Supporting information for the manuscript

Photo-isomerization of the cyclononatetraenyl ligand and related rare earth complexes

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Summary

1. General information

All air- and moisture-sensitive reactions were performed using standard Schlenk-line techniques under dry N_2 or Ar atmosphere or in argon-filled gloveboxes (MBraun). All glassware was dried at 140 °C for at least 12 h prior to use. All solvents (Et_2O, toluene, benzene, pentane, C_6D_6, tol-d_8, THF-d_8) were dried over sodium, degassed, and transferred under reduced pressure in a cold flask. Acetonitrile and deuterated acetonitrile were dried over CaH_2, degassed, and transferred under reduced pressure in a cold flask. K_2Cot, KCnt was prepared according to literature procedures. All LnCotI(thf)$_n$ were synthesized according to a modified procedure published literature by using the corresponding LnI_3 except for Ln = Sm where another synthesis pathway was used.[1–4] For Ln = Lu, [(Cot)Lu(BH_4)(thf)]$_2$ was synthesized according to known procedure.[1] Ln(Cot)(*cis*-Cnt) were prepared according to known procedure Ln = Tb-Tm.[1] All other chemicals were obtained from commercial sources and used without further purification. ^{1}H NMR spectra were recorded in 5 mm tubes adapted with a J. Young valve on a Bruker Avance III-300 MHz spectrometer and chemical shifts are expressed relative to internal solvent references in ppm. UV-visible absorption spectra were recorded on a cary60 spectrometer in quartz cuvettes adapted with a J. Young valve. Irradiation were performed using Kessils lamps ans Prizmatix multi-Wavelength FC5-LED. Elemental analyses were obtained from Mikroanalytisches Labor Pascher (Remagen, Germany). IR spectra were recorded using Thermo Scientific Nicolet iS5 spectrometer equipped with the ATR iD7 accessory.

2. Experimental section

a. General procedures:

General procedure A: Synthesis of 2-Ln-*cis*

A mixture of LnCotI(thf)$_n$ (n = 2, 3) (1.05 equiv.) and KCnt (1 equiv.) in toluene and acetonitrile (10:1) was allowed to stir at room temperature. After 12 h, the vessel was protected from light and the solvent were removed under reduced pressure. The reaction mixture was then dissolved in toluene. The evaporation / dissolution in toluene step was repeated once. The colored supernatant was then filtered and concentrated to yield **2**-Ln-*cis*. The desired compound can be obtained as microcrystalline powder through toluene extraction and evaporation. XRD suitable crystals were obtained by concentration of the toluene solution at -40°C.

General procedure B: Synthesis of 2-Ln-*trans*

All steps are protected from light. A mixture or LnCotI(thf)$_n$ (n = 2, 3) (1 equiv.) and KCnt (1 equiv.) in toluene was protected from light with aluminum foil and allowed to stir. After 12 h, the supernatant was filtered, concentrated, and cooled to yield a mixture of isomers with a high ratio of **2**-Ln-*trans*. The desired compound can be obtained as microcrystalline powder through toluene extraction and slow evaporation of dryness. XRD suitable crystals were obtained by concentration of the toluene solution at -40°C.

b. Synthesis of 2-Ln-*cis*:

2-Y-*cis*: Synthesized according to general procedure **A** YCotI(thf)$_3$ (106 mg, 0.20 mmol, 1.0 equiv) and KCnt (31 mg, 0.20 mmol, 1.05 equiv) as yellow micro-crystalline powder (24.9 mg, 40%)
^{1}H NMR (300 MHz, toluene-d$_8$, 293 K): δ (ppm) 6.77 (s, 9H, Cnt), 5.93 (s, 8H, Cot)
Anal. Calcd. for $C_{17}H_{17}Y$ (310.23): C, 65.82; H, 5.52 Found: C, 63.65; H, 5.42.

2-La-*cis*: Synthesized according to general procedure **A** LaCotI(thf)$_3$ (61.1 mg, 0.10 mmol, 1.0 equiv) and KCnt (17.2 mg, 0.11 mmol, 1.05 equiv) as orange micro-crystalline powder (26.9 mg, 71%)
^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ (ppm) 7.53 (s, 9H, Cnt), 6.03 (s, 8H, Cot)
Anal. Calcd. for $C_{17}H_{17}La$ (360.04): C, 56.68; H, 4.76 Found: C, 56.75; H, 4.81

2-Ce-*cis*: Synthesized according to general procedure **A** CeCotI(thf)$_3$ (150 mg, 0.25 mmol, 1.0 equiv) and KCnt (42 mg, 0.26 mmol, 1.05 equiv) as green micro-crystalline powder (53 mg, 58%)
^{1}H NMR (300 MHz, toluene-d$_8$, 293 K): δ (ppm) 6.22 (s, 9H, Cnt), 4.56 (s, 8H, Cot)
Anal. Calcd. for $C_{17}H_{17}Ce$ (361.43): C, 56.49; H, 4.74 Found: C, 56.36; H, 4.79.

2-Pr-*cis*: Synthesized according to general procedure **A** PrCotI(thf)$_3$ (70.9 mg, 0.12 mmol, 1.0 equiv) and KCnt (19.9 mg, 0.13 mmol, 1.05 equiv) as light brown micro-crystalline powder (25.6 mg, 59%)
^{1}H NMR (300 MHz, toluene-d$_8$, 293 K): δ (ppm) -0.60 (s, 9H, Cnt), -12.07 (s, 8H, Cot)
Anal. Calcd. for $C_{17}H_{17}Pr$ (362.23): C, 56.37; H, 4.73 Found: C, 55.80; H, 4.74.

2-Nd-*cis*: Synthesized according to general procedure **A** NdCotI(thf)$_3$ (72.1 mg, 0.12 mmol, 1.0 equiv) and KCnt (20.4 mg, 0.13 mmol, 1.05 equiv) as greenish micro-crystalline powder (24.0 mg, 54 %)
^{1}H NMR (300 MHz, toluene-d$_8$, 293 K): δ (ppm), 0.27 (s, 9H, Cnt), -13.70 (br s, 8H, Cot)
Anal. Calcd. for $C_{17}H_{17}Nd$ (363.04): C, 55.86; H, 4.69 Found: C, 55.53; H, 4.68

2-Sm-*cis*: Synthesized according to general procedure **A** SmCotI(thf)$_3$ (100 mg, 0.17 mmol, 1 equiv.) and KCnt (25 mg, 0.18 mmol, 1 equiv.) as small green micro-crystalline powder (24 mg, 38 %)
^{1}H NMR (300 MHz, toluene-d$_8$, 293 K): δ (ppm) 16.47 (br s, 8H, Cot), 11.39 (s, 9H, Cnt)
Anal. Calcd. for $C_{17}H_{17}Sm$ (371.68): C, 54.89; H, 4.57; Found: C, 53.45; H, 4.56.

2-Gd-*cis*: Synthesized according to general procedure **A** GdCotI(thf)$_3$ (79.9 mg, 0.15 mmol, 1.0 equiv) and KCnt (24.8 mg, 0.16 mmol, 1.05 equiv) as small orange needles (22 mg. 36 %)
^{1}H NMR (300 MHz, toluene-d$_8$, 293 K): δ (ppm), 97.94 (br s), 23.50 (br s)
Anal. Calcd. for $C_{17}H_{17}Gd$ (379.06): C, 53.94; H, 4.53 Found: C, 49.18; H, 4.30.

2-Y-*trans*: Synthesized according to general procedure **B** YCotI(thf)$_3$ (29.1 mg, 0.0627 mmol, 1.00 equiv.) and KCnt (10.4 mg, 0.0661 mmol, 1.05 equiv.) as bright orange-red crystals (3.0 mg, 15%, 61% *trans*).
^{1}H NMR (300 MHz, toluene-d$_8$, 293 K): 6.77 (s, Cnt^{cis}), 6.55 (s br, Cnt^{trans}), 6.02 (s, Cot^{trans}), 5.94 (s, Cot^{cis}), -3.19 (t, Cnt^{trans})
Anal. Calcd. for $C_{17}H_{17}Y$ (310.23): C, 65.82; H, 5.52 Found: C, 53.32; H, 4.95.

2-La-*trans*: Synthesized according to general procedure **B** LaCotI(thf)$_3$ (64.7 mg, 0.11 mmol, 1.00 equiv) and KCnt (18.7 mg, 0.12 mmol, 1.09 equiv) as small orange crystalline needles (4.0 mg, 10%, 55% *trans*)
^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ (ppm) 7.52 (s, Cnt^{cis}), 7.50(s, 2H, Cnt^{trans}), 6.96 (m, 2H, Cnt^{trans}), 6.83(m, 4H, Cnt^{trans}), 6.12 (s, 8H, Cot-*trans*), 6.02(s, Cot-*cis*), -3.92 (t, 1H, Cnt^{trans}, J = 12 Hz)
Anal. Calcd. for $C_{17}H_{17}La$ (360.04): C, 56.68; H, 4.76 Found: C, 55.80; H, 4.71.

2-Ce-*trans*: Synthesized according to general procedure **B** CeCotI(thf)$_3$ (58.2 mg, 0.099 mmol, 1 equiv) and KCnt (15.8 mg, 0.10 mmol, 1.01 equiv) as small green crystalline needles (4.3 mg, 12%, 79 % *trans*)
^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ (ppm) 25.68 (s, 2H, Cnt^{trans}), 15.55 (s, 2H, Cnt^{trans}), 6.75 (br s, Cnt^{cis}), 4.46 (br s, Cot^{cis}), 3.36 (s, 8H, Cot^{trans}), -16.23 (s, 2H, Cnt^{trans}), -50.30 (s, 1H, Cnt^{trans})
Anal. Calcd. for $C_{17}H_{17}Ce$ (361.43): C, 56.49; H, 4.74 Found: C, 55.28; H, 4.66.

2-Pr-*trans*: Synthesized according to general procedure **B** PrCotI(thf)$_3$ (65.5 mg, 0.11 mmol, 1 equiv) and KCnt (18.9 mg, 0.12 mmol, 1.09 equiv) as small orange crystalline needles (5.6 mg, 14%)
^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ (ppm) 84.96 (s br, 1H, Cnt^{trans}), 7.67 (S, 2H, Cnt^{trans}), -0.21- -0.49 (m br, 4H, Cnt$^{trans/cis}$), -1.96 (s, 2H, Cnt^{trans}), -11.65 (s, 12H, Cot$^{trans/cis}$), -23.00 (s, 2H, Cnt^{trans})
Anal. Calcd. for $C_{17}H_{17}Pr$ (362.23): C, 56.37; H, 4.73 Found: C, 55.80; H, 4.74.

2-Nd-*trans*: Synthesized according to general procedure **B** NdCotI(thf)$_3$ (62.2 mg, 0.105 mmol, 1 equiv) and KCnt (17.2 mg, 0.109 mmol, 1.04 equiv) as small orange crystalline needles (5.3 mg, 14%)
^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ (ppm) 21.16 (s, 2H, Cnt^{trans}), 7.19 (s, 2H, Cnt^{trans}), 6.68 (s, 2H, Cnt^{trans}), -13.84 (s, 8H, Cot^{trans}), -26.83 (s, 2H, Cnt^{trans}).
Anal. Calcd. for $C_{17}H_{17}Nd$ (363.04): C, 55.86; H, 4.69 Found: C, 55.80; H, 4.63

2-Sm-*trans*: Synthesized according to general procedure **B** SmCotI(thf)$_3$ (52 mg, 0.1 mmol, 1 equiv) and KCnt (15 mg, 0.1 mmol, 1 equiv) as small green crystalline needles (5.2 mg, 15% yield, 89% *trans*).

^{1}H NMR (300 MHz, toluene-d_8, 293 K): δ (ppm) 16.45 (br, Cot^{cis}), 15.60 (s, 8H, Cot^{trans}), 15.02 (s, 2H, Cnt^{trans}), 14.59 (s, 2H Cnt^{trans}), 11.41 (s, Cnt^{cis}), 11.00 (s, 2H, Cnt^{trans}), 6.19 (s, 2H, Cnt^{trans}), -40.52 (s, 1H, Cnt^{trans})
Anal. Calcd. for $C_{17}H_{17}Sm$ (371.68): C, 54.89; H, 4.57; Found: C, 54.37; H, 4.55.

2-Gd-*trans*: Synthesized according to general procedure **B** GdCotI(thf)$_2$ (63.1 mg, 0.118 mmol, 1 equiv) and KCnt (19.1 mg, 0.121 mmol, 1.03 equiv) as small orange crystalline needles (6.5 mg, 17%)
^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ (ppm) 34.84-23.62 (br), 23.62 (br), 12.18 (br)
Anal. Calcd. for $C_{17}H_{17}Gd$ (379.06): C, 53.94; H, 4.53 Found: C, 52.14; H, 4.45.

2-Tb-*trans*: Synthesized according to general procedure **B** TbCotI(thf)$_2$ (42.2 mg, 0.079 mmol, 1.00 equiv) and KCnt (13.0 mg, 0.083 mmol, 1.05 equiv) as small orange crystalline needles (8.0 mg, 27% yield, 87% *trans*)
^{1}H NMR (300 MHz, toluene-d_8, 293 K): δ (ppm) 391.13 (s, 2H, Cnt^{trans}), 242.25 (s, Cot^{cis}), 225.40 (s, 8H, Cot^{trans}), 196.81 (s, 2H, Cnt^{trans}), 163.00 (s, 2H, Cnt^{trans}), 100.49 (s, Cnt^{cis}), -156.76 (s, 2H, Cnt^{trans})
Anal. Calcd. for $C_{17}H_{17}Tb$ (380.06): C, 53.70; H, 4.51 Found: C, 53.73; H, 4.54.

2-Dy-*trans*: Synthesized according to general procedure **B** DyCotI(thf)$_2$ (67.7 mg, 0.126 mmol, 1.00 equiv.) and KCnt (21.1 mg, 0.134 mmol, 1.06 equiv.) as small orange crystalline needles (4.5 mg, 9 %, 75% *trans*)
^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ (ppm), 158.33 (br s, 2H, Cnt^{trans}), 115.04 (br s, Cnt^{cis}), 99.55 (br s, 2H, Cnt^{trans}), 72.10 (br s, $Cot^{trans/cis}$), 44.47 (br s, 2H, Cnt^{trans}), -168.91 (br s, 2H, Cnt^{trans})
Anal. Calcd. for $C_{17}H_{17}Dy$ (383.82): C, 53.20; H, 4.46 Found: C, 52.76; H, 4.47.

2-Ho-*trans*: Synthesized according to general procedure **B** HoCotI(thf)$_2$ (54.8 mg, 0.101 mmol, 1.00 equiv.) and KCnt (16.6 mg, 0.106 mmol, 1.05 equiv.) as small orange crystalline needles (5.7 mg, 15 %)
^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ (ppm), 198.17 (br s, Cnt^{trans}), 101.99 (br s, Cnt^{trans}), 87.22 (br s, Cnt^{cis}), 66.81 (br s, Cot^{trans}), 57.81 (br s, Cot^{cis}), 18.98 (br s, Cnt^{trans}), -124.84 (br s, Cnt^{trans})
Anal. Calcd. for $C_{17}H_{17}Ho$ (386.06): C, 52.86; H, 4.44 Found: C, 47.75; H, 4.20

2-Er: Synthesized according to general procedure **B** ErCotI(thf)$_2$ (59.4 mg, 0.109 mmol, 1.00 equiv.) and KCnt (18.6 mg, 0.118 mmol, 1.08 equiv.) as bright orange crystals (4.4 mg, 10%) where only the *cis* product could be obtained.
^{1}H NMR (300 MHz, toluene-d_8, 293 K): δ (ppm), -3.94 (br s), -127.52 (br s)
Anal. Calcd. for $C_{17}H_{17}Er$ (388.58): C, 52.55; H, 4.41 Found: C, 51.37; H, 4.35

2-Tm: Synthesized according to general procedure **B** TmCotI(thf)$_2$ (57.4 mg, 0.105 mmol, 1.00 equiv.) and KCnt (17.4 mg, 0.111 mmol, 1.05 equiv.) as bright orange crystals (3.8 mg, 9%) where only the *cis* product could be obtained.
^{1}H NMR (300 MHz, toluene-d_8, 293 K): δ (ppm), -22.87 (br s), -227.25 (br s)
Anal. Calcd. for $C_{17}H_{17}Tm$ (390.07): C, 52.32; H, 4.39 Found: C, 45.77; H, 4.13.

2-Lu: Synthesized according to general procedure **B** [LuCot(thf)(BH_4)]$_2$ (146 mg, 0.33 mmol, 1.00 equiv.) and KCnt (52 mg, 0.33 mmol, 1.0 equiv.) as yellow needles (26 mg, 9%) where only the *cis* product could be obtained.

[1]H NMR (300 MHz, toluene-d$_8$, 293 K): δ (ppm), 6.58 (s, 9H, Cnt^{cis}), 5.88 (s, 8H, Cot^{cis})
Anal. Calcd. for $C_{17}H_{17}Lu$ (396.29): C, 51.52; H, 4.32 Found: C,51.14; H, 4.96

c. Synthesis of 1-*trans*

All steps are protected from light. A mixture or SmI_2 (49.1 mg, 12mmol, 1 equiv.) and KCnt (21 mg, 13 mmol, 1.1 equiv.) in toluene was protected from light with aluminum foil and allowed to stir. After 12 h, the supernatant was filtered, and cooled at -40 °C to yield small black blocks (5.2 mg, 11%, 100% *trans,trans*). No crystals suitable for XRD could be obtained without a considerable isomerization of the compound from **1**-*trans* to **1**-*cis*.
^{1}H NMR (300 MHz, toluene-d$_8$, 293 K): δ (ppm) 51.27 – 49.57 (s, 4H), 26.34 (s, 4H), 21.10 (s, 4H), 15.34 (s, 4H), -0.95 (s, 2H).
Anal. Calcd. for $C_{18}H_{18}Sm$ (384.70): C, 56.2; H, 4.72 Found: C, 52.83; H, 4.57.

3. [1]H NMR Spectroscopy

a. The KCnt ligand

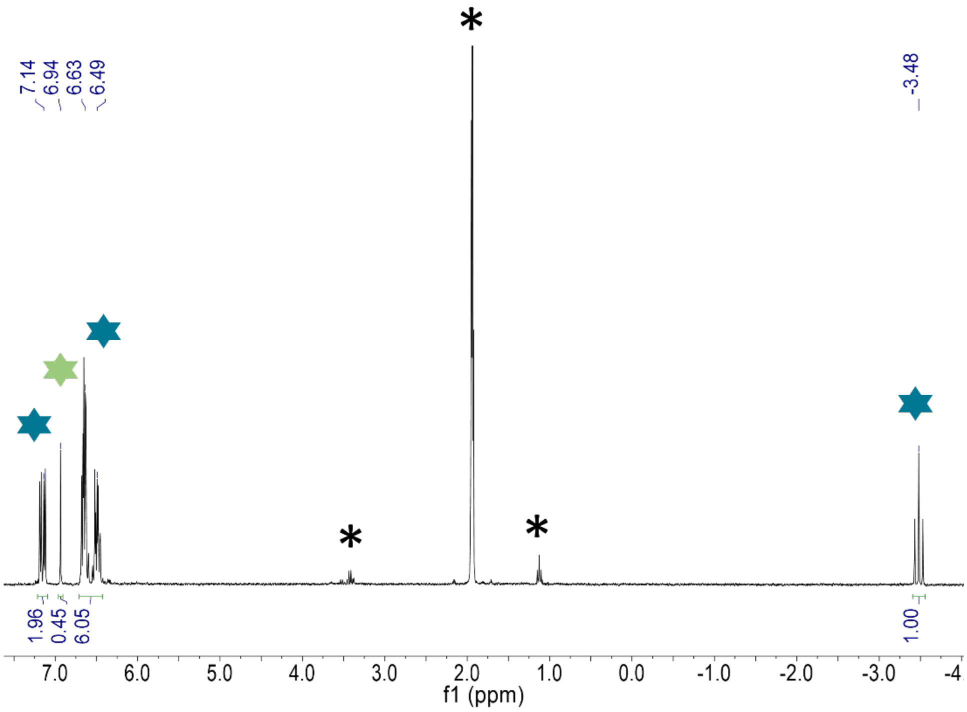

Figure S1: *¹H NMR of KCnt-trans in CD_3CN measured at 293 K (* residual protio signal of the solvent). Green star: signal attributed to KCnt-cis. Blue star: signal attributed to KCnt-trans*

b. Complexes **1**

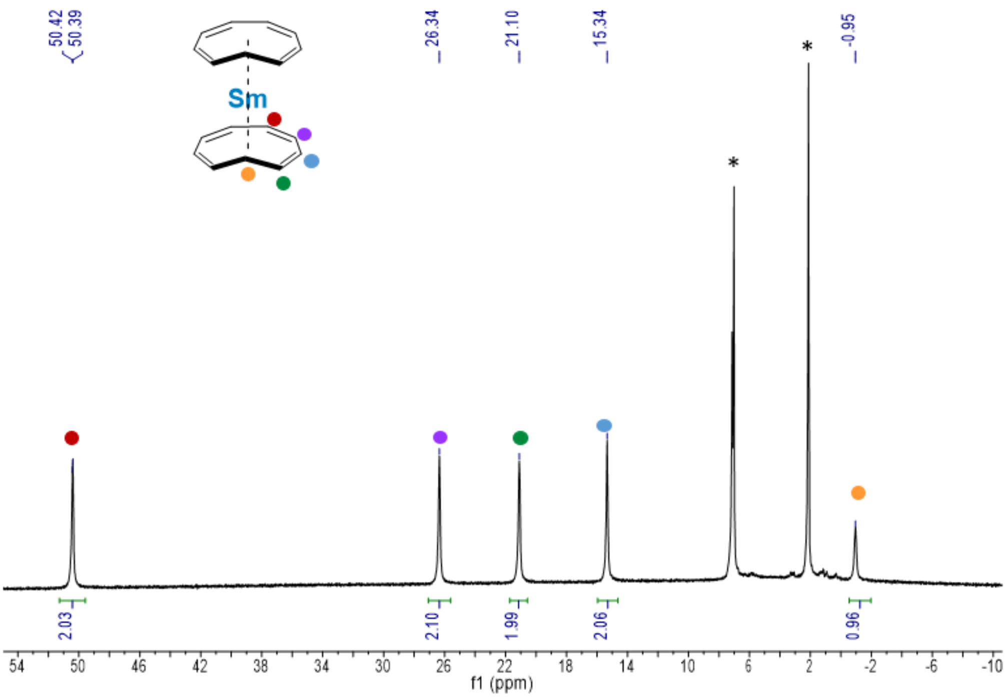

Figure S2: *¹H NMR of **1-trans** in toluene-d_8 measured at 293 K (* residual protio signal of the solvent).*

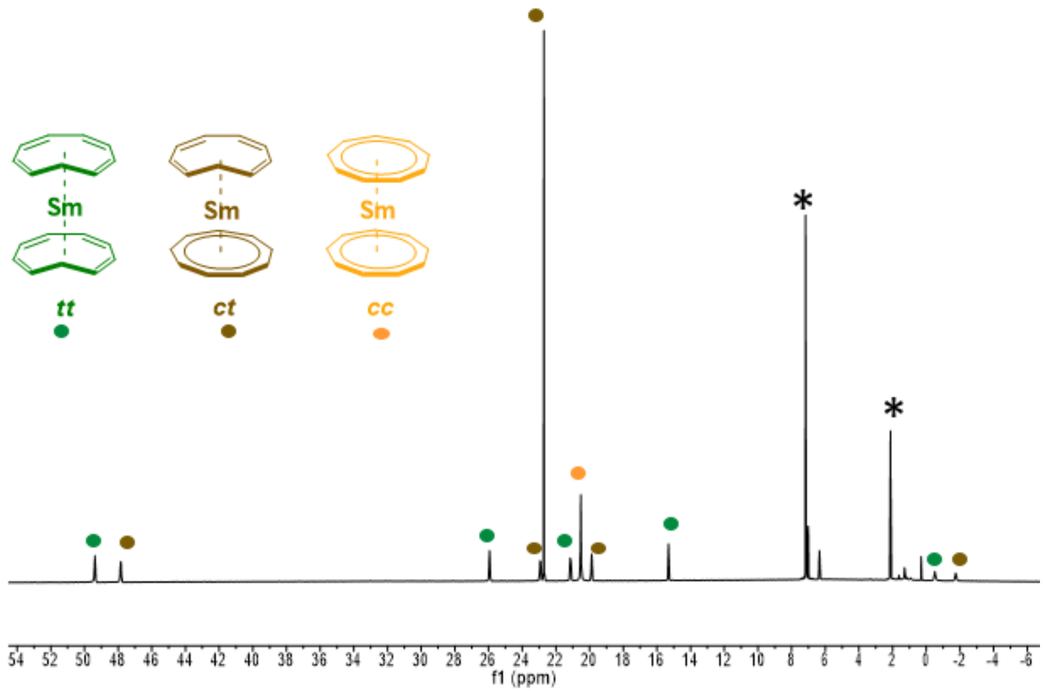

Figure S3: *[1]H NMR of **1** after crystallization in toluene-d$_8$ measured at 293 K (49 % of **1**-trans; 40 % **1**-cis-trans; 11 % of **1**-cis (* residual protio signal of the solvent).*

c. Complexes **2**

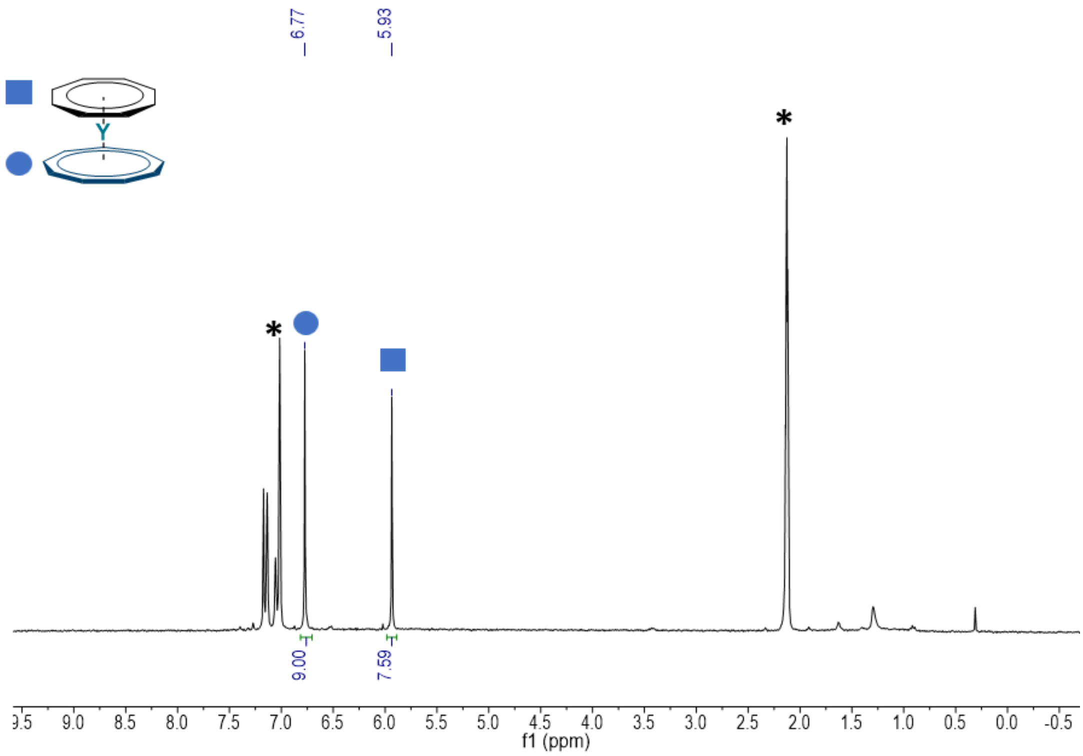

Figure S4: *[1]H NMR **2**-Y-cis in toluene-d$_8$ measured at 293 K (* residual protio signal of the solvent)*

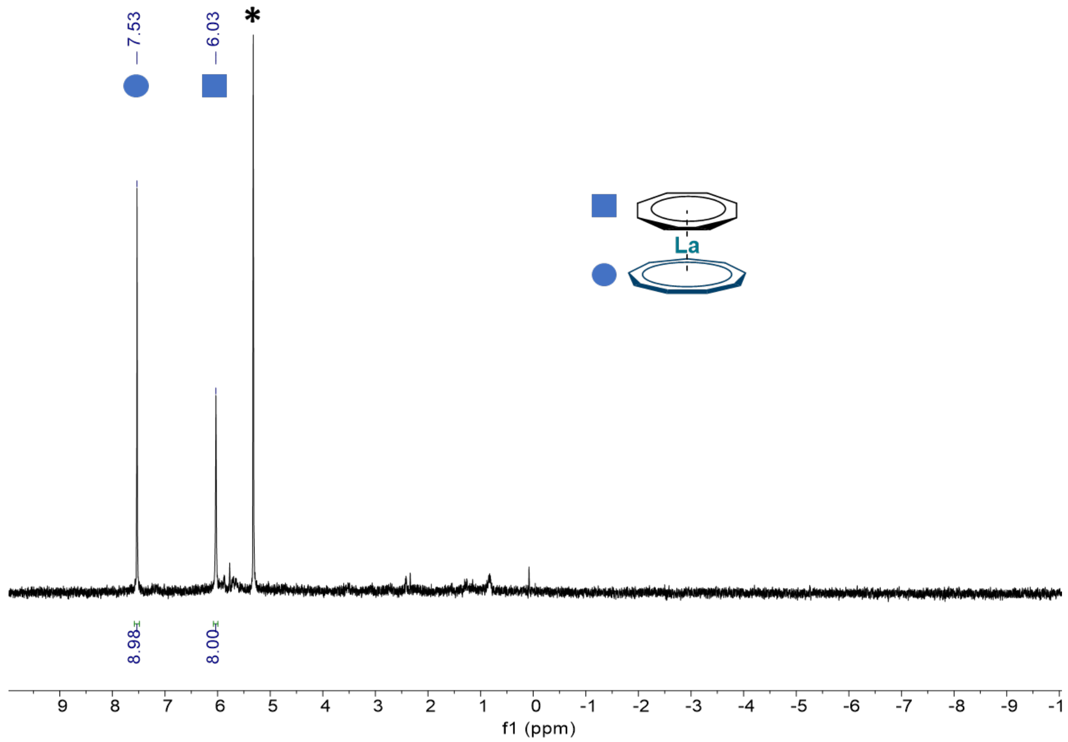

***Figure S5**: ^{1}H NMR of **2**-La-cis in CD_2Cl_2 measured at 293 K (* residual protio signal of the solvent)*

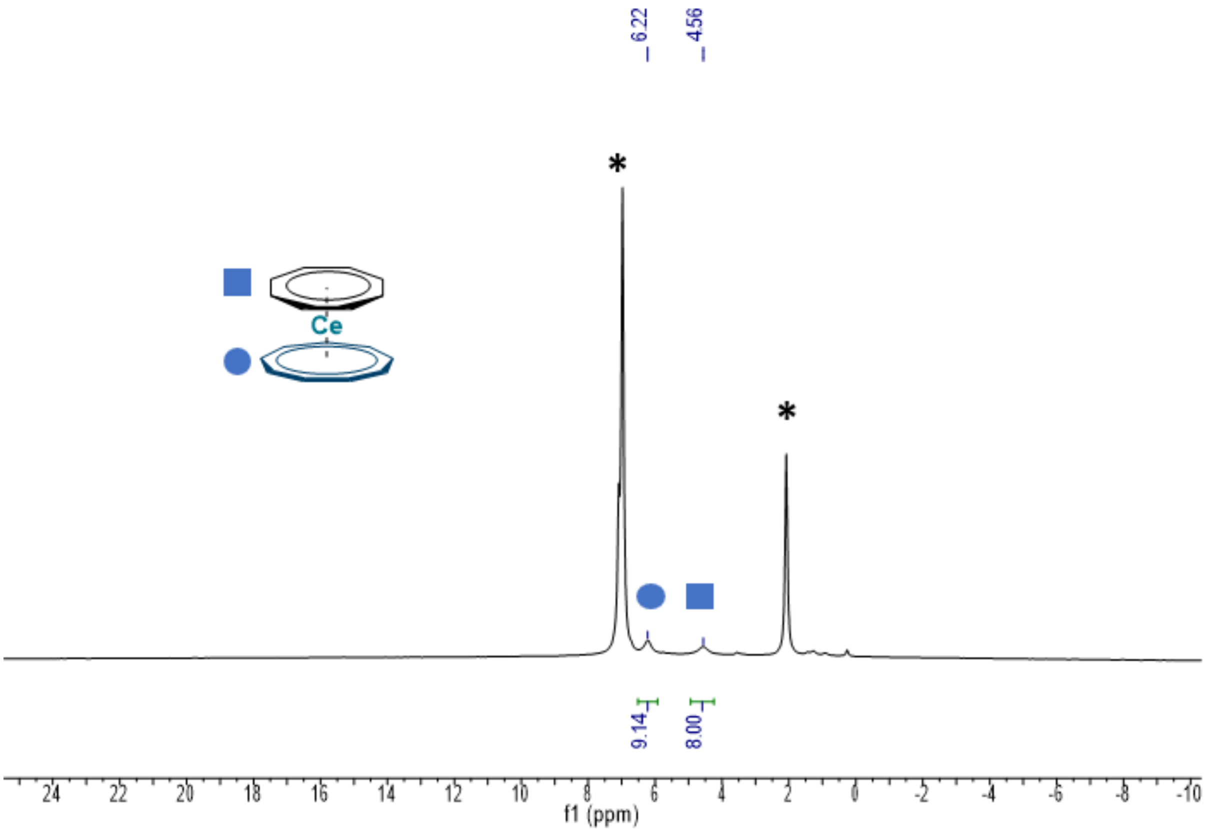

***Figure S6**: ^{1}H NMR of **2**-Ce-cis in toluene-d_8 measured at 293 K (* residual protio signal of the solvent)*

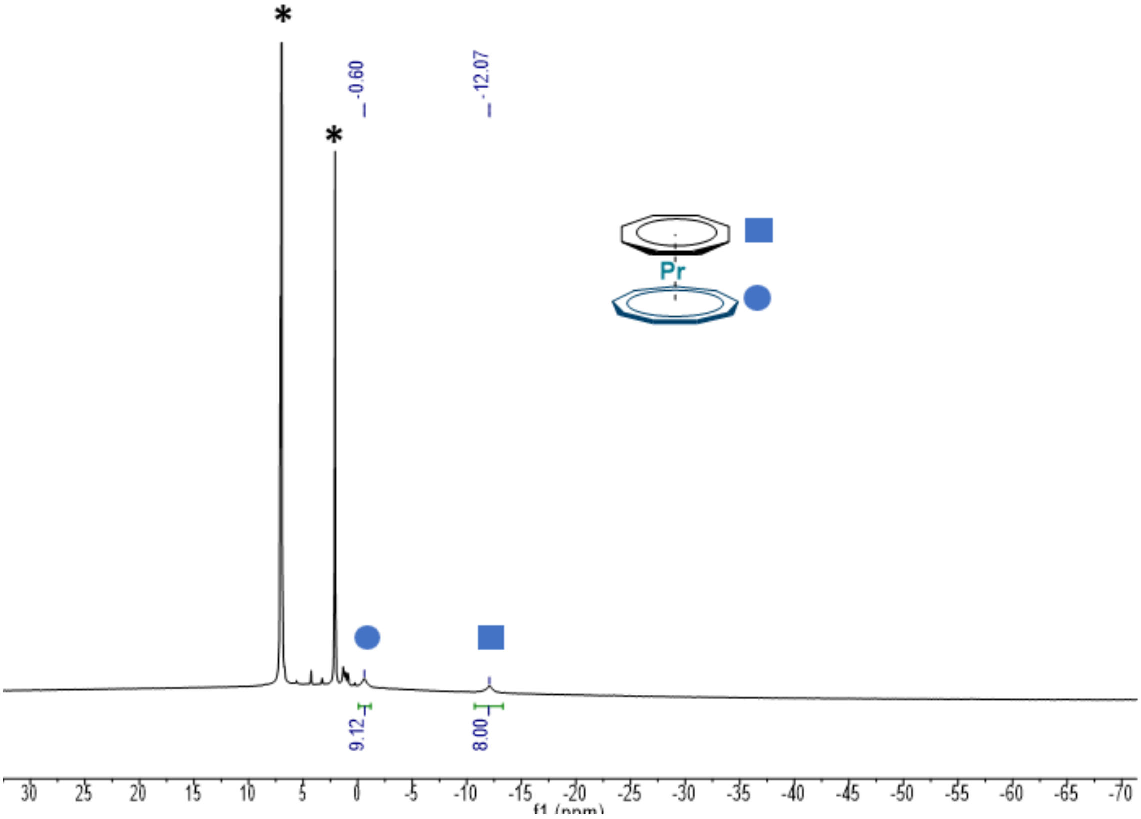

Figure S7: *[1]H NMR of **2**-Pr-cis in toluene-d$_8$ measured at 293 K (* residual protio signal of the solvent)*

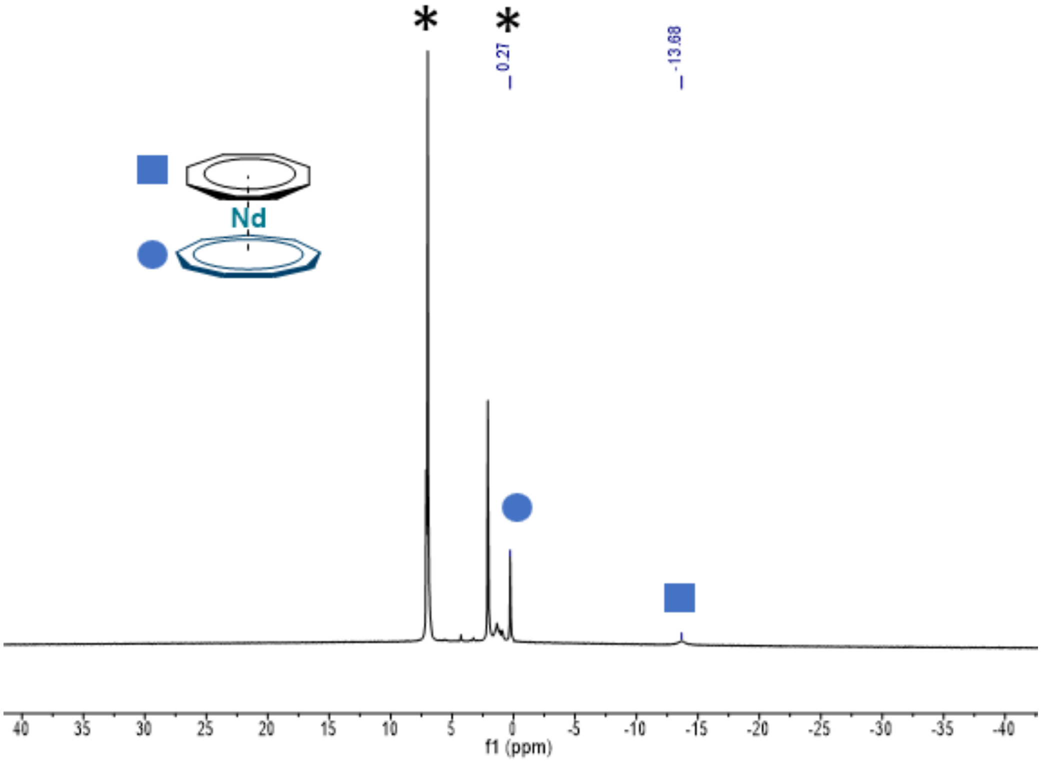

Figure S8: *[1]H NMR of **2**-Nd-cis in toluene-d$_8$ measured at 293 K (* residual protio signal of the solvent). The uncertainty of integration does not allow for specific attribution.*

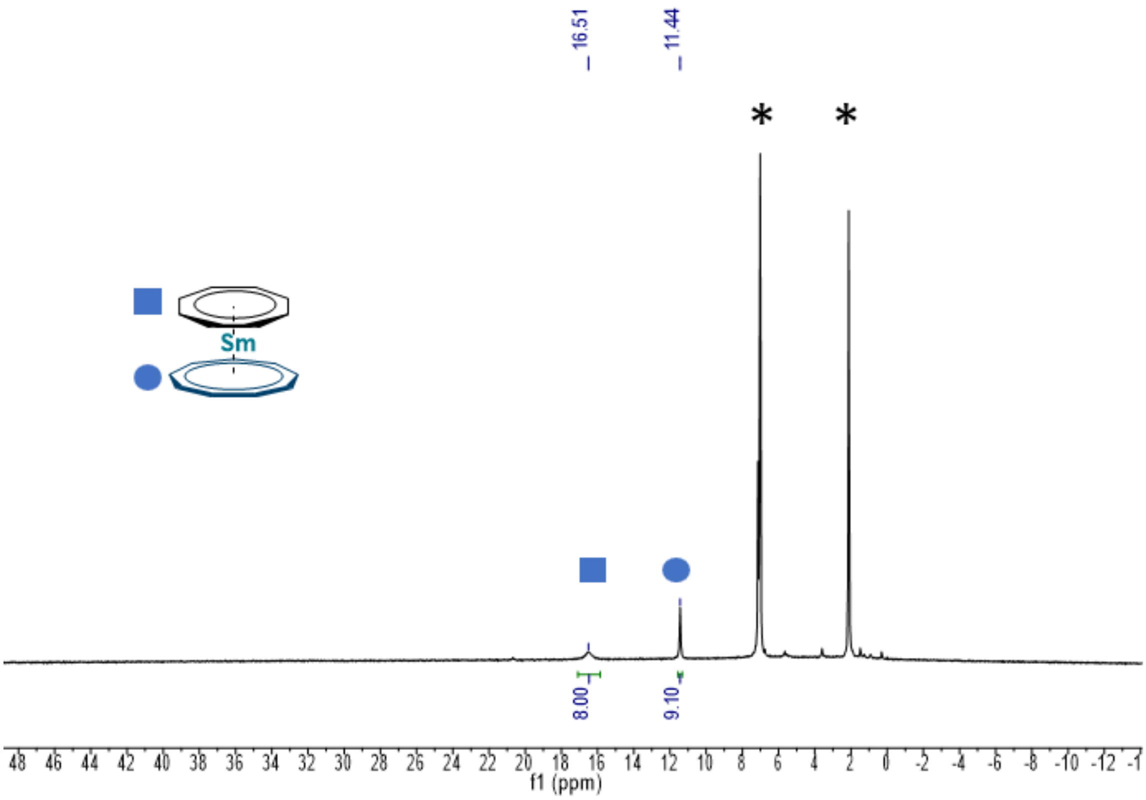

Figure S9:*[1]H NMR of **2**-Sm-cis in toluene-d*$_8$ *measured at 293 K (* residual protio signal of the solvent).*

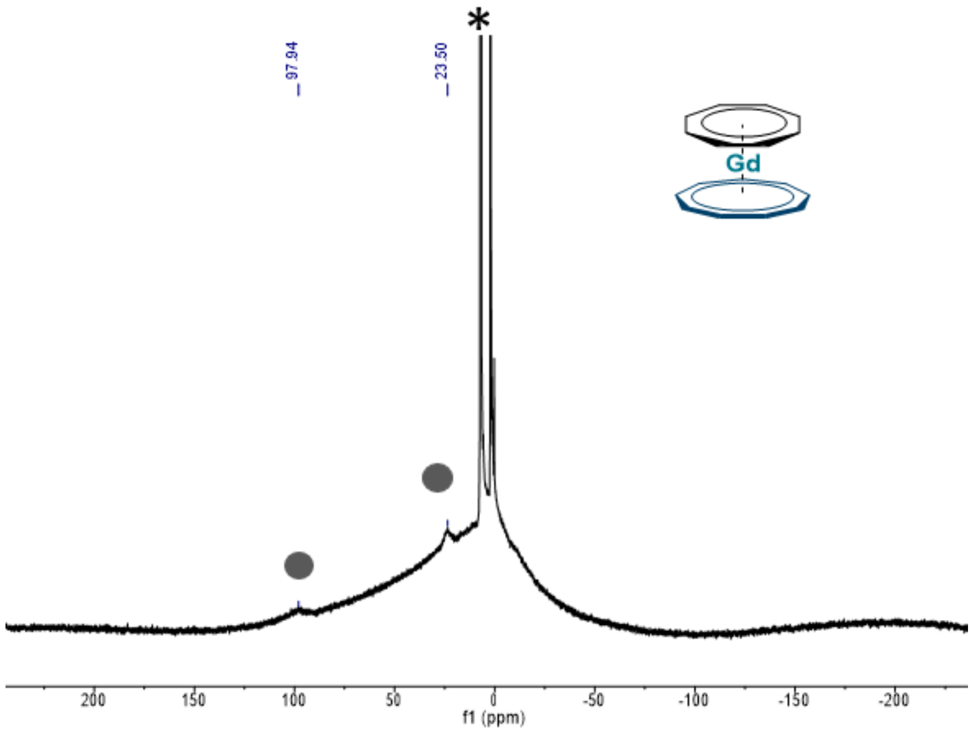

Figure S10: *[1]H NMR of **2**-Gd-cis in toluene-d*$_8$ *measured at 293 K (* residual protio signal of the solvent). The uncertainty of integration does not allow the attribution.*

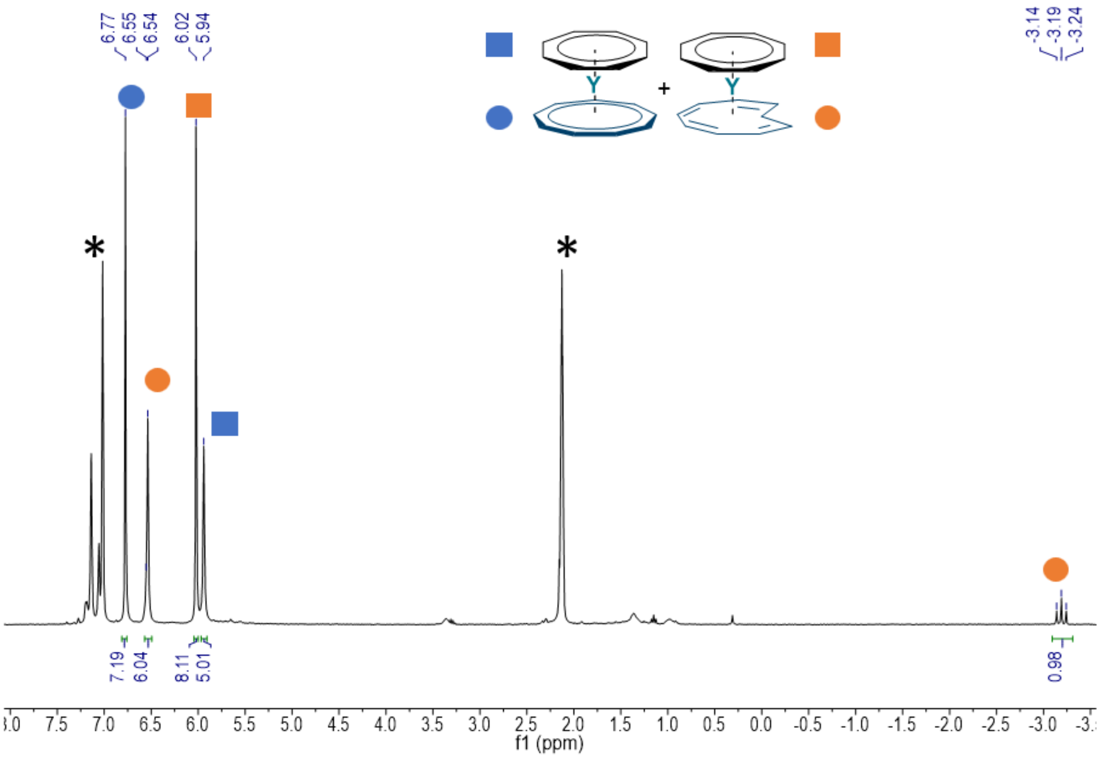

Figure S11: *[1]H NMR of **2**-Y-trans in toluene-d$_8$ measured at 293 K (* residual protio signal of the solvent).*

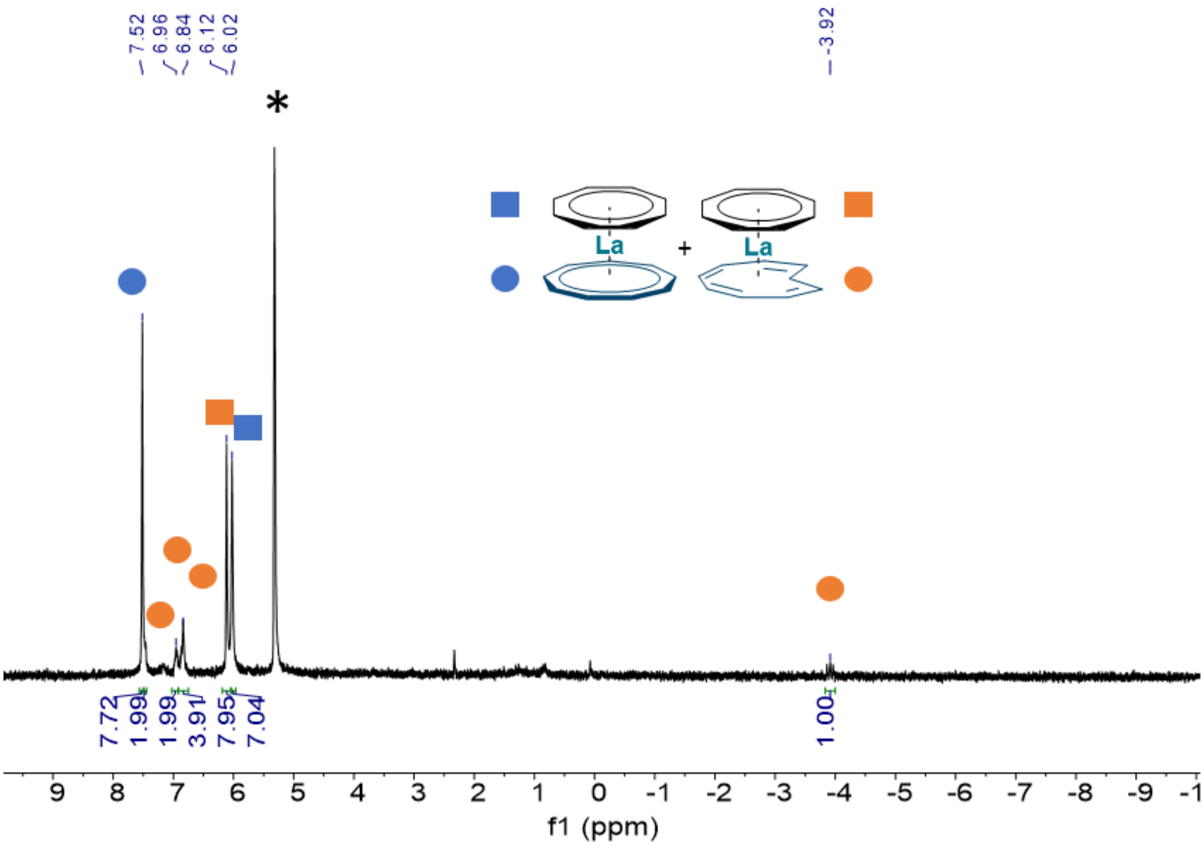

Figure S12: *[1]H NMR of **2**-La-trans in CD_2Cl_2 measured at 293 K (* residual protio signal of the solvent).*

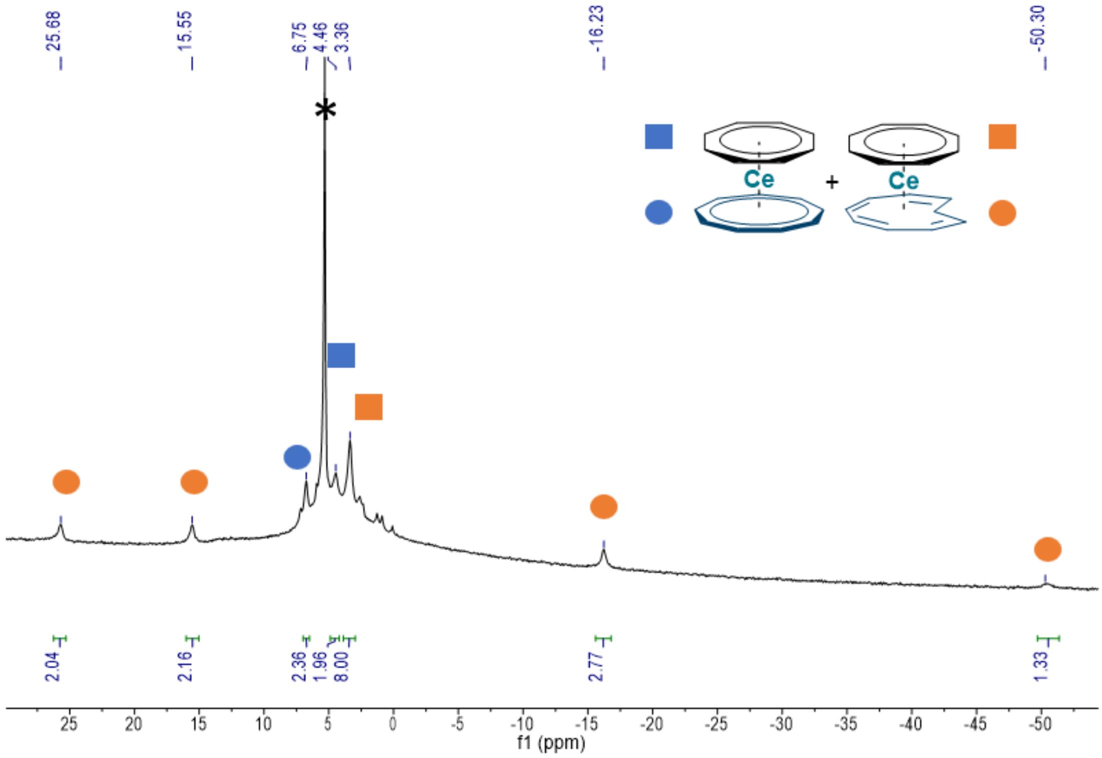

Figure S13: *[1]H NMR of **2**-Ce-trans in CD_2Cl_2 measured at 293 K (* residual protio signal of the solvent).*

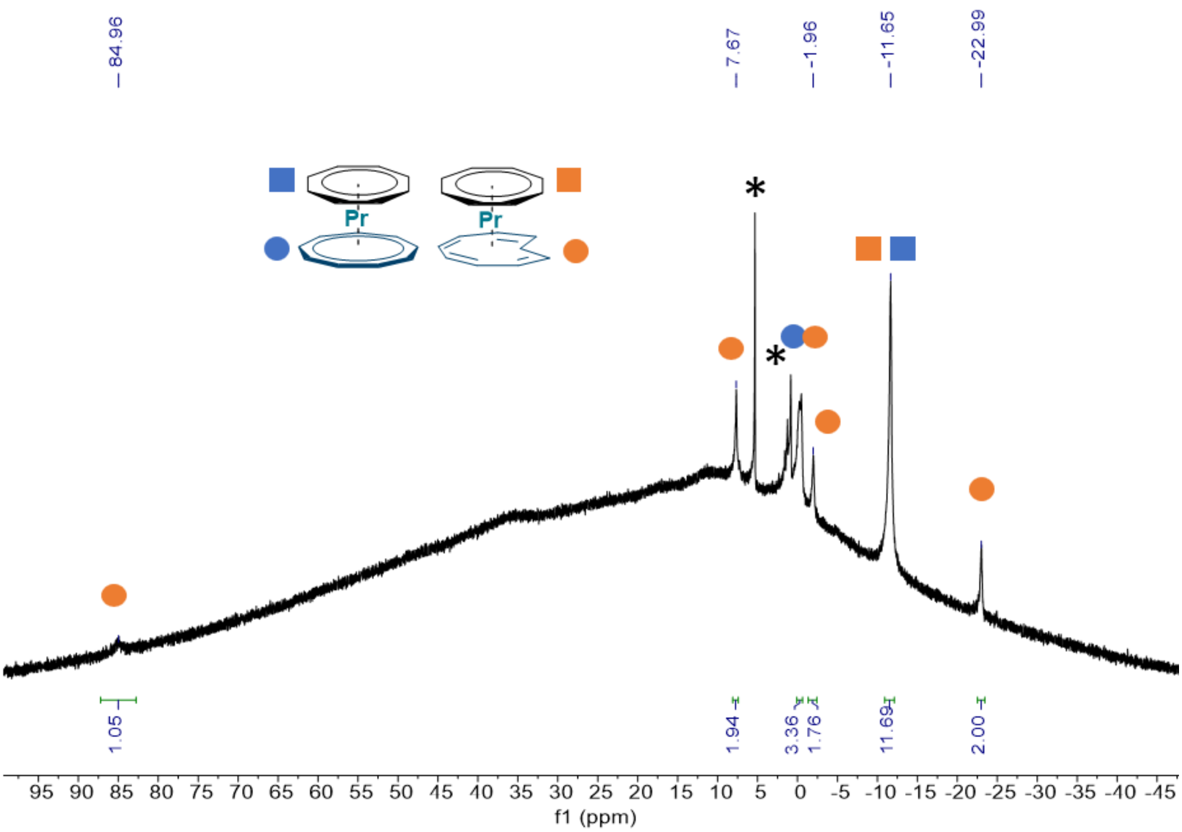

Figure S14: *[1]H NMR of **2**-Pr-trans in CD_2Cl_2 measured at 293 K (* residual protio signal of the solvent).*

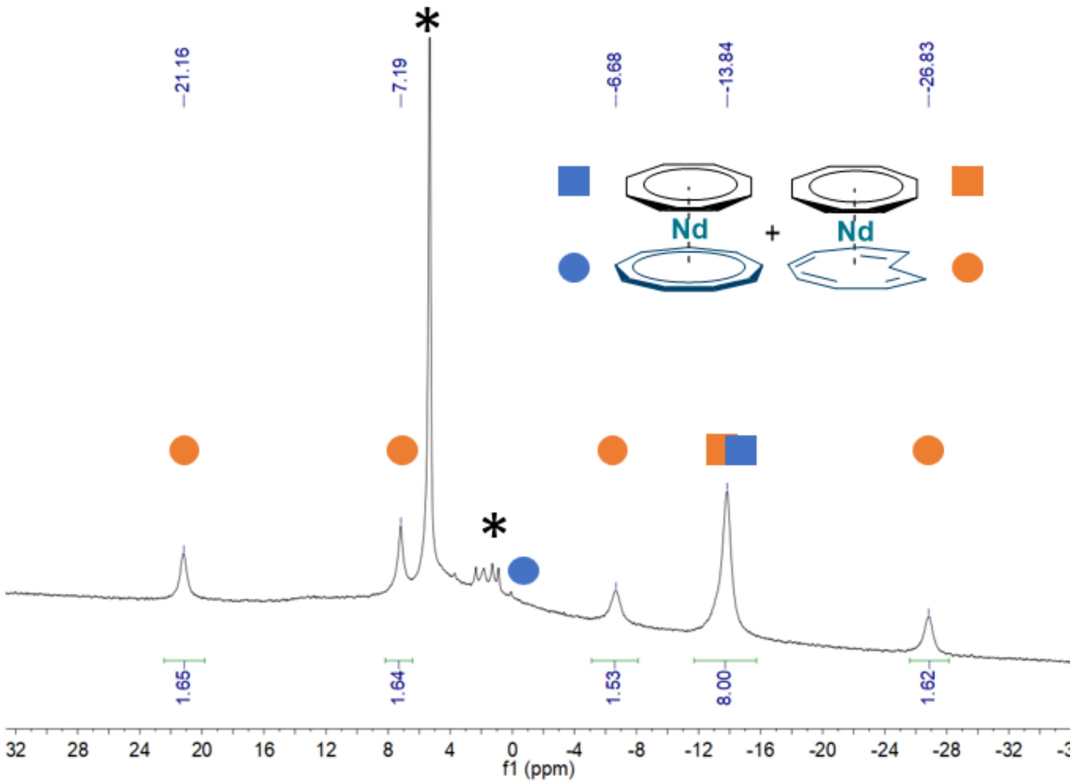

Figure S15: [1]H NMR of **2**-Nd-trans in CD_2Cl_2 measured at 293 K (* residual protio signal of the solvent).

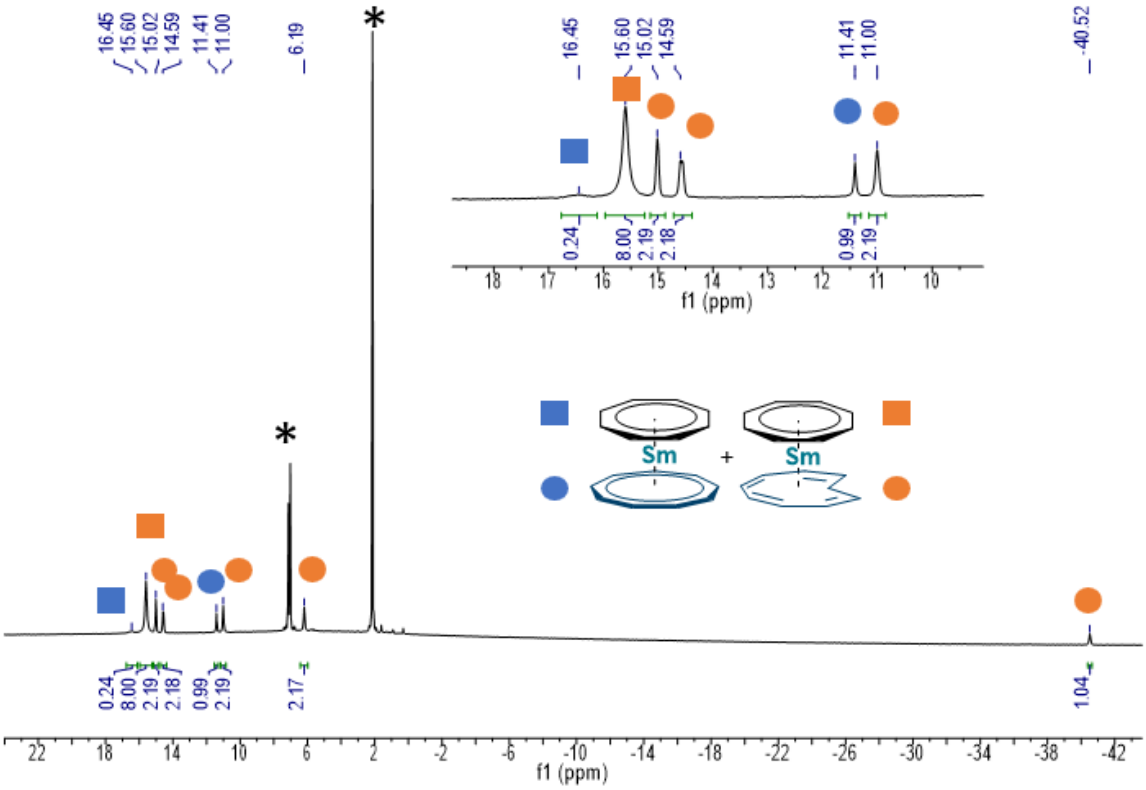

Figure S16: [1]H NMR of **2**-Sm-trans in CD_2Cl_2 measured at 293 K (* residual protio signal of the solvent).

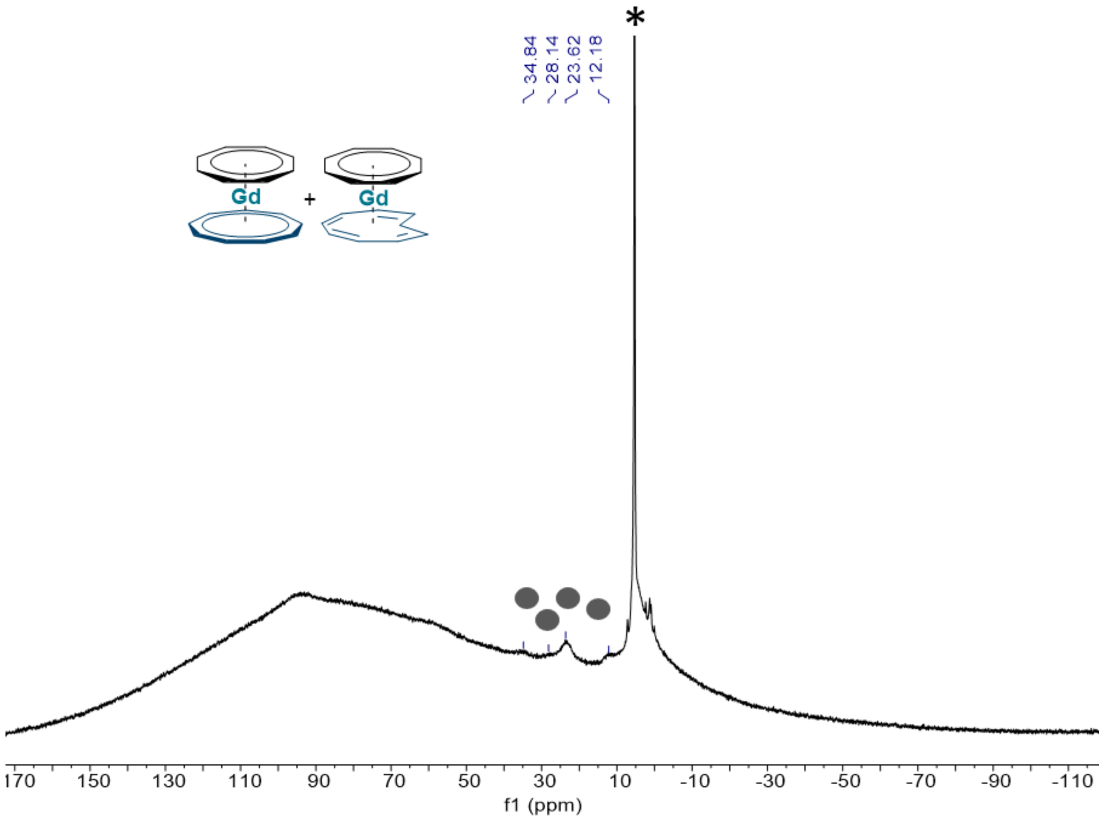

Figure S17: [1]H NMR of **2**-Gd-trans in CD_2Cl_2 measured at 293 K (* residual protio signal of the solvent). The uncertainty of integration does not allow the attribution.

