Structural and Electrochemical Characterization of a Cerium(IV) Hydroxamate Complex: Implications for the Beneficiation of Light Rare Earth Ores

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Supporting Information

Experimental Procedures.

General Methods. Unless otherwise noted, all reactions and manipulations were performed under an inert atmosphere (N_2) using standard Schlenk techniques or in a drybox equipped with a molecular sieves 13X / Q5 Cu–0226S catalyst purifier system. Glassware was oven-dried for at least 3 hrs at 150 °C prior to use. Chemical shifts were recorded in units of parts per million downfield from residual proteo solvent for ^{1}H–NMR and from characteristic solvent peaks for ^{13}C–NMR.

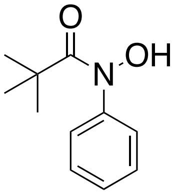
Materials. All solvents were sparged for 20 min with dry N_2 and dried using a commercial two-column solvent purification system comprising columns packed with Q5 reactant and neutral alumina respectively (for hexanes), or two columns of neutral alumina (for Et_2O, and CH_2Cl_2). Deuterated solvents were stored over potassium mirror overnight prior to use. Zinc dust (Acros), ammonium chloride (Acros), nitrobenzene (Acros), anhydrous sodium carbonate (Acros), pivaloyl chloride (Acros), cerium chloride (Strem), lithium *tert*-butoxide (Acros), and potassium bis(trimethylsilyl)amide (Sigma) were used as received. TEMPO (2,2,6,6-tetramethylpiperidine-N-oxyl) (Acros) was sublimed prior to use. *N*-phenylhydroxylamine was synthesized according to literature procedures.[1] $Ce[N(SiMe_3)_2]_3$ was synthesized according to literature procedures.[2]

Electrochemistry. All experiments were performed under an inert atmosphere (N_2) in a drybox with electrochemical cells that consisted of a 10 mL vial, glassy carbon disk (3 mm diameter) working electrode, a platinum wire counter electrode, and a silver wire plated with AgCl as a quasi-reference electrode. The working electrode surfaces were polished prior to each set of experiments. Potentials recorded in CH_2Cl_2 were referenced versus ferrocene, which was added as an internal standard for calibration at the end of each run. Solutions employed during CV studies were ~3 mM in analyte and 100 mM in [^{n}Pr$_4$N][BAr$^F_4$]. All data were collected in a positive-feedback IR compensation mode. The CH_2Cl_2 solution cell resistances were measured prior to each run to insure resistances ≤ ~500 Ω. Scan rate dependences of 50–1000 mV/s were performed to determine electrochemical reversibility.

X-Ray Crystallography. X-ray intensity data were collected on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at a temperature of 143(1) K. In all cases, rotation frames were integrated using SAINT, producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the SHELXTL program package for further processing and structure solution. The intensity data were corrected for Lorentz and polarization effects and for absorption using TWINABS or SADABS. The structures were solved by direct methods (SHELXS-97). Refinement was by full-matrix least squares based on F^2 using SHELXL-97. All reflections were used during refinements. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model.

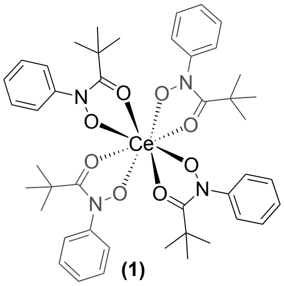
UV-Vis Absorption Spectroscopy. All UV-Vis Absorption measurements were performed using a Perkin Elmer 950 UV-Vis/NIR Spectrophotometer. 1 mm path length screw cap quartz cells were used with a blank measured before each run. All samples were prepared under an N_2 environment.

Synthetic Details and Characterization



(HL)

***N*-phenyl-pivalohydroxamic acid (HL).** The compound was prepared using a modified literature procedure.[3] To a stirring mixture of *N*-phenylhydroxylamine (3.95 g, 36.0 mmol, 1.00 equiv) and anhydrous sodium carbonate (4.00 g, 37.0 mmol, 1.05 equiv) in diethyl ether (200 mL) was added pivaloyl chloride (4.34 g, 36.0 mmol, 1.00 equiv) dropwise at 0 ºC. Stirring was continued at 0 ºC for 3 h. The resulting solid precipitate was removed by filtration and washed with copious amounts of diethyl ether. A saturated aqueous solution of ammonium chloride was added to the filtrate and the organic layer was separated from the aqueous layer. The aqueous layer was extracted three times with diethyl ether. The combined organic portions were dried with anhydrous magnesium sulfate. The mixture was filtered and the filtrate was concentrated under reduced pressure to yield a crude tan solid. Compound **1** was isolated as an off-white powder by cooling a hot, concentrated solution in hexanes. The powder was isolated by filtration and dried under reduced pressure. Yield 4.77 g, 69%. Analytical data were consistent with reported values.[4] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.88 (br, 1H, O-*H*), 7.41 (m, 5H, Ar-*H*), 1.15 (s, 9H, ^{t}Bu-*H*); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 175.6, 140.6, 129.3, 128.0, 39.18, 28.53.



(1)

Ce^{IV}[^{t}BuC(O)N(O)Ph]$_4$ (1). *Method 1*. To a solution of Ce[N(SiMe$_3$)$_2$]$_3$ (0.54 g, 0.86 mmol, 1.0 equiv) in diethyl ether (5 mL) was added a solution of **HL** (0.67 g, 3.5 mmol, 4.0 equiv) in diethyl ether (5 mL). The mixture was allowed to stand at room temperature for 3 d during which large, dark purple crystals formed. Compound **1** was isolated by filtration and dried under reduced pressure. Yield 0.39 g, 50%. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.37 (m, 8H, *ortho*-Ar-*H*), 7.30 (m, 12H, *meta*/*para*-Ar-*H*), 1.11 (s, 36H, ^{t}Bu-*H*); ^{13}C NMR (125.8 MHz, CDCl$_3$): δ 173.5, 143.3, 128.9, 128.8, 128.6, 38.02, 29.53; FT-IR (KBr, cm^{-1}) 3059, 2958, 1534, 1430, 1364, 1219, 1050, 1045, 1016, 961, 787, 780, 705, 695, 599, 502; Anal. Calcd. for CeC$_{44}$H$_{56}$N$_4$O$_8$: C, 58.13; H, 6.21; N, 6.16. Found: C, 58.38; H, 6.28; N, 6.11.

Method 2. To a solution of Ce[N(SiMe$_3$)$_2$]$_3$ (0.067 g, 0.11 mmol, 1.0 equiv) in diethyl ether (2 mL) was added a solution of **HL** (0.084 g, 0.44 mmol, 4.0 equiv) in diethyl ether (5 mL). To this mixture, a solution of TEMPO, 2,2,6,6-tetramethylpiperidine-N-oxyl, (0.017 g, 0.11 mmol, 1.0 equiv) in diethyl ether (2 mL) was added. The mixture was allowed to stand at room temperature for 18 h during which dark purple crystals formed. Compound **1** was isolated by filtration and dried under reduced pressure. Yield 0.075 g, 75%.

