Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Rare-earth Metal Complexes with Redox-Active Formazanate Ligands

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Table of Contents

I. NMR spectra

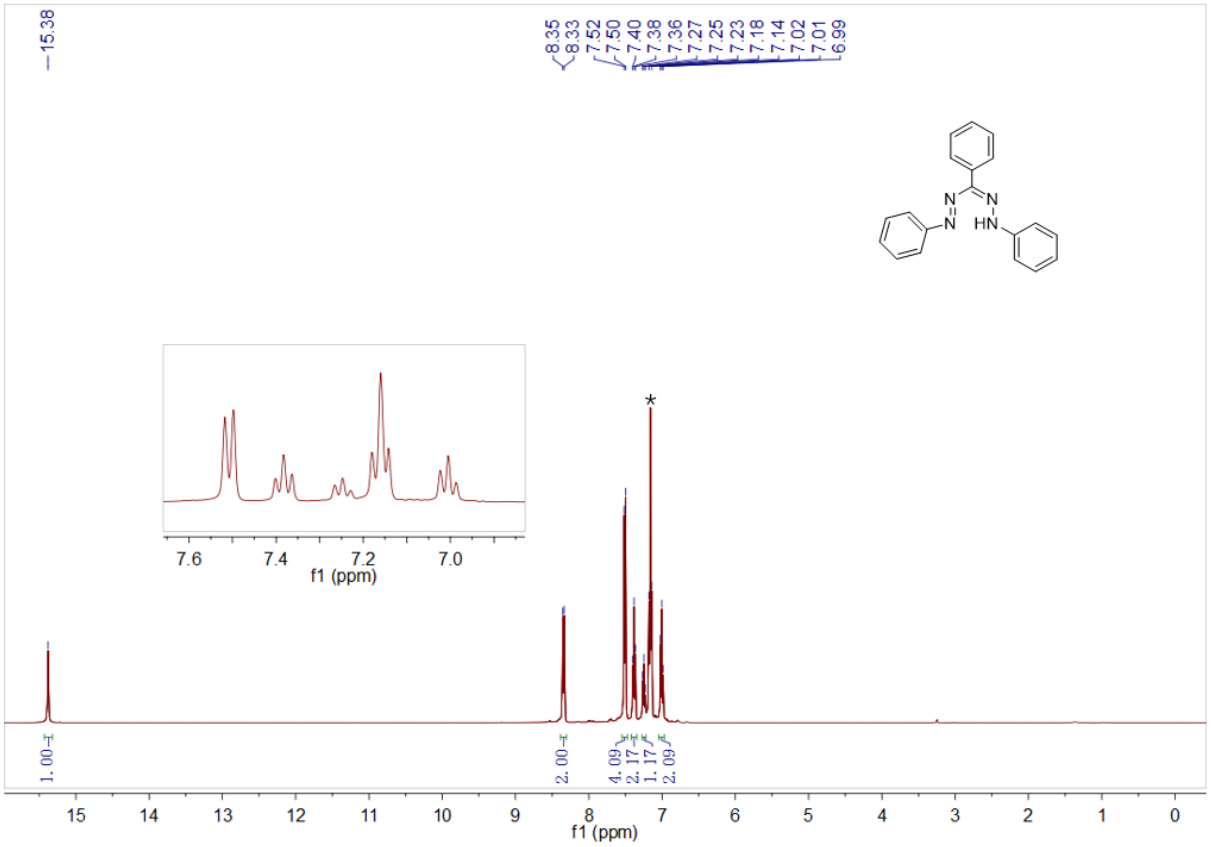

Fig. S1 ^{1}H NMR spectrum of [PhNNC(Ph)NNHPh] (**L^{1}H**) in C_6D_6, *, residual protio solvent signal.

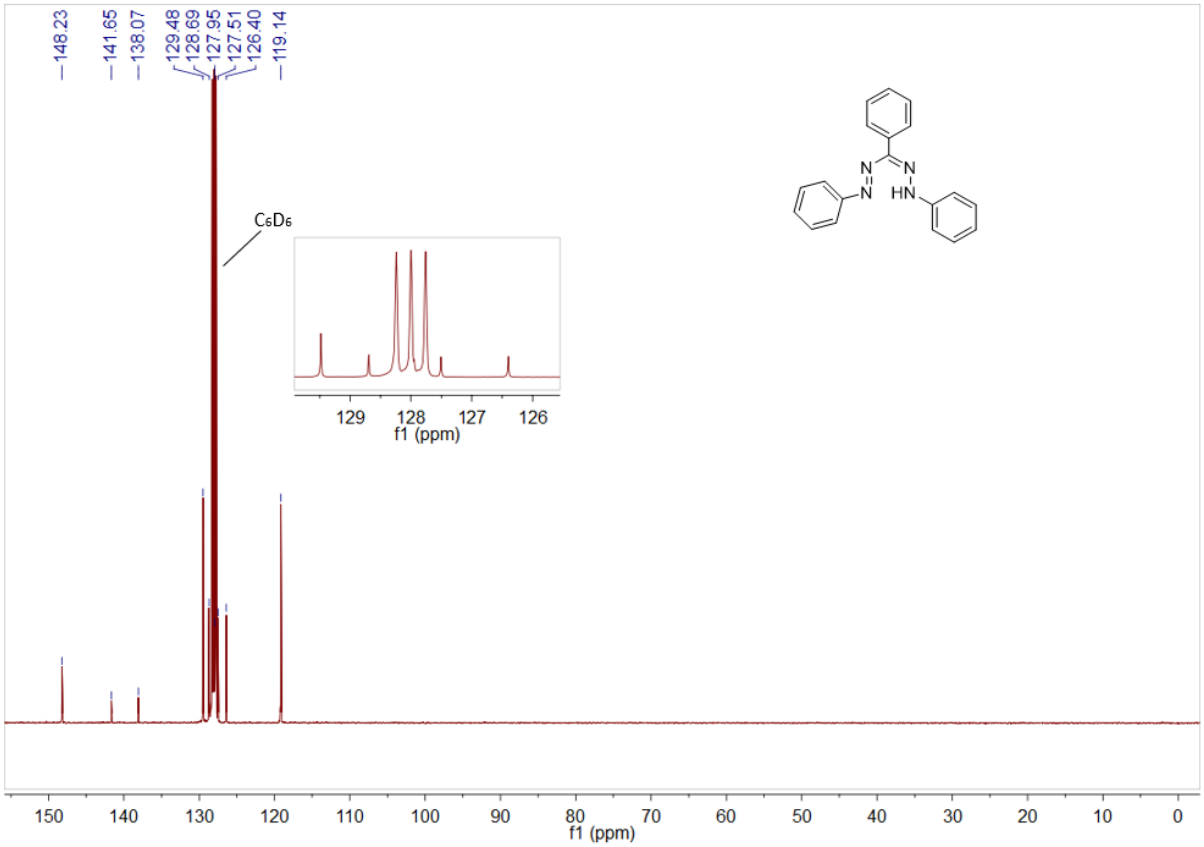

Fig. S2 ^{13}C{^{1}H} NMR spectrum of [PhNNC(Ph)NNHPh] (**L^{1}H**) in C_6D_6.

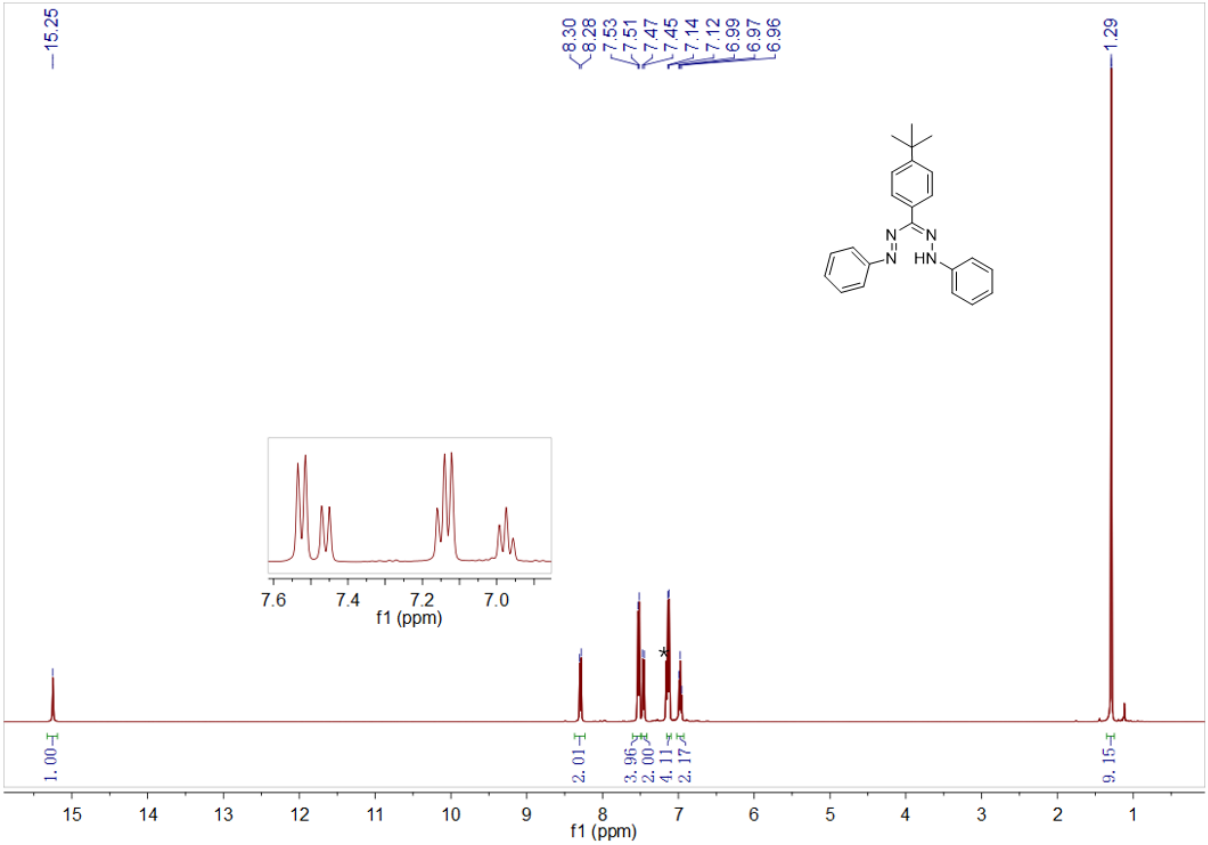

Fig. S3 ^{1}H NMR spectrum of [PhNNC(4-*t*BuPh)NNHPh] (**L^{2}H**) in C_6D_6, *, residual protio solvent signal.

