Synthesis and Reduction of $[(C_5H_4SiMe_3)_2Ln(\mu\text{-}OR)]_2$ (Ln = La, Ce) Complexes: Structural Effects of Bridging Alkoxides

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Electronic Supplementary Information

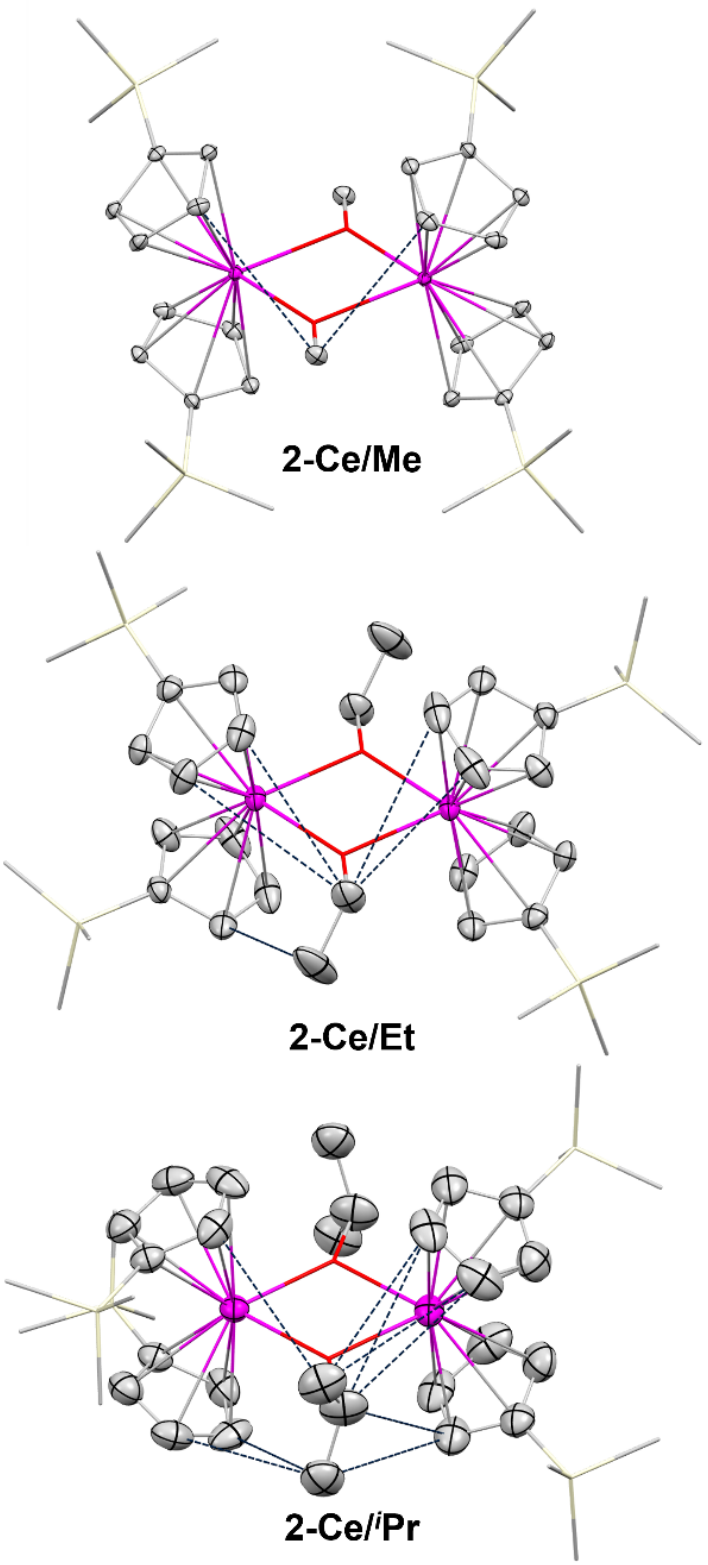

Fig S1. Crystal structures of **2-Ce/Me**,[1] **2-Ce/Et**, and **2-Ce/^{i}Pr** with blue dashed lines representing C···C distances less than 4.0 Å between -OR group and sp^2 carbon distances.

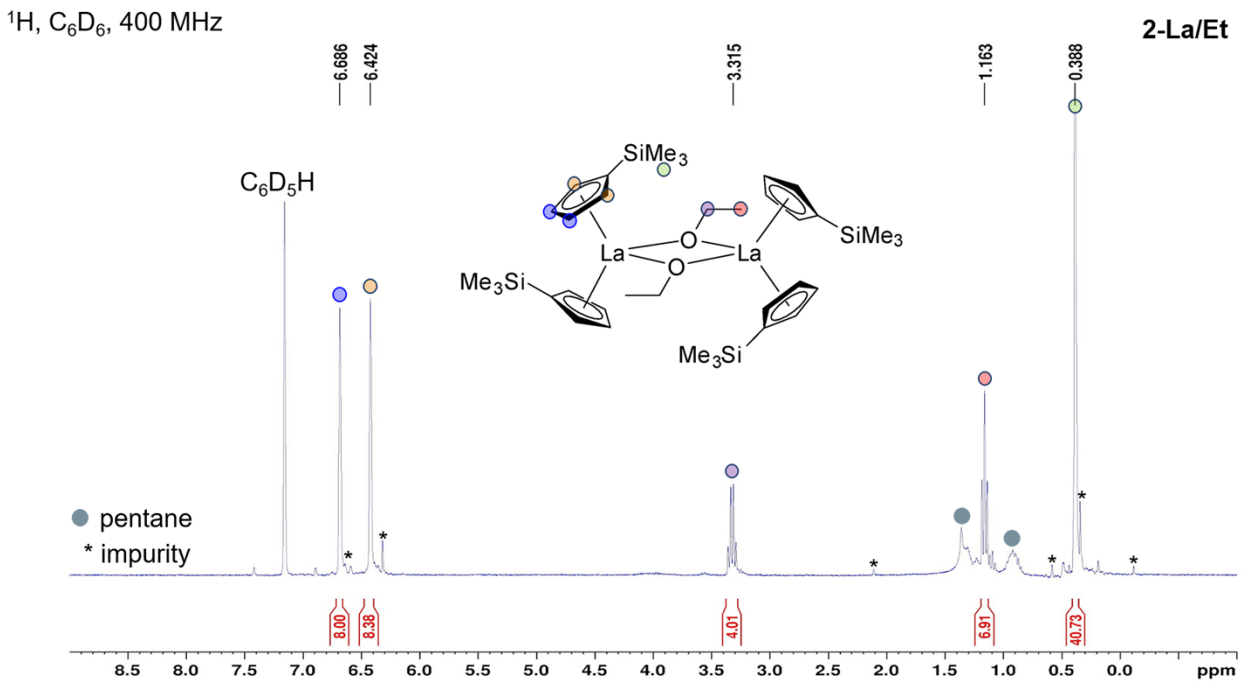

Fig S2. ^{1}H NMR spectrum of **2-La/Et** (C_6D_6, 400 MHz).

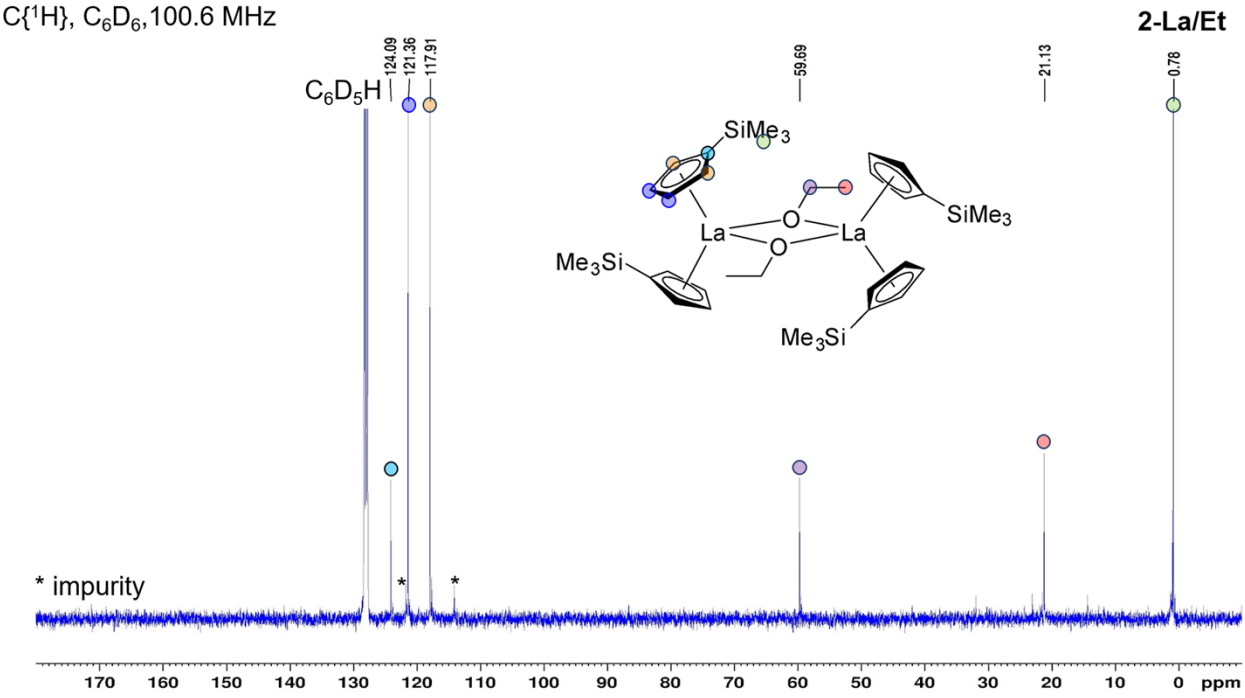

Fig S3. ^{13}C{^{1}H} NMR spectrum of **2-La/Et** (C_6D_6, 100.6 MHz).

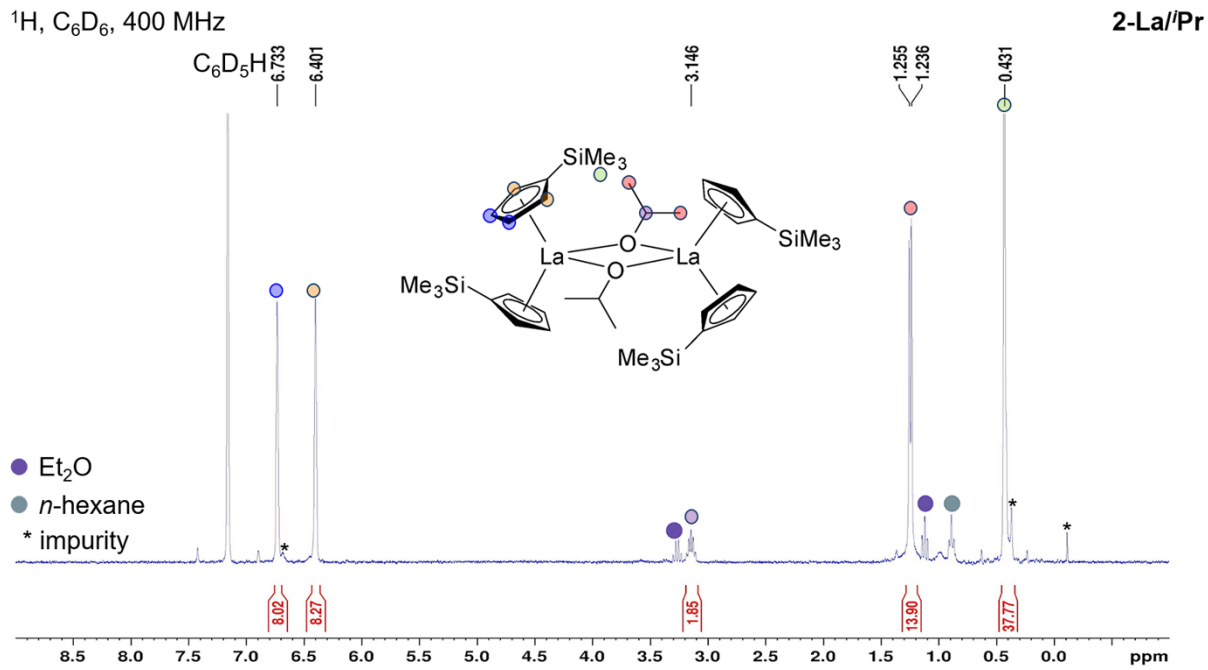

Fig S4. ^{1}H NMR spectrum of **2-La/^{i}Pr** (C_6D_6, 400 MHz).

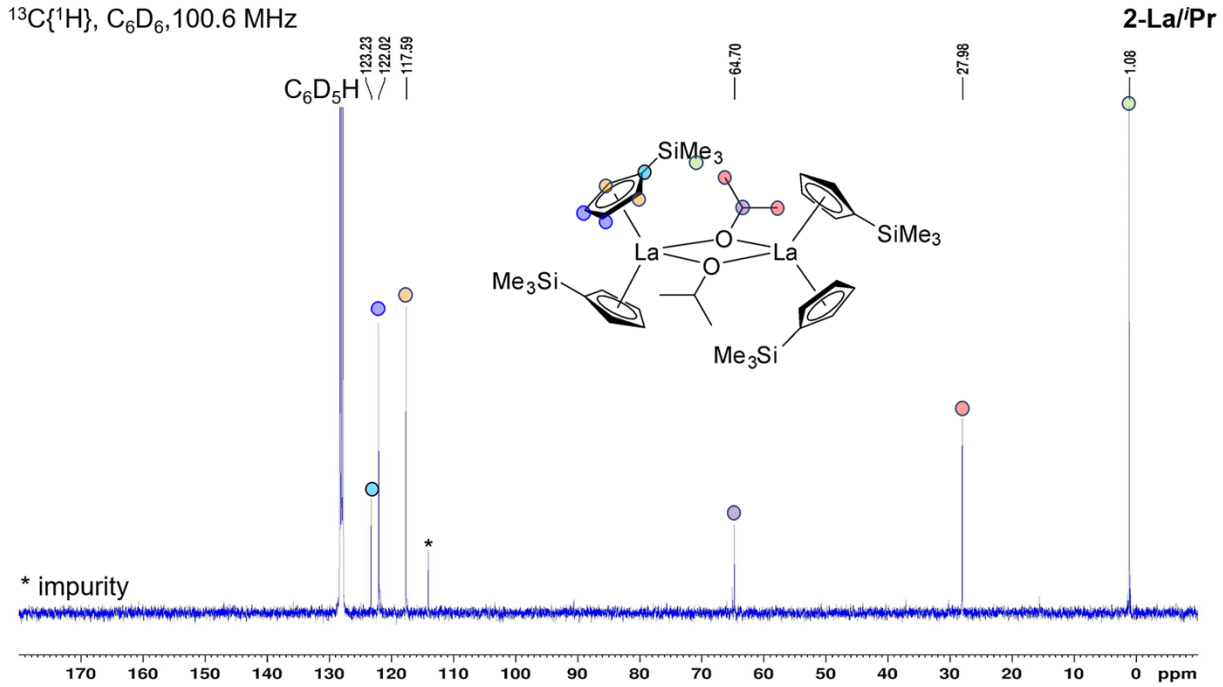

Fig S5. ^{13}C{^{1}H} NMR spectrum of **2-La/^{i}Pr** (C_6D_6, 100.6 MHz).

