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Supplementary Material

Synthesis and reactivity of a β-diketiminate Sm^{II} complex

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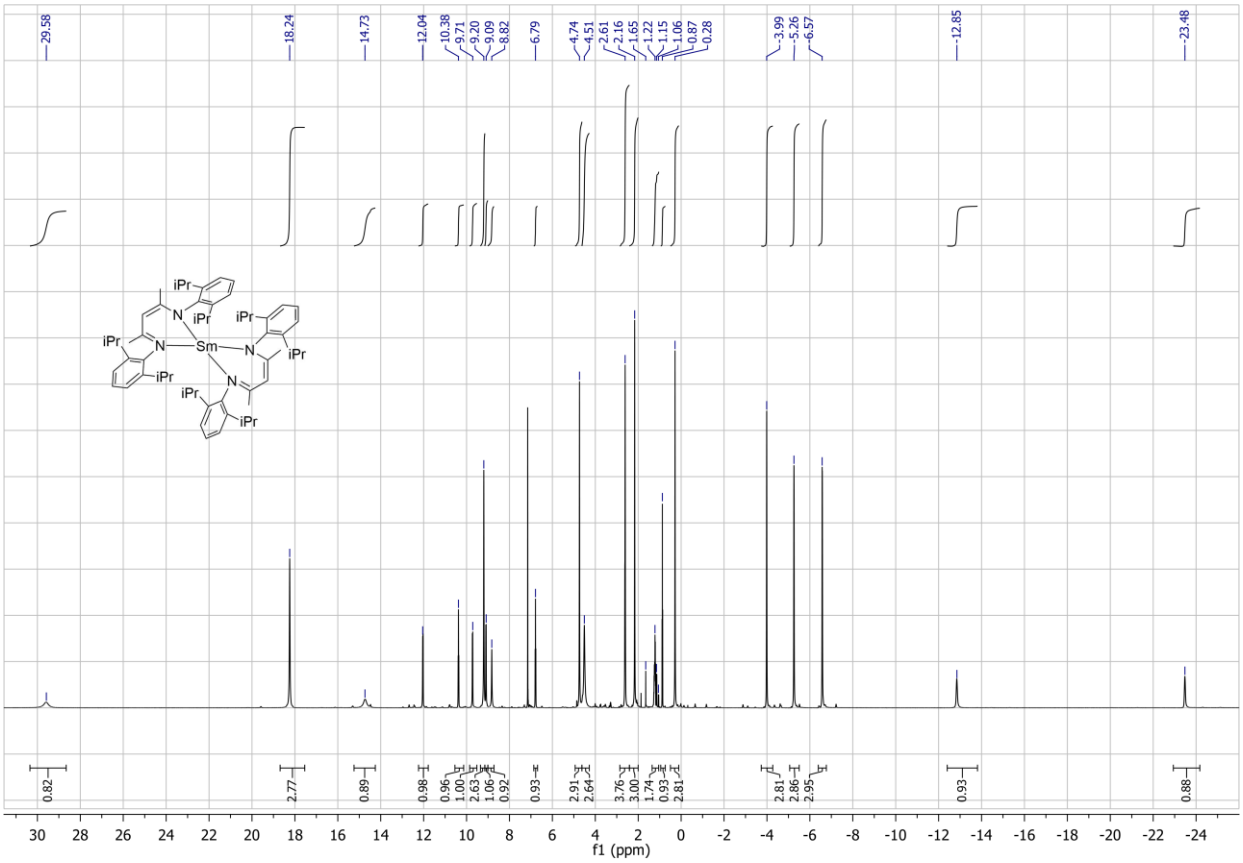

Figure S1. ^{1}H NMR spectrum of $(BDI)_2Sm$ (**2**) in C_6D_6

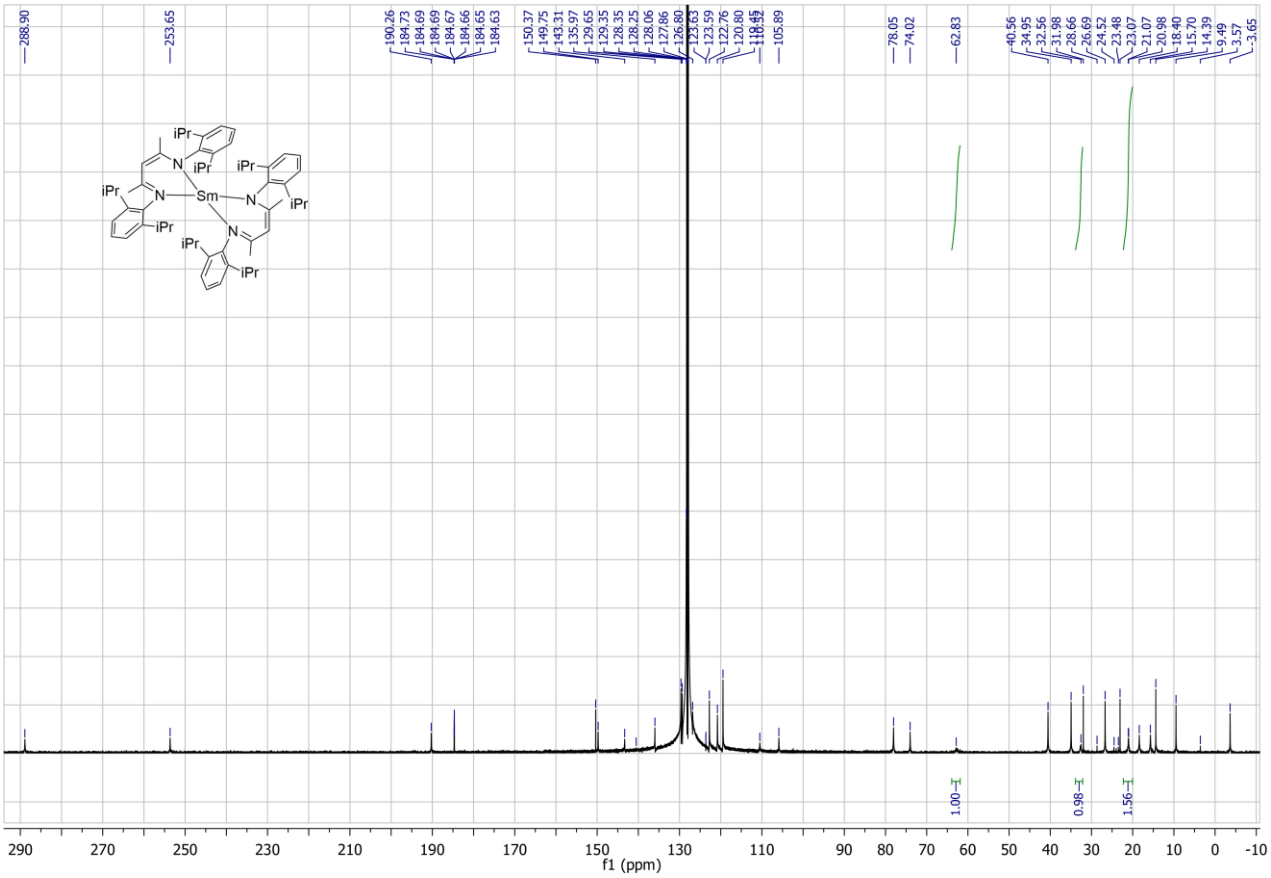

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of $(BDI)_2Sm$ (**2**) in C_6D_6