Method 3. To a solution of Ce[N(SiMe$_3$)$_2$]$_3$ (0.19 g, 0.30 mmol, 1.0 equiv) in diethyl ether (5 mL) was added a solution of **HL** (0.24 g, 1.2 mmol, 4.0 equiv) in diethyl ether (5 mL).

The mixture was exposed to air and allowed to stand at room temperature for 18 h during which dark purple crystals formed. Compound **1** was isolated by filtration and dried under reduced pressure. Yield 0.23 g, 84%.

Method 4. Under an ambient atmosphere, a suspension of anhydrous $CeCl_3$ (0.175 g, 0.710 mmol, 1.00 equiv) in DCM (5 mL) was treated with a solution of **HL** (0.549 g, 2.84 mmol, 4.00 equiv) in DCM (5 mL). To this mixture, LiO^{t}Bu (0.180 g, 2.25 mmol, 3.20 equiv) was added directly with concomitant and immediate change in color from clear colorless to dark red. After the mixture had been stirred at room temperature for 18 h, it was filtered and concentrated under reduced pressure. The residue was dissolved in pyridine. Dark purple crystals were obtained by layering this solution with hexanes. Compound **1** was isolated by filtration and dried under reduced pressure. Yield 0.165 g, 25 %.

Method 5. This is the method of choice for the preparation of **1**. Under an ambient atmosphere, a suspension of $Ce(NO_3)_3 \cdot 6H_2O$ (0.561 g, 1.29 mmol, 1.00 equiv) in DCM (5 mL) was treated with a solution of **HL** (1.09 g, 5.64 mmol, 4.40 equiv) in DCM (5 mL). To this mixture, LiO^{t}Bu (0.330 g, 4.10 mmol, 3.20 equiv) was added directly. An immediate change in color from clear colorless to dark red was observed. After the mixture had been stirred at room temperature for 2 h, it was filtered through Celite. The filtrate was layered with hexanes (10 mL) and allowed to stand at room temperature for 18 h. A small amount of clear, colorless crystals were removed by filtration. The filtrate was layered with hexanes (30 mL) and cooled in an ice bath. Compound **1** was isolated as dark purple microcrystals by filtration and dried under reduced pressure. Yield 1.13 g, 96 %.

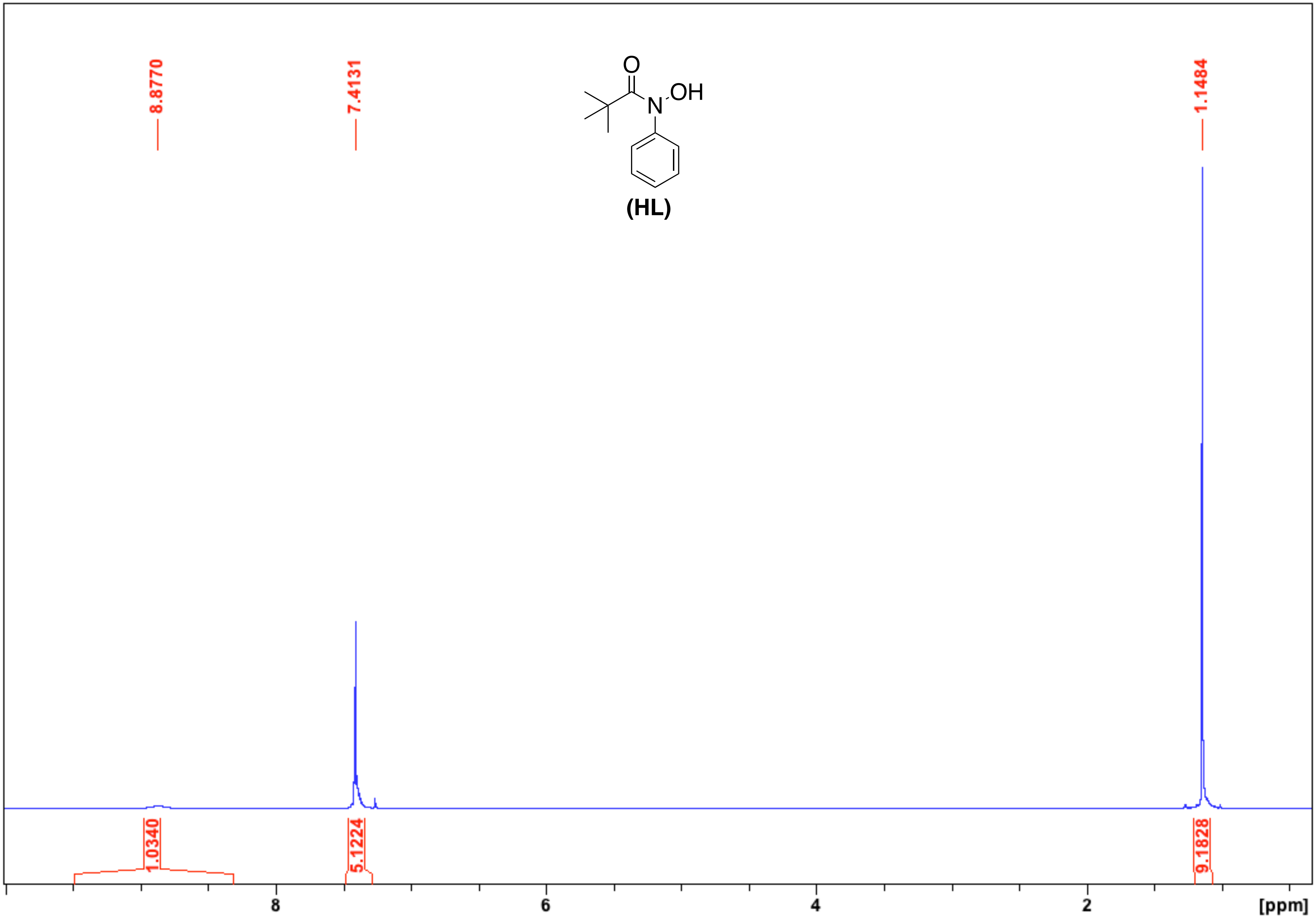


Figure S1. ^{1}H NMR of *N*-phenyl-pivalohydroxamic acid (**HL**) in $CDCl_3$.

