

## Supporting Information for:

# Harnessing magnetic fields for rare-earth complex crystallization-separations in aqueous solutions

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## Experimental Section

### General Considerations

All manipulations were carried out under ambient conditions. Unless otherwise stated, all chemicals and reagents were from major commercial suppliers and used as received or after extensive drying. Deuterated NMR solvents were purchased from Cambridge Isotope Laboratories (Tewksbury, MA, USA).  $^1\text{H}$  NMR spectra were collected on a 400 MHz Bruker UNI 400 FT NMR spectrometer (Bruker, Billerica, MA, USA) and referenced to the residual protio-solvent signal<sup>1</sup>. Chemical shifts ( $\delta$ ) are reported in units of ppm. The  $\text{Fe}_{14}\text{Nd}_2\text{B}$  magnets (1/2" square  $\times$  1/8" thick plate) were purchased from United Nuclear Scientific Equipment and Supplies.

### Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP–OES)

Inductively coupled plasma optical emission spectroscopy was conducted on a Spectro Genesis ICP-OES spectrometer (SPECTRO Analytical Instruments GmbH, Kleve, Germany) equipped with an integrated three-channel peristaltic pump and an ASX-260 auto-sampler (CETAC Technologies, Omaha, NE, USA). Samples solutions were delivered to the nebulizer using a Mod Lichte spray chamber and single-use PVC PT-2140PF tubing (Precision Glassblowing, Centennial, CO, USA). Each data acquisition was preceded by a 35-second rinse sequence at different pump speeds. Other relevant parameters were previously optimized to give the smallest RSD and are summarized in Table S1.

**Table S1.** Instrumental and operating conditions for ICP-OES measurements

Instrument Conditions	
Forward Power (W)	1350
Plasma gas flow rate ( $\text{L min}^{-1}$ )	13.50
Auxiliary gas flow rate ( $\text{L min}^{-1}$ )	1.00
Nebulizer flow rate ( $\text{L min}^{-1}$ )	0.90
Wavelengths (nm)	La 333.749 Nd 430.358 Dy 364.540 Er 326.478 Tm 342.508

Nitric acid (Fisher, Certified ACS Plus grade, 70% v/v), hydrogen peroxide (Fisher, 30% solution in water), and distilled-deionized water (Milli-Q, 18.2  $\text{M}\Omega\cdot\text{cm}$ , Millipore) were used for sample preparation and dilution. Samples were prepared by digestion in a (4:1)  $\text{HNO}_3:\text{H}_2\text{O}_2$  mixture at room temperature overnight, followed by dilution to a concentration of *ca.* 5%  $\text{HNO}_3$  to limit matrix effects. Analytical plasma standard solutions were obtained from Alfa Aesar (Specpure®),

1000 ppm RE<sub>2</sub>O<sub>3</sub> in 5% HNO<sub>3</sub>). Calibrations were performed before each set of measurements using a range of 7 standardized solutions (100–1 ppm) containing the elements of interest and a blank. Calibration curves were confirmed to have R<sup>2</sup> > 0.999 for the selected elements. Potential instrumental drift was monitored by continuously measuring Ar lines at 430.010 and 404.442 nm; the absence of drift was finally confirmed by measuring a standardized solution at the end of each measurement session. The wavelengths selected had the highest signal intensity, in agreement with the literature, and were the most relevant for the studied range of concentrations.

#### Separations Experiment without a Magnetic Field

To perform the experiments for the separations of rare earth ions, the binary mixtures of RE-DOTA were dissolved in 1 mL H<sub>2</sub>O (0.025 M for individual RE, 0.05 M combined) in a 4 mL vial, layered with 3 mL of acetone (3:1 acetone:H<sub>2</sub>O) and kept at 3°C for 72 hours to induce crystallization. After that time, the solid crystals were isolated by decantation, washed with acetone (~5 mL), and both the solid and filtrate portions were dried under vacuum. The isolated solid and filtrate portions were then subjected to digestion conditions for ICP-OES analysis as written above. These experiments for each binary pair of RE ions were triplicated and the enrichment and separation factors were averaged over these three experiments, which is likely the source of the experimental error shown in Table 1.

