Lanthanide(III) 2-Naphthoxide Complexes Stabilized by Interligand Non-Covalent Interactions

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Electronic Supplementary Information

Experimental Procedures

General Methods. Unless otherwise indicated all reactions and manipulations were performed under an inert atmosphere (N_2) using standard Schlenk techniques or in a Vacuum Atmospheres, Inc. Nexus II drybox equipped with a molecular sieves 13X / Q5 Cu-0226S catalyst purifier system. Glassware was oven-dried overnight at 150 °C prior to use. ^{1}H, ^{13}C, and ^{7}Li NMR spectra were obtained on a Bruker DMX-300, on a Bruker DMX-360, or on a Bruker DRX-400 Fourier transform NMR spectrometer at 300, 360, and 400 MHz respectively. Chemical shifts were recorded in units of parts per million downfield from residual proteo solvent peaks (^{1}H), or characteristic solvent peaks ($^{13}C\{^{1}H\}$). The $^{7}Li\{^{1}H\}$ spectra were referenced to external solution standards of LiCl in H_2O. Elemental analyses were performed at the University of California, Berkeley Microanalytical Facility using a Perkin-Elmer Series II 2400 CHNS analyzer.

Materials. Tetrahydrofuran, dimethoxyethane, toluene, fluorobenzene, hexane, 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 hexane and pentane), or two columns of neutral alumina (for THF and toluene). Pyridine was freeze-pump-thawed for 4 cycles and stored over 4 Å molecular sieves for three days before use. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. $CDCl_3$ was freeze-pump-thawed for 4 cycles and stored over 4 Å molecular sieves for three days before use. Pyridine-d_5 was stored over 4 Å molecular sieves for three days before use. The starting materials: $Ln[N(SiMe_3)_2]_3$ (Ln = La, Ce) were prepared following published procedures.[1] $Ce(OTf)_3$ was dried under vacuum at 150 °C for 12 hours. $Li[N(SiMe_3)_2]$ (Acros) was recrystallized from hot pentane prior to use. 2-

naphthol (Acros, Sigma Aldrich) was sublimed under reduced pressure prior to use. Lithium *tert*-butoxide was purchased from (Acros) and used without further purification. 1,1,3,3-tetramethylguanidine (Acros, Sigma Aldrich) was freeze-pump-thawed for 4 cycles and stored over 4 Å molecular sieves for three days before use.

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,[2] producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the SHELXTL[3] program package for further processing and structure solution on a Dell Pentium 4 computer. The intensity data were corrected for Lorentz and polarization effects and for absorption using TWINABS[4] or SADABS.[5] The structures were solved by direct methods (SHELXS-97).[6] Refinement was by full-matrix least squares based on F^2 using SHELXL-97.[6] All reflections were used during refinements. The weighting scheme used was $w=1/[\sigma^2(F_o^2)+ (0.0907P)^2 + 0.3133P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Complex **1** **(**$C_{90}H_{72}CeLi_3N_6O_6$, *M* = 1494.48) crystallizes in the rhombohedral space group $R\overline{3}$ (no. 148) with a = 20.7351(11) Å, c = 30.1140(18) Å, V = 11212.7(11) Å^3, Z = 6, and d_{calc} = 1.328 g/cm^3; *U* = 11212.7(11) Å^3. The molecule lies on a crystallographic 3-fold axis (at 1/3, 2/3, z); the asymmetric unit is 1/3 of a molecule. The naphthyl group C(11)–C(20) is disordered by a rotation of 180°, where each naphthyl group had an occupancy of 0.50. 114733 reflections were measured, 5743 unique (R_{int} = 0.027) which were used in all calculations for the structure determination. The final *R(F)* was 0.0277 (observed data). Complex **2** ($C_{116}H_{110}Ce_2Li_4O_{18}$, *M* = 2100.04) crystallizes in the triclinic space group $P\overline{1}$ (no. 2) with a = 11.7345(7) Å, b = 15.1830(9) Å, c = 16.6050(9) Å, α =

82.260(3)°, β = 74.755(3)°, γ = 87.099(3)°, V = 2828.0(3) Å^3, Z=1, and d_{calc} = 1.233 g/cm^3 ; U = 2828.0(3) Å^3. 80553 reflections were measured, 13008 unique (R_{int} = 0.027) which were used in all calculations for the structure determination. The final *R(F)* was 0.0267 (observed data).

Complex **3** ($C_{105}H_{105}Ce_2N_9O_9$, M = 1917.22) crystallizes in the monoclinic space group C2/c (no. 15) with a = 36.8108(18) Å, b = 20.6080(10) Å, c = 27.9312(13) Å, β = 108.529(2)°, V = 20090.2(17) Å^3, Z = 8, and d_{calc} = 1.268 g/cm^3; U = 20090.2(17) Å^3. The naphthyl rings exhibited varying degrees of disorder; naphthyls C(21)–C(30) and C(61)–C(70) were modeled with two contributing orientations. All naphthyl groups were refined as rigid units. The weighting scheme used for **3** was $w=1/[s^2(F_o^2)+(0.0943P)^2 + 92.6350P]$ where $P = (F_o^2 + 2F_c^2)/3$. 378757 reflections were measured, 23161 unique (R_{int} = 0.038) which were used in all calculations for the structure determination. The final *R(F)* was 0.0718 (observed data).

Synthetic Details and Characterization

Synthesis of [Li(THF)][naphO]. 2-naphthol (2.46 g, 17.1 mmol) was dissolved in 15 mL of THF in a 20 mL scintillation vial and the solution was chilled to –35 °C. Lithium *tert*-butoxide (1.37 g, 17.1 mmol, 1 equiv) was added to the cold mixture, which was stirred for 2 h resulting in a clear yellow solution. The THF solution was concentrated under reduced pressure and layered with 10 mL of hexanes. Colorless crystals of the product were collected by filtration, washed with hexanes and dried under reduced pressure. Yield 2.88 g, 13.0 mmol, 76 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (doublet, J = 8.0 Hz, 1H), 7.58 (doublet, J = 8.8 Hz, 1H), 7.47 (doublet, J = 8.2 Hz, 1H), 7.25 (triplet, J = 7.0 Hz, 1H), 7.07 (multiplet, 1H), 7.03 (doublet of doublets, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 6.94 (singlet, 1H). ^{7}Li NMR (400 MHz, $CDCl_3$) δ: 1.04 (s).

Synthesis of [Li(py)$_2$]$_3$[Ce(naphO)$_6$] (1). In a 20 mL scintillation vial, 2-naphthol (0.21 g, 1.45 mmol, 6 equiv) was dissolved in 5 mL of pyridine. Once dissolved, Li[N(SiMe$_3$)$_2$] (0.12 g, 0.73 mmol, 3 equiv) was added to the vial and the clear yellow solution was stirred for half an hour. After stirring, the pyridine was removed under reduced pressure, and the resulting gel-like pale yellow solid was re-dissolved in 2 mL of pyridine. Ce[N(SiMe$_3$)$_2$]$_3$ (0.15 g, 0.24 mmol, 1 equiv) was dissolved in 12 mL of hexanes and the bright yellow solution was layered over the clear, pale yellow pyridine solution. After two days, yellow crystals formed. The yellow crystals of the product were collected by filtration, washed with hexanes and dried under reduced pressure. Yield 0.21 g, 0.14 mmol, 57 %. ^{1}H NMR (360 MHz, CDCl$_3$) δ: 9.14 (broad singlet, 12H), 7.67 (broad singlet, 6H), 7.24 (broad singlet, 18H), 6.85 (broad singlet, 12H); ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) δ: 150.34, 136.63, 126.78, 124.30, 120.96; ^{7}Li{^{1}H} NMR (194 MHz, CDCl$_3$) δ: 1.99 (s). CHN analyses for compound **1** were consistently within ±0.5 % for the H and N values but the carbon value was consistently low on four attempts. We attribute the problem with the carbon value to incomplete combustion for this complex. The same result was obtained for complex **4**, the lanthanum analog of complex **1**.

