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Remarkable near-infrared chiroptical properties of chiral Yb, Tm and Er complexes

Oliver G. Willis,[a] Francesco Zinna,*[a] Gennaro Pescitelli,[a] Cosimo Micheletti,[a] and Lorenzo Di Bari *[a]

Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Moruzzi 13, 56124 Pisa, Italy.

E-mail: francesco.zinna@unipi.it, lorenzo.dibari@unipi.it

Synthesis

The synthesis of CsLn(hfbc)$_4$ (Ln = Yb, Tm, Er) complexes followed the literature procedure by Zinna *et al*.[S1] The series of [TMG-H$^+$]$_3$Ln(BINOLate)$_3$ (Ln = Yb, Tm, Er) complexes followed a modified procedure by Walsh and co-workers.[S2] The synthesis of [TMG-H$^+$]$_3$Ln(BINOLate)$_3$ is described below. The reagents and solvents were used as received from the supplier. The ^{1}H NMR spectra were recorded in deuterated CDCl$_3$ using an Agilent Inova 600 (^{1}H: 600 MHz). Elemental analysis of CHN were performed with a vario MICRO cube CHNOS Elemental Analyzer GmbH. [TMG-H+]$_3$Yb(BINOLate)$_3$ has been fully characterised previously by Walsh and co-workers.[S2]

General Procedure: [TMG-H+]$_3$Ln(BINOLate)$_3$ (Ln; Ln = Yb, Tm, Er).

[TMG-H+]$_3$Yb(BINOLate)$_3$: Under ambient atmosphere, a 20 mL glass vial was charged with ytterbium(III) trifluoromethanesulfonate (111.18 mg, 0.18 mmol, 1 equiv; FW: 620.25 g·mol^{-1}), CH$_3$CN (1 mL), glacial acetic acid (31 µL, 0.54 mmol, 3 equiv; FW: 60.05 g·mol^{-1}), and a Teflon-coated stir bar. The solution was stirred for 5 min and a solution of (*R*)-BINOL (154.32 mg, 0.54 mmol, 3 equiv; FW: 286.32 g·mol^{-1}) and TMG (135 µL, 1.08 mmol, 6 equiv; FW: 115.18 g·mol^{-1}) in CH$_3$CN (1 mL) was added dropwise over 1 min. TMG (68 µL, 0.54 mmol, 3 equiv; FW: 115.18 g·mol^{-1}) was added dropwise, and immediately formed an off-white precipitate. After ~1 min of additional stirring, the vial was sealed and centrifuged at 6000 RPM for 5 min. The supernatant was decanted and the precipitate was dried under reduced pressure on a rotary evaporator. The product was crystallized by layering a concentrated solution of CH$_2$Cl$_2$ with petroleum ether. After 12-24 h the crystalline solid was isolated by vacuum filtration. Yield: 150.68 mg (0.11 mmol, 61 %; FW: 1374.54 g mol^{-1}). NMR and analytical data are in agreement with those reported in the literature. [S2] **^{1}H-NMR** (600 MHz, CDCl$_3$) δ: 10.58 (s, 1H, H-4), 8.70 (s, 1H, H-7), 8.35 (s, 1H, H-5), 7.80 (s, 1H, H-6), 5.51 (s, 1H, H-8), 4.17 (s, 6H, CH$_3$), −14.32 (s, 1H, H-3). **^{13}C-NMR** (151 MHz, CDCl$_3$) δ: 169.52, 166.62, 155.72, 144.78, 143.29, 134.62, 130.07, 129.28, 128.46, 128.25, 128.07, 125.18, 124.89, 124.64, 120.96, 40.78.

[TMG-H+]$_3$Tm(BINOLate)$_3$: The title compound was prepared by General Procedure using thulium(III) trifluoromethanesulfonate (111.90 mg, 0.18 mmol, 1 equiv; FW: 616.14 g·mol^{-1}). Yield: 166.25 g (0.12 mmol, 67%; FW: 1370.43 g mol^{-1}). **^{1}H-NMR** (600 MHz, CDCl$_3$) δ: 21.77 (s, 1H), 13.80 (s, 1H), 11.52 (s, 1H), 10.96 (s, 1H), 9.50 (s, 6H), 1.34 (s, 1H), 0.35 (s, 1H). **^{13}C-NMR** (151 MHz, CDCl$_3$) δ: 197.00, 164.86, 140.10, 139.34, 133.12, 131.99, 127.04, 121.35, 115.96, 47.98. **Anal. Calcd** for $C_{75}H_{78}O_6N_9Tm\cdot 3H_2O\cdot 0.5C_6H_{14}$: C, 63.84; H, 6.25; N, 8.59. Found: C, 63.55; H, 6.35; N, 8.50.

