

Supporting Information:

**Tripodal tris(siloxide) Ligand Supported Trivalent Rare-earth Metal Complexes
and Redox Reactivity**

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1. Experimental

General. All operations were performed under an inert atmosphere of nitrogen using standard Schlenk-line or glovebox techniques. THF, *n*-hexane and THF-*d*₈ were dried over K-Na alloy, followed by vacuum transferred, and stored in the glovebox. CH₃CN were dried over CaH₂ and distilled under nitrogen prior to use. ¹H, ¹³C{¹H} spectra were recorded on a Bruker Ascend™ 400 spectrometer at 400 and 101 MHz, respectively. All chemical shifts were reported in δ units with references to the residual solvent resonance of the deuterated solvents for proton and carbon chemical shifts. LH₃ was synthesized via a modified procedure from the initial report,¹ LnCl₃ (Ln = Tb, Y, Lu) and LnI₃(THF)_x (Ln = Pr, Ce) were prepared according to the literature procedures.² Cyclic voltammetry measurements were carried out in a glovebox under a dinitrogen atmosphere using a CH Instruments electrochemical analyzer. A glassy carbon electrode and platinum wire were used as the working and auxiliary electrodes, respectively. The reference electrode was a Ag/AgNO₃ nonaqueous reference electrode assembled in THF or CH₃CN. Solutions of electrolyte (0.1 M [ⁿPr₄N][BAr₄^F] (Ar^F = 3,5-bis(trifluoromethyl)phenyl))³ and analytes were also prepared in the glovebox. All potentials are reported vs the Fc/Fc⁺ couple by comparison with an internal ferrocene reference added following data collection. Elemental analyses were performed by the Microanalytical Laboratory of Shanghai Institute of Organic Chemistry.

Synthesis of LH₃: A three-necked, round-bottomed flask was equipped with a magnetic stir bar and a gas inlet connected to an argon-vacuum manifold. The flame-dried flask was filled with argon and charged with 1,3,5-Tris(2-iodophenyl) benzene (5.00 g, 7.31 mmol). Et₂O (120 mL) was added and the stirred suspension was cooled to -80°C. A solution of ⁿBuLi (17.6 mL, 44.0 mmol, 2.5 M in *n*-hexane) was added over 10 min while the suspension was stirring. The mixture was allowed to warm to ambient temperature and stirring was continued for 1.5 h. The obtained brown suspension was again cooled to -80°C and a solution of diphenyldimethoxysilane (5.10 mL, 21.8 mmol) in Et₂O (30 mL) was added dropwise over 15 min. The reaction mixture was allowed to warm to ambient temperature and stirred for 12 h. The reaction was carefully quenched with water and the mixture was transferred into a separation funnel. The organic phase was separated and the aqueous solution was extracted with CH₂Cl₂ (3 x 50 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated in vacuo. Hexanes (50 mL) was added to precipitate a white solid product. (4.59 g, 65%). Following the previously reported procedure,¹ treatment of this solid with concentrated HCl solution in THF afforded LH₃ in nearly quantitative yield as a white solid. ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ (ppm) = 7.54 (d, ³J_{HH} = 6.8 Hz, 12H, ArH), 7.47-7.46 (m, 3H, ArH), 7.28-7.25 (m, 12H, ArH, partly overlapped with the solvent peak), 7.16 (t, ³J_{HH} = 7.4 Hz, 12H, ArH), 6.89-6.88 (m, 6H, ArH), 4.58 (br s, 3H, OH). The ¹H NMR spectrum is the same as that reported previously.

Synthesis of 1: LH₃ (200 mg, 0.22 mmol) in 5 mL of THF was slowly added to a slurry of KH (26 mg, 0.66 mmol) in 2 mL of THF at room temperature. The resulting orange reaction mixture was stirred at room temperature for 1 h and filtered through a pad of Celite. A slurry of CeI₃(THF)₄ (177 mg, 0.22 mmol) in 2 mL of THF was slowly added to the filtrate, which was allowed to stir at room temperature for 12 h. The reaction mixture was filtered through a pad of Celite, and the pale orange solution was concentrated under reduced pressure to about 5 mL, which was layered with 7 mL of *n*-hexane and stored at room temperature to afford pale yellow crystals of 1. Yield: 214 mg (80%). 1 is paramagnetic. ¹H NMR (THF-*d*₈, 400 MHz, 25 °C): δ (ppm) = 12.60 (br s, 12H, ArH), 9.25 (d, ³J_{HH} = 7.2 Hz, 3H, ArH), 8.75 (br s, 12H, ArH), 8.18 (br

s, 6H, ArH), 7.28 (t, $^3J_{\text{HH}} = 7.4$ Hz, 3H, ArH), 6.07 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3H, ArH), 3.62 (m, 12H, OCH₂CH₂), 2.80 (d, $^3J_{\text{HH}} = 7.2$ Hz, 3H, ArH), 1.79 (m, 12H, OCH₂CH₂), -2.27 (s, 3H, ArH). Anal. calcd for C₇₂H₆₉O₆Si₃Ce (1254.71 g/mol): C, 68.92; H, 5.54. Found: C, 69.05; H, 5.48.

Synthesis of 2: LH₃ (200 mg, 0.22 mmol) in 5 mL of THF was slowly added to a slurry of KH (26 mg, 0.66 mmol) in 2 mL of THF at room temperature. The resulting orange reaction mixture was stirred at room temperature for 1 h and filtered through a pad of Celite. A slurry of PrI₃(THF)₄ (140 mg, 0.22 mmol) in 2 mL of THF was slowly added to the filtrate, which was allowed to stir at room temperature for 12 h. The reaction mixture was filtered through a pad of Celite, and the pale orange solution was concentrated under reduced pressure to about 5 mL, which was layered with 7 mL of *n*-hexane and stored at room temperature to afford pale yellow crystals of **2**. Yield: 135 mg (53%). **2** is paramagnetic. ¹H NMR (THF-*d*₈, 400 MHz, 25 °C): δ (ppm) = 18.95 (br s, 6H, ArH), 17.46 (br s, 6H, ArH), 11.20 (d, $^3J_{\text{HH}} = 7.6$ Hz, 3H, ArH), 11.50-8.77 (br m, 18H, ArH), 7.48 (t, $^3J_{\text{HH}} = 7.6$ Hz, 3H, ArH), 5.00 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3H, ArH), 3.62 (m, 12H, OCH₂CH₂), 1.79 (m, 12H, OCH₂CH₂), -1.40 (d, $^3J_{\text{HH}} = 6.8$ Hz, 3H, ArH), -12.44 (s, 3H, ArH). Anal. calcd for C₇₂H₆₉O₆Si₃Pr (1255.50 g/mol): C, 68.88; H, 5.54. Found: C, 69.18; H, 5.83.

Synthesis of 3: LH₃ (200 mg, 0.22 mmol) in 5 mL of THF was slowly added to a slurry of KH (26 mg, 0.66 mmol) in 2 mL of THF at room temperature. The resulting orange reaction mixture was stirred at room temperature for 1 h and filtered through a pad of Celite. A slurry of TbCl₃ (58 mg, 0.22 mmol) in 2 mL of THF was slowly added to the filtrate, which was allowed to stir at room temperature for 12 h. The reaction mixture was filtered through a pad of Celite, and the pale orange solution was concentrated under reduced pressure to about 5 mL, which was layered with 7 mL of *n*-hexane and stored at room temperature to afford pale yellow crystals of **3**. Yield: 168 mg (60%). **3** is paramagnetic. ¹H NMR (THF-*d*₈, 400 MHz, 25 °C): δ (ppm) = 48.25 (s, 9H, ArH), 41.65 (s, 5H, ArH), 37.84 (br s, 6H, ArH), 32.91 (s, 5H, ArH), 25.13 (s, 5H, ArH), 9.33 (s, 5H, ArH), 3.65 (m, 12H, OCH₂CH₂), 1.79 (m, 12H, OCH₂CH₂), -13.69 (m, 5H, ArH), -72.76 (s, 5H, ArH). Anal. calcd for C₇₂H₆₉O₆Si₃Tb (1273.52 g/mol): C, 67.91; H, 5.46. Found: C, 67.49; H, 5.10.

Synthesis of 4: LH₃ (200 mg, 0.22 mmol) in 5 mL of THF was slowly added to a slurry of KH (26 mg, 0.66 mmol) in 2 mL of THF at room temperature. The resulting orange reaction mixture was stirred at room temperature for 1 h and filtered through a pad of Celite. A slurry of YCl₃ (43 mg, 0.22 mmol) in 2 mL of THF was slowly added to the filtrate, which was allowed to stir at room temperature for 12 h. The reaction mixture was filtered through a pad of Celite, and the pale orange solution was concentrated under reduced pressure to about 5 mL, which was layered with 7 mL of *n*-hexane and stored at room temperature to afford pale yellow crystals of **4**. Yield: 193 mg (73%). ¹H NMR (THF-*d*₈, 400 MHz, 25 °C): δ (ppm) = 7.84 (br s, 6H, ArH), 7.69 (br s, 6H, ArH), 7.62 (d, $^3J_{\text{HH}} = 7.2$ Hz, 3H, ArH), 7.27 (br s, 9H, ArH), 7.19 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3H, ArH), 7.14 (t, $^3J_{\text{HH}} = 7.4$ Hz, 3H, ArH), 7.04 (s, 6H, ArH), 6.82 (br s, 6H, ArH), 6.78 (d, $^3J_{\text{HH}} = 7.6$ Hz, 3H, ArH), 3.62 (m, 12H, OCH₂CH₂), 1.78 (m, 12H, OCH₂CH₂); ¹³C{¹H} NMR (THF-*d*₈, 101 MHz, 25 °C): δ (ppm) = 151.64 (s, ArC), 145.09 (s, ArC), 140.45 (s, ArC), 137.92 (s, ArC), 136.83 (s, ArC), 130.90 (s, ArC), 129.33 (s, ArC), 129.01 (s, ArC), 128.65 (s, ArC), 127.88 (s, ArC), 127.69 (s, ArC), 125.49 (s, ArC), 68.38 (s, OCH₂CH₂), 26.52 (s, OCH₂CH₂). Anal. calcd for C₇₂H₆₉O₆Si₃Y (1203.50 g/mol): C, 71.86; H, 5.78. Found: C, 72.28; H, 5.11.

Synthesis of 5: LH₃ (200 mg, 0.22 mmol) in 5 mL of THF was slowly added to a slurry of KH (26 mg, 0.66 mmol) in 2 mL of THF at room temperature. The resulting orange reaction mixture was stirred at room

temperature for 1 h and filtered through a pad of Celite. A slurry of LuCl_3 (62 mg, 0.22 mmol) in 2 mL of THF was slowly added to the filtrate, which was allowed to stir at room temperature for 12 h. The reaction mixture was filtered through a pad of Celite, and the pale orange solution was concentrated under reduced pressure to about 5 mL, which was layered with 7 mL of *n*-hexane and stored at room temperature to afford pale yellow crystals of **5**. Yield: 204 mg (72%). ^1H NMR (THF- d_8 , 400 MHz, 25 °C): δ (ppm) = 7.86 (d, $^3J_{\text{HH}} = 6.8$ Hz, 6H, ArH), 7.69 (br s, 6H, ArH), 7.63 (dd, $^3J_{\text{HH}} = 7.2$ Hz, $^4J_{\text{HH}} = 1.2$ Hz, 3H, ArH), 7.27 (br s, 9H, ArH), 7.19 (td, $^3J_{\text{HH}} = 7.2$ Hz, $^4J_{\text{HH}} = 1.2$ Hz, 3H, ArH), 7.14 (td, $^3J_{\text{HH}} = 7.4$ Hz, $^4J_{\text{HH}} = 1.2$ Hz, 3H, ArH), 7.03 (t, $^3J_{\text{HH}} = 7.4$ Hz, 3H, ArH), 7.01 (s, 3H, ArH), 6.80-6.78 (m, 9H, ArH), 3.62 (m, 12H, OCH_2CH_2), 1.78 (m, 12H, OCH_2CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 101 MHz, 25 °C): δ (ppm) = 151.73 (s, ArC), 145.06 (s, ArC), 144.82 (s, ArC), 143.46 (s, ArC), 140.67 (s, ArC), 137.97 (s, ArC), 137.00 (s, ArC), 136.93 (s, ArC), 130.80 (s, ArC), 129.30 (s, ArC), 129.04 (s, ArC), 128.61 (s, ArC), 127.93 (s, ArC), 127.57 (s, ArC), 125.50 (s, ArC), 68.38 (s, OCH_2CH_2), 26.52 (s, OCH_2CH_2). Anal. calcd for $\text{C}_{72}\text{H}_{69}\text{O}_6\text{Si}_3\text{Lu}$ (1289.56 g/mol): C, 67.06; H, 5.39. Found: C, 66.55; H, 5.14.