Synthesis of [Li(DME)]$_4$[Ce$_2$(naphO)$_{10}$] (2). In a 20 mL scintillation vial, 2-naphthol **(**0.17 g, 1.21 mmol, 10 equiv) was dissolved in 5 mL of DME to form a clear, colorless solution. Once dissolved, Li[N(SiMe$_3$)$_2$] (0.081 g, 0.48 mmol, 4 equiv) was added to the vial and stirred over a period of 0.5 hour. After stirring, the DME was removed under reduced pressure, and the white gel-like solid was re-dissolved in 2 mL of DME. A bright yellow solution of Ce[N(SiMe$_3$)$_2$]$_3$ (0.15 g, 0.24 mmol, 2 equiv) was prepared from in 12 mL hexanes and then layered over the clear, colorless DME solution. After two days, off-white needle-like crystals formed. The off-white crystals of the product were collected by filtration, washed with hexanes and dried under reduced pressure. Yield 0.19 g, 0.091 mmol, 75%. ^{1}H NMR (360 MHz, $CDCl_3$) δ: 7.0–6.2 (broad singlet, 6H), 5.76 (broad singlet, 2H), 4.65 (broad singlet, 4H), 4.06 (broad singlet, 6H); **^{13}**C NMR (360 MHz, $CDCl_3$) δ: 133.68, 126.62, 125.30, 124.01, 120.68, 73.05, 60.82; ^{7}Li{^{1}H} NMR (194 MHz, $CDCl_3$) δ: 17.18 (singlet). Analysis calculated for $C_{116}H_{110}O_{18}Ce_2Li_4$: C, 66.34; H, 5.28. Found: C, 66.09; H, 5.59.

Synthesis of $[HTMG]_3[Ce_2(naphO)_9]\cdot(THF)_2$ (3). In a 20 mL scintillation vial, 2-naphthol (0.21 g, 1.45 mmol, 9 equiv) was dissolved in 4 mL of THF. Once dissolved, 1,1,3,3-tetramethylguanidine (92 µL, 0.73 mmol, 3 equiv) was added by syringe and the clear, colorless solution was stirred over a period of 1 h. Then, $Ce[N(SiMe_3)_2]_3$ (0.209 g, 0.32 mmol, 2 equiv) was added to the clear, colorless solution. The clear yellow THF solution was concentrated to 2 mL after stirring for 2 h, and then layered with 20 mL hexanes. After 2 days, yellow crystals formed. The crystals were collected by filtration, washed with hexanes, and dried under reduced pressure. Yield: 0.23 g, 0.11 mmol, 68%. ^{1}H NMR (360 MHz, $CDCl_3$) δ: 11.80 (broad singlet, 3H), 7.65 (broad singlet, 20H), 7.30 (broad singlet, 17H), 7.10 (broad singlet, 14H), 2.84(broad singlet, 36H) ^{1}H NMR (360 MHz, THF-d_8) δ: 10.65 (broad singlet, 3H), 8.85 (broad singlet, 6H), 7.97 (singlet, 6H), 7.69 (singlet, 16H), 7.29 (singlet, 9H), 7.07 (singlet, 12H), 2.88 (singlet, 36H); ^{1}H NMR (360 MHz,-pyridine-d_5) δ: 9.87 (broad singlet, 3H), 8.83 (singlet, 4H), 8.39 (singlet, 6H), 8.01 (singlet, 9H), 7.88 (singlet, 9H), 7.48 (singlet, 9H), 7.23 (singlet, 9H), 2.35 (singlet, 36H); ^{13}C NMR (360 MHz, $CDCl_3$) δ: 162.37, 136.02, 128.40, 127.16, 126.77, 126.13, 125.02, 120.84, 113.98, 39.35, 31.69. Analysis calculated for $C_{113}H_{121}O_{11}N_9Ce_2$: C, 65.84; H, 5.92; N, 6.12. Found: C, 65.81; H, 5.70; N, 6.40. The product can also be crystallized from DME or pyridine by following the same procedure with those solvents.

Synthesis of $[Li(py)_2]_3[La(naphO)_6]$ (4). The synthesis of **4** was identical to that of **1**, except that $La[N(SiMe_3)_2]_3$ (0.10 g, 0.16 mmol, 1 equiv) was dissolved in hexanes and layered over a pyridine solution of 2-naphthol (0.14 g, 0.97 mmol, 6 equiv) and $Li[N(SiMe_3)_2]$ (0.082 g, 0.434 mmol, 3 equiv). Yield 0.18 g, 0.12 mmol, 74%. ^1H NMR (400 MHz, $CDCl_3$) δ: 8.13 (singlet, 12H), 7.53 (singlet, 6H), 7.43 (triplet, *J* = 7.0 Hz, 6H), 7.20 (singlet, 7H) 7.08 (singlet, 13H), 6.84 (singlet, 28H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ: 163.51, 149.61, 136.35, 136.10, 128.80, 127.38, 126.86, 125.72, 125.01, 124.09, 123.81, 120.68, 111.88; $^7Li\{^1H\}$ NMR (194 MHz, $CDCl_3$) δ: 2.04 (1Li), 1.95 (0.84 Li), 1.61 (0.24 Li). The CHN combustion analysis for compound **4** was within ±0.5 % for the H and N values but the carbon value was low. We attribute the problem with the carbon value to incomplete combustion for this complex. The same result was obtained for complex **1**, the cerium analog of complex **4**.

Synthesis of $[Li(DME)]_4[La_2(naphO)_{10}]$ (5). The synthesis of **5** was identical to that of **2**, except that $La[N(SiMe_3)_2]_3$ (1.00 g, 0.16 mmol, 2 equiv) was dissolved in hexanes and layered over a DME solution of 2-naphthol (0.12 g, 0.81 mmol, 10 equiv) and $LiN(SiMe_3)_2$ (0.054 g, 0.32 mmol, 4 equiv). Yield 0.087 g, 0.041 mmol, 51%. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.58 (singlet, 8H), 7.33 (singlet, 8H), 7.17 (multiplet, 16H), 7.11 (triplet, *J* = 7.0 Hz, 13H), 6.84 (singlet, 7H), 6.71 (singlet, 6H), 3.20 (singlet, 16H), 2.94 (singlet, 24H). $^7Li\{^1H\}$ NMR (194 MHz, $CDCl_3$) δ: 0.37 (1Li), 0.17 (0.7Li). Analysis calculated for $C_{116}H_{110}O_{18}La_2Li_4$: C, 66.42; H, 5.29. Found: C, 66.20; H, 5.70.