[TMG-H+]$_3$Er(BINOLate)$_3$: The title compound was prepared by General Procedure using erbium(III) trifluoromethanesulfonate (117.52 mg, 0.19 mmol, 1 equiv; FW: 614.47 g·mol^{-1}). Yield: 212.15 g (0.15 mmol, 81 %; FW: 1368.76 g mol^{-1}). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ: 25.26 (s, 1H), 15.03 (s, 1H), 12.40 (s, 1H), 11.14 (s, 1H), 9.52 (s, 6H), 1.30 (s, 1H), -1.43 (s, 1H). **^{13}C-NMR** (151 MHz, $CDCl_3$) δ: 173.06, 141.90, 141.03, 139.49, 135.20, 134.60, 127.70, 126.93, 121.30, 108.04, 47.81, 22.76. **Anal. Calcd** for $C_{75}H_{78}O_6N_9Er{\cdot}3.5H_2O{\cdot}0.5C_6H_{14}$: C, 63.13; H, 6.31; N, 8.50. Found: C, 63.06; H, 6.37; N, 8.32.

NMR analysis

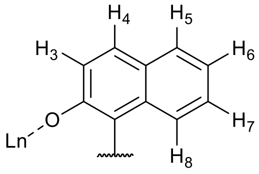

***Table S1.** Observed proton shift (δ^{obs}) and paramagnetic contribution ($\delta^{par} = \delta^{obs} - \delta^{diam}$), longitudinal relaxation time (T_1) and relaxation rate (ρ) of the specific nucleus for* [TMG-H+]$_3$Yb(BINOLate)$_3$. *As well as geometrical factors (GF) and distances between Yb and the observed nucleus ($r_{Yb\text{-}X}$) calculated from the crystal structures obtained by Walsh et al.*[S2]

H	δ^{obs} / ppm	δ^{para} / ppm	T_1 / ms	ρ (× 10^3) / s^{-1}	GF (× 10^3) / $Å^{-3}$ [a]	$r_{Yb\text{-}X}$ / Å [a]
3	-14.30	-21.30	12	83.3	-14.9	4.1
4	10.61	3.61	101	9.9	-1.36	5.9
5	8.37	1.37	364	2.7	1.10	7.5
6	7.83	0.83	609	1.6	1.33	8.7
7	8.73	1.73	471	2.1	1.84	8.1
8	5.53	-1.47	113	8.8	3.97	6.2

a) Calculated from the crystal structure reported in ref [S2]

The observed shift (δ^{obs}) is made up of both a paramagnetic (δ^{para}) and diamagnetic contribution (δ^{dia}). Thus subtraction of the diamagnetic component using a suitable reference ([TMG-H$^+$]$_3$La(BINOLate)$_3$) yields the paramagnetic shift. The term δ^{par} is also made of two contributions, namely the Fermi contact (δ^{FC}) and pseudocontact (δ^{PC}) terms.[S3] The pseudocontact term can be written as Equation S3 (axially symmetric complex), which shows proportionality to a geometrical factor term. The axial magnetic susceptibility anisotropy factor is denoted as $\mathscr{D}$. The distance between the observed nucleus and the paramagnetic centre (Yb) is denoted as r, and Ω is its azimuthal angle with respect to the C_n axis.[S3]

$$\delta^{obs} = \delta^{para} + \delta^{dia} \qquad \textbf{Eq. S1}$$

$$\delta^{para} = \delta^{FC} + \delta^{PC} \qquad \textbf{Eq. S2}$$

$$\delta^{PC} = \mathscr{D}\frac{(3\cos^2\Omega - 1)}{r^3} = \mathscr{D}(GF) \qquad \textbf{Eq. S3}$$