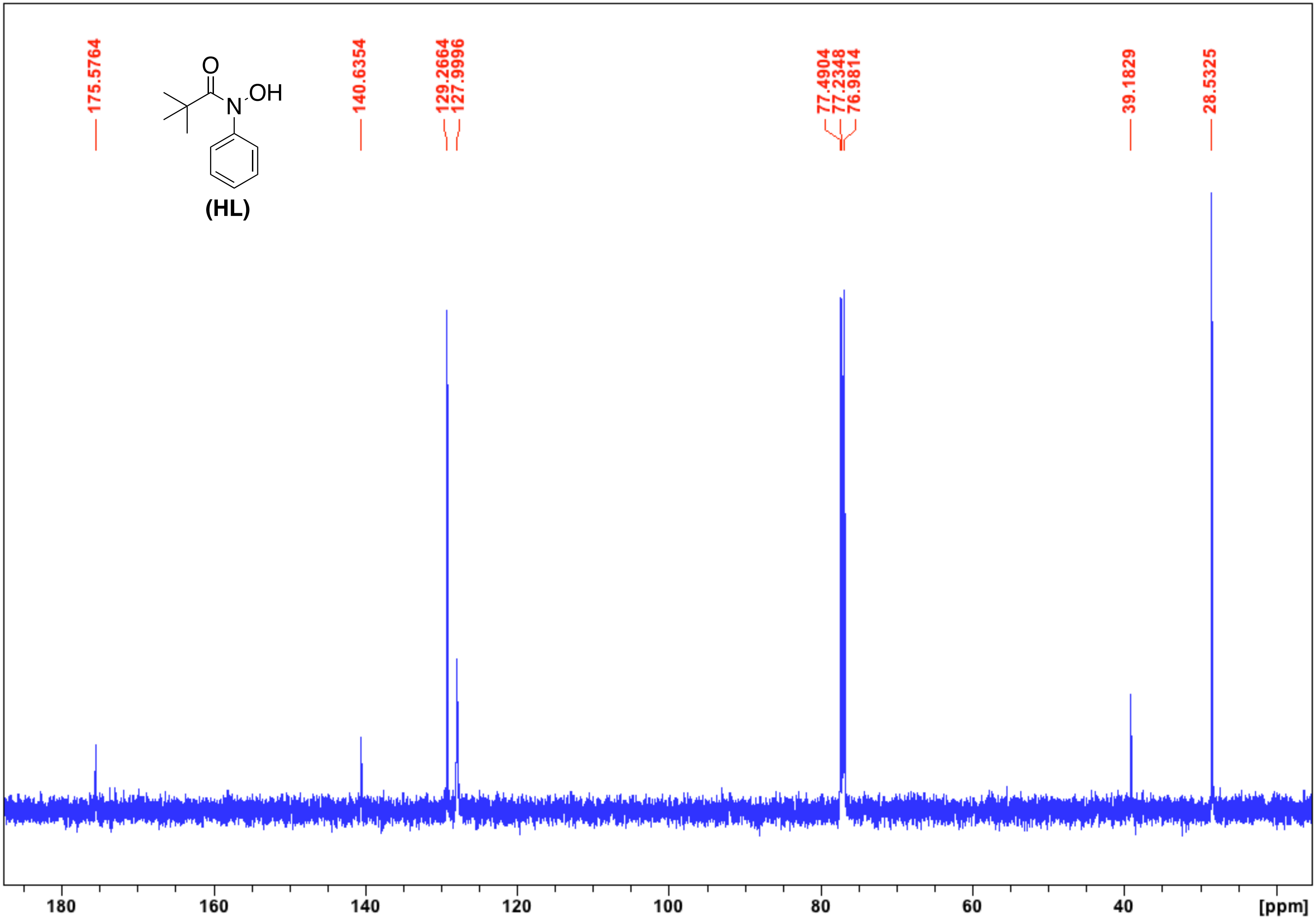


Figure S2. ^{13}C NMR of *N*-phenyl-pivalohydroxamic acid **(HL)** in $CDCl_3$.

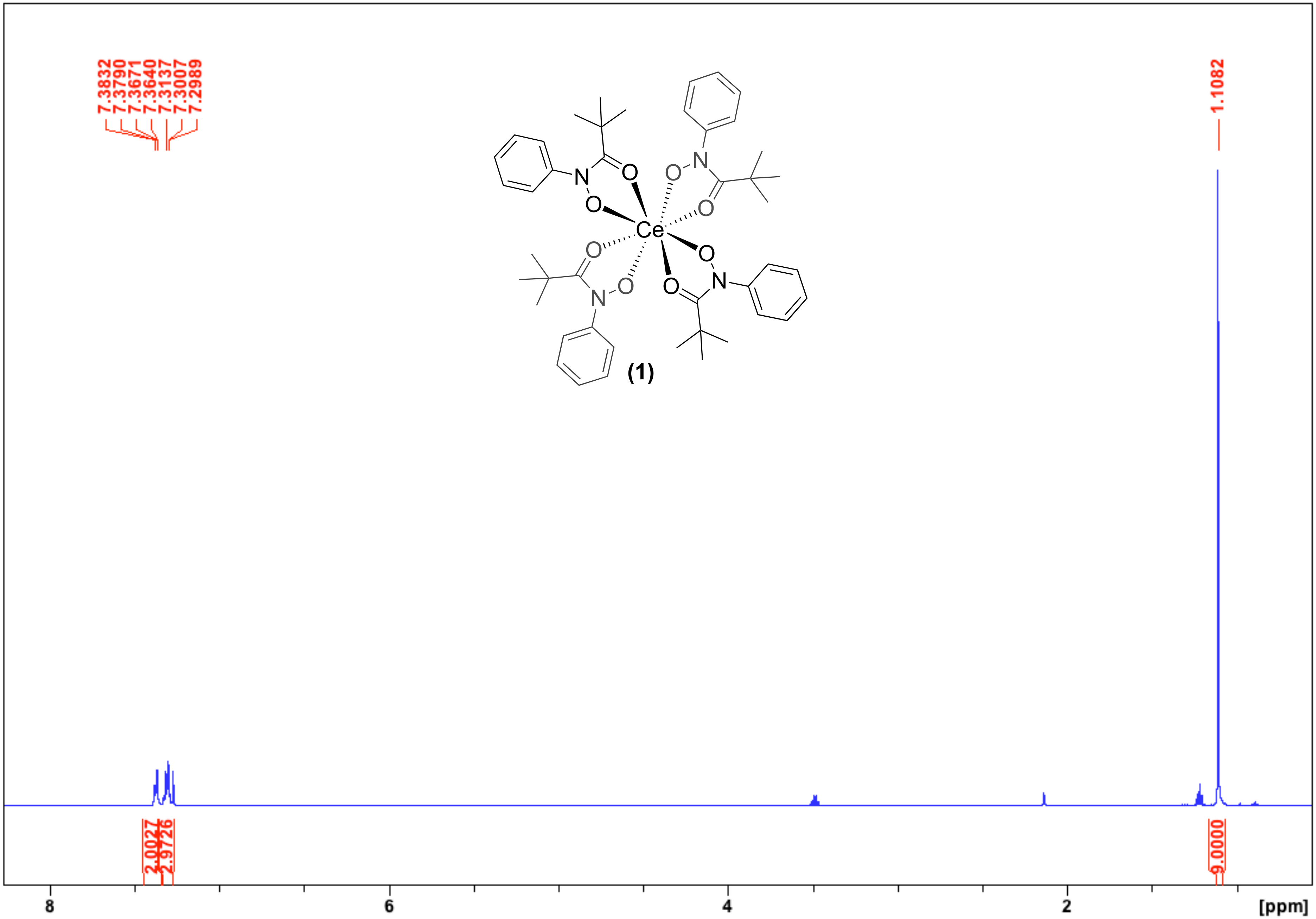


Figure S3. ^{1}H NMR of complex **1** in $CDCl_3$.

