Exploring sulfur donor atom coordination chemistry with La(II), Nd(II), and Tm(II) using a terphenylthiolate ligand

Kito Gilbert-Bass, Cary R. Stennett, Robin Grotjahn, Joseph W. Ziller, Filipp Furche*, William J. Evans*

Department of Chemistry, University of California, Irvine, Irvine, California 92697, United States

Supporting Information

The Supporting Information contains:

1. Experimental

General Considerations. All manipulations were performed by using modified Schlenk techniques or in a Vacuum/Atmospheres glovebox under argon. Solvents were degassed by sparging with dry argon before drying and collection using an S2 Grubbs-type[1] solvent purification system (JC Meyer). All physical measurements were recorded under strictly anaerobic and anhydrous conditions. Infrared spectra were recorded on compressed solid samples using an Agilent Cary 630 ATR/FTIR instrument. Electronic spectra were recorded as dilute solutions in the indicated solvent in quartz cuvettes (1 cm or 1 mm path length) using an Agilent Cary 60 UV/vis spectrophotometer. NMR spectra were recorded using a Bruker AVANCE 600 MHz spectrometer or a Bruker AVANCE 500 MHz spectrometer at 298 K unless otherwise stated and referenced to residual solvent signals. Assignment of the signals of NMR spectra have been provided where possible; but for the paramagnetic complexes, assignments were not possible due to broadening of the signals by the paramagnetism. Elemental analyses were conducted on a Thermo Scientific FlashSmart CHNS/O Elemental Analyzer at UC Irvine Materials Research Institute's TEMPR facility in Irvine, California. LaI_3 and NdI_3 were prepared using a modification of Meyer's procedure for the preparation of $LnCl_3$.[2] NdI_2 was prepared from neodymium metal and iodine as previously described.[3,4] $TmI_2(DME)_3$ was prepared from thulium metal and iodine in dimethoxyethane as previously described[5] and the final content of DME in the bulk material was determined by combustion analysis. $KSAr^{iPr6}$ was prepared by the reaction of $HSAr^{iPr6}$ with potassium metal in toluene as previously described.[6]

Synthesis of $La(SAr^{iPr6})_2I$, 1-La. A suspension of LaI_3 (0.12 g, 0.23 mmol) in toluene (20 mL) was added to a Teflon-tapped, heavy-walled flask. To this, a clear, colorless solution of $KSAr^{iPr6}$ (0.25 g, 0.452 mmol) in toluene (30 mL) was added. This was heated in an oil bath at 120-130 °C overnight, forming a white slurry. Solvent was removed under reduced pressure, and

the white residue was extracted in ca. 20 mL of hexane. The mixture was centrifuged and the supernatant was filtered to give a clear, colorless solution. Hexane was removed from the filtrate under reduced pressure. The product was recrystallized by heating to near-boiling in ca. 2 mL hexane until dissolution and allowing the solution to return to room temperature before placing in a freezer at −35 °C. Colorless, X-ray quality crystalline blocks were collected after overnight storage of this solution (0.044 g, 15%). Anal. Calcd for $LaIS_2C_{72}H_{98}$: C, 66.86; H, 7.64. Found: C, 68.36; H, 8.00. ^{1}H NMR (600 MHz, C_6D_6): δ = 8.21 (s, 2H, aryl H)), 7.45 (s, 2H, aryl H)), 7.27 (d, 4H, aryl H), 7.14 (d, 2H, aryl H), 6.89 (t, 2H, aryl H), 6.79 (d, 2H, aryl H), 3.43 (m, 4H, *p*-C*H*$(CH)_3$), 2.98 (m, 4H, *o*-C*H*$(CH)_3$), 2.84 (m, 4H, *o*-C*H*$(CH)_3$), 1.48-0.85 (m, 72H, *o,p*-CH$(CH_3)_3$).

Synthesis of Nd(Ar^{iPr6}S)$_2$I, 1-Nd. In a 100 mL Teflon-tapped, heavy-walled flask, NdI_3 (0.047 g, 0.090 mmol) and solid KSAr (0.10 g, 0.18 mmol) were combined in ca. 10 mL of toluene. The flask was sealed, and mixture was heated in an oil bath warmed to 120 °C and stirred for 18 h, after which the solution became pale green with concomitant formation of a colorless precipitate. The solvent was then removed under reduced pressure and the pale green residue was extracted in ca. 10 mL of hexane. The mixture was centrifuged, and the pale green supernatant was filtered. The solvent was then removed from the filtrate under reduced pressure to afford **1-Nd** as a pale green solid (0.084 g, 0.065 mmol, 72%). Crystals suitable for study by X-ray diffractometry were grown by overnight storage of a concentrated solution of **1-Nd** in hexane at -35 °C. Anal. Calcd for $NdIS_2C_{72}H_{98}$: C, 66.58; H, 7.61. Found: C, 65.93; H, 7.44. ^{1}H NMR (600 MHz, benzene-D_6): broad signals characteristic of **1-Nd** were found at δ = 8.49 ($\Delta\nu_{1/2}$ = 14 Hz) and 1.95 ($\Delta\nu_{1/2}$ > 620 Hz) No additional signals were observed in the region between -150 and 150 ppm. UV-vis: λ_{max}/nm (ε/$M^{-1}cm^{-1}$): 290 (shoulder, 18000), 325 (shoulder, 11000).

Synthesis of La(SAr^{iPr6})$_2$, 2-La. A clear, colorless solution of freshly prepared **1-La** (0.039 g, 0.030 mmol) in ca. 2 mL Et_2O was chilled to −35 °C for 30 minutes in a 20 mL scintillation vial. Similarly, a slurry of freshly made KC_8 (0.0082 g, 0.061 mmol) in ca. 2 mL Et_2O was chilled to −35 °C for 30 minutes in a separate scintillation vial. The solution of **1-La** was then added quickly by pipette into the vial containing KC_8. This was stirred for 2 minutes at room temperature and then placed back in the freezer overnight. The intense dark brown solution was then filtered through a pipette packed with ca. 1 cm of filter paper and the solvent was removed from the filtrate under reduced pressure. The intensely dark brown solid was extracted in ca. 2 mL hexanes and filtered through a pipette packed with ca. 1 cm of filter paper once more and stored for 18 h at -35 °C to afford intensely colored dark brown crystal blocks suitable for X-ray diffraction (0.028 g, 80% yield). Anal. Calcd for $LaS_2C_{72}H_{98}$: C, 74.13; H, 8.47. Found: C, 75.16; H, 8.62. ^{1}H NMR (600 MHz, C_6D_6): the 1H NMR spectrum of 2-La is essentially silent save for a broad signal of low intensity at $\delta = 8.47$ which was apparent across several experiments along with resonances of diamagnetic KSAr^{iPr6} which may be formed in small amounts during the reduction of **1-La** with KC_8.

Reduction of 1-La in the presence of [2.2.2]cryptand. A clear, colorless solution of freshly prepared **1-La** (0.052 g, 0.03 mmol) in ca. 2 mL THF was chilled to −35 °C for 30 minutes in a 20 mL scintillation vial. Similarly, a slurry of freshly prepared KC_8 (0.006 g, 0.06 mmol) in ca. 2 mL solution of 2.2.2-cryptand (0.016 g, 0.04 mmol) in THF was chilled to −35 °C for 30 minutes in a separate scintillation vial. The colorless solution of **1-La** was then quickly transferred by pipette into the vial containing KC_8. This was stirred for 5 minutes at room temperature and filtered immediately. The resulting yellow/green solution was then filtered using a pipette filter and the solvent was removed under reduced pressure. The yellow/green solids were extracted with

ca. 2 mL toluene and the extract was filtered through a glass pipette packed with ca. 1 cm of filter paper. The solvent was then removed under reduced pressure to afford 0.028 g of yellow/green powder. The EPR spectrum of a solution of this material dissolved in THF showed a characteristic 8-line pattern with g = 2.00 (A = 67.7 MHz) at 298 K. ^{1}H NMR (600 MHz, benzene-D_6, 298K): no resonances indicative of a new paramagnetic complex were observed in the ^{1}H NMR spectrum (see Figure S17).

Reduction of 1-La in the presence of 18-crown-6. A clear, colorless solution of freshly prepared **1-La** (52 mg, 0.030 mmol) in ca. 2 mL of THF was chilled to −35 °C for 30 minutes in a 20 mL scintillation vial. Similarly, a slurry of freshly made KC_8 (0.006 g, 0.06 mmol) in ca. 2 mL solution of 18-crown-6 (0.013 g, 0.05 mmol) in THF was chilled to −35 °C for 30 minutes in a separate scintillation vial. The black solution of **1-La** was then quickly transferred by pipette into the vial containing KC_8. This was stirred for 5 minutes at room temperature and then the mixture was filtered twice through a pipette packed with ca. 1 cm of filter paper to afford a dark brown/red solution. The solvent was then removed from the filtrate under reduced pressure. The dark brown solids were extracted with ca. 2mL of toluene and the extract was filtered through a glass pipette packed with ca. 1 cm of filter paper. The solvent was then removed from the filtrate under reduced pressure to afford 0.028 g of yellow/green powder. The EPR spectrum of a solution of this material dissolved in THF showed a characteristic 8-line pattern with g = 1.99 (A = 67.6 MHz) at 298 K. ^{1}H NMR (600 MHz, benzene-D_6, 298K): no resonances indicative of a new paramagnetic complex were observed in the ^{1}H NMR spectrum (see Figure S16).

Synthesis of Nd(SAr^{iPr6})$_2$, 2-Nd, by reduction of 1-Nd. Dark brown **1-Nd** (0.050 g, 0.043 mmol) was dissolved in ca. 5 mL of diethyl ether in a 20 mL vial. KC_8 (0.077 g, 0.090 mmol) was then added in one portion and the mixture was stirred for 4 h. The solvent was then removed under

reduced pressure and the residue was extracted in ca. 4 mL of hexane. The mixture was then centrifuged and the supernatant was filtered. The solvent was then removed from the filtrate under reduced pressure until small, dark brown crystals began to form on the wall of the vial. The vial was then sealed and gently warmed by hand until the crystalline material had dissolved and the vial was allowed to stand at ambient temperature. After ca. 18 h., a small amount of dark brown/orange crystals had grown from this solution which were suitable for study by X-ray diffraction experiments. The structural data showed a significant impurity of **1-Nd**, which has the same unit cell as **2-Nd**. Thus, a route to **2-Nd** through NdI_2 was pursued (vide infra). The formation of **2-Nd** was confirmed by ^{1}H NMR and IR spectroscopy (see Figures S6 and S19). No signals for **1-Nd** were apparent in the NMR spectrum, although several additional paramagnetically shifted and broadened signals were present which we have been unable to identify to date.

Synthesis of Nd(SAr$^{i\text{Pr6}}$)$_2$, 2-Nd, from NdI$_2$. NdI_2 (0.36 g, 0.90 mmol) and KSAr$^{i\text{Pr6}}$ (0.50 g, 0.90 mmol) were combined in a 20 mL vial. Diethyl ether (15 mL) was then added. The vial was canted by ca. 15 degrees to assure effective stirring of the insoluble NdI_2 and the mixture was stirred at room temperature. After stirring for 18 h, the mixture had become dark brown in color. The diethyl ether was removed from the mixture under reduced pressure and the residue was then extracted with ca. 5 mL of hexane. The mixture was then centrifuged and the supernatant was filtered through a pipette packed with ca. 1 cm of filter paper. The solvent was then completely removed from the filtrate under reduced pressure to afford 0.40 g (0.34 mmol, 76%) of **2-Nd** as dark brown, nearly black powder. Dark red/orange crystals which were suitable for study by X-ray diffraction experiments were grown from a concentrated hexane solution of **2-Nd** stored at ambient temperature for 24 h. Anal. Calcd. for $NdS_2C_{72}H_{98}$: C, 73.79; H, 8.43.

Found: C, 73.39; H, 7.33. ^{1}H NMR (600 MHz, C_6D_6): δ = 8.28 (d, br), 7.63 (d, br), 7.56 (t, br), 7.37 (s, $\Delta\nu_{1/2}$ = 14 Hz), 3.35 (s, $\Delta\nu_{1/2}$ = 99 Hz), 2.98 (mult.), 2.89 (mult.), 1.33-1.19 (mult.), 0.63 (s, $\Delta\nu_{1/2}$ = 36 Hz), -3.80 ($\Delta\nu_{1/2}$ = 112 Hz), -5.12 (s, $\Delta\nu_{1/2}$ = 45 Hz). UV-vis: λ_{max}/nm (ε/$M^{-1}cm^{-1}$): 272 (25000), 300 (shoulder, 15000).

Synthesis of Sm(SAr^{iPr6})$_2$, 2-Sm. The preparation of **2-Sm** by the reaction between KSAr^{iPr6} and excess SmI_2 has been previously described by Cofone and Niemeyer.[7] However, we have found that **2-Sm** may also be reliably obtained through the following route: $SmI_2(THF)_2$ (0.25 g, 0.45 mmol) and ca. 15 mL of diethyl ether were combined in a 20 mL vial. KSAr^{iPr6} (0.25 g, 0.45 mmol) was added to this mixture while stirring. The mixture was then stirred for 18 h. The solvent was removed under reduced pressure to afford a violet solid. The residue was extracted in ca. 10 mL of hexane and the mixture was centrifuged. The supernatant was then filtered through a pipette packed with ca. 1 cm of filter paper. The solvent was then removed from the filtrate under reduced pressure to afford 0.18 g (0.15 mmol, 68%) of **2-Sm** as a dark violet, microcrystalline solid. ^{1}H NMR (600 MHz, C_6D_6): δ = 29.54 ($\Delta\nu_{1/2}$ = 442 Hz), 25.42 ($\Delta\nu_{1/2}$ = 299 Hz), 7.25 ($\Delta\nu_{1/2}$ = 7 Hz), 7.21 ($\Delta\nu_{1/2}$ = 8 Hz), 4.92 ($\Delta\nu_{1/2}$ = 22 Hz), 3.76 ($\Delta\nu_{1/2}$ = 23 Hz), 3.61 ($\Delta\nu_{1/2}$ = 29 Hz), 0.12 ($\Delta\nu_{1/2}$ = 19 Hz), -0.20 ($\Delta\nu_{1/2}$ = 159 Hz), -0.67 ($\Delta\nu_{1/2}$ = 49 Hz), -0.76 ($\Delta\nu_{1/2}$ = 31 Hz), -1.19 ($\Delta\nu_{1/2}$ = 38 Hz), -3.43 ($\Delta\nu_{1/2}$ = 102 Hz), -7.31 ($\Delta\nu_{1/2}$ = 107 Hz). UV-vis: λ_{max}/nm (ε/$M^{-1}cm^{-1}$): 274 (25000), 300 (shoulder, 15000) 350 (shoulder, 6000).

Synthesis of Tm(SAr^{iPr6})$_2$, 2-Tm. In a 20 mL vial, solid KSAr^{iPr6} (0.15 g, 0.27 mmol) was added in one portion to a stirred mixture of $TmI_2(DME)_2$ (0.082 g, 0.14 mmol) in ca. 4 mL of diethyl ether. The mixture was stirred for 18 hours, after which a colorless precipitate had formed and the dark green $TmI_2(DME)_2$ had been consumed. The solvent was then removed under reduced pressure to afford a dark green, solid residue. The residue was extracted in ca. 4 mL of

hexane. The mixture was centrifuged, and the dark green supernatant was filtered. The solvent was then removed from the filtrate under reduced pressure to afford a dark green oil. The oil was dissolved in ca. 1 mL hexane and the solvent was again removed under reduced pressure. Another ca. 1 mL portion of hexane was added and the above process was repeated three times to afford 0.13 g (0.0.11 mmol, 78%) of **2-Tm** as a dark green, microcrystalline solid. Crystals suitable for study by X-ray diffractometry were grown by overnight storage at ambient temperature of a concentrated solution of **2-Tm** in hexane. Anal. Calcd. for $TmS_2C_{72}H_{98}$: C, 72.27; H, 8.26. Found: C, 72.29; H, 8.51. ^{1}H NMR (600 MHz, C_6D_6): δ = 12.99 ($\Delta\nu_{1/2}$ = 673 Hz), -2.24 ($\Delta\nu_{1/2}$ = 176 Hz), -2.74 ($\Delta\nu_{1/2}$ = 133 Hz), -3.73 ($\Delta\nu_{1/2}$ = 27 Hz), -6.80 ($\Delta\nu_{1/2}$ = 407 Hz), -8.14 ($\Delta\nu_{1/2}$ = 434 Hz), -10.80 ($\Delta\nu_{1/2}$ = 133 Hz), -53.56 ($\Delta\nu_{1/2}$ = 230 Hz). UV-vis: λ_{max}/nm ($\varepsilon/M^{-1}cm^{-1}$): 274 (24000), 300 (shoulder, 14000), 345 (5600).

Synthesis of Nd(SAr^{iPr6})$_2$(N$_2$Ph$_2$), 3-Nd. In a 20 mL vial, azobenzene (0.006 g, 0.034 mmol) was added in one portion to a stirred, dark brown solution of Nd(SAr^{iPr6})$_2$ (**2-Nd**, 0.040 g, 0.034 mmol) in ca. 2 mL of hexane at room temperature. The solution immediately became dark green and was stirred for 20 min. The solvent was then removed under reduced pressure to afford a dark green solid. A minimal amount of hexane (ca. 0.5 mL) was added dropwise to the dark green residue until it was dissolved, and the vial was then sealed and laid on its side. Dark red, almost black crystals of Nd(SAr^{iPr6})$_2$(N$_2$Ph$_2$), **3-Nd**, which were suitable for study by X-ray diffraction had grown on the walls of the vial after ca. 1 h (0.010 g, 0.0074 mmol, 34%). Anal. Calcd for $NdS_2C_{84}H_{108}N_2$: C, 74.51; H, 8.04; N, 2.07. Found: C, 75.03; H, 8.34; N, 2.48. ^{1}H NMR (500 MHz, C_6D_6): δ = 13.25 ($\Delta\nu_{1/2}$ = 153 Hz), 8.55 ($\Delta\nu_{1/2}$ = 12 Hz), 8.48 ($\Delta\nu_{1/2}$ = 18 Hz), 8.02 (d, br), 5.71 ($\Delta\nu_{1/2}$ = 51 Hz), 5.45 ($\Delta\nu_{1/2}$ = 30 Hz), 4.96 ($\Delta\nu_{1/2}$ = 85 Hz), 3.93 ($\Delta\nu_{1/2}$ = 21 Hz),

2.55 ($\Delta\nu_{1/2}$ = 61 Hz), 2.30 ($\Delta\nu_{1/2}$ = 21 Hz), 2.21 (d, br), 1.86 ($\Delta\nu_{1/2}$ = 30 Hz), 1.77 ($\Delta\nu_{1/2}$ = 53 Hz), 1.65 ($\Delta\nu_{1/2}$ = 34 Hz), 0.40 ($\Delta\nu_{1/2}$ = 114 Hz), -2.56 ($\Delta\nu_{1/2}$ = 24 Hz), -3.29 ($\Delta\nu_{1/2}$ = 27.2 Hz).

Synthesis of Sm(SAr^{iPr6})$_2$(N$_2$Ph$_2$), 3-Sm. In a 20 mL vial, azobenzene (0.008 g, 0.034 mmol) was added in one portion to a stirred, violet solution of Sm(SAr^{iPr6})$_2$ (**2-Sm**, 0.025 g, 0.021 mmol) in ca. 2 mL of hexane at room temperature. The solution immediately became dark green and was stirred for 20 min. The solvent was then removed under reduced pressure. A minimal amount of hexane (ca. 0.5 mL) was added dropwise to the dark green residue until it was dissolved, and the vial was then sealed and laid on its side. Dark red, almost black crystals of Sm(SAr^{iPr6})$_2$(N$_2$Ph$_2$), **3-Sm**, which were suitable for study by X-ray diffraction had grown on the walls of the vial after ca. 1 h (0.011 g, 0.008 mmol, 37 %). Anal. Calcd for $SmS_2C_{84}H_{108}N_2$: C, 74.17; H, 8.00; N, 2.06. Found: C, 74.40; H, 8.23; N, 2.35. ^{1}H NMR (600 MHz, C_6D_6): δ = 70.40 ($\Delta\nu_{1/2}$ = 412 Hz), 25.30 ($\Delta\nu_{1/2}$ = 347 Hz), 8.02 ($\Delta\nu_{1/2}$ = 89 Hz), 5.90 ($\Delta\nu_{1/2}$ = 172 Hz), 4.52 ($\Delta\nu_{1/2}$ = 175 Hz), 4.15 ($\Delta\nu_{1/2}$ = 128 Hz), 3.81 ($\Delta\nu_{1/2}$ = 155 Hz), 3.23 ($\Delta\nu_{1/2}$ = 133 Hz), 2.89 ($\Delta\nu_{1/2}$ = 142 Hz), 1.83 ($\Delta\nu_{1/2}$ = 128 Hz), 1.39-0.93 (mult.), 0.11 ($\Delta\nu_{1/2}$ = 170 Hz), -0.77 ($\Delta\nu_{1/2}$ = 202 Hz), -1.77 ($\Delta\nu_{1/2}$ = 200 Hz), -148.17 ($\Delta\nu_{1/2}$ = 573 Hz), -159.83 ($\Delta\nu_{1/2}$ = 344.2 Hz). UV-vis: λ_{max}/nm (ε/M^{-1}cm^{-1}): 277 (17000), 293 (shoulder, 15000), 315 (shoulder, 13000), 329 (shoulder, 10000), 345 (shoulder, 6000).

2. Infrared Spectra.

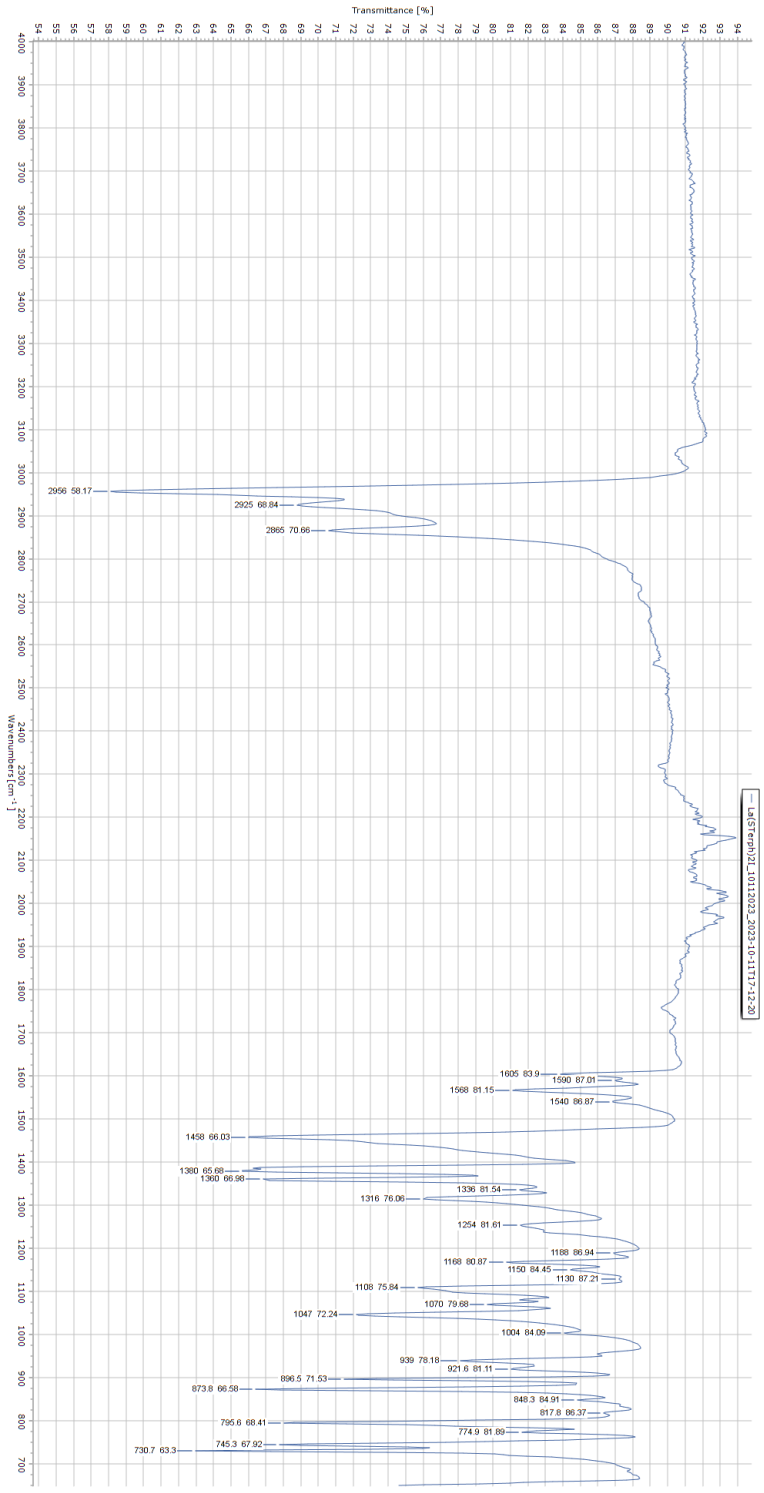


Figure S1. Infrared spectrum of La(SAr^{iPr6})$_2$I, **1-La**.

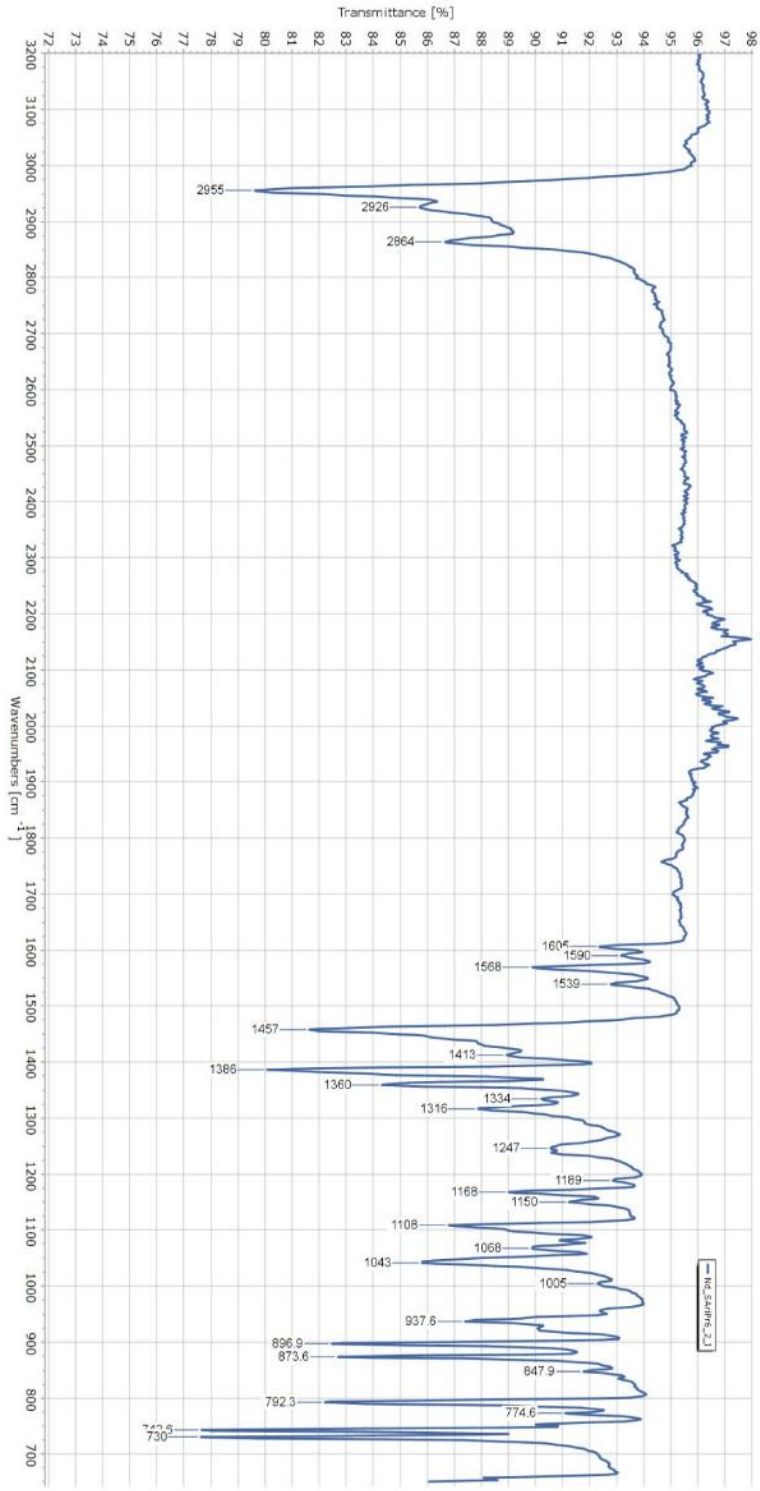


Figure S2. Infrared spectrum of $Nd(SAr^{iPr6})_2I$, **1-Nd**.

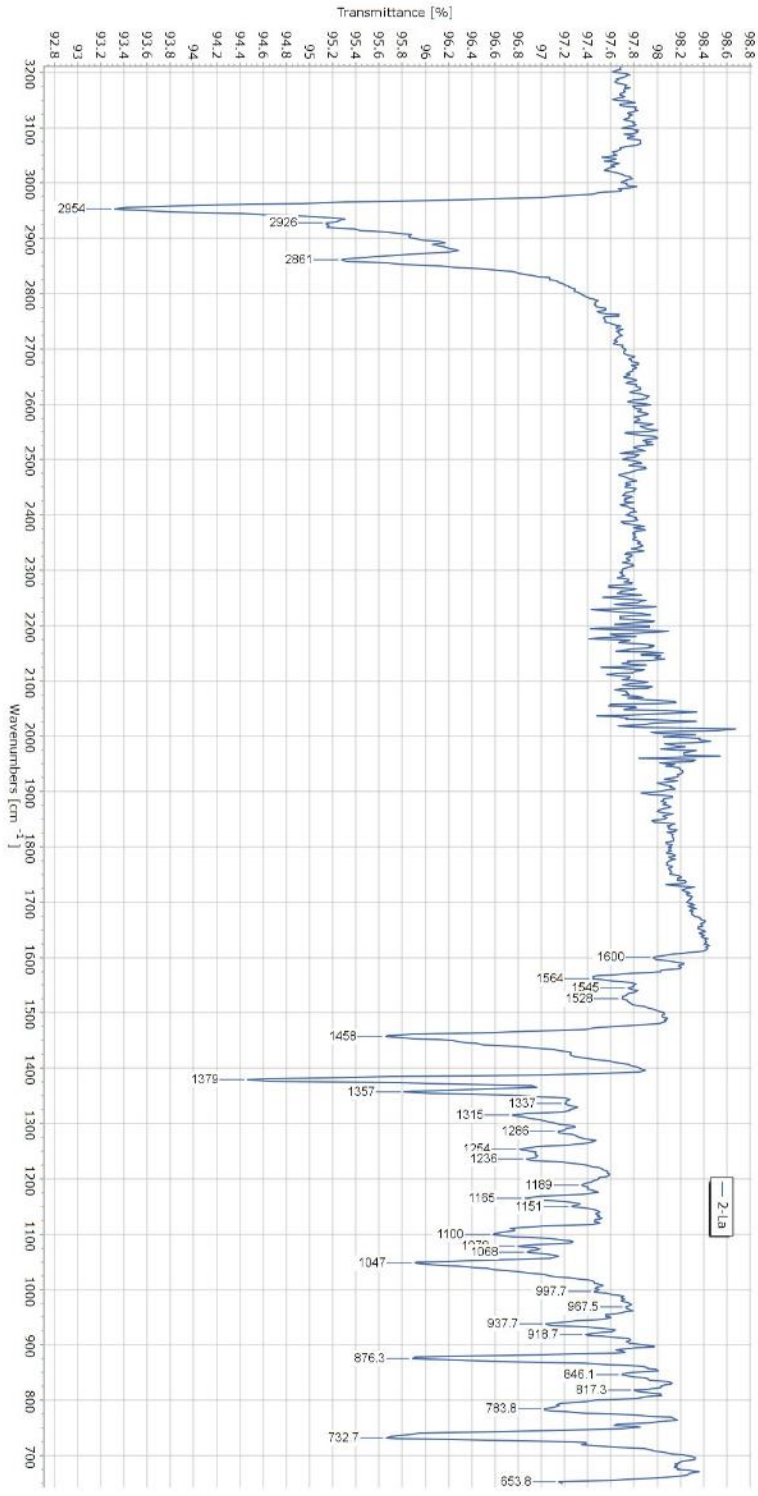


Figure S3. Infrared spectrum of La(SAr^{iPr6})$_2$, **2-La**.

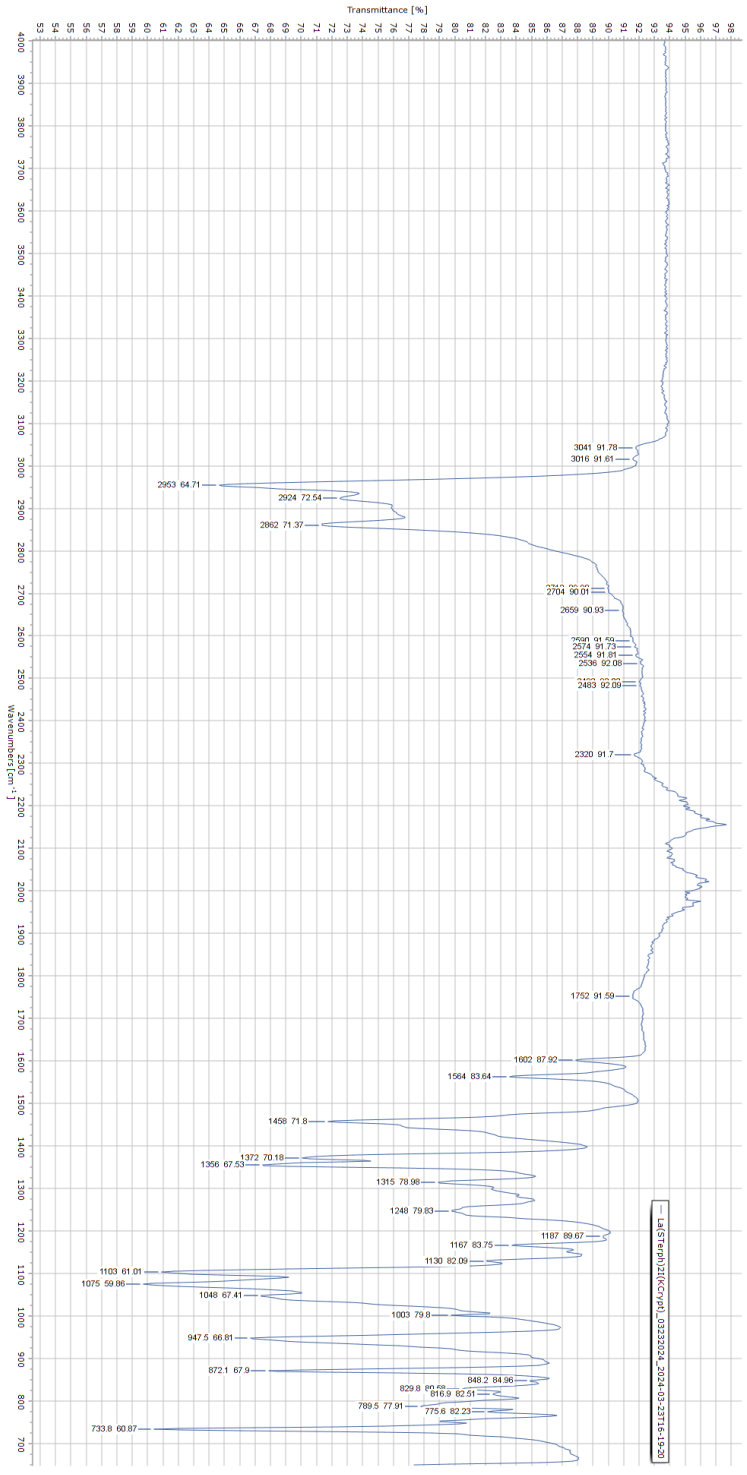


Figure S4. Infrared spectrum of La(SAr^{iPr6})$_2$I, **1-La** treated with 2.2.2-cryptand and KC_8

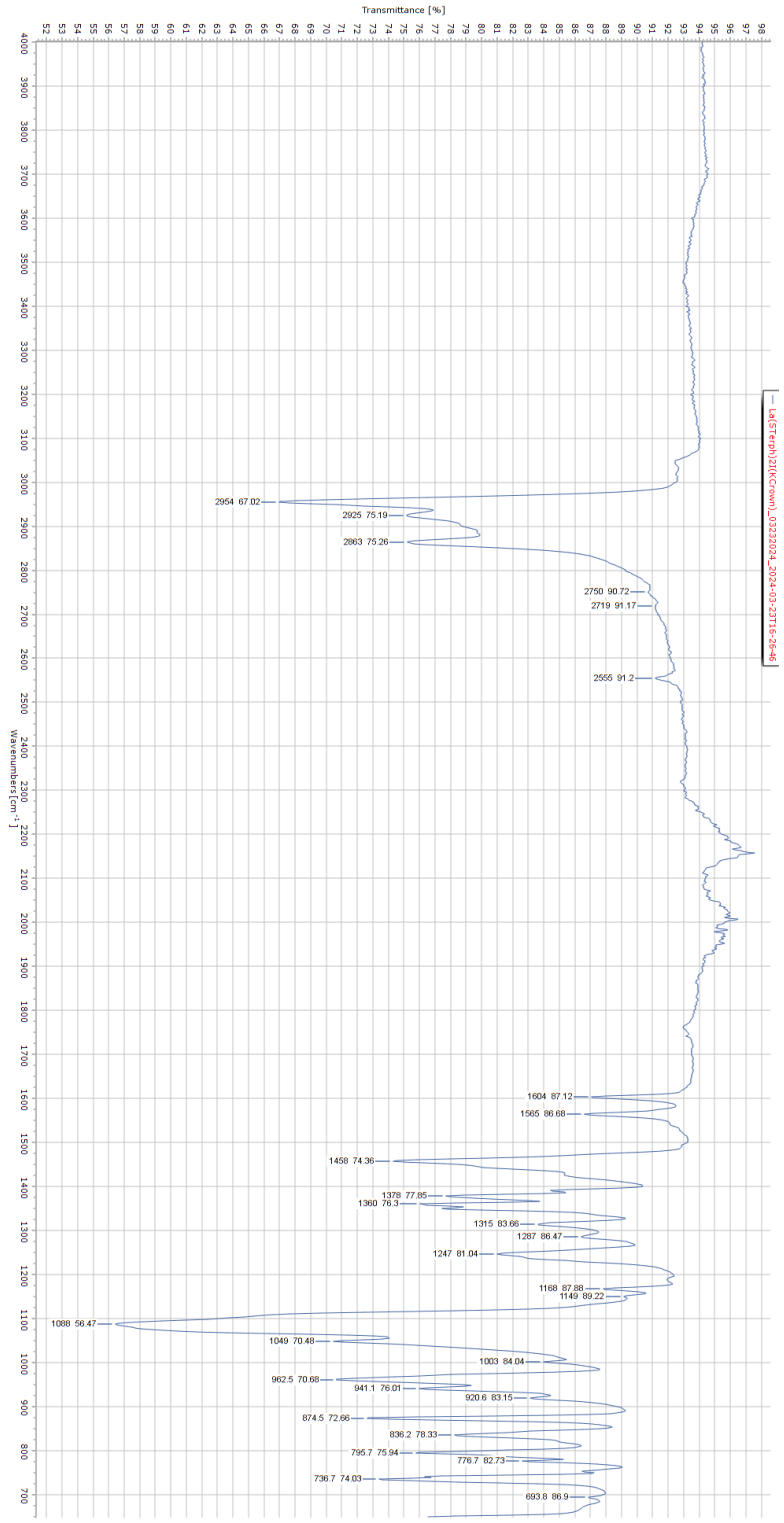


Figure S5. Infrared spectrum of La(SAr^{iPr6})$_2$I, **1-La** treated with 18-crown-6 and KC_8

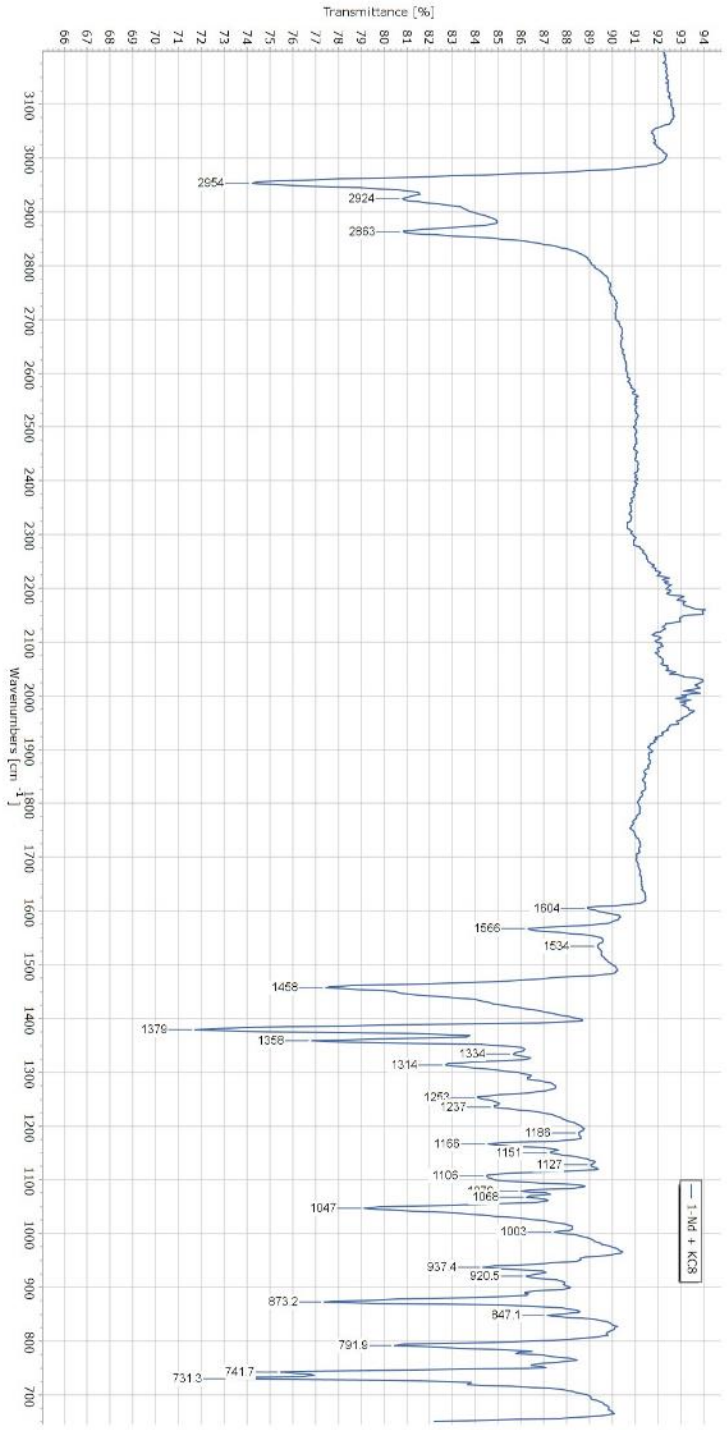


Figure S6. Infrared spectrum of $Nd(SAr^{iPr6})_2$, **2-Nd**, prepared by the reaction between **1-Nd** and and KC_8

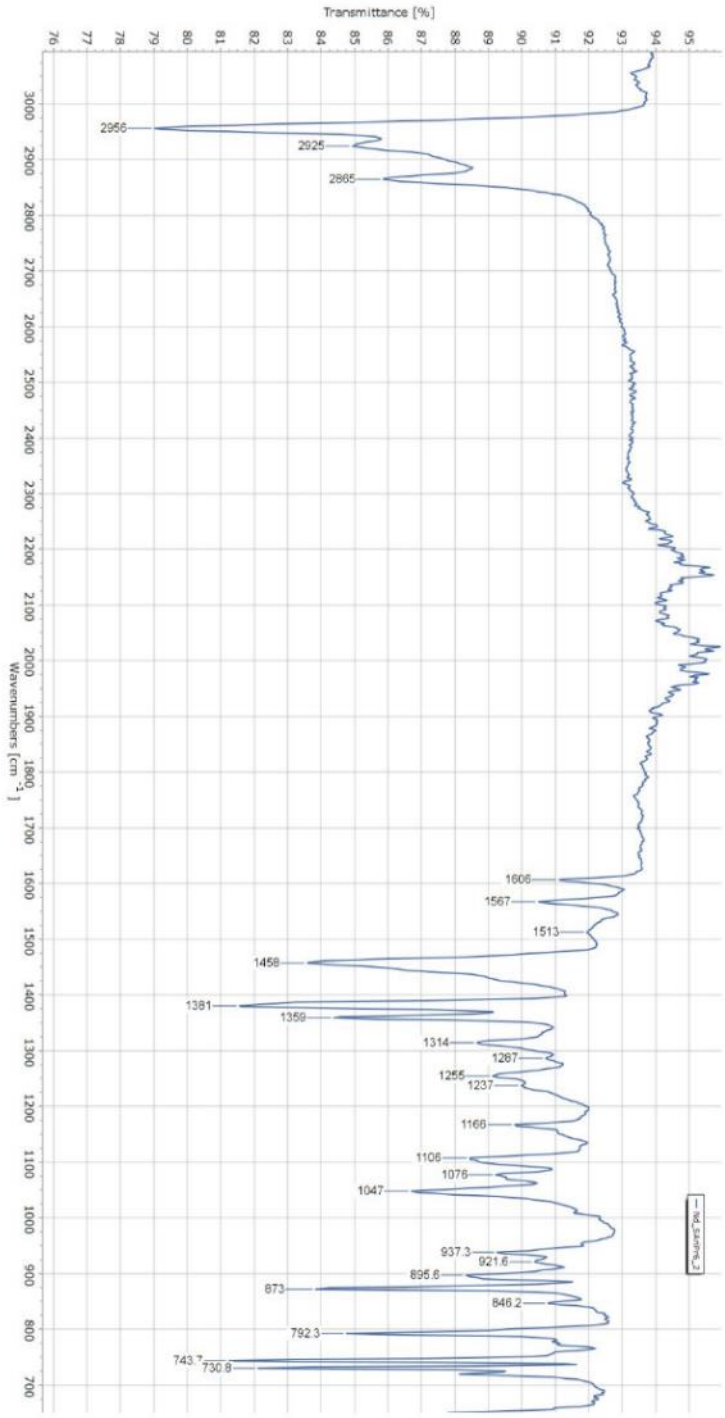


Figure S7. Infrared spectrum of $Nd(SAr^{iPr6})_2$, **2-Nd**, prepared by the reaction between NdI_2 and $KSAr^{iPr6}$

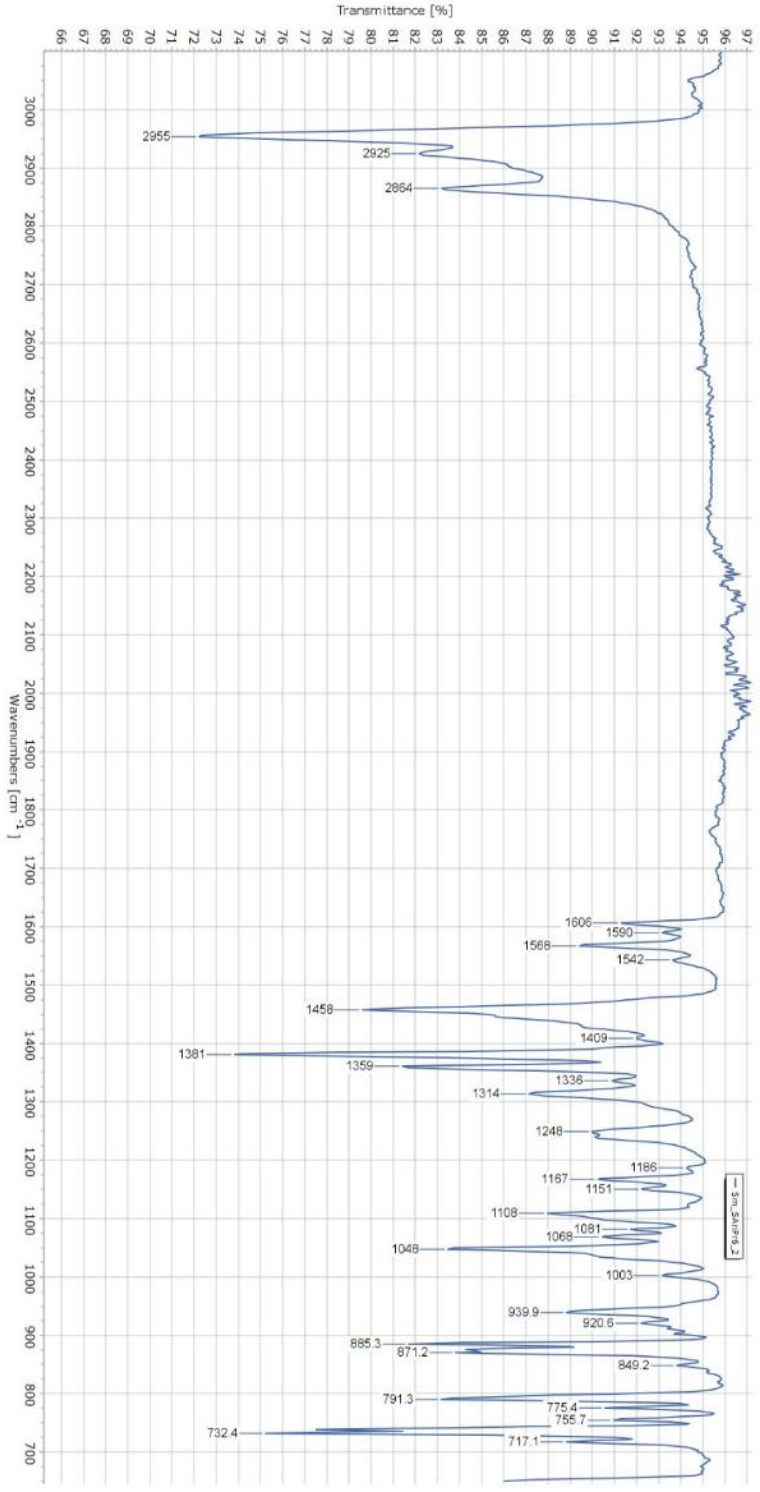


Figure S8. Infrared spectrum of $Sm(SAr^{iPr6})_2$, **2-Sm**.