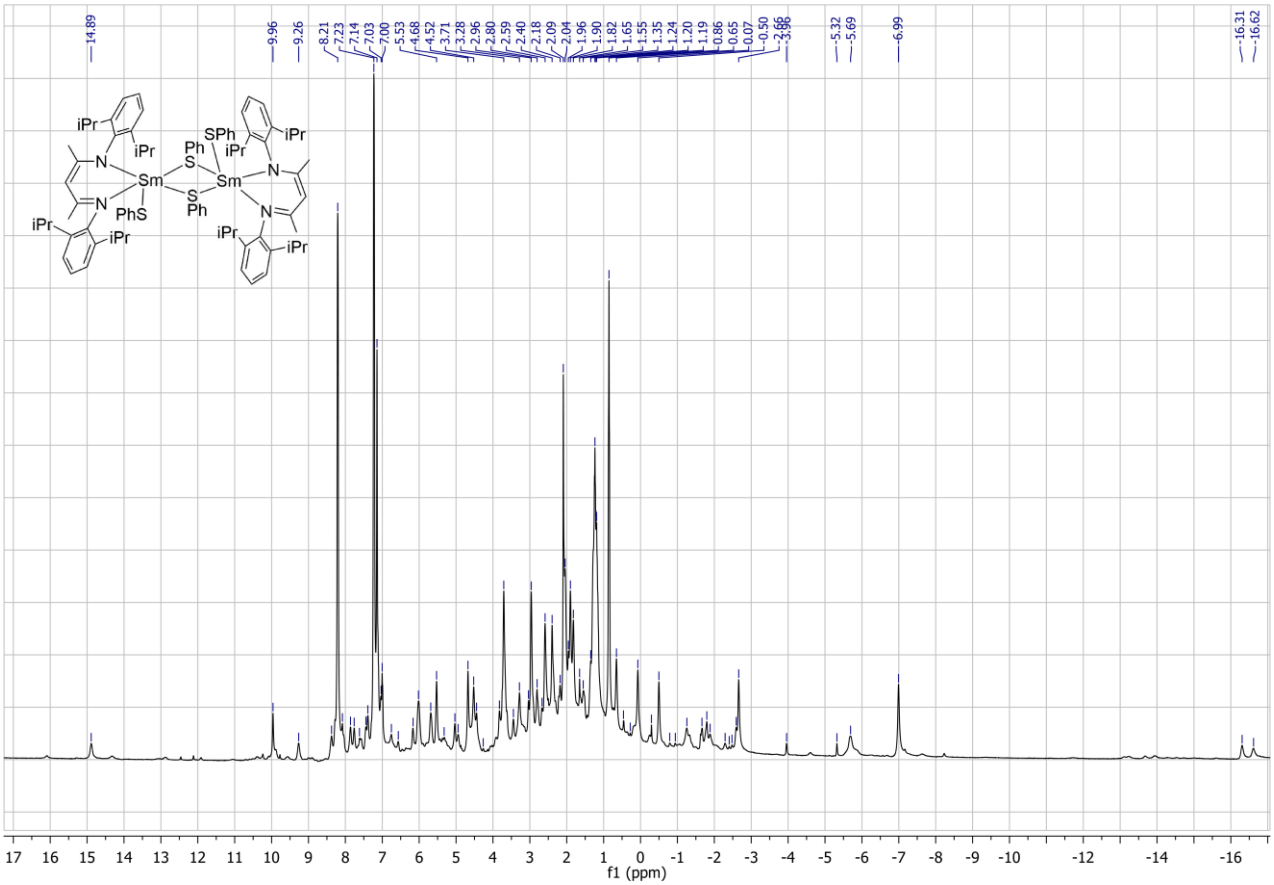

Figure S3. ^{1}H NMR spectrum of $[(BDI)_2Sm]_2(\mu\text{-}C_{12}H_8N_2)$ (**3**) in C_6D_6

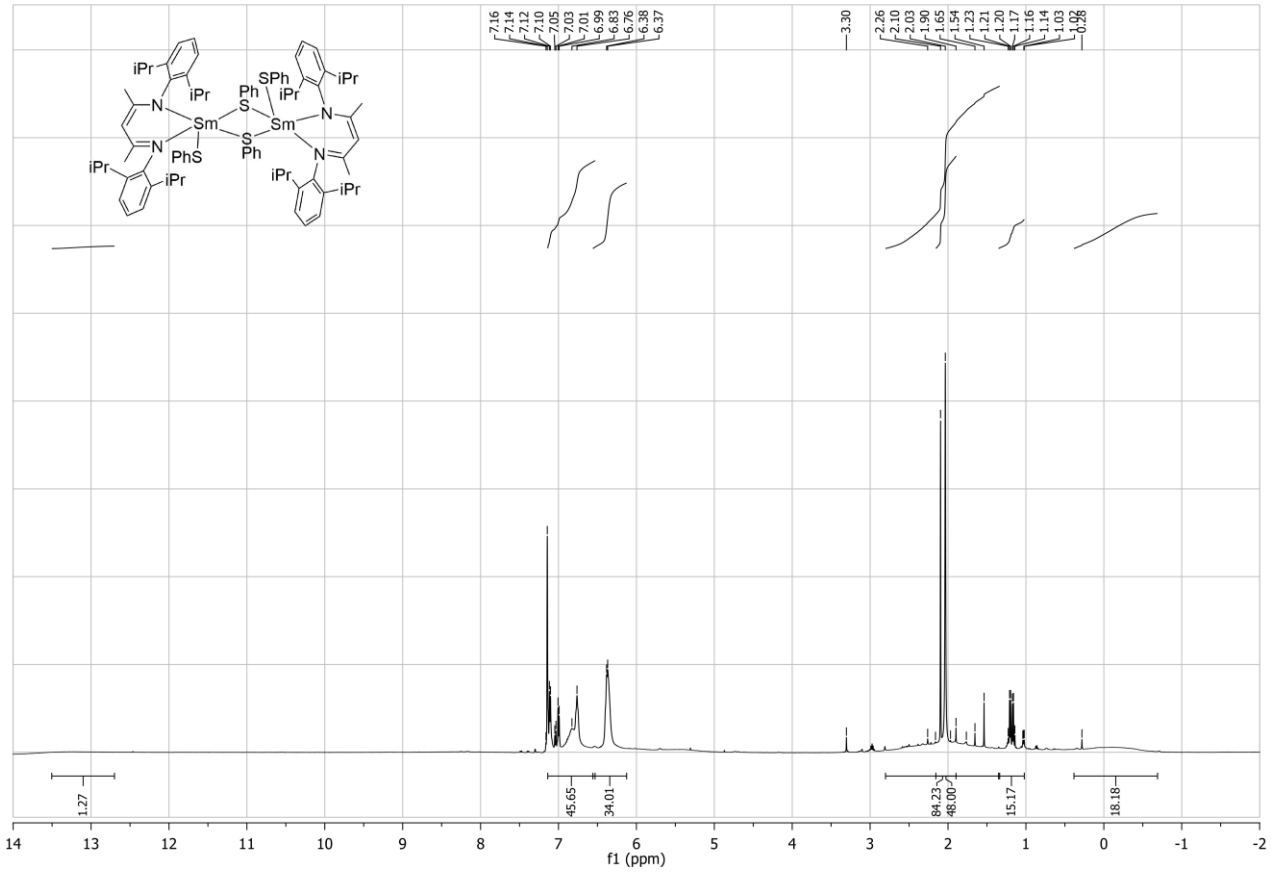

Figure S4. ^{1}H NMR spectrum of [(BDI)Sm(SPh)(μ-SPh)]$_2$ (**4**) in C_6D_6

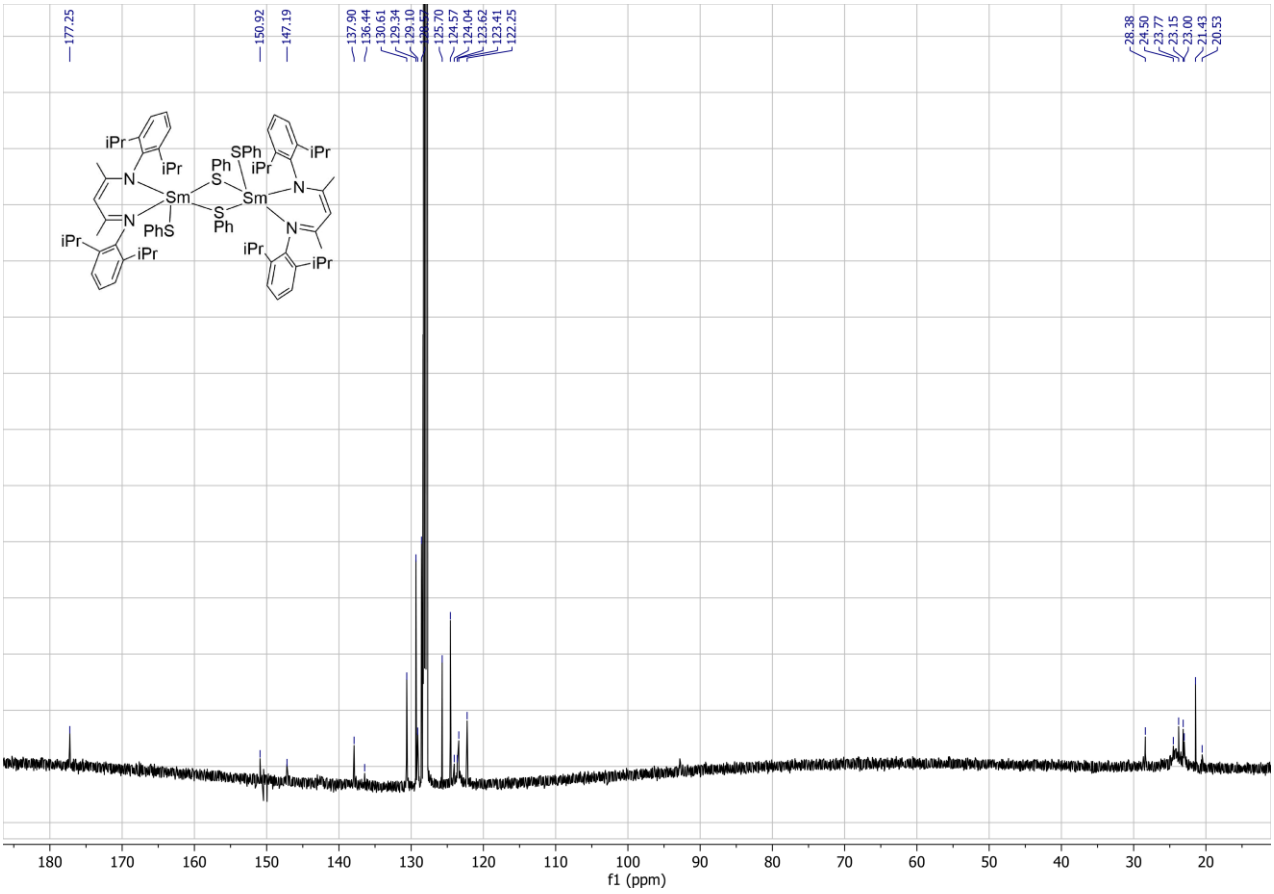

Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of [(BDI)Sm(SPh)(μ-SPh)]$_2$ (**4**) in C_6D_6

