

Electronic Supporting Information

Quantitative U=O bond activation in uranyl complexes via silyl radical transfer

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General Considerations: All air- and moisture-sensitive manipulations were carried out using standard high vacuum line, Schlenk, or cannula techniques or in an MBraun inert atmosphere drybox containing an atmosphere of purified dinitrogen. All solids were dried under high vacuum to bring into the glovebox. Solvents for air- and moisture-sensitive manipulations were dried and deoxygenated using a Glass Contour Solvent Purification System (Pure Process Technology, LLC) and stored over activated 4 Å molecular sieves (Fisher Scientific) prior to use. Deuterated solvents for ^1H NMR spectroscopy were purchased from Cambridge Isotope Laboratories, distilled from sodium metal (C_6D_6) after three freeze-pump-thaw cycles, and stored in the glovebox over activated 3 Å molecular sieves. Chemicals were purchased from commercial sources and used without further purification. 4-dimethylaminopyridine (DMAP) was purchased from Sigma-Aldrich and purified by recrystallization before being brought into the glove box. $^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{UO}_2(\text{THF})^1$, $\text{Pyz}(\text{SiMe}_3)_2^2$, and $\text{UO}_2\text{Cl}_2(\text{OPPh}_3)_2^3$ were synthesized following reported procedures.

Safety Considerations. Caution! Depleted uranium (primary isotope ^{238}U) is a weak α -emitter (4.197 MeV) with a half-life of 4.47×10^9 years; manipulations and reactions should be carried out in monitored fume hoods or in an inert atmosphere drybox in a radiation laboratory equipped with α - and β counting equipment.

X-ray Crystallography. Crystals of complexes $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{UO}_2(\text{DMAP})_2$ (**1**) and $(^{\text{Mes}}\text{PDP}^{\text{Ph}})\text{U}(\text{OSiMe}_3)_2(\text{DMAP})$ (**2**) were placed onto a thin glass optical fiber or a nylon loop and mounted on a Rigaku XtaLAB Synergy-S Dualflex diffractometer equipped with a HyPix-6000HE HPC area detector for data collection at 100.00(10) K. A preliminary set of cell constants and an orientation matrix were calculated from a small sampling of reflections.⁴ A short pre-experiment was run, from which an optimal data collection strategy was determined. The full data collection was carried out using a PhotonJet (Cu) X-ray source. After the intensity data were corrected for absorption, the final cell constants were calculated from the xyz centroids.⁴ See Table S1 (Supporting Information) for additional crystal and refinement information. The structure was solved using SHELXT⁵ and refined using SHELXL.⁶ Most or all non-hydrogen atoms were assigned from the solution; full-matrix least squares / difference Fourier

cycles were performed which located any remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

Synthesis of (^{Mes}PDP^{Ph})UO₂(DMAP)₂ (1)

In the glovebox, a 20 mL scintillation vial equipped with a magnetic stir bar was charged with (^{Mes}PDP^{Ph})UO₂(THF) (0.015 g, 0.016 mmol, 1.0 eq.) dissolved in 2 mL benzene. In a separate vial, dimethylaminopyridine (DMAP; 0.004 g, 0.032 mmol, 2.0 eq.) was dissolved in ~2 mL benzene. The DMAP solution was added dropwise to the (^{Mes}PDP^{Ph})UO₂(THF) solution with stirring and left to stir for ~1 hr. Volatiles were removed *in vacuo*, and the resulting powder was triturated with pentane. After being reduced to dryness, the product was dissolved in benzene, filtered through celite, and pumped dry again. The title compound is isolated as a bronze-brown powder (0.015 g, 0.014 mmol, 85 %). ¹H NMR (500 MHz, Benzene-d₆) δ = 8.55 (s, 2H), 7.96 (d, J = 7.2 Hz, 5H), 7.71 (d, J = 8.0 Hz, 2H), 7.38 (t, J = 7.6 Hz, 4H), 6.89 (t, J = 8.0 Hz, 2H), 6.69 (s, 2H), 6.52 (s, 4H), 6.17 (s, 1H), 5.70 (s, 1H), 2.52 (s, 12H), 2.29 (s, 7H), 1.81 (s, 5H). Brown crystals suitable for single crystal X-ray diffraction were grown from the slow diffusion of pentane into a toluene solution of the compound at -30°C. Anal. Calcd. for C₅₀H₄₇N₅O₂U (mol. wt. 987.988 g/mol): C, 62.14%; H, 4.97%; N, 6.77%. Found: C, 62.69%; H, 4.96%; N, 6.65%.

