Electronic Supplementary Material (ESI) for Dalton Transactions.

Homoleptic U(IV) and U(III) Amidate Complexes

Supplementary Information

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A. Experimental Section

Methods and Materials

Unless otherwise noted, all syntheses were performed using standard Schlenk techniques under an atmosphere of nitrogen or in an MBraun glovebox under an atmosphere of nitrogen. Glassware, cannulae, and Celite were stored in an oven at 160 ^{o}C for at least 12 hours prior to use. 3 Å and 4 Å molecular sieves were activated by heating under vacuum at 300 ^{o}C for 24 hours. Hexane, pentane, toluene, benzene, diethyl ether, tetrahydrofuran, 1,2-dimethoxyethane (DME), and acetonitrile were purified by passage through a column of activated alumina prior to use. Hexamethyldisiloxane (HMDSO) was stirred over sodium/benzophenone prior to distillation and stored over 4 Å molecular sieves. C_6D_6 and d^8-THF were purchased from Cambridge Isotope Labs and stored over 4 Å molecular sieves. C_5D_5N was purchased from Cambridge Isotope Labs, stirred over CaH_2, transferred under vacuum, and stored over 3 Å molecular sieves. $KN(SiMe_3)_2$ was recrystallized from hot toluene prior to use. H(TDA) **(1)** was prepared according to literature methods[1] and purified by sublimation at 250 ^{o}C, 10 mTorr. UI_4(1,4-dioxane)$_2$ and UI_3(1,4-dioxane)$_{1.5}$ were prepared according to literature methods.[2] All other chemicals were purchased from Sigma-Aldrich or Acros Organics and used as received. ^{1}H and ^{13}C NMR spectra were recorded at room temperature using Bruker AV-600, AV-500, and AVB-400 spectrometers. ^{1}H chemical shifts were referenced to C_6D_5H (δ = 7.16 ppm), C_5D_4HN (δ_1 = 8.74 ppm), and C_4D_7HO (δ_2 = 1.78 ppm). ^{13}C chemical shifts were referenced to C_6D_6 (δ = 128.39 ppm) and C_5D_5N (δ_1 = 150.35 ppm). Samples for IR spectroscopy were prepared as Nujol mulls, and spectra were taken in KBr plates using a Nicolet iS10 spectrometer. Melting points were determined in sealed tubes under an atmosphere of nitrogen using a Stanford Research Systems OptiMelt instrument and are reported uncorrected.

X-Ray Crystallography

X-ray structural determination was performed at CHEXRAY, University of California, Berkeley, on a Bruker APEX II Quazar diffractometer or at the Advanced Light Source (ALS) station 11.3.1 at Lawrence Berkeley National Laboratory. The Bruker Quazar is a Kappa geometry three-circle diffractometer that couples a charge-coupled device (CCD) detector with a sealed-tube source of monochromatized Mo Kα radiation. Structural data collected at ALS station 11.3.1 utilized a silicon monochromated beam of 16 keV (λ = 0.7749 Å) synchrotron radiation.

Crystals of appropriate size and quality were coated in Paratone-N oil and mounted on a Kaptan loop. The loop was transferred to the diffractometer, centered in the beam, and cooled by a nitrogen flow low-temperature apparatus that had been previously calibrated by a thermocouple placed at the same position as the crystal. All data collections were carried out at 100 K. The data were corrected for Lorentz and polarization effects; no correction for crystal decay was applied. An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS. All software used for diffraction data processing and crystal-structure solution and refinement are contained in the APEX3 program suite (Bruker AXS, Madison, WI). Thermal parameters for all non-hydrogen atoms were refined anisotropically.[3–7]

Due to a strongly disordered and unresolvable hexamethyldisiloxane (HMDSO) molecule in the structure of **4**, the SQUEEZE technique was applied for this molecular structure.[8] CCDC numbers for the compounds **3**, **4** and **5** can be found in *Table S1*. The CIF-Files can be downloaded free of charge from https://summary.ccdc.cam.ac.uk/structure-summary-form.

Synthesis of Ligand Precursors

K(TDA) (2): A THF solution (100 mL) of $KN(SiMe_3)_2$ (3.84 g, 19.3 mmol) was added to a stirred THF solution (150 mL) of **1** (5.00 g, 19.1 mmol) maintained at -78 ^{o}C via cannula. The resulting solution was slowly warmed to room temperature and stirred for 48 h, then the solvent was removed *in vacuo* to give an off-white powder. This powder was washed with hexane (50 mL) to remove impurities, then dried *in vacuo* to give the product as a colorless powder. (4.94 g, 86% yield) ^{1}H NMR (C_5D_5N, 400 MHz): δ 7.17 (d, 2H, Ph-*H*), 6.99 (t, 1H, Ph-*H*), 3.77 (m, 2H, $CH(CH_3)_2$, 1.68 (s, 9H, $C(CH_3)_3$), 1.32 and 1.26 (dd, 12H, $CH(CH_3)_2$). ^{13}C NMR (C_5D_5N, 600 MHz): δ 176.48 (NCO), 155.37 (CCN), 141.61 (Ph), 122.91 (Ph), 120.22 (Ph), 39.80 ($C(CH_3)_3$), 30.82 ($C(CH_3)_3$), 28.80 ($CH(CH_3)_2$), 24.00 ($CH(CH_3)_2$). IR (cm^{-1}): 1586 (w), 1542 (s), 1517 (s), 1433 (s), 1390 (m), 1349 (s), 1317 (m), 1255 (m), 1219 (m), 1176 (w), 1158 (w), 1101 (w), 1056 (w), 1041 (w), 914 (m), 883 (w), 848 (w), 808 (w), 791 (m), 751 (s).

K(TDA)(18c6) (3): A THF solution (5 mL) of 18-crown-6 (838 mg, 3.17 mmol) was added to a stirred THF solution (7 mL) of **2** (946 mg, 3.16 mmol) via pipette. The resulting solution was stirred for 1 h, then the solvent was removed *in vacuo*. The resulting off-white solids were triturated with hexane to give the product as a colorless powder. (1.73 g, 96% yield) ^{1}H NMR (C_6D_6, 600 MHz): δ 7.26 (d, 2H, Ph-*H*), 7.02 (t, 1H, Ph-*H*), 3.91 (m, 2H, C*H*(CH_3)$_2$, 3.05 (s, 24H, OC*H*$_2$), 1.83 (s, 9H, C(C*H*$_3$)$_3$),), 1.62 and 1.43 (dd, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR (C_6D_6, 600 MHz): δ 173.77 (N*C*O), 155.48 (C*C*N), 141.04 (Ph), 121.86 (Ph), 118.31 (Ph), 70.29 (O*C*H$_2$), 39.91 (*C*(CH_3)$_3$), 31.07 (C(*C*H$_3$)$_3$), 29.22 (*C*H(CH_3)$_2$), 24.23 (CH(*C*H$_3$)$_2$). IR (cm^{-1}): 1587 (w), 1551 (s), 1426 (m), 1392 (m), 1352 (m), 1302 (w), 1256 (w), 1225 (w), 1110 (s), 1082 (m), 960 (m), 910 (m), 839 (w), 781 (w), 741 (m).

Synthesis of Uranium Complexes

U(TDA)$_4$ (4):

Method 1: A THF solution (5 mL) of UI_4(1,4-dioxane)$_2$ (200 mg, 0.217 mmol) was slowly added to a stirred THF solution (10 mL) of **3** (489 mg, 0.868 mmol) via cannula. The reaction flask was heated to 60 °C and stirred for 3 d. Over the course of the reaction, the dark red solution turned cloudy green. The solvent was removed *in vacuo,* and HMDSO (10 mL) was added to the resulting green solids to give a pale green solution. This solution was filtered through Celite, concentrated to a volume of 3 mL, and cooled to -40 °C for 7 d, yielding pale green crystals, which were then dried *in vacuo*. (65 mg, 23% yield)

Method 2: A THF solution of $FcPF_6$ (6 mg, 0.018 mmol) was added dropwise to a stirred THF solution (2 mL) of **5** (30 mg, 0.019 mmol) via pipette. The deep red solution turned greenish-brown over the course of the reaction. The solution was stirred for 1 h, and then the solvent was removed *in vacuo*. The resulting brown-green solids were extracted into pentane and filtered through Celite, then the solvent was removed *in vacuo* to give a pale green waxy solid showing identical ^{1}H NMR shifts to the complex obtained from Method 1. (20 mg, 81% yield) ^{1}H NMR (C_6D_6, 600 MHz): δ 6.75 (s, 4H, Ph-*H* and 8H, Ph-*H*), 3.16 (s, 8H, C*H*(CH_3)$_2$), 1.66 (s, 36H, C(C*H*$_3$)$_3$), and 0.08 (s, 48H, CH(C*H*$_3$)$_2$). IR (cm^{-1}): 1468 (m), 1536 (m), 1397 (m), 1340 (w), 1313 (m), 1255 (w), 1211 (m), 1172 (m), 1125 (w), 1098 (w), 1029 (w), 925 (w), 803 (w), 764 (m), 736 (w), 656 (w), 585 (w). Melting point: 172-177 °C EA calcd for $C_{68}H_{104}N_4O_4U$: C: 63.83%, H: 8.19%, N: 4.38%. Found: C: 63.59%, H: 8.00%, N: 4.56%.

