Electronic Supplementary Material (ESI) for Dalton Transactions.

Synthesis of the first copper lanthanide BINOLate frameworks from a hydrogen bonding DBU-H^+ lanthanide BINOLate complex

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Supporting Information

Experimental Procedures

General Methods. For all reactions and manipulations performed under an inert atmosphere (N_2), standard Schlenk techniques or a Vacuum Atmospheres, Inc. Nexus II drybox equipped with a molecular sieves 13X / Q5 Cu–0226S catalyst purifier system were used. Glassware was oven-dried overnight at 150 °C prior to use. ^{1}H NMR spectra were obtained on a Brüker AM-500 or a Brüker UNI-400 Fourier transform NMR spectrometer at 500 or 400 MHz, respectively. ^{13}C{^{1}H} NMR spectra were recorded on a Brüker AM-500 Fourier transform NMR spectrometer at 126 MHz. All spectra were measured at 300 K unless otherwise specified. Chemical shifts were recorded in units of parts per million (ppm) downfield from residual proteo solvent peaks (^{1}H) or characteristic solvent peaks (^{13}C{^{1}H}). All coupling constants are reported in hertz. Elemental analyses were obtained on a Costech ECS 4010 instrument at the Earth and Environmental Science department of the University of Pennsylvania.

Materials.

Tetrahydrofuran, dichloromethane, toluene, and pentane were purchased from Fisher Scientific. The 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 and pentane), or two columns of neutral alumina (for THF). Deuterated tetrahydrofuran, chloroform and dichloromethane were purchased from Cambridge Isotope Laboratories, Inc. Deuterated tetrahydrofuran was stored for at least 12 h over potassium mirror prior to use. (*S*)-BINOL was purchased from AKScientific and dried at 25°C and 50 mtorr overnight. $LaCl_3$, $PrCl_3$, $EuCl_3$ (>99.9% purity) were purchased from Strem and used after drying at 140°C at 50

mtorr overnight. $La[N(SiMe_3)_2]_3$, $Pr[N(SiMe_3)_2]_3$, $Eu[N(SiMe_3)_2]_3$,[1] and copper mesitylene[2] were prepared according to literature procedures.

2D Exchange Spectroscopy (EXSY) NMR Experiments

All 2D ^1H experiments were performed on a Brüker UNI-400 Fourier transform NMR spectrometer at 400 and 155 MHz respectively using THF–d_8 as a solvent (sample concentrations listed below) and a conventional NOESY sequence. 2048 and 512 data points were used in the t_2 and t_1 domain respectively, where 8 scans were collected for each slice. Several t_{mix} were used for EXSY experiments performed at 300 K to determine the optimal value for each relevant exchange pathway. In addition to the values of t_{mix} listed, a reference was recorded at t_{mix} = 0 ms. Pseudo-first order rate constants (k, s^{-1}) were calculated using EXSYCalc 1.0 (Mestrelab Research)[3] from volume intensities obtained from the 2D spectra. Activation parameters were determined using Eyring plots generated from rate data obtained at several temperatures.

X-ray Crystallography

X-ray intensity data were collected on a Brüker APEXII CCD area detector or a Brüker APEXIII D8QUEST CMOS area detector, both employing graphite-monochromated Mo-K α radiation (λ= 0.71073 Å) at 100(1) K. Rotation frames were integrated using SAINT,[4] producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the SHELXT[4] program package for further processing and structure solution. The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS[5] or TWINABS.[6] Refinement was performed by full-matrix least squares based on F^2 using SHELXL.[7] All of the reflections were used during refinement. Non-

hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model.

Synthetic Details and Characterization

Synthesis of $[DBU\text{-}H^+]_3[(BINOLate)_3La]$ (1-La)

In an inert atmosphere glovebox, a 20 mL glass scintillation vial was charged with (*S*)-BINOL (258 mg, 0.90 mmol, 3 equiv; FW: 286.32 g · mol^{-1}), THF (6 mL), and a Teflon-coated stir bar. 1,8-Diazabicyclo(5.4.0)undec-7-ene (DBU, 137 mg, 0.90 mmol, 3 equiv; FW: 152.24 g · mol^{-1}) was added dropwise as a solution in THF (1 mL) to the stirring, colorless, BINOL solution. Upon complete addition, the solution became light yellow. $La[N(SiMe_3)_2]_3$ (200 mg, 0.300 mmol, 1 equiv; FW: 665.12 g · mol^{-1}) was added dropwise as a solution in THF (1 mL). After stirring for 1 h, the combined solution was filtered through a Celite packed, coarse porosity fritted filter. The resulting mixture was layered with pentane (12 mL) and allowed to crystallize for 16 h. The mother liquor was decanted and the solids washed with pentane (2 × 3 mL) over a medium porosity fritted glass filter. The remaining solid product was dried under vacuum for 3 h. Yield: 335 mg (0.230 mmol, 77%; 1451.59 g · mol^{-1}). ^1H NMR (500 MHz, CD_2Cl_2) δ: 11.18 (s, N*H*, 3H), 7.53 (d, *J* = 8.7 Hz, 6H), 7.50 (d, *J* = 7.9 Hz, 6H), 7.42 (d, *J* = 8.7 Hz, 6H), 6.79 (m, 12H), 6.74 (d, *J* = 8.4 Hz, 6H), 3.04 (t, *J* = 12.5 Hz, 3H), 2.69 (dd, *J* = 15.2 Hz, *J* = 6.8 Hz, 3H), 2.18 (bs, 6H), 2.00 (bs, 6H), 1.70 (bs, 3H), 1.37 (bs, 9H), 1.26 (bs, 3H) 1.06 (bs, 6H), 0.87 (bs, 3H), 0.36 (bs, 3H), 0.00 (bs, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2) δ: 163.12, 162.43, 135.70, 127.11, 126.73, 126.64, 126.48, 125.09, 123.44, 118.74, 118.48, 47.57, 37.13, 32.02, 28.99, 26.85, 23.74, 17.99. Anal. Calcd. for $C_{87}H_{87}LaN_6O_6 \bullet (C_5H_{12})$ C, 72.52; H, 6.55; N, 5.52. Found: C, 72.61; H, 6.44; N, 5.38. X-

ray quality crystals were obtained from layering concentrated solutions of **1-La** in THF with pentane (1:2 v/v).

1-Pr: The compound was prepared using an identical procedure as **1-La** using $Pr[N(SiMe_3)_2]_3 \cdot (Toluene)_{0.5}$ (200 mg, 0.300 mmol; FW: 667.12 g · mol^{-1}). Yield: 335 mg (0.268 mmol, 89%; 1452.58 g · mol^{-1}) Light yellow solid. Anal. Calcd. for $C_{87}H_{87}N_6O_6Pr$ C, 71.89; H, 6.03; N, 5.78. Found: C, 72.13; H, 5.92; N, 5.45. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.65 (bs, 6H), 7.47 (d, *J* = 7.9 Hz, 6H), 7.24 (bs, 6H), 7.09 (t, *J* = 7.5 Hz, 6H), 6.89 (t, *J* = 7.3 Hz, 6H), 5.77 (s, 6H), 5.30 (bs, 3H), 2.83 (bs, 3H), 2.40 (bs, 3H), 2.11 (bs, 6H), 1.98 (bs 3H), 1.62 (bs, 3H), 0.67 (bs, 3H), 0.37 (bs, 3H), 0.21 (bs, 9H), -1.22 (bs, 3H), -1.51 (bs, 6H), -3.90 (bs, 6H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 155.25, 134.45, 132.76, 128.37, 127.32, 126.51, 126.15, 125.34, 123.25, 119.82, 52.31, 47.74, 38.02, 28.01. Note: ^{13}C resonances were missing from the NMR due to broadening of the peaks. We postulate that the issue is short relaxation times. X-ray quality crystals were obtained from layering concentrated solutions of **2-Pr** in toluene with 3 equiv. of phenyl acetylene in toluene (1:1 v/v).

1-Eu: The compound was prepared using an identical procedure as **1-La** using $Eu[N(SiMe_3)_2)_3 \cdot (Toluene)_{0.5}$ (200 mg, 0.300 mmol; FW: 678.13 g · mol^{-1}). Yield: 335 mg (0.230 mmol, 77%; 1464.59 g · mol^{-1}) Yellow solid. Anal. Calcd. for $C_{87}H_{87}EuN_6O_6 \bullet (C_4H_8O)$ C, 71.12; H, 6.23; N, 5.47. Found: C, 71.47; H, 6.34; N, 5.70. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 23.94 (bs, 3H), 7.44 (s, 6H), 7.06 (s, 6H), 6.92 (s, 6H), 6.85 (s, 6H), 6.64 (s, 6H), 6.56 (s, 6H), 4.00 (s, 3H), 3.54 (s, 3H), 2.97 (s, 3H), 2.90, (s, 3H), 2.59 (s, 3H), 2.45 (s, 3H), 2.19 (s, 3H), 2.01 (s, 3H), 1.84 (s, 6H), 1.60 (s, 3H), 1.14 (s, 3H), 0.49 (s, 3H), 0.11 (s, 3H), -0.17 (s, 3H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ: 197.90,

165.63, 141.20, 127.68, 125.98, 124.31, 123.60, 117.68, 116.44, 114.24, 76.92, 53.66, 47.70, 37.18, 34.60, 29.83, 27.54, 25.52, 18.22. X-ray quality crystals were obtained from layering concentrated solutions of **1-Eu** in THF and with pentane (1:2 v/v).