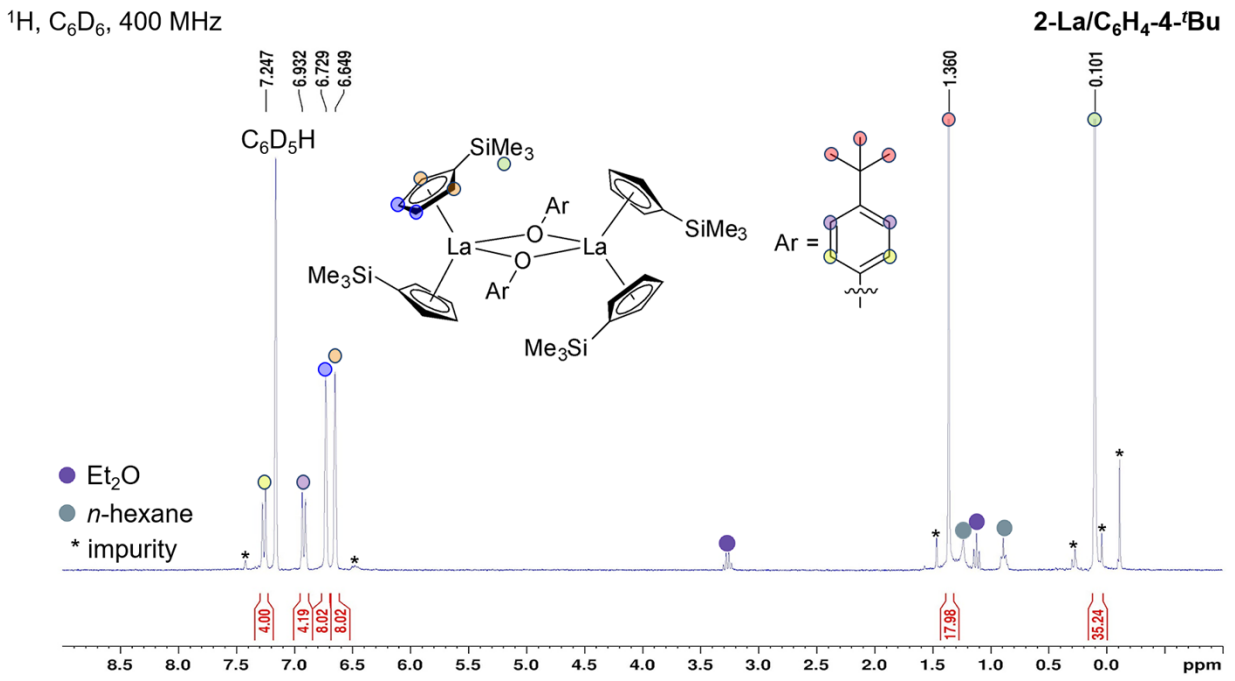

Fig S6. ^{1}H NMR spectrum of **2-La/C_6H_4-4-^{t}Bu** (C_6D_6, 400 MHz).

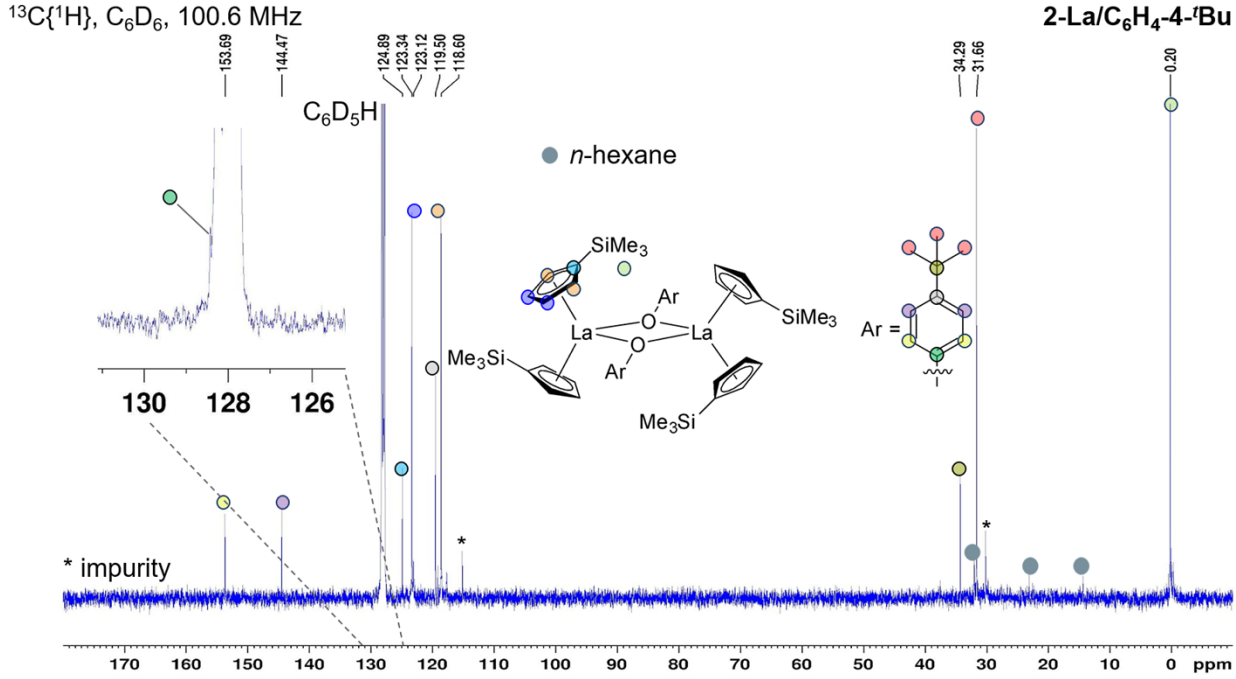

Fig S7. ^{13}C{^{1}H} NMR spectrum of **2-La/C_6H_4-4-^{t}Bu** (C_6D_6, 100.6 MHz).

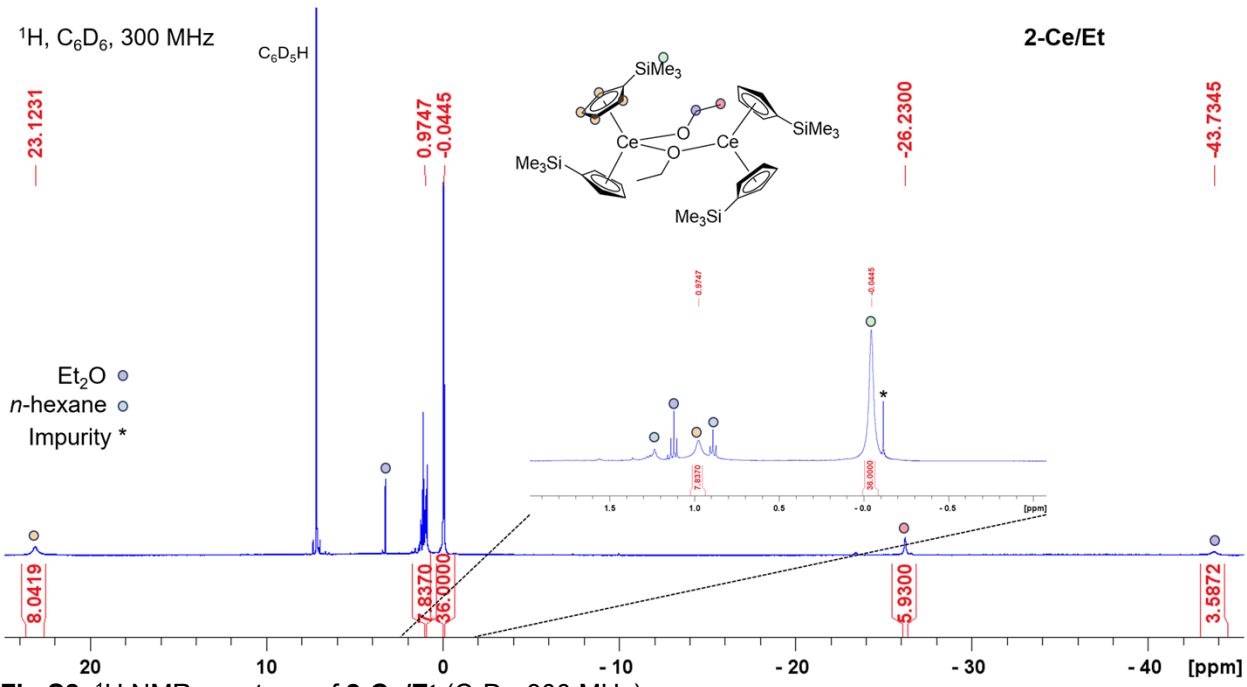

Fig S8. ^{1}H NMR spectrum of **2-Ce/Et** (C_6D_6, 300 MHz).

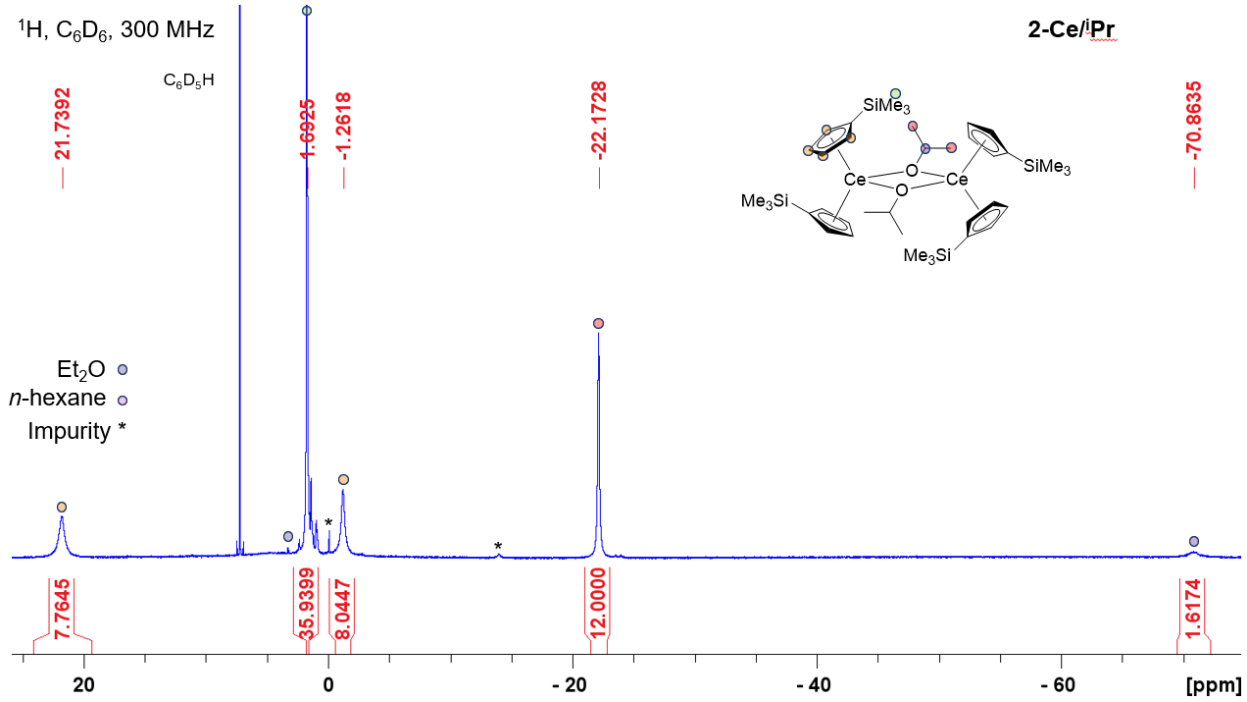

Fig S9. ^{1}H NMR spectrum of **2-Ce/^{i}Pr** (C_6D_6, 300 MHz).

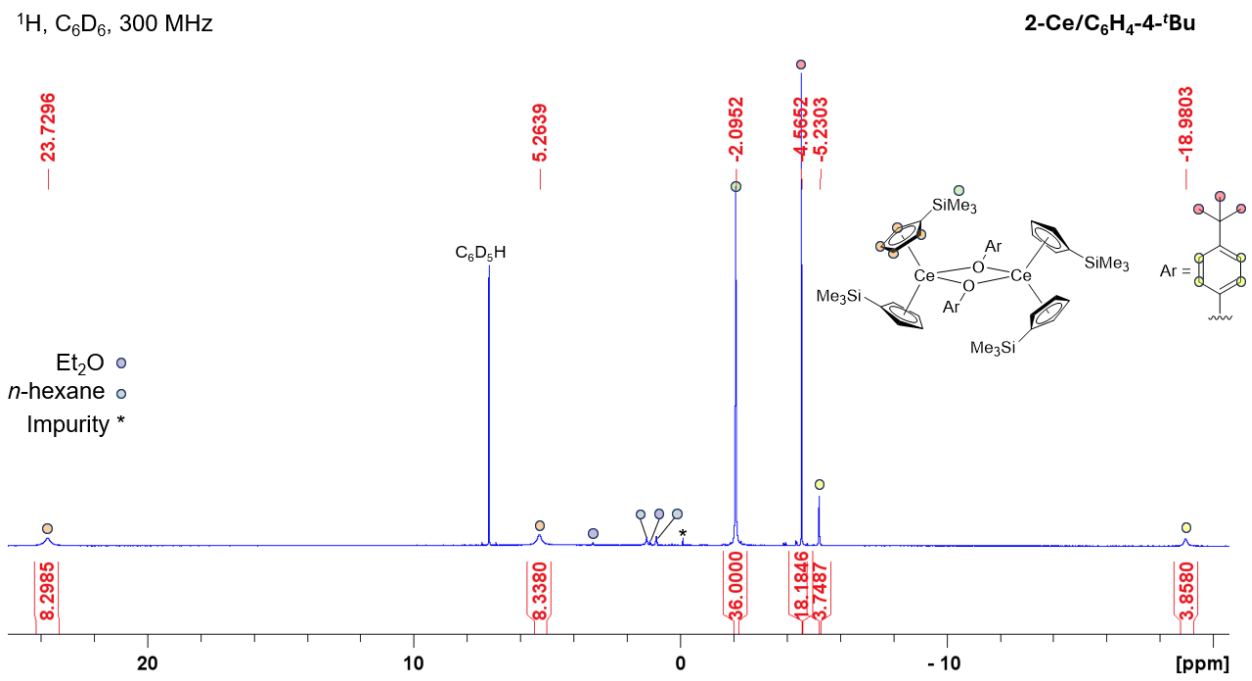

Fig S10. ^{1}H NMR spectrum of **2-Ce/C_6H_4-4-^{t}Bu** (C_6D_6, 300 MHz).

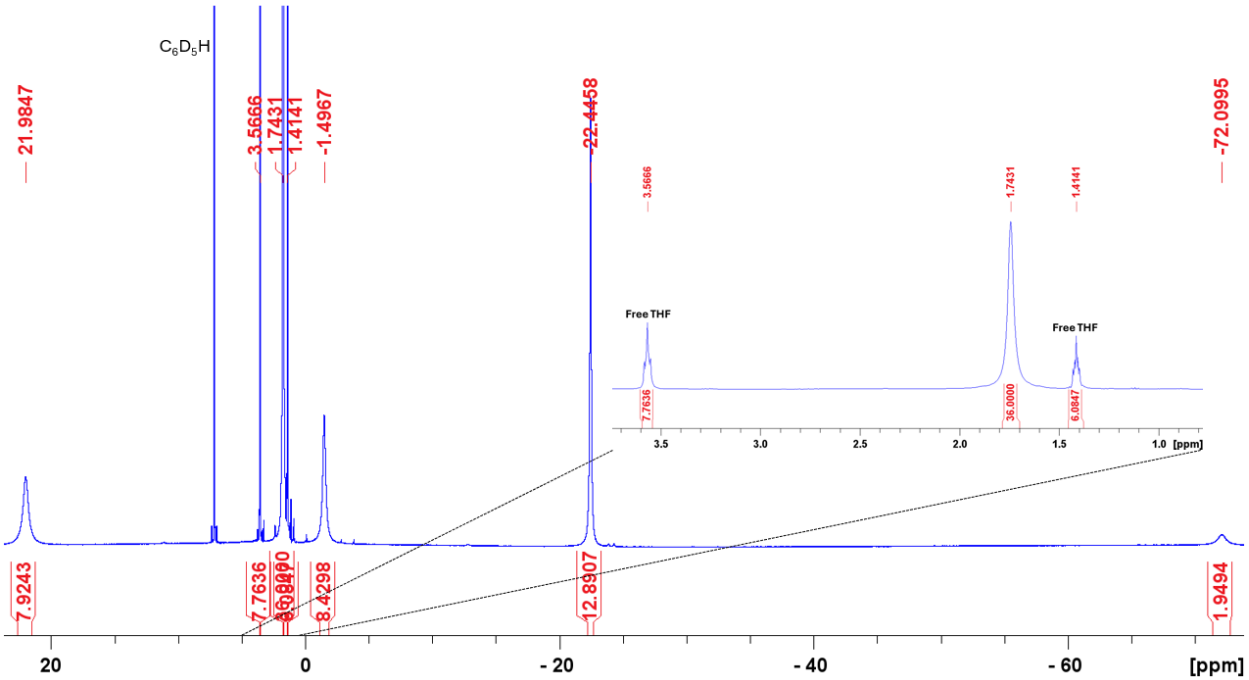

Fig S11. ^{1}H NMR spectrum of **2-Ce/^{i}Pr** with 2 equiv. of THF (C_6D_6, 300 MHz).