[U(TDA)$_4$]K(18c6) (5):

Method 1: A diethyl ether solution (7 mL) of **3** (300 mg, 0.532 mmol) was added dropwise to a stirred diethyl ether solution (3 mL) of $UI_3(diox)_{1.5}$ (130 mg, 0.173 mmol) via pipette. The dark blue solution turned cloudy red over the course of the reaction. The solution was stirred for 4 d, and then the solvent was removed *in vacuo*. The solution was filtered through Celite, concentrated to a volume of 2 mL, and cooled to -40 °C for 24 h, yielding dark red crystals, which were then washed twice with benzene and dried *in vacuo*. (140 mg, 66% yield) **Method 2:** A diethyl ether suspension (1 mL) of KC_8 (5 mg, 0.040 mmol) was added quickly to a stirred diethyl ether solution (2 mL) of **4** (33 mg, 0.026 mmol) and 18-crown-6 (8 mg, 0.032 mmol). The pale green solution turned reddish-brown over the course of the reaction. This solution was stirred for 2 min, and then the solvent was removed *in vacuo*. The resulting red solids were extracted into diethyl ether and filtered through Celite, then the solvent was removed *in vacuo* to give a dark red microcrystalline solid showing identical ^1H NMR shifts to the complex obtained from Method 1. (11 mg, 32% yield) ^1H NMR (C_5D_5N, 500 MHz): δ 6.61 (s, 4H, Ph-*H*), 6.44 (s, 8H, Ph-*H*), 3.46 (s, 24H, OC*H*$_2$), 2.47 (s, 8H, C*H*(CH$_3$)$_2$), 1.38 (s, 36H, C(C*H*$_3$)$_3$), 0.46 (s, 24H, CH(C*H*$_3$)$_2$), and -3.32 (s, 24H, CH(C*H*$_3$)$_2$). IR (cm^{-1}): 1647 (m), 1609 (m), 1584 (m), 1352 (w), 1294 (m), 1210 (w), 1160 (m), 1108 (m), 962 (m), 912 (m), 836 (w), 807 (w), 790 (w), 741 (m). Melting point: 201-205 °C; EA calcd for $C_{80}H_{128}N_4O_{10}UK$: C: 60.70%, H: 8.15%, N: 3.54%. Found: C: 60.41%, H: 8.23%, N: 3.20%.

