Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting information for the manuscript

N-aromatic heterocycle adducts of bulky $[1,2,4\text{-}(Me_3C)_3C_5H_2]_2Sm$. Synthesis, structure and solution analysis.

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1. Magnetism

Figure S1. Temperature dependent magnetic data, plot of χ *vs.* T (filled blue dots) and μ_{eff} vs. T (unfilled red dots) in the 5- 300 K temperature range for **1**.

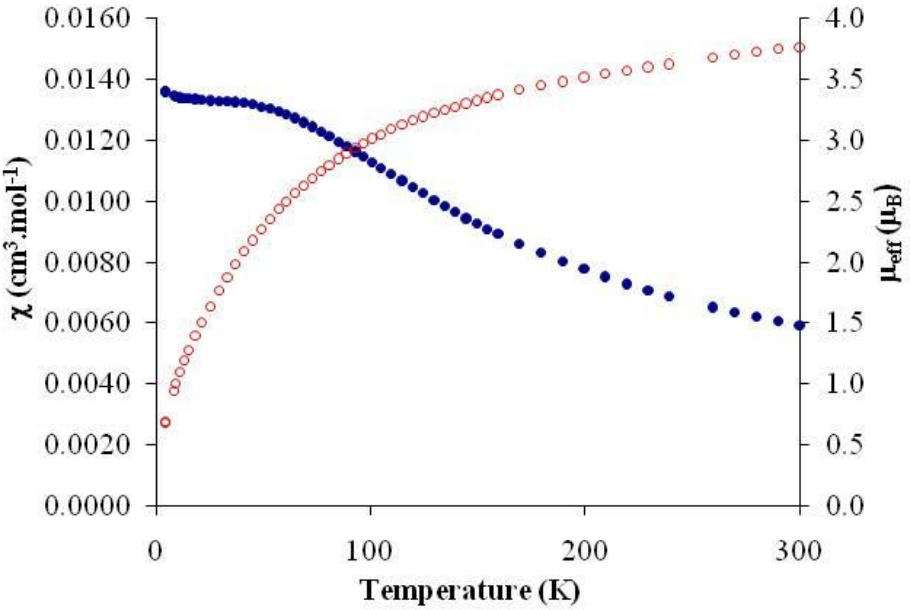


Figure S2. Temperature dependent magnetic data, plot of χ *vs.* T (filled blue dots) and μ_{eff} vs. T (unfilled red dots) in the 5- 300 K temperature range for **2**.

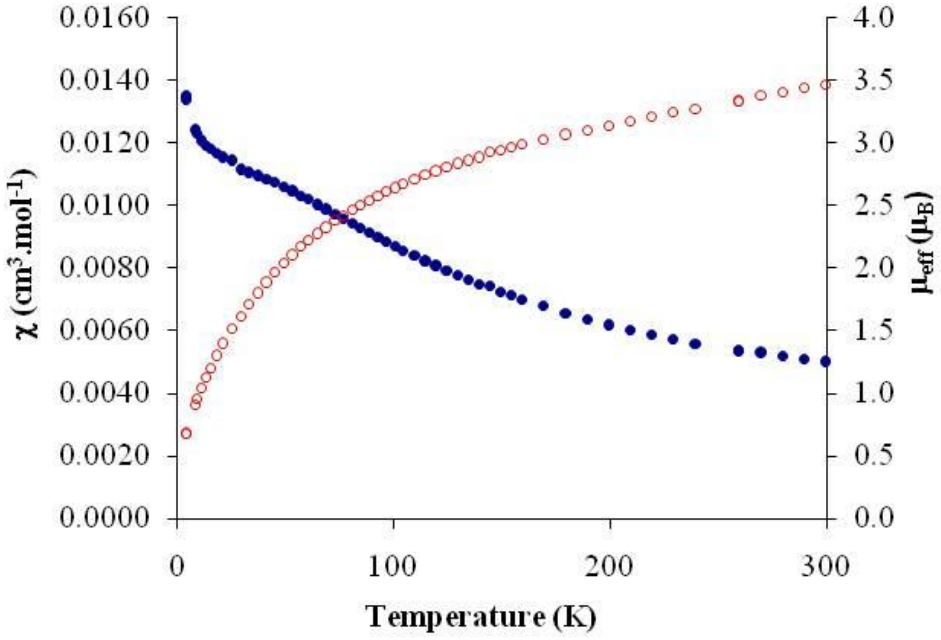


Figure S3. Temperature dependent magnetic data, plot of χ *vs.* T (filled blue dots) and μ_{eff} vs. T (unfilled red dots) in the 5- 300 K temperature range for **3**.

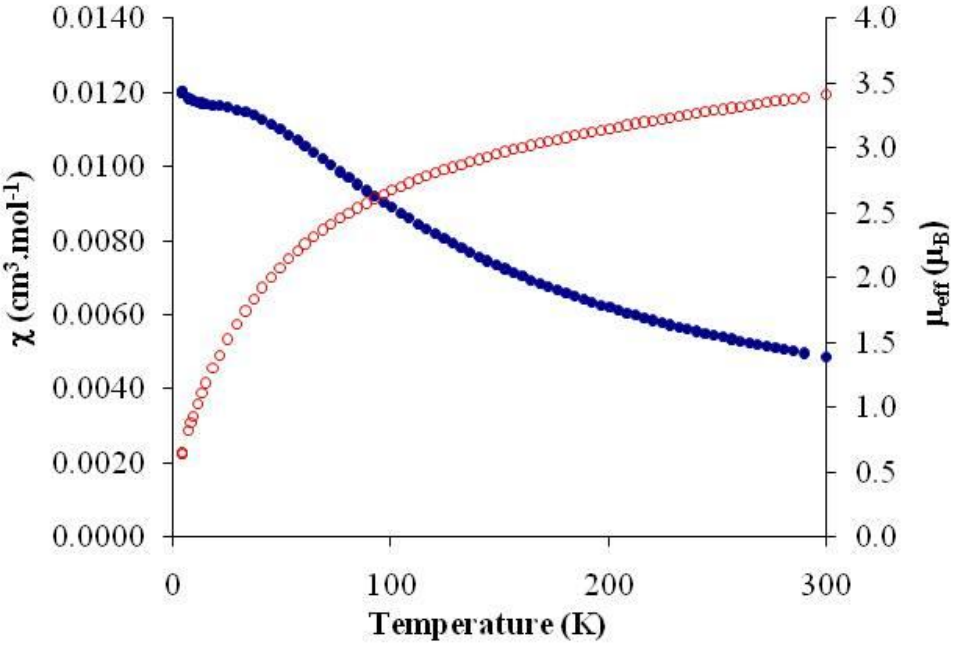


Figure S4. Temperature dependent magnetic data, plot of χ *vs.* T (filled blue dots) and μ_{eff} vs. T (unfilled red dots) in the 5- 300 K temperature range for **4**.