Synthesis of [DBU-Cu^{+}]$_3$[(BINOLate)$_3$La] (2-La)

In an inert atmosphere glovebox, **1-La** (200 mg, 0.14 mmol, 1 equiv) and copper mesitylene ($(CuMes)_n \cdot (Toluene)_{0.2}$, 102 mg, 0.51 mmol, 3 equiv; FW 201.09 g · mol^{-1}) and a Teflon coated stirbar were added to a 20 mL glass scintillation vial. Toluene (8 mL) was added and the suspension was stirred for 3 h; the scintillation vial was covered with aluminum foil during this period. More toluene (2 mL) was added and the suspension was heated to boiling to induce dissolution. The solution was moved to a –30°C freezer to cool for 1 h then the solution was layered with pentane (10 mL) and set at room temperature overnight to crystallize. The crystalline powder was collected by filtration over a medium porosity fritted glass filter and washed with pentane (2 × 3 mL), then dried for 3 h to yield the title compound as a crystalline powder. Yield: 212 mg (0.130 mmol, 94%; 1639.21 g · mol^{-1}) Off-white solid. Anal. Calcd. for $C_{87}H_{84}Cu_3LaN_6O_6$•2(C_7H_8) C, 66.53; H, 5.53; N, 4.61. Found: C, 66.84; H, 5.74; N, 4.72. ^{1}H-NMR (500 MHz, THF-d_8) δ: 7.57 (s, 12 H), 7.19 (s, 6 H), 6.87 (s, 6H), 6.80 (s, 6H), 6.77 (s, 6H), 2.91 (s, 3H), 2.84 (s, 3H), 2.74 (s, 6H), 2.27 (s, 6H), 1.89 (s, 3H), 1.73 (s, 3H), 1.30 (s, 9H), 1.23 (s, 9H), 0.90 (s, 6H). ^{13}C-NMR (126 MHz, THF-d_8) δ: 165.13, 163.28, 136.48, 128.46, 128.19, 127.65, 127.10, 126.91, 124.26, 119.90, 119.35, 53.90, 48.33, 47.08, 39.87, 29.91, 28.52, 22.14, 21.55. X-ray quality crystals were obtained from layering concentrated solutions of **2-La** in toluene and with pentane (1:1 v/v).

2-Pr: The compound was prepared using an identical procedure as **2-La** using **1-Pr** (200 mg, 0.14 mmol, 1 equiv). Yield: 167 mg (0.102 mmol, 74%; 1641.21 g · mol^{-1}) Light yellow solid. Anal. Calcd. for $C_{87}H_{84}Cu_3N_6O_6Pr$•2(C_7H_8) C, 66.45; H, 5.52; N, 4.60 Found: C, 66.13; H, 5.15; N, 4.14. ^{1}H-NMR (500 MHz, THF-d_8) δ: 12.94 (s, 6 H), 10.10 (s, 3H), 9.33 (s, 6H), 9.01 (s, 3H), 8.10 (s, 6H), 8.01 (s, 3H), 7.92 (s, 6H), 6.89 (s, 3H), 5.49 (s, 3H), 5.06 (s, 6H), 4.94 (s, 6H), 4.84 (s, 3H), 4.67 (s, 3H), 4.21 (s, 3H), 2.79 (s, 6H), 2.66 (s, 6H), 2.40 (s, 6H), -7.33 (s, 6H). ^{13}C-NMR (126 MHz, THF-d_8) δ: 174.05, 170.73, 143.16, 142.22, 134.07, 132.91, 128.78, 128.23, 126.78, 125.09, 123.07, 56.22, 51.50, 44.72, 31.50, 30.30, 27.77. . Note: ^{13}C resonances were missing from the NMR due to broadening of the peaks. We postulate that the issue is short relaxation times. X-ray quality crystals were obtained from layering concentrated solutions of **2-Pr** in toluene and layering with pentane (1:1 v/v).

2-Eu: The compound was prepared using an identical procedure as **2-La** using **1-Eu** (200 mg, 0.14 mmol, 1 equiv). Yield: 176 mg (0.107 mmol, 78%; 1652.27 g · mol^{-1}) Yellow solid. Anal. Calcd. for $C_{87}H_{84}Cu_3EuN_6O_6$•(C_7H_8) C, 64.72; H, 5.32; N, 4.82. Found: C, 64.87; H, 5.33; N, 4.82. ^{1}H-NMR (500 MHz, THF-d_8) δ: 18.38 (s, 6H), 9.02, (s, 6H), 7.31 (d, J = 7.7 Hz, 6H), 6.47 (t, J = 6.5 Hz, 6H), 4.99 (t, J = 7.0 Hz, 6H), 3.09 (d, J = 8.7 Hz, 6H), 1.52 (s, 6H), 1.17 (s, 3H), 1.01 (s, 3H), 0.57 (s, 3H), 0.51 (s, 3H), 0.35 (s, 3H), 0.20 (s, 3H), -0.33 (s, 3H), -0.51 (s, 3H), -1.05 (s, 3H), -1.45 (s, 6H), -2.00 (s, 3H), -2.47 (s, 3H), -2.58 (s, 3H). ^{13}C-NMR (126 MHz, THF-d_8) δ: 178.13, 161.19, 136.56, 129.37, 129.07, 124.08, 123.63, 121.73, 117.30, 104.70, 52.42, 46.31, 42.12, 36.64, 28.90, 27.43, 23.86, 19.40. Note: ^{13}C resonance signals were very weak. We postulate that the issue is short relaxation times. Solution NMR represents a 22.5 mM

sample. X-ray quality crystals were obtained from layering concentrated solutions of **2-Eu** in toluene and layering with pentane (1:1 v/v).