B. NMR Spectra

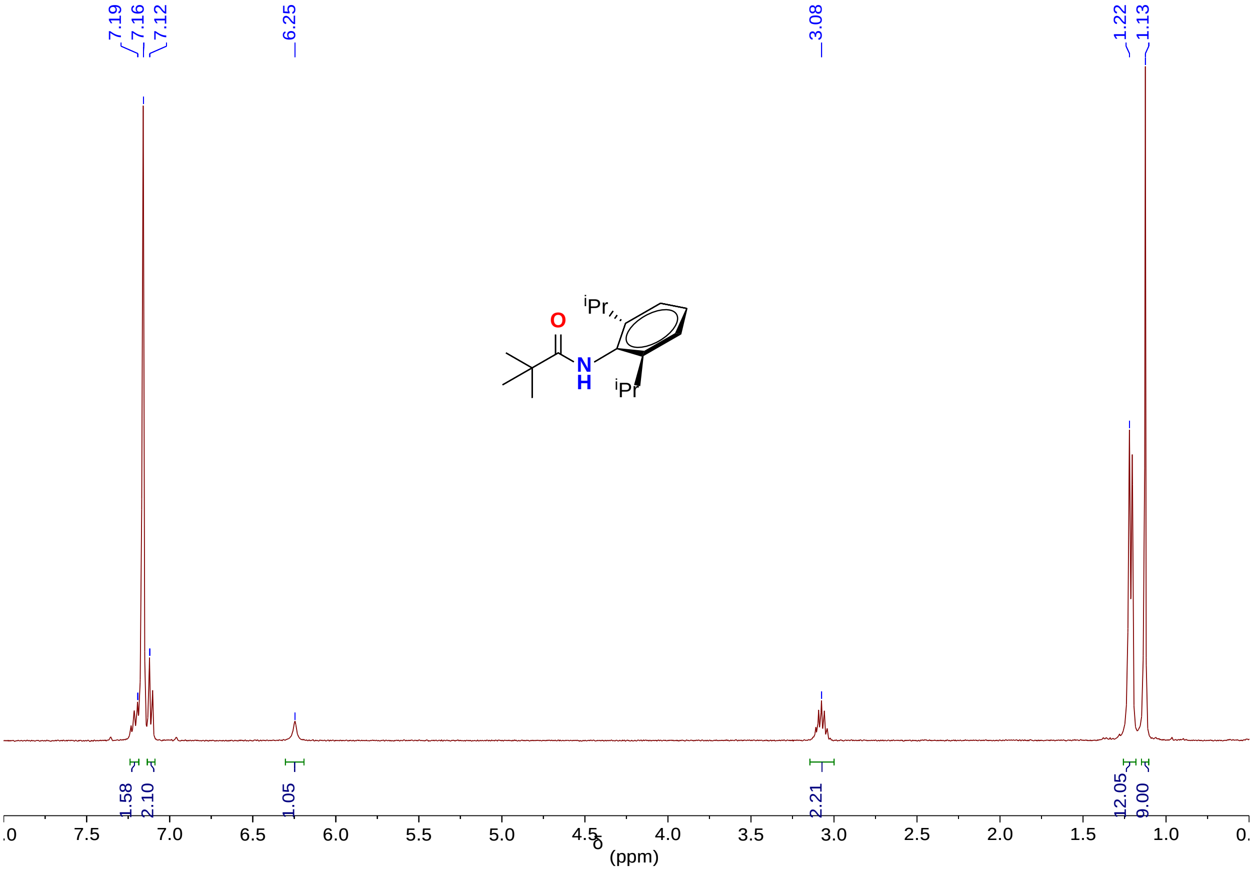

Figure S1: ^{1}H NMR spectrum of H(TDA) ***(1)*** *at 298 K in C_6D_6.*

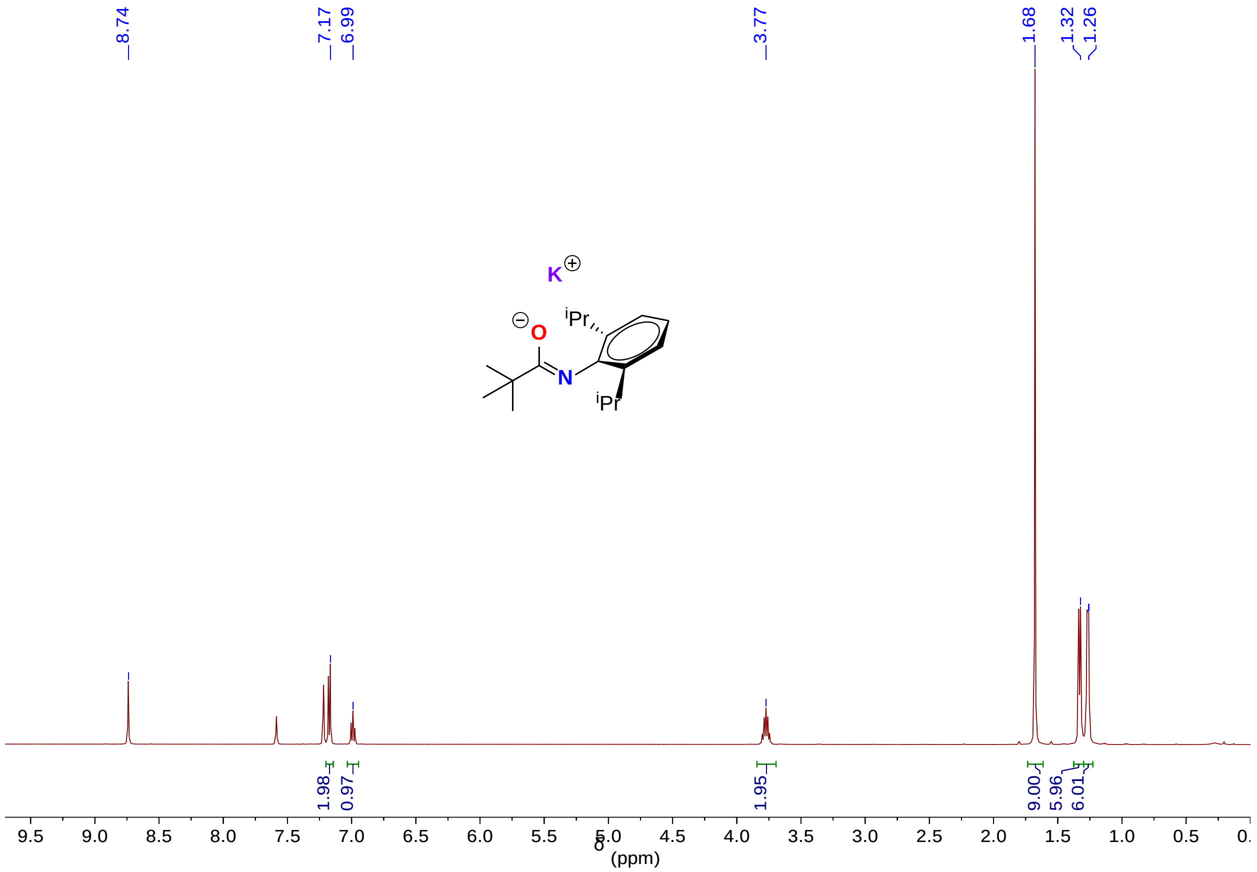

Figure S2: ^{1}H NMR spectrum of K(TDA) ***(2)*** *at 298 K in C_5D_5N.*

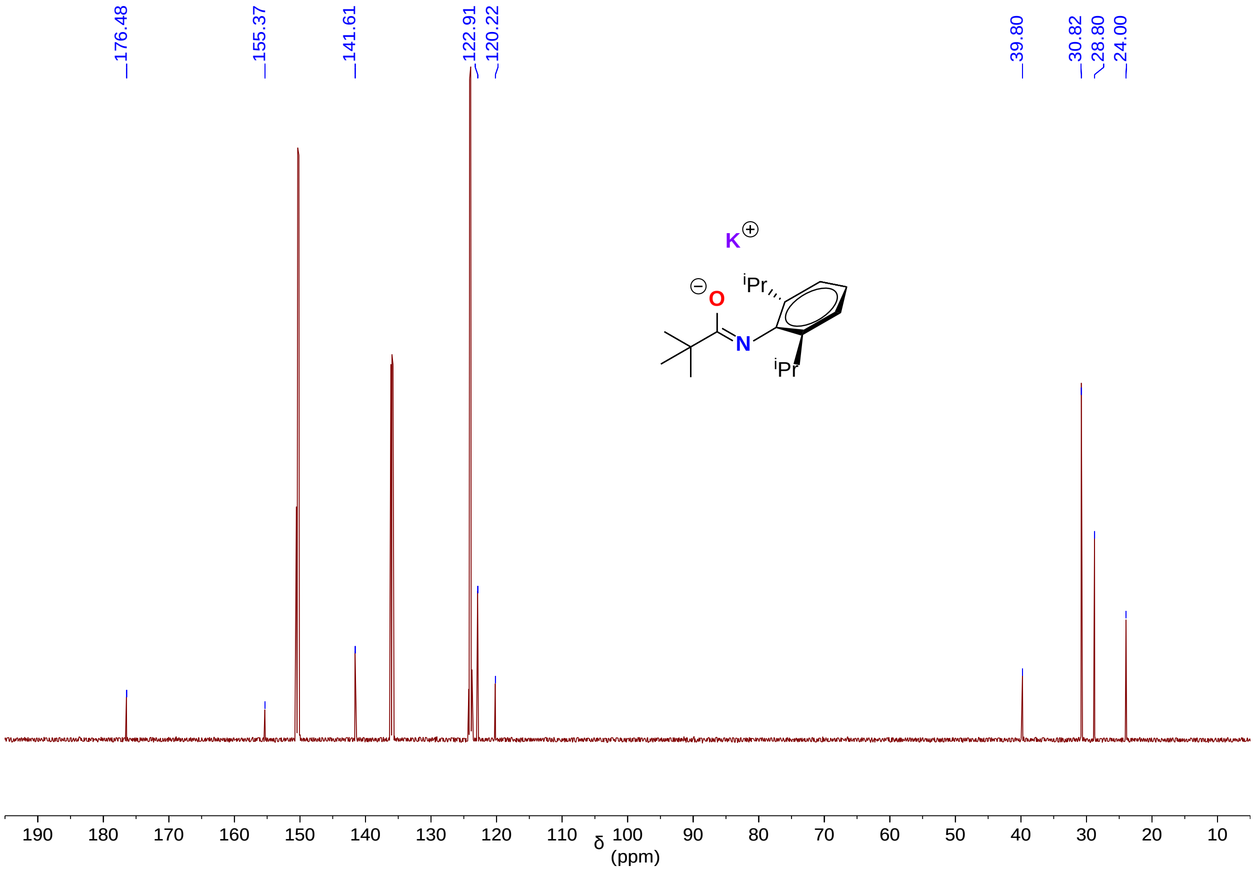

Figure S3: ^{13}C NMR spectrum of K(TDA) ***(2)*** *at 298 K in C_5D_5N.*

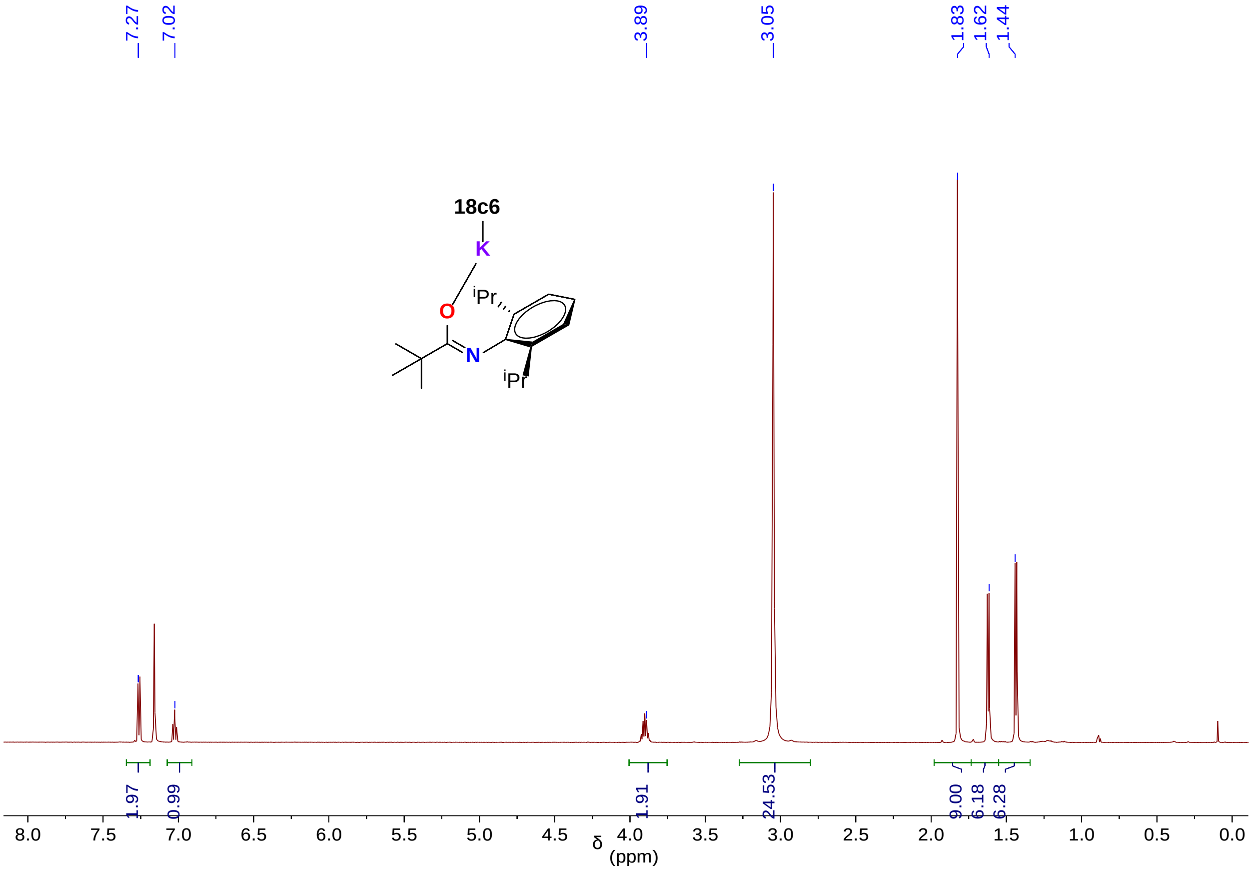

Figure S4: ^{1}H NMR spectrum of K(TDA)(18c6) ***(3)*** *at 298 K in C_6D_6.*

