Supporting information for the manuscript

Structure, Reactivity and Luminescence Studies of Triphenylsiloxide Complexes of Tetravalent Lanthanides

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A. Experimental Details

General considerations

Unless otherwise noted, all reactions were performed in an inert atmosphere MBraun glovebox under an atmosphere of purified argon (<1 ppm O_2/H_2O). Glassware was dried overnight at 150 °C prior to use. Syntheses were performed using glass covered stirring bars. Unless otherwise noted reagents were acquired from commercial suppliers and used without further purification. Anhydrous $LnCl_3$ (Ln = Ce, Pr, Nd, Gd), TbI_3 and $OPPh_3$ were acquired from Aldrich and used as such. $HOSiPh_3$ was purchased from Aldrich and dried under vacuum at 60 °C for 1 day prior to use. The solvents were purchased from Aldrich or Cortecnet (deuterated solvents) in their anhydrous form, conditioned under argon and vacuum distilled from K/benzophenone, Na/benzophenone (THF, toluene, n-hexane) and degassed prior to use. $AgBPh_4$,[1] $[Ln\{N(SiMe_3)_2\}_3]$ (Ln = Nd, Gd)[2], $KOSiPh_3$,[3,4] $[KLn(OSiPh_3)_4(THF)_x]$ (Ln = Pr and Tb), **1-Ln**,[3,4] and $[Ln(OSiPh_3)_4(MeCN)_2]$ (Ln = Pr and Tb), **3-Ln^{MeCN}**,[3,4] were prepared according to the respective published procedures. NMR experiments were carried out using NMR tubes adapted with J.Young valves. NMR spectra were recorded on Bruker 400 MHz spectrometers. ^1H chemical shifts are reported in ppm and were measured relative to residual solvent peaks. CHN elemental microanalysis were obtained using a Thermo Scientific Flash 2000 Organic Elemental Analyzer and performed under nitrogen by the analytical service at EPFL.

UV-Visible and FT-IR measurements

The UV-Visible spectra were recorded as 0.05 mM (for **1-Ln** and **3-Pr^{MeCN}**), 0.15 mM (for KL^{Ph}) solutions in THF or a 3 mM solution in toluene (for **4-Pr^{Ph}** and **4-Tb^{R}**) using 1mm cuvettes equipped with a J-Young valve and a Perkin Elmer 750 spectrometer. To ensure reliable photophysical data and avoid decomposition, the samples were prepared by dissolution of the corresponding compounds in the corresponding solvent in the glovebox and measured immediately after their preparation.

Infrared analyses were performed with a PerkinElmer Frontier FT-IR in presence of nujol in KBr cells. The compounds in solid state where ground using an agate mortar and pestle in presence of nujol. The corresponding formed glue was layered on a KBr cells and recovered with a second KBR cell in the glovebox.

Luminescence studies

A 5 mM toluene solution of each complex was transferred, in the glovebox, in a 1 cm cuvettes equipped with a J-Young valve. For the solutions studies of $[Pr(OSiPh_3)_4(MeCN)_2]$, **3-Pr^{MeCN}**, and $[Pr(OSiPh_3)_4(OPPh_3)(MeCN)]$, **4-Pr^{Ph}**, the solutions were immediately frozen with liquid nitrogen after dissolution. The emission and excitation spectra were recorded at room temperature or at 77K on a Horiba-Jobin Yvon Fluorolog FL-3-22 fluorimeter equipped with CW 450W Xenon source for fluorescence mode and a UV xenon flash tube for the phosphorescence mode. Data were collected by using a thermoelectrically cooled R2658P PMT (Hamamatsu, range 220-1010 nm) or a NIR PMT (950-1700 nm, thermoelectrically cooled H10330-75 NIR-PMT; Hamamatsu). A blank with toluene was recorded confirming that toluene does not affect the spectra. The spectra were corrected by the instrumental correction function. Data processing was performed with the program Origin 8®. Low temperature measurements were done in liquid nitrogen using a quartz Dewar. Luminescence decays were recorded by using TCSPC DeltaTime unit from Horiba and a xenon pulse lamp. The setup was used in phosphorescence mode with the delay set to 0 and in a range up to 340 μs which corresponds to a sampling width of 83 ns per channel. The full width at half maximum (FWHM) of the 276-nm flash pulse was found to be 230 ns, meaning that lifetimes down to ~1 μs can be determined without interference from the lamp. The decays were analysed by using the DAS software, and fitted with mono, bi- or tri-exponential functions; the best fits were kept. Data reported are averages of at least three independent measurements.

Electrochemistry. Voltammetry experiments were performed using a Bio-Logic SP300 potentiostat and the data were processed using EC-lab software. All experiments were performed in an Ar atmosphere glovebox using electrochemical cells consisting of a 4 mL vial, a glassy carbon (1 mm diameter) working electrode, a platinum wire counter electrode, and a silver wire plated with AgCl for the reference electrode. The working electrode surface was polished prior to each experiment. Solutions used contained 2 mM analyte and 100 mM $[NBu_4][B(C_6F_5)_4]$. Ferrocene was added as an internal standard for calibration at the end of each run.

Syntheses

Synthesis of [Nd(OSiPh$_3$)$_3$(THF)$_3$]. $[Nd(OSiPh_3)_3)_3(THF)_3]$[5] was synthetized in a similar manner as the previously reported $[Ln(OSiPh_3)_3)_3(THF)_3]$ (Ln = Ce, Pr) complexes.[4] A solution of $HOSiPh_3$

(228.0 mg, 0.825 mmol, 3 equiv.) in THF (1 mL) was added at room temperature to a solution of $[Nd\{N(SiMe_3)_2\}_3]$ (172.0 mg, 0.275 mmol, 1 equiv.) in THF (0.5 mL) resulting in the precipitation of a blue solid. The blue suspension was stirred 30 minutes at room temperature. The colorless supernatant was removed while the pale blue solid was washed with n-hexane (3 x 2 mL) and dried under vacuum for 1 hour affording $[Nd(OSiPh_3)_4(THF)_3]$ in 81 % yield (264.6.3 mg, 0.223 mmol). Anal. Calcd for $[Nd(OSiPh_3)_4(THF)_3]$ (1186.7 g mol^{-1}): $C_{66}H_{69}O_6Si_3Nd$: C, 66.80; H, 5.86. Found: C, 66.96; H, 5.85. ^1H NMR (THF-d_8, 400 MHz, 298 K): δ = 10.0 (br s, 18 H, Ph), 7.5 (s, 27 H, Ph) ppm. ^1H NMR (Tol-d_8, 400 MHz, 298 K): δ = 14.2 (br s, 18 H, Ph), 8.2 (s, 18 H, Ph), 7.8 (s, 9 H, Ph), −5.2 (br s, 12 H, THF), −10.6 (br s, 12 H, THF) ppm.

Synthesis of $[Gd(OSiPh_3)_3(THF)_3]$. $[Gd(OSiPh_3)_3)_3(THF)_3]$ was synthetized in a similar manner than the previously reported $[Ln(OSiPh_3)_3)_3(THF)_3]$ (Ln = Ce, Pr) complexes.[4] A solution of $HOSiPh_3$ (140.9 mg, 0.512 mmol, 3 equiv.) in THF (1 mL) was added at room temperature to a solution of $[Gd\{N(SiMe_3)_2\}_3]$ (109.0 mg, 0.171 mmol, 1 equiv.) in THF (0.5 mL) resulting in the precipitation of a white solid. The suspension was stirred 30 minutes at room temperature. The colorless supernatant was removed while the colorless solid was washed with n-hexane (3 x 1.5 mL) and dried under vacuum for 1 hour affording $[Gd(OSiPh_3)_4(THF)_3]$ in 90 % yield (185.3 mg, 0.155 mmol). Anal. Calcd for $[Gd(OSiPh_3)_4(THF)_3]$ (1199.8 g mol^{-1}): $C_{66}H_{69}O_6Si_3Gd$: C, 66.07; H, 5.80. Found: C, 66.08; H, 5.97. The ^1H NMR of $[Gd(OSiPh_3)_3)_3(THF)_3]$ in d_8-THF resulted silent.

Synthesis of $[KNd(OSiPh_3)_4(THF)_2]$, 1-Nd. A solution of $KOSiPh_3$ (62.5 mg, 0.199 mmol, 1 equiv.) in THF (1.5 mL) was added at room temperature to a blue suspension of $[Nd(OSiPh_3)_3(THF)_3]$ (236.0 mg, 0.199 mmol, 1 equiv.) in THF (0.5 mL). The resultant pale blue solution was stirred for 30 minutes at room temperature and filtered.

Layering of the concentrated reaction mixture with n-hexane resulted in the deposition of pale blue crystalline solid overnight. The pale blue residue was washed with *n*-hexane (3 x 2 mL) and dried for 30 min affording $[KNd(OSiPh_3)_4(THF)_3]$, **1-Nd**, in 75% yield (224.1 mg, 0.149 mmol). Anal. Calcd for $[KNd(OSiPh_3)_4(THF)_2]$ (1429.2 g mol^{-1}): $C_{80}H_{76}O_6Si_4KNd$: C, 67.23; H, 5.36. Found: C, 66.85; H, 5.64. ^1H NMR (THF-d_8, 400 MHz, 298 K): δ = 10.1 (br s, 24 H, Ph), 7.3 (s, 36 H, Ph) ppm. ^1H NMR (Tol-d_8, 400 MHz, 298 K): δ = 8.2 (br s, 24 H, Ph), 7.3 (s, 24 H, Ph), 7.1 (s, 12 H, Ph), −4.8 (br s, 8 H, THF), −9.3 (br s, 8 H, THF) ppm. Crystals of **1-Nd**, suitable for X-ray diffraction analysis were obtained from a concentrated toluene solution **1-Nd** stored at −40 °C for two days.

Synthesis of $[KGd(OSiPh_3)_4(THF)_3]$, 1-Gd. A solution of $KOSiPh_3$ (37.4 mg, 0.119 mmol, 1 equiv.) in THF (1 mL) was added at room temperature to a colorless slurry of $[Gd(OSiPh_3)_3(THF)_3]$ (142.7 mg, 0.119 mmol, 1 equiv.) in THF (0.5 mL). The resultant colorless solution was stirred for 30 minutes at room temperature and filtered. Layering of the concentrated filtrate with *n*-hexane resulted in the deposition of colorless crystalline solid overnight. The residue was washed with n-hexane (3 x 2 mL) and dried for 30 min affording $[KGd(OSiPh_3)_4(THF)_3]$, **1-Gd**, in 82% yield (148.7 mg, 0.098 mmol). Anal. Calcd for $[KGd(OSiPh_3)_4(THF)_3]$ (1514.2 g mol^{-1}): $C_{84}H_{84}O_7Si_4KGd$: C, 66.63; H, 5.59. Found: C, 66.69; H, 5.19. The ^1H NMR of **1-Gd** in d_8-THF resulted silent. Single crystals suitable for X-ray diffraction analysis were obtained from a THF solution of **1-Gd** layered with n-hexane at −40 °C.

Synthesis of $[K_2Nd(OSiPh_3)_4]$, 2-Nd. A solution of $KOSiPh_3$ (36.5 mg, 0.116 mmol, 1 equiv.) in toluene (1 mL) was added at room temperature to a blue solution of $[KNd(OSiPh_3)_4(THF)_2]$ (166 mg, 0.116 mmol, 1 equiv.) in toluene (0.5 mL). The blue solution was stirred for 15 minutes at room temperature and was then filtrated. Layering of the concentrated reaction mixture with *n*-hexane resulted in the deposition of pale blue crystalline solid overnight. The pale blue residue was washed with *n*-hexane (3 x 2 mL) and dried for 30 min affording $[K_2Nd(OSiPh_3)_5]$ in 78 % yield (151.8 mg, 0.095 mmol). Anal. Calcd for $[K_2Nd(OSiPh_3)_5].C_6H_{14}$ (1685.6 g mol^{-1}): $C_{96}H_{89}O_5Si_5K_2Nd$: C, 68.41; H, 5.32. Found: C, 68.22; H, 4.95. ^1H NMR (Tol-d_8, 400 MHz, 298 K): δ = 6.8 (s, 15 H, Ph), 6.1 (s, 30 H, Ph), 5.2 (br s, 30 H, Ph) ppm. Crystals of **2-Nd**, suitable for X-ray diffraction analysis were obtained from a saturated toluene solution **2-Nd** stored at −40 °C overnight.

Isolation of single crystals of $[KCe(OSiPh_3)_3)_4(THF)_2]$, 1-Ce. $[KCe(OSiPh_3)_4(THF)_2]$, 1-Ce, was prepared according to the published procedure[4] and single crystals suitable for X-ray diffraction analysis were obtained from a concentrated toluene solution of **1-Ce** stored at −40 °C for two hours.

Synthesis of $[Ce(OSiPh_3)_4(THF)_2]$, 3-Ce^{THF}. In the dark, a solution of $[KCe(OSiPh_3)_4(THF)_2]$, **1-Ce**, (210.0 mg, 0.140 mmol, 1 equiv.) in THF (3.5 mL) was added at room temperature to a slurry of $AgBPh_4$ (65.9 mg, 0.157 mmol, 1.1 equiv.) in THF (0.5 mL). The suspension immediately turned dark brown and was stirred in the dark for 2 hours. The suspension was filtered 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 (4 mL) and filtered. Slow diffusion of n-hexane (4 mL) on the concentrated yellow filtrate yielded colorless crystals, washed with toluene (2 x 1 mL) and n-hexane (3 x 2 mL), of $[Ce(OSiPh_3)_4(THF)_2]$, **3-Ce^{THF}**, in 61 % yield (118.4 mg, 0.085 mmol). Anal. Calcd for $[Ce(OSiPh_3)_4(THF)_2]$ (1385.9 g mol^{-1}): $C_{80}H_{76}O_6Si_4Ce$: C, 69.33; H, 5.53. Found: C, 69.21; H, 5.53. ^{1}H NMR (THF-d_8, 400 MHz, 298 K): δ = 7.7 ppm (d, 24H, Ph), 7.1 ppm (t, 12H, Ph), 6.9 ppm (t, 24H, Ph). Crystals of **3-Ce^{THF}**, suitable for X-ray diffraction analysis were obtained by storage of a concentrated THF solution of **3-Ce^{THF}** at −40 °C overnight.

Isolation of single crystals of $[Tb(OSiPh_3)_4(THF)_2]$, 3-Tb^{THF} . Single crystals of **3-Tb^{THF}** suitable for X-ray diffraction analysis were obtained from a concentrated THF solution of **3-Tb^{MeCN}** stored at −40 °C overnight.

Synthesis of $[Pr(OSiPh_3)_4(OPPh_3)(MeCN)]$, 4-Pr^{Ph}. A colorless solution of $OPPh_3$ (14.9 mg, 0.054 mmol, 1 equiv.) in toluene (0.8 mL) was added at room temperature to a dark red solution of **3-Pr^{MeCN}** (71.0 mg, 0.054 mmol, 1 equiv.) in toluene (0.8 mL). The dark red solution was stirred at room temperature for 5 minutes. Slow diffusion of *n*-hexane (4 mL) on the reaction mixture at −40 °C yielded dark brown crystals, washed with *n*-hexane (3 x 2 mL), of $[Pr(OSiPh_3)_4(OPPh_3)(MeCN)]$, **4-Pr^{Ph}**, in 90 % yield (76.3 mg, 0.049 mmol). Anal. Calcd for $[Pr(OSiPh_3)_4(OPPh_3)(MeCN)]$ (1561.8 g mol^{-1}): $C_{92}H_{78}NO_5Si_4PPr$: C, 70.75; H, 5.03; N, 0.90. Found: C, 70.85; H, 5.41; N, 0.58. ^{1}H NMR (Tol-d_8, 400 MHz, 298 K): δ = 7.2 ppm (t, 4H, Ph), 7.1 ppm (br, 11H, Ph), 6.9 ppm (br, 14H, Ph), 6.7 ppm (br, 46H, Ph). UV-Vis (toluene) λ_{max} = 375 nm (ε = 4500 M^{-1} cm^{-1}). Crystals of **4-Pr^{Ph}**, suitable for X-ray diffraction analysis were obtained by storage of a concentrated toluene solution of **4-Pr^{Ph}** at −40 °C for 5 days.

B. NMR spectroscopic data

The ^{1}H NMR spectrum of **1-Gd** remained silent, which is consistent with the presence of the $4f^7$ Gd(III) ion. The ^{1}H NMR spectrum of **1-Nd** in THF-d_8 at room temperature showed two signals at δ = 10.1 ppm and 7.3 ppm corresponding to the protons of the triphenylsiloxides (Fig. S3). At lower temperature (193 K) three signals are detected for these protons (Fig. S4) in agreement with the slowing down of ligand fluxional exchanges. Similarly, ^{1}H NMR spectroscopy indicated that ligand fluxionality is slowed down at low temperatures for **1-Pr** and **1-Tb** resulting in the observation of an increased number of signals for the siloxide ligands. On the other hand, decreasing the temperature only affects the broadening of the three signals observed in the ^{1}H NMR spectrum of **1-Ce** (Fig. S5) suggesting a higher fluxionality of the cerium complex. In toluene-d_8, the ^{1}H NMR spectrum at room temperature of **1-Ln** (Ln = Ce, Pr, Nd) shows three signals for the triphenylsiloxide protons, suggesting a reduced fluxionality of the species in a less polar solvent (Fig. S6, S7 and S8). The ^{1}H NMR spectrum of **2-Nd** in toluene-d_8 shows three signals at δ = 6.8 ppm, 6.1 ppm and 5.2 ppm (Fig. S11) corresponding to the 75 protons of the five triphenylsiloxide ligands belonging to the fluxional Nd(III) species. The ^{1}H NMR spectrum of **3-Ce^{THF}** in THF-d_8 shows three signals at δ = 7.7 ppm, 7.1 ppm and 6.9 ppm in agreement with fluxional phenyl groups present in solution (Fig. S13). Variable temperature ^{1}H NMR studies of **3-Ce^{THF}** in THF-d_8 suggest a reduced fluxionality of the species in solution at 233 K and 193 K where six signals corresponding to the 60 protons of the four siloxide ligands were identified in the spectra (Fig. S14). These features indicate a lower fluxionality of the siloxide ligands in the Ce(IV) species in THF compared to the Ce(III) precursor for which only three signals are identified in the ^{1}H NMR spectra at low temperature (Fig. S5).

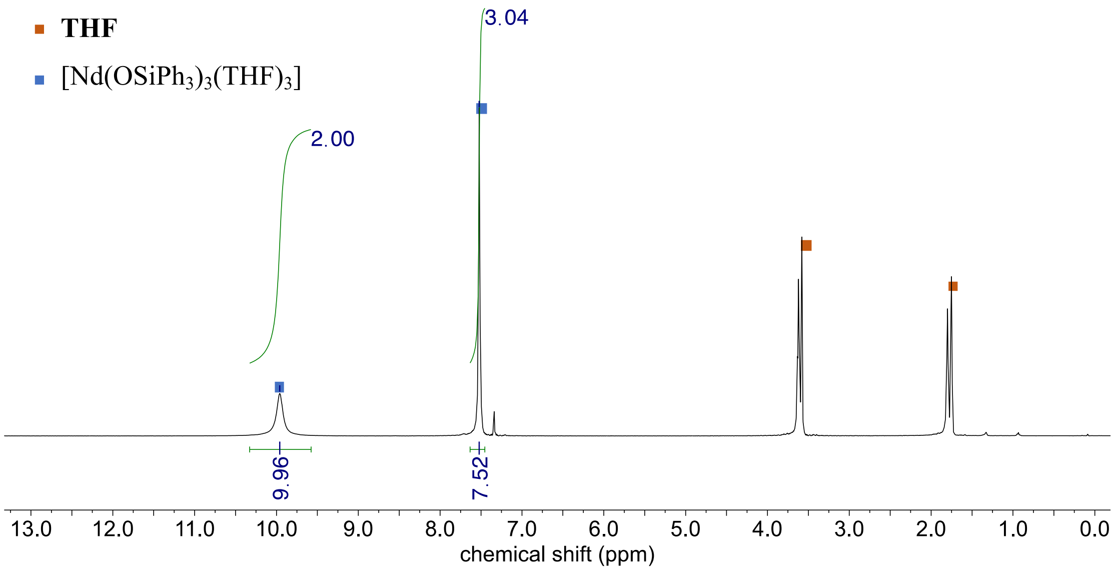


Fig. S1: ^{1}H NMR spectrum (400 MHz, 298 K, THF-d_8) of [Nd(OSiPh$_3$)$_3$(THF)$_3$] .

