Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPORTING INFORMATION FOR

Schiff Base Thorium(IV) and Uranium(IV) Chloro Complexes: Synthesis, Substitution and Oxidation Chemistry

Brian C. Stobbe, Douglas R. Powell and Robert K. Thomson*

Department of Chemistry and Biochemistry, University of Oklahoma, Norman, OK, USA 73019.

E-mail: rthomson@ou.edu

Contents

General Experimental Procedures

All experiments were performed under an atmosphere of dry N_2 in a VAC Atmospheres dry box. Solvents were purified using the appropriate VAC Atmospheres solvent purifier or dried over sodium benzophenone ketyl and distilled under an atmosphere of dry N_2. Solvents purified by these methods were subsequently degassed using successive freeze-pump-thaw methods, and brought into the dry box without exposure to air, and stored over activated 4 Å molecular sieves. Celite was activated and dried by heating under high vacuum (~ 0.3mm Hg) at > 200°C overnight. Deuterated NMR solvents, C_6D_6 and $CDCl_3$, were purchased from Cambridge Isotope Laboratories, degassed using freeze-pump-thaw cycles and stored over 4 Å molecular sieves. The Schiff base ligand (**L**)$\mathbf{H_2}$,[1] UCl_4[2] and $ThCl_4(DME)_2$[3] were synthesized by reported methods. ^1H NMR spectra were recorded using Varian VNMRS spectrometers operating at 300MHz or 400MHz for ^1H at room temperature in $CDCl_3$ unless otherwise specified. All chemical shifts herein are reported with reference to residual solvent peaks for $CDCl_3$ at δ 7.27. All infrared spectra were collected using an ATR adaptor on a Thermo Scientific Nicolet 6700 FT-IR instrument at room temperature. Microanalyses were performed at Atlantic Microlabs in Norcross, GA.

Synthesis of (L)UCl$_2$(THF)$_2$ (1):

Synthesis of K$_2$(L) generated for in situ use:

To a 20 mL scintillation vial charged with 14 mL of THF and a small stir bar, (0.250 g, 0.609 mmol) of the racemate of (±)-*trans*-6,6′-Diethoxy-2,2′-[cyclohexane-1,2-diylbis(nitrilomethanylylidene)]diphenol, **(L)H$_2$** was added. The resulting clear yellow solution was allowed to mix thoroughly, after which 2 equiv of KO^{t}Bu (0.136 g, 1.21 mmol) was added to the solution as a solid. The solution immediately became opaque, and a color change to a yellow-green was noted. The resulting solution was allowed to stir for 1.5 h prior to use in subsequent chemistry.

*Synthesis of (L)UCl$_2$(THF)$_2$ (**1**):*

To a 20 mL scintillation vial charged with 4 mL of THF and a small stir bar, (0.231 g, 0.608 mmol) of UCl$_4$ was added. The clear green solution was allowed to mix thoroughly, after which the solution of **K$_2$(L)** (*vide infra*) was added drop-wise over 5 min. The resulting solution turned dark brown and then became a cloudy golden yellow suspension during the addition of the dipotassium salt solution. The cloudy golden yellow suspension was allowed to stir overnight (approx. 12 h). Volatiles were then removed under vacuum, and the crude product was extracted with dichloromethane (~75 mL). The extraction products were then filtered over a bed of Celite on a 30 mL medium porosity frit under vacuum. The filtrate was then concentrated to dryness *in vacuo* and the product was isolated as a yellow powder. **Yield: 0.423 g, 81** %. The product was recrystallized from pyridine over the course of 2 weeks at room temperature. ^{1}H NMR (300 MHz, CDCl$_3$, 298 K): δ = 45.23 (2H), 41.73 (2H), 38.94 (2H), 28.30 (2H), 24.59 (2H), 23.97 (2H), 5.56 (6H,OCH_2CH_3), -10.29 (4H, THF), -11.19 (2H), -12.11 (2H), -15.58 (4H, THF), -19.93 (2H), -22.27 (2H), -89.80 (2H, *H*C=N). IR (cm^{-1}): 2973(C-H), 2927(C-H), 1614(C=N), 1598(C=C). Elemental analysis of $(L)UCl_2(THF)_2•CH_2Cl_2$: Theoretical C: 41.87, H: 4.90, N: 2.96; Actual: C: 42.30, H: 5.01, N: 3.17.

Synthesis of $(L)UCl_2(Py)_2$ ($1•Py_2$)

To a 20 mL scintillation vial charged with 8 mL of pyridine and a small stir bar, (0.250 g, 0.608 mmol) of **$(L)H_2$** was added. The clear yellow solution was allowed to mix thoroughly, after which 2 equiv of KO^tBu powder was added. The solution became cloudy upon addition of the KO^tBu, and was allowed to stir for 1 h. To a separate 20 mL scintillation vial charged with 3 mL of THF, 4 mL of Py and a small stir bar, (0.231 g, 0.608 mmol) of UCl_4 was added. The green solution was allowed to mix thoroughly, after which the solution of **$K_2(L)$** prepared separately was added drop-wise over 5 min. During the addition of **$K_2(L)$**, the solution turned cloudy yellow-green, and the resulting mixture was allowed to stir overnight (~18 h). Volatiles were removed *in vacuo* to afford a yellow-green powder. The crude product was then extracted with dichloromethane (~50 mL) and filtered over a bed of Celite on a medium porosity frit. The resulting yellow solution was collected in a 125 mL side arm flask and the volatiles were removed *in vacuo*, providing a yellow-green powder. **Yield: (0.423 g, 79 %)** ^1H NMR (400MHz, $CDCl_3$, 298 K) : δ 49.77 (2H), 44.54 (2H), 42.73 (2H), 31.14 (2H), 27.02 (2H), 25.02 (2H), 5.56 (6H, OCH_2CH_3), 0.47 (4H, Py), -4.37(1H, Py), -7.68(2H, Py), -11.44(2H), -12.85(2H), -20.51(2H), -22.29(2H), -90.82 (2H, *H*C=N).

Synthesis of (L)ThCl$_2$(THF)$_2$ (2):

A solution of **K$_2$(L)** was generated *in situ* by the method above using (0.200 g, 0.487 mmol) of the racemate of **(L)H$_2$** and (0.109 g, 0.971 mmol) of KO^{t}Bu. To a 20 mL scintillation vial charged with 5 mL of THF and a small stir bar, (0.270 g, 0.487 mmol) of ThCl$_4$(DME)$_2$ was added. The clear colorless solution was allowed to mix thoroughly, after which the solution of **K$_2$(L)** was added drop-wise over 5 min. The combined solution instantly turned cloudy and yellow upon addition of the dipotassium salt. The resulting suspension was allowed to stir overnight (~12 h), after which volatiles were removed *in vacuo*. The crude product was extracted with dicholormethane (~75 mL) and filtered over a bed of Celite on a 30 mL medium porosity frit. Volatiles were removed *in vacuo* to afford a yellow powder. **Yield: 0.302 g, 72 %**. The yellow powder was recrystallized from pyridine over 2 weeks at room temperature. ^{1}H NMR (400 MHz, D$_5$-Py, 298 K): δ = 8.70 (s, 2H, *H*C=N), 7.35 (d, 2H, $^3J_{HH}$ = 8 Hz, Ar-*H*), 7.20 (d, 2H, $^3J_{HH}$ = 8 Hz, Ar-*H*), 6.93 (t, 2H, $^3J_{HH}$ = 8 Hz, Ar-*H*), 4.66 (2H, m, cyclohexyl), 4.04 (4H, q, ^{3}J = 7 Hz, OCH_2CH$_3$), 2.25 (2H, m, cyclohexyl), 1.76 (2H, m, cyclohexyl), 1.40 (t, 6H, $^3J_{HH}$ = 8Hz, OCH$_2$CH_3), 1.17 (2H, m, cyclohexyl). ^{13}C NMR (100 MHz, D$_5$-Py, 298 K): δ = 163.41 (*C*=N), 152.76 (Ar-*C*), 149.10 (Ar-*C*), 127.32 (Ar-*C*), 125.00 (Ar-*C*), 117.48 (Ar-*C*), 115.98 (Ar-*C*), 67.76 (cyclohexyl), 63.51 (O*C*H$_2$CH$_3$) 30.50 (cyclohexyl), 24.66 (cyclohexyl), 15.03 (OCH$_2$*C*H$_3$). IR (cm^{-1}): 2973 (C-H), 2928 (C-H), 1611 (C=N), 1561 (C=C). Elemental analysis of (L)ThCl$_2$(THF)$_2$•(1.5 CH$_2$Cl$_2$): Theoretical: C: 41.29, H: 4.79, N: 2.83; Actual: C: 41.21, H:4.80, N: 3.27.

Synthesis of (L)U(N$_3$)$_2$(Py)$_2$ (3):

To a 20 mL scintillation vial charged with 8 mL of pyridine and a small stir bar, (0.115 g, 0.133 mmol) of (L)UCl$_2$(THF)$_2$ (**1**) was added. The resulting clear yellow-green solution was allowed to mix thoroughly and was heated to 70 °C, after which 6 equiv of NaN$_3$ (0.053 g, 0.800 mmol) was added. No immediate color changed was observed, but after 24 h the solution color changed from yellow-green to dark amber. The resulting solution was allowed to stir for 4 days, after which volatiles were removed under vacuum. The crude product was extracted with dichloromethane and filtered over a bed of Celite in a pasture pipette to afford a clear amber solution. Volatiles were removed under vacuum to yield a pale brown solid. The resulting solid was recrystallized slowly from dichloromethane and dark brown crystals were afforded within 24 h. **Yield 0.072 g, 61%**. ^{1}H NMR (300 MHz, CDCl$_3$, 298 K): δ 49.43 (2H), 42.37 (2H) ,40.25 (2H), 29.63 (2H), 26.20 (2H), 24.35 (2H), 5.32 (6H, OCH$_2$C*H$_3$*), -5.51 (1H), -10.95 (2H), -11.87 (2H), -19.66 (2H), -22.04 (2H), -86.81 (2H, *H*CN). IR (cm^{-1}): 2973 (C-H), 2055 (N$_3$), 1611 (C=N), 1599 (C=C). Elemental analysis of (L)U(N$_3$)$_2$(Py)$_2$•(1.5 Py, 1 CH$_2$Cl$_2$): Theoretical C: 46.73, H: 4.38, N: 14.75; Actual: C: 46.93, H: 4.64, N: 14.27.

Synthesis of (L)Th(N$_3$)$_2$(Py)$_2$ (4):

To a 20 mL scintillation vial charged with 10 mL of pyridine and 4 mL of THF, (0.075 g, 0.088 mmol) of (L)ThCl$_2$(THF)$_2$ (**2**) was added. The yellow translucent solution was allowed to mix thoroughly, after which approximately 8 equiv. of NaN$_3$ (0.046 g, 0.701 mmol) was added. The solution was heated to 80 °C and stirred for 4 days. The cloudy yellow suspension was filtered over Celite to give a pale-yellow solution and volatiles were removed *in vacuo* to afford a yellow solid. The crude product was then extracted with dichloromethane and filtered over Celite a second time, and volatiles were removed *in vacuo*. **Yield: 0.063 g, 82 %.** ^{1}H NMR (400 MHz, D$_5$-Py, 298 K): δ 8.85 (s, 2H, *H*C=N), 7.36 (d, 2H, $^3J_{HH}$ = 8Hz, Aryl), 7.18 (d, 2H, $^3J_{HH}$ = 8Hz, Ar-*H*), 6.92 (t, 2H, $^3J_{HH}$ = 8Hz, Ar-*H*), 4.28 (m, 2H, cyclohexyl), 4.04 (q, 4H, $^3J_{HH}$ = 8Hz, OCH_2CH_3), 2.36 (m, 2H, cyclohexyl), 1.77 (2H, m, cyclohexyl), 1.38 (m, 2H, cyclohexyl), 1.33 (t, 6H, $^3J_{HH}$ = 7 Hz, OCH_2CH_3). ^{13}C NMR (100 MHz, D$_5$-Py, 298 K): δ = 163.94 (*C*=N), 152.75 (Ar-*C*), 127.37 (Ar-*C*), 124.49 (Ar-*C*), 117.45 (Ar-*C*), 116.36 (Ar-*C*), 114.71 (Ar-*C*), 68.32 (cyclohexyl), 63.62 (OCH_2CH_3), 30.86 (cyclohexyl), 24.79 (cyclohexyl), 15.01 (OCH_2CH_3). IR (cm^{-1}): 2930 (C-H), 2061 (N_3), 1603 (C=N), 1558 (C=C). Elemental Analysis of $(L)Th(N_3)_2(Py)_2$•(1.5 CH_2Cl_2, 0.5 Py): Theoretical: C: 43.48, H: 4.18, N: 14.01; Actual: C: 43.46, H: 4.42, N: 13.69.