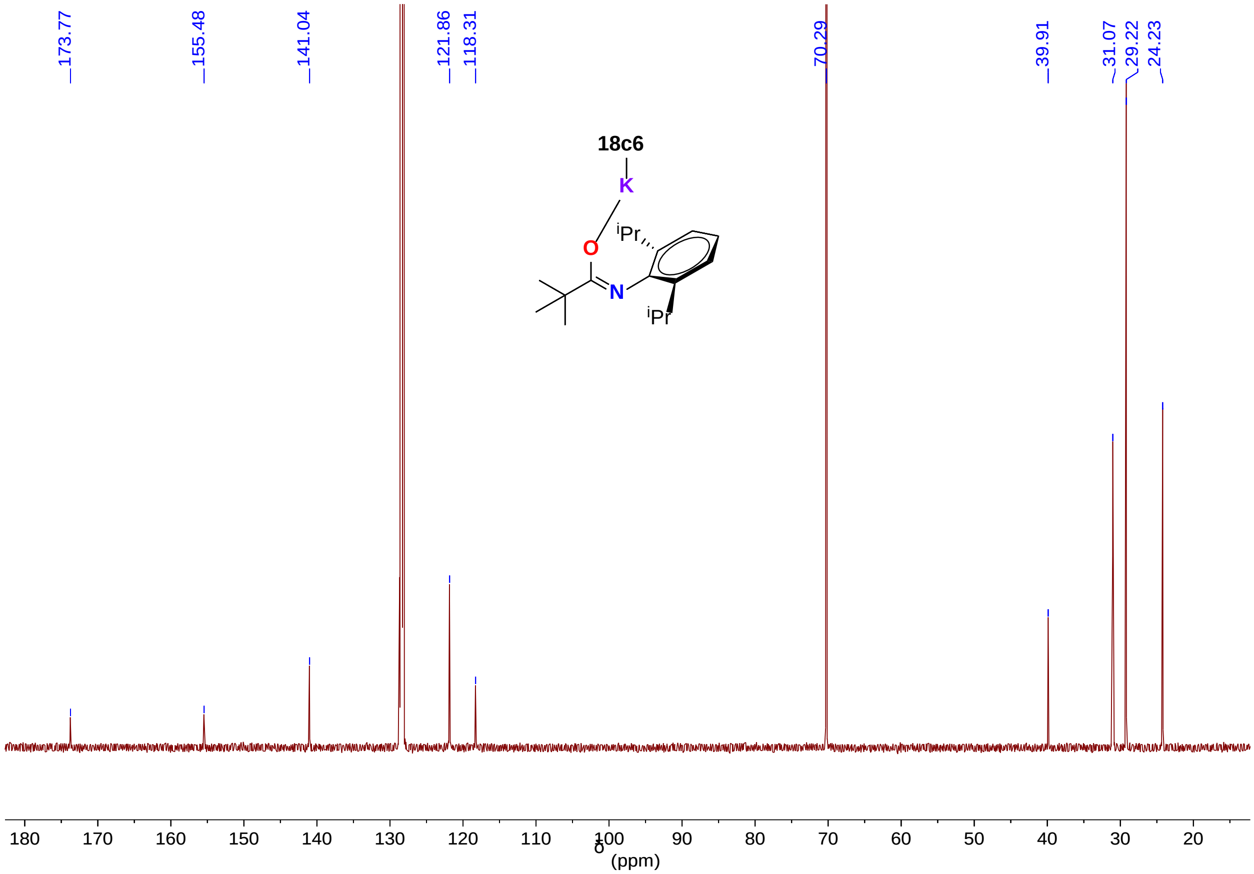

Figure S5: ^{13}C NMR spectrum of K(TDA)(18c6) **(3)** *at 298 K in C_6D_6.*

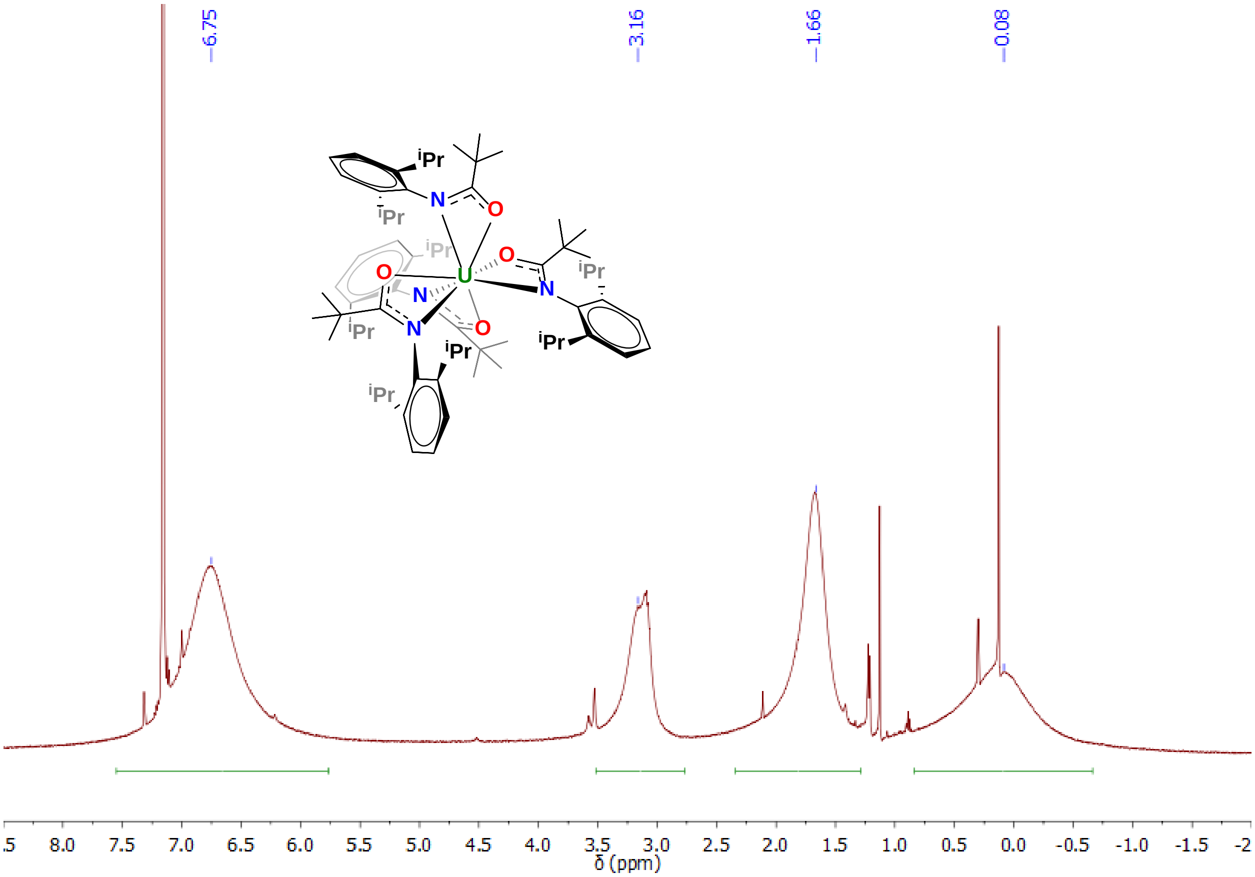

Figure S6: ^{1}H NMR spectrum of U(TDA)$_4$ ***(4)*** *at 298 K in C$_6$D$_6$. A small amount of* ***1*** *is present, resulting in the small peaks seen at 3.53 and 1.13 ppm. Residual solvent peaks are present at 1.23 and 0.89 ppm (hexane) and 0.09 ppm (HMDSO).*

