Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Synthesis and molecular structure of enantiomerically pure pentadienyl complexes of the rare-earth metals

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1. Crystallographic details

Table S1. Crystallographic data.

Compound reference	**1-La**	**1-Ce**	**1-Pr**	**1-Nd**
Chemical formula	$C_{39}H_{57}La$	$C_{39}H_{57}Ce$	$C_{39}H_{57}Pr$	$C_{39}H_{57}Nd$
Formula Mass	664.75	665.96	666.75	670.08
Crystal system	monoclinic	orthorhombic	monoclinic	orthorhombic
a/Å	9.5001(6)	9.9249(3)	9.4762(3)	9.9037(4)
b/Å	18.0623(18)	12.3230(4)	18.0442(7)	12.3136(7)
c/Å	19.7718(15)	27.7491(10)	19.7324(7)	27.6207(12)
α/°	90	90	90	90
β/°	97.105(6)	90	97.142(3)°	90
γ/°	90	90	90	90
Unit cell volume/Å^3	3366.7(5)	3393.84(19)	3347.9(2)	3368.4(3)
Temperature/K	100(2)	100(2)	100(2)	100(2)
Space group	$P2_1$	$P2_12_12_1$	$P2_1$	$P2_12_12_1$
No. of formula units per unit cell, *Z*	4	4	4	4
Radiation type	Mo Kα	Mo Kα	Mo Kα	Mo Kα
Absorption coefficient, *μ*/mm^{-1}	1.293	1.365	1.480	1.566
No. of reflections measured	144004	89141	154014	65007
No. of independent reflections	13782	9808	19885	9665
R_{int}	0.1899	0.0678	0.0997	0.1079
Final R_1 values ($I > 2\sigma(I)$)	0.0519	0.0344	0.0392	0.0418
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0698	0.0742	0.0629	0.0625
Final R_1 values (all data)	0.0789	0.0397	0.0578	0.0588
Final $wR(F^2)$ values (all data)	0.0845	0.0764	0.0689	0.0689
Goodness of fit on F^2	1.020	1.183	1.031	1.052
Flack parameter	-0.014(11)	-0.031(6)	-0.035(5)	-0.027(10)
Δρ / e Å^{-3}	1.115/-0.649	2.087/-0.912	0.999/-0.767	1.314/-1.016

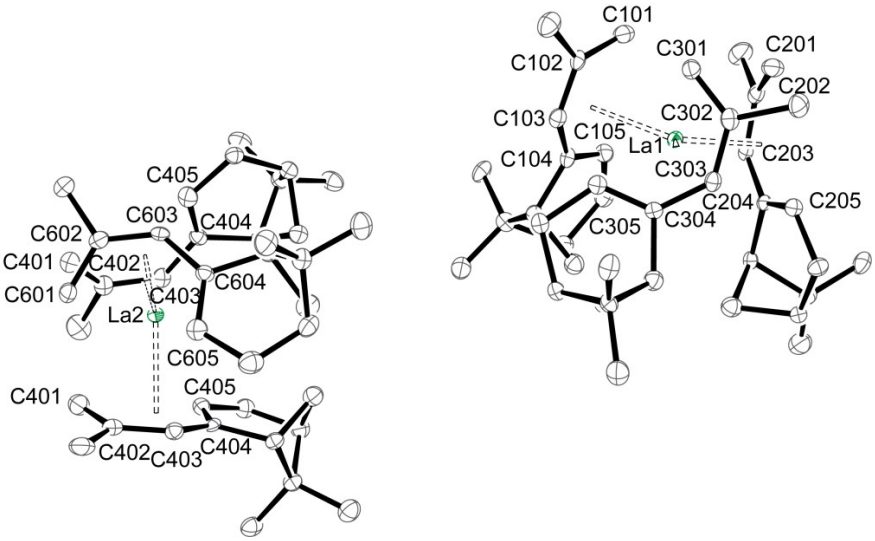

Figure S1. Molecular structure of **1-La** with two independent molecules in the asymmetric unit. Thermal ellipsoids are drawn at the 50% probability level.

