SUPPLEMENTARY INFORMATION

Widely contrasting outcomes from the use of tris(pentafluorophenyl)bismuth or pentafluorophenylsilver as oxidants in the reactions of lanthanoid metals with N,N'-diarylformamidines

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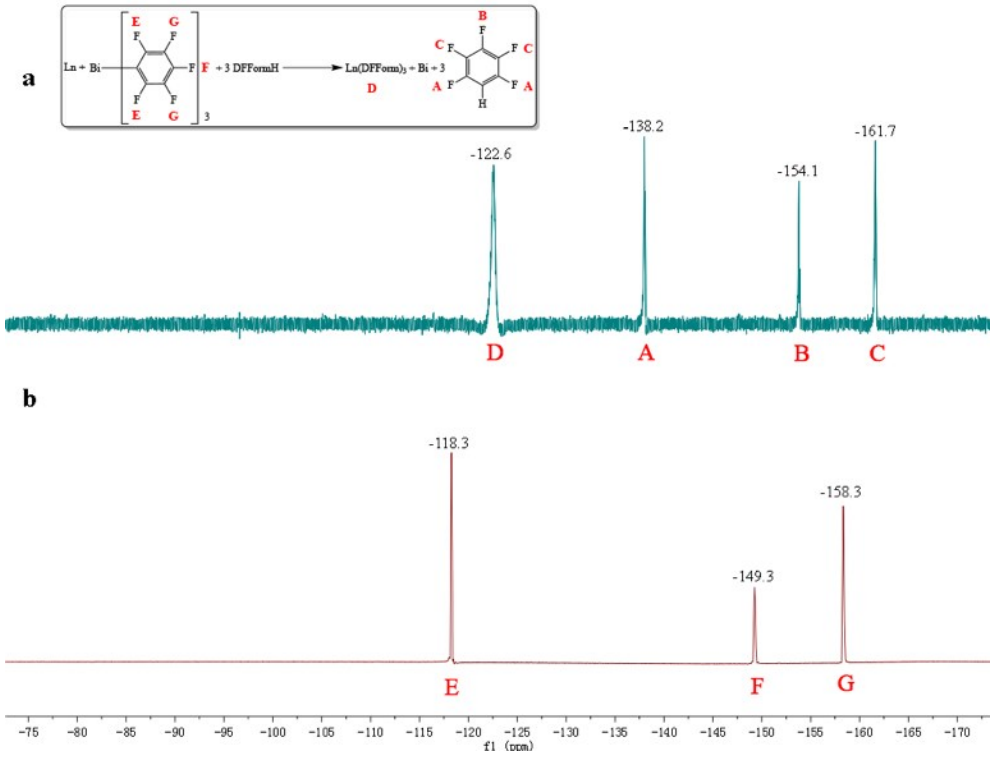

Figure S1. Typical $^{19}F\{^{1}H\}$ NMR spectra of (**a**) the reaction mixture after formation of [Ho(DFForm)$_3$(thf)] (**5**) (representative of **1-10**); (**b**) Bi(C_6F_5)$_3$

