The effect of the linker size in C_2-symmetrical chiral ligands on the self-assembly formation of luminescent triple-stranded *di*-metallic Eu(III) helicates in solution

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Supporting Information

All solvents and chemicals were purchased from commercial sources and used without further purification. Dichloromethane, chloroform, tetrahydrofuran were freshly distilled under argon atmosphere prior to use. Water was purified using a Millipore Milli-Q water purification system. 2,6-Dimethylaniline, cyclohexanone, 1,3-phenylenediamine, 1-hydroxybenzotriazole hydrate (HOBt), *N*-(3-Dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride (EDCI), dimethylaminopyridine (DMAP), trimethylamine (Et_3N), conc. HCl, NaOH, $NaHCO_3$, $MgSO_4$, pentane were purchased from Fluka and Sigma-Aldrich. Compounds **10** and **11** were synthesised and characterised as described in [1]. Stock solutions of $Eu(OTf)_3$ were prepared just before use in CH_3CN (spectroscopic grade). Exact concentrations of the solutions were determined by complexometric titrations using a standardized Na_2H_2EDTA solution in urotropine buffered medium and xylenol orange as the indicator. Deuterated solvent used for NMR analysis ($CDCl_3$) was purchased from Apollo Scientific. The ^1H and ^{13}C NMR spectra were recorded using a Bruker AV-600 instrument operating at either 600.1 MHz for ^1H NMR and 150.2 MHz for ^{13}C NMR or Bruker AV-400 instrument operating at 400.1 MHz for ^1H NMR and 100.6 MHz for ^{13} C NMR. Chemical shifts are reported in ppm using deuterated solvents as internal standards. ^1H NMR titrations were recorded using Bruker Spectrospin DPX-400 instrument operating at 400.1 MHz. The ^1H NMR titrations for the ligands **3**(*S*,*S*), **4**(*R*,*R*) and **5**(*S*,*S*), **6**(*R*,*R*) were started with the ligands at c $\approx 1.00\times10^{-3}$ M upon gradual addition of $Eu(CF_3SO_3)_3$ solution in CD_3CN. All NMR data acquisition were carried out at 293 K unless otherwise stated. Also, the data about NMR titrations needs to be added Mass-spectrometry was carried out using HPLC grade solvents. Electrospray mass spectra (ESI) were determined on a Micromass LCT spectrometer and high resolution mass spectra were determined relative to a standard of leucine enkephaline. Maldi-Q-Tof mass spectra were carried out on a MALDI-Q-TOF-Premier (Waters Corporation, Micromass MS technologies,

Manchester, UK) and high resolution mass spectrometry was performed using Glu-Fib with an internal reference peak of *m/z* 1570.6774. Melting points were determined using an Electrothermal IA9000 digital melting point apparatus. Mid-infrared spectra were recorded using a Perkin-Elmer Spectrum One FT-IR spectrometer equipped with a universal attenuated total reflection (ATR) sampling accessory. Elemental analysis was conducted at the Microanalytical Laboratory, School of Chemistry and Chemical Biology, University College Dublin. Complexation reactions were carried out in 2-5 mL Biotage Microwave Vials in a Biotage Initiator Eight EXP microwave reactor. Reactions were performed at 65 °C for 2 hours in HPLC grade methanol.

Photophysical measurements: Unless otherwise stated, all measurements were performed at 298 K in acetonitrile solutions (spectroscopy grade, Aldrich). UV-visible absorption spectra were measured in 1 cm quartz cuvettes on a Varian Cary 50 spectrophotometer. Baseline correction was applied for all spectra. Emission (fluorescence, phosphorescence (delay time – 0.10 ms; total decay time: 0.020 s) and excitation) spectra and life-times were recorded on a Varian Cary Eclipse Fluorimeter. Quartz cells with a 1 cm path length from Hellma were used for these measurements. The temperature was kept constant throughout the measurements at 298 K by using a thermostated unit block. Phosphorescence life-times of the Eu($^5D_0$) excited state were measured in CH_3CN in time-resolved mode at 298 K. They are averages of three independent measurements, which were made by monitoring the emission decay at 616 nm, which corresponds to the maxima of the Eu(III) $^5D_0 \rightarrow {}^7F_2$ transition, enforcing a 0.1 ms delay, and were analyzed using Origin 7.5®.

The quantum yields ($Q_{rel}^{Eu,L}$) were measured by relative method [2, 3] using $Cs_3[Eu(dpa)_3]\cdot 9H_2O$ complex in 0.1 M Tris buffer (pH = 7.45) ($Q_{abs}^{Eu} = 24.0 \pm 2.5\ \%$) [4] as a standard with known quantum yield, to which the absorbance and emission intensity of the sample are compared according to:

$$Q_{rel}^{Eu,L} = \frac{Q_x}{Q_r} = \frac{E_x}{E_r} \times \frac{A_r(\lambda_r)}{A_x(\lambda_x)} \times \frac{I_r(\lambda_r)}{I_x(\lambda_x)} \times \frac{n_x^2}{n_r^2} \qquad (2)$$

,

where subscript *r* – reference and *x* – sample; *E* – integrated luminescence intensity; *A* – absorbance at the excitation wavelength; *I* – intensity of the excitation light at the same

wavelength, *n* – refractive index of the solution. The estimated error for quantum yields is ±10%.

τ_R life-time was obtained using equation (3):

$$\frac{1}{\tau_R} = A_{MD,0} \cdot n^3 \cdot \left(\frac{I_{tot}}{I_{MD}}\right) \qquad (3),$$

where *n* is the refractive index of the solvent, $A_{MD,0}$ is the spontaneous emission probability for the $^5D_0 \rightarrow {}^7F_1$ transition *in vacuo*, and I_{tot}/I_{MD} is the ratio of the total area of the corrected Eu(III) emission spectrum to the area of the $^5D_0 \rightarrow {}^7F_1$ band ($A_{MD,0}$ = 14.65 s^{-1}).[5]

The quantum yield of the luminescence step (Φ_{Ln}^{Ln}) expresses how well the radiative process complete with non-radiative processes.

$$\Phi_{Ln}^{Ln} = \frac{\tau_{obs}}{\tau_R} \qquad (4),$$

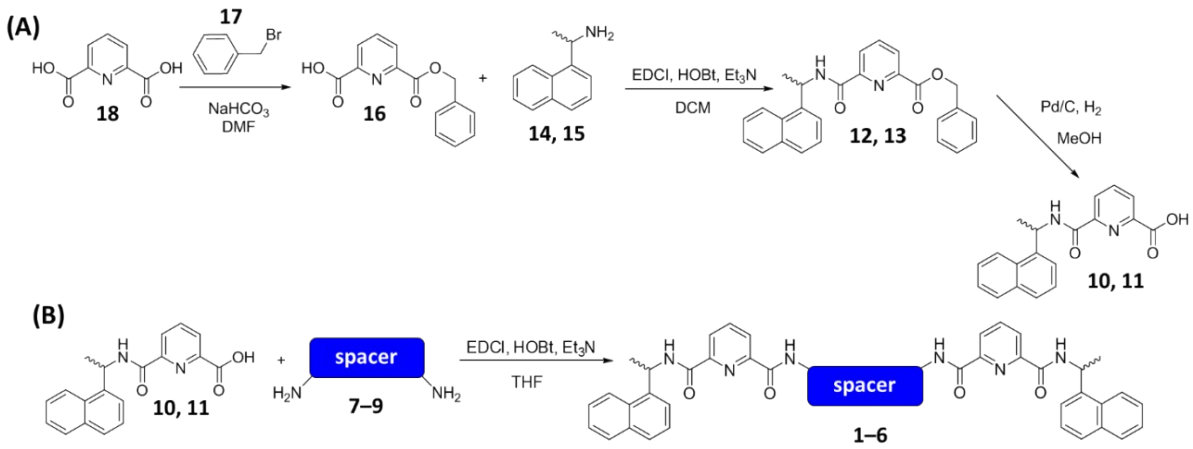
The efficiency of lanthanide sensitization (η_{sens}) is the ratio between Φ_{tot} (determined experimentally) and Φ_{Ln}^{Ln} (see equation (4)):

$$\eta_{sens} = \frac{\Phi_{tot}}{\Phi_{Ln}^{Ln}} \qquad (5).$$

CD spectra were recorded in acetonitrile solution on a Jasco J-810-150S spectropolarimeter. CD titrations were performed in CH_3CN media starting with the ligands at c = 1.40×10^{-5} M upon gradual addition from 0 to 4 equivalents of $Eu(CF_3SO_3)_3$ to the solution. CPL spectra were recorded by Dr. R. Peacock at the University of Glasgow. Excitation of Eu(III) (560-581nm) was accomplished by using a Coherent 599 tunable dye laser (0.03 nm resolution) with argon ion laser as a pump source. Calibration of the emission monochromator was accomplished by passing scattered light from a low power HeNe laser through the detection system. The optical detection system consisted of a photoelastic modulator (PEM, Hinds Int.) operating at 50 kHz and a linear polarizer, which together act as a circular analyzer, followed by a long pass filter, focusing lens and a 0.22 m double monochromator. The emitted light was detected by a cooled EM1-9558QB photomultiplier tube operating in photon counting mode. The 50 KHz

reference signal from the photoelastic modulator was used to direct the incoming pulses into two separated counters. An up counter, which counts every photon pulse and thus is a measure of the total luminescence signal $I = I_{left} + I_{right}$, and an up/down counter, which adds pulses when the analyzer is transmitting to the left circularly polarized light and subtracts pulses when the analyzer is transmitting right circularly polarized light. The second counter provides a measure of the differential emission intensity $\Delta I = I_{left} - I_{right}$.

Spectrophotometric titrations and binding constants: The formation of the luminescent $\mathbf{M_n:L_m}$ (M = Eu(III) and **L** = **1–6**) species was ascertained by both UV-visible, luminescence and CD titrations of a solution of **L** ($c_L \approx 1 \cdot 10^{-5}$ M) in CH_3CN with $Eu(CF_3SO_3)_3 \cdot 6H_2O$ (0→4 equivalents). The data were fitted using the non-linear regression analysis program, SPECFIT®.[6]



Scheme S1. Synthesis of the ligands **1–6**.

General procedure.

The synthesis and characterisation of compounds **10**, **11** was performed as described in [1].

Spacer molecules 1,3-bis(aminomethyl)benzene (**7**) and 1,3-benzenediamine (**8**) were commercially available and used as it is. Compound 1,1-bis(4-amino-3,5-dimethylphenyl)cyclohexane (**9**) was synthesised as described in [7]. Helicate ligands **1-6** were synthesised as previously described in [8].

General procedure for the synthesis of the ligands **3–6**: In a round bottom flask **10** or **11** (2 equiv.), spacer diamine (**7–9**, 1 equiv.), HOBt (2.1 equiv.), DMAP (1.2 equiv.) and Et_3N (2.1 equiv.) were mixed in freshly distilled THF. This mixture was placed under argon atmosphere,

cooled to 0 °C in an acetone/ice bath and left at this temperature for another hour. After this EDCI (124.6 mg, 0.65 mmol, 2.1 equiv.) was added to the reaction mixture and the resulting solution was left at 0 °C under argon atmosphere for another hour. The reaction was then allowed to gradually warm up to room temperature and left stirring for 48 hours. In the case solid was present in the resulting reaction mixture it was then filtered off through filter paper and solvent evaporated under reduced pressure yielding oily compound. It was then dissolved in DCM and solution was washed with 1.0 M HCl (3 x 25 mL), saturated solution of $NaHCO_3$ (1 x 25 mL) and H_2O (1 x 25 mL). The organic layer was then dried over $MgSO_4$, filtered and the solvent evaporated yielding off-white solid. The solid was purified using trituration.

1,1-bis(4-amino-3,5-dimethylphenyl)cyclohexane (9): In 250 mL round bottom flask 2,6-dimethylaniline (15 mL, 121.8 mmol), cyclohexanone (6.3 mL, 60.8 mmol) and concentrated HCl (15 mL) were mixed and refluxed for 48 hours. The products were then added in 250 mL of water and this solution was basified with 1M NaOH. The product was then extracted with 500 mL of chloroform which was then evaporated under reduced pressure. Upon addition of 250 mL of pentane the compound crystallised and the white powder was filtered and dried in air (5.86 g, Yield: 29.9%). m.p. 170 °C; HRMS (*m/z*) (ESI$^+$) calculated for $C_{22}H_{31}N_2$ *m/z* = 323.2488 $[M + H^+]^+$. Found *m/z* = 323.2487; ^{1}H NMR (400 MHz, $CDCl_3$, δ_H) ppm 6.84 (4H, s), 3.43 (4H, s), 2.18 (4H, br), 2.14 (12H, s), 1.53 (4H, br), 1.40 (2H, br); ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 140.02, 138.88, 127.10, 121.48, 44.63, 37.53, 26.69, 23.21, 18.22; IR ν_{max} (cm^{-1}): 3479.89, 3446.86, 3363.12, 3221.01, 2923.39, 2858.43, 2843.77, 2730.20, 1773.90, 1618.86, 1599.88, 1492.82, 1459.50, 1452.32, 1374.85, 1350.35, 1309.46, 1269.91, 1238.59, 1172.41, 1144.76, 1120.83, 1029.09, 1007.37, 992.37, 959.97, 948.46, 886.81, 865.58, 820.92, 779.57, 750.99, 736.94, 699.62.

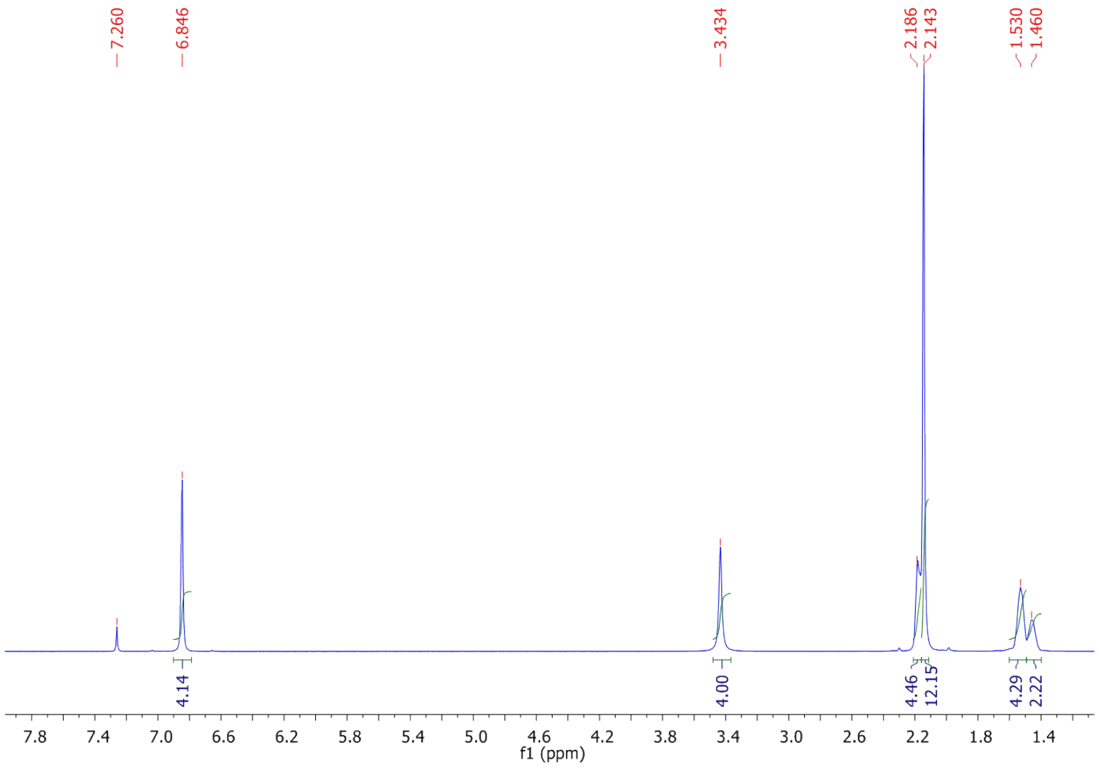


Figure S1. ^{1}H NMR of **9** ($CDCl_3$, 400.1 MHz).