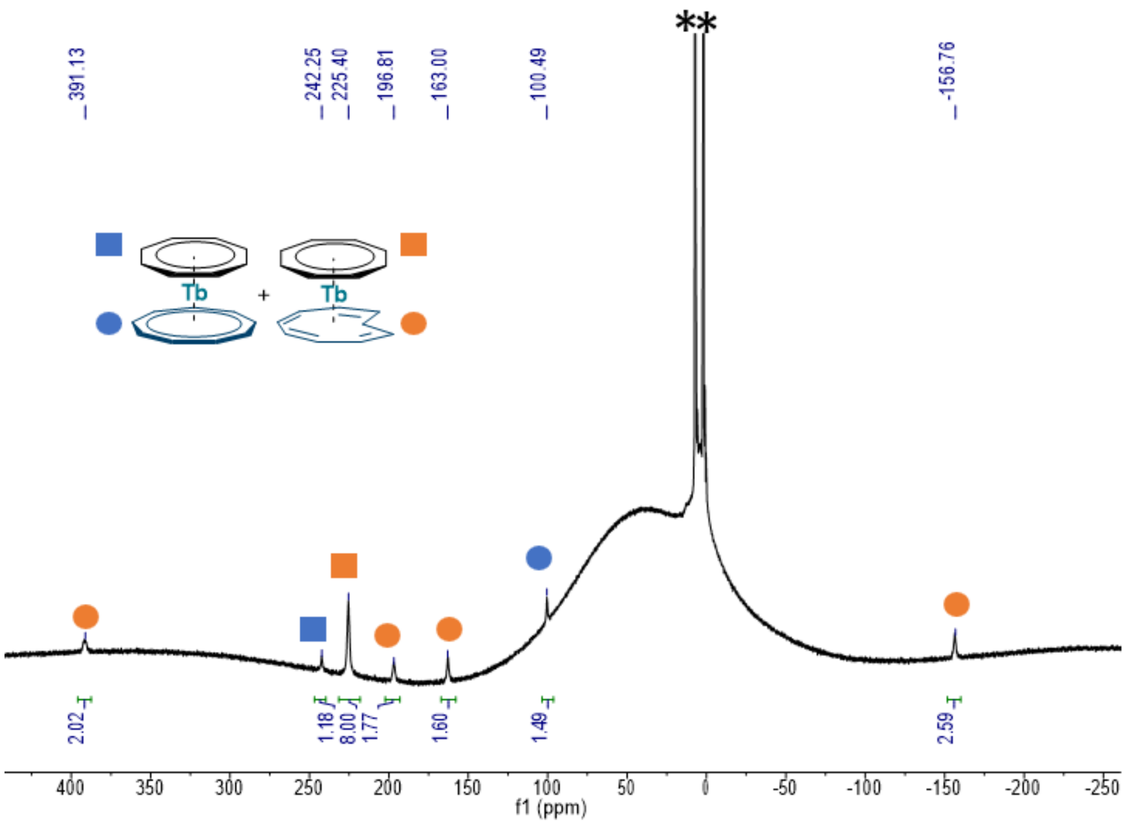

Figure S18: [1]H NMR of **2**-Tb-trans in toluene-d_8 measured at 293 K (* residual protio signal of the solvent).

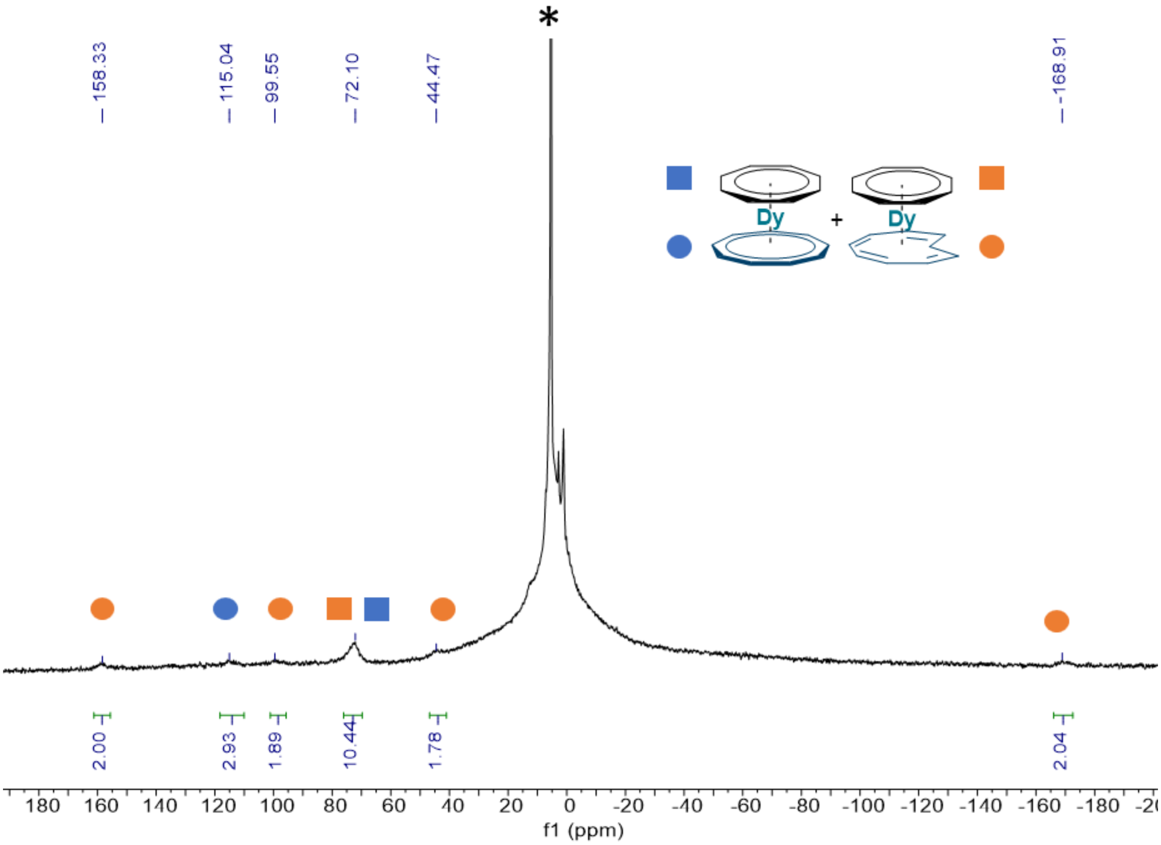

Figure S19: *[1]H NMR of **2**-Dy-trans in CD_2Cl_2 measured at 293 K (* residual protio signal of the solvent).*

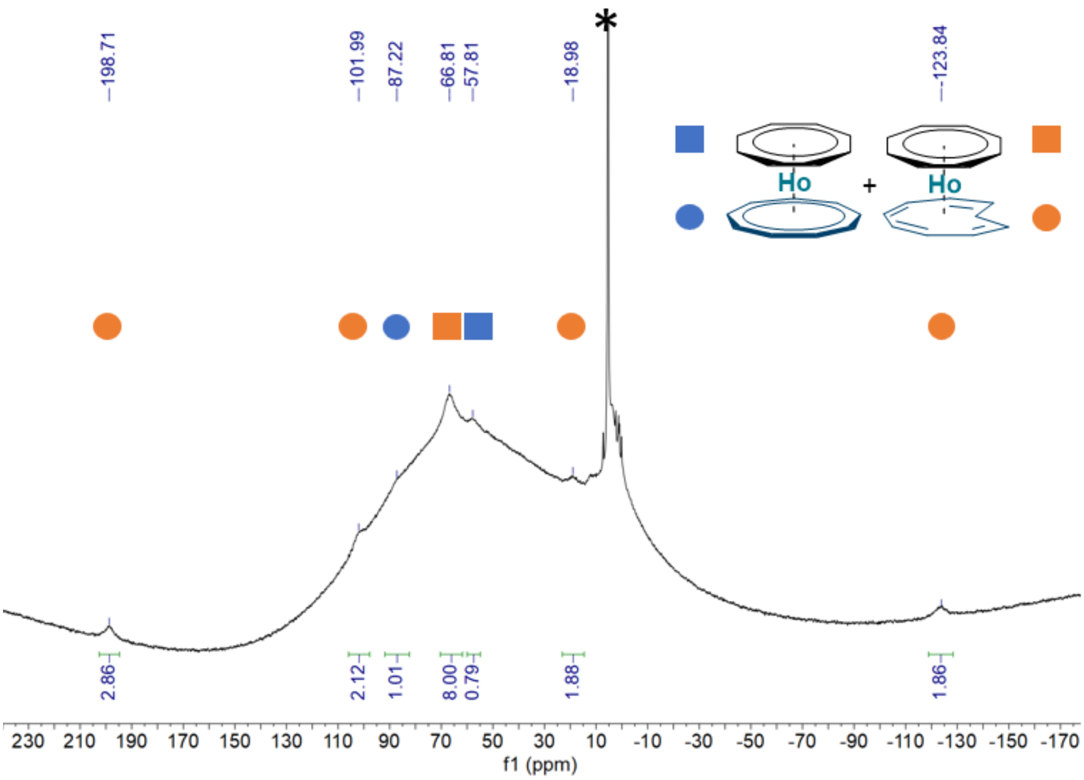

Figure S20: *[1]H NMR of **2**-Ho-trans in CD_2Cl_2 measured at 293 K (* residual protio signal of the solvent).*

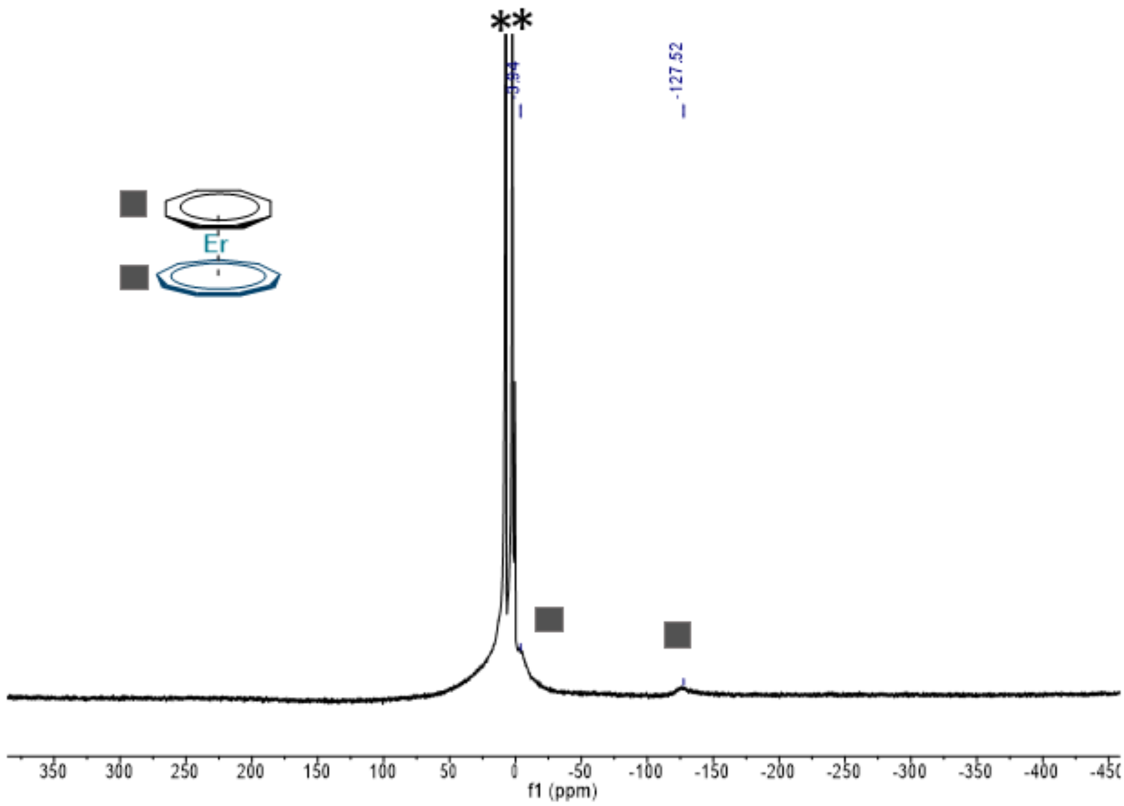

***Figure S21**:^{1}H NMR of **2**-Er-cis in toluene-d_8 measured at 293 K (* residual protio signal of the solvent).*

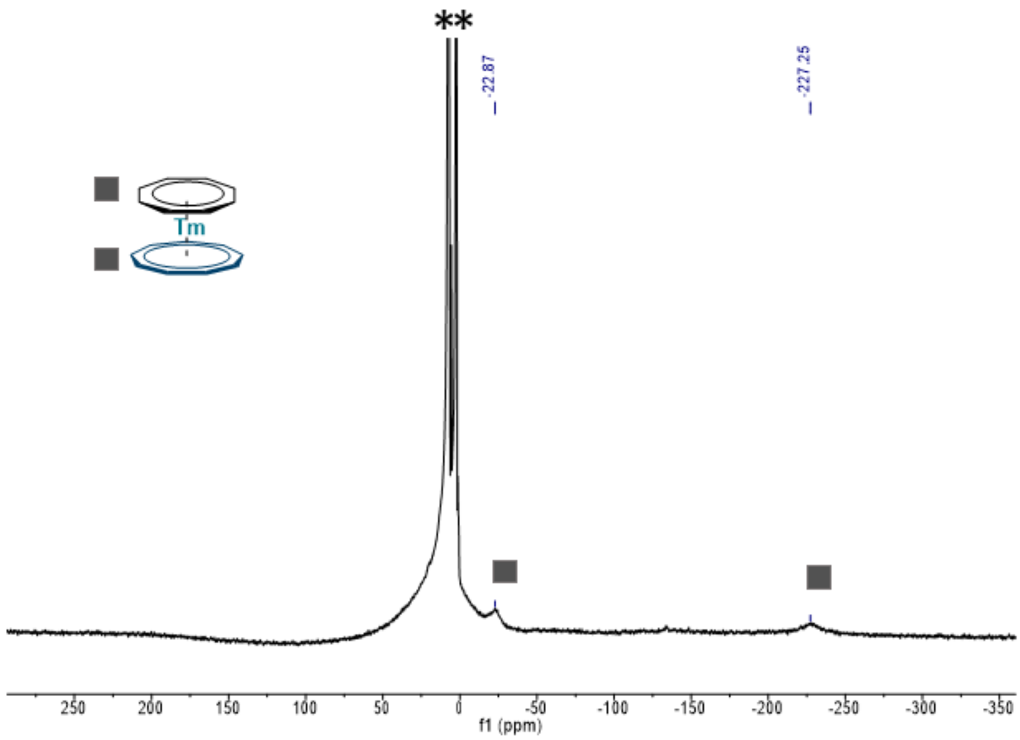

***Figure S22**: ^{1}H NMR of **2**-Tm-cis in toluene-d_8 measured at 293 K (* residual protio signal of the solvent).*

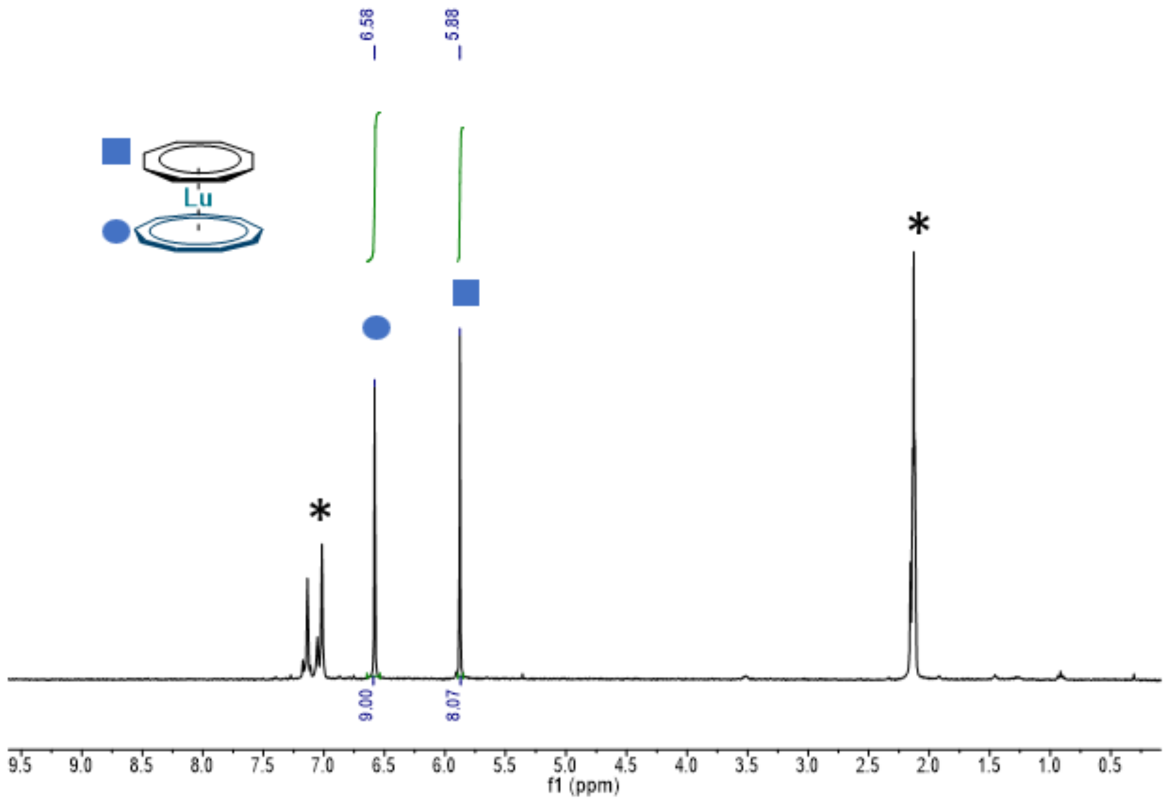

***Figure S23**: ^{1}H NMR of **2**-Lu-cis in toluene-d_8 measured at 293 K (* residual protio signal of the solvent).*

4. IR Spectra

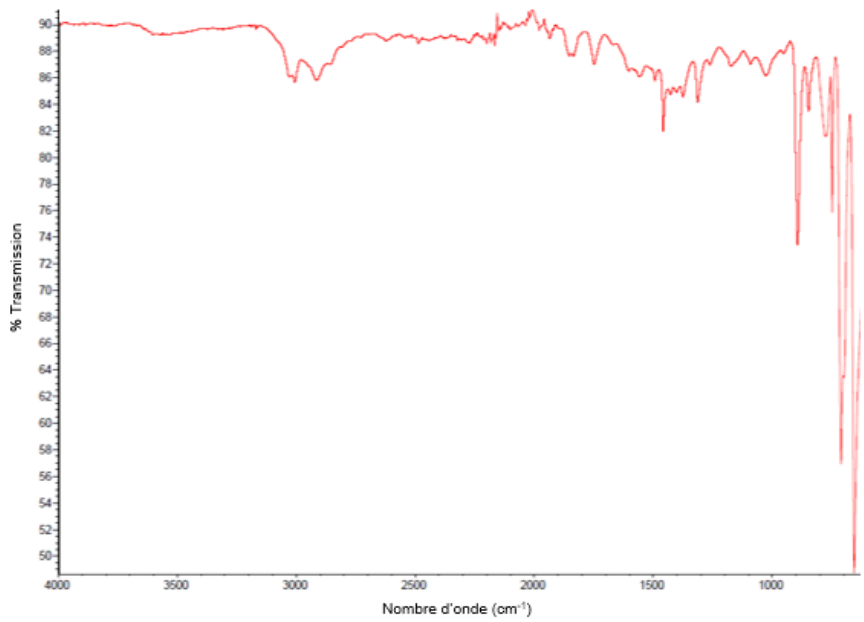

***Figure S24:** IR spectrum of **2**-Tb-cis*

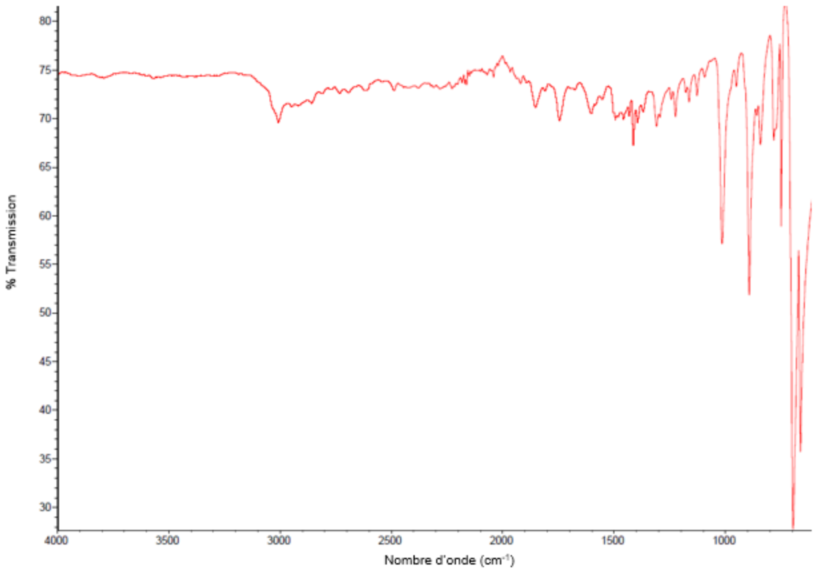

Figure S25: *IR spectrum of **2**-Tb-trans*

Table S1: *Summary of stretches observed in both isomers of **2**-Tb. The intensity of the signals is characterized by w = weak, m = medium, s = strong*

	2-Tb-*cis*	**2**-Tb-*trans*
Wavenumber (cm^{-1})	1457.20 (w)	1013.91 (m)
	892.06 (m)	891.95 (m)
	709.59 (s)	695.00 (s)
	654.30 (s)	661.54 (s)

5. X-ray crystallography

General details. Single crystals of the complexes suitable for X-ray analysis were mounted on a Kapton loop using a Paratone N oil. Two diffractometers were used during this for the data acquisition, either a Bruker diffractometer equipped with an APEX II CCD detector and a graphite Mo-Kα monochromator or a Stoe stadivari diffractometer with a Eiger2 detector and a Mo-Kα microsource. All measurements were done at 150 K (unless otherwise stated) and a refinement method was used for solving the structure. The resolution of the solid-state structure was accomplished using the SHELXS-97 or SHELXT programs. The refinement was performed with the SHELXL program using the Olex2 software. All atoms – except hydrogens – were refined anisotropically.

Atoms denoted C(X') refer to equivalent atoms constructed by the symmetry operation of the associated space group. For the Cnt ligand, the terme Cnt – 8C refers to the 8 atoms of the Cnt ligand excluding the isomerized atoms.

The molecular structure of **2** display as the thermal ellipsoids that are depicted at 50% probability level. The center atom represents the corresponding Ln and are depicted with different colors and carbon atoms are in grey. Hydrogen atoms and disorder of the Cot and the Cnt ligand are omitted for clarity. The blue and red spots represent the constructed centroids for Cnt-*cis* and Cot respectively. The purple and orange spots represent the constructed centroids for Cnt – 8C and Cnt-*trans* respectively. Moreover, the data presents a disorder, typical for this family of complexes. The heavy Y atom is disordered over two positions, close to the symmetry element, resulting with hight calculated residual electronic density. This peculiar disorder explains checkcif alerts about calculated residual electronic density. The C8 and C9 aromatic ligands are also disordered, resulting in low C-C bond precision.

For the modelisation of the **2-**Ln-*trans* three behaviors have been observed alongside the series. First for the late lanthanides the modelisation of a *trans*-Cnt allowed accurate portrayal of the electronic density showing very low amount of *cis*-Cnt present in the lattice. Then as demonstrated in Fig. S24, Gd and Sm did necessitate the modelisation of a disorder for one carbon atom between the *cis* and *trans* position. Finally, for La, Ce, Pr and Nd, two disordered and eclipsed Cnt rings were used to accurately represent the electronic density. One of them featuring a carbon in the *trans* position and the other one in the *cis* position as shown in Fig. S38-39.

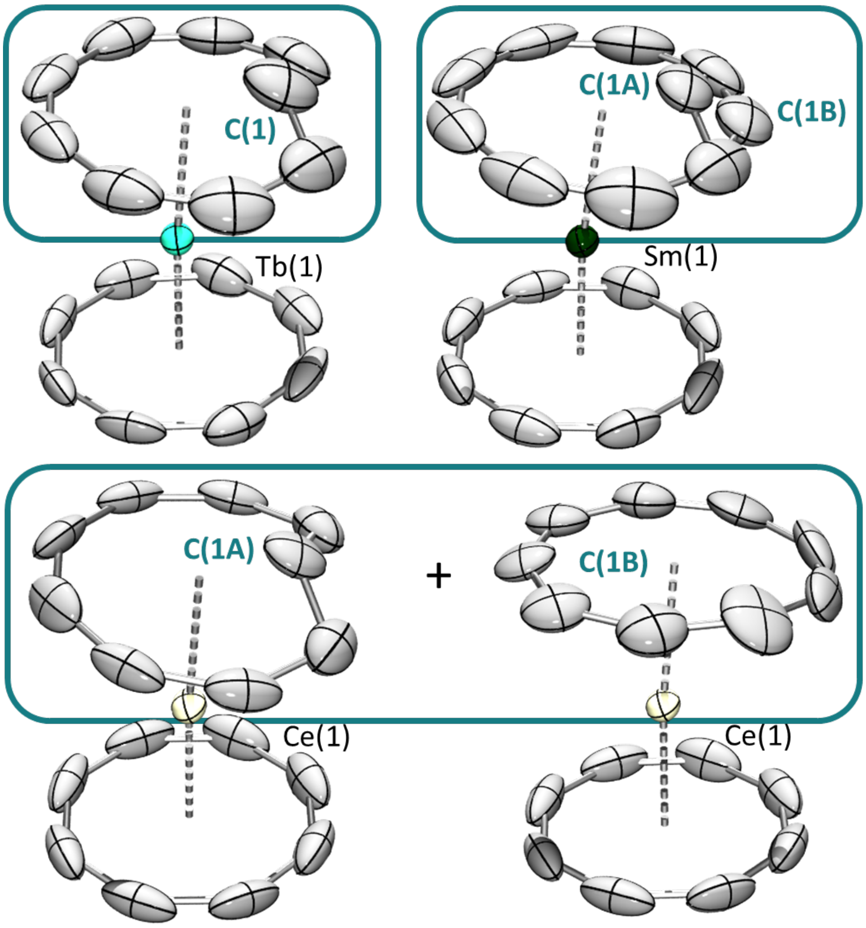

Figure S 26: Representation of the different model used for the LnCot(trans-Cnt) complexes

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*Table S 2: Crystallographic data, details of data collection and structure refinement parameters of all **2***

Compound	**YCot(Cnt-*cis*)**	**LaCot(Cnt-*cis*)**	**CeCot(Cnt-*cis*)**
Formula	$C_{17}H_{17}Y$	$C_{17}H_{17}La$	$C_{17}H_{17}Ce$
Crystal size (mm^3)	0.15x0.04x0.02	0.14 x 0.06 x 0.03	0.2x0.02x0.02
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/n$	Pnma	Pnma
Volume ($Å^3$)	671.15(10)	1392.9(6)	1381.6(3)
a (Å)	7.0169(6)	12.187(3)	12.1258(14)
b (Å)	8.7585(8)	12.736(3)	12.7752(16)
c (Å)	11.1560(9)	8.974(2)	8.9190(10)
α (deg)	90	90	90
β (deg)	101.791(6)	90	90
γ (deg)	90	90	90
Z	4	4	4
Formula weight (g/mol)	310.21	360.21	361.42
Density (calcd) (g/cm^3)	3.070	1.718	1.738
Absorption coefficient (mm^{-1})	8.645	3.046	3.273
F(000)	632.0	704.0	708.0
Temp (K)	150	150	150
diffractometer	Stoe Stadivari	Bruker APEX-II CCD	Bruker APEX-II CCD
Radiation	Mo Kα (λ = 0.71073)	MoKα (*λ* = 0.71073)	MoKα (*λ* = 0.71073)
2θ range for data collection (deg)	5.962 to 54.968	5.554 to 54.958	5.57 to 56.544
Absorption correction	Multi-scan	Multi-scan	Multi-scan
Total no. reflections	6569	21648	27170
Unique reflections [R_{int}]	1635 [R_{int} = 0.0446]	1674 [R_{int} = 0.1354]	1786 [R_{int} = 0.0965]
Final R indices [I>2σ(I)]	R_1 = 0.1254, wR_2 = 0.2668	R_1 = 0.0363, wR_2 = 0.0785	R_1 = 0.0267, wR_2 = 0.0562
R indices (all data)	R_1 = 0.1367, wR_2 = 0.2712	R_1 = 0.0879, wR_2 = 0.0980	R_1 = 0.0635, wR_2 = 0.0676
Largest diff. peak and hole ($e.A^{-3}$)	3.30/-4.35	0.72/-1.06	0.65/-0.76
GooF	1.171	1.011	1.009

Compound	**PrCot(Cnt-*cis*)**	**NdCot(Cnt-*cis*)**	**SmCot(Cnt-*cis*)**
Formula	$C_{17}H_{17}Pr$	$C_{17}H_{17}Nd$	$C_{17}H_{17}Sm$
Crystal size (mm^3)	0.12x0.03x0.03	0.24x0.03x0.02	-
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	Pnma	Pnma	Pnma
Volume ($Å^3$)	1365.3(8)	1368.1(14)	1356.78(15)
a (Å)	12.055(4)	12.0748(18)	11.9982(8)
b (Å)	12.777(5)	12.8129(19)	12.8760(8)
c (Å)	8.864(3)	8.8427(14)	8.7824(6)
α (deg)	90	90	90
β (deg)	90	90	90
γ (deg)	90	90	90
Z	4	4	4
Formula weight (g/mol)	362.21	365.54	371.65
Density (calcd) (g/cm^3)	1.762	1.775	1.819
Absorption coefficient (mm^{-1})	3.547	3.773	4.306
F(000)	712.0	716.0	724.0
Temp (K)	150	150	150
diffractometer	Bruker APEX-II CCD	Bruker APEX-II CCD	Bruker APEX-II CCD
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection (deg)	5.594 to 51.992	5.598 to 59.346	5.614 to 71.262
Absorption correction	Multi-scan	Multi-scan	Multi-scan
Total no. reflections	7946	28912	107017
Unique reflections [R_{int}]	1404 [R_{int} = 0.1682]	1986 [R_{int} = 0.1464]	3242 [R_{int} = 0.1536]
Final R indices [I>2σ(I)]	R_1 = 0.0528, wR_2 = 0.1097	R_1 = 0.0389, wR_2 = 0.0861	R_1 = 0.0324, wR_2 = 0.0679
R indices (all data)	R_1 = 0.1319, wR_2 = 0.1445	R_1 = 0.1015, wR_2 = 0.1087	R_1 = 0.0631, wR_2 = 0.0822
Largest diff. peak and hole ($e.A^{-3}$)	1.25/-1.22	1.96/-1.07	1.50/-1.41
GooF	1.007	1.022	1.009

Compound	**GdCot(Cnt-*cis*)**	**YCot(Cnt-*trans*)**	**LaCot(Cnt-*trans*)**
Formula	$C_{17}H_{17}Gd$	$C_{17}H_{17}Y$	$C_{17}H_{17}La$
Crystal size (mm^3)	0.14x0.03x0.03	0.17x0.08x0.04	0.12x0.06x0.03
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	Pnma	Pnma	Pnma
Volume ($Å^3$)	1348.0(3)	1335.5(3)	1385.3(2)
a (Å)	11.965(15)	11.7622(15)	12.1385(7)
b (Å)	12.9116(19)	13.1214(18)	12.7452(11)
c (Å)	8.7283(10)	8.6532(11)	8.9543(11)
α (deg)	90	90	90
β (deg)	90	90	90
γ (deg)	90	90	90
Z	4	4	4
Formula weight (g/mol)	378.55	310.21	360.21
Density (calcd) (g/cm^3)	1.865	1.543	1.727
Absorption coefficient (mm^{-1})	4.898	4.345	3.062
F(000)	732.0	632.0	704.0
Temp (K)	150	150	150
diffractometer	Bruker APEX-II CCD	Bruker APEX-II CCD	Stoe Stadivari
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection (deg)	5.634 to 54.954	5.64 to 55.28	5.56 to 58.68
Absorption correction	Multi-scan	Multi-scan	Multi-scan
Total no. reflections	8390	10027	14590
Unique reflections [R_{int}]	1618 [R_{int} = 0.1237]	1614 [R_{int} = 0.1667]	1840 [R_{int} = 0.0335]
Final R indices [I>2σ(I)]	R_1 = 0.0486, wR_2 = 0.0960	R_1 = 0.0536, wR_2 = 0.1128	R_1 = 0.0231, wR_2 = 0.0537
R indices (all data)	R_1 = 0.1100, wR_2 = 0.1171	R_1 = 0.1092, wR_2 = 0.1370	R_1 = 0.0378, wR_2 = 0.0554
Largest diff. peak and hole ($e.A^{-3}$)	0.88/-1.18	0.55/-0.79	1.24/-0.41
GooF	0.997	1.017	0.918

Compound	**CeCot(Cnt-*trans*)**	**PrCot(Cnt-*trans*)**	**NdCot(Cnt-*trans*)**
Formula	$C_{17}H_{17}Ce$	$C_{17}H_{17}Pr$	$C_{17}H_{17}Nd$
Crystal size (mm^3)	0.118x0.03x0.24	0.083x0.049x0.032	0.2x0.04x0.02
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	Pnma	Pnma	Pnma
Volume (Å^3)	1381.8(2)	1369.48(16)	1370.2(5)
a (Å)	12.0523(9)	12.0063(7)	11.983(2)
b (Å)	12.8172(12)	12.8295(10)	12.877(3)
c (Å)	8.9448(10)	8.8907(6)	8.8927(17)
α (deg)	90	90	90
β (deg)	90	90	90
γ (deg)	90	90	90
Z	4	4	4
Formula weight (g/mol)	361.52	362.21	365.54
Density (calcd) (g/cm^3)	1.738	1.757	1.769
Absorption coefficient (mm^{-1})	3.273	3.536	3.762
F(000)	708.0	712.0	716.0
Temp (K)	150	150	150
diffractometer	Stoe Stadivari	Stoe Stadivari	Bruker APEX-II CCD
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection (deg)	5.554 to 61.224	5.574 to 54.198	5.568 to 52.292
Absorption correction	Multi-scan	Multi-scan	Multi-scan
Total no. reflections	12034	5122	15587
Unique reflections [R_{int}]	2056 [R_{int} = 0.0622]	1536 [R_{int} = 0.0542]	1435 [R_{int} = 0.1352]
Final R indices [I>2σ(I)]	R1 = 0.0328, wR2 = 0.0629	R_1 = 0.0342, wR_2 = 0.0608	R_1 = 0.0396, wR_2 = 0.0849
R indices (all data)	R1 = 0.0714, wR2 = 0.0688	R_1 = 0.0771, wR_2 = 0.0663	R_1 = 0.0885, wR_2 = 0.1043
Largest diff. peak and hole (e.A^{-3})	1.08/-0.71	0.97/-0.64	0.90/-1.89
GooF	0.917	0.788	1.047

Compound	SmCot(Cnt-*trans*)	GdCot(Cnt-*trans*)	TbCot(Cnt-*trans*)
Formula	$C_{17}H_{17}Sm$	$C_{17}H_{17}Gd$	$C_{17}H_{17}Tb$
Crystal size (mm^3)	0.47 x 0.287 x 0.07	0.087x0.045x0.032	0.14x0.04x0.04
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	Pnma	Pnma	Pnma
Volume (Å^3)	1355.13(14)	1348.36(15)	1335.5(13)
a (Å)	11.8943(7)	11.8553(8)	11.781(6)
b (Å)	12.9414(6)	13.0113(8)	13.017(8)
c (Å)	8.8036(6)	8.7412(6)	8.708(5)
α (deg)	90	90	90
β (deg)	90	90	90
γ (deg)	90	90	90
Z	4	4	4
Formula weight (g/mol)	371.65	378.55	380.22
Density (calcd) (g/cm^3)	1.822	1.865	1.891
Absorption coefficient (mm^{-1})	4.311	4.897	5.273
F(000)	724.0	732.0	736.0
Temp (K)	150	150	150
diffractometer	Stoe Stadivari	Stoe Stadivari	Bruker APEX-II CCD
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection (deg)	5.596 to 54.2	5.614 to 54.206	5.628 to 54.204
Absorption correction	Multi-scan	Multi-scan	Multi-scan
Total no. reflections	7609	6971	17144
Unique reflections [R_{int}]	1454 [R_{int} = 0.0533]	1552 [R_{int} = 0.0699]	1539 [R_{int} = 0.1491]
Final R indices [I>2σ(I)]	R1 = 0.0323, wR2 = 0.0697	R_1 = 0.0397, wR_2 = 0.0866	R_1 = 0.0447, wR_2 = 0.1093
R indices (all data)	R1 = 0.0561, wR2 = 0.0763	R_1 = 0.0643, wR_2 = 0.0915	R_1 = 0.0726, wR_2 = 0.1274
Largest diff. peak and hole (e.A^{-3})	0.93/-0.67	1.38/-0.86	1.60/-2.27
GooF	0.958	0.933	1.101

Compound	**DyCot(Cnt-*trans*)**	**HoCot(Cnt-*trans*)**	**Sm(Cnt)₂***
Formula	$C_{17}H_{17}Dy$	$C_{17}H_{17}Ho$	$C_{18}H_{18}Sm$
Crystal size (mm^3)	0.64x0.08x0.06	0.1x0.04x0.02	0.097 × 0.09 × 0.055
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	Pnma	Pnma	$P2_1/n$
Volume ($Å^3$)	1336.6(2)	1336.0(2)	735.6(2)
a (Å)	11.8081(12)	11.7641(10)	7.3830(16)
b (Å)	13.057(10)	13.1227(12)	9.1133(11)
c (Å)	8.6690(9)	8.6544(9)	11.059(2)
α (deg)	90	90	90
β (deg)	90	90	98.630(16)
γ (deg)	90	90	90
Z	4	4	2
Formula weight (g/mol)	383.80	386.23	384.67
Density (calcd) (g/cm^3)	1.907	1.920	1.737
Absorption coefficient (mm^{-1})	5.568	5.900	3.974
F(000)	710.0	744.0	376.0
Temp (K)	150	150	150
diffractometer	Bruker APEX-II CCD	Bruker APEX-II CCD	Stoe Stadivari
Radiation	MoKα (λ = 0.71073)	MoKα (*λ* = 0.71073)	Mo Kα (λ = 0.71073)
2θ range for data collection (deg)	5.64 to 63.14	5.638 to 52.042	5.82 to 52.008
Absorption correction	Multi-scan	Multi-scan	Multi-scan
Total no. reflections	12046	18294	9911
Unique reflections [R_{int}]	2315 [R_{int} = 0.0701]	1376 [R_{int} = 0.1726]	1448 [R_{int} = 0.1487]
Final R indices [I>2σ(I)]	R_1 = 0.0384, wR_2 = 0.0776	R_1 = 0.0379, wR_2 = 0.0640	R_1 = 0.0959, wR_2 = 0.2434
R indices (all data)	R_1 = 0.0550, wR_2 = 0.0844	R_1 = 0.0615, wR_2 = 0.0677	R_1 = 0.1172, wR_2 = 0.2613
Largest diff. peak and hole ($e.A^{-3}$)	1.52/-1.68	1.10/-1.11	5.14/-2.66
GooF	1.082	0.842	1.004

**cis:trans* ratio of 18:82

*Table S3: Main metrics parameters for the **2** (trans and cis isomer). The carbon in trans formation is written in red. a) metrics taken from litterature[2]*

	Y		La		Ce		Pr		Nd		Sm	
	trans	cis	trans	cis	trans	cis	trans	cis	trans	cis	trans	cis
Ln - C(Cnt)	2.657(10)	2.87(2)	2.851(16)	2.93(2)	2.750(12)	2.891(13)	2.749(15)	2.89(4)	2.79(2)	2.84(1)	2.687(13)	2.824(9)
	2.827(9)	2.58(2)	2.931(8)	2.944(14)	2.878(15)	2.933(8)	2.87(2)	2.91(2)	2.89(2)	2.89(1)	2.857(9)	2.873(6)
	2.894(9)	2.51(2)	2.913(8)	2.971(13)	2.900(15)	2.942(8)	2.87(2)	2.93(2)	2.91(2)	2.92(1)	2.879(9)	2.892(7)
	2.812(9)	2.60(2)	2.901(8)	2.952(13)	2.887(15)	2.925(8)	2.88(2)	2.90(4)	2.85(2)	2.90(1)	2.834(9)	2.878(7)
	2.692(8)	2.81(3)	2.873(8)	2.927(13)	2.857(15)	2.905(8)	2.815(16)	2.85(2)	2.81(2)	2.86(1)	2.763(6)	2.831(6)
	-	3.13(3)	-	-	-	-	-	-	-	-	-	-
	-	3.53(2)	-	-	-	-	-	-	-	-	-	-
	-	3.60(2)	-	-	-	-	-	-	-	-	-	-
	-	3.30(2)	-	-	-	-	-	-	-	-	-	-
Ln-C(Cot)	2.524(7)	2.63(2)	2.686(4)	2.699(11)	2.640(4)	2.689(7)	2.637(5)	2.67(2)	2.619(8)	2.66(1)	2.594(5)	2.624(6)
	2.554(8)	2.46(3)	2.693(4)	2.694(12)	2.657(4)	2.675(8)	2.631(6)	2.65(2)	2.614(9)	2.65(1)	2.591(6)	2.627(7)
	2.554(8)	2.50(2)	2.693(4)	2.700(13)	2.656(4)	2.684(8)	2.639(6)	2.64(2)	2.641(9)	2.64(1)	2.601(6)	2.629(7)
	2.536(7)	2.43(2)	2.703(4)	2.686(13)	2.664(4)	2.657(8)	2.637(5)	2.64(2)	2.629(9)	2.64(1)	2.595(6)	2.618(6)
	-	2.54(2)	-	-	-	-	-	-	-	-	-	-
	-	2.61(2)	-	-	-	-	-	-	-	-	-	-
	-	2.48(3)	-	-	-	-	-	-	-	-	-	-
	-	2.65(2)	-	-	-	-	-	-	-	-	-	-
Plane (Cot) ^Plane (Cnt)	-	21.26 °	-	3.69 °	-	3.75°	-	3.86 °	-	3.62 °	-	3.02 °
Cent-Cot - Ln - Cent-Cnt	-	170.67 °	-	176.86 °	-	177.01 °	-	177.39 °	-	176.70 °	-	177.17 °
Ln-C(Cot) average	2.542(8)	2.54(2)	2.694(4)	2.695(12)	2.654(4)	2.676(8)	2.636(6)	2.65(1)	2.625(9)	2.65(1)	2.595(6)	2.624(7)
Ln-C(Cnt-C8) average	2.806(9)	-	2.905(8)	-	2.881(15)	-	2.86(2)	-	2.87(2)	-	2.833(8)	-
Ln-C(Cnt) average	2.776(9)	2.75(2)	2.894(10)	2.944(15)	2.85(1)	2.91(1)	2.84(2)	2.90(2)	2.85(2)	2.88(1)	2.804(9)	2.860(7)

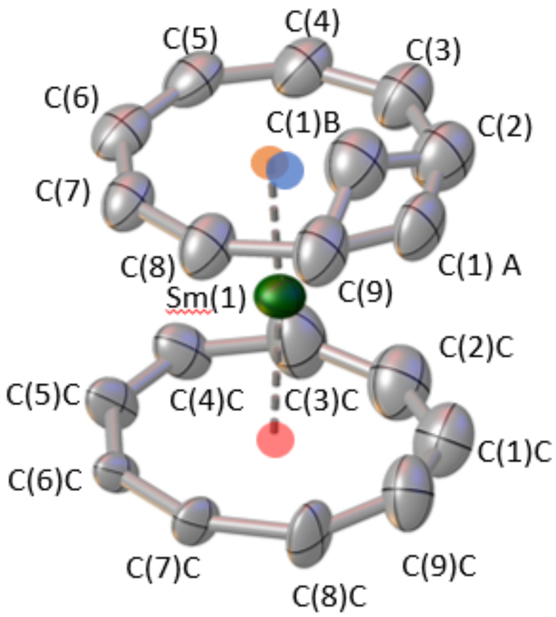
	Gd		Tb		Dy		Ho		Er	Tm	Lu
	trans	cis	trans	cis[a]	trans	cis[a]	trans	cis[a]	cis[a]	cis[a]	cis[a]
Ln - C(Cnt)	2.703(17)	2.77(3)	2.664(16)	2.78(2)	2.660(9)	2.675(17)	2.673(11)	2.56(2)	2.55(3)	2.54(3)	2.50(2)
	2.853((10))	2.817(18)	2.837(12)	2.839(16)	2.825(9)	2.723(16)	2.819(9)	2.61(2)	2.59(3)	2.57(2)	2.54(2)
	2.872(9)	2.873(19)	2.885(12)	2.874(15)	2.858(9)	2.738(16)	2.86(1)	2.821(16)	2.61(3)	2.64(2)	2.6(2)
	2.828(10)	2.861(19)	2.828(12)	2.852(16)	2.806(6)	2.787(15)	2.805(8)	3.212(14)	2.881(16)	2.73(2)	2.68(2)
	2.749(9)	2.801(17)	2.722(10)	2.780(14)	2.720(6)	2.860(18)	2.684(7)	3.466(17)	3.443(13)	2.875(13)	2.943(12)
	-	-	-	-	-	2.953(18)	-	3.37(2)	3.763(13)	3.11(2)	3.14(2)
	-	-	-	-	-	2.959(17)	-	3.02(3)	3.597(15)	3.449(9)	3.59(10)
	-	-	-	-	-	2.857(16)	-	2.72(3)	3.10(2)	3.594(12)	3.719(13)
	-	-	-	-	-	2.736(16)	-	2.62(2)	2.69(3)	3.769(8)	3.930(9)
Ln-C(Cot)	2.559(7)	2.607(15)	2.537(9)	2.573(14)	2.534(5)	2.52(2)	2.518(7)	2.493(15)	2.470(13)	2.467(8)	2.461(10)
	2.575(7)	2.630(17)	2.563(11)	2.591(16)	2.544(5)	2.560(16)	2.529(8)	2.519(14)	2.499(15)	2.479(12)	2.457(12)
	2.582(6)	2.613(17)	2.566(9)	2.586(14)	2.543(5)	2.611(16)	2.524(7)	2.580(16)	2.50(12)	2.46(2)	2.465(17)
	2.565(7)	2.586(15)	2.540(9)	2.573(13)	2.544(5)	2.639(16)	2.534(6)	2.652(18)	2.55(3)	2.54(3)	2.495(19)
	-	-	-	-	-	2.600(16)	-	2.61(2)	2.51(3)	2.50(3)	2.45(2)
	-	-	-	-	-	2.615(15)	-	2.55(3)	2.52(3)	2.43(3)	2.44(2)
	-	-	-	-	-	2.590(15)	-	2.47(4)	2.45(3)	2.45(2)	2.47(2)
	-	-	-	-	-	2.536(17)	-	2.464(19)	2.448(16)	2.456(12)	2.468(13)
Plane (Cot) ^Plane (Cnt)	-	2.53 °	-	4.80 °	-	12.5 °	-	26.7 °	29.7 °	31.3 °	34.2 °
Cent-Cot - Ln - Cent-Cnt	-	177.34 °	-	177.4 °	-	172.0 °	-	169.6 °	174.7 °	173.8 °	174.2 °
Ln-C(Cot) average	2.570(7)	2.609(16)	2.552(10)	2.58(2)	2.541(5)	2.58(4)	2.478(7)	2.55(7)	2.50(4)	22.48(3)	2.46(1)
Ln-C(Cnt-C8) average	2.826(9)	-	2.818(11)	-	2.802(8)	-	2.792(9)	-	-	-	-
Ln-C(Cnt) average	2.801(11)	2.82(2)	2.787(13)	2.82(3)	2.774(8)	2.81(10)	2.768(9)	2.93(33)	2.74(21)	2.74(21)	2.73(26)

Table S4: *Main metrics for the **2**-Ln-trans. The carbon in trans formation is written in red.*

	Y	La	Ce	Pr	Nd	Sm	Gd	Tb	Dy	Ho
	trans	trans	trans	trans	trans	trans	trans	trans	trans	trans
Ln - C(Cnt)	2.657(10)	2.851(16)	2.750(12)	2.749(15)	2.79(2)	2.687(13)	2.703(17)	2.664(16)	2.660(9)	2.673(11)
	2.827(9)	2.931(8)	2.878(15)	2.87(2)	2.89(2)	2.857(9)	2.853(10)	2.837(12)	2.825(9)	2.819(9)
	2.894(9)	2.913(8)	2.900(15)	2.87(2)	2.91(2)	2.879(9)	2.872(9)	2.885(12)	2.858(9)	2.86(1)
	2.812(9)	2.901(8)	2.887(15)	2.88(2)	2.85(2)	2.834(9)	2.828(10)	2.828(12)	2.806(6)	2.805(8)
	2.692(8)	2.873(8)	2.857(15)	2.815(16)	2.81(2)	2.763(6)	2.749(9)	2.722(10)	2.720(6)	2.684(7)
Ln-C(Cot)	2.524(7)	2.686(4)	2.640(4)	2.637(5)	2.619(8)	2.594(5)	2.559(7)	2.537(9)	2.534(5)	2.518(7)
	2.554(8)	2.693(4)	2.657(4)	2.631(6)	2.614(9)	2.591(6)	2.575(7)	2.563(11)	2.544(5)	2.529(8)
	2.554(8)	2.693(4)	2.656(4)	2.639(6)	2.641(9)	2.601(6)	2.582(6)	2.566(9)	2.543(5)	2.524(7)
	2.536(7)	2.703(4)	2.664(4)	2.637(5)	2.629(9)	2.595(6)	2.565(7)	2.540(9)	2.544(5)	2.534(6)
Ln-C(Cot) average	2.542(8)	2.694(4)	2.654(4)	2.636(6)	2.625(9)	2.595(6)	2.570(7)	2.552(10)	2.541(5)	2.478(7)
Ln-C(Cnt-C8) average	2.806(9)	2.905(8)	2.881(15)	2.86(2)	2.87(2)	2.833(8)	2.826(9)	2.818(11)	2.802(8)	2.792(9)
Ln-C(Cnt)all average	2.776(9)	2.894(10)	2.85(1)	2.84(2)	2.85(2)	2.804(9)	2.801(11)	2.787(13)	2.774(8)	2.768(9)

***Table S5**: Main metrics for the **2**-Ln-cis. a) Metrics taken from known literature*

	Y	La	Ce	Pr	Nd	Sm	Gd	Tb	Dy	Ho	Er	Tm	Lu
	cis	cis	cis	cis	cis	cis	cis	cis[a]	cis[a]	cis[a]	cis[a]	cis[a]	cis[a]
	2.87(2)	2.93(2)	2.891(13)	2.89(4)	2.84(1)	2.824(9)	2.77(3)	2.78(2)	2.675(17)	2.56(2)	2.55(3)	2.54(3)	2.50(2)
	2.58(2)	2.944(14)	2.933(8)	2.91(2)	2.89(1)	2.873(6)	2.817(18)	2.839(16)	2.723(16)	2.61(2)	2.59(3)	2.57(2)	2.54(2)
	2.51(2)	2.971(13)	2.942(8)	2.93(2)	2.92(1)	2.892(7)	2.873(19)	2.874(15)	2.738(16)	2.821(16)	2.61(3)	2.64(2)	2.6(2)
	2.60(2)	2.952(13)	2.925(8)	2.90(4)	2.90(1)	2.878(7)	2.861(19)	2.852(16)	2.787(15)	3.212(14)	2.881(16)	2.73(2)	2.68(2)
Ln - C(Cnt)	2.81(3)	2.927(13)	2.905(8)	2.85(2)	2.86(1)	2.831(6)	2.801(17)	2.780(14)	2.860(18)	3.466(17)	3.443(13)	2.875(13)	2.943(12)
	3.13(3)	-	-	-	-	-	-	-	2.953(18)	3.37(2)	3.763(13)	3.11(2)	3.14(2)
	3.53(2)	-	-	-	-	-	-	-	2.959(17)	3.02(3)	3.597(15)	3.449(9)	3.59(10)
	3.60(2)	-	-	-	-	-	-	-	2.857(16)	2.72(3)	3.10(2)	3.594(12)	3.719(13)
	3.30(2)	-	-	-	-	-	-	-	2.736(16)	2.62(2)	2.69(3)	3.769(8)	3.930(9)
	2.63(2)	2.699(11)	2.689(7)	2.67(2)	2.66(1)	2.624(6)	2.607(15)	2.573(14)	2.52(2)	2.493(15)	2.470(13)	2.467(8)	2.461(10)
	2.46(3)	2.694(12)	2.675(8)	2.65(2)	2.65(1)	2.627(7)	2.630(17)	2.591(16)	2.560(16)	2.519(14)	2.499(15)	2.479(12)	2.457(12)
	2.50(2)	2.700(13)	2.684(8)	2.64(2)	2.64(1)	2.629(7)	2.613(17)	2.586(14)	2.611(16)	2.580(16)	2.50(12)	2.46(2)	2.465(17)
Ln-C(Cot)	2.43(2)	2.686(13)	2.657(8)	2.64(2)	2.64(1)	2.618(6)	2.586(15)	2.573(13)	2.639(16)	2.652(18)	2.55(3)	2.54(3)	2.495(19)
	2.54(2)	-	-	-	-	-	-	-	2.600(16)	2.61(2)	2.51(3)	2.50(3)	2.45(2)
	2.61(2)	-	-	-	-	-	-	-	2.615(15)	2.55(3)	2.52(3)	2.43(3)	2.44(2)
	2.48(3)	-	-	-	-	-	-	-	2.590(15)	2.47(4)	2.45(3)	2.45(2)	2.47(2)
	2.65(2)	-	-	-	-	-	-	-	2.536(17)	2.464(19)	2.448(16)	2.456(12)	2.468(13)
Plane (Cot) ^Plane (Cnt)	21.26 °	3.69 °	3.75°	3.86 °	3.62 °	3.02 °	2.53 °	4.80 °	12.5 °	26.7 °	29.7 °	31.3 °	34.2 °
Cent-Cot - Ln - Cent-Cnt	170.67 °	176.86 °	177.01 °	177.39 °	176.70 °	177.17 °	177.34 °	177.4 °	172.0 °	169.6 °	174.7 °	173.8 °	174.2 °
Ln-C(Cot) average	2.54(2)	2.695(12)	2.676(8)	2.65(1)	2.65(1)	2.624(7)	2.609(16)	2.58(2)	2.58(4)	2.55(7)	2.50(4)	22.48(3)	2.46(1)
Ln-C(Cnt) average	2.75(2)	2.944(15)	2.91(1)	2.90(2)	2.88(1)	2.860(7)	2.82(2)	2.82(3)	2.81(10)	2.93(33)	2.74(21)	2.74(21)	2.73(26)



18% *trans*

Figure S27: *Molecular structure of **1-trans** (18% trans ratio)*

Table S6: *Summary of bond length and angles from the ligands to the metal center in **1**.*

	Main distances in Å
Sm-C1C(Cnt)	2.83(4)
Sm – C2 (Cnt)	2.89(4)
Sm – C3 (Cnt)	2.92(3)
Sm – C4 (Cnt)	2.77(6)
Sm – C5 (Cnt)	2.90(4)
Sm– C6 (Cnt)	2.92(3)
Sm – C7 (Cnt)	2.95(2)
Sm – C8 (Cnt)	2.92(3)
Sm – C9 (Cnt)	2.92(4)
Sm – Cent (Cnt cis)	2.058 (12)
Sm – C1A (Cnt)	2.85(5)
Sm-C1B(Cnt)	2.72(7)
Sm – C2 (Cnt)	2.81(3)
Sm – C3 (Cnt)	2.83(3)
Sm – C4 (Cnt)	2.82(3)
Sm – C5 (Cnt)	2.82(3)
Sm– C6 (Cnt)	2.85(3)
Sm – C7 (Cnt)	2.84(3)
Sm – C8 (Cnt)	2.87(3)
Sm – C9 (Cnt)	2.87(4)
Sm – Cent (Cnt)	2,075 (13)
Sm – Cent (Cnt) –9C cis	2,022 (9)
Plane (Cnt cis) ^Plane (Cnt trans)	2,7
Cent-Cntcis -Sm- Cent-Cnttrans	176,2
Plane (C2/C1/C2^1) ^Plane (Cnt 9C cis)	48

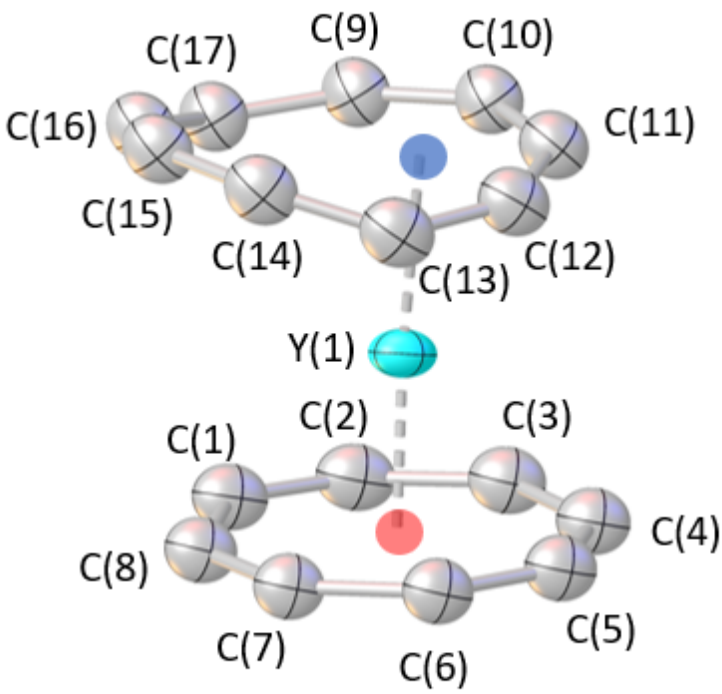


Figure S28: *Molecular structure of* ***2****-Y-cis*

Table S7: *Summary of bond length and angles from the ligands to the metal center.[1] Only the C coordinated to the metal are taken into account.*

	Main distances in Å
Y(1) – C(1) (Cot)	2.63(2)
Y(1) – C(2) (Cot)	2.46(3)
Y(1) – C(3) (Cot)	2.50(2)
Y(1) – C(4) (Cot)	2.43(2)
Y(1) – C(5) (Cot)	2.54(2)
Y(1) – C(6) (Cot)	2.61(2)
Y(1) – C(7) (Cot)	2.48(3)
Y(1) – C(8) (Cot)	2.65(2)
Y(1) – Cent (Cot)	1.734(9)
Y(1) – C(9) (Cnt)	2.87(2)
Y(1) – C(10) (Cnt)	2.58(2)
Y(1) – C(11) (Cnt)	2.51(2)
Y(1) – C(12) (Cnt)	2.60(2)
Y(1) – C(13) (Cnt)	2.81(3)
Y(1) – C(14) (Cnt)	3.13(3)
Y(1) – C(15) (Cnt)	3.53(2)
Y(1) – C(16) (Cnt)	3.60(2)
Y(1) – C(17) (Cnt)	3.30(2)
Y(1) – Cent (Cnt)[1]	2.081(11)
Plane (Cot) ^Plane (Cnt)[1]	21.26 °
Cent (Cot) - Y(1) – Cent (Cnt)[1]	170.67 °

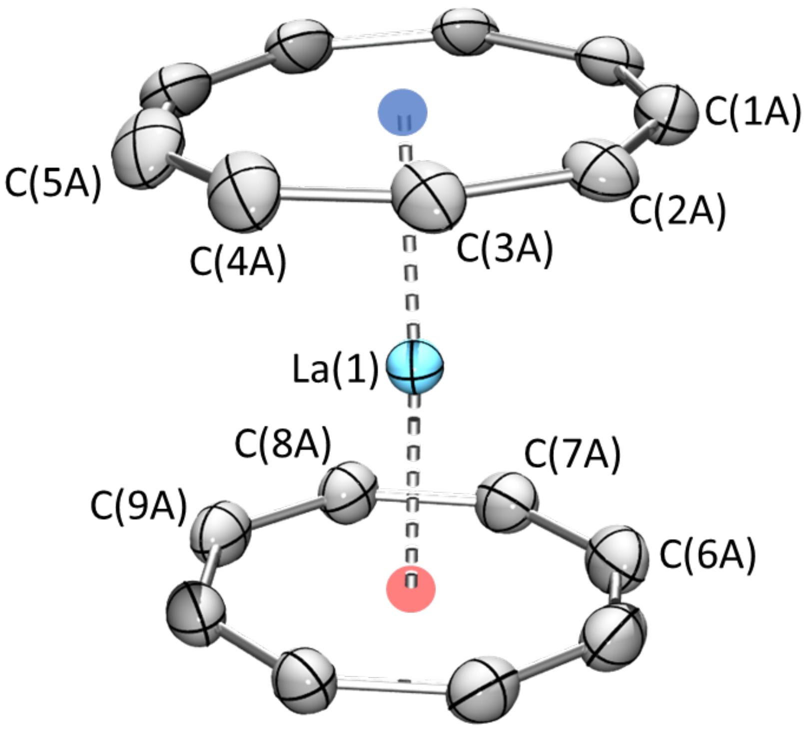


***Figure S29**: Molecular structure of **2**-La-cis*

***Table S8:** Summary of bond length and angles from the ligands to the metal center.*

	Main distances in Å
La(1) – C(6A) (Cot)	2.699(11)
La(1) – C(7A) (Cot)	2.694(12)
La(1) – C(8A) (Cot)	2.700(13)
La(1) – C(9A) (Cot)	2.686(13)
La(1) – Cent (Cot)	1.98
La(1) – C(1A) (Cnt)	2.93(2)
La(1) – C(2A) (Cnt)	2.944(14)
La(1) – C(3A) (Cnt)	2.971(13)
La(1) – C(4A) (Cnt)	2.952(13)
La(1) – C(5A) (Cnt)	2.927(13)
La(1) – Cent (Cnt)	2.14
Plane (Cot) ^Plane (Cnt)	3.69 °
Cent (Cot) - La(1) – Cent (Cnt)	176.86 °

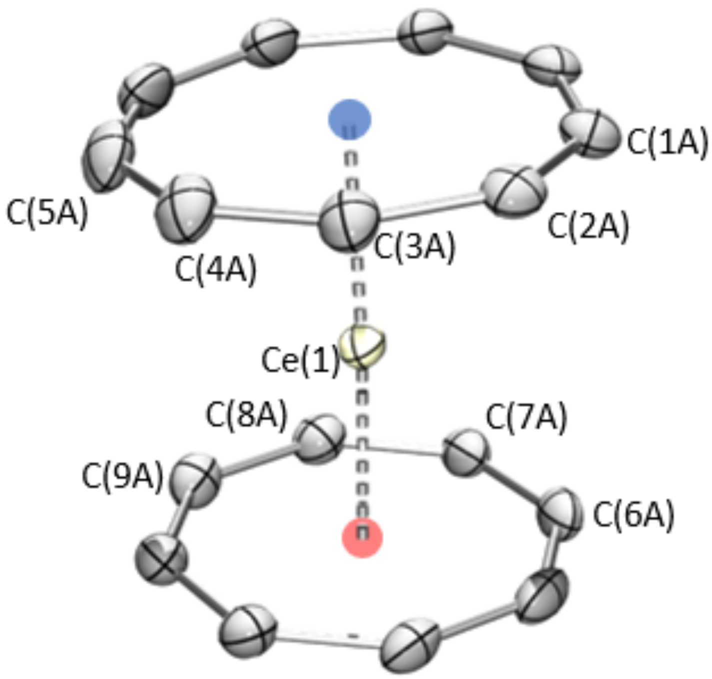


*Figure S 30: Molecular structure of **2**-Ce-cis*

Table S9: *Summary of bond length and angles from the ligands to the metal center.*

	Main distances in Å
Ce(1) – C(6A) (Cot)	2.689(7)
Ce(1) – C(7A) (Cot)	2.675(8)
Ce(1) – C(8A) (Cot)	2.684(8)
Ce(1) – C(9A) (Cot)	2.657(8)
Ce(1) – Cent (Cot)	1.947
Ce(1) – C(1A) (Cnt)	2.891(13)
Ce(1) – C(2A) (Cnt)	2.933(8)
Ce(1) – C(3A) (Cnt)	2.942(8)
Ce(1) – C(4A) (Cnt)	2.925(8)
Ce(1) – C(5A) (Cnt)	2.905(8)
Ce(1) – Cent (Cnt)	2.095
Plane (Cot) ^Plane (Cnt)	3.75°
Cent (Cot) - Ce(1) – Cent (Cnt)	177.01°

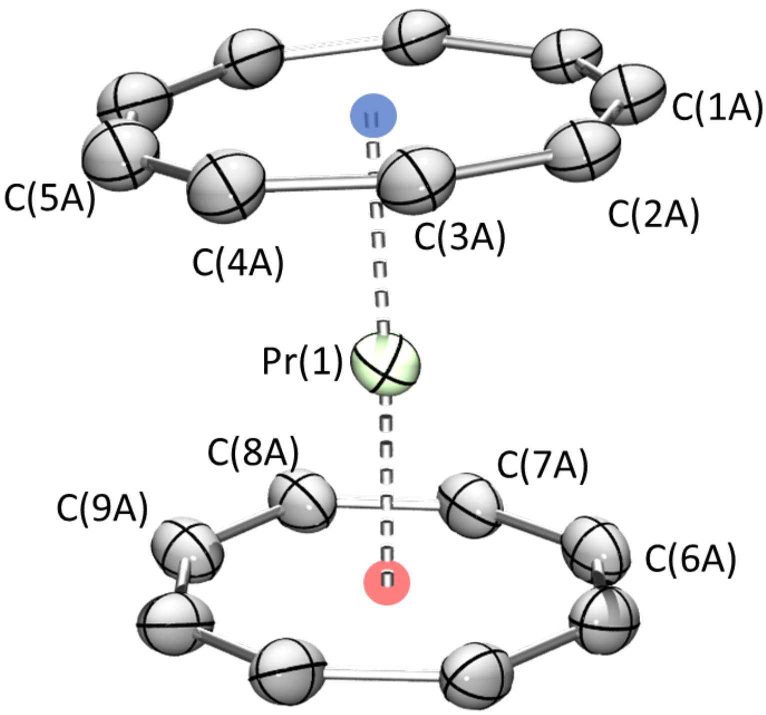


***Figure S31**: Molecular structure of **2**-Pr-cis*

***Table S10:** Summary of bond length and angles from the ligands to the metal center.*

	Main distances in Å
Pr(1) – C(6A) (Cot)	2.67(2)
Pr(1) – C(7A) (Cot)	2.65(2)
Pr(1) – C(8A) (Cot)	2.64(2)
Pr(1) – C(9A) (Cot)	2.64(2)
Pr(1) – Cent (Cot)	1.91
Pr(1) – C(1A) (Cnt)	2.89(4)
Pr(1) – C(2A) (Cnt)	2.91(2)
Pr(1) – C(3A) (Cnt)	2.93(2)
Pr(1) – C(4A) (Cnt)	2.90(4)
Pr(1) – C(5A) (Cnt)	2.85(2)
Pr(1) – Cent (Cnt)	2.07
Plane (Cot) ^Plane (Cnt)	3.86 °
Cent-Cot - Pr(1) - Cent-Cnt	177.39 °