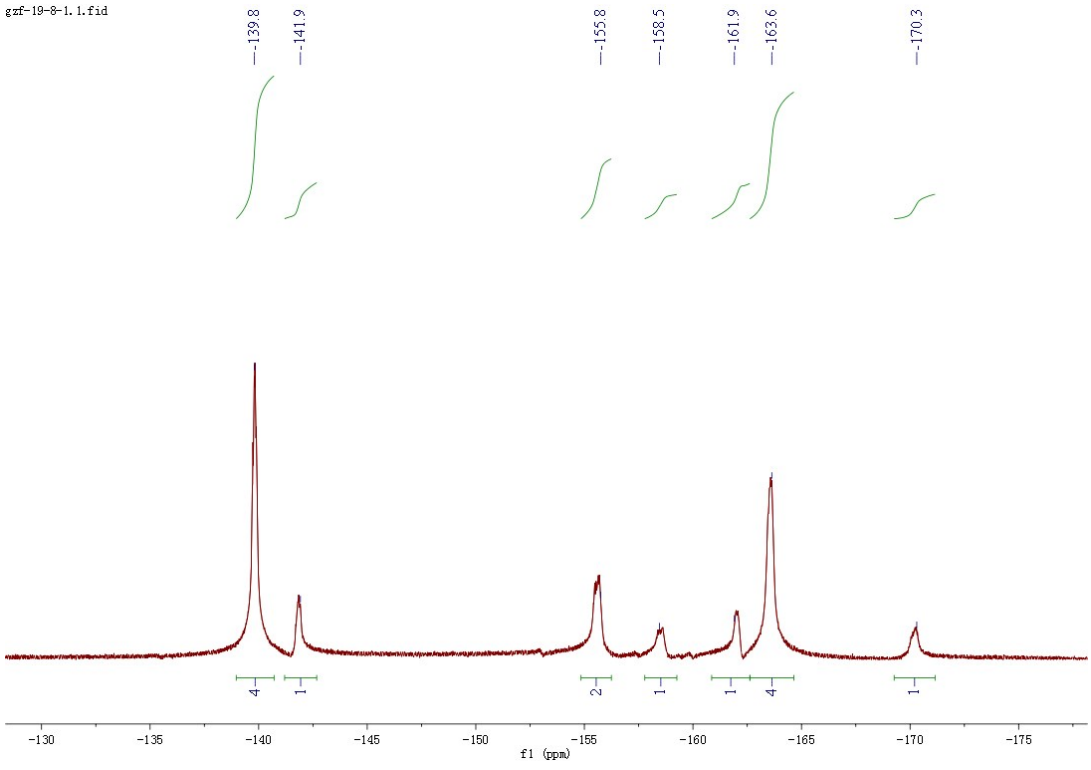

Figure S2. $^{19}F\{^{1}H\}$ NMR spectra of the reaction mixture after formation of **[Nd(DippForm)$_2$F(thf)$_2$] 12** and ***o*-HC$_6$F$_4$O(CH$_2$)$_4$DippForm** in C_6D_6

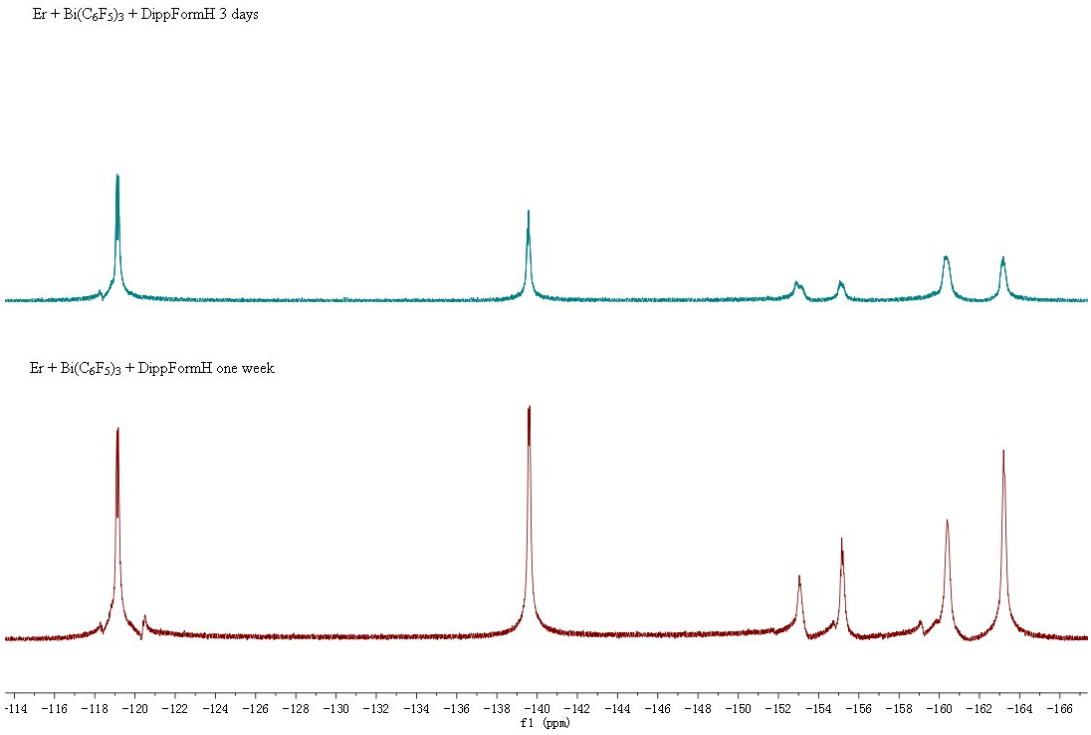

Figure S3. $^{19}F\{^{1}H\}$ NMR spectra of the reaction mixture of Er + $Bi(C_6F_5)_3$ + DippFormH after 3 days and 7 days