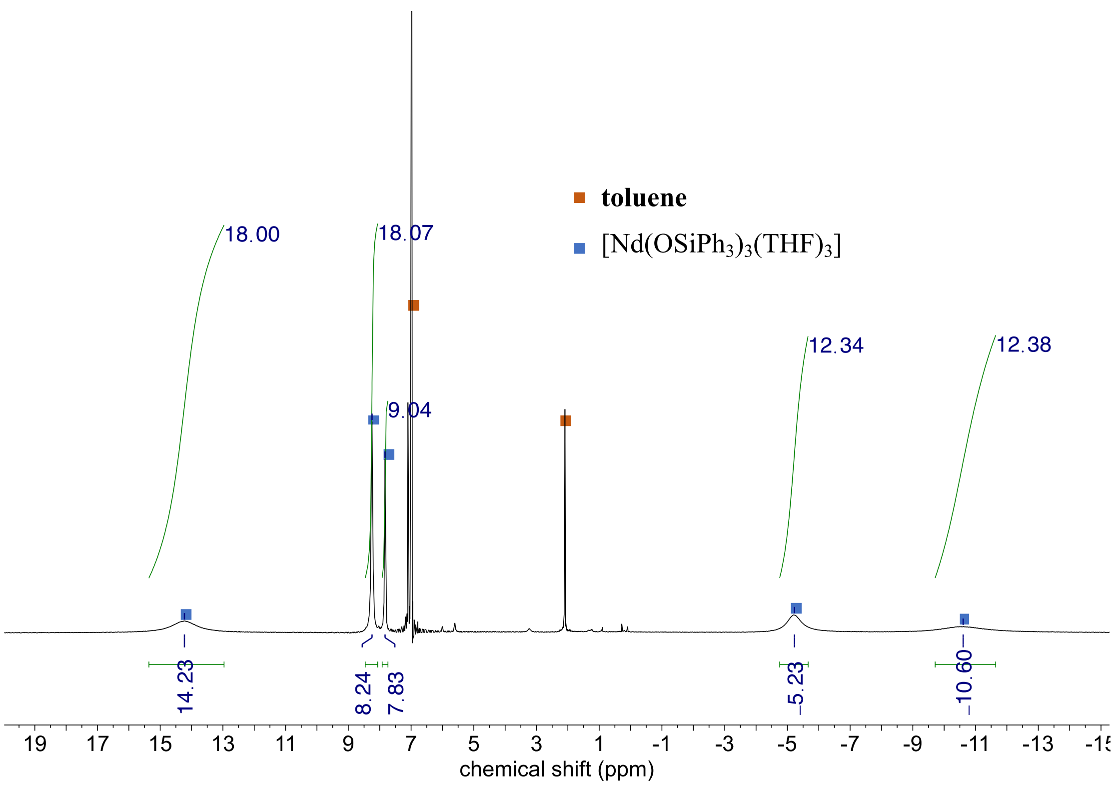


Fig. S2: ^{1}H NMR spectrum (400 MHz, toluene-d_8, 298 K) of [Nd(OSiPh$_3$)$_3$(THF)$_3$] .

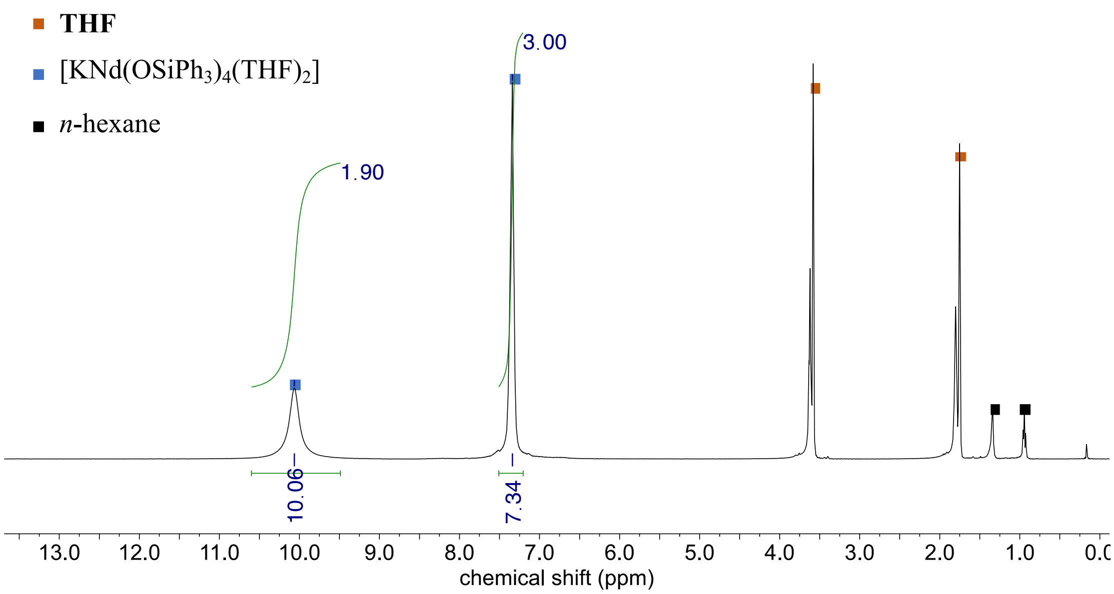


Fig. S3: ^{1}H NMR spectrum (400 MHz, 298 K, THF-d_8) of **1-Nd**.

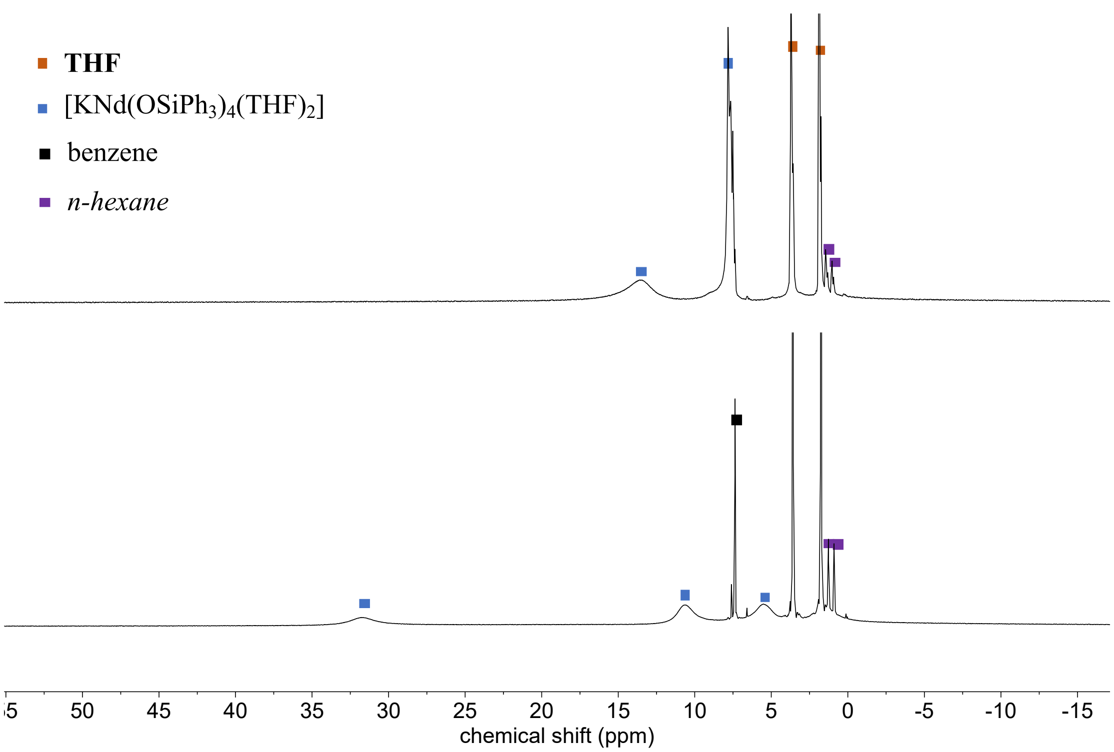


Fig. S4: Variable temperature ^{1}H NMR spectra (400 MHz, THF-d_8) of **1-Nd** at 233 K (top) and 193 K (bottom).

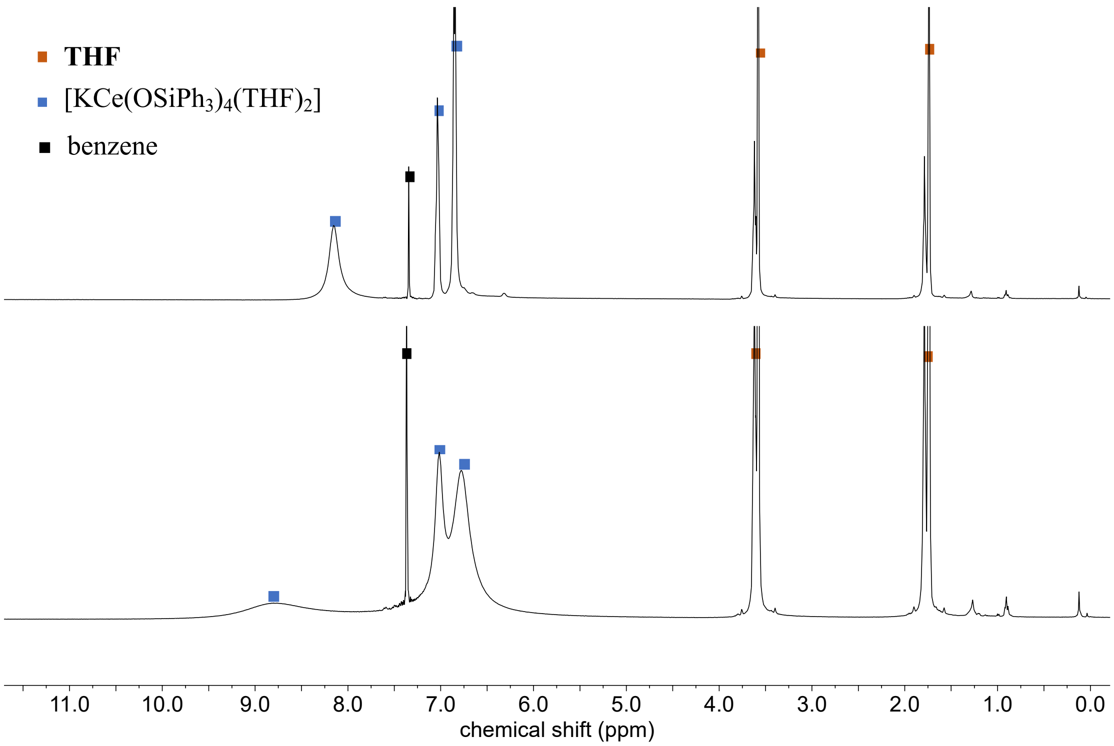


Fig. S5: Variable temperature [1]H NMR spectra (400 MHz, THF-d_8) of **1-Ce** at 233 K (top) and 193 K (bottom).

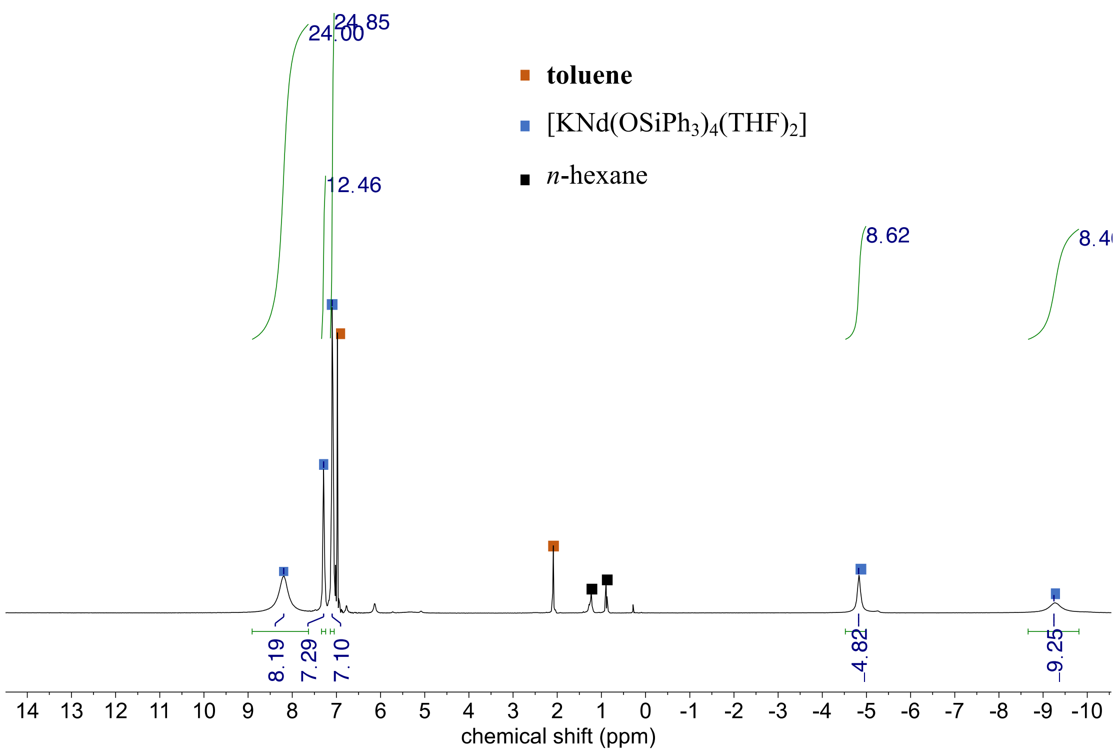


Fig. S6: [1]H NMR spectrum (400 MHz, toluene-d_8, 298 K) of **1-Nd**.

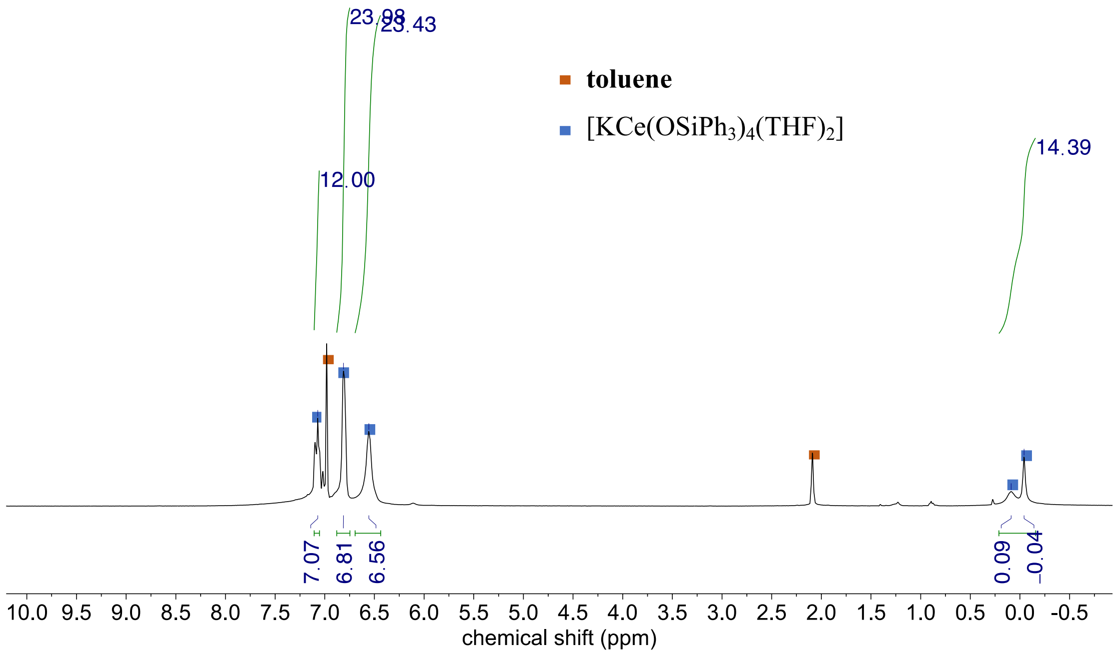


Fig. S7: ^{1}H NMR spectrum (400 MHz, toluene-d$_8$, 298 K) of **1-Ce**.

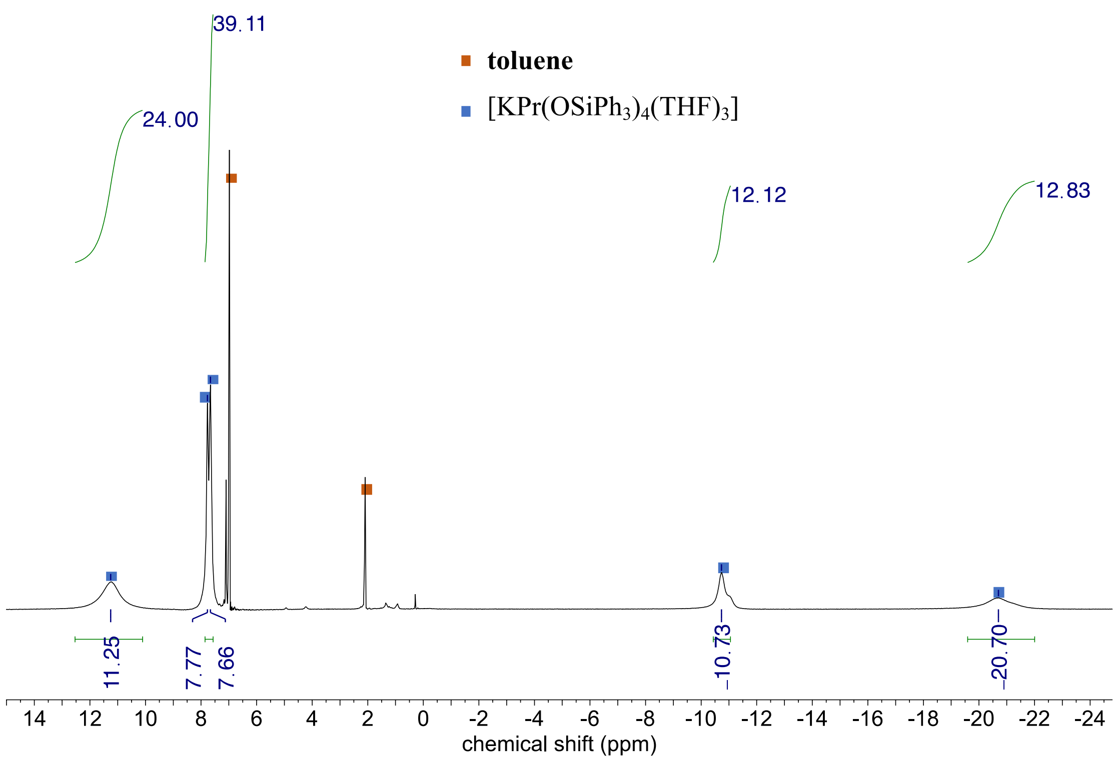


Fig. S8: ^{1}H NMR spectrum (400 MHz, toluene-d$_8$, 298 K) of **1-Pr**.

