

## Supporting Information

Photocatalytic dechlorination of chlorinated hydrocarbons including PVC by organolanthanide complexes

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## S1 General Details

All moisture and air sensitive materials were manipulated using standard high-vacuum Schlenk-line techniques and MBraun gloveboxes and stored under an atmosphere of dried and deoxygenated dinitrogen. All glassware items, cannulae and Fisherbrand 1.2  $\mu\text{m}$  retention glass microfiber filters were dried in a 160 °C oven overnight before use.

Hexanes, tetrahydrofuran (THF), diethyl ether ( $\text{Et}_2\text{O}$ ) and toluene for use with moisture and air sensitive compounds were dried using an MBRAUN SPS 800 Manual solvent purification system and stored over activated 3 Å molecular sieves. Benzene- $\text{D}_6$  was purchased from Cambridge Isotope Laboratories and refluxed over potassium metal for 24 hours, freeze-pump-thaw degassed and purified by trap-to-trap distillation prior to use. THF- $\text{D}_8$  was purchased from Cambridge Isotope Laboratories and dried over sodium/benzophenone before being freeze-pump-thaw degassed and purified by trap-to-trap distillation prior to use. All solvents were purchased from Sigma-Aldrich or Fisher Scientific and stored over 3 Å molecular sieves for 4 hours before being used.

$\text{PhICl}_2$  was prepared according to the literature procedure<sup>1</sup> and stored at  $-30$  °C. Dihydrocarbyl magnesium reagents<sup>2</sup>,  $\text{KC}_5\text{Me}_4\text{H}$ ,<sup>3</sup> lanthanide triiodides ( $\text{Ln} = \text{La}, \text{Ce}, \text{Nd}, \text{Sm}$ ),<sup>4,5</sup> lanthanide tris(tetramethylcyclopentadienyl) complexes **2-Ln** ( $\text{Ln} = \text{La}, \text{Ce}, \text{Nd}, \text{Sm}$ ),<sup>4,6</sup>  $[(\text{Cp}^{\text{Me}_4})_2\text{Ce}(\mu\text{-Cl})]_2$  (**3-Ce**)<sup>7</sup>,  $[(\text{Cp}^{\text{Me}_4})_2\text{Ln}(\mu\text{-Cl})]_2$  (**3-La**),<sup>7</sup> and  $\text{Mg}(\text{Cp}^{\text{Me}_4})_2$ <sup>8</sup> were all prepared using published methods. All other chemicals were purchased from commercial suppliers and degassed and/or dried under vacuum or over 3 Å molecular sieves for 12 hours before use.

The station for photochemical reactions was equipped with a fan to maintain constant temperature, and unless otherwise stated, a single 40 W Kessil A160WE 440 nm lamp. The reactions were conducted in J-Young valved NMR spectroscopy tubes fixed at a distance of 7.5 cm from the light source.

NMR spectra were recorded on Bruker Avance 500 and 600 MHz spectrometers and are referenced to residual protio solvent for  $^1\text{H}$  NMR spectroscopy. THF was used as solvents for No Deuterium (NoD) NMR spectroscopic experiments,<sup>10</sup> and was referenced to added tetramethylsilane (0.00 ppm for both  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopic experiments). Quantitative  $^1\text{H}$  NMR data were acquired with a minimum of 24, with the delay time set to 5x the longest  $T_1$  value present. Chemical shifts are quoted in ppm and coupling constants in Hz. Tetrakis(trimethylsilyl)silane (TMS\*) was used as internal standards for quantitative  $^1\text{H}$  NMR spectroscopy. NMR spectra were taken at 25°C unless otherwise noted. Elemental analyses were carried out by the microanalytic services in the College of Chemistry at the University of California, Berkeley. ATR-FTIR spectra were recorded on a Shimadzu IRSpirit FTIR spectrometer on neat powders.

X-ray diffraction data were collected at beamline 12.2.1 of the Advanced Light Source (ALS) at Lawrence Berkeley National Lab, using a Bruker D8 diffractometer coupled to a Bruker PhotonII CPAD detector with Si(111)-monochromated synchrotron radiation (17 keV radiation). All data were collected at 100 K and corrected for Lorentz and polarization effects; no correction for crystal decay was applied. An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS. All software used for diffraction data processing are contained in the APEX3 program suite (Bruker AXS, Madison, WI).<sup>9</sup> All structures were solved using SHELXT in Olex2 and refined using SHELXL in Olex2.<sup>10,11</sup>

## S2 Experimental Procedures and Characterization

### Synthesis of $[(\text{Cp}^{\text{Me4}})_2\text{Nd}(\mu\text{-Cl})_2]$ (3-Nd)

In a glovebox a vial was charged with  $(\text{Cp}^{\text{Me4}})_3\text{Nd}$  (94.5 mg, 0.186 mmol, 1.00 equiv.) in THF (5 mL), resulting in a green solution. With stirring, a colorless solution of  $\text{PhICl}_2$  (26.6 mg, 0.0968 mmol, 0.52 equiv.) in THF (1 mL) was added dropwise. After stirring for 1 hour at room temperature, a color change to turquoise was seen, and the solution continued to stir overnight. After this time the volatiles were removed under vacuum, resulting in a turquoise powder which was subsequently washed with cold hexanes (2 x 0.5 mL). The powder was redissolved in a minimum of THF (1 mL), layered with hexanes (3 mL) and stored at  $-30\text{ }^\circ\text{C}$  for 3 days to yield periwinkle blue blocks of  $[(\text{Cp}^{\text{Me4}})_2\text{NdCl}]_2$  that were suitable for X-ray diffraction studies. Yield: 56.0 mg, 70%.

$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  17.70 (br. s, 12H,  $\text{CH}_{3\text{cp}}$ ), 0.05 (br. s, 12H,  $\text{CH}_{3\text{cp}}$ ), -9.86 (br. s, 2H,  $\text{H}_{\text{cp}}$ ).

Anal. Calcd for:  $\text{C}_{36}\text{H}_{52}\text{Nd}_2\text{Cl}_2$ : C, 51.47; H, 5.76. Found: C, 50.78; H, 5.87.

### Synthesis of $[(\text{Cp}^{\text{Me4}})_2\text{Sm}(\mu\text{-Cl})_2]$ (3-Sm)

In a glovebox a vial was charged with  $(\text{Cp}^{\text{Me4}})_3\text{Sm}$  (95.9 mg, 0.186 mmol, 1.00 equiv.) in THF (5 mL), resulting in a red solution. With stirring, a colorless solution of  $\text{PhICl}_2$  (26.6 mg, 0.0968 mmol, 0.520 equiv.) in THF (1 mL) was added dropwise. After stirring for 16 hours at room temperature, a color change to orange was seen, and the volatiles were removed under vacuum resulting in an orange powder which was subsequently washed with cold hexanes (2 x 0.5 mL). The powder was redissolved in a minimum of THF (1 mL), layered with hexanes (3 mL) and stored at  $-30\text{ }^\circ\text{C}$  for 3 days to yield orange blocks that were suitable for X-ray diffraction studies. Yield: 60.3 mg, 77%.

$^1\text{H}$  NMR (500 MHz, THF- $\text{D}_8$ )  $\delta$  11.77 (br. s, 2H,  $\text{H}_{\text{cp}}$ ), 1.56 (br. s, 12H,  $\text{CH}_{3\text{cp}}$ ), 0.30 (br. s, 12H,  $\text{CH}_{3\text{cp}}$ ).

Anal. Calcd for:  $\text{C}_{36}\text{H}_{52}\text{Sm}_2\text{Cl}_2$ : C, 50.73; H, 5.68. Found: C, 51.03; H, 6.03.

## S3 Catalytic C-Cl activation

### Procedure

In a glovebox, a Young NMR tube was charged with metal complex (1-20 mol%),  $\text{MgBn}_2(\text{THF})_2$  (1 equiv.), internal standard, and THF (0.5 mL). Chlorinated substrate (1 equiv.) was then added, and the sample sealed, placed in front of a Kessil 440 nm lamp and monitored periodically by  $^1\text{H}$  NMR spectroscopy. Final time point measurements were collected after 24 hours unless stated otherwise.

## Results

**Table S1** - Calculated conversion R-Cl to R-H or R-Bn<sup>a</sup> with yields of dechlorinated product determined by <sup>1</sup>H NMR spectroscopy. No product formation was seen without irradiation with light.

Entry	Catalyst	Catalyst Loading (mol%)	Time (hr)	Substrate	Major Identified Product	Product Yield (%)
1	2-La	20	24	Chlorocyclohexane	Cyclohexane	52
2	2-La	5	24	Chlorocyclohexane	Cyclohexane	29
3	3-La	5	24	Chlorocyclohexane	Cyclohexane	28
3	1-Ce	20	24	Chlorocyclohexane	Cyclohexane	96
4	1-Ce	5	24	Chlorocyclohexane	Cyclohexane	37
5	2-Ce	20	24	Chlorocyclohexane	Cyclohexane	89
6	2-Ce	5	24	Chlorocyclohexane	Cyclohexane	93
7	2-Ce	5	24	Chlorobenzene	Benzene	64
8	2-Ce	5	48	Chlorobenzene	Benzene	100
9	2-Ce	5	24	241-Chloro-4-fluorobenzene	Fluorobenzene	100
10	2-Ce	5	24	(2-chloroethyl)benzene	Ethylbenzene	42
11	2-Ce	5	24	1-(chloromethyl)-4-(trifluoromethyl)benzene	1,2-bis(4-(trifluoromethyl)phenyl)ethane	89 <sup>a</sup>
12	2-Ce	5	24	1-Chloro-2-methylpropene	2-methylprop-1-ene	73
13	2-Ce	5	24	3-Chloro-2-methylpropene	(3-methylbut-3-en-1-yl)benzene	79 <sup>a</sup>
14	2-Ce	5	24	2-chloro-2-methylpropane	2-methylprop-1-ene <sup>b</sup>	20
15	2-Ce	5	24	Polyvinyl chloride <sup>c</sup>	Polyethylene	79 <sup>d</sup>
16	2-Ce	1	24	Chlorocyclohexane	Cyclohexane	96
17	3-Ce	20	24	Chlorocyclohexane	Cyclohexane	63
18	3-Ce	5	24	Chlorocyclohexane	Cyclohexane	76
19	3-Ce	5	24	Chlorobenzene	Benzene	15
20	3-Ce	5	48	Chlorobenzene	Benzene	82
21	3-Ce	1	24	Chlorocyclohexane	Cyclohexane	97
22	2-Nd	20	24	Chlorocyclohexane	Cyclohexane	37
23	2-Nd	5	24	Chlorocyclohexane	Cyclohexane	6.6
24	3-Nd	20	24	Chlorocyclohexane	Cyclohexane	27
25	2-Sm	20	24	Chlorocyclohexane	Cyclohexane	15
26	2-Sm	5	24	Chlorocyclohexane	Cyclohexane	2.2
27	3-Sm	20	24	Chlorocyclohexane	Cyclohexane	15
28	2-Dy	20	24	Chlorocyclohexane	Cyclohexane	0
29	2-Dy	5	24	Chlorocyclohexane	Cyclohexane	0