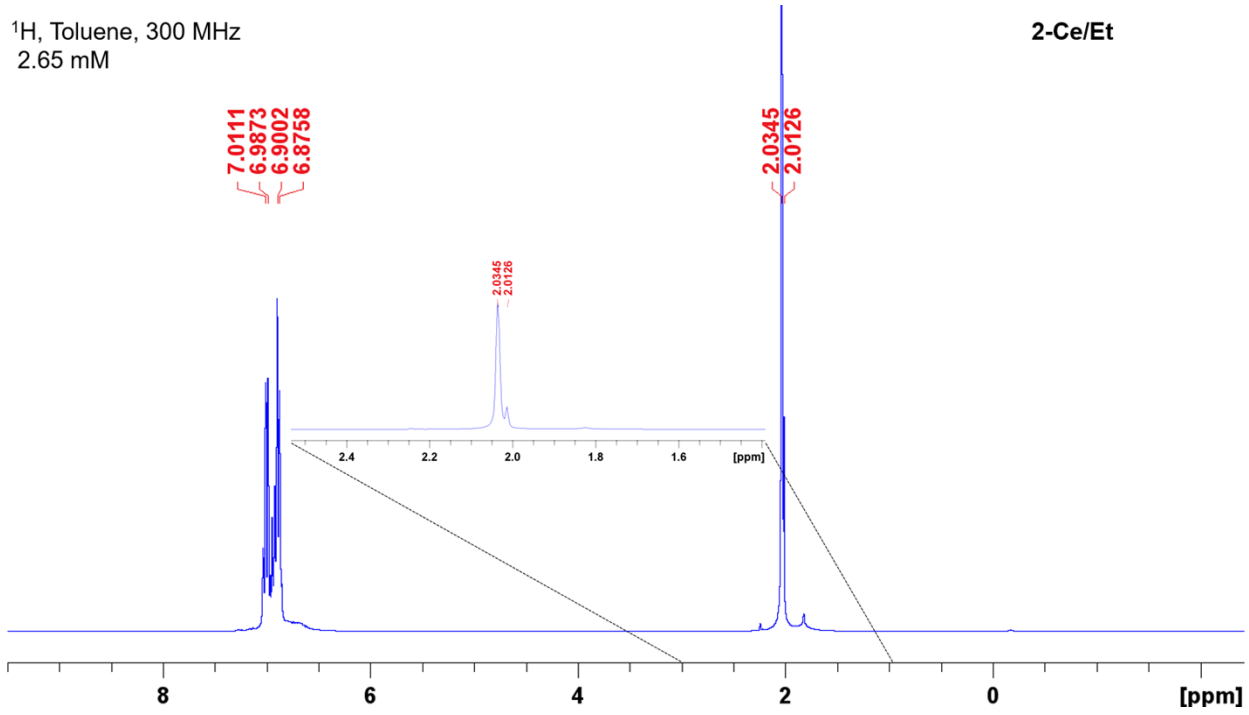

Fig S12. ^{1}H NMR spectrum Evans' Method of a 2.65 mM toluene solution of **2-Ce/Et** with toluene capillary: 1.28 μ_B. Low magnetic moment may be ascribed to antiferromagnetic coupling or superexchange due to the short Ce•••Ce distance: 3.8052(6) Å.

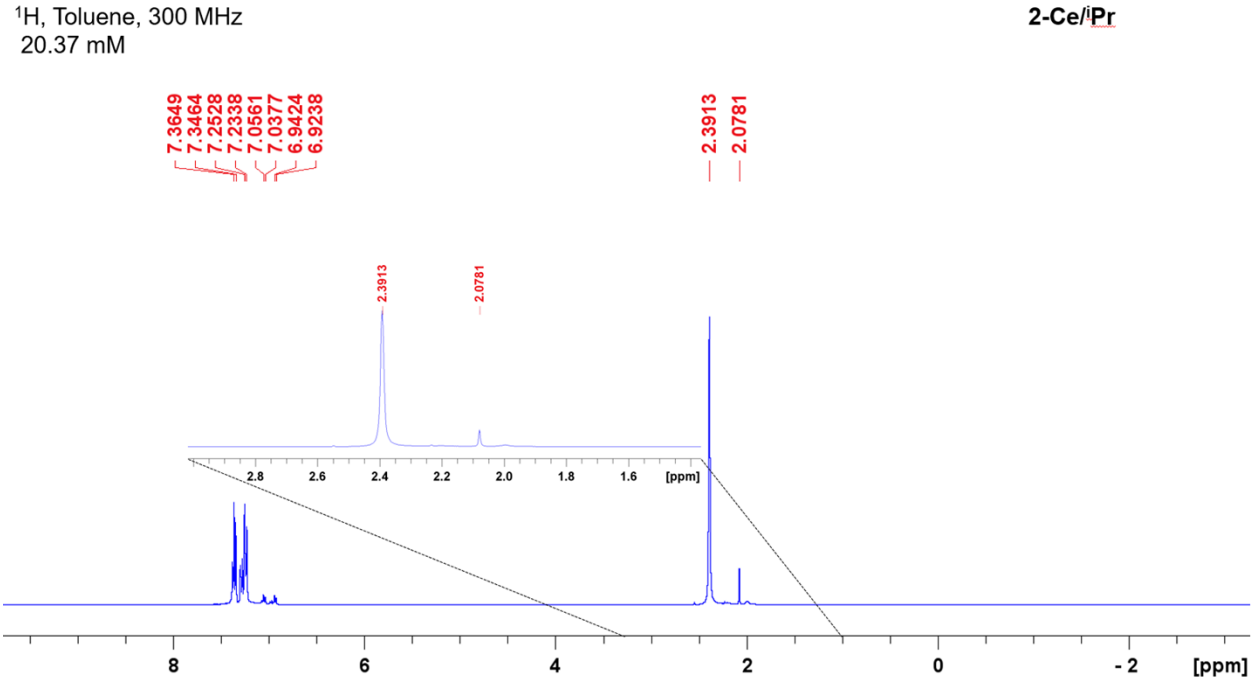

Fig S13. ^{1}H NMR spectrum Evans' Method of a 20.37 mM toluene solution of **2-Ce/^{i}Pr** with toluene capillary: 1.90 μ_B. Low magnetic moment may be ascribed to antiferromagnetic coupling or superexchange due to the short Ce•••Ce distance: 3.7977(8), 3.7810(8) Å.

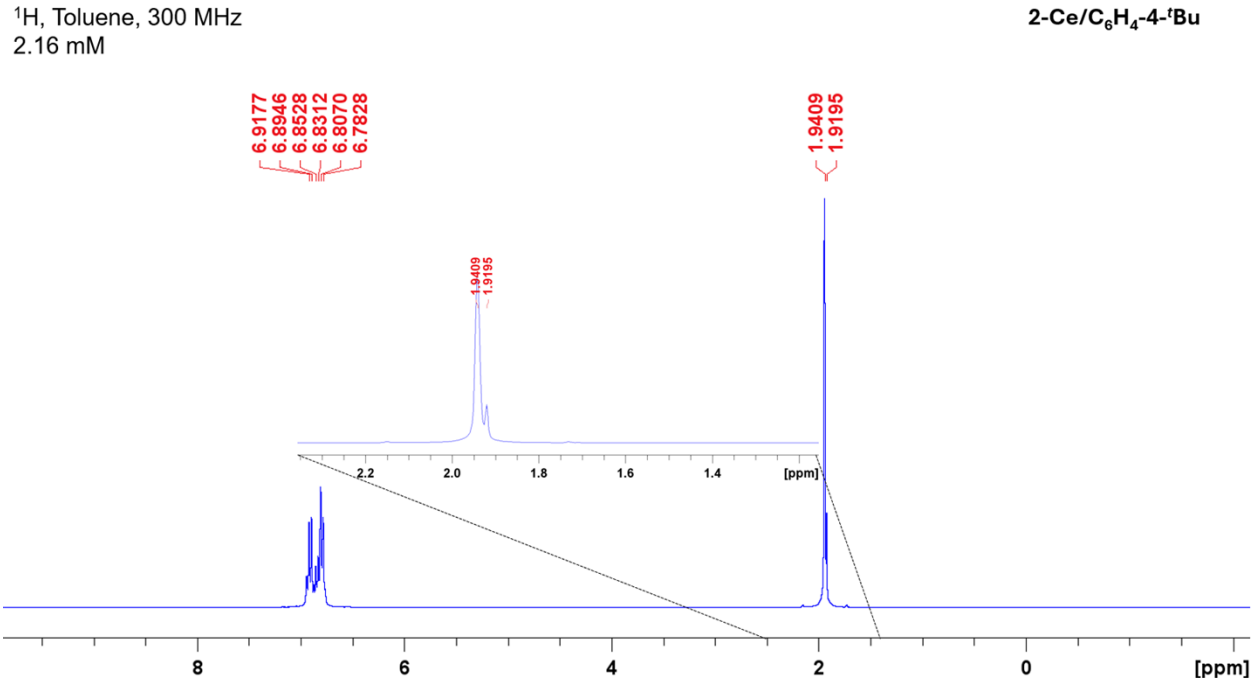

Fig S14. ^{1}H NMR spectrum Evans' Method of a 2.16 mM toluene solution of **2-Ce/C$_6$H$_4$-4-^{t}Bu** with toluene capillary: 1.34 μ_B. Low magnetic moment may be ascribed to antiferromagnetic coupling or superexchange due to short Ce•••Ce distances.

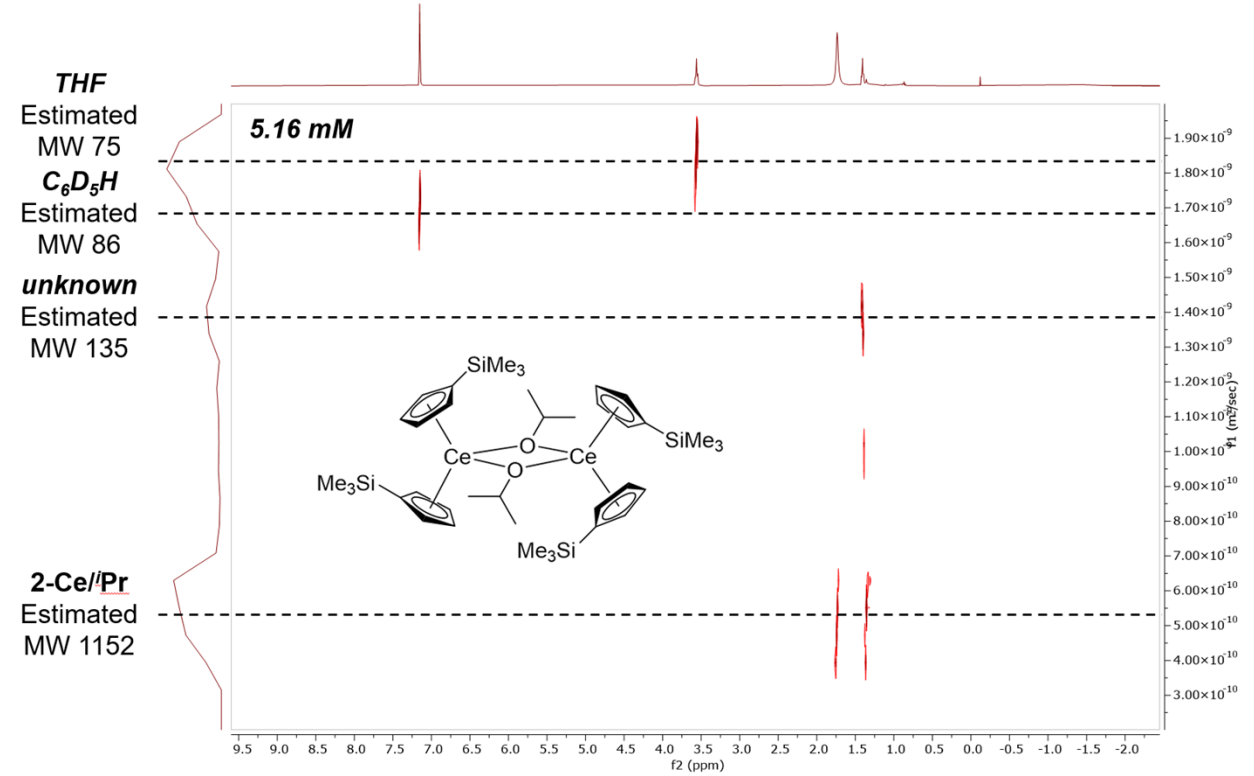

Fig S15. 2D ^{1}H DOSY NMR spectra of 5.16 mM **2-Ce/iPr** in C_6D_6 with 2 equiv. of THF.

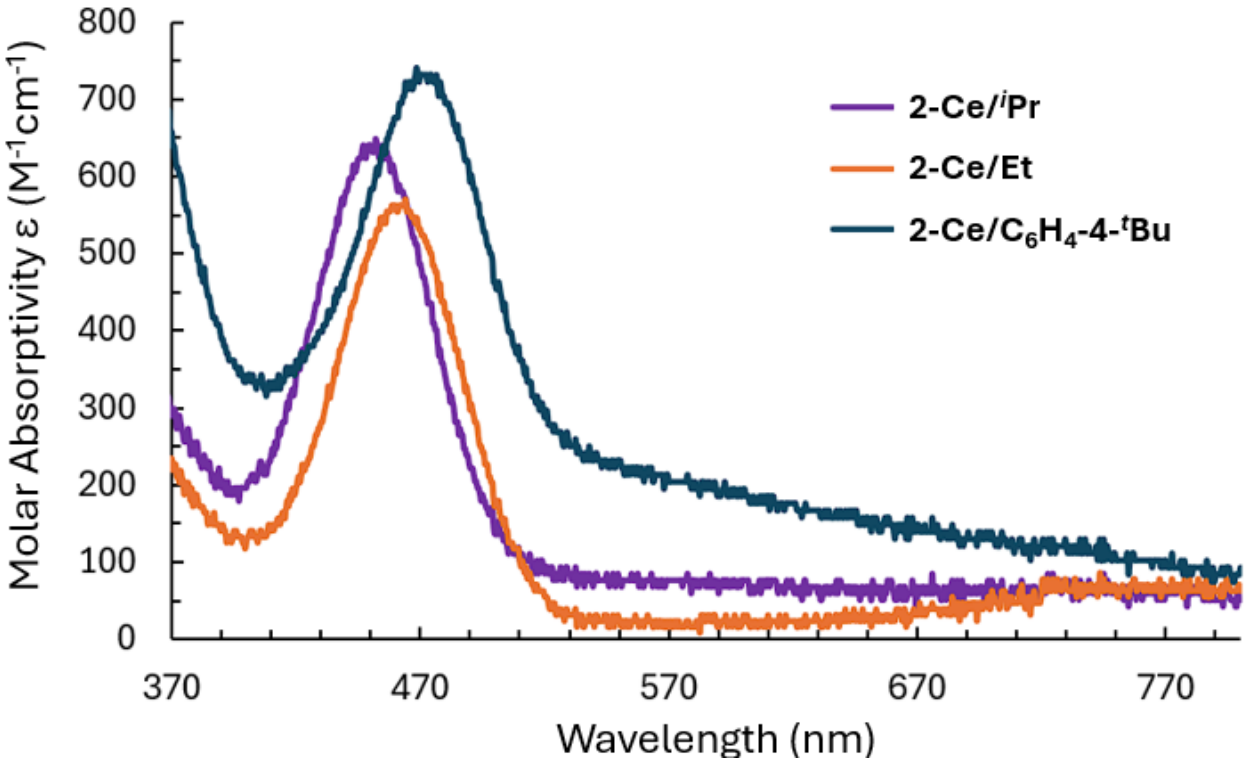

Fig S16. UV-vis spectra of **2-Ce/^{i}Pr** (purple trace; toluene; 230 μM; λ_{max} = 452 nm), **2-Ce/Et** (orange trace; toluene; 260 μM; λ_{max} = 458 nm) and **2-Ce/C$_6$H$_4$-4-^{t}Bu** (navy blue trace; toluene; 220 μM; λ_{max} = 471 nm).

