Supporting Information for:

Diethyl Ether Adducts of Trivalent Lanthanide Iodides

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Synthetic Procedures

General Considerations. Unless otherwise noted, all reagents were obtained from commercial suppliers and the syntheses and manipulations were conducted under argon with exclusion of oxygen and water using Schlenk techniques or in an inert atmosphere box (Vigor) under a dinitrogen (<0.1 ppm O_2/H_2O) atmosphere. The glovebox is equipped with two -35 ˚C freezers. All glassware and cannulae were stored in an oven over-night (>8 h) at a temperature of ca. 160˚C. Celite and molecular sieves were dried under vacuum at a temperature >250˚C for a minimum of 24 h. C_6D_6 was stored over 3 Å molecular sieves and then vacuum-transferred from purple sodium/benzophenone prior to use. Diethyl ether and tetrahydrofuran were purged with UHP-grade argon (Airgas) and passed through columns containing Q-5 and molecular sieves in a solvent purification system (JC Meyer Solvent Systems). All solvents in the glovebox were stored in bottles over 3 Å molecular sieves. NMR spectra were obtained on a Bruker Advance III 400 MHz spectrometer at 298 K, unless otherwise noted. ^{1}H NMR chemical shifts are reported in δ, parts per million. ^{1}H NMR are references to the residual ^{1}H resonances of the solvent. Peak position is listed, followed by peak multiplicity, integration value, and proton assignment, where applicable. Multiplicity and shape are indicated by one or more of the following abbreviations: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); td (triplet of doublets); m (multiplet); br (broad). Elemental analyses were determined at Robertson Microlit Laboratories (Ledgewood, NJ). Powder X-ray diffraction measurements were conducted in reflection mode with a PANalytical Empyrean diffractometer with Cu-Kα radiation. A continuous scan with a gonio axis and a scan rate of 0.0423 (degree/s) was used. An Anton Paar Domed sample holder was used for the measurement. The broad peak centered around 17° 2θ is due to the background from the Kapton dome.

Lanthanide metal content of **2-Ln**, [$LnI_3(THF)_4$], and **3-Ln**, [$LnI_2(THF)_5$][$LnI_4(THF)_2$] were determined by complexometric titration using the disodium salt of ethylenediaminetetraacetic acid (EDTA). A buffer solution was made using hexamethylenetetramine as the buffer buffer and Xylenol Orange as the indicator. Roughly 20-70 mg of either **2-Ln** or **3-Ln** was dissolved in the buffer solution. Then, a 0.150 M solution of EDTA in H_2O was used to titrate the sample. EDTA binds to lanthanides to form a Ln-EDTA complex. The endpoint of the titration is determined visually, when the solution changes color to yellow, signaling that the end-point has been reached. Titrations for each metal complex was completed in triplicate over a range of metal complex masses and the averages of the triplicate are reported. This procedure was developed based on a previous report.[1]

Two-step synthesis of 2-La via 1-La:

Synthesis of $LaI_3(Et_2O)_3$, **1-La:** To a slurry of lanthanum powder (1.15 g, 8.31 mmol, 1.0 equiv.) in 80 mL of diethyl ether in a 250 mL Schlenk flask was added a solution of iodine (3.143 g, 12.38 mmol, 1.49 equiv.) in diethyl ether (40 mL). The reaction mixture was stirred for 4 days at room temperature and a grey solid precipitated. The solid was isolated on a fine porosity, sintered glass frit and washed with diethyl ether (2x40 mL). The solid was dried *in vacuo* to yield a free flowing, gray microcrystalline powder (3.354 g). The precise composition of $LaI_3(Et_2O)_x$ after exposure to dynamic vacuum is dependent on absolute vacuum.

Synthesis of $LaI_3(THF)_4$, **2-La**: $LaI_3(Et_2O)_x$ (3.354g) is subjected to Soxhlet extraction with THF yielding a white powder (4.133 g, 62% for two steps based on iodine as limiting reagent). Found: La, 17.34%. $LaI_3(THF)_4$ requires 17.19%.

Two-step synthesis of 2-Ce via 1-Ce:

Synthesis of $CeI_3(Et_2O)_3$, **1-Ce**: To a slurry of cerium powder (0.500 g, 3.54 mmol, 1.0 equiv.) in 30 mL of diethyl ether in a 100 mL Schlenk flask was added a solution of iodine (1.339 g, 5.27 mmol, 1.49 equiv.) in diethyl ether (30 mL). The reaction mixture was stirred for 4 days at room temperature and a off-white solid precipitated. The solid was isolated on a fine porosity, sintered glass frit and washed with diethyl ether (2x35 mL). The solid was dried *in vacuo* to yield a free flowing, off-white microcrystalline powder (1.83 g). The precise composition of $CeI_3(Et_2O)_x$ depends on absolute vacuum and duration of exposure to vacuum. After three hours at 400 mtorr, elemental analysis found(calc'd) for $CeI_3(Et_2O)_{1.00}$: C, 8.15(8.08) H, 1.70(1.69). After nine hours at 30 mtorr, elemental analysis found(calc'd) for $CeI_3(Et_2O)_{0.62}$: C, 4.39(5.23), H, 1.09(1.10).

Synthesis of $CeI_3(THF)_4$, **2-Ce**: $CeI_3(Et_2O)_x$ (1.83g) is subjected to soxhlet extraction with THF yielding an off-white powder (2.08 g, 73%). Found: Ce, 17.55%. $CeI_3(THF)_4$ requires 17.31%.

Two-step synthesis of 2-Pr via 1-Pr:

Synthesis of $PrI_3(Et_2O)_3$, **1-Pr**: To a slurry of praseodymium powder (300 mg, 2.13 mmol, 1.0 equiv.) in 20 mL of diethyl ether in a 50 mL Schlenk flask was added a solution of iodine (806 mg, 3.17 mmol, 1.49 equiv.) in diethyl ether (16 mL). The reaction mixture was stirred for 4 days at room temperature and a pale green solid precipitated. The solid was isolated on a fine porosity, sintered glass frit and washed with diethyl ether (2x25 mL). The solid was dried *in vacuo* to yield a free flowing, pale green microcrystalline powder (945 mg). The precise composition of $PrI_3(Et_2O)_x$ depends on absolute vacuum.

Synthesis of $PrI_3(THF)_4$, **2-Pr**: $PrI_3(Et_2O)_x$ (945 mg) is subjected to soxhlet extraction with THF yielding a gray-green powder (1.195 g, 70%). Found: Pr, 17.49%. $PrI_3(THF)_4$ requires 17.40%.

Two-step synthesis of 3-Nd via 1-Nd:

Synthesis of $NdI_3(Et_2O)_3$, **1-Nd**: To a slurry of neodymium powder (1.081 g, 7.50 mmol, 1.0 equiv.) in 80 mL of diethyl ether in a 200 mL Schlenk flask was added a solution of iodine (2.817 g, 11.1 mmol, 1.48 equiv.) in diethyl ether (40 mL). The reaction mixture was stirred for 4 days at room temperature and a brown solid remained in a deep blue solution. The solid was isolated on a fine porosity, sintered glass frit and washed with diethyl ether (2x40 mL). Volatiles are removed from the combined filtrates to yield a blue microcrystalline powder (3.713 g). The precise composition of $NdI_3(Et_2O)_x$ depends on absolute vacuum.

Synthesis of $[NdI_2(THF)_5][NdI_4(THF)_2]$, **3-Nd**: $NdI_3(Et_2O)_x$ (3.713g) is subjected to soxhlet extraction with THF yielding a blue powder (4.038 g, 70%). Found: Nd, 18.61%. $NdI_3(THF)_{3.5}$ requires 18.56%.

Two-step synthesis of 3-Sm via 1-Sm:

Synthesis of $SmI_3(Et_2O)_3$, **1-Sm**: To a slurry of samarium powder (1.038 g, 6.90 mmol, 1.0 equiv.) in 80 mL of diethyl ether in a 200 mL Schlenk flask was added a solution of iodine (2.590 g, 10.2 mmol, 1.48 equiv.) in diethyl ether (40 mL). The reaction mixture was stirred for 4 days at room temperature and a yellow solid precipitated. The solid was isolated on a fine porosity, sintered glass frit and washed with diethyl ether (2x40 mL). The solid was dried *in vacuo* to yield a free flowing, yellow microcrystalline powder (3.810 g). The precise composition of $SmI_3(Et_2O)_x$ depends on absolute vacuum.

Synthesis of $[SmI_2(THF)_5][SmI_4(THF)_2]$, **3-Sm**: $SmI_3(Et_2O)_x$ (3.810 g) is subjected to soxhlet extraction with THF yielding a yellow powder (4.175 g, 77%). Found: Sm, 19.31%. $[SmI_2(THF)_5][SmI_4(THF)_2]$ requires 19.19%.

Direct Synthesis of 3-Eu:

Synthesis of $[EuI_2(THF)_5][EuI_4(THF)_2]$, **3-Eu**: To a slurry of europium powder (201 mg, 1.32 mmol, 1.0 equiv.) in 10 mL of THF in a 50 mL Schlenk flask was added a solution of iodine (495 mg, 1.95 mmol, 1.48 equiv.) in THF (14 mL). The reaction mixture was stirred for 4 days at room temperature and a tan-brown solid precipitated. The solid was isolated on a fine porosity, sintered glass frit and washed with THF (2x10 mL) until filtrate no longer had a greenish color to it. The solid was dried *in vacuo* to yield a free flowing, tan -brown microcrystalline powder (725 mg, 71%). Found: Eu, 19.12%. $[EuI_2(THF)_5][EuI_4(THF)_2]$ requires 19.35%.

Two-step synthesis of 3-Gd via 1-Gd:

Synthesis of $GdI_3(Et_2O)_3$, **1-Gd**: To a slurry of gadolinium powder (204 mg, 1.30 mmol, 1.0 equiv.) in 10 mL of diethyl ether in a 50 mL Schlenk flask was added a solution of iodine (488 mg, 1.92 mmol, 1.48 equiv.) in diethyl ether (14 mL). The reaction mixture was stirred for 4 days at room temperature and a tan solid precipitated. The solid was isolated on a fine porosity, sintered glass frit and washed with diethyl ether (2x10 mL). The solid was dried *in vacuo* to yield a free flowing, tan microcrystalline powder (675 mg). The precise composition of $GdI_3(Et_2O)_x$ depends on absolute vacuum.

Synthesis of $[GdI_2(THF)_5][GdI_4(THF)_2]$, **3-Gd**: $GdI_3(Et_2O)_x$ (675 mg) is subjected to soxhlet extraction with THF yielding a tan powder (815 mg, 80%). Found: Gd, 19.78%. $[GdI_2(THF)_5][GdI_4(THF)_2]$ requires 19.90%.

Two-step synthesis of 3-Tb via 1-Tb:

Synthesis of $TbI_3(Et_2O)_3$, **1-Tb**: To a slurry of terbium powder (1.039 g, 6.29 mmol, 1.0 equiv.) in 40 mL of diethyl ether in a 200 mL Schlenk flask was added a solution of iodine (2.378 g, 9.37 mmol, 1.49 equiv.) in diethyl ether (80 mL). The reaction mixture was stirred for 4 days at room temperature and a tan solid precipitated. The solid was isolated on a fine porosity, sintered glass frit and washed with diethyl ether (2x40 mL). The solid was dried *in vacuo* to yield a free flowing, white microcrystalline powder (4.067 g). The precise composition of $TbI_3(Et_2O)_x$ depends on absolute vacuum and duration of exposure to vacuum. After three hours at 400 mtorr, elemental analysis found(calc'd) for $TbI_3(Et_2O)_{1.88}$: C, 12.02(13.30) H, 2.79(2.79). After nine hours at 30 mtorr, elemental analysis found(calc'd) for $TbI_3(Et_2O)_{1.07}$: C, 7.33(8.84), H, 1.99(1.99).

Synthesis of $[TbI_2(THF)_5][TbI_4(THF)_2]$, **3-Tb**: $TbI_3(Et_2O)_x$ (4.067 mg) is subjected to soxhlet extraction with THF yielding a white powder (4.071 g, 82%). Found: 20.10%. $[TbI_2(THF)_5][TbI_4(THF)_2]$ requires 20.06%.

Two-step synthesis of 3-Dy via 1-Dy:

Synthesis of $DyI_3(Et_2O)_3$, **1-Dy**: To a slurry of dysprosium powder (1.020 g, 6.28 mmol, 1.0 equiv.) in 80 mL of diethyl ether in a 250 mL Schlenk flask was added a solution of iodine (2.374 g, 9.35 mmol, 1.49 equiv.) in diethyl ether (40 mL). The reaction mixture was stirred for 4 days at room temperature and a gray solid precipitated. The solid was isolated on a fine porosity, sintered glass frit and washed with diethyl ether (2x40 mL). The solid was dried *in vacuo* to yield a free flowing, gray microcrystalline powder (3.5067 g). The precise composition of $DyI_3(Et_2O)_x$ depends on absolute vacuum.