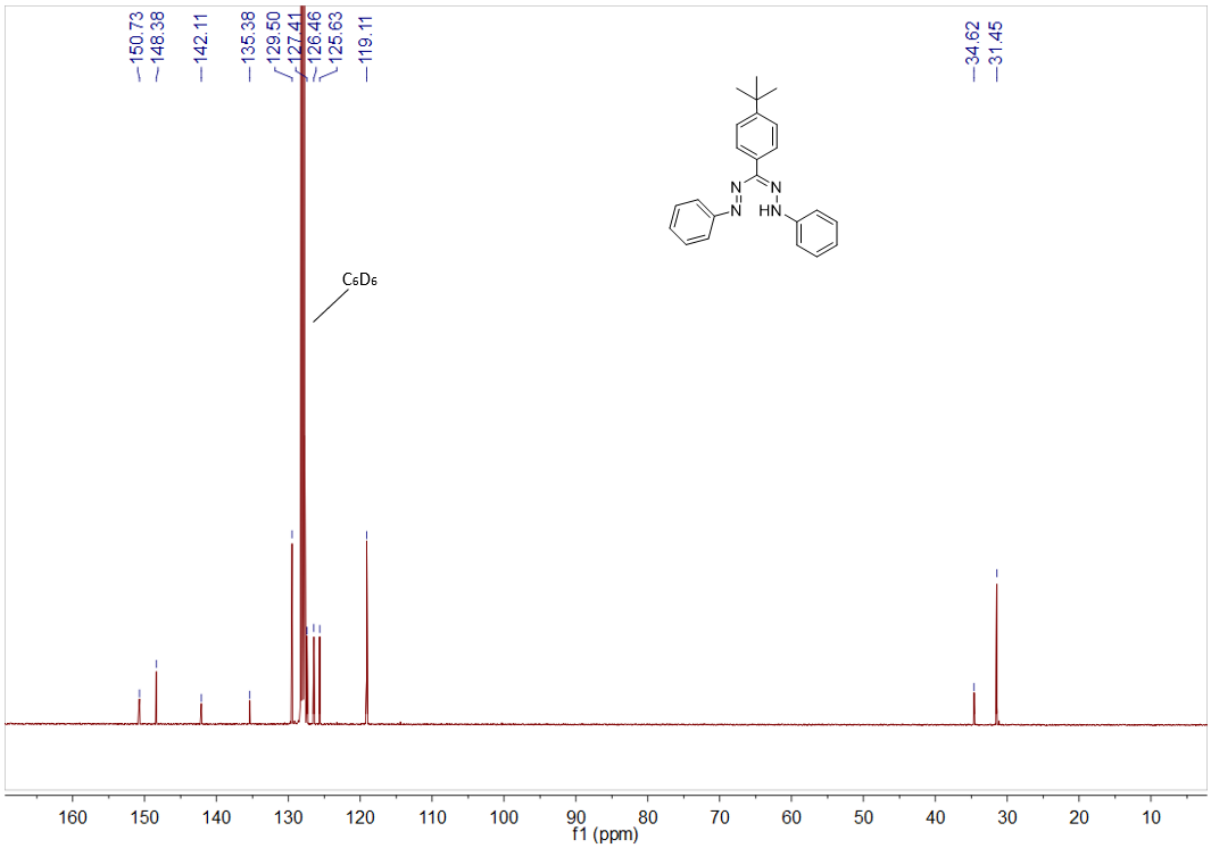

Fig. S4 ^{13}C{^{1}H} NMR spectrum of [PhNNC(4-*t*BuPh)NNHPh] (**L^{2}H**) in C_6D_6.

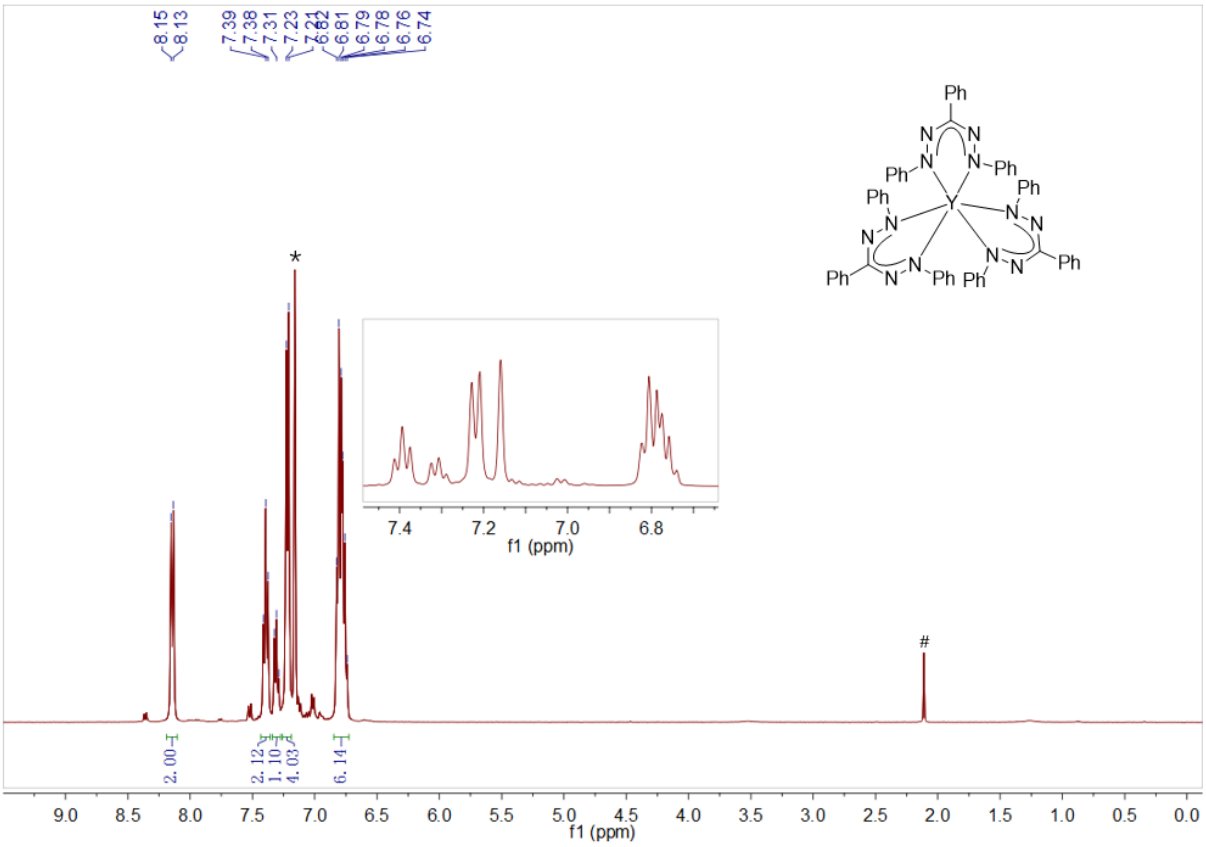

Fig. S5 ^{1}H NMR spectrum of [{PhNNC(Ph)NNPh}$_3$Y] (**1**) in C_6D_6: *, residual protio solvent signal; #, remaining toluene, which is due to incomplete drying of the crystals before measuring.

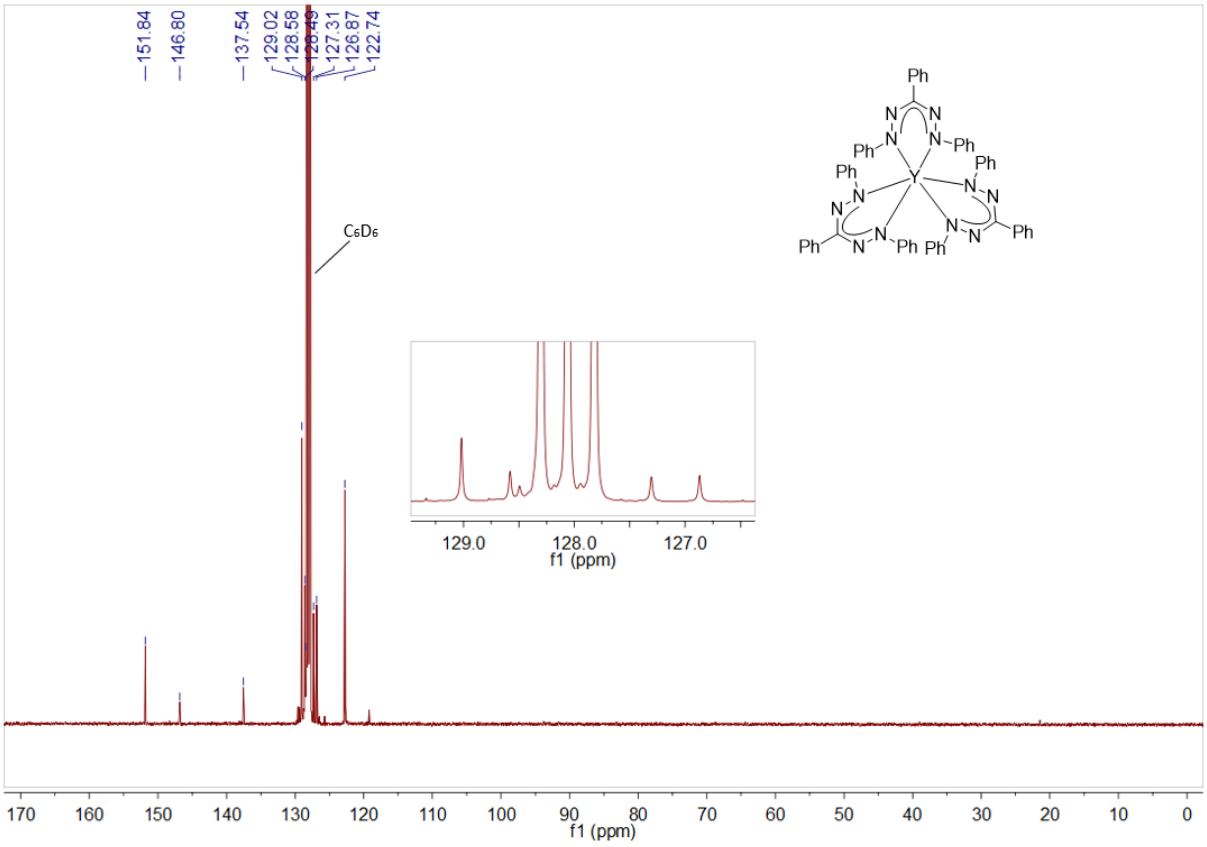

Fig. S6 ^{13}C{^{1}H} NMR spectrum of [{PhNNC(Ph)NNPh}$_3$Y] (**1**) in C_6D_6.