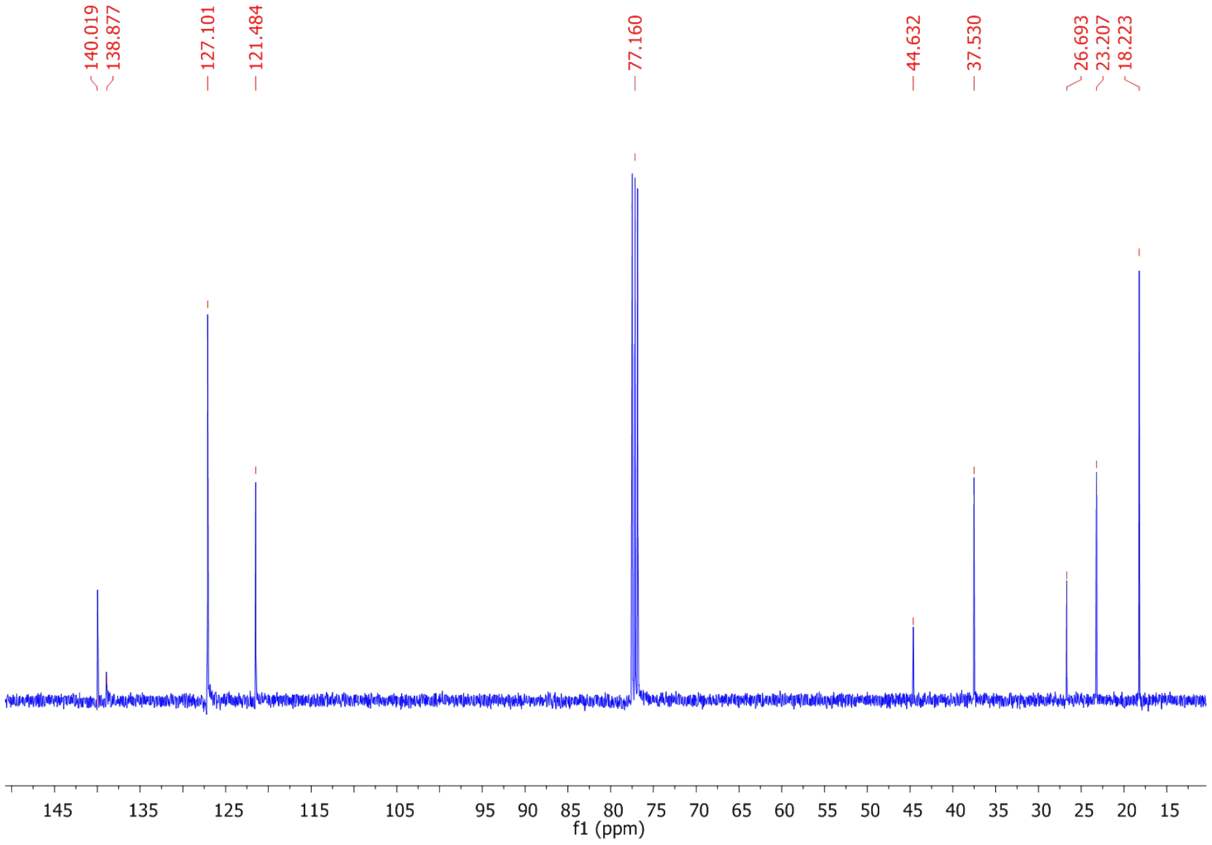


Figure S2. ^{13}C NMR of **9** ($CDCl_3$, 100.6 MHz).

***N2*-((*S*)-1-(naphthalen-1-yl)ethyl)-N6-(3-((6-((*S*)-1-(naphthalen-1-yl)ethylcarbamoyl)picolinamido)methyl)benzyl)pyridine-2,6-dicarboxamide (1)**

and

***N2*-((*S*)-1-(naphthalen-1-yl)ethyl)-N6-(3-((6-((*S*)-1-(naphthalen-1-yl)ethylcarbamoyl)picolinamido)methyl)benzyl)pyridine-2,6-dicarboxamide (2)** were synthesised and characterised as described in [8b].

***N2*-((*S*)-1-(naphthalen-1-yl)ethyl)-N6-(3-(6-((*S*)-1-(naphthalen-1-yl)ethylcarbamoyl)picolinamido)phenyl)pyridine-2,6-dicarboxamide (3**(*S*,*S*)**):** In a 100 mL round bottom flask **10** (200 mg, 0.62 mmol, 2 equiv.), 1,3-phenylenediamine (**8**, 33.8 mg, 0.31 mmol, 1 equiv.), HOBt (87.8 mg, 0.65 mmol, 2.1 equiv.), DMAP (45.4 mg, 0.37 mmol, 1.2 equiv.) and Et_3N (90.6 μL, 0.65 mmol, 2.1 equiv.) were mixed in 20 mL of freshly distilled THF. This mixture was placed under argon atmosphere, cooled to 0 °C in an acetone/ice bath and left at this temperature for another hour. After this EDCI (124.6 mg, 0.65 mmol, 2.1 equiv.) was added to the reaction mixture and the resulting solution was left at 0 °C under argon atmosphere for another hour. The reaction was then allowed to gradually warm up to room temperature and left stirring for 48 hours. As a result reddish-brown solution with a brown solid was obtained, the solid was filtered off through filter paper and solvent evaporated under reduced pressure yielding brown oil. It was then dissolved in DCM and solution was washed with 1.0 M HCl (3 x 25 mL), saturated solution of $NaHCO_3$ (1 x 25 mL) and H_2O (1 x 25 mL). The organic layer was then dried over $MgSO_4$, filtered and the solvent evaporated yielding off-white solid. The solid was then triturated in ethanol yielding 55 mg of solid (yield 25 %). HRMS (*m/z*) (ESI^+) calculated for $C_{44}H_{36}N_6O_4Na$ *m/z* = 735.2690 $[M + Na^+]^+$. Found *m/z* = 735.2669; ^1H NMR (600 MHz, $CDCl_3$, δ_H) ppm 9.38 (s, 2H, NH), 8.36 (d, 2H, J = 7.2 Hz, NH), 8.28 (d, 2H, J = 7.8 Hz, CH), 8.25 (br, 2H, CH), 8.17 (d, 2H, J = 8.4 Hz, CH), 7.97 (br, 2H, CH), 7.80 (d, 2H, J = 7.8 Hz, CH), 7.71 (d, 2H, J = 7.8 Hz, CH), 7.61 (d, 2H, J = 7.2 Hz, CH), 7.52 (t, 2H, CH), 7.45 (t, 2H, J = 7.2 Hz, CH), 7.41 (t, 2H, J = 7.2 Hz, CH), 7.08 (br, 2H, CH), 7.03 (br, 2H, CH), 6.11 (t, 2H, J = 6.6 Hz, CH), 1.81 (d, 6H, J = 6.0 Hz, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$, δ_C) 162.66, 161.57, 149.13, 148.65, 139.27, 138.26, 137.67, 134.08, 131.14, 129.47, 129.39, 129.00, 128.58, 126.72, 125.98, 125.77, 125.50, 125.25, 123.43, 123.22, 117.26, 45.57. IR ν_{max} (cm^{-1}): 3309, 3050, 2932, 2858, 1597, 1569, 1554, 1508, 1443, 1374, 1308, 1227, 1171, 1118, 1073,

1034, 999, 949, 857, 843, 799, 777, 750, 577. Anal. Calc. for $C_{44}H_{36}N_6O_4 \cdot 1.5H_2O$, %: C 71.43, H 5.31, N 11.36; Found, %: C 71.02, H 4.61, N 11.24.

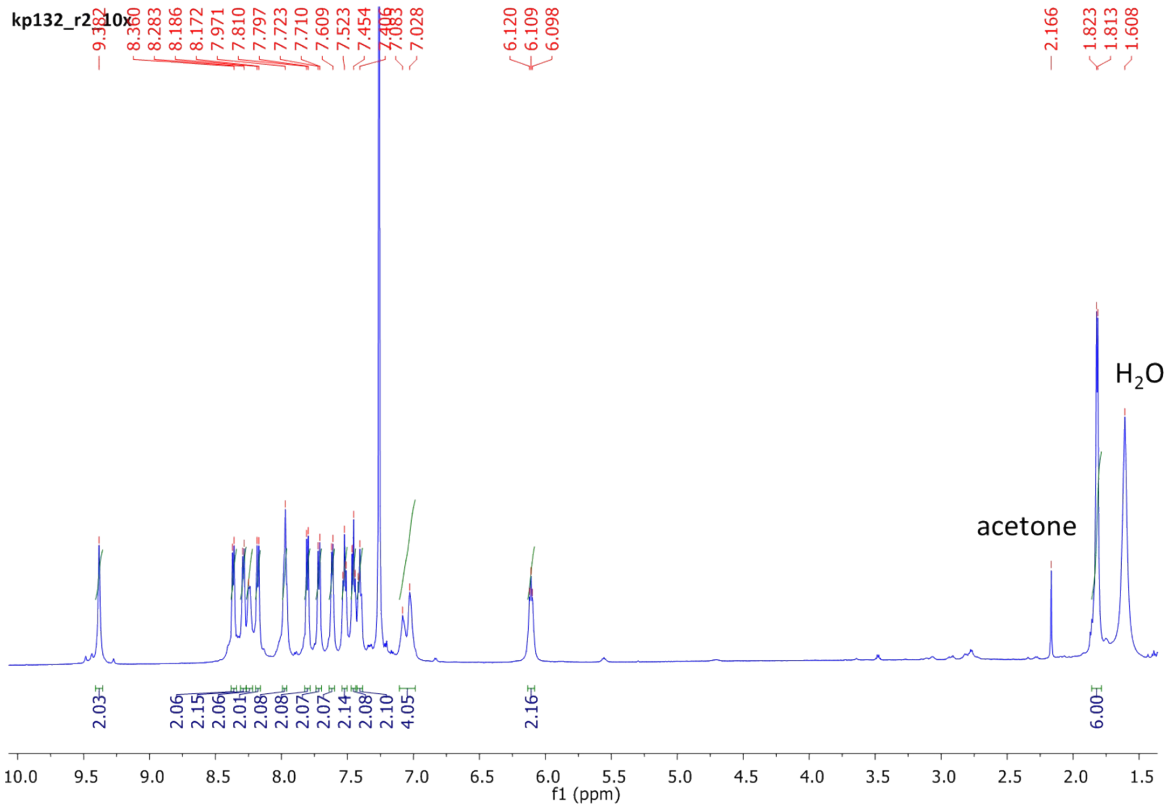


Figure S3. ^{1}H NMR of **3**(*S*,*S*) ($CDCl_3$, 600.1 MHz).

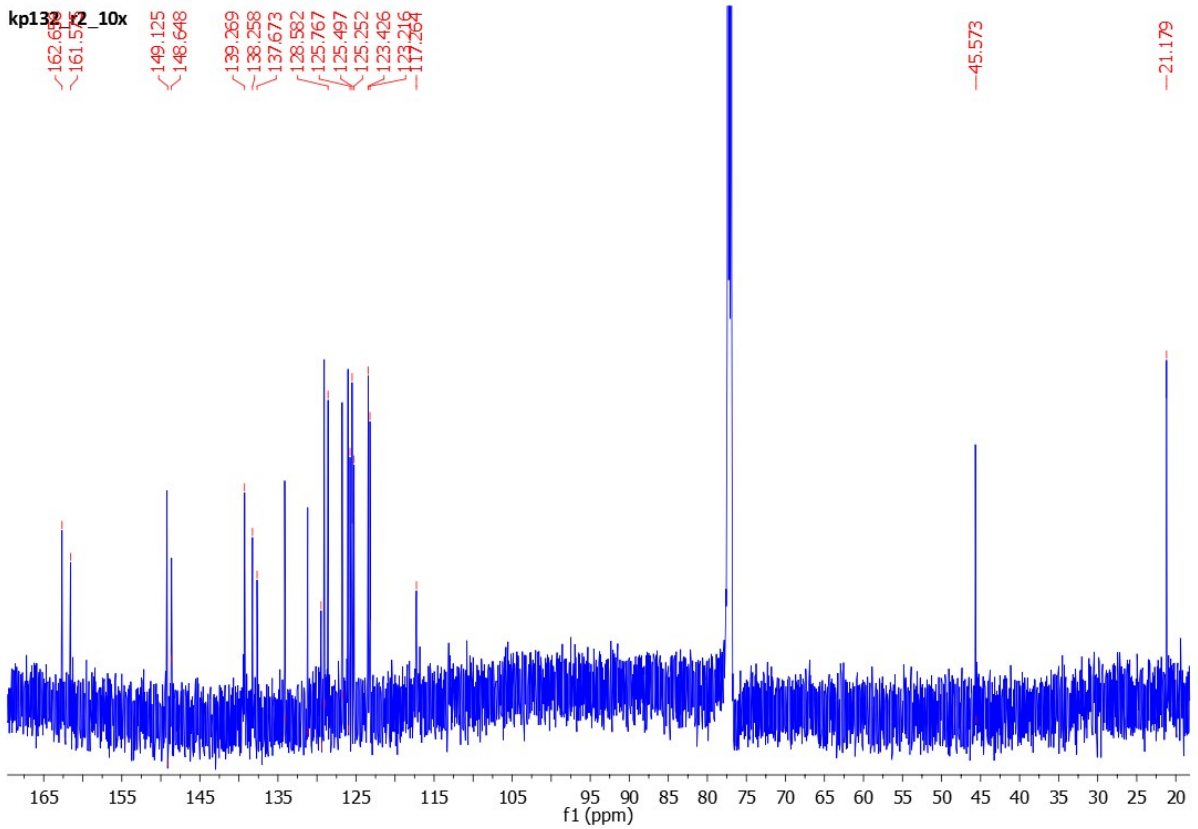


Figure S4. ^{13}C NMR of **3**(*S*,*S*) ($CDCl_3$, 150.2 MHz).

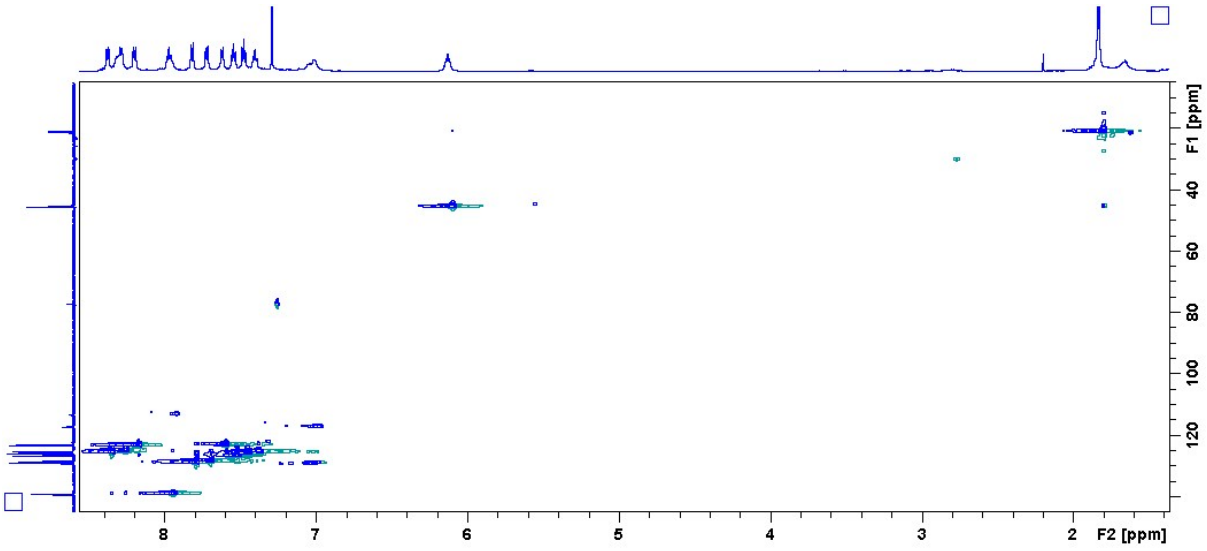


Figure S5. ^{1}H-^{13}C Heteronuclear single quantum coherence spectroscopy (HSQC, $CDCl_3$) NMR of **3**(*S*,*S*).