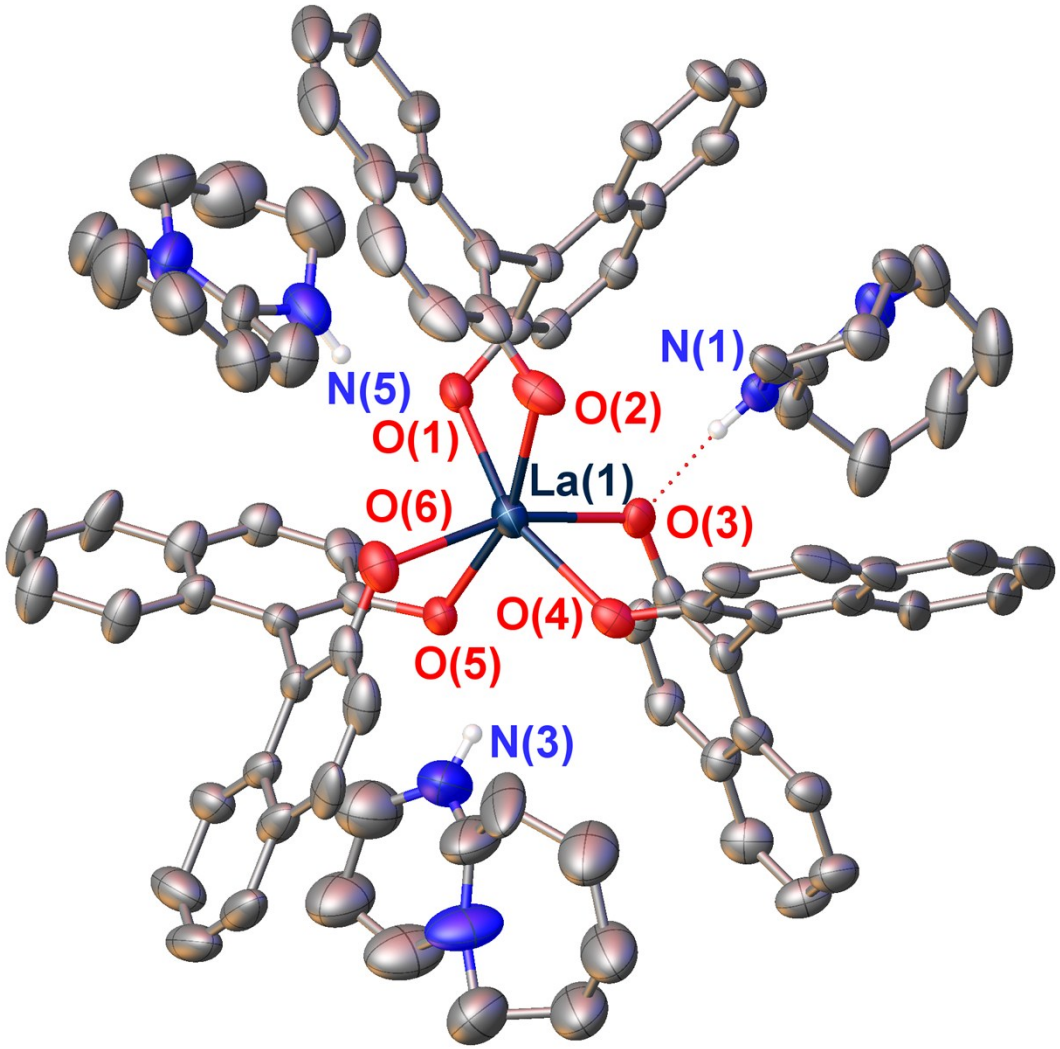

Figure S1. Thermal ellipsoid plot of **[DBU-H$^+$]$_3$[(BINOLate)$_3$La] (1-La)** at the 30% probability level. Selected bond length (Å): La(1)–O(1) 2.424(5), La(1)–O(2) 2.353(5), La(1)–O(3) 2.408(4), La(1)–O(4) 2.395(5), La(1)–O(5) 2.404(5), La(1)–O(6) 2.394(5), O(1)–N(5) 2.882(12), O(3)–N(1) 2.656(7), O(5)–N(3) 2.972(14). Selected angle (°) N(5)–H(5a)–O(1) 120.16, N(1)–H(1)–O(3) 172.74, N(3)–H(3a)–O(5) 113.61.

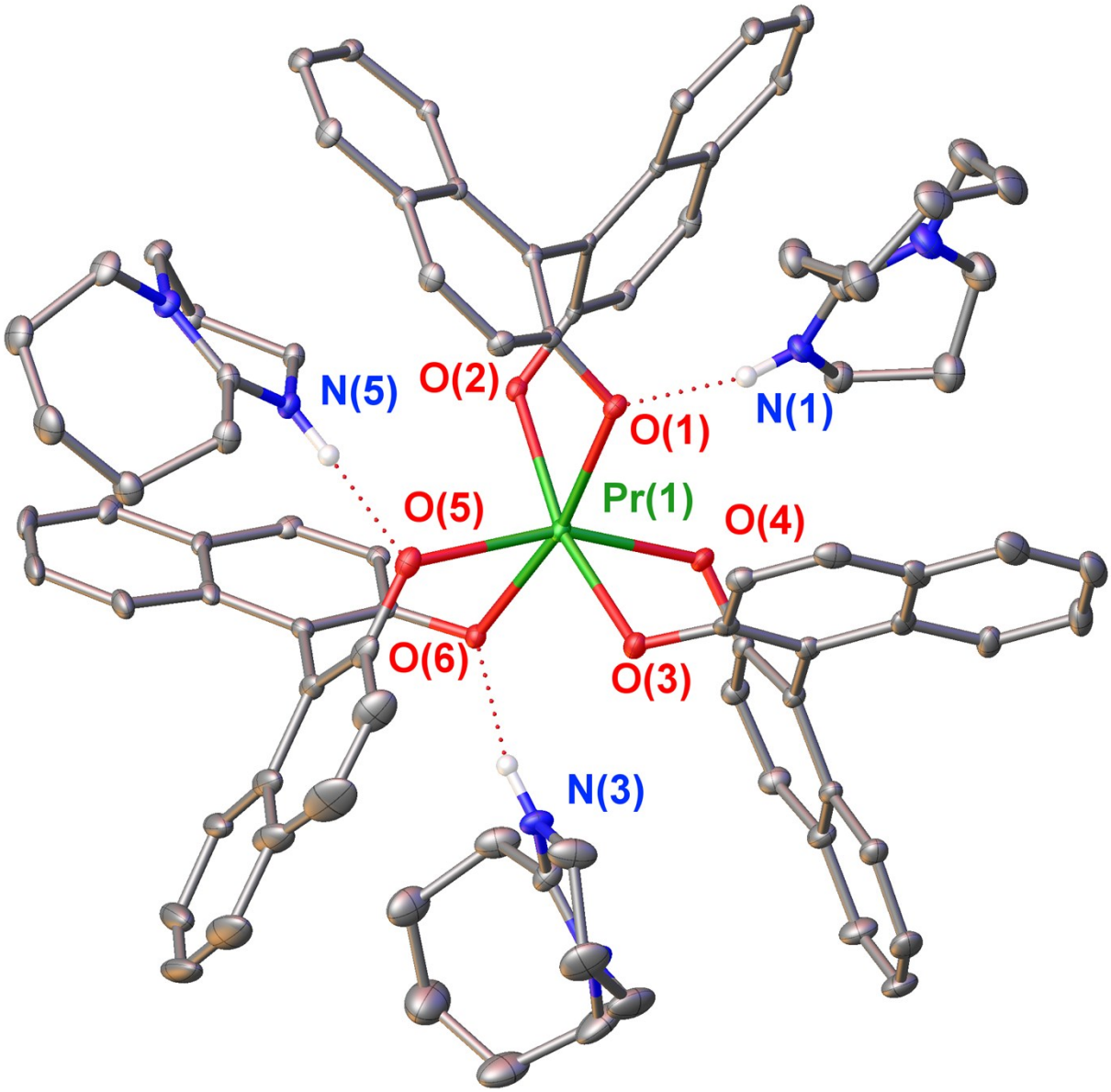

Figure S2. Thermal ellipsoid plot of **[DBU-H$^+$]$_3$[(BINOLate)$_3$Pr] (1-Pr)** at the 30% probability level, toluene and non-hydrogen bonding hydrogen atoms removed for clarity. Selected bond length (Å): Pr(1)–O(1) 2.400(3), Pr(1)–O(2) 2.325(2), Pr(1)–O(3) 2.333(3), Pr(1)–O(4) 2.308(3), Pr(1)–O(5) 2.406(3), Pr(1)–O(6) 2.393(3), O(1)–N(1) 2.700, O(5)–N(5) 2.724, O(6)–N(3) 2.757. Selected angle (°) N(1)–H(1)–O(1) 161.45, N(5)–H(5a)–O(5) 177.17, N(3)–H(3a)–O(6) 160.87.

