Table of Contents

Contents

X-ray Data Collection, Structure, Solution, Refinement

1-Gd in R32.
X-ray Data Collection, Structure Solution and Refinement for ajr46.

A blue crystal of approximate dimensions 0.283 x 0.106 x 0.103 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer. The APEX2[1] program package was used to determine the unit-cell parameters and for data collection (240 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[2] and SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. The systematic absences were consistent with the trigonal space group *R32*. The non-centrosymmetric space group *R*32 was assigned and later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analysis.

Hydrogen atoms were included using a riding model.

Least-squares analysis yielded wR2 = 0.0426 and Goof = 1.005 for 88 variables refined against 2478 data (0.80 Å), R1 = 0.0235 for those 2264 data with $I > 2.0\sigma(I)$.

There were several high residuals present in the final difference-Fourier map. It was not possible to determine the nature of the residuals although it was probable that toluene solvent was present. The SQUEEZE[7a] routine in the PLATON[7b] program package was used to account for the electrons in the solvent accessible voids.

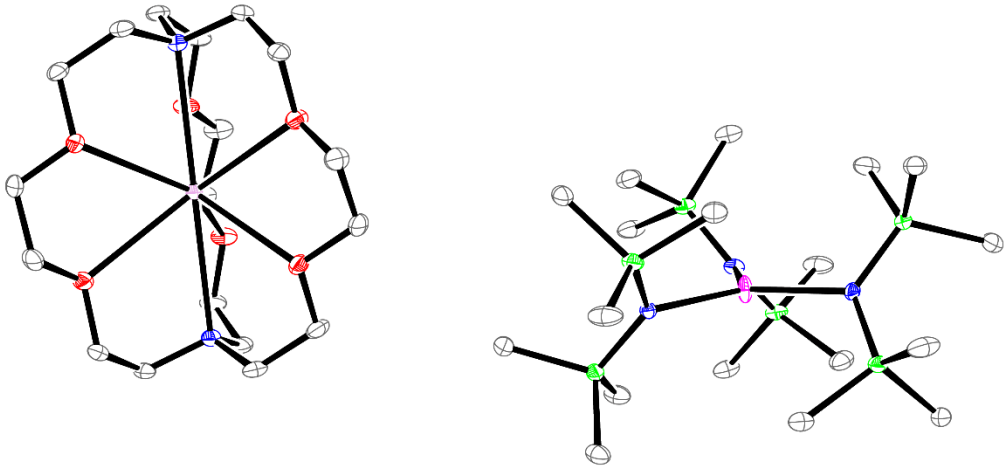


Figure S1. Ortep representation of **1-Gd** in R32 space group. Thermal ellipsoids drawn at the 50% probability level. H atoms excluded for clarity.

2-Dy. X-ray Data Collection, Structure Solution and Refinement for ajr19.

A dark blue crystal of approximate dimensions 0.140 x 0.145 x 0.192 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer. The APEX2[1] program package was used to determine the unit-cell parameters and for data collection (60 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[2] and SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space group $P2_1/n$ that was later determined to be correct.

The structure was solved by dual space methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analysis.

Hydrogen atoms were included using a riding model. Several atoms were disordered and included using multiple components, partial site-occupancy factors and isotropic thermal parameters. The Dy metal center was disordered over two positions and modeled with 95 and 5% occupancy.

At convergence, wR2 = 0.1025 and Goof = 1.023 for 553 variables refined against 16185 data (0.73Å), R1 = 0.0426 for those 12098 data with I > 2.0σ(I).

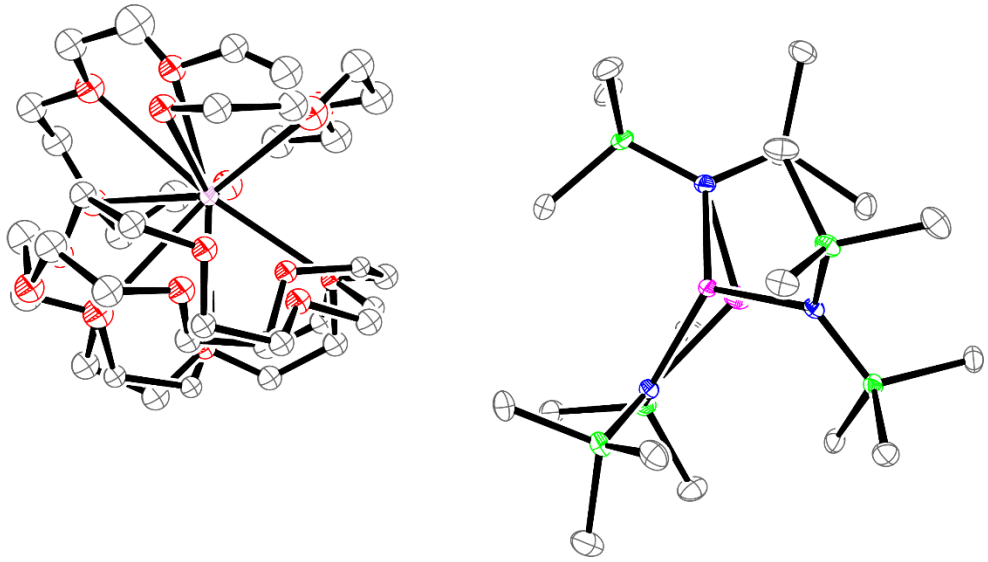


Figure S2. Ortep representation of **2-Dy** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms excluded for clarity.

2-Er X-ray Data Collection, Structure Solution and Refinement for ajr20.

A dark blue crystal of approximate dimensions 0.252 x 0.229 x 0.205 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer. The APEX2[1] program package was used to determine the unit-cell parameters and for data collection (60 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[2] and

SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space group $P2_1/n$ that was later determined to be correct.

The structure was solved by dual space methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Several atoms were disordered and included using multiple components, partial site-occupancy factors and isotropic thermal parameters. The Er metal center was disordered over tow positions and modeled with 97 and 3% occupancy.

Least-squares analysis yielded wR2 = 0.1081 and Goof = 1.091 for 553 variables refined against 15353 data (0.74, R1 = 0.0496 for those 12133 data with $I > 2.0\sigma(I)$.

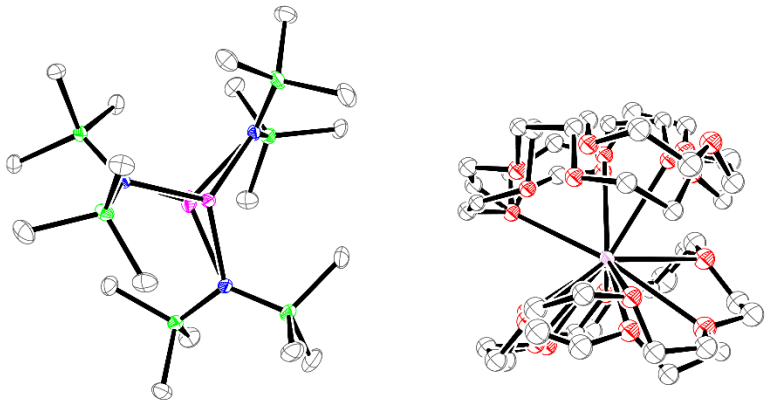


Figure S3. Ortep representation of **2-Er** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms excluded for clarity

2-Tb, X-ray Data Collection, Structure Solution and Refinement for ajr23.

A dark blue crystal of approximate dimensions 0.348 x 0.228 x 0.227 mm was in a cryoloop and transferred to a Bruker SMART APEX II diffractometer. The APEX2[1] program package was used to determine the unit-cell parameters and for data collection (30 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[2] and SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space group $P2_1/n$ that was later determined to be correct.

The structure was solved by dual space methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Several atoms were disordered and included using multiple components, partial site-occupancy factors and isotropic thermal parameters.

Least-squares analysis yielded wR2 = 0.0855 and Goof = 1.024 for 544 variables refined against 16174 data (0.73Å), R1 = 0.0356 for those 13695 data with $I > 2.0\sigma(I)$.

2-Y. X-ray Data Collection, Structure Solution and Refinement for ajr28.

A dark blue crystal of approximate dimensions 0.348 x 0.228 x 0.227 mm was mounted on a in a cryoloop and transferred to a Bruker SMART APEX II diffractometer. The APEX2[1] program package was used to determine the unit-cell parameters and for data collection (90 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[2] and SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space group $P2_1/n$ that was later determined to be correct.

The structure was solved by dual space methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analysis.

Hydrogen atoms were included using a riding model. Disorder in the 18-crown-6 units was modeled isotropically with multiple components. Disorder in the Y metal center was modeled in two parts with 97% and 3% occupancies.

Least-squares analysis yielded wR2 = 0.1383 and Goof = 1.025 for 553 variables refined against 15678 data (0.73 Å), R1 = 0.0516 for those 12476 data with $I > 2.0\sigma(I)$.

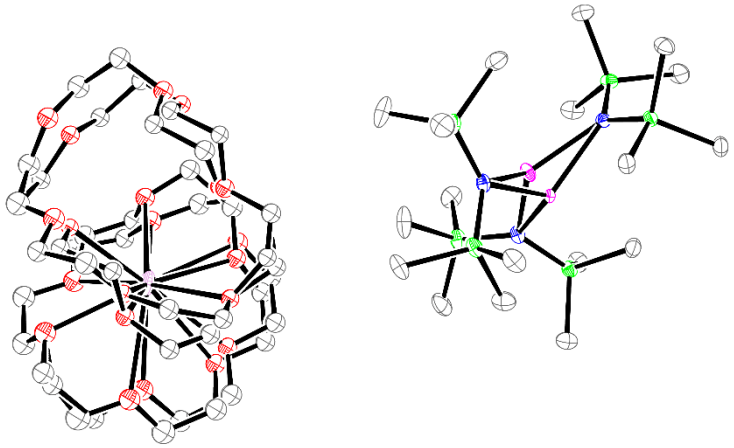


Figure S4. Ortep representation of **2-Y** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms excluded for clarity

2-Tm. X-ray Data Collection, Structure Solution and Refinement for ajr29.

A purple crystal of approximate dimensions 0.262 x 0.217 x 0.163 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer. The APEX2[1] program package was used to determine the unit-cell parameters and for data collection (90 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[2] and SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. The diffraction symmetry was *mmm* and the systematic absences were consistent with the orthorhombic space group $P2_12_12_1$ that was later determined to be correct.

The structure was solved by dual space methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model.

Least-squares analysis yielded wR2 = 0.1048 and Goof = 1.009 for 1042 variables refined against 26235 data (0.73Å), R1 = 0.0522 for those 18684 with I > 2.0σ(I).

