 1.00 equiv.) and CH<sub>3</sub>CN (2 mL). After the reaction mixture was stirred at 40 °C over night, it was cooled to room temperature, two thirds of the solvent were evaporated and diethyl ether (12 mL) was added to precipitate the yellowish crude product. The precipitation was separated from the yellow supernatant, washed with diethyl ether (3 x 6 mL) and dried in high vacuum to yield 40.0 mg (60.9 %) of 2 as off-white solid.

#### Synthesis of Coordination Compound 2 via Solid-State Photopolymerization

A solid-state powder sample of 1 (20.0 mg, 0.0170 mmol) was irradiated with 365 nm LED light at room temperature for 3 h. Every 30 min the powder was homogenized. According to XRPD and IR-spectroscopy the reaction was quantitative, no color change was observed.

#### Synthesis of Coordination Compound 3

Fe(ClO<sub>4</sub>)<sub>2</sub>•6H<sub>2</sub>O (17.3 mg, 0.0477 mmol, 1.00 equiv.) and a spatula tip of ascorbic acid were mixed in in CH<sub>3</sub>CN (1 mL), filtrated and added to a mixture of L2 (49.7 mg, 0.0953 mmol, 2.00 equiv.) and CH<sub>3</sub>CN (2 mL). After the reaction mixture was stirred at 40 °C over night, it was cooled to room temperature, two thirds of the solvent were evaporated and diethyl ether (12 mL) was added to precipitate the off-white crude product. The precipitation was separated from the supernatant, washed with diethyl ether (3 x 6 mL) and dried in high vacuum to yield 46.0 mg (70.0 %) of 3 as white solid.

## Spectroscopic Measurements

UV-Vis-NIR measurements were performed on a Lambda 900 spectrophotometer (PerkinElmer). Solid samples were measured in diffuse reflectance with a Harrick powder sample holder in "Praying Mantis" configuration against BaSO<sub>4</sub>. Diffuse reflectance data (R) were converted using the Kubelka-Munk function, defined as  $F(R) = \frac{(1-R)}{2R}$ .

IR spectra were recorded with a SpectrumTwo ATR-FT-IR-spectrometer (Perkin Elmer) using a diamond ATR-unit.

All PL spectra were recorded with a FluoTime 300 fluorescence lifetime spectrometer (PicoQuant) equipped with a coaxial UV-Xenon arc lamp, a high-resolution excitation and emission double monochromator, and a PMA hybrid 07 detector. Variable temperature experiments were performed using a liquid-nitrogen-filled cryostat Optistat DN connected to a Mercury ITC temperature controller (Oxford Instruments).

## Room Temperature Diffuse Reflectance and Emission Spectra

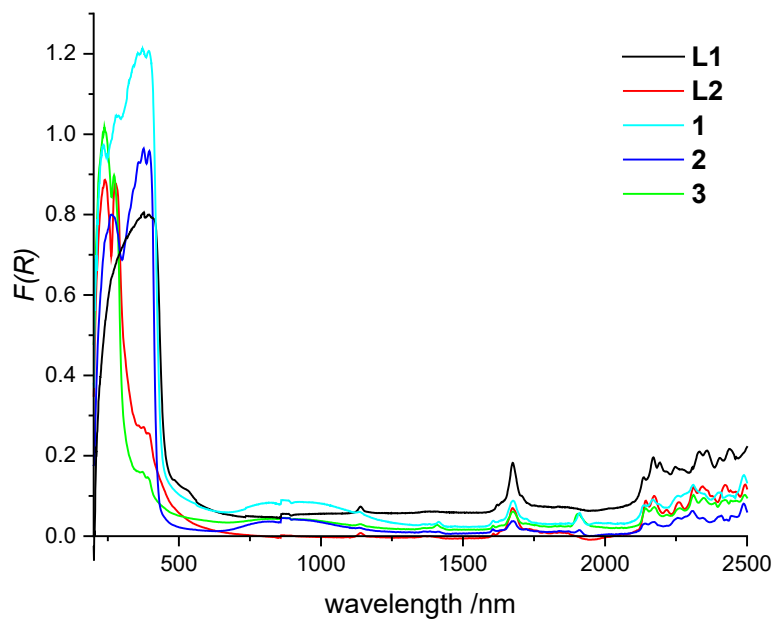


Figure S 1. UV-Vis-NIR spectra of L1, L2 and 1-3.

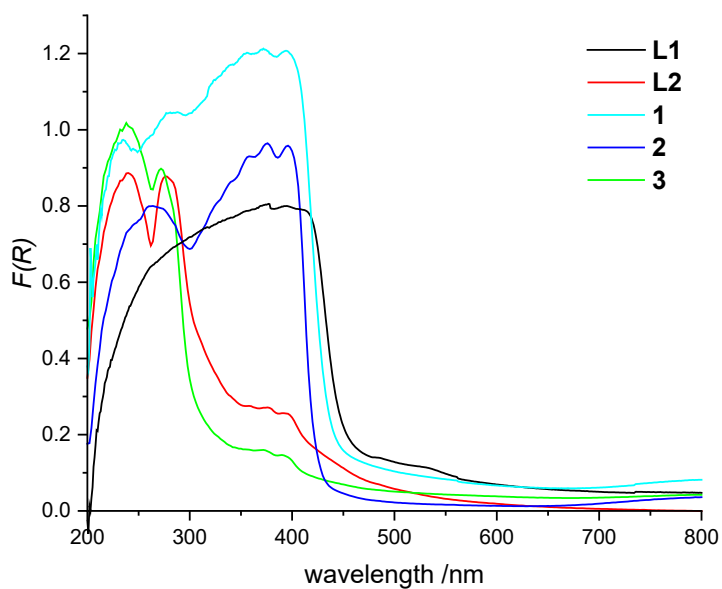
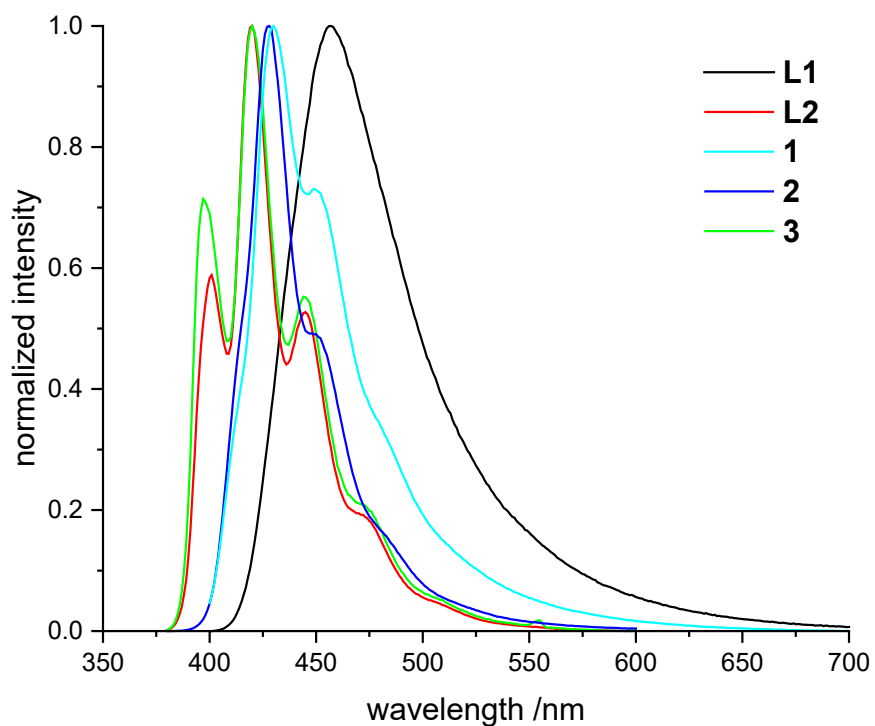
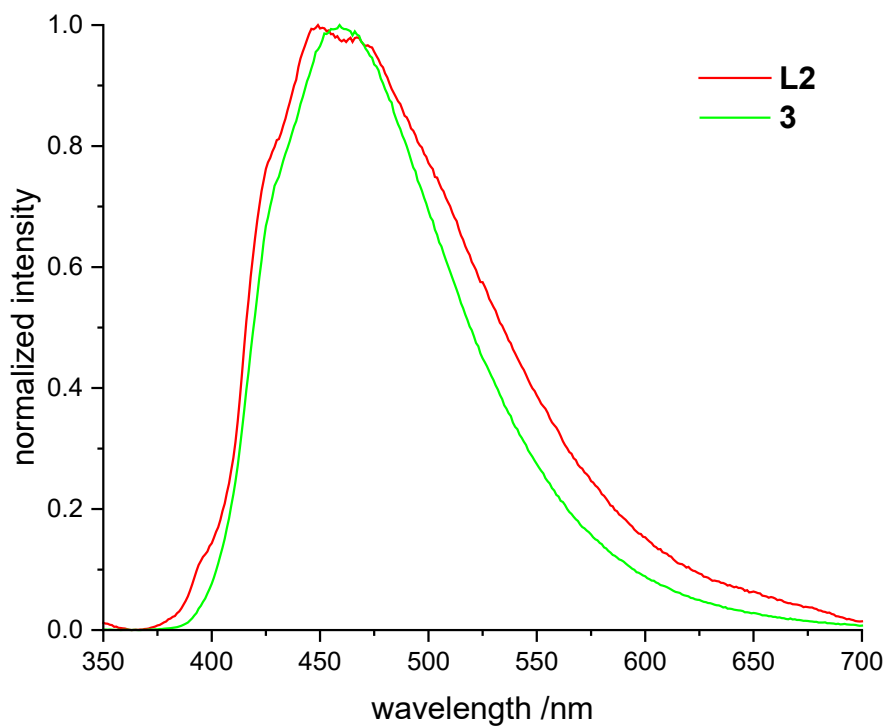


Figure S 2. UV-Vis range of L1, L2 and 1-3.



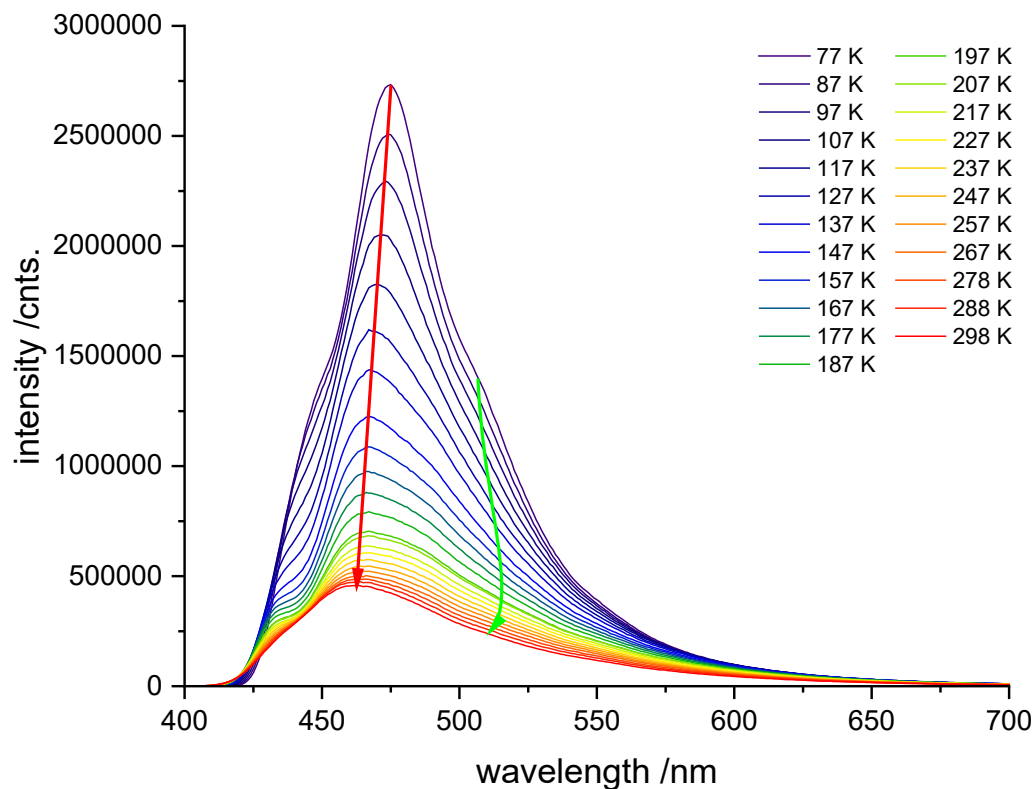
**Figure S 3.** Normalized solid state emission spectra of **L1, 1** ( $\lambda_{\text{exc.}} = 390 \text{ nm}$ ) and **L2, 2, 3** ( $\lambda_{\text{exc.}} = 370 \text{ nm}$ ).



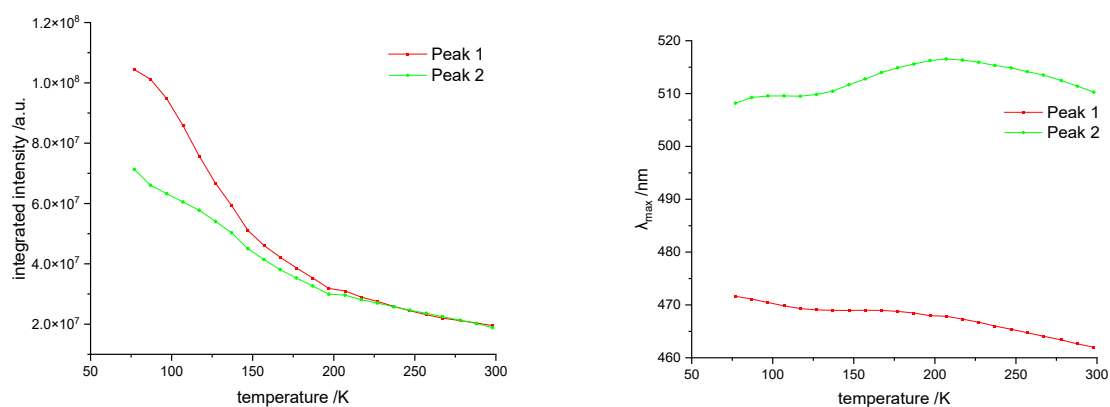
**Figure S 4.** Normalized solid state emission spectra of **L2** and **3** ( $\lambda_{\text{exc.}} = 276 \text{ nm}$ ).

# Variable-Temperature Emission Spectra

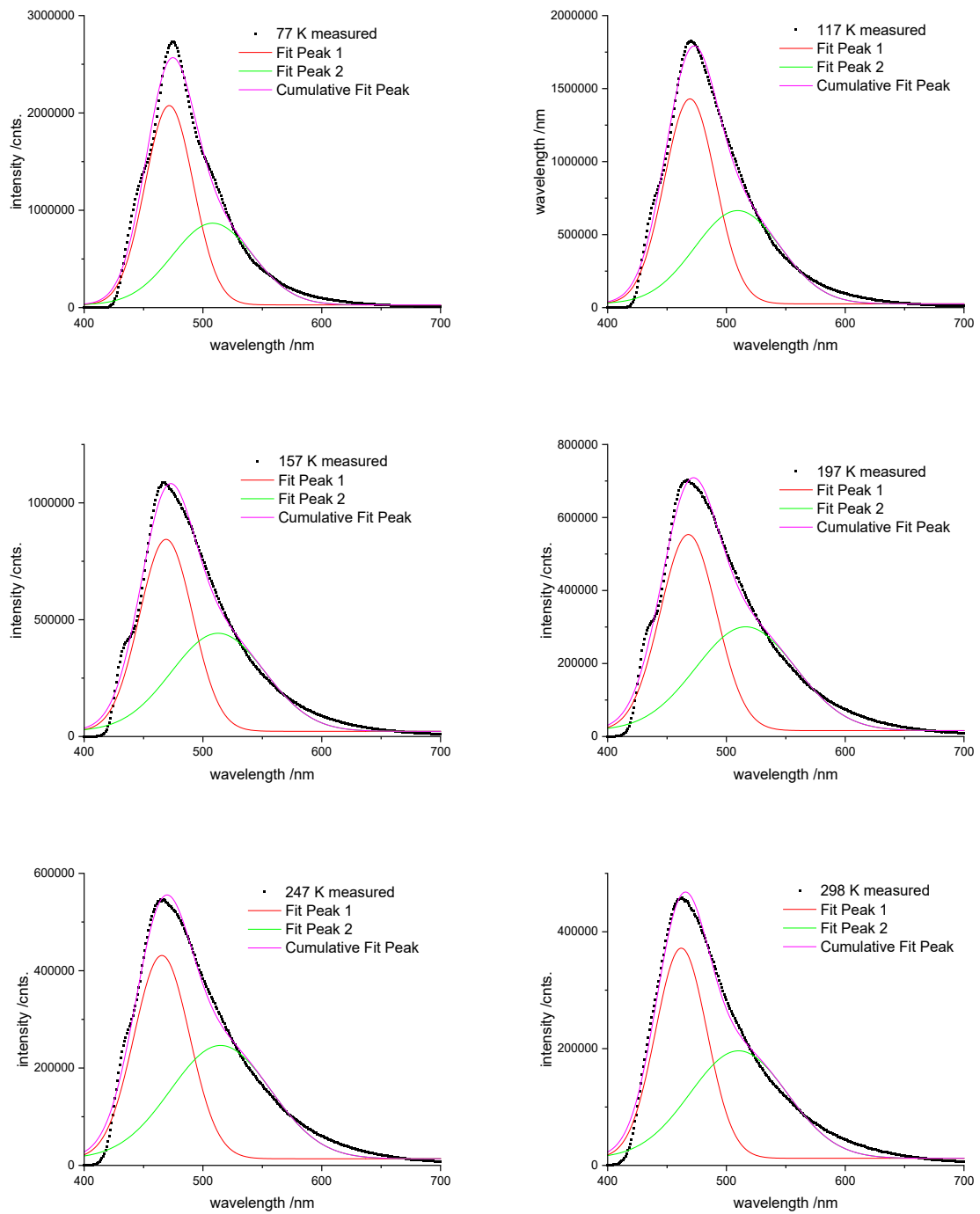
L1



**Figure S 5.** Temperature-dependent fluorescence emission spectra of L1.  $\lambda_{\text{exc.}} = 390$  nm. The colored arrows indicate the evolution of the respective fitted peaks with increasing temperature (red: Peak 1; green: Peak 2).

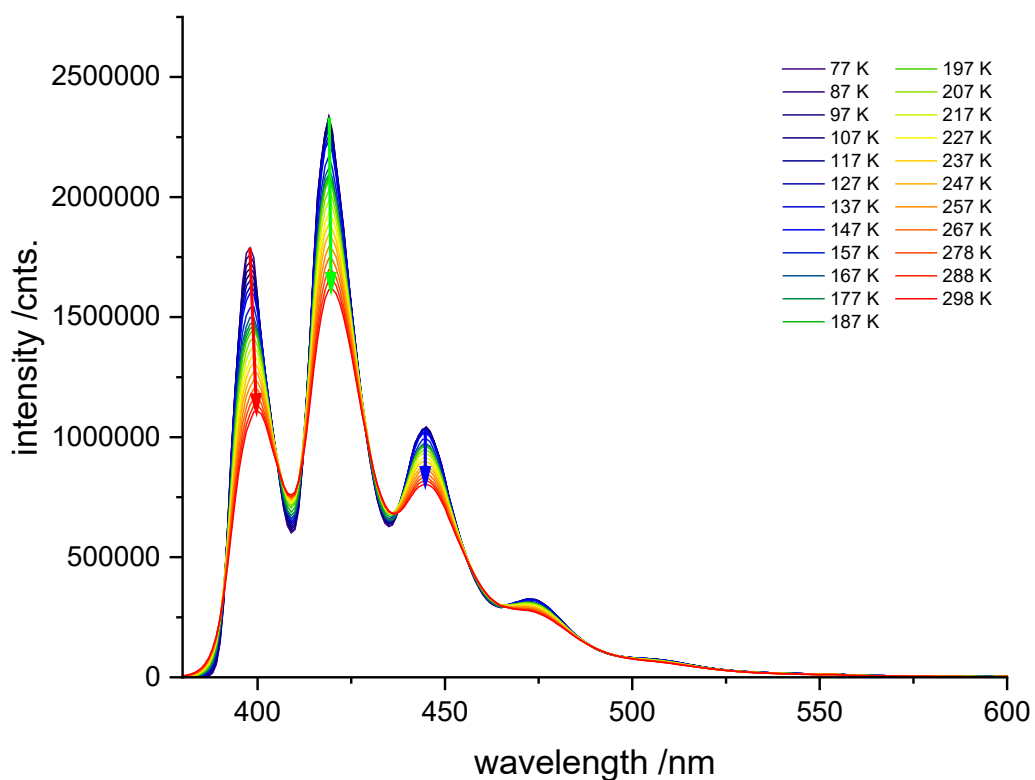


**Figure S 6.** Temperature dependence of the integrated intensity (left) and  $\lambda_{\text{max}}$  (right) of the fitted Peaks 1 and 2 for L1.

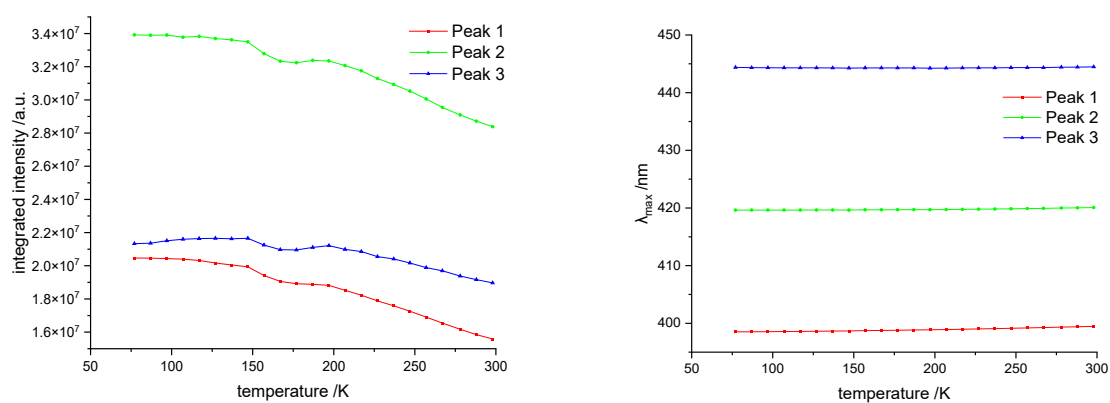


**Figure S 7.** Selected emission spectra at different temperatures of L1 fitted with two Gaussian functions.

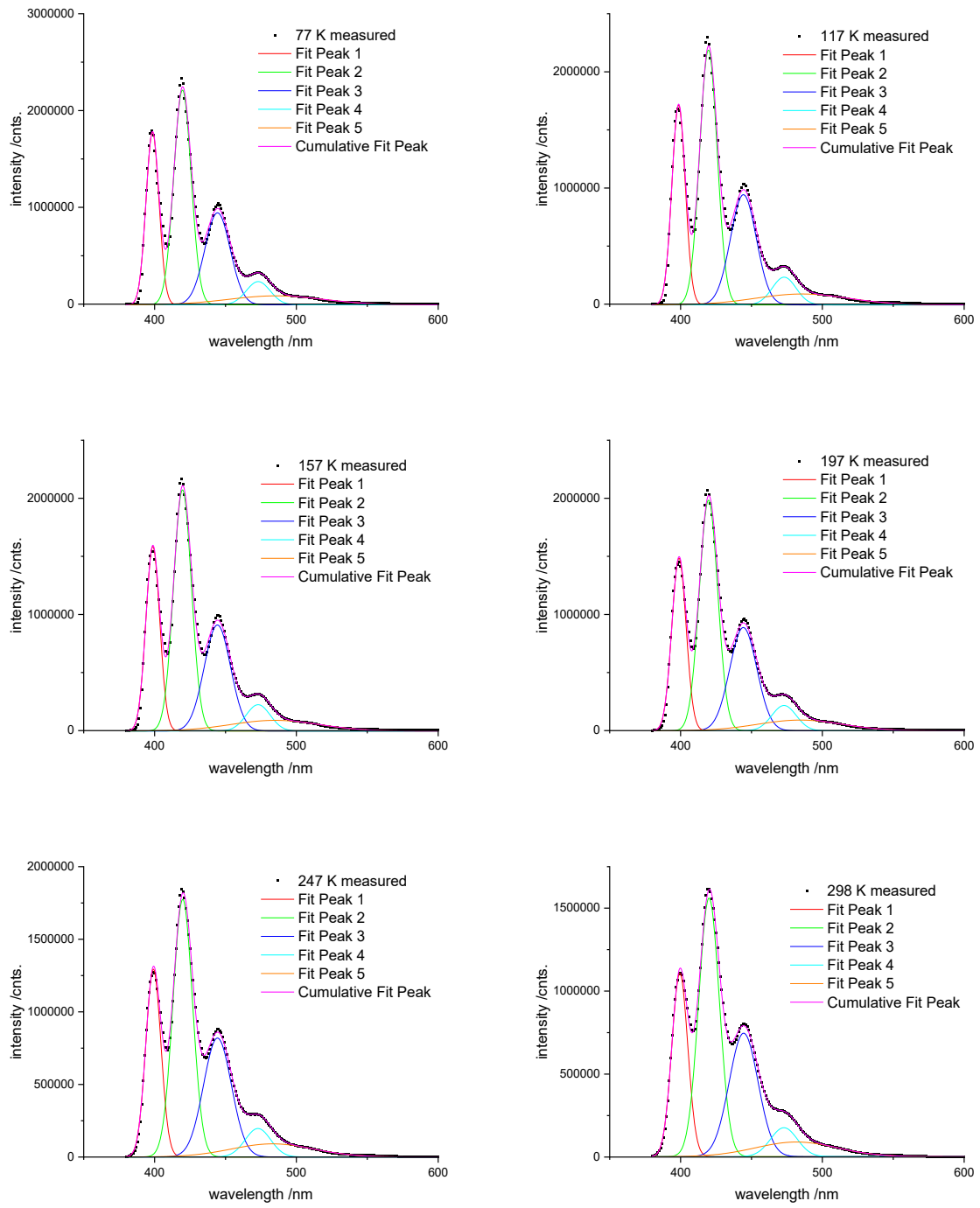
L2



**Figure S 8.** Temperature-dependent fluorescence emission spectra of **L2**.  $\lambda_{exc.} = 370$  nm. The colored arrows indicate the evolution of the respective fitted peaks with increasing temperature (red: Peak 1; green: Peak 2; blue: Peak 3).

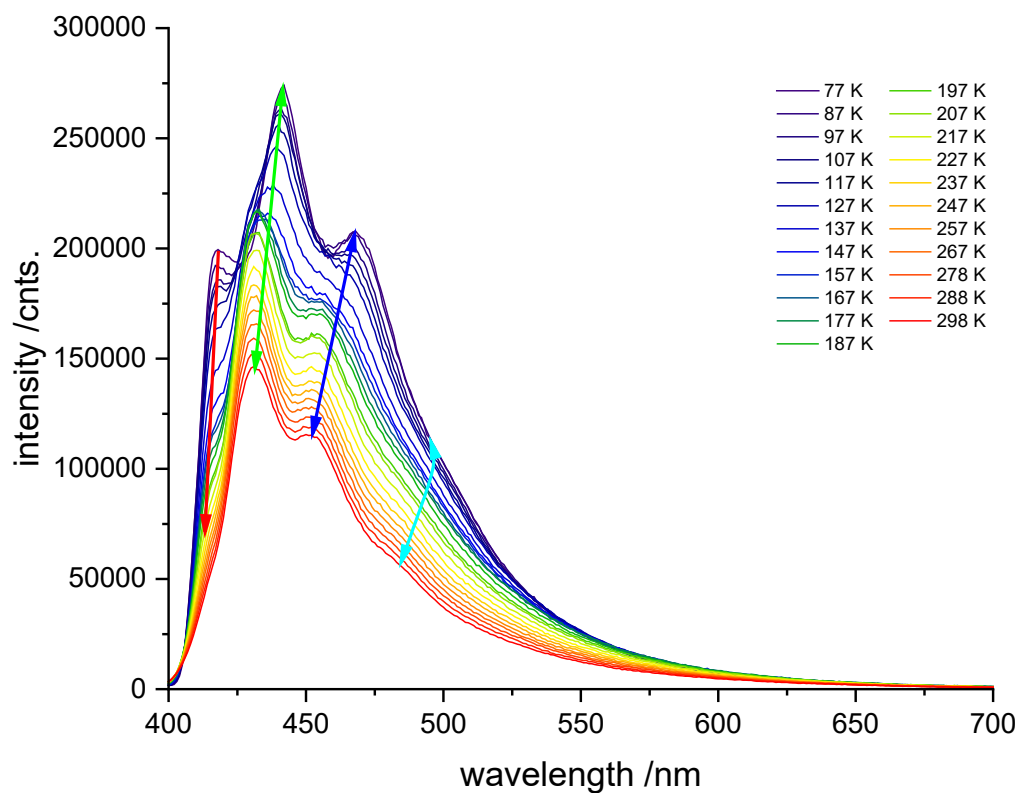


**Figure S 9.** Temperature dependence of the integrated intensity (left) and  $\lambda_{max}$  (right) of the fitted Peaks 1, 2 and 3 for **L2**.

