Supporting Information

Lanthanide Metal Organic Frameworks based on dicarboxyl-functionalized arylhydrazone of barbituric acid: Syntheses, Structures, Luminescence and Catalytic Aldehydes Cyanosilylation

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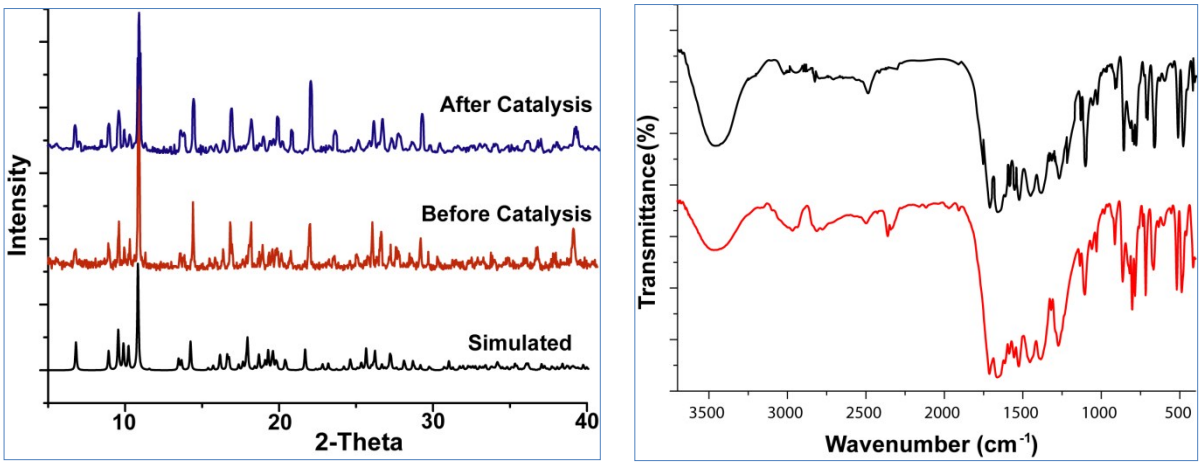


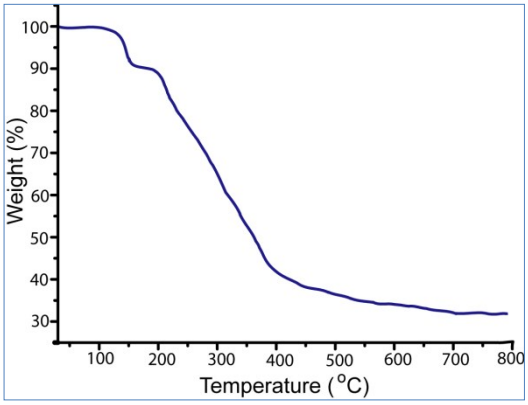
A B

Figure S1 (A) Powder XRD spectra of **2** (the red and blue curves refer to before and after the catalysis reaction and the black curve is the theoretical one). (B) FT-IR spectra of **2** before (red line) and after (black line) the cyanosilylation reaction.

Thermogravimetric analyses

Thermogravimetric analyses were carried out under dinitrogen in the range from room temperature to *ca.* 800˚C at a heating rate of 5 ˚C min^{-1}. Features of the thermal stability of frameworks **1**-**5** are illustrated in Figure S2. We have observed a similar type of decomposition in all cases.

These frameworks show a weight loss between 100 and 190˚C, corresponding to the loss of molecules of non-coordinated DMF. Upon further heating, the framework starts to decompose. We have not observed any sharp weight loss during the heating up process, but rather a continuous weight loss. This type of phenomenon was also observed in many previously reported Ln-frameworks.[1]



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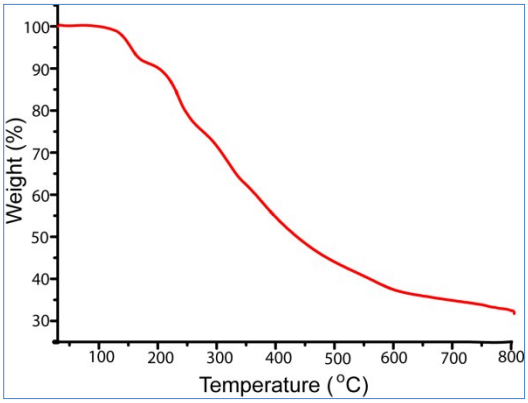