Synthesis of $(L)UO_2(Py)$ (5)

To a 20 mL scintillation vial charged with 8 mL of pyridine and a small stir bar, (0.100 g, 0.114 mmol) of $(L)UCl_2(Py)_2$ (**1-Py**) was added. The opaque yellow suspension was allowed to mix thoroughly, after which approximately 11 equiv of $NaNO_2$, (0.088 g, 1.26 mmol) were added to the solution. After approximately 1 h of stirring, the color of the solution changed from yellow to orange. The resulting solution was allowed to stir overnight (~12 h) at 60°C. Volatiles were removed *in vacuo* to afford an orange solid. The crude product was then extracted with dichloromethane (~14 mL) and filtered over a bed of Celite on a frit and volatiles were removed *in vacuo* to afford a bright orange solid. **Yield: 0.087g, quantitative yield**. The product was recrystallized slowly from $CDCl_3$ at room temperature as orange plate crystals. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ 10.81 (2H, Py), 9.26 (s, 2H, *H*C=N), 8.03 (1H, Py), 7.83 (2H, Py), 7.13 (d, 2H, $^3J_{HH}$ = 8 Hz, Ar-*H*), 7.11 (d, 2H, $^3J_{HH}$ = 8 Hz, Ar-*H*) 6.62 (*t*, 2H, $^3J_{HH}$ = 8 Hz, Ar-*H*), 4.15 (*q*, 4H, $^3J_{HH}$ = 7 Hz, OCH_2CH_3), 2.51 (m, 2H, cyclohexyl), 2.12 (m, 2H cyclohexyl), 1.93 (m, 2H, cyclohexyl), 1.58 (m, 2H, cyclohexyl) 1.53 (*t*, 6H, $^3J_{HH}$ = 8 Hz, OCH_2CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 165.84 (*C*=N), 159.68 (Ar-*C*), 150.62 (Ar-*C*), 125.76 (Ar-*C*), 123.83 (Ar-*C*), 117.02 (Ar-*C*), 116.47 (Ar-*C*), 71.04 (cyclohexyl-*C*), 64.34 (OCH_2CH_3), 32.11 (cyclohexyl-*C*), 25.14 (cyclohexyl-*C*), 15.44 (OCH_2CH_3). Elemental Analysis of (L)UO_2(Py)•(2 $CDCl_3$): Theoretical: C: 37.33, H: 3.64, N: 4.21; Actual: C: 36.88, H: 3.64, N: 4.18.

^{1}H, ^{13}C and HSQC NMR Spectra:

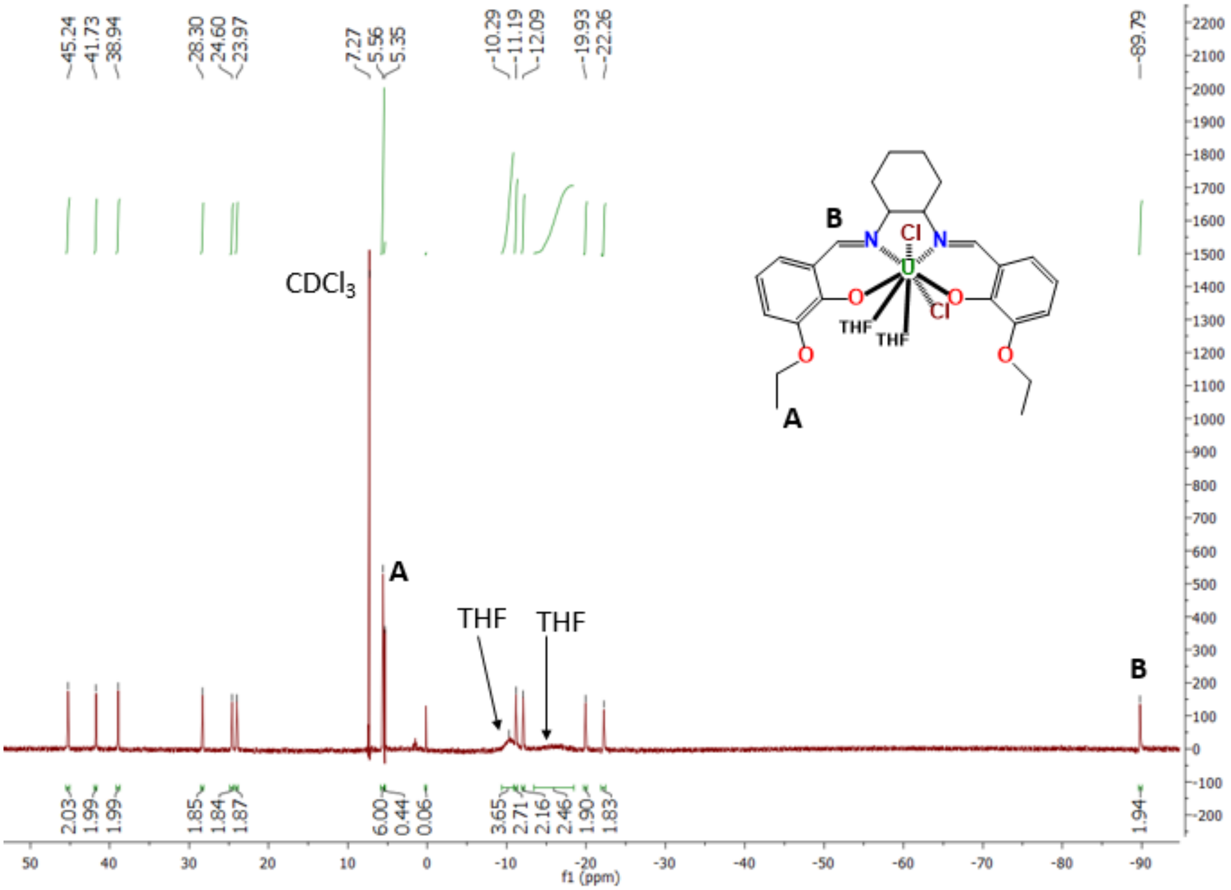

Figure S1-A. *^{1}H NMR spectrum of (L)UCl$_2$(THF)$_2$ (**1**) in CDCl$_3$.*

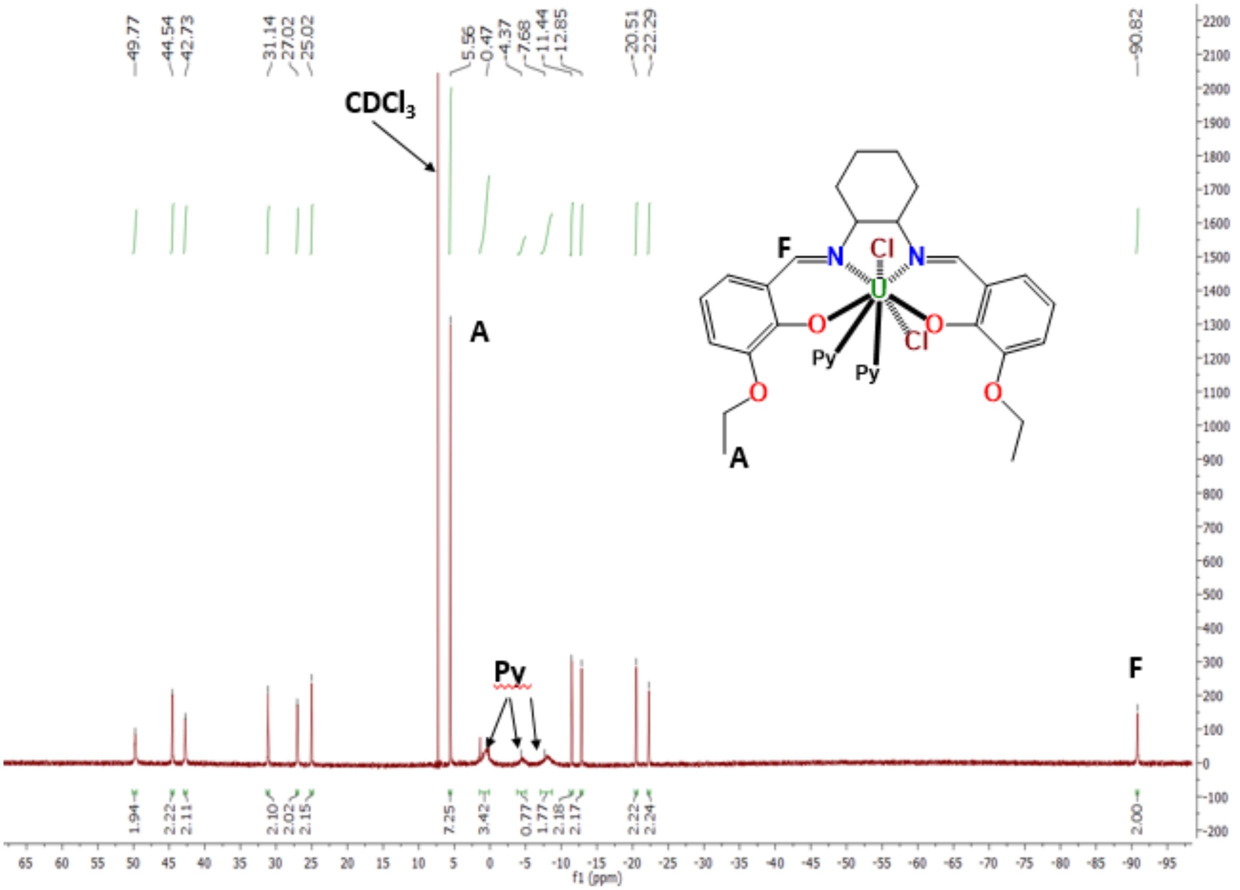

Figure S1-B: *^{1}H NMR Spectrum of (L)UCl$_2$(Py)$_2$ (**1•Py$_2$**) in CDCl$_3$.*

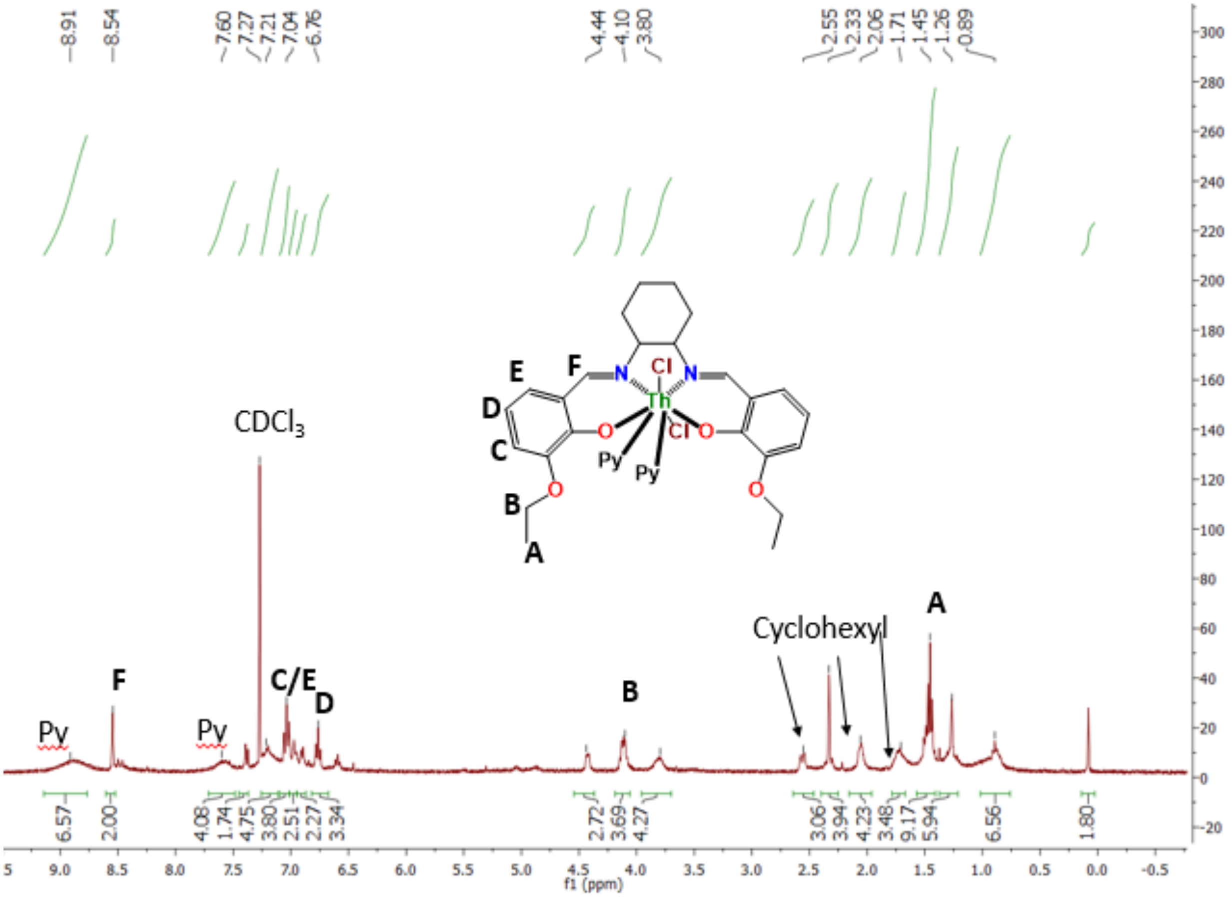

Figure S2-A. *^{1}H NMR Spectrum of (L)ThCl$_2$(Py)$_2$ (**2•Py$_2$**) in CDCl$_3$.*