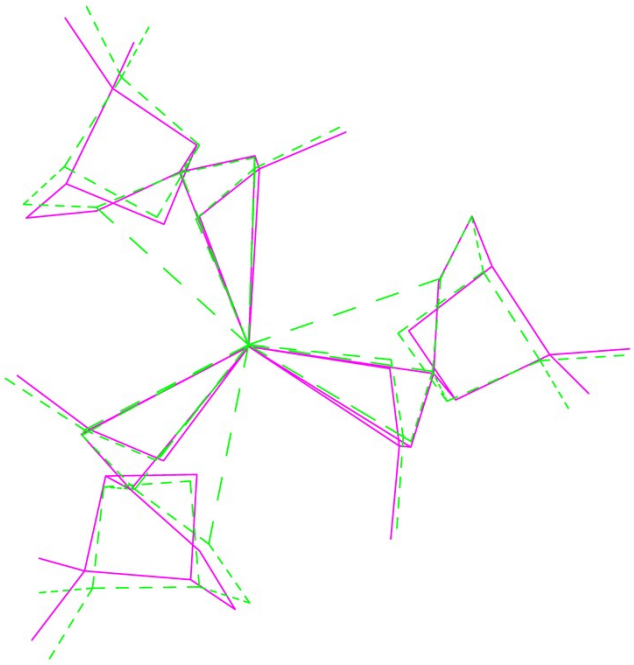

Figure S2. Least-squares fit of the two independent molecules of **1-La**. Molecule 1 is drawn in violet and molecule 2 in green.

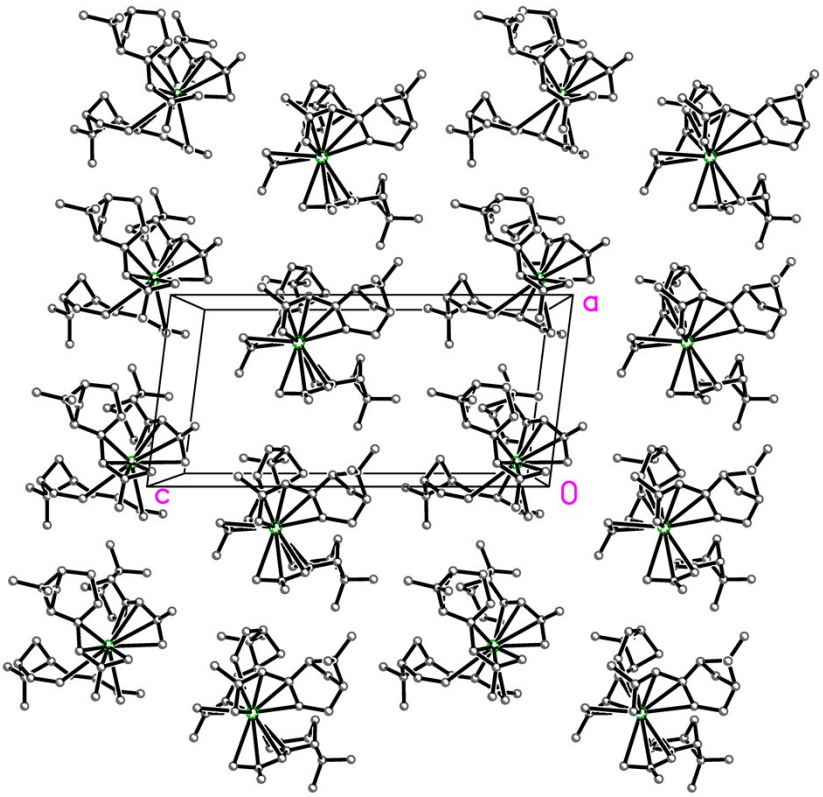

Figure S3. Packing diagram of **1-La** showing the formation of a hexagonal layer of molecules parallel to the *ac* plane at $y \approx ¼$. From left to right, the vertical rows are alternately composed of molecules 2 and 1 in that order. The orthorhombic derivatives display no simple packing patterns.