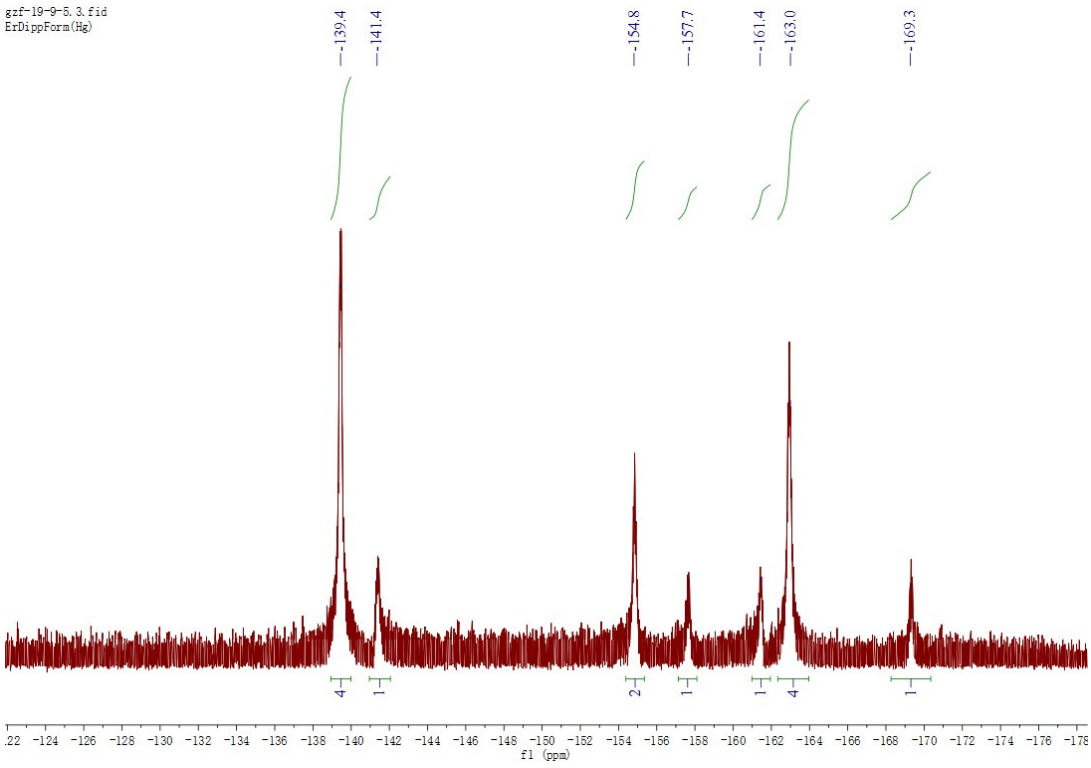

Figure S4. $^{19}F\{^{1}H\}$ NMR spectra of the reaction mixture after formation of **[Er(DippForm)$_2$F(thf)] 13** and ***o*-HC$_6$F$_4$O(CH$_2$)$_4$DippForm** in C_6D_6