Synthesis of $[DyI_2(THF)_5][DyI_4(THF)_2]$, **3-Dy**: $DyI_3(Et_2O)_x$ (3.5067 g) is subjected to soxhlet extraction with THF yielding a gray powder (4.533 g, 91%). Found: Dy, 20.45%. $[DyI_2(THF)_5][DyI_4(THF)_2]$ requires 20.43%.

Two-step synthesis of 3-Ho via 1-Ho:

Synthesis of $HoI_3(Et_2O)_3$, **1-Ho**: To a slurry of holmium powder (1.010 g, 6.12 mmol, 1.0 equiv.) in 80 mL of diethyl ether in a 250 mL Schlenk flask was added a solution of iodine (2.314 g, 9.12 mmol, 1.49 equiv.) in diethyl ether (40 mL). The reaction mixture was stirred for 4 days at room temperature and a gray solid precipitated. The solid was isolated on a fine porosity, sintered glass frit and washed with diethyl ether (2x40 mL). The solid was dried *in vacuo* to yield a free flowing, gray microcrystalline powder (3.3164 g). The precise composition of $HoI_3(Et_2O)_x$ depends on absolute vacuum.

Synthesis of $[HoI_2(THF)_5][HoI_4(THF)_2]$, **3-Ho**: $HoI_3(Et_2O)_x$ (3.3164 g) is subjected to soxhlet extraction with THF yielding a gray powder (3.957 g, 81%). Found: Ho, 20.52%. $[HoI_2(THF)_5][HoI_4(THF)_2]$ requires 20.65%.

Two-step synthesis of 3-Er via 1-Er:

Synthesis of $ErI_3(Et_2O)_3$, **1-Er**: To a slurry of erbium powder (221 mg, 1.32 mmol, 1.0 equiv.) in 14 mL of diethyl ether in a 50 mL Schlenk flask was added a solution of iodine (496 mg, 1.95 mmol, 1.48 equiv.) in diethyl ether (12 mL). The reaction mixture was stirred for 4 days at room temperature and a gray solid precipitated. The solid was isolated on a fine porosity, sintered glass frit and washed with diethyl ether (2x25 mL). The solid was dried *in vacuo* to yield a free flowing, gray-brown microcrystalline powder (682 mg). The precise composition of $ErI_3(Et_2O)_x$ depends on absolute vacuum.

Synthesis of $[ErI_2(THF)_5][ErI_4(THF)_2]$, **3-Er**: $ErI_3(Et_2O)_x$ (682 mg) is subjected to soxhlet extraction with THF yielding a gray powder (804 mg, 77%). Found 20.99%. $[ErI_2(THF)_5][ErI_4(THF)_2]$ requires 20.90%.

Two-step synthesis of 3-Tm via 1-Tm:

Synthesis of $TmI_3(Et_2O)_3$, **1-Tm**: To a slurry of thulium powder (200 mg, 1.184 mmol, 1.0 equiv.) in 12 mL of diethyl ether in a 50 mL Schlenk flask was added a solution of iodine (447 mg, 1.764 mmol, 1.49 equiv.) in diethyl ether (18 mL). The reaction mixture was stirred for 4 days at room temperature and a gray solid precipitated. The solid was isolated on a fine porosity, sintered glass frit and washed with diethyl ether (2x25 mL). The solid was dried *in vacuo* to yield a free flowing, gray-brown microcrystalline powder (860 mg). The precise composition of $ErI_3(Et_2O)_x$ depends on absolute vacuum.

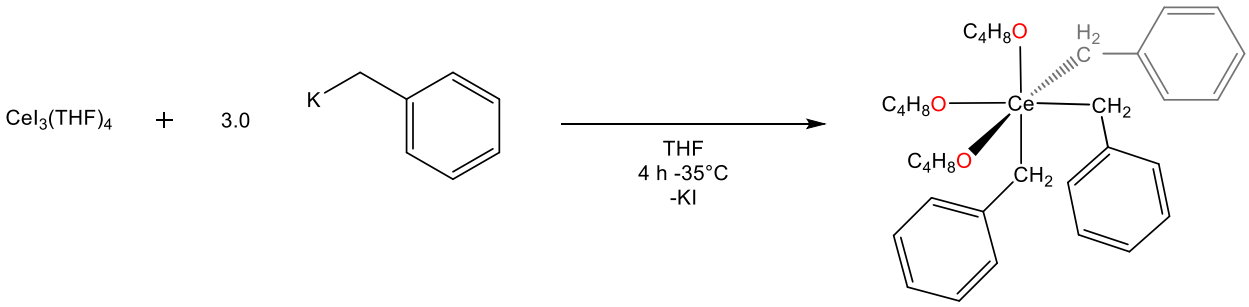
Synthesis of $[TmI_2(THF)_5][TmI_4(THF)_2]$, **3-Tm**: $TmI_3(Et_2O)_x$ (860 mg) is subjected to soxhlet extraction with THF yielding a gray powder (570 mg, 60%). Found: Tm, 21.48%. $[TmI_2(THF)_5][TmI_4(THF)_2]$ requires 21.06%.

Direct Synthesis of 3-Yb:

Synthesis of $[YbI_2(THF)_5][YbI_4(THF)_2]$, **3-Yb**: To a slurry of ytterbium powder (250 mg, 1.44 mmol, 1.0 equiv.) in 12 mL of THF in a 50 mL Schlenk flask was added a solution of iodine (542 mg, 2.14 mmol, 1.48 equiv.) in THF (20 mL). The reaction mixture was stirred for 4 days at room temperature and a red-brown solid precipitated. The solid was isolated on a fine porosity, sintered glass frit and washed with THF (2x10 mL). The solid was dried *in vacuo* to yield a free flowing, tan -brown microcrystalline powder (836 mg, 72%). Found: Yb, 21.31%. $[YbI_2(THF)_5][YbI_4(THF)_2]$ requires 21.45%.

Synthesis of $Ce[N\{Si(Me_3)_3\}_2]_3$. $CeI_3(THF)_4$ (2.20 g, 2.72 mmol, 1.00 equiv.) was suspended in 20 mL of toluene inside a 100-mL round-bottomed flask inside a glovebox.

A 20 mL toluene solution of $K[N(SiMe_3)_2]$ (1.63 g, 8.16 mmol, 3.00 equiv.) was added to the stirring suspension of $CeI_3(THF)_4$. The reaction mixture was stirred at room temperature for 24 hours. The resulting cloudy yellow solution was filtered through a fine-porosity glass frit with a plug of Celite. The product solution was dried *in vacuo* and collected as a free-flowing crystalline bright yellow solid (1.61 g, 95%). ^1H NMR, C_6D_6, δ (br-s) -3.39 ppm.



Synthesis of $Ce(C_7H_7)_3(THF)_3$. $CeI_3(THF)_4$ (441 mg, 0.545 mmol, 1.00 equiv.) was suspended in 5 mL of THF and chilled to -35°C. Potassium benzyl (213 mg, 1.63 mmol, 3.00 equiv.) was dissolved separately in 8 mL of THF and chilled to -35°C. The solution of potassium benzyl was added to the slurry of $CeI_3(THF)_4$ while cold. The reaction mixture is stirred for 4 hours at -35°C. The mixture is filtered over Celite using pre-chilled glass equipment. The filtrate is concentrated to approximately 5 mL of THF. The solution is layered with approximately 2 mL of cold hexanes and set to crystalize overnight at -35°C. The supernatant is decanted, and the dark orange crystals are collected and dried (203 mg, 59%). Powder XRD is used to confirm purity based on previous SCXRD result.

Crystallography

Crystals suitable for X-ray diffraction were covered in paratone oil in a glove box and transferred to the diffractometer in a 20 mL capped vial. Crystals were mounted on a loop with paratone oil on a Bruker D8 VENTURE diffractometer. The crystals were cooled and kept at T = 100(2) K during data collections. The structures were solved with the ShelXT structure solution program using the Intrinsic Phasing solution method and by using Olex2 as the graphical interface.[2-3] The model was refined with version 2014/7 of XL using Least Squares minimization.[4] XRD graphics are generated using POV-Ray.[5]

Table S1. Crystallographic Data

	1-Ce	***1-Pr***	***1-Nd***	***1-Sm***	***1-Gd***	***1-Tb***	***1-Tm***
Formula	$C_{12}H_{30}I_3O_3Ce$	$C_{12}H_{30}I_3O_3Pr$	$C_{12}H_{30}I_3O_3Nd$	$C_{12}H_{30}I_3O_3Sm$	$C_{12}H_{30}I_3O_3Gd$	$C_{12}H_{30}I_3O_3Tb$	$C_{12}H_{30}I_3O_3Tm$
Molecular weight	743.18	743.91	747.30	753.41	760.31	761.98	771.99
Color, Shape	Colorless Prism	Colorless Prism	Blue Prism	Yellow Prism	Colorless Prism	Colorless Prism	Colorless Prism
Size/mm	0.233×0.216×0.158	0.34×0.33×0.13	0.747×0.355×0.15	0.38×0.22×0.11	0.302×0.295×0.254	0.747×0.6×0.15	0.285×0.221×0.12
T/K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal System	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Triclinic
Space Group	Pbcn	Pbcn	$Pna2_1$	Pbcn	Pbcn	Pbcn	P-1
a/Å	10.1423	10.1152(4)	10.3268(6)	10.0662(7)	10.0525(12)	10.0273(6)	13.695(2)
b/Å	13.9652	13.9216(7)	16.1190(10)	13.8437(10)	13.8205(17)	13.7816(9)	17.532(3)
c/Å	15.8918	15.8716(8)	13.6707(10)	15.8345(11)	15.8047(19)	15.7910(11)	20.912(4)
α/°	90	90	90	90	90	90	65.386(7)
β/°	90	90	90	90	90	90	87.540(7)
γ/°	90	90	90	90	90	90	87.044(7)
V/Å³	2250.90(16)	2235.04(18)	2275.6(3)	2206.6(3)	2195.8(5)	2182.2(2)	4557.7(15)
Z	4	4	4	4	4	4	8
Wavelength/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Measured Reflections	24517	40923	63656	50414	114756	45138	140106
Unique Reflections	5427	3418	10888	5322	8912	3344	27718
Refl. I > 2σ	4012	2762	8725	3816	7567	2965	21667
R_{int}	0.0391	0.0567	0.0462	0.0619	0.0421	0.0606	0.0436
wR_2 *(all data)*	0.0645	0.0747	0.1497	0.1051	0.0547	0.0571	0.2680
wR_2	0.0556	0.0653	0.1332	0.0815	0.0501	0.0552	0.2493
R_1 *(all data)*	0.0494	0.0369	0.0772	0.0616	0.0320	0.0280	0.1232
R_1	0.0291	0.0255	0.0571	0.0342	0.0240	0.0235	0.1021
GooF	1.020	1.090	1.044	1.112	1.198	1.069	1.081

Table S2. Selected Bond lengths and Angles for **1-Ln**.

	1-Ce	***1-Pr***	***1-Nd***	***1-Sm***	***1-Gd***	***1-Tb***
Ln-$I_{1,ax}$	3.0993(3)	3.0812(3)	3.056(1)	3.0359(3)	3.0147(4)	3.0004(3)
Ln-$I_{2,ax}$	3.0993(3)	3.0812(3)	3.052(1)	3.0359(3)	3.0147(4)	3.0004(3)
Ln-$I_{3,eq}$	3.0621(4)	3.0441(4)	3.058(1)	3.0012(5)	2.9859(5)	2.9706(4)
Ln-$O_{1,ax}$	2.4249(19)	2.406(2)	2.427(8)	2.357(3)	2.3519(11)	2.3310(19)
Ln-$O_{2,ax}$	2.4249(19)	2.406(2)	2.39(1)	2.357(3)	2.3519(11)	2.3310(19)
Ln-$O_{3,eq}$	2.532(3)	2.522(4)	2.467(8)	2.479(4)	2.4479(16)	2.430(3)
$I_{1,ax}$-*Ln*-$I_{2,ax}$	178.265(10)	178.248(12)	165.15(3)	178.101(13)	178.022(5)	177.822(9)
$I_{1,ax}$-*Ln*-$I_{3,eq}$	89.132(5)	89.124(6)	95.08(3)	89.051(7)	89.011(3)	88.911(4)
$I_{2,ax}$-*Ln*-$I_{3,eq}$	89.132(5)	89.124(6)	97.17(3)	89.051(7)	89.011(2)	88.911(4)

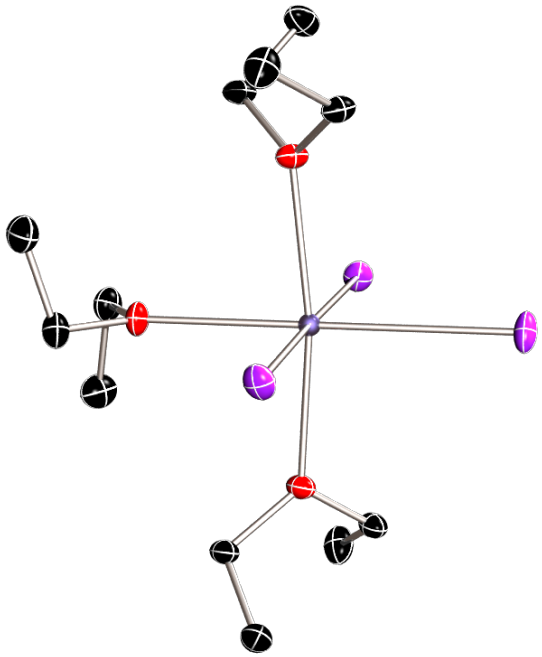


Figure S1. Molecular structure of **1-Ce** with thermal ellipsoids shown at 50% probability and H atoms are omitted for clarity.