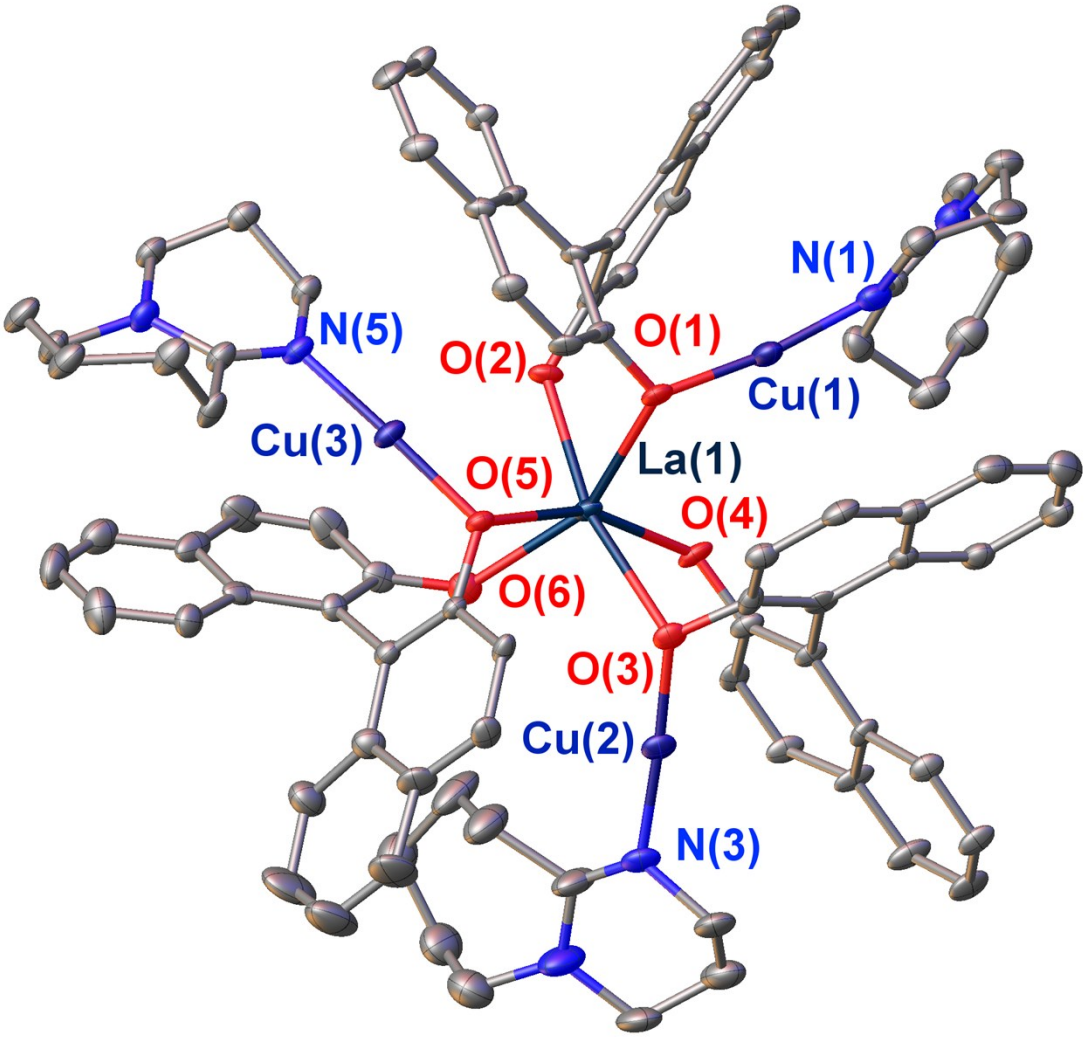

Figure S3. Thermal ellipsoid plot of **[Cu(DBU)]$_3$[(BINOLate)$_3$La] (2-La)** at the 30% probability level. Disorder, hydrogen atoms, and interstitial solvent removed for clarity. Selected bond length (Å): La(1)–O(1) 2.464(8), La(1)–O(2) 2.367(6), La(1)–O(3) 2.542(7), La(1)–O(4) 2.309(8), La(1)–O(5) 2.528(8), La(1)–O(6) 2.319(8), Cu(1)–O(1) 1.850(8), Cu(1)–N(1) 1.879(11), Cu(2)–O(3) 1.868(8), Cu(2)–N(3) 1.899(11), Cu(3)–O(5) 1.828(11), Cu(3)–N(5) 1.88(2). Selected angle (°) N(1)–Cu(1)–O(1) 172.2(4), N(3)–Cu(2)–O(3) 176.6(5), N(5)–Cu(3)–O(5) 175.9(9).

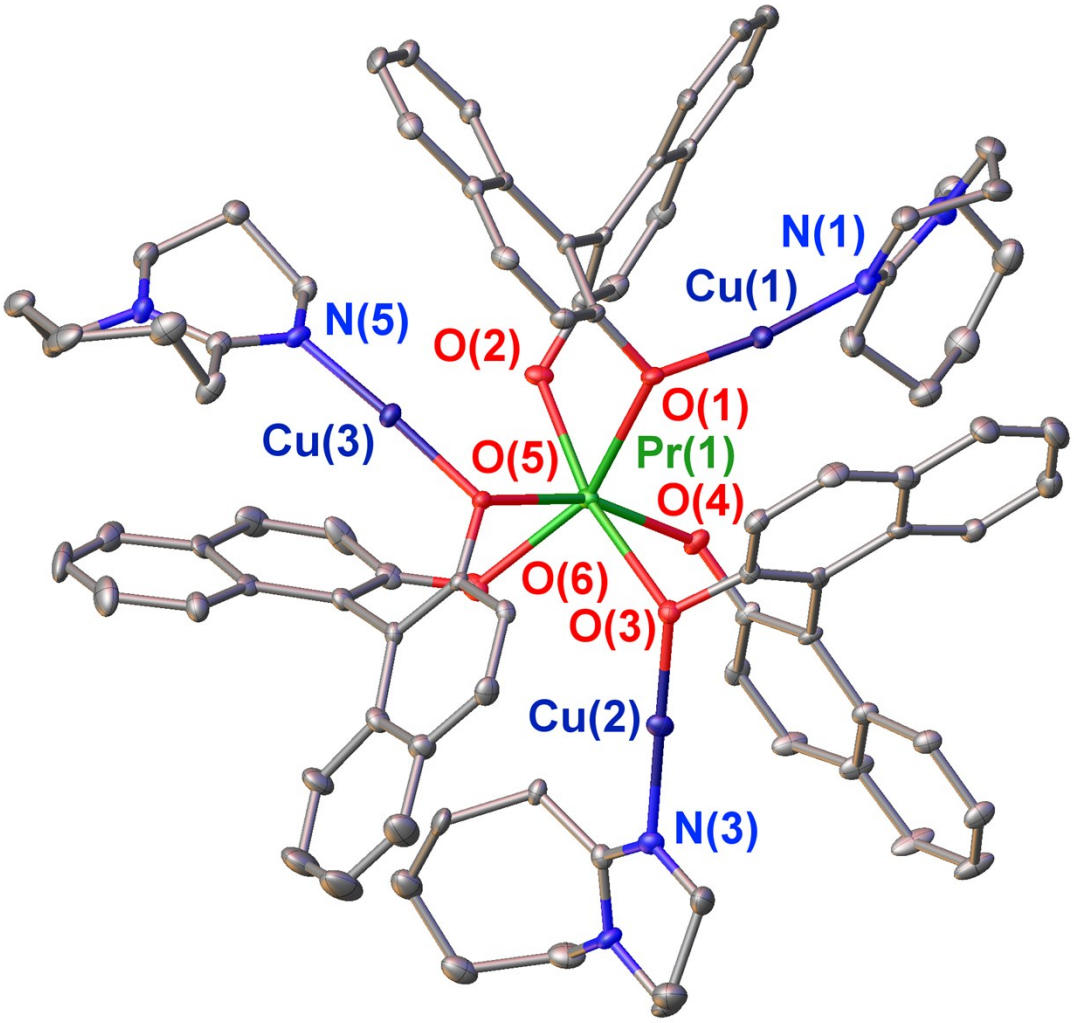

Figure S4. Thermal ellipsoid plot of **[Cu(DBU)]$_3$[(BINOLate)$_3$Pr] (2-Pr)** at the 30% probability level. Disorder, hydrogen atoms, and interstitial solvent removed for clarity. Selected bond length (Å): Pr(1)–O(1) 2.423(3), Pr(1)–O(2) 2.331(3), Pr(1)–O(3) 2.493(3), Pr(1)–O(4) 2.271(3), Pr(1)–O(5) 2.470(3), Pr(1)–O(6) 2.272(3), Cu(1)–O(1) 1.856(3), Cu(1)–N(1) 1.870(4), Cu(2)–O(3) 1.860(3), Cu(2)–N(3) 1.86(5), Cu(3)–O(5) 1.842(4), Cu(3)–N(5) 1.863(9). Selected angle (°) N(1)–Cu(1)–O(1) 171.76(16), N(3)–Cu(2)–O(3) 175.9(11), N(5)–Cu(3)–O(5) 177.1(4).

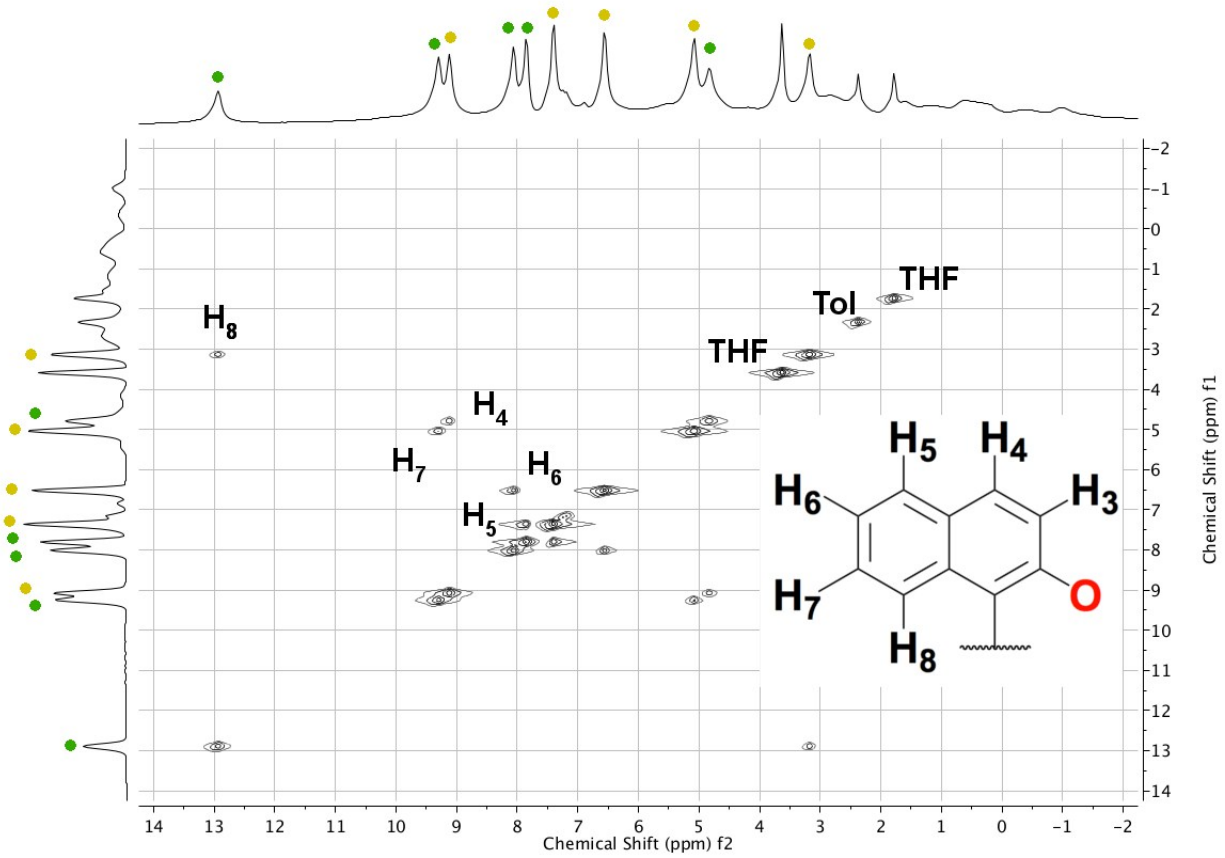

Figure S5. Representative 2D ^{1}H-NMR EXSY experiment of **2-Pr** and **2-Eu** (15.0 mM / 14.6 mM; tmix = 170 ms; 300 K) in THF-d_8. • = **2-Pr** (green) •□= **2-Eu** (yellow). H_3 relaxation time was too short and the cross peak was not obvious in the experiment.