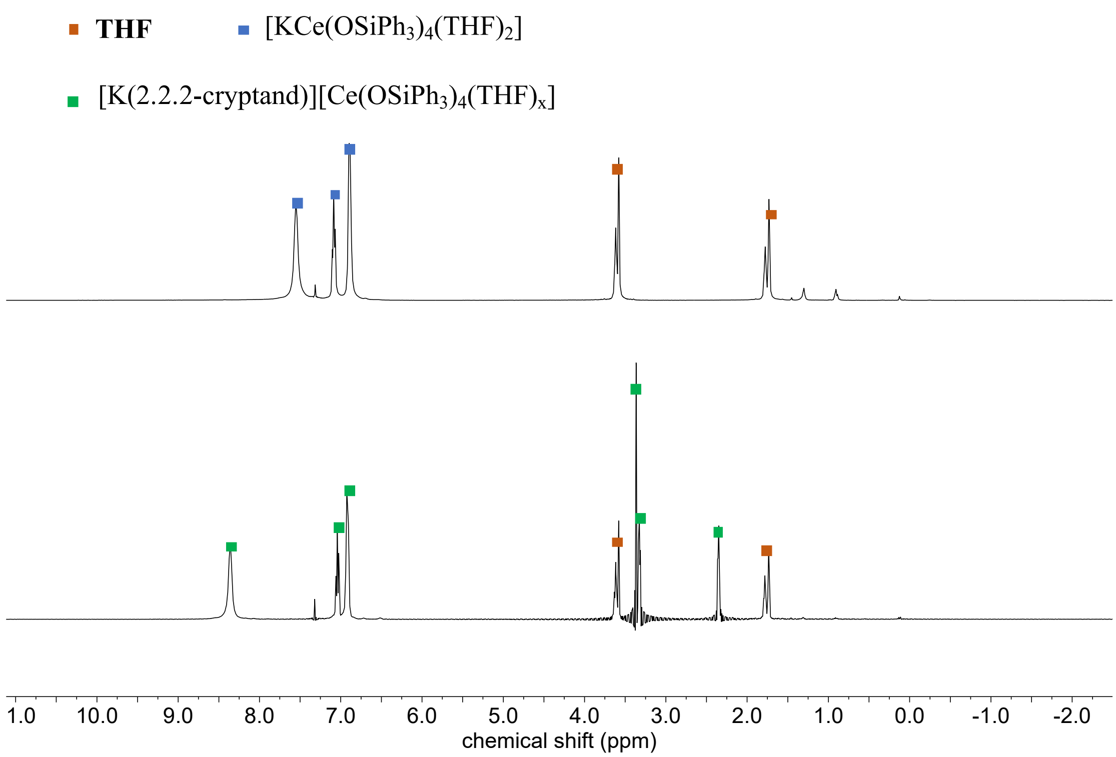


Fig. S9: ^{1}H NMR spectra (400 MHz, THF-d_8, 298 K) of **1-Ce**, before (top)[6] and after (bottom) addition of 1 equivalent 2.2.2-cryptand.

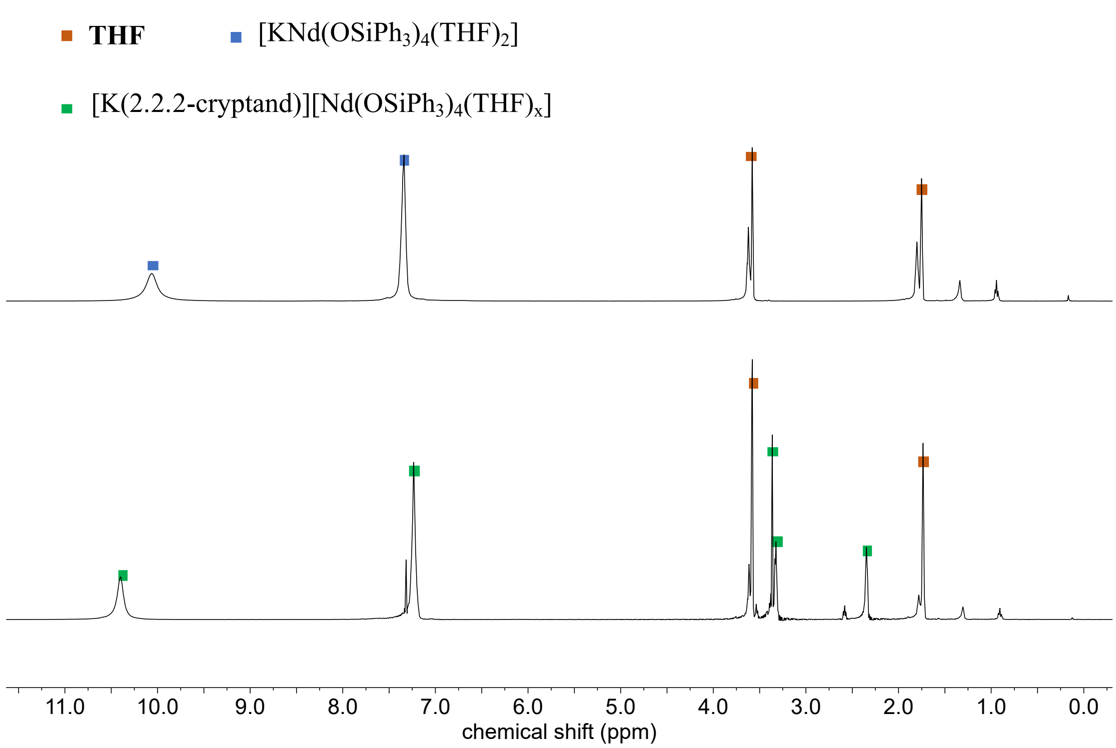


Fig. S10: ^{1}H NMR spectra (400 MHz, THF-d_8, 298 K) of **1-Nd**, before (top) and after (bottom) addition of 1 equivalent 2.2.2-cryptand.

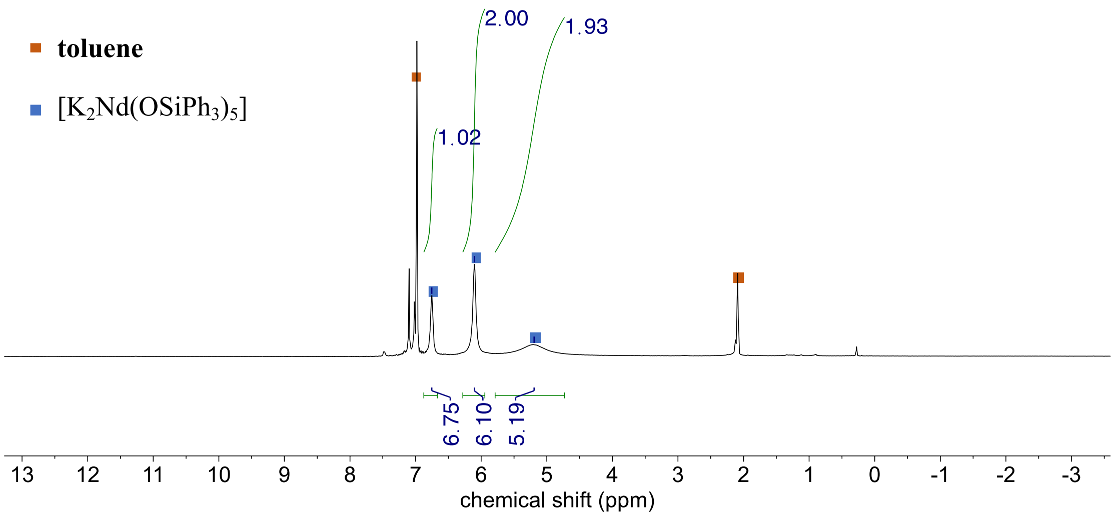


Fig. S11: ^{1}H NMR spectrum (400 MHz, toluene-d_8, 298 K) of **2-Nd**.

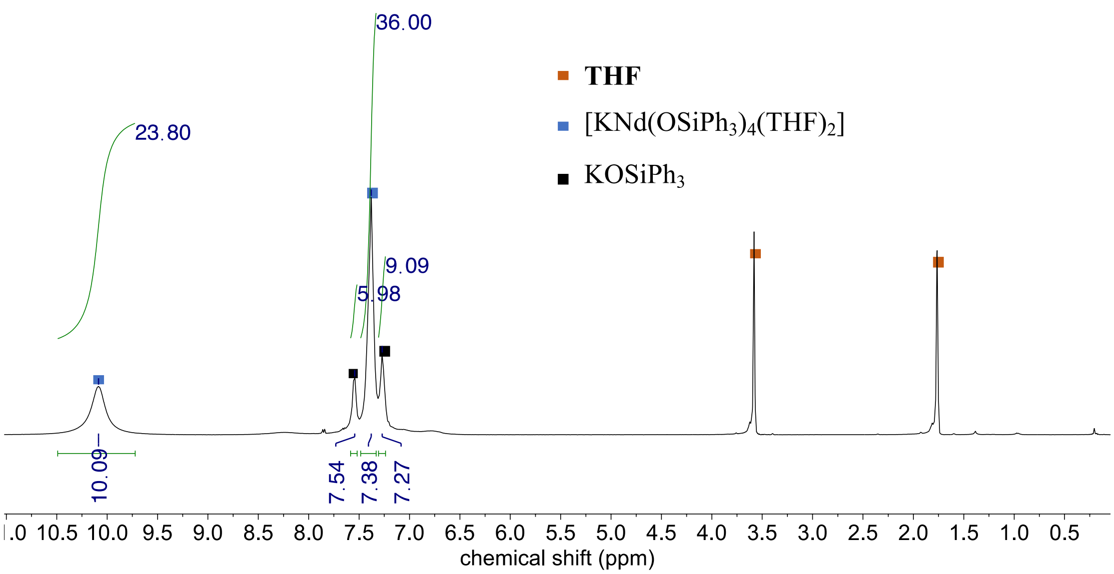


Fig. S12: ^{1}H NMR spectrum (400 MHz, THF-d_8, 298 K) of **2-Nd** after dissolution in THF-d_8.

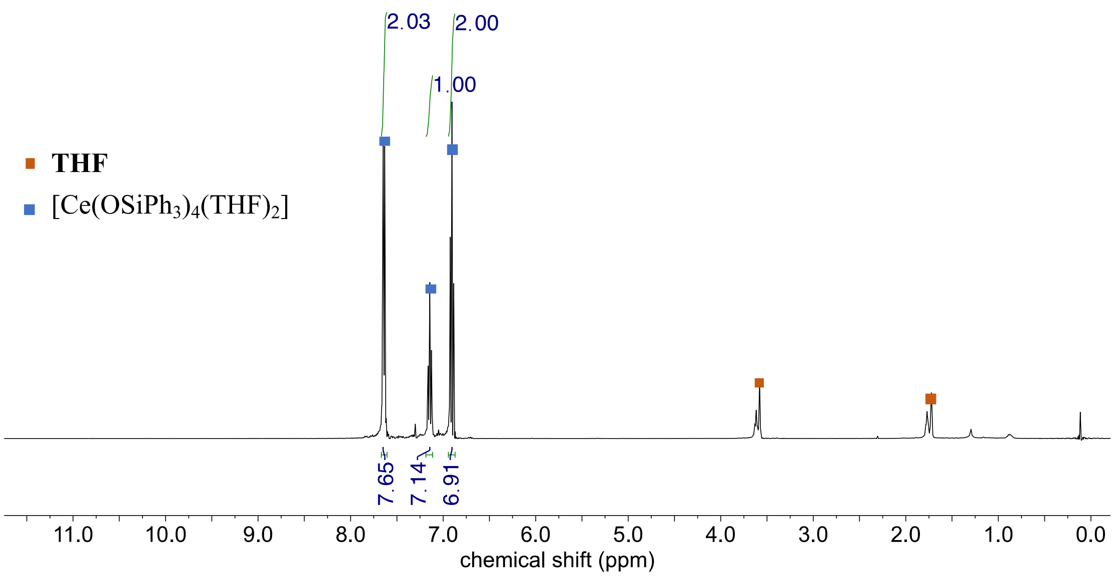


Fig. S13: ^{1}H NMR spectrum (400 MHz, 298 K, THF-d_8) of **3-Ce^{THF}**.

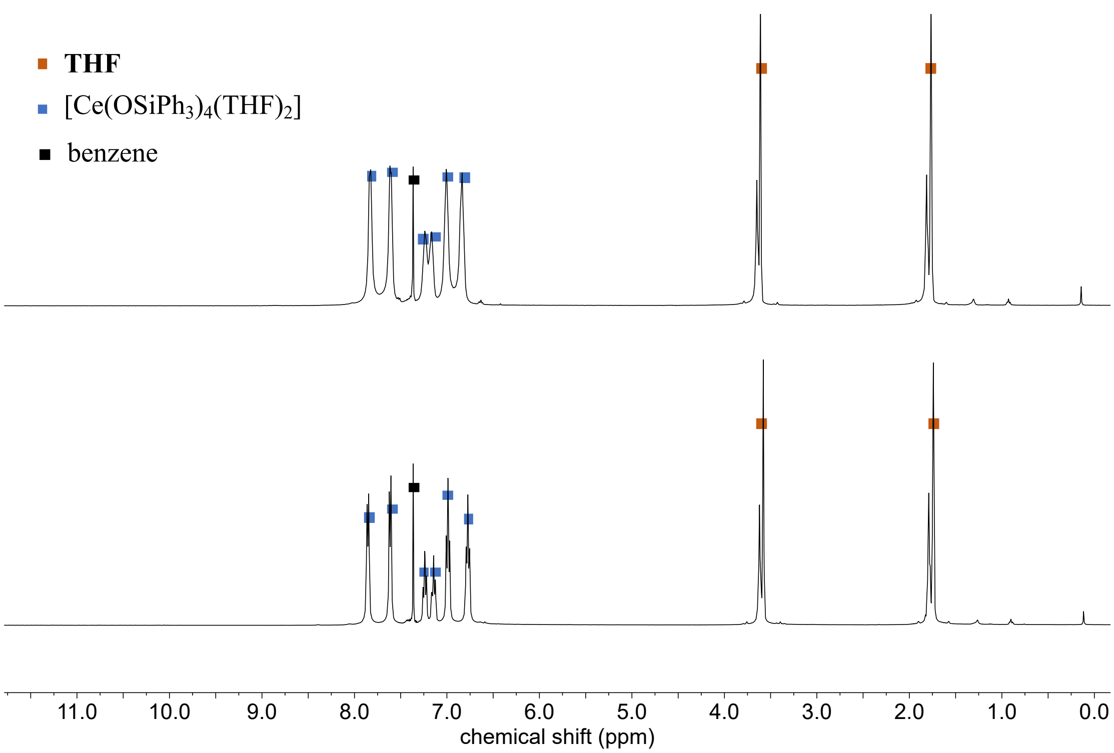


Fig. S14: ^{1}H NMR spectrum (400 MHz, THF-d_8) **3-Ce^{THF}** at 233 K (top) and 193 K (bottom).

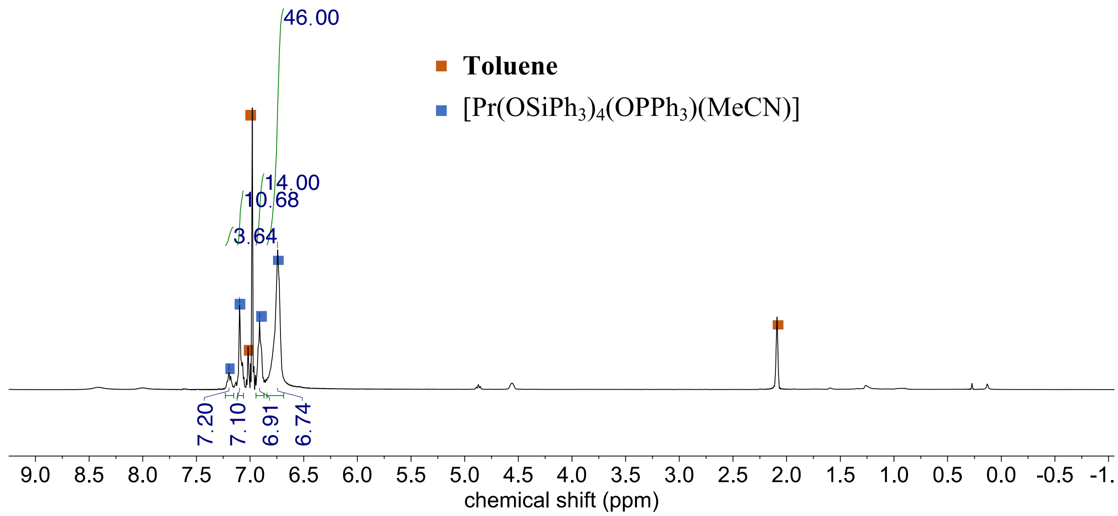


Fig. S15: ^{1}H NMR spectrum (400 MHz, 298 K, Toluene-d_8) of **4-Pr^{Ph}**.

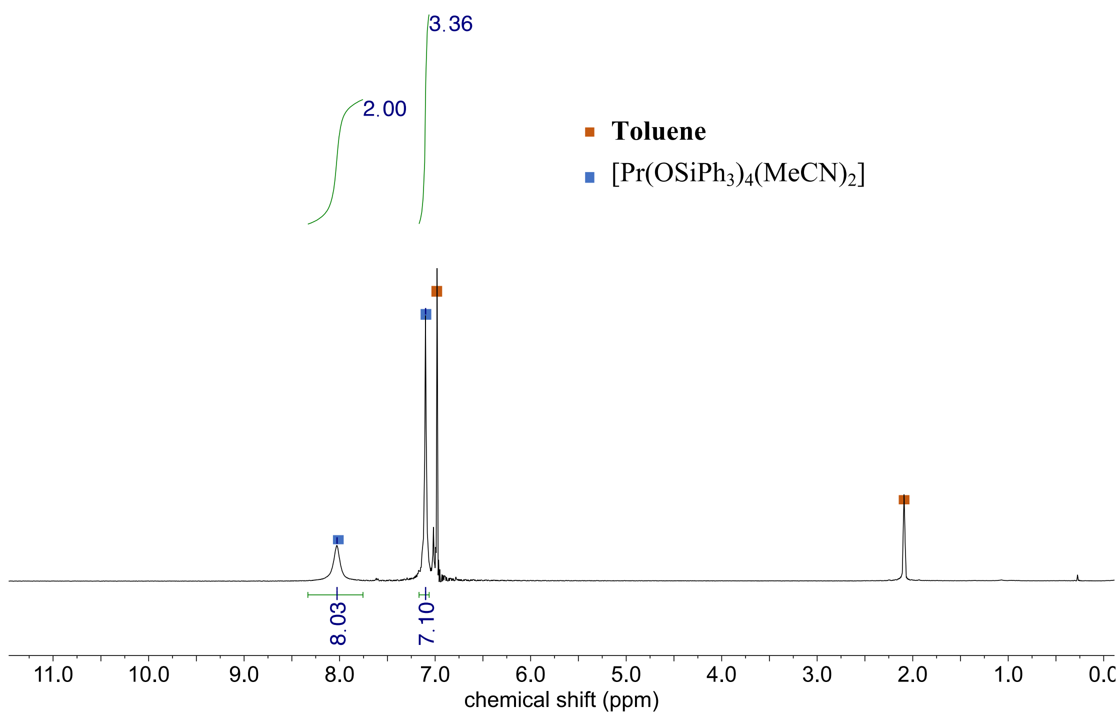


Fig. S16: ^{1}H NMR spectrum (400 MHz, 298 K, Toluene-d_8) of **3-Pr^{MeCN}**.