Synthesis of **6**: $[\text{N}(\text{C}_6\text{H}_4\text{Br})_3][\text{SbCl}_6]$ (60 mg, 0.073 mmol) in 2 mL of CH_3CN was slowly added to compound **1** (90 mg, 0.072 mmol) in 4 mL of mixed solvent of THF/ CH_3CN (v/v = 1:3) at room temperature. The blue reaction mixture was stirred at for 10 h, during which time the blue color gradually faded and yellow solid precipitated, which was isolated by centrifugation and washed twice with minimum of acetonitrile to afford **6**. Yield: 56 mg (60%). ^1H NMR (THF- d_8 , 400 MHz, 25 °C): δ (ppm) = 7.79 (s, 12H, ArH), 7.53 (d, $^2J_{\text{HH}} = 6.4$ Hz, 3H, ArH), 7.46-7.06 (m, 21H, ArH), 7.04 (s, 6H, ArH), 6.83 (d, $^2J_{\text{HH}} = 7.2$ Hz, 3H, ArH), 3.62 (m, 8H, OCH_2), 1.77 (m, 8H, CH_2). Due to its low solubility in common solvents, satisfactory $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum was not obtained. Anal. calcd for $\text{C}_{68}\text{H}_{61}\text{O}_5\text{Si}_3\text{CeCl}$ (1250.99 g mol $^{-1}$): C, 65.29; H, 4.92. Found: C, 65.65; H, 4.23.

Synthesis of 7: NaO t Bu (4.7 mg, 0.049 mmol) in 1 mL of THF was slowly added to compound **6** (60 mg, 0.049 mmol) in 3 mL of THF at room temperature. The yellow reaction mixture was stirred at room temperature for 1 h and filtered through a pad of Celite. The yellow solution was concentrated to about 2 mL under reduced pressure, which was layered with 4 mL of *n*-hexane and stored at room temperature to afford yellow crystals of **7**. Yield: 35 mg (57%). ^1H NMR (THF- d_8 , 400 MHz, 25 °C): δ (ppm) = 7.82 (br s, 12H, ArH), 7.54 (dd, $^3J_{\text{HH}} = 7.2$ Hz, $^4J_{\text{HH}} = 1.4$ Hz, 3H, ArH), 7.28 (br s, 15H, ArH), 7.21 (td, $^3J_{\text{HH}} = 7.6$ Hz, $^4J_{\text{HH}} = 1.2$ Hz, 3H, ArH), 7.16 (td, $^3J_{\text{HH}} = 7.4$ Hz, $^4J_{\text{HH}} = 1.6$ Hz, 3H, ArH), 6.94 (s, 3H, ArH), 6.86 (br s, 3H, ArH), 6.76 (d, $^3J_{\text{HH}} = 7.4$ Hz, $^4J_{\text{HH}} = 0.8$ Hz, 3H, ArH), 3.63 (m, 8H, OCH_2CH_2), 1.79 (m, 8H, OCH_2CH_2), 0.52 (s, 9H, $\text{C}(\text{CH}_3)_3$); $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 101 MHz, 25 °C): δ (ppm) = 151.31 (s, ArC), 145.03 (s, ArC), 142.26 (br s, ArC), 139.07 (s, ArC), 138.18 (s, ArC), 136.80 (br s, ArC), 130.75 (s, ArC), 129.65 (s, ArC), 129.38 (s, ArC), 127.98 (s, ArC), 125.86 (s, ArC), 84.05 (s, $\text{C}(\text{CH}_3)_3$), 68.38 (s, OCH_2CH_2), 32.96 (s, $\text{C}(\text{CH}_3)_3$), 25.87 (s, OCH_2CH_2). Anal. calcd for $\text{C}_{72}\text{H}_{70}\text{O}_6\text{Si}_3\text{Ce}$ (1255.72 g/mol): C, 68.87; H, 5.62. Found: C, 68.59; H, 6.20.

Reactions of 1 with oxidants: Complex **1** (20 mg, 0.016 mmol) in 2 mL of THF was treated with AgI (3.8 mg, 0.016 mmol), C_2Cl_6 (3.8 mg, 0.016 mmol) and I_2 (4.1 mg, 0.016 mmol) in 1 mL of THF at room temperature, respectively. The pale-yellow reaction solution remained unchanged for AgI and C_2Cl_6 , while for the I_2 the color turned brown. After 12h, the solution was filtered and evaporated to give pale-yellow solid. The ^1H NMR spectra of these solid only showed signals of **1**. Performing these reactions at -35 °C led to the same results.

Reactions of 6 with anionic nucleophiles: 1. Complex **6** (20 mg, 0.016 mmol) in 2 mL of THF was treated with $K[o\text{-CH}_2\text{C}_6\text{H}_4\text{NMe}_2]$ (3 mg, 0.017 mmol) in 1 mL of THF at -60°C . The pale-yellow reaction solution remained largely unchanged while small amount of white solid was generated. ^1H NMR spectrum taken after 30 min showed the formation of Ce(III) complex **1** as the major species.

2. Complex **6** (20 mg, 0.016 mmol) in 2 mL of THF was treated with $\text{KN}(\text{SiMe}_3)_2$ (3.3 mg, 0.017 mmol) in 1 mL of THF at -60°C . The pale-yellow reaction solution turned brown. ^1H NMR spectrum taken after 30 min showed the formation of Ce(III) complex **1** as the major species.

3. Complex **6** (20 mg, 0.016 mmol) in 2 mL of THF was treated with KNHDipp (3.6 mg, 0.017 mmol) in 1 mL of THF at -60°C . The pale-yellow reaction solution remained largely unchanged while small amount of white solid was generated. ^1H NMR spectrum taken after 30 min showed the formation of Ce(III) complex **1** as the major species.

2. NMR Spectroscopic Data

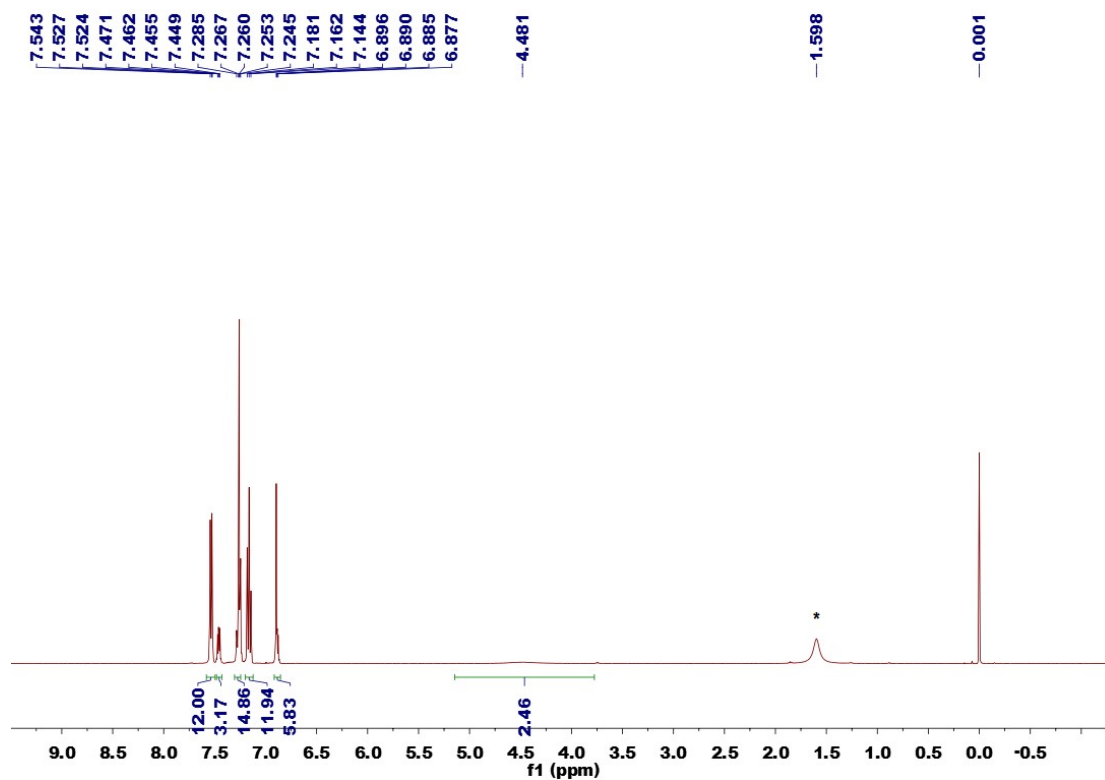


Figure S1. ^1H NMR spectrum of LH_3 in CDCl_3 at $25\text{ }^\circ\text{C}$. (* denotes residual water in CDCl_3)

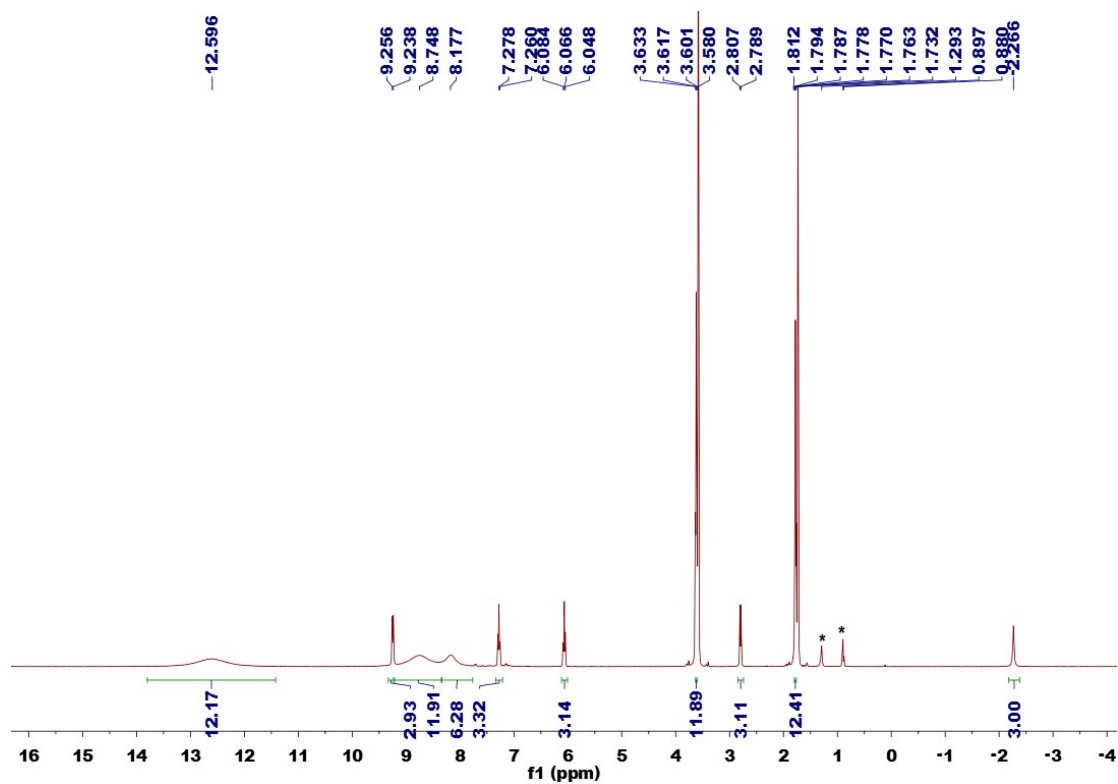


Figure S2. ^1H NMR spectrum of **1** in $\text{THF-}d_8$ at $25\text{ }^\circ\text{C}$. (* denotes small amount of hexane)