Synthesis of (^{Mes}PDP^{Ph})U(OSiMe₃)₂(DMAP) (2)

In the glovebox, a 20 mL scintillation vial was loaded with (^{Mes}PDP^{Ph})UO₂(DMAP)₂ (0.010 g, 0.009 mmol, 1.0 eq.) dissolved in 3 mL of dichloromethane. In a separate vial equipped with a magnetic stirrer, Pyz(SiMe₃)₂ (0.002 g, 0.009 mmol, 1.0 eq.) was dissolved in 3 mL of dichloromethane. Both solutions were placed in a liquid nitrogen cold well and frozen. Upon thawing, the (^{Mes}PDP^{Ph})UO₂(DMAP)₂ solution was added dropwise to the stirring solution of Pyz(SiMe₃)₂. Within five minutes, the color of the solution turned a bright orange and after 15 minutes the solution was a luminescent yellow; the reaction mixture was left to stir for ~12 hrs. The vial was reduced to dryness, affording the title compound (0.009 g, 0.008 mmol, 90 %). ¹H NMR (400 MHz, Benzene-d₆) δ = 49.94 (s, 18H), 15.22 (s, 2H), 12.13 (s, 12H), -6.50 (s, 4H), -8.68

(s, 4H), -10.82 (s, 2H), -11.34 (t, $J = 9.6$ Hz, 1H), -11.46 (s, 5H), -13.41 (s, 6H), -19.36 (s, 2H), -25.38 (s, 2H). Yellow crystals suitable for single crystal X-ray diffraction were grown from a concentrated diethyl ether solution of the compound at -30 °C. Anal. Calcd. for $C_{56}H_{65}N_5O_2Si_2U$ (mol. wt. 1134.368 g/mol): C, 61.13%; H, 5.95%; N, 5.82%. Found: C, 61.28%; H, 5.50%; N, 5.59%.

Synthesis of $(OSiMe_3)_2UCl_2(OPPh_3)_2$

In the glovebox, a 20 mL scintillation vial was loaded with $UO_2Cl_2(OPPh_3)_2$ (0.015 g, 0.011 mmol, 1 eq.) dissolved in 3 mL of dichloromethane. In a separate vial equipped with a magnetic stirrer, $Pyz(SiMe_3)_2$ (0.003 g, 0.013 mmol, 1 eq.) was dissolved in 3 mL dichloromethane. Both solutions were placed in a liquid nitrogen cold well and frozen. Upon thawing, the $UO_2Cl_2(OPPh_3)_2$ solution appears cloudy, and is added dropwise to the stirring solution of $Pyz(SiMe_3)_2$. Within ten minutes, the solution was homogeneous and slightly yellow in color; the reaction mixture was left to stir ~4 hrs. The vial was reduced to dryness and triturated with pentane, affording the title compound as a slightly oily material (0.017 g, 0.011 mmol, 98%). Characterization of this molecule matched that reported previously.³ 1H NMR (400 MHz, Benzene- d_6) δ 50.33 (s, 18H), 4.11 (s, 7H), 2.54 (s, 14H), -17.54 (s, 20H).

Table S1. Crystallographic parameters for molecular structures of (^{Mes}PDP^{Ph})UO₂(DMAP)₂ (**1**) and (^{Mes}PDP^{Ph})U(OSiMe₃)₂(DMAP) (**2**).

Compound	(^{Mes} PDP ^{Ph})UO ₂ (DMAP) ₂ (1)	(^{Mes} PDP ^{Ph})U(OSiMe ₃) ₂ (DMAP) (2)
Empirical formula	C ₅₇ H ₅₇ N ₇ O ₂ U	C ₆₀ H ₇₅ N ₅ O ₃ Si ₂ U
Formula weight	1110.12	1208.46
Temperature / K	100.00(10)	100.00(11)
Wavelength / Å	1.54184	1.54184
Crystal group	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>P2₁/n</i>
Unit cell dimensions	<i>a</i> = 30.86731(15) Å <i>b</i> = 18.79028(9) Å <i>c</i> = 19.81812(9) Å <i>α</i> = 90° <i>β</i> = 97.3495(5)° <i>γ</i> = 90°	<i>a</i> = 13.21430(10) Å <i>b</i> = 22.69980(10) Å <i>c</i> = 19.21290(10) Å <i>α</i> = 90° <i>β</i> = 96.1300(10)° <i>γ</i> = 90°
Volume / Å ³	11400.18(10)	5730.19(6)
<i>Z</i>	8	4
Reflections collected	74323	97688
Independent reflections	12275	12409
Completeness (theta)	99.9% (74.504°)	100% (74.504°)
Goodness-of-fit on <i>F</i> ²	1.095	1.106
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0250	<i>R</i> 1 = 0.0286
Largest diff. peak and hole	1.059 and -1.312 e.Å ⁻³	1.707 and -1.873 e.Å ⁻³