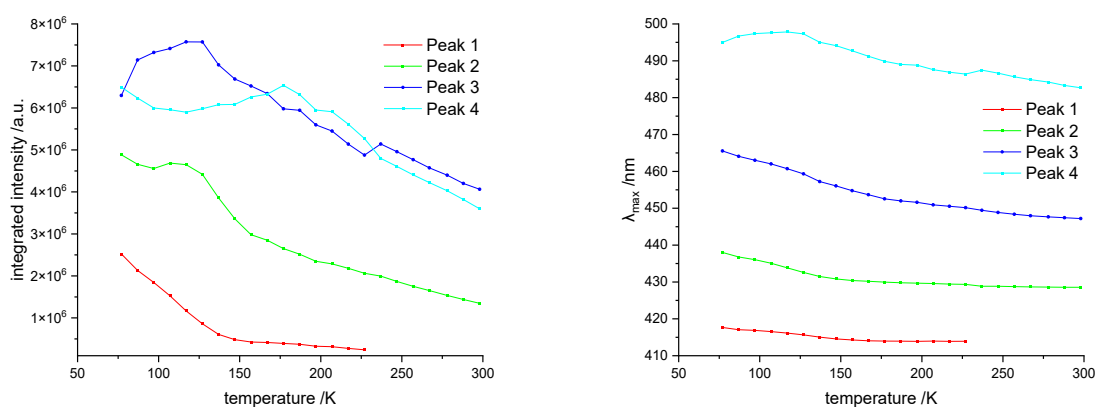


**Figure S 10.** Selected emission spectra at different temperatures of L2 fitted with five Gaussian functions.

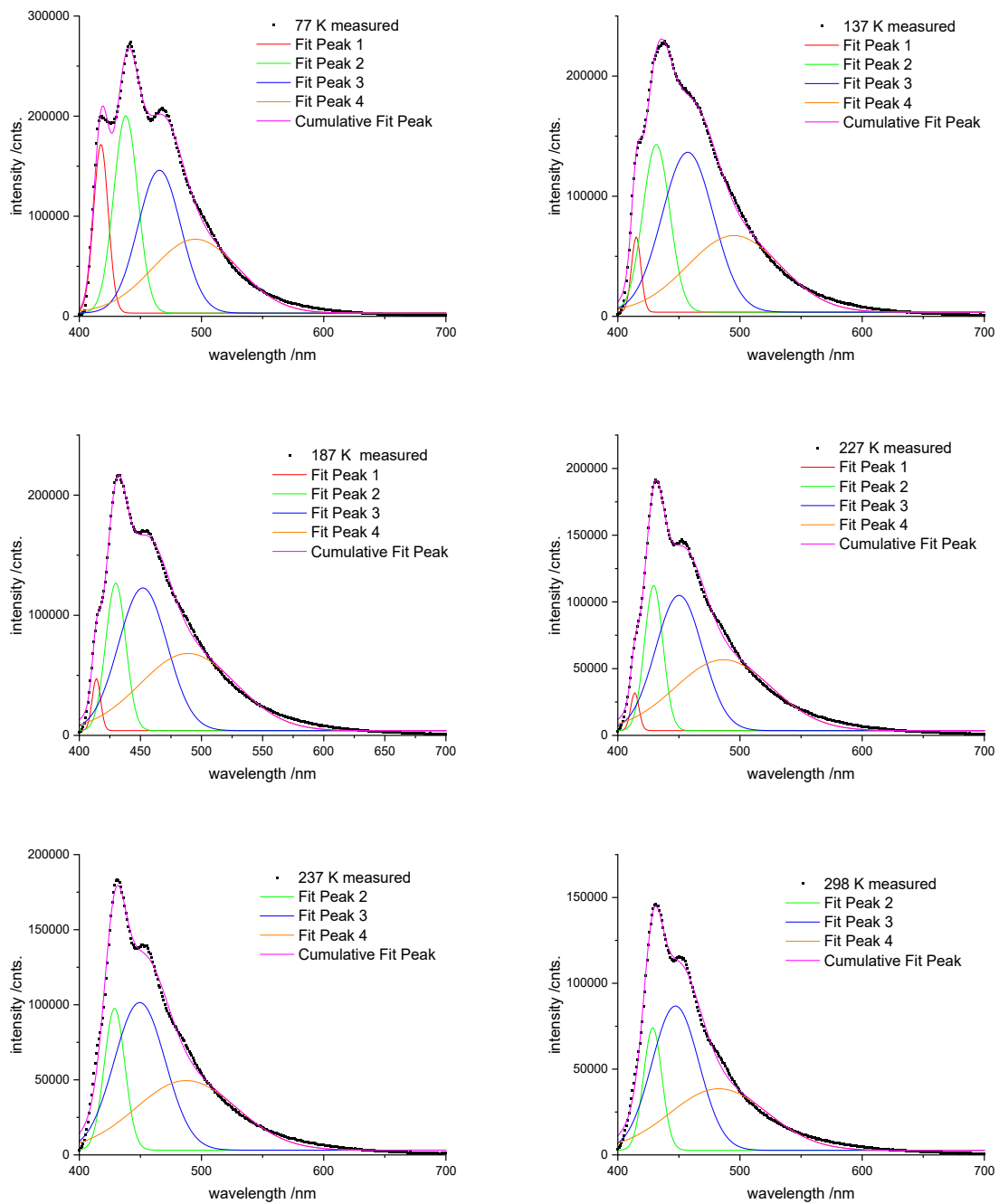
## Coordination Compound 1



**Figure S 11.** Temperature-dependent fluorescence emission spectra of 1.  $\lambda_{exc.} = 390$  nm. The colored arrows indicate the evolution of the respective fitted peaks with increasing temperature (red: Peak 1; green: Peak 2; blue: Peak 3; cyan: Peak 4).

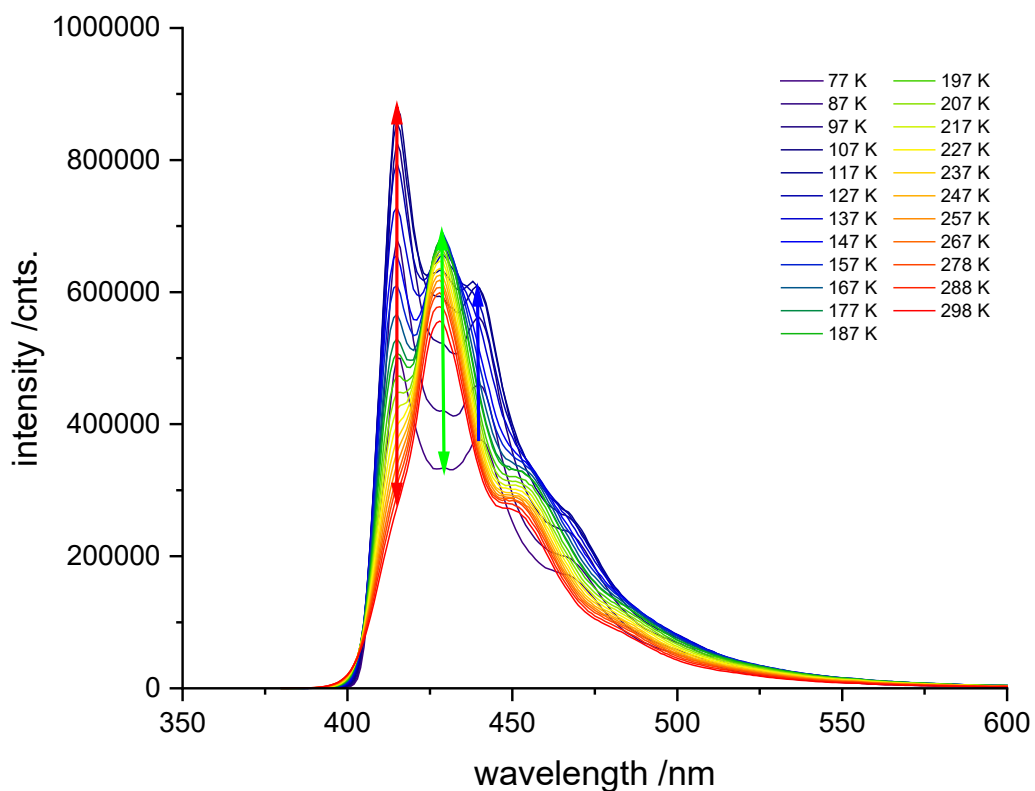


**Figure S 12.** Temperature dependence of the integrated intensity (left) and  $\lambda_{max}$  (right) of the fitted Peaks 1, 2, 3 and 4 for 1.

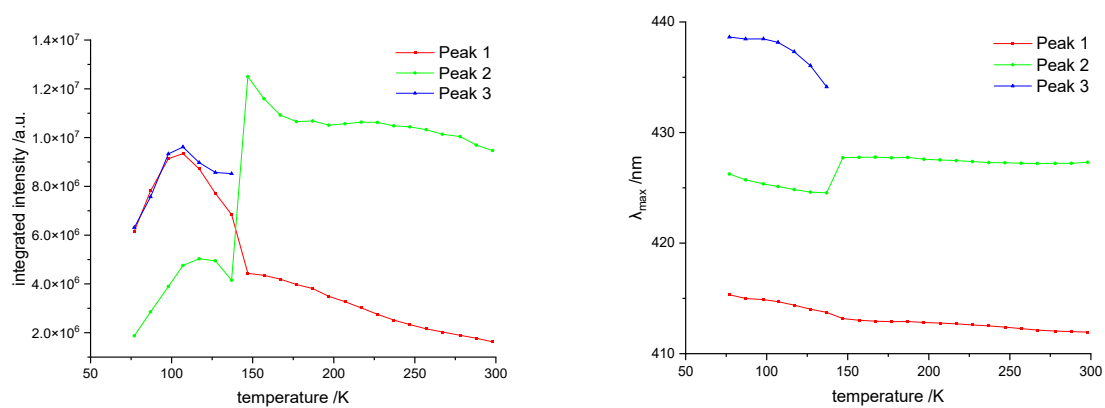


**Figure S 13.** Selected emission spectra at different temperatures of **1** fitted with multiple Gaussian functions.

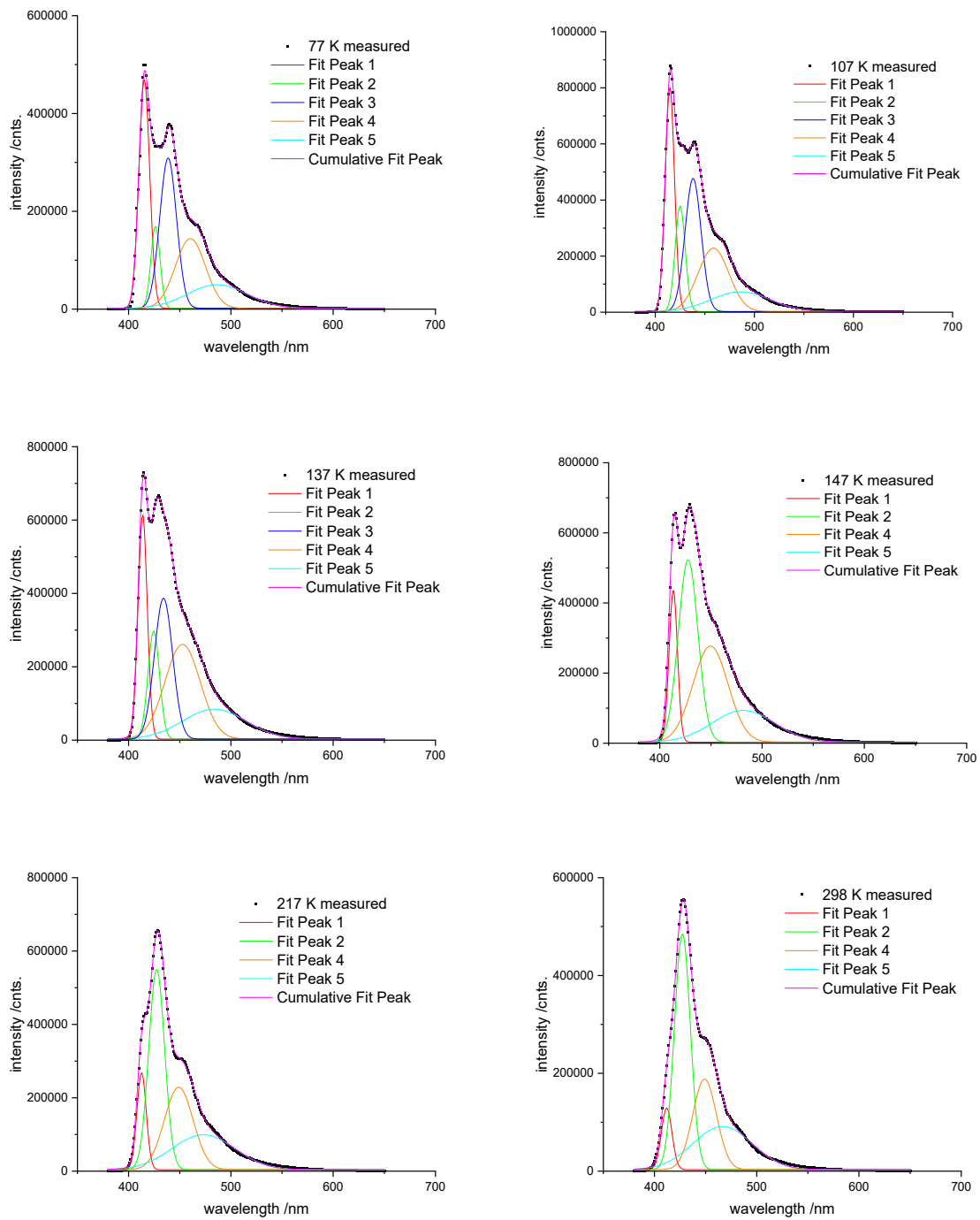
## Coordination Compound 2



**Figure S 14.** Temperature-dependent fluorescence emission spectra of **2**.  $\lambda_{exc.} = 370$  nm. The colored arrows indicate the evolution of the respective fitted peaks with increasing temperature (red: Peak 1; green: Peak 2; blue: Peak 3).

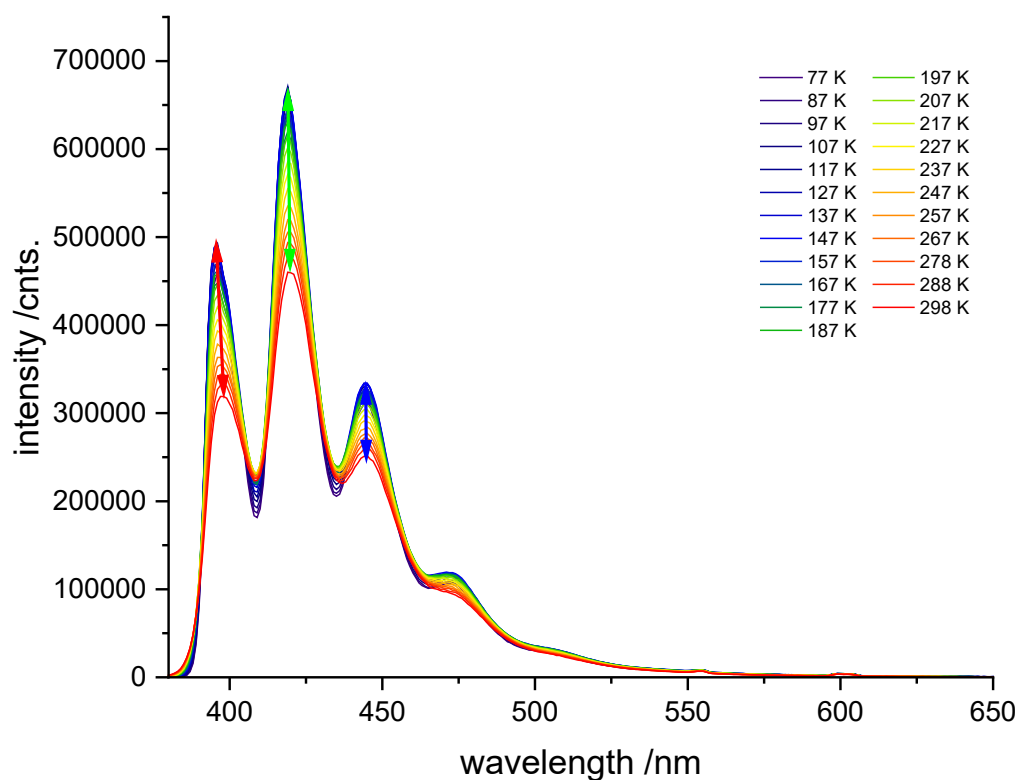


**Figure S 15.** Temperature dependence of the integrated intensity (left) and  $\lambda_{max}$  (right) of the fitted Peaks 1, 2 and 3 for **2**.

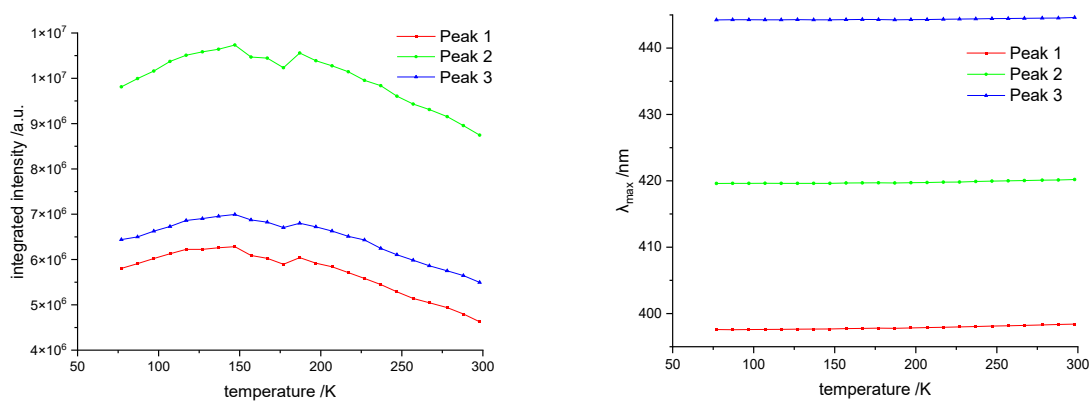


**Figure S 16.** Selected emission spectra at different temperatures of **2** fitted with multiple Gaussian functions.

### Coordination Compound 3



**Figure S17.** Temperature-dependent fluorescence emission spectra of **3**.  $\lambda_{\text{exc.}} = 370$  nm. The colored arrows indicate the evolution of the respective fitted peaks with increasing temperature (red: Peak 1; green: Peak 2; blue: Peak 3).



**Figure S18.** Temperature dependence of the integrated intensity (left) and  $\lambda_{\text{max}}$  (right) of the fitted Peaks 1, 2 and 3 for **3**.

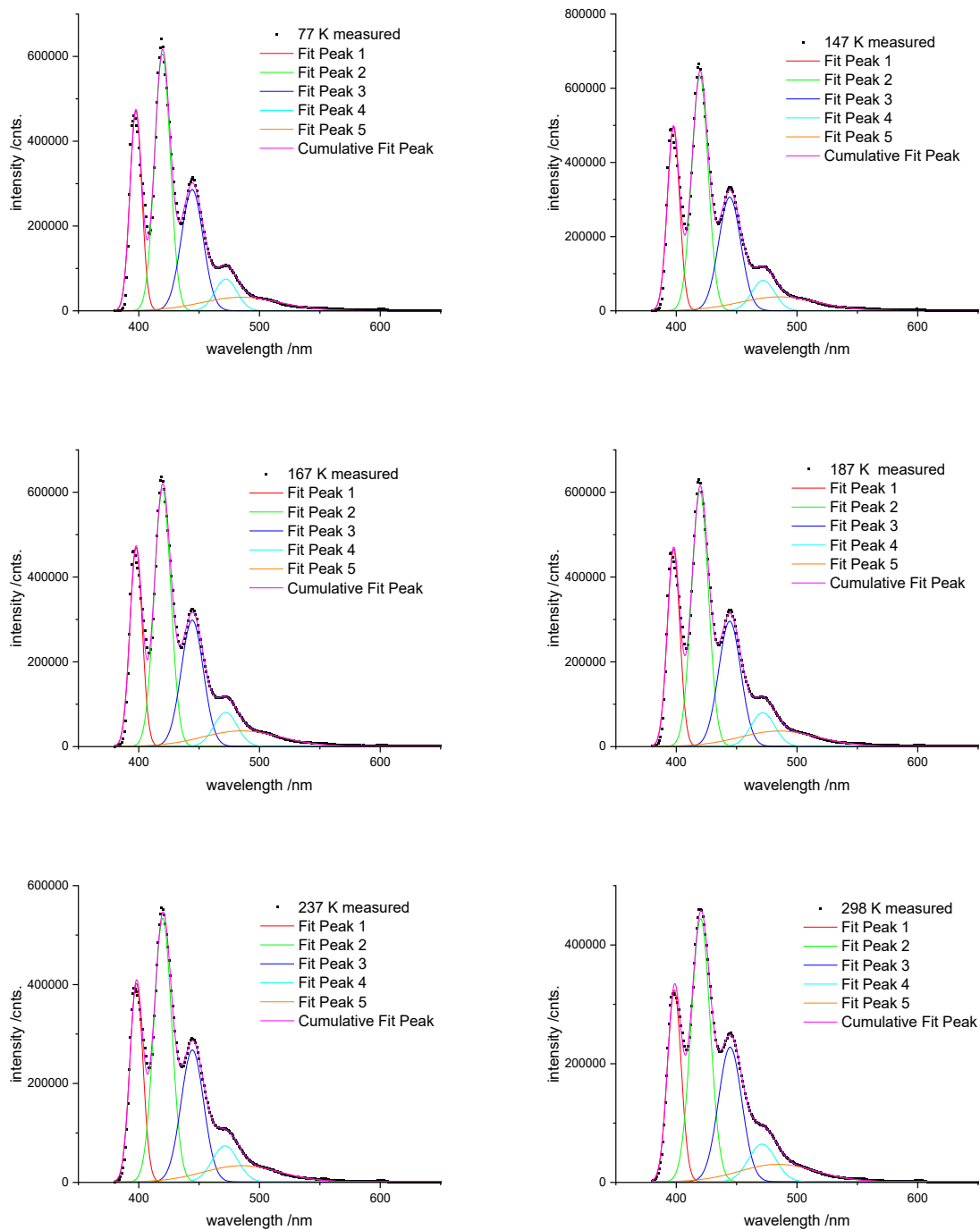
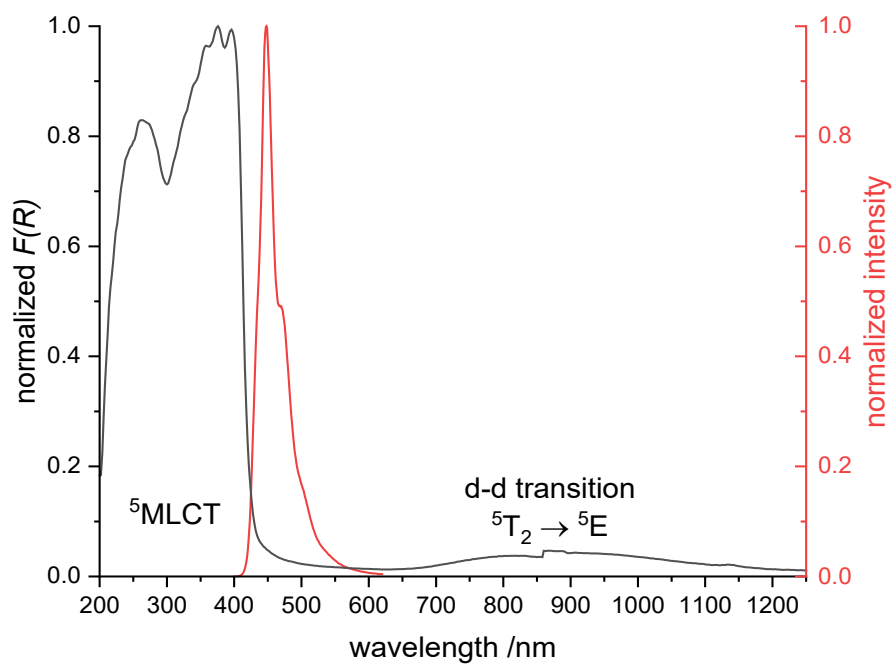
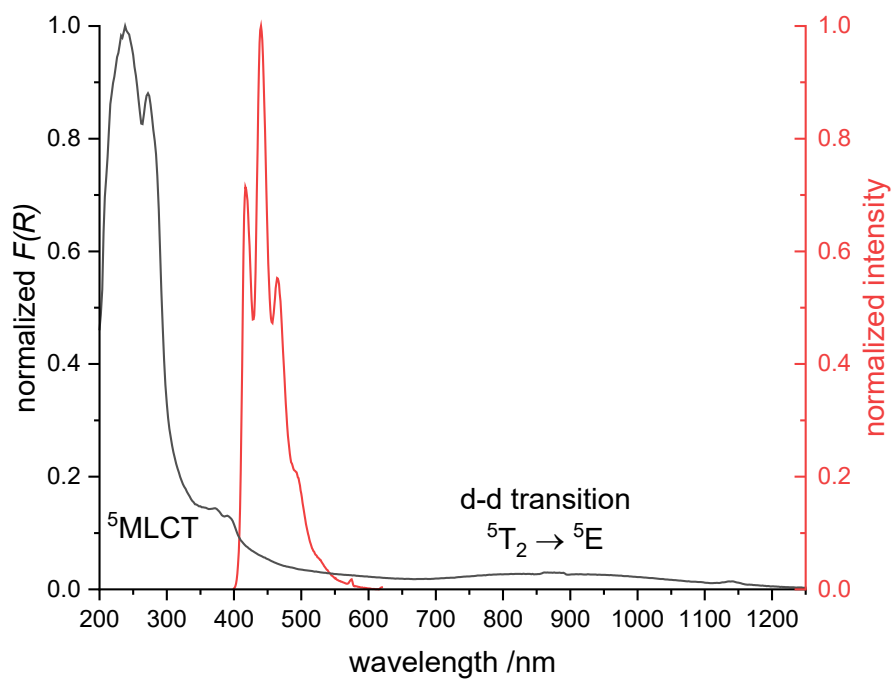


Figure S 19. Selected emission spectra at different temperatures of **3** fitted with five Gaussian functions.

## Spectral Overlap of Absorption and Emission Spectra



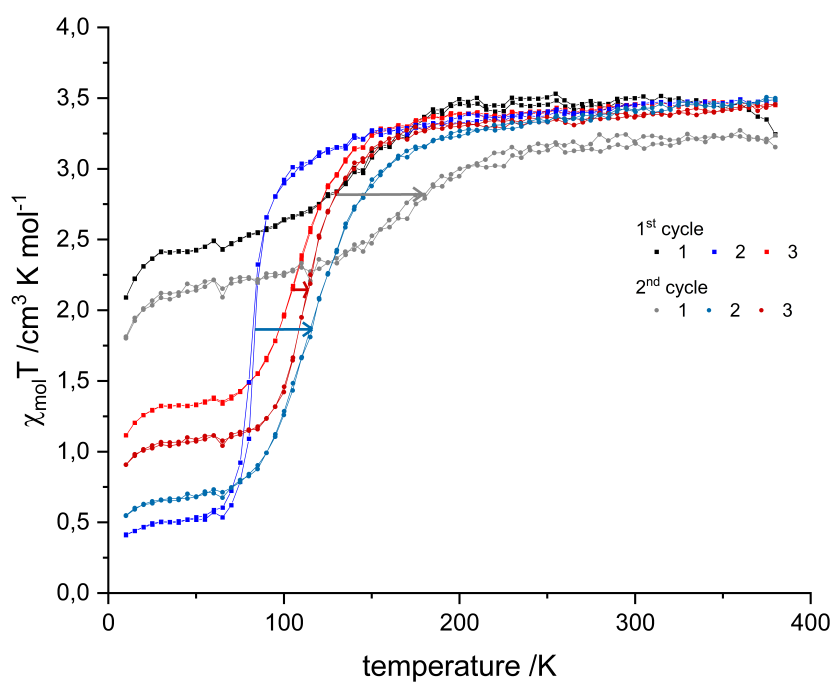
**Figure S 20.** Room temperature absorption (black) and fluorescence emission spectra (red) of **2**; excitation at 370 nm.



**Figure S 21.** Room temperature absorption (black) and fluorescence emission spectra (red) of **3**; excitation at 370 nm.

## Magnetic Measurements

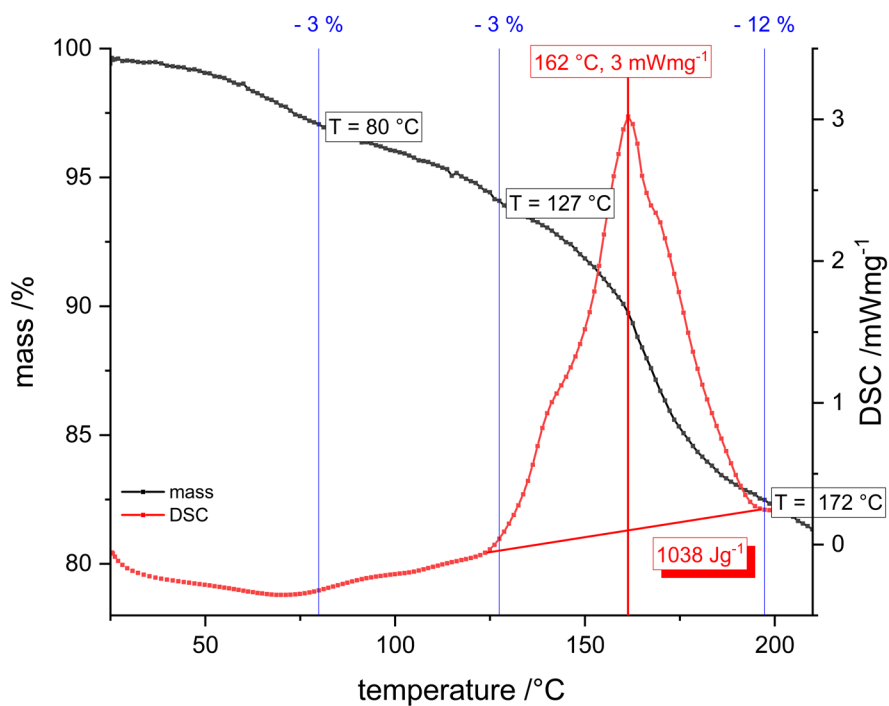
Magnetic measurements were performed using a Physical Property Measurement System (Quantum Design). The measurement setup employed a vibrating sample magnetometer (VSM) insert, and brass sample holders with polypropylene powder containers. The magnetic moment was measured by applying an external field of 1 T, first in cooling mode from 300 K to 10 K, and subsequently in heating mode from 10 K to 380 K, with data collection in 5 K steps after a thermal stabilization of 1 s and a sweeping rate of 10 K/min (settle mode). Corrections for the diamagnetic contribution of the sample holder were applied by subtracting results of blank measurements and contributions of the ligand by using tabulated Pascal's constants.



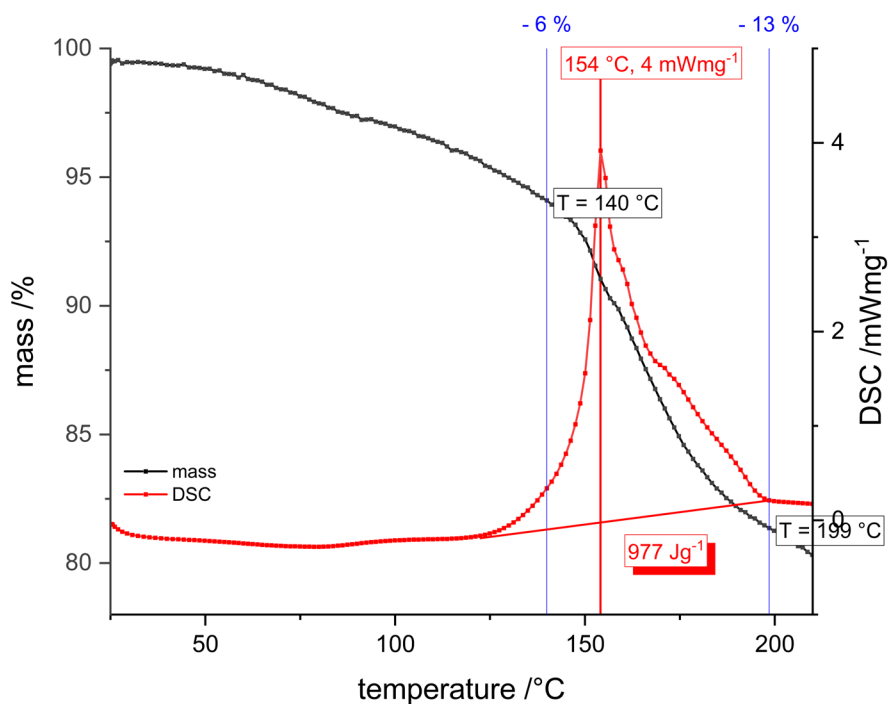
**Figure S 22.** Two cycles of temperature-dependent magnetic susceptibility measurements for **1-3**.