2. ^{1}H NMR Studies

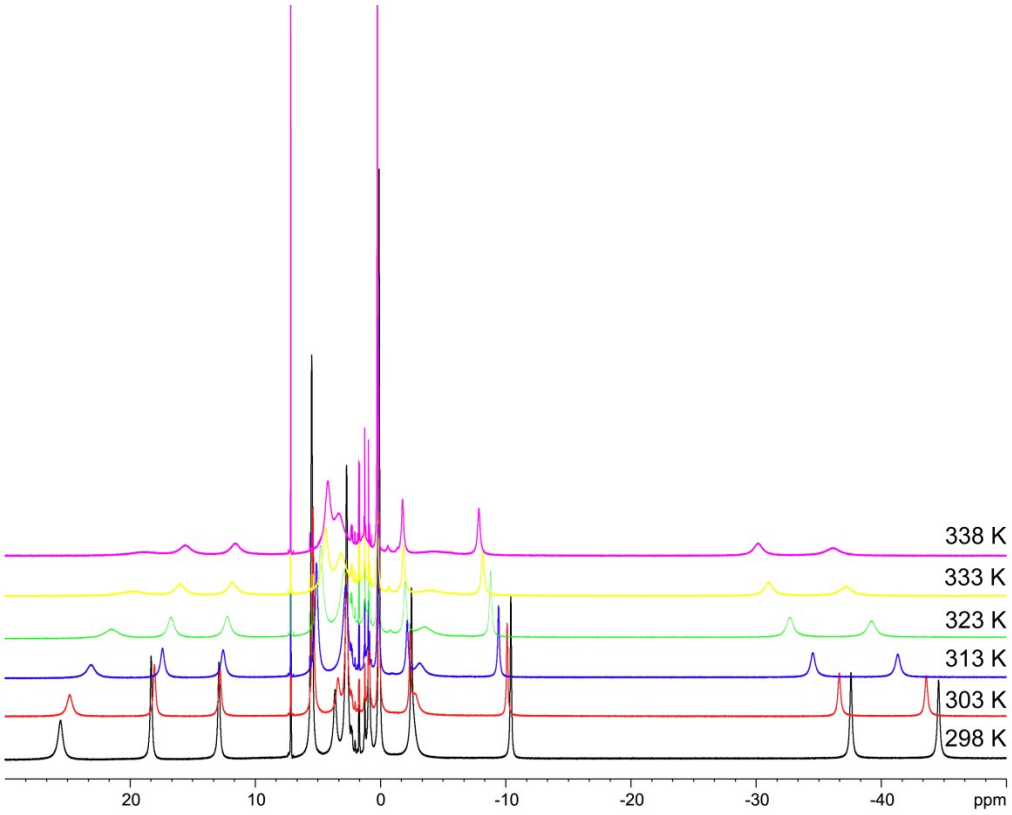

Figure S4. Variable temperature (VT) 1H NMR spectra for **1-Nd** recorded in C_6D_6 between *T* = 298 K and 338 K.

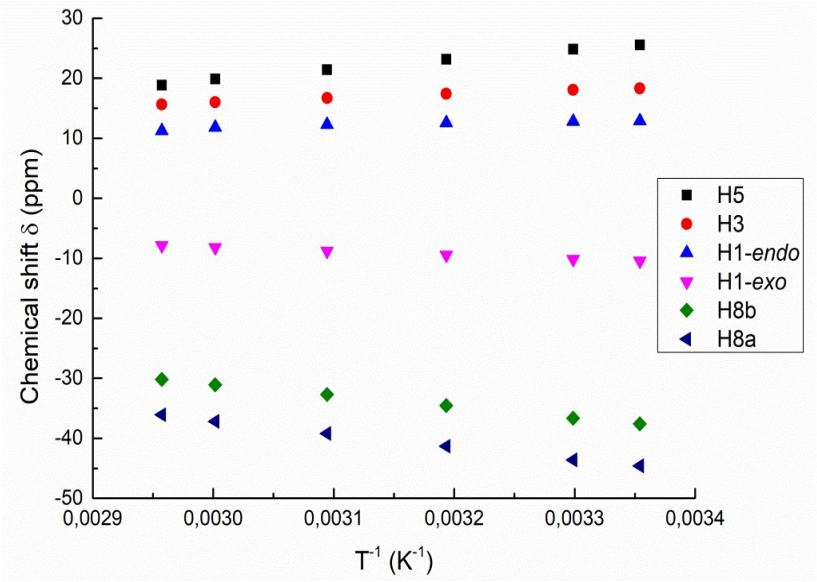

Figure S5. δ vs. T^{-1} plot for selected ^{1}H NMR resonances of **1-Nd** recorded in C_6D_6 between *T* = 298 K and 338 K (assigments according to Table S2).

Table S2. Correlation between G(r,θ) and δ^{para}.