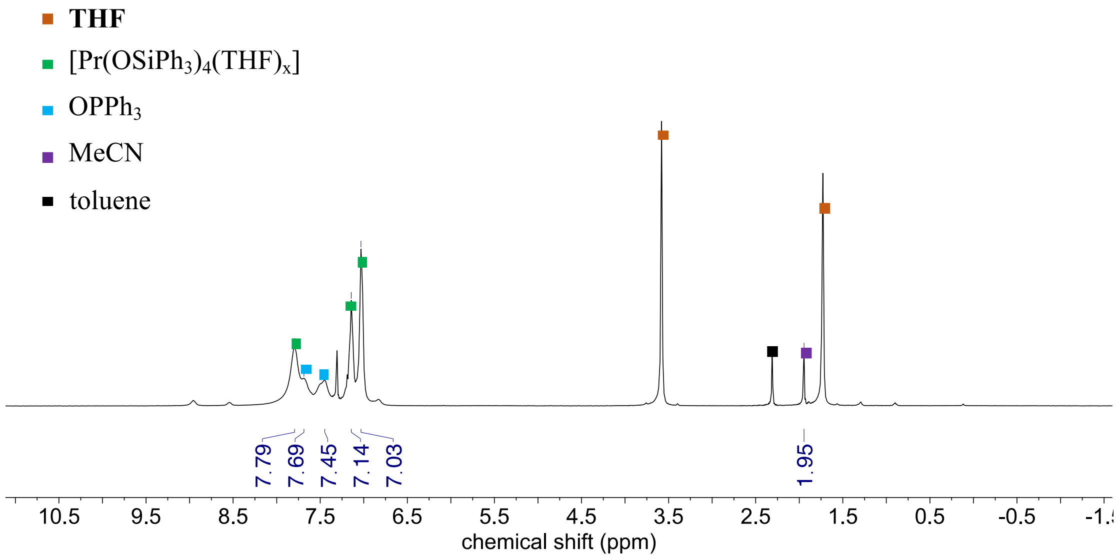


Fig. S17: ^{1}H NMR spectrum of **4-Pr^{Ph}** immediately after dissolution in THF-d_8 at room temperature (400 MHz, 298 K, THF-d_8).

C. IR spectra

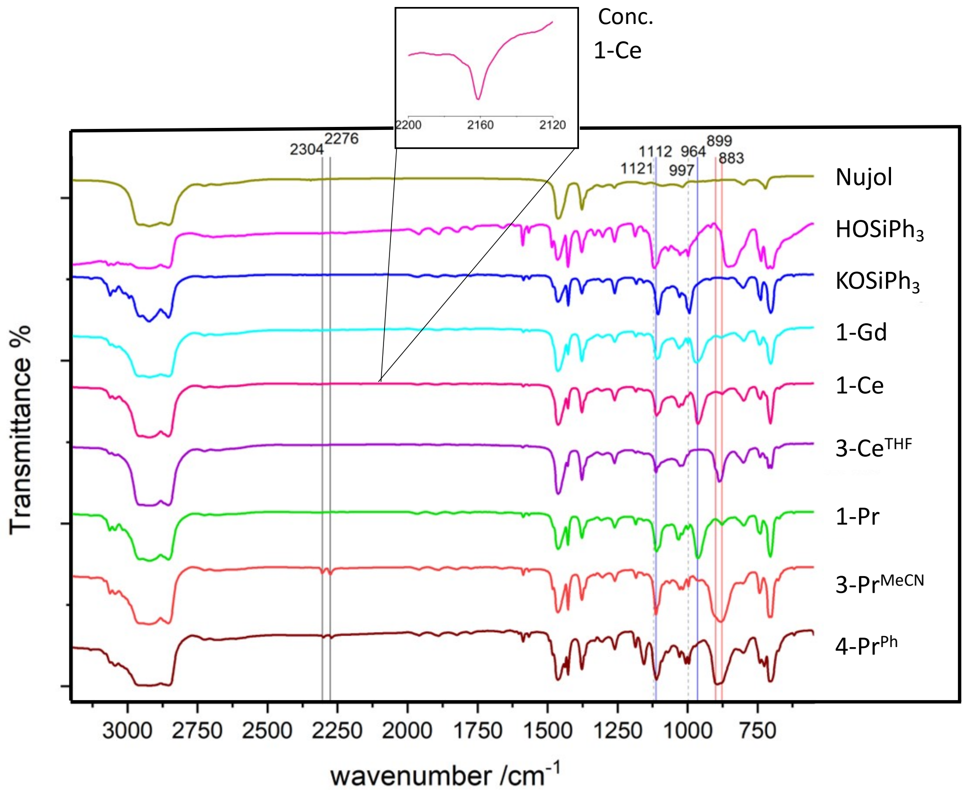


Fig. S18: Infrared spectra of $HOSiPh_3$, $KOSiPh_3$, **1-Ln** (Ln = Ce, Pr, Gd), **3-Ce^{THF}**, **3-Pr^{MeCN}** and **4-Pr^{Ph}** recorded between 3000 cm^{-1} and 550 cm^{-1} in nujol.

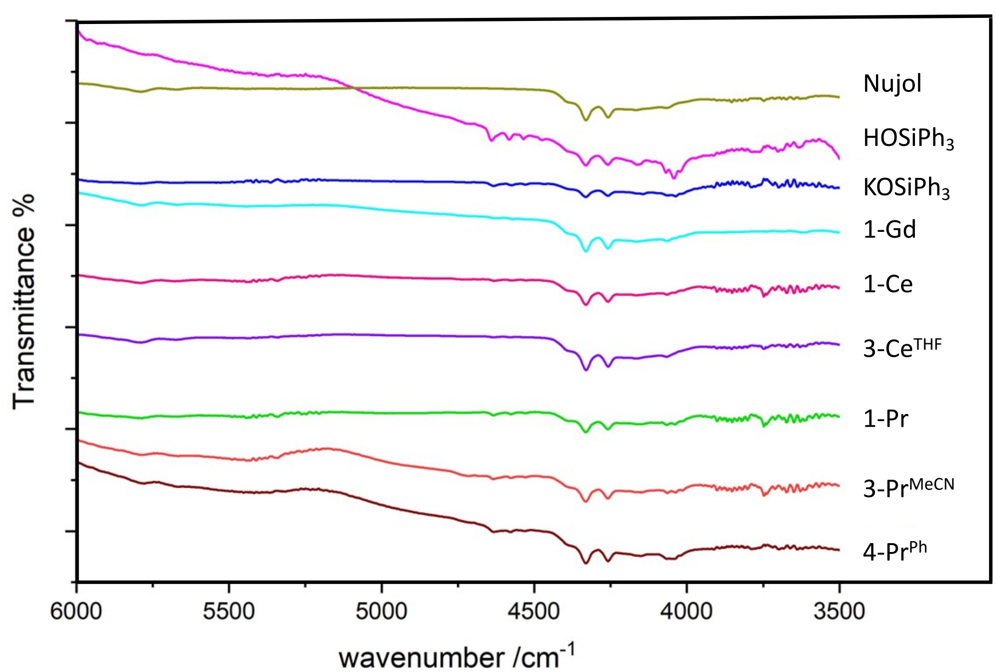


Fig. S19: Infrared spectra of $HOSiPh_3$, $KOSiPh_3$, **1-Ln** (Ln = Ce, Pr, Gd), **3-Ce^{THF}**, **3-Pr^{MeCN}** and **4-Pr^{Ph}** recorded between 6000 cm^{-1} and 3500 cm^{-1} in nujol.

D. UV-Visible spectra

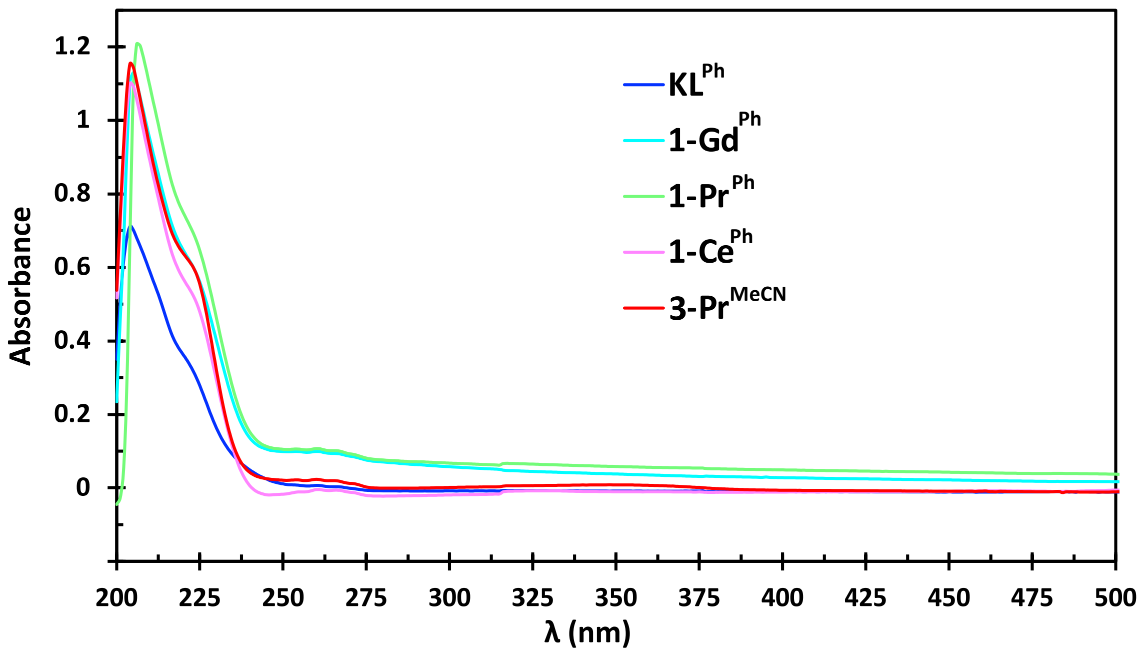


Fig. S20: UV-Visible spectra of $KOSiPh_3$ (0.15 mM), **1-Ln** (Ln = Ce, Pr, Gd) (0.05 mM) and **3-Pr^{MeCN}** (0.05 mM).

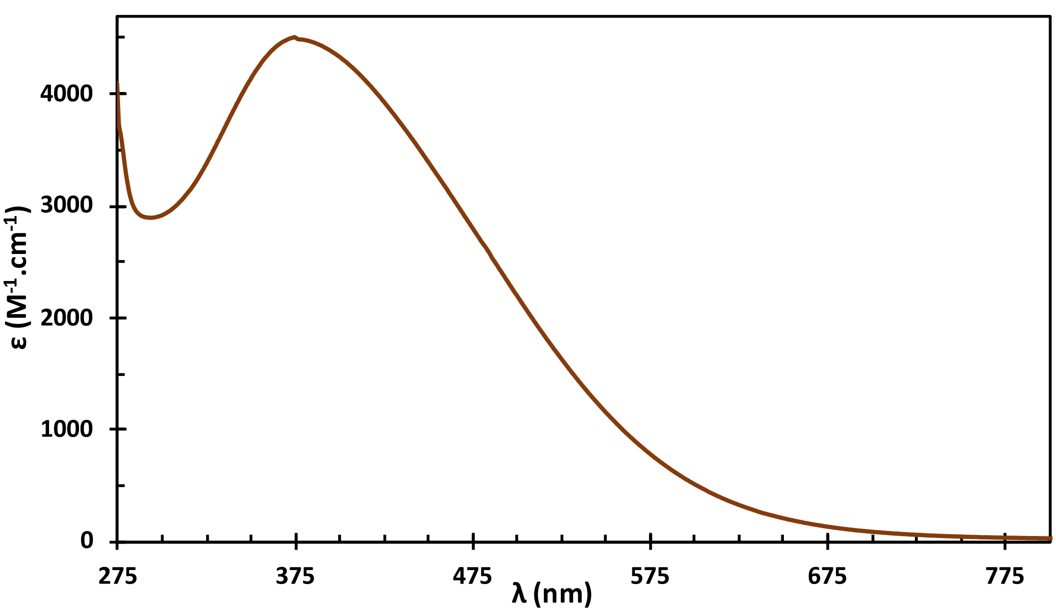


Fig. S21: UV-Visible spectra of **4-Pr^{Ph}** immediately after dissolution in toluene (3 mM).

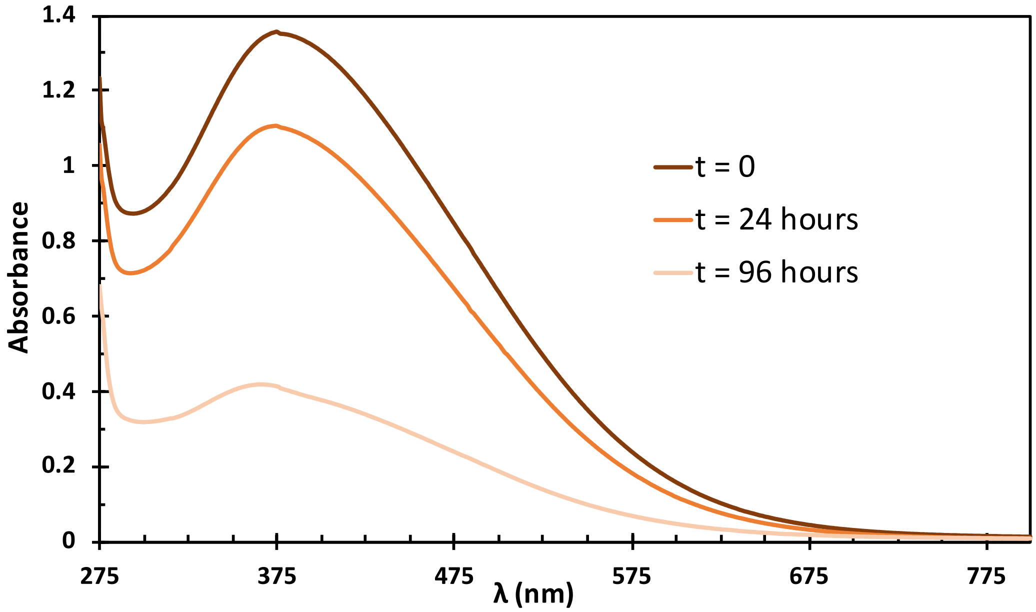


Fig. S22: UV-Visible spectra of **4-Pr^{Ph}** in toluene (3 mM) after "t" hours at room temperature.

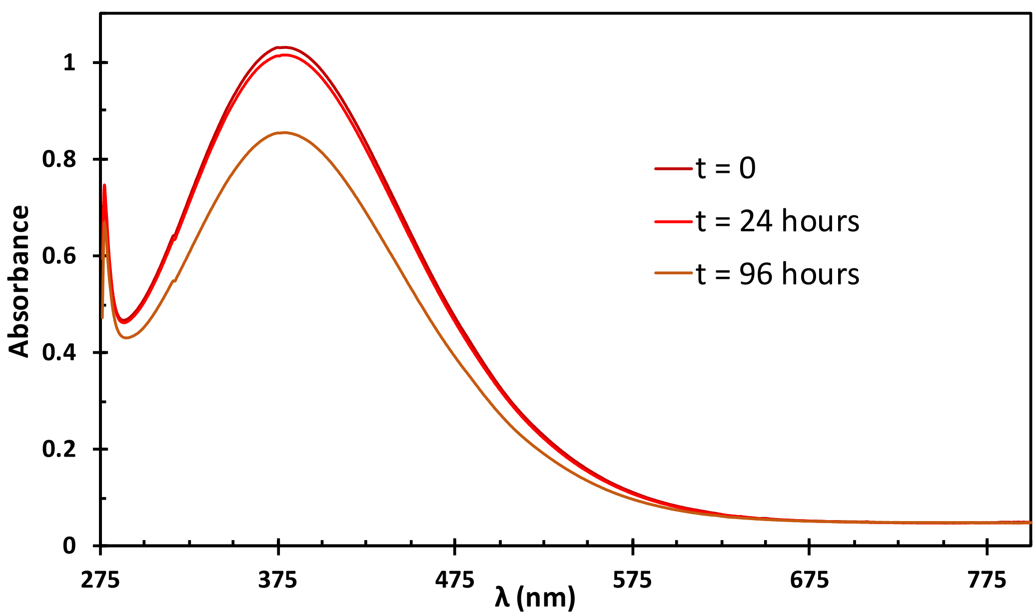


Fig. S23: UV-Visible spectra of **4-Tb^{Ph}** (3 mM) in toluene after "t" hours at room temperature.

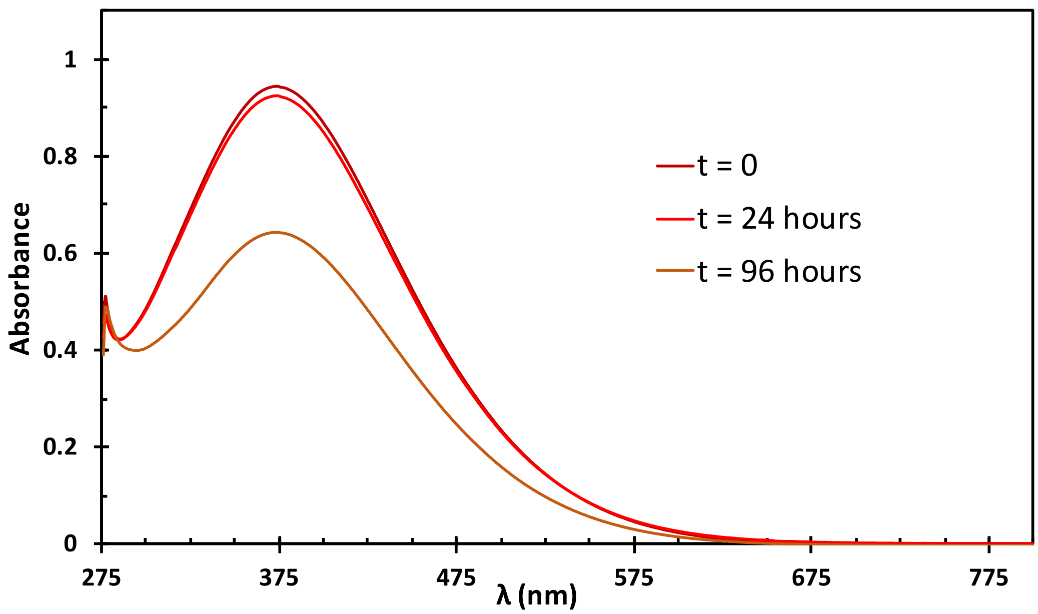


Fig. S24: UV-Visible spectra of **4-Tb^{Et}** (3 mM) in toluene after "t" hours at room temperature.

E. Luminescence spectra

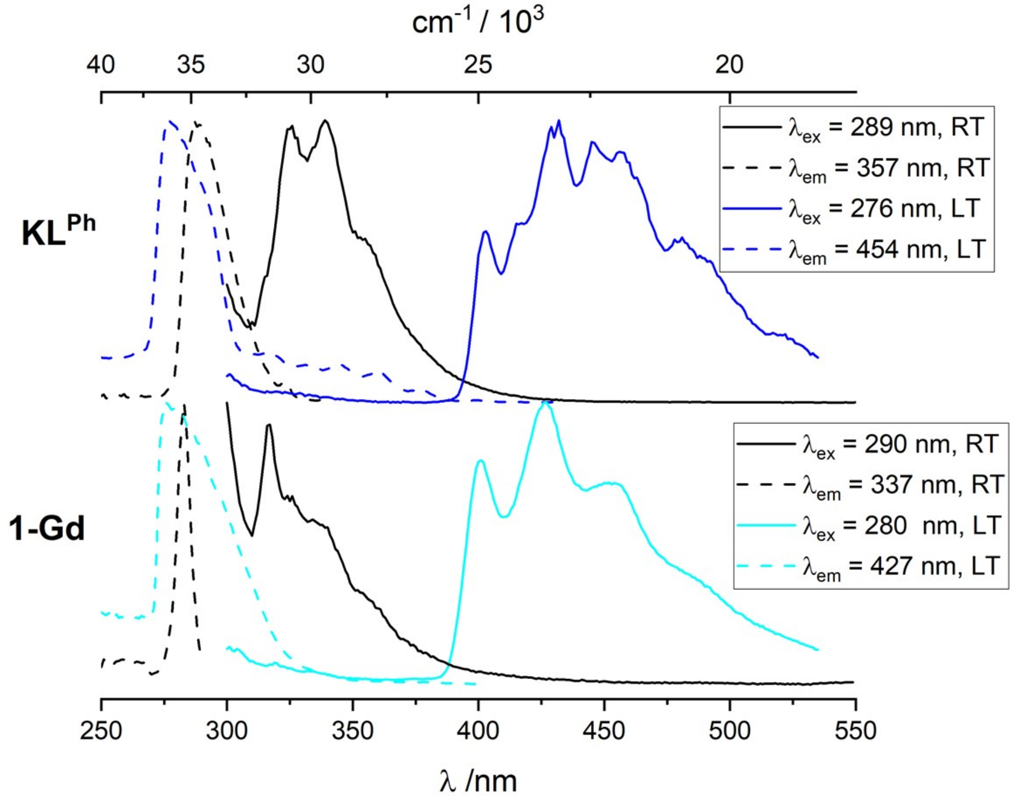


Fig. S25: Excitation and emission spectra of $KOSiPh_3$ and **1-Gd** at room temperature (RT) and low temperature (LT, 77K) in toluene (5mM).

