Siloxide tripodal ligands as a scaffold for stabilizing lanthanides in the +IV oxidation state.

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S1. Materials and Physical Measurements

General Considerations

Unless otherwise noted, all manipulations were carried out at ambient temperature under an inert argon or nitrogen atmosphere using Schlenk techniques and an MBraun glovebox equipped with a purifier unit. The water and oxygen levels were always kept at less than 0.1 ppm. Glassware was dried overnight at 140 °C before use.

NMR experiments were carried out using NMR tubes adapted with J-Young valves. NMR spectra were recorded on Bruker 400, 500, or 600 MHz spectrometers and referenced to residual solvent resonances of THF (d_8-THF), toluene (d_8-toluene), or Acetonitrile (d_3-MeCN) in Pyrex NMR tubes adapted with J-Young valves.

Elemental analyses were performed under an inert atmosphere of nitrogen with a ThermoScientific Flash 2000 Organic Elemental Analyzer.

Cyclic voltammetry data were carried out at room temperature in an argon-filled glovebox described above. Data were collected using a Biologic SP-300 potentiostat connected to a personal computer. All samples were measured with 0.1 M $[NBu_4][B(C_6F_5)_4]$[1] supporting electrolyte in THF solution. The experiments were carried out with a platinum disk (d = 5 mm) working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode. Potential calibration was performed at the end of each data collection cycle using the decamethylferrocene/decamethylferrocenium couple as an internal standard.

Starting materials Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Anhydrous solvents were purchased from Aldrich and further distilled from K/benzophenone (THF, Et_2O and toluene), sodium sand/benzophenone (n-hexane) or CaH_2 (MeCN). Deuterated solvents for NMR spectroscopy were purchased from Cortecnet, freeze-degassed and distilled over K/benzophenone (THF-d_8, toluene-d_8) or CaH_2 (MeCN-d_3). Potassium bis(trimethylsilyl)amide (KHMDS), cerium chloride, triphenylsilanol ($HOSiPh_3$) and sodium *tert*-butoxide (NaO^tBu) were purchased from Sigma-Aldrich and dried under high vacuum prior to use. *Tert*-butyllithium solution (1.7 M in pentane), imidazole, dimethoxydiphenylsilane, and $[N(C_6H_4Br)_3][SbCl_6]$ were purchased from Sigma-Aldrich and used as received. $AgBPh_4$[2], $KOSiPh_3$[3] $[Ln(N(SiMe_3)_2)_3]$[4,5] (Ln=Ce, Pr and Tb), $(HOSiPh_2Ar)_3$-arene[6], $(HOSi(O^tBu)_2Ar)_3$-arene)[7], 2-KOAd[22] (AdOH= 1-adamantanol) and $[Ce((OSi(O^tBu)_2Ar)_3\text{-arene})(THF)]$[7] (**1-Ce^{OtBu}**) were prepared according to the published procedure.

EPR analysis were performed on a Bruker Elexsys E500 spectrometer working at 9.4 GHz frequency with an Oxford ESR900 cryostat for 4-300 K operation. Simulations were performed with the Easyspin 5.1.3 program.[8]

Magnetization were performed using a QuantumDesign MPMS3 superconducting quantum interference device (SQUID) magnetometer in a temperature range 2-300 K. The powder sample was constrained in eicosane and enclosed in an evacuated quartz capsule and placed inside a plastic straw. The measurement was performed with applied magnetic field of 1 T in the zero-field cooled (ZFC) regime and performed on two independent samples for reproducibility. Diamagnetic corrections were applied using Pascal's constants.[9] The magnetic moment was calculated using the formula:

$$\mu_{eff} = \sqrt{8\chi T}$$

UV/Vis data were recorded using 1.0 mm cuvettes equipped with a J-Young valve and a Perkin Elmer 950 spectrometer.

IR spectra were recorded with a Perkin Elmer 1600 Series FTIR spectrophotometer flushed with nitrogen.

ICP-MS samples were submitted to acidic digestion with 5 mL of concentrated HNO3 (69%, ROTIPURAN Supra, Roth) in PP digestion vials using heating block system (DigiPREP Jr. 15ml, 40 Pos, SCP Science). Digestion program was the following: 10 min to heat up to 100°C and keep at 100°C for 60 min. After the digestion samples were further diluted 300 times with 2% HNO3 solution and their Tb & Dy content was analyzed by ICP-MS using KED mode with He as a collision gas on NexIon 350 D ICP-MS instrument (PerkinElmer). Hf was added as an internal standard at concentration of 2 ppb to all the solution and absolute quantitation was performed using external calibration curve with standards in 0.05-50 ppb range. All measurements were performed in triplicates.

X-ray crystallography data for the analyzed crystal structures were selected and mounted on various Rigaku diffractometers (XtaLAB Synergy R, DW system, HyPix-Arc 150 detector or SuperNova, Dual, Cu at home/near, AtlasS type detectors). The crystals were kept at a steady T = 140.00(10) K during data collection. Data were measured using ω scans with Cu K_α radiation. The diffraction patterns were indexed and the total number of runs and images were based on the strategy calculation from the program CrysAlisPro 1.171.42.72a (Rigaku OD, 2022).[10] The unit cells were refined using CrysAlisPro 1.171.42.72a (Rigaku OD, 2022).[10] Data reduction, scaling and absorption corrections were performed using CrysAlisPro 1.171.42.72a (Rigaku OD, 2022).[10] The structures were solved with the **ShelXT** (Sheldrick, 2015)[11] solution program using dual methods and by using **Olex2** 1.5 (Dolomanov et al., 2009)[12] as the graphical interface. The models were refined with **ShelXL** 2018/3 (Sheldrick, 2015)[13] using full matrix least squares minimization on $\boldsymbol{F^2}$. All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atom were calculated geometrically and refined using the riding model. Several structures displayed problems dealing with disorder (disordered ligands or solvent) or twinning. The major employed technique was the split model combined with a series of restraints and constraints. The restraints and constraints are used in order to get acceptable bond lengths and angles and/or anisotropic behavior. In some cases, the twinning treatment has been used for real twins or for multi-crystals, in order to properly separate the different domains. Finally, in some structures the solvent molecules were difficult to handle and the mask algorithm (by Olex2) was used to squeeze them completely from the final model.

CCDC numbers are 2296828 (complex **1-Tb^{OtBu}**), 2296833 (complex **1-Ce^{Ph}**), 2296827 (complex **1-Tb^{Ph}**), 2296886 (complex **1-Pr^{Ph}**), 2296835 (complex **2-Ce^{OtBu}**), 2296831 (complex **2-Tb^{OtBu}**), 2296830 (complex **2-Tb^{Ph}**), 2296887 (complex **2-Pr^{Ph}**), 2291801 (complex **3-Ce^{OtBu}**), 2296834 (complex **3-Ce^{Ph}**), 2296832 (complex **3-Tb^{Ph}**), 2296829 (MeCN adduct of **1-Pr^{Ph}**) and 2330604 (complex **2-Tb^{Ph}-MeCN·(Et$_2$O)**).

S2. Synthesis

S2.1. Synthesis and reactivity of cerium complexes

Synthesis of [Ce^{III}((OSiPh_2Ar)$_3$-arene)(THF)$_3$] (1-Ce^{Ph}): A cold (-40 °C) yellow solution of [Ce(N($SiMe_3$)$_2$)$_3$] (147.0 mg, 0.2366 mmol, 1.0 equiv.) in THF (1.0 mL) was added to a cold (-40 °C) stirring colorless solution of free ligand (HOSiPh_2Ar)$_3$-arene (213.3 mg, 0.2367 mmol, 1.0 equiv.) in THF (3.0 mL). The reaction mixture was then warmed to room temperature and stirred for 16 h, yielding a colorless solution. The resulting solution was stored at -40 °C overnight affording white powder of complex **1-Ce^{Ph}** (243.9 mg, 82%). H NMR (400 MHz, THF-d_8, 298 K): δ 12.54 ppm (br s, 12H, -OSiPh_2), δ 9.22 ppm (d, *J* = 7.5 Hz, 3H, tripodal arene), δ 8.73 ppm (br s, 12H, -OSiPh_2), δ 8.15 ppm (br s, 6H, -OSiPh_2), δ 7.27 ppm (t, *J* = 7.2 Hz, 3H, tripodal arene), δ 6.08 ppm (t, *J* = 7.3 Hz, 3H, tripodal arene), δ 2.86 ppm (d, *J* = 7.3 Hz, 3H, tripodal arene), δ -2.12 ppm (s, 3H, tripodal arene)(**Figure S2)**. *Anal. Calcd.* for **1-Ce^{Ph}**·(THF)$_{1.5}$, $C_{78}H_{81}O_{7.5}Si_3Ce$: C: 68.74; H: 5.99; N: 0.00. *Found*: C: 68.17; H: 5.62; N: 0.00. The fractional THF content is residual solvent from the bulk synthesis. X-ray quality crystals of **1-Ce^{Ph}·2toluene** could be isolated from concentrated toluene solution at room temperature.

Synthesis of [K(THF)$_6$][Ce^{III}((OSi(O^{t}Bu)$_2$Ar)$_3$-arene)(OSiPh_3)](2-Ce^{OtBu}): A colorless solution of KOSiPh_3 (15.3 mg, 0.0486 mmol, 1.0 equiv.) in THF (1.0 mL) was added to a light-yellow solution of complex [Ce((OSi(O^{t}Bu)$_2$Ar)$_3$-arene)(THF)](**1-Ce^{OtBu}**) (52.9 mg, 0.0487 mmol, 1.0 equiv.) in THF (2.0 mL). The reaction mixture was stirred for 30 mins at room temperature. The solution was concentrated under vacuum and the resulting solution was stored at -40 °C overnight affording pale yellow powder of complex **2-Ce^{OtBu}** (55.6 mg, 86%). X-ray quality crystals of **2-Ce^{OtBu}** could be isolated from concentrated THF solution at room temperature. ^{1}H NMR (400 MHz, THF-d_8, 298 K): δ 8.86 ppm (s, 3H, tripodal arene), δ 7.24 ppm (t, *J* = 7.4 Hz, 3H, tripodal arene), δ 6.68 – 6.61 ppm (m, 6H, tripodal arene and -OSiPh_3), δ 6.52 ppm (t, *J* = 6.5 Hz, 6H, -OSiPh_3), δ 5.00 ppm (d, *J* = 7.1 Hz, 3H, tripodal arene), δ 4.45 ppm (s, 6H, -OSiPh_3), δ 3.37 ppm (s, 3H, tripodal arene), δ 2.34 ppm (s, 54H, -OSi(O^{t}Bu)$_2$)(**Figure S4**). *Anal. Calcd.* for [K(THF)$_{0.4}$][Ce^{III}((OSi(O^{t}Bu)$_2$Ar)$_3$-arene)(OSiPh_3), $C_{67.6}H_{87.2}KO_{10.4}Si_4Ce$: C: 59.80; H: 6.47; N: 0.00. *Found*: C: 59.44; H: 6.74; N: 0.00. The potassium bound THF was lost during the drying process.

Synthesis of [K(toluene){Ce^{III}((OSiPh_2Ar)$_3$-arene)(OSiPh_3)}](2-Ce^{Ph}): A colorless solution of KOSiPh_3 (13.2 mg, 0.0420 mmol, 1.0 equiv.) in THF (1.0 mL) was added to a colorless solution of complex [Ce((OSiPh_2Ar)$_3$-arene)(THF)$_3$] (**1-Ce^{Ph}**) (52.0 mg, 0.0414 mmol, 1.0 equiv.) in THF (4.0 mL). The reaction mixture was stirred for 30 mins at room temperature. The volatiles were removed under vacuum and the residue was dissolved in toluene (0.2 mL). The resulting solution was stored at -40 °C overnight affording pale yellow powder of complex **2-Ce^{Ph}** (55.1 mg, 92%). X-ray quality crystals were obtained by cooling a concentrated toluene solution to -40 °C. ^{1}H NMR (400 MHz, THF-d_8, 298 K): δ 9.65 ppm (s, 12H, -OSiPh_2), δ 8.19 ppm (d, *J* = 7.4 Hz, 3H, tripodal arene), δ δ 7.56 – 7.45 ppm (m, 18H, -OSiPh_2 and -OSiPh_3), δ 7.42 ppm (t, *J* = 7.2 Hz, 6H, -OSiPh_3), δ 7.05 – 6.98 ppm (m, 6H, tripodal arene), δ 6.81 ppm (s, 6H, -OSiPh_2), δ 6.49 ppm (t, *J* = 7.3 Hz, 3H, -OSiPh_3), δ 4.86 ppm (d, *J* = 7.5 Hz, 3H, tripodal arene), δ 3.49 ppm (s, 3H, tripodal arene)(**Figure S6**). *Anal. Calcd.* for [K{Ce^{III}((OSiPh_2Ar)$_3$-arene)(OSiPh_3)}], $C_{78}H_{60}KO_4Si_4Ce$: C: 69.25; H: 4.47; N: 0.00. *Found*: C: 68.87; H: 4.78; N: 0.00. The potassium bound toluene was lost during the drying process.

Reaction of complex 2-Ce^{Ph} with 1.1 equiv. of 2.2.2-cryptand in THF: A 2.2.2-cryptand (1.9 mg, 0.0050 mmol, 1.1 equiv.) solution in THF-d_8 (0.1 mL) was added to a light-yellow solution of **2-Ce^{Ph}** (6.7 mg, 0.0046 mmol, 1.0 equiv.) in THF-d_8 (0.4 mL). The ^{1}H NMR spectrum of the resulting solution showed the appearance of a new set of resonances, indicating the K^+ ion was bound in the **2-Ce^{Ph}** in THF solution (**Figure S7)**.

Synthesis [Ce^{IV}((OSi(O^{t}Bu)$_2$Ar)$_3$-arene)(OSiPh_3)](3-Ce^{OtBu}): A white suspension of $AgBPh_4$ (23.0 mg, 0.0539 mmol, 1.1 equiv.) in THF (1.0 mL) was added to a light-yellow solution of complex **2-Ce^{OtBu}** (64.7 mg, 0.0489 mmol, 1.0 equiv.) in THF (2.0 mL). The reaction mixture was stirred at room temperature for 2 h, resulting in a gray suspension. The suspension was filtered on a porosity 4 glass frit and the volatiles of the yellow filtrate were removed under vacuum. The pale-yellow residue was dried under vacuum for 30 minutes, dissolved in toluene (1.0 mL) and filtered. The resulting solution was stored at -40 °C overnight affording yellow powder of complex **3-Ce^{OtBu}** (50.9 mg, 81%) that was thoroughly dried under vacuum to remove co-crystallized toluene. X-ray quality crystals were obtained by cooling a concentrated toluene solution to -40 °C. ^{1}H NMR (500 MHz, THF-d_8, 298 K): δ 8.40 ppm (d, *J* = 1.5 Hz, 3H, tripodal arene), δ 7.88 ppm (d, *J* = 7.9 Hz, 3H, tripodal arene), δ 7.60 ppm (d, *J* = 7.5 Hz, 6H, -OSiPh_3), δ 7.39 – 7.36 ppm (m, 6H, tripodal arene

and -OSiPh$_3$), δ 7.32 ppm – 7.28 ppm (m, 6H, tripodal arene), δ 7.22 ppm (t, J = 7.6 Hz, 6H, -OSiPh$_3$), δ 1.12 ppm (s, 54H, -OSi(O^{t}Bu)$_2$))(**Figure S9**). ^{13}C{^{1}H} NMR (126 MHz, THF-d_8, 298 K): δ 147.40 ppm, δ 145.52 ppm, δ 138.80 ppm, δ 138.06 ppm, δ 137.26 ppm, δ 136.18 ppm, δ 130.50 ppm, δ 130.29 ppm, δ 129.73 ppm, δ 129.62 ppm, δ 127.88 ppm, δ 126.82 ppm, δ 73.51 ppm, δ 32.36 ppm (**Figure S10**). ^{29}Si{^{1}H} NMR (79.5 MHz, THF-d_8, 298 K): δ -80.62 ppm (-OSi(O^{t}Bu)$_2$ and -OSiPh$_2$)(**Figure S11**). *Anal. Calcd.* for **3-Ce^{OtBu}**, $C_{66}H_{84}O_{10}Si_4Ce$: C: 61.46; H: 6.56; N: 0.00. *Found*: C: 61.50; H: 6.77; N: 0.00.

Synthesis [Ce^{IV}((OSiPh$_2$Ar)$_3$-arene)(OSiPh$_3$)(THF)$_2$](3-Ce^{Ph}): A white suspension of AgBPh$_4$ (20.3 mg, 0.0475 mmol, 1.1 equiv.) in THF (1.0 mL) was added to a light-yellow solution of complex **2-Ce^{Ph}** (59.9 mg, 0.0414 mmol, 1.0 equiv.) in THF (2.0 mL). The reaction mixture was stirred at room temperature for 2 h, resulting in a gray suspension. The suspension was filtered on a porosity 4 glass frit and the volatiles of the yellow filtrate were removed under vacuum. The pale-yellow residue was dried under vacuum for 30 minutes, dissolved in toluene (1.5 mL) and filtered. The volatiles were removed under vacuum and the residue was dissolved in THF (0.2 mL) and Et$_2$O (2 drops). The resulting solution was stored at -40 °C overnight affording yellow powder of complex **3-Ce^{Ph}** (51.4 mg, 85%). X-ray quality crystals were obtained by cooling a concentrated THF solution to -40 °C. ^{1}H NMR (500 MHz, THF-d_8, 298 K): δ 7.80 ppm (d, J = 7.4 Hz, 12H, -OSiPh$_2$), δ 7.51 ppm (dd, J = 6.9, 2.2 Hz, 3H, tripodal arene), δ 7.25 – 7.20 ppm (m, 6H, tripodal arene and -OSiPh$_3$), δ 7.17 ppm (t, J = 7.4 Hz, 6H, -OSiPh$_2$), δ 7.11 ppm (s, 3H, tripodal arene), δ 7.06 – 7.03 ppm (m, 9H, tripodal arene and -OSiPh$_3$), δ 6.95 ppm (t, J = 7.4 Hz, 12H, -OSiPh$_2$), δ 6.84 ppm (dd, J = 6.7, 2.0 Hz, 3H, tripodal arene), δ 6.79 ppm (t, J = 7.5 Hz, 6H, -OSiPh$_3$)(**Figure S13**). ^{13}C{^{1}H} NMR (126 MHz, THF-d_8, 298 K): δ 150.72 ppm, δ 144.81 ppm, δ 141.02 ppm, δ 139.45 ppm, δ 138.66 ppm, δ 138.00 ppm, δ 135.51 ppm, δ 136.08 ppm, δ 130.53 ppm, δ 129.53 ppm, δ 129.26 ppm, δ 129.21 ppm, δ 128.82 ppm, δ 127.91 ppm, δ 127.57 ppm, δ 125.76 ppm (**Figure S14**). ^{29}Si{^{1}H} NMR (79.5 MHz, THF-d_8, 298 K): δ -24.13 ppm (-OSiPh$_2$ and -OSiPh$_3$)(**Figure S15**). *Anal. Calcd.* for **3-Ce^{Ph}**·(THF)$_{2.5}$, $C_{96}H_{96}O_{8.5}Si_4Ce$: C: 70.38; H: 5.91; N: 0.00. *Found*: C: 69.91; H: 5.45; N: 0.00. The fractional THF content is residual co-crystallized solvent left from partial drying.

S2.2. Synthesis and reactivity of terbium complexes

Synthesis of [Tb^{III}((OSi(O^{t}Bu)$_2$Ar)$_3$-arene)(THF)] (1-Tb^{OtBu}): Following the procedure used for the synthesis of **1-Ce^{OtBu}**,[7] a cold (-40 °C) colorless solution of [Tb(N(SiMe$_3$)$_2$)$_3$] (53.4 mg, 0.0834 mmol, 1.0 equiv.) in THF (2 mL) was added to a cold (-40 °C) stirring colorless solution of the (HOSi(O^{t}Bu)$_2$Ar)$_3$-arene) ligand (73.2 mg, 0,0834 mmol, 1.0 equiv.) in THF (0.5 mL) and then warmed to room temperature to stir for 16 h, yielding a colorless solution. The volatiles were then removed under vacuum and the residue was dissolved in toluene (0.3 mL). The resulting solution was stored at -40 °C overnight affording colorless crystals of complex **1-Tb^{OtBu}** (61.1 mg, 66%). X-ray quality crystals of **1-Tb^{OtBu}** were obtained by cooling a concentrated toluene solution to -40 °C. ^{1}H NMR (400 MHz, THF-d$_8$, 298 K): δ 65.47 ppm (s, 3H, tripodal arene), δ 63.00 ppm (br s, 54H, -OSi(O^{t}Bu)$_2$), δ 20.73 ppm (s, 3H, tripodal arene), δ -8.67 ppm (s, 3H, tripodal arene), δ -95.92 ppm (s, 3H, tripodal arene), δ -181.83 ppm (br s, 3H, tripodal arene) (**Figure S17**). *Anal. Calcd.* for **1-Tb^{OtBu}**·(toluene)$_{0.7}$, $C_{56.9}H_{82.6}O_{10}Si_3Tb$: C: 58.16; H: 7.10; N: 0.00. *Found*: C: 58.41; H: 7.13; N: 0.00. The fractional toluene content is residual solvent from the bulk synthesis.

Synthesis of [Tb^{III}((OSiPh$_2$Ar)$_3$-arene)(THF)$_3$] (1-Tb^{Ph}): Following the procedure used for the synthesis of **1-Ce^{Ph}**, addition of [Tb(N(SiMe$_3$)$_2$)$_3$] (142.8 mg, 0.223 mmol, 1.0 equiv.) in THF (2.0 mL) to the (HOSiPh$_2$Ar)$_3$-arene ligand (201.1 mg, 0.223 mmol, 1.0 equiv.) in THF (2.0 mL) afforded analytically pure **1-Tb^{Ph}** as a white powder (232.8 mg, 82%). X-ray quality crystals of **1-Tb^{Ph}** were obtained by cooling a concentrated toluene solution at room temperature. ^{1}H NMR (400 MHz, THF-d$_8$, 298 K): δ 122.79 ppm (s, 6H, -OSiPh$_2$), δ 97.58 ppm (br s, 6H, -OSiPh$_2$), δ 47.08 ppm (s, 6H, -OSiPh$_2$), δ 40.68 ppm (s, 3H), δ 36.94 ppm (br s, 6H, -OSiPh$_2$), δ 32.10 ppm (s, 3H), δ 24.51 ppm (s, 3H), δ 9.03 ppm (s, 3H), -13.47 ppm (s, 3H), δ -71.14 ppm (s, 3H), δ -180.42 ppm (s, 3H) (**Figure S19**). *Anal. Calcd.* for **1-Tb^{Ph}**·(toluene)$_{1.7}$, $C_{83.9}H_{82.6}O_6Si_3Tb$: C: 70.46; H: 5.82; N: 0.00. *Found*: C: 70.28; H: 5.82; N: 0.00. The fractional toluene content is residual co-crystallized solvent.

Synthesis of [K(THF)$_6$][Tb^{III}((OSi(O^{t}Bu)$_2$Ar)$_3$-arene)(OSiPh$_3$)] (2-Tb^{OtBu}): Following the procedure used for the synthesis of **2-Ce^{OtBu}**, addition of KOSiPh$_3$ (21.7 mg, 0.069 mmol, 1.15 equiv.) in THF (1 mL) to **1-Tb^{OtBu}** (61.9 mg, 0.060 mmol, 1.0 equiv.) in THF (1.0 mL) afforded analytically pure **2-Tb^{OtBu}** as a white powder (66.5 mg, 82%). X-ray quality crystals of **2-Tb^{OtBu}** were obtained by cooling a concentrated THF solution to -40 °C. ^{1}H NMR (400 MHz, THF-d$_8$, 298

K): δ 30.37-26.77 ppm (br m, -OSi(O^{t}Bu)$_2$), δ 9.55 ppm (br s), δ -0.74 ppm (s), -1.29 ppm (br s), -2.17 ppm (s), -30.24 ppm (br s), -44.40 ppm (br s), -77.15 ppm (br, s) (**Figure S21**). *Anal. Calcd.* for [K(THF)$_{4.5}$][Tb^{III}((OSi(O^{t}Bu)$_2$Ar)$_3$-arene)(OSiPh$_3$)], $C_{84}H_{120}KO_{14.5}Si_4Tb$: C: 60.33; H: 7.23; N: 0.00. *Found*: C: 60.04; H: 7.46; N: 0.00. The potassium bound THF was lost during the drying process.

Synthesis of [K(toluene){Tb^{III}((OSiPh$_2$Ar)$_3$-arene)(OSiPh$_3$)}](2-Tb^{Ph}): Following the procedure used for the synthesis of **2-Ce^{Ph}**, the addition of KOSiPh$_3$ (54.2 mg, 0.172 mmol, 1.15 equiv.) in THF (1.0 mL) to **1-Tb^{Ph}** (191.0 mg, 0.150 mmol, 1.0 equiv.) in THF (2.0 mL) afforded analytically pure **2-Tb^{Ph}** as a white powder (138.5 mg, 67%). X-ray quality crystals of **2-Tb^{Ph}** were obtained by cooling a concentrated toluene solution to -40 °C. ^{1}H NMR (400 MHz, THF-d_8, 298 K): δ 40.77 ppm (br s), δ 26.54 ppm (br s), 17.60 ppm (s), δ 16.59 ppm (s), 13.38 ppm (s), δ 10.33 ppm (s), 6.37 ppm (s), -0.59 ppm (s), -20.46 ppm (br s), -47.24 (br s) (**Figure S23**). *Anal. Calcd.* for [K{Tb^{III}((OSiPh$_2$Ar)$_3$-arene)(OSiPh$_3$)}], $C_{78}H_{60}KO_4Si_4Tb$: C: 68.30; H: 4.41; N: 0.00. *Found*: C: 67.87; H: 4.89; N: 0.00. The potassium bound toluene was lost during the drying process.
Better quality crystals for X-ray diffraction analysis were also obtained by gas phase diffusion of Et$_2$O on a concentrated MeCN solution of [K(MeCN){Tb^{III}((OSiPh$_2$Ar)$_3$-arene)(OSiPh$_3$)(MeCN)}]$_2$, **2-Tb^{Ph}-MeCN** at -40 °C (**Figure S54**).

Reaction of complex 2-Tb^{Ph} with 1.1 equiv. of 2.2.2-cryptand in MeCN: A 2.2.2-cryptand (3.7 mg, 0.01 mmol, 1.0 equiv.) solution in MeCN-d_3 (0.1 mL) was added to a colorless solution of **2-Tb^{Ph}** (14.6 mg, 0.01 mmol, 1.0 equiv.) in MeCN-d_3 (0.4 mL). The ^{1}H NMR spectrum of the resulting solution showed the appearance of a new set of resonances, indicating the K^+ ion was bound in the **2-Tb^{Ph}** in MeCN (**Figure S24**).

Synthesis [Tb^{IV}((OSiPh$_2$Ar)$_3$-arene)(OSiPh$_3$)(MeCN)$_2$] (3-Tb^{Ph}): A large reaction tube equipped with a magnetic stirbar was charged with **2-Tb^{Ph}** (81.9 mg, 0.056 mmol, 1.0 equiv.) and 2.2.2-cryptand (21.1 mg, 0.056 mmol, 1.0 equiv.) and dissolved in 0.2 mL of MeCN. A separate 6 mL vial was charged with [N(C$_6$H$_4$Br)][SbCl$_6$] (50.6 mg, 0.062 mmol, 1.1 equiv.) and suspended in 0.9 mL MeCN. Both vials were chilled to -40 °C. The chilled solution of [N(C$_6$H$_4$Br)][SbCl$_6$] was added to the vial containing **2-Tb^{Ph}** and 2.2.2-cryptand, where upon addition, an orange solid crashed out. After 15 minutes stirring at -40 °C, the resulting orange solid was warmed to room temperature, then filtered and collected over a porosity 4 filter-frit, in which the solid was further washed with minimal MeCN (4 mL). The orange solid was collected and dried on high vacuum for 1 hour, then dissolved in toluene, resulting in a dark orange supernatant with precipitation of colorless solids. The colorless solids were removed by filtering the solution over a 0.22 μm porosity filter frit. The volatiles were removed under vacuum yielding a dark orange micro-crystalline solid of analytically pure complex **3-Tb^{Ph}** (41.8 mg, 53% yield). **Note**: the reaction can also be performed in the absence of 2.2.2-cryptand, however, the yield of **3-Tb^{Ph}** was slightly lower (43% yield). ^{1}H NMR (400 MHz, toluene-d_8, 298 K): silent due to the 4f^7 electronic configuration of the Tb(IV) ion (**Figure S27**). UV/Vis: λ_{max} = 285 and 355 nm. *Anal. Calcd.* for **3-Tb^{Ph}**, $C_{82}H_{66}N_2O_4Si_4Tb$: C: 69.62; H: 4.70; N: 1.98. *Found*: C: 69.45; H: 4.97; N: 1.78.
Single crystals suitable for XRD analysis were obtained from a similar, dilute small-scale reaction mixture: A 6 mL vial was charged with **2-Tb^{Ph}** (14.6 mg, 0.01 mmol, 1.0 equiv.) and 2.2.2-cryptand (3.7 mg, 0.01 mmol, 1.0 equiv.) and dissolved in 0.5 mL of MeCN. A separate 6 mL vial was charged with [N(C$_6$H$_4$Br)][SbCl$_6$] (8.2 mg, 0.01 mmol, 1.0 equiv.) and dissolved in 1.0 mL MeCN. Both vials were chilled to -40 °C. The chilled solution of [N(C$_6$H$_4$Br)][SbCl$_6$] was added to the vial containing **2-Tb^{Ph}**, where upon addition, the solution turned dark orange in color. The solution was allowed to stand at -40 °C for 24 hours resulting in a mixture of dark orange and pale-yellow crystals identified as complexes, **2-Tb^{Ph}** and the MeCN solvate analogue of **1-Tb^{Ph}**, **1-Tb^{Ph}-CH$_3$CN** (**Figure S50**), respectively. Complex **2-Tb^{Ph}** was the major product from this reaction mixture; however, isolation of analytically pure material through this pathway proved unsuccessful due to inability to separate the **1-Tb^{Ph}-CH$_3$CN** complex.

Reaction of complex 1-Tb^{Ph} with 1.0 equiv. of KOSi(O^{t}Bu)$_3$ in THF: A KOSi(O^{t}Bu)$_3$ (2.4 mg, 0.0079 mmol, 1.0 equiv.) solution in THF-d_8 (0.25 mL) was added to a colorless solution of **1-Tb^{Ph}** (10.0 mg, 0.0079 mmol, 1.0 equiv.) in THF-d_8 (0.25 mL). The ^{1}H NMR spectrum of the resulting solution showed the appearance of a new set of resonances, indicating the KOSi(O^{t}Bu)$_3$ was bound to the **1-Tb^{Ph}** complex in THF (**Figure S35**).

Reaction of complex 1-Tb^{Ph} with 1.1 equiv. of KOSiMe$_3$ in THF: A KOSiMe$_3$ (2.7 mg, 0.021 mmol, 1.1 equiv.) solution in THF-d_8 (0.25 mL) was added to a colorless solution of **1-Tb^{Ph}** (24.0 mg, 0.0188 mmol, 1.0 equiv.) in THF-d_8 (0.25 mL).

The ^{1}H NMR spectrum of the resulting solution showed the appearance of a new set of resonances, indicating the $KOSiMe_3$ was bound to the **1-Tb^{Ph}** complex in THF (**Figure S36)**.

Reaction of complex 1-Tb^{Ph} with 1.1 equiv. of 2-KOAd in THF: A 2-KOAd (3.2 mg, 0.017 mmol, 1.1 equiv.) solution in THF-d_8 (0.25 mL) was added to a colorless solution of **1-Tb^{Ph}** (19.4 mg, 0.0152 mmol, 1.0 equiv.) in THF-d_8 (0.25 mL). The ^{1}H NMR spectrum of the resulting solution showed the appearance of a new set of resonances, indicating the 2-KOAd was bound to the **1-Tb^{Ph}** complex in THF (**Figure S37**).

Reaction of complex 1-Tb^{Ph} with 1.0 equiv. of K(N(SiMe$_3$)$_2$) in THF: A K(N(SiMe$_3$)$_2$) (1.8 mg, 0.009 mmol, 1.1 equiv.) solution in THF-d_8 (0.25 mL) was added to a colorless solution of **1-Tb^{Ph}** (10.4 mg, 0.0082 mmol, 1.0 equiv.) in THF-d_8 (0.25 mL). The ^{1}H NMR spectrum of the resulting solution showed the appearance of a new set of resonances, indicating the K(N(SiMe$_3$)$_2$) was bound to the **1-Tb^{Ph}** complex in THF (**Figure S38**).

Reaction of complex 1-Tb^{Ph} with 1.1 equiv. of NaO^{t}Bu in THF: A NaO^{t}Bu (1.7 mg, 0.0177 mmol, 1.7 equiv.) solution in THF-d_8 (0.25 mL) was added to a colorless solution of **1-Tb^{Ph}** (14.7 mg, 0.0115 mmol, 1.0 equiv.) in THF-d_8 (0.25 mL). The ^{1}H NMR spectrum of the resulting solution showed the appearance of a new set of resonances, indicating the NaO^{t}Bu was bound to the **1-Tb^{Ph}** complex in THF (**Figure S39**).

S2.3. Synthesis and reactivity of praseodymium complexes

Synthesis of [Pr^{III}((OSiPh$_2$Ar)$_3$-arene)(THF)$_3$] (1-Pr^{Ph}): Following the procedure used for the synthesis of **1-Ce^{Ph}**, addition of [Pr(N(SiMe$_3$)$_2$)$_3$] (39.3 mg, 0.063 mmol, 1.0 equiv.) in THF (2.0 mL) to the (HOSiPh$_2$Ar)$_3$-arene ligand (57.0 mg, 0.063 mmol, 1.0 equiv.) in THF (0.5 mL) afforded analytically pure **1-Pr^{Ph}** as a white powder (57.8 mg, 73%). X-ray quality crystals of **1-Pr^{Ph}** were obtained by cooling a concentrated toluene solution at room temperature. ^{1}H NMR (400 MHz, THF-d$_8$, 298 K): δ 18.50 ppm (br s, 6H, -OSiPh$_2$), δ 17.46 ppm (br s, 6H, -OSiPh$_2$), δ 11.12 ppm (s, 3H), δ 10.54 ppm (br s, 6H, -OSiPh$_2$), δ 9.24 ppm (br s, 6H, -OSiPh$_2$), δ 7.46 ppm (s, 3H), δ 5.02 ppm (s, 3H), δ -1.27 ppm (s, 3H), -12.10 ppm (s, 3H) (**Figure S31**). *Anal. Calcd.* for **1-Pr^{Ph}·**(toluene), $C_{79}H_{77}O_6Si_3Pr$: C: 70.41; H: 5.76; N: 0.00. *Found*: C: 70.33; H: 5.73; N: 0.00. The fractional toluene content is residual co-crystallized solvent left from partial drying.

Synthesis of [K(toluene){Pr^{III}((OSiPh$_2$Ar)$_3$-arene)(OSiPh$_3$)}]: 2-Pr^{Ph} Following the procedure used for the synthesis of **2-Ce^{Ph}**, the addition of $KOSiPh_3$ (40.3 mg, 0.128 mmol, 1.15 equiv.) in THF (1.0 mL) to **1-Pr^{Ph}** (139.4 mg, 0.111 mmol, 1.0 equiv.) in THF (2.0 mL) afforded ,after recrystallization from toluene, analytically pure **2-Pr^{Ph}** as a white powder (128.5 mg, 86%). *Anal. Calcd.* for [K{Pr^{III}((OSiPh$_2$Ar)$_3$-arene)(OSiPh$_3$)}], $C_{78}H_{60}KO_4Si_4Pr$: C: 69.21; H: 4.47; N: 0.00. *Found*: C: 69.02; H: 4.74; N: 0.00. The potassium bound toluene was lost during the drying process.

Crystals of complex **2-Pr^{Ph} ·0.5 toluene** (isostructural to **2-Tb^{Ph} ·0.5 toluene**) could be obtained from toluene but their quality was not sufficient for a publishable structural determination, but X-ray quality crystals of [K(MeCN)$_2${Pr^{III}((OSiPh$_2$Ar)$_3$-arene)(OSiPh$_3$)(MeCN}]·4MeCN, **2-Pr^{Ph}-MeCN·4MeCN** were obtained by gas phase diffusion of Et_2O on a concentrated MeCN solution of **2-Pr^{Ph}** at -40 ºC. ^{1}H NMR (400 MHz, THF-d$_8$, 298 K): δ 16.49 ppm (br s), 15.97 ppm (br s), 10.31 ppm (s), δ 9.08 ppm (s), δ 8.55 ppm (s), 8.32 ppm (s), 8.22 ppm (s), δ 5.48 ppm (s), 0.96 ppm (br s), -3.73 ppm (br s) (**Figure S33**).

Reaction of complex 2-Pr^{Ph} with 1.1 equiv. of 2.2.2-cryptand in MeCN: A 2.2.2-cryptand (3.5 mg, 0.0093 mmol, 1.1 equiv.) solution in MeCN-d_3 (0.1 mL) was added to a colorless solution of **2-Pr^{Ph}** (11.4 mg, 0.0084 mmol, 1.0 equiv.) in MeCN-d_3 (0.4 mL). The ^{1}H NMR spectrum of the resulting solution showed the appearance of a new set of resonances, indicating the K^+ ion was bound in the **2-Pr^{Ph}** in MeCN (**Figure S34**).

Reaction of complex 2-Pr^{Ph} with 1.1 equiv. of [N(C$_6$H$_4$Br)$_3$][SbCl$_6$] in MeCN: A cold (-40 ºC) solution of [N(C$_6$H$_4$Br)][SbCl$_6$] (6.7 mg, 0.0082 mmol, 1.05 equiv.) in MeCN-d_3 (0.2 mL) was added to a cold (-40 ºC) suspension of **2-Pr^{Ph}** (10.6 mg, 0.0078 mmol, 1.0 equiv.) in MeCN-d_3 (0.4 mL). The reaction mixture immediately turned dark brown-orange but that color faded to yellow in less than 2 minutes while a white solid started to precipitate and then evolved to colorless after 10 minutes -40 ºC. Colorless crystals that grew from this reaction mixture were identified as the MeCN adduct of complex **1-Pr^{Ph}** (**Figure S53**)

Reaction of complex 1-Pr^{Ph} with 1.1 equiv. of KOSiMe$_3$ in THF: A KOSiMe$_3$ (4.2 mg, 0.0327 mmol, 1.1 equiv.) solution in THF-d_8 (0.25 mL) was added to a colorless solution of **1-Pr^{Ph}** (37.7 mg, 0.030 mmol, 1.0 equiv.) in THF-d_8 (0.25 mL). The ^{1}H NMR spectrum of the resulting solution showed the appearance of a new set of resonances, indicating the KOSiMe$_3$was bound to the **1-Pr^{Ph}** complex in THF (**Figure S40**).

Reaction of complex 1-Pr^{Ph} with 1.1 equiv. of 2-KOAd in THF: A 2-KOAd (2.7 mg, 0.014 mmol, 1.1 equiv.) solution in THF-d_8 (0.25 mL) was added to a colorless solution of **1-Pr^{Ph}** (16.0 mg, 0.0127 mmol, 1.0 equiv.) in THF-d_8 (0.25 mL). The ^{1}H NMR spectrum of the resulting solution showed the appearance of a new set of resonances, indicating the 2-KOAd was bound to the **1-Pr^{Ph}** complex in THF (**Figure S41**).

S2.4. Separation experiments

Oxidation with [N(C$_6$H$_4$Br)][SbCl$_6$] of the in situ prepared 1:1 mixture of 2-Tb ^{Ph} and 2-Dy^{Ph}: Following the procedure used for the synthesis of **1-Tb^{Ph}**, a solution of [Tb(N(SiMe$_3$)$_2$)$_3$] (45.0 mg, 0.0703 mmol, 1.0 equiv.) and [Dy(N(SiMe$_3$)$_2$)$_3$] (45.2 mg, 0.0703 mmol, 1.0 equiv.) in toluene (2.0 mL) was added to a solution of the (HOSiPh$_2$Ar)$_3$-arene ligand (126.7 mg, 0.1406 mmol, 2.0 equiv.) in toluene (1.0 mL) affording the desired 1:1 mixture of **1Tb ^{Ph}** and **1-Dy^{Ph}** as a white suspension. The suspension was taken to dryness and the residue was washed with hexane to remove the HN(SiMe$_3$)$_2$ byproduct. The resulting residue was suspended in toluene (1.0 mL) and a KOSiPh$_3$ (44.3 mg, 0.141 mmol, 1.0 equiv.) solution in toluene (1.0 mL) was added to the white suspension. The resulting solution was stirred for 30 minutes at room temperature affording a pale-yellow solution. The volatiles were removed under vacuum and the resulting solid was further dried for 2 h to obtain a 1:1 mixture of **2-Tb^{Ph}** :**2-Dy^{Ph}** (**Figure S43**).

The residue was transferred to a 6 mL vial equipped with a magnetic stir-bar and 2.2.2-cryptand (52.9 mg, 0.141mmol, 1.0 equiv.) and dissolved in 0.3 mL of MeCN. [N(C$_6$H$_4$Br)][SbCl$_6$] (126.6 mg, 0.155 mmol, 1.1 equiv.) was placed in a separate 6 mL vial and suspended in 1.5 mL MeCN. Both vials were chilled at -40 °C for 5 mins. The chilled solution of [N(C$_6$H$_4$Br)][SbCl$_6$] was added to the vial containing the 1:1 mixture of **2-Tb^{Ph}** and **2-Dy^{Ph}** and 2.2.2-cryptand, where upon addition, an orange solid crashed out. After 25 minutes stirring at -40 °C, the resulting orange solid was filtered and collected over a porosity 4 filter-frit, in which the solid was further washed with minimal MeCN (2 mL). The orange solid was collected and dried on high vacuum for 30 mins, then dissolved in toluene, resulting in a dark orange supernatant and colorless solids. The colorless solids were removed by filtering the solution over a 0.22 μm porosity filter frit. After dissolution in THF the colorless solid shows mainly the presence of **1-Dy^{Ph}** .
The volatiles were removed from the dark orange supernatant under vacuum yielding a dark orange micro-crystalline solid (36.0 mg) which contains only 6% **1-Dy^{Ph}** as measured by quantitative ^{1}H NMR in THF using CH_2Cl_2 as a standard. The ^{1}H NMR (400 MHz, 298 K) in toluene-d_8 of the solid obtained is silent (**Figure S44**) due to presence of Tb(IV), **2-Tb ^{Ph}** as major species. After dissolution in THF of obtained solid decomposition of the Tb(IV) occurs to yield a mixture of **1-Tb ^{Ph}** and **1-Dy^{Ph}** .

S3. NMR Spectroscopic Data

S3.1. NMR spectra for cerium complexes

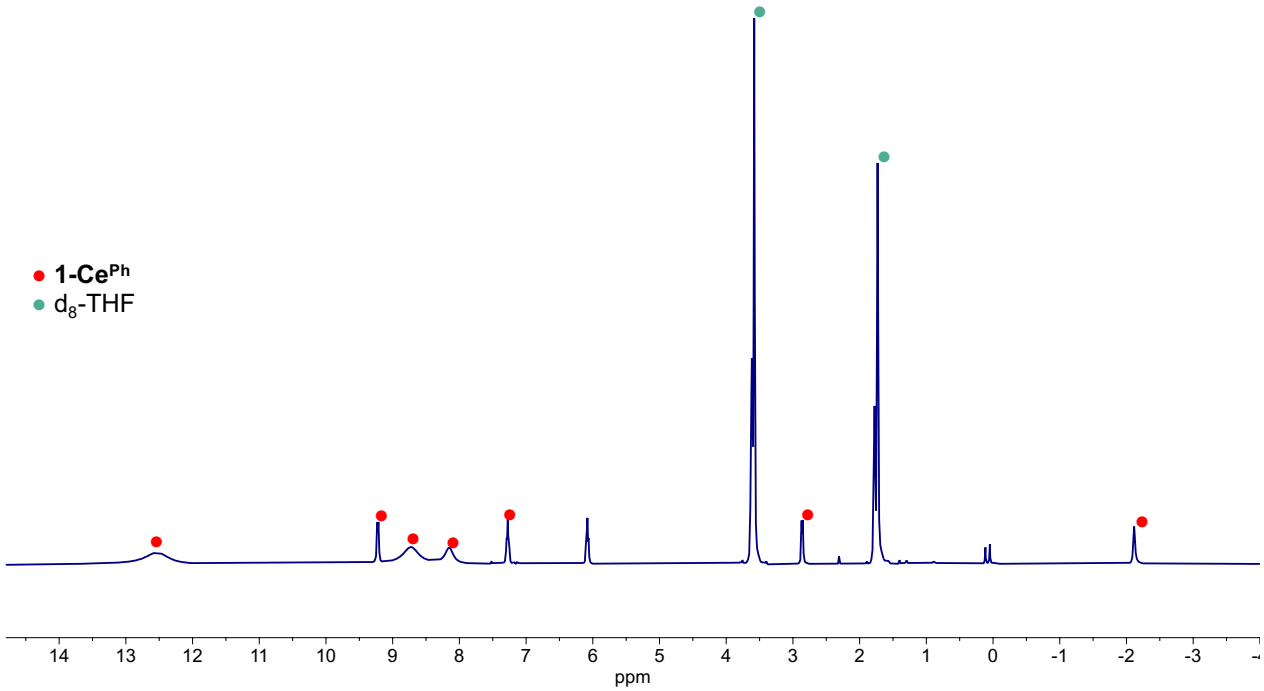


Figure S1. ^{1}H NMR spectrum (400 MHz, THF-d_8, 298 K) of the reaction mixture obtained after addition of 1.0 equiv. of [Ce(N(SiMe$_3$)$_2$)$_3$] to (HOSiPh$_2$Ar)$_3$-arene after 16 h, resulting in complex **1-Ce^{Ph}**.

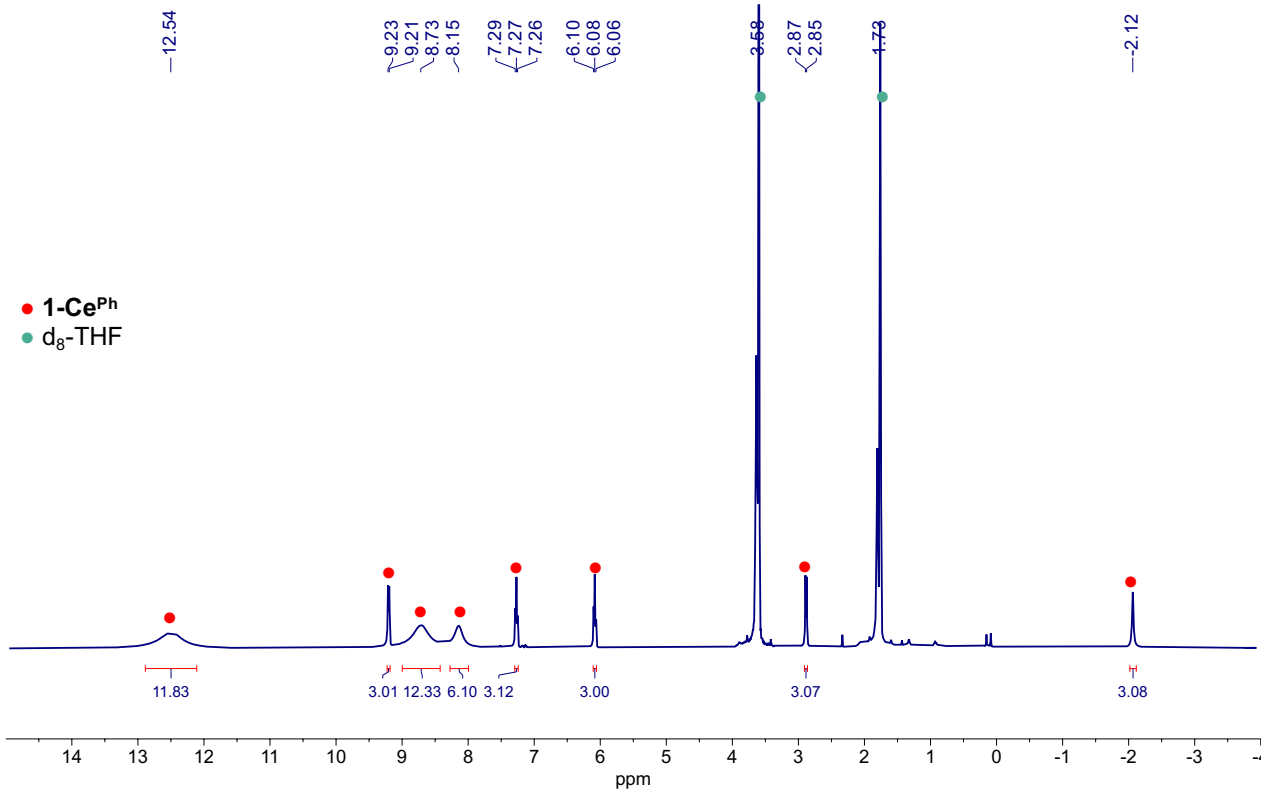


Figure S2. ^{1}H NMR spectrum (400 MHz, THF-d_8, 298 K) of isolated [Ce((OSiPh$_2$Ar)$_3$-arene)(THF)$_3$], **1-Ce^{Ph}**.