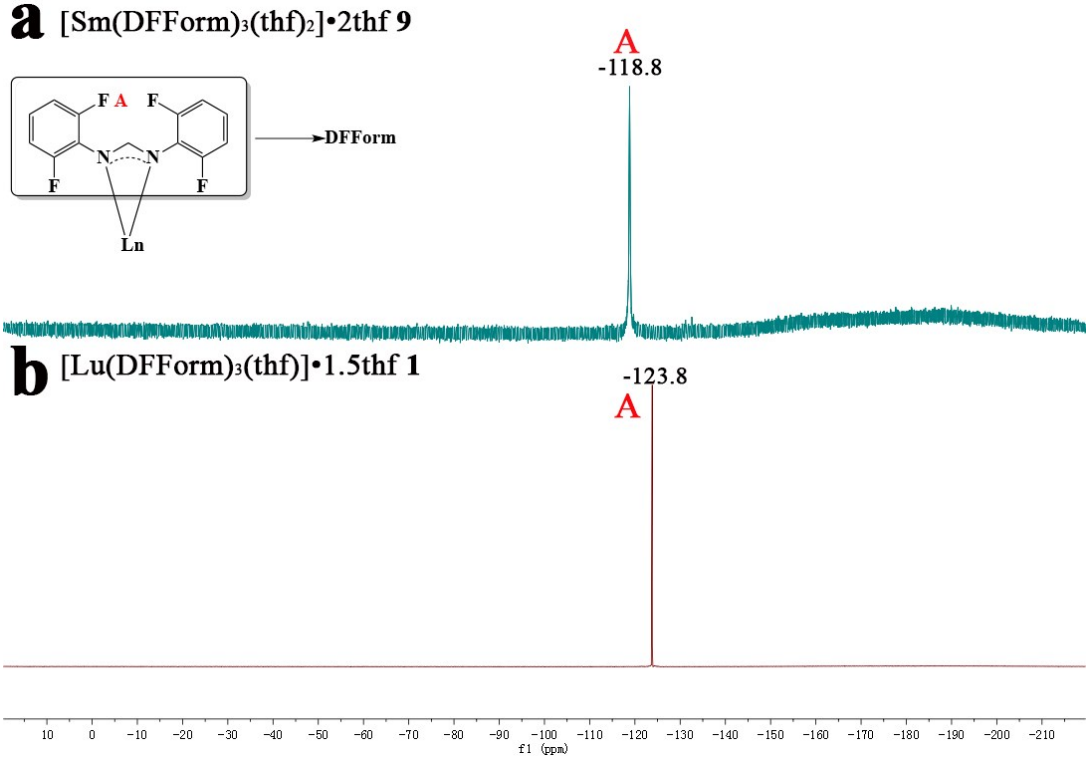

Figure S5. $^{19}F\{^{1}H\}$ NMR spectra of **[Sm(DFForm)$_3$(thf)$_2$]·2thf 9 (a)** and **[Lu(DFForm)$_3$(thf)]·1.5thf 1 (b)** in C_6D_6

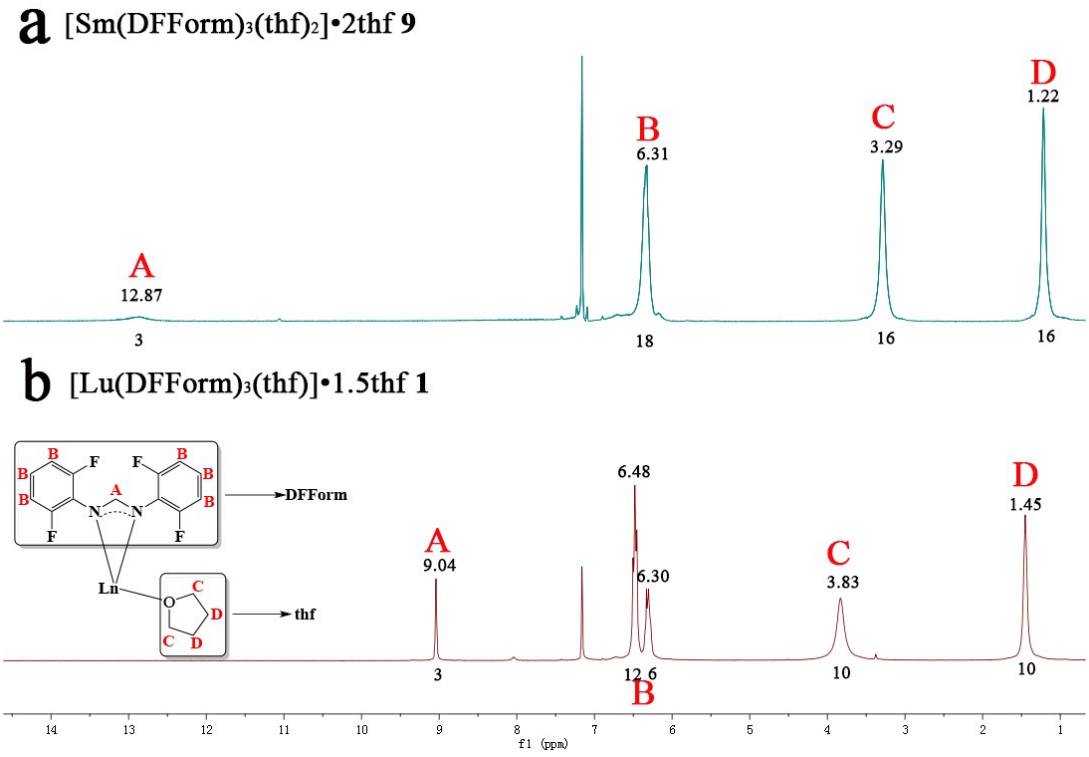

Figure S6. ^{1}H NMR spectra of **[Sm(DFForm)$_3$(thf)$_2$]·2thf 9 (a) and [Lu(DFForm)$_3$(thf)]·1.5thf 1 (b)** in C_6D_6

