Supporting Information for

Tetraanionic Biphenyl Lanthanide Complexes as Single-Molecule Magnets

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1. X-ray crystallography data

(NN^{TBS})DyI(THF)$_2$

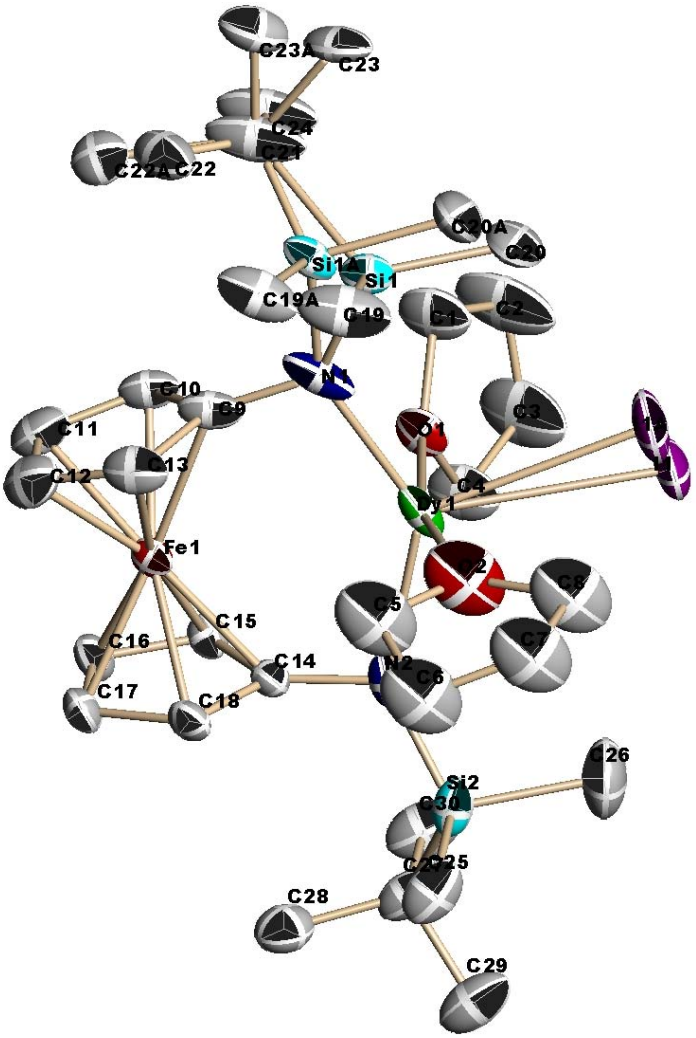

Figure S1. Thermal-ellipsoid (50% probability) representation of **(NN^{TBS})DyI(THF)$_2$**. Hydrogen atoms were omitted for clarity.

Single crystals suitable for X-ray diffraction were grown from a diethyl ether solution layered with *n*-pentane. One of the silyl groups and the iodide are disordered; this disorder was modeled over two sets of positions (see figure above). A total of 24706 reflections ($-15 \le h \le 15$, $-16 \le k \le 16$, $-22 \le l \le 22$) were collected at $T = 100(2)$ K with $2\theta_{max} = 61.24°$, of which 10016 were unique. The residual peak and hole electron densities were 3.17 and -5.22 eA^{-3}. The least-squares refinement converged normally with residuals of $R_1 = 0.0530$ and GOF = 1.078. Crystal and refinement data for **(NN^{TBS})DyI(THF)$_2$**: formula $C_{30}H_{54}N_2Si_2FeO_2DyI$, space group *P*-1, $a = 11.098(5)$, $b = 11.619(5)$, $c = 16.156(10)$, $\alpha = 101.744(7)$, $\beta = 91.826(6)$, $\gamma = 118.257(4)°$, $V = 1776.6(15)$ Å^3, $Z = 2$, $\mu = 3.459$ mm^{-1}, $F(000) = 874$, $R_1 = 0.0684$ and $wR_2 = 0.1296$ (based on all data, $I > 2\sigma(I)$).

[(NN^{TBS})Dy(THF)]$_2$(μ-biphenyl)[K(toluene)]$_2$ (Dy$_2$-biph)

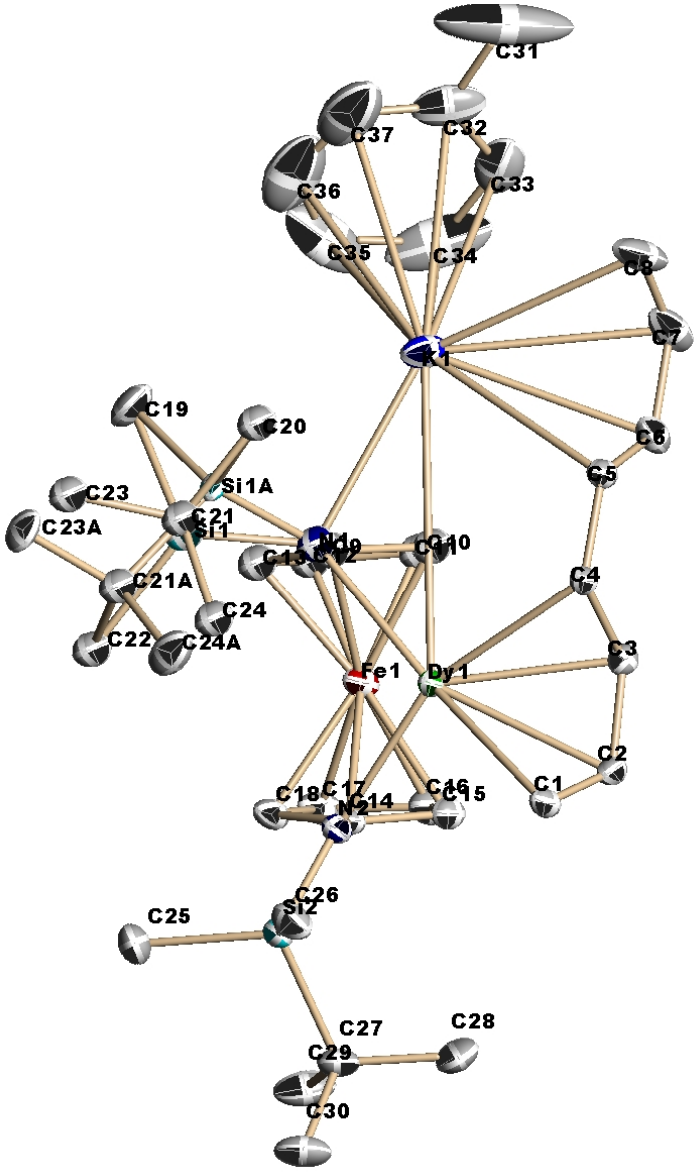

Figure S2. Thermal-ellipsoid (50% probability) representation of the crystallographically independent atoms in **Dy$_2$-biph**. Hydrogen and solvent atoms were omitted for clarity.

Single crystals suitable for X-ray diffraction were grown from a concentrated toluene solution layered with hexanes. One of the silyl groups is disordered; this disorder was modeled over two sets of positions (see figure above). A total of 58311 reflections ($-20 \le h \le 20$, $-30 \le k \le 29$, $-38 \le l \le 37$) were collected at T = 100(2) K with $2\theta_{max}$ = 61.70°, of which 12199 were unique. The residual peak and hole electron densities were 2.05 and -3.63 eA^{-3}. The least-squares refinement converged normally with residuals of R_1 = 0.0357 and GOF = 1.033. Crystal and refinement data for **Dy$_2$-biph**: formula $C_{56}H_{86}N_4Si_4Fe_2K_2Dy_2 \cdot 4(C_7H_8)$, space group $C2/c$, a = 14.320(3), b = 21.816(5), c = 26.408(6), β = 95.561(3)°, V = 8211(3) Å^3, Z = 4, μ = 2.350 mm^{-1}, F(000) = 3712, R_1 = 0.0437 and wR_2 = 0.0843 (based on all data, I > 2$\sigma(I)$).

[(NN^{TBS})Dy(THF)]$_2$(μ-bipheyl)[K(18-crown-6)(THF)$_{1.5}$]$_2$ (Dy$_2$-biph-crown$_2$)

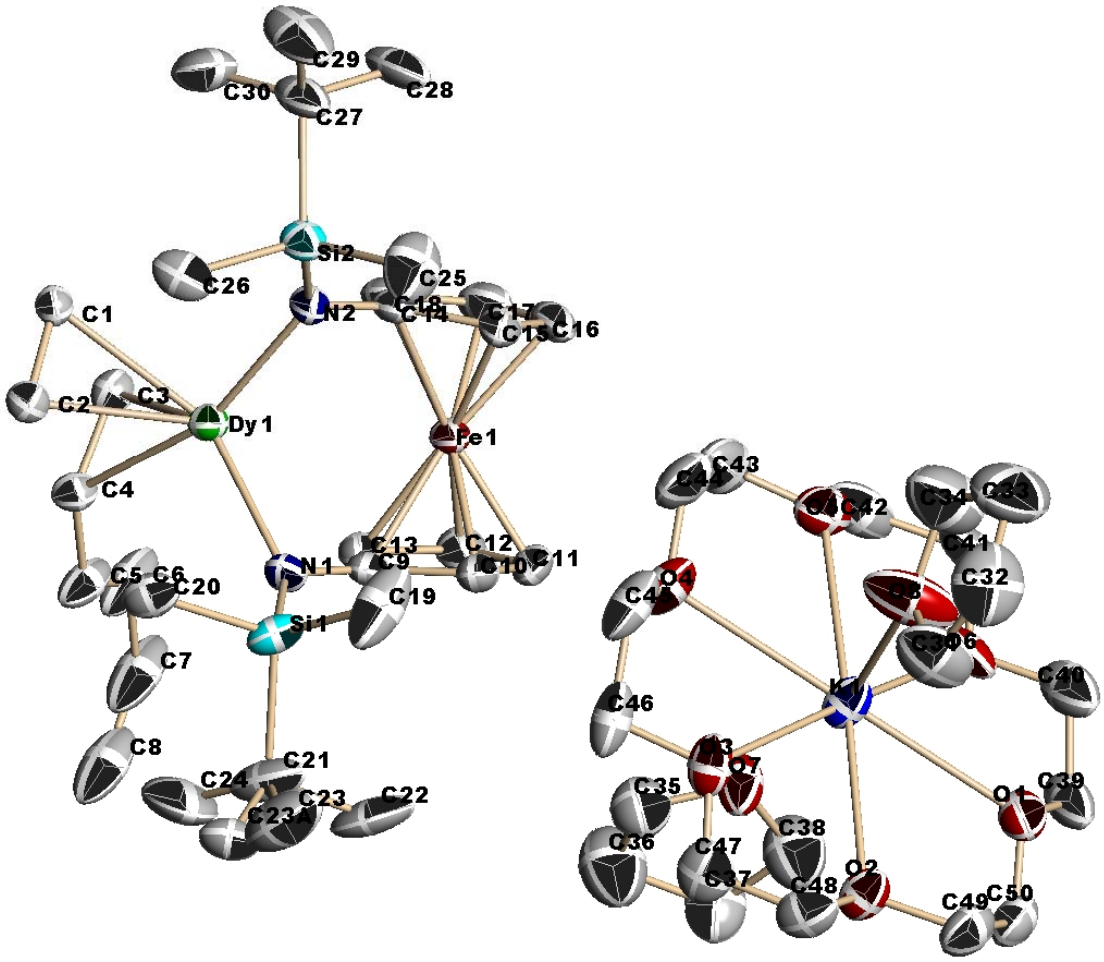

Figure S3. Thermal-ellipsoid (50% probability) representation of the crystallographically independent atoms in **Dy$_2$-biph-crown$_2$**. Hydrogen atoms were omitted for clarity.

Single crystals suitable for X-ray diffraction were grown from a THF solution layered with *n*-pentane. The unit cell contains large accessible voids; solvent molecules could not be modeled to fit this space (it is possible that some solvent was lost during crystal handling) and the program SQUEEZE was used. One of the *t*-butyl groups is disordered; this disorder was modeled over two sets of positions (see figure above). A total of 79111 reflections ($-24 \le h \le 24$, $-31 \le k \le 31$, $-49 \le l \le 46$) were collected at T = 100(2) K with $2\theta_{max}$ = 61.50°, of which 20024 were unique. The residual peak and hole electron densities were 0.67 and -0.90 eA^{-3}. The least-squares refinement converged normally with residuals of R_1 = 0.0376 and GOF = 0.997. Crystal and refinement data for **Dy$_2$-biph-crown$_2$**: formula $C_{92}H_{158}N_4Si_4Fe_2O_{15}Dy_2K_2$, space group $C222_1$, a = 17.237(6), b = 22.611(8), c = 34.538(13), V = 13461(9) Å^3, Z = 4, μ = 1.451 mm^{-1}, F(000) = 4544, R_1 = 0.0417 and wR_2 = 0.0937 (based on all data, $I > 2\sigma(I)$).

[(NN^{TBS})Gd(THF)]$_2$(μ-biphenyl)[K(toluene)]$_2$ (Gd$_2$-biph)

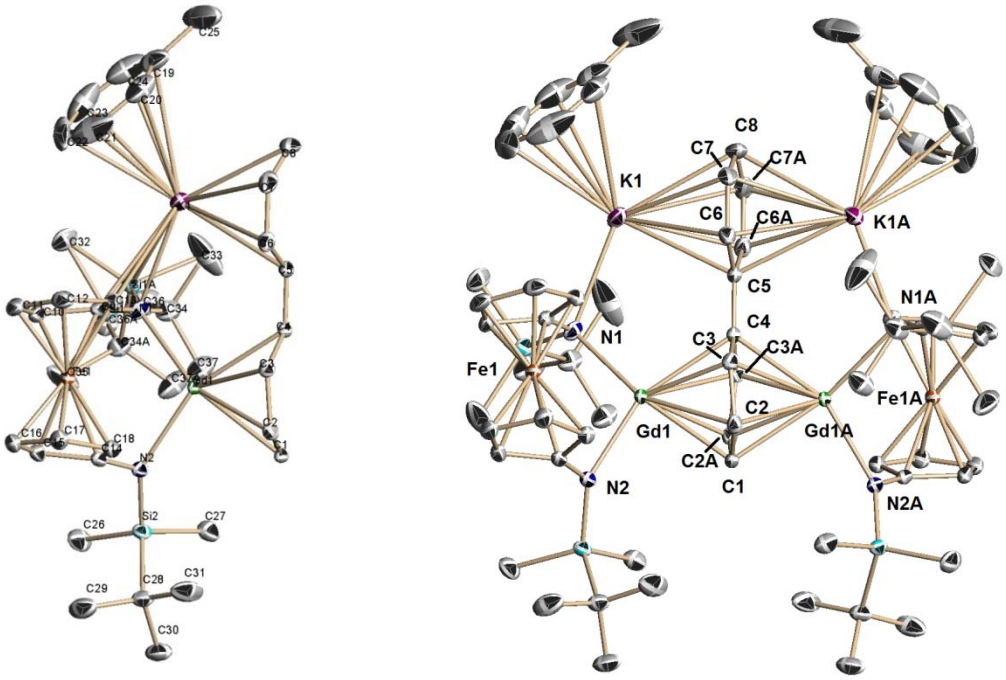

Figure S4. Thermal-ellipsoid (50% probability) representation of the crystallographically independent atoms in **Gd$_2$-biph** (left) and the full molecule (right). Hydrogen and solvent atoms and disordered counterparts were omitted for clarity.