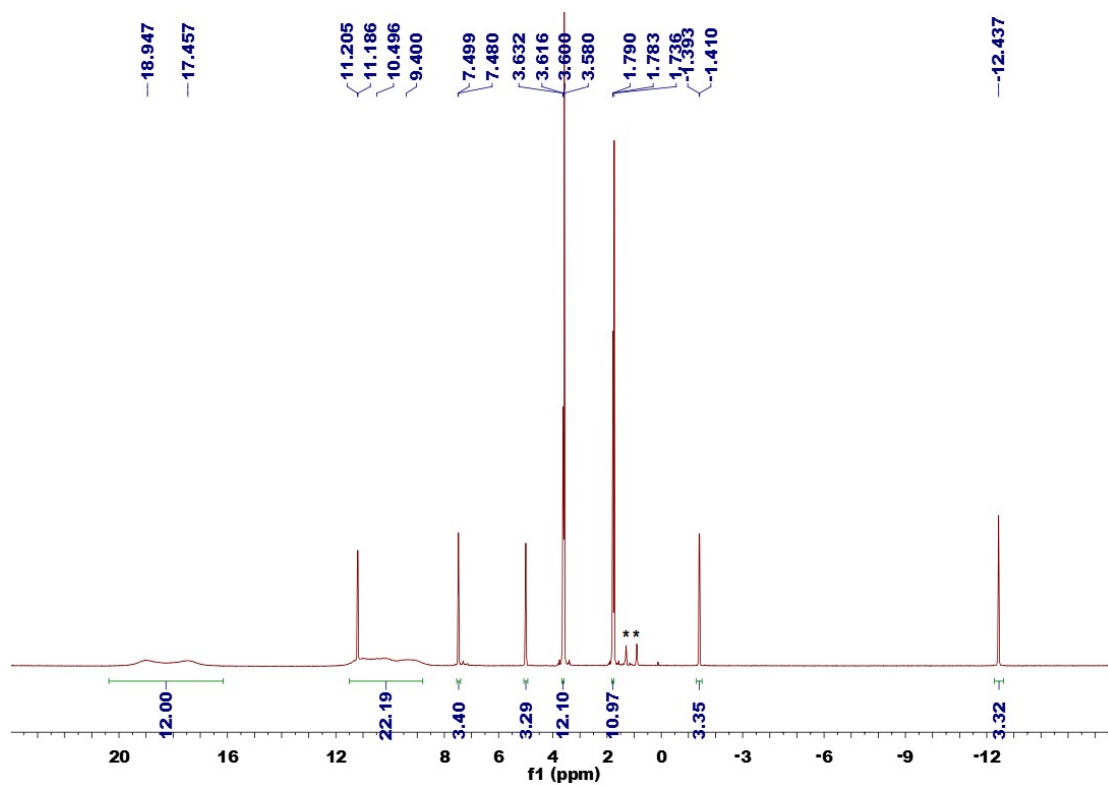


Figure S3. ^1H NMR spectrum of **2** in $\text{THF-}d_8$ at $25\text{ }^\circ\text{C}$. (* denotes small amount of hexane)

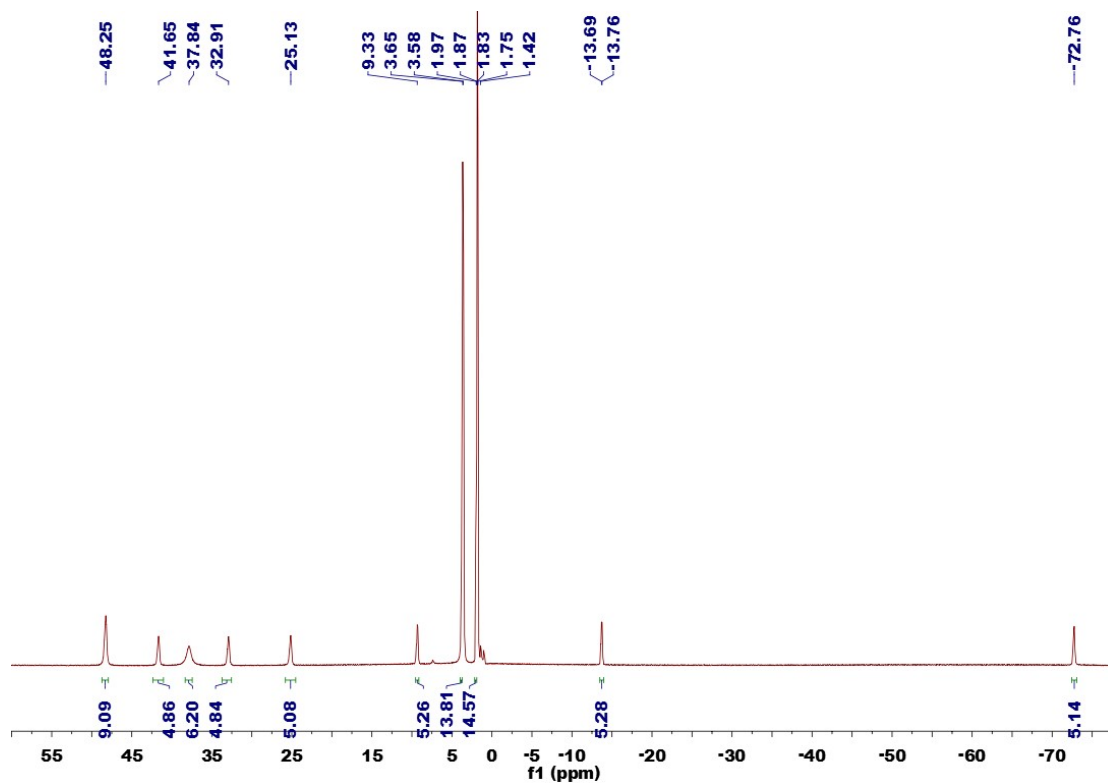


Figure S4. ^1H NMR spectrum of **3** in $\text{THF-}d_8$ at $25\text{ }^\circ\text{C}$.

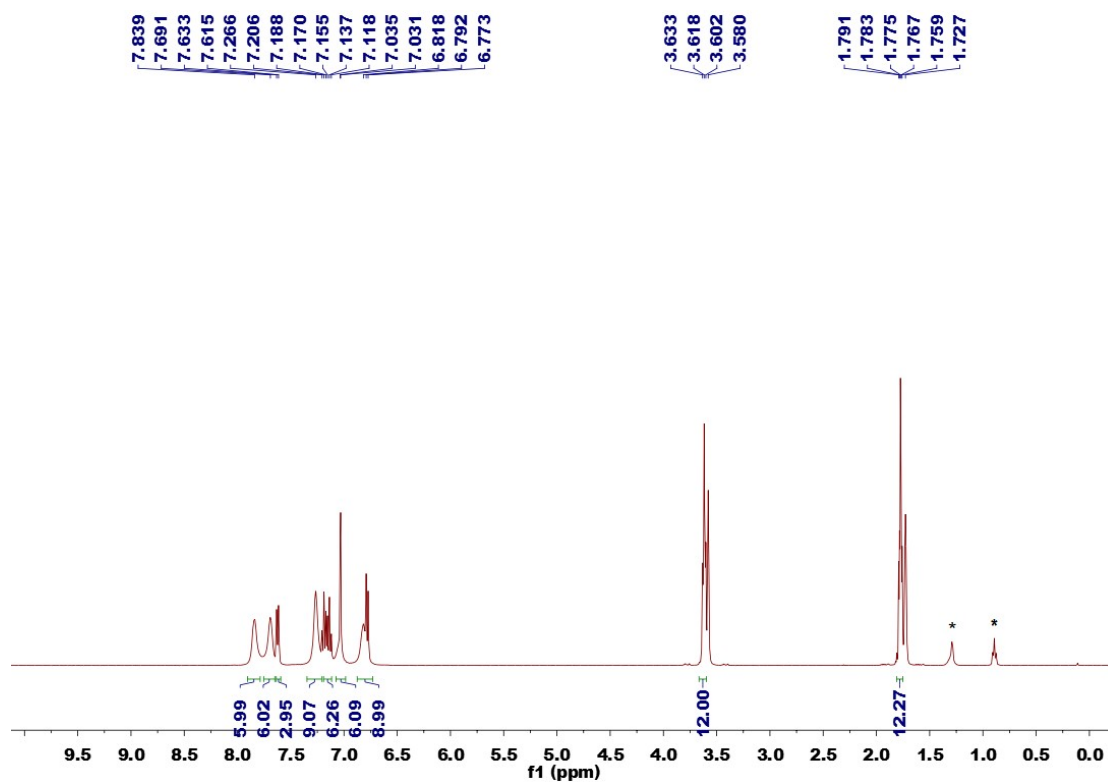


Figure S5. ^1H NMR spectrum of **4** in $\text{THF-}d_8$ at $25\text{ }^\circ\text{C}$. (* denotes small amount of hexane)

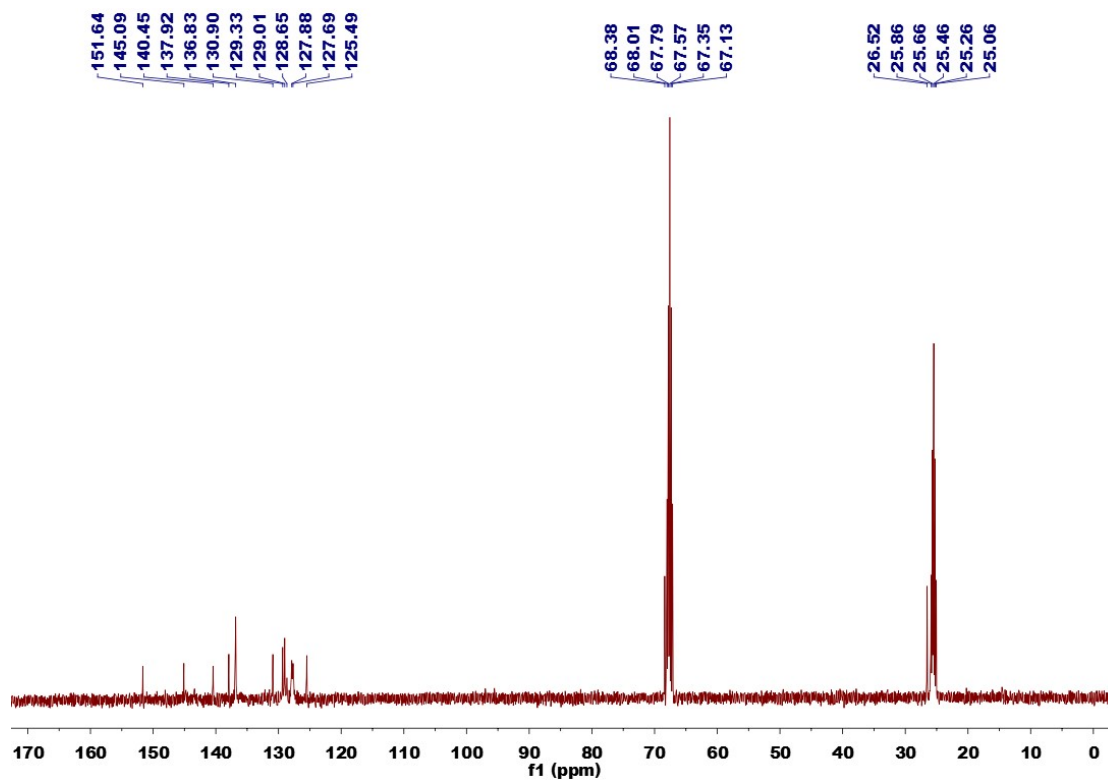


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4** in $\text{THF-}d_8$ at $25\text{ }^\circ\text{C}$.