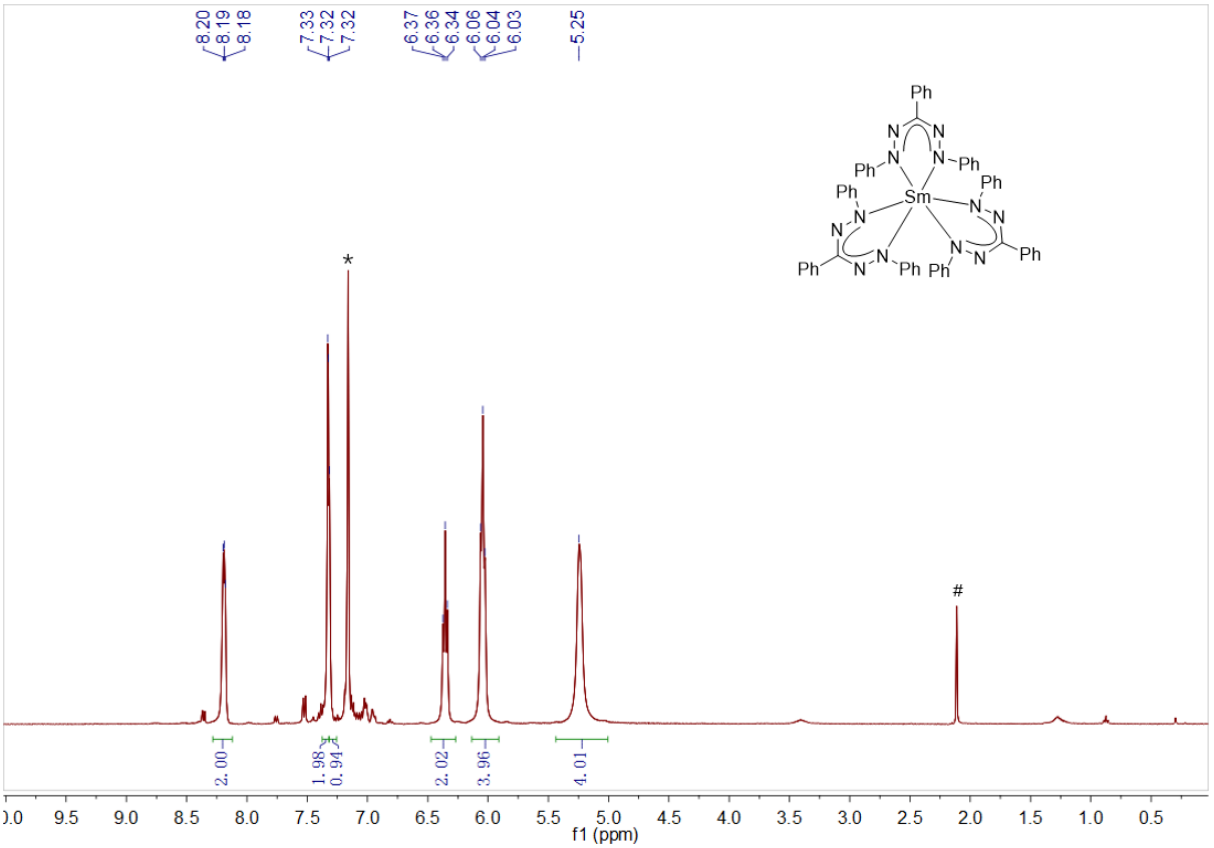

Fig. S7 ^{1}H NMR spectrum of [{PhNNC(Ph)NNPh}$_3$Sm] (**2**) in C_6D_6: *, residual protio solvent signal; #, remaining toluene, which is due to incomplete drying of the crystals before measuring.

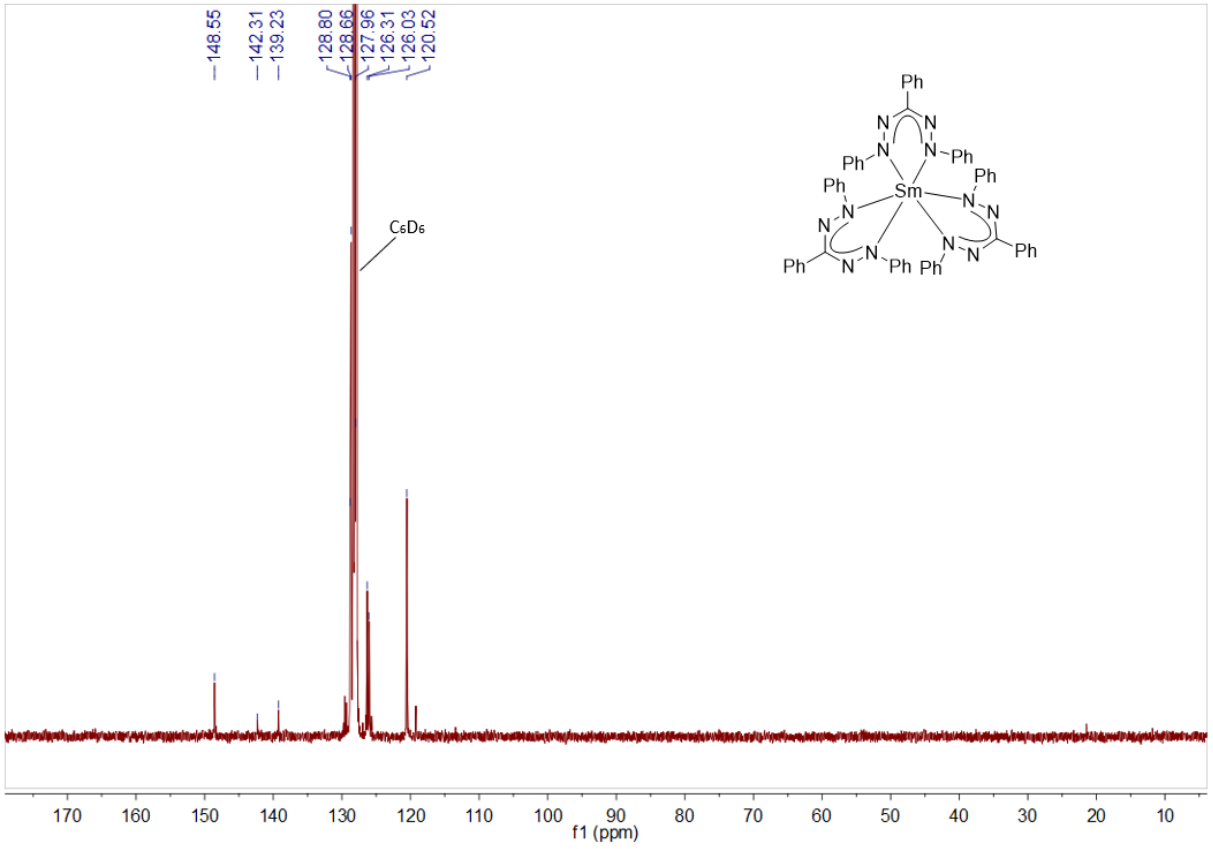

Fig. S8 ^{13}C{^{1}H} NMR spectrum of [{PhNNC(Ph)NNPh}$_3$Sm] (**2**) in C_6D_6.

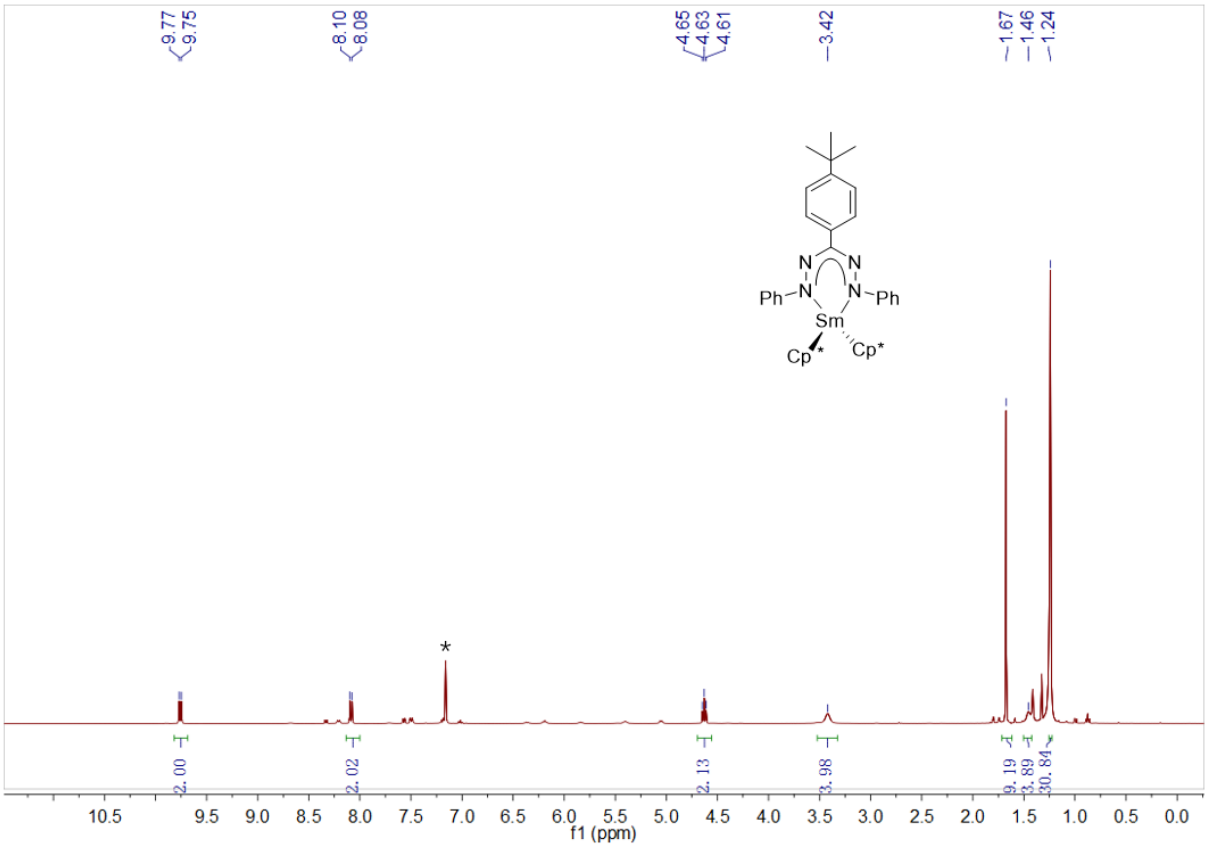

Fig. S9 ^{1}H NMR spectrum of [{PhNNC(4-*t*BuPh)NNPh}SmCp*$_2$] (**4**) in C_6D_6, *, residual protio solvent signal.