Single crystals suitable for X-ray diffraction were grown from a toluene solution layered with hexanes. One of the silyl groups is disordered; this disorder was modeled over two sets of positions. A total of 58108 reflections ($-20 \le h \le 19$, $-31 \le k \le 31$, $-37 \le l \le 37$) were collected at T = 100(2) K with $2\theta_{max}$ = 61.63°, of which 12214 were unique. The residual peak and hole electron densities were 1.88 and -1.54 eA^{-3}. The least-squares refinement converged normally with residuals of R_1 = 0.0252 and GOF = 1.037. Crystal and refinement data for **Gd$_2$-biph**: formula $C_{56}H_{86}N_4Si_4Fe_2K_2Gd_2 \cdot 4(C_7H_8)$, space group $C2/c$, a = 14.349(4), b = 21.880(6), c = 26.449(8), β = 95.136(3)°, V = 8270(4) Å^3, Z = 4, μ = 2.130 mm^{-1}, F(000) = 3696, R_1 = 0.0300 and wR_2 = 0.0633 (based on all data, I > 2$\sigma(I)$).

[(NN^{TBS})Gd(THF)]$_2$(μ-biphenyl)[K(18-crown-6)(THF)$_{1.5}$]$_2$ (Gd$_2$-biph-crown$_2$)

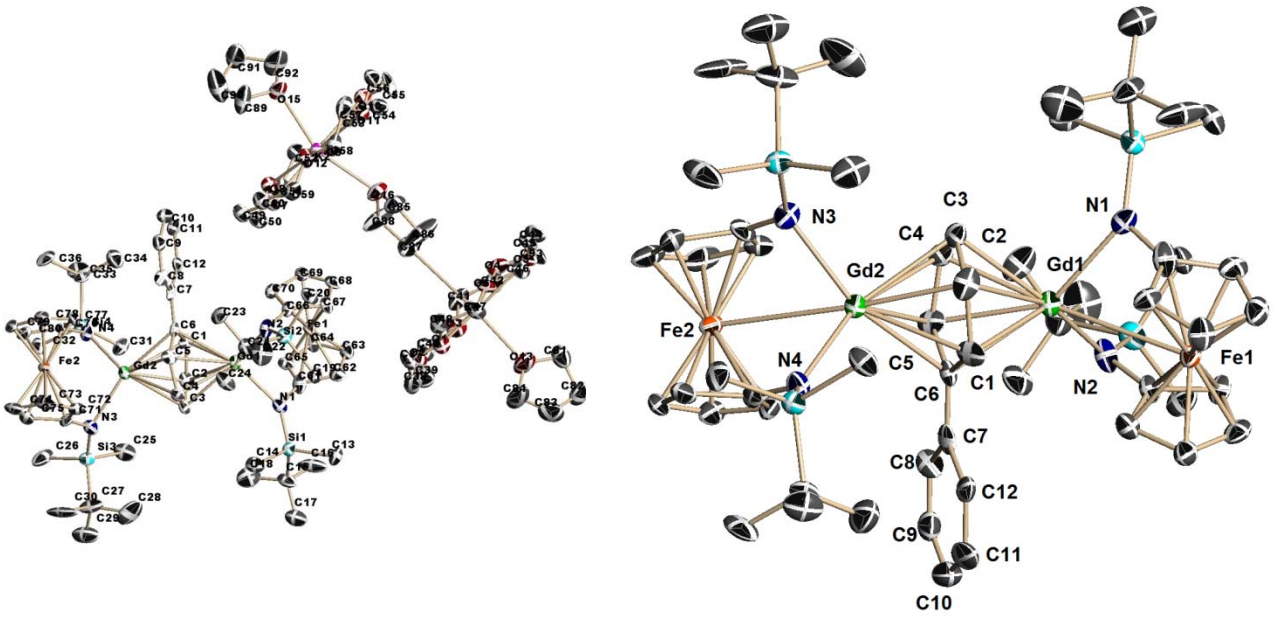

Figure S5. Thermal-ellipsoid (50% probability) representation of **Gd$_2$-biph-crown$_2$** (left) and the anion part (right). Hydrogen atoms were omitted for clarity.

Single crystals suitable for X-ray diffraction were grown from a THF solution layered with *n*-pentane. The unit cell contains large accessible voids; solvent molecules could not be modeled to fit this space (it is possible that some solvent was lost during crystal handling) and the program SQUEEZE was used. A total of 117257 reflections ($-23 \le h \le 23$, $-29 \le k \le 29$, $-46 \le l \le 46$) were collected at $T = 100(2)$ K with $2\theta_{max} = 56.62°$, of which 4661 were unique. The residual peak and hole electron densities were 5.21 and -1.89 eA^{-3}. The least-squares refinement converged normally with residuals of $R_1 = 0.0559$ and GOF = 1.056. Crystal and refinement data for **Gd$_2$-biph-crown$_2$**: formula $C_{92}H_{157}N_4Si_4Fe_2O_{15}Gd_2K_2$, space group $P2_12_12_1$, $a = 17.518(4)$, $b = 22.148(5)$, $c = 34.963(8)$, V = 13565(5) Å^3, Z = 4, μ = 1.316 mm^{-1}, F(000) = 4524, $R_1 = 0.0671$ and $wR_2 = 0.1455$ (based on all data, $I > 2\sigma(I)$).

[(NN^{TBS})Er(THF/Et$_2$O)]$_2$(μ-biphenyl)[K(Et$_2$O)]$_2$ (Er$_2$-biph)

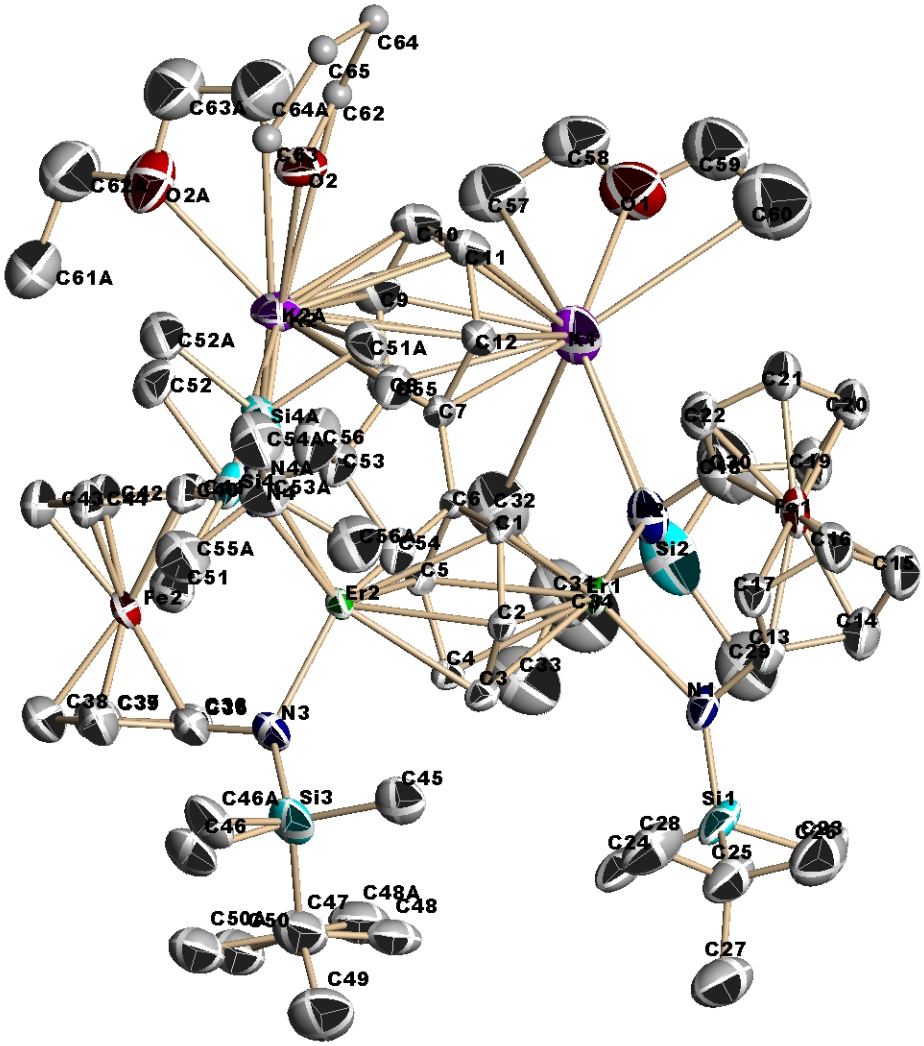

Figure S6. Thermal-ellipsoid (50% probability) representation of **Er$_2$-biph**. Hydrogen and solvent atoms were omitted for clarity.

Single crystals suitable for X-ray diffraction were grown from a diethyl ether solution. The quality of the crystal was not very good and several groups are disordered (see figure above). The most noticeable disorder is that of one of the potassium ions, K2, which was found to coordinate either a diethyl ether or a THF molecule. The THF carbon atoms were not refined anisotropically. As part of that disorder, the nitrogen atom coordinated to K2 and its silyl group are also disordered. In addition, another *t*-butyl group is disordered. All these disorders were modeled over two sets of positions. A total of 80158 reflections ($-19 \le h \le 19$, $-30 \le k \le 30$, $-31 \le l \le 31$) were collected at $T = 100(2)$ K with $2\theta_{max} = 56.54°$, of which 19525 were unique. The residual peak and hole electron densities were 4.42 and -2.43 eA^{-3}. The least-squares refinement converged normally with residuals of $R_1 = 0.0817$ and GOF = 1.197. Crystal and refinement data for **Er$_2$-biph**: formula $C_{132}H_{220}N_8Si_8Fe_4O_5Er_4K_4$, space group $P2_1/n$, a = 15.0037(19), b = 22.794(3), c = 23.376(3), β = 97.0190(15)°, V = 7934.5(18) Å^3, Z = 2, μ = 2.657 mm^{-1}, F(000) = 3344, $R_1 = 0.0977$ and $wR_2 = 0.1834$ (based on all data, $I > 2\sigma(I)$).

[(NN^{TBS})Er(THF)]$_2$(μ-biphenyl)[K(18-crown-6)(THF)$_{1.5}$]$_2$ (Er$_2$-biph-crown$_2$)

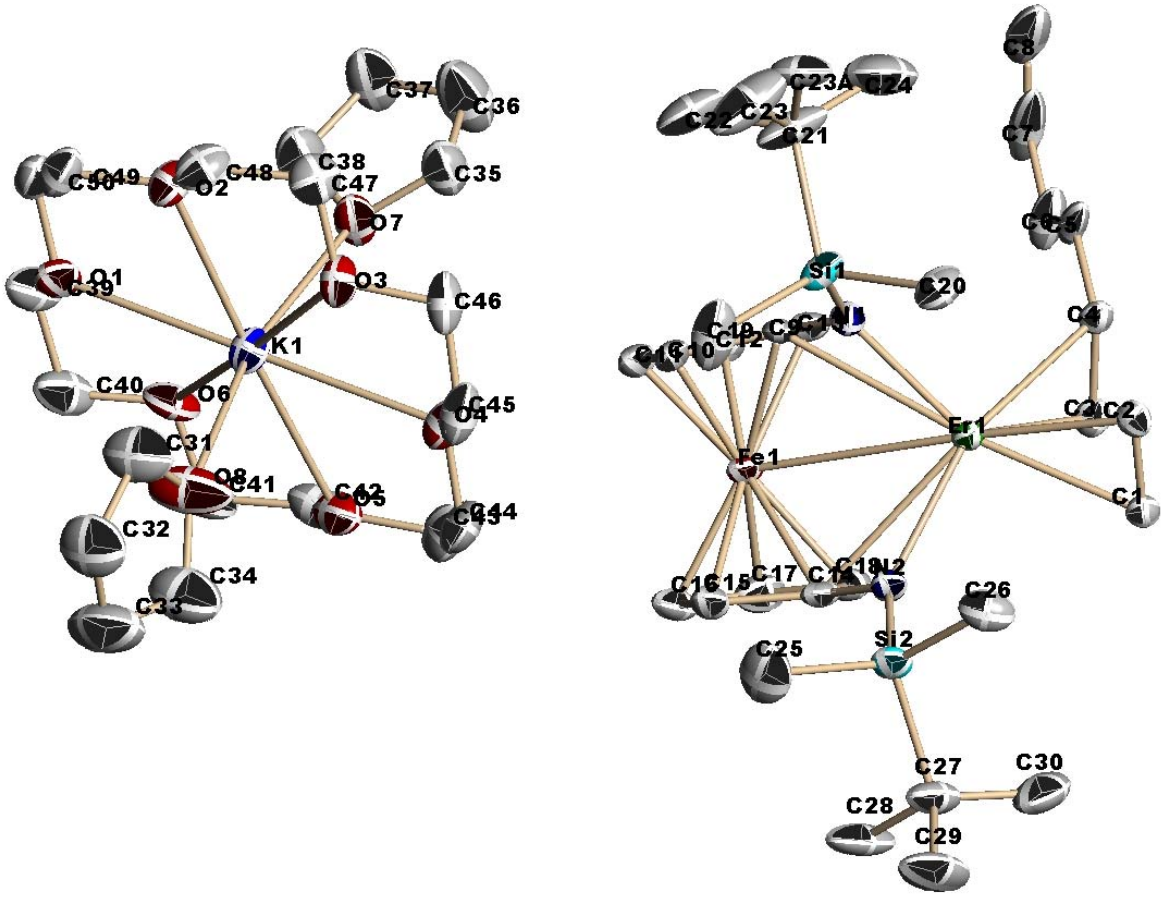

Figure S7. Thermal-ellipsoid (50% probability) representation of **Er$_2$-biph-crown$_2$**. Hydrogen and solvent atoms were omitted for clarity.