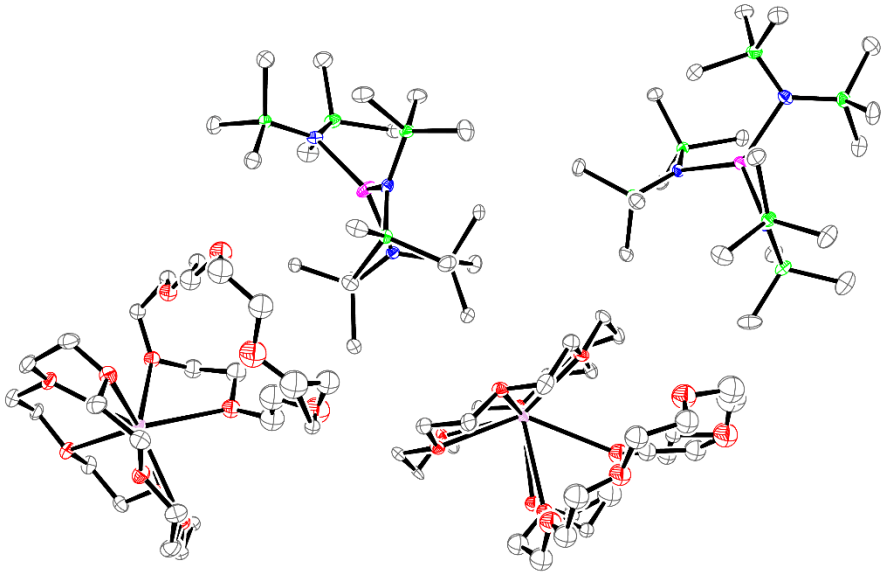


Figure S5. Ortep representation of **2-Tm** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms excluded for clarity.

2-Gd. X-ray Data Collection, Structure Solution and Refinement for ajr40.

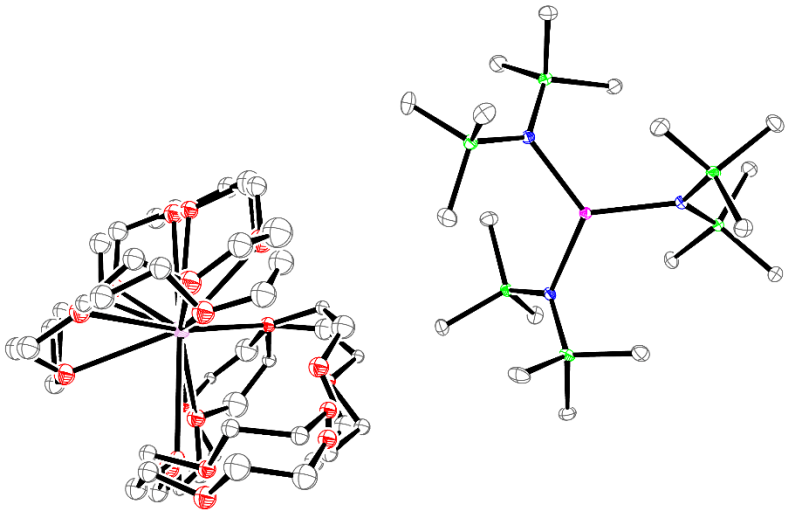
A dark blue crystal of approximate dimensions 0.253 x 0.239 x 0.192 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer. The APEX2[1] program package was used to determine the unit-cell parameters and for data collection (90 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[2] and SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space group $P2_1/n$ that was later determined to be correct.

The structure was solved by dual space methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analysis.

Hydrogen atoms were included using a riding model.

Least-squares analysis yielded wR2 = 0.0953 and Goof = 1.100 for 544 variables refined against 16163 data (0.73Å), R1 = 0.0466 for those 13374 data with I > 2.0σ(I).

Figure S6. Ortep representation of **2-Gd** with thermal ellipsoids drawn at the 50% probability



level. Hydrogen atoms excluded for clarity.

2-Ho. X-ray Data Collection, Structure Solution and Refinement for ajr43.

A blue crystal of approximate dimensions 0.378 x 0.375 x 0.367 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer. The APEX2[1] program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[2] and SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space group $P2_1/n$ that was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model.

Least-squares analysis yielded wR2 = 0.0914 and Goof = 1.028 for 553 variables refined against 156608 data (0.74Å), R1 = 0.0368 for those 14019 data with I > 2.0σ(I).

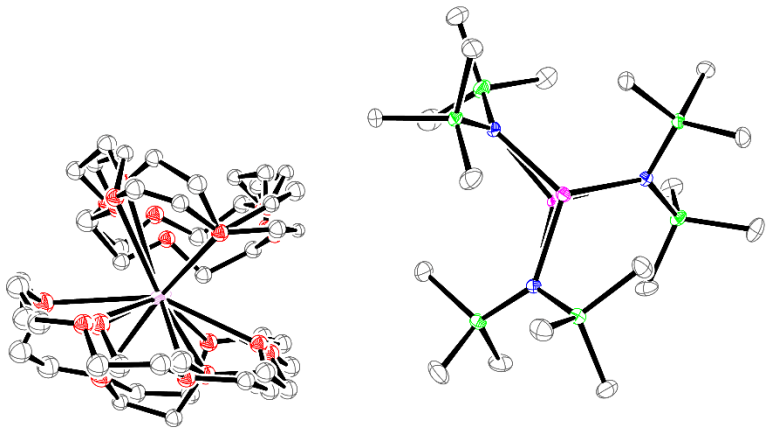


Figure S7. Ortep representation of **2-Ho** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms excluded for clarity.

3-Dy. X-ray Data Collection, Structure Solution and Refinement for ajr15.

A colorless crystal of approximate dimensions 0.048 x 0.141 x 0.264 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer. The APEX2[1] program package was used to determine the unit-cell parameters and for data collection (30 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[2] and

SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space groups *Cc* and *C*2/*c*. It was later determined that space group *C*2/*c* was correct.

The structure was solved by dual space methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analysis.

Hydrogen atoms were included using a riding model. The molecule was dimeric. There was a half-molecule located about an inversion center. Disorder in an Et2O solvent molecule was modeled isotropically.

Least-squares analysis yielded wR2 = 0.0846 and Goof = 1.113 for 567 variables refined against 15305 data (0.73 Å), R1 = 0.0373 for those 10683 data with $I > 2.0\sigma(I)$.

3-Ho. X-ray Data Collection, Structure Solution and Refinement for ajr26.

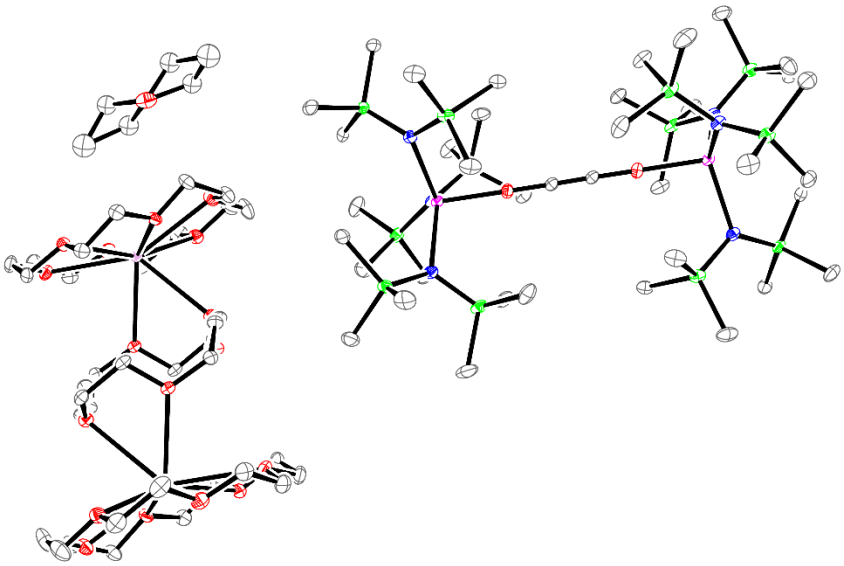
A yellow crystal of approximate dimensions 0.347 x 0.202 x 0.132 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer. The APEX2[1] program package was used to determine the unit-cell parameters and for data collection (30 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[2] and SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space groups *Cc* and *C*2/*c*. It was later determined that space group *C*2/*c* was correct.

The structure was solved by dual space methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analysis.

Hydrogen atoms were included using a riding model. The molecule was dimeric. There was a half-molecule located about an inversion center. Disorder in an Et2O solvent molecule was modeled isotropically in multiple parts.

Least-squares analysis yielded wR2 = 0.0590 and Goof = 1.026 for 559 variables refined against 14710 data (0.70 Å), R1 = 0.0251 for those 12462 data with I > 2.0σ(I).

Figure S8. Ortep representation of **3-Ho** with thermal ellipsoids drawn at the 50% probability



level. Hydrogen atoms excluded for clarity.

3-Tm. X-ray Data Collection, Structure Solution and Refinement for ajr41

A colorless crystal of approximate dimensions 0.214 x 0.200 x 0.196 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer. The APEX2[1] program package was used to determine the unit-cell parameters and for data collection (60 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[2] and SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space groups *Cc* and *C*2/*c*. It was later determined that space group *C*2/*c* was correct.

The structure was solved by dual space methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analysis. The molecule was dimeric. There was a half-molecules located about an inversion center. Disorder in an Et2O solvent molecule was modeled isotropically. Hydrogen atoms were included using a riding model.

Least-squares analysis yielded wR2 = 0.0554 and Goof = 1.011 for 559 variables refined against 15214 data (0.73Å), R1 = 0.0244 for those 12794 data with I > 2.0σ(I).

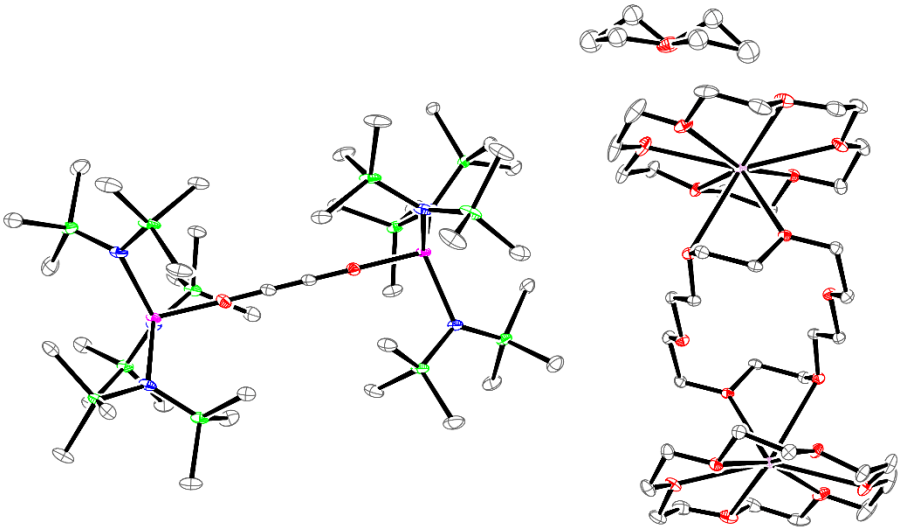


Figure S9. Ortep representation of **3-Tm** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms excluded for clarity.

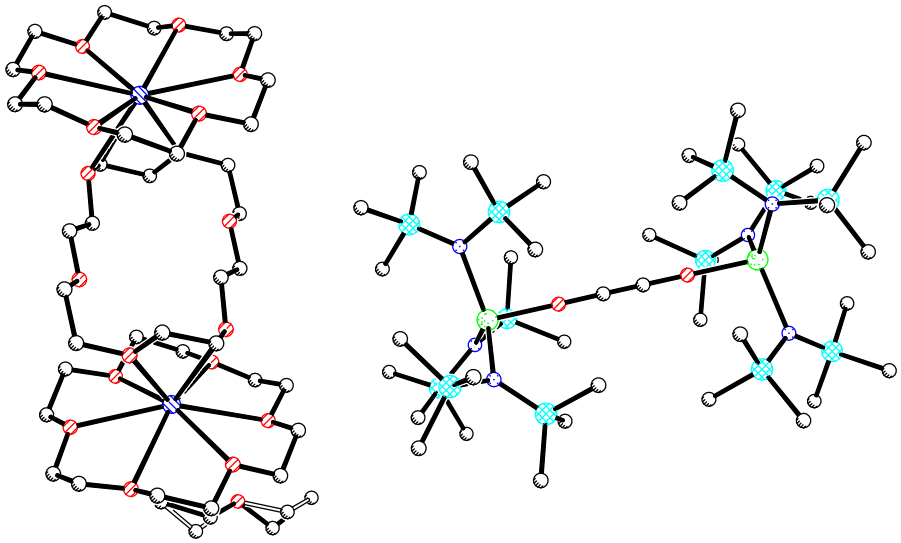


Figure S10. Ball and stick representation of connectivity structure of **3-Gd.** Hydrogen atoms excluded for clarity.