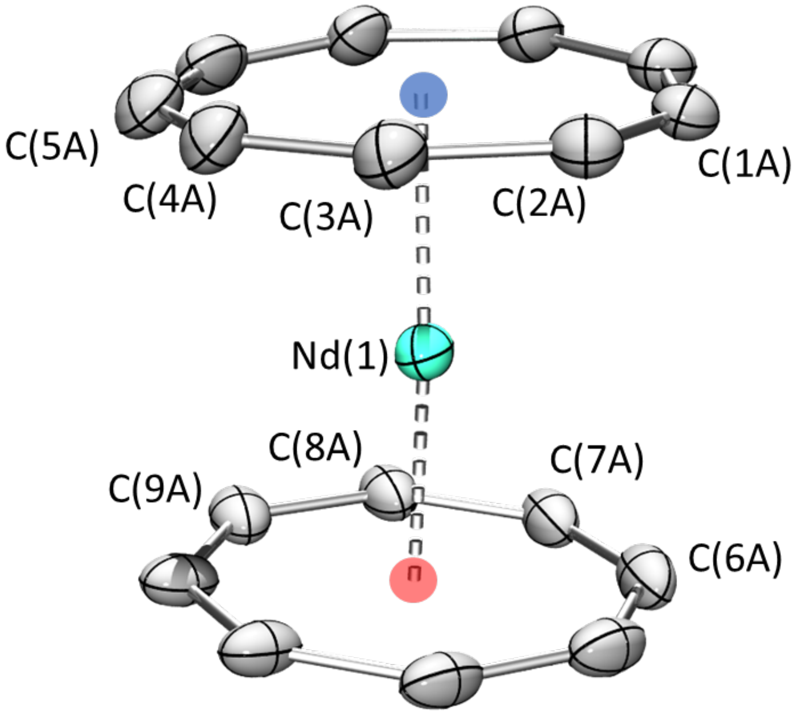


***Figure S32**: Molecular structure of **2**-Nd-cis*

***Table S11**: Summary of bond length and angles from the ligands to the metal center.*

	Main distances in Å
Nd(1) – C(6A) (Cot)	2.66(1)
Nd(1) – C(7A) (Cot)	2.65(1)
Nd(1) – C(8A) (Cot)	2.64(1)
Nd(1) – C(9A) (Cot)	2.64(1)
Nd(1) – Cent (Cot)	1.90
Nd(1) – C(1A) (Cnt)	2.84(1)
Nd(1) – C(2A) (Cnt)	2.89(1)
Nd(1) – C(3A) (Cnt)	2.92(1)
Nd(1) – C(4A) (Cnt)	2.90(1)
Nd(1) – C(5A) (Cnt)	2.86(1)
Nd(1) – Cent (Cnt)	2.05
Plane (Cot) ^Plane (Cnt)	3.62 °
Cent-Cot - Nd(1) - Cent-Cnt	176.70 °

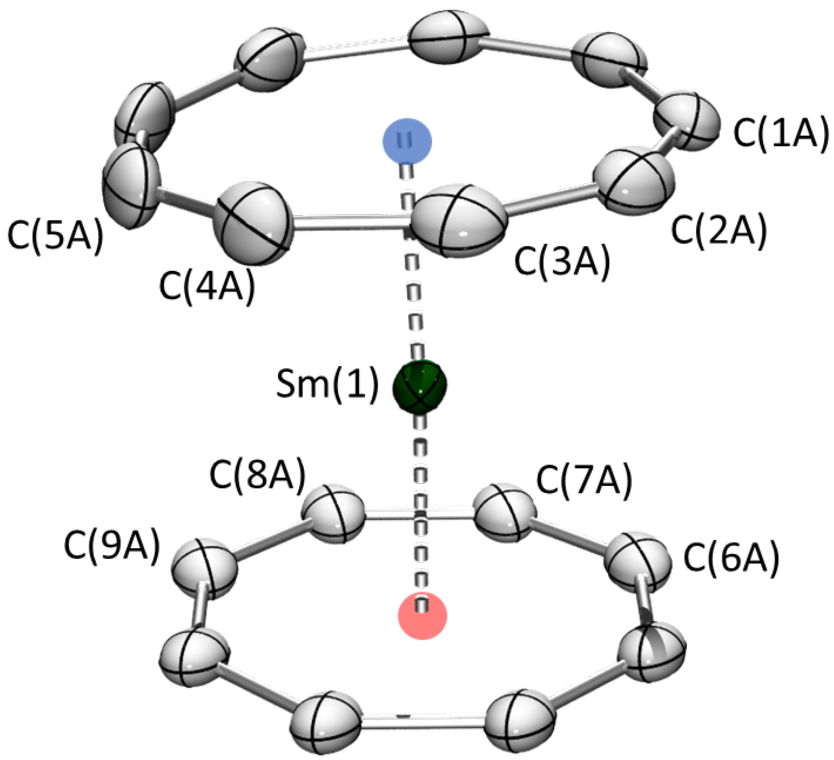


Figure S33: *Molecular structure of* ***2****-Sm-cis*

Table S12: *Summary of bond length and angles from the ligands to the metal center.*

	Main distances in Å
Sm(1) – C(6A) (Cot)	2.624(6)
Sm(1) – C(7A) (Cot)	2.627(7)
Sm(1) – C(8A) (Cot)	2.629(7)
Sm(1) – C(9A) (Cot)	2.618(6)
Sm(1) – Cent (Cot)	1.87
Sm(1) – C(1A) (Cnt)	2.824(9)
Sm(1) – C(2A) (Cnt)	2.873(6)
Sm(1) – C(3A) (Cnt)	2.892(7)
Sm(1) – C(4A) (Cnt)	2.878(7)
Sm(1) – C(5A) (Cnt)	2.831(6)
Sm(1) – Cent (Cnt)	2.01
Plane (Cot) ^Plane (Cnt)	3.02 °
Cent-Cot - Sm(1) - Cent-Cnt	177.17 °

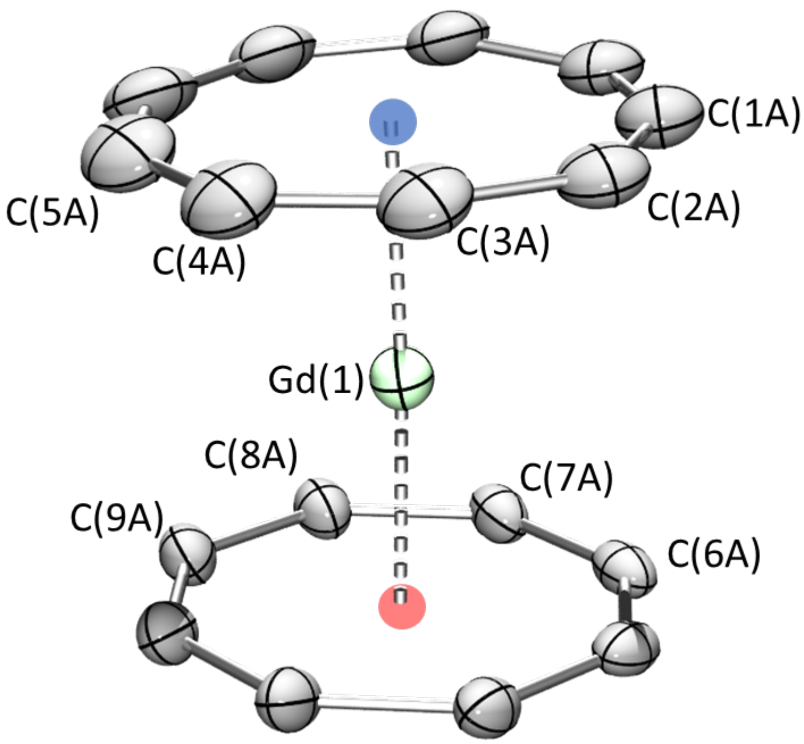


Figure S34: *Molecular structure of* ***2****-Gd-cis*

Table S13: *Summary of bond length and angles from the ligands to the metal center.*

	Main distances in Å
Gd(1) – C(6A) (Cot)	2.607(15)
Gd(1) – C(7A) (Cot)	2.630(17)
Gd(1) – C(8A) (Cot)	2.613(17)
Gd(1) – C(9A) (Cot)	2.586(15)
Gd(1) – Cent (Cot)	1.83
Gd(1) – C(1A) (Cnt)	2.77(3)
Gd(1) – C(2A) (Cnt)	2.817(18)
Gd(1) – C(3A) (Cnt)	2.873(19)
Gd(1) – C(4A) (Cnt)	2.861(19)
Gd(1) – C(5A) (Cnt)	2.801(17)
Gd(1) – Cent (Cnt)	2.00
Plane (Cot) ^Plane (Cnt)	2.53 °
Cent-Cot - Gd(1) - Cent-Cnt	177.34 °

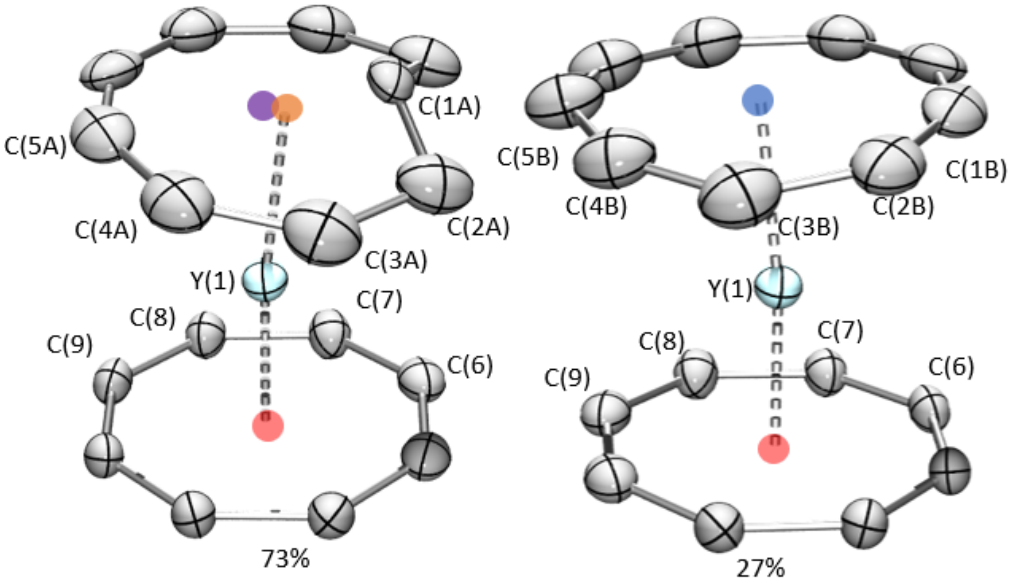


Figure S35: *Molecular structure of **2**-Y-trans (73% ratio).*

Table S14: *Summary of bond length and angles from the ligands to the metal center.*

	Main distances in Å
Y(1) – C(6) (Cot)	2.524(7)
Y(1) – C(7) (Cot)	2.554(8)
Y(1) – C(8) (Cot)	2.554(8)
Y(1) – C(9) (Cot)	2.536(7)
Y(1) – Cent (Cot)	1.758(4)
Y(1) – C(1A) (Cnt)	2.657(10)
Y(1) – C(1B) (Cnt)	2.66(6)
Y(1) – C(2A) (Cnt)	2.827(9)
Y(1) – C(2B) (Cnt)	2.83(3)
Y(1) – C(3A) (Cnt)	2.894(9)
Y(1) – C(3B) (Cnt)	2.93(2)
Y(1) – C(4A) (Cnt)	2.812(9)
Y(1) – C(4B) (Cnt)	3.00(2)
Y(1) – C(5A) (Cnt)	2.692(8)
Y(1) – C(5B) (Cnt)	2.85(2)
Y(1) – Cent (Cnt^{trans})	1.995(4)
Y(1) – Cent (Cnt^{cis})	2.050(13)
Y(1) – Cent (Cnt-8C)	1.948(5)
Plane (Cot) ^Plane (Cnt^{cis})	1.4 °
Plane (Cot) ^Plane (Cnt-8C)	4.3 °
Cent (Cot) - Y(1) – Cent (Cnt^{trans})	176.7 °
Cent (Cot) - Y(1) - Cent (Cnt^{cis})	175.9 °
Cent (Cot) - Y(1) - Cent (Cnt-8C)	179.1 °
Plane (C(2)/C(1)/C(2’)) ^Plane (Cnt^{cis})	47.9 °

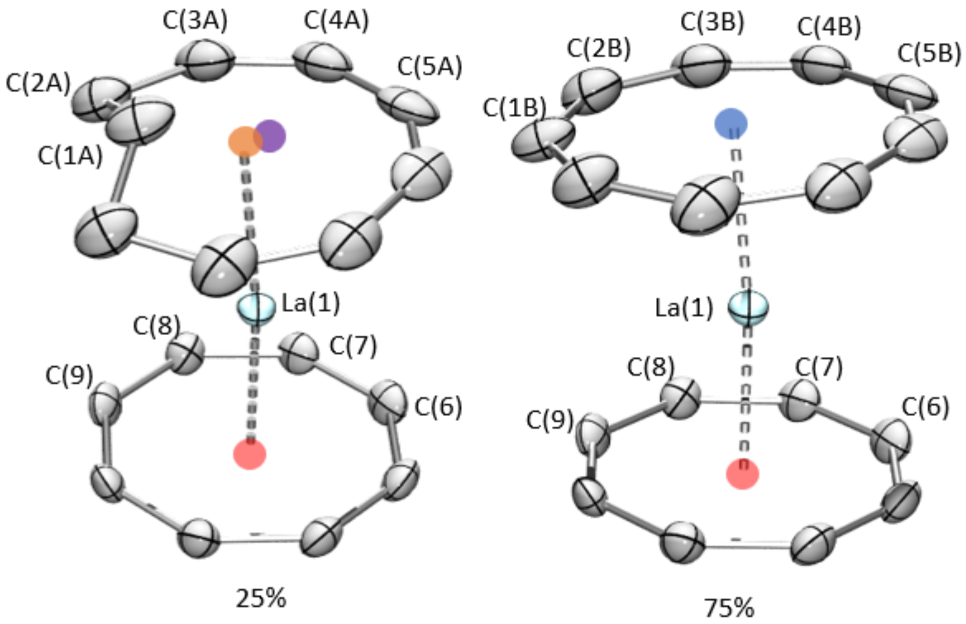


***Figure S36**: Molecular structure of **2**-La-trans (25% ratio).*

***Table S15**: Summary of bond length and angles from the ligands to the metal center.*

	Main distances in Å
La(1) – C(6) (Cot)	2.686(4)
La(1) – C(7) (Cot)	2.693(4)
La(1) – C(8) (Cot)	2.693(4)
La(1) – C(9) (Cot)	2.703(4)
La(1) – Cent (Cot)	1.970(2)
La(1) – C(1A) (Cnt)	2.851 (16)
La(1) – C(1B) (Cnt)	2.897(11)
La(1) – C(2A) (Cnt)	2.931(8)
La(1) – C(2B) (Cnt)	2.947(7)
La(1) – C(3A) (Cnt)	2.913(8)
La(1) – C(3B) (Cnt)	2.965(7)
La(1) – C(4A) (Cnt)	2.901(8)
La(1) – C(4B) (Cnt)	2.952(7)
La(1) – C(5A) (Cnt)	2.873(8)
La(1) – C(5B) (Cnt)	2.951(7)
La(1) – Cent (Cnt^{trans})	2.157(4)
La(1) – Cent (Cnt^{cis})	2.138(3)
La(1) – Cent (Cnt-8C)	2.110(4)
Plane (Cot) ^Plane (Cnt^{cis})	3.66 °
Plane (Cot) ^Plane (Cnt-8C)	5.03 °
Cent (Cot) - La(1) – Cent (Cnt^{trans})	177.13 °
Cent (Cot) - La(1) - Cent (Cnt^{cis})	176.25 °
Cent (Cot) - La(1) - Cent (Cnt-8C)	178.76 °
Plane (C(2)/C(1)/C(2')) ^Plane (Cnt^{cis})	32.4 °

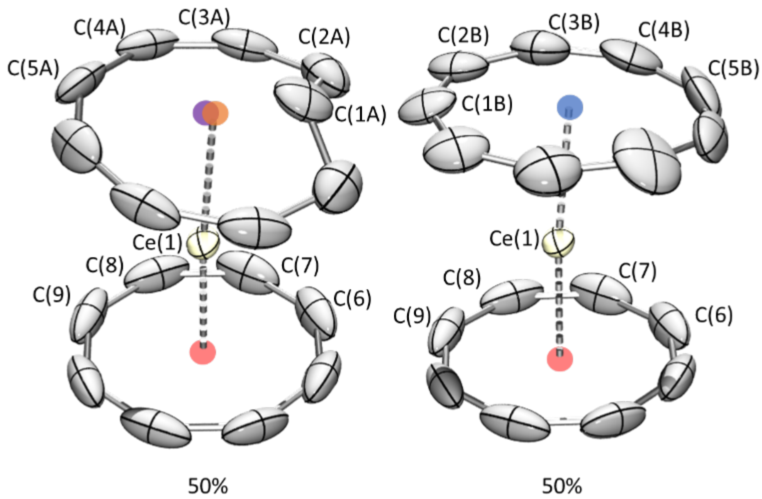


Figure S37*: Molecular structure of* ***2****-Ce-trans* (50% ratio).

Table S16*: Summary of bond length and angles from the ligands to the metal center.*

	Main distances in Å
Ce(1) – C(6) (Cot)	2.640(4)
Ce(1) – C(7) (Cot)	2.657(4)
Ce(1) – C(8) (Cot)	2.656(4)
Ce(1) – C(9) (Cot)	2.664(4)
Ce(1) – Cent (Cot)	1.94
Ce(1) – C(1A) (Cnt)	2.750(12)
Ce(1) – C(1B) (Cnt)	2.84(2)
Ce(1) – C(2A) (Cnt)	2.878(15)
Ce(1) – C(2B) (Cnt)	2.88(2)
Ce(1) – C(3A) (Cnt)	2.900(15)
Ce(1) – C(3B) (Cnt)	2.89(2)
Ce(1) – C(4A) (Cnt)	2.887(15)
Ce(1) – C(4B) (Cnt)	2.90(2)
Ce(1) – C(5A) (Cnt)	2.857(15)
Ce(1) – C(5B) (Cnt)	2.94(2)
Ce(1) – Cent (Cnt-*trans*)	2.08
Ce(1) – Cent (Cnt-*cis*)	2.14
Ce(1) – Cent (Cnt-8C)	2.04
Plane (Cot) ^Plane (Cnt-*cis*)	5.53 °
Plane (Cot) ^Plane (Cnt-8C)	3.39 °
Cent-Cot - Ce(1) - Cent-Cnt-*trans*	176.27 °
Cent-Cot - Ce(1)- Cent-Cnt-*cis*	176.41 °
Cent-Cot - Ce(1)- Cent-Cnt-8C	179.6 °
Plane (C(2)/C(1)/C(2’)) ^Plane (Cnt-*cis*)	5.53 °

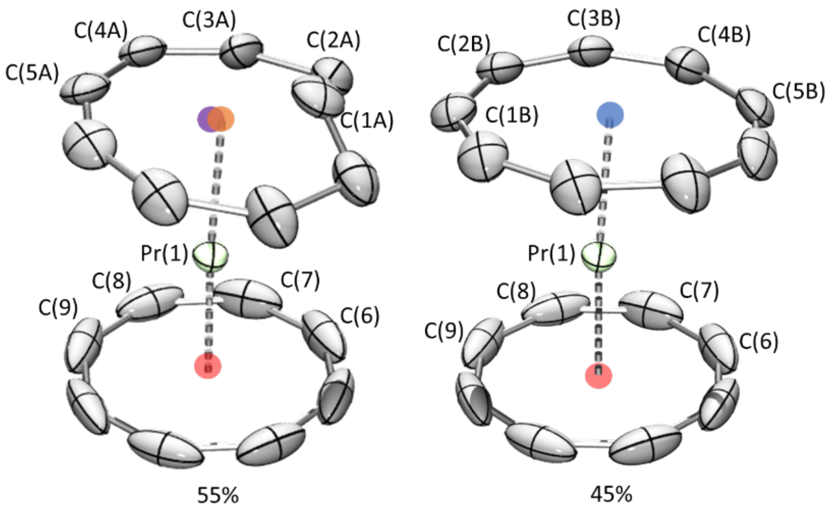


***Figure S38**: Molecular structure of **2**-Pr-trans (55% ratio).*

***Table S17**: Summary of bond length and angles from the ligands to the metal center.*

	Main distances in Å
Pr(1) – C(6) (Cot)	2.637(5)
Pr(1) – C(7) (Cot)	2.631(6)
Pr(1) – C(8) (Cot)	2.639(6)
Pr(1) – C(9) (Cot)	2.637(5)
Pr(1) – Cent (Cot)	1.91
Pr(1) – C(1A) (Cnt)	2.749(15)
Pr(1) – C(1B) (Cnt)	2.84(2)
Pr(1) – C(2A) (Cnt)	2.87(2)
Pr(1) – C(2B) (Cnt)	2.87(2)
Pr(1) – C(3A) (Cnt)	2.87(2)
Pr(1) – C(3B) (Cnt)	2.88(2)
Pr(1) – C(4A) (Cnt)	2.88(2)
Pr(1) – C(4B) (Cnt)	2.89(2)
Pr(1) – C(5A) (Cnt)	2.815(16)
Pr(1) – C(5B) (Cnt)	2.90(2)
Pr(1) – Cent (Cnt^{trans})	2.09
Pr(1) – Cent (Cnt^{cis})	2.08
Pr(1) – Cent (Cnt-8C)	2.04
Plane (Cot) ^Plane (Cnt^{cis})	5.12°
Plane (Cot) ^Plane (Cnt-8C)	2.88°
Cent (Cot) - Pr(1) – Cent (Cnt^{trans})	176.76°
Cent (Cot) - Pr(1)- Cent (Cnt^{cis})	176.16°
Cent (Cot) - Pr(1)- Cent (Cnt-8C)	178.99°
Plane (C(2)/C(1)/C(2')) ^Plane (Cnt^{cis})	47.68 °

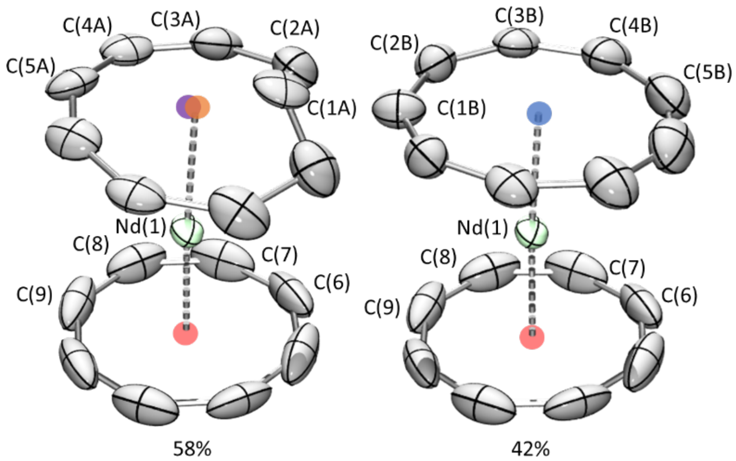


Figure S39: *Molecular structure of **2**-Nd-trans (58% ratio).*

Table S18: *Summary of bond length and angles from the ligands to the metal center.*

	Main distances in Å
Nd(1) – C(6) (Cot)	2.619(8)
Nd(1) – C(7) (Cot)	2.614(9)
Nd(1) – C(8) (Cot)	2.641(9)
Nd(1) – C(9) (Cot)	2.629(9)
Nd(1) – Cent (Cot)	1.90
Nd(1) – C(1A) (Cnt)	2.79(2)
Nd(1) – C(1B) (Cnt)	2.84(2)
Nd(1) – C(2A) (Cnt)	2.89(2)
Nd(1) – C(2B) (Cnt)	2.88(2)
Nd(1) – C(3A) (Cnt)	2.91(2)
Nd(1) – C(3B) (Cnt)	2.91(2)
Nd(1) – C(4A) (Cnt)	2.85(2)
Nd(1) – C(4B) (Cnt)	2.89(2)
Nd(1) – C(5A) (Cnt)	2.81(2)
Nd(1) – C(5B) (Cnt)	2.86(2)
Nd(1) – Cent (Cnt-*trans*)	2.08
Nd(1) – Cent (Cnt-*cis*)	2.06
Nd(1) – Cent (Cnt-8C)	2.03
Plane (Cot) ^Plane (Cnt-*cis*)	3.7 °
Plane (Cot) ^Plane (Cnt-8C)	4.44 °
Cent-Cot - Nd(1) - Cent-Cnt-*trans*	177.00 °
Cent-Cot - Nd(1)- Cent-Cnt-*cis*	176.8 °
Cent-Cot - Nd(1)- Cent-Cnt-8C	178.78 °
Plane (C(2)/C(1)/C(2’)) ^Plane (Cnt-*cis*)	50.15 °

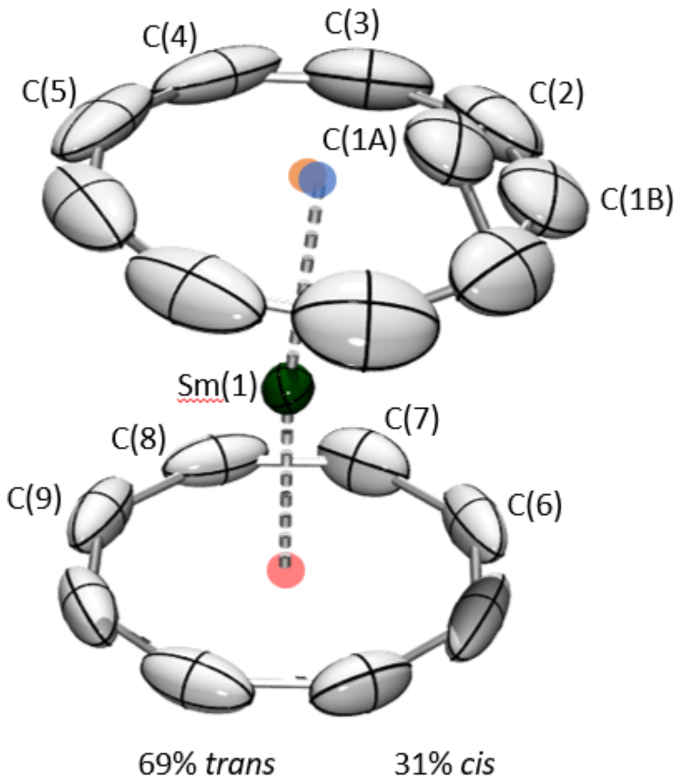


***Figure S40**: Molecular structure of **2**-Sm-trans (69% ratio).*

***Table S19**: Summary of bond length and angles from the ligands to the metal center.*

	Main distances in Å
Sm(1) – C(6) (Cot)	2.594(5)
Sm(1) – C(7) (Cot)	2.591(6)
Sm(1) – C(8) (Cot)	2.601(6)
Sm(1) – C(9) (Cot)	2.595(6)
Sm(1) – Cent (Cot)	1.85
Sm(1) – C(1A) (Cnt)	2.687(13)
Sm(1) – C(1B) (Cnt)	2.82(3)
Sm(1) – C(2) (Cnt)	2.857(9)
Sm(1) – C(3) (Cnt)	2.879(9)
Sm(1) – C(4) (Cnt)	2.834(9)
Sm(1) – C(5) (Cnt)	2.763(6)
Sm(1) – Cent (Cnt-*trans*)	2.054
Sm(1) – Cent (Cnt-*cis*)	2.01
Plane (Cot) ^Plane (Cnt-*cis*)	3.54 °
Cent-Cot - Sm(1) - Cent-Cnt-*trans*	175.96 °
Cent-Cot - Sm(1)- Cent-Cnt-*cis*	173.37 °
Plane (C(2)/C(1)/C(2')) ^Plane (Cnt-*cis*)	42.80 °

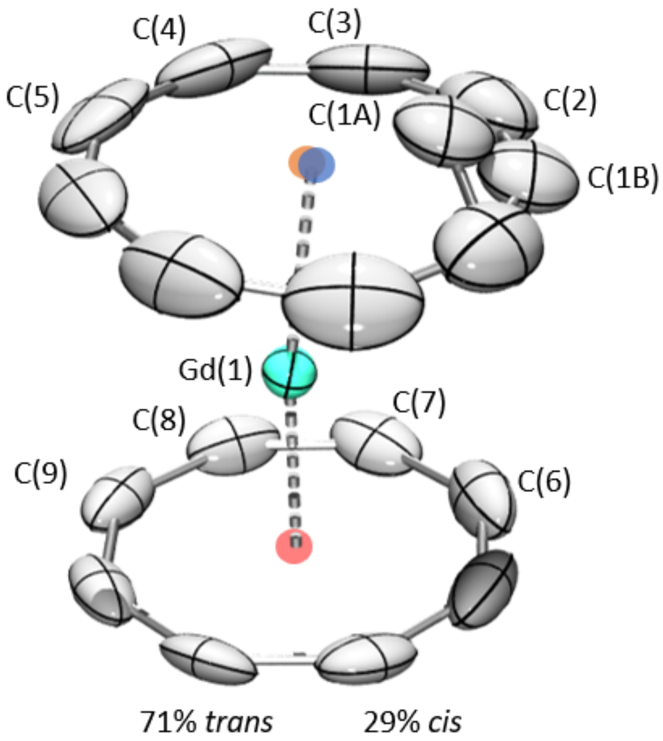


***Figure S41**: Molecular structure of **2**-Gd-trans (71% ratio).*

***Table S20**: Summary of bond length and angles from the ligands to the metal center.*

	Main distances in Å
Gd(1) – C(6) (Cot)	2.559(7)
Gd(1) – C(7) (Cot)	2.575(7)
Gd(1) – C(8) (Cot)	2.582(6)
Gd(1) – C(9) (Cot)	2.565(7)
Gd(1) – Cent (Cot)	1.82
Gd(1) – C(1A) (Cnt)	2.703(17)
Gd(1) – C(1B) (Cnt)	2.81(5)
Gd(1) – C(2) (Cnt)	2.853(10)
Gd(1) – C(3) (Cnt)	2.872(9)
Gd(1) – C(4) (Cnt)	2.828(10)
Gd(1) – C(5) (Cnt)	2.749(9)
Gd(1) – Cent (Cnt-*trans*)	2.04
Gd(1) – Cent (Cnt-*cis*)	2.003
Plane (Cot) ^Plane (Cnt-*cis*)	3.63 °
Cent-Cot - Gd(1) - Cent-Cnt-*trans*	175.04 °
Cent-Cot - Gd(1)- Cent-Cnt-*cis*	172.72 °
Plane (C(2)/C(1)/C(2')) ^Plane (Cnt-*cis*)	45.34 °

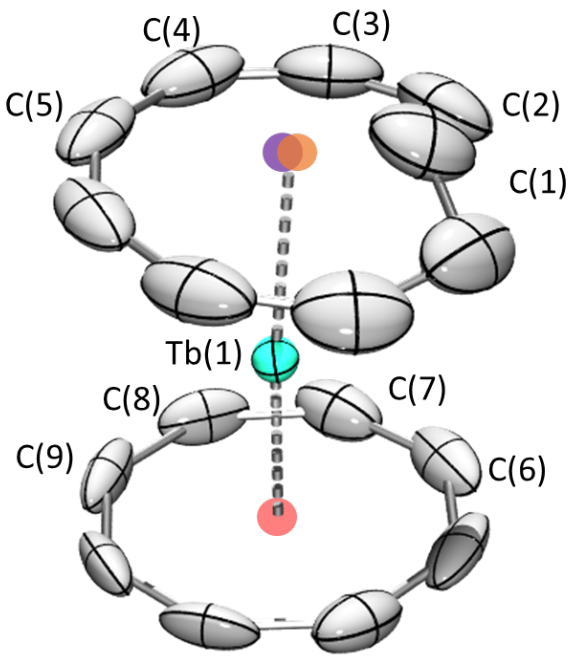


Figure S42: *Molecular structure of **2**-Tb-trans (100% ratio).*

Table S21*: Summary of bond length and angles from the ligands to the metal center.*

	Main distances in Å
Tb(1) – C(6) (Cot)	2.537(9)
Tb(1) – C(7) (Cot)	2.563(11)
Tb(1) – C(8) (Cot)	2.566(9)
Tb(1) – C(9) (Cot)	2.540(9)
Tb(1) – Cent (Cot)	1.80
Tb(1) – C(1) (Cnt)	2.664(16)
Tb(1) – C(2) (Cnt)	2.837(12)
Tb(1) – C(3) (Cnt)	2.885(12)
Tb(1) – C(4) (Cnt)	2.828(12)
Tb(1) – C(5) (Cnt)	2.722(10)
Tb(1) – Cent (Cnt)	2.01
Tb(1) – Cent (Cnt) –8C	1.97
Plane (Cot) ^Plane (Cnt 8C)	3.94 °
Cent-Cot - Tb(1) - Cent-Cnt	175.74 °
Cent-Cot - Tb(1)- Cent-Cnt 8C	179.97 °
Plane (C(2)/C(1)/C(2’)) ^Plane (Cnt 8C)	48.14 °

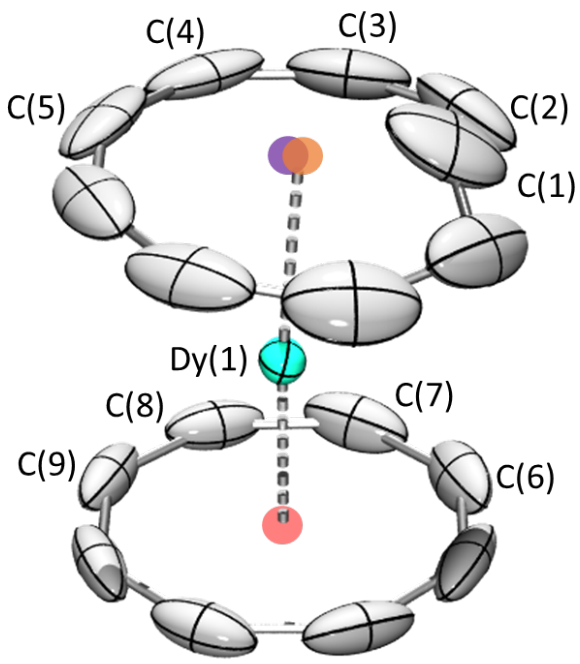


***Figure S43**: Molecular structure of **2**-Dy-trans (100% ratio).*

***Table S22**: Summary of bond length and angles from the ligands to the metal center.*

	Main distances in Å
Dy(1) – C(6) (Cot)	2.534(5)
Dy(1) – C(7) (Cot)	2.544(5)
Dy(1) – C(8) (Cot)	2.543(5)
Dy(1) – C(9) (Cot)	2.544(5)
Dy(1) – Cent (Cot)	1.78
Dy(1) – C(1) (Cnt)	2.660(9)
Dy(1) – C(2) (Cnt)	2.825(9)
Dy(1) – C(3) (Cnt)	2.858(9)
Dy(1) – C(4) (Cnt)	2.806(6)
Dy(1) – C(5) (Cnt)	2.720(6)
Dy(1) – Cent (Cnt)	1.99
Dy(1) – Cent (Cnt) –8C	1.96
Plane (Cot) ^Plane (Cnt 8C)	3.52 °
Cent-Cot - Dy(1) - Cent-Cnt	179.57 °
Cent-Cot - Dy(1)- Cent-Cnt 8C	175.75 °
Plane (C(2)/C(1)/C(2’)) ^Plane (Cnt 8C)	52.63 °

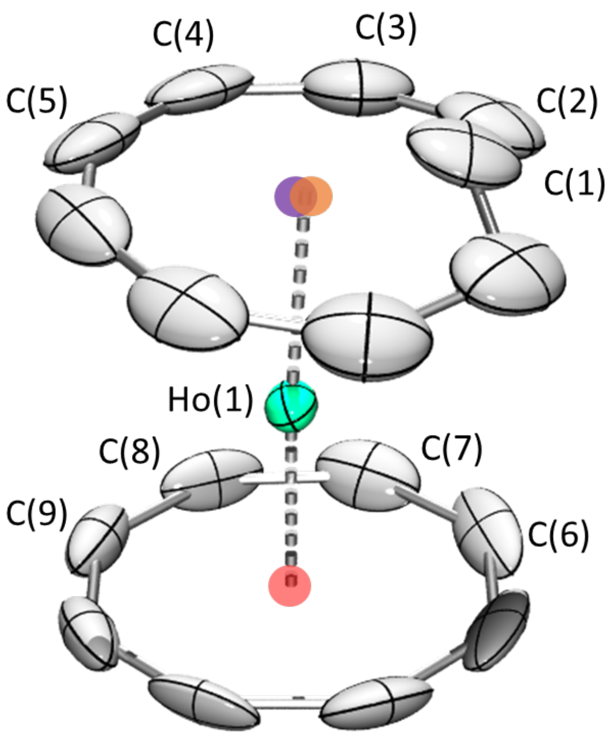


Figure S44: *Molecular structure of **2**-Ho-trans (100% ratio).*

Table S23: *Summary of bond length and angles from the ligands to the metal center.*

	Main distances in Å
Ho(1) – C(6) (Cot)	2.518(7)
Ho(1) – C(7) (Cot)	2.529(8)
Ho(1) – C(8) (Cot)	2.524(7)
Ho(1) – C(9) (Cot)	2.534(6)
Ho(1) – Cent (Cot)	1.76
Ho(1) – C(1) (Cnt)	2.673(11)
Ho(1) – C(2) (Cnt)	2.819(9)
Ho(1) – C(3) (Cnt)	2.86(1)
Ho(1) – C(4) (Cnt)	2.805(8)
Ho(1) – C(5) (Cnt)	2.684(7)
Ho(1) – Cent (Cnt)	2.00
Ho(1) – Cent (Cnt) –8C	1.95
Plane (Cot) ^Plane (Cnt 8C)	3.36 °
Cent-Cot - Ho(1) - Cent-Cnt	176.73 °
Cent-Cot - Ho(1)- Cent-Cnt 8C	178.81 °
Plane (C(2)/C(1)/C(2’)) ^Plane (Cnt 8C)	50.85 °

6. UV-visible Spectroscopy

a. KCnt

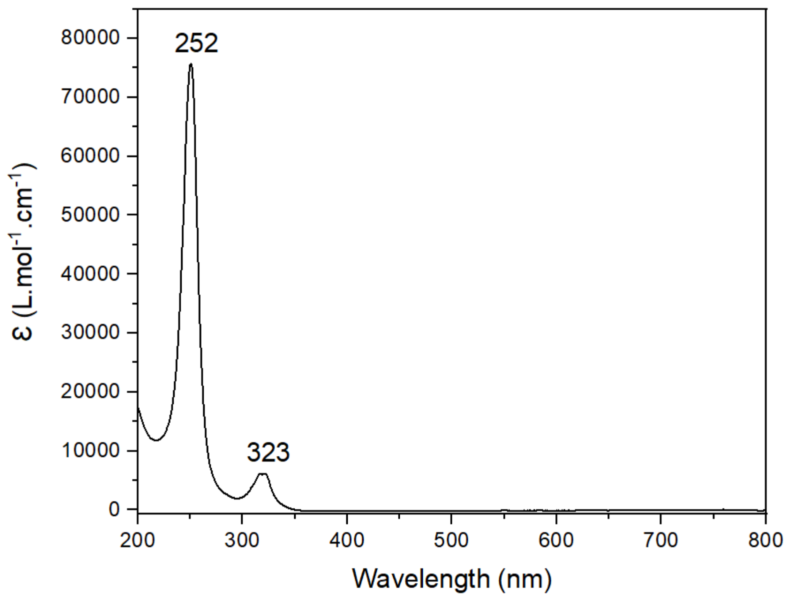


Figure S45: *UV-Visible spectrum of KCnt-cis in MeCN (3.0*10^{-5} M)*

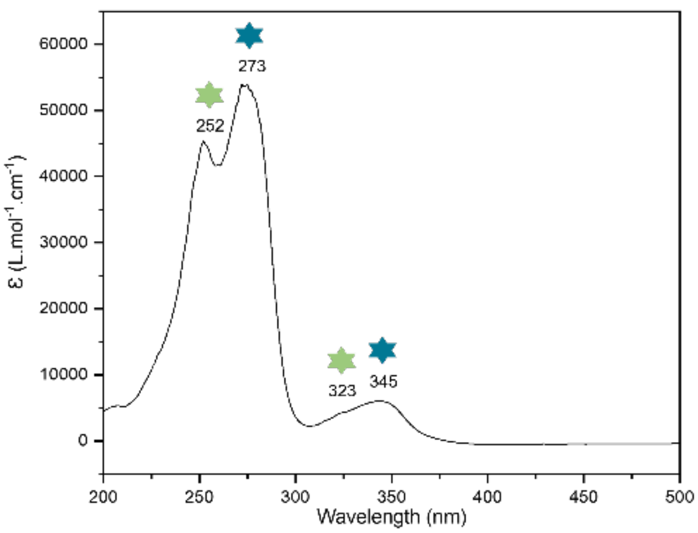


Figure S46: *UV-Visible spectrum of KCnt-trans in MeCN (3.07*10-4M). KCnt-trans in blue, KCnt-cis in green.*

b. LnCotCnt

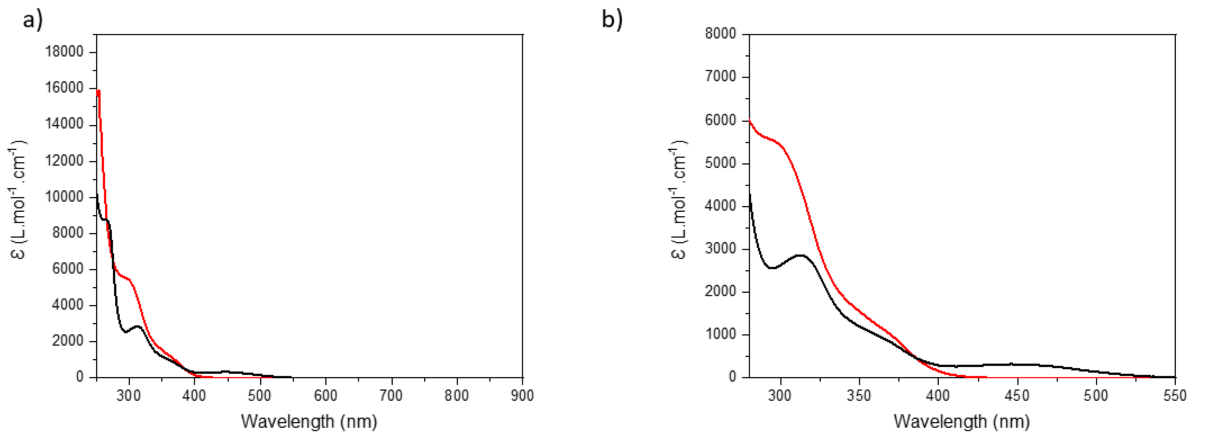


***Figure S47**: UV-Visible spectra of **2**-Y (trans isomer in black $1.16*10^{-3}$ M cis isomer in red $1.16*10^{-3}$M) in DCM. b) zoom in on the irradiation wavelength*

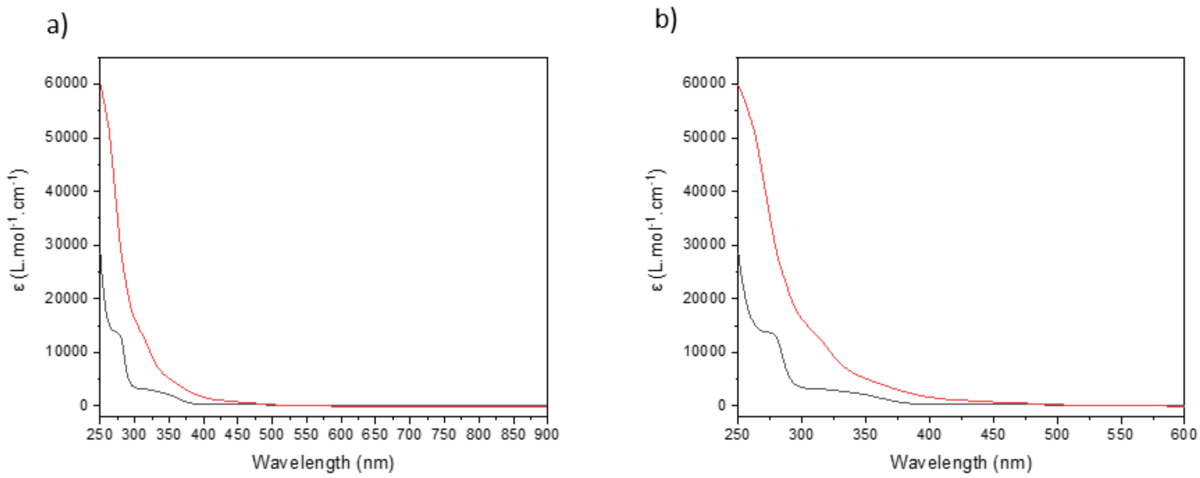


***Figure S48**: a) UV-Visible spectra of **2**-La (cis isomer in red $2.57*10^{-4}$ M, trans isomer in black $4.74*10^{-4}$ M) in DCM. b) zoom in on the irradiation wavelength*

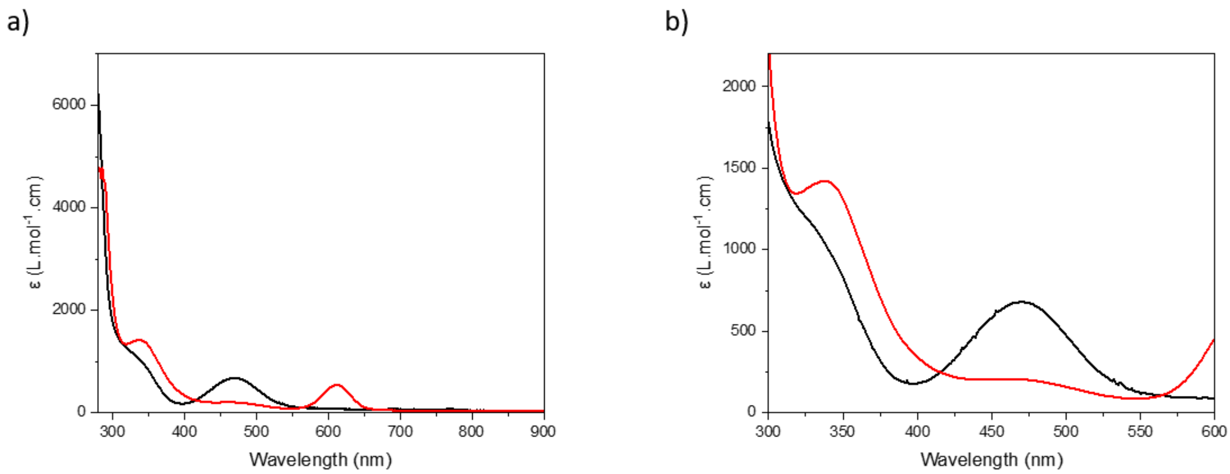


***Figure S49**: UV-Visible spectra of **2**-Ce (cis isomer in red $4.15*10^{-4}$ M, trans isomer in black $3.32*10^{-4}$ M) in DCM. b) zoom in on the irradiation wavelength*

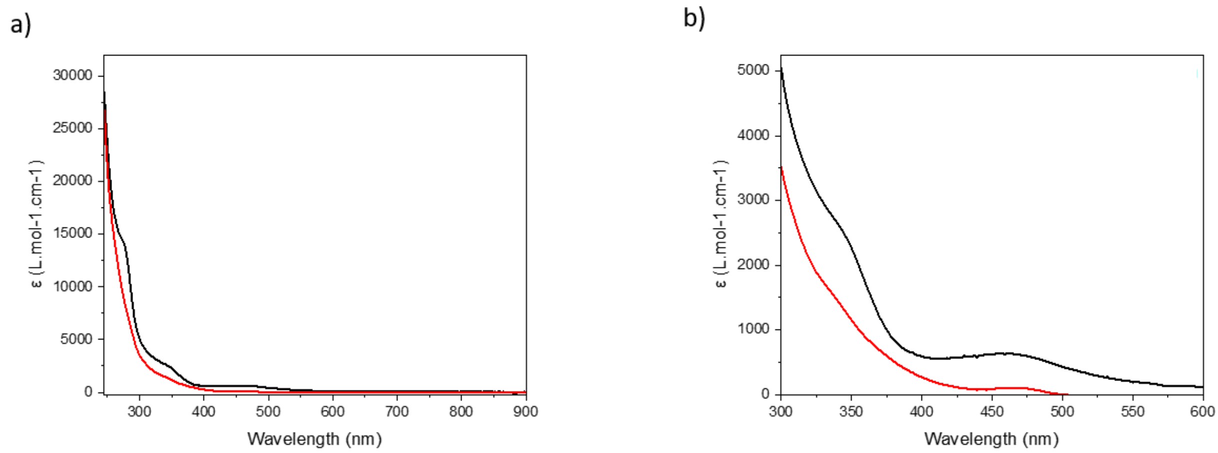


***Figure S50**: UV-Visible spectra of **2**-Pr (cis isomer in red 4.83*10^{-4} M, trans isomer in black 2.76*10^{-4} M) in DCM. b) zoom in on the irradiation wavelength*

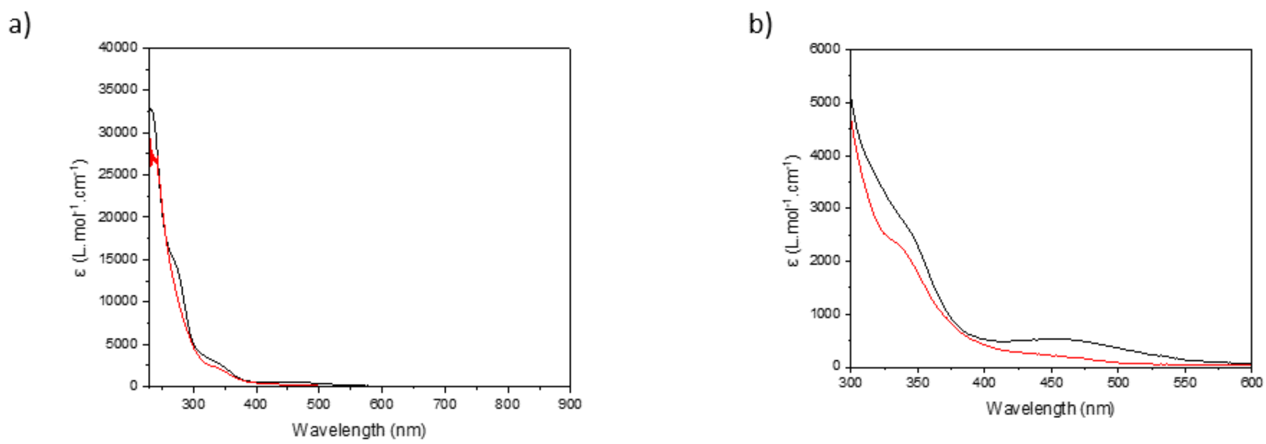


***Figure S51**: UV-Visible spectra of **2**-Nd (cis isomer in red 6.84*10^{-4} M, trans isomer in black 3.56*10^{-4} M) in DCM. b) zoom in on the irradiation wavelength*

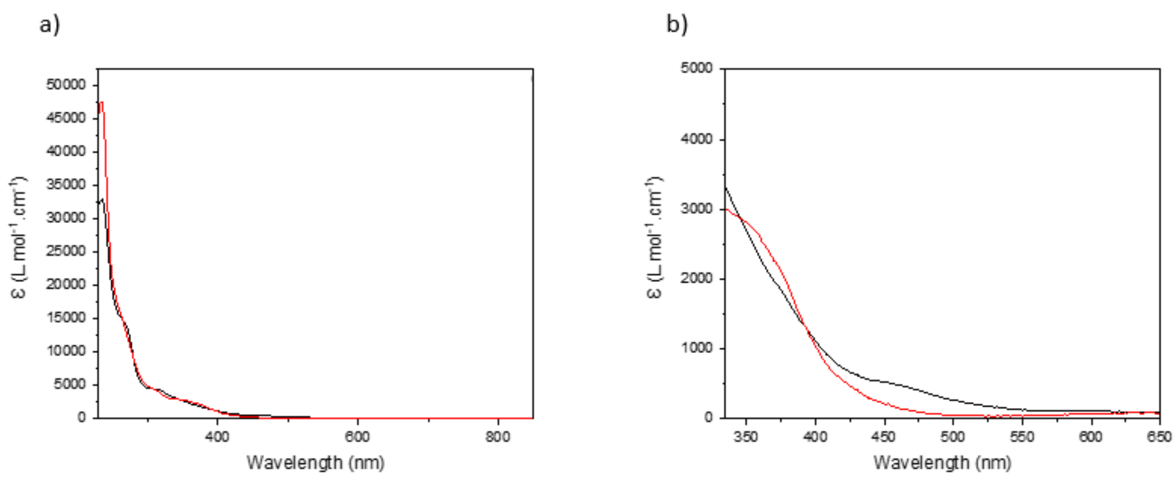


***Figure S52**: a) UV-Visible spectra of **2**-Sm (cis isomer in red 2.7*10^{-4} M, trans isomer in black 3.5*10^{-4} M) in DCM. b) zoom in on the irradiation wavelength*

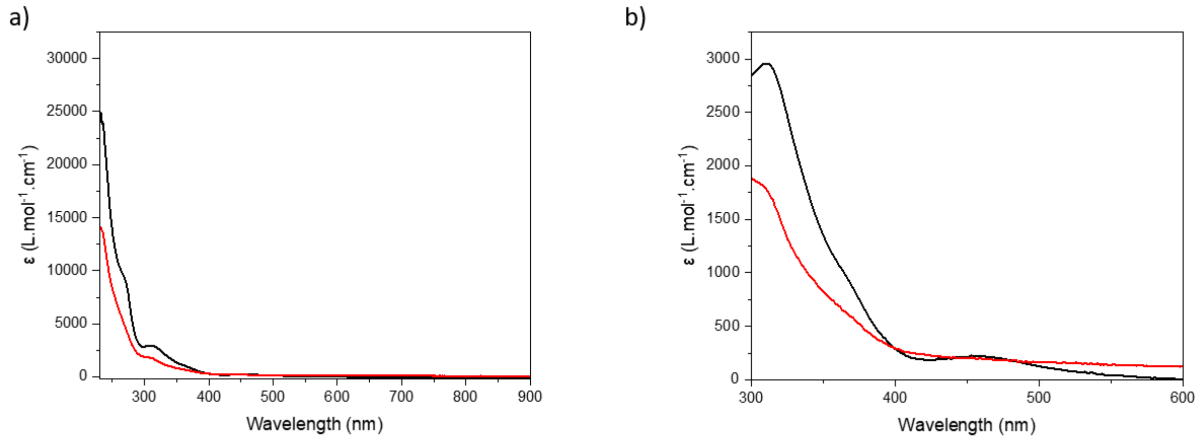


Figure S53: *UV-Visible spectrum of **2**-Gd (cis isomer in red 7.04*10^{-4} M, trans isomer in black 6.34*10^{-4} M) in DCM. b) zoom in on the irradiation wavelength*

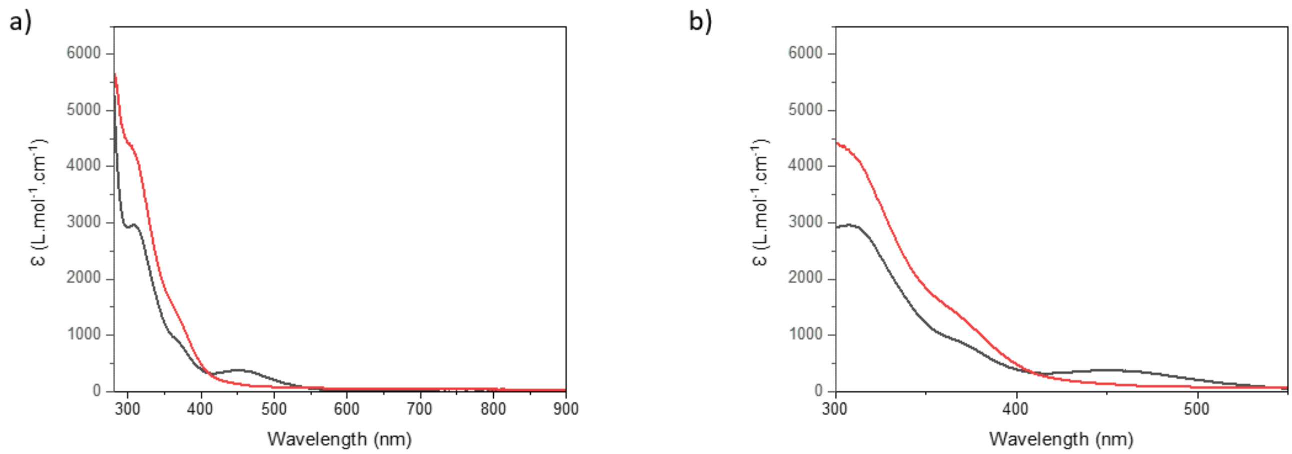


Figure S54: *UV-Visible spectrum of **2**-Tb (cis isomer in red 3.42*10^{-3} M, trans isomer in black 1.05*10^{-3} M) in DCM. b) zoom in on the irradiation wavelength*

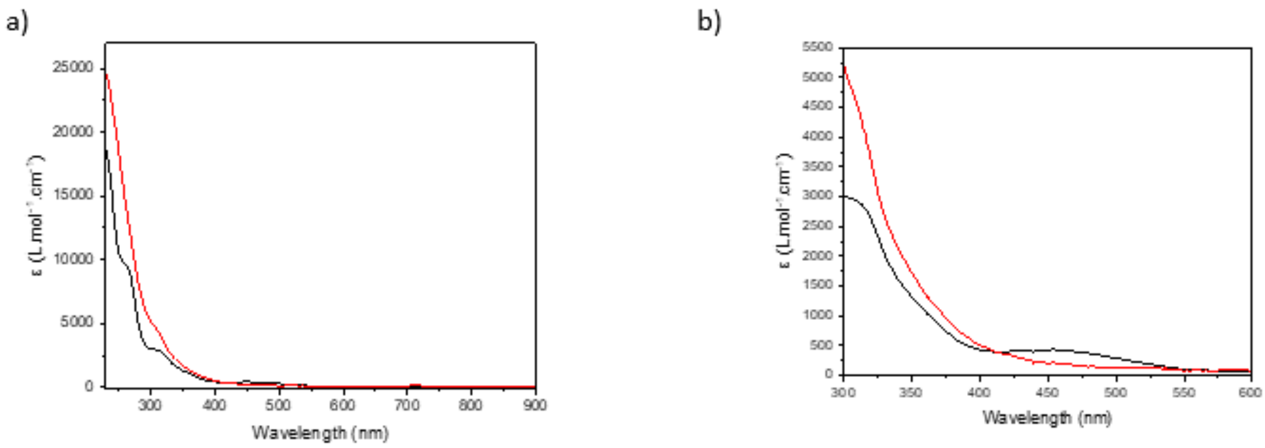


Figure S55: *UV-Visible spectrum of **2**-Dy (cis isomer in red 1.69*10^{-4} M, trans isomer in black 2.60*10^{-4} M) in DCM. b) zoom in on the irradiation wavelength*

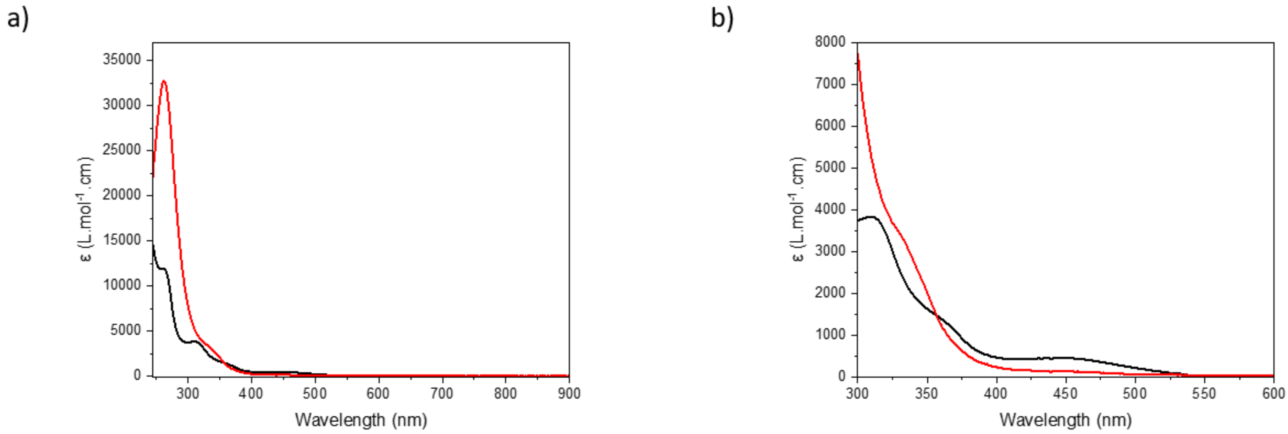


***Figure S56**: UV-Visible spectrum of **2**-Ho (cis isomer in red 2.80*10^{-4} M, trans isomer in black 3.37*10^{-4} M) in DCM. b) zoom in on the irradiation wavelength*

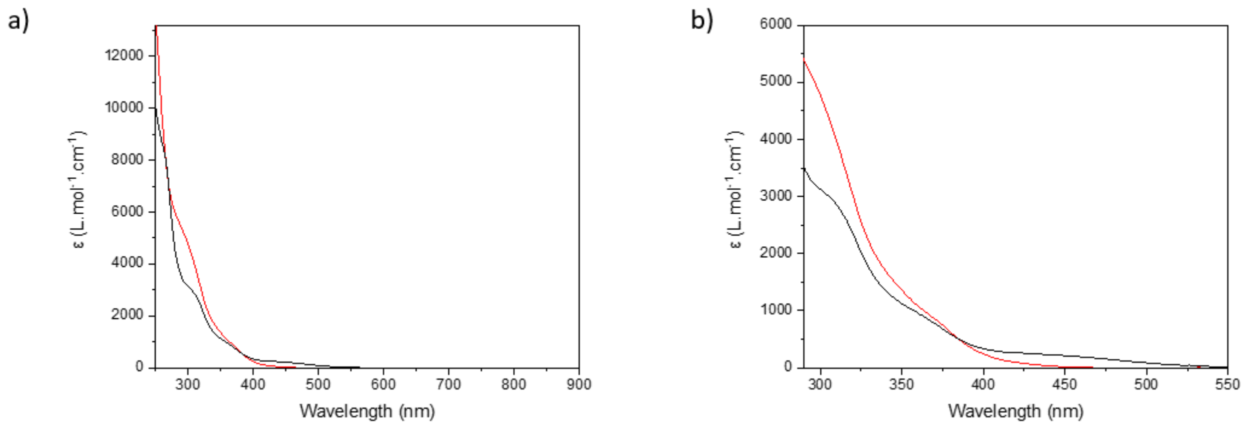


***Figure S57**: a) UV-Visible spectrum of **2**-Er (cis isomer in red 9.43*10^{-4} M, trans isomer in black 9.43*10-4 M) in DCM. b) zoom in on the irradiation wavelength. The trans isomer was generated through photoirradiation at 370nm for 10 min.*

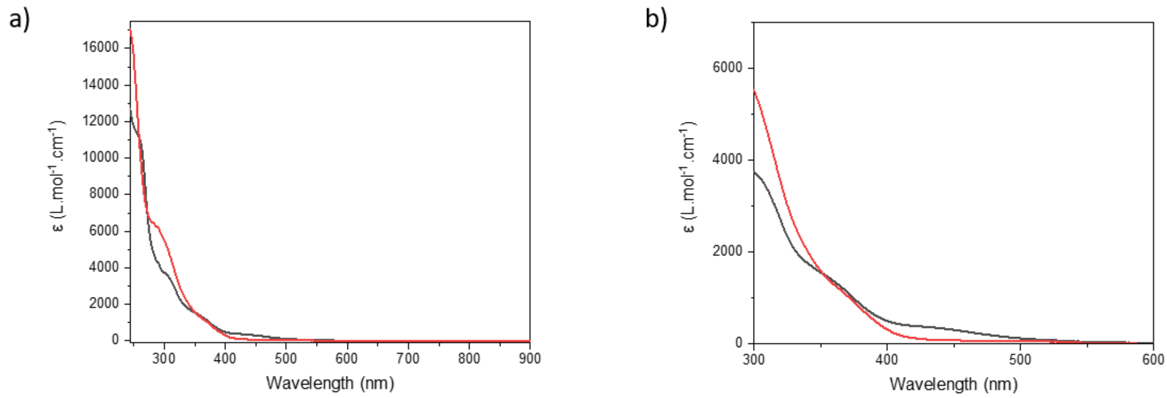


***Figure S58**: a) UV-Visible spectrum of **2**-Tm (cis isomer in red 7.68*10^{-4} M, trans isomer in black 7.68*10-4 M) in DCM. b) zoom in on the irradiation wavelength. The trans isomer was generated through photoirradiation at 370nm for 10 min.*

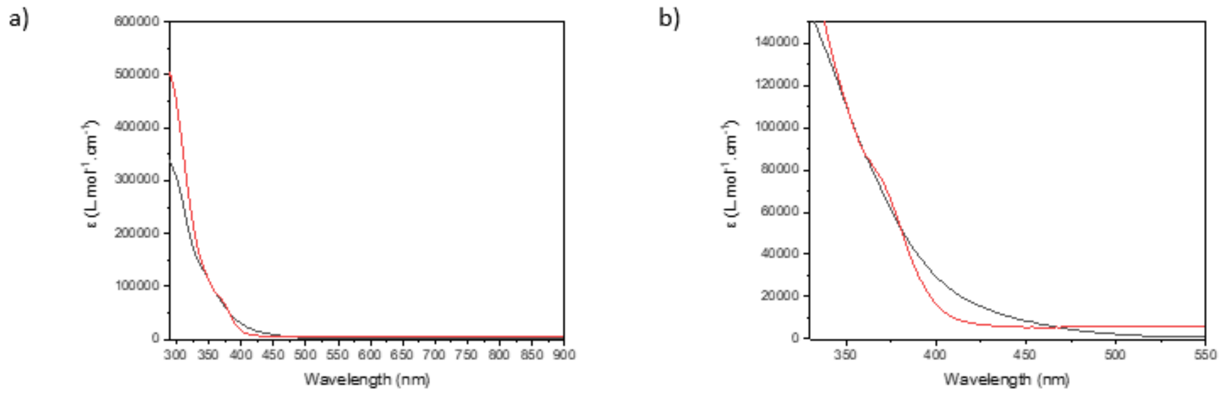


***Figure S59**: a) UV-Visible spectrum of **2**-Lu (cis isomer in red $3.28*10^{-3}$ M, trans isomer in black $3.28*10^{-3}$ M) in DCM. b) zoom in on the irradiation wavelength The trans isomer was generated through photoirradiation at 370nm for 10 min.*

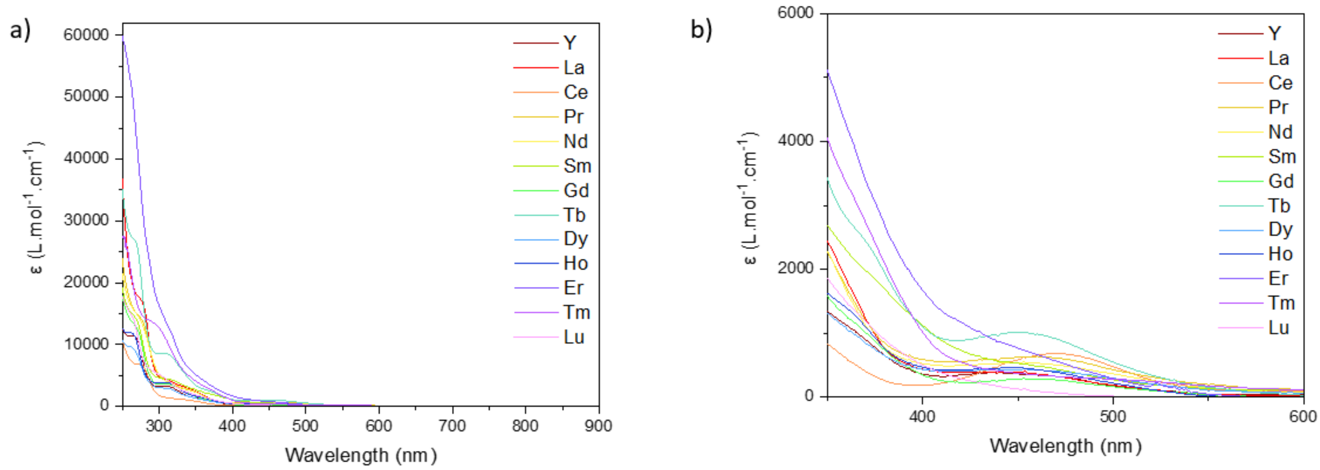


***Figure S60**: a) UV-Visible spectra of all **2**-Ln-trans in DCM. b) zoom in on the irradiation wavelength*

7. Isomerization study

General details. Studies were conducted in an NMR tube in toluene-*d*$_8$ and irradiated in a black box with an adapted NMR tube holder. All tubes were protected from the light in aluminum foil during the convoy from the irradiation box to the NMR spectrometer.