Synthesis of $[HTMG]_3[La_2(NaphO)_9]\cdot(DME)_2$ (6). The synthesis of **6** was identical to that of **3**, except that $La[N(SiMe_3)_2]_3$ (0.11 g, 0.16 mmol, 2 equiv) was reacted with 2-naphthol (0.11 g, 0.73 mmol, 9 equiv) and 1,1,3,3-tetramethylguanidine (33 μL, 0.24 mmol, 3 equiv) in either THF or DME. Yield 0.11 g, 0.050 mmol, 62%. ^1H NMR (360 MHz, $CDCl_3$) δ: 7.60 (doublet, *J* = 7.6

Hz, 9H), 7.50 (doublet, J = 7.6 Hz, 9H), 7.29 (multiplet, 21H), 7.21 (triplet, J = 6.7 Hz, 15H), 7.10 (triplet, J = 7.2 Hz, 9H), 1.89 (singlet, 36H); ^{13}C NMR (360 MHz, $CDCl_3$) δ: 163.63, 161.42, 136.27, 128.73, 127.47, 126.96, 125.86, 125.22, 124.70, 120.72, 112.04, 38.51. Analysis calculated for $C_{113}H_{125}O_{13}N_9La_2$: C, 64.78; H, 6.01; N, 6.02. Found: C, 64.60; H, 5.75; N, 5.78.

Diffusion Coefficient Experiments:

The NMR experiments for the determination of the self-diffusion coefficients and hydrodynamic radii were performed at 300 K on a Bruker Avance DRX 600 MHz spectrometer equipped with a 5 mm TXI probe with a z-axis gradient coil. The gradient system was calibrated with a doped water sample. In Bipolar-LED experiments, diffusion time (Δ) was 100 ms for all samples, and the duration (δ) of the sine shaped gradients was set to 1.4 ms. Data processing was accomplished with Bruker TOPSPIN 1.3 DOSY software and Bruker TOPSPIN 1.3 T1/T2 software. The experiments were run in $CDCl_3$ with benzene used as an internal standard.[7] The diffusion coefficient for benzene in $CDCl_3$ was determined to be 2.2×10^{-9} m^2s^{-1} with a standard deviation of 0.1×10^{-9} m^2s^{-1}, which is in good agreement with literature values.[7, 8] The hydrodynamic radii (r) of **3**–**6** were determined using the ratios of the diffusion constant of benzene ($D_{0\ reference}$) with that of the samples ($D_{0\ sample}$) and the hydrodynamic radius of benzene ($r_{reference}$), which was set to 2.54 Å (Eq 1).[8]

$$r = \left(\frac{D_{0\ reference}}{D_{0\ sample}} \right) \times r_{reference} \qquad (1)$$

This relationship is derived from the Stokes-Einstein equation (Eq 2),[7, 9] by referencing against the internal standard to minimize errors due to variations in viscosity and temperature within the samples. [7, 9-11]

$$D_0 = \frac{kT}{6\pi\eta r} \qquad (2)$$

Following Stokes-Einstein relation, D_0 is the diffusion coefficient, k is Boltzmann's constant, T is the temperature, η is the viscosity of the solution, and r is the hydrodynamic radius.

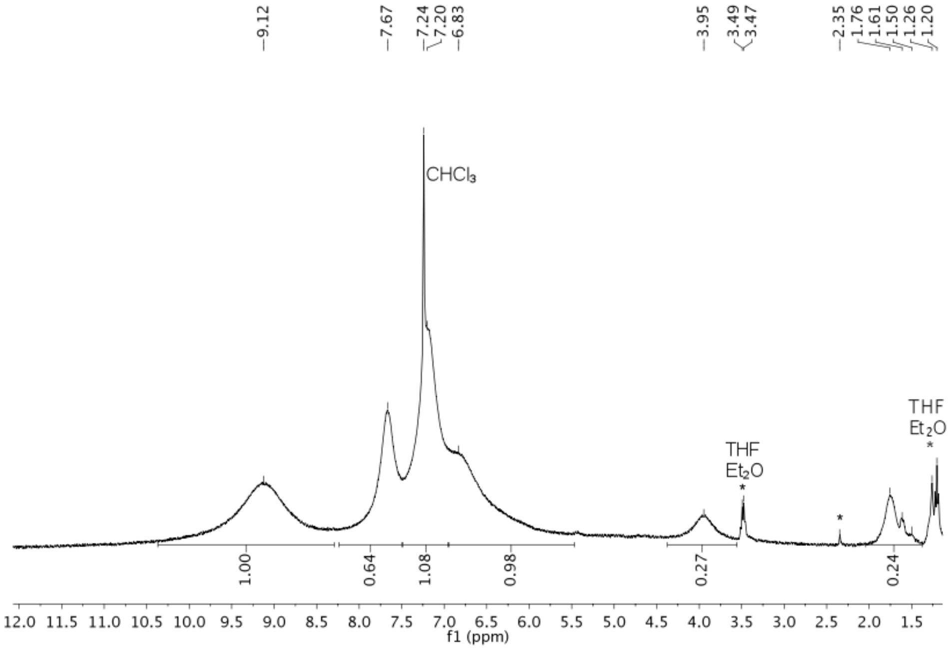

Figure S1. ^{1}H NMR spectrum of $[Li(py)_2]_3[Ce(naphO)_6]$ (**1**) collected in $CDCl_3$. The asterisks indicate exogenous solvent peaks.

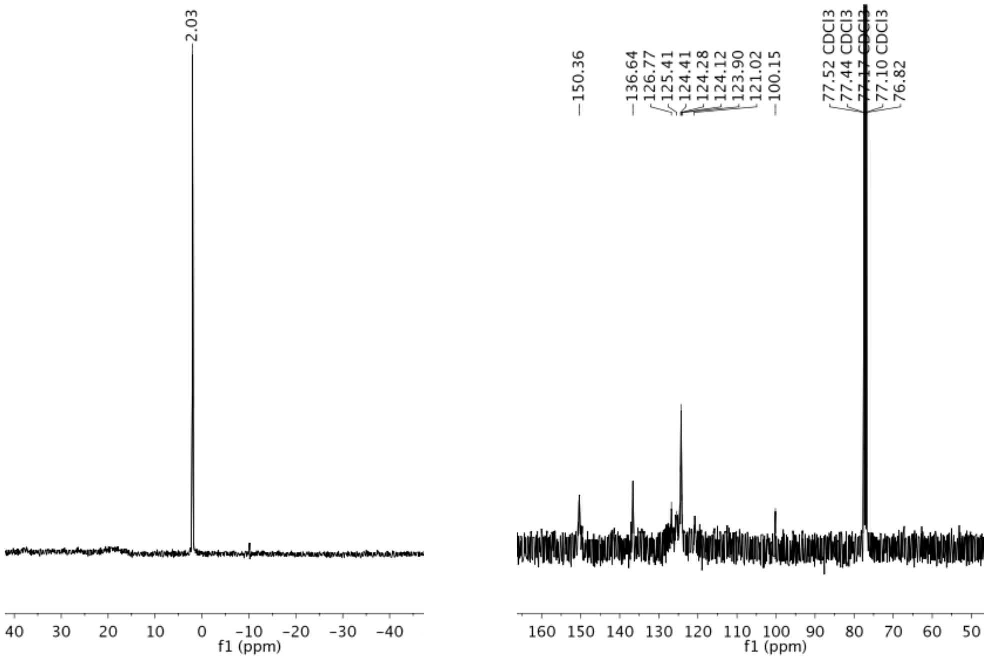

Figure S2. ^{7}Li NMR spectrum (left) and ^{13}C NMR spectrum (right) of $[Li(py)_2]_3[Ce(naphO)_6]$ (**1**) collected in $CDCl_3$.

