Electronic Supplementary Material (ESI) for Dalton Transactions.

Highly NIR-emitting ytterbium complexes containing 2-(tosylaminobenzylidene)-N-benzoylhydrazone anions: structure in solution and use for bioimaging

SUPPORTING INFORMATION

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Notes

♦Associated with shielding of paired electrons. It can be estimated as a chemical shift in the spectrum of an analogue complex with a diamagnetic ion.

♥Associated with the presence of unpaired electron density near the resonating nuclei due to the polarization of the filled electron shells of the ligand by the exchange interaction with the incompletely filled electron shell of the paramagnetic cation.

♠ Due to the dipole-dipole interaction of the magnetic moment of the resonating nucleus with the electron magnetic moment associated with the incompletely filled 4f electron shell of the lanthanide cation.

♣ The Fermi-contact shift δ_{FC} can be determined by the formula $\boldsymbol{\delta_{FC} =< S_F > F,}$ where the values of the $<S_F> = g_J(g_J - 1)J(J + 1)$ constant (J is the quantum number of the total angular momentum for the ground state, g_J is the Lange factor associated with this state) do not virtually depend on the ligand and can be determined solely by the lanthanide cation. The parameter F describes the relative contact interaction between the lanthanide cation and the resonating nucleus, i.e. this parameter is individual for each nucleus of the ligand under study.

Synthesis of compounds

Synthesis of the organic ligand

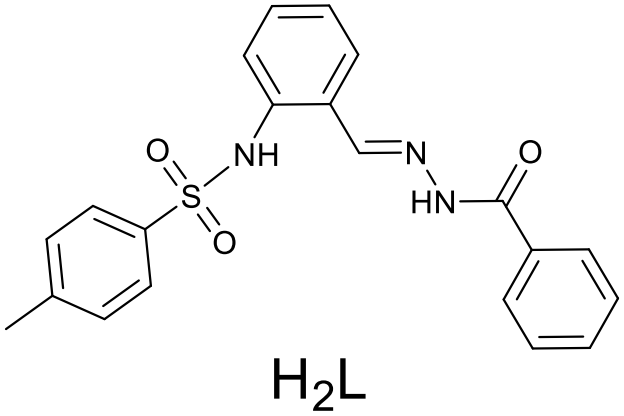

Figure 1 Structure of the organic ligand H_2L, 2-(tosylamino)-benzylidene-N-(benzoyl)hydrazone or N-[(E)-[2-(p-tolylsulfonylamino)phenyl]methyleneamino]benzamide

Ligand H_2L, 2-(tosylamino)-benzylidene-N-(benzoyl)hydrazone or N-[(E)-[2-(p-tolylsulfonylamino)phenyl]methyleneamino]benzamide (Figure 1) was synthesized according to the literature procedure previously reported by our team[1].

[1] Dalton Trans., 2015, **44**, 12660 DOI: 10.1039/c5dt01161b

Synthesis of the lanthanide complexes

Complexes **Ln(L)(HL)** (Ln = Lu, Yb) were synthesized according to the literature procedure previously reported by our team[2].

Complexes **$K(H_2O)_3[Ln(L)_2]$** (Ln = Lu, Yb) were synthesized according to the reaction

$$Ln(L)(HL) + KOH + 2H_2O \rightarrow K(H_2O)_3[Ln(L)_2]$$

by the following procedure: 0.10 mmol of Ln(L)(HL) (96 mg, Ln = Lu, Yb) were dispersed in 50 ml of boiling ethanol under stirring. 0.090 mmol (5.0 mg) of KOH was added, the mixture was stirred for 15 min, hot-filtered and cooled down to room temperature. During the evaporation of the solution, a crystalline precipitate was obtained, which was filtered, washed with ethanol and dried.

Elemental analyses (C, H, N) were performed on a Vario Micro Cube analyzer (Elementar, Germany). Elemental analyses is in agreement with the composition $K(H_2O)_3[Ln(L)_2]$ (Ln = Lu, Yb) consisting three water molecules.

$K(H_2O)_3[Lu(L)_2]$ ($C_{42}H_{40}O_9N_6S_2LuK$), calcd (found) (%):C, 48.00 (48.37); H, 3.84(4.05); N, 8.00 (7.78); calcd. for $K(EtOH)_3[Lu(L)_2]$ ($C_{48}H_{52}O_9N_6S_2LuK$) (%):C, 50.79; H, 4.62; N, 7.40.

$K(H_2O)_3[Yb(L)_2]$ ($C_{42}H_{40}O_9N_6S_2YbK$), calcd. (found) (%):C, 18.08(47.61); H, 3.84(3.82); N, 8.01(7.71), calcd. for $K(EtOH)_3[Yb(L)_2]$ ($C_{48}H_{52}O_9N_6S_2YbK$) (%):C, 50.87; H, 4.63; N, 7.42.

[2] Dalton Trans., 2018, **47**, 4524–4533 DOI: 10.1039/c7dt04387b

Thermal analysis

Thermal analyses were carried out on a thermoanalyzer STA 409 PC Luxx (NETZSCH, Germany) in the temperature range of 20-1000 ºC in air, heating rate 10 ºC/min.

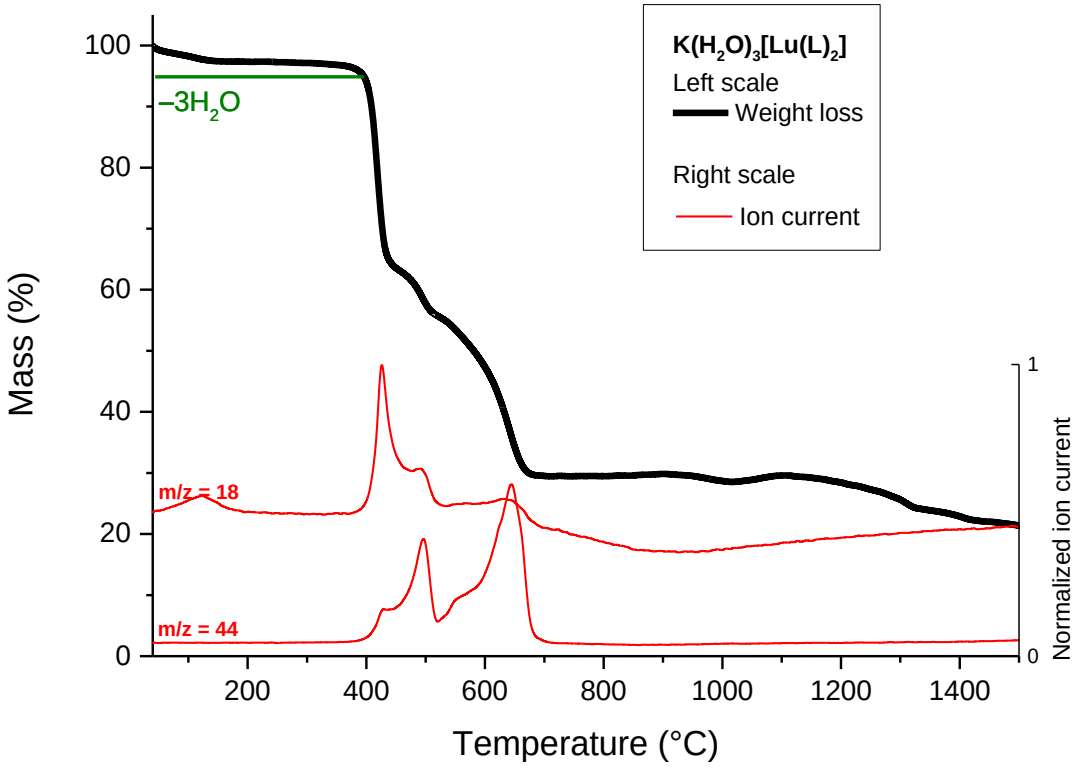

Figure 2 Thermal analysis of $K(H_2O)_3[Lu(L)_2]$. The black curve corresponds to the weight loss (left scale), red curves correspond to the normalized ion current of the detector of the coupled to the thermoanalyzer mass spectrometer.

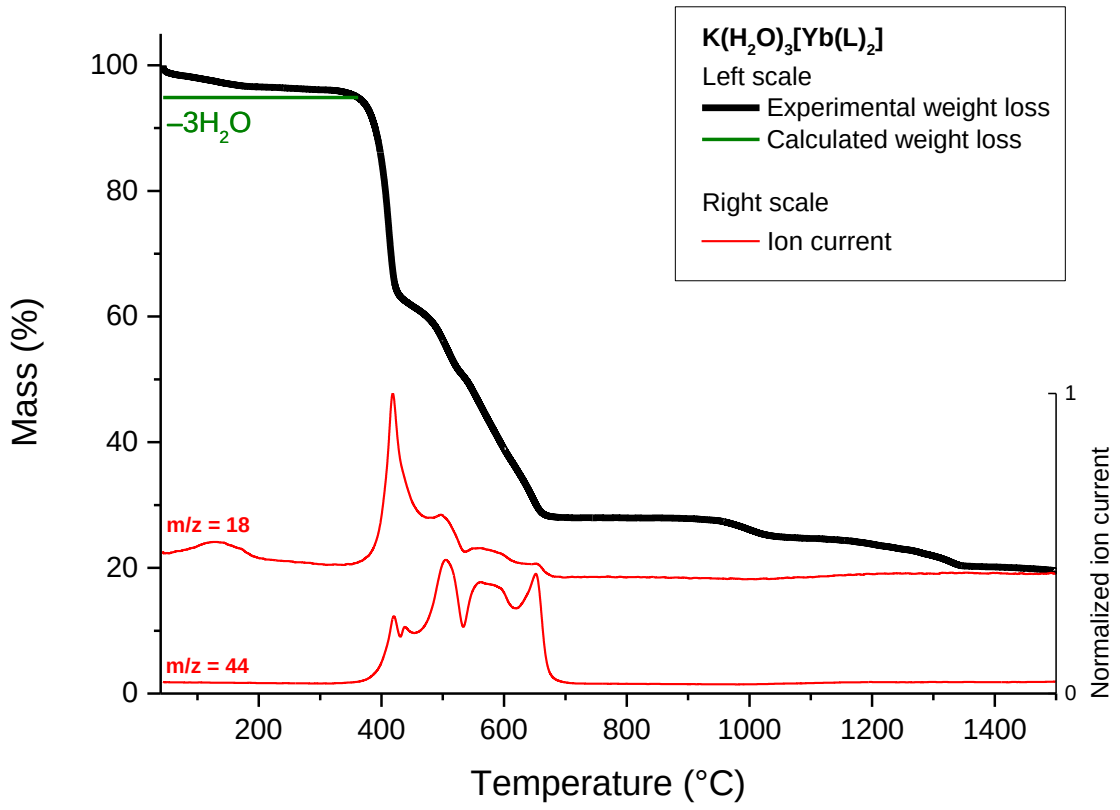

Figure 3 Thermal analysis of $K(H_2O)_3[Yb(L)_2]$. The black curve corresponds to the weight loss (left scale), blue and red curves correspond to the normalized ion current of the detector of the coupled to the thermoanalyzer mass spectrometer.

The experimental weight loss (78.6% for $K(H_2O)_3[Lu(L)_2]$ and 80.5% for $K(H_2O)_3[Yb(L)_2]$) in thermal analyses is in agreement with its decomposition into the lanthanide oxides (81.1% and 81.2% for $K(H_2O)_3[Ln(L)_2]$, Ln = Lu, Yb, correspondingly) and additionally allows to prove the number of solvent molecules in complexes. The first stage of the weight loss of about 5% up to ~380°C correspond to the loss of tree water molecules (calcd. 5.1% for both $K(H_2O)_3[Ln(L)_2]$, Ln = Lu, Yb; loss of ethanol molecules would correspond to 12.2% weight loss for both $K(EtOH)_3[Ln(L)_2]$ for both Ln = Lu, Yb). Additionally, loss of water solvent molecules is confirmed by a presence of the peak in this range with m/z= 18 on the ion current curves of the coupled mass spectrometer detector. Further heating decomposes complexes into the lanthanide oxides.

Infrared spectroscopy

IR spectra in the ATR mode were recorded on a spectrometer Spectrum One (Perkin-Elmer) in the region of 400-4000 cm^{-1}.

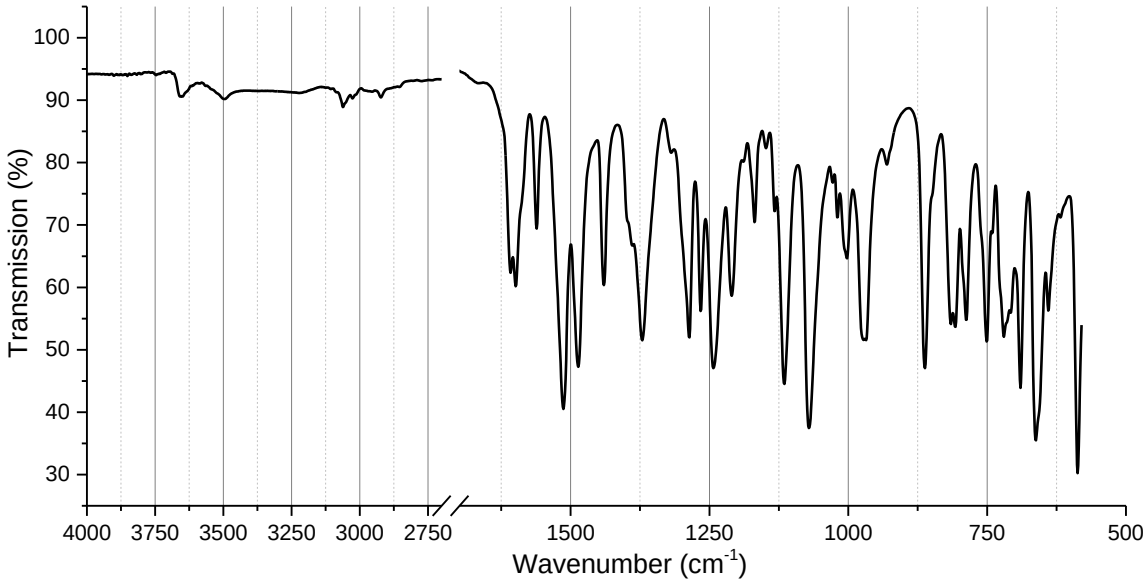

Figure 4 IR spectrum of $K(H_2O)_3[Lu(L)_2]$

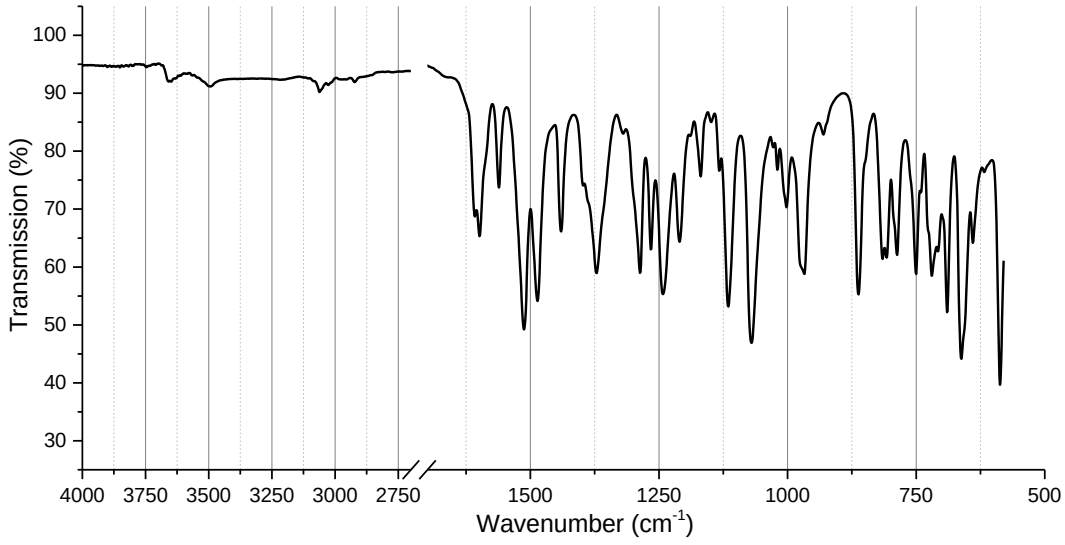

Figure 5 IR spectrum of $K(H_2O)_3[Yb(L)_2]$

Luminescence spectroscopy

Photoluminescence and excitation spectra of $K(H_2O)_3[Yb(L)_2]$ were measured using Fluorolog FL3-22 spectrofluorometer at room temperature. Quantum yield of $K(H_2O)_3[Yb(L)_2]$ was determined using Fluorolog FL3-22 spectrofluorometer at room temperature under excitation into ligand states, according to an absolute method, using an integrating sphere.

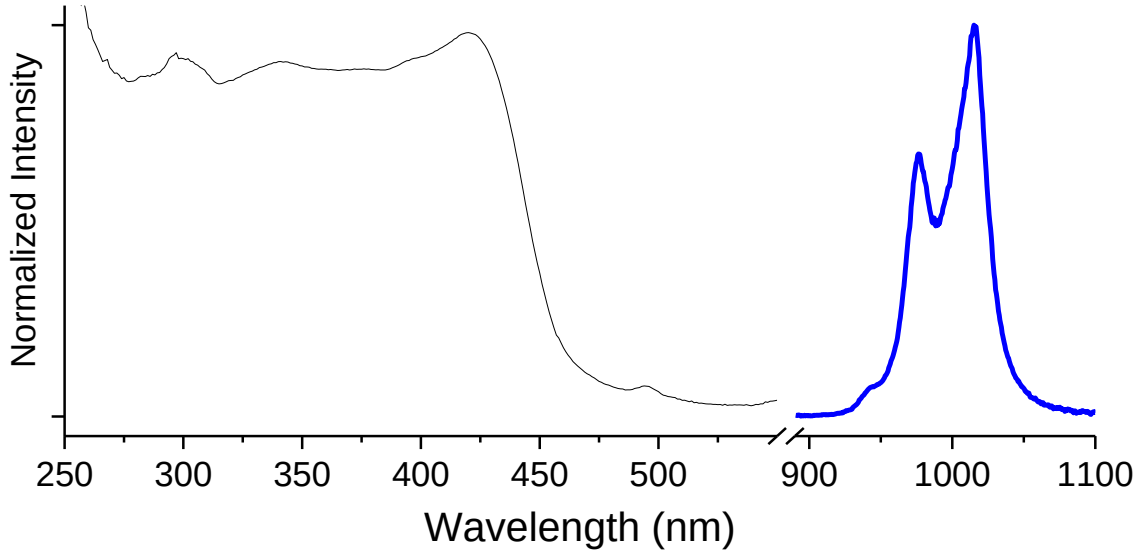

Figure 6 Luminescence and excitation spectra of $K(H_2O)_3[Yb(L)_2]$ in powder at 298 K

The lifetime in NIR range of $K(H_2O)[Yb(L)_2]$ emission (luminescence at 980 nm upon 365 nm excitation) was measured using an Edinburgh Instruments FLS980 Fluorescence Spectrometer equipped with 450 W Xenon lamp. The R5509-72 photomultiplier tube from Hamamatsu in nitrogen-flow cooled housing was used as a detector for near infrared range. The dependence of the luminescence intensity of $K(H_2O)[Yb(L)_2]$ (at 980 nm upon 365 nm excitation) on time was fitted with a single exponential decay function, providing the observed lifetime of ytterbium emission $\tau_{obs} = 12 \pm \mu s$.

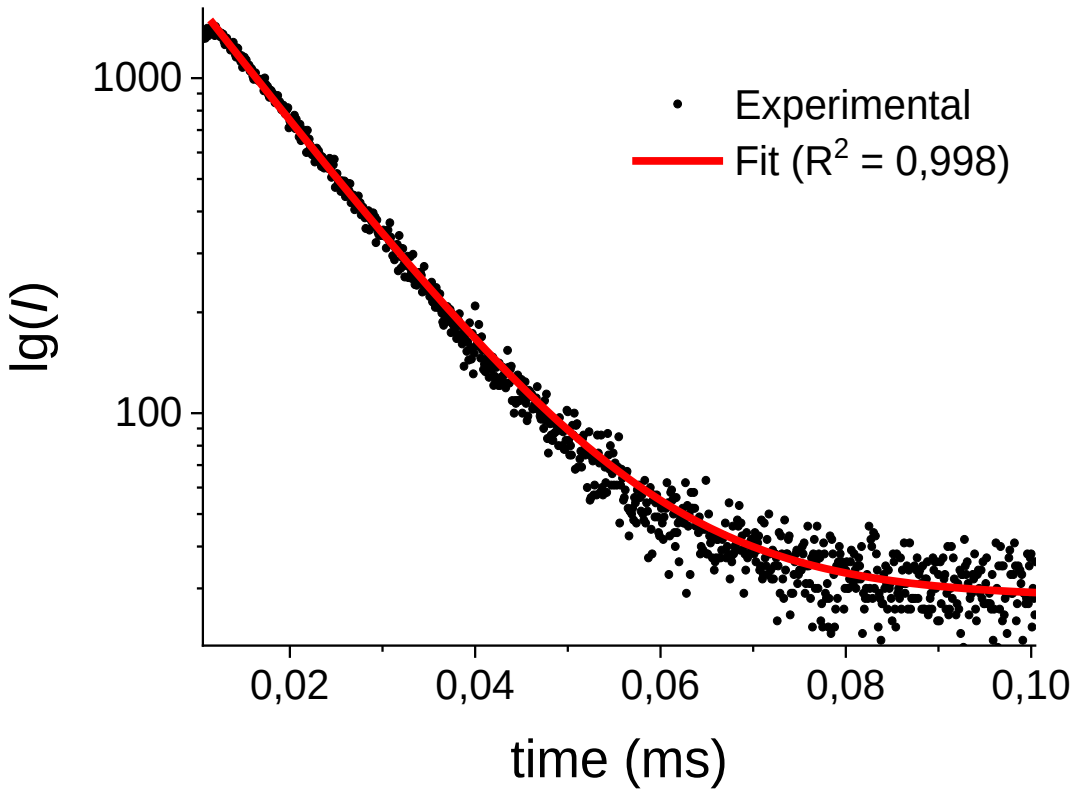

Figure 7 Dependence of the logarithm of the luminescence intensity of $K(H_2O)[Yb(L)_2]$ (at 980 nm upon 365 nm excitation) on time. The single exponential decay fit provides the observed lifetime of ytterbium emission τ_{obs} = 12 ± 1 µs.

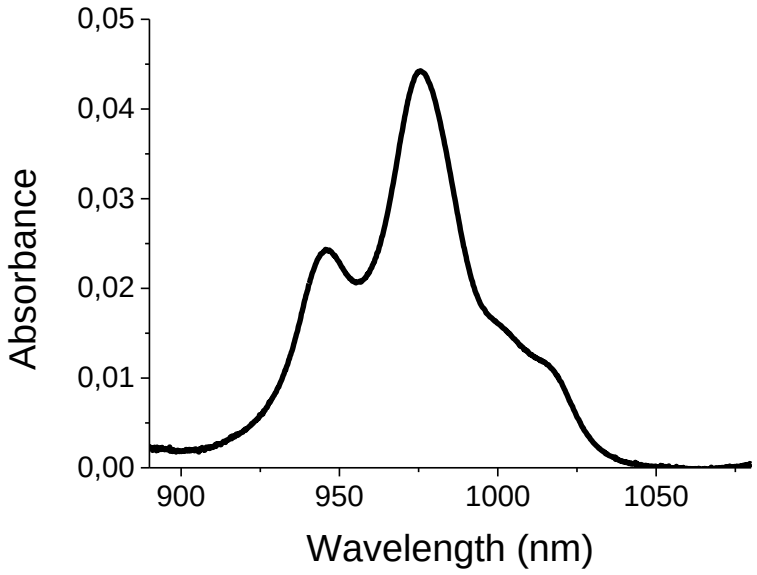

Figure 8 Absorption spectrum of $K(H_2O)[Yb(L)_2]$ in DMSO at 16.9 mM (*l* = 1 cm).

The radiative lifetime of ytterbium ion can be calculated from the absorption spectrum corresponding to the emission spectrum with the help of the modified Einstein's equation[3]:

$$\frac{1}{\tau_{rad}} = 2303 \times \frac{8\pi c n^2 \tilde{\nu}_m^{\ 2}(2J+1)}{N_A(2J'+1)} \int \varepsilon(\tilde{\nu}) d\tilde{\nu}$$

where c is the speed of light in vacuum (cm sec^{-1}), n is refractive index, N_A is Avogadro's number, J and J' are the quantum numbers for the ground and excited states, respectively, $\int \varepsilon(\tilde{\nu}) d\tilde{\nu}$ is the integrated spectrum of the f-f transition, $\tilde{\nu}_m = \frac{\int \tilde{\nu}\varepsilon(\tilde{\nu}) d\tilde{\nu}}{\int \varepsilon(\tilde{\nu}) d\tilde{\nu}}$ is the barycenter of the transition. Using the modified Einstein's equation and the absorption spectrum of K(H_2O)[Yb(L)$_2$] in DMSO, the radiative lifetime of the ytterbium emission in K(H_2O)[Yb(L)$_2$] was calculated to be τ_{rad}= 0.83 ms (where the integrated spectrum of the f-f transition was found to be 1327 M^{-1} and the barycenter of the transition is 10235 cm^{-1}).

Knowing the observed and radiative lifetimes of ytterbium emission in K(H_2O)[Yb(L)$_2$] DMSO solution though the ligand excitation, the intrinsic quantum yield can be calculated by the formula $Q_{Yb}^{Yb} = \frac{\tau_{obs}}{\tau_{rad}} =$ 1.4%.

The sensitization efficiency of the ytterbium emission by the ligand can be calculated by the formula $\eta_{sens} = \frac{Q_{Yb}^{L}}{Q_{Yb}^{Yb}}$ ~90%, where $Q_{Yb}^{L} = 1.3 \pm 0.2\%$ – overall quantum yield of K(H_2O)[Yb(L)$_2$] luminescence.