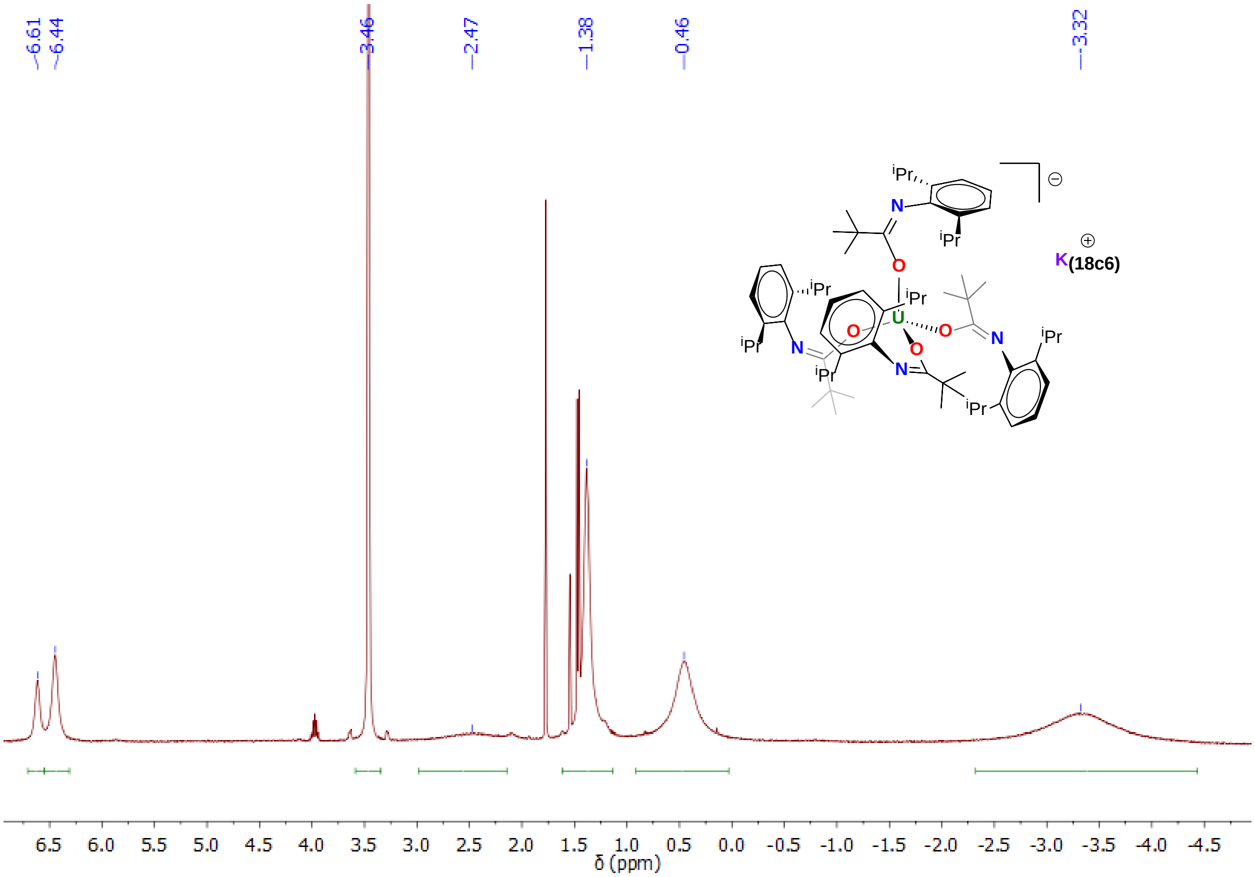

Figure S7: ^{1}H NMR spectrum of [U(TDA)$_4$]K(18c6) ***(5)*** *at 298 K in C_5D_5N. Small amounts of* ***1*** *and* ***3*** *are present, resulting in the peaks seen at 3.97, 1.78, 1.55, and 1.47 ppm.*

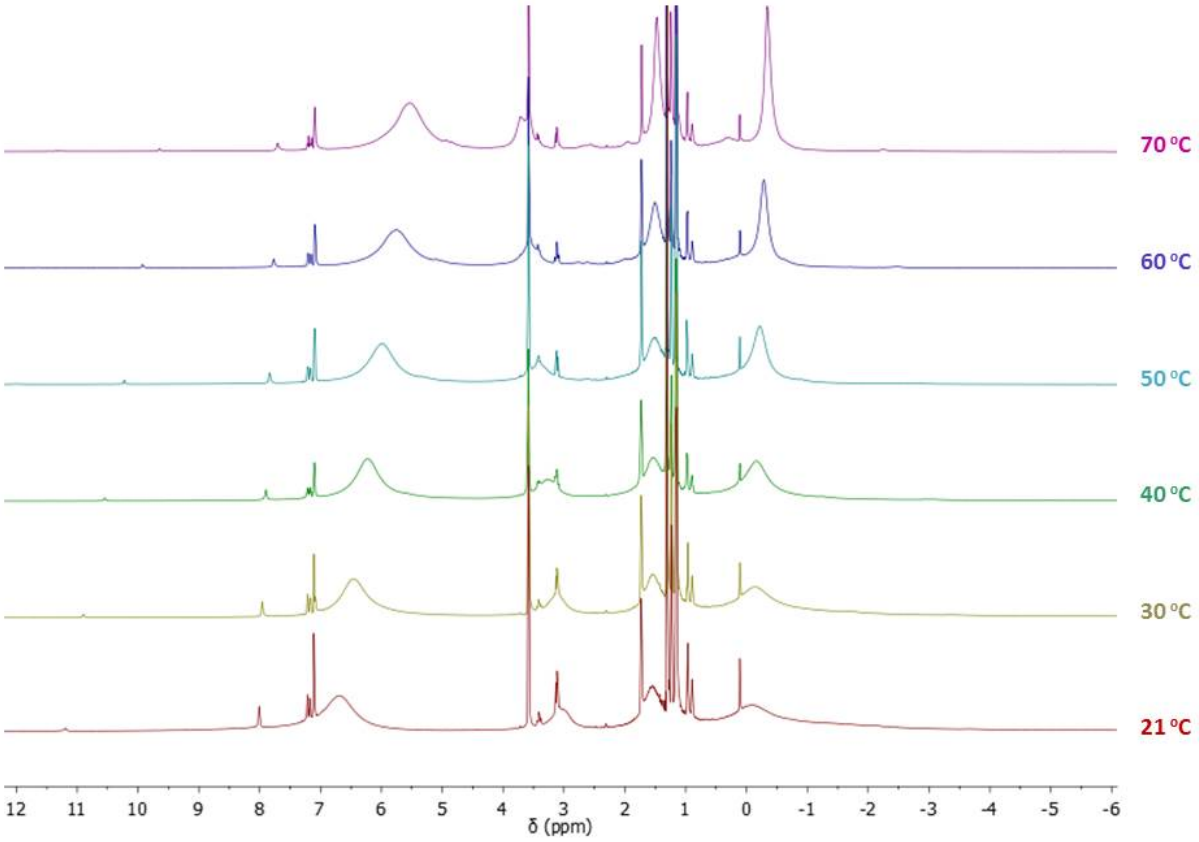

Figure S8: Variable-temperature ^1H NMR spectrum of $U(TDA)_4$ ***(4)*** *in d^8-THF from 21 °C to 70 °C.*

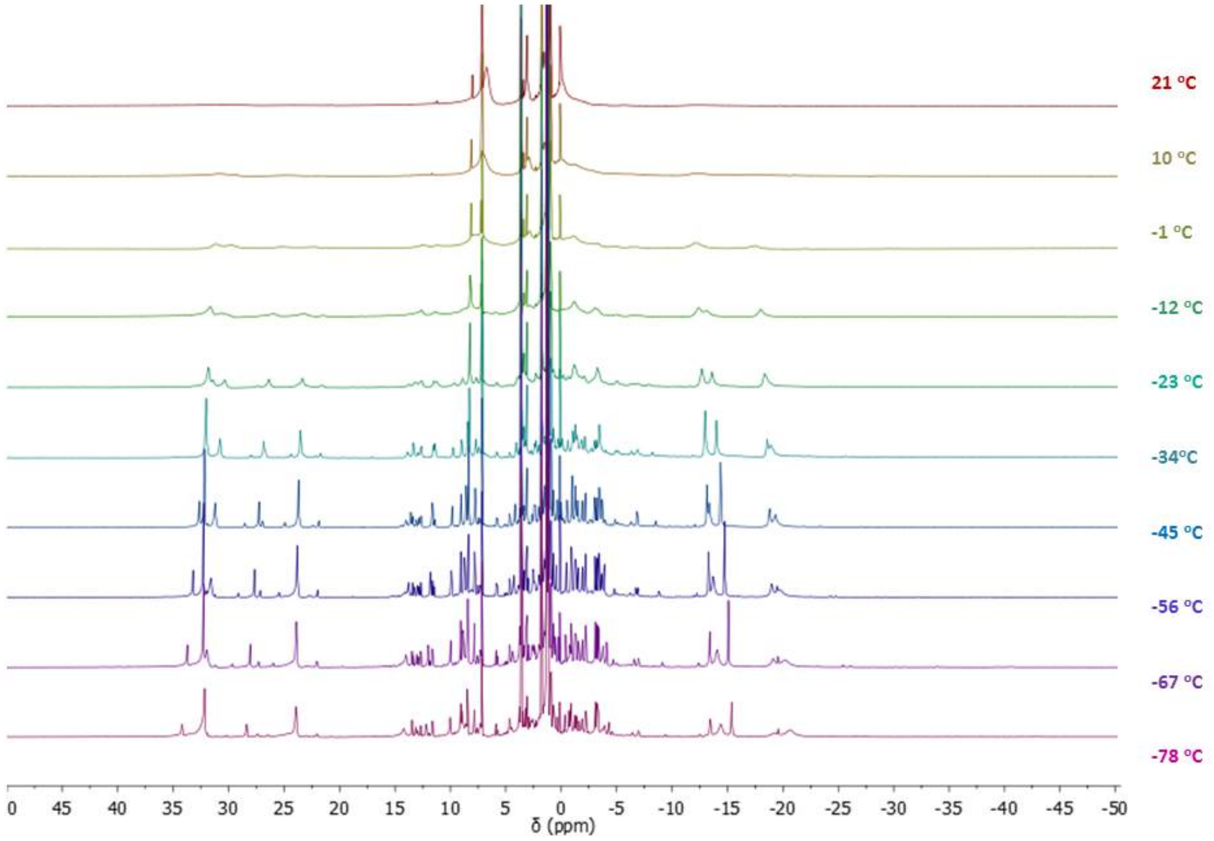

Figure S9: Variable-temperature ^{1}H NMR spectrum of U(TDA)$_4$ ***(4)*** *in d^8-THF from 21 °C to -78 °C.*