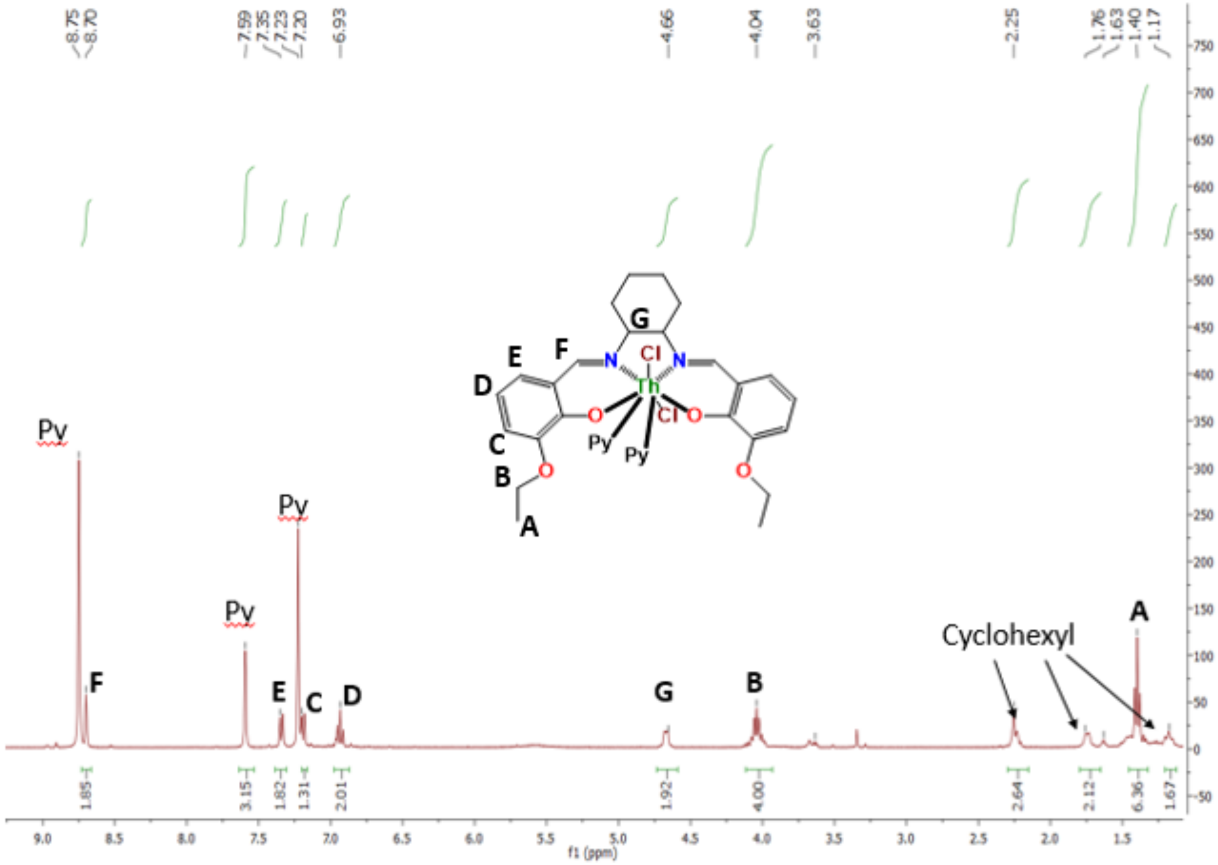

***Figure S2-B**: ^{1}H NMR Spectrum of (L)ThCl$_2$(Py)$_2$ (**2•Py$_2$**) in D$_5$-Py.*

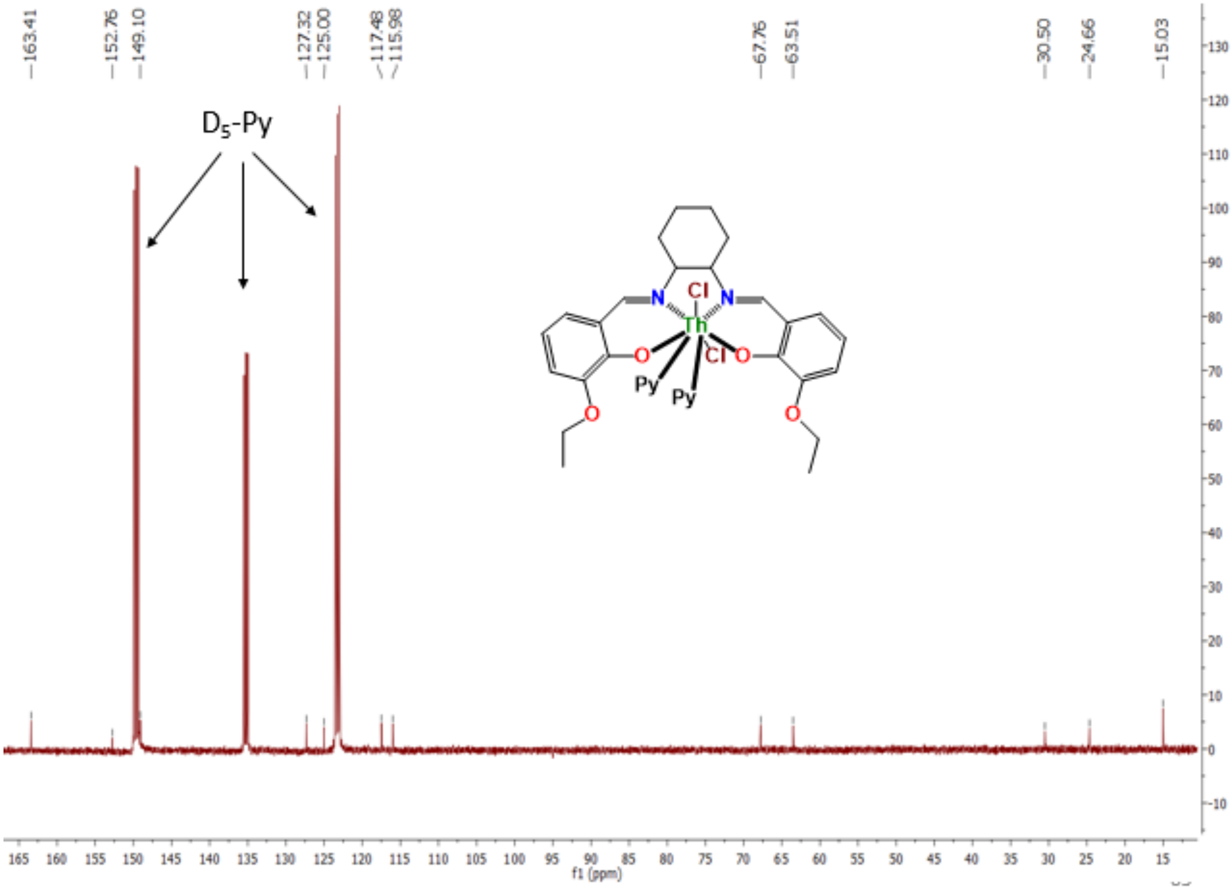

Figure S2-C: ^{13}C NMR Spectrum of (L)ThCl$_2$(Py)$_2$ (**2•Py$_2$**) in D$_5$-Py.