4- Gd. X-ray Data Collection, Structure Solution and Refinement for ajr32.

A colorless crystal of approximate dimensions 0.241 x 0.127 x 0.119 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer. The APEX2[1] program package was used to determine the unit-cell parameters and for data collection (90 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[2] and SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct.

The structure was solved by dual space methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analysis.

Hydrogen atoms were included using a riding model.

Least-squares analysis yielded wR2 = 0.0672 and Goof = 0.989 for 769 variables refined against 19003 data (0.70 Å), R1 = 0.0332 for those 14746 data with $I > 2.0\sigma(I)$.

Table S1. Crystal data and structure refinement for ajr19 (2-Dy).

Identification code	ajr19	
Empirical formula	C42 H102 Dy K N3 O12 Si6	
Formula weight	1211.40	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 11.0616(10) Å	□= 90°.
	b = 27.199(2) Å	□= 103.8855(12)°.
	c = 21.7721(19) Å	□ = 90°.
Volume	6359.0(10) $Å^3$	
Z	4	
Density (calculated)	1.265 Mg/m^3	
Absorption coefficient	1.403 mm^{-1}	
F(000)	2560	
Crystal color	blue	
Crystal size	0.348 x 0.228 x 0.227 mm^3	
Theta range for data collection	1.781 to 29.158°	
Index ranges	-14 <= h <= 15, -36 <= k <= 37, -28 <= l <= 28	
Reflections collected	78631	
Independent reflections	16185 [R(int) = 0.0587]	
Completeness to theta = 25.500°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4319 and 0.3886	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	16185 / 0 / 553
Goodness-of-fit on F^2	1.023
Final R indices [I>2sigma(I) = 12098 data]	R1 = 0.0426, wR2 = 0.0928
R indices (all data, 0.73 Å)	R1 = 0.0678, wR2 = 0.1025
Extinction coefficient	n/a
Largest diff. peak and hole	1.467 and -0.704 e.$Å^{-3}$

Table S2. Bond lengths [Å] for ajr19(2-Dy).

Dy(1)-N(3)	2.273(3)
Dy(1)-N(2)	2.278(3)
Dy(1)-N(1)	2.288(3)
Dy(1)-Si(5)	3.3919(10)
Dy(1)-Si(3)	3.3929(10)
Dy(1)-Si(1)	3.4012(10)
Dy(2)-N(1)	2.257(5)
Dy(2)-N(3)	2.320(5)
Dy(2)-N(2)	2.337(5)
Dy(2)-C(5)	2.973(6)
Dy(2)-Si(2)	3.136(4)
Dy(2)-Si(4)	3.218(4)
Dy(2)-Si(6)	3.241(4)
Si(1)-N(1)	1.714(3)
Si(1)-C(2)	1.874(4)
Si(1)-C(1)	1.874(4)

Si(1)-C(3)	1.878(4)
Si(2)-N(1)	1.710(3)
Si(2)-C(5)	1.874(4)
Si(2)-C(4)	1.877(4)
Si(2)-C(6)	1.878(4)
Si(3)-N(3)	1.726(3)
Si(3)-C(7)	1.870(4)
Si(3)-C(8)	1.876(4)
Si(3)-C(9)	1.886(4)
Si(4)-N(3)	1.708(3)
Si(4)-C(11)	1.879(4)
Si(4)-C(10)	1.882(4)
Si(4)-C(12)	1.883(4)
Si(5)-N(2)	1.713(3)
Si(5)-C(14)	1.870(4)
Si(5)-C(15)	1.879(4)
Si(5)-C(13)	1.880(4)
Si(6)-N(2)	1.705(3)
Si(6)-C(18)	1.879(3)
Si(6)-C(17)	1.879(3)
Si(6)-C(16)	1.887(3)

Table S3. Crystal data and structure refinement for ajr20 (2-Er).

Identification code	ajr20
Empirical formula	C42 H102 Er K N3 O12 Si6

Formula weight	1216.16	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 11.064(3) Å	□= 90°.
	b = 27.080(6) Å	□= 103.991(3)°.
	c = 21.797(5) Å	□ = 90°.
Volume	6337(2) $Å^3$	
Z	4	
Density (calculated)	1.275 Mg/m^3	
Absorption coefficient	1.553 mm^{-1}	
F(000)	2568	
Crystal color	blue	
Crystal size	0.348 x 0.228 x 0.227 mm^3	
Theta range for data collection	1.222 to 28.872°	
Index ranges	-14 <= h <= 14, -34 <= k <= 34, -28 <= l <= 28	
Reflections collected	76237	
Independent reflections	15353 [R(int) = 0.0511]	
Completeness to theta = 25.500°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7458 and 0.6642	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15353 / 0 / 553	
Goodness-of-fit on F^2	1.091	

Final R indices [I>2sigma(I) = 12133 data]	R1 = 0.0496, wR2 = 0.1012
R indices (all data, 0.74 Å)	R1 = 0.0703, wR2 = 0.1081
Extinction coefficient	n/a
Largest diff. peak and hole	1.060 and -0.957 e.Å^{-3}

Table S4. Bond lengths [Å] for ajr20(2-Er).

Er(1)-N(3)	2.246(3)
Er(1)-N(1)	2.249(3)
Er(1)-N(2)	2.249(3)
Er(1)-Si(3)	3.3812(13)
Er(1)-Si(1)	3.3850(12)
Er(1)-Si(5)	3.3856(13)
Er(2)-N(1)	2.256(8)
Er(2)-N(2)	2.289(8)
Er(2)-N(3)	2.354(8)
Er(2)-C(5)	2.961(9)
Er(2)-Si(2)	3.119(8)
Er(2)-Si(6)	3.185(7)
Er(2)-Si(4)	3.243(8)
Si(1)-N(1)	1.708(3)
Si(1)-C(1)	1.871(5)
Si(1)-C(2)	1.877(5)
Si(1)-C(3)	1.882(5)
Si(2)-N(1)	1.714(3)
Si(2)-C(5)	1.875(4)

Si(2)-C(4)	1.876(4)
Si(2)-C(6)	1.877(5)
Si(3)-N(3)	1.715(3)
Si(3)-C(8)	1.863(5)
Si(3)-C(7)	1.870(5)
Si(3)-C(9)	1.882(5)
Si(4)-N(3)	1.711(3)
Si(4)-C(12)	1.872(5)
Si(4)-C(10)	1.878(4)
Si(4)-C(11)	1.880(4)
Si(5)-N(2)	1.709(3)
Si(5)-C(14)	1.872(5)
Si(5)-C(15)	1.875(5)
Si(5)-C(13)	1.880(4)
Si(6)-N(2)	1.704(3)
Si(6)-C(17)	1.871(4)
Si(6)-C(18)	1.880(4)
Si(6)-C(16)	1.889(4)

Table S5. Crystal data and structure refinement for ajr23(2-Tb).

Identification code	ajr23
Empirical formula	C42 H102 K N3 O12 Si6 Tb
Formula weight	1207.82
Temperature	133(2) K
Wavelength	0.71073 Å

Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 11.1324(18) Å □= 90°.
	b = 27.081(4) Å □= 103.924(2)°.
	c = 21.775(4) Å □ = 90°.
Volume	6372.0(18) $Å^3$
Z	4
Density (calculated)	1.259 Mg/m^3
Absorption coefficient	1.337 mm^{-1}
F(000)	2556
Crystal color	blue
Crystal size	0.348 x 0.228 x 0.227 mm^3
Theta range for data collection	1.786 to 29.178°
Index ranges	-15 <= h <= 14, -36 <= k <= 35, -28 <= l <= 29
Reflections collected	78537
Independent reflections	16174 [R(int) = 0.0363]
Completeness to theta = 25.500°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.4318 and 0.3744
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	16174 / 0 / 544
Goodness-of-fit on F^2	1.024
Final R indices [I>2sigma(I) = 13695 data]	R1 = 0.0356, wR2 = 0.0804
R indices (all data, 0.73 Å)	R1 = 0.0461, wR2 = 0.0855
Extinction coefficient	n/a

Largest diff. peak and hole	1.489 and -0.680 e.Å^{-3}

Table S6. Bond lengths [Å] for ajr23 (2-Tb).

Tb(1)-N(2)	2.291(2)
Tb(1)-N(3)	2.294(2)
Tb(1)-N(1)	2.295(2)
Si(1)-N(1)	1.709(2)
Si(1)-C(1)	1.875(3)
Si(1)-C(3)	1.878(3)
Si(1)-C(2)	1.879(3)
Si(2)-N(1)	1.709(2)
Si(2)-C(5)	1.878(3)
Si(2)-C(4)	1.880(3)
Si(2)-C(6)	1.880(3)
Si(3)-N(3)	1.714(2)
Si(3)-C(7)	1.875(3)
Si(3)-C(8)	1.876(3)
Si(3)-C(9)	1.884(3)
Si(4)-N(3)	1.707(2)
Si(4)-C(10)	1.881(3)
Si(4)-C(12)	1.882(3)
Si(4)-C(11)	1.886(3)
Si(5)-N(2)	1.711(2)
Si(5)-C(14)	1.878(3)

Si(5)-C(13)	1.881(3)
Si(5)-C(15)	1.886(3)
Si(6)-N(2)	1.704(2)
Si(6)-C(17)	1.879(3)
Si(6)-C(18)	1.881(3)
Si(6)-C(16)	1.886(3)

Table S7. Crystal data and structure refinement for ajr28 (2-Y).

Identification code	ajr28	
Empirical formula	C42 H102 K N3 O12 Si6 Y	
Formula weight	1137.81	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 11.0774(7) Å	□= 90°.
	b = 27.0905(18) Å	□= 104.0003(9)°.
	c = 21.7959(14) Å	□ = 90°.
Volume	6346.5(7) $Å^3$	
Z	4	
Density (calculated)	1.191 Mg/m^3	
Absorption coefficient	1.147 mm^{-1}	
F(000)	2452	
Crystal color	violet	
Crystal size	0.348 x 0.228 x 0.227 mm^3	
Theta range for data collection	1.221 to 28.909°	
Index ranges	-14 <= h <= 14, -36 <= k <= 35, -28 <= l <= 29	
Reflections collected	76302	
Independent reflections	15678 [R(int) = 0.0364]	
Completeness to theta = 25.500°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7458 and 0.6480	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15678 / 0 / 553	

Goodness-of-fit on F^2	1.026
Final R indices [I>2sigma(I) = 12476 data]	R1 = 0.0516, wR2 = 0.1294
R indices (all data, 0.73 Å)	R1 = 0.0690, wR2 = 0.1384
Extinction coefficient	n/a
Largest diff. peak and hole	1.241 and -0.673 e.$Å^{-3}$

Table S8. Bond lengths [Å] for ajr28 (2-Y).