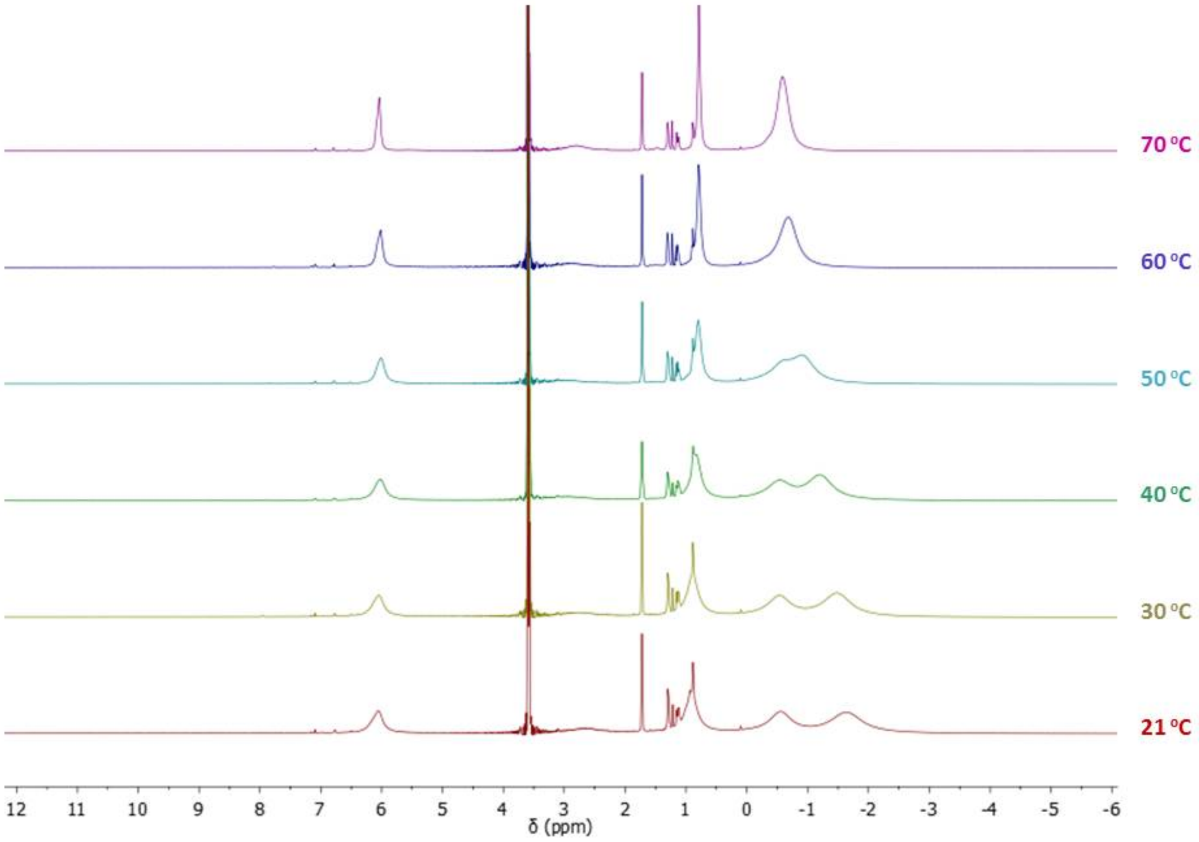

Figure S10: Variable-temperature ^{1}H NMR spectrum of [U(TDA)$_4$]K(18c6) ***(5)*** *in d^8-THF from 25 °C to 70 °C.*

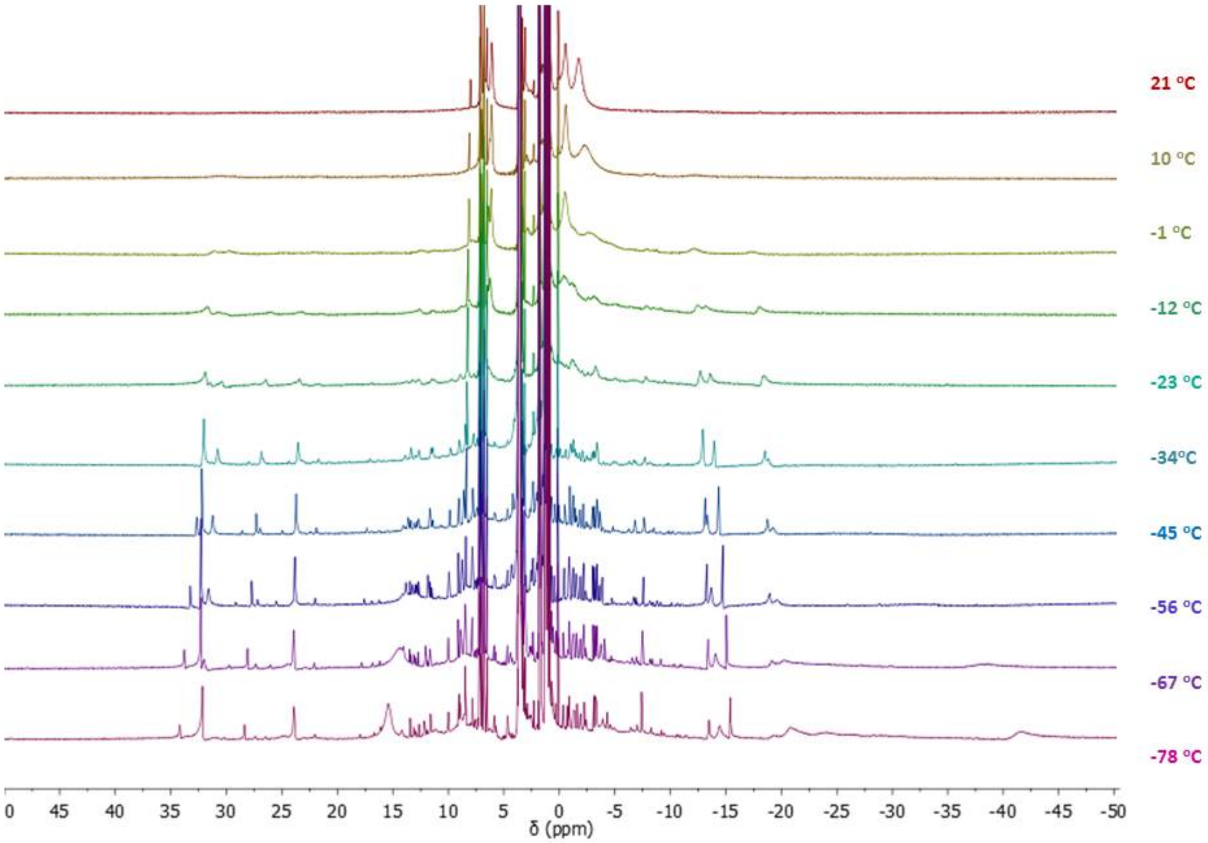

Figure S11: Variable-temperature ^{1}H NMR spectrum of [U(TDA)$_4$]K(18c6) ***(5)*** *in d^8-THF from 21 °C to -78 °C.*