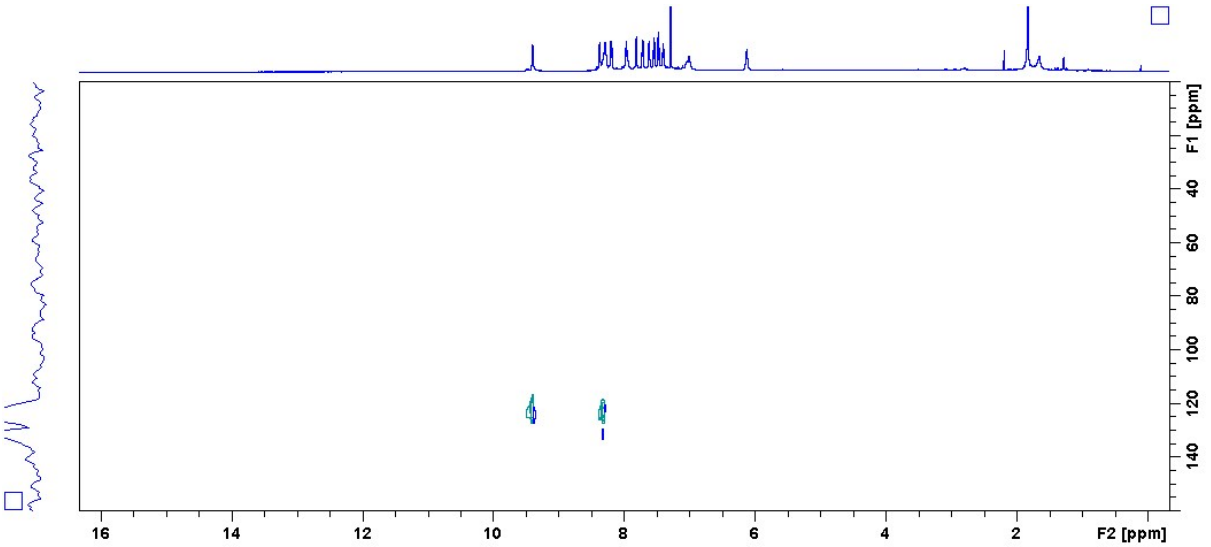


Figure S6. Heteronuclear single quantum coherence spectroscopy (HSQC, $CDCl_3$) NMR of **3**(*S*,*S*).

***N2*-((*R*)-1-(naphthalen-1-yl)ethyl)-N6-(3-(6-((*R*)-1-(naphthalen-1-yl)ethylcarbamoyl)picolinamido)phenyl)pyridine-2,6-dicarboxamide (4(*R*,*R*)):** In a 100 mL round bottom flask **11** (200 mg, 0.62 mmol, 2 equiv.), **8** (33.80 mg, 0.31 mmol, 1 equiv.), HOBt (87.8 mg, 0.65 mmol, 2.1 equiv.), DMAP (45.4 mg, 0.37 mmol, 1.2 equiv.) and Et_3N (90.6 μL, 0.65 mmol, 2.1 equiv.) were mixed in 20 mL of freshly distilled THF. This mixture was cooled down to 0 °C in an acetone/ice bath and left at this temperature for 1 hour under argon atmosphere. After this EDCI (124.6 mg, 0.65 mmol, 2.1 equiv.) was added to the mixture and it was left under argon at 0 °C for another hour. After this the solution was allowed to slowly warm up to room temperature and was let stirring for 24 hours. As a result of the reaction red-brown solution with brown solid was obtained. The solid was then filtered off and THF removed under reduced pressure yielding a brown oil. DCM (30 mL) was then added and organic phase was washed with 1.0 M HCl (3 x 25 mL), saturated solution of $NaHCO_3$ (2 x 25 mL) and H_2O (1 x 25 mL). Organic layer was then collected and dried over $MgSO_4$ which was then filtered off and the solvent evaporated under reduced pressure. The solid was then triturated in ethanol yielding 44 mg of solid (yield 20 %). HRMS (*m/z*) (ESI^+) calculated for $C_{44}H_{37}N_6O_4$ *m/z* = 713.2871 $[M + H^+]^+$. Found *m/z* = 713.2894; ^1H NMR (400 MHz, $CDCl_3$, δ_H) ppm 9.40 (s, 2H, NH), 8.35 (br, 4H, CH+NH), 8.22 (d, 2H, J = 7.6 Hz, CH), 8.15 (d, 2H, J= 8.4 Hz, CH), 7.91 (t, 2H, J = 7.6 Hz, CH), 7.86 (s, 2H, CH), 7.82 (d, 2H, J = 12.4 Hz, CH), 7.78 (d, 2H, J = 8.0 Hz, CH), 7.67 (d, 2H, J = 8.4 Hz, CH), 7.51 (t, 2H, J = 6.8 Hz, CH), 7.44 (t, 2H, J = 7.6 Hz, CH),

7.35 (t, 2H, J = 7.6 Hz, C<u>H</u>), 6.94 (s, 2H, C<u>H</u>), 6.07 (t, 2H, J = 7.2 Hz), 1.78 (d, 6H, J = 6.8 Hz, C<u>H</u>$_3$). ^{13}C NMR (101 MHz, $CDCl_3$, δ_C) 162.75, 161.66, 149.04, 148.48, 139.14, 138.18, 137.45, 134.03, 131.21, 129.29, 129.02, 128.50, 126.74, 125.99, 125.72, 125.41, 125.14, 123.43, 123.21, 117.59, 116.20, 113.62, 45.53, 21.04. IR ν_{max} (cm^{-1}): 3296, 2921, 1557, 1505, 1530, 1491, 1450, 1240, 1076, 845, 779, 750, 585. Anal. Calc. for $C_{44}H_{36}N_6O_4 \cdot 1.6H_2O$, %: C 71.26, H 5.33, N 11.33; Found, %: C 71.21, H 5.14, N 11.25.

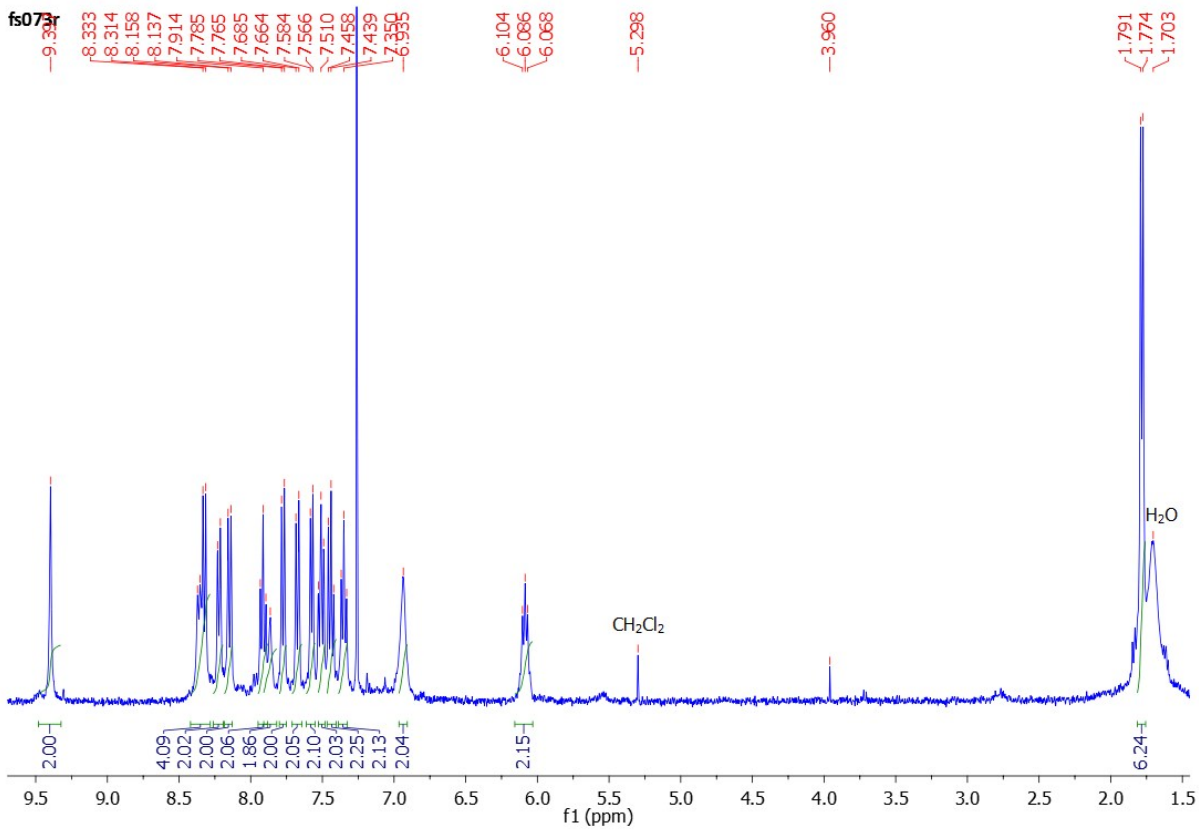


Figure S7. ^{1}H NMR of **4**(*R*,*R*) ($CDCl_3$, 400.1 MHz).

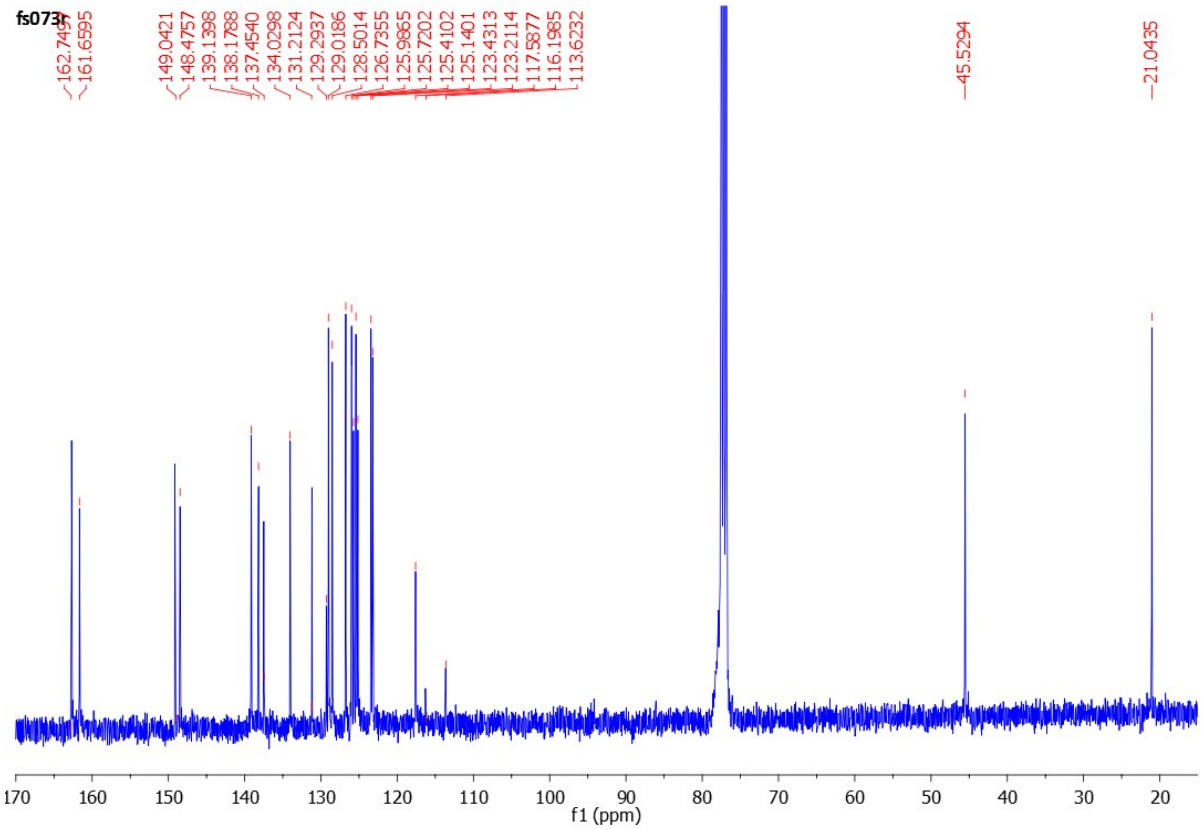


Figure S8. ^{13}C NMR of **4**(*R*,*R*) ($CDCl_3$, 100.6 MHz).

***N2*-(4-(1-(3,5-dimethyl-4-(6-((*S*)-1-(naphthalen-1-yl)ethylcarbamoyl)picolinamido)phenyl)cyclohexyl)-2,6-dimethylphenyl)-N6-((*S*)-1-(naphthalen-1-yl)ethyl)pyridine-2,6-dicarboxamide (5**(*S*,*S*)**):** In a 100 mL round bottom flask **9** (74.2 mg, 0.23 mmol, 1 equiv.), **10** (147.5 mg, 0.46 mmol, 2 equiv.), HOBt (64.9 mg, 0.48 mmol, 2.1 equiv.), DMAP (34.2 mg, 0.28 mmol, 1.2 equiv.) and Et_3N (67 μL, 0.48 mmol, 2.1 equiv.) were mixed in 20 mL of freshly distilled THF. This mixture was cooled down to 0 °C in an acetone/ice bath and left at this temperature for 1 hour under argon atmosphere. After this EDCI (92 mg, 0.48 mmol, 2.1 equiv.) was added to the mixture and it was left under argon at 0 °C for another hour. After this the solution was allowed to slowly warm up to room temperature and was let stirring for 24 hours. As a result of the reaction yellow solution containing solid was obtained. The solid was then filtered off and THF removed under reduced pressure yielding a yellow oil. DCM (30 mL) was then added and organic phase was washed with 1.0 M HCl (3 x 20 mL), saturated solution of $NaHCO_3$ (2 x 20 mL) and H_2O (1 x 25 mL). Organic layer was then collected and dried over $MgSO_4$ which was then filtered off and the solvent evaporated under reduced pressure. The solid was then dissolved in a minimum

amount of $CHCl_3$ and added to a swirling solution of diethyl ether. A white solid was then precipitated and was collected by filtration through Hirsch funnel yielding 41.2 mg of white solid (yield 19.6 %). HRMS (*m/z*) (ESI^+) calculated for $C_{60}H_{58}N_6O_4Na$ *m/z* = 949.4417 $[M + Na^+]^+$. Found *m/z* = 949.4379; ^1H NMR (400 MHz, $CDCl_3$, δ_H) ppm 8.84 (s, 2H, NH), 8.43 (br, 4H, CH), 8.19 (d, 2H, J = 8.8 Hz, CH), 8.08 (t, 2H, J= 7.6 Hz, CH), 7.91 (d, 2H, J = 8.8 Hz, CH), 7.85 (d, 2H, J = 7.6 Hz, CH), 7.80 (d, 2H, J = 8.0 Hz, CH), 7.60 (d, 2H, J = 6.8 Hz, CH), 7.46 (br, 6H, CH+NH), 7.02 (s, 4H, CH), 6.14 (q, 2H, J = 7.2 Hz, CH), 2.24 (br, 4H, CH_2), 2.13 (br, 12H, CH_3), 1.81 (d, 6H, J = 6.8 Hz, CH_3), 1.48 (br, 6H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$, δ_C) 162.46, 161.40, 148.90, 147.60, 139.34, 138.09, 134.80, 134.13, 131.13, 130.79, 129.08, 128.73, 127.18, 126.77, 126.04, 125.57, 125.42, 123.38, 122.96, 45.39, 37.14, 26.41, 23.00, 21.16, 19.02. IR ν_{max} (cm^{-1}): 3301, 3049, 2931, 2855, 1654, 1597, 1508, 1444, 1375, 1338, 1308, 1235, 1171, 1074, 1033, 999, 948, 858, 843, 799, 777, 751, 678. Anal. Calc. for $C_{60}H_{58}N_6O_4 \cdot 1.6H_2O$, %: C 75.38, H 6.45, N 8.79; Found, %: C 75.47, H 6.41, N 8.67.

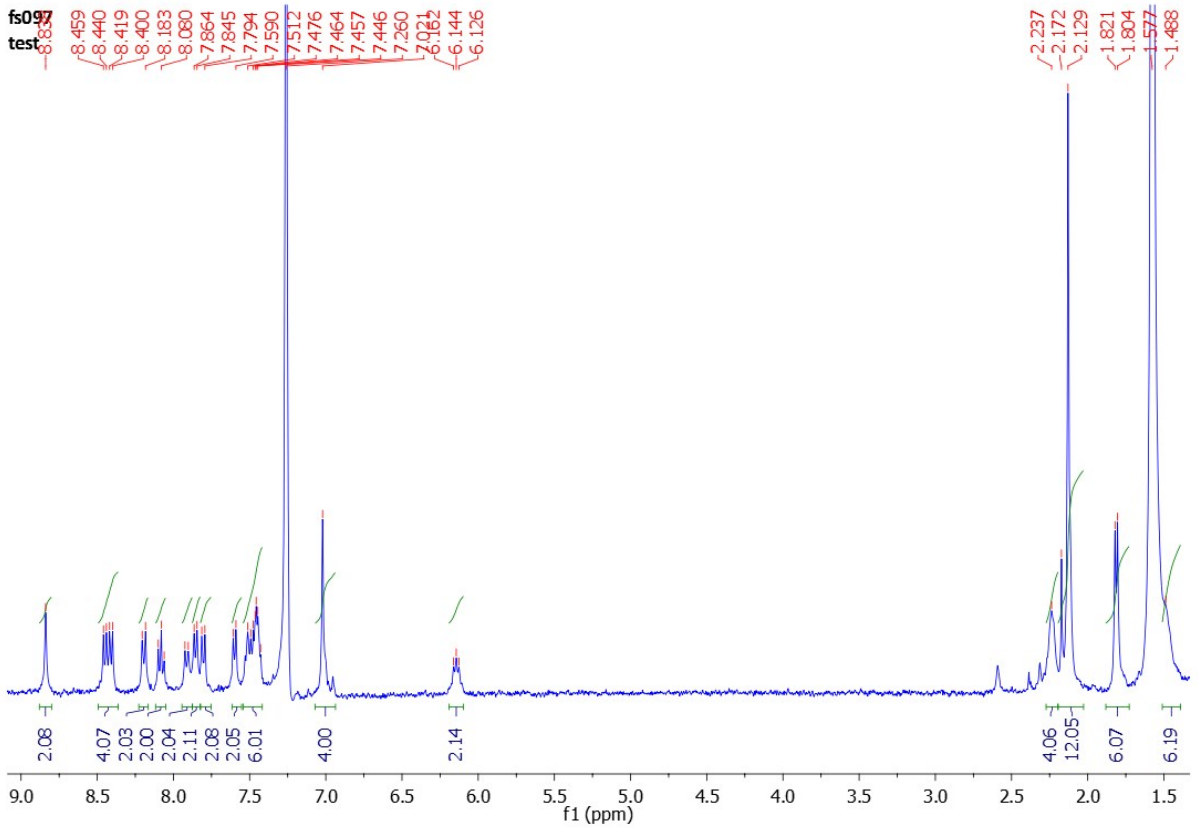


Figure S9. ^1H NMR of **5**(*S*,*S*) ($CDCl_3$, 400.1 MHz).