## Thermal Analysis

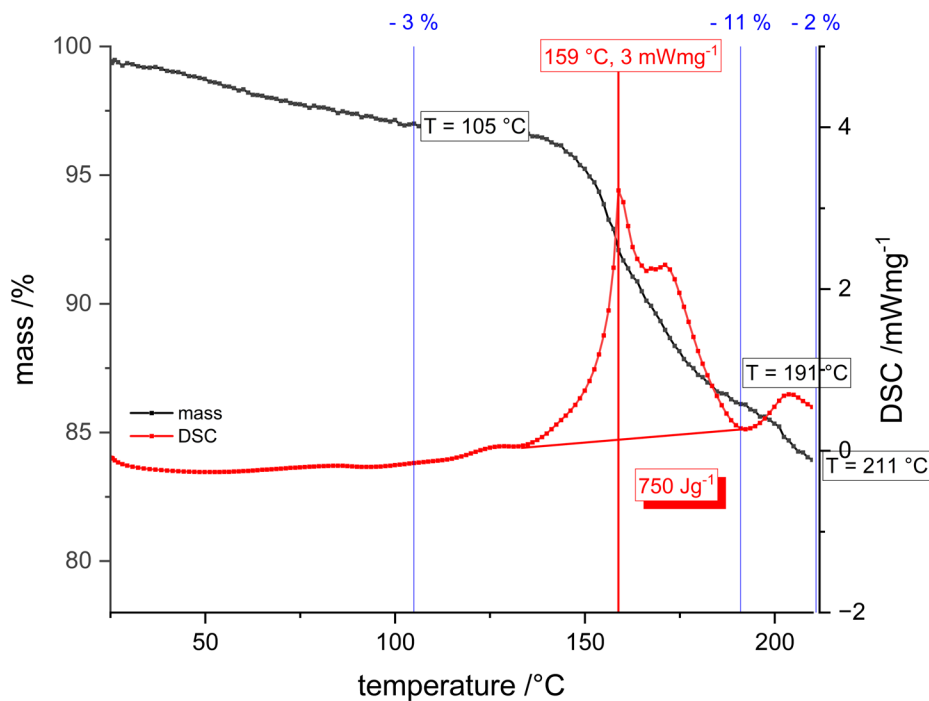
The TG/DSC analysis was performed on a NETZSCH STA 449 F1 Jupiter with a heating rate of 5 °Cmin<sup>-1</sup> from 25 to 210 °C under an nitrogen atmosphere. The sample was prepared by weighing approx. 9 mg in an aluminium crucible and crimping it with the responding cover. The measurement was calibrated with an empty, but crimped crucible running with the respective temperature scan.



**Figure S 23:** The TGA and DSC curves of compound **1** with the approx. mass losses of CH<sub>3</sub>CN (2 x 3 %) and ClO<sub>4</sub><sup>-</sup> (12 %), with an exothermic peak maximum at 162 °C and an enthalpy of 1038 Jg<sup>-1</sup>.



**Figure S 24:** The TGA and DSC curves of compound **2** with the approx. mass losses of  $\text{CH}_3\text{CN}$  (6 %) and  $\text{ClO}_4^-$  (13 %), with an exothermic peak maximum at 154 °C and an enthalpy of 977  $\text{Jg}^{-1}$ .

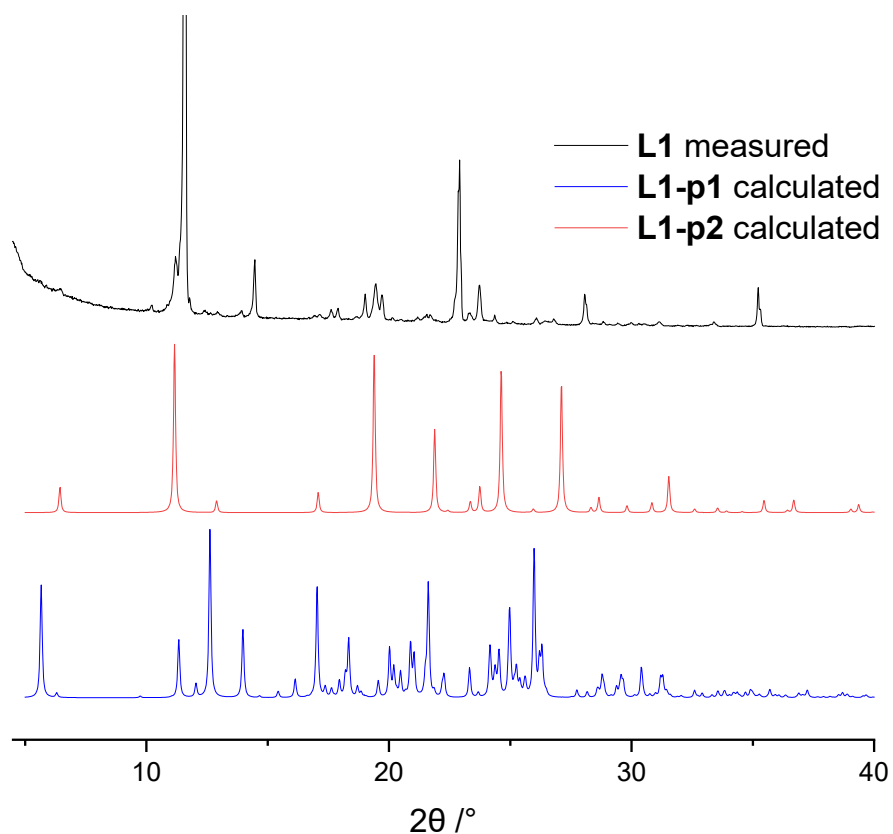


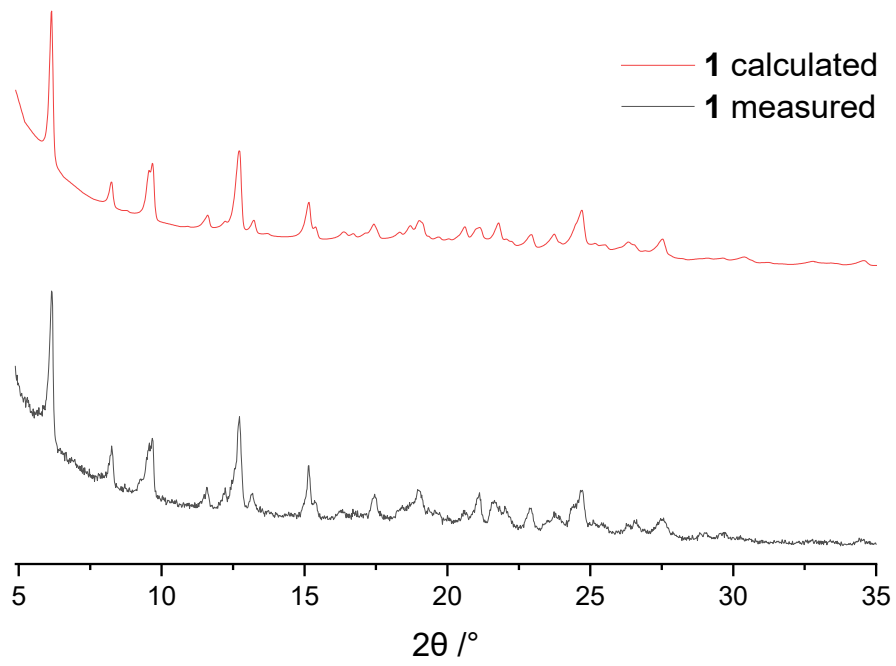
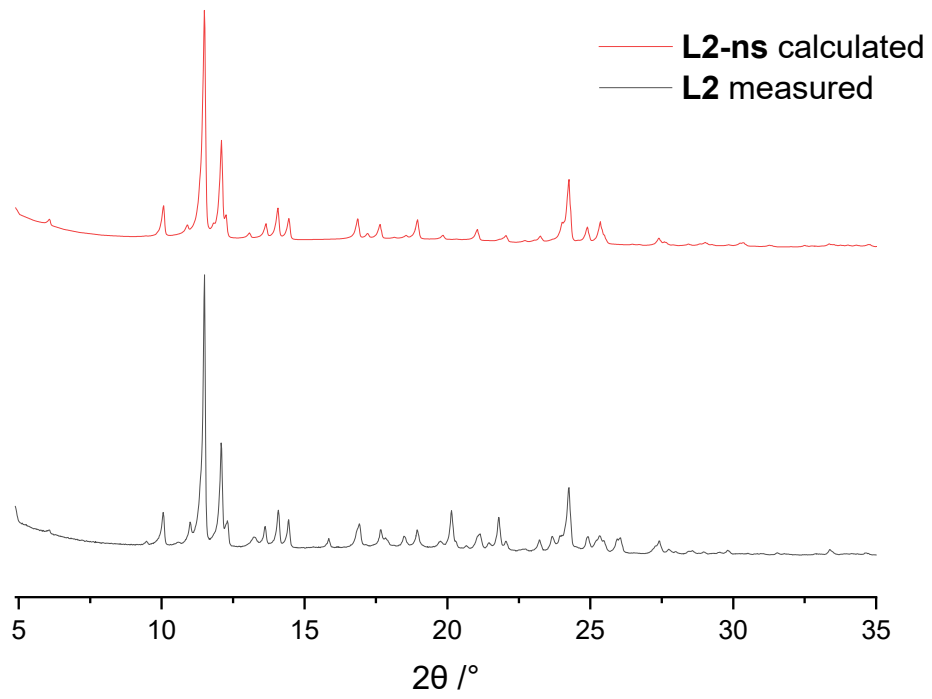
**Figure S 25:** The TGA and DSC curves of compound **3** with the approx. mass losses of  $\text{CH}_3\text{CN}$  (1 x 3 %) and  $\text{ClO}_4^-$  (11 %), with an exothermic peak maximum at 159 °C and an enthalpy of 750  $\text{Jg}^{-1}$ .

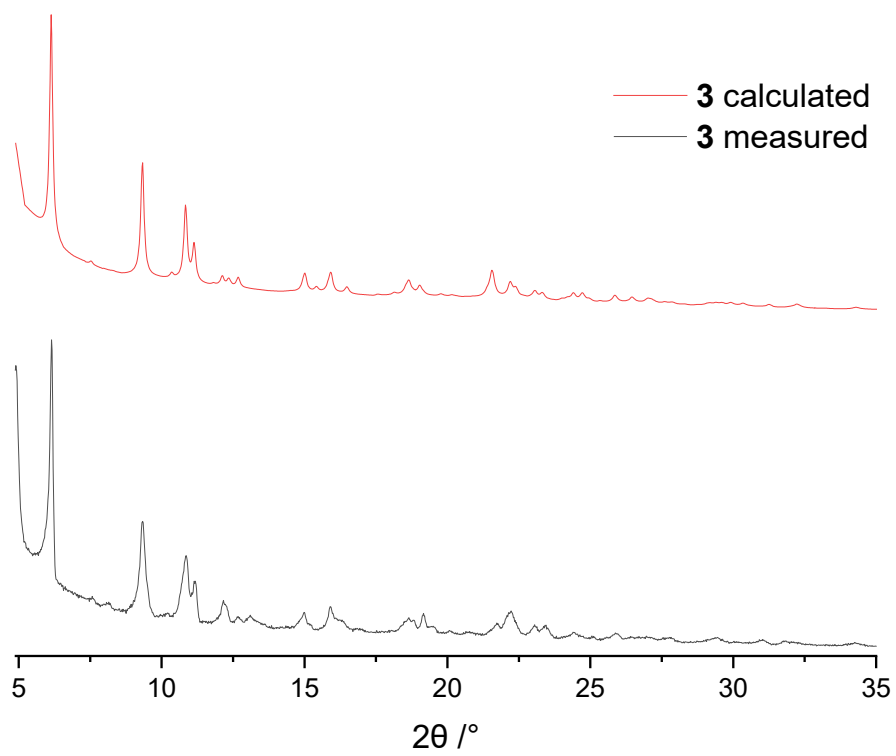
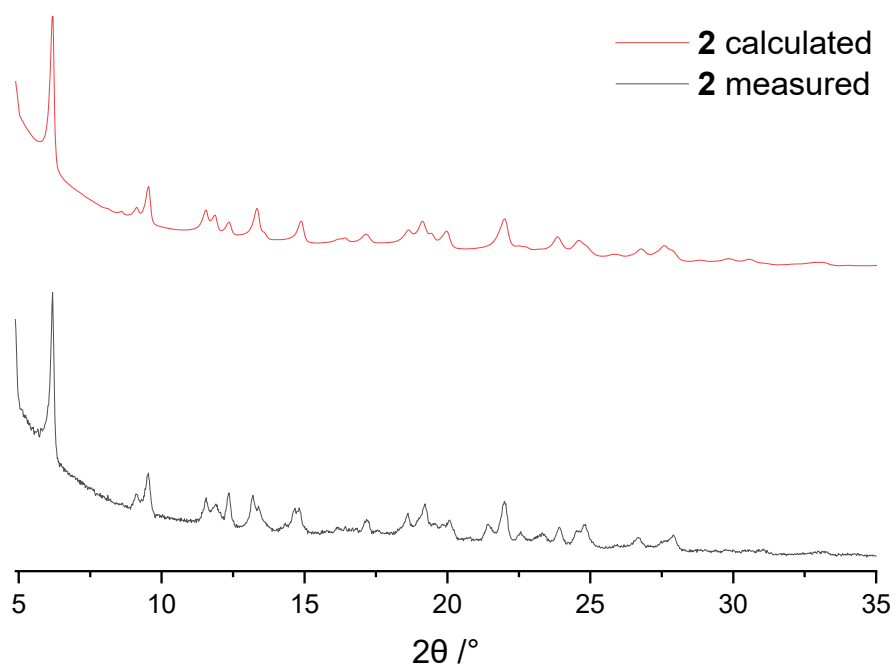
## XRPD Measurements

Powder X-ray diffraction experiments were performed on an “Empyrean” (Panalytical) diffractometer using Cu K- $\alpha$  radiation, a primary beam filter (Bragg-Brentano HD), a fixed  $\frac{1}{2}^\circ$  divergence slit, a 0.04 rad soller slit and a GaliPIX3D detector. Finely powdered bulk samples were positioned on a silicon single crystal cut along the (711) plane. It was measured from  $3^\circ$  to  $45^\circ$   $2\theta$  with a step size of  $0.014^\circ$ .

Diffractograms of **L2** and **1-3** were evaluated using the PANalytical program suite HighScorePlus<sup>3</sup>; background correction was applied, and a calculated diffraction pattern derived from single-crystal CIF data was subsequently refined via Rietveld analysis against the measured XRPD data to confirm phase purity and structural consistency.

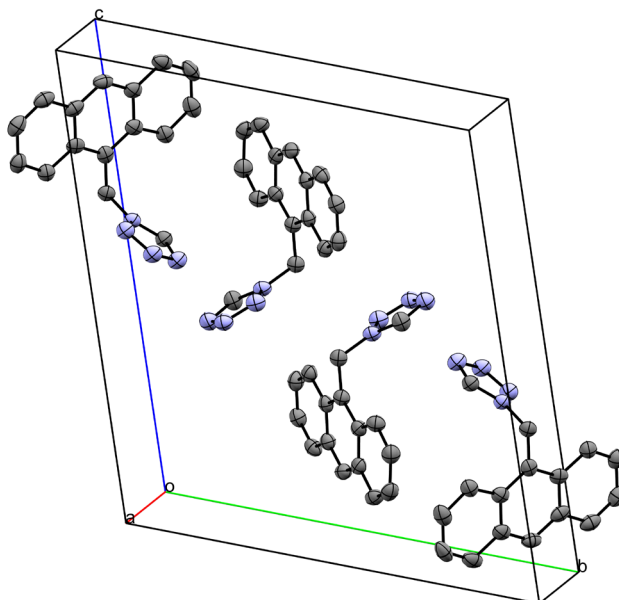




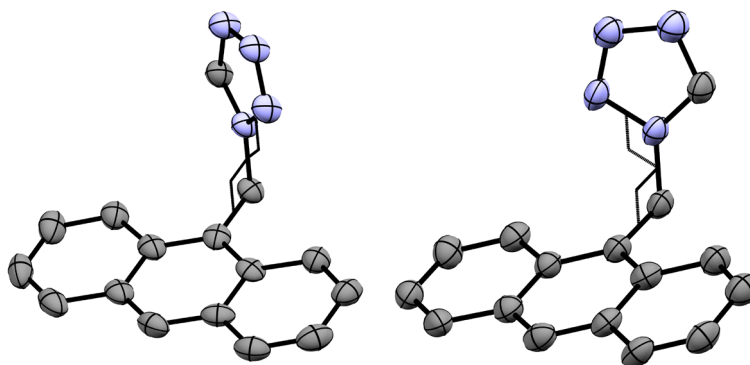


## X-Ray Structure Determination

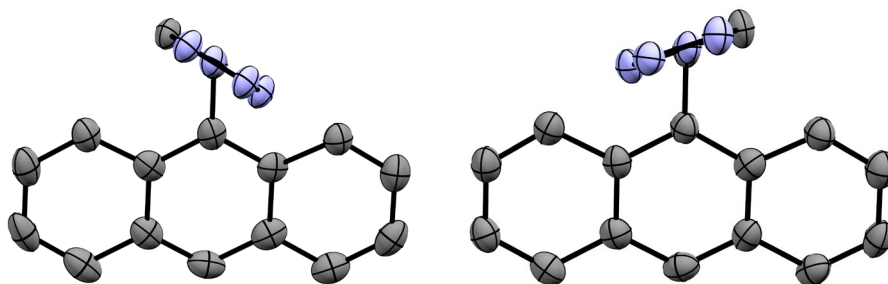
X-ray diffraction data of **1**, **2**, **L1-p1**, **L1-p2**, **L2-ns**, **L2-s1**, **L2-s2** (CSD 2427600–2427606) were collected at T = 100 K in a dry stream of nitrogen on a STOE STADIVARI diffractometer system equipped with a Dectris Eiger CdTe hybrid photon counting detector using Cu-K $\alpha$  radiation ( $\lambda = 1.54186 \text{ \AA}$ ). Data were reduced with X-Area (X-Area 1.31.194.0, LANA 2.8.4; STOE & Cie GmbH, Darmstadt, Germany, 2024). **L1-p1** and **L2-ns** were treated as twins with partial reflection overlap (HKL5-style reflection file). An absorption correction was applied with the multi-scan approach implemented in LANA. The structures were solved by the dual-space approach implemented in SHELXT<sup>4</sup> and refined against F<sup>2</sup> with SHELXL<sup>5</sup>.



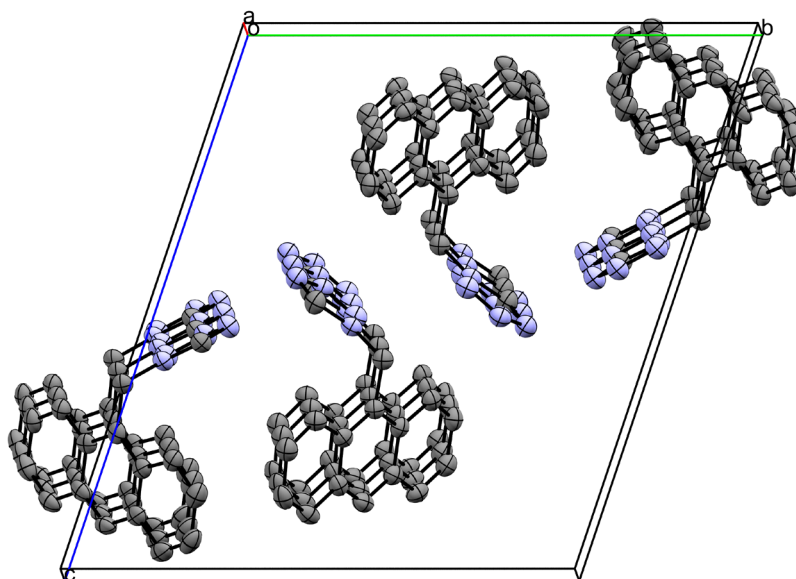
**Figure S 26.** Crystal packing of **L1-p1** (ellipsoids: 50 % probability level; atom color code: grey...C, blue...N; H-atoms are omitted for clarity).



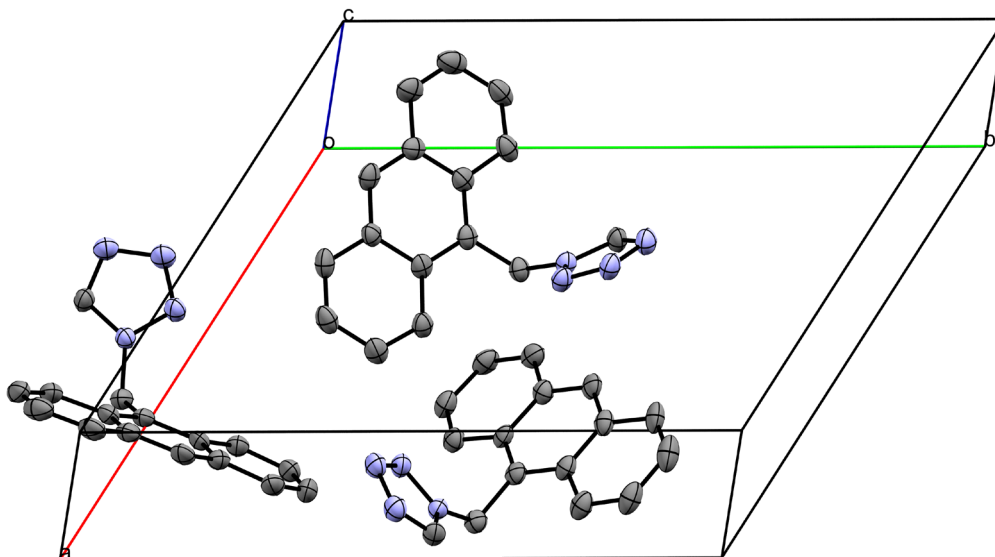
**Figure S 27.** Side view of the molecular structures of the two different conformers in **L1-p1**, showing the orientation of the tz moiety (ellipsoids: 50 % probability level; atom color code: grey...C, blue...N; H-atoms are omitted for clarity).



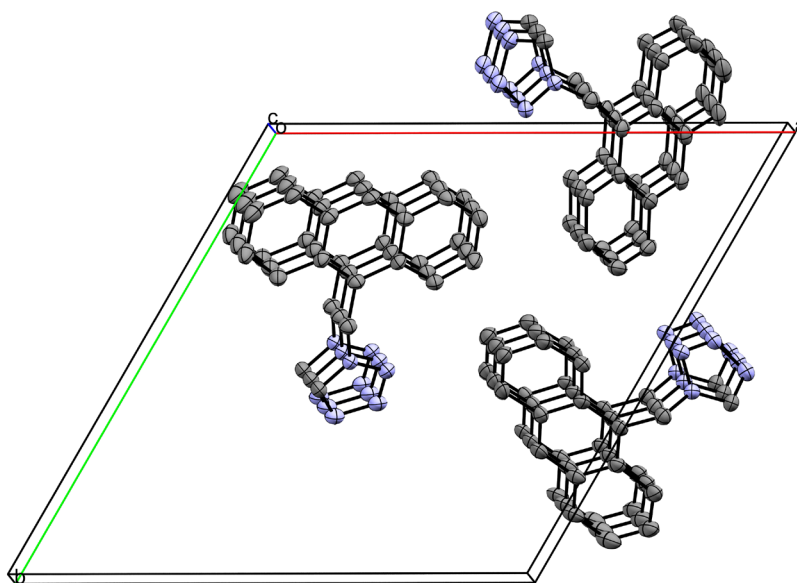
**Figure S 28.** Top view of the molecular structures of the two different conformers in **L1-p1**, showing the orientation of the tz moiety (ellipsoids: 50 % probability level; atom color code: grey...C, blue...N; H-atoms are omitted for clarity).



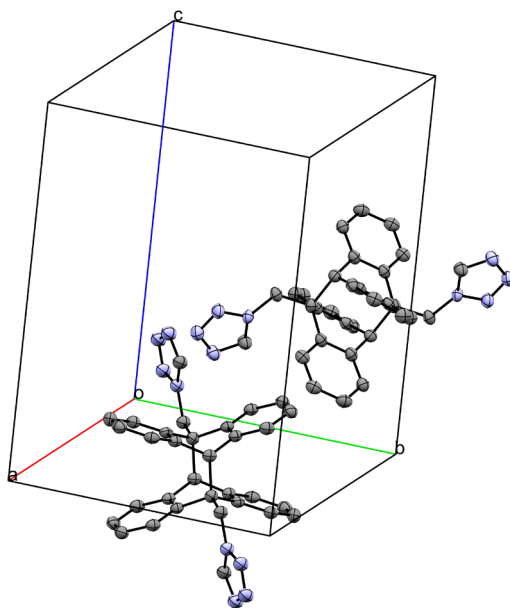
**Figure S 29.** Crystal packing with co-planar arrangement of **L1-p1** viewed along the crystallographic *a*-axis (ellipsoids: 50 % probability level; atom color code: grey...C, blue...N; H-atoms are omitted for clarity).



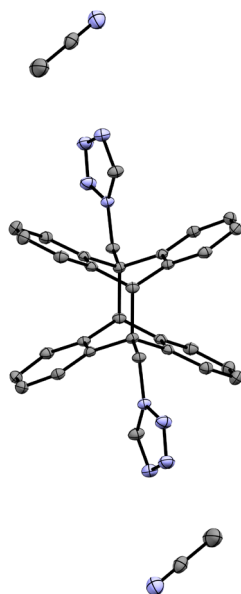
**Figure S 30.** Crystal packing of **L1-p2** (ellipsoids: 50 % probability level; atom color code: grey...C, blue...N; H-atoms are omitted for clarity).



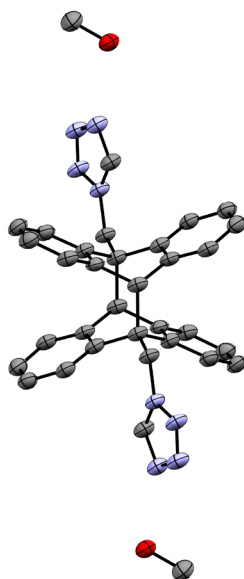
**Figure S 31.** Crystal packing with co-planar arrangement of **L1-p2** viewed along the crystallographic *c*-axis (ellipsoids: 50 % probability level; atom color code: grey...C, blue...N; H-atoms are omitted for clarity).



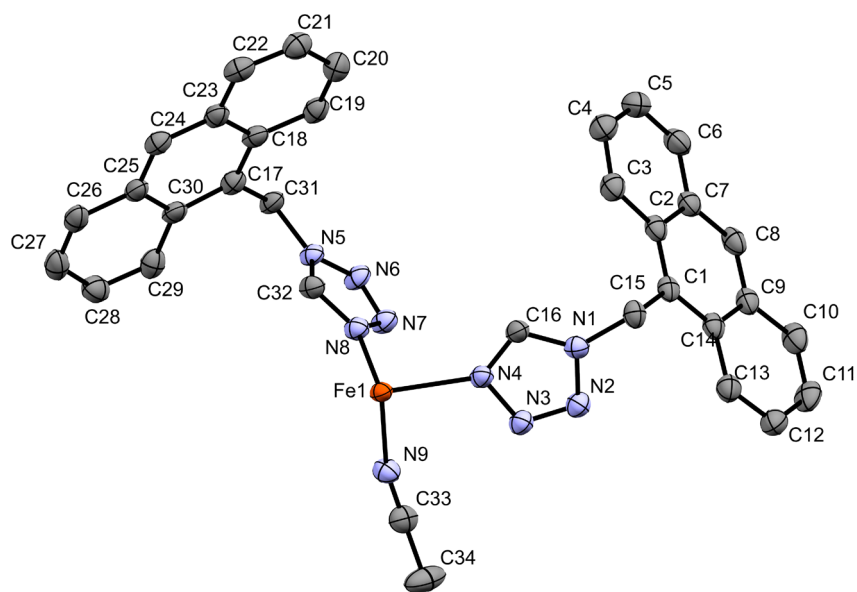
**Figure S 32.** Crystal packing of **L2-ns**, showing the two different conformers of **L2** (ellipsoids: 50 % probability level; atom color code: grey...C, blue...N; H-atoms are omitted for clarity).



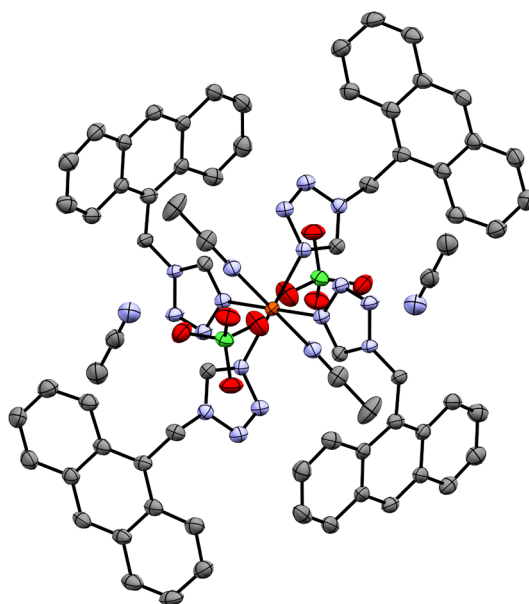
**Figure S 33.** Molecular structure of **L2-s1**, showing the relative positions of the two solvate molecules ( $\text{CH}_3\text{CN}$ ) (ellipsoids: 50 % probability level; atom color code: grey...C, blue...N; H-atoms are omitted for clarity).



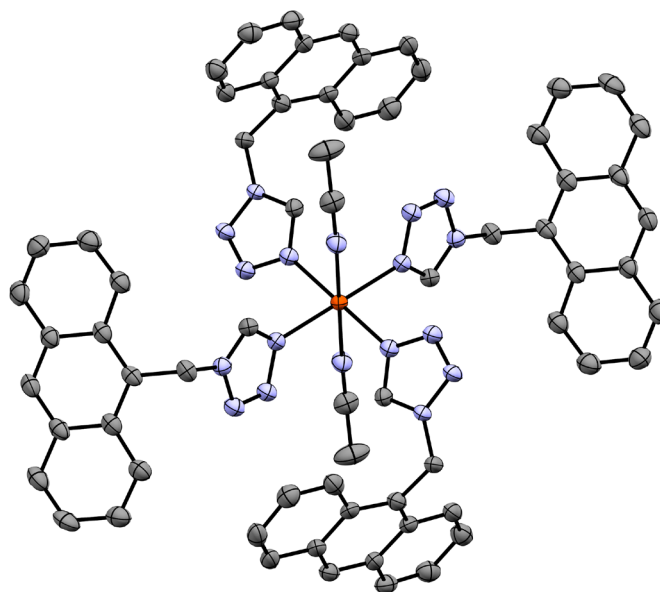
**Figure S 34.** Molecular structure of **L2-s2**, showing the relative positions of the two solvate molecules ( $\text{CH}_3\text{OH}$ ) (ellipsoids: 50 % probability level; atom color code: grey...C, blue...N, red...O; H-atoms are omitted for clarity).