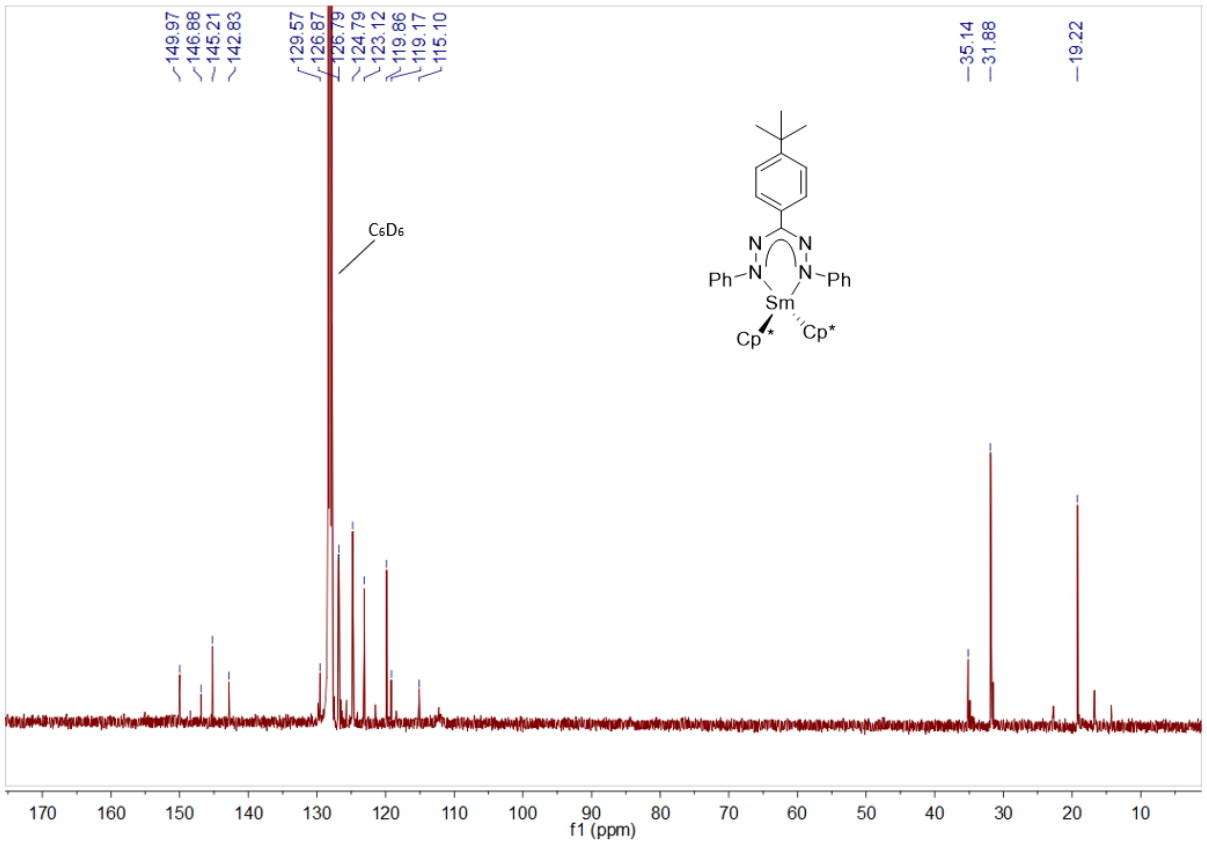

Fig. S10 ^{13}C{^{1}H} NMR spectrum of [{PhNNC(4-*t*BuPh)NNPh}SmCp*$_2$] (**4**) in C_6D_6.

II. IR spectra

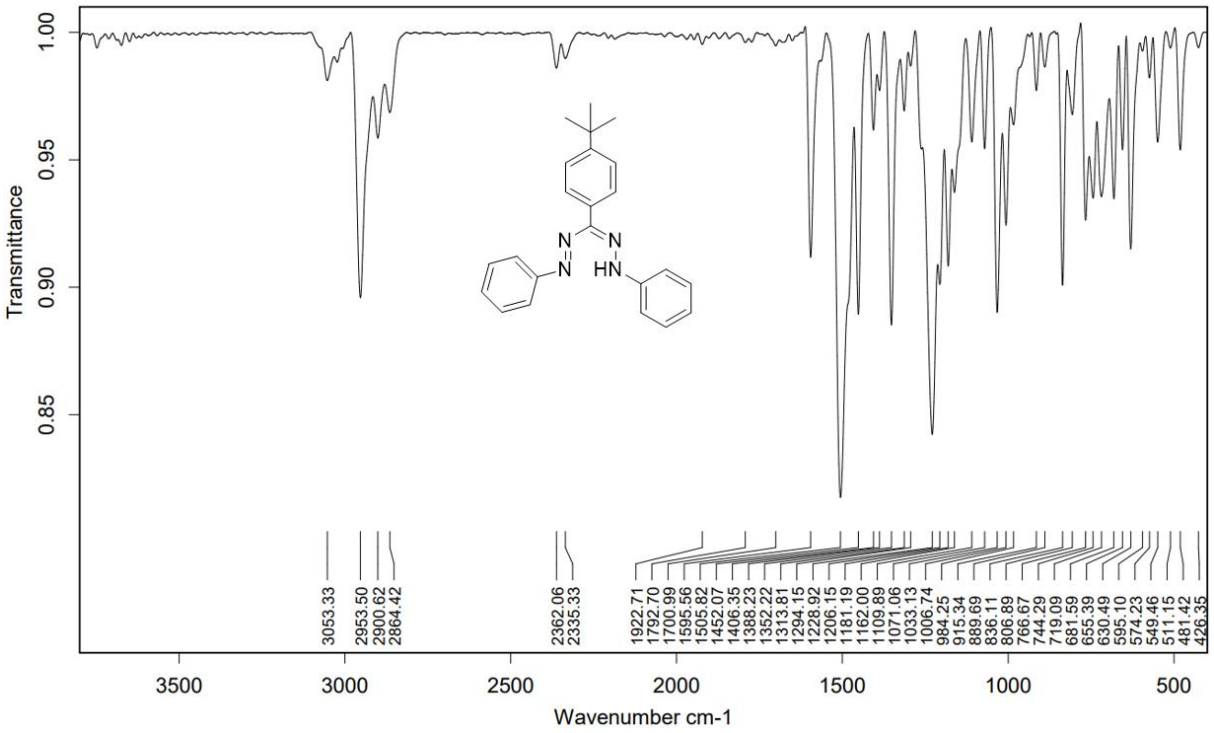

Fig. S11 IR spectrum of [PhNNC(4-*t*BuPh)NNHPh] (**L^{2}H**).

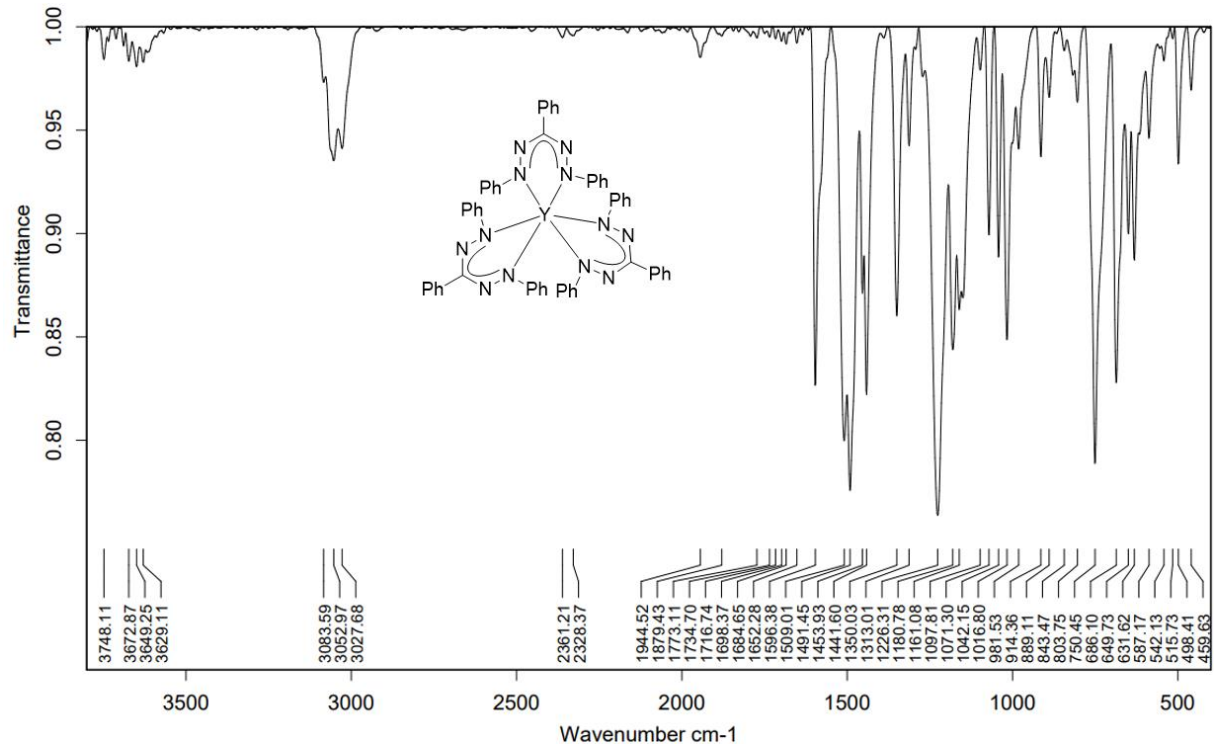

Fig. S12 IR spectrum of [{PhNNC(Ph)NNPh}$_3$Y] (**1**).

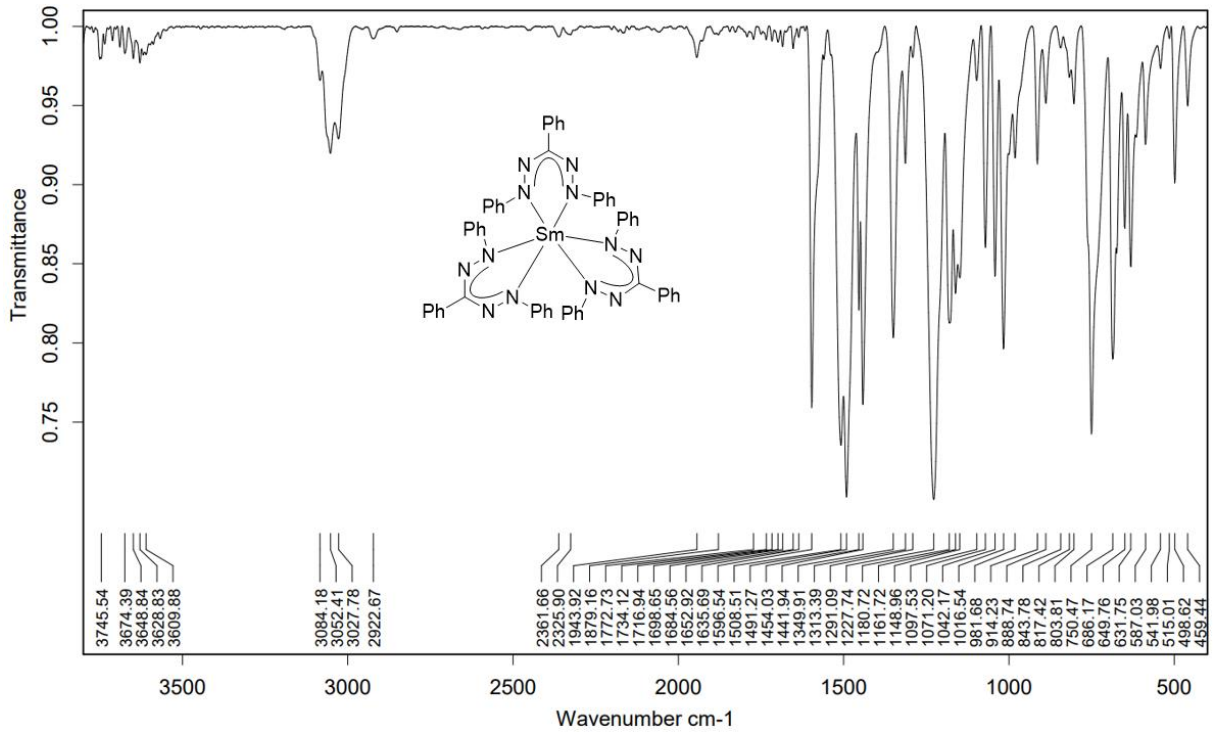

Fig. S13 IR spectrum of [{PhNNC(Ph)NNPh}$_3$Sm] (**2**).