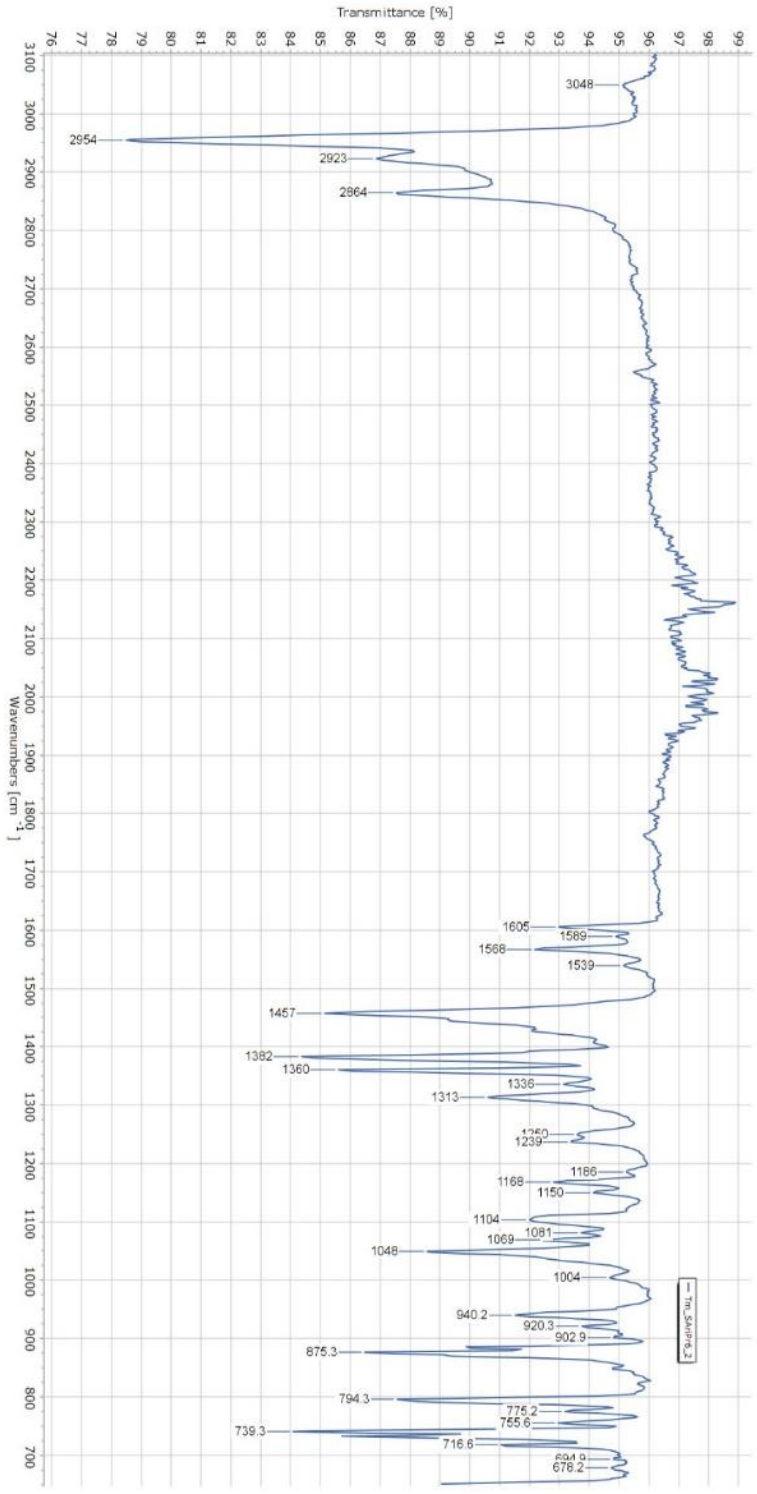


Figure S9. Infrared spectrum of $Tm(SAr^{iPr6})_2$, **2-Tm**.

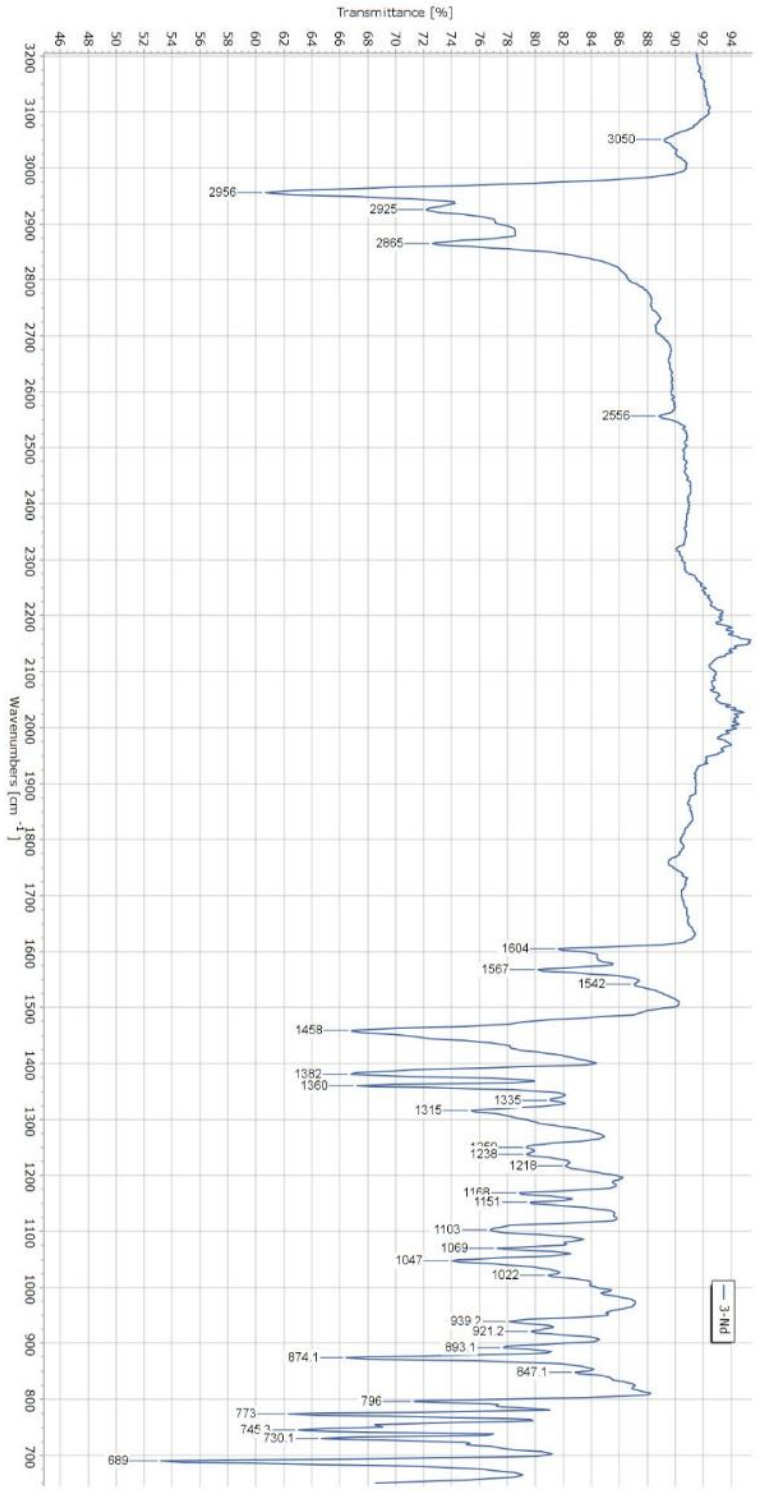


Figure S10. Infrared spectrum of $Nd(SAr^{iPr6})_2(N_2Ph_2)$, **3-Nd**.

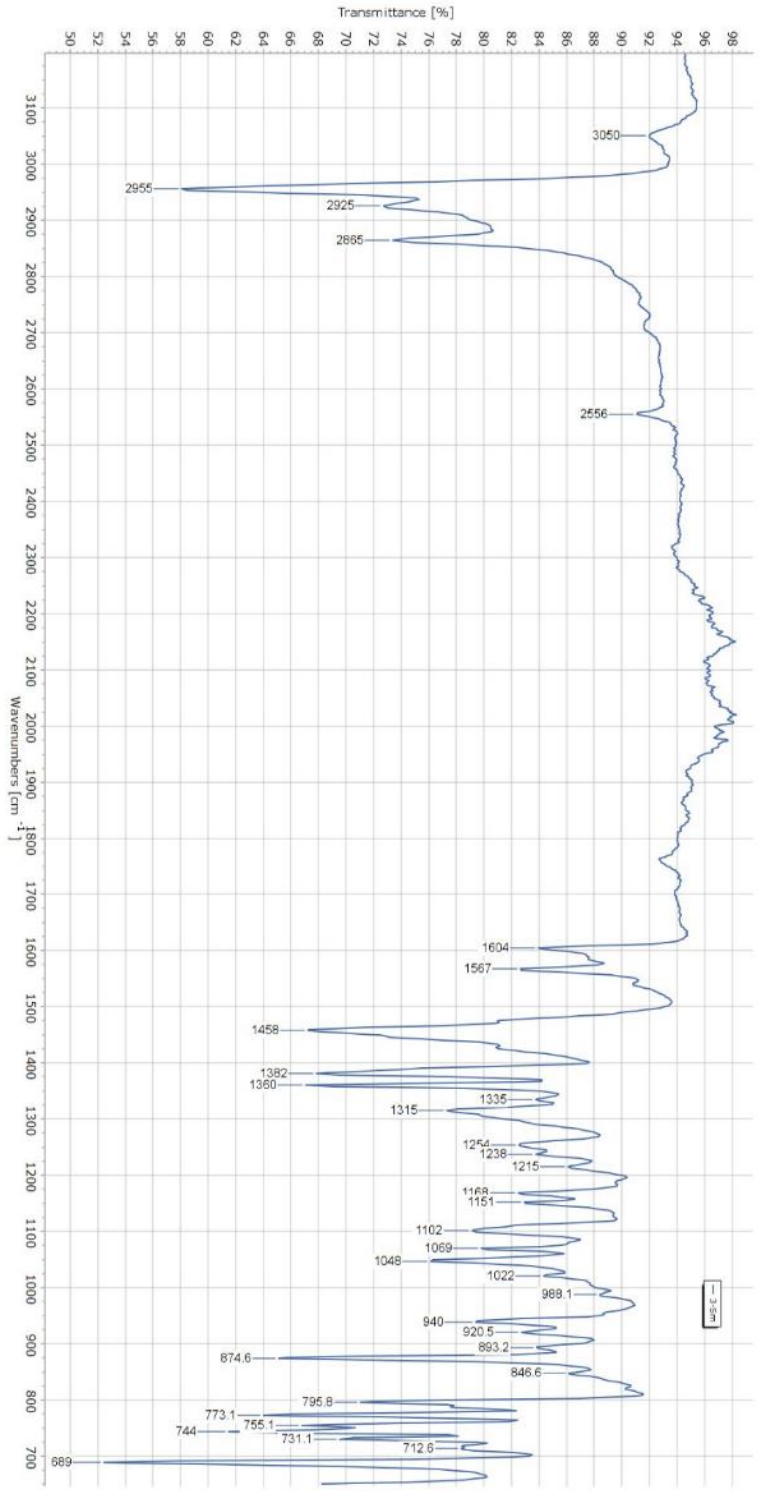


Figure S11. Infrared spectrum of $Sm(SAr^{iPr6})_2(N_2Ph_2)$, **3-Sm**.

3. NMR Spectra.

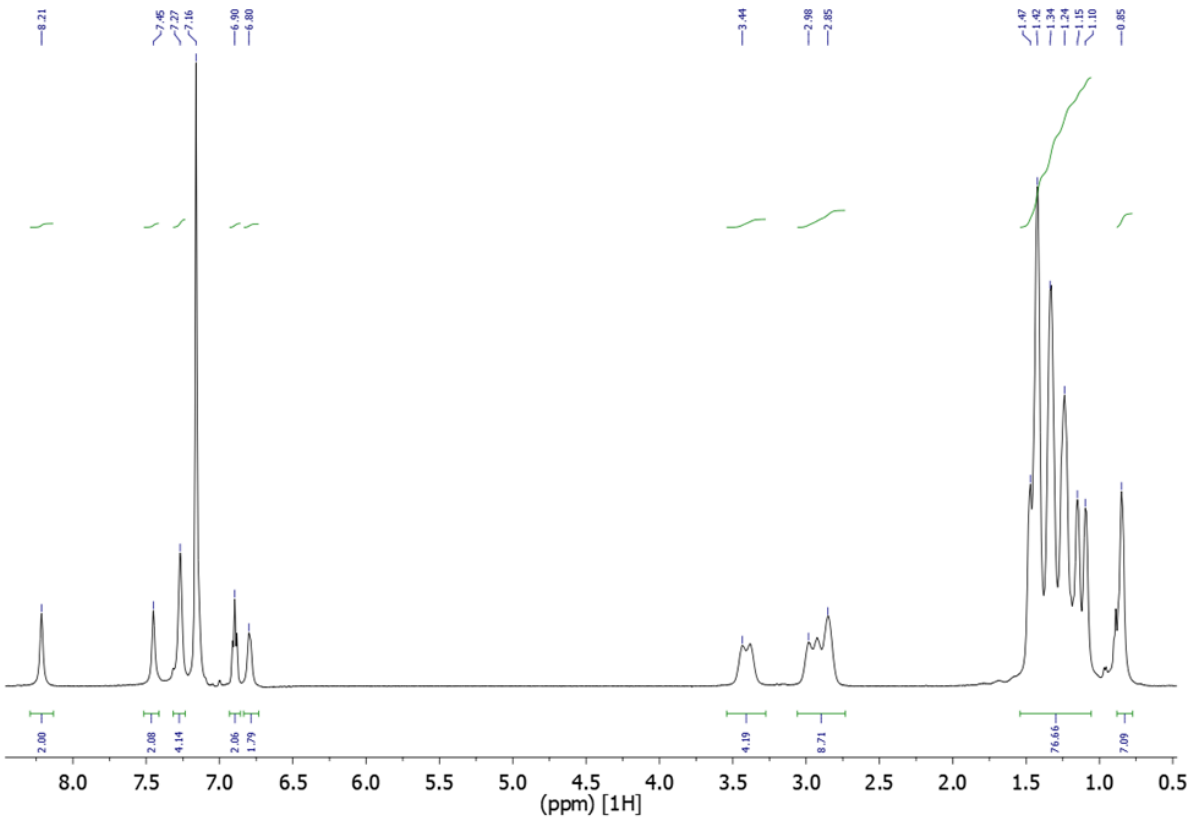


Figure S12. ^{1}H NMR (600 MHz, 298K) of **1-La** in benzene-D_6 (residual proton signal marked at 7.16 ppm). Note: Residual hexane solvent peaks are marked at 0.89 and 1.26 ppm.

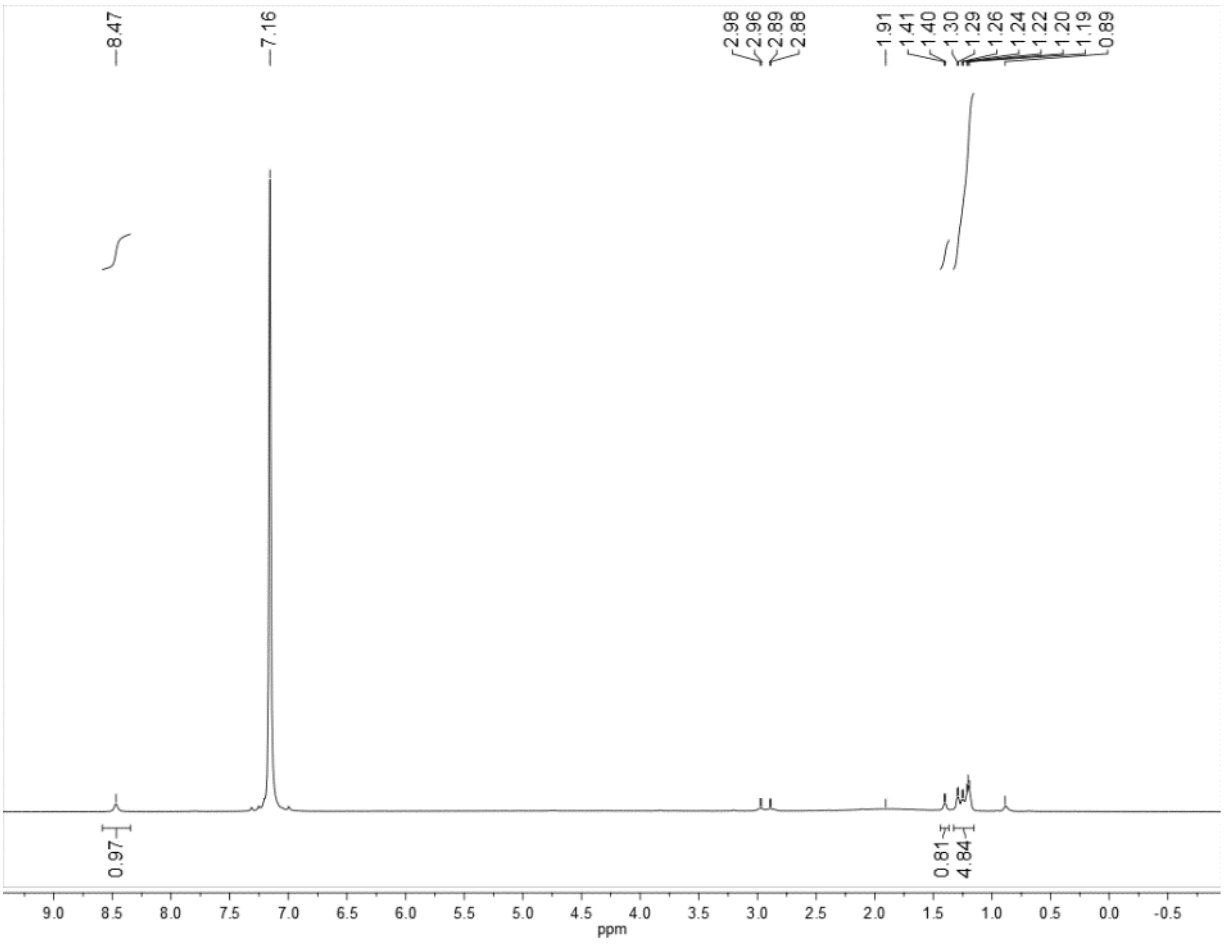


Figure S13. ^{1}H NMR spectrum (500 MHz, 298K) of **1-Nd** in benzene-D_6. The signal at 7.16 ppm is due to residual benzene in the deuterated solvent. Minor, unbroadened and unshifted signals at ca. 1.3 ppm and ca. 2.9 ppm are due minor impurities (hexane, residual KSAr$^{i\text{Pr}6}$).

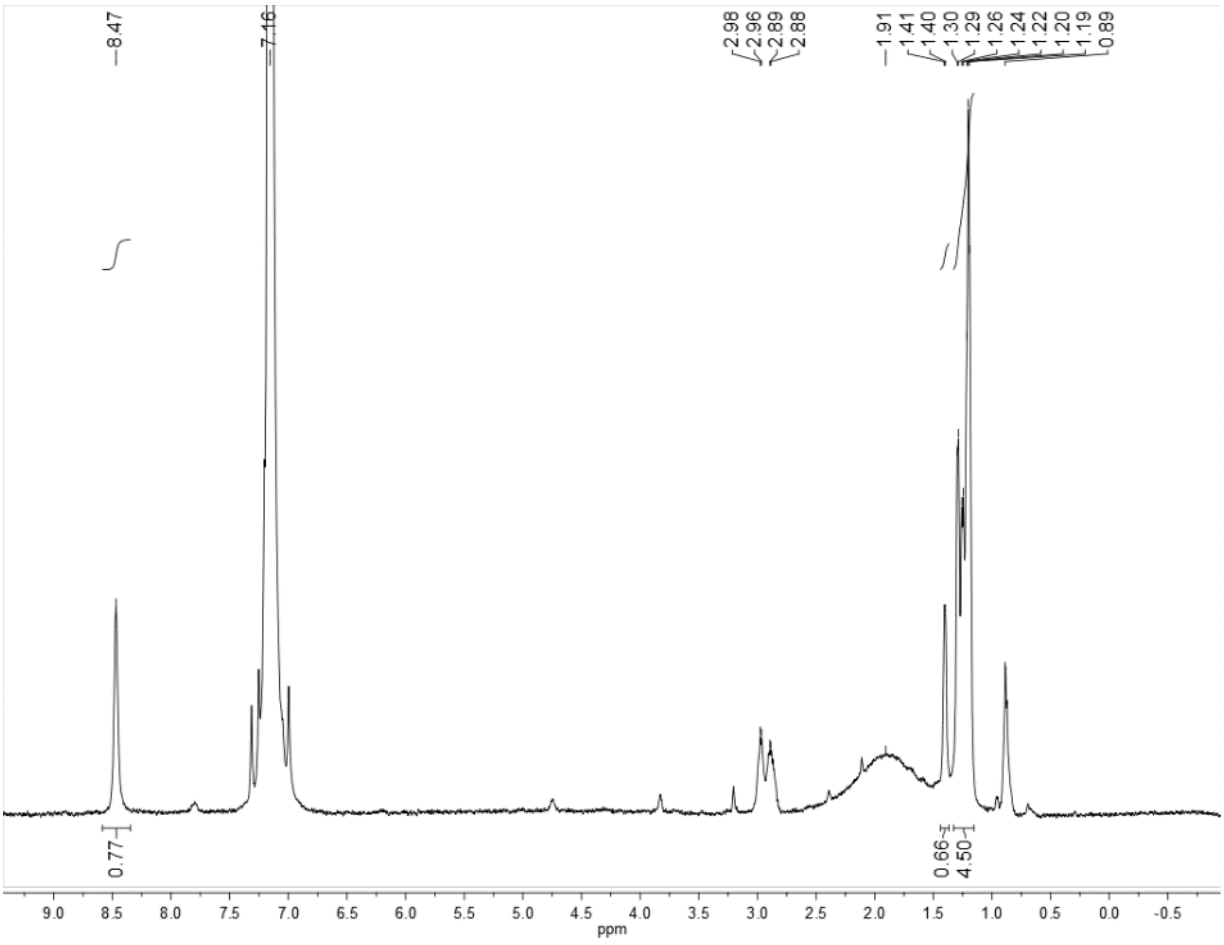


Figure S14. Magnified ^{1}H NMR spectrum (500 MHz, 298K) of **1-Nd** in benzene-D_6.

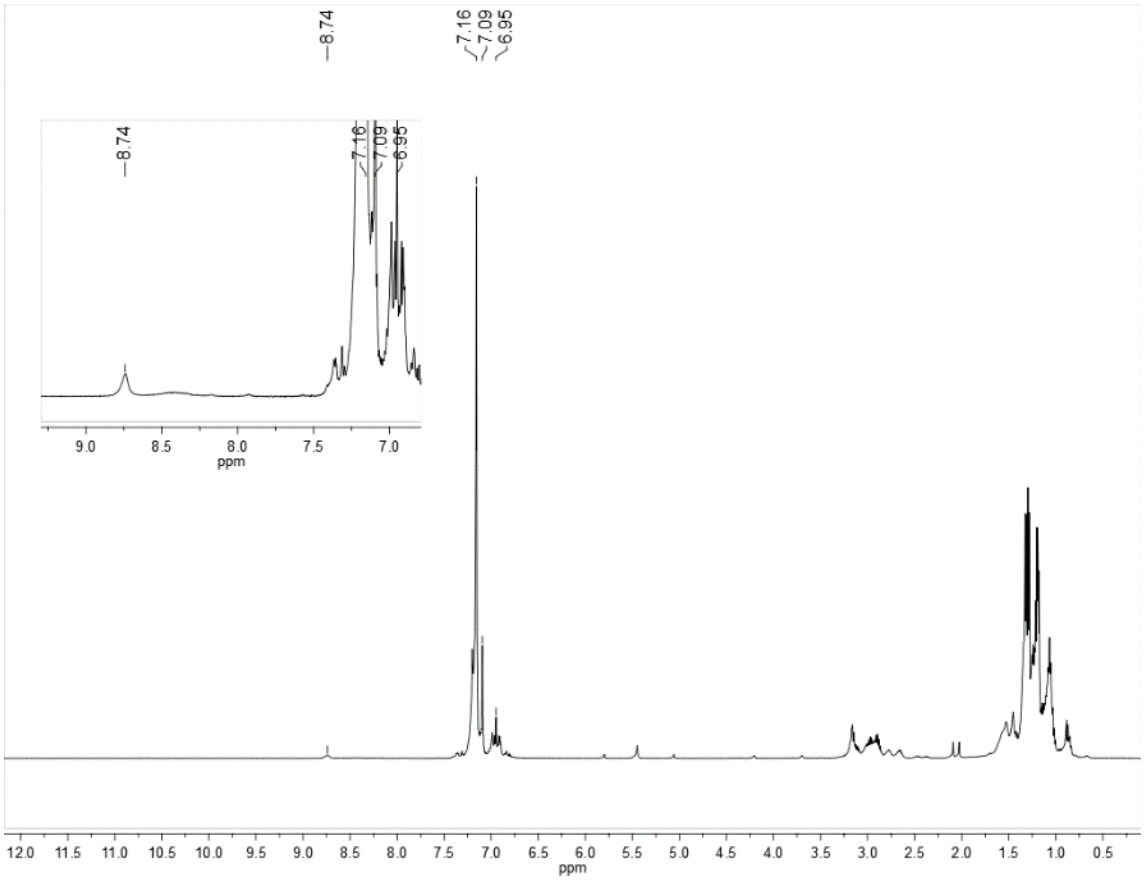


Figure S15. ^{1}H NMR (600 MHz, 298K) of **2-La** in benzene-D_6 (residual proton signal marked at δ = 7.16 ppm). The only resonance in the region of +100 to -100 ppm that is attributable to paramagnetic **2-La** is found at 8.74 ppm. The remainder of the signals shown here are due to diamagnetic impurities of KSAr$^{i\text{Pr}6}$.

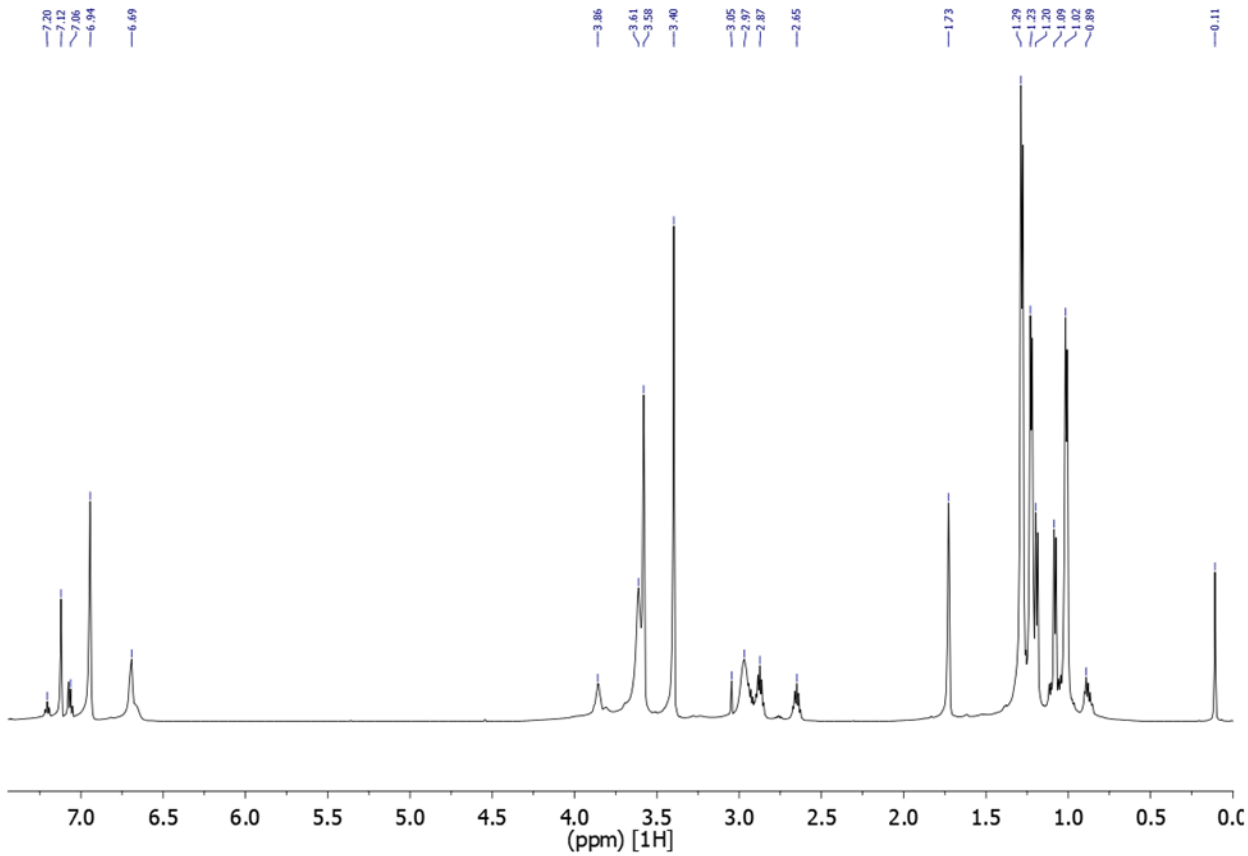


Figure S16. ^{1}H NMR (500 MHz, 298K) of **1-La** treated with 18-crown-6 and KC_8. Note: sample contains resonances of $HSAr^{iPr6}$ impurity, hexane at 0.89, silicon grease at 0.11, and residual THF-D_8 solvent at 3.58 and 1.73 ppm.

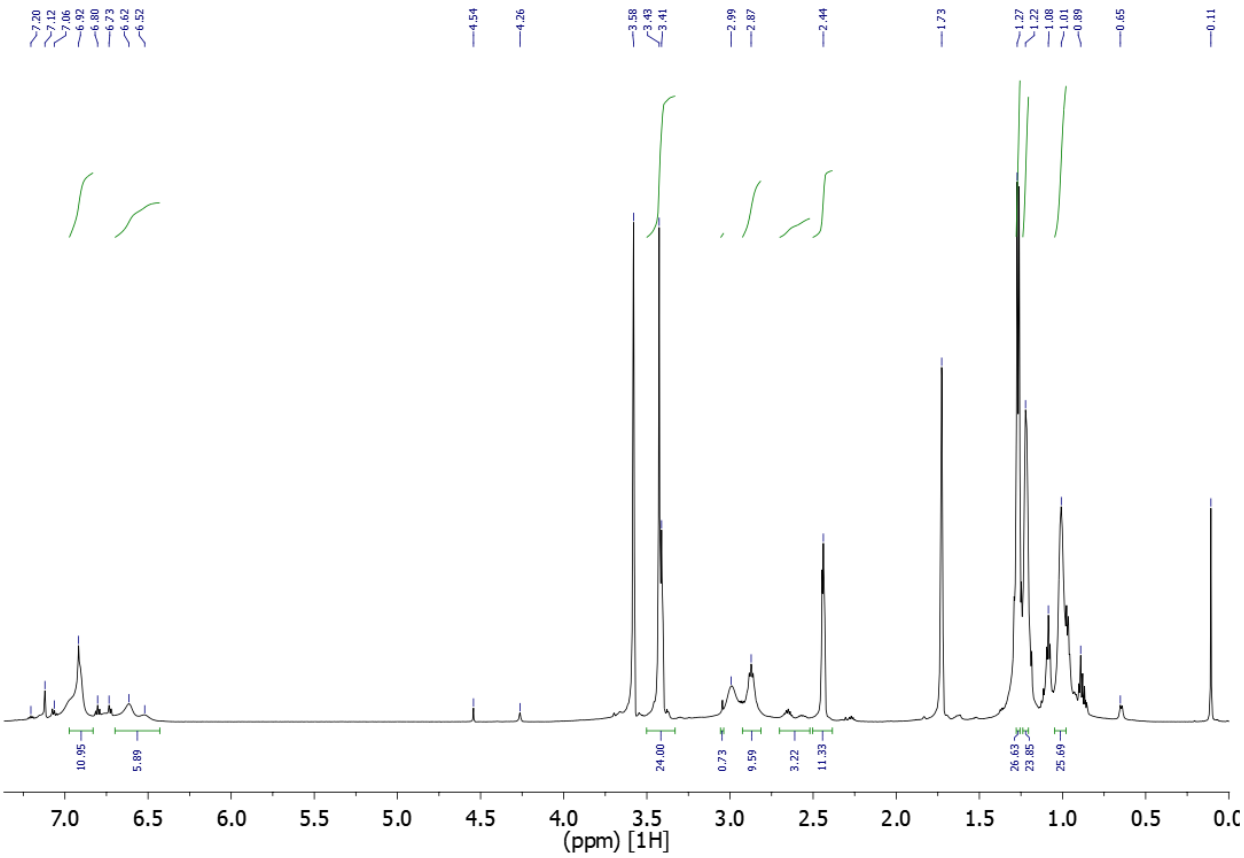


Figure S17. ^{1}H NMR (600 MHz, 298K) of **1-La** treated with 2.2.2-cryptand and KC_8. Note: resonance of of HSAr^{ipr6} impurity (Figure Sx), hexane impurity at 0.89, unknown impurities at 4.54, 4.26 and 0.65, silicon grease at 0.11, and residual THF-D_8 solvent at 3.58 and 1.73 ppm.

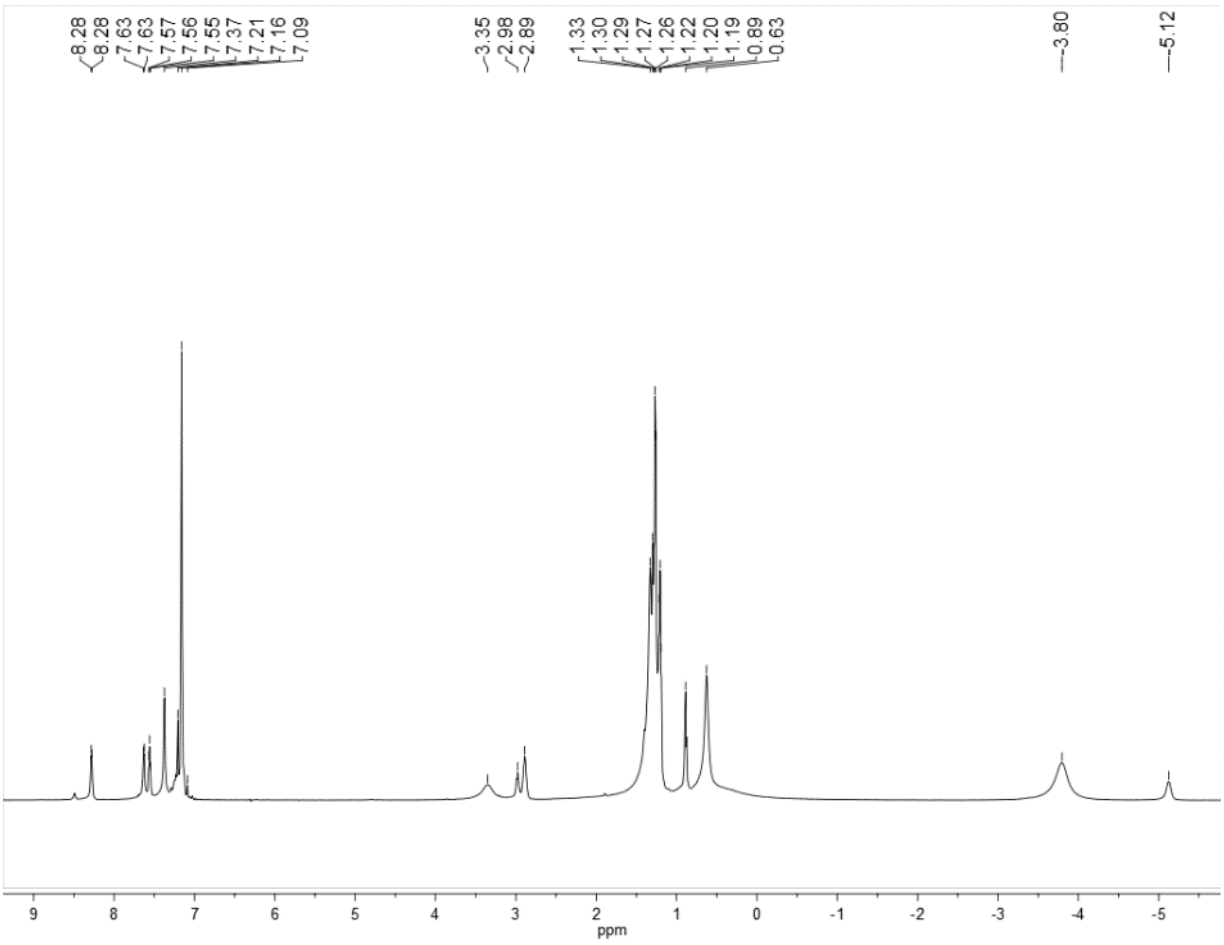


Figure S18. ^{1}H NMR spectrum (600 MHz, 298K) of **2-Nd** in benzene-D_6. The signal at 7.16 ppm is due to residual benzene in the deuterated solvent. The signal at 0.89 ppm is due to residual hexane solvent.

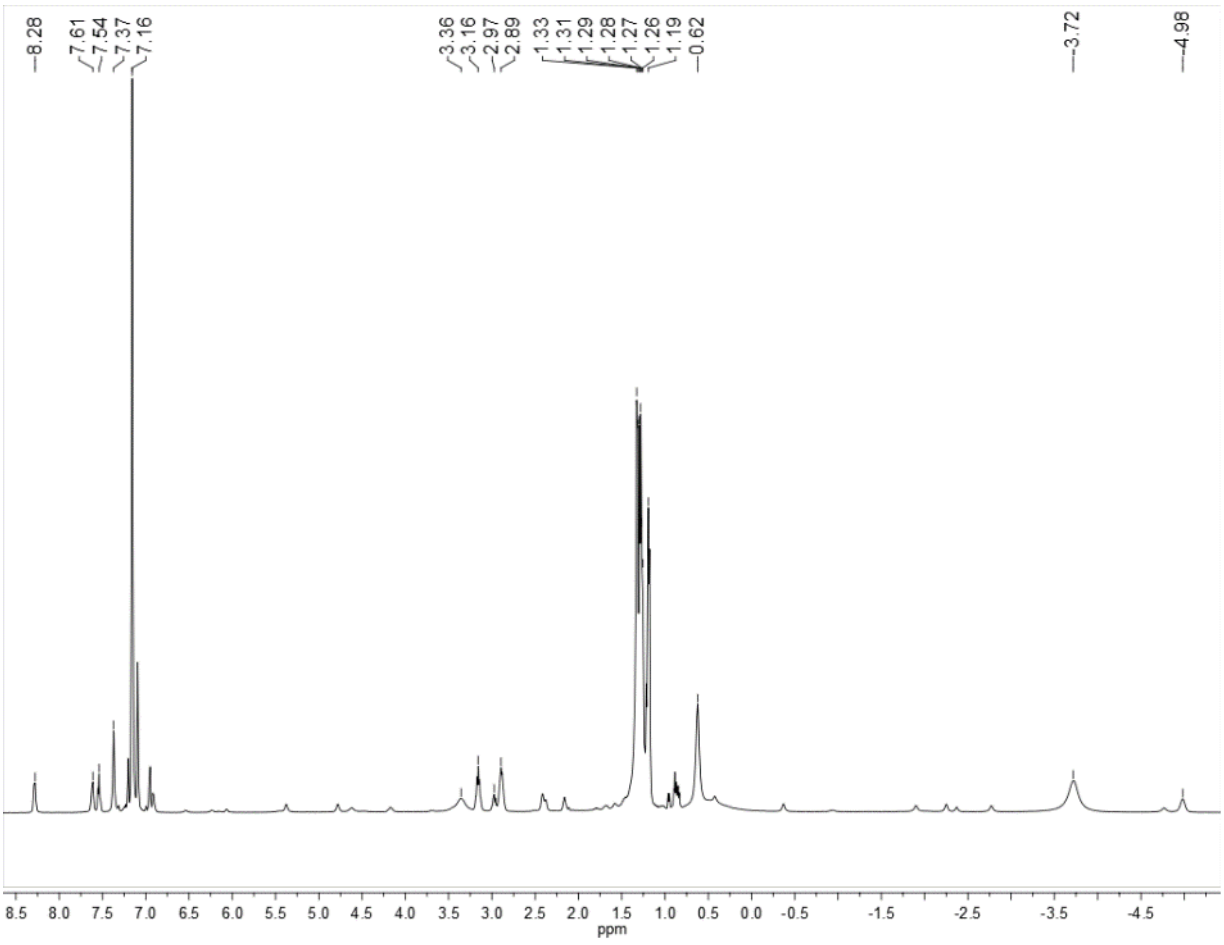


Figure S19. ^{1}H NMR spectrum (500 MHz, 298K, benzene-D_6) of the crude residue of the reaction between **1-Nd** and KC_8. Signals at 8.28, 7.61, 7.54, 7.37, 3.36, 2.97, 2.89, 1.30-1.20, 0.63, -3.72, and -4.98 are indicative of the formation of **2-Nd**. The signal at 7.16 ppm is due to residual benzene in the deuterated solvent. .