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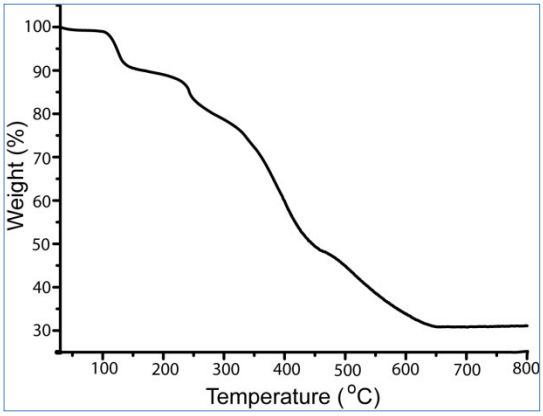

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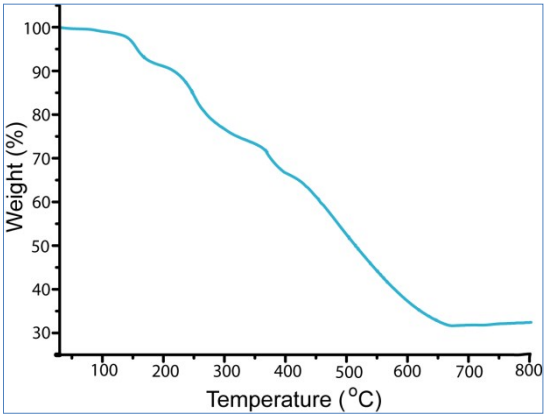

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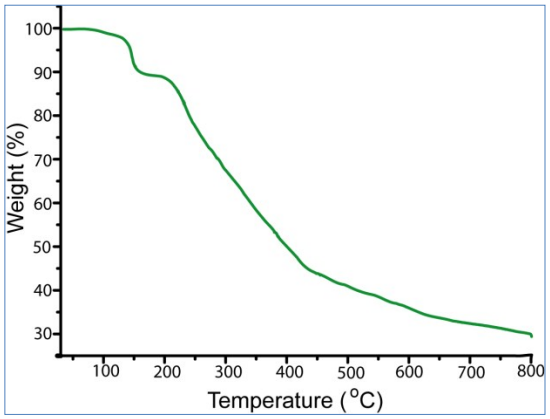


F

Figure S2 Thermogravimetric curves for **1** (A), **2** (B), **3** (C), **4** (D) and **5** (F).

Calculation of the yield in the cyanosilylation reaction

The -CH peak of benzaldehyde (reactant) appears as 10.048 ppm and that of the 2-phenyl-2-((trimethylsilyl)oxy)acetonitrile (product) appears at 5.531 ppm.

Total amount of benzaldehyde: unreacted benzaldehyde + 2-phenyl-2-((trimethylsilyl)oxy)acetonitrile = 1+ 15.9 = 16.9

Conversion of benzaldehyde (%) = yield (%) of 2-phenyl-2-((trimethylsilyl)oxy)acetonitrile = 15.9 X 100/ 16.9 = 94.0%