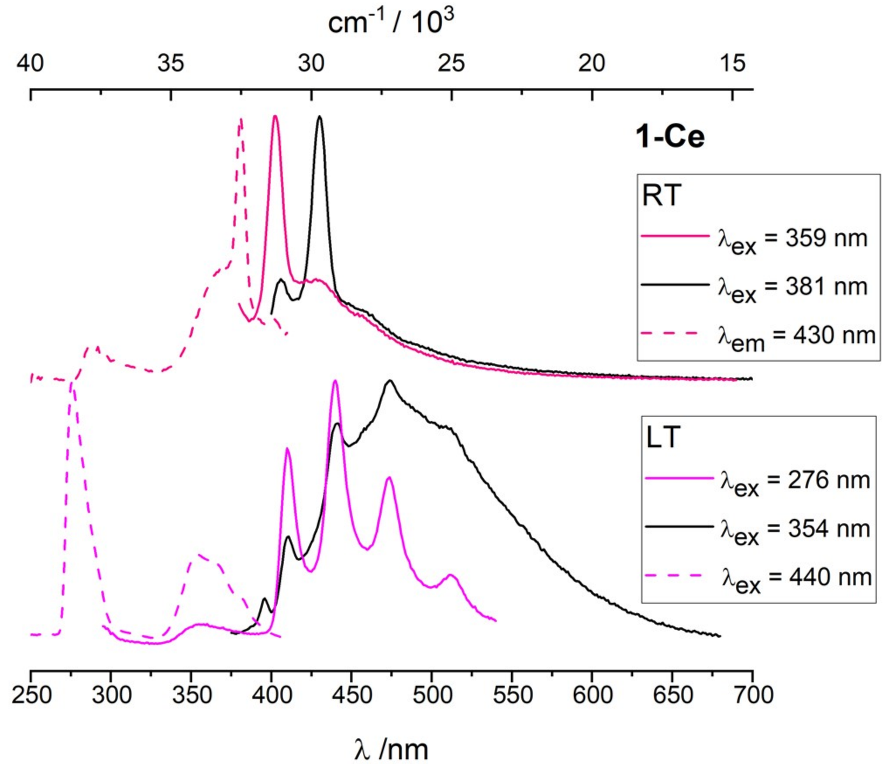


Fig. S26: Excitation and emission spectra of **1-Ce** at room temperature (RT) and low temperature (LT, 77K) in toluene (5mM).

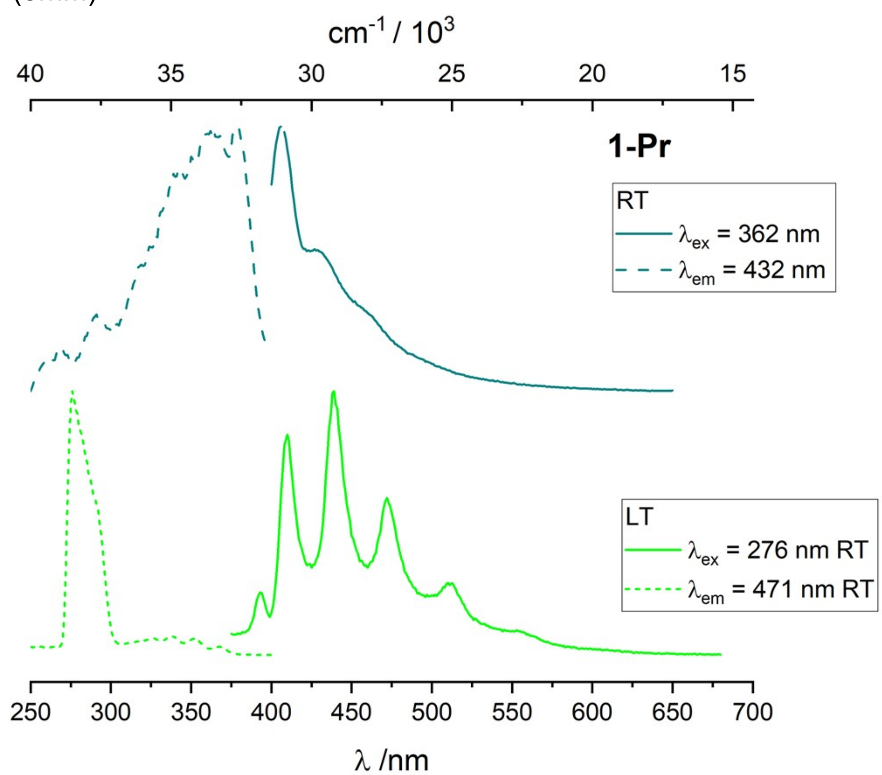


Fig. S27: Excitation and emission spectra of **1-Pr** at room temperature (RT) and low temperature (LT, 77K) in toluene (5mM).

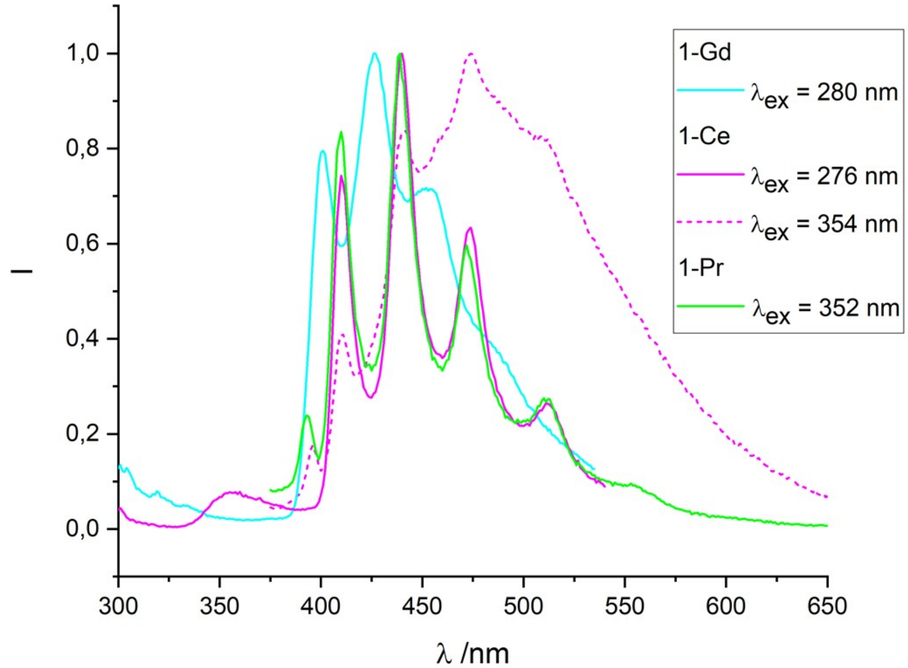


Fig. S28: Emission spectra of **1-Ln** (Ln = Gd, Ce, Pr) at low temperature (LT, 77K) in toluene (5mM).

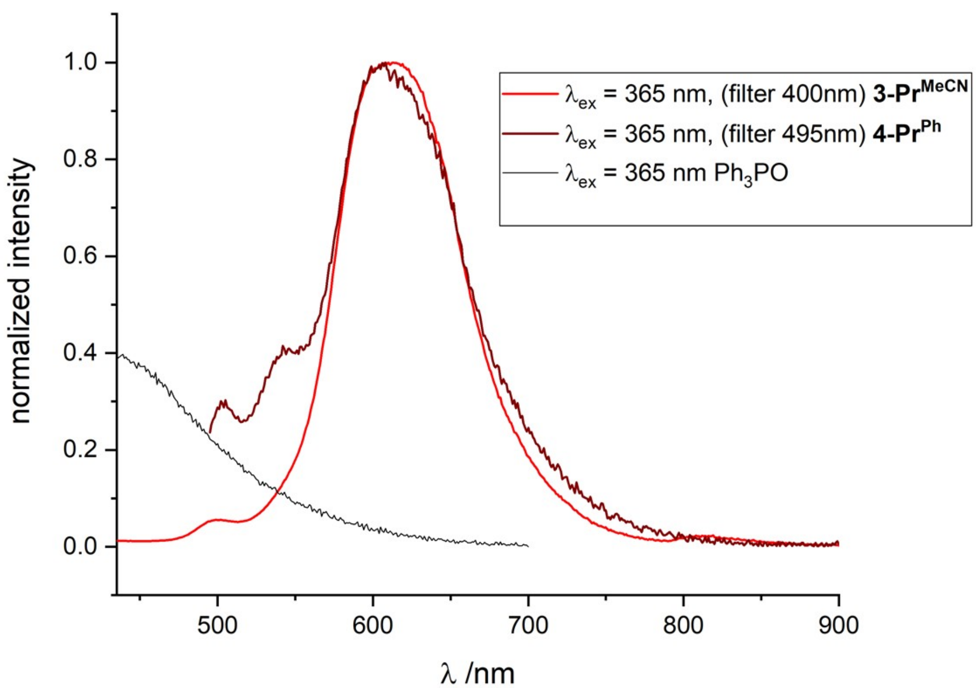


Fig. S29: Superposition of emission spectra of **3-Pr^{MeCN}**, **4-Pr^{Ph}** and Ph_3PO at low temperature (LT, 77K) in frozen toluene (5mM).

Table S1: Ligand-centered excitation and emission properties of $KOSiPh_3$ (**KL^Ph**), **1-Ln** (Ln = Ce, Pr, Gd)**, 3-Pr^MeCN** and **4-Pr^Ph**. The maxima of in bold. Sh= shoulder; w = weak.

Sample	toluene at RT		toluene at 77K	
	λ_{ex}/nm	λ_{em}/nm	λ_{ex}/nm	λ_{em}/nm
KL^Ph	**289**	315(sh) **325** **339** 357 370(sh)	276	403 416 **428** **431** 446 454 464 480 492 514(sh)
1-Gd	290	**317** 325 337 351	280 302(sh)	401 **427** 448 489(sh)
1-Ce	288(w) 359(sh) **381**	406 **430** 460(sh)	**276** 354(w)	395(w) 410 **440** 447 **474** 487 533
1-Pr	290(w) 302(w) 315(sh) 327(sh) 339(sh) 348 **363** **382**	**406** 432 461(sh)	**276** 290(sh) 327(w) 338(w) 352(w) 369(w)	392 410 **438** 471 512 554(w)
3-Pr^MeCN	/	/	**307** 349 365	500(w) **611** 816(w)
4-Pr^Ph	/	/	284 **306** 342 365	504 545 594 **608** 644(sh) 682

Table S2: Lifetime decays of the excited states of $KOSiPh_3$ (**KL^{Ph}**), **1-Ln** (Ln = Ce, Pr, Gd, Tb), **2-Pr^{MeCN}** and **3-Pr^{Ph}** in toluene frozen solutions (77 K)

Sample	λ_{ex}/nm	λ_{em}/nm	τ_1/µs	%τ_1	τ_2/µs	%τ_2	τ_{av}/µs$^{a)}$
KL^{Ph}	276	431	7.7±0.4	18	0.52±0.02	82	1.8±0.1
1-Gd	280	427	2.3±0.3	32	0.25±0.1	68	0.9±0.2
1-Ce	276	410	1.5±0.2	100	/	/	/
1-Pr	277	450	8.9±0.4	63	0.40±0.01	37	5.8±0.2
3-Pr^{MeCN}	307	611	3.4±0.2	100	/	/	/
4-Pr^{Ph}	345	599	7.3±0.2	42	0.67±0.01	58	3.45±0.17

a) Amplitude average lifetime: $\tau_{av} = \Sigma a_i \tau_i$

F. X-Ray Crystal Structure Determination Details

Bragg-intensities of **1-Ce • (toluene)$_2$, 1-Nd**, **1-Gd**, **2-Nd • (toluene)$_3$, 3-Ce^{THF}**, **3-Tb^{THF}** and **4-Pr^{Ph}** were collected at 140.00(10) K using Cu*Kα* radiation. A Rigaku SuperNova dual system diffractometer with an Atlas CCD detector was used for compounds **1-Ce • (toluene)$_2$, 1-Gd, 3-Ce^{THF}** and **3-Tb^{THF}**, and one equipped with an Atlas S2 CCD detector for compounds **1-Nd,** and **2-Nd • (toluene)$_3$**. A suitable crystal of **4-Pr^{Ph}** was selected and mounted on a XtaLAB Synergy R, DW system, HyPix-Arc 150 diffractometer. The datasets were reduced and corrected for absorption, with the help of a set of faces enclosing the crystals as snugly as possible, with *CrysAlis^{Pro}*.[7]

The solutions and refinements of the structures were performed by the latest available version of *ShelXT*[8] and *ShelXL.*[9] All non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on $|F|^2$. The hydrogen atoms were placed at calculated positions by means of the "riding" model in which each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent C-atom (1.5 U_{eq} for the methyl groups).

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif. The CCDC codes of each compound are given in Tables S2 and S3 containing the X-ray diffraction data (see below).

Table S3: Crystallographic parameters for complexes **1-Ln** (Ln = Ce, Nd, Gd), and **2-Nd**.

Compound	**1-Ce • (toluene)$_2$**	**1-Nd**	**1-Gd**	**2-Nd • (toluene)$_3$**
Formula	$C_{94}H_{92}CeKO_6Si_4$	$C_{80}H_{76}KNdO_6Si_4$	$C_{84}H_{84}GdKO_7Si_4$	$C_{111}H_{99}K_2NdO_5Si_5$
$D_{calc.}$/ g cm^{-3}	1.320	0.950	1.190	1.223
μ/mm^{-1}	5.796	5.091	6.438	5.576
Formula Weight	1609.25	1429.10	1514.22	1875.79
Colour	clear pale colourless	clear colourless	clear pale colourless	clear colourless
Shape	prism-shaped	prism	needle-shaped	plate
Size/mm^3	0.21×0.11×0.09	0.37×0.24×0.13	0.36×0.04×0.03	0.22×0.15×0.04
T/K	140.00(10)	139.99(11)	140.00(10)	140.00(10)
Crystal System	orthorhombic	monoclinic	monoclinic	monoclinic
Space Group	*Pbca*	$P2_1/c$	$P2_1/n$	$P2_1/n$
a/Å	15.5527(9)	15.07667(12)	13.4724(4)	19.0352(2)
b/Å	26.7995(12)	18.20509(11)	28.4527(9)	23.9418(2)
c/Å	38.849(2)	36.5229(3)	22.4563(8)	22.3713(3)
α/°	90	90	90	90
β/°	90	94.8279(8)	100.959(3)	92.2121(10)
γ/°	90	90	90	90
V/Å^3	16192.4(15)	9988.94(12)	8451.1(5)	10187.8(2)
Z	8	4	4	4
Z'	1	1	1	1
Wavelength/Å	1.54184	1.54184	1.54184	1.54184
Radiation type	CuK_α	CuK_α	CuK_α	CuK_α
Θ_{min}/°	3.298	3.434	3.106	2.992
Θ_{max}/°	72.602	72.870	72.769	74.881
Measured Refl's.	54117	84946	72125	83289
Ind't Refl's	15729	19622	16567	20610
Refl's with I > 2σ(I)	8219	18427	10539	17408
R_{int}	0.1776	0.0302	0.1171	0.0558
Parameters	998	993	893	1182
Restraints	224	823	75	392
Largest Peak/e Å^{-3}	0.823	0.526	1.159	3.837
Deepest Hole/e Å^{-3}	-0.797	-0.729	-0.945	-0.538
GooF	0.980	1.024	0.948	1.052
wR_2 (all data)	0.1858	0.1248	0.1413	0.1346
wR_2	0.1426	0.1228	0.1207	0.1262
R_1 (all data)	0.1530	0.0435	0.0970	0.0624
R_1	0.0679	0.0415	0.0531	0.0509
CCDC code	2104729	2104730	2104731	2104732

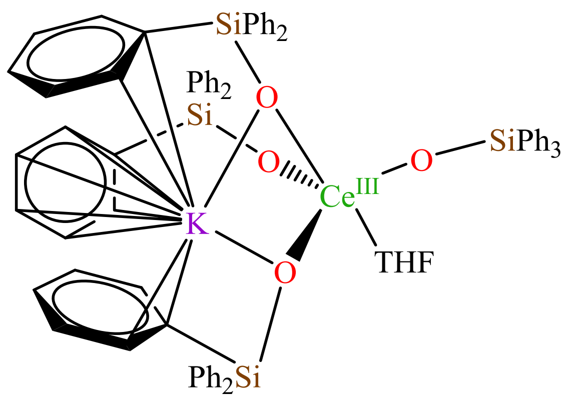
Table S4: Crystallographic parameters for complexes **3-Ce^{THF}**, **3-Tb^{THF}** and **4-Pr^{Ph}**.

Compound	**3-Ce^{THF} • THF**	**3-Tb^{THF} • THF**	**4-Pr^{Ph}**
Formula	$C_{84}H_{84}CeO_7Si_4$	$C_{84}H_{84}TbO_7Si_4$	$C_{92}H_{78}NO_5PPrSi_4$
$D_{calc.}$/ g cm^{-3}	1.169	1.195	1.216
μ/mm^{-1}	5.180	5.179	5.484
Formula Weight	1457.99	1476.79	1561.79
Colour	clear colourless	clear intense orange	clear intense orange
Shape	needle	prism-shaped	plate
Size/mm^3	0.34×0.09×0.09	0.14×0.06×0.04	0.10×0.07×0.01
T/K	140.00(10)	140.00(10)	140.00(10)
Crystal System	monoclinic	monoclinic	monoclinic
Space Group	$C2/c$	$C2/c$	$P2_1/c$
a/Å	16.5246(6)	16.4450(4)	14.39059(14)
b/Å	23.1693(9)	23.0841(7)	21.1314(2)
c/Å	21.7608(8)	21.7459(6)	28.0674(3)
α/°	90	90	90
β/°	95.951(4)	95.923(2)	91.3627(9)
γ/°	90	90	90
V/Å^3	8286.5(5)	8211.1(4)	8532.71(14)
Z	4	4	4
Z'	0.5	0.5	1
Wavelength/Å	1.54184	1.54184	1.54184
Radiation type	CuK_α	CuK_α	CuK_α
Θ_{min}/°	3.297	3.742	2.618
Θ_{max}/°	72.554	72.561	75.357
Measured Refl's.	30120	30838	107006
Ind't Refl's	8133	8008	17163
Refl's with I > 2σ(I)	6071	5726	14419
R_{int}	0.1352	0.0841	0.0325
Parameters	434	453	1000
Restraints	12	93	1757
Largest Peak/e Å^{-3}	1.401	0.935	0.795
Deepest Hole/e Å^{-3}	-1.509	-0.656	-0.599
GooF	0.987	0.924	1.048
wR_2 (all data)	0.1656	0.0988	0.0984
wR_2	0.1470	0.0904	0.0942
R_1 (all data)	0.0887	0.0699	0.0494
R_1	0.0626	0.0426	0.0395
CCDC code	2104733	2104734	2104735

G. Computational details

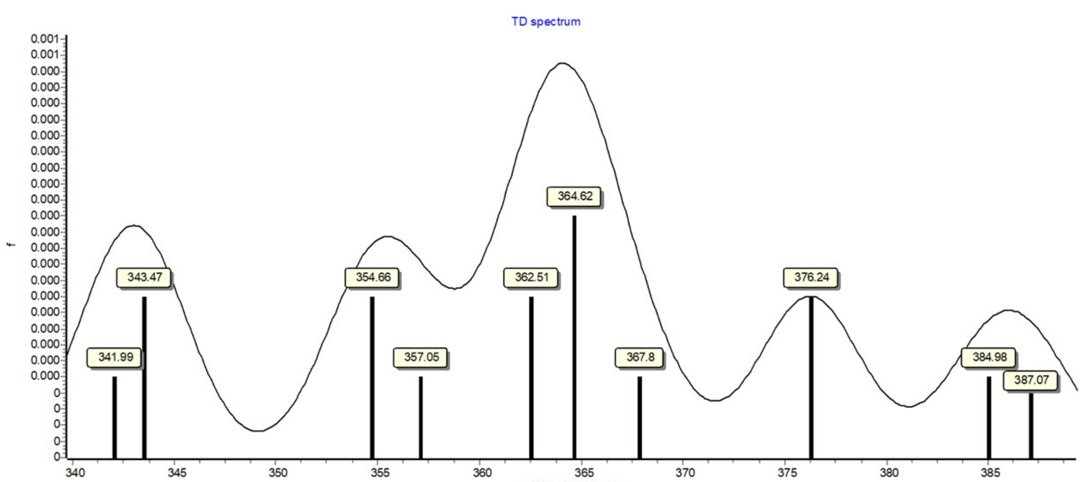
All calculations were performed using Gaussian09 suite of programs[10] using the Becke's 3-parameter hybrid functional[11] combined with the non-local correlation functional provided by Perdew/Wang.[12] The Ce, Pr, K and Si atoms were represented with a small-core Stuttgart-Dresden relativistic effective core potential associated with their adapted basis set [13-15]. Additionally, the Si basis set was augmented by a d-polarization function ($\alpha = 0.284$)[16] to represent the valence orbitals. All the other atoms C, O and H were described with a 6-31G (d,p), double –ζ quality basis set.[17] The enthalpy energy was computed at T=298 k in the gas phase.