Single crystals suitable for X-ray diffraction were grown from a THF solution layered with *n*-pentane. One of the *t*-butyl groups is disordered; this disorder was modeled over two sets of positions (see figure above). Most solvent atoms were also disordered; this disorder was modeled over two sets of positions (not shown). A total of 76862 reflections ($-22 \le h \le 22$, $-30 \le k \le 30$, $-45 \le l \le 44$) were collected at T = 100(2) K with $2\theta_{max}$ = 56.59°, of which 16722 were unique. The residual peak and hole electron densities were 0.79 and -0.87 eA^{-3}. The least-squares refinement converged normally with residuals of R_1 = 0.0316 and GOF = 1.038. Crystal and refinement data for **Er$_2$-biph-crown$_2$**: formula $C_{120}H_{214}N_4Si_4Fe_2O_{22}Er_2K_2$, space group $C222_1$, a = 17.2570(19), b = 22.701(3), c = 34.573(4), V = 13544(3) Å^3, Z = 4, μ = 1.596 mm^{-1}, F(000) = 5680, R_1 = 0.0341 and wR_2 = 0.0747 (based on all data, $I > 2\sigma(I)$).

2. Magnetic data

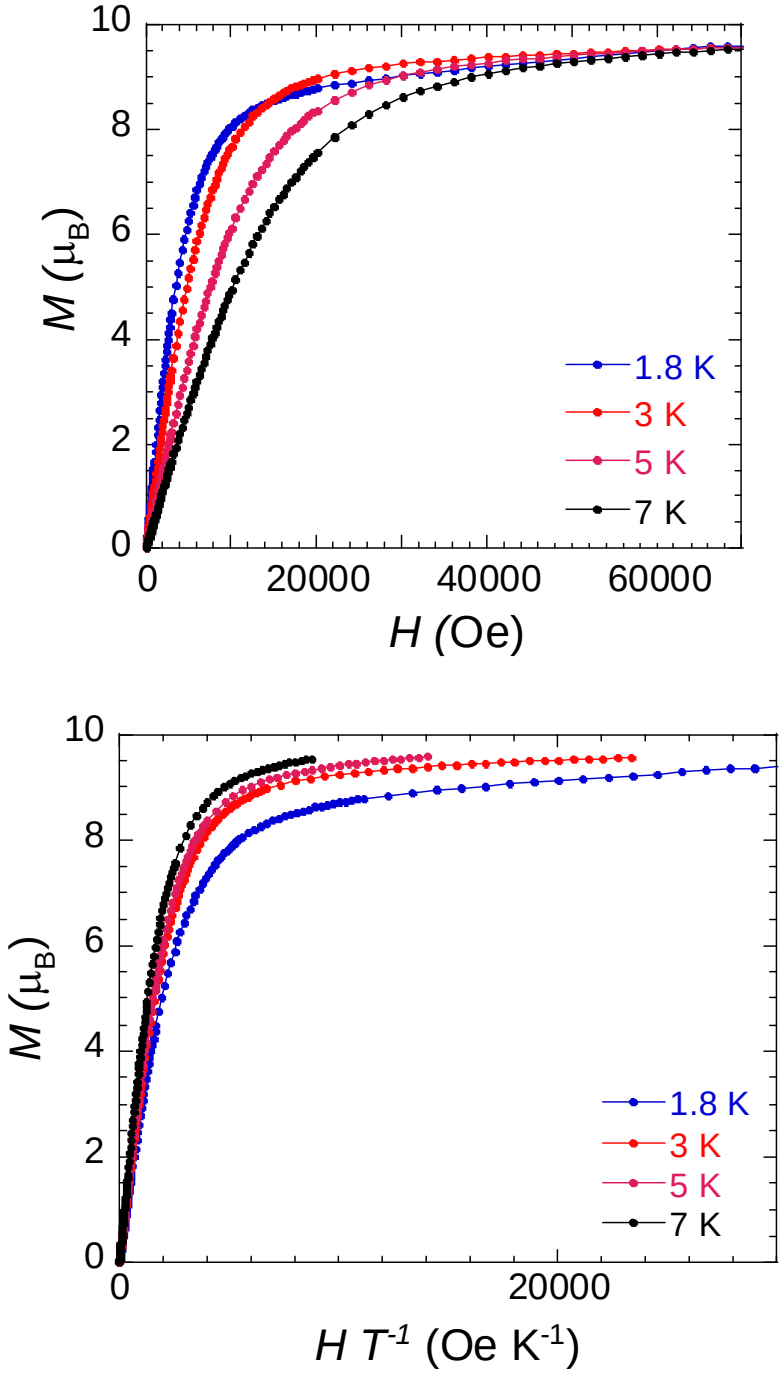

Figure S8. Field dependence of the magnetization (top) and reduced magnetization (bottom) for **Dy_2-biph** at 1.8, 3, 5, and 7 K.

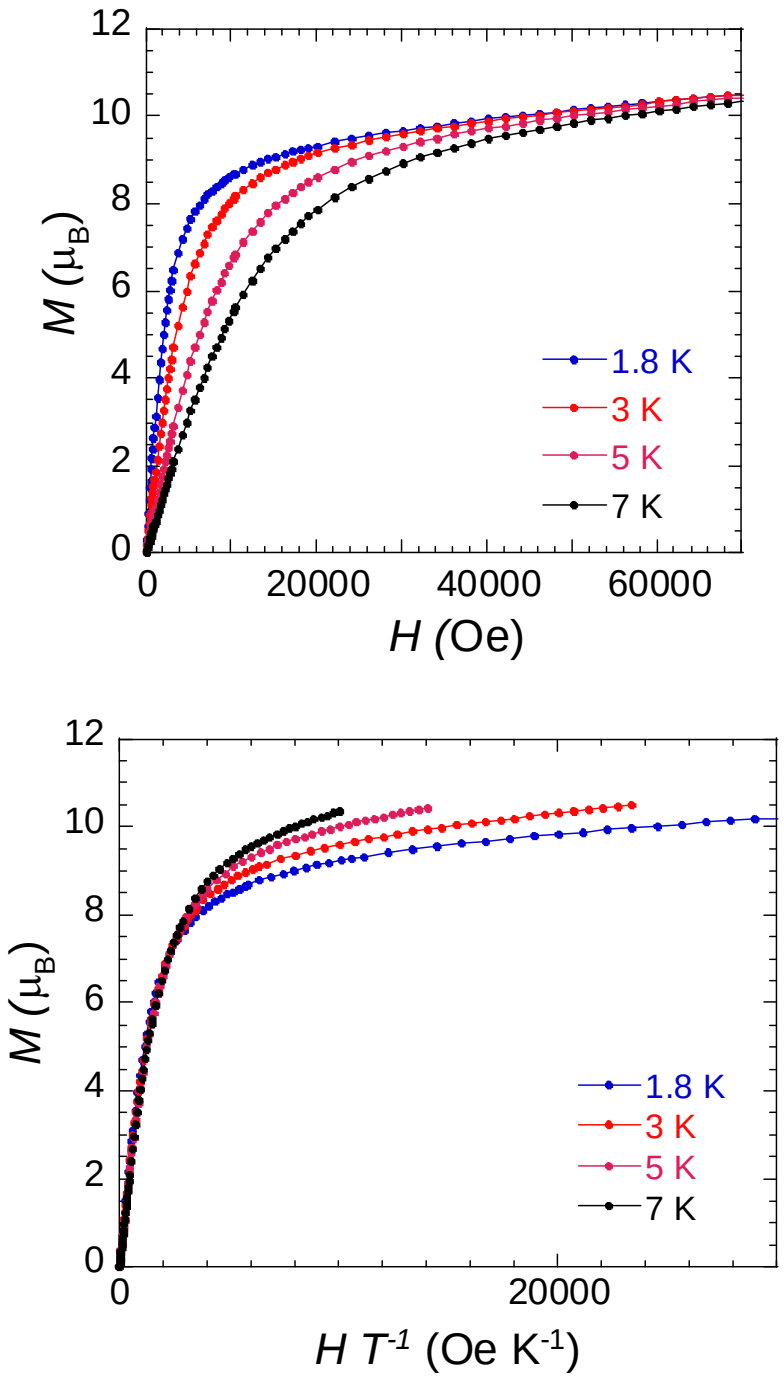

Figure S9. Field dependence of the magnetization (top) and reduced magnetization (bottom) for **Dy_2-biph-crown$_2$** at 1.8, 3, 5, and 7 K.

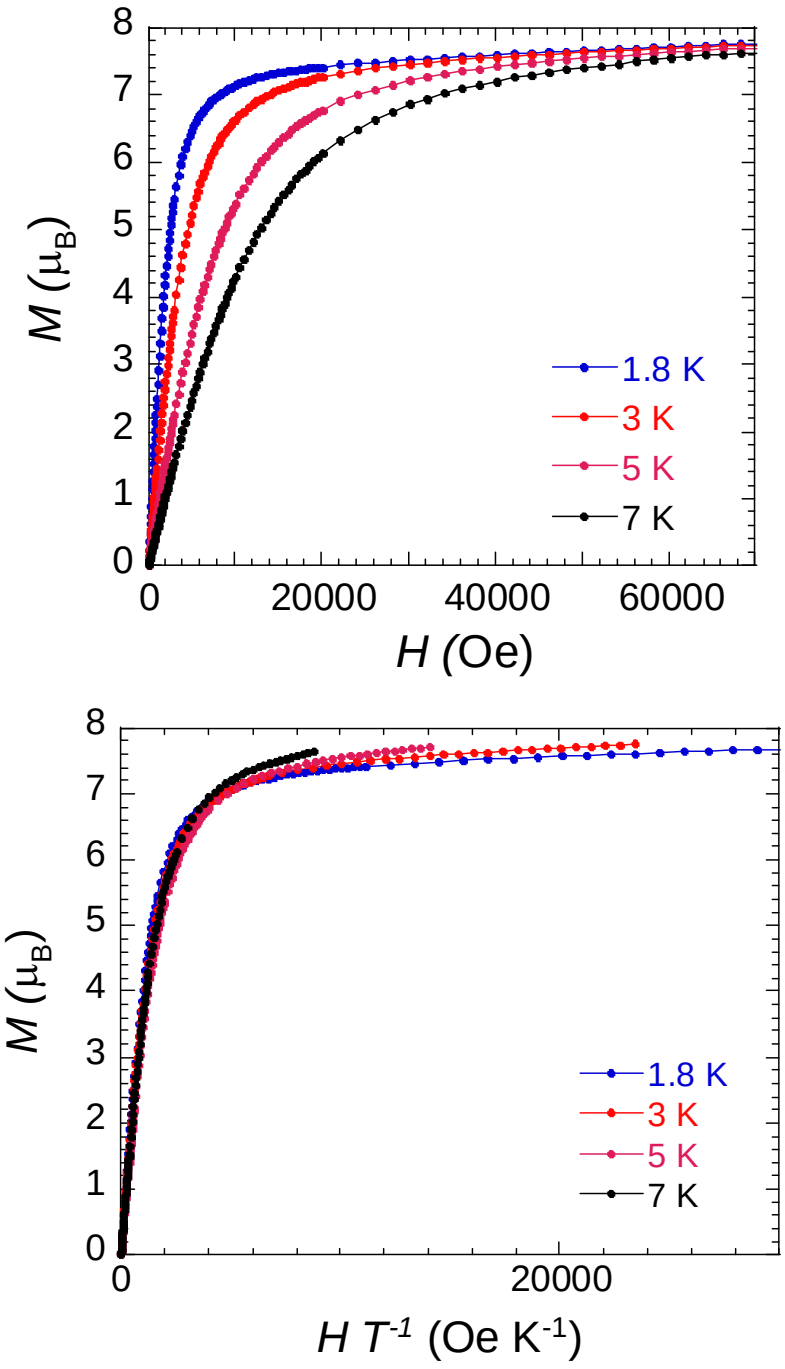

Figure S10. Field dependence of the magnetization (top) and reduced magnetization (bottom) for **Er_2-biph** at 1.8, 3, 5, and 7 K.