As δ^{PC} is usually much smaller than δ^{FC} for nuclei more than 3/4 bonds apart from the paramagnetic centre, here we assumed:

$$\delta^{para} \approx \delta^{PC}$$

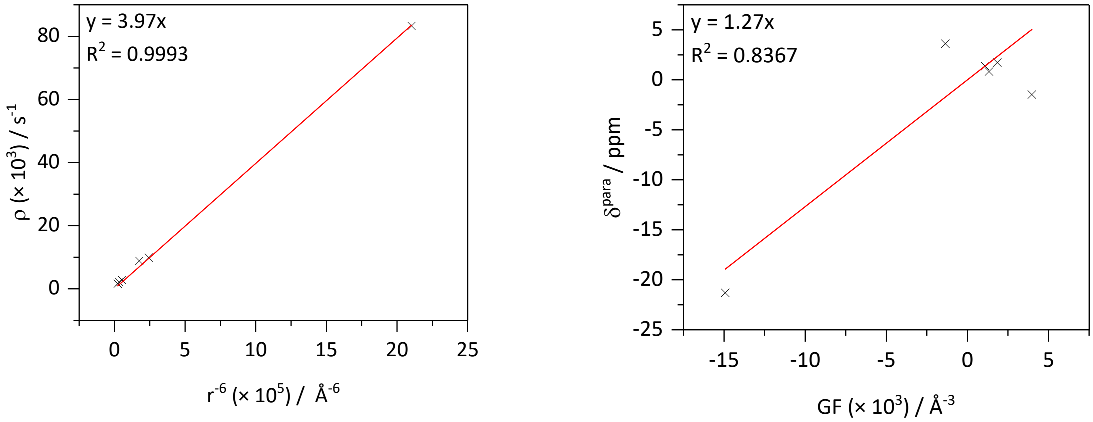

***Figure S1**. Left: The longitudinal relaxation rate (ρ_1) from the ^{1}H NMR of [TMG-H$^+$]$_3$Yb(BINOLate)$_3$ against r^{-6} calculated from the crystal structure of [TMG-H$^+$]$_3$La(BINOLate)$_3$. Right: The relation between δ^{PC} of [TMG-H$^+$]$_3$Yb(BINOLate)$_3$ and the geometrical factor (GF) calculated from the crystal structure of [TMG-H$^+$]$_3$La(BINOLate)$_3$.*

Instrumentation

NIR-CD/NIR-Abs measurements

NIR-CD measurements were performed using a Jasco J200 spectropolarimeter provided with an ADC system. Concentrations of solutions varied between 4-17 mM in either DCM or $CDCl_3$. All complexes were measured in 1 cm optical glass cells with parameters as follows: Scan speed 50 nm/min, slit width 2-4 nm, integration time 1-4 sec, accumulations 4. The spectra were baseline corrected by subtraction of the solvent spectrum. Solutions of the same concentrations were used to measure the corresponding NIR absorption spectra using a Cary 5000 UV-Vis-NIR spectrophotometer.

NIR-CPL measurements

NIR-CPL spectra were recorded used the home-built spectrofluoropolarimeter, equipped with a Hamamatsu R316 Ag-O-Cs photomultiplier tube, as described in ref [S4]. The spectra were collected under 365 nm irradiation from a commercial LED-source, using a 90° geometry between the excitation and detection direction. All the NIR-CPL spectra were recorded on 1 mM CH_2Cl_2 solutions in 1 cm semi-micro (aperture 4 mm) optical glass cells using the following parameters: scan-speed 0.5 nm/sec, integration time 2 sec, photomultiplier tube driving voltage 1100 V, accumulations 5-8.

UV-ECD measurements

UV-ECD spectra were recorded using a Jasco J710 spectropolarimeter on 1 mM CH_2Cl_2 solutions of $CsLn(hfbc)_4$ and 0.13 mM CH_2Cl_2 solutions of $[TMG\text{-}H^+]_3Ln(BINOLate)_3$ (Ln = Yb, Tm, Er) in 0.02 cm optical glass cells. The same solutions were used to record the corresponding UV absorption spectra.

