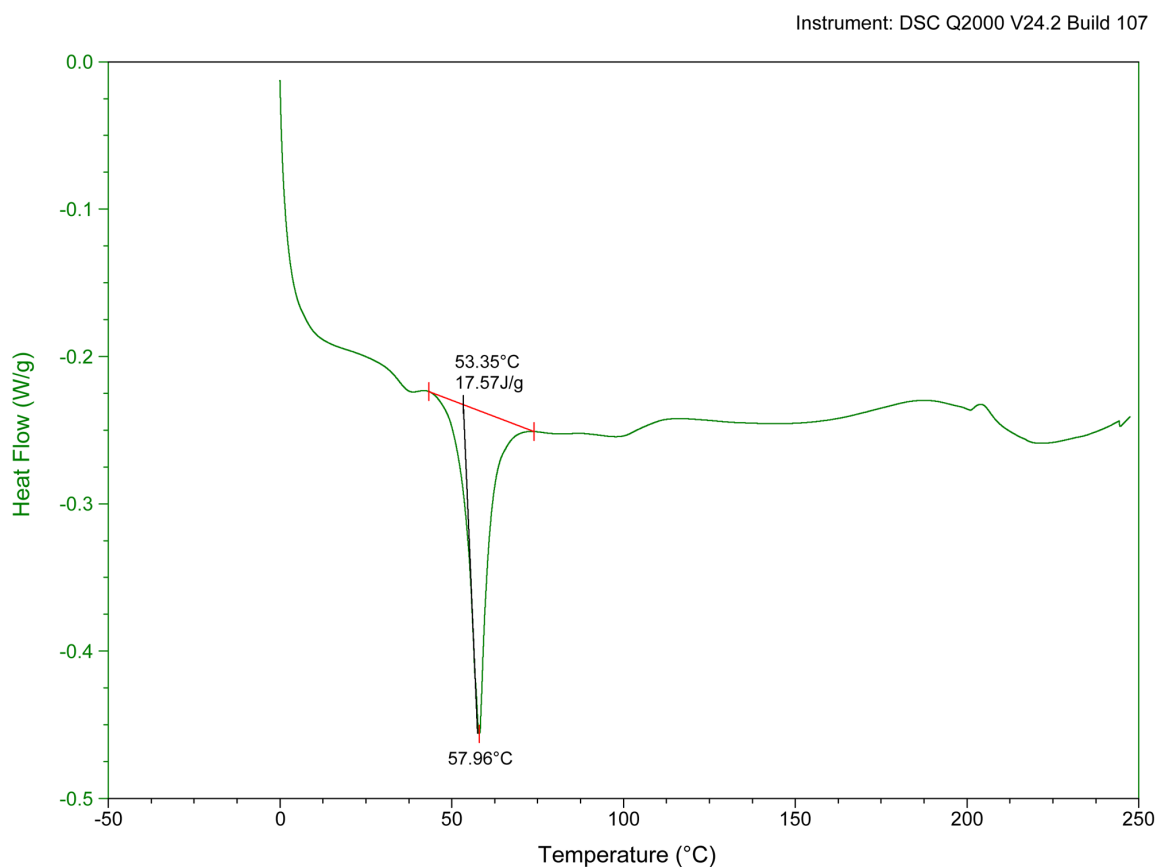


## Supporting Information For:

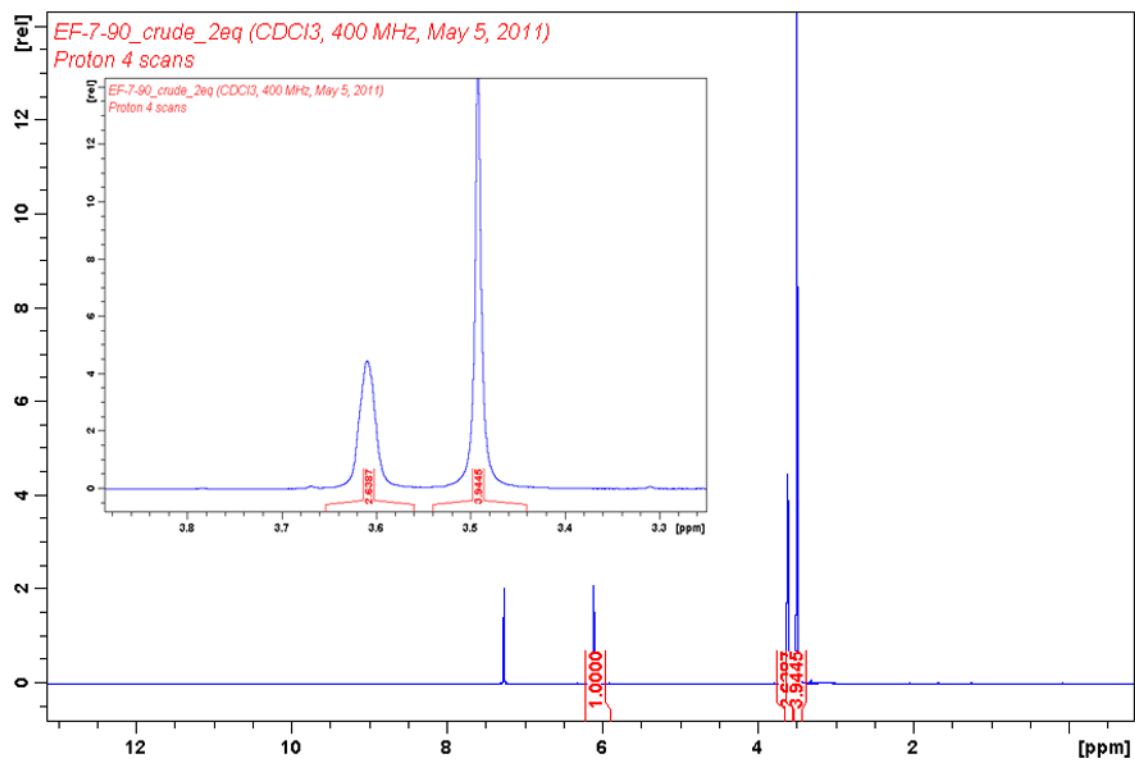
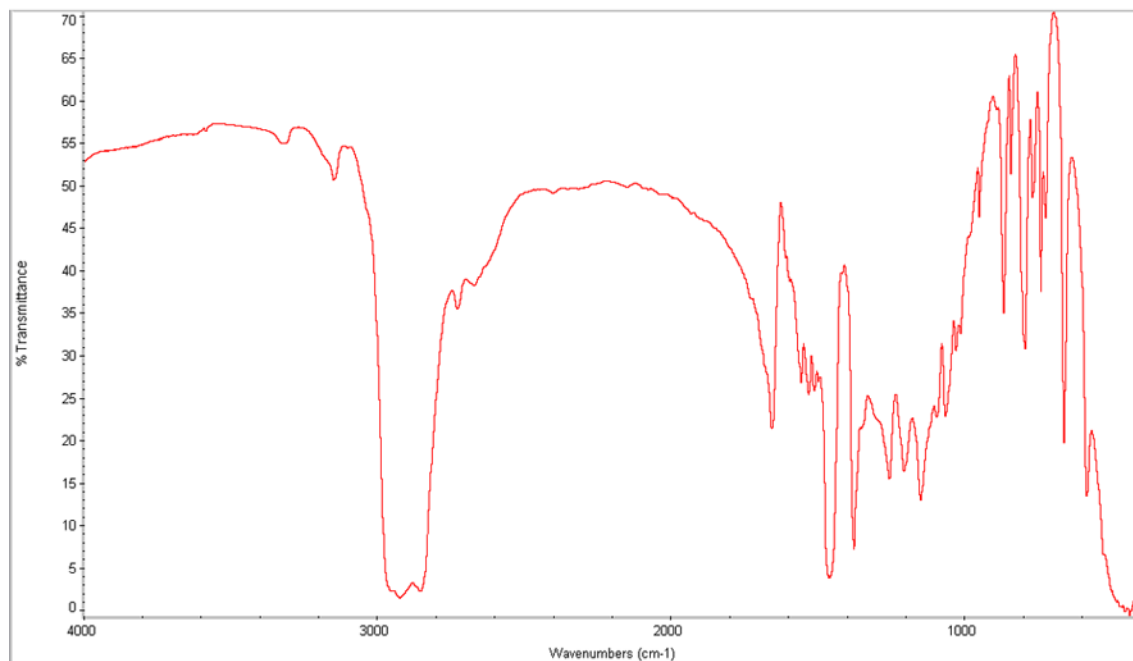
### Syntheses and Crystal Structures of Anhydrous $\text{Ln}(\text{hfac})_3(\text{monoglyme})$ . Ln = La, Ce, Pr, Sm, Eu, Gd, Tb, Dy, Er, Tm.