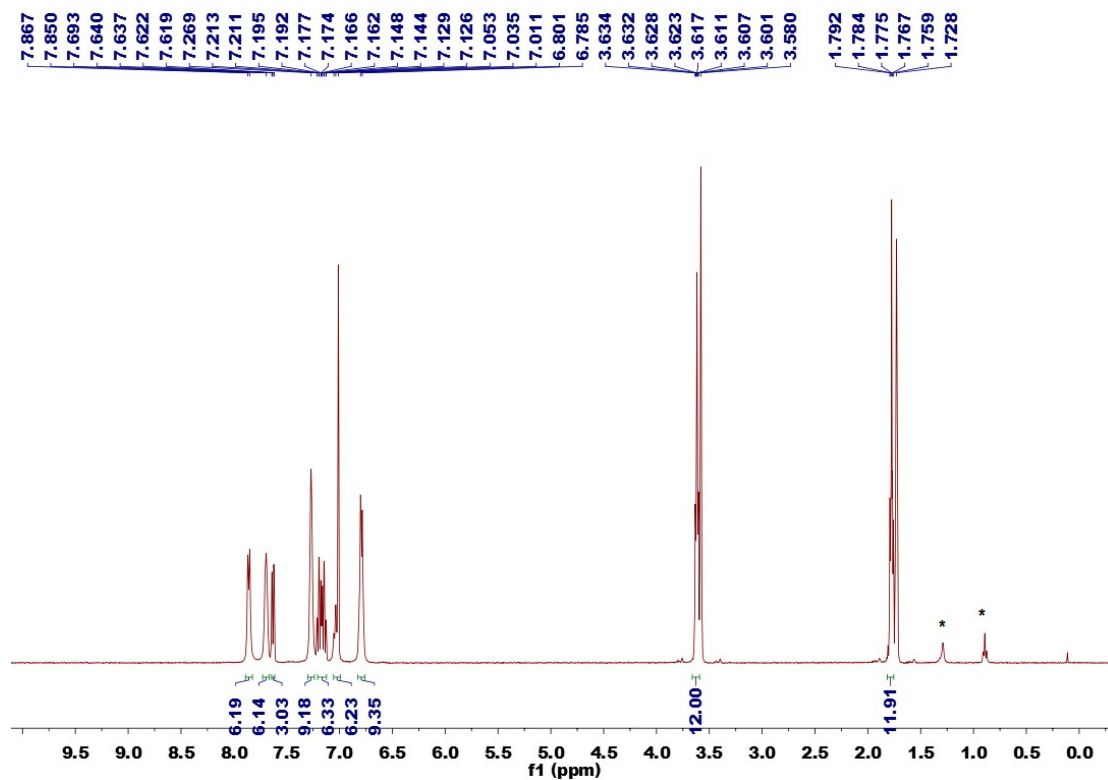


Figure S7. ^1H NMR spectrum of **5** in $\text{THF-}d_8$ at $25\text{ }^\circ\text{C}$. (* denotes small amount of hexane)

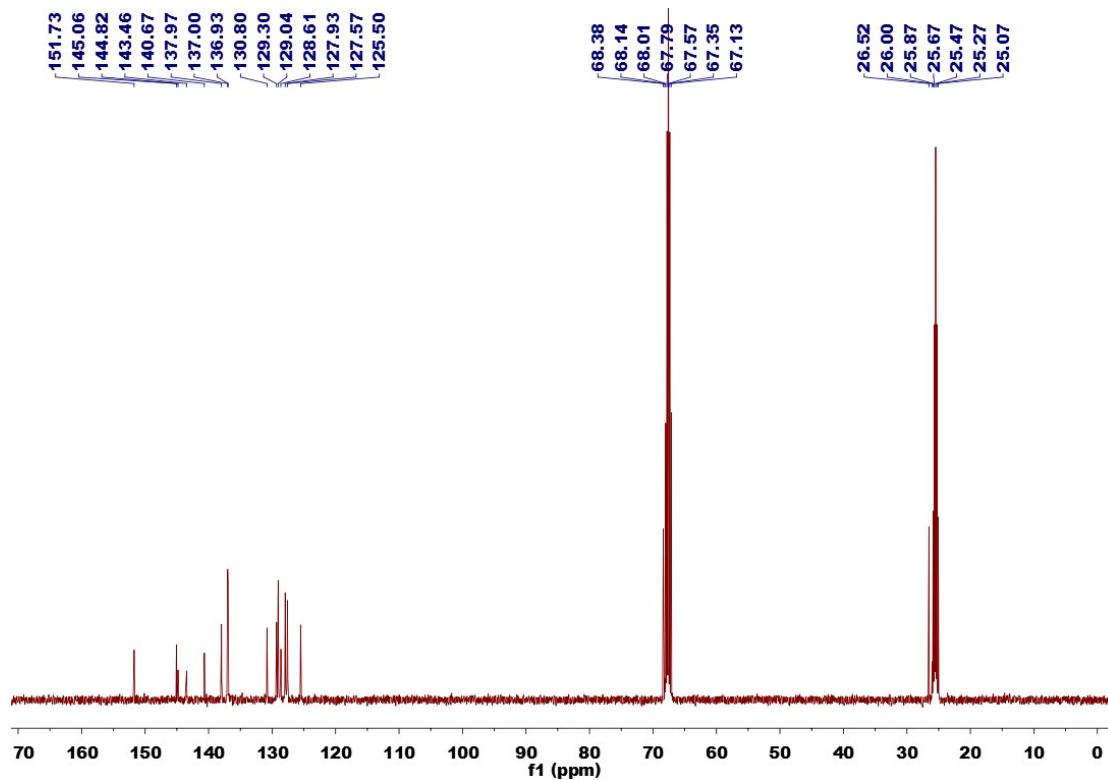


Figure S8. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5** in $\text{THF-}d_8$ at $25\text{ }^\circ\text{C}$.

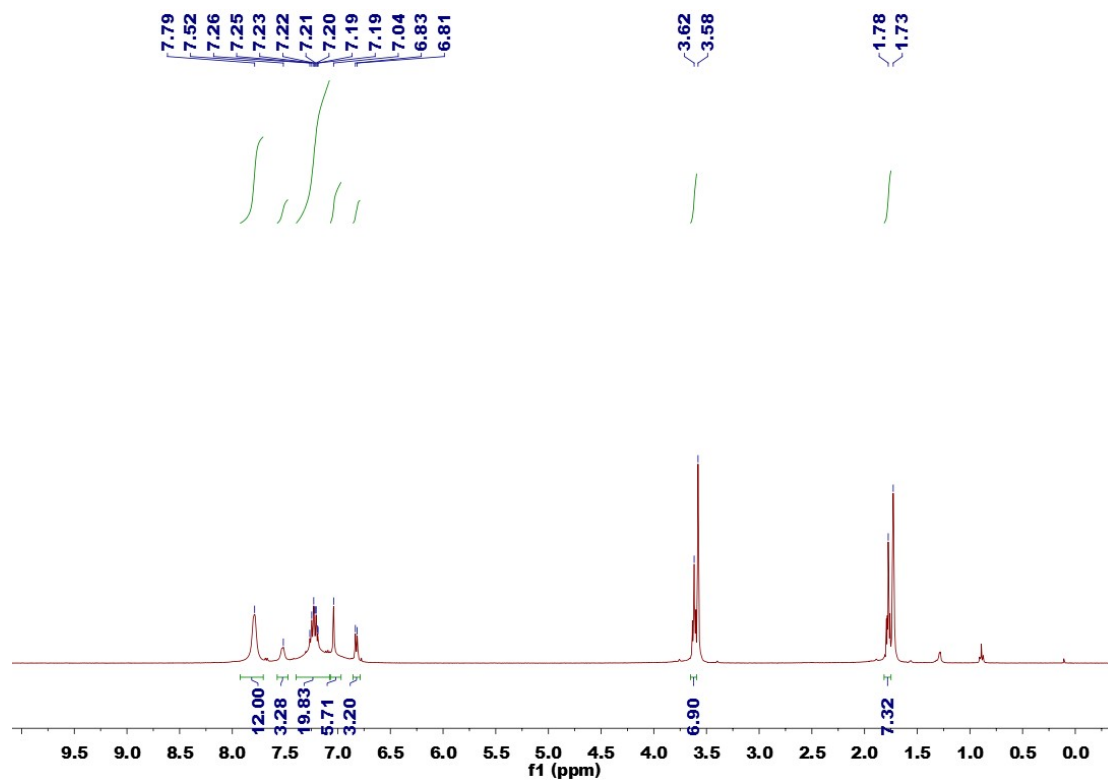


Figure S9. ^1H NMR spectrum of **6** in $\text{THF-}d_8$ at $25\text{ }^\circ\text{C}$.

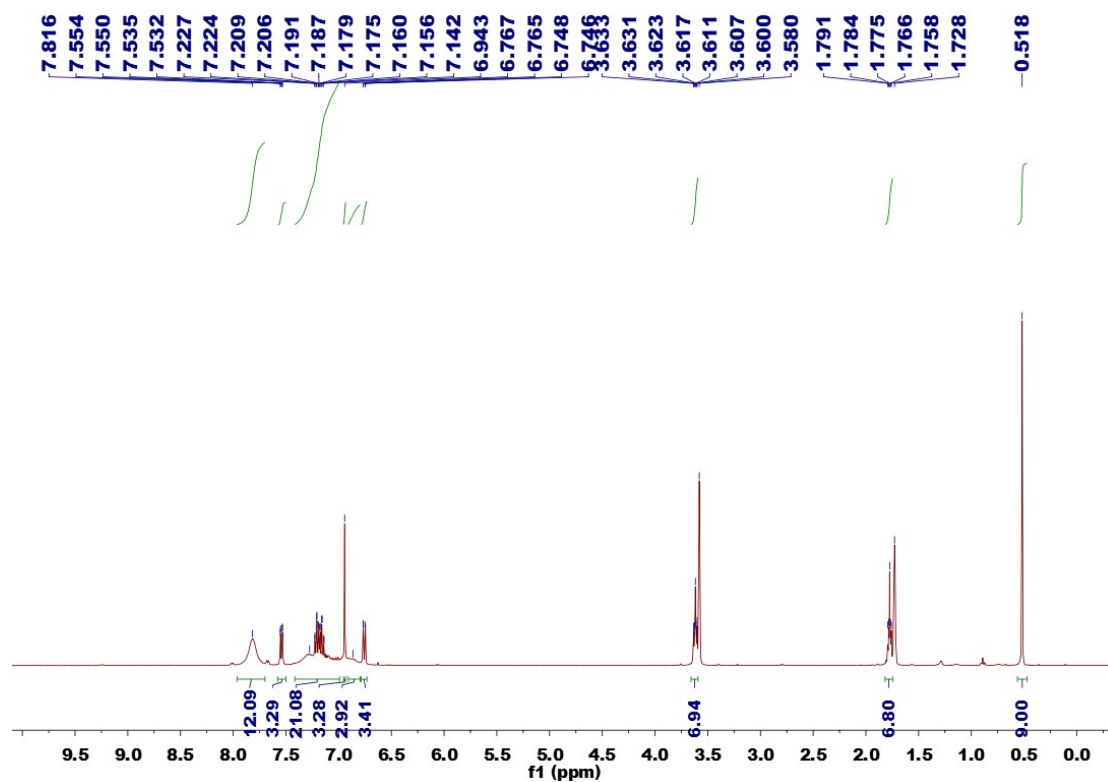


Figure S10. ^1H NMR spectrum of **7** in $\text{THF-}d_8$ at $25\text{ }^\circ\text{C}$.