For the Photo stationary state study, all samples were irradiated 30 min at each λ (2 X 15min) to ensure that the PSS was reached. The irradiation range was performed on Kessil's lamp (370 nm, 390 nm, 427 nm, 440 nm, 450 nm, 467 nm, and 525 nm). The irradiation started from 370 nm to 525 nm, and in order to test the reversibility of the isomerization, the samples were irradiated stepwise from 525 nm to 370 nm. For **2**-Ce, an additional lamp was used from Prizmatix FC5-LED Multi channel light source (655 nm). The irradiation took place inside the NMR with an adapted Young NMR tube to put an optic fiber inside. The irradiation lasted a total of 2h 50 min (1h 40 min + 50 min to reach the PSS)

It must be noted that all UV-Vis spectra of the **2**-Ln-*trans* display a mixture of the *cis* and *trans* isomer.

a) UV and NMR study

i. KCnt Isomerization

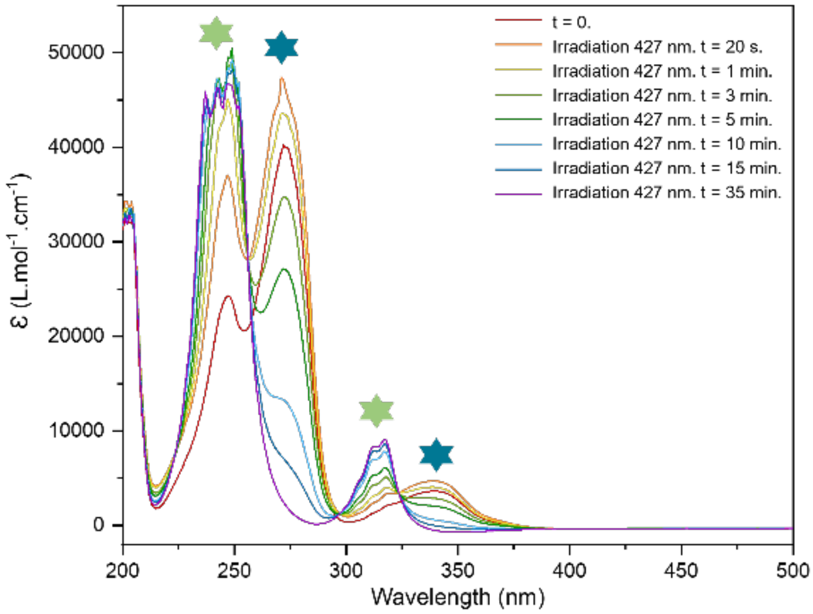


Figure S61*: Isomerization study by UV-visible spectroscopy of KCnt in THF. Green star: absorption band attributed to KCnt-cis; Blue star: absorption band attributed to KCnt-trans*

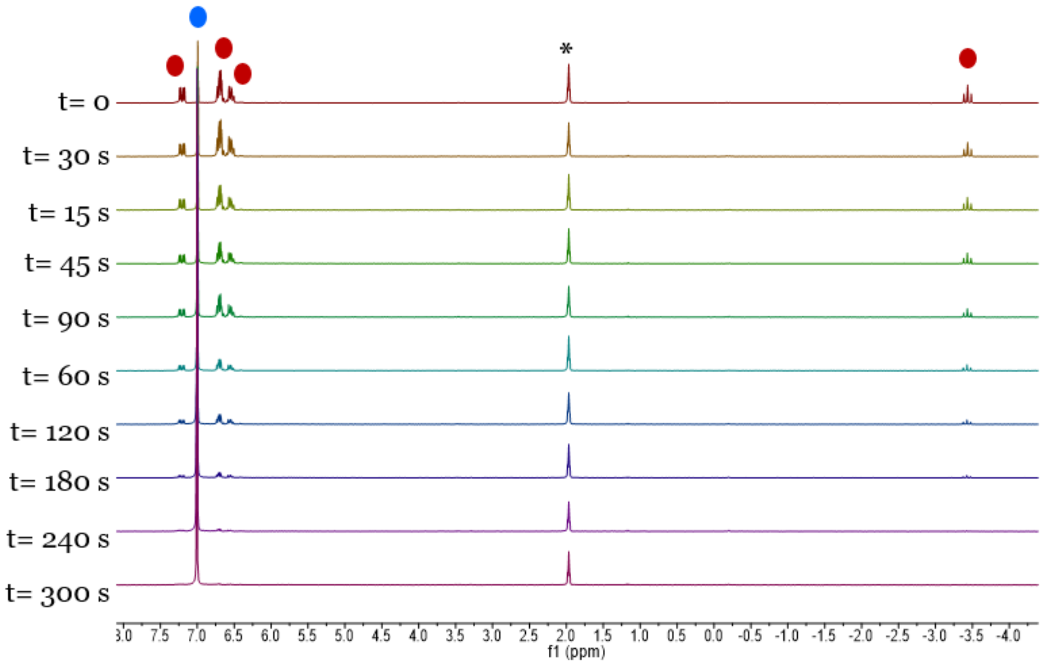


Figure S62*: Isomerization study by* ^{1}*H NMR of KCnt in* CD_3CN *at 427 nm. Red dots: signals attributed to the trans isomer; blue dot: signal attributed to the cis isomer*

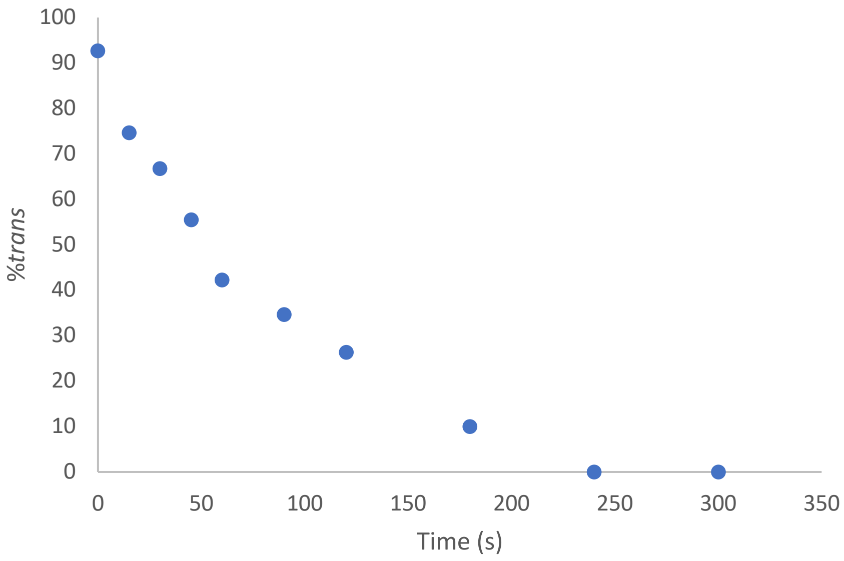


Figure S63: *Plotted data of KCnt isomerization*

ii. $Sm(Cnt)_2$

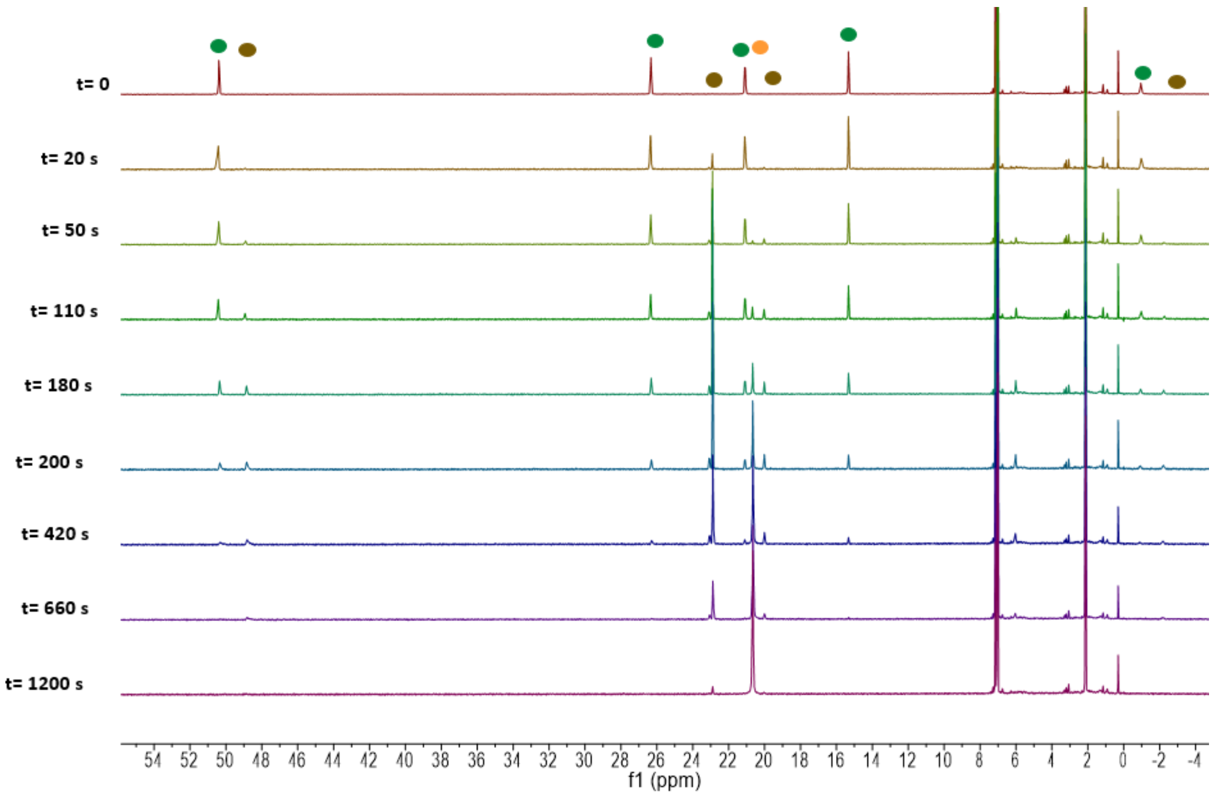


Figure S64: *Isomerization study by* [1]*H NMR of* ***1*** *in toluene at 427 nm. Green dots: signals attributed to the trans, trans isomer; brown dots: signals attributed to the cis, trans isomer; yellow dot: signals attributed to the cis, cis isomer.*

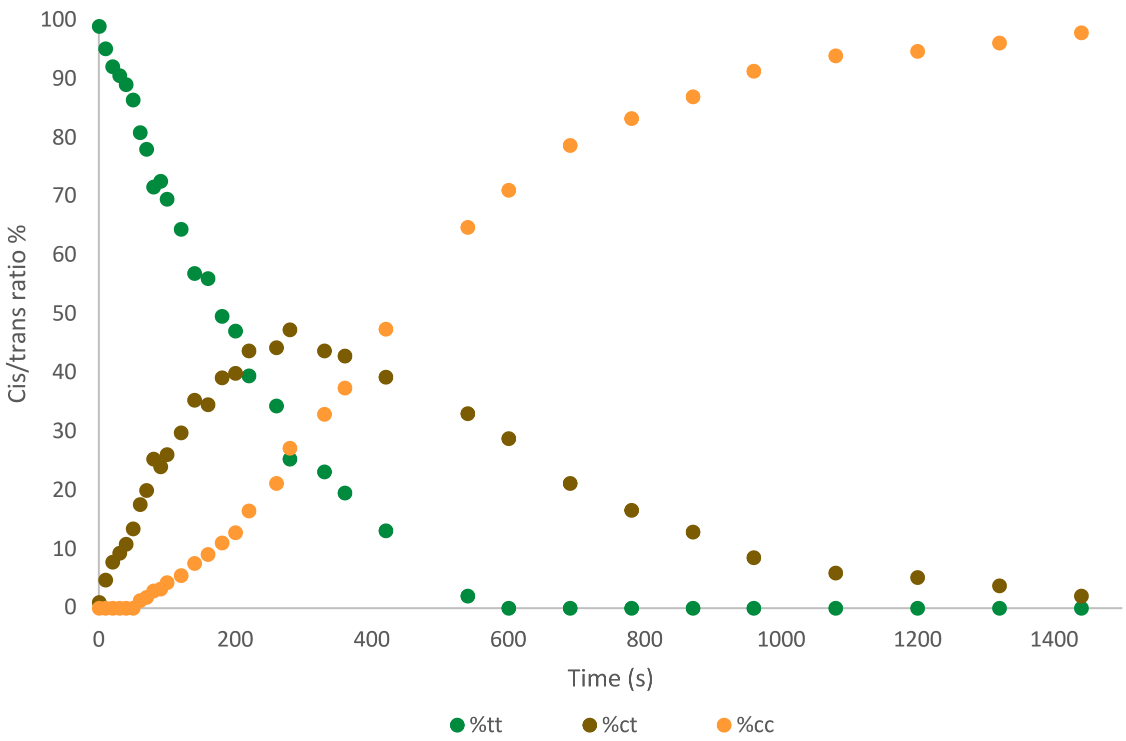


Figure S65: *Plotted data of **1** in toluene at 427 nm.*

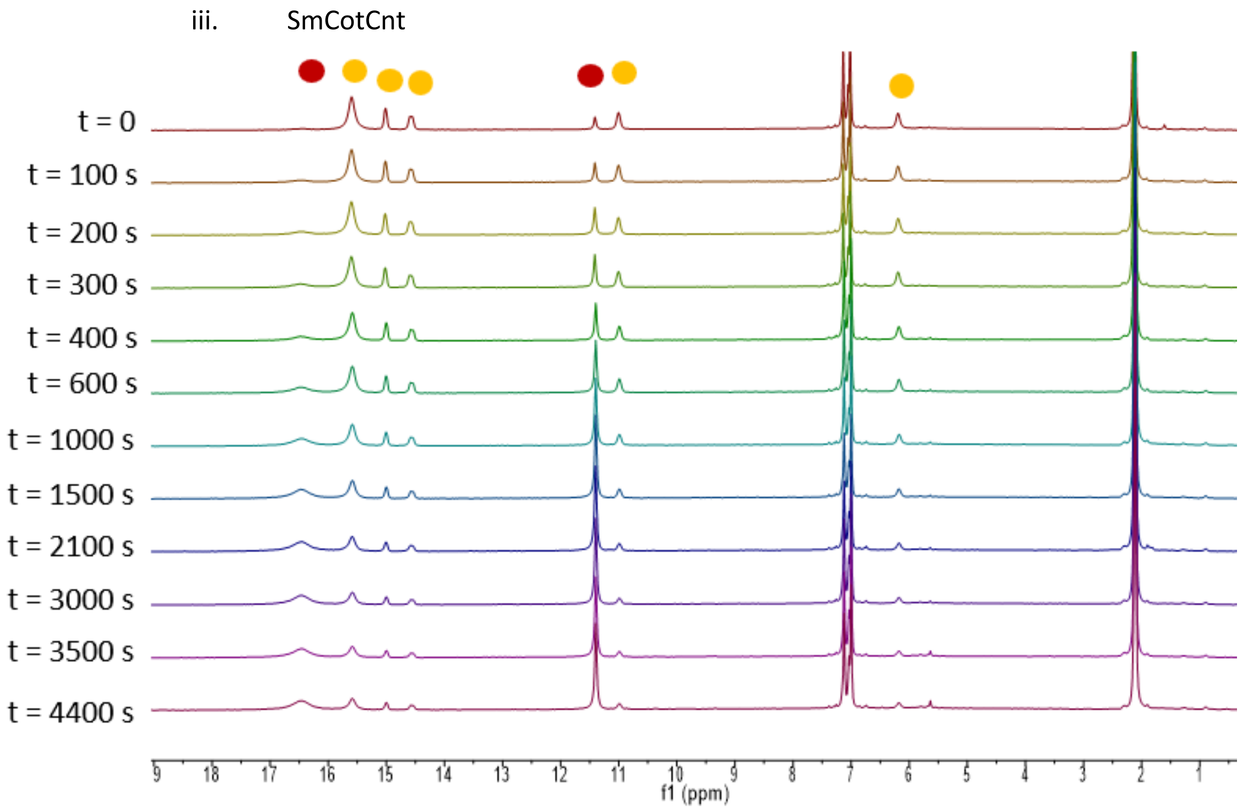


Figure S66: *Isomerization study by ^{1}H NMR of **2**-Sm in toluene at 427 nm. Red dots: signals attributed to the trans isomer; yellow dots: signals attributed to the cis isomer.*

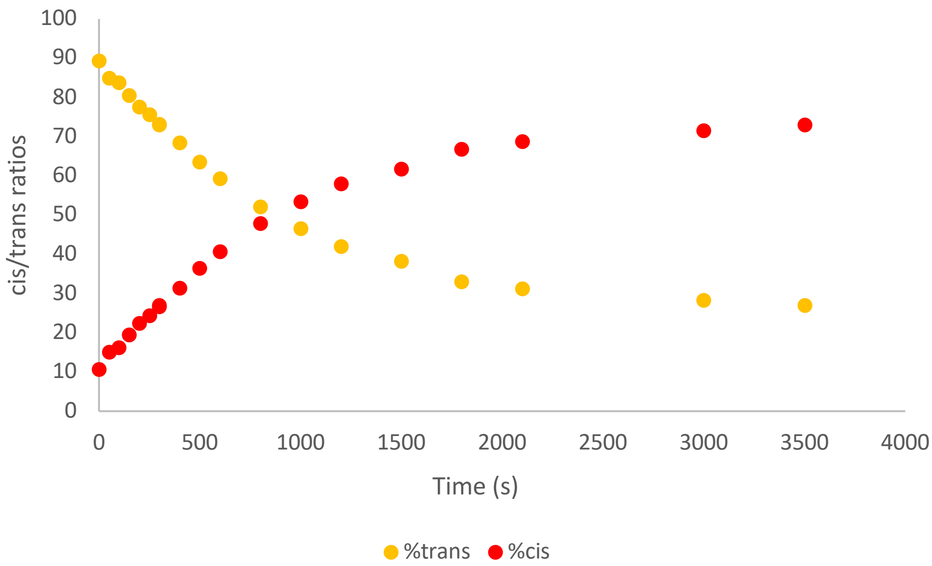


***Figure S67**: Plotted data of **2**-Sm in toluene at 427 nm*

b) Photostationary (PSS) study

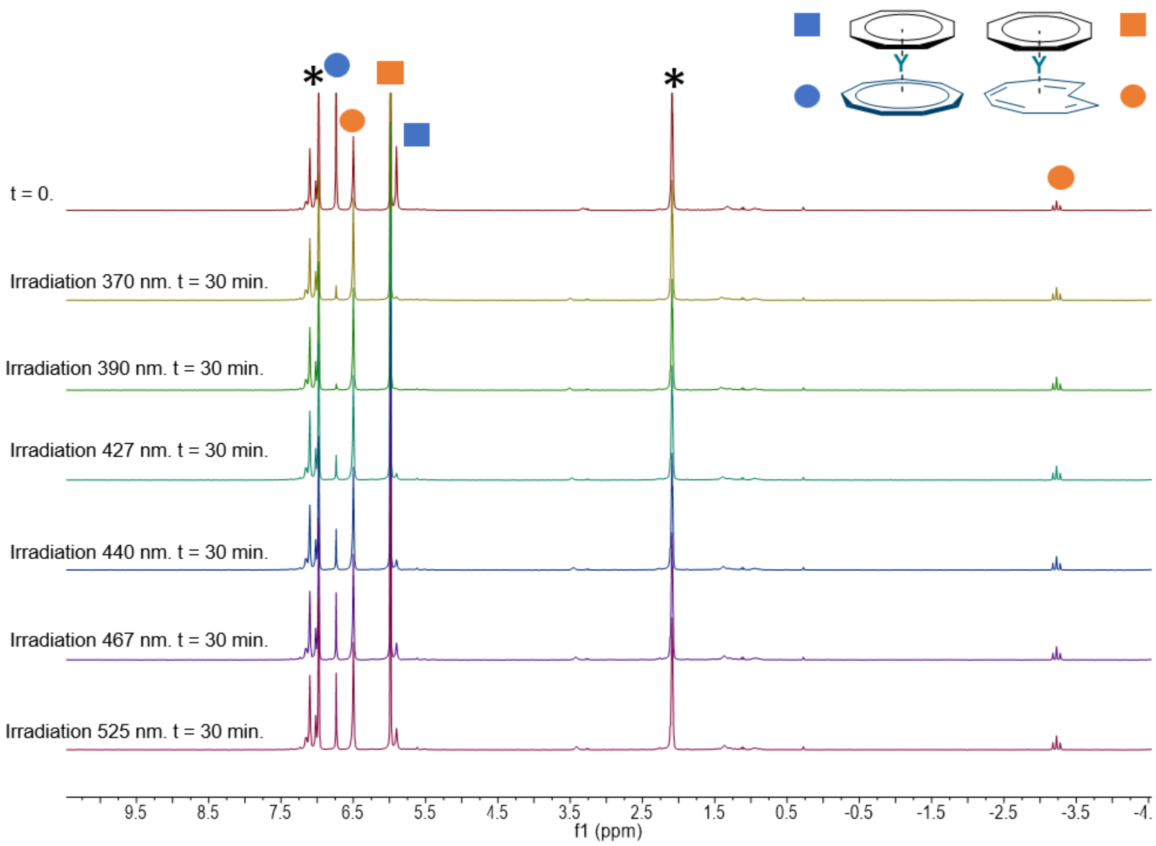


***Figure S68**: Isomerization study by ^{1}H NMR of **2**-Y in toluene-d_8 measured at 293 K at different wavelength (* residual protio signal of the solvent)*

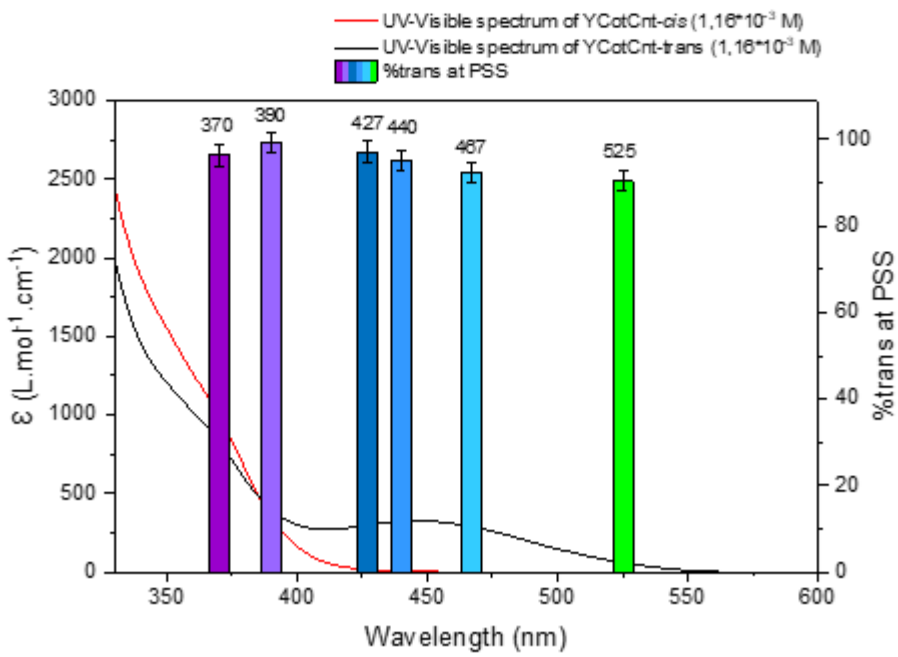


Figure S69*: Evolution of the trans/cis ratios of* ***2****-Y under different wavelengths superimposed with UV spectra of trans and cis isomer*

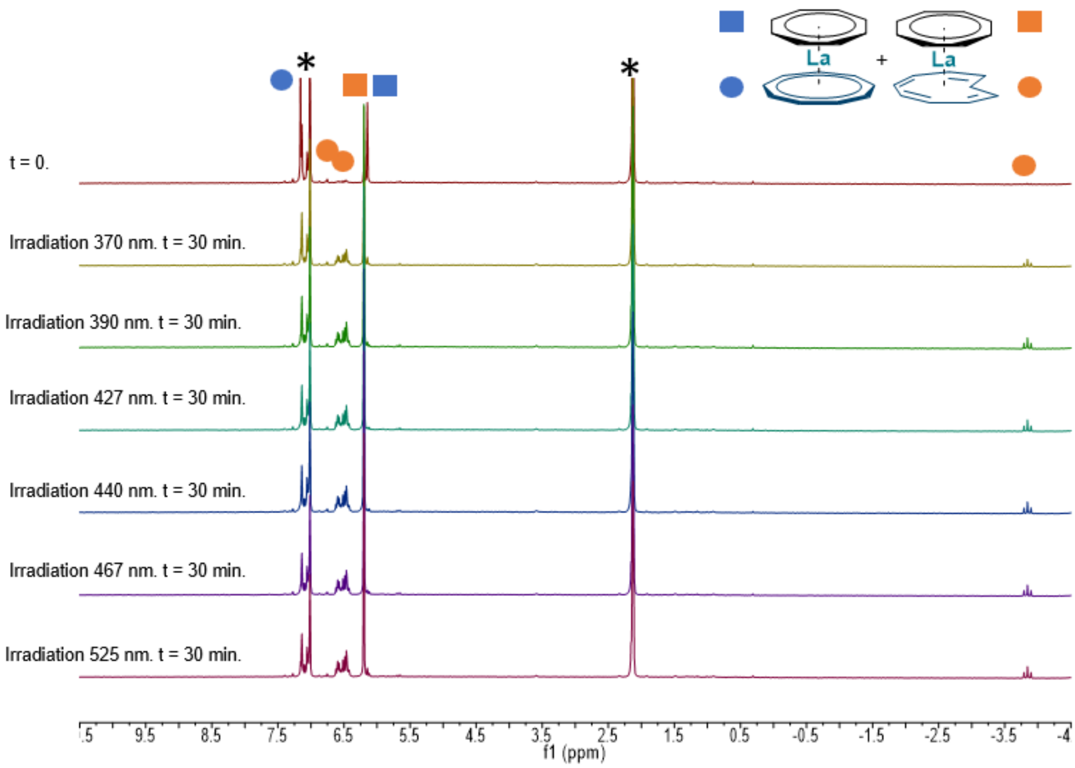


Figure S70*: Isomerization study by* ^{1}H *NMR of* ***2****-La in toluene-*d_8 *measured at 293 K at different wavelengths (* residual protio signal of the solvent)*

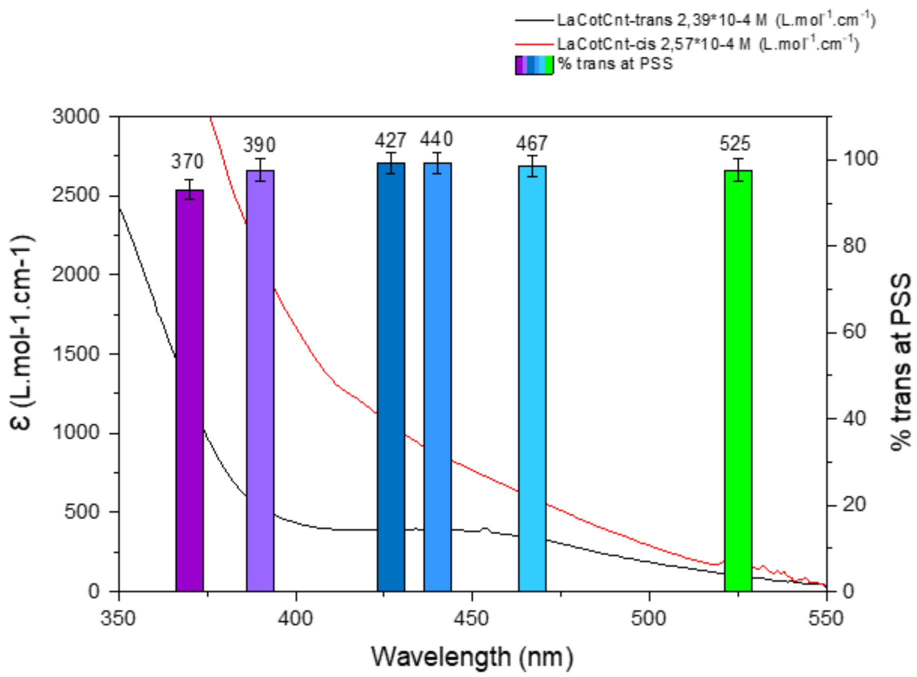


***Figure S71**: Evolution of the trans/cis ratios of **2**-La under different wavelengths superimposed with UV spectra of trans and cis isomer*

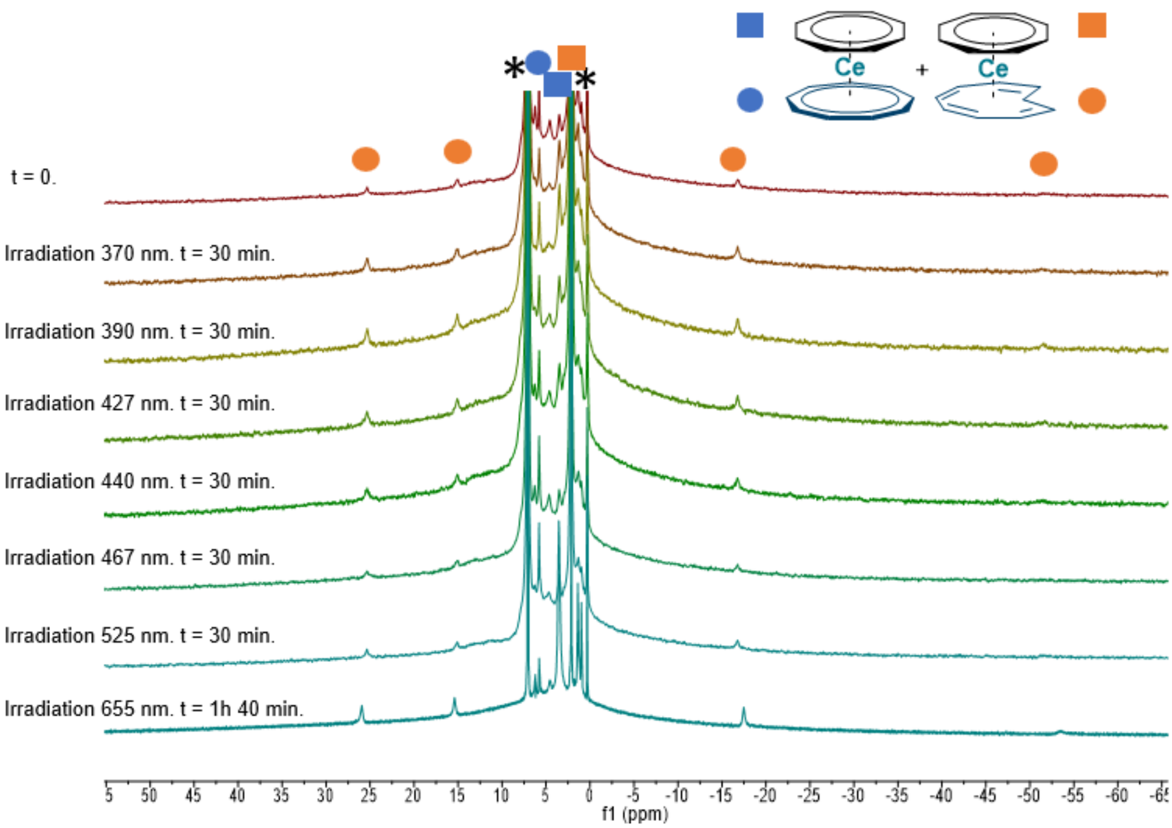


***Figure S72** : Isomerization study by ^1H NMR of **2**-Ce in toluene-d_8 measured at 293 K at different wavelengths (* residual protio signal of the solvent)*

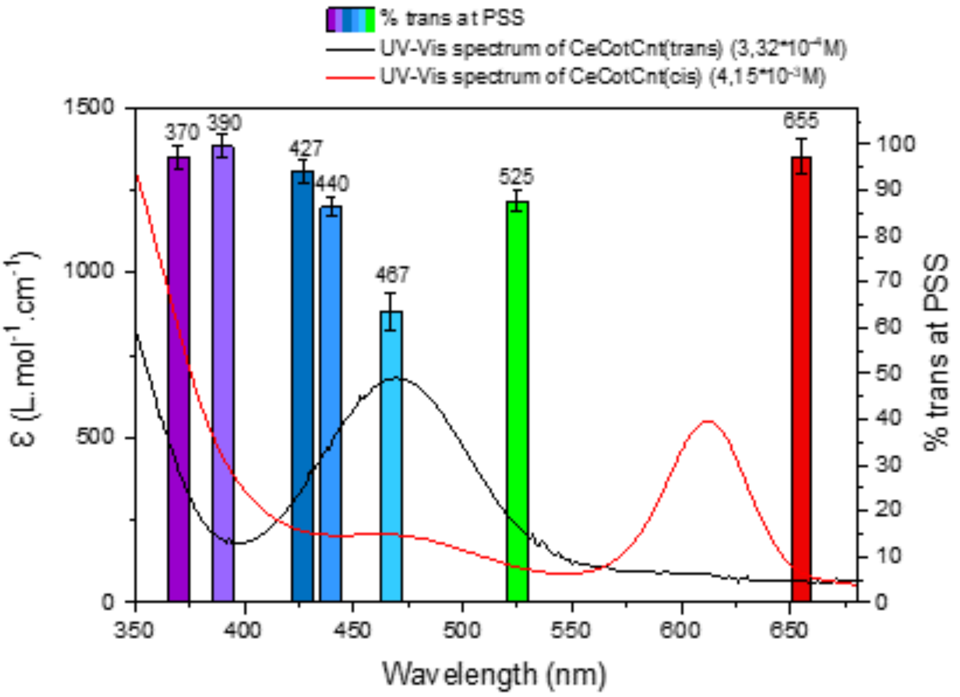


***Figure S73**: Evolution of the trans/cis ratios of **2**-Ce under different wavelengths superimposed with UV spectra of trans isomer*

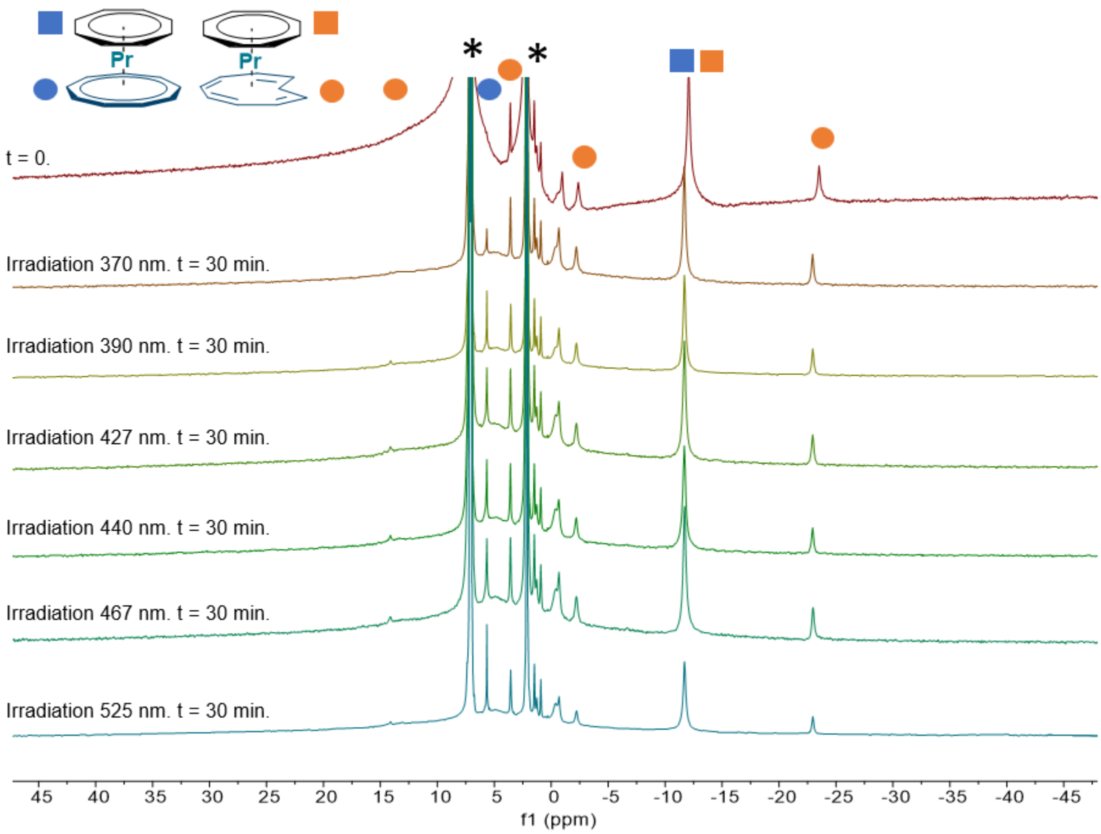


***Figure S74**: Isomerization study by ^{1}H NMR of **2**-Pr in toluene-d_8 measured at 293 K at different wavelengths (* residual protio signal of the solvent)*

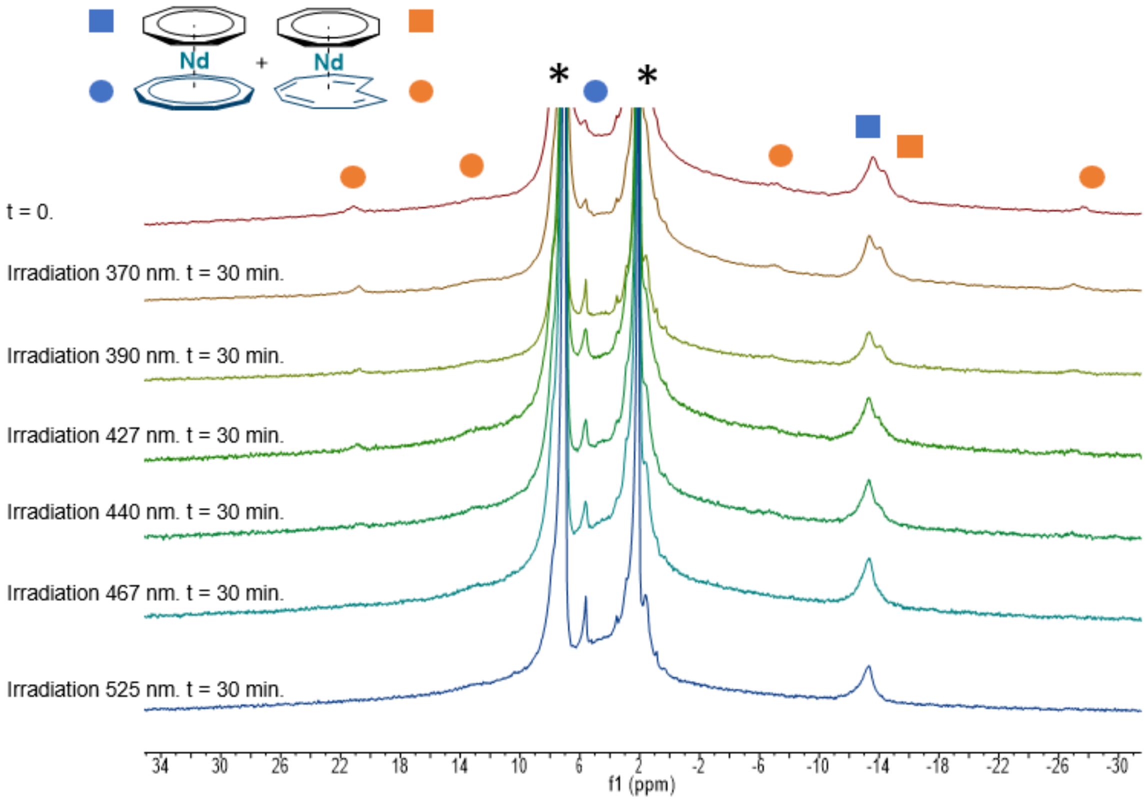


***Figure S75**: Isomerization study by ¹H NMR of **2**-Nd in toluene-d_8 measured at 293 K at different wavelengths (* residual protio signal of the solvent)*

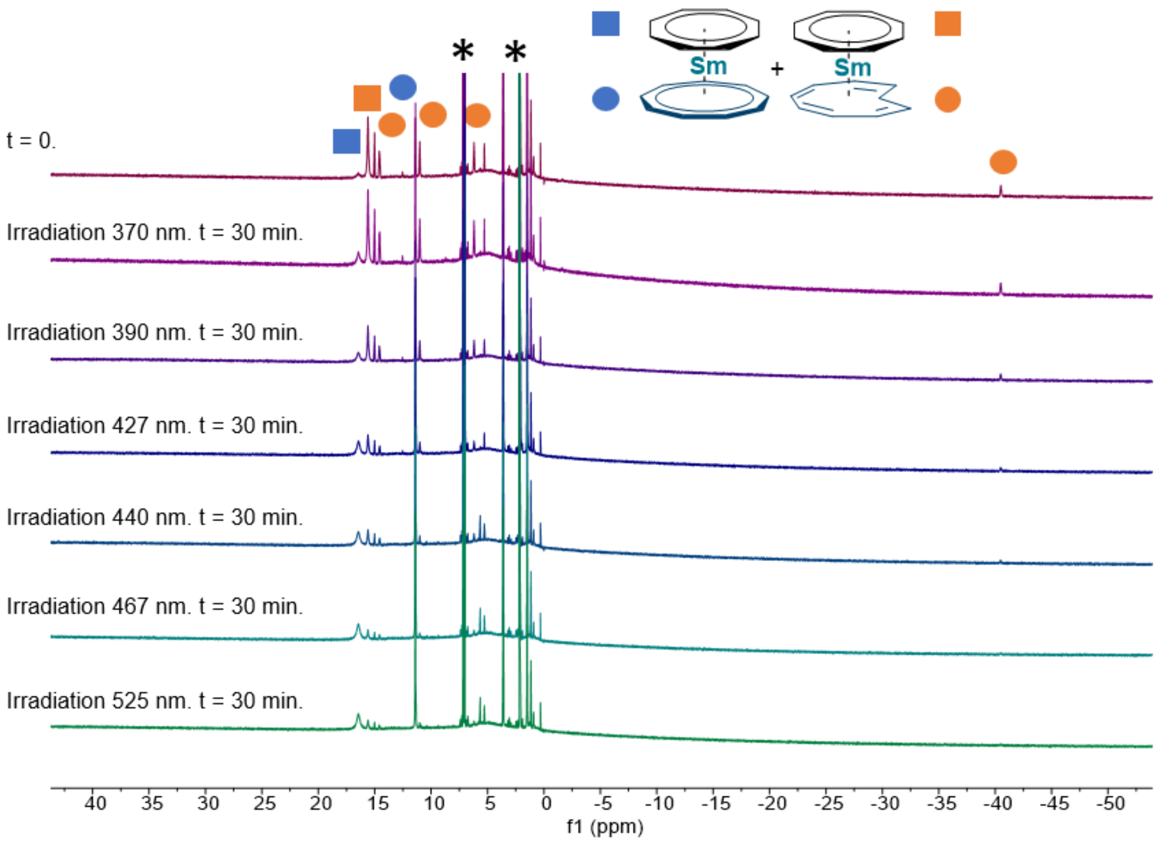


***Figure S76**: Isomerization study by ¹H NMR of **2**-Sm in toluene-d_8 measured at 293 K at different wavelengths (* residual protio signal of the solvent)*

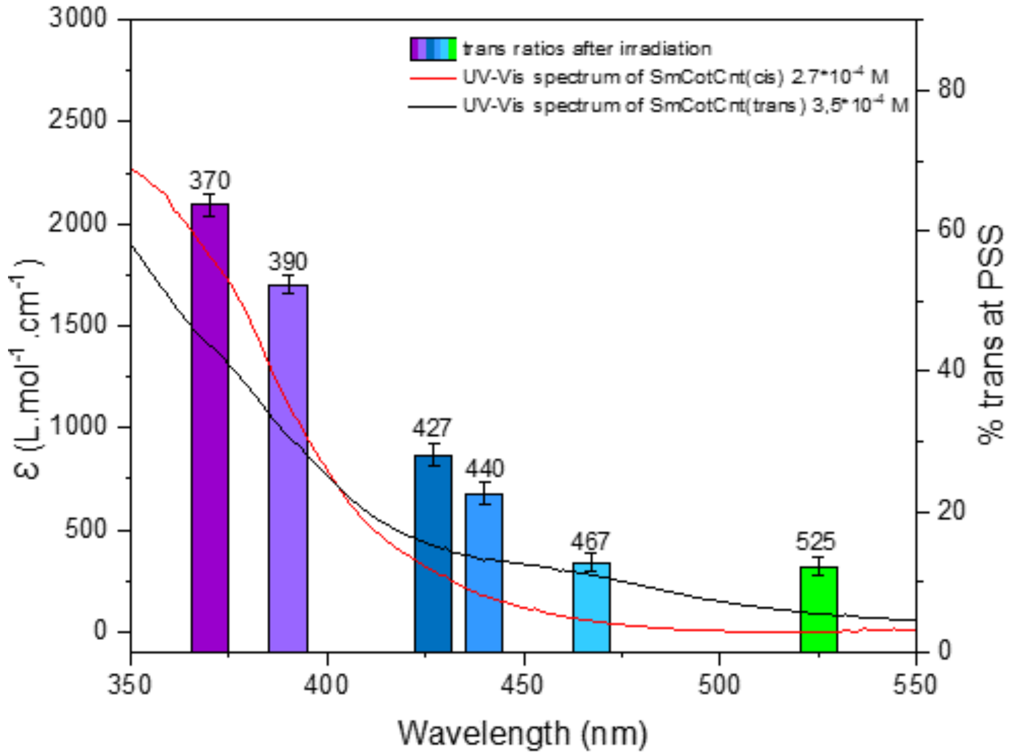


Figure S77: *Evolution of the trans/cis ratios of **2**-Sm under different wavelengths superimposed with UV spectra of the cis and trans isomers*

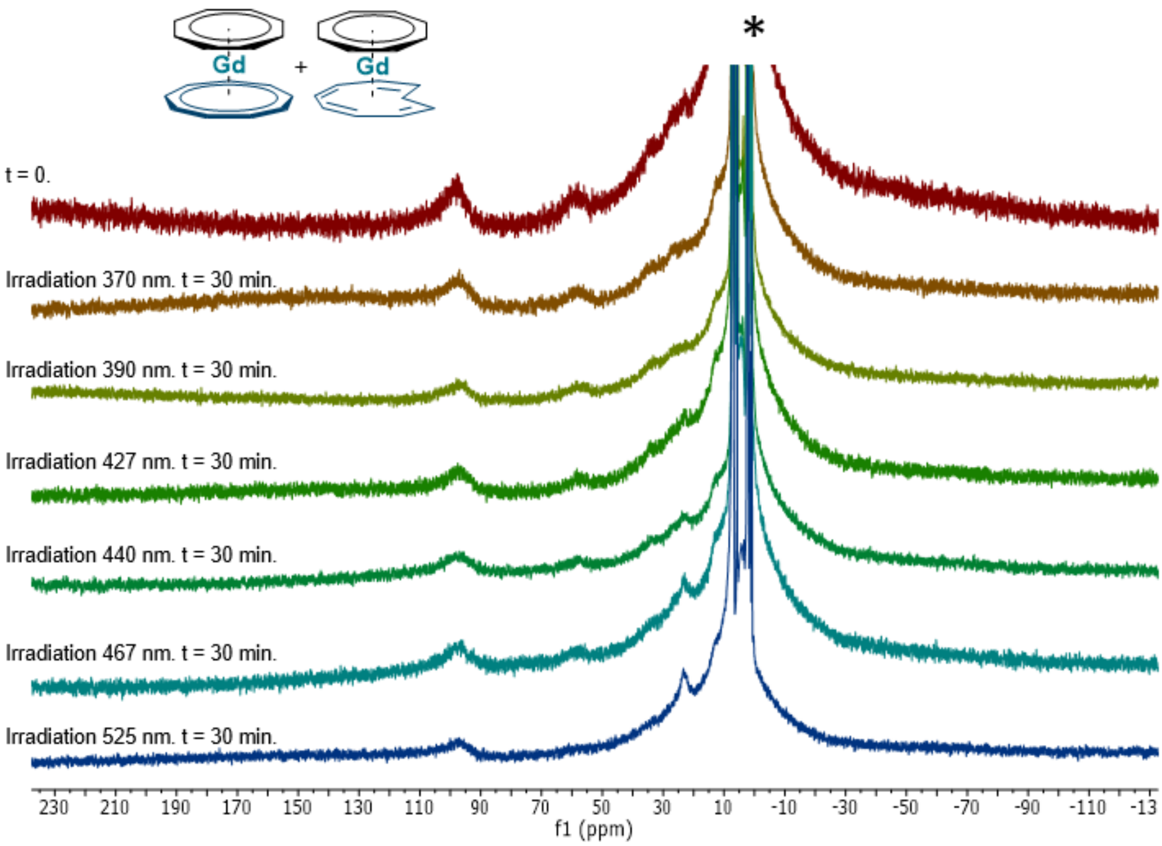


Figure S78: *Isomerization study by ^{1}H NMR of **2**-Gd in toluene-d_8 measured at 293 K at different wavelengths (* residual protio signal of the solvent)*

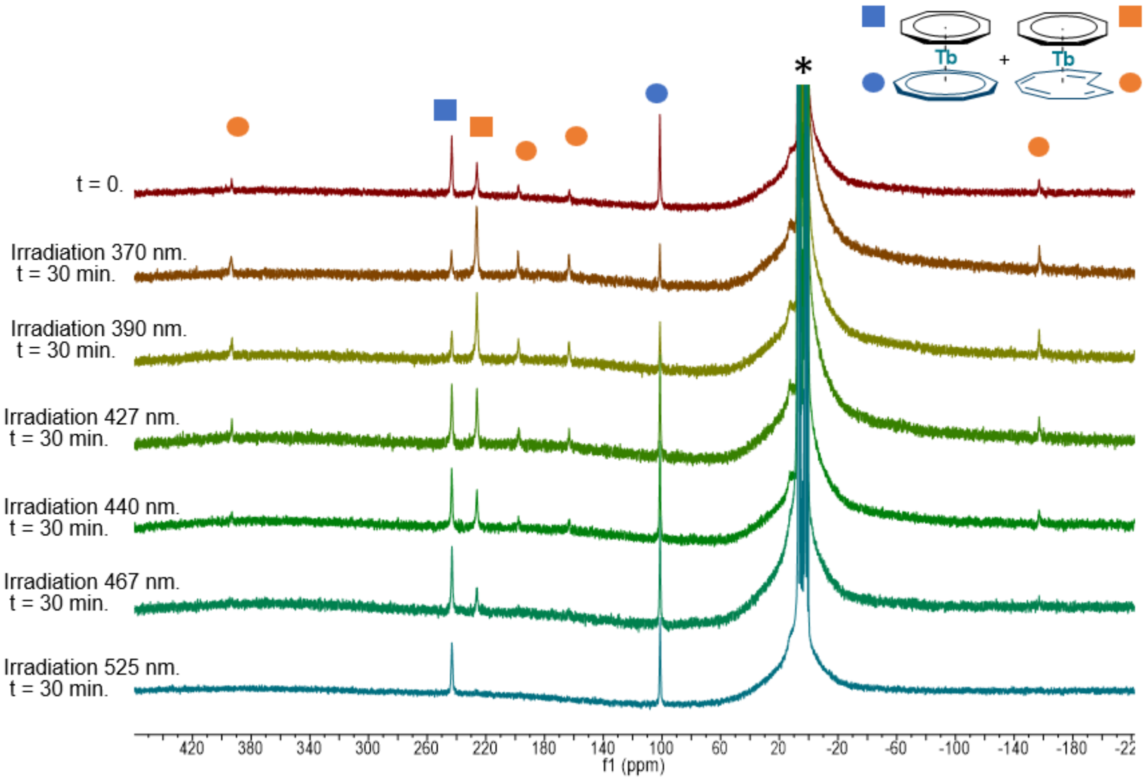


***Figure S79**: Isomerization study by [1]H NMR of **2**-Tb in toluene-d_8 measured at 293 K at different wavelengths (* residual protio signal of the solvent)*

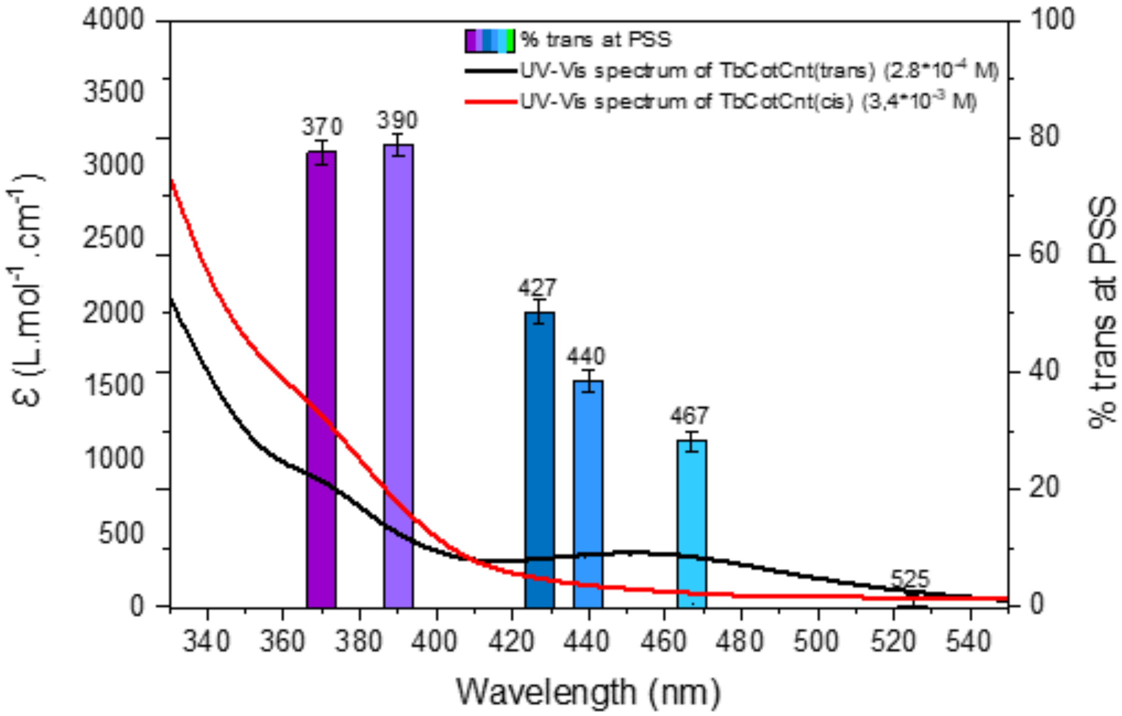


***Figure S80**: Evolution of the trans/cis ratios of **2**-Tb under different wavelength under different wavelengths superimposed with UV spectra of the trans isomers*

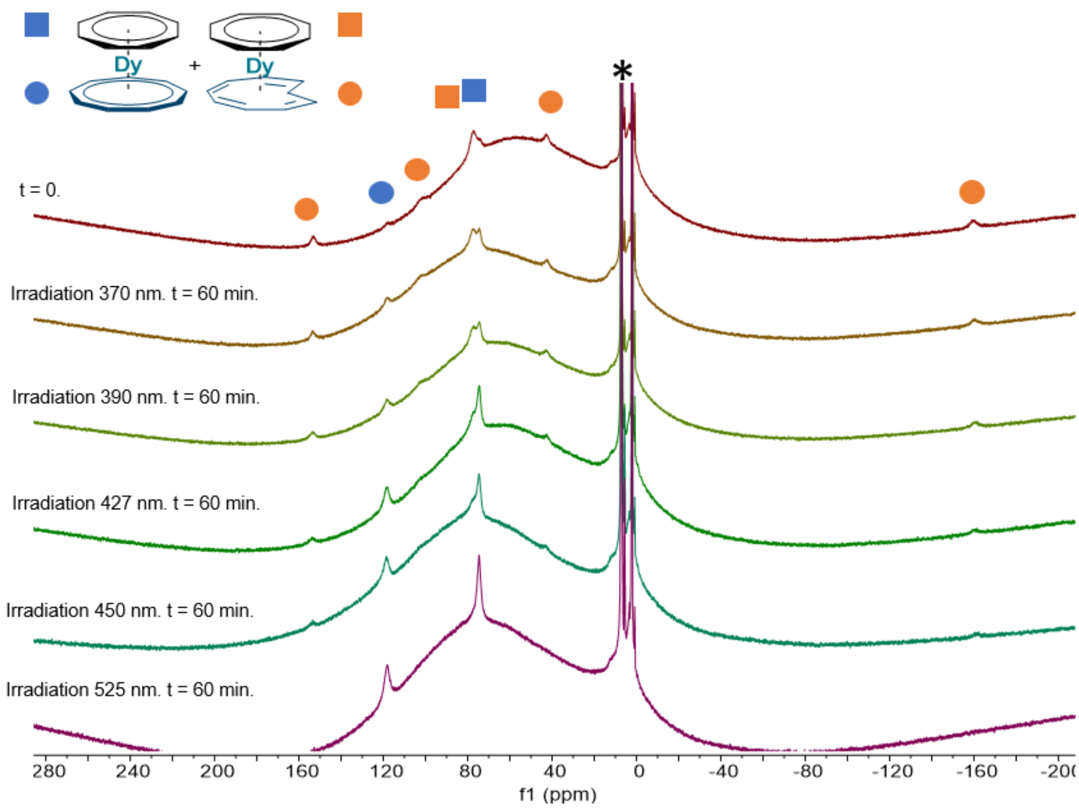


***Figure S81**: Isomerization study by ^{1}H NMR of **2**-Dy in toluene-d_8 measured at 293 K at different wavelengths (* residual protio signal of the solvent)*

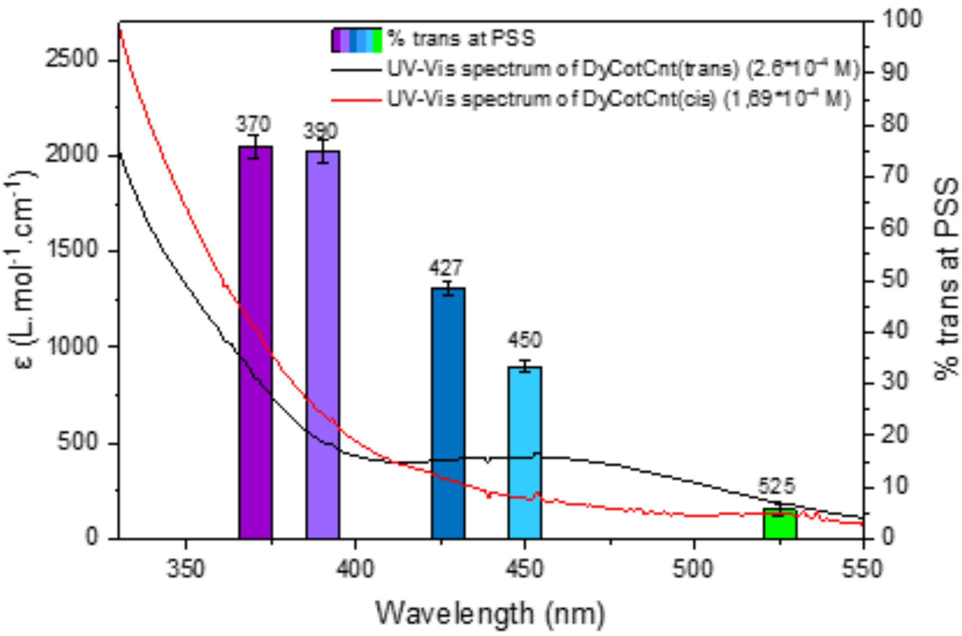


***Figure S82**: Evolution of the trans/cis ratios of **2**-Dy under different wavelengths superimposed with UV spectra of the trans isomers*

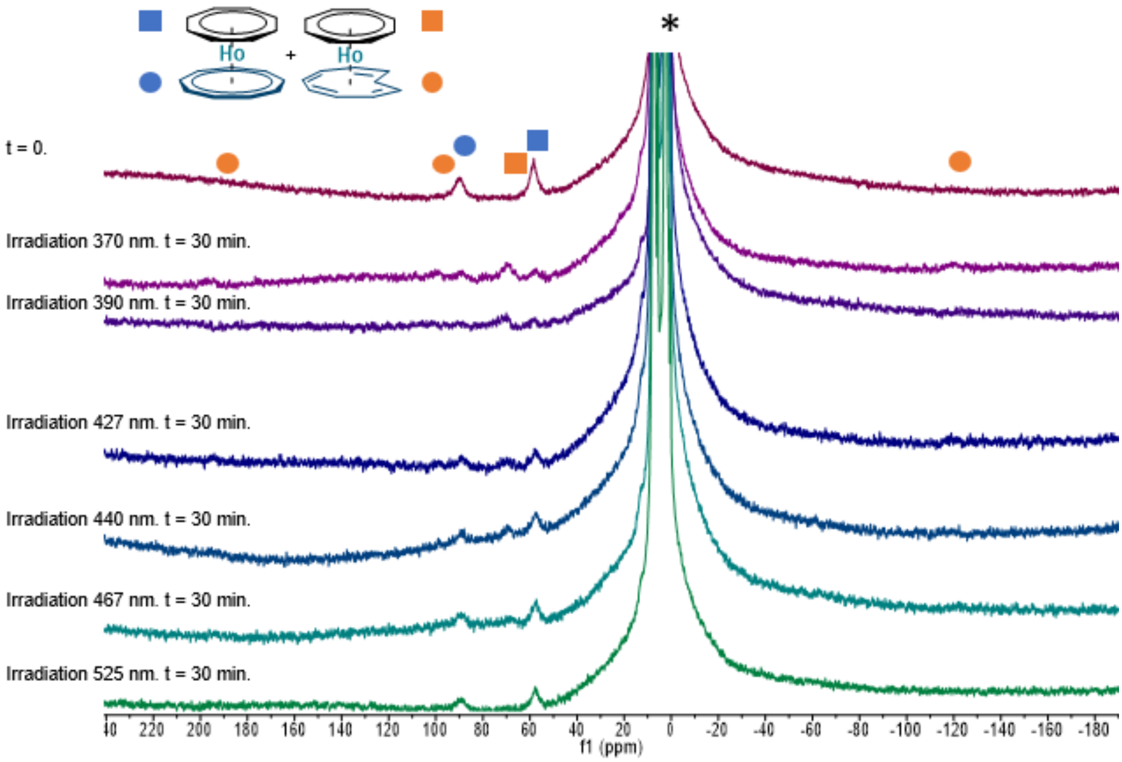


***Figure S83**: Isomerization study by ¹H NMR of **2**-Ho in toluene-d_8 measured at 293 K at different wavelengths (* residual protio signal of the solvent)*

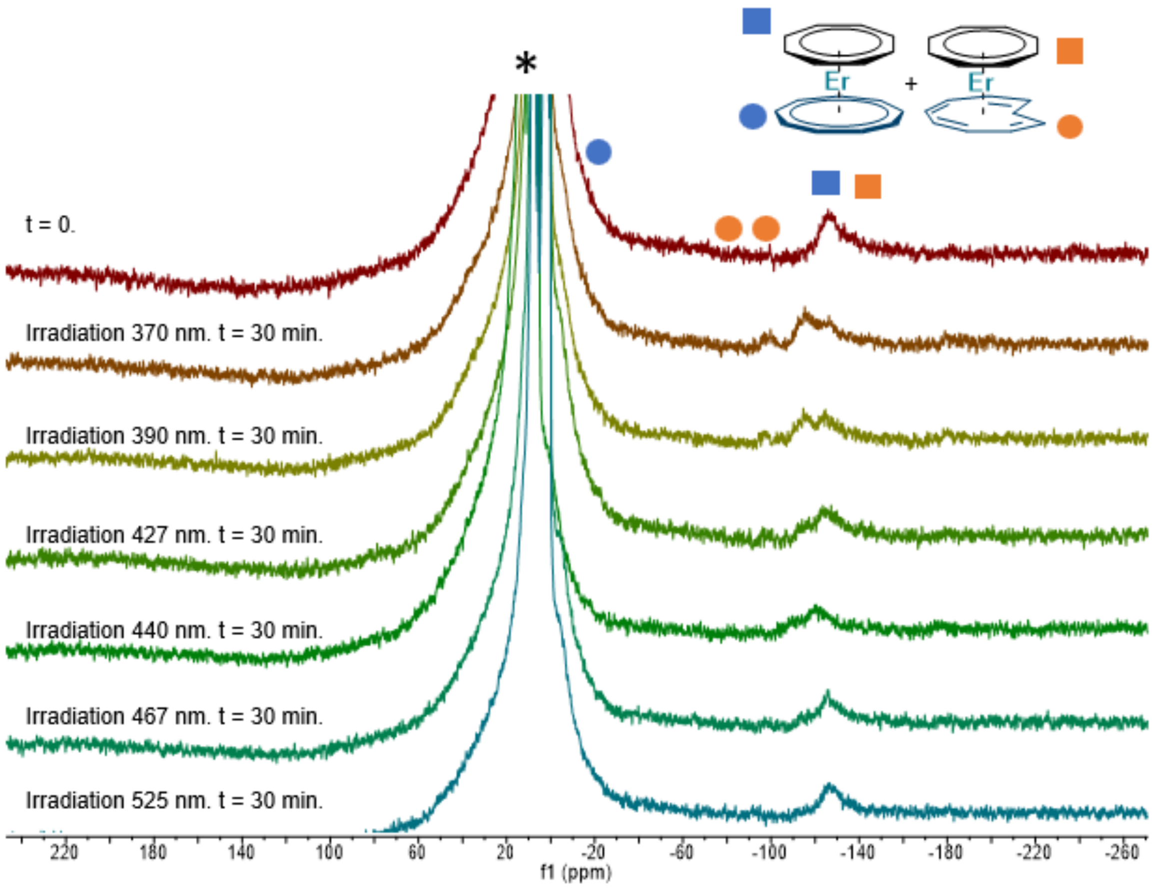


***Figure S84**: Isomerization study by ¹H NMR of **2**-Er in toluene-d_8 measured at 293 K at different wavelengths (* residual protio signal of the solvent).*