	1-Ce					1-Pr					1-Nd			
	δ	**δ^{dia}**	**δ^{para}** [a]	**G(r, θ) · 10^8**		**δ**	**δ^{dia}**	**δ^{para}** [a]	**G(r, θ) · 10^8**		**δ**	**δ^{dia}**	**δ^{para}** [a]	**G(r, θ) · 10^8**
H8a	-25,4	1,08	-26,48	-25,4		-64,9	1,08	-65,98	-35,3		-44,6	1,08	H5	-29,8
H1-*exo*	-20,2	4,04	-24,24	-20,2		-57,5	4,04	-61,14	-25,5		-37,6	4,04	-41,64	-22,9
H8b	-6,1	2,33	-8,43	-6,1		-18,5	2,33	-20,83	-12,4		-10,4	2,33	-12,73	-9,3
H6a	-0,6	2,4	-3	-0,6		-4,9	2,4	-7,3	-3,1		-2,5	2,4	-4,9	-7,3
H7	1,3	2,04	-0,74	-0,3		0,7	2,04	-2,84	-1,4		-2,5	2,04	-4,54	-4,1
H13 [b]	0,3	1,89	-1,59	-1,3		-0,8	1,89	-1,19	-0,3		0,1	1,89	-1,79	-0,9
H12 [b]	2,1	1,25	0,85	-2,1		2,5	1,25	1,25	2,7		2,7	1,25	1,45	-0,6
H9	3,5	2,25	1,25	3,5		8	2,25	5,75	2,9		2,7	2,25	0,45	1,2
H6b	4,2	2,67	1,53	3,7		6,1	2,67	3,43	3,8		3,6	2,67	0,93	1,5
H11 [b]	3,7	1,05	2,65	4,2		9,8	1,05	8,75	3,9		5,5	1,05	4,45	1,5
H1-*endo*	6,6	2,65	3,95	6,6		16,1	2,65	13,45	8,1		12,9	2,65	10,25	20,0
H3	16,4	4,35	12,05	16,4		32,5	4,35	28,15	27,7		18,3	4,35	13,95	27,0
H5	24,9	4,16	20,74	24,9		55,1	4,16	50,94	34,8		25,5	4,16	21,34	32,6

[a] $\delta^{para} = \delta - \delta^{dia}$. The values for δ^{dia} was taken from the diamagnetic representative within this series, i.e. **1-La**. [b] Averaged value for the H atoms of the Me-group.

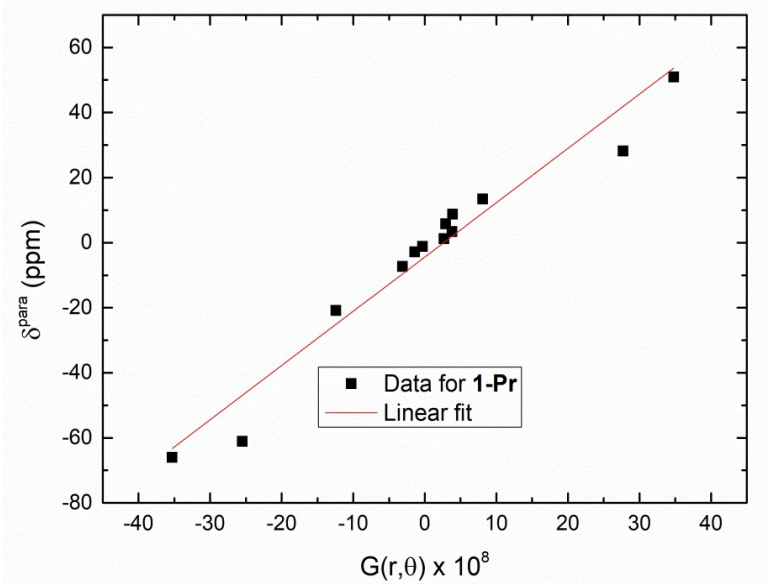

Figure S6. Correlation between δ^{para} and $G(r,\theta) = (3\cos^2\theta - 1)/r^3$ for compound **1-Pr**.

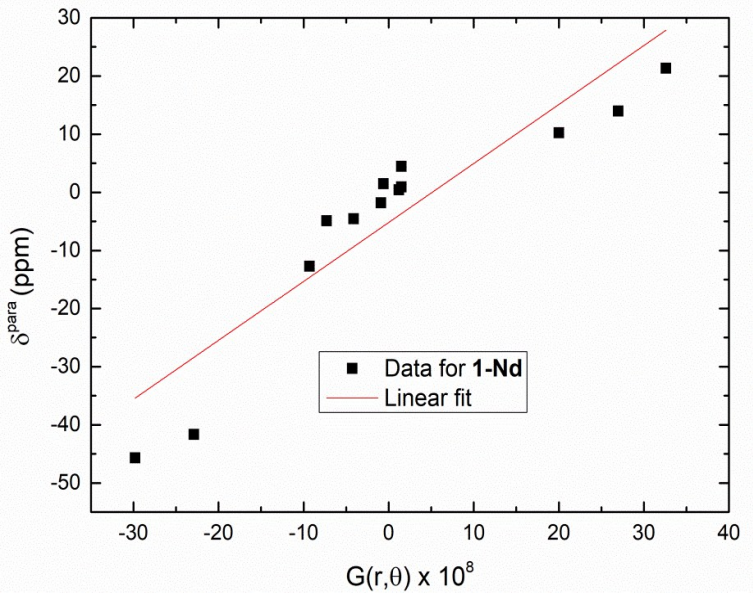

Figure S7. Correlation between δ^{para} and $G(r,\theta) = (3\cos^2\theta - 1)/r^3$ for compound **1-Nd**.