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and Kathryn E. Preuss\*<sup>a</sup>

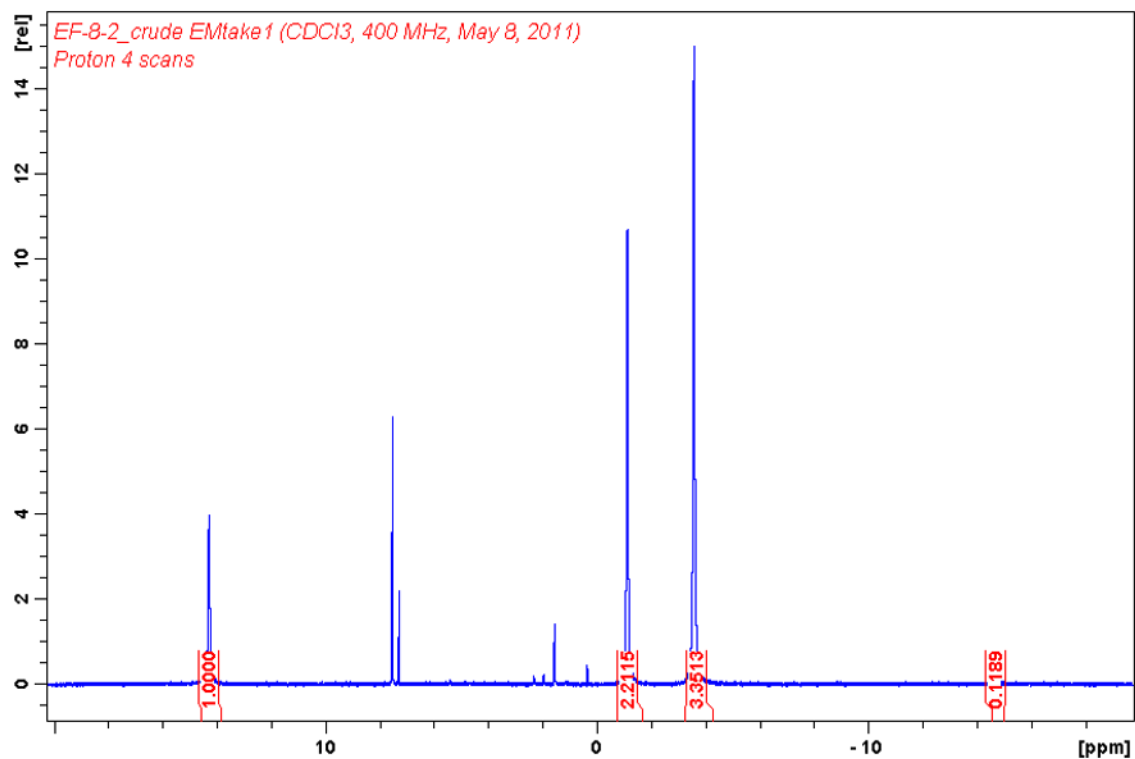
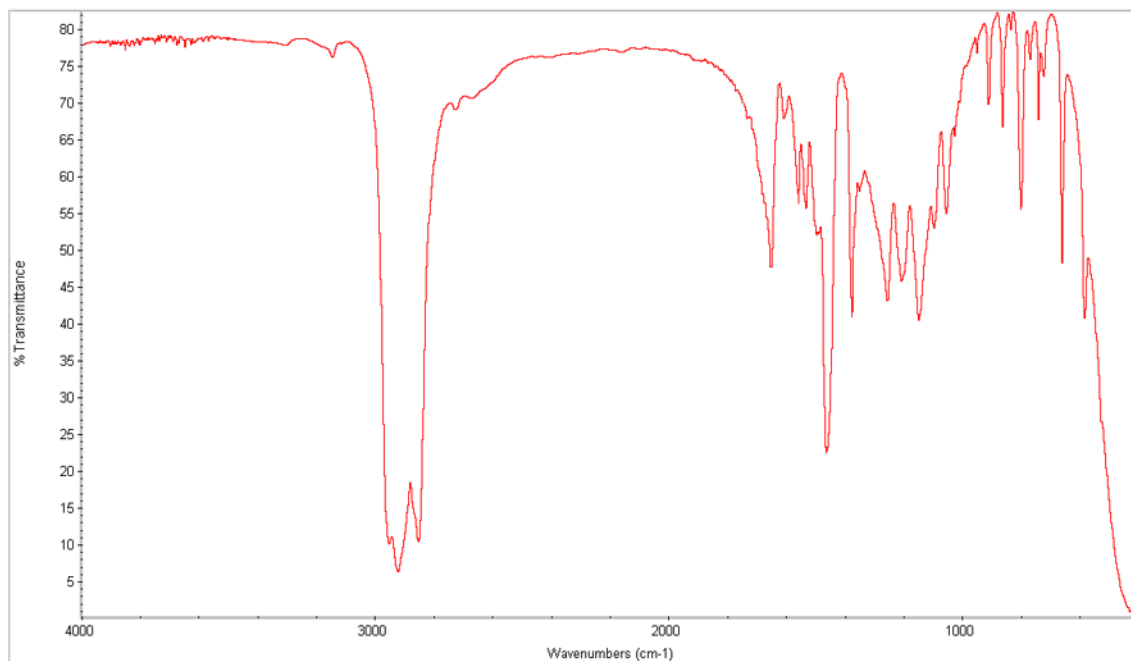
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**Figure S1.** Differential Scanning Calorimetry (DSC) graph of  $\text{La}(\text{hfac})_3(\text{monoglyme})$  showing the phase change at  $53.35^\circ\text{C}$ .