[3] Martinus H.V. Werts, Ronald T.F. Jukes, Jan W. Verhoeven, *PCCP*, 2002, **4**, 1542

Cellular experiments

The cellular experiments were performed using HeLa cells. Firstly, the cytotoxicity of $K(H_2O)_3[Yb(L)_2]$ solutions was determined. Because $K(H_2O)_3[Yb(L)_2]$ poorly soluble in water, the solutions were prepared by dilution of a stock 20 g/L DMSO solution of $K(H_2O)_3[Yb(L)_2]$ into a cell culture media. After that, the confocal microscopy experiments were performed using $K(H_2O)_3[Yb(L)_2]$ solution at a safe concentration (5 mg/L, 0.025% DMSO). In the absence of the detector in the micron-range attached to the confocal microscope, to show the proof of principle that $K(H_2O)_3[Yb(L)_2]$ can be used for luminescence bioimaging, the luminescence was detected in the range 600 – 750 nm which corresponded to the luminescence of the organic ligand.

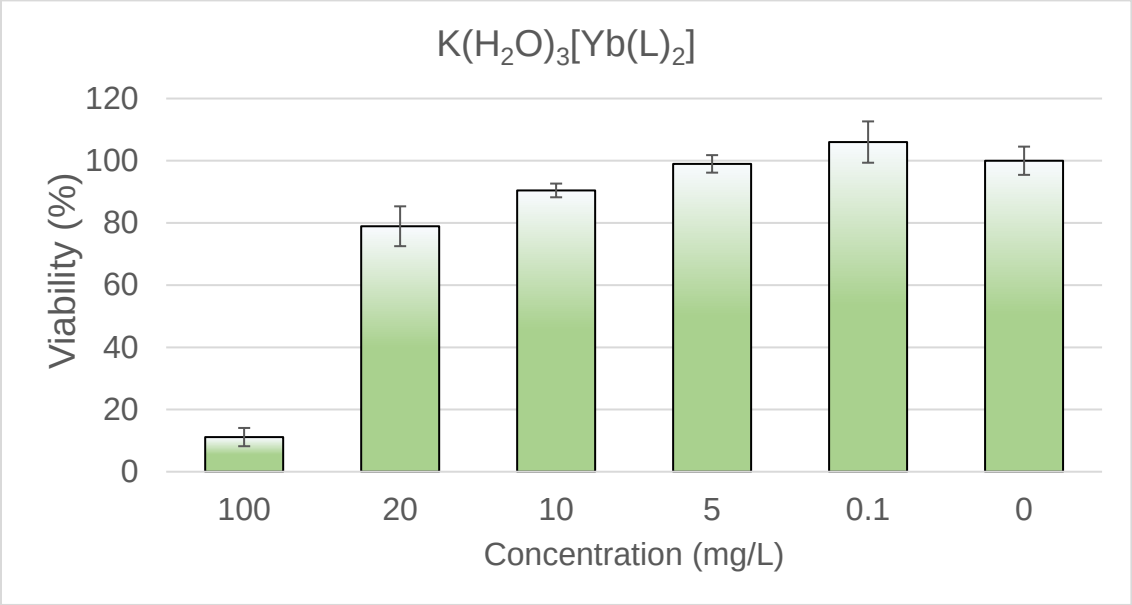

Figure 9 HeLa cell variability at different concentrations of $K(H_2O)_3[Yb(L)_2]$. Error bars correspond to 2s value.

Cytotoxicity was assessed using an MTT assay. To determine the toxic effect of the probes towards HeLa cells, the CellTiter 96® Non-Radioactive Cell Proliferation Assay (Promega) was used. This assay is based on the intracellular reduction of a tetrazolium salt (yellow) into a formazan product (blue), which

only takes place in metabolic active cells. The generated formazan is detectable at wavelengths between 630÷750 nm and is a direct measure for the viability of the cells. For this assay, each well of a 96 well plate (Cstar 3596, 96 Well Cell Culture Cluster, sterile) was seeded with 1×10^4 HeLa cells in 100 µl Dulbecco's modified Eagle's medium (DMEM, high glucose, Gibco) supplemented with 10% fetal calf serum (FCS, PAA), and 1 U/mL Penicillin/Streptomycin at 37 °C, 5% CO_2 and 95% humidity. After 24 h cells were incubated the samples at different concentrations. For each concentration, 6 wells were prepared and incubated for 72 h. A set of positive (cells treated with 5 µl of 20% triton) and negative (untreated cells) control wells, as well as the test samples, were treated with 15 µl of the Dye Solution and incubated for 4 h. 100 µl Solubilization Solution/Stop Mix is then added to each well to solubilize the formazan product, according to the manufacturer's manual. After 24 h incubation, the absorbance at 595 nm using a 96-well plate reader (Ultra Microplate Reader ELx808, BioTEK Instruments, INC) was measured. Data were averaged and the multiple determination of each substance and concentration made it possible to calculate the standard deviation

LD_{50} = 50 ±13 mg/L was calculated by a linear approximation in the least range containing 50% viability point and limited by two experimental points. Safe concentration (cell survival > 80%) is 20 mg/L.

Confocal microscopy. Two hours after seeding, 1×10^4 HeLa cells per a well plate were transferred into 8-well ibiTreat chamber slides (Ibidi, Martinsried, Germany) in 0.2 mL of the medium. After 24 h, cells were treated with the tested compounds at the desired concentrations. After the next 24 h, the cells were washed and then investigated using confocal microscope Leica TCS-SPE (DM2500), equipped with ACS APO 63x/1.30 OIL object-glass. Fluorescence excitation was performed by the 488-nm line or 405-nm line of an Ar-ion laser 15%, resolution 8 bit, line average 16, format 1024 × 1024 pixels, 200 Hz. Fluorescence detection took place in the red channel (600–750 nm). Additionally, brightfield images were

recorded in a third independent channel. The images were recorded and then analyzed using LAS-AF 2.0.2.4647 software.

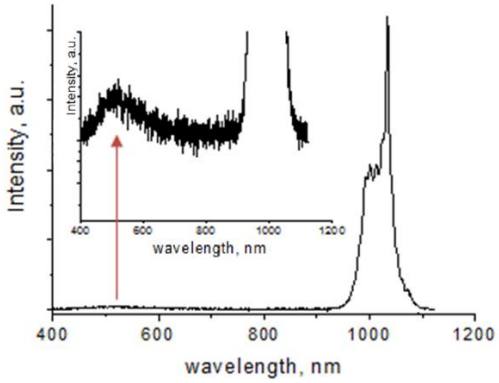

Figure 10 Photoluminescence spectrum of $K(H_2O)_3[Yb(L)_2]$. Insert shows the ligand luminescence band which was used for confocal microscopy.

Absorption spectroscopy

Absorption spectra were obtained using Perkin Elmer LAMBDA 950 spectrometer.

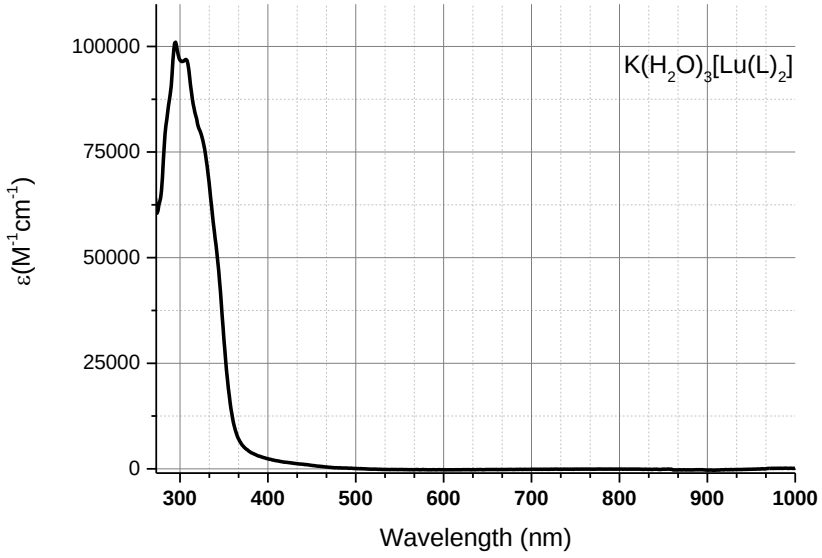

Figure 11 Absorption spectrum of $K(H_2O)_3[Lu(L)_2]$ in DMSO

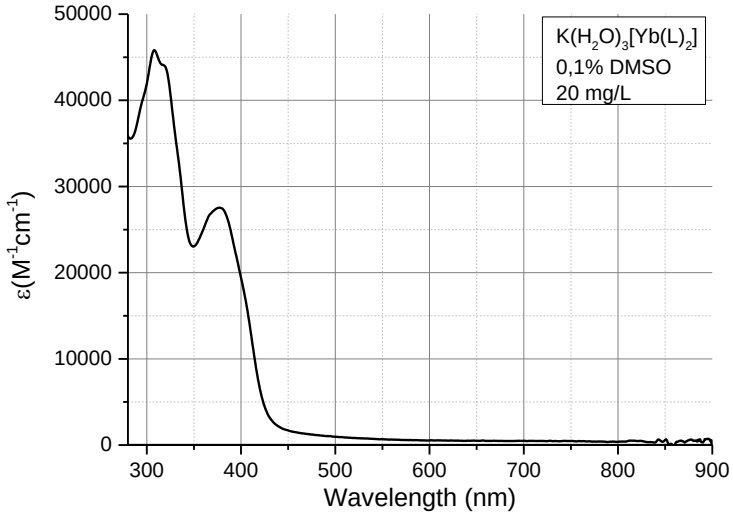

Figure 12 Absorption spectrum of $K(H_2O)_3[Yb(L)_2]$ in water – 0.1%DMSO at 20 mg/L.

MALDI data

MALDI spectroscopy was made on Autoflex II with time of flight detector (Bruker Daltonics, Germany).

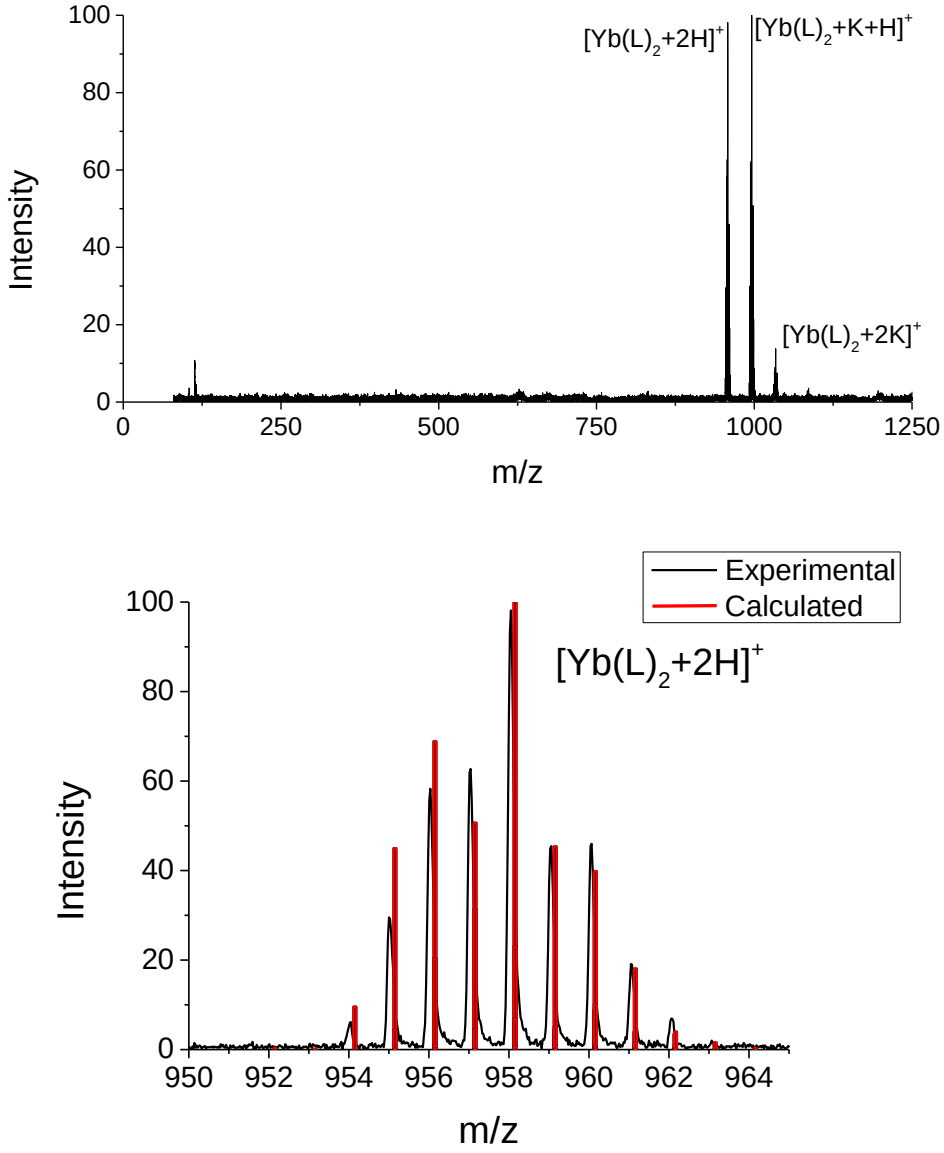

Figure 13 MALDI mass-spectrum of $K(H_2O)_3[Yb(L)_2]$.

Crystal structure data

Single crystals of $K(EtOH)_3[Yb(L)_2]$ ($C_{48}H_{52}KN_6O_9S_2Yb$) were grown from ethanol. A suitable crystal was selected and mounted on a glass fiber on Bruker APEX-II CCD diffractometer. The crystal was kept at 120 K during data collection. Using Olex2 [1], the structure was solved with the XS [2] structure solution program using Direct Methods and refined with the XL [2] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

Crystal Data for $C_{48}H_{52}KN_6O_9S_2Yb$ (M =1133.22 g/mol): triclinic, space group P-1 (no. 2), a = 9.2427(13) Å, b = 11.0807(15) Å, c = 24.563(3) Å, α = 86.803(2)°, β = 88.788(2)°, γ = 74.750(2)°, V = 2423.2(6) $Å^3$, Z = 2, T = 120 K, μ(MoKα) = 2.163 mm^{-1}, *Dcalc* = 1.553 g/cm^3, 25777 reflections measured ($1.66° \leq 2\Theta \leq 56.56°$), 11989 unique ($R_{int}$ = 0.0633, R_{sigma} = 0.0961) which were used in all calculations. The final R_1 was 0.0429 (>2sigma(I)) and wR_2 was 0.0832 (all data).

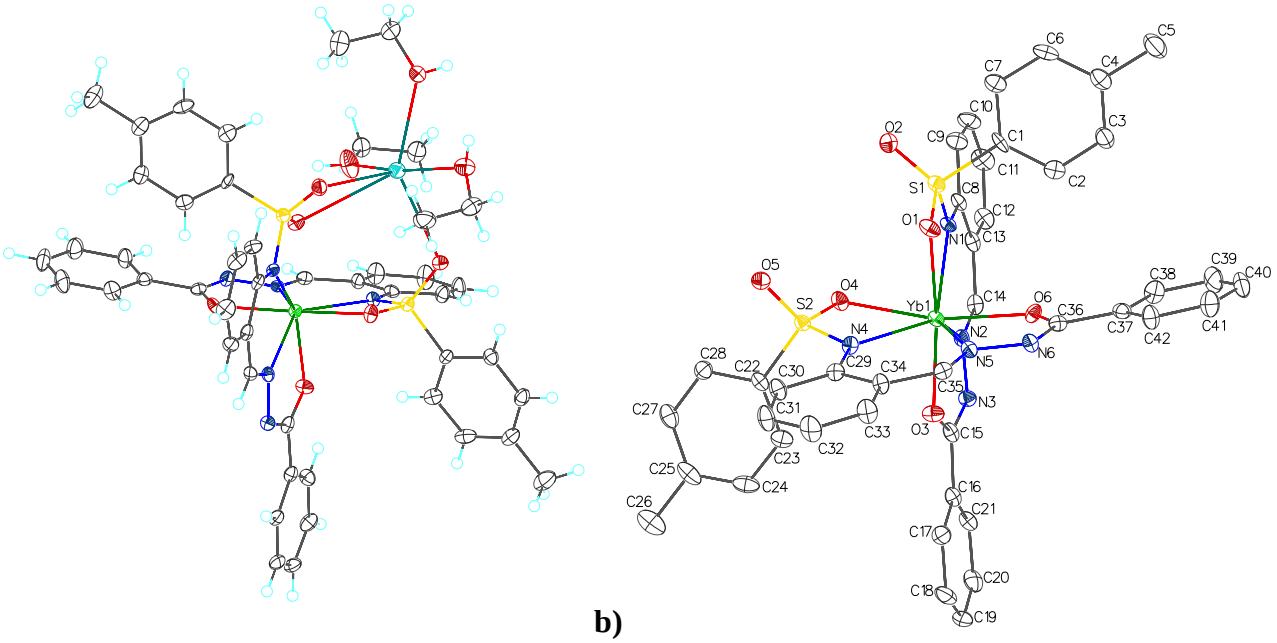

Figure 14 The general view of $K(EtOH)_3[Yb(L)_2]$ (CCDC 2016985). Atoms are represented a) by thermal displacement ellipsoids, b) by thermal displacement ellipsoids, hydrogen atoms are not shown.

Table 1 Crystal data and structure refinement for $K(EtOH)_3[Yb(L)_2]$ (CCDC 2016985)

Empirical formula	$C_{48}H_{52}KN_6O_9S_2Yb$
Formula weight	1133.22
Temperature/K	120
Crystal system	triclinic
Space group	P-1
a/Å	9.2427(13)
b/Å	11.0807(15)
c/Å	24.563(3)
α/°	86.803(2)
β/°	88.788(2)
γ/°	74.750(2)
Volume/Å^3	2423.2(6)
Z	2
ρ_{calc}g/cm^3	1.553
μ/mm^{-1}	2.163
F(000)	1150.0
Crystal size/mm^3	0.21 × 0.15 × 0.07
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	1.66 to 56.56
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -32 ≤ l ≤ 32
Reflections collected	25777
Independent reflections	11989 [R_{int} = 0.0633, R_{sigma} = 0.0961]
Data/restraints/parameters	11989/9/618
Goodness-of-fit on F^2	0.996
Final R indexes [I>=2σ (I)]	R_1 = 0.0429, wR_2 = 0.0740
Final R indexes [all data]	R_1 = 0.0647, wR_2 = 0.0832
Largest diff. peak/hole / e Å^{-3}	2.00/-1.80

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $K(EtOH)_3[Yb(L)_2]$ (CCDC 2016985). U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Yb1	9822.7(2)	504.29(19)	2389.80(8)	11.83(5)
S1	8930.8(11)	2403.4(10)	3279.5(4)	14.7(2)
S2	9295.2(11)	2585.2(10)	1495.1(4)	13.3(2)
O1	7984(3)	1955(3)	2903.8(12)	17.3(7)
O6	9753(3)	-957(3)	3042.4(12)	15.6(6)
O3	10875(3)	-817(3)	1760.6(12)	17.0(7)
O2	8695(3)	3739(3)	3245.6(12)	20.3(7)
O4	10449(3)	2231(3)	1921.3(12)	17.0(7)
O5	8416(3)	3876(3)	1487.0(12)	20.6(7)
N6	7472(4)	-1191(3)	2744.4(14)	15.3(8)
N1	10532(4)	1567(3)	3132.5(13)	12.3(7)
N4	8405(4)	1573(3)	1614.5(14)	13.5(7)
N2	12503(4)	-320(3)	2513.1(14)	13.7(7)
N3	13201(4)	-1281(3)	2162.1(14)	14.8(8)
N5	7651(4)	-319(3)	2318.2(14)	14.3(8)
C19	13910(5)	-4282(4)	655.6(19)	24.2(11)
C40	8336(6)	-3776(5)	4511(2)	30.3(12)
C20	14900(5)	-3981(4)	1015.2(18)	22.4(10)
C26	12325(6)	2053(5)	-722(2)	35.0(13)
C5	7050(6)	956(5)	5546(2)	35.7(13)
C32	4769(5)	1252(5)	670(2)	28.0(12)
C38	9659(5)	-2571(4)	3954.2(19)	22.6(10)
C11	14498(5)	1687(5)	3930.9(19)	23.8(11)
C18	12414(5)	-3607(4)	655.7(18)	23.8(11)
C39	9578(6)	-3331(5)	4412(2)	30.5(12)
C42	7250(5)	-2723(4)	3678.2(19)	22.7(10)
C41	7170(6)	-3468(5)	4141(2)	28.7(12)
C34	6328(5)	676(4)	1476.0(18)	16.1(9)
C8	11831(5)	1637(4)	3399.4(16)	13.5(9)
C13	13214(5)	795(4)	3262.6(17)	14.9(9)
C22	10220(4)	2395(4)	854.9(17)	13.6(9)
C1	8448(4)	1996(4)	3952.0(16)	15.5(9)
C2	8728(5)	741(4)	4120.8(18)	20.1(10)
C15	12263(5)	-1436(4)	1794.4(17)	15.4(9)
C35	6582(5)	-140(4)	1967.9(17)	15.0(9)
C29	7179(4)	1507(4)	1296.5(17)	14.1(9)
C36	8605(5)	-1417(4)	3090.9(17)	14.5(9)

Atom	*x*	*y*	*z*	U(eq)
C37	8495(5)	-2253(4)	3579.5(17)	16.4(9)
C12	14523(5)	853(4)	3538.5(18)	19.2(10)
C14	13451(4)	-128(4)	2859.5(17)	14.8(9)
C24	11233(5)	1145(5)	103.3(19)	22.9(11)
C16	12878(5)	-2393(4)	1390.4(17)	15.9(9)
C21	14395(5)	-3050(4)	1373.3(17)	17.4(9)
C25	11569(5)	2174(5)	-173.7(18)	22.6(11)
C30	6786(5)	2200(4)	798.8(18)	18.9(10)
C31	5614(5)	2054(5)	489.1(19)	24.7(11)
C7	7746(5)	2925(4)	4300.1(18)	20.2(10)
C23	10574(5)	1244(4)	618.1(18)	19.5(10)
C4	7560(5)	1327(5)	4991.3(18)	21.7(10)
C28	10548(5)	3429(4)	585.2(18)	18.3(10)
C33	5116(5)	581(5)	1159.9(19)	22.7(11)
C27	11232(5)	3299(5)	78.0(18)	22.0(10)
C17	11904(5)	-2680(4)	1022.1(18)	18.9(10)
C9	11831(5)	2504(4)	3800.2(18)	19.1(10)
C10	13144(5)	2515(4)	4061.7(18)	22.5(10)
C6	7313(5)	2577(5)	4816.2(18)	23.7(11)
C3	8291(5)	414(5)	4641.3(18)	23.0(11)
O1S	7717(4)	6587(3)	2142.2(13)	24.7(7)
C1S	9260(5)	6460(5)	2010(2)	28.1(12)
C2S	10303(6)	5743(5)	2451(2)	36.3(13)
O3S	4588(4)	6540(3)	2791.7(13)	27.2(8)
C6S	3670(7)	5385(5)	3507(2)	44.5(15)
C5S	3526(6)	6637(5)	3219(2)	31.1(12)
O2S	4964(4)	2970(3)	2460.4(16)	37.3(9)
C3S	3560(5)	2910(5)	2242(2)	25.3(11)
C4S	3317(5)	3731(5)	1726(2)	29.6(12)
K5	6628.8(11)	4604.6(9)	2388.6(4)	20.7(2)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for $K(EtOH)_3[Yb(L)_2]$ (CCDC 2016985). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Yb1	8.71(9)	16.23(10)	10.86(9)	-0.82(6)	-2.44(6)	-3.61(7)
S1	12.4(5)	18.2(6)	12.7(5)	-1.2(4)	-2.5(4)	-2.4(4)
S2	13.6(5)	15.2(5)	12.2(5)	-0.9(4)	-1.2(4)	-5.2(4)
O1	12.1(15)	27.9(18)	13.0(16)	-3.6(13)	-4.1(12)	-6.4(13)
O6	14.0(15)	11.5(15)	20.7(17)	1.4(12)	-6.4(12)	-2.5(12)
O3	10.6(15)	20.9(17)	19.0(17)	-6.2(13)	-5.3(12)	-2.0(13)
O2	23.9(17)	18.3(17)	17.7(17)	0.7(13)	-2.1(13)	-4.0(14)
O4	17.9(16)	22.0(17)	13.6(16)	1.5(13)	-5.6(12)	-9.8(13)
O5	23.3(17)	18.0(17)	18.4(17)	-2.0(13)	3.9(13)	-2.2(13)
N6	15.6(18)	18(2)	13.1(19)	1.5(15)	-0.9(14)	-5.9(15)
N1	11.1(17)	16.0(19)	9.5(18)	-1.3(14)	-1.1(13)	-2.9(14)
N4	10.4(17)	15.2(19)	16.2(19)	1.1(15)	-3.1(14)	-5.8(14)
N2	14.0(18)	14.1(19)	13.2(19)	0.9(14)	-2.8(14)	-4.5(15)
N3	14.4(18)	16.2(19)	14.4(19)	-2.2(15)	-2.7(14)	-4.6(15)
N5	10.3(17)	16.9(19)	13.0(19)	0.5(15)	0.7(14)	0.8(15)
C19	33(3)	21(3)	17(2)	-5.5(19)	9(2)	-5(2)
C40	42(3)	30(3)	19(3)	9(2)	-1(2)	-12(2)
C20	17(2)	28(3)	20(3)	3(2)	6.2(18)	-3(2)
C26	28(3)	54(4)	22(3)	-5(3)	2(2)	-10(3)
C5	47(3)	44(3)	19(3)	0(2)	4(2)	-18(3)
C32	26(3)	37(3)	25(3)	6(2)	-16(2)	-16(2)
C38	20(2)	23(3)	27(3)	2(2)	-4.5(19)	-8(2)
C11	20(2)	34(3)	22(3)	-3(2)	-5.5(19)	-15(2)
C18	30(3)	31(3)	13(2)	-5(2)	-0.7(19)	-10(2)
C39	34(3)	31(3)	24(3)	8(2)	-14(2)	-5(2)
C42	21(2)	26(3)	21(3)	7(2)	-5.0(19)	-7(2)
C41	30(3)	29(3)	29(3)	7(2)	1(2)	-12(2)
C34	11(2)	20(2)	16(2)	3.6(18)	-2.8(17)	-3.7(18)
C8	14(2)	20(2)	9(2)	1.0(17)	-0.3(16)	-8.8(18)
C13	13(2)	21(2)	13(2)	3.6(18)	-1.9(16)	-7.5(18)
C22	8(2)	22(2)	11(2)	0.8(17)	-1.8(16)	-5.1(17)
C1	12(2)	28(3)	6(2)	3.0(18)	-0.8(16)	-6.0(18)
C2	18(2)	23(3)	20(2)	-4.0(19)	0.6(18)	-6(2)
C15	15(2)	22(2)	12(2)	2.5(18)	-1.9(16)	-9.1(19)
C35	11(2)	16(2)	19(2)	-2.5(18)	0.9(17)	-5.2(17)
C29	9(2)	16(2)	17(2)	-1.1(17)	-1.3(16)	-1.2(17)
C36	12(2)	16(2)	16(2)	-3.3(17)	2.2(16)	-4.9(17)
C37	17(2)	17(2)	15(2)	-3.5(18)	0.9(17)	-1.8(18)
C12	12(2)	25(3)	19(2)	0.8(19)	-1.2(17)	-2.1(19)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C14	8(2)	18(2)	17(2)	3.4(18)	-1.6(16)	-2.7(17)
C24	15(2)	32(3)	22(3)	-12(2)	-0.4(18)	-4(2)
C16	14(2)	20(2)	14(2)	1.4(18)	-0.8(17)	-7.7(18)
C21	15(2)	24(3)	13(2)	0.3(18)	0.1(17)	-5.9(19)
C25	10(2)	44(3)	13(2)	-1(2)	-3.8(17)	-6(2)
C30	16(2)	25(3)	16(2)	3.5(19)	-3.8(17)	-5.7(19)
C31	23(3)	31(3)	20(3)	9(2)	-8.6(19)	-8(2)
C7	19(2)	26(3)	18(2)	-4.3(19)	-4.2(18)	-9(2)
C23	16(2)	25(3)	19(2)	-5.4(19)	-2.1(18)	-7.1(19)
C4	19(2)	31(3)	17(2)	-1(2)	-1.9(18)	-11(2)
C28	19(2)	18(2)	18(2)	-0.3(18)	-3.6(18)	-4.4(19)
C33	18(2)	31(3)	24(3)	4(2)	-8.8(19)	-14(2)
C27	16(2)	31(3)	19(2)	5(2)	0.3(18)	-6(2)
C17	18(2)	19(2)	19(2)	-1.2(19)	-4.6(18)	-3.9(19)
C9	15(2)	24(3)	19(2)	-4.8(19)	2.7(18)	-5.0(19)
C10	25(3)	30(3)	17(2)	-8(2)	-1.6(19)	-15(2)
C6	23(3)	33(3)	16(2)	-12(2)	2.7(19)	-8(2)
C3	27(3)	26(3)	17(2)	2(2)	-1.3(19)	-8(2)
O1S	23.2(18)	23.0(18)	30(2)	-7.3(15)	0.1(14)	-8.9(15)
C1S	31(3)	31(3)	27(3)	-7(2)	7(2)	-14(2)
C2S	24(3)	46(4)	33(3)	-3(3)	0(2)	2(2)
O3S	26.8(19)	24.4(19)	24.6(19)	2.9(15)	2.9(14)	2.6(15)
C6S	52(4)	41(4)	38(4)	10(3)	5(3)	-11(3)
C5S	30(3)	33(3)	29(3)	1(2)	7(2)	-6(2)
O2S	31(2)	36(2)	47(3)	13.8(18)	-20.3(17)	-15.3(18)
C3S	21(2)	28(3)	28(3)	3(2)	-2(2)	-9(2)
C4S	23(3)	37(3)	29(3)	5(2)	-3(2)	-10(2)
K5	17.5(5)	22.0(5)	21.5(5)	-0.7(4)	-0.2(4)	-3.1(4)