a) Product arising from benzylation of alkyl radical rather than hydrodechlorination. b) Product arising from tBu radical generation and subsequent formation of a closed shell molecule.<sup>12</sup> c) average  $M_w \sim 233,000$ , average  $M_n \sim 99,000$ , commercial sample. d) Yield indicates the percentage of Cl removed from PVC, as determined by Mohr's method, vide infra.

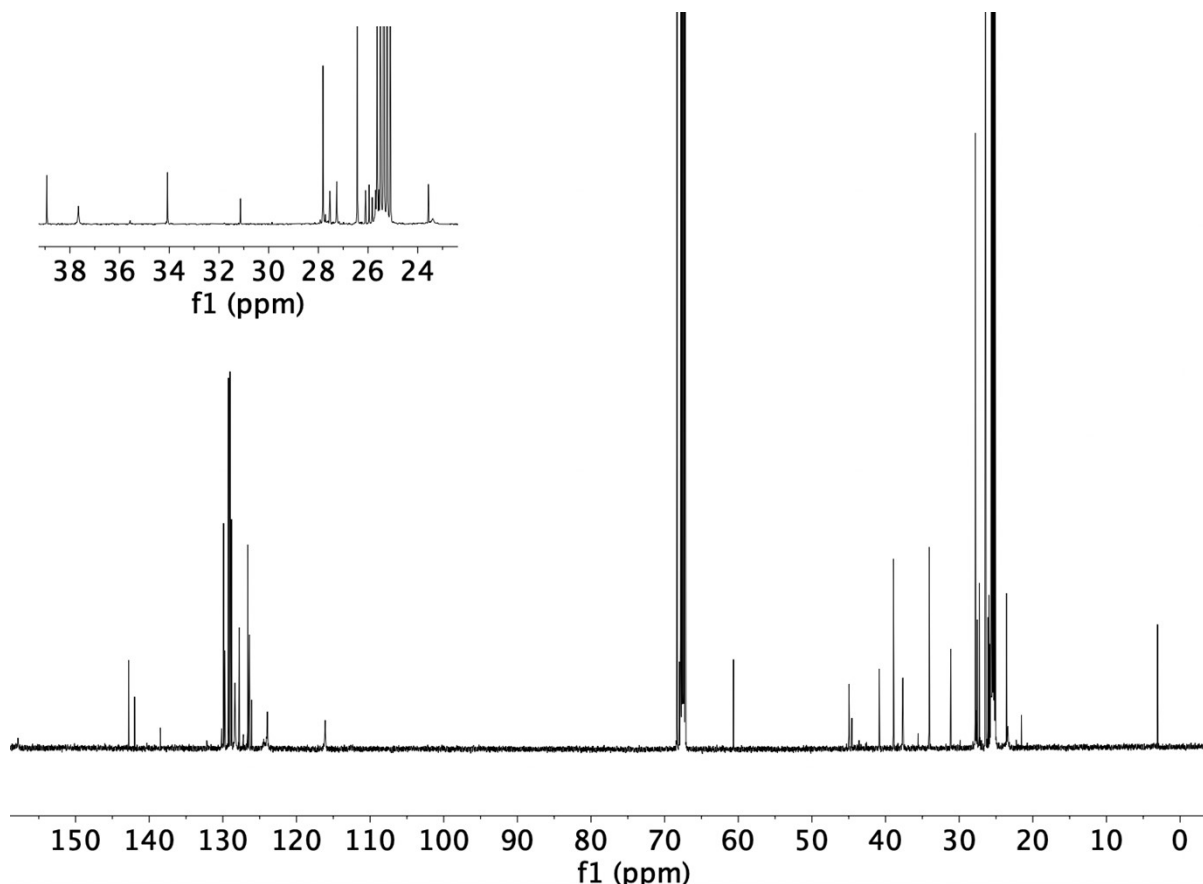
#### S4 Miscellaneous and Control Reactions

**Table S2** - Calculated conversion R-Cl to R-H with yields of dechlorinated product determined by <sup>1</sup>H NMR spectroscopy. Reactions carried out in 0.5 mL THF and irradiated with a Kessil 440 nm lamp for 24 hours unless otherwise specified. No product generation was seen without irradiation with light.

Entry	Catalyst	Catalyst Loading (mol%)	Turnover reagent	Substrate	Major Identified Product	Yield (%)
1	Mg(Cp <sup>Me4</sup> ) <sub>2</sub>	5	MgBn <sub>2</sub> (THF) <sub>2</sub>	Chlorocyclohexane	Cyclohexane	1.2
2	MgBn <sub>2</sub> (THF) <sub>2</sub>	20	MgBn <sub>2</sub> (THF) <sub>2</sub>	Chlorocyclohexane	Cyclohexane	0
3	MgPh <sub>2</sub> (THF) <sub>2</sub>	20	MgBn <sub>2</sub> (THF) <sub>2</sub>	Chlorocyclohexane	Cyclohexane	3.5
4	MgCl <sub>2</sub>	20	MgBn <sub>2</sub> (THF) <sub>2</sub>	Chlorocyclohexane	Cyclohexane	2.0
5	KCp <sup>Me4</sup>	5	MgBn <sub>2</sub> (THF) <sub>2</sub>	Chlorocyclohexane	Cyclohexane	3.0
6	1-Ce	20	Ce	Chlorocyclohexane	Cyclohexane	20
7	1-Ce	20	Zn	Chlorocyclohexane	Cyclohexane	20
8	1-Ce	20	MgPh <sub>2</sub> (THF) <sub>2</sub>	Chlorocyclohexane	Cyclohexane	23
9	2-Ce	5	NaH	Chlorocyclohexane	Cyclohexane	7.0
10	2-Ce	1	MgBn <sub>2</sub> (THF) <sub>2</sub>	Polyvinyl chloride <sup>a</sup>	Polyethylene	79 <sup>b</sup>
11 <sup>c</sup>	2-Ce	5	MgBn <sub>2</sub> (THF) <sub>2</sub>	Polyvinyl chloride <sup>a</sup>	Polyethylene	78 <sup>b</sup>

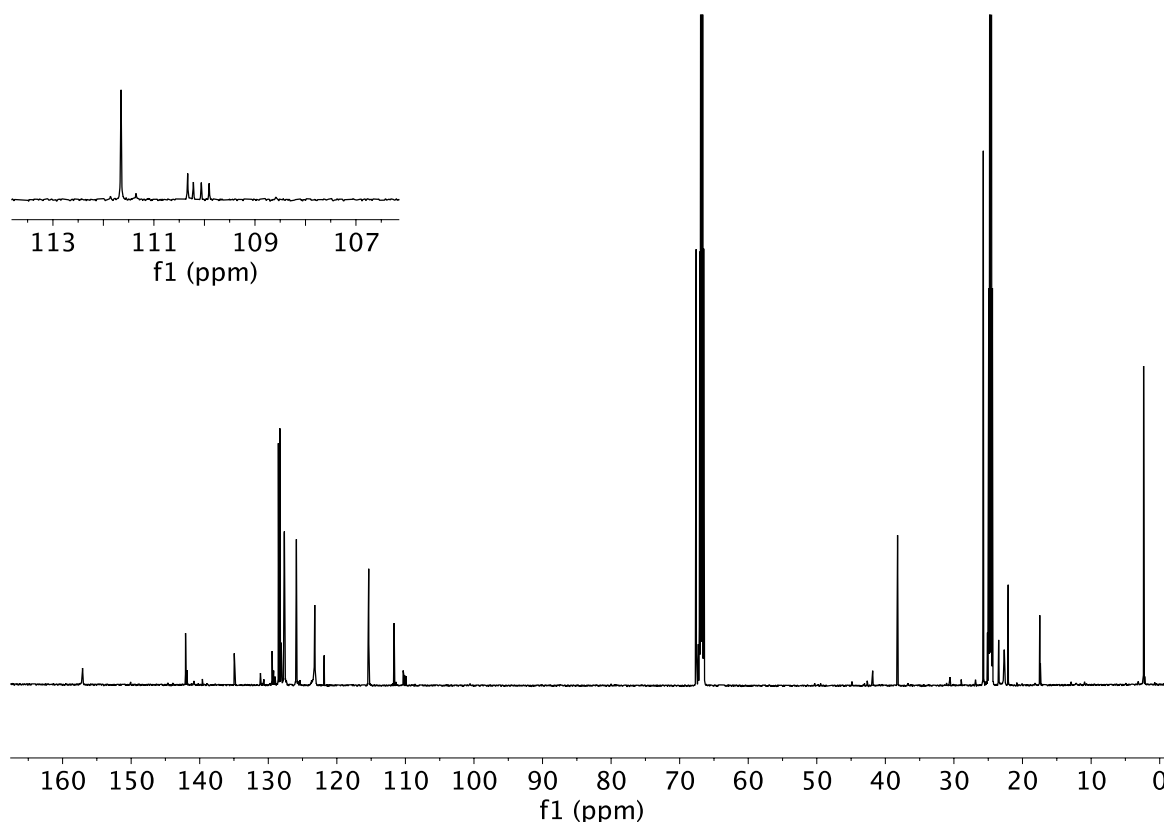
a) average M<sub>w</sub> ~ 233,000, average M<sub>n</sub> ~ 99,000, commercial sample. b) Yield indicates the percentage of Cl removed from PVC, as determined by Mohr's method, vide infra. c) Reaction time extended to 48 hours.