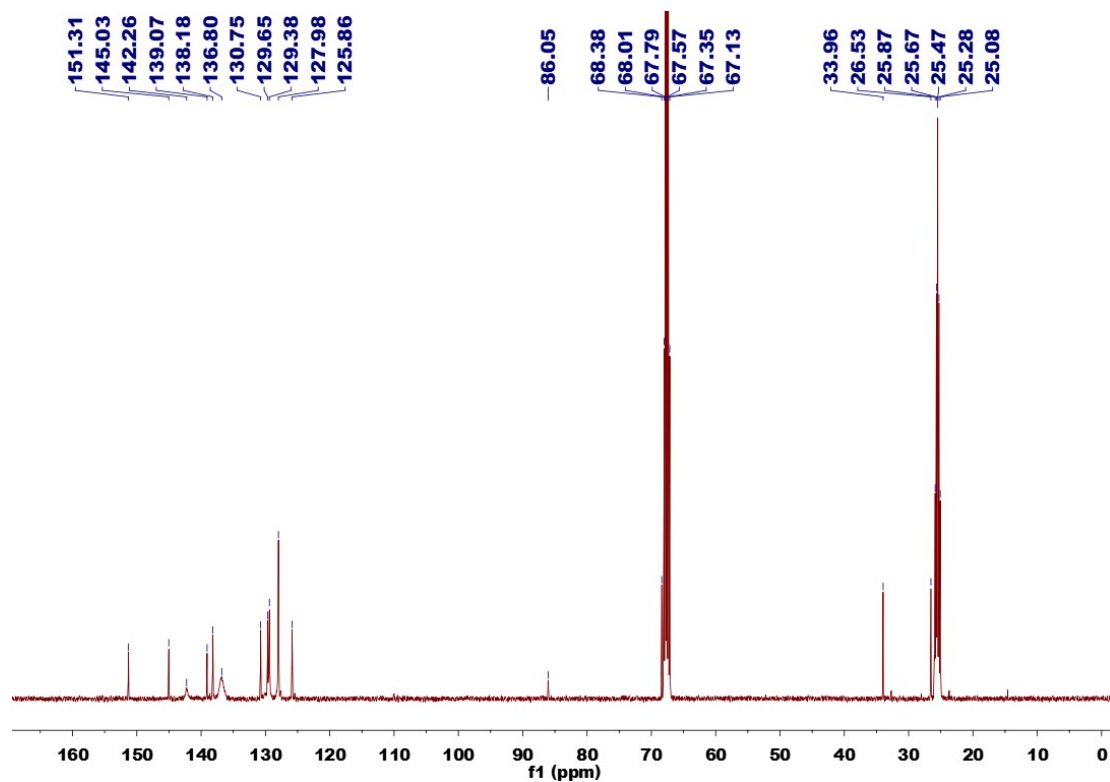


Figure S11. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **7** in $\text{THF-}d_8$ at $25\text{ }^\circ\text{C}$.

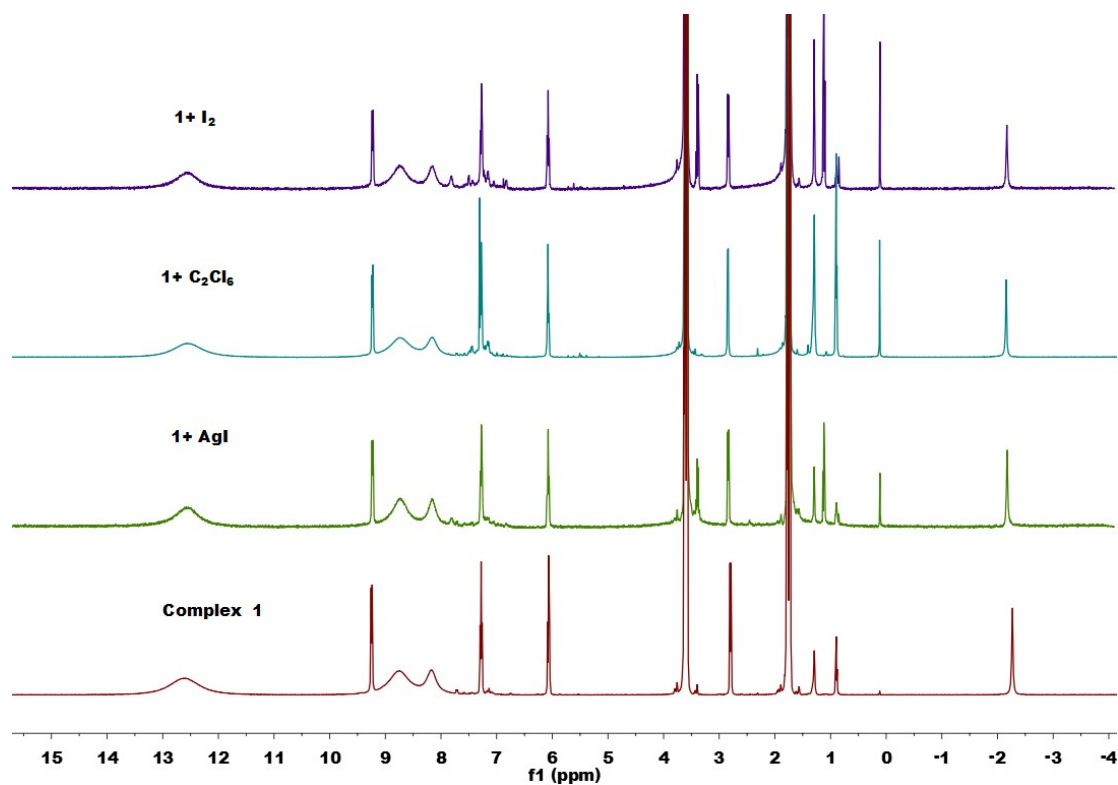


Figure S12. Stacked ^1H NMR spectra of reaction of **1** with various of oxidants ($\text{THF-}d_8$ at $25\text{ }^\circ\text{C}$.)

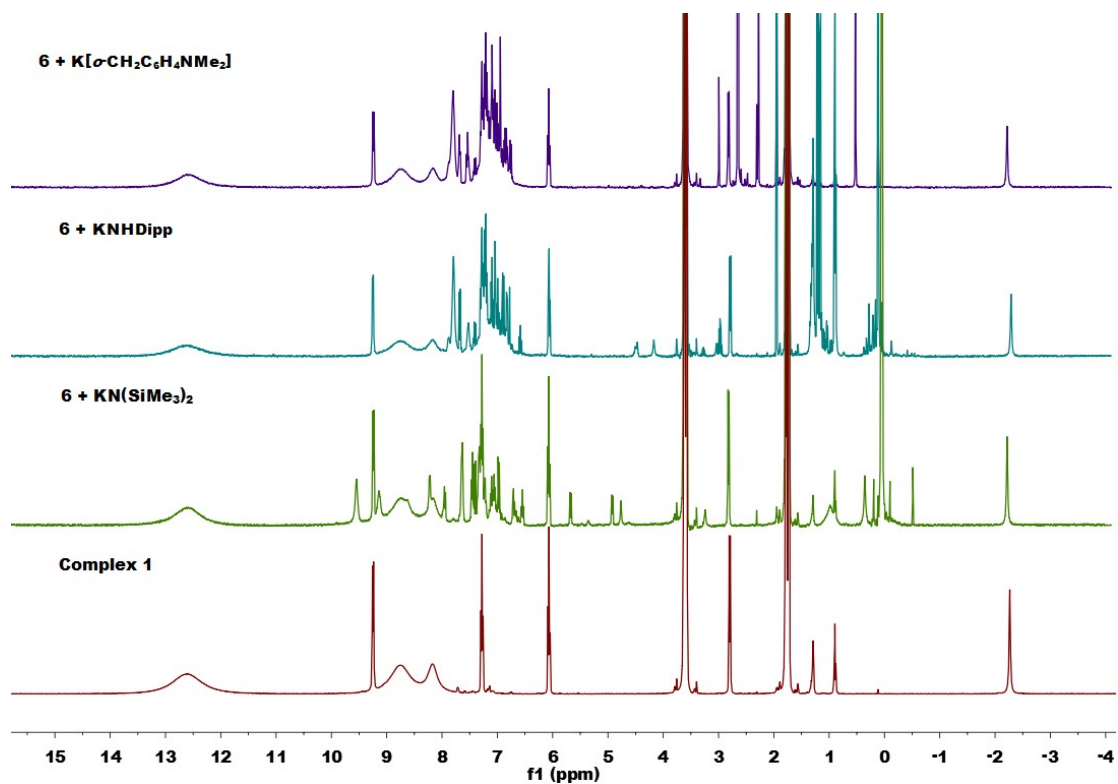


Figure S13. Stacked ^1H NMR spectra of reaction of **6** with various of anionic reagents (THF- d_8 at 25 $^\circ\text{C}$.)

3. X-ray Crystallography

X-ray Crystallography. Diffraction was performed on a Bruker SMART APEX II CCD area detector diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) and Bruker Platon II area detector diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) for complexes at 300 K, φ and ω scan technique. An empirical absorption correction was applied using the SADABS program.⁴ All structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations based on F^2 using the SHELXTL program package⁵ and Olex 2 program⁷. The hydrogen atom coordinates were calculated with SHELXTL by using an appropriate riding model with varied thermal parameters. The residual electron densities of solvent were squeezed by using PLATON.⁶ All crystal structural pictures drawn by Olex 2 program.⁷ Crystal parameters and refinement results are given in **Table S1-S2**.

Table S1. Crystallographic and Refinement Data for **1-4**.