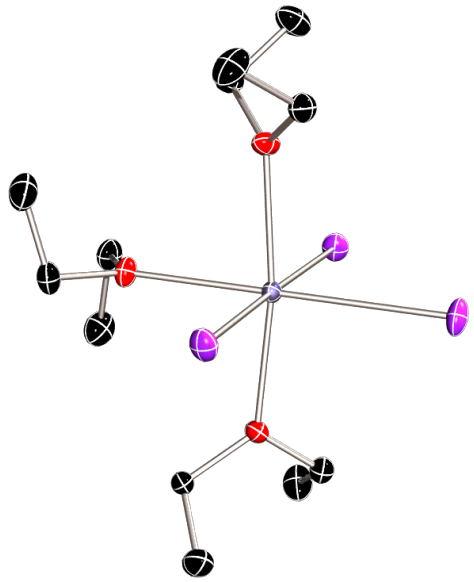


Figure S2. Molecular structure of **1-Pr** with thermal ellipsoids shown at 50% probability and H atoms are omitted for clarity.

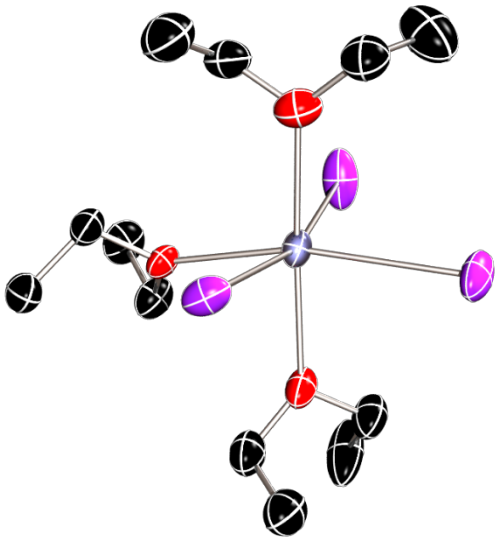


Figure S3. Molecular structure of **1-Nd** with thermal ellipsoids shown at 50% probability and H atoms are omitted for clarity.

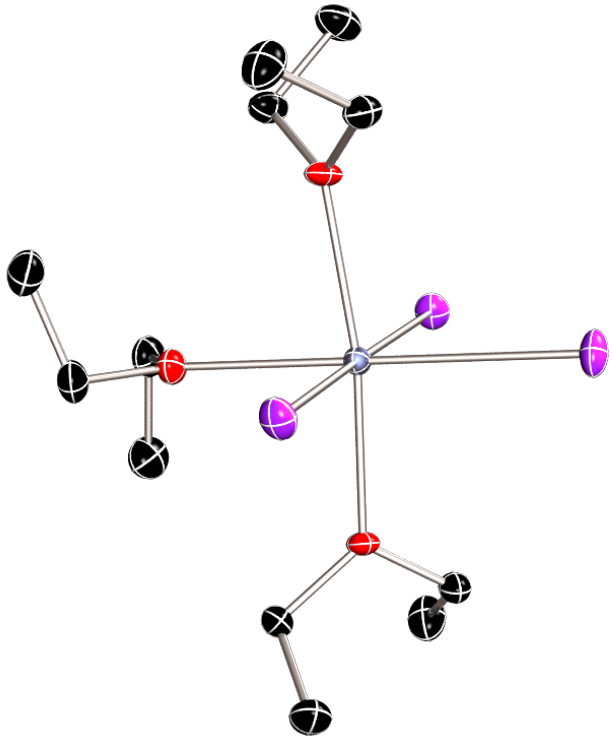


Figure S4. Molecular structure of **1-Sm** with thermal ellipsoids shown at 50% probability and H atoms are omitted for clarity.

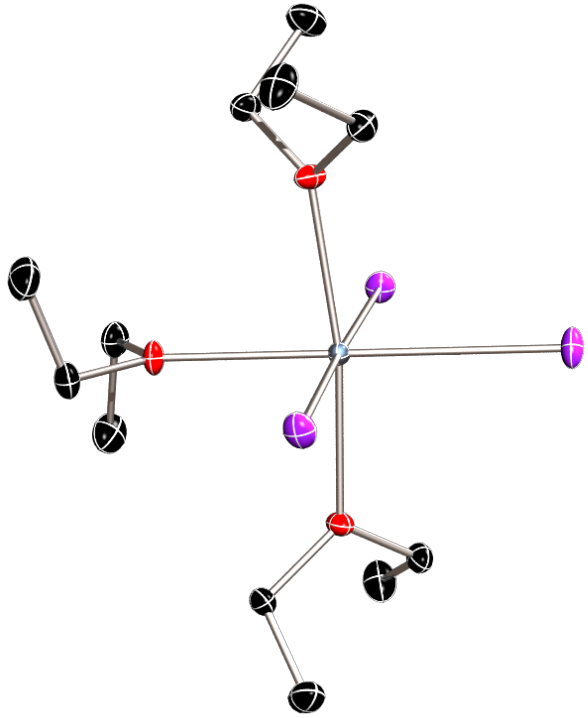


Figure S5. Molecular structure of **1-Gd** with thermal ellipsoids shown at 50% probability and H atoms are omitted for clarity.

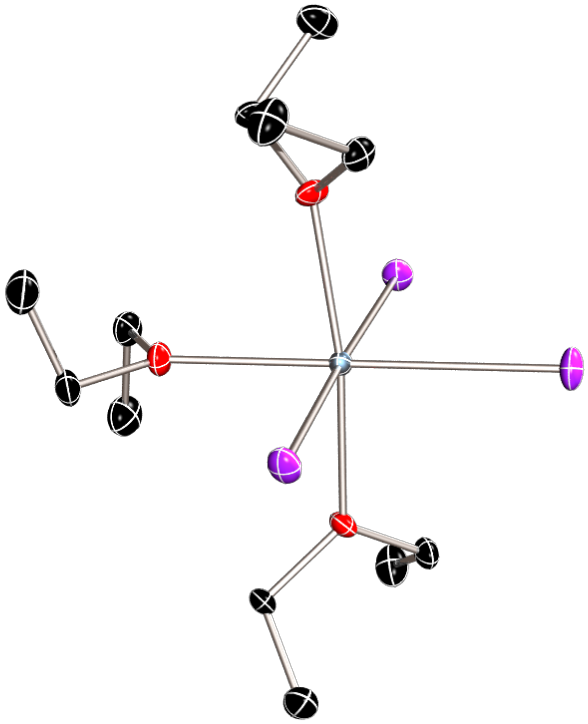


Figure S6. Molecular structure of **1-Tb** with thermal ellipsoids shown at 50% probability and H atoms are omitted for clarity.

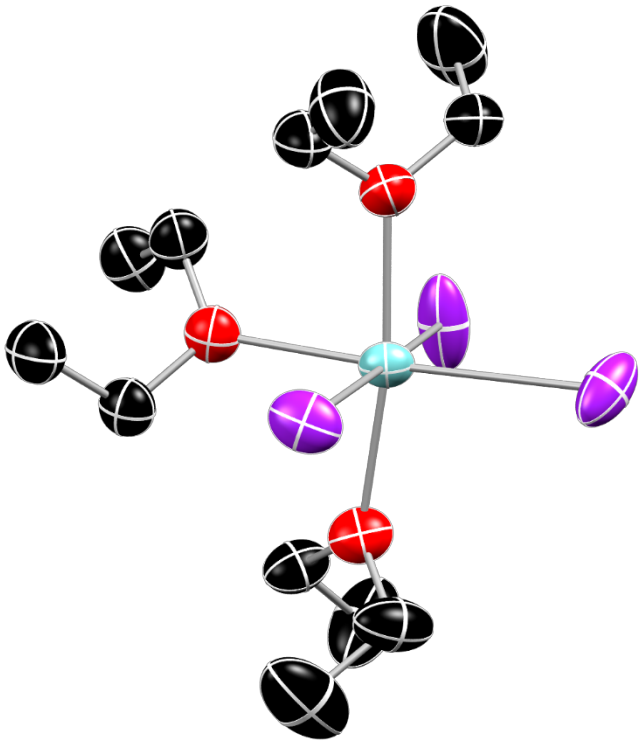


Figure S7. Molecular structure of **1-Tm** with thermal ellipsoids shown at 50% probability and H atoms are omitted for clarity.

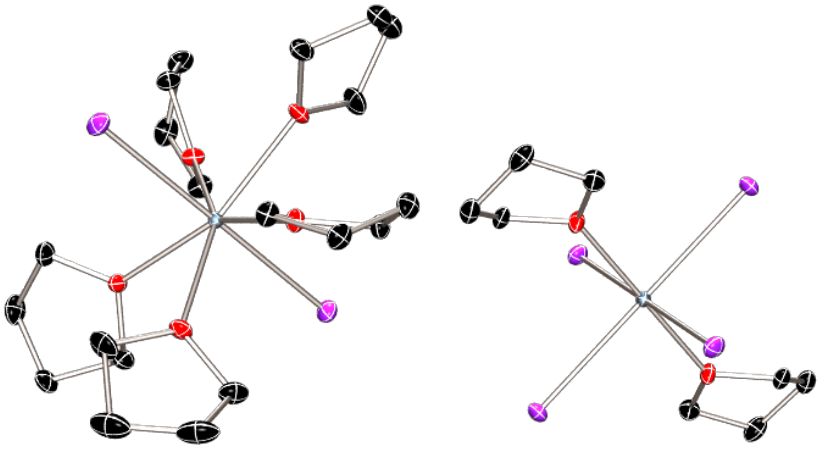


Figure S8. Molecular structure of **3-Tb** with thermal ellipsoids shown at 50% probability and H atoms are omitted for clarity.

1-Ce

Table S3: Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for **1-Ce**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
Ce1	5000	3716.1(2)	2500	10.89(4)
I1	7219.9(2)	3749.7(2)	3839.9(2)	19.35(4)
I2	5000	5908.8(2)	2500	21.22(6)
O1	5000	1903.0(19)	2500	18.5(4)
O2	3390.3(18)	3582.2(14)	3622.0(11)	16.7(3)
C5	3456(3)	4202(2)	4368.3(16)	18.0(4)
C3	2286(3)	2909(2)	3612.3(17)	18.3(4)
C4	970(3)	3405(2)	3587(2)	25.3(5)
C6	3747(3)	3654(2)	5159.7(18)	26.5(6)
C1	4201(3)	1316(2)	1929.0(18)	21.8(5)
C2	4943(3)	1097(2)	1132(2)	28.5(6)

Table S4: Anisotropic Displacement Parameters (×10⁴) for **1-Ce**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ce1	10.50(7)	10.42(8)	11.75(7)	0	0.12(6)	0
I1	15.54(7)	20.41(8)	22.09(8)	-0.37(7)	-6.38(6)	2.05(7)
I2	35.71(14)	10.57(10)	17.4(1)	0	-5.97(10)	0
O1	21.9(10)	11.8(9)	21.8(8)	0	-2.4(8)	0
O2	14.3(6)	20.4(7)	15.5(5)	-2.7(5)	2.5(5)	-3.6(5)
C5	19.0(10)	19.9(7)	15.0(6)	-2.2(5)	2.5(6)	-4.3(6)
C3	13.8(6)	20.2(7)	21.0(10)	-4.9(6)	4.3(6)	-3.3(5)
C4	14.3(6)	25.3(10)	36.5(15)	-6.2(11)	2.9(7)	-1.5(6)
C6	38.8(16)	24.6(11)	16.0(5)	-0.8(7)	-0.5(7)	-1.7(11)
C1	25.5(10)	16.8(10)	23.1(8)	-2.7(7)	-2.0(7)	-2.6(7)
C2	33.9(13)	26.0(14)	25.6(8)	-7.0(8)	1.7(8)	-4.1(11)

Table S5: Bond Lengths in Å for **1-Ce**.

Atom	Atom	Length/Å
Ce1	I1[1]	3.09923(18)
Ce1	I1	3.09924(19)
Ce1	I2	3.0620(3)
Ce1	O1	2.532(3)
Ce1	O2	2.4248(18)
Ce1	O2[1]	2.4248(18)
O1	C1	1.467(3)
O1	C1[1]	1.467(3)
O2	C5	1.470(3)
O2	C3	1.463(3)
C5	C6	1.501(4)
C3	C4	1.504(4)
C1	C2	1.504(4)

[1]1-x,+y,1/2-z

Table S6: Bond Angles in ° for **1-Ce**.