Y(1)-N(3)	2.264(2)
Y(1)-N(2)	2.2667(19)
Y(1)-N(1)	2.271(2)
Y(1)-Si(3)	3.3992(8)
Y(1)-Si(5)	3.4012(7)
Y(1)-Si(1)	3.4019(8)
Y(2)-N(1)	2.263(8)
Y(2)-N(2)	2.321(8)
Y(2)-N(3)	2.368(8)
Y(2)-C(5)	2.965(9)
Y(2)-Si(2)	3.124(8)
Y(2)-Si(6)	3.218(7)
Y(2)-Si(4)	3.249(8)
Si(1)-N(1)	1.708(2)
Si(1)-C(1)	1.868(3)
Si(1)-C(2)	1.871(3)
Si(1)-C(3)	1.881(4)
Si(2)-N(1)	1.705(2)
Si(2)-C(5)	1.872(3)
Si(2)-C(6)	1.876(3)
Si(2)-C(4)	1.881(3)
Si(3)-N(3)	1.713(2)
Si(3)-C(8)	1.870(3)
Si(3)-C(7)	1.872(3)
Si(3)-C(9)	1.881(3)
Si(4)-N(3)	1.705(2)
Si(4)-C(10)	1.875(3)

Si(4)-C(12)	1.879(3)
Si(4)-C(11)	1.884(3)
Si(5)-N(2)	1.709(2)
Si(5)-C(14)	1.869(3)
Si(5)-C(15)	1.874(3)
Si(5)-C(13)	1.875(3)
Si(6)-N(2)	1.701(2)
Si(6)-C(17)	1.875(3)
Si(6)-C(18)	1.876(3)
Si(6)-C(16)	1.883(3)

Table S9. Crystal data and structure refinement for ajr29 (2-Tm).

Identification code	ajr29	
Empirical formula	C42 H102 K N3 O12 Si6 Tm	
Formula weight	1217.83	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 21.956(2) Å	□= 90°.
	b = 22.554(2) Å	□= 90°.
	c = 25.737(3) Å	□ = 90°.
Volume	12745(2) $Å^3$	
Z	8	
Density (calculated)	1.269 Mg/m^3	
Absorption coefficient	1.620 mm^{-1}	
F(000)	5144	
Crystal color	purple	

Crystal size	0.262 x 0.217 x 0.163 mm^3
Theta range for data collection	1.200 to 26.481°
Index ranges	-27 <= h <= 27, -28 <= k <= 28, -32 <= l <= 32
Reflections collected	139038
Independent reflections	26235 [R(int) = 0.1045]
Completeness to theta = 25.500°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.4296 and 0.3637
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	26235 / 0 / 1042
Goodness-of-fit on F^2	1.009
Final R indices [I>2sigma(I) = 18684 data]	R1 = 0.0522, wR2 = 0.0910
R indices (all data, 0.73 Å)	R1 = 0.0941, wR2 = 0.1048
Absolute structure parameter	-0.006(3)
Extinction coefficient	n/a
Largest diff. peak and hole	0.981 and -1.073 $e.Å^{-3}$

Table S10. Bond lengths [Å] for ajr29 (2-Tm).

Tm(1)-N(2)	2.335(7)
Tm(1)-N(1)	2.353(7)
Tm(1)-N(3)	2.357(6)
Tm(1)-Si(3)	3.330(3)
Tm(1)-Si(2)	3.353(2)
Si(1)-N(1)	1.680(7)

Si(1)-C(1)	1.865(10)
Si(1)-C(3)	1.877(10)
Si(1)-C(2)	1.881(10)
Si(2)-N(1)	1.679(7)
Si(2)-C(4)	1.864(10)
Si(2)-C(5)	1.876(10)
Si(2)-C(6)	1.881(10)
Si(3)-N(2)	1.675(8)
Si(3)-C(9)	1.865(10)
Si(3)-C(7)	1.883(10)
Si(3)-C(8)	1.897(10)
Si(4)-N(2)	1.701(8)
Si(4)-C(12)	1.870(11)
Si(4)-C(11)	1.877(10)
Si(4)-C(10)	1.890(10)
Si(5)-N(3)	1.684(7)
Si(5)-C(15)	1.875(9)
Si(5)-C(13)	1.881(9)
Si(5)-C(14)	1.886(9)
Si(6)-N(3)	1.683(7)
Si(6)-C(16)	1.867(9)
Si(6)-C(17)	1.872(9)
Si(6)-C(18)	1.886(9)
Tm(2)-N(5)	2.338(7)
Tm(2)-N(4)	2.346(6)

Tm(2)-N(6)	2.348(7)

Table S11. Crystal data and structure refinement for ajr40 (2-Gd).

Identification code	ajr40	
Empirical formula	C42 H102 Gd K N3 O12 Si6	
Formula weight	1206.15	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 11.1493(11) Å	□= 90°.
	b = 27.059(3) Å	□= 104.0069(13)°.
	c = 21.755(2) Å	□ = 90°.
Volume	6368.1(11) $Å^3$	
Z	4	
Density (calculated)	1.258 Mg/m^3	
Absorption coefficient	1.269 mm^{-1}	
F(000)	2552	
Crystal color	purple	
Crystal size	0.253 x 0.239 x 0.192 mm^3	
Theta range for data collection	1.223 to 29.134°	
Index ranges	-15 <= h <= 15, -35 <= k <= 35, -28 <= l <= 28	
Reflections collected	78726	
Independent reflections	16163 [R(int) = 0.0511]	
Completeness to theta = 25.500°	100.0 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.4319 and 0.3744
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	16163 / 0 / 544
Goodness-of-fit on F^2	1.100
Final R indices [I>2sigma(I) = 13374 data]	R1 = 0.0466, wR2 = 0.0904
R indices (all data, 0.73 Å)	R1 = 0.0623, wR2 = 0.0953
Extinction coefficient	n/a
Largest diff. peak and hole	1.009 and -1.022 e.$Å^{-3}$

Table S12. Bond lengths [Å] for ajr40(2-Gd).

Gd(1)-N(2)	2.308(3)
Gd(1)-N(1)	2.310(3)
Gd(1)-N(3)	2.310(3)
Gd(1)-Si(6)	3.4562(9)
Gd(1)-Si(3)	3.4595(10)
Si(1)-N(1)	1.708(3)
Si(1)-C(3)	1.878(4)
Si(1)-C(1)	1.878(4)
Si(1)-C(2)	1.881(4)
Si(2)-N(1)	1.708(3)
Si(2)-C(6)	1.878(4)
Si(2)-C(5)	1.881(4)
Si(2)-C(4)	1.882(4)

Si(3)-N(3)	1.709(3)
Si(3)-C(8)	1.877(4)
Si(3)-C(7)	1.878(4)
Si(3)-C(9)	1.886(4)
Si(4)-N(3)	1.706(3)
Si(4)-C(12)	1.878(4)
Si(4)-C(10)	1.883(3)
Si(4)-C(11)	1.889(4)
Si(5)-N(2)	1.709(3)
Si(5)-C(13)	1.876(4)
Si(5)-C(15)	1.884(4)
Si(5)-C(14)	1.884(4)
Si(6)-N(2)	1.701(3)
Si(6)-C(17)	1.882(4)
Si(6)-C(18)	1.883(3)
Si(6)-C(16)	1.883(3)

Table S11. Crystal data and structure refinement for ajr43 (2-Ho).

Identification code	ajr43
Empirical formula	C42 H102 Ho K N3 O12 Si6
Formula weight	1213.83
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$

Unit cell dimensions	a = 11.0476(11) Å	□= 90°.
	b = 27.157(3) Å	□= 103.9052(12)°.
	c = 21.797(2) Å	□ = 90°.
Volume	6347.9(11) $Å^3$	
Z	4	
Density (calculated)	1.270 Mg/m^3	
Absorption coefficient	1.475 mm^{-1}	
F(000)	2564	
Crystal color	Blue	
Crystal size	0.378 x 0.375 x 0.367 mm^3	
Theta range for data collection	1.220 to 28.873°	
Index ranges	-14 <= h <= 14, -36 <= k <= 36, -29 <= l <= 29	
Reflections collected	75935	
Independent reflections	15608 [R(int) = 0.0434]	
Completeness to theta = 25.500°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7458 and 0.6626	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15608 / 0 / 553	
Goodness-of-fit on F^2	1.028	
Final R indices [I>2sigma(I) = 14019 data]	R1 = 0.0368, wR2 = 0.0883	
R indices (all data, 0.74 Å)	R1 = 0.0417, wR2 = 0.0914	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.859 and -0.882 $e.Å^{-3}$	

Table S12. Bond lengths [Å] for ajr43 (2-Ho).

Ho(1)-N(3)	2.262(2)
Ho(1)-N(2)	2.264(2)
Ho(1)-N(1)	2.274(2)
Ho(1)-Si(5)	3.3709(8)
Ho(1)-Si(3)	3.3832(9)
Ho(1)-Si(1)	3.3860(9)
Ho(2)-N(1)	2.258(5)
Ho(2)-N(3)	2.311(5)
Ho(2)-N(2)	2.318(4)
Ho(2)-C(5)	2.947(6)
Ho(2)-Si(2)	3.120(4)
Ho(2)-Si(4)	3.201(4)
Ho(2)-Si(6)	3.212(4)
Si(1)-N(1)	1.713(2)
Si(1)-C(1)	1.867(4)
Si(1)-C(2)	1.873(4)
Si(1)-C(3)	1.882(4)
Si(2)-N(1)	1.707(2)
Si(2)-C(5)	1.872(3)
Si(2)-C(6)	1.878(4)
Si(2)-C(4)	1.882(3)
Si(3)-N(3)	1.721(3)
Si(3)-C(8)	1.870(4)

Si(3)-C(7)	1.881(4)
Si(3)-C(9)	1.881(4)
Si(4)-N(3)	1.708(3)
Si(4)-C(11)	1.872(3)
Si(4)-C(10)	1.879(3)
Si(4)-C(12)	1.884(4)
Si(5)-N(2)	1.714(2)
Si(5)-C(14)	1.866(3)
Si(5)-C(13)	1.876(3)
Si(5)-C(15)	1.878(4)
Si(6)-N(2)	1.702(2)
Si(6)-C(17)	1.874(3)
Si(6)-C(18)	1.875(3)
Si(6)-C(16)	1.888(3)

Table S13. Crystal data and structure refinement for ajr15 (3-Dy).

Identification code	ajr15	
Empirical formula	C78 H190 Dy2 K2 N6 O21 Si12	
Formula weight	2288.63	
Temperature	88(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 25.4899(16) Å	□= 90°.
	b = 18.8304(12) Å	□= 103.1276(9)°.
	c = 25.7453(16) Å	□ = 90°.
Volume	12034.4(13) Å^3	
Z	4	
Density (calculated)	1.263 Mg/m^3	

Absorption coefficient	1.477 mm^{-1}
F(000)	4824
Crystal color	colorless
Crystal size	0.264 x 0.141 x 0.048 mm^3
Theta range for data collection	1.357 to 29.158°
Index ranges	-33 <= h <= 34, -25 <= k <= 25, -33 <= l <= 33
Reflections collected	74183
Independent reflections	15305 [R(int) = 0.0735]
Completeness to theta = 25.500°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.4319 and 0.3949
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	15305 / 0 / 567
Goodness-of-fit on F^2	1.114
Final R indices [I>2sigma(I) = 10683 data]	R1 = 0.0373, wR2 = 0.0667
R indices (all data, 0.73 Å)	R1 = 0.0738, wR2 = 0.0846
Extinction coefficient	n/a
Largest diff. peak and hole	0.614 and -0.651 e.$Å^{-3}$

Table S14. Bond lengths [Å] for ajr15 (3-Dy).