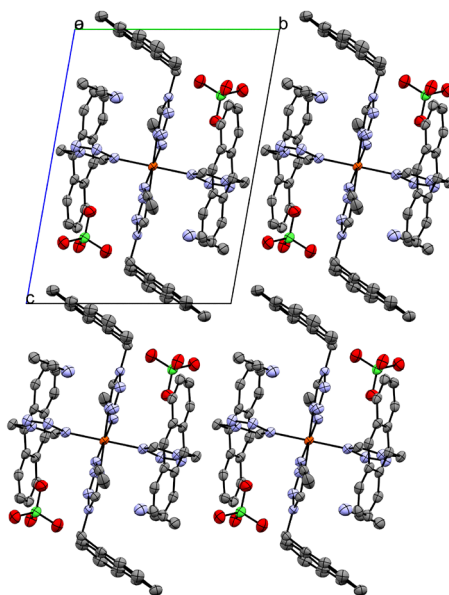
**Figure S 35.** Asymmetric unit of coordination compound **1** with atomic number labeling, showing the two different conformers of **L1** (ellipsoids: 50 % probability level; atom color code: grey...C, blue...N, orange...Fe; H-atoms, solvate molecules and anion molecules are omitted for clarity).



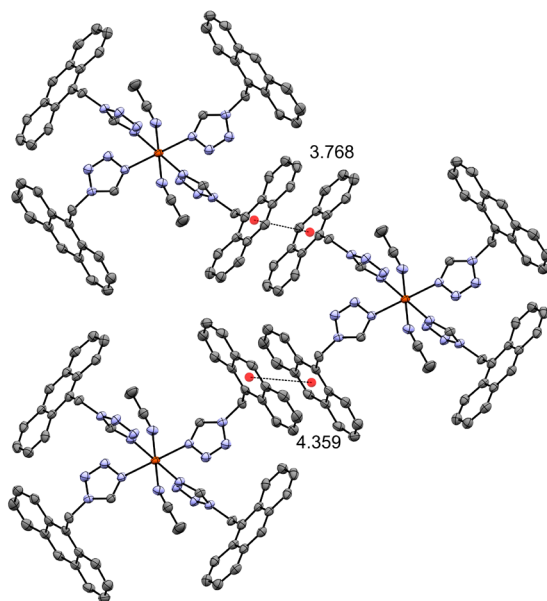
**Figure S 36.** Molecular structure of coordination compound **1**, showing the relative position of the solvate molecules ( $\text{CH}_3\text{CN}$ ) and the anion molecules ( $\text{ClO}_4^-$ ) (ellipsoids: 50 % probability level; atom color code: grey...C, blue...N, red...O, green...Cl, orange...Fe; H-atoms omitted for clarity).



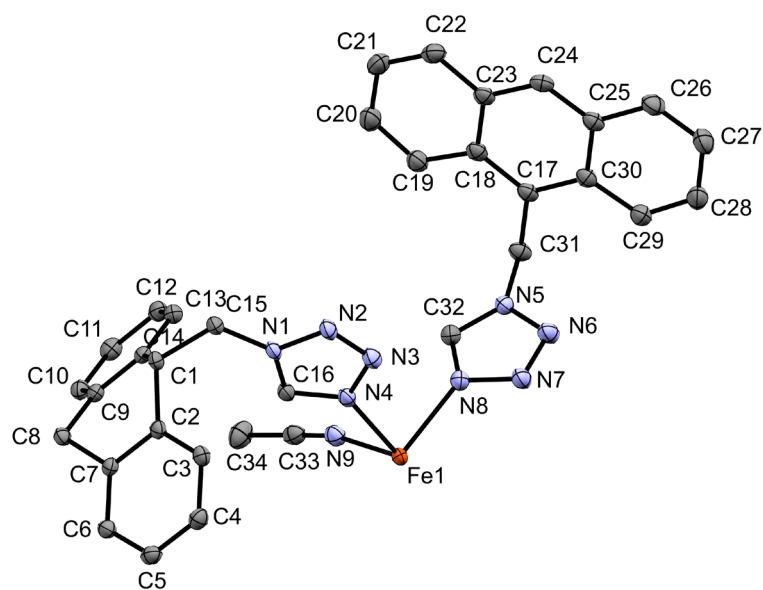
**Figure S 37.** Molecular structure of the mononuclear complex of coordination compound **1** (ellipsoids: 50 % probability level; atom color code: grey...C, blue...N, orange...Fe; H-atoms, solvate molecules and anion molecules are omitted for clarity).



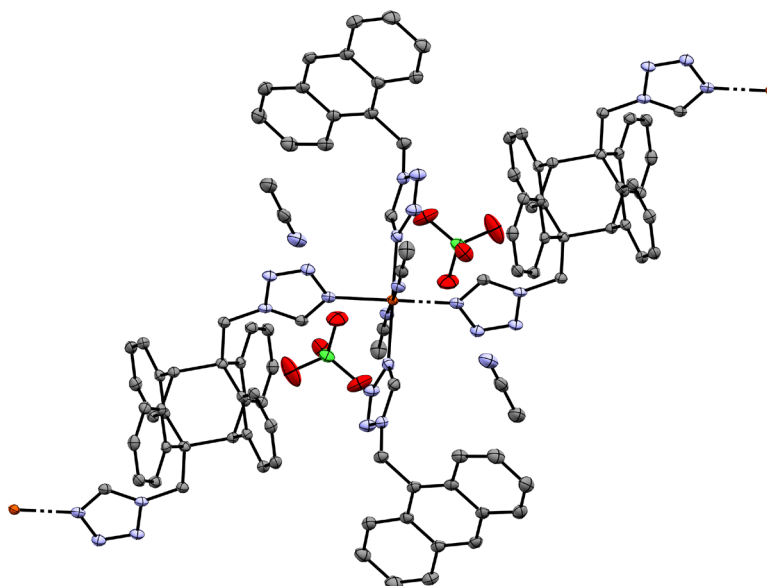
**Figure S 38.** Crystal packing of coordination compound **1** viewed along the crystallographic *a*-axis (ellipsoids: 50 % probability level; atom color code: grey...C, blue...N, red...O, green...Cl, orange...Fe; H-atoms omitted for clarity).



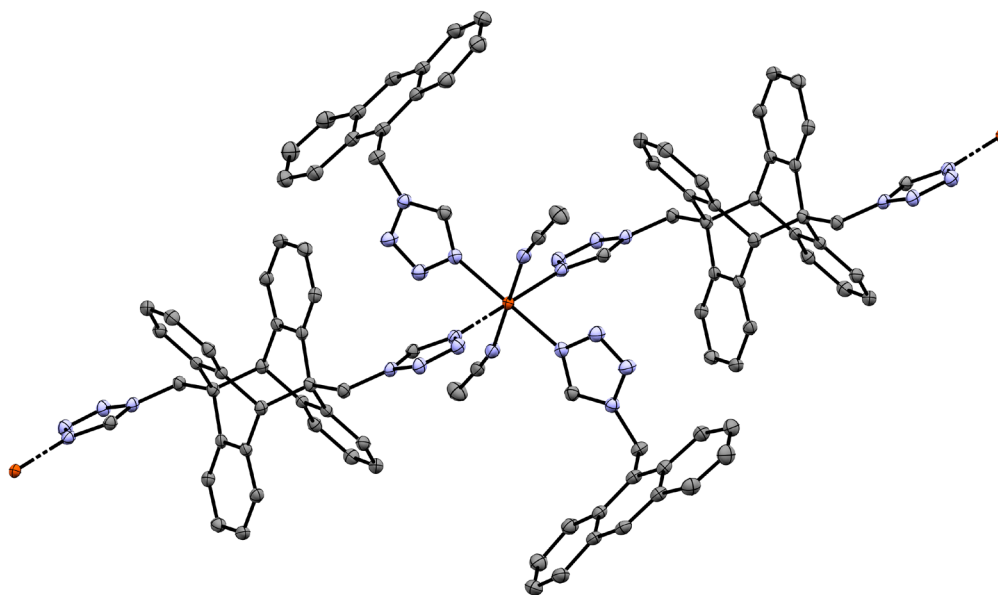
**Figure S 39.** Crystal packing of **1** with co-planar arrangement of anthracene moieties of the ligand **L1** of adjacent mononuclear complexes (ellipsoids: 50 % probability level; atom color code: grey...C, blue...N, orange...Fe; H-atoms, solvate molecules and anion molecules are omitted for clarity; interplane distance as dotted line (/ Å)).



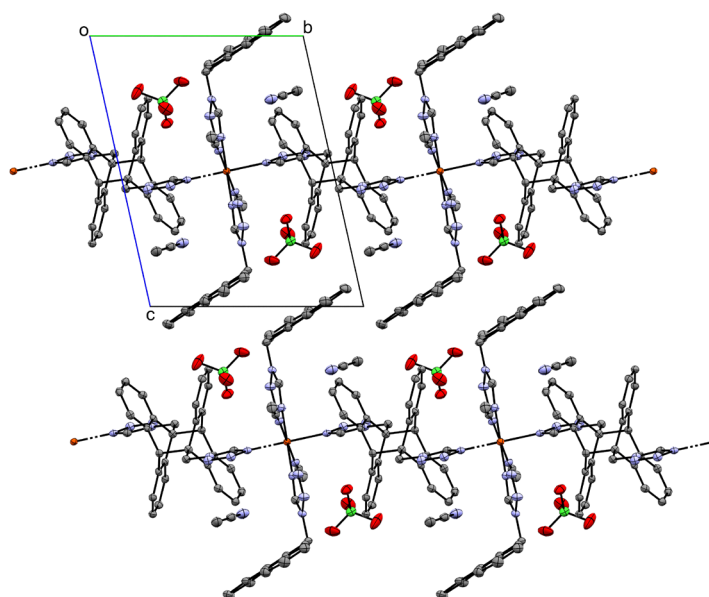
**Figure S 40.** Asymmetric unit of coordination compound **2** with atomic number labeling (ellipsoids: 50 % probability level; atom color code: grey...C, blue...N, orange...Fe; H-atoms, solvate molecules and anion molecules are omitted for clarity).



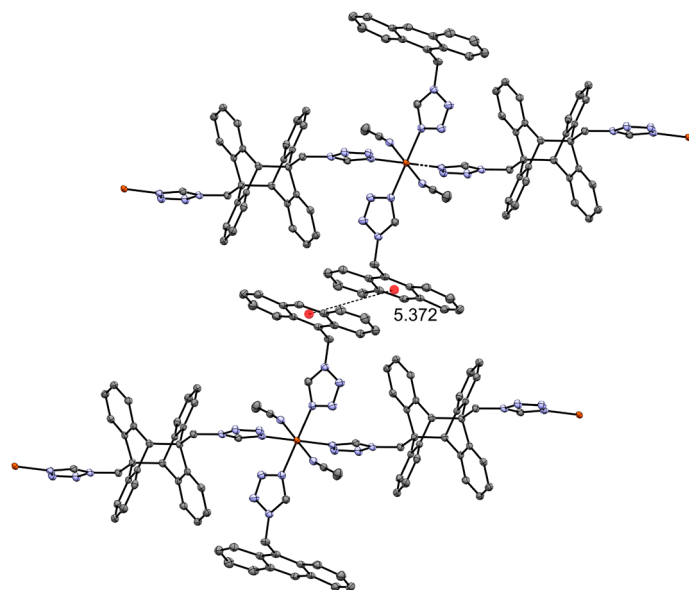
**Figure S 41.** Molecular structure of coordination compound **2**, showing the relative position of the solvate molecules ( $\text{CH}_3\text{CN}$ ) and the anion molecules ( $\text{ClO}_4^-$ ), as well as the bridging coordination mode of **L2** (ellipsoids: 50 % probability level; atom color code: grey...C, blue...N, red...O, green...Cl, orange...Fe; H-atoms omitted for clarity).



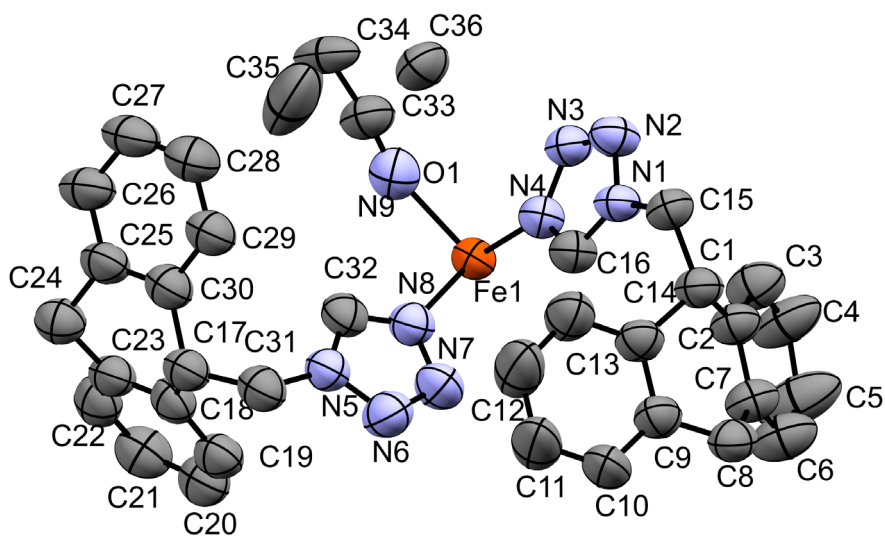
**Figure S 42.** Molecular structure of the 1D coordination polymer chain of coordination compound **2**, showing the bridging coordination mode of **L2** (ellipsoids: 50 % probability level; atom color code: grey...C, blue...N, orange...Fe; H-atoms, solvate molecules and anion molecules are omitted for clarity).



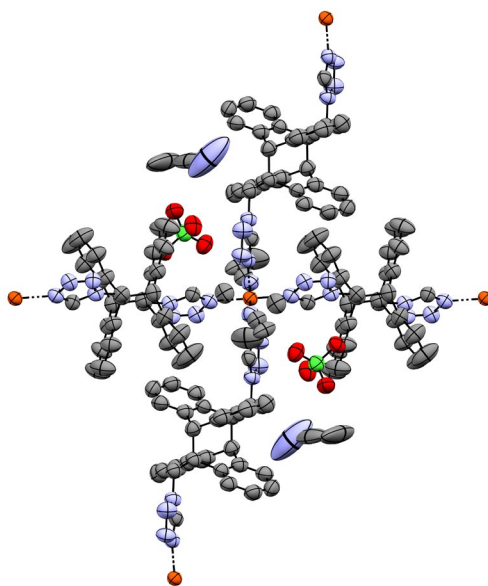
**Figure S 43.** Crystal packing of two parallel 1D coordination polymer chains of coordination compound **2** viewed along the crystallographic *a*-axis (ellipsoids: 50 % probability level; atom color code: grey...C, blue...N, red...O, green...Cl, orange...Fe; H-atoms omitted for clarity).



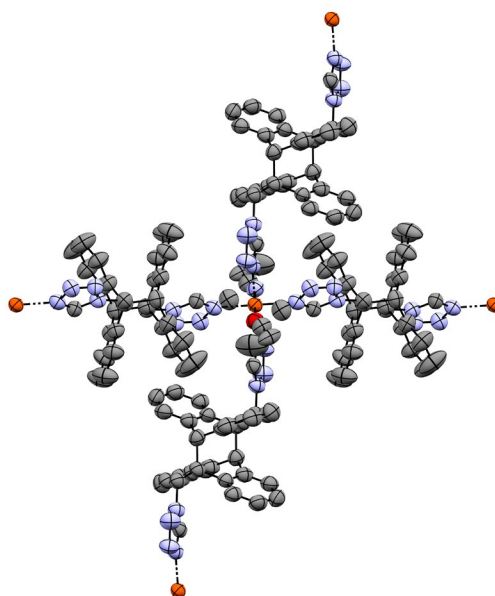
**Figure S 44.** Crystal packing of **2** with co-planar arrangement of anthracene moieties of the ligand **L1** of adjacent 1D coordination polymer chains (ellipsoids: 50 % probability level; atom color code: grey...C, blue...N, orange...Fe; H-atoms, solvate molecules and anion molecules are omitted for clarity; interplane distance as dotted line (*Å*)).



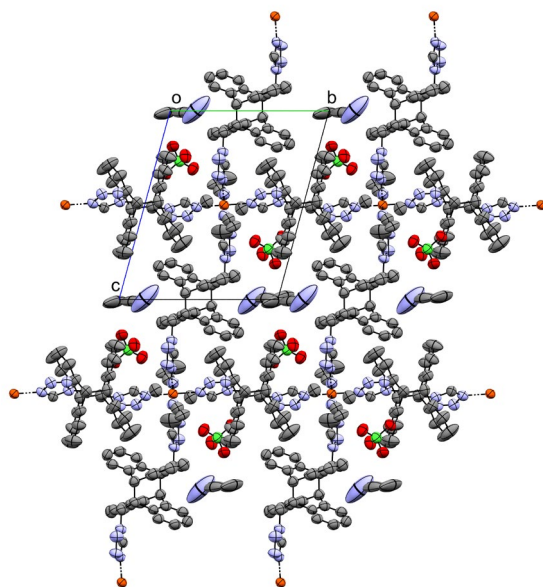
**Figure S 45.** Asymmetric unit of coordination compound **3** with atomic number labeling (ellipsoids: 50 % probability level; atom color code: grey...C, blue...N, orange...Fe; H-atoms, solvate molecules and anion molecules are omitted for clarity).



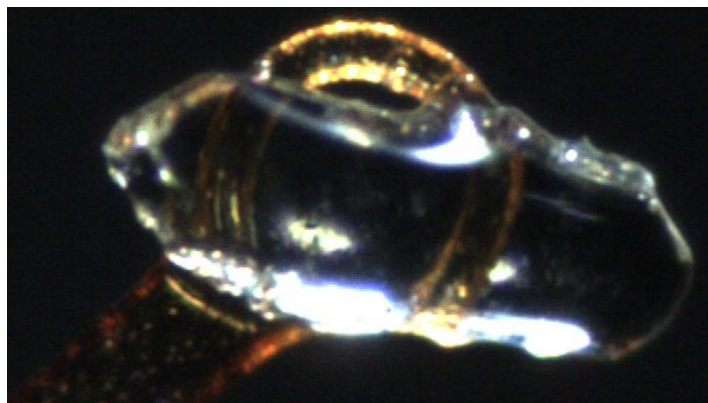
**Figure S 46.** Molecular structure of coordination compound **3**, showing the relative position of the solvate molecules (CH<sub>3</sub>CN) and the anion molecules (ClO<sub>4</sub><sup>-</sup>), as well as the bridging coordination mode of **L2** (ellipsoids: 50 % probability level; atom color code: grey...C, blue...N, red...O, green...Cl, orange...Fe; H-atoms omitted for clarity).



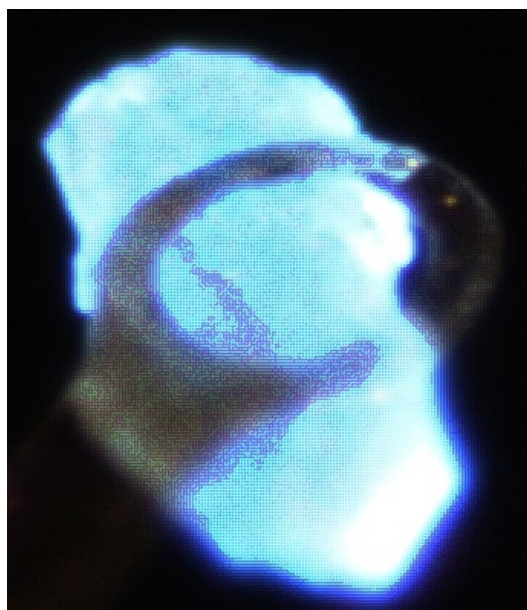
**Figure S 47.** Molecular structure of the 2D coordination polymer chain of coordination compound **3**, showing the bridging coordination mode of **L2** (ellipsoids: 50 % probability level; atom color code: grey...C, blue...N, orange...Fe; H-atoms, solvate molecules and anion molecules are omitted for clarity).



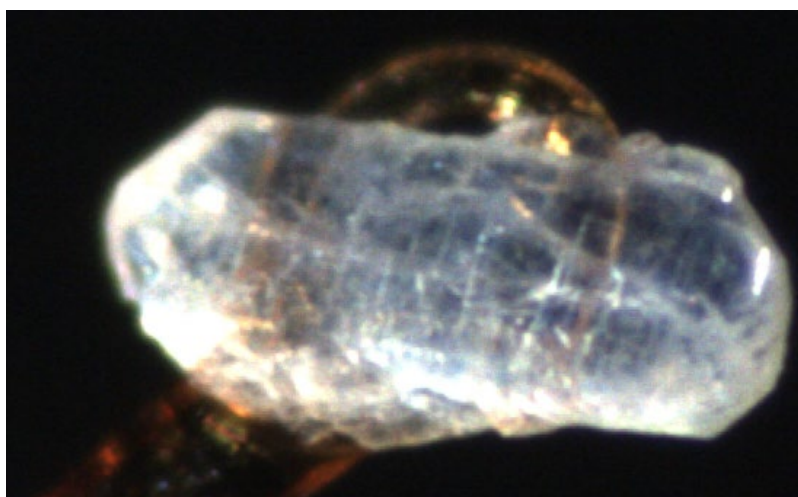
**Figure S 48.** Crystal packing of the 2D coordination polymer layer of coordination compound **2** viewed along the crystallographic *a*-axis (ellipsoids: 50 % probability level; atom color code: grey...C, blue...N, red...O, green...Cl, orange...Fe; H-atoms omitted for clarity).



**Figure S 49.** SC of **1** mounted on the crystal pin before irradiation with a 365 nm LED.



**Figure S 50.** SC of **1** mounted on the crystal pin during irradiation with a 365 nm LED.



**Figure S 51.** SC of **2** mounted on the crystal pin after irradiation of a SC of **1** with a 365 nm LED with clearly visible fragmentation.

**Table 1:** Hydrogens bond distances of polymorph **L1-p1**

donor atom (D)	H atom	acceptor atom (A)	D-H / Å	H...A / Å	D...A / Å	D-H...A /°
C32	H32	N4	0.93	4.48	3.143(8)	129
C16	H16	N3	0.93	2.35	3.265(7)	168
C13	H13	N2	0.93	2.60	3.429(8)	149
C31	H31A	N6	0.97	2.62	3.562(7)	165
C32	H32	N7	0.93	2.50	3.317(8)	146

**Table 2:** Hydrogen bond distances of polymorph L1-p2

donor atom (D)	H atom	acceptor atom (A)	D-H / Å	H...A / Å	D...A / Å	D-H...A / °
C16	H16	N4	0.95	2.51	3.373(9)	151
C15	H15A	N2	0.99	2.49	3.366(7)	147

**Table 3:** Octahedral distortion parameters of compound 1

<D>	2.165899
ζ	0.117186
Δ	0.000107
Σ	27.412707
Θ	73.871601
Volume	13.500000

**Table 4:** Octahedral distortion parameters of compound 2

<D>	2.141788
ζ	0.094145
Δ	0.000061
Σ	21.122430
Θ	50.718178
Volume	13.080000

**Table 5:** Octahedral distortion parameters of compound 3

<D>	2.1205
ζ	0.103597
Δ	0.000080
Σ	18.2745
Θ	53.1683
Volume	12.6900

**Table 6:** Crystal data of 1, 2, L1-p1, L1-p2

Chemical formula	C <sub>68</sub> H <sub>54</sub> FeN <sub>18</sub> +2(ClO <sub>4</sub> )+2(C <sub>2</sub> H <sub>3</sub> N)	C <sub>68</sub> H <sub>54</sub> FeN <sub>18</sub> +2(ClO <sub>4</sub> )+2(C <sub>2</sub> H <sub>3</sub> N)	C <sub>16</sub> H <sub>12</sub> N <sub>4</sub>	C <sub>16</sub> H <sub>12</sub> N <sub>4</sub>
<i>M<sub>r</sub></i>	1460.15	1460.15	260.30	260.30
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$	Trigonal, <i>P</i> 3 <sub>2</sub>
Temperature (K)	100	100	100	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.2758 (4), 11.0058 (4), 15.2855 (6)	10.4902 (3), 11.0975 (3), 14.7129 (5)	5.3803 (5), 14.8209 (13), 16.6040 (14)	15.8450 (7), 15.8450 (7), 4.2481 (2)
<i>α</i> , <i>β</i> , <i>γ</i> (°)	99.189 (3), 101.318 (3), 93.090 (3)	76.991 (2), 78.172 (2), 86.627 (2)	108.530 (7), 96.770 (7), 91.608 (7)	90, 90, 120
<i>V</i> (Å <sup>3</sup> )	1666.82 (11)	1633.26 (9)	1243.6 (2)	923.65 (9)
<i>Z</i>	1	1	4	3
Radiation type	Cu <i>Kα</i>	Cu <i>Kα</i>	Cu <i>Kα</i>	Cu <i>Kα</i>
μ (mm <sup>-1</sup> )	3.17	3.24	0.69	0.69
Crystal size (mm)	0.15 × 0.08 × 0.03 × 0.07 (radius)	0.16 × 0.09 × 0.02 × 0.04 (radius)	0.15 × 0.08 × 0.02 × 0.10 (radius)	0.3 × 0.12 × 0.03 × 0.05 (radius)

**Table 7:** Data collection of **1, 2, L1-p1, L1-p2**

Diffractionmeter	STOE STADIVARI	STOE STADIVARI	STOE STADIVARI	STOE STADIVARI
Absorption correction	Multi-scan STOE LANA, absorption correction by scaling of reflection intensities. J. Koziskova, F. Hahn, J. Richter, J. Kozisek, "Comparison of different absorption corrections on the model structure of tetrakis( $\mu$ 2-acetato)- diaqua-dicopper(II)", Acta Chimica Slovaca, vol. 9, no. 2, 2016, pp. 136 - 140. Afterwards a spherical absorption correction was performed within STOE LANA.	Multi-scan STOE LANA, absorption correction by scaling of reflection intensities. J. Koziskova, F. Hahn, J. Richter, J. Kozisek, "Comparison of different absorption corrections on the model structure of tetrakis( $\mu$ 2-acetato)- diaqua-dicopper(II)", Acta Chimica Slovaca, vol. 9, no. 2, 2016, pp. 136 - 140. Afterwards a spherical absorption correction was performed within STOE LANA.	Multi-scan STOE LANA, absorption correction by scaling of reflection intensities. J. Koziskova, F.Hahn, J. Richter, J. Kozisek, "Comparison of different absorption corrections on the model structure of tetrakis( $\mu$ 2-acetato)- diaquadi-copper(II)", Acta Chimica Slovaca, vol. 9, no. 2, 2016, pp. 136 - 140. Afterwards a spherical absorption correction was performed within STOE LANA.	Multi-scan STOE LANA, absorption correction by scaling of reflection intensities. J. Koziskova, F. Hahn, J. Richter, J. Kozisek, "Comparison of different absorption corrections on the model structure of tetrakis( $\mu$ 2-acetato)- diaqua-dicopper(II)", Acta Chimica Slovaca, vol. 9, no. 2, 2016, pp. 136 - 140. Afterwards a spherical absorption correction was performed within STOE LANA.
$T_{\min}, T_{\max}$	0.372, 0.551	0.527, 0.712	0.0000, 0.0000	0.780, 0.898
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	31264, 5911, 5456	21824, 6017, 5487	8027, 8027, 5553	9409, 1729, 1700
$R_{\text{int}}$	0.046	0.024	?	0.036
$(\sin \theta/\lambda)_{\text{max}}$ ( $\text{\AA}^{-1}$ )	0.604	0.612	0.602	0.605
Refinement $R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , $S$	0.061, 0.166, 1.10	0.042, 0.112, 1.05	0.089, 0.300, 1.08	0.050, 0.139, 1.14
No. of reflections	5911	6017	8027	1729
No. of parameters	468	468	362	182
No. of restraints	0	0	0	1
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ ( $\text{e \AA}^{-3}$ )	0.83, -0.35	0.48, -0.50	0.44, -0.40	0.21, -0.23

Absolute structure	–	–	–	Flack x determined using 571 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Absolute structure parameter	–	–	–	0.3 (9)

**Table 8:** Crystal data of **L2-ns**, **L2-s1**, **L2-s2**

Chemical formula	C <sub>32</sub> H <sub>24</sub> N <sub>8</sub>	C <sub>32</sub> H <sub>24</sub> N <sub>8</sub> +2(C <sub>2</sub> H <sub>3</sub> N)	2(CH <sub>4</sub> O)+C <sub>32</sub> H <sub>24</sub> N <sub>8</sub>
<i>M<sub>r</sub></i>	520.59	602.70	584.67
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	100	100	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.9531 (7), 10.6297 (9), 15.4615 (11)	8.3531 (6), 9.3239 (6), 9.6269 (7)	8.1947 (8), 9.5350 (9), 10.8960 (11)
$\alpha$ , $\beta$ , $\gamma$ (°)	94.965 (6), 104.688 (6), 114.640 (6)	95.204 (6), 92.686 (6), 94.521 (6)	114.584 (7), 107.805 (7), 93.255 (8)
<i>V</i> (Å <sup>3</sup> )	1262.45 (18)	743.26 (9)	720.28 (13)
<i>Z</i>	2	1	1
Radiation type	Cu <i>K</i> $\alpha$	Cu <i>K</i> $\alpha$	Cu <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.68	0.67	0.70
Crystal size (mm)	0.07 × 0.05 × 0.02	0.22 × 0.16 × 0.06 × 0.04 (radius)	0.15 × 0.08 × 0.02 × 0.05 (radius)