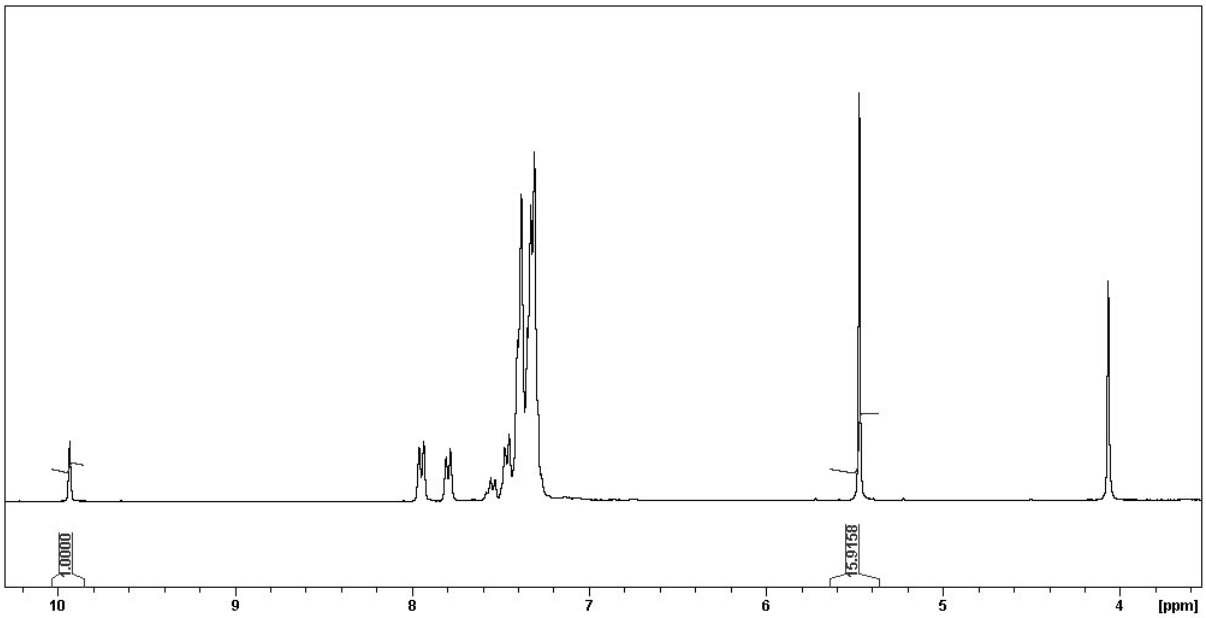
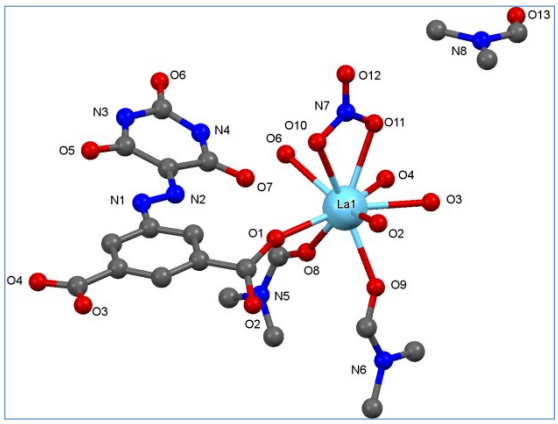
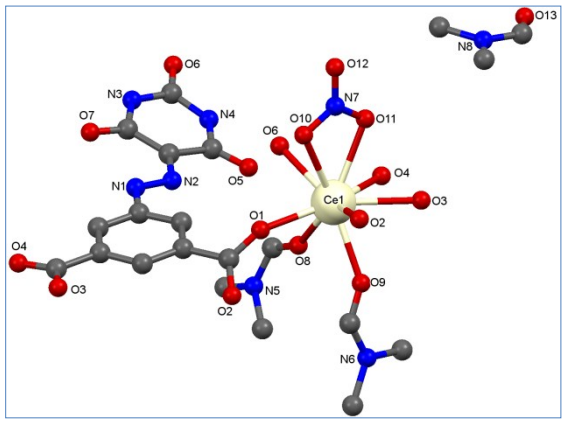


Figure S3: Example of integration in the ^{1}H-NMR spectrum for the determination of cyanosilylation reaction products (Table 1, Entry 2).

The accurateness of this procedure was confirmed by repeating a number of the ^{1}H NMR analyses in the presence of internal standard (1,2-dimethoxyethane) which was added to the $CDCl_3$ solution and this gave product yields similar to those obtained by the above method.



A



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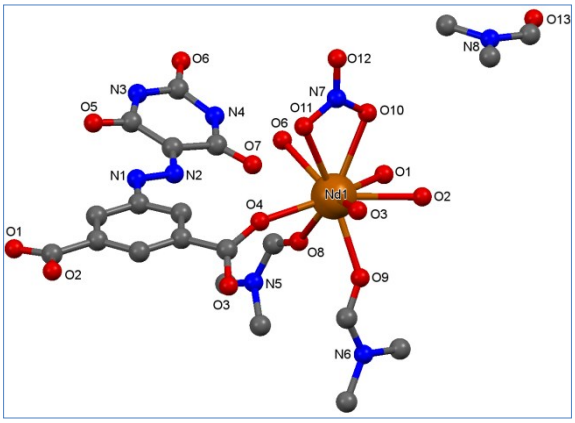

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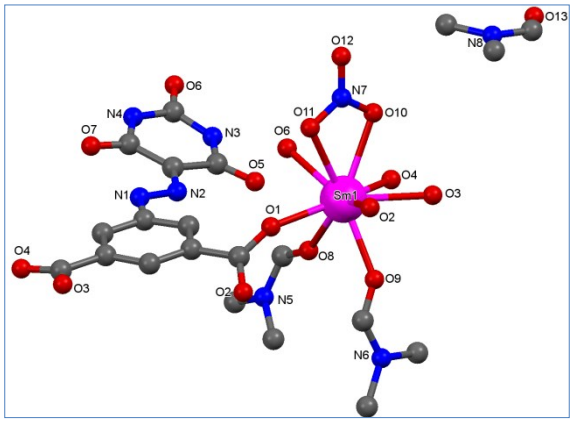

