

Supplementary Information for
**Multiply Engaged Molecular Gear composed of Cerium (IV) Double-
Decker of a triptycene-functionalized Porphyrin**

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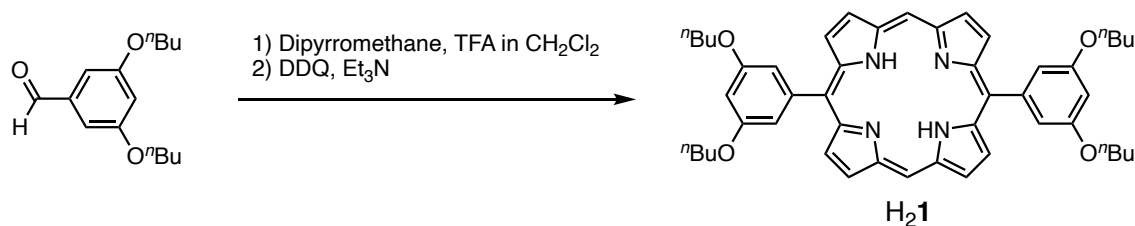
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General informations

Synthetic procedures were carried out under dry nitrogen atmosphere, unless otherwise specified. All reagents and solvents were purchased at the highest commercial quality available and used without further purification, unless otherwise stated. Trifluoroacetic acid, chloroform, copper iodide, methanol, *N*-bromosuccinimide, and zinc acetate dihydrate were purchased from FUJIFILM Wako Pure Chemical Corporation. Tris(acetylacetonato)cerium hydrate was purchased from Aldrich. Dichloromethane, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), anhydrous tetrahydrofuran and triethylamine were purchased from Nacalaitesque. Pyrrole and bis(triphenylphosphine) palladium(II)dichloride were purchased from TCI. 9-Ethynyltritycene,^[1] Dipyrromethanes,^[2] and 3,5-dibutoxybenzaldehyde^[3] were prepared according to the literature procedures. The complexation reaction of a porphyrin with zinc ion and cerium ion under microwave irradiation was carried out by utilizing CEM Discover SP in a glass pressure tube equipped with PTFE-coated magnetic stirring bar. ¹H, and ¹³C spectra were recorded on a JEOL JNM-ECA600 (600 MHz for ¹H; 150 MHz for ¹³C) spectrometer or a JEOL JNM-ECX400P (400 MHz for ¹H; 100 MHz for ¹³C) spectrometer at a constant temperature of 298 K. Tetramethylsilane (TMS) was used as an internal reference for ¹H and ¹³C NMR measurements in CDCl₃, DMSO-*d*₆, and toluene-*d*₈. Chemical shifts (δ) are reported in ppm. Coupling constants (*J*) are given in Hz and the following abbreviations have been used to describe the signals: singlet (s); broad singlet (br. s); doublet (d); triplet (t); quadruplet (q); quintuplet (quint); multiplet (m). Full assignments of ¹H and ¹³C NMR spectra were made with the assistance of COSY, NOESY, HMBC, and HSQC spectra when necessary. The MALDI-TOF mass spectrometry was performed using JEOL JMS-S300 spectrometer. Silica gel column chromatography and thin-layer (TLC) chromatography were performed using Wakosil® 60 and Merck silica gel 60 (F254) TLC plates, respectively.

Synthesis of porphyrin H₂1



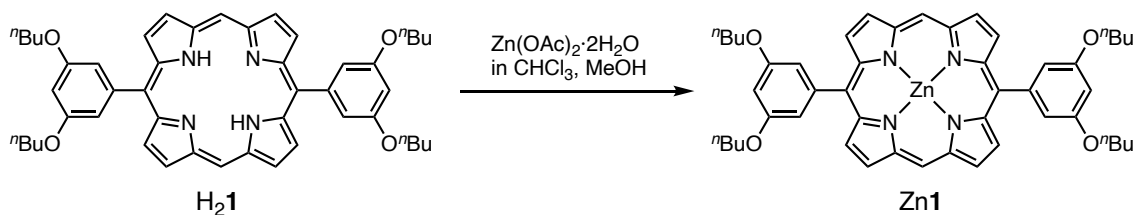
This reaction was performed under N₂ atmosphere and all the reaction vessels were dried up. 3,5-Dibutoxybenzaldehyde (2.51g, 10 mmol) and dipyrromethane (1.48 g, 10 mmol) was dissolved in CH₂Cl₂ (1000 mL) and the reaction vessels were protected from light by covering with aluminum foil. The resulting solution was deoxygenated by bubbling N₂ for 20 min. TFA (1.4 mL, 18 mmol) was added to the solution and the reaction mixture was stirred at room temperature for 30 min. Then, DDQ (3.41 g, 15 mmol) and Et₃N (2.4 mL, 20 mmol) was added. The reaction mixture was stirred at room temperature for an additional period of 30 min and then, silica gel (60 mL) was added. The resulting mixture was evaporated and the crude compound was purified by silica gel column chromatography (6φ × 16 cm, hexane : CH₂Cl₂ = 3 : 7) to afford crude purple solid, which was further purified by washing with acetone to afford H₂1 as a purple solid (1.55 g, 41%).

¹H NMR (400 MHz, CDCl₃/TMS): δ = 10.30 (s, 2H), 9.38 (d, *J* = 4.4 Hz, 4H), 9.19 (d, *J* = 4.4 Hz, 4H), 7.43 (d, *J* = 2.8 Hz, 4H), 6.92 (t, *J* = 2.2 Hz, 2H), 4.16 (t, *J* = 6.6 Hz, 8H), 1.88 (tt, *J* = 7.1, 7.1 Hz, 8H), 1.57 (tq, *J* = 7.5, 7.5 Hz, 9H, including H₂O), 1.01 (t, *J* = 7.4 Hz, 12H) -3,16 (s, 2H).

¹³C NMR (100 MHz, CDCl₃/TMS): δ = 158.6, 146.9, 145.2, 143.1, 131.5, 131.1, 119.0, 114.5, 105.2, 100.9, 68.1, 31.4, 19.3, 13.9.

HR-MS (MALDI, DCTB): *m/z* = 750.4152, calcd. for C₄₈H₅₄N₄O₄ [M]⁺: 750.4145.

Synthesis of porphyrin Zn1



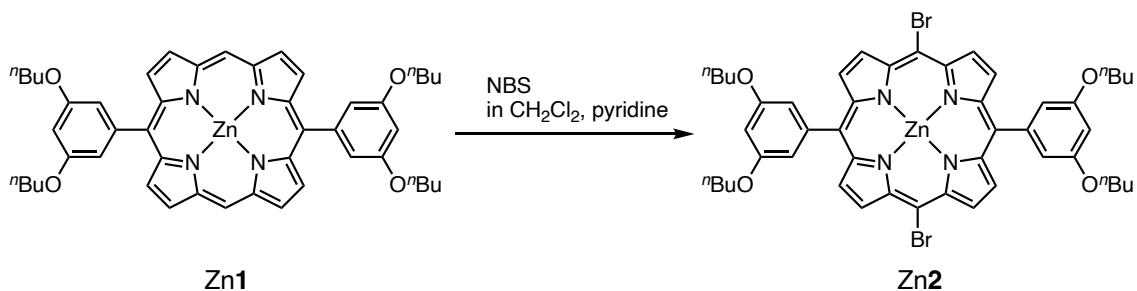
A mixture of CHCl₃ (10 mL) and MeOH (10 mL) containing porphyrin H₂1 (755 mg, 1.0 mmol) and Zn(OAc)₂·2H₂O (441 mg, 2.0 mmol) was added to the pressure tube. The resulting mixture was heated under microwave irradiation at 100 °C for 20 min. After finishing the reaction, the mixture was diluted with CH₂Cl₂ (150 mL). The organic phase was washed with H₂O (100 mL) and brine (100 mL), dried over anhydrous Na₂SO₄, filtered and evaporated to afford Zn1 as a purple solid (806 mg, quant.).

¹H NMR (400 MHz, CDCl₃/TMS): δ = 10.10 (d, *J* = 4.8 Hz, 2H), 9.21 (d, *J* = 4.4 Hz, 4H), 8.42 (d, *J* = 7.2 Hz, 6H), 7.43 (d, *J* = 2.4 Hz, 4H), 6.92 (t, *J* = 2.2 Hz, 2H), 4.15 (t, *J* = 6.4 Hz, 8H), 1.87 (tt, *J* = 7.1, 7.1 Hz, 8H), 1.55 (tq, *J* = 7.4, 7.4 Hz, 8H), 1.00 (t, *J* = 7.6 Hz, 12H).

¹³C NMR (100 MHz, CDCl₃/TMS): δ = 158.3, 149.9, 149.5, 144.3, 132.6, 131.6, 120.0, 114.4, 106.2, 100.8, 68.0, 31.5, 19.3, 13.9.

HR-MS (MALDI, DCTB): *m/z* = 812.3280, calcd for H₄₈H₅₂N₄O₄Zn [M]⁺: 812.3280.

Synthesis of porphyrin Zn2



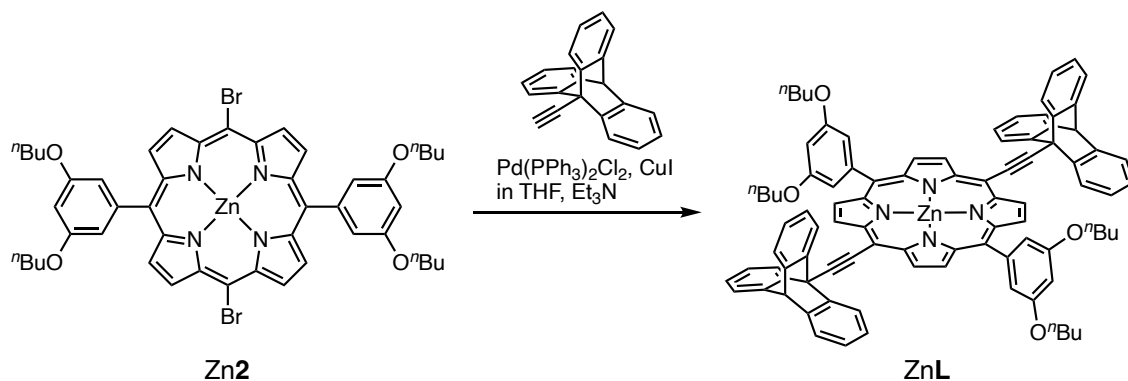
Zinc porphyrin **Zn1** (808 mg, 1.0 mmol) was dissolved in a mixture of CH₂Cl₂ (200 mL) and pyridine (4.0 mL) under N₂. After cooling the solution to -20 °C, NBS (357 mg, 2.0 mmol) was added to the mixture and the resulting solution was stirred at -20 °C for 12 hrs. Acetone (15 mL) was then added to quench the reaction and the volatiles were evaporated off. The residue was washed with MeOH to afford **Zn2** as a purple solid (930 mg, 96%).

¹H NMR (400 MHz, DMSO-*d*₆/TMS): δ = 9.61 (d, *J* = 4.4 Hz, 4H), 8.91 (d, *J* = 4.8 Hz, 4H), 7.27 (d, *J* = 2.0 Hz, 4H), 6.97 (t, *J* = 2.0 Hz, 2H), 4.17 (t, *J* = 6.2 Hz, 8H), 1.80 (tt, *J* = 7.0, 7.0 Hz, 8H), 1.50 (tq, *J* = 7.4, 7.4 Hz, 8H), 0.96 (t, *J* = 7.2 Hz, 12H).

¹³C NMR (100 MHz, CDCl₃ : pyridine-*d*₅ = 9 : 1 (v/v)/TMS): δ = 158.1, 150.5, 150.1, 144.4, 133.3, 132.8, 121.7, 114.6, 104.7, 100.5, 68.0, 31.4, 19.3, 13.9.

HR-MS (MALDI, DCTB): *m/z* = 968.1443, calcd for C₄₈H₅₀N₄O₄ZnBr₂ [M]⁺: 968.1490.