Additional spectra

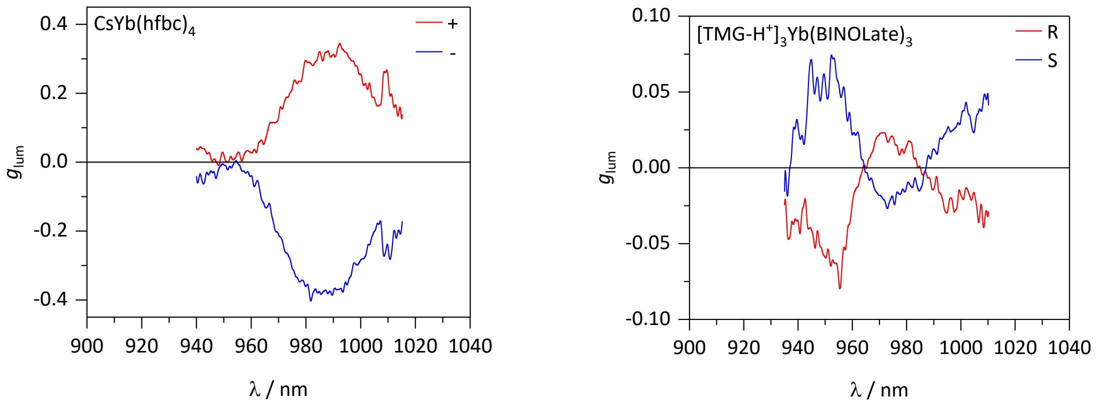

Figure S2. *The g_{lum} factor as a function of wavelength for the enantiomers of $CsYb(hfbc)_4$ (Left) and $[TMG\text{-}H^+]_3Yb(BINOLate)_3$ (Right)*

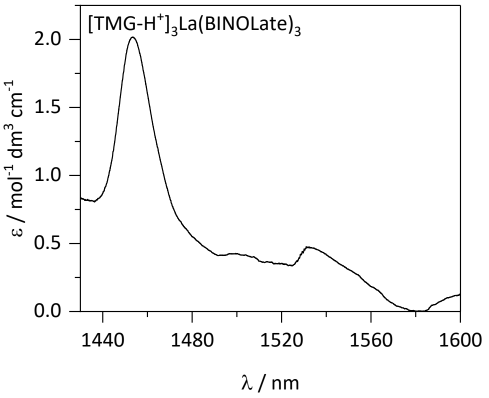

Figure S3. *The total absorption spectrum of $[TMG\text{-}H^+]_3La(BINOLate)_3$. Recorded in 10 mM solutions at room temperature.*

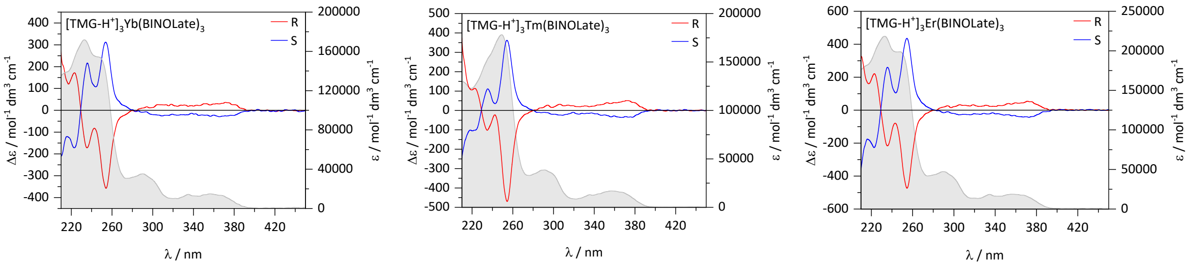

Figure S4. *ECD and average absorption spectra traced in the background of the enantiomers of $[TMG\text{-}H^+]_3Ln(BINOLate)_3$. Recorded in 0.13 mM solutions of DCM at room temperature.*

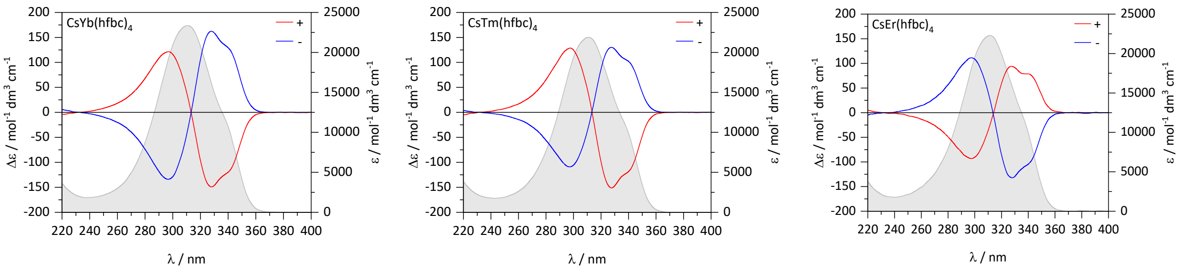

Figure S5. *ECD and average absorption spectra traced in the background of the enantiomers of CsLn(hfbc)$_4$. Recorded in 1 mM solutions of DCM at room temperature.*