#### Separations Experiment with a Magnetic Field

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#### Determination of Enrichment Factors and Separation Factors for La/Dy Pair

Enrichment factors were calculated using the following equations, where EF represents the enrichment factor and η represents millimolar of metal content in the sample used for ICP-OES analysis:

$$EF_{Dy,crystals} = \frac{\eta_{Dy}}{\eta_{La}}$$

$$EF_{La,motherliquor} = \frac{\eta_{La}}{\eta_{Dy}}$$

Separation factors were calculated using the following equation.

$$SF_{La:Dy} = EF_{Dy,crystals} \times EF_{La,motherliquor}$$

The enrichment factors and separation factors were calculated using ICP-OES spectroscopy. Sample calculations are shown below. The initial metal ratio of each homogenized mixture was analyzed by ICP by withdrawing an aliquot of the mixture before subjecting to crystallization.

	<b>Initial</b>	<b>Crystals</b>	<b>Mother Liquor</b>
$\eta_{La}$	0.251	0.080	0.121
$\eta_{Dy}$	0.245	0.273	0.010

$$EF_{Dy,initial} = \frac{\eta_{Dy,initial}}{\eta_{La,initial}} = \frac{0.245}{0.251} = 0.98$$

$$EF_{La,motherliquor} = \frac{\eta_{La}}{\eta_{Dy}} = \frac{0.121}{0.010} = 12.1$$

$$EF_{Dy,crystals} = \frac{\eta_{Dy}}{\eta_{La}} = \frac{0.273}{0.080} = 3.41$$

$$SF_{La:Dy} = EF_{Dy,crystals} \times EF_{La,motherliquor} = 3.41 \times 12.1 = 41.4$$