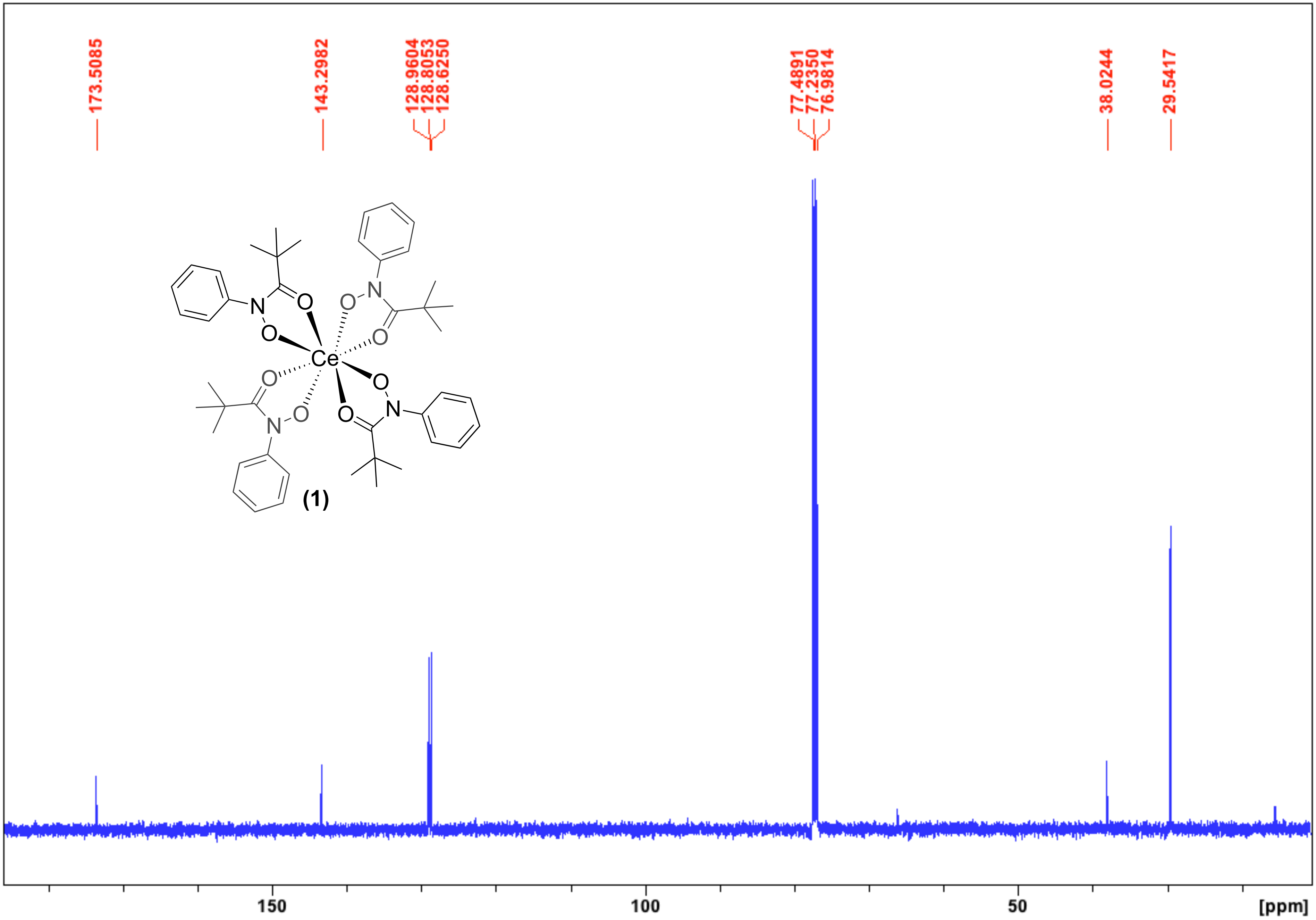


Figure S4. ^{13}C NMR of complex **1** in $CDCl_3$.

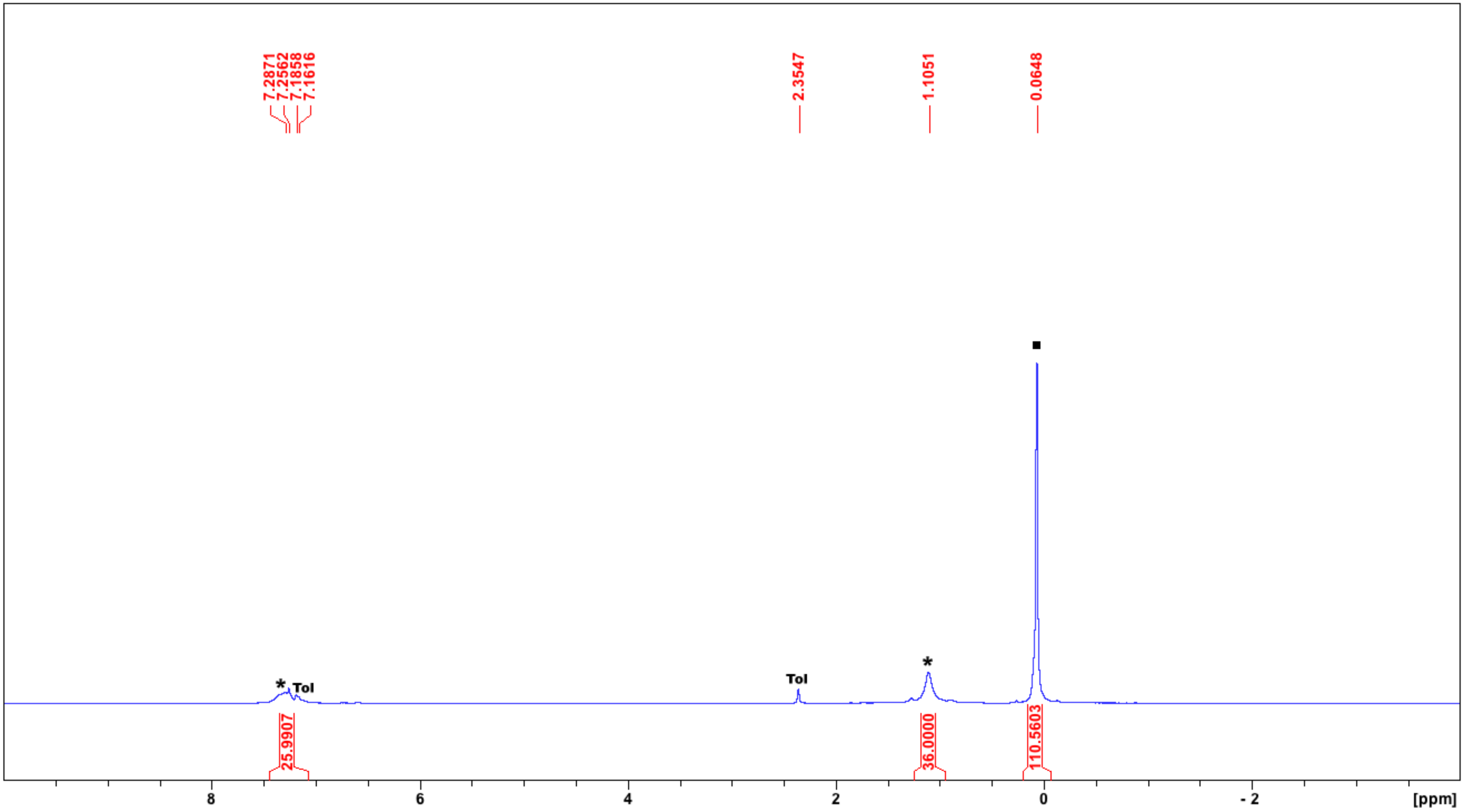


Figure S5. Formation of **1** from Ce[N(SiMe$_3$)$_2$]$_3$ and **HL** in CDCl$_3$ (* = **1**; ■ = H[N(SiMe$_3$)$_2$]), *Method 1*.