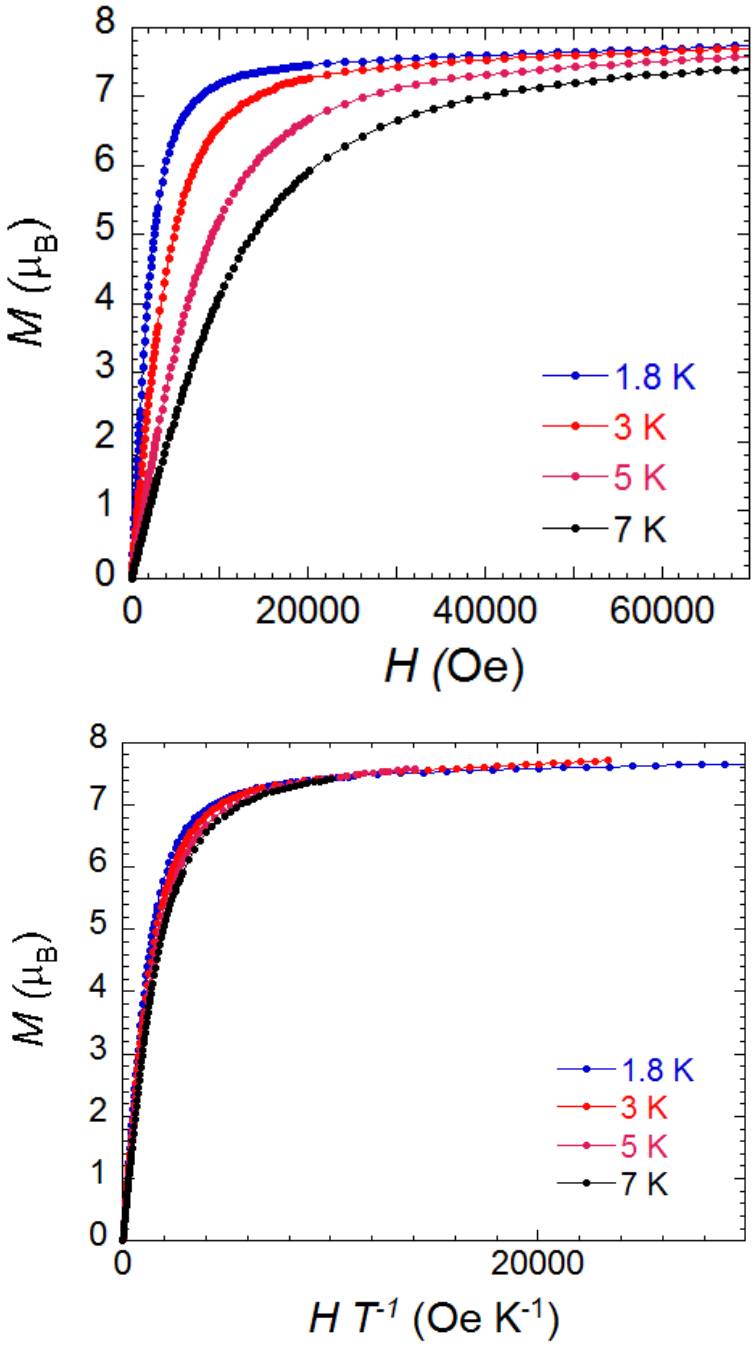

Figure S11. Field dependence of the magnetization (top) and reduced magnetization (bottom) for **Er_2-biph-$crown_2$** at 1.8, 3, 5, and 7 K.

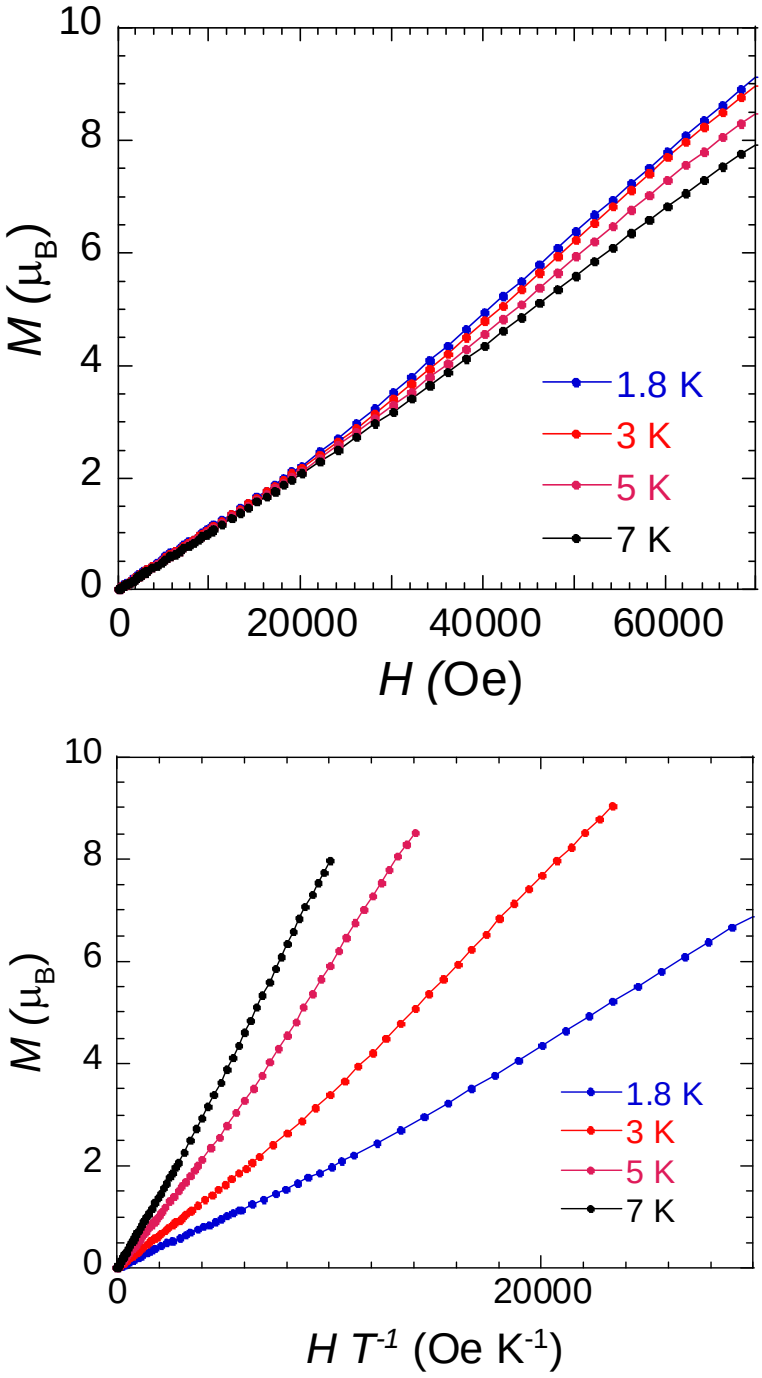

Figure S12. Field dependence of the magnetization (top) and reduced magnetization (bottom) for **Gd_2-biph** at 1.8, 3, 5, and 7 K.

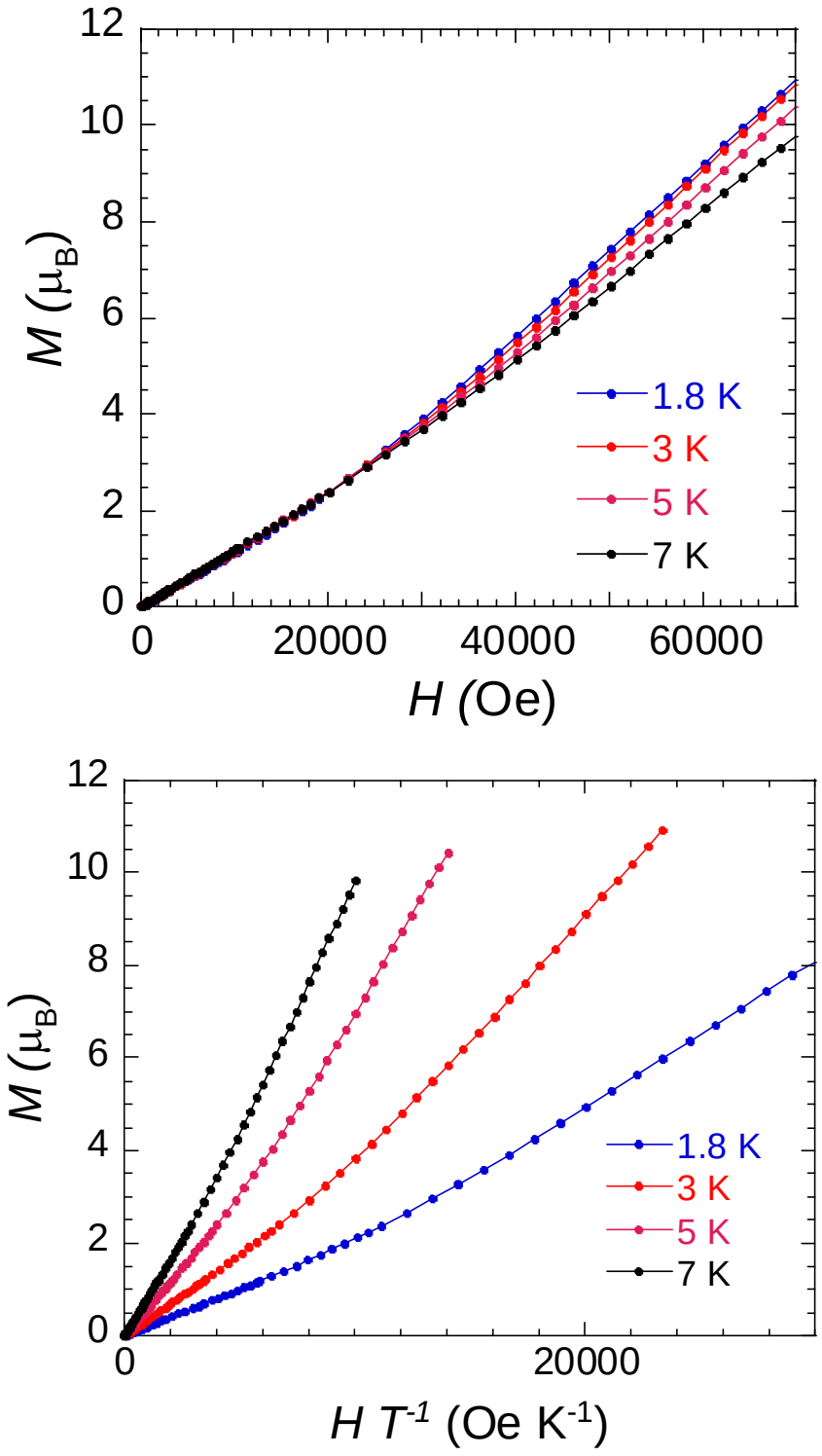

Figure S13. Field dependence of the magnetization (top) and reduced magnetization (bottom) for **Gd_2-biph-crown$_2$** at 1.8, 3, 5, and 7 K.

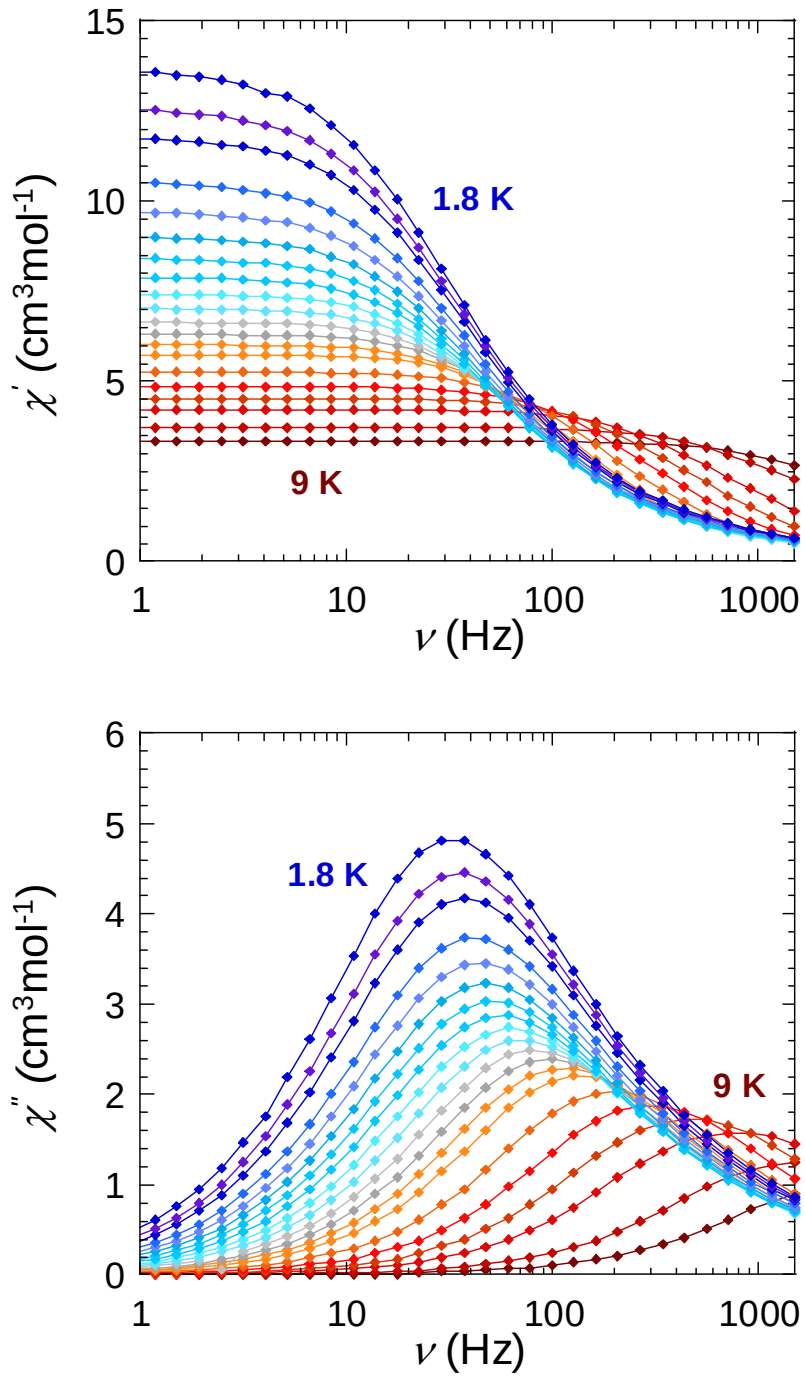

Figure S14. In-phase (top) and out-of phase (bottom) ac susceptibility of **Dy_2-biph** from 1.8-9 K under 0 applied dc field.

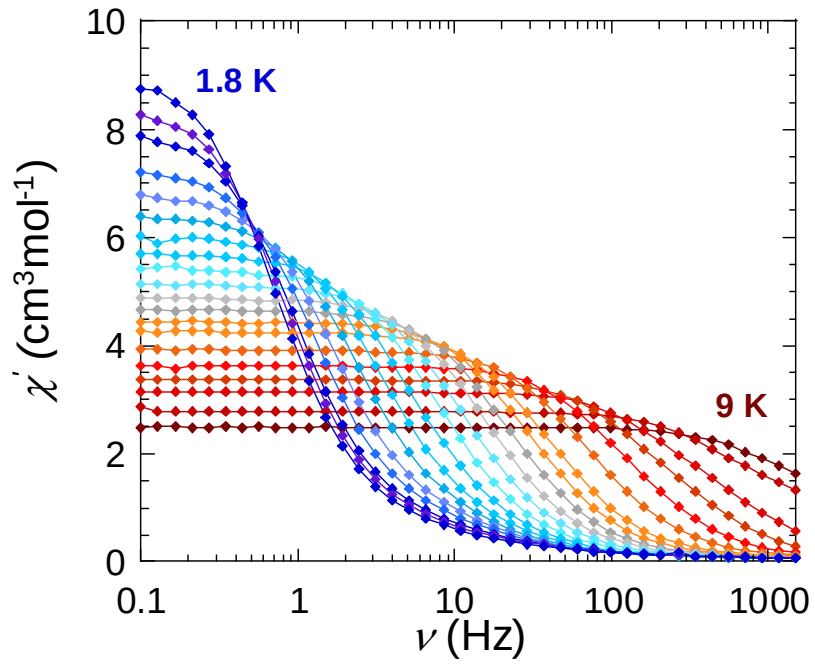

Figure S15. In-phase ac susceptibility for **Dy_2-biph** from 1.8-9 K under an applied dc field of 900 Oe.