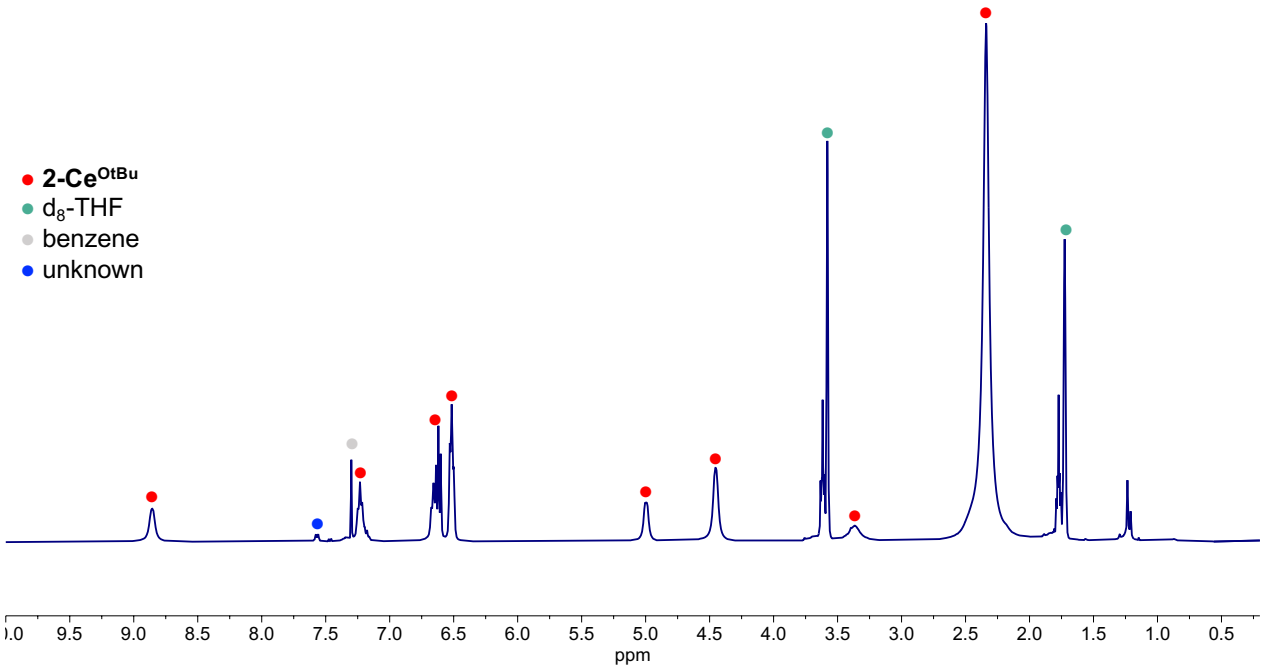


Figure S3. ^{1}H NMR spectrum (400 MHz, THF-d_8, 298 K) of the reaction mixture obtained after addition of 1.0 equiv. of $KOSiPh_3$ to [Ce((OSi(O^{t}Bu)$_2$)$_3$-arene)(THF)$_3$], **1-Ce^{OtBu}** after 30 mins, resulting in **2-Ce^{OtBu}**.

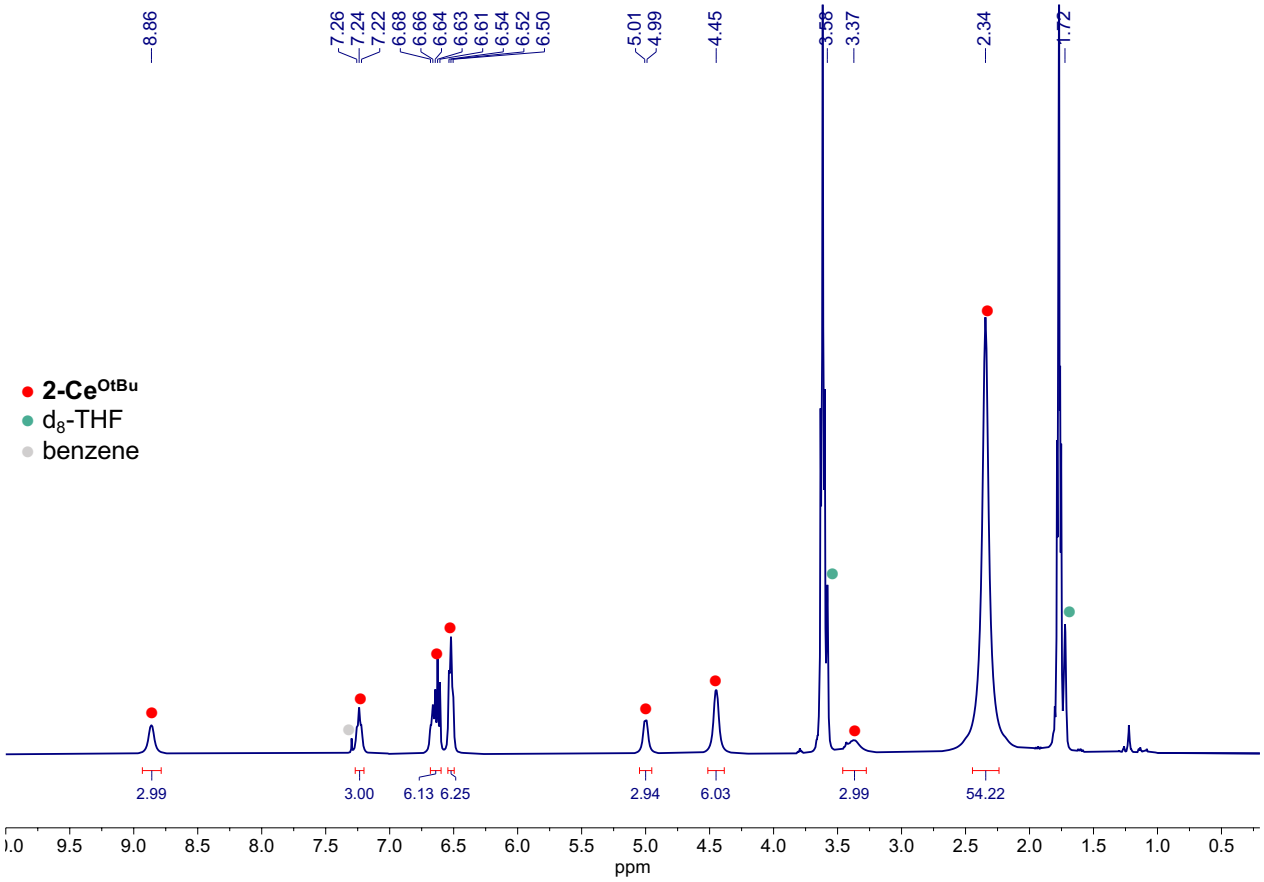


Figure S4. ^{1}H NMR spectrum (400 MHz, THF-d_8, 298 K) of isolated [Ce((OSiPh$_2$Ar)$_3$-arene)(THF)$_3$], **2-Ce^{OtBu}**.

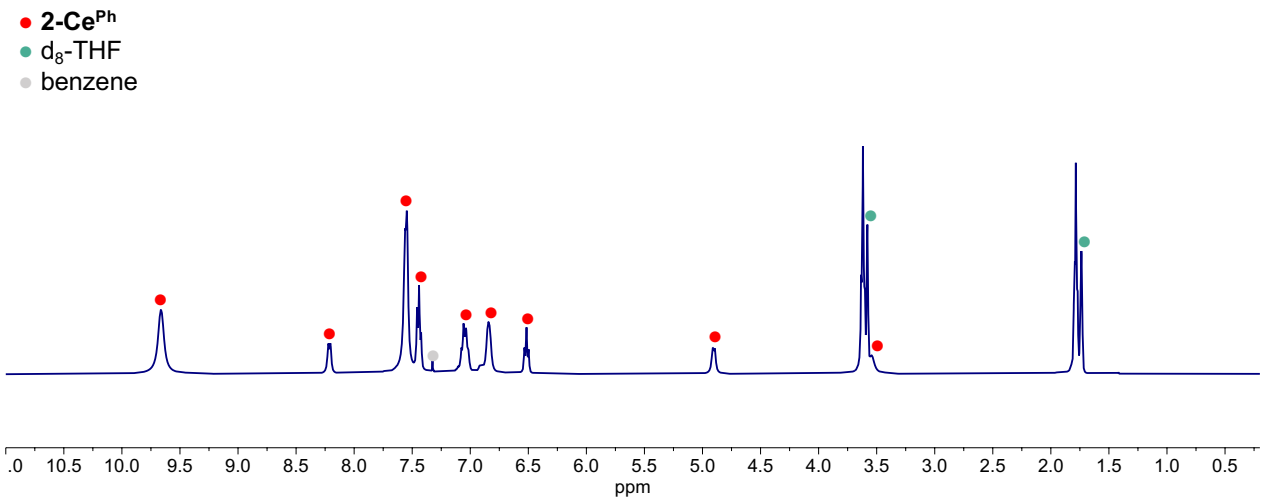


Figure S5. ^{1}H NMR spectrum (400 MHz, THF-d_8, 298 K) of the reaction mixture obtained after addition of 1.0 equiv. of $KOSiPh_3$ to [Ce((OSiPh$_2$Ar)$_3$-arene)(THF)$_3$], **1-Ce^{Ph}** after 30 mins, resulting in **2-Ce^{Ph}**.

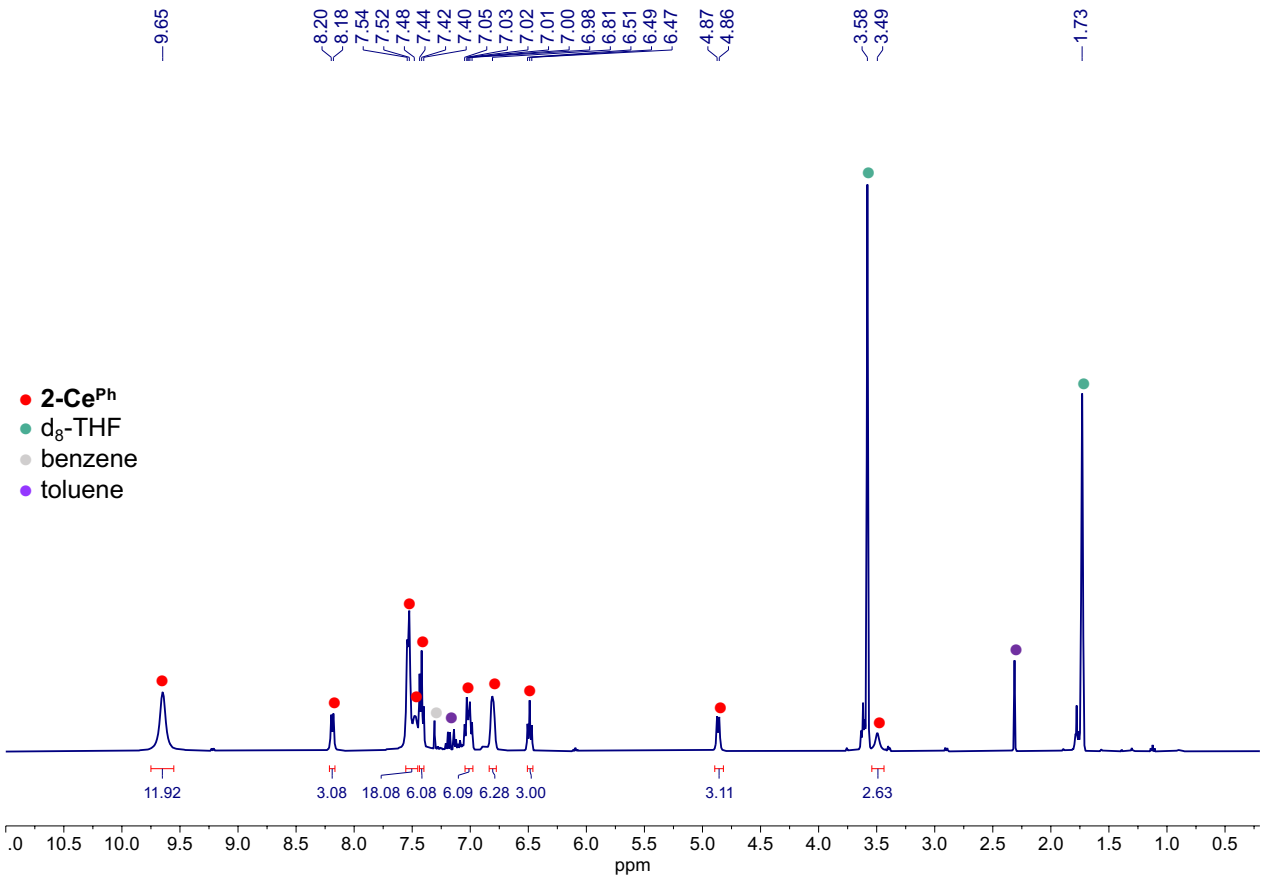


Figure S6. ^{1}H NMR spectrum (400 MHz, THF-d_8, 298 K) of isolated [K{Ce((OSiPh$_2$Ar)$_3$-arene)(OSiPh$_3$)(toluene)}], **2-Ce^{Ph}**.

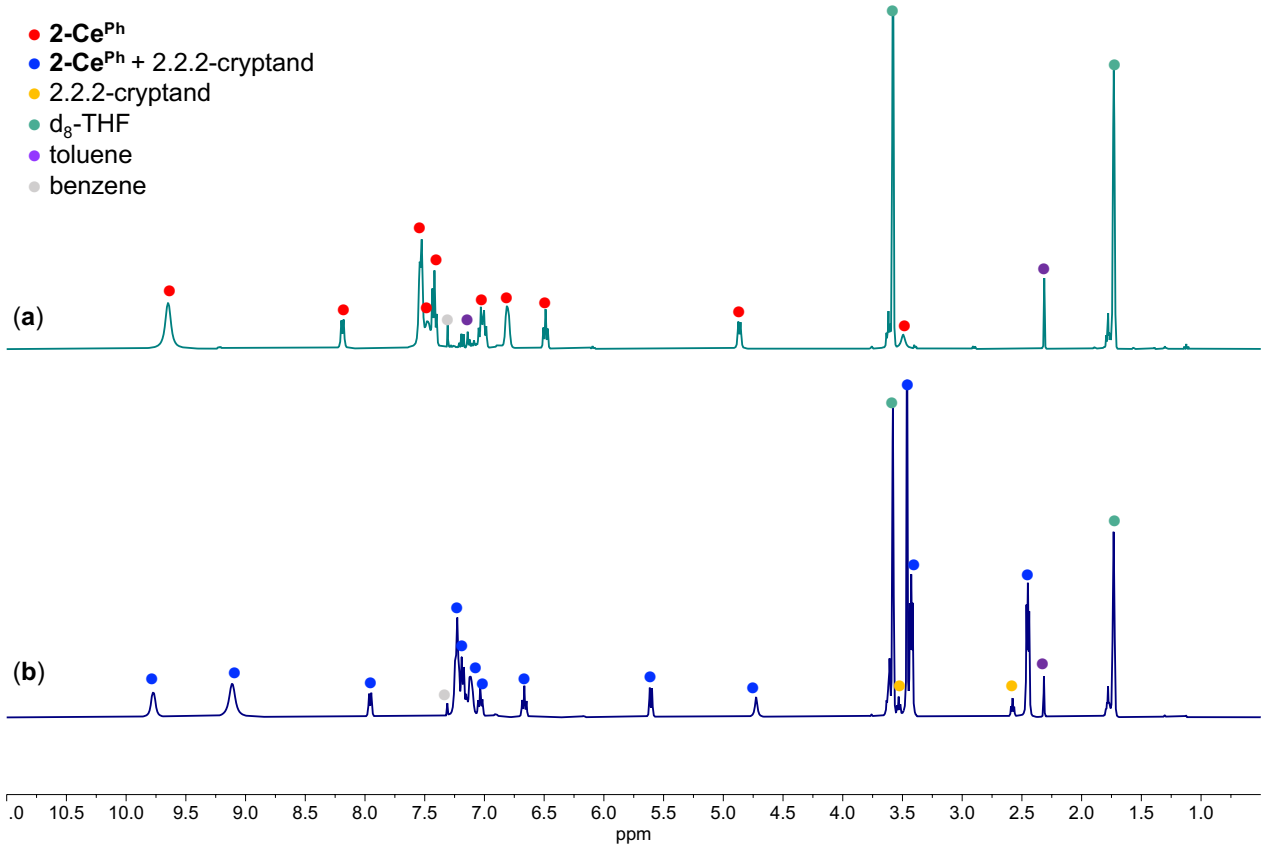


Figure S7. ^{1}H NMR spectra (400 MHz, THF-d_8, 298 K) of the reaction mixture obtained after addition of 1.1 equiv. of 2.2.2-cryptand: **2-Ce^{Ph}** before a) and immediately after b) addition of 1.1 equiv. of 2.2.2-cryptand.

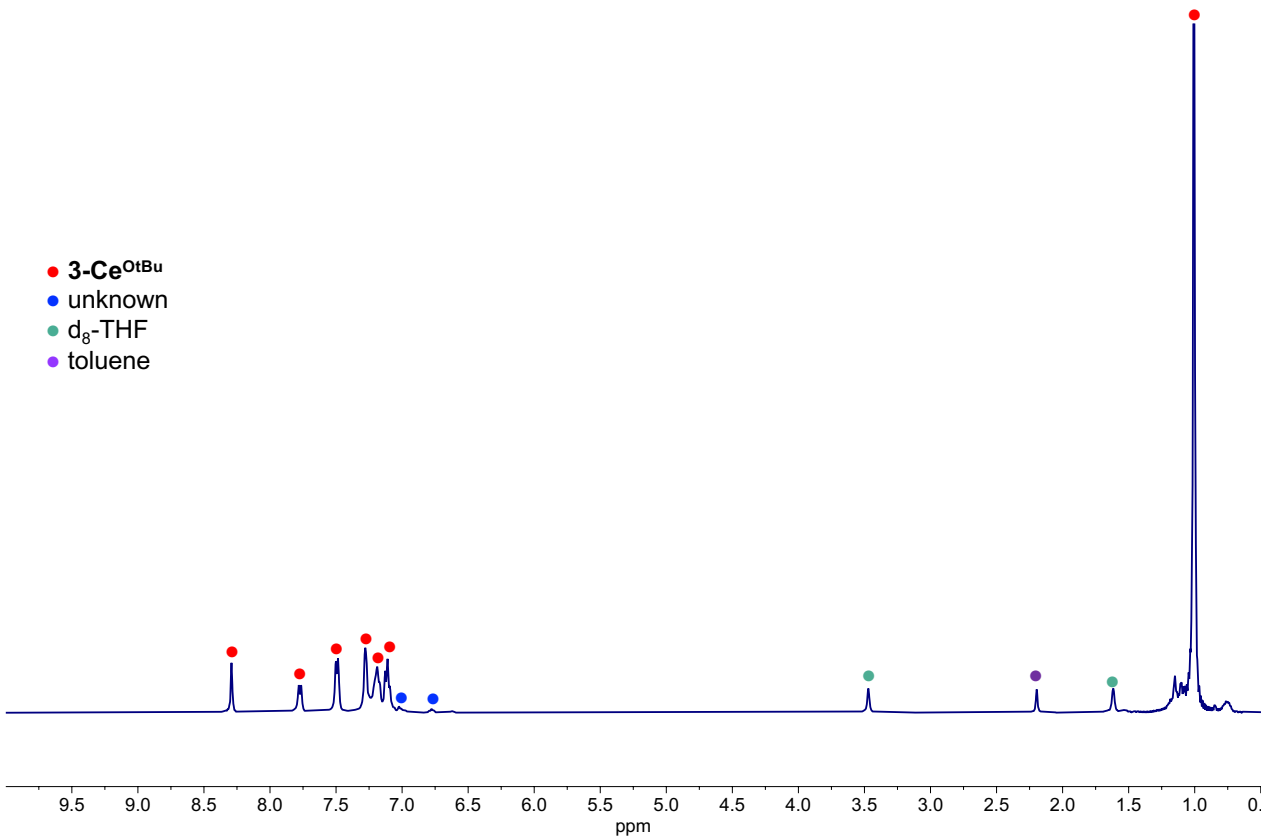


Figure S8. ^{1}H NMR spectrum (400 MHz, THF-d_8, 298 K) of the reaction mixture obtained after addition of 1.1 equiv. of $AgBPh_4$ to **2-Ce^{OtBu}** after 2 hours.

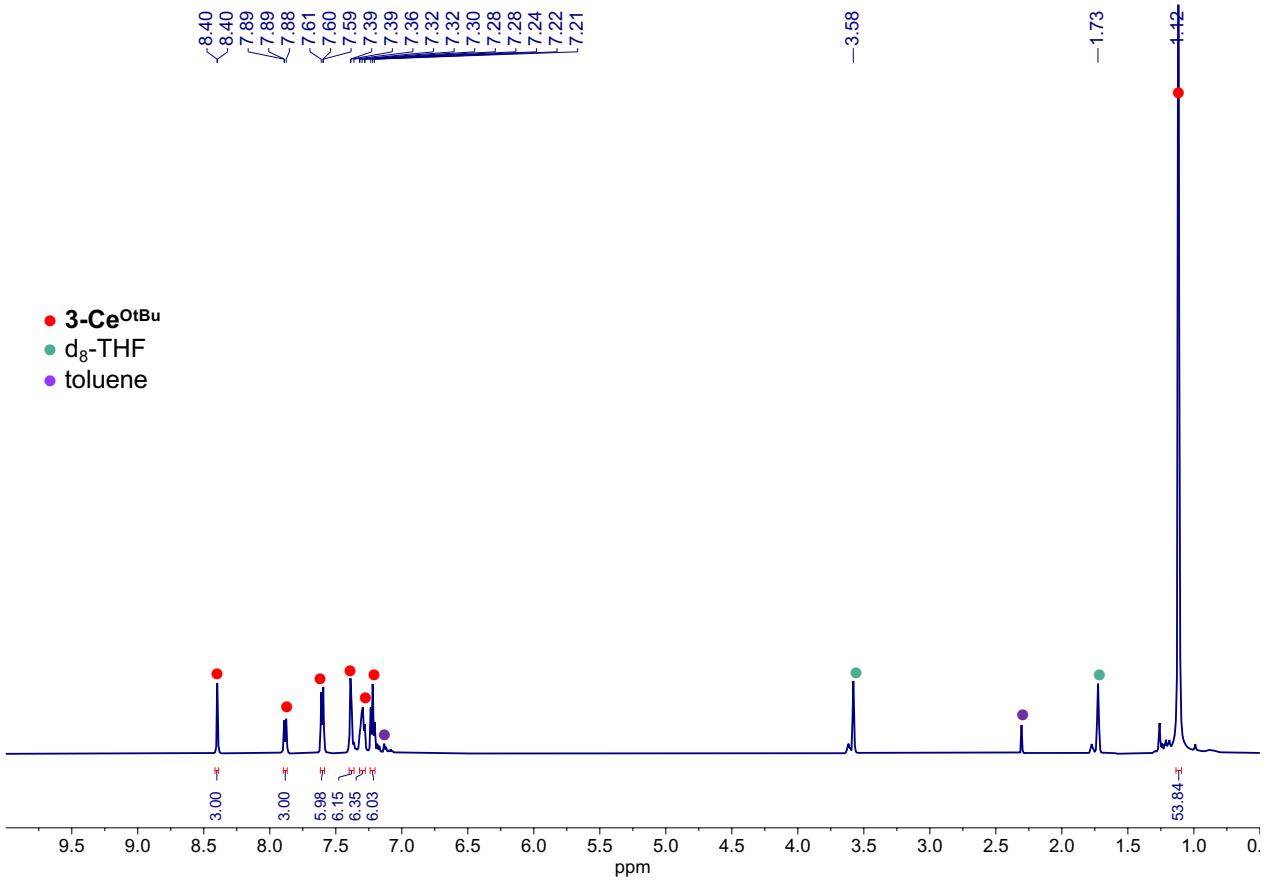


Figure S9. ^{1}H NMR spectrum (500 MHz, THF-d_8, 298 K) of isolated [Ce((OSi(O^{t}Bu)$_2$Ar)$_3$-arene)(OSiPh$_3$)], **3-Ce^{OtBu}**.

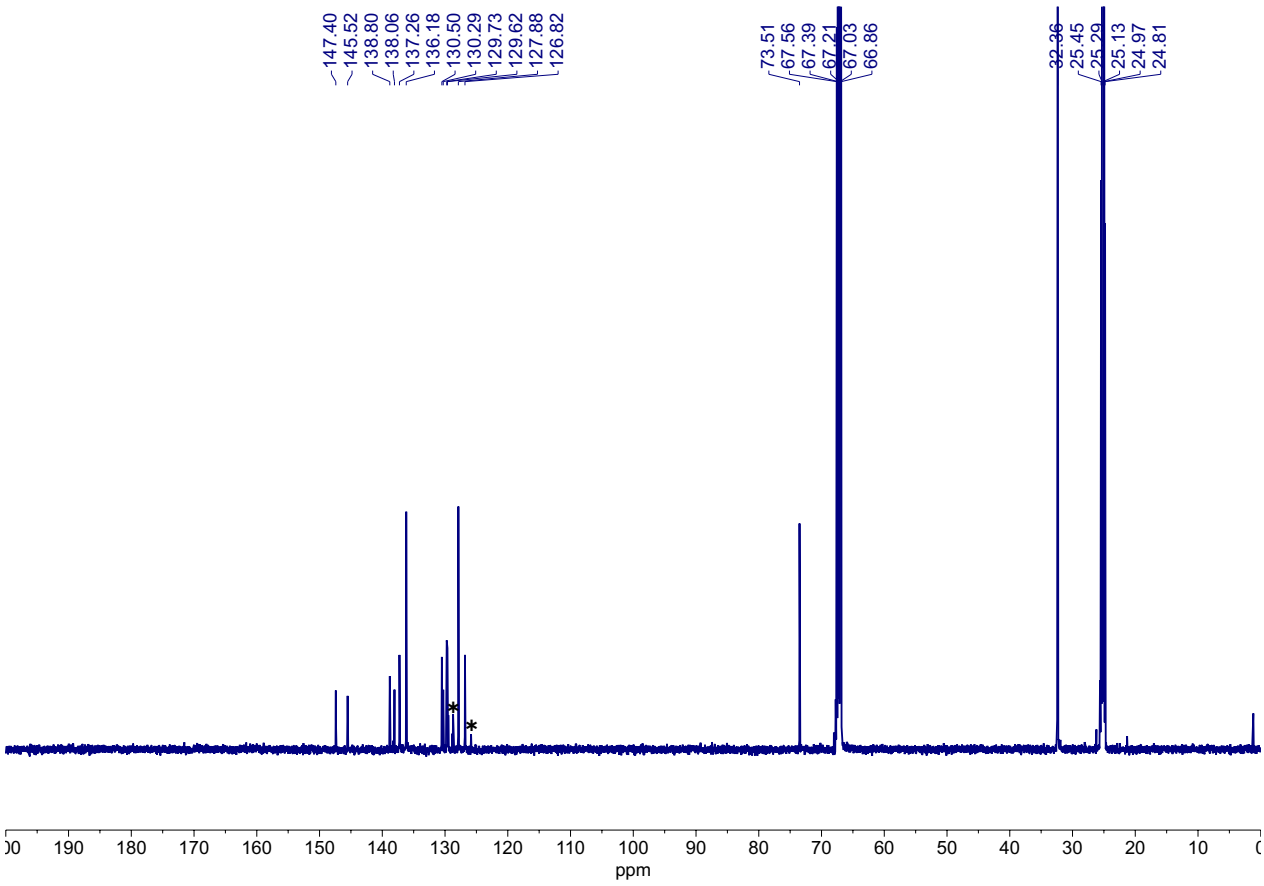


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, THF-d_8, 298 K) of isolated [Ce((OSi(O^{t}Bu)$_2$Ar)$_3$-arene)(OSiPh$_3$)], **3-Ce^{OtBu}** (✱toluene).

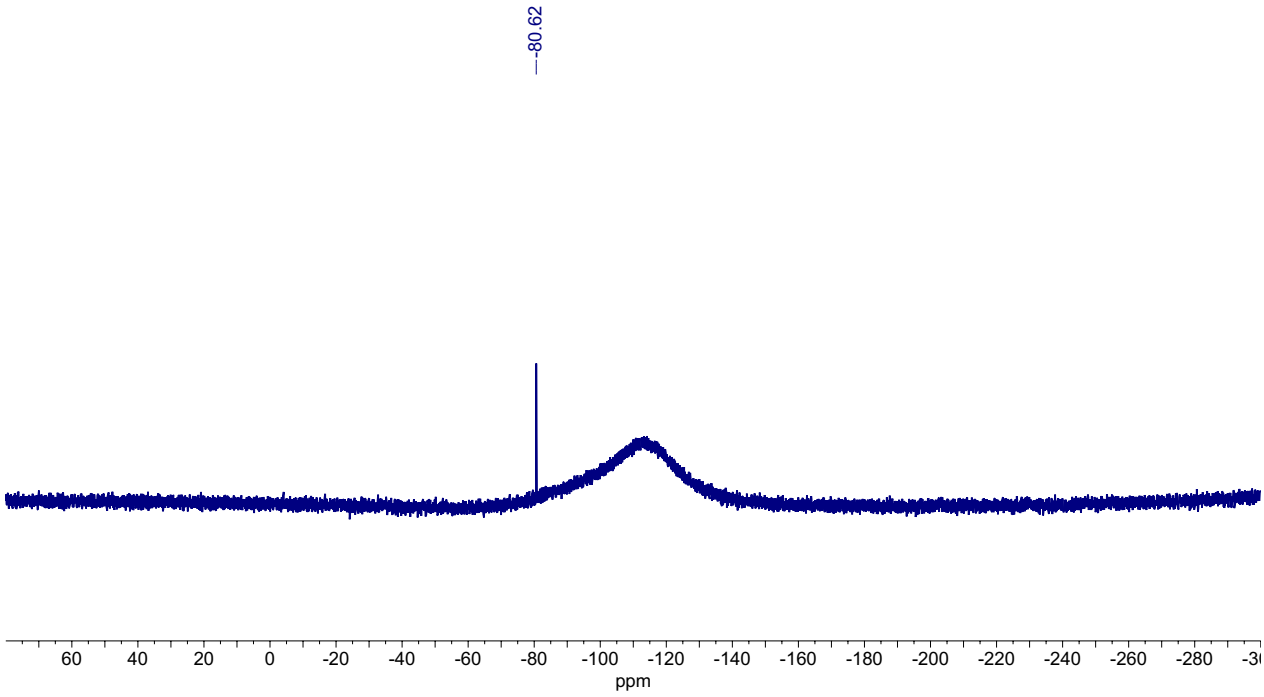


Figure S11. $^{29}Si\{^{1}H\}$ NMR spectrum (79.5 MHz, THF-d_8, 298 K) of isolated [Ce((OSi(O^{t}Bu)$_2$Ar)$_3$-arene)(OSiPh$_3$)], **3-Ce^{OtBu}**.

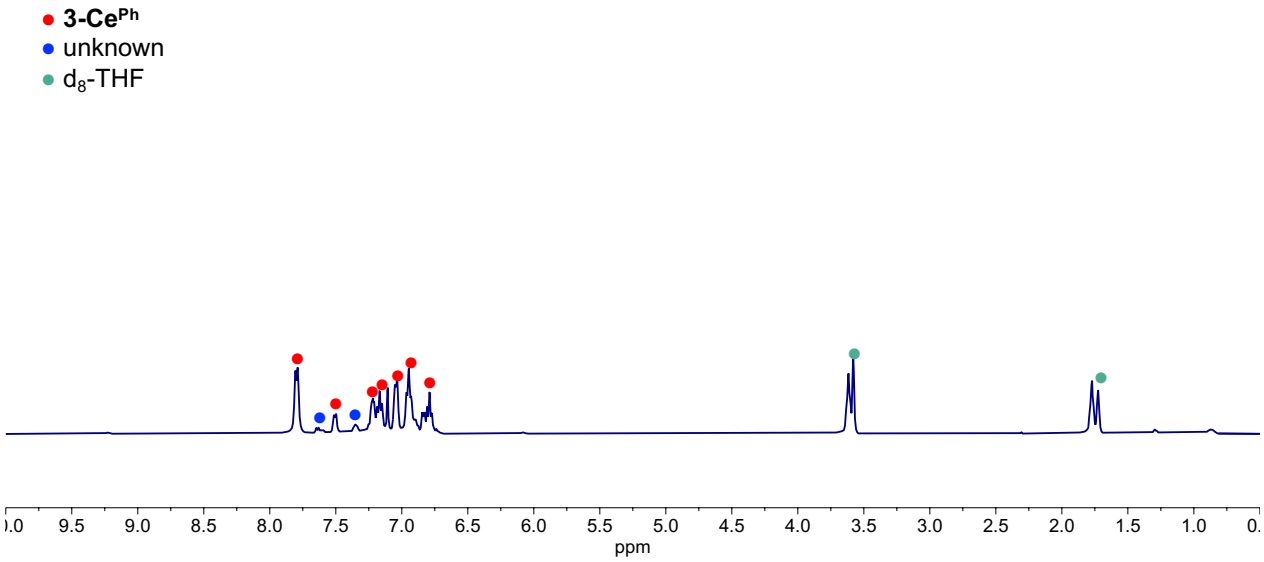


Figure S12. ^{1}H NMR spectrum (400 MHz, THF-d_8, 298 K) of the reaction mixture obtained after addition of 1.1 equiv. of $AgBPh_4$ to **2-Ce^{Ph}** after 2 hours.

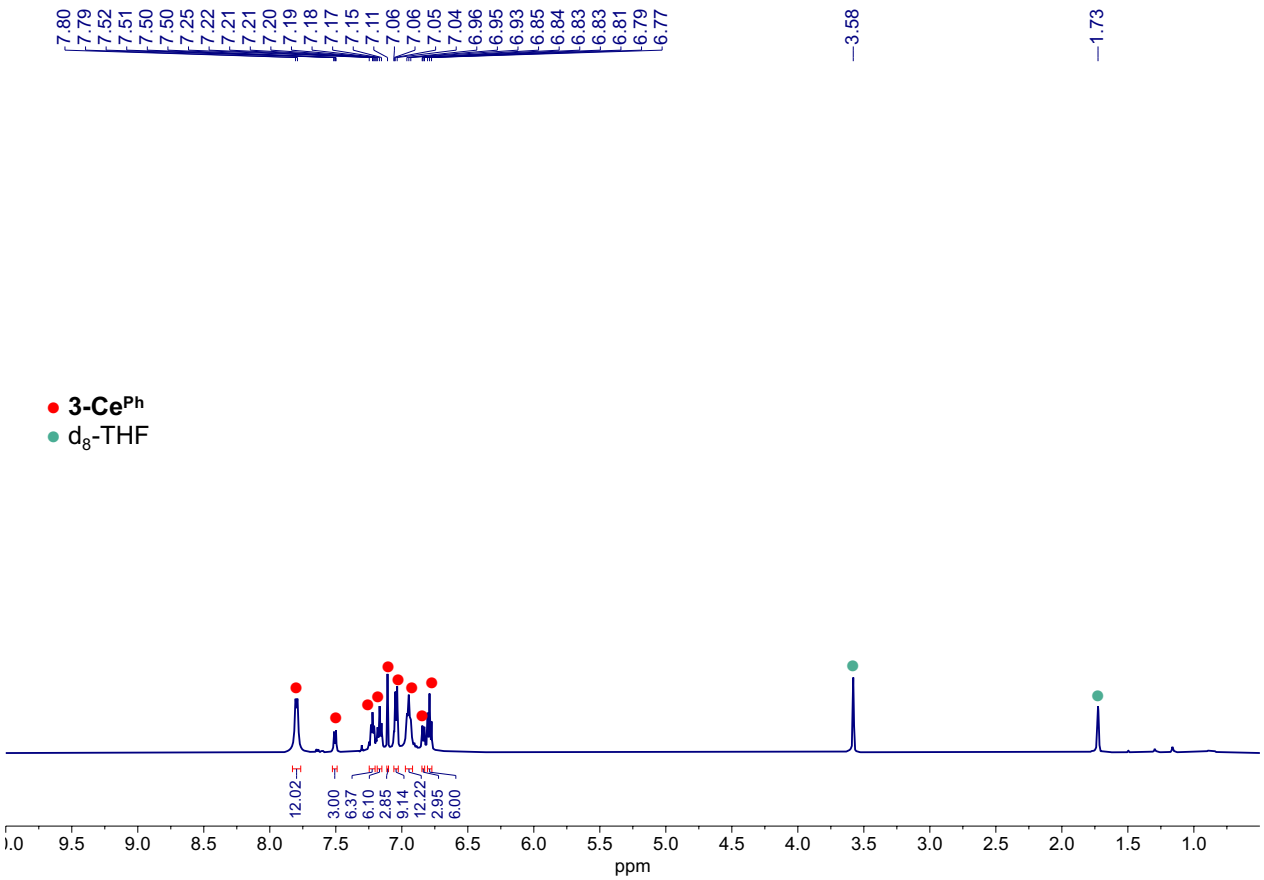


Figure S13. ^{1}H NMR spectrum (500 MHz, THF-d_8, 298 K) of isolated [Ce((OSiPh$_2$Ar)$_3$-arene)(OSiPh$_3$)(THF)$_2$], **3-Ce^{Ph}**.

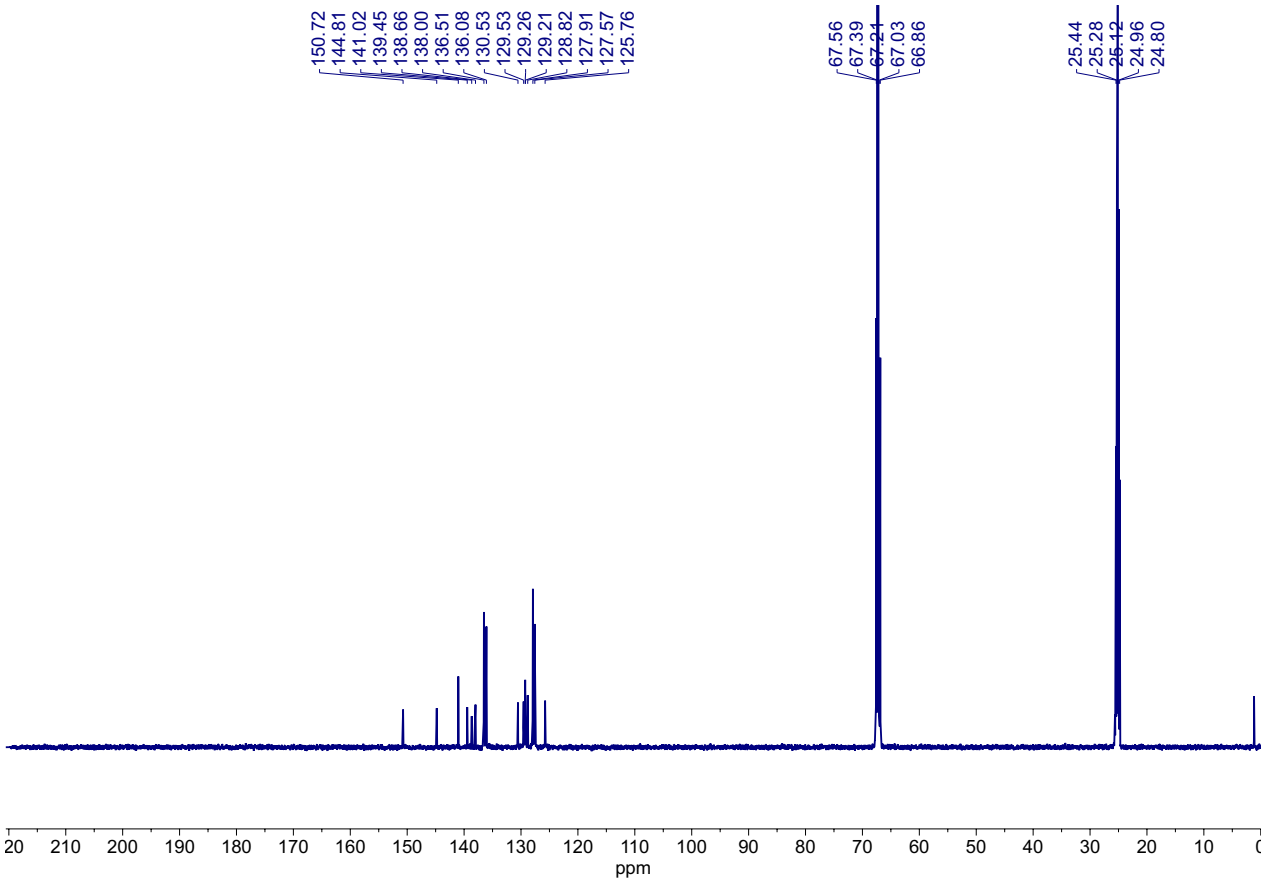


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, THF-d_8, 298 K) of isolated [Ce((OSiPh$_2$Ar)$_3$-arene)(OSiPh$_3$)(THF)$_2$], **3-Ce^{Ph}**.

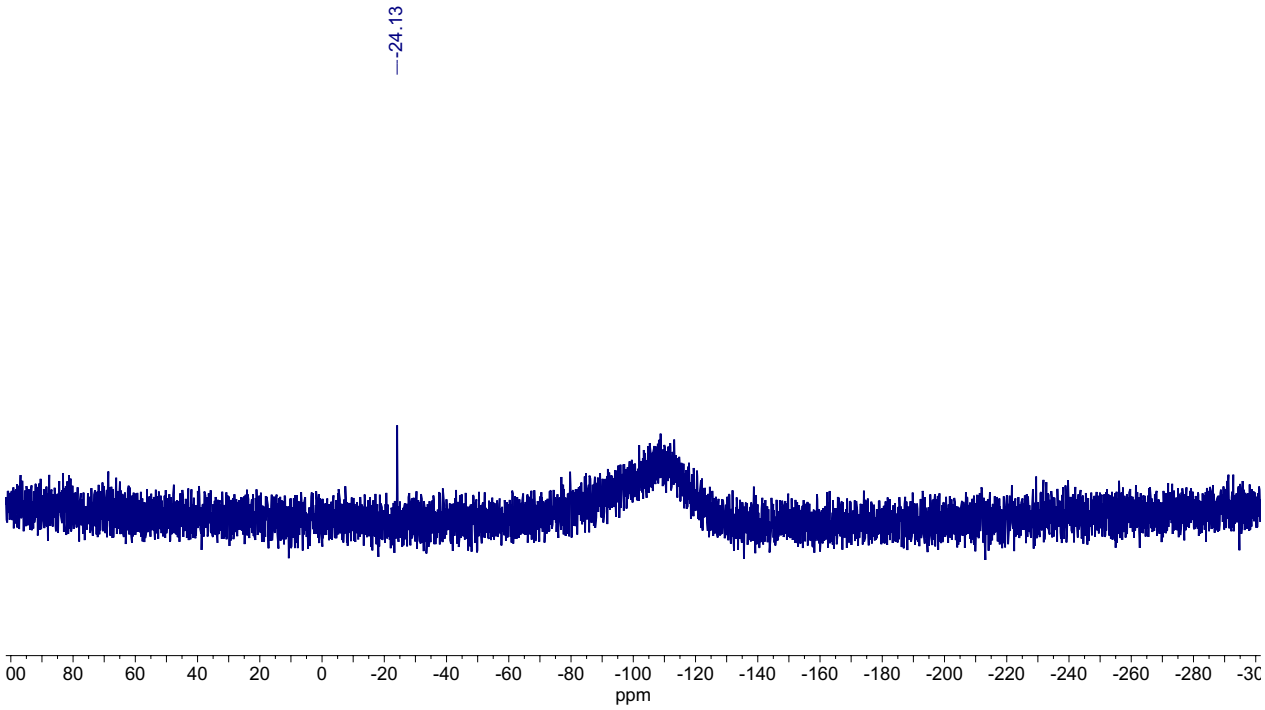


Figure S15. $^{29}Si\{^{1}H\}$ NMR spectrum (79.5 MHz, THF-d_8, 298 K) of isolated [Ce((OSiPh$_2$Ar)$_3$-arene)(OSiPh$_3$)(THF)$_2$], **3-Ce^{Ph}**.

S3.2. NMR spectra for terbium complexes

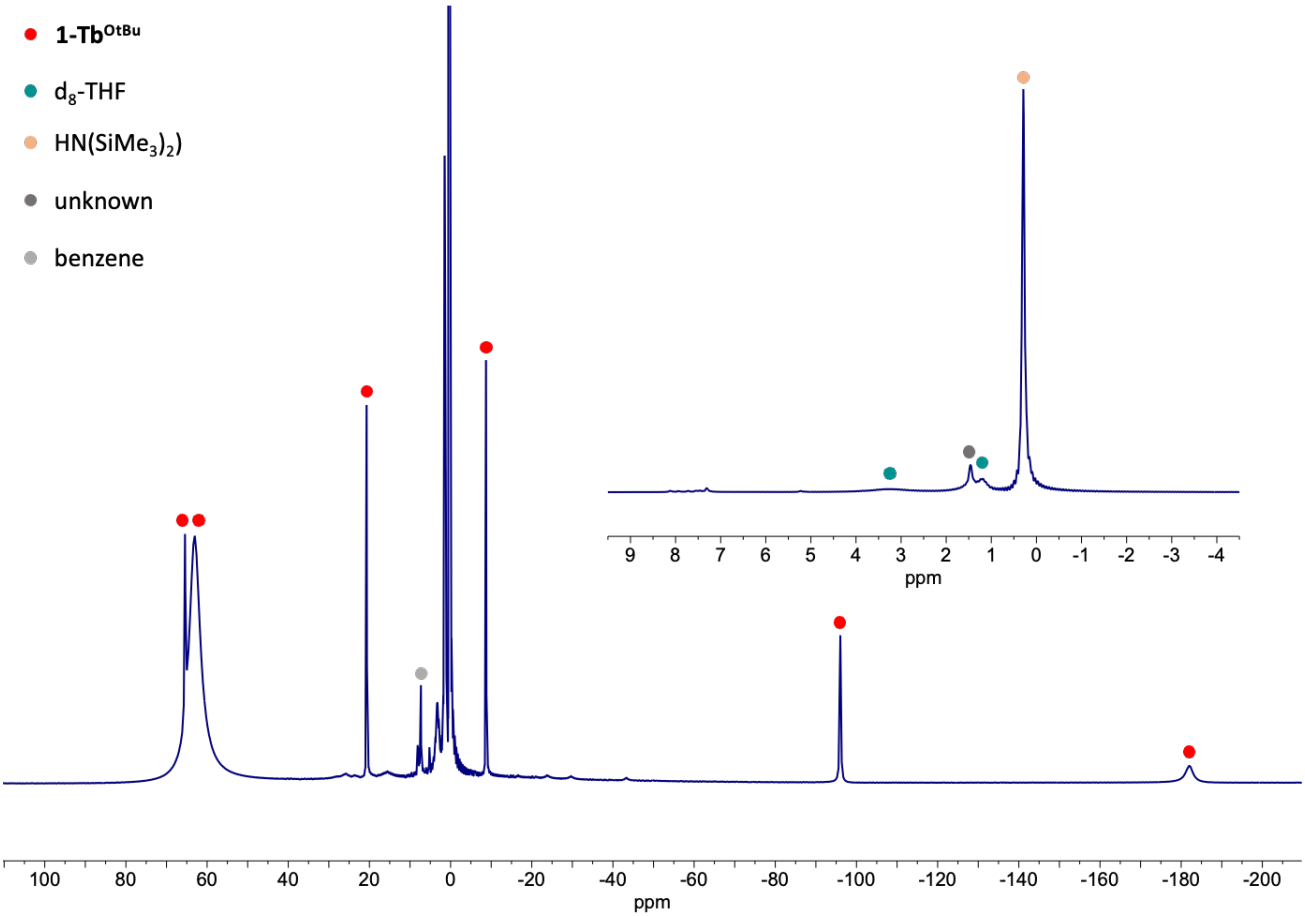


Figure S16. ^{1}H NMR spectrum (400 MHz, THF-d_8, 298 K) of the reaction mixture obtained after addition of 1.0 equiv. of [$Tb^{III}(N(SiMe_3)_2)_3$] to $(HOSi(O^tBu)_2Ar)_3$-arene after 15 minutes, resulting in complex **1-Tb^{OtBu}**.

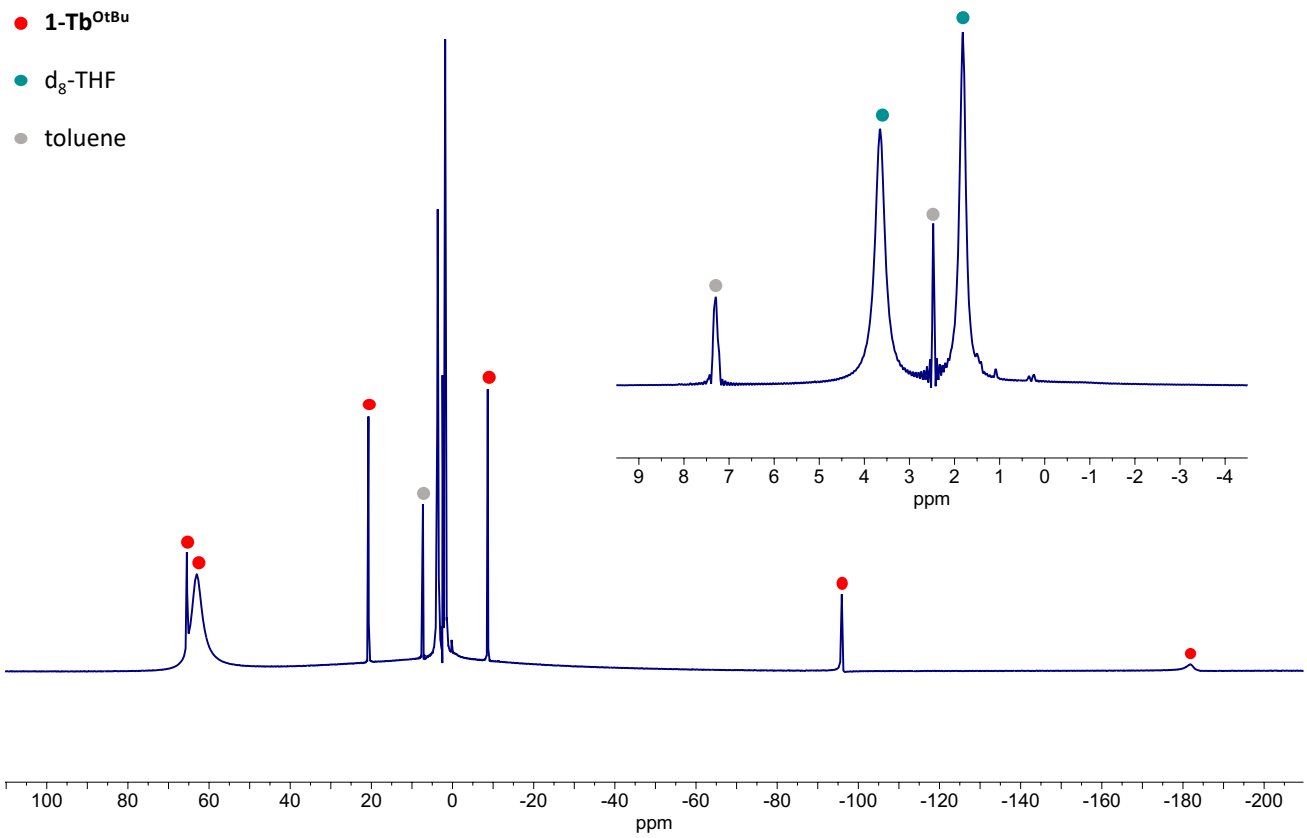


Figure S17. ^{1}H NMR spectrum (400 MHz, THF-d_8, 298 K) of isolated [Tb^{III}((OSi(O^{t}Bu)$_2$Ar)$_3$-arene)(THF)$_3$], **1-Tb^{OtBu}**.