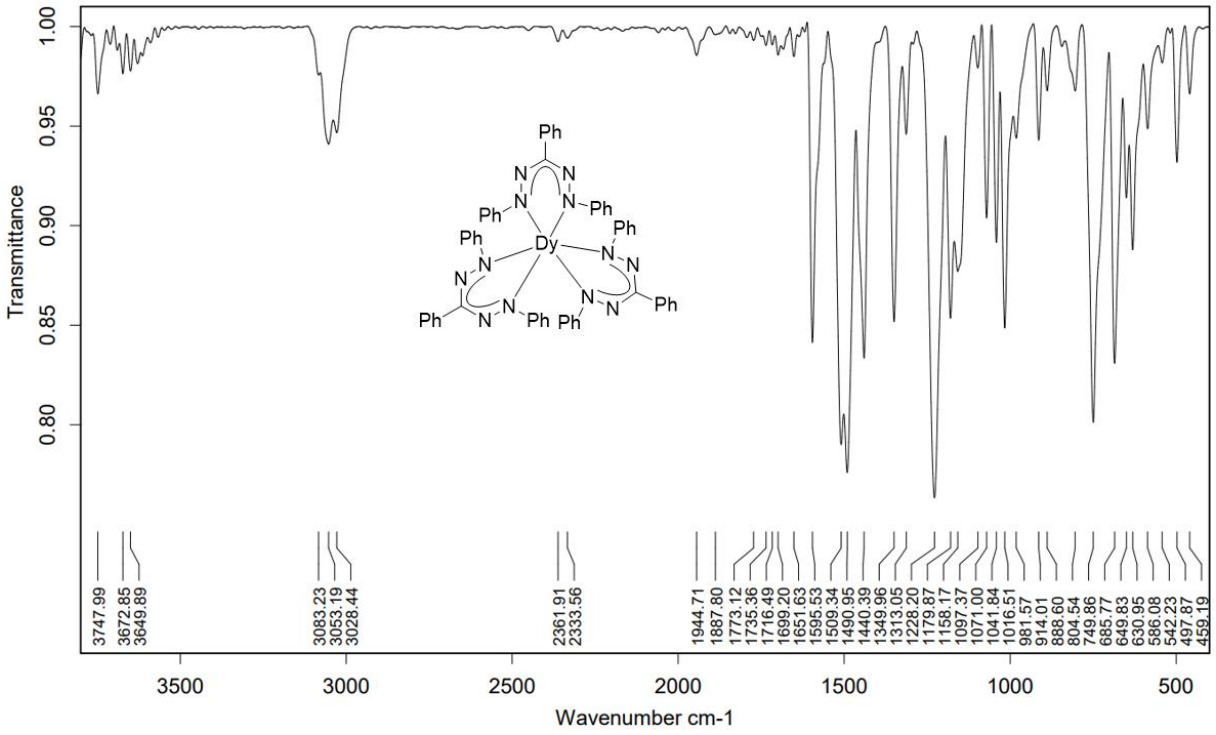

Fig. S14 IR spectrum of [{PhNNC(Ph)NNPh}$_3$Dy] (**3**).

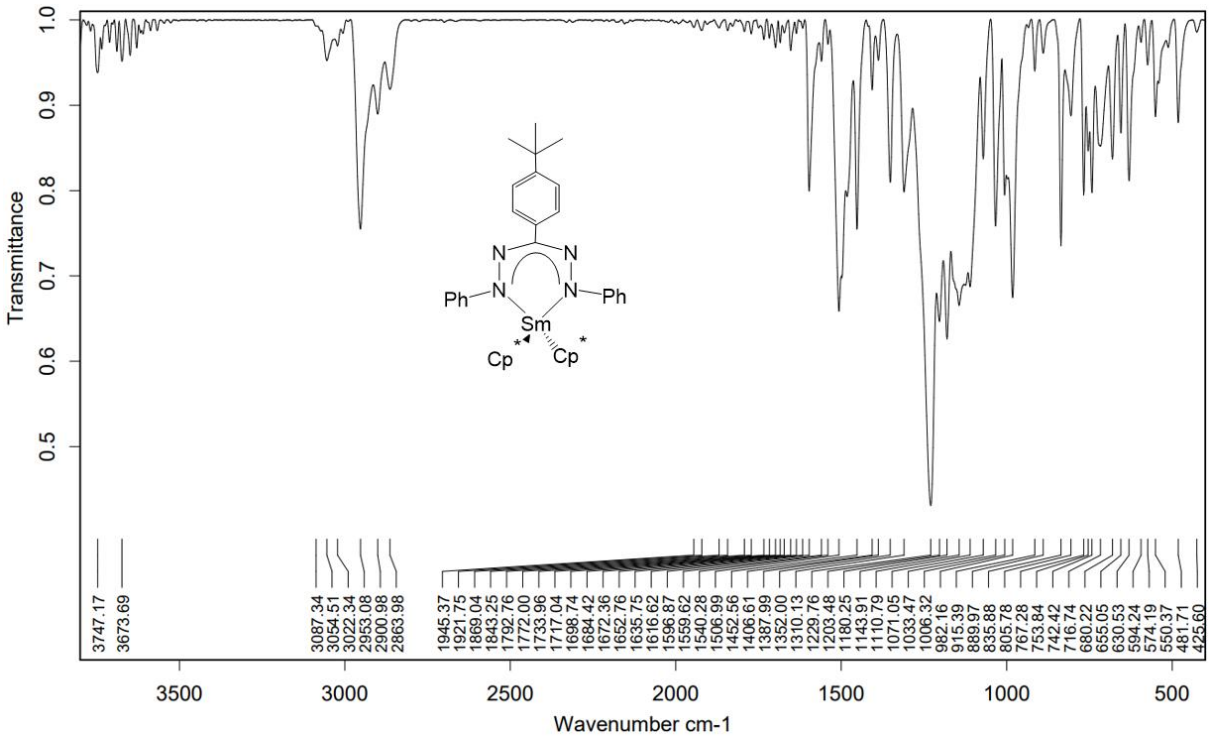

Fig. S15 IR spectrum of [{PhNNC(4-*t*BuPh)NNPh}SmCp*$_2$] (**4**).

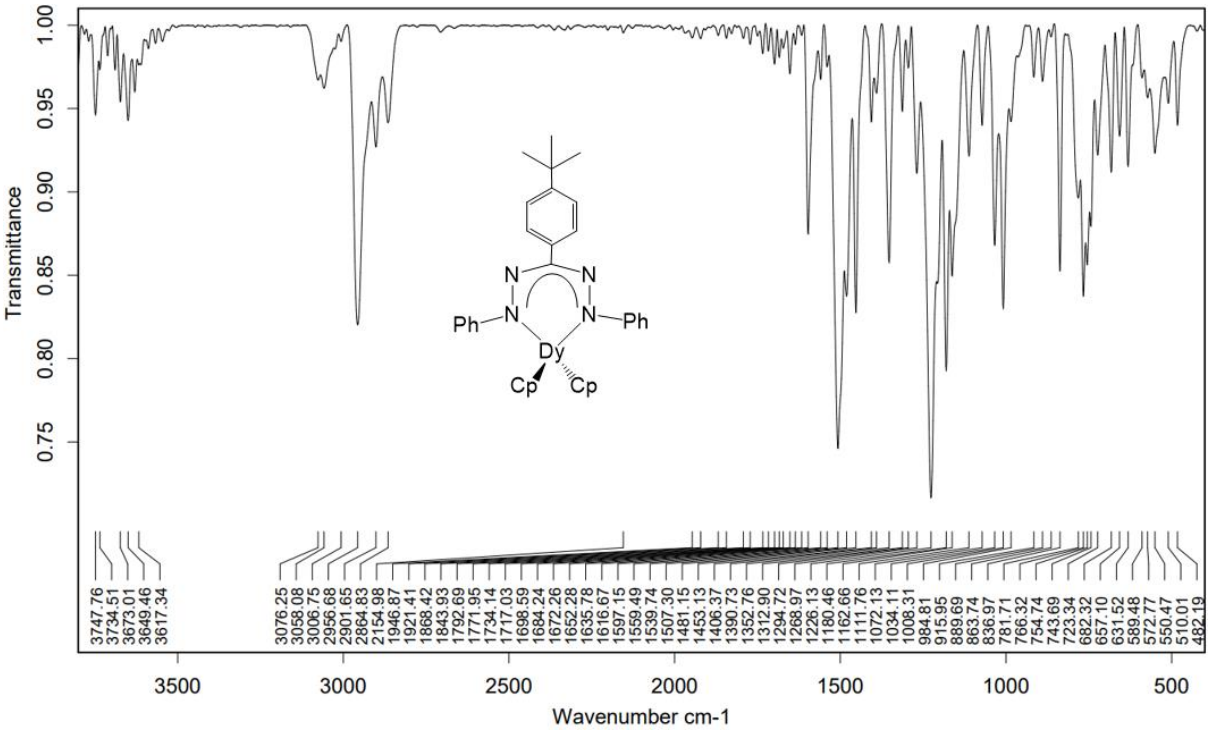

Fig. S16 IR spectrum of [{PhNNC(4-*t*BuPh)NNPh}DyCp$_2$] (**5**).

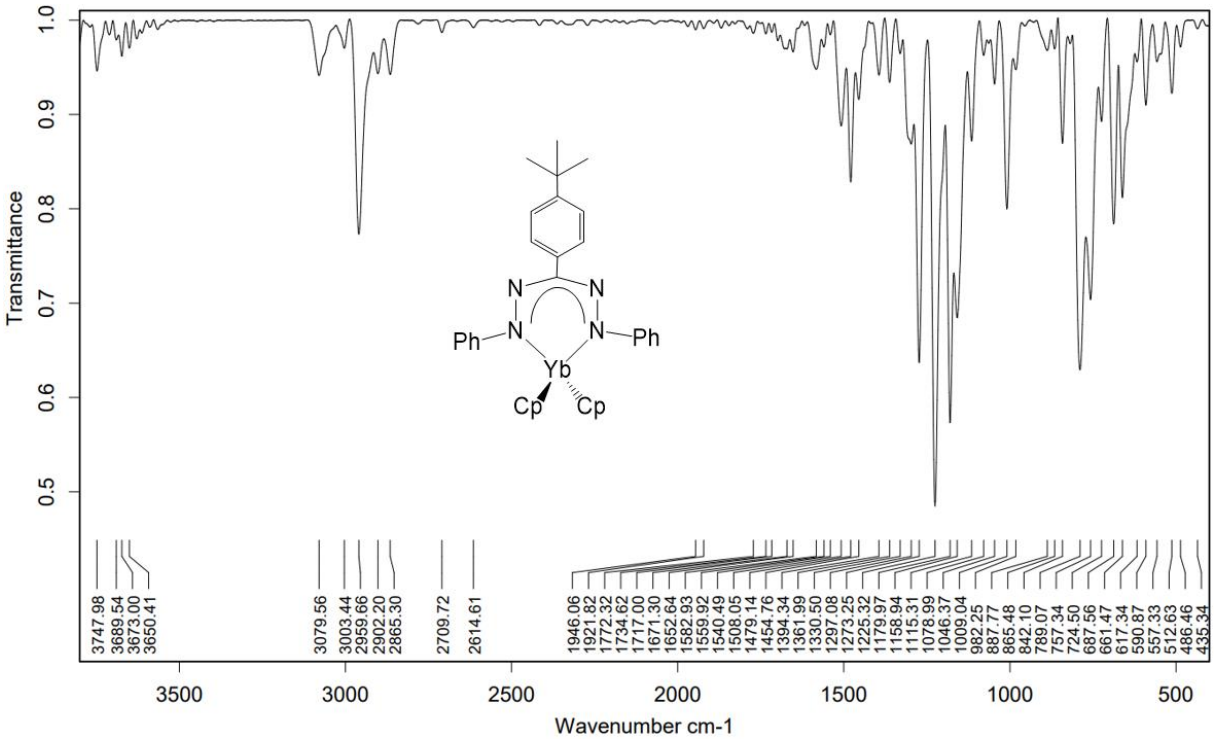

Fig. S17 IR spectrum of [{PhNNC(4-*t*BuPh)NNPh}YbCp$_2$] (**6**).