Synthesis of porphyrin ZnL



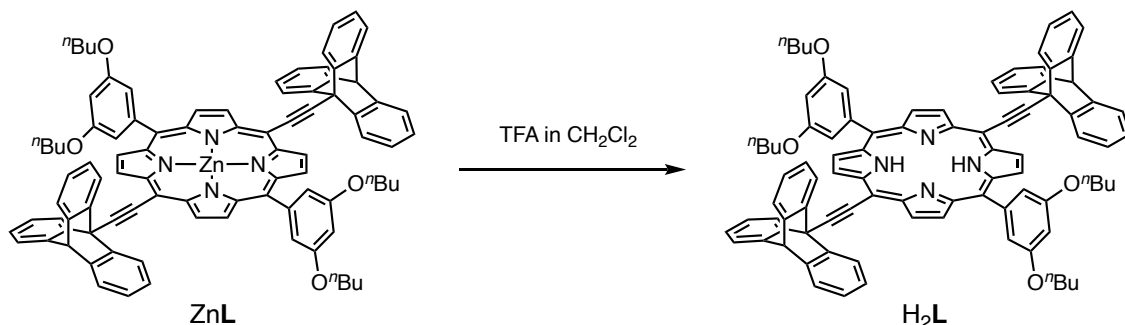
Zinc porphyrin **Zn2** (797 mg, 820 μ mol), 9-ethynyltriptycene (688 mg, 2.5 mmol), Pd(PPh₃)₂Cl₂ (58 mg, 82 μ mol) and CuI (19 mg, 100 μ mol) were suspended in a mixture of THF and Et₃N (4 : 1 (v/v), 40 mL). The resulting mixture was degassed by three successive freeze-pump-thaw cycles and refluxed for 3 hrs. The reaction mixture was filtered through Celite and the filtrate was evaporated. The crude compound was purified by silica gel column chromatography (4 ϕ \times 14 cm, hexane : CH₂Cl₂ = 5 : 5 – 4 : 6) to afford a crude green solid, which was further purified by reprecipitation of a CH₂Cl₂ solution with MeOH to afford **ZnL** as a green solid (1.08 g, 96%).

¹H NMR (400 MHz, CDCl₃/TMS): δ = 10.10 (d, J = 4.8 Hz, 4H), 9.21 (d, J = 4.4 Hz, 4H), 8.42 (d, J = 7.2 Hz, 6H), 7.56 (dd, J = 1.4, 7.6 Hz, 6H), 7.43 (d, J = 2.4 Hz, 4H), 7.26–7.21 (m, 6H), 7.19–7.16 (m, 6H), 6.91 (t, J = 2.2 Hz, 2H), 5.64 (s, 2H), 4.16 (t, J = 6.6 Hz, 8H), 1.87 (tt, J = 7.1, 7.1 Hz, 8H), 1.60–1.51 (m, 38 H, including H₂O), 1.00 (t, J = 7.6 Hz, 12H).

¹³C NMR (100 MHz, CDCl₃/TMS): δ = 158.4, 152.5, 150.3, 145.1, 144.7, 143.7, 133.5, 131.4, 126.0, 125.6, 123.8, 123.0, 122.9, 114.3, 101.2, 101.1, 94.9, 91.3, 68.1, 54.9, 53.5, 31.4, 19.3, 13.9.

HR-MS (MALDI, DCTB): m/z = 1364.5128, calcd for C₉₂H₇₆N₄O₄Zn [M]⁺: 1364.5158.

Synthesis of porphyrin H₂L



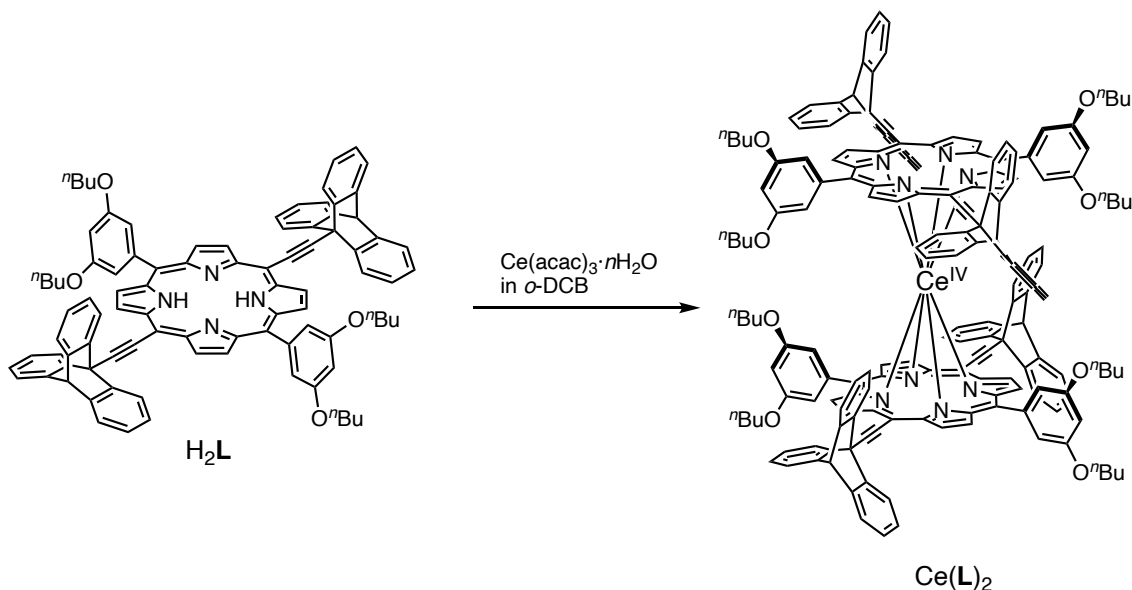
The zinc porphyrin ZnL (1.01 g, 742 μ mol) was dissolved in a mixture of CH₂Cl₂ (60 mL) and TFA (15 mL). The resulting solution was stirred at room temperature for 1 hr. The reaction mixture was diluted with CH₂Cl₂ (100 mL) and the organic phase was washed with H₂O (100 mL \times 2), saturated aqueous NaHCO₃ (50 mL \times 2) and brine (50 mL), dried over anhydrous Na₂SO₄, filtered and evaporated. The crude compound was purified by reprecipitation of a CH₂Cl₂ solution with MeOH to give H₂L as a purple solid (917 mg, 96%).

¹H NMR (400 MHz, CDCl₃/TMS): δ = 9.99 (d, J = 4.8 Hz, 4H), 9.11 (d, J = 4.8 Hz, 4H), 8.39 (d, J = 7.2 Hz, 6H), 7.56 (d, J = 6.6 Hz, 6H), 7.42 (d, J = 2.0 Hz, 4H), 7.26–7.15 (m, 23H, including CHCl₃), 6.91 (t, J = 2.4 Hz, 2H), 5.63 (s, 2H), 4.17 (t, J = 6.8 Hz, 8H), 1.88 (tt, J = 7.2, 7.2 Hz, 8H), 1.61–1.51 (m, 48H, including H₂O), 1.00 (t, J = 7.4 Hz, 12H), -1.99 (s, 2H).

¹³C NMR (100 MHz, CDCl₃/TMS): δ = 158.5, 145.0, 144.7, 143.0, 126.0, 125.6, 123.8, 122.9, 122.0, 114.3, 101.2, 100.5, 94.4, 91.9, 68.1, 54.9, 53.5, 31.4, 19.3, 13.9.

HR-MS (MALDI, DCTB): m/z = 1302.6034, calcd for C₉₂H₇₈N₄O₄ [M]⁺: 1302.6023.

Synthesis of double-decker complex Ce(L)₂



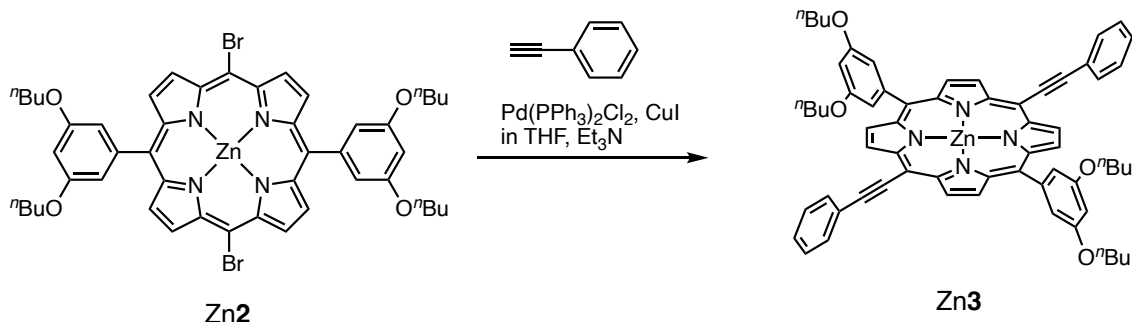
The porphyrin H₂L (133 mg, 1.0 mmol) and Ce(acac)₃·nH₂O (98 mg, 199 μmol), and *o*-DCB (10 mL) were added to the pressure tube. The resulting mixture was heated under microwave irradiation at 250 °C for 1 hr. Once back to room temperature, Ce(acac)₃·nH₂O (201 mg, 410 μmol) was added to the reaction mixture. The resulting mixture was further heated under microwave irradiation at 250 °C for 2.5 hrs. The reaction mixture was then purified by silica gel column chromatography (4ϕ × 14 cm, hexane : CH₂Cl₂ = 6 : 4). The main fraction was further purified by recycling GPC (JAIGEL 2H-2.5H, eluent : CHCl₃) to afford Ce(L)₂ as a blackish brown solid (80 mg, 58%).

¹H NMR (600 MHz, CDCl₃/TMS): δ = 9.85 (d, *J* = 4.2 Hz, 4H), 9.56 (d, *J* = 4.2 Hz, 4H), 9.10 (br, 4H), 8.90 (d, *J* = 4.2 Hz, 4H), 8.58 (d, *J* = 7.8 Hz, 12H), 8.50 (d, *J* = 4.2 Hz, 4H), 7.58 (d, *J* = 7.8 Hz, 12H), 7.08 (t, *J* = 6.9 Hz, 12H), 6.92–6.90 (m, 16H), 5.80 (t, *J* = 1.5 Hz, 4H), 5.67 (s, 4H), 4.76–4.72 (m, 4H), 4.65–4.61 (m, 4H), 3.77–3.70 (m, 8H), 1.91–1.79 (m, 8H), 1.56–1.48 (m, 18H, including H₂O), 1.46–1.38 (m, 4H), 1.25 (tq, *J* = 7.4, 7.4 Hz, 8H), 0.97 (t, *J* = 7.5 Hz, 12H), 0.75 (t, *J* = 7.5 Hz, 12H).

¹³C NMR (150 MHz, CDCl₃/TMS): δ = 158.9, 158.1, 155.2, 155.0, 152.9, 152.3, 145.5, 144.7, 143.0, 130.6, 129.0, 128.9, 127.3, 125.9, 125.8, 125.6, 123.6, 123.1, 115.6, 114.9, 103.6, 101.5, 93.7, 91.5, 69.0, 67.6, 54.6, 53.7, 31.6, 31.1, 19.4, 19.0, 14.1, 13.7.

HR-MS (MALDI, DCTB): *m/z* = 2741.0850, calcd for C₁₈₄H₁₅₂N₈O₈Ce [M]⁺: 2741.0787. Elemental Anal. calcd for C₁₈₄H₁₅₂N₈O₈Ce : C; 80.56, H; 5.58, N; 4.08, found: C; 80.42, H; 5.51, N; 4.16 (0.14% error).

Synthesis of porphyrin Zn3



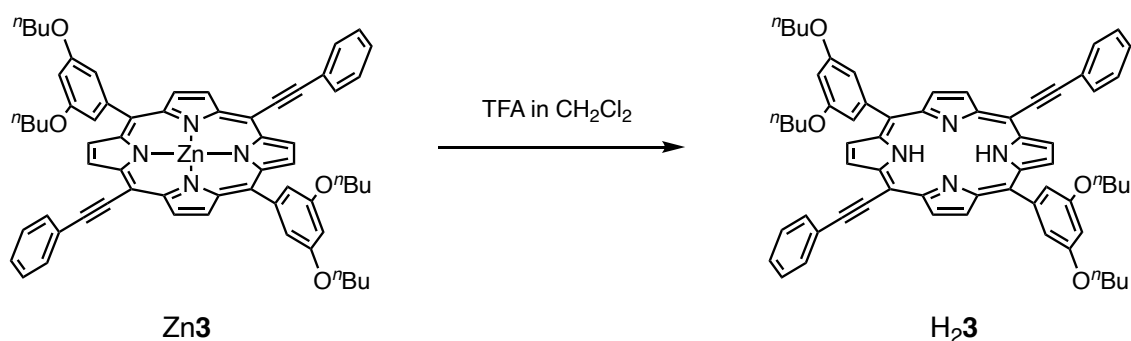
Zinc porphyrin **Zn2** (293 mg, 302 μmol), phenylacetylene (132 μL , 1.2 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (22 mg, 32 μmol) and CuI (6 mg, 33 μmol) were suspended in a mixture of THF and Et_3N (4 : 1 (v/v), 15 mL). The resulting mixture was degassed by four successive freeze-pump-thaw cycles and then refluxed for 3 hrs. The reaction mixture was filtered through Celite and the filtrate was evaporated. The crude compound was purified by silica gel column chromatography (4 ϕ \times 13 cm, hexane : CH_2Cl_2 = 4 : 6) to afford a crude green solid, which was further purified by reprecipitation of a CH_2Cl_2 solution with MeOH to afford **Zn3** as a green solid (253 mg, 83%).