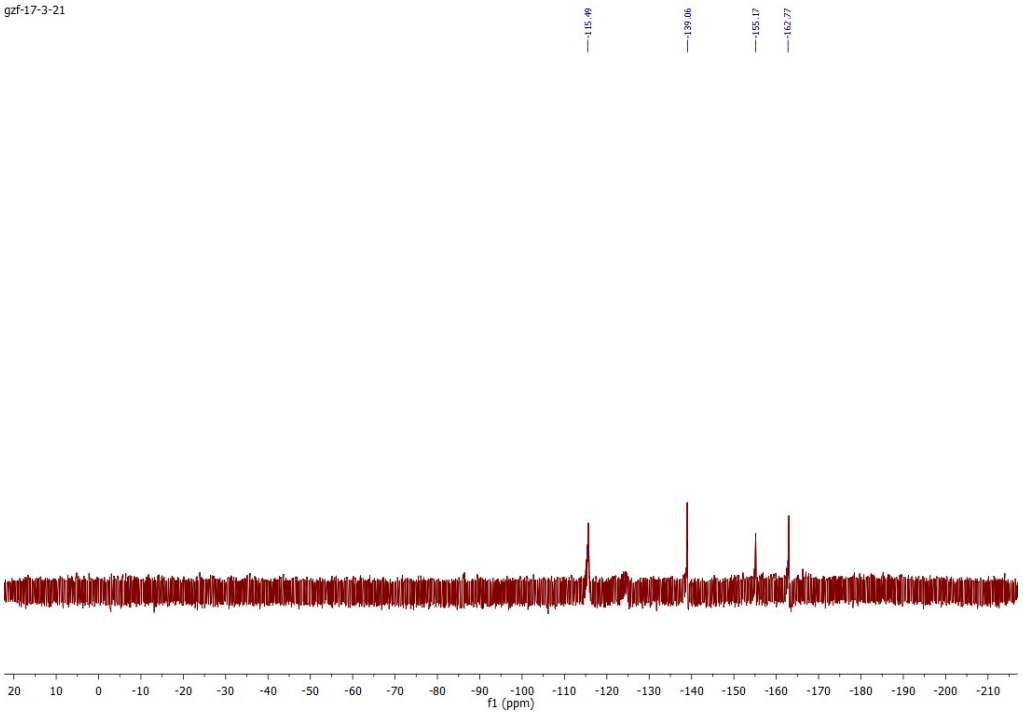

Figure S7. $^{19}F\{^{1}H\}$ NMR spectra of the reaction mixture of Yb + AgC_6F_5 + DFFormH in thf

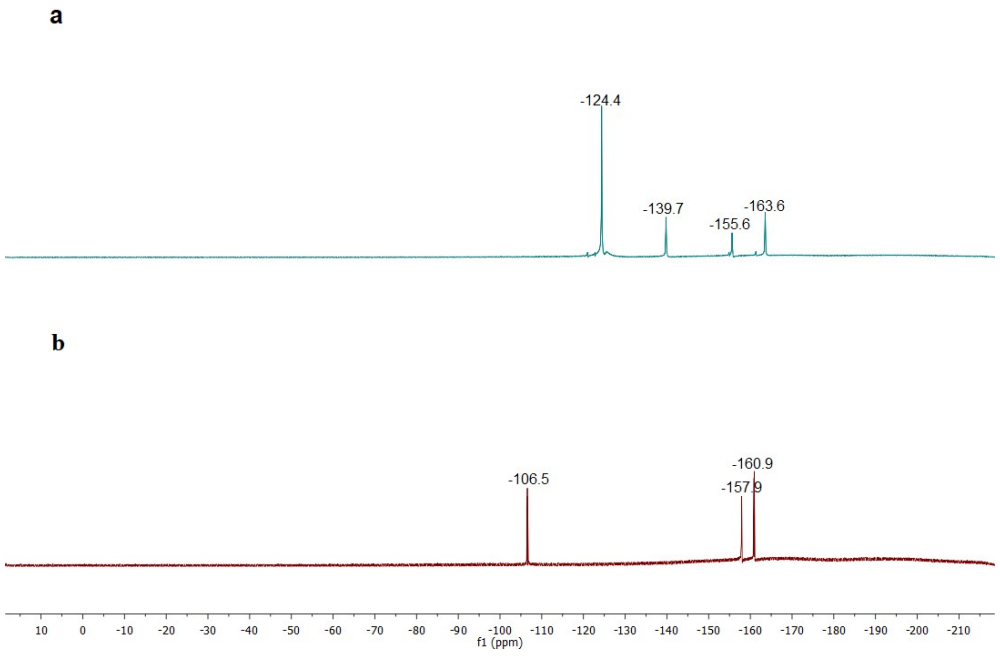

Figure S8. $^{19}F\{^{1}H\}$ NMR spectra of the reaction mixture of Er + I_2 + AgC_6F_5 + DFFormH stirring for 1h (**a**); b AgC_6F_5 (**b**)