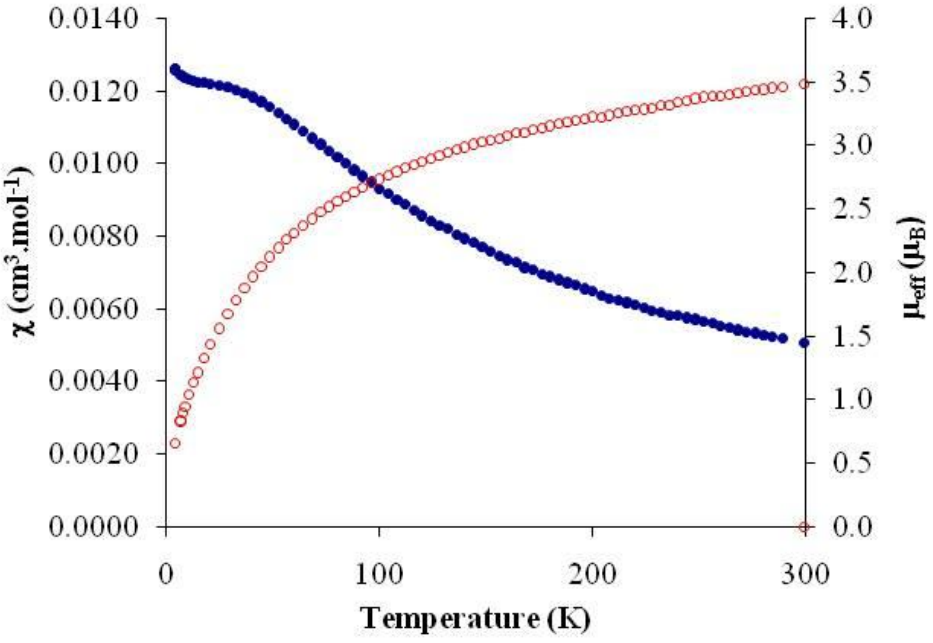


Figure S5. Temperature dependent magnetic data, plot of χ *vs.* T (filled blue dots) and μ_{eff} vs. T (unfilled red dots) in the 5- 300 K temperature range for **5**.

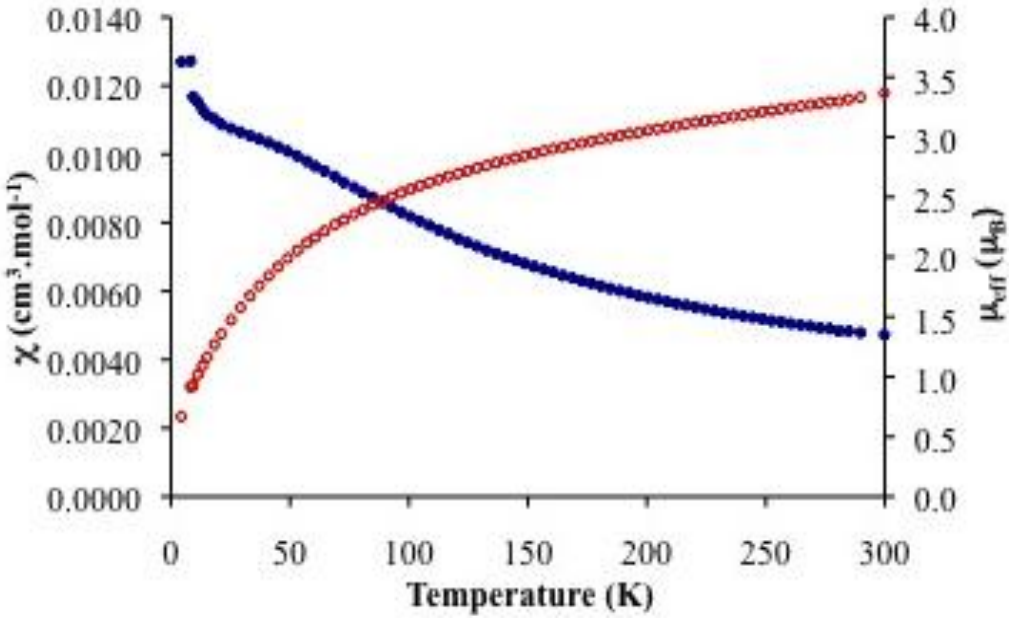


Figure S6. Temperature dependent magnetic data, plot of χ *vs.* T (filled blue dots) and μ_{eff} vs. T (unfilled red dots) in the 5- 300 K temperature range for **6**.

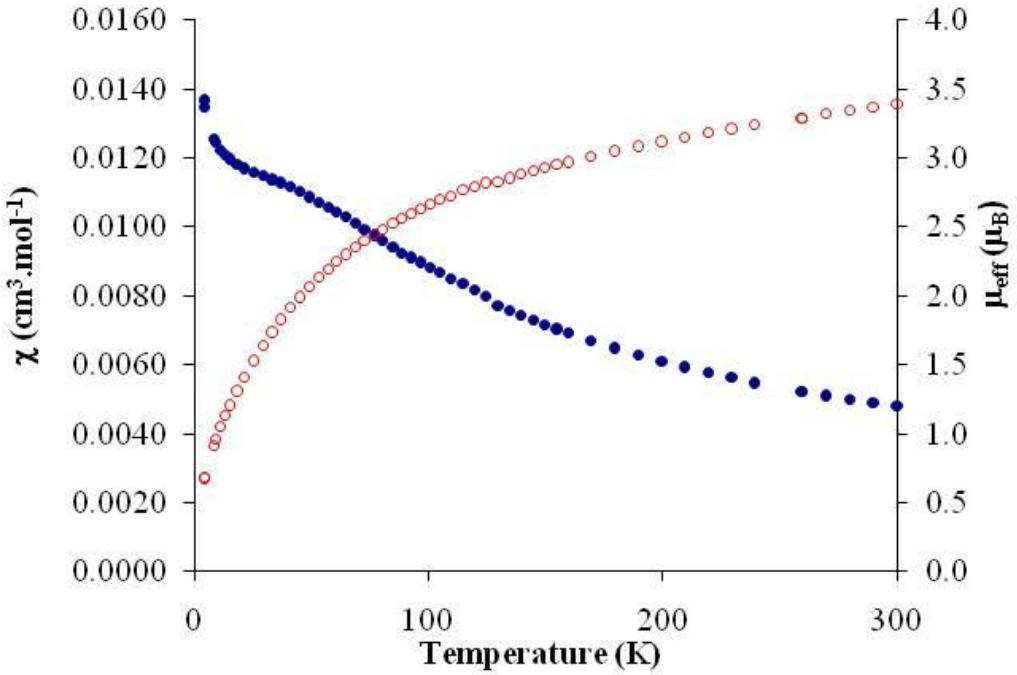


Figure S7. Temperature dependent magnetic data, plot of χ *vs.* T (filled blue dots) and μ_{eff} vs. T (unfilled red dots) in the 5- 300 K temperature range for **7**.