Table S6. Pseudo-first order rate constants obtained for BINOLate exchange between **2-Pr** and **2-Eu** from 2D ^{1}H-NMR EXSY experiments collected at t_{mix} = 170 ms at various temperatures.

Temperature (K)	k´($H_{(7)}$) (s^{-1})	
	2-Pr ⇝ 2-Eu	**2-Eu ⇝ 2-Pr**
300	2.63 ± 0.10	2. 63 ± 1.02
307	4.02 ± 0.95	4.35 ± 1.87
315	7.20 ± 2.51	7.21 ± 3.15
330	16.02 ± 6.28	11.27 ± 2.82

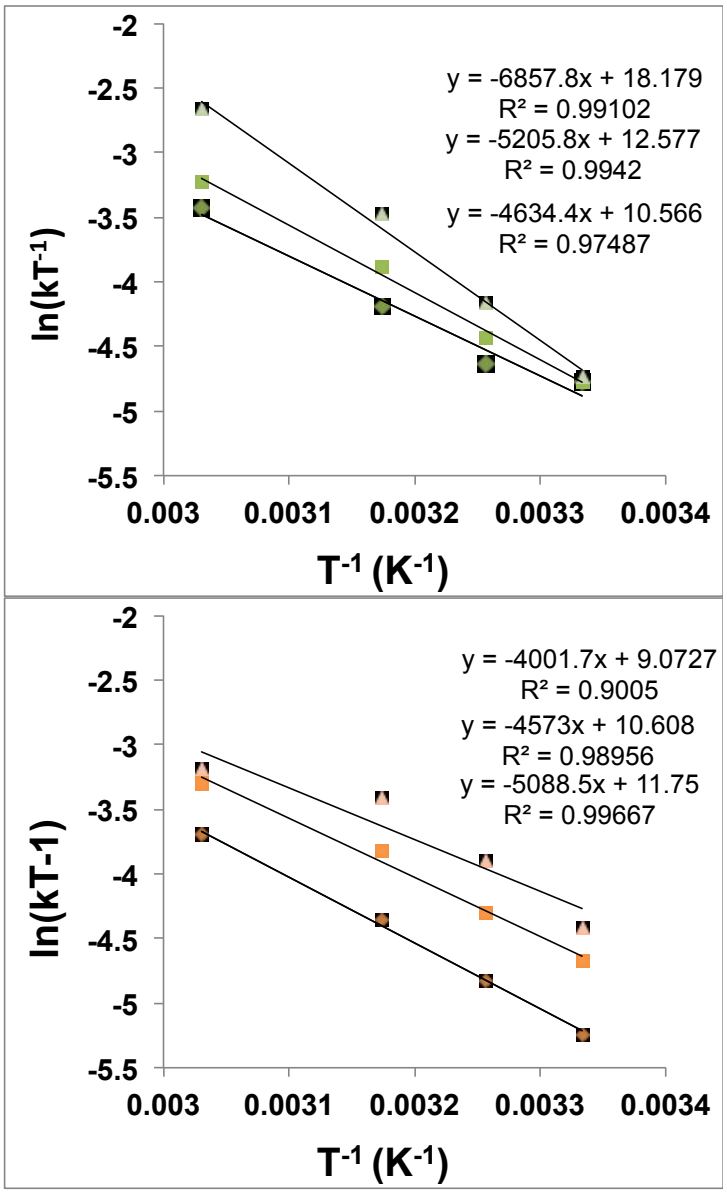

Figure S6. Eyring plots (*top* = **2-Pr** ⇝ **2-Eu**, *bottom* **2-Eu** ⇝ **2-Pr**) obtained for 2D ^{1}H-NMR EXSY experiments observing BINOLate exchange of **2-Pr**/**2-Eu** (15.0 mM / 14.6 mM) taken at 300, 307, 315, and 330 K ($H_{(7)}$; t_{mix}= 170 ms). Data for all three runs represented as 3 separate trendlines.

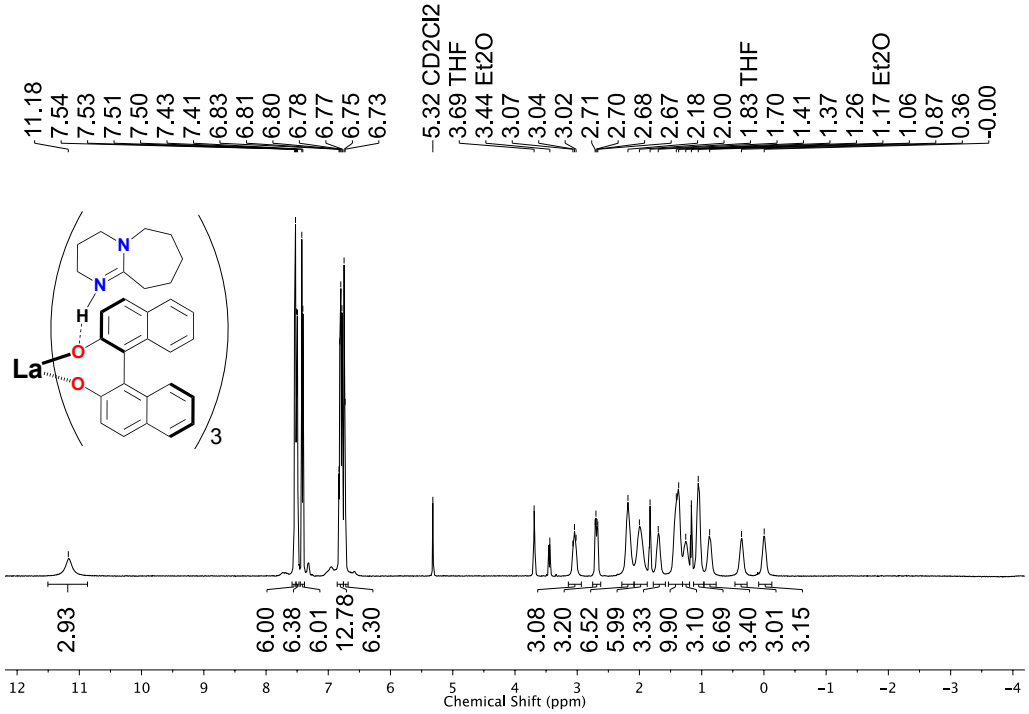

Figure S7a. ^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of **1-La.**

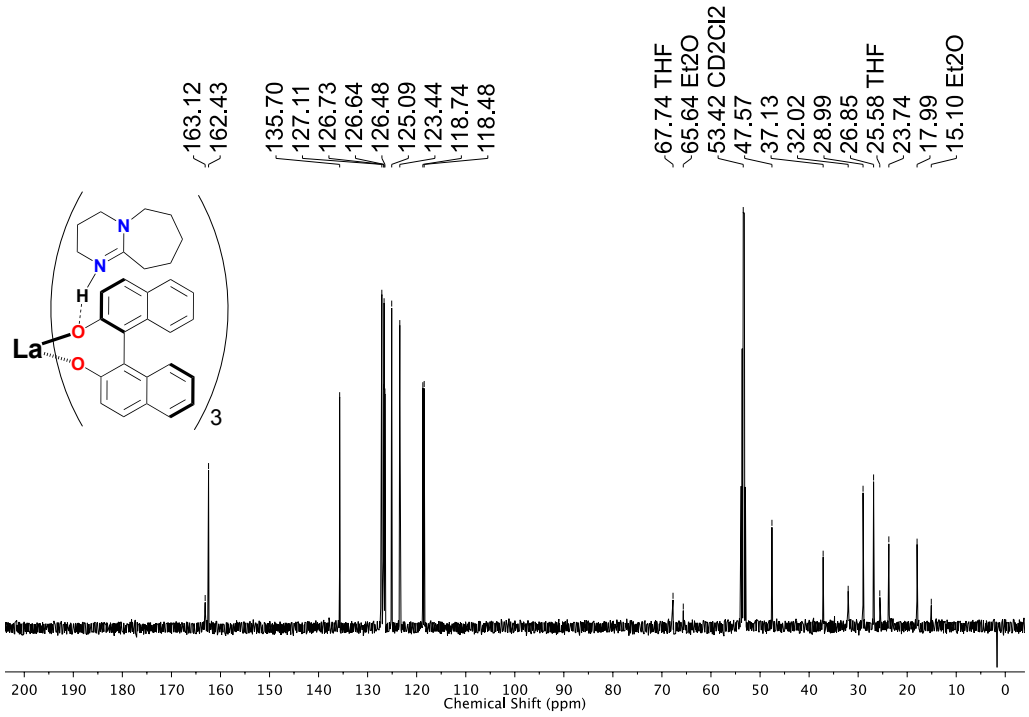

Figure S7b. $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2) spectrum of **1-La**.