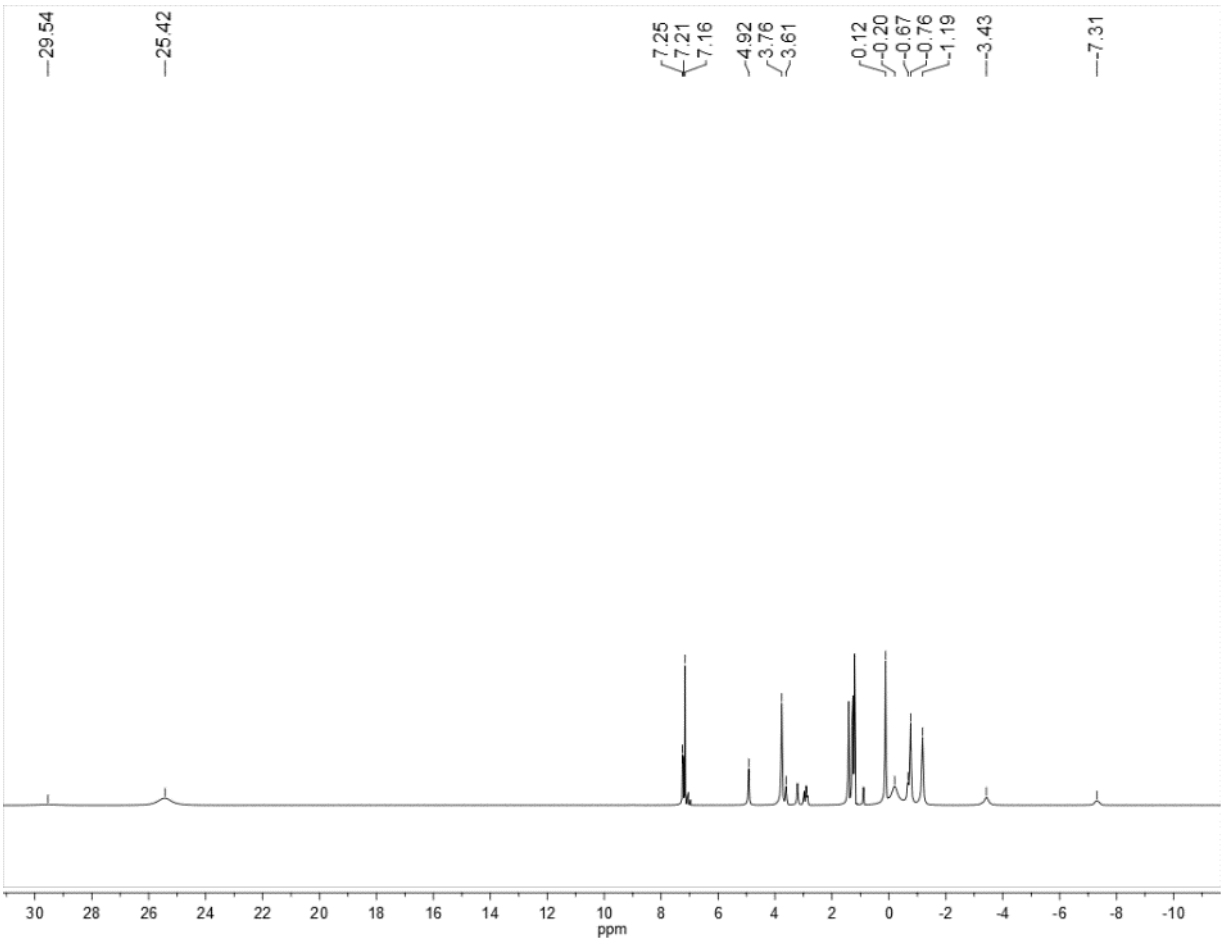


Figure S20. ^{1}H NMR spectrum (600 MHz, 298K) of **2-Sm** in benzene-D_6. The signal at 7.16 ppm is due to residual benzene in the deuterated solvent. The unmarked signals from ca. 1 – 3 ppm are due to an impurity of $KSAr^{iPr6}$.

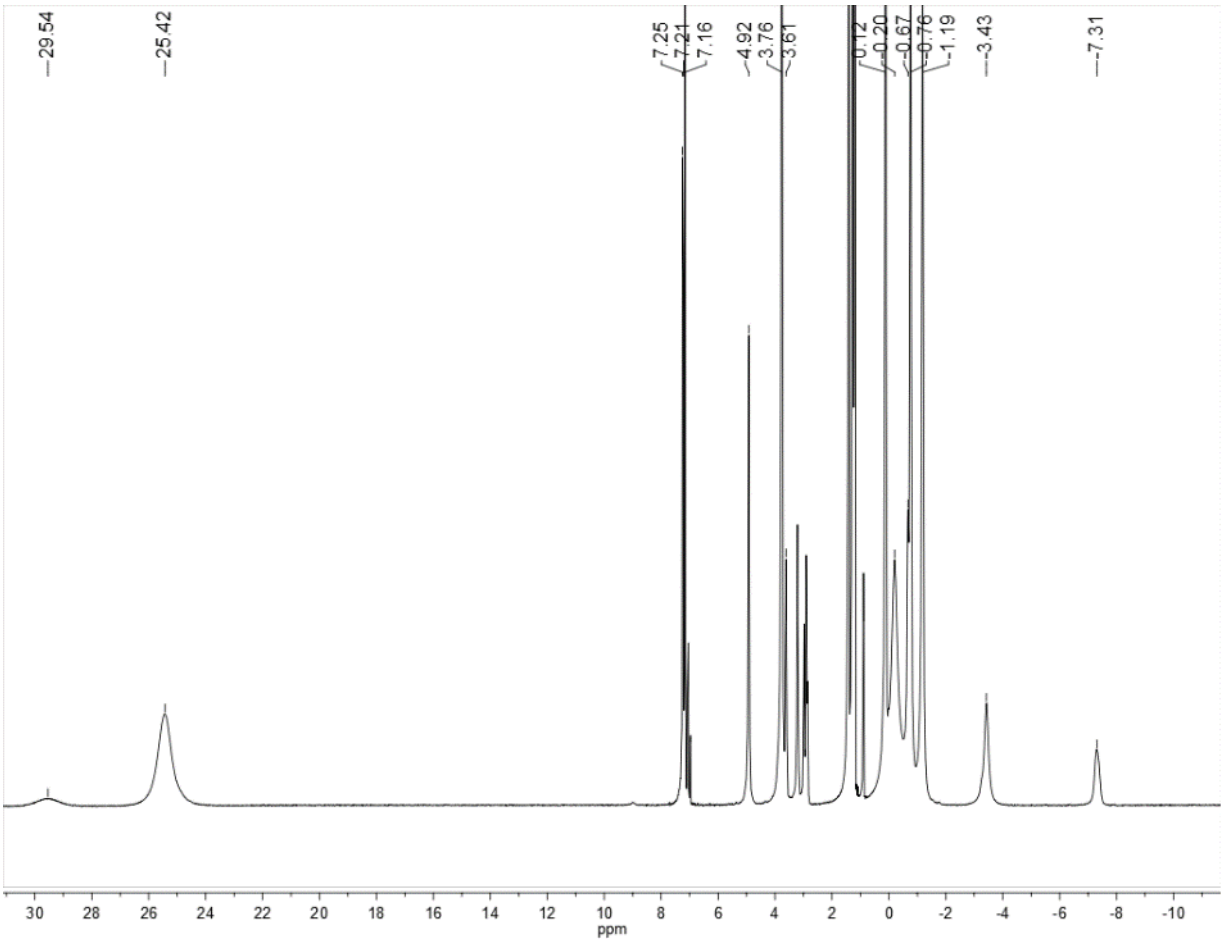


Figure S21. Magnified ^{1}H NMR spectrum (600 MHz, 298K) of **2-Sm** in benzene-D_6.

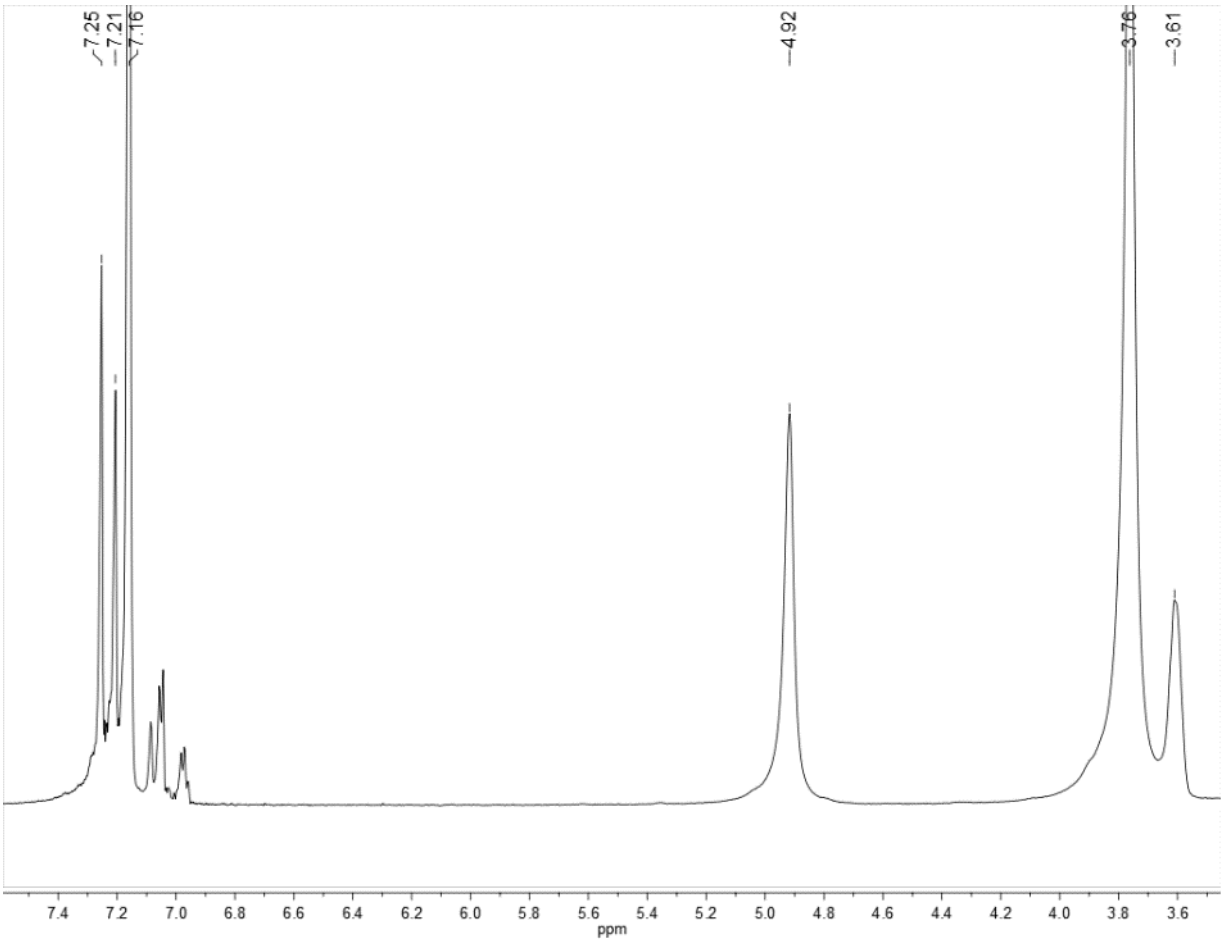


Figure S22. Magnified ^{1}H NMR spectrum (600 MHz, 298K, 7.5 – 3.5 ppm) of **2-Sm** in benzene-D_6.

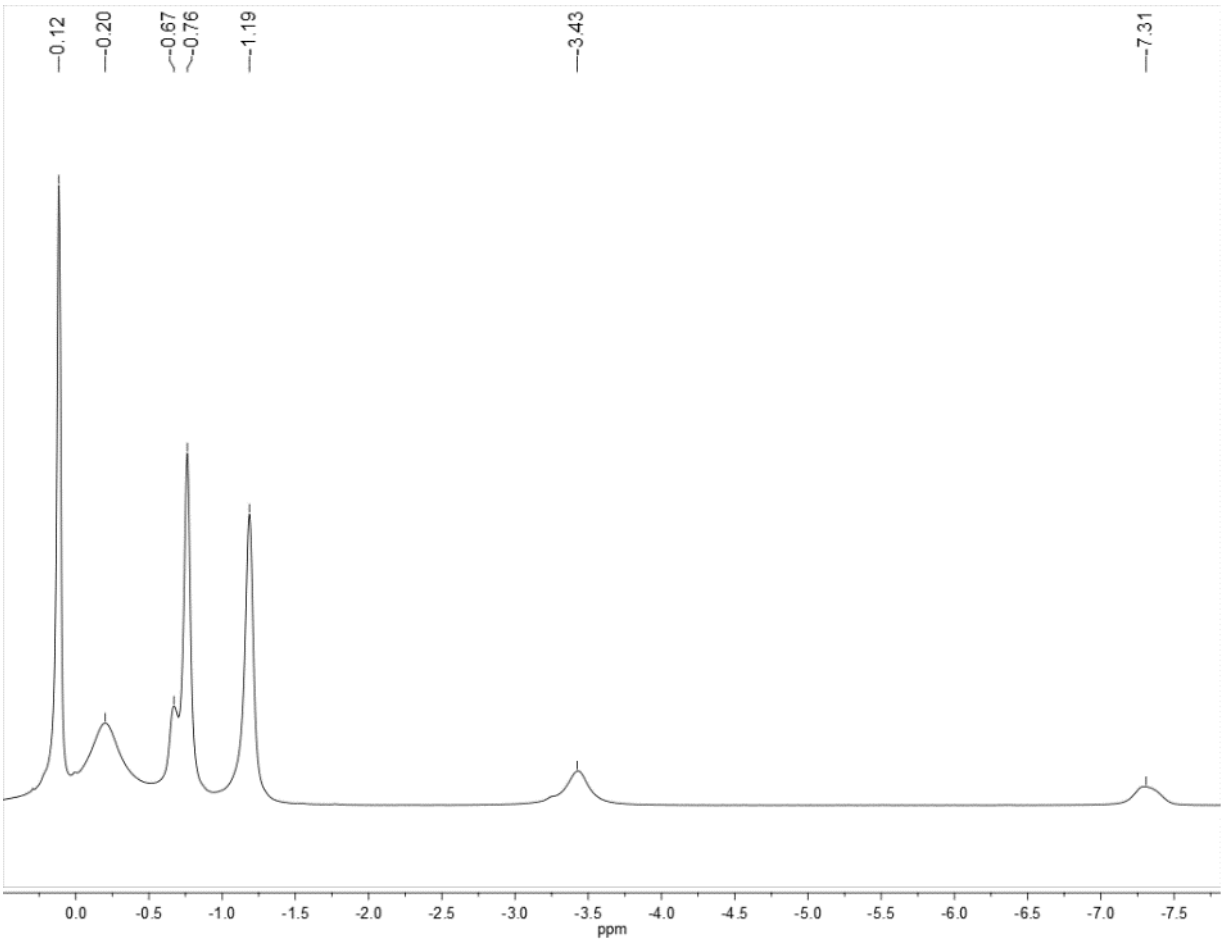


Figure S23. Magnified ^{1}H NMR spectrum (600 MHz, 298K, 0.75 – -8 ppm) of **2-Sm** in benzene-D_6.

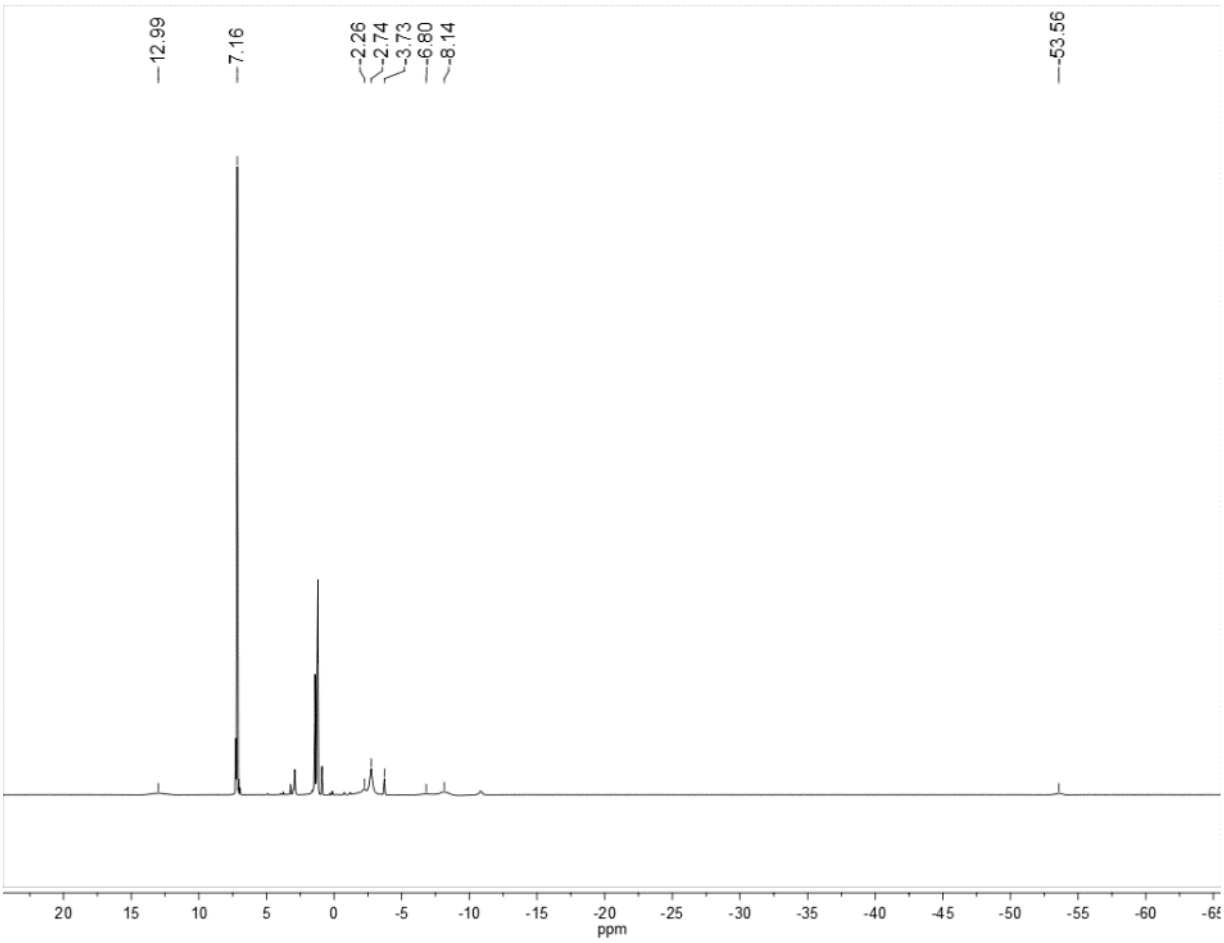


Figure S24. ^{1}H NMR spectrum (600 MHz, 298K) of **2-Tm** in benzene-D_6. The signal at 7.16 ppm is due to residual benzene in the deuterated solvent. Minor, unbroadened and unshifted signals from 0 ppm to 7.16 ppm are due to minor impurities (hexane, residual protonated ligand).

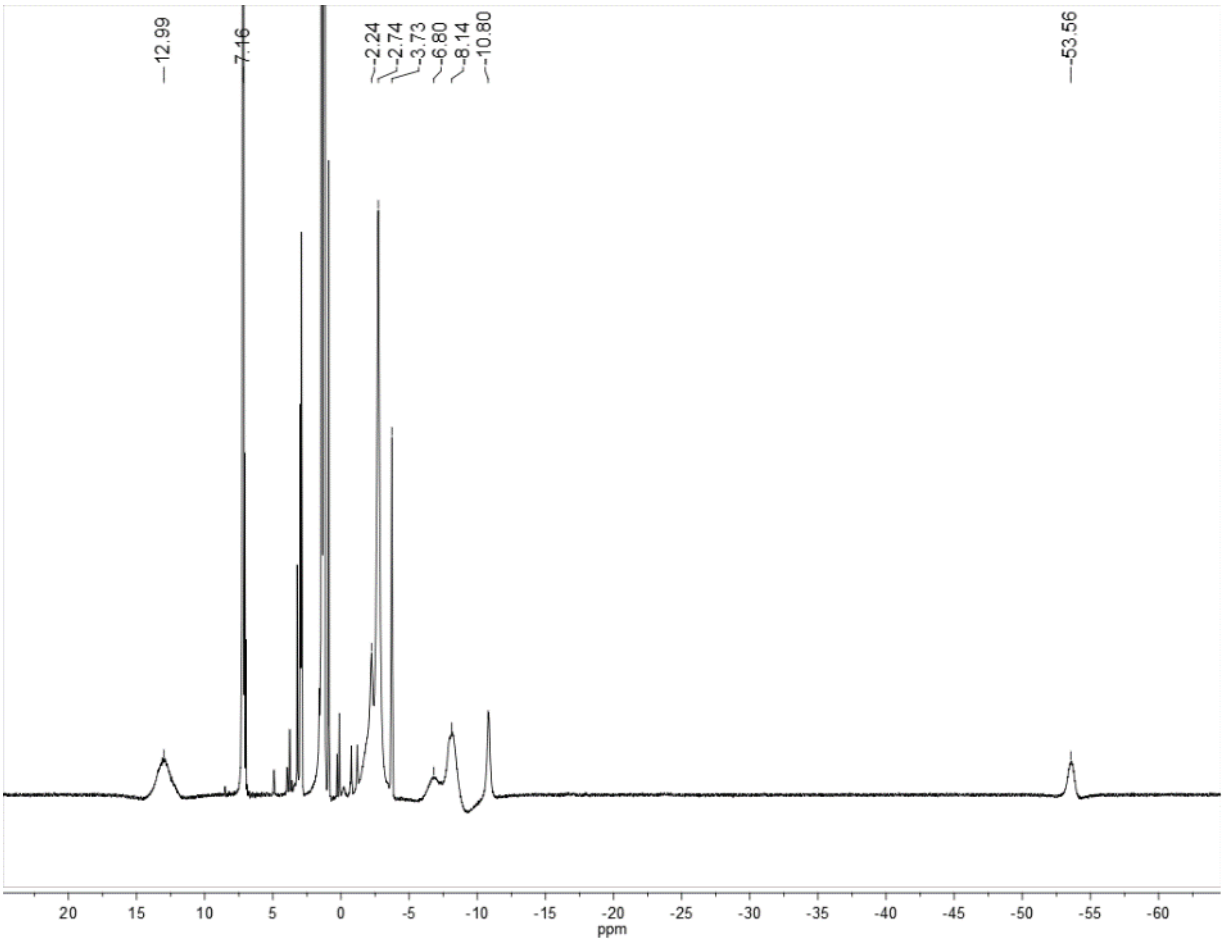


Figure S25. Magnified ^{1}H NMR spectrum (600 MHz, 298K) of Tm(SAr^{iPr6})$_2$, **2-Tm**, in benzene-D_6.

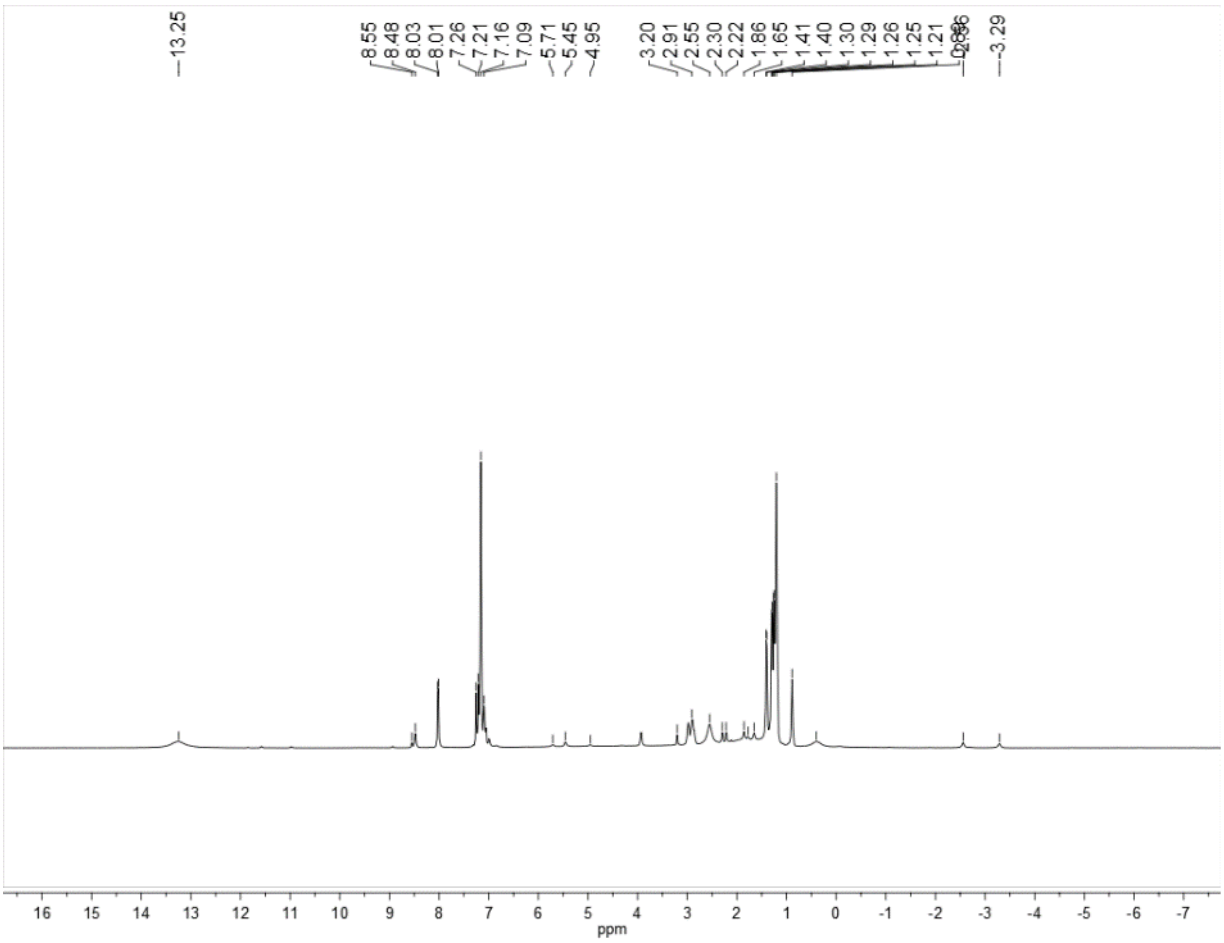


Figure S26. ^{1}H NMR spectrum (500 MHz, 298K) of Nd(SAr^{iPr6})$_2$(N_2Ph_2), **3-Nd,** in benzene-D_6.

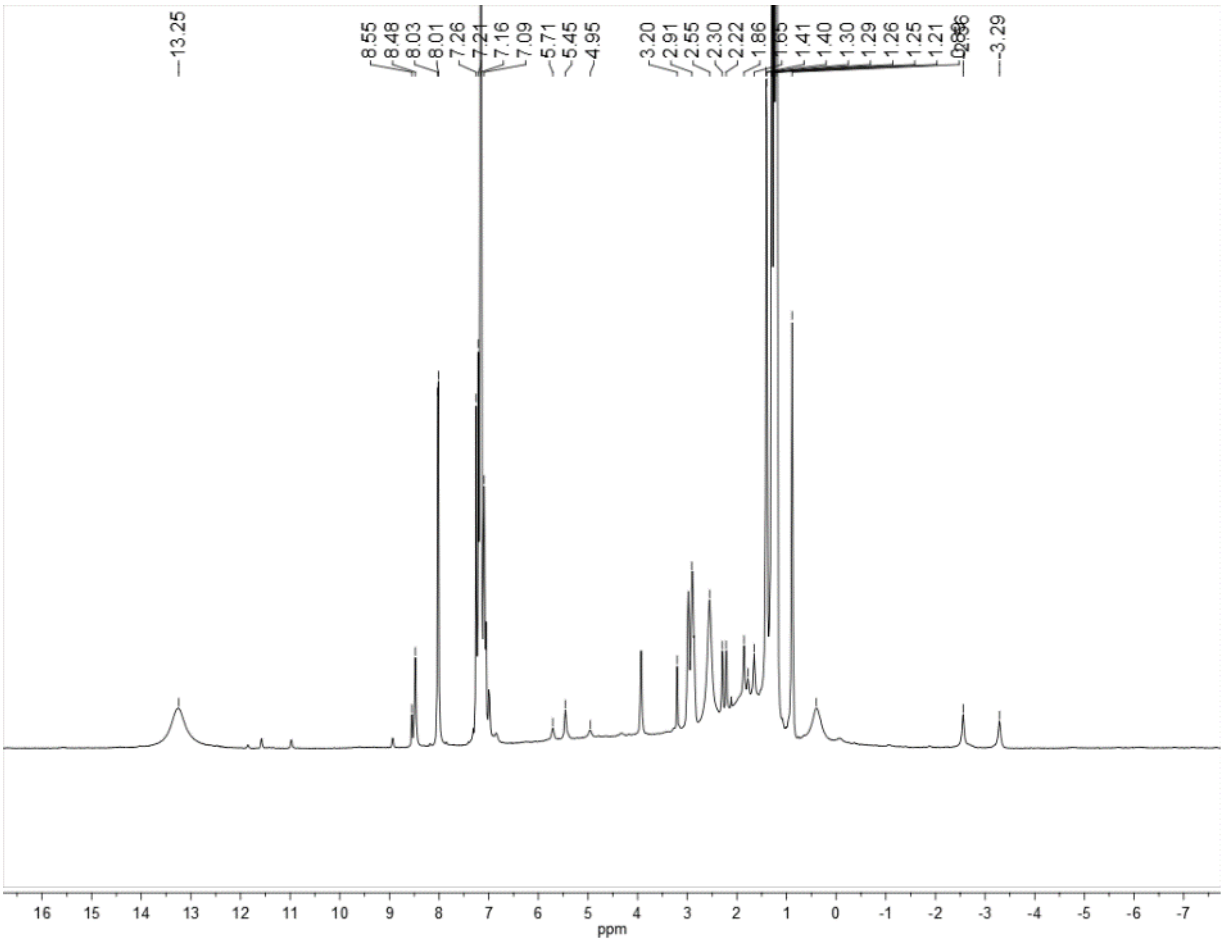


Figure S27. Magnified ^{1}H NMR spectrum (500 MHz, 298K) of Nd(SAr^{iPr6})$_2$(N_2Ph_2), **3-Nd,** in benzene-D_6.

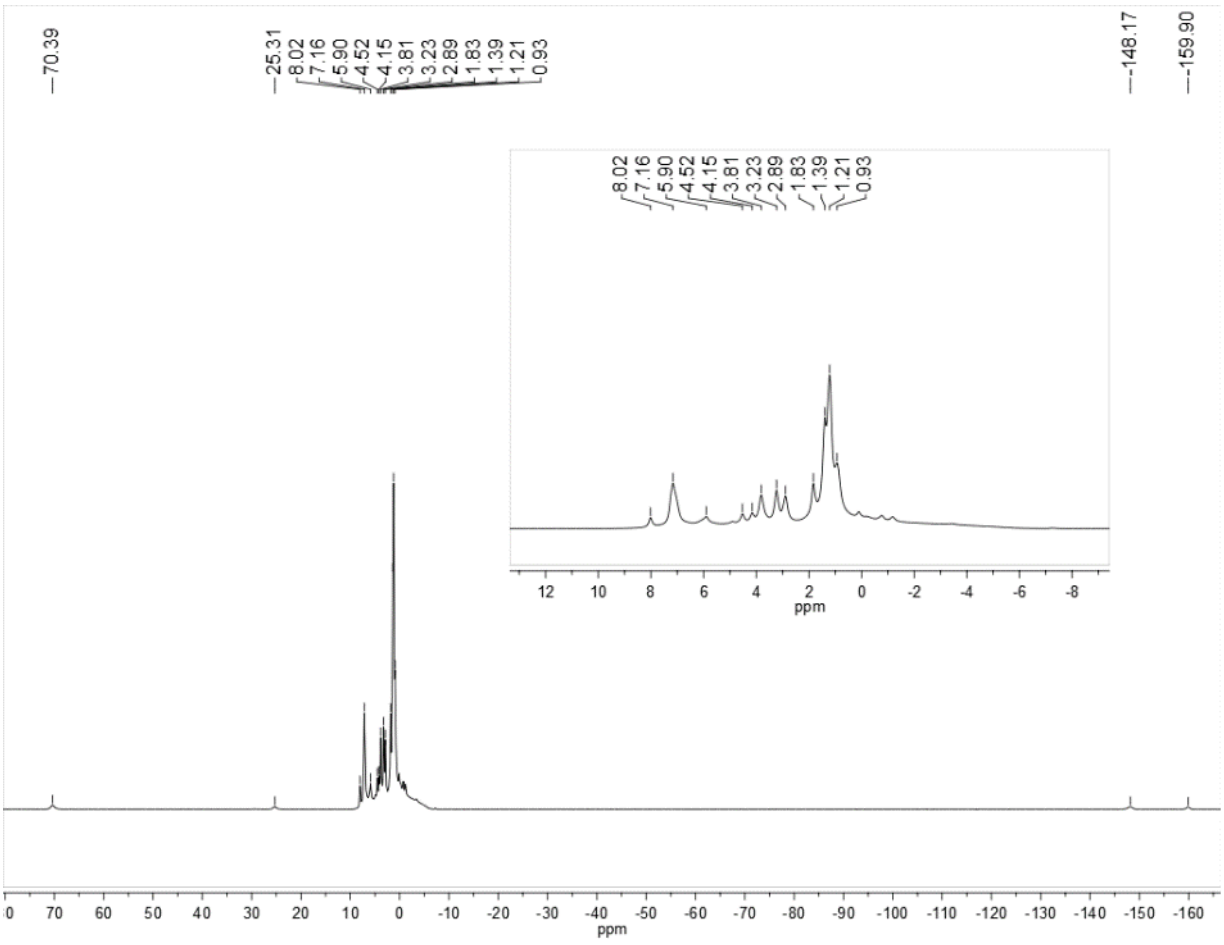


Figure S28. ^{1}H NMR spectrum (500 MHz, 298K) of Sm(SAr^{iPr6})$_2$(N_2Ph_2), **3-Sm,** in benzene-D_6. Inset: magnification of the region between ca. 12 ppm and -8 ppm.

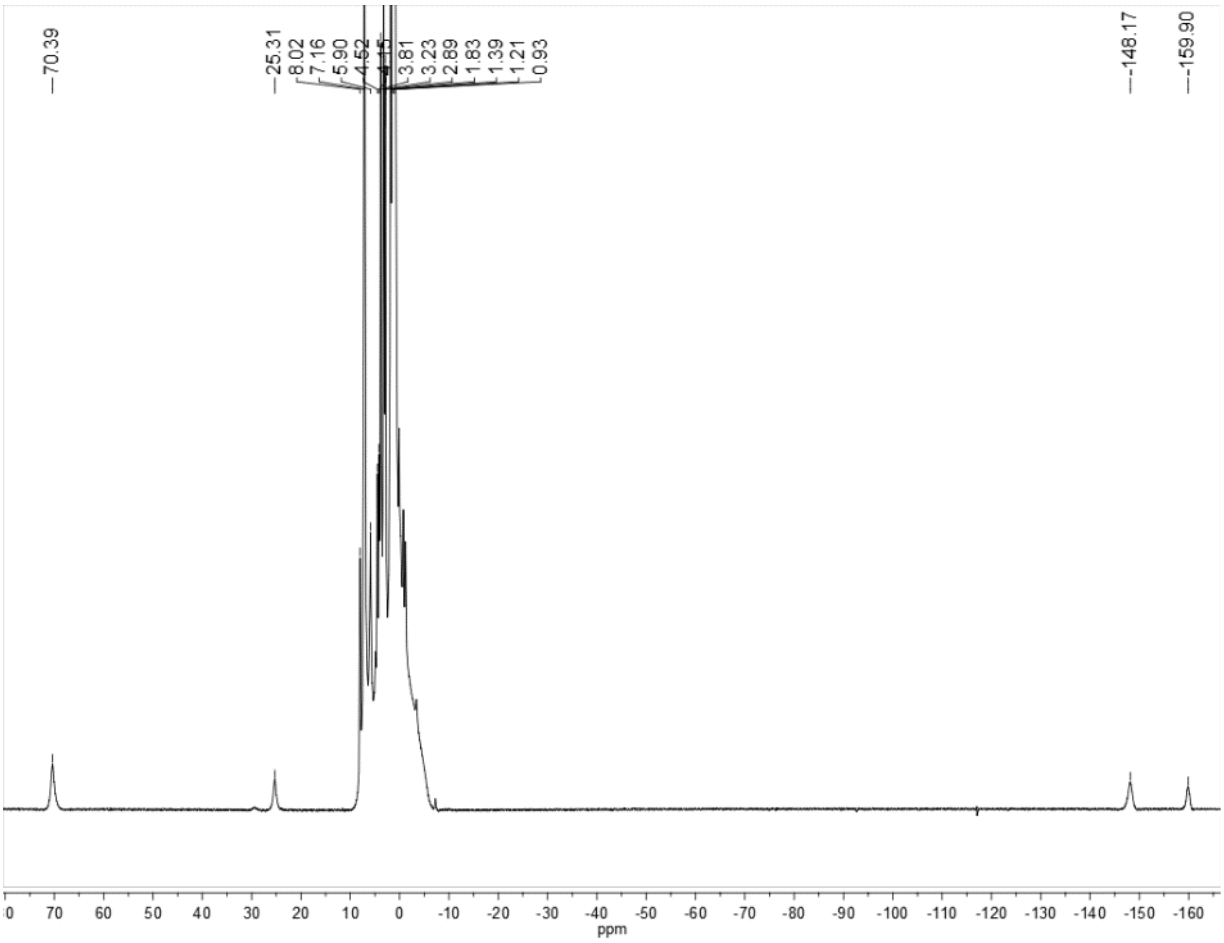


Figure S29. Magnified ^{1}H NMR spectrum (500 MHz, 298K) of $Sm(SAr^{iPr6})_2(N_2Ph_2)$, **3-Sm,** in benzene-$D_6$.

4. Electronic Spectra

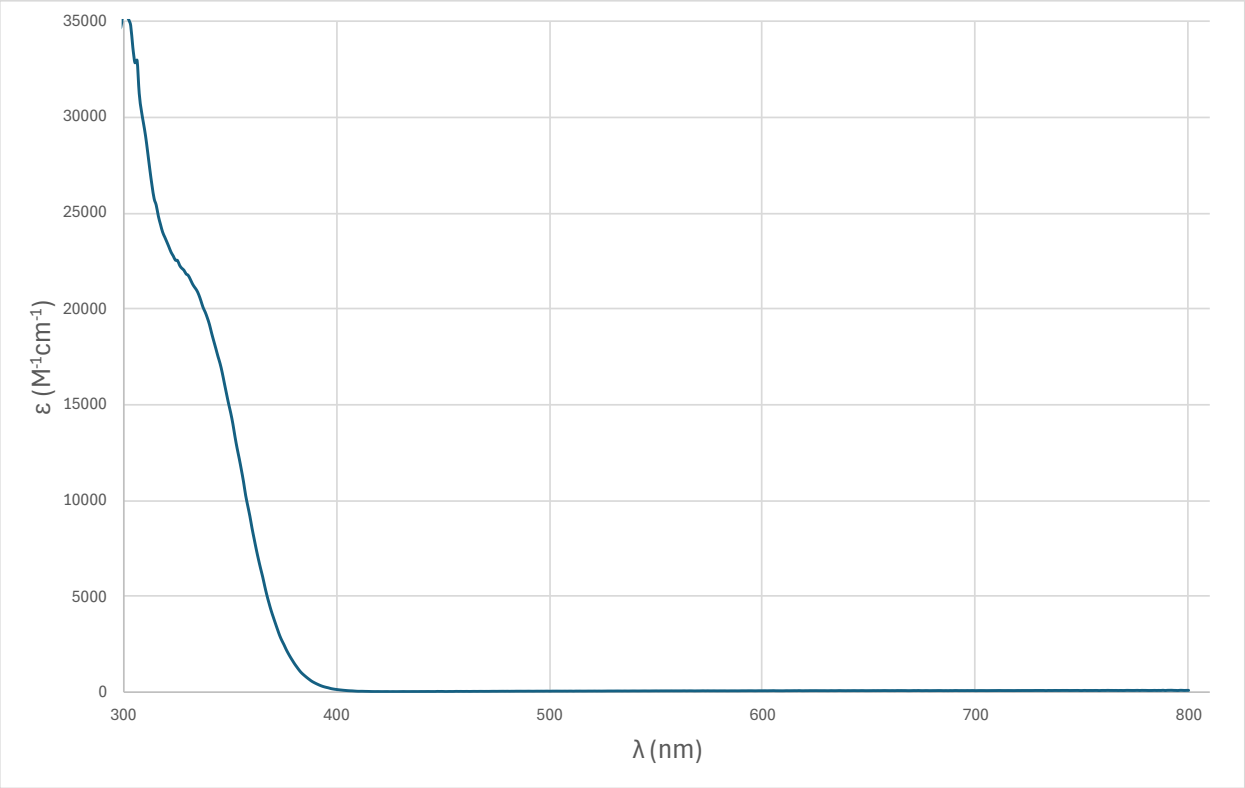


Figure S30. UV-vis spectrum of La(SAr^{iPr6})$_2$I, **1-La** (0.97 mM, toluene, 1 mm path length).

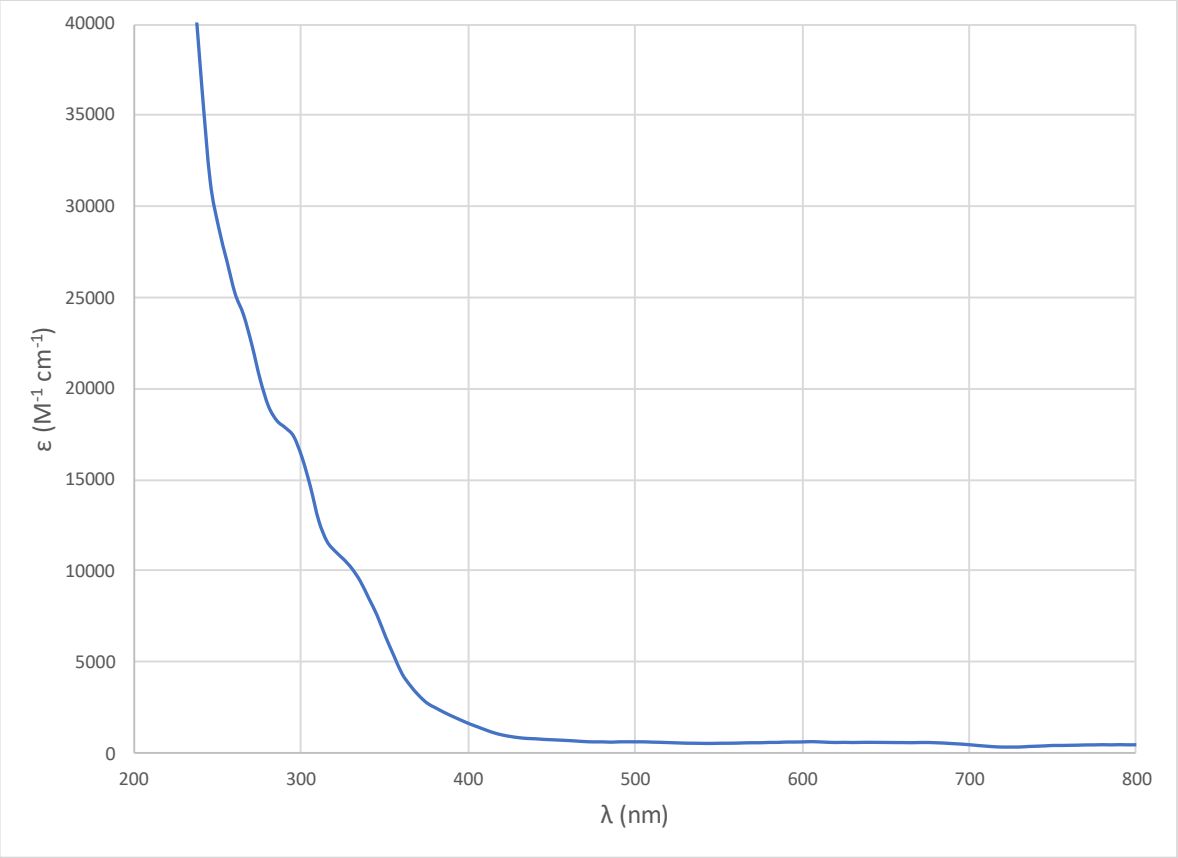


Figure S31. UV-vis spectrum of Nd(SAr^{iPr6})$_2$I, **1-Nd** (0.8 mM in hexane, 0.1 cm path length).