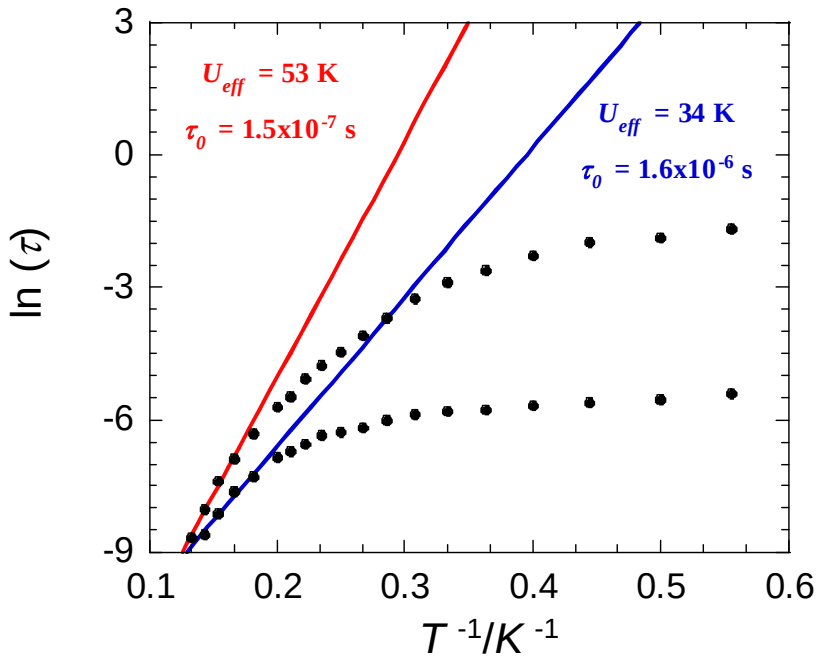

Figure S16. Relaxation time of the magnetization ln(τ) *vs.* T^{-1} (Arrhenius plot using ac data) for **Dy_2-biph** under zero field (blue) and 900 Oe (red) applied dc field. The lines correspond to the fit of the data.

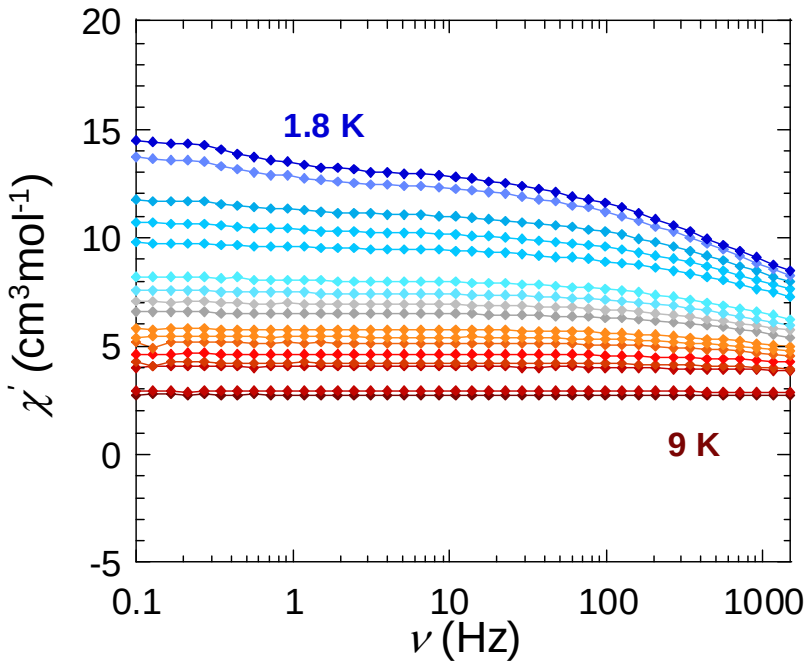

Figure S17. In-phase ac susceptibility of **Dy_2-biph-crown$_2$** from 1.8-9 K under an applied dc field of 900 Oe.

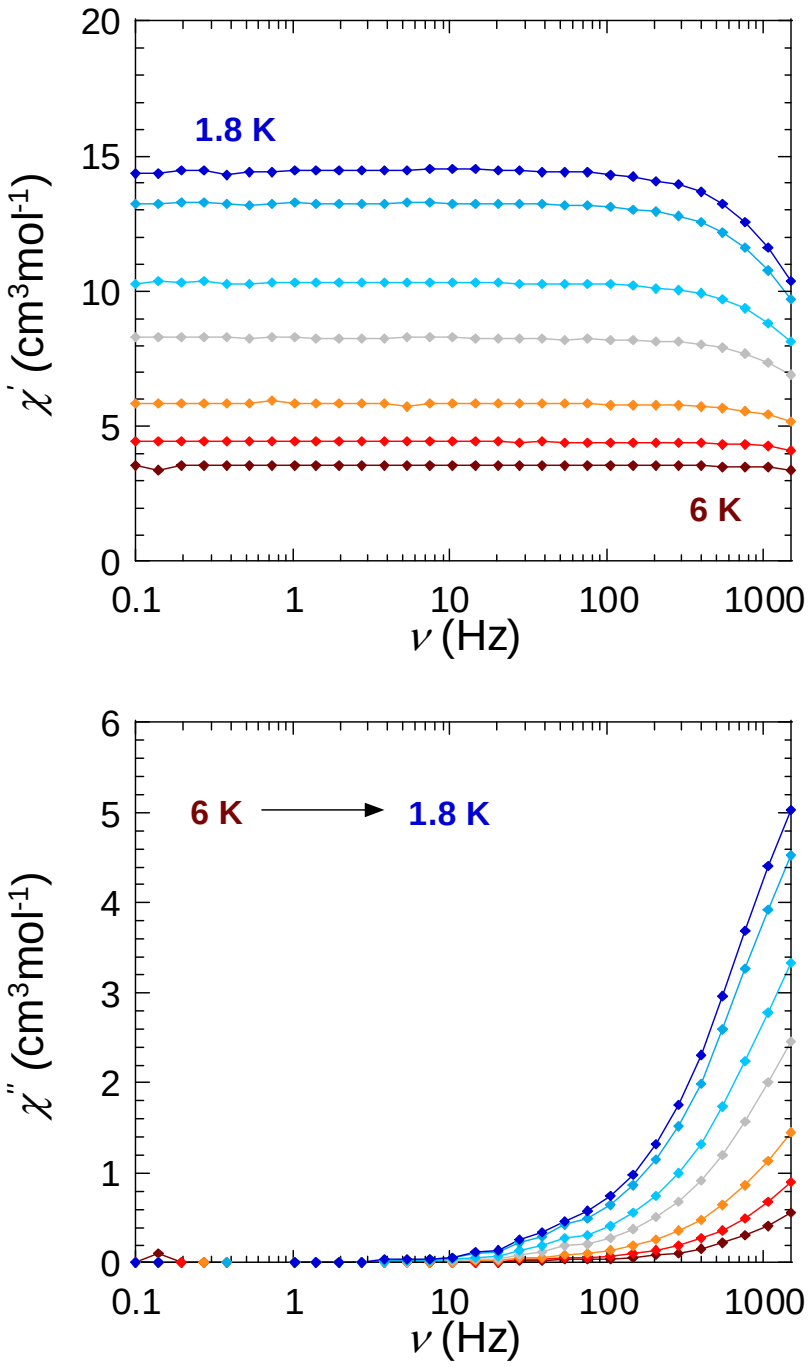

Figure S18. In-phase (top) and out-of phase (bottom) ac susceptibility of **Er_2-biph** from 1.8-6 K under 0 applied dc field.

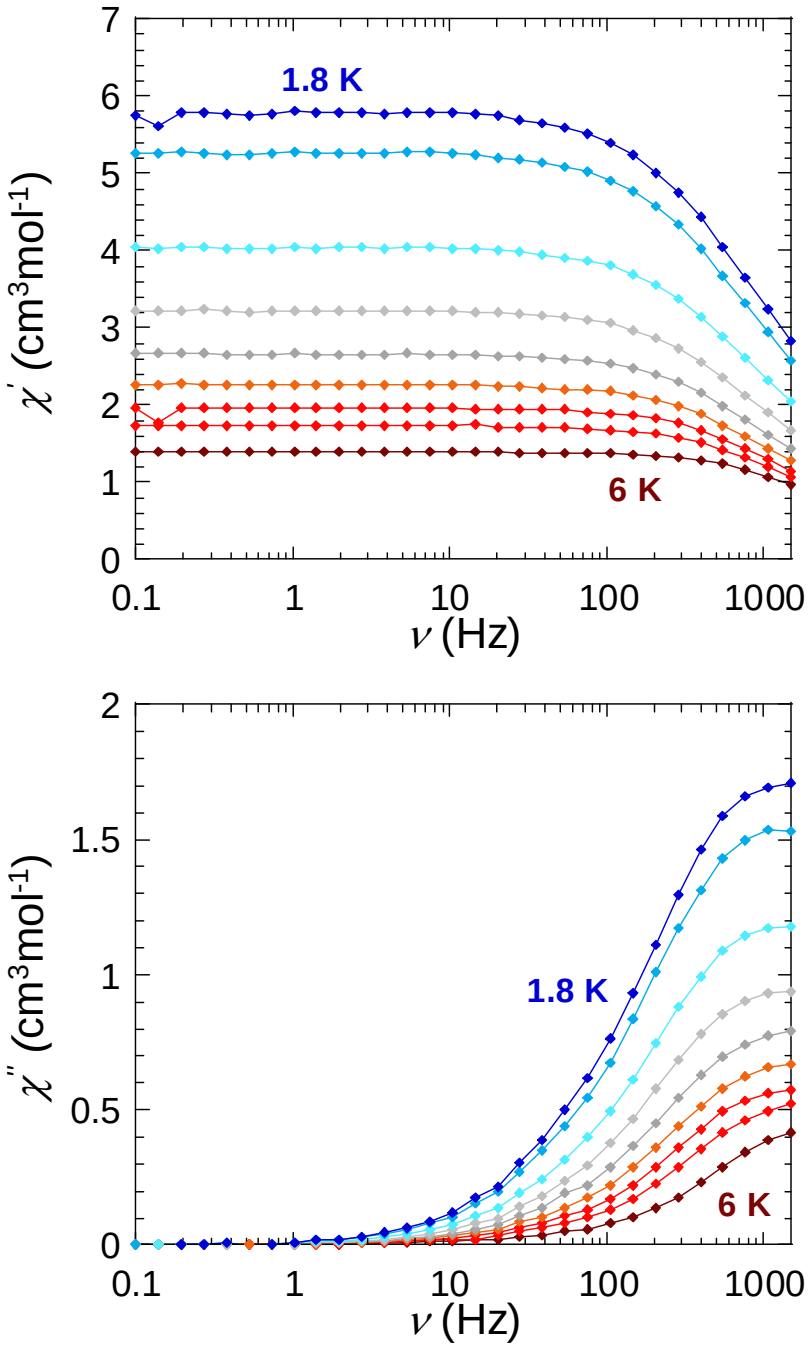

Figure S19. In-phase (top) and out-of phase (bottom) ac susceptibility of **Er_2-biph-$crown_2$** from 1.8-6 K under 0 applied dc field.

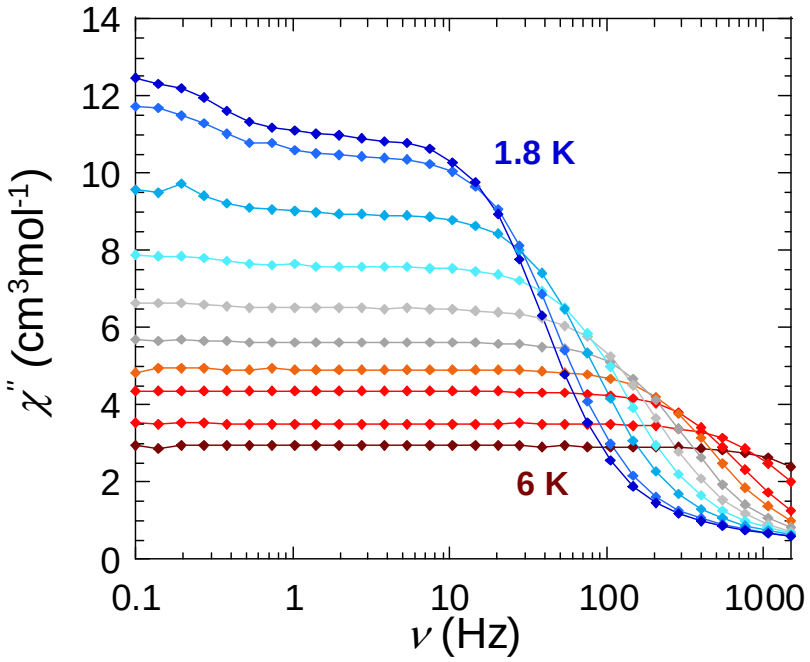

Figure S20. In-phase ac susceptibility of **Er_2-biph** from 1.8-6 K under an applied dc field of 900 Oe.