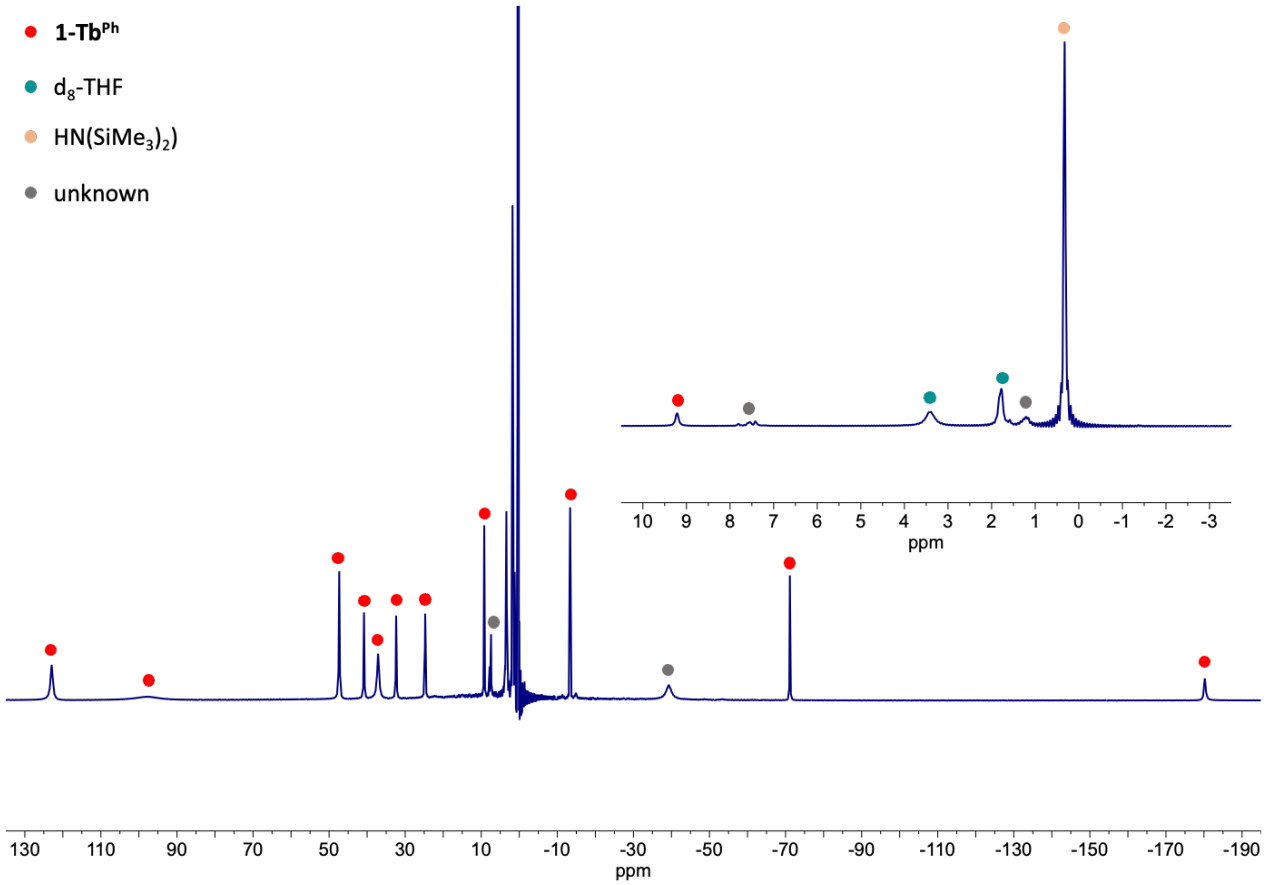


Figure S18. ^{1}H NMR spectrum (400 MHz, THF-d_8, 298 K) of the reaction mixture obtained after addition of 1.0 equiv. of [$Tb^{III}(N(SiMe_3)_2)_3$] to ($HOSiPh_2Ar)_3$-arene after 15 minutes, resulting in complex **1-Tb^{Ph}**.

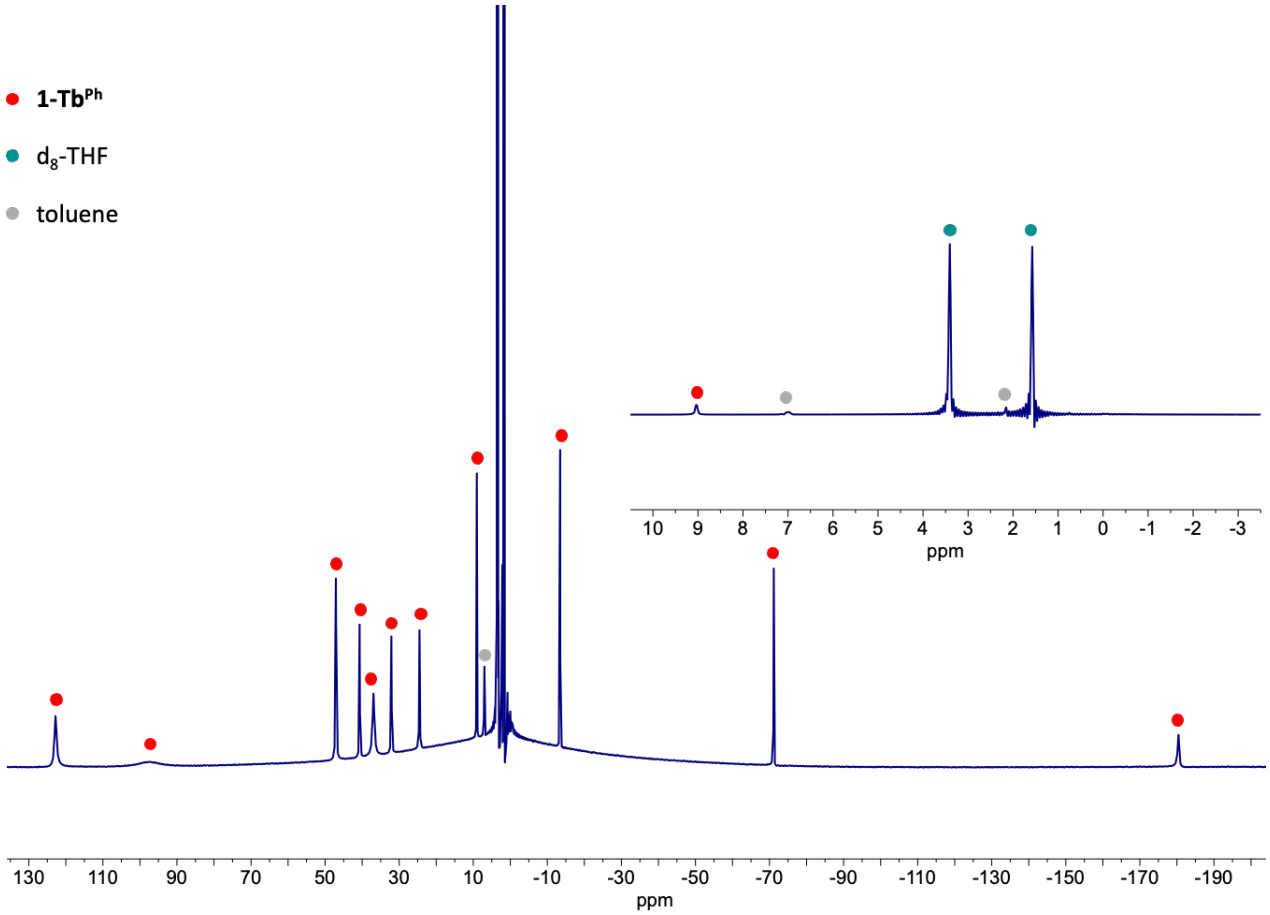


Figure S19. ^{1}H NMR spectrum (400 MHz, THF-d_8, 298 K) of isolated [Tb^{III}((OSiPh_2Ar)$_3$-arene)(THF)$_3$], **1-Tb^{Ph}**.

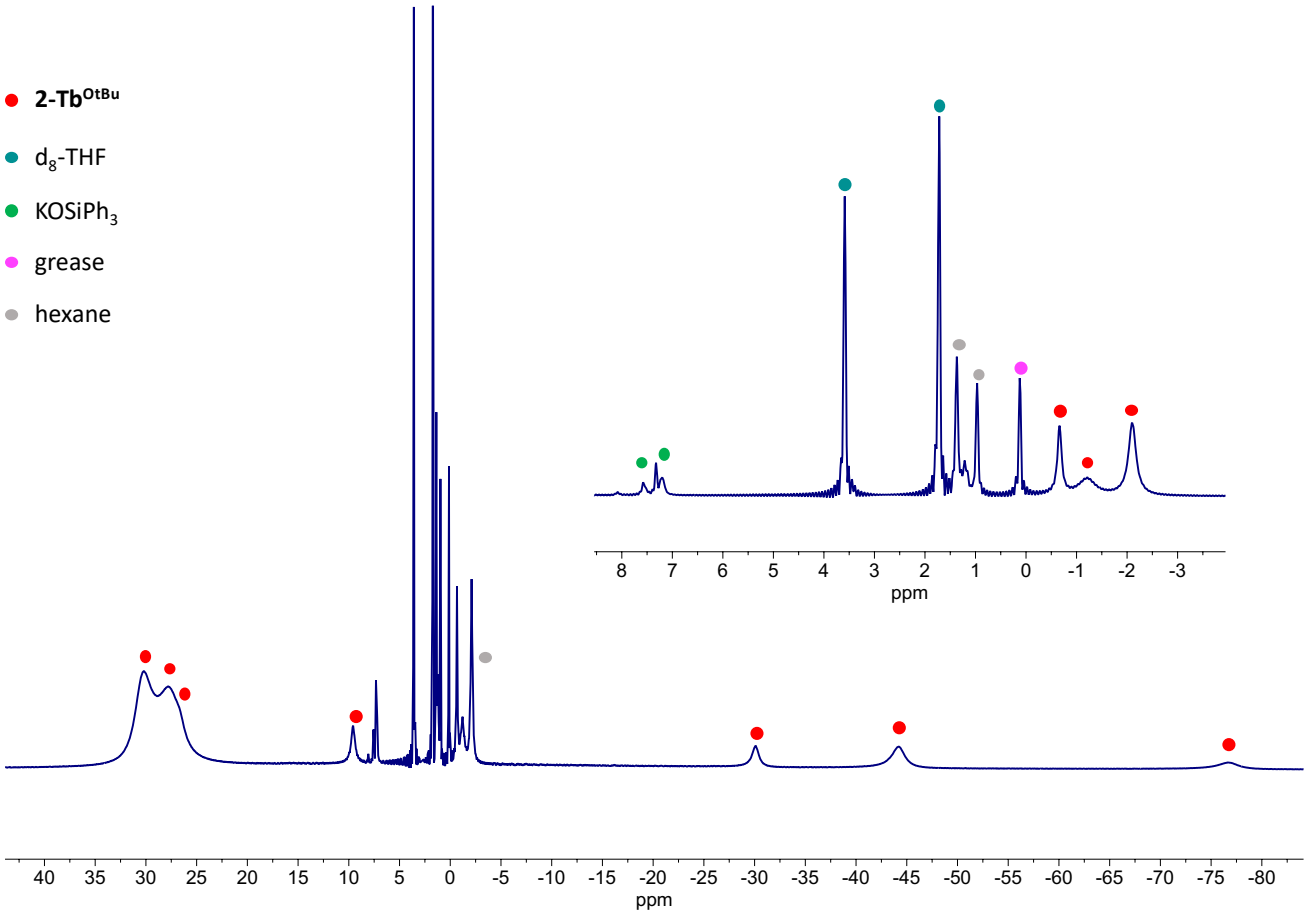


Figure S20. ^{1}H NMR spectrum (400 MHz, THF-d_8, 298 K) of the reaction mixture obtained after addition of 1.0 equiv. of $KOSiPh_3$ to [Tb^{III}((OSi(O^{t}Bu)$_2$)$_3$-arene)(THF)$_3$], **1-Tb^{OtBu}** after 30 mins, resulting in **2-Tb^{OtBu}**.

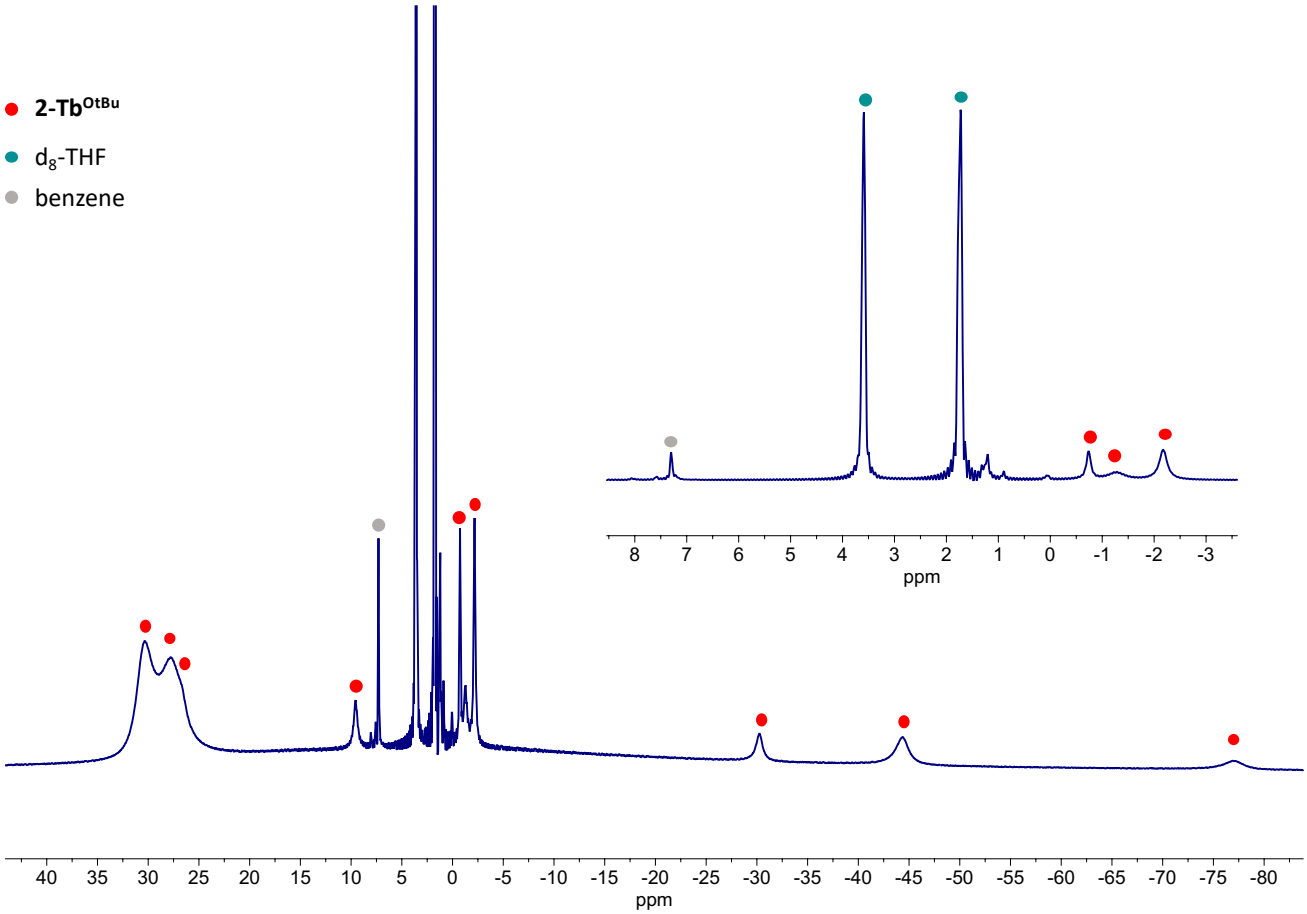


Figure S21. ^{1}H NMR spectrum (400 MHz, THF-d_8, 298 K) of isolated [K(THF)$_6$][Tb^{III}((OSi(O^{t}Bu)$_2$Ar)$_3$-arene)(OSiPh$_3$)], **2-Tb^{OtBu}**.

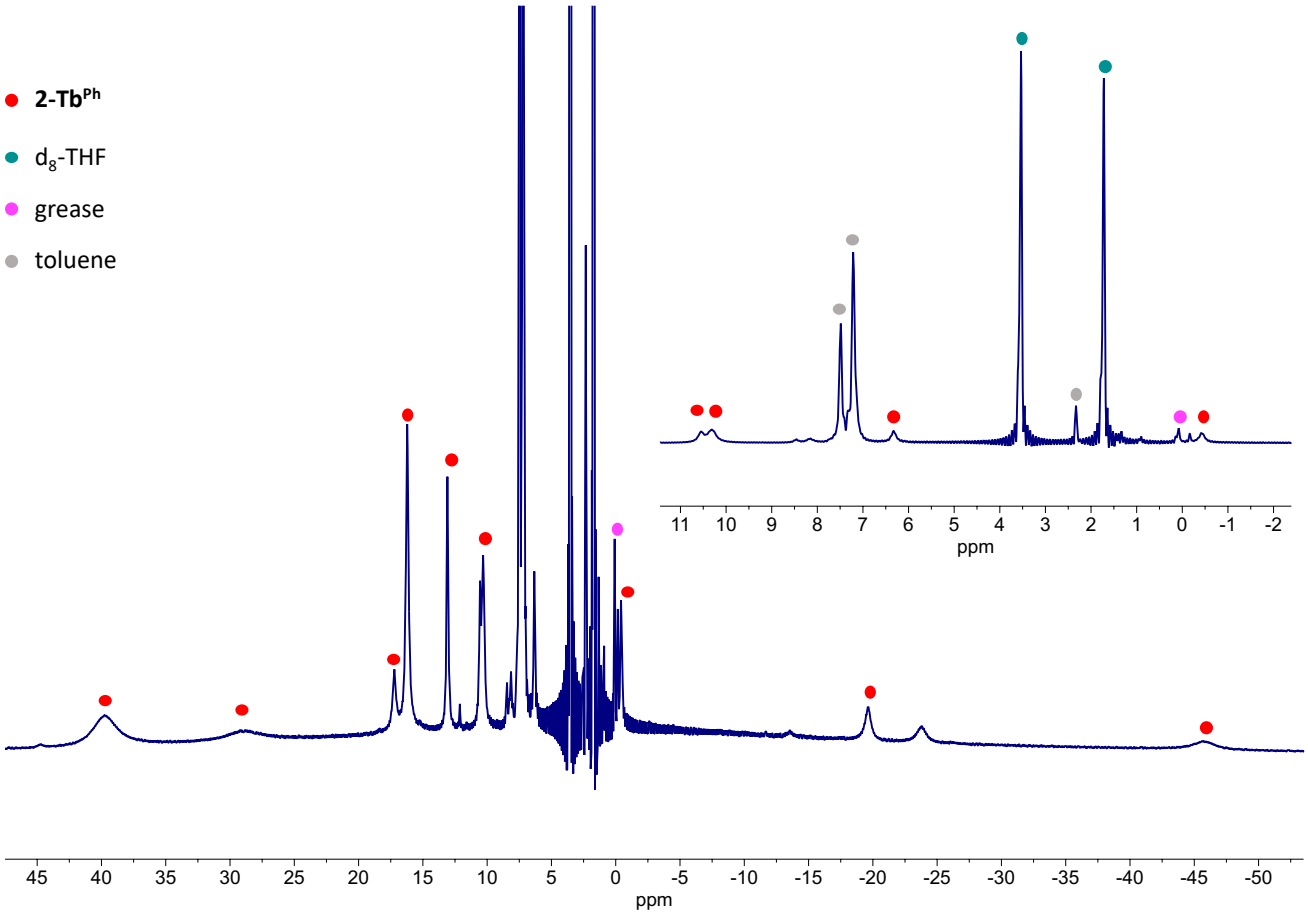


Figure S22. ^{1}H NMR spectrum (400 MHz, THF-d_8, 298 K) of the reaction mixture obtained after addition of 1.0 equiv. of $KOSiPh_3$ to [Tb^{III}($(OSiPh_2)_3$-arene)$(THF)_3$], **1-Tb^{Ph}** after 15 mins, resulting in **2-Tb^{Ph}**.

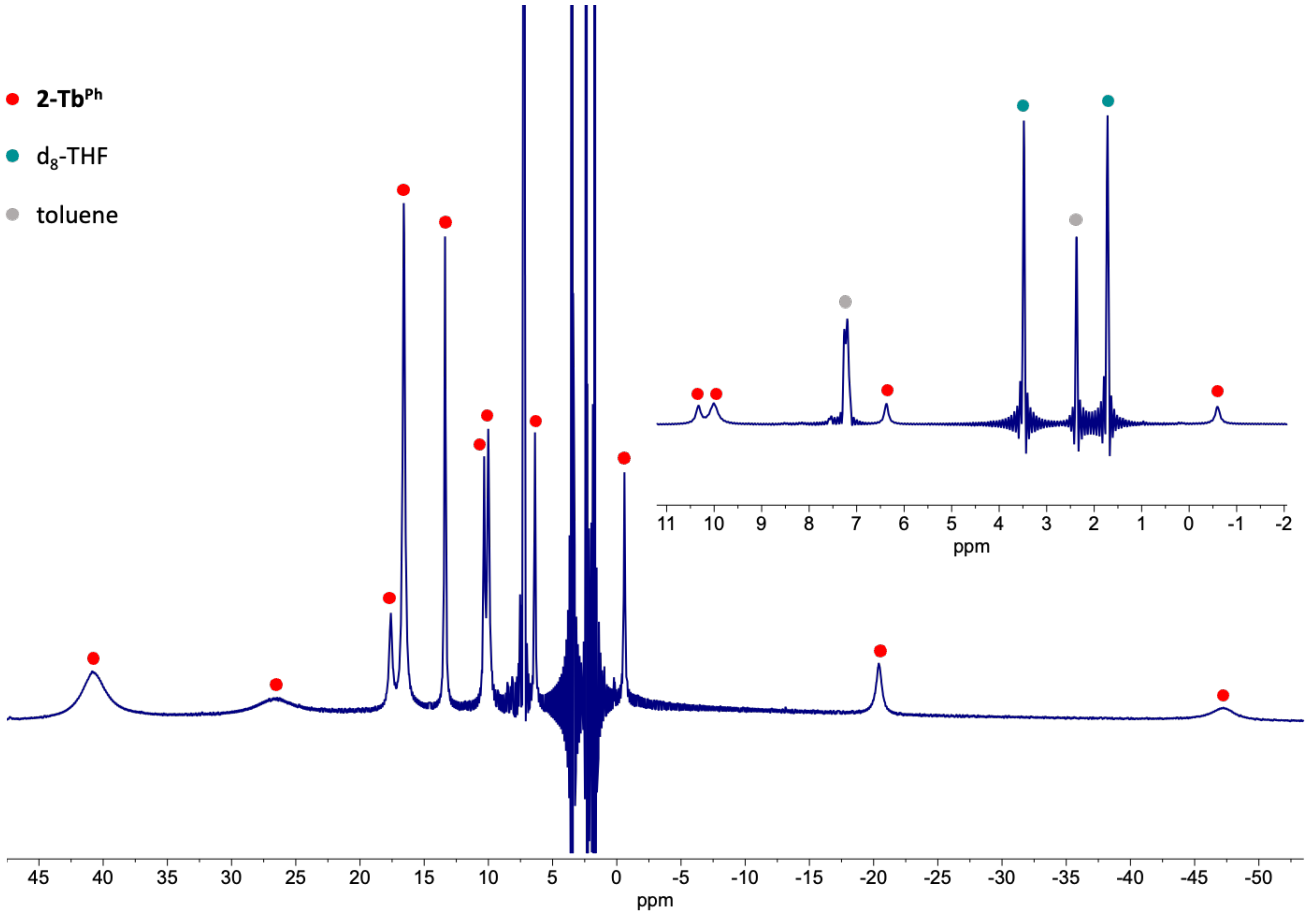


Figure S23. ^{1}H NMR spectrum (400 MHz, THF-d_8, 298 K) of isolated [K{Tb^{III}((OSiPh$_2$Ar)$_3$-arene)(OSiPh$_3$)(toluene)}], **2-Tb^{Ph}**.

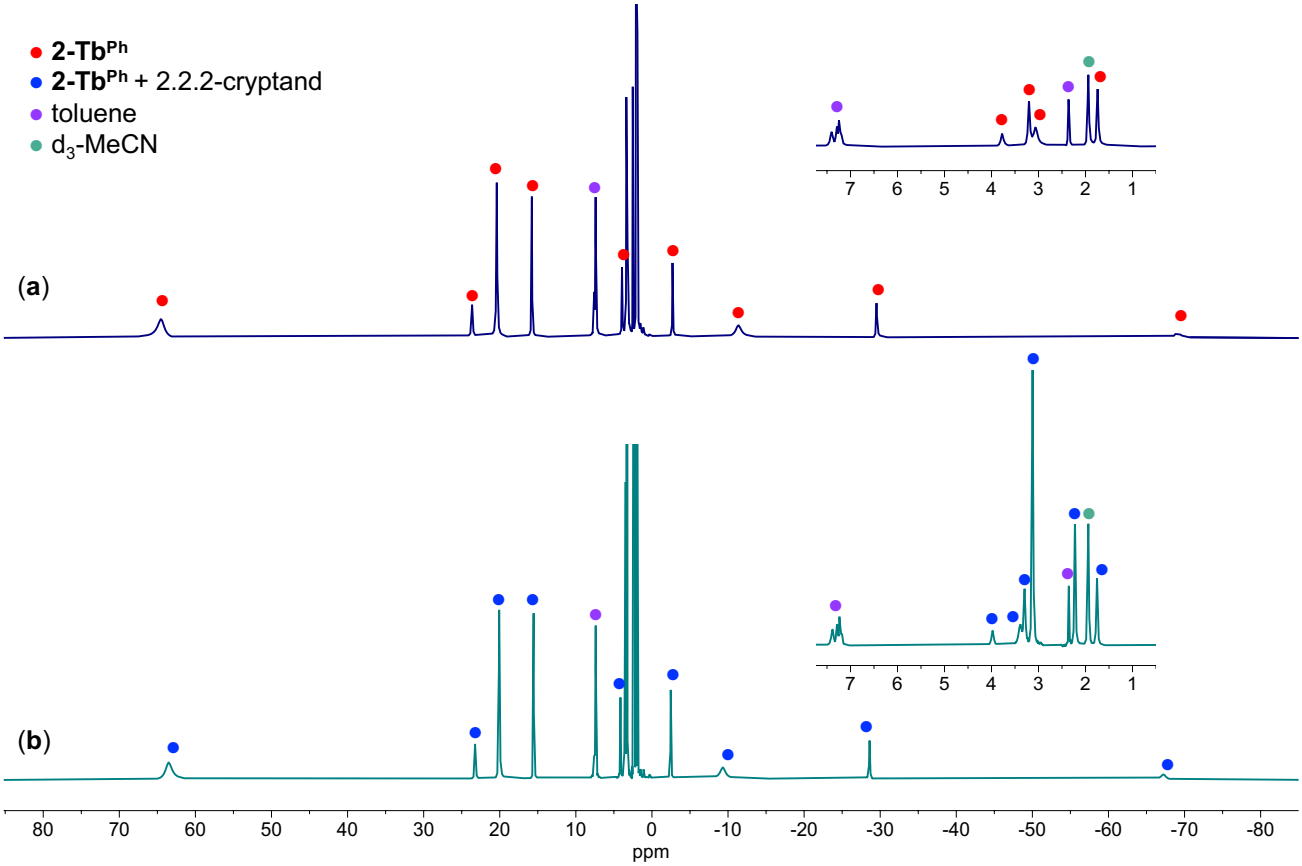


Figure S24. ^{1}H NMR spectra (400 MHz, MeCN-d_3, 298 K) of **2-Tb^{Ph}** before a) and immediately after b) addition of 1.1 equiv. of 2.2.2-cryptand.

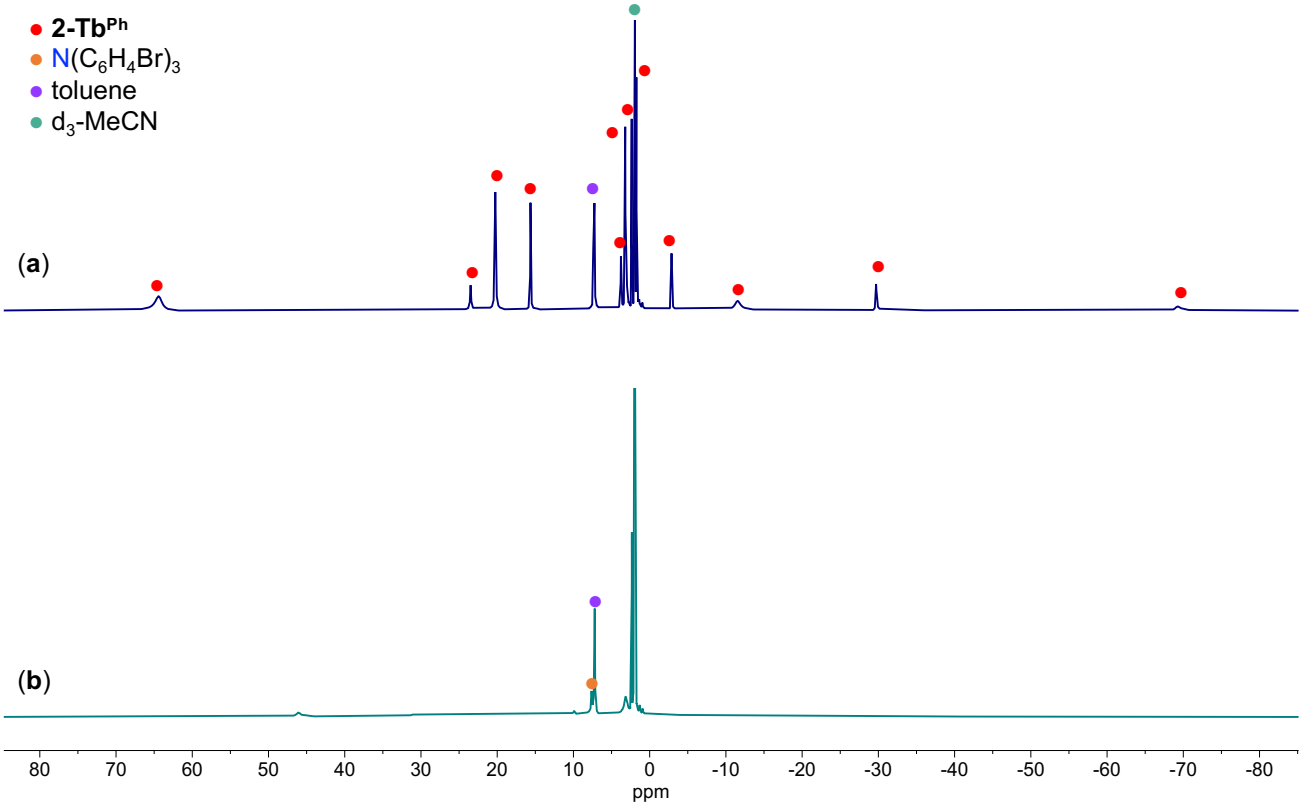


Figure S25. ^{1}H NMR spectrum (400 MHz, MeCN-d_3, 298 K) of the reaction mixture obtained after addition of 1.1 equiv. of [N(C_6H_4Br)][$SbCl_6$] to **2-Tb^{Ph}**, 15 minutes after addition showing complete disappearance of **2-Tb^{Ph}** and a silent spectrum.

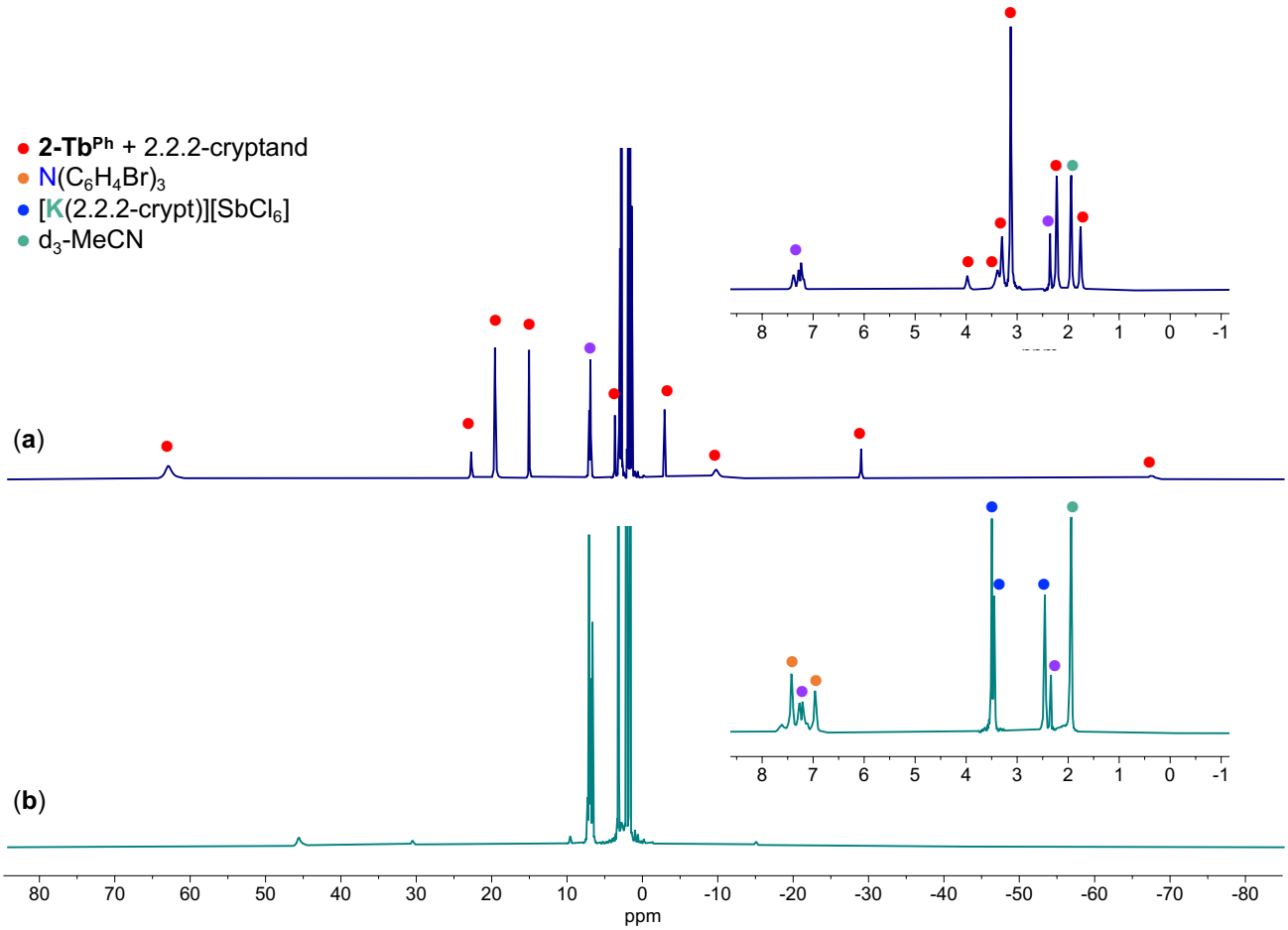


Figure S26. ^{1}H NMR spectrum (400 MHz, MeCN-d_3, 298 K) of the reaction mixture obtained after addition of 1.1 equiv. of [N(C$_6$H$_4$Br)][SbCl$_6$] to **2-Tb^{Ph}** and 2.2.2-cryptand, 15 minutes after addition.

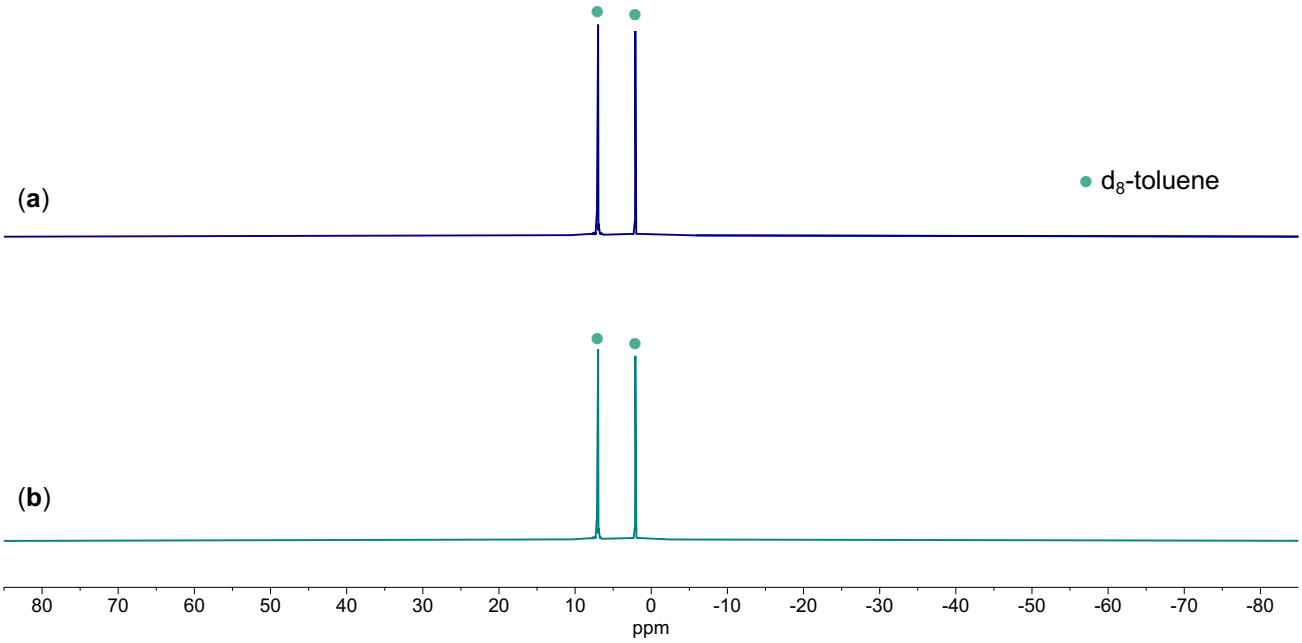


Figure S27. ^{1}H NMR spectrum (400 MHz, toluene-d_8, 298 K) of a) isolated [Tb^{IV}((OSiPh$_2$Ar)$_3$-arene)(OSiPh$_3$)(MeCN)$_2$], **3-Tb^{Ph}**. The spectrum is silent due to the Tb(IV) 4f^7 ion. b) ^{1}H NMR spectrum after 2 days.

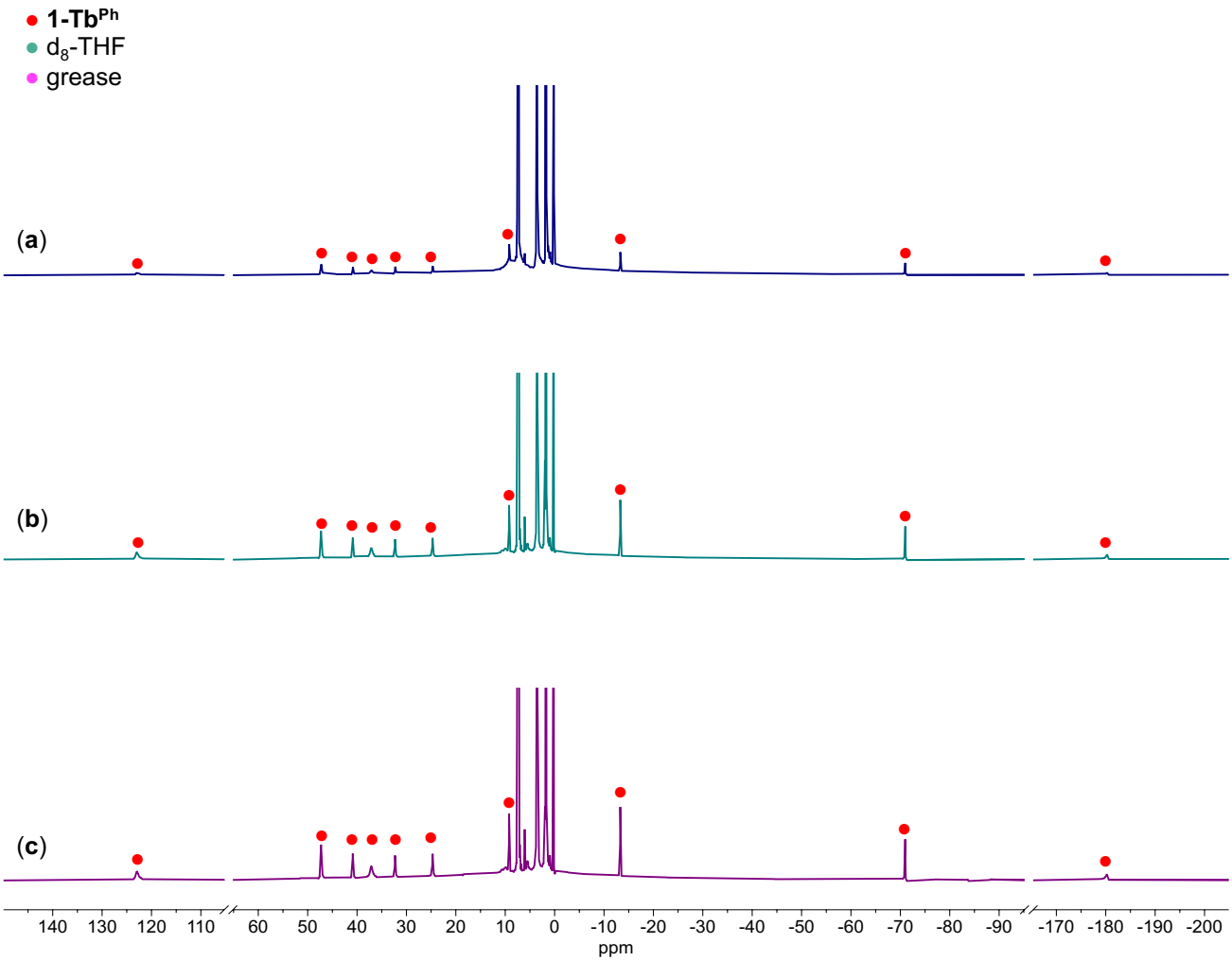


Figure S28. ^{1}H NMR spectrum (400 MHz, THF-d_8, 298 K) of isolated [Tb^{IV}((OSiPh$_2$Ar)$_3$-arene)(OSiPh$_3$)(MeCN)$_2$], **3-Tb^{Ph}** after a) 15 minutes, b) 9 hours, c) 24 hours.

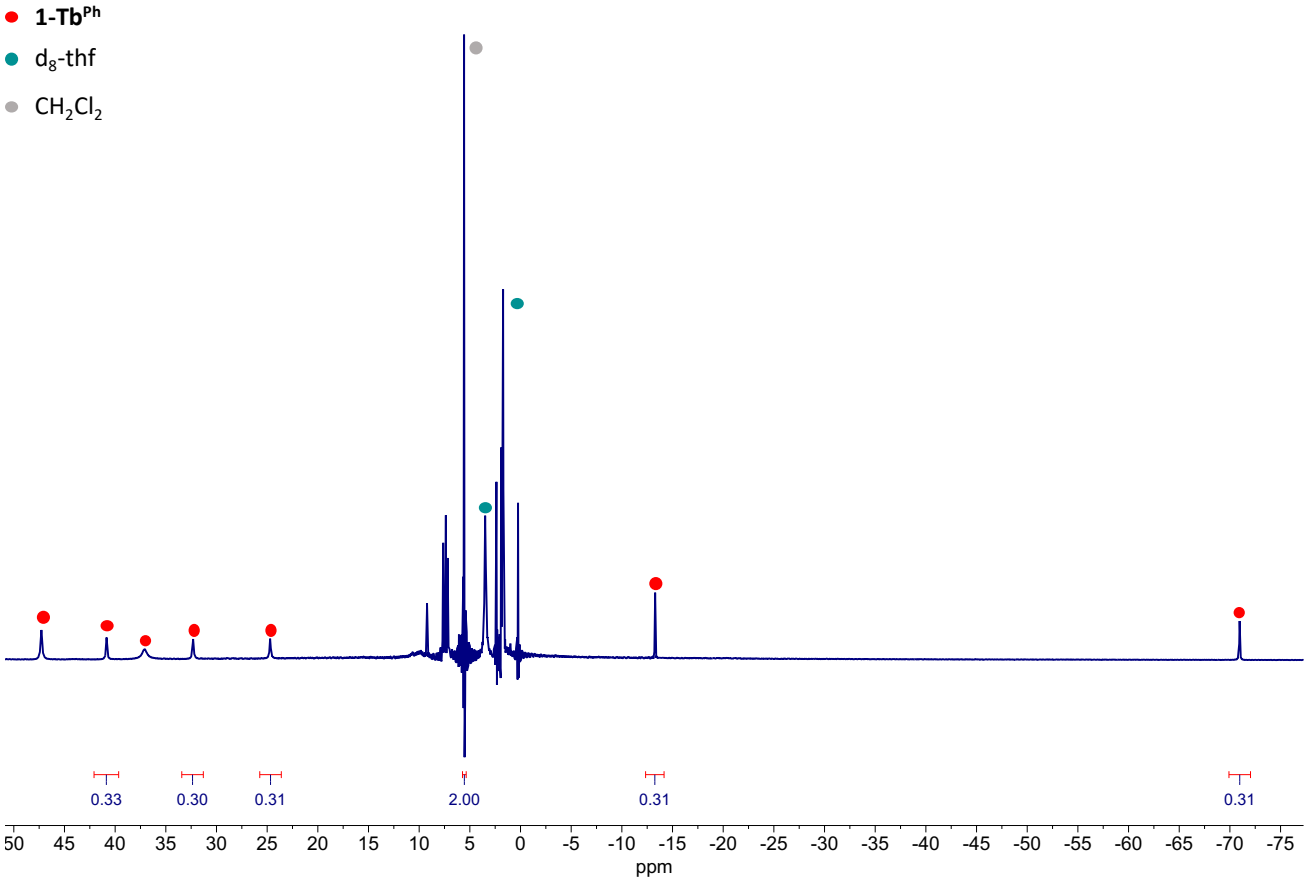


Figure S29. ^{1}H NMR spectrum (400 MHz, THF-d_8, 298 K) of 8.0 mg of isolated [Tb^{IV}((OSiPh$_2$Ar)$_3$-arene)(OSiPh$_3$)(MeCN)$_2$], **3-Tb^{Ph}** after 24 hours at room temperature, 3.0 µL of CH_2Cl_2 was added as internal standard to quantify the amount of **1-Tb^{Ph}** reformed (83%).

S3.3. NMR spectra for praseodymium complexes

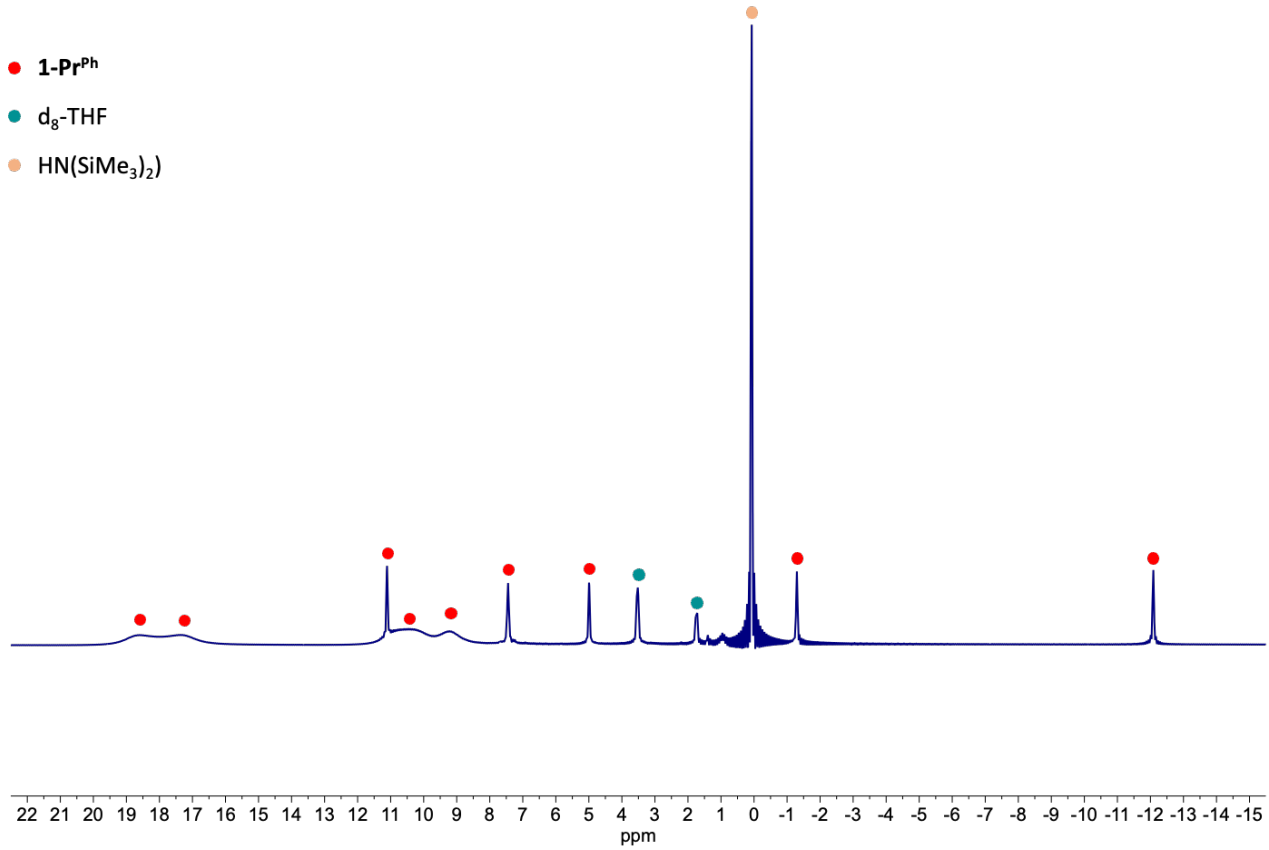


Figure S30. ^{1}H NMR spectrum (400 MHz, THF-d_8, 298 K) of the reaction mixture obtained after addition of 1.0 equiv. of [$Pr^{III}(N(SiMe_3)_2)_3$] to $(HOSiPh_2Ar)_3$-arene after 15 minutes, resulting in complex **1-Pr^{Ph}**.