Selected bond angles (°) and lengths (Å) for 2-5, 7, 8, and 10

2 Yb Yb-N(1) 2.409(4), Yb-N(2) 2.361(4), Yb-N(3) 2.367(4), Yb-N(4) 2.411(4), Yb-N(5) 2.362(4), Yb-N(6) 2.400(4), Yb-O(1) 2.311(3), C7-Yb-O1 118.94(14), C20-Yb-O1 102.03(13), C33-Yb-O1 84.79(14), C7-Yb-C20 96.92(14), C7-Yb-C33 116.66(14), C20-Yb-C33 137.32(14); **3** Tm-N(1) 2.388(3), Tm-N(2) 2.357(3), Tm-N(3) 2.395(3), Tm-N(4) 2.372(3), Tm-N(5) 2.388(3), Tm-N(6) 2.352(3), Tm-O(1) 2.319(3), C7-Tm-O1 132.10(10), C20-Tm-O1 93.66(10), C33-Tm-O1 90.85(10), C7-Tm-C20 105.80(11), C7-Tm-C33 101.87(10), C20-Tm-C33 137.70(10); **4 Er1** Er-N(1) 2.389(4), Er-N(2) 2.409(4), Er-N(3) 2.386(4), Er-N(4) 2.371(4), Er-N(5) 2.423(4), Er-N(6) 2.366(4), Er-O(1) 2.332(4), C7-Er-O1 133.54(15), C20-Er-O1 90.99(14), C33-Er-O1 88.83(14), C7-Er-C20 98.99(15), C7-Er-C33 108.63(15), C20-Er-C33 141.67(16); **4 Er2** Er-N(1) 2.423(4), Er-N(2) 2.361(4), Er-N(3) 2.421(4), Er-N(4) 2.398(5), Er-N(5) 2.349(5), Er-N(6) 2.384(4), Er-O(1) 2.332(4), C7-Er-O1 142.06(14), C20-Er-O1 89.63(15), C33-Er-O1 88.56(15), C7-Er-C20 102.28(16), C7-Er-C33 105.28(16), C20-Er-C33 136.83(16); **5** Ho-N(1) 2.371(5), Ho-N(2) 2.397(4), Ho-N(3) 2.372(5), Ho-N(4) 2.390(5), Ho-N(5) 2.418(5), Ho-N(6) 2.401(5), Ho-O(1) 2.328(4), C7-Ho-O1 132.33(16), C20-Ho-O1 93.33(15), C33-Ho-O1 91.12(16), C7-Ho-C20 106.66(17), C7-Ho-C33 101.07(17), C20-Ho-C33 137.48(16)

7 Tb2 Tb-N(1) 2.474(3), Tb-N(2) 2.558(3), Tb-N(3) 2.452(3), Tb-N(4) 2.527(3), Tb-N(5) 2.519(3), Tb-N(6) 2.454(3), Tb-O(1) 2.415(3), Tb-O(2) 2.404(3), O1-Tb-O2 151.24(10), C7-Tb-C20 136.56(12), C7-Tb-C33 104.25(11), C20-Tb-C33 119.16(12); **8 Gd2** Gd-N(1) 2.483(4), Gd-N(2) 2.518(4), Gd-N(3) 2.516(4), Gd-N(4) 2.526(4), Gd-N(5) 2.590(4), Gd-N(6) 2.474(4), Gd-O(1) 2.440(3), Gd-O(2) 2.419(3), O1-Gd-O2 144.35(11), C7-Gd-C20 148.44(13), C7-Gd-C33 104.93(13), C20-Gd-C33 106.55(13); **10 Nd2** Nd-N(1) 2.527(5), Nd-N(2) 2.569(4), Nd-N(3) 2.607(5), Nd-N(4) 2.541(5), Nd-N(5) 2.514(5), Nd-N(6) 2.608(5), Nd-O(1) 2.481(4), Nd-O(2) 2.477(4), O1-Nd-O2 151.34(14), C7-Nd-C20 135.91(18), C7-Nd-C33 103.82(15), C20-Nd-C33 120.19(17).

X-ray crystallography:

Single crystals coated with viscous hydrocarbon oil were mounted on glass fibres or loops. Complexes **4** were measured on a "Bruker APEX-II CCD' diffractometer equipped with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 123 K, mounted on a fibre loop in crystallography oil. Absorption corrections were completed using Apex II program suite using SADABS.[1] Complexes **1**, **3**, **9**, **12** and **18a** were measured on a Rigaku SynergyS diffractometer. The SynergyS operated using microsource Mo-Kα radiation (λ = 0.71073 Å) at 123 K. Data processing was conducted using CrysAlisPro.55 software suite.[2] Others (**2**, **5**, **6**, **7**, **8**, **10**, **13-19**, **17a** and **20**) were measured at the Australian Synchrotron on the MX1 beamline, data integration was completed using Blue-ice [3] and XDS [4] software programs. Structural solutions were obtained by either direct methods [5] or charge flipping [6] methods and refined using full-matrix least-squares methods against F^2 using SHELX2018,[7] in conjunction with the X-Seed [8] or Olex2 [6] graphical user interface. All hydrogen atoms were placed in calculated positions using the riding model. Crystal data and refinement details are given in

Table S1 and Table S2.

References

[1]. Sheldrick, G. M. SADABS; University of Gottingen, Gcottingen (Germany), 1996.