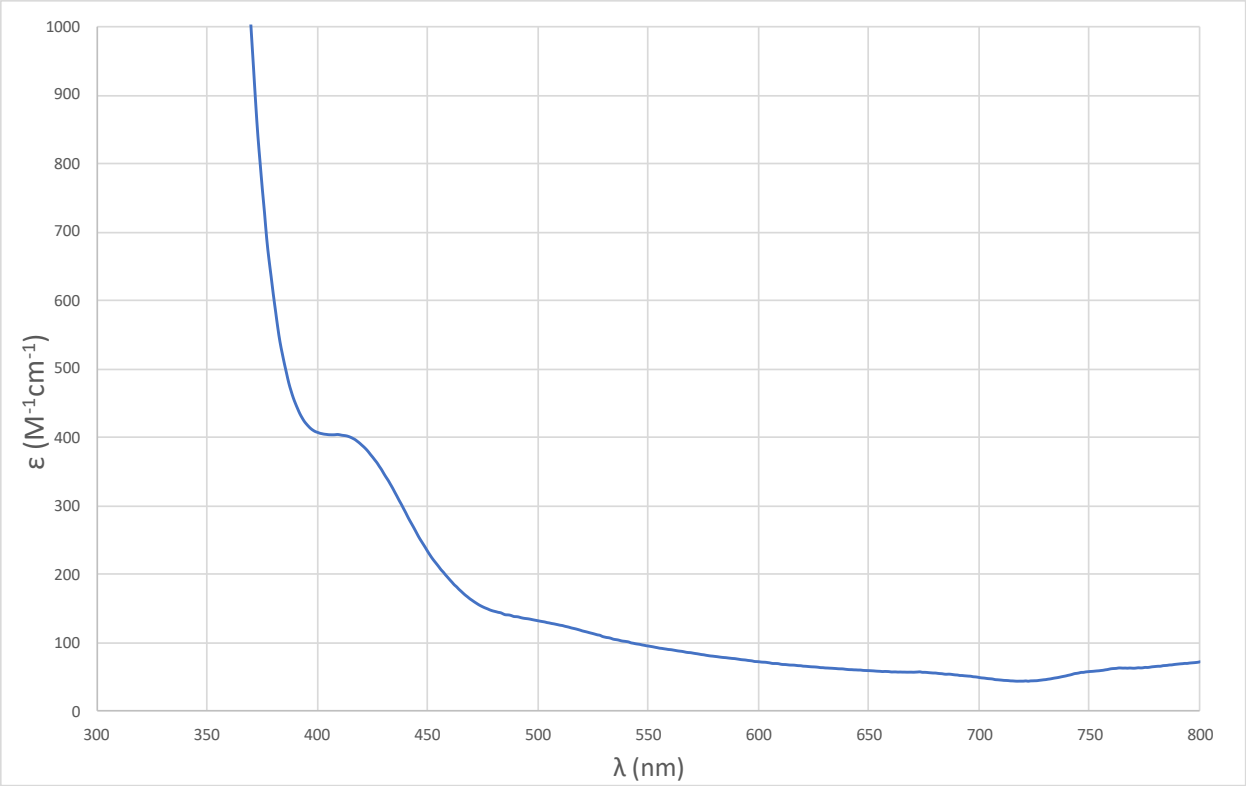


Figure S32. UV-vis spectrum of La(SAr^{iPr6})$_2$, **2-La** (1.2 mM, THF, 1 cm path length).

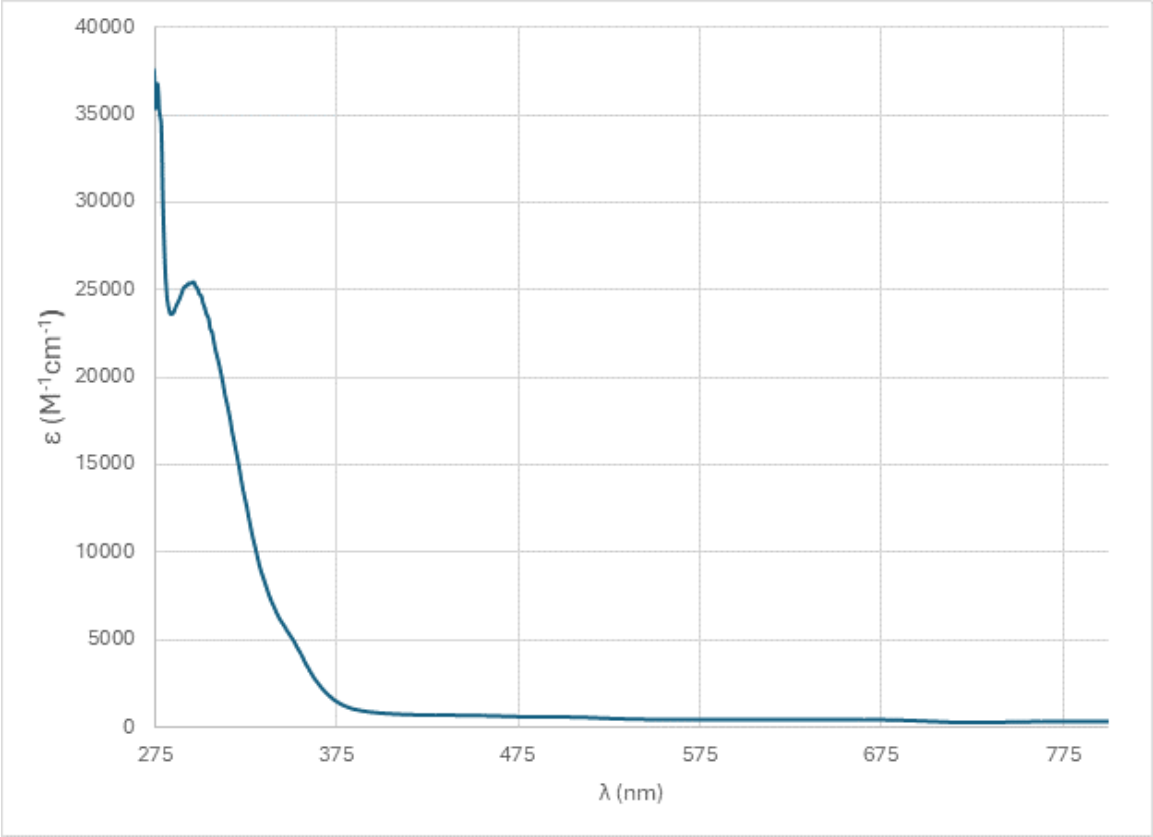


Figure S33. UV-Vis spectrum of La(SAr^{iPr6})$_2$I, **1-La** treated with 2.2.2-cryptand and KC_8. (1.1 mM, toluene, 1 mm path length).

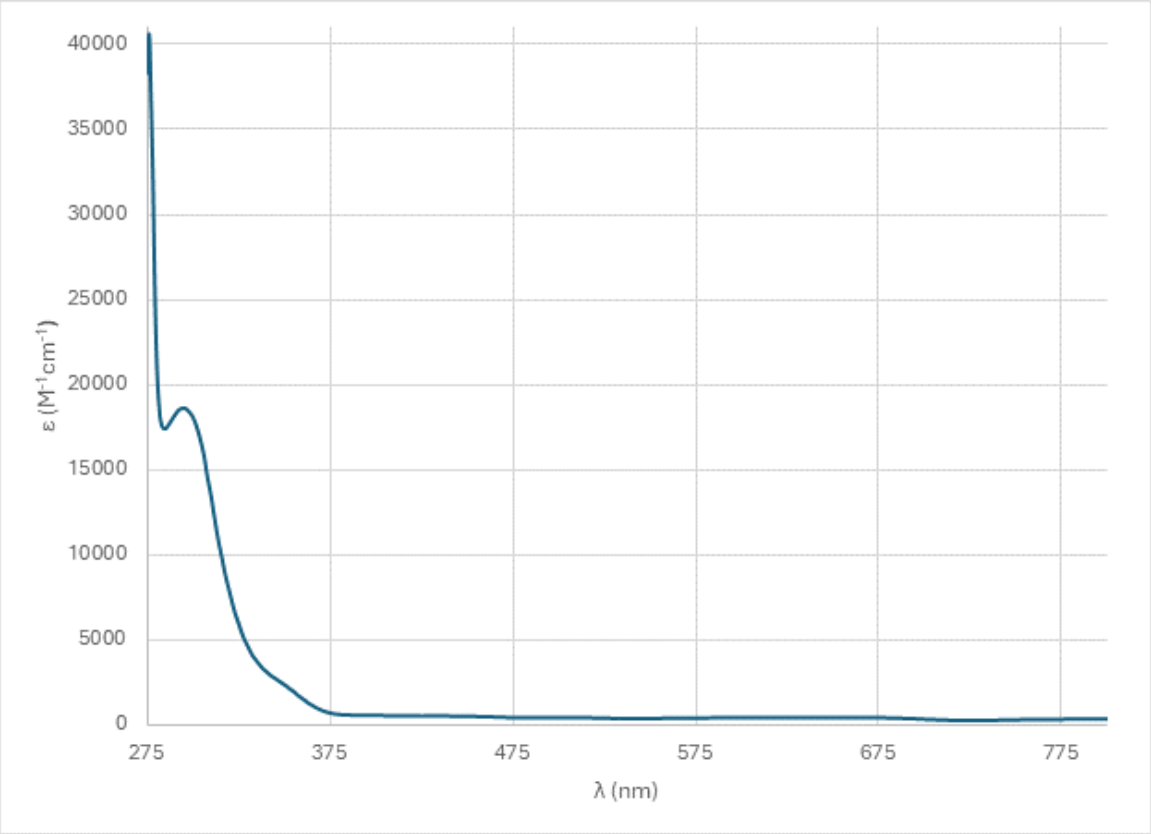


Figure S34. UV-Vis spectrum of La(SAr^{iPr6})$_2$I, **1-La** treated with 18-crown-6 and KC_8 (1.2 mM, toluene, 1 mm path length).

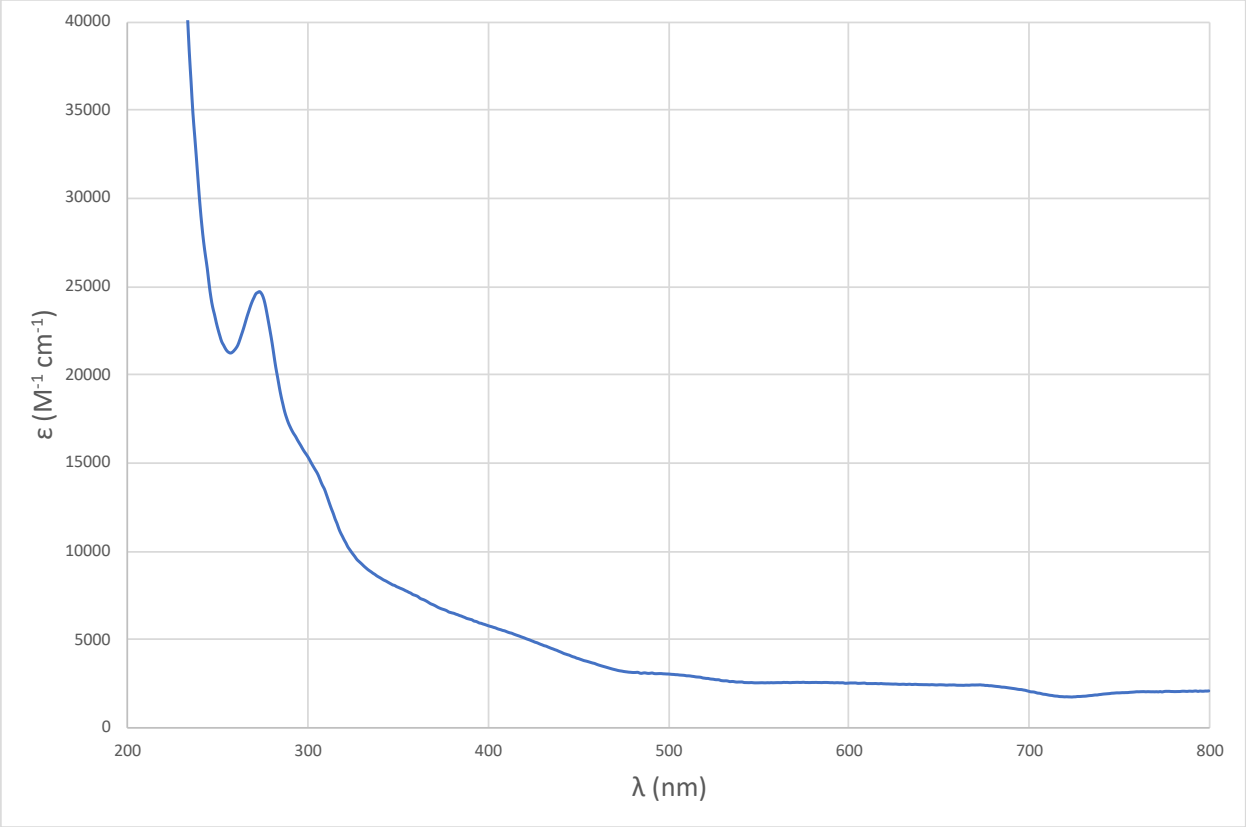


Figure S35. UV-vis spectrum of Nd(SAr^{iPr6})$_2$, **2-Nd** (0.3 mM in hexane, 0.1 cm path length).

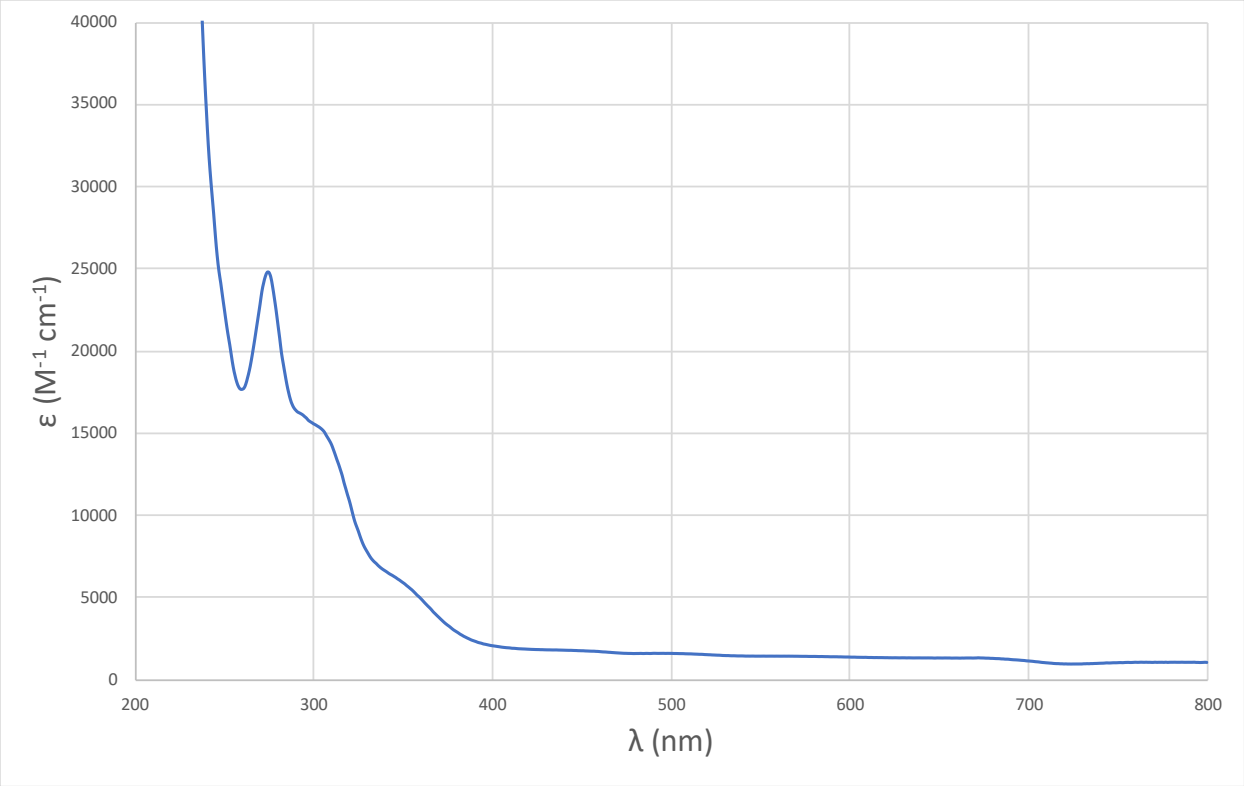


Figure S36. UV-vis spectrum of $Sm(SAr^{iPr6})_2$, **2-Sm** (0.5 mM in hexane, 0.1 cm path length).

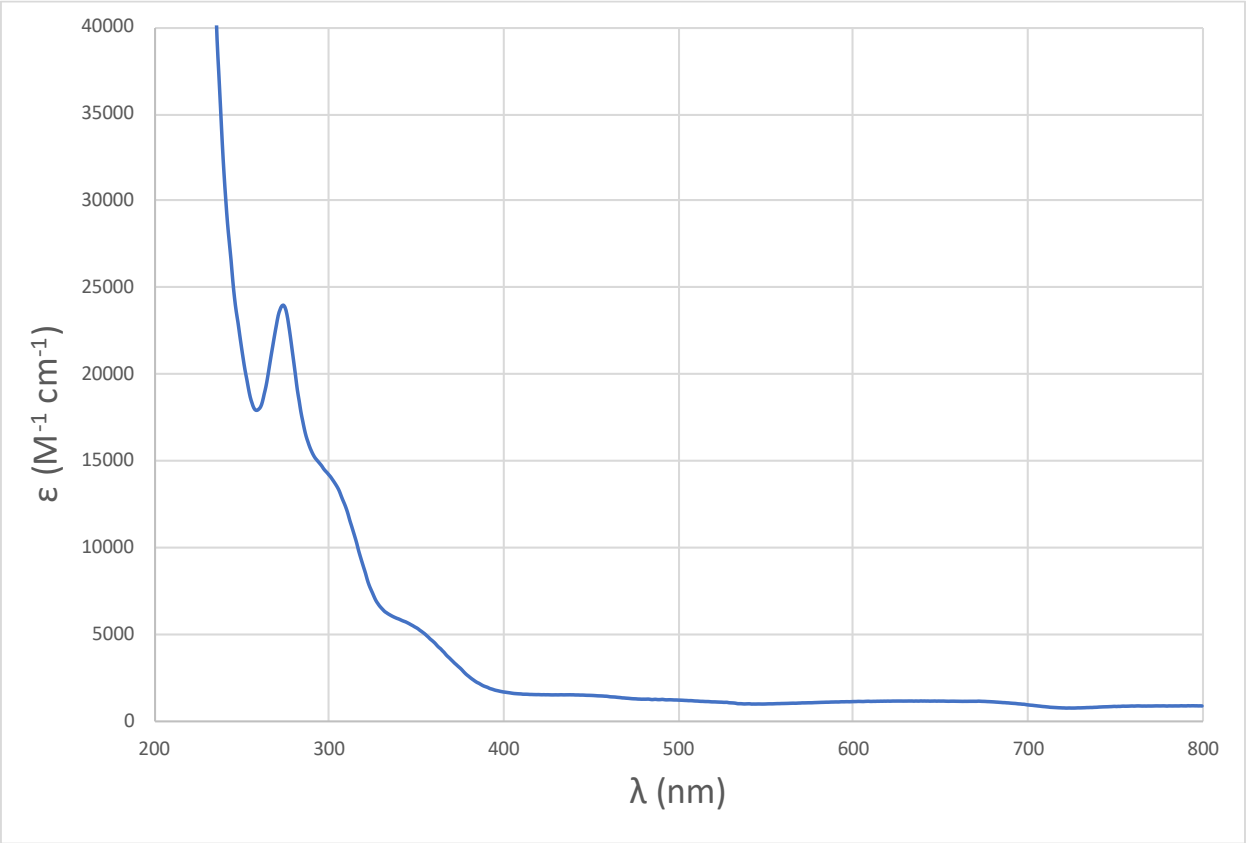


Figure S37. UV-vis spectrum of Tm(SAr^{iPr6})$_2$, **2-Tm** (0.6 mM in hexane, 0.1 cm path length).

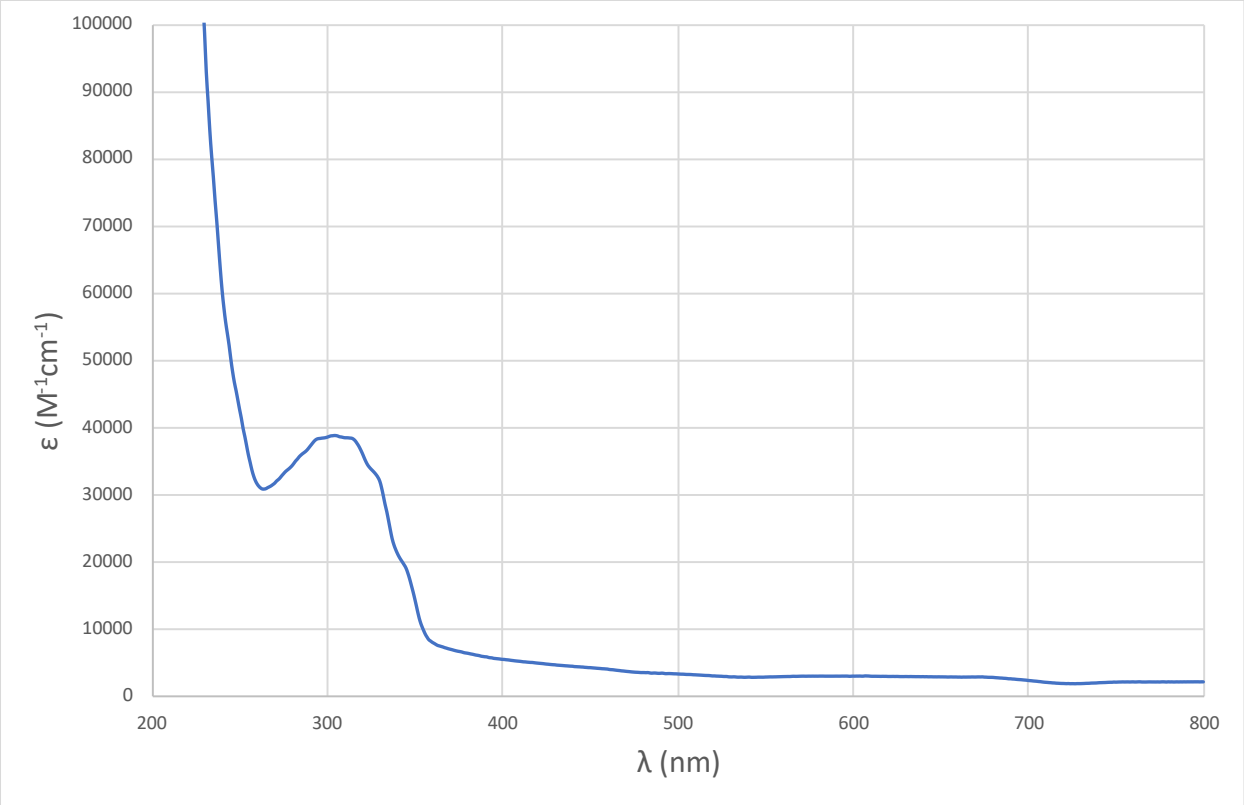


Figure S38. UV-vis spectrum of $Nd(SAr^{iPr6})_2(N_2Ph_2)$, **3-Nd** (0.25 mM in hexane, 0.1 cm path length).

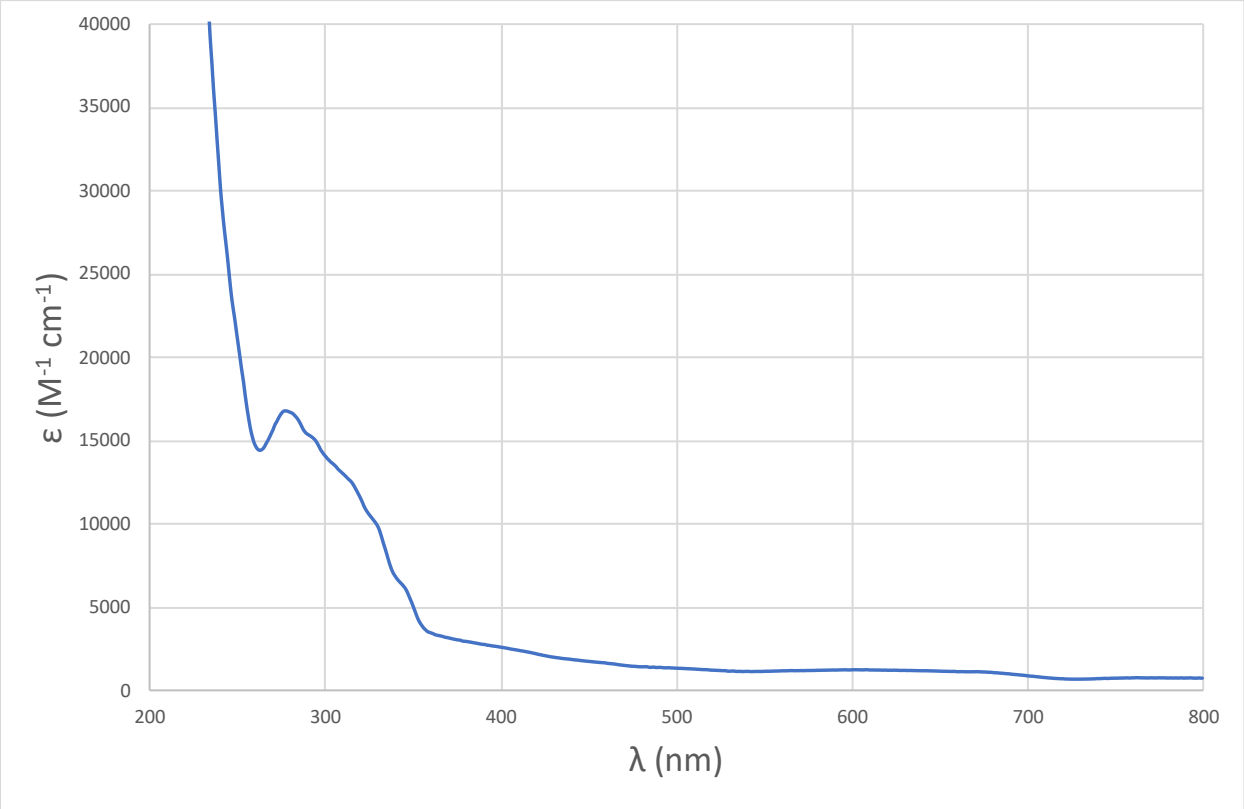


Figure S39. UV-vis spectrum of Sm(SAr^{iPr6})$_2$(PhNNPh), **3-Sm** (0.6 mM in hexane, 0.1 cm path length).

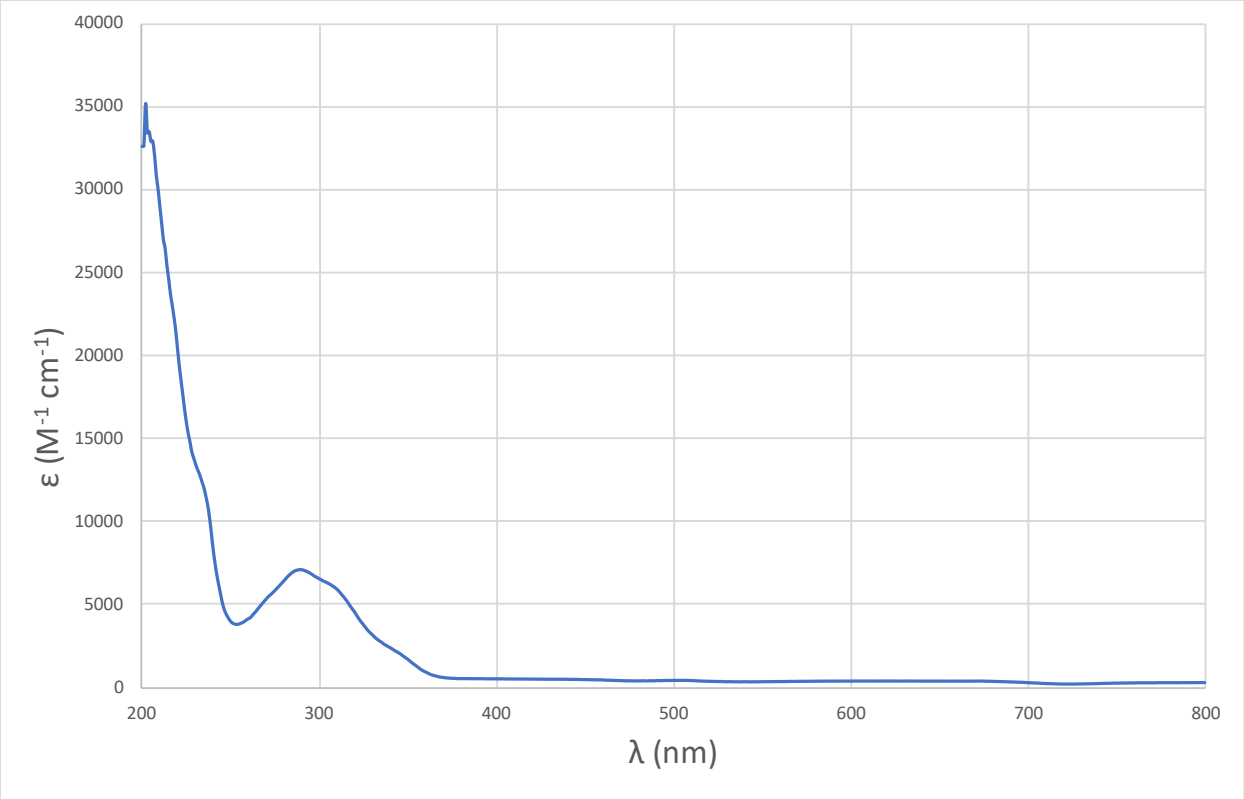


Figure S40. UV-vis spectrum of K(SAr^{iPr6}) (1.1 mM in hexane, 0.1 cm path length).

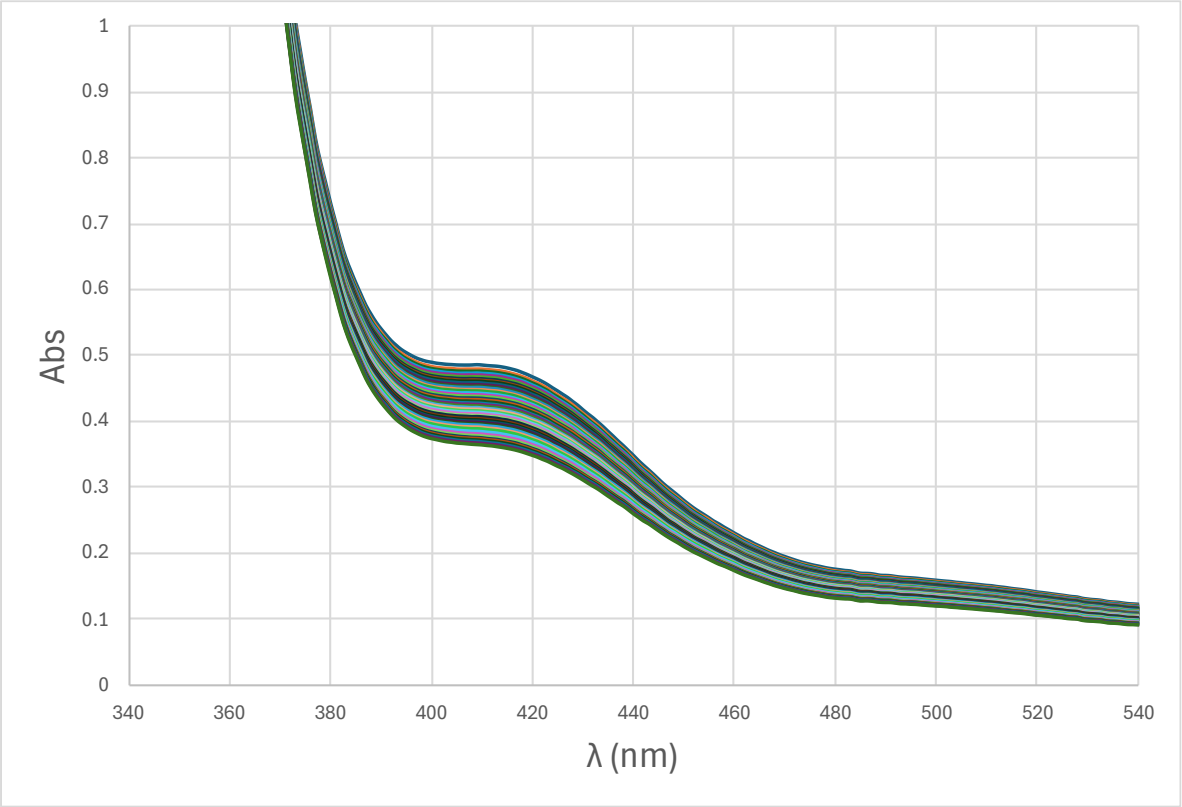


Figure S41. UV-vis spectrum of La(SAr^{iPr6})$_2$, **2-La**, (1.2 mM in hexane, 0.1 cm path length, ambient temperature). Spectra were recorded every 30 minutes for24 hours. The absorbance at 409 nm at t = 0 h is 0.49 and the absorbance at the same wavelength at t = 24 h is 0.36, which indicates that **2-La** has decomposed by ca. 26% during the period of this study.

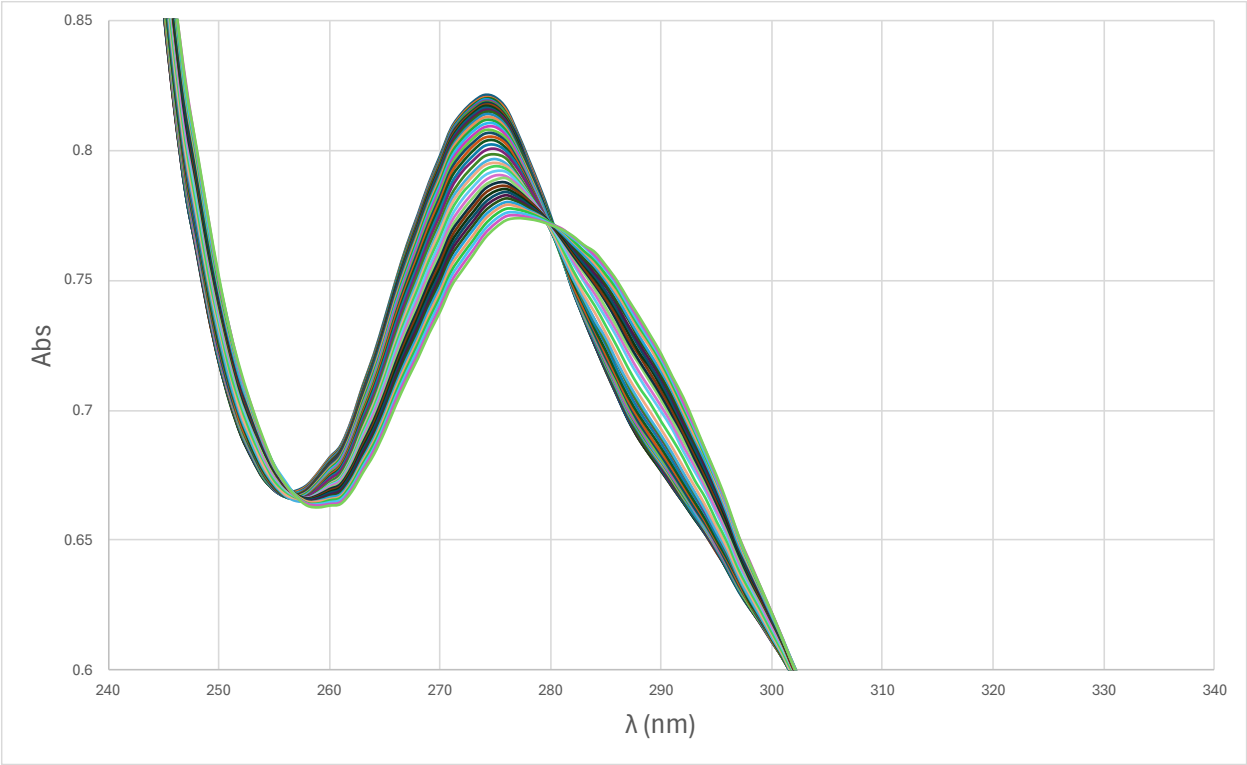


Figure S42. UV-vis spectrum of Nd(SAr^{iPr6})$_2$, **2-Nd**, (0.9 mM in hexane, 0.1 cm path length, ambient temperature). Spectra were recorded every hour for36 hours. The absorbance at 274 nm at t = 0 h is 0.82 and the absorbance at the same wavelength at t = 36 h is 0.78, which indicates that **2-Nd** has decomposed by ca. 5% during the period of this study.

5. EPR Data

Table S1. EPR Spectral Data of **2-La** and selected La(II) complexes.

Complex	Hyperfine Coupling (MHz)	Hyperfine Coupling (Gauss)	g
$La(SAr^{iPr6})_2$, **2-Ln**	67.3	24.2	1.99
"[K(crypt)][$La(SAr^{iPr6})_2I$]"	67.3	24.2	1.99
"[K(18-c-6)][$La(S\ Ar^{iPr6})_2I$]"	66.9	24.0	1.99
$[La\{OC_6H_2\text{-}2,6\text{-}(1\text{-}Ad)_2\text{-}4\text{-}tBu\}_3]^{1-}$ [8]	1840.0	657.3	2.00
$[La\{C_5H_4(SiMe_3)\}_3]^{1-}$ [9]	430.4	154	1.994
$[La\{C_5H_3\text{-}1,3\text{-}(SiMe_3)_2\}_3]^{1-}$ [10]	371.8	133.5	1.99
$[La(C_5H\text{-}1,2,3,4\text{-}Me_4)_3]^{1-}$ [11]	802.4	291	1.97
$[La\{C_5H_4(tBu)\}_3]^{1-}$ [12]	550.1 565.1	$A_{\|}$ = 197 $A_{\perp}$ = 208	$g_{\|}$ 1.995 $g_{\perp}$ = 1.941
$[La\{C_5H_4(Me)\}_3]^{1-}$ [13]	537.9	195	1.971
$[La\{C_5H_4{}^tBu_2\}_3]^{1-}$ [14]	A_z = 630.7 A_{xy} = 648.8	A_z = 233 A_{xy} = 232	g_z = 1.934 g_{xy} = 1.998

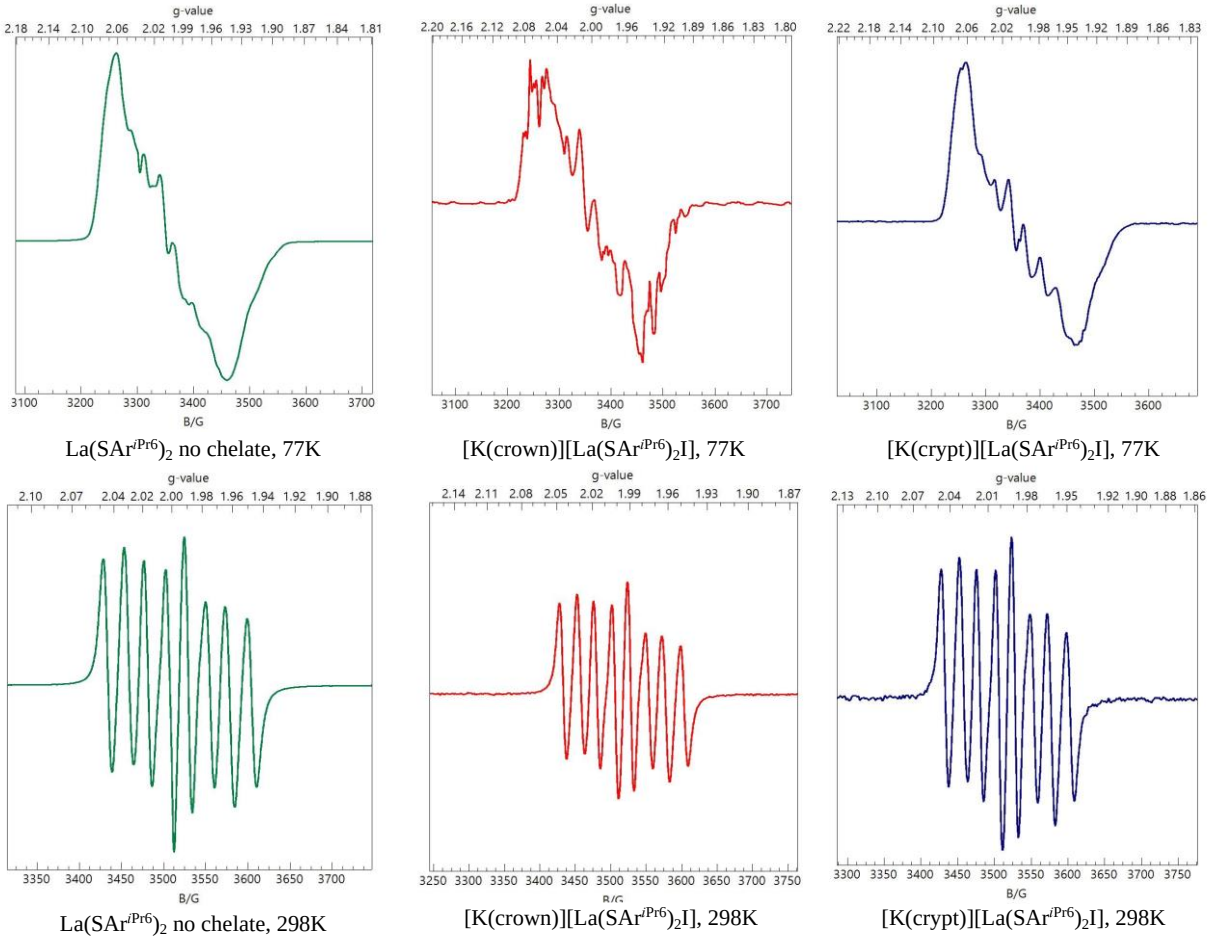


Figure S43. EPR spectra at 77K (top row) and 298 K (bottom row) of the products formed by reduction of **1-La** at −35 °C in THF with 1.1 equiv KC_8 with and without (**2-La**) chelates.

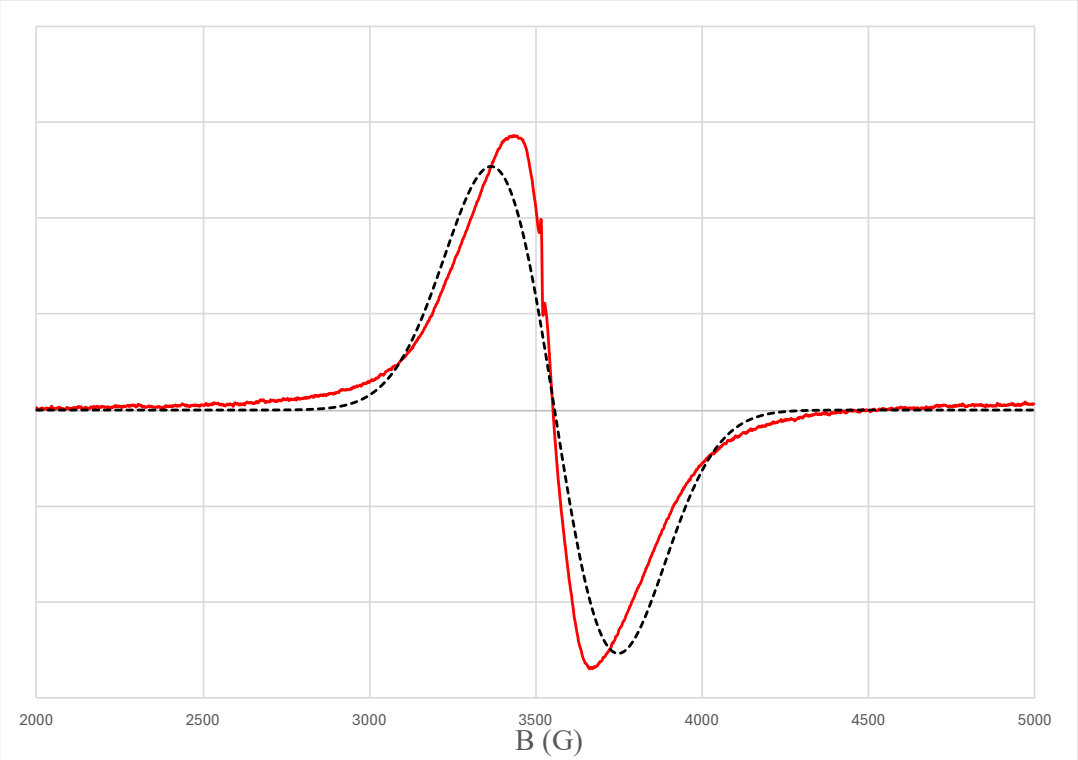


Figure S44. Experimental solid state EPR spectrum (300 K, red trace) and fitted spectrum (dashed black trace) of La(SAr^{iPr6})$_2$, **2-La**, with g = 1.98.

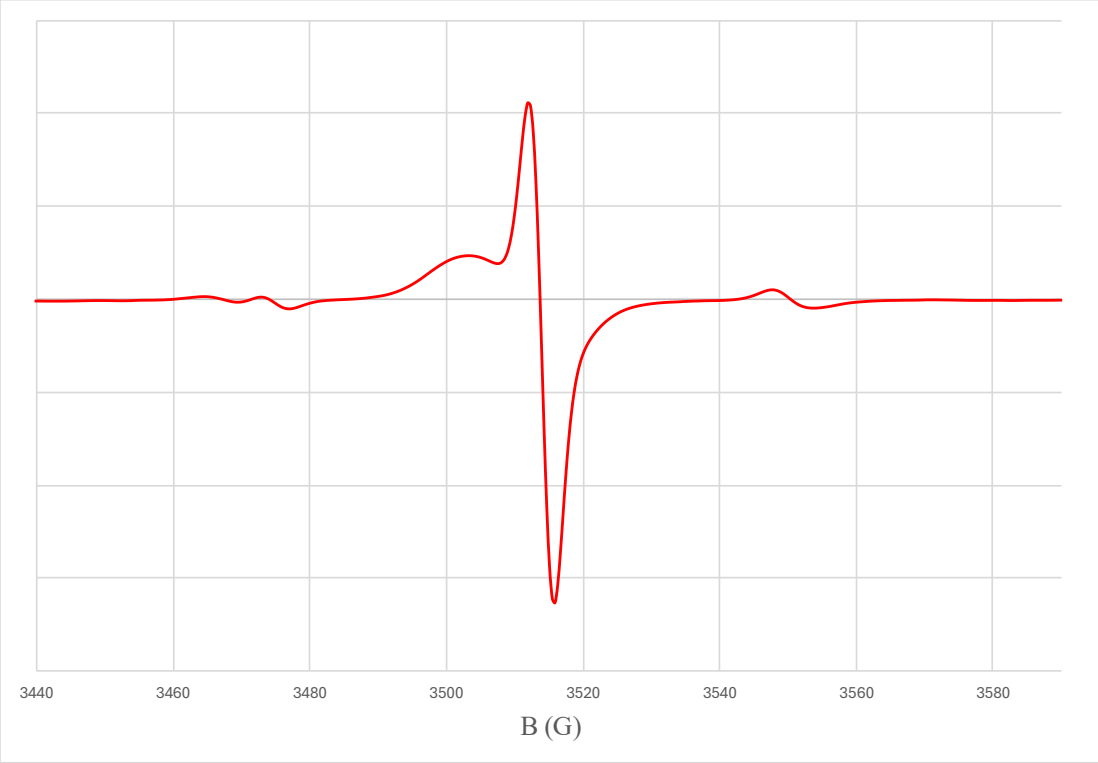


Figure S45. Experimental solid state EPR spectrum (300 K) of Nd(SAr^{iPr6})$_2$, **2-Nd**.