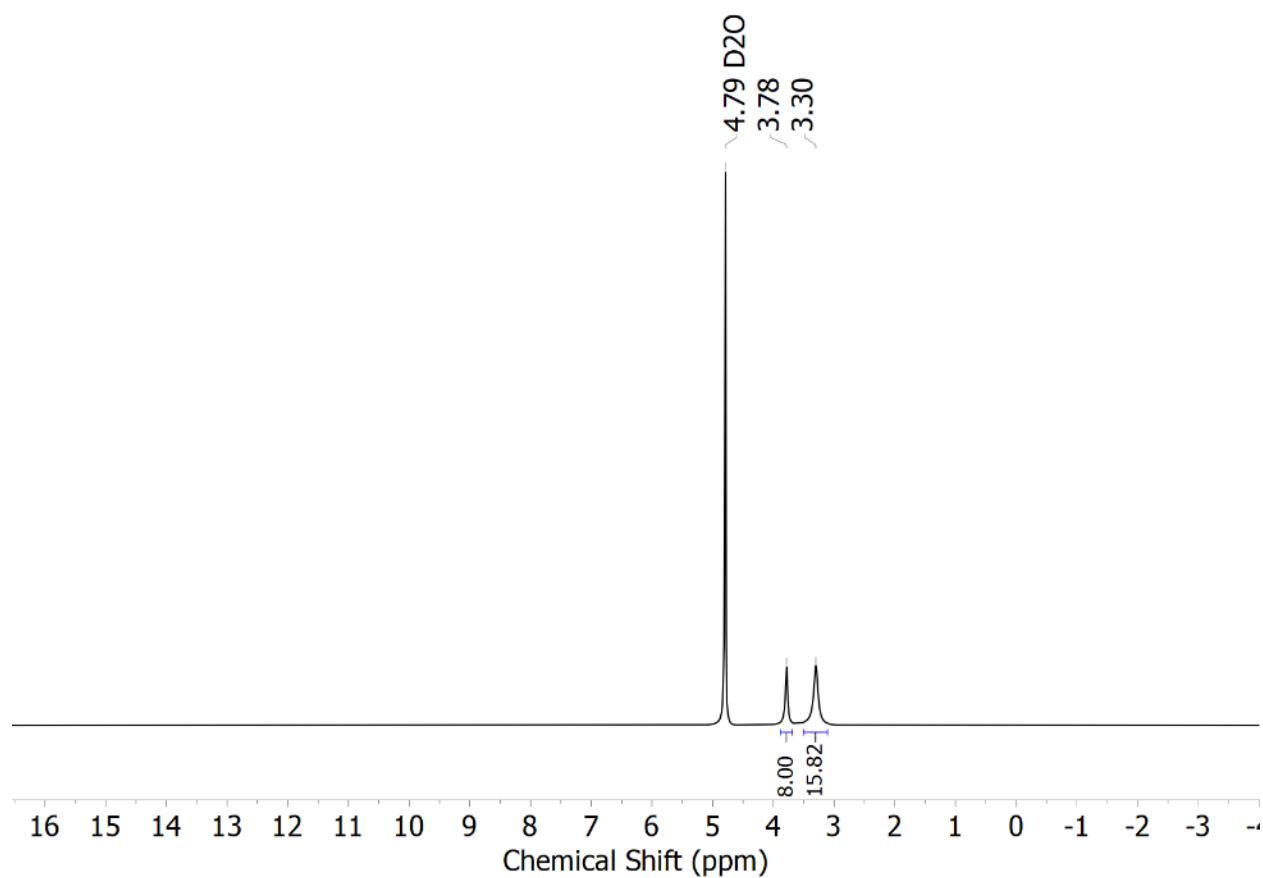
## Synthesis and Characterization

### **Synthesis of RE-DOTA (Na[RE(DOTA)(H<sub>2</sub>O)]•4H<sub>2</sub>O) Complexes**

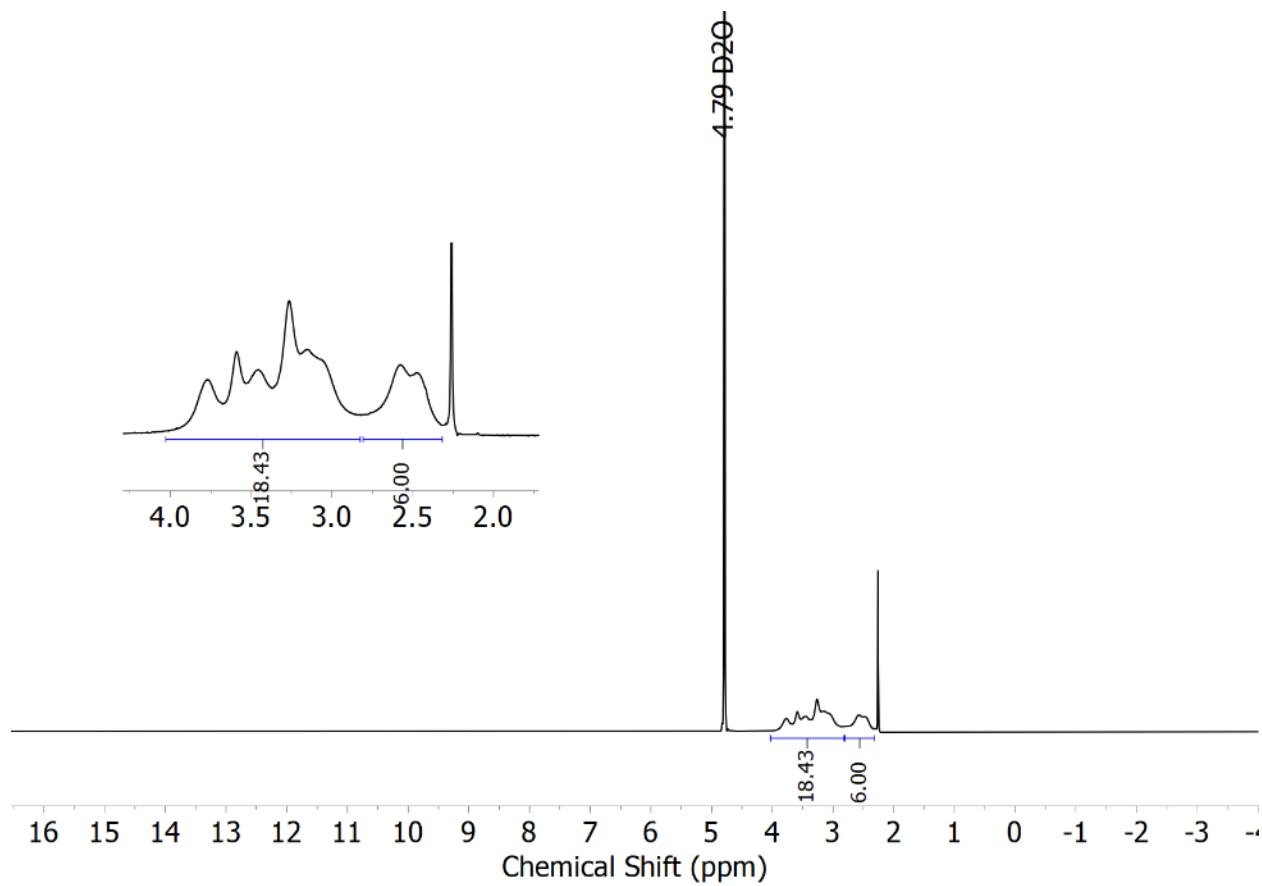
The RE-DOTA (RE = La, Nd, Dy, Er, Tm) complexes were prepared following the literature procedure with slight modification.<sup>2,3</sup> A mixture of RE<sub>2</sub>O<sub>3</sub> (0.371 mmol), H<sub>4</sub>DOTA (1,4,7,10-tetraazacyclododecane-*N,N',N'',N'''*-tetraacetic acid; 0.743 mmol) and NaOH (0.743 mmol) in 15 mL of distilled water was heated for 3–4 days with stirring at 90 °C. After that, the mixture was cooled to room temperature and filtered through a Celite bed on a medium porosity fritted filter. The resultant turbid filtrate was centrifuged and the supernatant solution was decanted to separate from the residual suspension. Single crystals of RE-DOTA complexes suitable for X-ray diffraction analysis were obtained by vapor diffusion of acetone into a concentrated solution of RE-DOTA complexes in water at room temperature. Unit cell determination of single crystals of RE-DOTA complexes confirmed the formation of the