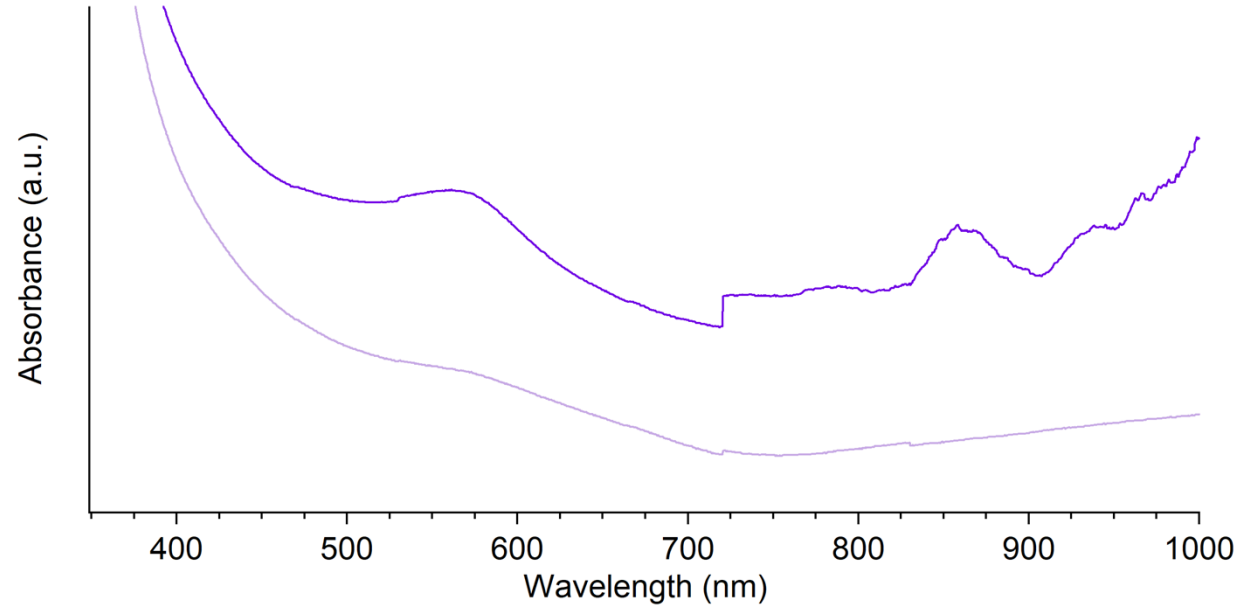

Fig S17. UV-vis spectrum of *in situ* reduction of **2-La/^{i}Pr** (50 mg, 0.053 mmol) using KC_8 (8 mg, 0.059 mmol) and 2.2.2-cryptand (22 mg, 0.059 mmol) in 2 mL of THF at –78 °C. Sample was transferred to an air-free cuvette while –78 °C. Prior to measurement, the sample was warmed to RT then immediately placed in the spectrometer for measurement (dark purple trace). After 5 mins, another spectrum was collected on the same sample (light purple trace).

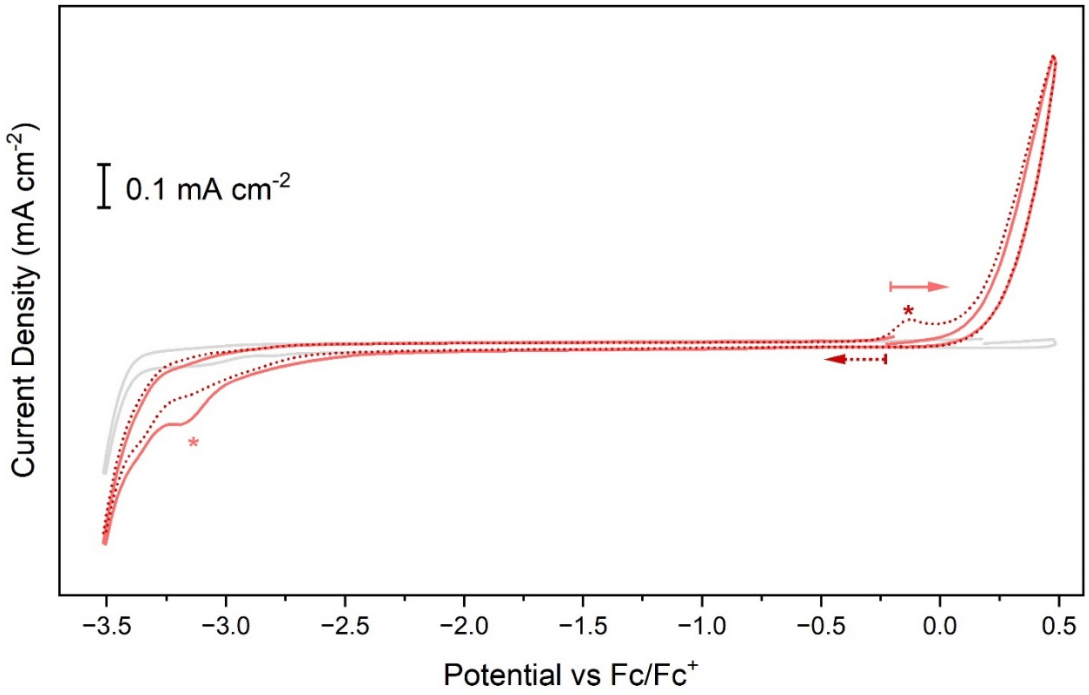

Fig. S18. CV traces (100 mV/s) of **2-La/^{i}Pr** (2.5 mM) in THF with [NBu_4][PF_6] (100 mM) as the supporting electrolyte, with arrows indicating the scanning direction. Background: gray, Cathodic: red (dashed), Anodic: pink (solid).

Note: The pronounced increase in current above 0 V vs Fc/Fc^+ was attributed to ligand oxidation, while the current response below -3.2 v vs Fc/Fc^+ was attributed to a $La^{III/II}$ reduction event. * correspond to redox peaks arising from decomposition products.

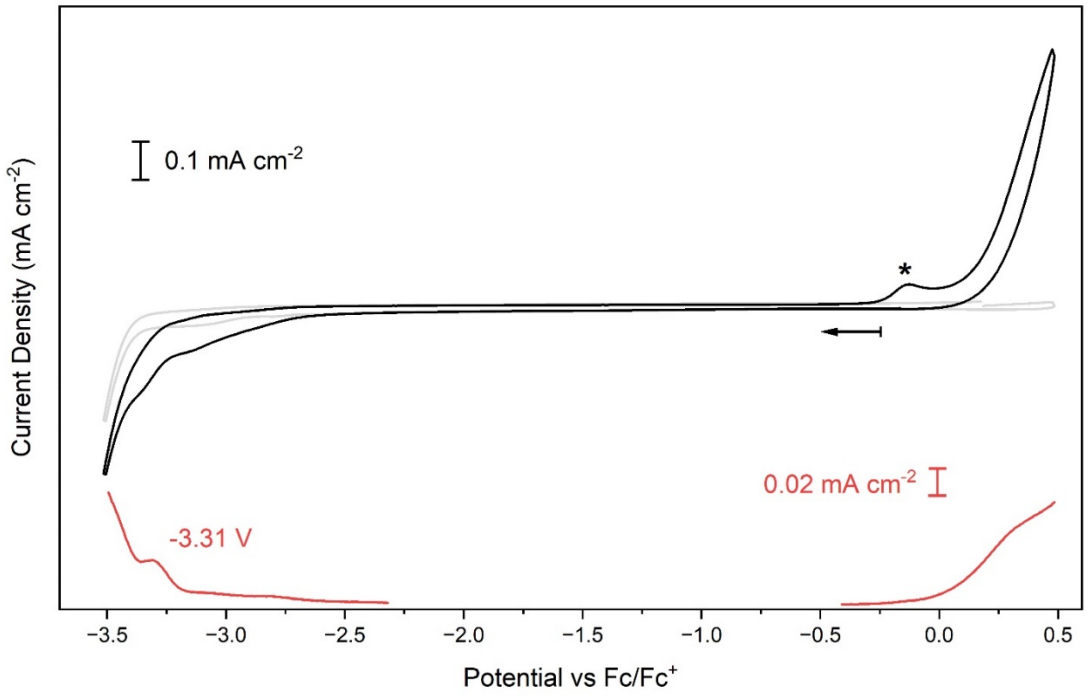

Fig. S19. (*Top*) CV trace (100 mV/s) of **2-La/^{i}Pr** (2.5 mM) in THF with [NBu_4][PF_6] (100 mM) as the supporting electrolyte, with arrows indicating the scanning direction. Background: gray, Anodic: black (solid), Anodic: pink (solid). * corresponds to redox peaks arising from decomposition products. (*Bottom*) DPV scans (red lines) at 10 mV/s, displayed with absolute values of the current density.

Note: DPV scans indicate a reduction event at –3.31 V *vs* Fc/Fc^+, in line with the a $La^{III/II}$ reduction event.

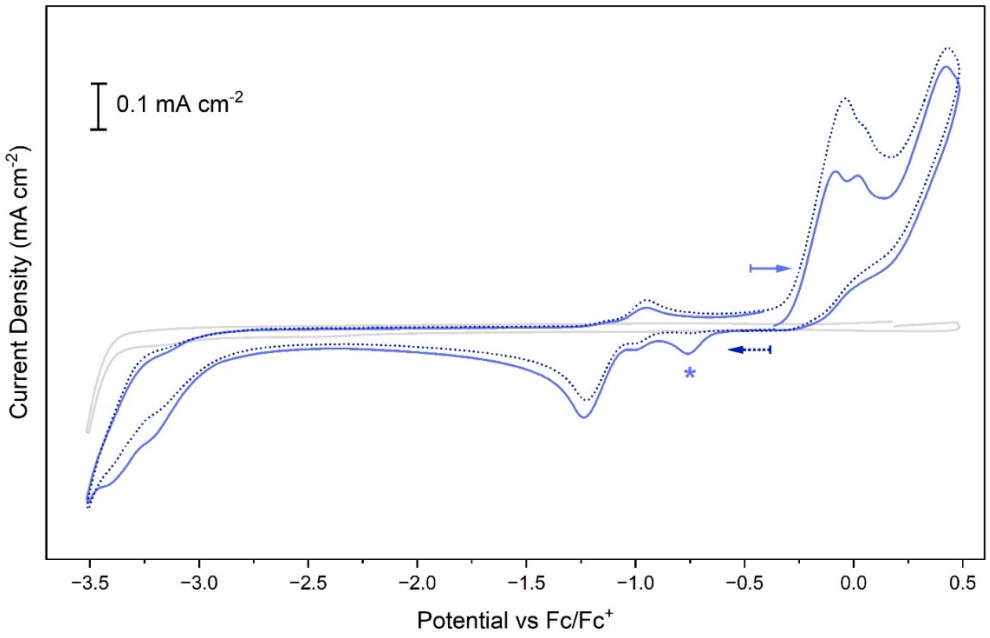

Fig. S20. CV traces (100 mV/s) of **2-Ce/^{i}Pr** (2.5 mM) in THF with $[NBu_4][PF_6]$ (100 mM) as the supporting electrolyte, with arrows indicating the scanning direction. Background: gray, Cathodic: blue (dashed), Anodic: light-blue (solid). * correspond to redox peaks arising from decomposition products.

Note: Ce^{III}/Ce^{IV} oxidation events were found to overlap with ligand oxidation at and above -0.2 V vs Fc/Fc^+, while the current response below –3.2 V vs Fc/Fc^+ is associated with a $Ce^{III/II}$ reduction event. The unexpected reduction event at –1.25 V vs Fc/Fc^+ arose due to the presence of a Ce^{IV} species generated by the reaction of **2-Ce/^{i}Pr** with small amounts of Ag^+ leached from the reference electrode.

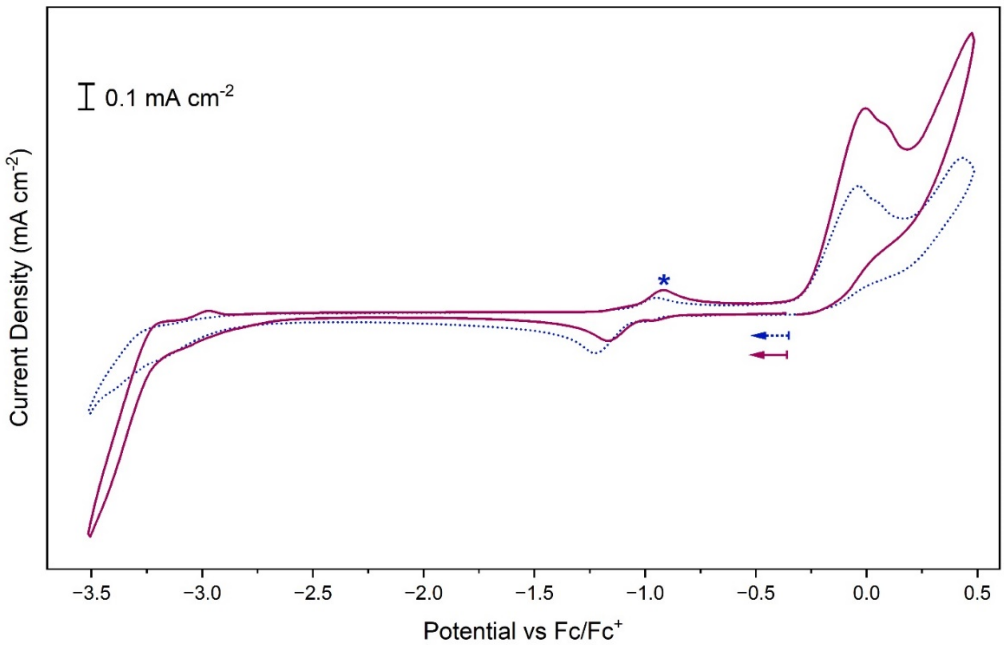

Fig. S21. CV traces (100 mV/s) of **2-Ce/^{i}Pr** at 2.5 mM (blue, dashed) and 5 mM (burgundy, solid) in THF with $[NBu_4][PF_6]$ (100 mM) as the supporting electrolyte, with arrows indicating the scanning direction. * correspond to redox peaks arising from decomposition products.