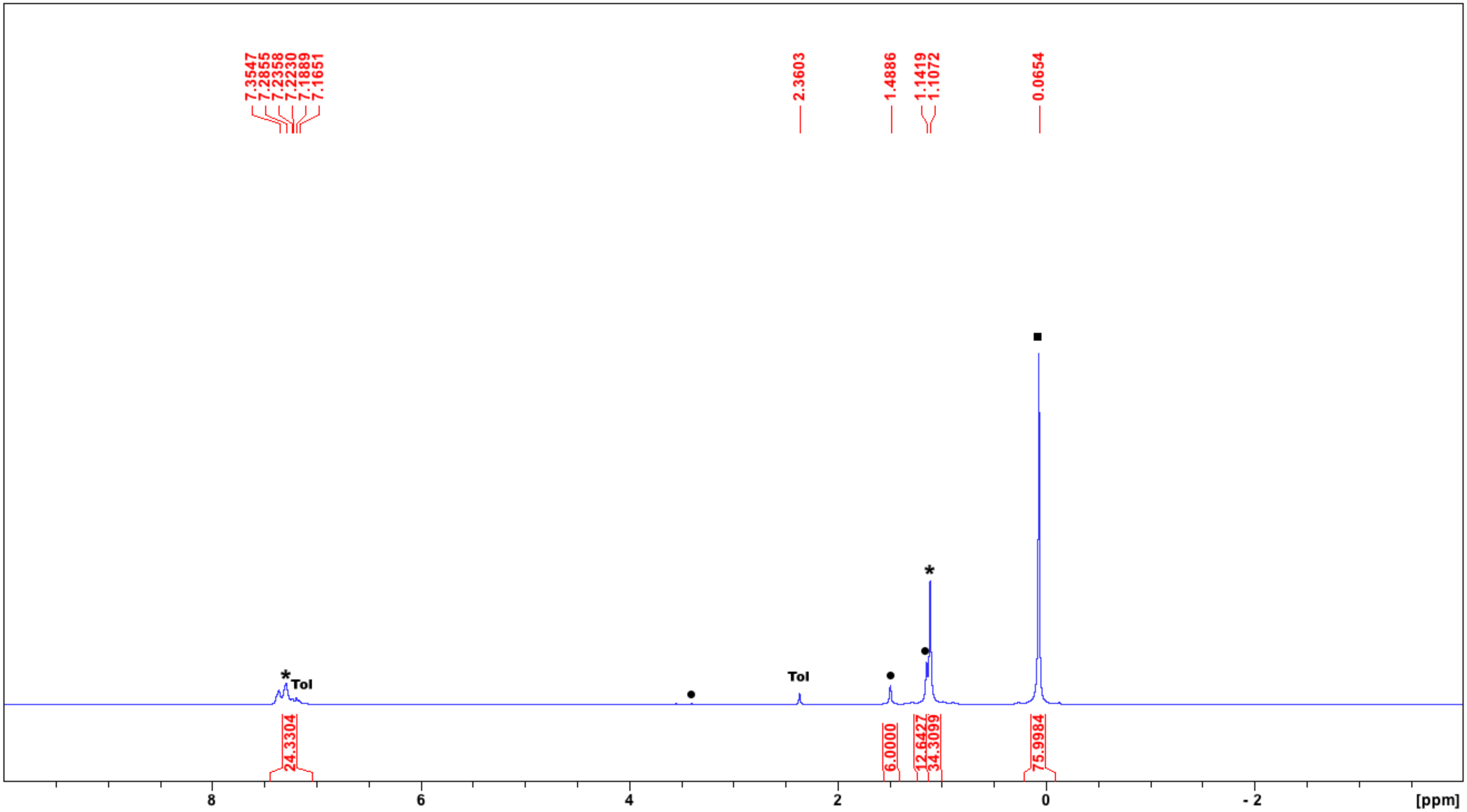


Figure S6. Formation of **1** from Ce[N(SiMe$_3$)$_2$]$_3$, **HL**, and TEMPO in CDCl$_3$ (* = **1**; ● = TEMPO-H/TEMPO-D; ■ = H[N(SiMe$_3$)$_2$]), *Method 2*.

