Supporting Information for:

A Novel Samarium(II) Complex Bearing a Dianionic Bis(phenolate) Cyclam Ligand: Synthesis, Structure and Electron-Transfer Reactions

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1. NMR Data

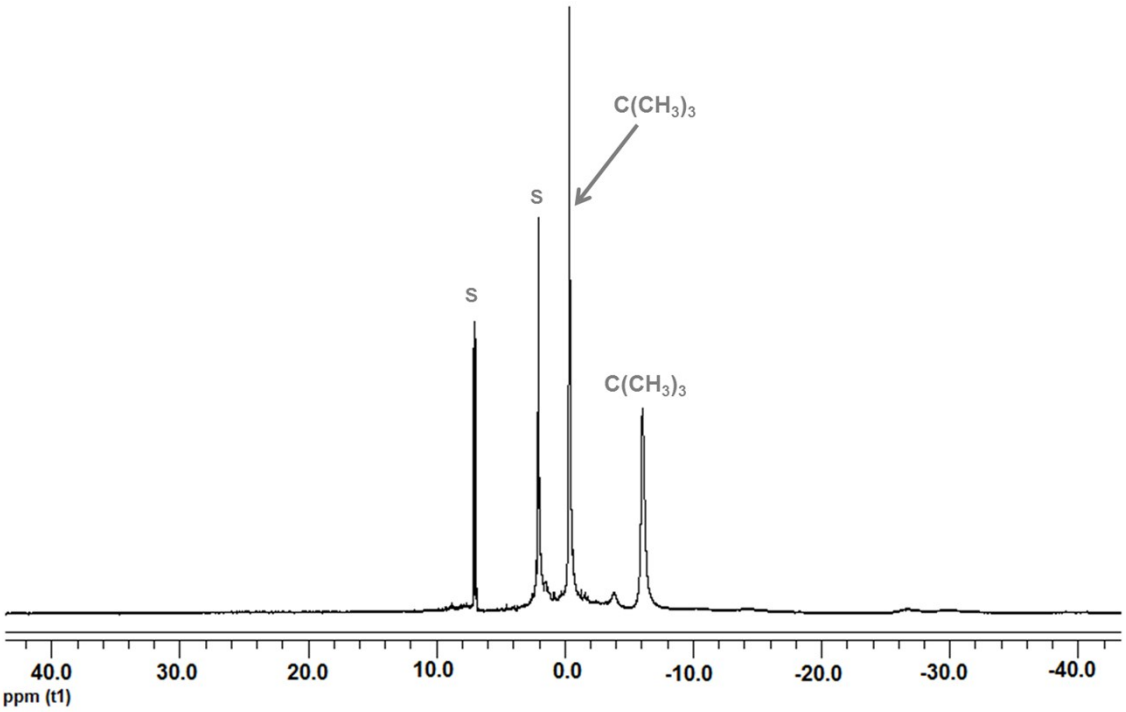


Figure S1. ^{1}H NMR spectrum of [Sm{(^{tBu2}OAr)$_2$Me$_2$-cyclam}] (**1**) in toluene-d_8 at 23 ºC.

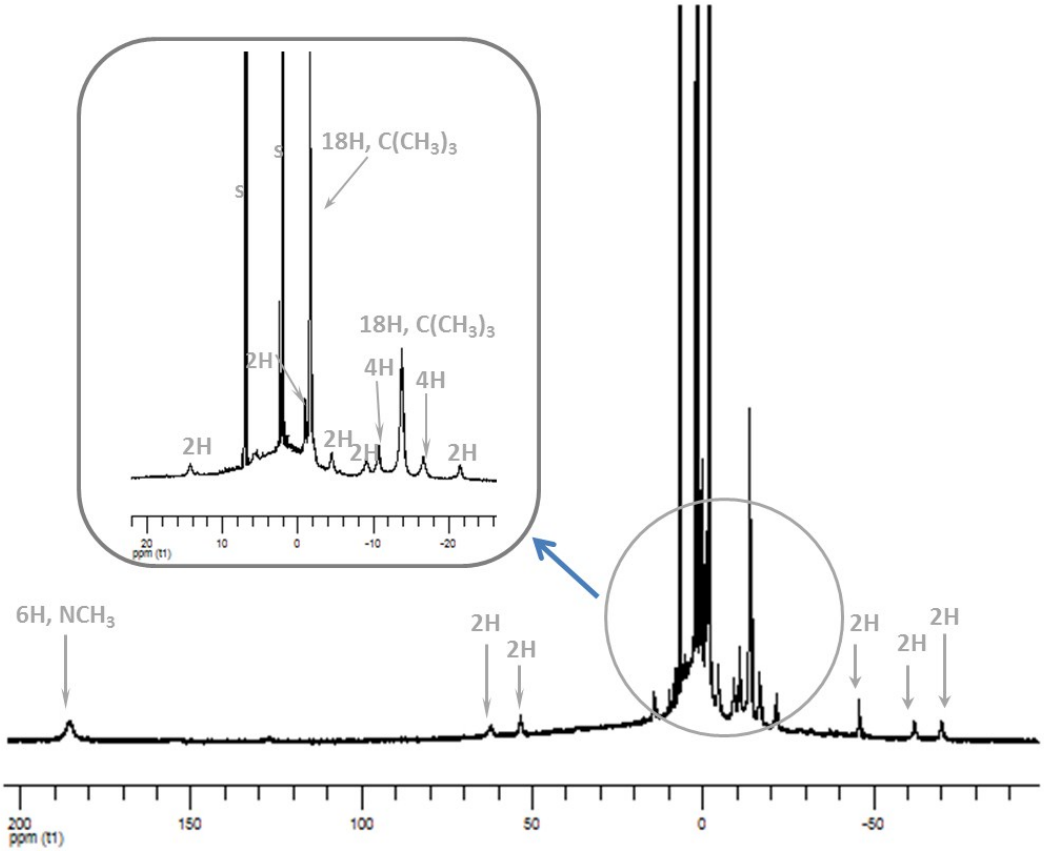


Figure S2. ^{1}H NMR of [Sm{(^{tBu2}OAr)$_2$Me$_2$-cyclam}](**1**) in toluene-d_8 at -40ºC.

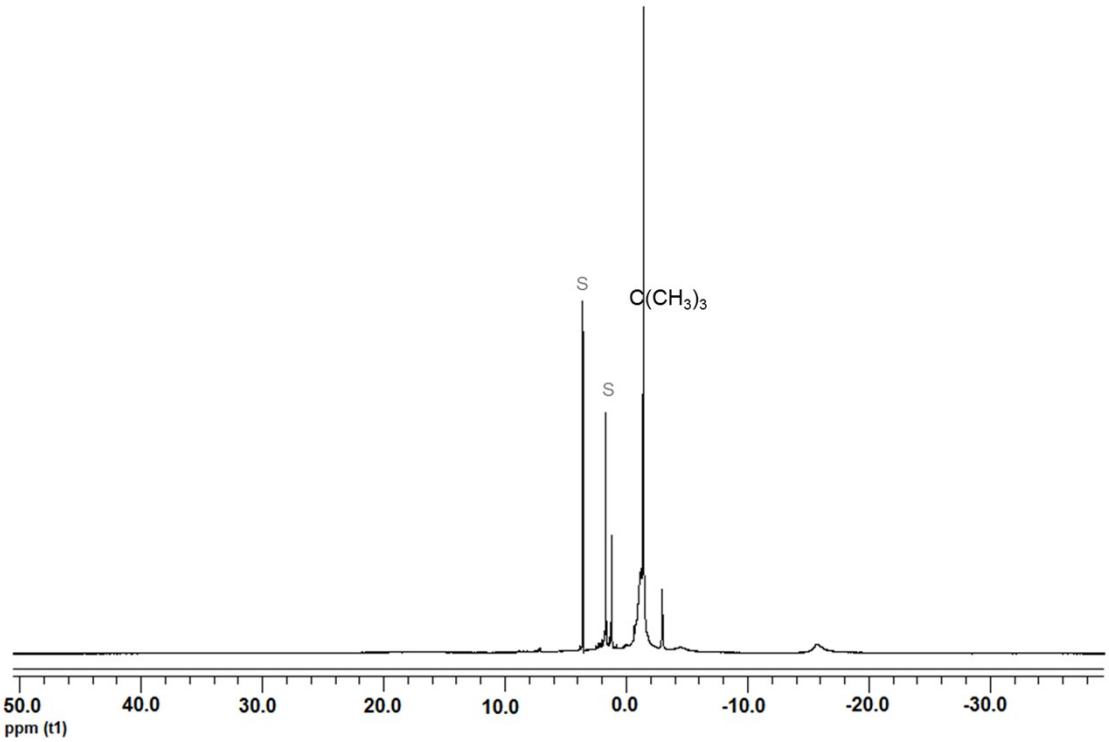


Figure S3. ^{1}H NMR of [Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}] (**1**) thf-d_8 at 25 ºC.