**Figure S2.** IR absorption spectrum (Nujol on NaCl plate) and <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of the pre-sublimation lanthanum species to illustrate that this species is anhydrous.



**Figure S3.** IR absorption spectrum (Nujol on NaCl plate) and <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>; note that there are two CHCl<sub>3</sub> peaks corresponding to the neat solvent and the solvent in the presence of the paramagnetic solute) of the pre-sublimation cerium species to illustrate that this species is anhydrous.

## Crystallographic Experimental Details.

### **Ln(hfac)<sub>3</sub>(monoglyme) coordination complexes**

**(Ln = La, Ce, Pr, Sm, Eu, Gd, Tb, Dy, Er, Tm):**

Single crystals of each of the products were grown by sublimation and cooled under a stream of N<sub>2</sub> for collection at low temperature (see Table). The majority of the data were collected on a Bruker-Nonius Kappa-CCD diffractometer using monochromated Mo-K $\alpha$  radiation and were measured using a combination of  $\phi$  scans and  $\omega$  scans with  $\kappa$  offsets, to fill the Ewald sphere.<sup>1</sup> The data were processed using the Denzo-SMN package. Absorption corrections were carried out using SORTAV.<sup>2</sup> Two of the data sets were collected with a Bruker APEX2 area detector diffractometer using APEX2 software, with Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using Bruker SAINT. The absorption correction was applied using SADABS.

In all cases, the reflection data and systematic absences were consistent with an orthorhombic space group: *Pbca*. The structures were solved (direct methods) and refined using SHELXTL V6.1<sup>3</sup> for full-matrix least-squares refinement that was based on  $F^2$ . Subsequent difference Fourier syntheses allowed the remaining atoms to be located. Independent molecules were formed. Most of the atoms were well ordered, however, it was typical to find some of the perfluoro butyl groups showing some disorder. They were modelled at various ratios (see Table), determined by refinement of the occupancy. All of the non-hydrogen atoms were refined with anisotropic thermal parameters (exceptions noted in Table). All H atoms were included in calculated positions and allowed to refine in riding-motion approximation with  $U_{\text{iso}}$  tied to the carrier atom. The largest residue electron density peak and Full-matrix least squares refinement values are reported in the Table below.

### **Ce(hfac)<sub>3</sub>(monoglyme)(H<sub>2</sub>O) coordination complex:**

Single crystals of [Ce(hfac)<sub>3</sub>(monoglyme)(H<sub>2</sub>O)] were grown from hexanes and cooled under a stream of N<sub>2</sub> for collection at low temperature (150 K). The data were collected on a Bruker-Nonius Kappa-CCD diffractometer using monochromated Mo-K $\alpha$  radiation and were measured using a combination of  $\phi$  scans and  $\omega$  scans with  $\kappa$  offsets, to fill the Ewald sphere.<sup>1</sup> The data were processed using the Denzo-SMN package. Absorption corrections were carried out using SORTAV.<sup>2</sup> The unit cell parameters were calculated and refined from the full data set.