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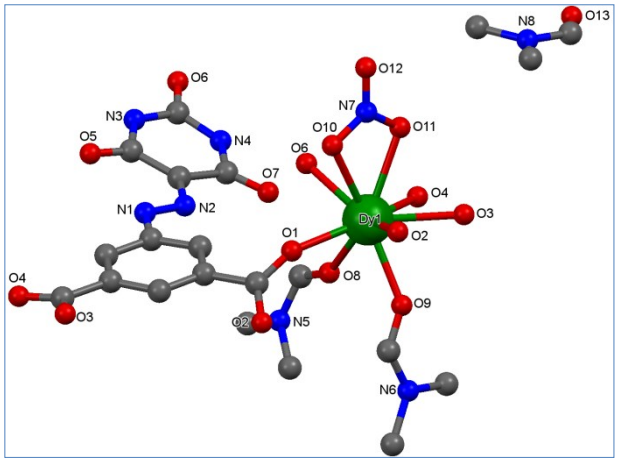


E

Figure S4: The molecular structures of Ln-frameworks **1** (A), **2** (B), **3** (C), **4** (D) and **5** (E).

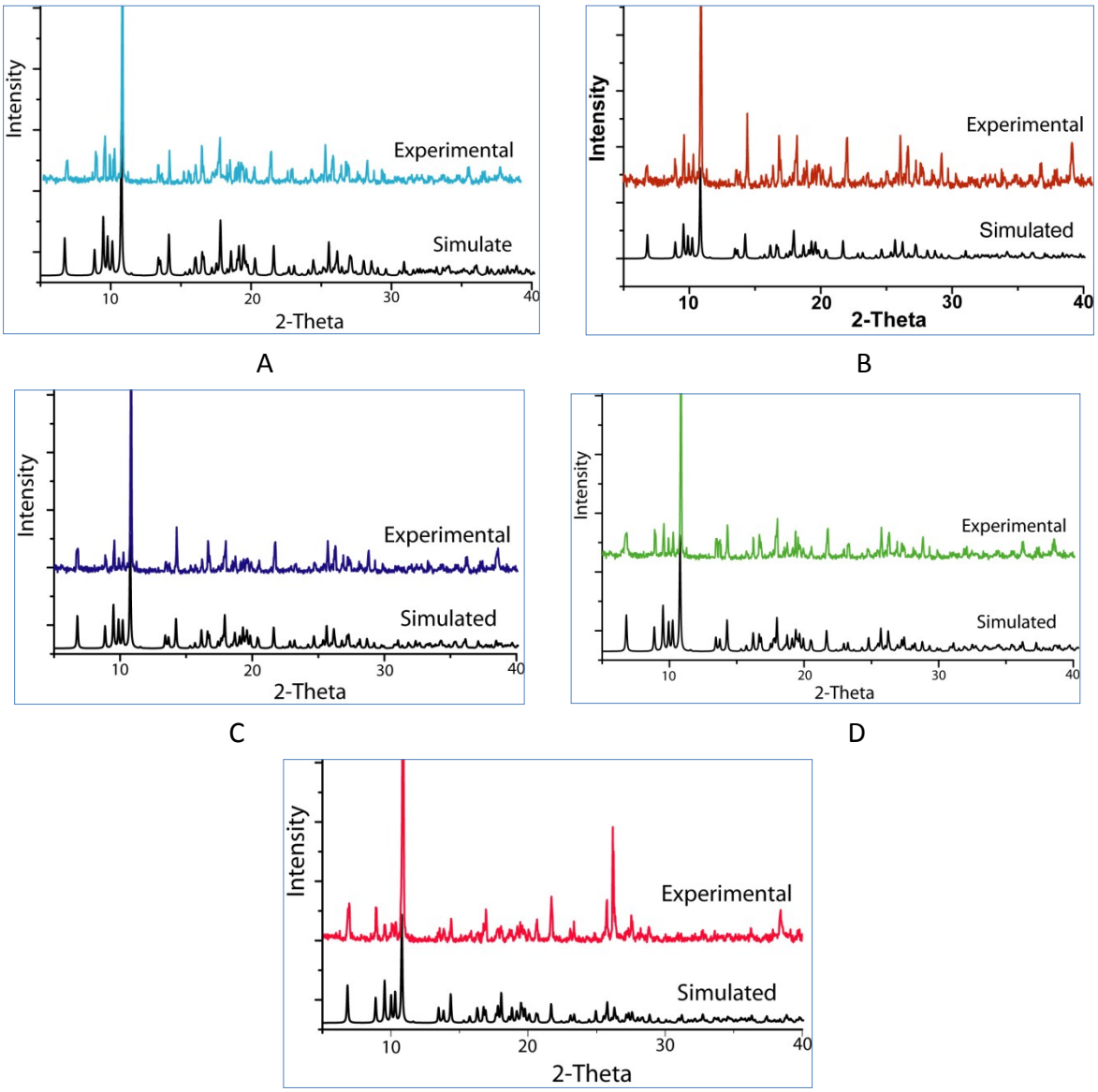
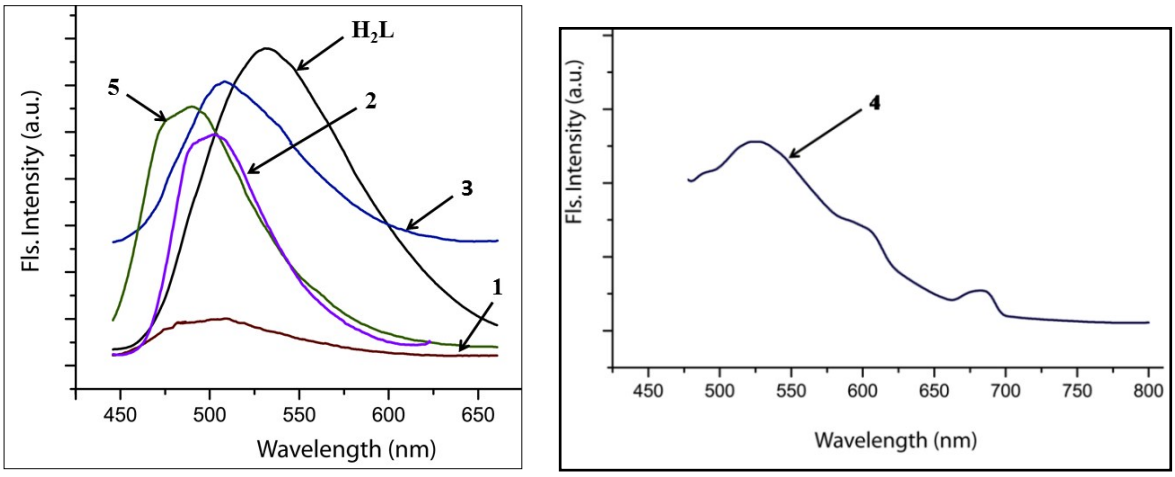