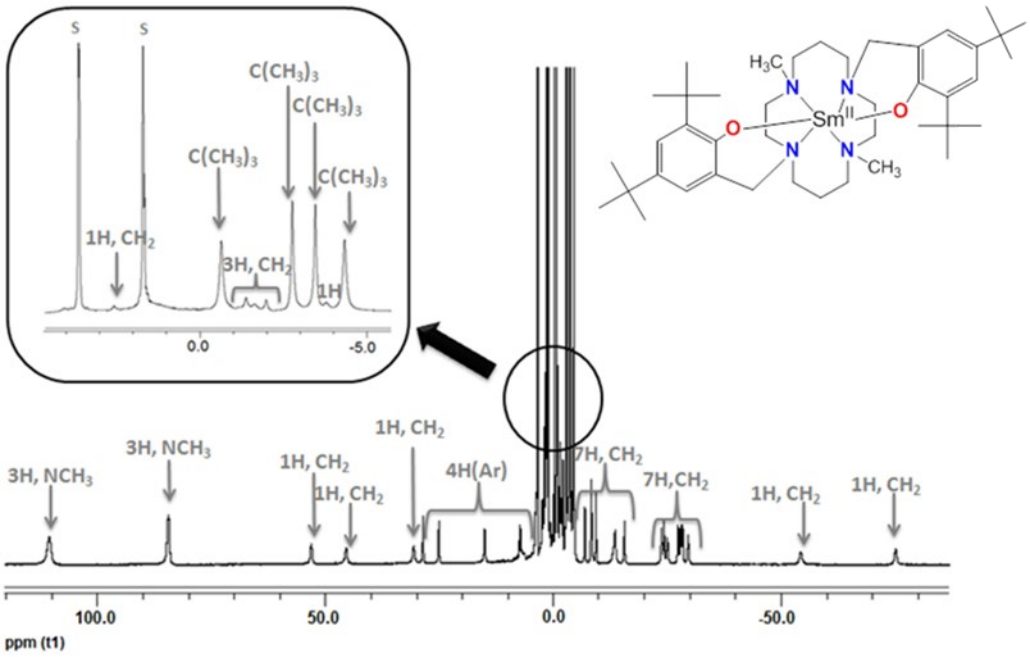


Figure S4. ^{1}H NMR spectrum of [Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}] (**1**) in thf-d_8 at -40ºC.

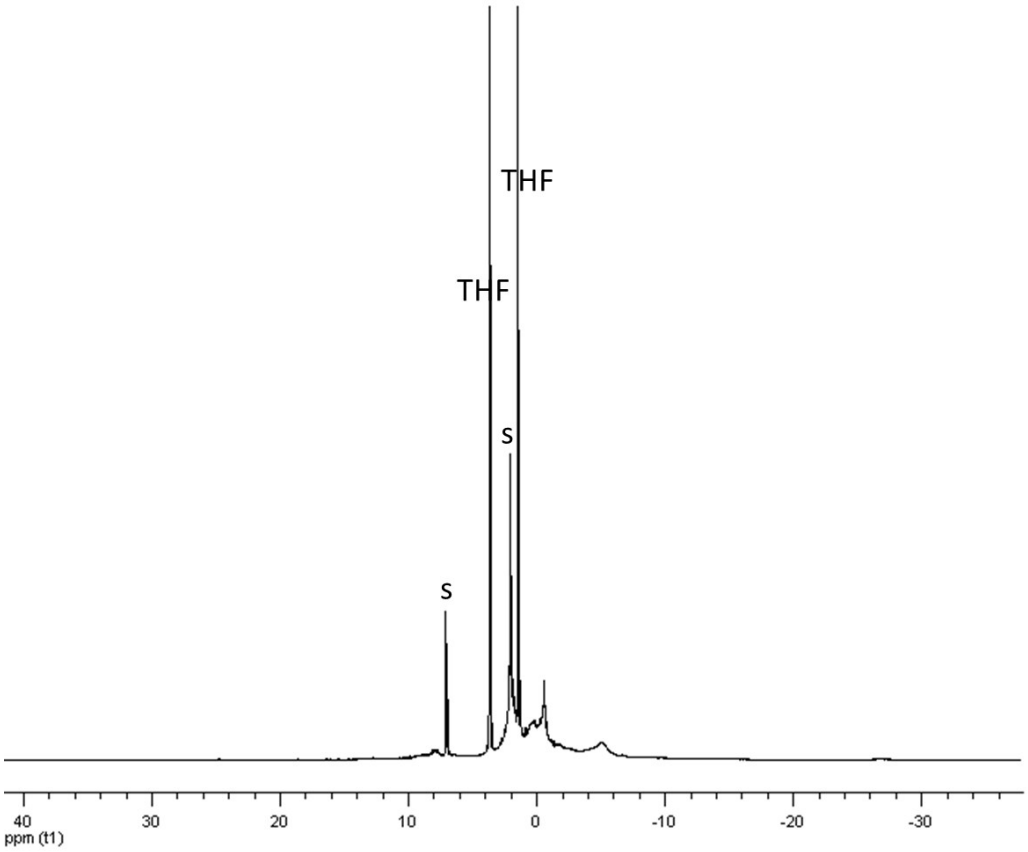


Figure S5. ^{1}H NMR spectrum of [Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}] (**1**) in toluene-d_8 with thf addition at 25ºC.

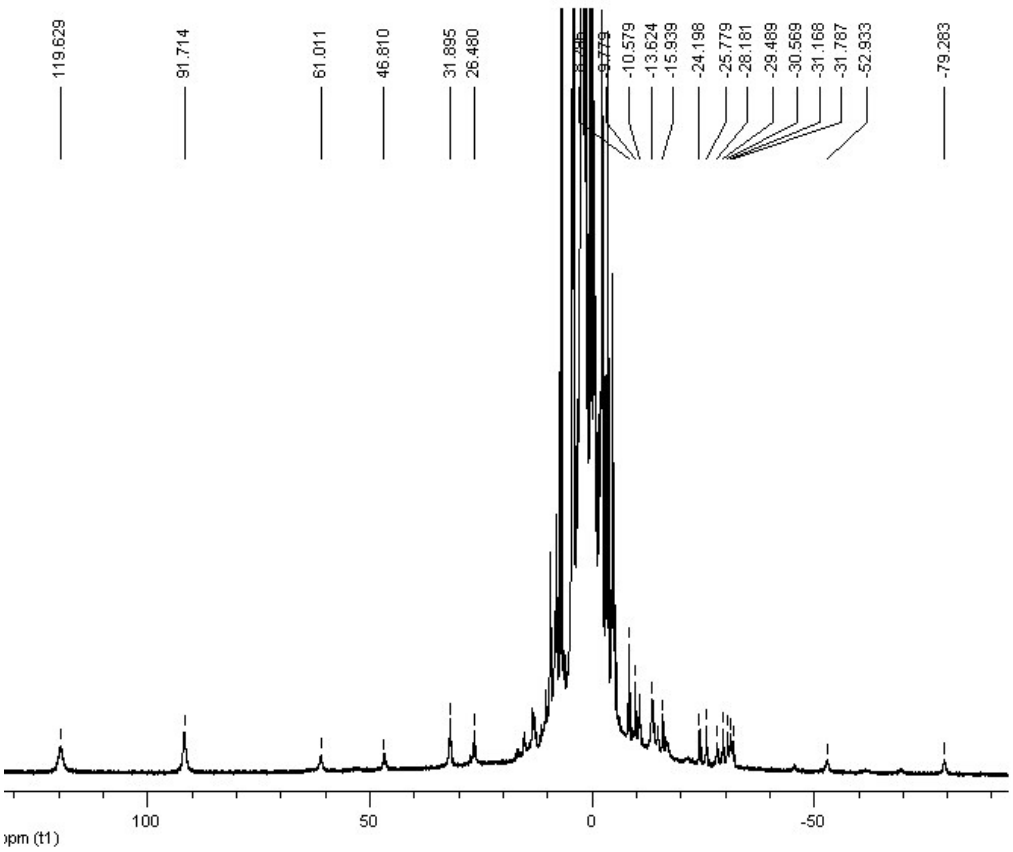


Figure S6. ^{1}H NMR spectrum of [Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}] (**1**) in toluene-d_8 with thf addition at -40ºC.