Ce(III)



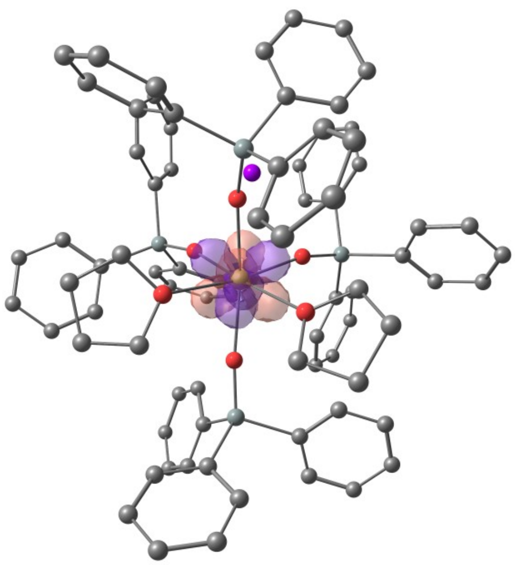
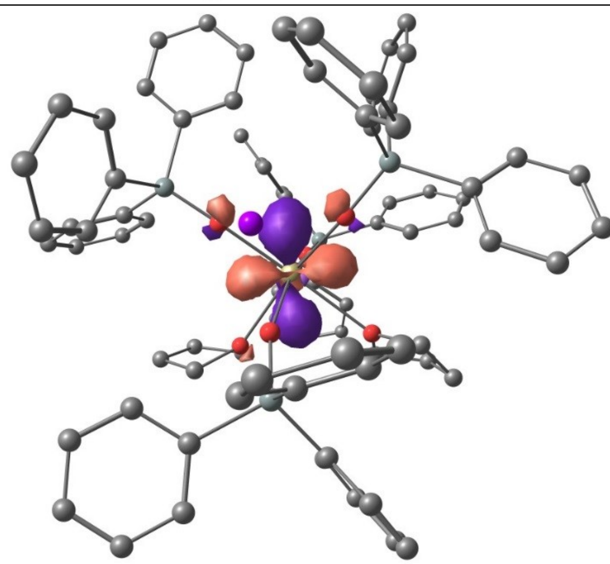
	Doublet	Quartet
Spin density on Ce	**1.023787**	**1.023359**
Energy Enthalpy (a.u)	**-4062.448211**	**-4062.323485**
Δ Energy (kcal.mol^{-1})	**78.3**	

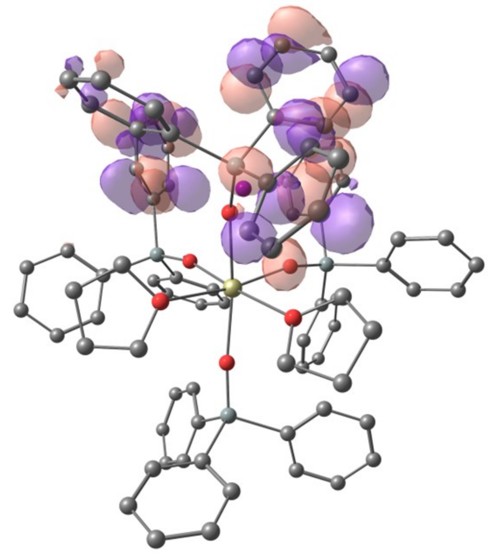
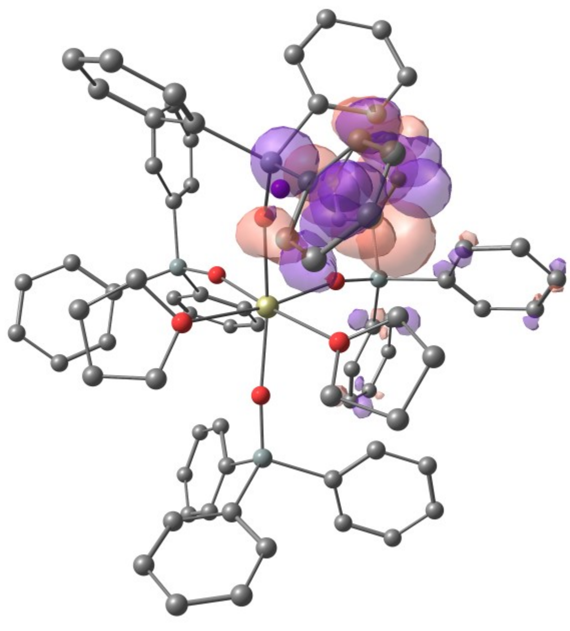
TDDFT Computed Absorption spectrum – Ce

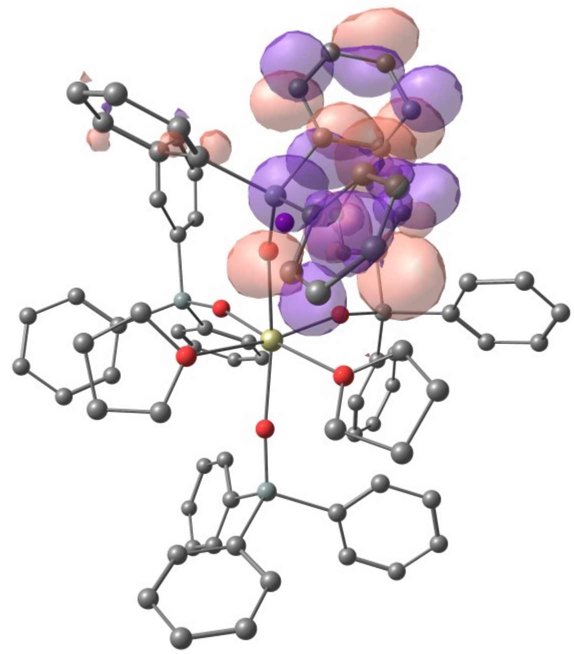
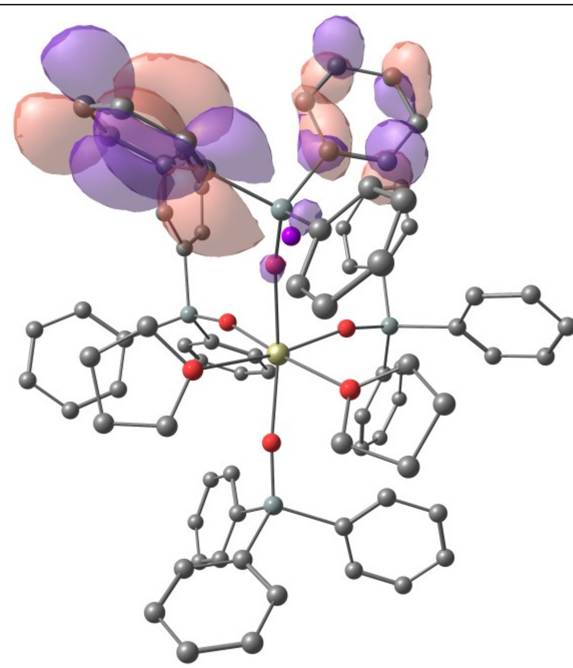


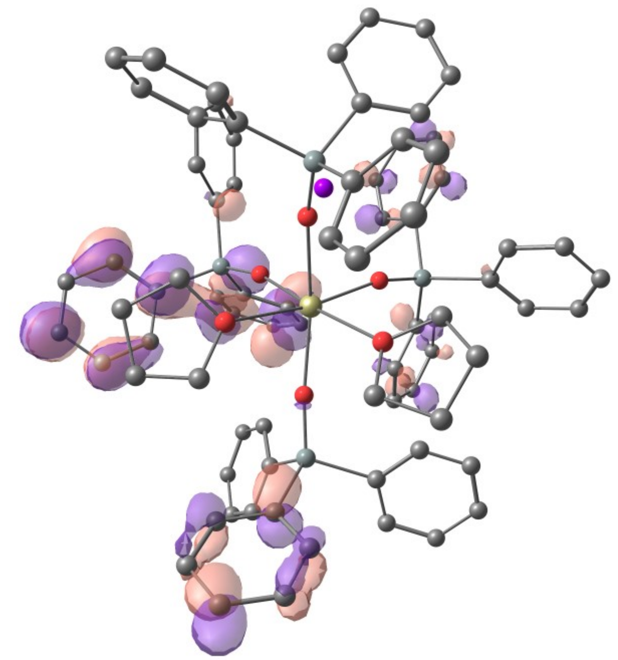
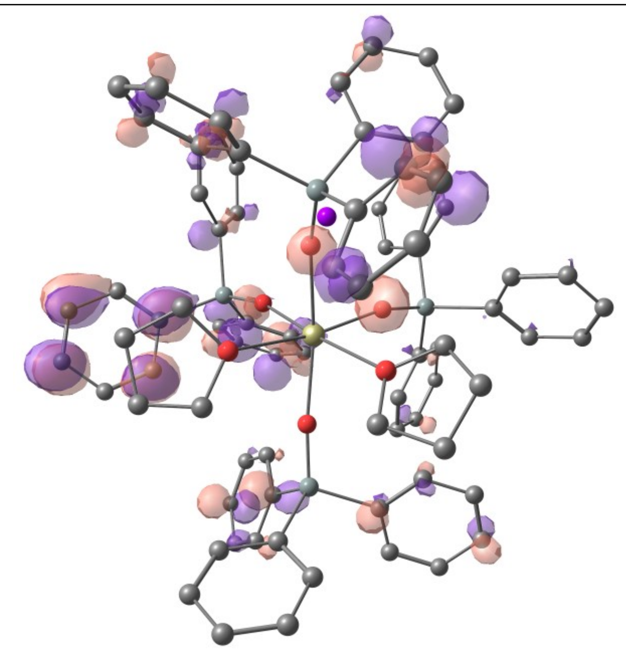
From	To	Coef.	Excitation	λ(nm)	Oscillator	S^2

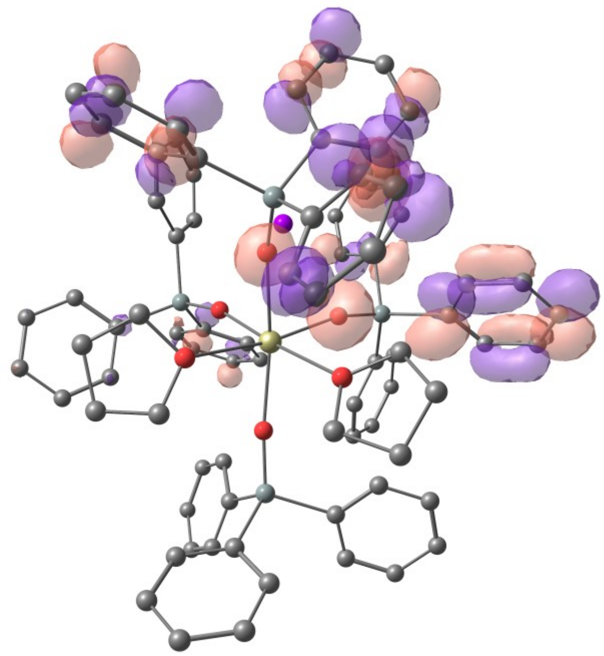
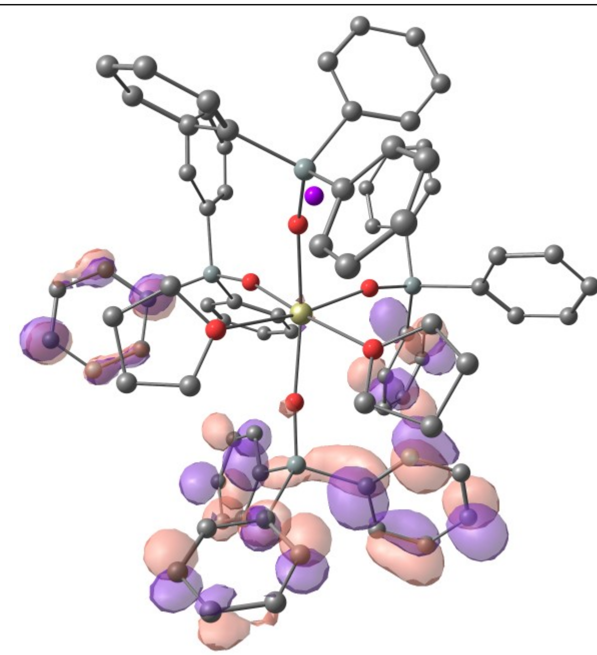
			energy (eV)		strength f	
330A	331A	0.96741	2.4454	507.07	0.0000	0.753
330A	335A	0.89741	3.2032	387.07	0.0001	0.753
330A	336A	0.94586	3.2206	384.98	0.0001	0.753
330A	337A	0.94263	3.2953	376.24	0.0002	0.753
330A	338A	0.96316	3.3710	367.80	0.0001	0.753
330A	340A	0.76869	3.4004	364.62	0.0003	0.753
330A	342A	0.74929	3.4201	362.51	0.0002	0.753
330A	343A	0.86423	3.4725	357.05	0.0001	0.753
330A	344A	0.93942	3.4959	354.66	0.0002	0.754
330A	347A	0.81041	3.6098	343.47	0.0002	0.759
330A	346A	0.90149	3.6254	341.99	0.0001	0.758

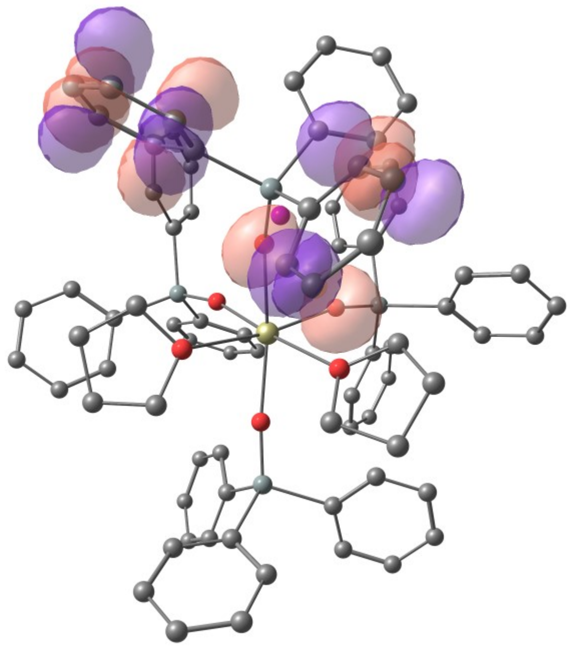
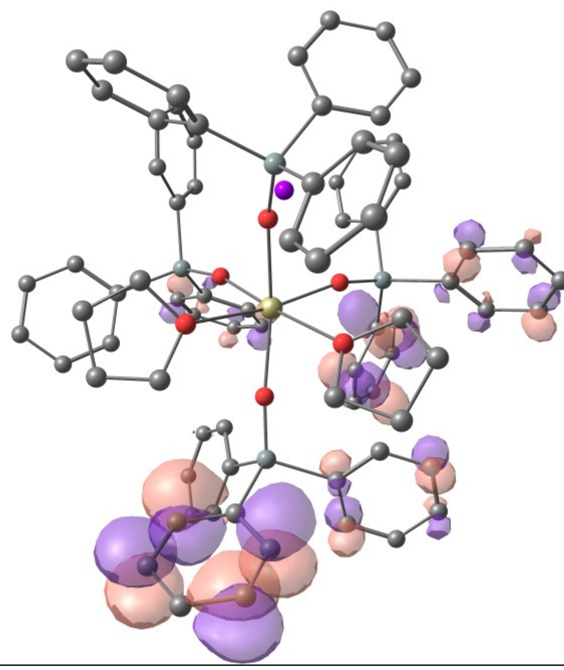
330A	
331A	

335A	
336A	

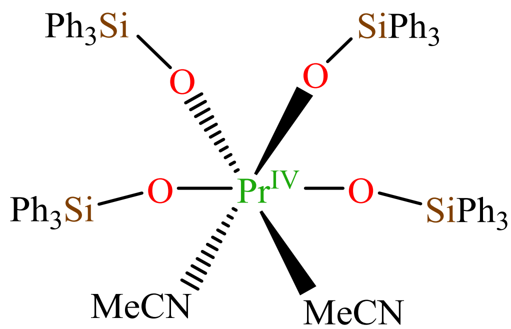
337A	
338A	

340A	
342A	

343A	
344A	

347A	
346A	

Pr(IV)

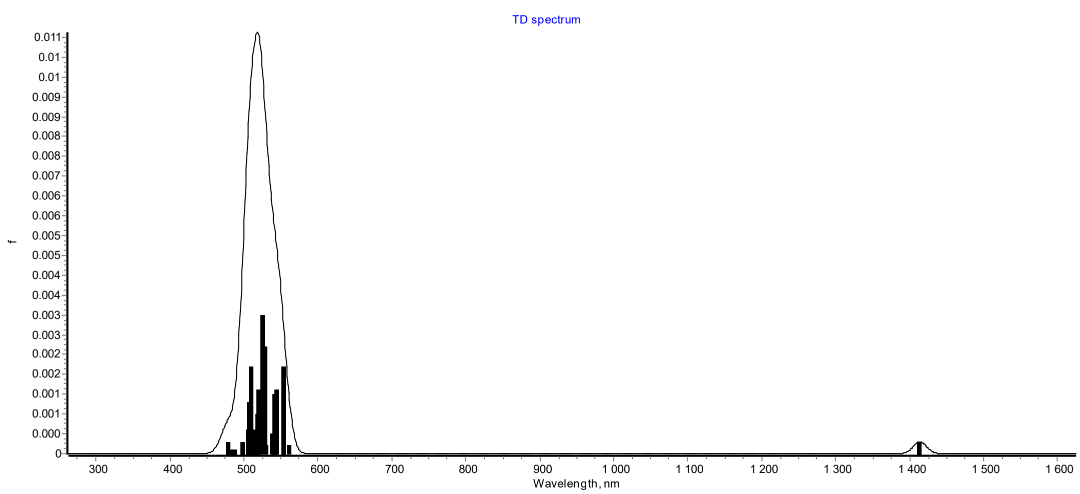


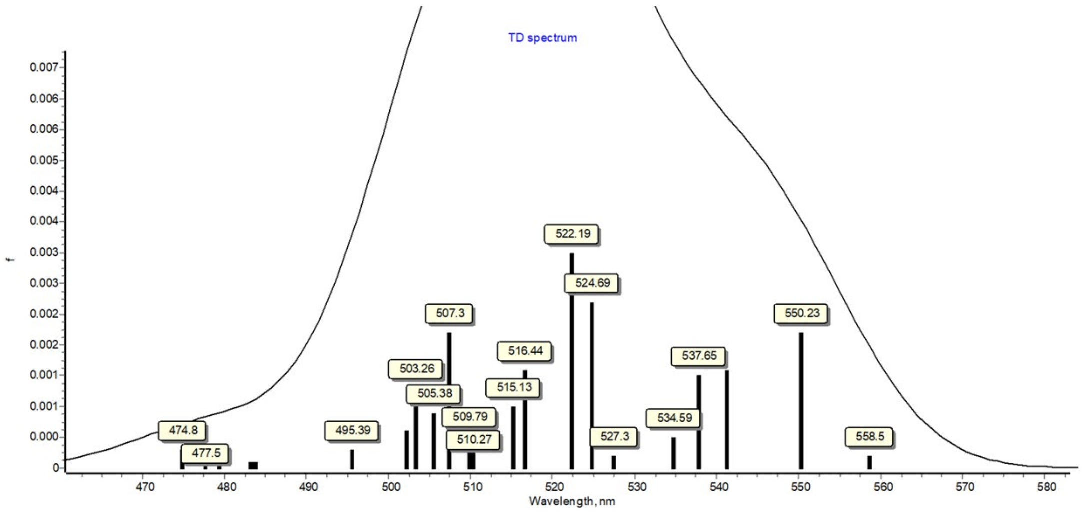
	Doublet	Quartet
Spin density on Pr	**1.149110**	**1.983118**
Energy Enthalpy (a.u)	**-3876.686140**	**-3876.612992**
Δ Energy (kcal.mol^{-1})	**45.9**	

Triplet state energy E^T

Since the triplet energy E^T cannot be obtained with TD DFT calculations, the geometry of this excited state was optimized and E^T was calculated as the difference with the ground state energy: 1.9 eV.