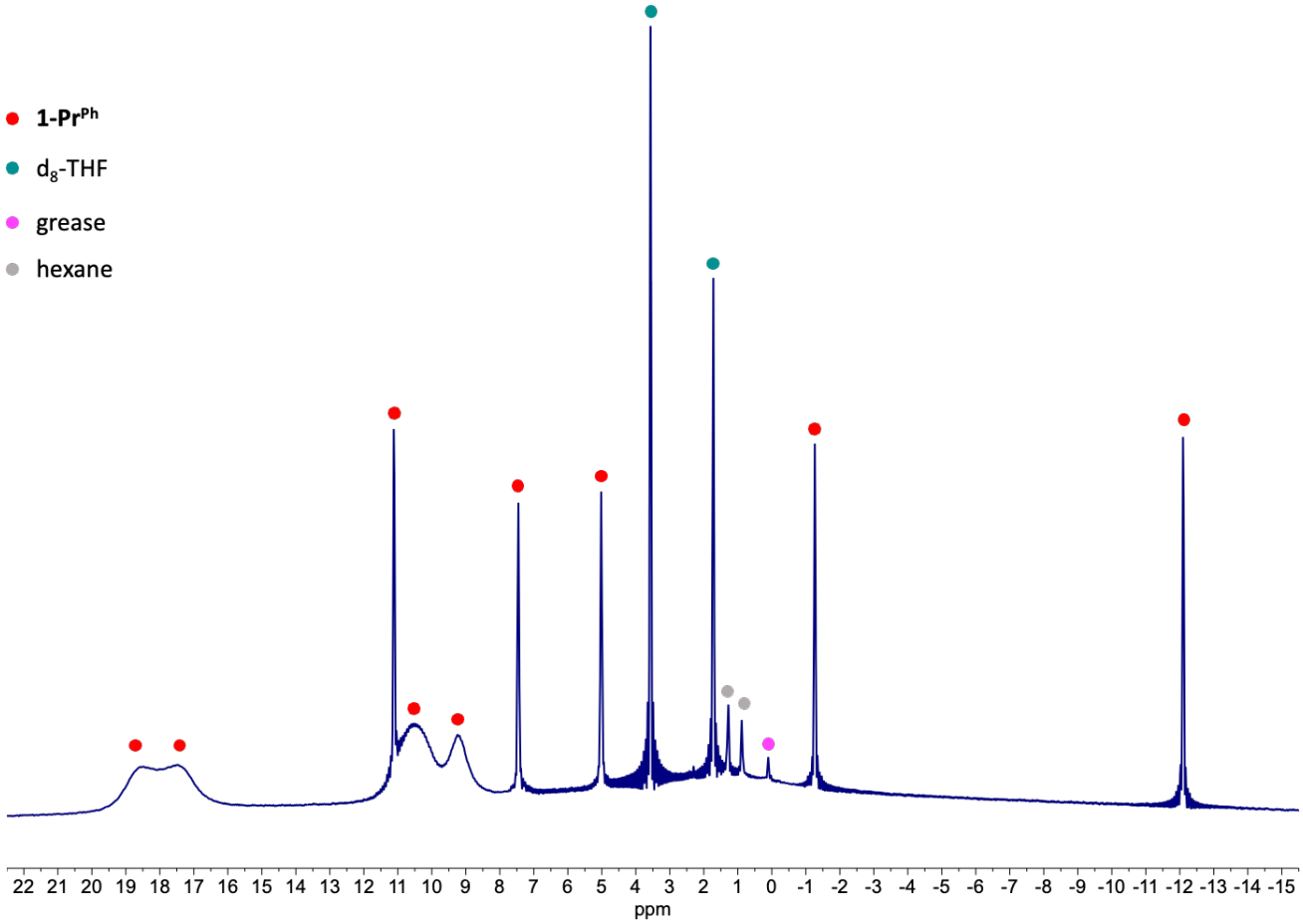


Figure S31. ^{1}H NMR spectrum (400 MHz, THF-d_8, 298 K) of isolated [Pr^{III}((OSiPh$_2$Ar)$_3$-arene)(THF)$_3$], **1-Pr^{Ph}**.

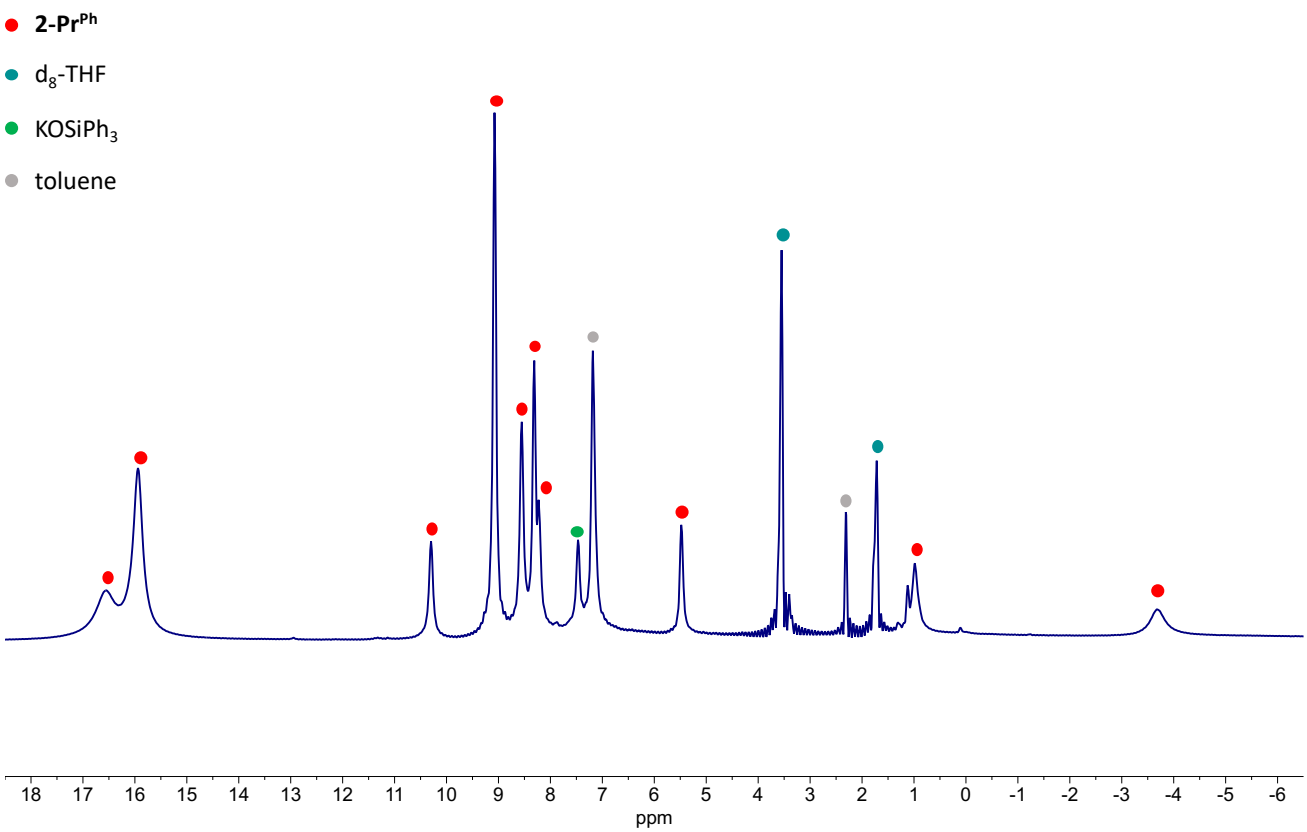


Figure S32. ^{1}H NMR spectrum (400 MHz, THF-d_8, 298 K) of the reaction mixture obtained after addition of 1.0 equiv. of $KOSiPh_3$ to [Pr^{III}(($OSiPh_2$)$_3$-arene)$(THF)_3$], **1-Pr^{Ph}** after 30 mins, resulting in **2-Pr^{Ph}**.

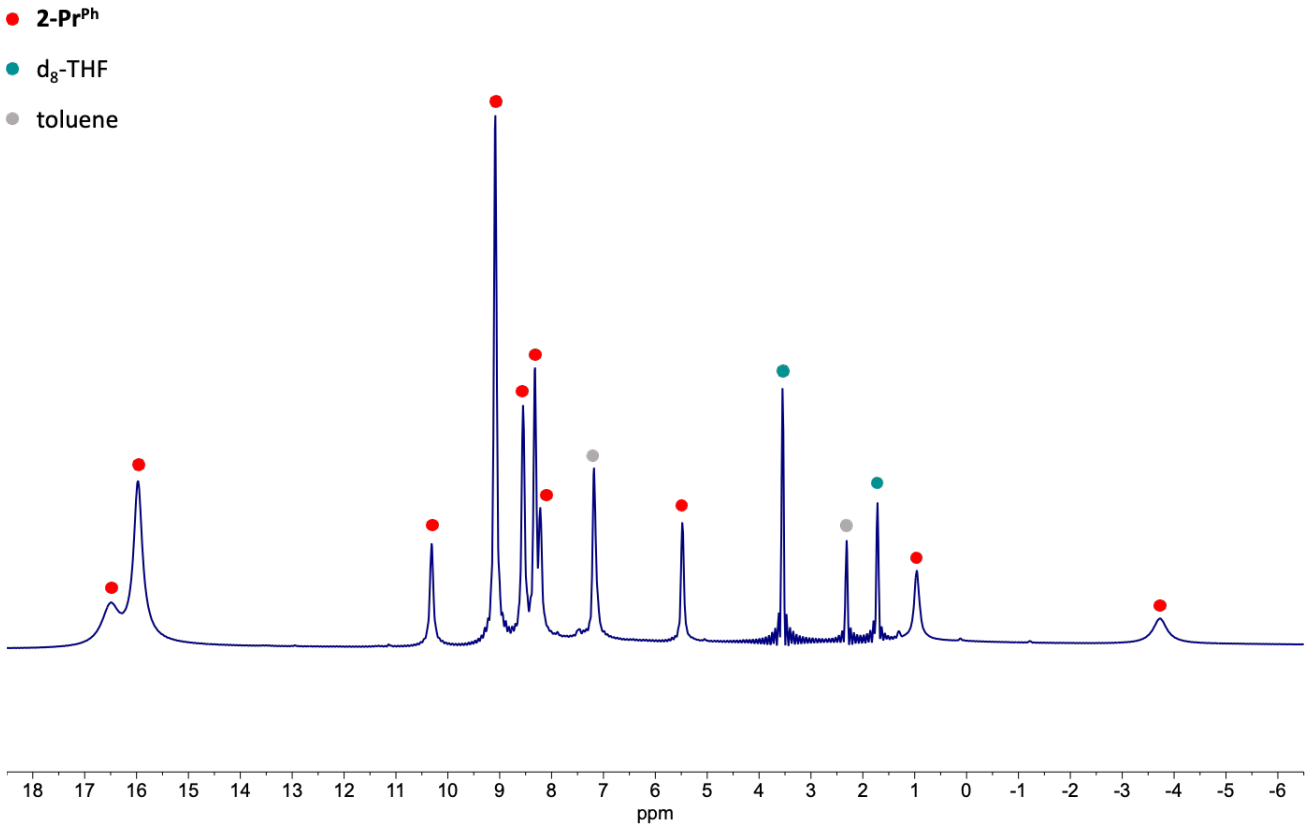


Figure S33. ^{1}H NMR spectrum (400 MHz, THF-d_8, 298 K) of isolated [K{Pr^{III}((OSiPh$_2$Ar)$_3$-arene)(OSiPh$_3$)(toluene)}], **2-Pr^{Ph}**.

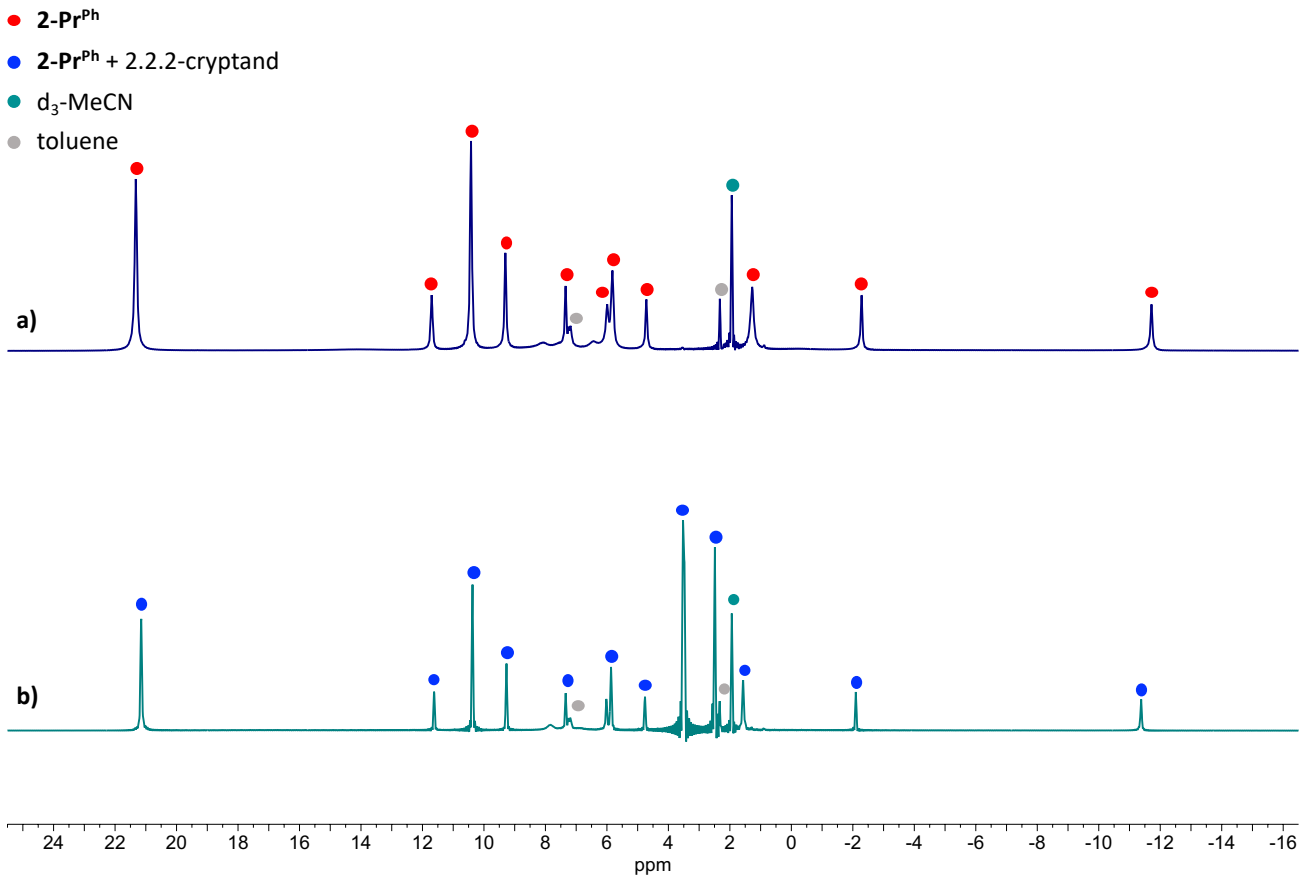


Figure S34. ^{1}H NMR spectra (400 MHz, MeCN-d_3, 298 K) of **2-Pr^{Ph}** a) and **2-Pr^{Ph}** + 1.1 equiv. of 2.2.2-cryptand b).

S3.4. NMR spectra of in-situ addition of KOSi(O^{t}Bu)$_3$, KOSiMe$_3$ and 2-KOAd and K(N(SiMe$_3$)$_2$) to 1-Tb^{Ph}

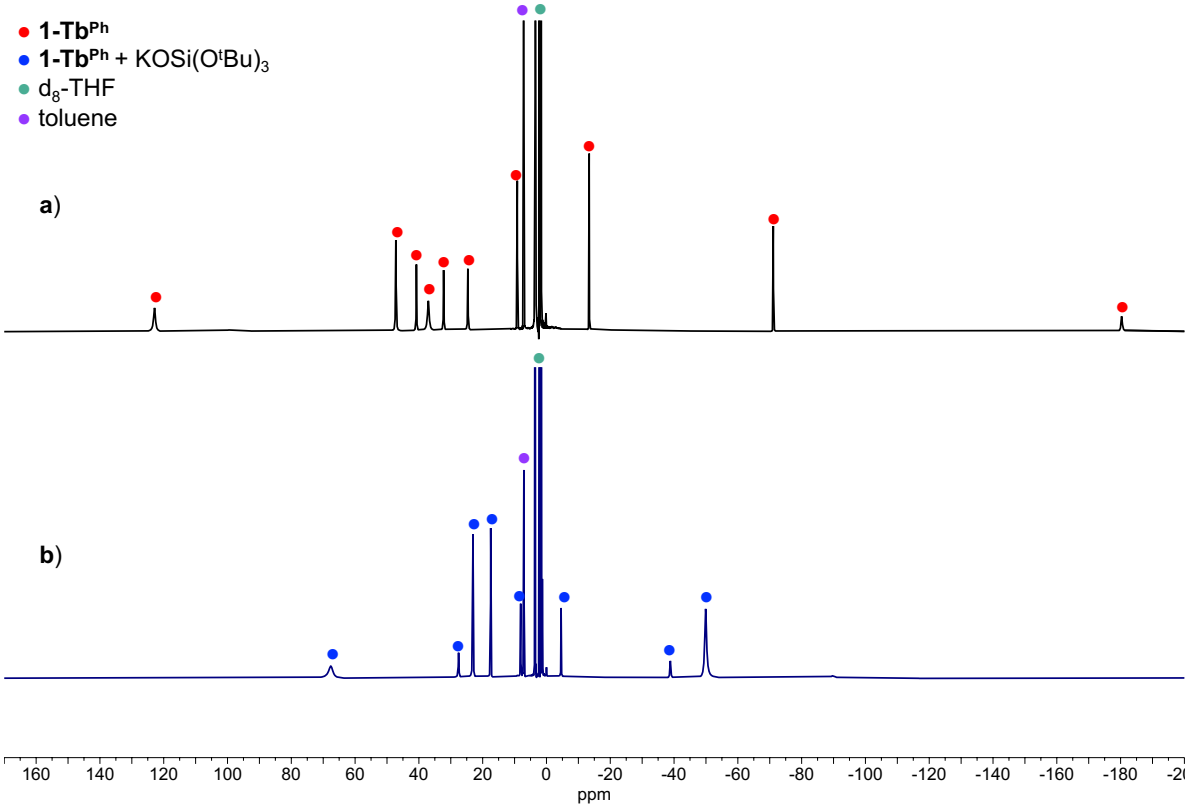


Figure S35. ^{1}H NMR spectra (400 MHz, THF-d_8, 298 K) of **1-Tb^{Ph}** a) and **1-Tb^{Ph}** + 1.0 equiv. of KOSi(O^{t}Bu)$_3$ after 6 hours, b).

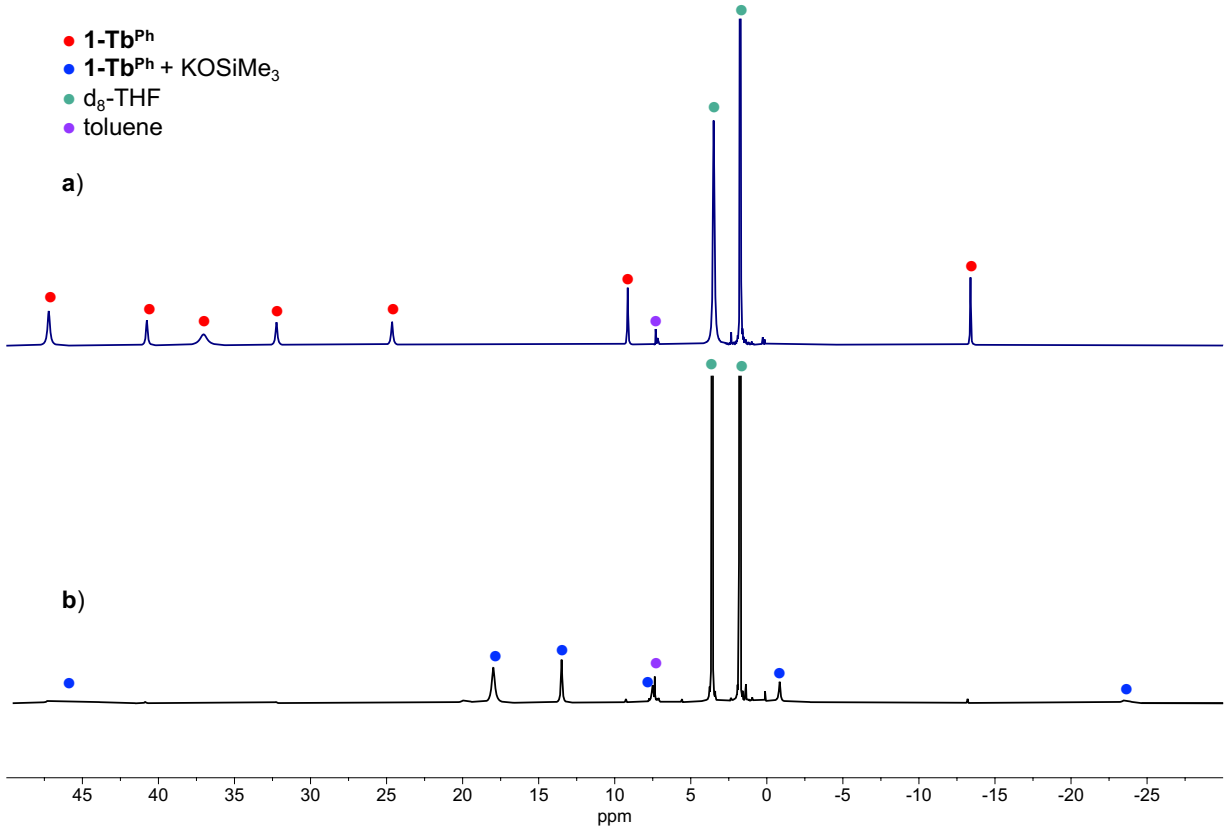


Figure S36. ^{1}H NMR spectra (400 MHz, THF-d_8, 298 K) of **1-Tb^{Ph}** a) and **1-Tb^{Ph}** + 1.1 equiv. of $KOSiMe_3$ after 3 h b).

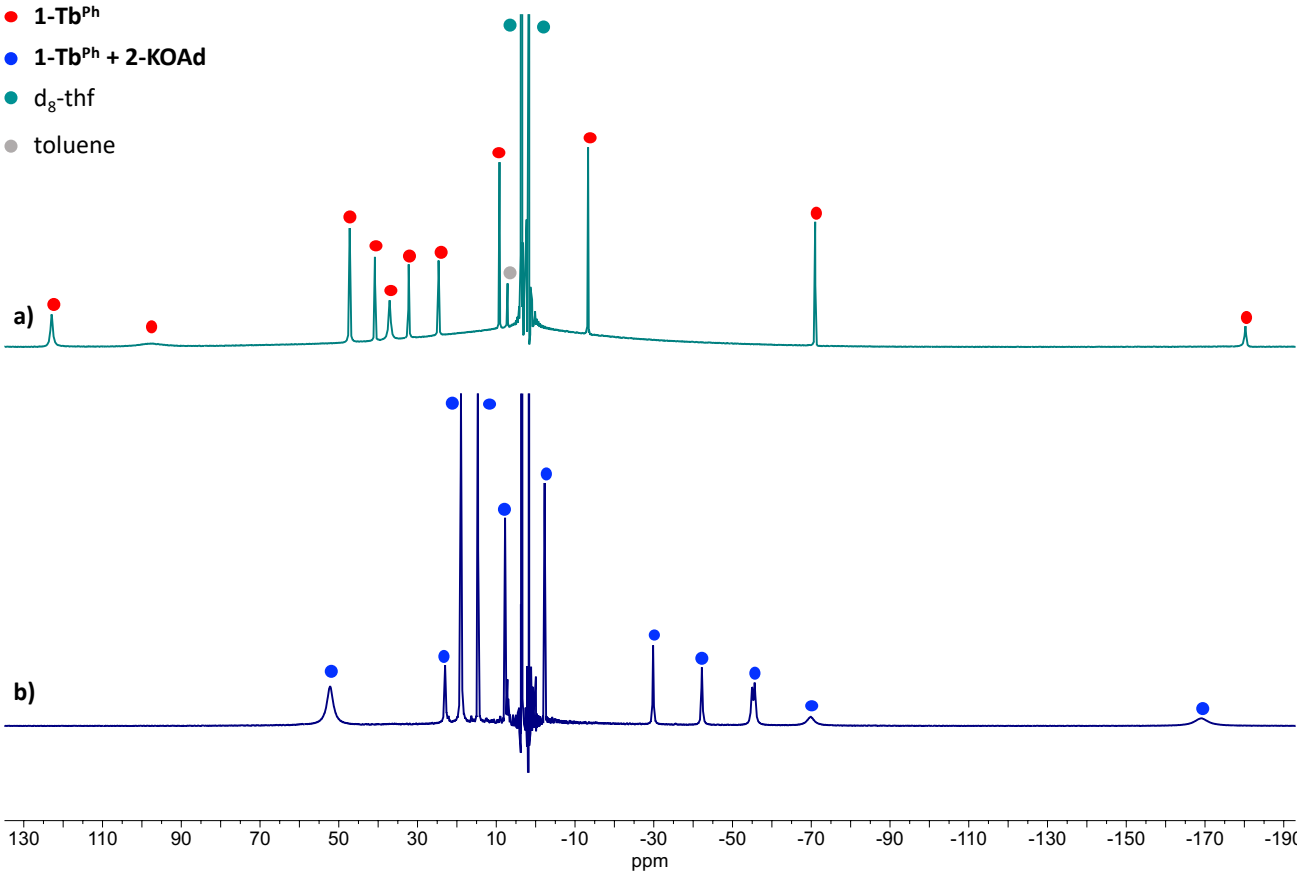


Figure S37. ^{1}H NMR spectra (400 MHz, THF-d_8, 298 K) of **1-Tb^{Ph}** a) and **1-Tb^{Ph}** + 1.1 equiv. of 2-KOAd after 3 h, b).

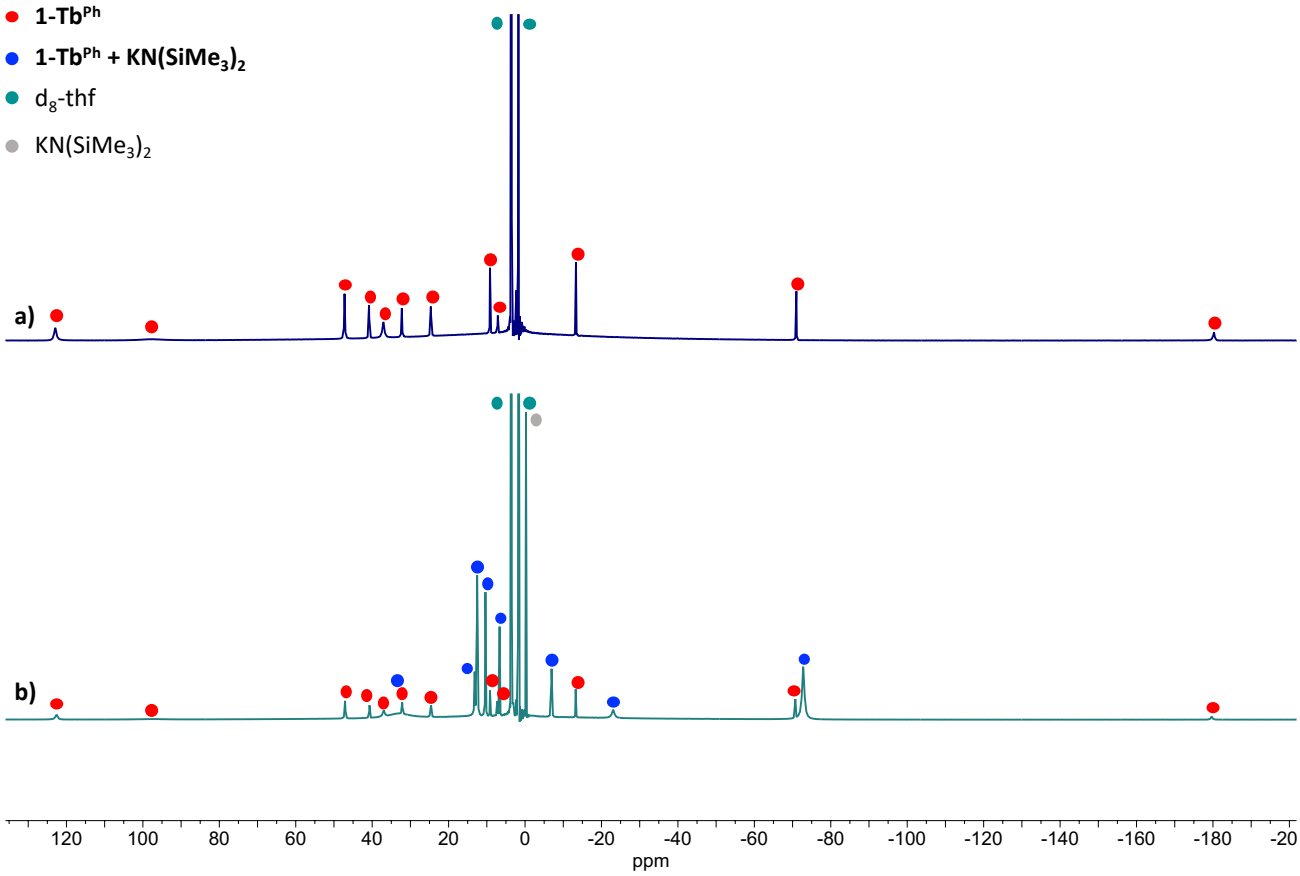


Figure S38. ^{1}H NMR spectra (400 MHz, THF-d_8, 298 K) of **1-Tb^{Ph}** a) and **1-Tb^{Ph}** + 1.1 equiv. of K(N(SiMe$_3$)$_2$) after 16 h, some **1-Tb^{Ph}** remained b). Almost no further conversion could be observed by adding an additional equivalent of K(N(SiMe$_3$)$_2$).

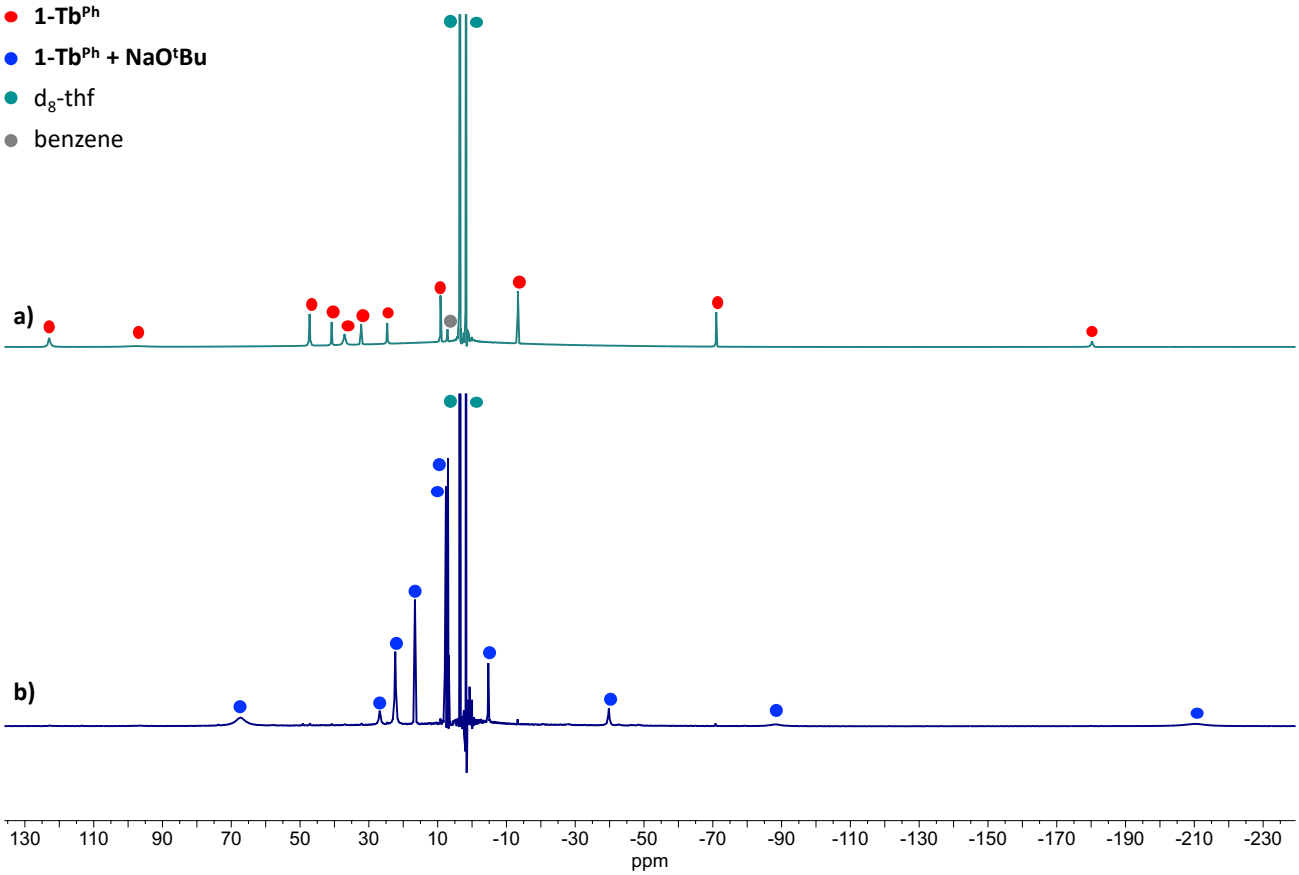


Figure S39. ^{1}H NMR spectra (400 MHz, THF-d_8, 298 K) of **1-Tb^{Ph}** a) and b) **1-Tb^{Ph}** + 1.5 equiv. of NaO^{t}Bu after 16 h.

S3.5. NMR spectra of in-situ addition of $KOSiMe_3$ and 2-KOAd to 1-Pr^{Ph}

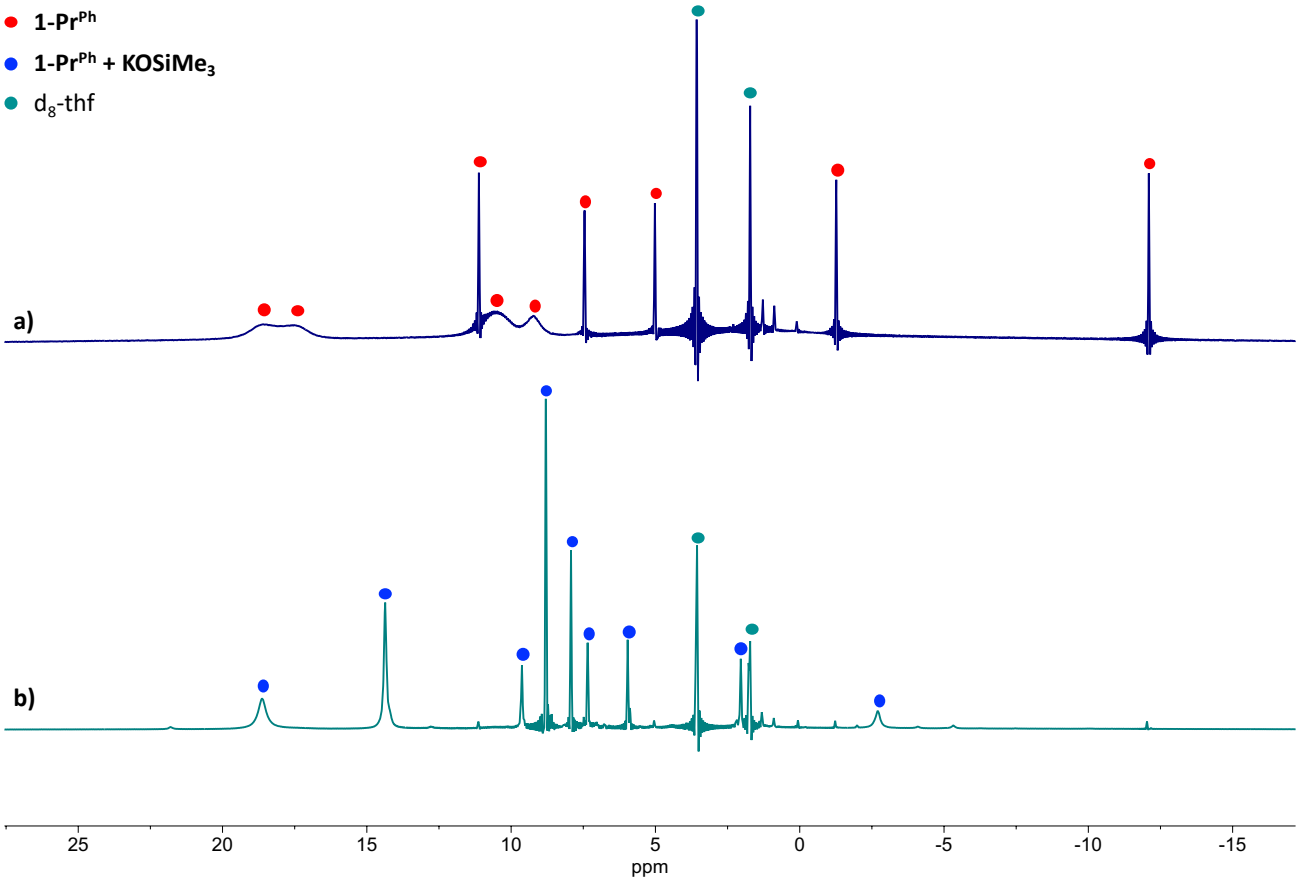


Figure S40. ^{1}H NMR spectra (400 MHz, THF-d_8, 298 K) of **1-Pr^{Ph}** a) and b) **1-Pr^{Ph}** + 1.1 equiv. of $KOSiMe_3$ after 1 h.

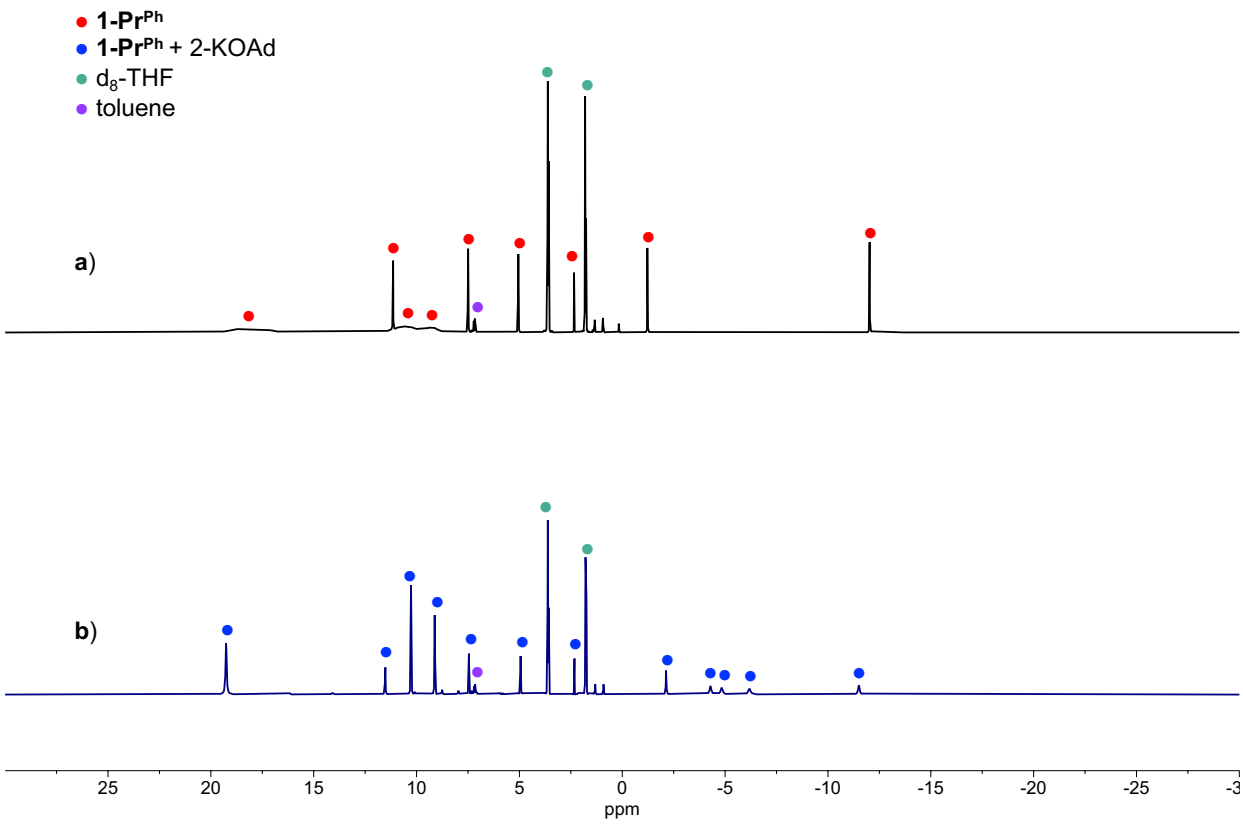


Figure S41. ^{1}H NMR spectra (400 MHz, THF-d_8, 298 K) of **1-Pr^{Ph}** a) and **1-Pr^{Ph}** + 1.1 equiv. of 2-KOAd after 3 h. b).

S3.6. NMR spectra of the Tb/Dy separation trials

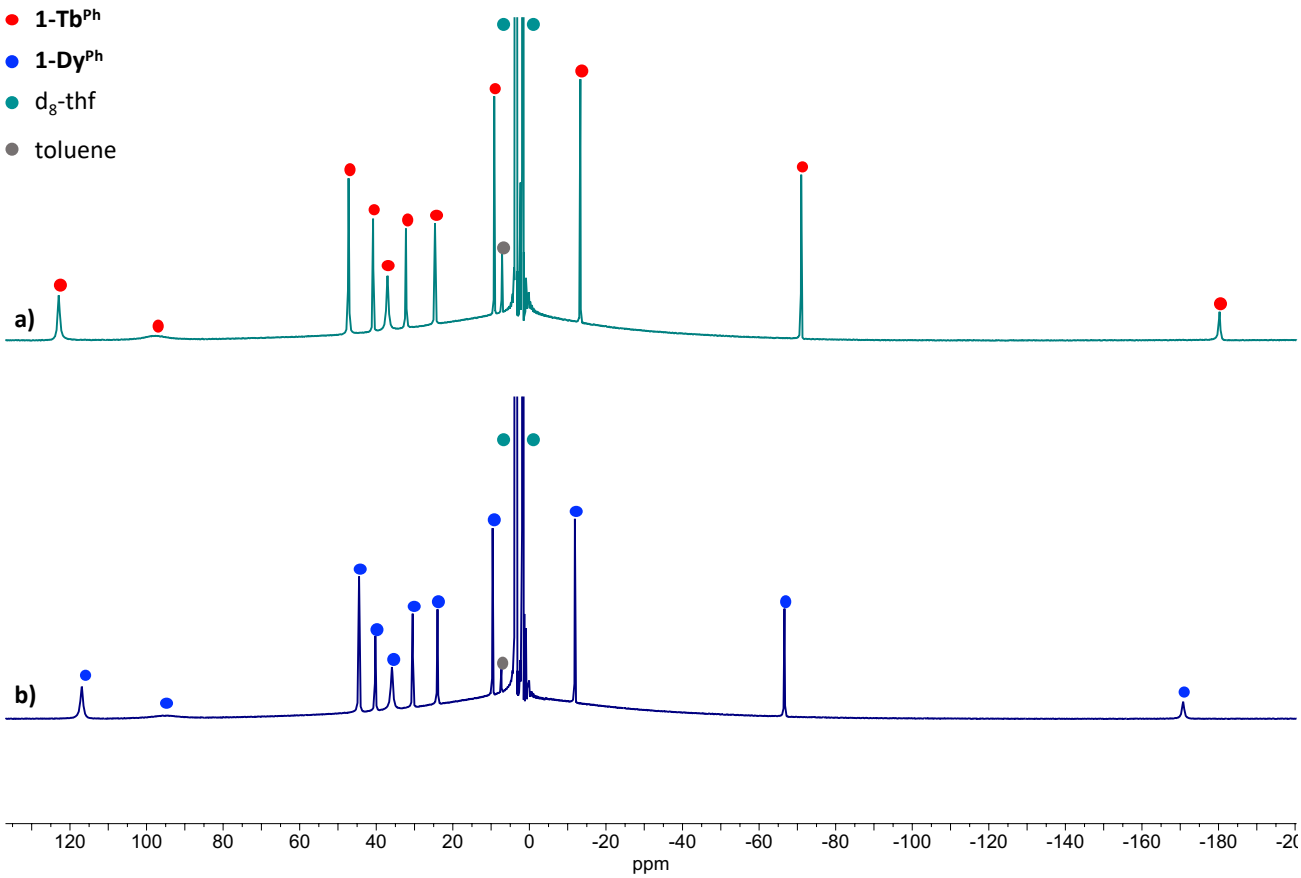


Figure S42. ^{1}H NMR spectrum (400 MHz, THF-d_8, 298 K) of a) **1-Tb^{Ph}**, b) **1-Dy^{Ph}**.

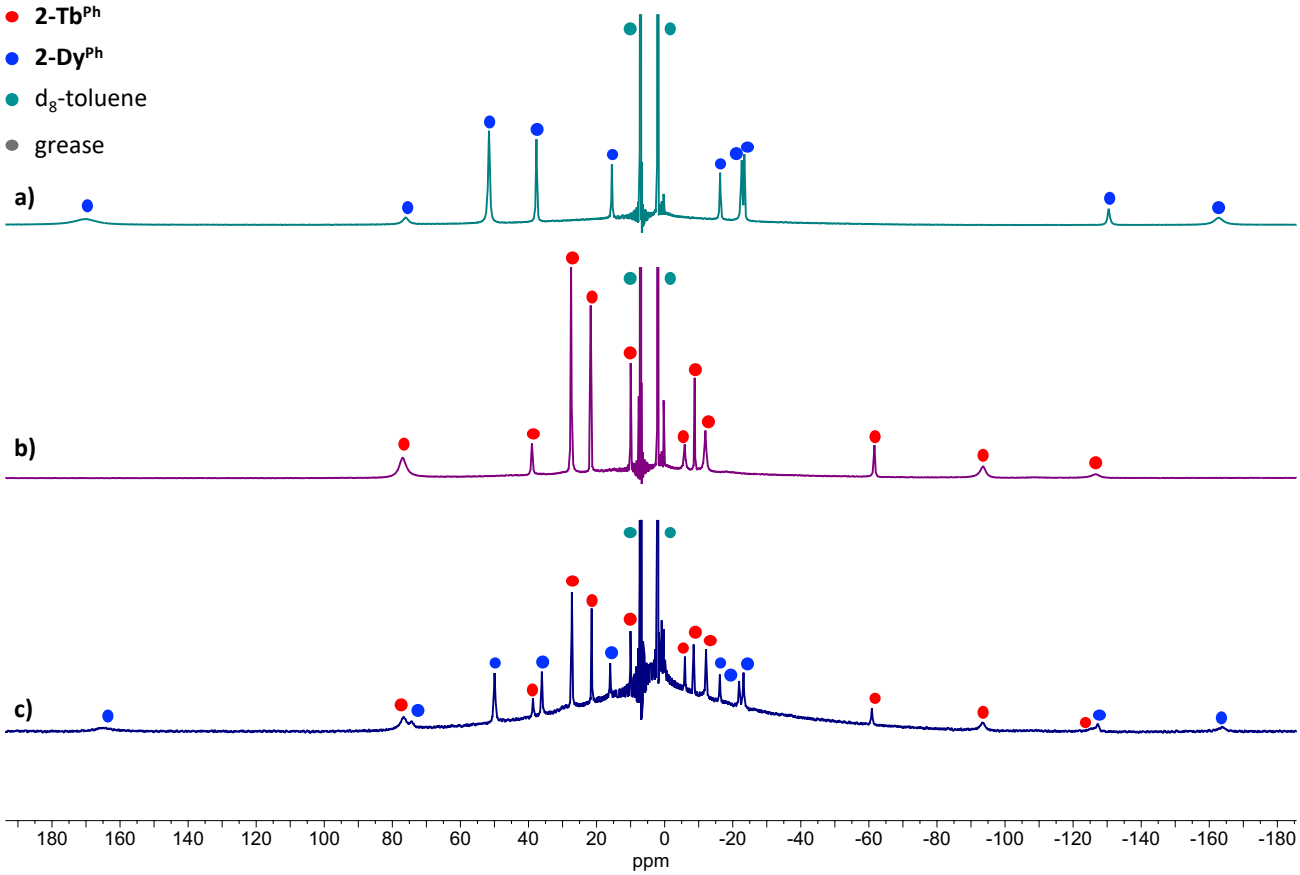


Figure S43. ^{1}H NMR spectrum (400 MHz, toluene-d_8, 298 K) of a) in-situ formed **2-Dy^{Ph}**, b) **2-Tb^{Ph}**, c) in-situ formed 1:1 mixture of **2-Tb^{Ph}: 2-Dy^{Ph}**.