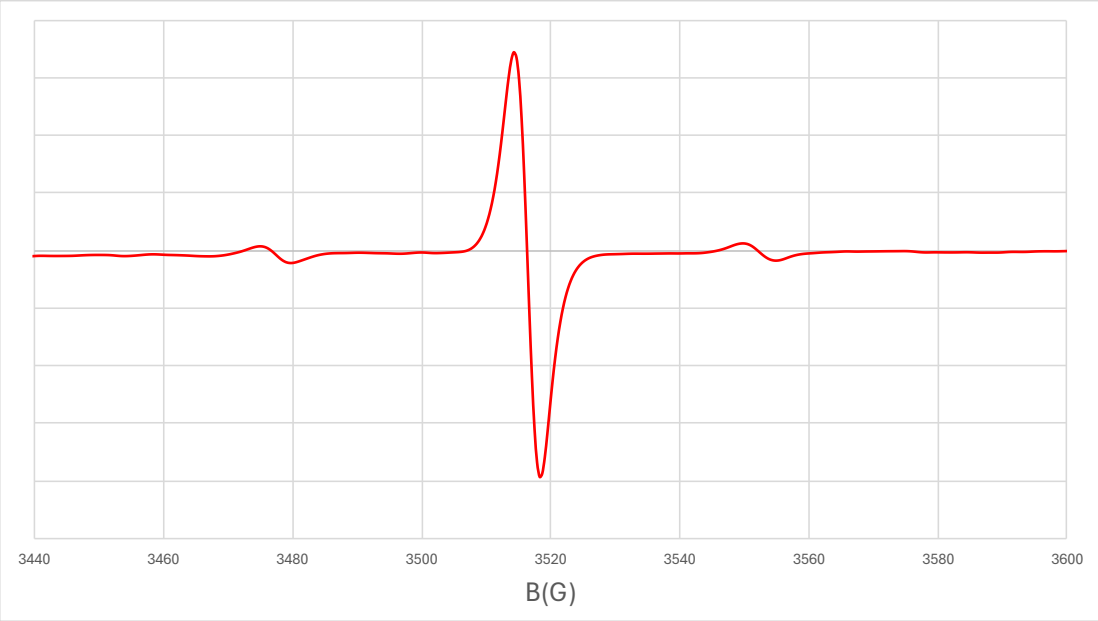


Figure S46. Experimental solution EPR spectrum (300 K, hexane) of Nd(SAr^{iPr6})$_2$, **2-Nd**.

6. Crystallographic Details

Table S2. X-ray Data Collection Parameters and Crystallographic Details of 1-La.

Empirical formula	$LaC_{72}S_2H_{98}I$
Formula weight	1293.43
Temperature/K	133.15
Crystal system	triclinic
Space group	P-1
a/Å	13.2786(13)
b/Å	14.2335(14)
c/Å	18.6780(19)
α/°	102.710(2)
β/°	94.255(2)
γ/°	99.004(2)
Volume/Å^3	3379.5(6)
Z	2
ρ_{calc}g/cm^3	1.271
μ/mm^{-1}	1.189
F(000)	1344.0
Crystal size/mm^3	0.187 × 0.163 × 0.092
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.98 to 61.242
Index ranges	$-18 \leq h \leq 18$, $-20 \leq k \leq 19$, $-26 \leq l \leq 26$
Reflections collected	72180
Independent reflections	19933 [R_{int} = 0.1107, R_{sigma} = 0.1327]
Data/restraints/parameters	19933/384/831
Goodness-of-fit on F^2	0.958
Final R indexes [I>=2σ (I)]	R_1 = 0.0518, wR_2 = 0.0887
Final R indexes [all data]	R_1 = 0.1234, wR_2 = 0.1099
Largest diff. peak/hole / e Å^{-3}	1.02/-1.05

X-ray Data Collection, Structure Solution and Refinement for La(SAr^{iPr6})$_2$I, 1-La.

A colorless crystal of approximate dimensions 0.092 x 0.163 x 0.187 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2[15] program package was used to determine the unit-cell parameters and for data collection (30 sec/frame scan time). The raw frame data was processed using SAINT[16] and SADABS[17] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[18] program package. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[19] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Disordered atoms were included using multiple components, partial site-occupancy-factors, and displacement (SIMU) constraints.

Least-squares analysis yielded $wR_2 = 0.0887$ and Goof = 0.958 for 831 variables refined against 19933 data (0.70 Å), $R_1 = 0.0518$ for those 11152 data with $I > 2.0\sigma(I)$.

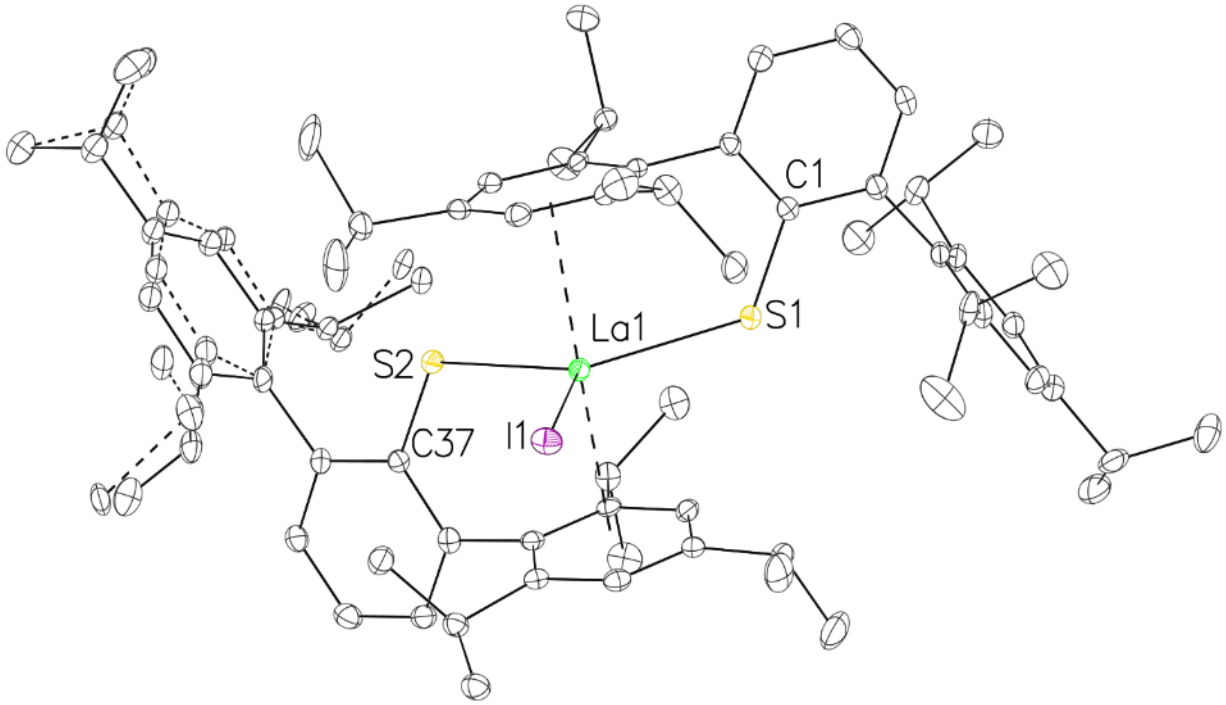


Figure S47. The molecular structure of La(SAr^{iPr6})$_2$I, **1-La**, showing modeled disorder. Thermal ellipsoids have been drawn at 30% probability. For clarity, hydrogen atoms are not shown.

Table S3. X-ray Data Collection Parameters and Crystallographic Details of **1-Nd**.

Empirical formula	$NdC_{72}S_2H_{98}I$
Formula weight	1298.76
Temperature/K	133.15
Crystal system	triclinic
Space group	P-1
a/Å	13.3492(8)
b/Å	14.1047(8)
c/Å	18.6556(11)
α/°	102.4330(10)
β/°	94.7210(10)
γ/°	99.2870(10)
Volume/Å^3	3360.2(3)
Z	2
ρ_{calc}g/cm^3	1.284
μ/mm^{-1}	1.332
F(000)	1350.0
Crystal size/mm^3	0.253 × 0.233 × 0.142
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.008 to 61.068
Index ranges	$-18 \leq h \leq 18$, $-20 \leq k \leq 19$, $-26 \leq l \leq 26$
Reflections collected	68604
Independent reflections	19753 [R_{int} = 0.0422, R_{sigma} = 0.0469]
Data/restraints/parameters	19753/468/872
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0344, wR_2 = 0.0745
Final R indexes [all data]	R_1 = 0.0504, wR_2 = 0.0809
Largest diff. peak/hole / e Å^{-3}	1.41/-1.40

X-ray Data Collection, Structure Solution and Refinement for Nd(SAr^{iPr6})$_2$I, 1-Nd.

A green crystal of approximate dimensions 0.142 x 0.233 x 0.253 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2[15] program package was used to determine the unit-cell parameters and for data collection (30 sec/frame scan time). The raw frame data was processed using SAINT[16] and SADABS[17] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[18] program package. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[19] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Disordered atoms were included using multiple components, partial site-occupancy-factors, and geometric (DFIX) and displacement (SIMU) constraints.

Least-squares analysis yielded $wR_2 = 0.0745$ and Goof = 1.023 for 872 variables refined against 19753 data (0.70 Å), $R_1 = 0.0344$ for those 15869 data with $I > 2.0\sigma(I)$.

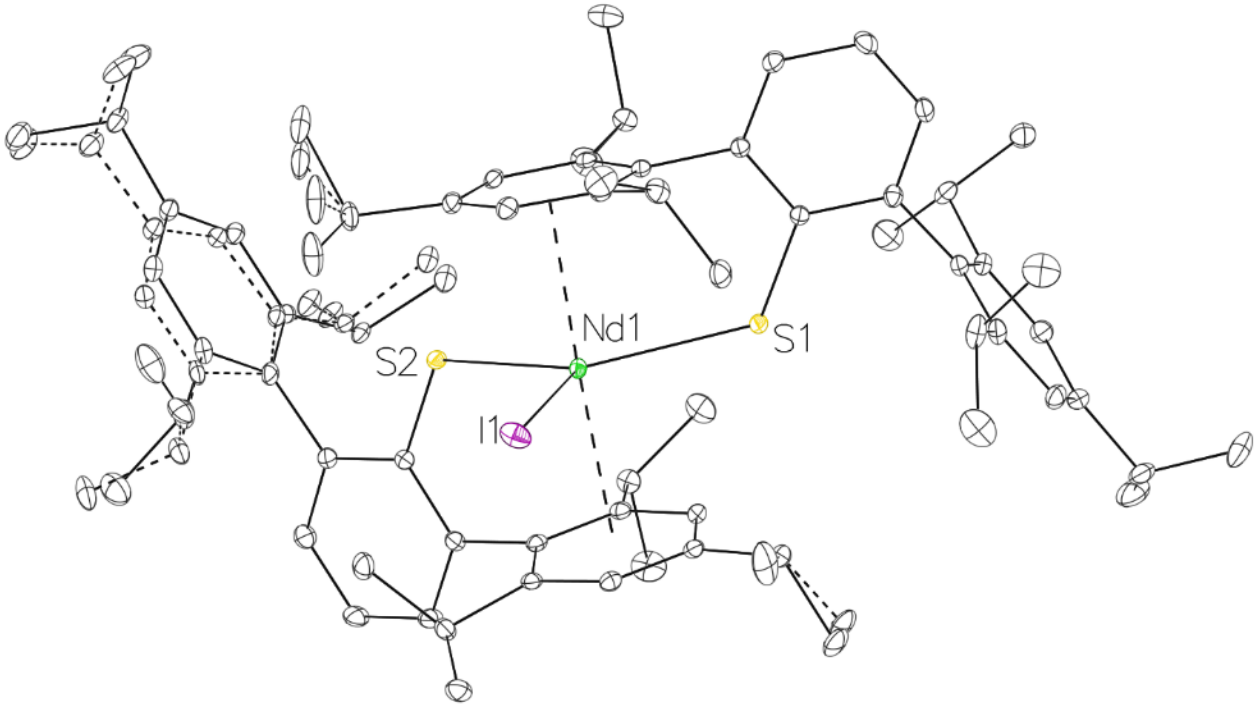


Figure S48. The molecular structure of Nd(SAr^{iPr6})$_2$I, **1-Nd**, showing modeled disorder. Thermal ellipsoids have been drawn at 30% probability. For clarity, hydrogen atoms are not shown.

Table S4. X-ray Data Collection Parameters and Crystallographic Details of 2-La.

Empirical formula	$LaC_{72}S_2H_{98}I_{0.13}$
Formula weight	1183.03
Temperature/K	92.85
Crystal system	triclinic
Space group	P-1
a/Å	13.2090(4)
b/Å	14.2623(4)
c/Å	18.5499(6)
α/°	104.544(2)
β/°	93.628(2)
γ/°	98.433(2)
Volume/Å^3	3327.73(18)
Z	2
ρ_{calc}g/cm^3	1.181
μ/mm^{-1}	6.291
F(000)	1252.0
Crystal size/mm^3	0.155 × 0.126 × 0.081
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.948 to 136.896
Index ranges	$-15 \leq h \leq 15$, $-17 \leq k \leq 17$, $-22 \leq l \leq 22$
Reflections collected	58509
Independent reflections	12145 [R_{int} = 0.1228, R_{sigma} = 0.0960]
Data/restraints/parameters	12145/36/750
Goodness-of-fit on F^2	0.813
Final R indexes [I>=2σ (I)]	R_1 = 0.0894, wR_2 = 0.2445
Final R indexes [all data]	R_1 = 0.1204, wR_2 = 0.2686
Largest diff. peak/hole / e Å^{-3}	1.46/-2.47

X-ray Data Collection, Structure Solution and Refinement for La(SAr^{iPr6})$_2$, 2-La.

An orange crystal of approximate dimensions 0.081 x 0.126 x 0.155 mm was mounted in a cryoloop and transferred to a Bruker X8 Prospector diffractometer system. The APEX3[20] program package was used to determine the unit-cell parameters and for data collection (30 sec/frame scan time). The raw frame data was processed using SAINT[16] and SADABS[17] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[18] program package. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[19] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Disordered atoms were included using multiple components, partial site-occupancy-factors, and displacement (SIMU) constraints. The crystal contained an iodide contaminant of ca. 13%.

Least-squares analysis yielded $wR_2 = 0.2220$ and Goof = 1.043 for 750 variables refined against 12145 data (0.83 Å), $R_1 = 0.0874$ for those 8321 data with $I > 2.0\sigma(I)$.

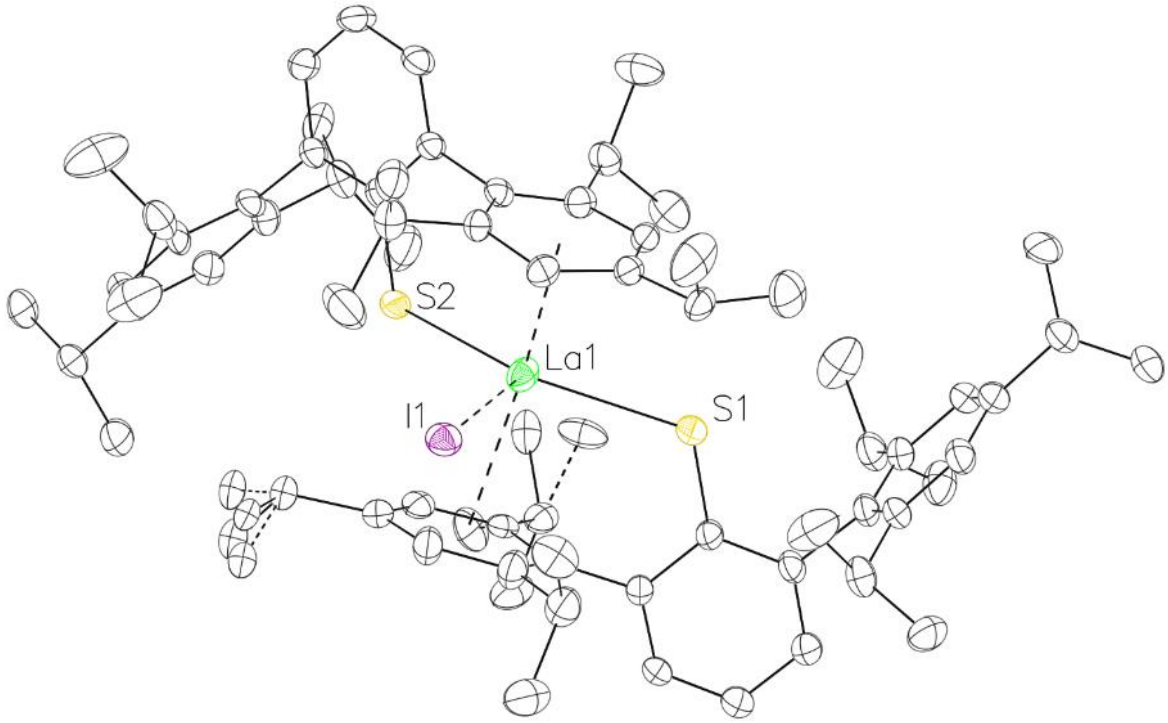


Figure S49. The molecular structure of La(SAr^{iPr6})$_2$, **2-La**, showing modeled disorder. Thermal ellipsoids have been drawn at 30% probability. For clarity, hydrogen atoms are not shown. The occupancy of the iodine atom in the crystal structure is 13%.

Table S5. X-ray Data Collection Parameters and Crystallographic Details of 2-Nd.

Empirical formula	$NdS_2C_{72}H_{98}$
Formula weight	1171.86
Temperature/K	93.15
Crystal system	triclinic
Space group	P-1
a/Å	13.2169(7)
b/Å	14.2162(8)
c/Å	18.5245(10)
α/°	104.9172(10)
β/°	93.8221(10)
γ/°	97.9184(10)
Volume/Å^3	3312.3(3)
Z	2
ρ_{calc}g/cm^3	1.175
μ/mm^{-1}	0.885
F(000)	1244.0
Crystal size/mm^3	0.327 × 0.263 × 0.16
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.248 to 61.156
Index ranges	$-18 \leq h \leq 18$, $-20 \leq k \leq 19$, $0 \leq l \leq 26$
Reflections collected	20371
Independent reflections	20371 [R_{int} = ?, R_{sigma} = 0.0445]
Data/restraints/parameters	20371/0/751
Goodness-of-fit on F^2	1.097
Final R indexes [I>=2σ (I)]	R_1 = 0.0545, wR_2 = 0.1393
Final R indexes [all data]	R_1 = 0.0641, wR_2 = 0.1441
Largest diff. peak/hole / e Å^{-3}	3.94/-1.03

X-ray Data Collection, Structure Solution and Refinement for Nd(SAr^{iPr6})$_2$, 2-Nd.

A red crystal of approximate dimensions 0.160 x 0.263 x 0.327 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2[15] program package and the CELL_NOW[21] were used to determine the unit-cell parameters. Data was collected using a 30 sec/frame scan time. The raw frame data was processed using SAINT[16] and TWINABS[22] to yield the reflection data file (HKLF5 format).[22] Subsequent calculations were carried out using the SHELXTL[18] program package. There were no systematic absences nor any diffraction symmetry other than the Friedel condition The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[19] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Disordered atoms were included using multiple components and partial site-occupancy-factors.

Least-squares analysis yielded $wR_2 = 0.1441$ and Goof = 1.097 for 751 variables refined against 20371 data (0.70 Å), $R_1 = 0.0545$ for those 17815 with $I > 2.0\sigma(I)$. The structure was refined as a three-component twin, BASF[18] = 0.051, 0.040.

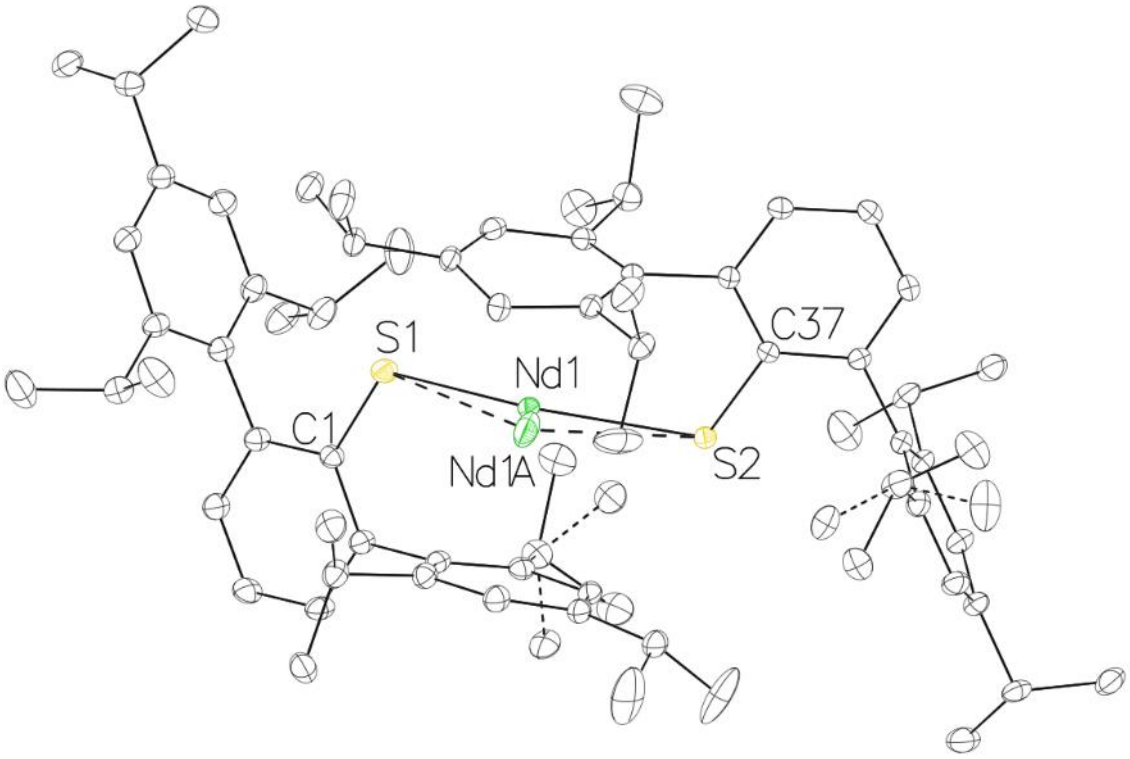


Figure S50. The molecular structure of Nd(SAr^{iPr6})$_2$, **2-Nd**, showing modeled disorder. Thermal ellipsoids have been drawn at 30% probability. For clarity, hydrogen atoms are not shown. The occupancy of the Nd1A in the crystal structure is 20%.

Table S6. X-ray Data Collection Parameters and Crystallographic Details of 2-Tm

Empirical formula	$TmC_{72}S_2H_{98}$
Formula weight	1196.55
Temperature/K	133.15
Crystal system	triclinic
Space group	P-1
a/Å	13.2573(10)
b/Å	14.2636(10)
c/Å	18.3627(13)
α/°	104.3400(10)
β/°	93.6930(10)
γ/°	98.5700(10)
Volume/Å^3	3307.9(4)
Z	2
ρ_{calc}g/cm^3	1.201
μ/mm^{-1}	1.442
F(000)	1262.0
Crystal size/mm^3	0.241 × 0.24 × 0.112
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.302 to 61.076
Index ranges	$-18 \leq h \leq 18$, $-20 \leq k \leq 20$, $-26 \leq l \leq 25$
Reflections collected	82334
Independent reflections	19517 [R_{int} = 0.0350, R_{sigma} = 0.0368]
Data/restraints/parameters	19517/0/760
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0331, wR_2 = 0.0728
Final R indexes [all data]	R_1 = 0.0452, wR_2 = 0.0774
Largest diff. peak/hole / e Å^{-3}	2.45/-0.95

X-ray Data Collection, Structure Solution and Refinement for $Tm(SAr^{iPr6})_2$, 2-Tm.

A green crystal of approximate dimensions 0.112 x 0.240 x 0.241 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX3[20] program package was used to determine the unit-cell parameters and for data collection (30 sec/frame scan time). The raw frame data was processed using SAINT[16] and SADABS[17] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[18] program package. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[19] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Disordered atoms were included using multiple components and partial site-occupancy-factors.

Least-squares analysis yielded $wR_2 = 0.0728$ and Goof = 1.030 for 760 variables refined against 19517 data (0.70 Å), $R_1 = 0.0331$ for those 16608 data with $I > 2.0\sigma(I)$.

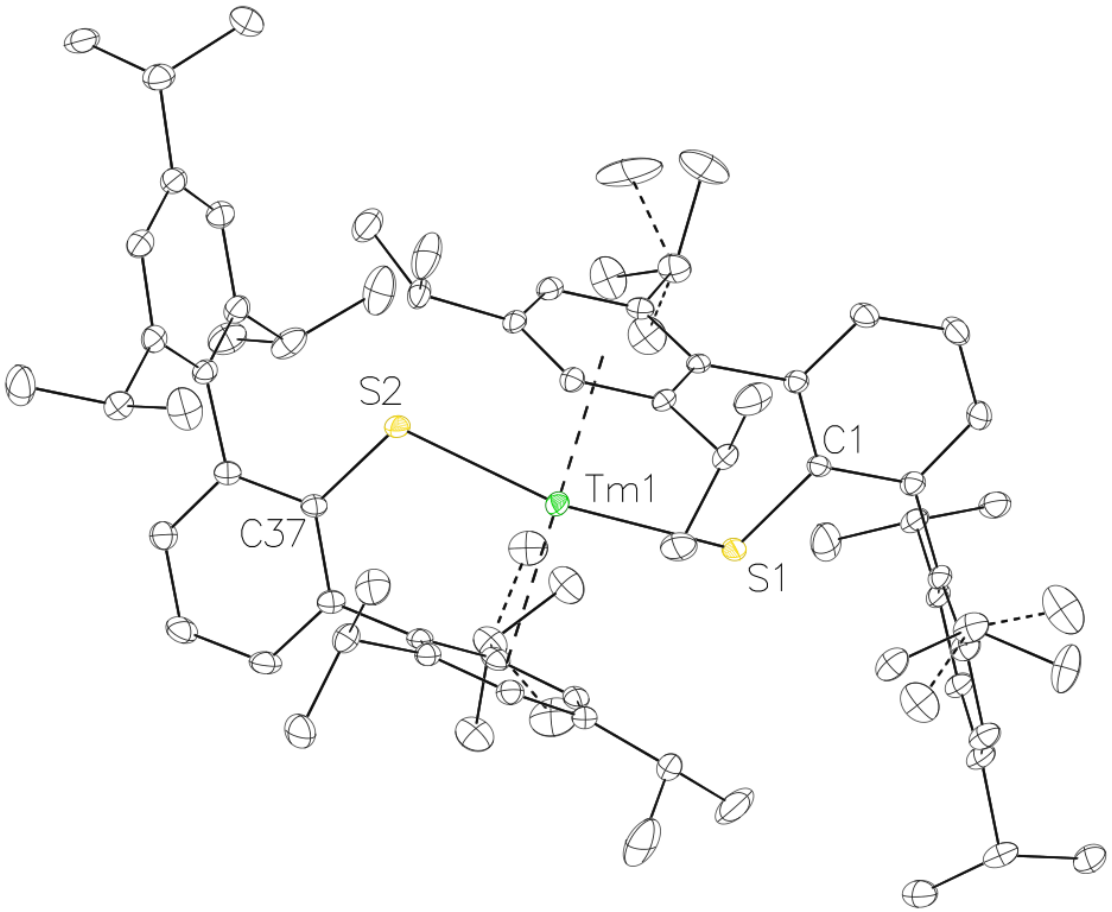


Figure S51. The molecular structure of $Tm(SAr^{iPr6})_2$, **2-Tm**, showing modeled disorder. Thermal ellipsoids have been drawn at 30% probability. For clarity, hydrogen atoms are not shown.

Table S7. X-ray Data Collection Parameters and Crystallographic Details of 3-Nd

Empirical formula	$NdC_{84}S_2N_2H_{108}$
Formula weight	1354.08
Temperature/K	93.15
Crystal system	orthorhombic
Space group	Pbcn
a/Å	15.9566(15)
b/Å	18.7918(17)
c/Å	24.254(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	7272.6(11)
Z	4
ρ_{calc}g/cm^3	1.237
μ/mm^{-1}	0.816
F(000)	2872.0
Crystal size/mm^3	0.305 × 0.222 × 0.152
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.218 to 61.302
Index ranges	$-22 \leq h \leq 22$, $-26 \leq k \leq 26$, $-34 \leq l \leq 34$
Reflections collected	96047
Independent reflections	11139 [R_{int} = 0.0636, R_{sigma} = 0.0389]
Data/restraints/parameters	11139/18/454
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0397, wR_2 = 0.0969
Final R indexes [all data]	R_1 = 0.0645, wR_2 = 0.1098
Largest diff. peak/hole / e Å^{-3}	1.47/-0.89

X-ray Data Collection, Structure Solution and Refinement for $Nd(SAr^{iPr6})_2(N_2Ph_2)$, 3-Nd.

A red crystal of approximate dimensions 0.152 x 0.222 x 0.305 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2[15] program package was used to determine the unit-cell parameters and for data collection (60 sec/frame scan time). The raw frame data was processed using SAINT[16] and SADABS[17] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[18] program package. The diffraction symmetry was *mmm* and the systematic absences were consistent with the orthorhombic space group *Pbcn* that was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[19] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Disordered atoms were included using multiple components, partial site-occupancy-factors, and displacement (SIMU) constraints.

Least-squares analysis yielded $wR_2 = 0.0969$ and Goof = 1.027 for 454 variables refined against 11139 data (0.70 Å), $R_1 = 0.0397$ for those 8027 data with $I > 2.0\sigma(I)$.

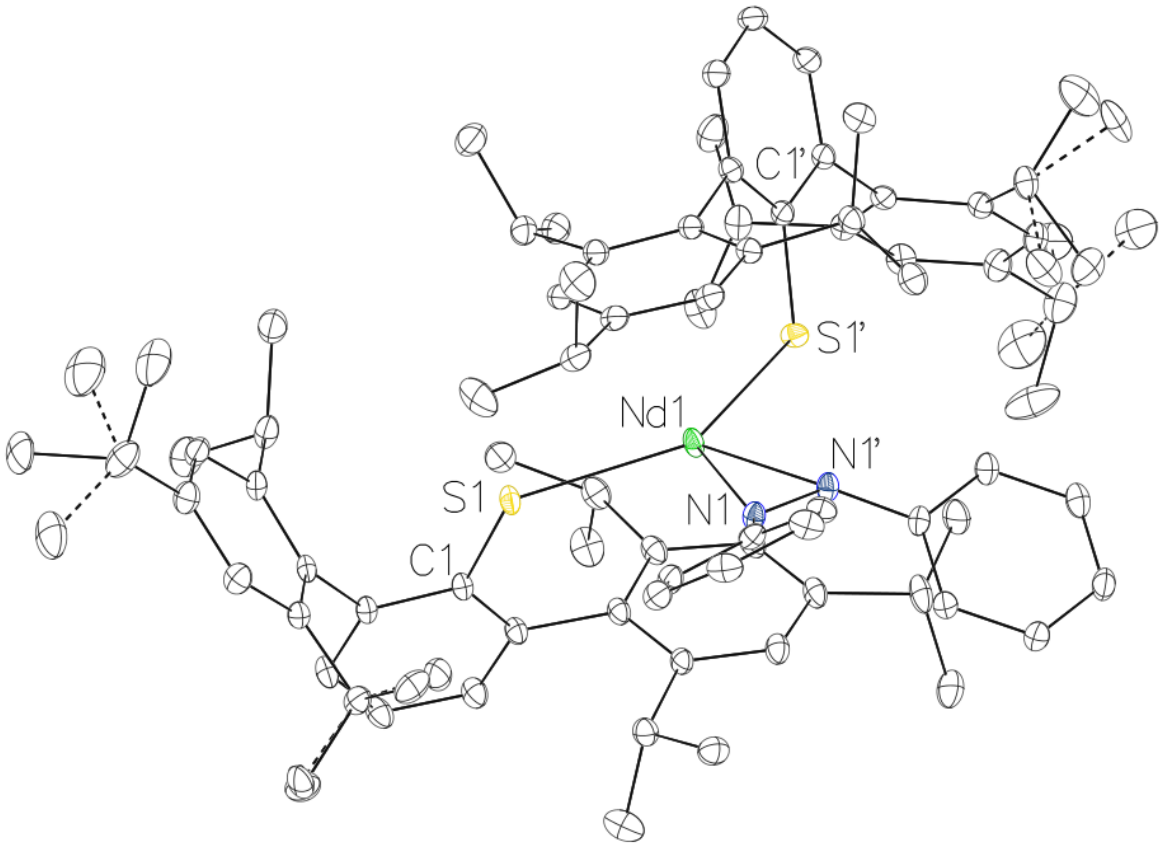


Figure S52. The molecular structure of $Nd(SAr^{iPr6})_2(N_2Ph_2)$, **3-Nd**, showing modeled disorder. Thermal ellipsoids have been drawn at 30% probability. For clarity, hydrogen atoms are not shown.

Table S8. X-ray Data Collection Parameters and Crystallographic Details of 3-Sm

Empirical formula	$SmC_{84}N_2S_2H_{108}$
Formula weight	1360.19
Temperature/K	93.15
Crystal system	orthorhombic
Space group	Pbcn
a/Å	16.0032(13)
b/Å	18.7417(15)
c/Å	24.3011(19)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	7288.6(10)
Z	4
ρ_{calc}g/cm^3	1.240
μ/mm^{-1}	0.908
F(000)	2880.0
Crystal size/mm^3	0.335 × 0.285 × 0.206
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.742 to 61.042
Index ranges	$-22 \leq h \leq 22$, $-26 \leq k \leq 26$, $-34 \leq l \leq 34$
Reflections collected	88008
Independent reflections	11106 [R_{int} = 0.0441, R_{sigma} = 0.0277]
Data/restraints/parameters	11106/26/458
Goodness-of-fit on F^2	1.146
Final R indexes [I>=2σ (I)]	R_1 = 0.0433, wR_2 = 0.0978
Final R indexes [all data]	R_1 = 0.0556, wR_2 = 0.1027
Largest diff. peak/hole / e Å^{-3}	0.53/-0.79

X-ray Data Collection, Structure Solution and Refinement for $Sm(SAr^{iPr6})_2(N_2Ph_2)$, 3-Sm.

A red crystal of approximate dimensions 0.206 x 0.285 x 0.335 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer system. The APEX2[15] program package was used to determine the unit-cell parameters and for data collection (60 sec/frame scan time). The raw frame data was processed using SAINT[16] and SADABS[17] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[18] program package. The diffraction symmetry was *mmm* and the systematic absences were consistent with the orthorhombic space group *Pbcn* that was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[19] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Disordered atoms were included using multiple components, partial site-occupancy-factors, and displacement (SIMU) constraints.

Least-squares analysis yielded $wR_2 = 0.1027$ and Goof = 1.146 for 458 variables refined against 11106 data (0.70 Å), $R_1 = 0.0433$ for those 9327 data with $I > 2.0\sigma(I)$.

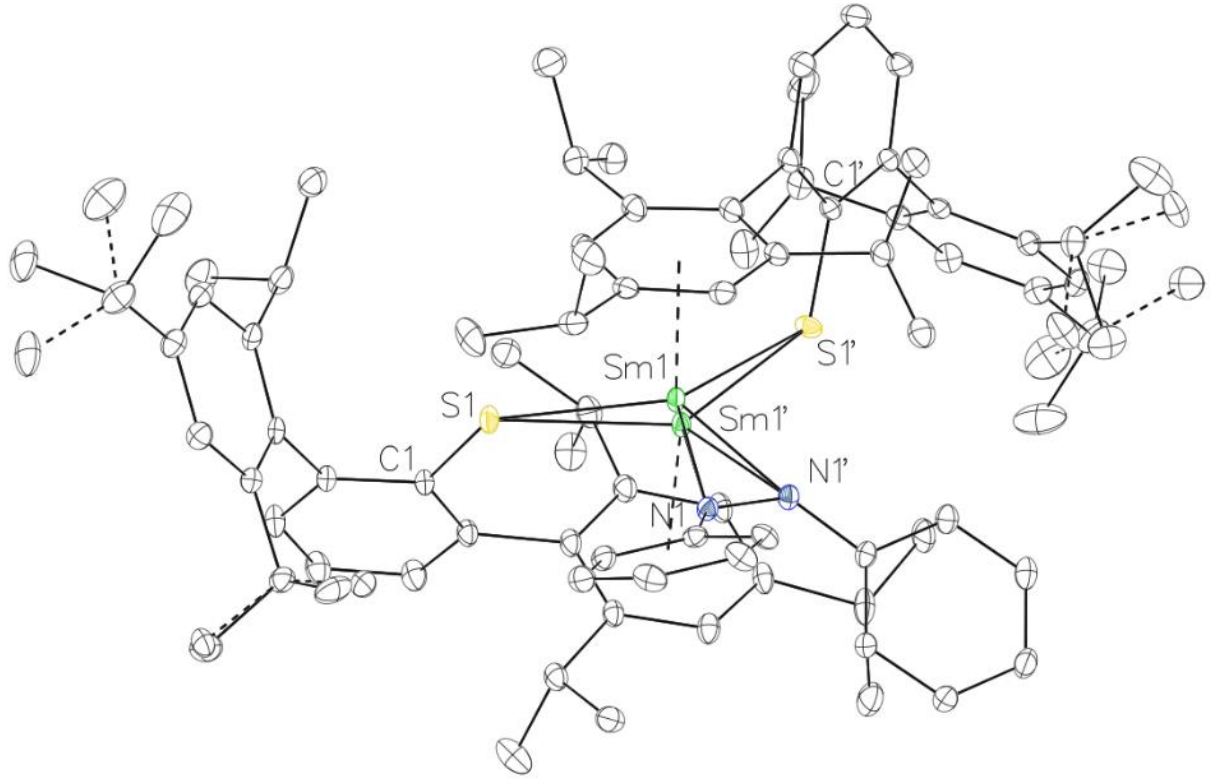


Figure S53. The molecular structure of $Sm(SAr^{iPr6})_2(N_2Ph_2)$, **3-Sm**, showing modeled disorder. Thermal ellipsoids have been drawn at 30% probability. For clarity, hydrogen atoms are not shown. Unlike the analogous complex **3-Nd**, the metal atom in **3-Sm** does not lie on the 2-fold crystallographic axis. Thus, the Sm atom resides on two sites of equal occupancy, with the Sm atom interacting with only one flanking ring of the ligand.

Table S9. Selected interatomic distances and angles in Ln(SAr^{iPr6})$_2$I complexes (1-Ln)

	1-La	**1-Nd**	**1-Gd**
Ln-I	3.1213(4)	3.0542(6)	2.9857(3)
Ln-S	2.8235(12), 2.8173(10)	2.7490(5), 2.7734(4)	2.7257(7), 2.7036(7)
Ln-C_{arene}	3.096 – 3.187(5); avg: 3.142(1)	3.0619(5) – 3.1876(5); avg: 3.1293(2)	3.047(3) – 3.288(3); avg: 3.151(1)
Ln-Cnt	2.8090(16), 2.8165(15)	2.7972(4), 2.7980(4)	2.7771(12), 2.8698(13)
S-Ln-S	125.32(3)	127.334(10)	128.46(2)
S-Ln-I	116.42(2), 118.26(2)	120.689(11), 111.977(7)	111.603(17), 119.898(17)
Cnt-Ln-Cnt	173.22(5)	175.2358(9)	176.55(4)
Cnt-Ln-I	93.52(4), 93.25(4)	92.741(12), 92.013(13)	93.16(3), 90.18(3)
Cnt-Ln-S	88.75(4), 87.71(4), 87.87(4), 89.45(4)	88.849(15), 88.957(14), 88.450(15), 89.561(14)	89.57(3), 90.10(3), 88.02(3), 89.46(3)

Table S10. Selected interatomic distances of Ln(SAr^{iPr6})$_2$ complexes (2-Ln)

	2-La	**2-Nd**	**2-Sm**[7]	**2-Eu (173 K)**[23]	**2-Eu (100 K)**[23]	**2-Tm**	**2-Yb**[24]
Ln-S	2.805(3), 2.810(3)	2.7763(11), 2.741(1)	2.8187(16), 2.8141(13)	2.8164(10), 2.8177(12)	2.8104(9), 2.8031(11), 2.8303(9), 2.8174(10)	2.7182(6), 2.7203(5)	2.696(3), 2.685(2)
Ln-C_{arene}	Ring1: 2.819(12) – 2.957(10) avg: 2.892(4) Ring 2: 3.073(13) – 3.201(11) avg: 3.137(4)	Ring 1: 2.697(3) – 2.858(3) avg: 2.779(1) Ring 2: 3.048(3) – 3.201(3) avg: 3.135(1)	2.993(6) – 3.149(5); avg: 3.071(2)	2.968(3) – 3.161(3); avg: 3.065(1)	2.973(4) – 3.240(4); avg: 3.095(2)	2.884(2) – 3.117(2); avg: 2.999(1)	2.823(9) – 3.139(8); avg: 2.974(3)
Ln-Cnt	2.524(4) 2.808(5)	2.3950(13), 2.8044(13)	2.726(2), 2.741(2)	2.7344(14), 2.7218(15)	2.7834(15), 2.7394(16), 2.7583(15), 2.7616(15)	2.6631(9), 2.6423(9)	2.624(4), 2.650(4)
S-Ln-S	135.97(10)	140.36(3)	139.76(4)	141.89(3)	139.04(3), 143.84(3)	143.31(2)	142.73(4)
Ln-S-C_{aryl}	118.8(4) 113.4(3)	118.71(11), 112.22(10)	116.11(18), 116.20(15)	115.43(10), 115.85(9)	115.50(12), 115.51(12), 115.69(11), 115.32(12)	115.76(7), 115.33(7)	115.0(3), 115.7(3)
Cnt-Ln-Cnt	170.92(17)	164.68(5)	168.88(7)	166.92(4)	172.61(4), 170.55(4)	164.09(3)	164.50(12)
Cnt-Ln-S	89.33(9) 87.71(8) 95.37(9) 94.23(9)	97.27(4), 96.77(4), 90.18(4), 85.74(4)	91.60(6), 91.93(6), 91.26(5), 92.84(6)	91.52(4), 94.08(4), 92.12(4), 90.68(4)	92.01(4), 90.51(4), 91.04(4), 91.59(4), 91.16(4), 95.81(9), 92.03(3), 91.67(4)	93.90(2), 91.03(2), 90.68(2), 94.38(2)	93.63(10), 93.80(9), 94.71(10), 87.43(9)

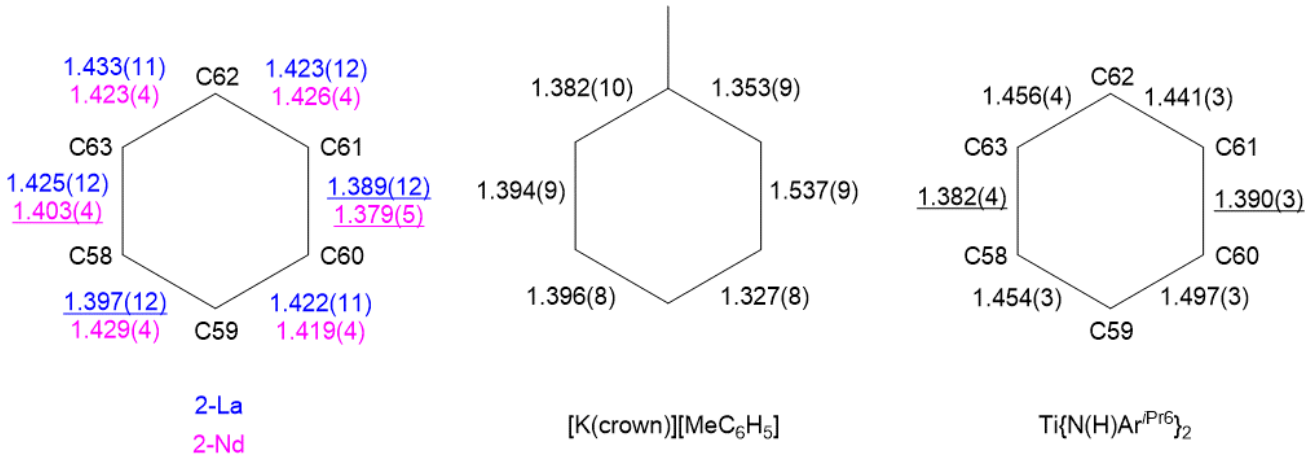


Figure S54. A comparison of interatomic C---C distances in the proximal flanking rings of **2-La** and **2-Nd** (left), the anion of [K(crown)][MeC_6H_5][25] (center), and the doubly reduced flanking ring of Ti[N(H)Ar^{iPr6}]$_2$[26] (right). The carbon atoms in the right diagram have been numbered to reflect their identical substitution to those of **2-Ln**. The two shortest C---C distances have been underlined in the left and right diagrams.