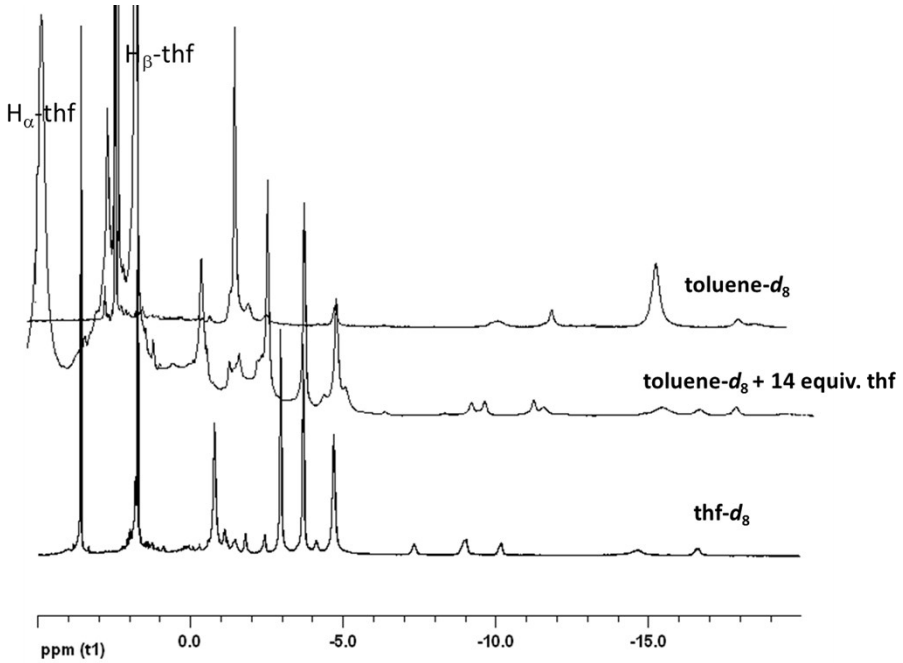


Figure S7. ^{1}H NMR of **1** spectrum in toluene-d_8, toluene-d_8 with addition of thf and in thf-d_8 at -50ºC.

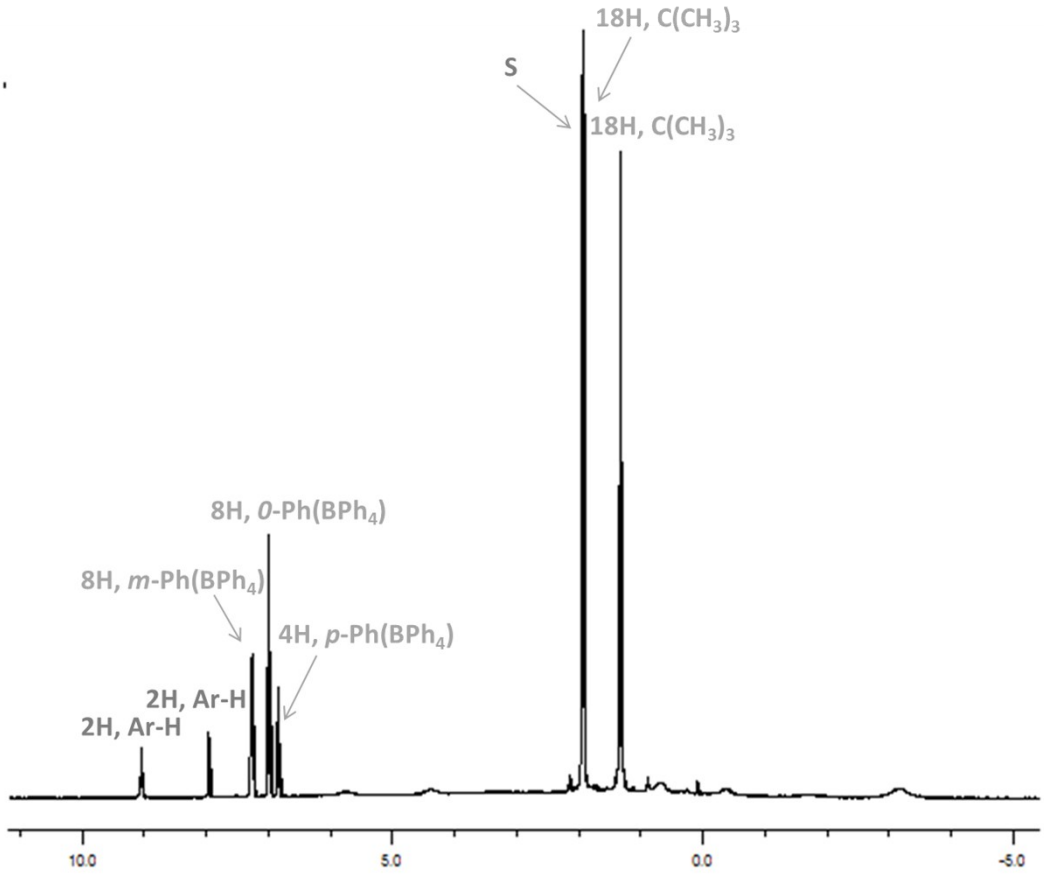


Figure S8. ^{1}H NMR of [Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}][BPh$_4$] (**2**) in acetonitrile-d_3 at 23 ºC.

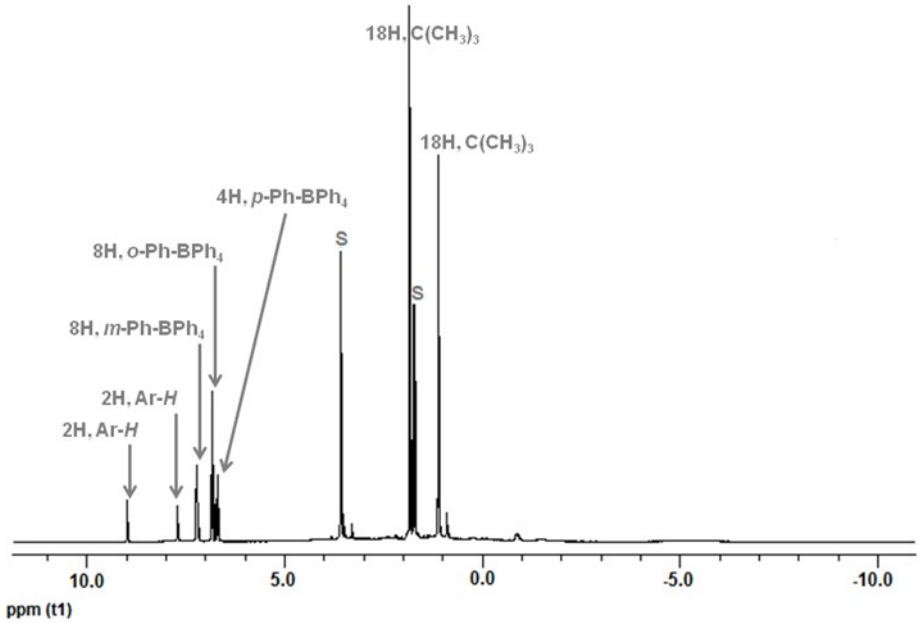


Figure S9. ^{1}H NMR of [Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}][BPh$_4$] (**2**) in thf-d_8 at 23 ºC.

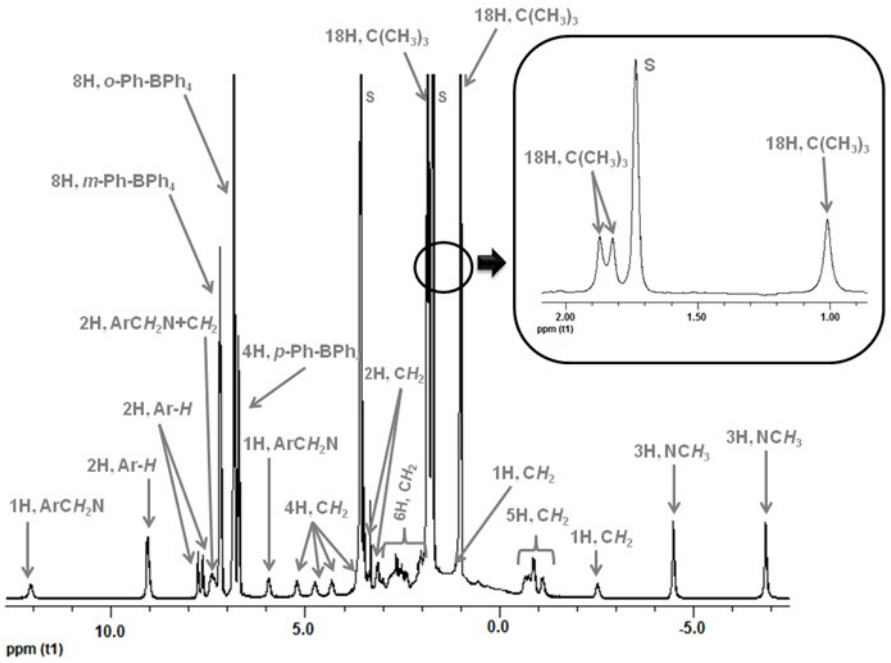


Figure S10. ^{1}H NMR of spectrum of [Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}][BPh$_4$] (**2**) in thf-d_8 at -30 ºC.