Note: Assignment of the reduction peak at –1.2 V as a decomposition product generated by adventitious Ag^+ leached from the reference electrode was made by assessing the current response from two different analyte concentrations. The current response at $E > -0.25$ V *vs* Fc/Fc^+ (Ce^{III} and ligand oxidation) and at $E < -3.2$ V *vs* Fc/Fc^+ (Ce^{III} reduction) increased with increasing analyte concentration, while the current response of the reduction peak at –1.2 V did not change significantly.

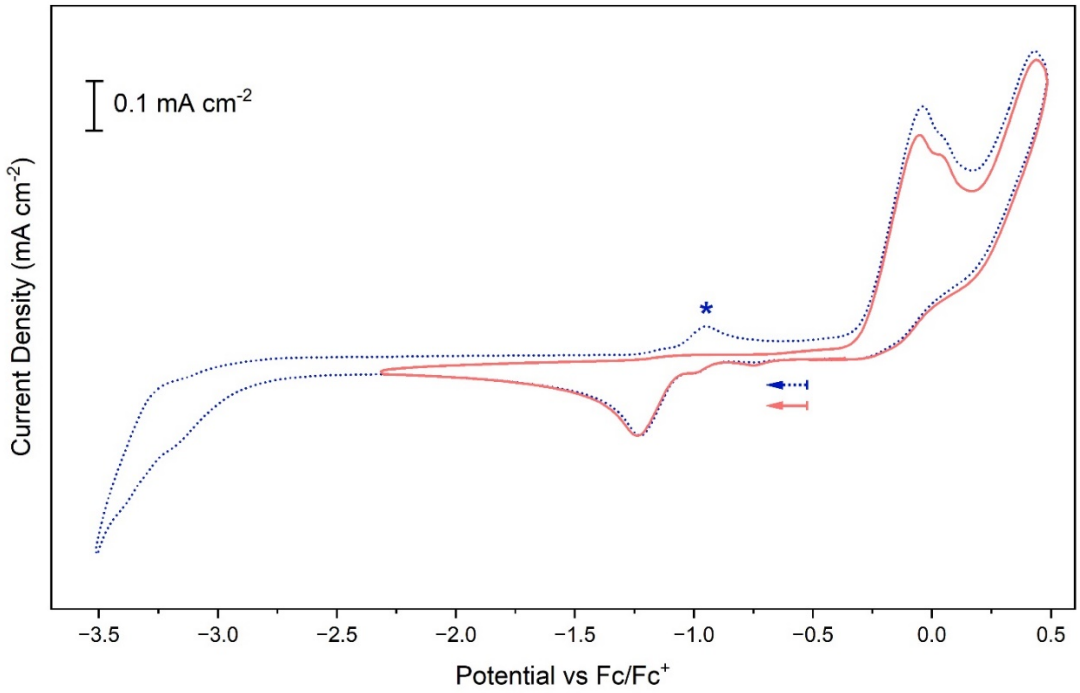

Fig. S22. CV traces (100 mV/s) of **2-Ce/^{i}Pr** (2.5 mM) in THF with [NBu_4][PF_6] (100 mM) as the supporting electrolyte, with arrows indicating the scanning direction. Cathodic, full-scan: blue (dashed), Cathodic, partial-scan: light-blue (dashed). * corresponds to redox peaks arising from decomposition products.
Note: The oxidation peak at –1.0 V *vs* Fc/Fc^+ was found to belong to a decomposition product generated upon $Ce^{III/II}$ reduction at < –3 V *vs* Fc/Fc^+.

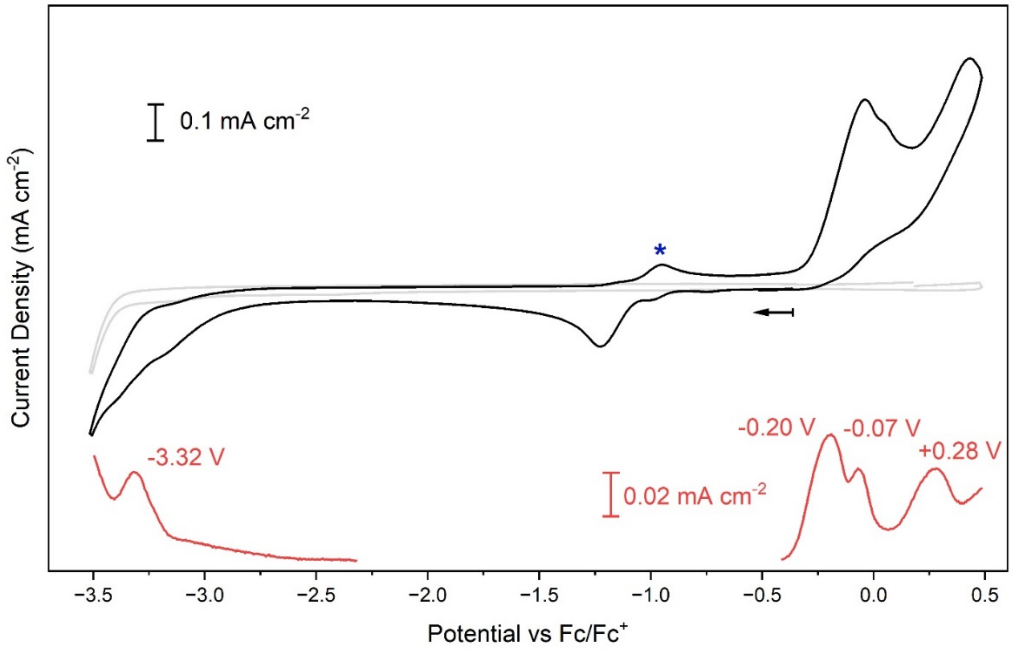

Fig. S23. CV trace (100 mV/s, background: gray) of **2-Ce/^{i}Pr** (2.5 mM, black solid-line) in THF with [NBu_4][PF_6] (100 mM) as the supporting electrolyte, with arrows indicating the scanning direction. * correspond to redox peaks arising from decomposition products.
Note: DPV scans indicate a reduction event at –3.32 V *vs* Fc/Fc^+, in line with the reduction of Ce^{III}. Ce oxidation events were observed above –0.4 V *vs* Fc/Fc^+, and overlapped with ligand oxidations.

Table S1. Crystallographic parameters for compounds **2-Ce/Et**, **2-Ce/^{i}Pr,** and **2-La/^{i}Pr**.

Identification code	**2-Ce/Et**	**2-La/^{i}Pr**	**2-Ce/^{i}Pr**
Empirical formula	$C_{18}H_{31}CeOSi_2$	$C_{38}H_{66}La_2O_2Si_4$	$C_{38}H_{66}Ce_2O_2Si_4$
Formula weight	459.73	945.08	947.50
Temperature/K	177.0	173.0	173.0
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	P2/n	P2/n
a/Å	13.433(2)	18.0071(7)	18.043(2)
b/Å	11.0399(16)	13.8430(6)	13.8611(19)
c/Å	14.619(2)	18.6821(7)	18.671(3)
α/°	90	90	90
β/°	96.647(5)	101.345(2)	100.767(5)
γ/°	90	90	90
Volume/Å^3	2153.4(6)	4565.9(3)	4587.3(11)
Z	4	4	4
ρ_{calc}g/cm^3	1.418	1.375	1.372
μ/mm^{-1}	2.225	1.978	2.091
F(000)	932.0	1920.0	1928.0
Crystal size/mm^3	0.2 × 0.18 × 0.17	0.16 × 0.12 × 0.1	0.08 × 0.05 × 0.03
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.368 to 55.002	4.112 to 56.362	4.116 to 55.464
Index ranges	-17 ≤ h ≤ 17, -14 ≤ k ≤ 14, -18 ≤ l ≤ 18	-23 ≤ h ≤ 23, -17 ≤ k ≤ 17, -24 ≤ l ≤ 24	-23 ≤ h ≤ 23, -18 ≤ k ≤ 18, -24 ≤ l ≤ 24
Reflections collected	57458	208523	125523
Independent reflections	4948 [R_{int} = 0.0555, R_{sigma} = 0.0270]	10533 [R_{int} = 0.0562, R_{sigma} = 0.0263]	10704 [R_{int} = 0.1295, R_{sigma} = 0.0702]
Data/restraints/parameters	4948/9/206	10533/36/474	10704/123/493
Goodness-of-fit on F^2	1.082	1.069	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0184, wR_2 = 0.0463	R_1 = 0.0226, wR_2 = 0.0529	R_1 = 0.0527, wR_2 = 0.1335
Final R indexes [all data]	R_1 = 0.0191, wR_2 = 0.0466	R_1 = 0.0259, wR_2 = 0.0550	R_1 = 0.0948, wR_2 = 0.1583
Largest diff. peak/hole / e Å^{-3}	0.33/-0.76	0.47/-0.40	1.11/-0.71
CCDC Deposition #	2372725	2372726	2372727

Table S2a. Bond lengths (Å) for **2-Ce/Et**.

Atom	Atom	Length (Å)	Atom	Atom	Length (Å)
Ce1	O1	2.3349(11)	Si2	C13	1.8572(16)
Ce1	O1^1	2.3600(11)	Si2	C14	1.865(2)
Ce1	C1	2.7981(15)	Si2	C15	1.861(2)
Ce1	C2	2.7912(18)	Si2	C16	1.868(2)
Ce1	C3	2.7974(16)	O1	C17	1.415(2)
Ce1	C4	2.8040(16)	C1	C2	1.404(2)
Ce1	C5	2.8179(15)	C1	C5	1.418(2)
Ce1	C9	2.8274(18)	C2	C3	1.402(3)
Ce1	C10	2.814(2)	C3	C4	1.398(3)
Ce1	C11	2.7982(18)	C4	C5	1.431(2)

Atom	Atom	Length (Å)	Atom	Atom	Length (Å)
Ce1	C12	2.8098(16)	C9	C10	1.416(3)
Ce1	C13	2.8401(15)	C9	C13	1.421(2)
Si1	C5	1.8574(16)	C10	C11	1.391(4)
Si1	C6	1.869(2)	C11	C12	1.394(3)
Si1	C7	1.862(2)	C12	C13	1.417(2)
Si1	C8	1.869(2)	C17	C18	1.491(3)

[1]1-X,1-Y,1-Z

Table S2b. Bond angles (˚) for **2-Ce/Et.**

Atom	Atom	Atom	Angle (˚)	Atom	Atom	Atom	Angle (˚)
O1	Ce1	O1[1]	71.71(4)	C11	Ce1	C10	28.70(7)
O1[1]	Ce1	C1	135.60(4)	C11	Ce1	C12	28.79(6)
O1	Ce1	C1	119.29(4)	C11	Ce1	C13	48.08(5)
O1[1]	Ce1	C2	128.59(5)	C12	Ce1	C5	130.79(5)
O1	Ce1	C2	90.25(5)	C12	Ce1	C9	47.38(5)
O1	Ce1	C3	80.76(5)	C12	Ce1	C10	47.24(6)
O1[1]	Ce1	C3	99.58(5)	C12	Ce1	C13	29.04(5)
O1[1]	Ce1	C4	88.71(5)	C5	Si1	C6	107.02(9)
O1	Ce1	C4	102.64(5)	C5	Si1	C7	111.33(9)
O1[1]	Ce1	C5	108.31(4)	C5	Si1	C8	110.79(10)
O1	Ce1	C5	129.08(4)	C6	Si1	C8	109.20(12)
O1	Ce1	C9	134.59(5)	C7	Si1	C6	109.01(12)
O1[1]	Ce1	C9	115.04(5)	C7	Si1	C8	109.42(12)
O1[1]	Ce1	C10	88.33(5)	C13	Si2	C14	111.78(9)
O1	Ce1	C10	117.32(6)	C13	Si2	C15	110.77(9)
O1[1]	Ce1	C11	88.03(5)	C13	Si2	C16	107.20(9)
O1	Ce1	C11	90.18(6)	C14	Si2	C16	108.27(12)
O1[1]	Ce1	C12	114.39(5)	C15	Si2	C14	109.63(11)
O1	Ce1	C12	87.92(5)	C15	Si2	C16	109.10(12)
O1	Ce1	C13	113.11(4)	Ce1	O1	Ce1[1]	108.29(4)
O1[1]	Ce1	C13	134.47(4)	C17	O1	Ce1[1]	112.78(10)
C1	Ce1	C4	47.68(5)	C17	O1	Ce1	137.17(11)
C1	Ce1	C5	29.24(5)	C2	C1	Ce1	75.18(9)
C1	Ce1	C9	88.06(5)	C2	C1	C5	109.69(15)
C1	Ce1	C10	116.17(6)	C5	C1	Ce1	76.15(9)
C1	Ce1	C12	109.10(5)	C1	C2	Ce1	75.73(10)
C1	Ce1	C13	83.76(5)	C3	C2	Ce1	75.72(10)
C2	Ce1	C1	29.09(5)	C3	C2	C1	107.63(15)
C2	Ce1	C3	29.06(6)	C2	C3	Ce1	75.22(10)
C2	Ce1	C4	47.84(5)	C4	C3	Ce1	75.80(9)
C2	Ce1	C5	48.56(5)	C4	C3	C2	108.21(15)
C2	Ce1	C9	111.70(6)	C3	C4	Ce1	75.28(10)
C2	Ce1	C10	140.73(6)	C3	C4	C5	109.19(15)
C2	Ce1	C11	141.17(6)	C5	C4	Ce1	75.80(9)
C2	Ce1	C12	112.46(6)	Si1	C5	Ce1	128.04(7)
C2	Ce1	C13	96.93(5)	C1	C5	Ce1	74.61(8)
C3	Ce1	C1	47.75(5)	C1	C5	Si1	126.63(12)
C3	Ce1	C4	28.91(6)	C1	C5	C4	105.29(14)
C3	Ce1	C5	48.49(5)	C4	C5	Ce1	74.72(9)
C3	Ce1	C9	135.74(6)	C4	C5	Si1	126.12(12)
C3	Ce1	C10	161.86(6)	C10	C9	Ce1	74.93(11)
C3	Ce1	C11	165.60(7)	C10	C9	C13	108.27(17)

Atom	Atom	Atom	Angle (˚)	Atom	Atom	Atom	Angle (˚)
C3	Ce1	C12	138.62(6)	C13	C9	Ce1	75.98(9)
C3	Ce1	C13	125.93(5)	C9	C10	Ce1	75.99(11)
C4	Ce1	C5	29.48(5)	C11	C10	Ce1	75.02(11)
C4	Ce1	C9	121.77(5)	C11	C10	C9	108.23(17)
C4	Ce1	C10	136.58(6)	C10	C11	Ce1	76.28(11)
C4	Ce1	C12	156.75(5)	C10	C11	C12	107.99(17)
C4	Ce1	C13	129.98(5)	C12	C11	Ce1	76.07(10)
C5	Ce1	C9	92.98(5)	C11	C12	Ce1	75.14(10)
C5	Ce1	C13	101.94(5)	C11	C12	C13	109.61(18)
C9	Ce1	C13	29.04(5)	C13	C12	Ce1	76.66(9)
C10	Ce1	C5	113.54(6)	Si2	C13	Ce1	126.93(7)
C10	Ce1	C9	29.08(6)	C9	C13	Ce1	74.98(9)
C10	Ce1	C13	47.99(5)	C9	C13	Si2	127.73(13)
C11	Ce1	C1	131.42(5)	C12	C13	Ce1	74.29(9)
C11	Ce1	C4	165.03(7)	C12	C13	Si2	124.83(13)
C11	Ce1	C5	140.22(6)	C12	C13	C9	105.89(16)
C11	Ce1	C9	47.69(6)	O1	C17	C18	112.78(16)

[1]1-X,1-Y,1-Z

Table S3a. Bond lengths (Å) for **2-La/^{i}Pr**.