5. Computational Details

General Considerations. All calculations were performed with the Turbomole software suite V7.8[27–29] (compiled on-site from the source code) using Kohn-Sham density functional theory for ground states and linear-response time-dependent density functional theory (TDDFT) for excited states. The resolution-of-the-identity approximation (RIJ) was used throughout.[30,31]

Starting from the XRD structures, exploratory ground state structure optimizations were performed with the TPSS[32] functional with empirical dispersion corrections (D3(BJ))[33,34] and def2-SVP basis sets[35] with effective core potentials[36,37] (def2-ecp) for the La atom (46 electrons) and the Nd atom (28 electrons). All final reported structures were obtained from subsequent calculations with the hybrid functional TPSSh[38] (also with D3(BJ) corrections) using def2-TZVP basis sets[35] with def2-ecp effective core potentials. A medium sized numerical quadrature grid (gridsize 3) and weight derivatives were used for the exchange-correlation integrals. Ground state energies were converged to smaller than 10^{-7} a.u. (scfconv 7) and ground sate maximum gradient norms were converged to smaller than 10^{-4} a.u. (-gcart 4). For **2-Nd**, structure optimizations were terminated at a maximum gradient norm of ca. 6×10^{-4} a.u. to avoid excessively long computation times as no significant changes in the structure and energy were observed. Additional structures for some of the property and spectra calculations described below were obtained at the TPSSh-D3(BJ)/def2-SVP level of theory using the COSMO continuum implicit solvation model[39,40] with parameters for hexane ($\varepsilon = 1.89$) and THF ($\varepsilon = 7.25$). Orbital and spin density plots were created using VMD.[41]

UV-vis-NIR absorption spectra were calculated at the TPSSh/def2-SVP(ECP) level using Turbomole's gauge-invariant current-density dependent meta generalized gradient approximation implementation.[42,43] The first 100 vertical excitation energies were used to simulate the spectra

using the Turbomole utility mkspec with an empirical line broadening for a line width of 1000 cm^{-1}. To evaluate the influence of the solvent on the absorption spectra, additional calculations using the COSMO continuum implicit solvation model[39,40] with parameters for hexane ($\varepsilon = 1.89$, $n_{ref} = 1.375$) were performed but showed no major qualitative differences.

EPR parameters for $La(SAr^{iPr6})_2$ were calculated within the quasi-relativistic one-electron exact two-component (X2C) framework[44,45] using the diagonal local approximation of the unitary decoupling transformation (DLU).[46,47] Spin-orbit coupling was considered at the level of a screened nuclear spin−orbit approach[48] with revised parameters.[49] A finite nucleus model was used for the charge densities of the nuclei.[50] The r^2SCAN[51] and ωB97X-D[52,53] functionals were used, for which previous benchmark studies comparing different GGA, MGGA, hybrid, and range-separated hybrids found the overall best agreement with experimental data for both EPR *g* tensors and hyperfine couplings.[46,47] Notably, good agreement was also found for a La(II) complex ($[La(OAr^*)_3]^-$ (OAr^* = 2,6-Ad_2-4-*t*-Bu-C_6H_2O)) with this functional.[46,47] The current dependent generalization of the kinetic energy density was used for r^2SCAN.[54] For La, a (contracted) x2c-QZVPall-2c basis set[55] was used, which was previously found to give results close to those of computationally more expensive fully uncontracted basis sets.[46,47] For all other atoms (S, C, H), (uncontracted) x2c-SVPall-2c-unc basis sets were used.[56] A finer numerical quadrature grid with additional radial points (gridsize 4a) was used.[57] Spectra were simulated using the python3 package EPRsim,[58] which is based on the methods used in EasySpin.[59] A rotational correlation time of 0.1 ns (0.9 ns) was used to simulated spectra at 298 K (77 K). A mixed Gaussian and Lorentzian broadening of 2 Gauss (FWHM) was used.

Table S11. Calculated structural parameters from TPSSh-D3(BJ)/def2-TZVP (gas phase) calculations.

	2-La		**2-Nd**
	symmetric	*asymmetric*	*asymmetric*
E_{tot} [Ha]	-3632.5092182	-3632.5086235	-4162.1260529
E_{tot} [kcal/mol]	E_0^{La}	E_0^{La} + 0.37	E_0^{Nd}
d(M–S_1) [Å]	2.8548	2.8508	2.7956
d(M–S_2) [Å]	2.8731	2.8610	2.7979
φ(S_1–M–S_2) [°]	120.45	134.97	139.73
d(M–Cnt_1) [Å]	2.5723	2.7422	2.8456
d(M–Cnt_2) [Å]	2.5968	2.4872	2.4529
φ(Cnt_1–M–Cnt_2) [°]	171.02	169.06	166.75

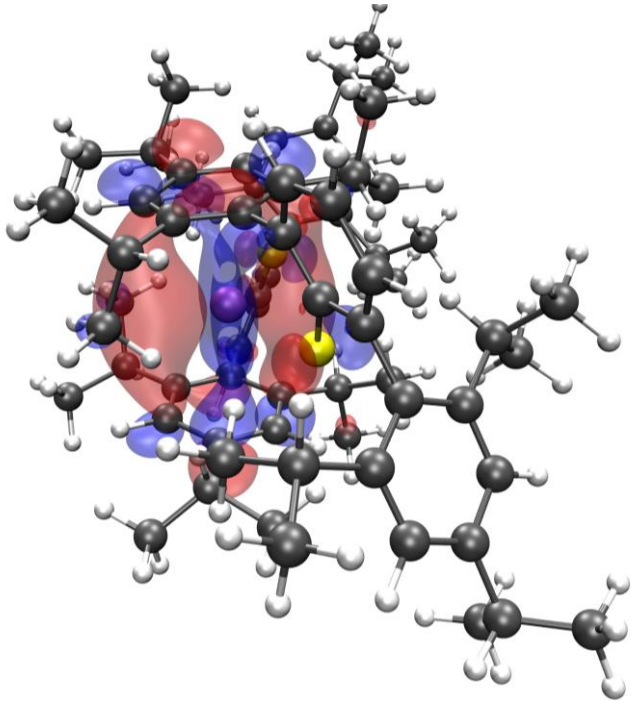
Table S12. Calculated structural parameters from TPSSh-D3(BJ)/def2-SVP (COSMO, hexane) calculations

	2-La		**2-Nd**
	symmetric	*asymmetric*	*asymmetric*
E_{tot} [Ha]	-3629.3687387	-3629.3689608	-4158.9752824
E_{tot} [kcal/mol]	E_0^{La} + 0.14	E_0^{La}	E_0^{Nd}
d(M–S_1) [Å]	2.8585	2.8476	2.8054
d(M–S_2) [Å]	2.8686	2.8504	2.8065
φ(S_1–M–S_2) [°]	121.38	133.98	138.43
d(M–Cnt_1) [Å]	2.5694	2.7978	2.8061
d(M–Cnt_2) [Å]	2.5997	2.4617	2.4696
φ(Cnt_1–M–Cnt_2) [°]	171.46	169.54	168.16

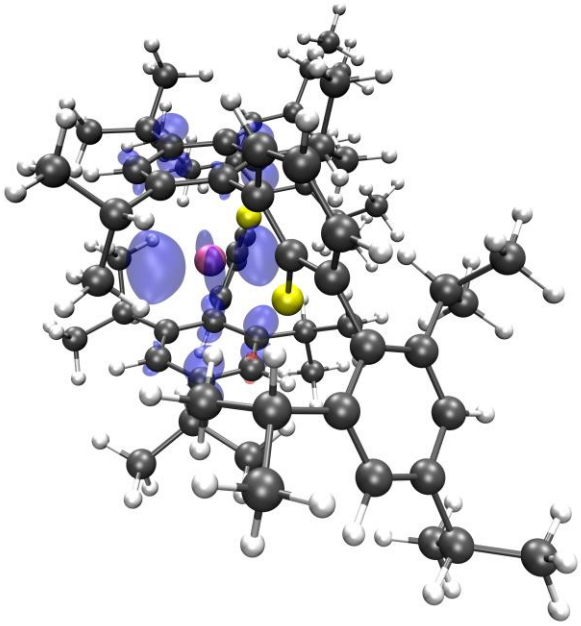
Table S13. Calculated structural parameters from TPSSh-D3(BJ)/def2-SVP (COSMO, THF) calculations

	2-La	
	symmetric	*asymmetric*
E_{tot} [Ha]	-3629.3743530	-3629.3744915
E_{tot} [kcal/mol]	E_0^{La} + 0.09	E_0^{La}
d(M–S_1) [Å]	2.8603	2.8502
d(M–S_2) [Å]	2.8723	2.8524
φ(S_1–M–S_2) [°]	119.43	133.42
d(M–Cnt_1) [Å]	2.5637	2.7964
d(M–Cnt_2) [Å]	2.5980	2.4602
φ(Cnt_1–M–Cnt_2) [°]	170.52	169.57

Isosurface Plots of Molecular Spin Orbitals and Spin Densities

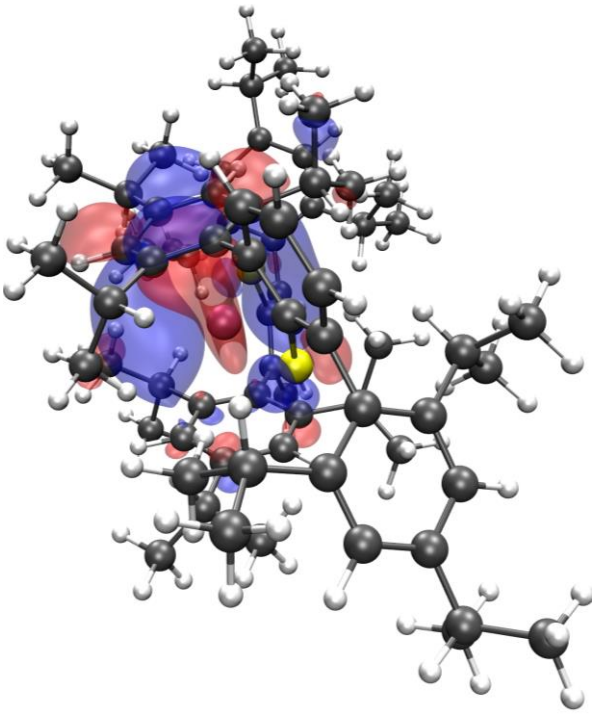


α 287a (–2.890 eV)
[1La Pop. 0.04285s 0.00891p 0.34350d 0.00150f]

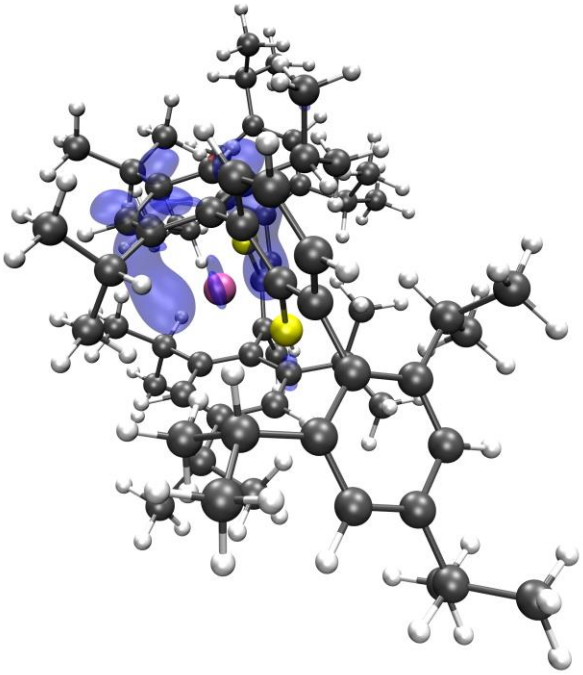


spin density
[1La Pop. 0.06068s 0.04405p 0.43047d 0.00129f]

Figure S55. Highest occupied spin orbital (iso value 0.03) and spin density (iso value 0.004) in **2-La** for the *symmetric* structure and Mulliken population analysis for the contributions from the La atomic orbitals.

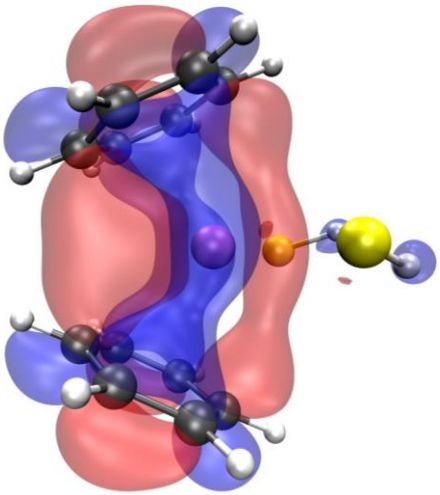


α 287a (–2.932 eV)
[1La Pop. 0.05678s 0.00540p 0.29640d 0.00447f]

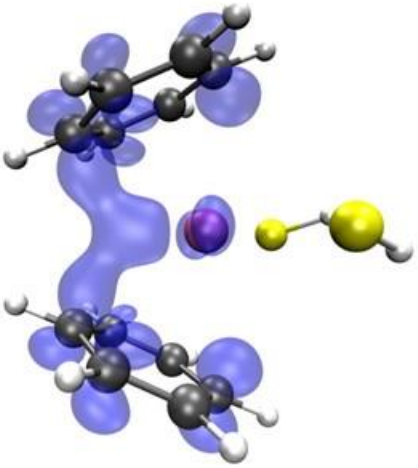


spin density
[1La Pop. 0.06719s 0.03347p 0.36610d 0.00412f]

Figure S56. Highest occupied spin orbital (iso value 0.03) and spin density (iso value 0.004) in **2-La** for the *asymmetric* structure and Mulliken population analysis for the contributions from the La atomic orbitals.

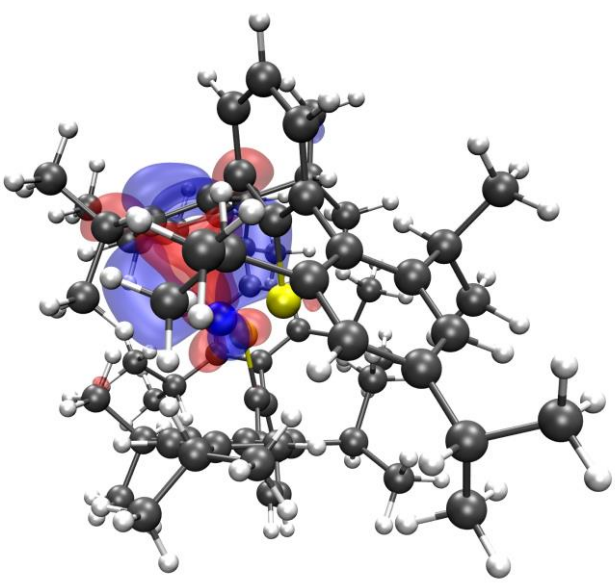


α 65a (–3.329 eV)
[1La Pop. 0.00115s 0.00207p 0.21126d 0.00808f]

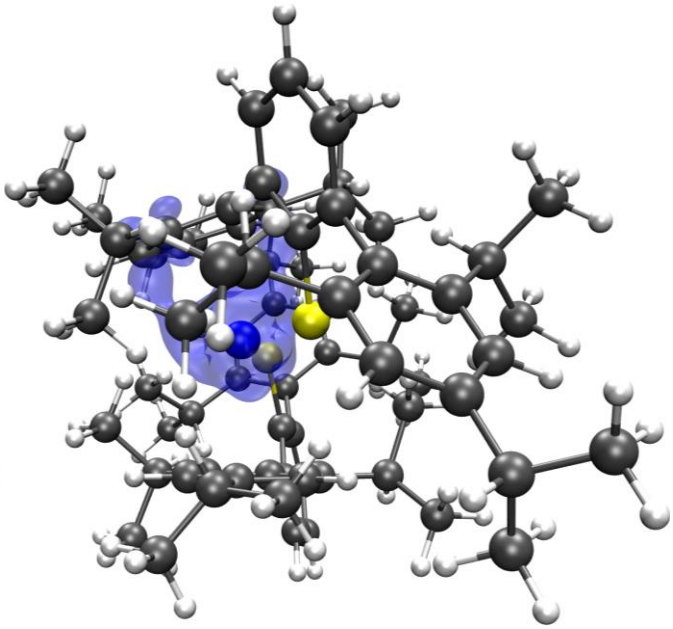


spindensity
[1La Pop. 0.01621s 0.00703p 0.23144d 0.00761f]

Figure S57. Highest occupied spin orbital (iso value 0.03) and spin density (iso value 0.004) in the model complex $La(SH)_2Bz_2$ (*symmetric* structure) and Mulliken population analysis for the contributions from the La atomic orbitals.



α 299a (–3.070 eV)
[1Nd Pop. 0.00443s 0.00343p 0.05105d 0.61520f]



spin density
[1Nd Pop. 0.02994s 0.02178p 0.12284d 3.57225f]

Figure S58. Highest occupied spin orbital (iso value 0.03) and spin density (iso value 0.004) in **2-Nd** for the *asymmetric* structure and Mulliken population analysis for the contributions from the Nd atomic orbitals.

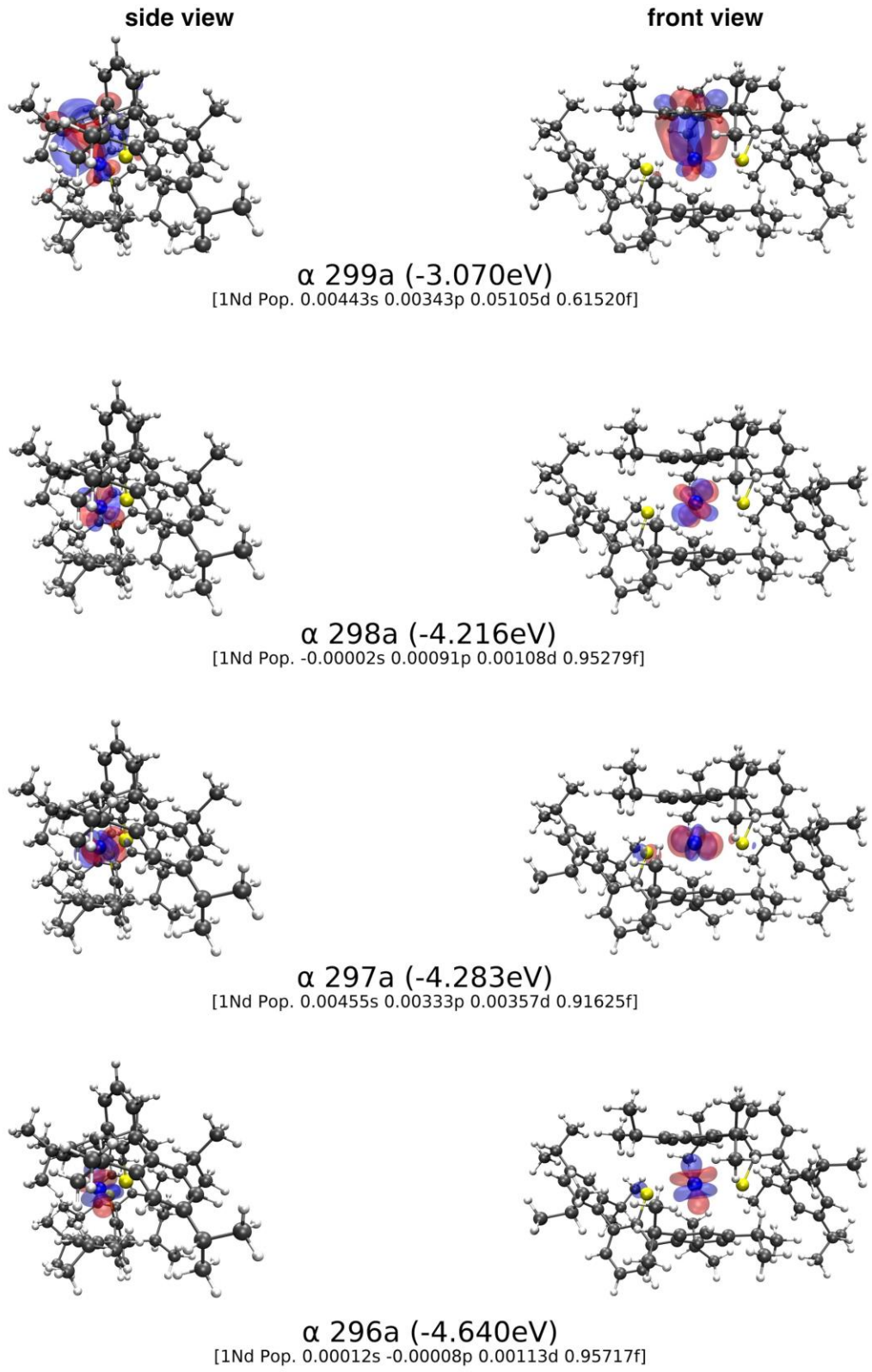
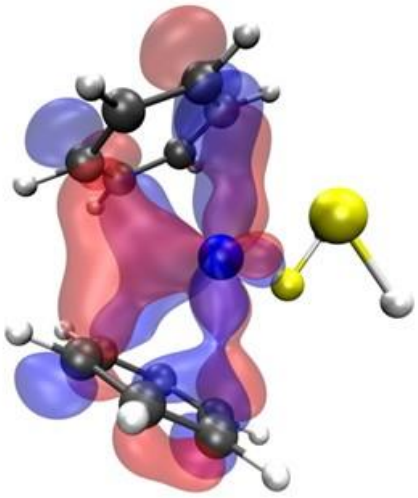
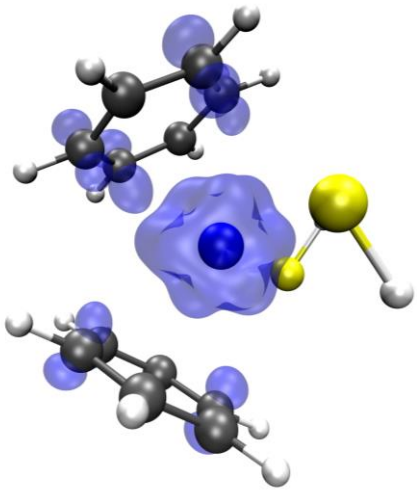


Figure S59. Highest occupied spin orbitals (iso value 0.03 in **2-Nd** for the *asymmetric* structure and Mulliken population analysis for the contributions from the Nd atomic orbitals. Two viewing angles are shown (left and right).



α 77a (–3.376 eV)
[1Nd Pop. 0.00022s 0.00136p 0.03503d 0.52314f]



spindensity
[1Nd Pop. 0.02087 0.01687p 0.11683d 3.46706f]

Figure S60. Highest occupied spin orbital (iso value 0.03) and spin density (iso value 0.004) in the model complex $Nd(SH)_2Bz_2$ (*symmetric* structure) and Mulliken population analysis for the contributions from the Nd atomic orbitals.

EPR Spectra from Quantum Chemical Calculations

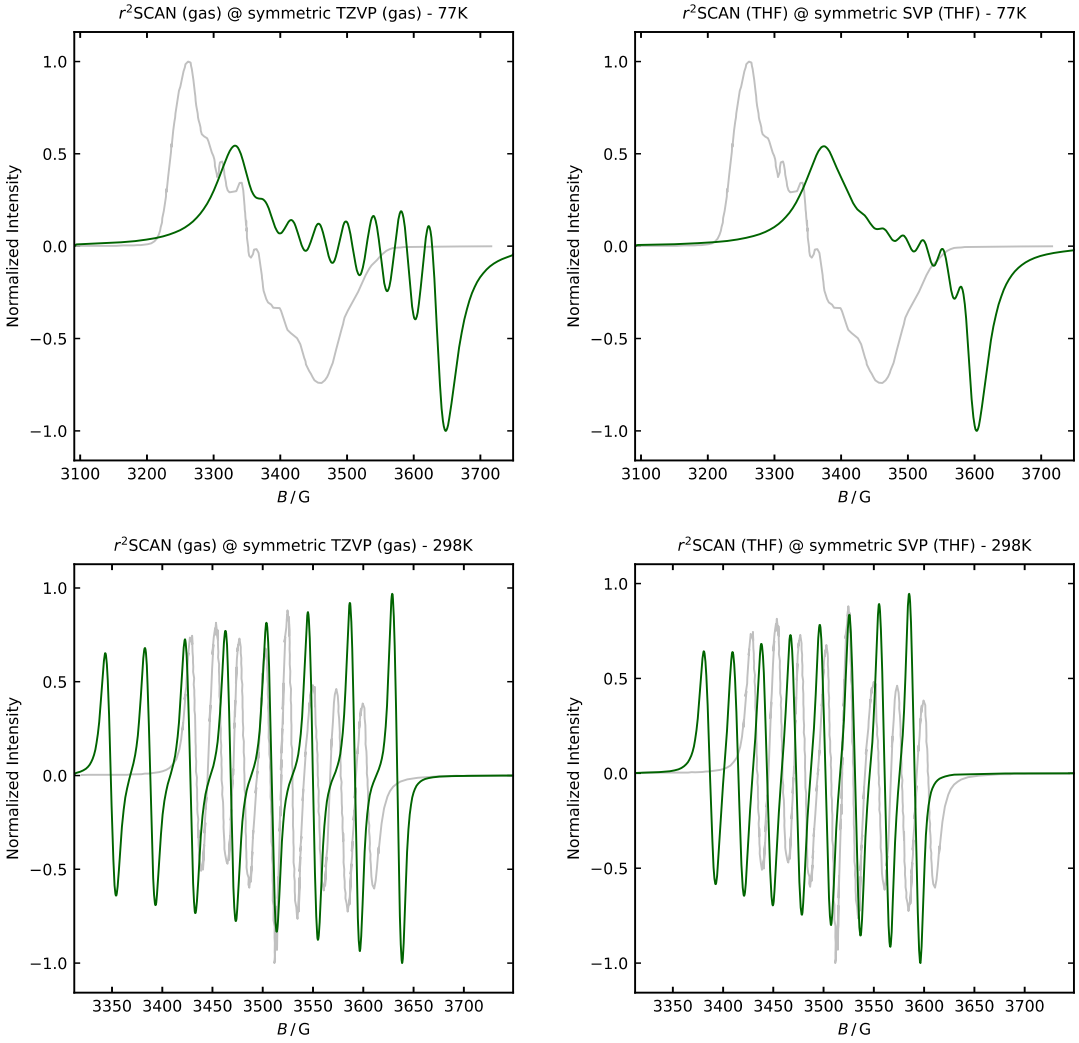


Figure S61. Simulated EPR spectra (green lines) of La(SAr^{iPr6})$_2$, **2-La**, using the *symmetric* structure optimized in the gas phase (left) or using the COSMO solvent model for THF (right) with a correlation time of 0.9 ns for the best visual match with the experimental spectrum (gray line) at 77 K (top) and of 0.1 ns for the spectrum at 298 K (bottom).

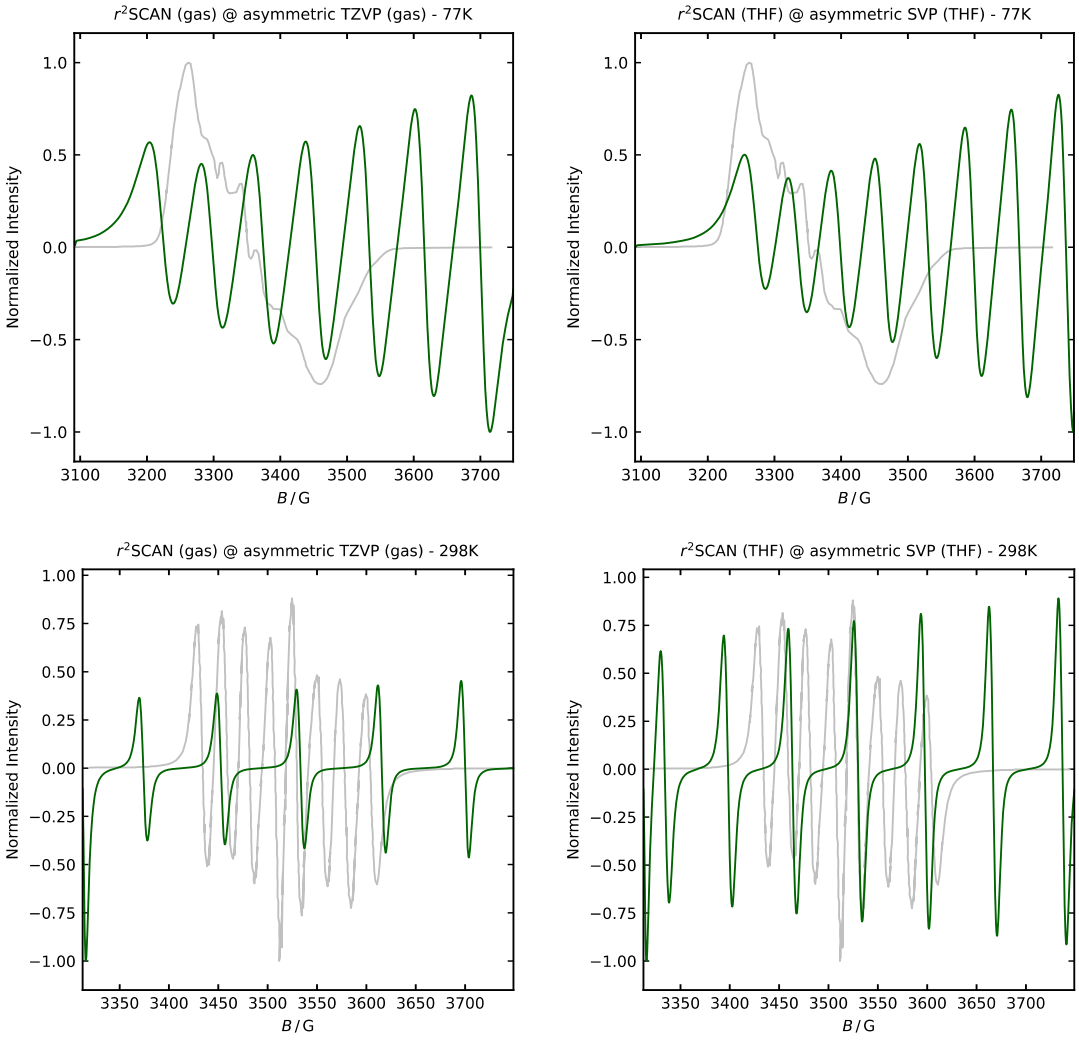


Figure S62. Simulated EPR spectra (green lines) of La(SAr^{iPr6})$_2$, **2-La**, using the *asymmetric* structure optimized in the gas phase (left) or using the COSMO solvent model for THF (right) with a correlation time of 0.9 ns for the best visual match with the experimental spectrum (gray line) at 77 K (top) and of 0.1 ns for the spectrum at 298 K (bottom).

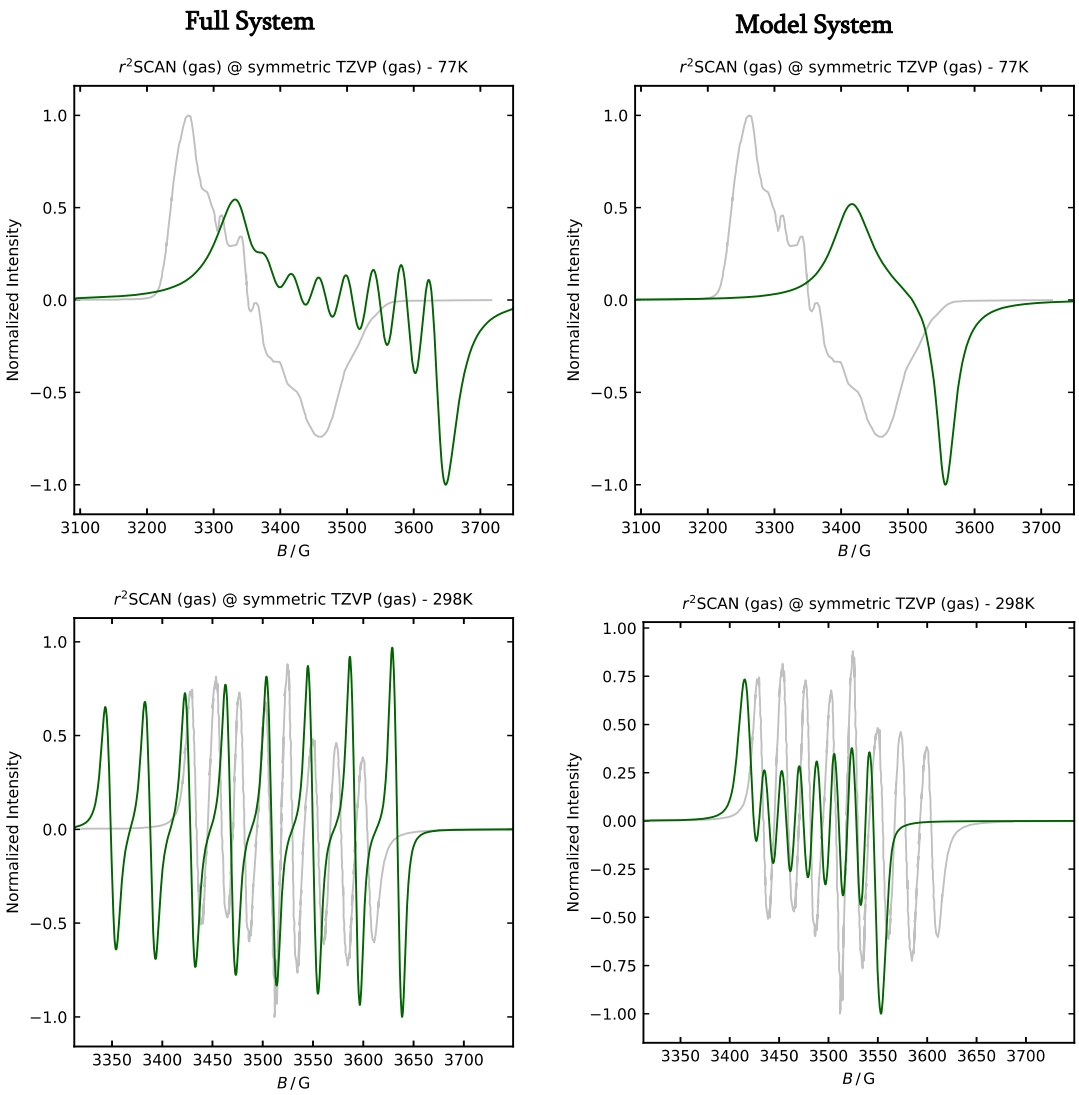


Figure S63. Simulated EPR spectra (green lines) of La(SAr^{iPr6})$_2$, **2-La** (full system, left) and the truncated model system La(SH)$_2$Bz$_2$ (right).

Table S14. Calculated EPR parameters (principal components of the g tensor and the principal components of the hyperfine coupling constant for La)[a]

System	DFA (environ)	Structure[b]		***g* Tensor**			**HFC Constant [MHz]**			
				g_{11}	g_{22}	g_{33}	A_{iso}	A_{11}	A_{22}	A_{33}
2-La (full system)	r^{2}SCAN (gas)	sym.	def2-TZVP (gas)	1.90932	1.98402	2.00034	111.9	104.1	109.6	122.2
	ωB97X-D (gas)	sym.	def2-TZVP (gas)	1.87949	1.98771	2.00025	81.0	59.0	88.0	96.1
	r^{2}SCAN (gas)	sym.	def2-SVP (THF)	1.91176	1.98569	2.00032	87.5	78.9	85.4	98.2
	r^{2}SCAN (THF)	sym.	def2-SVP (THF)	1.91146	1.98669	2.00051	80.1	71.2	77.9	91.3
	r^{2}SCAN (gas)	asym.	def2-TZVP (gas)	1.90523	1.97425	1.98860	220.5	214.4	217.7	229.4
	ωB97X-D (gas)	asym.	def2-TZVP (gas)	1.90783	1.98863	1.99712	180.9	168.3	185.7	188.7
	r^{2}SCAN (gas)	asym.	def2-SVP (THF)	1.90828	1.97444	1.98701	190.8	184.7	187.4	200.2
	r^{2}SCAN (THF)	asym.	def2-SVP (THF)	1.90863	1.97433	1.98658	182.1	175.9	178.7	191.7
La(SH)$_2$Bz$_2$ (model system)	r^{2}SCAN (gas)	sym.	def2-TZVP (gas)	1.91951	1.98882	1.99872	48.9	38.5	45.6	62.8

[a]EPR calculations used a DLU-X2C framework, the x2c-QZVPall-2c basis set for La and x2c-SVLall-2c-unc basis sets on all other atoms.

[b]All structures were optimized with the TPSSh-D3(BJ) functional.

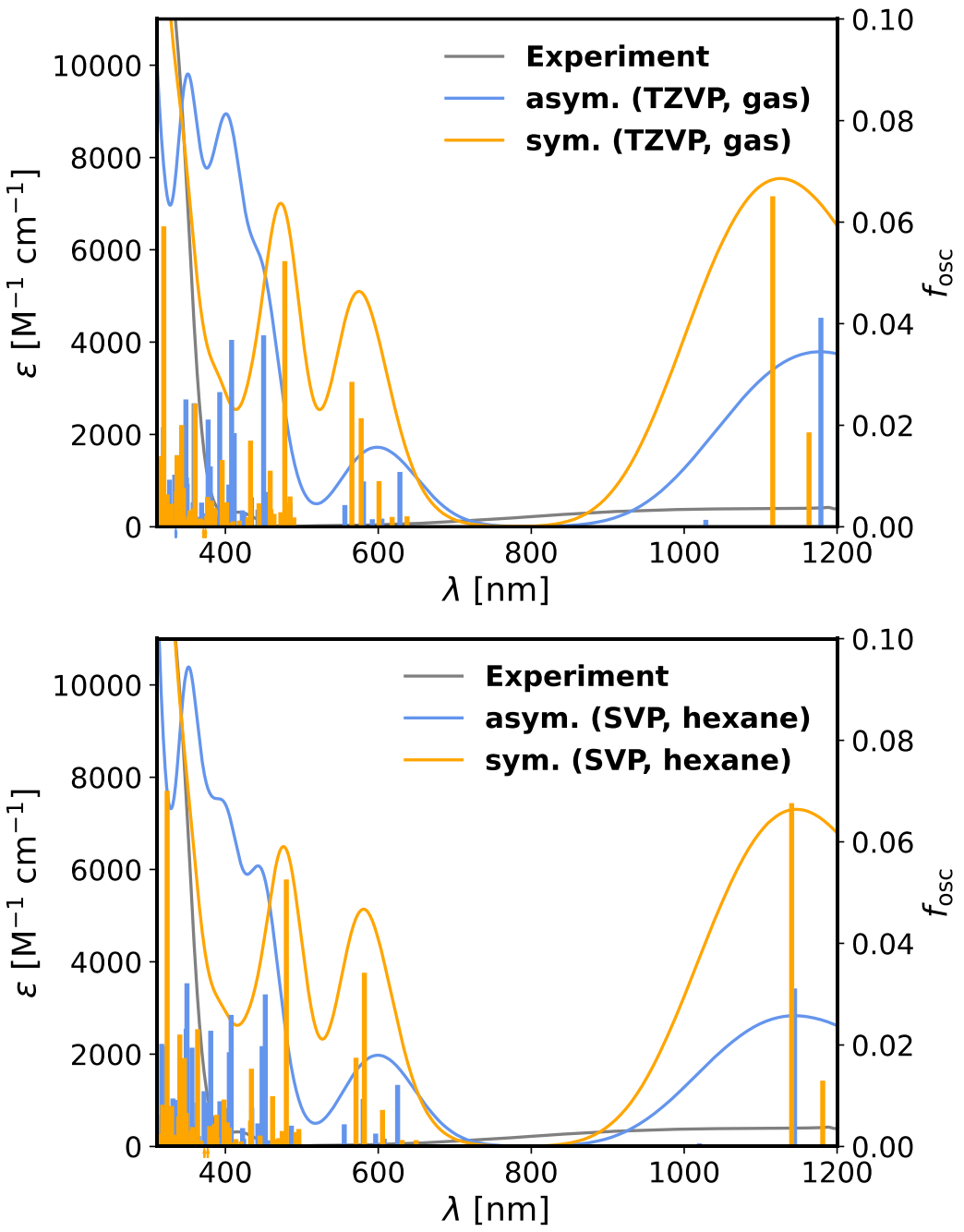


Figure S64. Simulated UV-vis-NIR spectra of La(SAr^{iPr6})$_2$, **2-La**, using the (a)symmetric structures optimized in the gas phase (TPSSh-D3(BJ)/def2-TZVP, top) or using the COSMO solvent model for hexane (TPSSh-D3(BJ)/def2-SVP, bottom). In both gases, the final TDDFT calculations were performed at the same level (TPSSh/def2-SVP level with the COSMO solvent model for hexane).

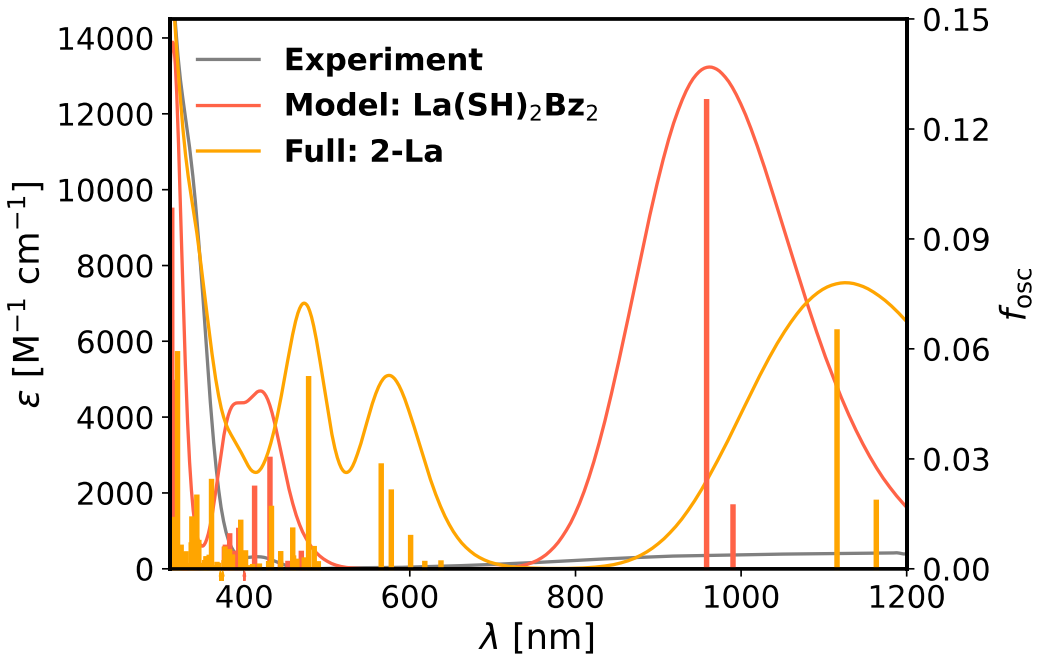


Figure S65. Simulated UV-vis-NIR spectra of La(SAr^{iPr6})$_2$, **2-La** (orange) and the model complex La(SH)$_2$Bz$_2$ (red), using the symmetric structure optimized in the gas phase (TPSSh-D3(BJ)/def2-TZVP). The final TDDFT calculations were performed at the same level (TPSSh/def2-SVP level with the COSMO solvent model for hexane).

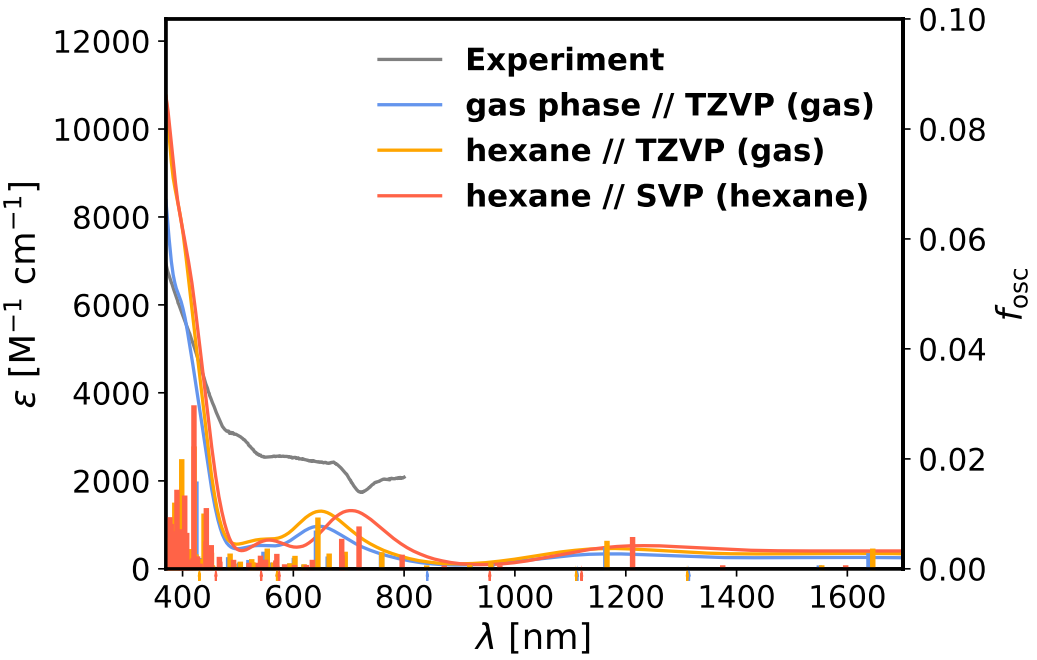


Figure S66. Simulated UV-vis-NIR spectra of Nd(SAr^{iPr6})$_2$, **2-Nd**, using the asymmetric structures optimized in the gas phase (TPSSh-D3(BJ)/def2-TZVP, blue and orange) or using the COSMO solvent model for hexane (TPSSh-D3(BJ)/def2-SVP, red). In both cases, the final TDDFT calculations were performed at the same level (TPSSh/def2-SVP) with or without the COSMO solvent model for hexane as indicated.