Atom	Atom	Atom	Angle/°
I1[1]	Ce1	I1	178.265(10)
I2	Ce1	I1	89.132(5)
I2	Ce1	I1[1]	89.133(5)
O1	Ce1	I1	90.868(5)
O1	Ce1	I1[1]	90.867(5)

Atom	Atom	Atom	Angle/°
O1	Ce1	I2	180.0
O2[1]	Ce1	I1	90.99(4)
O2	Ce1	I1[1]	90.99(4)
O2[1]	Ce1	I1[1]	89.15(4)
O2	Ce1	I1	89.15(4)
O2	Ce1	I2	94.42(4)
O2[1]	Ce1	I2	94.42(4)
O2	Ce1	O1	85.58(4)
O2[1]	Ce1	O1	85.58(4)
O2[1]	Ce1	O2	171.15(9)
C1[1]	O1	Ce1	124.00(15)
C1	O1	Ce1	124.00(15)
C1[1]	O1	C1	112.0(3)
C5	O2	Ce1	121.17(15)
C3	O2	Ce1	123.88(15)
C3	O2	C5	114.94(19)
O2	C5	C6	112.6(2)
O2	C3	C4	112.6(2)
O1	C1	C2	111.0(2)

[1]1-x,+y,1/2-z

Table S7: Hydrogen Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **CeI3ether**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H5A	2603.98	4540.51	4433.81	22
H5B	4149.91	4690.68	4282.46	22
H3A	2329.69	2500.49	4120.7	22
H3B	2366.79	2487.26	3114.13	22
H4A	965.32	3877.43	3131.22	38
H4B	813.69	3729.73	4125.14	38
H4C	272.61	2932.15	3489.85	38
H6A	4558.32	3283.36	5085.13	40
H6B	3013.49	3219.15	5282.25	40
H6C	3858.04	4103.42	5628.28	40
H1A	3377.12	1660.36	1789.47	26
H1B	3960.56	709.19	2212.77	26
H2A	4417.89	664.86	780.43	43
H2B	5784.05	789.25	1272.3	43
H2C	5111.86	1692.74	825.45	43

Coordination polyhedron

Ce1-I1 = 3.0993(3) Å

Ce1-O2 = 2.4248(18) Å

Ce1-I2 = 3.0621(5) Å

Ce1-O1 = 2.532(3) Å

Ce1-O2 = 2.4248(18) Å

Ce1-I1 = 3.0993(3) Å

The ether molecules bind highly asymmetrical. There is a correlation between the asymmetric binding of the ether molecules and the binding of the iodine atoms. The distortion index is 0.11291 and the bond angle variance is 7.7°.

Average bond length = 2.7737 Å

Polyhedral volume = 27.9370 Å^3

Distortion index (bond length) = 0.11291

Quadratic elongation = 1.0254

Bond angle variance = 7.6979 deg.^2

Effective coordination number = 3.3401

1-Pr

Table S8: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **1-Pr**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	Z	U_{eq}
Pr1	5000	6287.7(2)	2500	12.42(7)
I1	7216.7(2)	6253.8(2)	1168.8(2)	20.93(7)
I2	5000	4101.1(2)	2500	22.37(9)
O1	5000	8099(3)	2500	18.6(7)
O2	6596(2)	6416.6(17)	3617.9(16)	18.0(5)
C3	6535(4)	5797(2)	4360(2)	20.4(7)
C5	7707(3)	7093(3)	3607(2)	19.3(7)
C1	4201(4)	8685(3)	3068(3)	23.1(7)
C2	4945(5)	8903(3)	3869(3)	30.9(9)
C4	6252(5)	6344(3)	5158(3)	29.6(9)
C6	9025(4)	6600(3)	3584(3)	28.7(8)

Table S9: Anisotropic Displacement Parameters ($\times 10^4$) **1-Pr**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pr1	12.16(12)	10.66(12)	14.43(12)	0	-0.06(8)	0
I1	17.14(11)	20.67(12)	24.97(13)	-0.07(9)	6.30(8)	-1.77(9)
I2	36.14(19)	10.91(14)	20.05(16)	0	5.47(13)	0
O1	24.9(17)	13.7(15)	17.1(16)	0	3.1(14)	0
O2	14.5(11)	18.6(12)	20.9(12)	2.7(9)	-2.8(9)	-2.8(9)
C3	22.0(16)	17.4(16)	21.7(17)	2.2(13)	-1.8(13)	-1.4(13)
C5	18.1(15)	16.9(16)	22.8(17)	4.6(13)	-5.6(13)	-3.8(12)
C1	26.0(17)	15.6(16)	27.6(19)	-1.0(14)	2.5(14)	3.6(14)
C2	41(2)	23.8(19)	28(2)	-5.0(16)	0.3(17)	4.1(17)
C4	45(2)	28.4(19)	15.6(16)	-0.6(15)	0.2(17)	-6.1(17)
C6	18.6(16)	31(2)	36(2)	9.4(18)	-1.0(16)	-0.4(15)

Table S10: Bond Lengths in Å for **1-Pr**.

Atom	Atom	Length/Å
Pr1	$I1^1$	3.0812(2)
Pr1	I1	3.0812(2)
Pr1	I2	3.0441(4)
Pr1	O1	2.521(4)
Pr1	$O2^1$	2.406(2)
Pr1	O2	2.406(2)
O1	C1	1.460(4)
O1	$C1^1$	1.460(4)
O2	C3	1.461(4)
O2	C5	1.466(4)

Atom	Atom	Length/Å
C3	C4	1.506(5)
C5	C6	1.501(5)
C1	C2	1.509(6)

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[1]1-X,+Y,1/2-Z

Table S11: Bond Angles in ° for **1-Pr**.

Atom	Atom	Atom	Angle/°
I1[1]	Pr1	I1	178.248(12)
I2	Pr1	I1	89.124(6)
I2	Pr1	I1[1]	89.124(6)
O1	Pr1	I1	90.876(6)
O1	Pr1	I1[1]	90.876(6)
O1	Pr1	I2	180.0
O2	Pr1	I1	91.06(6)
O2[1]	Pr1	I1[1]	91.06(6)
O2	Pr1	I1[1]	89.08(6)
O2[1]	Pr1	I1	89.07(6)
O2[1]	Pr1	I2	94.28(6)
O2	Pr1	I2	94.28(6)
O2[1]	Pr1	O1	85.72(6)
O2	Pr1	O1	85.72(6)
O2	Pr1	O2[1]	171.45(12)
C1	O1	Pr1	124.01(19)
C1[1]	O1	Pr1	124.01(19)
C1[1]	O1	C1	112.0(4)
C3	O2	Pr1	121.5(2)
C3	O2	C5	114.9(3)
C5	O2	Pr1	123.6(2)
O2	C3	C4	112.8(3)
O2	C5	C6	112.7(3)
O1	C1	C2	110.9(3)

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[1]1-X,+Y,1/2-Z

Table S12: Hydrogen Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **1-Pr**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H3A	7388	5455	4421	24
H3B	5836	5309	4275	24
H5A	7661	7504	4116	23
H5B	7625	7515	3108	23
H1A	3373	8340	3206	28
H1B	3963	9294	2784	28
H2A	5097	8306	4181	46
H2B	4425	9346	4216	46
H2C	5796	9200	3730	46
H4A	6965	6806	5262	44
H4B	6194	5895	5632	44
H4C	5412	6689	5100	44
H6A	9180	6273	4122	43
H6B	9722	7076	3488	43
H6C	9033	6127	3126	43

1-Nd

Table S13: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **1-Nd**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
Nd1	2919.1(5)	5136.3(4)	4588.5(5)	29.56(13)
I1	5085.4(7)	4146.0(5)	3609.0(7)	41.63(19)
I2	2061.9(9)	6020.6(7)	2719.2(7)	54.4(3)

Atom	x	y	z	U_{eq}
I3	1246.4(11)	6125.9(8)	6010.8(8)	62.9(3)
O1	3231(7)	4177(5)	5985(6)	31.6(15)
O2	1300(8)	4101(5)	4205(7)	39.4(18)
O3	4540(10)	6158(6)	4871(9)	56(3)
C2	4693(14)	3017(9)	6294(12)	50(3)
C4	2212(19)	4097(12)	7598(12)	64(4)
C6	1665(18)	3029(11)	2903(13)	64(4)
C10	6620(20)	5851(14)	5603(17)	83(5)
C5	1614(18)	3232(9)	3971(12)	58(3)
C9	5161(19)	6141(12)	5814(16)	73(4)
C11	4867(16)	6921(12)	4256(14)	66(4)
C12	3970(20)	7577(13)	4470(30)	102(8)
C8	-1020(17)	3914(16)	4500(20)	101(9)
C7	-2(17)	4338(14)	3903(16)	77(6)
C3	2125(18)	3835(12)	6514(13)	61(4)
C1	4462(15)	3962(9)	6362(12)	50(3)

Table S14: Anisotropic Displacement Parameters ($\times 10^4$) **1-Nd**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Nd1	24.4(2)	38.7(3)	25.6(2)	7.0(3)	3.2(2)	2.2(2)
I1	31.1(3)	57.8(4)	35.9(4)	-15.6(4)	8.5(3)	-1.6(3)
I2	47.8(5)	70.5(6)	44.8(5)	30.8(5)	-8.4(4)	-10.5(4)
I3	59.7(6)	82.6(7)	46.4(5)	18.8(5)	24.5(5)	36.7(5)
O1	28(3)	38(4)	28(4)	-1(3)	0(3)	-7(3)
O2	26(4)	48(4)	44(5)	18(4)	-5(3)	-7(3)
O3	44(5)	53(5)	70(6)	-18(4)	11(4)	-8(4)
C2	42(7)	47(6)	62(9)	7(6)	-2(6)	4(5)
C4	76(11)	77(11)	40(7)	15(7)	26(7)	4(8)
C6	68(10)	62(9)	61(7)	3(6)	-6(7)	-19(8)
C10	73(9)	91(13)	83(13)	1(11)	-37(8)	-9(8)
C5	71(9)	47(5)	55(7)	19(5)	-3(6)	0(5)
C9	80(9)	56(9)	82(9)	30(8)	-8(7)	-15(7)
C11	50(8)	79(8)	70(10)	3(7)	-2(7)	-14(6)
C12	66(10)	82(10)	160(20)	2(13)	20(13)	-8(8)
C8	38(8)	150(20)	118(19)	74(17)	-10(9)	2(9)
C7	48(8)	90(13)	92(15)	36(11)	-18(8)	-8(8)
C3	65(10)	69(10)	50(8)	9(7)	-1(7)	-2(8)
C1	44(6)	52(6)	53(8)	-3(6)	-16(6)	-1(5)

Table S15: Bond Lengths in Å for **1-Nd**.

Atom	Atom	Length/Å
Nd1	I1	3.0537(9)
Nd1	I2	3.0534(10)
Nd1	I3	3.0475(11)
Nd1	O1	2.475(8)
Nd1	O2	2.417(8)
Nd1	O3	2.377(10)
O1	C3	1.458(19)
O1	C1	1.413(16)
O2	C5	1.472(18)
O2	C7	1.456(18)
O3	C9	1.44(2)
O3	C11	1.53(2)
C2	C1	1.54(2)
C4	C3	1.54(2)
C6	C5	1.50(2)
C10	C9	1.60(3)
C11	C12	1.44(3)
C8	C7	1.49(3)

Table S16: Bond Angles in ° for **1-Nd**.