Atom	Atom	Length (Å)	Atom	Atom	Length (Å)
La1	O1	2.3642(10)	La3	O2[2]	2.3604(10)
La1	O1[1]	2.3642(10)	La3	O2	2.3604(10)
La1	C1	2.8189(15)	La3	C20[2]	2.8543(16)
La1	C1[1]	2.8189(15)	La3	C20	2.8543(16)
La1	C2	2.8139(15)	La3	C21	2.8373(16)
La1	C2[1]	2.8139(15)	La3	C21[2]	2.8372(16)
La1	C3[1]	2.8439(16)	La3	C22[2]	2.8297(16)
La1	C3	2.8438(16)	La3	C22	2.8298(16)
La1	C4	2.8632(15)	La3	C23[2]	2.8372(15)
La1	C4[1]	2.8631(15)	La3	C23	2.8371(15)
La1	C5	2.8601(15)	La3	C24	2.8708(14)
La1	C5[1]	2.8601(15)	La3	C24[2]	2.8707(14)
La2	O1	2.3768(10)	La4	O2	2.4026(11)
La2	O1[1]	2.3768(10)	La4	O2[2]	2.4026(11)
La2	C9[1]	2.8446(15)	La4	C28	2.8478(17)
La2	C9	2.8446(15)	La4	C28[2]	2.8478(17)
La2	C10	2.8457(16)	La4	C29[2]	2.8211(16)
La2	C10[1]	2.8457(16)	La4	C29	2.8211(16)
La2	C11	2.8324(16)	La4	C30	2.8214(16)
La2	C11[1]	2.8323(16)	La4	C30[2]	2.8214(16)
La2	C12	2.8251(15)	La4	C31[2]	2.8446(16)
La2	C12[1]	2.8251(15)	La4	C31	2.8446(16)
La2	C13[1]	2.8452(14)	La4	C32	2.8770(16)
La2	C13	2.8452(14)	La4	C32[2]	2.8771(16)
Si1	C5	1.8641(17)	Si3	C24	1.8617(16)
Si1	C6	1.866(2)	Si3	C25	1.866(2)
Si1	C7	1.864(2)	Si3	C26	1.863(2)
Si1	C8	1.859(2)	Si3	C27	1.8627(19)
Si2	C13	1.8622(15)	Si4	C32	1.8554(18)
Si2	C14	1.865(2)	Si4	C33	1.870(3)
Si2	C15	1.868(2)	Si4	C34	1.848(3)
Si2	C16	1.8655(19)	Si4	C35	1.861(3)

Atom	Atom	Length (Å)	Atom	Atom	Length (Å)
O1	C17A	1.399(3)	Si4	C33A	1.778(14)
O1	C17B	1.395(3)	Si4	C34A	1.848(13)
C1	C2	1.409(2)	Si4	C35A	1.872(15)
C1	C5	1.427(2)	O2	C36	1.4240(18)
C2	C3	1.403(3)	C20	C21	1.406(2)
C3	C4	1.406(2)	C20	C24	1.420(2)
C4	C5	1.423(2)	C21	C22	1.398(3)
C9	C10	1.405(2)	C22	C23	1.402(2)
C9	C13	1.420(2)	C23	C24	1.420(2)
C10	C11	1.403(3)	C28	C29	1.402(3)
C11	C12	1.405(2)	C28	C32	1.418(2)
C12	C13	1.426(2)	C29	C30	1.401(3)
C18	C17A	1.523(4)	C30	C31	1.400(3)
C18	C17B	1.497(4)	C31	C32	1.421(2)
C19	C17A	1.490(4)	C36	C37	1.511(3)
C19	C17B	1.514(4)	C36	C38	1.519(2)

[1]3/2-X,+Y,3/2-Z; [2]3/2-X,+Y,1/2-Z

Table S3b. Bond angles (˚) for **2-La/^{i}Pr**.

Atom	Atom	Atom	Angle (˚)	Atom	Atom	Atom	Angle (˚)
O1	La1	O1[1]	73.19(5)	C18	C17B	C19	113.4(3)
O1[1]	La1	C1[1]	123.25(4)	C19	C17B	La1	126.9(2)
O1	La1	C1	123.25(4)	O2[2]	La3	O2	73.17(5)
O1	La1	C1[1]	131.03(4)	O2[2]	La3	C20	121.58(4)
O1[1]	La1	C1	131.03(4)	O2	La3	C20[2]	121.58(4)
O1[1]	La1	C2[1]	94.60(4)	O2	La3	C20	132.71(4)
O1	La1	C2[1]	123.75(5)	O2[2]	La3	C20[2]	132.71(4)
O1[1]	La1	C2	123.75(5)	O2[2]	La3	C21[2]	129.19(5)
O1	La1	C2	94.60(4)	O2	La3	C21	129.19(5)
O1[1]	La1	C3[1]	86.98(4)	O2	La3	C21[2]	92.98(5)
O1[1]	La1	C3	95.06(5)	O2[2]	La3	C21	92.98(5)
O1	La1	C3[1]	95.06(5)	O2[2]	La3	C22[2]	100.67(5)
O1	La1	C3	86.98(4)	O2[2]	La3	C22	81.91(4)
O1	La1	C4	109.05(4)	O2	La3	C22	100.67(5)
O1	La1	C4[1]	84.48(4)	O2	La3	C22[2]	81.90(4)
O1[1]	La1	C4[1]	109.05(4)	O2[2]	La3	C23	102.39(4)
O1[1]	La1	C4	84.48(4)	O2	La3	C23	87.61(4)
O1[1]	La1	C5	104.28(4)	O2[2]	La3	C23[2]	87.61(4)
O1[1]	La1	C5[1]	134.67(4)	O2	La3	C23[2]	102.39(4)
O1	La1	C5	134.67(4)	O2[2]	La3	C24	129.03(4)
O1	La1	C5[1]	104.28(4)	O2[2]	La3	C24[2]	105.07(4)
C1	La1	C1[1]	82.77(7)	O2	La3	C24[2]	129.03(4)
C1[1]	La1	C3[1]	47.36(5)	O2	La3	C24	105.07(4)
C1	La1	C3[1]	130.11(5)	C20	La3	C20[2]	83.10(7)
C1[1]	La1	C3	130.11(5)	C20[2]	La3	C24[2]	28.72(4)
C1	La1	C3	47.36(5)	C20	La3	C24	28.72(4)
C1[1]	La1	C4	117.73(5)	C20	La3	C24[2]	92.73(5)
C1[1]	La1	C4[1]	47.12(5)	C20[2]	La3	C24	92.73(5)
C1	La1	C4	47.12(5)	C21	La3	C20[2]	103.92(5)
C1	La1	C4[1]	117.73(5)	C21	La3	C20	28.59(5)
C1[1]	La1	C5	89.22(5)	C21[2]	La3	C20[2]	28.59(5)
C1	La1	C5[1]	89.22(5)	C21[2]	La3	C20	103.92(5)
C1[1]	La1	C5[1]	29.09(4)	C21[2]	La3	C21	129.59(8)

Atom	Atom	Atom	Angle (˚)	Atom	Atom	Atom	Angle (˚)
C1	La1	C5	29.10(5)	C21	La3	C24	47.58(4)
C2^{1}	La1	C1	106.31(5)	C21^{2}	La3	C24^{2}	47.58(4)
C2^{1}	La1	C1^{1}	28.96(5)	C21^{2}	La3	C24	101.69(5)
C2	La1	C1^{1}	106.31(5)	C21	La3	C24^{2}	101.69(5)
C2	La1	C1	28.96(5)	C22^{2}	La3	C20^{2}	47.04(5)
C2	La1	C2^{1}	133.35(7)	C22	La3	C20^{2}	129.81(5)
C2	La1	C3	28.71(5)	C22	La3	C20	47.04(5)
C2^{1}	La1	C3	149.27(5)	C22^{2}	La3	C20	129.81(5)
C2^{1}	La1	C3^{1}	28.71(5)	C22	La3	C21^{2}	148.74(5)
C2	La1	C3^{1}	149.27(5)	C22	La3	C21	28.56(5)
C2^{1}	La1	C4	124.49(5)	C22^{2}	La3	C21^{2}	28.56(5)
C2	La1	C4^{1}	124.49(5)	C22^{2}	La3	C21	148.74(5)
C2^{1}	La1	C4^{1}	47.17(5)	C22^{2}	La3	C22	176.83(7)
C2	La1	C4	47.17(5)	C22^{2}	La3	C23	150.64(5)
C2^{1}	La1	C5	101.56(5)	C22^{2}	La3	C23^{2}	28.66(5)
C2^{1}	La1	C5^{1}	48.03(5)	C22	La3	C23^{2}	150.64(5)
C2	La1	C5	48.03(5)	C22	La3	C23	28.66(5)
C2	La1	C5^{1}	101.56(5)	C22	La3	C24^{2}	130.00(5)
C3	La1	C3^{1}	177.46(7)	C22	La3	C24	47.67(5)
C3	La1	C4	28.52(5)	C22^{2}	La3	C24	130.00(5)
C3	La1	C4^{1}	150.72(5)	C22^{2}	La3	C24^{2}	47.68(5)
C3^{1}	La1	C4^{1}	28.52(5)	C23	La3	C20	46.84(5)
C3^{1}	La1	C4	150.72(5)	C23^{2}	La3	C20^{2}	46.84(5)
C3^{1}	La1	C5	130.27(5)	C23^{2}	La3	C20	121.53(5)
C3^{1}	La1	C5^{1}	47.74(5)	C23	La3	C20^{2}	121.53(5)
C3	La1	C5^{1}	130.27(5)	C23^{2}	La3	C21	126.17(5)
C3	La1	C5	47.74(5)	C23	La3	C21^{2}	126.17(5)
C4^{1}	La1	C4	163.51(6)	C23	La3	C21	47.01(5)
C5	La1	C4^{1}	134.97(5)	C23^{2}	La3	C21^{2}	47.01(5)
C5	La1	C4	28.80(4)	C23	La3	C23^{2}	167.64(7)
C5^{1}	La1	C4^{1}	28.80(4)	C23	La3	C24	28.81(4)
C5^{1}	La1	C4	134.97(5)	C23^{2}	La3	C24	139.19(5)
C5^{1}	La1	C5	107.49(6)	C23	La3	C24^{2}	139.19(5)
O1	La2	O1^{1}	72.74(5)	C23^{2}	La3	C24^{2}	28.81(4)
O1^{1}	La2	C9	85.38(4)	C24^{2}	La3	C24	112.71(6)
O1^{1}	La2	C9^{1}	105.48(4)	O2	La4	O2^{2}	71.69(5)
O1	La2	C9^{1}	85.38(4)	O2	La4	C28	134.85(5)
O1	La2	C9	105.49(4)	O2^{2}	La4	C28^{2}	134.85(5)
O1	La2	C10^{1}	96.53(5)	O2^{2}	La4	C28	120.06(5)
O1	La2	C10	83.81(4)	O2	La4	C28^{2}	120.06(5)
O1^{1}	La2	C10^{1}	83.81(4)	O2^{2}	La4	C29	91.56(5)
O1^{1}	La2	C10	96.52(5)	O2	La4	C29^{2}	91.56(5)
O1	La2	C11^{1}	125.12(5)	O2	La4	C29	127.21(5)
O1^{1}	La2	C11	125.12(5)	O2^{2}	La4	C29^{2}	127.21(5)
O1	La2	C11	92.75(4)	O2^{2}	La4	C30	82.99(5)
O1^{1}	La2	C11^{1}	92.75(4)	O2	La4	C30^{2}	82.99(5)
O1	La2	C12^{1}	131.73(4)	O2	La4	C30	98.52(5)
O1^{1}	La2	C12	131.73(4)	O2^{2}	La4	C30^{2}	98.52(5)
O1^{1}	La2	C12^{1}	121.38(4)	O2	La4	C31	88.58(5)
O1	La2	C12	121.38(4)	O2^{2}	La4	C31^{2}	88.58(5)
O1^{1}	La2	C13^{1}	131.51(4)	O2^{2}	La4	C31	105.23(5)
O1	La2	C13	131.51(4)	O2	La4	C31^{2}	105.23(5)
O1^{1}	La2	C13	104.70(4)	O2	La4	C32^{2}	130.60(4)

Atom	Atom	Atom	Angle (˚)	Atom	Atom	Atom	Angle (˚)
O1	La2	C13^{1}	104.70(4)	O2	La4	C32	108.39(4)
C9	La2	C9^{1}	166.71(6)	O2^{2}	La4	C32	130.59(4)
C9	La2	C10^{1}	151.31(5)	O2^{2}	La4	C32^{2}	108.39(4)
C9^{1}	La2	C10^{1}	28.59(5)	C28	La4	C28^{2}	83.87(8)
C9	La2	C10	28.59(5)	C28	La4	C32	28.67(5)
C9^{1}	La2	C10	151.31(5)	C28	La4	C32^{2}	89.47(5)
C9	La2	C13^{1}	138.04(5)	C28^{2}	La4	C32	89.47(5)
C9	La2	C13	28.91(4)	C28^{2}	La4	C32^{2}	28.67(5)
C9^{1}	La2	C13^{1}	28.91(4)	C29^{2}	La4	C28	107.33(6)
C9^{1}	La2	C13	138.04(4)	C29^{2}	La4	C28^{2}	28.63(6)
C10	La2	C10^{1}	179.59(7)	C29	La4	C28	28.63(6)
C11^{1}	La2	C9^{1}	47.07(5)	C29	La4	C28^{2}	107.33(6)
C11^{1}	La2	C9	126.26(5)	C29	La4	C29^{2}	134.12(9)
C11	La2	C9^{1}	126.26(5)	C29	La4	C30^{2}	149.79(6)
C11	La2	C9	47.07(5)	C29^{2}	La4	C30	149.79(6)
C11	La2	C10^{1}	151.07(5)	C29	La4	C30	28.75(6)
C11^{1}	La2	C10^{1}	28.60(5)	C29^{2}	La4	C30^{2}	28.75(6)
C11	La2	C10	28.60(5)	C29^{2}	La4	C31^{2}	47.04(5)
C11^{1}	La2	C10	151.07(5)	C29	La4	C31^{2}	124.54(6)
C11^{1}	La2	C11	134.46(7)	C29^{2}	La4	C31	124.54(6)
C11^{1}	La2	C13	103.26(5)	C29	La4	C31	47.04(5)
C11	La2	C13	47.94(4)	C29^{2}	La4	C32	102.13(5)
C11^{1}	La2	C13^{1}	47.94(4)	C29	La4	C32	47.57(5)
C11	La2	C13^{1}	103.26(5)	C29	La4	C32^{2}	102.13(5)
C12	La2	C9^{1}	120.68(5)	C29^{2}	La4	C32^{2}	47.57(5)
C12^{1}	La2	C9	120.68(5)	C30^{2}	La4	C28	130.99(6)
C12^{1}	La2	C9^{1}	47.10(5)	C30	La4	C28	47.17(6)
C12	La2	C9	47.10(5)	C30^{2}	La4	C28^{2}	47.17(6)
C12^{1}	La2	C10^{1}	47.24(5)	C30	La4	C28^{2}	130.99(6)
C12	La2	C10^{1}	132.34(5)	C30^{2}	La4	C30	178.15(8)
C12	La2	C10	47.24(5)	C30	La4	C31^{2}	150.84(5)
C12^{1}	La2	C10	132.34(5)	C30^{2}	La4	C31^{2}	28.60(5)
C12	La2	C11	28.75(5)	C30	La4	C31	28.60(5)
C12	La2	C11^{1}	107.85(5)	C30^{2}	La4	C31	150.84(5)
C12^{1}	La2	C11^{1}	28.75(5)	C30	La4	C32^{2}	130.87(6)
C12^{1}	La2	C11	107.85(5)	C30^{2}	La4	C32	130.87(6)
C12^{1}	La2	C12	85.10(7)	C30^{2}	La4	C32^{2}	47.66(5)
C12	La2	C13	29.12(4)	C30	La4	C32	47.66(5)
C12^{1}	La2	C13	92.01(5)	C31^{2}	La4	C28	117.78(5)
C12^{1}	La2	C13^{1}	29.12(4)	C31	La4	C28	46.80(5)
C12	La2	C13^{1}	92.01(5)	C31^{2}	La4	C28^{2}	46.80(5)
C13^{1}	La2	C10^{1}	47.86(4)	C31	La4	C28^{2}	117.78(5)
C13	La2	C10^{1}	131.83(5)	C31	La4	C31^{2}	163.12(7)
C13^{1}	La2	C10	131.83(5)	C31	La4	C32^{2}	134.56(5)
C13	La2	C10	47.86(4)	C31^{2}	La4	C32^{2}	28.76(5)
C13^{1}	La2	C13	110.62(6)	C31	La4	C32	28.76(5)
C5	Si1	C6	114.54(8)	C31^{2}	La4	C32	134.56(5)
C7	Si1	C5	107.40(9)	C32	La4	C32^{2}	106.83(7)
C7	Si1	C6	107.96(11)	C24	Si3	C25	108.62(9)
C8	Si1	C5	108.55(10)	C24	Si3	C26	109.23(9)
C8	Si1	C6	107.89(12)	C24	Si3	C27	111.92(8)
C8	Si1	C7	110.50(14)	C26	Si3	C25	109.38(12)
C13	Si2	C14	108.40(9)	C27	Si3	C25	109.28(11)