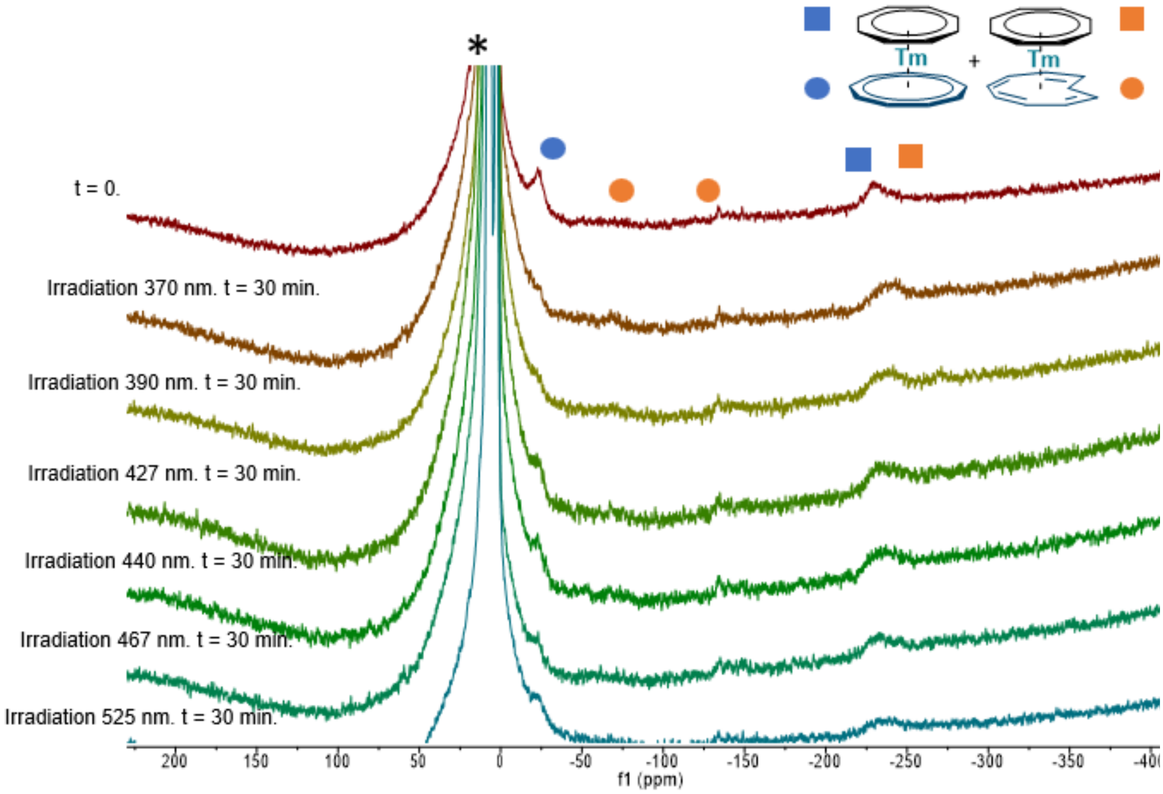


***Figure S85**: Isomerization study by ^{1}H NMR of **2**-Tm in toluene-d_8 measured at 293 K at different wavelengths (* residual protio signal of the solvent).*

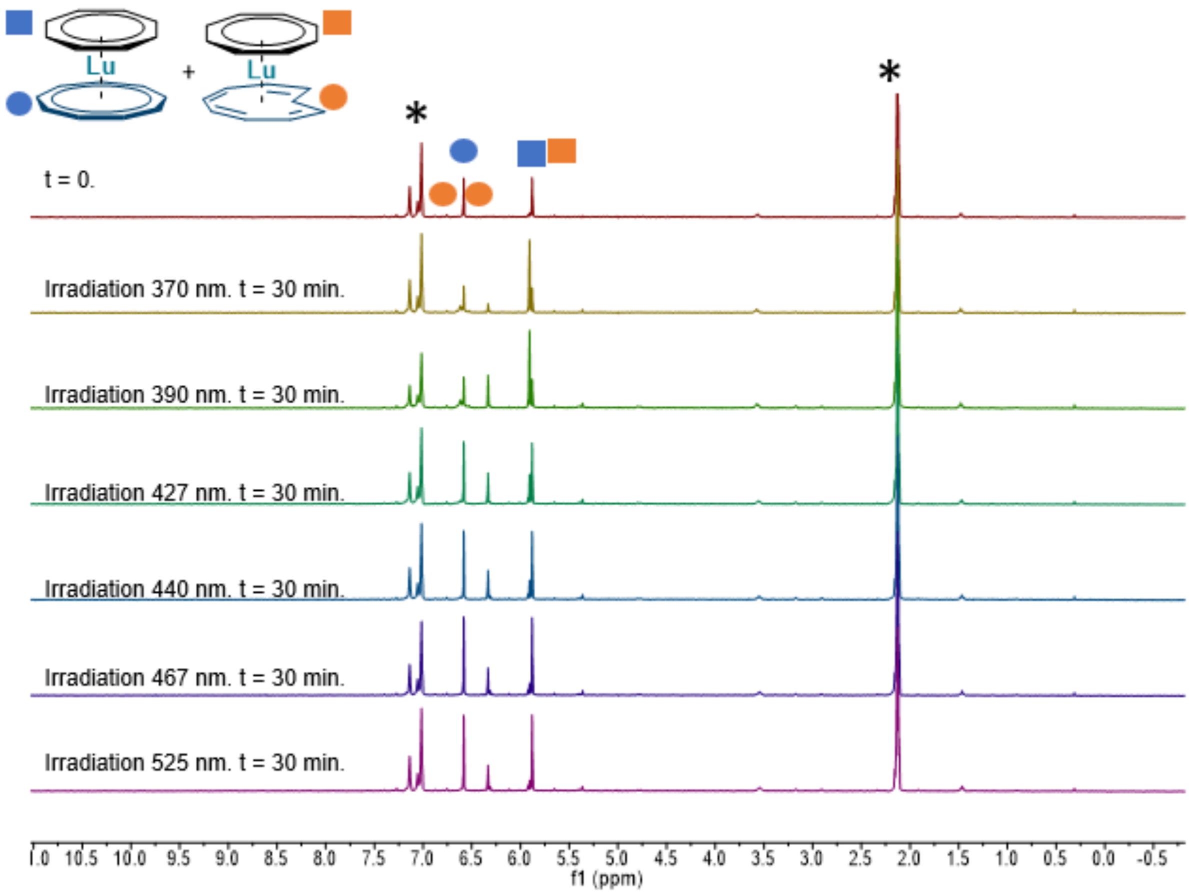


***Figure S86**: Isomerization study by ^{1}H NMR of **2**-Lu in toluene-d_8 measured at 293 K at different wavelengths (* residual protio signal of the solvent).*

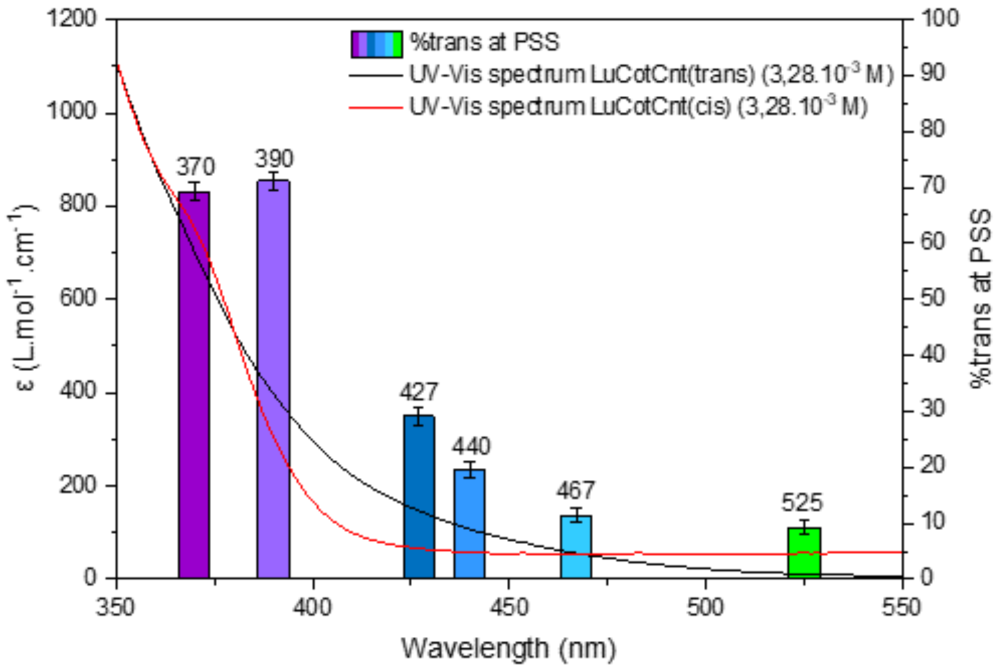


***Figure S87**: Evolution of the trans/cis ratios of **2**-Lu under different wavelengths superimposed with UV spectra of the trans isomers.*

8. Computational details

The optimization of reactants, transition states, IRC, and products were carried out by employing DFT hybrid functional (B3PW91)[5] along with small core pseudopotential Stuttgart basis set[6,7] for samarium atom and Pople basis set[8–10] (6-31G**) for the rest of the atoms. Frequency calculations were performed to locate saddle points for transition state structures, minima for the rest of the structures, and for obtaining thermal corrections over the energies. All the calculations were performed using Gaussian 16 suite of programs.[11] Dispersion corrections were accounted for using the GD3-BJ approach.

NCIS calculations were done using the GIAO method.[12–15]

Energetics (kcal/mol) between two isomers of [Sm(C8H8)(C9H9)], **2-Sm**

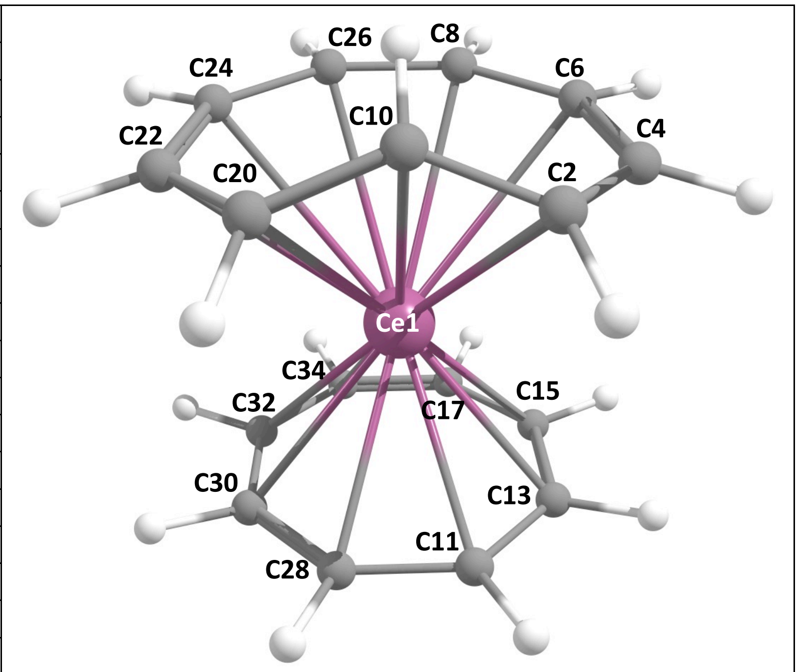
	ΔH	ΔG
1 (S=5/2)	6.9	4.9
2 (S=5/2)	0.0	0.0

Energetics (kcal/mol) between two isomers of [Ce(C8H8)(C9H9)], **2-Ce**

	ΔH	ΔG
3 (S=1/2)	3.7	4.3
4 (S=1/2)	0.0	0.0

Table S24**: Selected structural parameters (Dispersion) for **2-Ce-trans.

	Bond distance
Ce1-C2	2.98
Ce1-C4	3.97
Ce1-C6	3.00
Ce1-C8	2.91
Ce1-C10	2.86
Ce1-C11	2.66
Ce1-C13	2.66
Ce1-C15	2.66
Ce1-C17	2.67
Ce1-C20	2.98
Ce1-C22	3.07
Ce1-C24	3.00
Ce1-C26	2.91
Ce1-C28	2.66
Ce1-C30	2.66
Ce1-C32	2.66
Ce1-C34	2.67



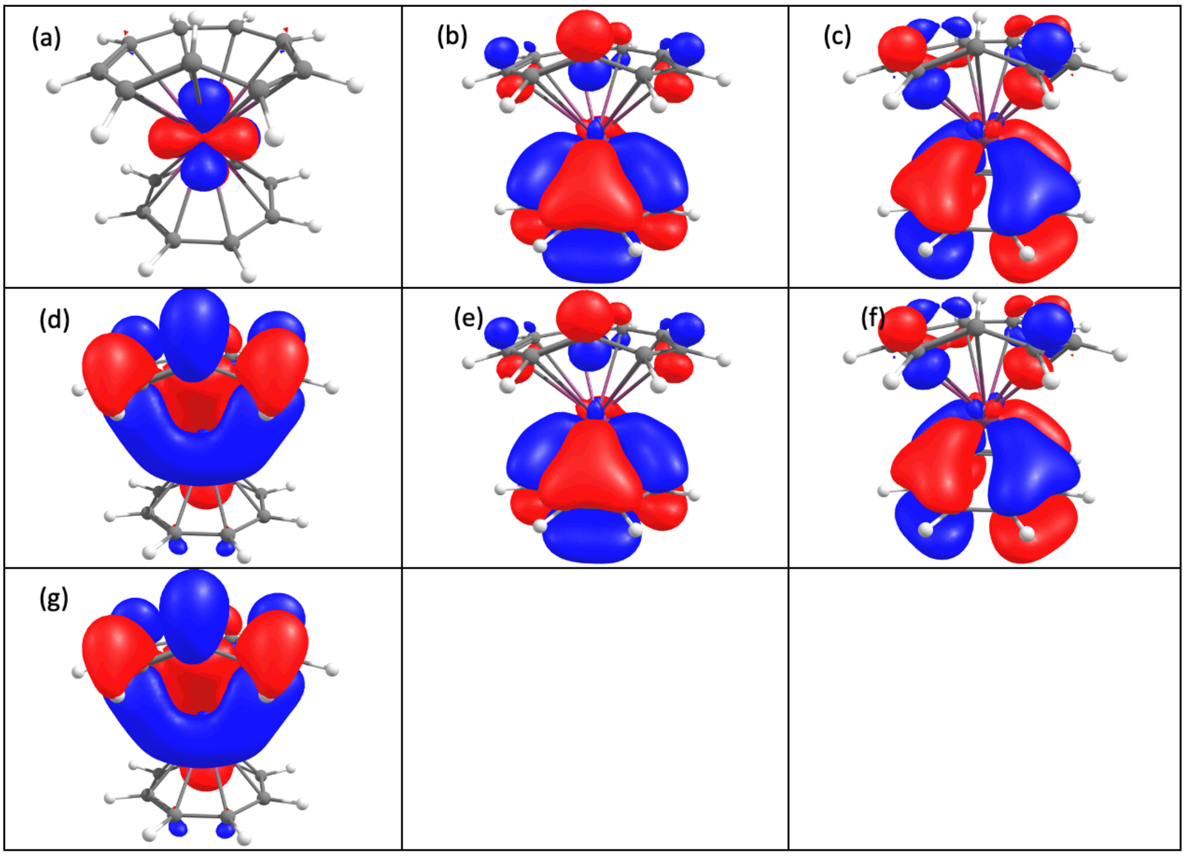
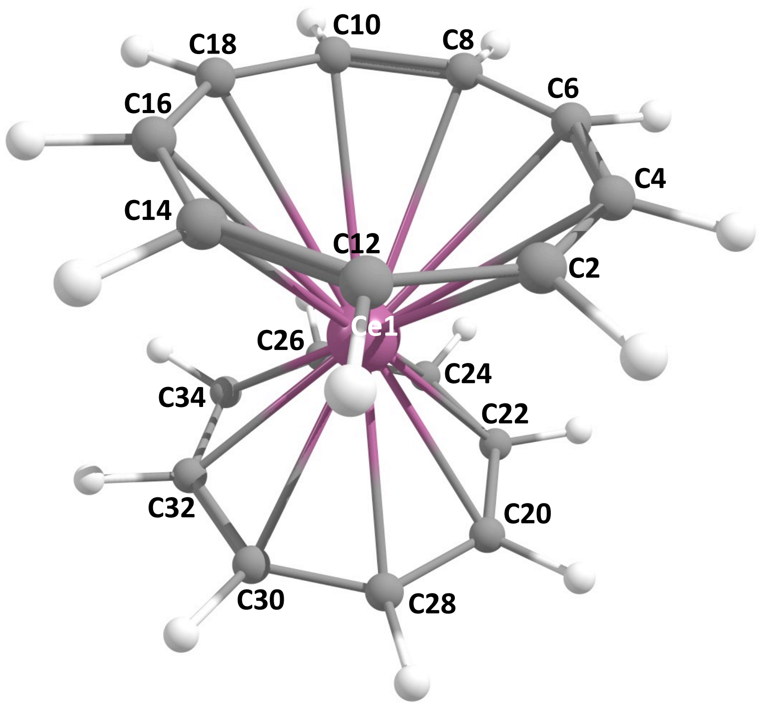


***Figure S88**: Computed MOs for **2-Ce-trans**. (a)AMO-HOMO-2 (b)AMO-HOMO-1 (c)AMO-HOMO (d)AMO-LUMO (e)BMO-HOMO-1 (f)BMO-HOMO (g)BMO-LUMO*

Table S25**: Selected structural parameters (Dispersion) for **2-Ce-cis.

	Bond distance	
Ce1-C2	3.01	
Ce1-C4	3.01	
Ce1-C6	3.02	
Ce1-C8	3.02	
Ce1-C10	2.89	
Ce1-C12	2.89	
Ce1-C14	2.89	
Ce1-C16	2.90	
Ce1-C18	2.89	
Ce1-C20	2.65	
Ce1-C22	2.65	
Ce1-C24	2.65	
Ce1-C26	2.65	
Ce1-C28	2.65	
Ce1-C30	2.65	

Ce1-C32	2.65	
Ce1-C34	2.65	

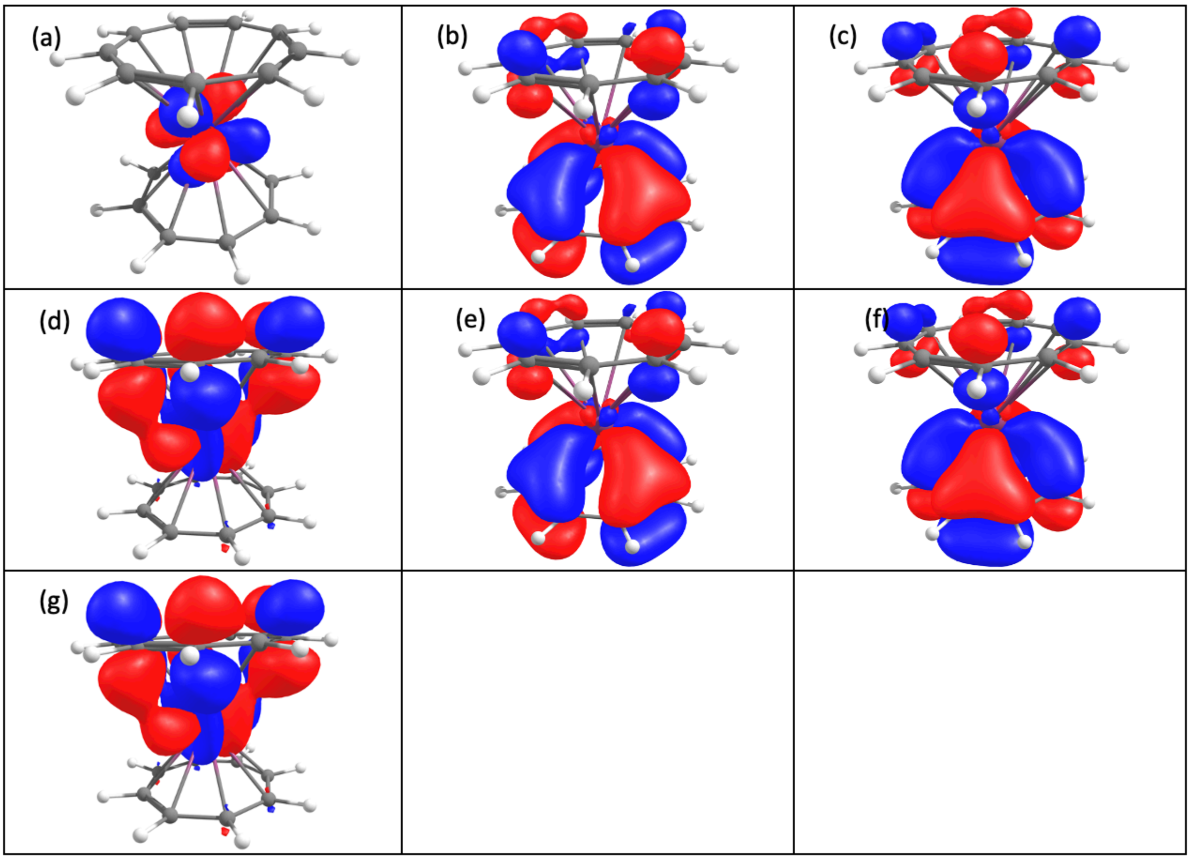


__Figure S89__: Computed MOs for __2-Ce-cis__. (a)AMO-HOMO-2 (b)AMO-HOMO-1 (c)AMO-HOMO (d)AMO-LUMO (e)BMO-HOMO-1 (f)BMO-HOMO (g)BMO-LUMO

Table S26: *Computed natural charges for* ***2-Ce-trans.***

Atom labels	Natural charges
Ce1	1.36079
C2	-0.29364
C4	-0.28918
C6	-0.33215
C8	-0.36598
C10	-0.31992
C11	-0.37842
C13	-0.37206
C15	-0.37218
C17	-0.37819
C20	-0.29364
C22	-0.28918
C24	-0.33215
C26	-0.36598
C28	-0.37842
C30	-0.37206
C32	-0.37218
C34	-0.37819

Table S27: *Computed Wiberg bond index for* ***2-Ce-trans.***

Atom labels	Wiberg bond index	Atom labels	Wiberg bond index	Atom labels	Wiberg bond index	Atom labels	Wiberg bond index
Ce1	0.0000	Ce1	0.0000	Ce1	0.0000	Ce1	0.0000
C2	0.1055	C4	0.0960	C6	0.1035	C8	0.1097
Atom labels	Wiberg bond index	Atom labels	Wiberg bond index	Atom labels	Wiberg bond index	Atom labels	Wiberg bond index
Ce1	0.0000	Ce1	0.0000	Ce1	0.0000	Ce1	0.0000
C10	0.1277	C11	0.2454	C13	0.2409	C15	0.2388
Atom labels	Wiberg bond index	Atom labels	Wiberg bond index	Atom labels	Wiberg bond index	Atom labels	Wiberg bond index
Ce1	0.0000	Ce1	0.0000	Ce1	0.0000	Ce1	0.0000
C17	0.2422	C20	0.1055	C22	0.0960	C24	0.1035
Atom labels	Wiberg bond index	Atom labels	Wiberg bond index	Atom labels	Wiberg bond index	Atom labels	Wiberg bond index
Ce1	0.0000	Ce1	0.0000	Ce1	0.0000	Ce1	0.0000
C26	0.1097	C28	0.2454	C30	0.2409	C32	0.2388
Atom labels	Wiberg bond index						
Ce1	0.0000						
C34	0.2422						

*Table S28: DFT computed NBO second order perturbation analysis for **2-Ce-trans.***

Donor NBO	Acceptor NBO	E(2) kcal/mol
(0.52166) LP (1) C 10 s(0.52%)p99.99(99.45%)d 0.06(0.03%)	(0.11692) LV (3)Ce 1 s(0.06%)p 3.95(0.24%)d99.99(98.98%)f11.35(0.68%)g 0.73(0.04%)	5.49
(0.52166) LP (1) C 10 s(0.52%)p99.99(99.45%)d 0.06(0.03%)	(0.07166) LV (5)Ce 1 s(3.03%)p 0.02(0.05%)d19.39(58.80%)f12.56(38.10%)g 0.01(0.02%)	13.79
(0.52166) LP (1) C 10 s(0.52%)p99.99(99.45%)d 0.06(0.03%)	(0.04854) LV (7)Ce 1 s(92.48%)p 0.01(0.90%)d 0.01(1.25%)f 0.06(5.29%)g 0.00(0.07%)	4.43
(0.83169) BD (2) C 2- C 4 (49.91%) 0.7065* C 2 s(0.58%)p99.99(99.35%)d 0.12(0.07%) (50.09%) 0.7077* C 4 s(0.31%)p99.99(99.64%)d 0.16(0.05%)	(0.11692) LV (3)Ce 1 s(0.06%)p 3.95(0.24%)d99.99(98.98%)f11.35(0.68%)g 0.73(0.04%)	3.00
(0.83169) BD (2) C 2- C 4 (49.91%) 0.7065* C 2 s(0.58%)p99.99(99.35%)d 0.12(0.07%) (50.09%) 0.7077* C 4 s(0.31%)p99.99(99.64%)d 0.16(0.05%)	(0.11537) LV (4)Ce 1 s(0.00%)p 1.00(0.17%)d99.99(98.31%)f 8.37(1.45%)g 0.40(0.07%)	4.58
(0.98776) BD (1) C 2- C 10 (49.37%) 0.7027* C 2 s(35.12%)p 1.85(64.82%)d 0.00(0.06%) (50.63%) 0.7115* C 10 s(36.72%)p 1.72(63.22%)d 0.00(0.06%)	(0.11692) LV (3)Ce 1 s(0.06%)p 3.95(0.24%)d99.99(98.98%)f11.35(0.68%)g 0.73(0.04%)	2.77
(0.98757) BD (1) C 4- C 6 (49.54%) 0.7038* C 4 s(35.58%)p 1.81(64.36%)d 0.00(0.07%) (50.46%) 0.7104* C 6 s(37.08%)p 1.70(62.86%)d 0.00(0.06%)	(0.11537) LV (4)Ce 1 s(0.00%)p 1.00(0.17%)d99.99(98.31%)f 8.37(1.45%)g 0.40(0.07%)	2.43
(0.85222) BD (2) C 6- C 8 (49.33%) 0.7024* C 6 s(0.40%)p99.99(99.56%)d 0.09(0.03%) (50.67%) 0.7118* C 8 s(0.37%)p99.99(99.60%)d 0.09(0.03%)	(0.11692) LV (3)Ce 1 s(0.06%)p 3.95(0.24%)d99.99(98.98%)f11.35(0.68%)g 0.73(0.04%)	3.05
(0.85222) BD (2) C 6- C 8 (49.33%) 0.7024* C 6 s(0.40%)p99.99(99.56%)d 0.09(0.03%) (50.67%) 0.7118* C 8 s(0.37%)p99.99(99.60%)d 0.09(0.03%)	(0.11537) LV (4)Ce 1 s(0.00%)p 1.00(0.17%)d99.99(98.31%)f 8.37(1.45%)g 0.40(0.07%)	3.60
(0.85222) BD (2) C 6- C 8 (49.33%) 0.7024* C 6 s(0.40%)p99.99(99.56%)d 0.09(0.03%) (50.67%) 0.7118* C 8 s(0.37%)p99.99(99.60%)d 0.09(0.03%)	(0.04854) LV (7)Ce 1 s(92.48%)p 0.01(0.90%)d 0.01(1.25%)f 0.06(5.29%)g 0.00(0.07%)	2.65
(0.98541) BD (1) C 8- C 26 (50.00%) 0.7071* C 8 s(37.45%)p 1.67(62.49%)d 0.00(0.06%)	(0.11692) LV (3)Ce 1 s(0.06%)p 3.95(0.24%)d99.99(98.98%)f11.35(0.68%)g 0.73(0.04%)	3.48

(50.00%) 0.7071* C 26 s(37.45%)p 1.67(62.49%)d 0.00(0.06%)		
(0.98541) BD (1) C 8- C 26 (50.00%) 0.7071* C 8 s(37.45%)p 1.67(62.49%)d 0.00(0.06%) (50.00%) 0.7071* C 26 s(37.45%)p 1.67(62.49%)d 0.00(0.06%)	(0.07166) LV (5)Ce 1 s(3.03%)p 0.02(0.05%)d19.39(58.80%)f12.56(38.10%)g 0.01(0.02%)	2.74
(0.98776) BD (1) C 10- C 20 (50.63%) 0.7115* C 10 s(36.72%)p 1.72(63.22%)d 0.00(0.06%) (49.37%) 0.7027* C 20 s(35.12%)p 1.85(64.82%)d 0.00(0.06%)	(0.11692) LV (3)Ce 1 s(0.06%)p 3.95(0.24%)d99.99(98.98%)f11.35(0.68%)g 0.73(0.04%)	2.77
(0.83170) BD (2) C 20- C 22 (49.91%) 0.7065* C 20 s(0.58%)p99.99(99.35%)d 0.12(0.07%) (50.09%) 0.7077* C 22 s(0.31%)p99.99(99.64%)d 0.16(0.05%)	(0.11692) LV (3)Ce 1 s(0.06%)p 3.95(0.24%)d99.99(98.98%)f11.35(0.68%)g 0.73(0.04%)	3.00
(0.83170) BD (2) C 20- C 22 (49.91%) 0.7065* C 20 s(0.58%)p99.99(99.35%)d 0.12(0.07%) (50.09%) 0.7077* C 22 s(0.31%)p99.99(99.64%)d 0.16(0.05%)	(0.11537) LV (4)Ce 1 s(0.00%)p 1.00(0.17%)d99.99(98.31%)f 8.37(1.45%)g 0.40(0.07%)	4.58
(0.98757) BD (1) C 22- C 24 (49.54%) 0.7038* C 22 s(35.58%)p 1.81(64.36%)d 0.00(0.07%) (50.46%) 0.7104* C 24 s(37.08%)p 1.70(62.86%)d 0.00(0.06%)	(0.11537) LV (4)Ce 1 s(0.00%)p 1.00(0.17%)d99.99(98.31%)f 8.37(1.45%)g 0.40(0.07%)	2.43
(0.85222) BD (2) C 24- C 26 (49.33%) 0.7024* C 24 s(0.40%)p99.99(99.56%)d 0.09(0.03%) (50.67%) 0.7118* C 26 s(0.37%)p99.99(99.60%)d 0.09(0.03%)	(0.11692) LV (3)Ce 1 s(0.06%)p 3.95(0.24%)d99.99(98.98%)f11.35(0.68%)g 0.73(0.04%)	3.05
(0.85222) BD (2) C 24- C 26 (49.33%) 0.7024* C 24 s(0.40%)p99.99(99.56%)d 0.09(0.03%) (50.67%) 0.7118* C 26 s(0.37%)p99.99(99.60%)d 0.09(0.03%)	(0.11537) LV (4)Ce 1 s(0.00%)p 1.00(0.17%)d99.99(98.31%)f 8.37(1.45%)g 0.40(0.07%)	3.60
(0.85222) BD (2) C 24- C 26 (49.33%) 0.7024* C 24 s(0.40%)p99.99(99.56%)d 0.09(0.03%) (50.67%) 0.7118* C 26 s(0.37%)p99.99(99.60%)d 0.09(0.03%)	(0.04854) LV (7)Ce 1 s(92.48%)p 0.01(0.90%)d 0.01(1.25%)f 0.06(5.29%)g 0.00(0.07%)	2.65
(0.97962) BD (1) C 11- C 13 (50.09%) 0.7078* C 11 s(35.29%)p 1.83(64.65%)d 0.00(0.06%) (49.91%) 0.7065* C 13 s(35.38%)p 1.82(64.55%)d 0.00(0.06%)	(0.11692) LV (3)Ce 1 s(0.06%)p 3.95(0.24%)d99.99(98.98%)f11.35(0.68%)g 0.73(0.04%)	4.53
(0.97962) BD (1) C 11- C 13 (50.09%) 0.7078* C 11 s(35.29%)p 1.83(64.65%)d 0.00(0.06%)	(0.11537) LV (4)Ce 1 s(0.00%)p 1.00(0.17%)d99.99(98.31%)f 8.37(1.45%)g 0.40(0.07%)	4.91

(49.91%) 0.7065* C 13 s(35.38%)p 1.82(64.55%)d 0.00(0.06%)		
(0.85428) BD (2) C 11- C 13 (49.87%) 0.7062* C 11 s(1.47%)p66.94(98.47%)d 0.04(0.06%) (50.13%) 0.7080* C 13 s(1.42%)p69.36(98.52%)d 0.04(0.06%)	(0.19683) LV (2)Ce 1 s(0.00%)p 0.00(0.00%)d 1.00(90.71%)f 0.10(9.24%)g 0.00(0.05%)	7.67
(0.85428) BD (2) C 11- C 13 (49.87%) 0.7062* C 11 s(1.47%)p66.94(98.47%)d 0.04(0.06%) (50.13%) 0.7080* C 13 s(1.42%)p69.36(98.52%)d 0.04(0.06%)	(0.11692) LV (3)Ce 1 s(0.06%)p 3.95(0.24%)d99.99(98.98%)f11.35(0.68%)g 0.73(0.04%)	5.84
(0.85428) BD (2) C 11- C 13 (49.87%) 0.7062* C 11 s(1.47%)p66.94(98.47%)d 0.04(0.06%) (50.13%) 0.7080* C 13 s(1.42%)p69.36(98.52%)d 0.04(0.06%)	(0.11537) LV (4)Ce 1 s(0.00%)p 1.00(0.17%)d99.99(98.31%)f 8.37(1.45%)g 0.40(0.07%)	6.97
(0.85428) BD (2) C 11- C 13 (49.87%) 0.7062* C 11 s(1.47%)p66.94(98.47%)d 0.04(0.06%) (50.13%) 0.7080* C 13 s(1.42%)p69.36(98.52%)d 0.04(0.06%)	(0.04854) LV (7)Ce 1 s(92.48%)p 0.01(0.90%)d 0.01(1.25%)f 0.06(5.29%)g 0.00(0.07%)	3.63
(0.97768) BD (1) C 11- C 28 (50.00%) 0.7071* C 11 s(36.66%)p 1.73(63.28%)d 0.00(0.06%) (50.00%) 0.7071* C 28 s(36.66%)p 1.73(63.28%)d 0.00(0.06%)	(0.11692) LV (3)Ce 1 s(0.06%)p 3.95(0.24%)d99.99(98.98%)f11.35(0.68%)g 0.73(0.04%)	10.45
(0.97768) BD (1) C 11- C 28 (50.00%) 0.7071* C 11 s(36.66%)p 1.73(63.28%)d 0.00(0.06%) (50.00%) 0.7071* C 28 s(36.66%)p 1.73(63.28%)d 0.00(0.06%)	(0.04854) LV (7)Ce 1 s(92.48%)p 0.01(0.90%)d 0.01(1.25%)f 0.06(5.29%)g 0.00(0.07%)	2.78
(0.97749) BD (1) C 13- C 15 (50.03%) 0.7073* C 13 s(36.84%)p 1.71(63.10%)d 0.00(0.06%) (49.97%) 0.7069* C 15 s(36.77%)p 1.72(63.16%)d 0.00(0.07%)	(0.11537) LV (4)Ce 1 s(0.00%)p 1.00(0.17%)d99.99(98.31%)f 8.37(1.45%)g 0.40(0.07%)	11.16
(0.97749) BD (1) C 13- C 15 (50.03%) 0.7073* C 13 s(36.84%)p 1.71(63.10%)d 0.00(0.06%) (49.97%) 0.7069* C 15 s(36.77%)p 1.72(63.16%)d 0.00(0.07%)	(0.04854) LV (7)Ce 1 s(92.48%)p 0.01(0.90%)d 0.01(1.25%)f 0.06(5.29%)g 0.00(0.07%)	2.67
(0.97994) BD (1) C 15- C 17 (49.95%) 0.7067* C 15 s(35.42%)p 1.82(64.52%)d 0.00(0.06%) (50.05%) 0.7075* C 17 s(35.32%)p 1.83(64.61%)d 0.00(0.06%)	(0.11692) LV (3)Ce 1 s(0.06%)p 3.95(0.24%)d99.99(98.98%)f11.35(0.68%)g 0.73(0.04%)	5.11
(0.97994) BD (1) C 15- C 17 (49.95%) 0.7067* C 15 s(35.42%)p 1.82(64.52%)d 0.00(0.06%)	(0.11537) LV (4)Ce 1 s(0.00%)p 1.00(0.17%)d99.99(98.31%)f 8.37(1.45%)g 0.40(0.07%)	4.85

(50.05%) 0.7075* C 17 s(35.32%)p 1.83(64.61%)d 0.00(0.06%)		
(0.97994) BD (1) C 15- C 17 (49.95%) 0.7067* C 15 s(35.42%)p 1.82(64.52%)d 0.00(0.06%) (50.05%) 0.7075* C 17 s(35.32%)p 1.83(64.61%)d 0.00(0.06%)	(0.04854) LV (7)Ce 1 s(92.48%)p 0.01(0.90%)d 0.01(1.25%)f 0.06(5.29%)g 0.00(0.07%)	2.34
(0.85292) BD (2) C 15- C 17 (49.82%) 0.7059* C 15 s(1.41%)p69.96(98.53%)d 0.04(0.06%) (50.18%) 0.7084* C 17 s(1.40%)p70.43(98.54%)d 0.04(0.06%)	(0.19683) LV (2)Ce 1 s(0.00%)p 0.00(0.00%)d 1.00(90.71%)f 0.10(9.24%)g 0.00(0.05%)	8.50
(0.85292) BD (2) C 15- C 17 (49.82%) 0.7059* C 15 s(1.41%)p69.96(98.53%)d 0.04(0.06%) (50.18%) 0.7084* C 17 s(1.40%)p70.43(98.54%)d 0.04(0.06%)	(0.11692) LV (3)Ce 1 s(0.06%)p 3.95(0.24%)d99.99(98.98%)f11.35(0.68%)g 0.73(0.04%)	6.75
(0.85292) BD (2) C 15- C 17 (49.82%) 0.7059* C 15 s(1.41%)p69.96(98.53%)d 0.04(0.06%) (50.18%) 0.7084* C 17 s(1.40%)p70.43(98.54%)d 0.04(0.06%)	(0.11537) LV (4)Ce 1 s(0.00%)p 1.00(0.17%)d99.99(98.31%)f 8.37(1.45%)g 0.40(0.07%)	6.98
(0.85292) BD (2) C 15- C 17 (49.82%) 0.7059* C 15 s(1.41%)p69.96(98.53%)d 0.04(0.06%) (50.18%) 0.7084* C 17 s(1.40%)p70.43(98.54%)d 0.04(0.06%)	(0.04854) LV (7)Ce 1 s(92.48%)p 0.01(0.90%)d 0.01(1.25%)f 0.06(5.29%)g 0.00(0.07%)	4.00
(0.97823) BD (1) C 17- C 34 (50.00%) 0.7071* C 17 s(36.71%)p 1.72(63.23%)d 0.00(0.06%) (50.00%) 0.7071* C 34 s(36.71%)p 1.72(63.23%)d 0.00(0.06%)	(0.11692) LV (3)Ce 1 s(0.06%)p 3.95(0.24%)d99.99(98.98%)f11.35(0.68%)g 0.73(0.04%)	11.43
(0.97823) BD (1) C 17- C 34 (50.00%) 0.7071* C 17 s(36.71%)p 1.72(63.23%)d 0.00(0.06%) (50.00%) 0.7071* C 34 s(36.71%)p 1.72(63.23%)d 0.00(0.06%)		
(0.97962) BD (1) C 28- C 30 (50.09%) 0.7078* C 28 s(35.29%)p 1.83(64.65%)d 0.00(0.06%) (49.91%) 0.7065* C 30 s(35.38%)p 1.82(64.55%)d 0.00(0.06%)	(0.11692) LV (3)Ce 1 s(0.06%)p 3.95(0.24%)d99.99(98.98%)f11.35(0.68%)g 0.73(0.04%)	4.53
(0.97962) BD (1) C 28- C 30 (50.09%) 0.7078* C 28 s(35.29%)p 1.83(64.65%)d 0.00(0.06%) (49.91%) 0.7065* C 30 s(35.38%)p 1.82(64.55%)d 0.00(0.06%)	(0.11537) LV (4)Ce 1 s(0.00%)p 1.00(0.17%)d99.99(98.31%)f 8.37(1.45%)g 0.40(0.07%)	4.92
(0.85428) BD (2) C 28- C 30 (49.87%) 0.7062* C 28 s(1.47%)p66.94(98.47%)d 0.04(0.06%)	(0.19683) LV (2)Ce 1 s(0.00%)p 0.00(0.00%)d 1.00(90.71%)f 0.10(9.24%)g 0.00(0.05%)	7.67

(50.13%) 0.7080* C 30 s(1.42%)p69.36(98.52%)d 0.04(0.06%)		
(0.85428) BD (2) C 28- C 30 (49.87%) 0.7062* C 28 s(1.47%)p66.94(98.47%)d 0.04(0.06%) (50.13%) 0.7080* C 30 s(1.42%)p69.36(98.52%)d 0.04(0.06%)	(0.11692) LV (3)Ce 1 s(0.06%)p 3.95(0.24%)d99.99(98.98%)f11.35(0.68%)g 0.73(0.04%)	5.84
(0.85428) BD (2) C 28- C 30 (49.87%) 0.7062* C 28 s(1.47%)p66.94(98.47%)d 0.04(0.06%) (50.13%) 0.7080* C 30 s(1.42%)p69.36(98.52%)d 0.04(0.06%)	(0.11537) LV (4)Ce 1 s(0.00%)p 1.00(0.17%)d99.99(98.31%)f 8.37(1.45%)g 0.40(0.07%)	6.97
(0.85428) BD (2) C 28- C 30 (49.87%) 0.7062* C 28 s(1.47%)p66.94(98.47%)d 0.04(0.06%) (50.13%) 0.7080* C 30 s(1.42%)p69.36(98.52%)d 0.04(0.06%)	(0.04854) LV (7)Ce 1 s(92.48%)p 0.01(0.90%)d 0.01(1.25%)f 0.06(5.29%)g 0.00(0.07%)	3.63
(0.97749) BD (1) C 30- C 32 (50.03%) 0.7073* C 30 s(36.84%)p 1.71(63.10%)d 0.00(0.06%) (49.97%) 0.7069* C 32 s(36.77%)p 1.72(63.16%)d 0.00(0.07%)	(0.11537) LV (4)Ce 1 s(0.00%)p 1.00(0.17%)d99.99(98.31%)f 8.37(1.45%)g 0.40(0.07%)	11.16
(0.97994) BD (1) C 32- C 34 (49.95%) 0.7067* C 32 s(35.42%)p 1.82(64.52%)d 0.00(0.06%) (50.05%) 0.7075* C 34 s(35.32%)p 1.83(64.61%)d 0.00(0.06%)	(0.11692) LV (3)Ce 1 s(0.06%)p 3.95(0.24%)d99.99(98.98%)f11.35(0.68%)g 0.73(0.04%)	5.11
(0.97994) BD (1) C 32- C 34 (49.95%) 0.7067* C 32 s(35.42%)p 1.82(64.52%)d 0.00(0.06%) (50.05%) 0.7075* C 34 s(35.32%)p 1.83(64.61%)d 0.00(0.06%)	(0.11537) LV (4)Ce 1 s(0.00%)p 1.00(0.17%)d99.99(98.31%)f 8.37(1.45%)g 0.40(0.07%)	4.84
(0.85292) BD (2) C 32- C 34 (49.82%) 0.7059* C 32 s(1.41%)p69.96(98.53%)d 0.04(0.06%) (50.18%) 0.7084* C 34 s(1.40%)p70.43(98.54%)d 0.04(0.06%)	(0.19683) LV (2)Ce 1 s(0.00%)p 0.00(0.00%)d 1.00(90.71%)f 0.10(9.24%)g 0.00(0.05%)	8.50
(0.85292) BD (2) C 32- C 34 (49.82%) 0.7059* C 32 s(1.41%)p69.96(98.53%)d 0.04(0.06%) (50.18%) 0.7084* C 34 s(1.40%)p70.43(98.54%)d 0.04(0.06%)	(0.11692) LV (3)Ce 1 s(0.06%)p 3.95(0.24%)d99.99(98.98%)f11.35(0.68%)g 0.73(0.04%)	6.75
(0.85292) BD (2) C 32- C 34 (49.82%) 0.7059* C 32 s(1.41%)p69.96(98.53%)d 0.04(0.06%) (50.18%) 0.7084* C 34 s(1.40%)p70.43(98.54%)d 0.04(0.06%)	(0.11537) LV (4)Ce 1 s(0.00%)p 1.00(0.17%)d99.99(98.31%)f 8.37(1.45%)g 0.40(0.07%)	6.97
(0.85292) BD (2) C 32- C 34 (49.82%) 0.7059* C 32 s(1.41%)p69.96(98.53%)d 0.04(0.06%)	(0.04854) LV (7)Ce 1 s(92.48%)p 0.01(0.90%)d 0.01(1.25%)f 0.06(5.29%)g 0.00(0.07%)	4.00

(50.18%) 0.7084* C 34 s(1.40%)p70.43(98.54%)d 0.04(0.06%)		

*Table S29: NBO analysis of canonical molecular orbitals for **2-Sm-trans.***

HOMO-2, MO 73 (occ): orbital energy = -0.19354 a.u. 0.983*[31]: LP (1)Ce 1(lp)	(0.98653) LP (1)Ce 1 s(0.01%)p 0.16(0.00%)d15.14(0.22%) f99.99(99.76%)g 0.04(0.00%)
HOMO-1, MO 74 (occ): orbital energy = -0.18388 a.u. -0.423*[127]: BD*(2) C32- C34* -0.423*[108]: BD*(2) C15- C17* 0.422*[122]: BD*(2) C28- C30* 0.422*[75]: BD*(2) C11- C13* 0.329*[76]: LV (1)Ce 1(lv)	(0.27020) BD*(2) C 32- C 34 (50.18%) 0.7084* C 32 s(1.41%)p69.96(98.53%)d 0.04(0.06%) (49.82%) -0.7059* C 34 s(1.40%)p70.43(98.54%)d 0.04(0.06%) (0.27020) BD*(2) C 15- C 17 (50.18%) 0.7084* C 15 s(1.41%)p69.96(98.53%)d 0.04(0.06%) (49.82%) -0.7059* C 17 s(1.40%)p70.43(98.54%)d 0.04(0.06%) (0.27043) BD*(2) C 28- C 30 (50.13%) 0.7080* C 28 s(1.47%)p66.94(98.47%)d 0.04(0.06%) (49.87%) -0.7062* C 30 s(1.42%)p69.36(98.52%)d 0.04(0.06%) (0.27043) BD*(2) C 11- C 13 (50.13%) 0.7080* C 11 s(1.47%)p66.94(98.47%)d 0.04(0.06%) (49.87%) -0.7062* C 13 s(1.42%)p69.36(98.52%)d 0.04(0.06%) (0.19843) LV (1)Ce 1 s(0.01%)p 0.06(0.00%)d99.99(89.61%) f99.99(10.33%)g 3.87(0.05%)
HOMO, MO 75 (occ): orbital energy = -0.18307 a.u. -0.421*[73]: BD (2) C32- C34 0.421*[54]: BD (2) C15- C17 0.421*[68]: BD (2) C28- C30 -0.421*[48]: BD (2) C11- C13 0.315*[77]: LV (2)Ce 1(lv)	(0.85292) BD (2) C 32- C 34 (49.82%) 0.7059* C 32 s(1.41%)p69.96(98.53%)d 0.04(0.06%) (50.18%) 0.7084* C 34 s(1.40%)p70.43(98.54%)d 0.04(0.06%) (0.85292) BD (2) C 15- C 17 (49.82%) 0.7059* C 15 s(1.41%)p69.96(98.53%)d 0.04(0.06%) (50.18%) 0.7084* C 17 s(1.40%)p70.43(98.54%)d 0.04(0.06%) (0.85428) BD (2) C 28- C 30 (49.87%) 0.7062* C 28 s(1.47%)p66.94(98.47%)d 0.04(0.06%) (50.13%) 0.7080* C 30 s(1.42%)p69.36(98.52%)d 0.04(0.06%) (0.85428) BD (2) C 11- C 13 (49.87%) 0.7062* C 11 s(1.47%)p66.94(98.47%)d 0.04(0.06%) (50.13%) 0.7080* C 13 s(1.42%)p69.36(98.52%)d 0.04(0.06%) (0.19683) LV (2)Ce 1

	s(0.00%)p 0.00(0.00%)d 1.00(90.71%) f 0.10(9.24%)g 0.00(0.05%)

Table S30**: Computed natural charges for **2-Ce-cis.

Atom labels	Natural charges
Ce1	1.41772
C2	-0.32989
C4	-0.32459
C6	-0.32283
C8	-0.32257
C10	-0.32787
C12	-0.32459
C14	-0.32283
C16	-0.32257
C18	-0.32787
C20	-0.37885
C22	-0.37291
C24	-0.37293
C26	-0.37875
C28	-0.37885
C30	-0.37291
C32	-0.37292
C34	-0.37875

Table S31**: Computed Wiberg bond index for **2-Ce-cis.

Atom labels	Wiberg bond index	Atom labels	Wiberg bond index	Atom labels	Wiberg bond index	Atom labels	Wiberg bond index
Ce1	0.0000	Ce1	0.0000	Ce1	0.0000	Ce1	0.0000
C2	0.0918	C4	0.0915	C6	0.0912	C8	0.0912
Atom labels	Wiberg bond index	Atom labels	Wiberg bond index	Atom labels	Wiberg bond index	Atom labels	Wiberg bond index
Ce1	0.0000	Ce1	0.0000	Ce1	0.0000	Ce1	0.0000
C10	0.0918	C12	0.0915	C14	0.0912	C16	0.0912
Atom labels	Wiberg bond index	Atom labels	Wiberg bond index	Atom labels	Wiberg bond index	Atom labels	Wiberg bond index
Ce1	0.0000	Ce1	0.0000	Ce1	0.0000	Ce1	0.0000
C18	0.0918	C20	0.2433	C22	0.2423	C24	0.2423
Atom labels	Wiberg bond index	Atom labels	Wiberg bond index	Atom labels	Wiberg bond index	Atom labels	Wiberg bond index
Ce1	0.0000	Ce1	0.0000	Ce1	0.0000	Ce1	0.0000
C26	0.2434	C28	0.2433	C30	0.2423	C32	0.2423
Atom labels	Wiberg bond index						
Ce1	0.0000						
C34	0.2434						

*Table S32: DFT computed NBO second-order perturbation analysis for **2-Ce-cis.***

Donor NBO	Acceptor NBO	E(2) kcal/mol
(0.53224) LP (1) C 6 s(0.38%)p99.99(99.60%)d 0.04(0.01%)	(0.11283) LV (4)Ce 1 s(0.00%)p 1.00(0.21%)d99.99(98.18%)f 7.40(1.57%)g 0.20(0.04%)	4.24
(0.84389) BD (2) C 2- C 4 (50.03%) 0.7073* C 2 s(0.15%)p99.99(99.82%)d 0.21(0.03%) (49.97%) 0.7069* C 4 s(0.15%)p99.99(99.82%)d 0.22(0.03%)	(0.11335) LV (3)Ce 1 s(0.00%)p 1.00(0.26%)d99.99(98.12%)f 6.01(1.57%)g 0.17(0.04%)	4.94
(0.98692) BD (1) C 2- C 12 (50.07%) 0.7076* C 2 s(37.32%)p 1.68(62.62%)d 0.00(0.06%) (49.93%) 0.7066* C 12 s(37.36%)p 1.67(62.58%)d 0.00(0.06%)	(0.11335) LV (3)Ce 1 s(0.00%)p 1.00(0.26%)d99.99(98.12%)f 6.01(1.57%)g 0.17(0.04%)	2.58
(0.98638) BD (1) C 4- C 6 (50.02%) 0.7073* C 4 s(37.31%)p 1.68(62.64%)d 0.00(0.06%) (49.98%) 0.7069* C 6 s(37.21%)p 1.69(62.73%)d 0.00(0.06%)	(0.11283) LV (4)Ce 1 s(0.00%)p 1.00(0.21%)d99.99(98.18%)f 7.40(1.57%)g 0.20(0.04%)	2.04
(0.98617) BD (1) C 6- C 8 (50.01%) 0.7072* C 6 s(37.19%)p 1.69(62.75%)d 0.00(0.06%) (49.99%) 0.7070* C 8 s(37.33%)p 1.68(62.61%)d 0.00(0.06%)	(0.11283) LV (4)Ce 1 s(0.00%)p 1.00(0.21%)d99.99(98.18%)f 7.40(1.57%)g 0.20(0.04%)	2.63
(0.84394) BD (2) C 8- C 10 (49.97%) 0.7069* C 8 s(0.15%)p99.99(99.81%)d 0.21(0.03%) (50.03%) 0.7073* C 10 s(0.15%)p99.99(99.81%)d 0.21(0.03%)	(0.11335) LV (3)Ce 1 s(0.00%)p 1.00(0.26%)d99.99(98.12%)f 6.01(1.57%)g 0.17(0.04%)	3.28
(0.84394) BD (2) C 8- C 10 (49.97%) 0.7069* C 8 s(0.15%)p99.99(99.81%)d 0.21(0.03%) (50.03%) 0.7073* C 10 s(0.15%)p99.99(99.81%)d 0.21(0.03%)	(0.11283) LV (4)Ce 1 s(0.00%)p 1.00(0.21%)d99.99(98.18%)f 7.40(1.57%)g 0.20(0.04%)	2.27
(0.98699) BD (1) C 10- C 18 (50.00%) 0.7071* C 10 s(37.34%)p 1.68(62.60%)d 0.00(0.06%) (50.00%) 0.7071* C 18 s(37.34%)p 1.68(62.60%)d 0.00(0.06%)	(0.11335) LV (3)Ce 1 s(0.00%)p 1.00(0.26%)d99.99(98.12%)f 6.01(1.57%)g 0.17(0.04%)	2.93
(0.98660) BD (1) C 12- C 14 (50.04%) 0.7074* C 12 s(37.18%)p 1.69(62.76%)d 0.00(0.06%) (49.96%) 0.7068* C 14 s(37.23%)p 1.68(62.71%)d 0.00(0.06%)	(0.11283) LV (4)Ce 1 s(0.00%)p 1.00(0.21%)d99.99(98.18%)f 7.40(1.57%)g 0.20(0.04%)	2.01

(0.84384) BD (2) C 12- C 14 (50.01%) 0.7072* C 12 s(0.16%)p99.99(99.81%)d 0.21(0.03%) (49.99%) 0.7071* C 14 s(0.16%)p99.99(99.81%)d 0.21(0.03%)	(0.11283) LV (4)Ce 1 s(0.00%)p 1.00(0.21%)d99.99(98.18%)f 7.40(1.57%)g 0.20(0.04%)	4.14
(0.98618) BD (1) C 14- C 16 (50.00%) 0.7071* C 14 s(37.35%)p 1.68(62.59%)d 0.00(0.06%) (50.00%) 0.7071* C 16 s(37.33%)p 1.68(62.61%)d 0.00(0.06%)	(0.11283) LV (4)Ce 1 s(0.00%)p 1.00(0.21%)d99.99(98.18%)f 7.40(1.57%)g 0.20(0.04%)	2.72
(0.84394) BD (2) C 16- C 18 (49.97%) 0.7069* C 16 s(0.15%)p99.99(99.81%)d 0.21(0.03%) (50.03%) 0.7073* C 18 s(0.15%)p99.99(99.81%)d 0.21(0.03%)	(0.11335) LV (3)Ce 1 s(0.00%)p 1.00(0.26%)d99.99(98.12%)f 6.01(1.57%)g 0.17(0.04%)	3.27
(0.84394) BD (2) C 16- C 18 (49.97%) 0.7069* C 16 s(0.15%)p99.99(99.81%)d 0.21(0.03%) (50.03%) 0.7073* C 18 s(0.15%)p99.99(99.81%)d 0.21(0.03%)	(0.11283) LV (4)Ce 1 s(0.00%)p 1.00(0.21%)d99.99(98.18%)f 7.40(1.57%)g 0.20(0.04%)	2.27
(0.97959) BD (1) C 20- C 22 (50.08%) 0.7077* C 20 s(35.29%)p 1.83(64.64%)d 0.00(0.06%) (49.92%) 0.7066* C 22 s(35.36%)p 1.83(64.58%)d 0.00(0.06%)	(0.11335) LV (3)Ce 1 s(0.00%)p 1.00(0.26%)d99.99(98.12%)f 6.01(1.57%)g 0.17(0.04%)	4.86
(0.97959) BD (1) C 20- C 22 (50.08%) 0.7077* C 20 s(35.29%)p 1.83(64.64%)d 0.00(0.06%) (49.92%) 0.7066* C 22 s(35.36%)p 1.83(64.58%)d 0.00(0.06%)	(0.11283) LV (4)Ce 1 s(0.00%)p 1.00(0.21%)d99.99(98.18%)f 7.40(1.57%)g 0.20(0.04%)	4.86
(0.97959) BD (1) C 20- C 22 (50.08%) 0.7077* C 20 s(35.29%)p 1.83(64.64%)d 0.00(0.06%) (49.92%) 0.7066* C 22 s(35.36%)p 1.83(64.58%)d 0.00(0.06%)	(0.04563) LV (7)Ce 1 s(96.49%)p 0.02(1.59%)d 0.01(0.71%)f 0.01(1.10%)g 0.00(0.11%)	2.42
(0.85266) BD (2) C 20- C 22 (50.06%) 0.7075* C 20 s(1.44%)p68.31(98.50%)d 0.04(0.06%) (49.94%) 0.7067* C 22 s(1.42%)p69.19(98.51%)d 0.04(0.06%)	(0.19853) LV (2)Ce 1 s(0.00%)p 0.00(0.00%)d 1.00(89.04%)f 0.12(10.92%)g 0.00(0.04%)	8.15
(0.85266) BD (2) C 20- C 22 (50.06%) 0.7075* C 20 s(1.44%)p68.31(98.50%)d 0.04(0.06%) (49.94%) 0.7067* C 22 s(1.42%)p69.19(98.51%)d 0.04(0.06%)	(0.11335) LV (3)Ce 1 s(0.00%)p 1.00(0.26%)d99.99(98.12%)f 6.01(1.57%)g 0.17(0.04%)	6.70
(0.85266) BD (2) C 20- C 22	(0.11283) LV (4)Ce 1 s(0.00%)p 1.00(0.21%)d99.99(98.18%)f 7.40(1.57%)g 0.20(0.04%)	6.75

(50.06%) 0.7075* C 20 s(1.44%)p68.31(98.50%)d 0.04(0.06%) (49.94%) 0.7067* C 22 s(1.42%)p69.19(98.51%)d 0.04(0.06%)		
(0.85266) BD (2) C 20- C 22 (50.06%) 0.7075* C 20 s(1.44%)p68.31(98.50%)d 0.04(0.06%) (49.94%) 0.7067* C 22 s(1.42%)p69.19(98.51%)d 0.04(0.06%)	(0.04563) LV (7)Ce 1 s(96.49%)p 0.02(1.59%)d 0.01(0.71%)f 0.01(1.10%)g 0.00(0.11%)	3.40
(0.97780) BD (1) C 20- C 28 (50.00%) 0.7071* C 20 s(36.76%)p 1.72(63.17%)d 0.00(0.06%) (50.00%) 0.7071* C 28 s(36.76%)p 1.72(63.17%)d 0.00(0.06%)	(0.11335) LV (3)Ce 1 s(0.00%)p 1.00(0.26%)d99.99(98.12%)f 6.01(1.57%)g 0.17(0.04%)	11.21
(0.97780) BD (1) C 20- C 28 (50.00%) 0.7071* C 20 s(36.76%)p 1.72(63.17%)d 0.00(0.06%) (50.00%) 0.7071* C 28 s(36.76%)p 1.72(63.17%)d 0.00(0.06%)	(0.04563) LV (7)Ce 1 s(96.49%)p 0.02(1.59%)d 0.01(0.71%)f 0.01(1.10%)g 0.00(0.11%)	2.86
(0.97717) BD (1) C 22- C 24 (50.00%) 0.7071* C 22 s(36.77%)p 1.72(63.16%)d 0.00(0.07%) (50.00%) 0.7071* C 24 s(36.77%)p 1.72(63.16%)d 0.00(0.07%)	(0.11283) LV (4)Ce 1 s(0.00%)p 1.00(0.21%)d99.99(98.18%)f 7.40(1.57%)g 0.20(0.04%)	11.01
(0.97717) BD (1) C 22- C 24 (50.00%) 0.7071* C 22 s(36.77%)p 1.72(63.16%)d 0.00(0.07%) (50.00%) 0.7071* C 24 s(36.77%)p 1.72(63.16%)d 0.00(0.07%)	(0.04563) LV (7)Ce 1 s(96.49%)p 0.02(1.59%)d 0.01(0.71%)f 0.01(1.10%)g 0.00(0.11%)	2.81
(0.97958) BD (1) C 24- C 26 (49.92%) 0.7065* C 24 s(35.36%)p 1.83(64.57%)d 0.00(0.06%) (50.08%) 0.7077* C 26 s(35.29%)p 1.83(64.65%)d 0.00(0.06%)	(0.11335) LV (3)Ce 1 s(0.00%)p 1.00(0.26%)d99.99(98.12%)f 6.01(1.57%)g 0.17(0.04%)	4.90
(0.97958) BD (1) C 24- C 26 (49.92%) 0.7065* C 24 s(35.36%)p 1.83(64.57%)d 0.00(0.06%) (50.08%) 0.7077* C 26 s(35.29%)p 1.83(64.65%)d 0.00(0.06%)	(0.11283) LV (4)Ce 1 s(0.00%)p 1.00(0.21%)d99.99(98.18%)f 7.40(1.57%)g 0.20(0.04%)	4.85
(0.97958) BD (1) C 24- C 26 (49.92%) 0.7065* C 24 s(35.36%)p 1.83(64.57%)d 0.00(0.06%) (50.08%) 0.7077* C 26 s(35.29%)p 1.83(64.65%)d 0.00(0.06%)	(0.04563) LV (7)Ce 1 s(96.49%)p 0.02(1.59%)d 0.01(0.71%)f 0.01(1.10%)g 0.00(0.11%)	2.41
(0.85263) BD (2) C 24- C 26 (49.95%) 0.7067* C 24 s(1.42%)p69.20(98.51%)d 0.04(0.06%)	(0.19853) LV (2)Ce 1 s(0.00%)p 0.00(0.00%)d 1.00(89.04%)f 0.12(10.92%)g 0.00(0.04%)	8.16

(50.05%) 0.7075* C 26 s(1.45%)p68.14(98.49%)d 0.04(0.06%)		
(0.85263) BD (2) C 24- C 26 (49.95%) 0.7067* C 24 s(1.42%)p69.20(98.51%)d 0.04(0.06%) (50.05%) 0.7075* C 26 s(1.45%)p68.14(98.49%)d 0.04(0.06%)	(0.11335) LV (3)Ce 1 s(0.00%)p 1.00(0.26%)d99.99(98.12%)f 6.01(1.57%)g 0.17(0.04%)	6.73
(0.85263) BD (2) C 24- C 26 (49.95%) 0.7067* C 24 s(1.42%)p69.20(98.51%)d 0.04(0.06%) (50.05%) 0.7075* C 26 s(1.45%)p68.14(98.49%)d 0.04(0.06%)	(0.11283) LV (4)Ce 1 s(0.00%)p 1.00(0.21%)d99.99(98.18%)f 7.40(1.57%)g 0.20(0.04%)	6.72
(0.85263) BD (2) C 24- C 26 (49.95%) 0.7067* C 24 s(1.42%)p69.20(98.51%)d 0.04(0.06%) (50.05%) 0.7075* C 26 s(1.45%)p68.14(98.49%)d 0.04(0.06%)	(0.04563) LV (7)Ce 1 s(96.49%)p 0.02(1.59%)d 0.01(0.71%)f 0.01(1.10%)g 0.00(0.11%)	3.36
(0.97777) BD (1) C 26- C 34 (50.00%) 0.7071* C 26 s(36.77%)p 1.72(63.17%)d 0.00(0.06%) (50.00%) 0.7071* C 34 s(36.77%)p 1.72(63.17%)d 0.00(0.06%)	(0.11335) LV (3)Ce 1 s(0.00%)p 1.00(0.26%)d99.99(98.12%)f 6.01(1.57%)g 0.17(0.04%)	11.25
(0.97777) BD (1) C 26- C 34 (50.00%) 0.7071* C 26 s(36.77%)p 1.72(63.17%)d 0.00(0.06%) (50.00%) 0.7071* C 34 s(36.77%)p 1.72(63.17%)d 0.00(0.06%)	(0.04563) LV (7)Ce 1 s(96.49%)p 0.02(1.59%)d 0.01(0.71%)f 0.01(1.10%)g 0.00(0.11%)	2.85
(0.97959) BD (1) C 28- C 30 (50.08%) 0.7077* C 28 s(35.29%)p 1.83(64.64%)d 0.00(0.06%) (49.92%) 0.7066* C 30 s(35.36%)p 1.83(64.58%)d 0.00(0.06%)	(0.11335) LV (3)Ce 1 s(0.00%)p 1.00(0.26%)d99.99(98.12%)f 6.01(1.57%)g 0.17(0.04%)	4.88
(0.97959) BD (1) C 28- C 30 (50.08%) 0.7077* C 28 s(35.29%)p 1.83(64.64%)d 0.00(0.06%) (49.92%) 0.7066* C 30 s(35.36%)p 1.83(64.58%)d 0.00(0.06%)	(0.11283) LV (4)Ce 1 s(0.00%)p 1.00(0.21%)d99.99(98.18%)f 7.40(1.57%)g 0.20(0.04%)	4.85
(0.97959) BD (1) C 28- C 30 (50.08%) 0.7077* C 28 s(35.29%)p 1.83(64.64%)d 0.00(0.06%) (49.92%) 0.7066* C 30 s(35.36%)p 1.83(64.58%)d 0.00(0.06%)	(0.04563) LV (7)Ce 1 s(96.49%)p 0.02(1.59%)d 0.01(0.71%)f 0.01(1.10%)g 0.00(0.11%)	2.42
(0.85266) BD (2) C 28- C 30 (50.06%) 0.7075* C 28 s(1.44%)p68.31(98.50%)d 0.04(0.06%) (49.94%) 0.7067* C 30 s(1.42%)p69.19(98.51%)d 0.04(0.06%)	(0.19853) LV (2)Ce 1 s(0.00%)p 0.00(0.00%)d 1.00(89.04%)f 0.12(10.92%)g 0.00(0.04%)	8.15

(0.85266) BD (2) C 28- C 30 (50.06%) 0.7075* C 28 s(1.44%)p68.31(98.50%)d 0.04(0.06%) (49.94%) 0.7067* C 30 s(1.42%)p69.19(98.51%)d 0.04(0.06%)	(0.11335) LV (3)Ce 1 s(0.00%)p 1.00(0.26%)d99.99(98.12%)f 6.01(1.57%)g 0.17(0.04%)	6.71
(0.85266) BD (2) C 28- C 30 (50.06%) 0.7075* C 28 s(1.44%)p68.31(98.50%)d 0.04(0.06%) (49.94%) 0.7067* C 30 s(1.42%)p69.19(98.51%)d 0.04(0.06%)	(0.11283) LV (4)Ce 1 s(0.00%)p 1.00(0.21%)d99.99(98.18%)f 7.40(1.57%)g 0.20(0.04%)	6.74
(0.85266) BD (2) C 28- C 30 (50.06%) 0.7075* C 28 s(1.44%)p68.31(98.50%)d 0.04(0.06%) (49.94%) 0.7067* C 30 s(1.42%)p69.19(98.51%)d 0.04(0.06%)	(0.04563) LV (7)Ce 1 s(96.49%)p 0.02(1.59%)d 0.01(0.71%)f 0.01(1.10%)g 0.00(0.11%)	3.40
(0.97717) BD (1) C 30- C 32 (50.00%) 0.7071* C 30 s(36.77%)p 1.72(63.16%)d 0.00(0.07%) (50.00%) 0.7071* C 32 s(36.77%)p 1.72(63.16%)d 0.00(0.07%)	(0.11283) LV (4)Ce 1 s(0.00%)p 1.00(0.21%)d99.99(98.18%)f 7.40(1.57%)g 0.20(0.04%)	11.01
(0.97717) BD (1) C 30- C 32 (50.00%) 0.7071* C 30 s(36.77%)p 1.72(63.16%)d 0.00(0.07%) (50.00%) 0.7071* C 32 s(36.77%)p 1.72(63.16%)d 0.00(0.07%)	(0.04563) LV (7)Ce 1 s(96.49%)p 0.02(1.59%)d 0.01(0.71%)f 0.01(1.10%)g 0.00(0.11%)	2.81
(0.97958) BD (1) C 32- C 34 (49.92%) 0.7065* C 32 s(35.36%)p 1.83(64.57%)d 0.00(0.06%) (50.08%) 0.7077* C 34 s(35.29%)p 1.83(64.65%)d 0.00(0.06%)	(0.11335) LV (3)Ce 1 s(0.00%)p 1.00(0.26%)d99.99(98.12%)f 6.01(1.57%)g 0.17(0.04%)	4.89
(0.97958) BD (1) C 32- C 34 (49.92%) 0.7065* C 32 s(35.36%)p 1.83(64.57%)d 0.00(0.06%) (50.08%) 0.7077* C 34 s(35.29%)p 1.83(64.65%)d 0.00(0.06%)	(0.11283) LV (4)Ce 1 s(0.00%)p 1.00(0.21%)d99.99(98.18%)f 7.40(1.57%)g 0.20(0.04%)	4.86
(0.85263) BD (2) C 32- C 34 (49.95%) 0.7067* C 32 s(1.42%)p69.21(98.51%)d 0.04(0.06%) (50.05%) 0.7075* C 34 s(1.45%)p68.14(98.49%)d 0.04(0.06%)	(0.19853) LV (2)Ce 1 s(0.00%)p 0.00(0.00%)d 1.00(89.04%)f 0.12(10.92%)g 0.00(0.04%)	8.16
(0.85263) BD (2) C 32- C 34 (49.95%) 0.7067* C 32 s(1.42%)p69.21(98.51%)d 0.04(0.06%) (50.05%) 0.7075* C 34 s(1.45%)p68.14(98.49%)d 0.04(0.06%)	(0.11335) LV (3)Ce 1 s(0.00%)p 1.00(0.26%)d99.99(98.12%)f 6.01(1.57%)g 0.17(0.04%)	6.71
(0.85263) BD (2) C 32- C 34	(0.11283) LV (4)Ce 1 s(0.00%)p 1.00(0.21%)d99.99(98.18%)f 7.40(1.57%)g 0.20(0.04%)	6.73

(49.95%) 0.7067* C 32 s(1.42%)p69.21(98.51%)d 0.04(0.06%) (50.05%) 0.7075* C 34 s(1.45%)p68.14(98.49%)d 0.04(0.06%)		
(0.85263) BD (2) C 32- C 34 (49.95%) 0.7067* C 32 s(1.42%)p69.21(98.51%)d 0.04(0.06%) (50.05%) 0.7075* C 34 s(1.45%)p68.14(98.49%)d 0.04(0.06%)	(0.04563) LV (7)Ce 1 s(96.49%)p 0.02(1.59%)d 0.01(0.71%)f 0.01(1.10%)g 0.00(0.11%)	3.36

Table S33**: NBO analysis of canonical molecular orbitals for **2-Ce-cis.