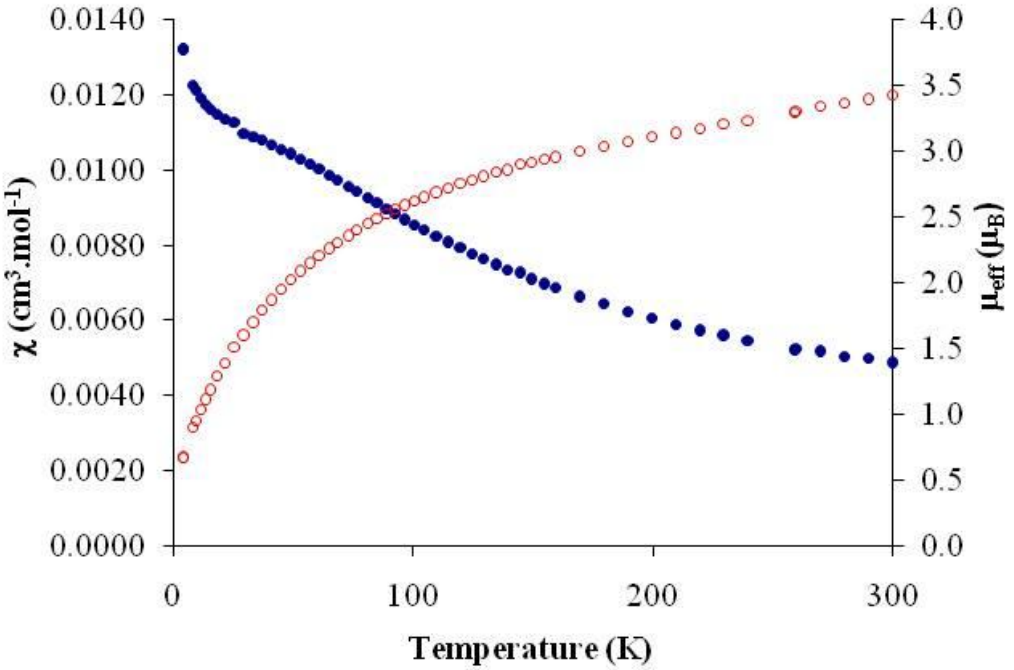
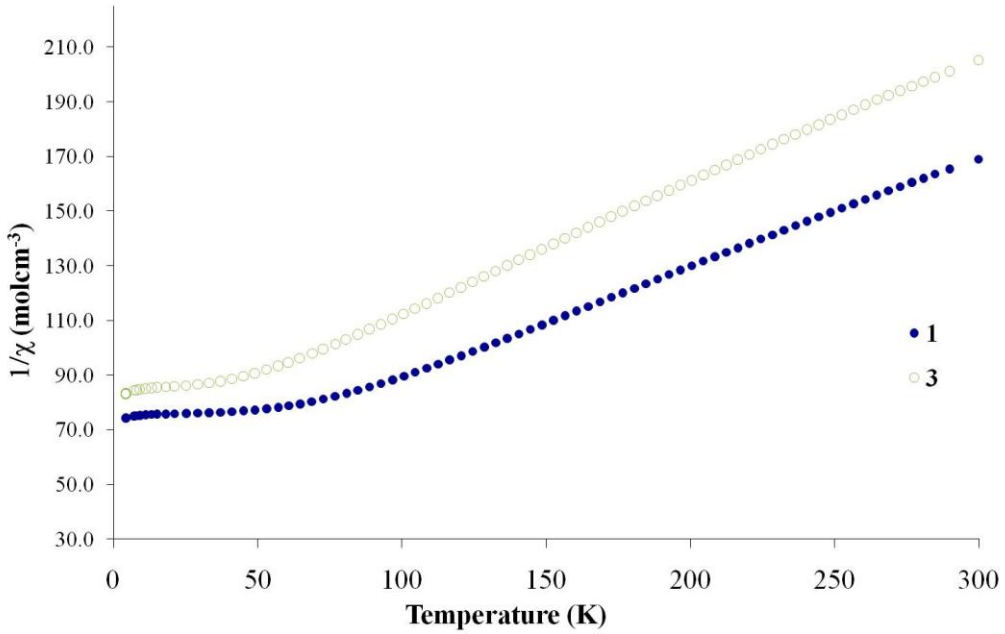


Figure S8. Temperature dependent magnetic data, plot of $1/\chi$ *vs.* T in the 5- 300 K temperature range for **1** and **3**.



2. Variable temperature ^{1}H NMR data

Figure S9. Variable temperature ^{1}H NMR data for **3.**

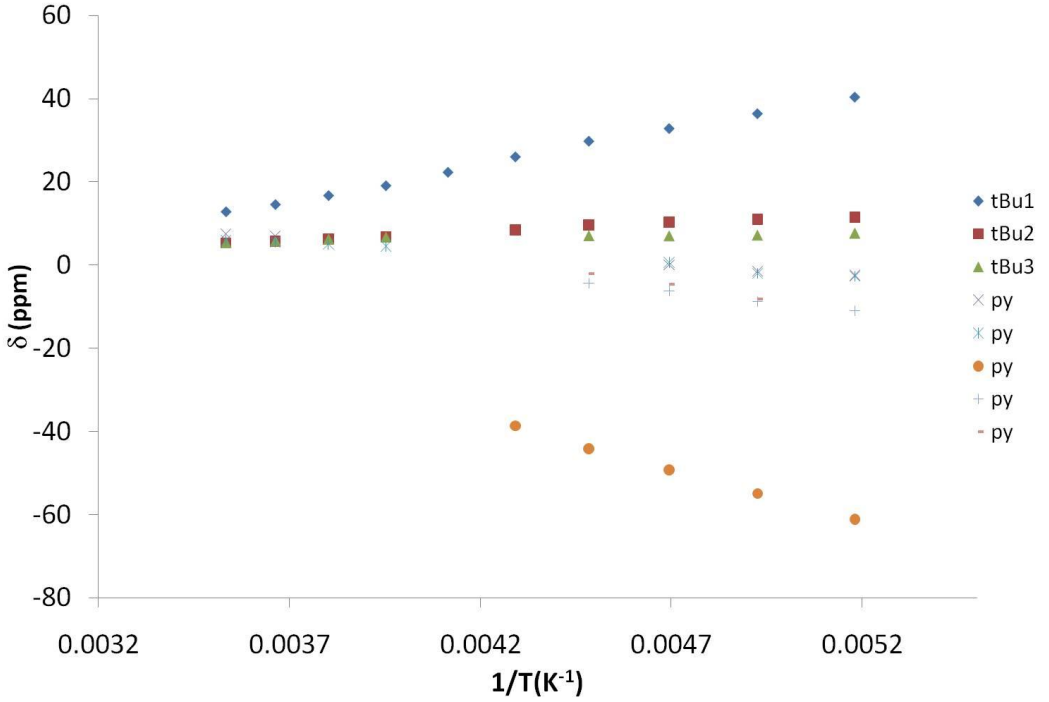


Figure S10. Variable temperature ^{1}H NMR data for **4**.