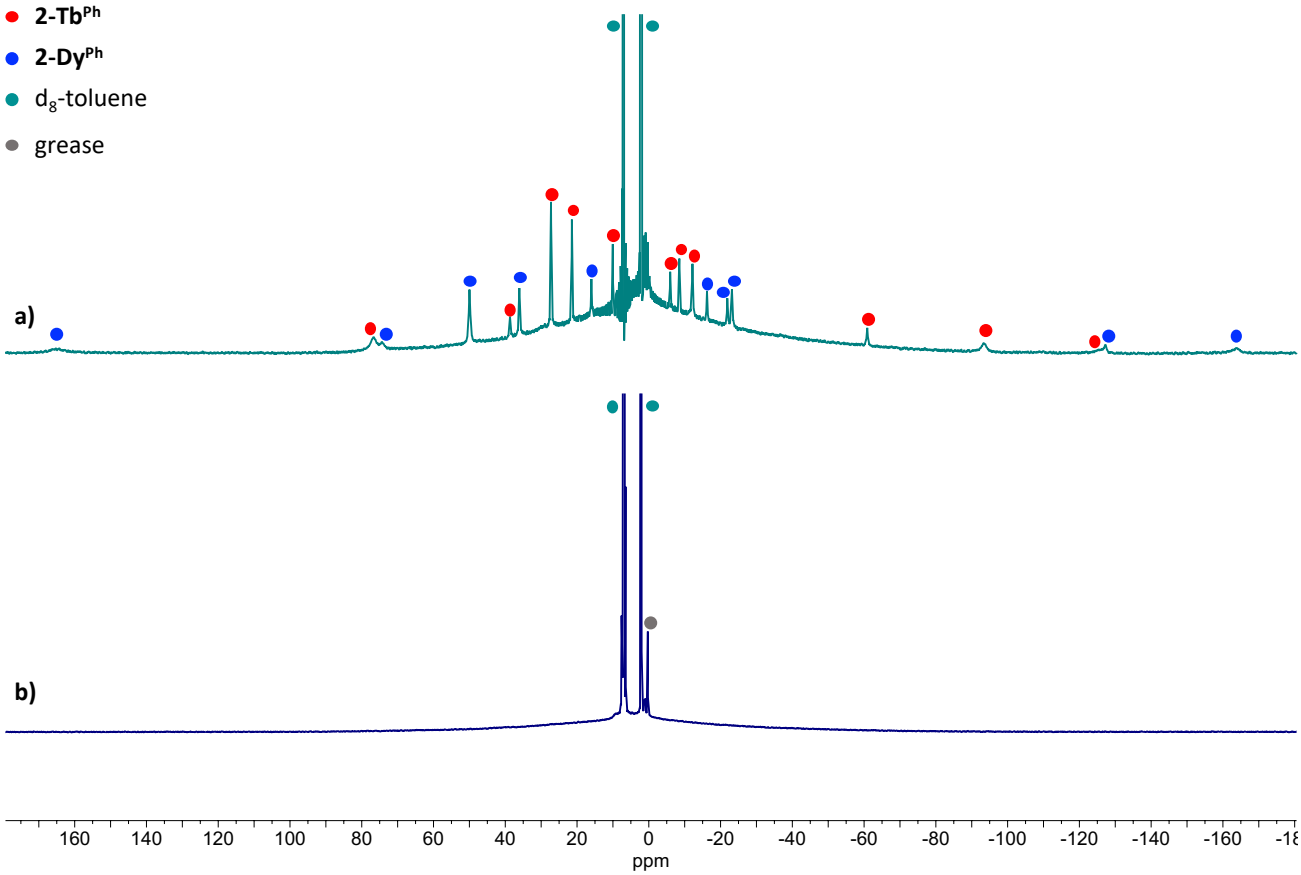


Figure S44. ^{1}H NMR spectrum (400 MHz, toluene-d_8, 298 K) of a) in-situ formed 1:1 mixture of **2-Tb^{Ph}: 2-Dy^{Ph}** b) Toluene solution obtained after extraction of the precipitate formed after oxidation of the in-situ formed 1:1 mixture of **2-Tb^{Ph}: 2-Dy^{Ph}**.

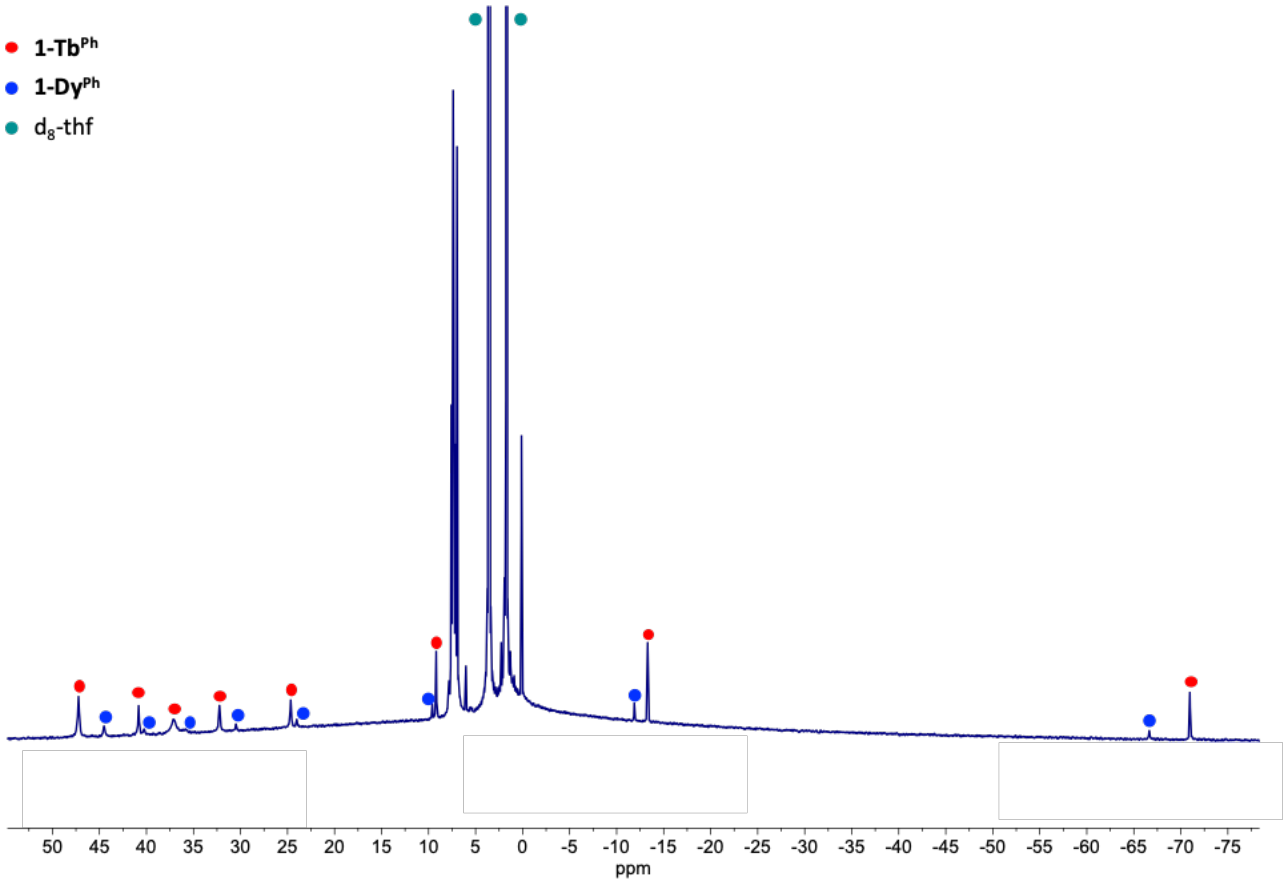


Figure S45. ^{1}H NMR spectrum (400 MHz, THF-d_8, 298 K) of the residue after oxidation of the in-situ formed 1:1 mixture of **2-Tb^{Ph}: 2-Dy^{Ph}** and extraction in toluene, in THF. The signals of **1-Dy^{Ph}** and **1-Tb^{h}** after 14 hours (quantitative integration of **1-Dy^{Ph}** showed that only 6% is left in the extracted solid.

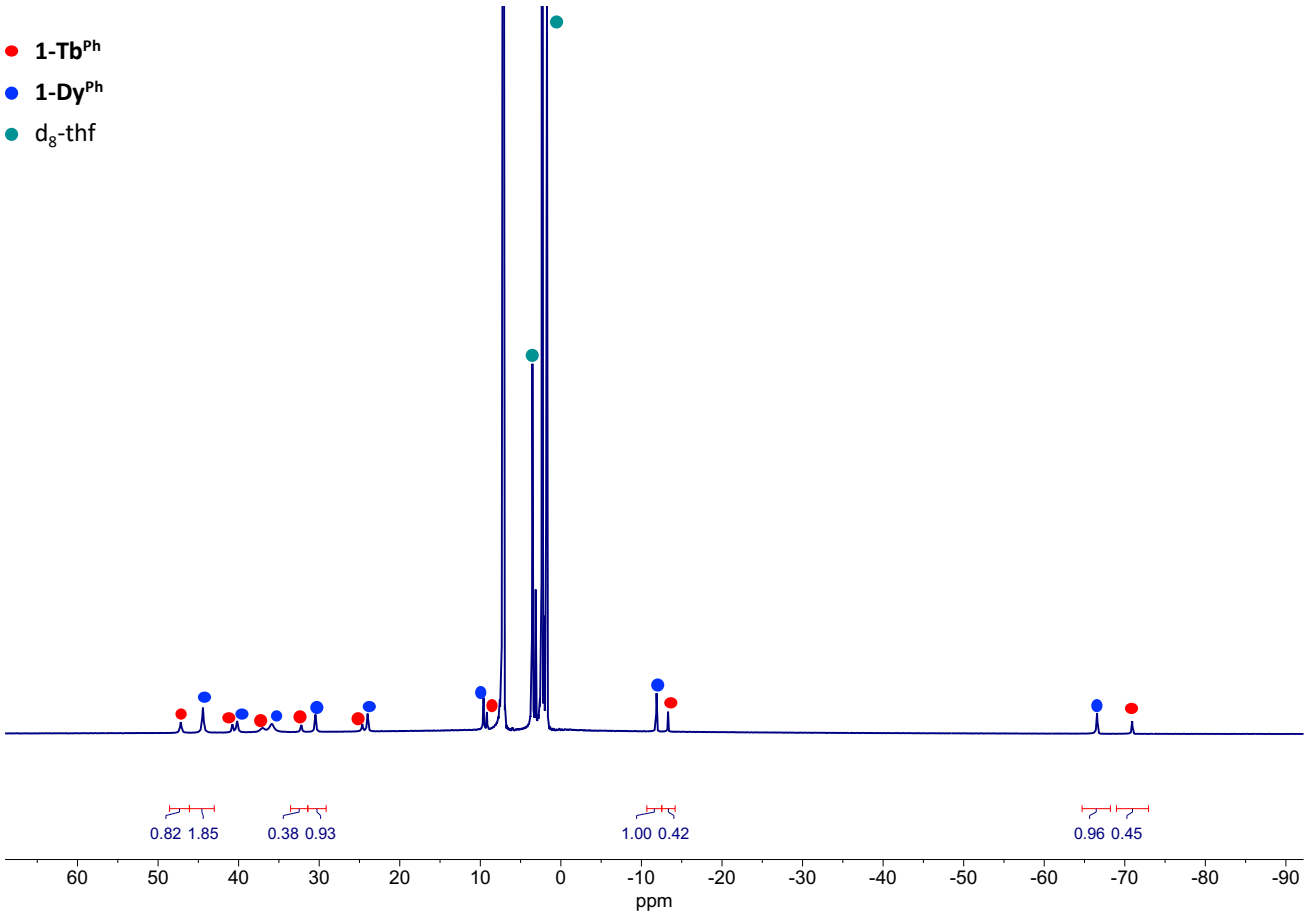


Figure S46. ^{1}H NMR spectrum (400 MHz, THF-d_8, 298 K) of the insoluble material left from the toluene extraction, after 14h in THF. The Tb:Dy ratio is 0.44:1 indicating a higher concentration of Dy in the insoluble material.

S4. X-ray Crystallography Data

Table S1. Crystal data and structural refinement parameters for complexes **1-Tb^{OtBu}**, **1-Ce^{Ph}·2(toluene)**, **1-Tb^{Ph}·2(toluene)**, **1-Pr^{Ph}·2(toluene)**

	1-Tb^{OtBu}	**1-Ce^{Ph}·2(toluene)**	**1-Tb^{Ph}·2(toluene)**	**1-Pr^{Ph}·2(toluene)**
Formula	$C_{52}H_{77}O_{10}Si_3Tb$	$C_{86}H_{85}CeO_6Si_3$	$C_{86}H_{85}O_6Si_3Tb$	$C_{86}H_{85}O_6PrSi_3$
$D_{calc.}$/ g cm^{-3}	1.331	1.289	1.338	1.294
μ/mm^{-1}	7.35	5.623	5.704	5.938
Formula Weight	1105.32	1438.92	1457.72	1439.71
Colour	clear pale colourless	clear pale colourless	clear pale colourless	clear pale colourless
Shape	irregular-shaped	prism-shaped	prism-shaped	prism-shaped
Size/mm^3	0.16×0.09×0.06	0.29×0.11×0.09	0.21×0.06×0.05	0.12×0.11×0.06
T/K	140.01(10)	200.00(11)	140.00(10)	200.00(10)
Crystal System	triclinic	triclinic	triclinic	triclinic
Space Group	P-1	P-1	P-1	P-1
a/Å	13.9674(4)	11.2033(3)	11.1371(2)	11.1967(4)
b/Å	18.1707(4)	14.3534(3)	14.2669(3)	14.3423(5)
c/Å	21.7736(4)	24.5094(5)	24.2013(5)	24.4587(6)
α/°	89.0799(15)	106.2354(18)	106.0855(17)	106.237(3)
β/°	88.765(2)	99.3584(18)	99.4980(18)	99.362(3)
γ/°	87.017(2)	93.8891(17)	93.6846(16)	93.699(3)
V/Å^3	5516.7(2)	3706.92(14)	3619.57(13)	3695.7(2)
Z	4	2	2	2
Z'	2	1	1	1
Wavelength/Å	1.54184	1.54184	1.54184	1.54184
Radiation type	Cu Kα	Cu Kα	Cu Kα	Cu Kα
Θ_{min}/°	3.148	3.23	3.246	3.231
Θ_{max}/°	72.726	77.152	72.633	72.48
Measured Refl's.	45368	40854	28022	32715
Indep't Refl's	21318	15358	13994	14258
Refl's I≥2 σ(I)	16912	13941	13011	13154
R_{int}	0.0435	0.0401	0.0333	0.0257
Parameters	1293	933	964	942
Restraints	230	454	420	418
Largest Peak	1.043	0.875	0.678	0.63
Deepest Hole	-1.382	-0.512	-0.946	-0.342
GooF	1.018	1.011	1.029	1.021
wR_2 (all data)	0.1072	0.0947	0.0786	0.0692
wR_2	0.0986	0.0891	0.0762	0.0668
R_1 (all data)	0.0585	0.0421	0.0356	0.0312
R_1	0.0421	0.0363	0.0316	0.027
Flack Parameter	/	/	/	/
Hooft Parameter	/	/	/	/

Table S2. Crystal data and structural refinement parameters for complexes **2-Ce^{OtBu}·0.9(THF)**, **2-Tb^{OtBu}·0.9(THF)**, **2-Tb^{Ph}·0.5(toluene)**, **2-Pr^{Ph}-MeCN·4(MeCN)**

	2-Ce^{OtBu}·0.9(THF)	**2-Tb^{OtBu}·0.9(THF)**	**2-Tb^{Ph}·0.5(toluene)**	**2-Pr^{Ph}-$_{MeCN}$·4(MeCN)**
Formula	$C_{88}H_{128}CeKO_{15.5}Si_4$	$C_{98.8}H_{149.6}KO_{18.2}Si_4Tb$	$C_{88.5}H_{72}KO_4Si_4Tb$	$C_{92}H_{81}KN_7O_4PrSi_4$
$D_{calc.}$/ g cm^{-3}	1.079	1.221	1.346	1.316
μ/mm^{-1}	4.508	4.568	6.186	5.951
Formula Weight	1725.48	1938.96	1509.921	1641
Colour	clear pale colourless	clear pale colourless	lustrous pale colourless	clear pale colourless
Shape	prism-shaped	irregular-shaped	irregular-shaped	prism-shaped
Size/mm^3	0.41×0.28×0.23	0.29×0.16×0.08	0.22×0.14×0.12	0.28×0.09×0.08
T/K	200.00(11)	199.99(12)	200.00(11)	139.99(10)
Crystal System	hexagonal	hexagonal	triclinic	monoclinic
Space Group	$P6_322$	$P6_322$	P-1	$P2_1/n$
a/Å	14.87393(16)	14.7864(3)	14.0838(14)	13.65640(10)
b/Å	14.87393(16)	14.7864(3)	14.2282(17)	43.2742(5)
c/Å	55.4259(7)	55.7285(10)	21.775(3)	14.24030(10)
α/°	90	90	77.38(1)	90
β/°	90	90	74.179(9)	100.1850(10)
γ/°	120	120	63.234(11)	90
V/Å^3	10619.3(3)	10551.9(4)	3724.9(8)	8282.97(13)
Z	4	4	2	4
Z'	0.333333	0.333333	1	1
Wavelength/Å	1.54184	1.54184	1.54184	1.54184
Radiation type	Cu Kα	Cu Kα	Cu Kα	Cu Kα
Θ_{min}/°	3.189	3.172	3.5	3.314
Θ_{max}/°	72.678	72.734	73	75.748
Measured Refl's.	86994	58647	29995	84003
Indep't Refl's	7038	6978	14275	16596
Refl's I≥2 σ(I)	6906	6285	9012	14190
R_{int}	0.0379	0.0585	0.0757	0.0684
Parameters	400	394	985	906
Restraints	551	484	630	0
Largest Peak	0.909	0.569	1.225	1.523
Deepest Hole	-0.6	-0.689	-1.2251	-1.476
GooF	1.088	1.074	1.0844	1.02
wR_2 (all data)	0.1561	0.1747	0.2509	0.161
wR_2	0.1554	0.1709	0.2142	0.1539
R_1 (all data)	0.0588	0.0751	0.1308	0.0693
R_1	0.0581	0.0695	0.085	0.0597
Flack Parameter	0.071(10)	0.429(12)	/	/
Hooft Parameter	-0.0349(11)	-0.007(2)	/	/

Table S3. Crystal data and structural refinement parameters for complexes **3-Ce^{OtBu}·3.5(toluene)**, **3-Ce^{Ph}·4(THF)**, **3-Tb^{Ph}·2.5(MeCN)** and **1-Tb^{Ph}-CH$_3$CN**

	3-Ce^{OtBu}·3.5(toluene)	**3-Ce^{Ph}·4(THF)**	**3-Tb^{Ph}·2.5(MeCN)**	**1-Tb^{Ph}-CH$_3$CN**
Formula	$C_{90.5}H_{112}CeO_{10}Si_4$	$C_{102}H_{108}CeO_{10}Si_4$	$C_{87}H_{73.5}N_{4.5}O_4Si_4Tb$	$C_{66}H_{54}N_3O_3Si_3Tb$
$D_{calc.}$/ g cm^{-3}	1.243	1.294	1.296	1.38
μ/mm^{-1}	5.052	4.902	5.474	7.113
Formula Weight	1612.27	1746.36	1517.28	1180.31
Colour	clear light yellow	clear pale colourless	clear dark orange	clear light yellow
Shape	plate-shaped	irregular-shaped	prism-shaped	prism-shaped
Size/mm^3	0.17×0.12×0.01	0.31×0.20×0.07	0.31×0.21×0.19	0.20×0.15×0.12
T/K	140.00(10)	139.99(10)	200.00(10)	140.00(10)
Crystal System	triclinic	orthorhombic	monoclinic	monoclinic
Space Group	P-1	$P2_12_12_1$	$P2_1/c$	$P2_1/n$
a/Å	14.49307(15)	15.94855(11)	17.6194(3)	13.79296(19)
b/Å	14.67810(14)	22.45159(16)	13.8469(3)	22.3194(2)
c/Å	20.2591(3)	25.03370(19)	31.8914(5)	18.4603(2)
α/°	89.6876(9)	90	90	90
β/°	88.7540(10)	90	91.3763(14)	91.7441(12)
γ/°	89.3655(8)	90	90	90
V/Å^3	4308.40(8)	8963.82(11)	7778.4(2)	5680.36(12)
Z	2	4	4	4
Z'	1	1	1	1
Wavelength/Å	1.54184	1.54184	1.54184	1.54184
Radiation type	Cu Kα	Cu Kα	Cu Kα	Cu Kα
Θ_{min}/°	3.011	3.286	2.772	3.107
Θ_{max}/°	74.677	72.628	72.539	74.747
Measured Refl's.	69611	39009	42724	57303
Indep't Refl's	16949	17348	15006	11268
Refl's I≥2σ(I)	15368	16665	11807	9232
R_{int}	0.0278	0.0272	0.0369	0.037
Parameters	1146	1035	868	784
Restraints	1139	534	36	421
Largest Peak/e Å^{-3}	0.753	0.592	0.73	1.732
Deepest Hole/e Å^{-3}	-0.59	-0.451	-0.467	-1.125
GooF	1.022	1.03	1.068	1.035
wR_2 (all data)	0.0887	0.1097	0.1069	0.1472
wR_2	0.0863	0.1073	0.0997	0.1396
R_1 (all data)	0.0408	0.0431	0.0555	0.065
R_1	0.0354	0.0409	0.0412	0.0516
Flack Parameter	/	-0.0133(17)	/	/
Hooft Parameter	/	-0.013(2)	/	/

Table S4. Crystal data and structural refinement parameters for complex **2-Tb^{Ph}-MeCN·(Et$_2$O)**

	2-Tb^{Ph}-MeCN·(Et$_2$O)
Formula	$C_{168}H_{142}K_2N_4O_9Si_8Tb_2$
$D_{calc.}$/ g cm^{-3}	1.391
μ/mm^{-1}	6.477
Formula Weight	2981.61
Colour	clear pale colourless
Shape	prism
Size/mm^3	0.22×0.13×0.09
T/K	139.99(10)
Crystal System	triclinic
Space Group	P-1
a/Å	14.6865(6)
b/Å	15.3137(6)
c/Å	18.9586(6)
α/°	87.191(3)
β/°	67.976(3)
γ/°	65.256(4)
V/Å^3	3560.2(3)
Z	1
Z'	0.5
Wavelength/Å	1.54184
Radiation type	Cu K$_\alpha$
Θ_{min}/°	2.535
Θ_{max}/°	72.469
Measured Refl's.	28996
Indep't Refl's	13709
Refl's I≥2σ(I)	12635
R_{int}	0.0322
Parameters	849
Restraints	0
Largest Peak/e Å^{-3}	0.634
Deepest Hole/e Å^{-3}	-0.699
GooF	1.018
wR_2 (all data)	0.0871
wR_2	0.0841
R_1 (all data)	0.0378
R_1	0.0335
Flack Parameter	/
Hooft Parameter	/

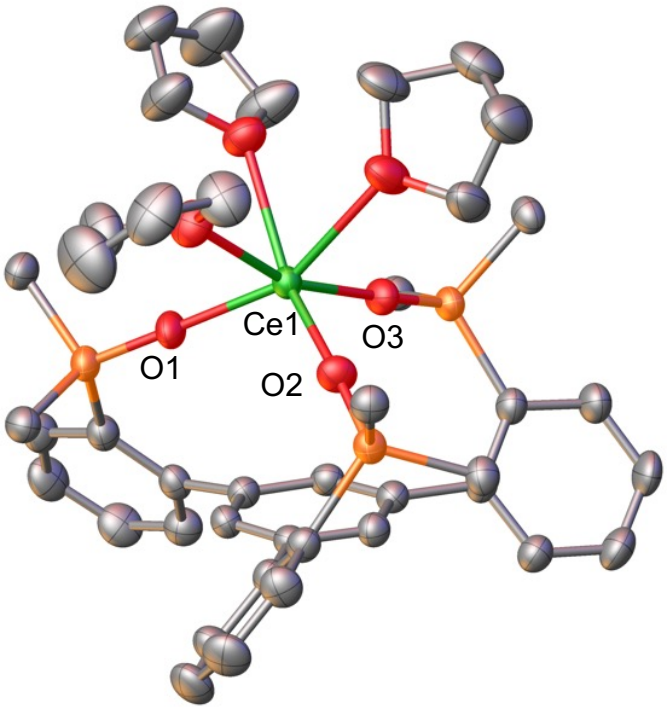


Figure S47. Molecular structure of complex, [Ce^{III}((OSiPh_2Ar)$_3$-arene)(THF)$_3$], **1-Ce^{Ph}** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms, some disordered substituents and the five carbon atoms of each phenyl groups have been omitted for clarity.

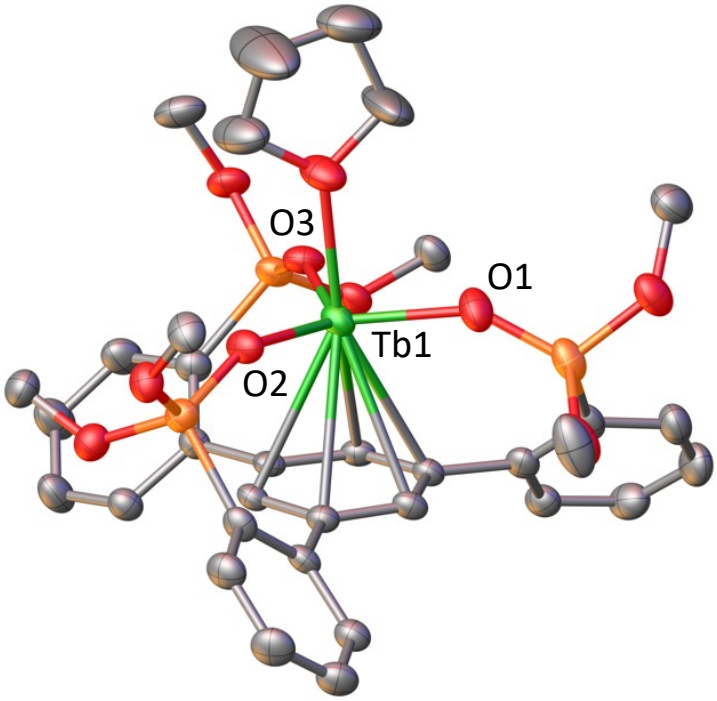


Figure S48. Molecular structure of complex, [Tb^{III}((OSi(O^{t}Bu)$_2$Ar)$_3$-arene)(THF)], **1-Tb^{OtBu}** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms, some disordered substituents and the methyl groups on the –O(SiO^{t}Bu)$_2$ arms have been omitted for clarity.

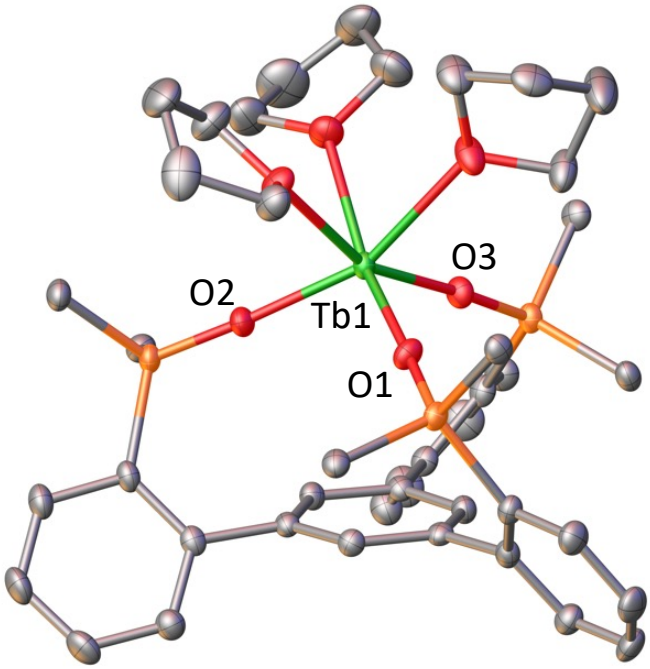


Figure S49. Molecular structure of complex, [Tb^{III}((OSiPh_2Ar)$_3$-arene)(THF)$_3$], **1-Tb^{Ph}** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms, some disordered substituents and the five carbon atoms of each phenyl groups have been omitted for clarity.

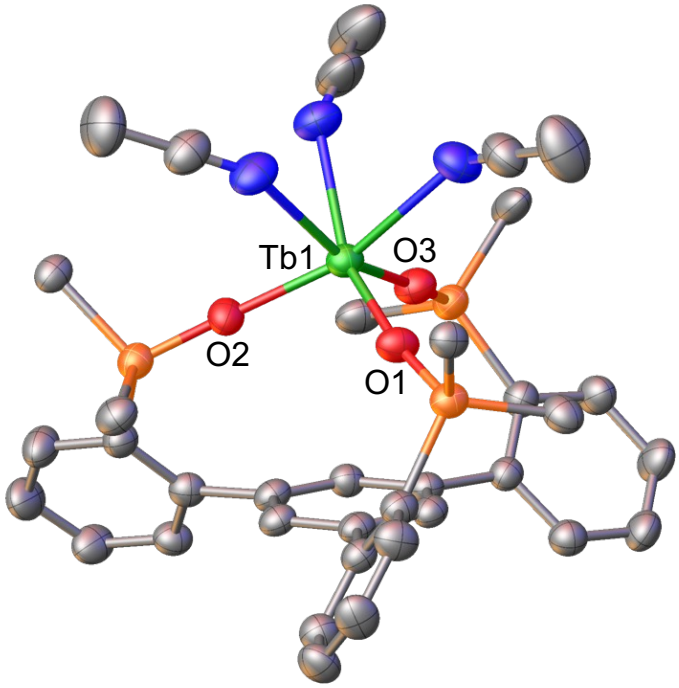


Figure S50. Molecular structure of the MeCN adduct of complex **1-Tb^{Ph}**, [Tb^{III}((OSiPh_2Ar)$_3$-arene)(MeCN)$_3$], with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms, some disordered substituents and the five carbon atoms of each phenyl groups have been omitted for clarity. Pertinent bond distances (Å) and angles (°): Tb1–O1: 2.120(3); Tb1–O2: 2.112(3); Tb1–O3: 2.107(3); Tb1–$C_{centroid}$; 3.960(2); O1–Tb1–O2: 102.72(13); O2–Tb1–O3: 102.61(13); O3–Tb1–O1: 103.89(14).

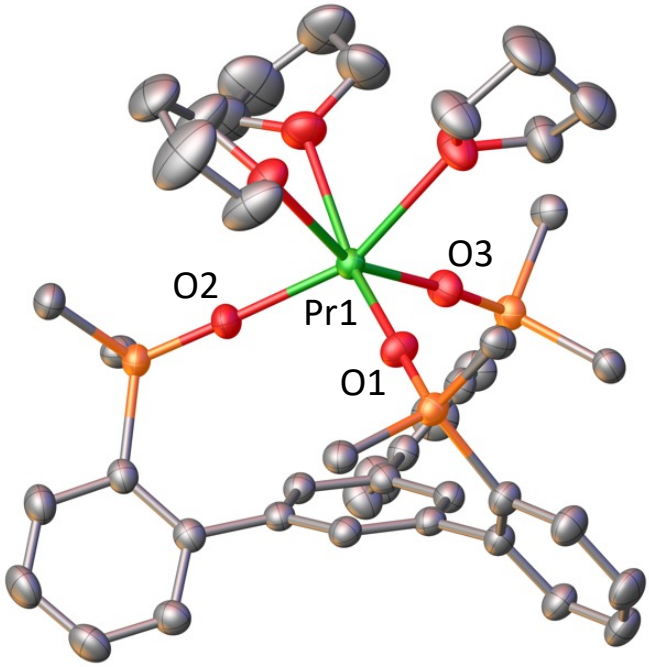


Figure S51. Molecular structure of complex, [Pr^{III}((OSiPh_2Ar)$_3$-arene)(THF)$_3$], **1-Pr^{Ph}** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms, some disordered substituents and the five carbon atoms of each phenyl groups have been omitted for clarity.

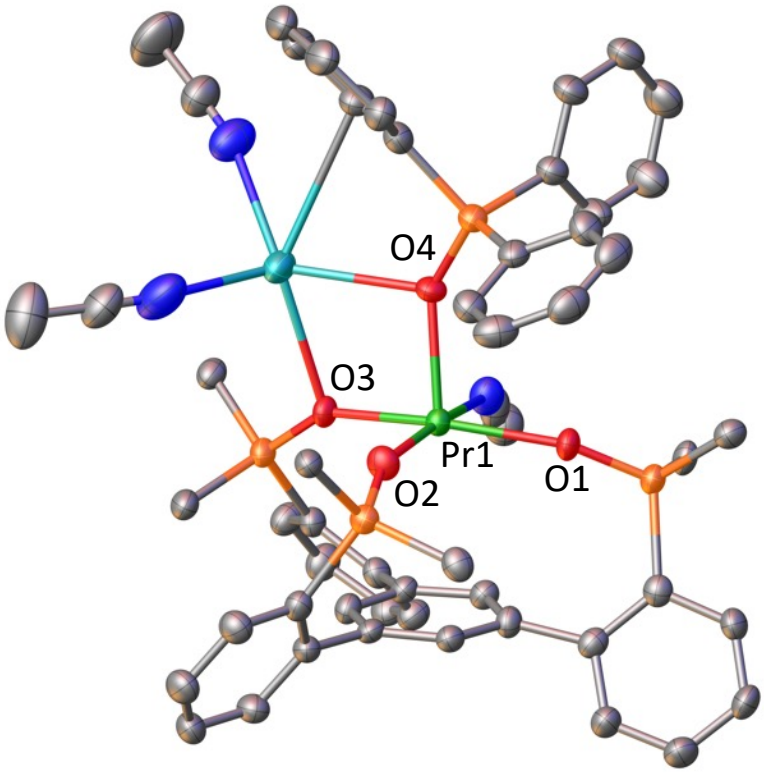


Figure S52. Molecular structure of complex, [K(MeCN)$_2${Pr^{III}((OSiPh_2Ar)$_3$-arene)(OSiPh_3)(MeCN)}], **2-Pr^{Ph}-MeCN·4(MeCN)** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms, some disordered substituents and the five carbon atoms of each phenyl groups of the (OSiPh_2Ar)$_3$-arene) ligand have been omitted for clarity.

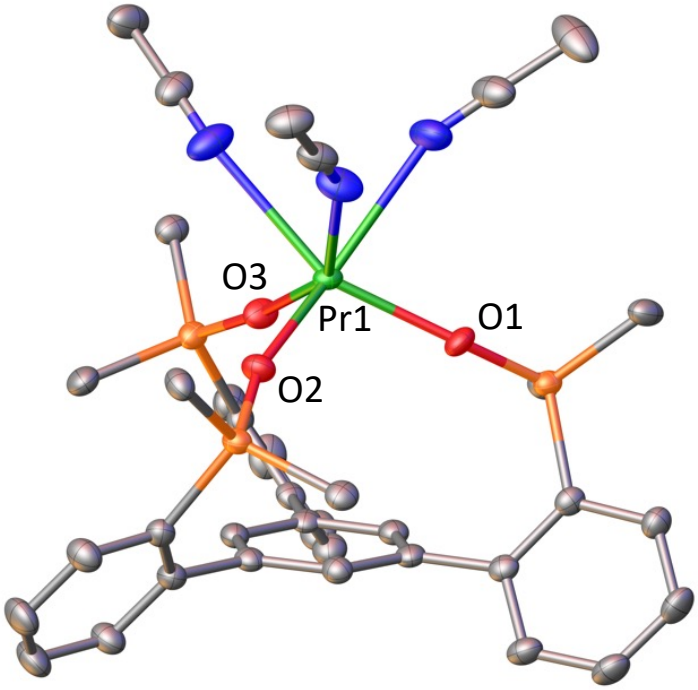


Figure S53. Molecular structure of complex [Pr^{III}((OSiPh_2Ar)$_3$-arene)(MeCN)$_3$], **1-Pr^{Ph}-CH_3CN**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms, some disordered substituents and the five carbon atoms of each phenyl groups have been omitted for clarity. Pertinent bond distances (Å) and angles (°): Pr1–O1: 2.202(1); Pr1–O2: 2.197(2); Pr1–O3: 2.191(2); Pr1–$C_{centroid}$; 4.163(1); O1–Pr1–O2: 103.48(8); O2–Pr1–O3: 100.44(9); O3–Pr1–O1: 101.86(8).

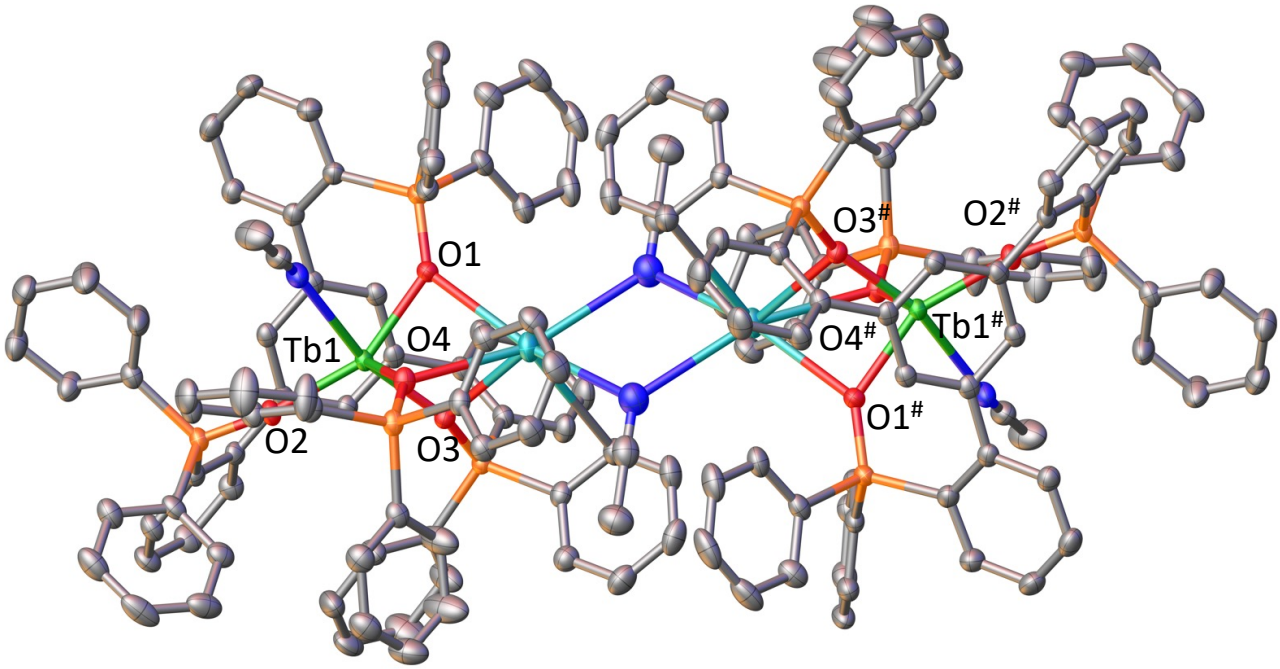


Figure S54. Molecular structure of complex [K(MeCN){Tb^{III}((OSiPh_2Ar)$_3$-arene)(OSiPh_3)(MeCN)}]$_2$, **2-$Tb^{Ph\text{-}MeCN}$**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Pertinent bond distances (Å) Tb1–O1 2.2170(18); Tb1–O2 2.1632(18); Tb1–O3 2.1784(17); Tb1–O4 2.1731(18).

Complex **2-Tb^{Ph}-MeCN·(Et_2O)** crystalizes in the *P-1* space group. The asymmetric unit is composed of one **2-Tb^{Ph}** moiety where which both K and Tb ions are coordinated by one MeCN molecule each. The overall structure is generated by symmetry and reveals a dimeric form with two MeCN molecules bound to potassium bridging the two **2-Tb^{Ph}** fragments.

S5. EPR Data

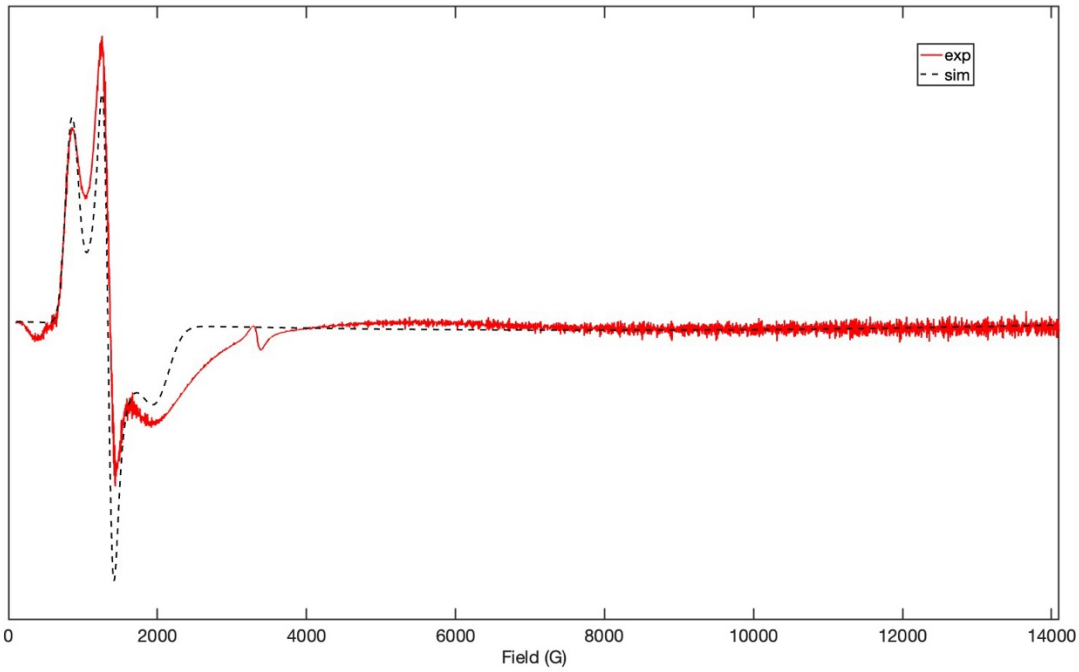


Figure S55. X-band (9.4 GHz) EPR spectrum of complex **3-Tb^{Ph}** in the solid-state at 6 K (*red line*, experiment; *black dashed line*, fit to $4f^7$ ion). The plot was fit to a rhombic set of *g*-values [7.90, 5.00, 3.35]

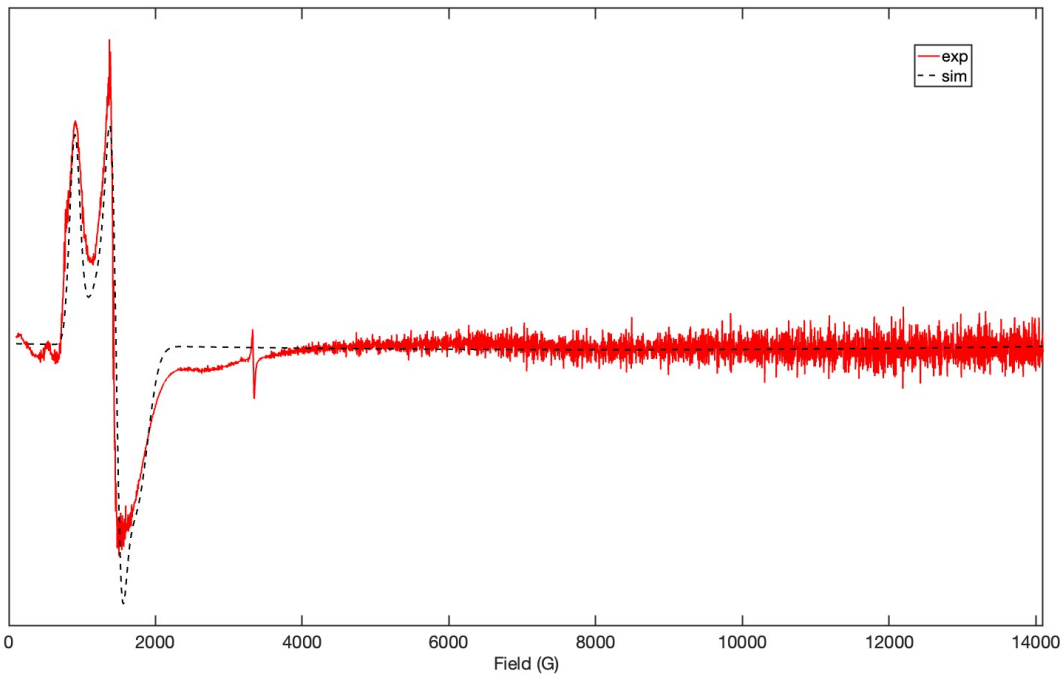


Figure S56. X-band (9.4 GHz) EPR spectrum of complex **3-Tb^{Ph}** in toluene (20 mM) at 6 K (*red line*, experiment; *black dashed line*, fit to $4f^7$ ion). The plot was fit to a rhombic set of *g*-values [7.45, 4.55, 3.75]

S6. Magnetization Data

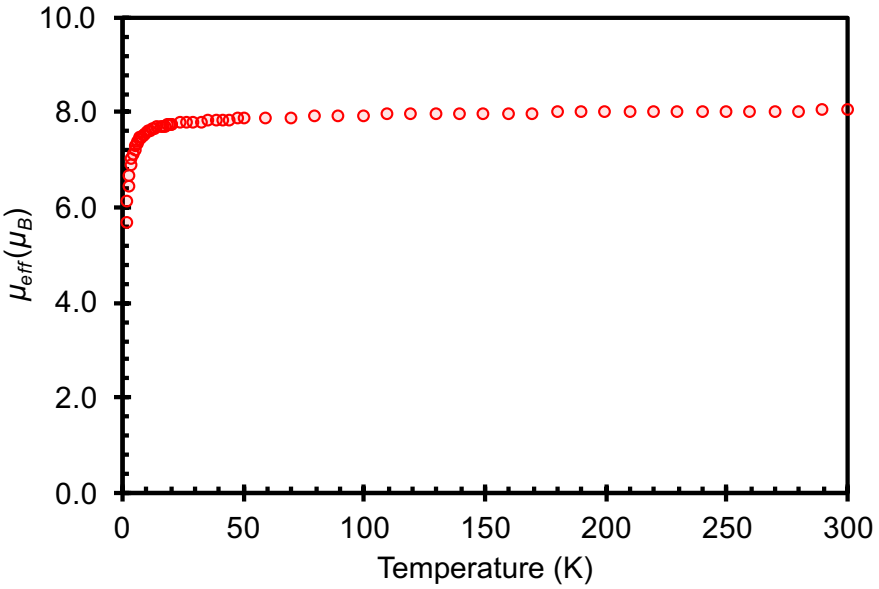


Figure S57. Temperature-dependent SQUID magnetization data (1 T) for complex **3-Tb^{Ph}**, plotted as the magnetic moment, μ_{eff}.

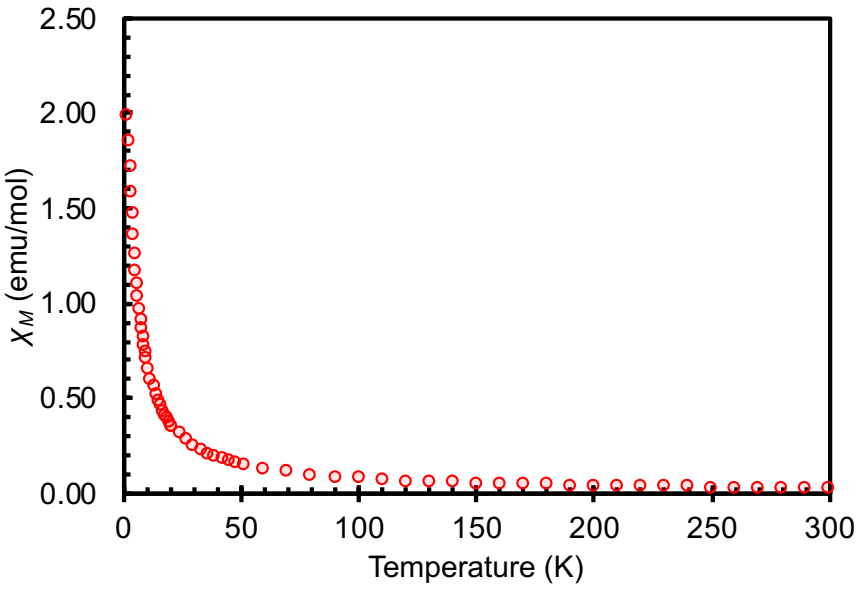


Figure S58. Temperature-dependent SQUID magnetization data (1 T) for complex **3-Tb^{Ph}**, plotted as the magnetic susceptibility, χ_M.

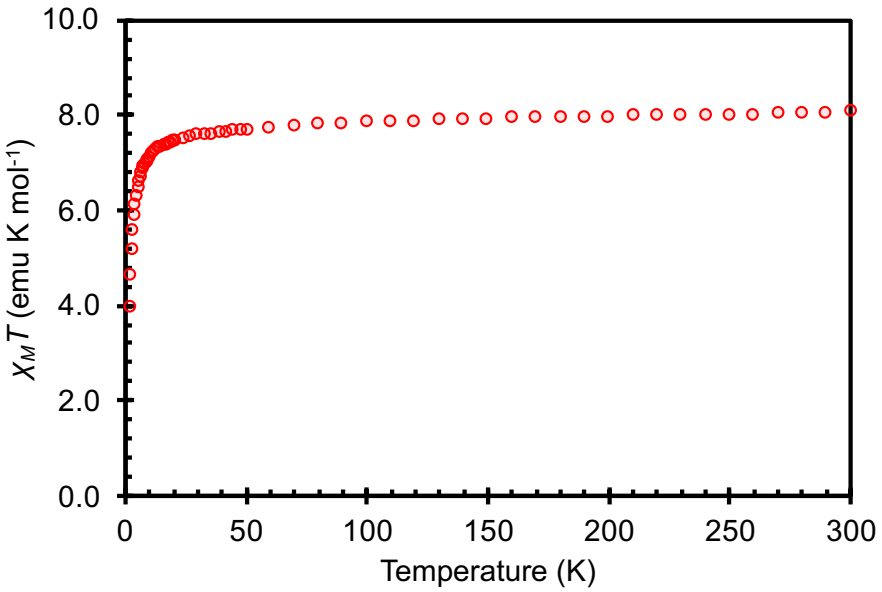


Figure S59. Temperature-dependent SQUID magnetization data (1 T) for complex **3-Tb^{Ph}**, plotted as the magnetic susceptibility versus temperature, $\chi_M T$.