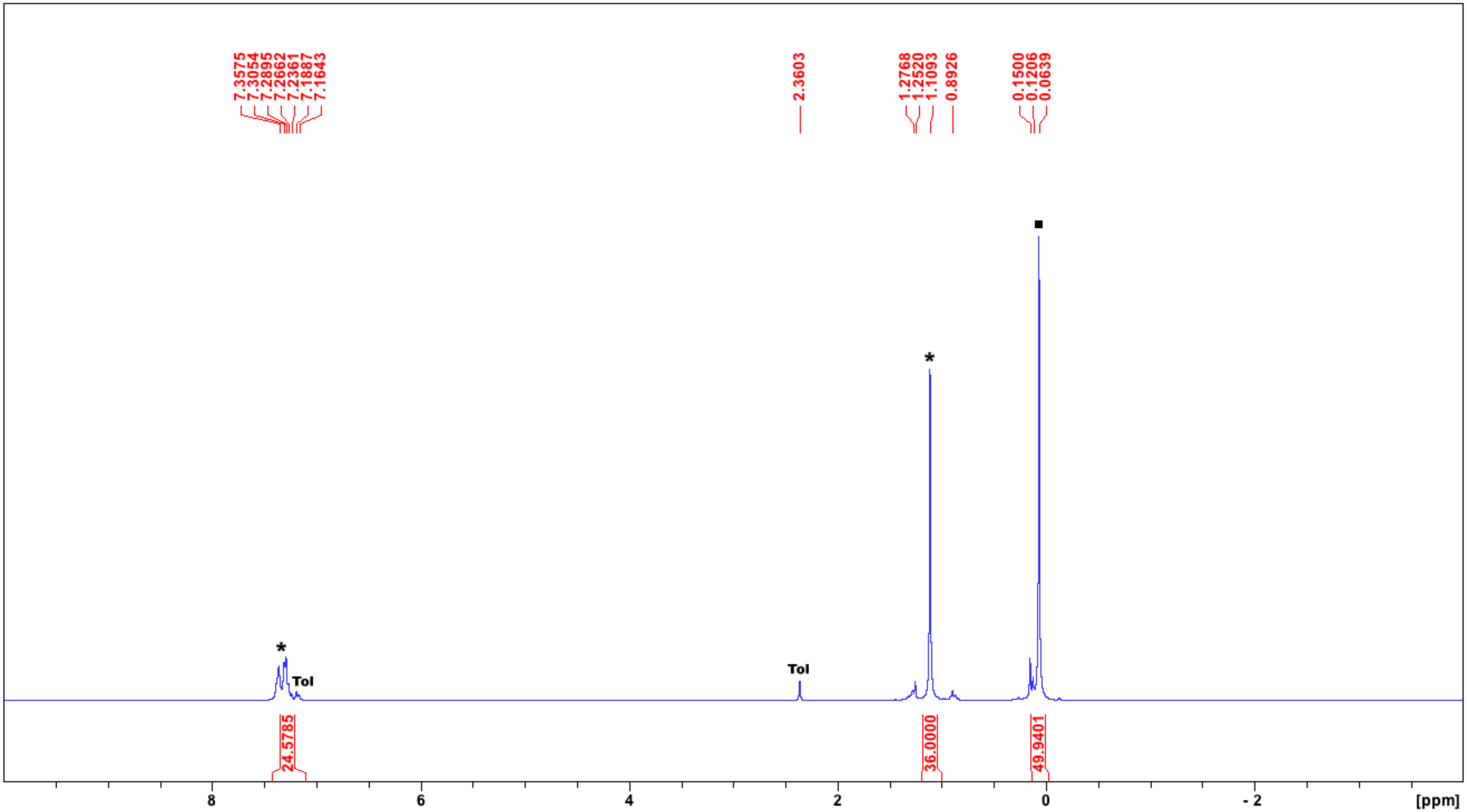


Figure S7. Formation of **1** from Ce[N(SiMe$_3$)$_2$]$_3$, **HL**, and dry O$_2$ in CDCl$_3$ (* = **1**; ■ = H[N(SiMe$_3$)$_2$]), *Method 3*, using dry O$_2$ instead of air.

Electrochemistry

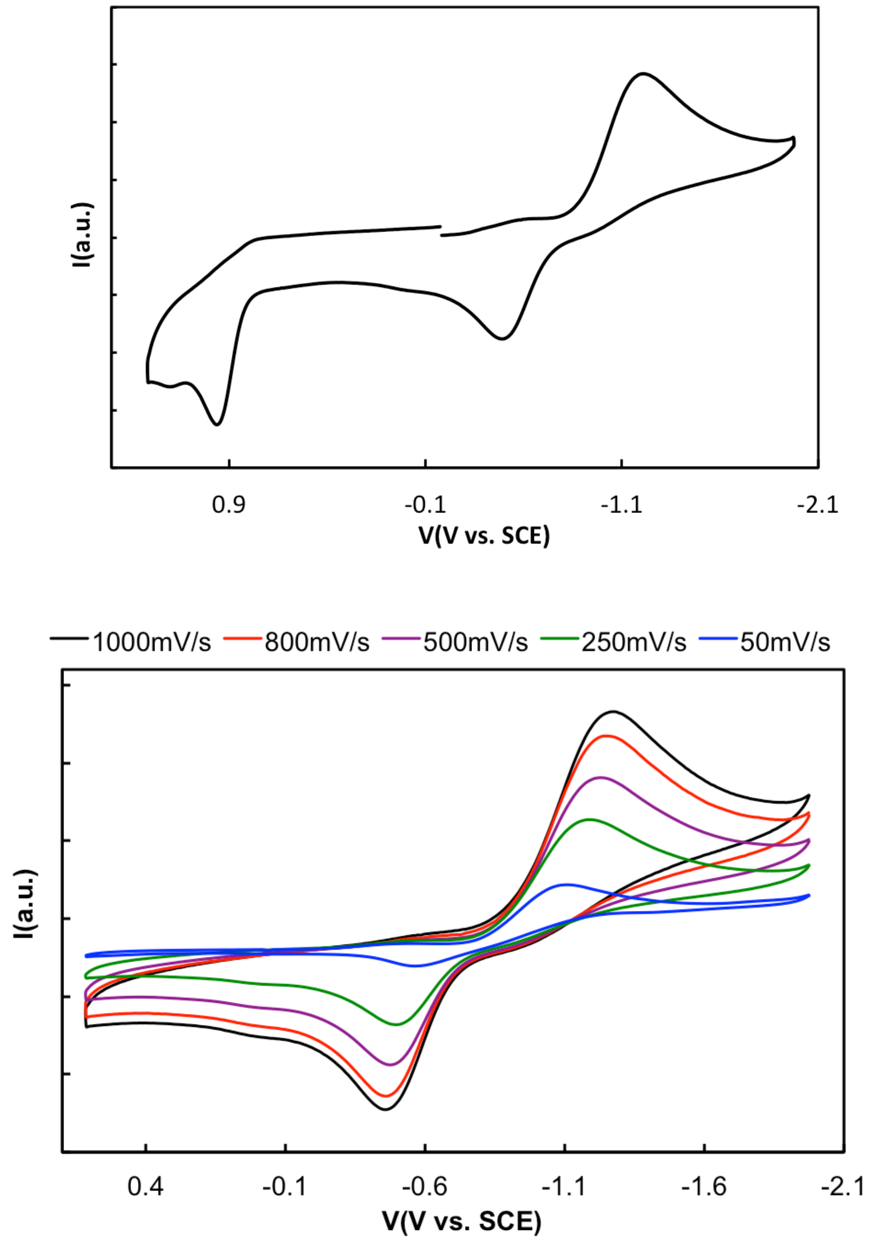


Figure S8. Cyclic voltammogram of complex **1** measured in 0.1 M [^{n}Pr$_4$N][BAr$^F_4$]/DCM versus an internal ferrocene standard (top). Scan rate dependent measurement of the isolated cerium based redox couple (bottom). The experimental rest potential was measured at –0.64 V vs. Fc/Fc$^+$. Potentials were corrected for the standard calomel electrode (SCE) by adding 0.46 V to the measured potential according to Connelly and Geiger.[5]