Figure S5 Powder XRD spectra of Ln-frameworks **1** (A), **2** (B), **3** (C), **4** (D) and **5** (E) obtained from the single-crystal X-ray diffraction data (Simulated) and after the catalysis experiments (Experimental)

Photoluminescence Studies

The luminescent properties of the free ligand H_2L and of its Ln-containing polymeric complexes **1**-**5** were investigated in the solid state at room temperature. The Ln-containing polymeric structures exhibit photoluminescence of a similar nature to that of the free ligand. As illustrated in Fig. S6 (emission spectra), the H_2L ligand exhibits an emission peak at 532, upon excitation at λ_{ex} = 370 nm, while complex **1** when excited at λ_{ex} = 380 nm exhibits an emission band at 498 with a blue shift of *ca.* 34 nm probably due to the intra-ligand emission.[2a] Similar spectral patterns are observed for complexes **2, 3** and **5** after excitation at 350, 380 and 400 nm, respectively. They display an emission band at 500 (**2**), 510 (**3**) and 488 (**5**) nm corresponding to blue shifts of *ca.* 32, 22 and 44 nm, in this order. The solid state luminescent study of the Sm^{3+} complex (**4**, λ_{ex} = 450 nm) exhibits three characteristic broad bands at 527 nm ($^4G_{5/2}\rightarrow{}^6H_{5/2}$), 604 nm ($^4G_{5/2}\rightarrow{}^6H_{7/2}$)

and 682 nm ($^4G_{5/2}\rightarrow{}^6H_{9/2}$) whose values are in accord with those of previously reported Sm^{3+} compounds.[2b-f]



(A) (B)

Figure S6: (A) Solid state emission spectra of H_2L and frameworks **1**, **2**, **3** and **5** at room temperature (**1** and **3**@λ_{ex}380 nm, **2**@λ_{ex}350 nm, **5**@λ_{ex}400 nm). (B) solid state emission spectrum of framework **4** at room temperature (λ_{ex} = 450 nm).