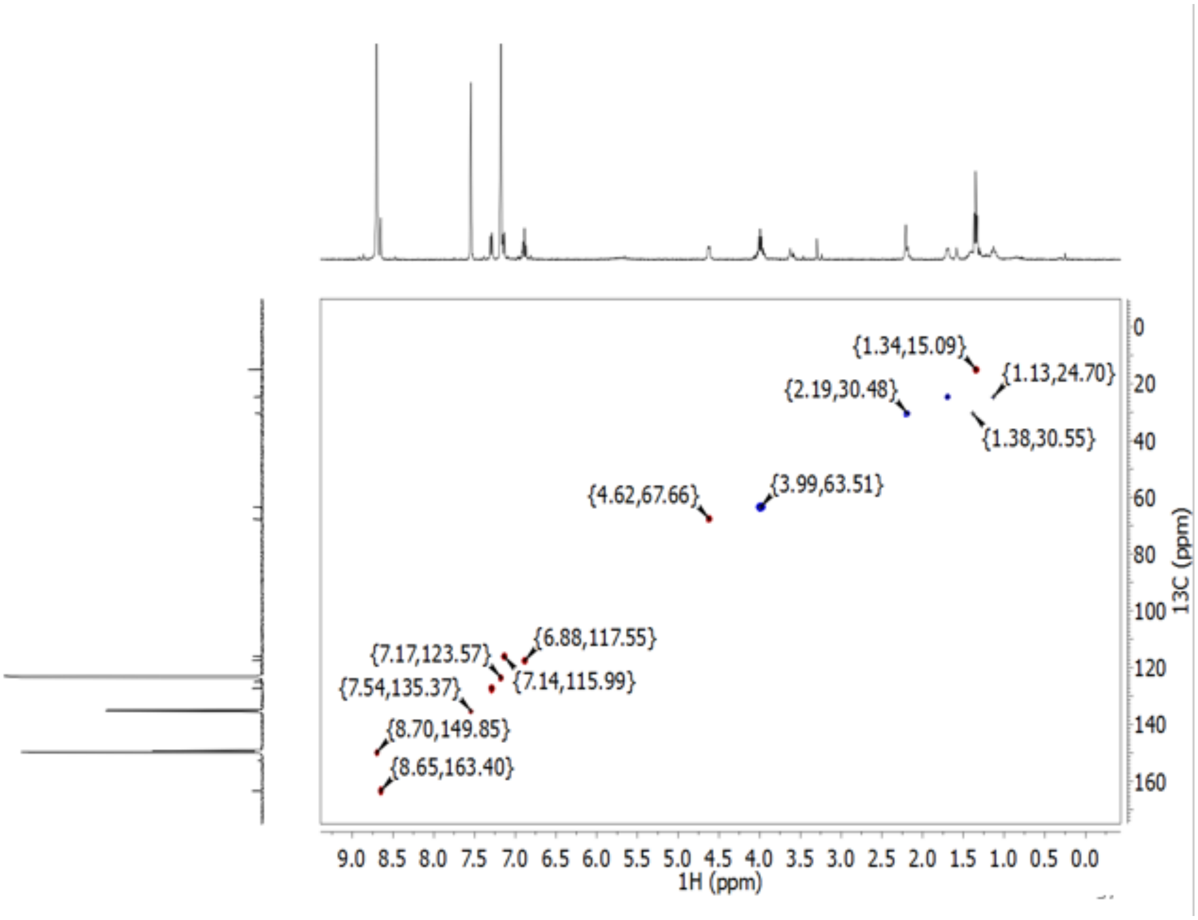

Figure S2-D: *HSQC Spectrum of (L)ThCl$_2$(Py)$_2$ (**2•Py$_2$**) in D$_5$-Py.*

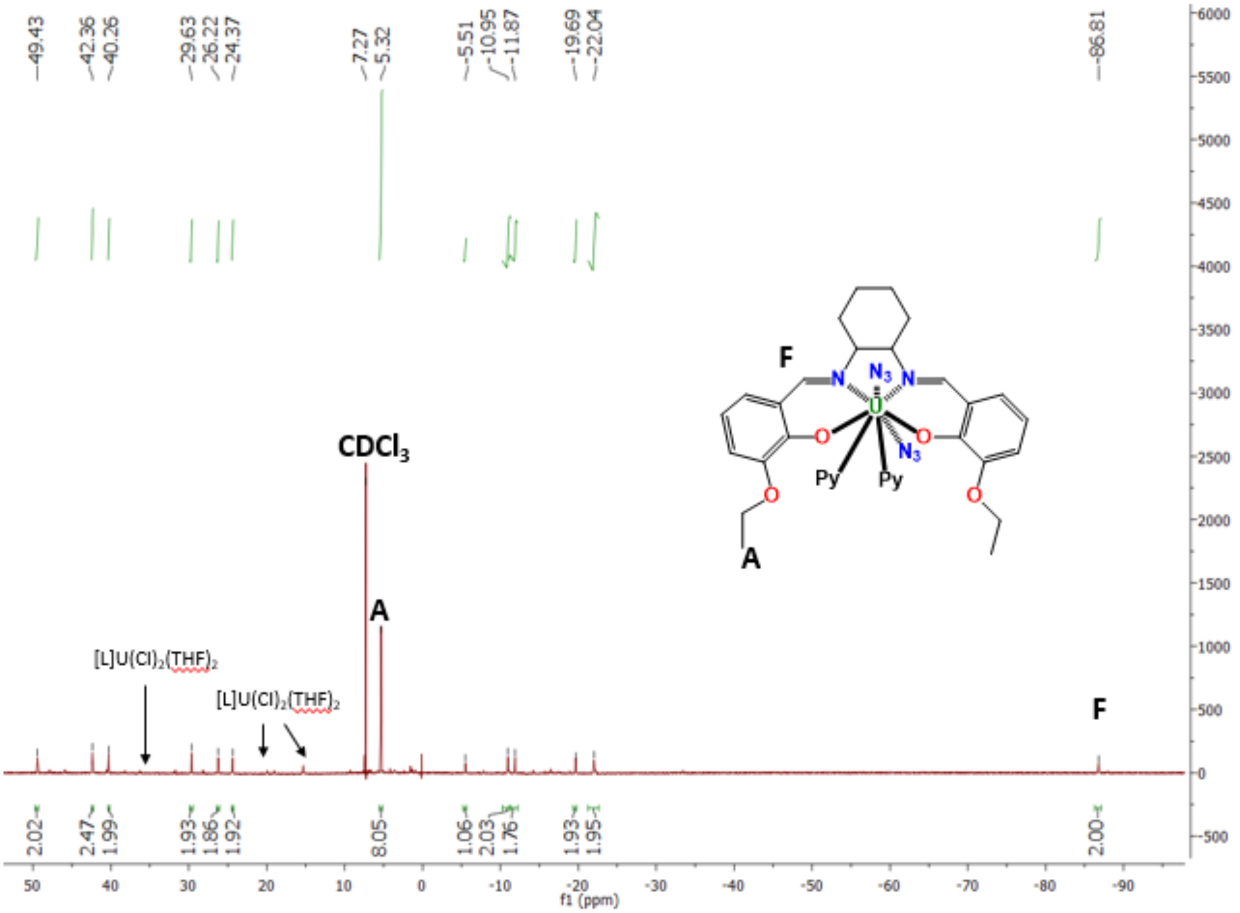

Figure S3. *^{1}H NMR Spectrum of (L)U(N_3)$_2$(Py)$_2$ (**3**) in $CDCl_3$*. (~3% (L)UCl_2(THF)$_2$ impurity).

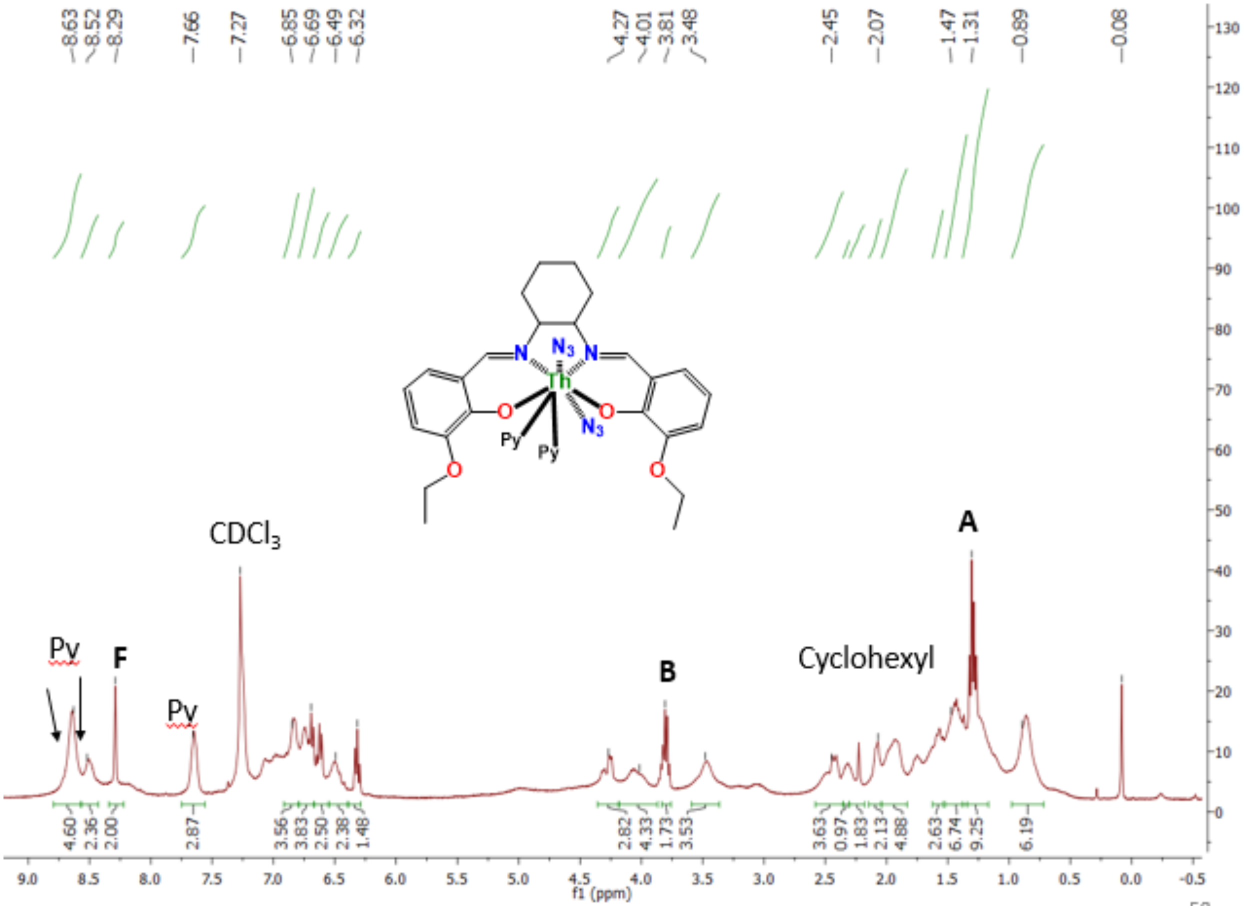

Figure S4-A. *^{1}H NMR Spectrum of (L)Th$(N_3)_2$(Py) (**4**) in $CDCl_3$.*

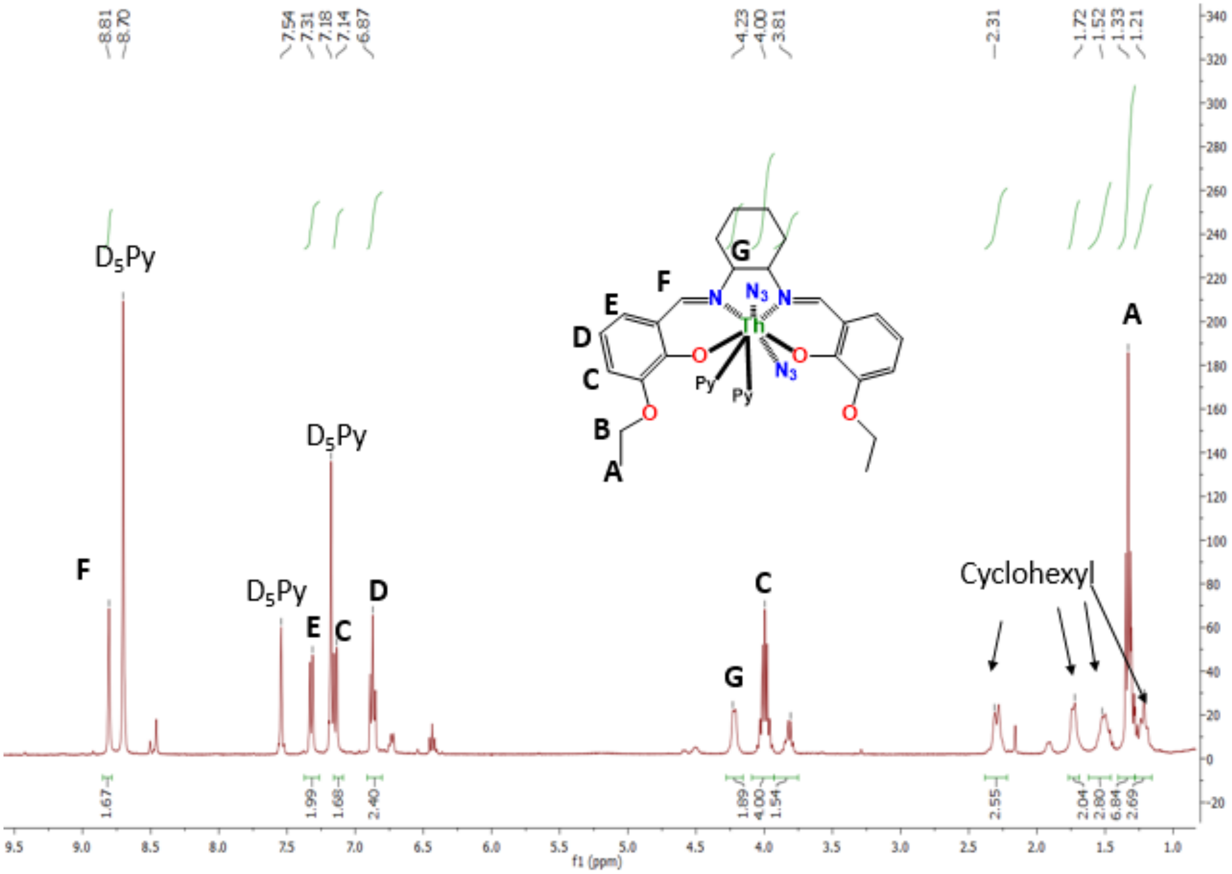

***Figure S4-B**: ^{1}H NMR Spectrum of (L)Th(N_3)$_2$(Py) (**4**) in D_5-Py (unassigned peaks are (L)ThCl$_2$(Py)$_2$) (**2**).*