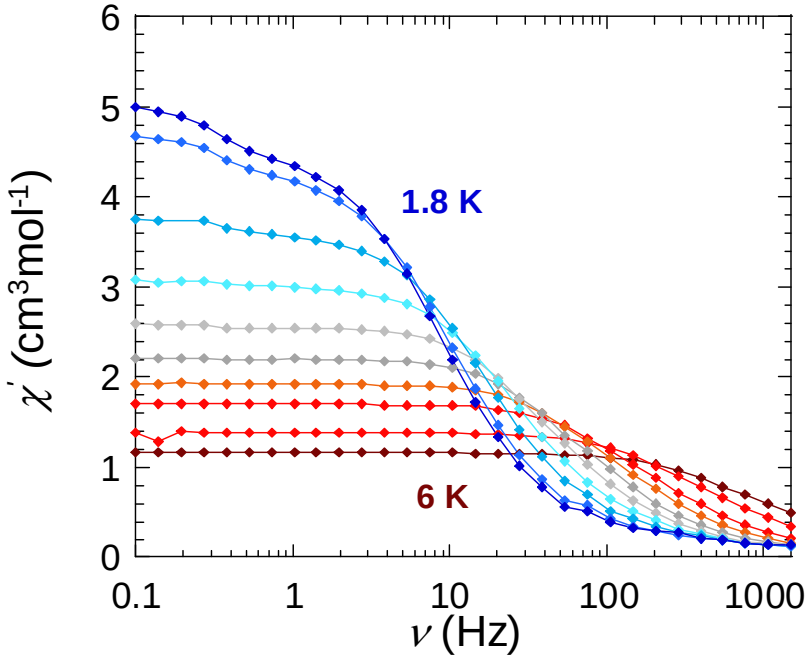

Figure S21. In-phase ac susceptibility of **Er_2-biph-crown$_2$** from 1.8-6 K under an applied dc field of 900 Oe.

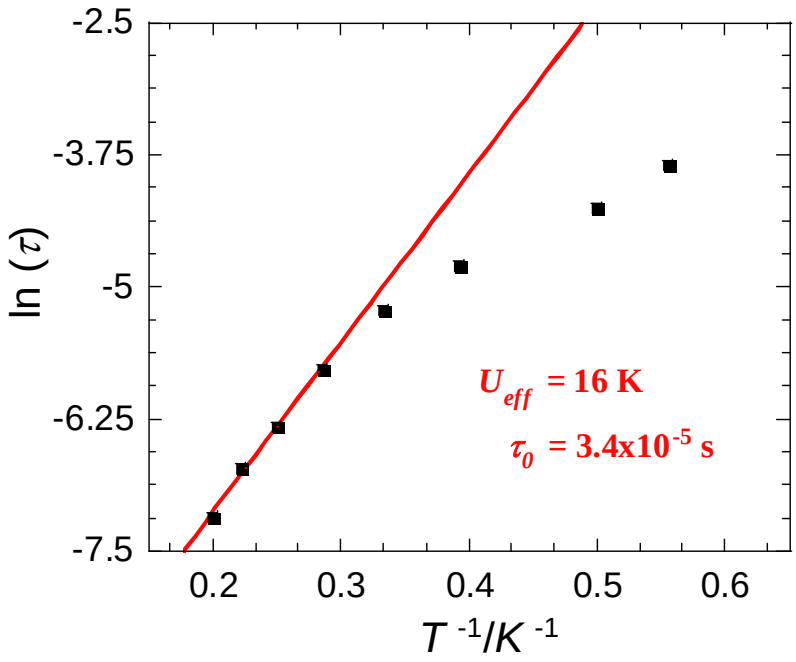

Figure S22. Relaxation time of the magnetization ln(τ) *vs.* T^{-1} (Arrhenius plot using ac data) for **Er_2-biph** under a 900 Oe applied dc field. The line corresponds to the fit of the data.

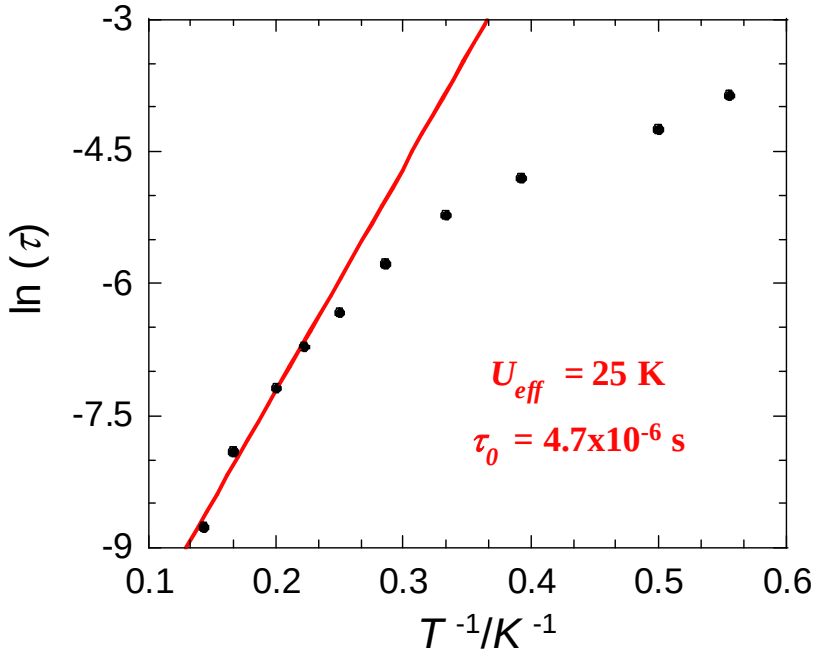

Figure S23. Relaxation time of the magnetization ln(τ) *vs.* T^{-1} (Arrhenius plot using ac data) for **Er_2-biph-crown$_2$** under a 900 Oe applied dc field. The line corresponds to the fit of the data.

4. Ab initio calculation data

All calculations on individual magnetic centers were done with MOLCAS 7.8 and are of CASSCF/RASSI/SINGLE_ANISO type.
For Dy^{3+}: Active space of the CASSCF included 9 electrons in seven 4f orbitals.
The spin-orbit coupling included the mixing of 21 sextets, 128 quartets and 130 doublet states.
For Er^{3+}: Active space of the CASSCF included 11 electrons in seven 4f orbitals.
The spin-orbit coupling included the mixing of 35 spin quartets, 112 spin doublet states.

Two structures were employed: complete structure and reduced structure.
In the reduced structure, all methyl and t-butyl groups were replaced by H.
Three basis sets were employed (MB (minimal), DZP (medium) and TZP (large).

Table S1: Energies of the low-lying Kramers doublets (cm^{-1}) on the Dy site for the Dy_2-biph compound.

reduced structure			complete structure		
MB	DZP	TZP	MB	DZP	TZP
0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000
180.298	85.449	88.994	180.245	83.097	90.494
180.298	85.449	88.994	180.245	83.097	90.494
400.323	225.603	228.993	400.720	230.246	233.486
400.323	225.603	228.993	400.720	230.246	233.486
612.424	372.338	375.217	614.638	381.414	383.485
612.424	372.338	375.217	614.638	381.414	383.485
820.986	531.938	541.228	823.403	544.668	550.658
820.986	531.938	541.228	823.403	544.668	550.658
1066.287	714.526	743.055	1066.855	734.014	750.312
1066.287	714.526	743.055	1066.855	734.014	750.312
1303.532	882.440	921.693	1304.409	909.909	920.933
1303.532	882.440	921.693	1304.409	909.909	920.933
1512.562	935.682	975.215	1500.816	957.913	979.518
1512.562	935.682	975.215	1500.816	957.913	979.518
…	…	…	…	…	…

Table S2: Main values of the g tensors of the low-lying Kramers doublets (cm^{-1}) on the Dy site for the Dy_2-biph compound.

KD		reduced structure			complete structure		
		MB	DZP	TZP	MB	DZP	TZP
1	g_X	0.017142	0.045991	0.042622	0.016216	0.048998	0.038809
	g_Y	0.031220	0.102235	0.096350	0.029369	0.114143	0.088397
	g_Z	19.300083	19.226461	19.289872	19.307409	19.143013	19.279351
2	g_X	0.188102	0.308754	0.311597	0.179946	0.277791	0.294539
	g_Y	0.239085	0.335739	0.343216	0.227816	0.324494	0.324103
	g_Z	16.262245	17.264460	17.764991	16.281031	17.076948	17.695418
3	g_X	1.211979	1.609514	1.675435	1.156921	1.524623	1.568740
	g_Y	1.369449	1.754391	1.889811	1.299730	1.674675	1.739327
	g_Z	13.088247	13.303037	13.247821	13.143349	13.342708	13.336910
4	g_X	3.771190	3.127815	3.236053	3.650848	3.101449	3.083869
	g_Y	4.591415	4.906644	5.149094	4.450459	4.789672	4.900284
	g_Z	8.856944	8.963048	8.702894	8.992167	9.021168	8.950048
5	g_X	3.587940	3.550826	3.457238	3.704748	3.662059	3.623550
	g_Y	4.062410	4.365620	4.134495	4.208759	4.437462	4.399527
	g_Z	9.696905	9.782851	10.002054	9.561345	9.703520	9.786191
6	g_X	0.991461	1.097781	0.901362	1.066351	1.101995	0.989832
	g_Y	1.068030	1.227373	1.086308	1.143652	1.254781	1.235748
	g_Z	13.905172	14.181694	14.048911	13.860481	14.089883	13.989891
7	g_X	0.160655	0.047070	0.026987	0.178724	0.132786	0.091158
	g_Y	0.175687	0.331728	0.304543	0.191978	0.333712	0.366198
	g_Z	17.546794	17.489168	17.396723	17.514330	17.011701	17.815698
8	g_X	0.011650	0.127376	0.130136	0.016016	0.169789	0.131739
	g_Y	0.022106	0.403359	0.312356	0.030597	0.512304	0.323658
	g_Z	19.554564	18.736736	19.041081	19.523586	18.622638	19.120837

Table S3: Energies of the low-lying Kramers doublets (cm^{-1}) on the Dy site for the Dy_2-biph-$crown_2$ compound.

reduced structure			complete structure		
MB	DZP	TZP	MB	DZP	TZP
0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000
165.087	62.887	50.492	162.210	59.330	50.854
165.087	62.887	50.492	162.210	59.330	50.854
369.950	191.263	190.788	364.835	194.856	191.129
369.950	191.263	190.788	364.835	194.856	191.129
584.955	332.164	328.739	577.948	338.626	330.001
584.955	332.164	328.739	577.948	338.626	330.001
811.104	503.512	507.180	802.025	512.624	506.619
811.104	503.512	507.180	802.025	512.624	506.619
1073.332	699.075	723.642	1060.274	714.277	718.954
1073.332	699.075	723.642	1060.274	714.277	718.954
1302.473	822.610	883.857	1283.466	850.564	873.000
1302.473	822.610	883.857	1283.466	850.564	873.000
1575.445	957.332	957.321	1557.798	961.822	942.655
1575.445	957.332	957.321	1557.798	961.822	942.655
…	…	…	…	…	…

.

Table S4: Main values of the g tensors of the low-lying Kramers doublets (cm^{-1}) on the Dy site for the Dy_2-biph-$crown_2$ compound.

KD		reduced structure			complete structure		
		MB	DZP	TZP	MB	DZP	TZP
1	g_X	0.048793	0.226771	0.291070	0.050086	0.244119	0.269292
	g_Y	0.102681	0.630363	0.922314	0.105682	0.720446	0.841108
	g_Z	19.200188	19.053801	18.887981	19.195581	18.911509	18.934429
2	g_X	0.421957	0.503524	0.117392	0.427625	0.362460	0.138184
	g_Y	0.538714	0.981759	0.998077	0.543264	0.954570	0.945478
	g_Z	15.858760	17.324860	17.543024	15.853755	17.069166	17.573116
3	g_X	1.954463	2.741874	2.954390	1.963844	2.702545	2.841677
	g_Y	2.074003	3.282475	3.527583	2.076300	3.169041	3.344238
	g_Z	12.381998	12.309128	12.442837	12.388583	12.406876	12.592117
4	g_X	4.131408	7.166769	7.217403	4.116060	7.173273	7.095866
	g_Y	5.873785	6.834366	6.643372	5.876150	6.815500	6.840032
	g_Z	7.766130	3.099305	2.855332	7.779674	3.143404	2.909480
5	g_X	2.823979	2.394728	2.400387	2.818304	2.485773	2.512494
	g_Y	3.139023	2.905328	2.777929	3.157816	2.974509	2.949563
	g_Z	10.522786	10.990331	11.120110	10.512015	10.959471	11.028300
6	g_X	0.713035	0.577282	0.469317	0.724994	0.587305	0.522659
	g_Y	0.731084	0.697426	0.601679	0.740323	0.711110	0.676203
	g_Z	14.190712	14.317021	14.234480	14.188394	14.300140	14.263769
7	g_X	0.097035	0.090376	0.065566	0.099318	0.083704	0.065258
	g_Y	0.104918	0.129525	0.133605	0.107602	0.134373	0.149642
	g_Z	17.745790	18.921800	18.653218	17.772784	18.918949	18.926726
8	g_X	0.000618	0.015358	0.005780	0.000912	0.013541	0.006302
	g_Y	0.004984	0.039383	0.041206	0.005453	0.044068	0.057293
	g_Z	19.622386	19.509917	19.418386	19.622219	19.475712	19.377001

Table S5: Energies of the low-lying Kramers doublets (cm^{-1}) on the Er1 site for the Er_2-biph compound.

reduced structure			complete structure		
MB	DZP	TZP	MB	DZP	TZP
0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000
53.816	40.018	60.397	52.663	47.586	57.917
53.816	40.018	60.397	52.663	47.586	57.917
199.640	155.750	161.632	199.543	159.004	158.780
199.640	155.750	161.632	199.543	159.004	158.780
270.596	185.969	194.177	270.426	192.200	194.810
270.596	185.969	194.177	270.426	192.200	194.810
329.507	213.754	219.039	330.069	220.195	217.160
329.507	213.754	219.039	330.069	220.195	217.160
397.418	286.802	301.389	396.864	294.121	296.000
397.418	286.802	301.389	396.864	294.121	296.000
591.784	446.640	470.193	592.133	461.556	470.840
591.784	446.640	470.193	592.133	461.556	470.840
693.700	513.587	535.631	693.856	529.013	536.430
693.700	513.587	535.631	693.856	529.013	536.430
…	…	…	…	…	…

Table S6: Main values of the g tensors of the low-lying Kramers doublets (cm^{-1}) on the Er1 site for the Er_2-biph compound.