desired compounds in all cases.  $^1\text{H}$  NMR spectra for all the complexes were collected in  $\text{D}_2\text{O}$  (Figures S1-S6).

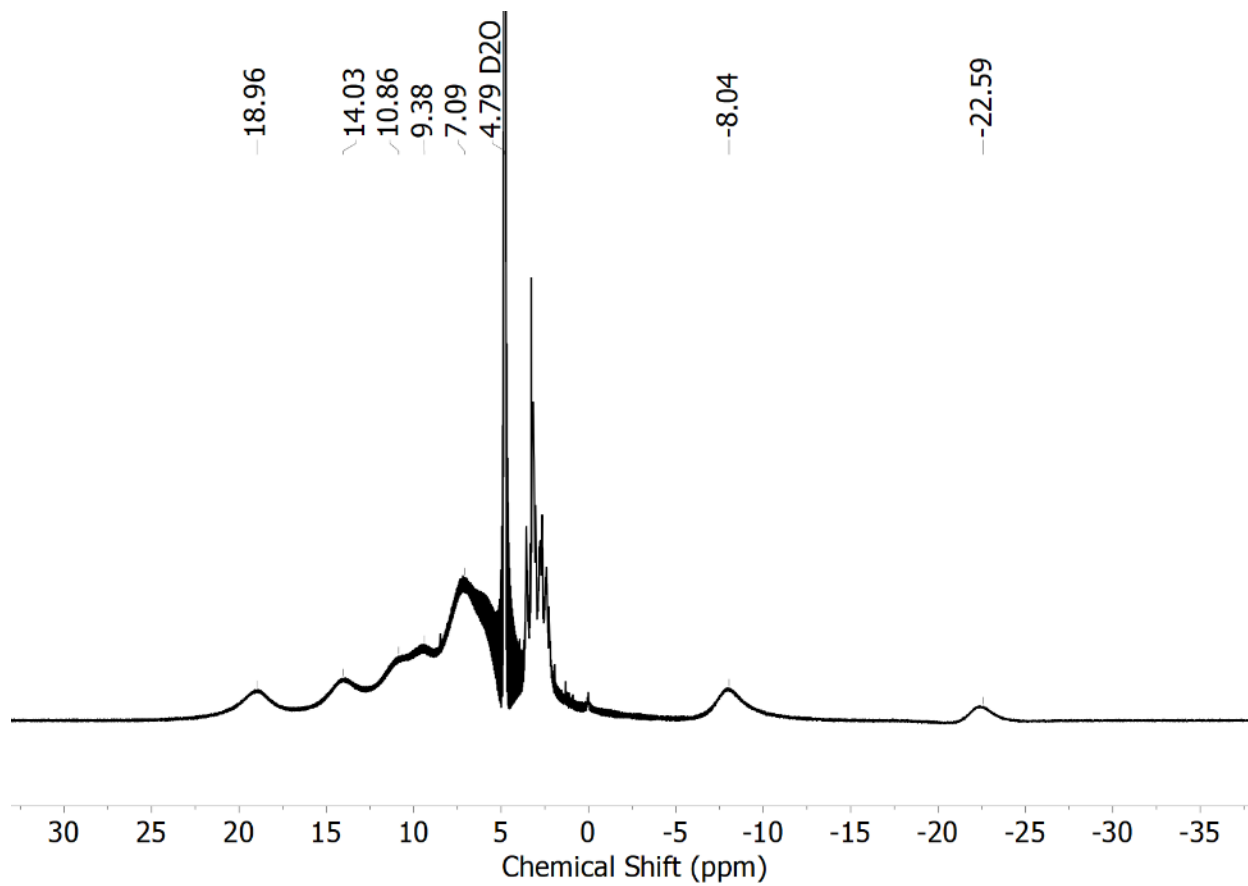
### NMR Spectra



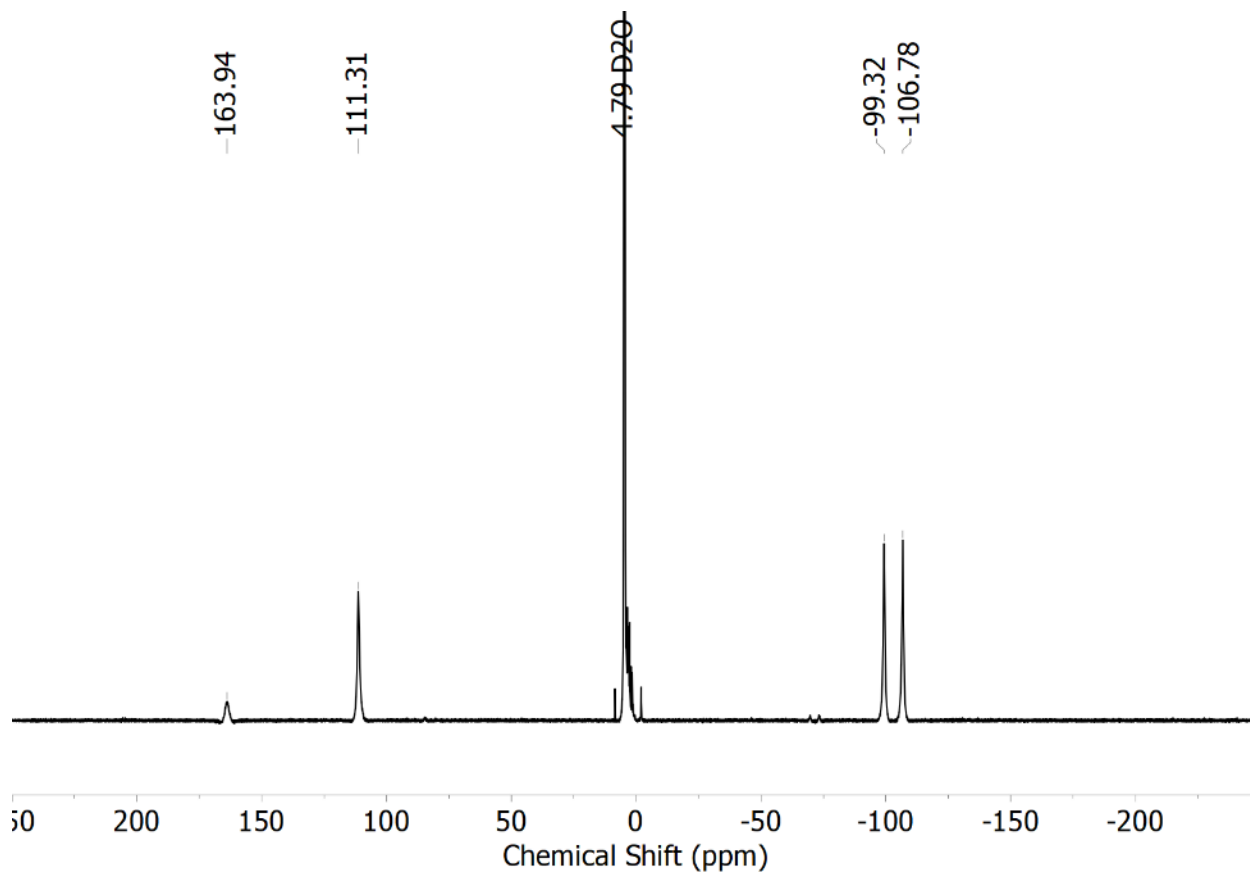
**Figure S1.**  $^1\text{H}$  NMR spectrum of  $\text{H}_4\text{DOTA}$  (400 MHz,  $\text{D}_2\text{O}$ ).