Atom	Atom	Atom	Angle/°
I1	Nd1	I2	95.13(3)
I3	Nd1	I1	165.11(4)
I3	Nd1	I2	97.17(3)
O1	Nd1	I1	85.21(19)
O1	Nd1	I2	166.59(17)
O1	Nd1	I3	84.77(19)
O2	Nd1	I1	92.9(2)
O2	Nd1	I2	86.6(2)
O2	Nd1	I3	96.2(2)
O2	Nd1	O1	80.0(3)
O3	Nd1	I1	85.3(2)
O3	Nd1	I2	91.0(3)
O3	Nd1	I3	86.2(2)
O3	Nd1	O1	102.4(3)
O3	Nd1	O2	176.8(4)
C3	O1	Nd1	121.0(8)
C1	O1	Nd1	123.4(8)
C1	O1	C3	115.5(12)
C5	O2	Nd1	123.4(9)
C5	O2	C7	121.3(10)
C7	O2	Nd1	113.0(13)
C9	O3	Nd1	116.5(9)
C9	O3	C11	114.2(12)
C11	O3	Nd1	128.6(10)
O2	C5	C6	115.3(12)
O3	C9	C10	105.2(17)
O3	C11	C12	109.7(16)
O2	C7	C8	112.1(14)
O1	C3	C4	109.1(14)
O1	C1	C2	111.1(11)

Table S17: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **1-Nd**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H2A	5300.38	2900.43	5759.12	76
H2B	3868.74	2735.12	6166.1	76
H2C	5057.96	2816.25	6912.58	76
H4A	2253.81	4703.9	7642.21	97
H4B	2993.08	3856.25	7892.56	97
H4C	1445.02	3896.86	7949.89	97
H6A	1909.85	3525.88	2532.46	96
H6B	810.59	2836.65	2685.3	96
H6C	2306.9	2590.35	2790.97	96
H10A	7120.59	6322.48	5352.61	124
H10B	6616.16	5404.26	5115.62	124
H10C	7013	5649.38	6211.25	124
H5A	959.4	2869.78	4284.59	69
H5B	2465.58	3097.04	4265.1	69
H9A	4719.63	5743.77	6256.6	87
H9B	5146.79	6698.52	6119.8	87
H11A	5760.73	7106.69	4403.5	79
H11B	4820.47	6778.52	3551.67	79
H12A	3879.23	7635.79	5183.05	153
H12B	3120.87	7444.34	4185.78	153
H12C	4287.64	8099.32	4193.17	153
H8A	-1876.77	4046.64	4230.32	152
H8B	-967.67	4106.27	5177.44	152
H8C	-882.51	3312.45	4474.98	152
H7A	-123.67	4193.97	3203.72	92
H7B	-102.1	4946.6	3969.68	92
H3A	2127.52	3222.11	6463.19	74
H3B	1308.24	4044.92	6224.84	74
H1A	4520.98	4139.4	7054.52	60
H1B	5142.82	4257.27	5988.29	60

Coordination polyhedron

Nd1-O2 = 2.417(9) Å
Nd1-I3 = 3.0475(14) Å
Nd1-O1 = 2.475(9) Å
Nd1-I2 = 3.0533(13) Å
Nd1-I1 = 3.0538(10) Å
Nd1-O3 = 2.377(11) Å

The ether molecules bind highly asymmetrically. There is a correlation between the asymmetric binding of the ether molecules and the binding of the iodine atoms. The distortion index is 0.11414 and the bond angle variance is **46.38°**

Average bond length = 2.7373 Å

Polyhedral volume = 26.4709 $Å^3$

Distortion index (bond length) = 0.1148

Quadratic elongation = 1.0355

Bond angle variance = **43.5** deg^2

Effective coordination number = 3.31

1-Sm

Table S18: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **1-Sm**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	Z	U_{eq}
Sm1	5000	6292.4(2)	2500	13.12(6)
I1	7203.5(3)	6256.1(2)	1191.3(2)	20.98(7)
I2	5000	4124.5(2)	2500	22.41(9)
O1	5000	8083(3)	2500	19.4(7)
O2	6570(3)	6423(2)	3598.5(19)	17.2(5)
C3	6517(4)	5795(3)	4350(3)	20.0(6)
C5	7689(4)	7099(3)	3592(3)	21.2(7)
C1	4198(5)	8677(3)	3071(3)	24.3(7)
C2	4948(6)	8899(4)	3870(3)	31.1(9)
C4	6249(6)	6349(3)	5145(3)	30.3(9)
C6	9020(4)	6601(4)	3580(3)	28.5(9)
I1'	7150(40)	6280(30)	3800(30)	20.98(7)

Table S19: Anisotropic Displacement Parameters (×10^4) **1-Sm**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sm1	12.39(11)	11.87(10)	15.10(11)	0	0.01(8)	0
I1	16.97(12)	21.32(12)	24.64(13)	0.20(9)	5.92(9)	-1.57(9)
I2	34.7(2)	11.98(13)	20.54(17)	0	4.65(14)	0
O1	20.6(17)	13.9(14)	23.8(16)	0	-0.9(13)	0
O2	12.5(10)	20.9(11)	18.1(11)	3.3(8)	-5.7(8)	-1.3(8)
C3	20.6(16)	20.1(13)	19.2(12)	2.9(10)	-4.1(11)	-3.7(11)
C5	16.9(12)	20.8(13)	25.8(18)	5.3(12)	-3.9(11)	-4.3(10)
C1	27.4(17)	16.1(15)	29.5(16)	-2.8(12)	1.9(13)	2.6(12)
C2	38(2)	24.7(19)	30.1(17)	-6.7(14)	-1.9(15)	2.3(17)
C4	44(3)	27.1(18)	20.3(14)	0.2(12)	-0.6(14)	-3.6(17)
C6	17.5(13)	31.1(19)	37(2)	6.9(18)	-2.7(13)	-0.4(12)
I1'	16.97(12)	21.32(12)	24.64(13)	0.20(9)	5.92(9)	-1.57(9)

Table S20: Bond Lengths in Å for **1-Sm**.

Atom	Atom	Length/Å
Sm1	I1[1]	3.0359(3)
Sm1	I1	3.0359(3)
Sm1	I2	3.0012(5)
Sm1	O1	2.479(4)
Sm1	O2	2.357(3)
Sm1	O2[1]	2.357(3)
O1	C1[1]	1.465(5)
O1	C1	1.465(5)
O2	C3	1.474(5)
O2	C5	1.466(5)
C3	C4	1.499(6)
C5	C6	1.507(6)
C1	C2	1.505(7)

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[1]1-X,+Y,1/2-Z

Table S21: Bond Angles in ° for **1-Sm**.

Atom	Atom	Atom	Angle/°
I1[1]	Sm1	I1	178.101(13)
I2	Sm1	I1	89.051(7)
I2	Sm1	I1[1]	89.051(7)
O1	Sm1	I1	90.949(7)
O1	Sm1	I1[1]	90.949(7)
O1	Sm1	I2	180.0
O2[1]	Sm1	I1	89.27(8)
O2	Sm1	I1[1]	89.28(8)
O2[1]	Sm1	I1[1]	90.87(8)
O2	Sm1	I1	90.87(8)
O2	Sm1	I2	94.39(7)
O2[1]	Sm1	I2	94.39(7)
O2	Sm1	O1	85.61(7)
O2[1]	Sm1	O1	85.61(7)
O2[1]	Sm1	O2	171.22(14)
C1	O1	Sm1	124.2(2)
C1[1]	O1	Sm1	124.2(2)
C1	O1	C1[1]	111.7(4)
C3	O2	Sm1	121.8(2)
C5	O2	Sm1	124.0(2)
C5	O2	C3	114.2(3)
O2	C3	C4	112.6(3)
O2	C5	C6	113.0(4)
O1	C1	C2	110.9(4)

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[1]1-X,+Y,1/2-Z

Table S22: Hydrogen Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **1-Sm**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H3A	7374	5450	4407	24
H3B	5811	5306	4271	24
H5A	7636	7517	4098	25
H5B	7617	7520	3088	25
H1A	3367	8331	3212	29
H1B	3956	9288	2785	29
H2A	5077	8303	4193	47
H2B	4440	9362	4210	47
H2C	5814	9178	3728	47
H4A	6967	6814	5241	45
H4B	6201	5900	5623	45
H4C	5403	6694	5092	45
H6A	9157	6262	4117	43
H6B	9724	7081	3502	43
H6C	9045	6134	3115	43

Table S23: Atomic Occupancies for all atoms that are not fully occupied in **1-Sm**.

Atom	Occupancy
I1	0.9926(10)
I1'	0.0074(10)

1-Gd

Table S24: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **1-Gd**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	Z	U_{eq}
Gd1	5000	3703.0(2)	2500	9.26(2)
I1	7195.7(2)	3740.7(2)	3798.8(2)	16.49(2)
I2	5000	5863.5(2)	2500	17.11(3)
O1	5000	1931.9(11)	2500	15.0(2)

Atom	x	y	Z	U_{eq}
O2	3432.2(11)	3574.6(8)	3598.7(7)	13.92(16)
C5	3491.7(17)	4202.7(11)	4342.2(9)	15.7(2)
C3	2322.3(15)	2898.9(11)	3587.7(11)	16.0(2)
C4	985.9(18)	3394.9(15)	3577.2(13)	23.1(3)
C6	3746(2)	3648.2(14)	5143.1(11)	24.9(3)
C1	4195.9(18)	1329.5(11)	1932.6(11)	18.6(2)
C2	4939(2)	1104.5(14)	1129.0(13)	25.9(3)

Table S15: Anisotropic Displacement Parameters ($\times 10^4$) **1-Gd**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Gd1	9.68(3)	8.24(3)	9.85(3)	0	-0.17(2)	0
I1	14.19(4)	17.02(4)	18.28(4)	0.08(3)	-5.56(3)	1.43(3)
I2	28.63(7)	8.39(4)	14.31(5)	0	-4.15(4)	0
O1	19.5(6)	7.6(4)	17.8(6)	0	-1.9(5)	0
O2	12.5(4)	15.8(4)	13.4(4)	-2.7(3)	3.0(3)	-3.0(3)
C5	19.0(6)	14.4(5)	13.8(5)	-2.4(4)	1.1(4)	-2.3(4)
C3	14.1(5)	14.5(5)	19.5(6)	-3.5(4)	2.3(4)	-3.6(4)
C4	14.8(6)	25.1(7)	29.5(8)	-7.4(6)	0.6(6)	-0.4(5)
C6	40.3(10)	21.9(7)	12.6(5)	1.0(5)	-0.3(6)	-4.2(7)
C1	21.4(7)	12.4(5)	22.0(6)	-2.3(4)	-2.4(5)	-3.4(5)
C2	36.5(10)	19.4(7)	21.8(7)	-6.0(6)	2.2(7)	-3.1(6)

Table S26: Bond Lengths in Å for **1-Gd**.

Atom	Atom	Length/Å
Gd1	I1	3.0144(2)
Gd1	I1[1]	3.0145(3)
Gd1	I2	2.9849(3)
Gd1	O1	2.4470(15)
Gd1	O2[1]	2.3517(11)
Gd1	O2	2.3517(11)
O1	C1	1.4663(18)
O1	C1[1]	1.4663(18)
O2	C5	1.4622(18)
O2	C3	1.4546(18)
C5	C6	1.502(2)
C3	C4	1.508(2)
C1	C2	1.506(3)

[1]1-x,+y,1/2-z

Table S27: Bond Angles in ° for **1-Gd**.

Atom	Atom	Atom	Angle/°
I1	Gd1	I1[1]	178.022(5)
I2	Gd1	I1	89.011(2)
I2	Gd1	I1[1]	89.011(2)
O1	Gd1	I1[1]	90.989(2)
O1	Gd1	I1	90.989(2)
O1	Gd1	I2	180.0
O2[1]	Gd1	I1[1]	89.35(3)
O2	Gd1	I1	89.35(3)
O2	Gd1	I1[1]	90.79(3)
O2[1]	Gd1	I1	90.79(3)
O2[1]	Gd1	I2	94.33(3)
O2	Gd1	I2	94.33(3)
O2[1]	Gd1	O1	85.67(3)
O2	Gd1	O1	85.67(3)
O2	Gd1	O2[1]	171.34(6)
C1	O1	Gd1	124.58(8)
C1[1]	O1	Gd1	124.58(8)
C1	O1	C1[1]	110.83(16)
C5	O2	Gd1	121.43(9)
C3	O2	Gd1	123.60(9)
C3	O2	C5	114.95(11)
O2	C5	C6	112.45(13)
O2	C3	C4	113.05(13)
O1	C1	C2	111.09(14)

[1]1-x,+y,1/2-z

Table S28: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **1-Gd**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H5A	2639.92	4557.35	4395.97	19
H5B	4208.49	4685.71	4262.39	19
H3A	2376.69	2477.76	4093.27	19
H3B	2398.27	2480.59	3081.48	19
H4A	969.21	3878.9	3124.18	35
H4B	834.05	3713.76	4122.55	35
H4C	285.75	2914.27	3478.21	35
H6A	4585.72	3292.07	5092.11	37
H6B	3016.57	3190.9	5240.14	37
H6C	3802.46	4099.84	5619.88	37
H1A	3359.13	1672.4	1793.41	22
H1B	3961.49	717.69	2222.71	22
H2A	4425.37	641.82	791.06	39
H2B	5807.11	823.64	1268.57	39
H2C	5067.89	1701.57	804.55	39

Coordination polyhedron

l(Gd1-O2) = 2.3519(12) Å

l(Gd1-I1) = 3.0147(4) Å

l(Gd1-O1) = 2.4479(16) Å

l(Gd1-I2) = 2.9859(6) Å

l(Gd1-I1) = 3.0147(4) Å

l(Gd1-O2) = 2.3519(12) Å

The ether molecules bind highly asymmetrically. There is a correlation between the asymmetric binding of the ether molecules and the binding of the iodine atoms. The distortion index is 0.11528 and the bond angle variance is 7.3°

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Average bond length = 2.6945 Å

Polyhedral volume = 25.6050 Å^3

Distortion index (bond length) = 0.11528

Quadratic elongation = 1.0260

Bond angle variance = 7.3546 deg.^2

Effective coordination number = 3.3106

1-Tb

Table S29: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **1-Tb**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
Tb1	5000	3695.9(2)	2500	10.79(6)
I1	7191.6(2)	3737.3(2)	3793.1(2)	18.17(6)
I2	5000	5851.4(2)	2500	18.78(7)
O1	5000	1933(2)	2500	16.7(5)
O2	3441.5(19)	3574.2(13)	3590.4(12)	15.6(4)
C5	3506(3)	4204.5(18)	4338.2(16)	16.7(5)
C3	2332(3)	2892.2(19)	3578.4(18)	17.5(5)
C4	996(3)	3393(2)	3575(2)	24.6(6)
C6	3743(4)	3647(2)	5140.5(18)	26.0(6)
C1	4193(3)	1329.4(18)	1931.4(19)	20.3(5)
C2	4938(3)	1105(2)	1127(2)	27.8(7)

Table S30: Anisotropic Displacement Parameters (×10^4) **1-Tb**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Tb1	9.59(9)	8.92(9)	13.87(9)	0	-0.10(5)	0
I1	14.14(10)	17.81(10)	22.55(10)	0.22(6)	-5.84(6)	1.40(6)
I2	28.64(15)	9.16(11)	18.53(12)	0	-4.44(9)	0
O1	19.2(14)	10.4(12)	20.5(13)	0	-1.4(10)	0
O2	12.9(9)	15.8(9)	18.2(8)	-1.9(7)	2.8(7)	-5.2(6)
C5	19.3(13)	14.1(11)	16.7(11)	-3.7(9)	0.5(9)	-4.5(9)
C3	12.9(12)	14.7(12)	25.0(13)	-4.0(10)	4.1(9)	-5.1(9)
C4	16.0(14)	25.0(14)	32.9(15)	-7.8(12)	-0.9(11)	-1.7(11)
C6	38.2(18)	22.5(14)	17.4(12)	-0.3(10)	1.0(12)	-3.9(11)
C1	20.4(14)	12.3(12)	28.1(14)	-3.5(10)	-2.1(10)	-3.1(9)
C2	35.4(19)	19.9(14)	28.2(16)	-4.9(12)	2.0(11)	-2.4(11)

Table S31: Bond Lengths in Å for **1-Tb**.