	1	2	3	4
formula	C72H69O6Si3Y	C72H69O6Si3Lu	C72H69O6Si3Ce	C72H69O6Si3Tb
Fw, g·mol ⁻¹	1203.45	1289.51	1254.66	1273.46
cryst size, mm	0.16x0.15x0.13	0.13x0.12x0.1	0.19x0.18x0.16	0.16x0.15x0.13
cryst. syst.	triclinic	monoclinic	monoclinic	monoclinic
space group	P -1	P 2 ₁ /c	P2 ₁ /m	P2 ₁ /n
T, K	300	300	300	300
a, Å	11.3274(9)	23.643(4)	13.7971(13)	13.9197(4)
b, Å	14.4251(11)	15.923(3)	18.7106(17)	18.7147(5)
c, Å	24.4081(17)	19.313(3)	14.0466(13)	23.9418(7)
α, °	106.098(2)	90	90	90
β, °	99.033(2)	108.165(2)	119.007(2)	91.9920(10)
γ, °	93.239(2)	90	90	90
V, Å ³	3763.3(5)	6908(2)	3171.3(5)	6233.1(3)
Z	2	4	2	4
Dcalcd, Kg·m ⁻³	1.062	1.24	1.314	1.357
F (000)	1260	2648	1298	2624
μ, mm ⁻¹	0.866	1.528	0.826	1.245
θ range /°	2.559-25.000	1.568-24.999	2.737-27.571	2.623- 27.480
refns collected	141216	48712	120329	206150
indep reflns (Rint)	13253 (0.1660)	12164 (0.1799)	7514 (0.0945)	14275 (0.0531)
reflns obsd [I > 2σ(I)]	8642	6262	6364	10786
data/restrnts/para ms	13253/452/ 813	12164/ 653/850	7514/168/ 616	14275/510/850
R1, wR2 (I > 2σ(I))	0.0622, 0.1423	0.0762, 0.1543	0.0467, 0.1154	0.0311, 0.0708
R1, wR2 (all data)	0.1066, 0.1707	0.1607, 0.1965	0.0598, 0.1241	0.0505, 0.0807
GOF on F2	1.024	1.018	1.070	1.124
Δρmax, min, e·Å ⁻³	0.540/ -0.314	1.357/-1.980	0.683/-0.784	0.786/ -0.772

$${}^aR1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, {}^b wR2 = \left\{ \frac{\sum w (F_o^2 - F_c^2)^2}{\sum w (F_o^2)^2} \right\}^{1/2}.$$

Table S2. Crystallographic and Refinement Data for 5-7.

	5	6	7
formula	C ₇₂ H ₆₉ O ₆ Si ₃ Pr	C ₇₂ H ₆₉ O ₆ Si ₃ ClCe	C ₇₂ H ₇₀ O ₆ Si ₃ Ce
Fw, g·mol ⁻¹	1255.45	1218.00	1255.67
cryst size, mm	0.1x0.2x0.3	0.15x0.13x0.12	0.18x0.15x0.13
cryst. syst.	monoclinic	triclinic	monoclinic
space group	P2 ₁ /n	P -1	P2 ₁ /n
T, K	300	300	300
<i>a</i> , Å	14.894(3)	13.824(2)	13.8866(11)
<i>b</i> , Å	30.171(6)	14.321(2)	18.9660(15)
<i>c</i> , Å	18.312(3)	19.077(3)	23.8269(18)
<i>α</i> , °	90	97.802(2)	90
<i>β</i> , °	102.716(3)	101.973(2)	92.3110(10)
<i>γ</i> , °	90	116.853(2)	90
<i>V</i> , Å ³	8027(3)	3180.1(9)	6270.3(8)
<i>Z</i>	4	2	4
<i>D</i> _{calcd.} , Kg·m ⁻³	1.039	1.272	1.330
<i>F</i> (000)	2600	1252	2600
<i>μ</i> , mm ⁻¹	0.692	0.861	0.835
<i>θ</i> range /°	1.325- 27.474	1.652- 27.713	2.312-27.104
refns collected	68983	28414	55011
indep reflns (<i>R</i> _{int})	18199 (0.1592)	14516 (0.1014)	14379 (0.0553)
reflns obsd [<i>I</i> > 2 <i>σ</i> (<i>I</i>)]	9006	6840	8684
data/restrnts/para ms	182199/1686/ 972	14516/1518/ 899	14379/ 1262/956
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2 <i>σ</i> (<i>I</i>))	0.0792, 0.1795	0.0750, 0.1485	0.0439, 0.0977
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1555, 0.2132	0.1805, 0.1903	0.0925, 0.1168
GOF on F ₂	0.987	0.958	1.005
<i>Δρ</i> _{max} , min, e·Å ⁻³	1.479/-1.115	1.492/-1.350	1.098/-0.929

$${}^a R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, \quad {}^b wR_2 = \left\{ \frac{\sum w (F_o^2 - F_c^2)^2}{\sum w (F_o^2)^2} \right\}^{1/2}.$$

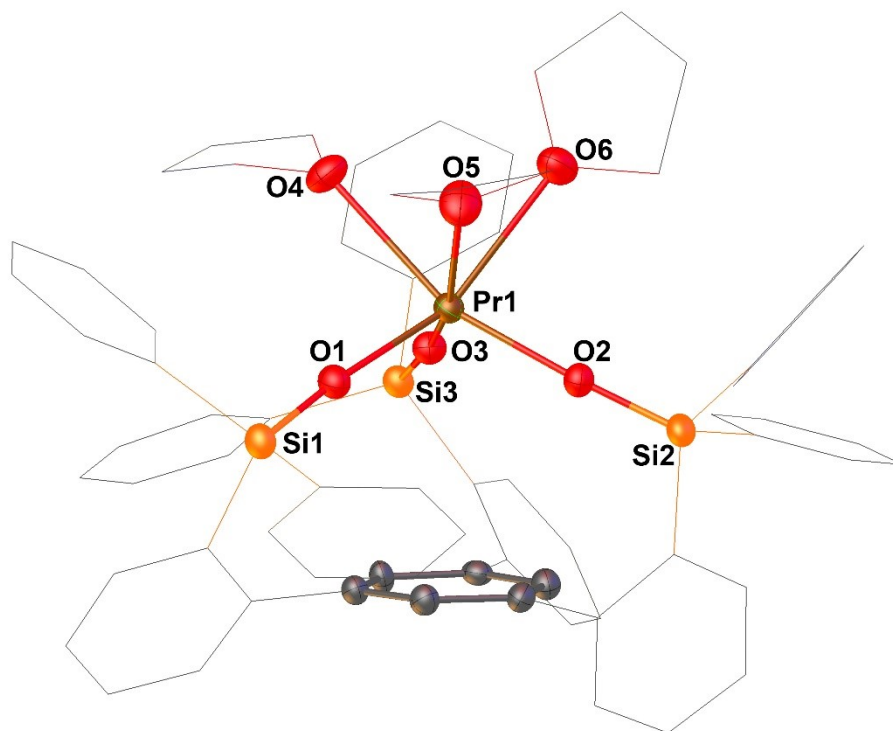


Fig. S14. Molecular structure of **2**. Hydrogen atoms were omitted for clarity. Disordered part in the structure was omitted.

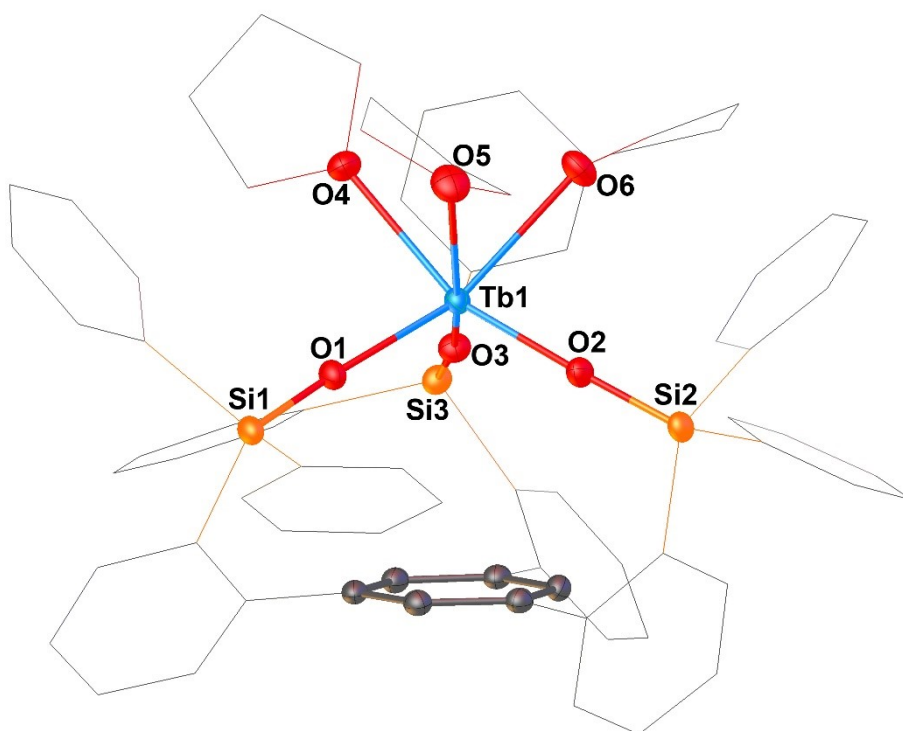


Fig. S15. Molecular structure of **3**. Hydrogen atoms were omitted for clarity. Disordered part in the structure was omitted.

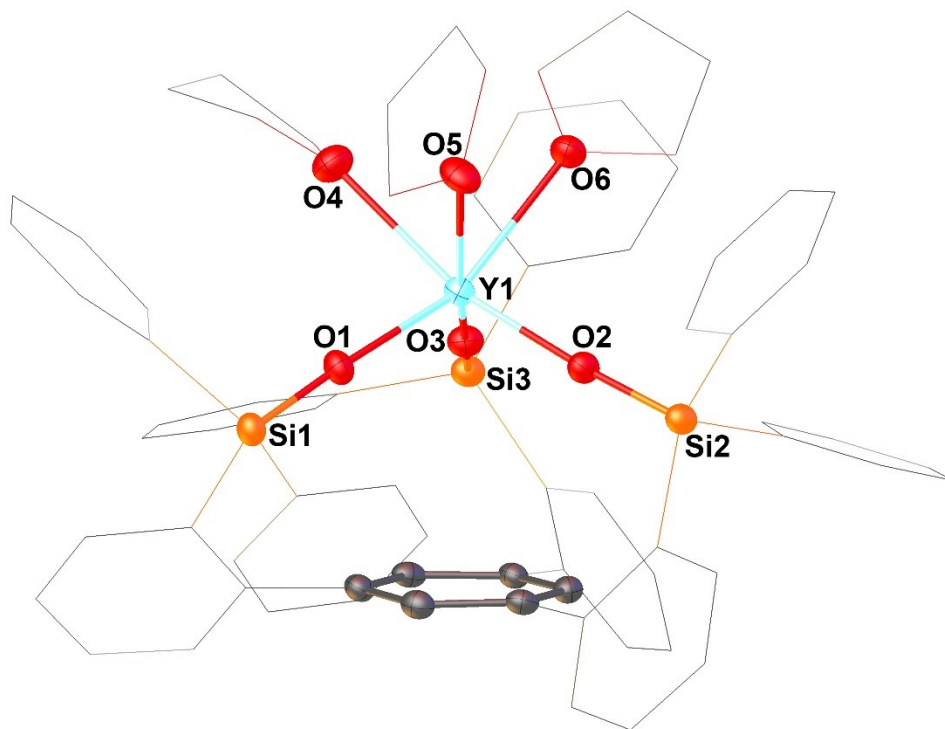


Fig. S16. Molecular structure of **4**. Hydrogen atoms were omitted for clarity. Disordered part in the structure was omitted.