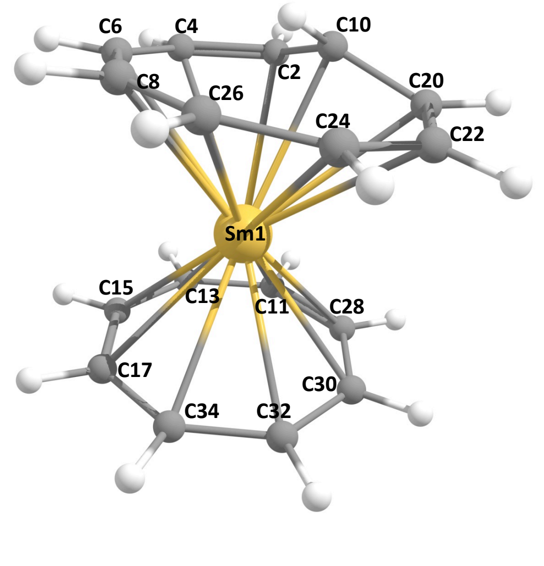
MO 73 (occ): orbital energy = -0.19089 a.u. 0.993*[31]: LP (1)Ce 1(lp)	(0.99737) LP (1)Ce 1 s(0.02%)p 0.03(0.00%)d 8.74(0.15%) f99.99(99.83%)g 0.04(0.00%)
MO 74 (occ): orbital energy = -0.18520 a.u. 0.419*[73]: BD (2) C32- C34 0.419*[57]: BD (2) C20- C22 -0.419*[68]: BD (2) C28- C30 -0.419*[63]: BD (2) C24- C26 0.323*[77]: LV (2)Ce 1(lv)	(0.85263) BD (2) C 32- C 34 (49.95%) 0.7067* C 32 s(1.42%)p69.21(98.51%)d 0.04(0.06%) (50.05%) 0.7075* C 34 s(1.45%)p68.14(98.49%)d 0.04(0.06%) (0.85266) BD (2) C 20- C 22 (50.06%) 0.7075* C 20 s(1.44%)p68.31(98.50%)d 0.04(0.06%) (49.94%) 0.7067* C 22 s(1.42%)p69.19(98.51%)d 0.04(0.06%) (0.85266) BD (2) C 28- C 30 (50.06%) 0.7075* C 28 s(1.44%)p68.31(98.50%)d 0.04(0.06%) (49.94%) 0.7067* C 30 s(1.42%)p69.19(98.51%)d 0.04(0.06%) (0.85263) BD (2) C 24- C 26 (49.95%) 0.7067* C 24 s(1.42%)p69.20(98.51%)d 0.04(0.06%) (50.05%) 0.7075* C 26 s(1.45%)p68.14(98.49%)d 0.04(0.06%)
MO 75 (occ): orbital energy = -0.18505 a.u. 0.423*[112]: BD*(2) C20- C22* 0.423*[118]: BD*(2) C24- C26* 0.423*[127]: BD*(2) C32- C34* 0.423*[75]: BD*(2) C28- C30* 0.323*[76]: LV (1)Ce 1(lv)	(0.19876) LV (1)Ce 1 s(0.00%)p 0.00(0.00%)d 1.00(89.02%)f 0.12(10.94%)g 0.00(0.04%)

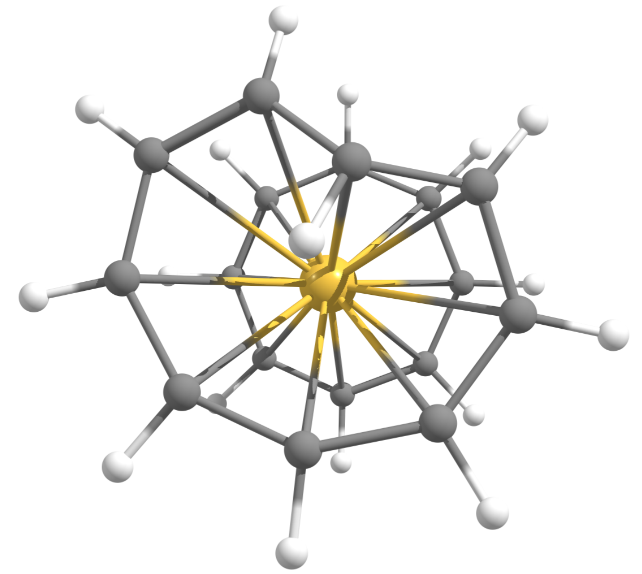
__Table S34__: Energetics of different spin states optimized for __2-Sm-trans.__

	DFT, ΔH (ΔG), kcal/mol	
	Dispersion	No dispersion
s=5/2	0.0	0.0
s=3/2	41.3 (44.8)	42.5 (42.9)
s=1/2	60.6 (64.6)	65.0 (66.1)

__Table S35__: Selected structural parameters for __2-Sm-trans.__

	No dispersion			Dispersion		
	s=5/2	s=3/2	s=1/2	s=5/2	s=3/2	s=1/2
Sm1-C2	2.89	2.89	2.89	2.87	2.87	2.86
Sm1-C4	2.98	2.97	2.98	2.96	2.94	2.94
Sm1-C6	2.91	2.90	2.90	2.89	2.87	2.87
Sm1-C8	2.82	2.81	2.81	2.80	2.79	2.79
Sm1-C10	2.77	2.75	2.76	2.75	2.74	2.74
Sm1-C11	2.69	2.63	2.62	2.65	2.61	2.60
Sm1-C13	2.69	2.63	2.62	2.66	2.62	2.61
Sm1-C15	2.69	2.64	2.63	2.66	2.62	2.61
Sm1-C17	2.69	2.63	2.62	2.66	2.61	2.61
Sm1-C20	2.89	2.89	2.89	2.87	2.87	2.86
Sm1-C22	2.98	2.97	2.99	2.96	2.94	2.94
Sm1-C24	2.91	2.90	2.91	2.89	2.87	2.87
Sm1-C26	2.82	2.81	2.81	2.80	2.79	2.79
Sm1-C28	2.69	2.63	2.62	2.65	2.61	2.60
Sm1-C30	2.69	2.63	2.63	2.66	2.62	2.61
Sm1-C32	2.69	2.64	2.63	2.66	2.62	2.61
Sm1-C34	2.69	2.63	2.62	2.66	2.61	2.61
Sm1-C8 (center of the ring)	1.96	1.88	1.86	1.92	1.86	1.84
Sm1-C9 (center of the ring)	2.10	2.09	2.09	2.07	2.06	2.06





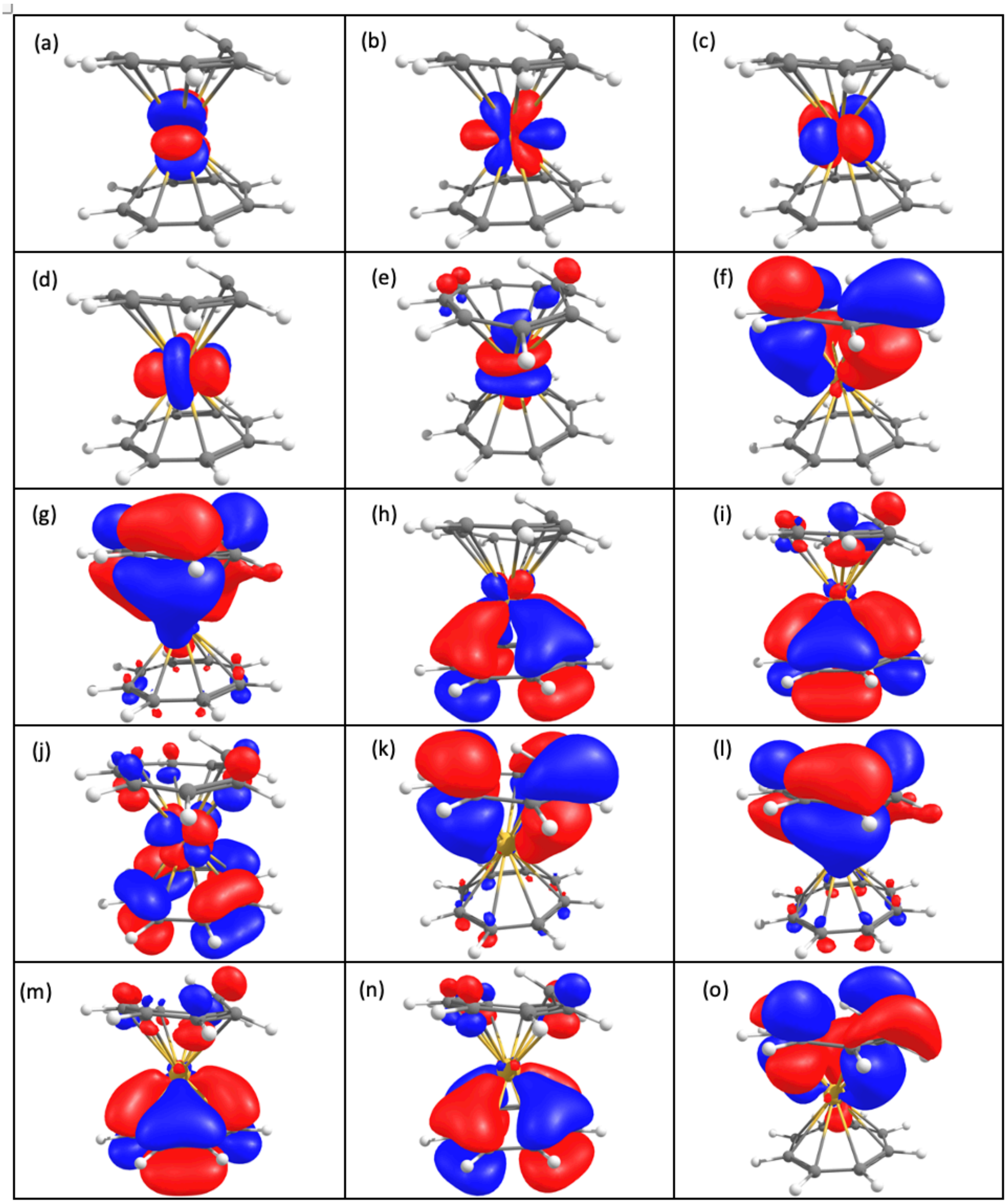


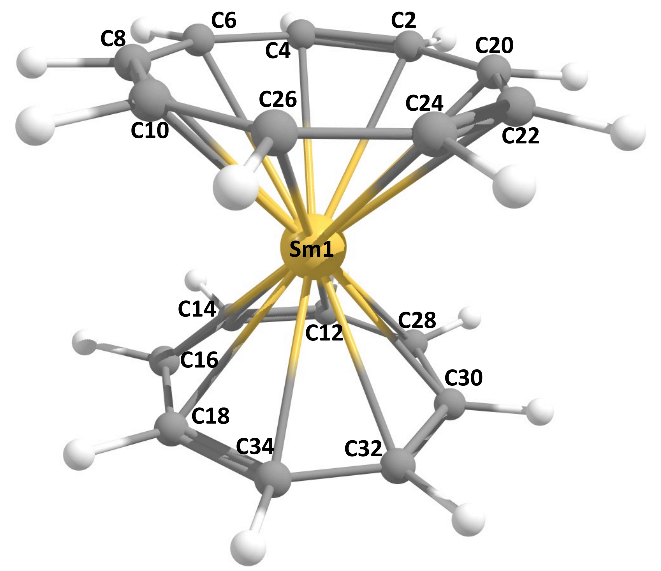
Figure S90: *DFT computed MO's for 1-disp (s=5/2). (a)AMO-HOMO-8 (b)AMO-HOMO-7 (c)AMO-HOMO-6 (d)AMO-HOMO-5 (e)AMO-HOMO-4 (f)AMO-HOMO-3 (g)AMO-HOMO-2 (h)AMO-HOMO-1 (i)AMO-HOMO (j)AMO-LUMO (k)BMO-HOMO-3 (l)BMO-HOMO-2 (m)BMO-HOMO-1 (n)BMO-HOMO (o)BMO-LUMO (p)spin density plot*

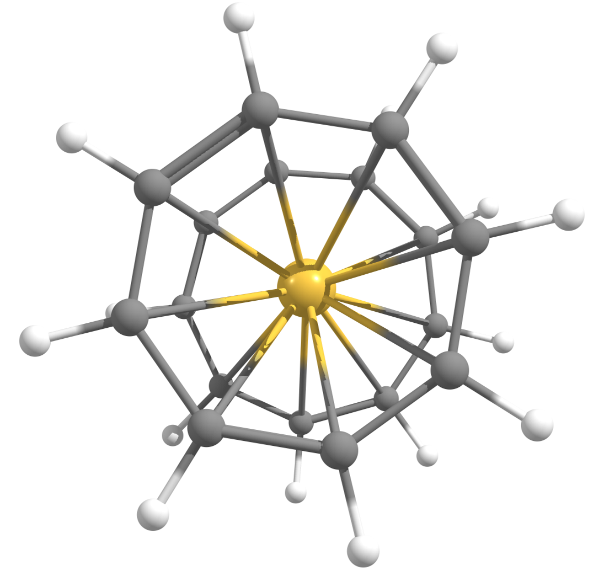
Table S36**: Energetics of different spin states optimized for **2-Sm-cis.

	DFT, ΔH (ΔG), kcal/mol	
	Dispersion	No dispersion
s=5/2	0.0	0.0
s=3/2	44.1 (44.7)	44.5 (45.1)
s=1/2	63.7 (64.8)	64.3 (65.3)

Table S37**: Selected structural parameters for **2-Sm-cis.

	No dispersion			Dispersion		
	s=5/2	s=3/2	s=1/2	s=5/2	s=3/2	s=1/2
Sm1-C2	2.91	2.90	2.90	2.89	2.88	2.88
Sm1-C4	2.91	2.90	2.90	2.89	2.88	2.88
Sm1-C6	2.91	2.90	2.90	2.89	2.88	2.88
Sm1-C8	2.92	2.90	2.90	2.90	2.88	2.88
Sm1-C10	2.91	2.90	2.90	2.89	2.88	2.88
Sm1-C12	2.68	2.63	2.62	2.65	2.62	2.60
Sm1-C14	2.68	2.63	2.62	2.65	2.62	2.61
Sm1-C16	2.68	2.63	2.62	2.65	2.62	2.60
Sm1-C18	2.68	2.63	2.62	2.65	2.62	2.61
Sm1-C20	2.91	2.90	2.90	2.89	2.88	2.88
Sm1-C22	2.91	2.90	2.90	2.89	2.88	2.88
Sm1-C24	2.92	2.90	2.90	2.90	2.88	2.88
Sm1-C26	2.91	2.90	2.90	2.89	2.88	2.88
Sm1-C28	2.68	2.63	2.62	2.65	2.62	2.60
Sm1-C30	2.68	2.63	2.62	2.65	2.62	2.61
Sm1-C32	2.68	2.63	2.62	2.65	2.62	2.60
Sm1-C34	2.68	2.63	2.62	2.65	2.62	2.61
Sm1-C8 (center of the ring)	1.94	1.88	1.86	1.90	1.86	1.84
Sm1-C9 (center of the ring)	2.06	2.05	2.05	2.04	2.02	2.02





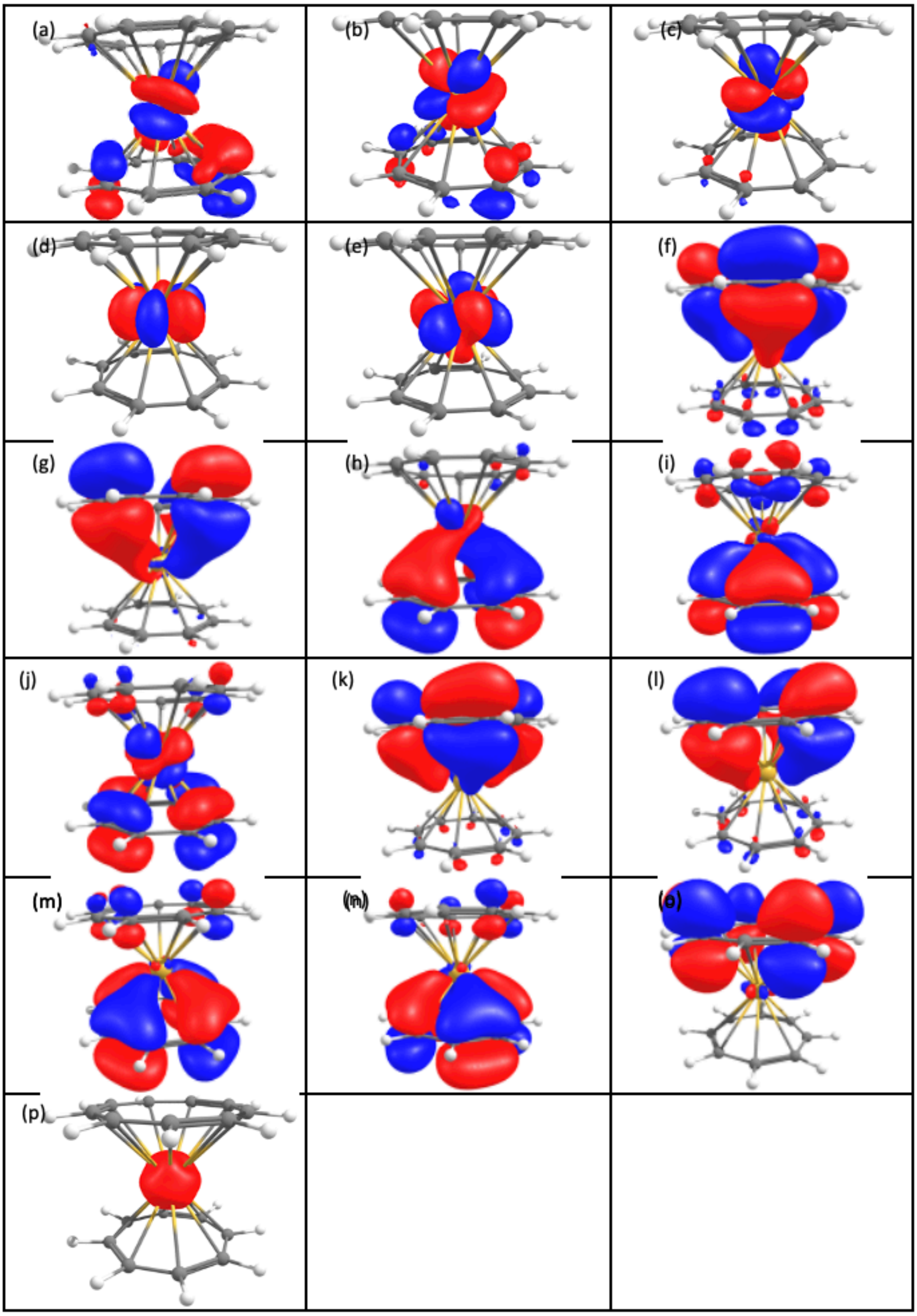


Figure S91: *DFT computed MO's for* ***2-Sm-cis****-disp (s=5/2). (a)AMO-HOMO-8 (b)AMO-HOMO-7 (c)AMO-HOMO-6 (d)AMO-HOMO-5 (e)AMO-HOMO-4 (f)AMO-HOMO-3 (g)AMO-HOMO-2 (h)AMO-HOMO-1 (i)AMO-HOMO (j)AMO-LUMO (k)BMO-HOMO-3 (l)BMO-HOMO-2 (m)BMO-HOMO-1 (n)BMO-HOMO (o)BMO-LUMO (p)spin density plot*

Table S38**: Computed natural charges for **2-Sm-trans.

Atom labels	Natural charges
Sm1	1.32085
C2	-0.29611
C4	-0.28653
C6	-0.33260
C8	-0.36719
C10	-0.31247
C11	-0.37112
C13	-0.36684
C15	-0.36724
C17	-0.37007
C20	-0.29607
C22	-0.28649
C24	-0.33262
C26	-0.36716
C28	-0.37164
C30	-0.36636
C32	-0.36775
C34	-0.36955

__Table S39__: Computed Wiberg bond index for __2-Sm-trans.__

Atom labels	Wiberg bond index	Atom labels	Wiberg bond index	Atom labels	Wiberg bond index	Atom labels	Wiberg bond index
Sm1	0.0000	Sm1	0.0000	Sm1	0.0000	Sm1	0.0000
C2	0.0946	C4	0.1056	C6	0.1005	C8	0.1117
Atom labels	Wiberg bond index	Atom labels	Wiberg bond index	Atom labels	Wiberg bond index	Atom labels	Wiberg bond index
Sm1	0.0000	Sm1	0.0000	Sm1	0.0000	Sm1	0.0000
C10	0.1366	C11	0.2333	C13	0.2233	C15	0.2225
Atom labels	Wiberg bond index	Atom labels	Wiberg bond index	Atom labels	Wiberg bond index	Atom labels	Wiberg bond index
Sm1	0.0000	Sm1	0.0000	Sm1	0.0000	Sm1	0.0000
C17	0.2282	C20	0.0946	C22	0.1057	C24	0.1003
Atom labels	Wiberg bond index	Atom labels	Wiberg bond index	Atom labels	Wiberg bond index	Atom labels	Wiberg bond index
Sm1	0.0000	Sm1	0.0000	Sm1	0.0000	Sm1	0.0000
C26	0.1118	C28	0.2328	C30	0.2238	C32	0.2220
Atom labels	Wiberg bond index						
Sm1	0.0000						
C34	0.2287						

__Table S40__: DFT computed NBO second order perturbation analysis for __2-Sm-trans.__

Donor NBO	Acceptor NBO	E(2) kcal/mol
(0.50122) LP (1) C 10 s(0.56%)p99.99(99.40%)d 0.07(0.04%)	(0.11728) LV (2)Sm 1 s(0.08%)p 1.60(0.12%)d99.99(99.75%)f 0.13(0.01%)g 0.42(0.03%)	8.06
(0.50122) LP (1) C 10 s(0.56%)p99.99(99.40%)d 0.07(0.04%)	(0.11091) LV (4)Sm 1 s(0.04%)p 0.12(0.00%)d99.99(88.33%)f99.99(11.58%)g 1.22(0.05%)	9.22
(0.50122) LP (1) C 10 s(0.56%)p99.99(99.40%)d 0.07(0.04%)	(0.05435) LV (5)Sm 1 s(94.83%)p 0.01(0.56%)d 0.05(4.33%)f 0.00(0.23%)g 0.00(0.05%)	7.70
(0.50122) LP (1) C 10 s(0.56%)p99.99(99.40%)d 0.07(0.04%)	(0.02782) LV (6)Sm 1 s(4.73%)p 0.03(0.14%)d19.07(90.18%) f 1.02(4.82%)g 0.03(0.13%)	6.10
(0.83135) BD (2) C 2- C 4 (51.09%) 0.7148* C 2 s(0.83%)p99.99(99.10%)d 0.09(0.07%) (48.91%) 0.6994* C 4 s(0.43%)p99.99(99.52%)d 0.13(0.06%)	(0.18206) LV (1)Sm 1 s(0.00%)p 0.00(0.01%)d 1.00(99.82%)f 0.00(0.14%)g 0.00(0.03%)	4.03
(0.83135) BD (2) C 2- C 4 (51.09%) 0.7148* C 2 s(0.83%)p99.99(99.10%)d 0.09(0.07%) (48.91%) 0.6994* C 4 s(0.43%)p99.99(99.52%)d 0.13(0.06%)	(0.11728) LV (2)Sm 1 s(0.08%)p 1.60(0.12%)d99.99(99.75%)f 0.13(0.01%)g 0.42(0.03%)	4.02

(0.83135) BD (2) C 2- C 4 (51.09%) 0.7148* C 2 s(0.83%)p99.99(99.10%)d 0.09(0.07%) (48.91%) 0.6994* C 4 s(0.43%)p99.99(99.52%)d 0.13(0.06%)	(0.11458) LV (3)Sm 1 s(0.00%)p 1.00(0.04%)d99.99(99.61%)f 6.81(0.31%)g 0.87(0.04%)	6.47
(0.98712) BD (1) C 2- C 10 (49.42%) 0.7030* C 2 s(35.16%)p 1.84(64.78%)d 0.00(0.07%) (50.58%) 0.7112* C 10 s(36.73%)p 1.72(63.21%)d 0.00(0.06%)	(0.11728) LV (2)Sm 1 s(0.08%)p 1.60(0.12%)d99.99(99.75%)f 0.13(0.01%)g 0.42(0.03%)	3.96
(0.98668) BD (1) C 4- C 6 (49.51%) 0.7036* C 4 s(35.64%)p 1.80(64.29%)d 0.00(0.07%) (50.49%) 0.7106* C 6 s(37.18%)p 1.69(62.76%)d 0.00(0.06%)	(0.11458) LV (3)Sm 1 s(0.00%)p 1.00(0.04%)d99.99(99.61%)f 6.81(0.31%)g 0.87(0.04%)	3.69
(0.98668) BD (1) C 4- C 6 (49.51%) 0.7036* C 4 s(35.64%)p 1.80(64.29%)d 0.00(0.07%) (50.49%) 0.7106* C 6 s(37.18%)p 1.69(62.76%)d 0.00(0.06%)	(0.11728) LV (2)Sm 1 s(0.08%)p 1.60(0.12%)d99.99(99.75%)f 0.13(0.01%)g 0.42(0.03%)	4.02
(0.85494) BD (2) C 6- C 8 (49.54%) 0.7038* C 6 s(0.52%)p99.99(99.44%)d 0.07(0.04%) (50.46%) 0.7104* C 8 s(0.43%)p99.99(99.53%)d 0.09(0.04%)	(0.11458) LV (3)Sm 1 s(0.00%)p 1.00(0.04%)d99.99(99.61%)f 6.81(0.31%)g 0.87(0.04%)	4.95
(0.85494) BD (2) C 6- C 8 (49.54%) 0.7038* C 6 s(0.52%)p99.99(99.44%)d 0.07(0.04%) (50.46%) 0.7104* C 8 s(0.43%)p99.99(99.53%)d 0.09(0.04%)	(0.05435) LV (5)Sm 1 s(94.83%)p 0.01(0.56%)d 0.05(4.33%)f 0.00(0.23%)g 0.00(0.05%)	3.42
(0.98400) BD (1) C 8- C 26 (50.00%) 0.7071* C 8 s(37.50%)p 1.66(62.44%)d 0.00(0.06%) (50.00%) 0.7071* C 26 s(37.50%)p 1.66(62.44%)d 0.00(0.06%)	(0.11728) LV (2)Sm 1 s(0.08%)p 1.60(0.12%)d99.99(99.75%)f 0.13(0.01%)g 0.42(0.03%)	5.24
(0.98711) BD (1) C 10- C 20 (50.58%) 0.7112* C 10 s(36.73%)p 1.72(63.21%)d 0.00(0.06%) (49.42%) 0.7030* C 20 s(35.16%)p 1.84(64.78%)d 0.00(0.07%)	(0.11728) LV (2)Sm 1 s(0.08%)p 1.60(0.12%)d99.99(99.75%)f 0.13(0.01%)g 0.42(0.03%)	3.95
(0.83121) BD (2) C 20- C 22 (51.09%) 0.7148* C 20 s(0.83%)p99.99(99.10%)d 0.09(0.07%) (48.91%) 0.6993* C 22 s(0.43%)p99.99(99.52%)d 0.13(0.06%)	(0.18206) LV (1)Sm 1 s(0.00%)p 0.00(0.01%)d 1.00(99.82%)f 0.00(0.14%)g 0.00(0.03%)	4.02
(0.83121) BD (2) C 20- C 22 (51.09%) 0.7148* C 20 s(0.83%)p99.99(99.10%)d 0.09(0.07%) (48.91%) 0.6993* C 22 s(0.43%)p99.99(99.52%)d 0.13(0.06%)	(0.11728) LV (2)Sm 1 s(0.08%)p 1.60(0.12%)d99.99(99.75%)f 0.13(0.01%)g 0.42(0.03%)	4.00
(0.83121) BD (2) C 20- C 22	(0.11458) LV (3)Sm 1	6.49

(51.09%) 0.7148* C 20 s(0.83%)p99.99(99.10%)d 0.09(0.07%) (48.91%) 0.6993* C 22 s(0.43%)p99.99(99.52%)d 0.13(0.06%)	s(0.00%)p 1.00(0.04%)d99.99(99.61%)f 6.81(0.31%)g 0.87(0.04%)	
(0.98668) BD (1) C 22- C 24 (49.51%) 0.7036* C 22 s(35.64%)p 1.80(64.29%)d 0.00(0.07%) (50.49%) 0.7106* C 24 s(37.18%)p 1.69(62.76%)d 0.00(0.06%)	(0.11458) LV (3)Sm 1 s(0.00%)p 1.00(0.04%)d99.99(99.61%)f 6.81(0.31%)g 0.87(0.04%)	3.69
(0.85489) BD (2) C 24- C 26 (49.55%) 0.7039* C 24 s(0.52%)p99.99(99.44%)d 0.07(0.04%) (50.45%) 0.7103* C 26 s(0.43%)p99.99(99.53%)d 0.09(0.04%)	(0.11728) LV (2)Sm 1 s(0.08%)p 1.60(0.12%)d99.99(99.75%)f 0.13(0.01%)g 0.42(0.03%)	4.04
(0.85489) BD (2) C 24- C 26 (49.55%) 0.7039* C 24 s(0.52%)p99.99(99.44%)d 0.07(0.04%) (50.45%) 0.7103* C 26 s(0.43%)p99.99(99.53%)d 0.09(0.04%)	(0.11458) LV (3)Sm 1 s(0.00%)p 1.00(0.04%)d99.99(99.61%)f 6.81(0.31%)g 0.87(0.04%)	4.93
(0.85489) BD (2) C 24- C 26 (49.55%) 0.7039* C 24 s(0.52%)p99.99(99.44%)d 0.07(0.04%) (50.45%) 0.7103* C 26 s(0.43%)p99.99(99.53%)d 0.09(0.04%)	(0.05435) LV (5)Sm 1 s(94.83%)p 0.01(0.56%)d 0.05(4.33%)f 0.00(0.23%)g 0.00(0.05%)	3.42
(0.98010) BD (1) C 11- C 13 (50.09%) 0.7078* C 11 s(35.29%)p 1.83(64.65%)d 0.00(0.06%) (49.91%) 0.7064* C 13 s(35.41%)p 1.82(64.53%)d 0.00(0.06%)	(0.11728) LV (2)Sm 1 s(0.08%)p 1.60(0.12%)d99.99(99.75%)f 0.13(0.01%)g 0.42(0.03%)	4.50
(0.98010) BD (1) C 11- C 13 (50.09%) 0.7078* C 11 s(35.29%)p 1.83(64.65%)d 0.00(0.06%) (49.91%) 0.7064* C 13 s(35.41%)p 1.82(64.53%)d 0.00(0.06%)	(0.11458) LV (3)Sm 1 s(0.00%)p 1.00(0.04%)d99.99(99.61%)f 6.81(0.31%)g 0.87(0.04%)	4.86
(0.86593) BD (2) C 11- C 13 (49.75%) 0.7054* C 11 s(1.11%)p88.74(98.83%)d 0.05(0.06%) (50.25%) 0.7089* C 13 s(1.03%)p96.43(98.91%)d 0.06(0.06%)	(0.18206) LV (1)Sm 1 s(0.00%)p 0.00(0.01%)d 1.00(99.82%)f 0.00(0.14%)g 0.00(0.03%)	5.76
(0.86593) BD (2) C 11- C 13 (49.75%) 0.7054* C 11 s(1.11%)p88.74(98.83%)d 0.05(0.06%) (50.25%) 0.7089* C 13 s(1.03%)p96.43(98.91%)d 0.06(0.06%)	(0.11728) LV (2)Sm 1 s(0.08%)p 1.60(0.12%)d99.99(99.75%)f 0.13(0.01%)g 0.42(0.03%)	5.91
(0.86593) BD (2) C 11- C 13 (49.75%) 0.7054* C 11 s(1.11%)p88.74(98.83%)d 0.05(0.06%) (50.25%) 0.7089* C 13 s(1.03%)p96.43(98.91%)d 0.06(0.06%)	(0.11458) LV (3)Sm 1 s(0.00%)p 1.00(0.04%)d99.99(99.61%)f 6.81(0.31%)g 0.87(0.04%)	6.71
(0.86593) BD (2) C 11- C 13	(0.05435) LV (5)Sm 1	4.16

(49.75%) 0.7054* C 11 s(1.11%)p88.74(98.83%)d 0.05(0.06%) (50.25%) 0.7089* C 13 s(1.03%)p96.43(98.91%)d 0.06(0.06%)	s(94.83%)p 0.01(0.56%)d 0.05(4.33%)f 0.00(0.23%)g 0.00(0.05%)	
(0.97903) BD (1) C 11- C 28 (50.00%) 0.7071* C 11 s(37.09%)p 1.69(62.84%)d 0.00(0.07%) (50.00%) 0.7071* C 28 s(37.09%)p 1.69(62.84%)d 0.00(0.07%)	(0.11728) LV (2)Sm 1 s(0.08%)p 1.60(0.12%)d99.99(99.75%)f 0.13(0.01%)g 0.42(0.03%)	10.92
(0.97880) BD (1) C 13- C 15 (50.01%) 0.7072* C 13 s(37.26%)p 1.68(62.67%)d 0.00(0.07%) (49.99%) 0.7070* C 15 s(37.23%)p 1.68(62.70%)d 0.00(0.07%)	(0.11458) LV (3)Sm 1 s(0.00%)p 1.00(0.04%)d99.99(99.61%)f 6.81(0.31%)g 0.87(0.04%)	11.05
(0.97880) BD (1) C 13- C 15 (50.01%) 0.7072* C 13 s(37.26%)p 1.68(62.67%)d 0.00(0.07%) (49.99%) 0.7070* C 15 s(37.23%)p 1.68(62.70%)d 0.00(0.07%)	(0.05435) LV (5)Sm 1 s(94.83%)p 0.01(0.56%)d 0.05(4.33%)f 0.00(0.23%)g 0.00(0.05%)	3.19
(0.98046) BD (1) C 15- C 17 (49.96%) 0.7068* C 15 s(35.46%)p 1.82(64.48%)d 0.00(0.06%) (50.04%) 0.7074* C 17 s(35.34%)p 1.83(64.60%)d 0.00(0.06%)	(0.11728) LV (2)Sm 1 s(0.08%)p 1.60(0.12%)d99.99(99.75%)f 0.13(0.01%)g 0.42(0.03%)	5.12
(0.98046) BD (1) C 15- C 17 (49.96%) 0.7068* C 15 s(35.46%)p 1.82(64.48%)d 0.00(0.06%) (50.04%) 0.7074* C 17 s(35.34%)p 1.83(64.60%)d 0.00(0.06%)	(0.11458) LV (3)Sm 1 s(0.00%)p 1.00(0.04%)d99.99(99.61%)f 6.81(0.31%)g 0.87(0.04%)	4.82
(0.86539) BD (2) C 15- C 17 (50.23%) 0.7087* C 15 s(1.01%)p98.42(98.93%)d 0.06(0.06%) (49.77%) 0.7055* C 17 s(1.02%)p96.51(98.91%)d 0.06(0.06%)	(0.18206) LV (1)Sm 1 s(0.00%)p 0.00(0.01%)d 1.00(99.82%)f 0.00(0.14%)g 0.00(0.03%)	6.61
(0.86539) BD (2) C 15- C 17 (50.23%) 0.7087* C 15 s(1.01%)p98.42(98.93%)d 0.06(0.06%) (49.77%) 0.7055* C 17 s(1.02%)p96.51(98.91%)d 0.06(0.06%)	(0.11728) LV (2)Sm 1 s(0.08%)p 1.60(0.12%)d99.99(99.75%)f 0.13(0.01%)g 0.42(0.03%)	7.03
(0.86539) BD (2) C 15- C 17 (50.23%) 0.7087* C 15 s(1.01%)p98.42(98.93%)d 0.06(0.06%) (49.77%) 0.7055* C 17 s(1.02%)p96.51(98.91%)d 0.06(0.06%)	(0.11458) LV (3)Sm 1 s(0.00%)p 1.00(0.04%)d99.99(99.61%)f 6.81(0.31%)g 0.87(0.04%)	7.15
(0.86539) BD (2) C 15- C 17 (50.23%) 0.7087* C 15 s(1.01%)p98.42(98.93%)d 0.06(0.06%) (49.77%) 0.7055* C 17 s(1.02%)p96.51(98.91%)d 0.06(0.06%)	(0.05435) LV (5)Sm 1 s(94.83%)p 0.01(0.56%)d 0.05(4.33%)f 0.00(0.23%)g 0.00(0.05%)	4.37
(0.97978) BD (1) C 17- C 34	(0.11728) LV (2)Sm 1	11.46

(50.00%) 0.7071* C 17 s(37.11%)p 1.69(62.82%)d 0.00(0.07%) (50.00%) 0.7071* C 34 s(37.11%)p 1.69(62.82%)d 0.00(0.07%)	s(0.08%)p 1.60(0.12%)d99.99(99.75%)f 0.13(0.01%)g 0.42(0.03%)	
(0.98010) BD (1) C 28- C 30 (50.10%) 0.7078* C 28 s(35.29%)p 1.83(64.65%)d 0.00(0.06%) (49.90%) 0.7064* C 30 s(35.41%)p 1.82(64.53%)d 0.00(0.06%)	(0.11728) LV (2)Sm 1 s(0.08%)p 1.60(0.12%)d99.99(99.75%)f 0.13(0.01%)g 0.42(0.03%)	4.48
(0.98010) BD (1) C 28- C 30 (50.10%) 0.7078* C 28 s(35.29%)p 1.83(64.65%)d 0.00(0.06%) (49.90%) 0.7064* C 30 s(35.41%)p 1.82(64.53%)d 0.00(0.06%)	(0.11458) LV (3)Sm 1 s(0.00%)p 1.00(0.04%)d99.99(99.61%)f 6.81(0.31%)g 0.87(0.04%)	4.88
(0.86595) BD (2) C 28- C 30 (49.85%) 0.7061* C 28 s(1.11%)p88.76(98.83%)d 0.05(0.06%) (50.15%) 0.7081* C 30 s(1.03%)p96.45(98.91%)d 0.06(0.06%)	(0.18206) LV (1)Sm 1 s(0.00%)p 0.00(0.01%)d 1.00(99.82%)f 0.00(0.14%)g 0.00(0.03%)	5.77
(0.86595) BD (2) C 28- C 30 (49.85%) 0.7061* C 28 s(1.11%)p88.76(98.83%)d 0.05(0.06%) (50.15%) 0.7081* C 30 s(1.03%)p96.45(98.91%)d 0.06(0.06%)	(0.11728) LV (2)Sm 1 s(0.08%)p 1.60(0.12%)d99.99(99.75%)f 0.13(0.01%)g 0.42(0.03%)	5.88
(0.86595) BD (2) C 28- C 30 (49.85%) 0.7061* C 28 s(1.11%)p88.76(98.83%)d 0.05(0.06%) (50.15%) 0.7081* C 30 s(1.03%)p96.45(98.91%)d 0.06(0.06%)	(0.11458) LV (3)Sm 1 s(0.00%)p 1.00(0.04%)d99.99(99.61%)f 6.81(0.31%)g 0.87(0.04%)	6.73
(0.86595) BD (2) C 28- C 30 (49.85%) 0.7061* C 28 s(1.11%)p88.76(98.83%)d 0.05(0.06%) (50.15%) 0.7081* C 30 s(1.03%)p96.45(98.91%)d 0.06(0.06%)	(0.05435) LV (5)Sm 1 s(94.83%)p 0.01(0.56%)d 0.05(4.33%)f 0.00(0.23%)g 0.00(0.05%)	4.16
(0.97880) BD (1) C 30- C 32 (50.01%) 0.7072* C 30 s(37.26%)p 1.68(62.67%)d 0.00(0.07%) (49.99%) 0.7070* C 32 s(37.23%)p 1.68(62.70%)d 0.00(0.07%)	(0.11458) LV (3)Sm 1 s(0.00%)p 1.00(0.04%)d99.99(99.61%)f 6.81(0.31%)g 0.87(0.04%)	11.05
(0.97880) BD (1) C 30- C 32 (50.01%) 0.7072* C 30 s(37.26%)p 1.68(62.67%)d 0.00(0.07%) (49.99%) 0.7070* C 32 s(37.23%)p 1.68(62.70%)d 0.00(0.07%)	(0.05435) LV (5)Sm 1 s(94.83%)p 0.01(0.56%)d 0.05(4.33%)f 0.00(0.23%)g 0.00(0.05%)	3.19
(0.98046) BD (1) C 32- C 34 (49.96%) 0.7068* C 32 s(35.46%)p 1.82(64.48%)d 0.00(0.06%) (50.04%) 0.7074* C 34 s(35.34%)p 1.83(64.60%)d 0.00(0.06%)	(0.11728) LV (2)Sm 1 s(0.08%)p 1.60(0.12%)d99.99(99.75%)f 0.13(0.01%)g 0.42(0.03%)	5.14
(0.98046) BD (1) C 32- C 34	(0.11458) LV (3)Sm 1	4.80

(49.96%) 0.7068* C 32 s(35.46%)p 1.82(64.48%)d 0.00(0.06%) (50.04%) 0.7074* C 34 s(35.34%)p 1.83(64.60%)d 0.00(0.06%)	s(0.00%)p 1.00(0.04%)d99.99(99.61%)f 6.81(0.31%)g 0.87(0.04%)	
(0.86536) BD (2) C 32- C 34 (50.34%) 0.7095* C 32 s(1.01%)p98.41(98.93%)d 0.06(0.06%) (49.66%) 0.7047* C 34 s(1.02%)p96.51(98.91%)d 0.06(0.06%)	(0.18206) LV (1)Sm 1 s(0.00%)p 0.00(0.01%)d 1.00(99.82%)f 0.00(0.14%)g 0.00(0.03%)	6.61
(0.86536) BD (2) C 32- C 34 (50.34%) 0.7095* C 32 s(1.01%)p98.41(98.93%)d 0.06(0.06%) (49.66%) 0.7047* C 34 s(1.02%)p96.51(98.91%)d 0.06(0.06%)	(0.11728) LV (2)Sm 1 s(0.08%)p 1.60(0.12%)d99.99(99.75%)f 0.13(0.01%)g 0.42(0.03%)	7.06
(0.86536) BD (2) C 32- C 34 (50.34%) 0.7095* C 32 s(1.01%)p98.41(98.93%)d 0.06(0.06%) (49.66%) 0.7047* C 34 s(1.02%)p96.51(98.91%)d 0.06(0.06%)	(0.11458) LV (3)Sm 1 s(0.00%)p 1.00(0.04%)d99.99(99.61%)f 6.81(0.31%)g 0.87(0.04%)	7.12
(0.86536) BD (2) C 32- C 34 (50.34%) 0.7095* C 32 s(1.01%)p98.41(98.93%)d 0.06(0.06%) (49.66%) 0.7047* C 34 s(1.02%)p96.51(98.91%)d 0.06(0.06%)	(0.05435) LV (5)Sm 1 s(94.83%)p 0.01(0.56%)d 0.05(4.33%)f 0.00(0.23%)g 0.00(0.05%)	4.37

*Table S 41: NBO analysis of canonical molecular orbitals for **2-Sm-trans.***

HOMO-3, MO 76 (occ): orbital energy = -0.22675 a.u. 0.445*[46]: BD (2) C 6- C 8 -0.445*[69]: BD (2) C24- C26 -0.384*[40]: BD (2) C 2- C 4 0.383*[64]: BD (2) C20- C22 0.323*[80]: LV (1)Sm 1(lv)	<u>(0.85494) BD (2) C 6- C 8</u> (49.54%) 0.7038* C 6 s(0.52%)p99.99(99.44%)d 0.07(0.04%) (50.46%) 0.7104* C 8 s(0.43%)p99.99(99.53%)d 0.09(0.04%) <u>(0.85489) BD (2) C 24- C 26</u> (49.55%) 0.7039* C 24 s(0.52%)p99.99(99.44%)d 0.07(0.04%) (50.45%) 0.7103* C 26 s(0.43%)p99.99(99.53%)d 0.09(0.04%) <u>(0.83135) BD (2) C 2- C 4</u> (51.09%) 0.7148* C 2 s(0.83%)p99.99(99.10%)d 0.09(0.07%) (48.91%) 0.6994* C 4 s(0.43%)p99.99(99.52%)d 0.13(0.06%) <u>(0.83121) BD (2) C 20- C 22</u> (51.09%) 0.7148* C 20 s(0.83%)p99.99(99.10%)d 0.09(0.07%) (48.91%) 0.6993* C 22 s(0.43%)p99.99(99.52%)d 0.13(0.06%) <u>(0.18206) LV (1)Sm 1</u> s(0.00%)p 0.00(0.01%)d 1.00(99.82%)f 0.00(0.14%)g 0.00(0.03%)

HOMO-2, MO 77 (occ): orbital energy = -0.22376 a.u. 0.412*[37]: LP (1) C10(lp) -0.391*[95]: BD*(2) C 6- C 8* -0.390*[118]: BD*(2) C24- C26* 0.339*[89]: BD*(2) C 2- C 4* 0.338*[113]: BD*(2) C20- C22* 0.305*[83]: LV (4)Sm 1(lv)	(0.50122) LP (1) C 10 s(0.56%)p99.99(99.40%)d 0.07(0.04%) (0.22752) BD*(2) C 6- C 8 (50.46%) 0.7104* C 6 s(0.52%)p99.99(99.44%)d 0.07(0.04%) (49.54%) -0.7038* C 8 s(0.43%)p99.99(99.53%)d 0.09(0.04%) (0.22754) BD*(2) C 24- C 26 (50.45%) 0.7103* C 24 s(0.52%)p99.99(99.44%)d 0.07(0.04%) (49.55%) -0.7039* C 26 s(0.43%)p99.99(99.53%)d 0.09(0.04%) (0.20396) BD*(2) C 2- C 4 (48.91%) 0.6994* C 2 s(0.83%)p99.99(99.10%)d 0.09(0.07%) (51.09%) -0.7148* C 4 s(0.43%)p99.99(99.52%)d 0.13(0.06%) (0.20400) BD*(2) C 20- C 22 (48.91%) 0.6993* C 20 s(0.83%)p99.99(99.10%)d 0.09(0.07%) (51.09%) -0.7148* C 22 s(0.43%)p99.99(99.52%)d 0.13(0.06%) (0.11091) LV (4)Sm 1 s(0.04%)p 0.12(0.00%)d99.99(88.33%)f99.99(11.58%)g 1.22(0.05%)
HOMO-1, MO 78 (occ): orbital energy = -0.18642 a.u. -0.629*[36]: LP (6)Sm 1(lp) -0.361*[102]: BD*(2) C11- C13* -0.361*[122]: BD*(2) C28- C30* -0.359*[127]: BD*(2) C32- C34* -0.359*[108]: BD*(2) C15- C17*	(0.02782) LV (6)Sm 1 s(4.73%)p 0.03(0.14%)d19.07(90.18%)f 1.02(4.82%)g 0.03(0.13%) (0.21943) BD*(2) C 28- C 30 (50.15%) 0.7081* C 28 s(1.11%)p88.76(98.83%)d 0.05(0.06%) (49.85%) -0.7061* C 30 s(1.03%)p96.45(98.91%)d 0.06(0.06%) (0.21632) BD*(2) C 32- C 34 (49.66%) 0.7047* C 32 s(1.01%)p98.41(98.93%)d 0.06(0.06%) (50.34%) -0.7095* C 34 s(1.02%)p96.51(98.91%)d 0.06(0.06%) (0.21632) BD*(2) C 15- C 17 (49.77%) 0.7055* C 15 s(1.01%)p98.42(98.93%)d 0.06(0.06%) (50.23%) -0.7087* C 17 s(1.02%)p96.51(98.91%)d 0.06(0.06%)
HOMO, MO 79 (occ): orbital energy = -0.16429 a.u. 0.433*[73]: BD (2) C28- C30 -0.433*[53]: BD (2) C11- C13 0.430*[59]: BD (2) C15- C17 -0.430*[78]: BD (2) C32- C34 0.250*[80]: LV (1)Sm 1(lv)	(0.86595) BD (2) C 28- C 30 (49.85%) 0.7061* C 28 s(1.11%)p88.76(98.83%)d 0.05(0.06%) (50.15%) 0.7081* C 30 s(1.03%)p96.45(98.91%)d 0.06(0.06%) (0.86593) BD (2) C 11- C 13 (49.75%) 0.7054* C 11 s(1.11%)p88.74(98.83%)d 0.05(0.06%)

	(50.25%) 0.7089* C 13 s(1.03%)p96.43(98.91%)d 0.06(0.06%) (0.86539) BD (2) C 15- C 17 (50.23%) 0.7087* C 15 s(1.01%)p98.42(98.93%)d 0.06(0.06%) (49.77%) 0.7055* C 17 s(1.02%)p96.51(98.91%)d 0.06(0.06%) (0.86536) BD (2) C 32- C 34 (50.34%) 0.7095* C 32 s(1.01%)p98.41(98.93%)d 0.06(0.06%) (49.66%) 0.7047* C 34 s(1.02%)p96.51(98.91%)d 0.06(0.06%) (0.18206) LV (1)Sm 1 s(0.00%)p 0.00(0.01%)d 1.00(99.82%)f 0.00(0.14%)g 0.00(0.03%)

Table S42**: Computed natural charges for **2-Sm-trans.

Atom labels	Natural charges
Sm1	1.32301
C2	-0.32685
C4	-0.32465
C6	-0.32069
C8	-0.32108
C10	-0.32467
C12	-0.36640
C14	-0.36370
C16	-0.35721
C18	-0.37023
C20	-0.32519
C22	-0.31942
C24	-0.32130
C26	-0.32547
C28	-0.36566
C30	-0.36258
C32	-0.36296
C34	-0.36422

Table S43**: Computed Wiberg bond index for **2-Sm-trans.

Atom labels	Wiberg bond index	Atom labels	Wiberg bond index	Atom labels	Wiberg bond index	Atom labels	Wiberg bond index
Sm1	0.0000	Sm1	0.0000	Sm1	0.0000	Sm1	0.0000
C2	0.1064	C4	0.0946	C6	0.1056	C8	0.0946
Atom labels	Wiberg bond index	Atom labels	Wiberg bond index	Atom labels	Wiberg bond index	Atom labels	Wiberg bond index
Sm1	0.0000	Sm1	0.0000	Sm1	0.0000	Sm1	0.0000
C10	0.1031	C12	0.2335	C14	0.2289	C16	0.2371
Atom labels	Wiberg bond index	Atom labels	Wiberg bond index	Atom labels	Wiberg bond index	Atom labels	Wiberg bond index
Sm1	0.0000	Sm1	0.0000	Sm1	0.0000	Sm1	0.0000
C18	0.2279	C20	0.0924	C22	0.1085	C24	0.0933
Atom labels	Wiberg bond index	Atom labels	Wiberg bond index	Atom labels	Wiberg bond index	Atom labels	Wiberg bond index
Sm1	0.0000	Sm1	0.0000	Sm1	0.0000	Sm1	0.0000
C26	0.1022	C28	0.2347	C30	0.2298	C32	0.2317
Atom labels	Wiberg bond index						
Sm1	0.0000						
C34	0.2334						

Table S44**: DFT computed NBO second-order perturbation analysis for **2-Sm-cis.

Donor NBO	Acceptor NBO	E(2) kcal/mol
(0.44813) LP (6)Sm 1 s(0.00%)p 0.00(0.00%)d 1.00(14.23%)f 6.03(85.77%)g 0.00(0.00%)	102. BD*(2) C 12- C 14	5.74
(0.44813) LP (6)Sm 1 s(0.00%)p 0.00(0.00%)d 1.00(14.23%)f 6.03(85.77%)g 0.00(0.00%)	108. BD*(2) C 16- C 18	4.99
(0.44813) LP (6)Sm 1 s(0.00%)p 0.00(0.00%)d 1.00(14.23%)f 6.03(85.77%)g 0.00(0.00%)	122. BD*(2) C 28- C 30	5.18
(0.44813) LP (6)Sm 1 s(0.00%)p 0.00(0.00%)d 1.00(14.23%)f 6.03(85.77%)g 0.00(0.00%)	127. BD*(2) C 32- C 34	4.43
(0.52209) LP (1) C 2 s(0.58%)p99.99(99.41%)d 0.03(0.02%)	(0.11000) LV (2)Sm 1 s(0.00%)p 1.00(0.12%)d99.99(99.39%)f 3.95(0.46%)g 0.24(0.03%)	6.39
(0.98560) BD (1) C 2- C 4 (50.07%) 0.7076* C 2 s(37.05%)p 1.70(62.89%)d 0.00(0.06%) (49.93%) 0.7066* C 4 s(37.36%)p 1.67(62.58%)d 0.00(0.06%)	(0.11000) LV (2)Sm 1 s(0.00%)p 1.00(0.12%)d99.99(99.39%)f 3.95(0.46%)g 0.24(0.03%)	3.25
(0.98535) BD (1) C 4- C 6	(0.10970) LV (3)Sm 1	4.02

(50.06%) 0.7075* C 4 s(37.12%)p 1.69(62.82%)d 0.00(0.06%) (49.94%) 0.7067* C 6 s(37.18%)p 1.69(62.76%)d 0.00(0.06%)	s(0.00%)p 1.00(0.10%)d99.99(99.68%)f 2.07(0.20%)g 0.28(0.03%)	
(0.84089) BD (2) C 4- C 6 (50.79%) 0.7127* C 4 s(0.22%)p99.99(99.74%)d 0.17(0.04%) (49.21%) 0.7015* C 6 s(0.24%)p99.99(99.72%)d 0.16(0.04%)	(0.10970) LV (3)Sm 1 s(0.00%)p 1.00(0.10%)d99.99(99.68%)f 2.07(0.20%)g 0.28(0.03%)	7.22
(0.98490) BD (1) C 6- C 8 (50.01%) 0.7072* C 6 s(37.33%)p 1.68(62.61%)d 0.00(0.06%) (49.99%) 0.7070* C 8 s(37.24%)p 1.68(62.70%)d 0.00(0.06%)	(0.10970) LV (3)Sm 1 s(0.00%)p 1.00(0.10%)d99.99(99.68%)f 2.07(0.20%)g 0.28(0.03%)	3.87
(0.98581) BD (1) C 8- C 10 (49.91%) 0.7065* C 8 s(37.21%)p 1.69(62.73%)d 0.00(0.06%) (50.09%) 0.7077* C 10 s(37.18%)p 1.69(62.77%)d 0.00(0.06%)	(0.11000) LV (2)Sm 1 s(0.00%)p 1.00(0.12%)d99.99(99.39%)f 3.95(0.46%)g 0.24(0.03%)	3.35
(0.84421) BD (2) C 8- C 10 (50.41%) 0.7100* C 8 s(0.22%)p99.99(99.75%)d 0.17(0.04%) (49.59%) 0.7042* C 10 s(0.24%)p99.99(99.73%)d 0.16(0.04%)	(0.11000) LV (2)Sm 1 s(0.00%)p 1.00(0.12%)d99.99(99.39%)f 3.95(0.46%)g 0.24(0.03%)	5.78
(0.98557) BD (1) C 10- C 26 (50.00%) 0.7071* C 10 s(37.29%)p 1.68(62.65%)d 0.00(0.06%) (50.00%) 0.7071* C 26 s(37.28%)p 1.68(62.66%)d 0.00(0.06%)	(0.11000) LV (2)Sm 1 s(0.00%)p 1.00(0.12%)d99.99(99.39%)f 3.95(0.46%)g 0.24(0.03%)	3.85
(0.83984) BD (2) C 20- C 22 (50.99%) 0.7141* C 20 s(0.22%)p99.99(99.74%)d 0.16(0.04%) (49.01%) 0.7001* C 22 s(0.25%)p99.99(99.71%)d 0.16(0.04%)	(0.11000) LV (2)Sm 1 s(0.00%)p 1.00(0.12%)d99.99(99.39%)f 3.95(0.46%)g 0.24(0.03%)	3.31
(0.83984) BD (2) C 20- C 22 (50.99%) 0.7141* C 20 s(0.22%)p99.99(99.74%)d 0.16(0.04%) (49.01%) 0.7001* C 22 s(0.25%)p99.99(99.71%)d 0.16(0.04%)	(0.10970) LV (3)Sm 1 s(0.00%)p 1.00(0.10%)d99.99(99.68%)f 2.07(0.20%)g 0.28(0.03%)	3.51
(0.84575) BD (2) C 24- C 26 (50.42%) 0.7101* C 24 s(0.22%)p99.99(99.75%)d 0.17(0.04%) (49.58%) 0.7041* C 26 s(0.23%)p99.99(99.73%)d 0.17(0.04%)	(0.10970) LV (3)Sm 1 s(0.00%)p 1.00(0.10%)d99.99(99.68%)f 2.07(0.20%)g 0.28(0.03%)	5.25
(0.98068) BD (1) C 12- C 14 (50.08%) 0.7077* C 12 s(36.19%)p 1.76(63.75%)d 0.00(0.06%)	(0.10970) LV (3)Sm 1 s(0.00%)p 1.00(0.10%)d99.99(99.68%)f 2.07(0.20%)g 0.28(0.03%)	7.41

(49.92%) 0.7065* C 14 s(36.17%)p 1.76(63.77%)d 0.00(0.07%)		
(0.86778) BD (2) C 12- C 14 (49.66%) 0.7047* C 12 s(1.05%)p94.28(98.88%)d 0.06(0.07%) (50.34%) 0.7095* C 14 s(1.06%)p93.62(98.88%)d 0.06(0.07%)	(0.18020) LV (1)Sm 1 s(0.00%)p 0.00(0.00%)d 1.00(86.88%)f 0.15(13.09%)g 0.00(0.03%)	5.67
(0.86778) BD (2) C 12- C 14 (49.66%) 0.7047* C 12 s(1.05%)p94.28(98.88%)d 0.06(0.07%) (50.34%) 0.7095* C 14 s(1.06%)p93.62(98.88%)d 0.06(0.07%)	(0.10970) LV (3)Sm 1 s(0.00%)p 1.00(0.10%)d99.99(99.68%)f 2.07(0.20%)g 0.28(0.03%)	10.29
(0.86778) BD (2) C 12- C 14 (49.66%) 0.7047* C 12 s(1.05%)p94.28(98.88%)d 0.06(0.07%) (50.34%) 0.7095* C 14 s(1.06%)p93.62(98.88%)d 0.06(0.07%)	(0.04915) LV (5)Sm 1 s(97.76%)p 0.01(0.73%)d 0.01(0.54%)f 0.01(0.85%)g 0.00(0.13%)	4.24
(0.97846) BD (1) C 12- C 28 (50.00%) 0.7071* C 12 s(36.41%)p 1.74(63.53%)d 0.00(0.06%) (50.00%) 0.7071* C 28 s(36.45%)p 1.74(63.49%)d 0.00(0.06%)	(0.11000) LV (2)Sm 1 s(0.00%)p 1.00(0.12%)d99.99(99.39%)f 3.95(0.46%)g 0.24(0.03%)	10.03
(0.97779) BD (1) C 14- C 16 (49.99%) 0.7070* C 14 s(36.33%)p 1.75(63.60%)d 0.00(0.07%) (50.01%) 0.7072* C 16 s(36.50%)p 1.74(63.43%)d 0.00(0.07%)	(0.10970) LV (3)Sm 1 s(0.00%)p 1.00(0.10%)d99.99(99.68%)f 2.07(0.20%)g 0.28(0.03%)	10.39
(0.98070) BD (1) C 16- C 18 (49.92%) 0.7066* C 16 s(36.22%)p 1.76(63.71%)d 0.00(0.07%) (50.08%) 0.7077* C 18 s(36.08%)p 1.77(63.85%)d 0.00(0.06%)	(0.11000) LV (2)Sm 1 s(0.00%)p 1.00(0.12%)d99.99(99.39%)f 3.95(0.46%)g 0.24(0.03%)	7.24
(0.86373) BD (2) C 16- C 18 (49.18%) 0.7013* C 16 s(1.04%)p94.97(98.89%)d 0.07(0.07%) (50.82%) 0.7129* C 18 s(1.05%)p94.29(98.89%)d 0.06(0.07%)	(0.18020) LV (1)Sm 1 s(0.00%)p 0.00(0.00%)d 1.00(86.88%)f 0.15(13.09%)g 0.00(0.03%)	6.59
(0.86373) BD (2) C 16- C 18 (49.18%) 0.7013* C 16 s(1.04%)p94.97(98.89%)d 0.07(0.07%) (50.82%) 0.7129* C 18 s(1.05%)p94.29(98.89%)d 0.06(0.07%)	(0.11000) LV (2)Sm 1 s(0.00%)p 1.00(0.12%)d99.99(99.39%)f 3.95(0.46%)g 0.24(0.03%)	9.87
(0.86373) BD (2) C 16- C 18 (49.18%) 0.7013* C 16 s(1.04%)p94.97(98.89%)d 0.07(0.07%) (50.82%) 0.7129* C 18 s(1.05%)p94.29(98.89%)d 0.06(0.07%)	(0.10970) LV (3)Sm 1 s(0.00%)p 1.00(0.10%)d99.99(99.68%)f 2.07(0.20%)g 0.28(0.03%)	3.07

(0.86373) BD (2) C 16- C 18 (49.18%) 0.7013* C 16 s(1.04%)p94.97(98.89%)d 0.07(0.07%) (50.82%) 0.7129* C 18 s(1.05%)p94.29(98.89%)d 0.06(0.07%)	(0.04915) LV (5)Sm 1 s(97.76%)p 0.01(0.73%)d 0.01(0.54%)f 0.01(0.85%)g 0.00(0.13%)	3.98
(0.97838) BD (1) C 18- C 34 (50.00%) 0.7071* C 18 s(36.40%)p 1.75(63.53%)d 0.00(0.06%) (50.00%) 0.7071* C 34 s(36.44%)p 1.74(63.50%)d 0.00(0.06%)	(0.11000) LV (2)Sm 1 s(0.00%)p 1.00(0.12%)d99.99(99.39%)f 3.95(0.46%)g 0.24(0.03%)	11.81
(0.98074) BD (1) C 28- C 30 (50.10%) 0.7078* C 28 s(36.15%)p 1.76(63.79%)d 0.00(0.06%) (49.90%) 0.7064* C 30 s(36.17%)p 1.76(63.76%)d 0.00(0.07%)	(0.11000) LV (2)Sm 1 s(0.00%)p 1.00(0.12%)d99.99(99.39%)f 3.95(0.46%)g 0.24(0.03%)	7.06
(0.86485) BD (2) C 28- C 30 (49.82%) 0.7058* C 28 s(1.06%)p93.41(98.87%)d 0.06(0.07%) (50.18%) 0.7084* C 30 s(1.04%)p94.65(98.89%)d 0.06(0.07%)	(0.18020) LV (1)Sm 1 s(0.00%)p 0.00(0.00%)d 1.00(86.88%)f 0.15(13.09%)g 0.00(0.03%)	6.34
(0.86485) BD (2) C 28- C 30 (49.82%) 0.7058* C 28 s(1.06%)p93.41(98.87%)d 0.06(0.07%) (50.18%) 0.7084* C 30 s(1.04%)p94.65(98.89%)d 0.06(0.07%)	(0.11000) LV (2)Sm 1 s(0.00%)p 1.00(0.12%)d99.99(99.39%)f 3.95(0.46%)g 0.24(0.03%)	9.71
(0.86485) BD (2) C 28- C 30 (49.82%) 0.7058* C 28 s(1.06%)p93.41(98.87%)d 0.06(0.07%) (50.18%) 0.7084* C 30 s(1.04%)p94.65(98.89%)d 0.06(0.07%)	(0.10970) LV (3)Sm 1 s(0.00%)p 1.00(0.10%)d99.99(99.68%)f 2.07(0.20%)g 0.28(0.03%)	3.43
(0.86485) BD (2) C 28- C 30 (49.82%) 0.7058* C 28 s(1.06%)p93.41(98.87%)d 0.06(0.07%) (50.18%) 0.7084* C 30 s(1.04%)p94.65(98.89%)d 0.06(0.07%)	(0.04915) LV (5)Sm 1 s(97.76%)p 0.01(0.73%)d 0.01(0.54%)f 0.01(0.85%)g 0.00(0.13%)	4.04
(0.97753) BD (1) C 30- C 32 (49.97%) 0.7069* C 30 s(36.34%)p 1.75(63.59%)d 0.00(0.07%) (50.03%) 0.7073* C 32 s(36.51%)p 1.74(63.42%)d 0.00(0.07%)	(0.10970) LV (3)Sm 1 s(0.00%)p 1.00(0.10%)d99.99(99.68%)f 2.07(0.20%)g 0.28(0.03%)	11.17
(0.98074) BD (1) C 32- C 34 (49.94%) 0.7067* C 32 s(36.20%)p 1.76(63.73%)d 0.00(0.07%) (50.06%) 0.7075* C 34 s(36.03%)p 1.77(63.90%)d 0.00(0.06%)	(0.10970) LV (3)Sm 1 s(0.00%)p 1.00(0.10%)d99.99(99.68%)f 2.07(0.20%)g 0.28(0.03%)	7.14
(0.86229) BD (2) C 32- C 34	(0.18020) LV (1)Sm 1 s(0.00%)p 0.00(0.00%)d 1.00(86.88%)f 0.15(13.09%)g 0.00(0.03%)	7.09

(50.30%) 0.7092* C 32 s(1.05%)p94.51(98.89%)d 0.06(0.07%) (49.70%) 0.7050* C 34 s(1.08%)p91.92(98.86%)d 0.06(0.07%)		
(0.86229) BD (2) C 32- C 34 (50.30%) 0.7092* C 32 s(1.05%)p94.51(98.89%)d 0.06(0.07%) (49.70%) 0.7050* C 34 s(1.08%)p91.92(98.86%)d 0.06(0.07%)	(0.11000) LV (2)Sm 1 s(0.00%)p 1.00(0.12%)d99.99(99.39%)f 3.95(0.46%)g 0.24(0.03%)	3.37
(0.86229) BD (2) C 32- C 34 (50.30%) 0.7092* C 32 s(1.05%)p94.51(98.89%)d 0.06(0.07%) (49.70%) 0.7050* C 34 s(1.08%)p91.92(98.86%)d 0.06(0.07%)	(0.10970) LV (3)Sm 1 s(0.00%)p 1.00(0.10%)d99.99(99.68%)f 2.07(0.20%)g 0.28(0.03%)	9.75
(0.86229) BD (2) C 32- C 34 (50.30%) 0.7092* C 32 s(1.05%)p94.51(98.89%)d 0.06(0.07%) (49.70%) 0.7050* C 34 s(1.08%)p91.92(98.86%)d 0.06(0.07%)	(0.04915) LV (5)Sm 1 s(97.76%)p 0.01(0.73%)d 0.01(0.54%)f 0.01(0.85%)g 0.00(0.13%)	4.16

Table S45**: NBO analysis of canonical molecular orbitals for **2-Sm-cis.