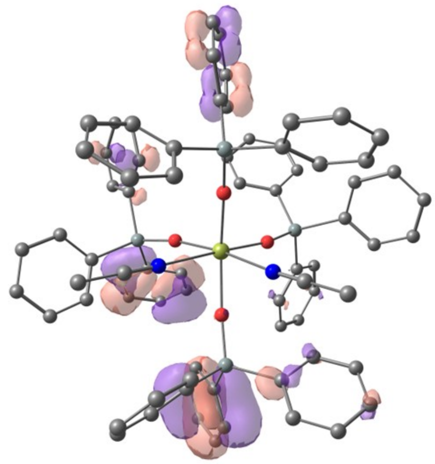
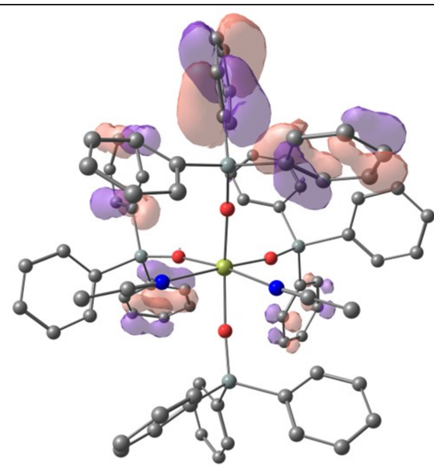
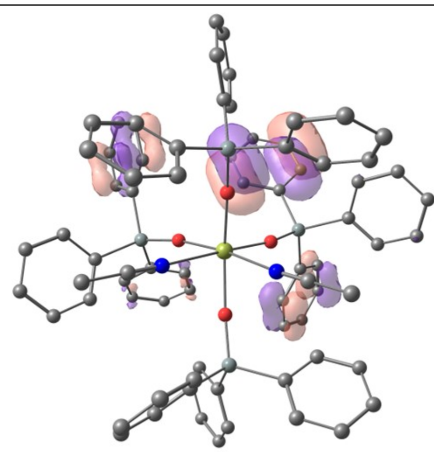
TDDFT Computed Absorption Spectrum – Pr(IV)

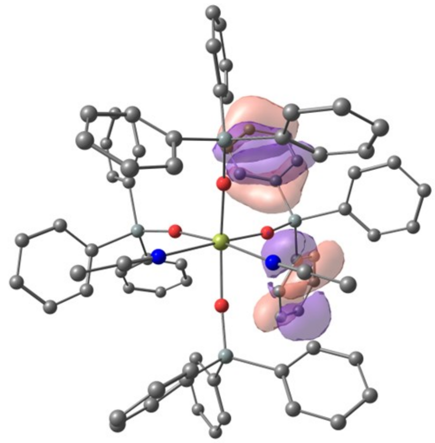
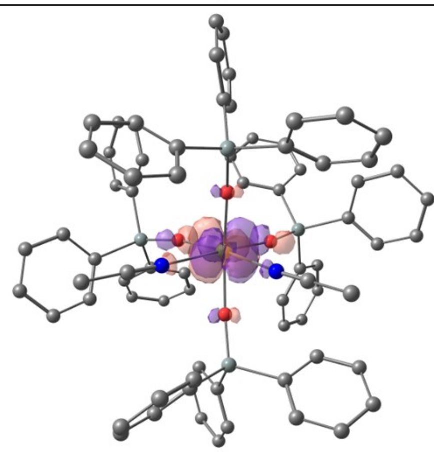
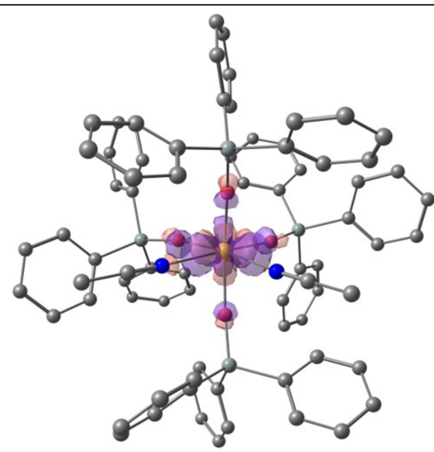


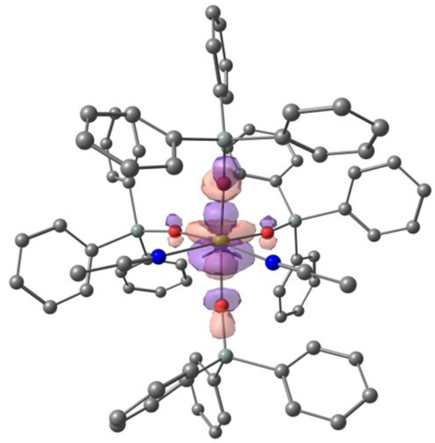
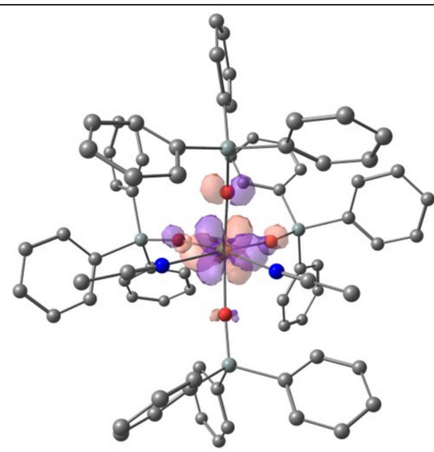
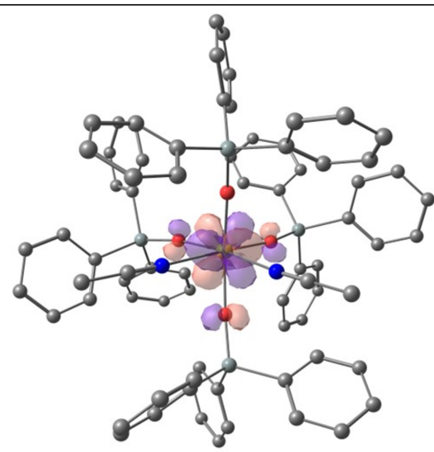


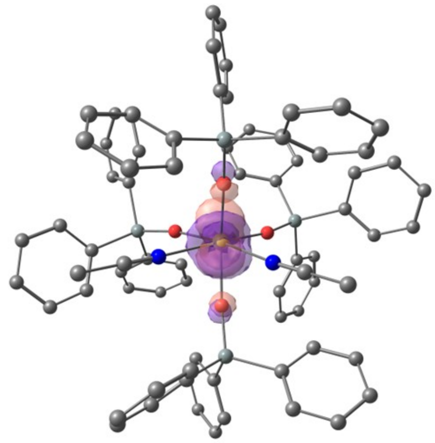
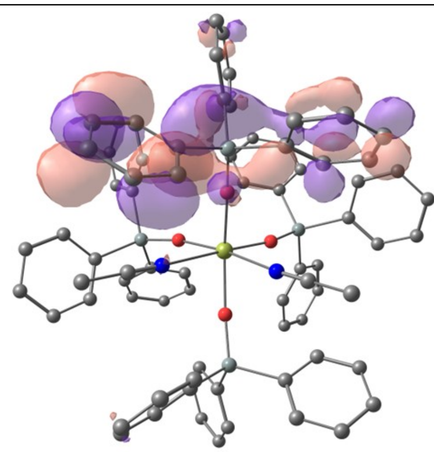
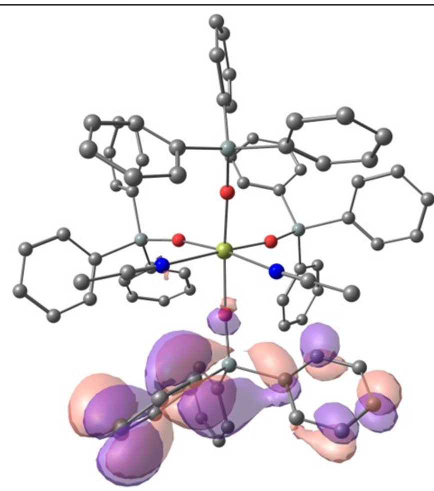
Other transitions not shown in the spectrum above:

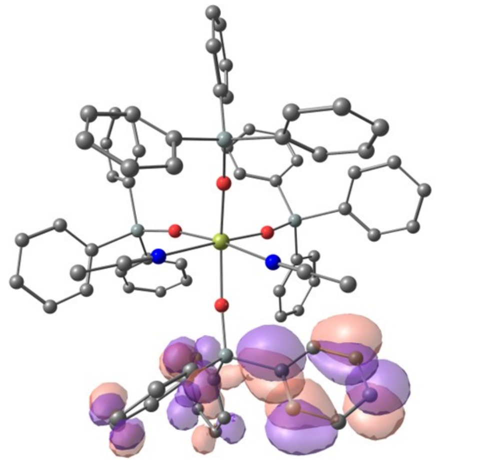
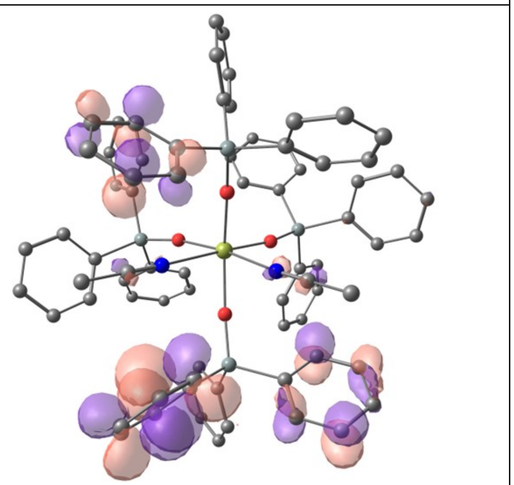
From	To	Coef	Excitation energy (eV)	λ(nm)	Oscillator strength f	S^2
301A	311A	0.22001	0.3527	3515.23	0.0001	3.772
305A	312A	0.51198	0.3527	3515.23	0.0001	3.772
301A	315A	0.11369	0.4087	3033.41	0.0001	3.772
305A	311A	0.27095	0.4087	3033.41	0.0001	3.772
301A	315A	0.35614	0.5146	2409.44	0.0001	3.771
301A	316A	0.19363	0.4087	3033.41	0.0001	3.772
301A	318A	0.63993	0.5968	2077.44	0.0003	3.772
305A	313A	0.23243	0.5968	2077.44	0.0003	3.772
301A	311A	0.21066	0.6344	1954.29	0.0004	3.772
301A	313A	0.22860	0.6344	1954.29	0.0004	3.772
305A	314A	0.22975	0.6344	1954.29	0.0004	3.772
305A	321A	0.44346	0.6344	1954.29	0.0004	3.772
305A	315A	0.32898	0.8007	1548.52	0.0017	3.771
309A	310A	0.88189	1.0324	1200.99	0.0004	3.782
301A	313A	0.32361	1.1115	1115.49	0.0001	3.779
305A	315A	0.40315	1.1115	1115.49	0.0001	3.779
301A	311A	0.24306	1.1902	1041.69	0.0003	3.804
305A	310A	0.26486	1.1902	1041.69	0.0003	3.804
305A	313A	0.23948	1.1902	1041.69	0.0003	3.804
309A	312A	0.42250	1.1902	1041.69	0.0003	3.804
309A	311A	0.48864	2.2395	553.62	0.0104	3.914
307A	310A	0.61544	2.3383	530.24	0.0169	3.917
308A	311A	0.48504	2.4479	506.48	0.0112	3.978

301A	
305A	
307A	

308A	
309A	
310A	

311A	
312A	
313A	

314A	
315A	
316A	

318A	
321A	

Cartesian coordinates of all optimized structures

168
KCeSi4C80H76O6 Doublet

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Si	10.533451000	16.343800000	26.774630000
Si	9.911241000	16.744607000	21.184079000
Si	4.963508000	16.151792000	24.461103000
O	9.290221000	20.349862000	24.416325000
O	9.505526000	16.985667000	25.652825000
O	9.039304000	17.237224000	22.500538000
O	6.497989000	16.747397000	24.529822000
O	6.597206000	19.797636000	22.758939000
O	6.797045000	19.379794000	26.353478000
C	10.438638000	22.207482000	22.457791000
C	9.707049000	21.575248000	21.442993000
H	8.986532000	20.805626000	21.710181000

C	9.900838000	21.902408000	20.099869000
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C	10.834024000	22.876381000	19.748659000
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H	12.307865000	24.271100000	20.475307000
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H	11.970325000	23.681348000	22.845223000
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H	14.243500000	23.636900000	26.589513000
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H	12.031128000	23.799352000	25.510044000
C	9.199849000	23.277340000	25.055212000
C	8.461148000	24.157044000	24.249467000
H	8.451783000	24.012299000	23.171280000
C	7.754340000	25.226432000	24.800682000
H	7.193461000	25.897686000	24.154768000
C	7.775725000	25.440179000	26.177992000
H	7.230327000	26.275518000	26.609964000
C	8.509401000	24.583191000	26.998379000
H	8.539320000	24.751114000	28.072256000
C	9.211706000	23.515884000	26.439235000
H	9.794649000	22.865704000	27.088358000
C	10.465018000	17.187691000	28.491032000
C	10.163903000	16.490942000	29.669767000
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C	10.153742000	17.135105000	30.908400000
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C	10.770904000	18.555440000	28.593989000
H	11.030557000	19.122546000	27.702831000
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C	12.639006000	16.708448000	24.835455000
H	11.826368000	16.946371000	24.152882000
C	13.955490000	16.722739000	24.370575000
H	14.158372000	16.970703000	23.332402000

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H	11.944422000	13.726741000	26.175678000
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H	11.292100000	11.345071000	26.296947000
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H	7.493786000	12.469149000	27.965040000
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C	9.433231000	12.547225000	20.801670000
H	8.754912000	11.872618000	20.285679000
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H	10.555026000	10.959499000	21.736132000
C	11.320215000	12.908211000	22.258862000
H	12.121812000	12.517172000	22.880254000
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H	7.070542000	16.447283000	20.270005000
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H	5.150512000	11.310307000	21.201492000
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H	4.827195000	11.136353000	23.658835000
C	4.850716000	13.269582000	23.968975000
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KCeSi4C80H76O6 Quartet

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Si	5.008804000	16.128088000	24.478398000
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O	6.578177000	16.631009000	24.452275000
O	6.634497000	19.548754000	22.638358000
O	6.946039000	19.205683000	26.409778000
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C	9.670522000	21.438934000	21.289390000
H	9.032136000	20.604569000	21.571084000
C	9.814990000	21.771890000	19.941487000
H	9.291555000	21.195475000	19.182864000
C	10.642043000	22.830631000	19.570178000
H	10.759435000	23.091042000	18.521199000
C	11.324716000	23.550710000	20.550385000
H	11.976429000	24.373558000	20.266794000
C	11.173822000	23.213386000	21.894712000
H	11.718544000	23.782871000	22.644743000
C	11.790134000	21.652980000	25.028327000
C	12.386885000	20.422487000	25.337027000
H	11.867446000	19.499639000	25.092568000
C	13.636641000	20.358847000	25.955354000
H	14.076317000	19.391479000	26.182526000

C	14.313339000	21.535004000	26.276899000
H	15.287270000	21.490006000	26.758029000
C	13.734572000	22.769568000	25.983676000
H	14.254615000	23.689753000	26.239178000
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H	12.035963000	23.795898000	25.168771000
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C	8.336388000	24.034495000	24.132967000
H	8.283705000	23.875006000	23.058022000
C	7.616582000	25.085570000	24.702122000
H	7.002193000	25.726222000	24.074088000
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H	8.569397000	24.688939000	27.939485000
C	9.210225000	23.453687000	26.293822000
H	9.845391000	22.834379000	26.923902000
C	10.427957000	17.260523000	28.508763000
C	9.885255000	16.638730000	29.642472000
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C	9.778600000	17.316885000	30.857970000
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H	10.142262000	19.164602000	31.906913000
C	10.767834000	19.270215000	29.845202000
H	11.125042000	20.294146000	29.921765000
C	10.870791000	18.588388000	28.633547000
H	11.311726000	19.096309000	27.778719000
C	12.409618000	16.461415000	26.287162000
C	12.751087000	16.613533000	24.936237000
H	11.964293000	16.736890000	24.196062000
C	14.085332000	16.633644000	24.527502000
H	14.326277000	16.776731000	23.477649000
C	15.103190000	16.490490000	25.470483000
H	16.143649000	16.503761000	25.155663000
C	14.783271000	16.342480000	26.820700000
H	15.574110000	16.240664000	27.559902000
C	13.447443000	16.334269000	27.223017000
H	13.211047000	16.236621000	28.280835000
C	10.154982000	14.504417000	27.083059000
C	11.133935000	13.501616000	27.008279000
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C	10.804820000	12.152923000	27.157080000
H	11.582735000	11.395458000	27.099613000
C	9.481506000	11.776808000	27.384694000
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C	8.490578000	12.756395000	27.464484000
H	7.458137000	12.476176000	27.655454000
C	8.826147000	14.103285000	27.313103000
H	8.037714000	14.851469000	27.381037000
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C	12.744366000	17.079856000	20.260313000
H	12.565453000	16.197065000	19.648795000
C	13.983071000	17.716311000	20.191510000
H	14.756942000	17.329722000	19.532779000
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C	13.227826000	19.342658000	21.807388000
H	13.405401000	20.225753000	22.413663000
C	11.991385000	18.699279000	21.873866000
H	11.222650000	19.097578000	22.530758000
C	10.494901000	14.824237000	20.996348000
C	9.675055000	13.842883000	20.255356000
H	9.373669000	14.037973000	19.229692000
C	9.274672000	12.722542000	20.916950000
H	8.608097000	12.005014000	20.442989000
C	9.838486000	12.405024000	22.205274000
H	9.560216000	11.475578000	22.693923000
C	11.011533000	13.117992000	22.654611000
H	11.615574000	12.696020000	23.455436000
C	11.413493000	14.242910000	21.999932000
H	12.351652000	14.736239000	22.239831000
C	9.109049000	17.119126000	19.505143000
C	9.669060000	18.003672000	18.571634000
H	10.638970000	18.450678000	18.773728000
C	9.001000000	18.322041000	17.387707000
H	9.455938000	19.007986000	16.677412000
C	7.755476000	17.759666000	17.114464000
H	7.235521000	18.004166000	16.191716000
C	7.179945000	16.878560000	18.030428000
H	6.207821000	16.436817000	17.825778000
C	7.852850000	16.566166000	19.211023000
H	7.385612000	15.882868000	19.915707000
C	4.783177000	14.713768000	23.199212000
C	5.644442000	14.634453000	22.094671000
H	6.428215000	15.382894000	21.984484000
C	5.503521000	13.630136000	21.135671000
H	6.186381000	13.584546000	20.291351000
C	4.488404000	12.682735000	21.265118000
H	4.374078000	11.899543000	20.520020000
C	3.618822000	12.745846000	22.353692000
H	2.825456000	12.009935000	22.458897000