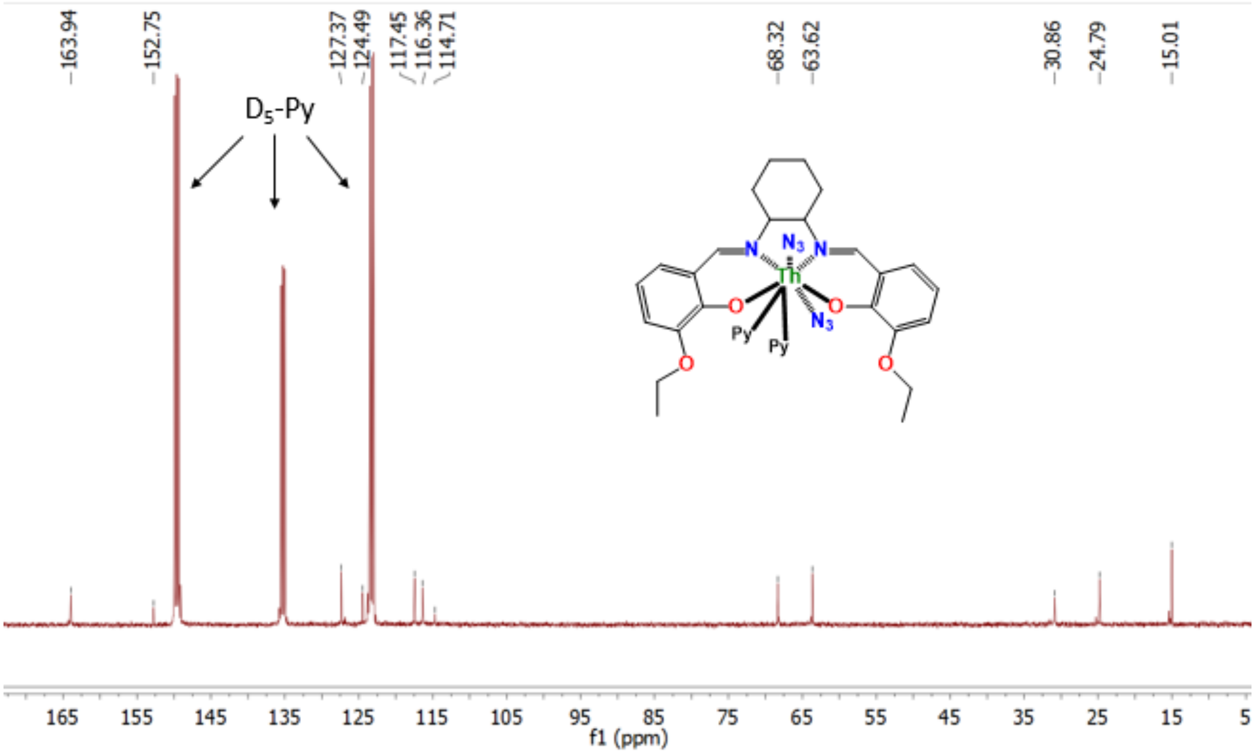

Figure S4-C: *^{13}C NMR Spectrum of (L)Th(N_3)$_2$(Py) (**4**) in D_5-Py.*

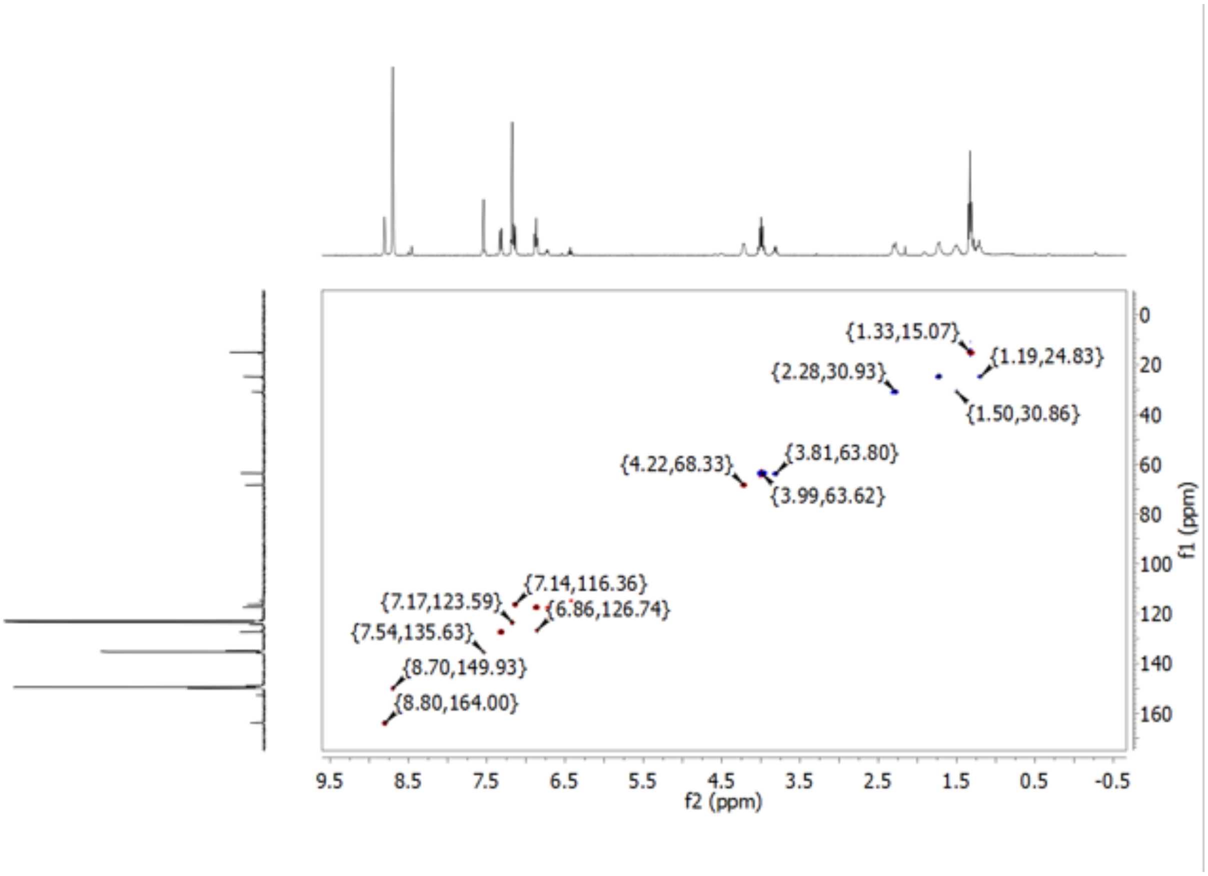

***Figure S4-D**: HSQC Spectrum of (L)Th(N_3)$_2$(Py) (**4**) in D_5-Py.*

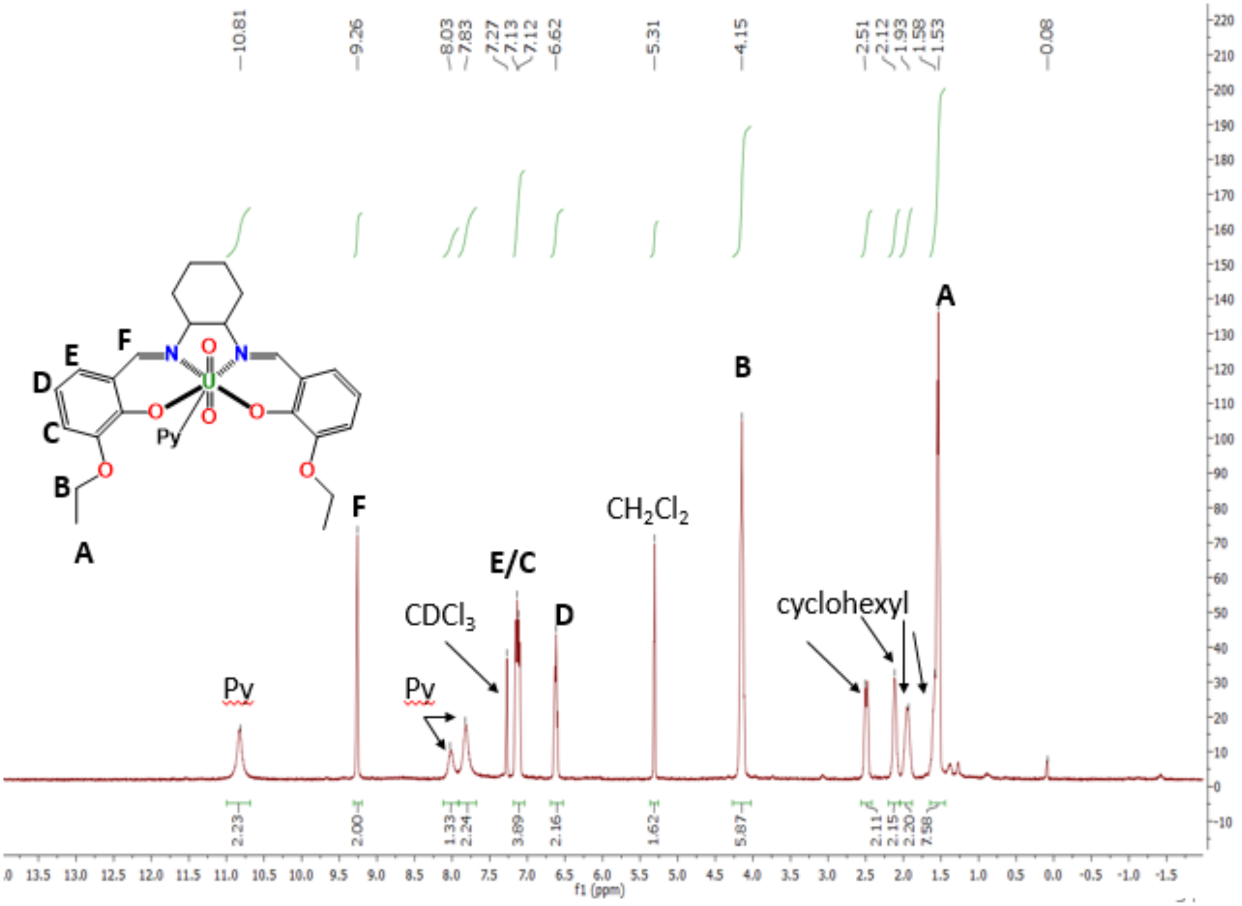

Figure S5-A. *^{1}H NMR Spectrum of (L)UO_2(Py) (**5**) in $CDCl_3$.*

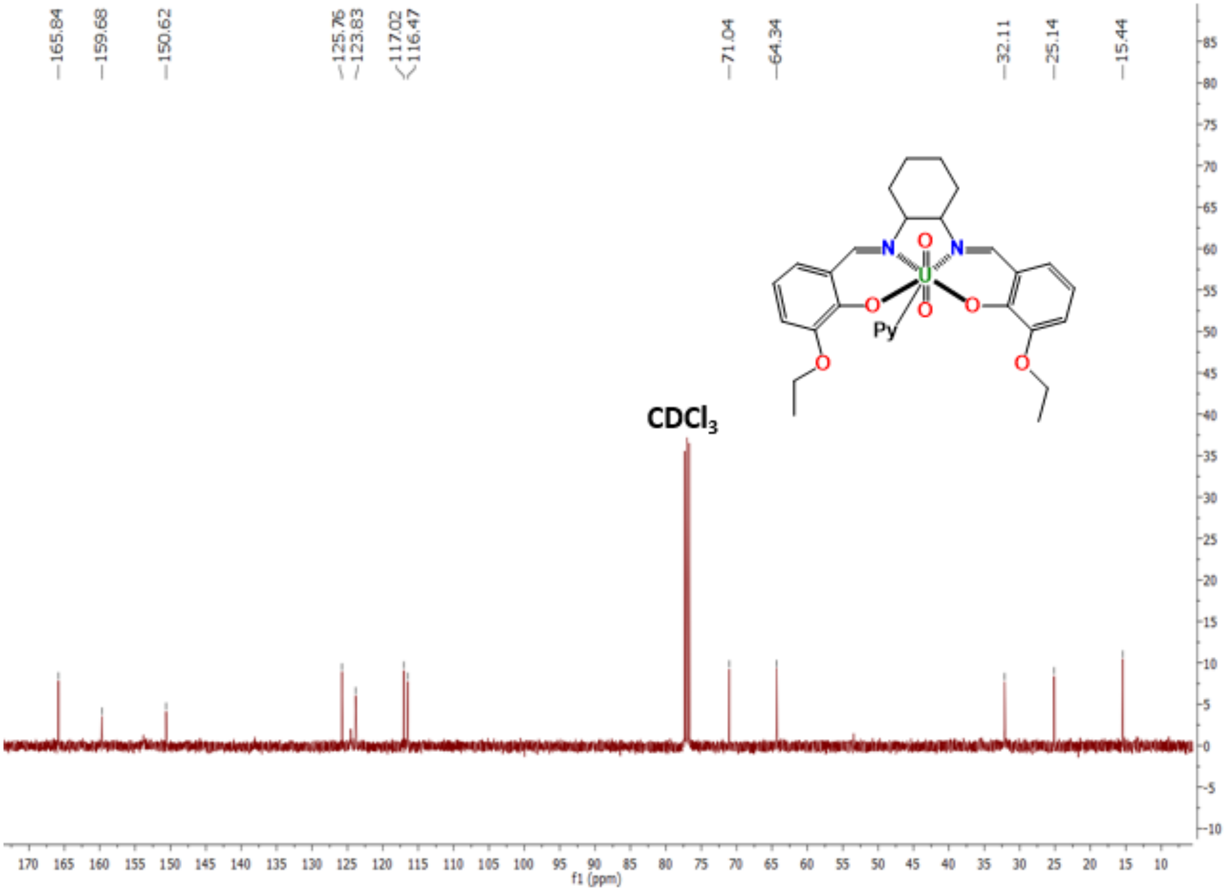

Figure S5-B: *^{13}C NMR Spectrum of (L)UO$_2$(Py) (**5**) in CDCl$_3$.*

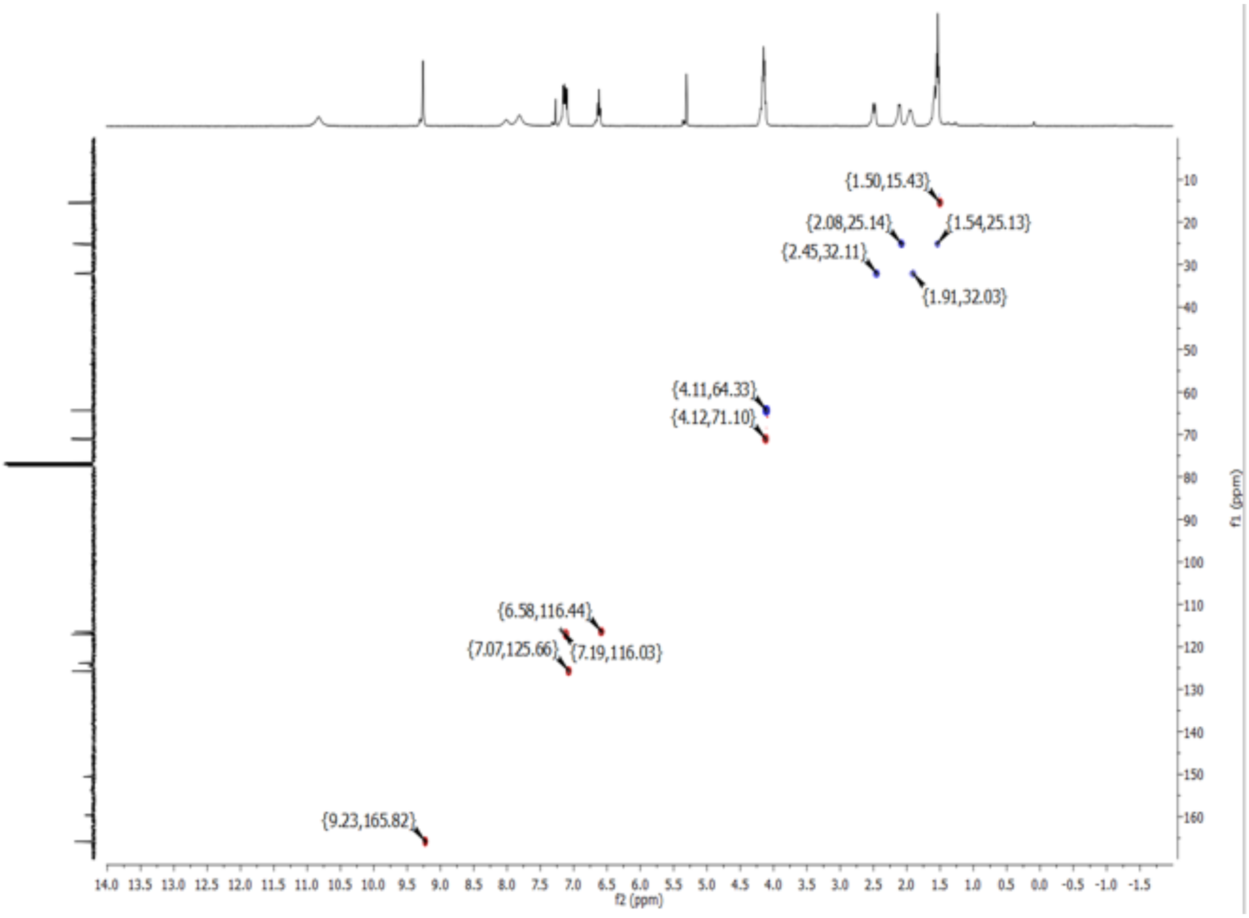

Figure S5-C: *HSQC Spectrum of (L)UO$_2$(Py) (**5**) in CDCl$_3$.*

IR Spectra:

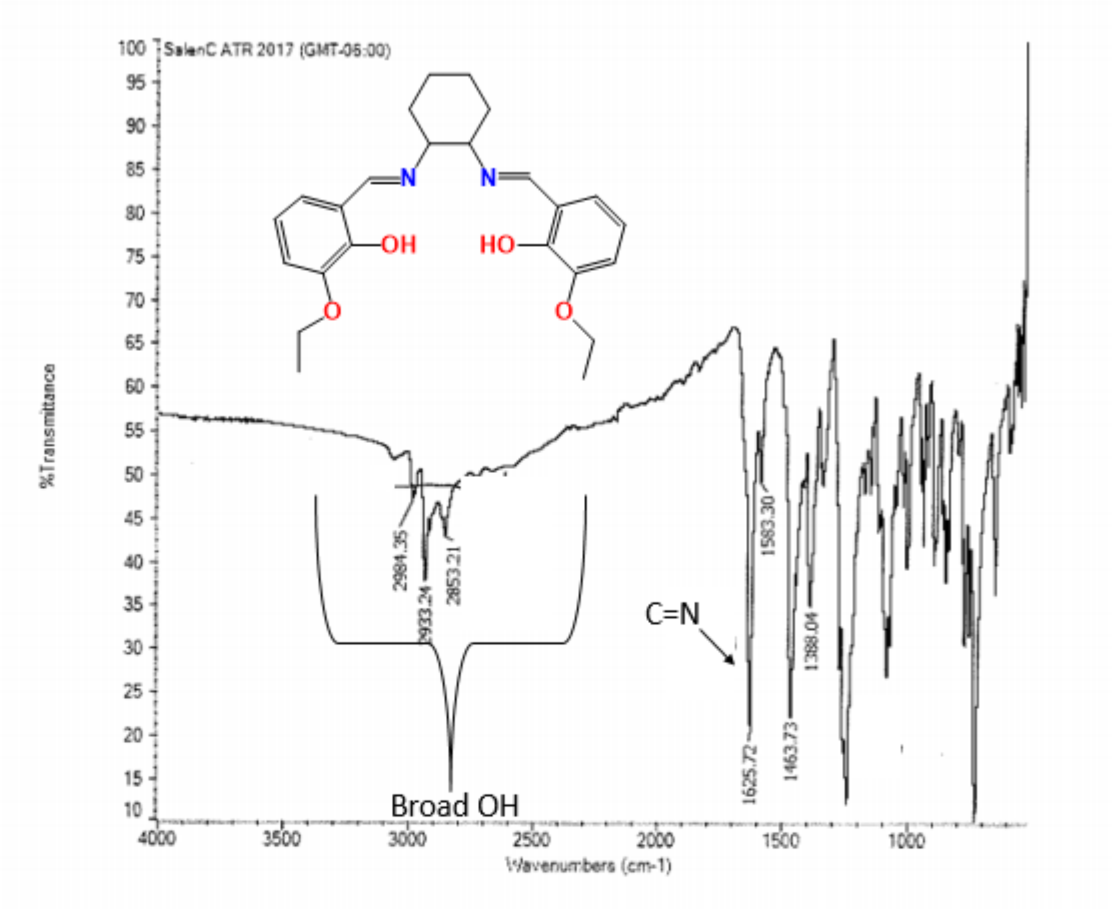

Figure S6. *Infrared Spectrum of Schiff Base Proligand (**L**)**H_2**.*

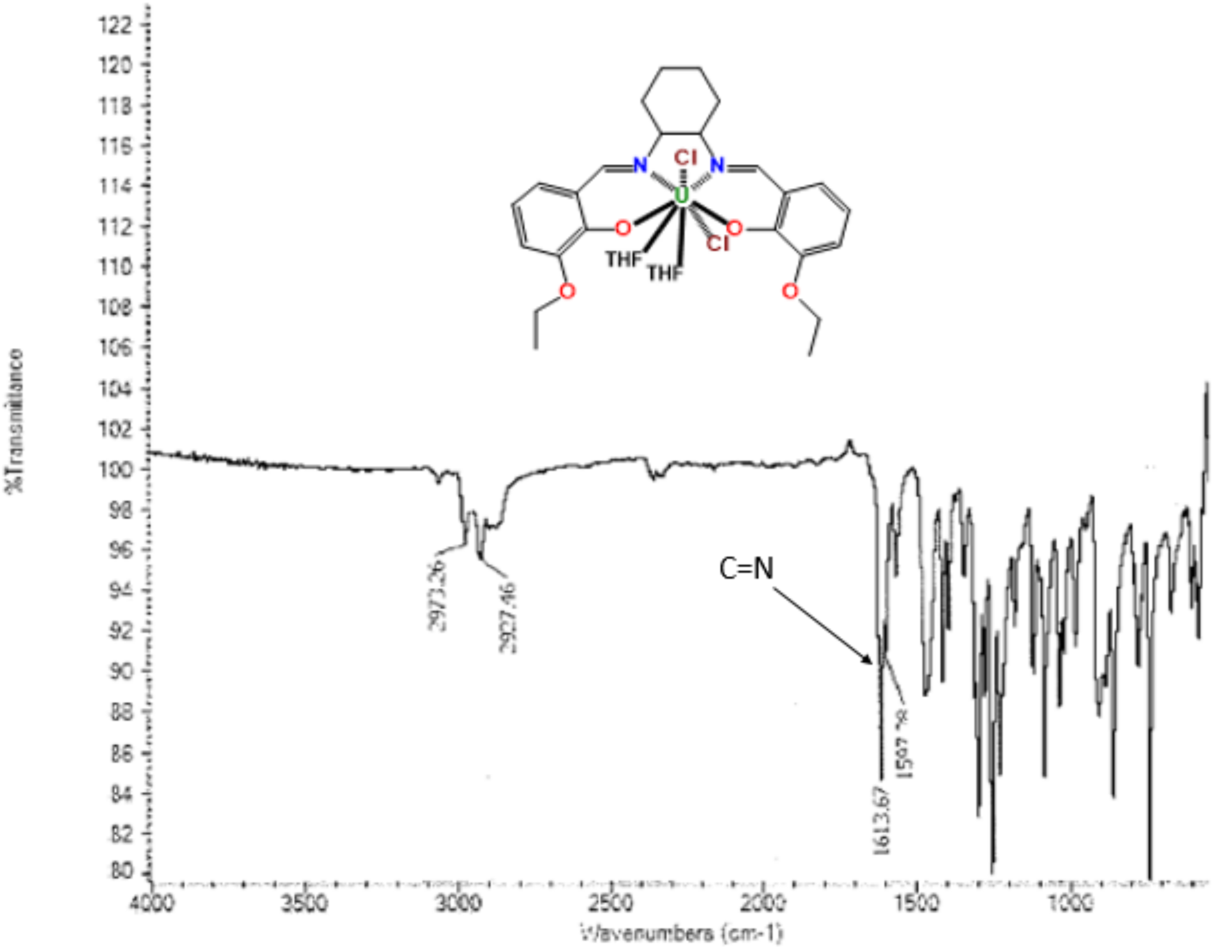

Figure S7. *Infrared Spectrum of* $(L)UCl_2(THF)_2$ *(**1**).*

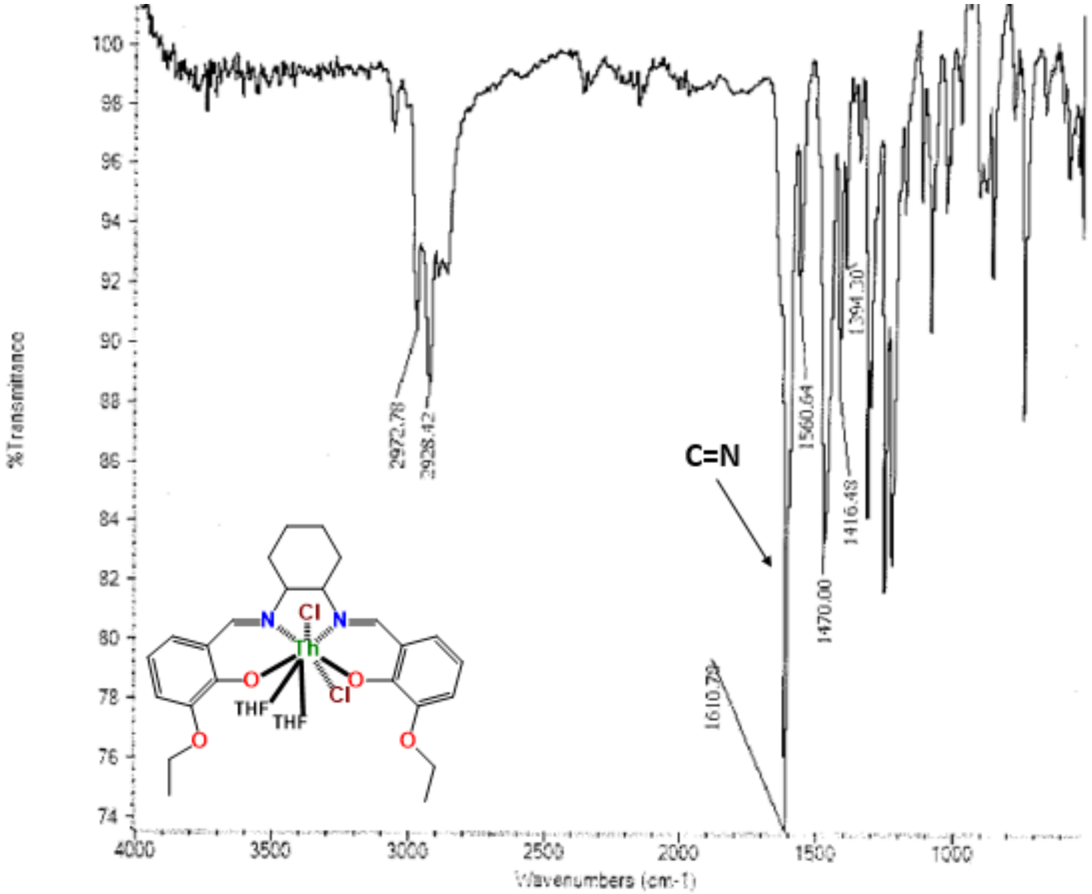

Figure S8. *Infrared Spectrum of (L)ThCl$_2$(THF)$_2$ (**2**).*