Atom	Atom	Length/Å
Tb1	I1	3.0003(2)
Tb1	I1[1]	3.0003(2)
Tb1	I2	2.9706(3)
Tb1	O1	2.430(3)
Tb1	O2	2.3313(19)
Tb1	O2[1]	2.3313(19)
O1	C1[1]	1.467(3)
O1	C1	1.467(3)
O2	C5	1.467(3)
O2	C3	1.457(3)
C5	C6	1.501(4)
C3	C4	1.507(4)
C1	C2	1.506(4)

[1]1-x,+y,1/2-z

Table S32: Bond Angles in ° for **1-Tb**.

Atom	Atom	Atom	Angle/°
I1	Tb1	I1[1]	177.822(8)
I2	Tb1	I1	88.911(4)
I2	Tb1	I1[1]	88.911(4)
O1	Tb1	I1[1]	91.089(4)
O1	Tb1	I1	91.089(4)
O1	Tb1	I2	180.0
O2	Tb1	I1[1]	90.75(5)
O2[1]	Tb1	I1	90.75(5)
O2[1]	Tb1	I1[1]	89.41(5)
O2	Tb1	I1	89.41(5)
O2	Tb1	I2	94.13(4)
O2[1]	Tb1	I2	94.13(4)
O2	Tb1	O1	85.87(4)
O2[1]	Tb1	O2	171.75(9)
C1[1]	O1	Tb1	124.52(14)
C1	O1	Tb1	124.52(14)
C1[1]	O1	C1	111.0(3)
C5	O2	Tb1	121.47(14)
C3	O2	Tb1	123.29(15)
C3	O2	C5	115.23(19)
O2	C5	C6	112.5(2)
O2	C3	C4	112.6(2)
O1	C1	C2	111.1(2)
O2[1]	Tb1	O2	171.75(9)

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[1]1-X,+Y,1/2-Z

Table S33: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **1-Tb**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H5A	2659.02	4568.66	4388.82	20
H5B	4234.57	4681.48	4261.34	20
H3A	2389.95	2466.43	4082	21
H3B	2404.58	2477.2	3068.76	21
H4A	971.38	3871.65	3116.08	37
H4B	857.63	3720.75	4118.34	37
H4C	289.32	2911.78	3487.17	37
H6A	4581.15	3285.15	5094.47	39
H6B	3005.22	3192.26	5232.56	39
H6C	3796.31	4098.67	5618.49	39
H1A	3354.83	1673.64	1792.45	24
H1B	3958.1	715.81	2221.19	24
H2A	4423.6	641.38	787.98	42
H2B	5808.35	823.31	1266.16	42
H2C	5067.27	1703.83	802.41	42

3-Tb

Table S34. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **3-Tb** . U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
Tb2	5000	4993.3(2)	2500	8.73(4)
Tb1	0	5000	5000	10.92(4)
I2	875.4(2)	5978.3(2)	5952.6(2)	17.23(5)
I1	297.2(2)	2669.7(2)	5379.6(2)	17.76(5)
I3	2888.1(2)	4978.6(2)	2831.8(2)	17.20(5)
O3	5000	6985(3)	2500	13.7(6)
O2	4520.4(19)	3391.2(19)	2021.7(8)	13.9(4)
O1	1728(2)	5042(2)	4833.2(9)	16.2(5)
O4	5831(2)	5622(2)	3265.4(8)	15.4(5)
C5	5227(3)	2517(3)	1889.3(13)	18.2(7)
C12	6792(3)	6311(3)	3349.5(13)	20.3(7)
C8	3422(3)	3135(3)	1814.1(12)	16.2(6)
C13	4462(3)	7690(3)	2810.7(12)	15.6(6)
C2	2760(3)	4699(3)	4236.7(13)	20.1(7)
C3	3318(3)	5625(3)	4545.4(15)	23.7(8)
C14	4899(3)	8845(3)	2757.2(12)	17.6(7)
C1	2154(3)	4132(3)	4579.6(13)	17.5(7)
C9	5449(4)	5423(4)	3720.1(12)	24.6(8)
C4	2482(3)	5984(3)	4850.9(13)	18.2(7)
C7	3521(3)	2249(3)	1448.5(13)	19.8(7)
C11	6745(4)	6865(4)	3815.1(15)	31.4(9)
C6	4491(3)	1609(3)	1672.8(14)	22.0(8)
C10	6268(4)	5964(4)	4089.3(15)	33.6(9)

Table S35. Anisotropic Displacement Parameters ($\times 10^4$) **3-Tb**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Tb2	9.31(9)	8.97(8)	7.95(9)	0	1.33(7)	0
Tb1	9.98(9)	12.19(9)	10.52(9)	-1.43(7)	1.24(7)	1.28(7)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I2	18.03(11)	20.86(10)	12.01(9)	-3.84(8)	-0.49(8)	-0.32(8)
I1	17.61(11)	15.23(9)	20.08(11)	2.27(8)	1.60(8)	4.50(8)
I3	12.94(10)	21.22(10)	18.45(11)	-2.34(8)	5.66(8)	-0.95(8)
O3	16.2(17)	10.2(14)	15.6(16)	0	4.6(13)	0
O2	12.8(11)	12.2(10)	15.9(11)	-3.0(9)	-0.3(9)	1.4(8)
O1	13.2(11)	15.7(11)	20.9(12)	-5.3(9)	6.8(10)	-0.5(9)
O4	18.8(12)	16.6(11)	9.7(10)	-2.7(8)	-1.1(9)	-1.2(9)
C5	19.3(17)	15.2(15)	20.5(17)	-3.8(13)	4.2(14)	2.4(12)
C12	20.5(16)	16.9(15)	21.8(15)	-5.4(12)	-2.8(12)	-0.4(12)
C8	15.2(16)	15.2(15)	17.6(16)	-3.5(12)	0.1(13)	-1.2(12)
C13	17.3(16)	13.5(14)	16.8(16)	-2.3(12)	4.6(13)	-0.3(12)
C2	23.7(19)	20.9(16)	16.5(16)	2.8(13)	6.1(14)	7.4(14)
C3	17.4(18)	22.8(17)	33(2)	3.7(16)	10.3(16)	2.1(14)
C14	19.5(17)	11.9(14)	21.8(17)	-2.9(12)	4.1(14)	-2.0(12)
C1	15.2(16)	17.7(15)	20.4(16)	-2.4(13)	4.9(13)	4.3(13)
C9	31.5(19)	32.1(19)	10.5(14)	-2.5(13)	3.9(13)	2.9(15)
C4	15.7(16)	16.2(15)	23.0(17)	-2.2(13)	4.1(14)	-4.1(13)
C7	20.8(18)	17.9(16)	19.9(17)	-8.3(13)	0.7(14)	-6.0(14)
C11	23.2(19)	39(2)	28.6(18)	-18.0(15)	-6.2(15)	5.1(15)
C6	27(2)	12.3(15)	27.9(19)	-5.2(14)	9.9(16)	-1.5(14)
C10	29(2)	51(2)	19.6(16)	-11.4(15)	-2.7(14)	10.0(17)

Table S36. Bond Lengths in Å for **3-Tb**.

Atom	Atom	Length/Å
Tb2	$I3^1$	2.9824(6)
Tb2	I3	2.9824(6)
Tb2	O3	2.393(3)
Tb2	$O2^1$	2.389(2)
Tb2	O2	2.389(2)
Tb2	$O4^1$	2.411(2)
Tb2	O4	2.411(2)
Tb1	I2	3.0284(5)
Tb1	$I2^2$	3.0285(5)
Tb1	$I1^2$	3.0074(6)
Tb1	I1	3.0073(6)
Tb1	O1	2.321(2)
Tb1	$O1^2$	2.321(2)
O3	C13	1.469(4)
O3	$C13^1$	1.469(4)
O2	C5	1.469(4)
O2	C8	1.470(4)
O1	C1	1.460(4)
O1	C4	1.480(4)
O4	C12	1.468(4)
O4	C9	1.475(4)
C5	C6	1.511(5)
C12	C11	1.499(5)
C8	C7	1.511(5)
C13	C14	1.512(5)
C2	C3	1.530(6)
C2	C1	1.499(5)
C3	C4	1.536(5)
C14	$C14^1$	1.532(7)
C9	C10	1.519(6)
C7	C6	1.516(6)
C11	C10	1.516(7)

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[1]1-X,+Y,1/2-Z; [2]-X,1-Y,1-Z

Table S37. Bond Angles in ° for **3-Tb**.

Atom	Atom	Atom	Angle/°
I3[1]	Tb2	I3	179.322(12)
O3	Tb2	I3	90.340(6)
O3	Tb2	I3[1]	90.339(6)
O3	Tb2	O4[1]	71.75(6)
O3	Tb2	O4	71.75(6)
O2[1]	Tb2	I3	88.83(6)
O2[1]	Tb2	I3[1]	90.63(6)
O2	Tb2	I3	90.63(6)
O2	Tb2	I3[1]	88.83(6)
O2[1]	Tb2	O3	143.68(6)
O2	Tb2	O3	143.68(6)
O2[1]	Tb2	O2	72.64(11)
O2	Tb2	O4[1]	71.95(8)
O2	Tb2	O4	144.54(8)
O2[1]	Tb2	O4[1]	144.54(8)
O2[1]	Tb2	O4	71.95(8)
O4[1]	Tb2	I3[1]	90.50(6)
O4	Tb2	I3[1]	89.71(6)
O4	Tb2	I3	90.50(6)
O4[1]	Tb2	I3	89.71(6)
O4[1]	Tb2	O4	143.50(12)
I2	Tb1	I2[2]	180.0
I1[2]	Tb1	I2	88.523(13)
I1[2]	Tb1	I2[2]	91.476(13)
I1	Tb1	I2	91.478(13)
I1	Tb1	I2[2]	88.522(13)
I1	Tb1	I1[2]	180.0
O1	Tb1	I2[2]	93.34(6)
O1	Tb1	I2	86.66(6)
O1[2]	Tb1	I2	93.34(6)
O1[2]	Tb1	I2[2]	86.66(6)
O1[2]	Tb1	I1	88.76(6)
O1	Tb1	I1	91.24(6)
O1	Tb1	I1[2]	88.75(6)
O1[2]	Tb1	I1[2]	91.25(6)
O1[2]	Tb1	O1	180.00(11)
C13[1]	O3	Tb2	125.21(17)
C13	O3	Tb2	125.21(17)
C13[1]	O3	C13	109.6(3)
C5	O2	Tb2	127.5(2)
C5	O2	C8	109.2(2)
C8	O2	Tb2	123.28(18)
C1	O1	Tb1	121.3(2)
C1	O1	C4	107.6(3)
C4	O1	Tb1	129.8(2)
C12	O4	Tb2	124.7(2)
C12	O4	C9	108.8(3)
C9	O4	Tb2	126.4(2)
O2	C5	C6	104.8(3)
O4	C12	C11	104.8(3)
O2	C8	C7	104.9(3)
O3	C13	C14	104.9(3)
C1	C2	C3	101.1(3)
C2	C3	C4	103.3(3)
C13	C14	C14[1]	102.3(2)
O1	C1	C2	104.5(3)
O4	C9	C10	105.2(3)
O1	C4	C3	105.5(3)
C8	C7	C6	102.1(3)
C12	C11	C10	102.4(3)
C5	C6	C7	103.0(3)
C11	C10	C9	103.4(3)

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[1]1-X,+Y,1/2-Z; [2]-X,1-Y,1-Z

Table S38. Hydrogen Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for **3-Tb**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H5A	5699	2238	2170	22
H5B	5668	2802	1658	22
H12A	6794	6870	3096	24
H12B	7437	5845	3364	24
H8A	3064	3805	1665	19
H8B	3013	2854	2058	19
H13A	4621	7435	3142	19
H13B	3684	7676	2712	19
H2A	2279	5005	3964	24
H2B	3276	4189	4122	24
H3A	3512	6251	4350	28
H3B	3966	5343	4743	28
H14A	5564	8966	2977	21
H14B	4377	9424	2812	21
H1A	1574	3670	4412	21
H1B	2627	3653	4799	21
H9A	5397	4615	3781	30
H9B	4742	5765	3721	30
H4A	2816	6127	5180	22
H4B	2114	6668	4723	22
H7A	3634	2582	1143	24
H7B	2885	1767	1398	24
H11A	6288	7534	3777	38
H11B	7462	7077	3972	38
H6A	4312	1088	1917	26
H6B	4813	1186	1433	26
H10A	5931	6287	4349	40
H10B	6814	5420	4223	40

Coordination Geometries of 1-Ln

Table S39 – Coordination Geometry Parameters I.