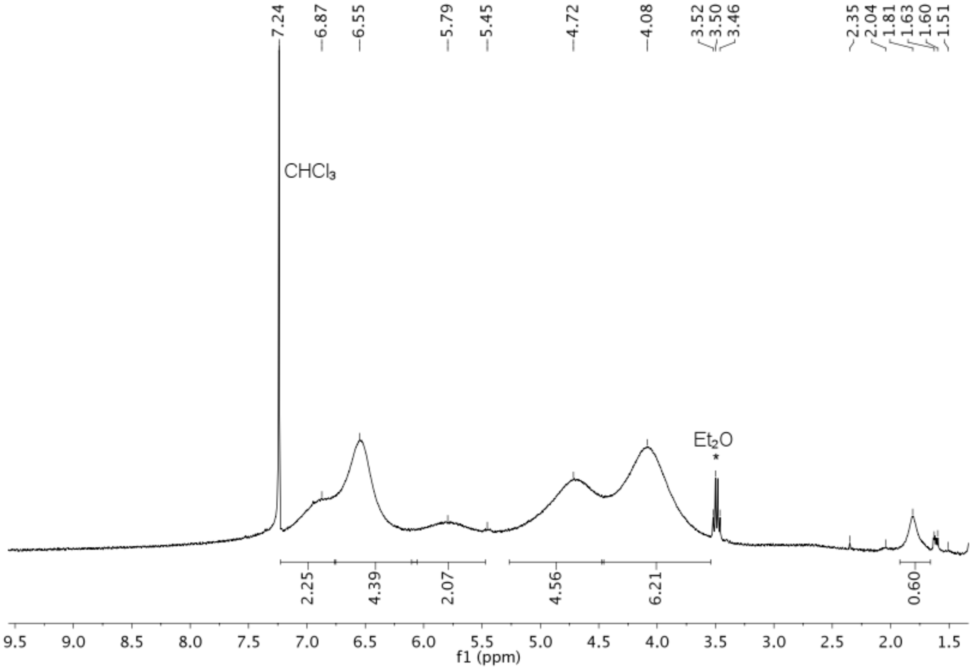

Figure S3. ^{1}H NMR spectrum of $[Li(DME)]_4[Ce_2(naphO)_{10}]$ (**2**) collected in $CDCl_3$. Asterisks indicate exogenous solvent species.

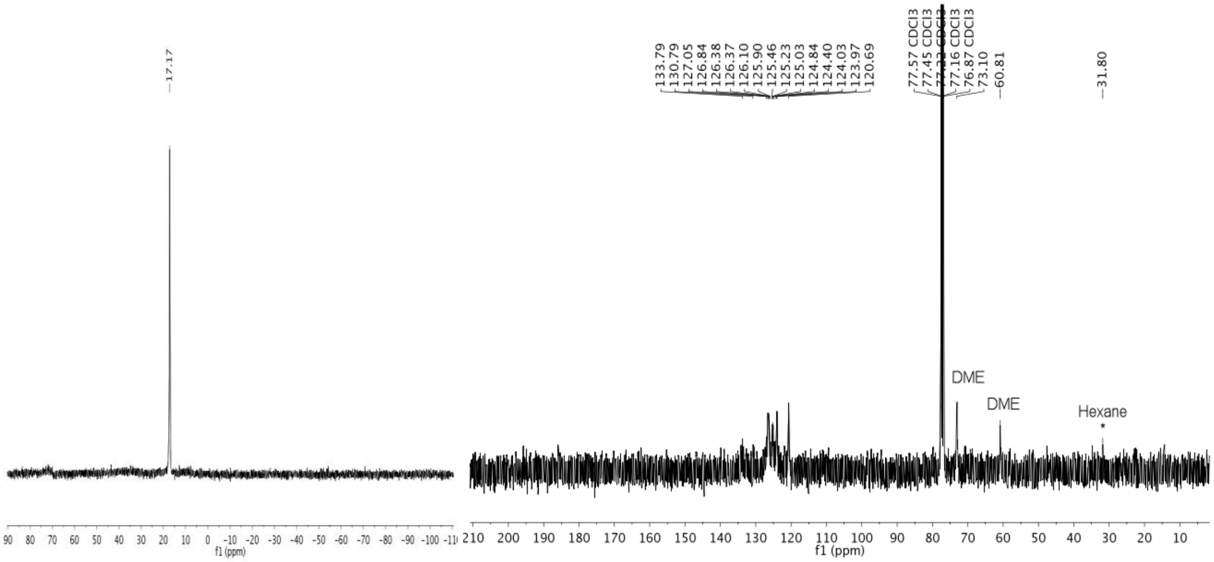

Figure S4. ^{7}Li NMR (left) and ^{13}C NMR (right) spectra of $[Li(DME)]_4[Ce_2(naphO)_{10}]$ (**2**) collected in $CDCl_3$. Asterisks indicate exogenous solvent species.

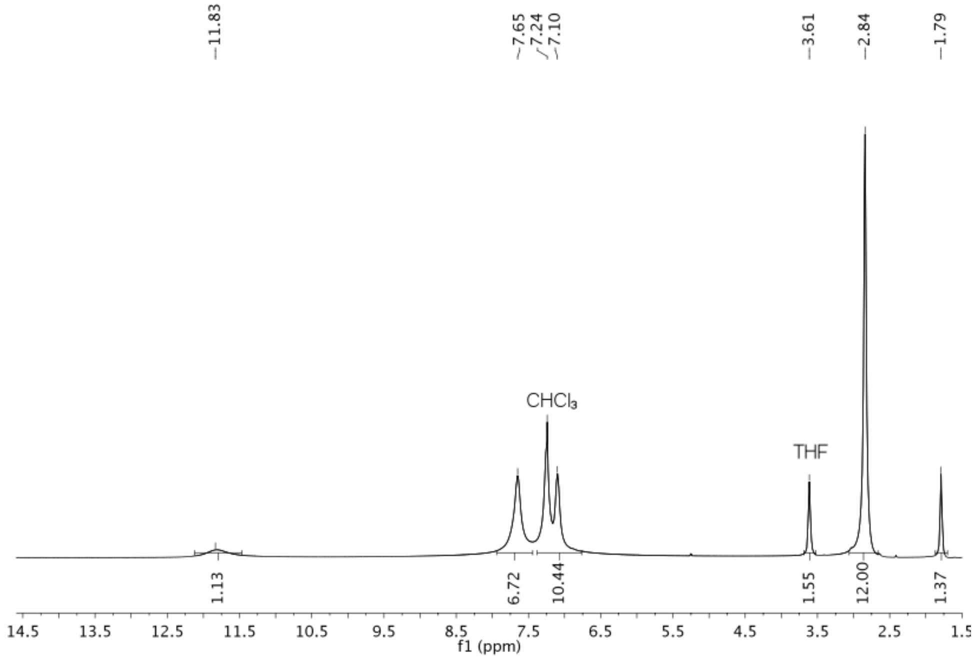

Figure S5. ^{1}H NMR spectrum of $[HTMG]_3[Ce_2(naphO)_9]$ (**3**) crystallized from THF collected in $CDCl_3$.