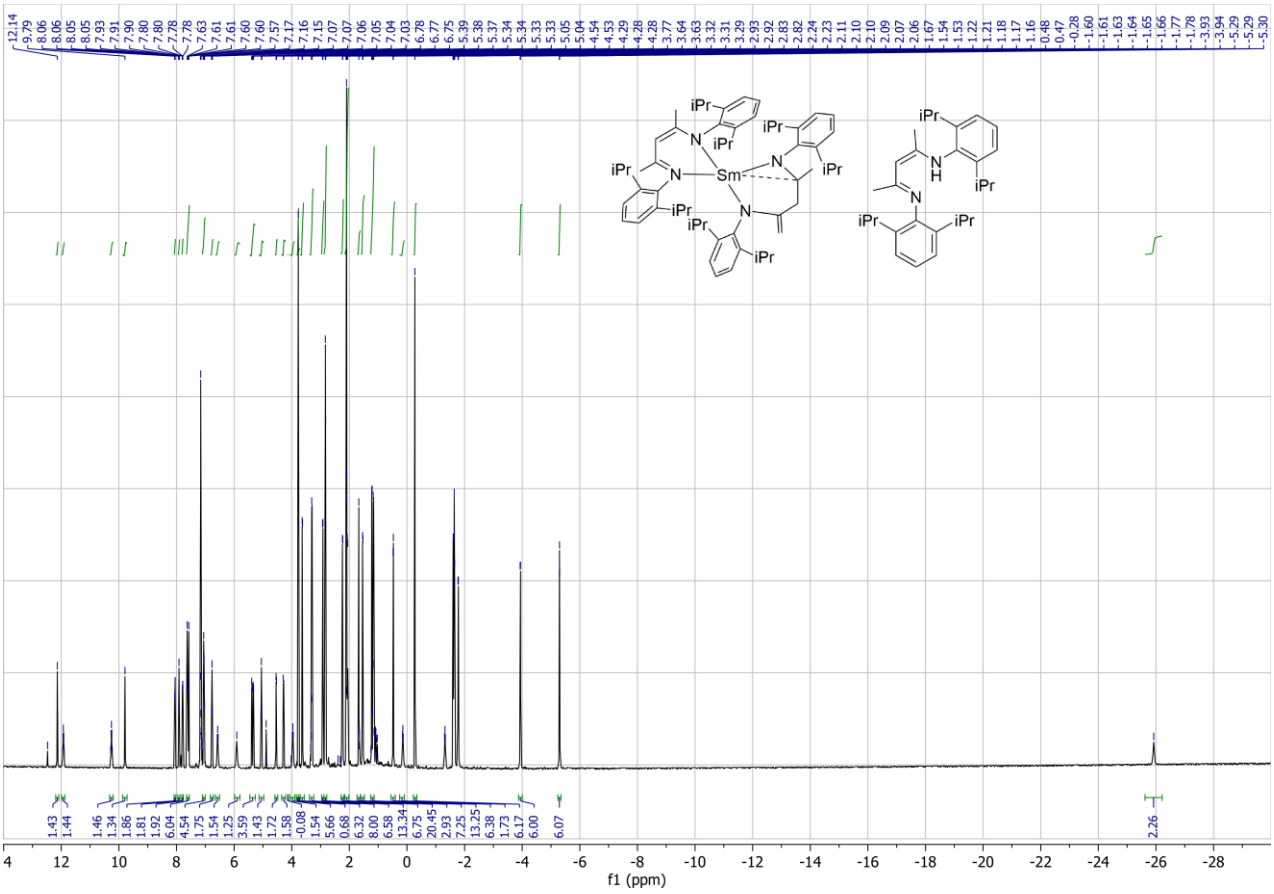

Figure S6. ^{1}H NMR spectrum of (BDI)(BDI-H)Sm·[(BDI)H] (**5a**) in C_6D_6

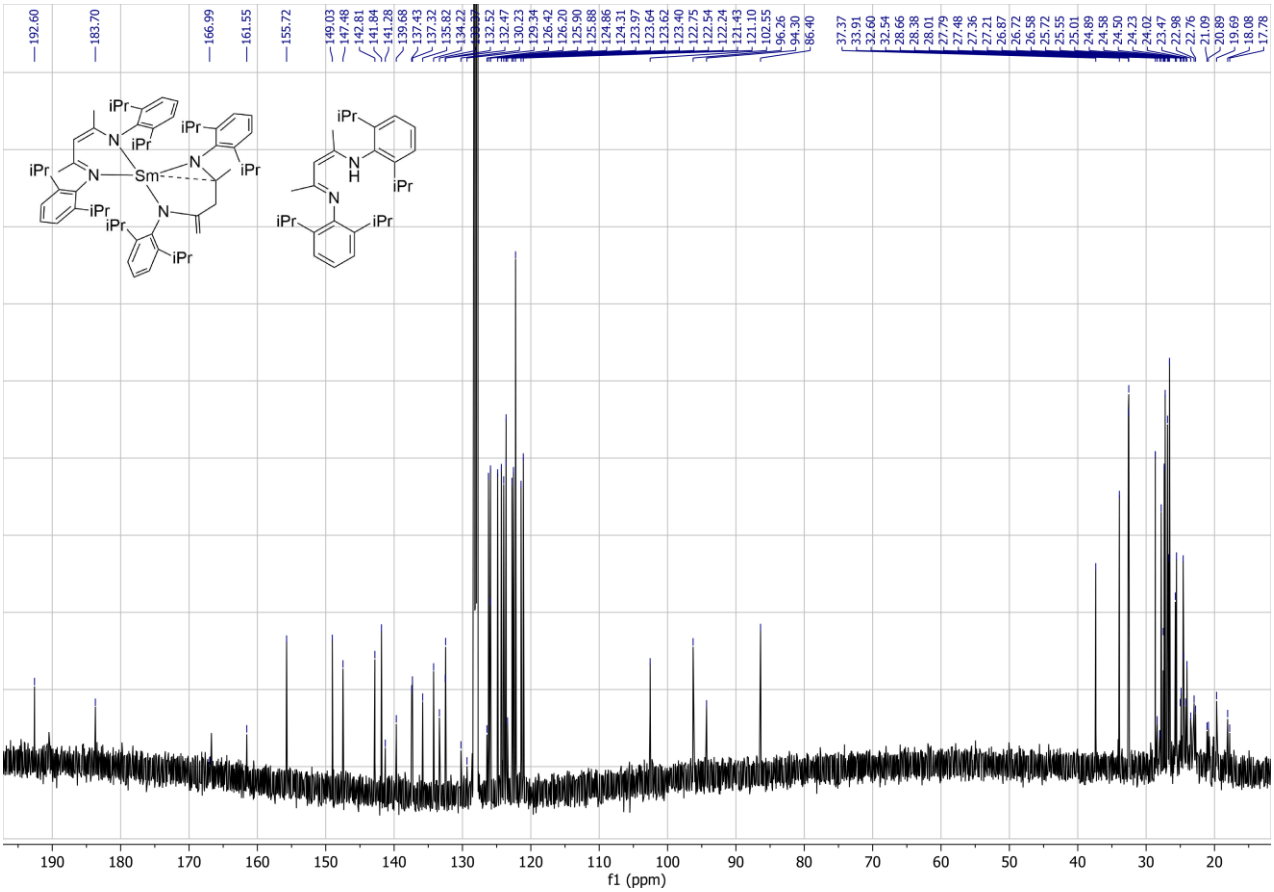

Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of (BDI)(BDI-H)Sm·[(BDI)H] (**5a**) in C_6D_6