KD		reduced structure			complete structure		
		MB	DZP	TZP	MB	DZP	TZP
1	g_X	0.253789	0.345765	0.184420	0.259533	0.266541	0.185469
	g_Y	0.678827	1.023995	0.408200	0.705360	0.693671	0.401741
	g_Z	16.951686	16.823176	17.423254	16.896660	17.152871	17.435804
2	g_X	0.014941	0.238480	0.204337	0.041475	0.029012	0.186227
	g_Y	0.692229	0.836509	0.633958	0.692457	0.717536	0.616845
	g_Z	15.182106	15.640670	16.451610	15.082287	16.106809	16.521585
3	g_X	2.877142	2.670033	1.838367	2.867844	2.612538	1.748891
	g_Y	3.524702	2.858839	2.190750	3.579548	2.722889	2.104617
	g_Z	11.639561	13.080723	14.008711	11.623104	13.432354	14.226151
4	g_X	8.006090	9.965835	1.809488	8.140319	10.018553	10.465211
	g_Y	7.172407	6.466928	6.064804	7.048221	6.498708	6.340486
	g_Z	1.791174	1.036781	11.122228	1.623598	1.011531	1.787724
5	g_X	1.032946	0.596986	0.583961	0.963205	0.440075	0.562565
	g_Y	3.246727	2.575858	2.996618	3.164183	2.914471	2.662310
	g_Z	11.041747	13.028107	12.145824	11.167670	12.724704	12.690393
6	g_X	2.025319	2.025130	1.942478	2.074199	2.216377	2.059118
	g_Y	3.146324	3.034015	2.954071	3.231406	3.117343	2.985731
	g_Z	12.321516	13.022346	13.108691	12.307116	12.867425	13.101523
7	g_X	0.116651	0.548639	0.735227	0.109417	0.560074	0.714887
	g_Y	0.508084	1.028810	1.089108	0.496181	0.990137	1.016544
	g_Z	14.593863	13.194134	13.085401	14.649732	13.219823	13.312122
8	g_X	0.138903	0.375596	0.405581	0.136518	0.366418	0.383520
	g_Y	0.453279	1.720389	1.951625	0.443971	1.677120	1.835586
	g_Z	16.487784	15.219695	15.024442	16.511073	15.212897	15.119851

Table S7: Energies of the low-lying Kramers doublets (cm^{-1}) on the Er2 site for the Er_2-biph compound.

reduced structure			complete structure		
MB	DZP	TZP	MB	DZP	TZP
0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000
84.215	66.526	87.978	82.195	76.658	87.316
84.215	66.526	87.978	82.195	76.658	87.316
218.573	171.308	177.389	218.005	174.321	174.285
218.573	171.308	177.389	218.005	174.321	174.285
286.904	190.872	198.217	286.102	199.170	200.997
286.904	190.872	198.217	286.102	199.170	200.997
343.273	217.212	225.355	342.100	224.478	222.575
343.273	217.212	225.355	342.100	224.478	222.575
428.723	315.056	330.117	424.979	322.113	323.958
428.723	315.056	330.117	424.979	322.113	323.958
615.557	471.280	496.512	614.957	486.612	497.479
615.557	471.280	496.512	614.957	486.612	497.479
690.293	524.058	548.505	689.695	540.388	549.109
690.293	524.058	548.505	689.695	540.388	549.109
…	…	…	…	…	…

Table S8: Main values of the g tensors of the low-lying Kramers doublets (cm^{-1}) on the Er2 site for the Er_2-biph compound.

KD		reduced structure			complete structure		
		MB	DZP	TZP	MB	DZP	TZP
1	g_X	0.098767	0.133013	0.084692	0.102915	0.106393	0.081517
	g_Y	0.195713	0.271871	0.148155	0.207640	0.201548	0.142975
	g_Z	17.487652	17.461883	17.592819	17.461871	17.538587	17.590989
2	g_X	0.215324	0.215099	0.342473	0.208597	0.278419	0.346804
	g_Y	0.418078	0.476931	0.458434	0.425302	0.459241	0.453593
	g_Z	16.062241	16.493527	16.655120	16.029837	16.626263	16.696633
3	g_X	2.101886	2.183611	1.352029	2.174675	1.922813	1.493446
	g_Y	2.564271	2.602358	1.831085	2.633603	2.378080	2.048839
	g_Z	12.687049	13.914858	14.538442	12.639084	14.270839	14.660538
4	g_X	9.294142	1.565313	2.258354	9.373925	1.729553	2.376429
	g_Y	6.770327	5.062866	4.452878	6.690062	4.978064	4.434250
	g_Z	1.974786	12.490995	13.026937	1.780491	12.454058	12.704873
5	g_X	9.411605	0.306736	0.136435	9.513342	0.037426	0.078514
	g_Y	5.331266	3.746026	4.159417	5.094882	4.310194	3.975842
	g_Z	0.085923	10.563910	9.749464	0.002349	9.850485	9.292925
6	g_X	2.180996	1.451909	1.476079	2.324133	1.708082	1.663453
	g_Y	3.092358	2.879282	2.827734	3.295784	2.940404	2.847795
	g_Z	12.249394	12.814703	12.849070	12.101910	12.726109	12.856253
7	g_X	0.414488	1.445597	1.439353	0.408315	1.366115	1.348491
	g_Y	0.917918	2.543967	3.012100	0.881311	2.390710	2.922682
	g_Z	13.370390	11.357194	11.117346	13.467503	11.615155	11.358016
8	g_X	0.343632	0.684096	0.710695	0.332582	0.653297	0.679402
	g_Y	1.476386	4.193115	4.622283	1.419858	3.926474	4.411927
	g_Z	15.465674	13.512626	13.166911	15.511927	13.689219	13.285507

Table S9: Energies of the low-lying Kramers doublets (cm^{-1}) on the Er site for the Er_2-biph-$crown_2$ compound.

reduced structure			complete structure		
MB	DZP	TZP	MB	DZP	TZP
0.000	0.000	0.000	0.000	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000
36.922	16.134	27.668	40.344	13.828	22.094
36.922	16.134	27.668	40.344	13.828	22.094
197.336	159.862	165.318	199.125	159.247	163.735
197.336	159.862	165.318	199.125	159.247	163.735
288.810	190.600	186.426	290.795	186.470	181.949
288.810	190.600	186.426	290.795	186.470	181.949
342.279	211.481	208.920	343.674	209.804	201.783
342.279	211.481	208.920	343.674	209.804	201.783
395.287	277.262	286.314	395.110	277.403	276.358
395.287	277.262	286.314	395.110	277.403	276.358
605.718	446.954	466.149	604.134	452.668	460.034
605.718	446.954	466.149	604.134	452.668	460.034
687.001	499.508	517.104	684.446	505.739	510.878
687.001	499.508	517.104	684.446	505.739	510.878
…	…	…	…	…	…

Table S10: Main values of the g tensors of the low-lying Kramers doublets (cm^{-1}) on the Er site for the Er_2-biph-$crown_2$ compound.

KD		reduced structure			complete structure		
		MB	DZP	TZP	MB	DZP	TZP
1	g_X	0.297995	0.519558	0.250886	0.262917	0.617734	0.331996
	g_Y	0.822492	2.116794	0.652471	0.676384	3.135653	0.973730
	g_Z	16.838042	15.884360	17.212284	17.028045	14.939693	16.946748
2	g_X	0.318181	0.706895	0.288156	0.186743	0.803997	0.480388
	g_Y	0.587171	1.621256	0.448170	0.553006	2.590784	0.608727
	g_Z	14.845590	14.752422	16.675250	15.151201	13.698181	16.356772
3	g_X	1.657936	1.691644	2.401521	1.636490	2.150455	3.007496
	g_Y	1.976978	2.588357	3.399340	1.951539	2.961935	3.739685
	g_Z	12.820864	13.228505	12.931231	12.804246	13.074371	12.233657
4	g_X	1.865464	10.516505	9.985599	1.913211	10.115100	9.437100
	g_Y	5.467287	6.924668	6.859218	5.462081	7.034012	6.689391
	g_Z	9.872580	1.304595	0.345213	9.864199	0.786746	0.304884
5	g_X	1.085750	10.104450	8.860129	1.084084	9.145795	8.624948
	g_Y	2.683678	6.371148	6.795954	2.715551	6.833030	6.722950
	g_Z	11.368218	0.760267	1.398750	11.394433	0.788756	1.394422
6	g_X	2.345145	2.675305	2.757004	2.338002	2.796770	2.843378
	g_Y	5.506830	3.219809	3.044836	5.505094	3.545226	3.331578
	g_Z	10.123148	12.167315	12.298383	10.147145	11.908067	12.121826
7	g_X	0.132778	1.156026	1.199083	0.137087	1.114204	1.129411
	g_Y	0.541649	1.728279	2.272855	0.533960	1.699419	2.156125
	g_Z	14.040523	12.315244	11.932081	14.054442	12.344652	12.115667
8	g_X	0.191723	0.534741	0.589098	0.190031	0.522024	0.559987
	g_Y	0.700305	2.921892	3.507835	0.695357	2.853637	3.310315
	g_Z	15.965993	14.266836	13.807060	15.966167	14.270374	13.924924

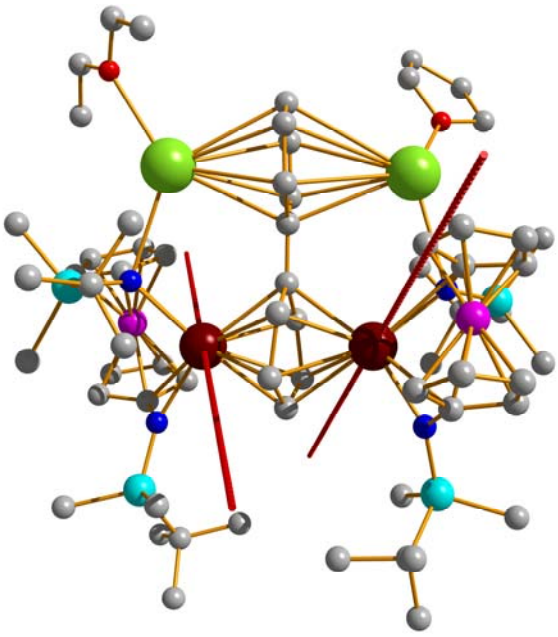

Figure S24. Main local anisotropy axes on Er sites in **Er_2-biph**.

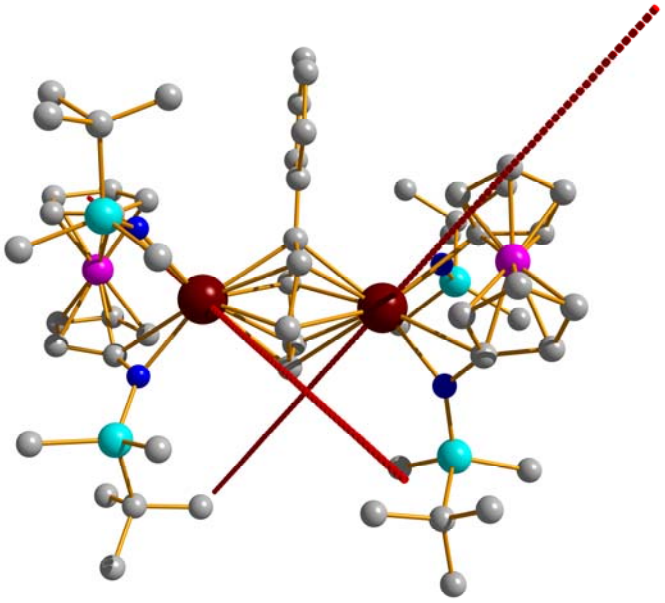

Figure S25. Main local anisotropy axes on Er sites in **Er_2-biph-crown$_2$**.

4. ^{1}H NMR spectra

(NN^{TBS})DyI($THF)_2$: scan from +425 to -425 ppm with the maximum width of 250 ppm per spectrum, only spectra having significant signal(s) are shown.

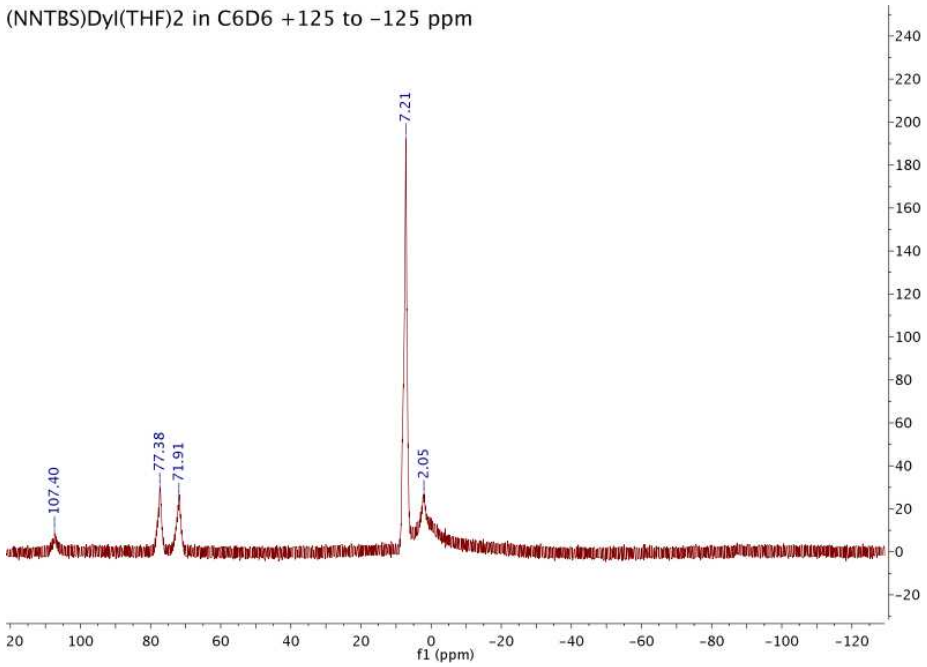

Figure S26. (NN^{TBS})DyI($THF)_2$ in C_6D_6 at 298 K (+125 to -125 ppm).