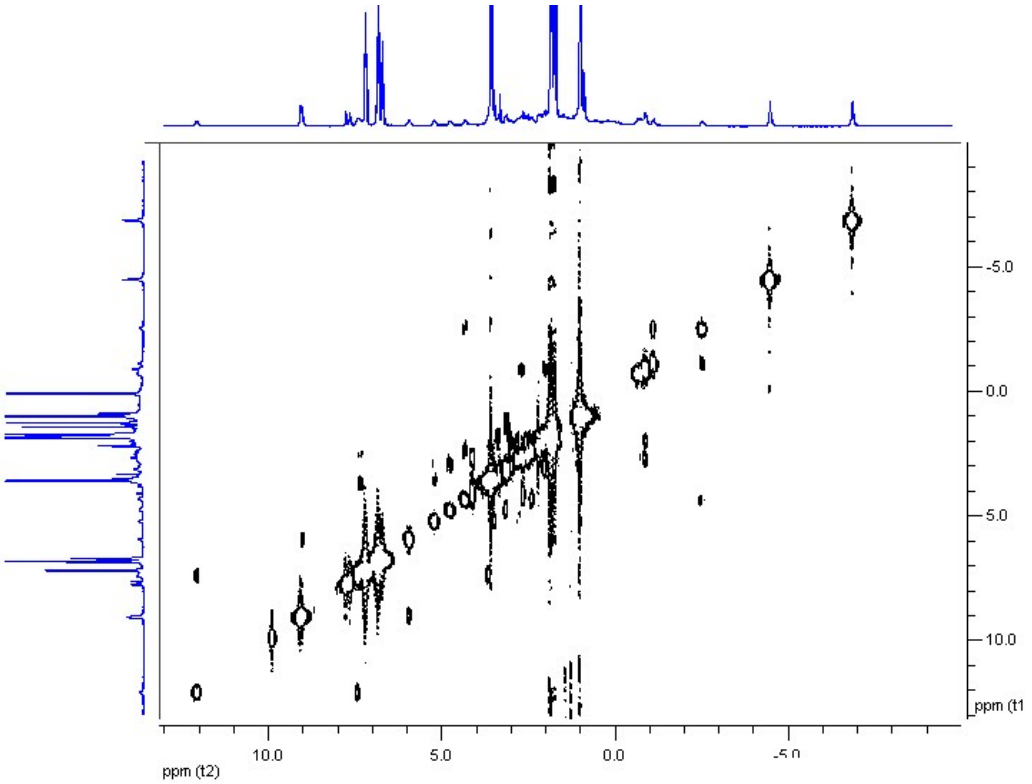


Figure S11. ^{1}H -^{1}H COSY of [Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}][BPh$_4$] (**2**) in thf-d_8 at -30 ºC.

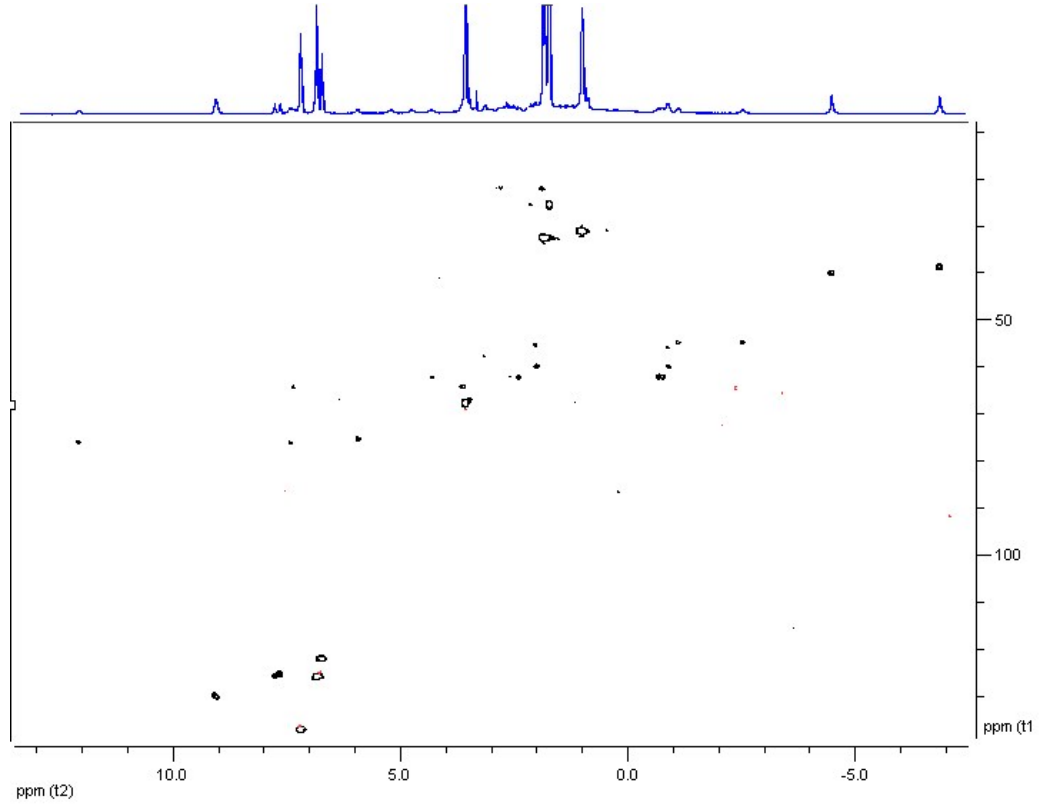
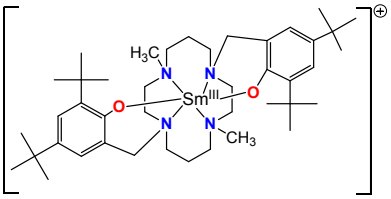


Figure S12. ^{1}H-^{13}C HSQC spectrum of [Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}][BPh$_4$] (**2**) in thf-d_8 at -30 ºC.

Table S1 ^{1}H and ^{13}C chemical shifts of [Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}][BPh$_4$] (**2**) in thf-d_8 at -30ºC[a)]



	Chemical Shift (δ, ppm)	
	^{1}H	**^{13}C**
ArC-H	9.08	129.91
ArC-H	9.04	129.91
ArC-H	7.77	125.48
ArC-H	7.64	125.12
ArCH$_2$N	12.08; 7.41	75.95
ArC*H*$_2$N	9.00; 5.94	75.20
CH$_2$	5.21, 3.50	66.84
CH$_2$	7.35, 3.63	64.18
CH$_2$	4.33, 2.43	62.14
CH$_2$	-0.70 (2H)	62.08
CH$_2$	2.03, -0.88	59.88
CH$_2$	2.20, -0.88	55.87
CH$_2$	-1.11, -2.53	54.72
CH$_2$	4.75, 3.14	57.38
CH$_2$	2.55, 2.17	25.46
CH$_2$	2.84, 1.91	22.04
C(C*H*$_3$)$_3$	1.87 (9H), 1.82 (9H)	32.43
C(C*H*$_3$)$_3$	1.01 (18H)	31.81
	[BPh$_4$]$^-$	
***m*-Ph-BPh$_4$**	7.20	137.00
***o*-Ph-BPh$_4$**	6.84	125.65
***p*-Ph-BPh$_4$**	6.72	121.79

a) The ^{13}C chemical shifts were extracted from the ^{1}H - ^{13}C HSQC experiment.

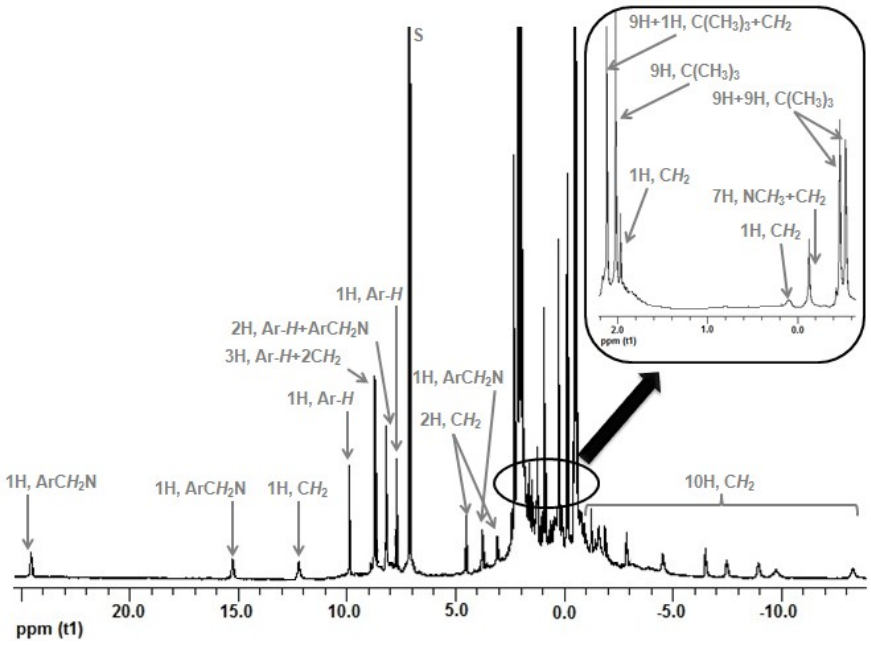


Figure S13. ^{1}H NMR of [({Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}})$_2$(μ-O)] (**3**) in benzene-d_6 at 23 ºC.