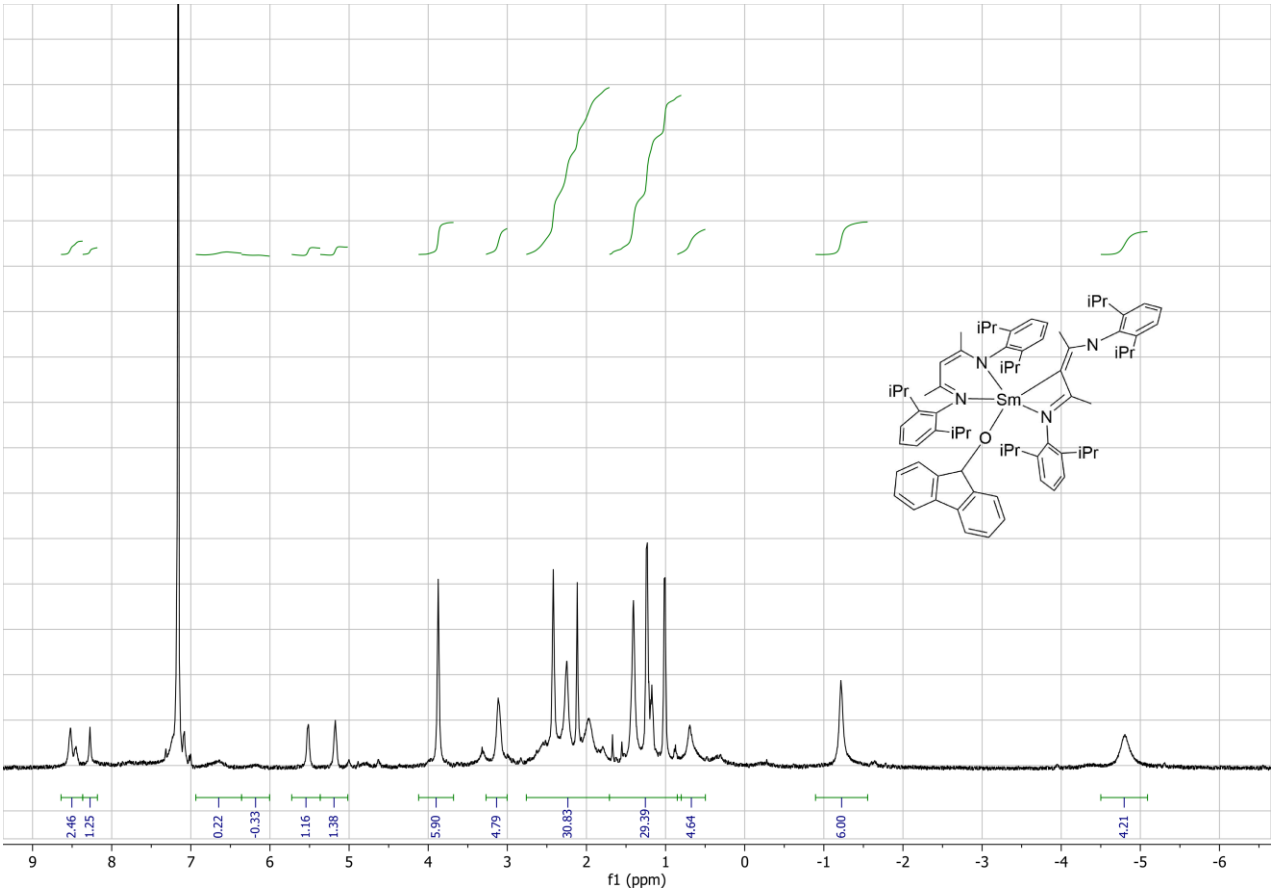

Figure S8. ^{1}H NMR spectrum $(BDI)_2Sm(OC_{13}H_8)$ (**6**) in C_6D_6

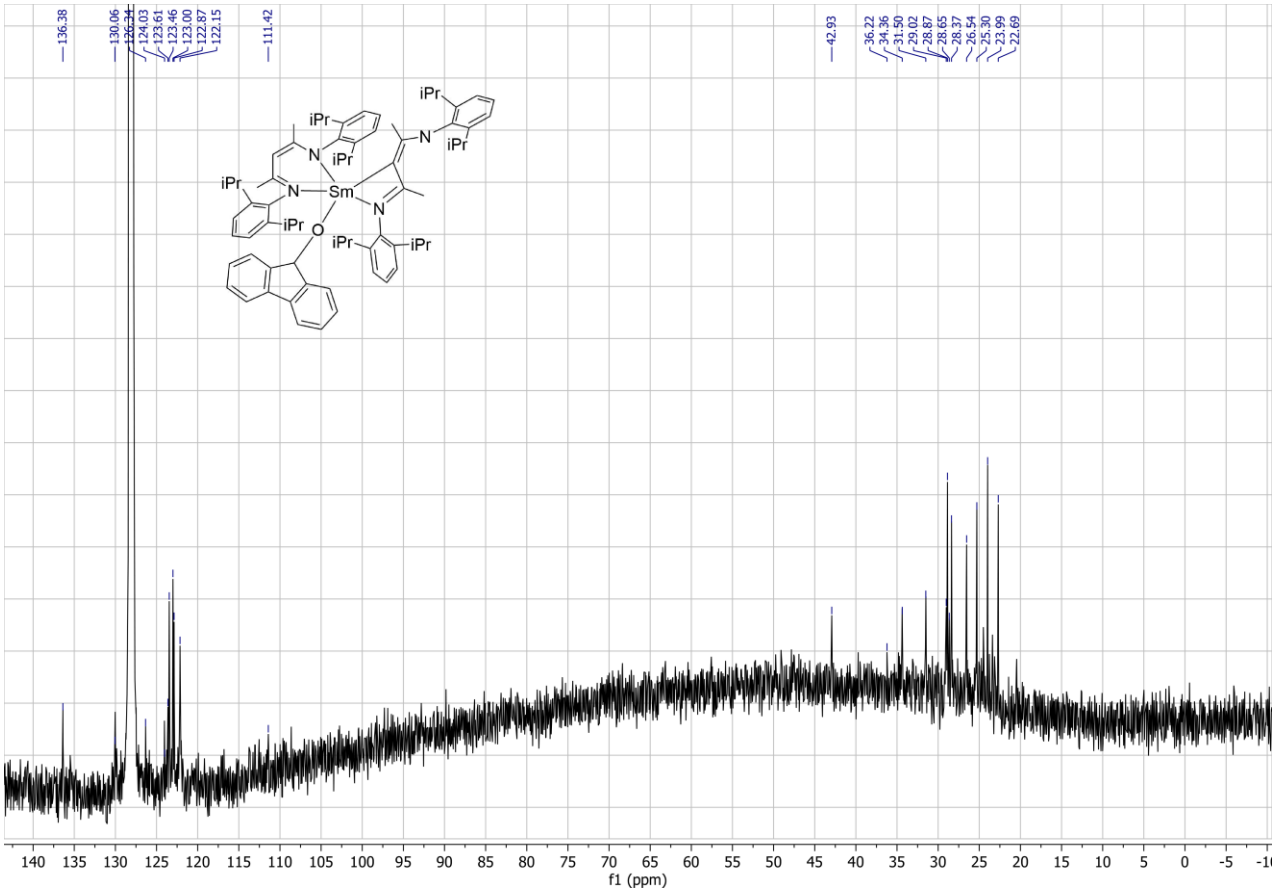

Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of $(BDI)_2Sm(OC_{13}H_8)$ (**6**) in C_6D_6