HOMO-3, MO 76 (occ): orbital energy = -0.23005 a.u. -0.454*[69]: BD (2) C24- C26 0.452*[48]: BD (2) C 8- C10 0.397*[64]: BD (2) C20- C22 -0.396*[43]: BD (2) C 4- C 6 0.271*[80]: LV (1)Sm 1(lv)	<u>(0.84575) BD (2) C 24- C 26</u> (50.42%) 0.7101* C 24 s(0.22%)p99.99(99.75%)d 0.17(0.04%) (49.58%) 0.7041* C 26 s(0.23%)p99.99(99.73%)d 0.17(0.04%) <u>(0.84421) BD (2) C 8- C 10</u> (50.41%) 0.7100* C 8 s(0.22%)p99.99(99.75%)d 0.17(0.04%) (49.59%) 0.7042* C 10 s(0.24%)p99.99(99.73%)d 0.16(0.04%) <u>(0.83984) BD (2) C 20- C 22</u> (50.99%) 0.7141* C 20 s(0.22%)p99.99(99.74%)d 0.16(0.04%) (49.01%) 0.7001* C 22 s(0.25%)p99.99(99.71%)d 0.16(0.04%) <u>(0.84089) BD (2) C 4- C 6</u> (50.79%) 0.7127* C 4 s(0.22%)p99.99(99.74%)d 0.17(0.04%) (49.21%) 0.7015* C 6 s(0.24%)p99.99(99.72%)d 0.16(0.04%) <u>(0.18020) LV (1)Sm 1</u> s(0.00%)p 0.00(0.00%)d 1.00(86.88%) f 0.15(13.09%)g 0.00(0.03%)
HOMO-2, MO 77 (occ): orbital energy = -0.22804 a.u. 0.433*[37]: LP (1) C 2(lp) 0.387*[97]: BD*(2) C 8- C10*	<u>(0.52209) LP (1) C 2</u> s(0.58%)p99.99(99.41%)d 0.03(0.02%) <u>(0.21317) BD*(2) C 8- C 10</u>

0.386*[118]: BD*(2) C24- C26* -0.343*[92]: BD*(2) C 4- C 6* -0.343*[113]: BD*(2) C20- C22* 0.297*[83]: LV (4)Sm 1(lv) -0.230*[43]: BD (2) C 4- C 6 -0.229*[64]: BD (2) C20- C22	(49.59%) 0.7042* C 8 s(0.22%)p99.99(99.75%)d 0.17(0.04%) (50.41%) -0.7100* C 10 s(0.24%)p99.99(99.73%)d 0.16(0.04%) (0.21339) BD*(2) C 24- C 26 (49.58%) 0.7041* C 24 s(0.22%)p99.99(99.75%)d 0.17(0.04%) (50.42%) -0.7101* C 26 s(0.23%)p99.99(99.73%)d 0.17(0.04%) (0.21588) BD*(2) C 4- C 6 (49.21%) 0.7015* C 4 s(0.22%)p99.99(99.74%)d 0.17(0.04%) (0.21684) BD*(2) C 20- C 22 (49.01%) 0.7001* C 20 s(0.22%)p99.99(99.74%)d 0.16(0.04%) (50.99%) -0.7141* C 22 s(0.25%)p99.99(99.71%)d 0.16(0.04%) (50.79%) -0.7127* C 6 s(0.24%)p99.99(99.72%)d 0.16(0.04%) (0.10344) LV (4)Sm 1 s(0.00%)p 0.00(0.01%)d 1.00(86.44%)f 0.16(13.52%)g 0.00(0.03%) (0.84089) BD (2) C 4- C 6 (50.79%) 0.7127* C 4 s(0.22%)p99.99(99.74%)d 0.17(0.04%) (49.21%) 0.7015* C 6 s(0.24%)p99.99(99.72%)d 0.16(0.04%) (0.83984) BD (2) C 20- C 22 (50.99%) 0.7141* C 20 s(0.22%)p99.99(99.74%)d 0.16(0.04%) (49.01%) 0.7001* C 22 s(0.25%)p99.99(99.71%)d 0.16(0.04%)
HOMO-1, MO 78 (occ): orbital energy = -0.18203 a.u. 0.659*[36]: LP (6)Sm 1(lp) 0.353*[127]: BD*(2) C32- C34* -0.352*[108]: BD*(2) C16- C18* 0.352*[122]: BD*(2) C28- C30* 0.351*[102]: BD*(2) C12- C14*	(0.44813) LP (6)Sm 1 s(0.00%)p 0.00(0.00%)d 1.00(14.23%)f 6.03(85.77%)g 0.00(0.00%) (0.20409) BD*(2) C 32- C 34 (49.70%) 0.7050* C 32 s(1.05%)p94.51(98.89%)d 0.06(0.07%) (50.30%) -0.7092* C 34 s(1.08%)p91.92(98.86%)d 0.06(0.07%) (0.20421) BD*(2) C 16- C 18 (50.82%) 0.7129* C 16 s(1.04%)p94.97(98.89%)d 0.07(0.07%) (49.18%) -0.7013* C 18 s(1.05%)p94.29(98.89%)d 0.06(0.07%) (0.20428) BD*(2) C 28- C 30 (50.18%) 0.7084* C 28 s(1.06%)p93.41(98.87%)d 0.06(0.07%) (49.82%) -0.7058* C 30 s(1.04%)p94.65(98.89%)d 0.06(0.07%) (0.20441) BD*(2) C 12- C 14

	(50.34%) 0.7095* C 12 s(1.05%)p94.28(98.88%)d 0.06(0.07%) (49.66%) -0.7047* C 14 s(1.06%)p93.62(98.88%)d 0.06(0.07%)
HOMO, MO 79 (occ): orbital energy = -0.17642 a.u. -0.434*[53]: BD (2) C12- C14 0.425*[73]: BD (2) C28- C30 0.425*[59]: BD (2) C16- C18 -0.419*[78]: BD (2) C32- C34 0.306*[80]: LV (1)Sm 1(lv)	(0.86778) BD (2) C 12- C 14 (49.66%) 0.7047* C 12 s(1.05%)p94.28(98.88%)d 0.06(0.07%) (50.34%) 0.7095* C 14 s(1.06%)p93.62(98.88%)d 0.06(0.07%) (0.86485) BD (2) C 28- C 30 (49.82%) 0.7058* C 28 s(1.06%)p93.41(98.87%)d 0.06(0.07%) (50.18%) 0.7084* C 30 s(1.04%)p94.65(98.89%)d 0.06(0.07%) (0.86373) BD (2) C 16- C 18 (49.18%) 0.7013* C 16 s(1.04%)p94.97(98.89%)d 0.07(0.07%) (50.82%) 0.7129* C 18 s(1.05%)p94.29(98.89%)d 0.06(0.07%) (0.86229) BD (2) C 32- C 34 (50.30%) 0.7092* C 32 s(1.05%)p94.51(98.89%)d 0.06(0.07%) (49.70%) 0.7050* C 34 s(1.08%)p91.92(98.86%)d 0.06(0.07%) (0.18020) LV (1)Sm 1 s(0.00%)p 0.00(0.00%)d 1.00(86.88%)f 0.15(13.09%)g 0.00(0.03%)

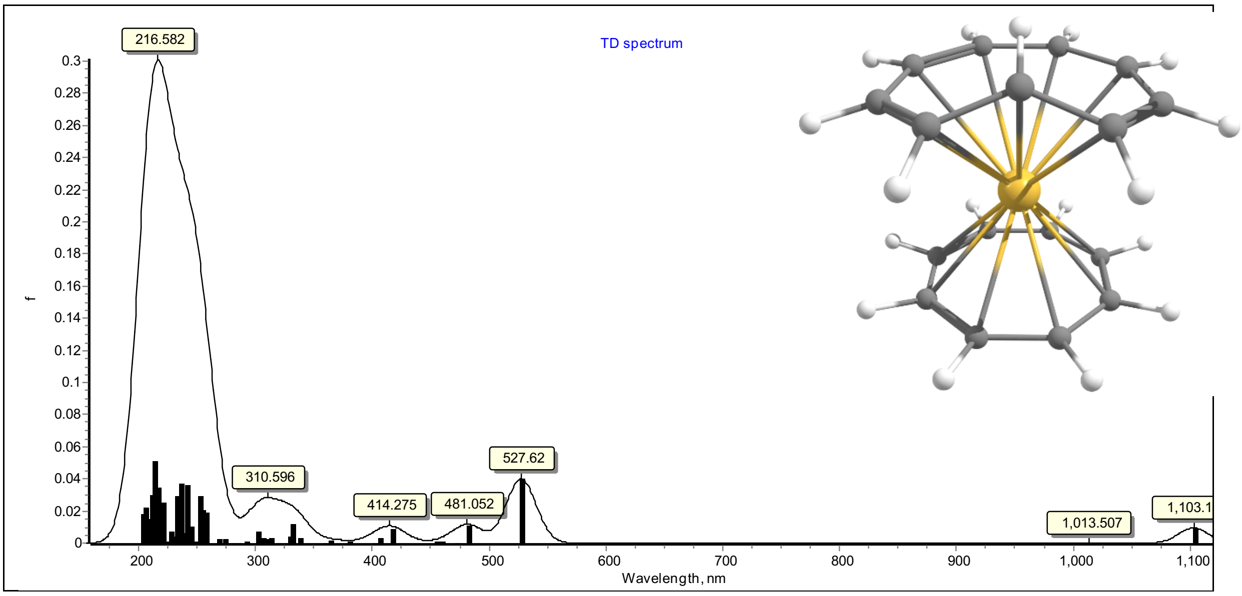
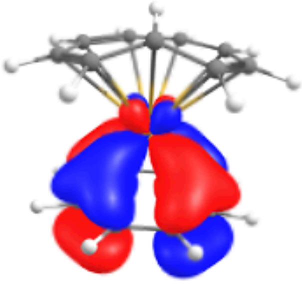
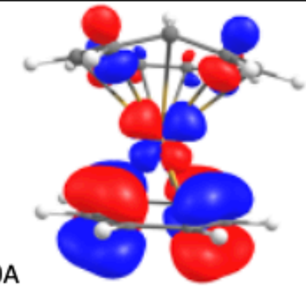
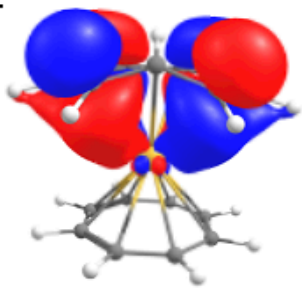
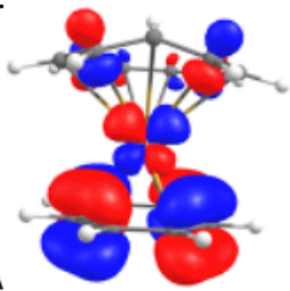
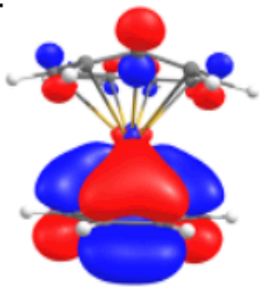
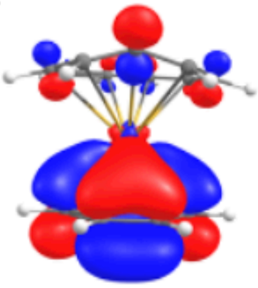
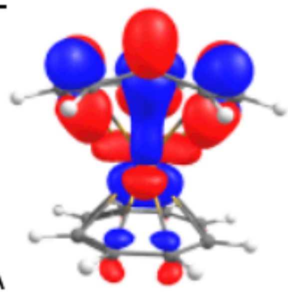
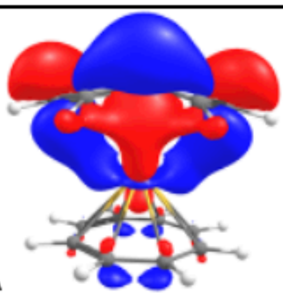
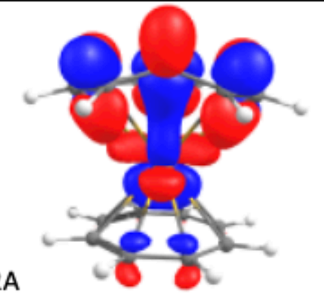
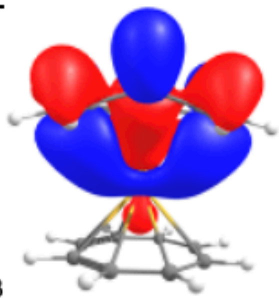
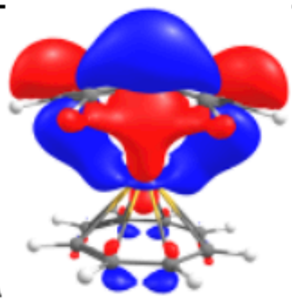
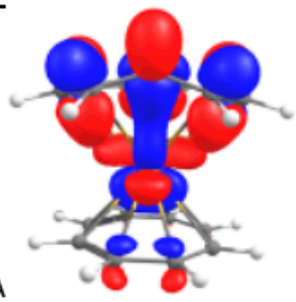
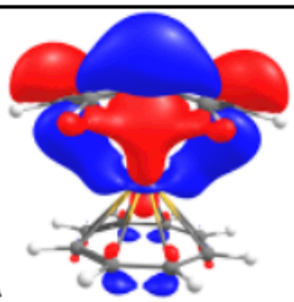
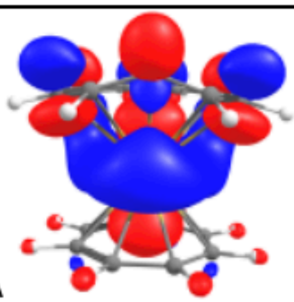
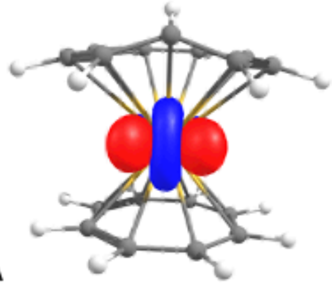
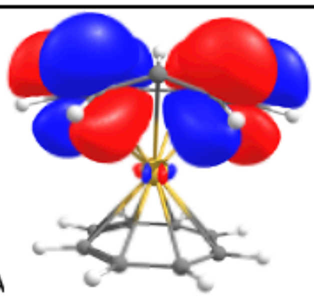
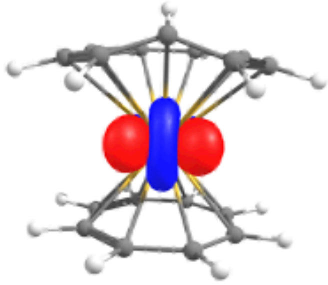
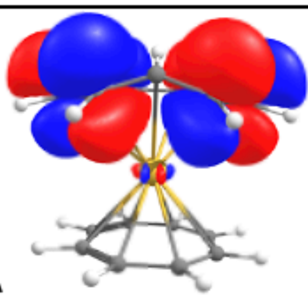
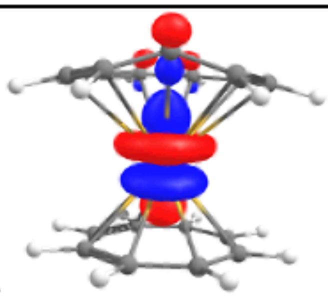
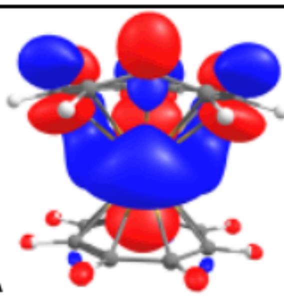
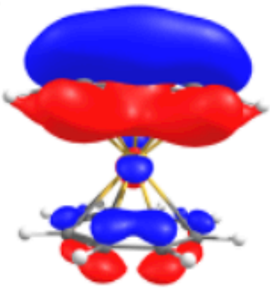
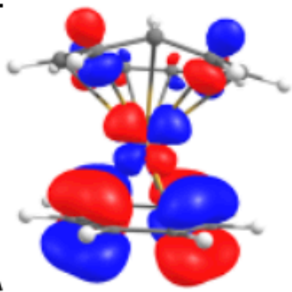
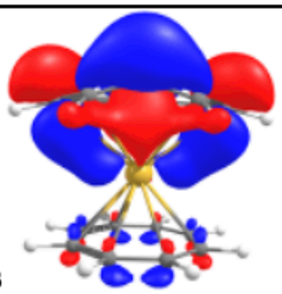
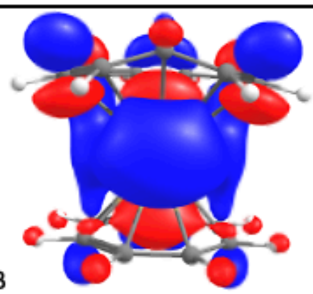
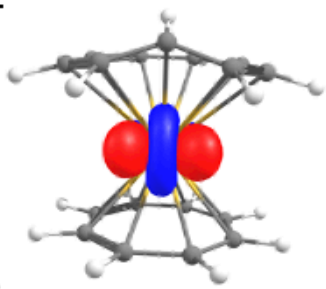
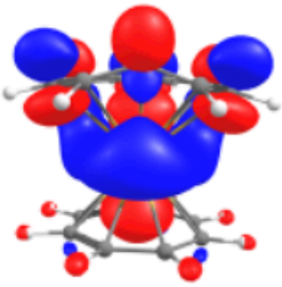
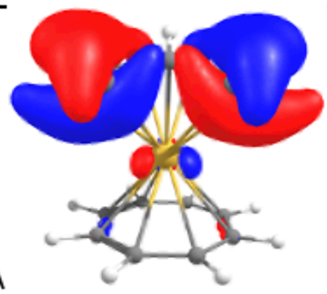
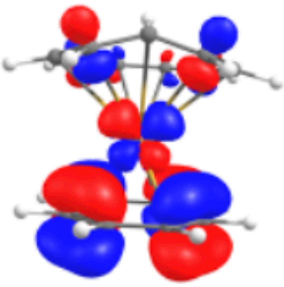
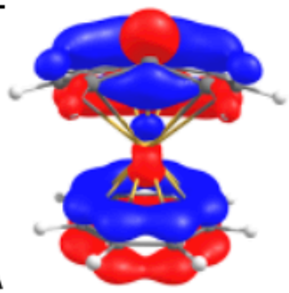
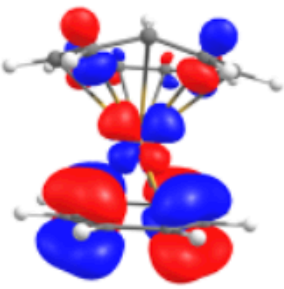


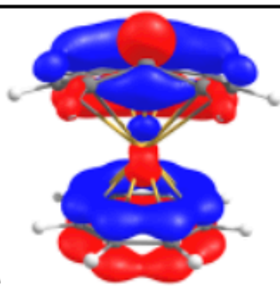
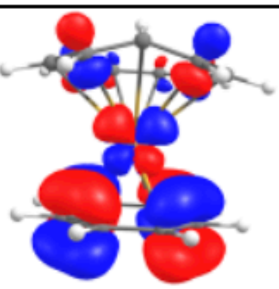
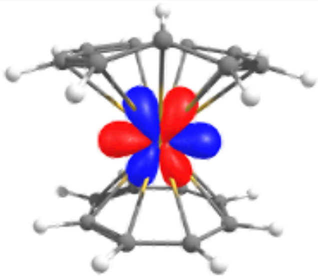
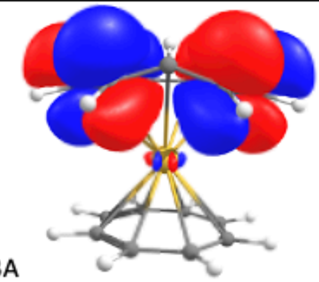
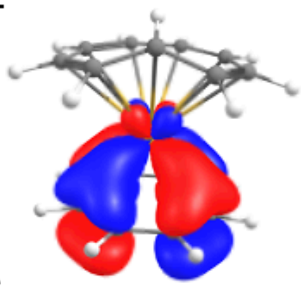
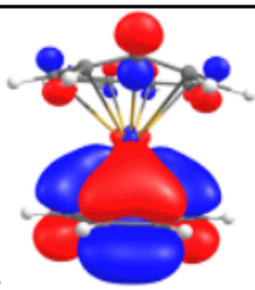
Figure S92**: Computed TD spectrum for **2-Sm-trans.

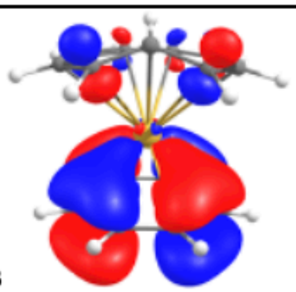
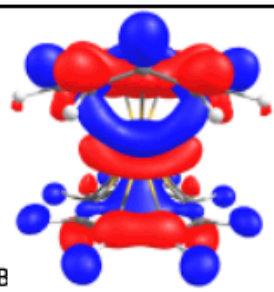
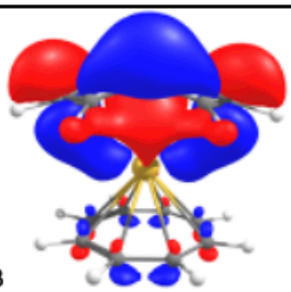
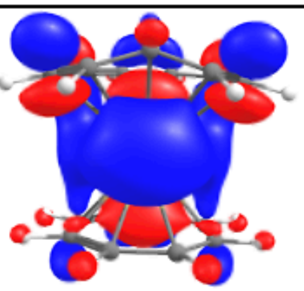
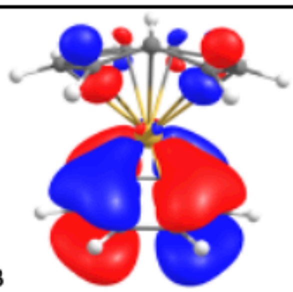
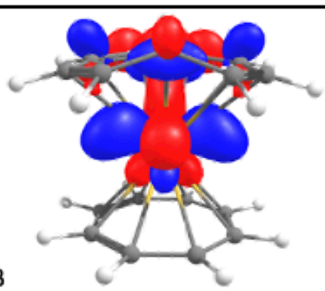
79A, 74B: HOMO		
Excited State 12: 6.255-?Sym 1.1242 eV 1102.88 nm f=0.0094 <S**2>=9.532 **78A -> 80A 0.91156** 79A -> 81A -0.27684 79A -> 82A -0.31260 79A <- 82A -0.12342	 78A	 80A
Excited State 15: 6.407-?Sym 2.3506 eV 527.45 nm f=0.0398 <S**2>=10.014 **76A -> 80A 0.79104** 78A -> 80A -0.19066 79A -> 81A -0.51500 79A -> 82A -0.10772 72B -> 75B -0.13367 73B -> 75B 0.10460	 76A	 80A
Excited State 16: 6.574-?Sym 2.5750 eV 481.50 nm f=0.0113 <S**2>=10.554 76A -> 80A 0.52647 77A -> 81A -0.12639 77A -> 82A 0.16114 78A -> 80A 0.13041 **79A -> 81A 0.64458** 79A -> 82A -0.22160 72B -> 75B 0.19522 73B -> 75B -0.37388	 79A	 81A
Excited State 20: 6.260-?Sym 2.9718 eV 417.20 nm f=0.0084 <S**2>=9.548 76A -> 80A 0.11676 78A -> 80A 0.20975 79A -> 81A -0.19456 **79A -> 82A 0.76280** 79A -> 84A -0.10641 73B -> 75B -0.47181 74B -> 76B -0.25561	 79A	 82A
Excited State 29: 6.460-?Sym 3.7475 eV 330.84 nm f=0.0118 <S**2>=10.182 73A -> 82A -0.11253 75A -> 81A -0.37725 75A -> 84A -0.14879 76A -> 83A 0.27591 **77A -> 81A 0.53057** **77A -> 82A 0.48288** 78A -> 83A -0.11078 71B -> 76B -0.36449	 77A	 81A

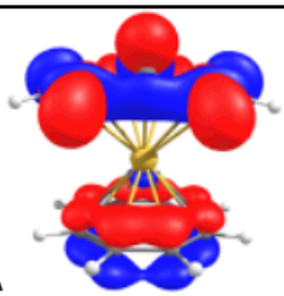
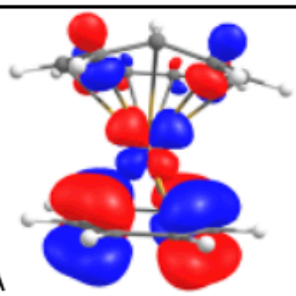
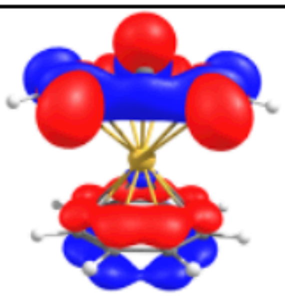
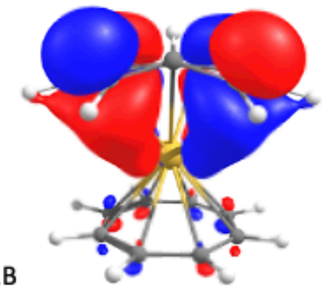
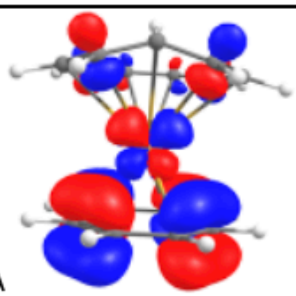
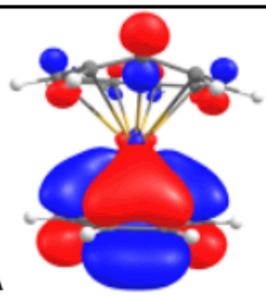
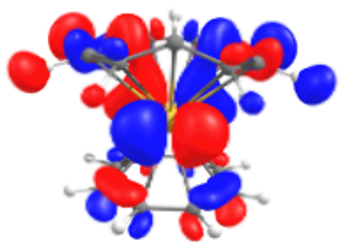
72B -> 75B 0.11989 74B -> 76B 0.16455		 82A
Excited State 39: 6.167-?Sym 4.1003 eV 302.38 nm f=0.0045 <S**2>=9.258 74A -> 81A 0.13868 74A -> 82A -0.16755 76A -> 81A 0.24562 76A -> 82A -0.55227 77A -> 83A 0.38545 **71B -> 75B 0.56034** 72B -> 76B 0.29581	 71B	 75B
Excited State 40: 6.165-?Sym 4.1010 eV 302.32 nm f=0.0072 <S**2>=9.252 72A -> 81A -0.28104 72A -> 82A 0.26941 72A -> 84A -0.15225 73A -> 82A -0.11594 75A -> 81A 0.12878 75A -> 82A -0.20150 76A -> 83A 0.28849 77A -> 81A -0.25645 **77A -> 82A 0.53432** 71B -> 76B 0.22393 72B -> 75B -0.48611	 77A	 82A
Excited State 52: 6.258-?Sym 4.8246 eV 256.98 nm f=0.0190 <S**2>=9.541 66A -> 80A -0.13806 74A -> 83A -0.46745 75A -> 81A -0.17572 75A -> 82A 0.18132 75A -> 84A 0.35394 76A -> 83A 0.29120 **77A -> 84A 0.56223** 79A -> 86A 0.11401 71B -> 76B 0.27639	 77A	 84A

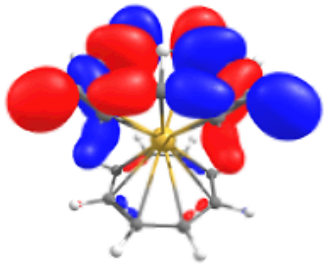
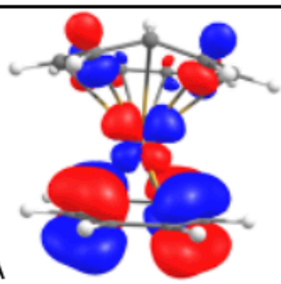
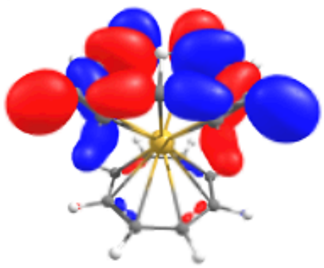
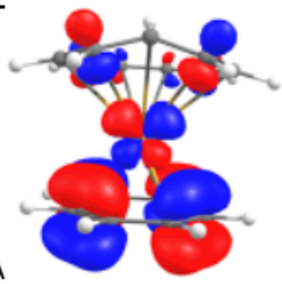
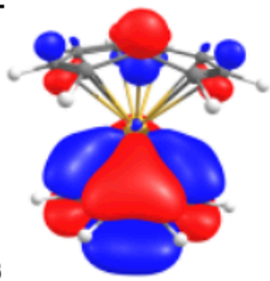
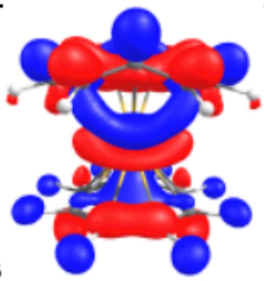
Excited State 54: 6.196-?Sym 4.8691 eV 254.63 nm f=0.0206 <S**2>=9.346 68A -> 80A 0.15460 **73A -> 83A 0.77626** 75A -> 83A -0.14989 76A -> 82A 0.10511 76A -> 84A -0.39828 77A -> 83A 0.27427 71B -> 75B -0.10504 72B -> 76B 0.23454	 73A	 83A
Excited State 56: 6.247-?Sym 4.9174 eV 252.13 nm f=0.0286 <S**2>=9.507 68A -> 80A -0.22767 72A -> 83A 0.10181 **73A -> 83A 0.62289** 75A -> 83A 0.13344 76A -> 81A 0.10964 76A -> 82A -0.13490 76A -> 84A 0.53905 77A -> 83A -0.27968 72B -> 76B -0.28954	 73A	 83A
Excited State 57: 6.189-?Sym 4.9294 eV 251.52 nm f=0.0291 <S**2>=9.327 66A -> 80A 0.19499 74A -> 83A -0.22906 75A -> 81A -0.15243 75A -> 82A 0.14133 **75A -> 84A 0.68134** 76A -> 83A -0.36165 77A -> 81A -0.12308 77A -> 82A 0.14635 77A -> 84A -0.21633 71B -> 76B -0.37170	 75A	 84A
Excited State 59: 6.300-?Sym 5.0847 eV 243.84 nm f=0.0106 <S**2>=9.673 67A -> 80A -0.21485 **68A -> 80A 0.58194** 74A -> 81A 0.16413 74A -> 82A -0.16473 74A -> 84A -0.53823 76A -> 84A 0.34480 77A -> 83A 0.16627 71B -> 78B -0.21467 72B -> 76B 0.10277	 68A	 80A

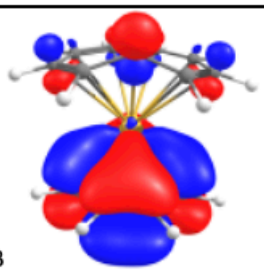
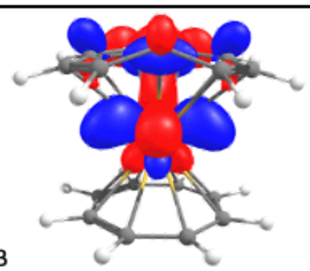
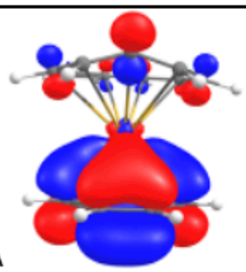
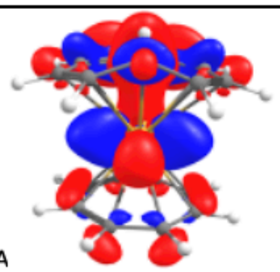
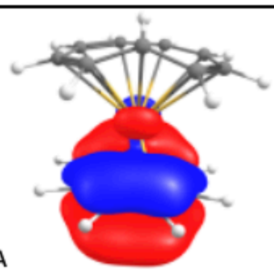
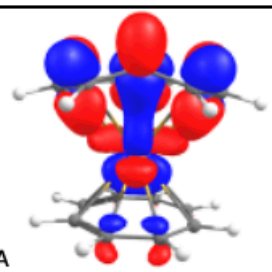
Excited State 63: 6.435-?Sym 5.1402 eV 241.20 nm f=0.0361 <S**2>=10.102 65A -> 80A 0.17559 66A -> 80A -0.14967 71A -> 83A -0.11361 73A -> 81A 0.11296 73A -> 82A -0.10705 73A -> 84A -0.35181 75A -> 84A 0.25689 76A -> 83A 0.33033 77A -> 84A -0.40775 79A -> 86A 0.10009 71B -> 76B 0.24768 72B -> 75B 0.17312 **72B -> 78B 0.49979** 73B -> 81B -0.11059	 72B	 78B
Excited State 64: 6.241-?Sym 5.2057 eV 238.17 nm f=0.0056 <S**2>=9.487 73A -> 81A -0.25764 73A -> 82A 0.24877 **73A -> 84A 0.80426** 74A -> 83A 0.11084 75A -> 84A 0.11427 77A -> 84A -0.16855 72B -> 78B 0.30126	 73A	 84A
Excited State 65: 6.325-?Sym 5.2326 eV 236.95 nm f=0.0064 <S**2>=9.750 65A -> 80A -0.18169 **66A -> 80A 0.86962** 72A -> 84A -0.14178 77A -> 84A 0.20327 71B -> 76B 0.12293 72B -> 78B 0.23330	 66A	 80A
Excited State 66: 6.397-?Sym 5.2522 eV 236.06 nm f=0.0372 <S**2>=9.981 59A -> 80A -0.10695 61A -> 80A -0.12509 **64A -> 80A 0.65707** 68A -> 80A 0.27642 74A -> 84A -0.16231 76A -> 84A -0.28062 77A -> 83A -0.23188 71B -> 75B 0.15719 71B -> 78B 0.36429 72B -> 76B -0.19757 74B -> 81B 0.15056	 64A	 80A

Excited State 68: 6.377-?Sym 5.3385 eV 232.25 nm f=0.0292 <S**2>=9.917 61A -> 80A -0.10605 **64A -> 80A 0.64638** 68A -> 80A -0.39719 77A -> 83A 0.16568 78A -> 88A -0.18745 78A -> 89A -0.10685 71B -> 75B -0.13342 71B -> 78B -0.41499 72B -> 76B 0.17251 74B -> 81B -0.17579	 64A	 80A
Excited State 70: 6.142-?Sym 5.3953 eV 229.80 nm f=0.0042 <S**2>=9.180 **71A -> 83A 0.97891**	 71A	 83A
Excited State 72: 6.262-?Sym 5.4601 eV 227.07 nm f=0.0074 <S**2>=9.552 78A -> 86A 0.48848 **78A -> 88A 0.51496** 78A -> 89A 0.25462 78A -> 92A 0.12499 79A -> 87A -0.40063 71B -> 78B -0.14086 73B -> 79B 0.32867 74B -> 80B -0.20562 74B -> 81B 0.10247	 78A	 88A
Excited State 80: 6.600-?Sym 5.6341 eV 220.06 nm f=0.0255 <S**2>=10.639 63A -> 80A 0.24782 66A -> 80A 0.13198 68A -> 81A 0.15108 77A -> 84A -0.18722 77A -> 85A -0.13934 78A -> 90A 0.36632 78A -> 91A -0.16036 79A -> 86A -0.12816 **79A -> 88A 0.51868** 79A -> 89A 0.20985 68B -> 75B -0.13817 73B -> 81B 0.37245 73B -> 84B -0.20203 73B -> 91B -0.12245 74B -> 90B 0.16536	 79A	 88A

Excited State 83: 6.333-?Sym 5.6888 eV 217.94 nm f=0.0182 <S**2>=9.778 61A -> 80A -0.18809 69A -> 81A -0.12391 71A -> 84A -0.10348 76A -> 84A 0.24690 77A -> 83A 0.11490 79A -> 87A 0.13430 71B -> 77B -0.47020 72B -> 76B 0.12729 73B -> 79B -0.10626 **74B -> 81B 0.56918** 74B -> 82B -0.36860	 74B	 81B
Excited State 85: 6.287-?Sym 5.7352 eV 216.18 nm f=0.0347 <S**2>=9.631 62A -> 80A 0.15318 66A -> 80A -0.19793 68A -> 81A -0.17144 68A -> 82A 0.11191 70A -> 82A -0.13679 75A -> 84A -0.11734 76A -> 83A -0.18273 77A -> 84A 0.31358 78A -> 87A 0.21185 78A -> 90A 0.14042 79A -> 86A -0.18781 79A -> 88A 0.27720 79A -> 89A 0.11669 71B -> 76B -0.16284 72B -> 75B -0.13836 **72B -> 78B 0.48861** 73B -> 80B 0.10023 73B -> 81B -0.23867 73B -> 82B 0.17602 74B -> 79B -0.10267 74B -> 90B 0.11614	 72B	 78B
Excited State 86: 6.317-?Sym 5.7365 eV 216.13 nm f=0.0099 <S**2>=9.725 60A -> 80A 0.21398 61A -> 80A -0.14152 76A -> 84A 0.14917 71B -> 78B 0.16889 74B -> 81B 0.11287 **74B -> 82B 0.78376** 74B -> 84B -0.39664	 74B	 82B

Excited State 87: 6.329-?Sym 5.7749 eV 214.69 nm f=0.0089 <S**2>=9.763 59A -> 80A 0.22360 60A -> 80A -0.18872 **61A -> 80A 0.64513** 64A -> 80A 0.11646 76A -> 84A -0.13443 79A -> 90A 0.20198 71B -> 77B -0.16110 71B -> 78B -0.27971 74B -> 81B 0.38528 74B -> 82B 0.16220 74B -> 84B -0.11783	 61A	 80A
Excited State 88: 6.321-?Sym 5.8292 eV 212.69 nm f=0.0514 <S**2>=9.739 59A -> 80A 0.12389 60A -> 80A -0.19070 **61A -> 80A 0.47172** 64A -> 80A 0.19658 76A -> 84A 0.26480 77A -> 83A 0.15804 78A -> 88A 0.14695 79A -> 90A -0.38398 79A -> 91A 0.24363 71B -> 75B -0.12486 **71B -> 78B 0.41846** 72B -> 76B 0.16752	 61A  71B	 80A  78B
Excited State 89: 6.449-?Sym 5.8422 eV 212.22 nm f=0.0107 <S**2>=10.146 61A -> 80A 0.17481 76A -> 84A 0.12524 78A -> 88A -0.16532 78A -> 94A 0.10344 **79A -> 90A 0.69364** 79A -> 91A -0.26914 79A -> 93A 0.10164 71B -> 77B 0.13687 71B -> 78B 0.31240 74B -> 81B -0.31487 74B -> 82B -0.17071	 79A	90A 

Excited State 90: 6.469-?Sym 5.8473 eV 212.04 nm f=0.0082 <S**2>=10.213 **62A -> 80A 0.38232** 68A -> 81A -0.33425 68A -> 82A 0.13438 70A -> 82A -0.11674 75A -> 85A -0.31390 77A -> 84A -0.16024 78A -> 91A -0.13340 79A -> 89A 0.12651 79A -> 92A 0.14813 **68B -> 75B 0.39741** 70B -> 75B -0.21682 71B -> 76B 0.12049 72B -> 78B -0.33849 72B -> 81B 0.10228 72B -> 84B -0.10460 73B -> 82B 0.13377	62A 	 80A
Excited State 91: 6.327-?Sym 5.8572 eV 211.68 nm f=0.0073 <S**2>=9.757 **62A -> 80A 0.72655** 63A -> 80A -0.14402 75A -> 85A 0.33300 72B -> 78B 0.16722 73B -> 81B 0.33301 73B -> 82B -0.36038 73B -> 84B 0.12857	62A 	 80A
Excited State 93: 6.385-?Sym 5.8962 eV 210.28 nm f=0.0296 <S**2>=9.942 62A -> 80A -0.44773 63A -> 80A 0.10854 68A -> 81A -0.19202 70A -> 82A -0.13233 75A -> 85A -0.11214 77A -> 84A 0.10820 78A -> 91A -0.18317 78A -> 93A -0.10755 68B -> 75B 0.15351 70B -> 75B -0.11342 72B -> 77B 0.12350 72B -> 78B 0.22699 **73B -> 81B 0.51666** 73B -> 82B -0.38002 73B -> 84B 0.16440 74B -> 85B 0.10591	 73B	 81B

Excited State 96: 6.349-?Sym 5.9489 eV 208.42 nm f=0.0151 <S**2>=9.827 78A -> 91A 0.39644 78A -> 93A 0.19367 79A -> 88A -0.18866 72B -> 77B 0.11073 72B -> 78B 0.15377 73B -> 81B 0.50080 **73B -> 82B 0.57975** 73B -> 84B -0.19913 74B -> 90B -0.17551	 73B	 82B
Excited State 98: 6.506-?Sym 6.0447 eV 205.11 nm f=0.0218 <S**2>=10.332 70A -> 81A -0.21352 70A -> 82A 0.40742 77A -> 84A 0.11188 78A -> 87A -0.12325 79A -> 86A 0.19134 79A -> 88A -0.24673 **79A -> 89A 0.68558** 79A -> 92A 0.25361	 79A	 89A
Excited State 100: 6.471-?Sym 6.0882 eV 203.65 nm f=0.0184 <S**2>=10.218 68A -> 81A -0.18610 70A -> 81A -0.39425 **70A -> 82A 0.60026** 70A -> 84A -0.11603 78A -> 87A -0.14533 79A -> 88A 0.30610 79A -> 89A -0.41250 79A -> 94A -0.15408 73B -> 80B -0.11038	 70A	 82A

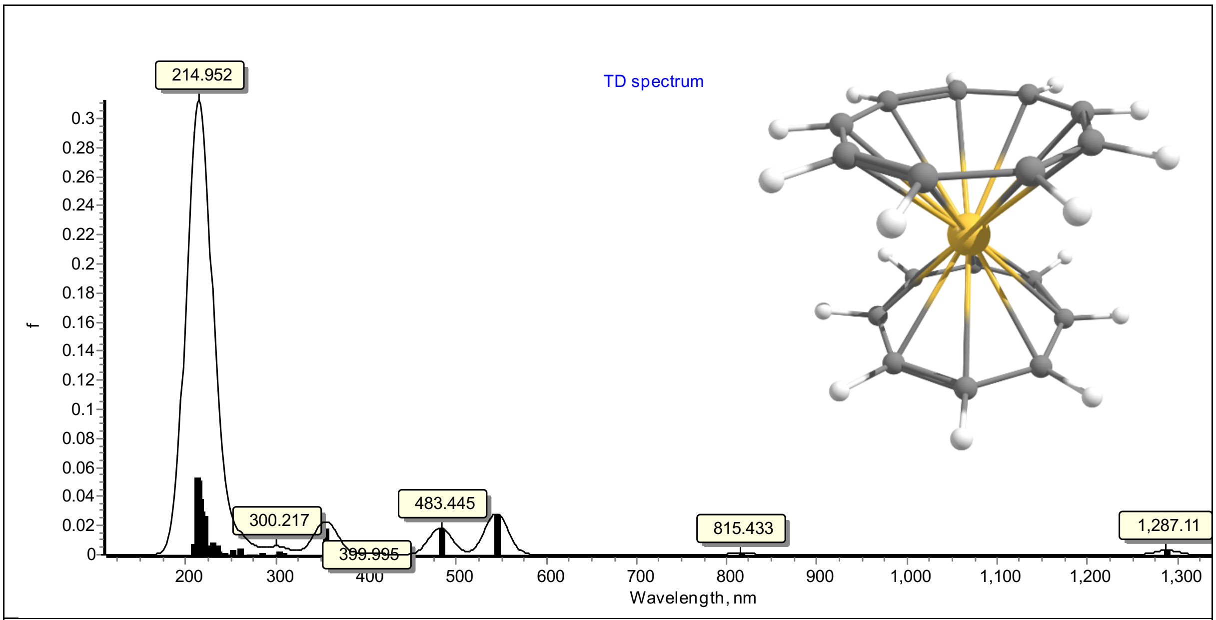
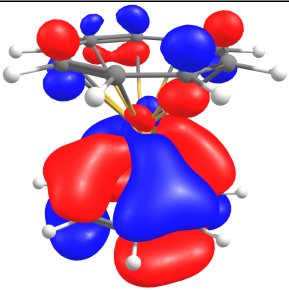
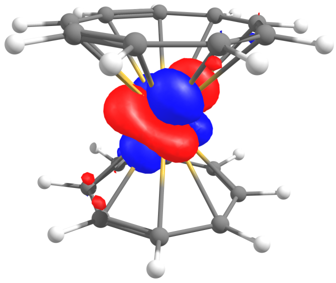
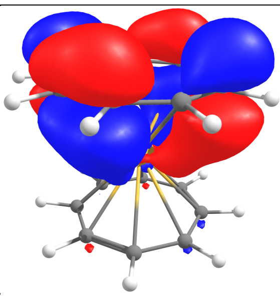
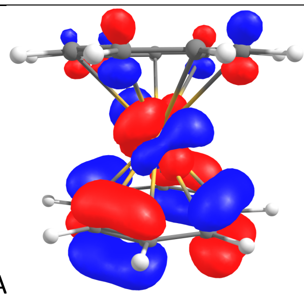
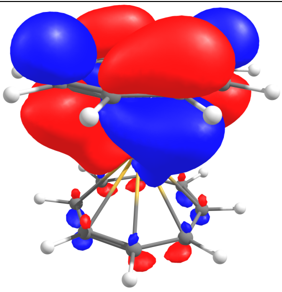
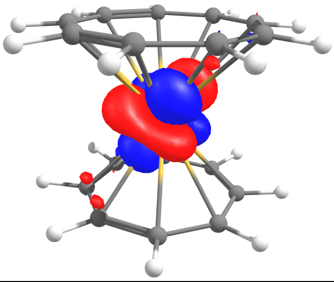
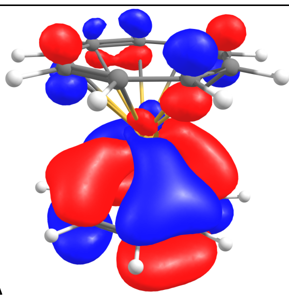
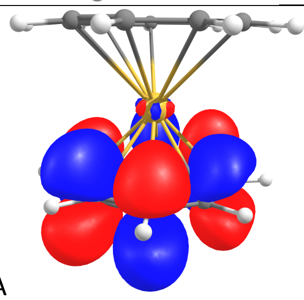
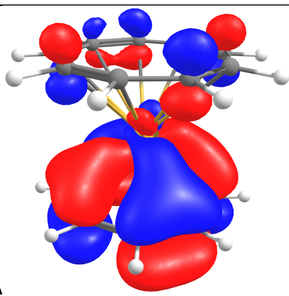
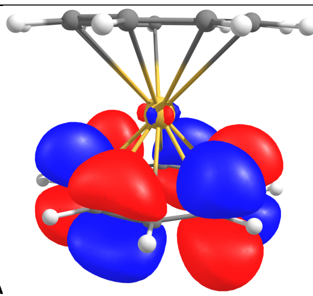
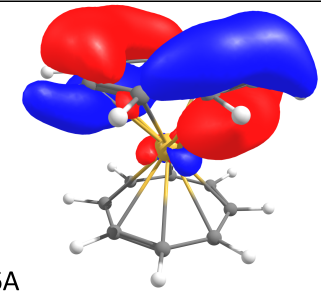
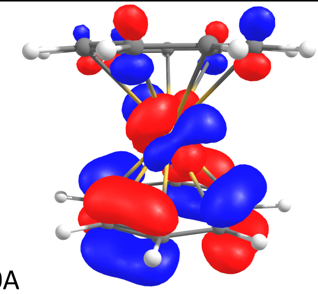
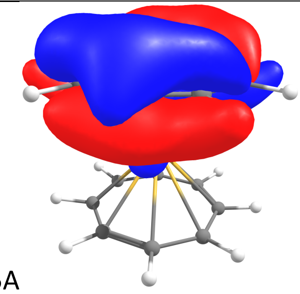
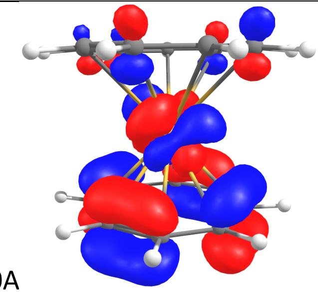
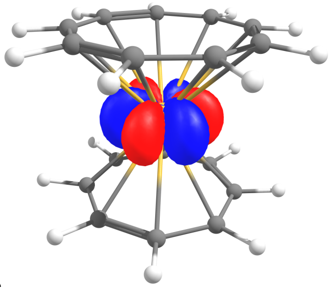
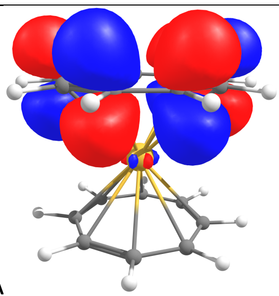
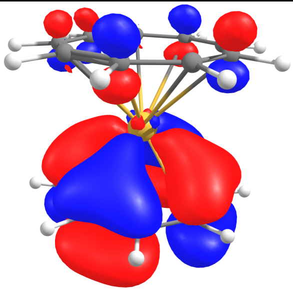
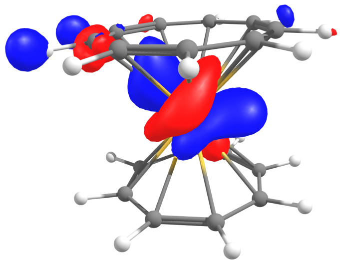
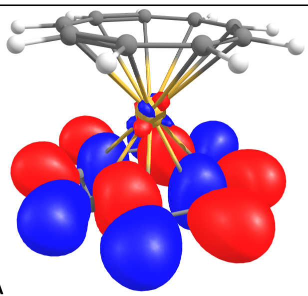
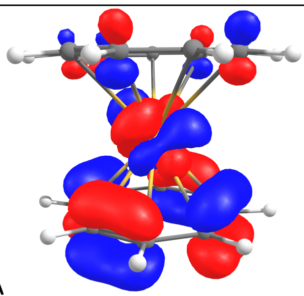
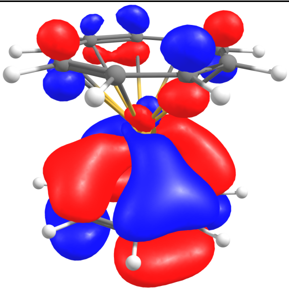
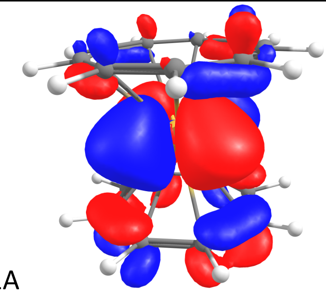
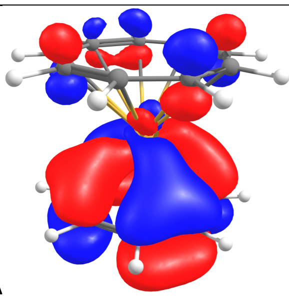
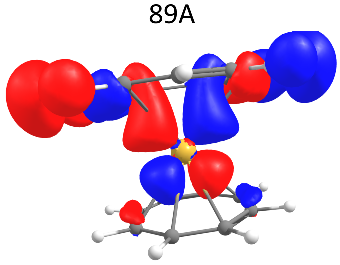
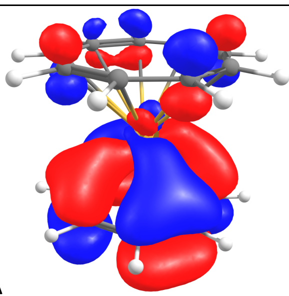
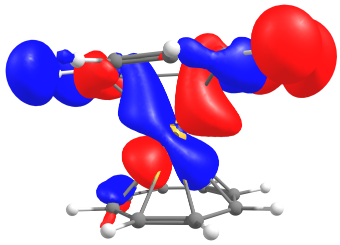
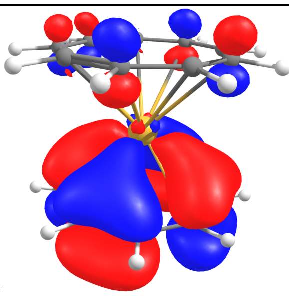
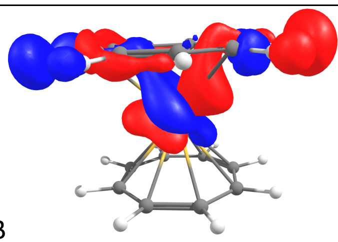
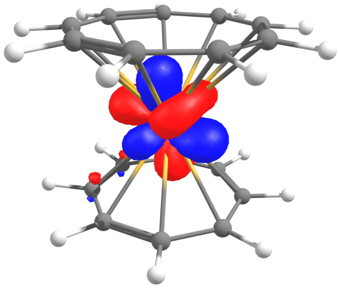
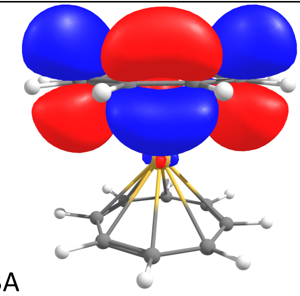
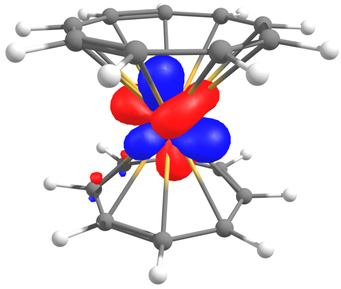
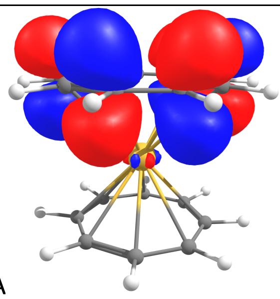
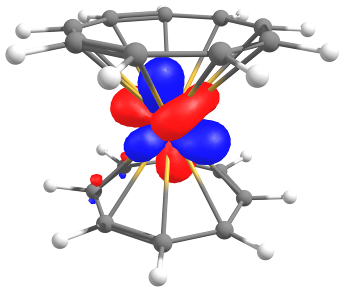
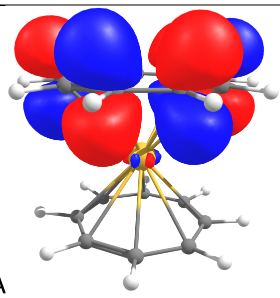


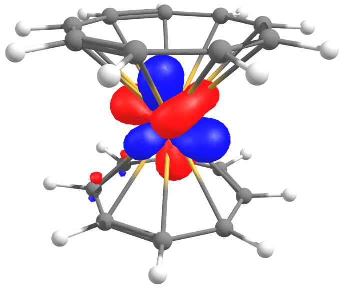
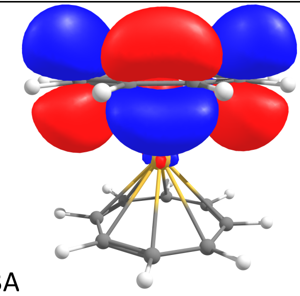
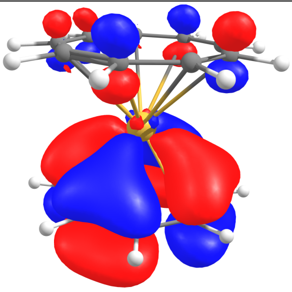
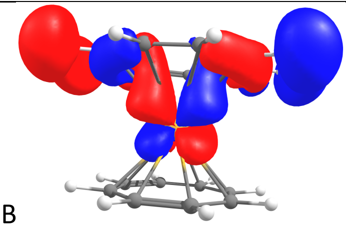
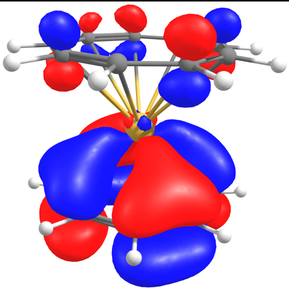
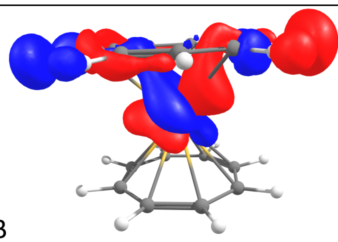
Figure S93**: Computed TD spectrum for **2-Sm-cis.