The reflection data and systematic absences were consistent with a monoclinic space group: *P2<sub>1</sub>/c*. The structures were solved (direct methods) and refined using SHELXTL V6.1<sup>3</sup> for full-matrix least-squares refinement that was based on  $F^2$ . Subsequent

difference Fourier syntheses allowed the remaining atoms to be located. Two independent molecules were formed. Most of the atoms were well ordered, however, two of the perfluoro butyl groups showed some disorder. They were modelled isotropically at 0.70/0.30 and 0.64/0.36 as determined by refinement of the occupancy. All of the non-hydrogen atoms were refined with anisotropic thermal parameters except for C66 which did not behave well. All H atoms were included in calculated positions and allowed to refine in riding-motion approximation with  $U_{\text{iso}}$  tied to the carrier atom. The largest residue electron density peak ( $2.11 \text{ e}/\text{\AA}^3$ ) was associated with one of the disordered fluorine atoms. Full-matrix least squares refinement on  $F^2$  gave  $R_1 = 4.85$  for  $2\sigma$  data and  $wR_2 = 12.04$  for all data (GOOF = 1.036).

### **La(hfac)<sub>3</sub>(monoglyme)<sub>2</sub> coordination complex:**

Single crystals of [La(hfac)<sub>3</sub>(monoglyme)<sub>2</sub>] were grown from hexane and cooled under a stream of N<sub>2</sub> for collection at low temperature (150 K). The data were collected on a Bruker APEX2 area detector diffractometer using APEX2 software, with Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Data were measured using a combination of  $\phi$  scans and  $\omega$  scans with  $\kappa$  offsets, to fill the Ewald sphere.<sup>1</sup> Crystal cell refinement and data reduction were carried out using Bruker SAINT. The absorption correction was applied using SADABS.

The reflection data and systematic absences were consistent with a monoclinic space group:  $P2_1/n$ . The structures were solved (direct methods) and refined using SHELXTL V6.1<sup>3</sup> for full-matrix least-squares refinement that was based on  $F^2$ . Subsequent difference Fourier syntheses allowed the remaining atoms to be located. A single independent molecule was located. Most of the atoms were well ordered, however, one of the perfluoro butyl groups showed some disorder. It was modelled anisotropically at a 50/50 ratio as determined by refinement of the occupancy. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. All H atoms were included in calculated positions and allowed to refine in riding-motion approximation with  $U_{\text{iso}}$  tied to the carrier atom. The largest residue electron density peak ( $1.461 \text{ e}/\text{\AA}^3$ ) was associated with one of the fluorine atoms. Full-matrix least squares refinement on  $F^2$  gave  $R_1 = 3.84$  for  $2\sigma$  data and  $wR_2 = 10.87$  for all data (GOOF = 1.054).

- (1) Otwinowski, Z.; Minor, W. In *Macromolecular Crystallography, Pt A*; Carter, C. W., Sweet, R. M., Eds.; Academic Press: London, 1997; Vol. 276, p 307.
- (2) Blessing, R. H. *Acta Cryst.* **1995**, *A51*, 33.
- (3) Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112.

	La	Ce	Pr	Sm	Eu	Gd	Tb	Dy	Er	Tm
Temp (K)	150	150	220	220	200	220	220	150	150	220
Data Collection						APEX 2		APEX 2		
-CF3	.60/.40	.60/.40	.65/.35	.52/.48	.70/.30	.60/.40	.75/.25	.60/.40	.59/.41	.79/.21
-CF3	.60/.40	.57/.43	.52/.48	.52/.48	.64/.36	.54/.46	.58/.42	.60/.40	.57/.43	.57/.43
-CF3	.50/.50	.54/.46			.52/.48	.52/.48		ξ	.53/.47	
$e/\text{Å}^3$	1.65	1.71	0.74	0.97	1.92	1.05	1.32	1.14	1.61	1.16
$R_1$	4.88	5.78	4.46	4.44	6.24	3.66	4.68	4.40	3.94	4.51
$wR_2$	14.26	18.44	12.80	13.44	21.96	10.25	13.96	11.72	10.93	13.05

ξ disordered fluorines kept isotropic