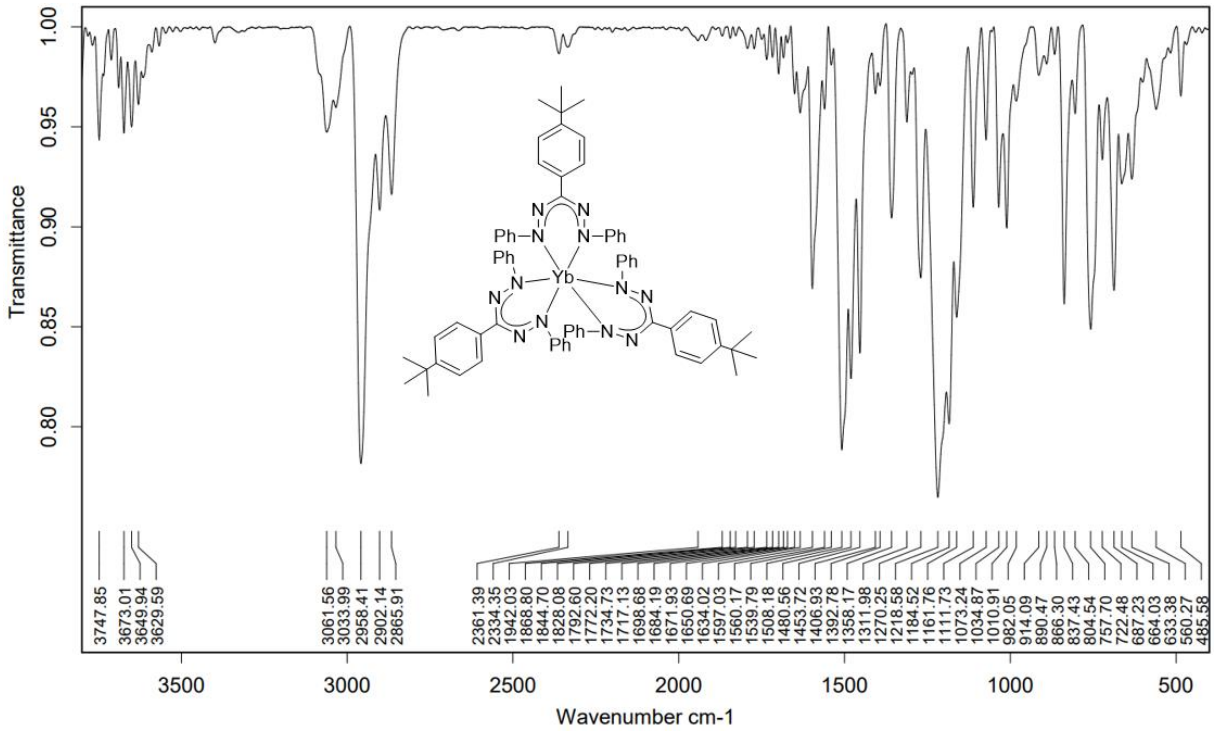

Fig. S18 IR spectrum of [{PhNNC(4-*t*BuPh)NNPh}$_3$Yb] (**7**).

III. Cyclic voltammetry (CV)

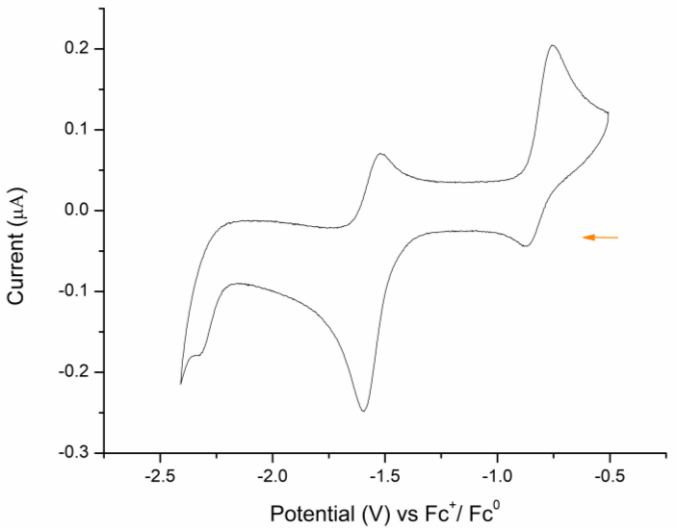

Fig. S19 Cyclic voltammogram of **L^2H** (THF, 0.1 M $[Bu_4N][PF_6]$) recorded at 250 mVs^{-1}

Table S1. Electrochemical parameters for formazan ligand (L^2H)

	E^0 vs $Fc^{/+}$ [V]				
	$(L^2)^{0/1-}(I/I')$	$(L^2)^{1-/2-}(II/II')$	$(L^2)^{2-/3-}(III/III')$	Δ'	Δ''
L^2H	-0.81	-1.55	-2.29	0.74	0.74

Table S2. Electrochemical parameters for tris-formazanate complexes

	E^0 vs $Fc^{/+}$ [V]				
	$(L^n)_3Ln^{0/1-}(I/I')$	$(L^n)_3Ln^{1-/2-}(II/II')$	$(L^n)_3Ln^{2-/3-}(III/III')$	Δ'	Δ''
$(L^1)_3Y$ (**1**)	-0.77	-1.51	-2.22	0.74	0.71
$(L^1)_3Sm$ (**2**)	-0.95	-1.71	-2.54	0.76	0.83
$(L^1)_3Dy$ (**3**)	-0.76	-1.60	-2.46	0.84	0.86
$(L^2)_3Yb$ (**7**)	-0.76	-1.53	-2.32	0.77	0.79

n = 1 or 2

Table S3. Electrochemical parameters for mono-formazanate complexes

	E^0 vs $Fc^{/+}$ [V]				
	$L^2LnR_2^{0/1-}(I/I')$	$L^2LnR_2^{1-/2-}(II/II')$	$L^2LnR_2^{2-/3-}(III/III')$	Δ'	Δ''
$L^2SmCp^*_2$ (**4**)	-0.78	-1.60	-2.42	0.82	0.82
L^2DyCp_2 (**5**)	-0.82	-1.57	-2.30	0.75	0.73
L^2YbCp_2 (**6**)	-0.76	-1.51	-2.25	0.75	0.74

R = Cp or Cp^*

IV. UV-Vis spectroscopy

Table S4. UV-Vis spectroscopic data for compounds **1**–**7**

Subestance	Absorption Max / nm	Extinction coefficient ($L \cdot mol^{-1} \cdot cm^{-1}$)
Compound **1**	300, 489,540	251474, 171878, 117488
Compound **2**	300, 489,540	210340, 135800, 100800
Compound **3**	300, 489, 540	184230, 120874, 79056
Compound **4**	299, 410, 484	77710, 40266, 40724
Compound **5**	301, 410, 480	62370, 51100, 30394
Compound **6**	296, 405, 479	88800, 83140, 46920
Compound **7**	300, 494	72880, 40658, 31044

See also video for the experimental setup.

V. X-ray crystallographic studies

1) General methods

A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fiber. The crystal was transferred directly to the cold stream of a STOE IPDS 2 or a STOE StadiVari diffractometer. All structures were solved by using the program SHELXS/T[1, 2] and Olex2.[3] The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F^2 by using the program SHELXL.[1, 2] In each case, the locations of the largest peaks in the final difference Fourier map calculations, as well as the magnitude of the residual electron densities, were of no chemical significance. Specific comments for each data set are given below.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC 2120929-2120935. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+(44)1223-336-033; email: deposit@ccdc.cam.ac.uk). Summary of the crystal data, data collection and refinement for compounds are given in Table S5 and Table S6.

The following special comments apply to the models of the structures:

-In the crystal structure of **4**, the *t*Bu group (C8-C11) is disordered over two positions with an occupancy of 0.53/0.46.

-In the crystal structure of **5**, the *t*Bu group (C8-C11) is disordered over two positions with an occupancy of 0.51/0.49.

2) Summary of crystal data

Table S5: Crystal data and structure refinement of **1**-**3**.

Compound	1	2	3
Formula	$C_{57}H_{45}N_{12}Y$	$C_{57}H_{45}N_{12}Sm$	$C_{57}H_{45}N_{12}Dy$
$D_{calc.}$/ g cm^{-3}	1.405	1.496	1.524
μ/mm^{-1}	1.304	1.316	1.672
Formula Weight	986.96	1048.41	1060.55
Colour	red	red	red
Shape	fragment	fragment	plate
Size/mm^3	0.36x0.31x0.29	0.25x0.16x0.08	0.15x0.11x0.05
***T*/K**	150	100	100
Crystal System	triclinic	triclinic	triclinic
Space Group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
***a*/Å**	12.7048(6)	12.7070(9)	12.6707(8)
***b*/Å**	13.1743(5)	13.1135(10)	13.1442(8)
***c*/Å**	15.8425(7)	15.8352(9)	15.7479(13)
α/°	97.320(3)	97.146(6)	97.226(6)
β/°	91.965(3)	92.198(5)	92.117(6)
γ/°	116.855(3)	116.609(6)	116.709(5)
***V*/Å^3**	2333.74(18)	2327.7(3)	2311.3(3)
Z	2	2	2
Z'	1	1	1
Wavelength/Å	0.71073	0.71073	0.71073
Radiation type	MoK_α	MoK_α	MoK_α
Θ_{min}/°	1.755	1.759	1.809
Θ_{max}/°	29.264	31.410	31.397
Measured Refl.	24350	22800	20709
Independent Refl.	12536	12300	12170
Reflections with I > 2(I)	9751	10797	9617
R_{int}	0.0239	0.0289	0.0659
Parameters	631	631	631
Restraints	0	0	0
Largest Peak	0.52	1.06	2.45
Deepest Hole	-0.20	-0.87	-1.75
GooF	1.020	1.035	1.018
wR_2 **(all data)**	0.1040	0.0784	0.1538
wR_2	0.0975	0.0747	0.1397
R_1 **(all data)**	0.0580	0.0397	0.0829
R_1	0.0394	0.0315	0.0596

Table S6: Crystal data and structure refinement of **4-7**.