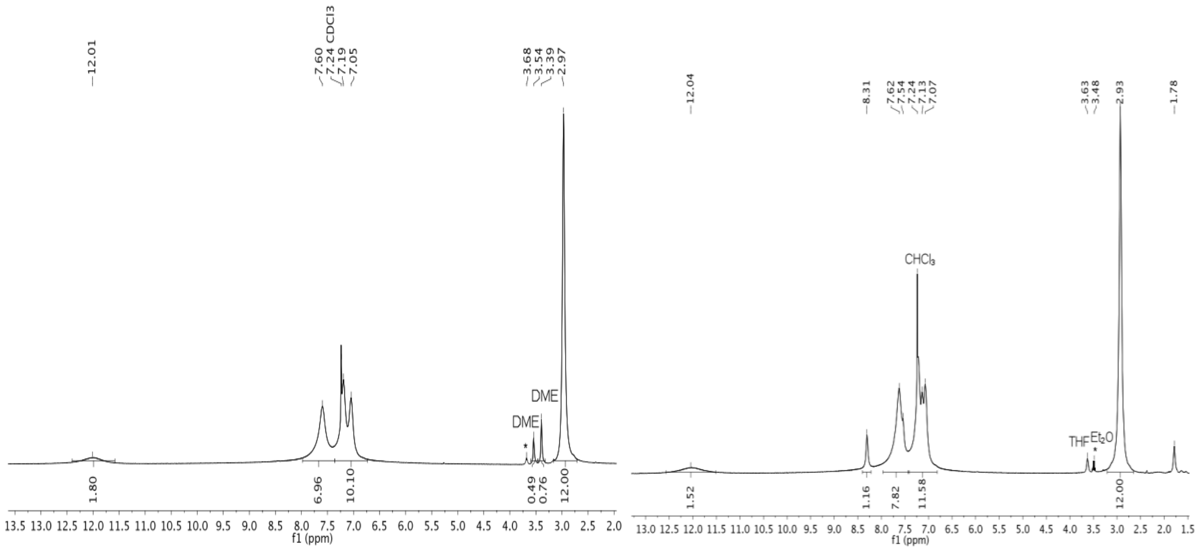

Figure S6. ^{1}H NMR spectrum of $[HTMG]_3[Ce_2(naphO)_9]$ (**3**) crystallized from DME (left) and pyridine (right) collected in $CDCl_3$. Asterisks indicate exogenous solvent peaks.

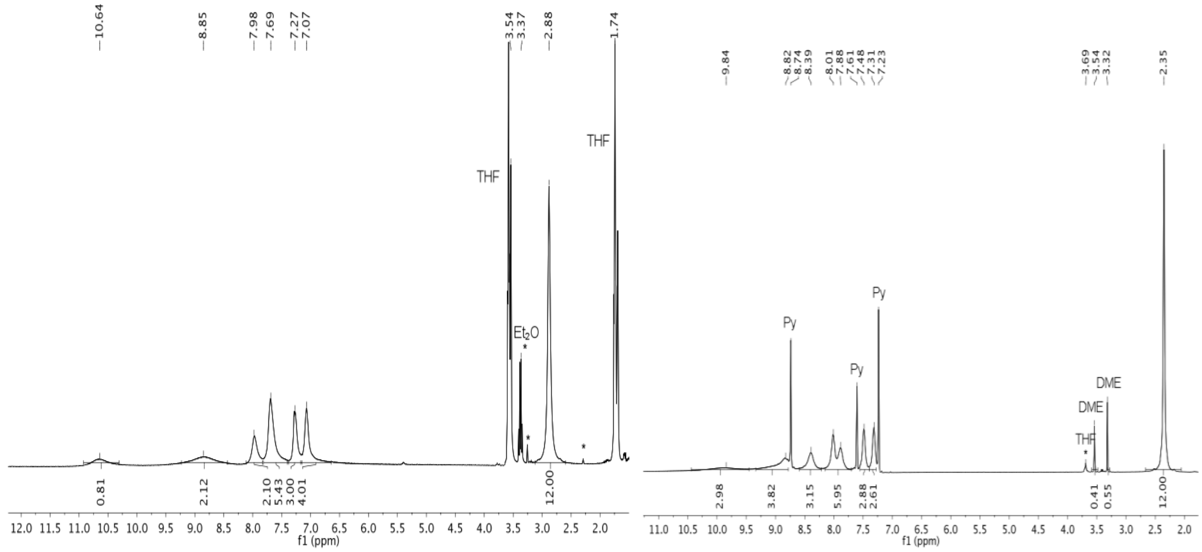

Figure S7. ^{1}H NMR spectrum of $[HTMG]_3[Ce_2(naphO)_9]$ (**3**) crystallized from DME collected in THF–d_8 (left) and pyridine–d_5. Asterisks indicate the exogenous solvent species present.

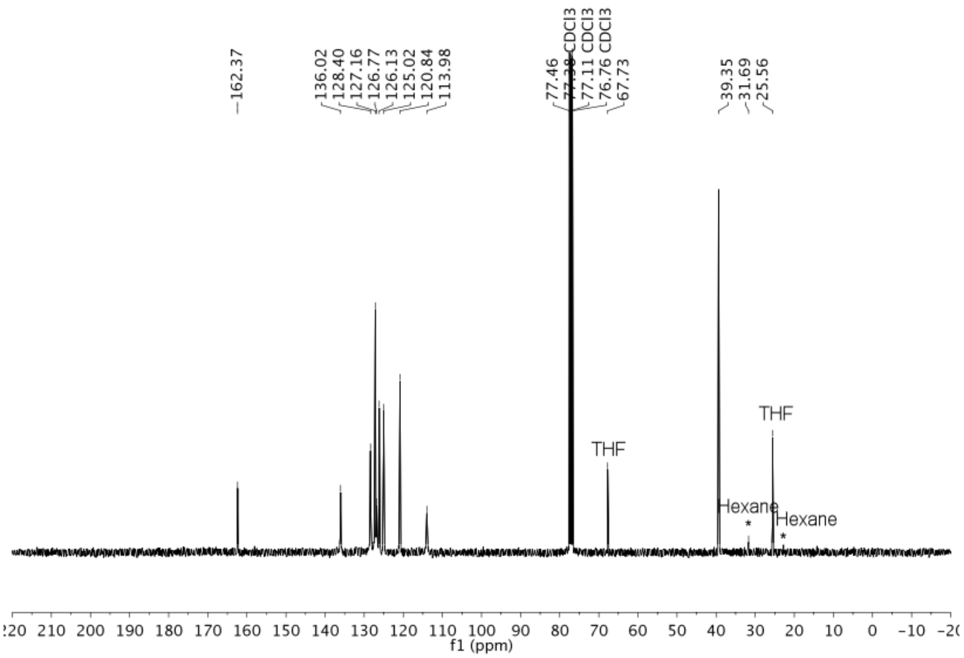

Figure S8. ^{13}C NMR spectrum of $[HTMG]_3[Ce_2(naphO)_9]$ (**3**) crystallized from THF collected in $CDCl_3$. Asterisks indicate exogenous solvent species present.