79A,74B: HOMO		
Excited State 14: 6.398-?Sym 2.2764 eV 544.66 nm f=0.0280 <S**2>=9.984 72A -> 81A 0.21663 76A -> 81A 0.11243 77A -> 80A -0.46410 78A -> 80A -0.42772 **79A -> 81A 0.73873** 78A <- 80A 0.18161	 79A	81A 
Excited State 16: 6.360-?Sym 2.5685 eV 482.72 nm f=0.0182 <S**2>=9.861 71A -> 80A -0.18864 76A -> 81A 0.16330 **77A -> 80A 0.85501** 78A -> 80A -0.23750 79A -> 81A 0.33430	 77A	 80A
Excited State 28: 6.431-?Sym 3.5026 eV 353.98 nm f=0.0181 <S**2>=10.090 72A -> 81A -0.13570 **76A -> 81A 0.96807** 79A -> 81A -0.11552	 76A	81A 
Excited State 49: 6.592-?Sym 4.7879 eV 258.95 nm f=0.0044 <S**2>=10.613 69A -> 81A -0.16307 70A -> 80A 0.34176 78A -> 87A 0.28728 **79A -> 86A 0.54295** 73B -> 80B 0.47509 74B -> 79B 0.45812	 79A	 86A
Excited State 50: 6.592-?Sym 4.7892 eV 258.88 nm f=0.0045 <S**2>=10.613 69A -> 80A -0.31312 70A -> 81A -0.18044 71A -> 80A 0.15642 78A -> 86A -0.29043 **79A -> 87A 0.54191** 73B -> 79B -0.47241 74B -> 80B 0.45995	 79A	 87A

Excited State 63: 6.320-?Sym 5.3074 eV 233.61 nm f=0.0067 <S**2>=9.736 62A -> 80A -0.13540 63A -> 80A 0.19812 **66A -> 80A 0.90873** 71A -> 84A -0.11427 76A -> 82A -0.17135 77A -> 83A -0.16465 72B -> 75B 0.10075	 66A	 80A
Excited State 64: 6.322-?Sym 5.3179 eV 233.15 nm f=0.0053 <S**2>=9.741 64A -> 80A -0.25526 **65A -> 80A 0.89118** 72A -> 84A -0.15247 76A -> 83A 0.15539 77A -> 82A -0.14959 78A -> 91A 0.14379	 65A	 80A
Excited State 73: 6.174-?Sym 5.4335 eV 228.18 nm f=0.0042 <S**2>=9.279 **74A -> 82A 0.86171** 75A -> 83A 0.11266 78A -> 90A 0.11461 78A -> 92A 0.29121 74B -> 83B 0.34786 74B -> 84B -0.11603	 74A	 82A
Excited State 78: 6.238-?Sym 5.5190 eV 224.65 nm f=0.0045 <S**2>=9.479 61A -> 80A 0.27873 74A -> 82A -0.37799 75A -> 83A -0.13455 78A -> 90A 0.29890 78A -> 92A 0.18750 79A -> 91A 0.27013 **74B -> 83B 0.68361** 74B -> 86B -0.14385	 74B	83B 
Excited State 83: 6.371-?Sym 5.5945 eV 221.62 nm f=0.0060 <S**2>=9.896 **61A -> 80A 0.70874** 74A -> 82A 0.10114 78A -> 90A 0.39765 78A -> 92A -0.20075 78A -> 94A -0.16530 79A -> 91A -0.41177 74B -> 83B -0.19892	 61A	 80A

Excited State 85: 6.507-?Sym 5.6300 eV 220.22 nm f=0.0267 <S**2>=10.334 61A -> 80A 0.36482 74A -> 82A 0.13124 78A -> 92A -0.18152 **79A -> 91A 0.75075** 73B -> 81B -0.10824 73B -> 89B -0.25997 74B -> 83B -0.24494 74B -> 90B 0.25462	 79A	 91A
Excited State 89: 6.359-?Sym 5.7397 eV 216.01 nm f=0.0302 <S**2>=9.860 66A -> 80A 0.11094 73A -> 83A -0.13819 76A -> 82A 0.19943 77A -> 83A 0.19366 **79A -> 89A 0.81627** 79A -> 93A -0.22217 71B -> 76B 0.18806 72B -> 75B -0.18338 74B -> 84B -0.12284	 79A	89A 
Excited State 90: 6.346-?Sym 5.7505 eV 215.61 nm f=0.0388 <S**2>=9.817 65A -> 80A -0.13202 73A -> 82A 0.11290 76A -> 83A 0.22404 77A -> 82A -0.22019 79A -> 88A 0.17400 **79A -> 90A 0.68238** 79A -> 92A -0.36894 79A -> 94A -0.21440 71B -> 75B 0.20839 72B -> 76B 0.21423 74B -> 79B -0.10421	 79A	90A 
Excited State 91: 6.095-?Sym 5.7829 eV 214.40 nm f=0.0048 <S**2>=9.038 73A -> 83A 0.18201 **74B -> 84B 0.82656** 74B -> 86B -0.44009	 74B	 84B

Excited State 92: 6.179-?Sym 5.8133 eV 213.28 nm f=0.0429 <S**2>=9.294 66A -> 80A -0.13130 72A -> 82A -0.10484 **73A -> 83A 0.71267** 76A -> 82A -0.22161 77A -> 83A -0.21942 78A -> 86A -0.15237 79A -> 87A 0.14084 79A -> 89A 0.37392 79A -> 93A -0.11016 71B -> 76B -0.21540 72B -> 75B 0.20979 73B -> 79B 0.12637	73A 	 83A
Excited State 93: 6.163-?Sym 5.8138 eV 213.26 nm f=0.0190 <S**2>=9.246 65A -> 80A -0.11137 **73A -> 82A 0.84460** 76A -> 83A 0.14260 77A -> 82A -0.14974 78A -> 87A 0.10522 79A -> 88A -0.16944 79A -> 90A -0.27908 79A -> 92A 0.11107 71B -> 75B 0.13199 72B -> 76B 0.14904	73A 	 82A
Excited State 95: 6.167-?Sym 5.8411 eV 212.26 nm f=0.0507 <S**2>=9.260 65A -> 80A 0.14727 72A -> 83A -0.13244 **73A -> 82A 0.48132** 76A -> 83A -0.25489 77A -> 82A 0.23552 78A -> 87A -0.19477 79A -> 86A -0.17782 79A -> 90A 0.33079 79A -> 92A -0.11104 79A -> 94A -0.10986 71B -> 75B -0.24750 72B -> 76B -0.23909 73B -> 80B 0.16267 73B -> 84B -0.28883 73B -> 86B 0.21124 74B -> 79B 0.11386 74B -> 85B -0.15865 74B -> 87B -0.18554	73A 	 82A

Excited State 96: 6.160-?Sym 5.8578 eV 211.66 nm f=0.0532 <S**2>=9.238 66A -> 80A 0.16964 72A -> 82A 0.14740 **73A -> 83A 0.64601** 76A -> 82A 0.25553 77A -> 83A 0.24187 78A -> 86A 0.18665 79A -> 87A -0.18354 79A -> 89A -0.24945 71B -> 76B 0.25215 72B -> 75B -0.24521 73B -> 79B -0.15719 74B -> 80B 0.12044 74B -> 84B -0.17131	73A 	 83A
Excited State 97: 6.091-?Sym 5.8608 eV 211.55 nm f=0.0041 <S**2>=9.026 **74B -> 85B 0.76434** 74B -> 87B 0.56771 74B -> 89B 0.14049	 74B	 85B
Excited State 98: 6.175-?Sym 5.8774 eV 210.95 nm f=0.0184 <S**2>=9.283 73A -> 82A 0.10812 76A -> 83A -0.13190 77A -> 82A 0.13347 79A -> 90A 0.12873 71B -> 75B -0.12913 72B -> 76B -0.13009 73B -> 83B 0.13559 **73B -> 84B 0.80505** 73B -> 86B -0.39485	 73B	 84B

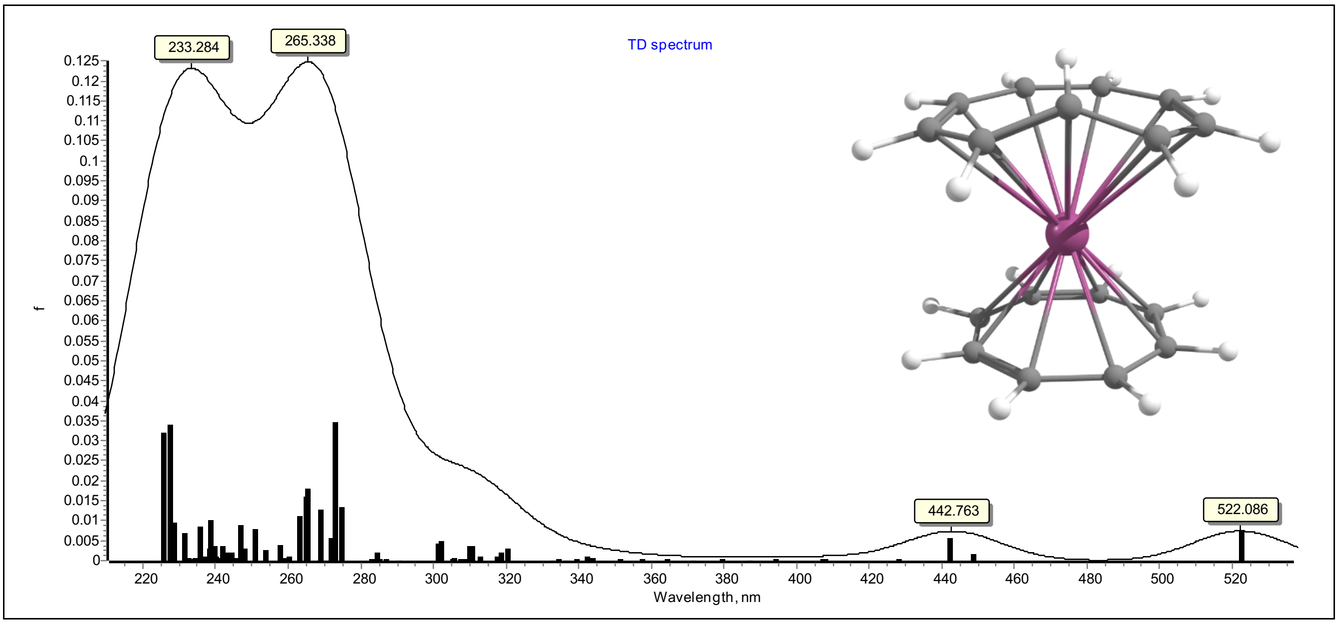
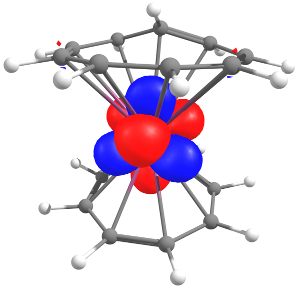
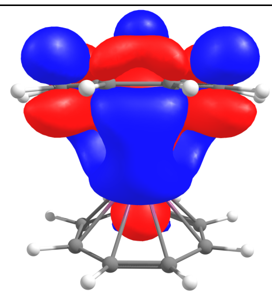
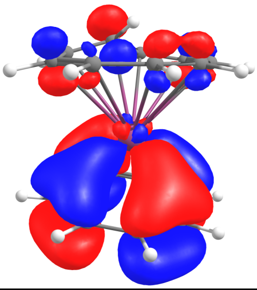
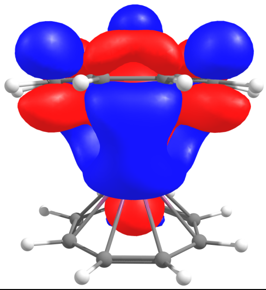
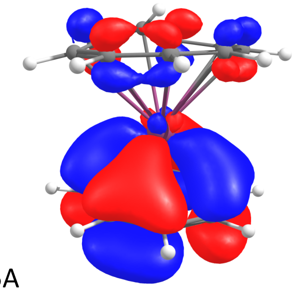
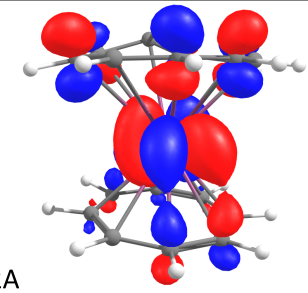
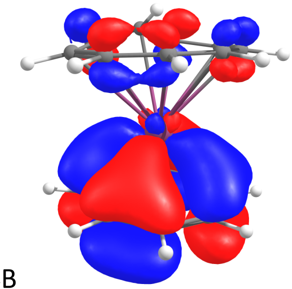
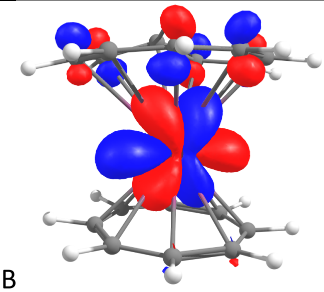
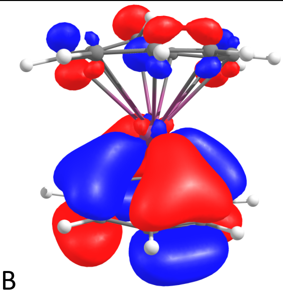
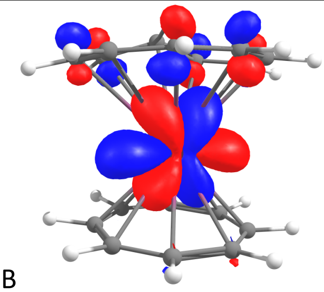
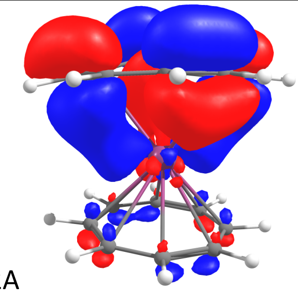
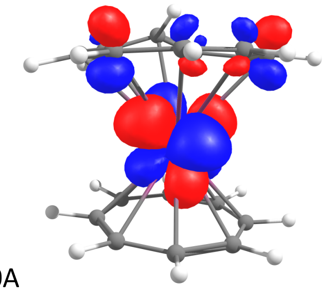
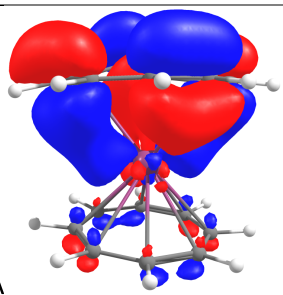
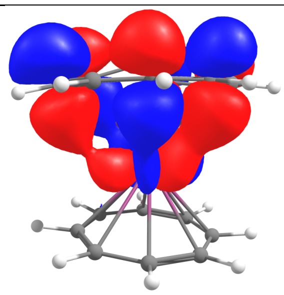
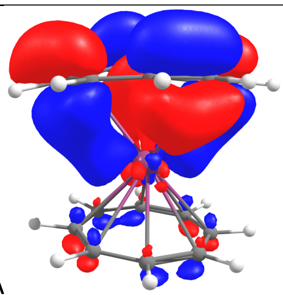
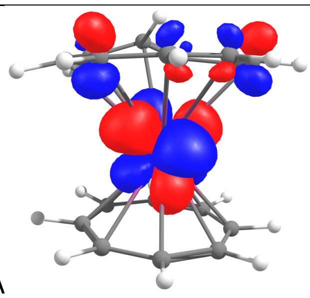
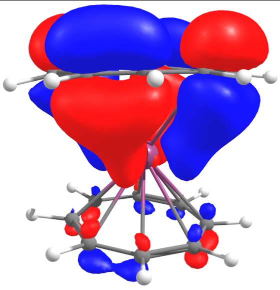
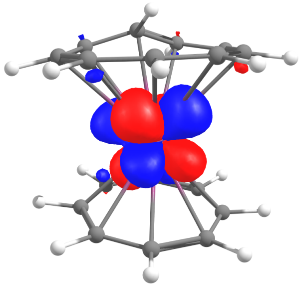
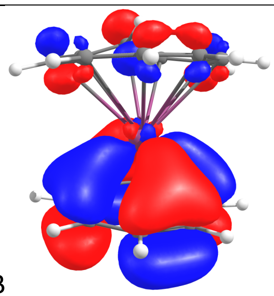
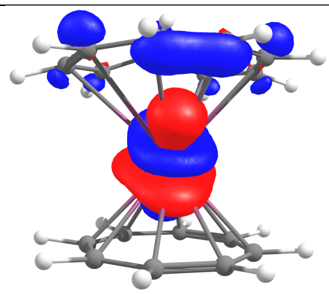
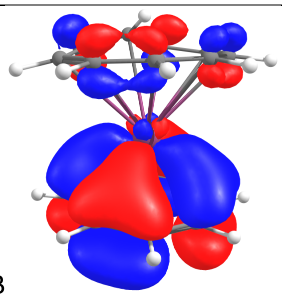
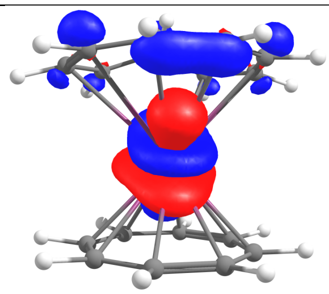
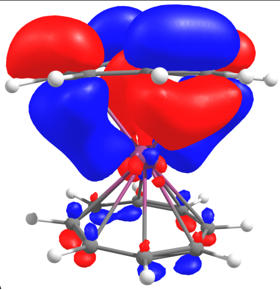
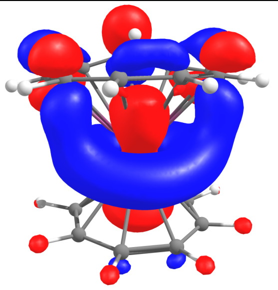
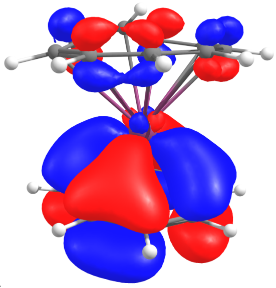
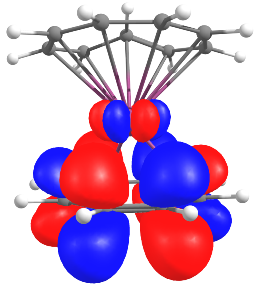
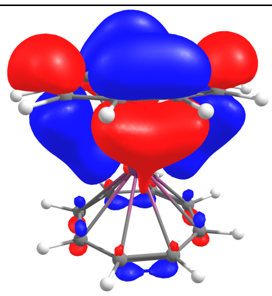
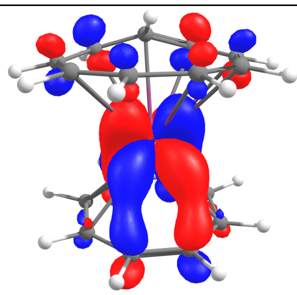


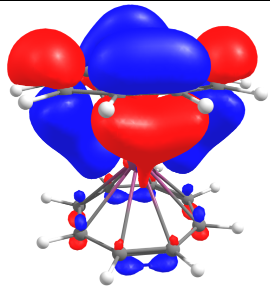
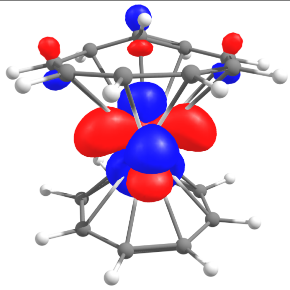
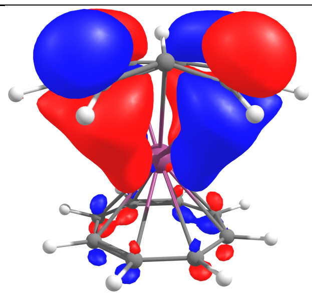
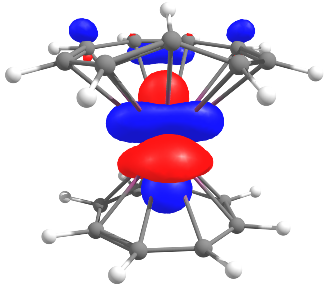
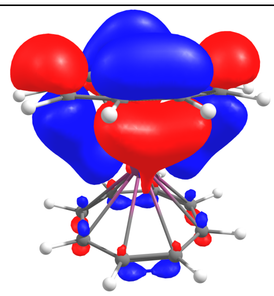
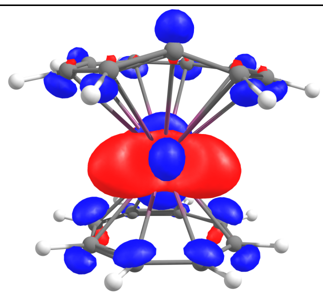
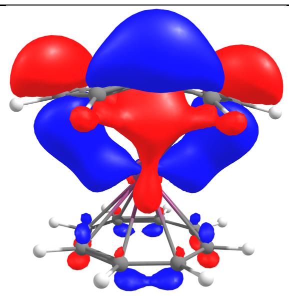
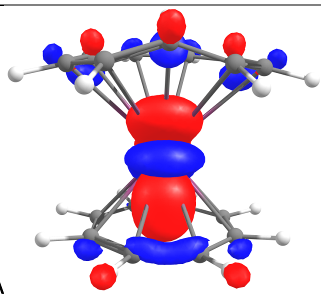
Figure S94**: Computed TD spectrum for **2-Ce-trans.

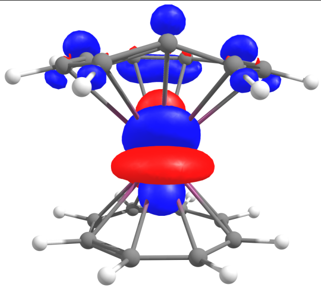
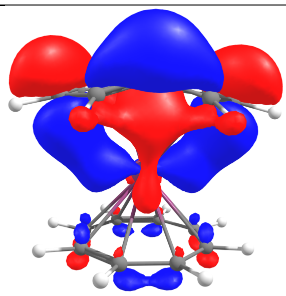
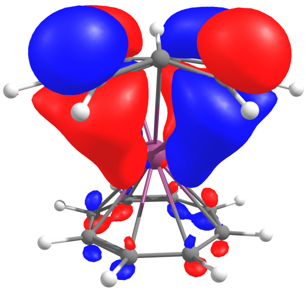
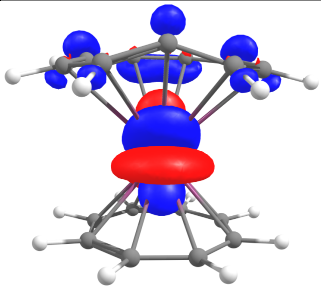
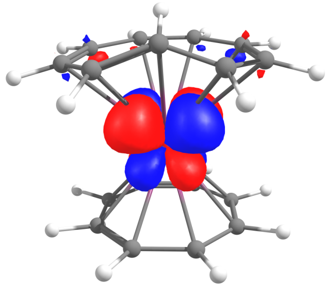
75A and 74B: HOMO		
Excited State 7: 2.015-?Sym 2.3746 eV **522.12** nm f=0.0074 <S**2>=0.765 **73A -> 76A 0.85893** 73A -> 80A -0.11851 73A -> 81A 0.45661	 73A	 76A
Excited State 11: 2.144-?Sym 2.8053 eV **441.97** nm f=0.0056 <S**2>=0.899 72A -> 76A 0.11227 **74A -> 76A 0.67846** 74A -> 81A 0.12618 **73B -> 75B 0.66309** 74B -> 76B -0.15041	74A (73B) 	76A (75B) 
Excited State 43: 2.954-?Sym 4.0024 eV **309.77** nm f=0.0035 <S**2>=1.932 71A -> 77A -0.40987 75A -> 77A -0.29122 **75A -> 82A 0.53320** 75A -> 83A -0.45897 71B -> 76B 0.22155 72B -> 75B 0.19255 73B -> 82B 0.26234 74B -> 83B 0.20979	 75A	 82A
Excited State 49: 2.658-?Sym 4.1106 eV **301.62** nm f=0.0049 <S**2>=1.516 71A -> 77A -0.11900 74A -> 81A -0.10164 75A -> 82A -0.12304 71B -> 76B 0.24754 73B -> 82B 0.13278 73B -> 84B -0.11077 74B -> 76B 0.24246 74B -> 79B -0.42606 **74B -> 81B 0.72942** 74B -> 83B 0.15442	 74B	 81B

Excited State 50: 2.624-?Sym 4.1169 eV **301.16** nm f=0.0043 <S**2>=1.472 74A -> 82A -0.14367 72B -> 76B 0.25692 73B -> 76B 0.23005 73B -> 79B -0.41885 **73B -> 81B** 0.67980 73B -> 83B 0.38944	 73B	 81B
Excited State 59: 2.561-?Sym 4.5213 eV **274.22** nm f=0.0135 <S**2>=1.389 71A -> 77A 0.42315 71A -> 79A 0.23642 71A -> 83A -0.14003 **72A -> 80A** 0.54680 71B -> 76B 0.36051 72B -> 75B 0.11473 72B -> 77B 0.40639 73B -> 80B -0.10888 73B -> 85B -0.23370	 72A	 80A
Excited State 60: 2.425-?Sym 4.5477 eV **272.63** nm f=0.0346 <S**2>=1.220 71A -> 76A -0.18540 71A -> 78A -0.16972 71A -> 80A -0.33073 **72A -> 77A** 0.42156 72A -> 82A 0.23841 72A -> 83A -0.15227 71B -> 75B -0.21729 71B -> 77B -0.37649 72B -> 76B 0.39699 74B -> 80B 0.14323 74B -> 85B 0.34449	 72A	 77A
Excited State 61: 2.768-?Sym 4.5654 eV **271.57** nm f=0.0055 <S**2>=1.665 71A -> 77A -0.22476 71A -> 79A 0.27958 71A -> 82A -0.12322 **72A -> 80A** 0.63813 73A -> 84A -0.23945 73A -> 85A -0.23815 71B -> 76B -0.18554 72B -> 75B -0.10761 72B -> 77B -0.39637 73B -> 85B 0.22892	 72A	 80A

Excited State 63: 2.834-?Sym 4.6175 eV **268.51** nm f=0.0127 <S**2>=1.758 71A -> 77A -0.21368 **71A -> 79A** 0.56896 71A -> 83A 0.10882 72A -> 76A -0.12307 72A -> 78A -0.21156 72A -> 81A -0.49393 74A -> 87A 0.11144 71B -> 76B -0.30253 72B -> 77B 0.22558 73B -> 85B -0.23440	 71A	 79A
Excited State 65: 2.843-?Sym 4.6787 eV **265.00** nm f=0.0179 <S**2>=1.771 71A -> 77A 0.17300 71A -> 79A 0.42721 71A -> 82A 0.17033 72A -> 80A -0.26624 73A -> 84A -0.16121 73A -> 85A -0.12416 73A -> 86A 0.22598 73A -> 87A -0.19960 74A -> 86A -0.17140 74A -> 87A -0.18039 75A -> 88A -0.10628 71B -> 76B 0.12455 71B -> 83B -0.11432 72B -> 82B 0.10991 **73B -> 85B** 0.49742 73B -> 86B 0.10086 74B -> 83B -0.12036 74B -> 87B 0.15151	 73B	 85B
Excited State 66: 2.789-?Sym 4.6815 eV **264.84** nm f=0.0160 <S**2>=1.694 71A -> 76A 0.10116 71A -> 78A 0.14864 71A -> 80A -0.40270 71A -> 81A 0.16417 72A -> 77A -0.17910 72A -> 82A -0.28513 73A -> 89A 0.31989 75A -> 86A -0.18892 75A -> 87A -0.21133 71B -> 77B 0.12272 72B -> 76B -0.12434 73B -> 87B -0.13524 74B -> 78B 0.10169 **74B -> 85B** 0.56194	 74B	 85B

74B -> 86B 0.13926		
Excited State 67: 3.099-?Sym 4.7157 eV **262.92** nm f=0.0110 <S**2>=2.150 71A -> 79A 0.39050 72A -> 80A -0.19410 **72A -> 81A** 0.47865 74A -> 86A 0.10037 74A -> 87A 0.16787 75A -> 88A 0.11893 71B -> 76B 0.13974 71B -> 83B -0.10546 72B -> 77B -0.36396 72B -> 82B 0.15742 73B -> 82B 0.10326 73B -> 85B -0.42261 73B -> 86B -0.10729 74B -> 87B -0.11350	 72A	 81A
Excited State 74: 2.946-?Sym 4.9452 eV **250.71** nm f=0.0078 <S**2>=1.919 71A -> 77A 0.12711 71A -> 83A -0.20567 72A -> 81A -0.35504 72A -> 84A 0.24139 72A -> 85A -0.20245 73A -> 86A -0.24463 73A -> 87A 0.13450 **75A -> 88A** 0.43686 72B -> 77B -0.26775 72B -> 78B 0.22056 72B -> 80B -0.14672 73B -> 85B 0.23498 74B -> 87B -0.38785	 75A	 88A
Excited State 77: 2.913-?Sym 5.0285 eV **246.56** nm f=0.0088 <S**2>=1.871 71A -> 81A 0.39119 71A -> 84A -0.18908 71A -> 85A 0.15562 73A -> 89A 0.11432 73A -> 91A -0.19933 74A -> 88A 0.21505 75A -> 86A 0.14555 75A -> 87A 0.19361 71B -> 77B 0.31975 71B -> 78B -0.30119 71B -> 80B 0.18254 72B -> 76B 0.12686 **72B -> 79B** 0.48572 72B -> 81B -0.11330	 72B	 79B

73B -> 87B -0.20114 74B -> 86B -0.12657 74B -> 88B -0.14334		
Excited State 88: 2.841-?Sym 5.2006 eV **238.40** nm f=0.0102 <S**2>=1.768 71A -> 82A 0.14948 71A -> 83A -0.18155 72A -> 85A -0.11378 73A -> 90A 0.29129 73A -> 92A 0.18877 71B -> 76B -0.13254 71B -> 79B 0.18970 71B -> 81B 0.49600 71B -> 83B 0.12227 72B -> 77B 0.11810 **72B -> 82B** 0.59280 72B -> 84B 0.17147	 72B	 82B
Excited State 96: 2.704-?Sym 5.3611 eV **231.27** nm f=0.0070 <S**2>=1.578 72A -> 82A -0.10185 71B -> 78B -0.10818 71B -> 80B -0.36256 71B -> 82B 0.38810 **71B -> 84B** 0.78815 72B -> 79B -0.10451 72B -> 81B 0.10245	 71B	 84B
Excited State 97: 3.182-?Sym 5.4300 eV **228.33** nm f=0.0094 <S**2>=2.281 72A -> 84A -0.24022 72A -> 85A -0.31392 71B -> 81B -0.14804 71B -> 83B -0.34128 72B -> 78B 0.39596 **72B -> 80B** 0.64956 72B -> 84B 0.26654	 72B	 80B
Excited State 99: 2.570-?Sym 5.4607 eV **227.05** nm f=0.0341 <S**2>=1.401 71A -> 82A 0.10059 **72A -> 84A** 0.53125 **72A -> 85A** 0.51786 71B -> 83B -0.52455 72B -> 80B 0.11405 72B -> 82B 0.21782 72B -> 84B -0.11946	 72A	 84A

		 85A
Excited State 100: 2.165-?Sym 5.4986 eV **225.48** nm f=0.0320 <S**2>=0.922 71A -> 82A -0.11971 72A -> 84A 0.28117 **72A -> 85A** 0.40535 73A -> 86A -0.10891 73A -> 87A -0.16459 71B -> 81B 0.11677 **71B -> 83B** 0.40901 72B -> 78B 0.19893 72B -> 80B 0.35291 72B -> 82B -0.25174 72B -> 84B 0.39366 73B -> 86B 0.16818 74B -> 89B 0.16732	 72A  71B	 85A  83B

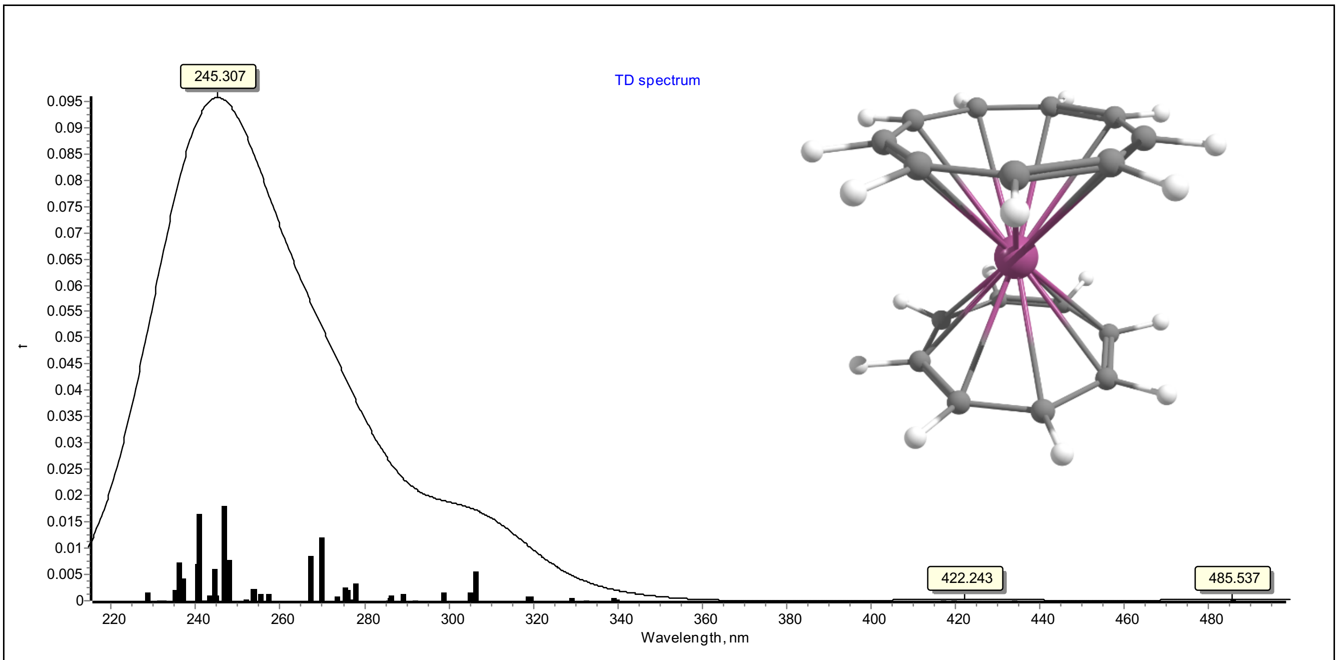
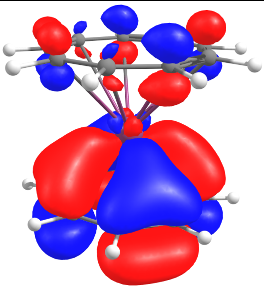
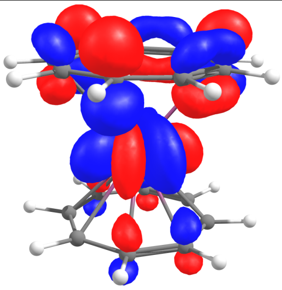
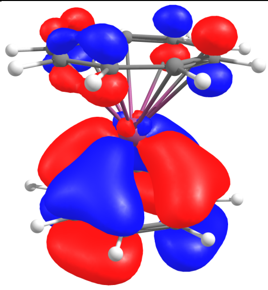
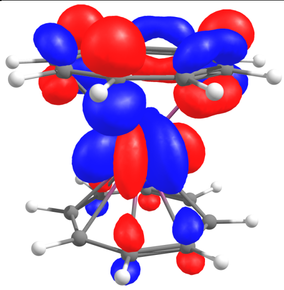
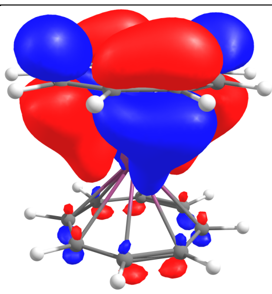
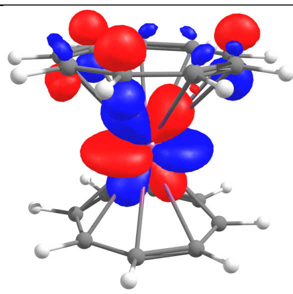
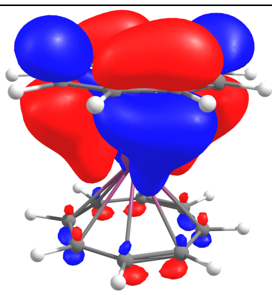
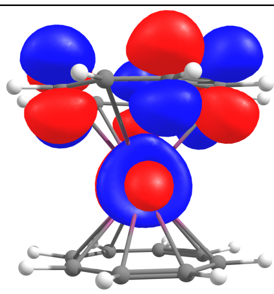
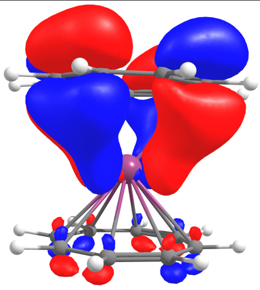
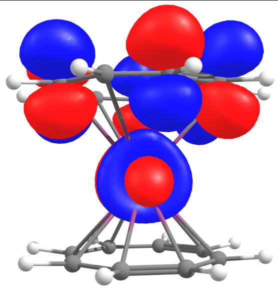
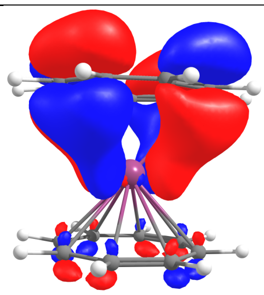
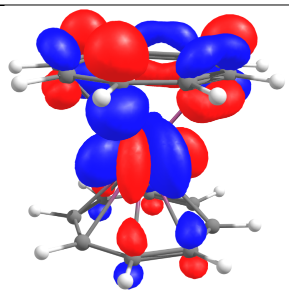
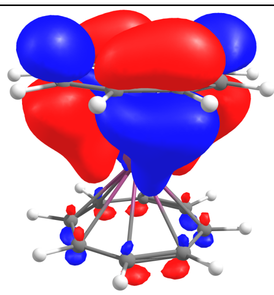
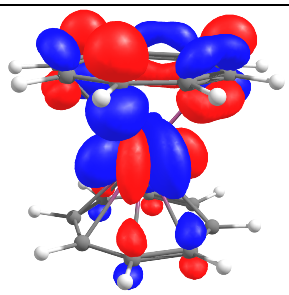
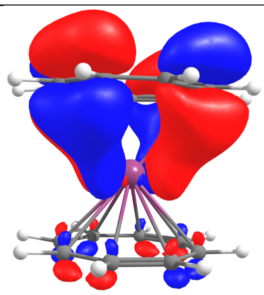
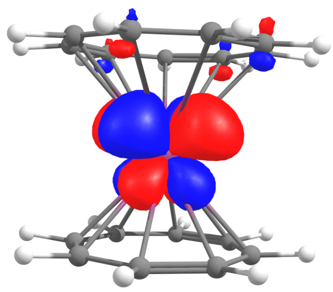
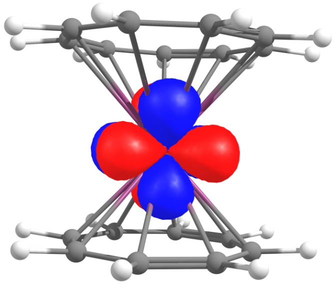
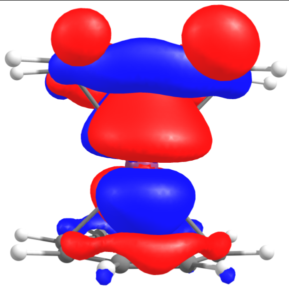
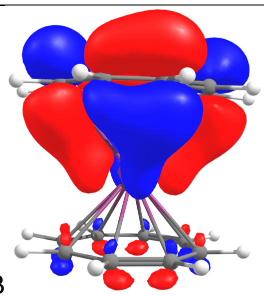
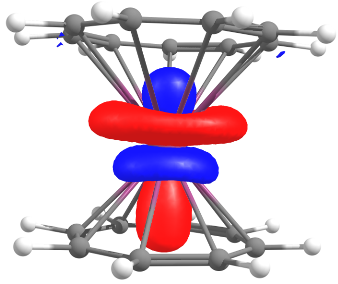
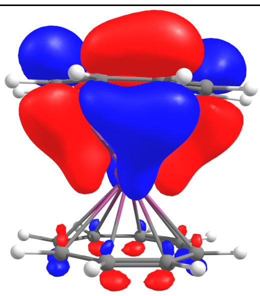
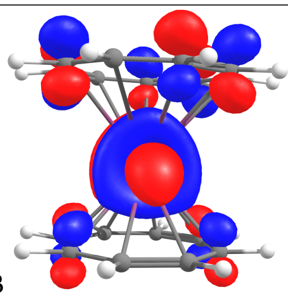
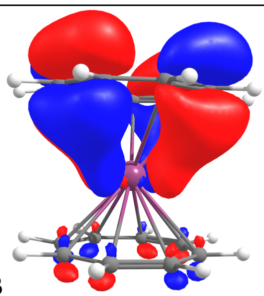
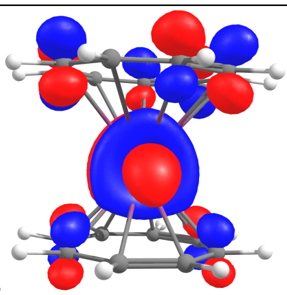
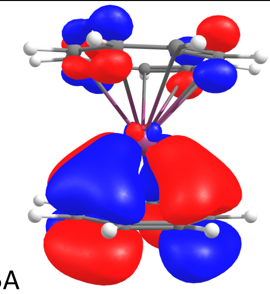
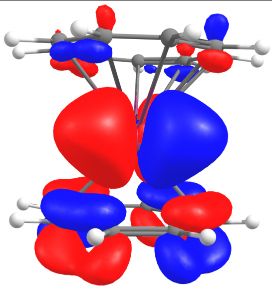
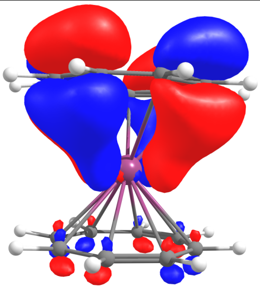
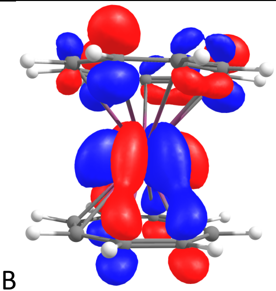
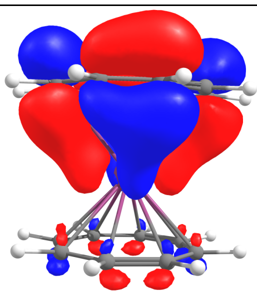
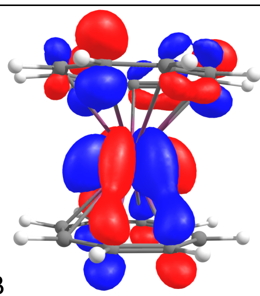


Figure S95**: Computed TD spectrum for **2-Ce-trans

75A and 74B: HOMO		
Excited State 43: 2.633-?Sym 4.0495 eV 306.17 nm f=0.0049 <S**2>=1.483 72A -> 77A -0.29714 74A -> 77A -0.24321 74A -> 79A 0.17003 **74A -> 83A 0.62727** 71B -> 75B 0.20132 72B -> 76B 0.18002 73B -> 82B 0.27399 74B -> 76B 0.16439 74B -> 81B -0.45996 74B -> 85B -0.12250	 74A	 83A
Excited State 44: 2.315-?Sym 4.0508 eV 306.08 nm f=0.0054 <S**2>=1.089 71A -> 77A -0.23997 72A -> 76A -0.30091 74A -> 81A 0.21539 75A -> 77A -0.20968 75A -> 79A 0.15162 **75A -> 83A 0.62482** 72B -> 75B 0.17370 73B -> 81B 0.17562 74B -> 75B -0.10517 74B -> 82B 0.49663	 75A	 83A
Excited State 58: 2.771-?Sym 4.4635 eV 277.77 nm f=0.0032 <S**2>=1.670 71A -> 76A -0.27219 71A -> 81A -0.22225 72A -> 77A 0.21385 **72A -> 79A 0.83361** 72B -> 76B -0.19728 74B -> 85B 0.24478	 72A	 79A
Excited State 67: 2.678-?Sym 4.6418 eV 267.11 nm f=0.0084 <S**2>=1.543 71A -> 77A 0.28870 71A -> 79A -0.30547 71A -> 83A 0.13573 72A -> 76A 0.18387 **72A -> 81A 0.74747** 72B -> 75B 0.40823	 72A	 81A

Excited State 68: 2.634-?Sym 4.6427 eV 267.05 nm f=0.0084 <S**2>=1.485 71A -> 76A 0.16550 **71A -> 81A 0.70196** 72A -> 77A -0.26998 72A -> 79A 0.37840 72A -> 83A -0.13882 73A -> 87A -0.16094 71B -> 75B -0.41436	 71A	 81A
Excited State 75: 2.815-?Sym 5.0087 eV 247.54 nm f=0.0078 <S**2>=1.731 71A -> 77A 0.15962 **71A -> 83A 0.58867** 72A -> 81A -0.15237 72A -> 84A -0.33932 73A -> 89A -0.42714 73A -> 91A 0.12270 75A -> 88A 0.26879 71B -> 76B 0.20231 71B -> 81B 0.18133 72B -> 79B -0.10894 74B -> 86B -0.21416	 71A	 83A
Excited State 76: 3.021-?Sym 5.0103 eV 247.46 nm f=0.0073 <S**2>=2.032 71A -> 81A 0.15811 71A -> 84A -0.11976 72A -> 77A 0.15043 **72A -> 83A 0.63991** 73A -> 87A -0.35691 74A -> 88A 0.37029 71B -> 79B 0.12752 71B -> 82B -0.11076 72B -> 76B -0.18962 72B -> 81B -0.17980 73B -> 86B -0.30482 74B -> 85B 0.12747	 72A	 83A
Excited State 78: 2.970-?Sym 5.0293 eV 246.52 nm f=0.0180 <S**2>=1.955 **71A -> 84A 0.76960** 72A -> 83A 0.11670 73A -> 90A 0.41443 73A -> 93A -0.10933 75A -> 84A -0.11653 75A -> 87A 0.15224 71B -> 78B -0.11192 71B -> 80B 0.14637 71B -> 83B 0.18341	 71A	84A 

72B -> 84B -0.23758		
Excited State 81: 2.339-?Sym 5.0762 eV 244.25 nm f=0.0059 <S**2>=1.118 71A -> 84A -0.40126 **73A -> 90A 0.81339** 73A -> 93A -0.20560 73A -> 95A -0.14595 74A -> 89A 0.10117 71B -> 83B -0.16005 72B -> 84B 0.11375 73B -> 88B -0.12299	 73A	 90A
Excited State 87: 2.808-?Sym 5.1539 eV 240.56 nm f=0.0042 <S**2>=1.721 73A -> 90A 0.11700 71B -> 77B -0.13279 **71B -> 78B 0.74986** 71B -> 80B -0.59254 72B -> 84B -0.13940	 71B	78B 
Excited State 88: 3.027-?Sym 5.1571 eV 240.42 nm f=0.0165 <S**2>=2.040 71A -> 83A -0.26753 74A -> 86A -0.19163 75A -> 88A -0.10653 71B -> 76B 0.16805 **71B -> 81B 0.66936** 72B -> 75B 0.19575 72B -> 82B 0.43583 73B -> 87B 0.24384 74B -> 86B 0.22114	 71B	 81B
Excited State 89: 3.072-?Sym 5.1612 eV 240.22 nm f=0.0069 <S**2>=2.109 72A -> 83A 0.17318 73A -> 87A 0.18538 74A -> 89A 0.25753 75A -> 86A -0.18742 75A -> 87A -0.28876 71B -> 75B -0.12636 71B -> 79B 0.20357 71B -> 82B -0.17738 72B -> 76B 0.11320 **72B -> 81B 0.60111** 73B -> 86B -0.16295 73B -> 88B -0.28641 74B -> 87B 0.23375 74B -> 90B 0.22015	 72B	 81B

Excited State 90: 3.269-?Sym 5.1623 eV 240.17 nm f=0.0037 <S**2>=2.422 71A -> 84A -0.18428 72A -> 83A 0.10007 73A -> 87A 0.12533 74A -> 89A -0.36718 75A -> 86A -0.12673 **75A -> 87A 0.43950** 71B -> 79B 0.14285 71B -> 82B -0.13033 72B -> 81B 0.39392 73B -> 86B -0.10929 **73B -> 88B 0.42412** 74B -> 87B 0.15606 74B -> 90B -0.32362	 75A	 87A
Excited State 91: 2.581-?Sym 5.2397 eV 236.63 nm f=0.0042 <S**2>=1.416 71A -> 83A 0.10781 72A -> 81A -0.19861 71B -> 81B -0.55304 **72B -> 82B 0.75165** 72B -> 83B -0.14074	 72B	 82B
Excited State 92: 2.554-?Sym 5.2573 eV 235.83 nm f=0.0073 <S**2>=1.380 71A -> 81A 0.19729 72A -> 83A 0.13430 73A -> 87A -0.12713 71B -> 75B 0.10071 **71B -> 82B 0.81990** 72B -> 76B -0.10215 72B -> 81B 0.40081 72B -> 84B 0.10540 73B -> 86B 0.10404	 71B	 82B

Optimized structure

3-disp

Ce	4.577791000	3.235332000	4.478832000
C	1.912585000	4.517356000	4.107971000
H	1.496519000	4.775668000	5.079991000
C	2.717308000	5.427973000	3.407535000
H	2.740962000	6.463965000	3.737212000
C	3.605211000	5.113529000	2.350205000
H	4.097291000	6.002171000	1.960703000
C	4.113146000	3.951845000	1.698845000
H	4.875098000	4.274114000	0.990636000
C	1.871955000	3.235404000	3.563154000
C	4.555302000	3.942013000	7.044089000
H	3.740918000	4.358746000	7.631978000
C	5.315568000	4.936055000	6.391385000
H	4.937522000	5.937230000	6.584552000
C	6.378318000	4.936268000	5.461183000
H	6.623086000	5.937809000	5.115482000
C	7.127827000	3.941664000	4.796894000
H	7.817873000	4.358558000	4.067139000
H	2.132183000	3.235374000	2.509816000
C	1.912499000	1.953469000	4.108021000
H	1.496415000	1.695225000	5.080051000
C	2.717162000	1.042771000	3.407623000
H	2.740746000	0.006790000	3.737343000
C	3.605088000	1.357111000	2.350282000
H	4.097111000	0.468421000	1.960816000
C	4.113099000	2.518736000	1.698875000
H	4.875030000	2.196388000	0.990679000
C	4.555361000	2.528539000	7.044061000
H	3.741011000	2.111715000	7.631931000
C	5.315706000	1.534586000	6.391314000
H	4.937741000	0.533372000	6.584440000
C	6.378453000	1.534497000	5.461109000
H	6.623302000	0.532989000	5.115367000
C	7.127882000	2.529189000	4.796862000
H	7.817963000	2.112383000	4.067089000

4-disp

Ce	4.507571000	3.235360000	4.616365000
C	1.496798000	3.235352000	4.546377000
H	0.792927000	3.235354000	5.376205000
C	1.830006000	4.554977000	4.200999000
H	1.300531000	5.252807000	4.846498000
C	2.676817000	5.256802000	3.328305000
H	2.594161000	6.326356000	3.511021000
C	3.643153000	5.013074000	2.339094000
H	4.072176000	5.953513000	1.999111000
C	4.276734000	3.937579000	1.696636000
H	5.042929000	4.308786000	1.019030000
C	1.830001000	1.915727000	4.201001000
H	1.300522000	1.217897000	4.846498000
C	2.676827000	1.213898000	3.328322000

H	2.594178000	0.144346000	3.511048000
C	3.643165000	1.457623000	2.339113000
H	4.072201000	0.517184000	1.999147000
C	4.276739000	2.533116000	1.696645000
H	5.042942000	2.161907000	1.019049000
C	4.692375000	3.941635000	7.169573000
H	3.921039000	4.355764000	7.814281000
C	5.390067000	4.940011000	6.455660000
H	5.028208000	5.939996000	6.682330000
C	6.372947000	4.939991000	5.441921000
H	6.588336000	5.939979000	5.073254000
C	7.064966000	3.941646000	4.722509000
H	7.685411000	4.355737000	3.931525000
C	4.692362000	2.529056000	7.169561000
H	3.921023000	2.114928000	7.814265000
C	5.390046000	1.530687000	6.455630000
H	5.028172000	0.530701000	6.682277000
C	6.372945000	1.530710000	5.441912000
H	6.588340000	0.530724000	5.073241000
C	7.064966000	2.529059000	4.722508000
H	7.685408000	2.114970000	3.931521000

1-disp, s=5/2

Sm	4.438188000	3.235350000	4.562342000
C	1.548011000	3.235350000	4.596266000
H	0.843057000	3.235350000	5.424458000
C	1.883544000	4.553679000	4.251770000
H	1.360590000	5.251328000	4.901905000
C	2.736738000	5.254179000	3.386372000
H	2.662608000	6.322222000	3.578137000
C	3.703665000	5.012580000	2.397250000
H	4.138250000	5.952484000	2.064873000
C	4.338509000	3.937860000	1.760429000
H	5.113747000	4.307335000	1.093020000
C	4.634957000	3.945213000	7.106222000
H	3.868815000	4.355599000	7.759658000
C	5.322257000	4.937927000	6.394265000
H	4.972179000	5.940264000	6.627755000
C	6.304443000	4.934782000	5.369759000
H	6.514965000	5.935930000	5.001155000
C	6.991631000	3.944895000	4.652431000
H	7.616968000	4.357486000	3.864682000
C	1.883545000	1.917021000	4.251770000
H	1.360591000	1.219372000	4.901905000
C	2.736738000	1.216521000	3.386373000
H	2.662608000	0.148478000	3.578138000
C	3.703665000	1.458120000	2.397250000
H	4.138251000	0.518216000	2.064873000
C	4.338509000	2.532841000	1.760429000
H	5.113747000	2.163365000	1.093020000
C	4.634957000	2.525487000	7.106221000
H	3.868814000	2.115102000	7.759657000
C	5.322257000	1.532772000	6.394264000
H	4.972179000	0.530436000	6.627754000
C	6.304442000	1.535917000	5.369759000
H	6.514965000	0.534769000	5.001155000

C	6.991631000	2.525805000	4.652431000
H	7.616967000	2.113215000	3.864681000

1-disp, s=3/2

Sm	4.456149000	3.235350000	4.564075000
C	1.578302000	3.235350000	4.622477000
H	0.885541000	3.235350000	5.460799000
C	1.911292000	4.553937000	4.278457000
H	1.392658000	5.250364000	4.933187000
C	2.759468000	5.255200000	3.409115000
H	2.689963000	6.322903000	3.603522000
C	3.724995000	5.010523000	2.421297000
H	4.167574000	5.949120000	2.095914000
C	4.353925000	3.936597000	1.773978000
H	5.126751000	4.307865000	1.105014000
C	4.602677000	3.940389000	7.080479000
H	3.828343000	4.355044000	7.721144000
C	5.297475000	4.936944000	6.363382000
H	4.926826000	5.935798000	6.580633000
C	6.280999000	4.938814000	5.352447000
H	6.492017000	5.938380000	4.980705000
C	6.974173000	3.940754000	4.636927000
H	7.589361000	4.353955000	3.841335000
C	1.911293000	1.916763000	4.278457000
H	1.392659000	1.220336000	4.933188000
C	2.759468000	1.215499000	3.409115000
H	2.689963000	0.147797000	3.603522000
C	3.724995000	1.460177000	2.421297000
H	4.167574000	0.521580000	2.095914000
C	4.353925000	2.534103000	1.773979000
H	5.126751000	2.162835000	1.105014000
C	4.602677000	2.530310000	7.080479000
H	3.828344000	2.115656000	7.721145000
C	5.297475000	1.533756000	6.363382000
H	4.926826000	0.534902000	6.580633000
C	6.280999000	1.531886000	5.352447000
H	6.492016000	0.532320000	4.980705000
C	6.974173000	2.529946000	4.636927000
H	7.589361000	2.116745000	3.841336000

1-disp, s=1/2

Sm	4.461367000	3.235322000	4.568253000
C	1.584855000	3.235605000	4.629785000
H	0.892181000	3.235633000	5.468081000
C	1.918844000	4.553757000	4.285304000
H	1.402653000	5.250329000	4.941817000
C	2.766551000	5.255183000	3.415926000
H	2.698157000	6.322641000	3.611893000
C	3.730761000	5.011279000	2.426311000
H	4.172552000	5.949940000	2.100182000
C	4.360435000	3.937216000	1.781496000
H	5.135397000	4.307763000	1.114633000
C	4.594706000	3.940873000	7.071830000
H	3.816186000	4.354446000	7.708047000
C	5.291498000	4.937562000	6.358711000
H	4.919649000	5.936312000	6.574088000
C	6.271377000	4.937725000	5.344191000
H	6.476942000	5.936406000	4.967081000
C	6.968750000	3.939784000	4.630516000

H	7.581613000	4.353588000	3.833520000
C	1.918729000	1.917483000	4.285309000
H	1.402572000	1.220870000	4.941792000
C	2.767023000	1.216209000	3.416363000
H	2.699391000	0.148832000	3.612980000
C	3.731170000	1.460060000	2.426606000
H	4.173368000	0.521401000	2.101047000
C	4.360451000	2.534001000	1.781301000
H	5.135345000	2.163521000	1.114336000
C	4.594702000	2.529341000	7.071571000
H	3.815921000	2.115742000	7.707491000
C	5.291672000	1.532417000	6.358886000
H	4.920403000	0.533621000	6.575017000
C	6.271873000	1.532267000	5.344588000
H	6.478450000	0.533483000	4.968285000
C	6.969235000	2.530247000	4.631053000
H	7.582208000	2.116393000	3.834142000

1, s=5/2

Sm	4.491774000	3.235350000	4.447602000
C	1.917403000	4.513888000	4.111436000
H	1.487309000	4.775311000	5.076825000
C	2.738128000	5.422144000	3.424451000
H	2.755905000	6.458661000	3.754010000
C	3.645168000	5.109651000	2.385768000
H	4.141414000	6.000259000	2.005501000
C	4.166307000	3.950126000	1.736465000
H	4.935030000	4.276202000	1.037391000
C	1.866671000	3.235389000	3.560381000
C	4.546258000	3.935424000	7.039686000
H	3.760293000	4.357422000	7.662622000
C	5.300736000	4.938903000	6.366778000
H	4.943018000	5.940953000	6.593983000
C	6.333367000	4.938629000	5.422714000
H	6.591324000	5.940600000	5.086344000
C	7.072833000	3.935047000	4.733978000
H	7.761287000	4.357077000	4.004925000
H	2.141027000	3.235362000	2.509725000
C	1.917347000	1.956910000	4.111487000
H	1.487242000	1.695544000	5.076887000
C	2.738032000	1.048590000	3.424539000
H	2.755762000	0.012085000	3.754139000
C	3.645086000	1.361000000	2.385844000
H	4.141293000	0.470355000	2.005613000
C	4.166277000	2.520477000	1.736495000
H	4.934984000	2.194338000	1.037434000
C	4.546295000	2.535159000	7.039653000
H	3.760352000	2.113091000	7.662569000
C	5.300824000	1.531749000	6.366699000
H	4.943156000	0.529671000	6.593856000
C	6.333455000	1.532120000	5.422634000
H	6.591462000	0.530178000	5.086216000
C	7.072868000	2.535772000	4.733943000
H	7.761343000	2.113812000	4.004870000

1, s=3/2

Sm	4.528968000	3.235341000	4.455653000
C	1.954971000	4.515628000	4.154902000
H	1.527121000	4.776723000	5.120865000

C	2.773766000	5.421408000	3.467097000
H	2.801607000	6.455794000	3.801697000
C	3.673013000	5.107856000	2.418961000
H	4.173358000	5.997574000	2.042465000
C	4.183827000	3.951463000	1.761931000
H	4.950422000	4.276383000	1.060237000
C	1.910339000	3.235388000	3.605765000
C	4.502954000	3.941342000	6.990042000
H	3.698844000	4.359944000	7.591356000
C	5.261368000	4.934484000	6.331531000
H	4.888183000	5.936542000	6.532615000
C	6.312492000	4.937129000	5.389987000
H	6.558621000	5.939766000	5.047641000
C	7.049227000	3.941372000	4.711996000
H	7.728362000	4.357979000	3.971261000
H	2.175447000	3.235365000	2.552848000
C	1.954911000	1.955163000	4.154944000
H	1.527048000	1.694120000	5.120915000
C	2.773665000	1.049323000	3.467170000
H	2.801457000	0.014947000	3.801804000
C	3.672928000	1.362799000	2.419024000
H	4.173231000	0.473046000	2.042556000
C	4.183793000	2.519147000	1.761955000
H	4.950372000	2.194168000	1.060270000
C	4.502994000	2.529249000	6.990017000
H	3.698906000	2.110580000	7.591314000
C	5.261464000	1.536172000	6.331470000
H	4.888334000	0.534087000	6.532521000
C	6.312586000	1.533619000	5.389925000
H	6.558770000	0.531007000	5.047543000
C	7.049264000	2.529442000	4.711969000
H	7.728421000	2.112900000	3.971217000

1, s=1/2

Sm	4.518720000	3.240110000	4.479438000
C	1.949900000	4.510694000	4.143827000
H	1.514939000	4.766421000	5.108308000
C	2.768591000	5.424029000	3.463346000
H	2.785041000	6.459450000	3.795508000
C	3.679685000	5.111405000	2.427918000
H	4.182779000	6.000309000	2.053210000
C	4.201258000	3.951220000	1.782298000
H	4.981485000	4.275212000	1.095313000
C	1.909637000	3.233346000	3.589768000
C	4.517610000	3.943884000	7.007732000
H	3.721400000	4.364235000	7.618113000
C	5.265774000	4.936224000	6.332328000
H	4.896787000	5.938822000	6.537601000
C	6.310556000	4.937241000	5.383357000
H	6.552010000	5.939458000	5.036657000
C	7.034511000	3.940928000	4.691745000
H	7.702415000	4.358138000	3.941259000
H	2.180260000	3.233704000	2.538447000
C	1.948490000	1.952518000	4.141865000
H	1.505730000	1.692698000	5.101613000
C	2.769451000	1.043799000	3.462470000
H	2.789597000	0.008367000	3.794447000
C	3.683625000	1.359757000	2.428430000
H	4.188289000	0.471615000	2.054077000

C	4.200338000	2.519495000	1.780416000
H	4.980616000	2.196633000	1.092916000
C	4.512755000	2.533445000	7.002300000
H	3.715370000	2.114643000	7.612282000
C	5.264122000	1.537038000	6.333560000
H	4.892089000	0.535743000	6.539398000
C	6.301938000	1.534858000	5.380045000
H	6.537745000	0.532388000	5.029690000
C	7.029990000	2.528893000	4.686762000
H	7.697526000	2.110530000	3.937023000

2-disp, s=5/2

Sm	4.438188000	3.235350000	4.562342000
C	1.548011000	3.235350000	4.596266000
H	0.843057000	3.235350000	5.424458000
C	1.883544000	4.553679000	4.251770000
H	1.360590000	5.251328000	4.901905000
C	2.736738000	5.254179000	3.386372000
H	2.662608000	6.322222000	3.578137000
C	3.703665000	5.012580000	2.397250000
H	4.138250000	5.952484000	2.064873000
C	4.338509000	3.937860000	1.760429000
H	5.113747000	4.307335000	1.093020000
C	4.634957000	3.945213000	7.106222000
H	3.868815000	4.355599000	7.759658000
C	5.322257000	4.937927000	6.394265000
H	4.972179000	5.940264000	6.627755000
C	6.304443000	4.934782000	5.369759000
H	6.514965000	5.935930000	5.001155000
C	6.991631000	3.944895000	4.652431000
H	7.616968000	4.357486000	3.864682000
C	1.883545000	1.917021000	4.251770000
H	1.360591000	1.219372000	4.901905000
C	2.736738000	1.216521000	3.386373000
H	2.662608000	0.148478000	3.578138000
C	3.703665000	1.458120000	2.397250000
H	4.138251000	0.518216000	2.064873000
C	4.338509000	2.532841000	1.760429000
H	5.113747000	2.163365000	1.093020000
C	4.634957000	2.525487000	7.106221000
H	3.868814000	2.115102000	7.759657000
C	5.322257000	1.532772000	6.394264000
H	4.972179000	0.530436000	6.627754000
C	6.304442000	1.535917000	5.369759000
H	6.514965000	0.534769000	5.001155000
C	6.991631000	2.525805000	4.652431000
H	7.616967000	2.113215000	3.864681000

2-disp, s=3/2

Sm	4.456149000	3.235350000	4.564075000
C	1.578302000	3.235350000	4.622477000
H	0.885541000	3.235350000	5.460799000
C	1.911292000	4.553937000	4.278457000
H	1.392658000	5.250364000	4.933187000
C	2.759468000	5.255200000	3.409115000
H	2.689963000	6.322903000	3.603522000
C	3.724995000	5.010523000	2.421297000
H	4.167574000	5.949120000	2.095914000
C	4.353925000	3.936597000	1.773978000

H	5.126751000	4.307865000	1.105014000
C	4.602677000	3.940389000	7.080479000
H	3.828343000	4.355044000	7.721144000
C	5.297475000	4.936944000	6.363382000
H	4.926826000	5.935798000	6.580633000
C	6.280999000	4.938814000	5.352447000
H	6.492017000	5.938380000	4.980705000
C	6.974173000	3.940754000	4.636927000
H	7.589361000	4.353955000	3.841335000
C	1.911293000	1.916763000	4.278457000
H	1.392659000	1.220336000	4.933188000
C	2.759468000	1.215499000	3.409115000
H	2.689963000	0.147797000	3.603522000
C	3.724995000	1.460177000	2.421297000
H	4.167574000	0.521580000	2.095914000
C	4.353925000	2.534103000	1.773979000
H	5.126751000	2.162835000	1.105014000
C	4.602677000	2.530310000	7.080479000
H	3.828344000	2.115656000	7.721145000
C	5.297475000	1.533756000	6.363382000
H	4.926826000	0.534902000	6.580633000
C	6.280999000	1.531886000	5.352447000
H	6.492016000	0.532320000	4.980705000
C	6.974173000	2.529946000	4.636927000
H	7.589361000	2.116745000	3.841336000

2-disp, s=1/2

Sm	4.461367000	3.235322000	4.568253000
C	1.584855000	3.235605000	4.629785000
H	0.892181000	3.235633000	5.468081000
C	1.918844000	4.553757000	4.285304000
H	1.402653000	5.250329000	4.941817000
C	2.766551000	5.255183000	3.415926000
H	2.698157000	6.322641000	3.611893000
C	3.730761000	5.011279000	2.426311000
H	4.172552000	5.949940000	2.100182000
C	4.360435000	3.937216000	1.781496000
H	5.135397000	4.307763000	1.114633000
C	4.594706000	3.940873000	7.071830000
H	3.816186000	4.354446000	7.708047000
C	5.291498000	4.937562000	6.358711000
H	4.919649000	5.936312000	6.574088000
C	6.271377000	4.937725000	5.344191000
H	6.476942000	5.936406000	4.967081000
C	6.968750000	3.939784000	4.630516000
H	7.581613000	4.353588000	3.833520000
C	1.918729000	1.917483000	4.285309000
H	1.402572000	1.220870000	4.941792000
C	2.767023000	1.216209000	3.416363000
H	2.699391000	0.148832000	3.612980000
C	3.731170000	1.460060000	2.426606000
H	4.173368000	0.521401000	2.101047000
C	4.360451000	2.534001000	1.781301000
H	5.135345000	2.163521000	1.114336000
C	4.594702000	2.529341000	7.071571000
H	3.815921000	2.115742000	7.707491000
C	5.291672000	1.532417000	6.358886000
H	4.920403000	0.533621000	6.575017000
C	6.271873000	1.532267000	5.344588000

H	6.478450000	0.533483000	4.968285000
C	6.969235000	2.530247000	4.631053000
H	7.582208000	2.116393000	3.834142000

2, s=5/2

Sm	4.438216000	3.235347000	4.556735000
C	1.529510000	3.235352000	4.580234000
H	0.819198000	3.235353000	5.404567000
C	1.864000000	4.554651000	4.234544000
H	1.334469000	5.253075000	4.879363000
C	2.714815000	5.255480000	3.365722000
H	2.632688000	6.324892000	3.549520000
C	3.680388000	5.013573000	2.373878000
H	4.106153000	5.954658000	2.031832000
C	4.314501000	3.938390000	1.735285000
H	5.080678000	4.308388000	1.056920000
C	4.654686000	3.946727000	7.126921000
H	3.895447000	4.357028000	7.789345000
C	5.343162000	4.938578000	6.417265000
H	5.001778000	5.942632000	6.658796000
C	6.330852000	4.935754000	5.393720000
H	6.553109000	5.938918000	5.036023000
C	7.019546000	3.946525000	4.679418000
H	7.658758000	4.358789000	3.901899000
C	1.863995000	1.916052000	4.234544000
H	1.334463000	1.217630000	4.879363000
C	2.714808000	1.215221000	3.365721000
H	2.632676000	0.145809000	3.549519000
C	3.680382000	1.457125000	2.373877000
H	4.106144000	0.516039000	2.031832000
C	4.314498000	2.532306000	1.735285000
H	5.080674000	2.162306000	1.056919000
C	4.654689000	2.523969000	7.126921000
H	3.895453000	2.113664000	7.789346000
C	5.343169000	1.532120000	6.417265000
H	5.001789000	0.528065000	6.658796000
C	6.330859000	1.534949000	5.393720000
H	6.553119000	0.531786000	5.036023000
C	7.019549000	2.524180000	4.679417000
H	7.658764000	2.111919000	3.901899000

2, s=3/2

Sm	4.461632000	3.235350000	4.568566000
C	1.559274000	3.235350000	4.605772000
H	0.858063000	3.235350000	5.437780000
C	1.892361000	4.554794000	4.261499000
H	1.365666000	5.252022000	4.909742000
C	2.740467000	5.256523000	3.391034000
H	2.663084000	6.325558000	3.578104000
C	3.706169000	5.011768000	2.402162000
H	4.141136000	5.951542000	2.068297000
C	4.335190000	3.937041000	1.754301000
H	5.101027000	4.308705000	1.076691000
C	4.623061000	3.940816000	7.101745000
H	3.855152000	4.356035000	7.750639000
C	5.318333000	4.938036000	6.384292000
H	4.954849000	5.938368000	6.609369000
C	6.302789000	4.939914000	5.373032000
H	6.522036000	5.940907000	5.008393000

C	6.996600000	3.941217000	4.657299000
H	7.621088000	4.355002000	3.868558000
C	1.892362000	1.915906000	4.261499000
H	1.365666000	1.218678000	4.909742000
C	2.740467000	1.214177000	3.391034000
H	2.663084000	0.145142000	3.578104000
C	3.706169000	1.458932000	2.402162000
H	4.141136000	0.519158000	2.068297000
C	4.335190000	2.533659000	1.754301000
H	5.101027000	2.161996000	1.076691000
C	4.623061000	2.529884000	7.101745000
H	3.855152000	2.114665000	7.750639000
C	5.318333000	1.532664000	6.384292000
H	4.954849000	0.532332000	6.609368000
C	6.302789000	1.530786000	5.373032000
H	6.522036000	0.529793000	5.008393000
C	6.996600000	2.529483000	4.657299000
H	7.621088000	2.115697000	3.868559000

2, s=1/2

Sm	4.467377000	3.235362000	4.574846000
C	1.564564000	3.235672000	4.611752000
H	0.862617000	3.235797000	5.443062000
C	1.900444000	4.554516000	4.268644000
H	1.376088000	5.252169000	4.918318000
C	2.748407000	5.256247000	3.397497000
H	2.672556000	6.324982000	3.586885000
C	3.712872000	5.012799000	2.407866000
H	4.146957000	5.952574000	2.072996000
C	4.342239000	3.937154000	1.761366000
H	5.109543000	4.308406000	1.085196000
C	4.615959000	3.940068000	7.094756000
H	3.843949000	4.354400000	7.739361000
C	5.309673000	4.938852000	6.376739000
H	4.945682000	5.938964000	6.601005000
C	6.295785000	4.938665000	5.367300000
H	6.508096000	5.938850000	4.996002000
C	6.988525000	3.941249000	4.649254000
H	7.610150000	4.355438000	3.858637000
C	1.900525000	1.917005000	4.269068000
H	1.376440000	1.219325000	4.918922000
C	2.749024000	1.215220000	3.398130000
H	2.673868000	0.146584000	3.588279000
C	3.713032000	1.458534000	2.408226000
H	4.147560000	0.518769000	2.073909000
C	4.342589000	2.534144000	1.761667000
H	5.109922000	2.162850000	1.085578000
C	4.616943000	2.529631000	7.095606000
H	3.844941000	2.115231000	7.740235000
C	5.309809000	1.531035000	6.377018000
H	4.946753000	0.530779000	6.602150000
C	6.296004000	1.531305000	5.367156000
H	6.509157000	0.531084000	4.996480000
C	6.988813000	2.528865000	4.649738000
H	7.610119000	2.114724000	3.858786000

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