**Table 9:** Data collection of of **L2-ns**, **L2-s1**, **L2-s2**

Diffractometer	STOE STADIVARI	STOE STADIVARI	STOE STADIVARI
Absorption correction	Multi-scan STOE LANA, absorption correction by scaling of reflection intensities. J. Koziskova, F. Hahn, J. Richter, J. Kozisek, "Comparison of different absorption corrections on the model structure of tetrakis( $\mu$ 2-acetato)- diaqua-dicopper(II)", Acta Chimica Slovaca, vol. 9, no. 2, 2016, pp. 136 - 140.	Multi-scan STOE LANA, absorption correction by scaling of reflection intensities. J. Koziskova, F. Hahn, J. Richter, J. Kozisek, "Comparison of different absorption corrections on the model structure of tetrakis( $\mu$ 2-acetato)-diaqua-di-copper(II)", Acta Chimica Slovaca, vol. 9, no. 2, 2016, pp. 136 - 140.	Multi-scan STOE LANA, absorption correction by scaling of reflection intensities. J. Koziskova, F. Hahn, J. Richter, J. Kozisek, "Comparison of different absorption corrections on the model structure of tetrakis( $\mu$ 2-acetato)- diaqua-di-copper(II)", Acta Chimica Slovaca, vol. 9, no. 2, 2016, pp. 136 - 140. Afterwards a spherical absorption correction was performed within STOE LANA.
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.954, 0.987	0.863, 0.961	0.686, 0.949
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	25734, 25734, 19209	10260, 2721, 2495	8615, 2500, 1864
<i>R<sub>int</sub></i>	?	0.022	0.069
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.599	0.610	0.600
Refinement <i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.063, 0.180, 1.03	0.037, 0.101, 1.04	0.068, 0.187, 1.07
No. of reflections	25734	2721	2500
No. of parameters	363	210	201
No. of restraints	0	0	0

H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\max}, \Delta\rho_{\min}$ ( $e \text{ \AA}^{-3}$ )	0.41, -0.34	0.22, -0.22	0.27, -0.25
Absolute structure	–	–	–
Absolute structure parameter	–	–	–

**Table 10:** Geometric parameters of compound **1** ( $\text{\AA}$ ,  $^\circ$ ), symmetry code: (i)  $-x+1, -y+1, -z+1$

Fe1—N4	2.195(3)	C15—H15A	0.9900
Fe1—N4 <sup>i</sup>	2.195(3)	C15—H15B	0.9900
Fe1—N8 <sup>i</sup>	2.162(3)	C16—H16	0.9500
Fe1—N8	2.162(3)	C17—C18	1.391(5)
Fe1—N9 <sup>i</sup>	2.141(3)	C17—C30	1.428(5)
Fe1—N9	2.141(3)	C17—C31	1.522(5)
N1—N2	1.352(4)	C18—C19	1.423(5)
N1—C15	1.474(4)	C18—C23	1.451(5)
N1—C16	1.327(4)	C19—H19	0.9500
N2—N3	1.291(4)	C19—C20	1.371(6)
N3—N4	1.374(4)	C20—H20	0.9500
N4—C16	1.316(4)	C20—C21	1.418(5)
N5—N6	1.347(4)	C21—H21	0.9500
N5—C31	1.470(4)	C21—C22	1.350(6)
N5—C32	1.323(4)	C22—H22	0.9500
N6—N7	1.288(4)	C22—C23	1.419(5)
N7—N8	1.356(4)	C23—C24	1.393(5)
N8—C32	1.310(4)	C24—H24	0.9500
N9—C33	1.166(5)	C24—C25	1.401(5)
C1—C2	1.399(5)	C25—C26	1.438(5)
C1—C14	1.409(5)	C25—C30	1.444(5)
C1—C15	1.519(5)	C26—H26	0.9500
C2—C3	1.431(5)	C26—C27	1.323(6)
C2—C7	1.447(5)	C27—H27	0.9500
C3—H3	0.9500	C27—C28	1.424(6)
C3—C4	1.363(6)	C28—H28	0.9500
C4—H4	0.9500	C28—C29	1.368(5)
C4—C5	1.413(6)	C29—H29	0.9500
C5—H5	0.9500	C29—C30	1.423(5)
C5—C6	1.359(6)	C31—H31A	0.9900
C6—H6	0.9500	C31—H31B	0.9900
C6—C7	1.425(5)	C32—H32	0.9500
C7—C8	1.392(5)	C33—C34	1.438(6)
C8—H8	0.9500	C34—H34A	0.9800
C8—C9	1.389(5)	C34—H34B	0.9800
C9—C10	1.433(5)	C34—H34C	0.9800
C9—C14	1.437(5)	C11—O1	1.443(3)
C10—H10	0.9500	C11—O2	1.436(3)
C10—C11	1.354(6)	C11—O3	1.434(3)
C11—H11	0.9500	C11—O4	1.429(3)
C11—C12	1.423(6)	N10—C35	1.146(6)
C12—H12	0.9500	C35—C36	1.454(6)
C12—C13	1.360(5)	C36—H36A	0.9800
C13—H13	0.9500	C36—H36B	0.9800
C13—C14	1.435(5)	C36—H36C	0.9800
N4 <sup>i</sup> —Fe1—N4	180.0	C1—C15—H15A	109.1
N8—Fe1—N4	92.96(10)	C1—C15—H15B	109.1
N8 <sup>i</sup> —Fe1—N4 <sup>i</sup>	92.96(10)	H15A—C15—H15B	107.8
N8 <sup>i</sup> —Fe1—N4	87.04(10)	N1—C16—H16	125.4
N8—Fe1—N4 <sup>i</sup>	87.05(10)	N4—C16—N1	109.1(3)
N8 <sup>i</sup> —Fe1—N8	180.0	N4—C16—H16	125.4
N9 <sup>i</sup> —Fe1—N4 <sup>i</sup>	89.42(11)	C18—C17—C30	121.8(3)
N9—Fe1—N4	89.42(11)	C18—C17—C31	120.3(3)
N9—Fe1—N4 <sup>i</sup>	90.58(11)	C30—C17—C31	117.9(3)

N9 <sup>i</sup> —Fe1—N4	90.58(11)	C17—C18—C19	123.5(3)
N9 <sup>i</sup> —Fe1—N8	86.70(11)	C17—C18—C23	119.6(3)
N9 <sup>i</sup> —Fe1—N8 <sup>i</sup>	93.30(11)	C19—C18—C23	116.8(3)
N9—Fe1—N8 <sup>i</sup>	86.70(11)	C18—C19—H19	119.3
N9—Fe1—N8	93.30(11)	C20—C19—C18	121.4(3)
N9—Fe1—N9 <sup>i</sup>	180.0	C20—C19—H19	119.3
N2—N1—C15	121.1(3)	C19—C20—H20	119.5
C16—N1—N2	108.0(3)	C19—C20—C21	121.0(4)
C16—N1—C15	130.9(3)	C21—C20—H20	119.5
N3—N2—N1	107.5(3)	C20—C21—H21	120.2
N2—N3—N4	109.4(3)	C22—C21—C20	119.6(4)
N3—N4—Fe1	122.7(2)	C22—C21—H21	120.2
C16—N4—Fe1	129.9(2)	C21—C22—H22	119.2
C16—N4—N3	106.0(3)	C21—C22—C23	121.5(4)
N6—N5—C31	122.9(3)	C23—C22—H22	119.2
C32—N5—N6	108.3(3)	C22—C23—C18	119.6(3)
C32—N5—C31	128.8(3)	C24—C23—C18	118.9(3)
N7—N6—N5	106.7(3)	C24—C23—C22	121.5(3)
N6—N7—N8	110.0(3)	C23—C24—H24	119.1
N7—N8—Fe1	128.6(2)	C23—C24—C25	121.7(3)
C32—N8—Fe1	125.0(2)	C25—C24—H24	119.1
C32—N8—N7	106.3(3)	C24—C25—C26	121.6(3)
C33—N9—Fe1	157.2(3)	C24—C25—C30	120.3(3)
C2—C1—C14	121.1(3)	C26—C25—C30	118.1(3)
C2—C1—C15	119.6(3)	C25—C26—H26	119.3
C14—C1—C15	119.3(3)	C27—C26—C25	121.4(4)
C1—C2—C3	123.9(3)	C27—C26—H26	119.3
C1—C2—C7	119.3(3)	C26—C27—H27	119.5
C3—C2—C7	116.8(3)	C26—C27—C28	120.9(4)
C2—C3—H3	119.1	C28—C27—H27	119.5
C4—C3—C2	121.9(4)	C27—C28—H28	119.7
C4—C3—H3	119.1	C29—C28—C27	120.5(4)
C3—C4—H4	119.6	C29—C28—H28	119.7
C3—C4—C5	120.8(4)	C28—C29—H29	119.8
C5—C4—H4	119.6	C28—C29—C30	120.4(4)
C4—C5—H5	120.0	C30—C29—H29	119.8
C6—C5—C4	119.9(4)	C17—C30—C25	117.5(3)
C6—C5—H5	120.0	C29—C30—C17	124.1(3)
C5—C6—H6	119.3	C29—C30—C25	118.4(3)
C5—C6—C7	121.4(4)	N5—C31—C17	109.2(3)
C7—C6—H6	119.3	N5—C31—H31A	109.8
C6—C7—C2	119.3(3)	N5—C31—H31B	109.8
C8—C7—C2	118.8(3)	C17—C31—H31A	109.8
C8—C7—C6	121.9(3)	C17—C31—H31B	109.8
C7—C8—H8	118.8	H31A—C31—H31B	108.3
C9—C8—C7	122.4(3)	N5—C32—H32	125.7
C9—C8—H8	118.8	N8—C32—N5	108.7(3)
C8—C9—C10	121.6(3)	N8—C32—H32	125.7
C8—C9—C14	119.1(3)	N9—C33—C34	178.6(4)
C10—C9—C14	119.2(4)	C33—C34—H34A	109.5
C9—C10—H10	119.5	C33—C34—H34B	109.5
C11—C10—C9	121.1(4)	C33—C34—H34C	109.5
C11—C10—H10	119.5	H34A—C34—H34B	109.5
C10—C11—H11	119.8	H34A—C34—H34C	109.5
C10—C11—C12	120.4(4)	H34B—C34—H34C	109.5
C12—C11—H11	119.8	O2—C11—O1	109.10(17)
C11—C12—H12	119.9	O3—C11—O1	110.13(18)
C13—C12—C11	120.1(4)	O3—C11—O2	109.99(18)
C13—C12—H12	119.9	O4—C11—O1	109.64(19)
C12—C13—H13	119.0	O4—C11—O2	108.4(2)
C12—C13—C14	122.0(4)	O4—C11—O3	109.59(18)
C14—C13—H13	119.0	N10—C35—C36	179.4(5)
C1—C14—C9	119.3(3)	C35—C36—H36A	109.5
C1—C14—C13	123.6(3)	C35—C36—H36B	109.5

C13—C14—C9	117.1(3)	C35—C36—H36C	109.5
N1—C15—C1	112.7(3)	H36A—C36—H36B	109.5
N1—C15—H15A	109.1	H36A—C36—H36C	109.5
N1—C15—H15B	109.1	H36B—C36—H36C	109.5
Fe1—N4—C16—N1	167.0(2)	C15—N1—C16—N4	-178.3(3)
Fe1—N8—C32—N5	177.4(2)	C15—C1—C2—C3	0.8(5)
N1—N2—N3—N4	0.1(4)	C15—C1—C2—C7	179.0(3)
N2—N1—C15—C1	74.6(4)	C15—C1—C14—C9	-177.8(3)
N2—N1—C16—N4	-0.4(4)	C15—C1—C14—C13	1.5(5)
N2—N3—N4—Fe1	-168.1(2)	C16—N1—N2—N3	0.2(4)
N2—N3—N4—C16	-0.3(4)	C16—N1—C15—C1	-107.7(4)
N3—N4—C16—N1	0.4(4)	C17—C18—C19—C20	-177.2(3)
N5—N6—N7—N8	0.6(4)	C17—C18—C23—C22	179.4(3)
N6—N5—C31—C17	-170.9(3)	C17—C18—C23—C24	0.7(5)
N6—N5—C32—N8	0.8(4)	C18—C17—C30—C25	4.6(5)
N6—N7—N8—Fe1	-177.8(2)	C18—C17—C30—C29	-173.8(3)
N6—N7—N8—C32	-0.1(4)	C18—C17—C31—N5	91.0(4)
N7—N8—C32—N5	-0.4(4)	C18—C19—C20—C21	-1.7(6)
C1—C2—C3—C4	177.3(4)	C18—C23—C24—C25	0.9(5)
C1—C2—C7—C6	-178.9(3)	C19—C18—C23—C22	2.3(5)
C1—C2—C7—C8	-1.2(5)	C19—C18—C23—C24	-176.3(3)
C2—C1—C14—C9	0.4(5)	C19—C20—C21—C22	1.7(6)
C2—C1—C14—C13	179.8(3)	C20—C21—C22—C23	0.4(6)
C2—C1—C15—N1	91.3(4)	C21—C22—C23—C18	-2.4(5)
C2—C3—C4—C5	1.3(6)	C21—C22—C23—C24	176.2(3)
C2—C7—C8—C9	0.5(5)	C22—C23—C24—C25	-177.7(3)
C3—C2—C7—C6	-0.5(5)	C23—C18—C19—C20	-0.3(5)
C3—C2—C7—C8	177.1(3)	C23—C24—C25—C26	179.4(3)
C3—C4—C5—C6	-0.2(6)	C23—C24—C25—C30	0.2(5)
C4—C5—C6—C7	-1.3(6)	C24—C25—C26—C27	-177.7(3)
C5—C6—C7—C2	1.6(6)	C24—C25—C30—C17	-2.9(5)
C5—C6—C7—C8	-175.9(4)	C24—C25—C30—C29	175.6(3)
C6—C7—C8—C9	178.1(3)	C25—C26—C27—C28	1.6(6)
C7—C2—C3—C4	-0.9(5)	C26—C25—C30—C17	177.9(3)
C7—C8—C9—C10	-178.1(3)	C26—C25—C30—C29	-3.6(5)
C7—C8—C9—C14	0.7(5)	C26—C27—C28—C29	-2.6(6)
C8—C9—C10—C11	179.4(4)	C27—C28—C29—C30	0.4(6)
C8—C9—C14—C1	-1.1(5)	C28—C29—C30—C17	-178.9(3)
C8—C9—C14—C13	179.5(3)	C28—C29—C30—C25	2.7(5)
C9—C10—C11—C12	0.7(6)	C30—C17—C18—C19	173.2(3)
C10—C9—C14—C1	177.6(3)	C30—C17—C18—C23	-3.6(5)
C10—C9—C14—C13	-1.8(5)	C30—C17—C31—N5	-88.3(4)
C10—C11—C12—C13	-0.8(6)	C30—C25—C26—C27	1.5(5)
C11—C12—C13—C14	-0.4(6)	C31—N5—N6—N7	178.0(3)
C12—C13—C14—C1	-177.7(3)	C31—N5—C32—N8	-178.0(3)
C12—C13—C14—C9	1.7(5)	C31—C17—C18—C19	-6.1(5)
C14—C1—C2—C3	-177.5(3)	C31—C17—C18—C23	177.1(3)
C14—C1—C2—C7	0.7(5)	C31—C17—C30—C25	-176.0(3)
C14—C1—C15—N1	-90.5(4)	C31—C17—C30—C29	5.6(5)
C14—C9—C10—C11	0.6(6)	C32—N5—N6—N7	-0.8(4)
C15—N1—N2—N3	178.3(3)	C32—N5—C31—C17	7.7(5)

**Table 11:** Geometric parameters of compound **2** (Å, °), symmetry codes: (i) -x+1, -y+1, -z+1; (ii) -x, -y+2, -z+1

Fe1—N4	2.1313(18)	C11—H11	0.9500
Fe1—N4 <sup>i</sup>	2.1314(18)	C11—C12	1.392(3)
Fe1—N8	2.1653(18)	C12—H12	0.9500
Fe1—N8 <sup>i</sup>	2.1653(18)	C12—C13	1.388(3)
Fe1—N9	2.1288(19)	C13—H13	0.9500
Fe1—N9 <sup>i</sup>	2.1289(19)	C13—C14	1.393(3)
Cl1—O1	1.421(2)	C15—H15A	0.9900
Cl1—O2	1.4281(18)	C15—H15B	0.9900
Cl1—O3	1.4325(17)	C16—H16	0.9500

C11—O4	1.435(2)	C17—C18	1.411(3)
N1—N2	1.355(2)	C17—C30	1.415(3)
N1—C15	1.476(3)	C17—C31	1.513(3)
N1—C16	1.328(3)	C18—C19	1.436(3)
N2—N3	1.292(3)	C18—C23	1.435(3)
N3—N4	1.352(2)	C19—H19	0.9500
N4—C16	1.318(3)	C19—C20	1.365(3)
N5—N6	1.356(2)	C20—H20	0.9500
N5—C31	1.475(3)	C20—C21	1.413(4)
N5—C32	1.333(3)	C21—H21	0.9500
N6—N7	1.292(3)	C21—C22	1.354(3)
N7—N8	1.372(2)	C22—H22	0.9500
N8—C32	1.310(3)	C22—C23	1.428(3)
N9—C33	1.142(3)	C23—C24	1.394(3)
N10—C35	1.142(3)	C24—H24	0.9500
C1—C2	1.526(3)	C24—C25	1.394(3)
C1—C8 <sup>ii</sup>	1.631(3)	C25—C26	1.429(3)
C1—C14	1.534(3)	C25—C30	1.435(3)
C1—C15	1.534(3)	C26—H26	0.9500
C2—C3	1.393(3)	C26—C27	1.353(4)
C2—C7	1.406(3)	C27—H27	0.9500
C3—H3	0.9500	C27—C28	1.418(3)
C3—C4	1.393(3)	C28—H28	0.9500
C4—H4	0.9500	C28—C29	1.360(3)
C4—C5	1.382(3)	C29—H29	0.9500
C5—H5	0.9500	C29—C30	1.435(3)
C5—C6	1.390(3)	C31—H31A	0.9900
C6—H6	0.9500	C31—H31B	0.9900
C6—C7	1.384(3)	C32—H32	0.9500
C7—C8	1.510(3)	C33—C34	1.455(3)
C8—C1 <sup>ii</sup>	1.631(3)	C34—H34A	0.9800
C8—H8	1.0000	C34—H34B	0.9800
C8—C9	1.516(3)	C34—H34C	0.9800
C9—C10	1.388(3)	C35—C36	1.451(4)
C9—C14	1.404(3)	C36—H36A	0.9800
C10—H10	0.9500	C36—H36B	0.9800
C10—C11	1.389(3)	C36—H36C	0.9800
N4—Fe1—N4 <sup>i</sup>	180.0	C12—C13—H13	119.5
N4—Fe1—N8 <sup>i</sup>	88.35(6)	C12—C13—C14	120.91(19)
N4 <sup>i</sup> —Fe1—N8 <sup>i</sup>	91.65(6)	C14—C13—H13	119.5
N4—Fe1—N8	91.65(6)	C9—C14—C1	116.59(18)
N4 <sup>i</sup> —Fe1—N8	88.35(6)	C13—C14—C1	124.36(18)
N8—Fe1—N8 <sup>i</sup>	180.0	C13—C14—C9	119.04(19)
N9 <sup>i</sup> —Fe1—N4	91.69(7)	N1—C15—C1	114.98(16)
N9—Fe1—N4 <sup>i</sup>	91.69(7)	N1—C15—H15A	108.5
N9 <sup>i</sup> —Fe1—N4 <sup>i</sup>	88.31(7)	N1—C15—H15B	108.5
N9—Fe1—N4	88.31(7)	C1—C15—H15A	108.5
N9 <sup>i</sup> —Fe1—N8	88.05(7)	C1—C15—H15B	108.5
N9—Fe1—N8	91.95(7)	H15A—C15—H15B	107.5
N9—Fe1—N8 <sup>i</sup>	88.05(7)	N1—C16—H16	125.7
N9 <sup>i</sup> —Fe1—N8 <sup>i</sup>	91.94(7)	N4—C16—N1	108.52(18)
N9—Fe1—N9 <sup>i</sup>	180.00(7)	N4—C16—H16	125.7
O1—C11—O2	109.79(14)	C18—C17—C30	120.60(19)
O1—C11—O3	109.86(12)	C18—C17—C31	119.84(19)
O1—C11—O4	110.11(16)	C30—C17—C31	119.55(19)
O2—C11—O3	108.99(12)	C17—C18—C19	123.8(2)
O2—C11—O4	107.99(12)	C17—C18—C23	119.42(19)
O3—C11—O4	110.07(11)	C23—C18—C19	116.8(2)
N2—N1—C15	118.72(16)	C18—C19—H19	119.3
C16—N1—N2	107.99(17)	C20—C19—C18	121.3(2)
C16—N1—C15	133.29(17)	C20—C19—H19	119.3
N3—N2—N1	106.94(16)	C19—C20—H20	119.4
N2—N3—N4	109.95(16)	C19—C20—C21	121.2(2)
N3—N4—Fe1	124.53(13)	C21—C20—H20	119.4

C16—N4—Fe1	128.87(14)	C20—C21—H21	120.1
C16—N4—N3	106.60(17)	C22—C21—C20	119.8(2)
N6—N5—C31	120.95(17)	C22—C21—H21	120.1
C32—N5—N6	108.10(17)	C21—C22—H22	119.4
C32—N5—C31	130.94(18)	C21—C22—C23	121.2(2)
N7—N6—N5	107.05(17)	C23—C22—H22	119.4
N6—N7—N8	109.58(17)	C22—C23—C18	119.8(2)
N7—N8—Fe1	122.17(13)	C24—C23—C18	119.3(2)
C32—N8—Fe1	130.60(15)	C24—C23—C22	120.9(2)
C32—N8—N7	106.48(17)	C23—C24—H24	119.0
C33—N9—Fe1	165.94(18)	C25—C24—C23	122.0(2)
C2—C1—C8 <sup>ii</sup>	109.73(16)	C25—C24—H24	119.0
C2—C1—C14	108.49(16)	C24—C25—C26	121.2(2)
C2—C1—C15	112.85(16)	C24—C25—C30	119.3(2)
C14—C1—C8 <sup>ii</sup>	109.56(15)	C26—C25—C30	119.4(2)
C15—C1—C8 <sup>ii</sup>	103.40(15)	C25—C26—H26	119.5
C15—C1—C14	112.68(17)	C27—C26—C25	121.1(2)
C3—C2—C1	124.22(18)	C27—C26—H26	119.5
C3—C2—C7	119.21(19)	C26—C27—H27	119.9
C7—C2—C1	116.48(17)	C26—C27—C28	120.3(2)
C2—C3—H3	119.8	C28—C27—H27	119.9
C2—C3—C4	120.34(19)	C27—C28—H28	119.8
C4—C3—H3	119.8	C29—C28—C27	120.4(2)
C3—C4—H4	120.0	C29—C28—H28	119.8
C5—C4—C3	119.95(19)	C28—C29—H29	119.1
C5—C4—H4	120.0	C28—C29—C30	121.9(2)
C4—C5—H5	119.9	C30—C29—H29	119.1
C4—C5—C6	120.2(2)	C17—C30—C25	119.3(2)
C6—C5—H5	119.9	C17—C30—C29	123.8(2)
C5—C6—H6	119.9	C25—C30—C29	116.9(2)
C7—C6—C5	120.27(19)	N5—C31—C17	112.01(17)
C7—C6—H6	119.9	N5—C31—H31A	109.2
C2—C7—C8	118.18(18)	N5—C31—H31B	109.2
C6—C7—C2	119.99(19)	C17—C31—H31A	109.2
C6—C7—C8	121.82(18)	C17—C31—H31B	109.2
C1 <sup>ii</sup> —C8—H8	107.6	H31A—C31—H31B	107.9
C7—C8—C1 <sup>ii</sup>	112.39(16)	N5—C32—H32	125.6
C7—C8—H8	107.6	N8—C32—N5	108.79(19)
C7—C8—C9	108.86(16)	N8—C32—H32	125.6
C9—C8—C1 <sup>ii</sup>	112.64(16)	N9—C33—C34	178.0(2)
C9—C8—H8	107.6	C33—C34—H34A	109.5
C10—C9—C8	122.24(18)	C33—C34—H34B	109.5
C10—C9—C14	119.87(19)	C33—C34—H34C	109.5
C14—C9—C8	117.88(18)	H34A—C34—H34B	109.5
C9—C10—H10	119.7	H34A—C34—H34C	109.5
C9—C10—C11	120.60(19)	H34B—C34—H34C	109.5
C11—C10—H10	119.7	N10—C35—C36	179.1(3)
C10—C11—H11	120.1	C35—C36—H36A	109.5
C10—C11—C12	119.8(2)	C35—C36—H36B	109.5
C12—C11—H11	120.1	C35—C36—H36C	109.5
C11—C12—H12	120.1	H36A—C36—H36B	109.5
C13—C12—C11	119.7(2)	H36A—C36—H36C	109.5
C13—C12—H12	120.1	H36B—C36—H36C	109.5
Fe1—N4—C16—N1	179.01(13)	C14—C1—C2—C7	-45.1(2)
Fe1—N8—C32—N5	-170.35(14)	C14—C1—C15—N1	-65.7(2)
N1—N2—N3—N4	-0.2(2)	C14—C9—C10—C11	0.0(3)
N2—N1—C15—C1	-168.63(17)	C15—N1—N2—N3	179.75(17)
N2—N1—C16—N4	-0.1(2)	C15—N1—C16—N4	-179.6(2)
N2—N3—N4—Fe1	-178.94(13)	C15—C1—C2—C3	12.7(3)
N2—N3—N4—C16	0.1(2)	C15—C1—C2—C7	-170.74(17)
N3—N4—C16—N1	0.0(2)	C15—C1—C14—C9	170.40(17)
N5—N6—N7—N8	0.1(2)	C15—C1—C14—C13	-10.8(3)
N6—N5—C31—C17	-76.3(2)	C16—N1—N2—N3	0.2(2)
N6—N5—C32—N8	0.4(2)	C16—N1—C15—C1	10.8(3)

N6—N7—N8—Fe1	171.18(14)	C17—C18—C19—C20	-177.2(2)
N6—N7—N8—C32	0.1(2)	C17—C18—C23—C22	177.56(19)
N7—N8—C32—N5	-0.3(2)	C17—C18—C23—C24	0.7(3)
C1—C2—C3—C4	178.02(19)	C18—C17—C30—C25	1.3(3)
C1—C2—C7—C6	-177.10(18)	C18—C17—C30—C29	-176.6(2)
C1—C2—C7—C8	1.4(3)	C18—C17—C31—N5	-94.0(2)
C1 <sup>ii</sup> —C8—C9—C10	-97.6(2)	C18—C19—C20—C21	-0.2(4)
C1 <sup>ii</sup> —C8—C9—C14	82.0(2)	C18—C23—C24—C25	2.2(3)
C2—C1—C14—C9	44.7(2)	C19—C18—C23—C22	-0.5(3)
C2—C1—C14—C13	-136.5(2)	C19—C18—C23—C24	-177.39(19)
C2—C1—C15—N1	57.6(2)	C19—C20—C21—C22	-0.7(4)
C2—C3—C4—C5	-1.7(3)	C20—C21—C22—C23	0.9(4)
C2—C7—C8—C1 <sup>ii</sup>	-82.5(2)	C21—C22—C23—C18	-0.3(3)
C2—C7—C8—C9	43.0(2)	C21—C22—C23—C24	176.5(2)
C3—C2—C7—C6	-0.4(3)	C22—C23—C24—C25	-174.6(2)
C3—C2—C7—C8	178.09(18)	C23—C18—C19—C20	0.8(3)
C3—C4—C5—C6	0.6(3)	C23—C24—C25—C26	174.7(2)
C4—C5—C6—C7	0.6(3)	C23—C24—C25—C30	-3.4(3)
C5—C6—C7—C2	-0.7(3)	C24—C25—C26—C27	-178.3(2)
C5—C6—C7—C8	-179.13(18)	C24—C25—C30—C17	1.6(3)
C6—C7—C8—C1 <sup>ii</sup>	95.9(2)	C24—C25—C30—C29	179.64(19)
C6—C7—C8—C9	-138.61(19)	C25—C26—C27—C28	-0.8(4)
C7—C2—C3—C4	1.6(3)	C26—C25—C30—C17	-176.5(2)
C7—C8—C9—C10	137.02(19)	C26—C25—C30—C29	1.6(3)
C7—C8—C9—C14	-43.3(2)	C26—C27—C28—C29	0.6(4)
C8 <sup>ii</sup> —C1—C2—C3	-102.0(2)	C27—C28—C29—C30	0.8(4)
C8 <sup>ii</sup> —C1—C2—C7	74.5(2)	C28—C29—C30—C17	176.1(2)
C8 <sup>ii</sup> —C1—C14—C9	-75.1(2)	C28—C29—C30—C25	-1.8(3)
C8 <sup>ii</sup> —C1—C14—C13	103.7(2)	C30—C17—C18—C19	175.5(2)
C8 <sup>ii</sup> —C1—C15—N1	176.12(16)	C30—C17—C18—C23	-2.4(3)
C8—C9—C10—C11	179.63(18)	C30—C17—C31—N5	87.3(2)
C8—C9—C14—C1	-0.5(3)	C30—C25—C26—C27	-0.3(3)
C8—C9—C14—C13	-179.35(18)	C31—N5—N6—N7	-179.21(18)
C9—C10—C11—C12	0.2(3)	C31—N5—C32—N8	179.15(19)
C10—C9—C14—C1	179.18(18)	C31—C17—C18—C19	-3.1(3)
C10—C9—C14—C13	0.3(3)	C31—C17—C18—C23	178.90(18)
C10—C11—C12—C13	-0.6(3)	C31—C17—C30—C25	179.96(18)
C11—C12—C13—C14	0.9(3)	C31—C17—C30—C29	2.0(3)
C12—C13—C14—C1	-179.49(19)	C32—N5—N6—N7	-0.3(2)
C12—C13—C14—C9	-0.7(3)	C32—N5—C31—C17	105.1(2)
C14—C1—C2—C3	138.3(2)		

**Table 12:** Geometric parameters of L1-p1 (Å, °)

N1—N2	1.342(6)	N5—N6	1.358(6)
N1—C15	1.469(7)	N5—C31	1.461(7)
N1—C16	1.337(7)	N5—C32	1.342(8)
N2—N3	1.295(7)	N6—N7	1.295(7)
N3—N4	1.354(6)	N7—N8	1.346(7)
N4—C16	1.324(7)	N8—C32	1.314(8)
C1—C2	1.419(8)	C17—C18	1.419(8)
C1—C14	1.401(8)	C17—C30	1.415(8)
C1—C15	1.500(9)	C17—C31	1.515(8)
C2—C3	1.424(8)	C18—C19	1.439(8)
C2—C7	1.427(8)	C18—C23	1.428(8)
C3—H3	0.9300	C19—H19	0.9300
C3—C4	1.360(8)	C19—C20	1.358(9)
C4—H4	0.9300	C20—H20	0.9300
C4—C5	1.408(10)	C20—C21	1.389(9)
C5—H5	0.9300	C21—H21	0.9300
C5—C6	1.350(10)	C21—C22	1.360(9)
C6—H6	0.9300	C22—H22	0.9300
C6—C7	1.433(9)	C22—C23	1.430(8)