^1H NMR (400 MHz, CDCl_3/TMS): δ = 9.76 (d, J = 5.2 Hz, 4H), 9.06 (d, J = 4.4 Hz, 4H), 8.04–8.02 (m, 4H), 7.59–7.56 (m, 4H), 7.52–7.48 (m, 2H), 7.37 (d, J = 2.4 Hz, 4H), 6.91 (d, J = 2.4 Hz, 2H), 4.16 (t, J = 6.6 Hz, 8H), 1.88 (tt, J = 7.1, 7.1 Hz, 8H), 1.60–1.51 (m, 26H, including H_2O), 1.01 (t, J = 7.2 Hz, 12H).

^{13}C NMR (100 MHz, CDCl_3/TMS): δ = 158.3, 152.0, 149.8, 143.8, 132.8, 131.5, 130.9, 128.6, 128.5, 123.9, 122.7, 114.2, 101.6, 101.1, 96.5, 92.2, 68.1, 31.4, 19.3, 13.9.

HR-MS (MALDI, DCTB): m/z = 1012.3889, calcd for $\text{C}_{64}\text{H}_{60}\text{N}_4\text{O}_4\text{Zn}$ [M] $^+$: 1012.3906.

Synthesis of porphyrin H₂3



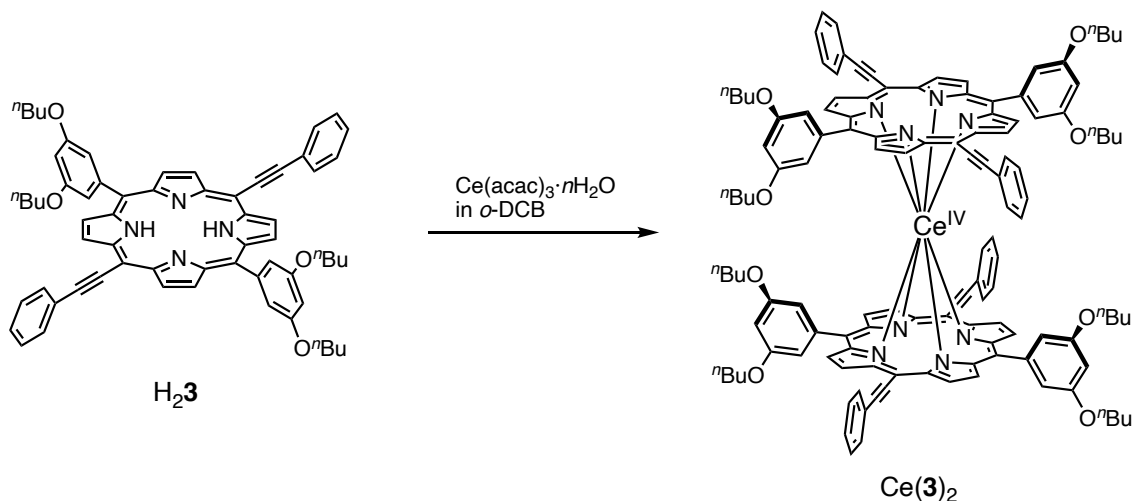
The zinc porphyrin **Zn3** (508 mg, 500 μ mol) was dissolved in the mixture of CH₂Cl₂ (40 mL) and TFA (10 mL). The resulting solution was stirred at room temperature for 1 hr. The reaction mixture was diluted with CH₂Cl₂ (150 mL) and the organic phase was washed with H₂O (100 mL \times 3), saturated aqueous Na₂CO₃ (100 mL) and brine (50 mL), dried over anhydrous Na₂SO₄, filtered and evaporated to give **H₂3** as a purple solid (475 mg, quant.).

¹H NMR (400 MHz, CDCl₃/TMS): δ = 9.72 (d, J = 4.4 Hz, 4H), 8.96 (d, J = 4.4 Hz, 4H), 8.05–8.02 (m, 4H), 7.61–7.57 (m, 4H), 7.54–7.50 (m, 2H), 7.36 (d, J = 2.4 Hz, 4H), 6.91 (t, J = 2.4 Hz, 2H), 4.16 (t, J = 6.4 Hz, 8H), 1.88 (tt, J = 7.0 Hz, 8H), 1.61–1.51 (m, 16H, including H₂O), 1.01 (t, J = 7.4 Hz, 12H), -2.01 (s, 2H).

¹³C NMR (100 MHz, CDCl₃/TMS): δ = 158.5, 143.0, 131.7, 128.7, 123.8, 121.8, 114.3, 101.2, 101.0, 97.2, 91.9, 68.1, 31.4, 19.3, 13.9.

HR-MS (MALDI, DCTB): m/z = 950.4774, calcd for C₆₄H₆₂N₄O₄ [M]⁺: 950.4771.

Synthesis of double-decker complex Ce(3)₂



The porphyrin **H₂3** (95 mg, 99 μmol), $\text{Ce}(\text{acac})_3 \cdot n\text{H}_2\text{O}$ (131 mg, 298 μmol) and *o*-DCB (5.0 mL) were added to the pressure tube. The resulting mixture was heated under microwave irradiation at 220 °C for 0.5 hr and then 240 °C for 0.5 hr with two cycles. The reaction mixture was purified by silica gel column chromatography (4 ϕ \times 15 cm, hexane : CH_2Cl_2 = 1 : 1 – 4 : 6) to yield **Ce(3)₂** as a blackish brown solid (31 mg, 31%).

¹H NMR (400 MHz, CDCl_3/TMS): δ = 9.42 (d, J = 4.8 Hz, 4H), 9.18 (d, J = 4.8 Hz, 4H), 8.96 (br, 4H), 8.52 (d, J = 4.8 Hz, 4H), 8.34 (d, J = 4.0 Hz, 4H), 8.18 (d, J = 6.8 Hz, 8H), 7.71 (dd, J = 7.4, 7.4 Hz, 8H), 7.61–7.57 (m, 4H), 6.90 (dd, J = 2.2, 2.2 Hz, 4H), 5.64 (dd, J = 1.6, 1.6 Hz, 4H), 4.85–4.74 (m, 8H), 3.69 (t, J = 5.6 Hz, 8H), 2.31–2.26 (m, 8H), 1.93–1.87 (m, 8H), 1.55–1.49 (m, 25H, including H_2O), 1.31–1.21 (m, 33H), 0.75 (t, J = 7.4 Hz, 12H).

¹³C NMR (100 MHz, CDCl_3/TMS): δ = 158.8, 158.0, 155.4, 151.8, 151.5, 150.3, 142.8, 132.4, 130.4, 128.8, 128.7, 128.2, 127.8, 127.6, 125.1, 123.8, 115.4, 115.0, 104.5, 101.3, 98.0, 90.7, 68.9, 67.6, 32.0, 31.0, 19.8, 19.0, 14.3, 13.7.

HR-MS (MALDI, DCTB): m/z = 2036.8296, calcd for $\text{C}_{128}\text{H}_{120}\text{N}_8\text{O}_8\text{Ce}$ [M]⁺: 2036.8283.

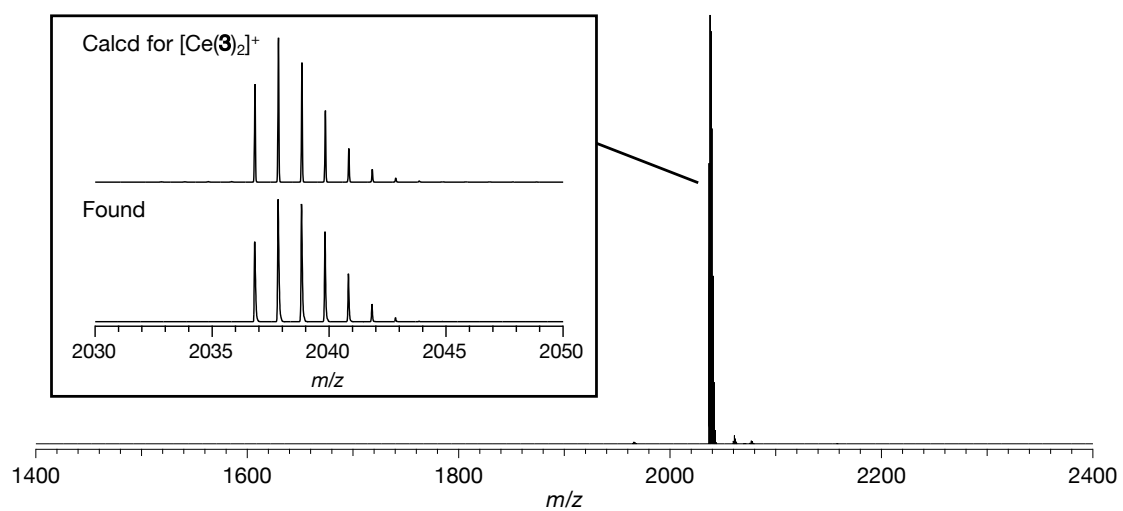
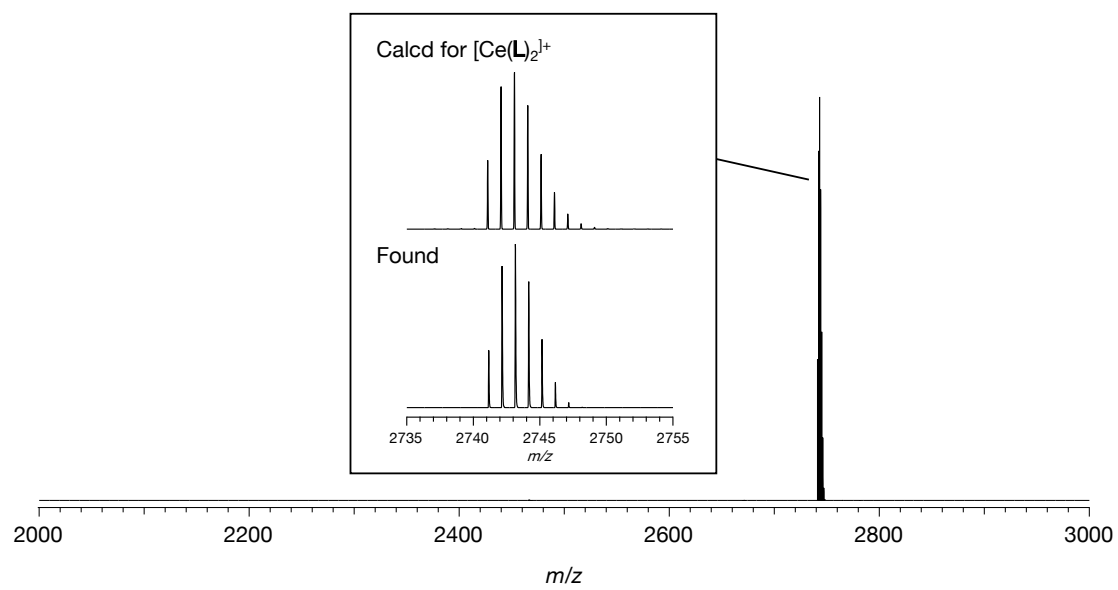


Figure S1. MALDI-TOF MS spectrum of $\text{Ce}(\mathbf{L})_2$ (top) and $\text{Ce}(\mathbf{3})_2$ (bottom)