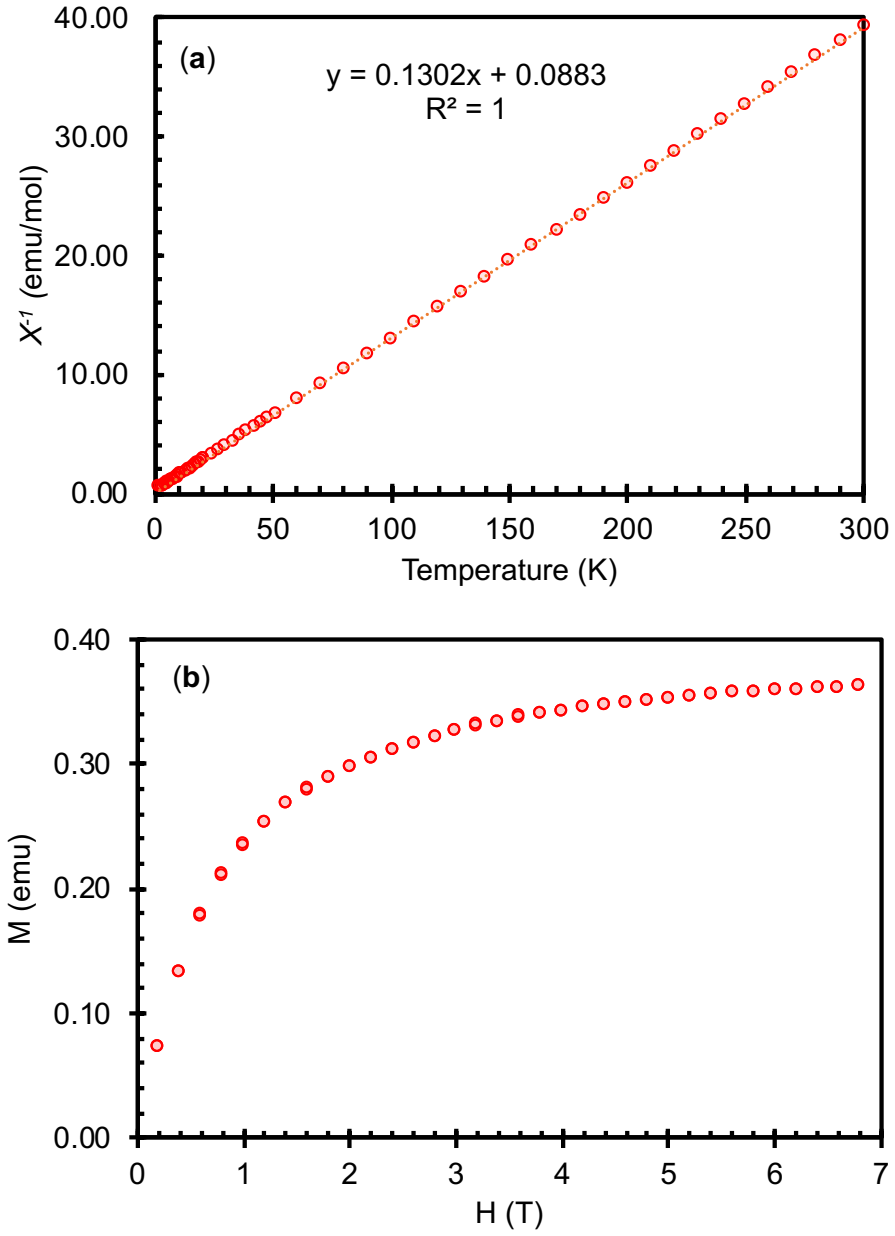


Figure S60. (a) Plot of χ^{-1} versus temperature for **3-Tb^{Ph}** under an applied field of 1 T. (b) Magnetization data at 2 K from 0 to 7 T.

S7. UV/Vis Data

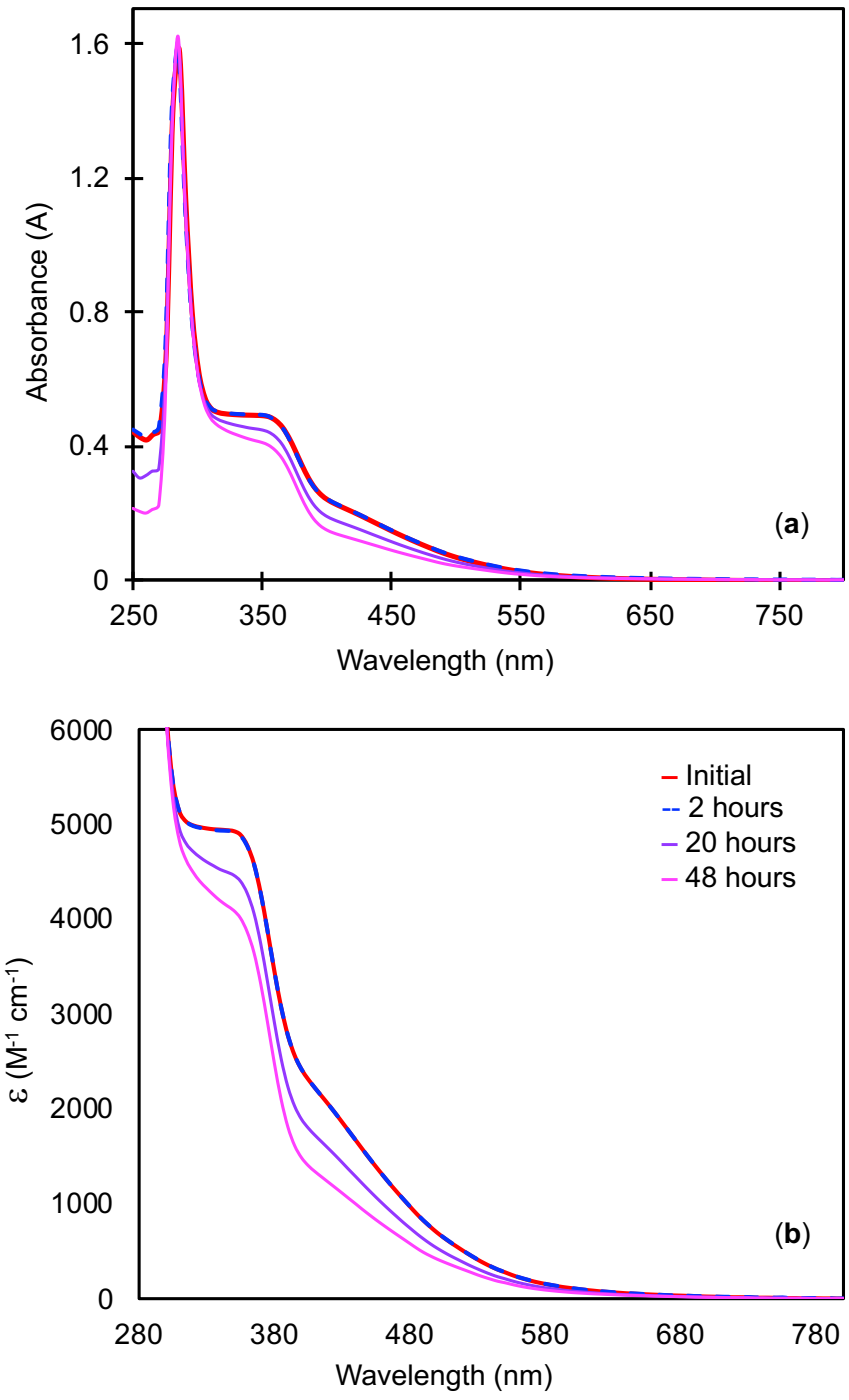


Figure S61. (a) UV/Vis spectra for complex **3-Tb^{Ph}** (1.0 mM) in toluene (*red*, initial); (*blue-dashed*, after 2 hours); (*purple*, after 20 hours); and (*pink*, after 48 hours. (b) Zoomed-in spectra of the absorption band at λ_{max} = 355 nm.

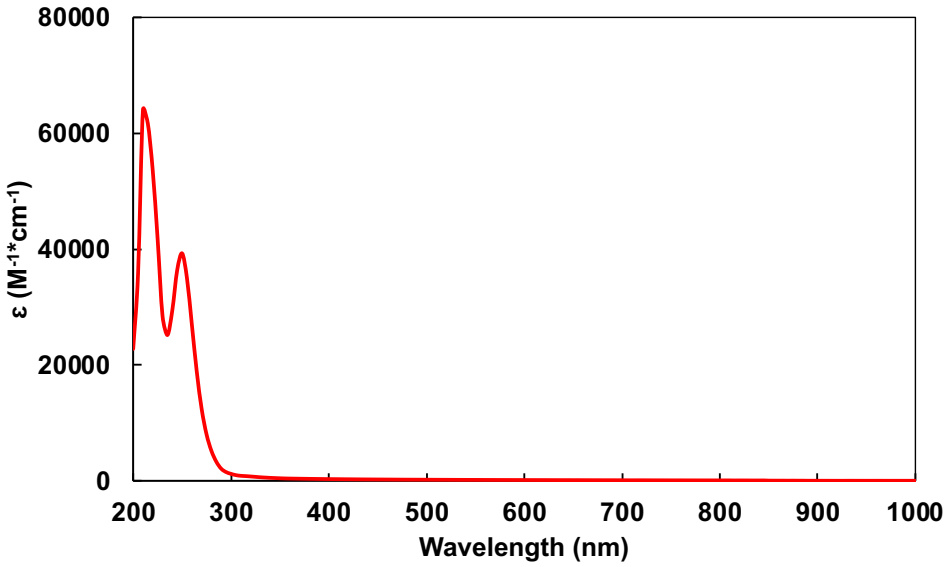


Figure S62. UV-Vis spectrum of a 0.4 mM solution of **2-Ce^{OtBu}** in THF at room temperature.

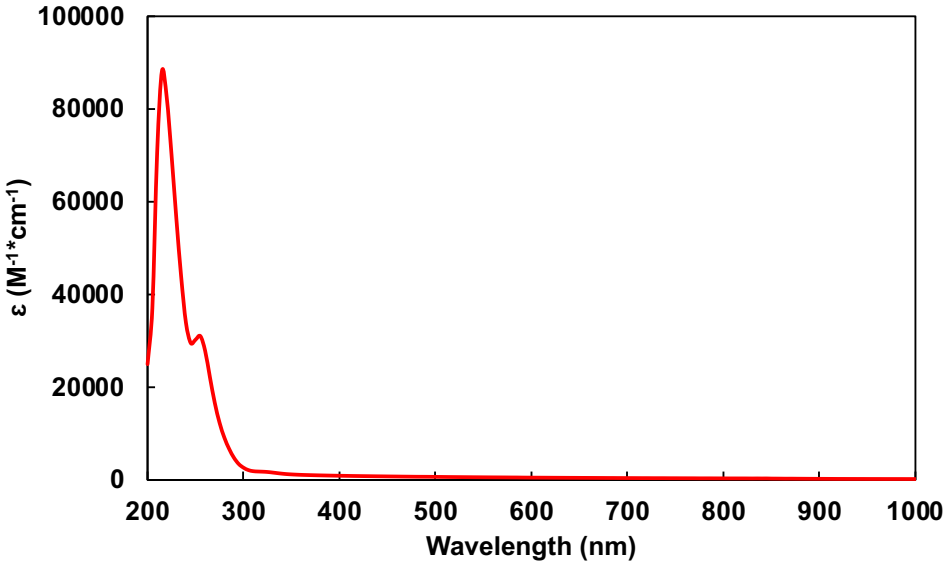


Figure S63. UV-Vis spectrum of a 0.4 mM solution of **2-Ce^{Ph}** in THF at room temperature.

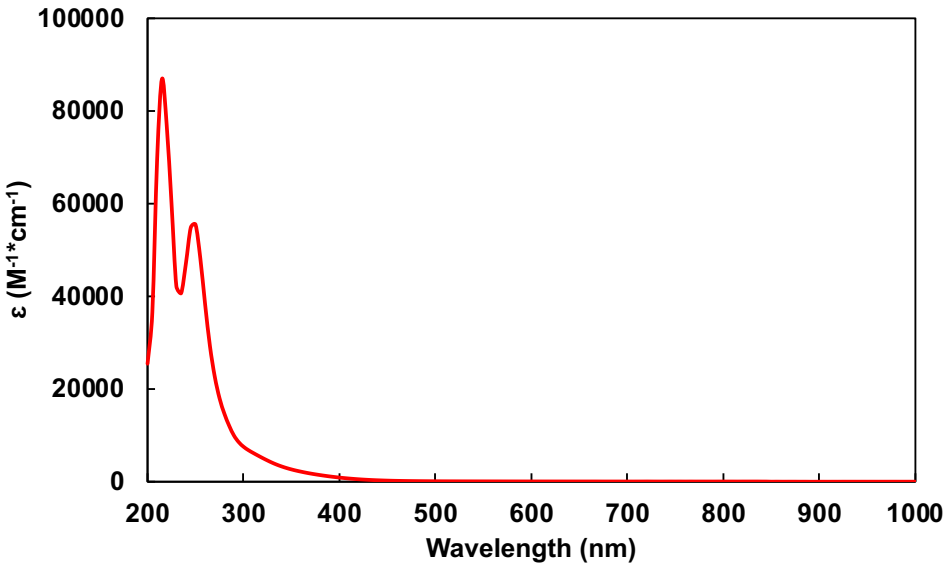


Figure S64. UV-Vis spectrum of a 0.4 mM solution of **3-Ce^{OtBu}** in THF at room temperature.

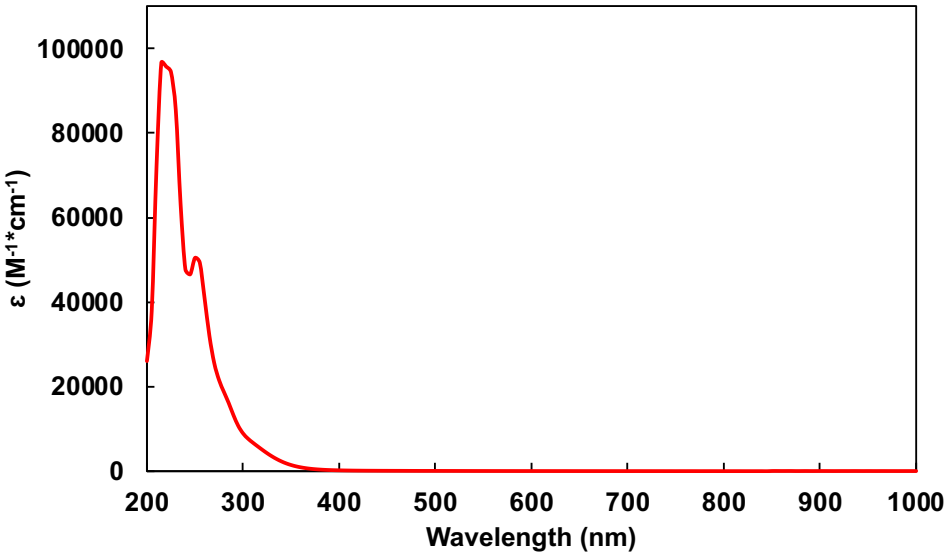


Figure S65. UV-Vis spectrum of a 0.4 mM solution of **3-Ce^{Ph}** in THF at room temperature.

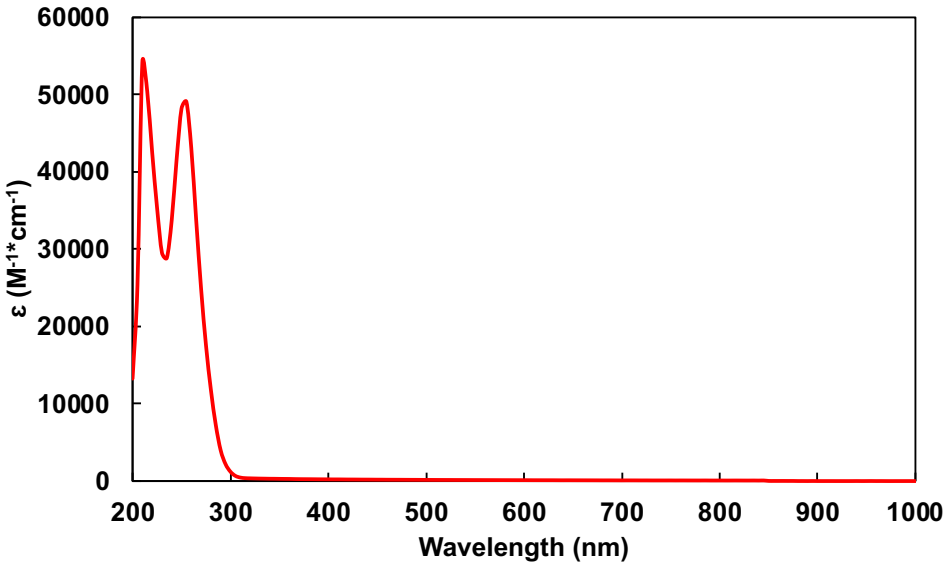


Figure S66. UV-Vis spectrum of a 0.4 mM solution of **1-Tb^{OtBu}** in THF at room temperature.

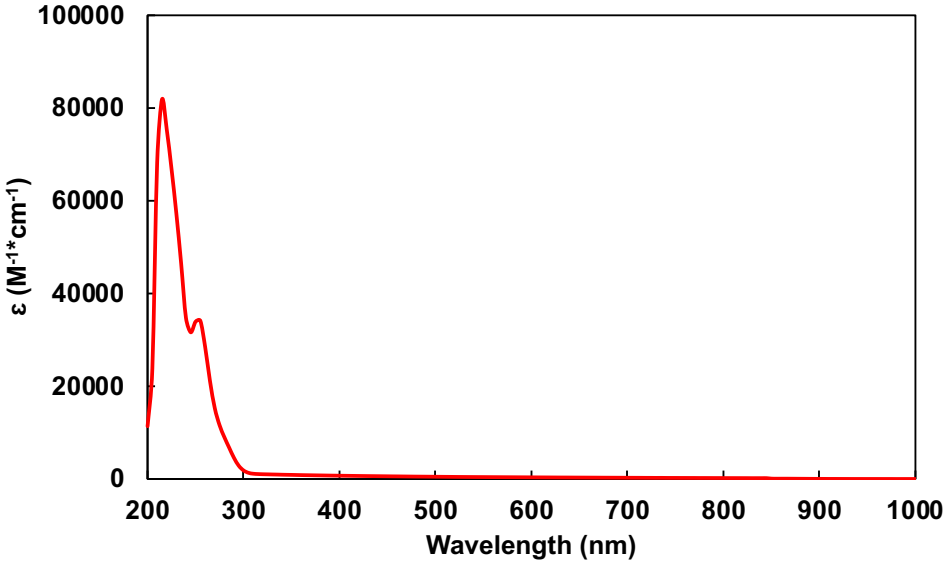


Figure S67. UV-Vis spectrum of a 0.4 mM solution of **1-Tb^{Ph}** in THF at room temperature.

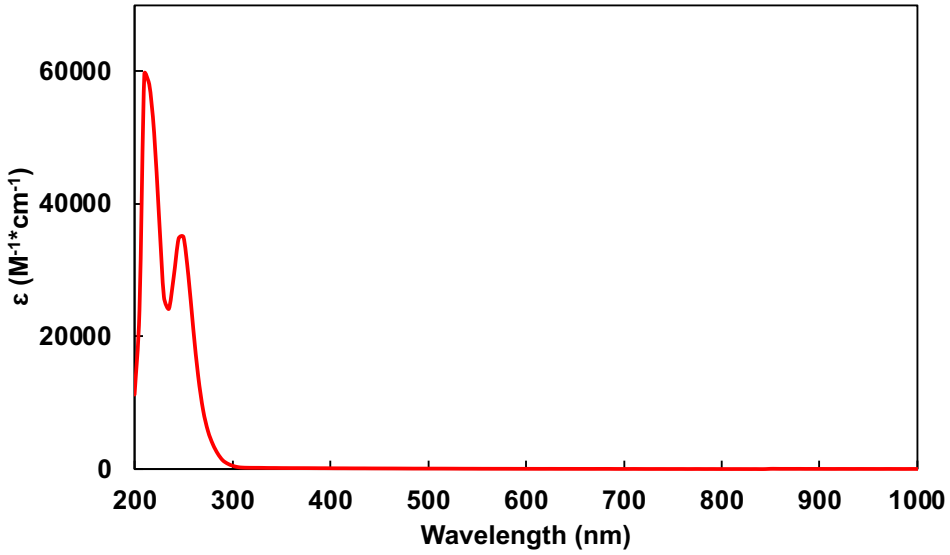


Figure S68. UV-Vis spectrum of a 0.4 mM solution of **2-Tb^{OtBu}** in THF at room temperature.

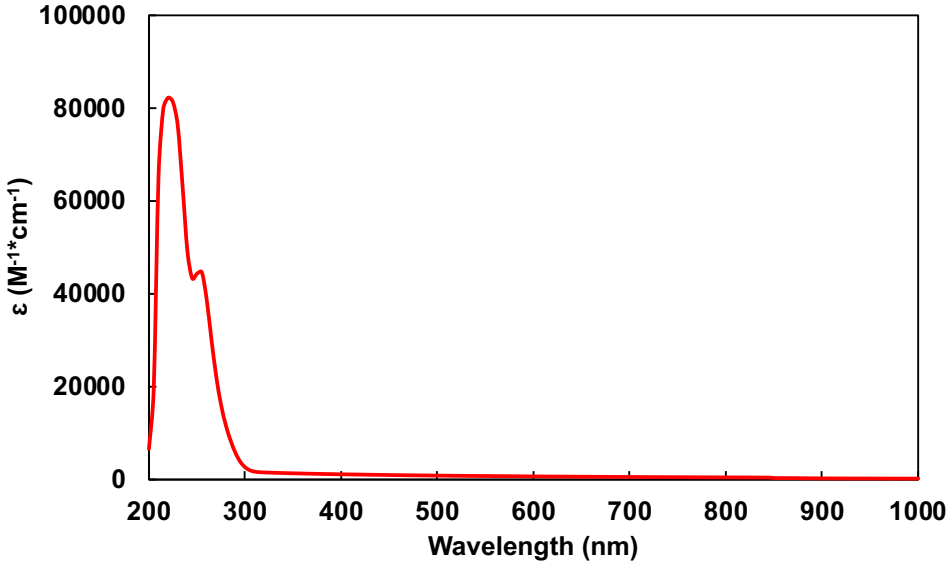


Figure S69. UV-Vis spectrum of a 0.4 mM solution of **2-Tb^{Ph}** in THF at room temperature.

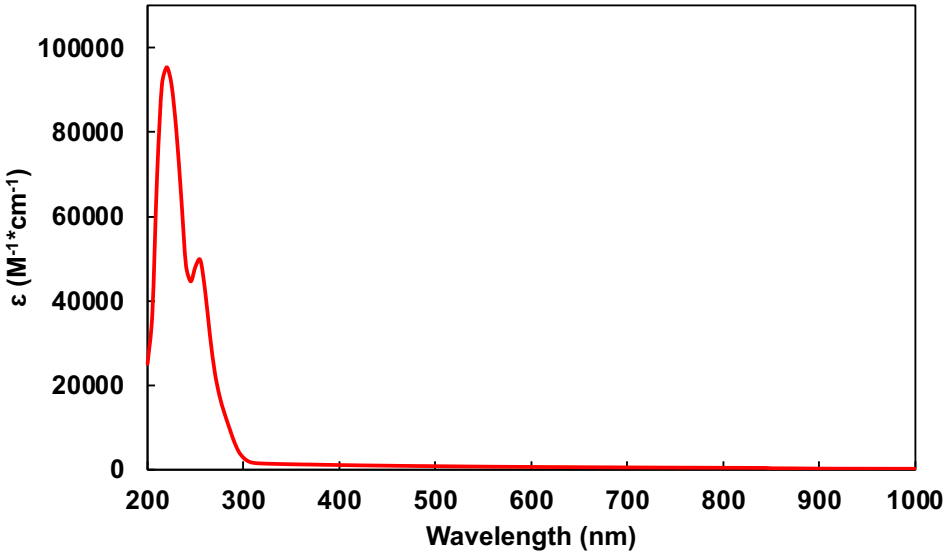


Figure S70. UV-Vis spectrum of a 0.4 mM solution of **1-Pr^{Ph}** in THF at room temperature.

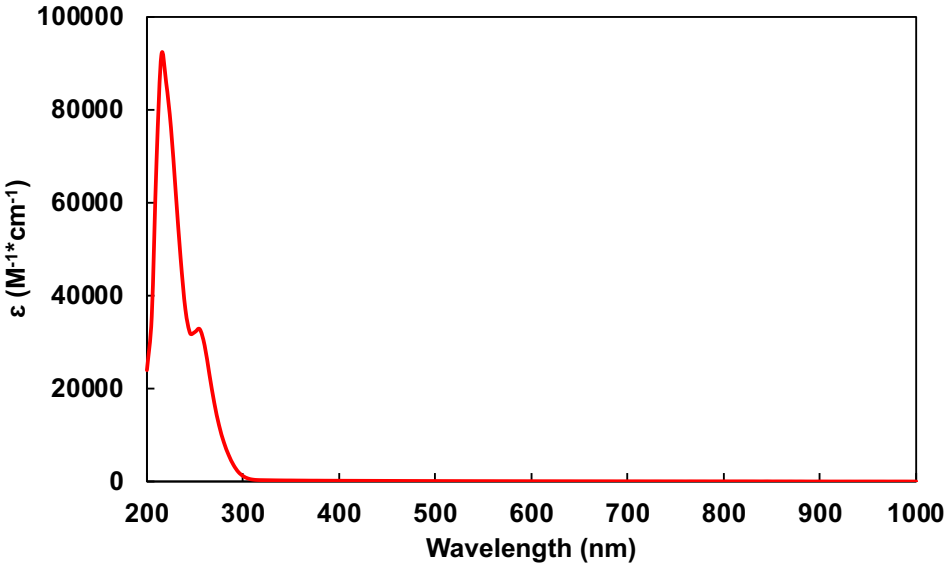


Figure S71. UV-Vis spectrum of a 0.4 mM solution of **2-Pr^{Ph}** in THF at room temperature.

S8. Electrochemistry Data

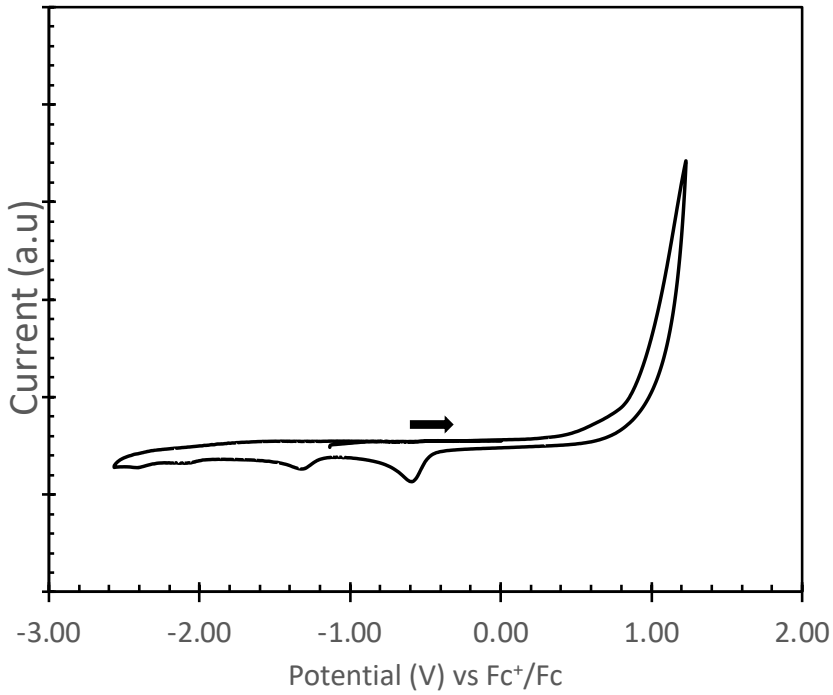


Figure S72. Cyclic voltammogram of NBu_4 $B(C_6F_5)_4$ electrolyte, in THF at room temperature with a 100mV/s scan rate.

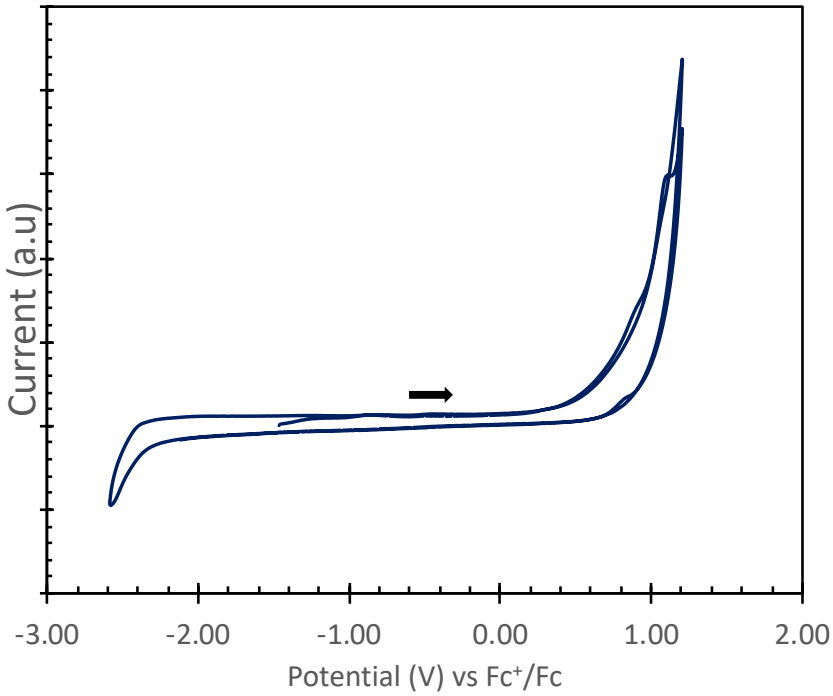


Figure S73. Cyclic voltammogram of the deprotonated free ligand $(KOSiPh_2Ar)_3$-arene, in THF at room temperature with a 100mV/s scan rate.

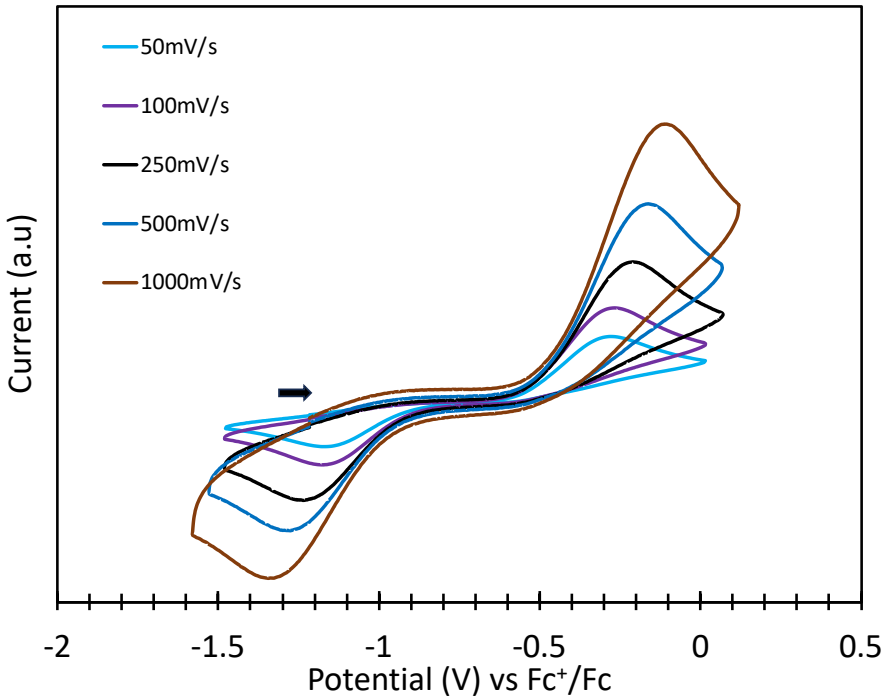


Figure S74. Cyclic voltammogram of **2-Ce^{OtBu}**, in THF at room temperature with varying scan rates.

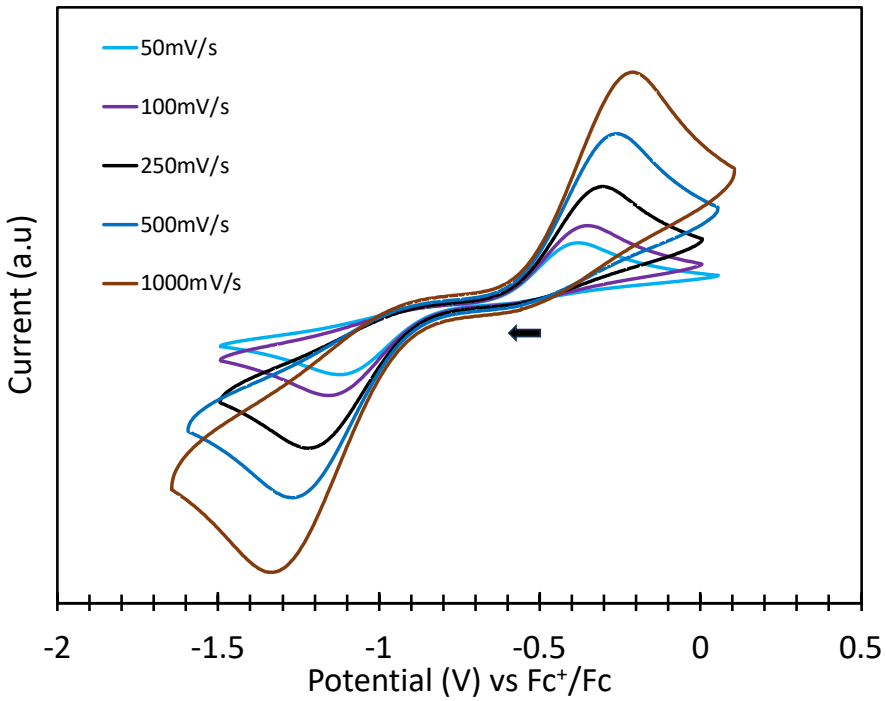


Figure S75. Cyclic voltammogram of **3-Ce^{OtBu}**, in THF at room temperature with varying scan rates.

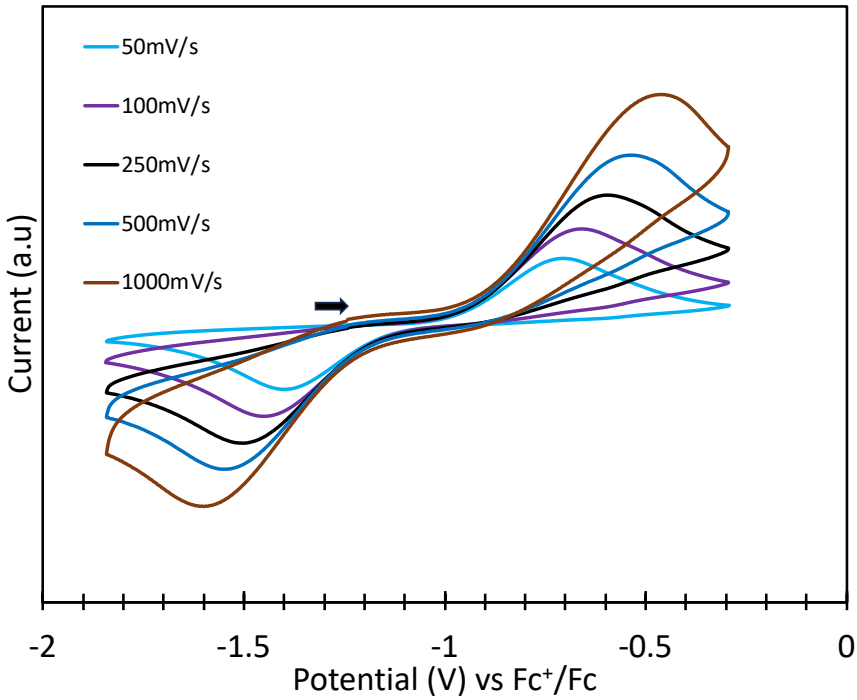


Figure S76. Cyclic voltammogram of **2-Ce^{Ph}**, in THF at room temperature with varying scan rates.

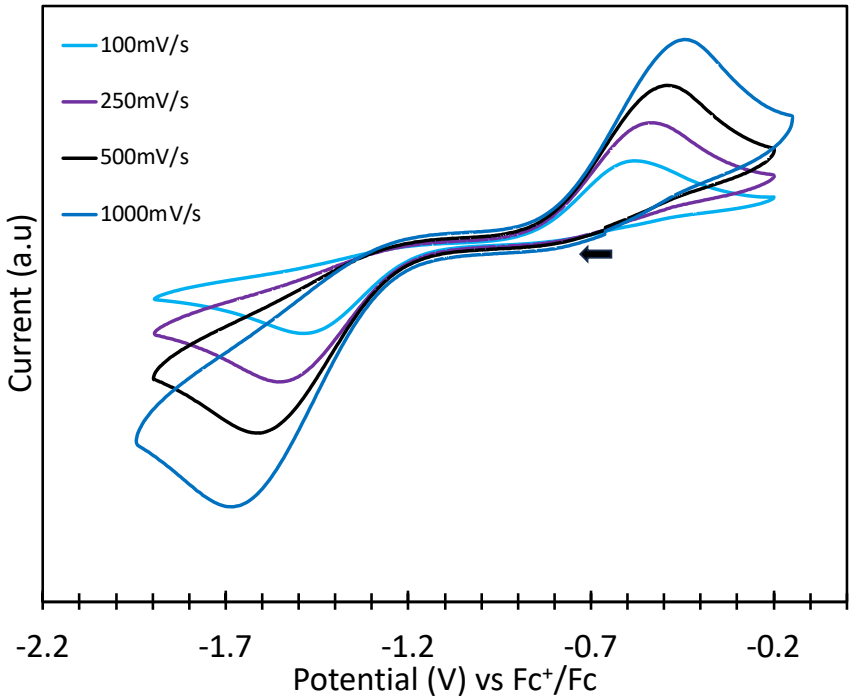


Figure S77. Cyclic voltammogram of **3-Ce^{Ph}**, in THF at room temperature with varying scan rates.

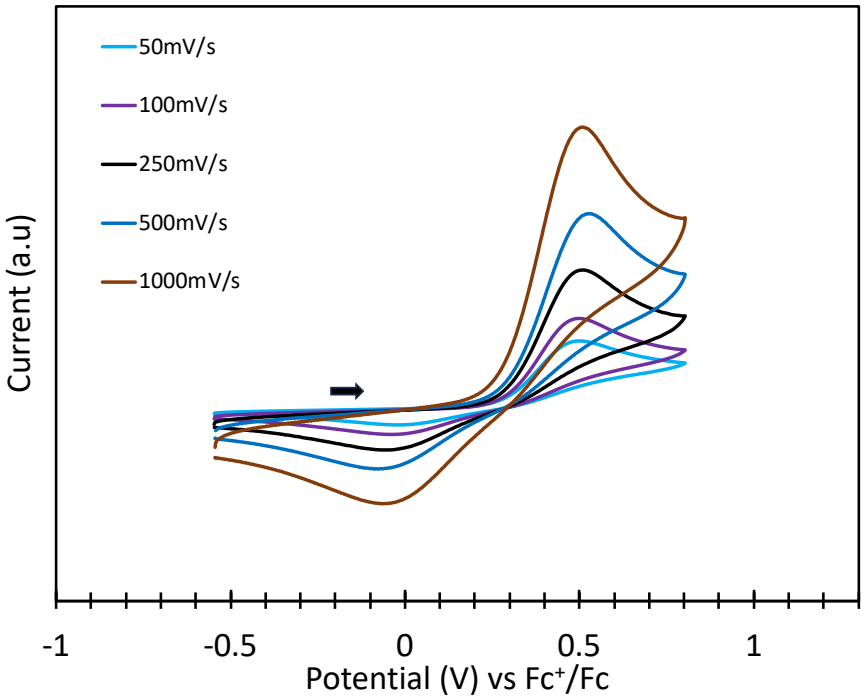


Figure S78. Cyclic voltammogram of **2-Tb^{Ph}**, in THF at room temperature with varying scan rates.

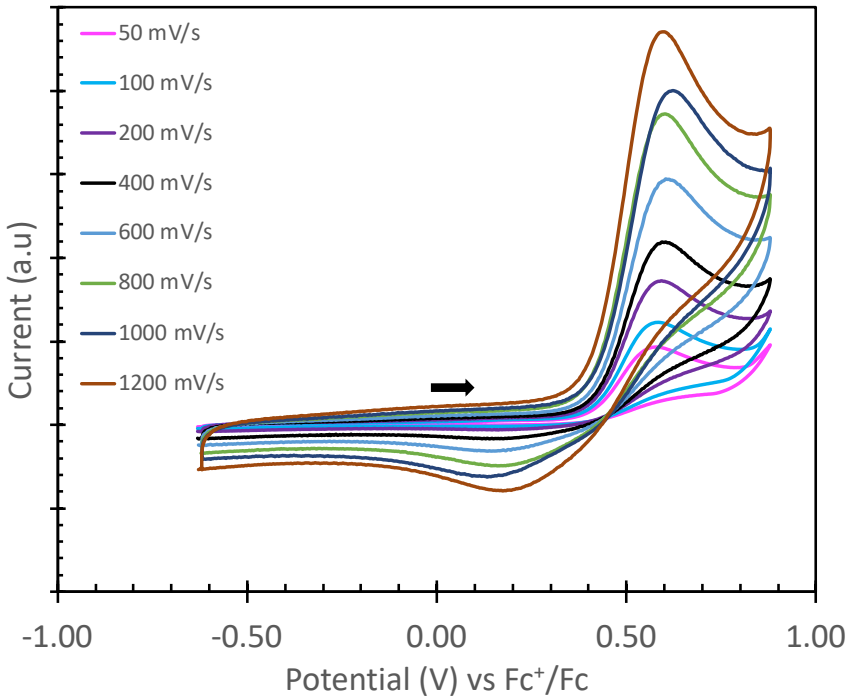


Figure S79. Cyclic voltammogram of **2-Pr^{Ph}**, in THF at room temperature with varying scan rates.

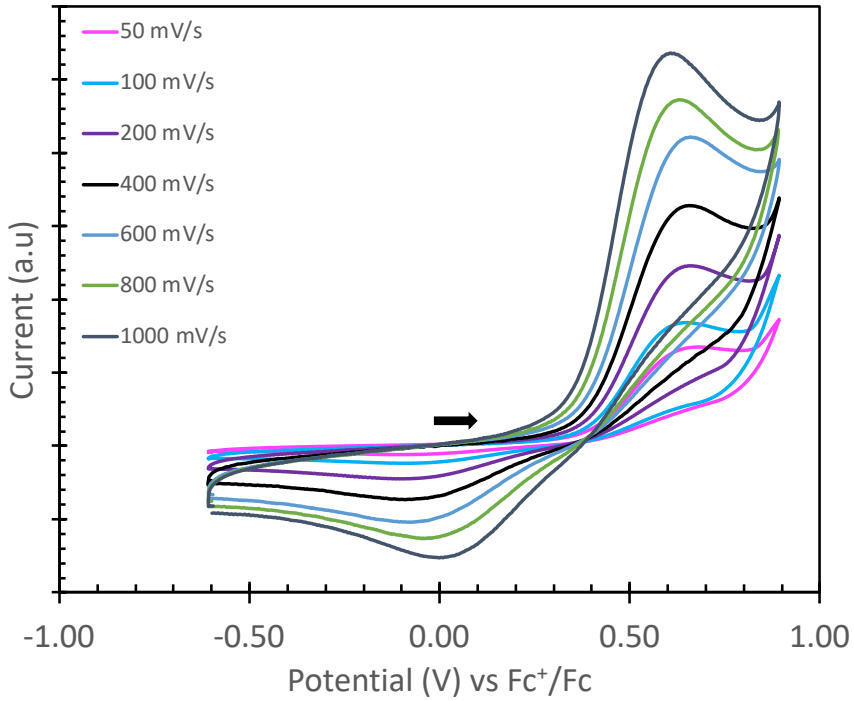


Figure S80. Cyclic voltammogram of **1-Tb^{Ph}** + 1.1 equiv. of KOSi(O^{t}Bu)$_3$, in THF at room temperature with varying scan rates.

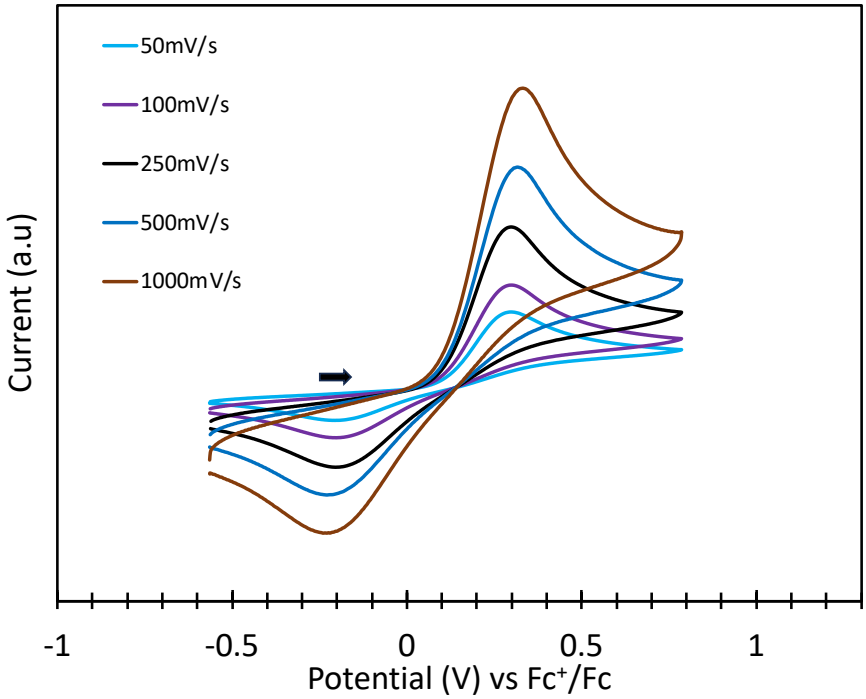


Figure S81. Cyclic voltammogram of **1-Tb^{Ph}** + 1.1 equiv. of KOSiMe$_3$, in THF at room temperature with varying scan rates.

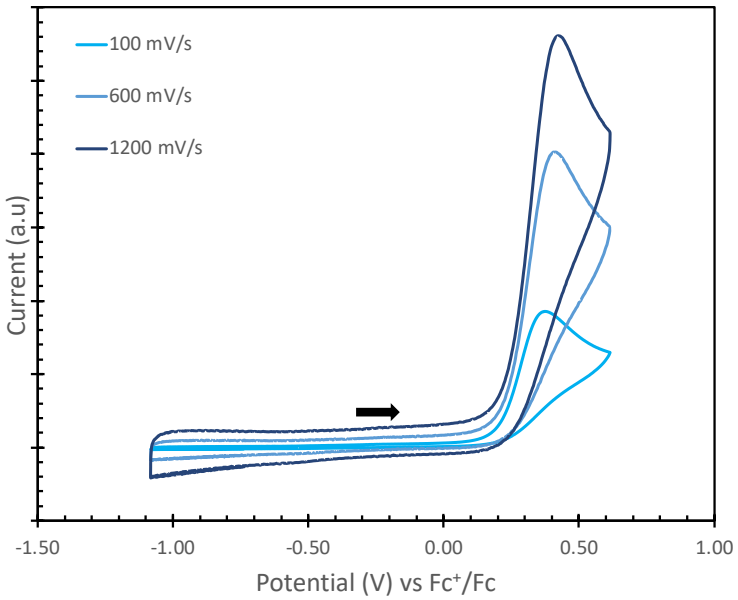


Figure S82. Cyclic voltammogram of **1-Tb^{Ph}** + 1.1 equiv. of $K(N(SiMe_3)_2$, in THF at room temperature with varying scan rates.

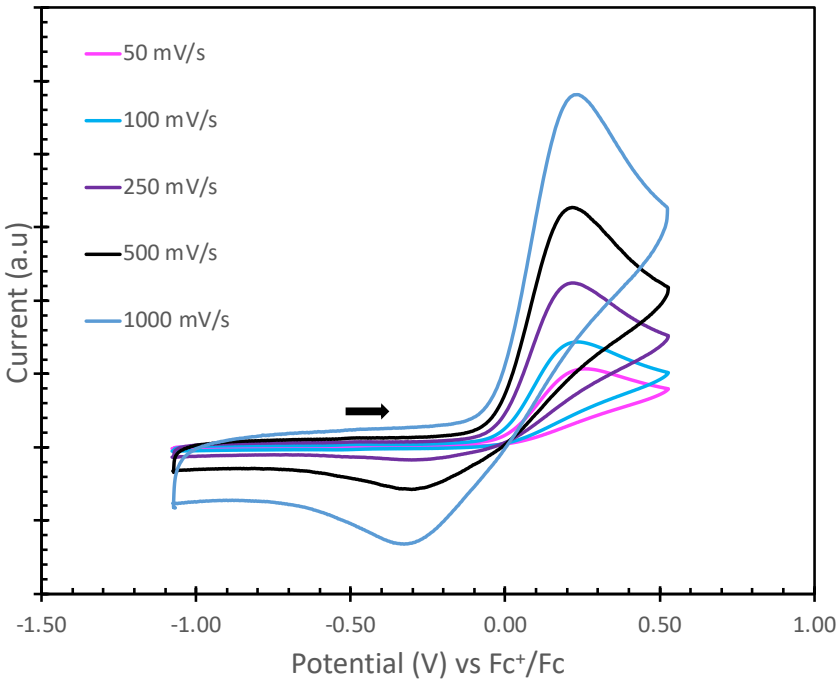


Figure S83. Cyclic voltammogram of **1-Tb^{Ph}** + 1.1 equiv. of 2-KOAd, in THF at room temperature with varying scan rates.

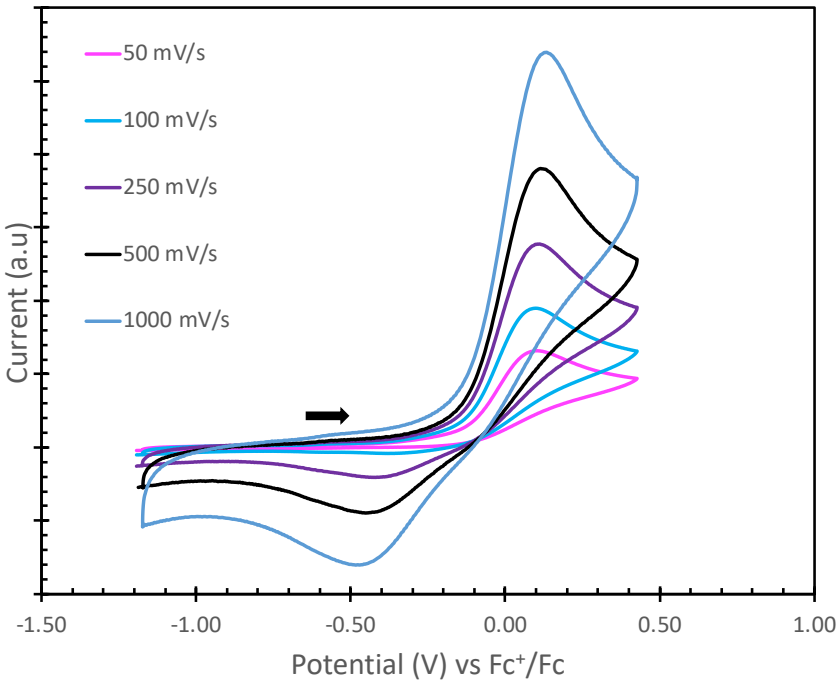


Figure S84. Cyclic voltammogram of **1-Tb^{Ph}** + 1.1 equiv. of NaO^{t}Bu, in THF at room temperature with varying scan rates.