C7—C8	1.392(9)	C23—C24	1.399(8)
C8—H8	0.9300	C24—H24	0.9300
C8—C9	1.386(9)	C24—C25	1.368(9)
C9—C10	1.429(9)	C25—C26	1.433(8)
C9—C14	1.433(9)	C25—C30	1.431(9)
C10—H10	0.9300	C26—H26	0.9300
C10—C11	1.369(10)	C26—C27	1.345(9)
C11—H11	0.9300	C27—H27	0.9300
C11—C12	1.398(11)	C27—C28	1.421(10)
C12—H12	0.9300	C28—H28	0.9300
C12—C13	1.353(8)	C28—C29	1.354(9)
C13—H13	0.9300	C29—H29	0.9300
C13—C14	1.431(9)	C29—C30	1.434(8)
C15—H15A	0.9700	C31—H31A	0.9700
C15—H15B	0.9700	C31—H31B	0.9700
C16—H16	0.9300	C32—H32	0.9300
N2—N1—C15	120.5(4)	N6—N5—C31	121.6(5)
C16—N1—N2	108.5(4)	C32—N5—N6	107.3(5)
C16—N1—C15	131.0(4)	C32—N5—C31	131.1(5)
N3—N2—N1	106.3(4)	N7—N6—N5	106.4(4)
N2—N3—N4	111.2(4)	N6—N7—N8	111.2(5)
C16—N4—N3	105.3(5)	C32—N8—N7	105.8(5)
C2—C1—C15	120.1(5)	C18—C17—C31	119.5(5)
C14—C1—C2	120.3(6)	C30—C17—C18	120.2(5)
C14—C1—C15	119.6(5)	C30—C17—C31	120.3(5)
C1—C2—C3	123.6(5)	C17—C18—C19	122.8(5)
C1—C2—C7	119.2(5)	C17—C18—C23	119.5(5)
C3—C2—C7	117.2(5)	C23—C18—C19	117.7(5)
C2—C3—H3	119.1	C18—C19—H19	119.8
C4—C3—C2	121.9(6)	C20—C19—C18	120.3(6)
C4—C3—H3	119.1	C20—C19—H19	119.8
C3—C4—H4	119.8	C19—C20—H20	119.0
C3—C4—C5	120.4(6)	C19—C20—C21	121.9(6)
C5—C4—H4	119.8	C21—C20—H20	119.0
C4—C5—H5	119.8	C20—C21—H21	119.8
C6—C5—C4	120.4(6)	C22—C21—C20	120.3(6)
C6—C5—H5	119.8	C22—C21—H21	119.8
C5—C6—H6	119.6	C21—C22—H22	119.7
C5—C6—C7	120.9(6)	C21—C22—C23	120.6(6)
C7—C6—H6	119.6	C23—C22—H22	119.7
C2—C7—C6	119.2(6)	C18—C23—C22	119.1(5)
C8—C7—C2	119.3(6)	C24—C23—C18	118.8(5)
C8—C7—C6	121.5(6)	C24—C23—C22	122.1(6)
C7—C8—H8	118.8	C23—C24—H24	118.7
C9—C8—C7	122.4(6)	C25—C24—C23	122.6(6)
C9—C8—H8	118.8	C25—C24—H24	118.7
C8—C9—C10	121.8(6)	C24—C25—C26	121.8(6)
C8—C9—C14	118.8(6)	C24—C25—C30	119.8(5)
C10—C9—C14	119.4(6)	C30—C25—C26	118.4(5)
C9—C10—H10	119.6	C25—C26—H26	119.1
C11—C10—C9	120.7(6)	C27—C26—C25	121.9(6)
C11—C10—H10	119.6	C27—C26—H26	119.1
C10—C11—H11	120.0	C26—C27—H27	120.2
C10—C11—C12	120.1(6)	C26—C27—C28	119.6(6)
C12—C11—H11	120.0	C28—C27—H27	120.2
C11—C12—H12	119.6	C27—C28—H28	119.5
C13—C12—C11	120.9(7)	C29—C28—C27	121.1(6)
C13—C12—H12	119.6	C29—C28—H28	119.5
C12—C13—H13	118.9	C28—C29—H29	119.5
C12—C13—C14	122.2(6)	C28—C29—C30	121.1(6)
C14—C13—H13	118.9	C30—C29—H29	119.5
C1—C14—C9	120.0(6)	C17—C30—C25	119.1(5)
C1—C14—C13	123.3(6)	C17—C30—C29	123.0(5)
C13—C14—C9	116.7(5)	C25—C30—C29	117.9(5)

N1—C15—C1	112.3(5)	N5—C31—C17	112.7(5)
N1—C15—H15A	109.1	N5—C31—H31A	109.1
N1—C15—H15B	109.1	N5—C31—H31B	109.1
C1—C15—H15A	109.1	C17—C31—H31A	109.1
C1—C15—H15B	109.1	C17—C31—H31B	109.1
H15A—C15—H15B	107.9	H31A—C31—H31B	107.8
N1—C16—H16	125.7	N5—C32—H32	125.4
N4—C16—N1	108.7(5)	N8—C32—N5	109.3(5)
N4—C16—H16	125.7	N8—C32—H32	125.4
N1—N2—N3—N4	0.1(6)	N5—N6—N7—N8	-0.5(6)
N2—N1—C15—C1	60.3(6)	N6—N5—C31—C17	-70.0(6)
N2—N1—C16—N4	-0.1(7)	N6—N5—C32—N8	0.0(7)
N2—N3—N4—C16	-0.1(7)	N6—N7—N8—C32	0.5(7)
N3—N4—C16—N1	0.1(6)	N7—N8—C32—N5	-0.3(7)
C1—C2—C3—C4	179.8(5)	C17—C18—C19—C20	-177.8(5)
C1—C2—C7—C6	179.6(5)	C17—C18—C23—C22	177.7(5)
C1—C2—C7—C8	-1.2(8)	C17—C18—C23—C24	-2.5(8)
C2—C1—C14—C9	-0.8(8)	C18—C17—C30—C25	2.8(8)
C2—C1—C14—C13	179.7(5)	C18—C17—C30—C29	-178.3(5)
C2—C1—C15—N1	-95.8(6)	C18—C17—C31—N5	91.3(6)
C2—C3—C4—C5	0.6(9)	C18—C19—C20—C21	0.2(9)
C2—C7—C8—C9	-0.6(8)	C18—C23—C24—C25	2.7(8)
C3—C2—C7—C6	-1.1(7)	C19—C18—C23—C22	-0.5(8)
C3—C2—C7—C8	178.2(5)	C19—C18—C23—C24	179.4(5)
C3—C4—C5—C6	-1.3(9)	C19—C20—C21—C22	-0.5(9)
C4—C5—C6—C7	0.7(9)	C20—C21—C22—C23	0.2(9)
C5—C6—C7—C2	0.5(8)	C21—C22—C23—C18	0.3(8)
C5—C6—C7—C8	-178.7(6)	C21—C22—C23—C24	-179.6(5)
C6—C7—C8—C9	178.6(5)	C22—C23—C24—C25	-177.5(5)
C7—C2—C3—C4	0.5(8)	C23—C18—C19—C20	0.3(8)
C7—C8—C9—C10	179.9(5)	C23—C24—C25—C26	-179.6(5)
C7—C8—C9—C14	1.6(8)	C23—C24—C25—C30	-0.1(9)
C8—C9—C10—C11	-177.8(6)	C24—C25—C26—C27	-179.4(6)
C8—C9—C14—C1	-0.9(8)	C24—C25—C30—C17	-2.7(8)
C8—C9—C14—C13	178.6(5)	C24—C25—C30—C29	178.4(5)
C9—C10—C11—C12	-0.6(9)	C25—C26—C27—C28	0.8(9)
C10—C9—C14—C1	-179.2(5)	C26—C25—C30—C17	176.9(5)
C10—C9—C14—C13	0.3(8)	C26—C25—C30—C29	-2.1(8)
C10—C11—C12—C13	0.0(9)	C26—C27—C28—C29	-1.8(9)
C11—C12—C13—C14	0.8(9)	C27—C28—C29—C30	0.8(9)
C12—C13—C14—C1	178.5(5)	C28—C29—C30—C17	-177.7(6)
C12—C13—C14—C9	-0.9(8)	C28—C29—C30—C25	1.2(9)
C14—C1—C2—C3	-177.4(5)	C30—C17—C18—C19	177.9(5)
C14—C1—C2—C7	1.9(8)	C30—C17—C18—C23	-0.2(8)
C14—C1—C15—N1	84.0(6)	C30—C17—C31—N5	-90.6(6)
C14—C9—C10—C11	0.5(8)	C30—C25—C26—C27	1.1(8)
C15—N1—N2—N3	-179.6(5)	C31—N5—N6—N7	178.8(5)
C15—N1—C16—N4	179.5(5)	C31—N5—C32—N8	-178.3(6)
C15—C1—C2—C3	2.4(8)	C31—C17—C18—C19	-4.1(8)
C15—C1—C2—C7	-178.3(5)	C31—C17—C18—C23	177.9(5)
C15—C1—C14—C9	179.4(5)	C31—C17—C30—C25	-175.3(5)
C15—C1—C14—C13	-0.1(8)	C31—C17—C30—C29	3.6(8)
C16—N1—N2—N3	0.0(6)	C32—N5—N6—N7	0.3(6)
C16—N1—C15—C1	-119.2(6)	C32—N5—C31—C17	108.0(7)

**Table 13:** Geometric parameters of L1-p2 (Å, °)

N1—N2	1.346(6)	C6—C7	1.418(7)
N1—C15	1.461(6)	C7—C8	1.399(7)
N1—C16	1.337(6)	C8—H8	0.9500
N2—N3	1.299(6)	C8—C9	1.385(7)
N3—N4	1.373(6)	C9—C10	1.424(7)
N4—C16	1.316(7)	C9—C14	1.428(7)

C1—C2	1.423(7)	C10—H10	0.9500
C1—C14	1.399(7)	C10—C11	1.344(9)
C1—C15	1.510(7)	C11—H11	0.9500
C2—C3	1.427(7)	C11—C12	1.407(9)
C2—C7	1.437(7)	C12—H12	0.9500
C3—H3	0.9500	C12—C13	1.347(8)
C3—C4	1.370(7)	C13—H13	0.9500
C4—H4	0.9500	C13—C14	1.446(7)
C4—C5	1.411(8)	C15—H15A	0.9900
C5—H5	0.9500	C15—H15B	0.9900
C5—C6	1.356(8)	C16—H16	0.9500
C6—H6	0.9500		
N2—N1—C15	122.7(4)	C9—C8—H8	118.8
C16—N1—N2	107.7(4)	C8—C9—C10	121.7(5)
C16—N1—C15	129.6(4)	C8—C9—C14	119.1(5)
N3—N2—N1	106.8(4)	C10—C9—C14	119.1(5)
N2—N3—N4	110.8(4)	C9—C10—H10	118.9
C16—N4—N3	104.6(4)	C11—C10—C9	122.3(6)
C2—C1—C15	119.7(4)	C11—C10—H10	118.9
C14—C1—C2	120.8(5)	C10—C11—H11	120.6
C14—C1—C15	119.5(4)	C10—C11—C12	118.7(5)
C1—C2—C3	124.0(5)	C12—C11—H11	120.6
C1—C2—C7	118.7(4)	C11—C12—H12	118.8
C3—C2—C7	117.3(4)	C13—C12—C11	122.3(5)
C2—C3—H3	119.5	C13—C12—H12	118.8
C4—C3—C2	121.0(5)	C12—C13—H13	119.7
C4—C3—H3	119.5	C12—C13—C14	120.7(5)
C3—C4—H4	119.5	C14—C13—H13	119.7
C3—C4—C5	120.9(5)	C1—C14—C9	119.9(4)
C5—C4—H4	119.5	C1—C14—C13	123.3(5)
C4—C5—H5	120.0	C9—C14—C13	116.8(5)
C6—C5—C4	120.1(5)	N1—C15—C1	112.9(4)
C6—C5—H5	120.0	N1—C15—H15A	109.0
C5—C6—H6	119.5	N1—C15—H15B	109.0
C5—C6—C7	121.0(5)	C1—C15—H15A	109.0
C7—C6—H6	119.5	C1—C15—H15B	109.0
C6—C7—C2	119.7(5)	H15A—C15—H15B	107.8
C8—C7—C2	119.1(4)	N1—C16—H16	124.9
C8—C7—C6	121.3(5)	N4—C16—N1	110.1(4)
C7—C8—H8	118.8	N4—C16—H16	124.9
C9—C8—C7	122.4(5)		
N1—N2—N3—N4	-0.1(5)	C8—C9—C10—C11	-178.6(6)
N2—N1—C15—C1	60.9(6)	C8—C9—C14—C1	-1.5(7)
N2—N1—C16—N4	1.2(6)	C8—C9—C14—C13	178.6(5)
N2—N3—N4—C16	0.8(6)	C9—C10—C11—C12	0.8(9)
N3—N4—C16—N1	-1.3(6)	C10—C9—C14—C1	-179.8(5)
C1—C2—C3—C4	-177.1(5)	C10—C9—C14—C13	0.3(7)
C1—C2—C7—C6	177.4(5)	C10—C11—C12—C13	-1.4(9)
C1—C2—C7—C8	-1.6(7)	C11—C12—C13—C14	1.4(9)
C2—C1—C14—C9	2.0(8)	C12—C13—C14—C1	179.3(5)
C2—C1—C14—C13	-178.1(5)	C12—C13—C14—C9	-0.9(8)
C2—C1—C15—N1	-99.8(5)	C14—C1—C2—C3	179.0(5)
C2—C3—C4—C5	-1.2(8)	C14—C1—C2—C7	-0.5(7)
C2—C7—C8—C9	2.1(8)	C14—C1—C15—N1	82.9(6)
C3—C2—C7—C6	-2.2(7)	C14—C9—C10—C11	-0.3(8)
C3—C2—C7—C8	178.9(5)	C15—N1—N2—N3	-178.4(4)
C3—C4—C5—C6	-0.5(9)	C15—N1—C16—N4	178.8(5)
C4—C5—C6—C7	0.7(9)	C15—C1—C2—C3	1.8(8)
C5—C6—C7—C2	0.6(8)	C15—C1—C2—C7	-177.8(4)
C5—C6—C7—C8	179.5(5)	C15—C1—C14—C9	179.3(4)
C6—C7—C8—C9	-176.8(5)	C15—C1—C14—C13	-0.8(8)
C7—C2—C3—C4	2.5(8)	C16—N1—N2—N3	-0.7(5)
C7—C8—C9—C10	177.7(5)	C16—N1—C15—C1	-116.3(6)
C7—C8—C9—C14	-0.6(8)		

**Table 14:** Geometric parameters of **L2-ns** (Å, °), symmetry codes: (i)  $-x+1, -y+2, -z+1$ ; (ii)  $-x+1, -y+1, -z$ 

N1—N2	1.343(4)	C12—C13	1.382(5)
N1—C15	1.476(4)	C13—H13	0.9500
N1—C16	1.323(5)	C13—C14	1.387(5)
N2—N3	1.297(4)	C15—H15A	0.9900
N3—N4	1.353(4)	C15—H15B	0.9900
N4—C16	1.314(5)	C16—H16	0.9500
N5—N6	1.351(4)	C17—C18	1.535(5)
N5—C31	1.480(4)	C17—C24 <sup>ii</sup>	1.646(5)
N5—C32	1.333(5)	C17—C30	1.528(5)
N6—N7	1.299(4)	C17—C31	1.535(5)
N7—N8	1.367(4)	C18—C19	1.392(5)
N8—C32	1.313(5)	C18—C23	1.405(5)
C1—C2	1.540(5)	C19—H19	0.9500
C1—C8 <sup>i</sup>	1.629(5)	C19—C20	1.386(5)
C1—C14	1.538(5)	C20—H20	0.9500
C1—C15	1.516(5)	C20—C21	1.382(5)
C2—C3	1.387(5)	C21—H21	0.9500
C2—C7	1.401(5)	C21—C22	1.387(5)
C3—H3	0.9500	C22—H22	0.9500
C3—C4	1.381(5)	C22—C23	1.383(5)
C4—H4	0.9500	C23—C24	1.514(5)
C4—C5	1.389(6)	C24—H24	1.0000
C5—H5	0.9500	C24—C25	1.498(5)
C5—C6	1.384(5)	C25—C26	1.391(5)
C6—H6	0.9500	C25—C30	1.400(5)
C6—C7	1.394(5)	C26—H26	0.9500
C7—C8	1.497(5)	C26—C27	1.381(5)
C8—H8	1.0000	C27—H27	0.9500
C8—C9	1.506(5)	C27—C28	1.379(6)
C9—C10	1.397(5)	C28—H28	0.9500
C9—C14	1.400(5)	C28—C29	1.391(5)
C10—H10	0.9500	C29—H29	0.9500
C10—C11	1.380(5)	C29—C30	1.389(5)
C11—H11	0.9500	C31—H31A	0.9900
C11—C12	1.389(6)	C31—H31B	0.9900
C12—H12	0.9500	C32—H32	0.9500
N2—N1—C15	117.7(3)	C1—C15—H15A	108.1
C16—N1—N2	108.0(3)	C1—C15—H15B	108.1
C16—N1—C15	134.3(3)	H15A—C15—H15B	107.3
N3—N2—N1	106.5(3)	N1—C16—H16	125.2
N2—N3—N4	110.7(3)	N4—C16—N1	109.6(3)
C16—N4—N3	105.3(3)	N4—C16—H16	125.2
N6—N5—C31	118.7(3)	C18—C17—C24 <sup>ii</sup>	109.3(3)
C32—N5—N6	107.9(3)	C18—C17—C31	112.5(3)
C32—N5—C31	133.3(3)	C30—C17—C18	109.2(3)
N7—N6—N5	106.6(3)	C30—C17—C24 <sup>ii</sup>	109.0(3)
N6—N7—N8	110.6(3)	C30—C17—C31	112.8(3)
C32—N8—N7	105.2(3)	C31—C17—C24 <sup>ii</sup>	103.8(3)
C2—C1—C8 <sup>i</sup>	110.9(3)	C19—C18—C17	124.8(3)
C14—C1—C2	107.5(3)	C19—C18—C23	118.7(3)
C14—C1—C8 <sup>i</sup>	109.4(3)	C23—C18—C17	116.4(3)
C15—C1—C2	113.3(3)	C18—C19—H19	119.6
C15—C1—C8 <sup>i</sup>	102.3(3)	C20—C19—C18	120.8(3)
C15—C1—C14	113.3(3)	C20—C19—H19	119.6
C3—C2—C1	124.4(3)	C19—C20—H20	119.9
C3—C2—C7	118.8(3)	C21—C20—C19	120.3(3)
C7—C2—C1	116.8(3)	C21—C20—H20	119.9
C2—C3—H3	119.8	C20—C21—H21	120.2
C4—C3—C2	120.4(3)	C20—C21—C22	119.5(3)
C4—C3—H3	119.8	C22—C21—H21	120.2
C3—C4—H4	119.5	C21—C22—H22	119.6
C3—C4—C5	120.9(4)	C23—C22—C21	120.8(3)

C5—C4—H4	119.5	C23—C22—H22	119.6
C4—C5—H5	120.3	C18—C23—C24	117.7(3)
C6—C5—C4	119.5(3)	C22—C23—C18	120.0(3)
C6—C5—H5	120.3	C22—C23—C24	122.3(3)
C5—C6—H6	120.1	C17 <sup>ii</sup> —C24—H24	107.6
C5—C6—C7	119.9(3)	C23—C24—C17 <sup>ii</sup>	111.6(3)
C7—C6—H6	120.1	C23—C24—H24	107.6
C2—C7—C8	117.5(3)	C25—C24—C17 <sup>ii</sup>	112.6(3)
C6—C7—C2	120.6(3)	C25—C24—C23	109.6(3)
C6—C7—C8	122.0(3)	C25—C24—H24	107.6
C1 <sup>i</sup> —C8—H8	107.2	C26—C25—C24	121.9(3)
C7—C8—C1 <sup>i</sup>	112.9(3)	C26—C25—C30	119.6(3)
C7—C8—H8	107.2	C30—C25—C24	118.4(3)
C7—C8—C9	108.9(3)	C25—C26—H26	119.7
C9—C8—C1 <sup>i</sup>	113.0(3)	C27—C26—C25	120.5(3)
C9—C8—H8	107.2	C27—C26—H26	119.7
C10—C9—C8	122.2(3)	C26—C27—H27	119.9
C10—C9—C14	120.0(3)	C28—C27—C26	120.1(4)
C14—C9—C8	117.8(3)	C28—C27—H27	119.9
C9—C10—H10	119.8	C27—C28—H28	120.1
C11—C10—C9	120.4(3)	C27—C28—C29	119.9(3)
C11—C10—H10	119.8	C29—C28—H28	120.1
C10—C11—H11	120.2	C28—C29—H29	119.7
C10—C11—C12	119.6(4)	C30—C29—C28	120.6(3)
C12—C11—H11	120.2	C30—C29—H29	119.7
C11—C12—H12	119.9	C25—C30—C17	116.4(3)
C13—C12—C11	120.1(3)	C29—C30—C17	124.2(3)
C13—C12—H12	119.9	C29—C30—C25	119.2(3)
C12—C13—H13	119.5	N5—C31—C17	115.6(3)
C12—C13—C14	121.1(3)	N5—C31—H31A	108.4
C14—C13—H13	119.5	N5—C31—H31B	108.4
C9—C14—C1	116.4(3)	C17—C31—H31A	108.4
C13—C14—C1	124.9(3)	C17—C31—H31B	108.4
C13—C14—C9	118.7(3)	H31A—C31—H31B	107.4
N1—C15—C1	116.8(3)	N5—C32—H32	125.1
N1—C15—H15A	108.1	N8—C32—N5	109.8(3)
N1—C15—H15B	108.1	N8—C32—H32	125.1
N1—N2—N3—N4	0.5(4)	C15—C1—C2—C7	172.1(3)
N2—N1—C15—C1	165.7(3)	C15—C1—C14—C9	-169.6(3)
N2—N1—C16—N4	0.9(4)	C15—C1—C14—C13	13.8(5)
N2—N3—N4—C16	0.1(4)	C16—N1—N2—N3	-0.8(4)
N3—N4—C16—N1	-0.6(4)	C16—N1—C15—C1	-15.9(5)
N5—N6—N7—N8	-0.2(4)	C17—C18—C19—C20	-175.0(3)
N6—N5—C31—C17	-169.0(3)	C17—C18—C23—C22	175.7(3)
N6—N5—C32—N8	0.0(4)	C17—C18—C23—C24	-1.9(4)
N6—N7—N8—C32	0.2(4)	C17 <sup>ii</sup> —C24—C25—C26	95.7(4)
N7—N8—C32—N5	-0.1(4)	C17 <sup>ii</sup> —C24—C25—C30	-81.0(4)
C1—C2—C3—C4	-177.9(3)	C18—C17—C30—C25	-43.1(4)
C1—C2—C7—C6	176.9(3)	C18—C17—C30—C29	142.3(3)
C1—C2—C7—C8	-2.4(4)	C18—C17—C31—N5	-67.1(4)
C1 <sup>i</sup> —C8—C9—C10	98.5(4)	C18—C19—C20—C21	-0.5(5)
C1 <sup>i</sup> —C8—C9—C14	-80.1(4)	C18—C23—C24—C17 <sup>ii</sup>	83.3(3)
C2—C1—C14—C9	-43.6(4)	C18—C23—C24—C25	-42.1(4)
C2—C1—C14—C13	139.8(3)	C19—C18—C23—C22	-0.3(5)
C2—C1—C15—N1	-58.6(4)	C19—C18—C23—C24	-177.9(3)
C2—C3—C4—C5	1.4(5)	C19—C20—C21—C22	0.0(5)
C2—C7—C8—C1 <sup>i</sup>	82.6(4)	C20—C21—C22—C23	0.3(5)
C2—C7—C8—C9	-43.8(4)	C21—C22—C23—C18	-0.1(5)
C3—C2—C7—C6	-1.0(5)	C21—C22—C23—C24	177.3(3)
C3—C2—C7—C8	179.7(3)	C22—C23—C24—C17 <sup>ii</sup>	-94.2(4)
C3—C4—C5—C6	-1.5(5)	C22—C23—C24—C25	140.4(3)
C4—C5—C6—C7	0.3(5)	C23—C18—C19—C20	0.6(5)
C5—C6—C7—C2	0.9(5)	C23—C24—C25—C26	-139.4(3)
C5—C6—C7—C8	-179.8(3)	C23—C24—C25—C30	43.8(4)

C6—C7—C8—C1 <sup>i</sup>	-96.7(4)	C24 <sup>ii</sup> —C17—C18—C19	101.0(3)
C6—C7—C8—C9	136.9(3)	C24 <sup>ii</sup> —C17—C18—C23	-74.8(4)
C7—C2—C3—C4	-0.1(5)	C24 <sup>ii</sup> —C17—C30—C25	76.3(3)
C7—C8—C9—C10	-135.1(3)	C24 <sup>ii</sup> —C17—C30—C29	-98.3(4)
C7—C8—C9—C14	46.2(4)	C24 <sup>ii</sup> —C17—C31—N5	174.8(3)
C8 <sup>i</sup> —C1—C2—C3	104.2(4)	C24—C25—C26—C27	-174.8(3)
C8 <sup>i</sup> —C1—C2—C7	-73.6(4)	C24—C25—C30—C17	-0.9(4)
C8 <sup>i</sup> —C1—C14—C9	76.9(4)	C24—C25—C30—C29	174.0(3)
C8 <sup>i</sup> —C1—C14—C13	-99.6(4)	C25—C26—C27—C28	-0.1(5)
C8 <sup>i</sup> —C1—C15—N1	-178.0(3)	C26—C25—C30—C17	-177.7(3)
C8—C9—C10—C11	-174.9(3)	C26—C25—C30—C29	-2.9(5)
C8—C9—C14—C1	-1.7(4)	C26—C27—C28—C29	-0.8(5)
C8—C9—C14—C13	175.1(3)	C27—C28—C29—C30	-0.2(5)
C9—C10—C11—C12	-1.6(5)	C28—C29—C30—C17	176.4(3)
C10—C9—C14—C1	179.6(3)	C28—C29—C30—C25	2.0(5)
C10—C9—C14—C13	-3.6(5)	C30—C17—C18—C19	-139.8(3)
C10—C11—C12—C13	-0.6(6)	C30—C17—C18—C23	44.4(4)
C11—C12—C13—C14	0.7(6)	C30—C17—C31—N5	57.0(4)
C12—C13—C14—C1	177.9(3)	C30—C25—C26—C27	1.9(5)
C12—C13—C14—C9	1.4(5)	C31—N5—N6—N7	176.1(3)
C14—C1—C2—C3	-136.1(3)	C31—N5—C32—N8	-175.2(3)
C14—C1—C2—C7	46.0(4)	C31—C17—C18—C19	-13.8(5)
C14—C1—C15—N1	64.3(4)	C31—C17—C18—C23	170.5(3)
C14—C9—C10—C11	3.8(5)	C31—C17—C30—C25	-169.0(3)
C15—N1—N2—N3	178.0(3)	C31—C17—C30—C29	16.4(5)
C15—N1—C16—N4	-177.7(3)	C32—N5—N6—N7	0.2(4)
C15—C1—C2—C3	-10.1(5)	C32—N5—C31—C17	5.8(6)

**Table 15:** Geometric parameters of **L2-s1** (Å, °), symmetry code: (i) -x+2, -y+1, -z+1)

N1—N2	1.3452(15)	C8—H8	1.0000
N1—C15	1.4731(15)	C8—C9	1.5151(16)
N1—C16	1.3335(16)	C9—C10	1.3899(17)
N2—N3	1.2977(16)	C9—C14	1.3988(16)
N3—N4	1.3598(16)	C10—H10	0.9500
N4—C16	1.3122(16)	C10—C11	1.3945(18)
N5—C17	1.1420(19)	C11—H11	0.9500
C1—C2	1.5366(16)	C11—C12	1.3820(18)
C1—C8 <sup>i</sup>	1.6230(16)	C12—H12	0.9500
C1—C14	1.5355(16)	C12—C13	1.3938(17)
C1—C15	1.5319(16)	C13—H13	0.9500
C2—C3	1.3893(17)	C13—C14	1.3952(17)
C2—C7	1.3970(17)	C15—H15A	0.9900
C3—H3	0.9500	C15—H15B	0.9900
C3—C4	1.3947(18)	C16—H16	0.9500
C4—H4	0.9500	C17—C18	1.451(2)
C4—C5	1.3817(18)	C18—H18A	0.9800
C5—H5	0.9500	C18—H18B	0.9800
C5—C6	1.3835(18)	C18—H18C	0.9800
C6—H6	0.9500	C18—H18D	0.9800
C6—C7	1.3914(17)	C18—H18E	0.9800
C7—C8	1.5062(16)	C18—H18F	0.9800
C8—C1 <sup>i</sup>	1.6230(16)		
N2—N1—C15	118.87(10)	C14—C9—C8	118.13(10)
C16—N1—N2	107.83(10)	C9—C10—H10	119.8
C16—N1—C15	133.11(10)	C9—C10—C11	120.39(11)
N3—N2—N1	106.32(10)	C11—C10—H10	119.8
N2—N3—N4	111.11(10)	C10—C11—H11	120.2
C16—N4—N3	104.88(10)	C12—C11—C10	119.57(11)
C2—C1—C8 <sup>i</sup>	109.78(9)	C12—C11—H11	120.2
C14—C1—C2	107.45(9)	C11—C12—H12	119.8
C14—C1—C8 <sup>i</sup>	110.58(9)	C11—C12—C13	120.31(12)
C15—C1—C2	113.15(10)	C13—C12—H12	119.8