C. IR Spectra

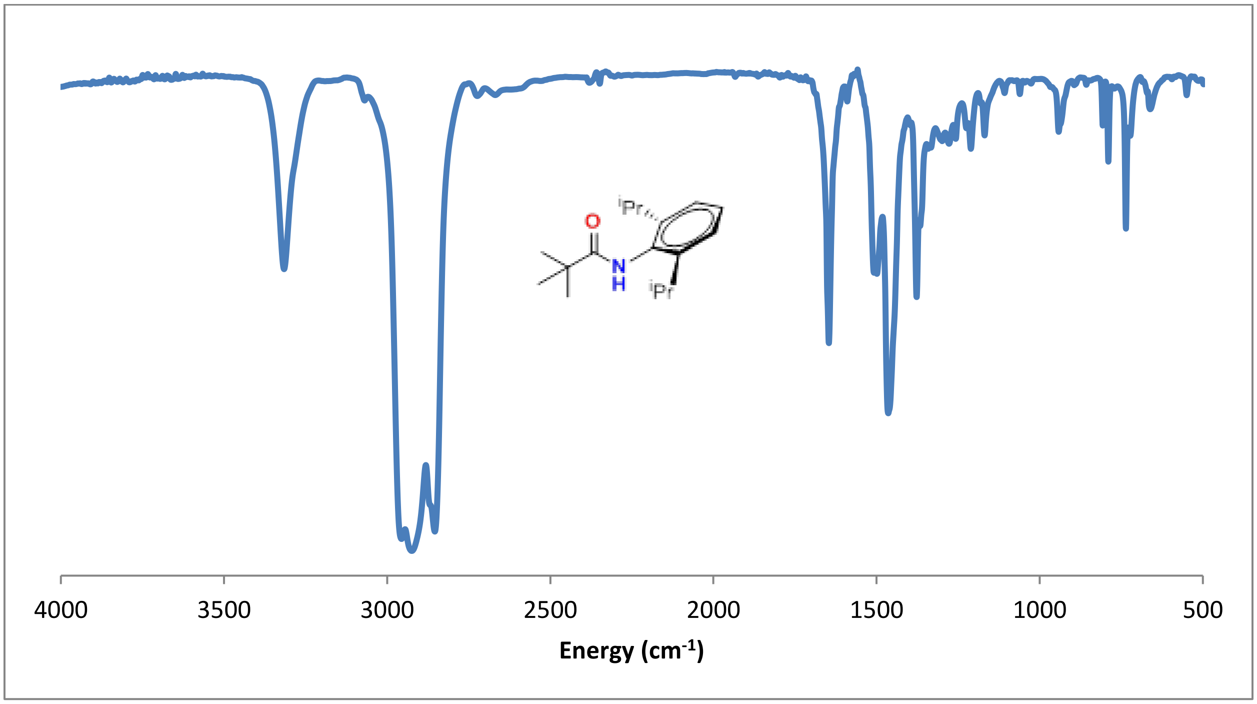

Figure S12: IR spectrum of H(TDA) ***(1)*** *prepared as a Nujol mull.*

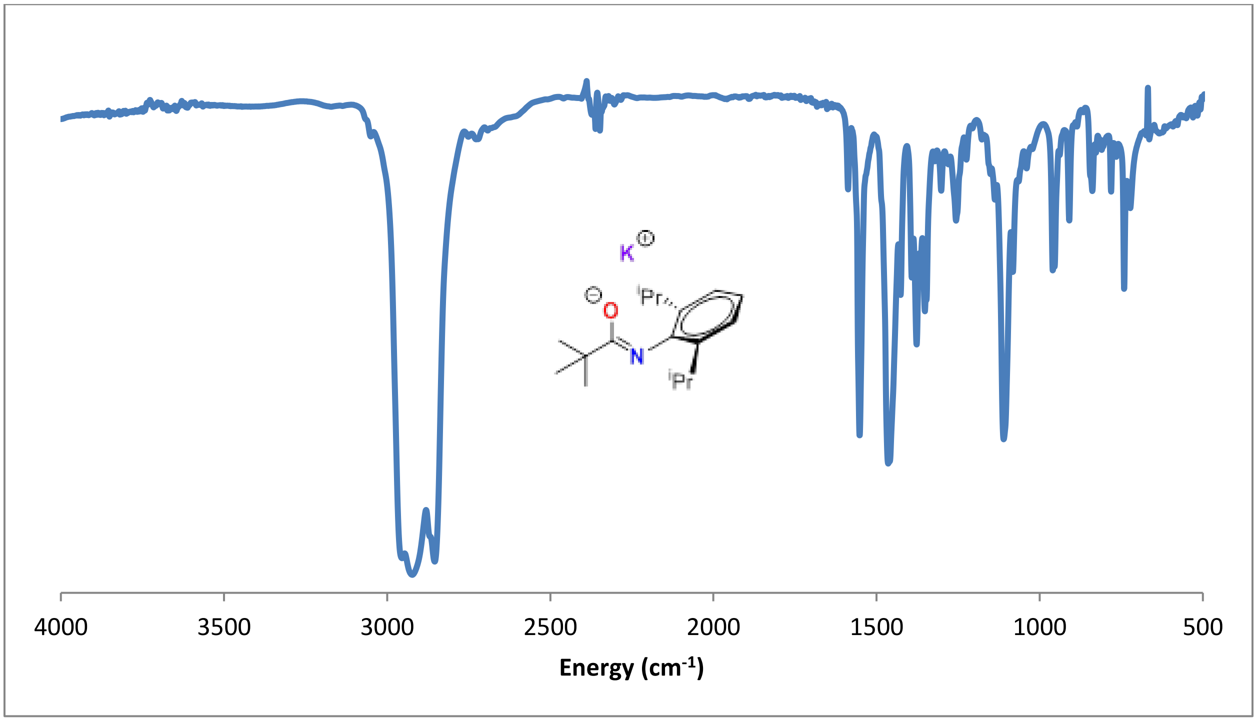

Figure S13: IR spectrum of K(TDA) ***(2)*** *prepared as a Nujol mull.*

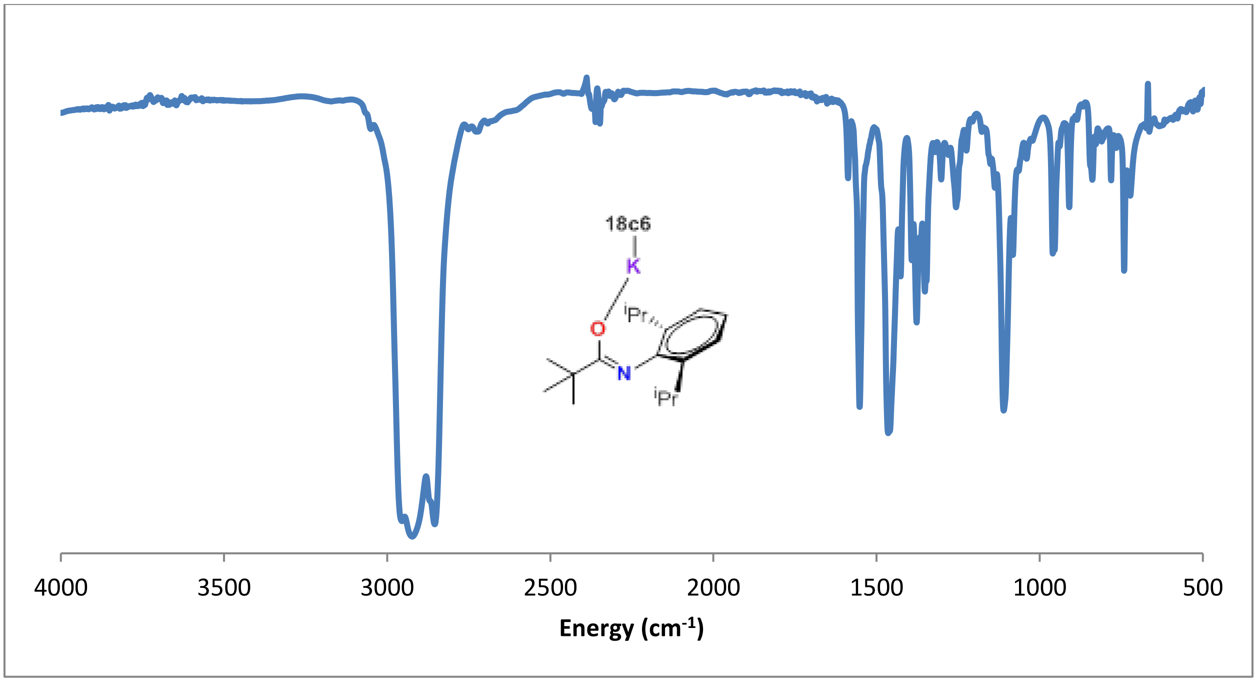

Figure S14: IR spectrum of K(TDA)(18c6) ***(3)*** *prepared as a Nujol mull.*

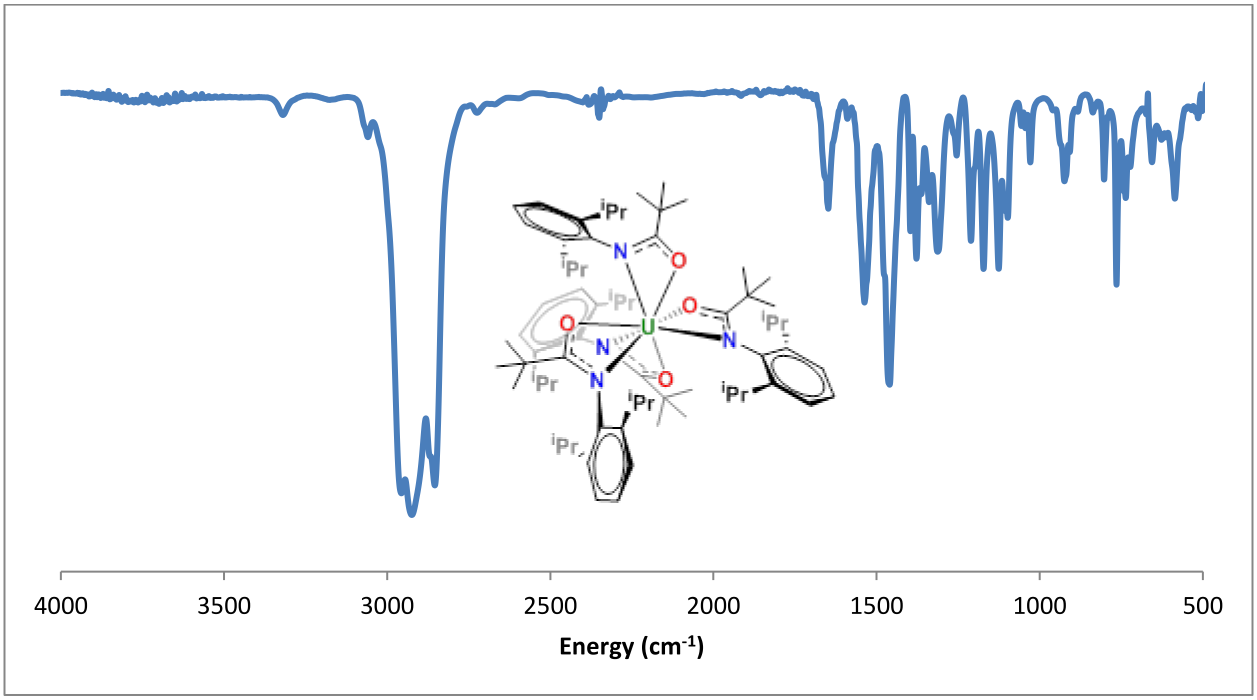

Figure S15: IR spectrum of U(TDA)$_4$ ***(4)*** *prepared as a Nujol mull. A small amount of* ***1*** *is present, resulting in the small peak at 3317 cm^{-1}.*

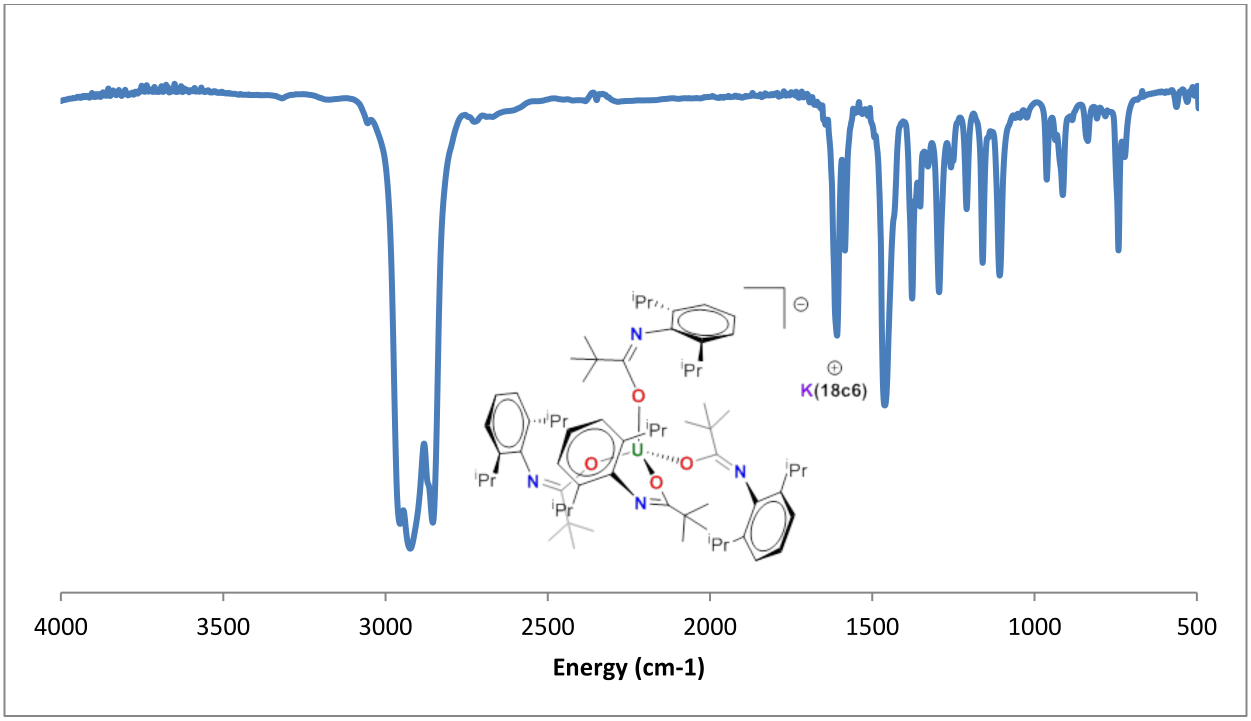

Figure S16: IR spectrum of [U(TDA)$_4$]K(18c6) ***(5)*** *prepared as a Nujol mull.*

D. X-Ray Crystallography

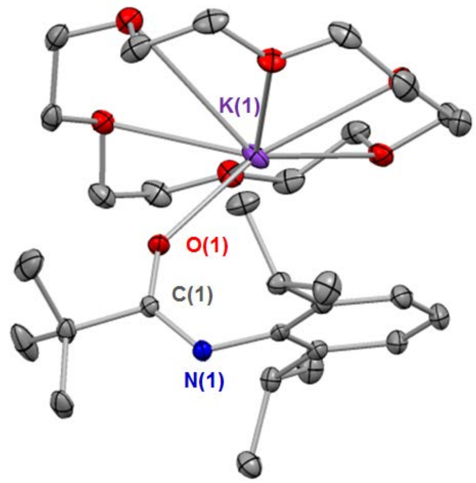

Figure S17: X-ray crystal structure of K(TDA)(18c6) ***(3)*** *with 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected atomic distances (Å) and angles (deg) for* ***3****: K(1)-O(1) 2.552(1), O(1)-C(1)-N(1) 127.43(9).*

Table S1: Crystal Data- General

	3	**4***	**5 · 3 Et_2O**
Chemical formula	$C_{29}H_{50}NO_7K$	$C_{68}H_{104}N_4O_4U_1$	$C_{80}H_{128}N_4O_{10}U_1K_1$ 3 $C_4H_{10}O$
M_r	563.80	1279.58	1805.34
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P\ 2_1/n$	P-1	P-1
a (Å)	9.692(5)	13.4219(5)	13.479(4)
b (Å)	21.888(13)	13.6222(6)	18.049(6)
c (Å)	14.814(9)	21.0557(9)	20.964(7)
α (°)	90	88.668(2)	87.530(7)
β (°)	101.007(4)	77.566(2)	79.614(10)
γ (°)	90	87.760(2)	74.365(6)
V ($Å^3$)	3085(3)	3756.1(3)	4831(3)
Z	4	2	2
Density (g/cm^3)	1.214	1.131	1.241