**Figure S2.**  $^1\text{H}$  NMR spectrum of La-DOTA (400 MHz,  $\text{D}_2\text{O}$ ).

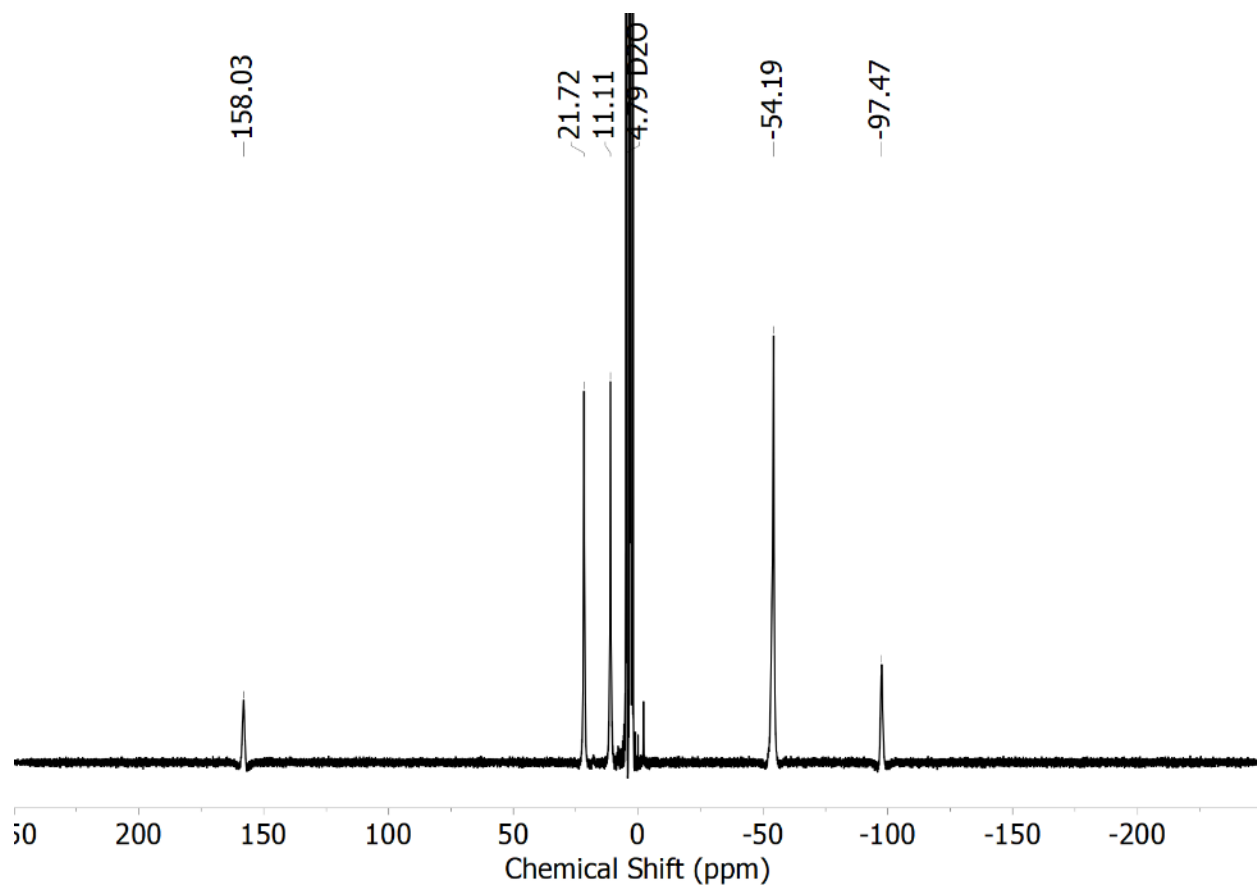


**Figure S3.**  $^1\text{H}$  NMR spectrum of Nd-DOTA (400 MHz,  $\text{D}_2\text{O}$ ).

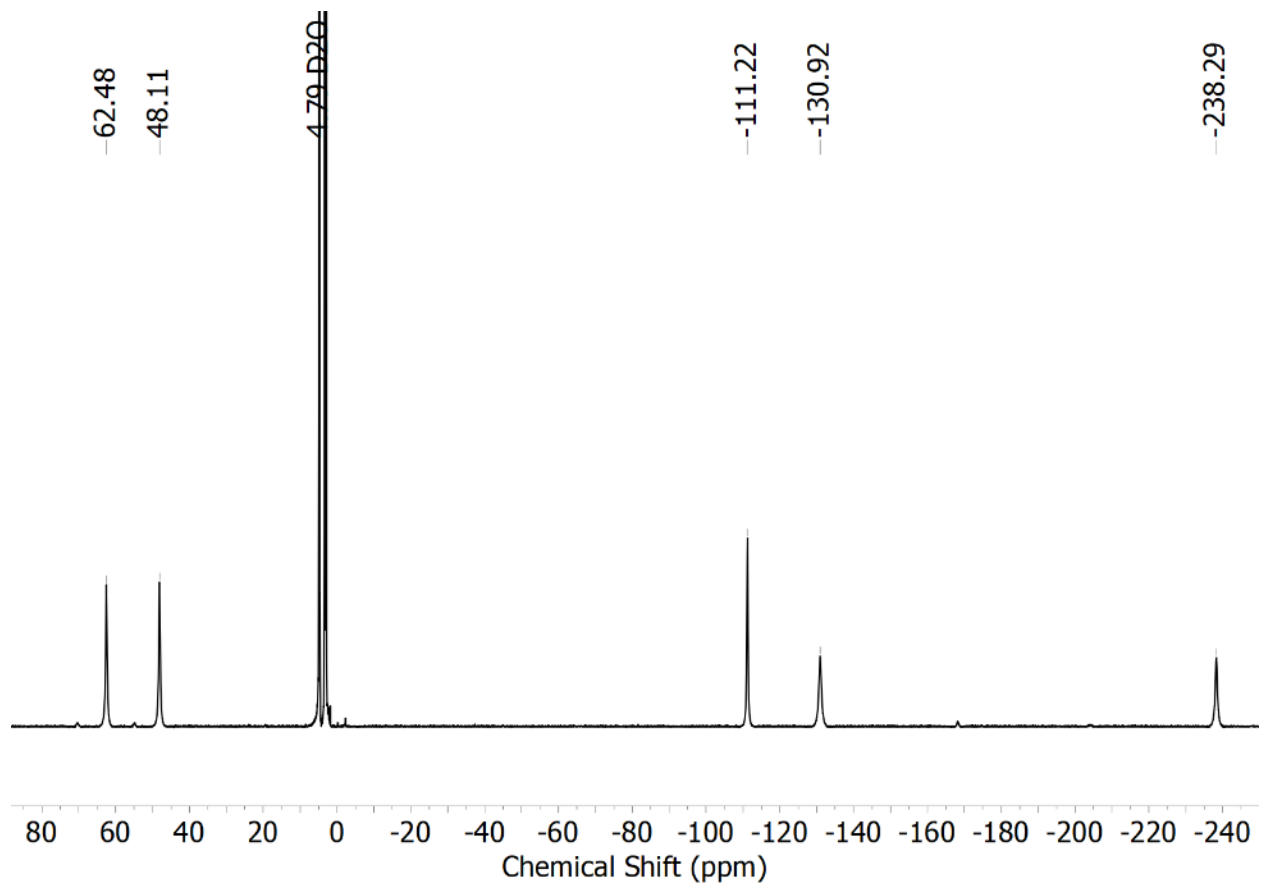


**Figure S4.**  $^1\text{H}$  NMR spectrum of Dy-DOTA (400 MHz,  $\text{D}_2\text{O}$ ).

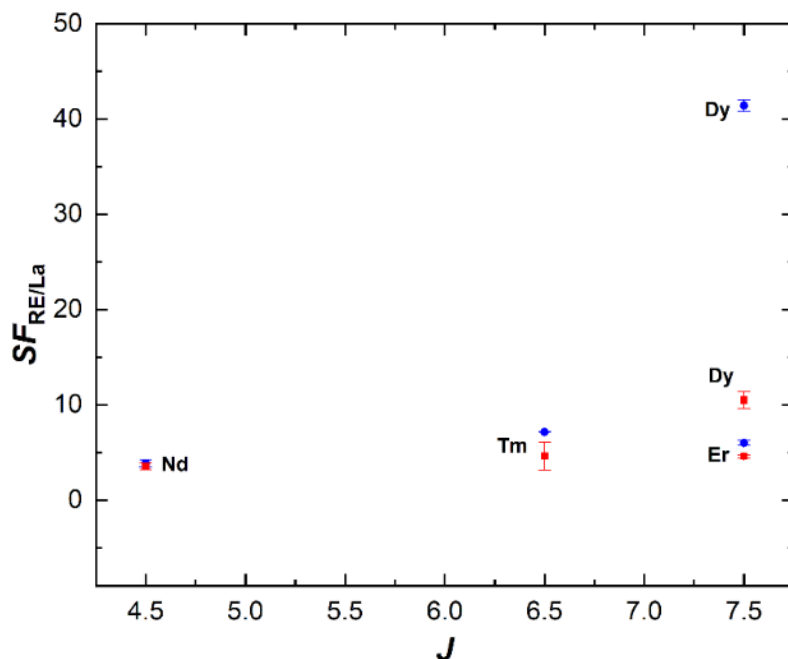




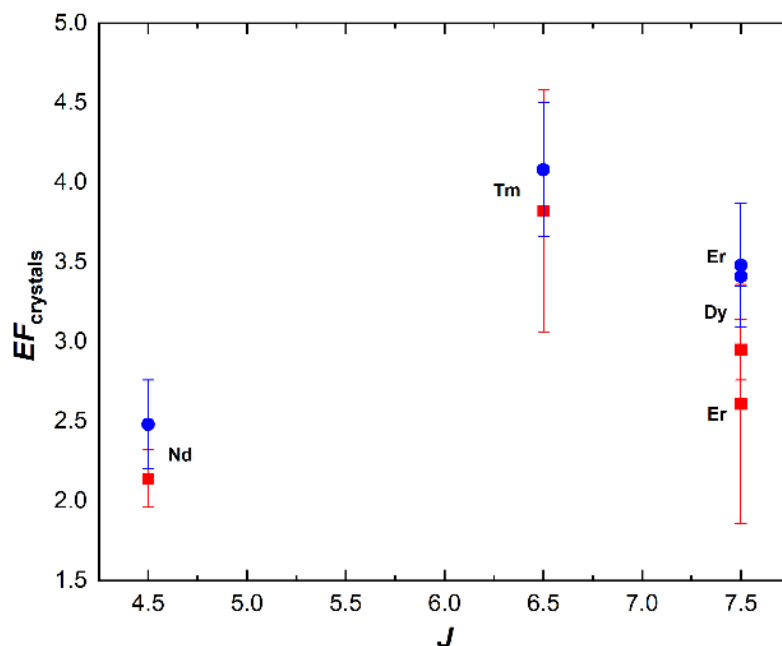
**Figure S5.**  $^1\text{H}$  NMR spectrum of Er-DOTA (400 MHz,  $\text{D}_2\text{O}$ ).



**Figure S6.**  $^1\text{H}$  NMR spectrum of Tm-DOTA (400 MHz,  $\text{D}_2\text{O}$ ).



**Figure S7.** Separation factor as a function of RE<sup>3+</sup> free ion angular momentum ( $J$ ) for La: RE-DOTA binary mixtures. Blue Circles: Separations performed in the presence of a magnetic field using FeNdB magnets. Red Squares: Separations performed without a magnetic field. Error bars in the data are a result of triplicate measurements.



**Figure S8.** Enrichment factor (crystals) as a function of RE<sup>3+</sup> free ion angular momentum ( $J$ ) for La: RE-DOTA binary mixtures. Blue Circles: Separations performed in the presence of a magnetic field using FeNdB magnets. Red Squares: Separations performed without a magnetic field. Error bars in the data are a result of triplicate measurements.

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- (1) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, *29*, 2176-2179.
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