Compound	4	5	6	7
Formula	$C_{43}H_{53}N_4Sm$	$C_{33}H_{33}N_4Dy$	$C_{33}H_{33}N_4Yb$	$C_{76}H_{86}N_{12}Yb$(1.5 pentane)
$D_{calc.}$/ g cm^{-3}	1.370	1.525	1.543	1.288
μ/mm^{-1}	1.594	2.675	3.340	1.397
Formula Weight	776.24	648.13	658.67	1347.62
Colour	dark red	dark red	dark red	dark red
Shape	plate	fragment	thin plate	block
Size/mm^3	0.22x0.17x0.11	0.52x0.40x0.20	0.27x0.20x0.06	0.32x0.22x0.15
***T*/K**	100	150	100	150
Crystal System	monoclinic	monoclinic	monoclinic	triclinic
Space Group	$P2_1/c$	$P2_1$	$P2_1$	$P\bar{1}$
***a*/Å**	22.8627(11)	10.179(2	10.179(2)	12.4474(10)
***b*/Å**	10.1803(5)	11.509(2)	11.509(2)	15.2412(10)
***c*/Å**	17.1284(8)	12.716(3)	12.716(3)	19.8619(19)
α/°	-	-	-	81.535(7)
β/°	109.217(4)	108.62(3)	108.62(3)	80.353(7)
γ/°	-	-	-	69.971(6)
***V*/Å^3**	3764.5(3)	1411.6(5)	1411.6(5)	3473.7(5)
Z	4	2	2	2
Z'	1	1	1	1
Wavelength/Å	0.71073	0.71073	0.71073	0.71073
Radiation type	MoK_α	MoK_α	MoK_α	MoK_α
Θ_{min}/°	2.212	1.690	2.111	1.686
Θ_{max}/°	30.061	29.848	31.708	29.527
Measured Refl.	17565	23042	21895	40105
Independent Refl.	9548	7733	5288	19291
Reflections with I > 2(I)	6259	7090	5028	15030
R_{int}	0.0636	0.0523	0.0780	0.0366
Parameters	486	386	346	842
Restraints	10	1	655	86
Largest Peak	1.88	2.53	3.61	1.94
Deepest Hole	-2.08	-3.06	-4.33	-1.48
GooF	0.959	1.026	1.239	0.977
wR_2 **(all data)**	0.1695	0.1421	0.1809	0.0954
wR_2	0.1498	0.1403	0.1872	0.0901
R_1 **(all data)**	0.0994	0.0582	0.0837	0.0582
R_1	0.0628	0.0546	0.0768	0.0395

3) Crystal structures

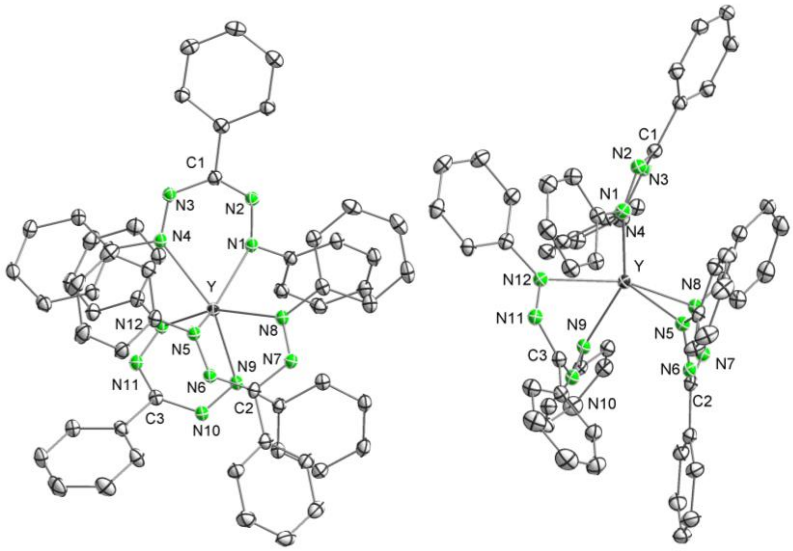

Fig. S20 Molecular structure of **1** in the solid state with thermal ellipsoids at the 30% probability level (left: front view; right: side view). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles [°]: Y-N1 2.315(2), Y-N4 2.429(2), Y-N5 2.377(2), Y-N8 2.392(2), Y-N9 2.351(2), Y-N12 2.382(2), N1-N2 1.315(2), N3-N4 1.303(2), N5-N6 1.320(2), N7-N8 1.316(2), N9-N10 1.322(2), N11-N12 1.306(2), N2-C1 1.336(2), N3-C1 1.362(2), N6-C2 1.345(2), N7-C2 1.351(2), N10-C3 1.359(2), N11-C3 1.358(2); N1-Y-N4 70.74(5), N5-Y-N8 66.71(5), N9-Y-N12 70.85(5), N2-N1-Y 132.77(12), N1-N2-C1 120.82(15), N4-N3-C1 121.3(2), N3-N4-Y 131.16(11), N6-N5-Y 115.19(12), N5-N6-C2 120.4(2), N8-N7-C2 119.36(15), N7-N8-Y 116.52(11), N10-N9-Y 105.67(11), N9-N10-C3 119.3(2), N12-N11-C3 121.21(15), N11-N12-Y 103.71(11), N2-C1-N3 129.1(2), N6-C2-N7 125.1(2), N10-C3-N11 126.8(2).

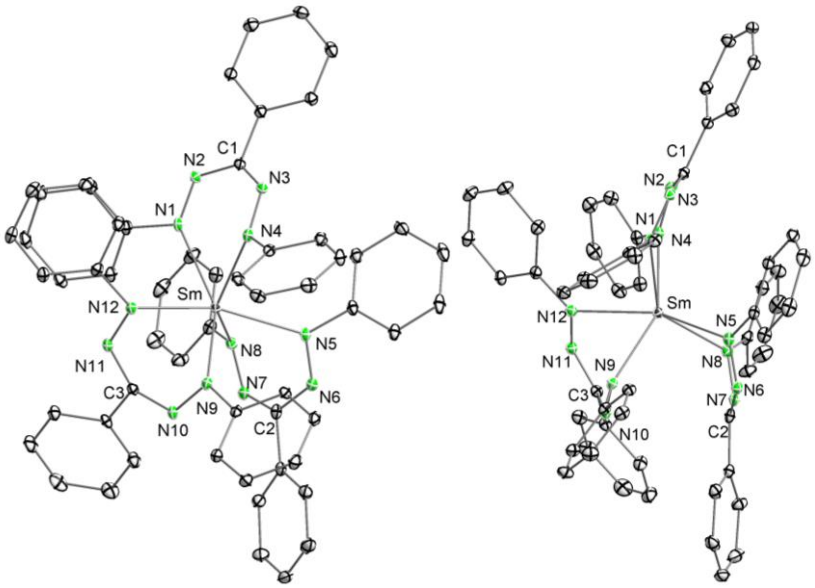

Fig. S21 Molecular structure of **2** in the solid state with thermal ellipsoids at the 30% probability level (left: front view; right: side view). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles [°]: Sm-N1 2.497(2), Sm-N4 2.373(2), Sm-N5 2.443(2), Sm-N8 2.434(2), Sm-N9 2.407(2), Sm-N12 2.435(2), N1-N2 1.302(3), N2-C1 1.356(3), N3-N4 1.317(3), N3-C1 1.338(3), N5-N6 1.310(3), N6-C2 1.347(3), N7-N8 1.318(3), N7-C2 1.352(3), N9-N10 1.313(3), N10-C3 1.363(3), N11-N12 1.300(3), N11-C3 1.358(3); N1-Sm-N4 68.02(6), N5-Sm-N8 65.12(6), N9-Sm-N12 69.59(6), N2-N1-Sm 132.93(14), N1-N2-C1 120.8 (2), N4-N3-C1 120.4(2), N3-N4-Sm 134.30(15), N6-N5-Sm 115.47(14), N5-N6-C2 119.6(2), N8-N7-C2 119.7(2), N7-N8-Sm 114.12(14), N10-N9-Sm 103.90(13), N9-N10-C3 119.3(2), N12-N11-C3 121.9(2), N11-N12-Sm 100.85(13), N2-C1-N3 129.0(2), N6-C2-N7 125.4(2), N10-C3-N11 126.9(2).

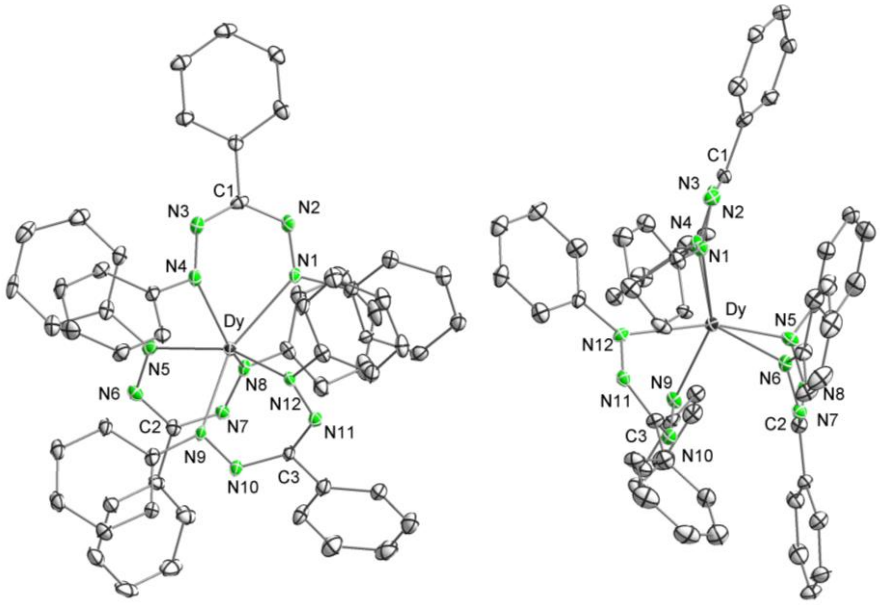

Fig. S22 Molecular structure of **3** in the solid state with thermal ellipsoids at the 30% probability level (left: front view; right: side view). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles [°]: Dy-N1 2.443(4), Dy-N4 2.327(5), Dy-N5 2.382(4), Dy-N8 2.385(4), Dy-N9 2.368(4), Dy-N12 2.379(4), N1-N2 1.305(6), N2-C1 1.355(6), N3-N4 1.313(6), N3-C1 1.335(7), N5-N6 1.307(6), N6-C2 1.356(7), N7-N8 1.309(6), N7-C2 1.351(6), N9-N10 1.315(6), N10-C3 1.365(6), N11-N12 1.316(6), N11-C3 1.355(6); N1-Dy-N4 70.46(14), N5-Dy-N8 66.29(14), N9-Dy-N12 70.44(14), N2-N1-Dy 130.4(3), N1-N2-C1 122.1(4), N4-N3-C1 120.1(4), N3-N4-Dy 133.4(3), N6-N5-Dy 117.1(3), N5-N6-C2 119.6(4), N8-N7-C2 120.7(4), N7-N8-Dy 115.2(3), N10-N9-Dy 104.9(3), N9-N10-C3 119.0(4), N12-N11-C3 120.8(4), N11-N12-Dy 102.9(3), N2-C1-N3 129.6(5), N6-C2-N7 124.0(5), N10-C3-N11 127.0(4).