	Ce	Pr	Nd	Sm	Gd	Tb	Tm
Average bond length (Å)	2.7737	2.7565	2.7423	2.7113	2.6945	2.6773	2.6196
Polyhedral volume (Å³)	27.9371	27.4178	26.60	26.067	25.605	25.1107	23.5003
Distortion index	0.11291	0.1130	0.11414	0.11551	0.11527	0.11699	0.12424
Quadratic elongation	1.0254	1.0254	1.0289	1.0267	1.0260	1.0266	1.0289
Bond angle variance (°²)	7.6874	7.6874	8.066	7.5856	7.3546	6.7864	8.0661
Volume of the Ln VDP (Å³)	21.230	20.822	20.780	19.805	19.451	19.057	17.976

Radius of the Spherical Lanthanum Voronoi–Dirichlet Domain (Rsd, Å)	1.718	1.707	1.706	1.678	1.668	1.657	1.625
Solid angles from the Voronoi–Dirichlet Polyhedron (S, °) with Ln as the central atom	O2	O1	O3	O3	O1	O2	O2
	20.12	20.17	20.85	20.27	20.15	20.21	20.25
	O3	O3	O2	O1	O3	O1	O1
	20.12	20.17	19.38	20.27	20.15	20.21	20.14
	O1	O2	O1	O2	O2	O3	O3
	17.23	17.20	17.89	17.15	17.34	17.40	17.78
	I2	I3	I3	I3	I3	I2	I1
	15.36	15.31	13.80	15.26	15.25	15.17	15.37
	I3	I2	I2	I2	I2	I1	I3
	13.59	13.57	13.23	13.52	13.55	13.50	13.19
	I1	I1	I1	I1	I1	I3	I2
	13.59	13.57	14.85	13.52	13.55	13.50	13.27

UV-vis-NIR Spectroscopy

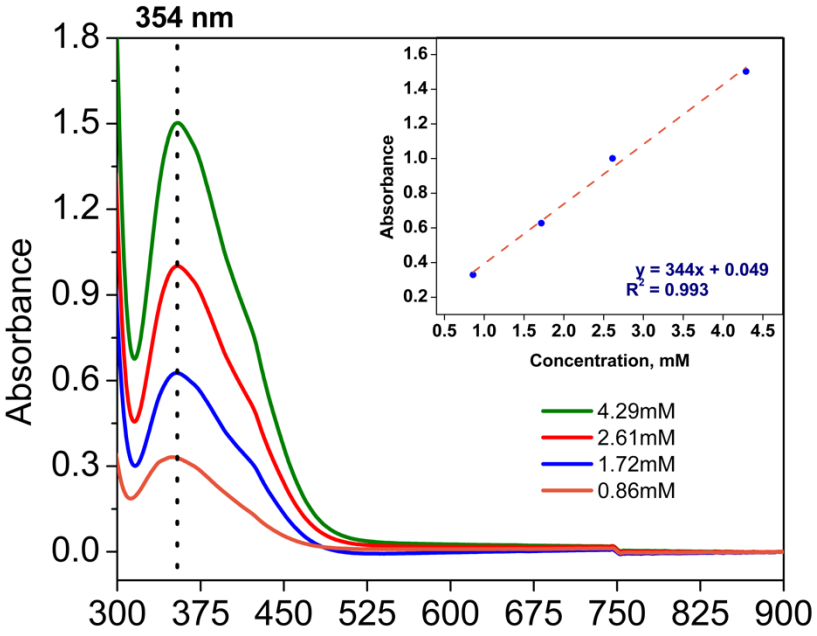

Figure S9. UV-vis spectra for varied concentrations for **1-Sm** in diethyl ether.

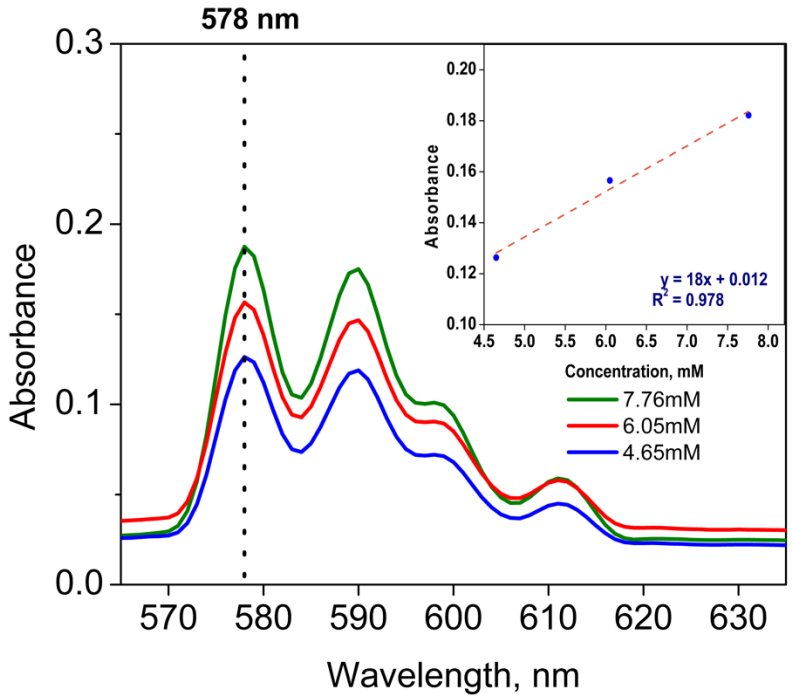

Figure S10. UV-vis spectra for varied concentrations for **1-Nd** in diethyl ether.

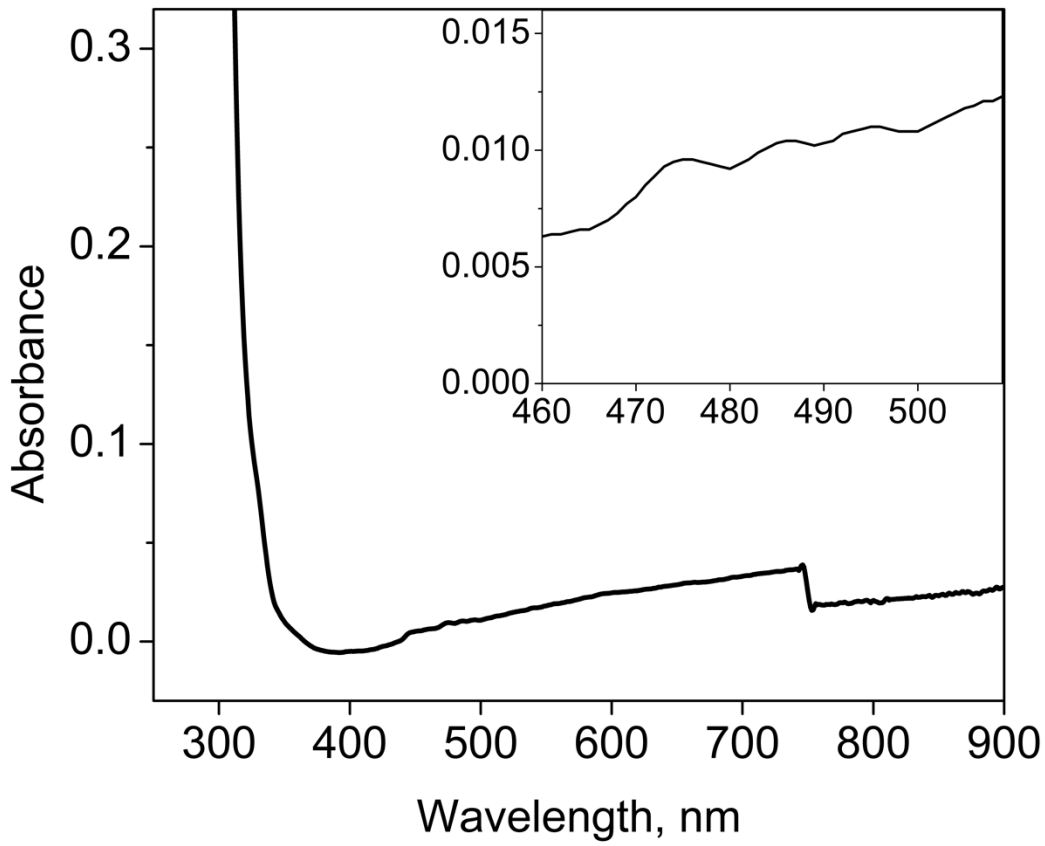

Figure S11. UV-vis spectra for near saturated concentration for **1-Pr** in diethyl ether.

NMR Spectroscopy

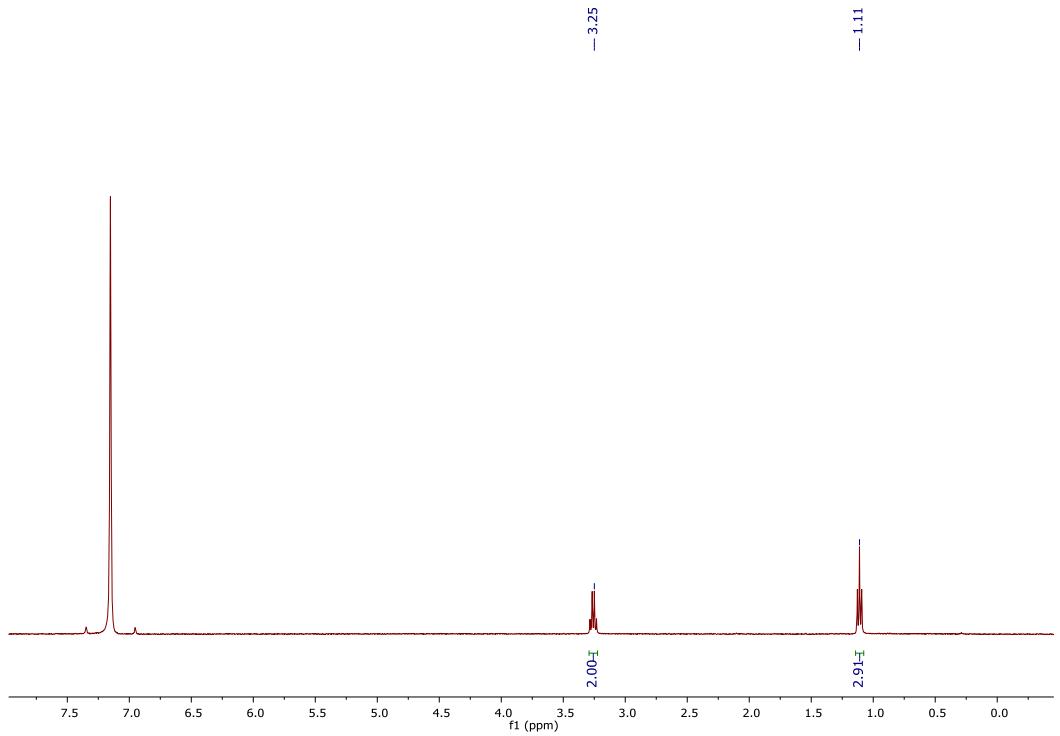

Figure S12. ^{1}H NMR of **1-Pr** in C_6D_6 (no precipitation observed, all of the complex is dissolved).