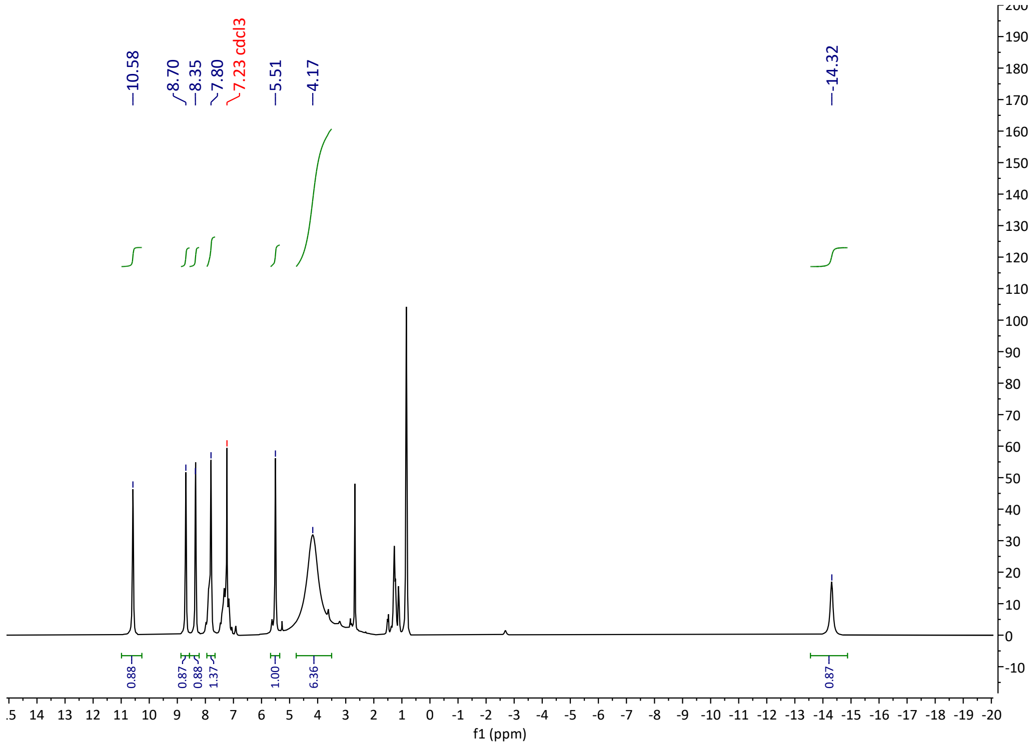

Figure S6. *^{1}H-NMR (600 MHz, CDCl$_3$) spectra of [TMG-H$^+$]$_3$Yb(BINOLate)$_3$.*