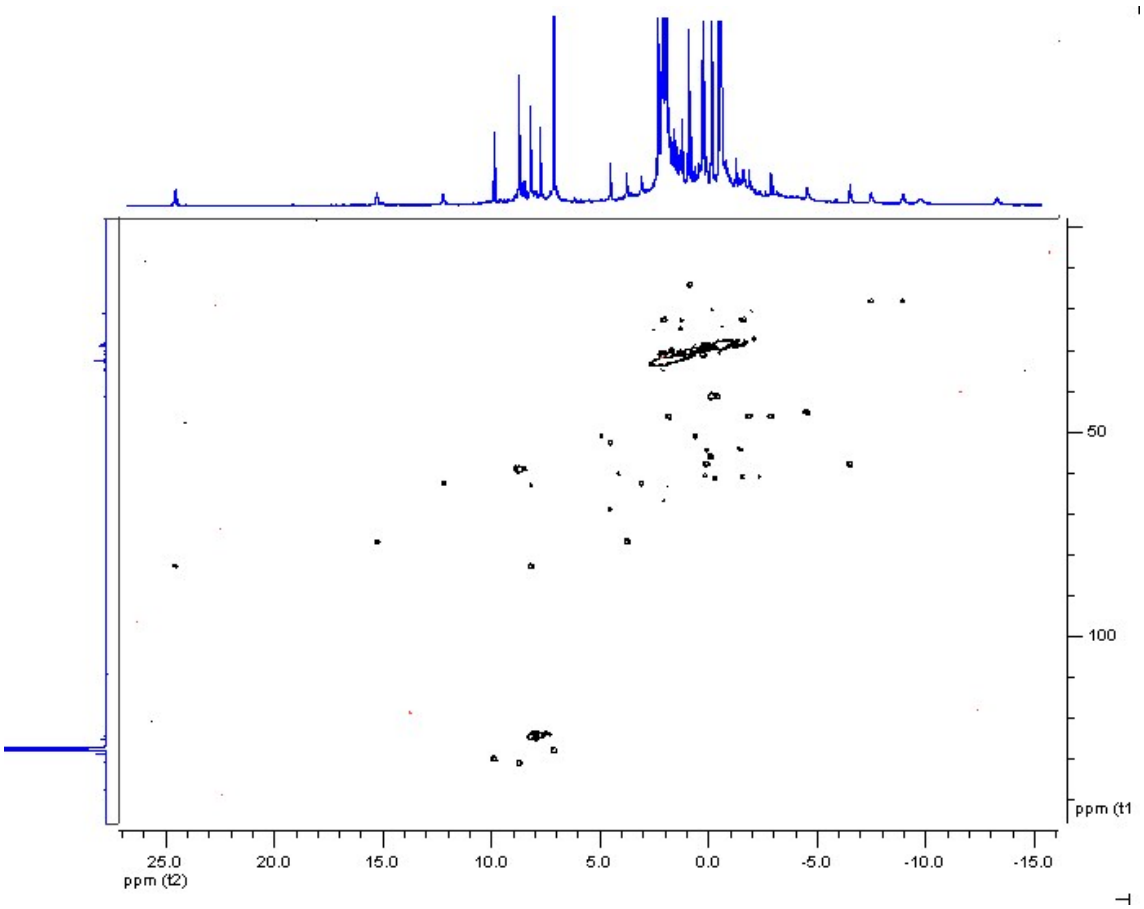


Figure S14. ^{1}H-^{13}C HSQC spectrum of [({Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}})$_2$(μ-O)] (**3**) in thf-d_8

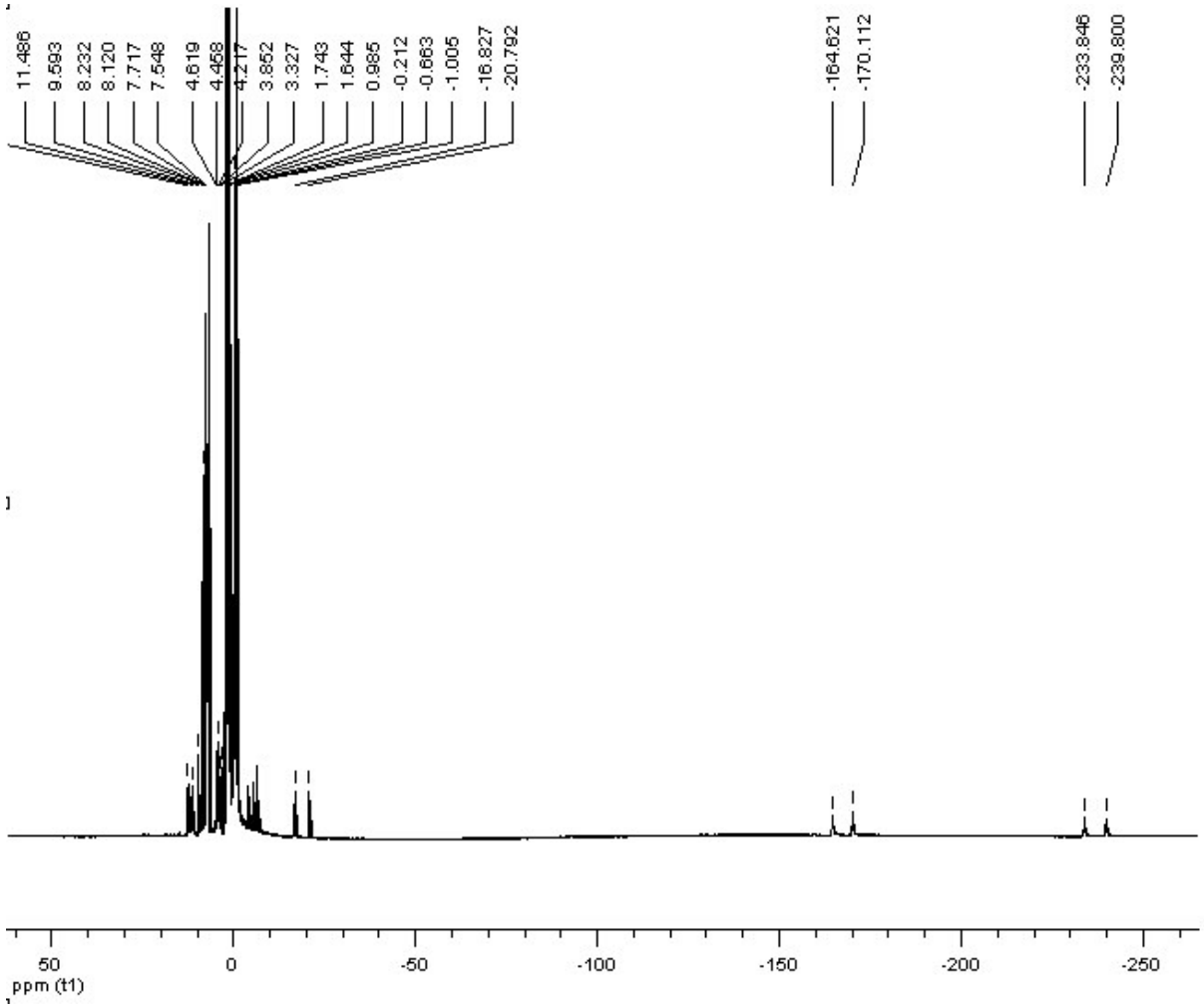


Figure S15. Full ^{1}H NMR spectrum of [Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}(bipy$^{\bullet-}$)] (**5**) in toluene-d_8 at 25 ºC from 60 to -260 ppm.