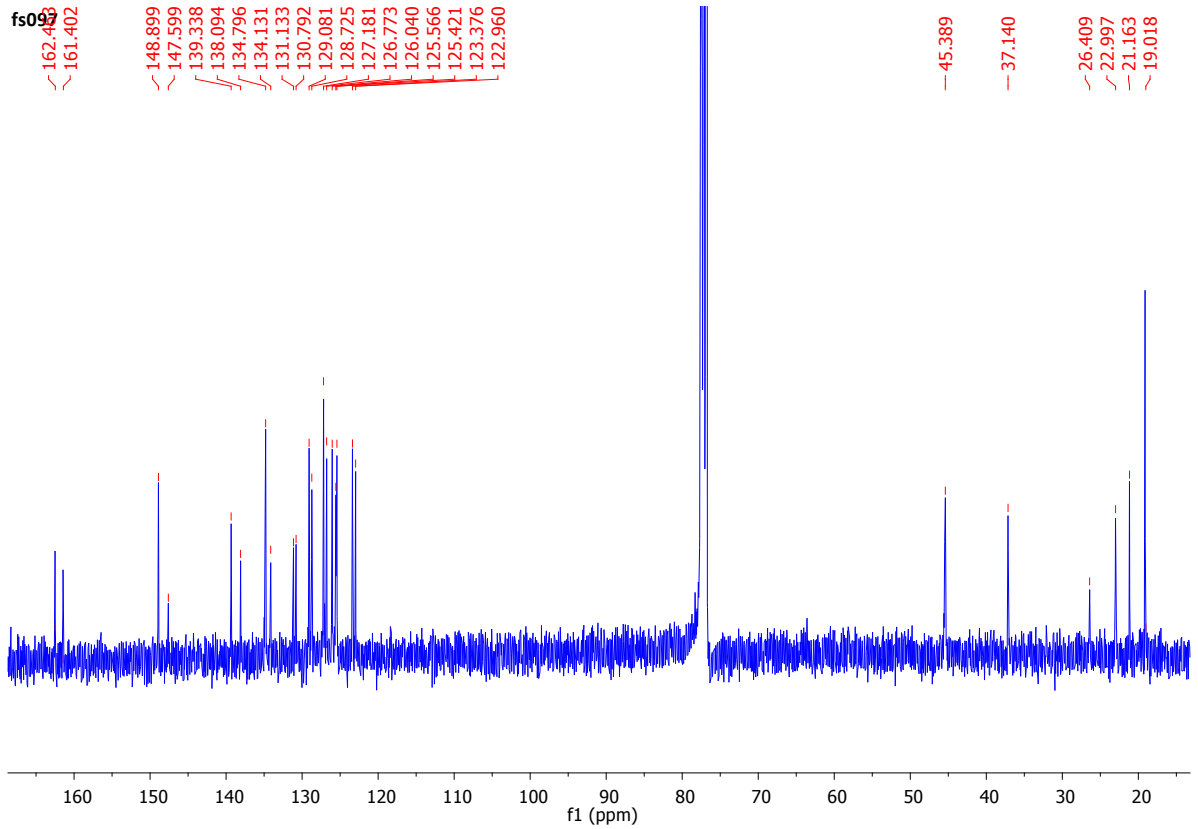


Figure S10. ^{13}C NMR of **5**(*S*,*S*) ($CDCl_3$, 100.6 MHz).

***N2*-(4-(1-(3,5-dimethyl-4-(6-((*R*)-1-(naphthalen-1-yl)ethylcarbamoyl)picolinamido)phenyl)cyclohexyl)-2,6-dimethylphenyl)-N6-((*R*)-1-(naphthalen-1-yl)ethyl)pyridine-2,6-dicarboxamide (6**(*R*,*R*)**):** In a 100 mL round bottom flask **9** (151.1 mg, 0.47 mmol, 1 equiv.), **11** (300.0 mg, 0.94 mmol, 2 equiv.), HOBt (133.0 mg, 0.98 mmol, 2.1 equiv.), DMAP (68.6 mg, 0.56 mmol, 1.2 equiv.) and Et_3N (99.5 µL, 0.71 mmol, 1.5 equiv.) were mixed in 20 mL of freshly distilled THF. This mixture was cooled down to 0 °C in an acetone/ice bath and left at this temperature for 1 hour under argon atmosphere. After this EDCI (188.4 mg, 0.98 mmol, 2.1 equiv.) was added to the mixture and it was left under argon at 0 °C for another hour. After this the solution was allowed to slowly warm up to room temperature and was let stirring for 24 hours. As a result of the reaction yellow solution containing solid was obtained. The solid was then filtered off and THF removed under reduced pressure yielding a yellow oil. DCM (30 mL) was then added and organic phase was washed with 1.0 M HCl (3 x 20 mL), saturated solution of $NaHCO_3$ (2 x 20 mL) and H_2O (1 x 25 mL). Organic layer was then collected and dried over $MgSO_4$ which was then filtered off and the solvent evaporated under reduced pressure. The solid was then dissolved in a minimum

amount of $CHCl_3$ and added to a swirling solution of diethyl ether. A white solid was then precipitated and was collected by filtration through Hirsch funnel yielding 82.8 mg of white solid (yield 19 %). HRMS (*m/z*) (ESI^+) calculated for $C_{60}H_{58}N_6O_4Na$ *m/z* = 949.4417 $[M + Na^+]^+$. Found *m/z* = 949.4434; ^1H NMR (600 MHz, $CDCl_3$, δ_H) ppm 8.99 (s, 2H, NH), 8.36 (t, 4H, J = 7.2 Hz, CH), 8.17 (d, 2H, J = 9.0 Hz, CH), 8.08 (d, 2H, J= 8.4 Hz, NH), 7.99 (t, 2H, J = 7.2 Hz, CH), 7.83 (d, 2H, J = 7.8 Hz, CH), 7.76 (d, 2H, J = 8.4 Hz, CH), 7.56 (d, 2H, J = 6.6 Hz, CH), 7.50 (t, 2H, J = 7.2 Hz, CH), 7.42 (m, 4H, CH), 7.03 (br, 4H, CH), 6.04 (q, 2H, J = 7.8 Hz, CH), 2.25 (br, 4H, CH_2), 2.14 (br, 12H, CH_3), 1.72 (d, 6H, J = 6.6 Hz, CH_3), 1.56 (br, 4H, CH_2), 1.48 (br, 2H, CH_2). ^{13}C NMR (150 MHz, $CDCl_3$, δ_C) 162.56, 161.51, 148.96, 148.93, 147.60, 139.28, 138.21, 134.82, 134.74, 134.14, 132.69, 131.15, 130.89, 129.08, 128.67, 127.15, 127.09, 127.05, 126.75, 126.02, 125.54, 125.45, 125.41, 123.39, 122.97, 45.46, 45.42, 37.22, 37.12, 26.43, 23.01, 21.19, 19.11, 19.07. IR ν_{max} (cm^{-1}): 3300, 3045, 2933, 2858, 1664, 1597, 1508, 1444, 1375, 1339, 1308, 1234, 1171, 1073, 1034, 999, 949, 857, 842, 825, 799, 775, 751, 723, 678. Anal. Calc. for $C_{60}H_{58}N_6O_4 \cdot 2H_2O$, %: C 74.87, H 6.22, N 8.74; Found, %: C 74.82, H 6.49, N 8.73.

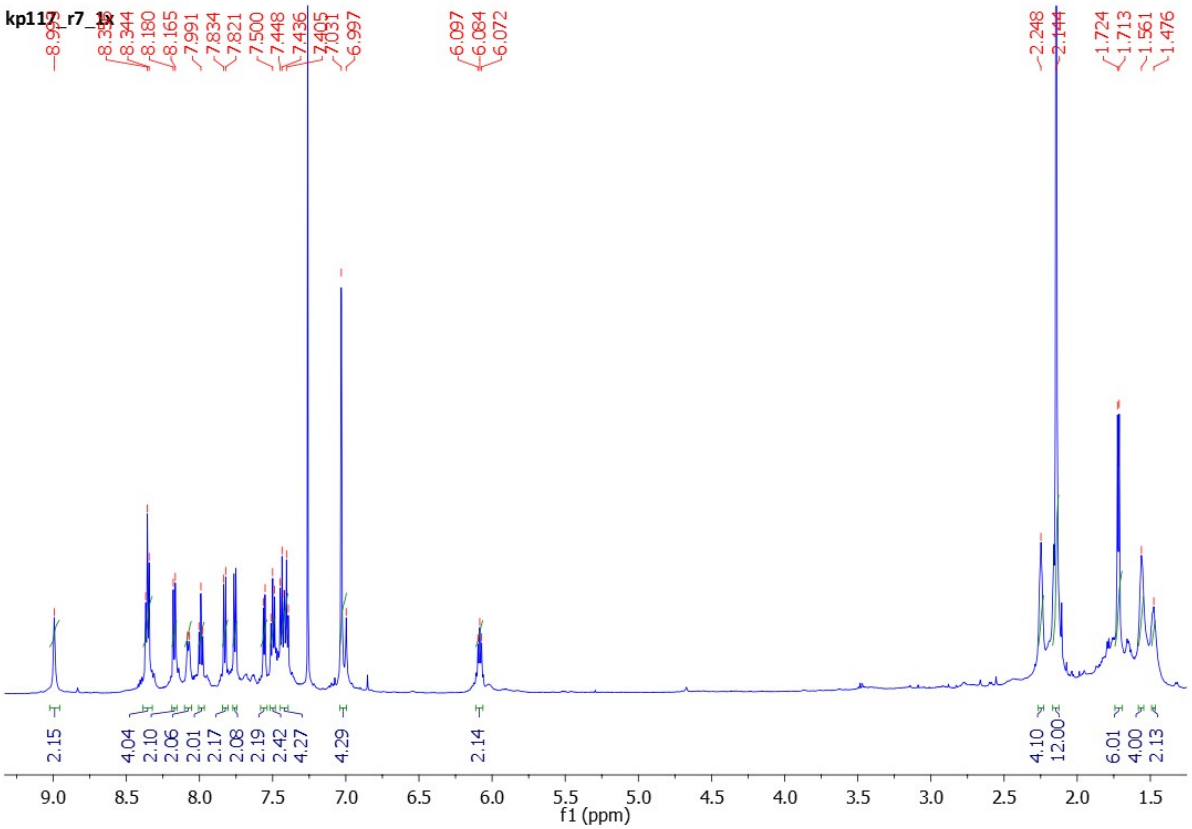


Figure S11. ^1H NMR of **6**(*R*,*R*) ($CDCl_3$, 600.1 MHz).

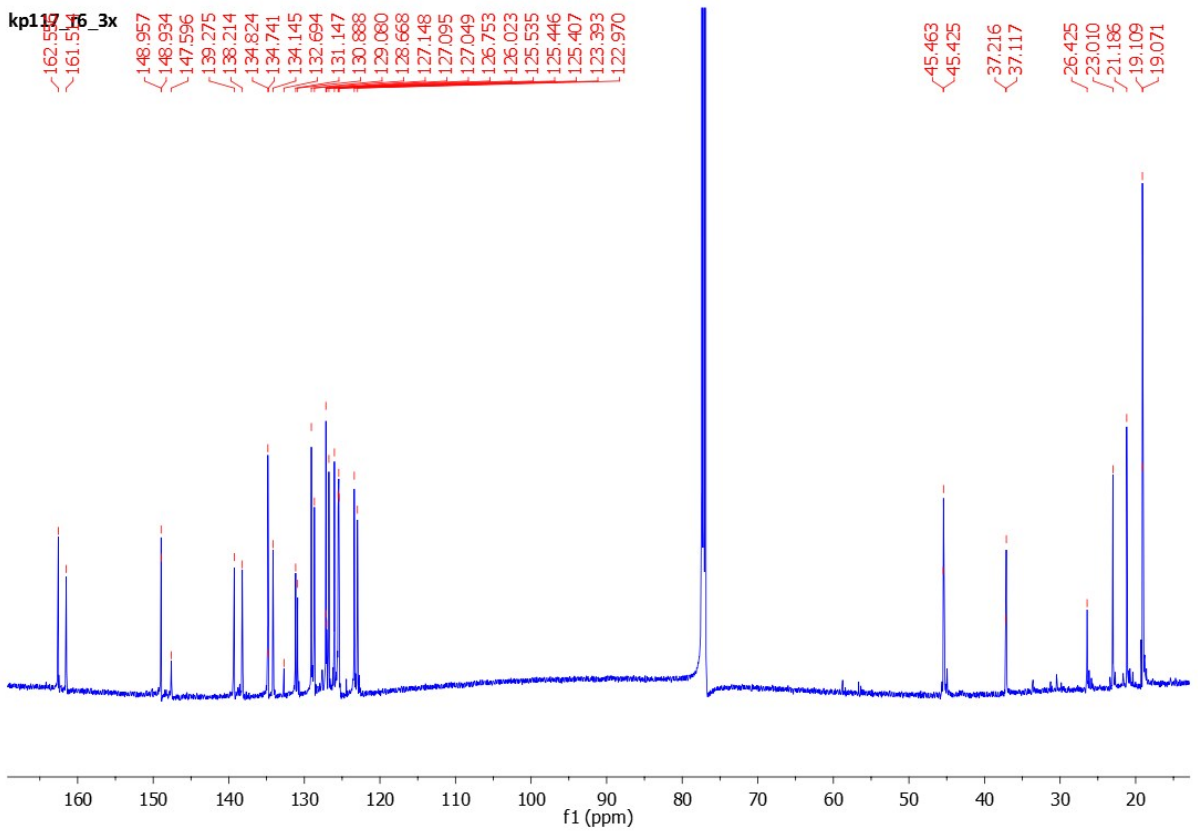


Figure S12. ^{13}C NMR of **6**(*R*,*R*) ($CDCl_3$, 150.2 MHz).

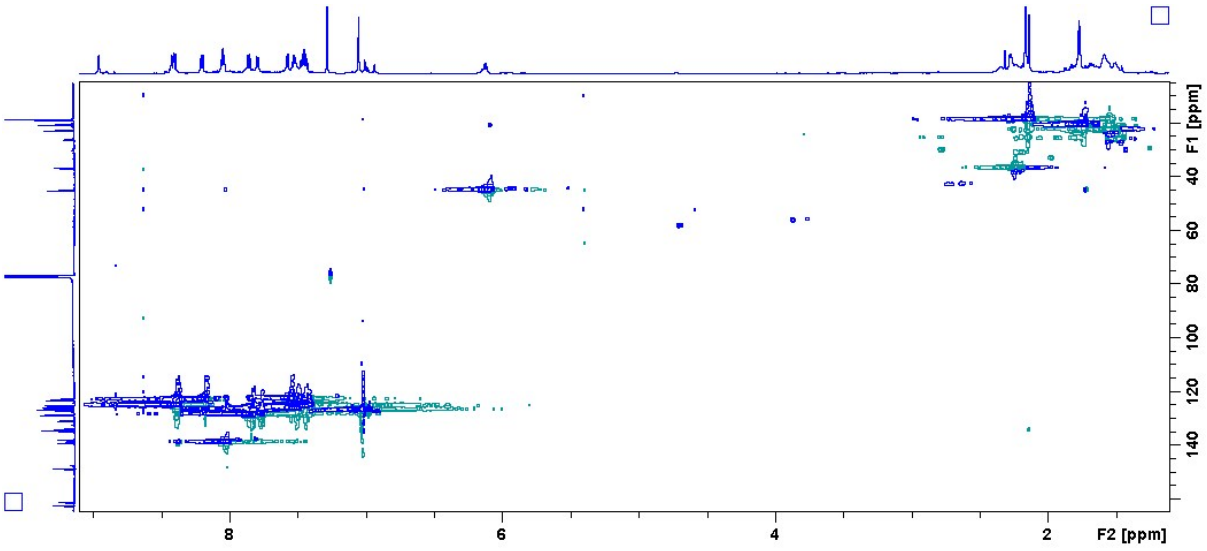


Figure S13. ^{1}H-^{13}C Heteronuclear single quantum coherence spectroscopy (HSQC, $CDCl_3$) NMR of **6**(*R*,*R*).