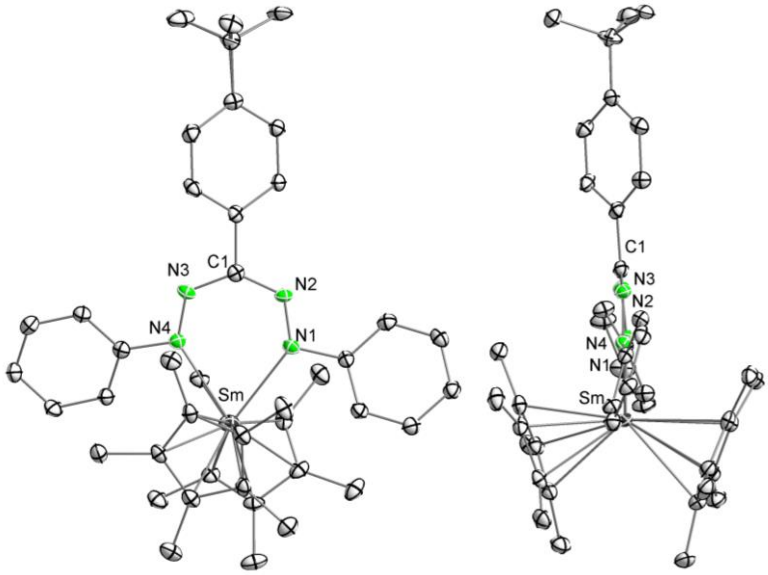

Fig. S23 Molecular structure of **4** in the solid state with thermal ellipsoids at the 30% probability level (left-front view; right-side view). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles [°]: Sm-N1 2.489(4), Sm-N4 2.475(5), N1-N2 1.306(6), N2-C1 1.335(7), N3-N4 1.290(6), N3-C1 1.349(7); N1-Sm-N4 72.15(15), N2-N1-Sm 133.3(4), N1-N2-C1 122.7(5), N4-N3-C1 122.3(5), N3-N4-Sm 134.3(4), N2-C1-N3 134.6(5).

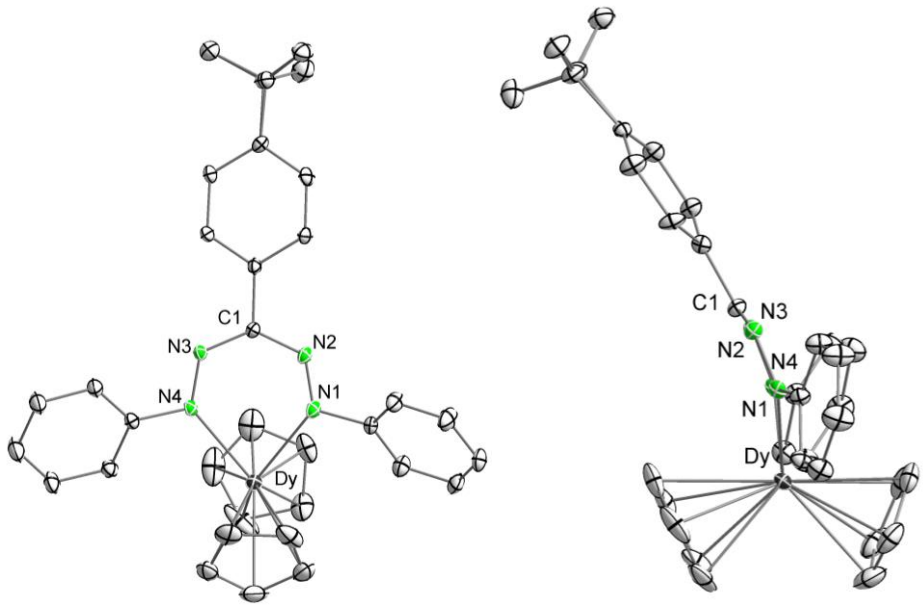

Fig. S24 Molecular structure of **5** in the solid state with thermal ellipsoids at the 25% probability level (left-front view; right-side view). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles [°]: Dy-N1 2.370(8), Dy-N4 2.366(7), N3-N4 1.309(10), N3-C1 1.329(10), N1-N2 1.286(11), N2-C1 1.346(10); N1-Dy-N4 74.0(3), N2-N1-Dy 131.1(6), N1-N2-C1 123.0(8), N4-N3-C1 122.8(7), N3-N4-Dy 130.5(5), N2-C1-N3 131.0(8).

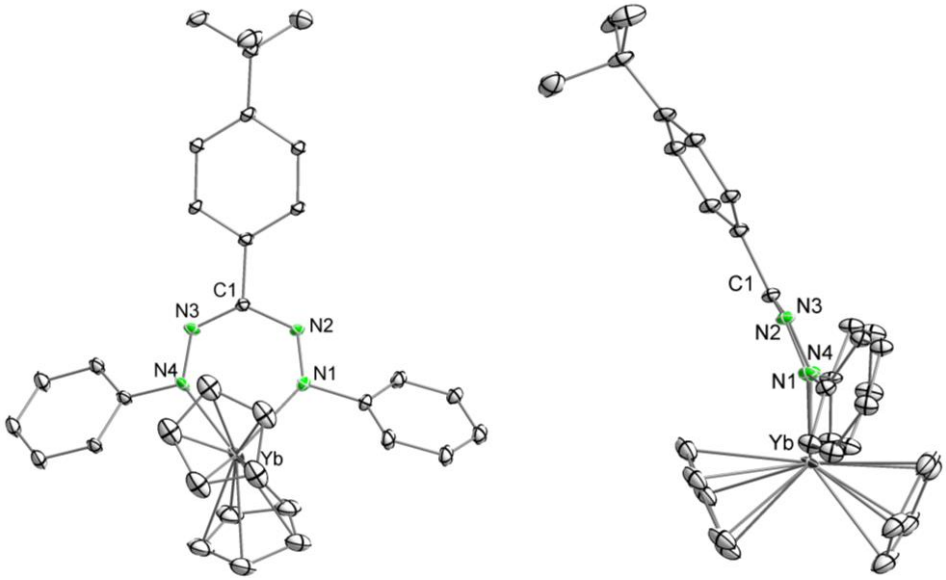

Fig. S25 Molecular structure of **6** in the solid state with thermal ellipsoids at the 25% probability level (left-front view; right-side view). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles [°]: Yb-N1 2.37(2), Yb-N4 2.335(15), N1-N2 1.26(3), C1-N2 1.39(3), N3-C1 1.31(3), N3-N4 1.29(2); N1-Yb-N4 73.8(7), N2-N1-Yb 130.4(15), N1-N2-C1 122(2), N4-N3-C1 124(2), N3-N4-Yb 129.5(13), N3-C1-N2 130(2).

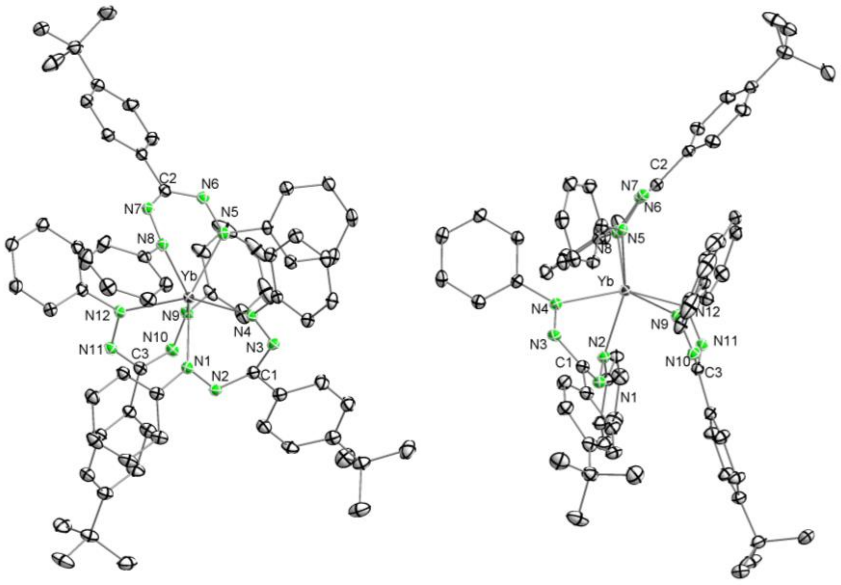

Fig. S26 Molecular structure of **7** in the solid state with thermal ellipsoids at the 25% probability level (left-front view; right-side view). All hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and bond angles [°]: Yb-N1 2.324(2), Yb-N4 2.344(2), Yb-N5 2.372(2), Yb-N8 2.287(2), Yb-N9 2.311(2), Yb-N12 2.345(2), N1-N2 1.322(3), C1-N2 1.347(4), N3-C1 1.346(4), N3-N4 1.307(3), N5-N6 1.321(3), N6-C2 1.345(4), N7-C2 1.350(4), N7-N8 1.312(3), N9-N10 1.317(3), C3-N10 1.351(3), C3-N11 1.347(4); N1-Yb-N4 69.38(8), N5-Yb-N8 71.70(8), N9-Yb-N12 68.39(8), N2-N1-Yb 110.0(2), N1-N2-C1 119.3(2), N4-N3-C1 120.3(2), N3-N4-Yb 111.5(2), N6-N5-Yb 122.8(2), N5-N6-C2 122.1(2), N8-N7-C2 119.8(2), N7-N8-Yb 125.8(2), N10-N9-Yb 120.3(2), N9-N10-C3 119.6(2), N12-N11-C3 120.1(2), N11-N12-Yb 120.2(2), N2-C1-N3 125.1(3), N6-C2-N7 127.9(3), N10-C3-N11 125.2(3).

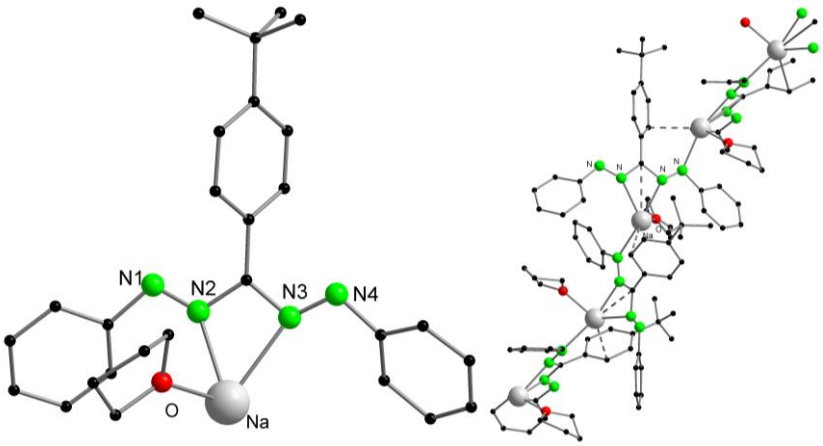

Fig. S27 Molecular structure of **L^2Na(thf)** in the solid state. All hydrogen atoms are omitted for clarity.

VI. References

[1] G. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, **64**, 112-122.
[2] G. Sheldrick, *Acta Crystallogr. Sect. C*, 2015, **71**, 3-8.
[3] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.