C15—C1—C8 <sup>i</sup>	103.18(9)	C12—C13—H13	119.8
C15—C1—C14	112.69(10)	C12—C13—C14	120.49(11)
C3—C2—C1	124.40(11)	C14—C13—H13	119.8
C3—C2—C7	118.71(11)	C9—C14—C1	116.64(10)
C7—C2—C1	116.88(10)	C13—C14—C1	124.40(10)
C2—C3—H3	119.8	C13—C14—C9	118.95(11)
C2—C3—C4	120.37(11)	N1—C15—C1	114.64(9)
C4—C3—H3	119.8	N1—C15—H15A	108.6
C3—C4—H4	119.8	N1—C15—H15B	108.6
C5—C4—C3	120.46(11)	C1—C15—H15A	108.6
C5—C4—H4	119.8	C1—C15—H15B	108.6
C4—C5—H5	120.2	H15A—C15—H15B	107.6
C4—C5—C6	119.67(12)	N1—C16—H16	125.1
C6—C5—H5	120.2	N4—C16—N1	109.86(11)
C5—C6—H6	119.9	N4—C16—H16	125.1
C5—C6—C7	120.13(11)	N5—C17—C18	179.14(16)
C7—C6—H6	119.9	C17—C18—H18A	109.5
C2—C7—C8	118.11(10)	C17—C18—H18B	109.5
C6—C7—C2	120.62(11)	C17—C18—H18C	109.5
C6—C7—C8	121.27(11)	C17—C18—H18D	109.5
C1 <sup>i</sup> —C8—H8	107.5	C17—C18—H18E	109.5
C7—C8—C1 <sup>i</sup>	112.97(9)	C17—C18—H18F	109.5
C7—C8—H8	107.5	H18A—C18—H18B	109.5
C7—C8—C9	107.72(9)	H18A—C18—H18C	109.5
C9—C8—C1 <sup>i</sup>	113.32(9)	H18B—C18—H18C	109.5
C9—C8—H8	107.5	H18D—C18—H18E	109.5
C10—C9—C8	121.63(10)	H18D—C18—H18F	109.5
C10—C9—C14	120.21(11)	H18E—C18—H18F	109.5
N1—N2—N3—N4	0.10(14)	C8 <sup>i</sup> —C1—C2—C3	103.01(13)
N2—N1—C15—C1	158.92(10)	C8 <sup>i</sup> —C1—C2—C7	-75.82(12)
N2—N1—C16—N4	0.14(14)	C8 <sup>i</sup> —C1—C14—C9	75.05(12)
N2—N3—N4—C16	-0.01(14)	C8 <sup>i</sup> —C1—C14—C13	-106.31(12)
N3—N4—C16—N1	-0.08(14)	C8 <sup>i</sup> —C1—C15—N1	-174.36(9)
C1—C2—C3—C4	178.99(11)	C8—C9—C10—C11	175.95(11)
C1—C2—C7—C6	-179.10(10)	C8—C9—C14—C1	0.30(15)
C1—C2—C7—C8	0.52(15)	C8—C9—C14—C13	-178.41(10)
C1 <sup>i</sup> —C8—C9—C10	101.22(12)	C9—C10—C11—C12	2.20(18)
C1 <sup>i</sup> —C8—C9—C14	-80.88(12)	C10—C9—C14—C1	178.24(10)
C2—C1—C14—C9	-44.74(13)	C10—C9—C14—C13	-0.48(17)
C2—C1—C14—C13	133.89(11)	C10—C11—C12—C13	-0.11(18)
C2—C1—C15—N1	-55.81(13)	C11—C12—C13—C14	-2.29(18)
C2—C3—C4—C5	0.87(19)	C12—C13—C14—C1	-176.04(11)
C2—C7—C8—C1 <sup>i</sup>	80.70(13)	C12—C13—C14—C9	2.57(17)
C2—C7—C8—C9	-45.23(13)	C14—C1—C2—C3	-136.68(11)
C3—C2—C7—C6	2.00(17)	C14—C1—C2—C7	44.49(13)
C3—C2—C7—C8	-178.38(10)	C14—C1—C15—N1	66.35(13)
C3—C4—C5—C6	0.71(19)	C14—C9—C10—C11	-1.91(18)
C4—C5—C6—C7	-0.91(19)	C15—N1—N2—N3	-175.79(10)
C5—C6—C7—C2	-0.45(18)	C15—N1—C16—N4	174.92(12)
C5—C6—C7—C8	179.94(11)	C15—C1—C2—C3	-11.65(16)
C6—C7—C8—C1 <sup>i</sup>	-99.68(12)	C15—C1—C2—C7	169.52(10)
C6—C7—C8—C9	134.39(11)	C15—C1—C14—C9	-170.05(10)
C7—C2—C3—C4	-2.20(18)	C15—C1—C14—C13	8.58(16)
C7—C8—C9—C10	-133.06(11)	C16—N1—N2—N3	-0.14(13)
C7—C8—C9—C14	44.85(13)	C16—N1—C15—C1	-15.40(18)

**Table 16:** Geometric parameters of **L2-s2** (Å, °), symmetry code: (i) -x+2, -y+2, -z+1

O1—H1	0.8400	C5—H5	0.9500
O1—C17	1.411(4)	C5—C6	1.387(5)
C17—H17A	0.9800	C6—H6	0.9500
C17—H17B	0.9800	C6—C7	1.388(5)
C17—H17C	0.9800	C7—C8	1.515(4)

N1—N2	1.350(4)	C8—C1 <sup>i</sup>	1.623(4)
N1—C15	1.472(4)	C8—H8	1.0000
N1—C16	1.323(4)	C8—C9	1.506(4)
N2—N3	1.298(4)	C9—C10	1.383(5)
N3—N4	1.355(4)	C9—C14	1.412(4)
N4—C16	1.322(4)	C10—H10	0.9500
C1—C2	1.534(4)	C10—C11	1.383(5)
C1—C8 <sup>i</sup>	1.623(4)	C11—H11	0.9500
C1—C14	1.531(4)	C11—C12	1.386(5)
C1—C15	1.532(4)	C12—H12	0.9500
C2—C3	1.395(4)	C12—C13	1.389(5)
C2—C7	1.402(5)	C13—H13	0.9500
C3—H3	0.9500	C13—C14	1.388(5)
C3—C4	1.388(5)	C15—H15A	0.9900
C4—H4	0.9500	C15—H15B	0.9900
C4—C5	1.388(5)	C16—H16	0.9500
C17—O1—H1	109.5	C6—C7—C2	120.6(3)
O1—C17—H17A	109.5	C6—C7—C8	121.9(3)
O1—C17—H17B	109.5	C1i—C8—H8	107.4
O1—C17—H17C	109.5	C7—C8—C1 <sup>i</sup>	112.8(2)
H17A—C17—H17B	109.5	C7—C8—H8	107.4
H17A—C17—H17C	109.5	C9—C8—C1 <sup>i</sup>	113.2(2)
H17B—C17—H17C	109.5	C9—C8—C7	108.5(2)
N2—N1—C15	119.2(3)	C9—C8—H8	107.4
C16—N1—N2	108.0(3)	C10—C9—C8	122.3(3)
C16—N1—C15	132.7(3)	C10—C9—C14	119.9(3)
N3—N2—N1	106.5(3)	C14—C9—C8	117.8(3)
N2—N3—N4	110.6(2)	C9—C10—H10	119.7
C16—N4—N3	105.4(3)	C11—C10—C9	120.7(3)
C2—C1—C8 <sup>i</sup>	109.8(2)	C11—C10—H10	119.7
C14—C1—C2	107.8(3)	C10—C11—H11	120.0
C14—C1—C8 <sup>i</sup>	110.2(2)	C10—C11—C12	119.9(3)
C14—C1—C15	113.0(3)	C12—C11—H11	120.0
C15—C1—C2	112.6(2)	C11—C12—H12	120.1
C15—C1—C8 <sup>i</sup>	103.2(2)	C11—C12—C13	119.8(3)
C3—C2—C1	124.5(3)	C13—C12—H12	120.1
C3—C2—C7	118.5(3)	C12—C13—H13	119.5
C7—C2—C1	117.0(3)	C14—C13—C12	121.1(3)
C2—C3—H3	119.7	C14—C13—H13	119.5
C4—C3—C2	120.6(3)	C9—C14—C1	116.6(3)
C4—C3—H3	119.7	C13—C14—C1	124.9(3)
C3—C4—H4	119.7	C13—C14—C9	118.5(3)
C3—C4—C5	120.6(3)	N1—C15—C1	115.4(3)
C5—C4—H4	119.7	N1—C15—H15A	108.4
C4—C5—H5	120.3	N1—C15—H15B	108.4
C6—C5—C4	119.3(3)	C1—C15—H15A	108.4
C6—C5—H5	120.3	C1—C15—H15B	108.4
C5—C6—H6	119.8	H15A—C15—H15B	107.5
C5—C6—C7	120.4(3)	N1—C16—H16	125.3
C7—C6—H6	119.8	N4—C16—N1	109.5(3)
C2—C7—C8	117.5(3)	N4—C16—H16	125.3
N1—N2—N3—N4	-0.1(3)	C8 <sup>i</sup> —C1—C2—C3	102.6(3)
N2—N1—C15—C1	160.8(3)	C8 <sup>i</sup> —C1—C2—C7	-75.3(3)
N2—N1—C16—N4	0.5(4)	C8 <sup>i</sup> —C1—C14—C9	75.2(3)
N2—N3—N4—C16	0.4(4)	C8 <sup>i</sup> —C1—C14—C13	-104.5(3)
N3—N4—C16—N1	-0.5(4)	C8 <sup>i</sup> —C1—C15—N1	-175.5(2)
C1—C2—C3—C4	179.5(3)	C8—C9—C10—C11	178.0(3)
C1—C2—C7—C6	-179.4(3)	C8—C9—C14—C1	0.2(4)
C1—C2—C7—C8	-0.3(4)	C8—C9—C14—C13	179.9(3)
C1 <sup>i</sup> —C8—C9—C10	98.5(3)	C9—C10—C11—C12	1.9(5)
C1 <sup>i</sup> —C8—C9—C14	-81.3(3)	C10—C9—C14—C1	-179.5(3)
C2—C1—C14—C9	-44.8(3)	C10—C9—C14—C13	0.2(4)
C2—C1—C14—C13	135.6(3)	C10—C11—C12—C13	0.4(5)
C2—C1—C15—N1	-57.1(4)	C11—C12—C13—C14	-2.5(5)

C2—C3—C4—C5	1.1(5)	C12—C13—C14—C1	-178.1(3)
C2—C7—C8—C1 <sup>i</sup>	81.5(3)	C12—C13—C14—C9	2.2(4)
C2—C7—C8—C9	-44.7(4)	C14—C1—C2—C3	-137.2(3)
C3—C2—C7—C6	2.6(4)	C14—C1—C2—C7	44.9(3)
C3—C2—C7—C8	-178.3(3)	C14—C1—C15—N1	65.5(3)
C3—C4—C5—C6	0.5(5)	C14—C9—C10—C11	-2.2(4)
C4—C5—C6—C7	-0.5(5)	C15—N1—N2—N3	-178.3(3)
C5—C6—C7—C2	-1.1(5)	C15—N1—C16—N4	178.1(3)
C5—C6—C7—C8	179.9(3)	C15—C1—C2—C3	-11.8(4)
C6—C7—C8—C1 <sup>i</sup>	-99.4(3)	C15—C1—C2—C7	170.3(3)
C6—C7—C8—C9	134.4(3)	C15—C1—C14—C9	-170.0(3)
C7—C2—C3—C4	-2.6(5)	C15—C1—C14—C13	10.4(4)
C7—C8—C9—C10	-135.6(3)	C16—N1—N2—N3	-0.2(3)
C7—C8—C9—C14	44.7(4)	C16—N1—C15—C1	-16.7(5)

**Table 17:** Crystal data of compound **3**

Chemical formula	C <sub>73.30</sub> H <sub>63.90</sub> Cl <sub>2</sub> FeN <sub>18.70</sub> O <sub>9.30</sub>
<i>M</i> <sub>r</sub>	1482.30
Crystal system, space group	Triclinic, <i>P</i> 1
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.7159 (10), 12.2753 (12), 15.1700 (15)
$\alpha$ , $\beta$ , $\gamma$ (°)	104.378 (8), 95.644 (8), 95.602 (8)
<i>V</i> (Å <sup>3</sup> )	1730.1 (3)
<i>Z</i>	1
Radiation type	Cu <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	3.07
Crystal size (mm)	0.07 × 0.05 × 0.02

**Table 18:** Data collection of compound **3**

Diffractometer	STOE STADIVARI
Absorption correction	Multi-scan STOE LANA, absorption correction by scaling of reflection intensities. J. Koziskova, F. Hahn, J. Richter, J. Kozisek, "Comparison of different absorption corrections on the model structure of tetrakis( $\mu$ 2-acetato)-diaqua-di-copper(II)", Acta Chimica Slovaca, vol. 9, no. 2, 2016, pp. 136 - 140.
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	1.000, 1.000
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	17074, 6305, 4650
<i>R</i> <sub>int</sub>	0.071
(sin $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.615
Refinement <i>R</i> [ <i>F</i> <sub>2</sub> > 2 $\sigma$ ( <i>F</i> <sub>2</sub> )], <i>wR</i> ( <i>F</i> <sub>2</sub> ), <i>S</i>	0.127, 0.401, 1.61
No. of reflections	6305
No. of parameters	486
H-atom treatment	H-atom parameters constrained
$\Delta\rho$ <sub>max</sub> , $\Delta\rho$ <sub>min</sub> (e Å <sup>-3</sup> )	0.88, -0.69

**Table 19:** Geometric parameters of compound **3** (Å, °), symmetry codes: (i) -x+1, -y+1, -z+1; (ii) -x+2, -y+2, -z+1; (iii) -x+1, -y+1, -z+2

Fe1—O1	2.094(7)	C15—H15A	0.9900
Fe1—N9	2.094(7)	C15—H15B	0.9900
Fe1—O1 <sup>i</sup>	2.094(7)	C16—H16	0.9500
Fe1—N9 <sup>i</sup>	2.094(7)	C17—C31	1.493(11)
Fe1—N4 <sup>i</sup>	2.127(6)	C17—C30	1.523(10)
Fe1—N4	2.127(6)	C17—C18	1.563(10)
Fe1—N8 <sup>i</sup>	2.139(5)	C17—C24 <sup>iii</sup>	1.653(9)
Fe1—N8	2.139(5)	C18—C23	1.366(11)
Cl1—O5	1.413(6)	C18—C19	1.408(11)

C11—O3	1.415(5)	C19—C20	1.362(12)
C11—O4	1.420(6)	C19—H19	0.9500
C11—O2	1.456(5)	C20—C21	1.400(14)
N1—C16	1.333(8)	C20—H20	0.9500
N1—N2	1.359(7)	C21—C22	1.362(13)
N1—C15	1.480(9)	C21—H21	0.9500
N2—N3	1.273(8)	C22—C23	1.382(11)
N3—N4	1.364(8)	C22—H22	0.9500
N4—C16	1.307(9)	C23—C24	1.527(10)
N5—C32	1.320(9)	C24—C25	1.481(11)
N5—N6	1.339(9)	C24—C17 <sup>iii</sup>	1.653(9)
N5—C31	1.481(9)	C24—H24	1.0000
N6—N7	1.291(9)	C25—C26	1.366(10)
N7—N8	1.339(9)	C25—C30	1.404(12)
N8—C32	1.292(9)	C26—C27	1.417(12)
N10—C38	1.34(5)	C26—H26	0.9500
C1—C2	1.517(10)	C27—C28	1.360(14)
C1—C15	1.521(9)	C27—H27	0.9500
C1—C14	1.525(9)	C28—C29	1.360(12)
C1—C8 <sup>ii</sup>	1.689(10)	C28—H28	0.9500
C2—C3	1.395(10)	C29—C30	1.404(10)
C2—C7	1.403(10)	C29—H29	0.9500
C3—C4	1.366(12)	C31—H31A	0.9900
C3—H3	0.9500	C31—H31B	0.9900
C4—C5	1.414(14)	C32—H32	0.9500
C4—H4	0.9500	C33—O1	1.165(10)
C5—C6	1.361(13)	C33—N9	1.165(10)
C5—H5	0.9500	C33—C36	1.361(17)
C6—C7	1.391(11)	C33—C35	1.39(2)
C6—H6	0.9500	C33—C34	1.41(3)
C7—C8	1.511(10)	C37—C38	1.59(4)
C8—C9	1.464(11)	C37—H37A	0.9800
C8—C1 <sup>ii</sup>	1.689(10)	C37—H37B	0.9800
C8—H8	1.0000	C37—H37C	0.9800
C9—C10	1.392(10)	C34—H34A	0.9800
C9—C14	1.405(10)	C34—H34B	0.9800
C10—C11	1.377(14)	C34—H34C	0.9800
C10—H10	0.9500	C35—H35A	0.9800
C11—C12	1.374(15)	C35—H35B	0.9800
C11—H11	0.9500	C35—H35C	0.9800
C12—C13	1.377(13)	C36—H36A	0.9800
C12—H12	0.9500	C36—H36B	0.9800
C13—C14	1.404(11)	C36—H36C	0.9800
C13—H13	0.9500		
O1—Fe1—O1 <sup>i</sup>	180.0	C1—C15—H15A	108.4
N9—Fe1—N9 <sup>i</sup>	180.0	N1—C15—H15B	108.4
O1—Fe1—N4 <sup>i</sup>	87.7(2)	C1—C15—H15B	108.4
N9—Fe1—N4 <sup>i</sup>	87.7(2)	H15A—C15—H15B	107.5
O1 <sup>i</sup> —Fe1—N4 <sup>i</sup>	92.3(2)	N4—C16—N1	107.9(6)
N9 <sup>i</sup> —Fe1—N4 <sup>i</sup>	92.3(2)	N4—C16—H16	126.0
O1—Fe1—N4	92.3(2)	N1—C16—H16	126.0
N9—Fe1—N4	92.3(2)	C31—C17—C30	114.4(6)
O1 <sup>i</sup> —Fe1—N4	87.7(2)	C31—C17—C18	113.6(6)
N9 <sup>i</sup> —Fe1—N4	87.7(2)	C30—C17—C18	106.6(6)
N4 <sup>i</sup> —Fe1—N4	180.0	C31—C17—C24 <sup>iii</sup>	104.2(6)
O1—Fe1—N8 <sup>i</sup>	92.0(2)	C30—C17—C24 <sup>iii</sup>	109.2(6)
N9—Fe1—N8 <sup>i</sup>	92.0(2)	C18—C17—C24 <sup>iii</sup>	108.8(5)
O1 <sup>i</sup> —Fe1—N8 <sup>i</sup>	88.0(2)	C23—C18—C19	118.2(7)
N9 <sup>i</sup> —Fe1—N8 <sup>i</sup>	88.0(2)	C23—C18—C17	118.4(6)
N4 <sup>i</sup> —Fe1—N8 <sup>i</sup>	89.7(2)	C19—C18—C17	123.2(7)
N4—Fe1—N8 <sup>i</sup>	90.3(2)	C20—C19—C18	120.2(8)
O1—Fe1—N8	88.0(2)	C20—C19—H19	119.9
N9—Fe1—N8	88.0(2)	C18—C19—H19	119.9
O1 <sup>i</sup> —Fe1—N8	92.0(2)	C19—C20—C21	121.2(8)

N9 <sup>i</sup> —Fe1—N8	92.0(2)	C19—C20—H20	119.4
N4 <sup>i</sup> —Fe1—N8	90.3(2)	C21—C20—H20	119.4
N4—Fe1—N8	89.7(2)	C22—C21—C20	117.8(7)
N8 <sup>i</sup> —Fe1—N8	180.0(3)	C22—C21—H21	121.1
O5—C11—O3	109.4(4)	C20—C21—H21	121.1
O5—C11—O4	110.3(4)	C21—C22—C23	121.7(8)
O3—C11—O4	109.5(4)	C21—C22—H22	119.2
O5—C11—O2	108.4(4)	C23—C22—H22	119.2
O3—C11—O2	110.2(4)	C18—C23—C22	120.7(7)
O4—C11—O2	109.1(3)	C18—C23—C24	117.3(6)
C16—N1—N2	108.7(5)	C22—C23—C24	121.9(7)
C16—N1—C15	133.5(5)	C25—C24—C23	109.5(6)
N2—N1—C15	117.8(5)	C25—C24—C17 <sup>iii</sup>	112.2(6)
N3—N2—N1	106.1(5)	C23—C24—C17 <sup>iii</sup>	112.8(6)
N2—N3—N4	110.8(5)	C25—C24—H24	107.4
C16—N4—N3	106.4(5)	C23—C24—H24	107.4
C16—N4—Fe1	130.7(5)	C17 <sup>iii</sup> —C24—H24	107.4
N3—N4—Fe1	122.3(4)	C26—C25—C30	120.4(7)
C32—N5—N6	105.7(6)	C26—C25—C24	122.3(8)
C32—N5—C31	135.0(6)	C30—C25—C24	117.4(7)
N6—N5—C31	119.2(6)	C25—C26—C27	119.7(9)
N7—N6—N5	109.0(6)	C25—C26—H26	120.1
N6—N7—N8	107.9(6)	C27—C26—H26	120.1
C32—N8—N7	107.3(6)	C28—C27—C26	119.8(8)
C32—N8—Fe1	130.0(5)	C28—C27—H27	120.1
N7—N8—Fe1	122.7(4)	C26—C27—H27	120.1
C2—C1—C15	113.3(5)	C27—C28—C29	120.7(8)
C2—C1—C14	108.4(6)	C27—C28—H28	119.6
C15—C1—C14	113.5(6)	C29—C28—H28	119.6
C2—C1—C8 <sup>ii</sup>	109.5(6)	C28—C29—C30	121.1(8)
C15—C1—C8 <sup>ii</sup>	103.0(5)	C28—C29—H29	119.5
C14—C1—C8 <sup>ii</sup>	108.8(5)	C30—C29—H29	119.5
C3—C2—C7	118.0(7)	C25—C30—C29	118.2(7)
C3—C2—C1	124.1(6)	C25—C30—C17	118.5(6)
C7—C2—C1	117.9(6)	C29—C30—C17	123.2(7)
C4—C3—C2	122.0(8)	N5—C31—C17	116.9(6)
C4—C3—H3	119.0	N5—C31—H31A	108.1
C2—C3—H3	119.0	C17—C31—H31A	108.1
C3—C4—C5	119.2(8)	N5—C31—H31B	108.1
C3—C4—H4	120.4	C17—C31—H31B	108.1
C5—C4—H4	120.4	H31A—C31—H31B	107.3
C6—C5—C4	119.5(9)	N8—C32—N5	110.0(7)
C6—C5—H5	120.2	N8—C32—H32	125.0
C4—C5—H5	120.2	N5—C32—H32	125.0
C5—C6—C7	121.2(9)	O1—C33—C36	109.1(10)
C5—C6—H6	119.4	O1—C33—C35	130(2)
C7—C6—H6	119.4	C36—C33—C35	121(2)
C6—C7—C2	119.9(7)	N9—C33—C34	172.3(15)
C6—C7—C8	122.9(7)	C38—C37—H37A	109.5
C2—C7—C8	117.2(6)	C38—C37—H37B	109.5
C9—C8—C7	108.5(6)	H37A—C37—H37B	109.5
C9—C8—C1 <sup>ii</sup>	112.6(6)	C38—C37—H37C	109.5
C7—C8—C1 <sup>ii</sup>	112.0(6)	H37A—C37—H37C	109.5
C9—C8—H8	107.9	H37B—C37—H37C	109.5
C7—C8—H8	107.9	N10—C38—C37	169(2)
C1 <sup>ii</sup> —C8—H8	107.9	C33—N9—Fe1	160.7(6)
C10—C9—C14	118.4(7)	C33—C34—H34A	109.5
C10—C9—C8	122.3(7)	C33—C34—H34B	109.5
C14—C9—C8	119.0(6)	H34A—C34—H34B	109.5
C11—C10—C9	121.1(8)	C33—C34—H34C	109.5
C11—C10—H10	119.4	H34A—C34—H34C	109.5
C9—C10—H10	119.4	H34B—C34—H34C	109.5
C12—C11—C10	119.5(8)	C33—O1—Fe1	160.7(6)
C12—C11—H11	120.3	C33—C35—H35A	109.5

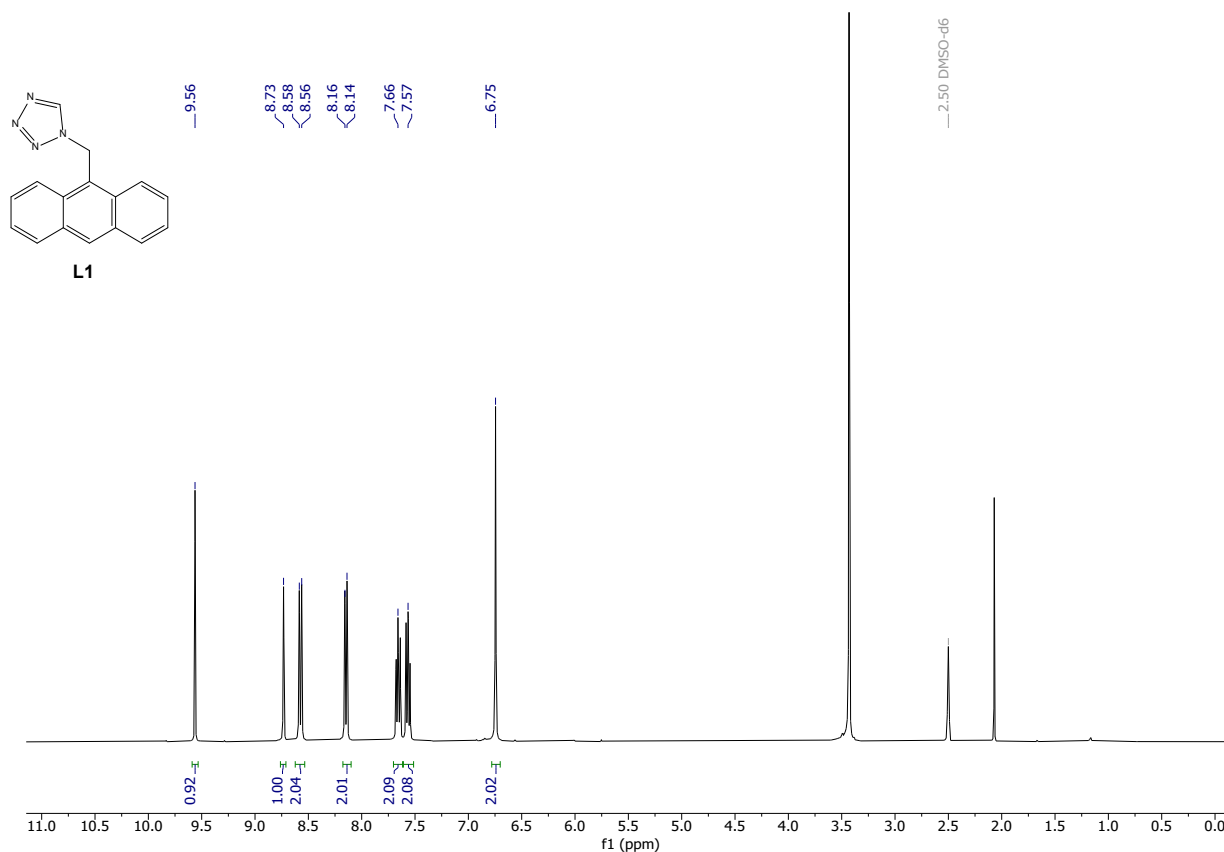
C10—C11—H11	120.3	C33—C35—H35B	109.5
C11—C12—C13	121.7(9)	H35A—C35—H35B	109.5
C11—C12—H12	119.1	C33—C35—H35C	109.5
C13—C12—H12	119.1	H35A—C35—H35C	109.5
C12—C13—C14	118.7(9)	H35B—C35—H35C	109.5
C12—C13—H13	120.6	C33—C36—H36A	109.5
C14—C13—H13	120.6	C33—C36—H36B	109.5
C13—C14—C9	120.3(7)	H36A—C36—H36B	109.5
C13—C14—C1	123.0(6)	C33—C36—H36C	109.5
C9—C14—C1	116.7(6)	H36A—C36—H36C	109.5
N1—C15—C1	115.4(6)	H36B—C36—H36C	109.5
N1—C15—H15A	108.4		
C16—N1—N2—N3	0.2(7)	N3—N4—C16—N1	0.7(7)
C15—N1—N2—N3	177.5(5)	Fe1—N4—C16—N1	171.8(4)
N1—N2—N3—N4	0.2(7)	N2—N1—C16—N4	-0.6(7)
N2—N3—N4—C16	-0.6(7)	C15—N1—C16—N4	-177.3(6)
N2—N3—N4—Fe1	-172.6(4)	C31—C17—C18—C23	-168.5(6)
C32—N5—N6—N7	0.6(8)	C30—C17—C18—C23	-41.7(8)
C31—N5—N6—N7	-177.0(6)	C24 <sup>iii</sup> —C17—C18—C23	75.9(8)
N5—N6—N7—N8	-1.2(8)	C31—C17—C18—C19	15.9(9)
N6—N7—N8—C32	1.3(8)	C30—C17—C18—C19	142.8(7)
N6—N7—N8—Fe1	-177.4(5)	C24 <sup>iii</sup> —C17—C18—C19	-99.6(7)
C15—C1—C2—C3	13.4(11)	C23—C18—C19—C20	4.3(10)
C14—C1—C2—C3	140.5(8)	C17—C18—C19—C20	179.9(6)
C8 <sup>ii</sup> —C1—C2—C3	-101.0(9)	C18—C19—C20—C21	-1.3(11)
C15—C1—C2—C7	-168.7(7)	C19—C20—C21—C22	-1.8(12)
C14—C1—C2—C7	-41.7(9)	C20—C21—C22—C23	2.0(12)
C8 <sup>ii</sup> —C1—C2—C7	76.9(8)	C19—C18—C23—C22	-4.2(10)
C7—C2—C3—C4	3.6(14)	C17—C18—C23—C22	-180.0(6)
C1—C2—C3—C4	-178.6(9)	C19—C18—C23—C24	174.6(6)
C2—C3—C4—C5	0.1(18)	C17—C18—C23—C24	-1.2(9)
C3—C4—C5—C6	-4(2)	C21—C22—C23—C18	1.0(11)
C4—C5—C6—C7	4(2)	C21—C22—C23—C24	-177.7(7)
C5—C6—C7—C2	0.0(17)	C18—C23—C24—C25	44.7(9)
C5—C6—C7—C8	178.9(12)	C22—C23—C24—C25	-136.5(7)
C3—C2—C7—C6	-3.6(12)	C18—C23—C24—C17 <sup>iii</sup>	-81.0(8)
C1—C2—C7—C6	178.4(8)	C22—C23—C24—C17 <sup>iii</sup>	97.8(8)
C3—C2—C7—C8	177.4(8)	C23—C24—C25—C26	135.1(7)
C1—C2—C7—C8	-0.6(10)	C17 <sup>iii</sup> —C24—C25—C26	-98.8(8)
C6—C7—C8—C9	-134.4(9)	C23—C24—C25—C30	-43.2(9)
C2—C7—C8—C9	44.6(9)	C17 <sup>iii</sup> —C24—C25—C30	82.8(8)
C6—C7—C8—C1 <sup>ii</sup>	100.7(9)	C30—C25—C26—C27	-4.0(11)
C2—C7—C8—C1 <sup>ii</sup>	-80.3(8)	C24—C25—C26—C27	177.7(7)
C7—C8—C9—C10	141.0(8)	C25—C26—C27—C28	3.2(12)
C1 <sup>ii</sup> —C8—C9—C10	-94.5(9)	C26—C27—C28—C29	-2.4(13)
C7—C8—C9—C14	-46.1(9)	C27—C28—C29—C30	2.5(13)
C1 <sup>ii</sup> —C8—C9—C14	78.5(8)	C26—C25—C30—C29	4.0(10)
C14—C9—C10—C11	6.4(14)	C24—C25—C30—C29	-177.6(6)
C8—C9—C10—C11	179.4(10)	C26—C25—C30—C17	-179.9(6)
C9—C10—C11—C12	-5.7(18)	C24—C25—C30—C17	-1.5(9)
C10—C11—C12—C13	1.5(19)	C28—C29—C30—C25	-3.2(11)
C11—C12—C13—C14	1.8(17)	C28—C29—C30—C17	-179.1(7)
C12—C13—C14—C9	-0.9(13)	C31—C17—C30—C25	169.5(6)
C12—C13—C14—C1	179.5(9)	C18—C17—C30—C25	43.2(8)
C10—C9—C14—C13	-3.1(11)	C24 <sup>iii</sup> —C17—C30—C25	-74.1(8)
C8—C9—C14—C13	-176.3(7)	C31—C17—C30—C29	-14.5(9)
C10—C9—C14—C1	176.5(7)	C18—C17—C30—C29	-140.9(7)
C8—C9—C14—C1	3.3(9)	C24 <sup>iii</sup> —C17—C30—C29	101.8(8)
C2—C1—C14—C13	-139.8(7)	C32—N5—C31—C17	36.9(11)
C15—C1—C14—C13	-12.9(10)	N6—N5—C31—C17	-146.4(7)
C8 <sup>ii</sup> —C1—C14—C13	101.2(8)	C30—C17—C31—N5	-71.4(8)
C2—C1—C14—C9	40.6(8)	C18—C17—C31—N5	51.2(8)
C15—C1—C14—C9	167.5(6)	C24 <sup>iii</sup> —C17—C31—N5	169.4(6)
C8 <sup>ii</sup> —C1—C14—C9	-78.4(7)	N7—N8—C32—N5	-0.9(8)