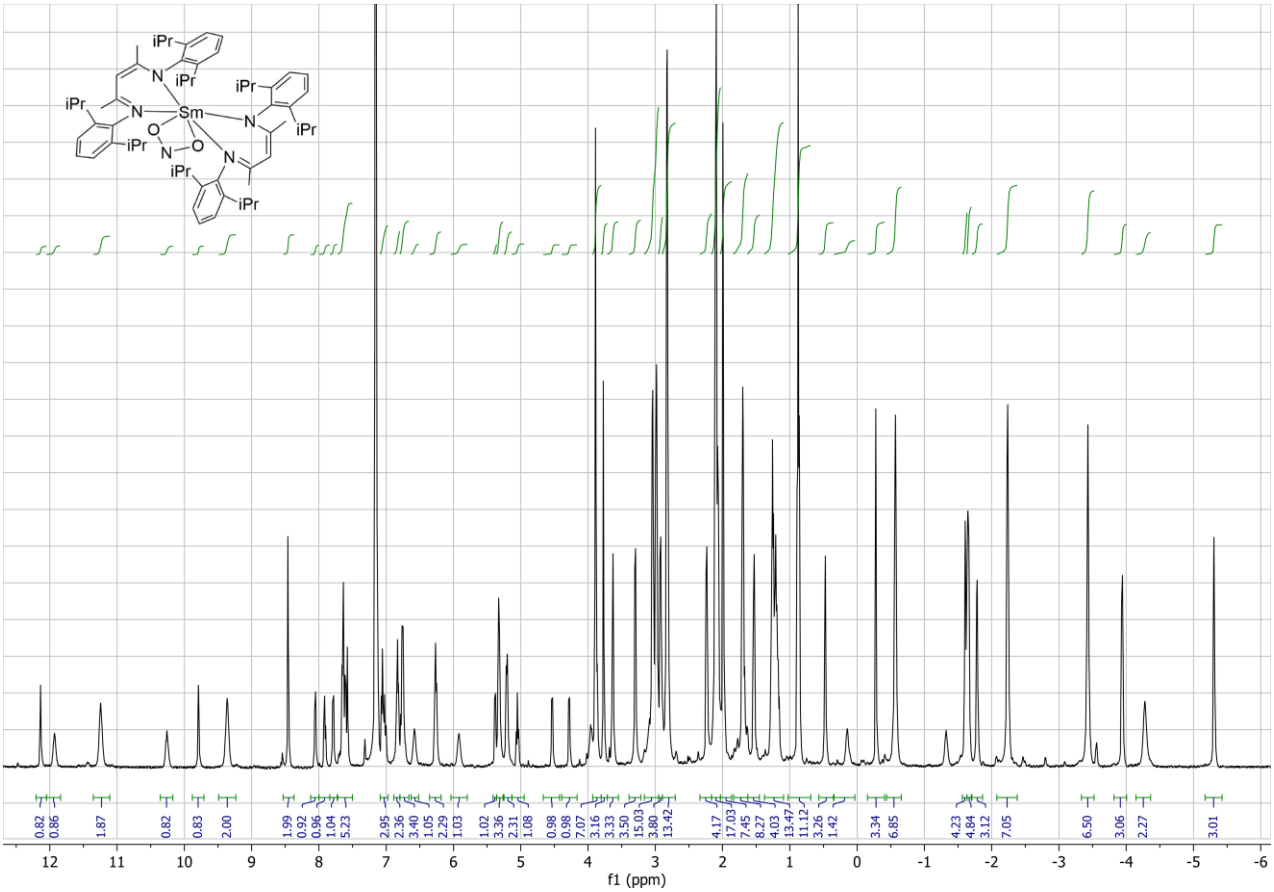

Figure S10. ^{1}H NMR spectrum of $(BDI)_2Sm(NO_2)$ (**7**) in C_6D_6

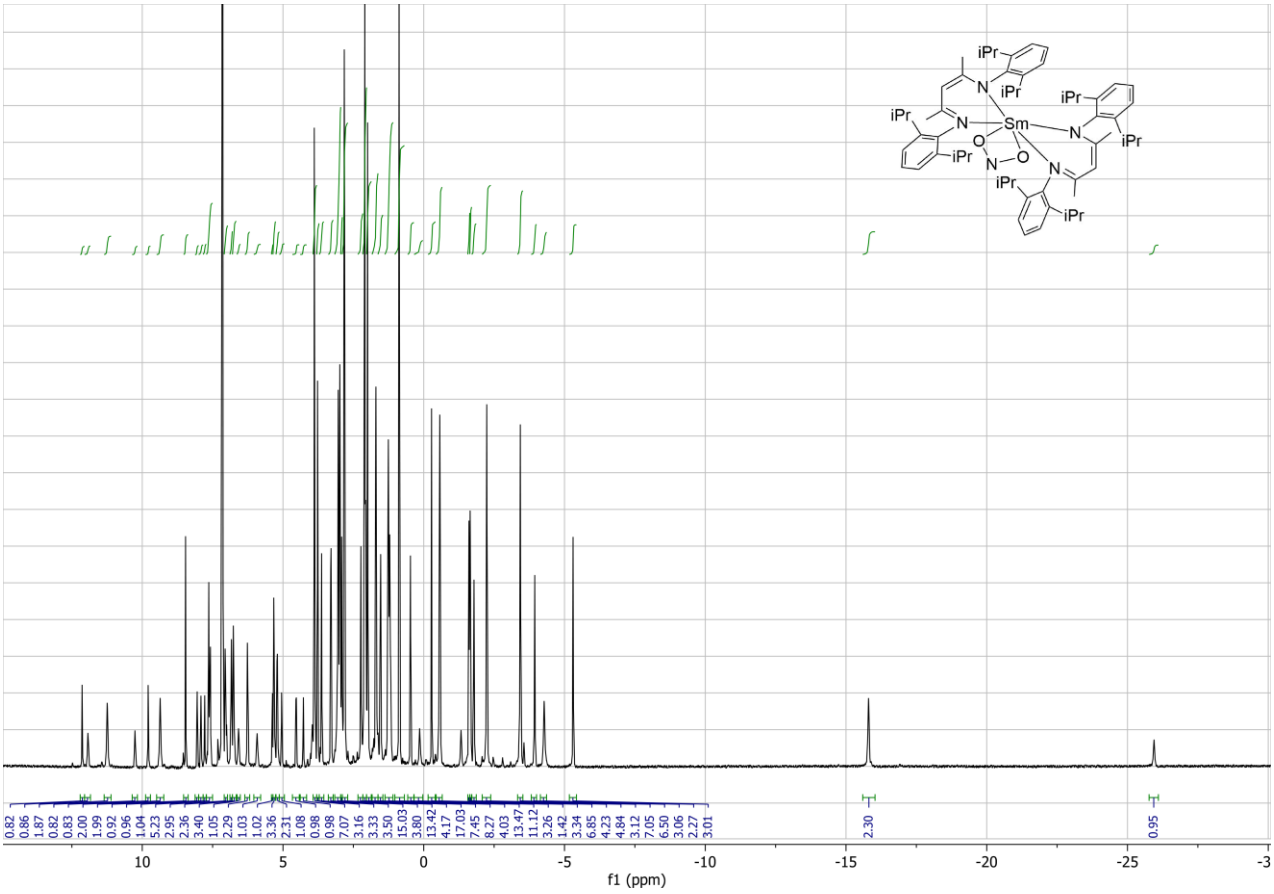

Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of $(BDI)_2Sm(NO_2)$ (**7**) in C_6D_6

2. Crystal data

Experimental section

All crystal structures have been measured on a SuperNova (Agilent) diffractometer with dual Cu and Mo microfocus sources and an Atlas S2 detector. Crystals were covered in paraffin oil, mounted on a flexible MiTeGen microloop and immediately transferred to a cold N_2 stream. The temperature of the N_2 stream was set to 100 K for all structures except **2**, for which 153 K N_2 was used. Structures were determined using Olex2,[S1] ShelXT[S2] for the structure solution by Direct Methods and ShelXL[S3] for least squares refinement. Unless noted otherwise, the hydrogen atoms have been placed at idealized calculated positions and were refined isotropically using a riding model.

Remarks on structure refinement:

$(BDI)_2Sm$ (**2**): The structure solution shows slight disorder in some of the iPr groups which were refined with slightly increased anisotropy.

$[(BDI)_2Sm]_2(\mu\text{-}C_{12}H_8N_2)$ (**3**): The structure contains incorporated benzene solvent which is only slightly disordered and was refined with somewhat larger anisotropic displacement parameters.

$[(BDI)Sm(SPh)(\mu\text{-}SPh)]_2$ (**4**): The asymmetric unit contains one disordered molecule of toluene. A suitable disorder model could not be found and refinement with enlarged displacement factors was preferred over SQUEEZE methods.

(BDI)(BDI-H)Sm·[(BDI)H] (**5a**): All hydrogen atoms have been place on idealized calculated positions and were refined isotropically in a riding mode, except for the H atoms at the CH2 group of one of the nacnac ligands which were found in the difference Fourier map and refined isotropically. The asymmetric unit contains one molecule of hexane which is somewhat disordered but was refined with enlarged displacement factors and DFIX instruction to fix the terminal C-C bonds. The N-H hydrogen atom at the neutral (BDI)H molecule was not found but calculated to be located at one of the N atoms and refined in riding mode. It is, however, likely delocalized over both N atoms (as is evident from equal C-C and C-N bond distances in the NCCCN backbone).

$(BDI)_2Sm(OC_{13}H_8)$ (**6**): All hydrogen atoms have been place on idealized calculated positions and were refined isotropically in a riding mode, except for the C-H hydrogen atoms in the backbone of the BDI ligands which have been refined isotropically with a fixed displacement factor.

$(BDI)_2Sm(NO_2)$ (**7**): The asymmetric unit contains one disordered molecule of pentane. A suitable disorder model could not be found and refinement with enlarged displacement factors was preferred over SQUEEZE methods.