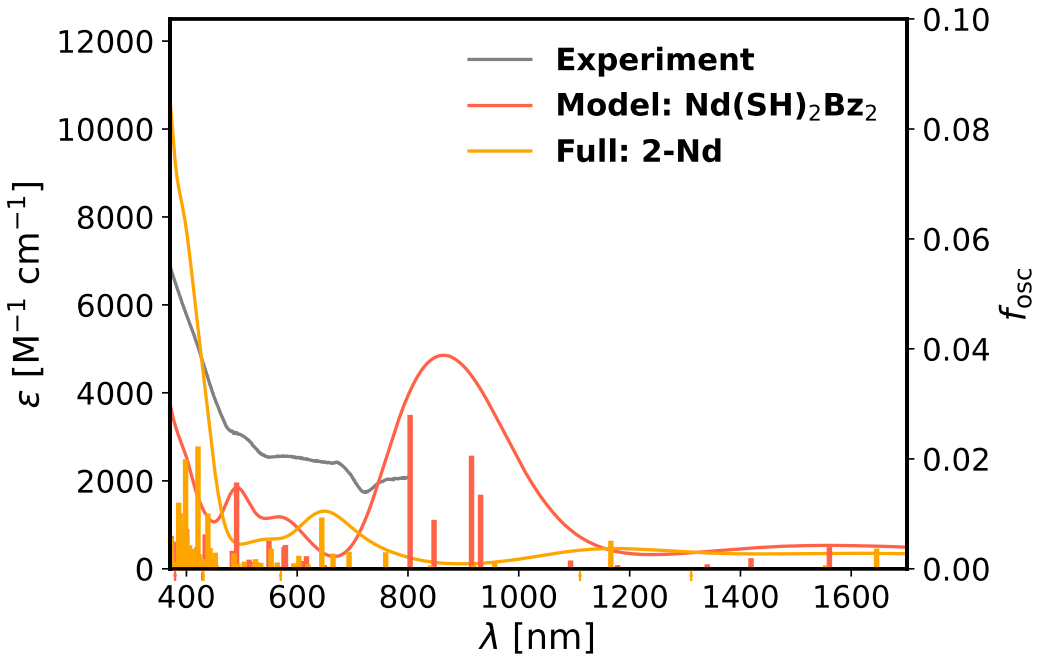


Figure S67. Simulated UV-vis-NIR spectra of Nd(SAr^{iPr6})$_2$, **2-Nd** (orange) and the model complex Nd(SH)$_2$Bz$_2$ (red), using structures optimized in the gas phase (TPSSh-D3(BJ)/def2-TZVP). The final TDDFT calculations were performed at the same level (TPSSh/def2-SVP level with the COSMO solvent model for hexane).

Understanding the Electronic Structure of 2-Nd from a Truncated Model Complex

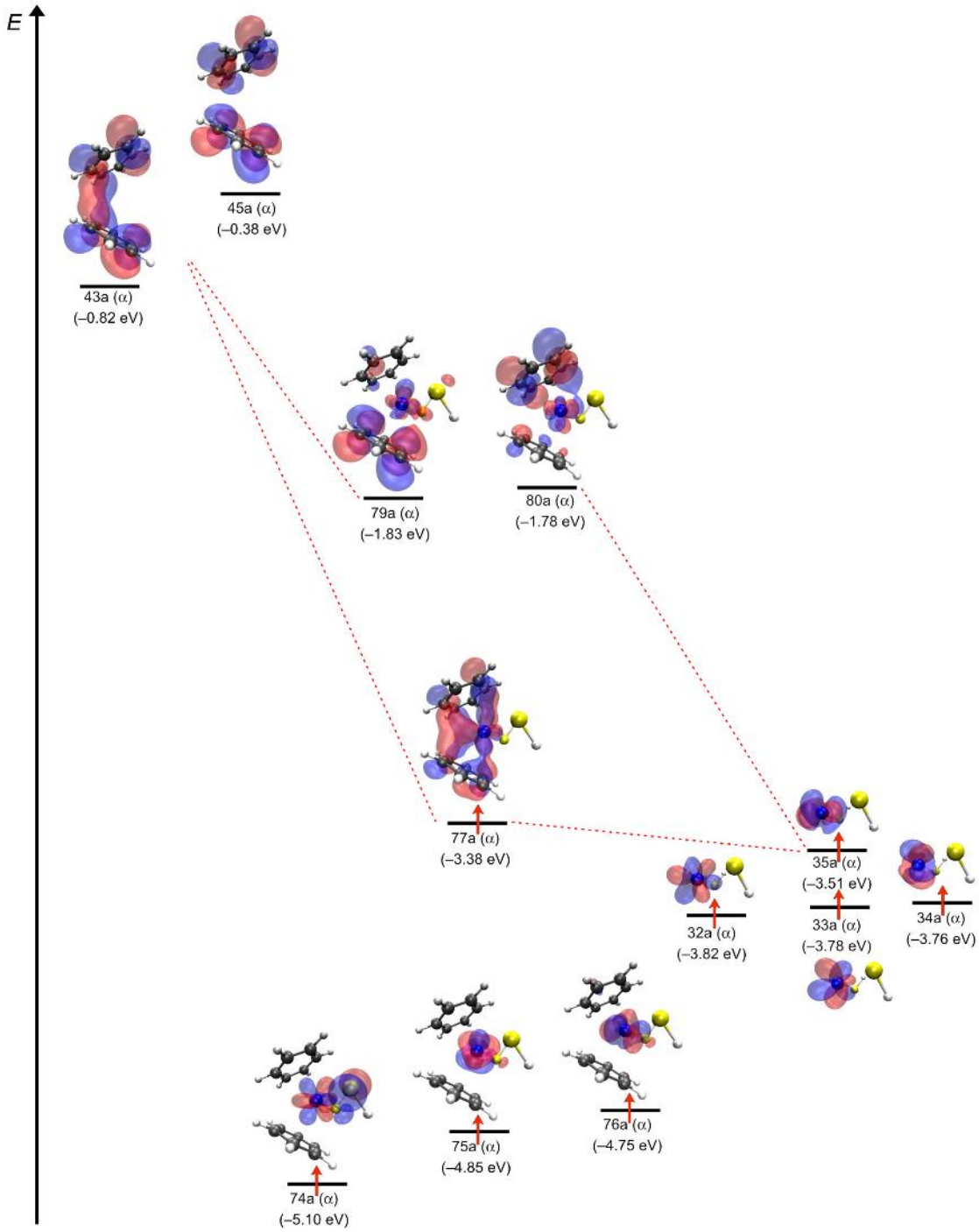


Figure S68. Orbital diagram for the Bz_2 fragment (left), the $Nd(SH)_2$ fragment (right) and the $Nd(SH)_2Bz_2$ model complex for the full complex **2-Nd**. All orbitals are plotted at a contour value of 0.03. The interaction of the occupied f_{xyz}-like orbital (35a) of the $Nd(SH)_2$ fragment with the two virtual π*-like orbitals of the Bz_2 fragment yielding the bonding orbital 77a and the antibonding orbitals 79a and 80a is indicated. Although qualitatively obtained as the antibonding linear combination, 79a and 80a also have some bonding character from a 2-3% contribution of Nd *d* orbitals.

Cartesian Coordinates of DFT optimized structures in Å

(coordinate blocks in the format <atom> <x> <y> <z>, separated by single spaces)

2-La *symmetric* TPSSh-D3(BJ)/def2-TZVP (gas phase)

La -0.0008835 -0.0161236 0.0207419
S -2.5180263 0.4004843 -1.3002119
S 2.4352522 0.8184823 -1.2115998
C 4.4838350 2.6119085 -0.8405618
C -2.6002903 -2.3456015 -1.6263830
C 1.6008728 -2.4575400 -0.5796015
C -3.2849567 -1.1181301 -1.7340149
C 0.0327585 2.9290573 0.1090766
C -4.6110683 -1.1139349 -2.2264133
C 1.1605484 -2.0153367 -1.8349021
C -1.1686304 -2.3595629 -1.2325044
C 3.1841511 2.2120444 -0.4515563
C -6.6731285 2.6401498 -2.6043284
C -0.7546155 -2.8389792 0.0272081
C 3.1136505 4.0651800 1.1202039
C -0.5939982 -1.5436968 -3.5926286
C 2.5102366 2.9526906 0.5359846
C -6.3268368 0.5336424 -1.4308859
C 5.0520125 3.7421948 -0.2558499
C 3.0825752 -2.5573986 -0.2500345
C 6.2627544 0.9387121 -1.4025199
C -5.2192391 -2.3213588 -2.5618391

C -0.1871507 -1.9323194 -2.1867515

C -5.0454540 1.0354478 -3.4395816

C -1.5095380 1.9192711 1.7384795

C 0.6094935 -2.8307772 0.3605399

C -3.2431571 -3.5387938 -1.9584230

C -4.0369300 0.6207259 -4.4950533

C -1.2544596 2.6166094 0.5465775

C -4.5521364 -3.5351101 -2.4215309

C 5.2389856 1.8005237 -1.8347964

C 4.8867952 1.8575252 -3.1954980

C -5.7122091 2.2504751 -3.5381387

C 6.5287343 0.1327209 -3.6862527

C 5.5378324 1.0222136 -4.0970460

C -8.1283526 4.1507401 -4.0142221

C 3.8441876 2.8520867 -3.6712219

C -6.9719634 1.7650884 -1.5687611

C -7.3549107 3.9894925 -2.6993244

C -0.4006536 1.4856464 2.4908063

C 4.3814317 4.4709364 0.7216365

C 0.2608840 3.7647128 -1.1340547

C -5.3504929 0.1711791 -2.3691986

C 1.1382471 2.5495606 0.9361387

C 6.8865962 0.1180144 -2.3425077

C -6.6906411 -0.3679447 -0.2645490

C 0.3062495 -0.4758291 -4.2114896

C 4.5106473 4.1941401 -4.0102298

C 7.1885390 -0.8123819 -4.6689813

C 6.6450825 0.8640530 0.0683659

C -4.7441301 -0.1157026 -5.6426821

C 3.9712721 -2.4756035 -1.4932105

C 0.9154048 1.8359439 2.1239158

C -1.7960412 -3.2553614 1.0544599

C -2.9452301 1.6695422 2.1624643

C 2.0766044 1.3760135 2.9885584

C -0.6501283 -2.7969474 -4.4813126

C 8.0843078 0.4035398 0.3073939

C -1.2474456 -4.1534297 2.1621129

C -6.3431776 5.1303504 -2.5186109

C 7.8782438 -0.0626676 -5.8156176

C -3.1914584 1.7821485 -5.0197150

C 3.0037723 2.3428044 -4.8424964

C 1.9015680 1.7923824 4.4520984

C 2.2783714 -0.1386429 2.8566661

C 6.1775385 -1.8322856 -5.2129438

C 3.4038374 -3.8250229 0.5532270

C -2.4509287 -2.0021193 1.6507119

C -8.1233597 -0.9002107 -0.4026513

C -6.4982132 0.3392235 1.0815830

C -3.0766877 1.0153708 3.5370797

C 5.6618683 -0.0256308 0.8423105

C 0.1896409 5.2563026 -0.7684184

C -0.6966316 3.4346092 -2.2784686

C -3.7576651 2.9736880 2.1295633

H 1.8995345 -1.7165372 -2.5644736

H 2.5764889 4.6178177 1.8839141

H -1.6013872 -1.1294685 -3.5316255

H 6.0439116 4.0457059 -0.5733627

H 3.3393668 -1.6928902 0.3732785

H -6.2365023 -2.3014261 -2.9371450

H 0.9090919 -3.2037622 1.3291533

H -2.6957823 -4.4719987 -1.8735797

H -3.3528528 -0.0867029 -4.0224386

H -2.0965283 2.9185367 -0.0626295

H -5.0422860 -4.4640220 -2.6872331

H -5.4705268 2.9175701 -4.3580156

H 5.2580419 1.0572773 -5.1440609

H -8.8653756 3.3538834 -4.1361384

H -8.6497924 5.1117680 -4.0393547

H -7.4506081 4.1153323 -4.8714381

H 3.1609350 3.0254532 -2.8368327

H -7.7217710 2.0569142 -0.8388913

H -8.0754058 4.0444761 -1.8755432

H -0.5563915 0.9518934 3.4186195

H 4.8416825 5.3453518 1.1656673

H 1.2745185 3.5484094 -1.4771845

H 7.6687263 -0.5627974 -2.0242989

H -6.0148567 -1.2255716 -0.2831004

H 1.3197485 -0.8463157 -4.3873392

H -0.1000534 -0.1649710 -5.1765943

H 0.3760257 0.4019456 -3.5661177

H 5.2220116 4.0749214 -4.8325462

H 3.7599969 4.9313812 -4.3101090

H 5.0519469 4.5879063 -3.1472659

H 7.9576731 -1.3652055 -4.1178786

H 6.5525018 1.8725319 0.4792375

H -5.4614762 0.5443210 -6.1386903

H -4.0184871 -0.4563138 -6.3872309

H -5.2854085 -0.9869068 -5.2677163

H 3.7040824 -3.2511232 -2.2179029

H 3.9006732 -1.4970965 -1.9705228

H 5.0151230 -2.6243897 -1.2100634

H -2.5727663 -3.8060027 0.5187851

H -3.3752941 0.9973126 1.4090669

H 2.9750100 1.8603103 2.6030721

H 0.3428860 -3.2462663 -4.5739937

H -1.3302390 -3.5442078 -4.0685820

H -1.0011147 -2.5325939 -5.4822911

H 8.2236841 -0.6459258 0.0331830

H 8.7969085 1.0012779 -0.2659409

H 8.3323609 0.4978314 1.3678677

H -0.5488538 -3.6121803 2.8072218

H -2.0687679 -4.5017197 2.7922683

H -0.7329198 -5.0277790 1.7570540

H -5.6027745 5.1194791 -3.3230678

H -6.8459372 6.1015502 -2.5348232

H -5.8092166 5.0312946 -1.5706625

H 7.1502578 0.4941584 -6.4116644

H 8.6131228 0.6489915 -5.4327990

H 8.3893193 -0.7636613 -6.4815552

H -3.7893281 2.4956440 -5.5939125

H -2.7133881 2.3135320 -4.1956672

H -2.4100815 1.4041302 -5.6842439

H 3.5919910 2.2596115 -5.7608500

H 2.5764316 1.3658966 -4.6135224

H 2.1837631 3.0377611 -5.0414095

H 1.0367760 1.3049327 4.9102910

H 2.7855596 1.5118855 5.0299392

H 1.7649887 2.8725689 4.5381207

H 1.3998036 -0.6899097 3.2057517

H 2.4736236 -0.4066920 1.8124935

H 3.1422873 -0.4680392 3.4393884

H 5.3845704 -1.3298035 -5.7737859

H 6.6677644 -2.5430859 -5.8843955

H 5.7098143 -2.3900033 -4.3985989

H 3.1395766 -4.7223370 -0.0132903

H 4.4739455 -3.8612079 0.7699290

H 2.8753045 -3.8587916 1.5078219

H -1.6938556 -1.4131573 2.1868980

H -2.8996614 -1.3766728 0.8754060

H -3.2279108 -2.2672729 2.3718206

H -8.8466095 -0.0799015 -0.3949157

H -8.2499517 -1.4477146 -1.3392852

H -8.3659608 -1.5733527 0.4247989

H -7.1747418 1.1918132 1.1857068

H -6.6976698 -0.3492726 1.9080306

H -5.4759297 0.7064810 1.1738835

H -2.6849048 1.6679126 4.3232517

H -4.1302079 0.8265461 3.7529958

H -2.5532471 0.0597810 3.5936048

H 5.7462264 -1.0626661 0.5078360

H 5.8762951 0.0064868 1.9149203

H 4.6331460 0.2994015 0.6790284

H -0.8084843 5.5131577 -0.4021331

H 0.9159414 5.5067575 0.0068876

H 0.4011943 5.8712634 -1.6468505

H -1.7344076 3.6731764 -2.0312446

H -0.4257234 4.0170233 -3.1624900

H -0.6526034 2.3746753 -2.5356536

H -3.3305052 3.7105428 2.8155404

H -3.7862824 3.4090242 1.1302772

H -4.7882752 2.7775965 2.4333077

2-La *asymmetric* TPSSh-D3(BJ)/def2-TZVP (gas phase)

La 0.0089386 0.0054656 0.0101160

S -2.6506445 -0.4834782 -0.9241220

S 2.6030516 -0.0600747 -1.1703614

C -3.1770829 -2.1603887 -0.9073533

C -4.4863520 -2.4778030 -1.3341618

C -4.9045327 -3.8062276 -1.3411694

H -5.9104491 -4.0307636 -1.6785528

C -4.0642607 -4.8310623 -0.9166201

H -4.4032810 -5.8599117 -0.9302746

C -2.7900831 -4.5181026 -0.4604577

H -2.1273145 -5.3012257 -0.1072478

C -2.3440339 -3.1965355 -0.4496942

C -5.4102187 -1.3784919 -1.7305257

C -5.3931174 -0.8836506 -3.0451797

C -6.2032212 0.1997687 -3.3700237

H -6.1834591 0.5841761 -4.3849061

C -7.0224669 0.8125765 -2.4230751

C -7.0405262 0.2909114 -1.1345114

H -7.6810212 0.7590714 -0.3924011

C -6.2521622 -0.7999954 -0.7681909

C -4.5157358 -1.5237747 -4.1041717

H -3.8375669 -2.2112191 -3.5932424

C -5.3632173 -2.3472203 -5.0844363

H -5.9282383 -3.1220665 -4.5609984

H -4.7273202 -2.8294124 -5.8325112

H -6.0783476 -1.7060773 -5.6077359

C -3.6561345 -0.4957045 -4.8438448

H -4.2691888 0.1910161 -5.4343513

H -2.9679884 -0.9989698 -5.5287651

H -3.0720255 0.0874212 -4.1328436

C -7.8574420 2.0263415 -2.7750932

H -8.4201243 2.3006904 -1.8756556

C -8.8697020 1.7232137 -3.8872802

H -9.4923963 2.5989733 -4.0906077

H -9.5215706 0.8927184 -3.6072652

H -8.3605188 1.4514931 -4.8159790

C -6.9677318 3.2184863 -3.1540938

H -6.3827591 2.9963082 -4.0509005

H -6.2688082 3.4553668 -2.3489565

H -7.5750824 4.1047930 -3.3586940

C -6.2912068 -1.3124406 0.6606724

H -5.7065719 -2.2341914 0.6954764

C -7.7173488 -1.6542420 1.1069897

H -7.7088621 -2.0809278 2.1140239

H -8.1763808 -2.3784035 0.4299916

H -8.3528143 -0.7647075 1.1283970

C -5.6331021 -0.3162468 1.6242831

H -6.1797323 0.6309208 1.6393201

H -4.6061988 -0.1124462 1.3153111

H -5.6229948 -0.7171923 2.6425746

C -0.9924159 -2.8829595 0.0849760

C -0.8574600 -2.4539773 1.4232649

C 0.4247614 -2.2206023 1.9452583

H 0.5187173 -1.9177273 2.9808377

C 1.5859885 -2.4456105 1.1842068

C 1.4167462 -2.8387253 -0.1460282

H 2.2939748 -2.9888503 -0.7572500

C 0.1591744 -3.0654862 -0.7186411

C -2.0865025 -2.2782148 2.2973023

H -2.9357819 -2.1401167 1.6258741

C -2.3317578 -3.5538572 3.1154531

H -2.4509923 -4.4182781 2.4599371

H -3.2407892 -3.4494760 3.7130676

H -1.4956082 -3.7484816 3.7933267

C -2.0117839 -1.0475014 3.2032027

H -1.2216311 -1.1312305 3.9540859

H -2.9593158 -0.9194697 3.7307861

H -1.8309714 -0.1369831 2.6220748

C 2.9705909 -2.2959914 1.7979691

H 3.1325776 -1.2282262 1.9839398

C 3.0536141 -3.0262931 3.1468792

H 2.3190256 -2.6581175 3.8655738

H 4.0450366 -2.8868781 3.5836505

H 2.8877957 -4.0988492 3.0132416

C 4.0925952 -2.7644067 0.8710391

H 3.9654716 -3.8176094 0.6017385

H 5.0524644 -2.6659857 1.3814682

H 4.1389535 -2.1643425 -0.0390521

C 0.0426813 -3.5302900 -2.1603812

H -0.8225288 -4.1970601 -2.2047176

C 1.2699701 -4.3102713 -2.6382735

H 2.1461586 -3.6646643 -2.7354666

H 1.0694600 -4.7343728 -3.6244861

H 1.5196529 -5.1282953 -1.9578384

C -0.2410444 -2.3456745 -3.0979620

H -1.1646868 -1.8367793 -2.8179396

H -0.3338127 -2.6936215 -4.1303695

H 0.5806107 -1.6237114 -3.0531077

C 3.2638874 1.5438342 -1.4517486

C 4.5852085 1.6774479 -1.9306729

C 5.0905380 2.9508240 -2.1899794

H 6.1029661 3.0391132 -2.5692173

C 4.3335847 4.0921388 -1.9485955

H 4.7438402 5.0743633 -2.1504843

C 3.0506387 3.9607148 -1.4287890

H 2.4569824 4.8406827 -1.2069488

C 2.5092278 2.6998934 -1.1861916

C 5.4412988 0.4671547 -2.0736688

C 6.3758108 0.1641249 -1.0678109

C 7.1065728 -1.0200878 -1.1655262

H 7.8184710 -1.2740432 -0.3869780

C 6.9436745 -1.9002121 -2.2295079

C 6.0320230 -1.5647143 -3.2287515

H 5.9001954 -2.2350221 -4.0714594

C 5.2738203 -0.3996619 -3.1676752

C 6.5372428 1.0637857 0.1470377

H 6.2362827 2.0709101 -0.1479315

C 5.5863856 0.6193851 1.2682648

H 4.5611741 0.5513885 0.8989536

H 5.6176333 1.3261389 2.1030682

H 5.8767399 -0.3660232 1.6428824

C 7.9783173 1.1468537 0.6571298

H 8.3197226 0.1930422 1.0684109

H 8.0478002 1.8892527 1.4567458

H 8.6662303 1.4365078 -0.1407116

C 7.7258537 -3.1962517 -2.2868224

H 8.3841179 -3.2136714 -1.4110271

C 6.7895936 -4.4098828 -2.1989547

H 6.1829788 -4.3699029 -1.2914572

H 7.3617001 -5.3420485 -2.1942501

H 6.1099262 -4.4349652 -3.0552118

C 8.6065444 -3.2758744 -3.5404600

H 7.9944874 -3.2754225 -4.4464817

H 9.2005446 -4.1941669 -3.5379745

H 9.2869630 -2.4232821 -3.5947117

C 4.3054746 -0.0534134 -4.2830111

H 3.6041223 0.6838476 -3.8855886

C 3.4810486 -1.2552133 -4.7500820

H 4.1022968 -2.0108039 -5.2392340

H 2.7241447 -0.9348637 -5.4711777

H 2.9737185 -1.7171530 -3.9023454

C 5.0527333 0.5966625 -5.4569152

H 5.5854245 1.4933479 -5.1324427

H 4.3535899 0.8797056 -6.2491768

H 5.7852474 -0.0974462 -5.8790560

C 1.1399081 2.5654063 -0.6204558

C 0.0216371 2.4193543 -1.5070908

C -1.2687759 2.4400287 -0.9274707

H -2.1255360 2.4067805 -1.5871293

C -1.4892235 2.4701716 0.4461546

C -0.3525104 2.4325659 1.3101288

H -0.4857279 2.4989140 2.3812588

C 0.9512084 2.5793631 0.7669638

C 0.2163727 2.4805455 -3.0071323

H 1.2288567 2.1203316 -3.2089695

C -0.7622984 1.5911566 -3.7719832

H -0.7296749 0.5626965 -3.4072116

H -0.5176224 1.5897801 -4.8370380

H -1.7907137 1.9471409 -3.6728669

C 0.1197791 3.9330482 -3.5035733

H -0.8754969 4.3388217 -3.2999934

H 0.2944420 3.9821096 -4.5818872

H 0.8567170 4.5680706 -3.0096878

C -2.8858271 2.5374598 1.0411593

H -3.0583221 1.5941026 1.5754225

C -3.9906527 2.6840202 -0.0044922

H -3.8521721 3.5995864 -0.5880574

H -4.9602418 2.7483599 0.4933311

H -4.0243360 1.8295626 -0.6814657

C -2.9829973 3.6782286 2.0671779

H -2.2561996 3.5739243 2.8745285

H -3.9802160 3.6921558 2.5133006

H -2.8123929 4.6431454 1.5817474

C 2.1319396 2.6894782 1.7120133

H 3.0381795 2.5826763 1.1133290

C 2.1332410 1.5728069 2.7606390

H 1.2835814 1.6481391 3.4437636

H 3.0499068 1.6128314 3.3534920

H 2.0987301 0.5877392 2.2833072

C 2.1595428 4.0711163 2.3780391

H 2.2099905 4.8627629 1.6280088

H 3.0309537 4.1609594 3.0318778

H 1.2616324 4.2316556 2.9812786

2-La *symmetric* TPSSh-D3(BJ)/def2-SVP (COSMO, hexane)

La -0.0018137 0.0144899 -0.0703907

S -2.5060665 0.3980779 -1.4158186

S 2.4674826 0.8205860 -1.2636111

C 4.5261678 2.6102103 -0.8459535

C -2.5742383 -2.3660209 -1.7082634

C 1.6297529 -2.4254237 -0.5990867

C -3.2736685 -1.1397007 -1.8161406

C 0.0384620 2.9707036 -0.0546080

C -4.6158888 -1.1488187 -2.2834812

C 1.2012381 -2.0102861 -1.8766138

C -1.1442192 -2.3606338 -1.2935149

C 3.2069591 2.2205244 -0.4867087

C -6.6890446 2.6354430 -2.2995987

C -0.7438832 -2.8137091 -0.0104192

C 3.1028834 4.1019849 1.0685984

C -0.5485132 -1.5695439 -3.6679200

C 2.5045949 2.9805524 0.4762562

C -6.3103154 0.4271852 -1.3104062

C 5.0877841 3.7509166 -0.2568985

C 3.1113754 -2.4971262 -0.2424870

C 6.3121074 0.9060849 -1.3421824

C -5.2135606 -2.3655578 -2.6357090

C -0.1498722 -1.9381335 -2.2481660

C -5.1159816 1.0800591 -3.3487532

C -1.5934437 1.9999109 1.5330904

C 0.6225287 -2.7848068 0.3424502

C -3.2074147 -3.5706690 -2.0508966

C -4.1620196 0.7319528 -4.4838342

C -1.2761250 2.6776949 0.3357058

C -4.5225756 -3.5769297 -2.5196052

C 5.2989793 1.7743449 -1.8118573

C 4.9663215 1.8061814 -3.1864552

C -5.7765692 2.3111308 -3.3156888

C 6.6065306 0.0433931 -3.6170429

C 5.6253637 0.9391086 -4.0636969

C -8.1668122 4.3051789 -3.5116972

C 3.9440225 2.8099960 -3.7021297

C -6.9503018 1.6767662 -1.3179874

C -7.3506234 4.0030297 -2.2454059

C -0.5130347 1.5744640 2.3473890

C 4.3904215 4.4975696 0.6988814

C 0.3234829 3.7832379 -1.3075546

C -5.3792523 0.1330687 -2.3289202

C 1.1102077 2.5952302 0.8293722

C 6.9451404 0.0547732 -2.2598356

C -6.6429061 -0.5780016 -0.2136397

C 0.3406930 -0.4885556 -4.2878061

C 4.6381011 4.1369770 -4.0549793

C 7.2704616 -0.9350508 -4.5725212

C 6.6653950 0.8571520 0.1424661

C -4.9231161 0.0203226 -5.6158441

C 4.0219979 -2.4481193 -1.4749132

C 0.8270433 1.9056694 2.0293899

C -1.8009529 -3.2024344 1.0199296

C -3.0512597 1.7469114 1.8949975

C 1.9557551 1.4361688 2.9398208

C -0.5850703 -2.8346310 -4.5447327

C 8.0951360 0.3830660 0.4248223

C -1.2721204 -4.0943229 2.1459413

C -6.3106111 5.1040943 -1.9761707

C 7.9870170 -0.2208604 -5.7289152

C -3.3674834 1.9313872 -5.0090003

C 3.1035024 2.2845477 -4.8694617

C 1.7274961 1.8272522 4.4051844

C 2.1803060 -0.0760410 2.7785071

C 6.2562626 -1.9663224 -5.0962591

C 3.4386862 -3.7169268 0.6325931

C -2.4572355 -1.9316894 1.5861992

C -8.0591271 -1.1451202 -0.4072686

C -6.4680045 0.0075879 1.1941351

C -3.2464971 1.2282313 3.3222161

C 5.6449539 0.0091677 0.9203705

C 0.2766467 5.2853828 -0.9729889

C -0.6018294 3.4440572 -2.4797268

C -3.9203849 2.9945161 1.6571091

H 1.9537537 -1.7213412 -2.6088044

H 2.5435921 4.6712854 1.8159391

H -1.5702338 -1.1650657 -3.6171698

H 6.0968896 4.0494034 -0.5531833

H 3.3417070 -1.5908954 0.3458730

H -6.2453454 -2.3566907 -2.9961237

H 0.9163339 -3.1317375 1.3316651

H -2.6478672 -4.5063317 -1.9662052

H -3.4298478 0.0176409 -4.0771193

H -2.0906562 2.9822713 -0.3215157

H -5.0047016 -4.5164377 -2.7980721

H -5.5659802 3.0466311 -4.0955229

H 5.3603256 0.9555973 -5.1234590

H -8.9230852 3.5250592 -3.6902435

H -8.6841775 5.2740912 -3.4191263

H -7.5180971 4.3565919 -4.4013910

H 3.2478194 3.0140502 -2.8745423

H -7.6676043 1.9162452 -0.5267309

H -8.0505346 3.9876219 -1.3920214

H -0.7134557 1.0599439 3.2870266

H 4.8468798 5.3813848 1.1494975

H 1.3508637 3.5382290 -1.6153446

H 7.7184699 -0.6344606 -1.9119174

H -5.9350854 -1.4147583 -0.3082338

H 1.3697624 -0.8447205 -4.4568042

H -0.0664305 -0.1829673 -5.2640723

H 0.3942624 0.3993952 -3.6402164

H 5.3639372 3.9956939 -4.8730536

H 3.8992687 4.8898377 -4.3763890

H 5.1803418 4.5379194 -3.1845893

H 8.0338520 -1.4830198 -3.9932330

H 6.5816930 1.8857806 0.5258882

H -5.6864596 0.6862091 -6.0515215

H -4.2326850 -0.2847223 -6.4197753

H -5.4314971 -0.8807254 -5.2396594

H 3.7813367 -3.2600314 -2.1816943

H 3.9412452 -1.4810536 -1.9922227

H 5.0722190 -2.5643573 -1.1688142

H -2.5827148 -3.7586230 0.4807946

H -3.4083117 0.9769682 1.1847139

H 2.8713170 1.9360910 2.5930057

H 0.4201720 -3.2796783 -4.6294661

H -1.2633248 -3.5915684 -4.1234655

H -0.9375263 -2.5861693 -5.5587519

H 8.2304514 -0.6810012 0.1708473

H 8.8347693 0.9657492 -0.1465228

H 8.3234206 0.4941623 1.4968541

H -0.5652196 -3.5518796 2.7953090

H -2.1080327 -4.4272970 2.7798927

H -0.7620039 -4.9869381 1.7522740

H -5.5805147 5.1628698 -2.7999811

H -6.7958445 6.0894604 -1.8814739

H -5.7539495 4.9003072 -1.0480043

H 7.2711965 0.3307846 -6.3599087

H 8.7281274 0.4999967 -5.3500255

H 8.5088284 -0.9480949 -6.3722367

H -4.0125100 2.6612854 -5.5256735

H -2.8500424 2.4434722 -4.1849384

H -2.6095269 1.5935003 -5.7338987

H 3.7024560 2.1539718 -5.7858515

H 2.6456350 1.3197742 -4.6089881

H 2.2962808 2.9968870 -5.1035141

H 0.8491831 1.3176835 4.8336990

H 2.6024036 1.5476359 5.0126860

H 1.5728744 2.9127388 4.5040892

H 1.2960033 -0.6542548 3.0964459

H 2.4097479 -0.3211219 1.7263644

H 3.0413892 -0.4123458 3.3773163

H 5.4648352 -1.4748391 -5.6857106

H 6.7503495 -2.7086098 -5.7445775

H 5.7718132 -2.4991876 -4.2636070

H 3.1954200 -4.6567374 0.1099094

H 4.5135004 -3.7261313 0.8713193

H 2.8926198 -3.7076155 1.5880750

H -1.7032821 -1.3263724 2.1252841

H -2.8990682 -1.3157558 0.7875941

H -3.2519442 -2.1797531 2.3068865

H -8.8164894 -0.3471989 -0.3331323

H -8.1641215 -1.6157408 -1.3970183

H -8.2858575 -1.9027417 0.3610008

H -7.1590969 0.8463082 1.3770921

H -6.6664465 -0.7616166 1.9583224

H -5.4423875 0.3754381 1.3341720

H -2.8959167 1.9629230 4.0660568

H -4.3156918 1.0457117 3.5079226

H -2.7181056 0.2806799 3.5025831

H 5.7276610 -1.0504676 0.6317649

H 5.8216426 0.0844176 2.0062320

H 4.6179603 0.3388109 0.7065499

H -0.7343415 5.5800612 -0.6463975

H 0.9854234 5.5359279 -0.1697744

H 0.5393935 5.8829763 -1.8605251

H -1.6456159 3.7376610 -2.2836372

H -0.2719596 3.9802904 -3.3830995

H -0.5937782 2.3645518 -2.6925398

H -3.5613399 3.8477653 2.2557545

H -3.9332021 3.2882025 0.5980498

H -4.9614496 2.7828763 1.9445772

2-La *asymmetric* TPSSh-D3(BJ)/def2-SVP (COSMO, hexane)

La -0.0172370 0.0347613 -0.0128404

S -2.6454402 -0.4819004 -0.9876485

S 2.5776575 -0.0498039 -1.1825369

C -3.1849533 -2.1609990 -0.9116341

C -4.5129995 -2.4679388 -1.3114228

C -4.9526547 -3.7977601 -1.2806919

H -5.9762490 -4.0177805 -1.5943184

C -4.1144579 -4.8296388 -0.8457264

H -4.4717262 -5.8614440 -0.8286596

C -2.8202563 -4.5251146 -0.4184426

H -2.1579184 -5.3165842 -0.0575793

C -2.3508039 -3.2032570 -0.4457485

C -5.4247397 -1.3554554 -1.7158348

C -5.3392662 -0.8147304 -3.0201899

C -6.1356469 0.2858666 -3.3503861

H -6.0651126 0.7085206 -4.3554259

C -7.0083848 0.8712877 -2.4210324

C -7.0883209 0.3088117 -1.1439858

H -7.7663908 0.7607206 -0.4143303

C -6.3125754 -0.7990415 -0.7700103

C -4.4091070 -1.4488299 -4.0451967

H -3.5890171 -1.9179868 -3.4793850

C -5.1393028 -2.5630900 -4.8146071

H -5.5331593 -3.3268661 -4.1269123

H -4.4571184 -3.0585664 -5.5251517

H -5.9879104 -2.1486382 -5.3837002

C -3.7754232 -0.4367344 -5.0044206

H -4.5172330 0.0020521 -5.6920523

H -3.0078300 -0.9306914 -5.6214092

H -3.2946865 0.3781985 -4.4457359

C -7.8327851 2.0969898 -2.7805942

H -8.4236803 2.3590045 -1.8858009

C -8.8215905 1.8081049 -3.9214743

H -9.4471294 2.6916872 -4.1291088

H -9.4845051 0.9672731 -3.6647611

H -8.2899450 1.5468639 -4.8511713

C -6.9327268 3.2988596 -3.1117659

H -6.3215541 3.1000318 -4.0073337

H -6.2470988 3.5183664 -2.2789777

H -7.5387696 4.1980578 -3.3101579

C -6.3701096 -1.3289932 0.6579032

H -5.9485610 -2.3454666 0.6436655

C -7.7988496 -1.4307839 1.2074246

H -7.7912194 -1.9060674 2.2016667

H -8.4406643 -2.0309342 0.5433723

H -8.2638377 -0.4380447 1.3218969

C -5.4739185 -0.4830335 1.5787245

H -5.8627349 0.5451483 1.6631467

H -4.4525744 -0.4237124 1.1731985

H -5.4335985 -0.9182048 2.5913631

C -0.9807707 -2.8987933 0.0614205

C -0.8135162 -2.4669575 1.4045653

C 0.4878429 -2.2459846 1.9029916

H 0.6047095 -1.9422707 2.9452097

C 1.6383149 -2.4750818 1.1160676

C 1.4379176 -2.8767722 -0.2167334

H 2.3078675 -3.0325874 -0.8508155

C 0.1615186 -3.1012568 -0.7642673

C -2.0238082 -2.2848936 2.3112306

H -2.8982742 -2.1729932 1.6540902

C -2.2387567 -3.5496457 3.1590591

H -2.3620740 -4.4336946 2.5159831

H -3.1444541 -3.4453859 3.7772563

H -1.3817064 -3.7276535 3.8292857

C -1.9387254 -1.0279089 3.1850927

H -1.1185442 -1.0814920 3.9189995

H -2.8776767 -0.8931481 3.7428847

H -1.7870481 -0.1214526 2.5728981

C 3.0394215 -2.3160406 1.7010570

H 3.1907675 -1.2362770 1.8759584

C 3.1582262 -3.0322366 3.0576788

H 2.4318310 -2.6578834 3.7946846

H 4.1649197 -2.8786632 3.4759204

H 2.9973331 -4.1165290 2.9413602

C 4.1483499 -2.7705391 0.7475374

H 4.0322402 -3.8339362 0.4791932

H 5.1275094 -2.6554614 1.2352347

H 4.1650071 -2.1660663 -0.1712367

C 0.0143754 -3.5596868 -2.2107980

H -0.8715102 -4.2131448 -2.2431622

C 1.2171059 -4.3686452 -2.7115202

H 2.1153832 -3.7402088 -2.8176934

H 0.9927948 -4.7859631 -3.7049416

H 1.4580698 -5.2029989 -2.0340085

C -0.2661957 -2.3626747 -3.1380537

H -1.1849125 -1.8381819 -2.8379530

H -0.3823026 -2.7034358 -4.1792756

H 0.5700425 -1.6443258 -3.1016113

C 3.2478358 1.5634019 -1.4418267

C 4.5799093 1.6969427 -1.9114766

C 5.0922655 2.9785165 -2.1600007

H 6.1150777 3.0695447 -2.5349735

C 4.3312755 4.1248913 -1.9122428

H 4.7484202 5.1158113 -2.1042426

C 3.0375947 3.9922042 -1.3992516

H 2.4402160 4.8786216 -1.1716246

C 2.4876419 2.7235016 -1.1714092

C 5.4338142 0.4791721 -2.0493851

C 6.3689464 0.1715291 -1.0339618

C 7.0979639 -1.0229545 -1.1278828

H 7.8095738 -1.2812269 -0.3391760

C 6.9314188 -1.9116189 -2.1948778

C 6.0154340 -1.5733586 -3.2005747

H 5.8786373 -2.2511652 -4.0470546

C 5.2595859 -0.3972290 -3.1450688

C 6.5209193 1.0706521 0.1887027

H 6.2375855 2.0883854 -0.1174080

C 5.5318710 0.6434018 1.2868948

H 4.5104618 0.5771106 0.8834114

H 5.5395473 1.3629122 2.1223690

H 5.8030648 -0.3481698 1.6837824

C 7.9544341 1.1393734 0.7286489

H 8.2826047 0.1746589 1.1489451

H 8.0182333 1.8856447 1.5367809

H 8.6672016 1.4254005 -0.0608303

C 7.7131731 -3.2145385 -2.2487289

H 8.3549906 -3.2401069 -1.3511148

C 6.7756013 -4.4317888 -2.1870715

H 6.1394244 -4.3937105 -1.2894014

H 7.3530807 -5.3705493 -2.1652277

H 6.1128141 -4.4636513 -3.0673613

C 8.6307805 -3.2797159 -3.4801022

H 8.0431109 -3.2675525 -4.4126520

H 9.2301356 -4.2048667 -3.4727922

H 9.3195701 -2.4211024 -3.5042873

C 4.2902457 -0.0460375 -4.2651639

H 3.5726057 0.6800168 -3.8535604

C 3.4773134 -1.2503052 -4.7532165

H 4.1077723 -1.9955274 -5.2658960

H 2.7045312 -0.9241051 -5.4677260

H 2.9771194 -1.7386948 -3.9045656

C 5.0362380 0.6418569 -5.4213532

H 5.5591274 1.5447077 -5.0694019

H 4.3344493 0.9389228 -6.2182120

H 5.7874589 -0.0357288 -5.8602137

C 1.1077850 2.5808049 -0.6217108

C -0.0032664 2.4186479 -1.5316237

C -1.3104541 2.4453565 -0.9644490

H -2.1635622 2.4171130 -1.6426268

C -1.5518789 2.4689348 0.4120116

C -0.4197189 2.4218359 1.2999926

H -0.5707869 2.4927990 2.3774928

C 0.8989947 2.5855521 0.7698668

C 0.2103402 2.4852711 -3.0344505

H 1.2350312 2.1264678 -3.2231206

C -0.7503227 1.5841987 -3.8154029

H -0.7097552 0.5474055 -3.4504302

H -0.4934391 1.5883099 -4.8863782

H -1.7929664 1.9278070 -3.7254141

C 0.1195285 3.9399475 -3.5324287

H -0.8881849 4.3488215 -3.3498818

H 0.3200747 3.9943922 -4.6149642

H 0.8483182 4.5825244 -3.0173259

C -2.9610257 2.5256639 0.9910790

H -3.1236272 1.5750826 1.5329015

C -4.0603948 2.6391678 -0.0682862

H -3.9442503 3.5629951 -0.6593927

H -5.0462808 2.6744046 0.4192031

H -4.0611499 1.7753135 -0.7486019

C -3.0837276 3.6696642 2.0146127

H -2.3551605 3.5774125 2.8337663

H -4.0911186 3.6712212 2.4594915

H -2.9232953 4.6446993 1.5258861

C 2.0732527 2.6670399 1.7338464

H 2.9901440 2.5808418 1.1325442

C 2.0686496 1.5018480 2.7341842

H 1.2162752 1.5500980 3.4303276

H 2.9941311 1.5038396 3.3302514

H 2.0287536 0.5300116 2.2103997

C 2.1023915 4.0260045 2.4493948

H 2.1667818 4.8487482 1.7212898

H 2.9743540 4.0898938 3.1198791

H 1.1933782 4.1765016 3.0544814

2-La *symmetric* TPSSh-D3(BJ)/def2-SVP (COSMO, THF)