Table 4 Bond Lengths for $K(EtOH)_3[Yb(L)_2]$ (CCDC 2016985).

Atom	Atom	Length (Å)	Atom	Atom	Length (Å)
Yb1	S1	3.0672(11)	C32	C33	1.376(6)
Yb1	S2	3.0452(11)	C38	C39	1.380(7)
Yb1	O1	2.401(3)	C38	C37	1.391(6)
Yb1	O6	2.226(3)	C11	C12	1.368(6)
Yb1	O3	2.218(3)	C11	C10	1.387(6)
Yb1	O4	2.373(3)	C18	C17	1.385(6)
Yb1	N1	2.417(3)	C42	C41	1.380(6)
Yb1	N4	2.405(3)	C42	C37	1.394(6)
Yb1	N2	2.424(3)	C34	C35	1.453(6)
Yb1	N5	2.426(4)	C34	C29	1.408(6)
Yb1	C15	3.084(4)	C34	C33	1.406(6)
Yb1	C36	3.088(4)	C8	C13	1.417(6)
S1	O1	1.476(3)	C8	C9	1.414(6)
S1	O2	1.436(3)	C13	C12	1.416(6)
S1	N1	1.572(3)	C13	C14	1.435(6)
S1	C1	1.767(4)	C22	C23	1.388(6)
S1	K5	3.4838(14)	C22	C28	1.391(6)
S2	O4	1.472(3)	C1	C2	1.387(6)
S2	O5	1.446(3)	C1	C7	1.391(6)
S2	N4	1.569(4)	C2	C3	1.390(6)
S2	C22	1.770(4)	C15	C16	1.486(6)
S2	K5	3.6490(14)	C29	C30	1.408(6)
O1	K5	3.083(3)	C36	C37	1.493(6)
O6	C36	1.293(5)	C24	C25	1.396(7)
O3	C15	1.288(5)	C24	C23	1.389(6)
O2	K5	2.825(3)	C16	C21	1.400(6)
O5	K5	2.762(3)	C16	C17	1.395(6)
N6	N5	1.422(5)	C25	C27	1.381(7)
N6	C36	1.327(5)	C30	C31	1.385(6)
N1	C8	1.401(5)	C7	C6	1.386(6)
N4	C29	1.409(5)	C4	C6	1.389(7)
N2	N3	1.418(5)	C4	C3	1.389(6)
N2	C14	1.298(5)	C28	C27	1.382(6)
N3	C15	1.314(5)	C9	C10	1.387(6)
N5	C35	1.292(5)	O1S	C1S	1.427(5)
C19	C20	1.398(7)	O1S	K5	2.682(3)
C19	C18	1.389(6)	C1S	C2S	1.508(7)
C40	C39	1.375(7)	O3S	C5S	1.411(5)
C40	C41	1.385(7)	O3S	K5	2.677(3)

Atom	Atom	Length (Å)	Atom	Atom	Length (Å)
C20	C21	1.374(6)	C6S	C5S	1.496(7)
C26	C25	1.500(6)	O2S	C3S	1.434(5)
C5	C4	1.503(6)	O2S	K5	2.664(4)
C32	C31	1.379(7)	C3S	C4S	1.503(6)

Table 5 Bond Angles for $K(EtOH)_3[Yb(L)_2]$ (CCDC 2016985).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
S1	Yb1	C15	149.74(8)	N3	N2	Yb1	114.9(2)
S1	Yb1	C36	90.54(8)	C14	N2	Yb1	133.7(3)
S2	Yb1	S1	91.71(3)	C14	N2	N3	111.3(3)
S2	Yb1	C15	97.43(8)	C15	N3	N2	111.5(3)
S2	Yb1	C36	148.73(8)	N6	N5	Yb1	115.6(2)
O1	Yb1	S1	28.09(7)	C35	N5	Yb1	133.8(3)
O1	Yb1	S2	85.65(7)	C35	N5	N6	110.6(4)
O1	Yb1	N1	58.51(10)	C18	C19	C20	119.2(4)
O1	Yb1	N4	84.14(11)	C39	C40	C41	119.3(5)
O1	Yb1	N2	131.06(11)	C21	C20	C19	120.6(4)
O1	Yb1	N5	78.56(11)	C33	C32	C31	119.3(4)
O1	Yb1	C15	176.60(11)	C39	C38	C37	120.7(5)
O1	Yb1	C36	81.83(10)	C12	C11	C10	118.8(4)
O6	Yb1	S1	86.44(8)	C17	C18	C19	120.1(4)
O6	Yb1	S2	169.46(7)	C40	C39	C38	120.7(4)
O6	Yb1	O1	87.88(10)	C41	C42	C37	120.6(4)
O6	Yb1	O4	159.99(10)	C42	C41	C40	120.4(5)
O6	Yb1	N1	83.22(11)	C29	C34	C35	126.2(4)
O6	Yb1	N4	140.15(11)	C33	C34	C35	114.5(4)
O6	Yb1	N2	82.14(11)	C33	C34	C29	119.3(4)
O6	Yb1	N5	67.57(11)	N1	C8	C13	118.5(4)
O6	Yb1	C15	89.29(11)	N1	C8	C9	123.3(4)
O6	Yb1	C36	21.19(10)	C9	C8	C13	118.2(4)
O3	Yb1	S1	169.71(8)	C8	C13	C14	126.5(4)
O3	Yb1	S2	87.67(8)	C12	C13	C8	118.5(4)
O3	Yb1	O1	161.58(9)	C12	C13	C14	115.0(4)
O3	Yb1	O6	95.98(11)	C23	C22	S2	120.7(3)
O3	Yb1	O4	93.36(11)	C23	C22	C28	120.5(4)
O3	Yb1	N1	139.77(10)	C28	C22	S2	118.8(3)
O3	Yb1	N4	81.38(11)	C2	C1	S1	119.2(3)
O3	Yb1	N2	67.36(11)	C2	C1	C7	120.6(4)
O3	Yb1	N5	86.26(11)	C7	C1	S1	120.2(4)
O3	Yb1	C15	21.01(10)	C1	C2	C3	119.4(4)
O3	Yb1	C36	95.31(11)	O3	C15	Yb1	38.11(19)
O4	Yb1	S1	81.43(7)	O3	C15	N3	124.7(4)
O4	Yb1	S2	28.21(7)	O3	C15	C16	118.8(4)
O4	Yb1	O1	88.82(10)	N3	C15	Yb1	86.7(3)
O4	Yb1	N1	78.24(11)	N3	C15	C16	116.5(4)
O4	Yb1	N4	58.88(11)	C16	C15	Yb1	156.5(3)
O4	Yb1	N2	85.20(11)	N5	C35	C34	128.8(4)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O4	Yb1	N5	130.87(10)	C34	C29	N4	118.4(4)
O4	Yb1	C15	93.20(11)	C34	C29	C30	118.0(4)
O4	Yb1	C36	170.63(10)	C30	C29	N4	123.5(4)
N1	Yb1	S1	30.49(8)	O6	C36	Yb1	38.48(18)
N1	Yb1	S2	100.37(8)	O6	C36	N6	125.5(4)
N1	Yb1	N2	72.74(11)	O6	C36	C37	118.7(4)
N1	Yb1	N5	128.80(11)	N6	C36	Yb1	87.2(3)
N1	Yb1	C15	119.25(11)	N6	C36	C37	115.8(4)
N1	Yb1	C36	97.26(11)	C37	C36	Yb1	156.3(3)
N4	Yb1	S1	103.15(8)	C38	C37	C42	118.3(4)
N4	Yb1	S2	30.68(8)	C38	C37	C36	119.5(4)
N4	Yb1	N1	123.66(11)	C42	C37	C36	122.1(4)
N4	Yb1	N2	130.81(11)	C11	C12	C13	122.5(4)
N4	Yb1	N5	72.59(11)	N2	C14	C13	128.8(4)
N4	Yb1	C15	99.24(11)	C23	C24	C25	121.2(4)
N4	Yb1	C36	119.03(11)	C21	C16	C15	122.7(4)
N2	Yb1	S1	103.21(8)	C17	C16	C15	119.0(4)
N2	Yb1	S2	108.37(8)	C17	C16	C21	118.3(4)
N2	Yb1	N5	137.48(11)	C20	C21	C16	120.7(4)
N2	Yb1	C15	46.54(11)	C24	C25	C26	121.0(5)
N2	Yb1	C36	101.42(11)	C27	C25	C26	120.7(5)
N5	Yb1	S1	103.87(8)	C27	C25	C24	118.3(4)
N5	Yb1	S2	102.93(8)	C31	C30	C29	121.1(4)
N5	Yb1	C15	102.08(11)	C32	C31	C30	120.6(4)
N5	Yb1	C36	46.51(11)	C6	C7	C1	119.0(4)
C15	Yb1	C36	96.17(11)	C22	C23	C24	119.1(4)
Yb1	S1	K5	92.03(3)	C6	C4	C5	121.2(4)
O1	S1	Yb1	50.00(12)	C6	C4	C3	118.6(4)
O1	S1	N1	101.11(18)	C3	C4	C5	120.2(5)
O1	S1	C1	107.65(19)	C27	C28	C22	119.3(4)
O1	S1	K5	62.13(12)	C32	C33	C34	121.6(4)
O2	S1	Yb1	130.02(13)	C25	C27	C28	121.6(4)
O2	S1	O1	113.59(18)	C18	C17	C16	121.0(4)
O2	S1	N1	118.01(19)	C10	C9	C8	121.0(4)
O2	S1	C1	106.6(2)	C11	C10	C9	120.9(4)
O2	S1	K5	51.58(12)	C7	C6	C4	121.5(4)
N1	S1	Yb1	51.25(13)	C4	C3	C2	120.9(5)
N1	S1	C1	109.49(19)	C1S	O1S	K5	122.3(3)
N1	S1	K5	124.96(13)	O1S	C1S	C2S	112.8(4)
C1	S1	Yb1	123.20(16)	C5S	O3S	K5	133.2(3)
C1	S1	K5	125.48(14)	O3S	C5S	C6S	110.4(4)
Yb1	S2	K5	89.26(3)	C3S	O2S	K5	135.7(3)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O4	S2	Yb1	49.60(12)	O2S	C3S	C4S	106.7(4)
O4	S2	N4	101.06(18)	S1	K5	S2	75.86(3)
O4	S2	C22	107.74(18)	O1	K5	S1	25.03(6)
O4	S2	K5	92.65(12)	O1	K5	S2	66.72(6)
O5	S2	Yb1	131.55(13)	O2	K5	S1	23.47(6)
O5	S2	O4	114.94(18)	O2	K5	S2	87.98(7)
O5	S2	N4	115.91(18)	O2	K5	O1	48.47(8)
O5	S2	C22	105.79(19)	O5	K5	S1	94.14(7)
O5	S2	K5	42.53(12)	O5	K5	S2	20.73(6)
N4	S2	Yb1	51.47(13)	O5	K5	O1	87.40(8)
N4	S2	C22	111.3(2)	O5	K5	O2	101.43(9)
N4	S2	K5	87.49(13)	O1S	K5	S1	112.59(8)
C22	S2	Yb1	122.53(14)	O1S	K5	S2	93.21(7)
C22	S2	K5	148.21(15)	O1S	K5	O1	134.00(9)
Yb1	O1	K5	118.33(11)	O1S	K5	O2	92.26(10)
S1	O1	Yb1	101.91(15)	O1S	K5	O5	77.08(10)
S1	O1	K5	92.84(14)	O3S	K5	S1	119.43(8)
C36	O6	Yb1	120.3(2)	O3S	K5	S2	163.50(8)
C15	O3	Yb1	120.9(3)	O3S	K5	O1	129.73(9)
S1	O2	K5	104.96(16)	O3S	K5	O2	104.30(10)
S2	O4	Yb1	102.19(15)	O3S	K5	O5	142.86(10)
S2	O5	K5	116.74(16)	O3S	K5	O1S	75.60(10)
C36	N6	N5	110.6(3)	O2S	K5	S1	82.60(8)
S1	N1	Yb1	98.27(16)	O2S	K5	S2	90.67(10)
C8	N1	Yb1	139.2(3)	O2S	K5	O1	60.76(9)
C8	N1	S1	122.4(3)	O2S	K5	O2	102.55(10)
S2	N4	Yb1	97.84(16)	O2S	K5	O5	102.85(12)
C29	N4	Yb1	139.6(3)	O2S	K5	O1S	164.81(11)
C29	N4	S2	122.5(3)	O2S	K5	O3S	97.20(12)

Table 6 Torsion Angles for $K(EtOH)_3[Yb(L)_2]$ (CCDC 2016985).

A	B	C	D	Angle/°
Yb1	S1	O1	K5	-119.74(14)
Yb1	S1	O2	K5	52.62(19)
Yb1	S1	N1	C8	177.5(4)
Yb1	S1	C1	C2	11.8(4)
Yb1	S1	C1	C7	-166.0(3)
Yb1	S1	K5	S2	-23.21(3)
Yb1	S1	K5	O1	41.73(13)
Yb1	S1	K5	O2	-142.49(17)
Yb1	S1	K5	O5	-33.07(7)
Yb1	S1	K5	O1S	-110.79(8)
Yb1	S1	K5	O3S	163.49(10)
Yb1	S1	K5	O2S	69.37(10)
Yb1	S2	O5	K5	-7.3(3)
Yb1	S2	N4	C29	-179.7(4)
Yb1	S2	C22	C23	33.7(4)
Yb1	S2	C22	C28	-148.2(3)
Yb1	S2	K5	S1	23.37(3)
Yb1	S2	K5	O1	-1.29(6)
Yb1	S2	K5	O2	43.71(7)
Yb1	S2	K5	O5	174.52(19)
Yb1	S2	K5	O1S	135.86(8)
Yb1	S2	K5	O3S	-177.6(3)
Yb1	S2	K5	O2S	-58.82(8)
Yb1	O1	K5	S1	-105.15(18)
Yb1	O1	K5	S2	1.86(9)
Yb1	O1	K5	O2	-107.40(15)
Yb1	O1	K5	O5	0.38(13)
Yb1	O1	K5	O1S	-68.83(17)
Yb1	O1	K5	O3S	-179.50(12)
Yb1	O1	K5	O2S	106.67(16)
Yb1	O6	C36	N6	7.4(5)
Yb1	O6	C36	C37	-171.2(3)
Yb1	O3	C15	N3	-5.9(6)
Yb1	O3	C15	C16	174.6(3)
Yb1	N1	C8	C13	-7.6(6)
Yb1	N1	C8	C9	172.6(3)
Yb1	N4	C29	C34	8.6(6)
Yb1	N4	C29	C30	-169.2(3)
Yb1	N2	N3	C15	7.1(4)
Yb1	N2	C14	C13	-8.4(7)
N1	Yb1	N2	N3	178.0(3)
N1	Yb1	N2	C14	3.2(4)
N1	Yb1	N5	N6	-55.9(3)
N1	Yb1	N5	C35	124.2(4)
N1	Yb1	C15	O3	-169.3(3)
N1	Yb1	C15	N3	5.8(3)
N1	Yb1	C15	C16	178.6(7)
N1	Yb1	C36	O6	-48.9(3)
N1	Yb1	C36	N6	137.1(2)
N1	Yb1	C36	C37	-29.4(7)
N1	S1	O1	Yb1	-4.10(19)
N1	S1	O1	K5	-123.83(15)
N1	S1	O2	K5	113.99(17)
N1	S1	C1	C2	-44.0(4)
N1	S1	C1	C7	138.2(3)
N1	S1	K5	S2	19.10(17)
N1	S1	K5	O1	84.0(2)
N1	S1	K5	O2	-100.2(2)
N1	S1	K5	O5	9.24(18)
N1	S1	K5	O1S	-68.48(19)
N1	S1	K5	O3S	-154.20(19)
N1	S1	K5	O2S	111.68(19)
N1	C8	C13	C12	-179.0(4)
N1	C8	C13	C14	1.8(6)
N1	C8	C9	C10	178.5(4)
N4	Yb1	S1	O1	48.68(18)
N4	Yb1	S1	O2	-40.03(19)
N4	Yb1	S1	N1	-136.48(18)
N4	Yb1	S1	C1	134.32(18)
N4	Yb1	S1	K5	-1.50(9)
N4	Yb1	S2	O4	-178.5(2)
N4	Yb1	S2	O5	92.3(2)
N4	Yb1	S2	C22	-92.4(2)
N4	Yb1	S2	K5	87.39(16)
N4	Yb1	O1	S1	-132.68(17)
N4	Yb1	O1	K5	-32.83(12)
N4	Yb1	O6	C36	-5.6(4)
N4	Yb1	O3	C15	148.0(3)
N4	Yb1	O4	S2	0.90(14)
N4	Yb1	N1	S1	53.7(2)

A	B	C	D	Angle/°
Yb1	N5	C35	C34	-0.6(7)
Yb1	C15	C16	C21	-176.0(5)
Yb1	C15	C16	C17	2.1(10)
Yb1	C36	C37	C38	-17.1(9)
Yb1	C36	C37	C42	162.3(5)
S1	Yb1	S2	O4	68.20(16)
S1	Yb1	S2	O5	-20.97(18)
S1	Yb1	S2	N4	-113.31(16)
S1	Yb1	S2	C22	154.29(17)
S1	Yb1	S2	K5	-25.92(3)
S1	Yb1	O1	K5	99.85(19)
S1	Yb1	O6	C36	100.8(3)
S1	Yb1	O3	C15	31.1(7)
S1	Yb1	O4	S2	-110.19(14)
S1	Yb1	N1	C8	-176.7(5)
S1	Yb1	N4	S2	70.51(15)
S1	Yb1	N4	C29	-109.9(4)
S1	Yb1	N2	N3	177.1(2)
S1	Yb1	N2	C14	2.3(4)
S1	Yb1	N5	N6	-75.8(3)
S1	Yb1	N5	C35	104.4(4)
S1	Yb1	C15	O3	-169.5(2)
S1	Yb1	C15	N3	5.6(4)
S1	Yb1	C15	C16	178.5(6)
S1	Yb1	C36	O6	-78.7(3)
S1	Yb1	C36	N6	107.3(2)
S1	Yb1	C36	C37	-59.2(7)
S1	O1	K5	S2	107.01(13)
S1	O1	K5	O2	-2.24(11)
S1	O1	K5	O5	105.53(14)
S1	O1	K5	O1S	36.3(2)
S1	O1	K5	O3S	-74.35(18)
S1	O1	K5	O2S	-148.18(18)
S1	O2	K5	S2	-57.81(15)
S1	O2	K5	O1	2.38(12)
S1	O2	K5	O5	-73.68(17)
S1	O2	K5	O1S	-150.95(16)
S1	O2	K5	O3S	133.34(16)
S1	O2	K5	O2S	32.43(19)
S1	N1	C8	C13	176.3(3)
S1	N1	C8	C9	-3.6(6)
S1	C1	C2	C3	-177.2(3)
N4	Yb1	N1	C8	-123.1(4)
N4	Yb1	N2	N3	-62.1(3)
N4	Yb1	N2	C14	123.1(4)
N4	Yb1	N5	N6	-175.4(3)
N4	Yb1	N5	C35	4.7(4)
N4	Yb1	C15	O3	-32.0(3)
N4	Yb1	C15	N3	143.1(3)
N4	Yb1	C15	C16	-44.1(7)
N4	Yb1	C36	O6	175.9(3)
N4	Yb1	C36	N6	1.9(3)
N4	Yb1	C36	C37	-164.6(7)
N4	S2	O4	Yb1	-1.20(18)
N4	S2	O5	K5	53.0(2)
N4	S2	C22	C23	-23.3(4)
N4	S2	C22	C28	154.8(3)
N4	S2	K5	S1	74.84(13)
N4	S2	K5	O1	50.18(14)
N4	S2	K5	O2	95.18(14)
N4	S2	K5	O5	-134.0(2)
N4	S2	K5	O1S	-172.67(15)
N4	S2	K5	O3S	-126.1(3)
N4	S2	K5	O2S	-7.36(15)
N4	C29	C30	C31	176.8(4)
N2	Yb1	S1	O1	-173.23(18)
N2	Yb1	S1	O2	98.06(19)
N2	Yb1	S1	N1	1.61(19)
N2	Yb1	S1	C1	-87.59(19)
N2	Yb1	S1	K5	136.59(9)
N2	Yb1	S2	O4	-36.33(18)
N2	Yb1	S2	O5	-125.5(2)
N2	Yb1	S2	N4	142.16(18)
N2	Yb1	S2	C22	49.76(19)
N2	Yb1	S2	K5	-130.45(9)
N2	Yb1	O1	S1	8.8(2)
N2	Yb1	O1	K5	108.61(15)
N2	Yb1	O6	C36	-155.4(3)
N2	Yb1	O3	C15	6.8(3)
N2	Yb1	O4	S2	145.65(16)
N2	Yb1	N1	S1	-178.35(19)
N2	Yb1	N1	C8	4.9(4)
N2	Yb1	N4	S2	-50.3(2)
N2	Yb1	N4	C29	129.3(4)