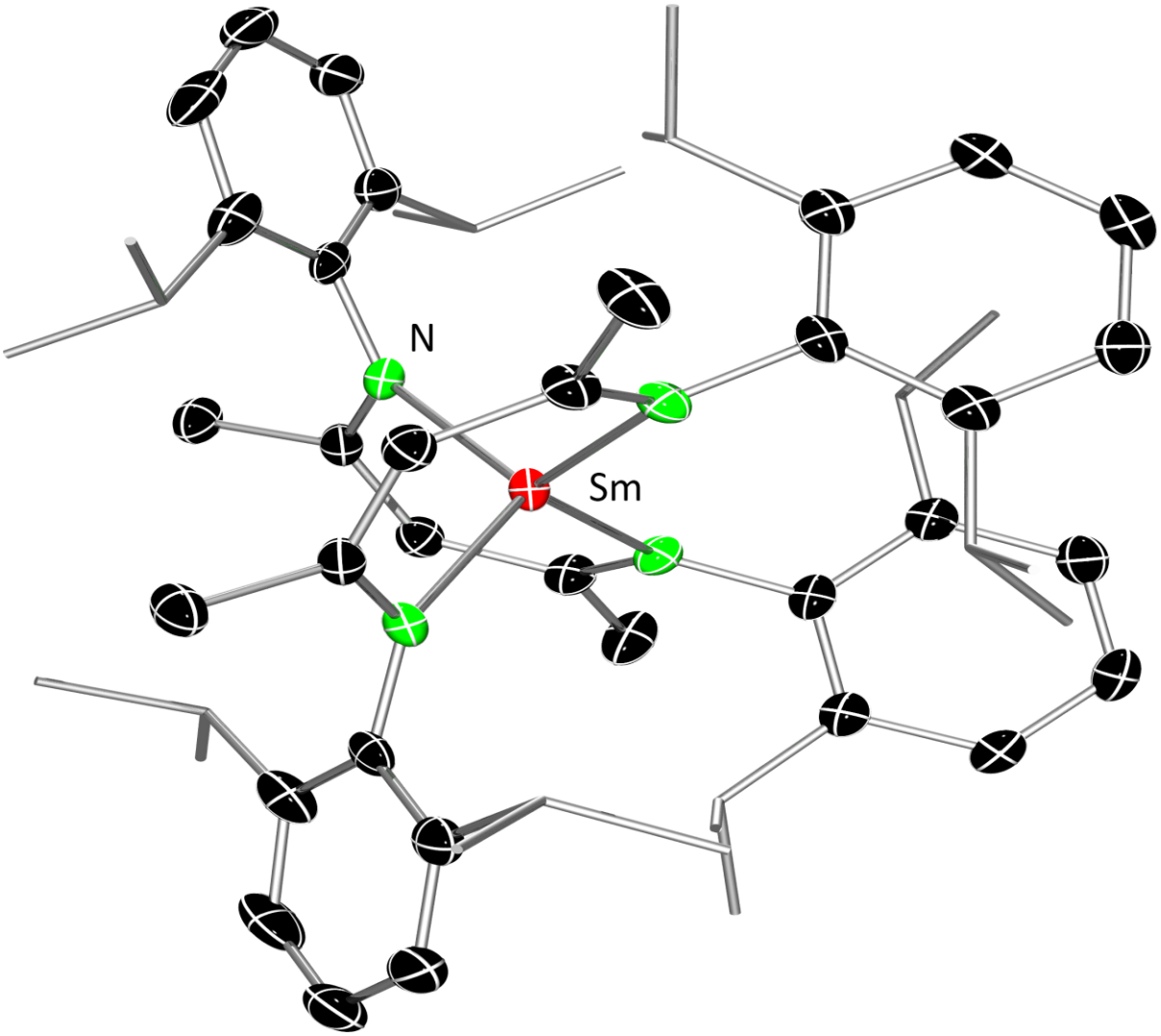

Figure S12. ORTEP drawing of $(BDI)_2Sm$ (**2**) with thermal displacement parameters drawn at 50% probability. For clarity reasons, the *iso*-propyl groups on the aryl rings are depicted as sticks.

Table S1. Crystal Structure data for $(BDI)_2Sm$ (**2**)

Identification code	molan329b
Empirical Formula	$C_{58}H_{82}N_4Sm$
Formula weight	985.62
Temperature/K	153(2)
Crystal system	monoclinic
Space group	C 2/c
a/Å	19.5636(14)
b/Å	12.6480(19)
c/Å	22.1427(19)
α/°	90
β/°	100.455(6)
γ/°	90
Volume/Å^3	5388.0(10)
Z	4
ρ_{calc}/g·cm^{-3}	1.215 g
μ/mm^{-1}	1.128
F(000)	2080
Crystal size/mm^3	0.21 x 0.17 x 0.05
Crystal colour	intense dark-red
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.634−54.300
Index ranges	-25 ≤ h ≤ 25, -16 ≤ k ≤ 16, -28 ≤ l ≤ 28
Reflections collected	82108
Independent reflections	5885 [R_{int} = 0.0682, R_{sigma} = 0.0271]
Data/restraints/parameters	5885/0/287
Goodness-of-fit on F^2	1.200
Final R indexes [>=2σ (I)]	R_1 = 0.0403, wR_2 = 0.0863
Final R indexes [all data]	R_1 = 0.0468, wR_2 = 0.0899
Largest diff. peak/hole/e·Å^3	1.901/-1.877

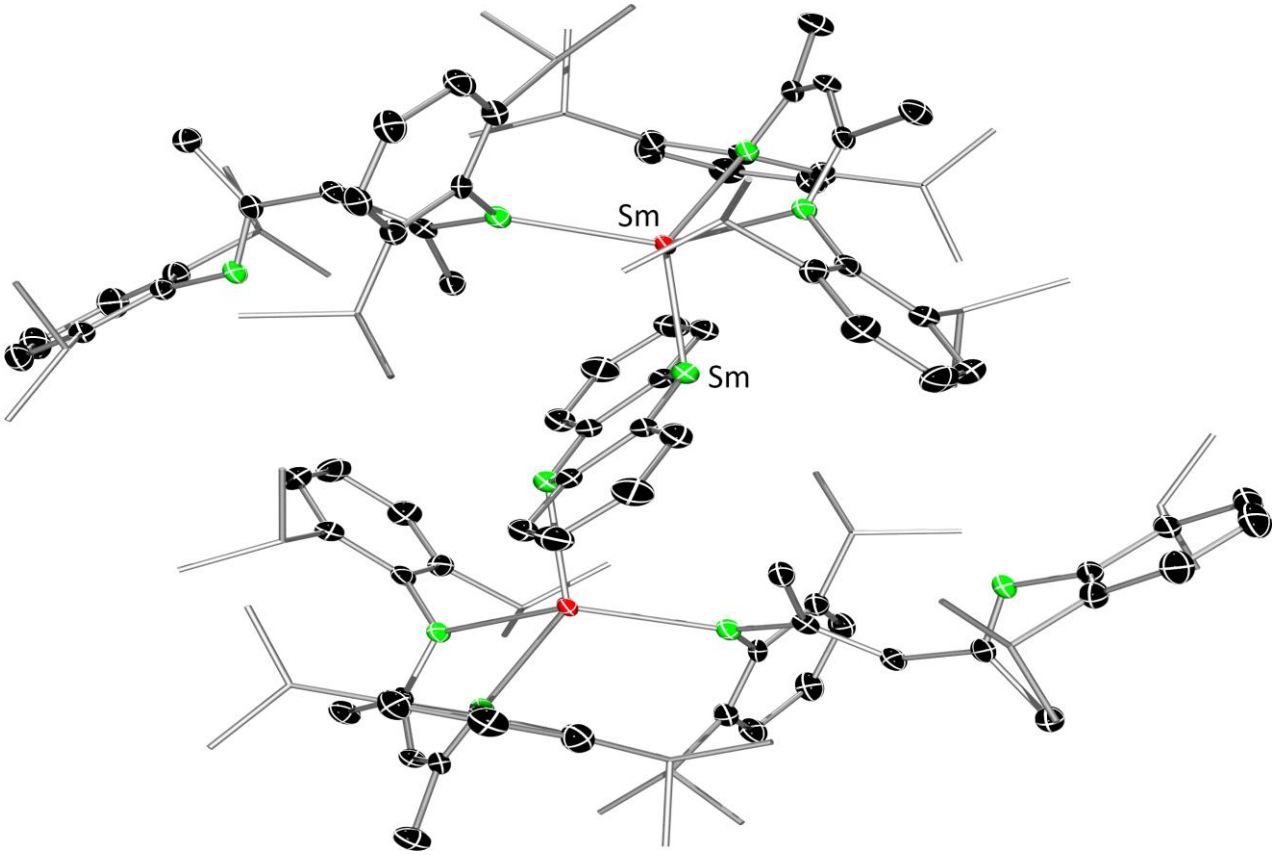

Figure S13. ORTEP drawing of $[(BDI)_2Sm]_2(\mu\text{-}C_{12}H_8N_2)$ (**3**) with thermal displacement parameters drawn at 50% probability. For clarity reasons, the *iso*-propyl groups on the aryl rings are depicted as sticks.

Table S2. Crystal Structure data for $[(BDI)_2Sm]_2(\mu\text{-}C_{12}H_8N_2)$ (**3**)

Identification code	molan334
Empirical Formula	$C_{140}H_{184}N_{10}Sm_2$
Formula weight	2307.66
Temperature/K	100(2)
Crystal system	triclinic
Space group	P −1
a/Å	13.6989(6)
b/Å	15.8652(7)
c/Å	16.8455(7)
α/°	114.098(2)
β/°	101.038(2)
γ/°	105.791(2)
Volume/Å^3	3019.1(2)
Z	1
ρ_{calc}/g·cm^{-3}	1.269
μ/mm^{-1}	1.018 mm^{-1}
F(000)	1218
Crystal size/mm^3	0.19 x 0.13 x 0.08
Crystal colour	dark-red with metallic lustre
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.468 – 55.886
Index ranges	-17 ≤ h ≤ 17, -20 ≤ k ≤ 20, -22 ≤ l ≤ 22
Reflections collected	100317
Independent reflections	14416
Data/restraints/parameters	14416/0/705
Goodness-of-fit on F^2	1.099
Final R indexes [>=2σ (I)]	R_1 = 0.0405, wR_2 = 0.0889
Final R indexes [all data]	R_1 = 0.0545, wR_2 = 0.0985
Largest diff. peak/hole/e·Å^3	2.216/-0.947