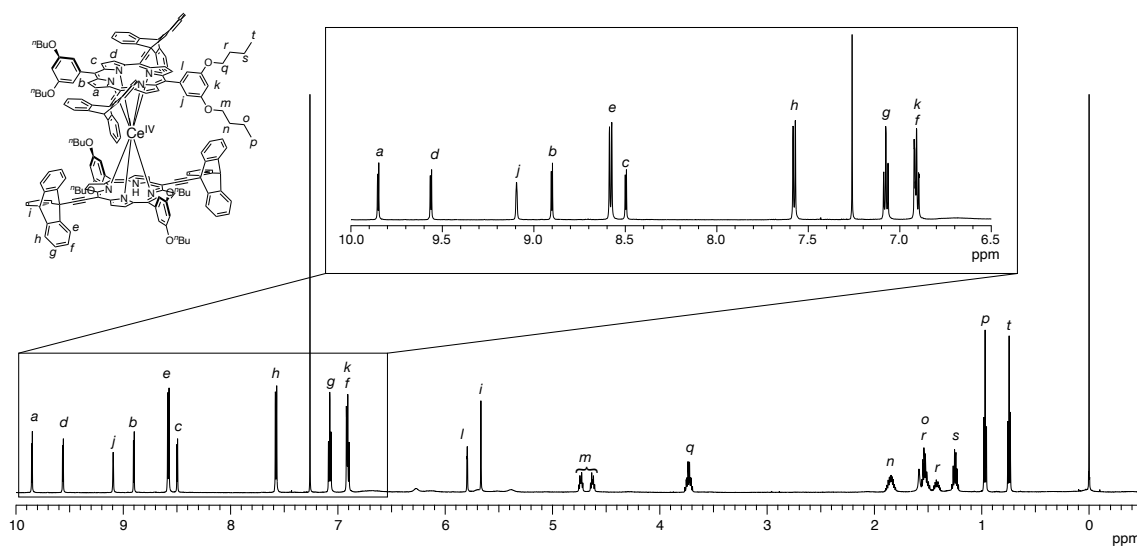


Figure S2. ¹H-NMR spectrum of Ce(L)₂ in CDCl₃.

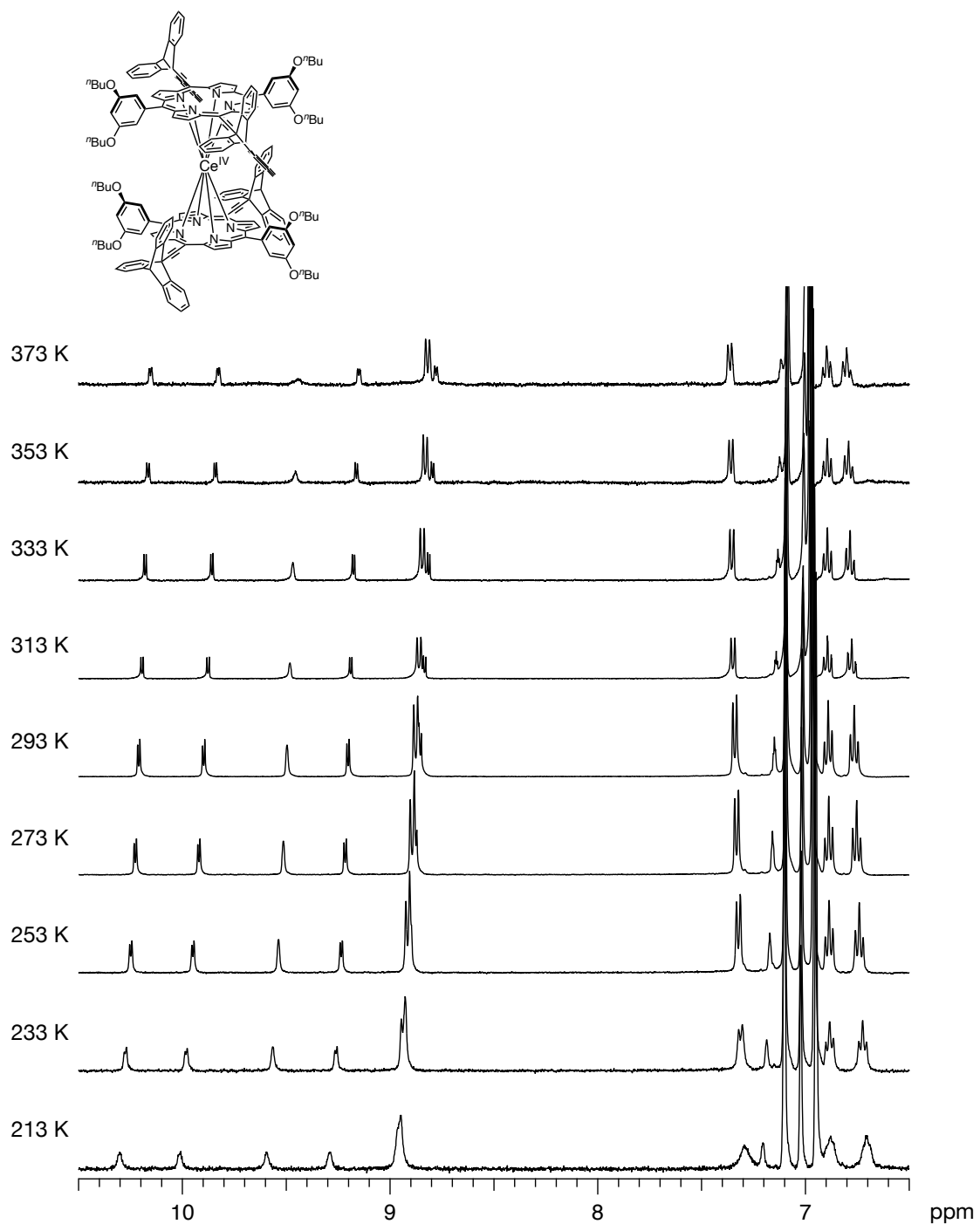


Figure S3. Aromatic region of VT $^1\text{H-NMR}$ spectra of $\text{Ce}(\text{L})_2$ in $\text{toluene-}d_8$ (400 MHz).

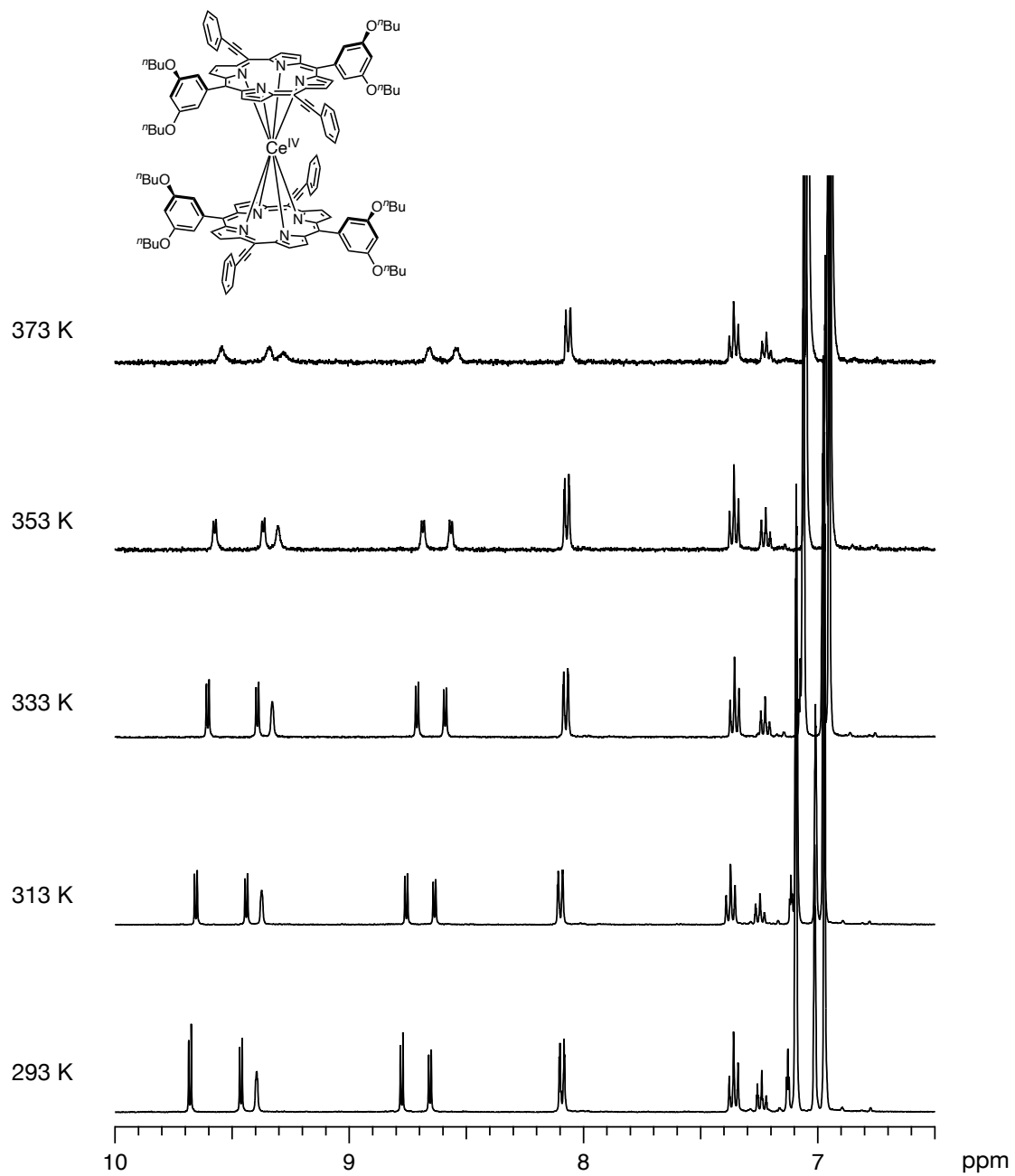
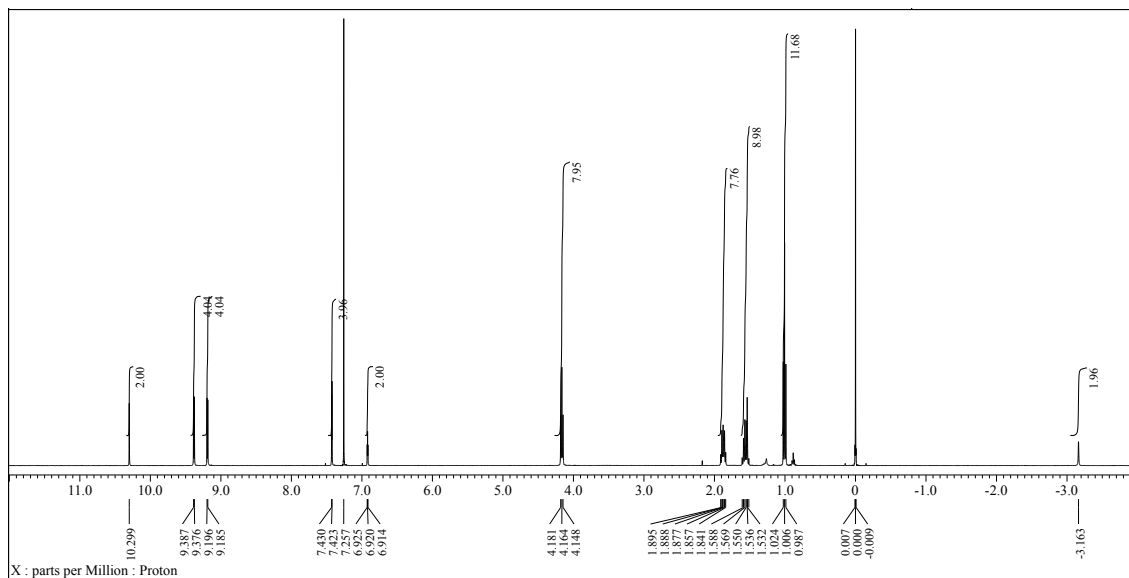


Figure S4. Aromatic region of VT $^1\text{H-NMR}$ spectra of $\text{Ce}(\mathbf{3})_2$ in $\text{toluene-}d_8$ (400 MHz).