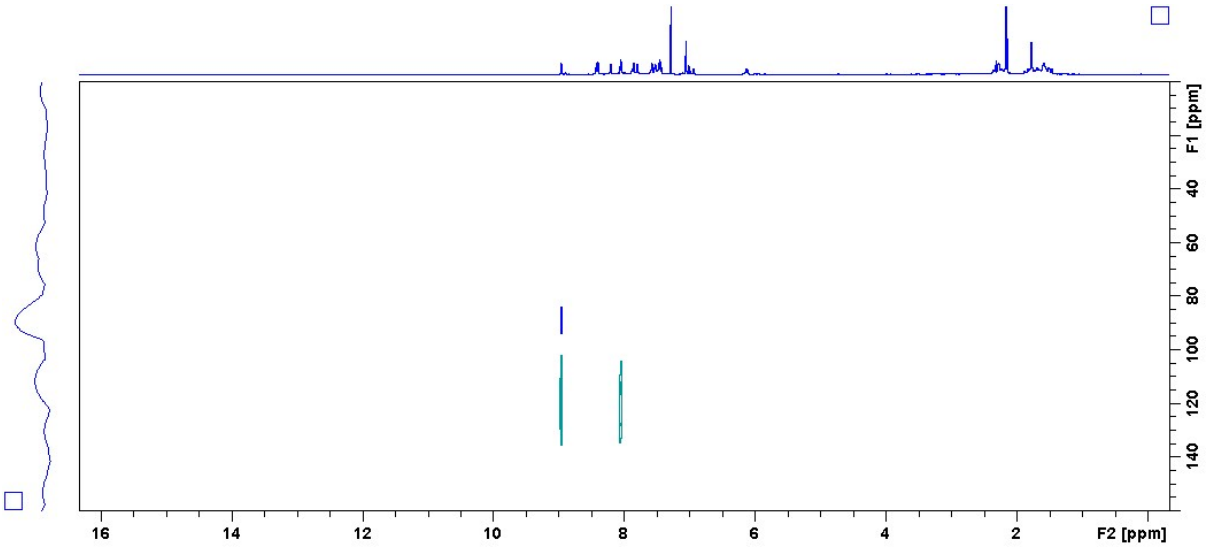


Figure S14. Heteronuclear single quantum coherence spectroscopy (HSQC, $CDCl_3$) NMR of **6**(*R*,*R*).

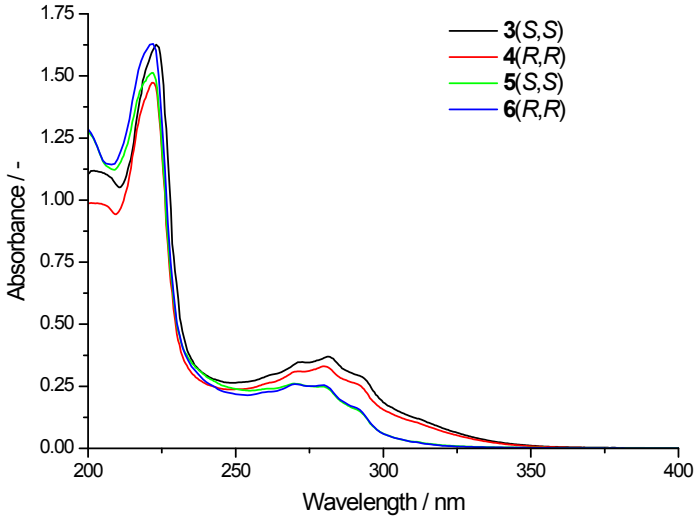


Figure S15. UV-visible spectra for ligands **3**(*S*,*S*) (c = 1.06×10^{-5} M), **4**(*R*,*R*) (c = 7.36×10^{-6} M) and **5**(*S*,*S*) (c = 1.06×10^{-5} M), **6**(*R*,*R*) (c = 1.09×10^{-5} M) in CH_3CN; T = 25 °C.

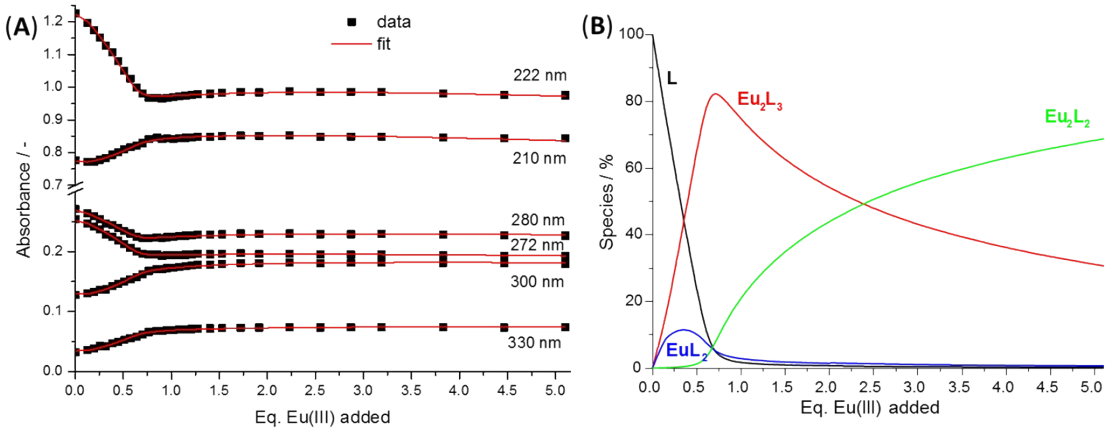


Figure S16. (A) Experimental binding isotherms for the UV-visible titration of **4**(*R*,*R*) ($c = 7.84\times10^{-6}$ M) with $Eu(OTf)_3$ (0→5 equiv.) in CH_3CN at T = 25 °C and their corresponding fits by means of SPECFIT(—), (B) Speciation-distribution diagram obtained from the fit.

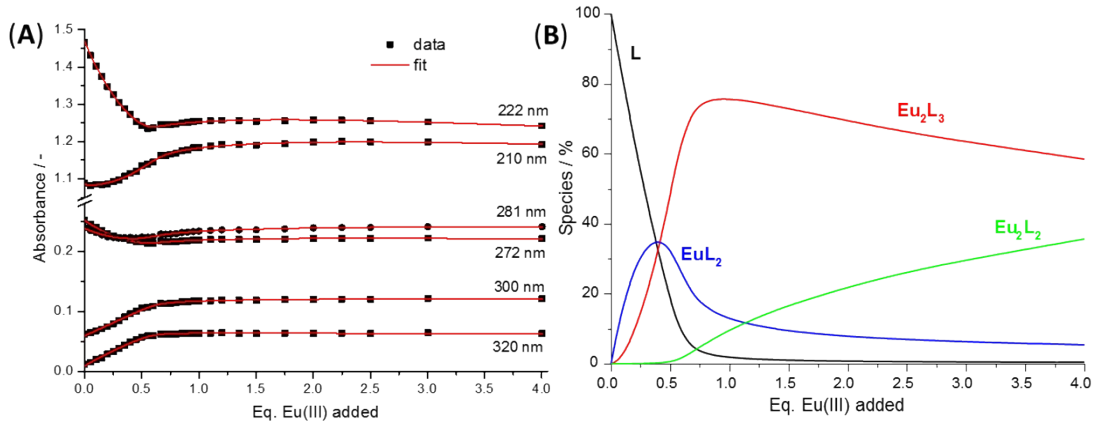


Figure S17. (A) Experimental binding isotherms for the UV-visible titration of **5**(*S*,*S*) ($c = 1.00\times10^{-5}$ M) with $Eu(OTf)_3$ (0→4 equiv.) in CH_3CN at T = 25 °C and their corresponding fits by means of SPECFIT(—), (B) Speciation-distribution diagram obtained from the fit.

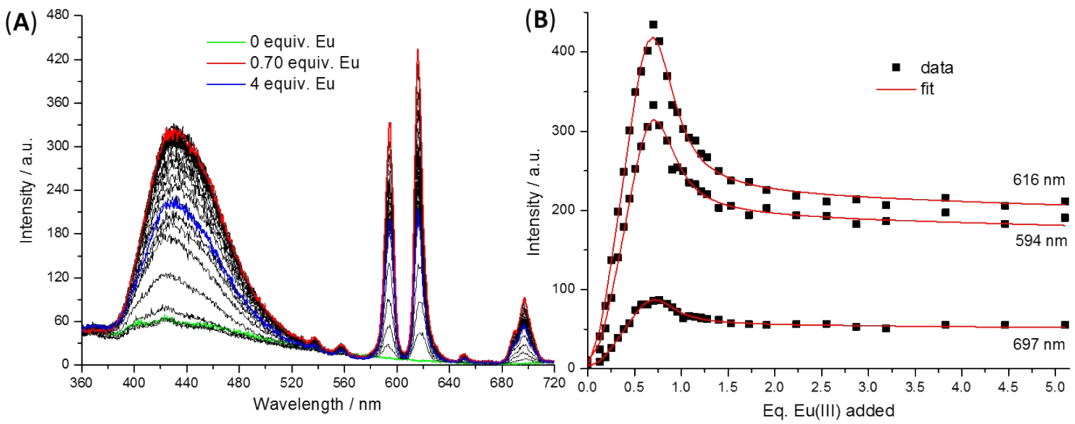


Figure S18. (A) The changes in the fluorescence spectrum of **4**(*R*,*R*) (c = 7.84×10^{-6} M) upon addition of Eu(OTf)$_3$ (0→5 equiv.) in CH_3CN at T = 25 °C, λ_{ex} = 281 nm; (B) experimental binding isotherms for the same titration and their corresponding fits by means of SPECFIT.

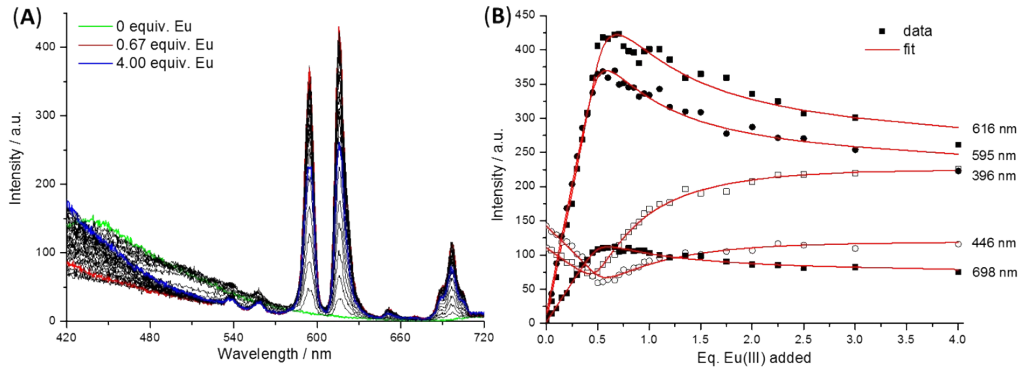


Figure S19. (A) The changes in the fluorescence spectrum of **5**(*S*,*S*) (c = 1.00×10^{-5} M) upon addition of Eu(OTf)$_3$ (0→4 equiv.) in CH_3CN at T = 25 °C, λ_{ex} = 281 nm; (B) experimental binding isotherms for the same titration and their corresponding fits by means of SPECFIT.

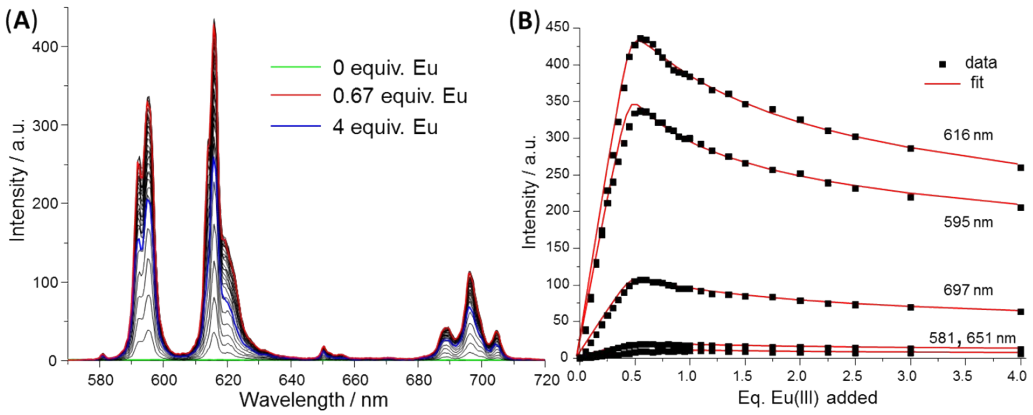


Figure S20. (A) The changes in the Eu(III)-centred emission spectrum of **5**(*S*,*S*) (c = 1.00×10^{-5} M) upon addition of $Eu(OTf)_3$ (0→4 equiv.) in CH_3CN at T = 25 °C, λ_{ex} = 281 nm; (B) experimental binding isotherms for the same titration and their corresponding fits by means of SPECFIT.

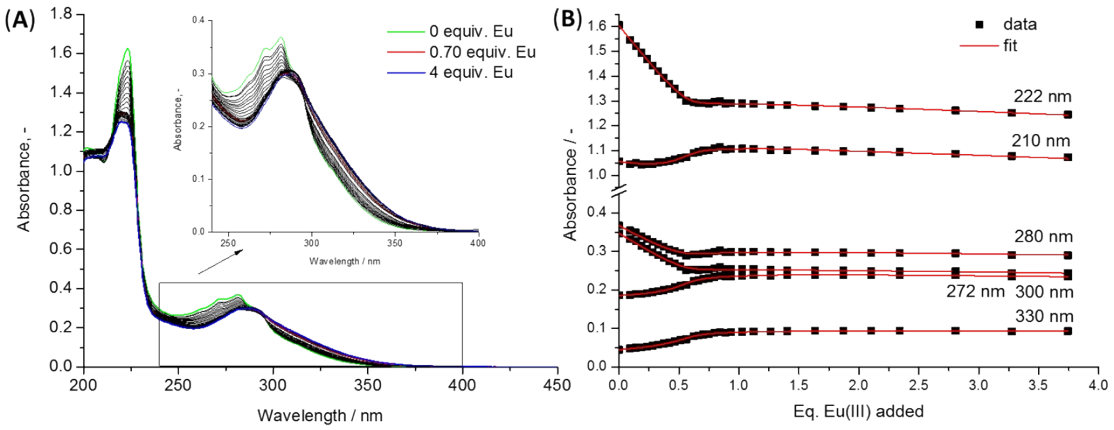


Figure S21. The changes in the absorption spectrum of (A) **3**(*S,S*) (c = 1.07×10^{-5} M) upon addition of $Eu(OTf)_3$ (0→4 equiv.) in CH_3CN at 25 °C and (B) experimental binding isotherms for the same titration and their corresponding fits by means of SPECFIT.

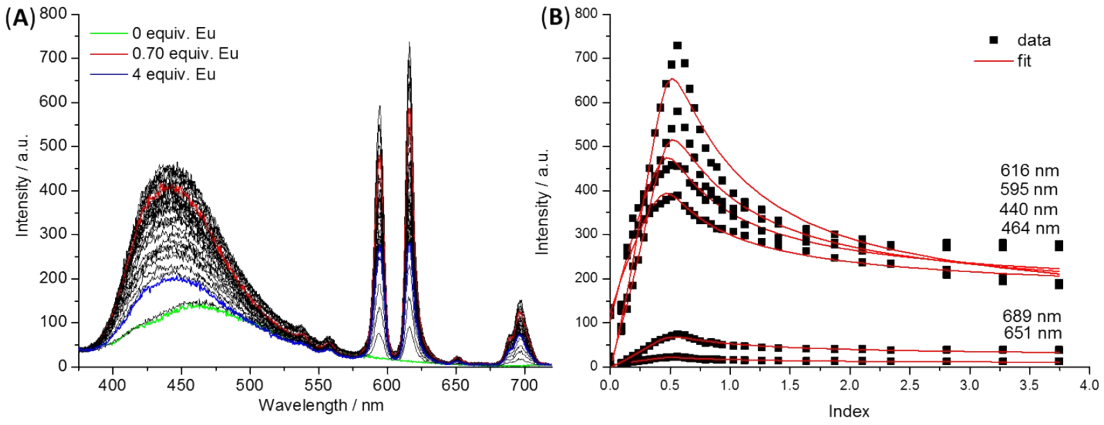


Figure S22. The changes in the fluorescence spectrum of (A) **3**(*S*,*S*) (c = 1.07×10^{-5} M) upon addition of $Eu(OTf)_3$ (0→4 equiv.) in CH_3CN at 25 °C (λ_{ex} = 281 nm) and (B) experimental binding isotherms for the same titration and their corresponding fits by means of SPECFIT.