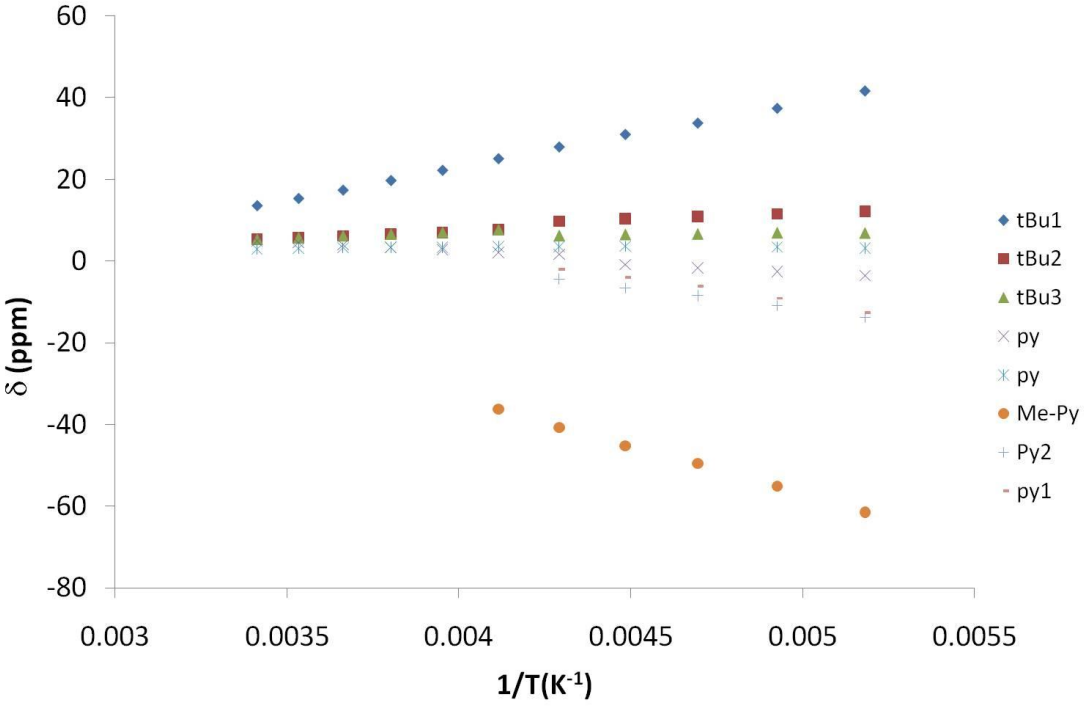


Figure S11. Variable temperature ^{1}H NMR data for **5.**

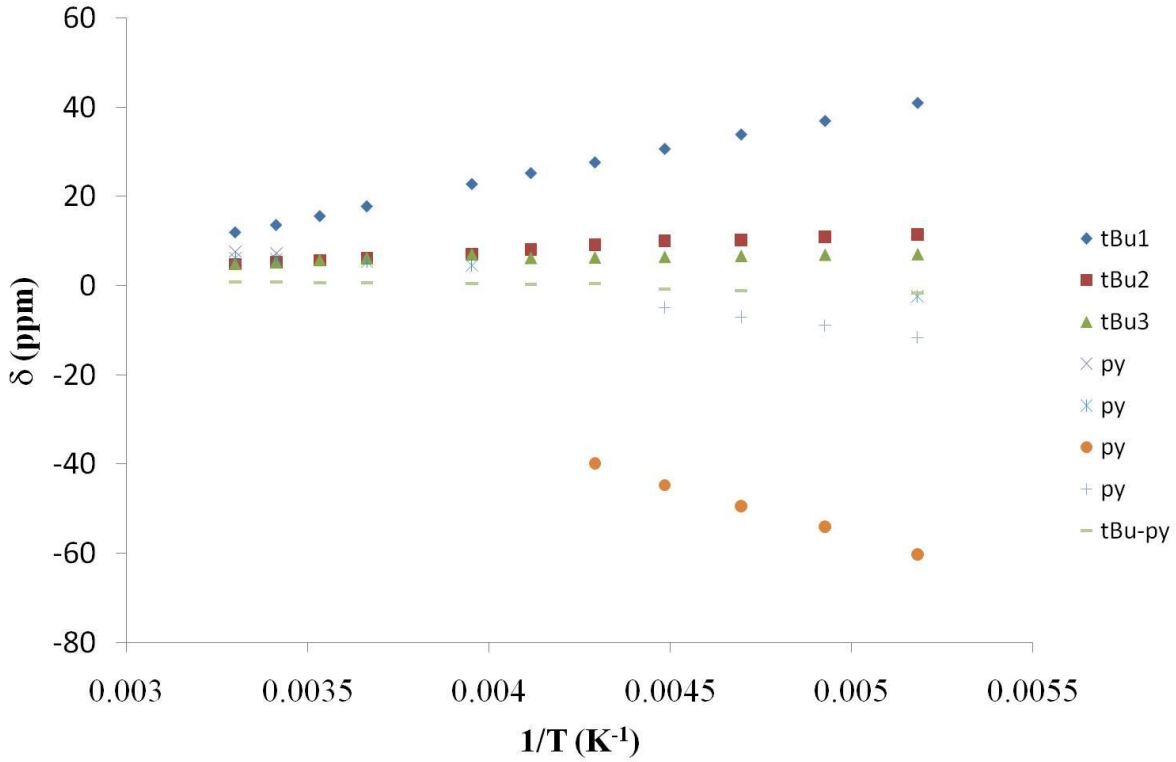
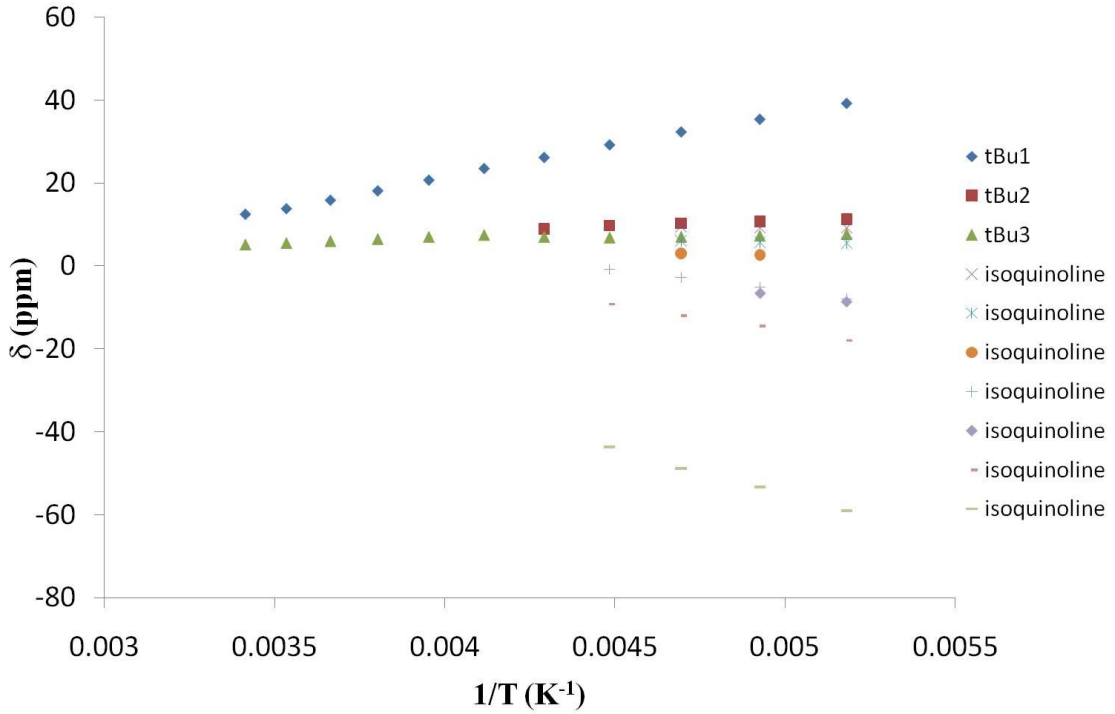