Dy(1)-O(1)	2.070(2)
Dy(1)-N(1)	2.282(3)
Dy(1)-N(2)	2.290(2)
Dy(1)-N(3)	2.296(3)
Dy(1)-Si(3)	3.3846(10)
Dy(1)-Si(6)	3.3882(9)
Dy(1)-Si(1)	3.4043(9)
K(1)-O(10)	2.776(2)
K(1)-O(7)	2.815(2)
K(1)-O(6)	2.834(2)
K(1)-O(3)	2.840(2)
K(1)-O(5)	2.845(2)
K(1)-O(2)	2.883(2)
K(1)-O(9)	2.894(2)

K(1)-O(4)	2.896(2)
K(1)-C(35)	3.388(3)
Si(1)-N(1)	1.714(3)
Si(1)-C(3)	1.871(4)
Si(1)-C(4)	1.881(3)
Si(1)-C(2)	1.884(4)
Si(2)-N(1)	1.707(3)
Si(2)-C(7)	1.878(4)
Si(2)-C(5)	1.885(4)
Si(2)-C(6)	1.886(4)
Si(3)-N(3)	1.719(3)
Si(3)-C(8)	1.873(3)
Si(3)-C(9)	1.883(4)
Si(3)-C(10)	1.885(3)
Si(4)-N(3)	1.707(3)
Si(4)-C(13)	1.871(4)
Si(4)-C(11)	1.882(3)
Si(4)-C(12)	1.884(3)
Si(5)-N(2)	1.704(3)
Si(5)-C(14)	1.877(3)
Si(5)-C(15)	1.884(4)
Si(5)-C(16)	1.886(4)
Si(6)-N(2)	1.720(3)
Si(6)-C(18)	1.871(4)
Si(6)-C(19)	1.878(3)
Si(6)-C(17)	1.884(4)
O(1)-C(1)	1.311(4)
O(2)-C(21)	1.418(4)
O(2)-C(22)	1.425(4)
O(3)-C(24)	1.422(4)
O(3)-C(23)	1.423(4)
O(4)-C(25)	1.417(4)
O(4)-C(26)	1.430(4)
O(5)-C(28)	1.411(4)
O(5)-C(27)	1.422(4)
O(6)-C(30)	1.423(4)

O(6)-C(29)	1.423(4)
O(7)-C(20)	1.419(4)
O(7)-C(31)	1.425(4)
O(8)-C(32)	1.420(3)
O(8)-C(33)	1.423(3)
O(9)-C(34)	1.428(3)
O(9)-C(35)	1.439(3)
O(10)-C(36)	1.425(3)
O(10)-C(37)	1.429(4)
C(1)-C(1)#1	1.183(6)
C(20)-C(21)	1.506(4)
C(22)-C(23)	1.499(5)
C(24)-C(25)	1.499(5)
C(26)-C(27)	1.491(5)
C(28)-C(29)	1.495(5)
C(30)-C(31)	1.494(5)
C(32)-C(37)#2	1.510(4)
C(33)-C(34)	1.502(4)
C(35)-C(36)	1.511(4)
C(37)-C(32)#2	1.510(4)
O(11)-C(44)#3	1.357(10)
O(11)-C(44)	1.357(10)
O(11)-C(45)#3	1.496(9)
O(11)-C(45)	1.496(9)
C(44)-C(46)	1.509(11)
C(45)-C(46)	1.422(10)

Table S15. Crystal data and structure refinement for ajr26 (3-Ho).

Identification code	ajr26
Empirical formula	C78 H190 Ho2 K2 N6 O21 Si12
Formula weight	2293.49
Temperature	133(2) K
Wavelength	0.71073 Å

Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 25.514(3) Å	□= 90°.
	b = 18.800(2) Å	□= 103.1674(15)°.
	c = 25.712(3) Å	□ = 90°.
Volume	12009(2) $Å^3$	
Z	4	
Density (calculated)	1.269 Mg/m^3	
Absorption coefficient	1.553 mm^{-1}	
F(000)	4832	
Crystal color	yellow	
Crystal size	0.347 x 0.202 x 0.132 mm^3	
Theta range for data collection	1.358 to 28.864°	
Index ranges	-33 <= h <= 33, -25 <= k <= 25, -34 <= l <= 32	
Reflections collected	61845	
Independent reflections	14710 [R(int) = 0.0318]	
Completeness to theta = 25.500°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4316 and 0.3733	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14710 / 0 / 559	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2sigma(I) = 12462 data]	R1 = 0.0251, wR2 = 0.0554	
R indices (all data, 0.73 Å)	R1 = 0.0345, wR2 = 0.0589	
Extinction coefficient	n/a	

Largest diff. peak and hole	0.631 and -0.377 e.Å^{-3}

Table S16. Bond lengths [Å] for ajr26 (3-Ho).

Ho(1)-O(1)	2.0598(14)
Ho(1)-N(1)	2.2716(15)
Ho(1)-N(2)	2.2780(16)
Ho(1)-N(3)	2.2802(16)
Ho(1)-Si(6)	3.3691(6)
Ho(1)-Si(3)	3.3723(7)
Ho(1)-Si(1)	3.3834(6)
Si(1)-N(1)	1.7140(18)
Si(1)-C(3)	1.873(2)
Si(1)-C(4)	1.874(2)
Si(1)-C(2)	1.887(2)
Si(2)-N(1)	1.7015(18)
Si(2)-C(7)	1.868(3)
Si(2)-C(6)	1.879(3)
Si(2)-C(5)	1.882(2)
Si(3)-N(3)	1.7161(18)
Si(3)-C(8)	1.872(2)
Si(3)-C(10)	1.878(2)
Si(3)-C(9)	1.879(2)
Si(4)-N(3)	1.7063(18)
Si(4)-C(13)	1.871(2)

Si(4)-C(11)	1.883(2)
Si(4)-C(12)	1.883(2)
Si(5)-N(2)	1.7059(17)
Si(5)-C(14)	1.873(2)
Si(5)-C(16)	1.878(2)
Si(5)-C(15)	1.884(2)
Si(6)-N(2)	1.7145(18)
Si(6)-C(18)	1.870(3)
Si(6)-C(19)	1.875(2)
Si(6)-C(17)	1.884(3)
O(1)-C(1)	1.301(2)
C(1)-C(1)#1	1.186(4)
K(1)-O(10)	2.7717(14)
K(1)-O(7)	2.8118(15)
K(1)-O(6)	2.8347(15)
K(1)-O(3)	2.8387(15)
K(1)-O(5)	2.8464(15)
K(1)-O(2)	2.8779(15)
K(1)-O(9)	2.8972(15)
K(1)-O(4)	2.8974(15)
K(1)-C(35)	3.394(2)
O(2)-C(21)	1.415(2)
O(2)-C(22)	1.420(3)
O(3)-C(24)	1.417(3)
O(3)-C(23)	1.422(3)

O(4)-C(25)	1.419(3)
O(4)-C(26)	1.422(3)
O(5)-C(28)	1.406(3)
O(5)-C(27)	1.416(3)
O(6)-C(29)	1.416(3)
O(6)-C(30)	1.419(3)
O(7)-C(20)	1.418(2)
O(7)-C(31)	1.420(2)
O(8)-C(32)	1.420(2)
O(8)-C(33)	1.426(2)
O(9)-C(34)	1.424(2)
O(9)-C(35)	1.432(2)
O(10)-C(36)	1.423(2)
O(10)-C(37)	1.428(2)
C(20)-C(21)	1.498(3)
C(22)-C(23)	1.498(3)
C(24)-C(25)	1.498(3)
C(26)-C(27)	1.495(4)
C(28)-C(29)	1.501(4)
C(30)-C(31)	1.501(3)
C(32)-C(37)#2	1.504(3)
C(33)-C(34)	1.504(3)
C(35)-C(36)	1.503(3)
C(37)-C(32)#2	1.504(3)
O-C(44)#3	1.355(6)

O-C(44)	1.355(6)
O-C(45)#3	1.496(6)
O-C(45)	1.496(6)
C(44)-C(46)	1.514(7)
C(45)-C(46)	1.421(7)

Table S17. Crystal data and structure refinement for ajr41 (3-Tm).

Identification code	ajr41	
Empirical formula	C78 H190 K2 N6 O21 Si12 Tm2	
Formula weight	2301.49	
Temperature	88(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 25.453(3) Å	□= 90°.
	b = 18.757(2) Å	□= 103.1418(15)°.
	c = 25.744(3) Å	□ = 90°.
Volume	11969(2) $Å^3$	
Z	4	
Density (calculated)	1.277 Mg/m^3	
Absorption coefficient	1.719 mm^{-1}	
F(000)	4848	
Crystal color	colourless	
Crystal size	0.214 x 0.200 x 0.196 mm^3	
Theta range for data collection	1.361 to 29.125°	

Index ranges	-34 <= h <= 34, -24 <= k <= 24, -33 <= l <= 34
Reflections collected	73762
Independent reflections	15214 [R(int) = 0.0304]
Completeness to theta = 25.500°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7458 and 0.6513
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	15214 / 0 / 559
Goodness-of-fit on F^2	1.011
Final R indices [I>2sigma(I) = 12794 data]	R1 = 0.0244, wR2 = 0.0509
R indices (all data, 0.73 Å)	R1 = 0.0349, wR2 = 0.0554
Extinction coefficient	n/a
Largest diff. peak and hole	0.652 and -1.122 e.Å^{-3}

Table S18. Bond lengths [Å] ajr41 (3-Tm).

Tm(1)-O(1)	2.0428(14)
Tm(1)-N(1)	2.2465(17)
Tm(1)-N(2)	2.2533(16)
Tm(1)-N(3)	2.2548(16)
Tm(1)-Si(3)	3.3487(7)
Tm(1)-Si(6)	3.3502(6)
Tm(1)-Si(1)	3.3632(7)
K(1)-O(10)	2.7714(13)
K(1)-O(7)	2.8168(14)

K(1)-O(6)	2.8296(15)
K(1)-O(3)	2.8375(15)
K(1)-O(5)	2.8441(15)
K(1)-O(2)	2.8833(14)
K(1)-O(9)	2.8911(14)
K(1)-O(4)	2.8979(15)
K(1)-C(35)	3.388(2)
Si(1)-N(1)	1.717(2)
Si(1)-C(3)	1.876(3)
Si(1)-C(4)	1.879(2)
Si(1)-C(2)	1.891(2)
Si(2)-N(1)	1.705(2)
Si(2)-C(7)	1.871(3)
Si(2)-C(5)	1.879(2)
Si(2)-C(6)	1.885(2)
Si(3)-N(3)	1.721(2)
Si(3)-C(8)	1.875(2)
Si(3)-C(9)	1.881(2)
Si(3)-C(10)	1.883(2)
Si(4)-N(3)	1.7092(18)
Si(4)-C(13)	1.873(2)
Si(4)-C(11)	1.885(2)
Si(4)-C(12)	1.886(2)
Si(5)-N(2)	1.7069(17)
Si(5)-C(14)	1.877(2)

Si(5)-C(16)	1.882(2)
Si(5)-C(15)	1.887(2)
Si(6)-N(2)	1.7203(17)
Si(6)-C(18)	1.874(3)
Si(6)-C(19)	1.879(2)
Si(6)-C(17)	1.882(2)
O(1)-C(1)	1.303(2)
O(2)-C(21)	1.421(2)
O(2)-C(22)	1.422(2)
O(3)-C(23)	1.425(3)
O(3)-C(24)	1.428(3)
O(4)-C(25)	1.417(3)
O(4)-C(26)	1.427(3)
O(5)-C(28)	1.414(3)
O(5)-C(27)	1.426(3)
O(6)-C(30)	1.424(3)
O(6)-C(29)	1.428(3)
O(7)-C(20)	1.422(2)
O(7)-C(31)	1.425(2)
O(8)-C(32)	1.423(2)
O(8)-C(33)	1.424(2)
O(9)-C(34)	1.425(2)
O(9)-C(35)	1.435(2)
O(10)-C(36)	1.426(2)
O(10)-C(37)	1.428(2)

C(1)-C(1)#1	1.184(4)
C(20)-C(21)	1.498(3)
C(22)-C(23)	1.499(3)
C(24)-C(25)	1.494(3)
C(26)-C(27)	1.494(4)
C(28)-C(29)	1.489(4)
C(30)-C(31)	1.502(3)
C(32)-C(37)#2	1.511(3)
C(33)-C(34)	1.504(3)
C(35)-C(36)	1.505(3)
C(37)-C(32)#2	1.511(3)
O(11)-C(44)#3	1.359(6)
O(11)-C(44)	1.359(6)
O(11)-C(45)	1.523(6)
O(11)-C(45)#3	1.523(6)
C(44)-C(46)	1.520(7)
C(45)-C(46)	1.396(7)

Table S19. Crystal data and structure refinement for ajr32 (4-Gd).