C	3.768778000	13.750677000	23.309894000
H	3.090847000	13.780483000	24.160187000
C	3.749055000	17.516812000	24.067716000
C	3.848230000	18.776099000	24.681732000
H	4.686130000	18.984100000	25.344550000
C	2.893671000	19.767645000	24.451479000
H	2.980443000	20.731777000	24.947206000
C	1.826346000	19.523676000	23.586378000
H	1.081336000	20.294615000	23.406637000
C	1.720874000	18.285626000	22.954365000
H	0.894664000	18.090193000	22.275208000
C	2.672105000	17.293596000	23.197918000
H	2.574532000	16.330648000	22.701888000
C	4.450964000	15.394393000	26.170935000
C	3.635898000	16.114549000	27.057177000
H	3.277178000	17.100563000	26.772042000
C	3.259077000	15.585620000	28.292388000
H	2.625342000	16.164441000	28.959726000
C	3.684321000	14.312285000	28.665348000
H	3.386316000	13.894067000	29.623279000
C	4.483327000	13.570941000	27.794926000
H	4.799288000	12.567581000	28.070825000
C	4.862519000	14.111103000	26.566487000
H	5.467751000	13.508721000	25.891269000
C	6.005359000	18.961020000	21.475356000
H	5.458475000	18.068525000	21.790052000
H	6.796876000	18.669770000	20.778424000
C	5.093008000	20.043012000	20.899370000
H	4.083793000	19.948469000	21.313042000
H	5.024285000	19.981991000	19.809913000
C	5.751078000	21.334409000	21.393827000
H	5.063060000	22.183803000	21.426811000
H	6.604790000	21.606761000	20.764147000
C	6.228530000	20.921897000	22.777702000
H	7.087816000	21.481879000	23.150644000
H	5.412102000	20.981295000	23.508956000
C	6.783137000	18.373877000	27.586441000
H	7.734797000	17.869755000	27.780120000
H	6.018673000	17.623753000	27.372195000
C	6.416598000	19.327194000	28.718448000
H	5.331478000	19.475704000	28.766468000
H	6.754500000	18.954396000	29.688514000
C	7.116932000	20.618789000	28.289768000
H	6.702550000	21.516819000	28.755776000
H	8.184327000	20.565468000	28.527524000
C	6.907665000	20.599539000	26.783367000

H	7.676845000	21.120536000	26.212098000
H	5.923458000	21.008387000	26.514263000

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PrSi4C76N2H66O4 Doublet

C	4.452628000	-0.894364000	-3.695301000
C	3.515090000	-1.648233000	-2.975612000
C	2.640756000	-2.475129000	-3.698206000
C	2.705749000	-2.554558000	-5.088858000
C	3.649612000	-1.798594000	-5.787045000
C	4.521997000	-0.966289000	-5.087270000
Si	3.402602000	-1.535256000	-1.065204000
O	2.003558000	-0.770600000	-0.562512000
Pr	-0.037570000	-0.258115000	-0.243285000
N	0.010387000	-0.060140000	-2.868389000
C	0.083824000	0.226566000	-3.985419000
C	0.178917000	0.587784000	-5.385483000
C	3.467405000	-3.317533000	-0.367509000
C	4.071238000	-4.367169000	-1.074546000
C	4.155001000	-5.649915000	-0.529950000
C	3.629642000	-5.904346000	0.736225000
C	3.020813000	-4.871960000	1.453067000
C	2.942306000	-3.591988000	0.904535000
C	4.902187000	-0.547879000	-0.423679000
C	6.184706000	-1.114877000	-0.388201000
C	7.281352000	-0.378803000	0.057639000
C	7.109737000	0.939230000	0.481975000
C	5.840224000	1.515659000	0.461645000
C	4.746018000	0.775395000	0.011220000
N	-0.156501000	-2.879970000	-0.781017000
C	-0.185110000	-4.035767000	-0.759083000
C	-0.220508000	-5.484581000	-0.710136000
O	-0.069241000	-0.573008000	1.830802000
Si	-0.226723000	-0.530852000	3.501287000
C	-0.950787000	-2.169059000	4.170816000
C	-0.123512000	-3.163114000	4.713531000
C	-0.650974000	-4.375326000	5.158996000
C	-2.021293000	-4.615394000	5.065383000
C	-2.860856000	-3.639183000	4.527718000
C	-2.327433000	-2.429000000	4.084520000
O	-2.115733000	-0.529730000	-0.607277000
Si	-3.616225000	-0.964269000	-1.206399000
C	-4.946335000	0.102970000	-0.350793000
C	-6.276881000	0.108580000	-0.795351000
C	-7.254308000	0.841916000	-0.124419000
C	-6.915559000	1.578350000	1.011129000

C	-5.599135000	1.578197000	1.470601000
C	-4.623686000	0.845805000	0.792658000
O	0.106096000	1.839381000	-0.316218000
Si	0.433658000	3.451647000	-0.634819000
C	0.899082000	3.747970000	-2.471031000
C	2.160054000	3.371982000	-2.960664000
C	2.511793000	3.596461000	-4.291083000
C	1.603624000	4.204759000	-5.160025000
C	0.342678000	4.577376000	-4.693620000
C	-0.003346000	4.347986000	-3.360820000
C	-1.389024000	0.895024000	4.007806000
C	-1.541221000	2.019110000	3.183461000
C	-2.339231000	3.094218000	3.575531000
C	-2.997698000	3.060694000	4.804770000
C	-2.860554000	1.949160000	5.635690000
C	-2.063680000	0.876225000	5.237560000
C	1.511003000	-0.271742000	4.249597000
C	2.639553000	-0.196168000	3.422361000
C	3.912215000	0.002220000	3.960933000
C	4.072036000	0.128607000	5.339996000
C	2.958141000	0.059356000	6.177711000
C	1.689849000	-0.137039000	5.634522000
C	-3.737942000	-0.729983000	-3.102842000
C	-3.215508000	-1.690745000	-3.982668000
C	-3.259652000	-1.505579000	-5.364410000
C	-3.823484000	-0.343814000	-5.894239000
C	-4.336490000	0.628502000	-5.036101000
C	-4.291380000	0.434449000	-3.655426000
C	-3.953890000	-2.803399000	-0.789060000
C	-3.433897000	-3.351049000	0.393158000
C	-3.730558000	-4.660956000	0.770721000
C	-4.553362000	-5.451028000	-0.034311000
C	-5.079808000	-4.922537000	-1.211992000
C	-4.784088000	-3.609372000	-1.580745000
C	1.893528000	4.039454000	0.441627000
C	2.667638000	5.150849000	0.075204000
C	3.693833000	5.613804000	0.898769000
C	3.967379000	4.964079000	2.102333000
C	3.214916000	3.850670000	2.476808000
C	2.185788000	3.396248000	1.652692000
C	-1.130283000	4.470717000	-0.240910000
C	-1.045881000	5.827817000	0.102617000
C	-2.195052000	6.576098000	0.354244000
C	-3.450623000	5.973728000	0.271059000
C	-3.552270000	4.622749000	-0.060194000
C	-2.399341000	3.878720000	-0.314093000

H	2.519917000	-0.288755000	2.345817000
H	4.773245000	0.059660000	3.300631000
H	5.061900000	0.281981000	5.762634000
H	3.078266000	0.161364000	7.253440000
H	0.830837000	-0.182119000	6.301130000
H	0.944799000	-2.979600000	4.802436000
H	0.005856000	-5.129667000	5.585324000
H	-2.435744000	-5.556462000	5.418541000
H	-3.931094000	-3.816769000	4.459632000
H	-2.994987000	-1.671202000	3.680309000
H	-1.036939000	2.057970000	2.221110000
H	-2.443548000	3.954080000	2.919694000
H	-3.616280000	3.899328000	5.114753000
H	-3.377033000	1.915986000	6.591830000
H	-1.978497000	0.008687000	5.888792000
H	-2.789810000	-2.747841000	1.027698000
H	-3.329683000	-5.055638000	1.701290000
H	-4.791251000	-6.470269000	0.260399000
H	-5.724888000	-5.530581000	-1.841500000
H	-5.205253000	-3.211906000	-2.501698000
H	-6.557244000	-0.462896000	-1.678203000
H	-8.279924000	0.837419000	-0.485132000
H	-7.677551000	2.147392000	1.537917000
H	-5.325331000	2.144774000	2.356489000
H	-3.599671000	0.852057000	1.156237000
H	-2.777180000	-2.602400000	-3.583243000
H	-2.864102000	-2.270585000	-6.028466000
H	-3.871246000	-0.201735000	-6.971235000
H	-4.777233000	1.535422000	-5.442217000
H	-4.701901000	1.196793000	-2.997764000
H	-0.071574000	6.304491000	0.187473000
H	-2.111226000	7.626335000	0.622399000
H	-4.347491000	6.555021000	0.470376000
H	-4.525426000	4.141886000	-0.109600000
H	-2.485748000	2.822571000	-0.557153000
H	2.882536000	2.909704000	-2.292213000
H	3.496290000	3.305323000	-4.648296000
H	1.882012000	4.395589000	-6.193749000
H	-0.366839000	5.056173000	-5.364061000
H	-0.984561000	4.651826000	-3.004001000
H	2.476628000	5.655351000	-0.869863000
H	4.282164000	6.477719000	0.599500000
H	4.765909000	5.324077000	2.746328000
H	3.427971000	3.331908000	3.407291000
H	1.608567000	2.526569000	1.954629000
H	0.975279000	0.004323000	-5.855579000

H	0.413281000	1.653164000	-5.467254000
H	-0.774401000	0.380795000	-5.879036000
H	1.900849000	-3.068697000	-3.166513000
H	2.027300000	-3.211162000	-5.628649000
H	3.710223000	-1.866399000	-6.870574000
H	5.261545000	-0.378136000	-5.624898000
H	5.143259000	-0.248192000	-3.158950000
H	6.330975000	-2.146593000	-0.702205000
H	8.268261000	-0.834324000	0.080173000
H	7.963899000	1.513507000	0.832053000
H	5.694627000	2.537895000	0.799856000
H	3.757194000	1.226624000	0.010063000
H	2.462960000	-2.798256000	1.471567000
H	2.612265000	-5.061956000	2.442453000
H	3.699925000	-6.900418000	1.166503000
H	4.630848000	-6.448943000	-1.093250000
H	4.475915000	-4.185378000	-2.067874000
H	0.609803000	-5.842530000	-0.094757000
H	-0.123564000	-5.897286000	-1.717610000
H	-1.173391000	-5.805436000	-0.280046000

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PrSi4C76N2H66O4 Quartet

C	5.061754000	-0.880235000	-3.517594000
C	3.836615000	-1.375596000	-3.049063000
C	2.850049000	-1.690174000	-3.997331000
C	3.080892000	-1.524551000	-5.362559000
C	4.308687000	-1.033596000	-5.808922000
C	5.299325000	-0.710585000	-4.883111000
Si	3.500068000	-1.627059000	-1.173806000
O	2.076594000	-0.932790000	-0.701568000
Pr	0.030838000	-0.147269000	-0.695040000
N	-0.313010000	0.454347000	-3.317533000
C	-0.110541000	1.025467000	-4.303539000
C	0.153320000	1.750355000	-5.531036000
C	3.465671000	-3.521395000	-0.855054000
C	4.029398000	-4.439488000	-1.752558000
C	4.017601000	-5.810696000	-1.487691000
C	3.435073000	-6.288689000	-0.314065000
C	2.864207000	-5.390183000	0.590074000
C	2.880467000	-4.022251000	0.318800000
C	4.960615000	-0.871209000	-0.202645000
C	6.165296000	-1.564910000	-0.015474000
C	7.232918000	-0.979279000	0.664758000
C	7.108720000	0.313093000	1.175157000

C	5.915060000	1.014233000	1.006475000
C	4.851267000	0.424245000	0.323432000
N	-0.260282000	-2.609675000	-1.925791000
C	-0.150497000	-3.761724000	-1.977556000
C	-0.009139000	-5.204262000	-2.025400000
O	-0.662130000	-0.686183000	1.433865000
Si	-0.911392000	-0.335145000	3.069998000
C	-1.793259000	-1.755367000	3.991344000
C	-1.042941000	-2.768721000	4.607946000
C	-1.668023000	-3.836196000	5.251589000
C	-3.060269000	-3.907658000	5.289373000
C	-3.822023000	-2.910539000	4.681914000
C	-3.193092000	-1.845397000	4.038037000
O	-2.302566000	-0.495081000	-0.298993000
Si	-3.722562000	-1.417409000	-0.364642000
C	-4.998386000	-0.785189000	0.892391000
C	-6.013739000	-1.625503000	1.371972000
C	-6.980148000	-1.144619000	2.254303000
C	-6.938304000	0.184689000	2.675980000
C	-5.931177000	1.030458000	2.212398000
C	-4.970013000	0.548772000	1.323497000
O	0.336511000	2.007771000	-0.619083000
Si	0.812081000	3.574630000	-0.863249000
C	1.637899000	3.821689000	-2.582154000
C	2.672221000	2.969091000	-3.001551000
C	3.320889000	3.164384000	-4.220668000
C	2.947505000	4.225859000	-5.047420000
C	1.918377000	5.080845000	-4.652539000
C	1.269660000	4.874971000	-3.431856000
C	-1.864180000	1.293361000	3.332621000
C	-1.801158000	2.324831000	2.383883000
C	-2.434975000	3.546130000	2.612740000
C	-3.137214000	3.756314000	3.799864000
C	-3.206570000	2.742669000	4.754499000
C	-2.576730000	1.520435000	4.519203000
C	0.848272000	-0.162925000	3.816057000
C	2.005438000	-0.510777000	3.107000000
C	3.265052000	-0.400323000	3.698741000
C	3.383049000	0.056707000	5.010012000
C	2.240037000	0.412631000	5.726705000
C	0.984353000	0.306509000	5.131365000
C	-4.369013000	-1.089923000	-2.138757000
C	-3.689136000	-1.606410000	-3.252500000
C	-4.155716000	-1.369688000	-4.544227000
C	-5.304672000	-0.603548000	-4.742231000
C	-5.983807000	-0.074814000	-3.645613000

C	-5.516176000	-0.313745000	-2.353526000
C	-3.432867000	-3.286511000	-0.128420000
C	-2.521230000	-3.753866000	0.830307000
C	-2.365066000	-5.121008000	1.057683000
C	-3.116868000	-6.044041000	0.328224000
C	-4.019572000	-5.594783000	-0.635708000
C	-4.173854000	-4.225909000	-0.860727000
C	2.091328000	4.115040000	0.449229000
C	3.016441000	5.137529000	0.190799000
C	3.928905000	5.544691000	1.163920000
C	3.937082000	4.924276000	2.413080000
C	3.031583000	3.898423000	2.683980000
C	2.116152000	3.501151000	1.709590000
C	-0.712135000	4.731657000	-0.785106000
C	-0.630076000	6.034396000	-0.273391000
C	-1.749021000	6.867775000	-0.242707000
C	-2.974636000	6.406946000	-0.722520000
C	-3.076999000	5.110962000	-1.229018000
C	-1.955013000	4.283407000	-1.257842000
H	1.932971000	-0.858471000	2.079469000
H	4.151106000	-0.662478000	3.127912000
H	4.363820000	0.140739000	5.471311000
H	2.326346000	0.776458000	6.747607000
H	0.103374000	0.599429000	5.698710000
H	0.043173000	-2.714208000	4.595146000
H	-1.069495000	-4.607834000	5.729588000
H	-3.550098000	-4.737021000	5.793543000
H	-4.907241000	-2.960591000	4.705086000
H	-3.801471000	-1.077055000	3.568162000
H	-1.253628000	2.181916000	1.455158000
H	-2.373378000	4.331761000	1.864953000
H	-3.625317000	4.710669000	3.981816000
H	-3.753083000	2.901195000	5.680950000
H	-2.651632000	0.733082000	5.266111000
H	-1.930077000	-3.045346000	1.403559000
H	-1.665193000	-5.462888000	1.815390000
H	-3.004566000	-7.109306000	0.515242000
H	-4.606717000	-6.308463000	-1.208340000
H	-4.876707000	-3.887488000	-1.618798000
H	-6.044468000	-2.667923000	1.062578000
H	-7.762278000	-1.806905000	2.616965000
H	-7.687346000	0.558925000	3.369245000
H	-5.882156000	2.061431000	2.550570000
H	-4.178787000	1.209835000	0.981473000
H	-2.789375000	-2.199086000	-3.109260000
H	-3.623096000	-1.782874000	-5.397261000

H	-5.669860000	-0.419254000	-5.749412000
H	-6.879163000	0.522939000	-3.795576000
H	-6.052432000	0.101247000	-1.503882000
H	0.317130000	6.398569000	0.118544000
H	-1.665874000	7.873862000	0.161020000
H	-3.848212000	7.053628000	-0.697427000
H	-4.032559000	4.744024000	-1.595675000
H	-2.047739000	3.269221000	-1.639789000
H	2.981578000	2.140975000	-2.368111000
H	4.116894000	2.488645000	-4.522114000
H	3.458538000	4.387038000	-5.993562000
H	1.624357000	5.911024000	-5.290556000
H	0.468637000	5.547682000	-3.133305000
H	3.035220000	5.614955000	-0.786997000
H	4.637964000	6.339496000	0.945301000
H	4.649129000	5.237932000	3.172575000
H	3.037705000	3.403083000	3.651070000
H	1.417668000	2.699273000	1.932306000
H	0.947139000	1.246802000	-6.088366000
H	0.484282000	2.764542000	-5.286364000
H	-0.752020000	1.794957000	-6.142193000
H	1.886508000	-2.069429000	-3.664806000
H	2.306719000	-1.786398000	-6.080694000
H	4.493680000	-0.908562000	-6.873031000
H	6.259009000	-0.329191000	-5.223370000
H	5.842237000	-0.622878000	-2.805357000
H	6.269694000	-2.579400000	-0.395536000
H	8.158795000	-1.532595000	0.802135000
H	7.939422000	0.770285000	1.707102000
H	5.805535000	2.017519000	1.409239000
H	3.919414000	0.972819000	0.211745000
H	2.431299000	-3.333200000	1.030121000
H	2.411210000	-5.756584000	1.508124000
H	3.429482000	-7.354966000	-0.101637000
H	4.464300000	-6.504921000	-2.195464000
H	4.480326000	-4.079602000	-2.674798000
H	0.957886000	-5.487034000	-1.598218000
H	-0.064660000	-5.552881000	-3.059999000
H	-0.814354000	-5.661242000	-1.443071000

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