Table S1: Crystal data and structure refinement details for compounds 1-5					
Identification name	**1**	**2**	**3**	**4**	**5**
Formulae	$C_{21}H_{27}LaN_8O_{13}$	$C_{21}H_{27}CeN_8O_{13}$	$C_{21}H_{27}N_8NdO_{13}$	$C_{21}H_{27}N_8O_{13}Sm$	$C_{21}H_{27}DyN_8O_{13}$
Mol. wt.	738.41	739.62	743.74	749.85	762.00
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1	P-1	P-1
Temperature /K	296	296	296	296	296
Wavelength /Å	0.71073	0.71073	0.71073	0.71073	0.71073
a /Å	11.0950(3)	11.0424(3)	10.9927(3)	10.9386(3)	10.8661(4)
b /Å	11.1629(3)	11.1343(3)	11.1065(3)	11.0774(3)	11.0292(5)
c /Å	14.1758(4)	14.1570(4)	14.1247(4)	14.0776(4)	14.0228(6)
α/°	83.7360(10)	83.8450(10)	84.0120(10)	84.0560(10)	84.312(2)
β/°	68.205(2)	68.087(2)	67.888(2)	67.7610(10)	67.6040(10)
γ/°	63.6940(10)	63.8570(10)	64.1610(10)	64.3570(10)	64.7230(10)
V/ $Å^3$	1458.14(7)	1446.21(7)	1434.23(7)	1419.69(7)	1400.96(10)
Z	2	2	2	2	2
Density/Mgm^{-3}	1.682	1.698	1.722	1.754	1.806
Abs. Coeff. /mm^{-1}	1.541	1.651	1.888	2.147	2.746
F(000)	740	742	746	750	758
Refl. collected	14640	20269	20942	21303	23464
Refl. unique	5871	5897	5653	5807	5752
Max. 2θ/°	26.373	26.373	26.054	26.387	26.425
Ranges (h, k, l)	-13<= h <=13 -13 <= k <=13 -16<= l <=17	-13<= h <=13 -13<= k <=13 -17<= l <= 17	-13<= h <=13 -13<= k <=13 -17<= l <= 17	-13<= h <=13 -13<= k <=13 -17<= l <= 17	-13<= h <=13 -13<= k <=13 -17<= l <= 17

Complete to 2θ (%)	98.6	99.7	99.6	99.7	99.7
Refl. with I > 2σ(I)	5296	5190	5223	5080	5212
Data/Restraints/Parameters	5871/0/394	5897/2/394	5653/0/394	5807/0/394	5752/ 0 / 394
Goof (F^2)	1.134	1.021	1.029	1.073	1.159
R1 [I > 2s(I)]	0.0266	0.0264	0.0244	0.0251	0.0249
wR2 [I > 2s(I)]	0.0658	0.0615	0.0613	0.0340	0.0599
R1 [all data]	0.0316	0.0342	0.0278	0.0556	0.0300
wR2 [all data]	0.0680	0.0645	0.0631	0.0583	0.0620