Atom	Atom	Atom	Angle (˚)	Atom	Atom	Atom	Angle (˚)
C13	Si2	C15	107.59(8)	C27	Si3	C26	108.39(11)
C13	Si2	C16	113.76(8)	C32	Si4	C33	109.89(12)
C14	Si2	C15	111.38(11)	C32	Si4	C35	113.27(11)
C14	Si2	C16	108.02(9)	C32	Si4	C35A	102.2(6)
C16	Si2	C15	107.74(10)	C34	Si4	C32	109.77(12)
La1	O1	La2	107.03(4)	C34	Si4	C33	107.9(2)
C17A	O1	La1	143.9(2)	C34	Si4	C35	108.2(2)
C17A	O1	La2	109.1(2)	C35	Si4	C33	107.56(19)
C17B	O1	La1	110.4(2)	C33A	Si4	C32	108.4(6)
C17B	O1	La2	142.5(3)	C33A	Si4	C34A	122.0(11)
C2	C1	La1	75.32(9)	C33A	Si4	C35A	112.2(11)
C2	C1	C5	109.07(15)	C34A	Si4	C32	103.2(6)
C5	C1	La1	77.05(9)	C34A	Si4	C35A	106.7(11)
C1	C2	La1	75.71(9)	La3	O2	La4	107.57(4)
C3	C2	La1	76.83(9)	C36	O2	La3	144.19(10)
C3	C2	C1	107.99(15)	C36	O2	La4	108.24(9)
C2	C3	La1	74.46(9)	C21	C20	La3	75.03(9)
C2	C3	C4	107.95(15)	C21	C20	C24	109.16(15)
C4	C3	La1	76.50(9)	C24	C20	La3	76.28(9)
C3	C4	La1	74.97(9)	C20	C21	La3	76.38(9)
C3	C4	C5	109.32(15)	C22	C21	La3	75.42(10)
C5	C4	La1	75.48(9)	C22	C21	C20	108.02(15)
Si1	C5	La1	124.50(7)	C21	C22	La3	76.02(9)
C1	C5	La1	73.85(9)	C21	C22	C23	107.84(15)
C1	C5	Si1	126.47(12)	C23	C22	La3	75.96(9)
C4	C5	La1	75.72(9)	C22	C23	La3	75.38(9)
C4	C5	Si1	126.87(12)	C22	C23	C24	109.42(15)
C4	C5	C1	105.66(14)	C24	C23	La3	76.91(8)
C10	C9	La2	75.75(9)	Si3	C24	La3	124.70(7)
C10	C9	C13	109.56(14)	C20	C24	La3	74.99(8)
C13	C9	La2	75.57(8)	C20	C24	Si3	127.15(12)
C9	C10	La2	75.66(9)	C20	C24	C23	105.57(14)
C11	C10	La2	75.17(9)	C23	C24	La3	74.28(8)
C11	C10	C9	107.69(14)	C23	C24	Si3	126.27(12)
C10	C11	La2	76.23(9)	C29	C28	La4	74.63(10)
C10	C11	C12	108.08(14)	C29	C28	C32	109.22(17)
C12	C11	La2	75.34(9)	C32	C28	La4	76.81(9)
C11	C12	La2	75.91(9)	C28	C29	La4	76.74(10)
C11	C12	C13	109.17(14)	C30	C29	La4	75.64(10)
C13	C12	La2	76.22(8)	C30	C29	C28	108.06(17)
Si2	C13	La2	125.29(7)	C29	C30	La4	75.61(10)
C9	C13	La2	75.52(8)	C31	C30	La4	76.62(9)
C9	C13	Si2	126.48(12)	C31	C30	C29	107.69(17)
C9	C13	C12	105.50(13)	C30	C31	La4	74.78(10)
C12	C13	La2	74.66(8)	C30	C31	C32	109.45(17)
C12	C13	Si2	126.67(12)	C32	C31	La4	76.89(9)
O1	C17A	La2	45.91(15)	Si4	C32	La4	128.40(7)
O1	C17A	C18	111.1(3)	C28	C32	La4	74.52(9)
O1	C17A	C19	113.6(3)	C28	C32	Si4	126.25(14)
C18	C17A	La2	125.70(19)	C28	C32	C31	105.58(16)
C19	C17A	La2	121.01(19)	C31	C32	La4	74.36(9)
C19	C17A	C18	113.3(3)	C31	C32	Si4	126.27(13)
O1	C17B	La1	44.94(17)	O2	C36	C37	111.50(14)

Atom	Atom	Atom	Angle (˚)	Atom	Atom	Atom	Angle (˚)
O1	C17B	C18	112.9(3)	O2	C36	C38	110.88(14)
O1	C17B	C19	112.3(3)	C37	C36	C38	111.81(15)
C18	C17B	La1	119.7(2)				

[1]3/2-X,+Y,3/2-Z; [2]3/2-X,+Y,1/2-Z

Table S4a. Bond lengths (Å) for **2-Ce/^{i}Pr**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ce1	O1[1]	2.339(4)	Ce3	O2[2]	2.339(4)
Ce1	O1	2.339(4)	Ce3	O2	2.339(4)
Ce1	C1	2.786(6)	Ce3	C00S[2]	2.857(6)
Ce1	C1[1]	2.786(6)	Ce3	C00S	2.857(6)
Ce1	C2	2.785(6)	Ce3	C20	2.828(6)
Ce1	C2[1]	2.785(6)	Ce3	C20[2]	2.828(6)
Ce1	C3	2.805(6)	Ce3	C21	2.789(6)
Ce1	C3[1]	2.805(6)	Ce3	C21[2]	2.789(6)
Ce1	C4[1]	2.825(6)	Ce3	C22	2.783(6)
Ce1	C4	2.825(6)	Ce3	C22[2]	2.783(6)
Ce1	C5[1]	2.847(6)	Ce3	C23	2.805(6)
Ce1	C5	2.847(6)	Ce3	C23[2]	2.805(6)
Ce2	O1	2.347(4)	Ce4	O2[2]	2.361(4)
Ce2	O1[1]	2.347(4)	Ce4	O2	2.361(4)
Ce2	C9[1]	2.814(6)	Ce4	C27[2]	2.808(7)
Ce2	C9	2.814(6)	Ce4	C27	2.808(7)
Ce2	C10	2.810(6)	Ce4	C28[2]	2.772(6)
Ce2	C10[1]	2.810(6)	Ce4	C28	2.772(6)
Ce2	C11[1]	2.797(6)	Ce4	C29	2.785(7)
Ce2	C11	2.797(6)	Ce4	C29[2]	2.784(7)
Ce2	C12[1]	2.790(6)	Ce4	C30[2]	2.805(7)
Ce2	C12	2.790(6)	Ce4	C30	2.805(7)
Ce2	C13[1]	2.829(6)	Ce4	C31	2.847(6)
Ce2	C13	2.829(6)	Ce4	C31[2]	2.847(6)
Si1	C5	1.855(7)	Si3	C00S	1.851(6)
Si1	C6	1.853(8)	Si3	C24	1.856(9)
Si1	C7	1.844(9)	Si3	C25	1.835(8)
Si1	C8	1.845(8)	Si3	C26	1.857(8)
Si2	C13	1.853(6)	Si4	C31	1.859(7)
Si2	C14	1.851(8)	Si4	C32	1.814(13)
Si2	C15	1.848(7)	Si4	C33	1.865(14)
Si2	C16	1.870(8)	Si4	C34	1.841(13)
O1	C17	1.398(12)	Si4	C32A	1.81(2)
O1	C17A	1.408(11)	Si4	C33A	1.87(2)
C1	C2	1.405(9)	Si4	C34A	1.797(19)
C1	C5	1.419(9)	O2	C35	1.414(7)
C2	C3	1.389(10)	C00S	C20	1.423(9)
C3	C4	1.397(9)	C00S	C23	1.448(9)
C4	C5	1.418(8)	C20	C21	1.394(9)
C9	C10	1.394(9)	C21	C22	1.378(10)
C9	C13	1.422(8)	C22	C23	1.380(10)
C10	C11	1.394(9)	C27	C28	1.338(10)
C11	C12	1.403(9)	C27	C31	1.410(9)
C12	C13	1.418(8)	C28	C29	1.402(11)
C17	C18	1.50(3)	C29	C30	1.401(10)
C17	C19	1.47(2)	C30	C31	1.399(9)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C17A	C18A	1.51(3)	C35	C36	1.475(10)
C17A	C19A	1.49(2)	C35	C37	1.509(10)

[1]3/2-X,+Y,1/2-Z; [2]1/2-X,+Y,1/2-Z

Table S4b. Bond angles (˚) for **2-Ce/^{i}Pr**.

Atom	Atom	Atom	Angle (˚)	Atom	Atom	Atom	Angle (˚)
O1[1]	Ce1	O1	72.56(19)	O2	Ce3	C00S	129.91(16)
O1	Ce1	C1[1]	131.65(17)	O2[2]	Ce3	C00S	105.63(16)
O1[1]	Ce1	C1[1]	123.54(17)	O2[2]	Ce3	C00S[2]	129.90(16)
O1	Ce1	C1	123.55(17)	O2	Ce3	C00S[2]	105.63(16)
O1[1]	Ce1	C1	131.65(17)	O2[2]	Ce3	C20	133.41(17)
O1	Ce1	C2[1]	124.56(19)	O2	Ce3	C20	122.04(18)
O1[1]	Ce1	C2[1]	94.57(18)	O2	Ce3	C20[2]	133.41(17)
O1	Ce1	C2	94.57(18)	O2[2]	Ce3	C20[2]	122.04(18)
O1[1]	Ce1	C2	124.56(19)	O2[2]	Ce3	C21	129.56(19)
O1	Ce1	C3[1]	95.82(19)	O2[2]	Ce3	C21[2]	93.32(18)
O1	Ce1	C3	86.74(18)	O2	Ce3	C21[2]	129.55(19)
O1[1]	Ce1	C3	95.82(19)	O2	Ce3	C21	93.32(18)
O1[1]	Ce1	C3[1]	86.74(18)	O2	Ce3	C22	82.63(18)
O1[1]	Ce1	C4	85.05(16)	O2[2]	Ce3	C22[2]	82.62(18)
O1[1]	Ce1	C4[1]	108.73(17)	O2	Ce3	C22[2]	100.9(2)
O1	Ce1	C4[1]	85.05(16)	O2[2]	Ce3	C22	100.9(2)
O1	Ce1	C4	108.73(17)	O2[2]	Ce3	C23	87.48(17)
O1	Ce1	C5	134.67(16)	O2	Ce3	C23	102.53(18)
O1[1]	Ce1	C5[1]	134.67(16)	O2	Ce3	C23[2]	87.48(17)
O1	Ce1	C5[1]	104.78(16)	O2[2]	Ce3	C23[2]	102.53(18)
O1[1]	Ce1	C5	104.77(16)	C00S[2]	Ce3	C00S	111.2(3)
C1	Ce1	C1[1]	81.9(3)	C20[2]	Ce3	C00S	91.21(19)
C1	Ce1	C3	47.4(2)	C20	Ce3	C00S[2]	91.21(19)
C1[1]	Ce1	C3	129.4(2)	C20	Ce3	C00S	28.98(17)
C1	Ce1	C3[1]	129.4(2)	C20[2]	Ce3	C00S[2]	28.98(17)
C1[1]	Ce1	C3[1]	47.4(2)	C20	Ce3	C20[2]	81.9(3)
C1	Ce1	C4	47.22(19)	C21[2]	Ce3	C00S[2]	48.06(18)
C1	Ce1	C4[1]	117.35(19)	C21	Ce3	C00S[2]	100.4(2)
C1[1]	Ce1	C4[1]	47.22(19)	C21	Ce3	C00S	48.06(18)
C1[1]	Ce1	C4	117.34(19)	C21[2]	Ce3	C00S	100.4(2)
C1[1]	Ce1	C5	88.62(19)	C21[2]	Ce3	C20[2]	28.72(19)
C1	Ce1	C5[1]	88.63(19)	C21	Ce3	C20[2]	103.1(2)
C1	Ce1	C5	29.16(18)	C21[2]	Ce3	C20	103.1(2)
C1[1]	Ce1	C5[1]	29.16(18)	C21	Ce3	C20	28.72(19)
C2	Ce1	C1[1]	105.5(2)	C21	Ce3	C21[2]	128.9(3)
C2[1]	Ce1	C1[1]	29.22(19)	C21[2]	Ce3	C23	125.5(2)
C2	Ce1	C1	29.22(19)	C21	Ce3	C23[2]	125.5(2)
C2[1]	Ce1	C1	105.5(2)	C21	Ce3	C23	47.6(2)
C2	Ce1	C2[1]	132.7(3)	C21[2]	Ce3	C23[2]	47.6(2)
C2[1]	Ce1	C3[1]	28.8(2)	C22[2]	Ce3	C00S	128.9(2)
C2	Ce1	C3[1]	148.7(2)	C22[2]	Ce3	C00S[2]	47.84(19)
C2	Ce1	C3	28.8(2)	C22	Ce3	C00S	47.84(19)
C2[1]	Ce1	C3	148.7(2)	C22	Ce3	C00S[2]	128.9(2)
C2[1]	Ce1	C4	124.0(2)	C22	Ce3	C20	47.0(2)
C2	Ce1	C4[1]	124.0(2)	C22[2]	Ce3	C20	128.7(2)
C2[1]	Ce1	C4[1]	47.5(2)	C22	Ce3	C20[2]	128.6(2)
C2	Ce1	C4	47.5(2)	C22[2]	Ce3	C20[2]	47.0(2)