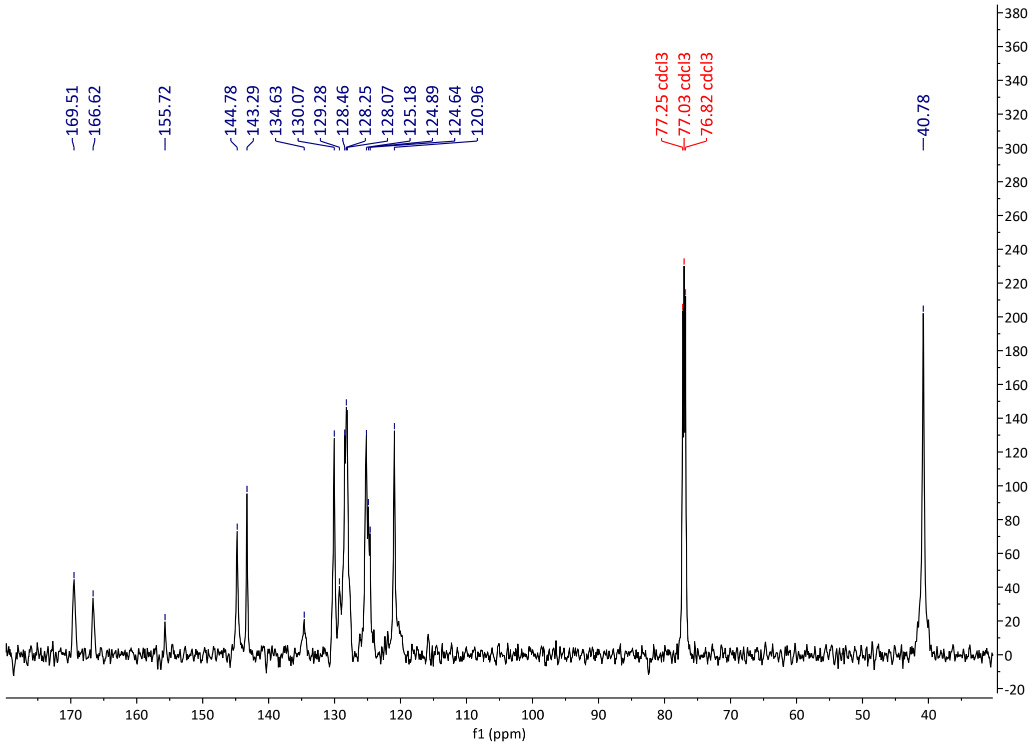

Figure S7. *^{13}C-NMR (151 MHz, $CDCl_3$) spectra of [TMG-H^+]$_3$Yb(BINOLate)$_3$.*

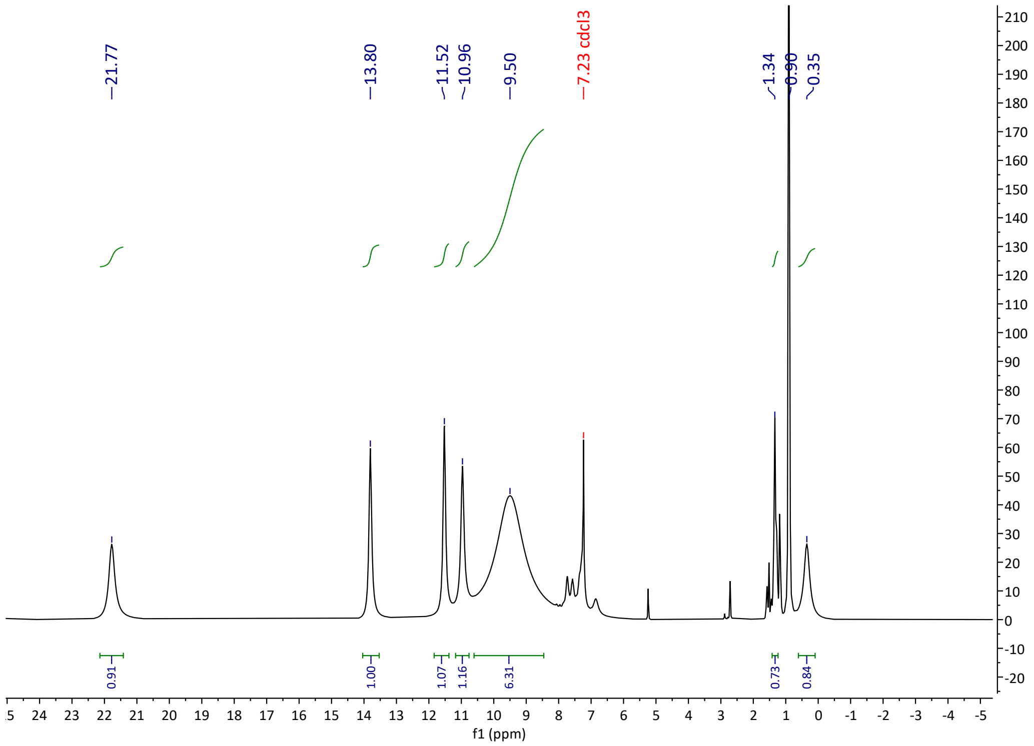

Figure S8. *^{1}H-NMR (600 MHz, $CDCl_3$) spectra of [TMG-H^+]$_3$Tm(BINOLate)$_3$.*