La -0.0069354 -0.0271929 0.0263079

S -2.5169398 0.3889245 -1.3066729

S 2.4124418 0.8360824 -1.2317349

C 4.4623654 2.6431281 -0.8419962

C -2.5946082 -2.3766810 -1.5962980

C 1.6326540 -2.4460133 -0.5645265

C -3.2832420 -1.1443552 -1.7230998

C -0.0028803 2.9248087 0.1217692

C -4.6115024 -1.1441469 -2.2303167

C 1.1774136 -2.0180521 -1.8284038

C -1.1578729 -2.3782925 -1.2042492

C 3.1605892 2.2278369 -0.4485812

C -6.5816200 2.6787651 -2.6266950

C -0.7290159 -2.8530470 0.0627843

C 3.0843589 4.0747991 1.1503371

C -0.5973101 -1.5749687 -3.5875541

C 2.4823321 2.9571601 0.5550138

C -6.3089558 0.5461943 -1.4495259

C 5.0288100 3.7790989 -0.2480867

C 3.1221397 -2.5188074 -0.2420617

C 6.2453335 0.9629500 -1.4223529

C -5.2230241 -2.3602640 -2.5606710

C -0.1797208 -1.9462497 -2.1742569

C -4.9943187 1.0136705 -3.4631523

C -1.5542047 1.8951306 1.7516203

C 0.6435208 -2.8246153 0.3900635

C -3.2408226 -3.5795354 -1.9216948

C -3.9879193 0.5646834 -4.5138182

C -1.2970338 2.6041463 0.5583048

C -4.5536104 -3.5792978 -2.3984529

C 5.2139970 1.8335136 -1.8466393

C 4.8400810 1.8869490 -3.2102749

C -5.6252145 2.2564976 -3.5635691

C 6.4728064 0.1386655 -3.7200408

C 5.4762560 1.0386293 -4.1226867

C -7.9725969 4.2693492 -4.0320159

C 3.7935987 2.8912691 -3.6741311

C -6.9170973 1.8050319 -1.5890797

C -7.2108533 4.0600220 -2.7138521

C -0.4372512 1.4554688 2.5050549

C 4.3533948 4.4967676 0.7454884

C 0.2230623 3.7748350 -1.1183978

C -5.3342534 0.1531258 -2.3895614

C 1.1083339 2.5413821 0.9516221

C 6.8526448 0.1289864 -2.3734164

C -6.7070596 -0.3549392 -0.2874784

C 0.2842675 -0.4954321 -4.2202224

C 4.4646053 4.2305771 -4.0250556

C 7.1100844 -0.8235830 -4.7097110

C 6.6481810 0.8919849 0.0488905

C -4.7084297 -0.1562656 -5.6658400

C 4.0042883 -2.4472008 -1.4940816

C 0.8849911 1.8119179 2.1402047

C -1.7649594 -3.2580600 1.1072682

C -2.9938281 1.6395102 2.1772306

C 2.0530684 1.3236242 2.9878991

C -0.6513934 -2.8392301 -4.4645883

C 8.0891778 0.4208217 0.2743416

C -1.2083437 -4.1387614 2.2282367

C -6.1549036 5.1585400 -2.5014846

C 7.7969417 -0.0903469 -5.8725581

C -3.0901694 1.6957553 -5.0251735

C 2.9190865 2.3796644 -4.8223973

C 1.8941516 1.6917465 4.4684982

C 2.2576196 -0.1871103 2.7912900

C 6.0811994 -1.8449163 -5.2241937

C 3.4708181 -3.7519391 0.6057346

C -2.4306326 -1.9950668 1.6787859

C -8.1413574 -0.8807217 -0.4610567

C -6.5262852 0.3395242 1.0692670

C -3.1242285 1.0029883 3.5636216

C 5.6601636 0.0254427 0.8479246

C 0.1447279 5.2658310 -0.7424787

C -0.7228272 3.4385626 -2.2746315

C -3.8266384 2.9326881 2.1088238

H 1.9147814 -1.7200484 -2.5719587

H 2.5442162 4.6197268 1.9292404

H -1.6161655 -1.1670314 -3.5226202

H 6.0243863 4.0975324 -0.5689585

H 3.3653821 -1.6226578 0.3559907

H -6.2449324 -2.3454667 -2.9485399

H 0.9563129 -3.1830731 1.3694659

H -2.6924989 -4.5203106 -1.8214506

H -3.3303369 -0.1700222 -4.0265221

H -2.1446478 2.9156284 -0.0532217

H -5.0460433 -4.5187251 -2.6593640

H -5.3548912 2.9215449 -4.3872949

H 5.1785798 1.0706185 -5.1734461

H -8.7485956 3.4995780 -4.1675998

H -8.4604743 5.2577050 -4.0462256

H -7.2908998 4.2195016 -4.8969188

H 3.1250635 3.0723882 -2.8191736

H -7.6657962 2.1221230 -0.8561710

H -7.9409126 4.1331278 -1.8893384

H -0.5914933 0.9073907 3.4344467

H 4.8131172 5.3771930 1.1998604

H 1.2476362 3.5646168 -1.4593960

H 7.6368068 -0.5647283 -2.0603209

H -6.0316711 -1.2235771 -0.2993159

H 1.3142513 -0.8480787 -4.3911534

H -0.1283021 -0.2006618 -5.1972613

H 0.3355407 0.3976707 -3.5796895

H 5.1657577 4.1094923 -4.8678070

H 3.7098870 4.9821812 -4.3108886

H 5.0300831 4.6214926 -3.1646036

H 7.8874111 -1.3819026 -4.1599539

H 6.5737054 1.9139426 0.4518304

H -5.4014231 0.5280589 -6.1833681

H -3.9829677 -0.5355868 -6.4048494

H -5.2911903 -1.0102602 -5.2864947

H 3.7496276 -3.2483000 -2.2084002

H 3.9094488 -1.4724508 -1.9946261

H 5.0614413 -2.5661646 -1.2134685

H -2.5450820 -3.8280825 0.5804849

H -3.4130688 0.9419188 1.4277151

H 2.9545305 1.8247532 2.6074957

H 0.3516163 -3.2857094 -4.5674917

H -1.3228534 -3.5957414 -4.0311797

H -1.0214142 -2.5893233 -5.4722380

H 8.2207718 -0.6380288 -0.0025027

H 8.8065550 1.0174488 -0.3113039

H 8.3523047 0.5155464 1.3399575

H -0.4993770 -3.5848638 2.8654023

H -2.0316905 -4.4796519 2.8741461

H -0.6929932 -5.0261552 1.8294823

H -5.4011977 5.1379941 -3.3056460

H -6.6226587 6.1568053 -2.4994850

H -5.6290197 5.0183535 -1.5439484

H 7.0656829 0.4734455 -6.4747369

H 8.5504109 0.6219537 -5.5010576

H 8.2998957 -0.8076061 -6.5416148

H -3.6555453 2.4443784 -5.6044595

H -2.5956540 2.2024153 -4.1839793

H -2.3103308 1.2876823 -5.6877562

H 3.4878694 2.2733844 -5.7609922

H 2.4809645 1.4052699 -4.5640476

H 2.0962449 3.0872300 -5.0128604

H 1.0276169 1.1860962 4.9244581

H 2.7908125 1.3886168 5.0312735

H 1.7601586 2.7775759 4.5918071

H 1.3890013 -0.7659638 3.1479378

H 2.4292478 -0.4158153 1.7242644

H 3.1472977 -0.5378308 3.3373279

H 5.2757322 -1.3433502 -5.7856295

H 6.5585876 -2.5768163 -5.8964226

H 5.6179347 -2.3907257 -4.3877230

H 3.2202366 -4.6834219 0.0714586

H 4.5501715 -3.7609328 0.8234662

H 2.9422602 -3.7592996 1.5707937

H -1.6761037 -1.3802370 2.2060545

H -2.8929955 -1.3851831 0.8868185

H -3.2088142 -2.2524955 2.4137383

H -8.8685345 -0.0516949 -0.4649292

H -8.2501005 -1.4285324 -1.4103562

H -8.4089343 -1.5628683 0.3628100

H -7.1956945 1.2085851 1.1758545

H -6.7479362 -0.3582296 1.8934166

H -5.4915469 0.6904939 1.1816306

H -2.7411493 1.6757232 4.3486819

H -4.1840729 0.8002162 3.7798889

H -2.5845501 0.0484518 3.6386168

H 5.7344695 -1.0275773 0.5347606

H 5.8791741 0.0795961 1.9272523

H 4.6246521 0.3555506 0.6815448

H -0.8638589 5.5222867 -0.3781487

H 0.8694063 5.5141574 0.0474564

H 0.3637778 5.8943843 -1.6205837

H -1.7741616 3.6672130 -2.0362092

H -0.4483107 4.0276974 -3.1636869

H -0.6665694 2.3708218 -2.5338447

H -3.4043878 3.7055969 2.7717234

H -3.8728820 3.3372493 1.0875362

H -4.8602454 2.7314927 2.4292748

2-La *asymmetric* TPSSh-D3(BJ)/def2-SVP (COSMO, THF)

La -0.0160331 0.0376802 -0.0058449

S -2.6418748 -0.4820961 -0.9910802

S 2.5739791 -0.0467344 -1.1926426

C -3.1782831 -2.1621543 -0.9131295

C -4.5050180 -2.4726929 -1.3148054

C -4.9428513 -3.8032261 -1.2825198

H -5.9654674 -4.0271395 -1.5972038

C -4.1036086 -4.8327959 -0.8430835

H -4.4592229 -5.8653066 -0.8237228

C -2.8106658 -4.5248135 -0.4132191

H -2.1486730 -5.3145114 -0.0479817

C -2.3436050 -3.2021370 -0.4428532

C -5.4178983 -1.3617673 -1.7213777

C -5.3324862 -0.8220047 -3.0264595

C -6.1290530 0.2783296 -3.3585044

H -6.0577046 0.7007533 -4.3636269

C -7.0013662 0.8654955 -2.4292471

C -7.0815333 0.3042288 -1.1512773

H -7.7574328 0.7587620 -0.4211351

C -6.3059754 -0.8039279 -0.7761472

C -4.3997832 -1.4557660 -4.0494461

H -3.5801537 -1.9227042 -3.4813002

C -5.1264014 -2.5723866 -4.8190048

H -5.5211097 -3.3355279 -4.1306941

H -4.4413946 -3.0682003 -5.5267405

H -5.9736597 -2.1598775 -5.3919361

C -3.7661471 -0.4436239 -5.0086654

H -4.5081620 -0.0049920 -5.6962722

H -2.9979133 -0.9380263 -5.6246648

H -3.2860926 0.3709883 -4.4488063

C -7.8224970 2.0935311 -2.7886774

H -8.4140351 2.3562112 -1.8946782

C -8.8098314 1.8093268 -3.9321810

H -9.4315699 2.6956872 -4.1393938

H -9.4772456 0.9710688 -3.6774647

H -8.2768524 1.5476840 -4.8611639

C -6.9181589 3.2930250 -3.1172825

H -6.3070020 3.0931998 -4.0127430

H -6.2328369 3.5086806 -2.2831203

H -7.5218977 4.1940678 -3.3144276

C -6.3635408 -1.3314256 0.6526639

H -5.9389420 -2.3466402 0.6406292

C -7.7928617 -1.4356675 1.2007302

H -7.7841916 -1.9071897 2.1967819

H -8.4319701 -2.0413316 0.5385688

H -8.2608213 -0.4437191 1.3104579

C -5.4707052 -0.4811592 1.5728012

H -5.8624860 0.5461429 1.6543550

H -4.4491353 -0.4202966 1.1683097

H -5.4300533 -0.9149511 2.5858674

C -0.9749265 -2.8949144 0.0665142

C -0.8103057 -2.4622935 1.4099172

C 0.4901487 -2.2412211 1.9110486

H 0.6050281 -1.9372853 2.9534757

C 1.6417963 -2.4694800 1.1258066

C 1.4439578 -2.8711066 -0.2075513

H 2.3149942 -3.0274360 -0.8399403

C 0.1687571 -3.0969696 -0.7571191

C -2.0214850 -2.2786177 2.3148163

H -2.8960576 -2.1715749 1.6569102

C -2.2335304 -3.5397642 3.1689769

H -2.3527076 -4.4277798 2.5302323

H -3.1401991 -3.4341348 3.7855527

H -1.3766072 -3.7105956 3.8410961

C -1.9371017 -1.0173546 3.1827151

H -1.1151265 -1.0663585 3.9145284

H -2.8751902 -0.8814742 3.7416424

H -1.7885701 -0.1134427 2.5656226

C 3.0417411 -2.3126487 1.7137545

H 3.1936528 -1.2334427 1.8915685

C 3.1563304 -3.0314638 3.0694578

H 2.4280038 -2.6570609 3.8043447

H 4.1622369 -2.8789780 3.4901030

H 2.9949323 -4.1154204 2.9498754

C 4.1515517 -2.7670707 0.7612306

H 4.0339088 -3.8298827 0.4911729

H 5.1297492 -2.6545199 1.2515392

H 4.1706378 -2.1614868 -0.1568215

C 0.0249620 -3.5578037 -2.2033565

H -0.8570882 -4.2163761 -2.2353551

C 1.2319072 -4.3613184 -2.7027127

H 2.1269345 -3.7278999 -2.8083775

H 1.0096746 -4.7803405 -3.6959353

H 1.4766172 -5.1936029 -2.0240332

C -0.2612527 -2.3637967 -3.1327174

H -1.1822873 -1.8426854 -2.8337250

H -0.3748739 -2.7075736 -4.1733149

H 0.5715338 -1.6413578 -3.0961983

C 3.2443356 1.5670607 -1.4454409

C 4.5761920 1.7025267 -1.9161368

C 5.0895997 2.9847953 -2.1594179

H 6.1124884 3.0781717 -2.5341650

C 4.3293972 4.1308853 -1.9055570

H 4.7471352 5.1226954 -2.0927746

C 3.0359438 3.9963165 -1.3913134

H 2.4402382 4.8826156 -1.1585732

C 2.4855478 2.7268240 -1.1684056

C 5.4285180 0.4839930 -2.0580363

C 6.3618941 0.1707560 -1.0422655

C 7.0848220 -1.0278778 -1.1367414

H 7.7915560 -1.2925422 -0.3457187

C 6.9148079 -1.9147152 -2.2051874

C 6.0026399 -1.5698455 -3.2126328

H 5.8626970 -2.2465318 -4.0594912

C 5.2518142 -0.3902388 -3.1554420

C 6.5179031 1.0675574 0.1816369

H 6.2381909 2.0866669 -0.1232267

C 5.5282696 0.6426319 1.2802524

H 4.5063566 0.5800067 0.8776944

H 5.5389140 1.3619405 2.1157371

H 5.7965078 -0.3500591 1.6760117

C 7.9523211 1.1299096 0.7204504

H 8.2775068 0.1623904 1.1365976

H 8.0184078 1.8732414 1.5311607

H 8.6654015 1.4173924 -0.0686211

C 7.6858543 -3.2241639 -2.2565188

H 8.3257488 -3.2544418 -1.3578618

C 6.7370832 -4.4328541 -2.1953973

H 6.0984384 -4.3867496 -1.2998278

H 7.3070152 -5.3761139 -2.1693522

H 6.0770823 -4.4605784 -3.0780003

C 8.6045751 -3.2994719 -3.4866558

H 8.0181239 -3.2829938 -4.4200711

H 9.1945280 -4.2306113 -3.4766356

H 9.3028557 -2.4481489 -3.5102430

C 4.2828792 -0.0342149 -4.2745512

H 3.5667615 0.6918759 -3.8603789

C 3.4678092 -1.2357626 -4.7658457

H 4.0975931 -1.9809058 -5.2795132

H 2.6960617 -0.9056523 -5.4798277

H 2.9664522 -1.7246193 -3.9181487

C 5.0295589 0.6552649 -5.4295032

H 5.5552361 1.5560515 -5.0754611

H 4.3277458 0.9564016 -6.2249667

H 5.7782566 -0.0234614 -5.8713742

C 1.1062951 2.5829078 -0.6173400

C -0.0053365 2.4182176 -1.5273102

C -1.3128553 2.4461386 -0.9595221

H -2.1661537 2.4177231 -1.6375462

C -1.5534612 2.4700626 0.4170277

C -0.4205761 2.4226733 1.3051494

H -0.5708186 2.4904433 2.3829855

C 0.8982073 2.5882111 0.7742387

C 0.2080367 2.4860208 -3.0300604

H 1.2324723 2.1264508 -3.2189698

C -0.7528184 1.5857285 -3.8116940

H -0.7120437 0.5489066 -3.4466838

H -0.4961465 1.5911635 -4.8828923

H -1.7953417 1.9294528 -3.7201208

C 0.1176776 3.9410019 -3.5275997

H -0.8906757 4.3491193 -3.3461305

H 0.3195296 3.9963746 -4.6100541

H 0.8453567 4.5834070 -3.0102228

C -2.9621352 2.5254983 0.9972401

H -3.1232852 1.5743462 1.5383383

C -4.0621979 2.6390406 -0.0613768

H -3.9471714 3.5636347 -0.6517151

H -5.0477690 2.6724393 0.4269977

H -4.0619321 1.7761091 -0.7429125

C -3.0847965 3.6678413 2.0227398

H -2.3551444 3.5740616 2.8407169

H -4.0918867 3.6673923 2.4685015

H -2.9261667 4.6439020 1.5349253

C 2.0720633 2.6665872 1.7388493

H 2.9893291 2.5825794 1.1377237

C 2.0651180 1.4971250 2.7343593

H 1.2122788 1.5436783 3.4297233

H 2.9900516 1.4951645 3.3311608

H 2.0249322 0.5272889 2.2064342

C 2.1008805 4.0223706 2.4606940

H 2.1652985 4.8489472 1.7365464

H 2.9727330 4.0821439 3.1317010

H 1.1919163 4.1686526 3.0668763

2-Nd *asymmetric* TPSSh-D3(BJ)/def2-TZVP (gas phase)

Nd 0.0031811 -0.0029902 0.0269628

S -2.6104682 -0.5198999 -0.8198881

S 2.6149927 -0.0190683 -0.9762616

C -3.1525406 -2.1913487 -0.8195438

C -4.4814467 -2.4873016 -1.1971816

C -4.9114692 -3.8123523 -1.2205449

H -5.9327826 -4.0205860 -1.5202670

C -4.0636322 -4.8536783 -0.8558741

H -4.4130282 -5.8790133 -0.8785215

C -2.7685071 -4.5623557 -0.4463592

H -2.0989802 -5.3592610 -0.1395512

C -2.3086052 -3.2453258 -0.4241946

C -5.4199598 -1.3773814 -1.5243375

C -5.4181678 -0.8072262 -2.8086318

C -6.2715673 0.2582019 -3.0770916

H -6.2688740 0.6949900 -4.0706286

C -7.1160435 0.7864406 -2.1019572

C -7.1032310 0.2053448 -0.8393200

H -7.7537040 0.6142745 -0.0717139

C -6.2725061 -0.8724269 -0.5299005

C -4.5097445 -1.3484168 -3.8966065

H -3.7741614 -1.9965307 -3.4145648

C -5.3065966 -2.2031131 -4.8921510

H -5.8083870 -3.0301703 -4.3845720

H -4.6469637 -2.6191474 -5.6592989

H -6.0718032 -1.6007560 -5.3903466

C -3.7396542 -0.2351230 -4.6123192

H -4.4084123 0.4152089 -5.1831562

H -3.0153031 -0.6621725 -5.3114467

H -3.2003459 0.3735489 -3.8860762

C -8.0137442 1.9699704 -2.3990974

H -8.5643526 2.1942246 -1.4786153

C -9.0402270 1.6446652 -3.4923793

H -9.7081945 2.4944664 -3.6594190

H -9.6453754 0.7783042 -3.2159415

H -8.5425633 1.4177428 -4.4392397

C -7.1941028 3.2132693 -2.7708267

H -6.6242618 3.0431461 -3.6883517

H -6.4853321 3.4647093 -1.9790816

H -7.8495419 4.0730542 -2.9362744

C -6.2536029 -1.4298519 0.8826441

H -5.7105660 -2.3770714 0.8565567

C -7.6583166 -1.7191819 1.4211685

H -7.5968021 -2.1857690 2.4083793

H -8.2021366 -2.3934288 0.7554318

H -8.2462633 -0.8033545 1.5254210

C -5.4821162 -0.4882199 1.8184858

H -5.9830224 0.4816458 1.8899648

H -4.4726955 -0.3214238 1.4363911

H -5.4160950 -0.9130191 2.8250467

C -0.9300721 -2.9634203 0.0573606

C -0.7312754 -2.5450497 1.3928413

C 0.5748222 -2.3765640 1.8694116

H 0.7180662 -2.0887993 2.9048087

C 1.6995997 -2.6136259 1.0659875

C 1.4720245 -2.9765456 -0.2633902

H 2.3216385 -3.1237636 -0.9141843

C 0.1857501 -3.1660083 -0.7827041

C -1.9134916 -2.3342227 2.3213778

H -2.7998798 -2.2305573 1.6940742

C -2.1078520 -3.5663918 3.2154696

H -2.2527044 -4.4619278 2.6079856

H -2.9862138 -3.4389882 3.8532769

H -1.2364645 -3.7251239 3.8571872

C -1.7867371 -1.0548520 3.1517367

H -0.9403001 -1.0894897 3.8430300

H -2.6918634 -0.8995265 3.7427655

H -1.6703709 -0.1757675 2.5064675

C 3.1021344 -2.5049763 1.6431771

H 3.2545620 -1.4540897 1.9118012

C 3.2300830 -3.3453256 2.9238610

H 2.4995866 -3.0578036 3.6827244

H 4.2266565 -3.2195061 3.3535434

H 3.0865081 -4.4064149 2.7021644

C 4.1999009 -2.8816074 0.6498863

H 4.0849464 -3.9155310 0.3095399

H 5.1753318 -2.7985056 1.1326124

H 4.2017739 -2.2166281 -0.2149749

C 0.0028885 -3.5508493 -2.2410794

H -0.9455066 -4.0872372 -2.3169859

C 1.1109172 -4.4675338 -2.7669739

H 2.0701203 -3.9483771 -2.8359404

H 0.8543427 -4.8110064 -3.7716542

H 1.2413619 -5.3445730 -2.1281796

C -0.1119625 -2.2816823 -3.0994736

H -0.9633677 -1.6759373 -2.7787502

H -0.2507875 -2.5391940 -4.1527196

H 0.7998349 -1.6823977 -3.0127839

C 3.3241034 1.5843713 -1.0925547

C 4.6682582 1.7418989 -1.4958228

C 5.1898646 3.0287005 -1.6329616

H 6.2193785 3.1380497 -1.9571374

C 4.4271003 4.1561823 -1.3488797

H 4.8521804 5.1465091 -1.4608719

C 3.1170770 3.9994774 -0.9086130

H 2.5134402 4.8663419 -0.6623285

C 2.5645041 2.7273950 -0.7824155

C 5.5312827 0.5465523 -1.7110877

C 6.4644037 0.1788278 -0.7246367

C 7.2264782 -0.9739601 -0.9168652

H 7.9400369 -1.2744602 -0.1569591

C 7.0932172 -1.7650865 -2.0526177

C 6.1762837 -1.3708833 -3.0245449

H 6.0662108 -1.9689150 -3.9226634

C 5.3913669 -0.2316662 -2.8736537

C 6.5905062 0.9762445 0.5641532

H 6.3141011 2.0080602 0.3382011

C 5.5883934 0.4604407 1.6078215

H 4.5821407 0.4168226 1.1866774

H 5.5766250 1.1105422 2.4881182

H 5.8626560 -0.5476097 1.9314066

C 8.0098603 0.9957622 1.1363062

H 8.3171376 0.0085494 1.4919260

H 8.0594158 1.6783521 1.9889065

H 8.7349399 1.3264779 0.3889099

C 7.9125995 -3.0290467 -2.2143856

H 8.5833453 -3.0894907 -1.3501196

C 7.0147215 -4.2744378 -2.2029157

H 6.4306106 -4.3265859 -1.2815834

H 7.6145390 -5.1853477 -2.2857909

H 6.3146496 -4.2531131 -3.0427559

C 8.7778661 -2.9930556 -3.4807142

H 8.1545415 -2.9491529 -4.3779565

H 9.3987034 -3.8908967 -3.5487384

H 9.4326150 -2.1187564 -3.4838071

C 4.4332719 0.1858033 -3.9739458

H 3.7058542 0.8689725 -3.5304670

C 3.6499023 -0.9917997 -4.5588054

H 4.2987069 -1.6802669 -5.1075652

H 2.8903001 -0.6296062 -5.2569586

H 3.1487793 -1.5455762 -3.7635579

C 5.1880653 0.9501102 -5.0720142

H 5.6963568 1.8246039 -4.6597187

H 4.4990367 1.2886038 -5.8513988

H 5.9428620 0.3093636 -5.5369581

C 1.1626046 2.5585177 -0.3159715

C 0.1119275 2.4910258 -1.2661589

C -1.2222549 2.4471645 -0.8020722

H -2.0247664 2.4483887 -1.5272958

C -1.5392225 2.4002517 0.5548112

C -0.4701127 2.3135261 1.4732204

H -0.6850214 2.2587366 2.5337614

C 0.8761623 2.4380152 1.0523702

C 0.4079970 2.5875570 -2.7492760

H 1.4643333 2.3416822 -2.8786718

C -0.4097970 1.5969445 -3.5795451

H -0.2765782 0.5736713 -3.2223312

H -0.0906834 1.6304385 -4.6242209

H -1.4767856 1.8272306 -3.5515766

C 0.1896737 4.0257206 -3.2430082

H -0.8525422 4.3266385 -3.1020298

H 0.4256572 4.1038135 -4.3075996

H 0.8246372 4.7276834 -2.6991975

C -2.9704249 2.4609313 1.0644272

H -3.1675467 1.5169706 1.5848565

C -4.0161430 2.6091933 -0.0391748

H -3.8593277 3.5351867 -0.6015698

H -5.0117826 2.6553605 0.4068916

H -4.0046744 1.7629687 -0.7273208

C -3.1209750 3.6024109 2.0840382

H -2.4297835 3.5018475 2.9227374

H -4.1380379 3.6113542 2.4831240

H -2.9338680 4.5682353 1.6065585

C 1.9823686 2.4009230 2.0866038

H 2.9299660 2.3722275 1.5459998

C 1.8940020 1.1288435 2.9365990

H 0.9641150 1.0844841 3.5098922

H 2.7274198 1.0775998 3.6409815

H 1.9577387 0.2395216 2.2992559

C 1.9685478 3.6611003 2.9598439

H 2.0804774 4.5578351 2.3468401

H 2.7894853 3.6335110 3.6811412

H 1.0307049 3.7455870 3.5159870

2-Nd *asymmetric* TPSSh-D3(BJ)/def2-SVP (COSMO, hexane)

Nd 0.0139335 -0.0241091 0.1061830

S -2.5965882 -0.5130412 -0.7974306

S 2.6253101 -0.0186840 -0.9219140

C -3.1312596 -2.1945782 -0.7935181

C -4.4624692 -2.4984244 -1.1841542

C -4.8889393 -3.8331738 -1.2048571

H -5.9152876 -4.0502301 -1.5120225

C -4.0331105 -4.8743613 -0.8305543

H -4.3811729 -5.9093682 -0.8508182

C -2.7317483 -4.5759904 -0.4203096

H -2.0541825 -5.3755842 -0.1087944

C -2.2754453 -3.2494175 -0.3990783

C -5.3923536 -1.3854948 -1.5429360

C -5.3158676 -0.7966492 -2.8264121

C -6.1512402 0.2835755 -3.1279044

H -6.0912006 0.7390517 -4.1192858

C -7.0519302 0.8060346 -2.1881056

C -7.1139470 0.2040658 -0.9279375

H -7.8108512 0.6094557 -0.1888403

C -6.3008972 -0.8868382 -0.5843058

C -4.3519596 -1.3545847 -3.8645855

H -3.5336165 -1.8385519 -3.3096971

C -5.0415629 -2.4383943 -4.7104498

H -5.4279259 -3.2483157 -4.0727232

H -4.3356317 -2.8784681 -5.4342869

H -5.8907549 -2.0134457 -5.2710166

C -3.7198238 -0.2720585 -4.7449571

H -4.4558430 0.1943169 -5.4206474

H -2.9263785 -0.7079142 -5.3730060

H -3.2720159 0.5150582 -4.1218157

C -7.9300892 2.0024676 -2.5188363

H -8.5226377 2.2238059 -1.6142910

C -8.9177425 1.6889690 -3.6544566

H -9.5822797 2.5480694 -3.8434227

H -9.5420329 0.8170626 -3.4045539

H -8.3843933 1.4640609 -4.5925845

C -7.0887943 3.2487290 -2.8390491

H -6.4815360 3.0934646 -3.7456931

H -6.4029908 3.4843551 -2.0107641

H -7.7370931 4.1230127 -3.0139754

C -6.3334435 -1.4569096 0.8285166

H -5.9103774 -2.4716320 0.7784292

C -7.7490822 -1.5759058 1.4061265

H -7.7198261 -2.0807387 2.3852746

H -8.4053782 -2.1563709 0.7387248

H -8.2115774 -0.5875189 1.5611735

C -5.4174631 -0.6326476 1.7499130

H -5.8132534 0.3888548 1.8758240

H -4.4093679 -0.5513700 1.3152472

H -5.3436568 -1.0975301 2.7474130

C -0.8956990 -2.9551850 0.0870775

C -0.7021731 -2.5499637 1.4348354

C 0.6079862 -2.3716900 1.9221191

H 0.7414148 -2.0975512 2.9712313

C 1.7441420 -2.5851315 1.1161532

C 1.5206798 -2.9401866 -0.2258922

H 2.3792867 -3.0737029 -0.8805508

C 0.2335211 -3.1418872 -0.7555236

C -1.8877184 -2.3455091 2.3678680

H -2.7882756 -2.3113152 1.7393011

C -2.0286321 -3.5331198 3.3327476

H -2.1379265 -4.4769853 2.7775813

H -2.9169261 -3.4049846 3.9715982

H -1.1448046 -3.6200331 3.9860815

C -1.8013898 -1.0116620 3.1202752

H -0.9515739 -0.9814367 3.8212050

H -2.7197904 -0.8372037 3.7007739

H -1.7074036 -0.1656345 2.4156007

C 3.1519587 -2.4596634 1.6913000

H 3.3065249 -1.3888806 1.9098216

C 3.2830665 -3.2359213 3.0132258

H 2.5663299 -2.8909258 3.7737486

H 4.2951658 -3.1057901 3.4268291

H 3.1153971 -4.3135906 2.8526295

C 4.2485526 -2.8719082 0.7056963

H 4.1261583 -3.9201181 0.3852282

H 5.2337039 -2.7843431 1.1872058

H 4.2564330 -2.2202317 -0.1802589

C 0.0606961 -3.5241544 -2.2213741

H -0.8357172 -4.1608581 -2.2804650

C 1.2447789 -4.3163890 -2.7883373

H 2.1471754 -3.6909167 -2.8804847

H 0.9964453 -4.6798560 -3.7972051

H 1.4919437 -5.1869299 -2.1602797

C -0.2116392 -2.2659045 -3.0656866

H -1.1137079 -1.7429325 -2.7144226

H -0.3530201 -2.5319219 -4.1253475

H 0.6423255 -1.5704758 -2.9991793

C 3.3142837 1.6004711 -1.0510568

C 4.6584475 1.7678901 -1.4757190

C 5.1788314 3.0637326 -1.6056716

H 6.2102367 3.1829949 -1.9479972

C 4.4120109 4.1908678 -1.2937616

H 4.8373642 5.1916114 -1.3956719

C 3.0986830 4.0249905 -0.8444532

H 2.4900138 4.8937353 -0.5806631

C 2.5457389 2.7428910 -0.7301624

C 5.5027303 0.5625843 -1.7318354

C 6.4509367 0.1503983 -0.7663435

C 7.1747506 -1.0293338 -0.9941749

H 7.8997188 -1.3682181 -0.2498243

C 6.9880268 -1.8048728 -2.1432491

C 6.0583846 -1.3644258 -3.0946073

H 5.9050663 -1.9495863 -4.0048791

C 5.3099500 -0.1970062 -2.9086568

C 6.6256877 0.9328292 0.5321642

H 6.4287151 1.9903856 0.2996710

C 5.5720401 0.5007169 1.5673369

H 4.5618066 0.5321861 1.1331780

H 5.6006038 1.1586230 2.4520214

H 5.7626525 -0.5318227 1.9010504

C 8.0392193 0.8504279 1.1191696

H 8.2750687 -0.1646789 1.4786280

H 8.1306231 1.5306470 1.9810554

H 8.8008346 1.1325917 0.3752418

C 7.7603769 -3.1001050 -2.3359428

H 8.4363373 -3.2010305 -1.4691616

C 6.8166935 -4.3142822 -2.3335701

H 6.2234779 -4.3488913 -1.4068179

H 7.3867258 -5.2542109 -2.4170761

H 6.1132587 -4.2683808 -3.1812288

C 8.6294706 -3.0705132 -3.6030689

H 8.0079061 -2.9817529 -4.5090497

H 9.2214965 -3.9961214 -3.6919811

H 9.3241431 -2.2163562 -3.5855663

C 4.3333366 0.2662165 -3.9815139

H 3.6322783 0.9652094 -3.5011562

C 3.4968807 -0.8789158 -4.5639627

H 4.1098863 -1.5832374 -5.1502908

H 2.7194862 -0.4800802 -5.2355401

H 3.0008507 -1.4359979 -3.7560820

C 5.0792307 1.0407457 -5.0814198

H 5.6205991 1.9008099 -4.6577015

H 4.3751655 1.4179210 -5.8415723

H 5.8153552 0.3933549 -5.5863405

C 1.1404065 2.5610507 -0.2657122

C 0.0890954 2.4668793 -1.2246357

C -1.2508220 2.4165245 -0.7649281

H -2.0546485 2.4029328 -1.4997742

C -1.5775447 2.3835808 0.5998596

C -0.5069170 2.3264300 1.5273763

H -0.7285114 2.2791055 2.5955731

C 0.8463977 2.4537318 1.1108012

C 0.3956927 2.5286333 -2.7135950

H 1.4306476 2.1719742 -2.8370485

C -0.5167060 1.6210846 -3.5459573

H -0.5328279 0.5920489 -3.1576780

H -0.1671756 1.5870196 -4.5894903

H -1.5554092 1.9860490 -3.5565559

C 0.3331871 3.9811164 -3.2180830

H -0.6813064 4.3941204 -3.0912585

H 0.5908971 4.0276113 -4.2886032

H 1.0372226 4.6225220 -2.6682123

C -3.0203272 2.4284707 1.0965183

H -3.2143264 1.4625526 1.5946360

C -4.0567196 2.5793403 -0.0205834

H -3.9034587 3.5174636 -0.5802505

H -5.0673047 2.6090583 0.4137716

H -4.0265382 1.7312756 -0.7198942

C -3.1951013 3.5431022 2.1444501

H -2.5192264 3.4195891 3.0038412

H -4.2277391 3.5407117 2.5266755

H -2.9985403 4.5314307 1.6974483

C 1.9569127 2.4162395 2.1485833

H 2.9095060 2.4270725 1.5990339

C 1.9058220 1.1061183 2.9481304

H 0.9929200 1.0259585 3.5605085

H 2.7727565 1.0244988 3.6218588

H 1.9556602 0.2412193 2.2625836

C 1.9242714 3.6509911 3.0600294

H 2.0156719 4.5742854 2.4675370

H 2.7575171 3.6198190 3.7800766

H 0.9834287 3.7050038 3.6320530

$La(SH)_2Bz_2$ TPSSh-D3(BJ)/def2-TZVP (gas phase)

La 0.1131107 0.0095372 0.0311339

S 2.4129087 0.0726698 -1.5542644

S -1.8602555 -0.0773957 -1.9517073

C -0.0967133 2.9531176 -0.1602635

C 1.1164595 2.7588584 0.5299749

C 1.1236680 2.1510832 1.7811435

C -0.0898930 1.7052580 2.3606764

C -1.3147366 1.9910082 1.7079953

C -1.3145350 2.5939040 0.4567753

C -1.2256974 -2.6106673 0.4206619

C -1.2821175 -2.0036983 1.6700571

C -0.0893101 -1.6873591 2.3615343

C 1.1552442 -2.1053834 1.8248588

C 1.2039986 -2.7178157 0.5774564

C 0.0212713 -2.9451031 -0.1515364

H 2.0610958 1.9984364 2.3023171

H -2.2522070 1.7105632 2.1731216

H 2.1590166 -2.9887305 0.1468512

H 1.7503759 -0.2888484 -2.6685792

H -1.0167224 0.3197641 -2.9220341

H -0.0968801 3.3890166 -1.1496323

H 2.0487388 3.0553525 0.0674613

H -0.0900549 1.2659657 3.3486122

H -2.2473346 2.7590677 -0.0654869

H -2.2416172 -1.7460188 2.1025911

H -0.1343844 -1.2438223 3.3465365

H 2.0706185 -1.9243199 2.3749440

H 0.0635106 -3.3829270 -1.1391067

H -2.1359904 -2.8065111 -0.1302139

$Nd(SH)_2Bz_2$ TPSSh-D3(BJ)/def2-TZVP (gas phase)

Nd -0.0230372 -0.0314469 -0.0004288

S 0.5590110 2.1184173 1.6099168

S -0.5427741 -2.3851143 1.2998761

C 2.8835716 0.3885523 -0.0727246

C 2.4132085 1.2025200 -1.1148850

C 1.7784149 0.6307178 -2.2149481

C 1.5929847 -0.7636052 -2.2774288

C 2.0879768 -1.5791174 -1.2475078

C 2.7321438 -1.0037964 -0.1528430

C -2.8531061 -0.5986591 -0.3537432

C -2.3020785 -0.9446984 -1.5909986

C -1.6693513 0.0225673 -2.3760563

C -1.6045454 1.3620533 -1.9327462

C -2.2027787 1.7160571 -0.7138031

C -2.8124508 0.7447625 0.0768994

H 1.4224676 1.2605070 -3.0205694

H 1.9440391 -2.6508346 -1.2861915

H -2.1505122 2.7396463 -0.3671476

H -0.5519936 1.9621497 2.3536290

H 0.5618176 -2.3401274 2.0680206

H 3.3496683 0.8377751 0.7932574

H 2.5277707 2.2768316 -1.0506589

H 1.1085931 -1.2114176 -3.1349653

H 3.0890107 -1.6344356 0.6516007

H -2.3393761 -1.9739974 -1.9258316

H -1.2513760 -0.2507489 -3.3362978

H -1.1361878 2.1208069 -2.5455247

H -3.2410541 1.0167873 1.0331285

H -3.3068662 -1.3556830 0.2706867

$Nd(SH)_2Bz_2^+$ TPSSh-D3(BJ)/def2-TZVP (gas phase)

Nd -0.0095508 -0.0686591 -0.0683097

S 0.4841802 1.7494270 1.7629646

S -0.5541311 -2.4086790 0.9953437

C 2.9237603 0.4667486 -0.0313009

C 2.4703692 1.2660908 -1.0888178

C 1.9033713 0.6690448 -2.2179008

C 1.7798593 -0.7249736 -2.2900497

C 2.2403034 -1.5245753 -1.2371195

C 2.8132772 -0.9254334 -0.1102034

C -2.9513668 -0.4668199 -0.2377881

C -2.4944750 -0.9496932 -1.4716557

C -1.8769205 -0.0801395 -2.3737948

C -1.7074832 1.2719781 -2.0444241

C -2.1705067 1.7560885 -0.8160130

C -2.7931322 0.8846770 0.0846883

H 1.5684556 1.2842397 -3.0444144

H 2.1478805 -2.6015746 -1.2893660

H -2.0423068 2.7991836 -0.5572784

H -0.5680823 1.3876131 2.5230204

H 0.4313289 -2.2702215 1.9050509

H 3.3591602 0.9264729 0.8458459

H 2.5630489 2.3432557 -1.0291213

H 1.3513359 -1.1875610 -3.1710313

H 3.1649938 -1.5423111 0.7074186

H -2.6215465 -1.9955442 -1.7216480

H -1.5370406 -0.4494362 -3.3339869

H -1.2416181 1.9490375 -2.7501371

H -3.1458337 1.2588957 1.0376268

H -3.4241399 -1.1406616 0.4641170

8. References.

1 A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, **15**, 1518–1520.

2 G. Meyer, E. Garcia and J. D. Corbett, in *Inorg. Synth.*, 1989, pp. 146–150.

3 W. J. Evans, N. T. Allen, P. S. Workman and J. C. Meyer, *Inorg. Chem.*, 2003, **42**, 3097–3099.

4 M. N. Bochkarev and A. A. Fagin, *Chem. – A Eur. J.*, 1999, **5**, 2990–2992.

5 M. N. Bochkarev, I. L. Fedushkin, A. A. Fagin, T. V Petrovskaya, J. W. Ziller, R. N. R. Broomhall-Dillard and W. J. Evans, *Angew. Chem. Int. Ed.*, 1997, **36**, 133–135.

6 M. Niemeyer and P. P. Power, *Inorg. Chem.*, 1996, **35**, 7264–7272.

7 A. Cofone and M. Niemeyer, *Z. Anorg. Allg. Chem.*, 2006, **632**, 1930–1932.

8 K. Kundu, J. R. K. White, S. A. Moehring, J. M. Yu, J. W. Ziller, F. Furche, W. J. Evans and S. Hill, *Nat. Chem.*, 2022, **14**, 392–397.

9 M. E. Fieser, M. R. MacDonald, B. T. Krull, J. E. Bates, J. W. Ziller, F. Furche and W. J. Evans, *J. Am. Chem. Soc.*, 2015, **137**, 369–382.

10 P. B. Hitchcock, M. F. Lappert, L. Maron and A. V. Protchenko, *Angew. Chem. Int. Ed.*, 2008, **47**, 1488–1491.

11 T. F. Jenkins, D. H. Woen, L. N. Mohanam, J. W. Ziller, F. Furche and W. J. Evans, *Organometallics*, 2018, **37**, 3863–3873.

12 M. A. Angadol, D. H. Woen, C. J. Windorff, J. W. Ziller and W. J. Evans, *Organometallics*, 2019, **38**, 1151–1158.

13 D. H. Woen, D. N. Huh, J. W. Ziller and W. J. Evans, *Organometallics*, 2018, **37**, 3055–3063.

14 J. Liu, L. E. Nodaraki, D. O. T. A. Martins, M. J. Giansiracusa, P. J. Cobb, J. Emerson-King, F. Ortu, G. F. S. Whitehead, G. K. Gransbury, E. J. L. Mclnnes, F. Tuna and D. P. Mills, *Eur. J. Inorg. Chem.*, 2023, **26**, e202300552.

15 APEX2 Version 2014.11-0. Bruker AXS, Inc.; Madison, WI 2014.

16 SAINT Version 8.34a. Bruker AXS, Inc.; Madison, WI 2013.

17 G. M. Sheldrick, SADABS, Version 2014/5. Bruker AXS, Inc.; Madison, WI 2014.

18 G. M. Sheldrick, SHELXTL, Version 2014/7. Bruker AXS, Inc.; Madison, WI 2014.

19 *International Tables for Crystallography, Vol. C*, Dordrecht: Kluwer Academic Publishers, 1992.

20 APEX3 Version 2018/1-0. Bruker AXS, Inc.; Madison, WI 2018.

21 G. M. Sheldrick, *Cell_Now*, University of Göttingen, Germany, 2008.

22 G. M. Sheldrick, *TWINABS*, University of Göttingen, Germany, 2012.

23 J. Angelkort, S. van Smaalen, S. O. Hauber and M. Niemeyer, *Z. Anorg. Allg. Chem.*, 2007, **633**, 1031–1035.

24 M. Niemeyer, *Eur. J. Inorg. Chem.*, 2001, **2001**, 1969–1981.

25 P. B. Hitchcock, M. F. Lappert and A. V Protchenko, *J. Am. Chem. Soc.*, 2001, **123**, 189–190.

26 J. N. Boynton, J.-D. Guo, F. Grandjean, J. C. Fettinger, S. Nagase, G. J. Long and P. P.

Power, *Inorg. Chem.*, 2013, **52**, 14216–14223.

27 S. G. Balasubramani, G. P. Chen, S. Coriani, M. Diedenhofen, M. S. Frank, Y. J. Franzke, F. Furche, R. Grotjahn, M. E. Harding, C. Hättig, A. Hellweg, B. Helmich-Paris, C. Holzer, U. Huniar, M. Kaupp, A. Marefat Khah, S. Karbalaei Khani, T. Müller, F. Mack, B. D. Nguyen, S. M. Parker, E. Perlt, D. Rappoport, K. Reiter, S. Roy, M. Rückert, G. Schmitz, M. Sierka, E. Tapavicza, D. P. Tew, C. van Wüllen, V. K. Voora, F. Weigend, A. Wodyński and J. M. Yu, *J. Chem. Phys.*, 2020, **152**, 184107.

28 Y. J. Franzke, C. Holzer, J. H. Andersen, T. Begušić, F. Bruder, S. Coriani, F. Della Sala, E. Fabiano, D. A. Fedotov, S. Fürst, S. Gillhuber, R. Grotjahn, M. Kaupp, M. Kehry, M. Krstić, F. Mack, S. Majumdar, B. D. Nguyen, S. M. Parker, F. Pauly, A. Pausch, E. Perlt, G. S. Phun, A. Rajabi, D. Rappoport, B. Samal, T. Schrader, M. Sharma, E. Tapavicza, R. S. Treß, V. Voora, A. Wodyński, J. M. Yu, B. Zerulla, F. Furche, C. Hättig, M. Sierka, D. P. Tew and F. Weigend, *J. Chem. Theory Comput.*, 2023, **19**, 6859–6890.

29 TURBOMOLE V7.7 2022, a Development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; Available from https://www.Turbomole.org.

30 R. Bauernschmitt, M. Häser, O. Treutler and R. Ahlrichs, *Chem. Phys. Lett.*, 1997, **264**, 573–578.

31 K. Eichkorn, O. Treutler, H. Öhm, M. Häser and R. Ahlrichs, *Chem. Phys. Lett.*, 1995, **240**, 283–289.

32 J. Tao, J. P. Perdew, V. N. Staroverov and G. E. Scuseria, *Phys. Rev. Lett.*, 2003, **91**, 146401.

33 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.

34 A. D. Becke and E. R. Johnson, *J. Chem. Phys.*, 2005, **123**, 154101.

35 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.

36 M. Dolg, H. Stoll, A. Savin and H. Preuss, *Theor. Chim. Acta*, 1989, **75**, 173–194.

37 M. Dolg, H. Stoll and H. Preuss, *Theor. Chim. Acta*, 1993, **85**, 441–450.

38 V. N. Staroverov, G. E. Scuseria, J. Tao and J. P. Perdew, *J. Chem. Phys.*, 2003, **119**, 12129–12137.

39 A. Klamt and G. Schüürmann, *J. Chem. Soc., Perkin Trans. 2*, 1993, **0**, 799–805.

40 A. Schäfer, A. Klamt, D. Sattel, J. C. W. Lohrenz and F. Eckert, *Phys. Chem. Chem. Phys.*, 2000, **2**, 2187–2193.

41 W. Humphrey, A. Dalke and K. Schulten, *J. Molec. Graph.*, 1996, **14**, 33–38.

42 J. E. Bates and F. Furche, *J. Chem. Phys.*, 2012, **137**, 164105.

43 J. E. Bates, M. C. Heiche, J. Liang and F. Furche, *J. Chem. Phys.*, 2022, **156**, 159902.

44 W. Kutzelnigg and W. Liu, *J. Chem. Phys.*, 2005, **123**, 241102.

45 D. Peng, N. Middendorf, F. Weigend and M. Reiher, *J. Chem. Phys.*, 2013, **138**, 184105.

46 Y. J. Franzke and J. M. Yu, *J. Chem. Theory Comput.*, 2021, **18**, 323–343.

47 Y. J. Franzke and J. M. Yu, *J. Chem. Theory Comput.*, 2022, **18**, 2246–2266.

48 J. C. Boettger, *Phys. Rev. B*, 2000, **62**, 7809–7815.

49 M. Filatov, W. Zou and D. Cremer, *J. Chem. Phys.*, 2013, **139**, 14106.

50 L. Visscher and K. G. Dyall, *At. Data Nucl. Data Tables*, 1997, **67**, 207–224.

51 J. W. Furness, A. D. Kaplan, J. Ning, J. P. Perdew and J. Sun, *J. Phys. Chem. Lett.*, 2020, **11**, 8208–8215.

52 J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615–6620.

53 J.-D. Chai and M. Head-Gordon, *J. Chem. Phys.*, 2008, **128**, 84106.

54 Y. J. Franzke and C. Holzer, *J. Chem. Phys.*, 2022, **157**, 31102.

55 Y. J. Franzke, L. Spiske, P. Pollak and F. Weigend, *J. Chem. Theory Comput.*, 2020, **16**, 5658–5674.

56 P. Pollak and F. Weigend, *J. Chem. Theory Comput.*, 2017, **13**, 3696–3705.

57 Y. J. Franzke, R. Treß, T. M. Pazdera and F. Weigend, *Phys. Chem. Chem. Phys.*, 2019, **21**, 16658–16664.

58 S. Rein, EPRsim. 2019.

https://urldefense.com/v3/__https://pypi.org/project/EPRsim/__;!!CzAuKJ42GuquVTTmVmPViYEvSg!MTIFMYu8QvooUGH6zvVdD7sLF6yYLh6oospK7uBAtBOSW_2hnGz3D-09DQy5zEa1bK1xtp3xBdt-R1T9$

59 S. Stoll and A. Schweiger, *J. Magn. Reson.*, 2006, **178**, 42–55.