Atom	Atom	Atom	Angle (˚)	Atom	Atom	Atom	Angle (˚)
C2	Ce1	C5^{1}	100.7(2)	C22	Ce3	C21	28.6(2)
C2^{1}	Ce1	C5^{1}	48.47(19)	C22^{2}	Ce3	C21	147.7(2)
C2^{1}	Ce1	C5	100.7(2)	C22^{2}	Ce3	C21^{2}	28.6(2)
C2	Ce1	C5	48.47(19)	C22	Ce3	C21^{2}	147.7(2)
C3	Ce1	C3^{1}	176.8(3)	C22	Ce3	C22^{2}	175.6(3)
C3^{1}	Ce1	C4	150.3(2)	C22^{2}	Ce3	C23	150.4(2)
C3^{1}	Ce1	C4^{1}	28.73(19)	C22^{2}	Ce3	C23^{2}	28.6(2)
C3	Ce1	C4	28.74(19)	C22	Ce3	C23^{2}	150.4(2)
C3	Ce1	C4^{1}	150.3(2)	C22	Ce3	C23	28.6(2)
C3	Ce1	C5^{1}	129.5(2)	C23^{2}	Ce3	C00S^{2}	29.61(18)
C3	Ce1	C5	48.02(19)	C23	Ce3	C00S^{2}	138.43(19)
C3^{1}	Ce1	C5	129.5(2)	C23	Ce3	C00S	29.61(18)
C3^{1}	Ce1	C5^{1}	48.02(19)	C23^{2}	Ce3	C00S	138.43(19)
C4	Ce1	C4^{1}	163.3(3)	C23^{2}	Ce3	C20^{2}	47.62(19)
C4	Ce1	C5^{1}	134.59(18)	C23	Ce3	C20^{2}	120.8(2)
C4	Ce1	C5	28.95(17)	C23	Ce3	C20	47.62(19)
C4^{1}	Ce1	C5^{1}	28.95(17)	C23^{2}	Ce3	C20	120.8(2)
C4^{1}	Ce1	C5	134.59(18)	C23^{2}	Ce3	C23	167.7(3)
C5	Ce1	C5^{1}	107.1(2)	O2^{2}	Ce4	O2	71.79(19)
O1	Ce2	O1^{1}	72.28(19)	O2	Ce4	C27	88.63(19)
O1	Ce2	C9	106.22(16)	O2^{2}	Ce4	C27^{2}	88.63(19)
O1^{1}	Ce2	C9^{1}	106.22(17)	O2	Ce4	C27^{2}	105.55(18)
O1	Ce2	C9^{1}	85.54(16)	O2^{2}	Ce4	C27	105.55(18)
O1^{1}	Ce2	C9	85.54(16)	O2^{2}	Ce4	C28^{2}	98.2(2)
O1^{1}	Ce2	C10^{1}	84.66(17)	O2	Ce4	C28	98.2(2)
O1	Ce2	C10^{1}	96.82(18)	O2^{2}	Ce4	C28	83.87(19)
O1^{1}	Ce2	C10	96.82(18)	O2	Ce4	C28^{2}	83.87(19)
O1	Ce2	C10	84.66(17)	O2^{2}	Ce4	C29	91.43(19)
O1	Ce2	C11^{1}	125.61(18)	O2	Ce4	C29	127.3(2)
O1	Ce2	C11	93.90(17)	O2^{2}	Ce4	C29^{2}	127.3(2)
O1^{1}	Ce2	C11^{1}	93.90(17)	O2	Ce4	C29^{2}	91.43(19)
O1^{1}	Ce2	C11	125.61(18)	O2^{2}	Ce4	C30	120.33(19)
O1	Ce2	C12^{1}	132.11(16)	O2^{2}	Ce4	C30^{2}	134.85(19)
O1	Ce2	C12	122.86(17)	O2	Ce4	C30^{2}	120.33(19)
O1^{1}	Ce2	C12^{1}	122.86(17)	O2	Ce4	C30	134.85(19)
O1^{1}	Ce2	C12	132.11(16)	O2^{2}	Ce4	C31	131.05(17)
O1	Ce2	C13^{1}	104.81(15)	O2	Ce4	C31	108.41(17)
O1	Ce2	C13	132.74(16)	O2^{2}	Ce4	C31^{2}	108.41(17)
O1^{1}	Ce2	C13^{1}	132.74(16)	O2	Ce4	C31^{2}	131.05(17)
O1^{1}	Ce2	C13	104.81(15)	C27^{2}	Ce4	C27	162.7(3)
C9	Ce2	C9^{1}	165.7(3)	C27^{2}	Ce4	C31^{2}	28.87(19)
C9^{1}	Ce2	C13	136.77(19)	C27	Ce4	C31	28.87(19)
C9	Ce2	C13	29.19(17)	C27	Ce4	C31^{2}	134.0(2)
C9	Ce2	C13^{1}	136.77(19)	C27^{2}	Ce4	C31	134.0(2)
C9^{1}	Ce2	C13^{1}	29.19(17)	C28	Ce4	C27	27.7(2)
C10^{1}	Ce2	C9	150.8(2)	C28^{2}	Ce4	C27	151.5(2)
C10^{1}	Ce2	C9^{1}	28.71(19)	C28	Ce4	C27^{2}	151.5(2)
C10	Ce2	C9	28.71(19)	C28^{2}	Ce4	C27^{2}	27.7(2)
C10	Ce2	C9^{1}	150.8(2)	C28	Ce4	C28^{2}	177.5(3)
C10^{1}	Ce2	C10	178.2(3)	C28	Ce4	C29	29.2(2)
C10	Ce2	C13^{1}	130.31(19)	C28^{2}	Ce4	C29^{2}	29.2(2)
C10	Ce2	C13	48.28(18)	C28	Ce4	C29^{2}	148.8(3)
C10^{1}	Ce2	C13	130.31(19)	C28^{2}	Ce4	C29	148.8(3)

Atom	Atom	Atom	Angle (˚)	Atom	Atom	Atom	Angle (˚)
C10[1]	Ce2	C13[1]	48.28(18)	C28	Ce4	C30[2]	130.4(2)
C11	Ce2	C9	47.2(2)	C28[2]	Ce4	C30	130.4(2)
C11[1]	Ce2	C9[1]	47.2(2)	C28[2]	Ce4	C30[2]	47.1(2)
C11[1]	Ce2	C9	125.3(2)	C28	Ce4	C30	47.1(2)
C11	Ce2	C9[1]	125.3(2)	C28	Ce4	C31	47.2(2)
C11	Ce2	C10	28.79(19)	C28[2]	Ce4	C31[2]	47.2(2)
C11[1]	Ce2	C10	149.7(2)	C28	Ce4	C31[2]	130.8(2)
C11[1]	Ce2	C10[1]	28.79(19)	C28[2]	Ce4	C31	130.8(2)
C11	Ce2	C10[1]	149.7(2)	C29	Ce4	C27	47.3(2)
C11[1]	Ce2	C11	132.5(3)	C29[2]	Ce4	C27[2]	47.3(2)
C11	Ce2	C13	48.23(18)	C29[2]	Ce4	C27	124.2(2)
C11[1]	Ce2	C13	101.56(19)	C29	Ce4	C27[2]	124.2(2)
C11[1]	Ce2	C13[1]	48.23(18)	C29[2]	Ce4	C29	134.2(4)
C11	Ce2	C13[1]	101.56(19)	C29[2]	Ce4	C30	107.0(3)
C12	Ce2	C9[1]	119.26(18)	C29	Ce4	C30	29.0(2)
C12	Ce2	C9	47.45(18)	C29	Ce4	C30[2]	107.0(3)
C12[1]	Ce2	C9	119.26(18)	C29[2]	Ce4	C30[2]	29.0(2)
C12[1]	Ce2	C9[1]	47.45(18)	C29[2]	Ce4	C31	101.6(2)
C12	Ce2	C10[1]	130.4(2)	C29	Ce4	C31[2]	101.6(2)
C12[1]	Ce2	C10	130.4(2)	C29	Ce4	C31	48.0(2)
C12[1]	Ce2	C10[1]	47.78(19)	C29[2]	Ce4	C31[2]	48.0(2)
C12	Ce2	C10	47.78(19)	C30	Ce4	C27	46.8(2)
C12	Ce2	C11	29.09(18)	C30	Ce4	C27[2]	117.4(2)
C12[1]	Ce2	C11	105.6(2)	C30[2]	Ce4	C27[2]	46.8(2)
C12	Ce2	C11[1]	105.6(2)	C30[2]	Ce4	C27	117.4(2)
C12[1]	Ce2	C11[1]	29.09(18)	C30	Ce4	C30[2]	83.3(3)
C12	Ce2	C12[1]	82.6(3)	C30	Ce4	C31[2]	88.9(2)
C12[1]	Ce2	C13[1]	29.23(16)	C30[2]	Ce4	C31[2]	28.66(19)
C12[1]	Ce2	C13	90.21(18)	C30[2]	Ce4	C31	88.9(2)
C12	Ce2	C13[1]	90.21(18)	C30	Ce4	C31	28.66(19)
C12	Ce2	C13	29.23(17)	C31	Ce4	C31[2]	106.2(3)
C13[1]	Ce2	C13	109.3(2)	C00S	Si3	C24	108.5(4)
C6	Si1	C5	115.1(3)	C00S	Si3	C26	108.9(4)
C7	Si1	C5	108.4(4)	C24	Si3	C26	108.3(5)
C7	Si1	C6	108.2(5)	C25	Si3	C00S	112.9(3)
C7	Si1	C8	109.9(5)	C25	Si3	C24	108.8(5)
C8	Si1	C5	107.5(4)	C25	Si3	C26	109.4(5)
C8	Si1	C6	107.6(4)	C31	Si4	C33	114.3(5)
C13	Si2	C16	108.1(4)	C31	Si4	C33A	102.0(11)
C14	Si2	C13	107.7(3)	C32	Si4	C31	110.4(5)
C14	Si2	C16	111.2(5)	C32	Si4	C33	106.2(9)
C15	Si2	C13	114.1(3)	C32	Si4	C34	109.4(8)
C15	Si2	C14	107.9(4)	C34	Si4	C31	110.9(5)
C15	Si2	C16	107.9(4)	C34	Si4	C33	105.4(8)
Ce1	O1	Ce2	107.58(15)	C32A	Si4	C31	106.0(14)
C17	O1	Ce1	141.2(7)	C32A	Si4	C33A	103.6(18)
C17	O1	Ce2	111.2(7)	C34A	Si4	C31	110.9(10)
C17A	O1	Ce1	109.3(6)	C34A	Si4	C32A	125.9(19)
C17A	O1	Ce2	143.1(6)	C34A	Si4	C33A	105.7(18)
C2	C1	Ce1	75.4(4)	Ce3	O2	Ce4	107.81(15)
C2	C1	C5	109.9(6)	C35	O2	Ce3	140.6(4)
C5	C1	Ce1	77.8(3)	C35	O2	Ce4	111.6(4)
C1	C2	Ce1	75.4(3)	Si3	C00S	Ce3	126.3(3)

Atom	Atom	Atom	Angle (˚)	Atom	Atom	Atom	Angle (˚)
C3	C2	Ce1	76.4(4)	C20	C00S	Ce3	74.4(3)
C3	C2	C1	107.2(6)	C20	C00S	Si3	127.4(5)
C2	C3	Ce1	74.8(4)	C20	C00S	C23	104.8(6)
C2	C3	C4	108.5(6)	C23	C00S	Ce3	73.2(3)
C4	C3	Ce1	76.4(3)	C23	C00S	Si3	126.7(5)
C3	C4	Ce1	74.9(4)	C00S	C20	Ce3	76.6(4)
C3	C4	C5	109.6(6)	C21	C20	Ce3	74.1(4)
C5	C4	Ce1	76.4(3)	C21	C20	C00S	109.5(6)
Si1	C5	Ce1	125.4(3)	C20	C21	Ce3	77.2(4)
C1	C5	Ce1	73.0(3)	C22	C21	Ce3	75.4(4)
C1	C5	Si1	126.7(5)	C22	C21	C20	107.7(6)
C4	C5	Ce1	74.7(3)	C21	C22	Ce3	75.9(4)
C4	C5	Si1	127.5(5)	C21	C22	C23	110.0(6)
C4	C5	C1	104.8(6)	C23	C22	Ce3	76.6(4)
C10	C9	Ce2	75.5(4)	C00S	C23	Ce3	77.2(3)
C10	C9	C13	110.0(6)	C22	C23	Ce3	74.8(4)
C13	C9	Ce2	76.0(3)	C22	C23	C00S	108.0(6)
C9	C10	Ce2	75.8(4)	C28	C27	Ce4	74.6(4)
C11	C10	Ce2	75.1(4)	C28	C27	C31	109.9(7)
C11	C10	C9	107.5(6)	C31	C27	Ce4	77.1(4)
C10	C11	Ce2	76.1(4)	C27	C28	Ce4	77.6(4)
C10	C11	C12	108.3(6)	C27	C28	C29	109.8(7)
C12	C11	Ce2	75.2(3)	C29	C28	Ce4	75.9(4)
C11	C12	Ce2	75.7(3)	C28	C29	Ce4	74.9(4)
C11	C12	C13	109.1(6)	C30	C29	Ce4	76.3(4)
C13	C12	Ce2	76.9(3)	C30	C29	C28	105.4(7)
Si2	C13	Ce2	126.5(3)	C29	C30	Ce4	74.7(4)
C9	C13	Ce2	74.8(3)	C31	C30	Ce4	77.3(4)
C9	C13	Si2	126.4(5)	C31	C30	C29	109.9(7)
C12	C13	Ce2	73.8(3)	Si4	C31	Ce4	128.5(3)
C12	C13	Si2	127.2(5)	C27	C31	Ce4	74.0(4)
C12	C13	C9	105.1(5)	C27	C31	Si4	126.0(6)
O1	C17	C18	112.2(18)	C30	C31	Ce4	74.0(4)
O1	C17	C19	115.5(18)	C30	C31	Si4	127.3(6)
C19	C17	C18	115(2)	C30	C31	C27	105.0(6)
O1	C17A	C18A	111.6(19)	O2	C35	C36	114.3(6)
O1	C17A	C19A	111.0(18)	O2	C35	C37	112.8(6)
C19A	C17A	C18A	112(2)	C36	C35	C37	114.0(6)
O2[2]	Ce3	O2	72.6(2)				

[1]3/2-X,+Y,1/2-Z; [2]1/2-X,+Y,1/2-Z

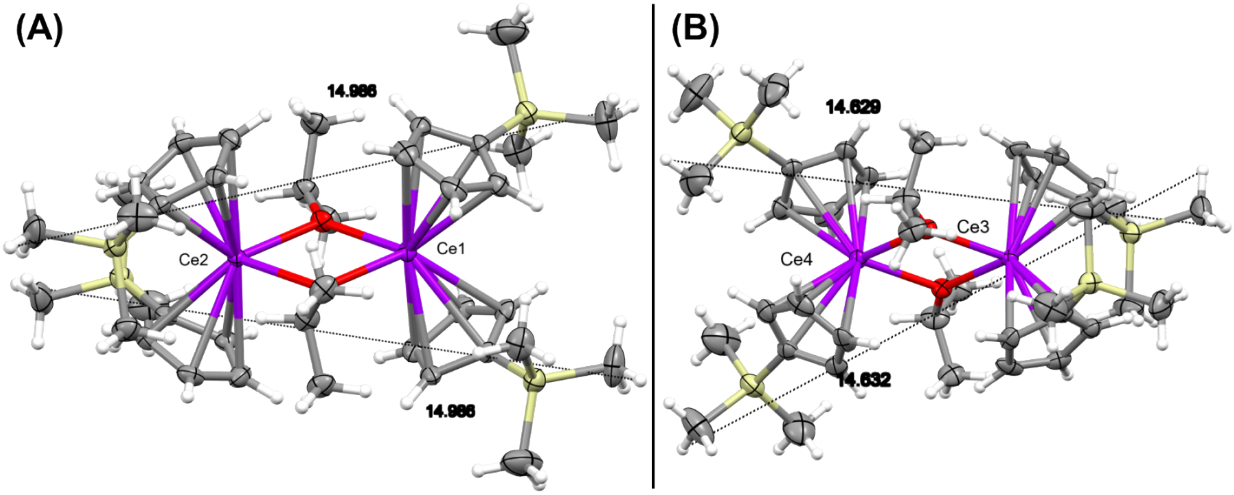

Fig S24. Points used for determination of $r_{H(theo)}$ from the crystal structure of **2-Ce/^{i}Pr**, where $r_{H(theo)}$ is estimated as half the longest distance observed in the crystal structure.

References

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