Identification code	ajr32	
Empirical formula	C52 H124 Gd2 K2 N4 O16 Si8	
Formula weight	1678.96	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.6614(13) Å	□= 94.4758(13)°.
	b = 15.5498(15) Å	□= 94.0831(13)°.
	c = 21.205(2) Å	□ = 105.7458(12)°.

Volume	3987.4(7) $Å^3$
Z	2
Density (calculated)	1.398 Mg/m^3
Absorption coefficient	1.929 mm^{-1}
F(000)	1740
Crystal color	colorless
Crystal size	0.241 x 0.127 x 0.119 mm^3
Theta range for data collection	0.968 to 28.896°
Index ranges	-16 <= h <= 17, -20 <= k <= 21, -27 <= l <= 28
Reflections collected	48467
Independent reflections	19003 [R(int) = 0.0368]
Completeness to theta = 25.500°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.4316 and 0.3793
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	19003 / 0 / 769
Goodness-of-fit on F^2	0.989
Final R indices [I>2sigma(I) = 14746 data]	R1 = 0.0332, wR2 = 0.0614
R indices (all data, 0.73 Å)	R1 = 0.0538, wR2 = 0.0672
Extinction coefficient	n/a
Largest diff. peak and hole	1.126 and -0.482 $e.Å^{-3}$

Table S20. Bond lengths [Å] for ajr32 (4-Gd).

Gd(1)-O(1)	2.2667(19)
Gd(1)-O(2)#1	2.2791(19)
Gd(1)-N(2)	2.322(2)
Gd(1)-N(1)	2.354(2)
Gd(1)-O(2)	2.3694(19)
Gd(1)-C(1)	2.929(3)
Gd(1)-C(2)	2.999(3)
Gd(1)-Si(4)	3.4382(9)
Gd(1)-Gd(1)#1	3.8719(4)
K(1)-O(1)	2.745(2)
K(1)-O(8)	2.803(2)

K(1)-O(5)	2.865(2)
K(1)-O(11)	2.895(8)
K(1)-O(10)	2.904(3)
K(1)-O(6)	2.910(2)
K(1)-O(7)	2.957(2)
K(1)-O(9)	3.011(8)
K(1)-O(12)	3.028(4)
K(1)-C(1)	3.271(3)
K(1)-C(10)	3.467(3)
K(1)-C(34)	3.479(7)
Si(1)-N(1)	1.709(3)
Si(1)-C(5)	1.871(3)
Si(1)-C(7)	1.874(3)
Si(1)-C(6)	1.882(3)
Si(2)-N(1)	1.705(3)
Si(2)-C(10)	1.872(3)
Si(2)-C(8)	1.881(3)
Si(2)-C(9)	1.882(3)
Si(3)-N(2)	1.706(3)
Si(3)-C(11)	1.876(3)
Si(3)-C(12)	1.877(3)
Si(3)-C(13)	1.877(3)
Si(4)-N(2)	1.705(3)
Si(4)-C(16)	1.879(3)
Si(4)-C(14)	1.882(3)
Si(4)-C(15)	1.884(3)
O(1)-C(1)	1.354(3)
O(2)-C(2)	1.367(3)
O(2)-Gd(1)#1	2.2791(19)
O(5)-C(29)	1.419(4)
O(5)-C(47)	1.440(6)
O(5)-C(48)	1.473(13)
O(6)-C(30)	1.419(3)
O(6)-C(31)	1.425(4)
O(7)-C(33)	1.373(12)
O(7)-C(32)	1.417(4)

O(7)-C(34)	1.459(6)
O(8)-C(36)	1.294(6)
O(8)-C(37)	1.314(10)
O(8)-C(38)	1.495(5)
O(8)-C(35)	1.738(11)
O(9)-C(39)	1.376(13)
O(9)-C(41)	1.430(14)
O(10)-C(40)	1.425(6)
O(10)-C(42)	1.427(6)
O(11)-C(45)	1.418(14)
O(11)-C(43)	1.421(13)
O(12)-C(46)	1.419(6)
O(12)-C(44)	1.424(6)
C(1)-C(2)	1.334(4)
C(29)-C(30)	1.486(5)
C(31)-C(32)	1.485(4)
C(33)-C(35)	1.486(16)
C(34)-C(36)	1.489(8)
C(37)-C(39)	1.468(15)
C(38)-C(40)	1.495(7)
C(41)-C(43)	1.450(16)
C(42)-C(44)	1.489(7)
C(45)-C(48)	1.479(17)
C(46)-C(47)	1.488(8)
Gd(2)-O(3)	2.2598(19)
Gd(2)-O(4)#2	2.2795(19)
Gd(2)-N(4)	2.329(2)
Gd(2)-N(3)	2.356(2)
Gd(2)-O(4)	2.3738(19)
Gd(2)-C(3)	2.985(3)
Gd(2)-C(4)	3.050(3)
Gd(2)-Si(6)	3.4316(9)
Gd(2)-Gd(2)#2	3.8758(4)
K(2)-O(3)	2.778(2)
K(2)-O(18)	2.794(3)
K(2)-O(16)	2.870(2)

K(2)-O(13)	2.885(2)
K(2)-O(19)	2.888(2)
K(2)-O(14)	2.958(2)
K(2)-O(15)	2.962(2)
K(2)-O(17)	3.083(7)
K(2)-C(3)	3.282(3)
K(2)-C(61)	3.507(11)
Si(5)-N(3)	1.711(2)
Si(5)-C(19)	1.864(3)
Si(5)-C(17)	1.879(3)
Si(5)-C(18)	1.881(3)
Si(6)-N(3)	1.710(2)
Si(6)-C(22)	1.876(3)
Si(6)-C(20)	1.878(3)
Si(6)-C(21)	1.883(3)
Si(7)-N(4)	1.700(2)
Si(7)-C(24)	1.871(3)
Si(7)-C(23)	1.879(3)
Si(7)-C(25)	1.882(3)
Si(8)-N(4)	1.717(2)
Si(8)-C(28)	1.866(3)
Si(8)-C(27)	1.879(3)
Si(8)-C(26)	1.893(3)
O(3)-C(3)	1.351(3)
O(4)-C(4)	1.378(3)
O(4)-Gd(2)#2	2.2794(19)
O(13)-C(57)	1.421(3)
O(13)-C(56)	1.427(4)
O(14)-C(55)	1.416(4)
O(14)-C(54)	1.425(3)
O(15)-C(52)	1.425(3)
O(15)-C(53)	1.427(3)
O(16)-C(51)	1.422(3)
O(16)-C(50)	1.426(3)
O(17)-C(61)	1.410(12)
O(17)-C(49)	1.452(8)

O(18)-C(60)	1.412(5)
O(18)-C(49)	1.451(4)
O(19)-C(58)	1.411(4)
O(19)-C(59)	1.432(4)
C(3)-C(4)	1.331(4)
C(49)-C(50)	1.501(4)
C(51)-C(52)	1.493(4)
C(53)-C(54)	1.496(4)
C(55)-C(56)	1.509(4)
C(57)-C(58)	1.481(4)
C(59)-C(60)	1.497(5)
C(59)-C(61)	1.614(11)

Table S21. Crystal data and structure refinement for ajr46 (1-Gd).

Identification code	ajr46	
Empirical formula	C36 H90 Gd K N5 O6 Si6	
Formula weight	1053.99	
Temperature	88(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	R32	
Unit cell dimensions	a = 18.564(3) Å	□= 90°.
	b = 18.564(3) Å	□= 90°.
	c = 18.050(3) Å	□ = 120°.
Volume	5387(2) $Å^3$	
Z	3	
Density (calculated)	0.975 Mg/m^3	
Absorption coefficient	1.112 mm^{-1}	

F(000)	1668
Crystal color	Blue
Crystal size	0.283 x 0.106 x 0.103 mm^3
Theta range for data collection	1.696 to 26.389°
Index ranges	-23 <= h <= 23, -23 <= k <= 23, -22 <= l <= 22
Reflections collected	13308
Independent reflections	2478 [R(int) = 0.0525]
Completeness to theta = 25.500°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7454 and 0.6134
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2478 / 0 / 88
Goodness-of-fit on F^2	1.005
Final R indices [I>2sigma(I) = 2264 data]	R1 = 0.0235, wR2 = 0.0411
R indices (all data, 0.8 Å)	R1 = 0.0304, wR2 = 0.0426
Absolute structure parameter	-0.026(6)
Extinction coefficient	n/a
Largest diff. peak and hole	0.372 and -0.271 e.$Å^{-3}$

Table S22. Bond lengths [Å] and angles [°] for ajr46 (1-Gd).