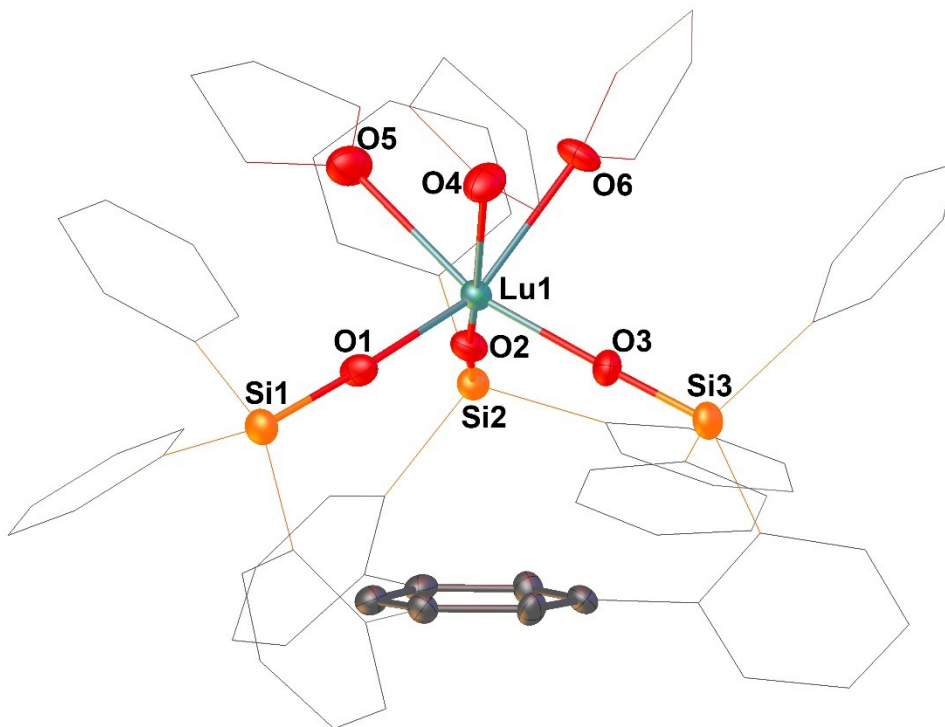


Fig. S17. Molecular structure of **5**. Hydrogen atoms were omitted for clarity. Disordered part in the structure was omitted.

4. Cyclic voltammograms.

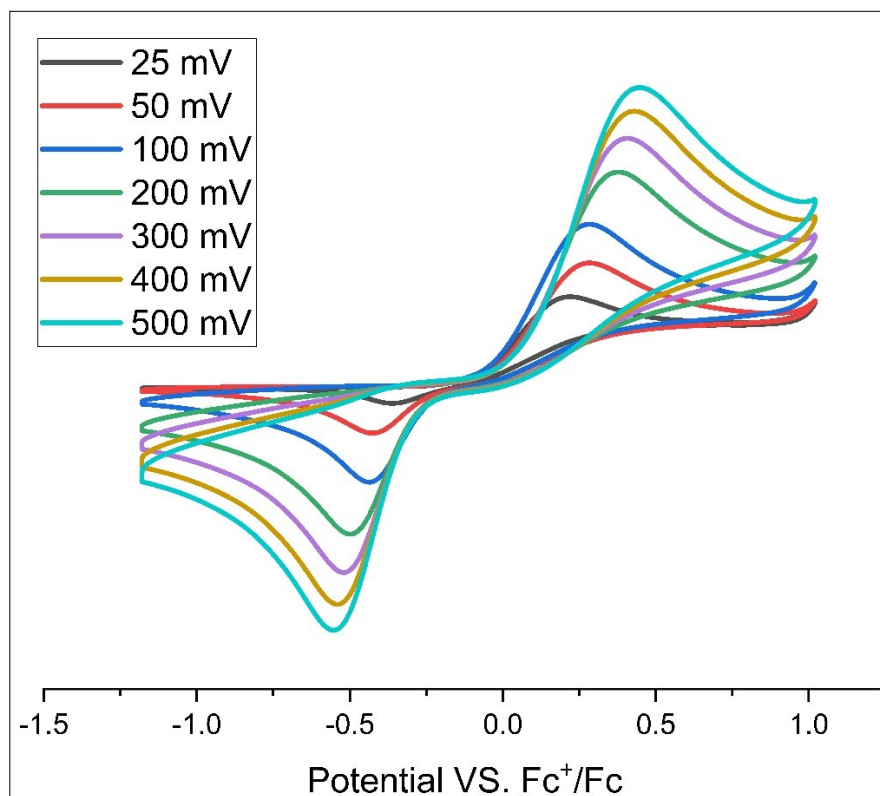


Figure S18. CVs of **1** at different scan rates with $[\text{Pr}_4\text{N}][\text{BAR}^{\text{F}}_4]$ 0.1 M in THF.

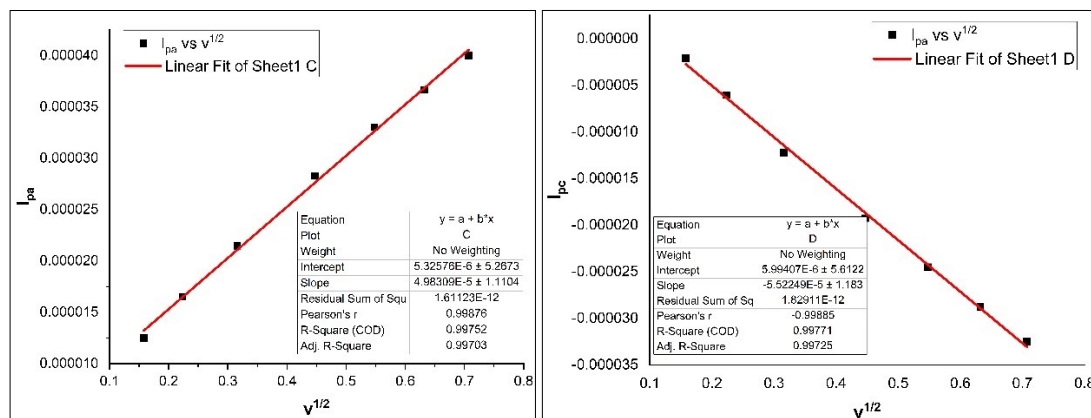


Figure S19. I_p versus $v^{1/2}$ plot for **1** (Left: anodic peak currents; Right: cathodic peak currents)

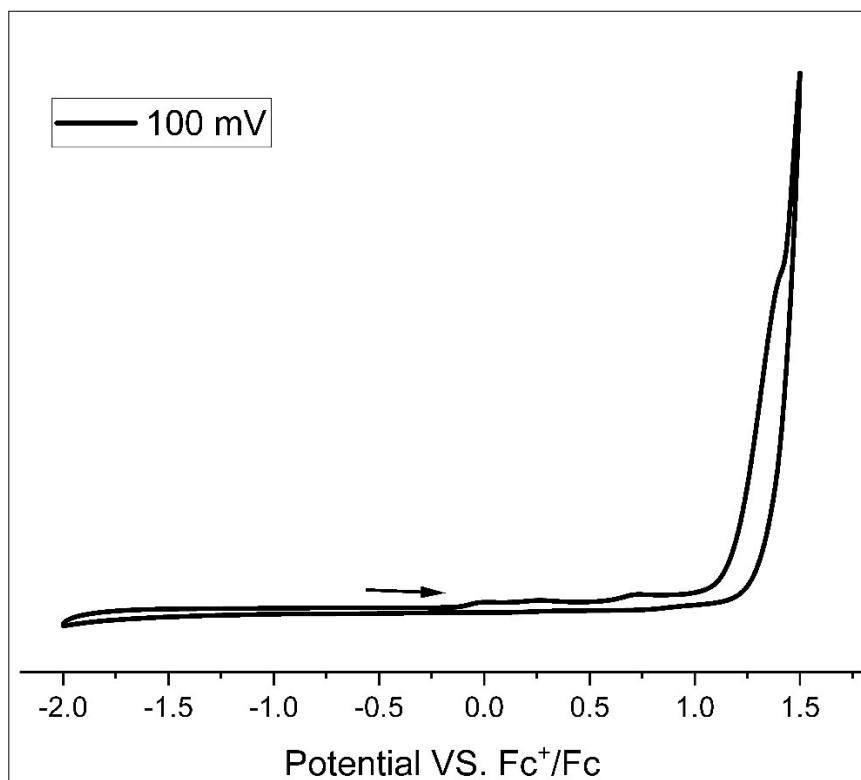


Figure S20. CVs of **2** at scan rate of 100 mV with $[\text{Pr}_4\text{N}][\text{BARF}_4]$ 0.1 M in THF.

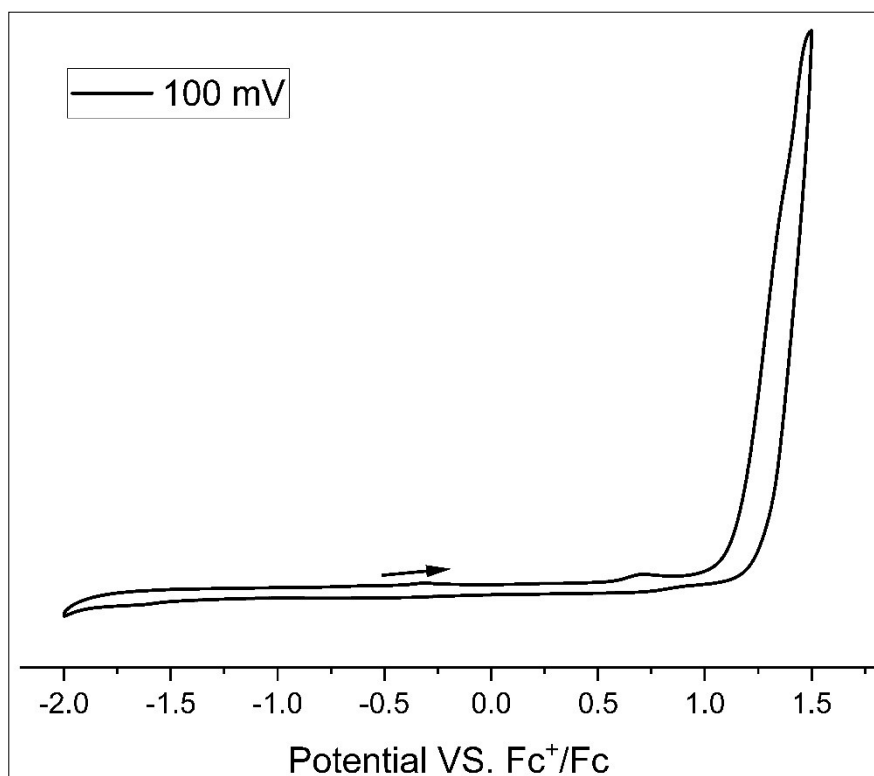


Figure S21. CVs of **3** at scan rate of 100 mV with $[\text{Pr}_4\text{N}][\text{BARF}_4]$ 0.1 M in THF.

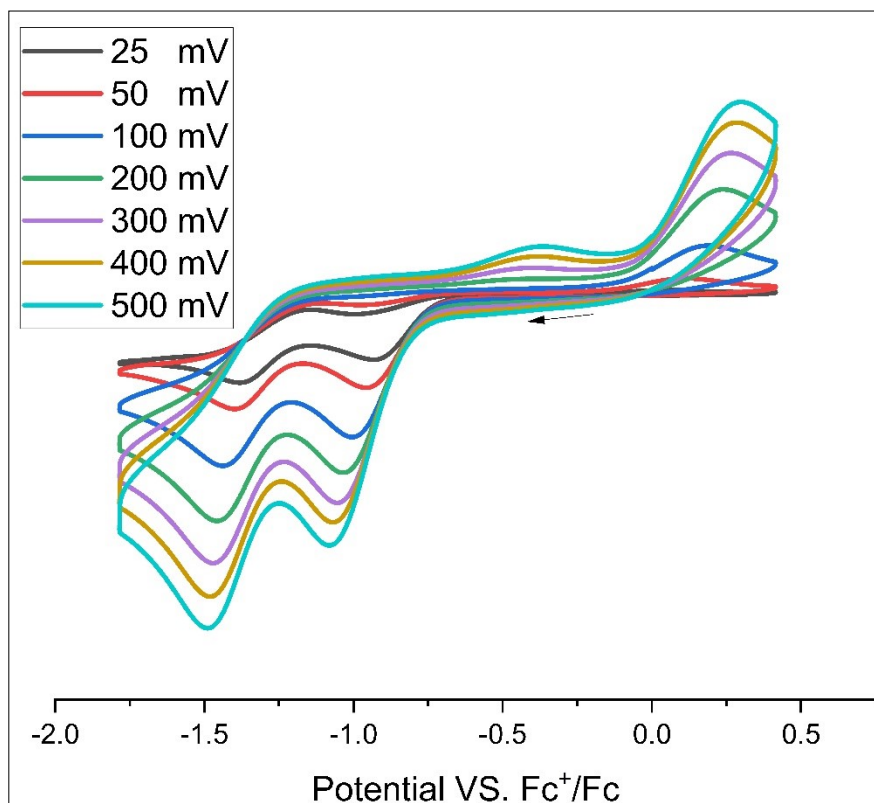


Figure S22. CVs of **6** at different scan rates with $[\text{Pr}_4\text{N}][\text{BARF}_4]$ 0.1 M in THF.