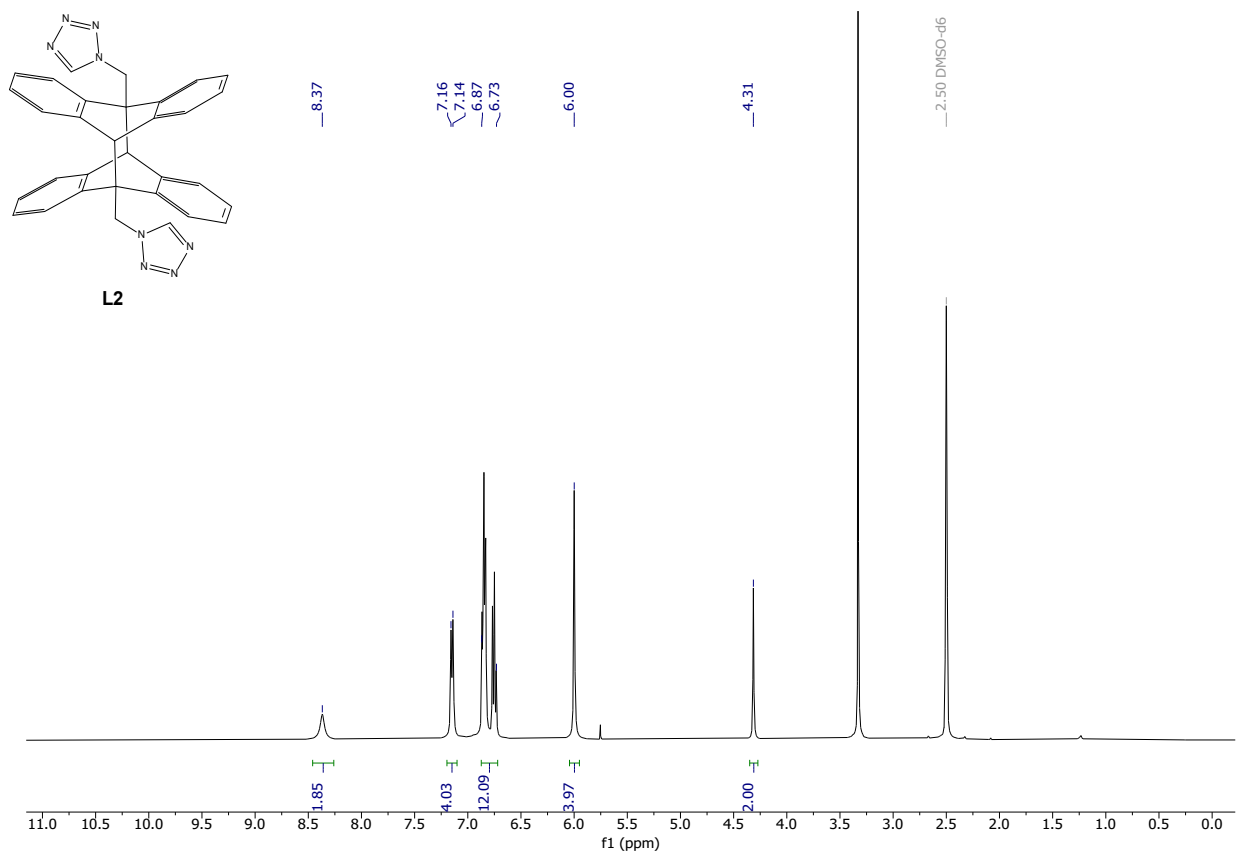
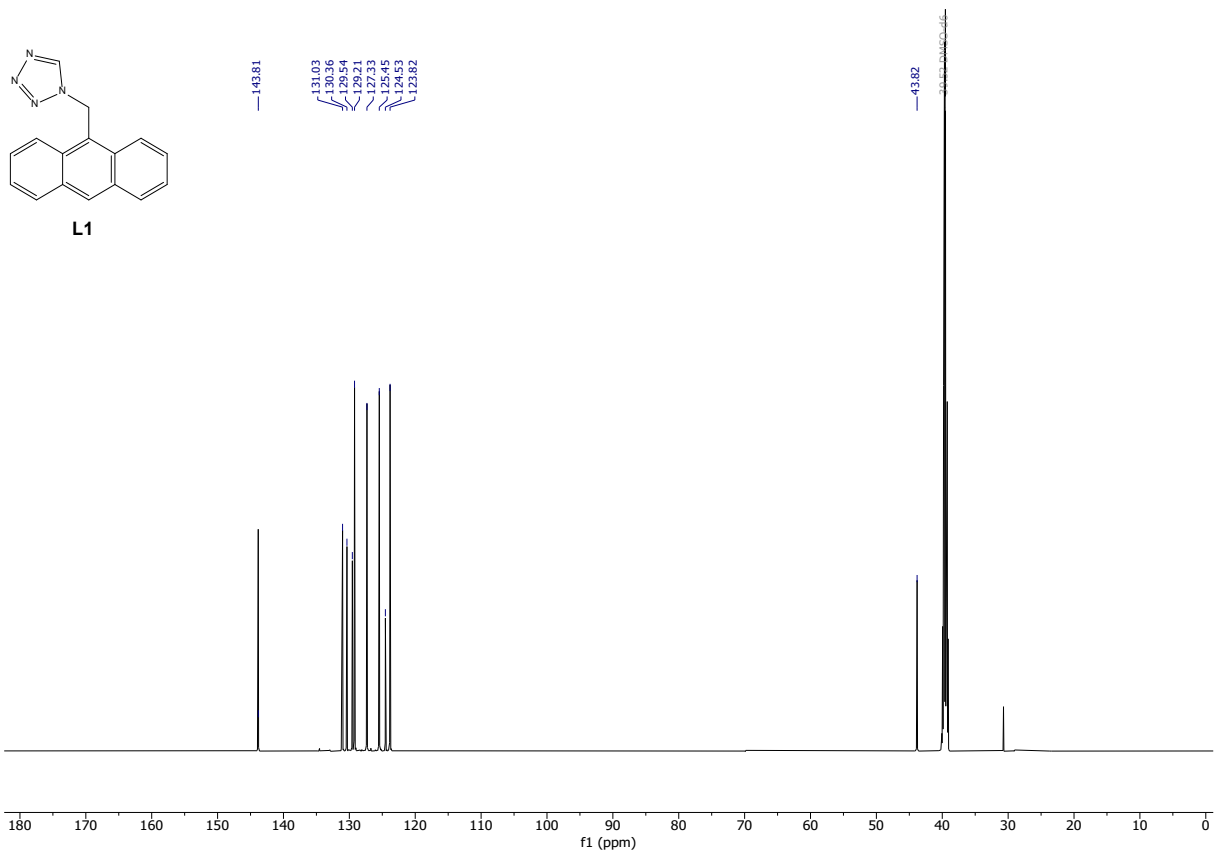
C16—N1—C15—C1	23.5(10)	Fe1—N8—C32—N5	177.7(4)
N2—N1—C15—C1	-152.9(6)	N6—N5—C32—N8	0.2(8)
C2—C1—C15—N1	54.3(8)	C31—N5—C32—N8	177.2(7)
C14—C1—C15—N1	-70.0(7)	C36—C33—O1—Fe1	22(2)
C8 <sup>ii</sup> —C1—C15—N1	172.6(5)	C35—C33—O1—Fe1	-163(2)

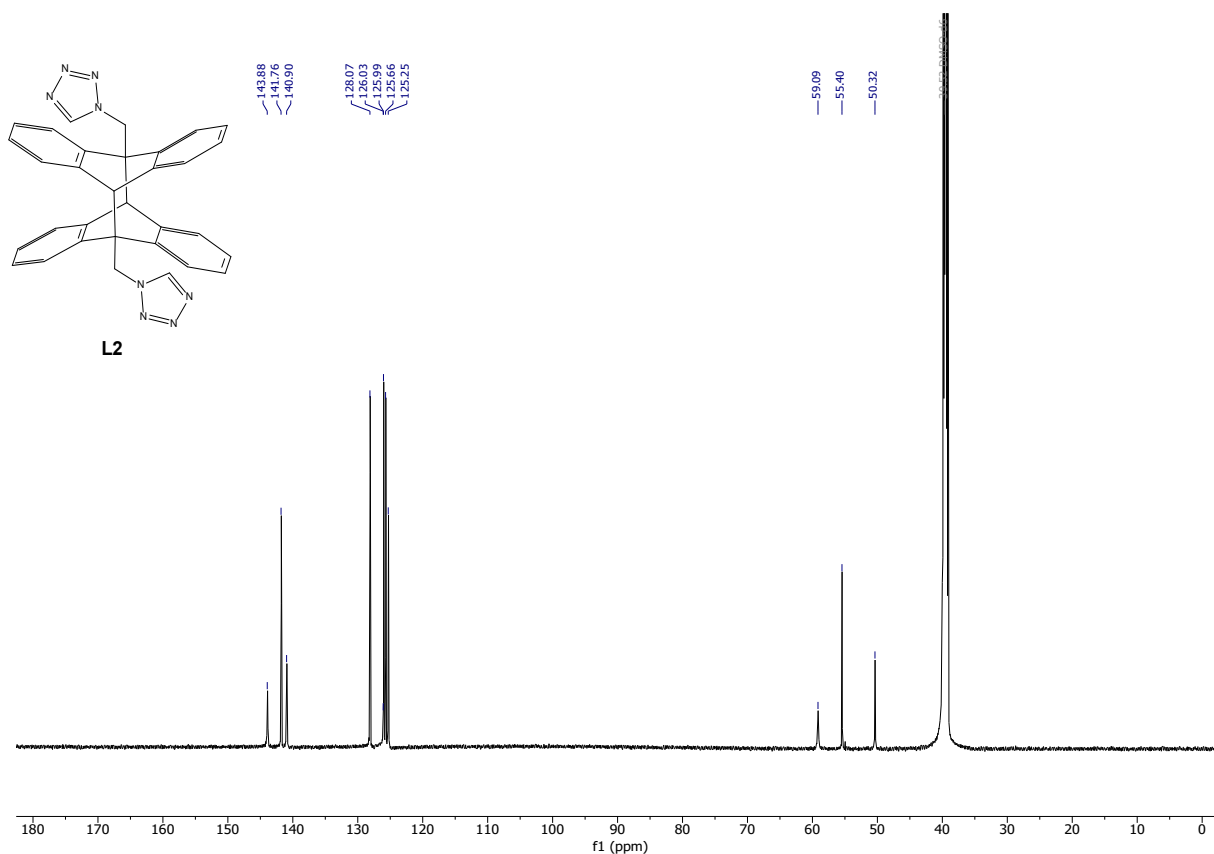
## References

1. J. Singh, N. Steck, D. De, A. Hofer, A. Ripp, I. Captain, M. Keller, P. A. Wender, R. Bhandari and H. J. Jessen, A Phosphoramidite Analogue of Cyclotriphosphate Enables Iterative Polyphosphorylations, *Angew. Chem. Int. Ed.*, 2019, **58**, 3928-3933.
2. *Germany Pat.*, DE P 21 47 023.5, 1971.
3. T. Degen, M. Sadki, E. Bron, U. König and G. Nénert, The HighScore suite, *Powder Diffr.*, 2014, **29**, 13-18.
4. G. M. Sheldrick, SHELXT - integrated space-group and crystal-structure determination, *Acta Crystallogr. Sect. A: Found. Crystallogr.*, 2015, **71**, 3-8.
5. G. M. Sheldrick, Crystal structure refinement with SHELXL, *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.*, 2015, **71**, 3-8.

## NMR Spectra







## Photocycloreversion experiments in the solid state

The thermal stability of the dimerized ligand **L2** was followed in the solid state via  $^1\text{H-NMR}$  spectroscopy in DMSO from 50 – 250 °C in 25 °C steps under inert atmosphere. For this, a spatula tip of the ligand was put into a screwcap vial which was lowered into an oil bath at the respective temperature for 10 min. For a better mixing, the vial was softly shaken periodically. The ligand is stable up to 175 °C, where first signals of monomer (10 %) appeared in the spectrum. A color change of the powder from white to yellow was visible at this point. At 200 °C it turned brown, the amount of monomer increased to 94 %, unwanted side products were formed as well. At 225 °C, the amount for monomer increased to 97 %. At 250 °C side products started to take over, the amount of monomer decreased, traces of dimer were also still visible. With this study, it could be shown that the results of the temperature dependent solid-state measurements, VSM and TGA/DSC are not affected by photocycloreversion of the ligand.

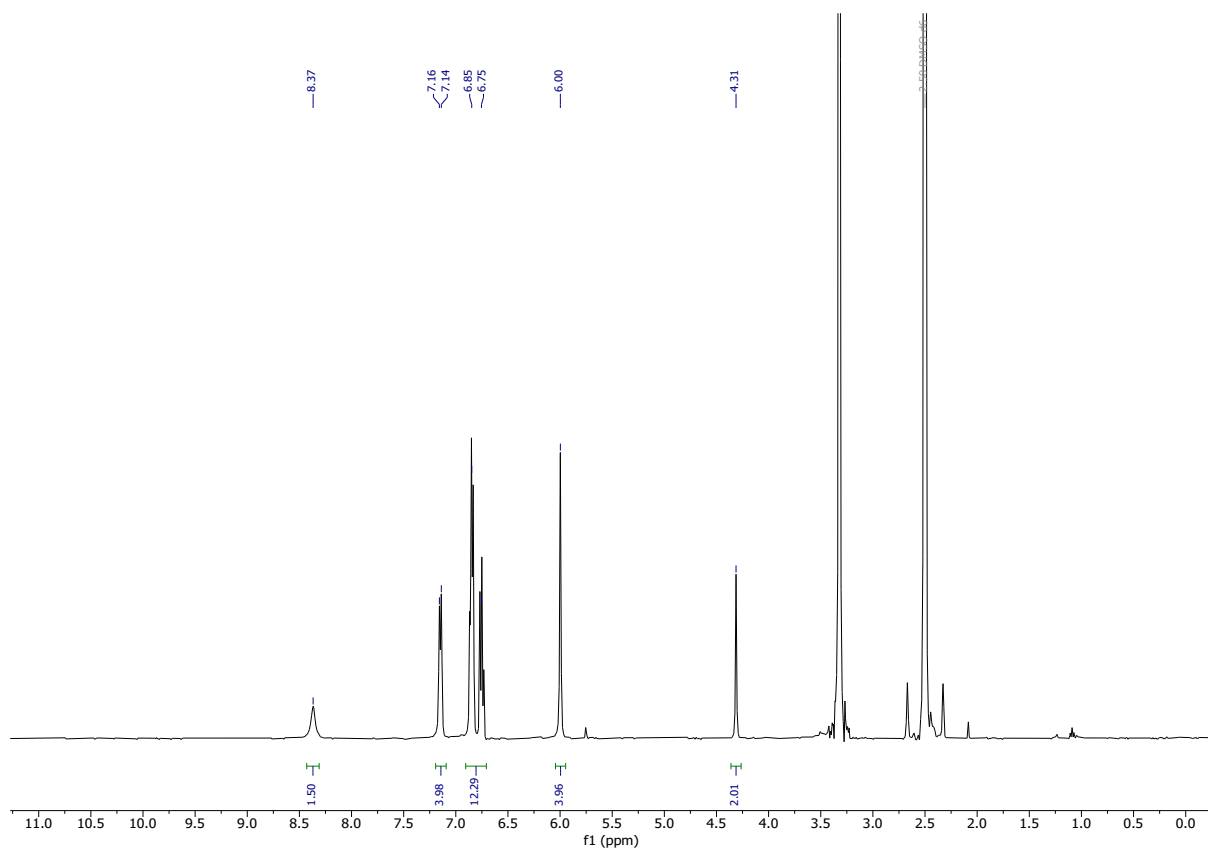


Figure S 52:  $^1\text{H}$ -NMR spectrum in  $\text{DMSO-d}_6$  of the solid sample being heated to  $150\text{ }^\circ\text{C}$  for 10 min.

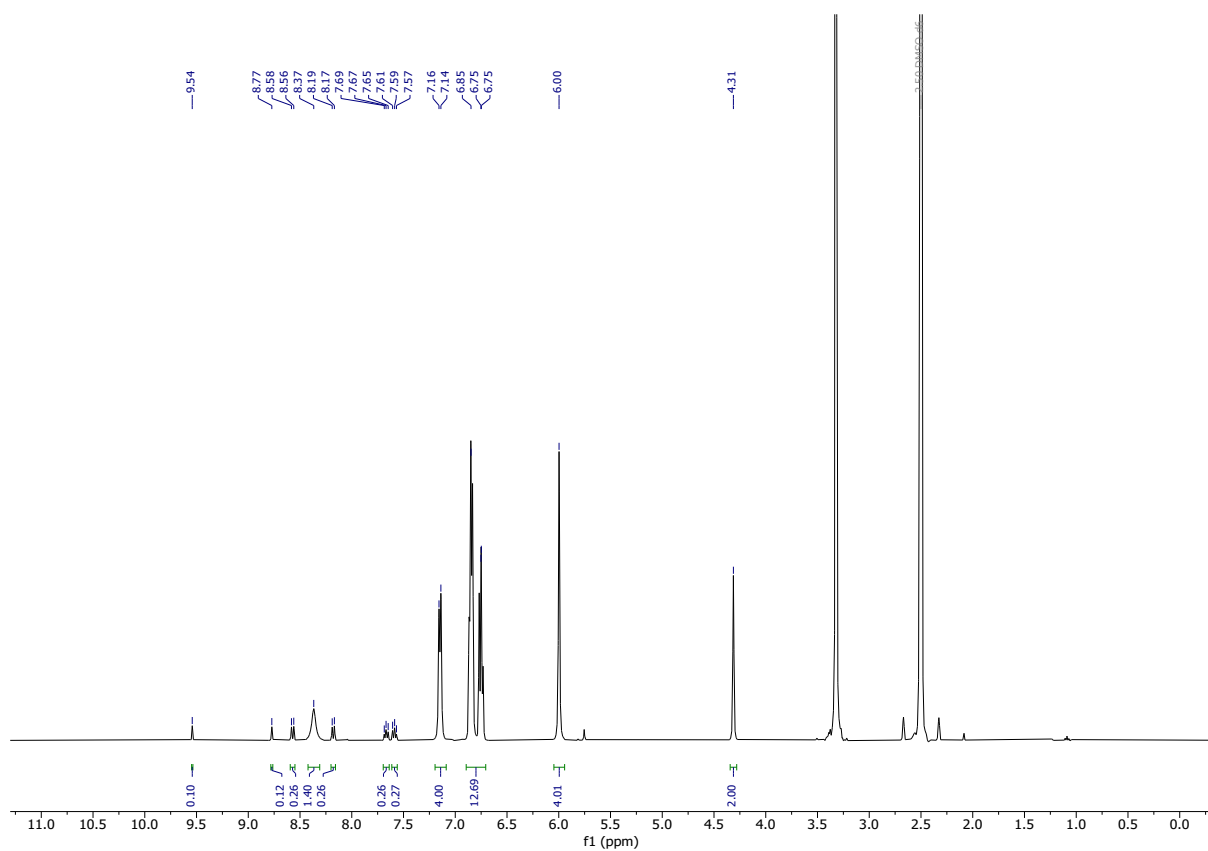


Figure S 53:  $^1\text{H}$ -NMR spectrum in  $\text{DMSO-d}_6$  of the solid sample being heated to  $175\text{ }^\circ\text{C}$  for 10 min.

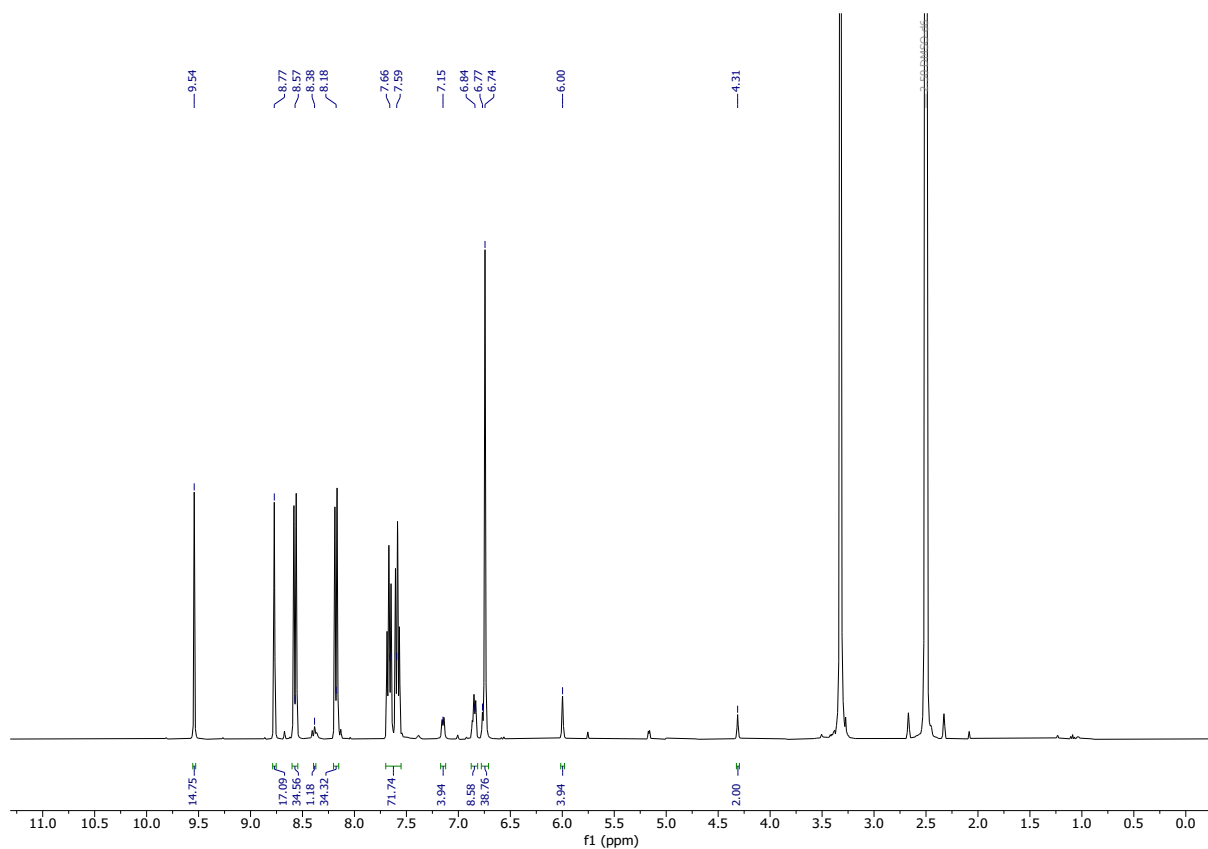


Figure S 54:  $^1\text{H-NMR}$  spectrum in  $\text{DMSO-d}_6$  of the solid sample being heated to  $200\text{ }^\circ\text{C}$  for 10 min.

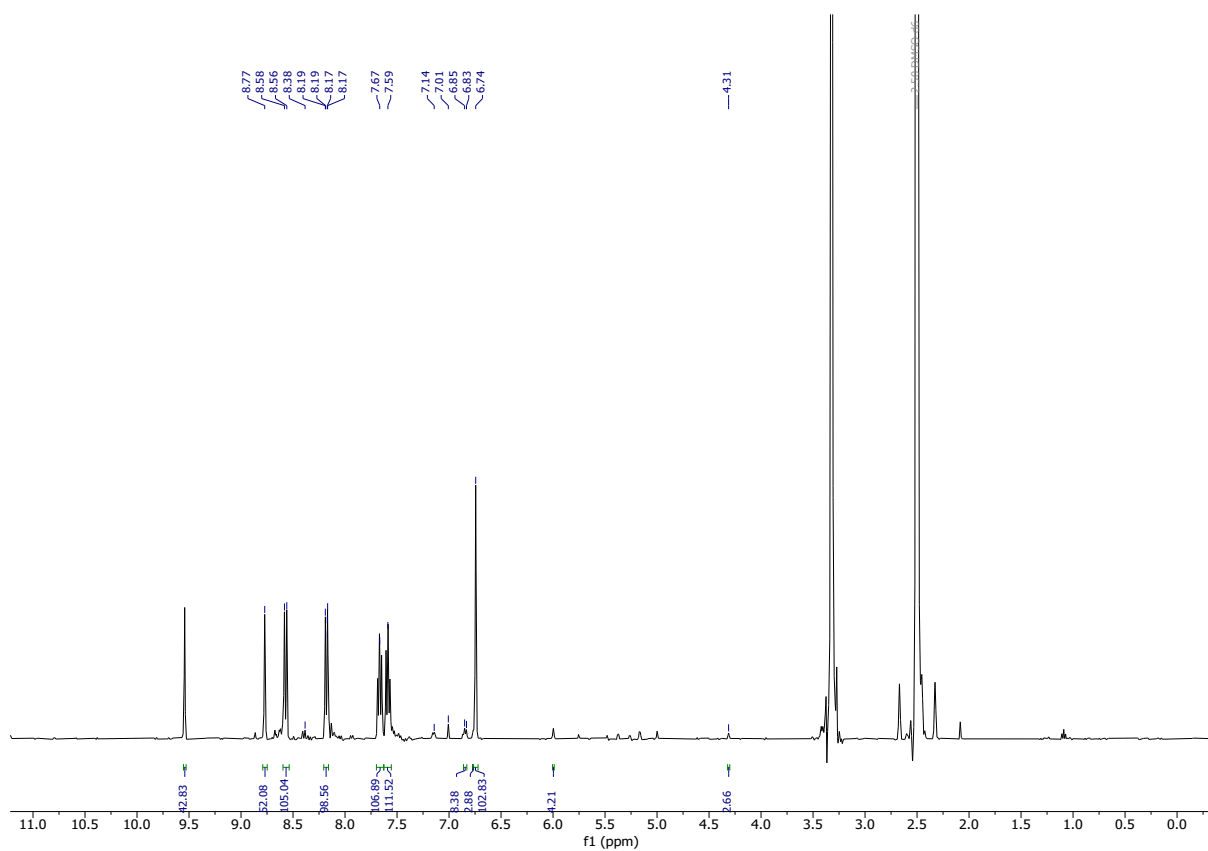
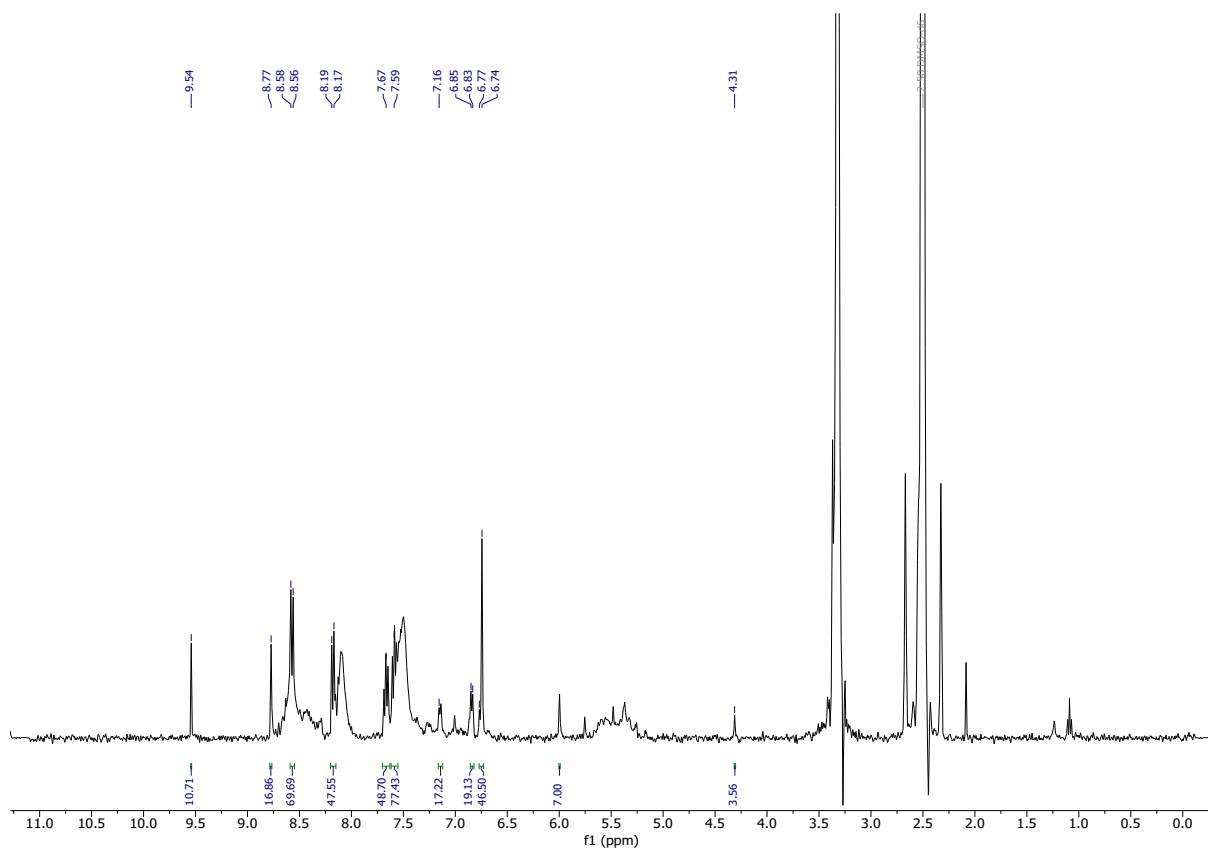


Figure S 55:  $^1\text{H-NMR}$  spectrum in  $\text{DMSO-d}_6$  of the solid sample being heated to  $225\text{ }^\circ\text{C}$  for 10 min.



**Figure S 56:**  $^1\text{H}$ -NMR spectrum in  $\text{DMSO-d}_6$  of the solid sample being heated to  $250\text{ }^\circ\text{C}$  for 10 min.

# IR Spectra