(a)



(b)

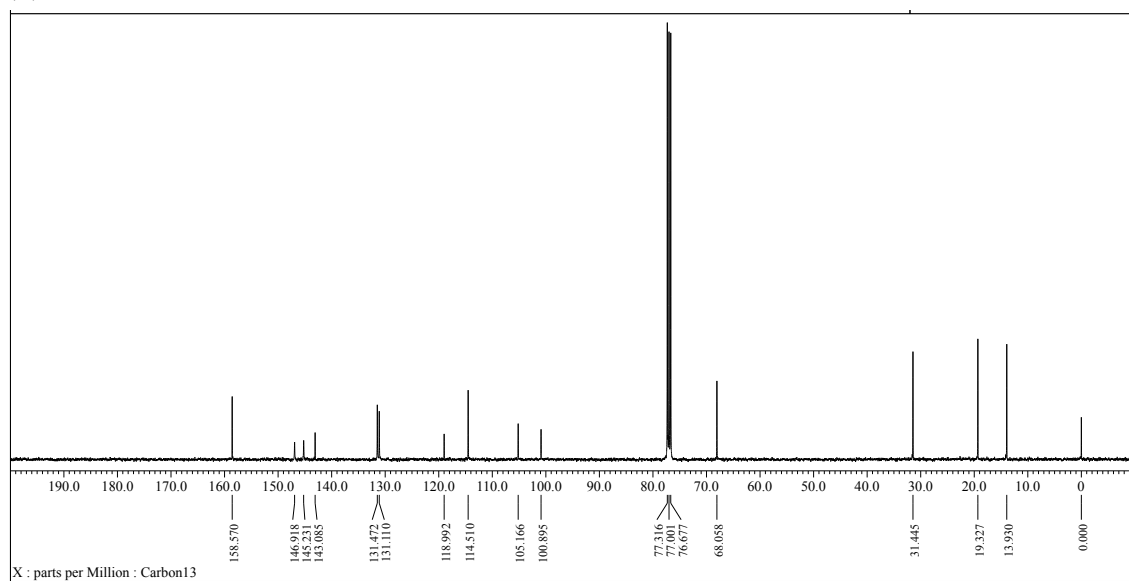
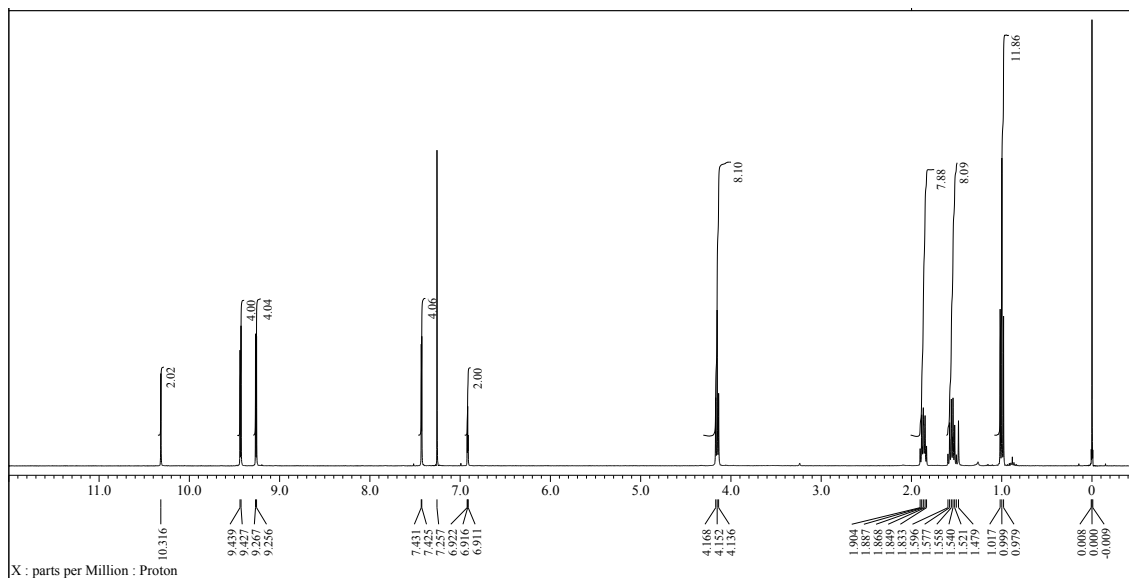


Figure S5. (a) ^1H and (b) ^{13}C NMR spectra of $\text{H}_2\mathbf{1}$ in CDCl_3

(a)



(b)

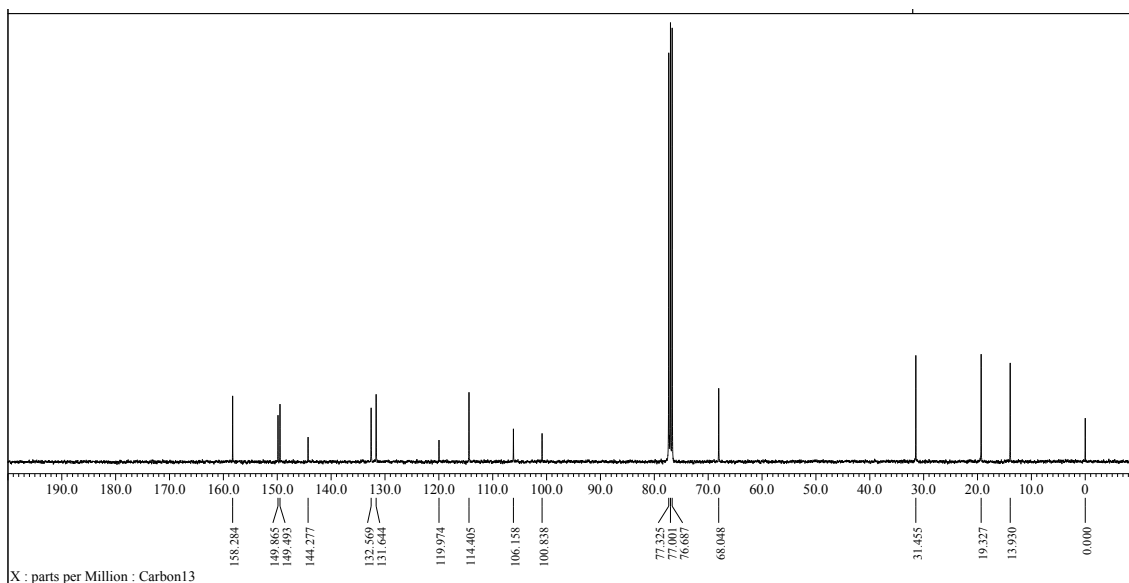
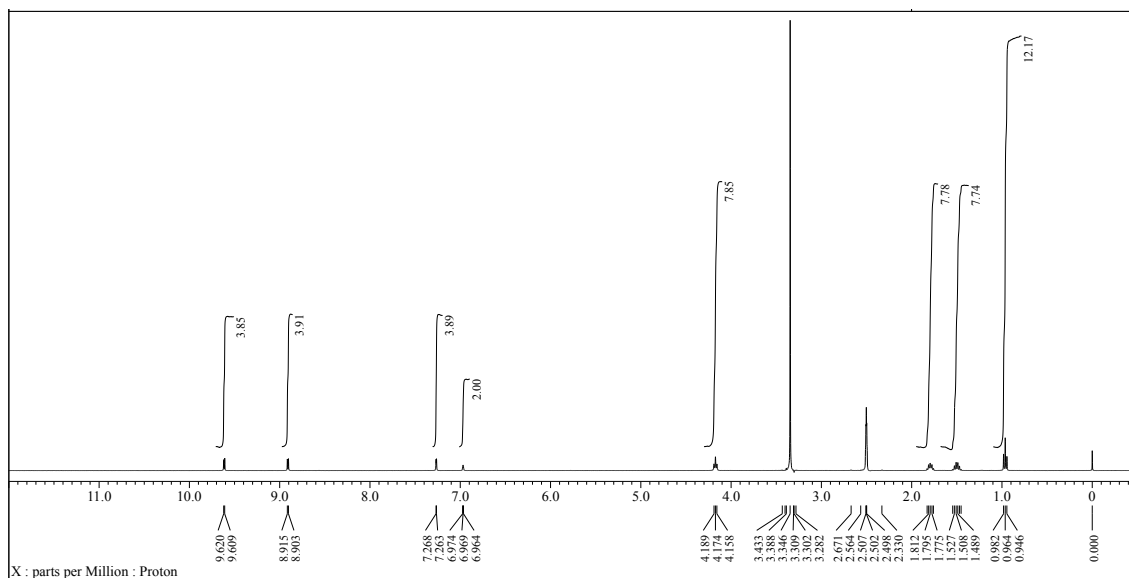


Figure S6. (a) ¹H and (b) ¹³C NMR spectra of Zn1 in CDCl₃.

(a)



(b)

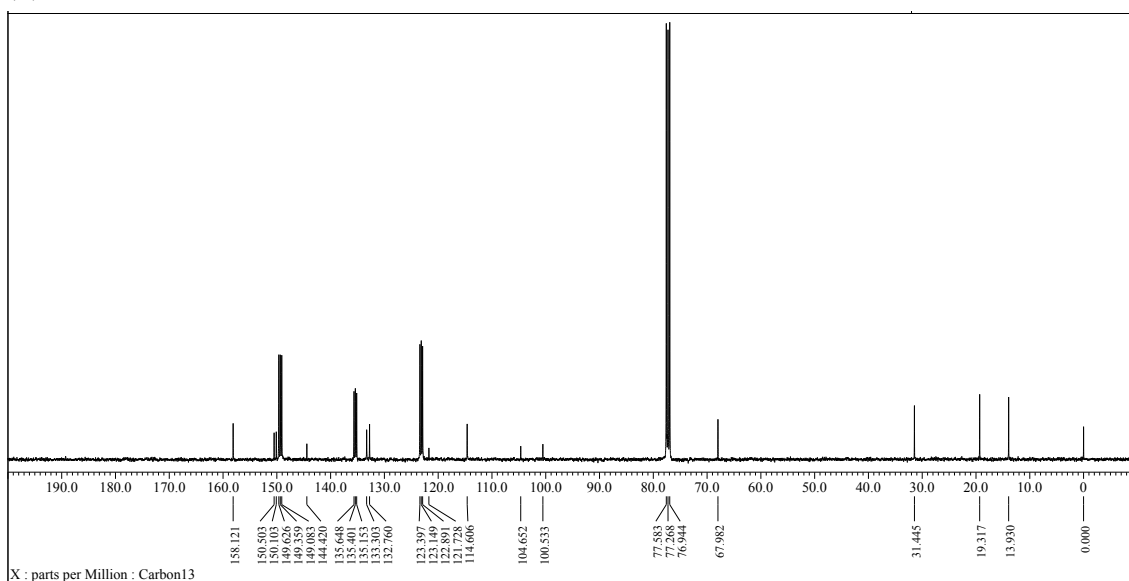
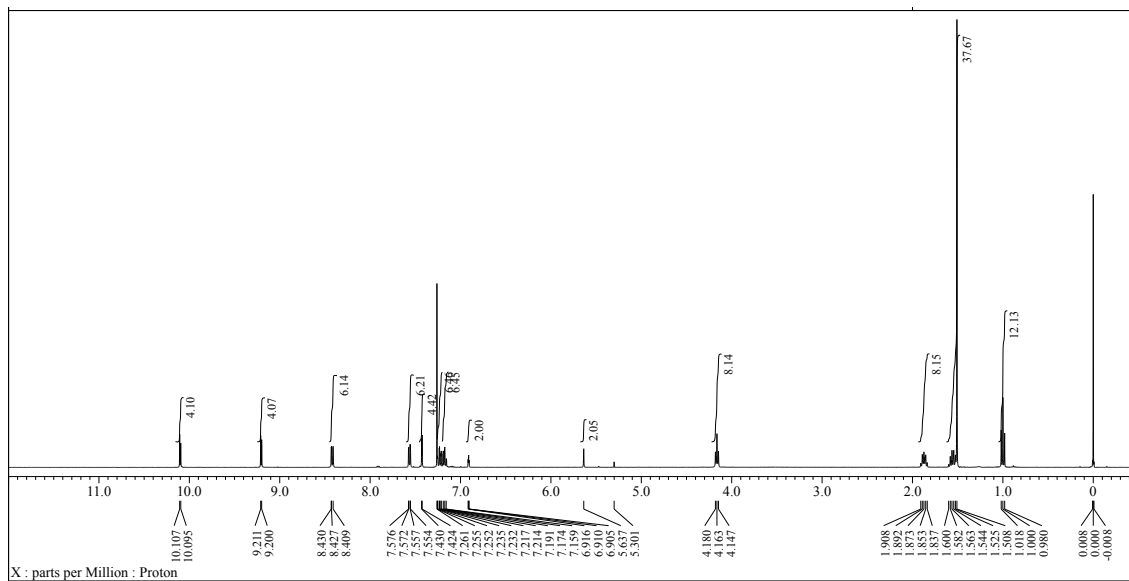


Figure S7. (a) ^1H spectrum in $\text{DMSO-}d_6$ and (b) ^{13}C NMR spectrum in CDCl_3 : pyridine- d_5 (9:1 (v/v)) of Zn2 .