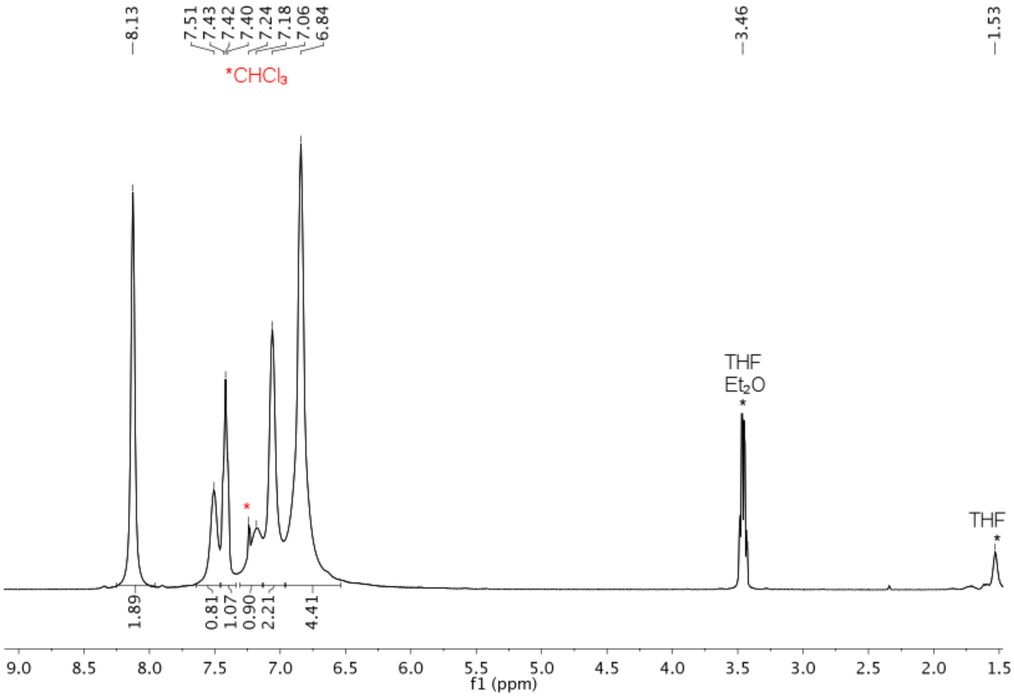

Figure S9. ^{1}H NMR spectrum of $[Li(py)_2]_3[La(naphO)_6]$ (**4**) collected in $CDCl_3$. Asterisks indicate exogenous solvent peaks.

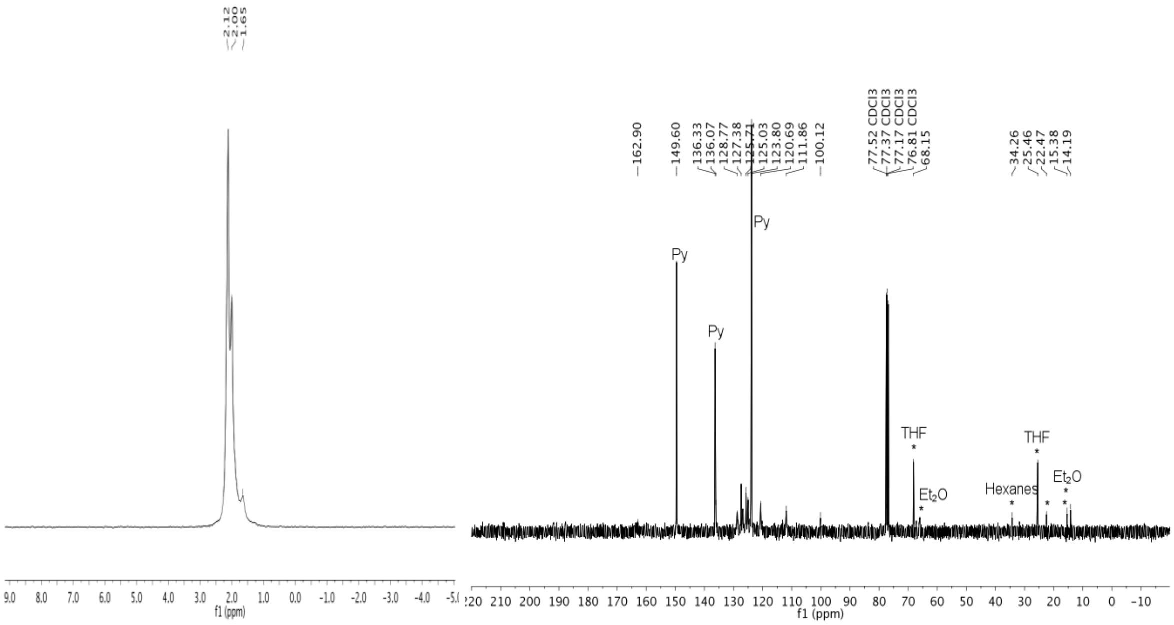

Figure S10. ^{7}Li NMR spectrum (left) and ^{13}C NMR spectrum (right) of $[Li(py)_2]_3[La(naphO)_6]$ (**4**) collected in $CDCl_3$. Asterisks indicate exogenous solvent peaks.

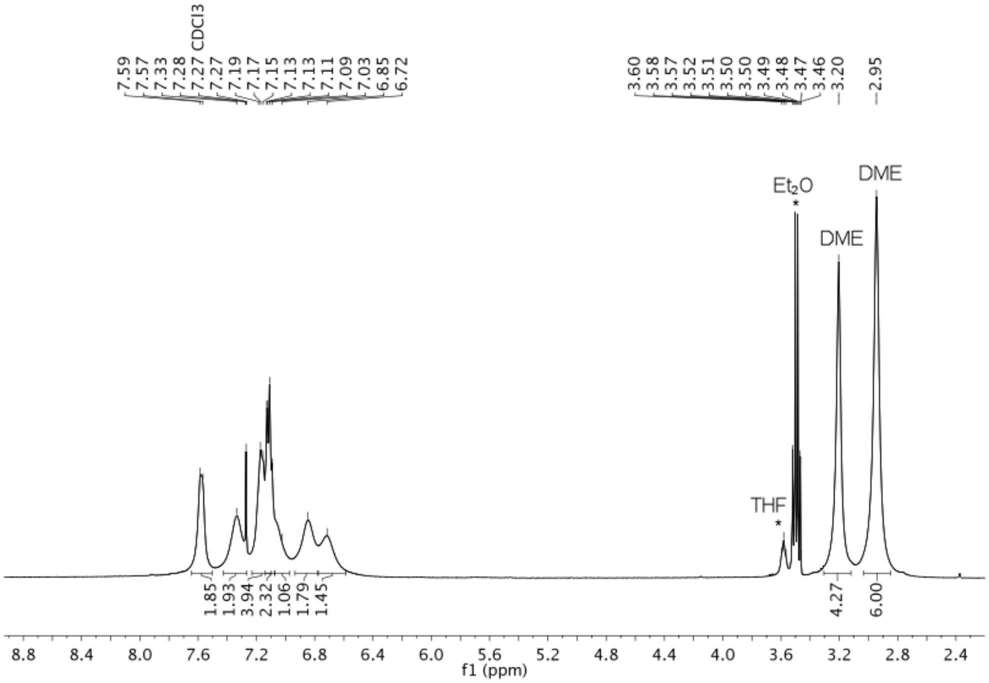

Figure S11. ^{1}H NMR spectrum of $[Li(DME)]_4[La_2(naphO)_{10}]$ (**5**) collected in $CDCl_3$. Asterisks indicate exogenous solvent species.