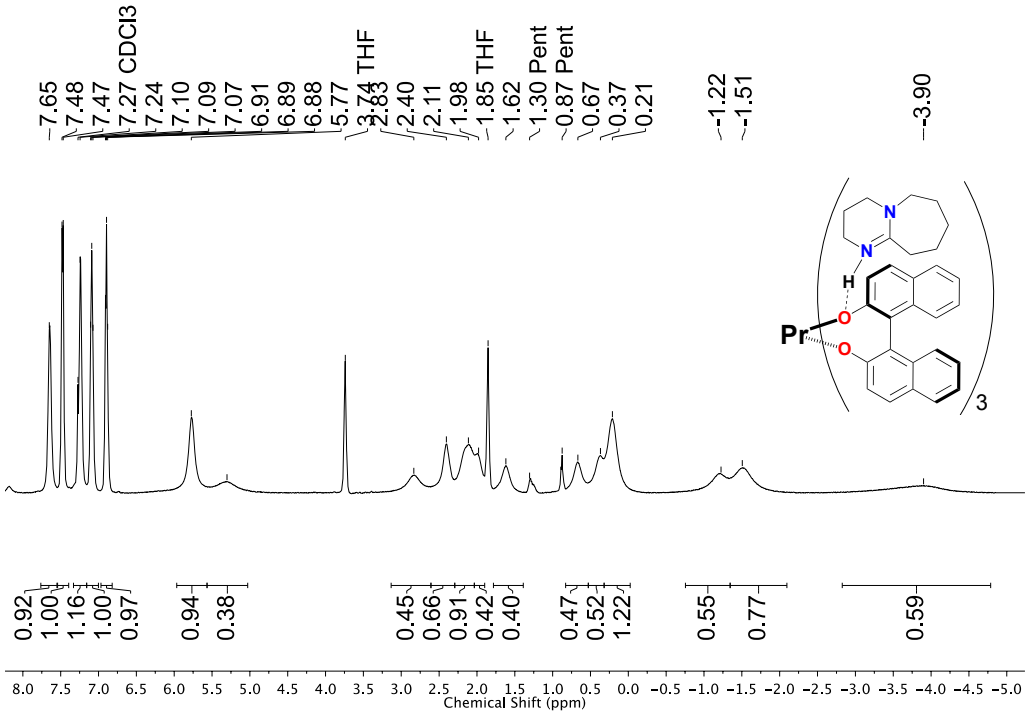

Figure S8a. ^{1}H NMR(500 MHz, $CDCl_3$) spectrum of **1-Pr.**

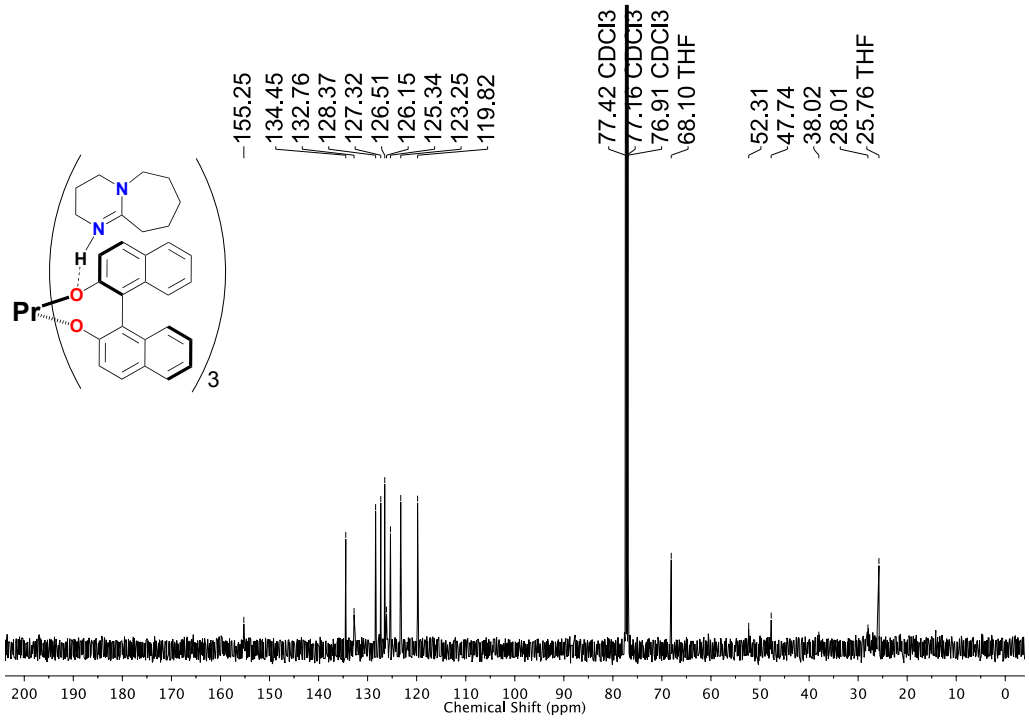

Figure S8b. $^{13}C\{^{1}H\}$ NMR(126 MHz, $CDCl_3$) spectrum of **1-Pr.**

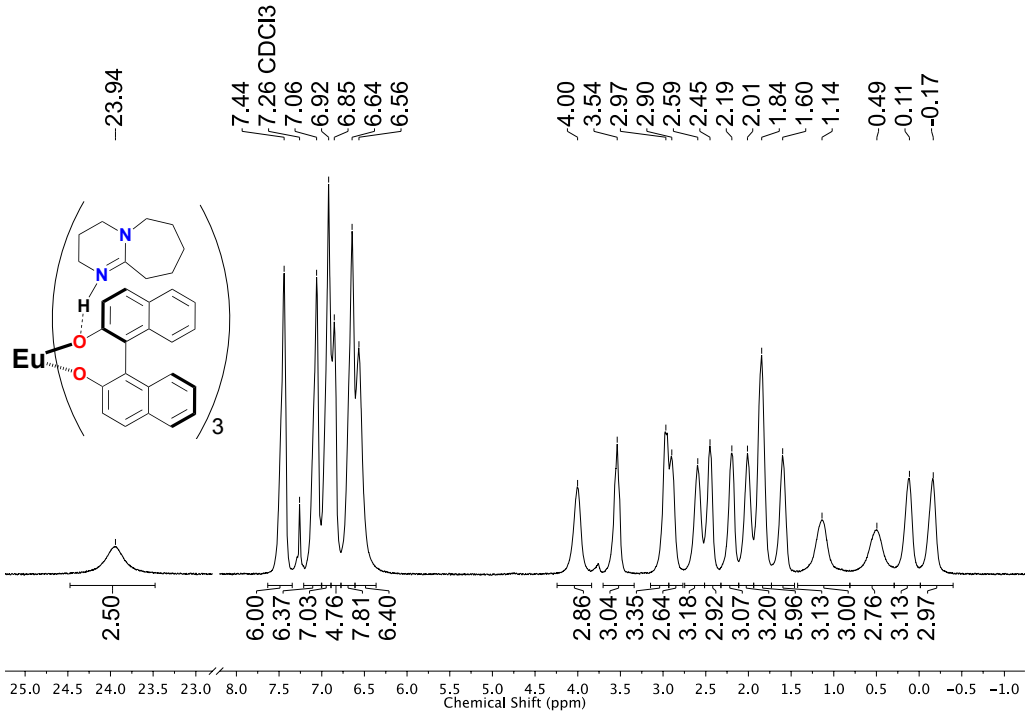

Figure S9a. ^{1}H NMR(500 MHz, $CDCl_3$) spectrum of **1-Eu.**