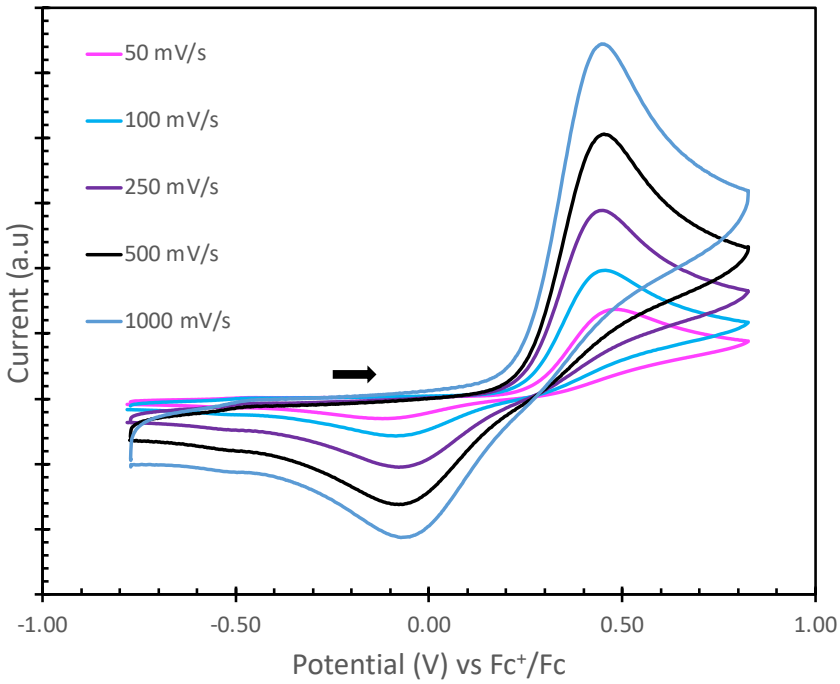


Figure S85. Cyclic voltammogram of **1-Pr^{Ph}** + 1.1 equiv. of $KOSiMe_3$, in THF at room temperature with varying scan rates.

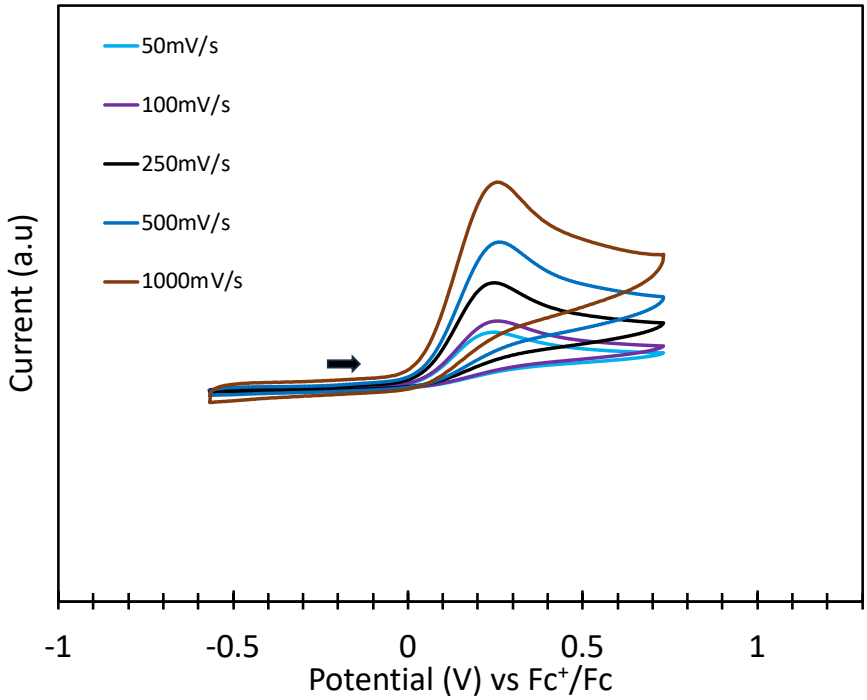


Figure S86. Cyclic voltammogram of **1-Pr^{Ph}** + 1.1 equiv. of 2-KOAd, in THF at room temperature with varying scan rates.

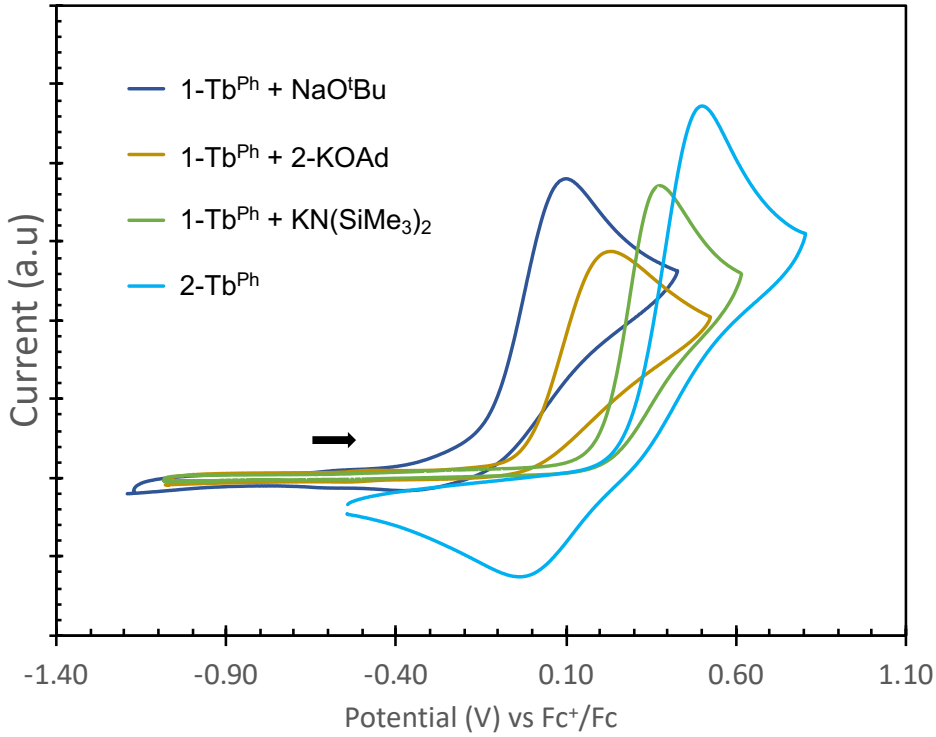


Figure S87. Cyclic voltammogram of **2-Tb^{Ph}** compared with **1-Tb^{Ph}** + 1.1 equiv. of K(N(SiMe$_3$)$_2$, **1-Tb^{Ph}** + 1.1 equiv. of 2-KOAd and **1-Tb^{Ph}** + 1.1 equiv. of NaO^{t}Bu, in THF at room temperature with a 100 mV/s scan rate.

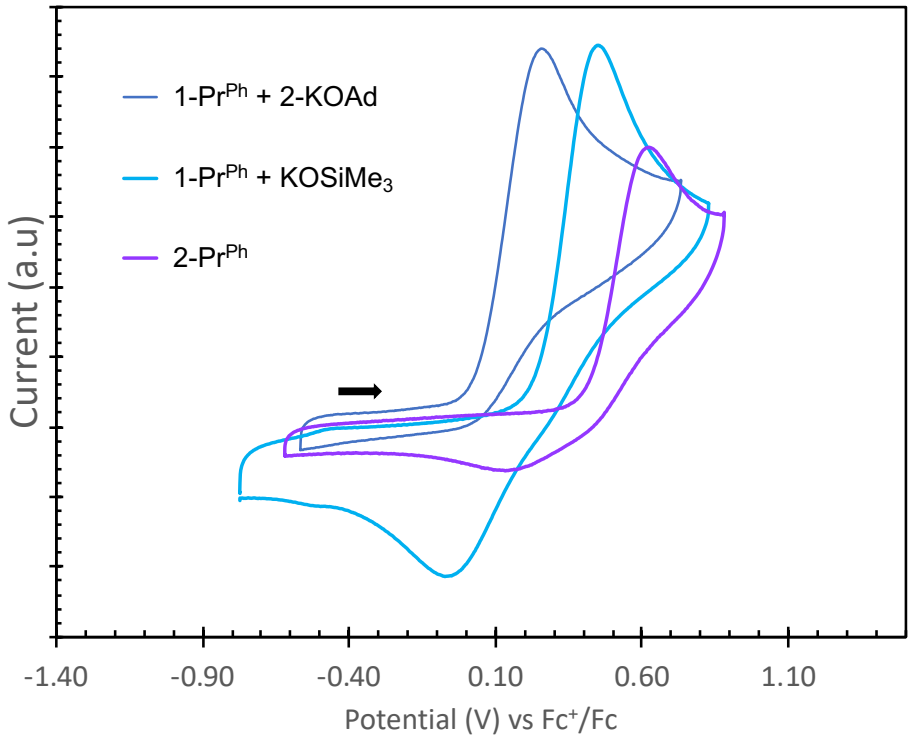


Figure S88. Cyclic voltammogram of **2-Pr^{Ph}** compared with **1-Pr^{Ph}** + 1.1 equiv. of $KOSiMe_3$ and **1-Pr^{Ph}** + 1.1 equiv. of 2-KOAd, in THF at room temperature with a 1000 mV/s scan rate.

S9. Infrared (IR) spectra

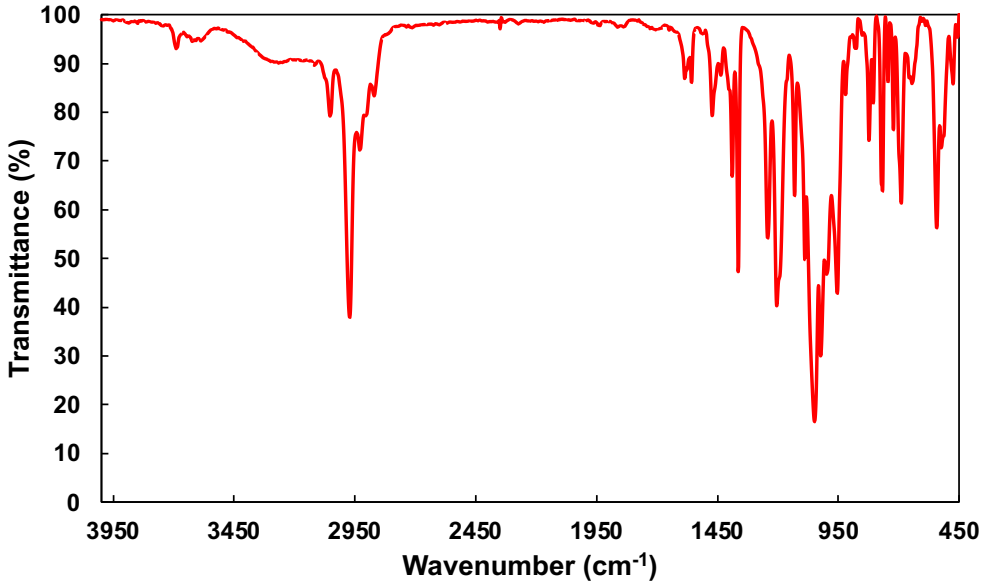


Figure S89. Infrared (IR) spectra for **1-Tb^{OtBu}** prepared as a KBr pellet.

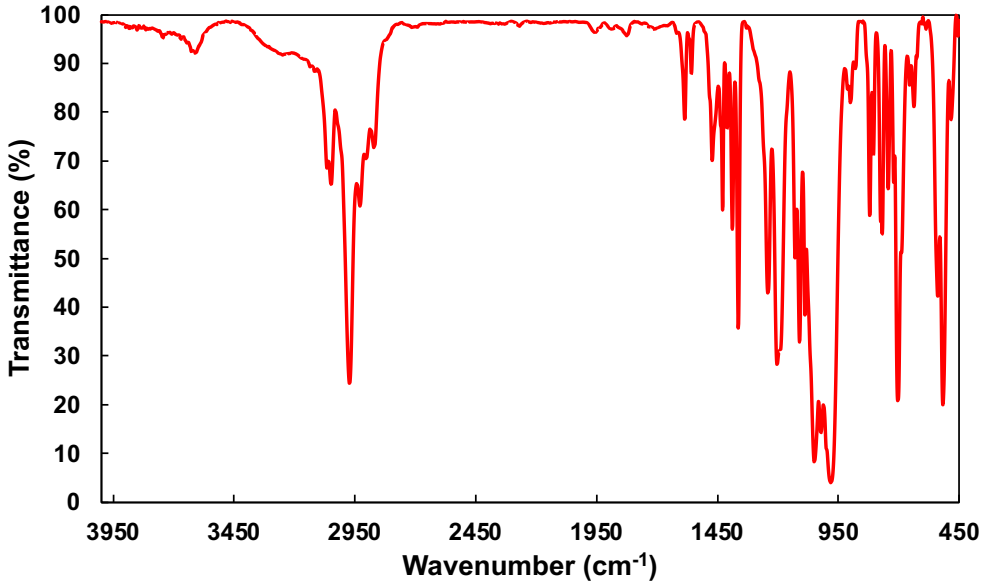


Figure S90. Infrared (IR) spectra for **2-Tb^{OtBu}** prepared as a KBr pellet.

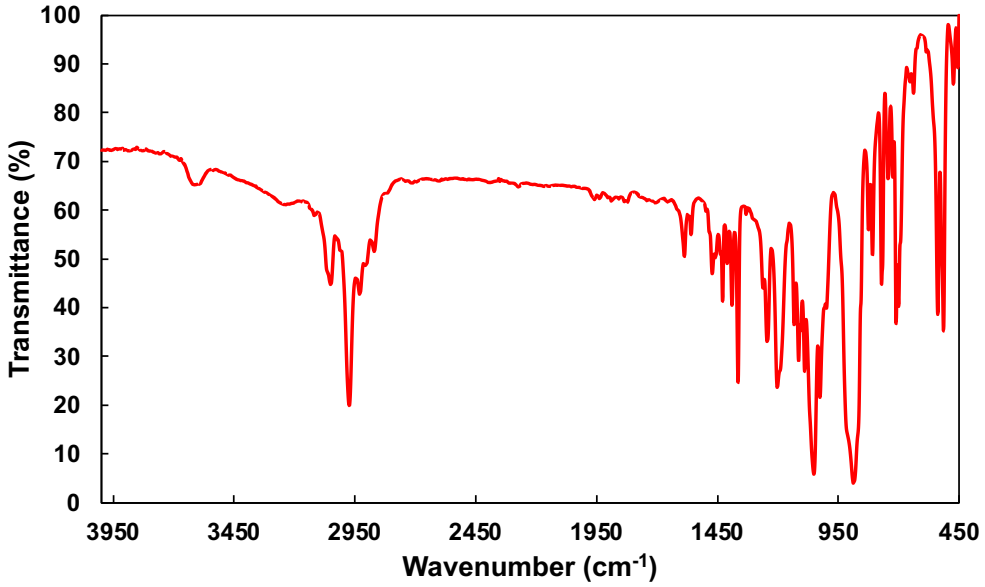


Figure S91. Infrared (IR) spectra for **2-Ce^{OtBu}** prepared as a KBr pellet.

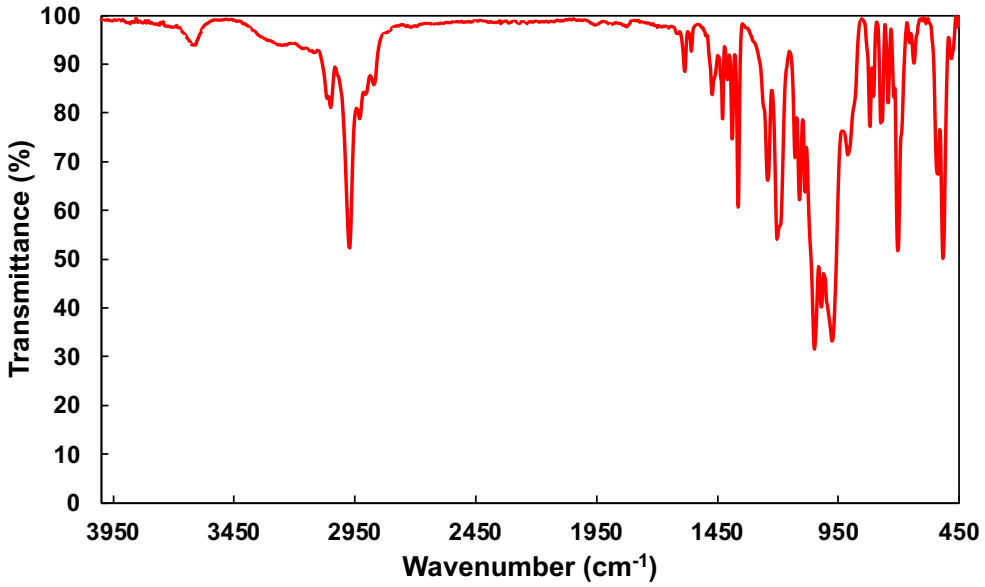


Figure S92. Infrared (IR) spectra for **3-Ce^{OtBu}** prepared as a KBr pellet.

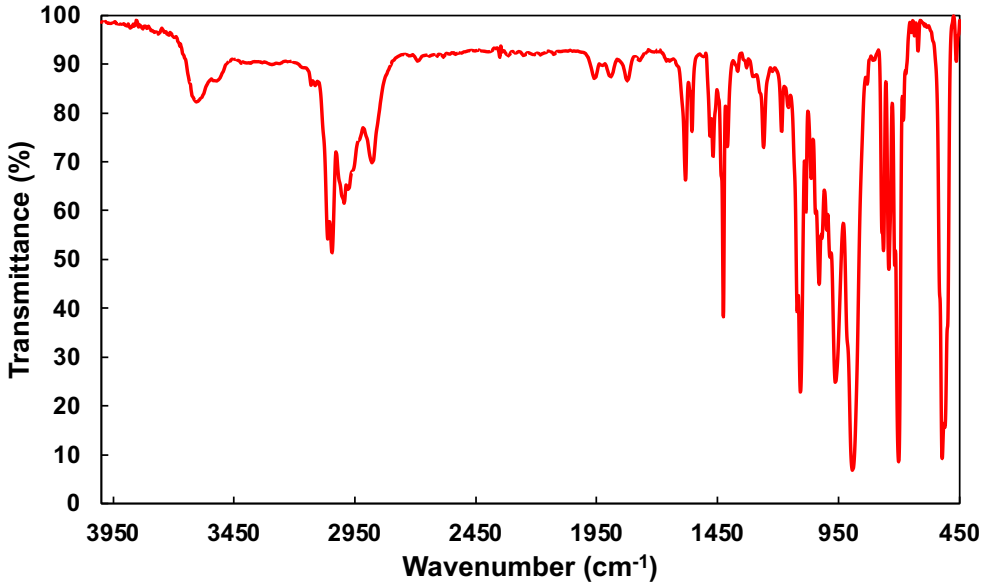


Figure S93. Infrared (IR) spectra for **1-Ce^{Ph}** prepared as a KBr pellet.

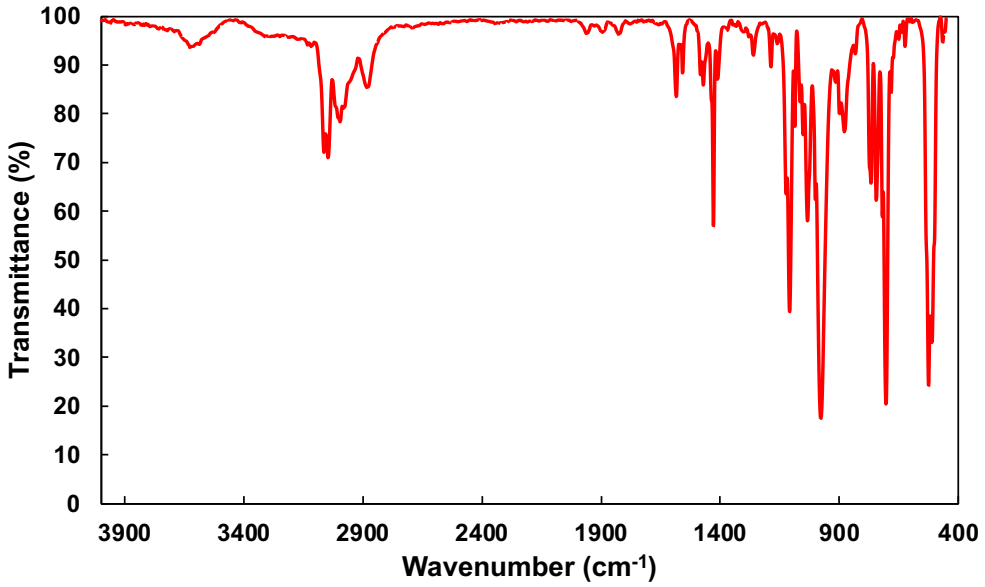


Figure S94. Infrared (IR) spectra for **1-Tb^{Ph}** prepared as a KBr pellet.

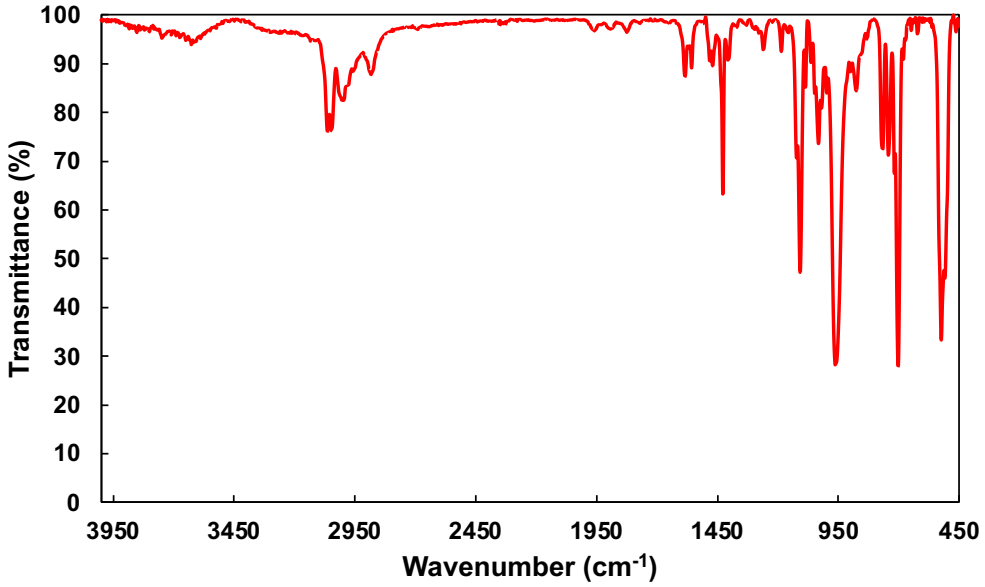


Figure S95. Infrared (IR) spectra for **1-Pr^{Ph}** prepared as a KBr pellet.

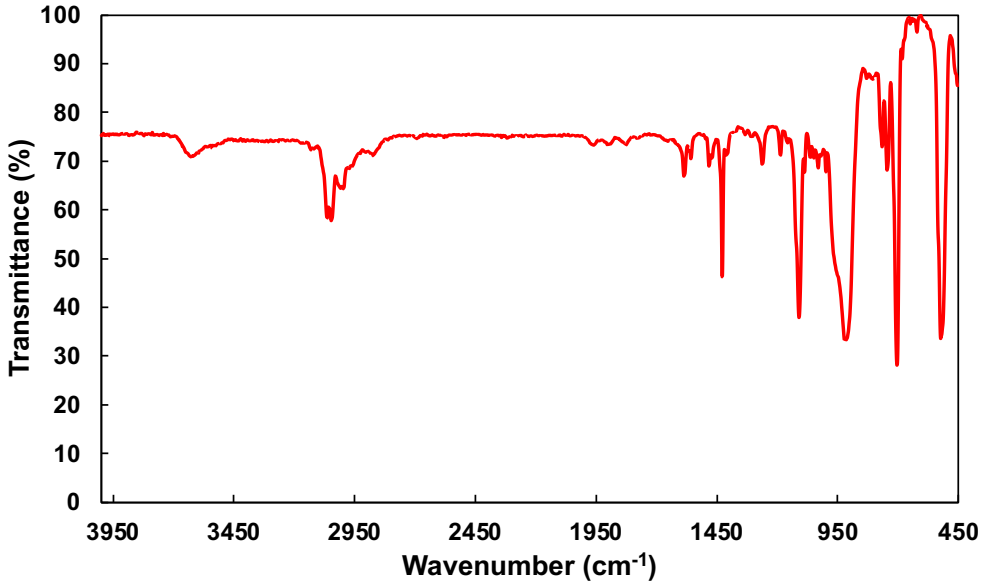


Figure S96. Infrared (IR) spectra for **2-Ce^{Ph}** prepared as a KBr pellet.

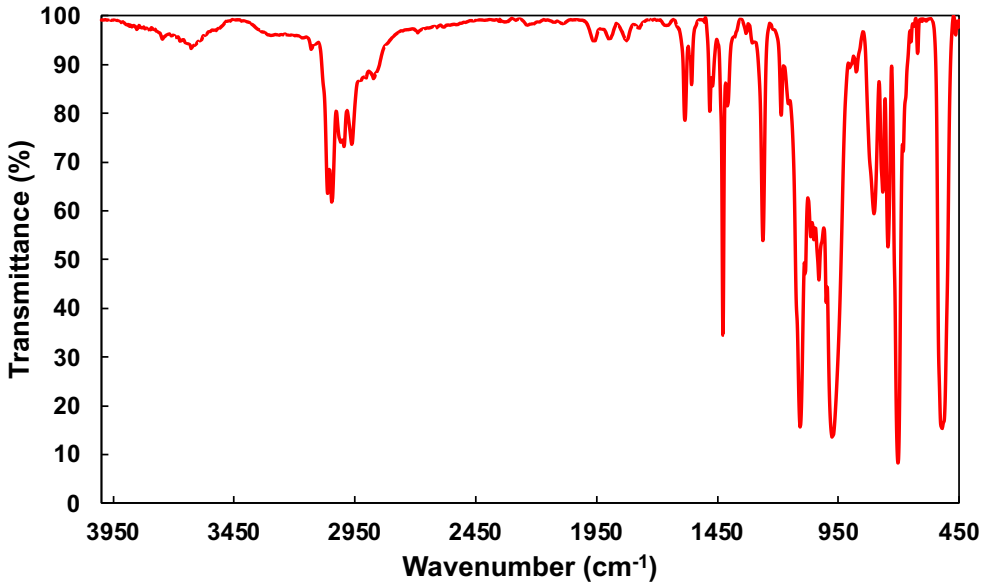


Figure S97. Infrared (IR) spectra for **2-Tb^{Ph}** prepared as a KBr pellet.

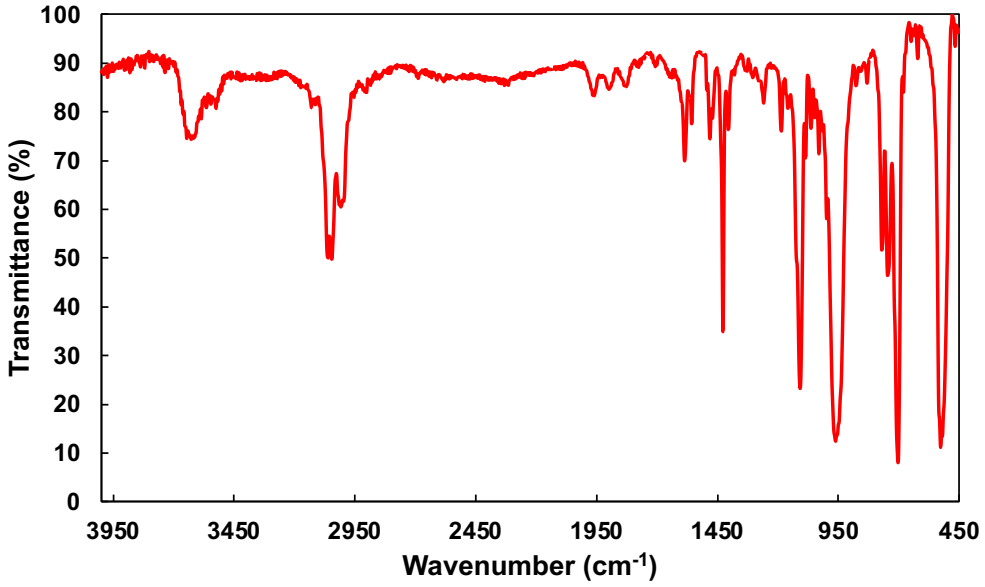


Figure S98. Infrared (IR) spectra for **2-Pr^{Ph}** prepared as a KBr pellet.

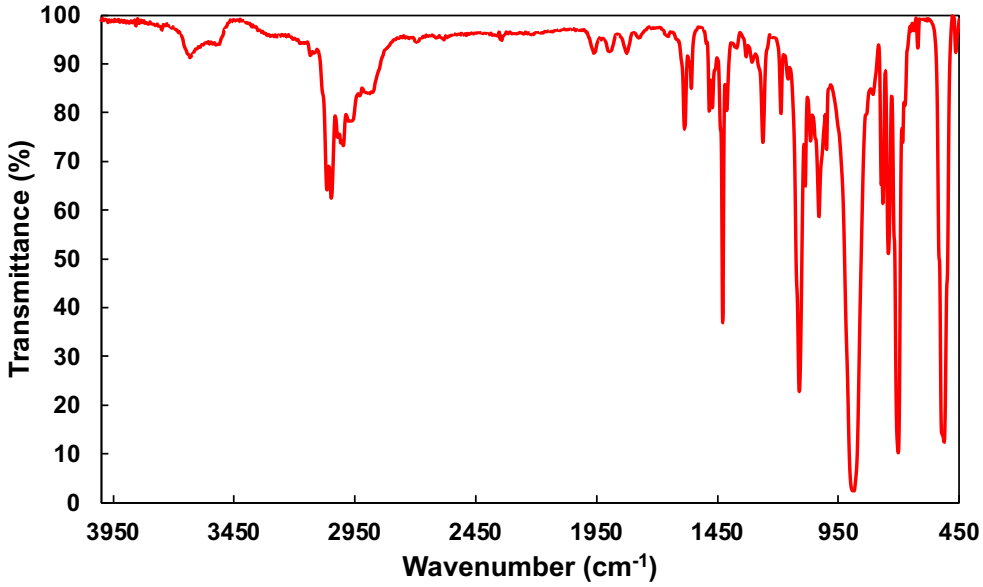


Figure S99. Infrared (IR) spectra for **3-Ce^{Ph}** prepared as a KBr pellet.

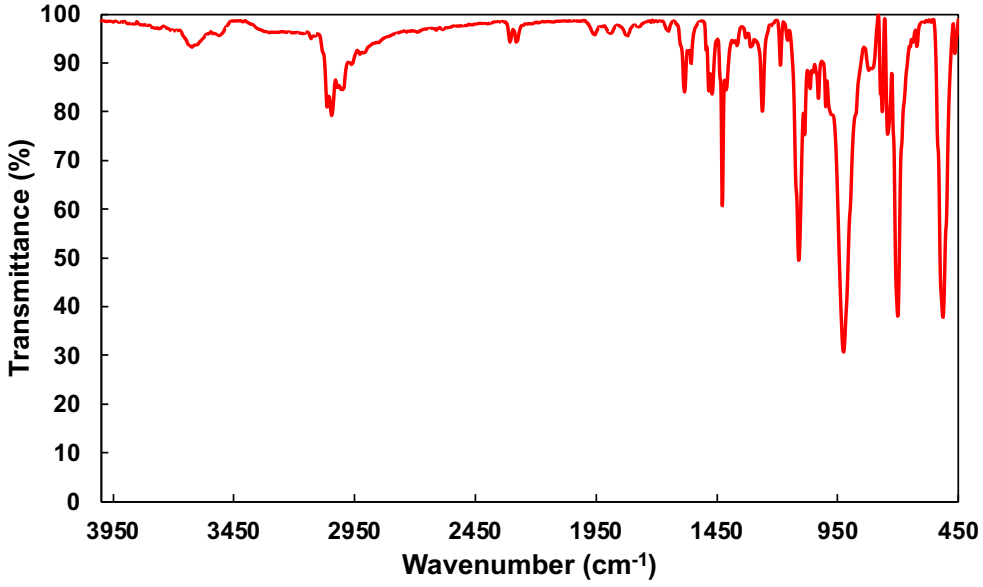


Figure S100. Infrared (IR) spectra for **3-Tb^{Ph}** prepared as a KBr pellet.

S10. Determination of Enrichment and Separation factors

The Tb:Dy separations factors were determined by the following equation:

$$S = D_{residualsolid} \cdot D_{extractedsolid} = \frac{\eta_{Tb}}{\eta_{Dy}} \cdot \frac{\eta_{Dy}}{\eta_{Tb}}$$

The molar ratios (η_{Ln}) were determined both by integration of the Tb and Dy peaks in the thf-d_8 ^{1}H NMR spectra after 24h or by ICP-MS analyses.

Table S5. Enrichment factors for the fraction obtained after extraction in toluene (η_{Tb}/η_{Dy}) and for the solid fraction (η_{Dy}/η_{Tb}).

	^{1}H NMR	ICP-MS
$D_{extractedsolid}$	4.44	3.72
$D_{residualsolid}$	2.27	2.30
S	10.1	8.56

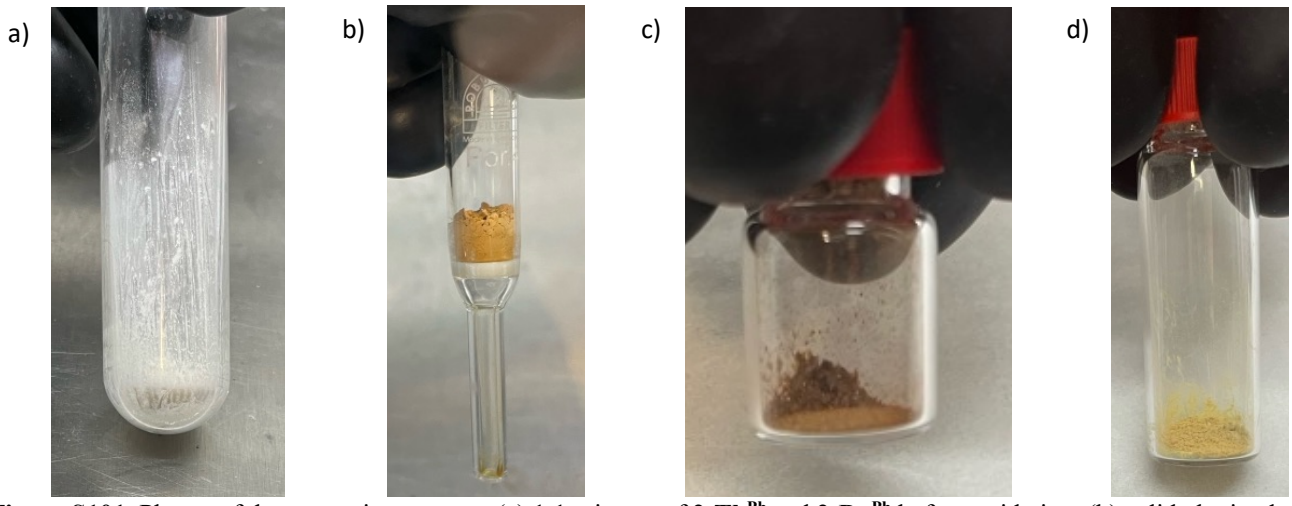


Figure S101. Photos of the separation process. (a) 1:1 mixture of **2-Tb^{Ph}** and **2-Dy^{Ph}** before oxidation, (b) solid obtained after the oxidation, (c) solid obtained after drying the fraction extracted in toluene. (d) residual insoluble in toluene solid after extraction.

S11. Computational details

The optimization of cerium and terbium complexes were carried out by employing DFT hybrid functional (B3PW91)[14] along with small core pseudopotential Stuttgart basis set[15] for terbium (oxidation state, +3), cerium, potassium and silicon atoms (polarization functions[16] were added for silicon and potassium atoms). Pople basis set[17] (6-31G**) were employed for the rest of the atoms. Large core pseudopotential Stuttgart basis set for terbium was employed to converge the IV oxidation state in complexes **3** and $\mathbf{3}^{\mathbf{OtBu}}$.[18] Frequency calculations were performed to confirm the minima for optimized structures. Disperison corrections were included in our calculations by employing D3 version of Grimme's dispersion with Becke-Johnson damping.[19] All the calculations were performed using Gaussian 09 suite of programs.[20] NBO analysis were carried out using NBO 6.0 version as implemented in the Gaussian program.[21]

Table S6. Selected structural parameters of Ce(III) (**1-Ce^{Ph}**) for s=1/2

Atom Label	Bond distance (Å)	
	DFT	X-ray
Ce1-O5	2.20	2.21
Ce1-O6	2.19	2.20
Ce1-O7	2.19	2.21
Ce1-O8	2.62	2.61
Ce1-O9	2.63	2.58
Ce1-O10	2.62	2.60
Ce1-X (center of phenyl ring)	4.02	3.93

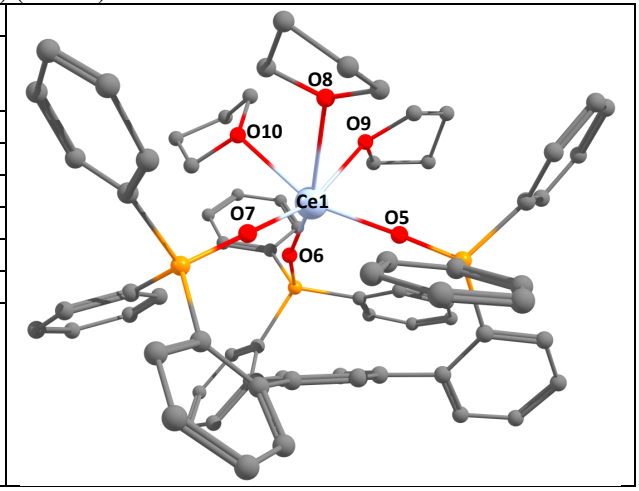


Table S7. Computed Natural charges for complex **1-Ce^{Ph}** for s=1/2

Atom Label	Natural charges
Ce1	1.93891
O5	-1.27410
O6	-1.27304
O7	-1.26882
O8	-0.63424
O9	-0.63470
O10	-0.63002

Table S8. Computed Wiberg bond index for complex **1-Ce^{Ph}** for s=1/2

Atom Label	Wiberg bond index	Atom Label	Wiberg bond index	Atom Label	Wiberg bond index
Ce1	0.0000	Ce1	0.0000	Ce1	0.0000
O5	0.4582	O6	0.4645	O7	0.4761
Atom Label	Wiberg bond index	Atom Label	Wiberg bond index	Atom Label	Wiberg bond index
Ce1	0.0000	Ce1	0.0000	Ce1	0.0000
O8	0.1341	O9	0.1285	O10	0.1362

Table S9. Bonding orbitals from NBO analysis for complex **1-Ce^{Ph}**

(0.99097) BD (1)Ce 1- O 7
(5.08%) 0.2254*Ce 1 s(0.89%)p 0.80(0.71%)d73.53(65.27%) f36.94(32.79%)g 0.39(0.34%)
(94.92%) 0.9743* O 7 s(55.07%)p 0.82(44.92%)d 0.00(0.00%)

Table S10. Second order perturbation analysis for complex **1-Ce^{Ph}**

Donor NBO	Acceptor NBO	E(2) kcal/mol
(0.94276) LP (1) O 5	(0.07843) LV (2)Ce 1	38.15

s(54.91%)p 0.82(45.08%)d 0.00(0.01%)	s(0.84%)p 0.76(0.63%)d79.59(66.81%)f37.39(31.38%)g 0.40(0.34%)	
(0.91935) LP (2) O 5 s(0.00%)p 1.00(99.98%)d 0.00(0.02%)	(0.08101) LV (1)Ce 1 s(0.02%)p 1.50(0.03%)d99.99(98.39%)f76.08(1.37%)g10.58(0.19%)	5.49
(0.94260) LP (1) O 6 s(55.00%)p 0.82(44.99%)d 0.00(0.01%)	(0.07767) LV (4)Ce 1 s(0.93%)p 0.77(0.72%)d70.12(65.25%)f35.18(32.74%)g 0.38(0.36%)	38.21
(0.91874) LP (2) O 6 s(0.01%)p 1.00(99.97%)d 0.00(0.02%)	(0.08101) LV (1)Ce 1 s(0.02%)p 1.50(0.03%)d99.99(98.39%)f76.08(1.37%)g10.58(0.19%)	4.41
(0.91830) LP (1) O 7 s(0.01%)p 1.00(99.98%)d 0.00(0.02%)	(0.07803) LV (3)Ce 1 s(0.00%)p 1.00(0.02%)d99.99(97.51%)f94.21(2.29%)g 6.88(0.17%)	7.18
(0.95834) LP (2) O 8 s(20.67%)p 3.84(79.30%)d 0.00(0.03%)	(0.07767) LV (4)Ce 1 s(0.93%)p 0.77(0.72%)d70.12(65.25%)f35.18(32.74%)g 0.38(0.36%)	3.25
(0.95834) LP (2) O 8 s(20.67%)p 3.84(79.30%)d 0.00(0.03%)	(0.02444) LV (7)Ce 1 s(0.40%)p 1.55(0.61%)d36.10(14.30%)f99.99(84.35%)g 0.86(0.34%)	5.86
(0.95989) LP (2) O 9 s(21.30%)p 3.69(78.68%)d 0.00(0.02%)	(0.02293) LV (8)Ce 1 s(0.16%)p 4.11(0.67%)d78.65(12.83%)f99.99(85.89%)g 2.73(0.45%)	3.08
(0.95815) LP (2) O 10 s(20.62%)p 3.85(79.36%)d 0.00(0.03%)	(0.02293) LV (8)Ce 1 s(0.16%)p 4.11(0.67%)d78.65(12.83%)f99.99(85.89%)g 2.73(0.45%)	4.04

Table S11. DFT computed MO's for **1-Ce^{Ph}**. (a)AMO-HOMO-1 (b)AMO-HOMO (c) spin density plot (AMO: Alpha Molecular Orbital)

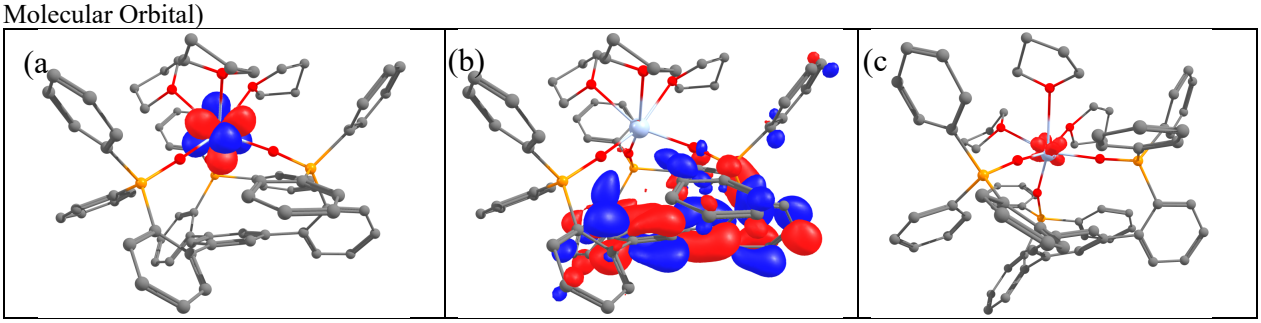


Table S12. Selected structural parameters of Tb(III) (**2-Tb^{Ph}**) for s=3

Atom Label	Bond distance (Å)	
	DFT	X-ray
Tb1-O7	2.15	2.19
Tb1-O8	2.09	2.14
Tb1-O9	2.10	2.13
Tb1-O10	2.16	2.19
Tb1-X (center of phenyl ring)	3.51	3.23

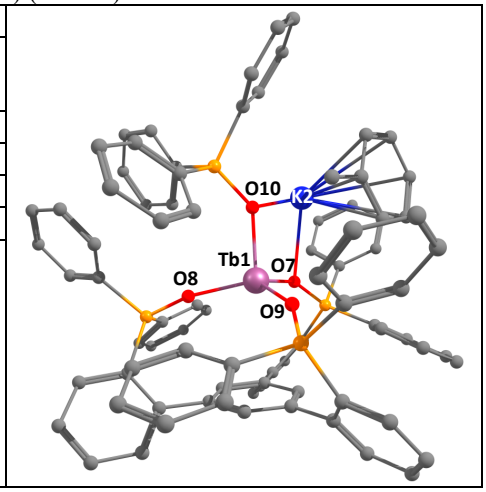


Table S13. Computed Natural charges for complex **2-Tb^{Ph}** for s=3

Atom Label	Natural charges
Tb1	2.01870
K2	0.95973
O7	-1.32287
O8	-1.30182
O9	-1.29923
O10	-1.32332

Table S14. Computed Wiberg bond index for complex **2-Tb^{Ph}** for s=3

Atom Label	Wiberg bond index	Atom Label	Wiberg bond index	Atom Label	Wiberg bond index
Tb1	0.0000	Tb1	0.0000	Tb1	0.0000
O7	0.3874	O8	0.4361	O9	0.4216
Atom Label	Wiberg bond index				
Tb1	0.0000				
O10	0.3985				

Table S15. Second order perturbation analysis for complex **2-Tb^{Ph}**

Donor NBO	Acceptor NBO	E(2) kcal/mol
(0.95430) LP (1) O 7 s(40.28%)p 1.48(59.70%)d 0.00(0.02%)	(0.09748) LV (2)Tb 1 s(0.26%)p 1.14(0.30%)d99.99(99.36%)f 0.17(0.04%)g 0.15(0.04%)	14.33
(0.95430) LP (1) O 7 s(40.28%)p 1.48(59.70%)d 0.00(0.02%)	(0.08283) LV (5)Tb 1 s(1.67%)p 0.15(0.24%)d58.71(97.89%)f 0.11(0.18%)g 0.01(0.02%)	7.16
(0.93008) LP (2) O 7 s(0.68%)p99.99(99.30%)d 0.03(0.02%)	(0.08466) LV (4)Tb 1 s(2.27%)p 0.08(0.18%)d42.84(97.39%)f 0.06(0.13%)g 0.01(0.02%)	4.97
(0.95113) LP (1) O 8 s(37.26%)p 1.68(62.72%)d 0.00(0.01%)	(0.09909) LV (1)Tb 1 s(0.00%)p 1.00(0.53%)d99.99(99.32%)f 0.22(0.11%)g 0.07(0.04%)	8.89
(0.95113) LP (1) O 8 s(37.26%)p 1.68(62.72%)d 0.00(0.01%)	(0.09748) LV (2)Tb 1 s(0.26%)p 1.14(0.30%)d99.99(99.36%)f 0.17(0.04%)g 0.15(0.04%)	11.14
(0.95113) LP (1) O 8 s(37.26%)p 1.68(62.72%)d 0.00(0.01%)	(0.08283) LV (5)Tb 1 s(1.67%)p 0.15(0.24%)d58.71(97.89%)f 0.11(0.18%)g 0.01(0.02%)	6.01
(0.92489) LP (2) O 8 s(0.97%)p99.99(99.01%)d 0.02(0.02%)	(0.08466) LV (4)Tb 1 s(2.27%)p 0.08(0.18%)d42.84(97.39%)f 0.06(0.13%)g 0.01(0.02%)	4.23
(0.95219) LP (1) O 9 s(39.23%)p 1.55(60.75%)d 0.00(0.02%)	(0.09909) LV (1)Tb 1 s(0.00%)p 1.00(0.53%)d99.99(99.32%)f 0.22(0.11%)g 0.07(0.04%)	20.19
(0.92530) LP (2) O 9 s(0.82%)p99.99(99.16%)d 0.03(0.02%)	(0.09748) LV (2)Tb 1 s(0.26%)p 1.14(0.30%)d99.99(99.36%)f 0.17(0.04%)g 0.15(0.04%)	4.95
(0.91908) LP (3) O 9 s(0.05%)p99.99(99.93%)d 0.45(0.02%)	(0.09072) LV (3)Tb 1 s(0.08%)p 0.97(0.08%)d99.99(99.76%)f 0.69(0.06%)g 0.29(0.02%)	7.56
(0.95553) LP (1) O 10 s(42.19%)p 1.37(57.78%)d 0.00(0.03%)	(0.09072) LV (3)Tb 1 s(0.08%)p 0.97(0.08%)d99.99(99.76%)f 0.69(0.06%)g 0.29(0.02%)	4.22
(0.95553) LP (1) O 10 s(42.19%)p 1.37(57.78%)d 0.00(0.03%)	(0.08466) LV (4)Tb 1 s(2.27%)p 0.08(0.18%)d42.84(97.39%)f 0.06(0.13%)g 0.01(0.02%)	8.39
(0.95553) LP (1) O 10	(0.08283) LV (5)Tb 1	11.33

s(42.19%)p 1.37(57.78%)d 0.00(0.03%)	s(1.67%)p 0.15(0.24%)d58.71(97.89%)f 0.11(0.18%)g 0.01(0.02%)	
(0.93027) LP (2) O 10 s(0.31%)p99.99(99.66%)d 0.08(0.03%	(0.08283) LV (5)Tb 1 s(1.67%)p 0.15(0.24%)d58.71(97.89%)f 0.11(0.18%)g 0.01(0.02%)	7.48
(0.92727) LP (3) O 10 s(0.02%)p99.99(99.94%)d 1.43(0.03%)	(0.09072) LV (3)Tb 1 s(0.08%)p 0.97(0.08%)d99.99(99.76%)f 0.69(0.06%)g 0.29(0.02%)	5.69

Table S16. DFT computed MO's for **2-Tb^{Ph}**. (a)AMO-HOMO-90 (b)AMO-HOMO-89 (c)AMO-HOMO-88 (d)AMO-HOMO-87 (e)AMO-HOMO-84 (f)AMO-HOMO-83 (g)AMO-HOMO-81 (h)AMO-HOMO (i)BMO-LUMO-1 (AMO:Alpha Molecular Orbital, BMO: Beta Molecular Orbital)