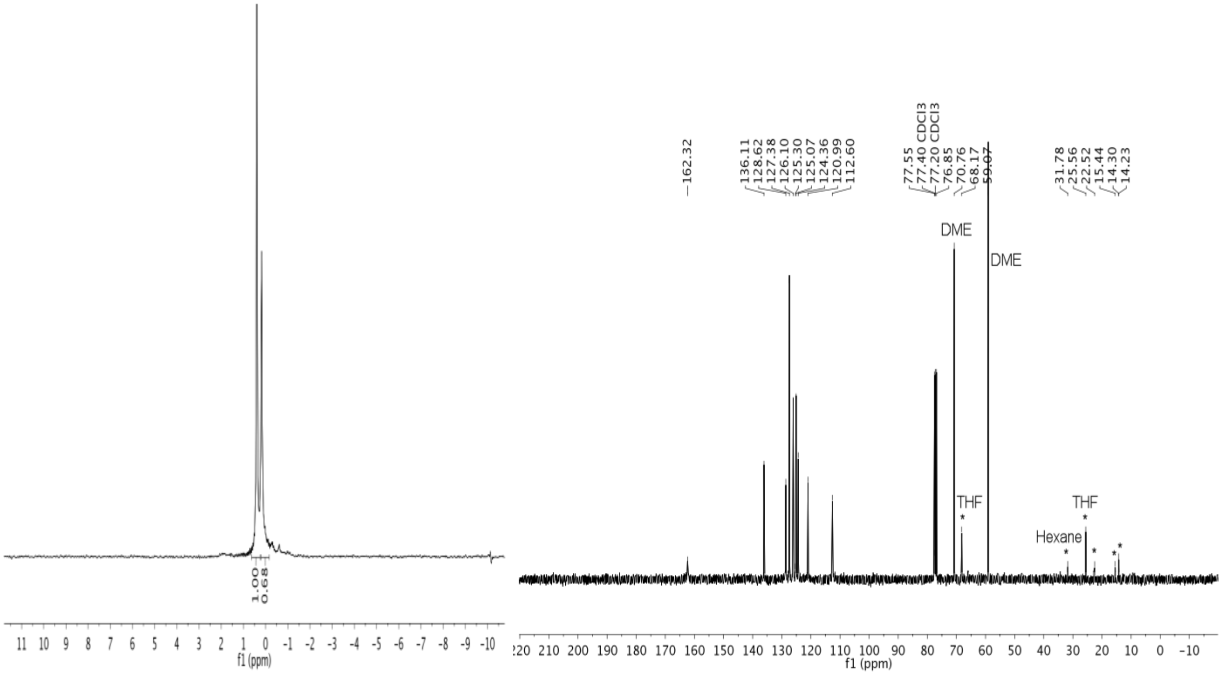

Figure S12. ^{7}Li NMR (left) and ^{13}C NMR (right) spectra of [Li(DME)]$_4$[La$_2$(naphO)$_{10}$] (**5**) collected in CDCl$_3$. Asterisks indicate exogenous solvent species.

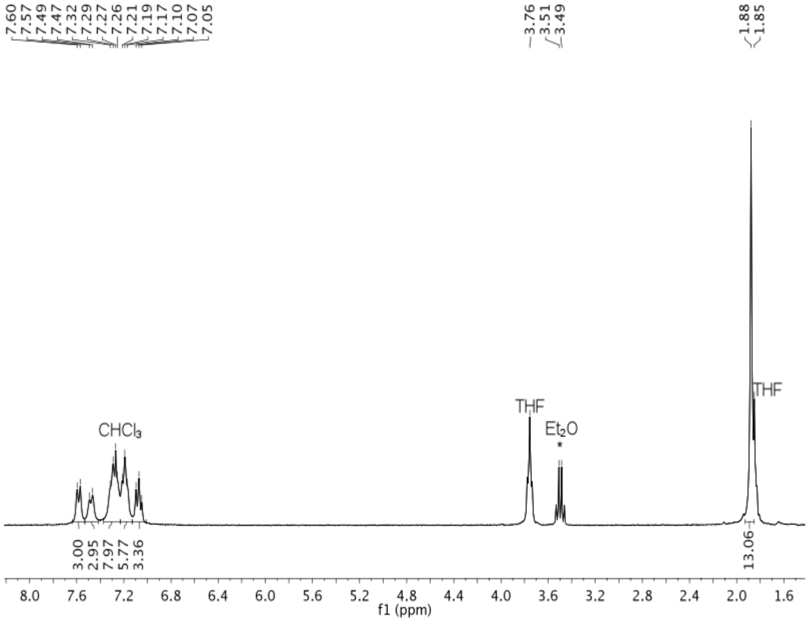

Figure S13. ^{1}H NMR spectrum of [HTMG]$_3$[La$_2$(naphO)$_9$] (**6**) crystallized from DME collected in CDCl$_3$. Asterisks indicate exogenous solvent species present.

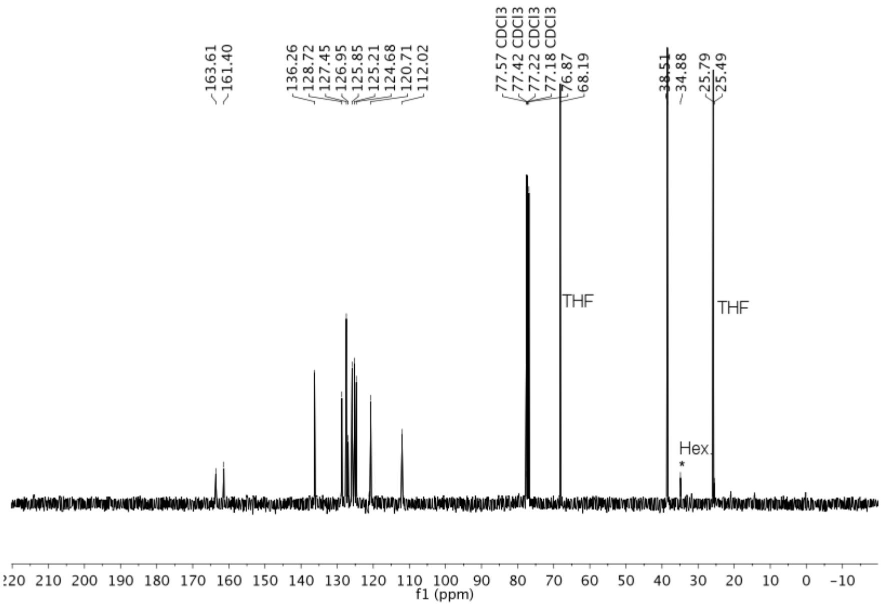

Figure S14. ^{13}C NMR spectrum of [HTMG]$_3$[La$_2$(naphO)$_9$] (**6**) crystallized from THF collected in CDCl$_3$. Asterisks indicate exogenous solvent species present.