Figure S12. Variable temperature ^{1}H NMR data for **6.**



3. Vis-NIR data

Figure S13. Vis-NIR spectra of **4** at 40 °C in toluene (red line) and methylcyclohexane (red line).

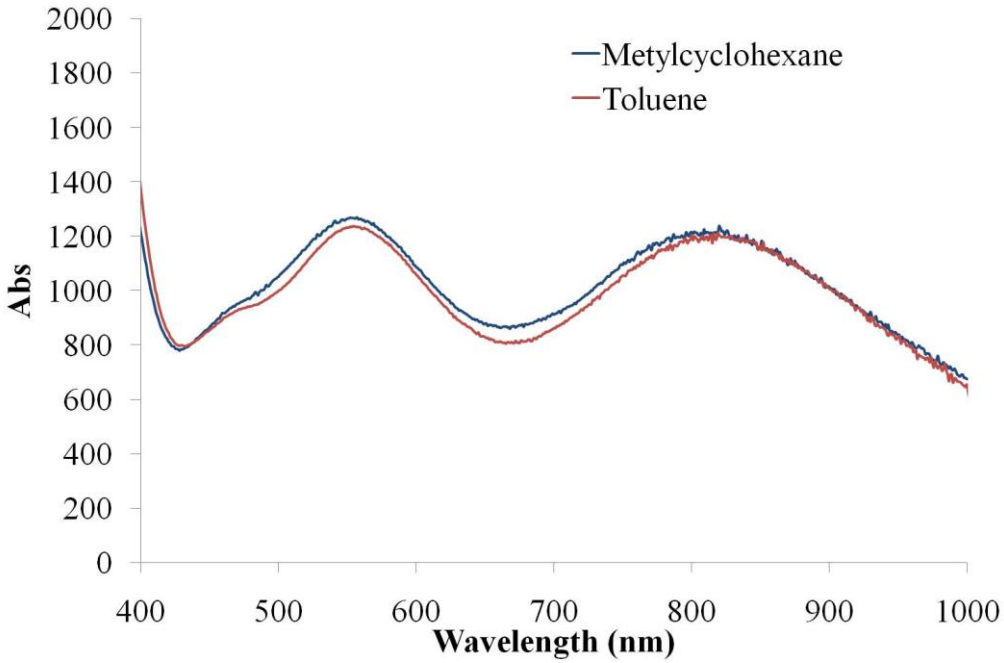
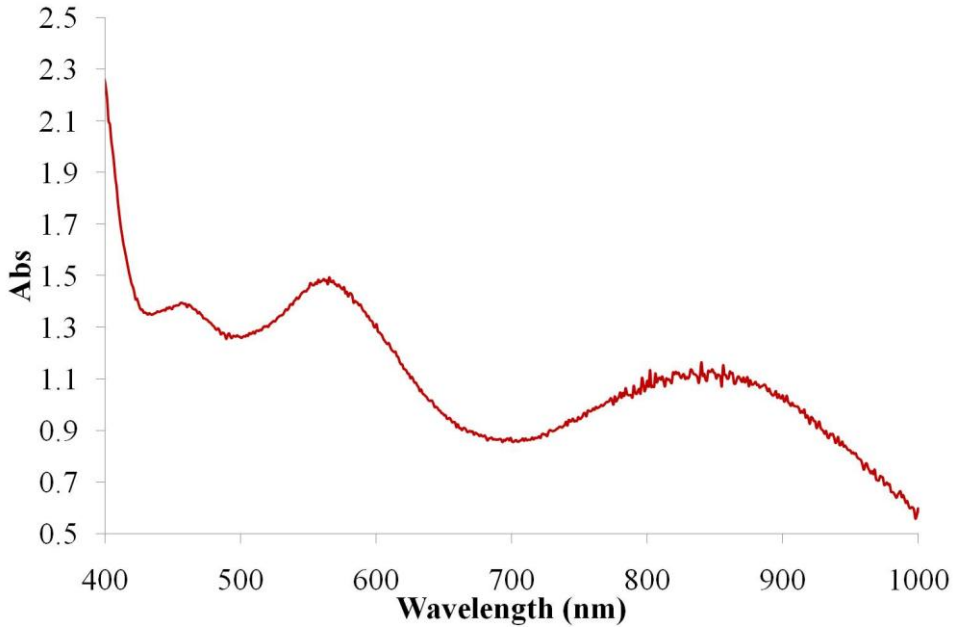


Figure S14. Tentative Vis-NIR spectrum of **4** at low temperature (between -10 °C and -20 °C).