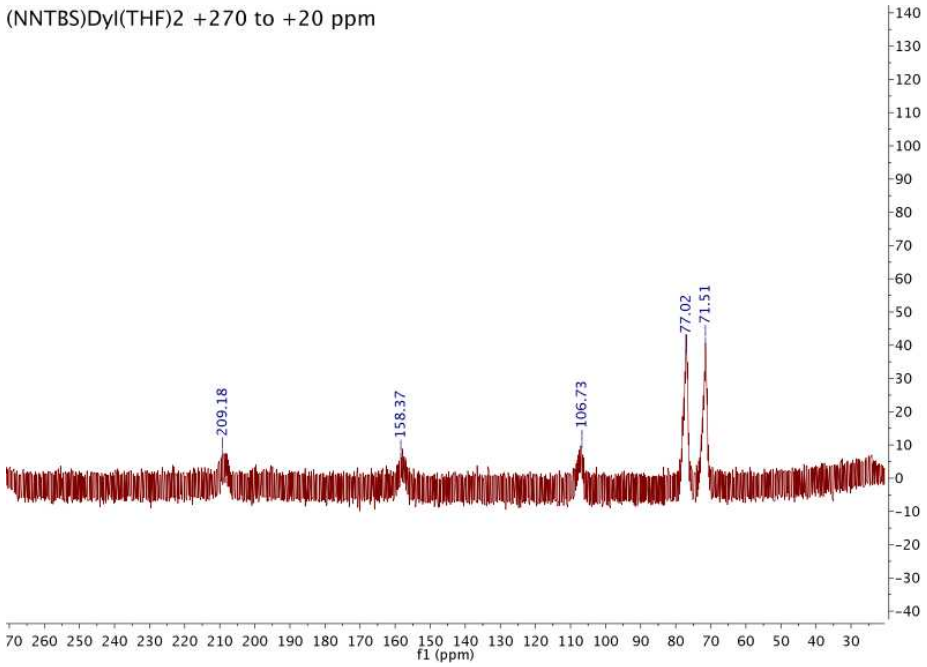

Figure S27. (NN^{TBS})DyI($THF)_2$ in C_6D_6 at 298 K (+270 to +20 ppm).

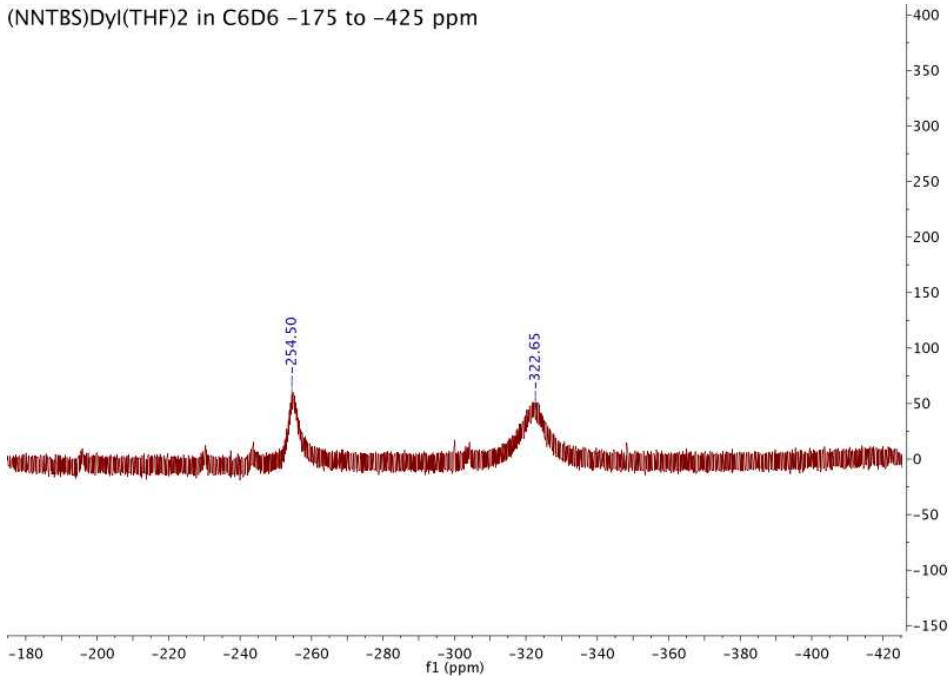

Figure S28. (NN^{TBS})DyI(THF)$_2$ in C_6D_6 at 298 K (-175 to -425 ppm).

Dy_2K_2-biph

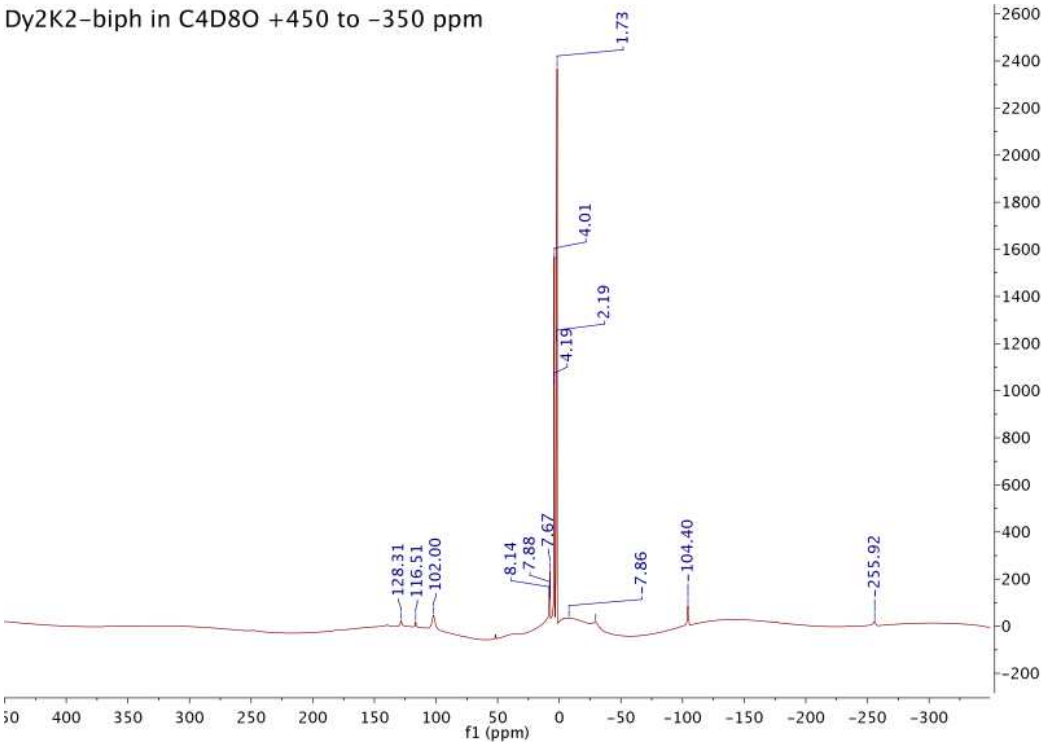

Figure S29. Dy_2K_2-biph in C_4D_8O at 298 K (+450 to -350 ppm).

Er_2K_2-biph: scan from +250 to -250 ppm with the maximum width of 200 ppm per spectrum, only spectra having significant signal(s) are shown.

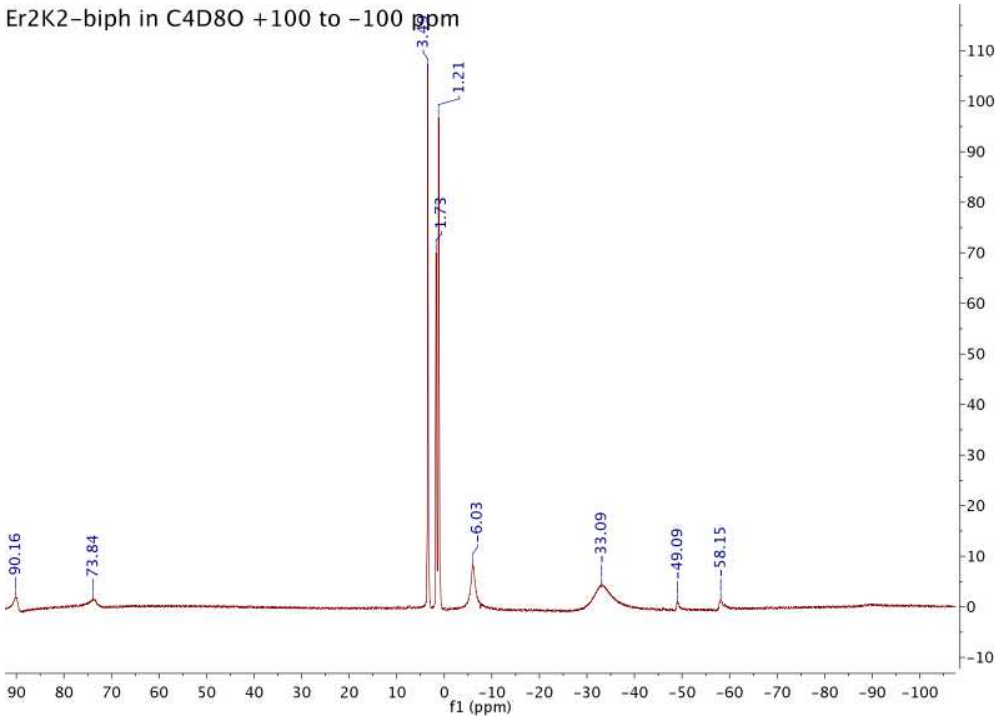

Figure S30. Er_2K_2-biph in C_4D_8O at 298 K (+100 to -100 ppm).

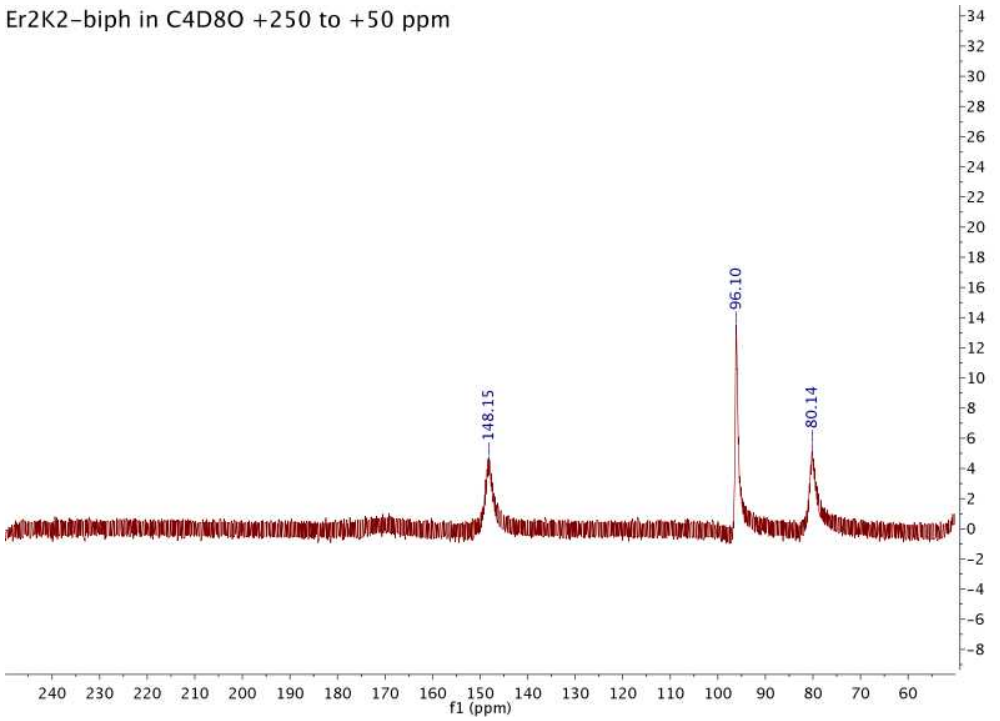

Figure S31. Er_2K_2-biph in C_4D_8O at 298 K (+250 to 50 ppm).

Gd_2K_2-biph

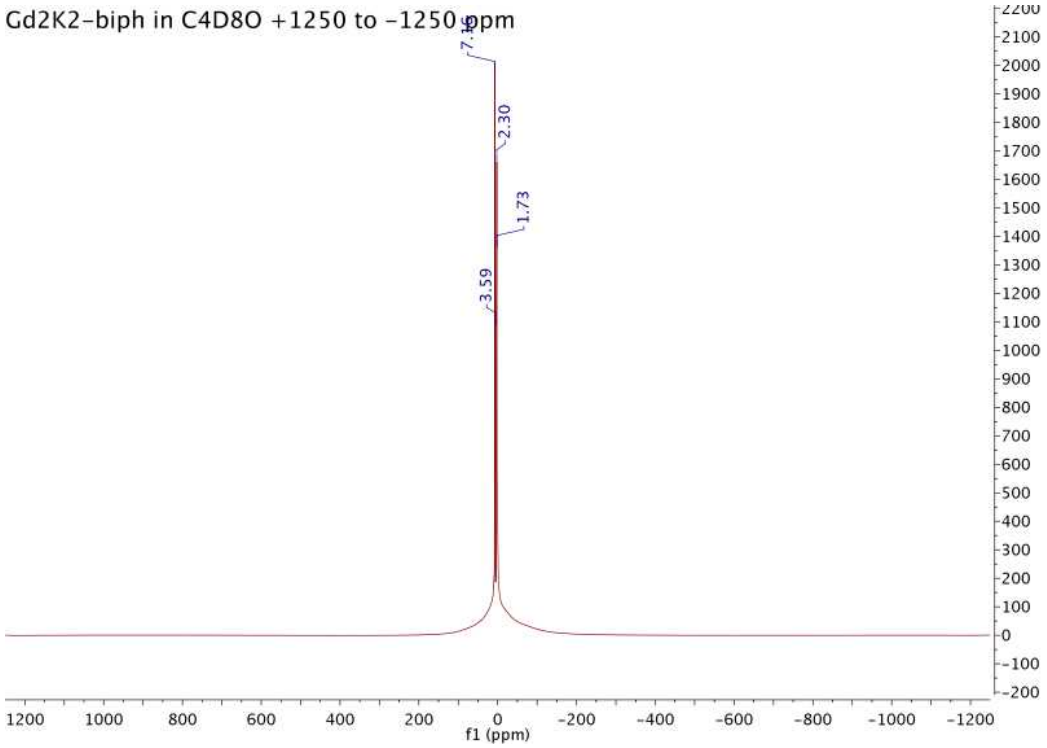

Figure S32. Gd_2K_2-biph in C_4D_8O at 298 K (+1250 to -1250 ppm).