Table S2: Selected bond distances (Å) and angles (°) for compounds **1**-**5**	
1	La1-O1 2.4042(18); La1-O2 2.4641(17); La1-O3 2.5720(19); La1-O4 2.5835(18); La1-O6 2.6152(18); La1-O8 2.530(2); La1-O9 2.495(2); La1-O10 2.631(3); La1-O11 2.649(3). <O1-La1-O2 85.43(6); <O1-La1-O9 88.41(8); <O2-La1-O9 73.96(7); <O1-La1-O8 73.34(8); <O2-La1-O8 138.01(7); <O9-La1-O8 69.75(8); <O1-La1-O3 158.01(7); <O2-La1-O3 78.72(6); <O9-La1-O3 72.68(8); <O8-La1-O3 108.99(8); <O1-La1-O4 145.91(6); <O2-La1-O4 128.34(6); <O9-La1-O4 96.25(7); <O8-La1-O4 76.71(7); <O3-La1-O4 50.52(6); <O1-La1-O6 80.40(6); <O2-La1-O6 140.28(7); <O9-La1-O6 141.69(8); <O8-La1-O6 71.94(7); <O3-La1-O6 121.43(6); <O4-La1-O6 75.13(6); <O1-La1-O10 77.27(9); <O2-La1-O10 73.14(8); <O9-La1-O10 144.94(8); <O8-La1-O10 133.03(8); <O3-La1-O10 111.91(9); <O4-La1-O10 113.57(8); <O6-La1-O10 67.61(8); <O1-La1-O11 124.39(9); <O2-La1-O11 85.04(9); <O9-La1-O11 139.66(9); <O8-La1-O11 136.82(10); <O3-La1-O11 69.62(9); <O4-La1-O11 70.27(9); <O6-La1-O11 73.25(9); <O10-La1-O11 47.60(9).
2	Ce1-O1 2.3767(18); Ce1-O2 2.4384(18); Ce1-O3 2.551(2); Ce1-O4 2.5542(18); Ce1-O6 2.595(2); Ce1-O8 2.505(2); Ce1-O9 2.473(2); Ce1-O10 2.612(3); Ce1-O11 2.624(3). <O1-Ce1-O2 85.09(6); <O1-Ce1-O9 88.61(8); <O2-Ce1-O9 74.10(8); <O1-Ce1-O8 73.44(8); <O2-Ce1-O8 137.84(7); <O9-Ce1-O8 69.63(8); <O1-Ce1-O3 157.50(7); <O2-Ce1-O3 78.18(6); <O9-Ce1-O3 72.48(8); <O8-Ce1-O3 109.64(8); <O1-Ce1-O4 146.05(6); <O2-Ce1-O4 128.47(6); <O9-Ce1-O4 95.59(8); <O8-Ce1-O4 76.56(7); <O3-Ce1-O4 51.07(6); <O1-Ce1-O6 80.39(7); <O2-Ce1-O6 140.27(7); <O9-Ce1-O6 141.51(8); <O8-Ce1-O6 71.88(8); <O3-Ce1-O6 122.03(6); <O4-Ce1-O6 75.48(6); <O1-Ce1-O10 76.98(9); <O2-Ce1-O10 73.15(8); <O9-Ce1-O10 145.12(8); <O8-Ce1-O10 132.87(9); <O3-Ce1-O10 111.70(9); <O4-Ce1-O10 114.13(8); <O6-Ce1-O10 67.62(8); <O1-Ce1-O11 124.54(9); <O2-Ce1-O11 85.38(9); <O9-Ce1-O11 139.53(10); <O8-Ce1-O11 136.65(10); <O3-Ce1-O11 69.33(9); <O4-Ce1-O11 70.34(9); <O6-Ce1-O11 73.30(9); <O10-Ce1-O11 48.04(9).
3	Nd1-O1 2.5172(19); Nd1-O2 2.528(2); Nd1-O3 2.4069(18); Nd1-O4 2.3470(19); Nd1-O6 2.5589(19); Nd1-O8 2.481(2); Nd1-O9 2.440(2); Nd1-O10 2.588(3); Nd1-O11 2.584(3). <O4-Nd1-O3 84.82(7); <O4-Nd1-O9 88.80(8); <O3-Nd1-O9 74.47(8); <O4-Nd1-O8 73.28(8); <O3-Nd1-O8 137.66(8); <O9-Nd1-O8 69.40(9); <O4-Nd1-O1 146.22(7); <O3-Nd1-O1 128.43(6); <O9-Nd1-O1 94.44(8); <O8-Nd1-O1 76.48(8); <O4-Nd1-O2 156.60(7); <O3-Nd1-O2 77.43(7); <O9-Nd1-O2 71.93(9); <O8-Nd1-O2 110.38(8); <O1-Nd1-O2 51.66(6); <O4-Nd1-O6 80.68(7); <O3-Nd1-O6 140.06(7); <O9-Nd1-O6 141.51(8); <O8-Nd1-O6 72.11(8); <O1-Nd1-O6 75.98(6); <O2-Nd1-O6 122.68(6); <O4-Nd1-O11 76.48(9); <O3-Nd1-O11 73.05(8); <O9-Nd1-O11 145.30(8); <O8-Nd1-O11 132.47(9); <O1-Nd1-O11 115.28(8); <O2-Nd1-O11 111.95(9); <O6-Nd1-O11 67.44(8); <O4-Nd1-O10 124.63(9); <O3-Nd1-O10 85.00(9); <O9-Nd1-O10 139.13(10); <O8-Nd1-O10 137.22(10); <O1-Nd1 -O10 71.14(9); <O2-Nd1-O10 69.27(9); <O6-Nd1-O10 73.48(9); <O11-Nd1-O10 48.54(9).
4	Sm1-O1 2.3188(19); Sm1-O2 2.3758(19); Sm1-O3 2.505(2); Sm1-O4 2.4842(19); Sm1-O6 2.531(2); Sm1-O8 2.459(2); Sm1-O9 2.407(2); Sm1-O10 2.560(3); Sm1-O11 2.562(3). <O1-Sm1-O2 84.52(7); <O1-Sm1-O9 89.05(9); <O2-Sm1-O9 74.82(8); <O1-Sm1-O8 73.40(8); <O2-Sm1-O8 137.61(8); <O9-Sm1-O8 69.20(9); <O1-Sm1-O4 146.29(7); <O2-Sm1-O4 128.56(7); <O9-Sm1-O4 93.59(8); <O8-Sm1-O4 76.21(8); <O1-Sm1-O3 156.16(7); <O2-Sm1-O3 76.93(7); <O9-Sm1-O3 71.85(9); <O8-Sm1-O3 111.04(8); <O4-Sm1-O3 52.16(6); <O1-Sm1-O6 80.63(7);