4. Cyclic Voltammetry

Figure S15. Cyclic voltammogram of **2** at a 5 mm Pt disk electrode in ~ 0.1 M $[NBu_4][BPh_4]$/THF solution at room temperature at 200 mVs^{-1}.

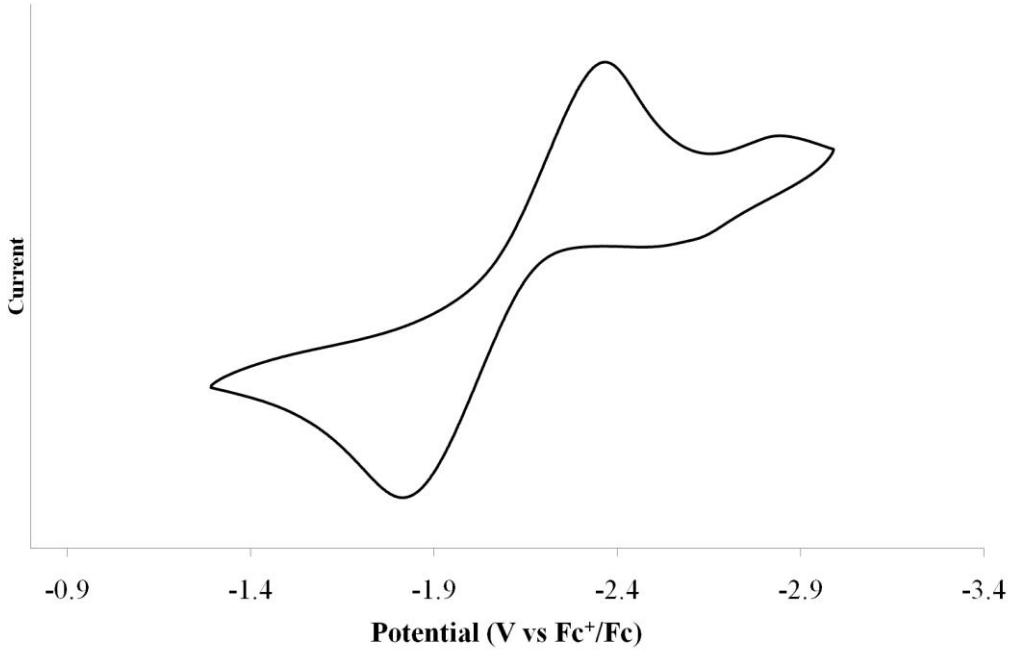
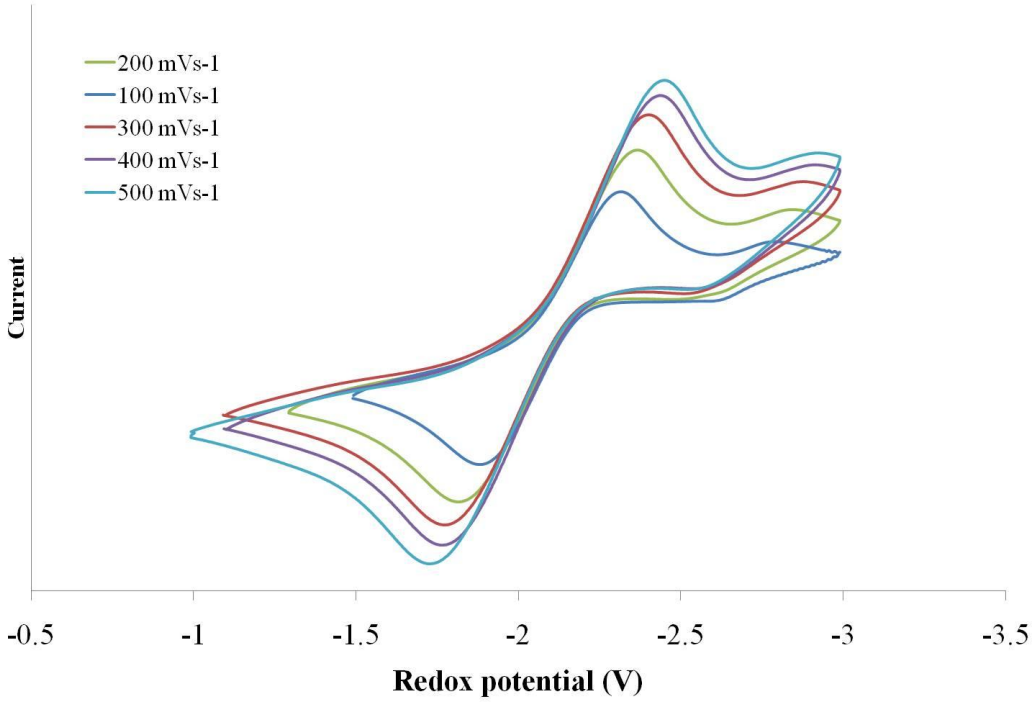


Figure S16. Cyclic voltammogram of **2** at a 5 mm Pt disk electrode in ~ 0.1 M $[NBu_4][BPh_4]$/THF solution at room temperature with different scan rate.



5. X-ray crystallography

Figure S17. ORTEP of **3** with thermal ellipsoid at 50% level. Sm is represented in green, and C in dark grey. Hydrogen atoms have been omitted for clarity.

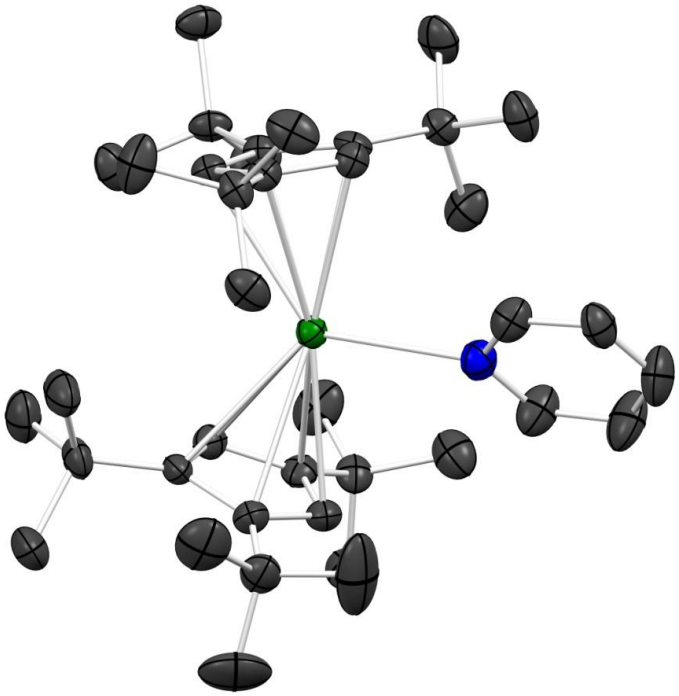


Figure S18. ORTEP of **4** with thermal ellipsoid at 50% level. Sm is represented in green, and C in dark grey. Hydrogen atoms have been omitted for clarity.