A	B	C	D	Angle/°
S1	C1	C7	C6	176.8(3)
S2	Yb1	S1	O1	77.45(16)
S2	Yb1	S1	O2	-11.26(17)
S2	Yb1	S1	N1	-107.71(17)
S2	Yb1	S1	C1	163.09(17)
S2	Yb1	S1	K5	27.26(3)
S2	Yb1	O1	S1	-101.91(15)
S2	Yb1	O1	K5	-2.05(10)
S2	Yb1	O6	C36	20.6(6)
S2	Yb1	O3	C15	117.8(3)
S2	Yb1	N1	S1	75.47(15)
S2	Yb1	N1	C8	-101.3(4)
S2	Yb1	N4	C29	179.6(5)
S2	Yb1	N2	N3	-86.6(3)
S2	Yb1	N2	C14	98.7(4)
S2	Yb1	N5	N6	-170.8(2)
S2	Yb1	N5	C35	9.3(4)
S2	Yb1	C15	O3	-63.0(3)
S2	Yb1	C15	N3	112.1(2)
S2	Yb1	C15	C16	-75.0(7)
S2	Yb1	C36	O6	-172.9(2)
S2	Yb1	C36	N6	13.1(3)
S2	Yb1	C36	C37	-153.4(6)
S2	O5	K5	S1	27.98(18)
S2	O5	K5	O1	3.85(18)
S2	O5	K5	O2	50.5(2)
S2	O5	K5	O1S	140.2(2)
S2	O5	K5	O3S	-176.30(17)
S2	O5	K5	O2S	-55.4(2)
S2	N4	C29	C34	-171.8(3)
S2	N4	C29	C30	10.3(6)
S2	C22	C23	C24	176.8(3)
S2	C22	C28	C27	-178.2(3)
O1	Yb1	S1	O2	-88.7(2)
O1	Yb1	S1	N1	174.8(2)
O1	Yb1	S1	C1	85.6(2)
O1	Yb1	S1	K5	-50.18(16)
O1	Yb1	S2	O4	95.65(17)
O1	Yb1	S2	O5	6.48(19)
O1	Yb1	S2	N4	-85.86(17)
O1	Yb1	S2	C22	-178.26(18)
O1	Yb1	S2	K5	1.53(7)

A	B	C	D	Angle/°
N2	Yb1	N5	N6	52.4(3)
N2	Yb1	N5	C35	-127.5(4)
N2	Yb1	C15	O3	-171.3(4)
N2	Yb1	C15	N3	3.8(2)
N2	Yb1	C15	C16	176.7(8)
N2	Yb1	C36	O6	24.9(3)
N2	Yb1	C36	N6	-149.1(2)
N2	Yb1	C36	C37	44.4(7)
N2	N3	C15	Yb1	-5.0(3)
N2	N3	C15	O3	-1.4(6)
N2	N3	C15	C16	178.1(3)
N3	N2	C14	C13	176.7(4)
N3	C15	C16	C21	-3.9(6)
N3	C15	C16	C17	174.2(4)
N5	Yb1	S1	O1	-26.32(18)
N5	Yb1	S1	O2	-115.03(19)
N5	Yb1	S1	N1	148.52(18)
N5	Yb1	S1	C1	59.32(18)
N5	Yb1	S1	K5	-76.50(9)
N5	Yb1	S2	O4	172.85(17)
N5	Yb1	S2	O5	83.7(2)
N5	Yb1	S2	N4	-8.66(18)
N5	Yb1	S2	C22	-101.07(18)
N5	Yb1	S2	K5	78.73(8)
N5	Yb1	O1	S1	153.95(18)
N5	Yb1	O1	K5	-106.20(13)
N5	Yb1	O6	C36	-5.8(3)
N5	Yb1	O3	C15	-139.0(3)
N5	Yb1	O4	S2	-9.2(2)
N5	Yb1	N1	S1	-40.6(2)
N5	Yb1	N1	C8	142.7(4)
N5	Yb1	N4	S2	171.15(18)
N5	Yb1	N4	C29	-9.2(4)
N5	Yb1	N2	N3	48.8(3)
N5	Yb1	N2	C14	-126.0(4)
N5	Yb1	C15	O3	42.0(3)
N5	Yb1	C15	N3	-142.9(3)
N5	Yb1	C15	C16	30.0(7)
N5	Yb1	C36	O6	172.6(3)
N5	Yb1	C36	N6	-1.4(2)
N5	Yb1	C36	C37	-168.0(8)
N5	N6	C36	Yb1	1.9(3)

A	B	C	D	Angle/°
O1	Yb1	O6	C36	72.7(3)
O1	Yb1	O3	C15	-173.4(3)
O1	Yb1	O4	S2	-82.97(15)
O1	Yb1	N1	S1	-2.84(13)
O1	Yb1	N1	C8	-179.6(4)
O1	Yb1	N4	S2	91.34(16)
O1	Yb1	N4	C29	-89.0(4)
O1	Yb1	N2	N3	172.9(2)
O1	Yb1	N2	C14	-1.9(5)
O1	Yb1	N5	N6	-88.1(3)
O1	Yb1	N5	C35	92.1(4)
O1	Yb1	C15	O3	142.5(17)
O1	Yb1	C15	N3	-42(2)
O1	Yb1	C15	C16	130.5(17)
O1	Yb1	C36	O6	-105.5(3)
O1	Yb1	C36	N6	80.5(2)
O1	Yb1	C36	C37	-86.0(7)
O1	S1	O2	K5	-4.1(2)
O1	S1	N1	Yb1	4.02(18)
O1	S1	N1	C8	-178.5(3)
O1	S1	C1	C2	65.1(4)
O1	S1	C1	C7	-112.7(4)
O1	S1	K5	S2	-64.94(13)
O1	S1	K5	O2	175.8(2)
O1	S1	K5	O5	-74.80(15)
O1	S1	K5	O1S	-152.52(15)
O1	S1	K5	O3S	121.76(16)
O1	S1	K5	O2S	27.64(16)
O6	Yb1	S1	O1	-92.17(17)
O6	Yb1	S1	O2	179.12(19)
O6	Yb1	S1	N1	82.68(18)
O6	Yb1	S1	C1	-6.53(18)
O6	Yb1	S1	K5	-142.35(8)
O6	Yb1	S2	O4	147.9(4)
O6	Yb1	S2	O5	58.7(5)
O6	Yb1	S2	N4	-33.6(5)
O6	Yb1	S2	C22	-126.0(4)
O6	Yb1	S2	K5	53.8(4)
O6	Yb1	O1	S1	86.41(16)
O6	Yb1	O1	K5	-173.74(12)
O6	Yb1	O3	C15	-72.1(3)
O6	Yb1	O4	S2	-163.5(2)

A	B	C	D	Angle/°
N5	N6	C36	O6	-2.7(6)
N5	N6	C36	C37	175.9(3)
C19	C20	C21	C16	0.8(7)
C19	C18	C17	C16	1.0(7)
C20	C19	C18	C17	-2.3(7)
C26	C25	C27	C28	-179.4(4)
C5	C4	C6	C7	-178.3(4)
C5	C4	C3	C2	178.0(4)
C18	C19	C20	C21	1.5(7)
C39	C40	C41	C42	-0.1(8)
C39	C38	C37	C42	-0.2(7)
C39	C38	C37	C36	179.3(4)
C41	C40	C39	C38	0.9(8)
C41	C42	C37	C38	1.0(7)
C41	C42	C37	C36	-178.4(4)
C34	C29	C30	C31	-1.1(6)
C8	C13	C12	C11	0.1(7)
C8	C13	C14	N2	5.9(8)
C8	C9	C10	C11	1.0(7)
C13	C8	C9	C10	-1.4(6)
C22	S2	O4	Yb1	-117.97(18)
C22	S2	O5	K5	176.82(17)
C22	S2	N4	Yb1	115.32(17)
C22	S2	N4	C29	-64.4(4)
C22	S2	K5	S1	-157.0(3)
C22	S2	K5	O1	178.4(3)
C22	S2	K5	O2	-136.6(3)
C22	S2	K5	O5	-5.8(3)
C22	S2	K5	O1S	-44.5(3)
C22	S2	K5	O3S	2.1(4)
C22	S2	K5	O2S	120.8(3)
C22	C28	C27	C25	1.5(7)
C1	S1	O1	Yb1	-118.88(17)
C1	S1	O1	K5	121.38(16)
C1	S1	O2	K5	-122.45(17)
C1	S1	N1	Yb1	117.43(18)
C1	S1	N1	C8	-65.1(4)
C1	S1	K5	S2	-157.47(19)
C1	S1	K5	O1	-92.5(2)
C1	S1	K5	O2	83.2(2)
C1	S1	K5	O5	-167.3(2)
C1	S1	K5	O1S	114.9(2)

A	B	C	D	Angle/°
O6	Yb1	N1	S1	-94.51(16)
O6	Yb1	N1	C8	88.8(4)
O6	Yb1	N4	S2	170.91(13)
O6	Yb1	N4	C29	-9.5(5)
O6	Yb1	N2	N3	92.7(3)
O6	Yb1	N2	C14	-82.1(4)
O6	Yb1	N5	N6	4.4(2)
O6	Yb1	N5	C35	-175.5(4)
O6	Yb1	C15	O3	108.8(3)
O6	Yb1	C15	N3	-76.0(3)
O6	Yb1	C15	C16	96.8(7)
O6	Yb1	C36	N6	-174.0(4)
O6	Yb1	C36	C37	19.5(6)
O6	C36	C37	C38	-3.4(6)
O6	C36	C37	C42	176.0(4)
O3	Yb1	S1	O1	163.8(5)
O3	Yb1	S1	O2	75.1(5)
O3	Yb1	S1	N1	-21.3(5)
O3	Yb1	S1	C1	-110.5(5)
O3	Yb1	S1	K5	113.7(4)
O3	Yb1	S2	O4	-101.53(17)
O3	Yb1	S2	O5	169.30(19)
O3	Yb1	S2	N4	76.97(18)
O3	Yb1	S2	C22	-15.44(18)
O3	Yb1	S2	K5	164.35(8)
O3	Yb1	O1	S1	-171.0(3)
O3	Yb1	O1	K5	-71.1(4)
O3	Yb1	O6	C36	-89.3(3)
O3	Yb1	O4	S2	78.73(16)
O3	Yb1	N1	S1	174.23(14)
O3	Yb1	N1	C8	-2.5(5)
O3	Yb1	N4	S2	-100.08(16)
O3	Yb1	N4	C29	79.5(4)
O3	Yb1	N2	N3	-7.2(2)
O3	Yb1	N2	C14	178.0(4)
O3	Yb1	N5	N6	102.4(3)
O3	Yb1	N5	C35	-77.5(4)
O3	Yb1	C15	N3	175.1(5)
O3	Yb1	C15	C16	-12.0(6)
O3	Yb1	C36	O6	92.8(3)
O3	Yb1	C36	N6	-81.2(2)
O3	Yb1	C36	C37	112.3(7)

A	B	C	D	Angle/°
C1	S1	K5	O3S	29.2(2)
C1	S1	K5	O2S	-64.9(2)
C1	C2	C3	C4	0.9(7)
C1	C7	C6	C4	-0.2(7)
C2	C1	C7	C6	-0.9(6)
C15	Yb1	S1	O1	-174.6(2)
C15	Yb1	S1	O2	96.7(2)
C15	Yb1	S1	N1	0.2(2)
C15	Yb1	S1	C1	-89.0(2)
C15	Yb1	S1	K5	135.20(16)
C15	Yb1	S2	O4	-82.88(17)
C15	Yb1	S2	O5	-172.1(2)
C15	Yb1	S2	N4	95.61(18)
C15	Yb1	S2	C22	3.20(18)
C15	Yb1	S2	K5	-177.00(8)
C15	Yb1	O1	S1	52.7(19)
C15	Yb1	O1	K5	152.6(18)
C15	Yb1	O6	C36	-109.2(3)
C15	Yb1	O4	S2	99.77(16)
C15	Yb1	N1	S1	-179.87(14)
C15	Yb1	N1	C8	3.4(4)
C15	Yb1	N4	S2	-88.99(16)
C15	Yb1	N4	C29	90.6(4)
C15	Yb1	N2	N3	-3.9(2)
C15	Yb1	N2	C14	-178.6(5)
C15	Yb1	N5	N6	88.5(3)
C15	Yb1	N5	C35	-91.4(4)
C15	Yb1	C36	O6	71.7(3)
C15	Yb1	C36	N6	-102.3(2)
C15	Yb1	C36	C37	91.2(7)
C15	C16	C21	C20	176.0(4)
C15	C16	C17	C18	-176.9(4)
C35	C34	C29	N4	0.3(6)
C35	C34	C29	C30	178.2(4)
C35	C34	C33	C32	-177.2(4)
C29	C34	C35	N5	-3.9(7)
C29	C34	C33	C32	2.1(7)
C29	C30	C31	C32	2.1(7)
C36	Yb1	S1	O1	-71.36(18)
C36	Yb1	S1	O2	-160.07(19)
C36	Yb1	S1	N1	103.48(18)
C36	Yb1	S1	C1	14.28(18)

A	B	C	D	Angle/°
O3	C15	C16	C21	175.6(4)
O3	C15	C16	C17	-6.3(6)
O2	S1	O1	Yb1	123.34(16)
O2	S1	O1	K5	3.61(18)
O2	S1	N1	Yb1	-120.47(17)
O2	S1	N1	C8	57.0(4)
O2	S1	C1	C2	-172.7(3)
O2	S1	C1	C7	9.5(4)
O2	S1	K5	S2	119.28(16)
O2	S1	K5	O1	-175.8(2)
O2	S1	K5	O5	109.42(17)
O2	S1	K5	O1S	31.70(18)
O2	S1	K5	O3S	-54.02(19)
O2	S1	K5	O2S	-148.14(19)
O4	Yb1	S1	O1	103.79(17)
O4	Yb1	S1	O2	15.08(18)
O4	Yb1	S1	N1	-81.36(18)
O4	Yb1	S1	C1	-170.57(18)
O4	Yb1	S1	K5	53.61(7)
O4	Yb1	S2	O5	-89.2(2)
O4	Yb1	S2	N4	178.5(2)
O4	Yb1	S2	C22	86.1(2)
O4	Yb1	S2	K5	-94.12(16)
O4	Yb1	O1	S1	-73.85(16)
O4	Yb1	O1	K5	26.01(12)
O4	Yb1	O6	C36	153.4(3)
O4	Yb1	O3	C15	90.2(3)
O4	Yb1	N1	S1	93.06(16)
O4	Yb1	N1	C8	-83.7(4)
O4	Yb1	N4	S2	-0.83(13)
O4	Yb1	N4	C29	178.8(4)
O4	Yb1	N2	N3	-102.9(3)
O4	Yb1	N2	C14	82.3(4)
O4	Yb1	N5	N6	-166.4(2)
O4	Yb1	N5	C35	13.8(4)
O4	Yb1	C15	O3	-91.0(3)
O4	Yb1	C15	N3	84.1(3)
O4	Yb1	C15	C16	-103.0(7)
O4	Yb1	C36	O6	-109.5(6)
O4	Yb1	C36	N6	76.5(7)
O4	Yb1	C36	C37	-90.1(9)
O4	S2	O5	K5	-64.4(2)

A	B	C	D	Angle/°
C36	Yb1	S1	K5	-121.54(8)
C36	Yb1	S2	O4	162.1(2)
C36	Yb1	S2	O5	72.9(2)
C36	Yb1	S2	N4	-19.4(2)
C36	Yb1	S2	C22	-111.8(2)
C36	Yb1	S2	K5	67.95(15)
C36	Yb1	O1	S1	106.82(17)
C36	Yb1	O1	K5	-153.33(13)
C36	Yb1	O3	C15	-93.4(3)
C36	Yb1	O4	S2	-78.9(7)
C36	Yb1	N1	S1	-78.60(16)
C36	Yb1	N1	C8	104.7(4)
C36	Yb1	N4	S2	168.60(13)
C36	Yb1	N4	C29	-11.8(4)
C36	Yb1	N2	N3	83.8(3)
C36	Yb1	N2	C14	-91.0(4)
C36	Yb1	N5	N6	1.5(2)
C36	Yb1	N5	C35	-178.4(4)
C36	Yb1	C15	O3	88.8(3)
C36	Yb1	C15	N3	-96.1(3)
C36	Yb1	C15	C16	76.7(7)
C36	N6	N5	Yb1	-2.7(4)
C36	N6	N5	C35	177.2(3)
C37	C38	C39	C40	-0.8(8)
C37	C42	C41	C40	-0.9(8)
C12	C11	C10	C9	-0.1(7)
C12	C13	C14	N2	-173.3(4)
C14	N2	N3	C15	-177.0(4)
C14	C13	C12	C11	179.4(4)
C24	C25	C27	C28	-1.5(7)
C21	C16	C17	C18	1.3(7)
C25	C24	C23	C22	1.2(6)
C31	C32	C33	C34	-1.2(8)
C7	C1	C2	C3	0.5(6)
C23	C22	C28	C27	-0.1(6)
C23	C24	C25	C26	178.0(4)
C23	C24	C25	C27	0.2(7)
C28	C22	C23	C24	-1.3(6)
C33	C32	C31	C30	-0.9(8)
C33	C34	C35	N5	175.3(4)
C33	C34	C29	N4	-178.9(4)
C33	C34	C29	C30	-0.9(6)

A	B	C	D	Angle/°
O4	S2	N4	Yb1	1.17(18)
O4	S2	N4	C29	-178.5(3)
O4	S2	C22	C23	86.6(4)
O4	S2	C22	C28	-95.3(4)
O4	S2	K5	S1	-26.13(12)
O4	S2	K5	O1	-50.79(14)
O4	S2	K5	O2	-5.79(14)
O4	S2	K5	O5	125.0(2)
O4	S2	K5	O1S	86.36(14)
O4	S2	K5	O3S	132.9(3)
O4	S2	K5	O2S	-108.32(14)
O5	S2	O4	Yb1	124.39(17)
O5	S2	N4	Yb1	-123.77(17)
O5	S2	N4	C29	56.5(4)
O5	S2	C22	C23	-150.0(3)
O5	S2	C22	C28	28.1(4)
O5	S2	K5	S1	-151.15(19)
O5	S2	K5	O1	-175.8(2)
O5	S2	K5	O2	-130.8(2)
O5	S2	K5	O1S	-38.7(2)
O5	S2	K5	O3S	7.9(4)
O5	S2	K5	O2S	126.7(2)
N6	N5	C35	C34	179.5(4)
N6	C36	C37	C38	177.9(4)
N6	C36	C37	C42	-2.7(6)
N1	Yb1	S1	O1	-174.8(2)
N1	Yb1	S1	O2	96.4(2)
N1	Yb1	S1	C1	-89.2(2)
N1	Yb1	S1	K5	134.97(17)
N1	Yb1	S2	O4	38.77(17)
N1	Yb1	S2	O5	-50.4(2)
N1	Yb1	S2	N4	-142.74(18)
N1	Yb1	S2	C22	124.86(18)
N1	Yb1	S2	K5	-55.35(8)
N1	Yb1	O1	S1	3.06(14)
N1	Yb1	O1	K5	102.92(15)
N1	Yb1	O6	C36	131.2(3)
N1	Yb1	O3	C15	14.5(4)
N1	Yb1	O4	S2	-141.01(17)
N1	Yb1	N4	S2	45.7(2)
N1	Yb1	N4	C29	-134.7(4)
C17	C16	C21	C20	-2.2(7)
C9	C8	C13	C12	0.8(6)
C9	C8	C13	C14	-178.4(4)
C10	C11	C12	C13	-0.4(7)
C6	C4	C3	C2	-1.9(7)
C3	C4	C6	C7	1.5(7)
C1S	O1S	K5	S1	44.3(3)
C1S	O1S	K5	S2	-31.7(3)
C1S	O1S	K5	O1	28.6(4)
C1S	O1S	K5	O2	56.4(3)
C1S	O1S	K5	O5	-44.8(3)
C1S	O1S	K5	O3S	160.6(3)
C1S	O1S	K5	O2S	-136.3(5)
C5S	O3S	K5	S1	-46.2(4)
C5S	O3S	K5	S2	157.3(3)
C5S	O3S	K5	O1	-18.3(5)
C5S	O3S	K5	O2	-65.6(4)
C5S	O3S	K5	O5	161.9(4)
C5S	O3S	K5	O1S	-154.2(4)
C5S	O3S	K5	O2S	39.4(4)
C3S	O2S	K5	S1	178.5(4)
C3S	O2S	K5	S2	-105.9(4)
C3S	O2S	K5	O1	-168.5(5)
C3S	O2S	K5	O2	166.0(4)
C3S	O2S	K5	O5	-89.0(4)
C3S	O2S	K5	O1S	-1.0(8)
C3S	O2S	K5	O3S	59.6(4)
K5	S1	O1	Yb1	119.74(14)
K5	S1	N1	Yb1	-59.61(18)
K5	S1	N1	C8	117.9(3)
K5	S1	C1	C2	133.0(3)
K5	S1	C1	C7	-44.7(4)
K5	S2	O4	Yb1	86.76(10)
K5	S2	N4	Yb1	-91.05(10)
K5	S2	N4	C29	89.2(3)
K5	S2	C22	C23	-145.9(3)
K5	S2	C22	C28	32.2(5)
K5	O1S	C1S	C2S	-56.2(5)
K5	O3S	C5S	C6S	3.2(7)
K5	O2S	C3S	C4S	24.8(6)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for K(EtOH)$_3$[Yb(L)$_2$] (CCDC 2016985).

Atom	*x*	*y*	*z*	U(eq)
H19	14257	-4939	414	29
H40	8279	-4288	4830	36
H20	15930	-4425	1012	27
H26A	13411	1734	-674	52
H26B	12103	2875	-917	52
H26C	11955	1471	-932	52
H5A	7782	1015	5820	54
H5B	6965	92	5549	54
H5C	6072	1518	5631	54
H32	3958	1163	459	34
H38	10519	-2263	3894	27
H11	15394	1700	4111	29
H18	11739	-3782	404	29
H39	10388	-3549	4662	37
H42	6450	-2529	3425	27
H41	6309	-3773	4206	34
H2	9214	109	3883	24
H35	5865	-605	2042	18
H12	15452	290	3448	23
H14	14433	-672	2844	18
H24	11459	363	-63	27
H21	15083	-2849	1612	21
H30	7334	2777	673	23
H31	5389	2510	149	30
H7	7567	3784	4186	24
H23	10368	533	806	23
H28	10304	4216	748	22
H33	4522	41	1288	27
H27	11477	4002	-102	26
H17	10875	-2232	1023	23
H9	10919	3089	3892	23
H10	13114	3097	4334	27
H6	6836	3209	5056	28
H3	8496	-445	4759	28
H1S	7470(30)	7250(20)	2333(14)	37
H1SA	9427	7304	1950	34
H1SB	9502	6023	1666	34
H2SA	11340	5722	2349	54
H2SB	10198	4885	2493	54

Atom	*x*	*y*	*z*	U(eq)
H2SC	10048	6156	2795	54
H3S	4410(40)	7247(16)	2619(14)	41
H6SA	3442	4810	3252	67
H6SB	2965	5475	3815	67
H6SC	4696	5051	3641	67
H5SA	2502	6961	3070	37
H5SB	3687	7236	3482	37
H2S	5180(40)	2430(40)	2727(15)	56
H3SA	2737	3214	2506	30
H3SB	3592	2037	2163	30
H4SA	4101	3386	1460	44
H4SB	3359	4578	1806	44
H4SC	2333	3764	1576	44

Refinement model description

Number of restraints - 9, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups, All O(H) groups
2. Restrained distances
 O3S-H3S
 0.85 with sigma of 0.01
 O1S-H1S
 0.85 with sigma of 0.01
 O2S-H2S
 0.85 with sigma of 0.01
 C5S-H3S
 1.873851 with sigma of 0.02
 K5-H3S
 3.175585 with sigma of 0.02
 C1S-H1S
 1.88629 with sigma of 0.02
 K5-H1S
 3.286641 with sigma of 0.02
 C3S-H2S
 1.895492 with sigma of 0.02
 K5-H2S
 3.125781 with sigma of 0.02
3.a Secondary CH2 refined with riding coordinates:
 C1S(H1SA,H1SB), C5S(H5SA,H5SB), C3S(H3SA,H3SB)
3.b Aromatic/amide H refined with riding coordinates:
 C19(H19), C40(H40), C20(H20), C32(H32), C38(H38), C11(H11), C18(H18),
 C39(H39), C42(H42), C41(H41), C2(H2), C35(H35), C12(H12), C14(H14), C24(H24),
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C21(H21), C30(H30), C31(H31), C7(H7), C23(H23), C28(H28), C33(H33), C27(H27),

C17(H17), C9(H9), C10(H10), C6(H6), C3(H3)

3.c Idealised Me refined as rotating group:

C26(H26A,H26B,H26C), C5(H5A,H5B,H5C), C2S(H2SA,H2SB,H2SC), C6S(H6SA,H6SB,

H6SC), C4S(H4SA,H4SB,H4SC)

This report has been created with Olex2, compiled on 2020.02.04 svn.rd84adfe8 for OlexSys.

Nuclear magnetic resonance data

Experimental details

^{1}H and ^{13}C NMR spectra, as well as 2D spectra (1H-1H COSY, 1H-13C HSQC, 1H-13C HMBC, 1H-1H NOESY, DOSY), were recorded from the DMSO-*d*$_6$ solutions with a Bruker Avance 600 NMR spectrometer (^{1}H NMR frequency: 600.15 MHz). The measurements were done using the residual signals of the deuterated solvent (^{1}H 2.50 ppm, ^{13}C 39.52 ppm). The following acquisition parameters were used: ^{1}H (acquisition time 2.18 s. relaxation delay 3-4 s, number of scans 8-16), ^{13}C (acquisition time 0.5 s. relaxation delay 1.5 s), NOESY (mixing time 0.3-0.6 s), DOSY (acquisition time 1 s. relaxation delay 3 s, number of scans 1, diffusion delay 0.2 s, diffusion gradient length 1.5 - 2.5 ms). Acquisition time and relaxation delay were reduced to 0.2 s for paramagnetic complexes due to fast nuclear relaxation.

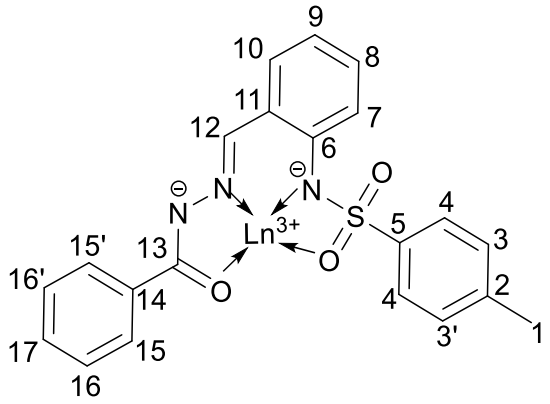

Figure 15 Atom numbering in (L)$^{2-}$ anion

Table 8 Assignments of ^{1}H and ^{13}C NMR signals of H_2L, $[Lu(L)]^+$, $[Lu(L)_2]^-$-A, $[Lu(L)_2]^-$-B, $[Lu(L)_2]^-$-C, $[Yb(L)]^+$ in DMSO-d_6. For $[Yb(L)]^+$ presented experimental values (exp.) as well as chemical shift calculated by formula (4) (see the main text).