**Incorporation of deuterium into cyclohexane (Figure S1).** In a glovebox, a vial was charged with  $\text{MgBn}_2(\text{THF})_2$ , (35.0 mg, 0.100 mmol, 1.00 equiv.) chlorocyclohexane (11.8  $\mu\text{L}$ , 0.100 mmol, 1.00 equiv.) and  $\text{THF-D}_8$  (0.5 mL). The solution was then used to dissolve **2-Ce** (2.5 mg, 5.00  $\mu\text{mol}$ , 0.0500 equiv.), and the reaction mixture transferred to a Young's valve-equipped NMR tube. The sample was irradiated with a Kessil 440 nm lamp and monitored periodically by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, with a time point measured after 24 hours. Following this time coupling arising from the formation of cyclohexane- $\text{D}_1$  was observed by  $^{13}\text{C}$  NMR spectroscopy, but no diagnostic peaks could be observed by  $^1\text{H}$  NMR spectroscopy because the peaks of cyclohexane-D coalesce at room temperature.



**Figure S1.**  $^{13}\text{C}$  NMR in  $\text{THF-D}_8$  of catalysis reaction mixture of the dechlorination of chlorocyclohexane by **2-Ce** carried out in  $\text{THF-D}_8$  under otherwise standard conditions. The incorporation of deuterium into cyclohexane- $\text{D}_1$  is highlighted in the spectrum, a yield of 3% is observed by  $^1\text{H}$  NMR.

**Incorporation of deuterium into 2-methylpropene (Figure S2).** In a glovebox, a vial was charged with  $\text{MgBn}_2(\text{THF})_2$ , (35.0 mg, 0.100 mmol, 1.00 equiv.) 1-chloro-2-methylpropene (9.84  $\mu\text{L}$ , 0.100 mmol, 1.00 equiv.) and  $\text{THF-D}_8$  (0.5 mL). The solution was then used to dissolve **2-Ce** (2.5 mg, 5.00  $\mu\text{mol}$ , 0.0500 equiv.), and the reaction mixture transferred to a Young's valve-equipped NMR tube. The sample was irradiated with a Kessil 440 nm lamp and monitored periodically by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, with a time point measured after 24 hours. 2.4% in situ yield of 2-methylprop-1-ene-1-D was observed by  $^1\text{H}$  NMR spectroscopy.



**Figure S2.**  $^{13}\text{C}$  NMR in THF- $\text{D}_8$  of catalysis reaction mixture of the dechlorination of 1-chloro-2-methylpropene by **2-Ce** carried out in THF- $\text{D}_8$  under otherwise standard conditions. The incorporation of deuterium into 2-methylprop-1-ene-1-D is highlighted in the spectrum, a yield of 3% is observed by  $^1\text{H}$  NMR.

**Equilibrium between  $(\text{Cp}^{\text{Me}_4})_3\text{Ce}$  (**2-Ce**),  $(\text{Cp}^{\text{Me}_4})_2(\text{Bn})(\text{THF})$  (**6-Ce**) and  $\text{MgBn}_2(\text{THF})_2$  (440 nm).** In a glovebox, a Young's valve-equipped NMR tube was charged with **2-Ce** (5.0 mg, 0.010 mmol, 1.00 equiv.),  $\text{MgBn}_2(\text{THF})_2$  (70.0 mg, 0.200 mmol, 20.0 equiv.), THF (0.5 mL) and an internal standard. The NMR tube was sealed and the mixture immediately analyzed by  $^1\text{H}$  NMR spectroscopy. An equilibrium constant of 2.5 was calculated based on the relative concentrations of **2-Ce**, **6-Ce**,  $\text{MgBn}_2(\text{THF})_2$  and  $\text{Mg}(\text{Cp}^{\text{Me}_4})_2$  present in solution. Yields: 99% conversion to **6-Ce**, 92% conversion to  $\text{Mg}(\text{Cp}^{\text{Me}_4})_2$ .

**Reaction to investigate the formation of **3-Ce** from dechlorination catalysis mixtures.** In a glovebox, a Young's valve-equipped NMR tube was charged with **2-Ce** (5.0 mg, 0.010 mmol, 1.00 equiv.),  $\text{MgBn}_2(\text{THF})_2$  (70.0 mg, 0.200 mmol, 20.0 equiv.), THF (0.5 mL) and an internal standard. Chlorocyclohexane (23.6  $\mu\text{L}$ , 0.200 mmol, 20.0 equiv.) was then added before the NMR tube was sealed and irradiated for 24 hours under a 440 nm lamp. Following this time, the complete conversion from **2-Ce** to **3-Ce** was observed by  $^1\text{H}$  NMR spectroscopy.

**Reaction of **3-Ce** and  $\text{MgBn}_2(\text{THF})_2$  in the dark.** In a glovebox, a Young's valve-equipped NMR tube was charged with **3-Ce** (4.26 mg, 5.00  $\mu\text{mol}$ , 0.5 equiv.),  $\text{MgBn}_2(\text{THF})_2$  (70.0 mg, 0.200 mmol, 20.0 equiv.), THF (0.5 mL) and an internal standard. The NMR tube was sealed, wrapped in aluminum foil and stored in the dark for 24 hours. Following this time, a color change from bright yellow to darker yellow had occurred but no conversion to **6-Ce** was observed by  $^1\text{H}$  NMR spectroscopy.

**Reaction of **3-Ce** and  $\text{MgBn}_2(\text{THF})_2$  under 440 nm light irradiation.** In a glovebox, a Young's valve-equipped NMR tube was charged with **3-Ce** (4.26 mg, 5.00  $\mu\text{mol}$ , 0.500 equiv.),  $\text{MgBn}_2(\text{THF})_2$  (70.0 mg, 0.200 mmol, 20.0 equiv.), THF (0.5 mL) and an internal standard. the NMR tube was sealed and

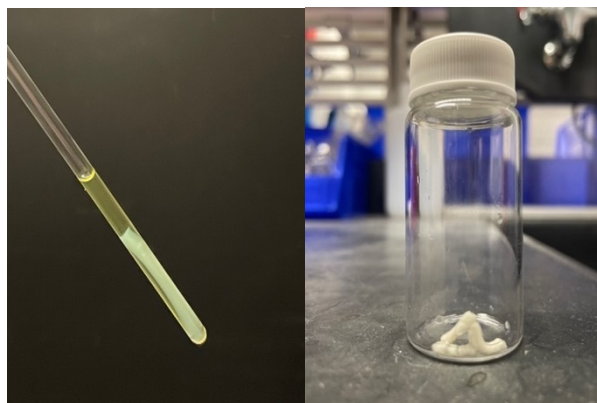
irradiated for 24 hours under a 440 nm lamp. Following this time a color change from bright yellow to a yellow-green had occurred and 96% conversion to **6-Ce** was observed by  $^1\text{H}$  NMR spectroscopy.

## **S5 Characterization of products arising from dechlorination of polyvinyl chloride (PVC)**

We aimed to characterize the sample arising from the dechlorination of PVC by Gel Permeation Chromatography (GPC) and matrix-assisted laser desorption/ionization (MALDI). However, the sample was not sufficiently soluble in organic solvents for these characterization techniques to be possible.

### **S5.1 Determination of the extent of dechlorination of PVC**

In a glovebox, a Young NMR tube was charged with **2-Ce** (0.005 mmol, 2.5 mg),  $\text{MgBn}_2(\text{THF})_2$  (0.100 mmol, 35.1 mg), a commercial sample of PVC (0.100 mmol, 6.25 mg, average  $M_w \sim 233,000$ , average  $M_n \sim 99,000$ ) and THF (0.5 mL). The sample was then sealed and placed in front of a Kessil 440 nm lamp for 24 hours. During this time, the precipitation of the dechlorinated polymer as a colourless solid (Figure S1, left) was observed, alongside generation of a yellow solution shown to contain **3-Ce** by  $^1\text{H}$  NMR spectroscopy.



**Figure S3** – Solution and polymer precipitate resulting from the dechlorination of PVC by **2-Ce** (left); isolated dechlorinated polymer (right).

Mohr's method was then used to determine the amount of  $\text{MgCl}_2$  and other chloride-containing species resulting from the dechlorination of polyvinyl chloride. The Young NMR tube was opened to air, and the white solid manually separated from the solution (Figure S1, right). The solution was evaporated to dryness and the resulting solids redissolved in water suitable for trace metal analyses. Potassium chromate indicator was added, and a 25 mM solution of silver nitrate was titrated against the solution until the end point was reached. The extent of dechlorination in the polymer was determined to be 79%.