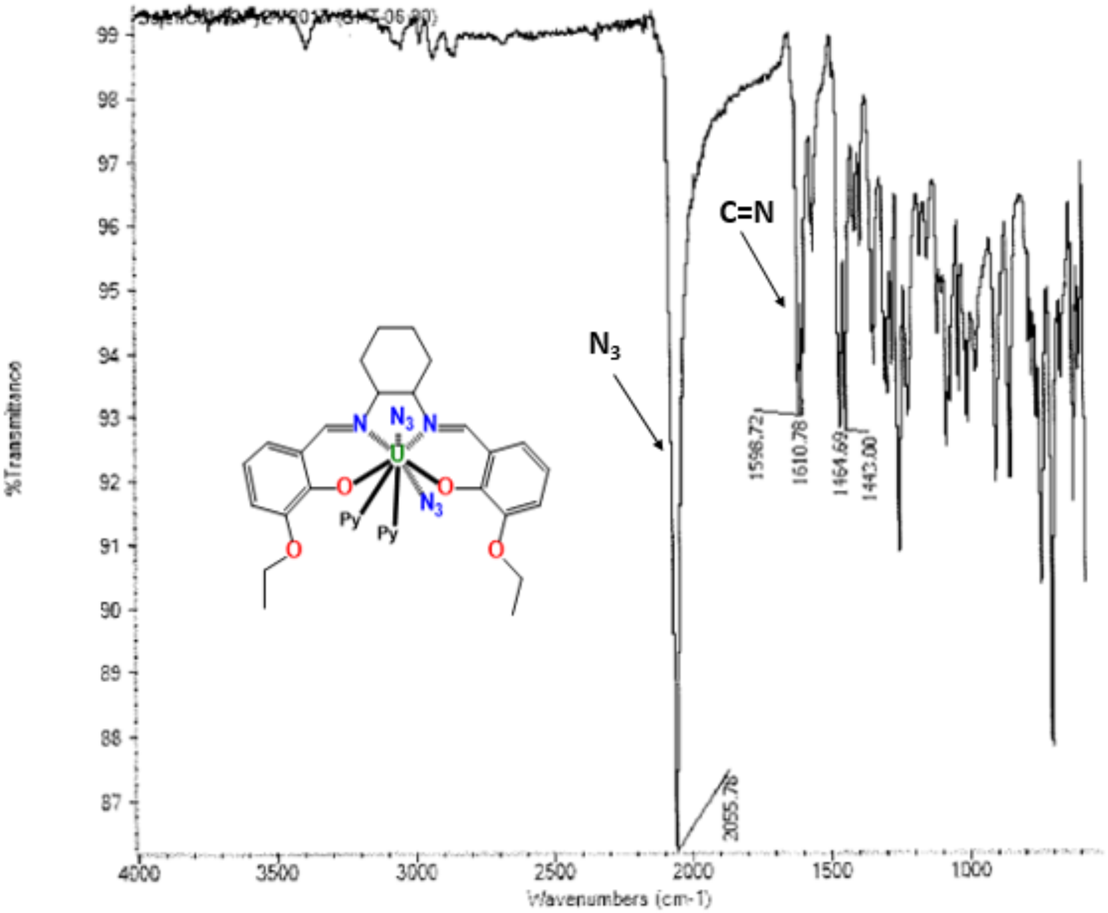

Figure S9. *Infrared Spectrum of (L)U(N_3)$_2$(Py)$_2$ (**3**).*

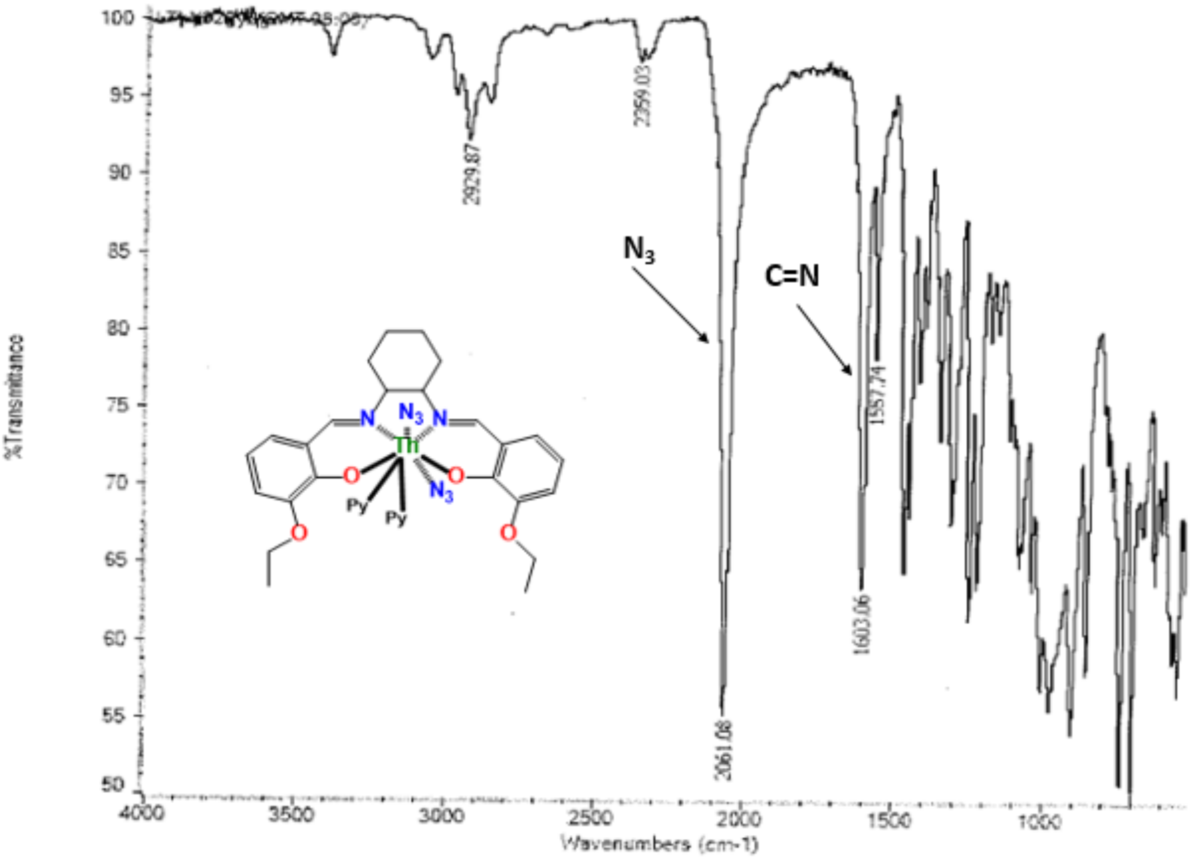

__Figure S10.__ Infrared Spectrum of (L)Th$(N_3)_2(Py)_2$ (__4__).

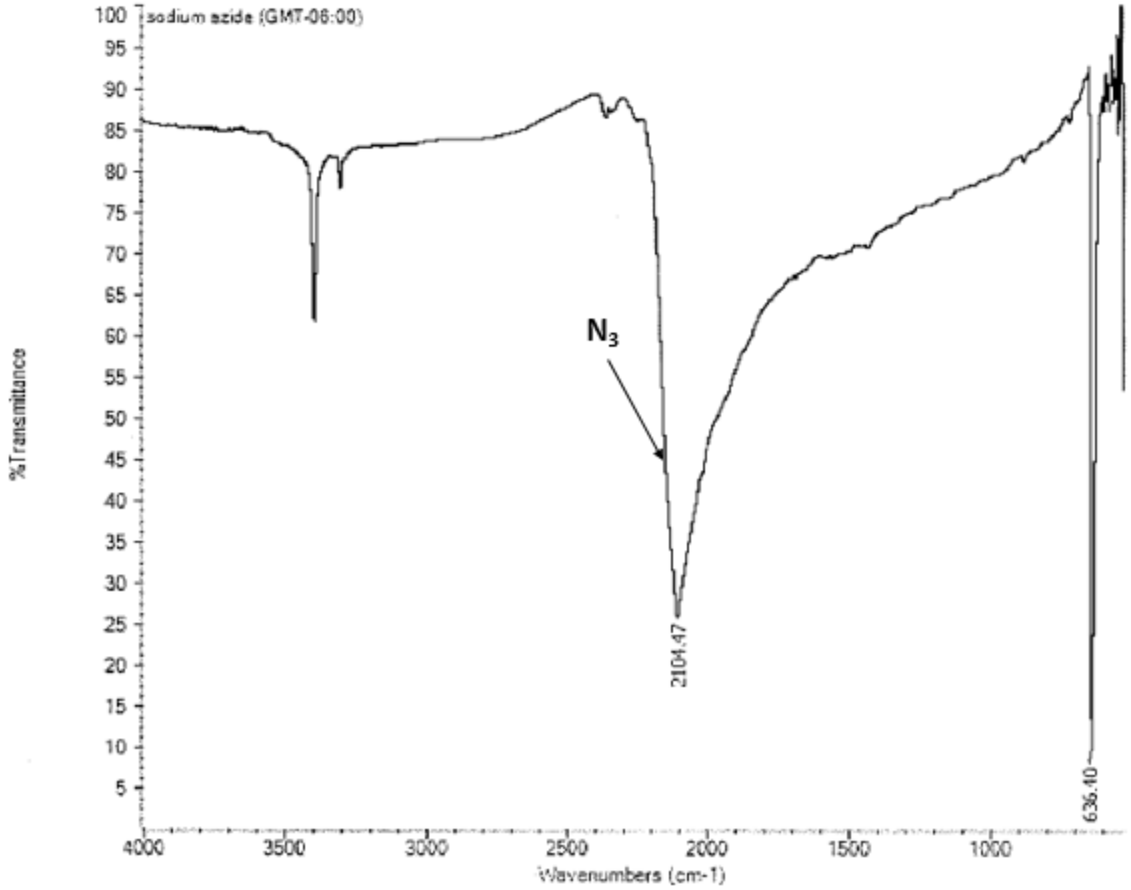

Figure S11. *Infrared Spectrum of* NaN_3.