UV-Visible Spectroscopy

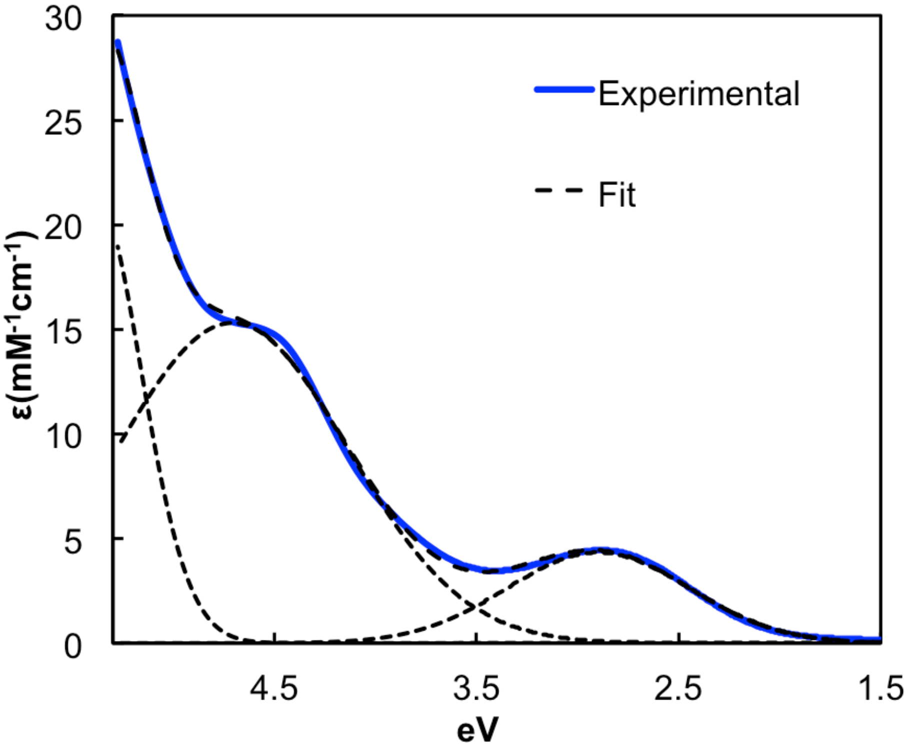


Figure S9. UV-Vis spectrum of complex **1** measured in CH_2Cl_2. The fit of the experimental data to three Gaussian curves was made with the fityk software (M. J. Wojdyr, *Appl. Cryst.,* 2010, **43,** 1126-1128.)

Table S2. Shape parameters[a] for compound **1**.

	Compound **1**	**Ideal square antiprism**[6]	**Ideal dodecahedron**[6]
ϕ	21.25, 24.50	24.50, 24.5	0, 0
δ_b	4.22, 20.02, 53.06, 54.74	0, 0, 52.4, 52.4	29.5, 29.5, 29.5, 29.5

[a] O_N atoms taken as the B vertices, and O_C atoms taken as the A vertices.[7] ϕ is the torsion angle of the BAAB trapezoid. δ_{edge} is the dihedral angle between the faces of the polyhedron containing the edge.

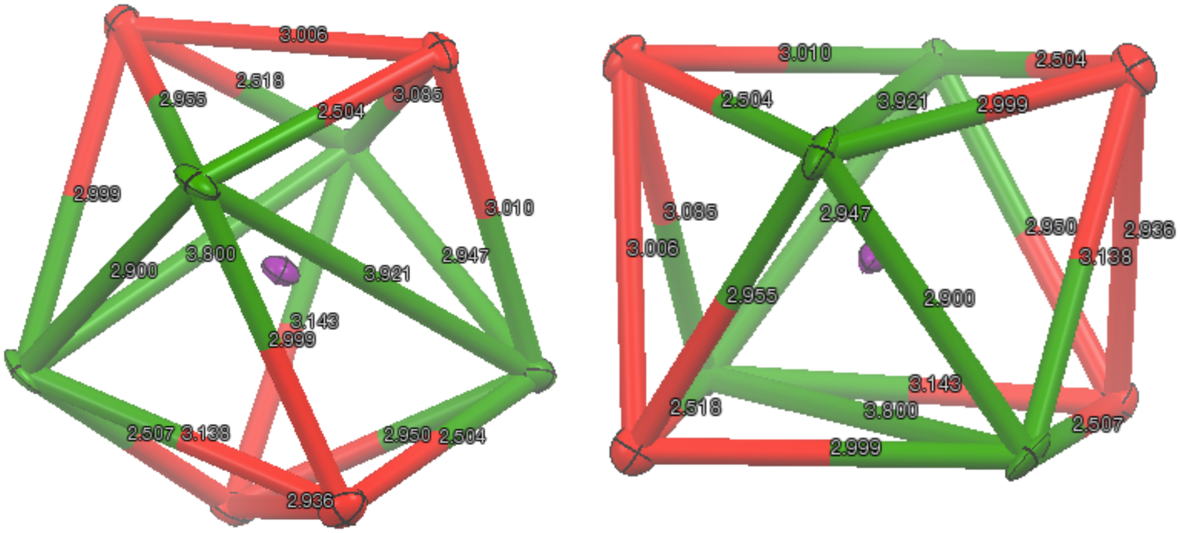
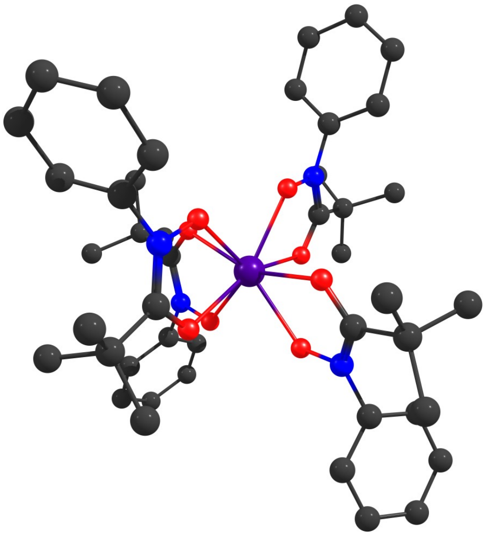


Figure S10. The coordination polyhedron of compound **1** presented in two suggestive perspectives: dodecahedron (left) and square antiprism (right). The Ce atom is presented in purple. The O_N atoms are presented in green. The O_C atoms are presented in red. The length of the edges of the polyhedron are given in Å.

Computational details

All calculations were performed with Gaussian '09,[8] using the B3LYP hybrid DFT method. Geometry optimizations were carried out using the ECP28MWB pseudopotential for the cerium cation,[9] and the CPCM SCRF method with acetonitrile as the solvent. The default UFF radii were used. All frequency calculations found no imaginary frequencies, supporting that the optimized structures are energy minima. Molecular orbital analysis was performed using Chemcraft.[10]

Table S2. Optimized coordinates of complex **1**.