	H_2L		$[Lu(L)]^+$		$[Lu(L)_2]^-$-A		$[Lu(L)_2]^-$-B		$[Lu(L)_2]^-$-C		$[Yb(L)]^+$	
№	^{1}H (ppm)	^{13}C (ppm)	^{1}H (ppm)	^{13}C (ppm)	^{1}H (ppm)	^{13}C (ppm)	^{1}H (ppm)	^{13}C (ppm)	^{1}H (ppm)	^{13}C (ppm)	^{1}H, exp. (ppm)	^{1}H, calc. (ppm)
1	2.31	20.93	2.37	20.89	2.15	20.88	2.15	20.88	2.37	20.93	4.18	3.56
2		143.57		143.09		142.04		142.14		142.36		
3	7.32	129.64	7.39	129.60	6.88	129.11	6.88	129.11	6.86	129.34	11.68	11.49
4	7.69	126.97	8.01	127.83	8.04	128.09	8.03	128.09	8.09j	128.23	23.68	23.90
5		136.49		137.77		138.42		138.89		138.05		
6		124.35		123.17		123.47		123.58		123.77		
7	7.32	121.21	6.92	117.86	6.98	117.96	6.98	117.96	6.95	117.96	-14.05	-14.65
8	7.32	130.47	7.14	131.90	7.10	131.06	7.10	131.06	7.04	131.06	-0.62	-0.24
9	7.18	124.67	6.86	120.03	6.82	119.11	6.82	119.11	6.79	119.11	1.32	1.38
10	7.60	132.04	7.53	135.92	7.47	135.50	7.47	135.50	7.47	135.35	-2.21	-2.42
11		136.26		142.00		142.87		142.86		142.57		
12	8.57	147.98	8.58	157.28	8.52	156.25	8.52	156.21	8.54	155.46	-15.55	-15.62
13		163.01		169.48		168.70		168.70		169.45		
14		132.80		135.29		135.81		135.81		136.34		
15	7.99	127.93	8.11	127.78	8.03	12,71	8.03	127.71	7.93	127.52	-18.36	-17.90
16	7.58	128.55	7.43	128.07	7.39	127.81	7.39	127.81	7.33	127.93	-1.13	-1.68
17	7.55	130.60	7.47	130.16	7.40	129.59	7.40	129.59	7.40	129.45	1.26	0.72

Spectra of H_2L

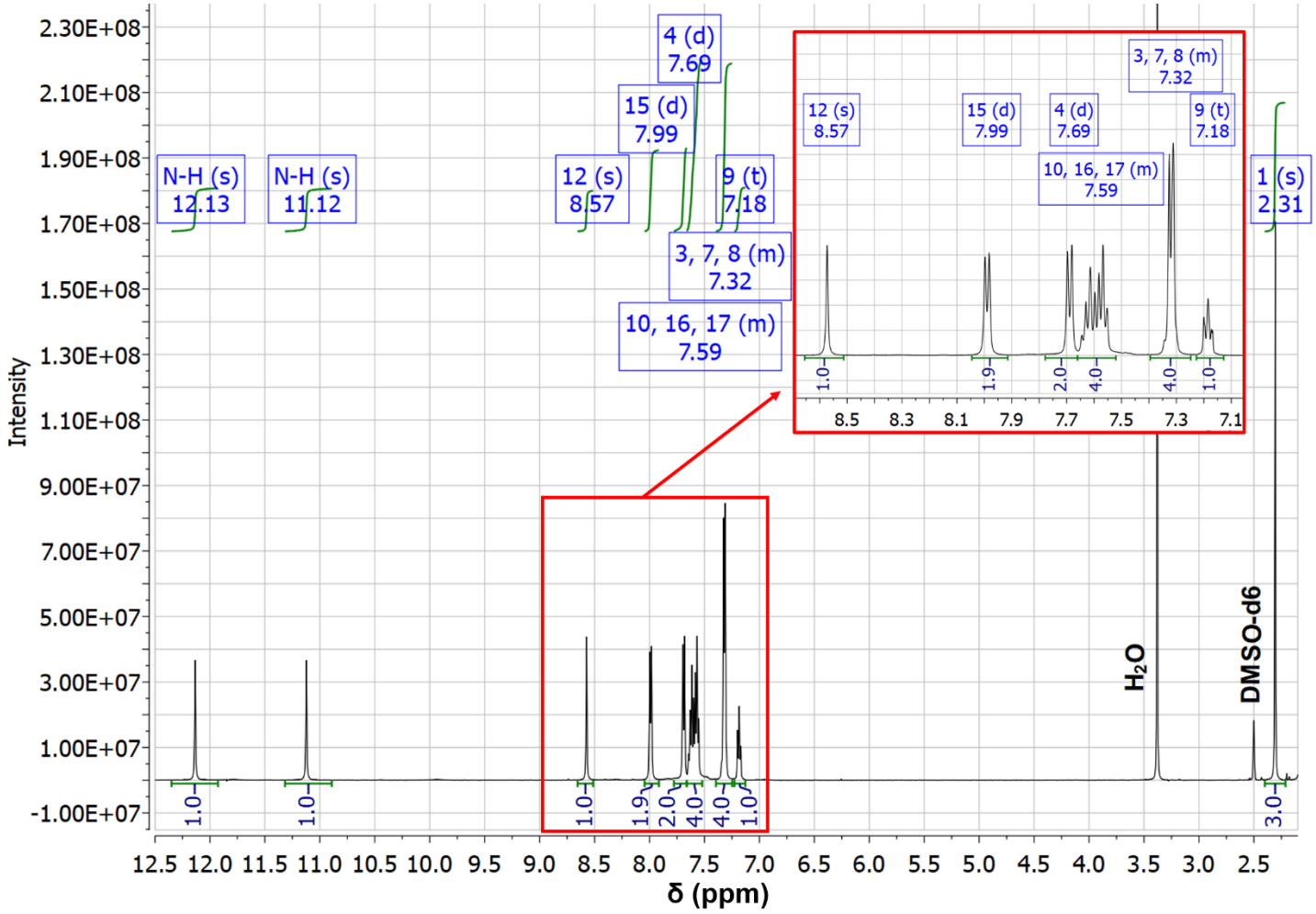

Figure 16 ^{1}H NMR spectrum of 2-(tosylamino)-benzylidene-N-(benzoy)-lhydrazone (H_2L) in DMSO-d_6

^{1}H NMR in DMSO-d_6 (δ, ppm): 12.13 (s, 1H), 11.12 (s, 1H), 8.57 (s, 1H), 7.99 (d, J = 7.4 Hz, 2H), 7.69 (d, J = 7.9 Hz, 2H), 7.66 – 7.54 (m, 4H), 7.37 – 7.27 (m, 4H), 7.18 (t, J = 17.6 Hz, 1H), 2.31 (s, 3H).

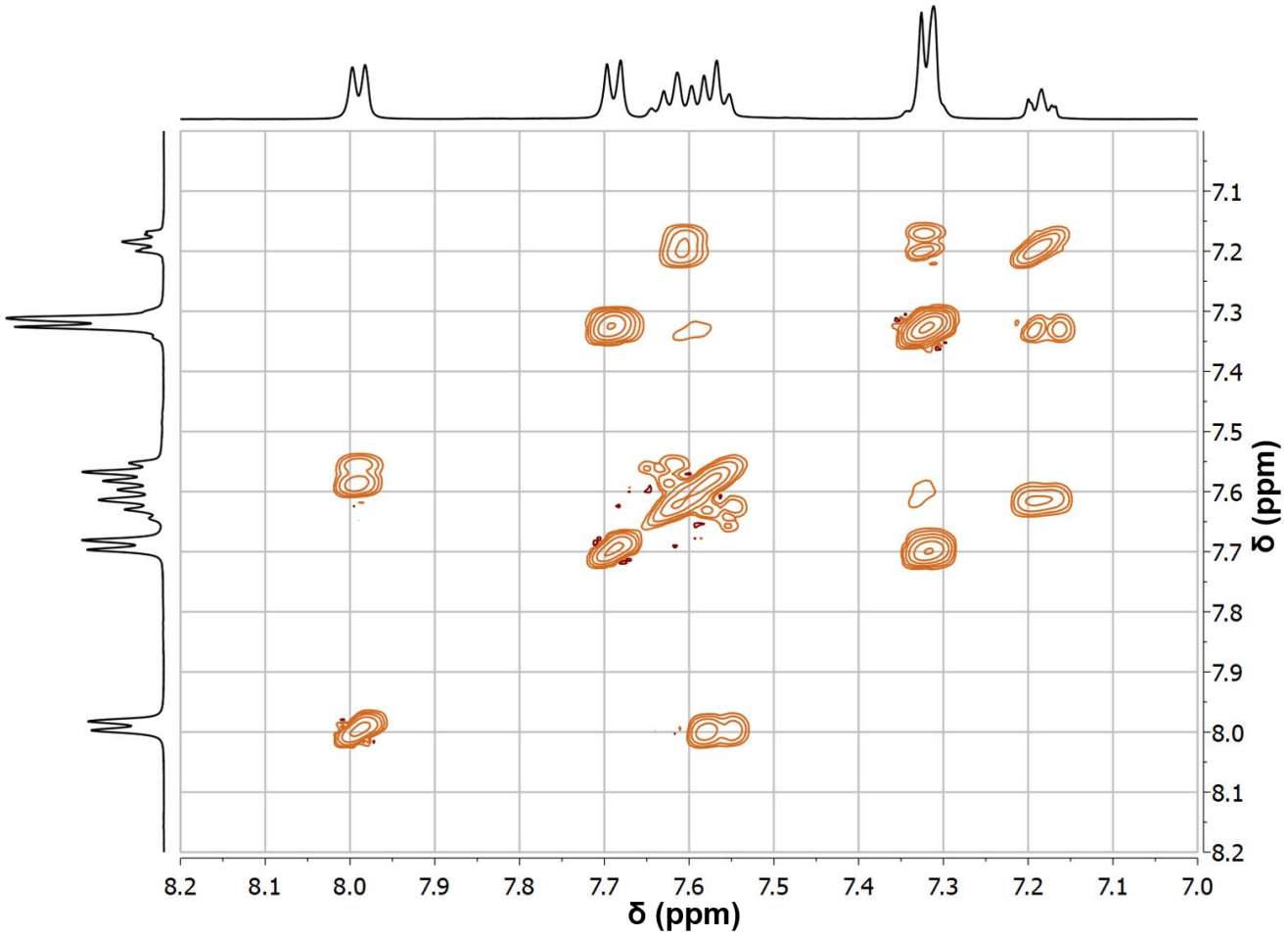

Figure 17 Fragment of ^{1}H COSY spectrum of H_2L in DMSO-d_6

Spectra of $Lu(HL)_2Cl$

In DMSO, $Lu(HL)_2Cl$ dissociate according to the reaction (see reaction (1) in the main text):

$$Lu(HL)_2Cl = H_2L + [Lu(L)]^+ + Cl,$$

thus, in its NMR spectra, signals of both H_2L and $[Lu(L)]^+$ are present.

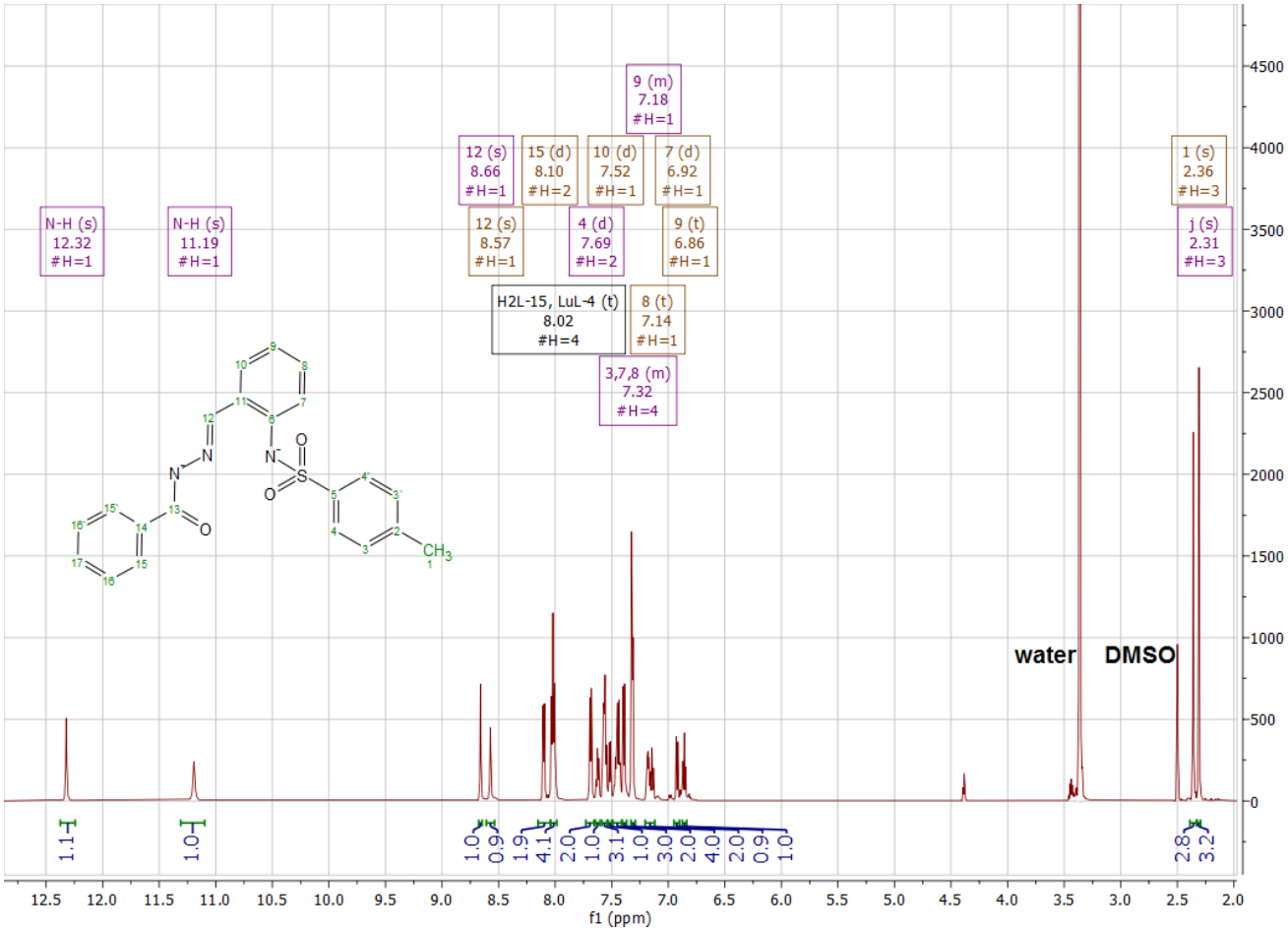

Figure 18 ^{1}H NMR spectrum of $Lu(HL)_2Cl$ in DMSO-d_6. Violet signals correspond to H_2L, brown signals – to $[Lu(L)]^+$, black signals are a mixture of both H_2L and $[Lu(L)]^+$.

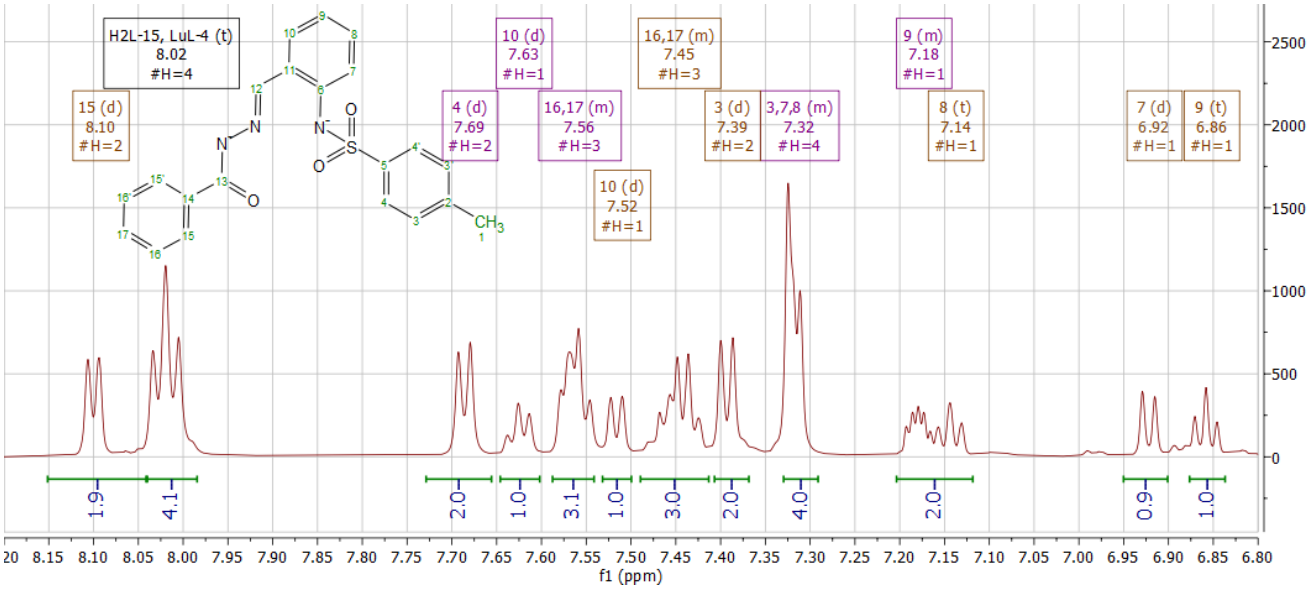

Figure 19 ^{1}H NMR spectrum of $Lu(HL)_2Cl$ in DMSO-d_6 in the range 6.80 – 8.20 ppm. Violet signals correspond to H_2L, brown signals – to $[Lu(L)]^+$, black signals are a mixture of both H_2L and $[Lu(L)]^+$.

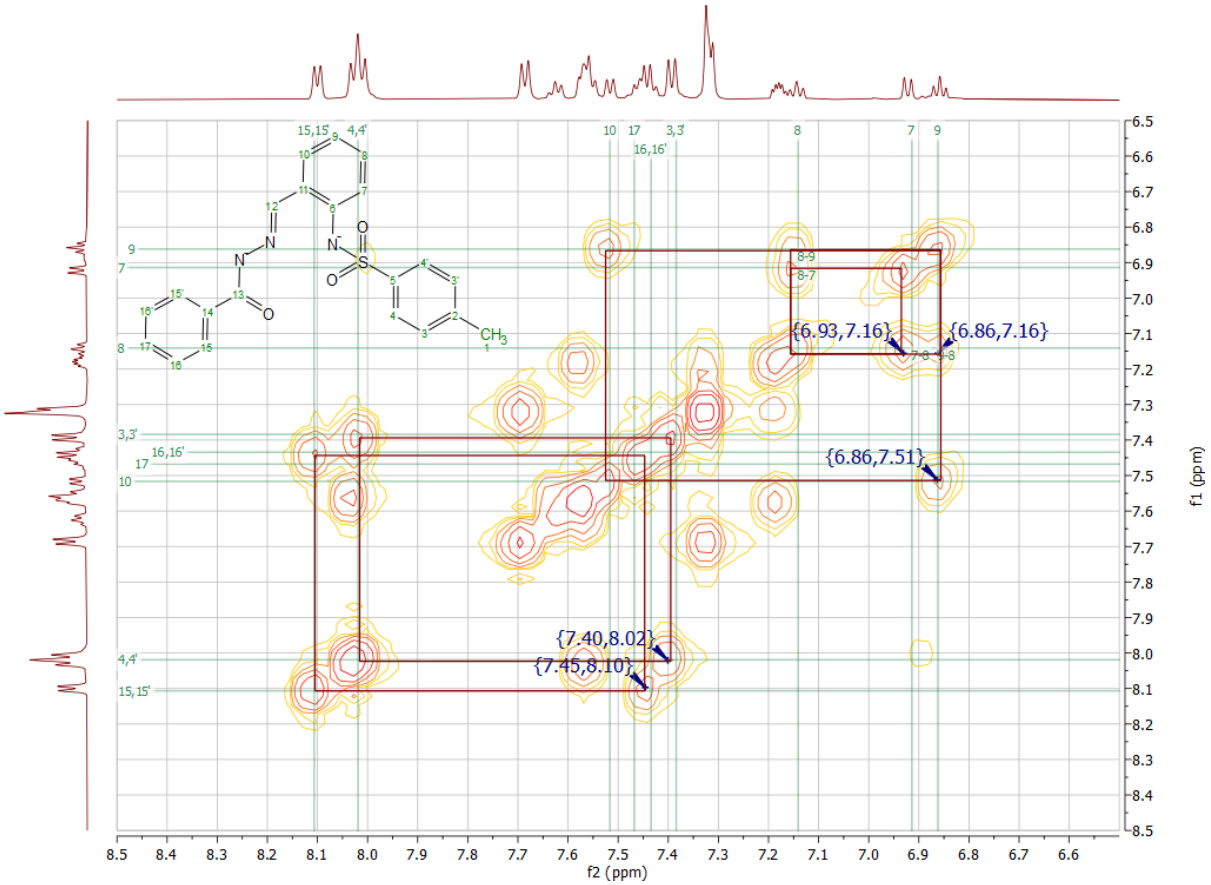

Figure 20 Fragment of a COSY spectrum of $Lu(HL)_2Cl$ in DMSO-d_6. For clearance, only signals of $[Lu(L)]^+$ are highlighted.

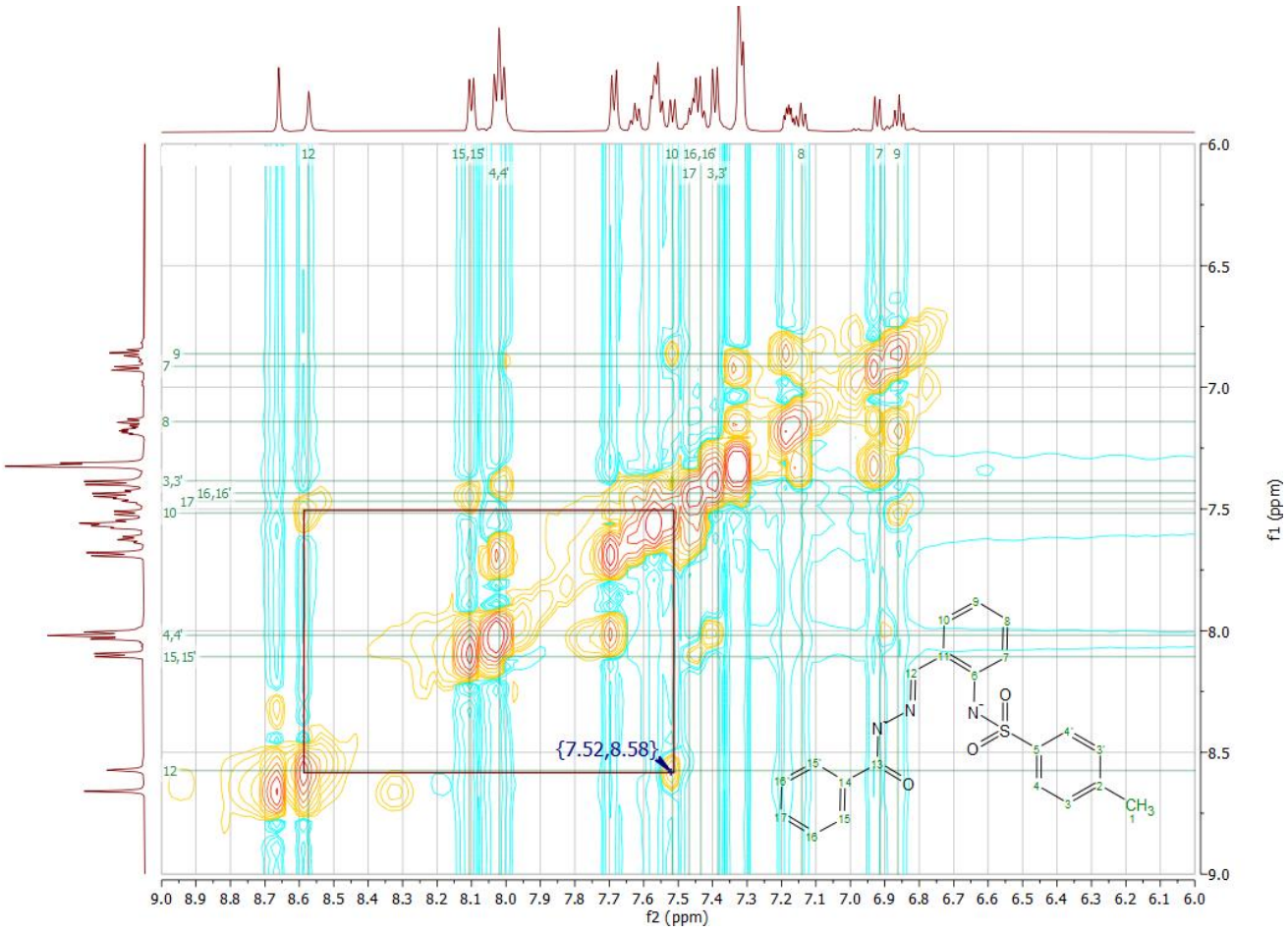

Figure 21 Fragment of the NOESY spectrum of $Lu(HL)_2Cl$ in DMSO-d_6. For clearance, only signals of $[Lu(L)]^+$ which bring information additional to ^1H and COSY spectra are highlighted.