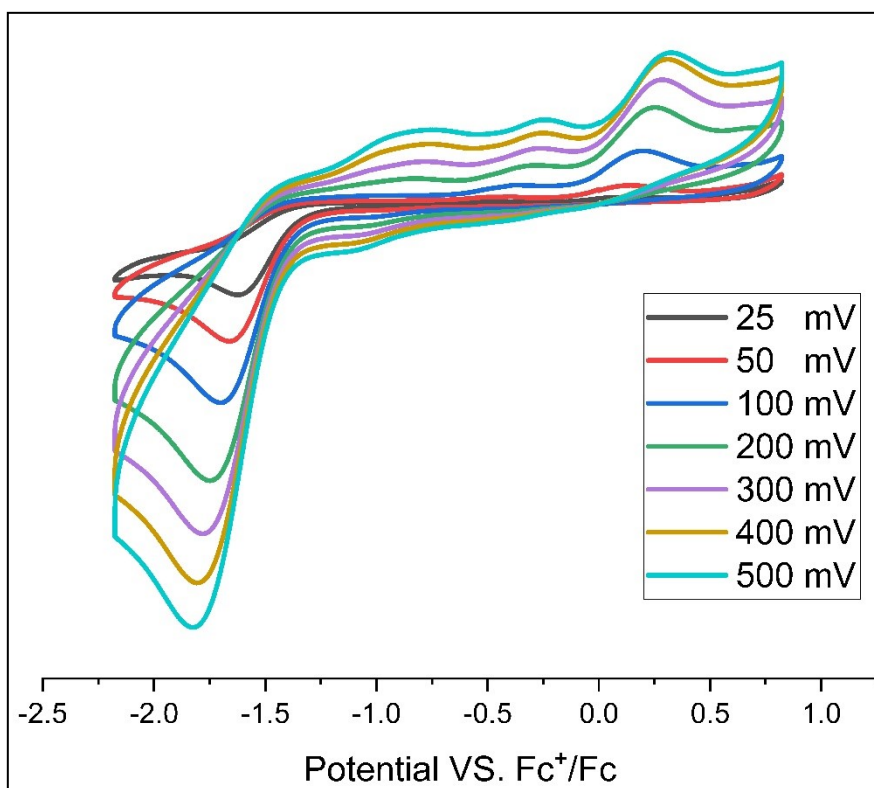


Figure S23. CVs of **7** at different scan rates with $[\text{Pr}_4\text{N}][\text{BARF}_4]$ 0.1 M in THF.

5. UV-Vis Spectra.

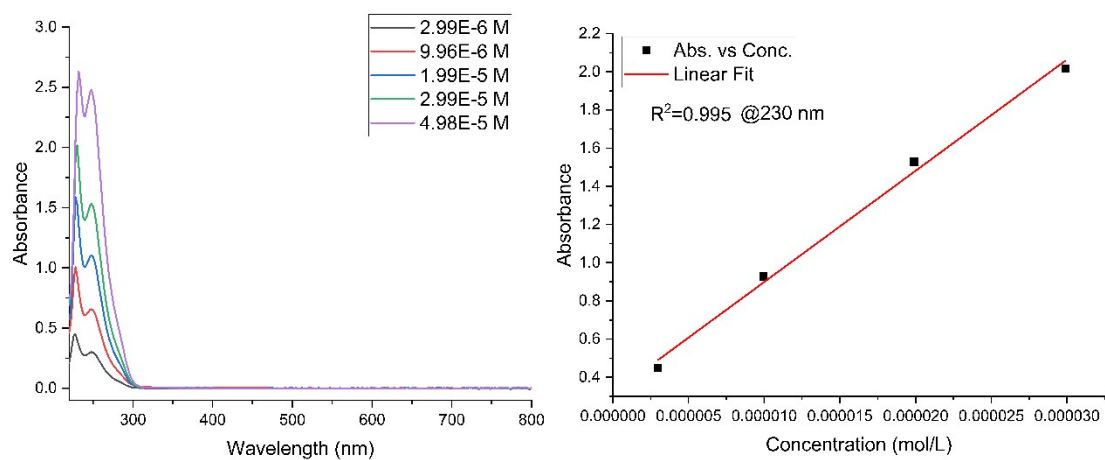


Figure S24. UV-Vis spectra of LH_3 in THF.

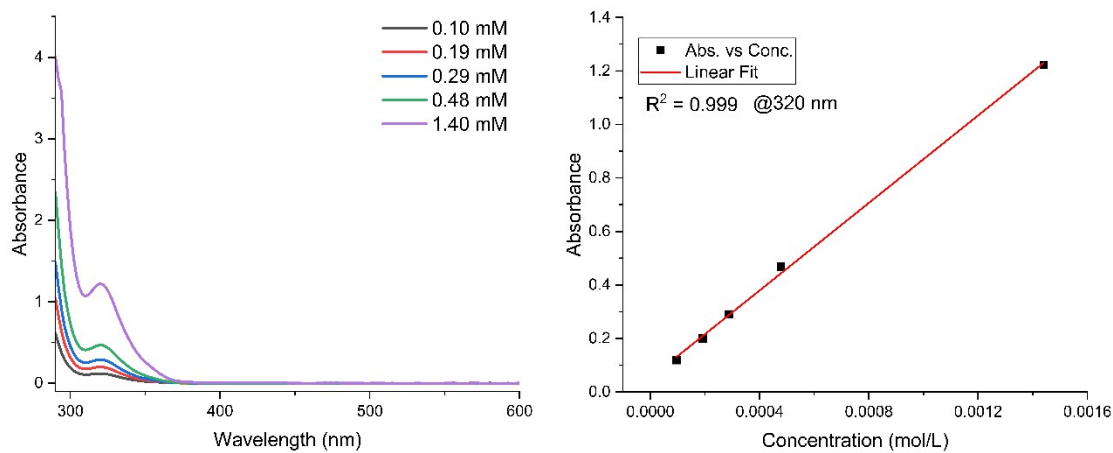


Figure S25. UV-Vis spectra of **1** in THF.

Coplot of UV-vis-NIR absorption spectra of 1-Ce

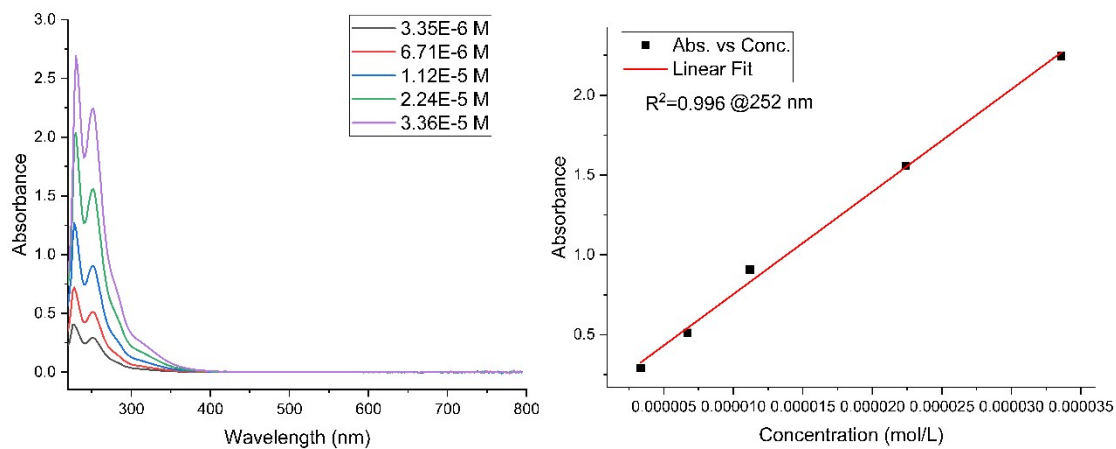


Figure S26. UV-Vis spectra of **6** in THF.

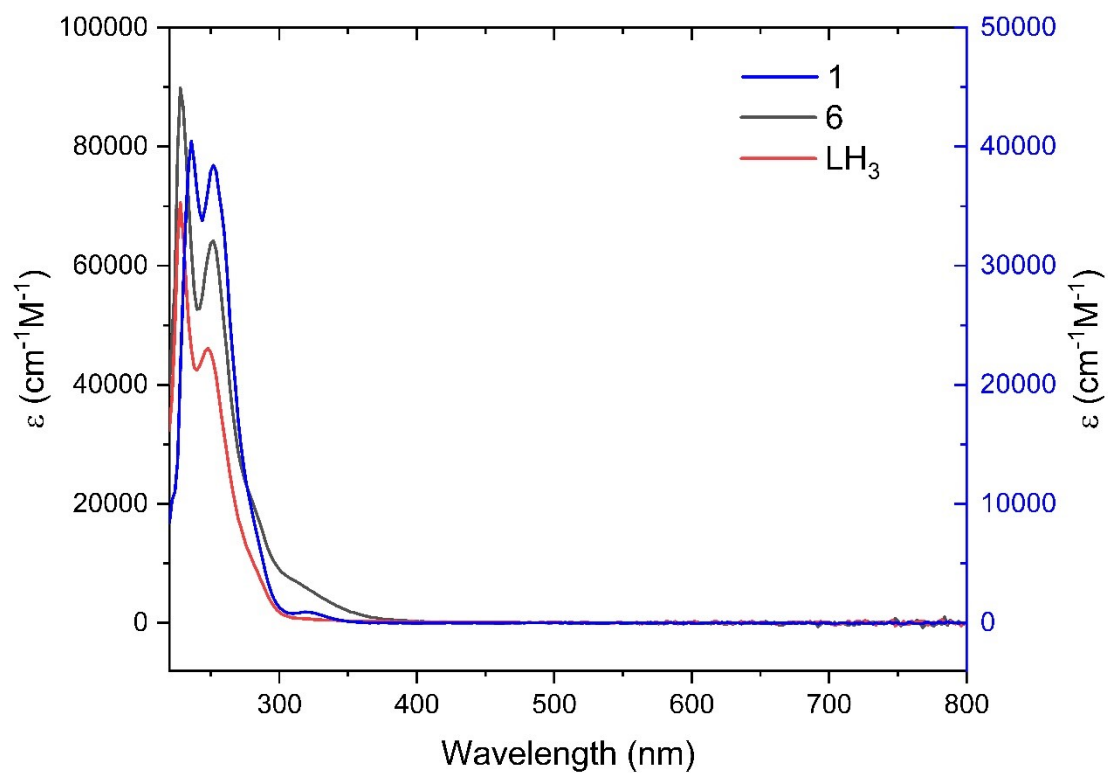


Figure S27. Coplot of UV-Vis spectra of LH₃, 1 and 6 in THF.

6. References

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