(a)



(b)

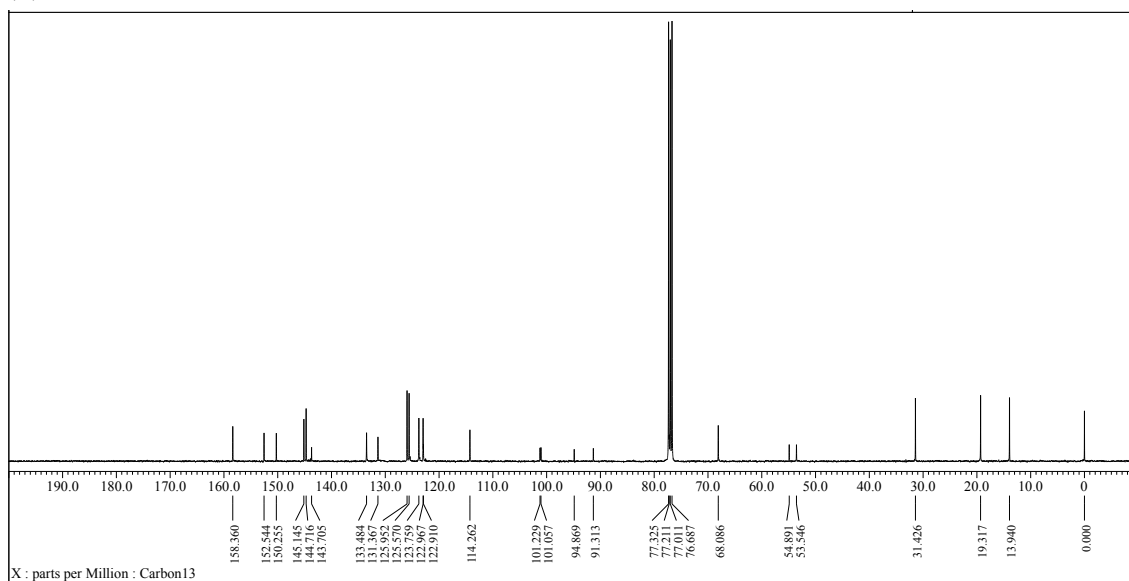
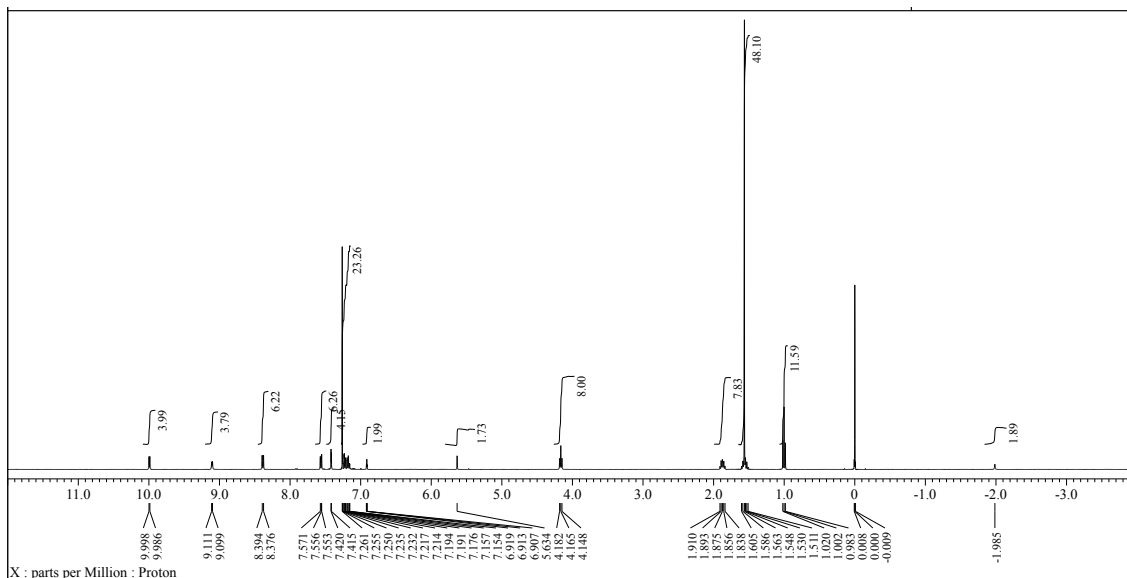


Figure S8. (a) ¹H and (b) ¹³C NMR spectra of ZnL in CDCl₃.

(a)



(b)

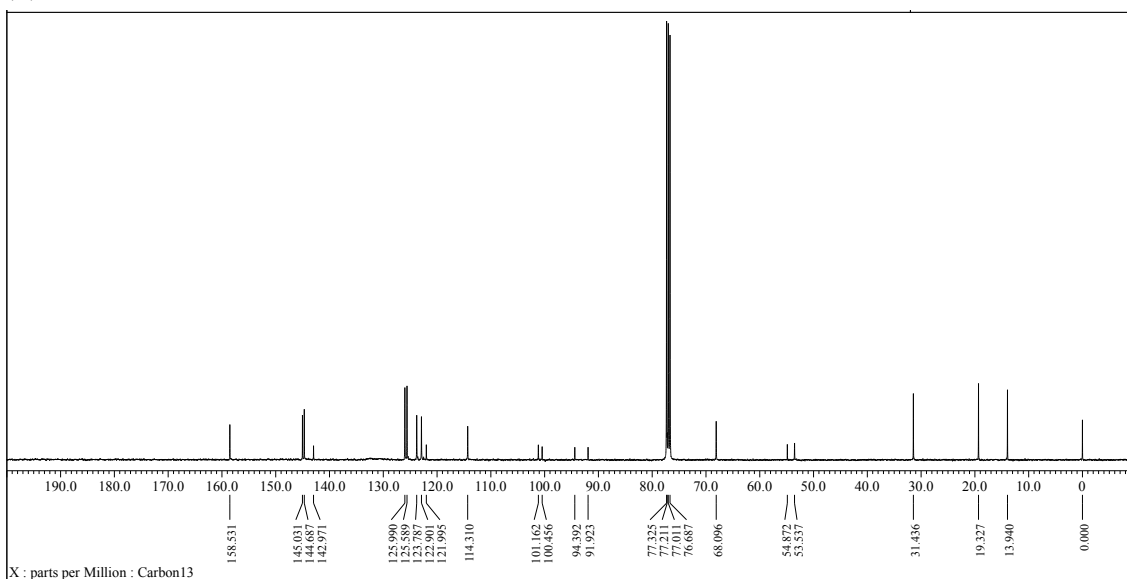
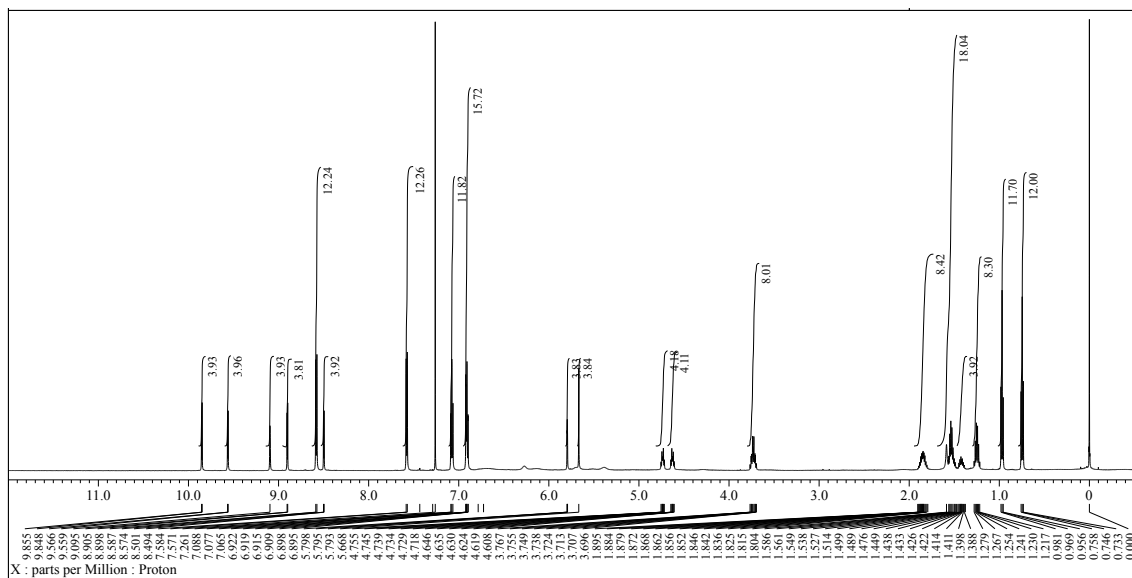


Figure S9. (a) ^1H and (b) ^{13}C NMR spectra of H_2L in CDCl_3 .

(a)



(b)

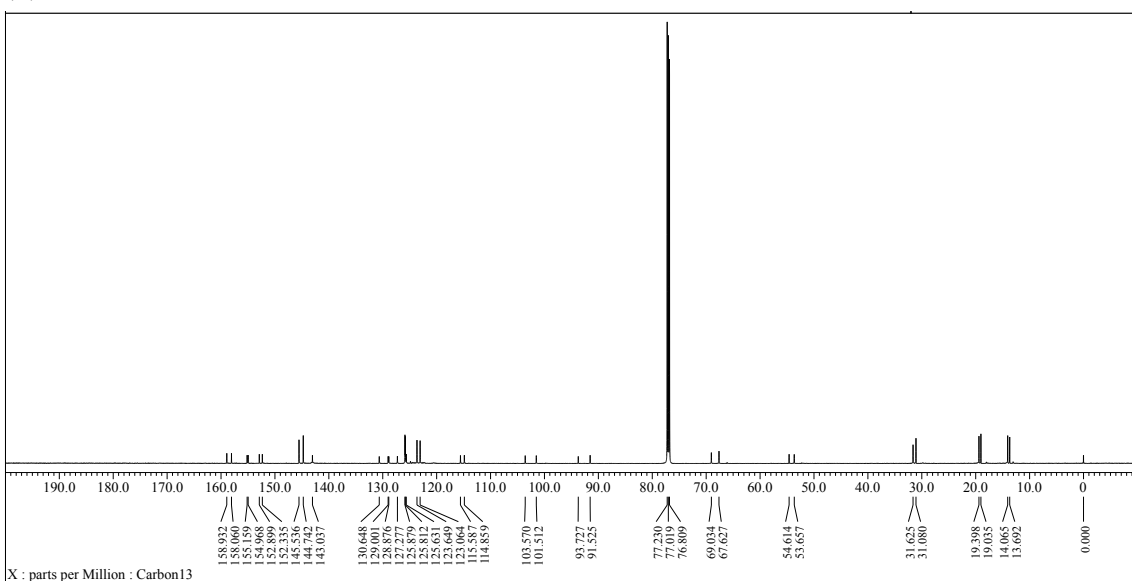


Figure S10. (a) ^1H and (b) ^{13}C NMR spectra of $\text{Ce}(\text{L})_2$ in CDCl_3 .