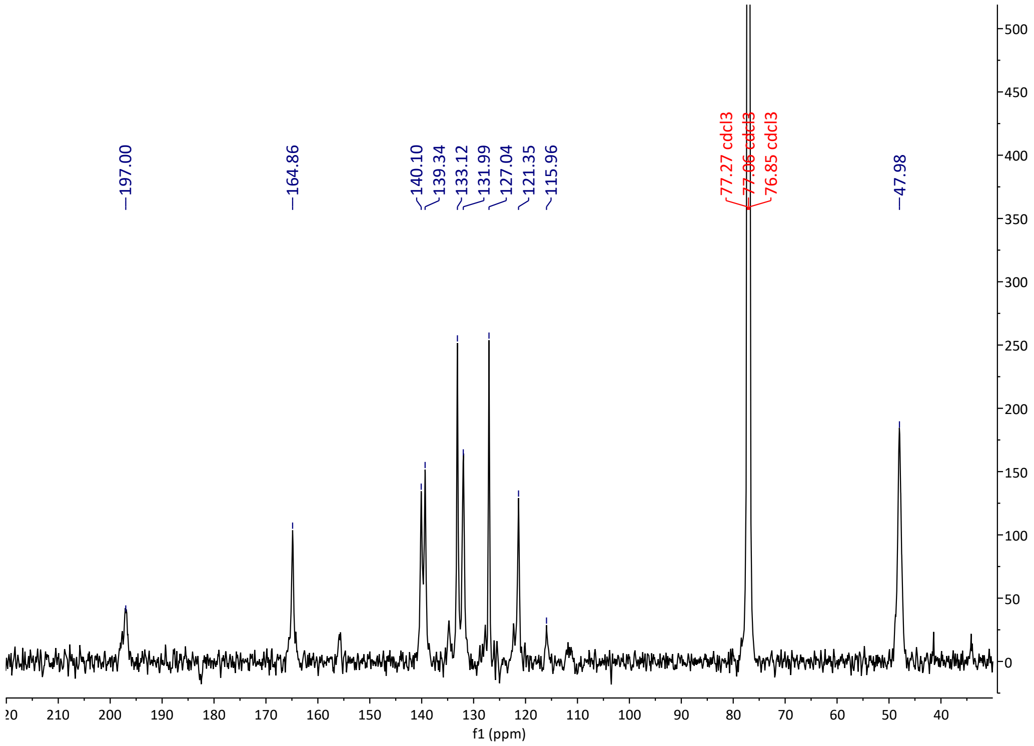

Figure S9. *^{13}C-NMR (151 MHz, $CDCl_3$) spectra of [TMG-H$^+$]$_3$Tm(BINOLate)$_3$.*