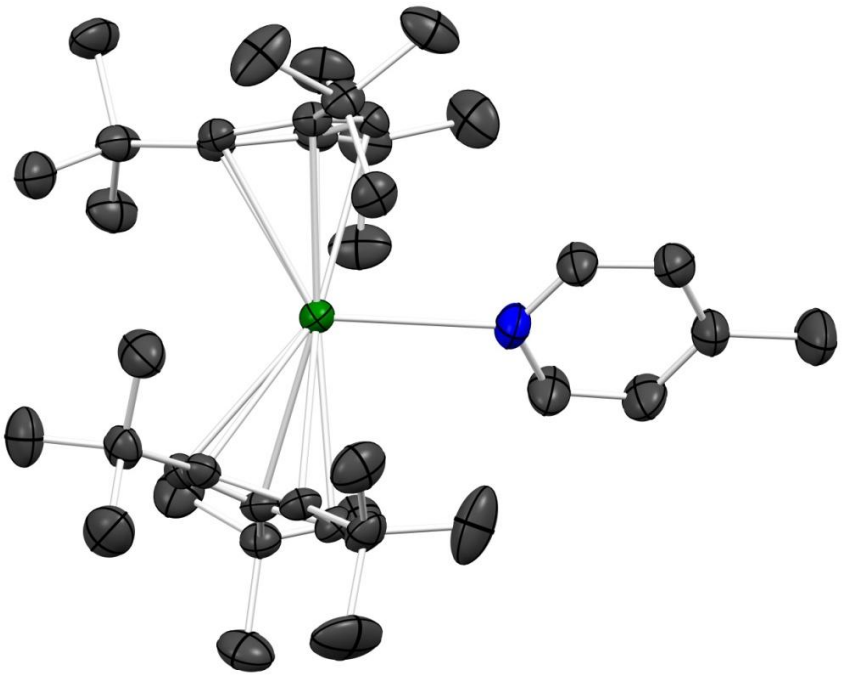


Figure S19. ORTEP of **5** with thermal ellipsoid at 50% level. Sm is represented in green, and C in dark grey. Hydrogen atoms have been omitted for clarity.

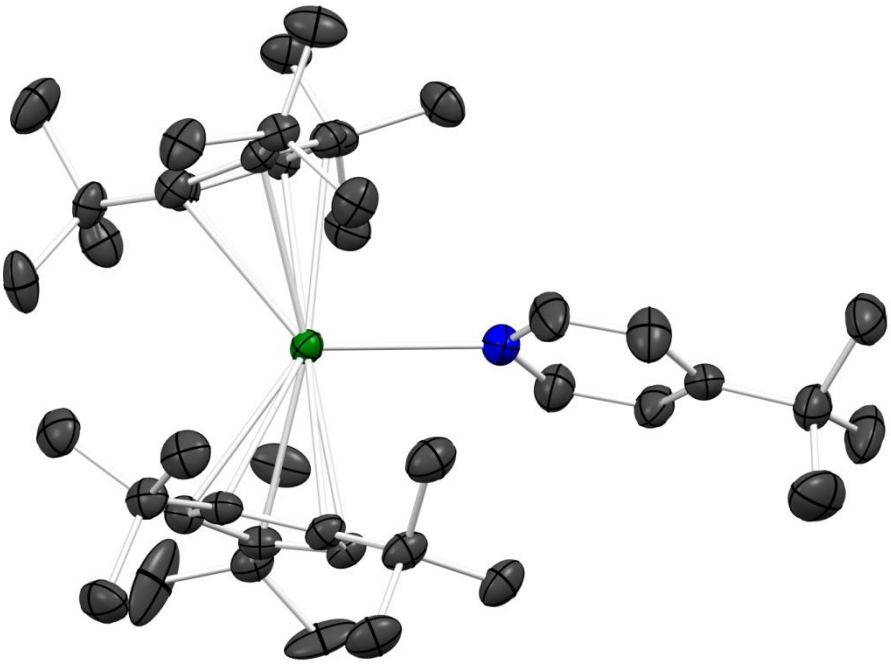


Figure S20. ORTEP of **6** with thermal ellipsoid at 50% level. Sm is represented in green, and C in dark grey. Hydrogen atoms have been omitted for clarity.

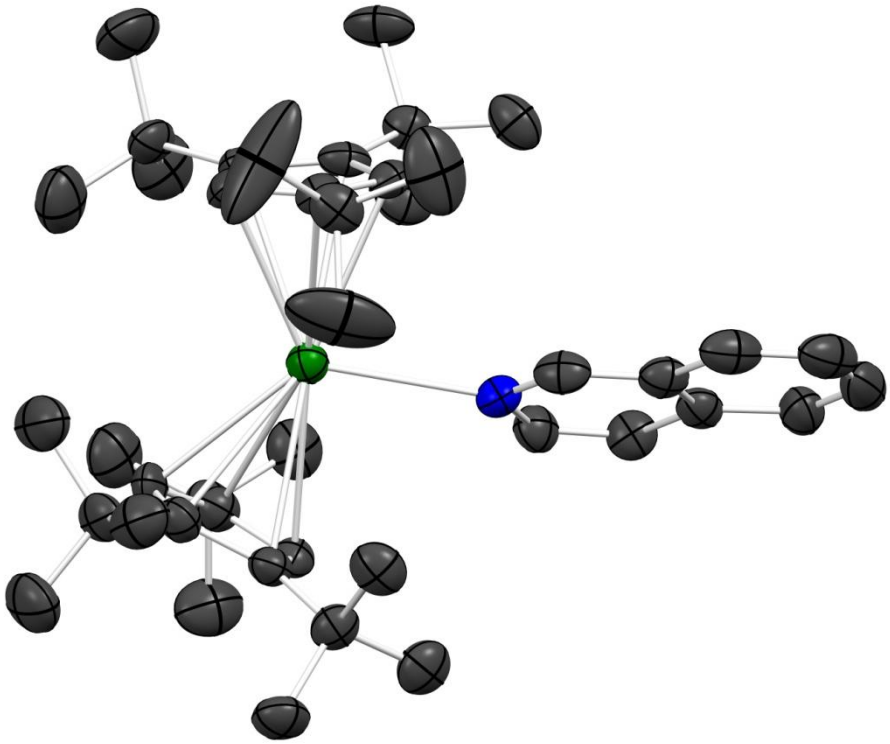


Figure S21. ORTEP of **7** with thermal ellipsoid at 50% level. Sm is represented in green, and C in dark grey. Hydrogen atoms have been omitted for clarity.