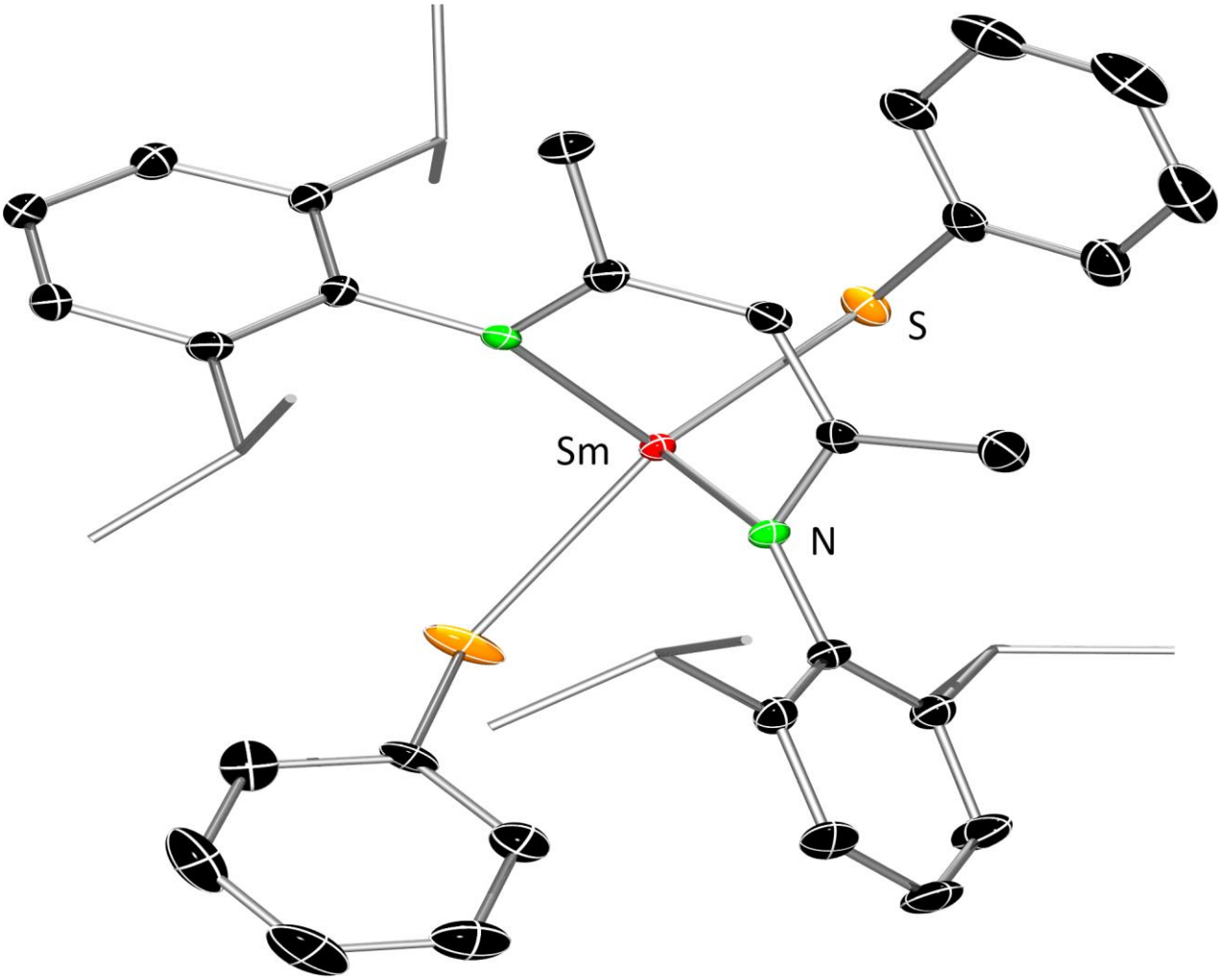

Figure S14. ORTEP drawing of [(BDI)Sm(SPh)(μ-SPh)]$_2$ (**4**) with thermal displacement parameters drawn at 50% probability. For clarity reasons, the *iso*-propyl groups on the aryl rings are depicted as sticks.

Table S3. Crystal Structure data for [(BDI)Sm(SPh)(μ-SPh)]$_2$ (**4**)

Identification code	molan341
Empirical Formula	$C_{96}H_{118}N_4S_4Sm_2$
Formula weight	1756.88
Temperature/K	100(2)
Crystal system	triclinic
Space group	P −1
a/Å	11.4508(4)
b/Å	14.5434(5)
c/Å	15.2437(6)
α/°	92.3100(10) °
β/°	111.4810(10) °
γ/°	111.4750(10) °
Volume/Å^3	2153.23(14) Å^3
Z	1
ρ_{calc}/g·cm^{-3}	1.355
μ/mm^{-1}	1.495
F(000)	910
Crystal size/mm^3	0.35 x 0.12 x 0.05
Crystal color	yellow
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.698−61.150
Index ranges	-14 ≤ h ≤ 16, -20 ≤ k ≤ 18, -21 ≤ l ≤ 21
Reflections collected	26097
Independent reflections	12563
Data/restraints/parameters	12563/0/489
Goodness-of-fit on F^2	1.128
Final R indexes [>=2σ (I)]	R_1 = 0.0449, wR_2 = 0.1067
Final R indexes [all data]	R_1 = 0.0532, wR_2 = 0.1144
Largest diff. peak/hole/e·Å^3	2.664/-2.625

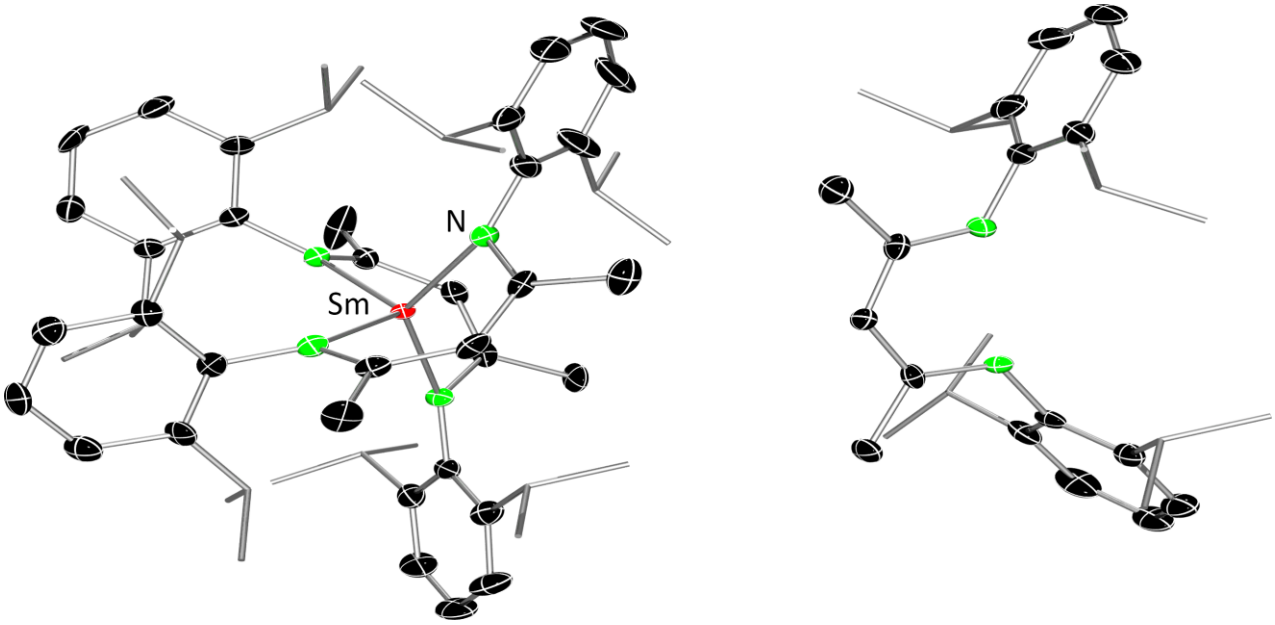

Figure S15. ORTEP drawing of (BDI)(BDI-H)Sm·[(BDI)H] (**5a**) with thermal displacement parameters drawn at 50% probability. For clarity reasons, the *iso*-propyl groups on the aryl rings are depicted as sticks. H atoms at the deprotonated backbone Me group have been found and were refined isotropically.

Table S4. Crystal Structure data for (BDI)(BDI-H)Sm·[(BDI)H] (**5a**)

Identification code	molan370
Empirical Formula	$C_{90}H_{130}N_6Sm$
Formula weight	1446.34
Temperature/K	100(2)
Crystal system	triclinic
Space group	P −1
a/Å	10.9463(8)
b/Å	16.7436(13)
c/Å	24.6176(17)
α/°	70.572(3)
β/°	83.173(3)
γ/°	75.143(3)
Volume/Å^3	4110.0(5)
Z	2
ρ_{calc}/g·cm^{-3}	1.169
μ/mm^{-1}	0.761
F(000)	1548
Crystal size/mm^3	0.15 x 0.04 x 0.02
Crystal color	red
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.220−53.544
Index ranges	-13 ≤ h ≤ 13, -21 ≤ k ≤ 21, -29 ≤ l ≤ 31
Reflections collected	52476
Independent reflections	17316
Data/restraints/parameters	17316/1/882
Goodness-of-fit on F^2	1.072
Final R indexes [>=2σ (I)]	R_1 = 0.0641, wR_2 = 0.1433
Final R indexes [all data]	R_1 = 0.0933, wR_2 = 0.1632
Largest diff. peak/hole/e·Å^3	2.812/-1.498