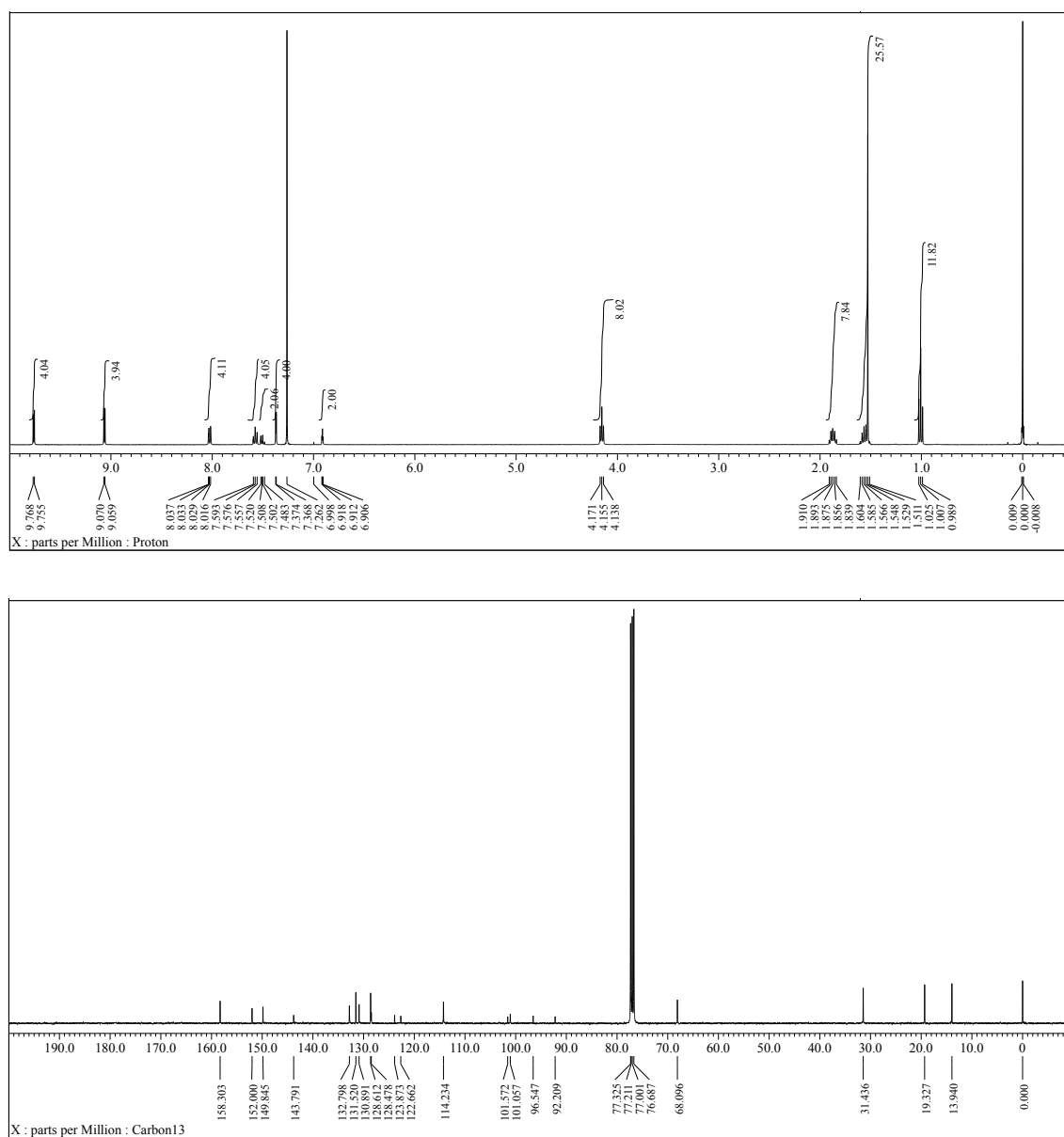


Figure S11. (a) ^1H and (b) ^{13}C NMR spectra of Zn3 in CDCl_3 .

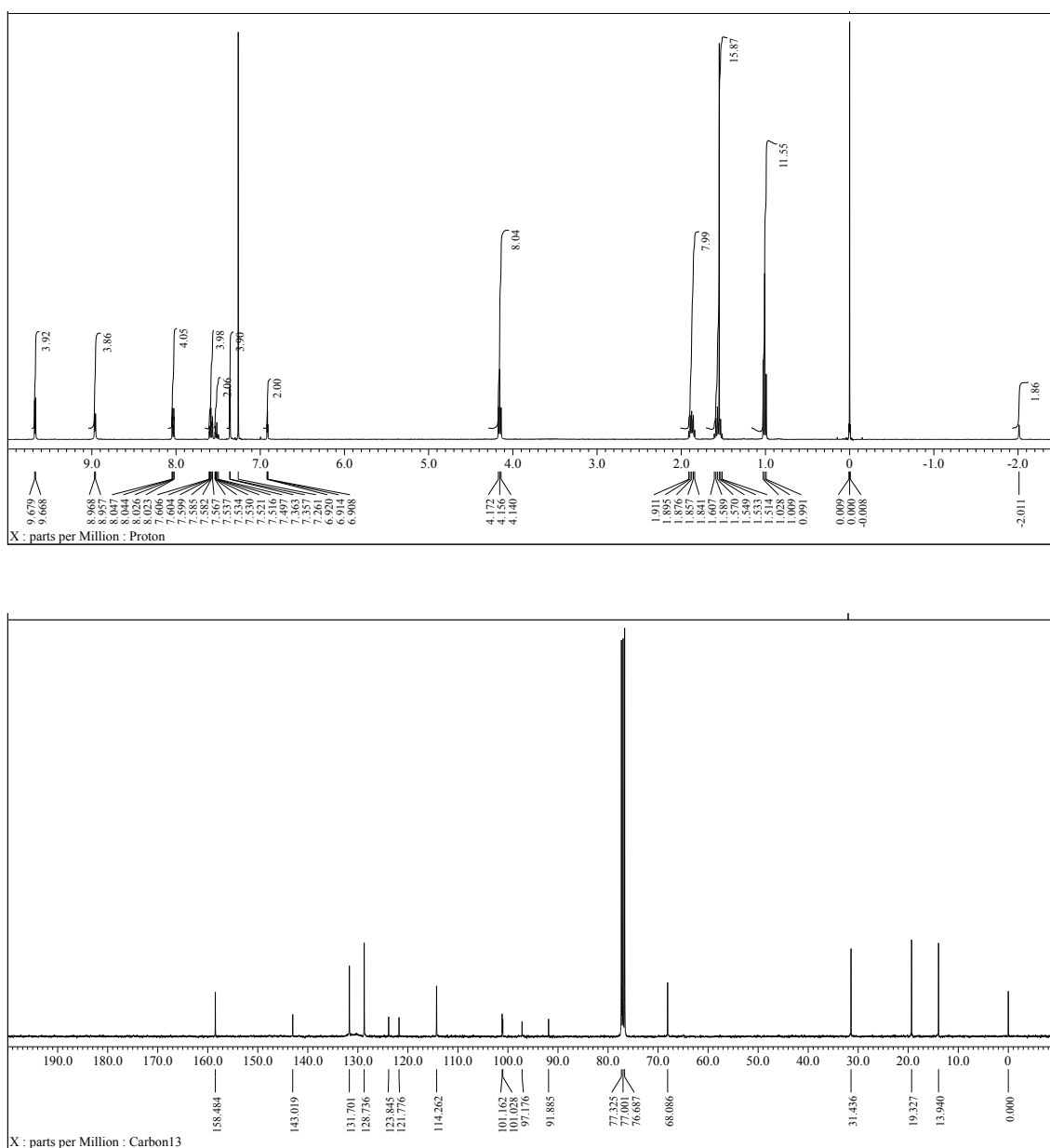


Figure S12. (a) ^1H and (b) ^{13}C NMR spectra of $\text{H}_2\mathbf{3}$ in CDCl_3 .

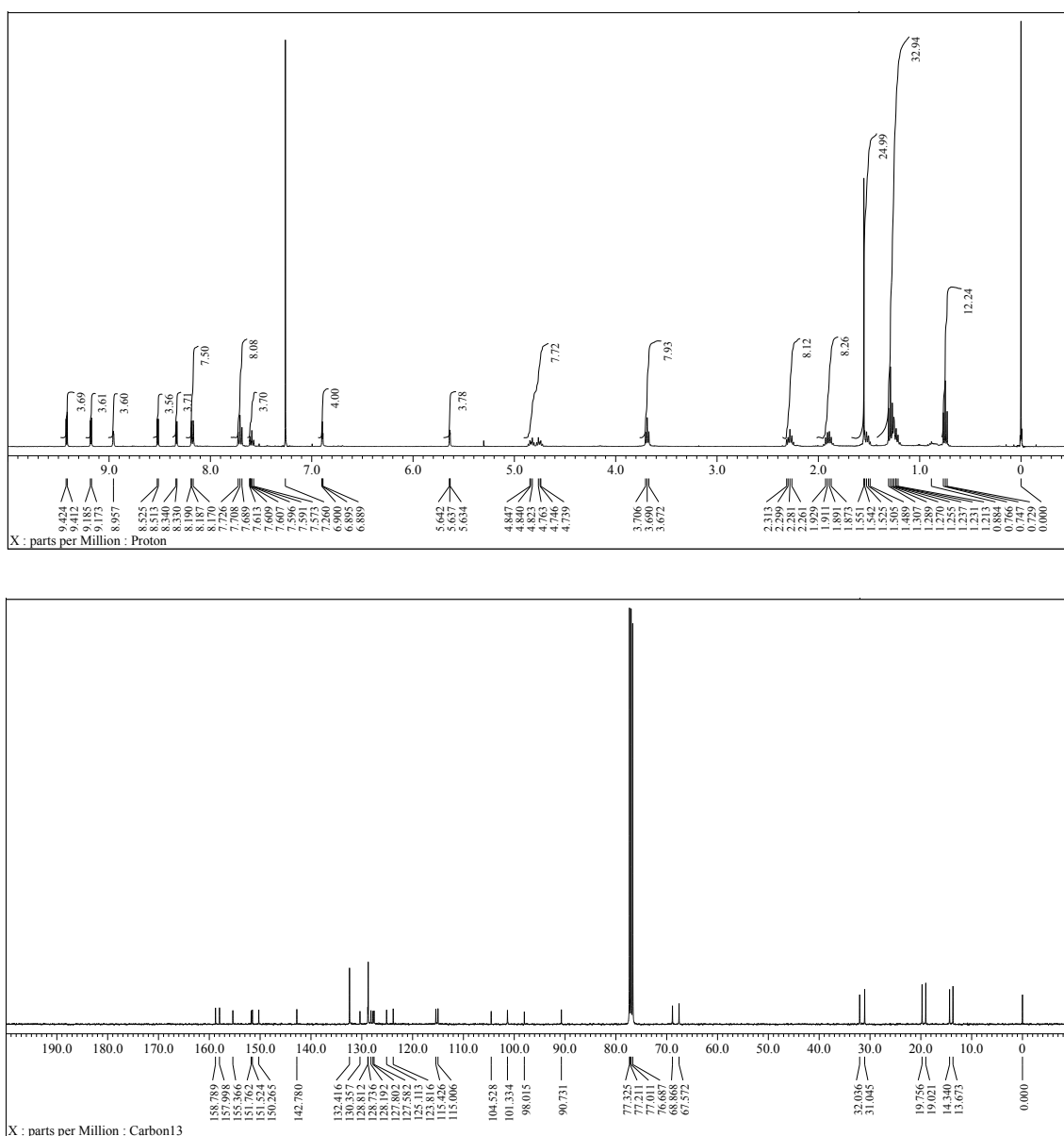


Figure S13. (a) ^1H and (b) ^{13}C NMR spectra of $\text{Ce}(\mathbf{3})_2$ in CDCl_3 .