## S5.2 Further characterization

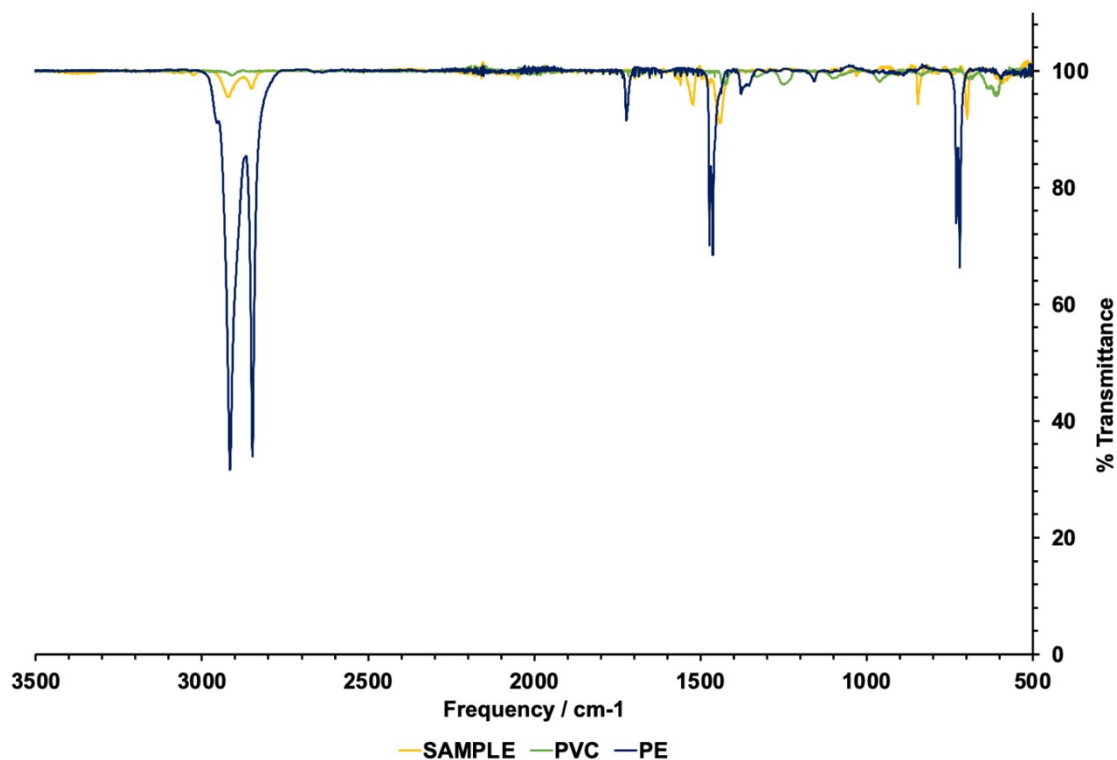


Figure S4. IR spectrum of PVC, polyethylene and the dechlorinated sample. Sample possesses similar features to commercial sample of polyethylene, alongside evidence of unreacted PVC.

## S6 Photophysical measurements

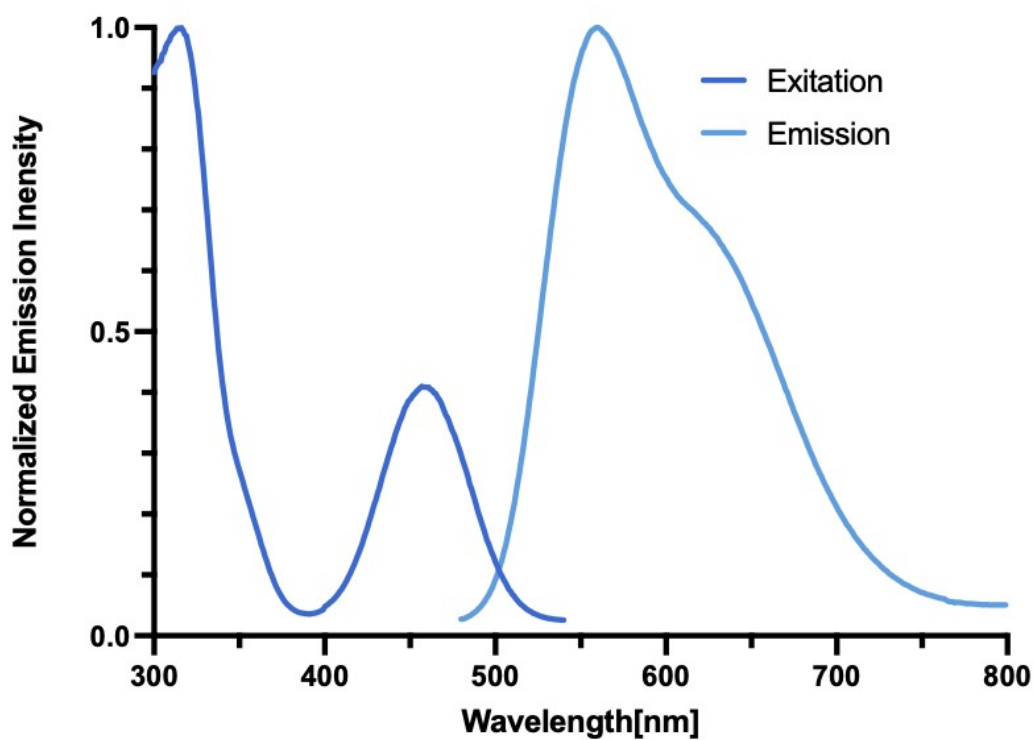


Figure S5 - Emission and excitation spectra of **3-Ce** recorded in THF. The emission spectrum was collected with an excitation wavelength of 300 nm; the excitation was monitored at an emission wavelength of 559 nm. All data were calibrated to the detector efficiency and normalized.

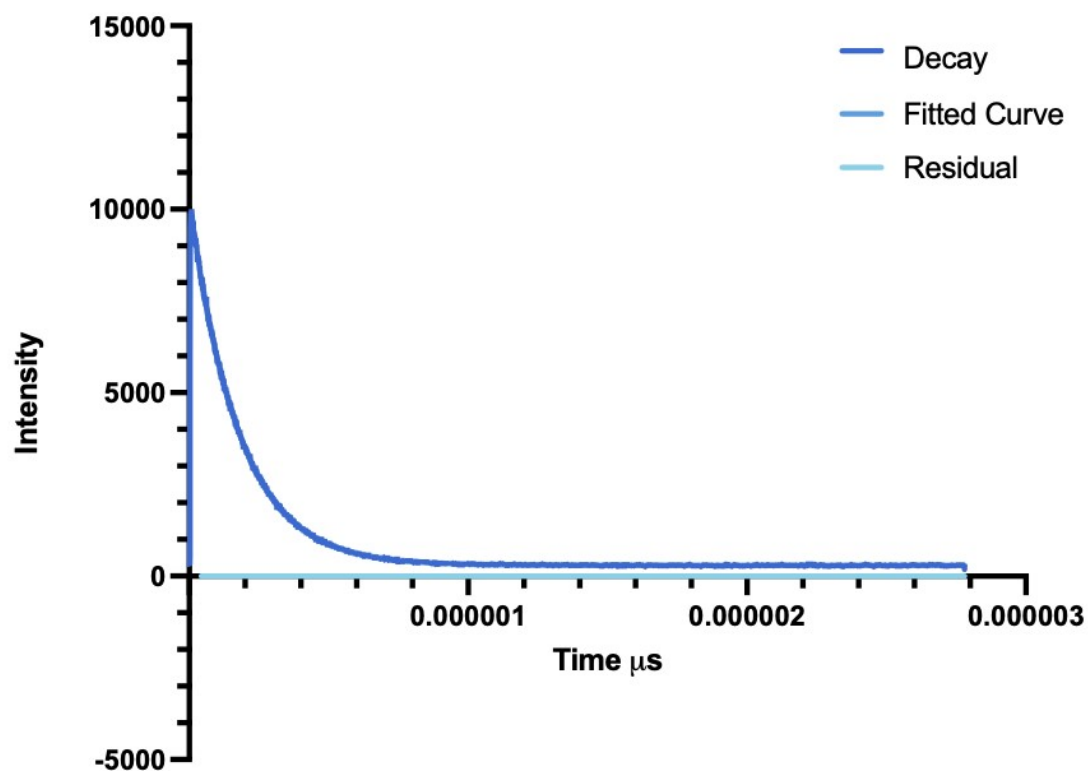


Figure S6 - Lifetime decay of 3-Ce recorded in THF.  $\tau_1[\text{ns}] = 175.10 \pm 0.16$ .

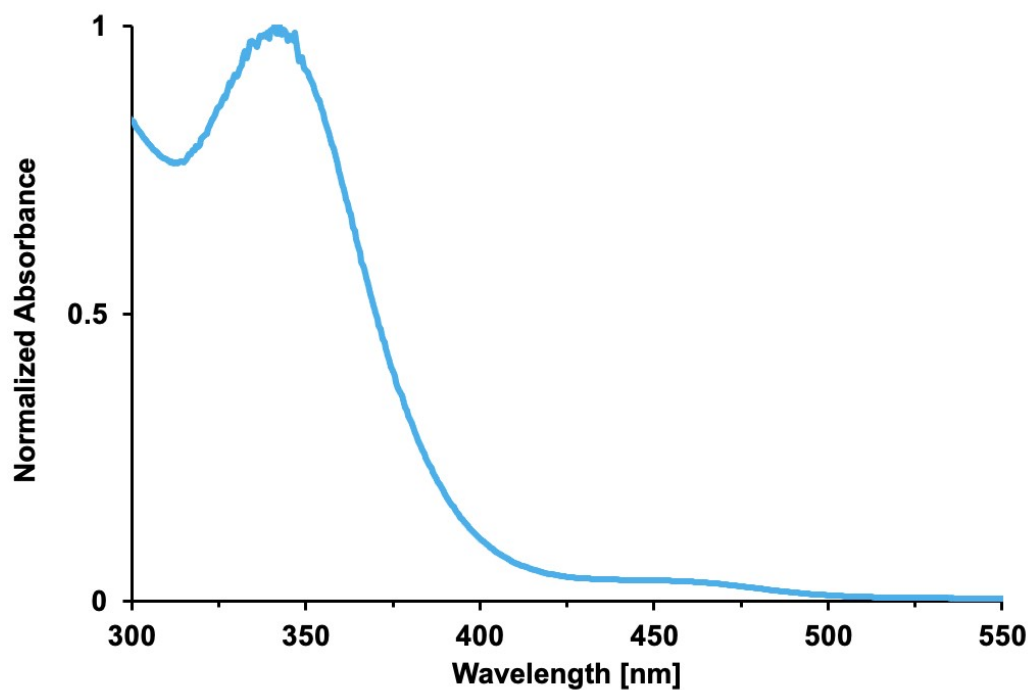


Figure S7 – Absorbance spectrum of 4-Ce in THF.