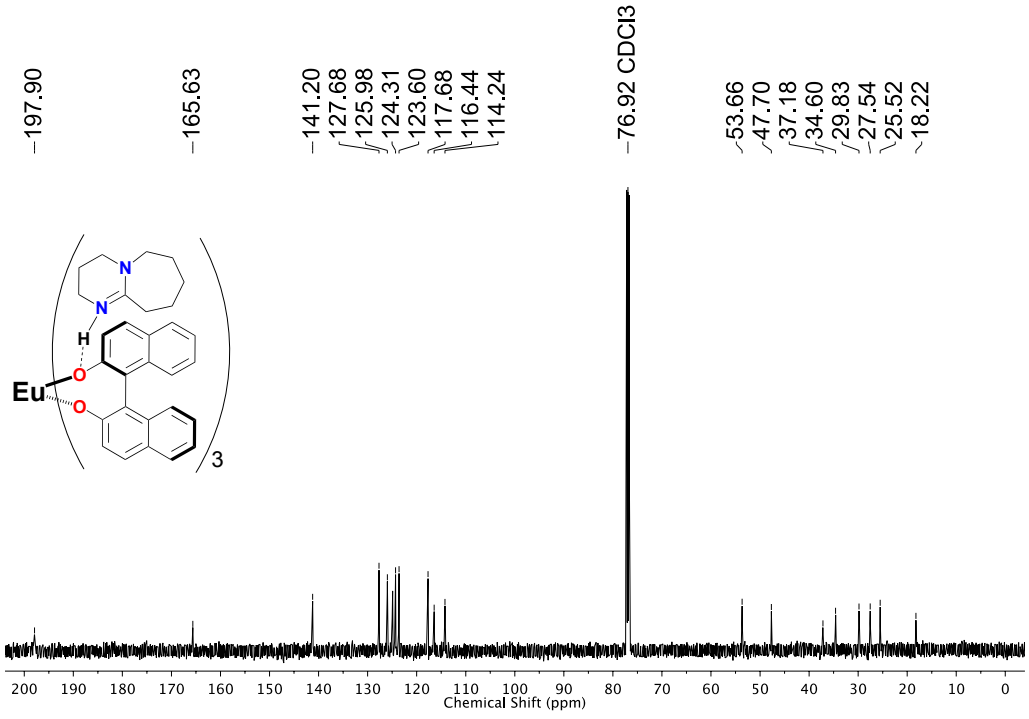

Figure S9b. $^{13}C\{^{1}H\}$ NMR(126 MHz, $CDCl_3$) spectrum of **1-Eu**.

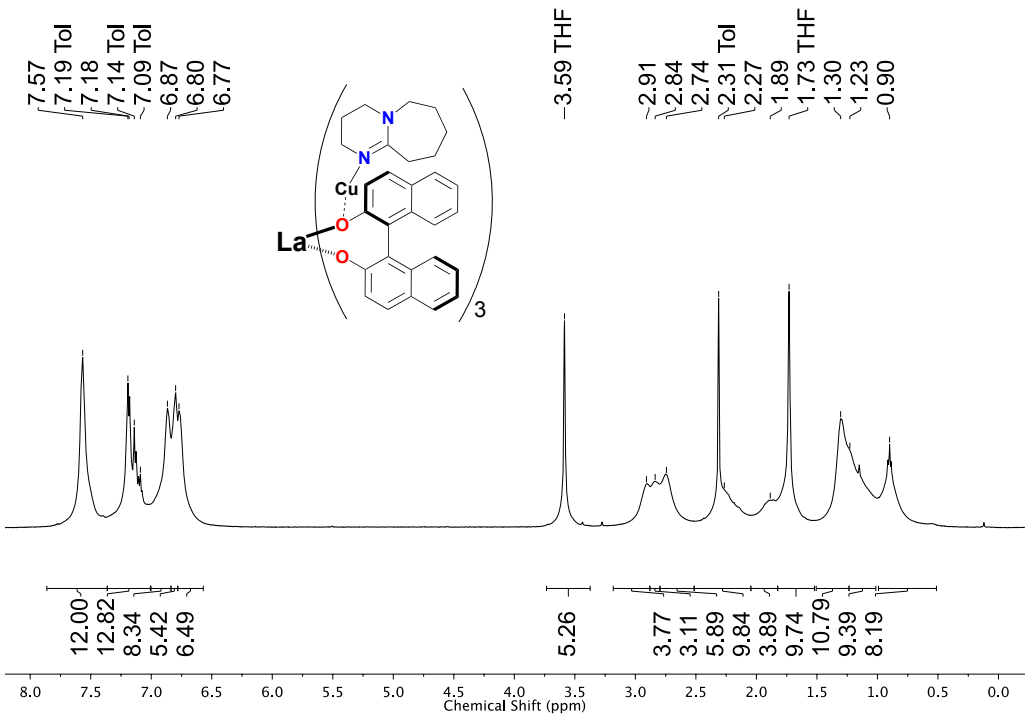

Figure S10a. ^{1}H NMR(500 MHz, THF-d_8) spectrum of **2-La.**

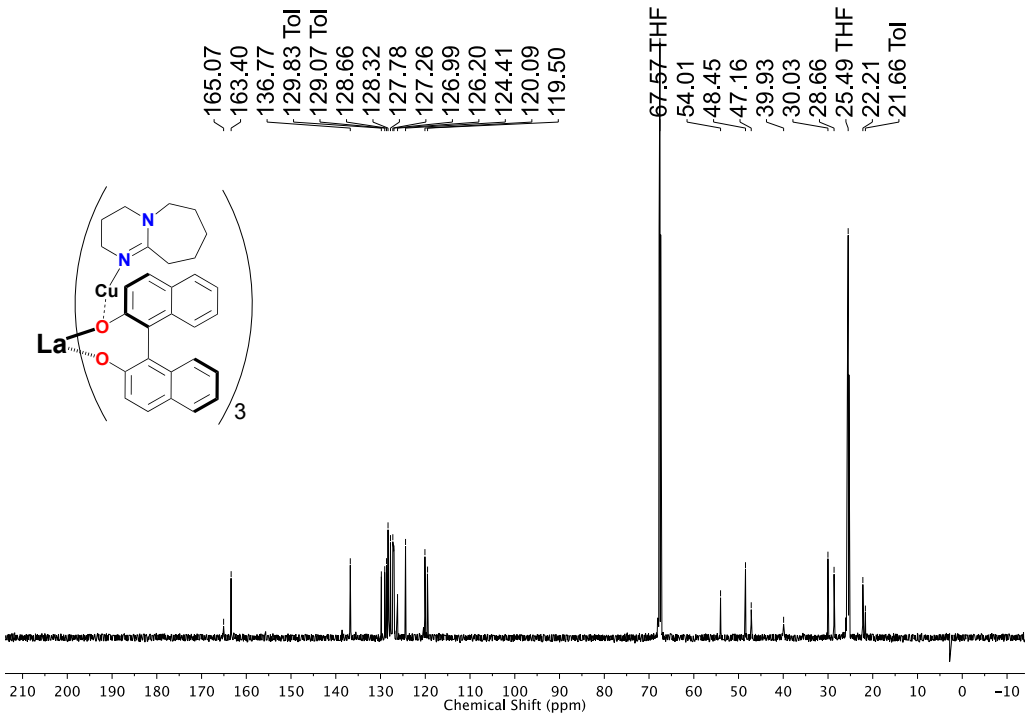

Figure S10b. ^{13}C{^{1}H} NMR(126 MHz, THF-d_8) spectrum of **2-La**.