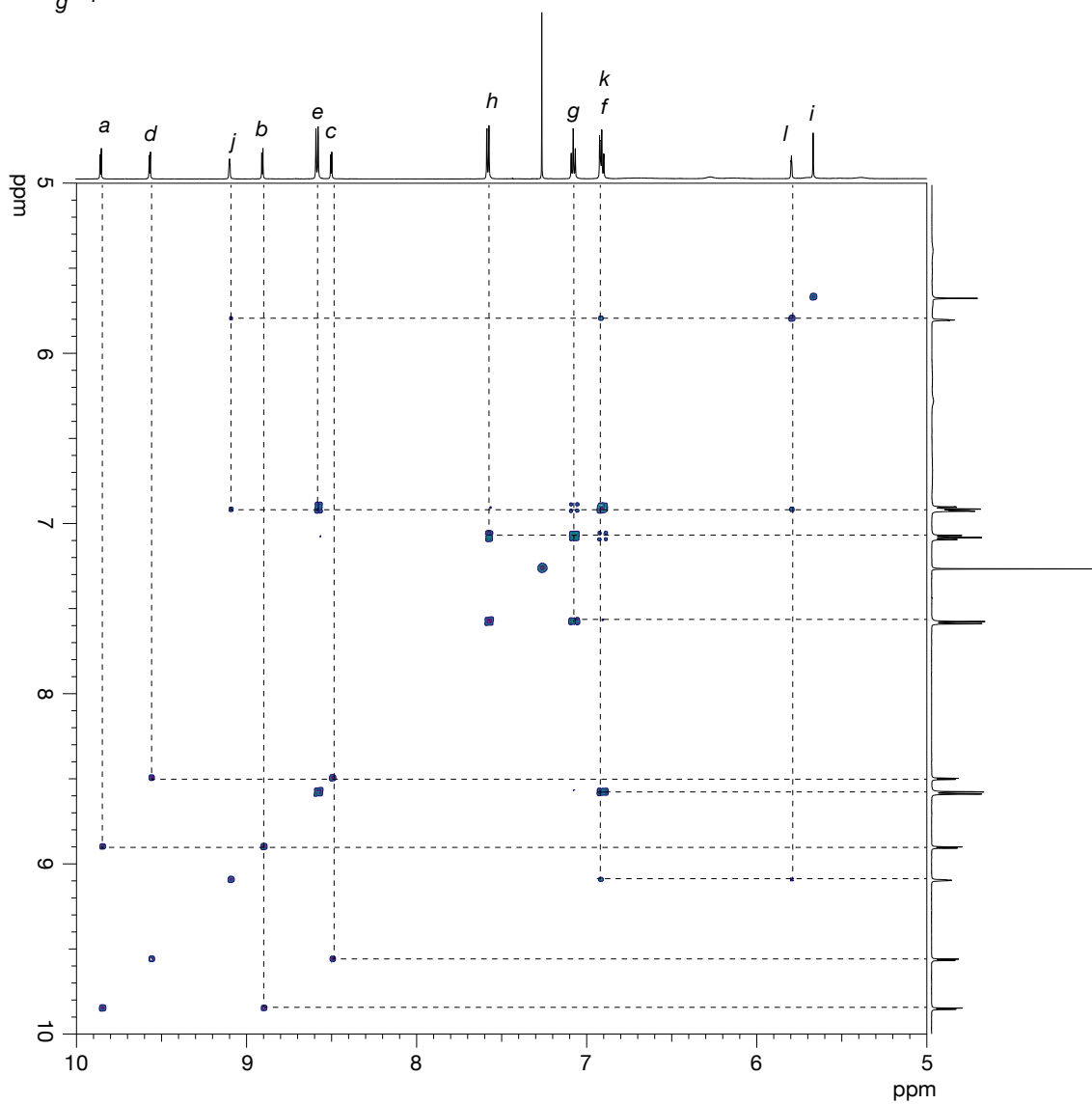
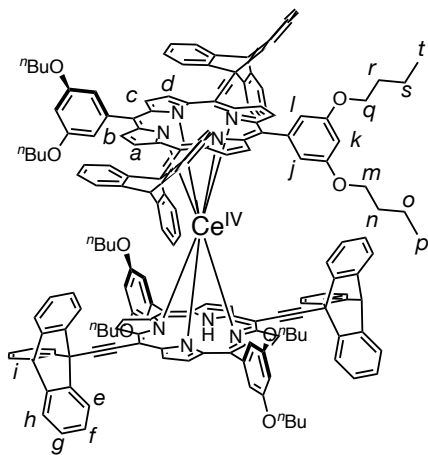


Figure S14. COSY spectrum of $\text{Ce}(\text{L})_2$ in CDCl_3 .

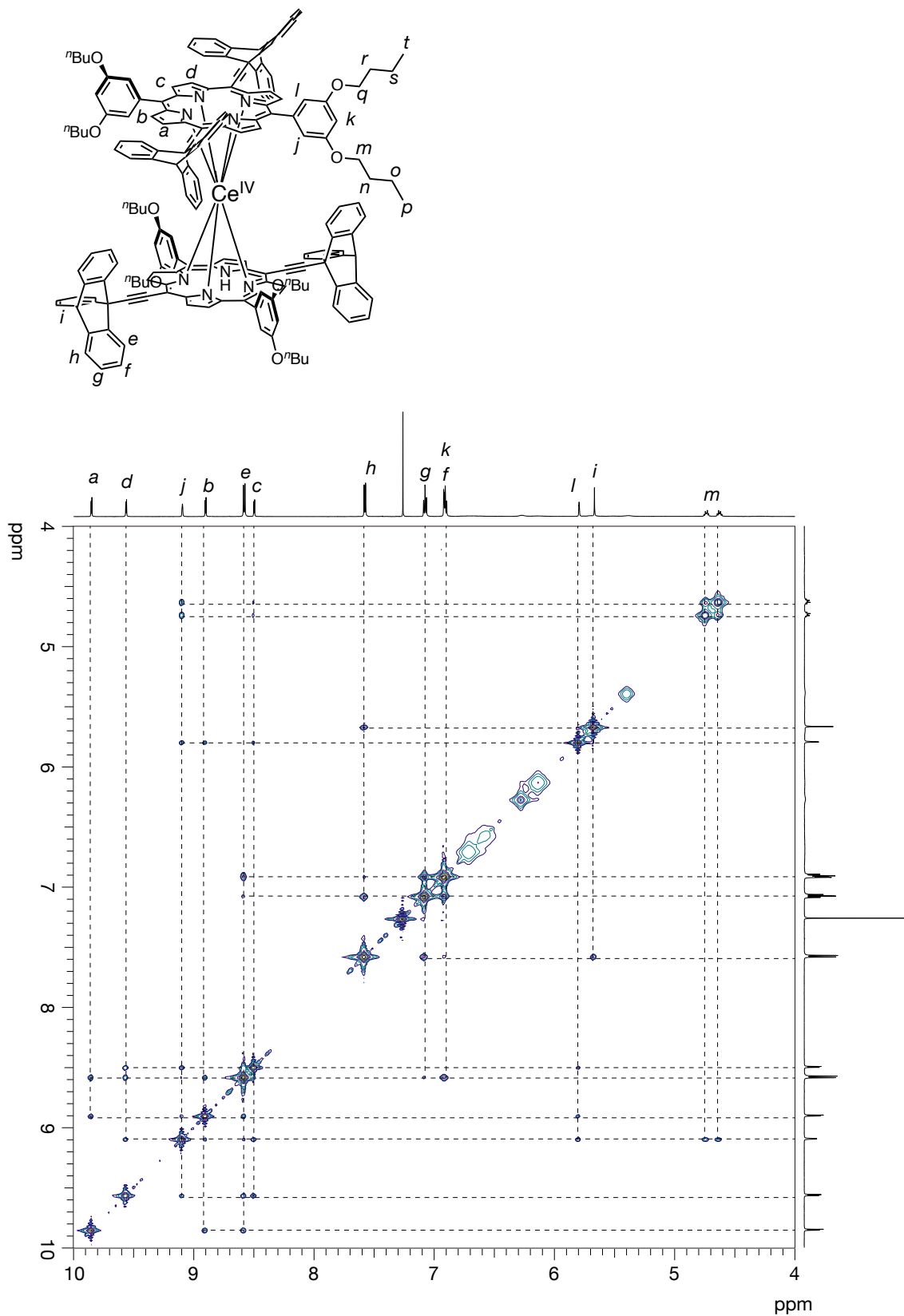


Figure S15. NOESY spectrum of $Ce(1)_2$.

Single crystal X-ray analysis of Ce(L)₂

Single crystals suitable for the single crystal X-ray analysis were obtained by slow diffusion of MeOH into a CHCl₃ solution of Ce(L)₂. The single crystal X-ray diffraction data was collected on a Rigaku VariMax RAPID (1.2kW) diffractometer equipped with confocal mirror optics MoK α radiation and IP detector. The collected X-ray diffraction data were processed using the Rapid Auto software. The structure was solved by SHELXT^[4] and refined by full-matrix least-squares on *F*² using the SHELXL-2019/2^[5] and Olex2.^[6] The geometrical restraints, i.e. DFIX, SIMU and RIGU on peripheral alkyl chains as well as the triptycene moiety, were used in the refinements. The Solvent Mask function of Olex2 was employed to remove the disordered chloroform and methanol molecules which were used for the preparation of single crystals since the diffraction of these crystalline solvent molecules was weak and the electron density of solvent molecules hardly be modeled.

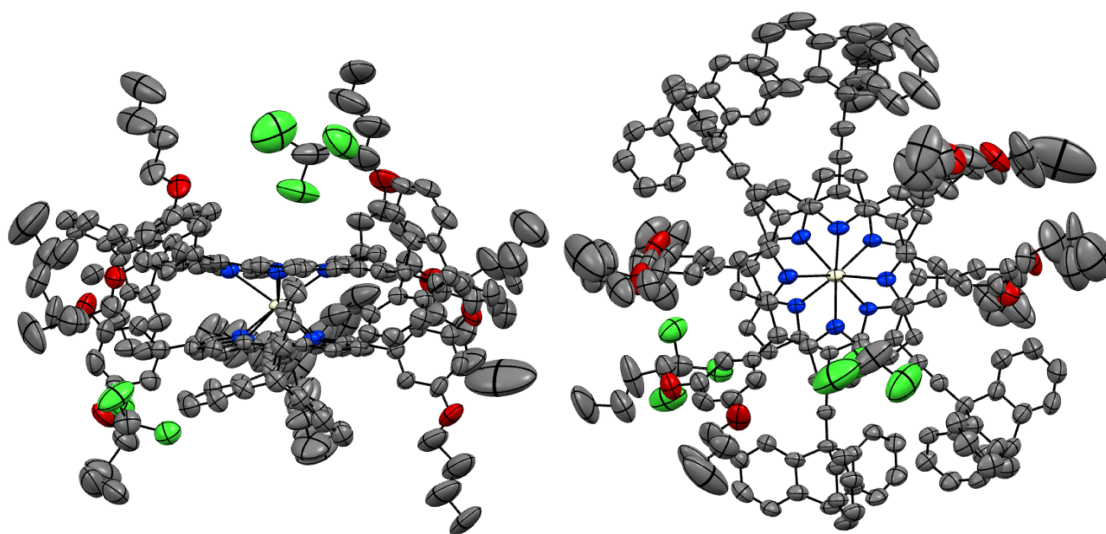


Figure S16. ORTEP representation of a side view (left) and a top view (right) of Ce(L)₂. Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms and solvent molecules are omitted for clarity. (CCDC deposit number: 2258829)

Table S1. Crystal data and structure refinement for Ce(L)₂ (CCDC deposit number: 2258829)

Empirical formula	C186 H154 Ce Cl6 N8 O8
Formula weight	2981.98
Temperature	103.15 K
Wavelength	0.71075 Å
Crystal system	trigonal
Space group	R-3 (#148)
Unit cell dimensions	a = 41.9814(5) Å b = 41.9814(8) Å c = 53.6321(10) Å $\alpha = 90^\circ$ $\beta = 90^\circ$ $\gamma = 120^\circ$
Volume	81860(3) Å ³
Z	18
Density (calculated)	1.089 g/cm ³
Absorption coefficient	0.392 mm ⁻¹
F(000)	27900.0
Crystal size	0.2 x 0.19 x 0.14 mm ³
Theta range for data collection	1.887 to 25.351 °
Index ranges	-50 ≤ h ≤ 50, -50 ≤ k ≤ 50, -64 ≤ l ≤ 64
Reflections collected	391865
Independent reflections	33301 [R _{int} = 0.0679, R _{sigma} = 0.0295]
Completeness to theta = 25.351°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.644 and 1.000
Refinement method	Full-matrix least-square on F ²
Data / restraints / parameters	33301 / 239 / 1926
Goodness-of-fit on F ²	1.170
Final R indices [I > 2σ(I)]	R1 = 0.0860, wR2 = 0.2678
R indices (all data)	R1 = 0.1018, wR2 = 0.2866
Largest diff. peak and hole	1.77 and -1.08 e.Å ⁻³

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