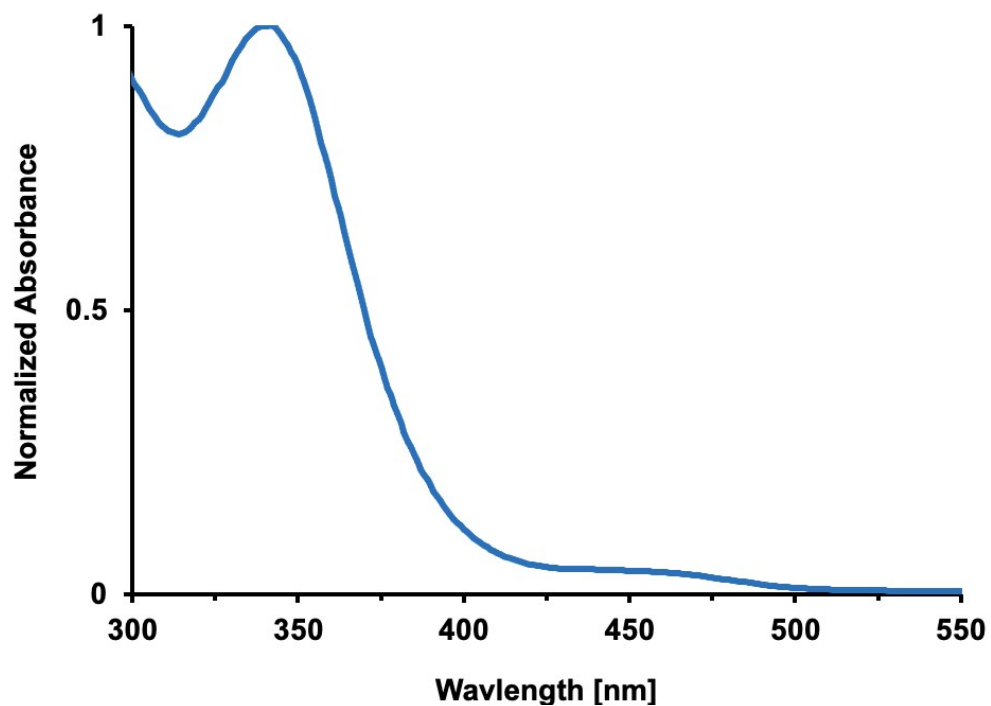


Figure S8 - Absorbance spectrum of 4-Ce and 1  $\mu$ L chlorocyclohexane in THF.

### S7 Crystallography

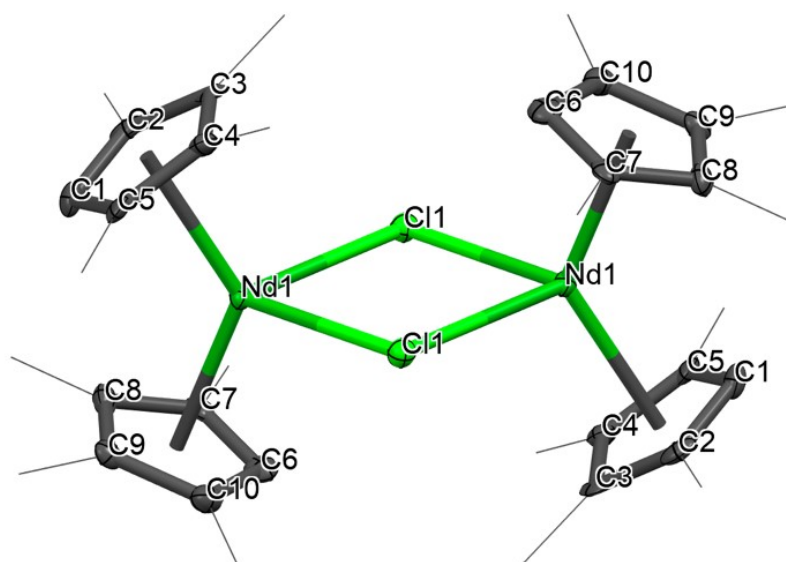
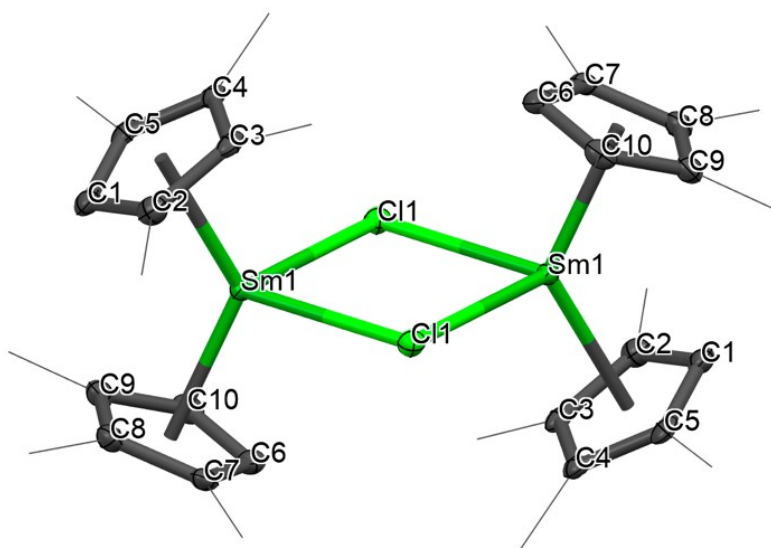


Figure S9 - ORTEP diagram of 3-Nd. Ellipsoids shown at 50% probability, hydrogen atoms have been omitted for clarity.



**Figure S10** - ORTEP diagram of **3-Sm**. Ellipsoids shown at 50% probability, hydrogen atoms have been omitted for clarity.

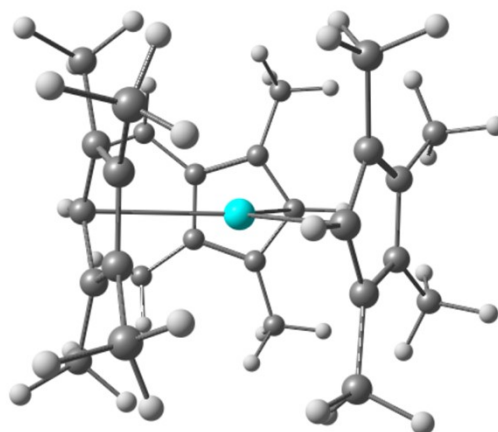
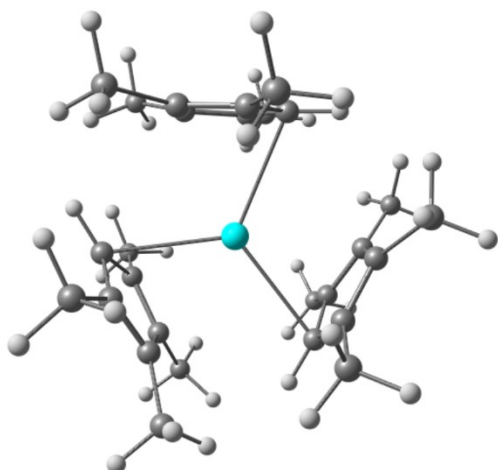
**Table S3** - Crystal data and structure refinement for **3-Nd** and **3-Sm**.

	<b>3-Nd</b>	<b>3-Sm</b>
Empirical formula	C <sub>36</sub> H <sub>52</sub> Cl <sub>2</sub> Nd <sub>2</sub>	C <sub>36</sub> H <sub>52</sub> Cl <sub>2</sub> Sm <sub>2</sub>
Formula weight	844.15	856.37
Temperature/K	100	100
Crystal system	monoclinic	monoclinic
Space group	P2 <sub>1</sub> /n	P2 <sub>1</sub> /n
a/Å	8.504(13)	8.5346(12)
b/Å	10.398(14)	10.3557(14)
c/Å	19.24(3)	19.111(3)
α/°	90	90
β/°	91.801(8)	91.674(5)
γ/°	90	90
Volume/Å <sup>3</sup>	1700(4)	1688.4(4)
Z	2	2
ρ <sub>calc</sub> /cm <sup>3</sup>	1.649	1.684
μ/mm <sup>-1</sup>	3.395	3.859
F(000)	844.0	852.0
Crystal size/mm <sup>3</sup>	0.1 × 0.04 × 0.02	0.2 × 0.1 × 0.1
Radiation	synchrotron (λ = 0.7288)	synchrotron (λ = 0.7288)
2θ range for data collection/°	4.344 to 52.074	4.588 to 58.288
Index ranges	-10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -23 ≤ l ≤ 23	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -25 ≤ l ≤ 25
Reflections collected	21497	25987
Independent reflections	3104 [R <sub>int</sub> = 0.1314, R <sub>sigma</sub> = 0.0838]	4208 [R <sub>int</sub> = 0.0807, R <sub>sigma</sub> = 0.0554]
Data/restraints/parameters	3104/0/189	4208/0/189
Goodness-of-fit on F <sup>2</sup>	0.986	1.037
Final R indexes [I >= 2σ (I)]	R <sub>1</sub> = 0.0482, wR <sub>2</sub> = 0.1196	R <sub>1</sub> = 0.0349, wR <sub>2</sub> = 0.0902
Final R indexes [all data]	R <sub>1</sub> = 0.0585, wR <sub>2</sub> = 0.1275	R <sub>1</sub> = 0.0419, wR <sub>2</sub> = 0.0940
Largest diff. peak/hole / e Å <sup>-3</sup>	0.98/-1.11	0.85/-1.11