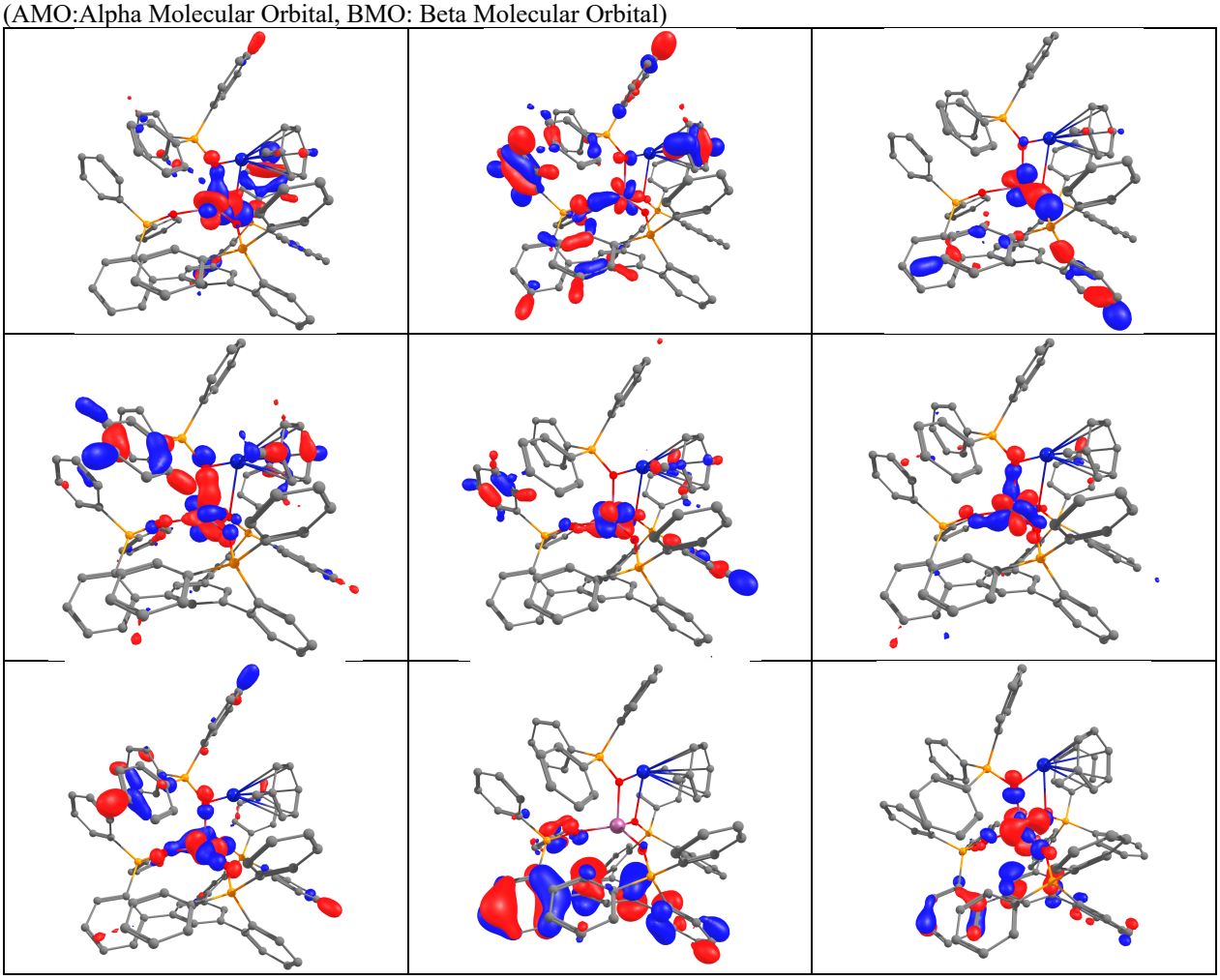


Table S17. Selected structural parameters of Tb(IV) (**3-Tb^{Ph}**)

Atom Label	Bond distance (Å)	
	DFT	X-ray
Tb1-O6	2.01	2.03
Tb1-O7	2.07	2.08
Tb1-O8	2.03	2.04
Tb1-O9	2.05	2.07
Tb1-N10	2.52	2.51
Tb1-N11	2.52	2.47

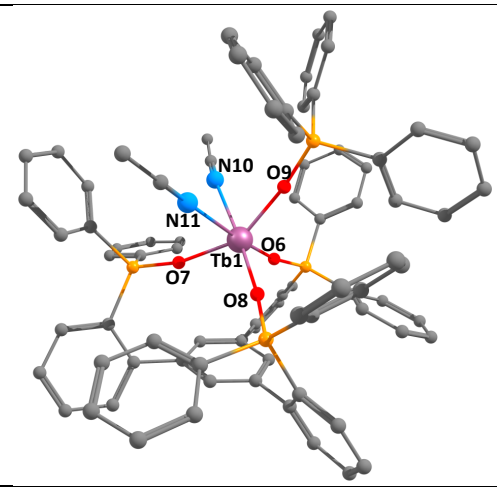
Tb1-X (center of phenyl ring)	4.02	4.04	

Table S18. Computed Natural charges for complex **3-Tb^{Ph}**

Atom Label	Natural charges
Tb1	2.55352
O6	-1.28907
O7	-1.30485
O8	-1.29957
O9	-1.28604
N10	-0.43686
N11	-0.45080

Table S19. Computed Wiberg bond index for complex **3-Tb^{Ph}**

Atom Label	Wiberg bond index	Atom Label	Wiberg bond index	Atom Label	Wiberg bond index
Tb1	0.0000	Tb1	0.0000	Tb1	0.0000
O6	0.5164	O7	0.4419	O8	0.4937
Atom Label	Wiberg bond index	Atom Label	Wiberg bond index	Atom Label	Wiberg bond index
Tb1	0.0000	Tb1	0.0000	Tb1	0.0000
O9	0.5044	N10	0.1864	N11	0.1859

Table S20. Second order perturbation analysis for complex **3-Tb^{Ph}**

Donor NBO	Acceptor NBO	E(2) kcal/mol
(1.89505) LP (1) O 6 s(36.66%)p 1.73(63.33%)d 0.00(0.02%)	(0.28440) LV (1)Tb 1 s(0.00%)p 1.00(0.17%)d99.99(99.78%)f 0.24(0.04%)	41.67
(1.89505) LP (1) O 6 s(36.66%)p 1.73(63.33%)d 0.00(0.02%)	(0.28093) LV (2)Tb 1 s(0.02%)p 9.05(0.17%)d99.99(99.74%)f 3.76(0.07%)	11.22
(1.89505) LP (1) O 6 s(36.66%)p 1.73(63.33%)d 0.00(0.02%)	(0.26365) LV (3)Tb 1 s(0.30%)p 0.74(0.22%)d99.99(99.45%)f 0.09(0.03%)	15.37
(1.90710) LP (1) O 7 s(34.56%)p 1.89(65.43%)d 0.00(0.01%)	(0.26365) LV (3)Tb 1 s(0.30%)p 0.74(0.22%)d99.99(99.45%)f 0.09(0.03%)	49.20
(1.84462) LP (2) O 7 s(1.71%)p57.59(98.28%)d 0.01(0.01%)	(0.28093) LV (2)Tb 1 s(0.02%)p 9.05(0.17%)d99.99(99.74%)f 3.76(0.07%)	8.32
(1.84211) LP (3) O 7 s(1.67%)p58.70(98.31%)d 0.01(0.02%)	(0.28440) LV (1)Tb 1 s(0.00%)p 1.00(0.17%)d99.99(99.78%)f 0.24(0.04%)	7.31
(1.89742) LP (1) O 8	(0.28440) LV (1)Tb 1	31.10

s(35.67%)p 1.80(64.31%)d 0.00(0.01%)	s(0.00%)p 1.00(0.17%)d99.99(99.78%)f 0.24(0.04%)	
(1.89742) LP (1) O 8 s(35.67%)p 1.80(64.31%)d 0.00(0.01%)	(0.28093) LV (2)Tb 1 s(0.02%)p 9.05(0.17%)d99.99(99.74%)f 3.76(0.07%)	20.44
(1.89742) LP (1) O 8 s(35.67%)p 1.80(64.31%)d 0.00(0.01%)	(0.26365) LV (3)Tb 1 s(0.30%)p 0.74(0.22%)d99.99(99.45%)f 0.09(0.03%)	16.27
(1.84728) LP (2) O 8 s(0.18%)p99.99(99.81%)d 0.06(0.01%)	(0.28440) LV (1)Tb 1 s(0.00%)p 1.00(0.17%)d99.99(99.78%)f 0.24(0.04%)	7.75
(1.84728) LP (2) O 8 s(0.18%)p99.99(99.81%)d 0.06(0.01%)	(0.28093) LV (2)Tb 1 s(0.02%)p 9.05(0.17%)d99.99(99.74%)f 3.76(0.07%)	15.93
(1.90321) LP (1) O 9 s(39.13%)p 1.56(60.86%)d 0.00(0.01%)	(0.26365) LV (3)Tb 1 s(0.30%)p 0.74(0.22%)d99.99(99.45%)f 0.09(0.03%)	61.40
(1.84056) LP (2) O 9 s(1.11%)p89.29(98.88%)d 0.01(0.01%)	(0.28093) LV (2)Tb 1 s(0.02%)p 9.05(0.17%)d99.99(99.74%)f 3.76(0.07%)	26.04
(1.88575) LP (1) N 10 s(46.95%)p 1.13(53.02%)d 0.00(0.03%)	(0.28440) LV (1)Tb 1 s(0.00%)p 1.00(0.17%)d99.99(99.78%)f 0.24(0.04%)	28.59
(1.88575) LP (1) N 10 s(46.95%)p 1.13(53.02%)d 0.00(0.03%)	(0.28093) LV (2)Tb 1 s(0.02%)p 9.05(0.17%)d99.99(99.74%)f 3.76(0.07%)	12.22
(1.88575) LP (1) N 10 s(46.95%)p 1.13(53.02%)d 0.00(0.03%)	(0.26365) LV (3)Tb 1 s(0.30%)p 0.74(0.22%)d99.99(99.45%)f 0.09(0.03%)	16.14
(1.88555) LP (1) N 11 s(46.95%)p 1.13(53.02%)d 0.00(0.04%)	(0.28440) LV (1)Tb 1 s(0.00%)p 1.00(0.17%)d99.99(99.78%)f 0.24(0.04%)	33.61
(1.88555) LP (1) N 11 s(46.95%)p 1.13(53.02%)d 0.00(0.04%)	(0.28093) LV (2)Tb 1 s(0.02%)p 9.05(0.17%)d99.99(99.74%)f 3.76(0.07%)	9.71
(1.88555) LP (1) N 11 s(46.95%)p 1.13(53.02%)d 0.00(0.04%)	(0.26365) LV (3)Tb 1 s(0.30%)p 0.74(0.22%)d99.99(99.45%)f 0.09(0.03%)	12.96

Table S21. Selected structural parameters of [Tb^{IV}(($OSiPh_2Ar)_3$-arene)($OCMe_3$)($MeCN)_2$] (**3-Tb^{Ph}-O^tBu**)

Atom Label	Bond distance (Å), DFT
Tb1-O5	2.02
Tb1-O6	2.09
Tb1-O7	2.03
Tb1-O8	2.02
Tb1-N9	2.53
Tb1-N10	2.57
Tb1-X (center of phenyl ring)	4.15

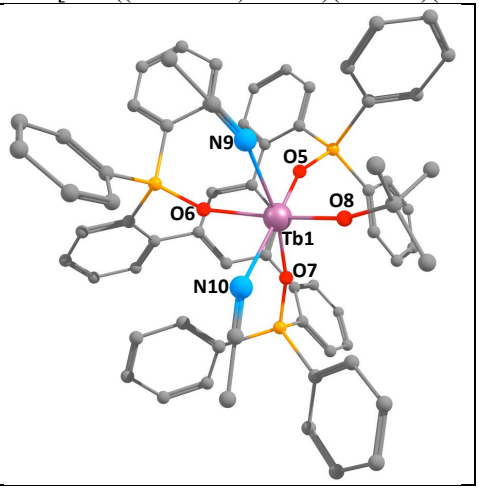


Table S22. Computed Natural charges for complex **3-Tb^{Ph}-O^{t}Bu**

Atom Label	Natural charges
Tb1	2.47268
O5	-1.28318
O6	-1.30415
O7	-1.29378
O8	-0.93883
N9	-0.43942
N10	-0.43909

Table S23. Computed Wiberg bond index for complex **3-Tb^{Ph}-O^{t}Bu**

Atom Label	Wiberg bond index	Atom Label	Wiberg bond index	Atom Label	Wiberg bond index
Tb1	0.0000	Tb1	0.0000	Tb1	0.0000
O5	0.5257	O6	0.4309	O7	0.5051
Atom Label	Wiberg bond index	Atom Label	Wiberg bond index	Atom Label	Wiberg bond index
Tb1	0.0000	Tb1	0.0000	Tb1	0.0000
O8	0.5983	N9	0.2022	N10	0.1958

Table S24. Bonding orbitals between Ce and atoms in the first coordination sphere for **3-Tb^{Ph}-O^{t}Bu**

(1.93420) BD (1)Tb 1- O 7
(5.52%) 0.2350*Tb 1 s(0.10%)p 4.27(0.44%)d99.99(98.56%)f 8.74(0.90%)
(94.48%) 0.9720* O 7 s(0.30%)p99.99(99.69%)d 0.04(0.01%)
(1.95983) BD (1)Tb 1- O 8
(7.08%) 0.2661*Tb 1 s(0.08%)p 6.66(0.50%)d99.99(98.52%)f12.04(0.90%)
(92.92%) 0.9640* O 8 s(1.41%)p70.09(98.59%)d 0.00(0.00%)
(1.95619) BD (2)Tb 1- O 8
(6.84%) 0.2616*Tb 1 s(0.02%)p27.07(0.54%)d99.99(98.46%)f48.65(0.98%)
(93.16%) 0.9652* O 8 s(0.05%)p99.99(99.94%)d 0.13(0.01%)

Table S25. Second order perturbation analysis for complex **3-Tb^{Ph}-O^{t}Bu**

Donor NBO	Acceptor NBO	E(2) kcal/mol
(1.88881) LP (1) O 5 s(36.19%)p 1.76(63.80%)d 0.00(0.02%)	(0.28303) LV (1)Tb 1 s(0.04%)p 6.68(0.24%)d99.99(99.67%)f 1.63(0.06%)	49.28
(1.88881) LP (1) O 5 s(36.19%)p 1.76(63.80%)d 0.00(0.02%)	(0.26227) LV (2)Tb 1 s(0.74%)p 0.24(0.18%)d99.99(99.05%)f 0.04(0.03%)	6.56
(1.88881) LP (1) O 5 s(36.19%)p 1.76(63.80%)d 0.00(0.02%)	(0.10486) LV (3)Tb 1 s(98.54%)p 0.00(0.10%)d 0.01(1.32%)f 0.00(0.05%)	6.09
(1.85001) LP (2) O 5 s(0.00%)p 1.00(99.98%)d 0.00(0.01%)	(0.16527) BD*(1)Tb 1- O 8 (92.92%) 0.9640* Tb 1 s(0.08%)p 6.66(0.50%)d99.99(98.52%)f12.04(0.90%) (7.08%) -0.2661* O 8 s(1.41%)p70.09(98.59%)d 0.00(0.00%)	7.25
(1.85001) LP (2) O 5 s(0.00%)p 1.00(99.98%)d 0.00(0.01%)	(0.17948) BD*(2)Tb 1- O 8 (93.16%) 0.9652* Tb 1 s(0.02%)p27.07(0.54%)d99.99(98.46%)f48.65(0.98%) (6.84%) -0.2616* O 8 s(0.05%)p99.99(99.94%)d 0.13(0.01%)	6.34
(1.82744) LP (3) O 5 s(0.01%)p 1.00(99.98%)d 0.00(0.01%)	(0.14313) BD*(1)Tb 1- O 7 (94.48%) 0.9720* Tb 1 s(0.10%)p 4.27(0.44%)d99.99(98.56%)f 8.74(0.90%) (5.52%) -0.2350* O 7 s(0.30%)p99.99(99.69%)d 0.04(0.01%)	21.07
(1.90567) LP (1) O 6	(0.26227) LV (2)Tb 1	43.07

s(33.92%)p 1.95(66.06%)d 0.00(0.01%)	s(0.74%)p 0.24(0.18%)d99.99(99.05%)f 0.04(0.03%)	
(1.90567) LP (1) O 6 s(33.92%)p 1.95(66.06%)d 0.00(0.01%)	(0.10486) LV (3)Tb 1 s(98.54%)p 0.00(0.10%)d 0.01(1.32%)f 0.00(0.05%)	12.35
(1.84641) LP (2) O 6 s(2.40%)p40.58(97.58%)d 0.01(0.02%)	(0.16527) BD*(1)Tb 1- O 8 (92.92%) 0.9640* Tb 1 s(0.08%)p 6.66(0.50%)d99.99(98.52%)f12.04(0.90%) (7.08%) -0.2661* O 8 s(1.41%)p70.09(98.59%)d 0.00(0.00%)	20.04
(1.84282) LP (3) O 6 s(1.18%)p83.45(98.80%)d 0.01(0.02%)	(0.17948) BD*(2)Tb 1- O 8 (93.16%) 0.9652*Tb 1 s(0.02%)p27.07(0.54%)d99.99(98.46%)f48.65(0.98%) (6.84%) -0.2616* O 8 s(0.05%)p99.99(99.94%)d 0.13(0.01%)	13.10
(1.89231) LP (1) O 7 s(34.83%)p 1.87(65.16%)d 0.00(0.01%)	(0.28303) LV (1)Tb 1 s(0.04%)p 6.68(0.24%)d99.99(99.67%)f 1.63(0.06%)	37.59
(1.89231) LP (1) O 7 s(34.83%)p 1.87(65.16%)d 0.00(0.01%)	(0.26227) LV (2)Tb 1 s(0.74%)p 0.24(0.18%)d99.99(99.05%)f 0.04(0.03%)	26.58
(1.89231) LP (1) O 7 s(34.83%)p 1.87(65.16%)d 0.00(0.01%)	(0.10486) LV (3)Tb 1 s(98.54%)p 0.00(0.10%)d 0.01(1.32%)f 0.00(0.05%)	6.61
(1.85031) LP (2) O 7 s(0.85%)p99.99(99.14%)d 0.01(0.01%)	(0.16527) BD*(1)Tb 1- O 8 (92.92%) 0.9640* Tb 1 s(0.08%)p 6.66(0.50%)d99.99(98.52%)f12.04(0.90%) (7.08%) -0.2661* O 8 s(1.41%)p70.09(98.59%)d 0.00(0.00%)	8.71
(1.85031) LP (2) O 7 s(0.85%)p99.99(99.14%)d 0.01(0.01%)	(0.17948) BD*(2)Tb 1- O 8 (93.16%) 0.9652* Tb 1 s(0.02%)p27.07(0.54%)d99.99(98.46%)f48.65(0.98%) (6.84%) -0.2616* O 8 s(0.05%)p99.99(99.94%)d 0.13(0.01%)	11.70
(1.89106) LP (1) O 8 s(58.42%)p 0.71(41.56%)d 0.00(0.02%)	(0.26227) LV (2)Tb 1 s(0.74%)p 0.24(0.18%)d99.99(99.05%)f 0.04(0.03%)	58.53
(1.89106) LP (1) O 8 s(58.42%)p 0.71(41.56%)d 0.00(0.02%)	(0.10486) LV (3)Tb 1 s(98.54%)p 0.00(0.10%)d 0.01(1.32%)f 0.00(0.05%)	14.23
(1.87958) LP (1) N 9 s(47.05%)p 1.12(52.92%)d 0.00(0.03%)	(0.28303) LV (1)Tb 1 s(0.04%)p 6.68(0.24%)d99.99(99.67%)f 1.63(0.06%)	27.89
(1.87958) LP (1) N 9 s(47.05%)p 1.12(52.92%)d 0.00(0.03%)	(0.26227) LV (2)Tb 1 s(0.74%)p 0.24(0.18%)d99.99(99.05%)f 0.04(0.03%)	24.82
(1.87958) LP (1) N 9 s(47.05%)p 1.12(52.92%)d 0.00(0.03%)	(0.10486) LV (3)Tb 1 s(98.54%)p 0.00(0.10%)d 0.01(1.32%)f 0.00(0.05%)	7.75
(1.88015) LP (1) N 10 s(48.16%)p 1.08(51.80%)d 0.00(0.04%)	(0.28303) LV (1)Tb 1 s(0.04%)p 6.68(0.24%)d99.99(99.67%)f 1.63(0.06%)	42.55
(1.88015) LP (1) N 10 s(48.16%)p 1.08(51.80%)d 0.00(0.04%)	(0.26227) LV (2)Tb 1 s(0.74%)p 0.24(0.18%)d99.99(99.05%)f 0.04(0.03%)	6.56
(1.88015) LP (1) N 10 s(48.16%)p 1.08(51.80%)d 0.00(0.04%)	(0.10486) LV (3)Tb 1 s(98.54%)p 0.00(0.10%)d 0.01(1.32%)f 0.00(0.05%)	7.07

Optimized geometries

1-Ce^{Ph}

Ce	3.014189000	2.330986000	17.375604000
Si	3.863528000	2.428644000	21.058055000
Si	4.356265000	5.626556000	16.122934000
Si	5.539612000	-0.116412000	15.990114000
O	3.399218000	2.677203000	19.512477000
O	3.878987000	4.090384000	16.397393000
O	4.422653000	0.762080000	16.796103000
O	1.319121000	0.405680000	17.914221000
O	0.765342000	3.603036000	17.864625000
O	1.627724000	1.997218000	15.178071000
C	6.450103000	3.688948000	19.478553000
C	6.575330000	4.477305000	18.330325000
H	6.374656000	5.540727000	18.390376000
C	6.970491000	3.919802000	17.112586000
C	7.268153000	2.554307000	17.058470000
H	7.610931000	2.119411000	16.126925000
C	7.140067000	1.743350000	18.188512000
C	6.748181000	2.326781000	19.397710000
H	6.690724000	1.713969000	20.289561000
C	6.086757000	4.304099000	20.777352000
C	6.794694000	5.443270000	21.179427000
H	7.560127000	5.842889000	20.520399000
C	6.547629000	6.051551000	22.405512000
H	7.109307000	6.935559000	22.694120000
C	5.591096000	5.512903000	23.261021000
H	5.399130000	5.967227000	24.229163000
C	4.867499000	4.391709000	22.859075000
H	4.098995000	4.000204000	23.519937000
C	5.076472000	3.776365000	21.615368000
C	2.307916000	2.575305000	22.135884000
C	1.694723000	3.823705000	22.331235000
H	2.183060000	4.722427000	21.962951000
C	0.473010000	3.937435000	22.990658000
H	0.027129000	4.917191000	23.142810000
C	-0.176318000	2.793306000	23.456239000
H	-1.130915000	2.877887000	23.968357000
C	0.409106000	1.543379000	23.265811000
H	-0.089585000	0.648460000	23.628791000
C	1.639763000	1.440693000	22.616848000
H	2.091155000	0.460925000	22.481256000
C	4.545757000	0.682606000	21.276159000
C	4.843370000	0.173243000	22.548238000
H	4.634860000	0.774558000	23.431139000
C	5.410489000	-1.090988000	22.703346000
H	5.634718000	-1.467731000	23.697842000
C	5.705572000	-1.862974000	21.580135000
H	6.169738000	-2.838634000	21.695217000
C	5.422604000	-1.370758000	20.307373000
H	5.694759000	-1.945385000	19.426959000
C	4.837317000	-0.115224000	20.159195000
H	4.655222000	0.260935000	19.155074000
C	7.143311000	4.781259000	15.917614000
C	8.366196000	4.720812000	15.239013000
H	9.126982000	4.031525000	15.593986000
C	8.623552000	5.535920000	14.141735000
H	9.580405000	5.470376000	13.631503000
C	7.655944000	6.440028000	13.713000000

H	7.848888000	7.093349000	12.866575000
C	6.427155000	6.489500000	14.368706000
H	5.665414000	7.173042000	14.003184000
C	6.132978000	5.661089000	15.462439000
C	3.223673000	6.326033000	14.771436000
C	3.338356000	5.866341000	13.449535000
H	4.155337000	5.199648000	13.184172000
C	2.428043000	6.248080000	12.466758000
H	2.546429000	5.890376000	11.447139000
C	1.363568000	7.089247000	12.791957000
H	0.648749000	7.384842000	12.028945000
C	1.225670000	7.551895000	14.099134000
H	0.401145000	8.210868000	14.358545000
C	2.150908000	7.176461000	15.073608000
H	2.038765000	7.552822000	16.087609000
C	4.130556000	6.673667000	17.676673000
C	4.281992000	8.067111000	17.646506000
H	4.487091000	8.565736000	16.701118000
C	4.181483000	8.827700000	18.810708000
H	4.302228000	9.906935000	18.767080000
C	3.942891000	8.199851000	20.032792000
H	3.887277000	8.786699000	20.945613000
C	3.794231000	6.814763000	20.083375000
H	3.654663000	6.314356000	21.037326000
C	3.874444000	6.061697000	18.913828000
H	3.779039000	4.980200000	18.979377000
C	7.499513000	0.305851000	18.124907000
C	8.410306000	-0.178196000	19.071811000
H	8.792039000	0.504047000	19.825988000
C	8.843522000	-1.499523000	19.048310000
H	9.549560000	-1.851139000	19.795386000
C	8.380392000	-2.357618000	18.055216000
H	8.723962000	-3.387521000	18.012231000
C	7.457700000	-1.888872000	17.122041000
H	7.077860000	-2.576759000	16.371578000
C	6.978916000	-0.569783000	17.142611000
C	4.692959000	-1.729143000	15.458412000
C	4.399581000	-2.728756000	16.399851000
H	4.771393000	-2.631575000	17.416413000
C	3.644642000	-3.848737000	16.058418000
H	3.444253000	-4.615868000	16.802200000
C	3.146608000	-3.984040000	14.762015000
H	2.555374000	-4.855015000	14.492548000
C	3.414743000	-2.998149000	13.814659000
H	3.030865000	-3.097857000	12.802713000
C	4.183553000	-1.887247000	14.161904000
H	4.394840000	-1.128851000	13.412023000
C	6.113574000	0.778185000	14.430420000
C	6.854595000	0.121083000	13.437797000
H	7.075770000	-0.939217000	13.542862000
C	7.317977000	0.805037000	12.314588000
H	7.890882000	0.278253000	11.555912000
C	7.057499000	2.167861000	12.172933000
H	7.433251000	2.707308000	11.307612000
C	6.328909000	2.840203000	13.153003000
H	6.159773000	3.910340000	13.072932000
C	5.855848000	2.147080000	14.264572000
H	5.314653000	2.690302000	15.034217000
C	1.351818000	-0.138845000	19.251297000
H	0.354531000	-0.033800000	19.697682000

H	2.060732000	0.447907000	19.837859000
C	1.747122000	-1.594077000	19.076968000
H	1.426116000	-2.218187000	19.914444000
H	2.834408000	-1.673091000	18.985729000
C	1.070682000	-1.941778000	17.751014000
H	-0.000354000	-2.119609000	17.901590000
H	1.505326000	-2.812669000	17.257398000
C	1.301087000	-0.673806000	16.943481000
H	2.271349000	-0.694343000	16.437887000
H	0.517454000	-0.457186000	16.214070000
C	0.074530000	3.194325000	19.071359000
H	0.826195000	2.846232000	19.786402000
H	-0.593724000	2.369760000	18.811723000
C	-0.636744000	4.440973000	19.575491000
H	-0.755848000	4.420052000	20.660148000
H	-1.626609000	4.538347000	19.115195000
C	0.292073000	5.552966000	19.086497000
H	-0.183606000	6.535596000	19.039659000
H	1.175832000	5.628147000	19.727154000
C	0.697903000	5.037373000	17.717812000
H	-0.047866000	5.276253000	16.948106000
H	1.673418000	5.389760000	17.381522000
C	0.294580000	2.473763000	14.925710000
H	-0.080287000	2.900841000	15.857099000
H	-0.337817000	1.622729000	14.635594000
C	0.450186000	3.464256000	13.784403000
H	0.822339000	4.423321000	14.159054000
H	-0.483298000	3.638773000	13.243366000
C	1.524946000	2.776989000	12.941134000
H	2.041161000	3.462906000	12.267585000
H	1.086452000	1.967928000	12.346376000
C	2.458459000	2.223919000	14.009007000
H	2.943095000	1.281369000	13.743560000
H	3.221355000	2.955007000	14.288881000

2-Tb^{Ph}

Tb	18.889067000	9.372392000	15.235495000
K	15.915708000	9.141509000	17.290434000
Si	15.817901000	7.987571000	13.806087000
Si	21.416720000	6.747565000	15.530185000
Si	20.111185000	12.097167000	13.150717000
Si	19.181726000	10.042595000	18.699280000
O	16.973478000	8.467971000	14.870102000
O	20.515487000	8.110300000	15.570119000
O	19.244455000	11.138626000	14.157598000
O	18.379417000	9.893035000	17.269255000
C	18.625411000	7.140995000	12.239800000
C	19.941191000	6.841094000	12.610699000
H	20.166140000	5.863356000	13.017053000
C	20.969731000	7.776043000	12.460956000
C	20.671291000	9.021685000	11.895651000
H	21.465953000	9.744517000	11.753012000
C	19.368358000	9.342905000	11.500385000
C	18.355870000	8.389590000	11.667897000
H	17.355177000	8.613310000	11.319348000
C	17.562894000	6.113433000	12.363169000
C	17.850685000	4.830333000	11.883163000
H	18.834374000	4.636733000	11.466265000
C	16.901912000	3.814849000	11.916481000
H	17.153208000	2.827948000	11.538889000

C	15.633495000	4.074916000	12.424405000
H	14.876417000	3.295992000	12.444282000
C	15.343194000	5.344061000	12.920569000
H	14.357530000	5.526862000	13.339446000
C	16.289441000	6.380723000	12.921116000
C	14.299369000	7.619914000	14.899542000
C	14.373716000	6.579120000	15.845732000
H	15.212749000	5.887294000	15.810576000
C	13.401357000	6.420792000	16.832898000
H	13.478944000	5.606227000	17.548494000
C	12.321671000	7.306357000	16.892266000
H	11.559073000	7.186010000	17.656757000
C	12.220259000	8.335790000	15.956833000
H	11.377477000	9.020910000	15.993617000
C	13.200302000	8.489206000	14.973276000
H	13.120778000	9.305615000	14.260907000
C	15.353846000	9.380450000	12.627870000
C	14.238072000	9.278219000	11.784973000
H	13.608592000	8.391240000	11.826370000
C	13.923032000	10.295243000	10.884028000
H	13.053254000	10.199451000	10.239716000
C	14.734504000	11.426111000	10.800100000
H	14.503645000	12.211053000	10.085551000
C	15.855698000	11.538632000	11.620807000
H	16.517477000	12.394361000	11.528389000
C	16.153226000	10.528783000	12.531158000
H	17.044544000	10.627132000	13.144019000
C	22.360384000	7.442972000	12.855146000
C	23.386286000	7.708947000	11.941306000
H	23.133933000	8.142162000	10.977527000
C	24.712392000	7.416906000	12.244386000
H	25.492244000	7.632508000	11.519533000
C	25.030845000	6.851429000	13.475446000
H	26.063122000	6.620771000	13.723935000
C	24.016493000	6.600884000	14.398529000
H	24.276064000	6.203810000	15.376797000
C	22.673249000	6.887402000	14.118171000
C	20.300690000	5.233894000	15.331329000
C	20.828498000	3.978346000	14.998484000
H	21.901310000	3.867407000	14.853039000
C	19.999825000	2.872241000	14.812648000
H	20.430144000	1.909423000	14.550012000
C	18.618882000	3.007619000	14.944298000
H	17.966958000	2.155248000	14.776684000
C	18.074144000	4.250478000	15.260468000
H	16.996124000	4.370892000	15.310418000
C	18.908240000	5.347651000	15.455368000
H	18.458821000	6.316372000	15.655391000
C	22.334069000	6.576883000	17.162498000
C	22.728658000	5.341985000	17.693527000
H	22.556318000	4.429501000	17.127933000
C	23.303103000	5.256103000	18.959855000
H	23.595259000	4.288797000	19.360360000
C	23.480837000	6.410393000	19.720645000
H	23.910087000	6.344619000	20.716873000
C	23.097071000	7.647396000	19.206044000
H	23.222926000	8.550727000	19.794126000
C	22.533918000	7.729003000	17.935790000
H	22.210827000	8.693039000	17.554333000
C	19.082702000	10.635814000	10.830061000

C	18.425111000	10.590608000	9.595038000
H	18.128208000	9.625463000	9.194442000
C	18.167323000	11.751113000	8.872859000
H	17.655818000	11.690935000	7.916401000
C	18.579549000	12.980751000	9.377354000
H	18.398338000	13.894268000	8.817793000
C	19.215651000	13.035024000	10.616468000
H	19.501825000	14.003616000	11.017049000
C	19.466887000	11.882824000	11.376746000
C	19.795871000	13.883970000	13.677556000
C	18.529296000	14.462572000	13.496674000
H	17.772607000	13.932686000	12.923447000
C	18.213554000	15.702074000	14.045284000
H	17.224610000	16.126609000	13.895600000
C	19.166428000	16.392262000	14.795542000
H	18.923239000	17.358574000	15.228919000
C	20.429096000	15.835751000	14.989451000
H	21.173768000	16.366645000	15.576332000
C	20.737058000	14.594439000	14.433564000
H	21.722789000	14.167353000	14.595682000
C	21.954973000	11.742048000	13.310460000
C	22.895852000	12.547012000	12.650613000
H	22.558413000	13.398942000	12.063360000
C	24.260164000	12.274096000	12.733806000
H	24.973495000	12.908894000	12.214771000
C	24.707115000	11.181305000	13.477050000
H	25.769013000	10.958532000	13.534184000
C	23.788443000	10.369462000	14.138826000
H	24.123244000	9.507342000	14.706960000
C	22.427766000	10.653151000	14.056829000
H	21.737002000	9.992072000	14.571135000
C	19.395929000	8.339332000	19.466620000
C	19.374982000	7.199959000	18.651931000
H	19.215506000	7.312057000	17.584759000
C	19.618902000	5.931800000	19.171703000
H	19.625450000	5.072343000	18.508317000
C	19.892144000	5.785088000	20.530159000
H	20.104257000	4.801152000	20.938731000
C	19.900438000	6.903760000	21.363591000
H	20.106798000	6.789248000	22.424486000
C	19.647620000	8.167748000	20.835457000
H	19.642489000	9.031906000	21.496689000
C	20.841054000	10.895511000	18.465399000
C	21.760721000	10.931259000	19.524711000
H	21.499439000	10.478993000	20.478790000
C	23.013824000	11.518044000	19.369839000
H	23.714938000	11.530844000	20.200124000
C	23.372178000	12.078368000	18.143225000
H	24.354327000	12.524393000	18.014022000
C	22.469885000	12.061603000	17.082762000
H	22.744869000	12.482694000	16.121714000
C	21.213882000	11.479211000	17.247444000
H	20.523118000	11.491998000	16.408439000
C	18.164818000	11.058070000	19.934570000
C	18.494628000	12.380361000	20.260779000
H	19.405750000	12.814774000	19.856927000
C	17.676727000	13.145087000	21.092449000
H	17.949454000	14.169922000	21.328877000
C	16.507263000	12.596004000	21.617389000
H	15.865255000	13.191934000	22.259962000

C	16.175529000	11.270882000	21.331862000
H	15.281022000	10.828952000	21.763396000
C	17.005541000	10.513089000	20.508409000
H	16.766674000	9.463853000	20.332136000
C	16.643279000	12.761156000	16.672064000
C	16.118074000	12.347358000	15.439465000
H	16.769227000	12.347622000	14.571677000
C	14.793468000	11.923291000	15.322575000
H	14.420788000	11.604291000	14.353983000
C	13.964164000	11.901841000	16.448115000
H	12.930751000	11.577642000	16.361148000
C	14.478126000	12.302778000	17.686259000
H	13.844557000	12.292554000	18.570148000
C	15.805114000	12.725778000	17.796294000
H	16.197255000	13.023980000	18.764219000
C	18.060059000	13.242912000	16.764215000
H	18.485732000	13.035355000	17.746051000
H	18.677177000	12.766216000	16.002310000
H	18.115403000	14.323364000	16.591628000

3-Tb^{Ph}

Tb	4.215131000	6.978173000	10.896513000
Si	5.673217000	3.985456000	12.256382000
Si	4.548526000	6.482571000	7.303562000
Si	0.681717000	6.489440000	11.506966000
Si	5.037030000	9.189969000	13.675605000
O	5.085579000	5.210974000	11.323559000
O	4.072564000	6.750048000	8.845711000
O	2.318844000	6.447528000	11.369933000
O	4.829128000	8.002669000	12.556517000
N	6.405182000	7.826661000	9.993121000
N	3.054756000	9.158008000	10.409078000
C	3.936268000	2.911996000	9.697881000
C	3.672172000	3.512765000	8.462121000
H	4.426553000	3.481059000	7.684386000
C	2.459443000	4.165209000	8.220816000
C	1.484984000	4.172041000	9.224275000
H	0.535744000	4.664092000	9.041055000
C	1.718694000	3.563723000	10.459603000
C	2.942752000	2.924697000	10.680099000
H	3.125539000	2.441361000	11.633567000
C	5.241543000	2.249481000	9.951218000
C	5.693457000	1.304237000	9.023282000
H	5.079933000	1.093312000	8.151936000
C	6.896315000	0.628930000	9.207133000
H	7.223949000	-0.100751000	8.471950000
C	7.668715000	0.886634000	10.336009000
H	8.605719000	0.359984000	10.494341000
C	7.238225000	1.842192000	11.254868000
H	7.867513000	2.071512000	12.111360000
C	6.037695000	2.546390000	11.084583000
C	4.470155000	3.570154000	13.639818000
C	3.198120000	4.157863000	13.679734000
H	2.908077000	4.860287000	12.904563000
C	2.285982000	3.828098000	14.679481000
H	1.297288000	4.276210000	14.674600000
C	2.639898000	2.911012000	15.667884000
H	1.928368000	2.649155000	16.446248000
C	3.906802000	2.326503000	15.653327000
H	4.186898000	1.612713000	16.423350000

C	4.811054000	2.652304000	14.643616000
H	5.793810000	2.185019000	14.639136000
C	7.271747000	4.620167000	13.024535000
C	7.321395000	5.023030000	14.366065000
H	6.460850000	4.858344000	15.007894000
C	8.451323000	5.651322000	14.887178000
H	8.462400000	5.971695000	15.924807000
C	9.558418000	5.879285000	14.073784000
H	10.437843000	6.371901000	14.478251000
C	9.526363000	5.492863000	12.733524000
H	10.386052000	5.674966000	12.093393000
C	8.389477000	4.878386000	12.215478000
H	8.365598000	4.601342000	11.164723000
C	2.187606000	4.830833000	6.921152000
C	0.997784000	4.519254000	6.252600000
H	0.323140000	3.792838000	6.696898000
C	0.678141000	5.111024000	5.034211000
H	-0.251499000	4.851556000	4.535478000
C	1.552685000	6.028821000	4.459454000
H	1.313882000	6.494887000	3.507505000
C	2.730152000	6.361516000	5.127126000
H	3.387013000	7.114198000	4.697560000
C	3.069086000	5.784683000	6.358954000
C	6.071303000	5.378282000	7.198501000
C	6.628251000	5.041464000	5.955971000
H	6.162634000	5.397988000	5.039197000
C	7.758117000	4.228827000	5.868461000
H	8.175310000	3.980884000	4.896119000
C	8.336530000	3.717282000	7.029486000
H	9.204326000	3.066663000	6.965663000
C	7.776210000	4.014494000	8.271680000
H	8.183552000	3.565665000	9.172646000
C	6.659609000	4.843515000	8.355040000
H	6.212305000	5.036813000	9.325269000
C	4.983512000	8.172182000	6.572193000
C	6.034154000	8.421805000	5.679388000
H	6.656028000	7.599500000	5.334768000
C	6.312765000	9.715758000	5.236268000
H	7.131721000	9.887995000	4.542504000
C	5.541190000	10.786600000	5.684402000
H	5.759091000	11.795294000	5.344343000
C	4.491640000	10.557982000	6.574314000
H	3.892195000	11.390367000	6.933402000
C	4.218255000	9.264346000	7.010415000
H	3.415585000	9.092132000	7.721553000
C	0.678497000	3.569772000	11.517340000
C	0.306079000	2.345486000	12.084696000
H	0.789074000	1.438253000	11.732871000
C	-0.671889000	2.276361000	13.071784000
H	-0.944554000	1.314180000	13.496104000
C	-1.296980000	3.440927000	13.508928000
H	-2.062584000	3.399208000	14.278558000
C	-0.912754000	4.666863000	12.969938000
H	-1.363191000	5.577405000	13.357222000
C	0.074718000	4.762284000	11.978362000
C	-0.057543000	7.162283000	9.911647000
C	0.775662000	7.344449000	8.795928000
H	1.823257000	7.065504000	8.853849000
C	0.276460000	7.857441000	7.601099000
H	0.936516000	7.958527000	6.744513000

C	-1.069918000	8.211044000	7.504798000
H	-1.462985000	8.612593000	6.574704000
C	-1.917028000	8.023917000	8.597739000
H	-2.970583000	8.278881000	8.520048000
C	-1.414328000	7.493674000	9.785977000
H	-2.094589000	7.325557000	10.618132000
C	0.297795000	7.615707000	12.972946000
C	1.070412000	7.406717000	14.127522000
H	1.859634000	6.661774000	14.121975000
C	0.860210000	8.149759000	15.285334000
H	1.480944000	7.970910000	16.157870000
C	-0.127708000	9.135646000	15.304647000
H	-0.291922000	9.723665000	16.203427000
C	-0.894310000	9.372194000	14.164589000
H	-1.662884000	10.140956000	14.175049000
C	-0.683304000	8.613962000	13.011228000
H	-1.295135000	8.804676000	12.133081000
C	6.850598000	9.683117000	13.659375000
C	7.792982000	8.803208000	13.107863000
H	7.465291000	7.844029000	12.717934000
C	9.141770000	9.148410000	13.053545000
H	9.856630000	8.452315000	12.624584000
C	9.571508000	10.375797000	13.556002000
H	10.623762000	10.645070000	13.512788000
C	8.648361000	11.258143000	14.116750000
H	8.979170000	12.215615000	14.510525000
C	7.299645000	10.911403000	14.164604000
H	6.583858000	11.613358000	14.587373000
C	4.488403000	8.459940000	15.318907000
C	4.329890000	7.069465000	15.402147000
H	4.518027000	6.463597000	14.521965000
C	3.917949000	6.459244000	16.584737000
H	3.789385000	5.381231000	16.616992000
C	3.657849000	7.241676000	17.710675000
H	3.333704000	6.773372000	18.636311000
C	3.807695000	8.628056000	17.645971000
H	3.598659000	9.238522000	18.520604000
C	4.218868000	9.229898000	16.457384000
H	4.316925000	10.312563000	16.413827000
C	3.985125000	10.693814000	13.250238000
C	4.461330000	11.683494000	12.378998000
H	5.485152000	11.629932000	12.017404000
C	3.640987000	12.732276000	11.965932000
H	4.028148000	13.492905000	11.292830000
C	2.325578000	12.809187000	12.424534000
H	1.688025000	13.633577000	12.114019000
C	1.833464000	11.829633000	13.287889000
H	0.809373000	11.875882000	13.648252000
C	2.657979000	10.782012000	13.692794000
H	2.260625000	10.020117000	14.354680000
C	7.301314000	7.884237000	9.265835000
C	8.397360000	7.916741000	8.322470000
H	8.088272000	8.489759000	7.443784000
H	8.617590000	6.889342000	8.016679000
H	9.279841000	8.372180000	8.778030000
C	2.081203000	9.779562000	10.354942000
C	0.836361000	10.509184000	10.268013000
H	0.231801000	10.081317000	9.462829000
H	1.036904000	11.566666000	10.086058000
H	0.310794000	10.403571000	11.220059000

3-Tb^{OtBu}

Tb	4.237172000	7.141480000	11.017272000
Si	5.752516000	4.099915000	12.214780000
Si	4.470934000	6.548198000	7.408833000
Si	0.693271000	6.500949000	11.493416000
O	5.193796000	5.393622000	11.356448000
O	4.063578000	6.916686000	8.949795000
O	2.331669000	6.601681000	11.464234000
O	4.767558000	8.099879000	12.715527000
N	6.349362000	8.130465000	10.049686000
N	3.042842000	9.364314000	10.535757000
C	3.972415000	2.979636000	9.735275000
C	3.655325000	3.579896000	8.513506000
H	4.384403000	3.562335000	7.712638000
C	2.422882000	4.205861000	8.315996000
C	1.478951000	4.180311000	9.347530000
H	0.507866000	4.633107000	9.187129000
C	1.775549000	3.592979000	10.580041000
C	3.020285000	2.980441000	10.757049000
H	3.247121000	2.508188000	11.705651000
C	5.301170000	2.350615000	9.927676000
C	5.747230000	1.422681000	8.980740000
H	5.106597000	1.186897000	8.135658000
C	6.982424000	0.795973000	9.115461000
H	7.307541000	0.076950000	8.368654000
C	7.792781000	1.090518000	10.208165000
H	8.756705000	0.602954000	10.325405000
C	7.367420000	2.034224000	11.141428000
H	8.024977000	2.297777000	11.966214000
C	6.131759000	2.685247000	11.021374000
C	4.529231000	3.600429000	13.546544000
C	3.436995000	4.419363000	13.864416000
H	3.300313000	5.364265000	13.350383000
C	2.482500000	4.010140000	14.791170000
H	1.622406000	4.640971000	14.992399000
C	2.610477000	2.774922000	15.423677000
H	1.856879000	2.448813000	16.134972000
C	3.694741000	1.950180000	15.126141000
H	3.793040000	0.982741000	15.611568000
C	4.643261000	2.359883000	14.190179000
H	5.466470000	1.693920000	13.938108000
C	7.378475000	4.639503000	12.995287000
C	7.715697000	4.363492000	14.324965000
H	7.033814000	3.781787000	14.940344000
C	8.898311000	4.851909000	14.880404000
H	9.140667000	4.636782000	15.917619000
C	9.761438000	5.628024000	14.109759000
H	10.678857000	6.016273000	14.543746000
C	9.441800000	5.911913000	12.781350000
H	10.110674000	6.521824000	12.179618000
C	8.260963000	5.420082000	12.232361000
H	8.005551000	5.663414000	11.204047000
C	2.114956000	4.880415000	7.031579000
C	0.926552000	4.555185000	6.369699000
H	0.264759000	3.817489000	6.814567000
C	0.593000000	5.148844000	5.156213000
H	-0.334994000	4.879042000	4.659938000
C	1.452317000	6.081480000	4.583084000
H	1.203827000	6.547814000	3.633671000

C	2.626369000	6.431266000	5.248632000
H	3.267728000	7.196293000	4.818171000
C	2.979235000	5.854077000	6.476170000
C	5.963636000	5.402447000	7.298996000
C	6.342800000	4.844015000	6.069003000
H	5.746035000	5.039466000	5.179784000
C	7.450729000	4.003328000	5.971586000
H	7.723407000	3.573485000	5.011305000
C	8.195593000	3.699315000	7.110611000
H	9.048757000	3.030368000	7.042580000
C	7.821463000	4.229163000	8.344067000
H	8.364739000	3.954768000	9.242991000
C	6.714509000	5.069581000	8.435753000
H	6.392518000	5.420408000	9.410241000
C	5.000647000	8.176255000	6.592742000
C	5.801868000	8.247935000	5.444293000
H	6.111759000	7.333485000	4.945381000
C	6.242359000	9.473059000	4.945025000
H	6.864895000	9.505602000	4.054753000
C	5.895333000	10.656246000	5.598515000
H	6.245907000	11.611982000	5.218376000
C	5.096809000	10.605916000	6.741765000
H	4.825915000	11.523924000	7.256788000
C	4.651597000	9.377549000	7.227691000
H	4.047229000	9.336979000	8.129116000
C	0.791917000	3.607395000	11.690039000
C	0.494678000	2.404011000	12.337898000
H	0.986301000	1.494447000	12.005036000
C	-0.419681000	2.357300000	13.385692000
H	-0.634951000	1.410181000	13.872332000
C	-1.052247000	3.523528000	13.805871000
H	-1.766247000	3.498074000	14.624365000
C	-0.744946000	4.731848000	13.182694000
H	-1.204385000	5.646400000	13.549610000
C	0.173519000	4.802770000	12.126477000
C	-0.044521000	6.944462000	9.817757000
C	0.775443000	7.419929000	8.783411000
H	1.851227000	7.452702000	8.922242000
C	0.234530000	7.788678000	7.554184000
H	0.892204000	8.122037000	6.757650000
C	-1.137090000	7.679600000	7.333376000
H	-1.556513000	7.953003000	6.369169000
C	-1.965248000	7.188941000	8.342545000
H	-3.032404000	7.080465000	8.167562000
C	-1.420294000	6.822675000	9.572463000
H	-2.073425000	6.409899000	10.339047000
C	0.120890000	7.846175000	12.693991000
C	1.084444000	8.458988000	13.509607000
H	2.111817000	8.107191000	13.474029000
C	0.750134000	9.535495000	14.330727000
H	1.513752000	10.001072000	14.947166000
C	-0.559250000	10.016386000	14.354625000
H	-0.820774000	10.856745000	14.992036000
C	-1.532579000	9.414075000	13.556213000
H	-2.553805000	9.785571000	13.568926000
C	-1.189994000	8.343117000	12.732827000
H	-1.953153000	7.907599000	12.093140000
C	7.111469000	8.302785000	9.196985000
C	8.036249000	8.473892000	8.098120000
H	7.633104000	9.213550000	7.400356000

H	8.128988000	7.514084000	7.581435000
H	9.013511000	8.795404000	8.466504000
C	2.006035000	9.876413000	10.597827000
C	0.692590000	10.479184000	10.670917000
H	-0.024508000	9.788531000	10.218575000
H	0.682462000	11.429690000	10.131583000
H	0.422431000	10.635859000	11.718993000
C	5.475560000	8.767338000	13.726142000
C	6.478309000	9.726689000	13.081551000
H	7.039883000	10.283236000	13.839593000
H	7.186028000	9.164264000	12.466527000
H	5.955308000	10.440532000	12.437113000
C	6.205578000	7.721815000	14.571025000
H	6.730302000	8.184114000	15.414201000
H	5.490635000	6.991364000	14.961127000
H	6.934550000	7.184918000	13.960192000
C	4.469459000	9.543465000	14.579671000
H	3.898150000	10.230226000	13.947113000
H	3.771276000	8.848683000	15.056679000
H	4.970219000	10.120996000	15.363839000

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