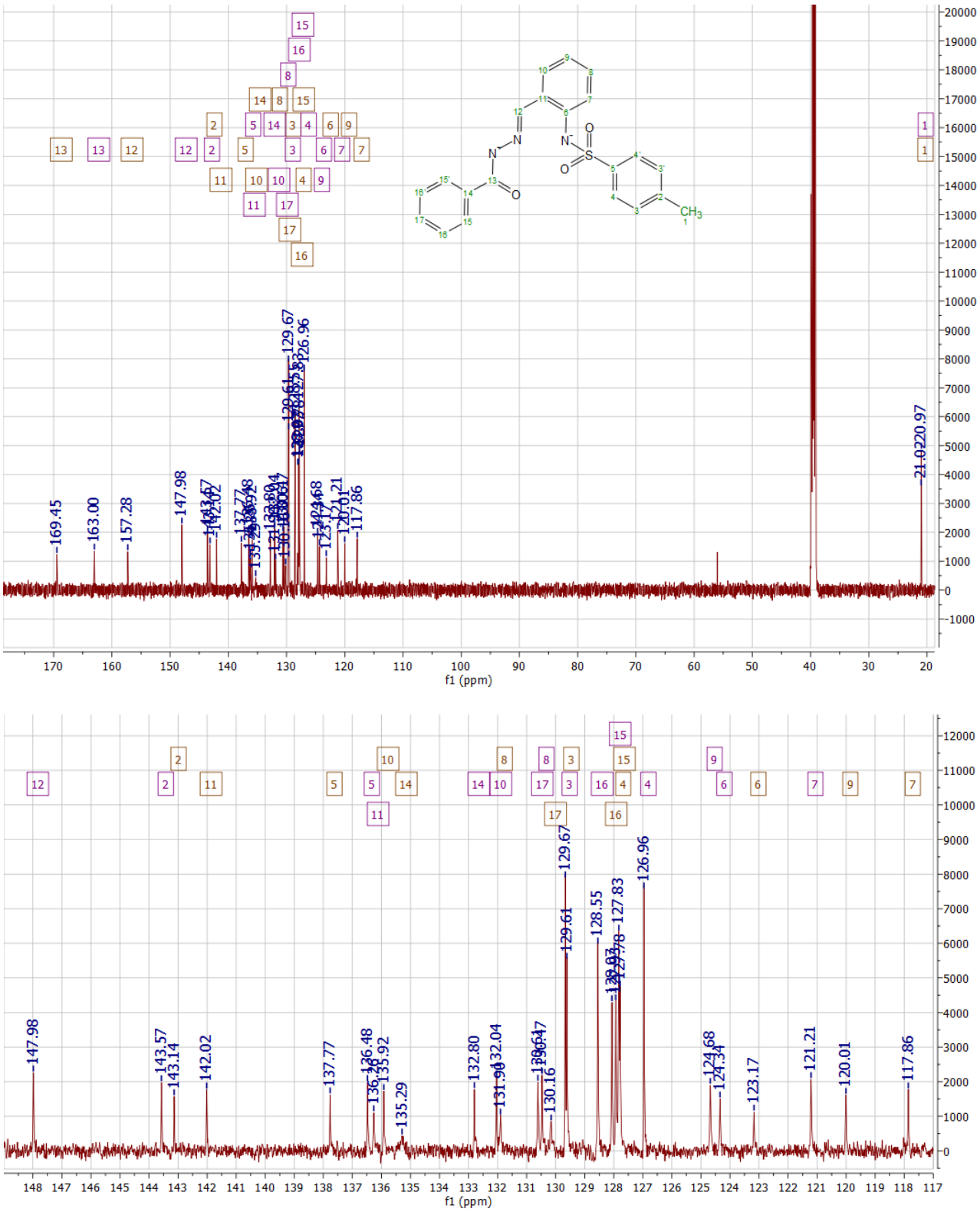

Figure 22 ^{13}C NMR spectrum of $Lu(HL)_2Cl$ in DMSO-d_6. Violet signals correspond to H_2L, brown signals – to $[Lu(L)]^+$.

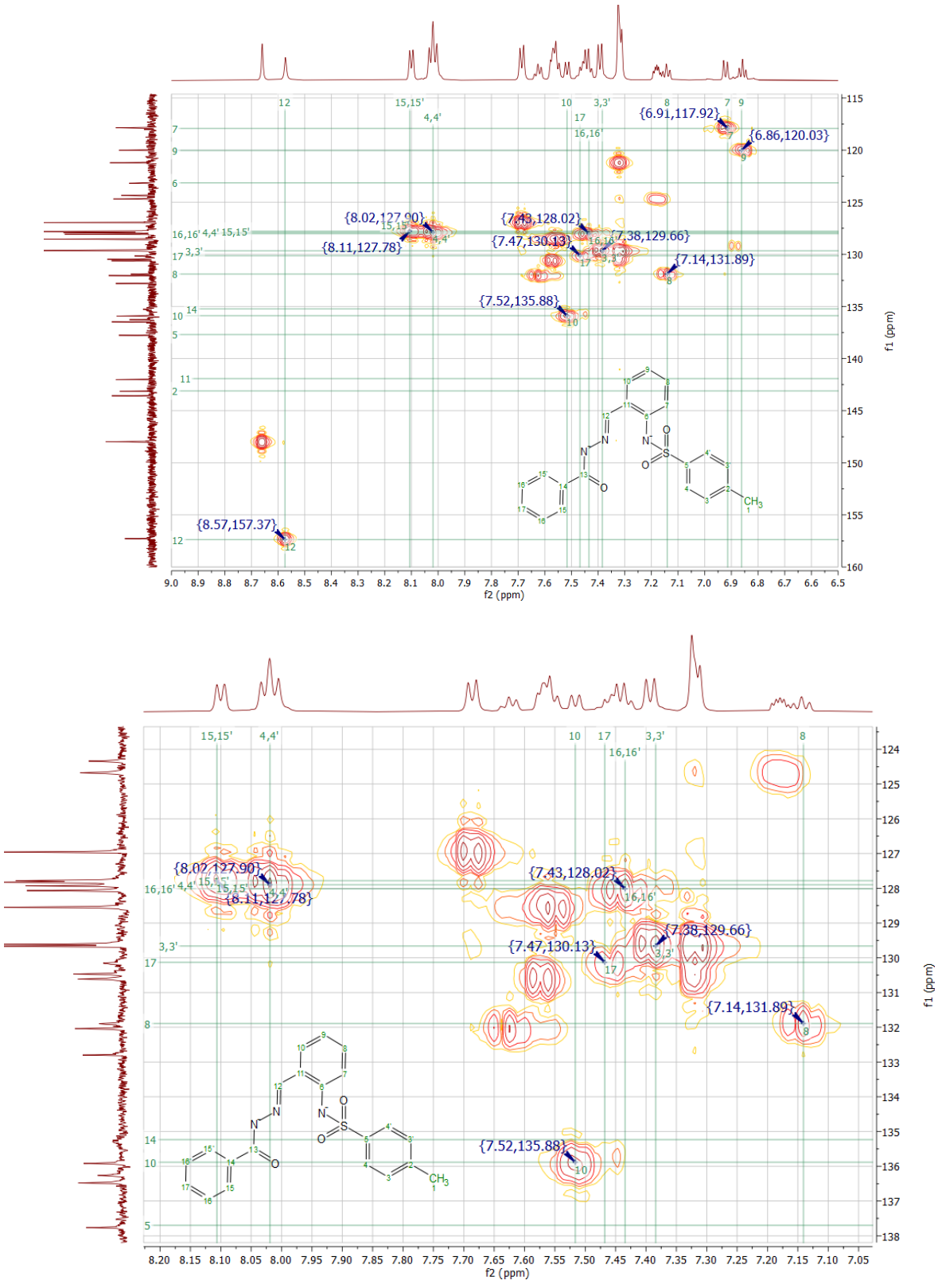

Figure 23 HMQC spectrum of $Lu(HL)_2Cl$ in DMSO-d_6. For clearance, only signals of $[Lu(L)]^+$ are highlighted.

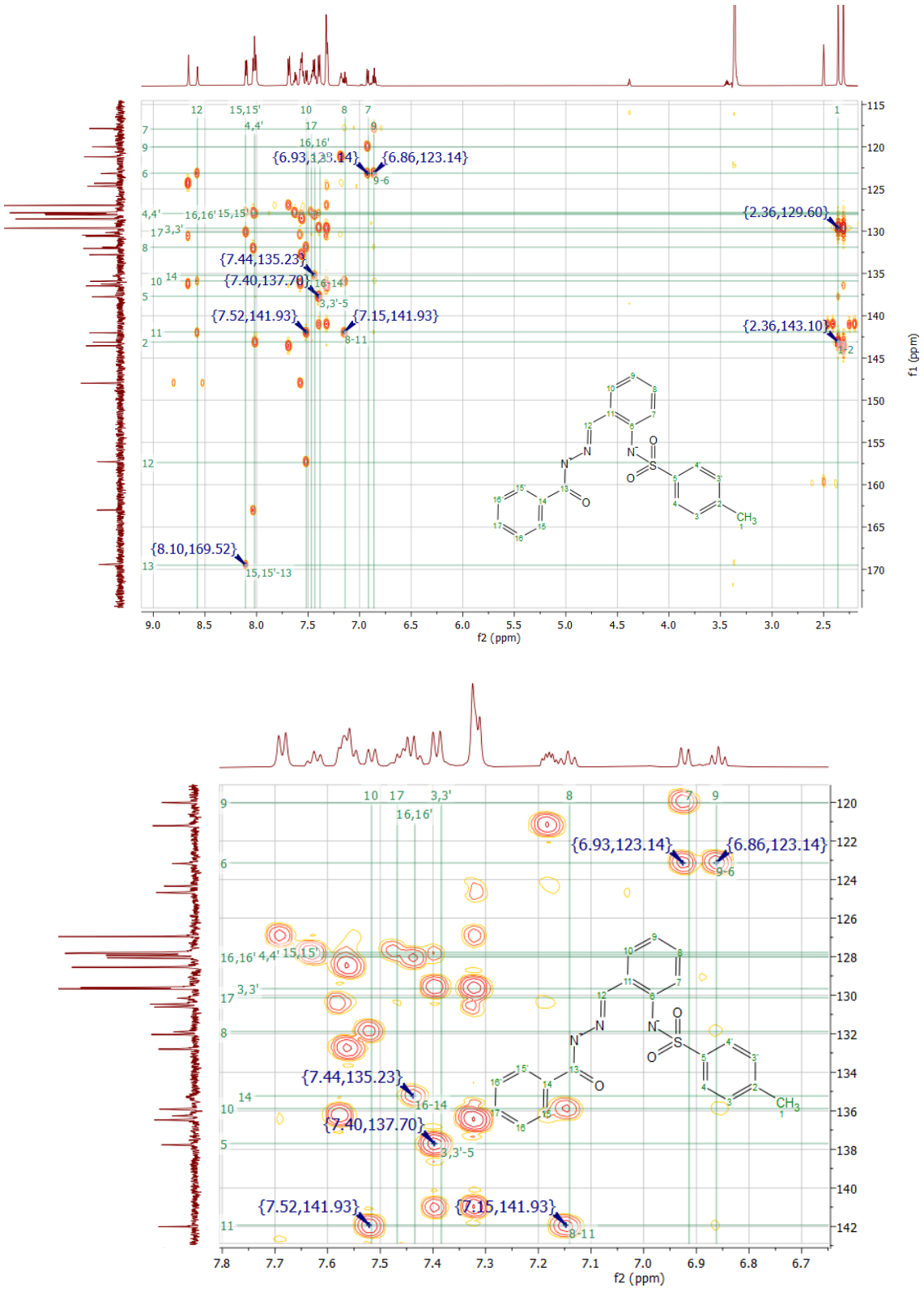

Figure 24 HMBC spectrum of $Lu(HL)_2Cl$ in DMSO-d_6. For clearance, only signals of $[Lu(L)]^+$ which brings additional to HMQC spectrum information, are highlighted.

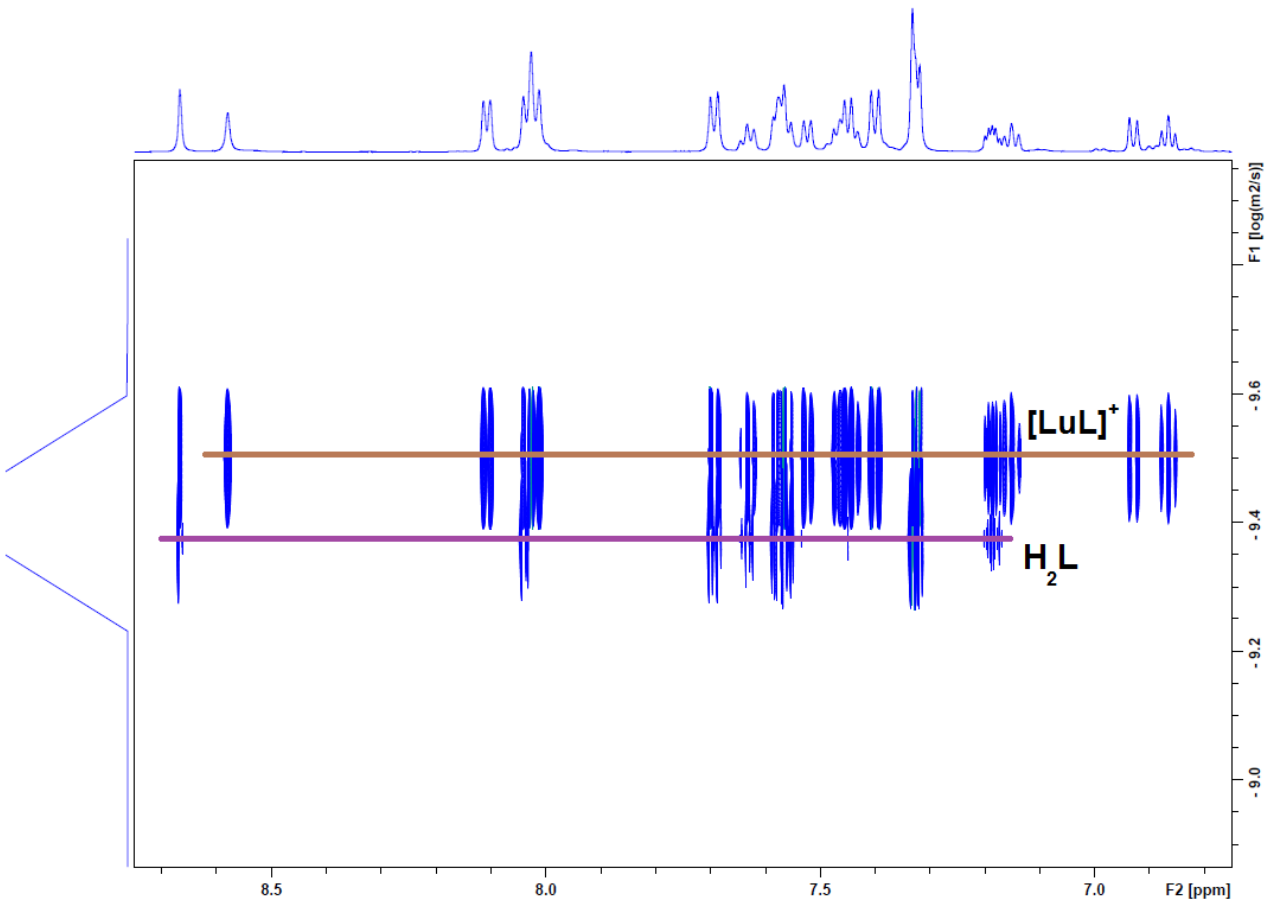

Figure 25 DOSY spectrum of $Lu(HL)_2Cl$ in DMSO-d_6. Violet signals correspond to H_2L, brown signals – to $[Lu(L)]^+$.

Spectra of $K(H_2O)_3[Lu(L)_2]$

Spectra of $K(H_2O)_3[Lu(L)_2]$ correspond to the spectra of the anionic complex $[Lu(L)_2]^-$. Signals of H_2L or $[Lu(L)]^+$ are not observed in spectra of $K(H_2O)_3[Lu(L)_2]$.

At least 3 different forms (A, B and C, see Table 8) of the ligand anion $\{(L)^-\}$ appear in the spectra of $K(H_2O)_3[Lu(L)_2]$, which can correspond to coordination isomers and/or non-equivalent positions of the coordinated ligand. Signals of three forms A, B and C in ^1H and ^{13}C spectra are present for most carbon and hydrogen nuclei. It can be shown on the example of atoms 1 and 12 (see Figure 26). Nevertheless, sums of integral intensities of forms A, B and C are in agreement with the composition of the ligand.

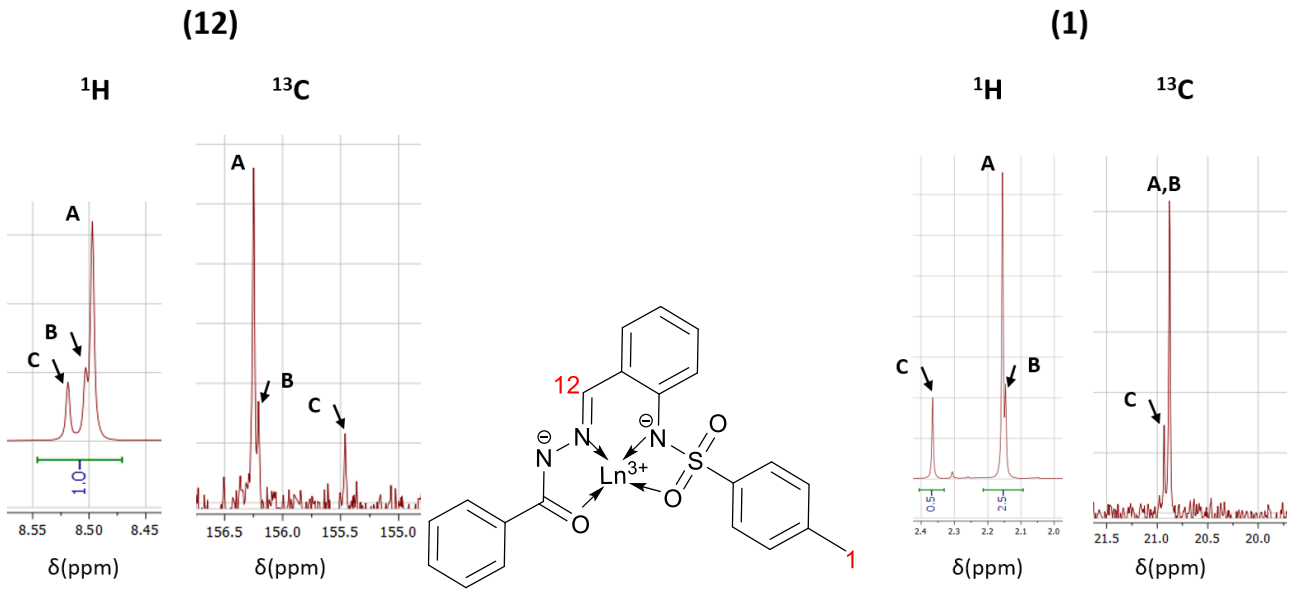

Figure 26 Fragments of ^{1}H and ^{13}C NMR spectra of $K(H_2O)_3[Lu(L)_2]$ in DMSO-d_6 showing ligand forms A, B and C on the example of nuclei 1 and 12.

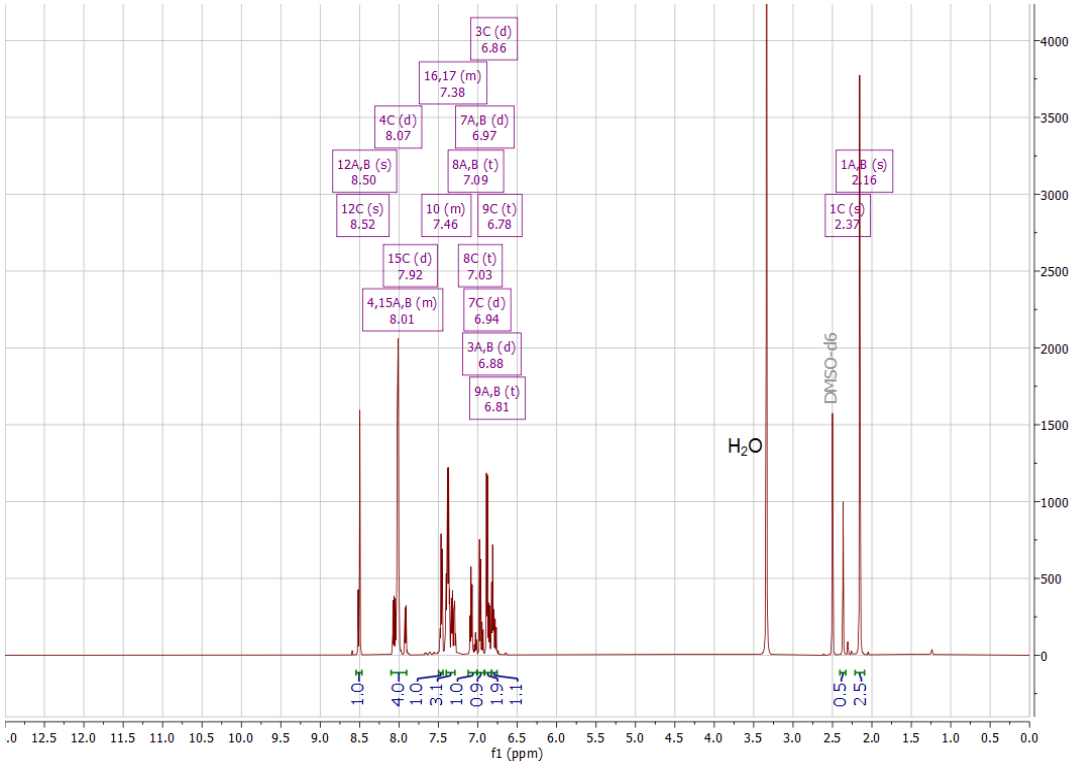

Figure 27 ^{1}H NMR spectrum of $K(H_2O)_3[Lu(L)_2]$ in DMSO-d_6.

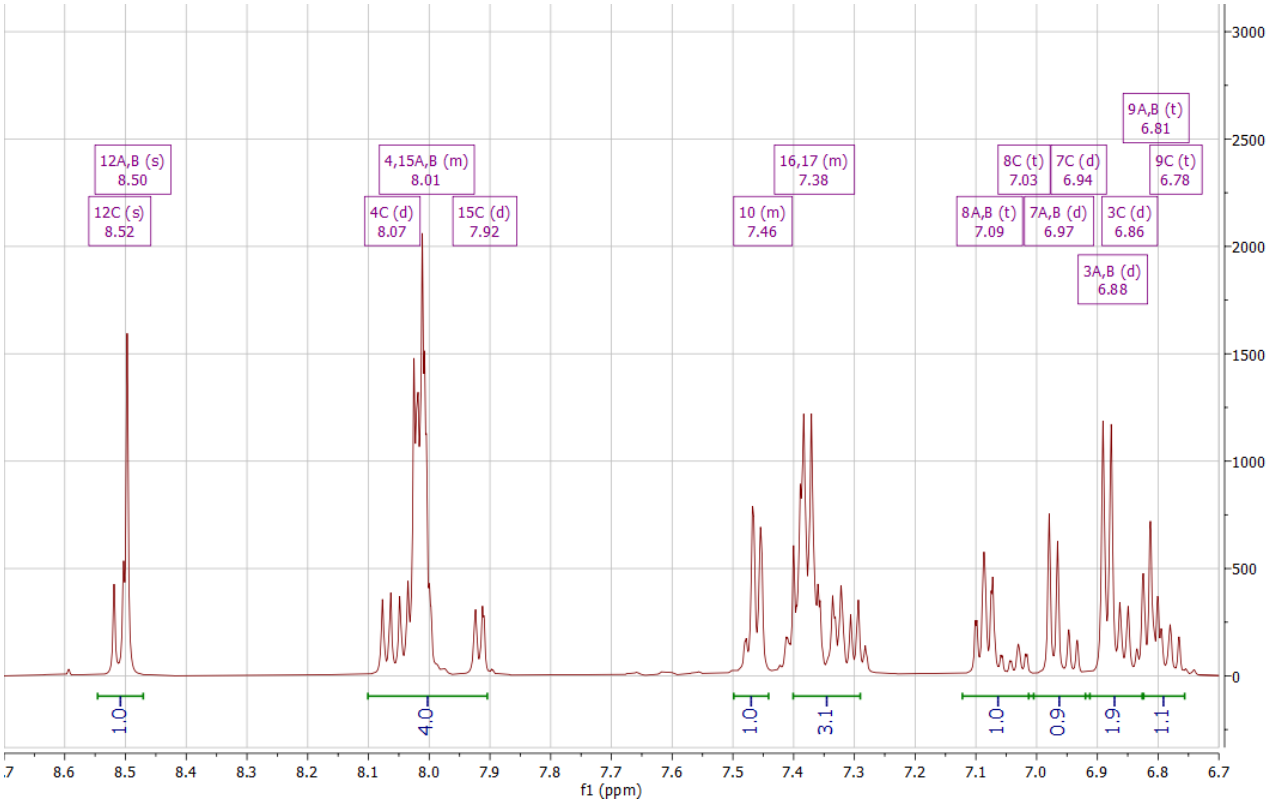

Figure 28 ^{1}H NMR spectrum of $K(H_2O)_3[Lu(L)_2]$ in DMSO-d_6 in the range 6.7 – 8.7 ppm.