## **S8 Computational details**

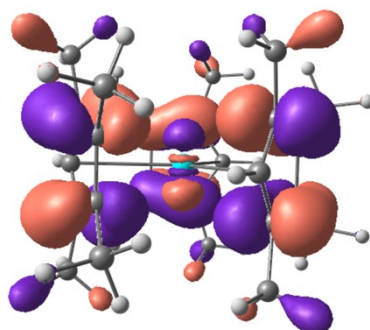
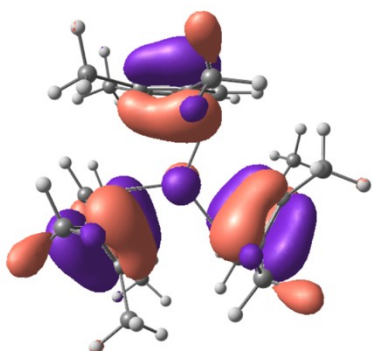
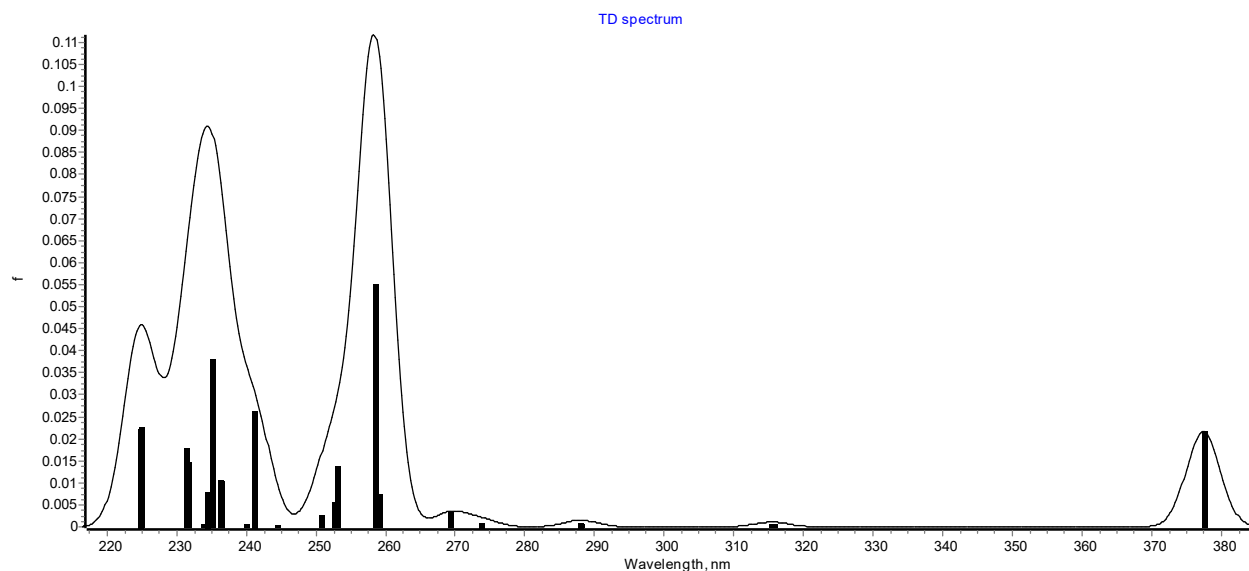
All DFT and TDDFT calculations were carried out using Gaussian 09<sup>13</sup> software package. Optimizations, frequency calculations and population analysis were performed using the B3PW91<sup>14,15</sup> functional. Ce, La and Cl atoms were treated with a Stuttgart effective core potential and the associated basis set.<sup>16,17</sup> In the case of Cl, a set of polarization functions<sup>18</sup> was added. The 6-31G\*\* basis set<sup>19,20</sup> was employed for C and H atoms. Single point calculations including THF solvent were carried out to correct the TDDFT spectra using the SMD model.

### S8.1 2-La



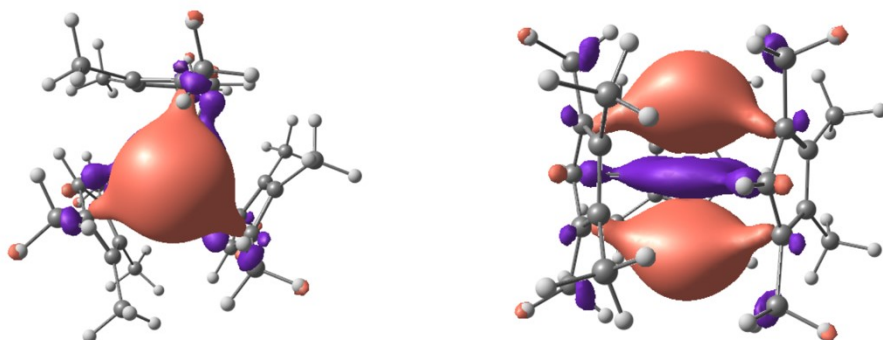
#### **First excitation :**

Excited State 2: Singlet-?Sym 3.2853 eV 377.39 nm f=0.0216 <S\*\*2>=0.000  
HOMO-1 -> LUMO 0.70421



**HOMO-1**

## LUMO

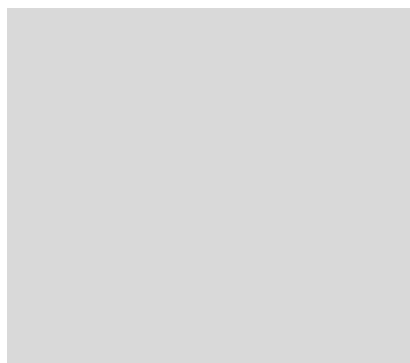
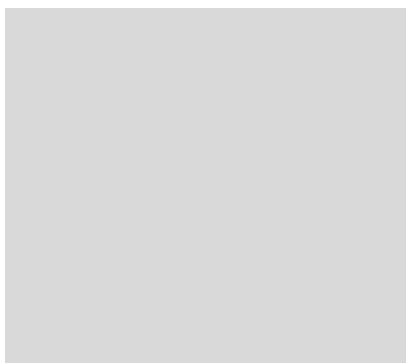


## Including solvent (THF, single point)

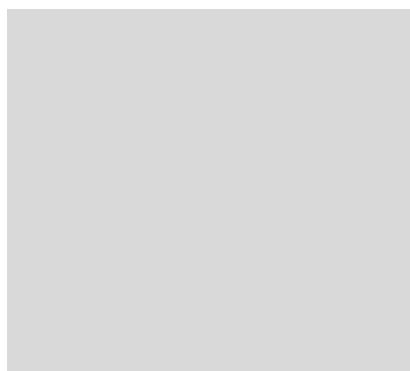
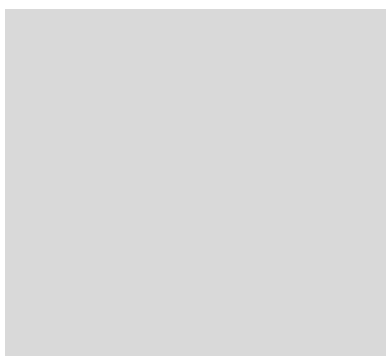
Excited State 2: Singlet-?Sym 2.9146 eV 425.92 nm f=0.0216 <S\*\*2>=0.000

HOMO-1 -> LUMO 0.70421

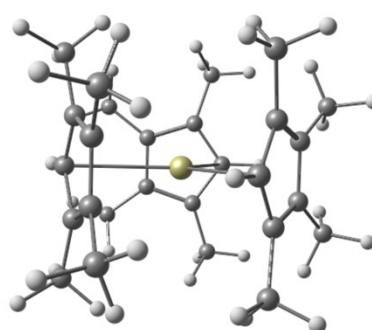
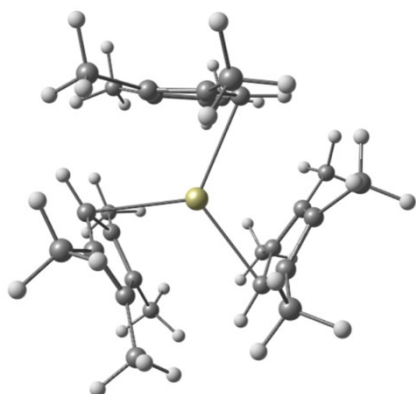
## HOMO-1



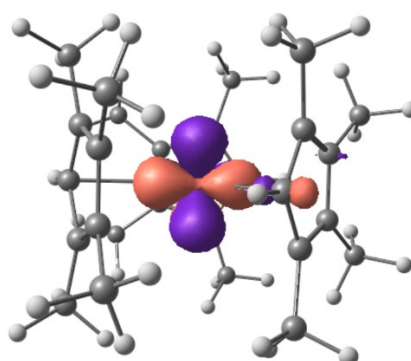
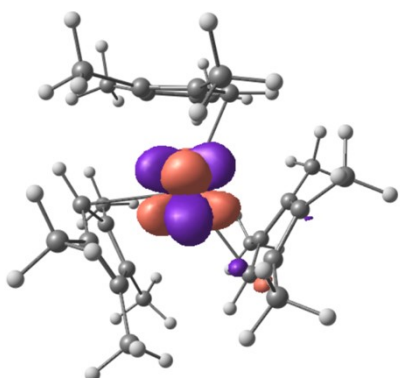
LUMO