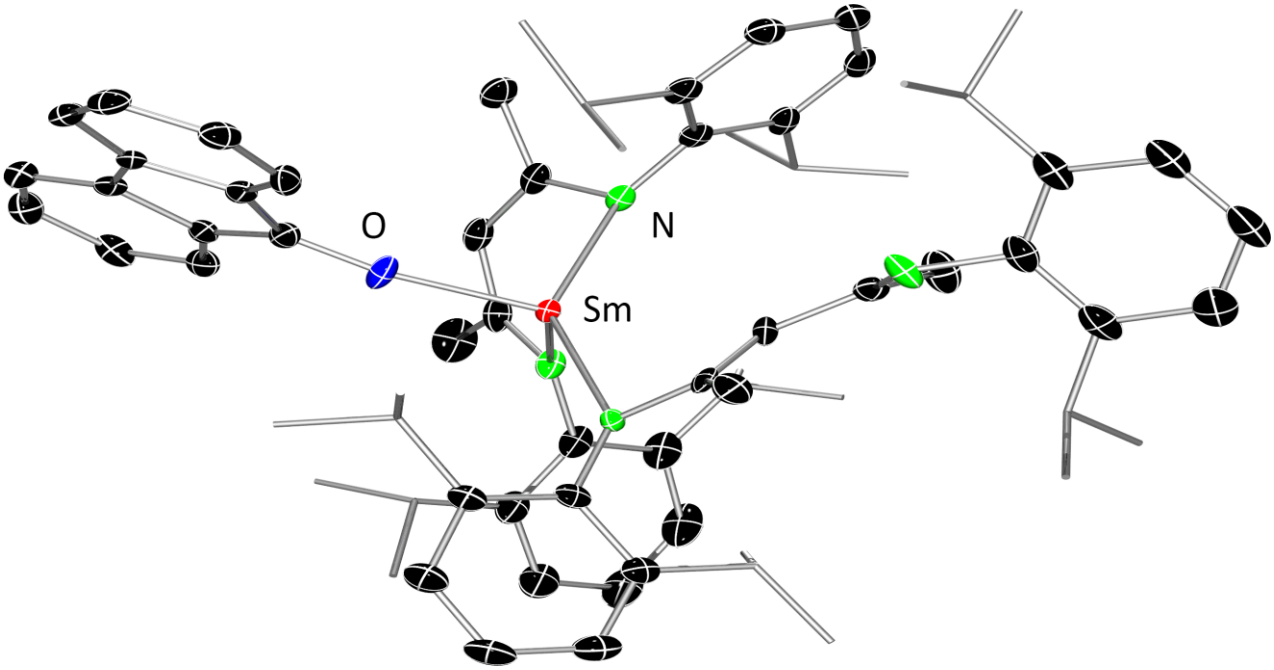

Figure S16. ORTEP drawing of $(BDI)_2Sm(OC_{13}H_8)$ (**6**) with thermal displacement parameters drawn at 50% probability. For clarity reasons, the *iso*-propyl groups on the aryl rings are depicted as sticks.

Table S5. Crystal Structure data for $(BDI)_2Sm(OC_{13}H_8)$ (**6**)

Identification code	molan342
Empirical Formula	$C_{71}H_{90}N_4OSm$
Formula weight	1165.81
Temperature/K	100(2)
Crystal system	triclinic
Space group	P −1
a/Å	12.2882(5)
b/Å	12.8092(6)
c/Å	20.4675(9)
α/°	89.062(2)
β/°	77.387(2)
γ/°	78.214(2)
Volume/Å^3	3076.3(2)
Z	2
ρ_{calc}/g·cm^{-3}	1.259
μ/mm^{-1}	1.000
F(000)	1228
Crystal size/mm^3	0.12 x 0.04 x 0.02
Crystal colour	red
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.402−52.936
Index ranges	-15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -25 ≤ l ≤ 25
Reflections collected	63823
Independent reflections	12612
Data/restraints/parameters	12612/0/720
Goodness-of-fit on F^2	1.094
Final R indexes [>=2σ (I)]	R_1 = 0.0545, wR_2 = 0.0778
Final R indexes [all data]	R_1 = 0.0462, wR_2 = 0.0812
Largest diff. peak/hole/e·Å^3	1.518/-1.696

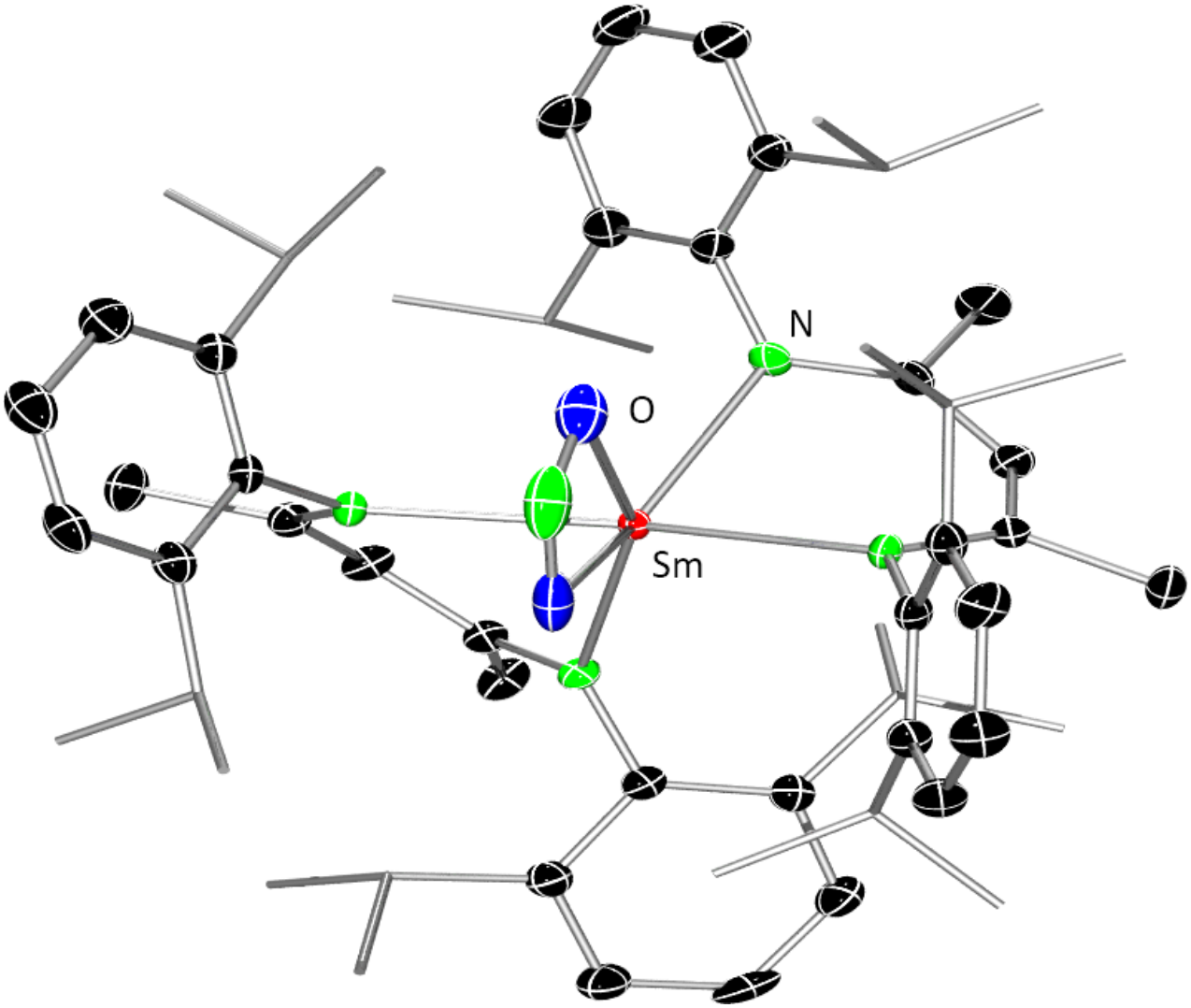

Figure S17. ORTEP drawing of $(BDI)_2Sm(NO_2)$ (**7**) with thermal displacement parameters drawn at 50% probability. For clarity reasons, the *iso*-propyl groups on the aryl rings are depicted as sticks.

Table S6. Crystal Structure data for $(BDI)_2Sm(NO_2)$ (**7**)

Identification code	molan373
Empirical Formula	$C_{63}H_{93}N_5O_2Sm$
Formula weight	1102.77
Temperature/K	100(2)
Crystal system	triclinic
Space group	P −1
a/Å	12.0367(6)
b/Å	12.1936(5)
c/Å	20.7640(9)
α/°	83.648(2)
β/°	83.196(2)
γ/°	76.595(2)
Volume/Å^3	2932.7(2)
Z	2
ρ_{calc}/g·cm^{-3}	1.249
μ/mm^{-1}	1.047
F(000)	1700
Crystal size/mm^3	0.12 x 0.09 x 0.05
Crystal color	yellow
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.950−65.968
Index ranges	-18 ≤ h ≤ 17, -18 ≤ k ≤ 17, -31 ≤ l ≤ 30
Reflections collected	68402
Independent reflections	19242
Data/restraints/parameters	19242/0/662
Goodness-of-fit on F^2	1.201
Final R indexes [>=2σ (I)]	R_1 = 0.0722, wR_2 = 0.1239
Final R indexes [all data]	R_1 = 0.0518, wR_2 = 0.1093
Largest diff. peak/hole/e·Å^3	1.910/-2.186

3. References

[1] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339-341
[2] G. M. Sheldrick, *Acta Cryst.* **2015**, *A71*, 3-8
[3] G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122