Gd(1)-N(1)	2.315(3)
Gd(1)-N(1)#1	2.316(3)
Gd(1)-N(1)#2	2.316(3)
Si(1)-N(1)	1.7059(18)
Si(1)-C(2)	1.875(3)

Si(1)-C(1)	1.880(3)
Si(1)-C(3)	1.886(3)
N(1)-Si(1)#3	1.7059(18)
K(1)-O(1)#4	2.841(2)
K(1)-O(1)#5	2.841(2)
K(1)-O(1)#6	2.841(2)
K(1)-O(1)#7	2.841(2)
K(1)-O(1)	2.841(2)
K(1)-O(1)#8	2.841(2)
K(1)-N(2)#5	2.983(4)
K(1)-N(2)	2.983(4)
O(1)-C(6)	1.429(4)
O(1)-C(5)	1.433(4)
N(2)-C(4)#6	1.475(3)
N(2)-C(4)	1.475(3)
N(2)-C(4)#8	1.475(3)
C(4)-C(5)	1.494(5)
C(6)-C(6)#5	1.481(7)
N(1)-Gd(1)-N(1)#1	120.0
N(1)-Gd(1)-N(1)#2	120.000(1)
N(1)#1-Gd(1)-N(1)#2	120.0
N(1)-Si(1)-C(2)	113.49(12)
N(1)-Si(1)-C(1)	110.92(15)
C(2)-Si(1)-C(1)	106.80(15)
N(1)-Si(1)-C(3)	113.64(13)

C(2)-Si(1)-C(3)	106.05(16)
C(1)-Si(1)-C(3)	105.35(17)
Si(1)-N(1)-Si(1)#3	123.5(2)
Si(1)-N(1)-Gd(1)	118.23(10)
Si(1)#3-N(1)-Gd(1)	118.23(10)
O(1)#4-K(1)-O(1)#5	98.09(6)
O(1)#4-K(1)-O(1)#6	119.23(9)
O(1)#5-K(1)-O(1)#6	137.51(9)
O(1)#4-K(1)-O(1)#7	98.09(6)
O(1)#5-K(1)-O(1)#7	98.09(6)
O(1)#6-K(1)-O(1)#7	59.51(9)
O(1)#4-K(1)-O(1)	137.51(9)
O(1)#5-K(1)-O(1)	59.52(9)
O(1)#6-K(1)-O(1)	98.09(6)
O(1)#7-K(1)-O(1)	119.23(9)
O(1)#4-K(1)-O(1)#8	59.52(9)
O(1)#5-K(1)-O(1)#8	119.24(9)
O(1)#6-K(1)-O(1)#8	98.09(6)
O(1)#7-K(1)-O(1)#8	137.51(9)
O(1)-K(1)-O(1)#8	98.09(6)
O(1)#4-K(1)-N(2)#5	60.70(4)
O(1)#5-K(1)-N(2)#5	60.70(4)
O(1)#6-K(1)-N(2)#5	119.30(4)
O(1)#7-K(1)-N(2)#5	60.70(4)
O(1)-K(1)-N(2)#5	119.30(4)

O(1)#8-K(1)-N(2)#5	119.30(4)
O(1)#4-K(1)-N(2)	119.30(4)
O(1)#5-K(1)-N(2)	119.30(4)
O(1)#6-K(1)-N(2)	60.70(4)
O(1)#7-K(1)-N(2)	119.30(4)
O(1)-K(1)-N(2)	60.70(4)
O(1)#8-K(1)-N(2)	60.70(4)
N(2)#5-K(1)-N(2)	180.0
C(6)-O(1)-C(5)	111.5(2)
C(6)-O(1)-K(1)	115.51(18)
C(5)-O(1)-K(1)	117.35(17)
C(4)#6-N(2)-C(4)	109.62(18)
C(4)#6-N(2)-C(4)#8	109.62(18)
C(4)-N(2)-C(4)#8	109.62(18)
C(4)#6-N(2)-K(1)	109.32(18)
C(4)-N(2)-K(1)	109.32(18)
C(4)#8-N(2)-K(1)	109.32(18)
N(2)-C(4)-C(5)	114.5(3)
O(1)-C(5)-C(4)	109.4(3)
O(1)-C(6)-C(6)#5	109.7(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+y,-x,z #2 -y,x-y,z #3 x-y,-y,-z+1 #4 x-y+1/3,-y+2/3,-z+2/3