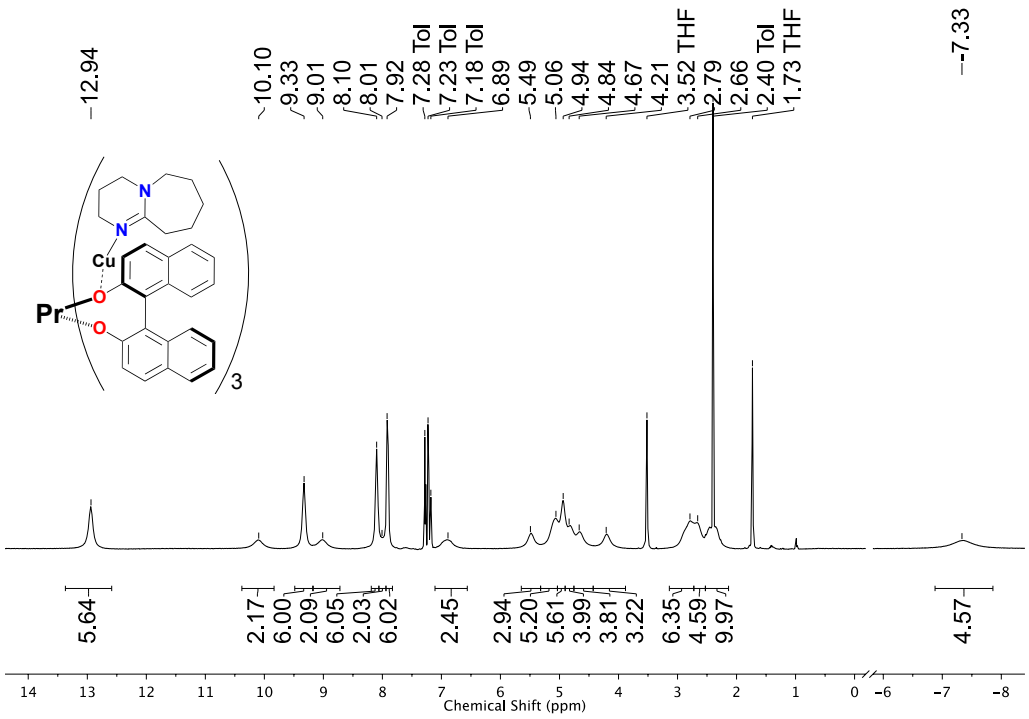

Figure S11a. ^{1}H NMR(500 MHz, THF-d_8) spectrum of **2-Pr.**

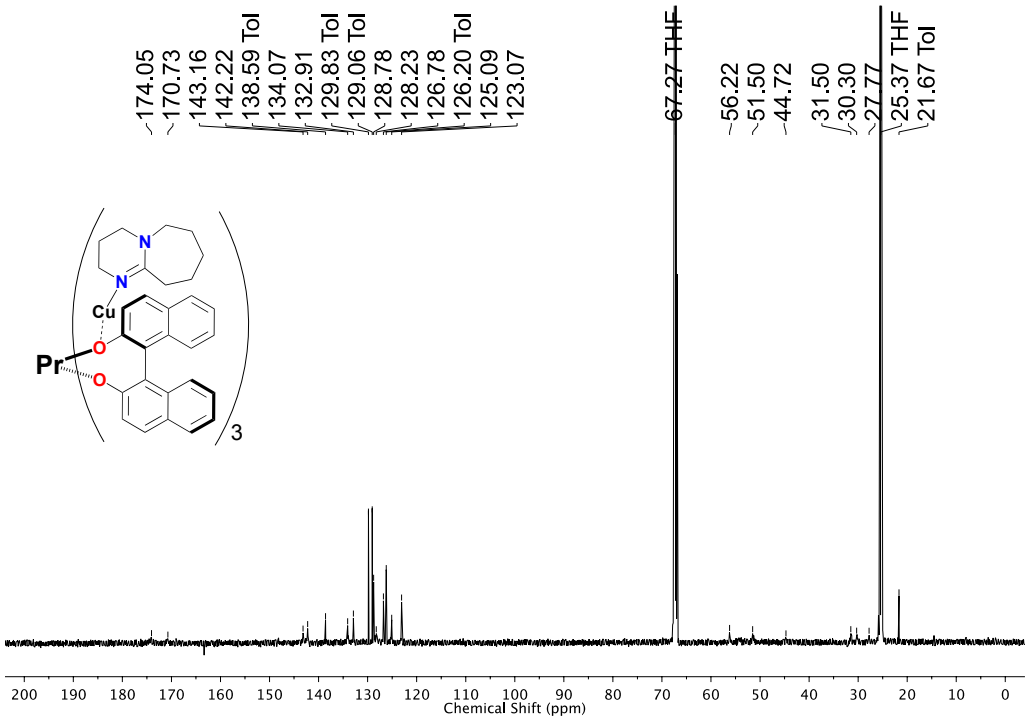

Figure S11b. ^{13}C{^{1}H} NMR(126 MHz, THF-d_8) spectrum of **2-Pr**.

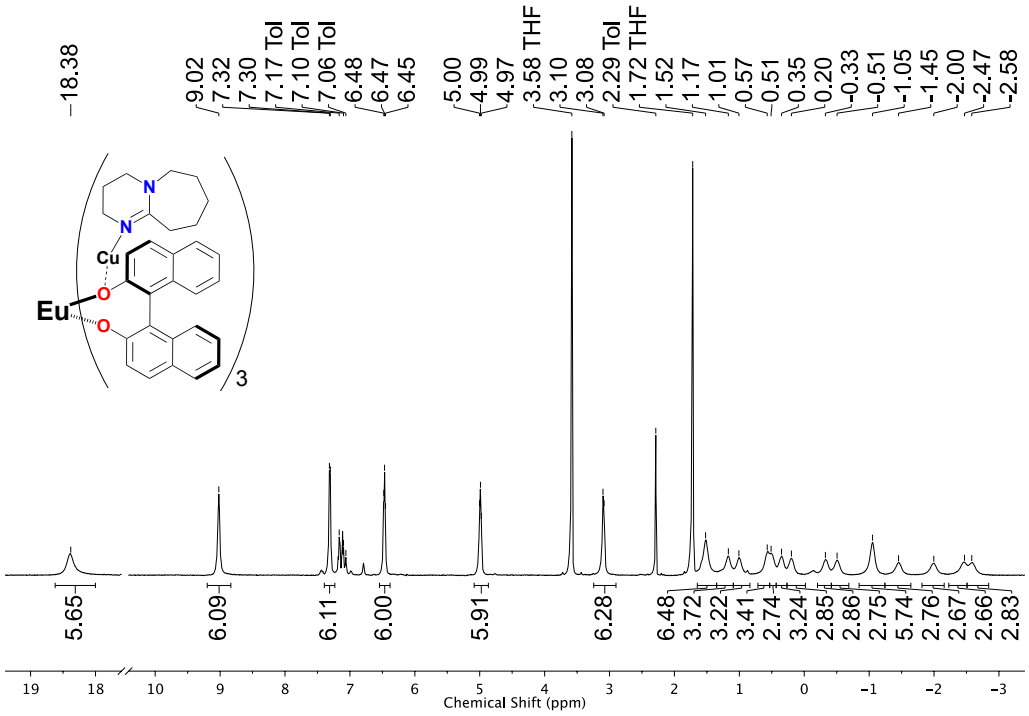

Figure S12a. ^{1}H NMR(500 MHz, THF-d_8) spectrum of **2-Eu.**

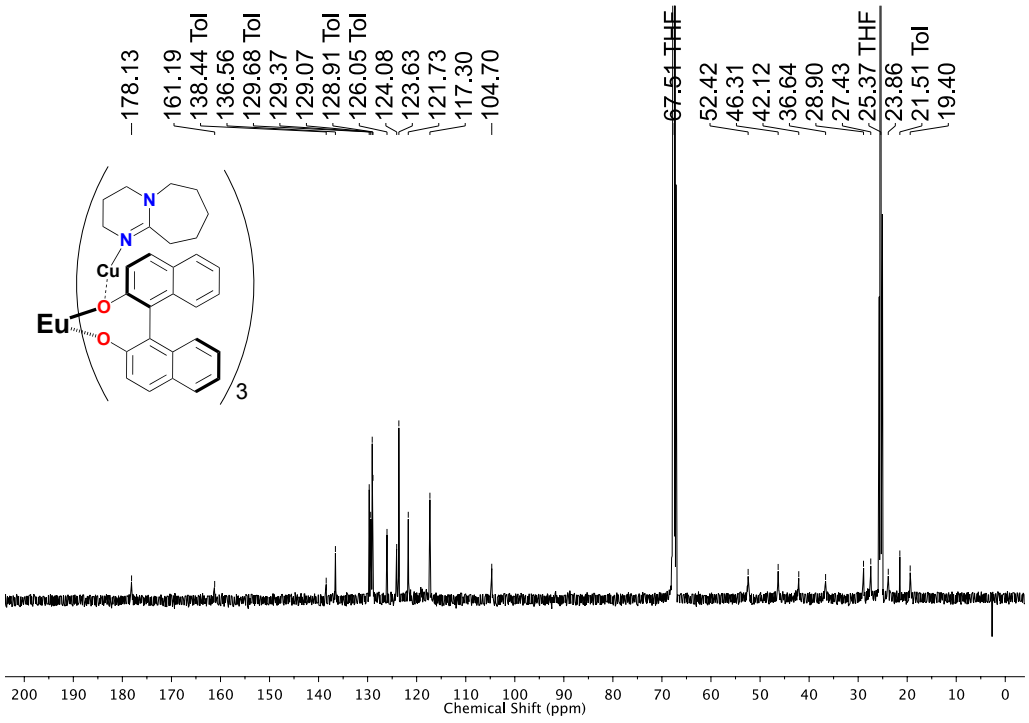

Figure S12b. ^{13}C{^{1}H} NMR(126 MHz, THF-d_8) spectrum of **2-Eu**.

References:

1. Bradley, D. C.; Ghotra, J. S.; Hart, F. A., *Dalton Trans.* **1973**, 1021-1027.
2. Pape, F.; Thiel Niklas, O.; Teichert Johannes, F., *Chem. -Eur. J.* **2015,** *21* (45), 15934-15938.
3. Cobas, J. C.; Martin-Pastor, M. *EXSYCalc*, 1.0; Mestrelab Research: Santiago De Compostela.
4. Bruker, SHELXTL. Bruker AXS Inc.: Madison, Wisconsin, USA, 2009.; SAINT v8.38A: Bruker-AXS Madison, Wisconsin, USA (2014).
5. SADABS v2016/2: Krause, L., Herbst-Irmer, R., Sheldrick, G.M. & Stalke, D., J. Appl. Cryst., 48, 3-10 (2015).
6. Sheldrick, G. M., TWINABS. University of Gottingen, Germany, 2008.
7. Sheldrick, G.M., Acta Cryst., A, 71, 3-8 (2015).
8. J. R. Robinson, J. Gu, P. J. Carroll, E. J. Schelter and P. J. Walsh, *J. Am. Chem. Soc.*, 2015, **137**, 7135-7144.