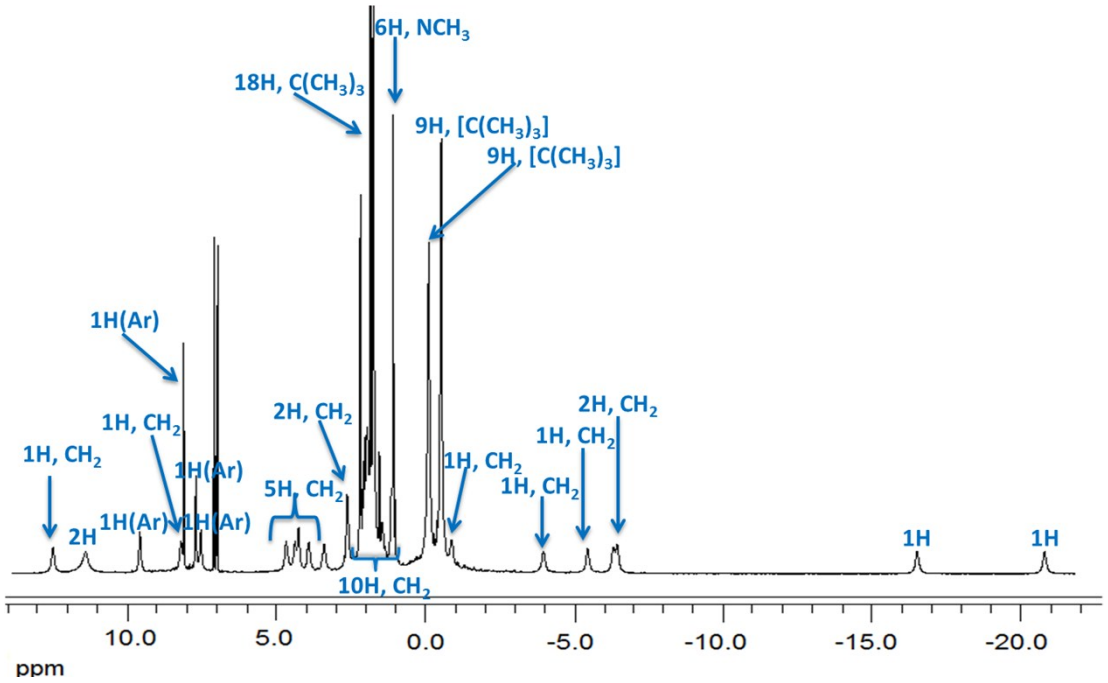


Figure S16. ^{1}H NMR spectrum of [Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam} (bipy$^{\bullet-}$)] (**5**) in toluene-d_8 at 25 ºC from 14 to -22 ppm.

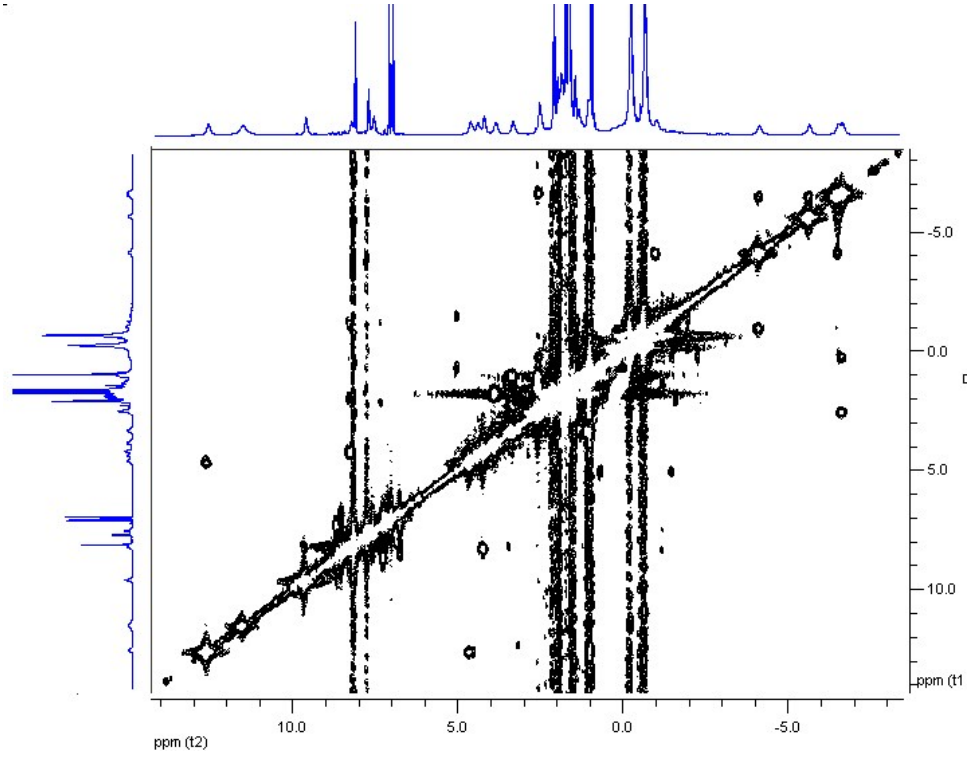


Figure S17. ^{1}H- ^{1}H gCOSY spectrum of [Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam} (bipy$^{\bullet-}$)] (**5**) in toluene-d_8 at 25 ºC from 14 to -8 ppm

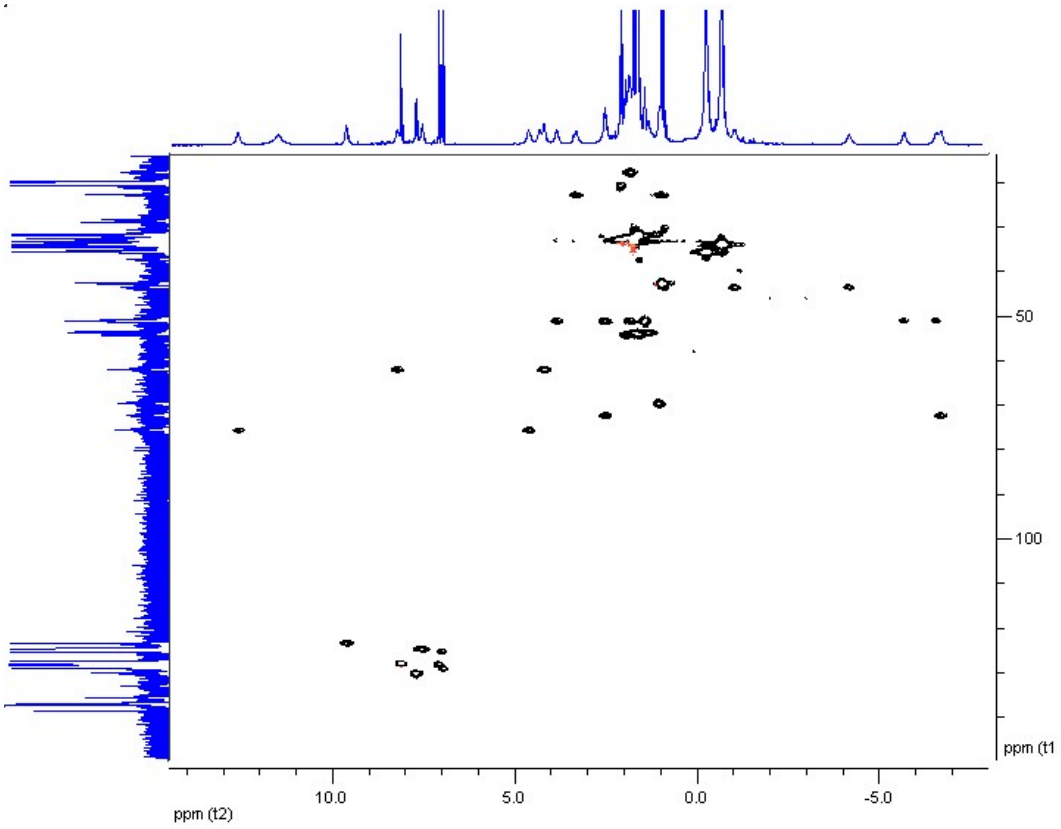


Figure S18. $^{1}H - ^{13}C$ HSQC spectrum of [Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}(bipy$^{\bullet-}$)] (**5**) in toluene-d_8 at 25 ºC from 11 to -22 ppm