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5	Dy1-O1 2.263(2); Dy1-O2 2.326(2); Dy1-O3 2.472(2); Dy1-O4 2.432(2); Dy1-O6 2.478(2); Dy1-O8 2.422(2); Dy1-O9 2.353(3); Dy1-O10 2.526(3); Dy1-O11 2.516(3). <O1-Dy1-O2 84.08(8); <O1-Dy1-O9 89.26(10); <O2-Dy1-O9 75.30(9); <O1-Dy1-O8 73.21(9); <O2-Dy1-O8 137.32(9); <O9-Dy1-O8 68.89(10); <O1-Dy1-O4 146.34(8); <O2-Dy1 O4 128.76(7); <O9-Dy1-O4 92.37(9); <O8-Dy1-O4 76.08(9); <O1-Dy1-O3 155.23(8); <O2-Dy1-O3 76.06(8); <O9-Dy1-O3 71.63(10); <O8-Dy1-O3 112.24(9); <O4-Dy1-O3 53.07(7); <O1-Dy1-O6 80.88(8); <O2-Dy1-O6 139.50(8); <O9-Dy1-O6 141.30(9); <O8-Dy1-O6 72.43(9); <O4-Dy1-O6 76.98(7); <O3-Dy1-O6 123.88(7); <O1-Dy1-O11 124.99(10); <O2-Dy1-O11 85.29(11); <O9-Dy1-O11 138.74(11); <O8-Dy1-O11 137.31(11); <O4-Dy1-O11 71.90(10); <O3-Dy1-O11 68.47(10); <O6-Dy1-O11 73.40(10); <O1-Dy1-O10 75.75(10); <O2-Dy1-O10 72.71(9); <O9-Dy1-O10 145.78(10); <O8-Dy1-O10 132.02(10); <O4-Dy1-O10 117.15(9); <O3-Dy1-O10 111.33(10); <O6-Dy1-O10 67.20(9); <O11-Dy1-O10 49.61(10).

Table S3: Hydrogen bond geometry (Å, °) in compounds 1-5

Compound	D-H···A	D···H (Å)	H···A (Å)	D···A (Å)	<D–H···A(°)
1	N1-H1N···O5	0.86	1.96	2.626(3)	133.7
	N3-H3N···O4	0.86	1.91	2.729(3)	159.9
	N4-H4N···O13	0.86	2.02	2.880(3)	173.0
	C13-H13···O7	0.93	2.34	3.241(4)	162.9
	C16-H16···O10	0.93	2.44	3.305(5)	153.9
	C17-H17A···O10	0.96	2.46	3.374(7)	158.0
2	N1-H1N···O7	0.86	1.96	2.625(3)	133.8
	N3-H3N···O4	0.86	1.91	2.728(3)	159.2
	C16-H16···O10	0.93	2.44	3.295(4)	153.8
	N4-H4N···O13	0.86	2.01	2.869(3)	173.0
	C13-H13···O5	0.93	2.33	3.236(4)	163.0
	C18-H18C···O10	0.96	2.45	3.365(7)	158.3
3	N1-H1N···O5	0.86	1.96	2.628(3)	133.7
	N3-H3N···O1	0.86	1.90	2.722(3)	158.7
	C13-H13···O7	0.93	2.35	3.241(4)	161.3
	N4-H4N···O13	0.86	2.01	2.866(3)	173.1
	C16-H16···O11	0.93	2.42	3.277(4)	152.6
	C18-H18A···O11	0.96	2.45	3.359(7)	157.9
4	N1-H1N···O7	0.86	1.96	2.629(3)	133.8
	N3-H3N···O13	0.86	2.01	2.862(3)	173.0
	C16-H16···O11	0.93	2.41	3.261(5)	151.8
	C18-H18A···O11	0.96	2.44	3.344(6)	157.4
	N4-H4···O4	0.86	1.90	2.717(3)	158.2
	C13-H13···O5	0.93	2.34	3.239(4)	161.3
	C15-H15A···O5	0.96	2.63	3.514(6)	153.0

5	N4-H4N···O13	0.86	2.00	2.852(4)	173.0
	N3-H3N···O4	0.86	1.89	2.703(3)	156.4
	N1-H1N···O5	0.86	1.96	2.632(3)	133.8
	C16-H16···O10	0.93	2.40	3.238(5)	150.6
	C17-H17A···O10	0.96	2.44	3.343(7)	156.5
	C13-H13···O7	0.93	2.35	3.241(4)	159.7
	C14-H14C···O7	0.96	2.57	3.470(6)	155.2

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