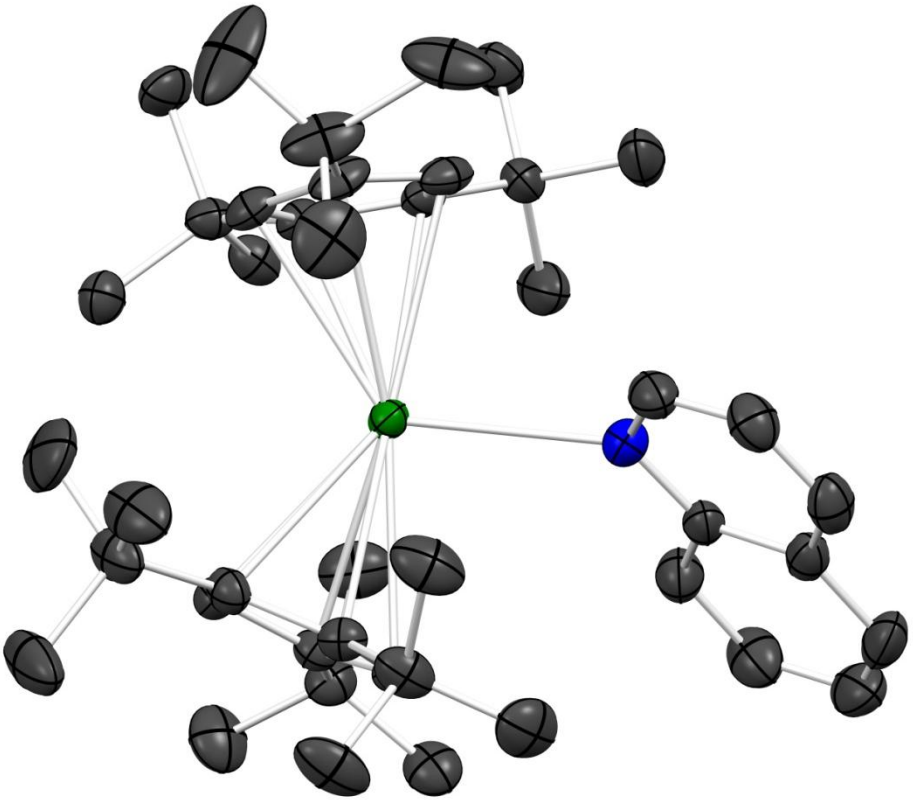


Table S1. Selected Crystal Data and Data Collection Parameters for complexes **1**, **3-7**.

	$Cp^{‡}_2Sm$ (**1**)	$Cp^{‡}_2Sm(py)$ (**3**)	$Cp^{‡}_2Sm(4\text{-Me-py})$ (**4**)	$Cp^{‡}_2Sm(4\text{-}^tBu\text{-py})\cdot 4\text{-}^tBu\text{-py}$ (**5**).	$Cp^{‡}_2Sm(isoquinoline)$ (**6**)	$Cp^{‡}_2Sm(quinoline)$ (**7**)
Formula	$C_{34}H_{53}NSm$	$C_{39}H_{63}NSm$	$C_{40}H_{65}NSm$	$C_{43}H_{71}NSm,C_9H_{13}N$	$C_{43}H_{65}NSm$	$C_{43}H_{65}NSm$
Crystal size (mm)	0.15 x 0.15 x 0.05	0.20 x 0.10 x 0.05	0.20 x 0.20 x 0.10	0.20 x 0.20 x 0.20	0.15 x 0.05 x 0.02	0.30 x 0.30 x 0.20
cryst system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	P -1	P -1	$P2_1/c$
volume (Å)	6523.5(6)	7512.4(7)	7704.7(7)	2431.5(3)	4036.7(5)	3991.1(4)
a (Å)	19.360(1)	20.330(1)	20.575(1)	10.426(1)	11.621(1)	18.313(1)
b (Å)	18.224(1)	19.811(1)	19.641(1)	15.174(1)	19.215(1)	13.041(1)
c (Å)	19.633(1)	19.622(1)	19.820(1)	16.268(1)	19.645(1)	17.303(1)
α (deg)	90.00	90.00	90.00	102.872(1)	105.725(1)	90.00
β (deg)	109.649(1)	108.088(1)	105.859(1)	103.379(1)	98.579(1)	105.021(1)
γ (deg)	90.00	90.00	90.00	91.822(1)	101.698(1)	90.00
Z	4	8	8	2	2	4
formula weight (g/mol)	617.16	696.25	710.28	887.56	746.31	746.31
density (calcd) (g cm^{-3})	1.257	1.231	1.225	1.212	1.228	1.242
absorption coefficient (mm^{-1})	1.818	1.588	1.549	1.241	1.482	1.499
F(000)	2592	2928	2292	944	1568	1568
absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Tmin / Tmax	0.7721 / 0.8391	0.7419 / 0.9248	0.7469 / 0.8605	0.7894 / 0.7894	0.8083/ 0.9710	0.6620/ 0.7537
Diffractometer	KappaCCD	KappaCCD	KappaCCD	KappaCCD	KappaCCD	KappaCCD
X-ray source	MoKα	MoKα	MoKα	MoKα	MoKα	MoKα
λ(Å)	0.71069	0.71069	0.71069	0.71069	0.71069	0.71069
Monochromator	graphite	graphite	graphite	graphite	graphite	graphite
T (K)	150.0(1)	150.0(1)	150.0(1)	150.0(1)	150.0(1)	150.0(1)
Scan mode	phi and omega scans	phi and omega scans	phi and omega scans	phi and omega scans	phi and omega scans	phi and omega scans
Maximum θ	27.48	27.52	27.48	30.00	26.37	30.09
HKL ranges	-19.25 ; -23.22 ; -25.25	-26 16 ; -25 24 ; -24 25	-26 24 ; -23 25 ; -18 25	-14 14 ; -21 20 ; -22 18	-13 14 ; -24 24 ; -24 19	-25 21 ; -18 15 ; -16 24
Reflections measured	36782	49839	52632	28492	29040	25000
Reflections used	11325 [0.0486]	12513 [0.0706]	13065 [0.0681]	13969 [0.0470]	12421 [0.0489]	11599 [0.0427]
Refinement type	Fsqd	Fsqd	Fsqd	Fsqd	Fsqd	Fsqd
wR2	0.0967	0.1100	0.0946	0.1069	0.1264	0.1022
R_1	0.0536	0.0635	0.0541	0.0532	0.0680	0.0525
GoF	1.086	1.084	1.058	1.155	1.131	1.071
difference peak / hole (e $Å^{-3}$)	0.932/ -1.117	1.305/ -0.825	0.898/ -0.600	1.447/ -1.052	1.260 / -0.986	0.914/ -1.060