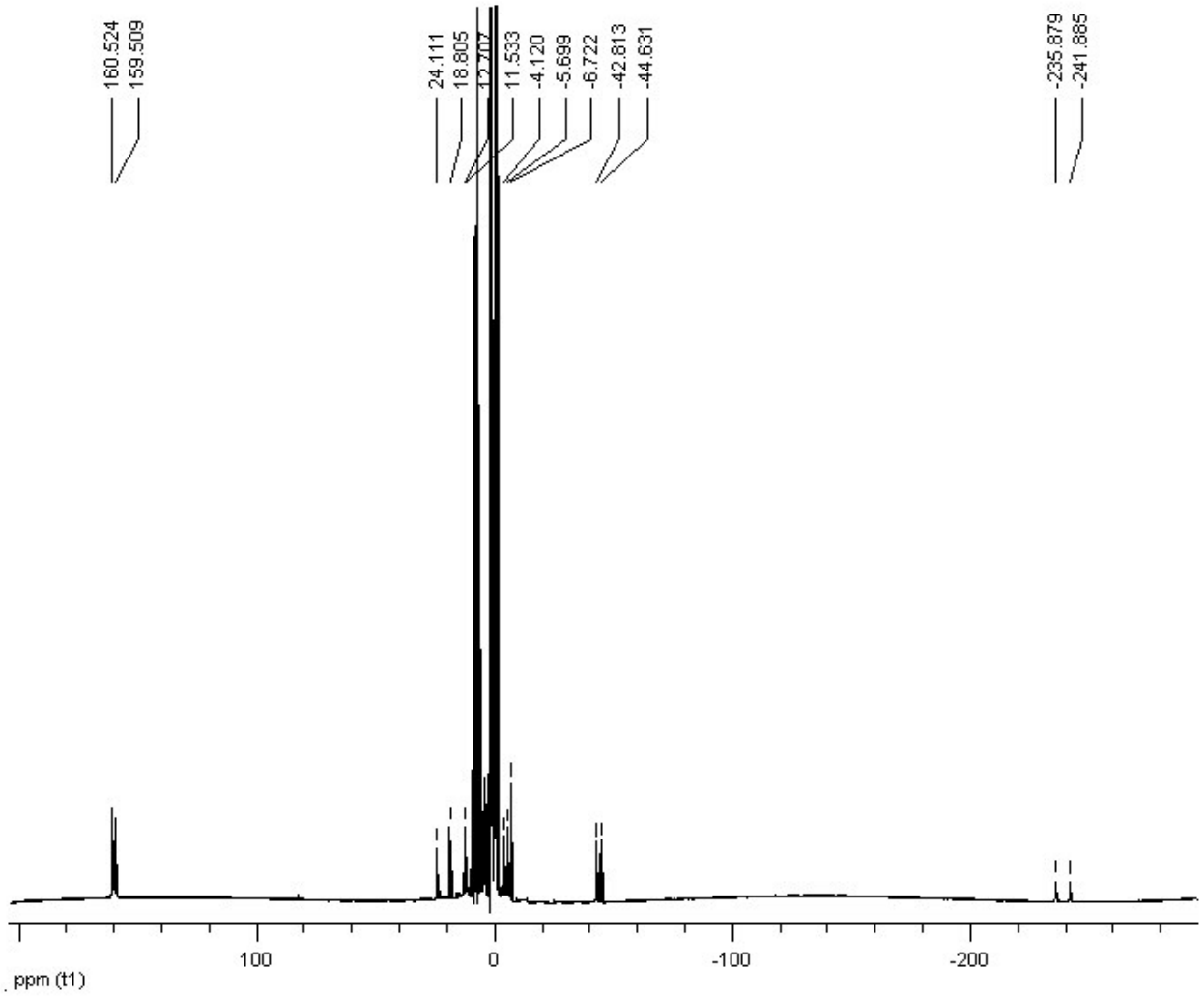


Figure S19. Full ^{1}H NMR spectrum of [{Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}}(Me$_2$-bipy$^{\bullet-}$)] (**6**) in toluene-d_8 at 25 ºC from 200 to -290 ppm.

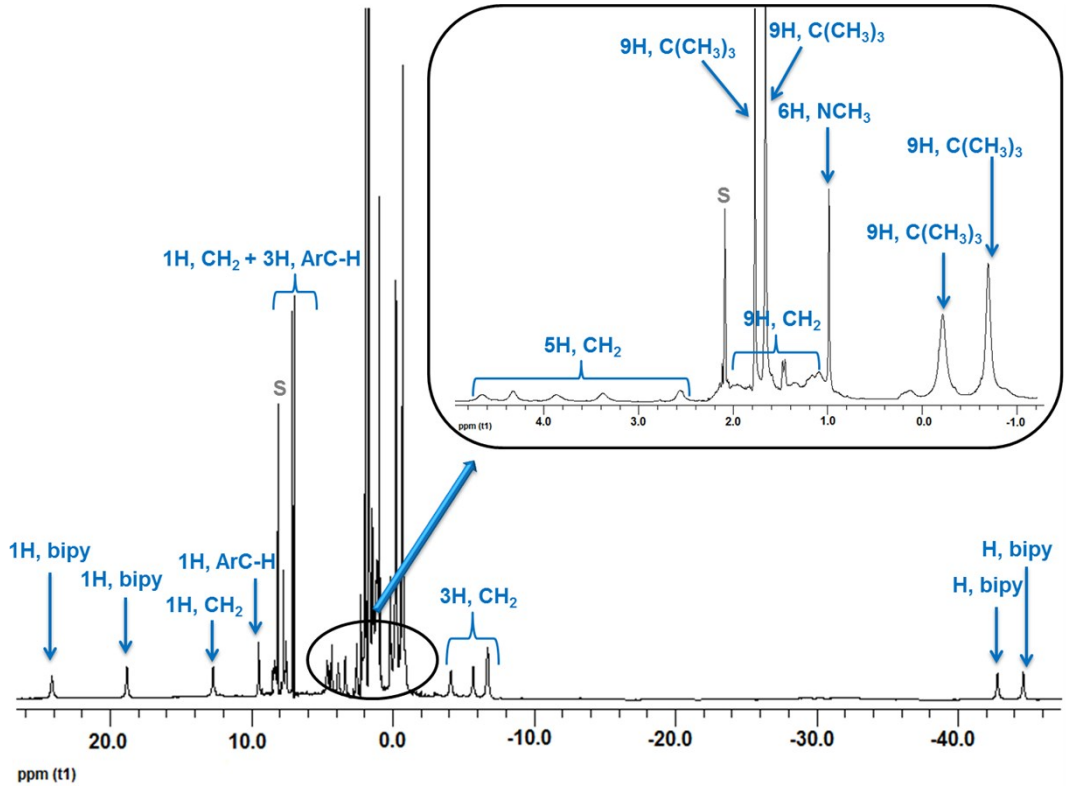


Figure S20. ^{1}H NMR spectrum of [Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam} (Me$_2$-bipy$^{\bullet-}$)] (**6**) in toluene-d_8 at 25 ºC from 26 to -46 ppm.

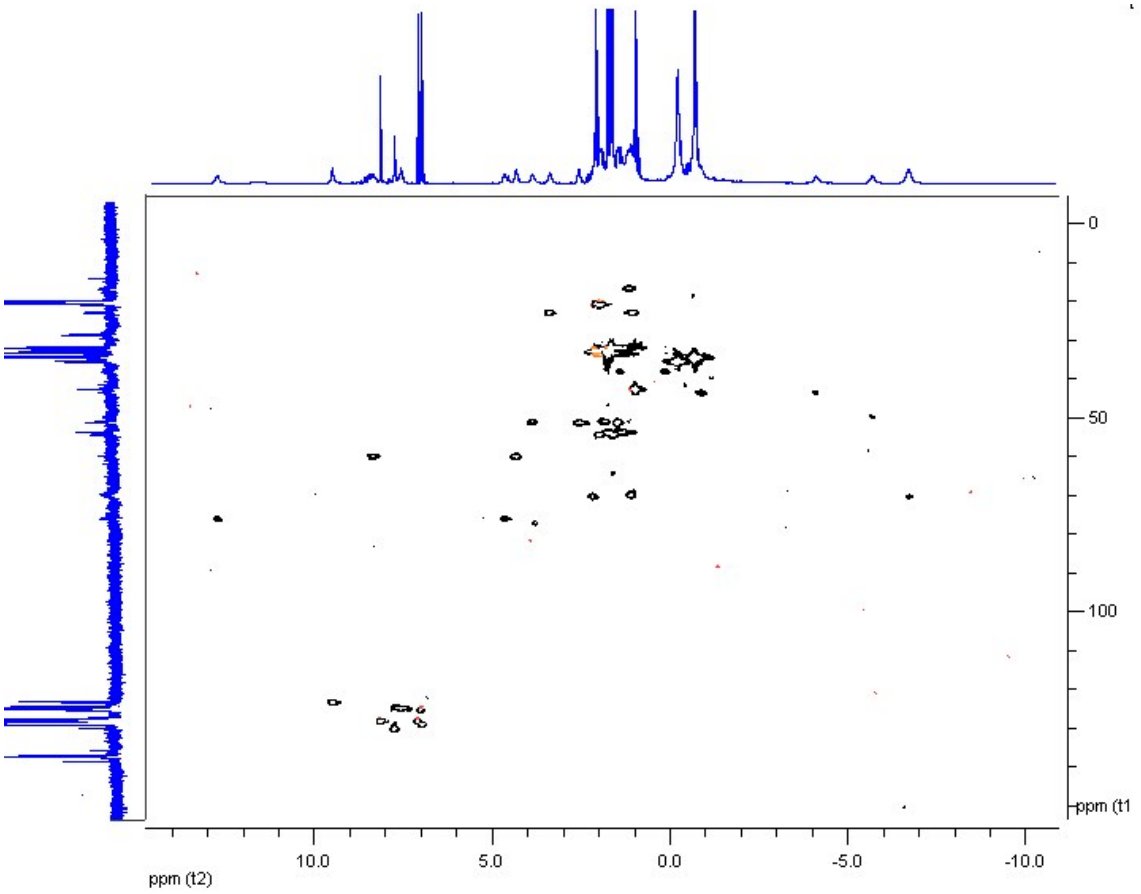


Figure S21. $^{1}H - ^{13}C$ HSQC spectrum of [Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}(Me$_2$-bipy$^{\bullet-}$)] (**6**) in toluene-d_8 at 25 ºC from 14 to -11 ppm