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Table S1. Crystal data and structural refinement for lanthanoids complexes **1-13**						
	1	**2**	**3**	**4**	**5**	**6**
	Lu(DFForm)$_3$(thf)]·1.5thf	[Yb(DFForm)$_3$(thf)]·thf	[Tm(DFForm)$_3$(thf)]	[Er(DFForm)$_3$(thf)]·0.25thf	[Ho(DFForm)$_3$(thf)]	[Dy(DFForm)$_3$(thf)]
Formula	$C_{98}H_{82}F_{24}Lu_2N_{12}O_5$	$C_{47}H_{37}N_6O_2F_{12}Yb$	$C_{43}H_{29}F_{12}N_6OTm$	$C_{176}H_{124}Er_4F_{48}N_{24}O_5$	$C_{43}H_{29}F_{12}HoN_6O$	$C_{43}H_{29}DyF_{12}N_6O$
M_r	2313.69	1118.86	1042.65	4236.02	1038.65	1036.22
Space group	**P**-1	**P**-1	**P**2$_1$/c	**P**-1	**P**2$_1$/c	**P**2$_1$/c
a (Å)	10.6678 (1)	10.075 (2)	12.7928 (3)	14.4237 (10)	12.763 (3)	12.807 (3)
b (Å)	11.6671 (1)	11.999 (2)	15.9417 (3)	16.3753 (12)	15.850 (2)	15.953 (3)
c (Å)	19.4498 (2)	20.207 (4)	19.8550 (4)	19.3779 (14)	19.836 (4)	19.959 (4)
α (°)	82.422(1)	84.61(3)	90	69.357(2)	90	90
β (°)	77.196(1)	82.90(3)	99.849 (2)	85.193(3)	99.86 (3)	100.06 (3)
γ (°)	88.771(1)	66.73(3)	90	69.548(2)	90	90
V (Å^3)	2339.69(4)	2224.2(9)	3989.53(15)	4009.0(5)	3953.4(14)	4015.1(14)
Z	1	2	4	1	4	4
ρ_{calc}, g cm^{-3}	1.642	1.671	1.736	1.755	1.745	1.714
μ, mm^{-1}	2.206	2.200	2.324	2.195	2.103	1.961
N_τ	49954	54985	43707	65596	28356	53465
N (R_{int})	9557(0.0503)	8997(0.0642)	8138(0.0765)	14141(0.1182)	7877(0.0854)	8110(0.0571)
$R_1(I > 2\sigma(I))$	0.0241	0.0429	0.0362	0.0439	0.0464	0.0329
wR_2 (all data)	0.0574	0.1138	0.0969	0.1208	0.1165	0.0866
GOF	1.057	1.079	1.033	1.046	0.996	1.043

	7	**8**	**9**	**10**	**12**	**13**
	[Tb(DFForm)$_3$(thf)$_2$]·thf	[Gd(DFForm)$_3$(thf)$_2$]·thf	[Sm(DFForm)$_3$(thf)$_2$]·2thf	[Nd(DFForm)$_3$(thf)$_2$]·thf	[Nd(DippForm)$_2$F(thf)$_2$]	[Er(DippForm)$_2$F(thf)]
Formula	$C_{51}H_{45}F_{12}N_6O_3Tb$	$C_{51}H_{45}F_{12}GdN_6O_3$	$C_{55}H_{53}F_{12}N_6O_4Sm$	$C_{51}H_{45}F_{12}N_6NdO_3$	$C_{58}H_{86}FN_4NdO_2$	$C_{54}H_{78}ErFN_4O$
M_r	1176.85	1175.18	1240.38	1162.17	1034.54	985.46
Space group	**P**-1	**P**-1	**P**$2_12_12_1$	**P**-1	**P**2_1/**n**	**P**2_1/**n**
a (Å)	13.510 (3)	13.550 (3)	15.0846 (2)	13.580 (3)	10.5982 (2)	20.470 (4)
b (Å)	18.030 (4)	18.070 (4)	17.6395 (3)	18.100 (4)	22.8059 (4)	12.133 (2)
c (Å)	22.570 (5)	22.500 (5)	19.6763 (3)	22.510 (5)	22.1814 (4)	21.508 (4)
α (°)	85.87(3)	85.81(3)	90	85.52(3)	90	90
β (°)	75.52(3)	75.52(3)	90	75.40(3)	95.019(2)	110.27(3)
γ (°)	69.45(3)	69.65(3)	90	69.60(3)	90	90
V (Å^3)	4983(2)	5001(2)	5235.56(14)	5018(2)	5340.72(17)	5011(2)
Z	4	4	4	4	4	4
ρ_{calc}, g cm^{-3}	1.569	1.561	1.574	1.538	1.287	1.306
μ, mm^{-1}	1.513	1.420	1.217	1.128	1.020	1.719
N_τ	104447	105125	41672	104237	61941	60702
N (R_{int})	19931(0.0529)	20032(0.0641)	10615(0.0434)	20050(0.0896)	13754(0.0436)	9826(0.0276)
$R_1(I > 2\sigma(I))$	0.0423	0.0462	0.0291	0.0557	0.0345	0.0268
wR_2 (all data)	0.1189	0.1301	0.0704	0.1612	0.0830	0.0696
GOF	1.054	1.042	1.035	1.025	1.032	1.054