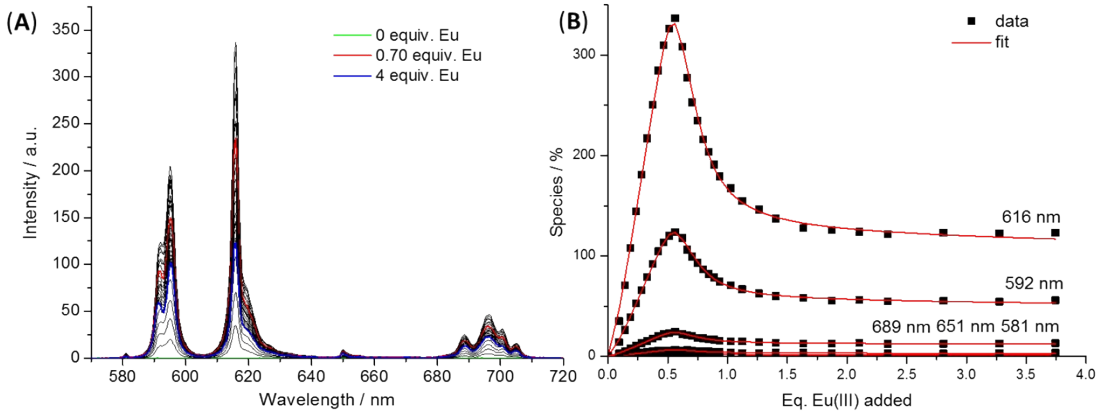


Figure S23. The changes in the Eu(III)-centred emission spectrum of (A) **3**(*S*,*S*) (c = 1.07×10^{-5} M) upon addition of $Eu(OTf)_3$ (0→4 equiv.) in CH_3CN at 25 °C (λ_{ex} = 281 nm) and (B) experimental binding isotherms for the same titration and their corresponding fits by means of SPECFIT.

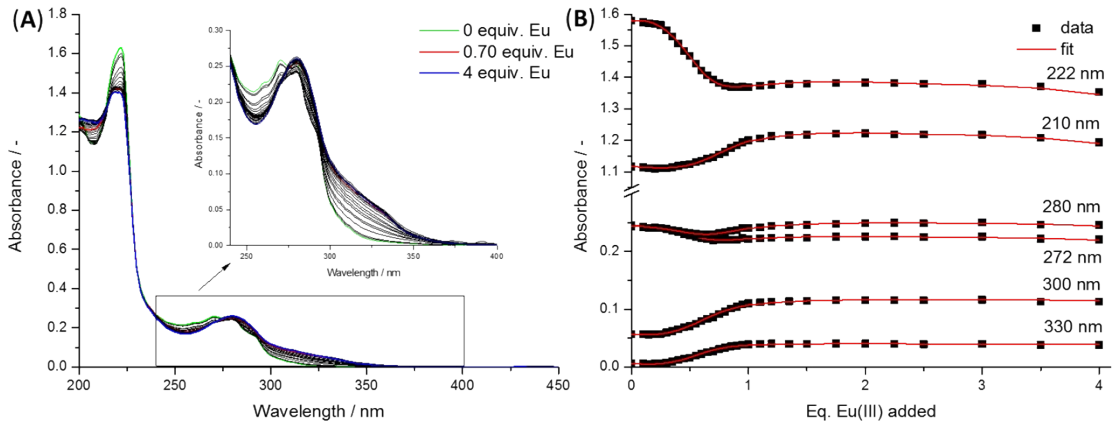


Figure S24. The changes in the absorption spectrum of (A) **6**(*R*,*R*) (c = 1.09×10^{-5} M) upon addition of $Eu(OTf)_3$ (0→4 equiv.) in CH_3CN at 25 °C and (B) experimental binding isotherms for the same titration and their corresponding fits by means of SPECFIT.

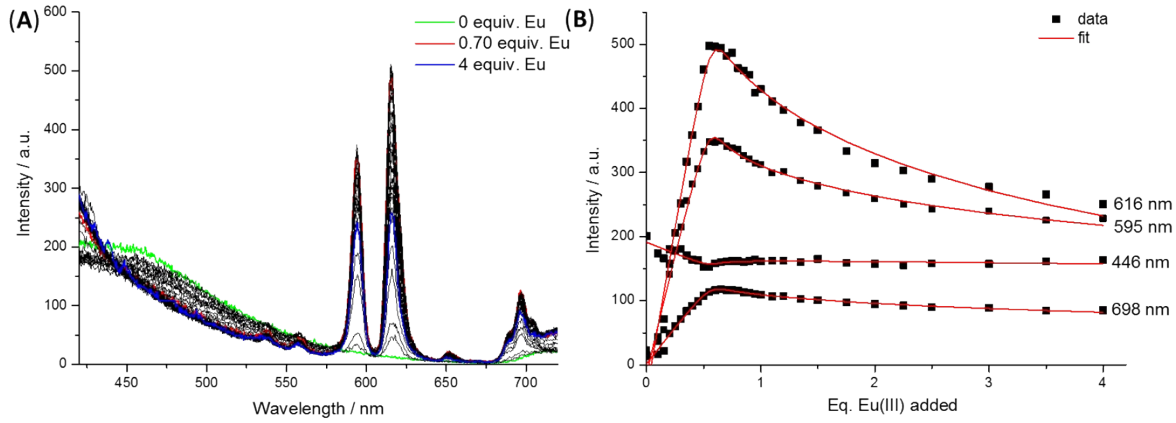


Figure S25. The changes in the fluorescence spectrum of (A) **6**(*R*,*R*) (c = 1.09×10^{-5} M) upon addition of $Eu(OTf)_3$ (0→4 equiv.) in CH_3CN at 25 °C (λ_{ex} = 281 nm) and (B) experimental binding isotherms for the same titration and their corresponding fits by means of SPECFIT.

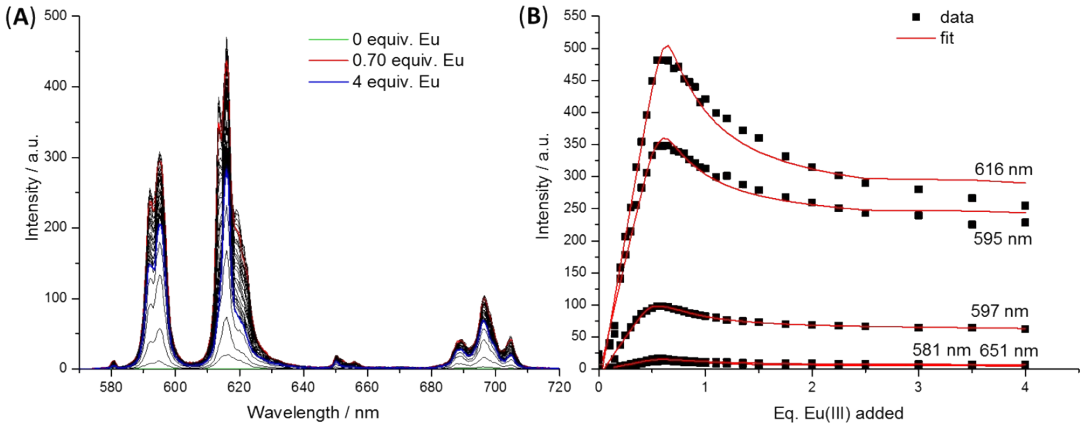


Figure S26. The changes in the Eu(III)-centred emission spectrum of (A) **6**(*R*,*R*) (c = 1.09×10^{-5} M) upon addition of $Eu(OTf)_3$ (0→4 equiv.) in CH_3CN at 25 °C (λ_{ex} = 281 nm) and (B) experimental binding isotherms for the same titration and their corresponding fits by means of SPECFIT.

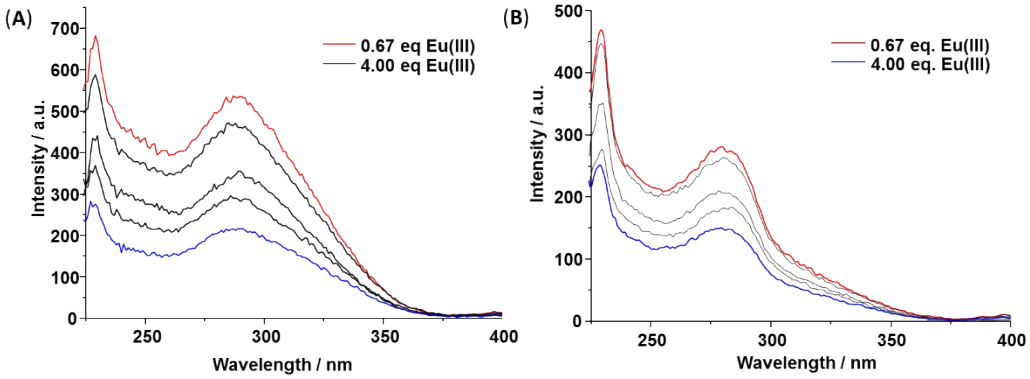


Figure S27. Excitation spectra recorded during the titration experiments for (A) **3**(*S*,*S*) (c = 1.07×10^{-5} M) and (B) **6**(*R*,*R*) (c = 1.09×10^{-5} M) upon addition of Eu(III) (0→4 equiv.) where the emission was monitored at the emission maximum λ_{em} = 616 nm with time delay of 0.1 ms.

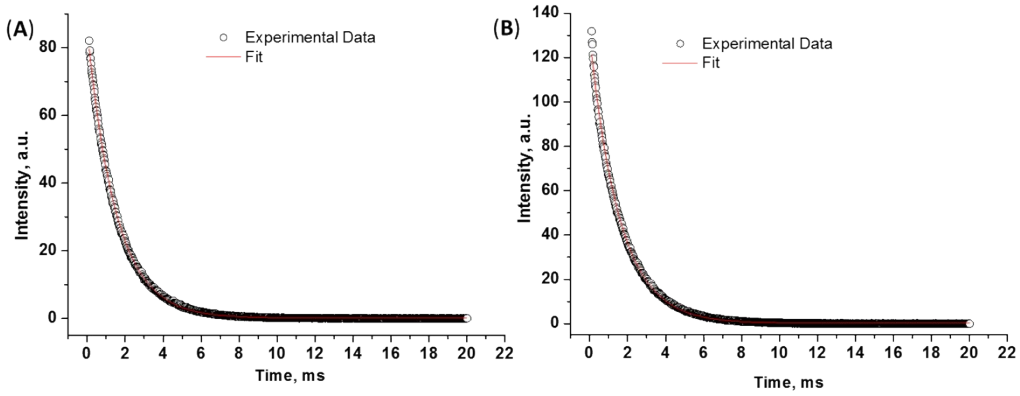


Figure S28. Phosphorescence life-times of the Eu($^5D_0$) excited state recorded during the course of the titration experiments for (A) **4**(*R*,*R*) and (B) **6**(*R*,*R*) upon addition of 0.67 equiv. of Eu(III).

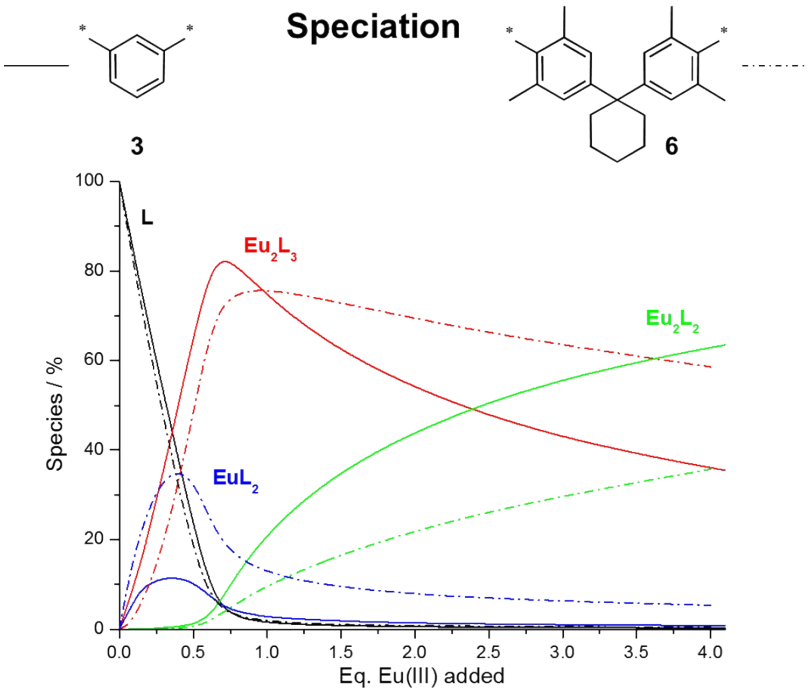


Figure S29. Comparison of speciation-distribution diagrams obtained from the fit of the titrations of **4**(*R*,*R*) and **5**(S,S) upon addition of $Eu(OTf)_3$ (0→4 equiv.) in CH_3CN at T = 25 °C.

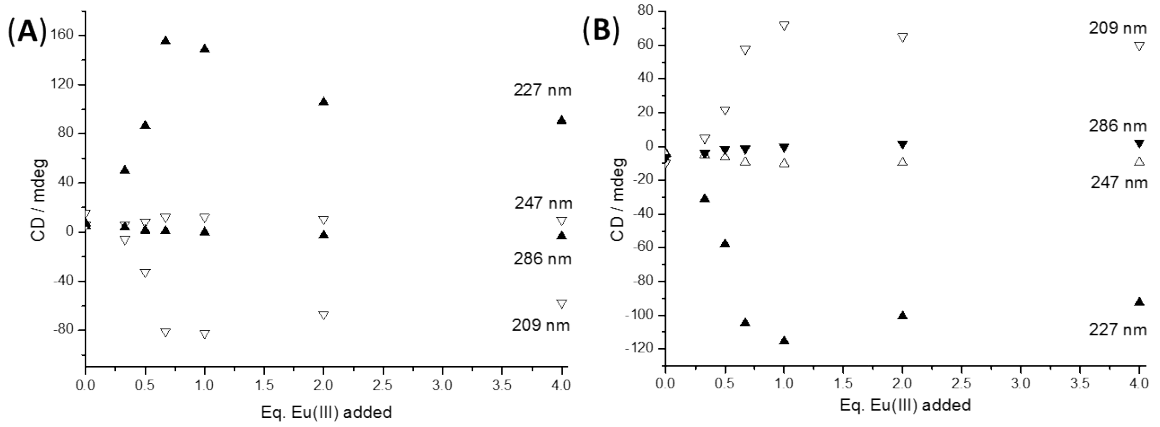


Figure S30. Experimental binding isotherms for the CD titrations of (A) **5**(*S*,*S*) (c = 1.40 x 10^{-5} M) and (B) **6**(*R*,*R*) (c = 1.34×10^{-5} M) upon addition of $Eu(OTf)_3$ (0→4 equiv.).