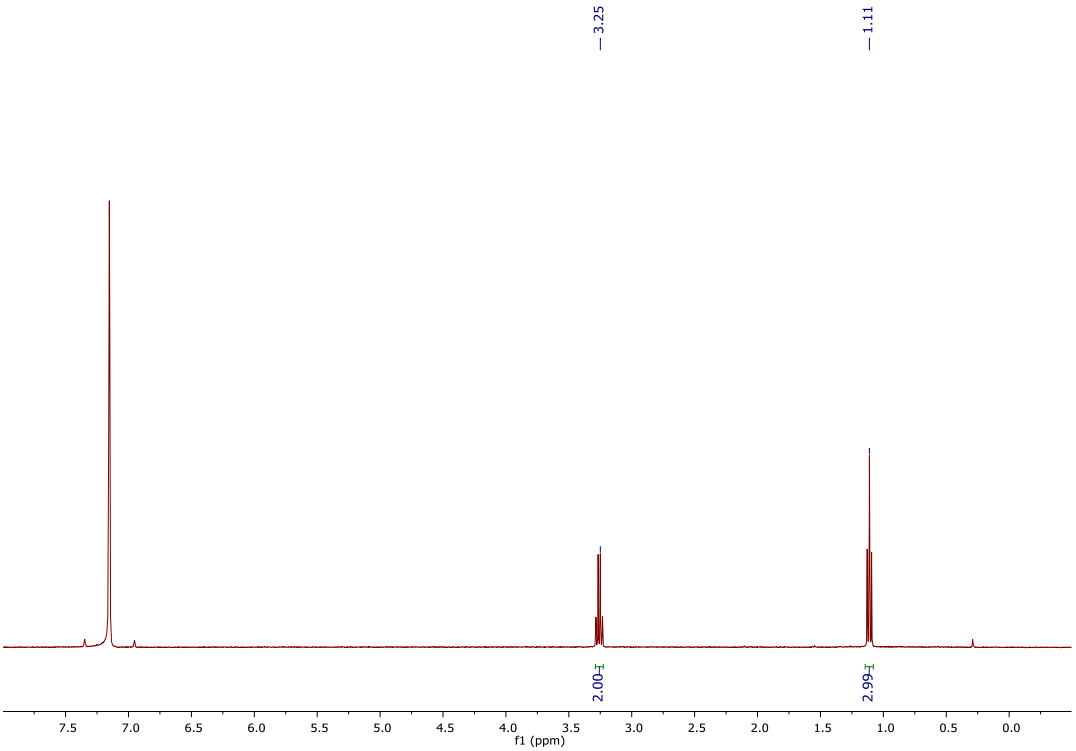

Figure S13. ^{1}H NMR of **1-Ce** in C_6D_6 (no precipitation observed, all of the complex is dissolved).

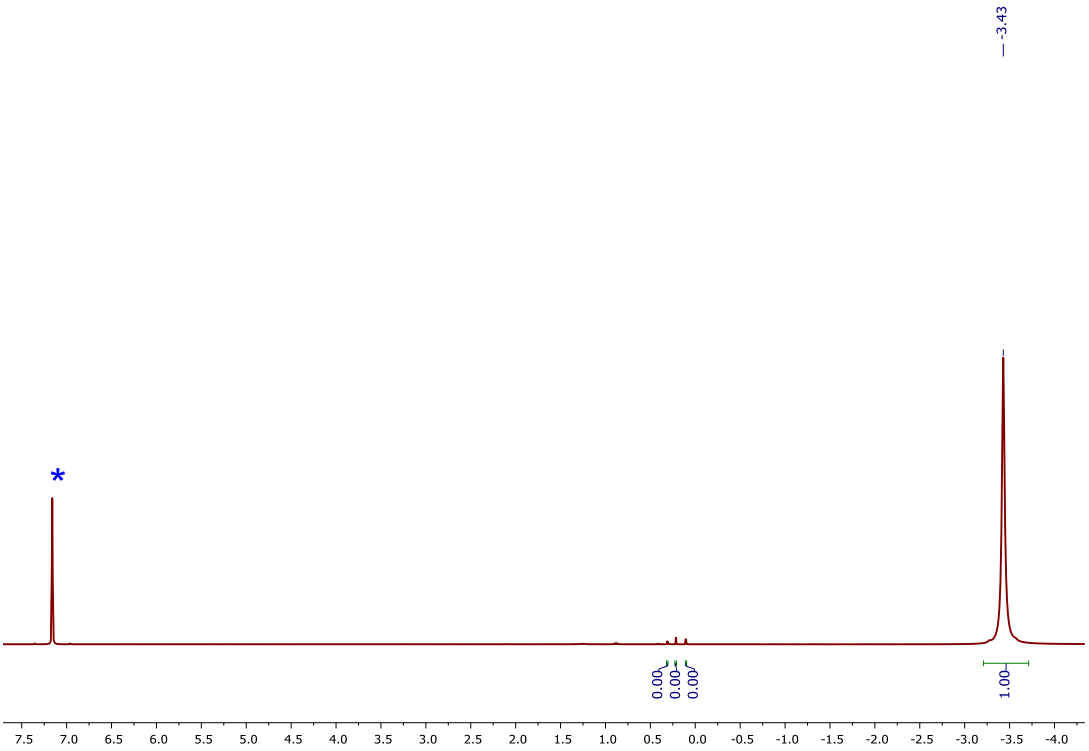

Figure S14. ^{1}H NMR of **Ce[N{Si(Me)$_3$}$_2$]$_3$** in C_6D_6. Peak of C_6D_5H is noted as *.

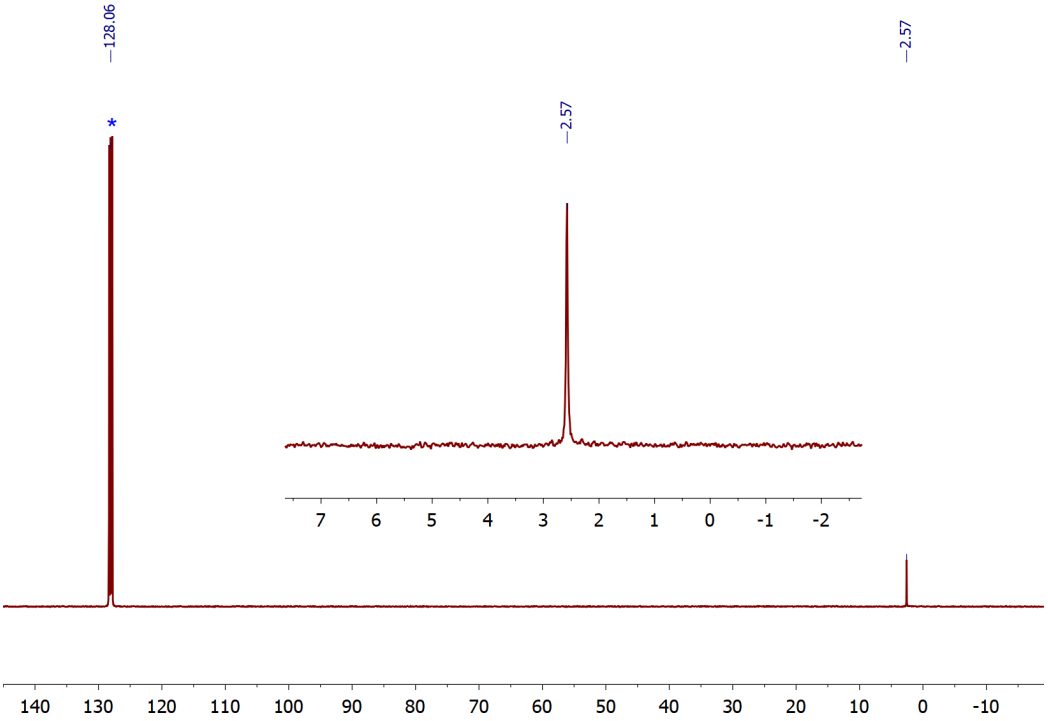

Figure S15. ^{13}C NMR of **Ce[N(Si(CH$_3$)$_3$)$_2$]$_3$** in C_6D_6. Peak of C_6D_5H is noted as *.

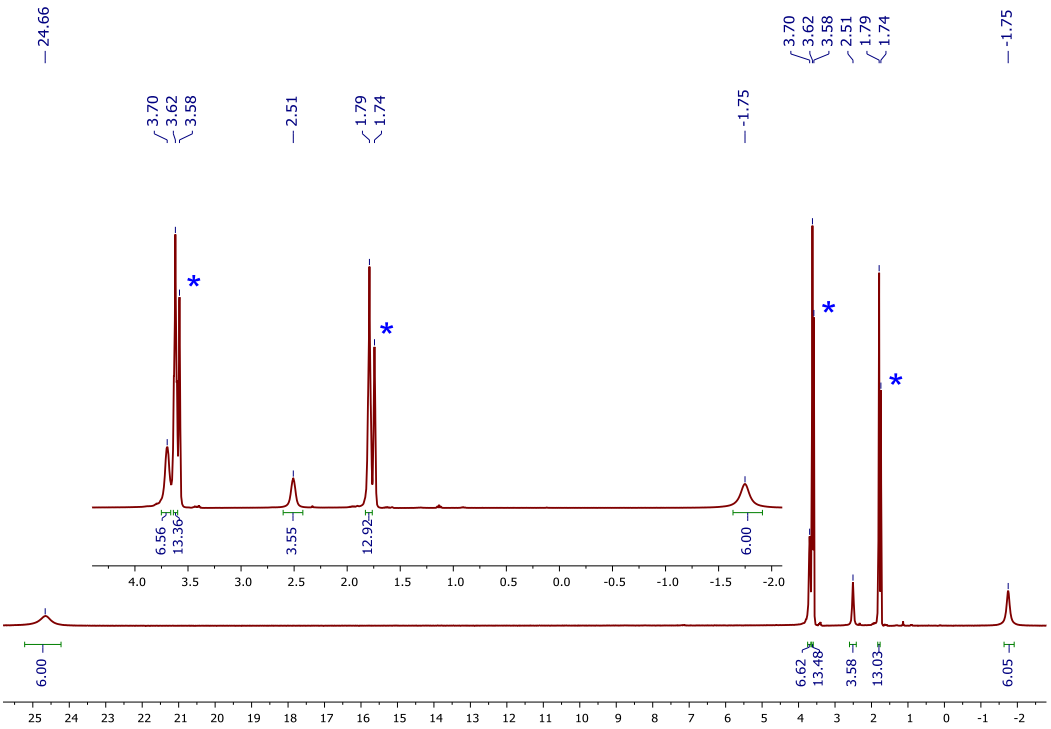

Figure S16. ^{1}H NMR of **$Ce(C_7H_7)_3(THF)_3$** in d_8-THF. Peaks of OC_4D_7H noted as *.

Powder X-ray Diffraction Patterns

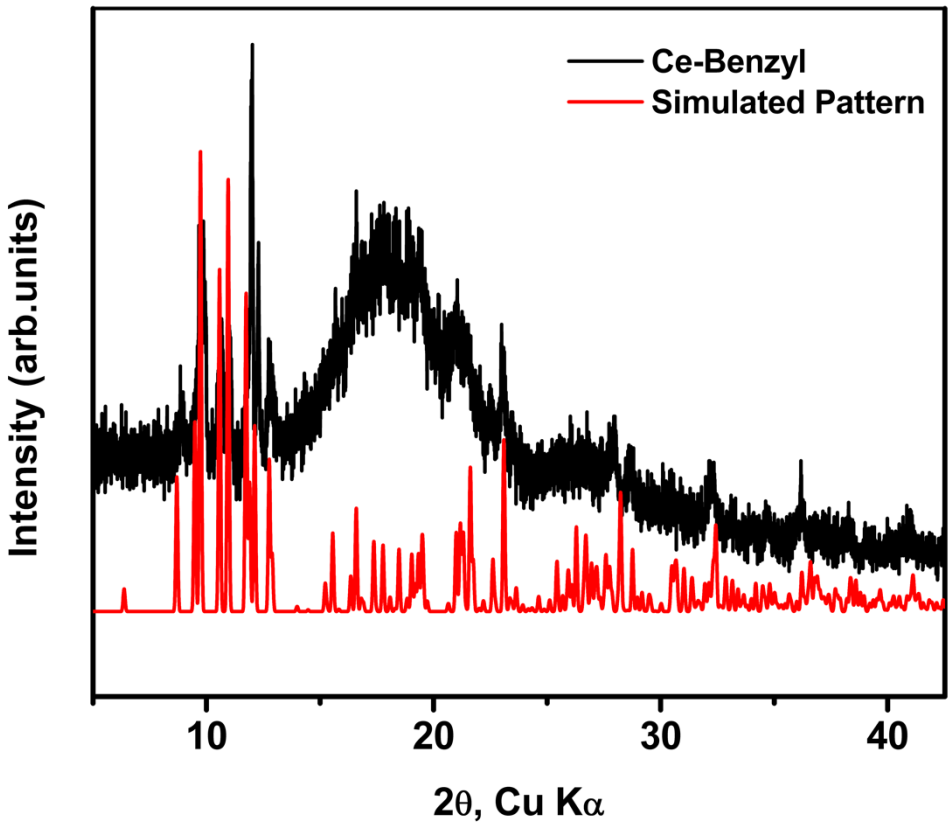

Figure S14. Powder XRD pattern for $Ce(C_7H_7)_3(THF)_3$. Simulated pattern is based on previously reported single crystal XRD data.[6]

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