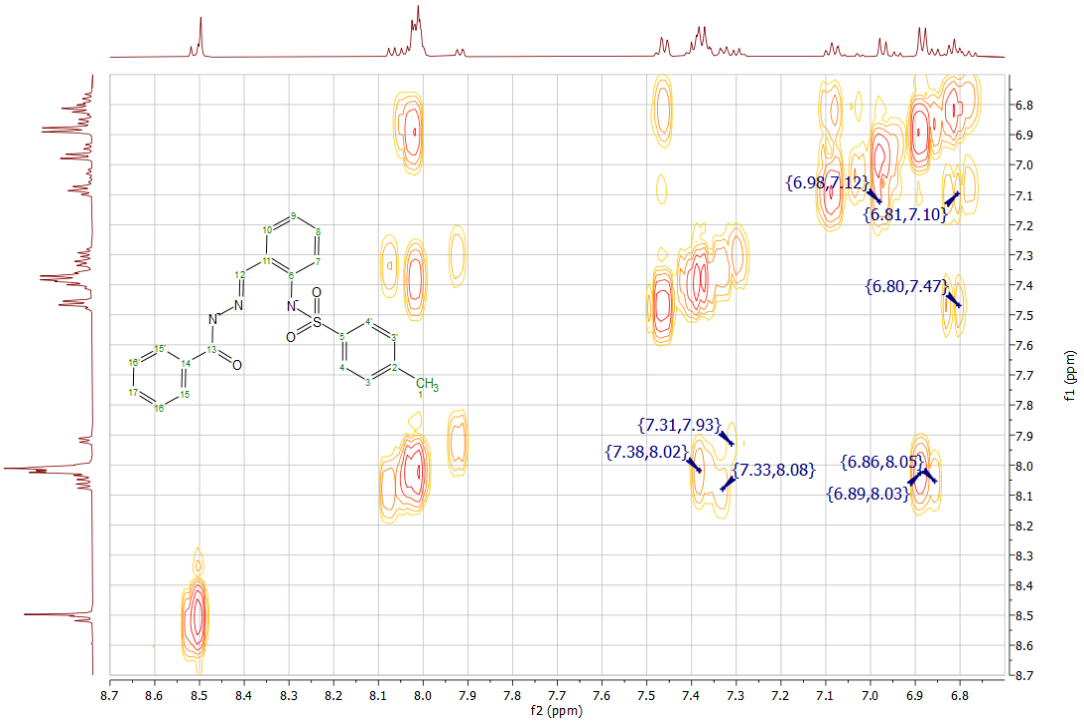

Figure 29 Fragment of the COSY spectrum of $K(H_2O)_3[Lu(L)_2]$ in DMSO-d_6.

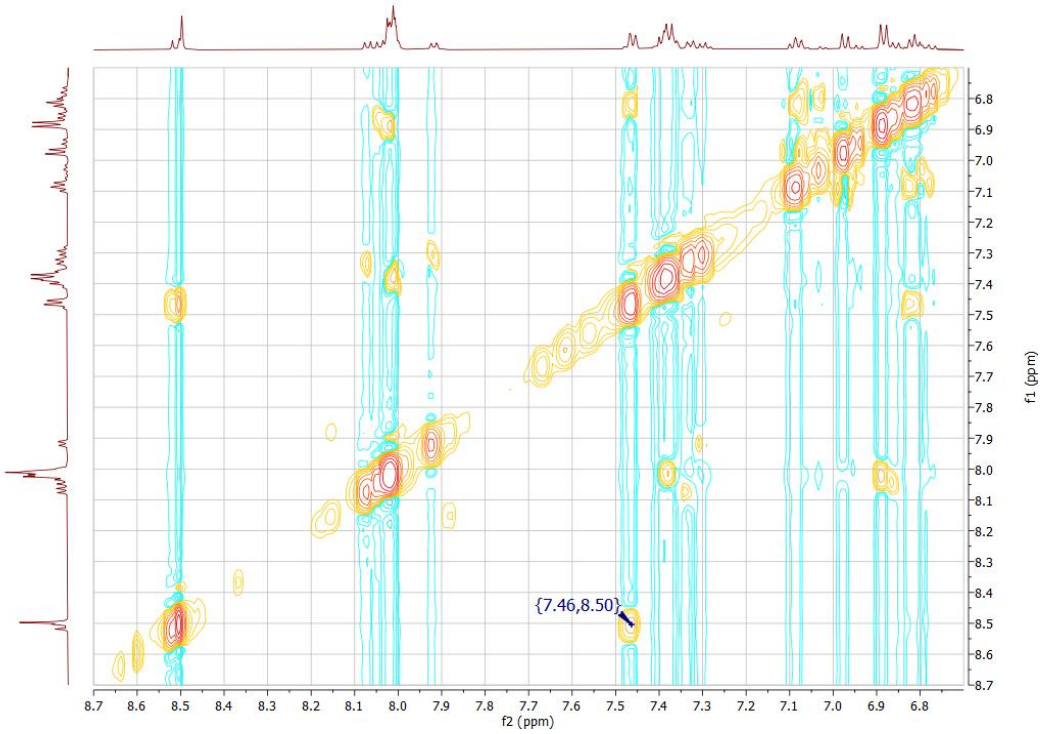

Figure 30 Fragment of the NOESY spectrum of $K(H_2O)_3[Lu(L)_2]$ in DMSO-d_6. For clearance, only interaction of protons 12-10, which brings additional to COSY spectrum information, is highlighted.

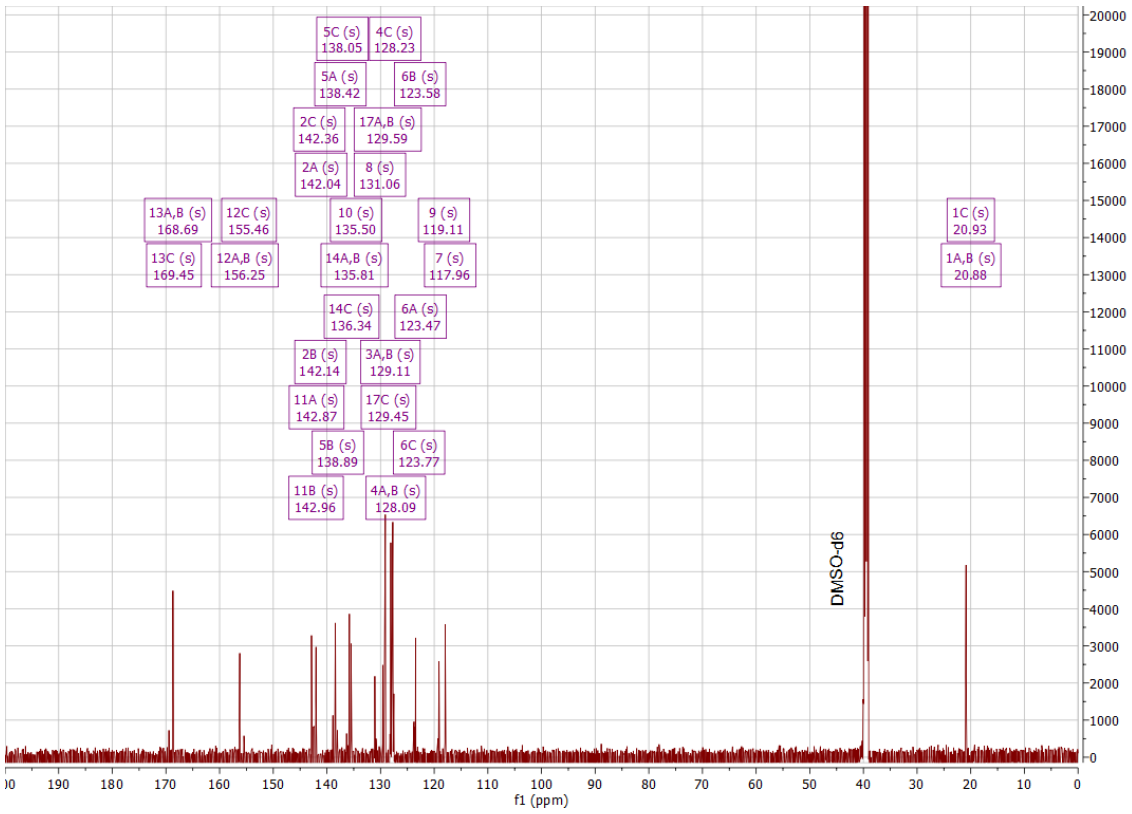

Figure 31 ^{13}C NMR spectrum of $K(H_2O)_3[Lu(L)_2]$ in DMSO-d_6.

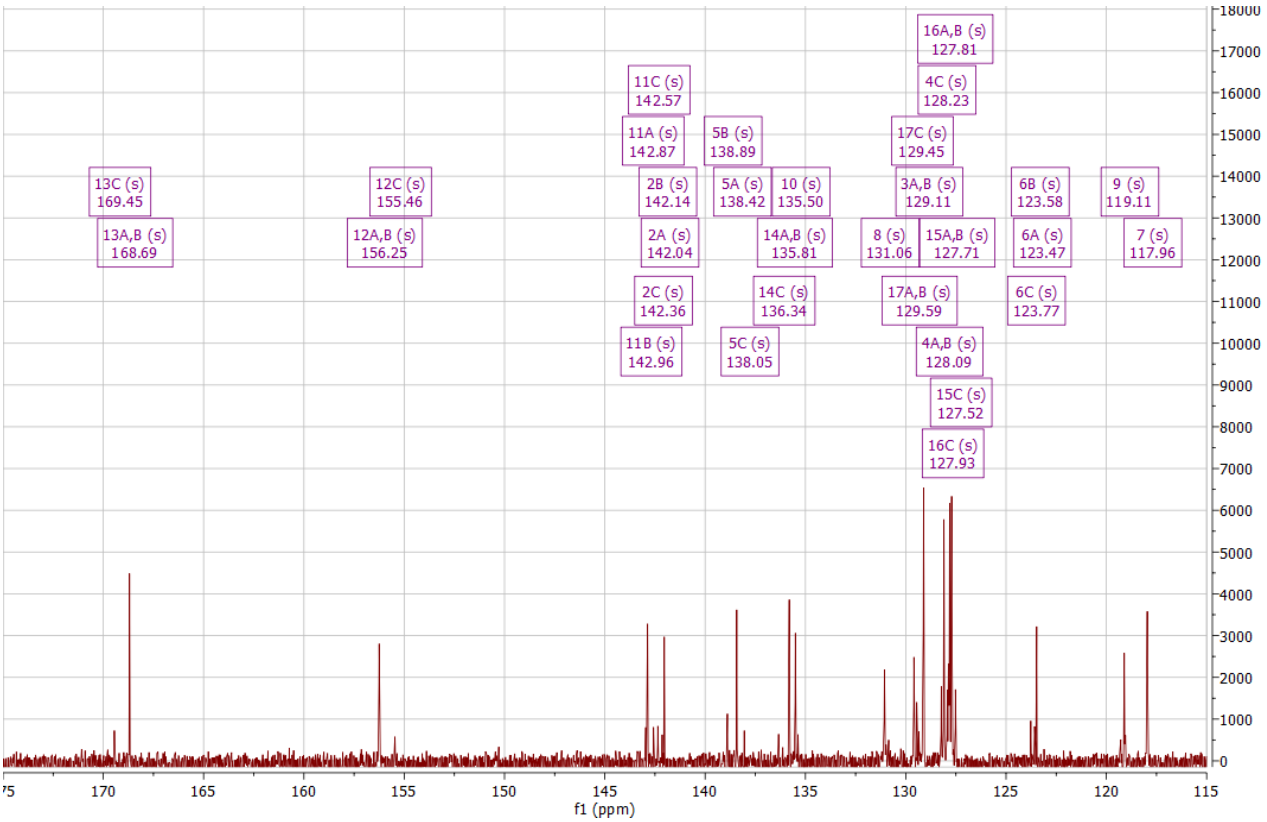

Figure 32 ^{13}C NMR spectrum of $K(H_2O)_3[Lu(L)_2]$ in DMSO-d_6 in the range 175 – 115 ppm.

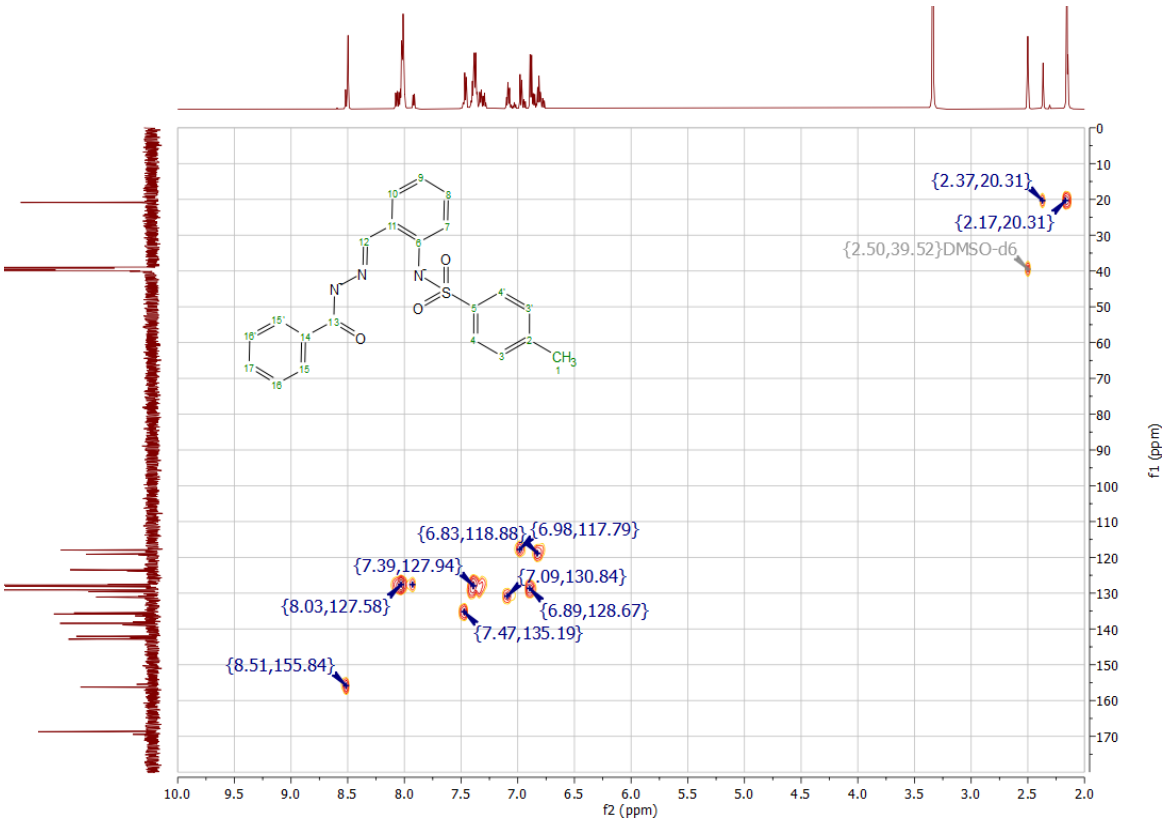

Figure 33 HSQC spectrum of $K(H_2O)_3[Lu(L)_2]$ in DMSO-d_6.

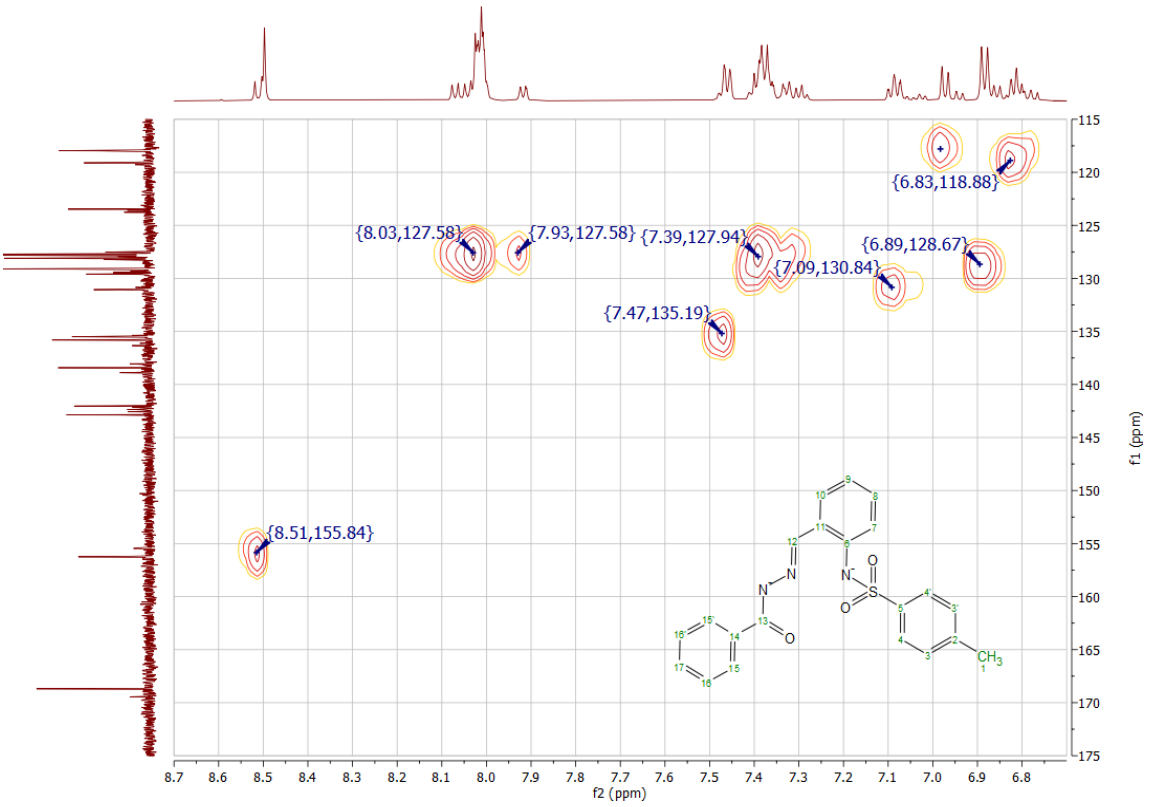

Figure 34 Fragment of $K(H_2O)_3[Lu(L)_2]$ HSQC spectrum in DMSO-d_6.

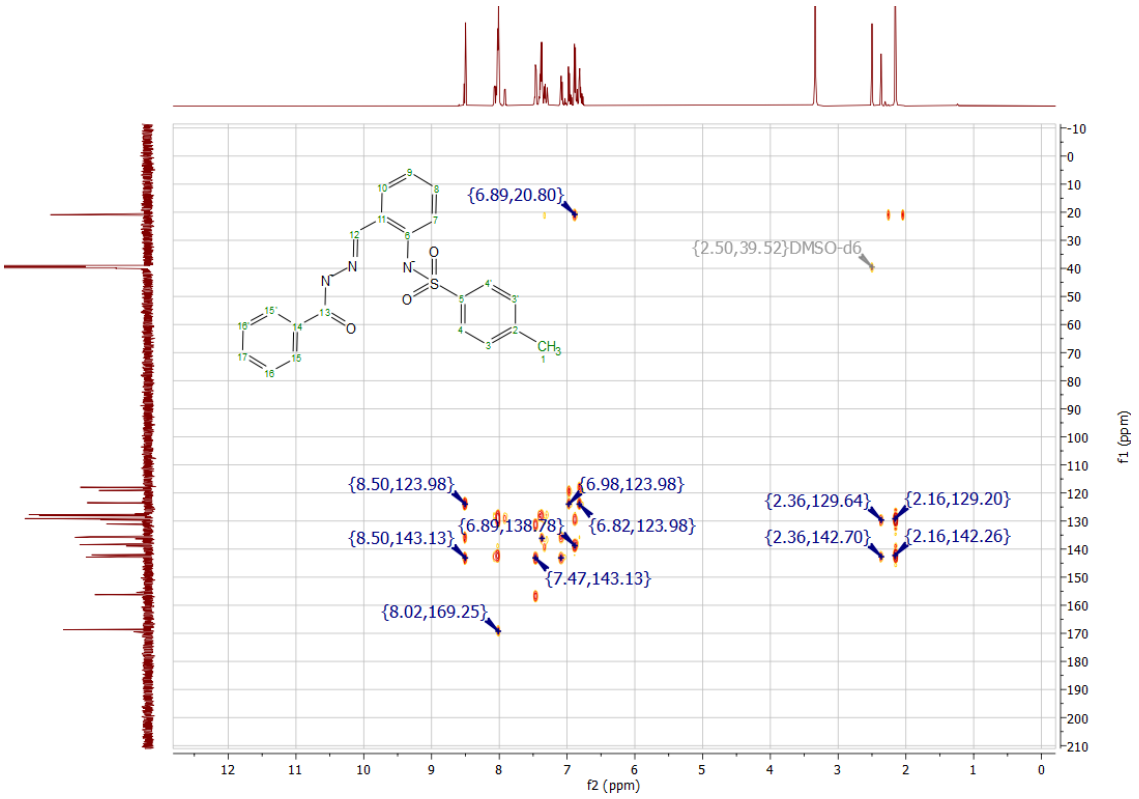

Figure 35 HMBC spectrum of $K(H_2O)_3[Lu(L)_2]$ in DMSO-d_6.

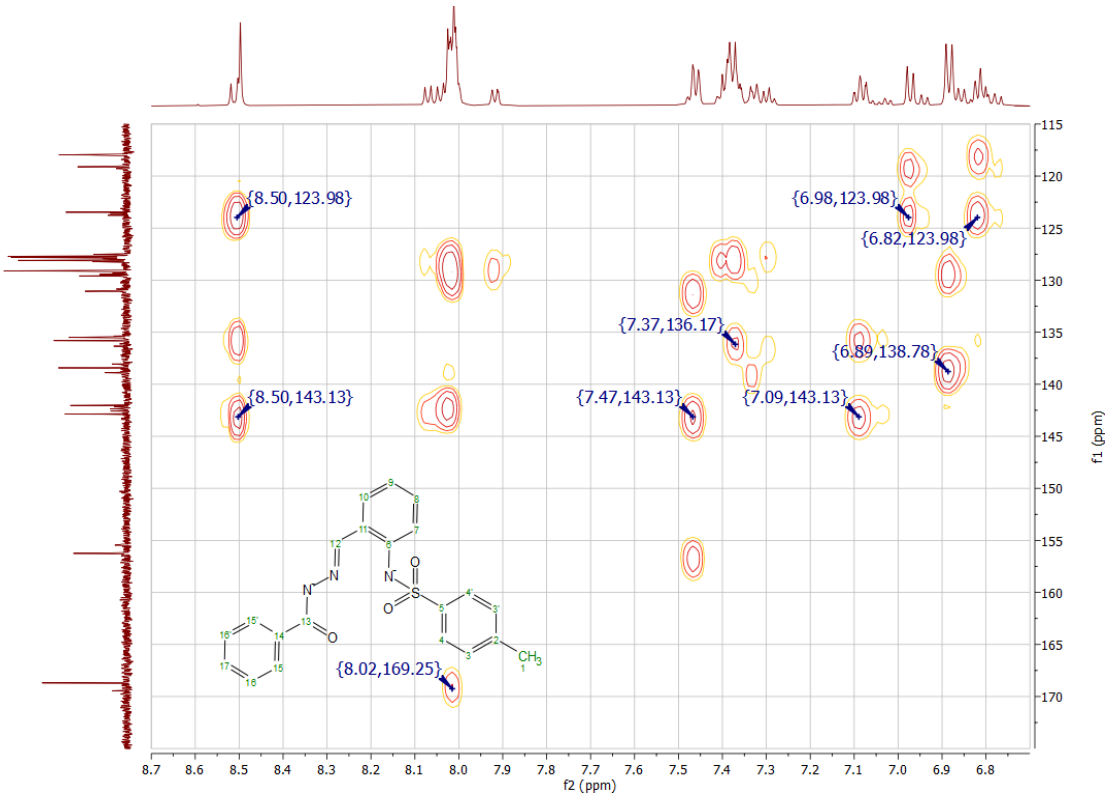

Figure 36 Fragment of $K(H_2O)_3[Lu(L)_2]$ HMBC spectrum in DMSO-d_6. For clearance, only interactions which bring additional to HSQC spectrum information are highlighted.

Spectra of Lu(L)(HL)

In DMSO, Lu(L)(HL) dissociate according to the reaction (see reaction (2) in the main text):

$$2Lu(L)(HL) = H_2L + [Lu(L)]^+ + [Lu(L)_2]^-,$$

thus, in its NMR spectra signals of H_2L, $[Lu(L)]^+$ and $[Lu(L)_2]^-$ are present.

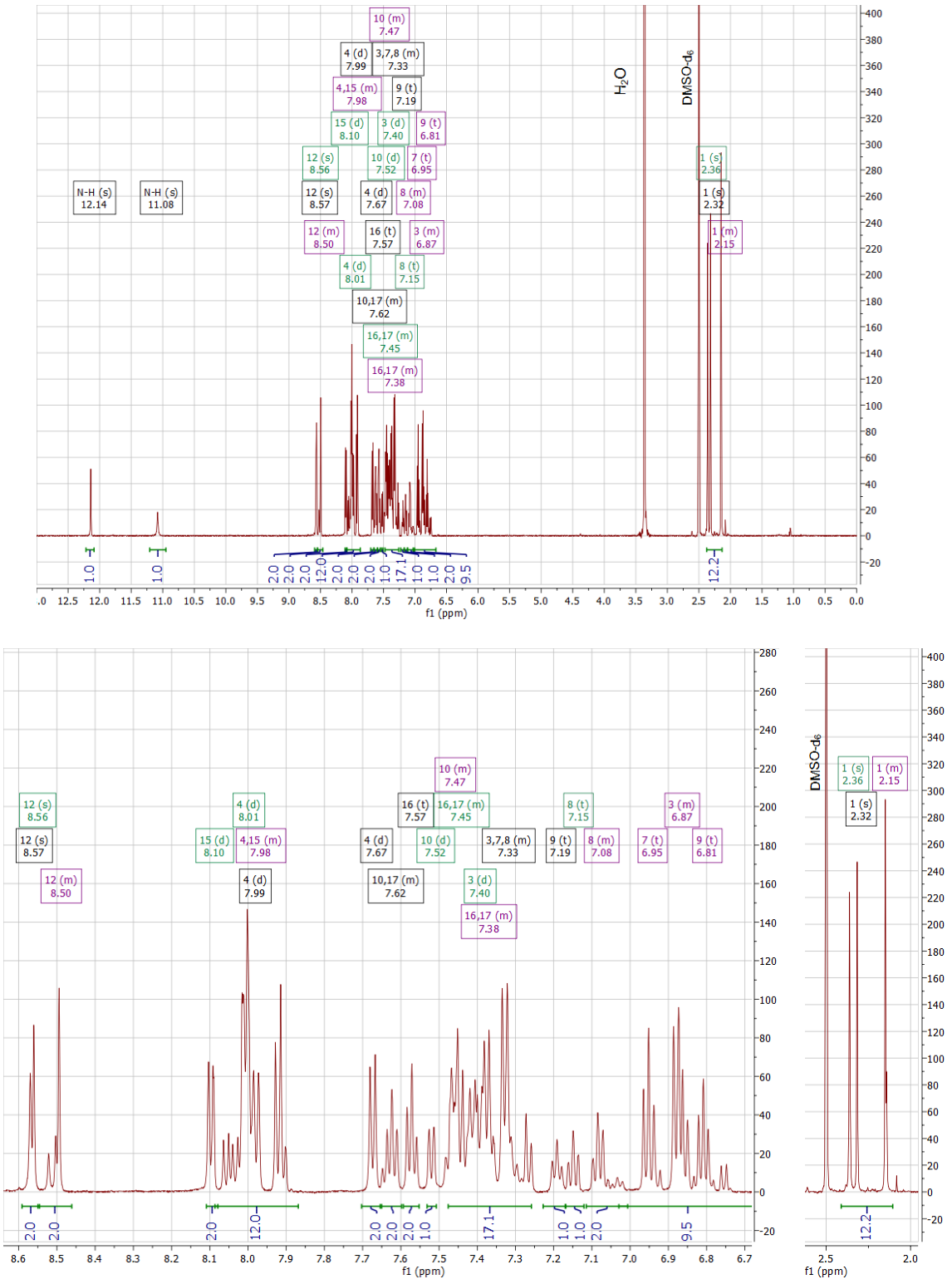

Figure 37 ^{1}H spectrum of Lu(L)(HL) in DMSO-d_6. H_2L signals are black, $[LuL]^+$ signals are green and $[Lu(L)_2]^-$ signals are violet.