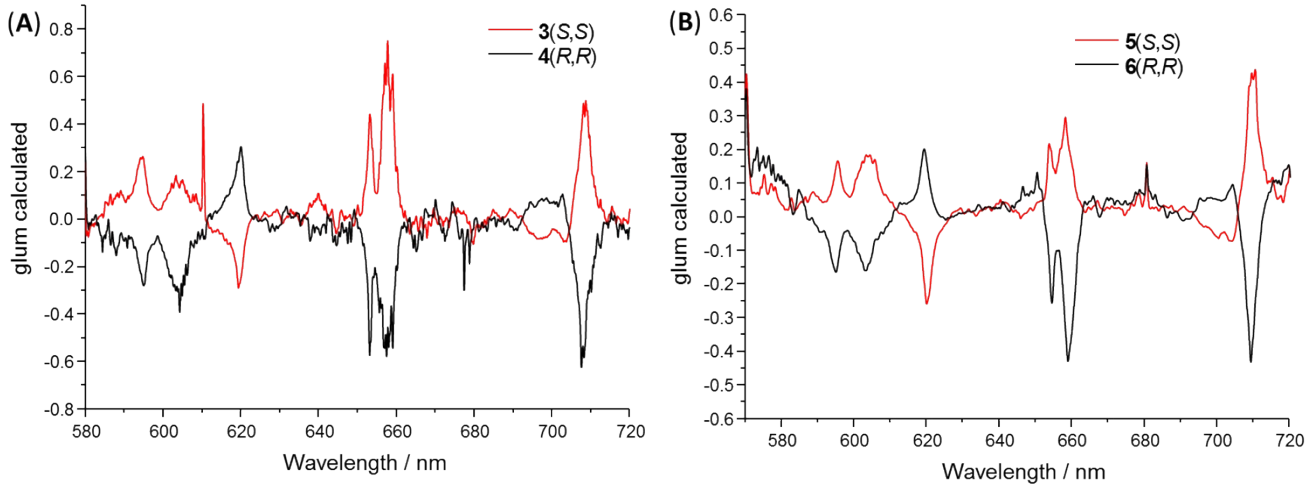


Figure S31. G-value plots derived from circularly polarised luminescence spectra and total luminescence emission of $\mathbf{Eu_2L_3}$ complexes in CH_3CN (c = 3.33×10^{-5} M) where **L** is (A) **3**(*S*,*S*), **4**(*R*,*R*) and (B) **L** = **5**(*S*,*S*), **6**(*R*,*R*) (λ_{ex} = 281 nm) (see Figure 5 – main text).

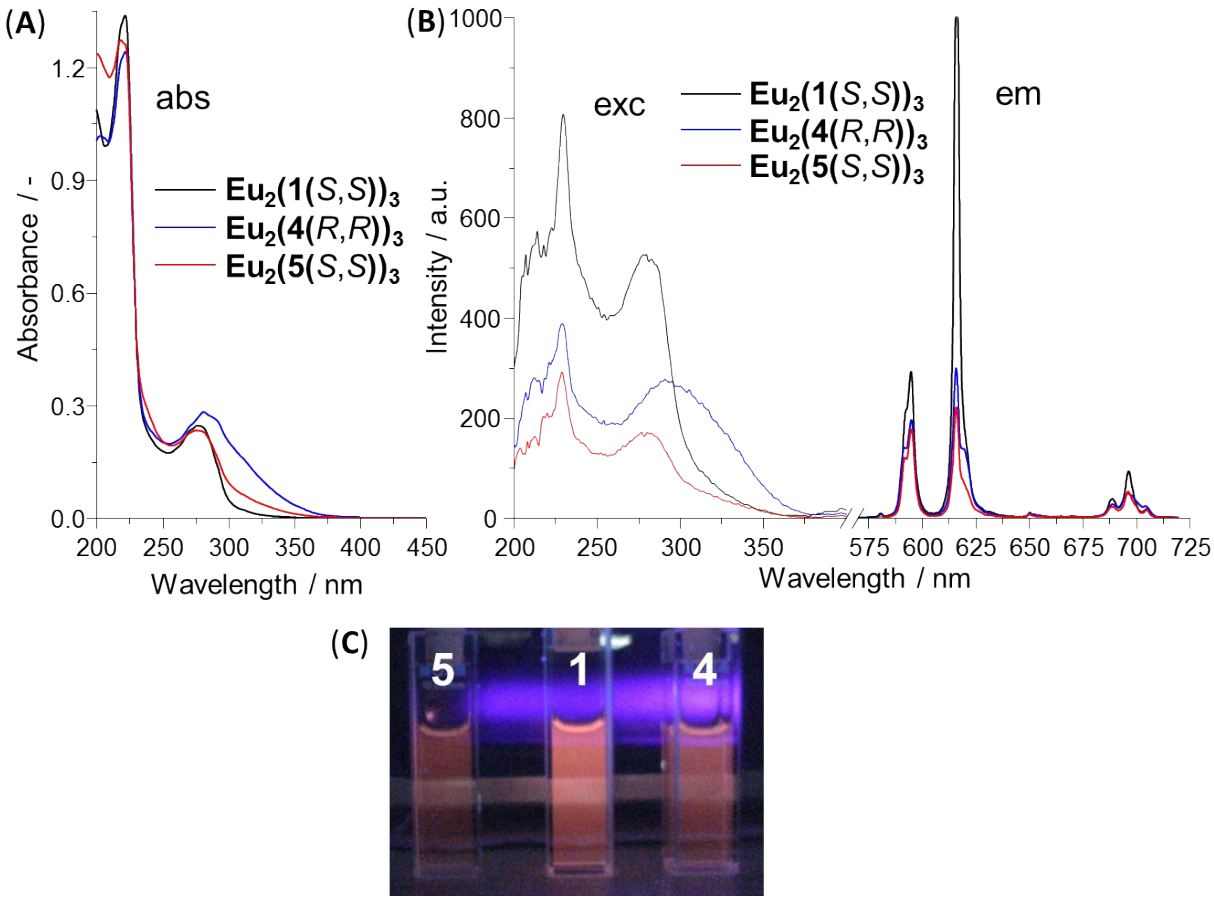


Figure S32. Comparison of luminescent properties between Eu(III) helicate complexes **Eu_2:L_3** (**L** = **1**(*S*,*S*), **4**(*R*,*R*), **5**(*S*,*S*)) (c = 3.33×10^{-6} M) in CH_3CN (λ_{ex} = 281 nm).

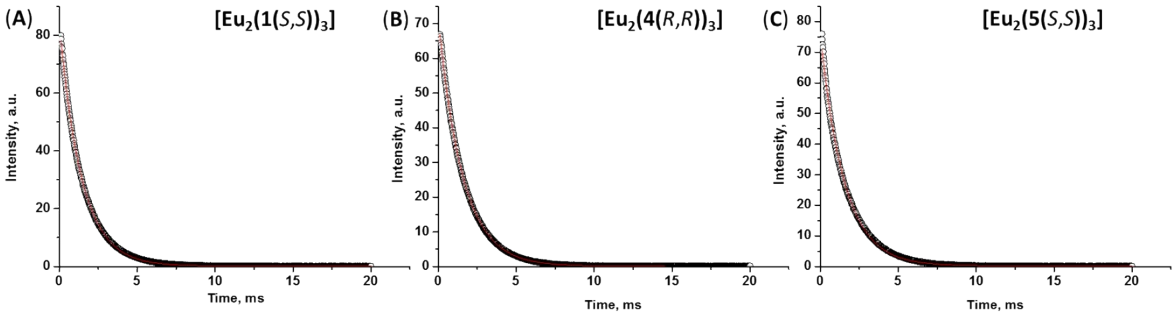


Figure S33. Experimental $^5D_0 \rightarrow {}^7F_2$ emission decay of Eu(III) luminescence (ooo) upon ligand excitation at 279 nm and their corresponding fit (–) for (A) [**Eu_2(1**(*S*,*S*)$_3$], (B) [**Eu_2(4**(*R*,*R*)$_3$] and (C) [**Eu_2(5**(*S*,*S*)$_3$]. All the curves were best fitted to mono-exponential decays.

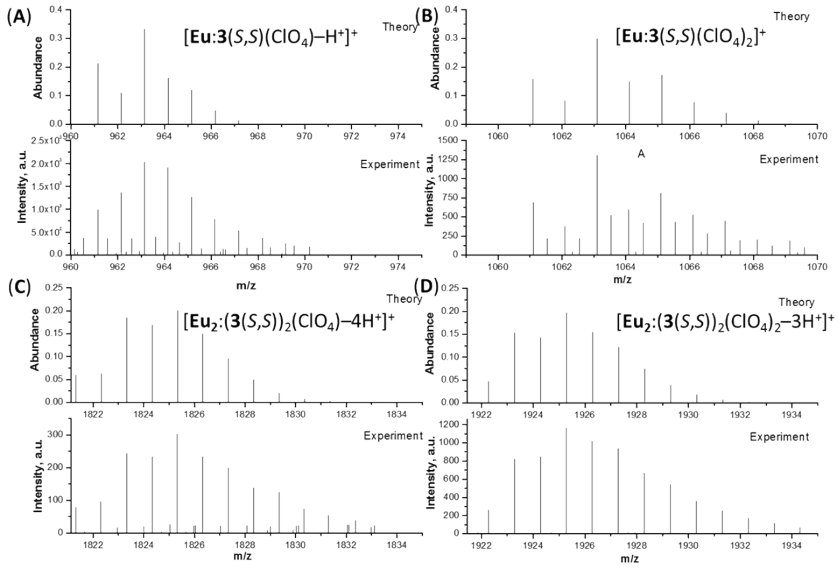


Figure S34. MALDI-MS spectra of $Eu_2(\mathbf{3}(S,S))_3(ClO_4)_6$.

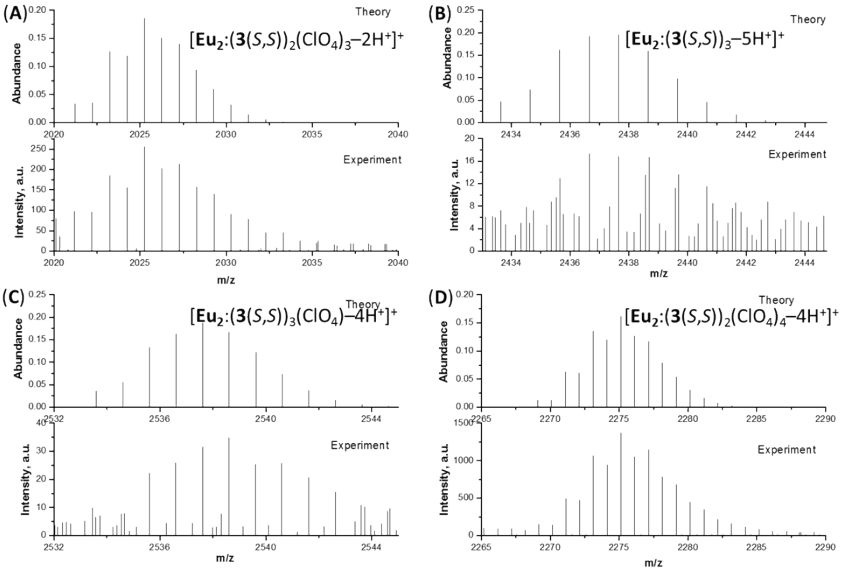


Figure S35. MALDI-MS spectra of $Eu_2(\mathbf{3}(S,S))_3(ClO_4)_6$.

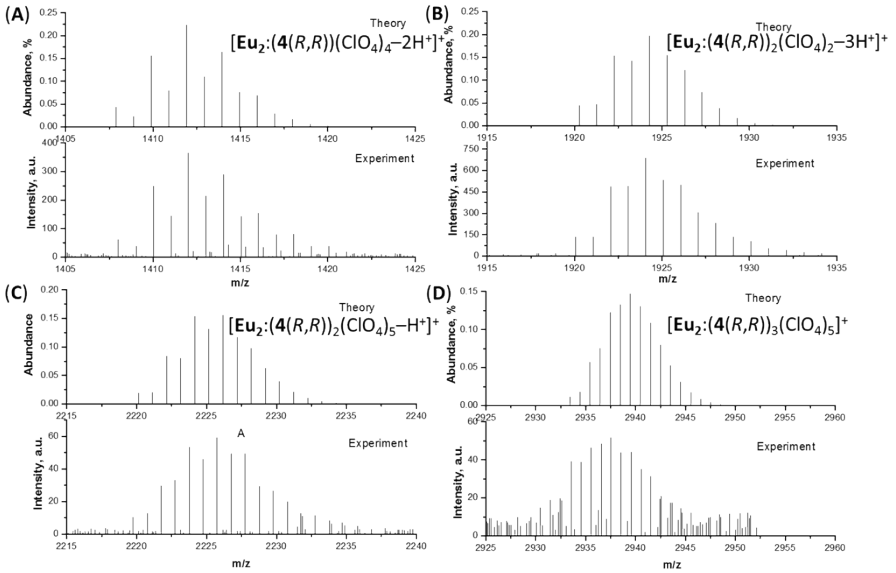


Figure S36. MALDI-MS spectra of $Eu_2(\mathbf{4}(R,R))_3(ClO_4)_6$.

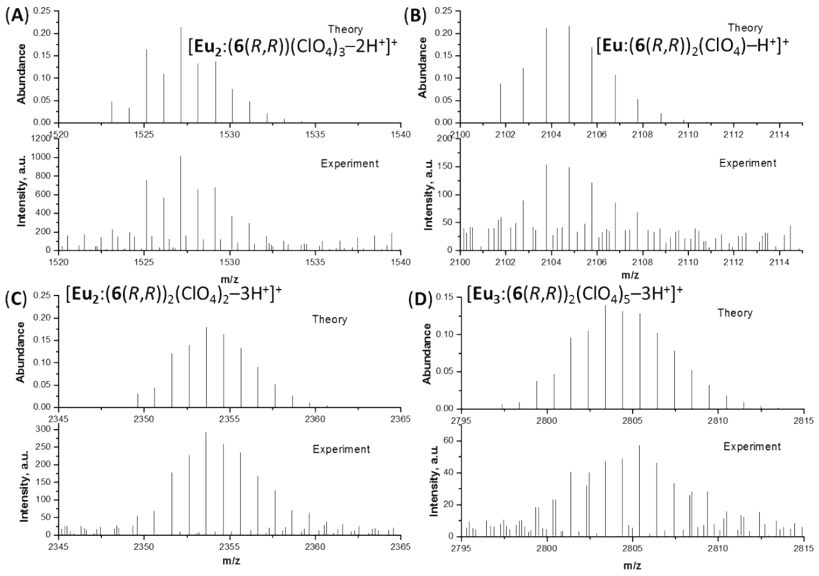


Figure S37. MALDI-MS spectra of $Eu_2(\mathbf{6}(R,R))_3(ClO_4)_6$.

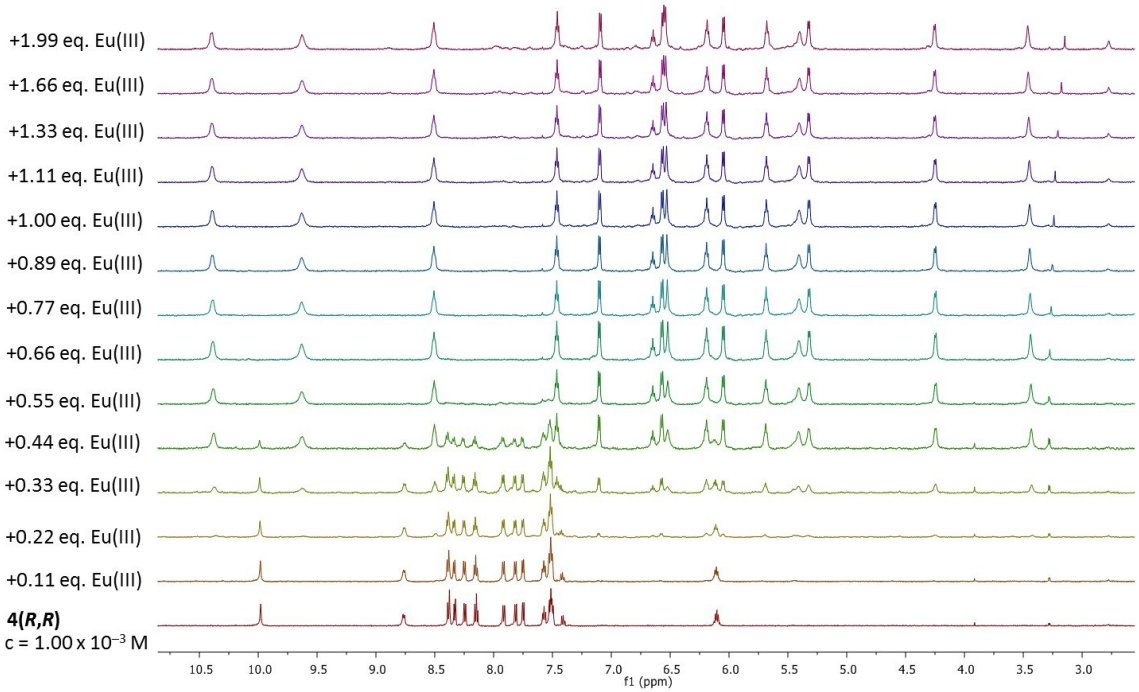


Figure S38. The changes in ^{1}H NMR of **4**(*R*,*R*) (c = 1.00 × 10^{-3} M) upon addition of Eu(CF_3SO_3)$_3$ (0→1.99 equiv.) in CD_3CN (600.1 MHz, T = 25 °C).