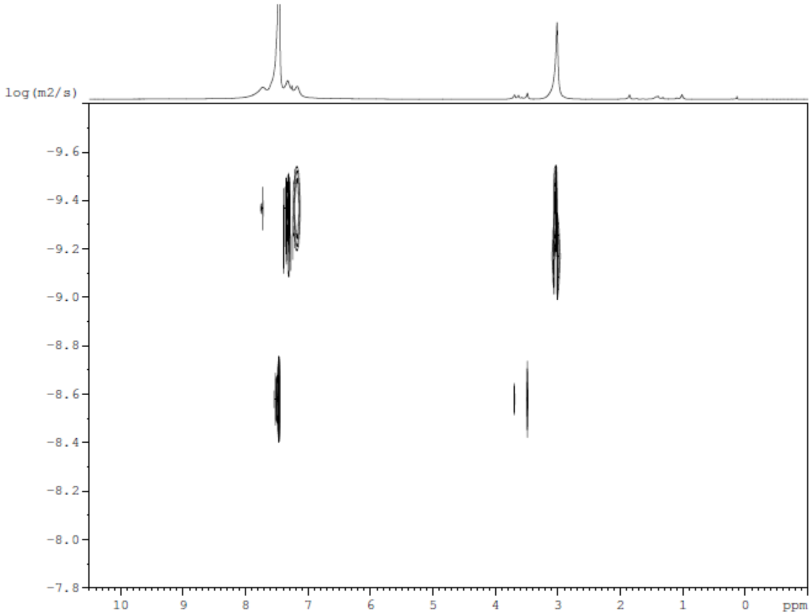

Figure S15. Representative ^{1}H DOSY NMR spectrum of $[HTMG]_3[Ce_2(naphO)_9]$ (**3**) in $CDCl_3$ with benzene as an internal reference.

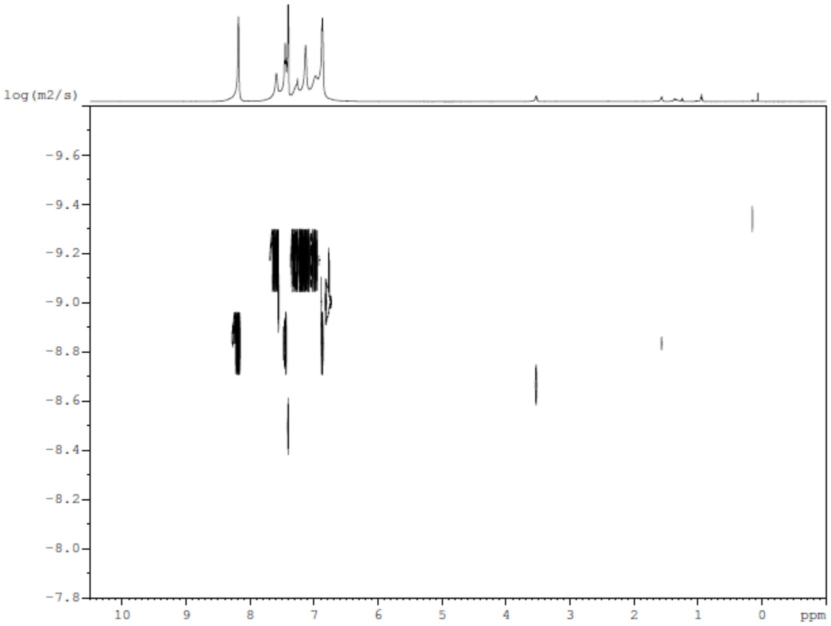

Figure S16. Representative ^{1}H DOSY NMR spectrum of $[Li(py)_2]_3[La(naphO)_6]$ (**4**) in $CDCl_3$ with benzene as an internal reference.

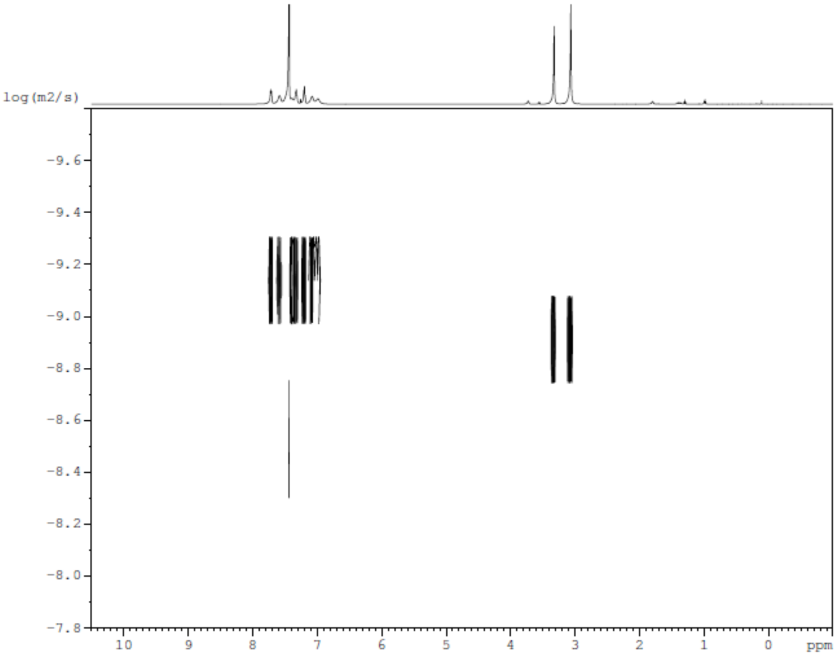

Figure S17. Representative ^{1}H DOSY NMR spectrum of $[Li(DME)]_4[La_2(naphO)_{10}]$ (**5**) in $CDCl_3$ with benzene as an internal reference.

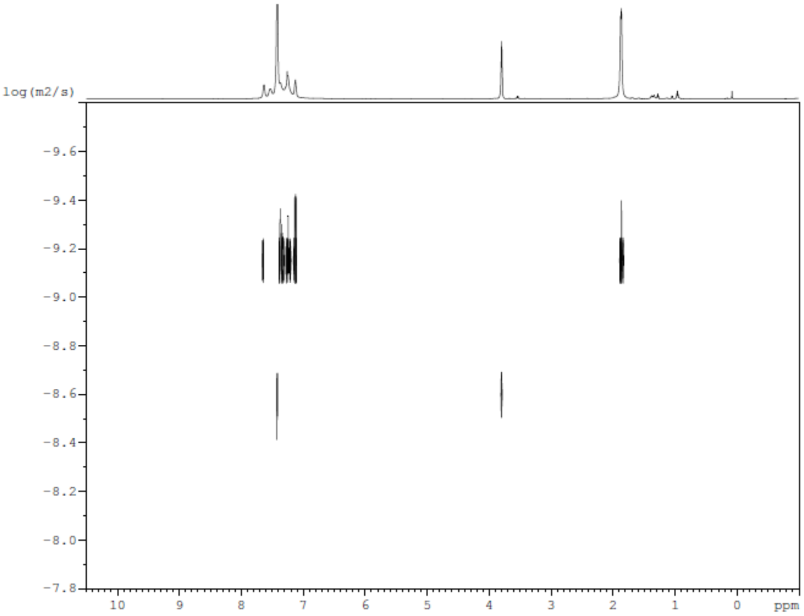

Figure S18. Representative ^{1}H DOSY NMR spectrum of $[HTMG]_3[La_2(naphO)_9]$ (**6**) in $CDCl_3$ with benzene as an internal reference.

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