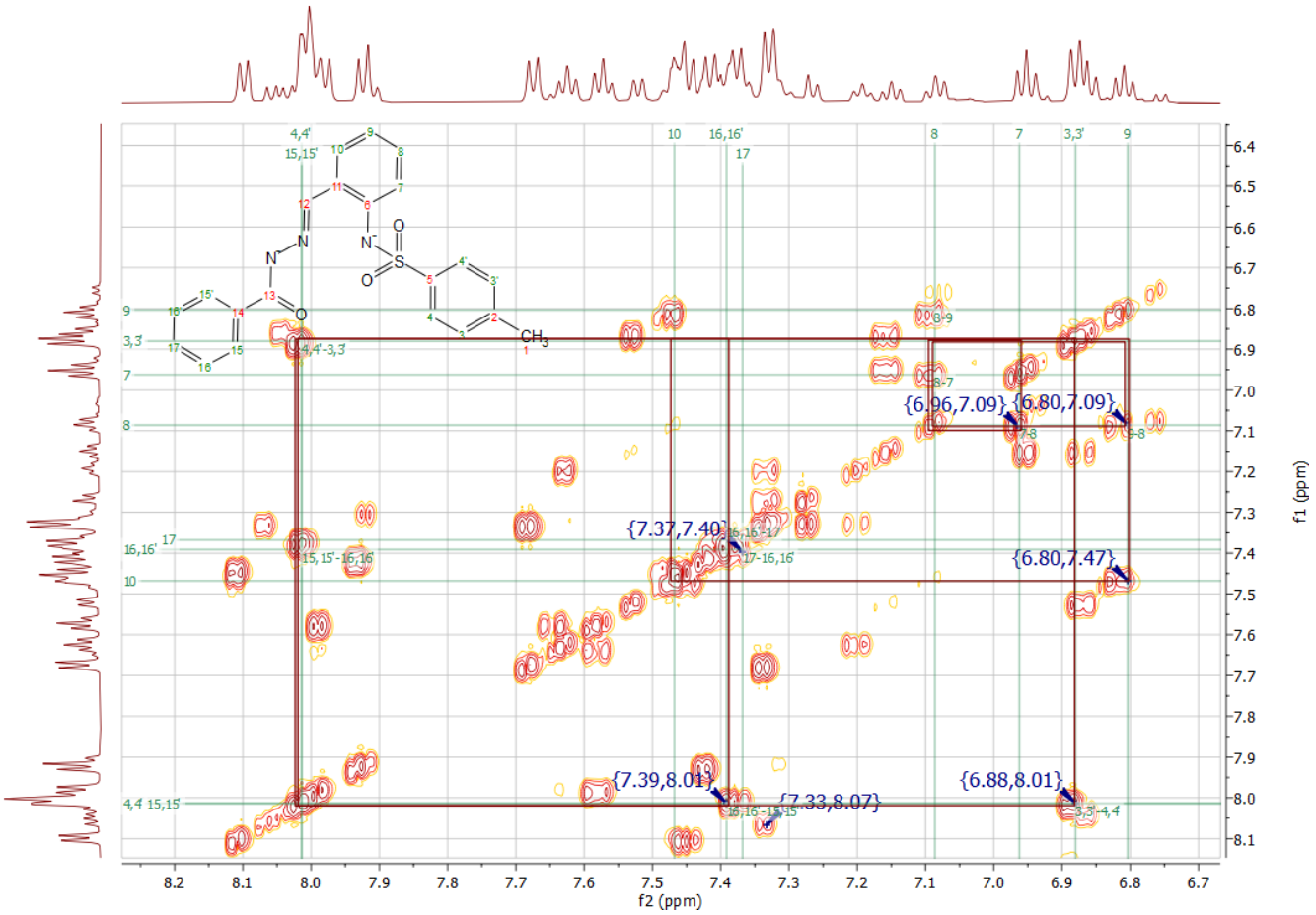

Figure 38 Fragment of the COSY spectrum of Lu(L)(HL) in DMSO-d_6. For clearance, only signals of $[Lu(L)_2]^-$ are highlighted.

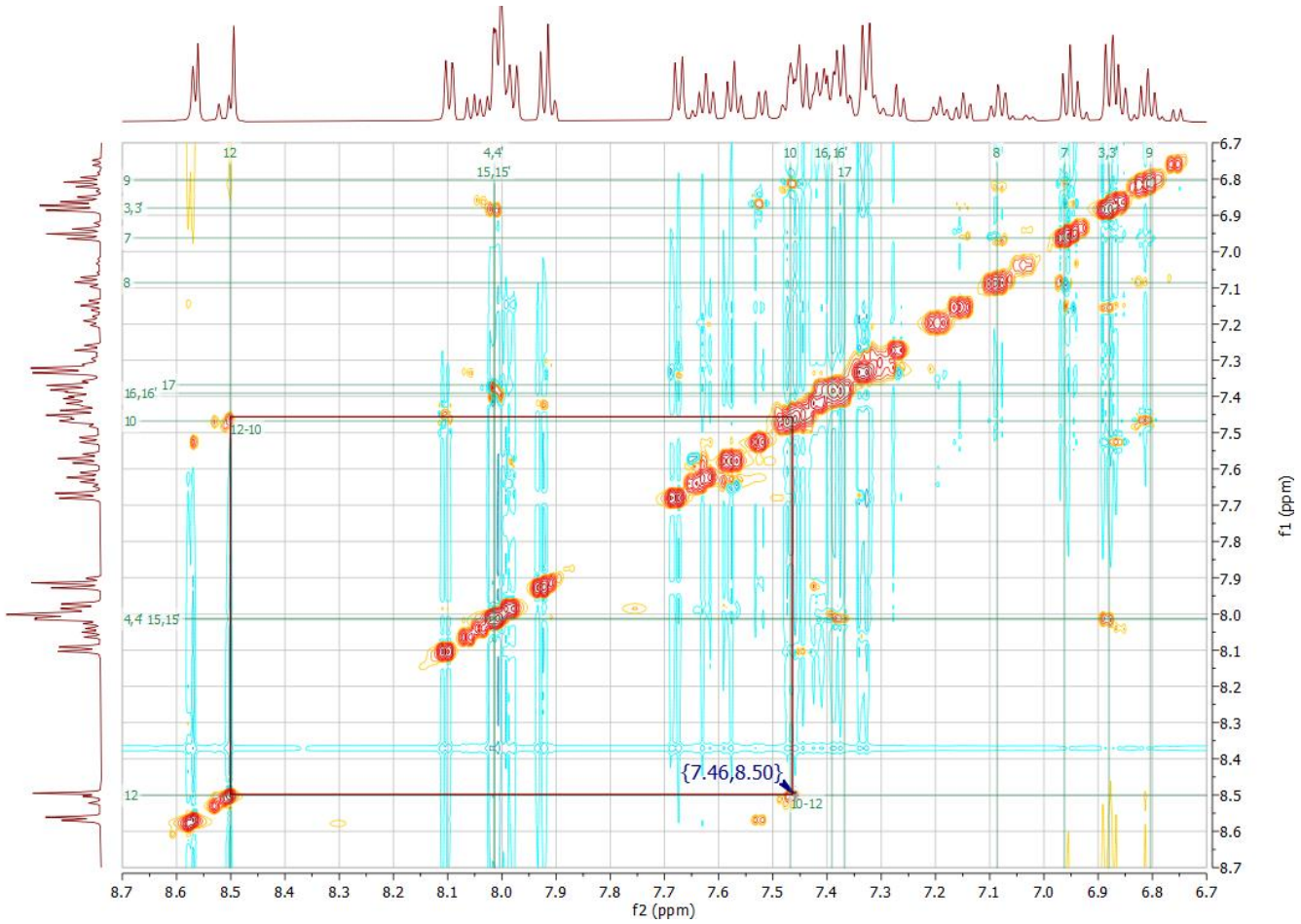

Figure 39 Fragment of the NOESY spectrum of Lu(L)(HL) in DMSO-d_6. For clearance, only signals of $[Lu(L)_2]^-$ which bring information additional to ^1H and COSY spectra are highlighted.

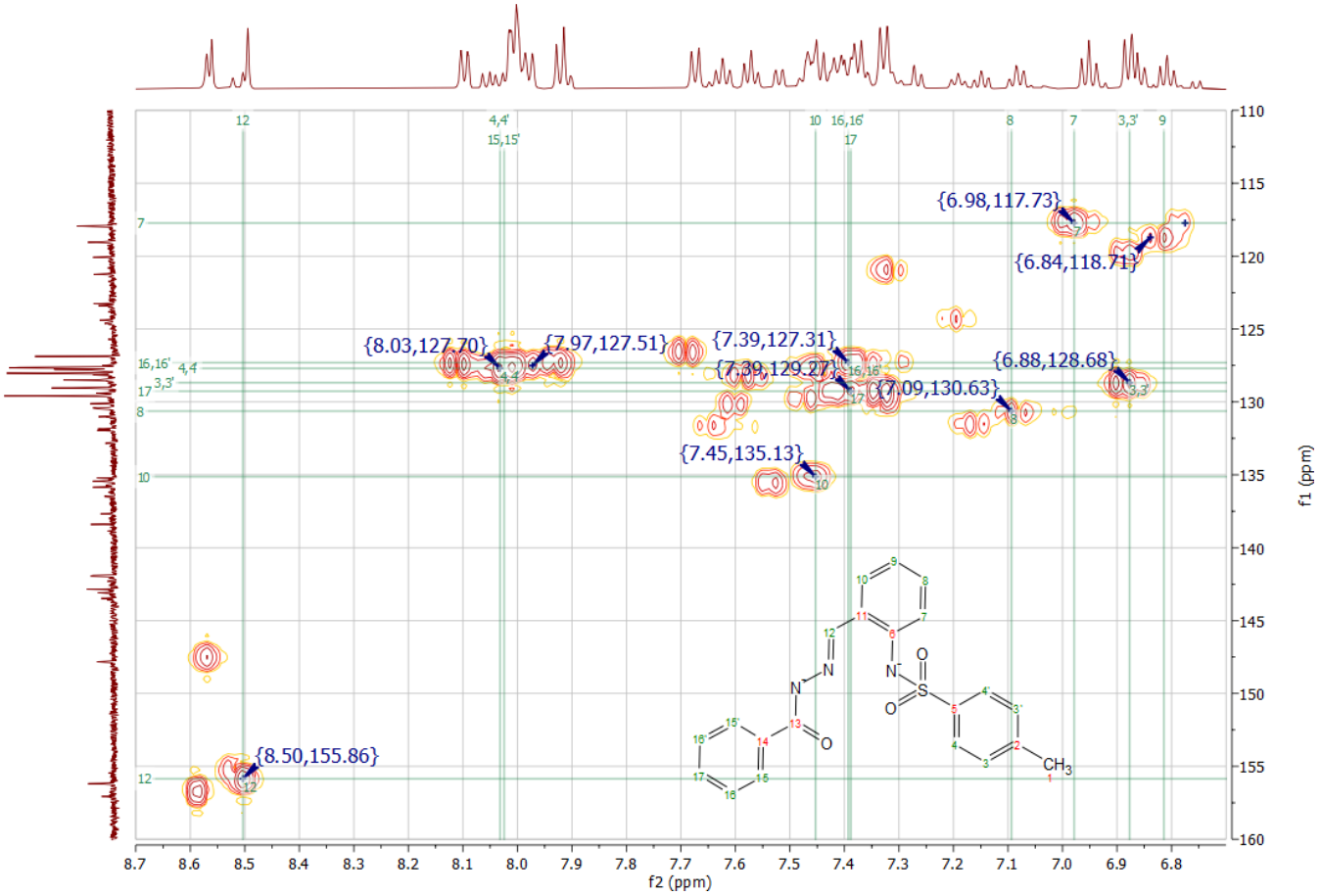

Figure 40 HMQC spectrum of Lu(L)(HL) in DMSO-d_6. For clearance, only signals of $[Lu(L)_2]^-$ are highlighted.

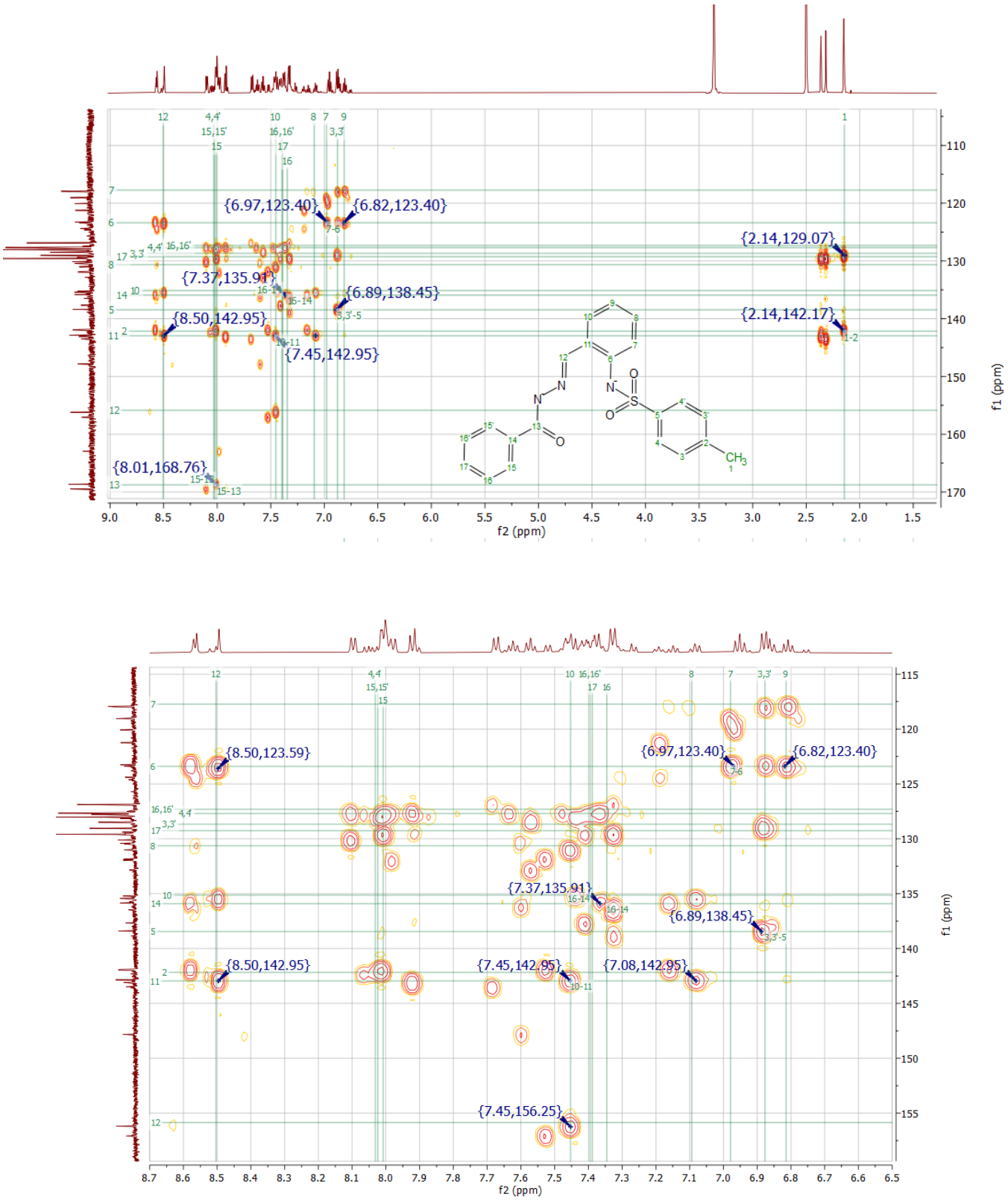

Figure 41 HMBC spectrum of Lu(L)(HL) in DMSO-d_6. For clearance, only signals of $[Lu(L)_2]^-$ which bring additional to HMQC spectrum information are highlighted.

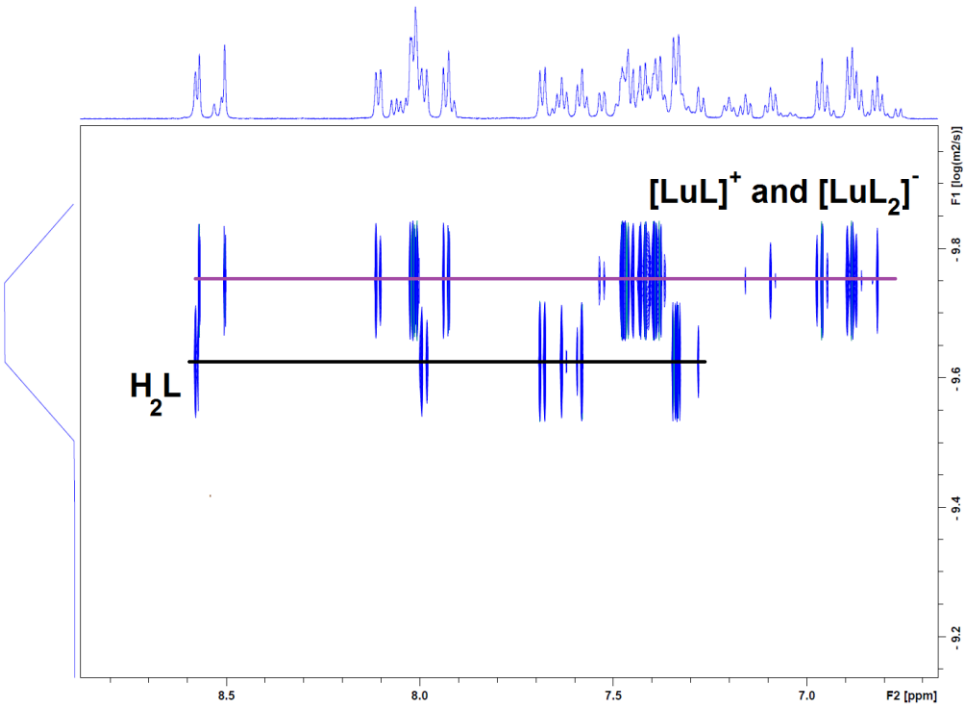

Figure 42 DOSY spectrum of Lu(L)(HL) in DMSO-d_6.

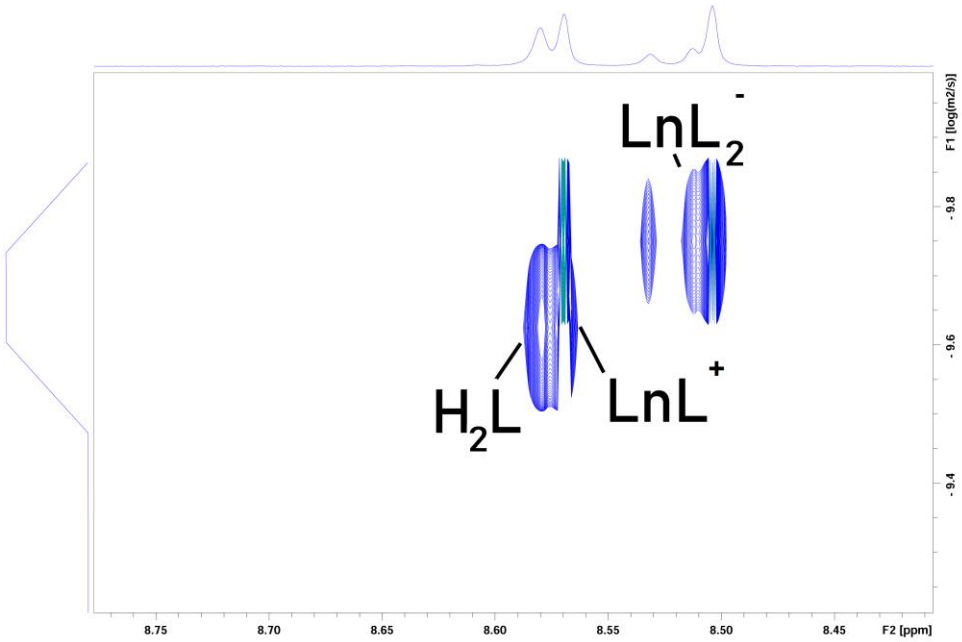

Figure 43 DOSY spectrum of Lu(L)(HL) in DMSO-d_6 in the range 8.80 – 8.40 ppm showing signals of protons 12.

Spectra of $Yb(HL)_2Cl$

In DMSO, $Yb(HL)_2Cl$ dissociate according to the reaction (see the reaction (1) in the main text):

$$Yb(HL)_2Cl = H_2L + [Yb(L)]^+ + Cl.$$

Thus, in its NMR spectra, signals of both H_2L and $[Yb(L)]^+$ are presented.

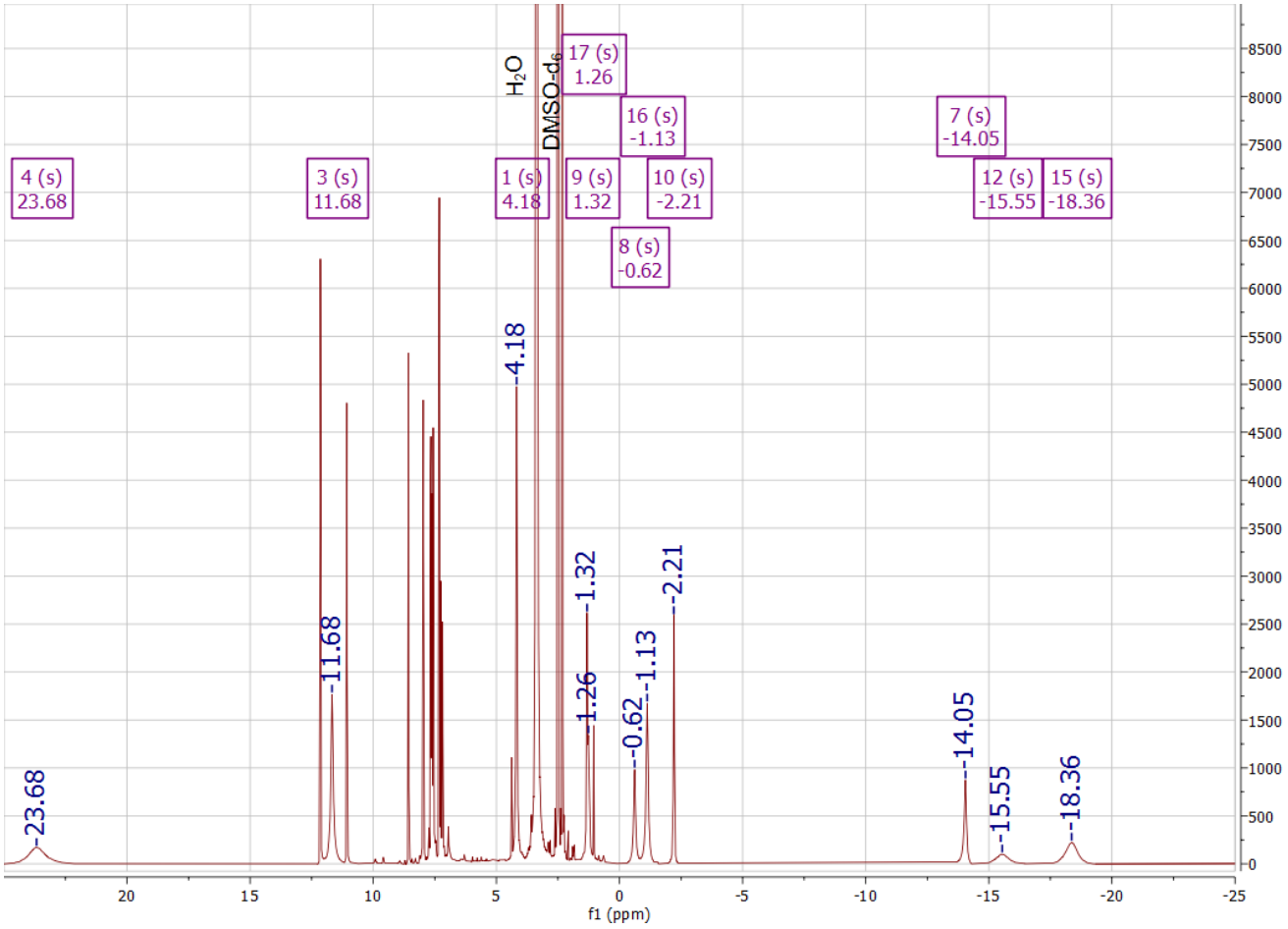

Figure 44 ^1H spectrum of $Yb(HL)_2Cl$ in DMSO-d_6. For clearance, only signals of $[Yb(L)]^+$ are named.