#5 y+1/3,x-1/3,-z+2/3 #6 -y+1,x-y,z #7 -x+4/3,-x+y+2/3,-z+2/3

#8 -x+y+1,-x+1,z

UV-Visible spectra

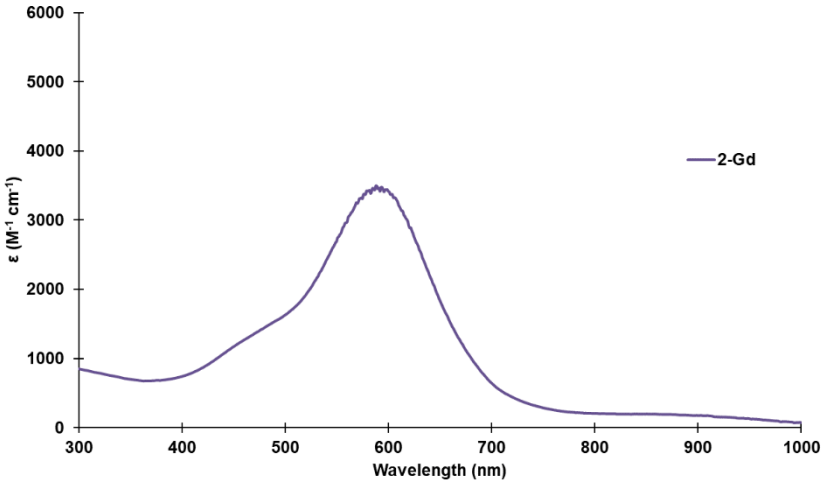


Figure S11. UV-visible spectrum of 2-Gd in Et_2O

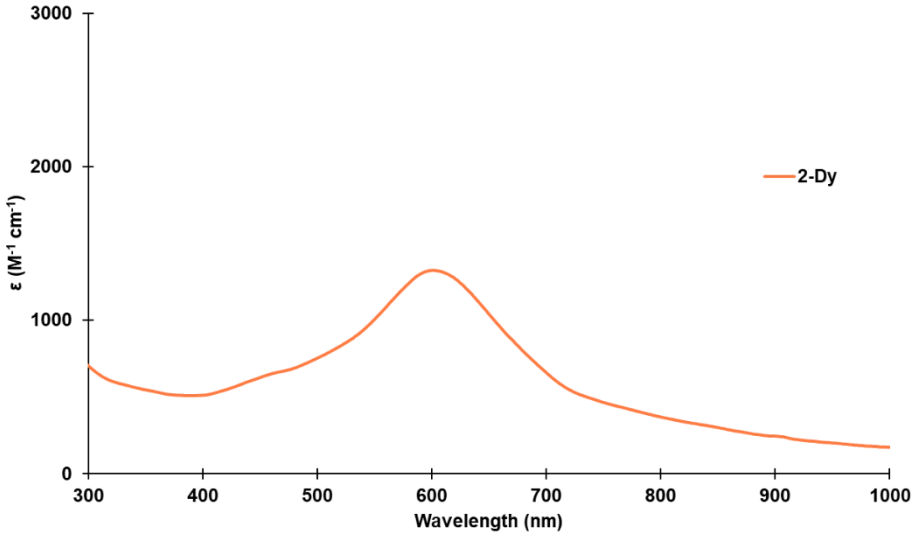


Figure S12. UV-visible spectrum of 2-Dy in Et_2O

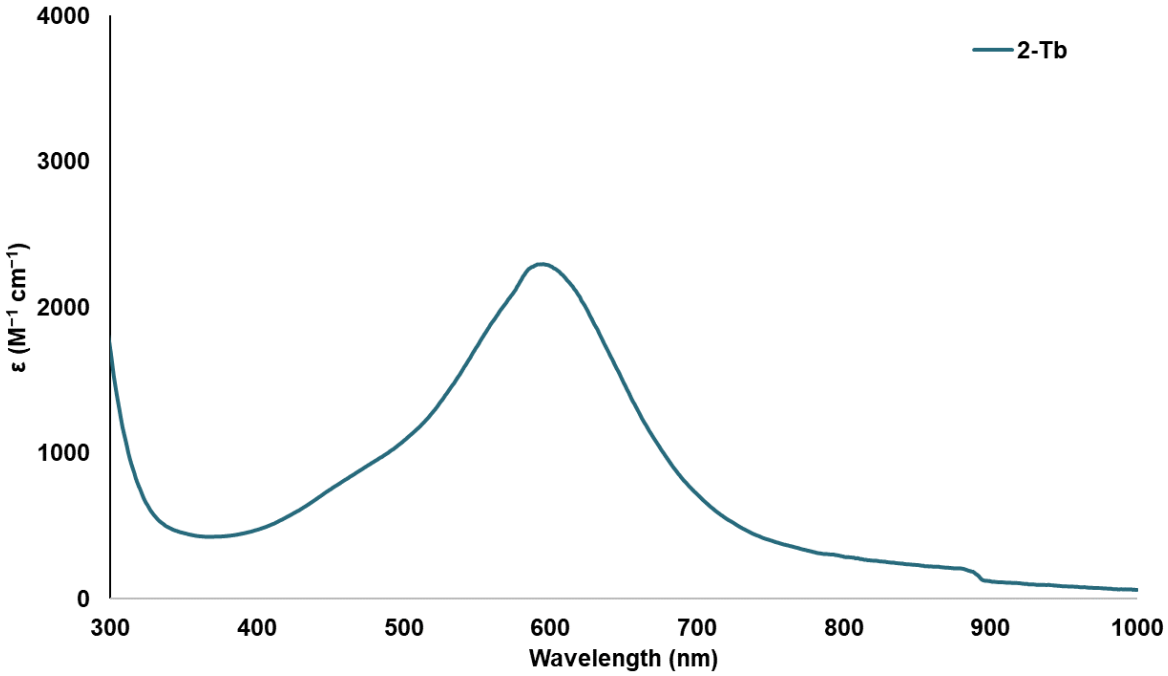


Figure S13. UV-visible spectrum of 2-Tb in Et_2O

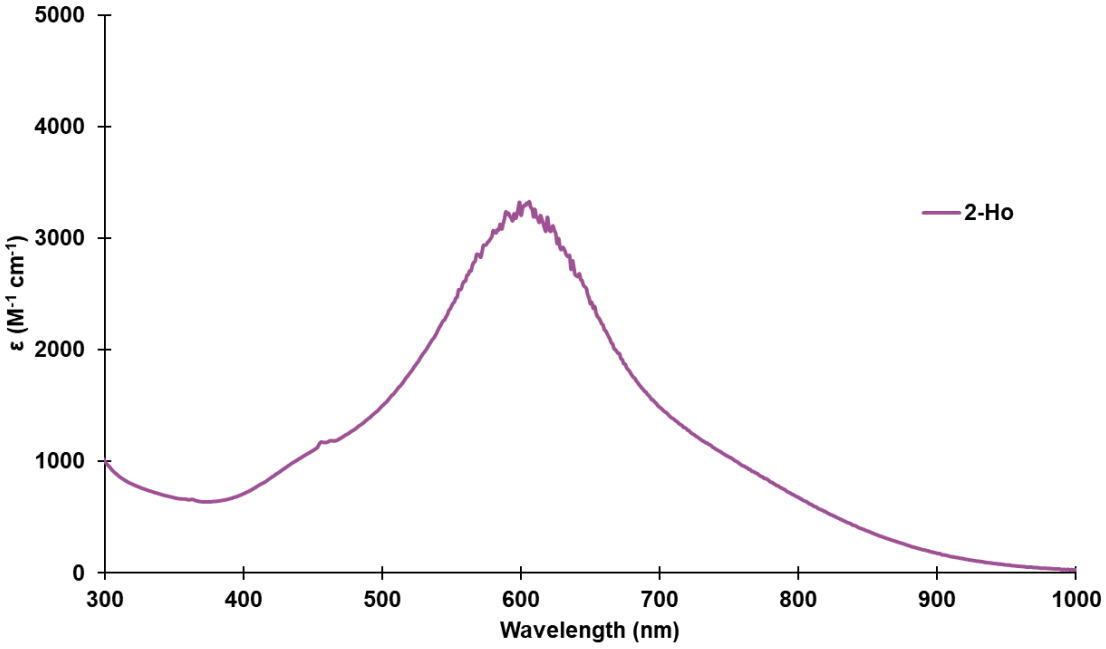


Figure S14. UV-visible spectrum of 2-Ho in Et_2O

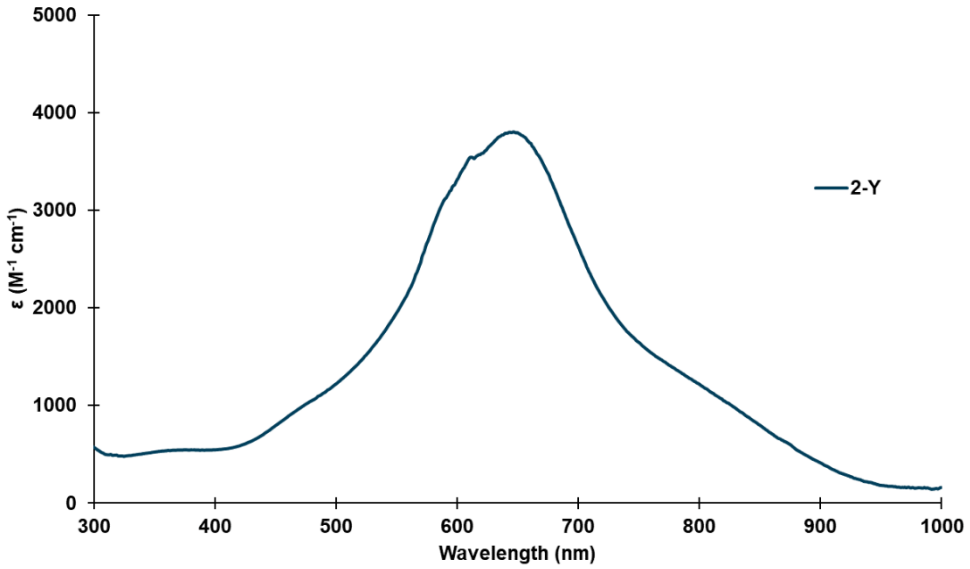


Figure S15. UV-visible spectrum of 2-Y in Et_2O

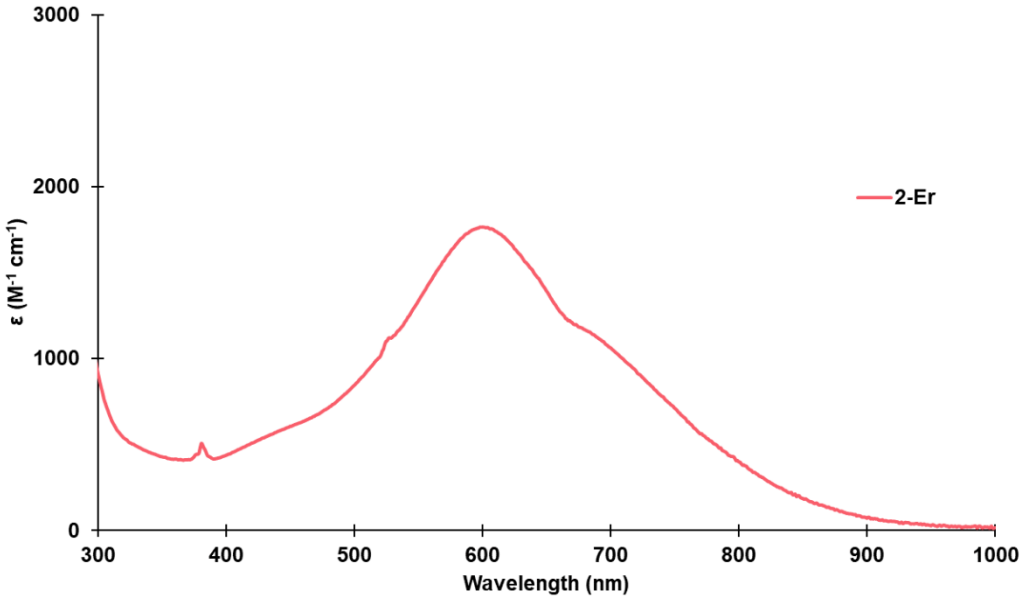


Figure S16. UV-visible spectrum of 2-Er in Et_2O

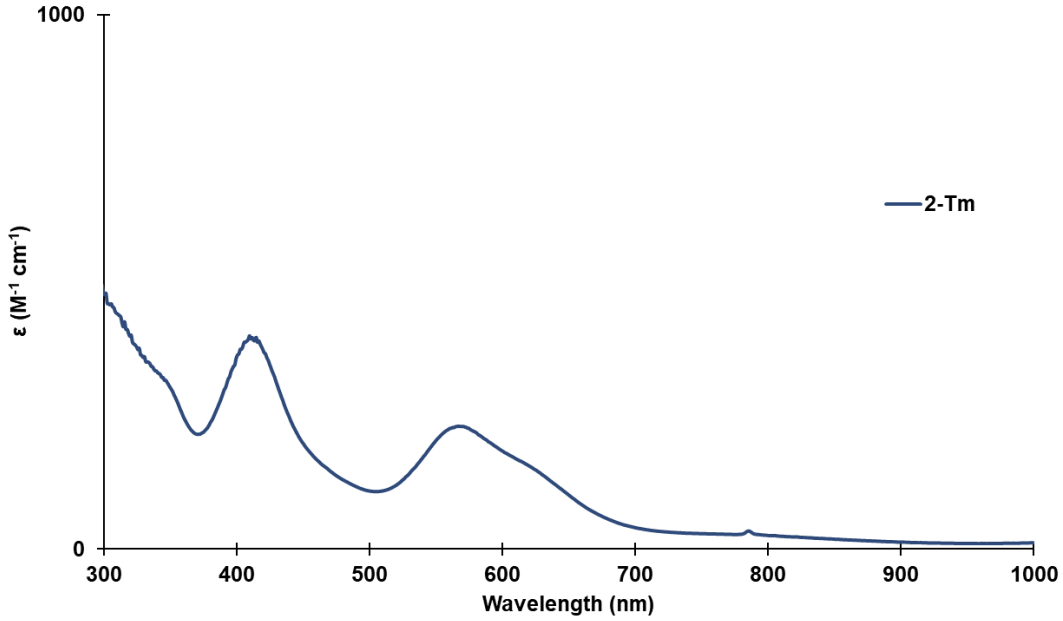


Figure S17. UV-visible spectrum of 2-Tm in Et_2O

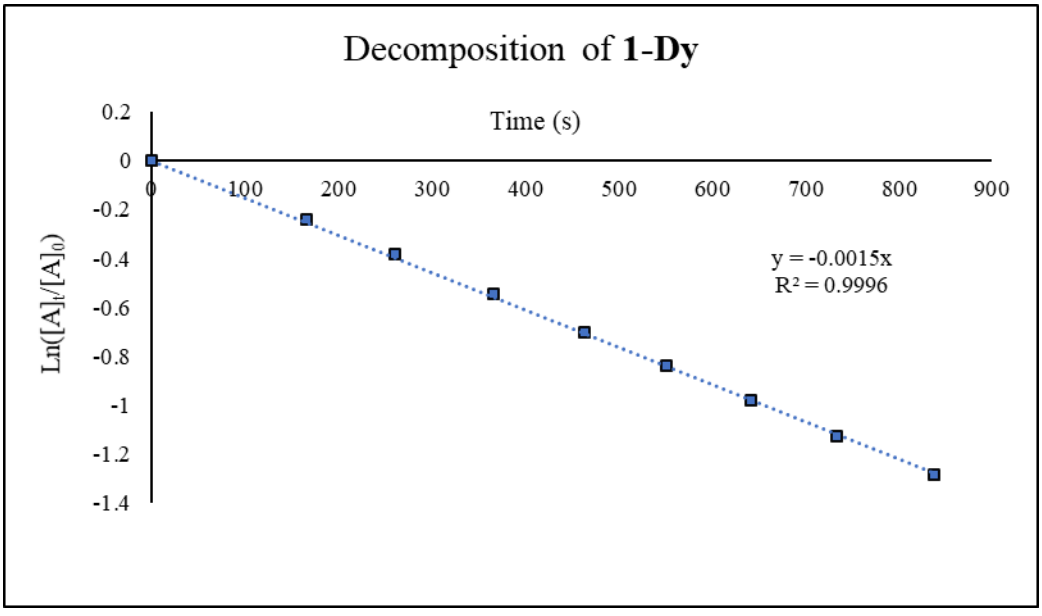


Figure S18. Decomposition of 1-Dy 3mM in THF

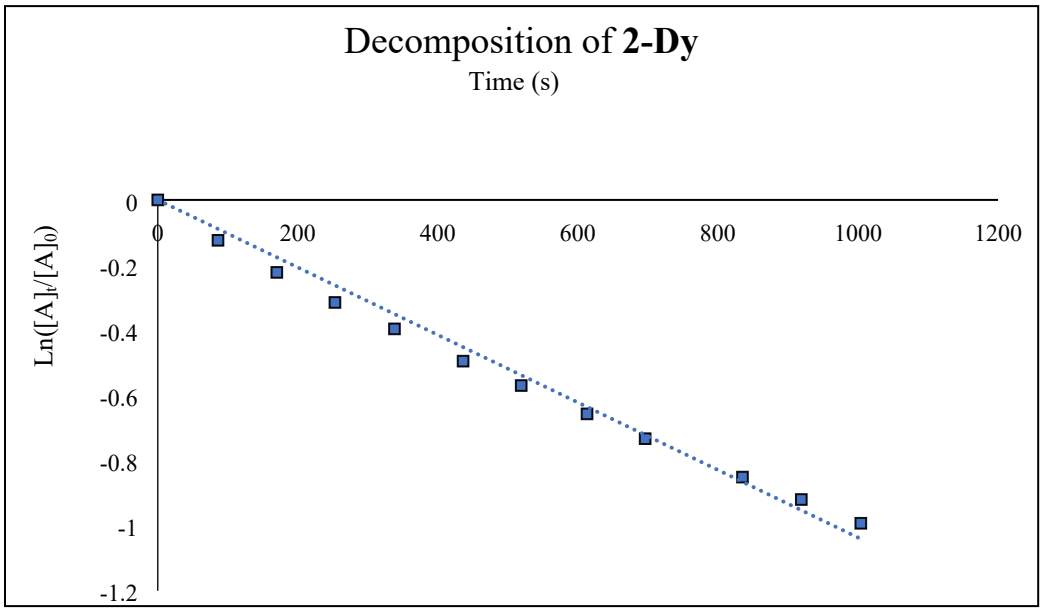


Figure S19. Decomposition of 2-Dy 3mM in Et_2O

H-Tube Schematic

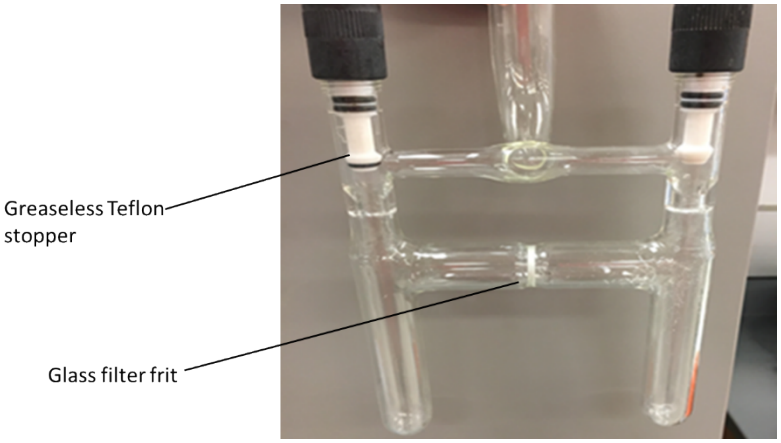


Figure S20. Schematic of H tube used in reactions to form **3-Ln** and **4-Ln**