X-Ray Diffraction Data:

*X-Ray Diffraction Data for (L)UCl$_2$(Py)$_2$ (**1•Py$_2$**).*

Empirical formula	$C_{34}H_{38}Cl_2N_4O_4U$	
Formula weight	875.61	
Crystal system	monoclinic	
Space group	*C2/c*	
Unit cell dimensions	*a* = 19.233(6) Å	α= 90°
	b = 19.034(6) Å	β= 122.796(3)°
	c = 12.202(4) Å	γ= 90°
Volume	3755(2) Å^3	
Z, Z'	4, 0.5	
Density (calculated)	1.549 Mg/m^3	
Wavelength	0.71073 Å	
Temperature	100(2) K	
F(000)	1712	
Absorption coefficient	4.504 mm^{-1}	
Absorption correction	semi-empirical from equivalents	
Max. and min. transmission	0.687 and 0.411	
Theta range for data collection	1.653 to 27.517°	
Reflections collected	24171	
Independent reflections	4301 [R(int) = 0.0666]	
Data / restraints / parameters	4301 / 0 / 204	
wR(F^2 all data)	*wR*2 = 0.1424	
R(*F* obsd data)	*R*1 = 0.0424	
Goodness-of-fit on F^2	1.020	
Observed data [I > 2σ(I)]	3346	
Largest and mean shift / s.u.	0.000 and 0.000	
Largest diff. peak and hole	2.368 and -2.619 e/Å^3	

$wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$

$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$

*X-ray Diffraction Data for (L)ThCl$_2$(Py)$_2$ (**2•Py$_2$**).*

Empirical formula	$(C_{34}H_{38}Cl_2N_4O_4Th) \cdot (C_5H_5N)$ $C_{39}H_{43}Cl_2N_5O_4Th$	
Formula weight	948.72	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 16.806(13) Å	α= 90°
	b = 14.283(11) Å	β= 92.515(14)°
	c = 15.268(12) Å	γ= 90°
Volume	3661(5) Å^3	
Z, Z'	4, 1	
Density (calculated)	1.721 Mg/m^3	
Wavelength	0.71073 Å	
Temperature	100(2) K	
F(000)	1872	
Absorption coefficient	4.267 mm^{-1}	
Absorption correction	semi-empirical from equivalents	
Max. and min. transmission	0.726 and 0.675	
Theta range for data collection	2.268 to 22.464°	
Reflections collected	85853	
Independent reflections	4595 [R(int) = 0.2301]	
Data / restraints / parameters	4595 / 493 / 462	
$wR(F^2$ all data)	$wR2$ = 0.2203	
$R(F$ obsd data)	$R1$ = 0.1052	
Goodness-of-fit on F^2	1.071	
Observed data [$I > 2\sigma(I)$]	2708	
Largest and mean shift / s.u.	0.004 and 0.000	
Largest diff. peak and hole	2.233 and -1.716 e/Å^3	

$wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$

$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$

*X-ray Diffraction Data for (L)U$(N_3)_2$$(Py)_2$ (**3**).*

Comment:

This sample was a 3-component twin. The intensity data were effectively detwinned by the data reduction and scaling programs. A dichloromethane molecule was severely disordered and was eliminated using the Squeeze program.[4]

Empirical formula	$C_{34} H_{38} N_{10} O_4 U$	
Formula weight	888.77	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 16.872(4) Å	α= 90°
	b = 15.338(3) Å	β= 93.301(2)°
	c = 15.062(3) Å	γ= 90°
Volume	3891.3(14) $Å^3$	
Z, Z'	4, 1	
Density (calculated)	1.517 Mg/m^3	
Wavelength	0.71073 Å	
Temperature	100(2) K	
F(000)	1744	
Absorption coefficient	4.219 mm^{-1}	
Absorption correction	semi-empirical from equivalents	
Max. and min. transmission	0.237 and 0.154	
Theta range for data collection	1.897 to 26.257°	
Reflections collected	81766	
Independent reflections	7117 [R(int) = 0.1176]	
Data / restraints / parameters	7117 / 0 / 442	
wR(F^2 all data)	$wR2$ = 0.1202	
R(F obsd data)	$R1$ = 0.0468	
Goodness-of-fit on F^2	1.001	
Observed data [I > 2σ(I)]	4959	
Largest and mean shift / s.u.	0.003 and 0.000	
Largest diff. peak and hole	1.574 and -1.971 e/$Å^3$	

$wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o{}^2)^2] \}^{1/2}$

$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$

*X-ray Diffraction Data for exo-(L)U(N_3)$_2$(Py)$_2$ (**3-exo**).*

Comment:

The selected crystal was split. The intensity data were corrected by data reduction and scaling programs.[5-7] Three parts of the structure were disordered. The occupancies of atoms C(1) and C(2) refined to 0.727(8) and 0.273(8) for the unprimed and primed atoms, respectively. The occupancies of atoms C(10) – C(15) refined to 0.750(5) and 0.250(5) for the unprimed and primed atoms, respectively. The occupancies of the toluene molecule refined to 0.660(5) and 0.340(5) for the A- and B-labeled atoms, respectively. Restraints on the positional parameters of the disordered atoms and the displacement parameters of all atoms were required.

Empirical formula	$(C_{34}H_{38}N_{10}O_4U) \cdot (C_7H_8)$	
	$C_{41}H_{46}N_{10}O_4U$	
Formula weight	980.91	
Crystal system	triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 9.572(5) Å	α= 76.878(2)°
	b = 13.791(7) Å	β= 86.987(2)°
	c = 16.103(2) Å	γ= 71.973(2)°
Volume	1968.2(15) $Å^3$	
Z, Z'	2, 1	
Density (calculated)	1.655 Mg/m^3	
Wavelength	0.71073 Å	
Temperature	100(2) K	
$F(000)$	972	
Absorption coefficient	4.179 mm^{-1}	
Absorption correction	semi-empirical from equivalents	
Max. and min. transmission	0.680 and 0.279	
Theta range for data collection	1.299 to 31.673°	
Reflections collected	90881	
Independent reflections	11866 [R(int) = 0.0574]	
Data / restraints / parameters	11866 / 1149 / 648	
$wR(F^2$ all data)	$wR2$ = 0.0945	
$R(F$ obsd data)	$R1$ = 0.0420	
Goodness-of-fit on F^2	0.990	
Observed data [$I > 2\sigma(I)$]	9414	
Largest and mean shift / s.u.	0.003 and 0.000	
Largest diff. peak and hole	2.478 and -1.960 e/$Å^3$	

$wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^{\ 2})^2] \}^{1/2}$

$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$

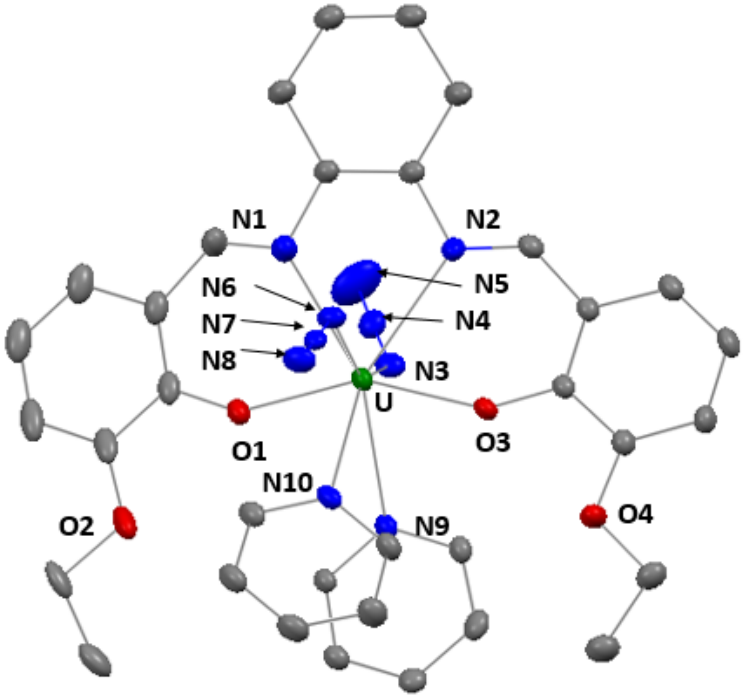

Figure S12. *ORTEP Depiction of exo-(L)U(N$_3$)$_2$(Py)$_2$ (**3-exo**).*

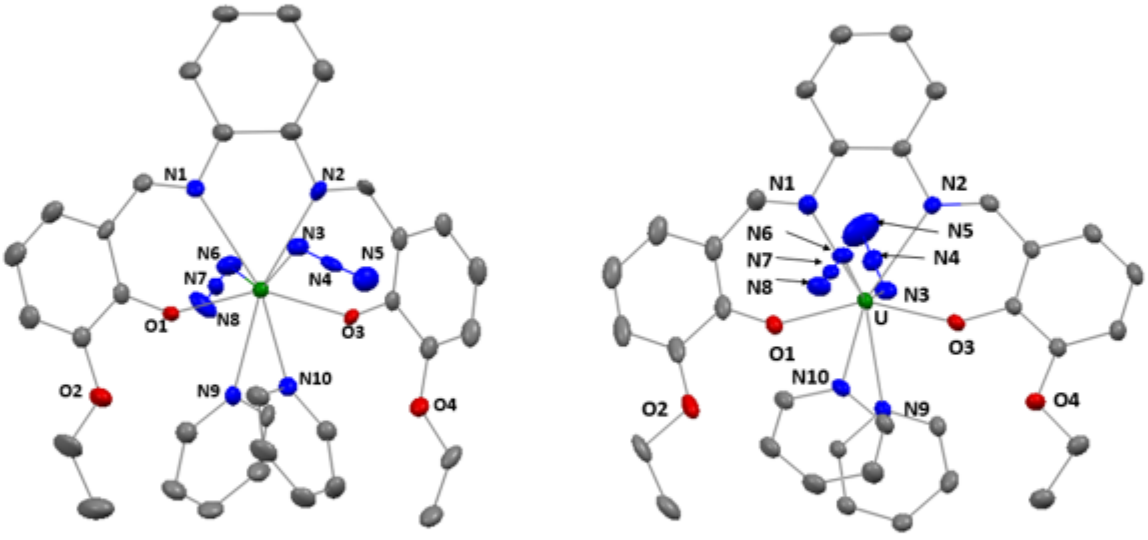

Figure S13. *Comparison of Solid-State Structures of Complexes (**3**) (left) and (**3-exo**) (right).*

*X-ray Diffraction Data for (L)UO_2(Py) (**5**).*

Empirical formula	$(C_{29}H_{33}N_3O_6U) \cdot (CDCl_3)$ $C_{30}H_{33}Cl_3DN_3O_6U$	
Formula weight	877.99	
Crystal system	monoclinic	
Space group	*C*2/*c*	
Unit cell dimensions	*a* = 27.313(4) Å	α= 90°
	b = 9.2102(13) Å	β= 97.694(2)°
	c = 26.618(4) Å	γ= 90°
Volume	6635.7(17) Å^3	
Z, Z'	8, 1	
Density (calculated)	1.758 Mg/m^3	
Wavelength	0.71073 Å	
Temperature	295(2) K	
F(000)	3408	
Absorption coefficient	5.179 mm^{-1}	
Absorption correction	semi-empirical from equivalents	
Max. and min. transmission	0.860 and 0.297	
Theta range for data collection	1.505 to 28.359°	
Reflections collected	76032	
Independent reflections	8293 [R(int) = 0.0561]	
Data / restraints / parameters	8293 / 38 / 433	
wR(F^2 all data)	*wR*2 = 0.1016	
R(*F* obsd data)	*R*1 = 0.0355	
Goodness-of-fit on F^2	0.977	
Observed data [I > 2σ(I)]	6454	
Largest and mean shift / s.u.	0.001 and 0.000	
Largest diff. peak and hole	1.579 and -1.017 e/Å^3	

$wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o{}^2)^2] \}^{1/2}$

$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$

References

1. Constable, E.C.; Zhang, G.; Housecroft, C. E.; Neuburger, M.; Schaffner, S. *CrystEngComm* **2009**, *11*, 657-662.

2. Kiplinger, J. L.; Morris, D. E.; Scott, B. L.; Burns, C. J. *Organometallics* **2002**, *21*, 5978.

3. Cantat, T., Scott, B. L., Kiplinger, J. *Chem. Commun.* **2010**, *46*, 919-921.

4. Spek, A. L. *Acta Cryst.* **2015**, *C71*, 9.

5. (a) Data Collection: APEX2 (**2007**) Bruker AXS Inc., Madison, Wisconsin, USA. (b) Data Reduction: SAINT (**2007**) Bruker AXS Inc., Madison, Wisconsin, USA.

6. Krause, L.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D. *J. Appl. Cryst.* **2015**, *48*, 3-10.

7. (a) Sheldrick, G. M. *Acta Cryst.* **2015**, *A71*, 3. (b) Sheldrick, G. M. *Acta Cryst.* **2015**, *C71*, 3.