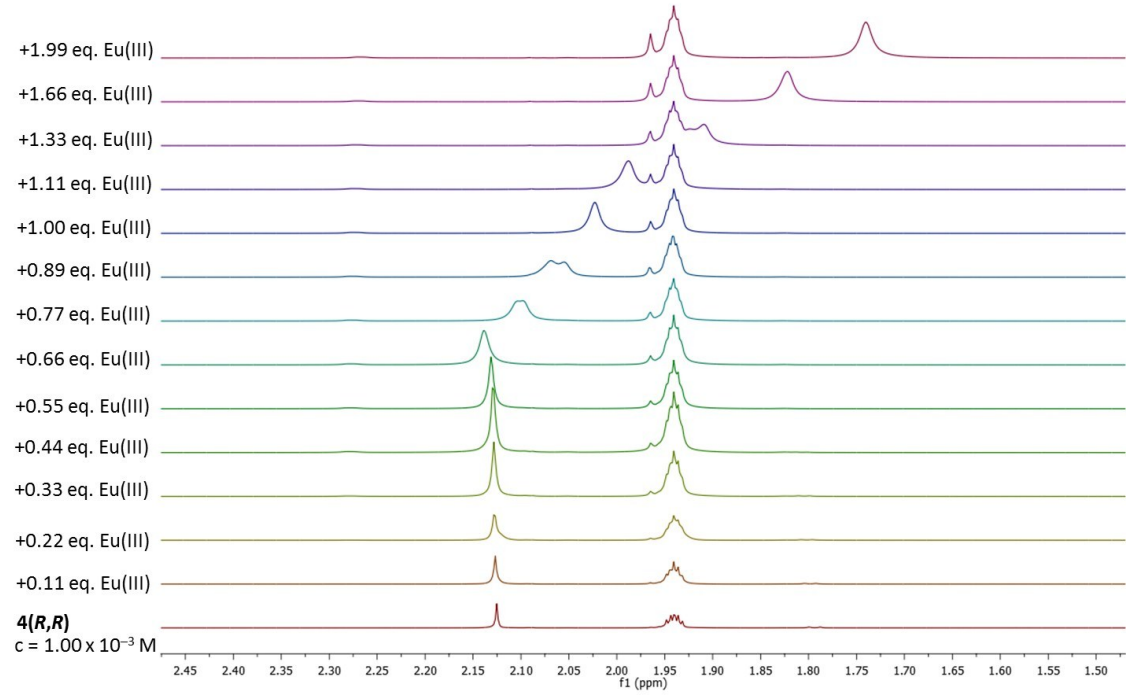


Figure S39. The changes in ^{1}H NMR of **4**(*R*,*R*) (c = 1.00 × 10^{-3} M) upon addition of Eu(CF_3SO_3)$_3$ (0→1.99 equiv.) in CD_3CN (600.1 MHz, T = 25 °C) showing the shift of the water peak signal.

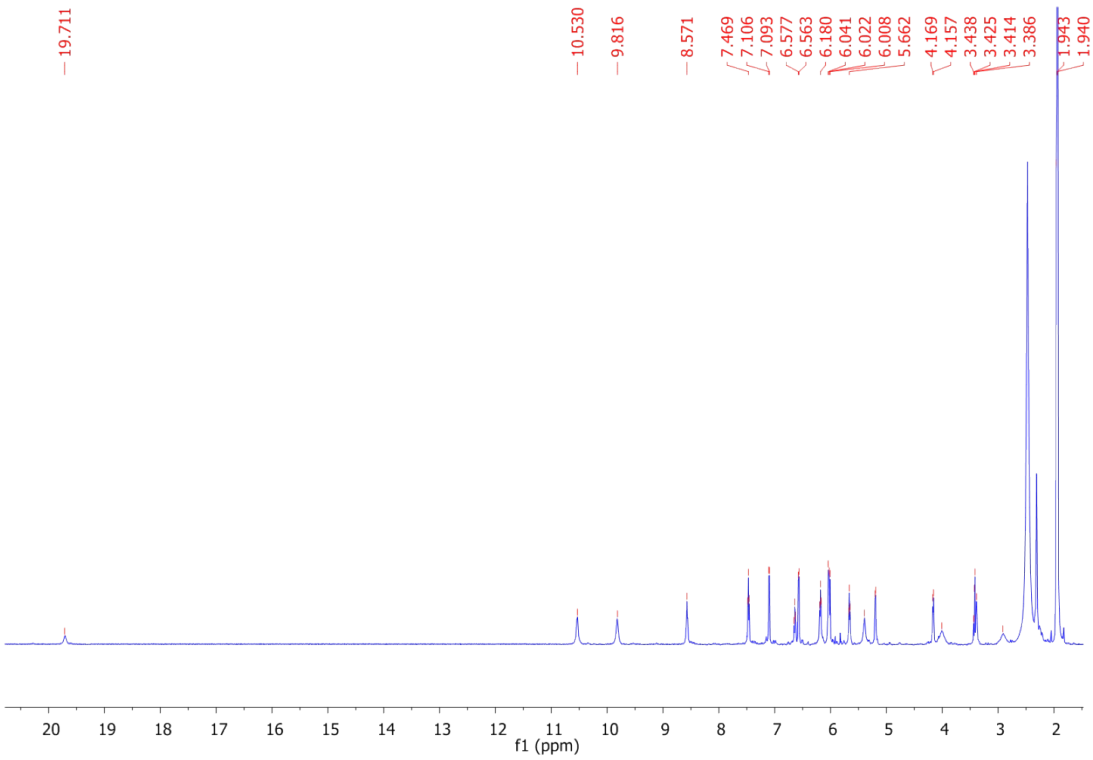


Figure S40. ^{1}H NMR of Eu_2(**3**(*S*,*S*))$_3(ClO_4)_6$ in CD_3CN (600.1 MHz, T = 25 °C).

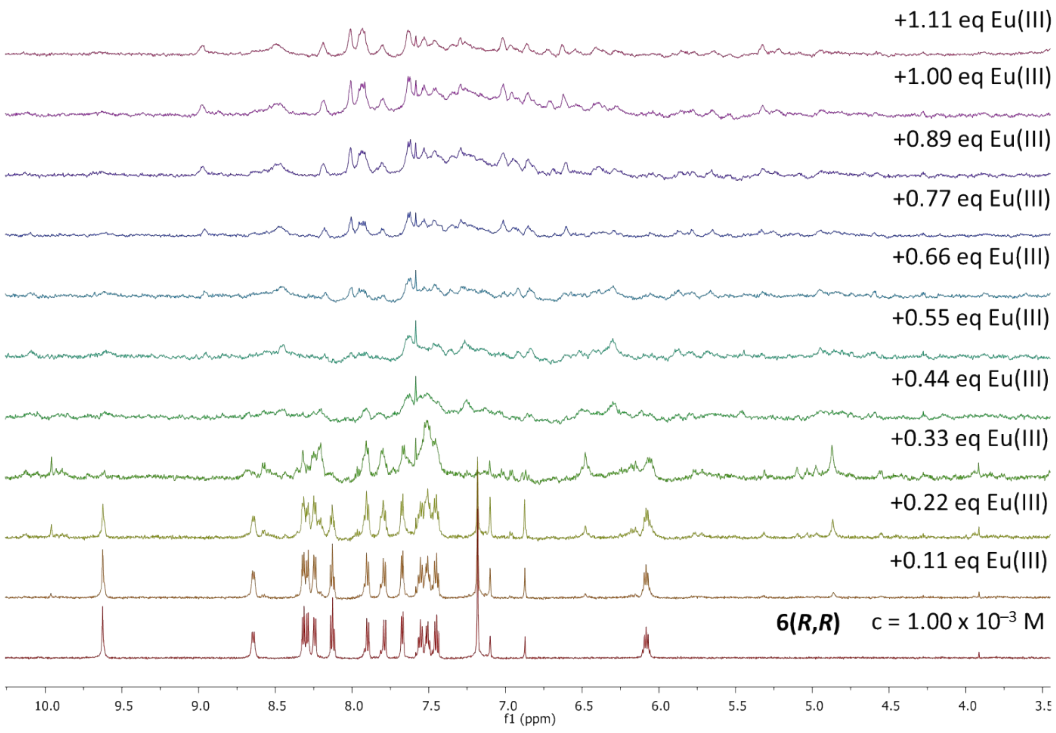


Figure S41. The changes in ^{1}H NMR of **6**(*R*,*R*) (c = 1.00 × 10^{-3} M) upon addition of $Eu(CF_3SO_3)_3$ (0→1.11 equiv.) in CD_3CN (600.1 MHz, T = 25 °C).

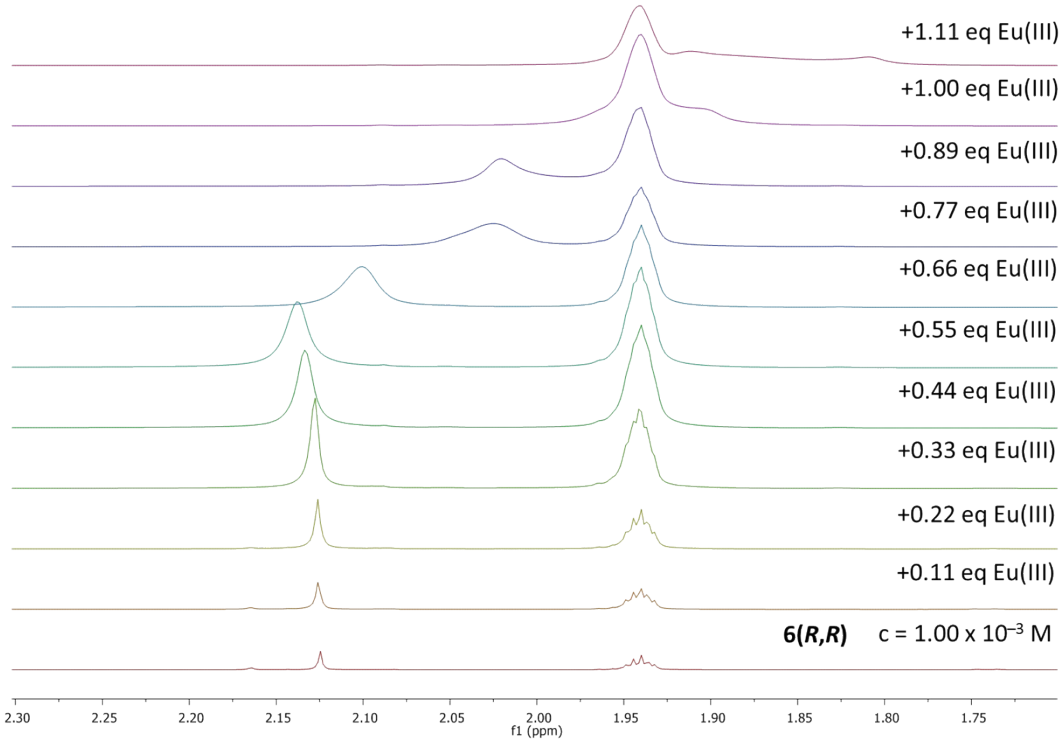


Figure S42. The changes in ^{1}H NMR of **6**(*R*,*R*) (c = 1.00 × 10^{-3} M) upon addition of $Eu(CF_3SO_3)_3$ (0→1.11 equiv.) in CD_3CN (600.1 MHz, T = 25 °C) showing the shift of water signal.

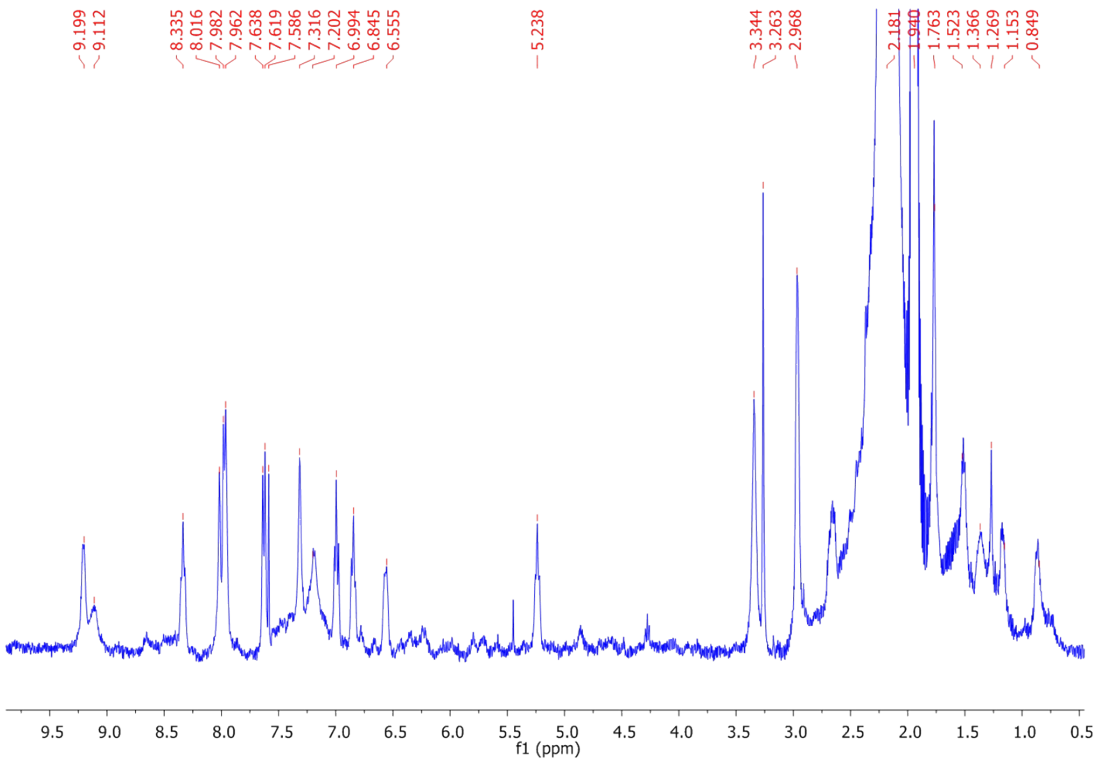


Figure S43. ^{1}H NMR of Eu_2(**5**(*S*,*S*))$_3(ClO_4)_6$ in CD_3CN (400.1 MHz, T = 20 °C).

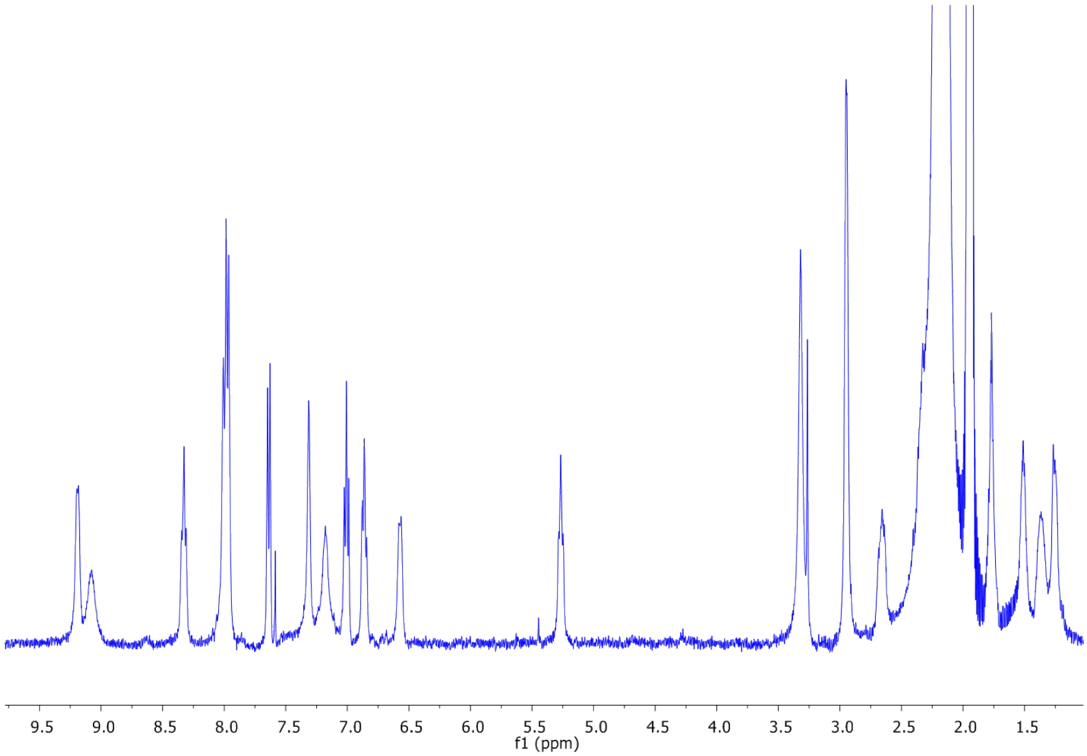


Figure S44. ^{1}H NMR of Eu_2(**5**(*S*,*S*))$_3(ClO_4)_6$ in CD_3CN (400.1 MHz, T = 22 °C), the sample was cooled down to 22 ° after being heated to 40 °C.

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