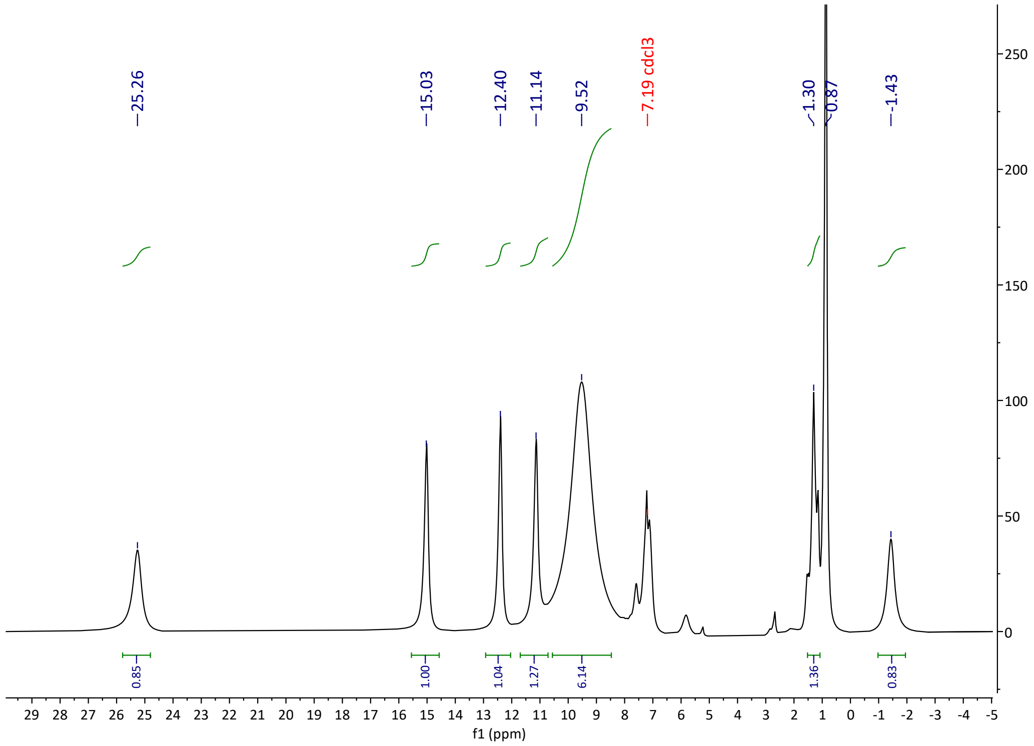

Figure S10. *^{1}H-NMR (600 MHz, $CDCl_3$) spectra of [TMG-H$^+$]$_3$Er(BINOLate)$_3$.*

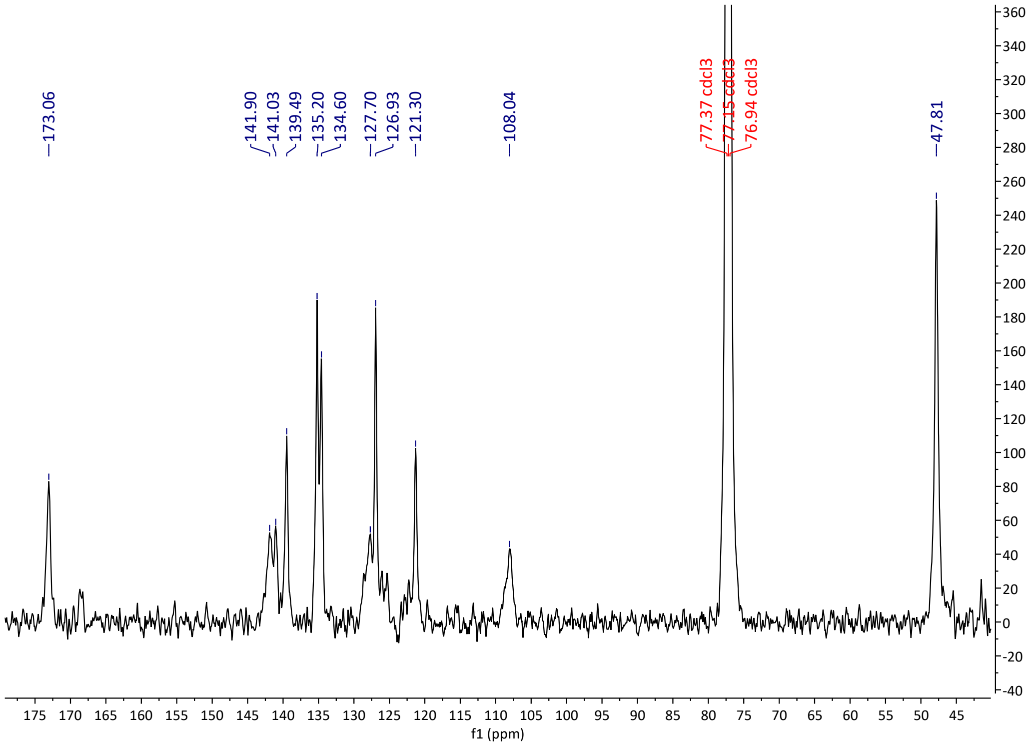

Figure S11. *^{13}C-NMR (151 MHz, CDCl$_3$) spectra of [TMG-H$^+$]$_3$Er(BINOLate)$_3$.*

References

S1 F. Zinna, U. Giovanella and L. Di Bari, *Adv. Mater.*, 2015, **27**, 1791–1795.

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S3 L. Di Bari, M. Lelli, G. Pintacuda, G. Pescitelli, F. Marchetti and P. Salvadori, *J. Am. Chem. Soc.*, 2003, **125**, 5549–5558.

S4 F. Zinna, L. Arrico and L. Di Bari, *Chem. Commun.*, 2019, **55**, 6607–6609.