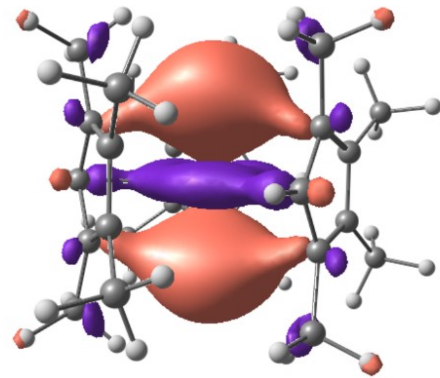
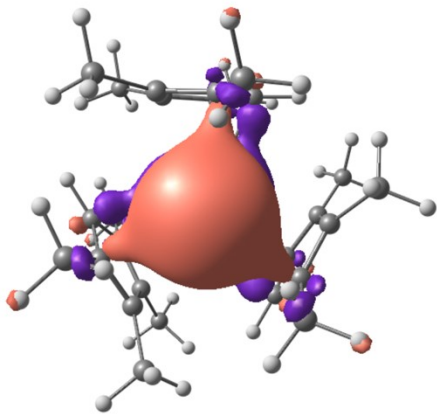
S8.2 2-Ce



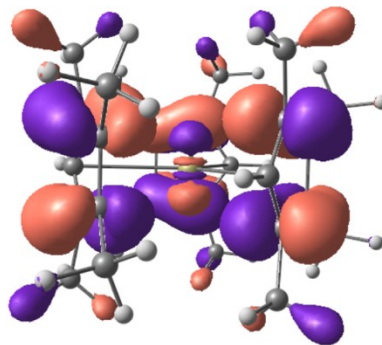
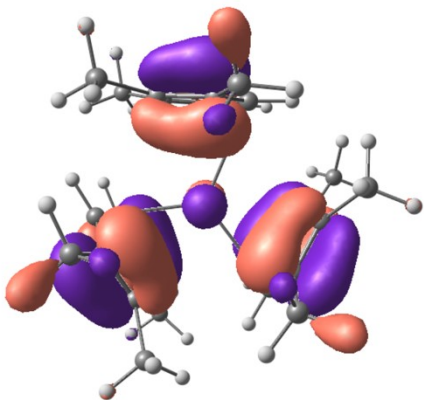
SOMO



## LUMO



## HOMO-1



## First observable excitations:

Excited State 9: 3.425-?Sym 3.0242 eV 409.98 nm  $f=0.0006$   $\langle S^2 \rangle = 2.683$

f

f



SOMO -> LUMO 0.79134  
HOMO-1 -> LUMO -0.56170

Excited State 14: 2.061-?Sym 3.2471 eV 381.83 nm f=0.0209 <S\*\*2>=0.812

SOMO -> LUMO 0.57443  
HOMO-1 -> LUMO 0.80932

### Including solvent (THF, single point)

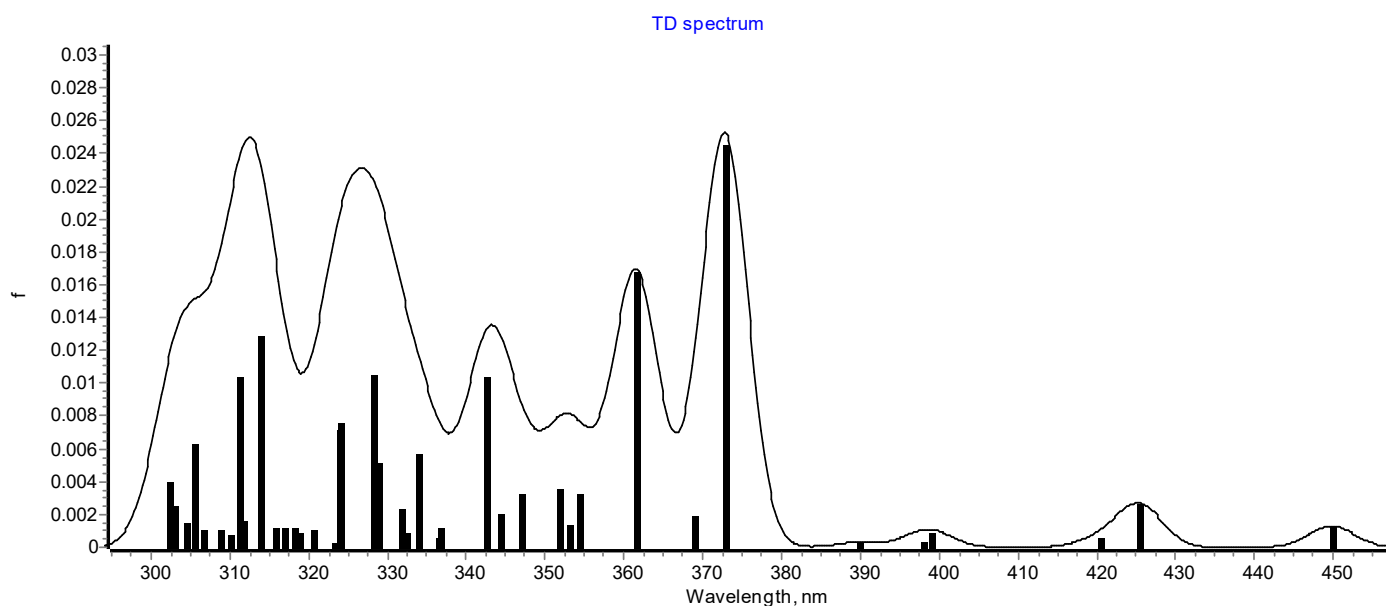
Excited State 9: 3.425-?Sym 2.7552 eV 449.98 nm f=0.0006 <S\*\*2>=2.683

SOMO -> LUMO 0.79134  
HOMO-1 -> LUMO -0.56170

Excited State 14: 2.061-?Sym 2.9146 eV 425.92 nm f=0.0209 <S\*\*2>=0.812

SOMO -> LUMO 0.57443  
HOMO-1 -> LUMO 0.80932

### S8.3 Chloroalkyl adduct to 4-Ce



Excited State 8: 2.594-?Sym 2.9146 eV 425.40 nm f=0.0026 <S\*\*2>=1.432

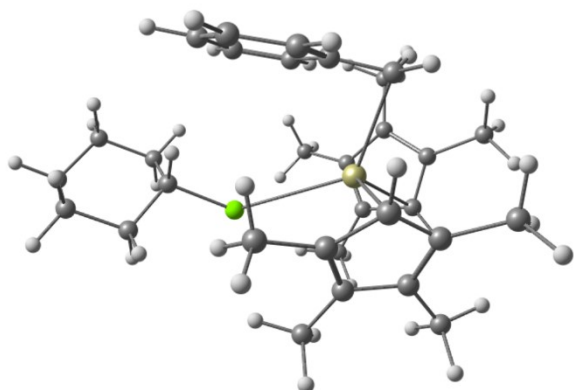
132A ->135A -0.13457  
133A ->135A 0.55554  
133A ->136A 0.14504  
133A ->137A 0.22292  
133A ->138A 0.26988  
133A ->140A 0.19525  
133A ->145A -0.12899  
133A ->147A 0.11695  
133A ->148A -0.11153

134A ->135A	-0.17874
134A ->136A	0.38889
133B ->134B	-0.13876
133B ->135B	-0.34078
133B ->136B	-0.10498

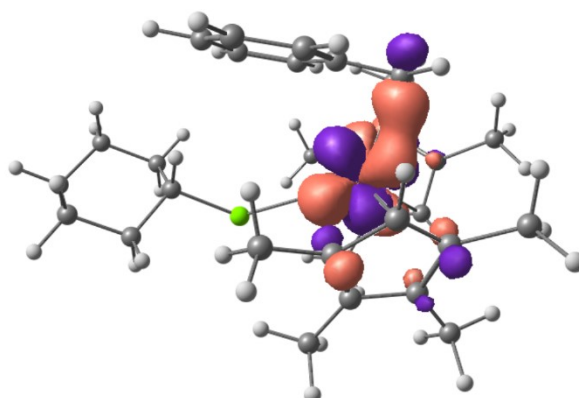
**Including solvent (THF, single point)**

Excited State 8: 2.594-?Sym 2.7675 eV 447.98 nm f=0.0026 <S\*\*2>=1.432

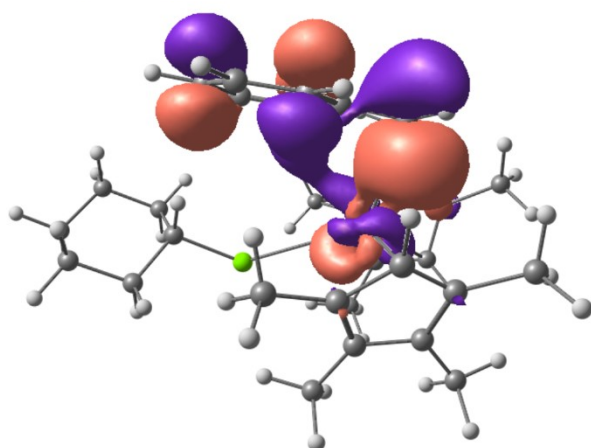
132A ->135A	-0.13457
133A ->135A	0.55554
133A ->136A	0.14504
133A ->137A	0.22292
133A ->138A	0.26988
133A ->140A	0.19525
133A ->145A	-0.12899
133A ->147A	0.11695
133A ->148A	-0.11153
134A ->135A	-0.17874
134A ->136A	0.38889
133B ->134B	-0.13876
133B ->135B	-0.34078
133B ->136B	-0.10498