F(000)	1224	1328	1906
Radiation Type	Synchrotron	MoK_α	MoK_α
μ (mm^{-1})	0.268	2.202	1.781
Abs. corr. type	Multi-scan	Multi-scan	Multi-scan
Abs. corr. T_{min}	0.623	0.639	0.653
Abs. corr. T_{max}	0.746	0.745	0.745
Crystal size (mm)	0.19 x 0.17 x 0.12	0.15 x 0.15 x 0.13	0.15 x 0.12 x 0.11
Meas. Refl.	32500	98499	100876
Indep. Refl.	7183	13844	19634
Obsvd. [$I > 2\sigma(I)$] refl.	6509	12424	16754
R_{int}	0.0254	0.0403	0.0586
R [$F^2 > 2\sigma(F^2)$], wR(F^2)	0.0300, 0.0814	0.0302, 0.0736	0.0394, 0.0840
S	1.049	1.088	1.079
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.342, -0.288	2.863, -0.999	2.723, -0.522
CCDC	1559383	1559385	1559386

*****Due to a strongly disordered and unresolvable hexamethyldisiloxane (HMDSO) molecule in the lattice, the SQUEEZE technique was applied for this molecular structure.

Table S2: Bonds (Å) and Angles (deg)

Atoms	**3**	**4**	**5 · 3 Et_2O**
K1 – O1	2.552(1)	-	-
U1 – O1	-	2.270(2)	2.234(2)
U1 – O2	-	2.321(2)	2.235(2)
U1 – O3	-	2.316(2)	2.236(2)
U1 – O4	-	2.276(2)	2.253(2)
U1 – N1	-	2.721(3)	-
U1 – N2	-	2.535(2)	-
U1 – N3	-	2.535(2)	-
U1 – N4	-	2.713(2)	-
C1 – O1	1.274(1)	1.315(4)	1.334(4)
C2 – O2	-	1.314(4)	1.323(3)
C3 – O3	-	1.313(4)	1.334(3)
C4 – O4	-	1.317(4)	1.327(4)
C1 – N1	1.298(1)	1.293(4)	1.271(4)
C2 – N2	-	1.305(4)	1.282(4)
C3 – N3	-	1.309(4)	1.277(4)
C4 – N4	-	1.297(4)	1.284(4)
O1 – C1 – N1	127.43(9)	114.7(3)	126.5(3)
O2 – C2 – N2	-	113.6(3)	125.4(3)
O3 – C3 – N3	-	113.8(3)	124.9(3)
O4 – C4 – N4	-	114.6(3)	125.1(3)

E. References

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