Table S2. ^{1}H chemical shifts of [Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}(R$_2$-bipy$^{\bullet-}$)] in toluene-d_8 at 25ºC

	Chemical Shift (δ, ppm)	
	5 (R = H)	**6** (R = CH_3)
	(^{tBu2}ArO)$_2$Me$_2$-cyclam^{2-}	
NCH_3	0.98 (6H)	0.98 (6H)
$C(CH_3)_3$	1.74 (9H), 1,64 (9H) -0.21 (9H), -0,66 (9H)	1.77 (9H), 1.66 (9H) -0.22 (9H), -0.69 (9H)
ArC-H	9.59, 8.12, 7.72, 7.54,	9.49, 8.15, 7.74, 7.56
$ArCH_2N+CH_2$	12.54, 8.23, 4.62, 4.46, 4.22, 3.85, 3.32, 2.53 (2H), 2.00-1.10 (8H), 1.10-0.80 (2H), -1.00, -4.16 -5.68, -6.56, -6.69	12.73, 8.35, 4.65, 4.32, 3.87, 3.38, 2.56 2.15-1.10 (9H), -0.90, -4.11, -5.68, -6.71
	4,4'-R$_2$-2,2'-bipy	
Ar-H	11.48 (2H), -16.83, -20.79, -164.6, -170.1, -233.8, -239.8	24.13, 18.82, -42.82, -44.64, -235.9, -242.0
Ar-CH_3	-	160.6 (3H), 159.6 (3H)

2. UV-vis-NIR data

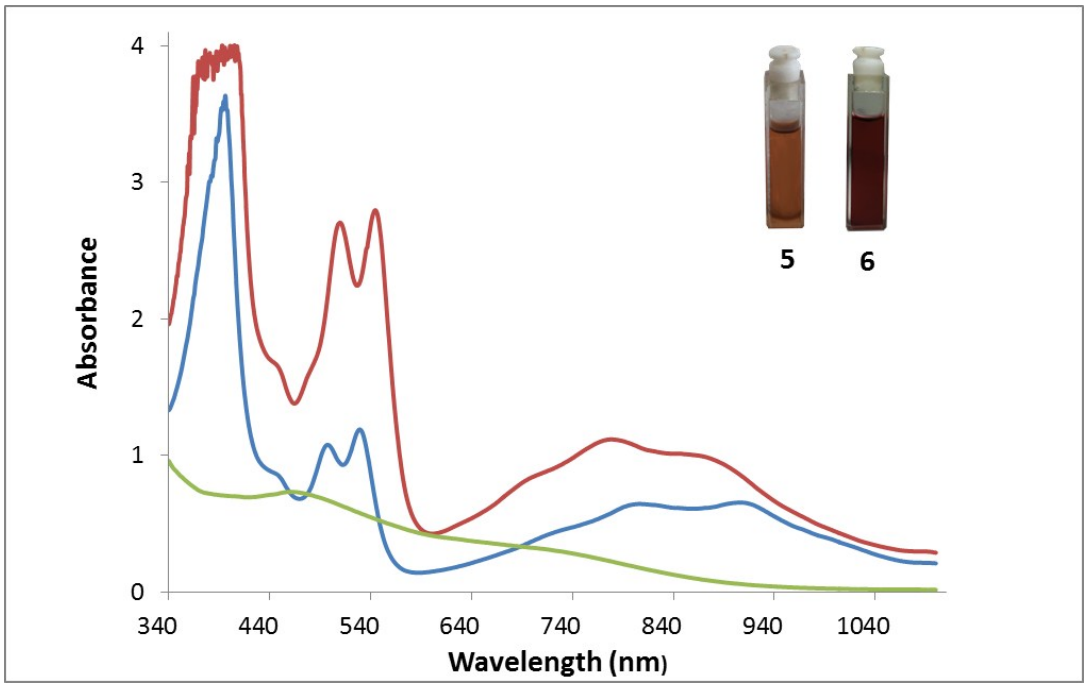


Figure S22. UV-vis-NIR spectra (23ºC) of toluene solutions of **1** (green line), **5** (blue line) and **6** (red line).

3. X-ray crystallography data

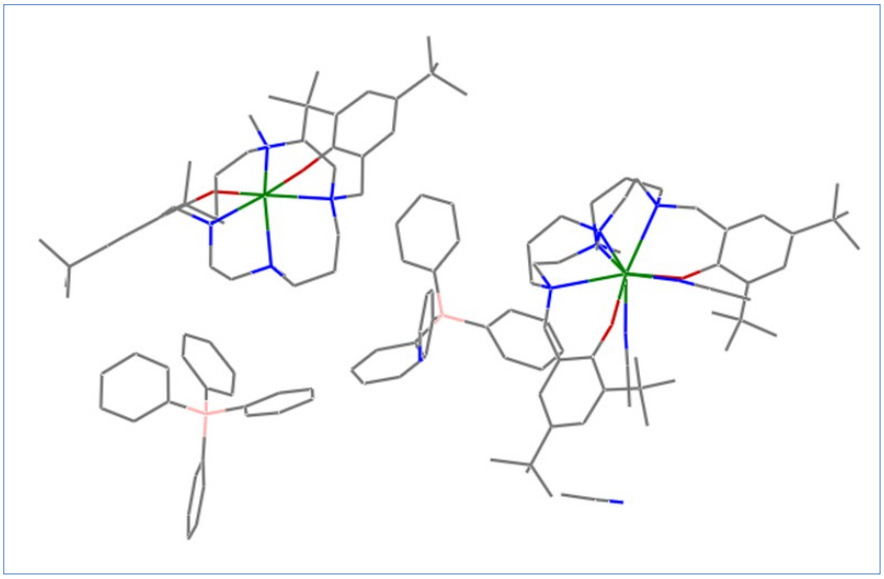


Figure S23: Diagram of the asymmetric unit of compound [Sm{(^{tBu2}ArO)$_2$Me$_2$-cyclam}][BPh$_4$]$_2$ (**2**).

Table S3 : Selected Crystal Data and Data Collection Parameters for complexes **1-4** and **6**

	1	**2.**CH_3CN	**3.**$(C_4H_8O)_2$	**4.**C_6H_{14}	**6**
Empirical formula	$C_{54}H_{82}N_4O_2Sm$	$C_{138}H_{189}B_2N_{11}O_4Sm_2$	$C_{96}H_{164}N_8O_8Sm_2$	$C_{90}H_{150}N_8O_4SSm_2$	$C_{54}H_{82}N_6O_2Sm$
Crystal size (mm)	0.22 x 0.12 x 0.04	0.25 x 018 x 0.04	0.22 x 0.16 x 0.04	0.40 x 0.10 x 0.08	0.30 x 0.20 x 0.10
Formula weight	813.17	2388.32	1859.07	1740.94	997.61
Cryst. System	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	C2/c	$P2_1/n$	$P2_1/n$
a [Å]	26.2754(14)	40.1363(7)	20.7329(14)	15.8177(3)	17.906(5)
b[Å]	9.0495(5)	18.3016(3)	30.8997(19)	37.3695(8)	14.892(5)
c [Å]	17.5199(10)	17.6719(3)	15.2338(10)	18.0889(4)	21.375(5)
α [º]	90	90	90	90	90
β [º]	93.263(2)	100.442(1)	97.093(2)	115.1330(10)	104.623(5)
γ [º]	90	90	90	90	90
V[$Å^3$]	4159.1(4)	12766.1(4)	9684.7(11)	9680.0(3)	5515(3)
Z	4	4	4	4	4
Calculated density (mg/m^{-3})	1.299	1.243	1.275	1.195	1.201
μ (mm^{-1})	1.449	0.967	1.257	1.271	1.106
T_{min}/T_{max}	0.7410/0.944	0.749/0.962	0.770/0.951	0.630/0.905	0.733/0.897
F(000)	1712	5040	3936	3672	2104
θ_{max} (º)	25.03	25.68	25.03	25.03	12.91
Reflections collected	23262	98512	23205	68171	12014
Unique refl. (R_{int})	7326 (0.0919)	24192 (0.0906)	8482 (0.0907)	16883 (0.0709)	1415(0.0860)
R_1[I>2σ(I)]	0.0717	0.0525	0.0510	0.0605	0.0731
wR2 (all data)	0.1624	0.1137	0.1064	0.1507	0.2070
Parameters	457	1476	529	960	314
GOF on F^2	1.054	1.026	0.894	1.057	1.088
Largest diff. peak , hole/e $Å^{-3}$	1.131, -2.361	1.581, -1.285	1.339, -0.905	5.285, -1.634	1.470, -0.444