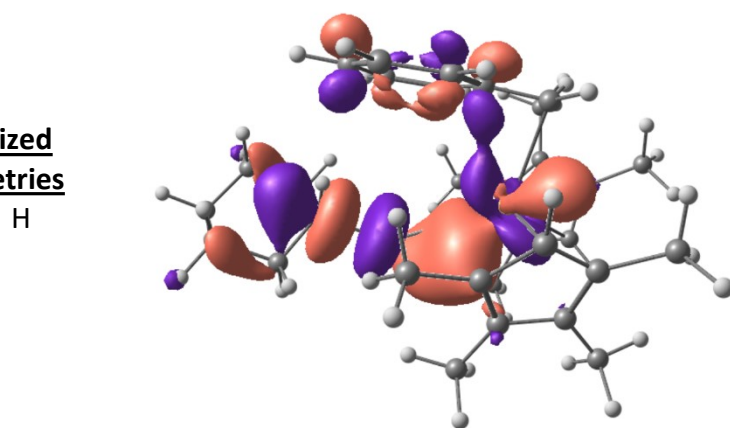
HOMO-1



LUMO



**S8.4**  
**Optimized**  
**geometries**



H

**2-La**

La	-0.001751	-0.001934	12.375711
C	2.460921	-0.820264	11.223000
C	1.945785	-2.072326	11.665674
C	1.945665	-2.072125	13.086399
C	2.460729	-0.819944	13.528818
C	2.789848	-0.066560	12.375835
C	2.760853	-0.451026	9.796715
C	1.690819	-3.254343	10.777747
C	1.690437	-3.253838	13.974664
C	2.760224	-0.450285	14.955089
H	3.242478	0.917073	12.375715
H	3.054550	0.598243	9.713562
H	3.588978	-1.051524	9.397553
H	1.910705	-0.611948	9.120878
H	1.350193	-2.953920	9.781690
H	2.609386	-3.840172	10.633098
H	0.943836	-3.939322	11.190242
H	2.608877	-3.839767	14.119566

0.943379 -3.938816 13.562324

H	1.349782	-2.953016	14.970593
H	3.055945	0.598437	15.037652
H	3.586787	-1.052139	15.355354
H	1.909209	-0.608944	15.630429
C	-0.518402	2.537563	11.223022
C	0.823200	2.720453	11.665375
C	0.823716	2.720346	13.086013
C	-0.517551	2.537292	13.529281
C	-1.334896	2.444039	12.376428
C	-0.987536	2.605943	9.796231
C	1.974777	3.096701	10.780626
C	1.975830	3.096686	13.970024
C	-0.985820	2.605119	14.956385
H	-2.412414	2.339544	12.376813
H	-2.053292	2.376940	9.720328
H	-0.841570	3.610624	9.378354
H	-0.452972	1.915423	9.130440
H	1.874875	2.676811	9.774724
H	2.035846	4.187620	10.661595

H	2.939518	2.770720	11.181279	H	0.931451	-3.937204	11.185401
H	2.036960	4.187605	14.088815	H	2.601891	-3.829771	14.107981
H	2.940336	2.770654	13.568877	H	0.931435	-3.936195	13.568031
H	1.876481	2.676958	14.976044	H	1.347547	-2.950567	14.973819
H	-2.051533	2.376096	15.032773	H	3.035263	0.605237	15.036793
H	-0.839617	3.609594	15.374599	H	3.550569	-1.049729	15.357109
H	-0.450907	1.914286	15.621602	H	1.876379	-0.590846	15.628335
C	-1.943159	-1.719940	11.222213	C	-0.512510	2.509676	11.222458
C	-2.769930	-0.647482	11.665045	C	0.827008	2.699546	11.665780
C	-2.770025	-0.647585	13.085773	C	0.827086	2.699356	13.086374
C	-1.943358	-1.720130	13.528560	C	-0.512374	2.509319	13.529800
C	-1.456363	-2.382176	12.375372	C	-1.329008	2.411674	12.376159
C	-1.771438	-2.161872	9.795574	C	-0.980921	2.581669	9.795576
C	-3.667610	0.166013	10.780144	C	1.976004	3.085861	10.782475
C	-3.667762	0.165776	13.970749	C	1.976228	3.085438	13.969588
C	-1.771866	-2.162208	14.955183	C	-0.980630	2.580776	14.956754
H	-0.829706	-3.265304	12.375348	H	-2.406139	2.307597	12.376221
H	-1.023064	-2.954103	9.715228	H	-2.048403	2.361575	9.719664
H	-2.710183	-2.559981	9.388449	H	-0.826949	3.585443	9.378539
H	-1.465864	-1.348365	9.124477	H	-0.452221	1.887046	9.129476
H	-3.245475	0.302064	9.779377	H	1.874299	2.675565	9.772947
H	-4.639429	-0.329892	10.647469	H	2.033724	4.178068	10.674170
H	-3.875732	1.159416	11.189220	H	2.942771	2.759116	11.177604
H	-4.639301	-0.330503	14.103867	H	2.033965	4.177621	14.078147
H	-3.876454	1.158967	13.561469	H	2.942908	2.758798	13.574153
H	-3.245367	0.302281	14.971354	H	1.874729	2.674870	14.979019
H	-1.023881	-2.954786	15.035510	H	-2.048138	2.360792	15.032656
H	-2.710791	-2.559878	15.362266	H	-0.826496	3.584351	15.374210
H	-1.465903	-1.348871	15.626338	H	-0.451968	1.885797	15.622516

## 2-Ce

Ce	-0.004371	0.003643	12.375680	C	-1.918739	-1.704130	11.222143
C	2.430262	-0.810051	11.222553	C	-2.749274	-0.635211	11.665052
C	1.920889	-2.064111	11.665722	C	-2.749432	-0.635299	13.085944
C	1.921099	-2.063642	13.086114	C	-1.918971	-1.704241	13.528913
C	2.430731	-0.809339	13.528322	C	-1.429391	-2.364244	12.375540
C	2.758508	-0.055719	12.375148	C	-1.748474	-2.145343	9.795212
C	2.729237	-0.442136	9.795753	C	-3.654550	0.170152	10.780694
C	1.678822	-3.249170	10.778728	C	-3.654948	0.169906	13.970200
C	1.679084	-3.248045	13.973999	C	-1.749116	-2.145726	14.955804
C	2.730291	-0.440697	14.954813	H	-0.802579	-3.246712	12.375584
H	3.211162	0.927430	12.374766	H	-1.010748	-2.947267	9.715493
H	3.031085	0.604625	9.712574	H	-2.691452	-2.529904	9.384988
H	3.551483	-1.049147	9.394402	H	-1.429799	-1.334735	9.126739
H	1.875949	-0.595716	9.122239	H	-3.237440	0.303959	9.777636
H	1.346935	-2.952495	9.778786	H	-4.623850	-0.332341	10.654669
H	2.601719	-3.830781	10.644891	H	-3.867326	1.164081	11.186105
				H	-4.624129	-0.332827	14.096194
				H	-3.867962	1.163747	13.564700

H	-3.237945	0.303882	14.973279
H	-1.010904	-2.947188	15.035698
H	-2.692048	-2.531019	15.365456
H	-1.431314	-1.335074	15.624628

#### Chloroalkyl adduct to 4-Ce

Ce	1.789326	6.162344	9.808599
C	3.725542	8.209133	9.565158
C	4.013137	7.277919	8.527664
C	-0.367834	5.074937	11.407860
C	-0.803809	6.381040	11.041349
C	2.597853	3.961055	6.851221
H	3.636480	3.674689	6.996969
C	1.717626	3.913207	7.970671
C	2.168325	3.654448	9.312272
H	3.169632	3.237063	9.409425
H	1.441902	3.159339	9.956985
C	0.064839	7.326057	11.654792
C	2.152809	4.293192	5.581913
H	2.855298	4.276369	4.751493
C	4.471602	6.261060	10.549228
C	4.019088	7.584580	10.813093
C	1.034320	6.591969	12.387364
H	1.806955	7.023235	13.013149
C	0.773477	5.205295	12.243597
C	3.369113	9.656678	9.384539
H	2.880215	9.839585	8.423775
H	4.265275	10.291833	9.418219
H	2.694624	10.020142	10.167197
C	4.464966	6.085969	9.143603
H	4.767585	5.185403	8.622072
C	3.971757	7.539827	7.050185
H	3.833787	6.612494	6.486806
H	4.904137	8.004497	6.702059
H	3.157610	8.218314	6.774979
C	-0.097000	8.820175	11.671068
H	0.853722	9.321216	11.879706
H	-0.801722	9.134475	12.452817
H	-0.477908	9.217391	10.724344
C	0.369648	4.294560	7.712272
H	-0.357212	4.224303	8.519588
C	4.069653	8.287312	12.138174

H	3.233442	8.980044	12.281183
H	4.990648	8.879509	12.229893
H	4.061846	7.582688	12.974821
C	0.808956	4.622186	5.348183
H	0.461610	4.847844	4.344035
C	1.467597	4.092891	12.975048
H	1.671963	3.228806	12.333828
H	0.858522	3.732358	13.814936
H	2.422309	4.426776	13.391808
C	-2.066158	6.698051	10.292029
H	-2.053231	7.713512	9.887620
H	-2.944756	6.620274	10.947002
H	-2.236355	6.015481	9.451844
C	-1.112389	3.797706	11.150687
H	-1.747378	3.856647	10.260762
H	-1.776338	3.557297	11.992612
H	-0.443682	2.939933	11.023719
C	-0.071642	4.618839	6.425697
H	-1.124336	4.844623	6.269217
C	4.996721	5.274900	11.552080
H	4.490821	5.356130	12.519510
H	6.067884	5.429262	11.739115
H	4.872464	4.246108	11.200906
Cl	0.196343	8.365762	7.991907
C	-0.126897	8.298331	6.168648
C	0.502903	9.514504	5.509908
C	0.207090	9.499486	4.002884
C	-1.295710	9.417744	3.726694
C	-1.919043	8.209750	4.429066
C	-1.627335	8.221949	5.936971
H	1.582006	9.529450	5.689848
H	0.085068	10.423157	5.962066
H	0.637938	10.395608	3.542526
H	0.711904	8.639193	3.542092
H	-1.480804	9.366118	2.647775
H	-1.781080	10.336542	4.084806
H	-3.003317	8.186695	4.272318
H	-1.521263	7.285204	3.988445
H	-2.038536	7.330999	6.420761
H	-2.106588	9.094324	6.399536
H	0.363830	7.372619	5.855737

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