	14	**15**	**16**	**17a**	**17**
	$[Ag_2(DFForm)_2]\cdot 3thf$	$[Lu(DFForm)_2(py)(thf)I]$	$\{[Tm(DFForm)_2(py)(thf)I]\cdot 1.5thf\}_2$	$[Er(DFForm)_3(py)]\cdot thf$	$\{[Er(DFForm)_2(py)(thf)I]\cdot 1.5thf\}_2$
Formula	$C_{38}H_{38}Ag_2F_8N_4O_3$	$C_{82}H_{78}F_{16}I_2Lu_2N_{10}O_5$	$C_{82}H_{78}F_{16}I_2N_{10}O_5Tm_2$	$C_{48}H_{34}ErF_{12}N_7O$	$C_{82}H_{78}Er_2F_{16}I_2N_{10}O_5$
M_r	966.46	2191.28	2179.20	1120.08	2175.86
Space group	**I2/m**	**C2/c**	**C2/c**	**P**-1	**C2/c**
a (Å)	8.8317(2)	26.598(5)	26.332(5)	11.510(2)	26.488(5)
b (Å)	17.4428(4)	20.753(4)	20.789(4)	12.020(2)	20.872(4)
c (Å)	12.0639(3)	17.735(4)	17.983(4)	16.940(3)	17.977(4)
α (°)	90	90	90	92.65(3)	90
β (°)	100.322(3)	123.82(3)	124.30(3)	96.67(3)	124.22(3)
γ (°)	90	90	90	107.52(3)	90
V (Å^3)	1828.36(8)	8133(4)	8132(4)	2211.7(9)	8218(4)
Z	2	4	4	2	4
ρ_{calc}, g cm^{-3}	1.756	1.790	1.780	1.682	1.759
μ, mm^{-1}	1.156	3.268	3.022	1.995	2.874
N_τ	13783	56724	28154	46380	50296
N (R_{int})	2654(0.0311)	8091(0.0312)	8017(0.0490)	8866(0.0284)	7587(0.1234)
$R_1(I > 2\sigma(I))$	0.0231	0.0326	0.0590	0.0242	0.0778
wR_2 (all data)	0.0548	0.0816	0.1615	0.0633	0.2351
GOF	1.057	1.080	1.072	1.102	1.097

	18a	**18**	**19**	**20**
	[Tb(DFForm)$_3$(py)]·2PhMe	[Tb(DFForm)$_2$(py)$_2$I]·PhMe	[Gd(DFForm)$_2$(py)$_2$I]·PhMe	[Yb$_2$(DippForm)$_2$O$_4$(py)$_4$]
Formula	$C_{58}H_{42}F_{12}N_7Tb$	$C_{43}H_{32}F_8IN_6Tb$	$C_{43}H_{32}F_8GdIN_6$	$C_{70}H_{90}N_8O_4Yb_2$
M_r	1223.90	1070.56	1068.89	1453.59
Space group	**P**-1	**P2/n**	**P2/n**	**P2$_1$/n**
a (Å)	11.2093(1)	11.232 (2)	11.166(2)	12.250(3)
b (Å)	11.5339(1)	13.487 (3)	13.357(3)	15.840(3)
c (Å)	20.2881(2)	13.952(3)	13.945(3)	17.389(4)
α (°)	90.183(1)	90	90	90
β (°)	103.137(1)	96.14(3)	96.10(3)	100.37(3)
γ (°)	92.010(1)	90	90	90
V (Å^3)	2552.60(4)	2101.4(7)	2068.0(7)	3319.1(12)
Z	2	2	2	2
ρ_{calc}, g cm^{-3}	1.592	1.692	1.717	1.454
μ, mm^{-1}	1.477	2.491	2.425	2.853
N_τ	48554	27124	24031	45312
N (R_{int})	10429(0.1385)	3976(0.1124)	4222(0.0369)	6495(0.0879)
$R_1(I > 2\sigma(I))$	0.0399	0.0506	0.0294	0.0441
wR_2 (all data)	0.1012	0.1250	0.0760	0.1141
GOF	1.020	1.100	1.113	1.057