Ce	-0.030565000	-0.000359000	0.001261000
O	0.859788000	-0.891962000	-1.900444000
N	1.967705000	-0.383561000	-2.536395000
C	2.375050000	-1.196267000	-3.647261000
C	3.259506000	-2.259167000	-3.438314000
H	3.685142000	-2.415904000	-2.452066000
C	3.581773000	-3.106620000	-4.500083000
H	4.275302000	-3.927213000	-4.341617000
C	3.009261000	-2.903160000	-5.758586000
H	3.261039000	-3.564408000	-6.582678000
C	2.106754000	-1.854075000	-5.955577000
H	1.653314000	-1.699327000	-6.930210000
C	1.780900000	-1.002707000	-4.898532000
H	1.073105000	-0.191108000	-5.035093000
C	2.467458000	0.752751000	-2.021620000
O	1.873835000	1.220945000	-1.007598000
C	3.696640000	1.490305000	-2.597963000
C	4.965998000	0.613786000	-2.491906000
H	4.919954000	-0.265629000	-3.137821000
H	5.129218000	0.277848000	-1.461309000
H	5.836956000	1.206489000	-2.793980000
C	3.460361000	1.914668000	-4.065693000
H	4.297769000	2.539625000	-4.396306000
H	2.541910000	2.504741000	-4.163707000
H	3.394513000	1.060458000	-4.742621000
C	3.915274000	2.764396000	-1.755161000
H	4.102627000	2.523780000	-0.704845000
H	3.047593000	3.428987000	-1.799447000
H	4.784329000	3.304008000	-2.146976000
O	-0.917337000	2.107209000	0.034565000

N	-2.005871000	2.486302000	-0.713235000
C	-2.345282000	3.866661000	-0.525119000
C	-1.895252000	4.828669000	-1.433162000
H	-1.325708000	4.522038000	-2.304722000
C	-2.180378000	6.176940000	-1.203709000
H	-1.840294000	6.926314000	-1.912414000
C	-2.890753000	6.559059000	-0.063125000
H	-3.109650000	7.608137000	0.113824000
C	-3.314342000	5.592311000	0.854912000
H	-3.861372000	5.888241000	1.745280000
C	-3.038265000	4.244123000	0.629356000
H	-3.361263000	3.481872000	1.331531000
C	-2.509043000	1.548987000	-1.531081000
O	-1.914607000	0.430749000	-1.541271000
C	-3.721334000	1.752616000	-2.464196000
C	-4.393732000	0.371698000	-2.641607000
H	-4.781497000	-0.004522000	-1.688043000
H	-3.694135000	-0.365971000	-3.039363000
H	-5.234804000	0.468996000	-3.336427000
C	-3.183573000	2.227618000	-3.836439000
H	-4.007210000	2.268428000	-4.558344000
H	-2.425714000	1.536753000	-4.221120000
H	-2.741241000	3.226895000	-3.772576000
C	-4.790117000	2.737795000	-1.947986000
H	-5.113929000	2.485405000	-0.932334000
H	-5.665847000	2.671655000	-2.603422000
H	-4.453165000	3.775458000	-1.954643000
O	-0.938666000	-2.099145000	-0.028160000
N	-2.028192000	-2.466019000	0.724365000
C	-2.390018000	-3.839793000	0.530161000
C	-3.095469000	-4.199230000	-0.622517000
H	-3.410250000	-3.427638000	-1.318201000
C	-3.394163000	-5.541471000	-0.854597000
H	-3.950860000	-5.823255000	-1.743564000
C	-2.980848000	-6.520344000	0.055220000
H	-3.217378000	-7.564730000	-0.126721000
C	-2.258180000	-6.156401000	1.194030000
H	-1.926208000	-6.915331000	1.896386000
C	-1.950360000	-4.814243000	1.429952000
H	-1.371606000	-4.522009000	2.300397000
C	-2.515048000	-1.524605000	1.547195000
O	-1.906498000	-0.413903000	1.556841000
C	-3.723049000	-1.715184000	2.488450000
C	-3.179678000	-2.194570000	3.856993000
H	-2.746032000	-3.197493000	3.790064000
H	-3.998504000	-2.228520000	4.584699000

H	-2.413333000	-1.510079000	4.236166000
C	-4.806227000	-2.689536000	1.981752000
H	-5.135220000	-2.434997000	0.968329000
H	-5.676072000	-2.612882000	2.643860000
H	-4.480713000	-3.730878000	1.987324000
C	-4.379839000	-0.327188000	2.669511000
H	-3.669168000	0.403998000	3.059465000
H	-5.215526000	-0.414587000	3.372079000
H	-4.772418000	0.051190000	1.718747000
O	0.878387000	0.881611000	1.898634000
N	1.984685000	0.362271000	2.528602000
C	2.404387000	1.169265000	3.639030000
C	1.817217000	0.976211000	4.893640000
H	1.104966000	0.168961000	5.032750000
C	2.155331000	1.822805000	5.950704000
H	1.707262000	1.668404000	6.927872000
C	3.062957000	2.866804000	5.750438000
H	3.324180000	3.524398000	6.574514000
C	3.628522000	3.069920000	4.488702000
H	4.326124000	3.886577000	4.327792000
C	3.294156000	2.227155000	3.426992000
H	3.714557000	2.383480000	2.438428000
C	2.471331000	-0.777898000	2.009912000
O	1.867998000	-1.239392000	0.998571000
C	3.696636000	-1.527522000	2.578847000
C	4.972427000	-0.660135000	2.475469000
H	5.839457000	-1.261692000	2.771277000
H	4.935018000	0.215259000	3.127348000
H	5.135755000	-0.318481000	1.446767000
C	3.459871000	-1.958642000	4.044581000
H	2.536908000	-2.541889000	4.140966000
H	3.402236000	-1.107802000	4.726522000
H	4.292877000	-2.592229000	4.369857000
C	3.904074000	-2.798246000	1.728162000
H	4.770126000	-3.346407000	2.114751000
H	4.090829000	-2.552873000	0.678810000
H	3.031744000	-3.456798000	1.770546000

References

1. D. A. Evans, H.-J. Song, and K. R. Fandrick, *Org. Lett.*, 2006, **8**, 3351–3354.
2. D. C. Bradley, J. S. Ghotra, and F. A. Hart, *J. Chem. Soc. Dalton Trans.*, 1973, 1021–1023.
3. J. Aires-de-Sousa, S. Prabhakar, A. M. Lobo, A. M. Rosa, M. J. S. Gomes, M. C. Corvo, D. J. Williams, and A. J. P. White, *Tetrahedron Asymmetry*, 2002, **12**, 3349–3365.
4. T. Saitoh, Y. Yamazaki, T. Kamidate, H. Watanabe, and K. Haraguchi, *Anal. Sci.*, 1992, **8**, 767–771.
5. N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877–910.
6. E. L. Muetterties and L. J. Guggenberger, *J. Am. Chem. Soc.*, 1974, **96**, 1748–56.
7. J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, 1963, **2**, 235–43.
8. M. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. Hratchian, A. Izmaylov, J. Bloino, G. Zheng, J. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, J. Peralta, F. Ogliaro, M. Bearpark, J. Heyd, E. Brothers, K. Kudin, V. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. Burant, S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. Millam, M. Klene, J. Knox, J. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. Stratmann, O. Yazyev, A. Austin, R. Cammi, C. Pomelli, J. Ochterski, R. Martin, K. Morokuma, V. Zakrzewski, G. Voth, P. Salvador, J. Dannenberg, S. Dapprich, A. Daniels, Farkas, J. Foresman, J. Ortiz, J. Cioslowski, and D. Fox, *Gaussian 09 Revis. B01 Gaussian Inc Wallingford Ct*, 2009.
9. X. Cao and M. Dolg, *J. Mol. Struct. Theochem*, 2002, **581**, 139–147.
10. http://www.chemcraftprog.com.