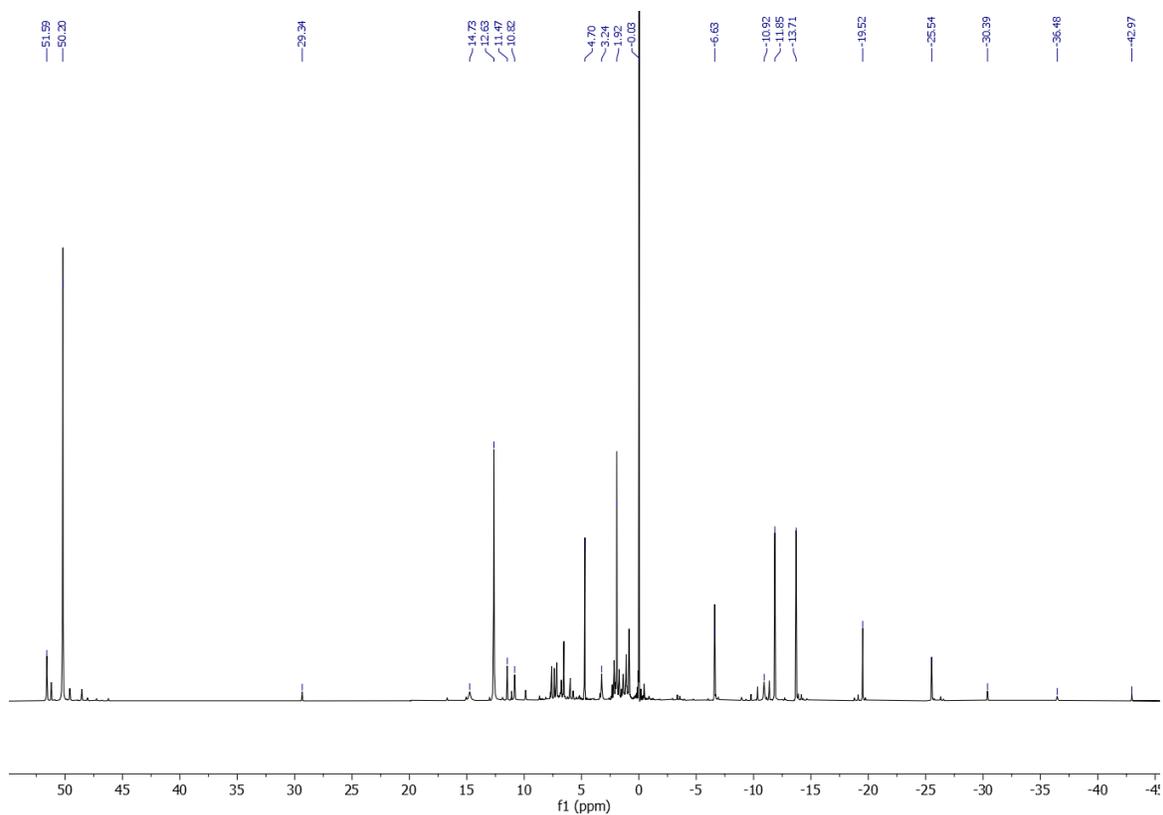


Figure S1. ^1H NMR spectrum (400 MHz) of $^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{UO}_2(\text{THF})$ reacted with 1 equiv. of $\text{Pyz}(\text{SiMe}_3)_2$ to form $^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{U}(\text{OSiMe}_3)_2(\text{THF})$ and other side products in C_6D_6 .

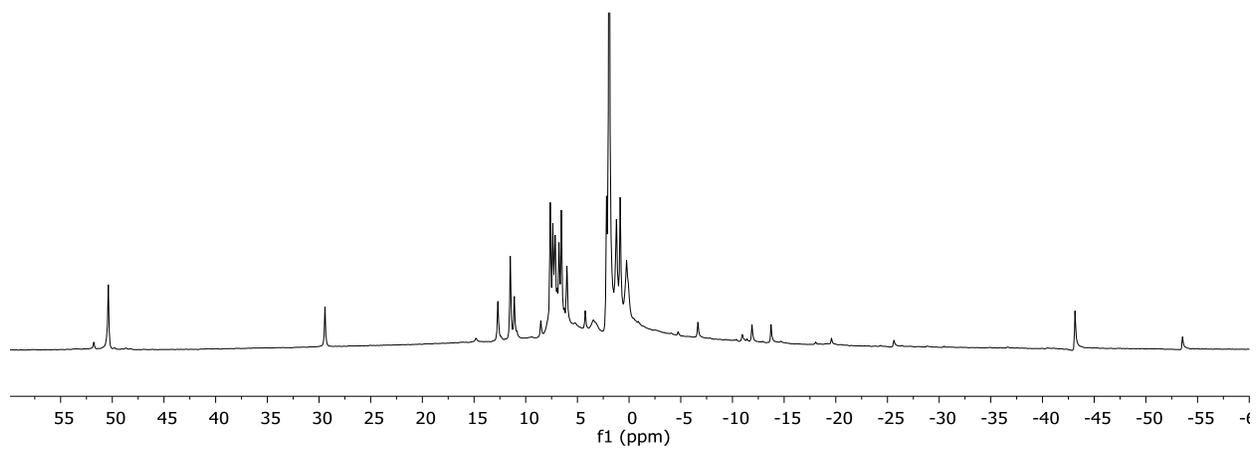
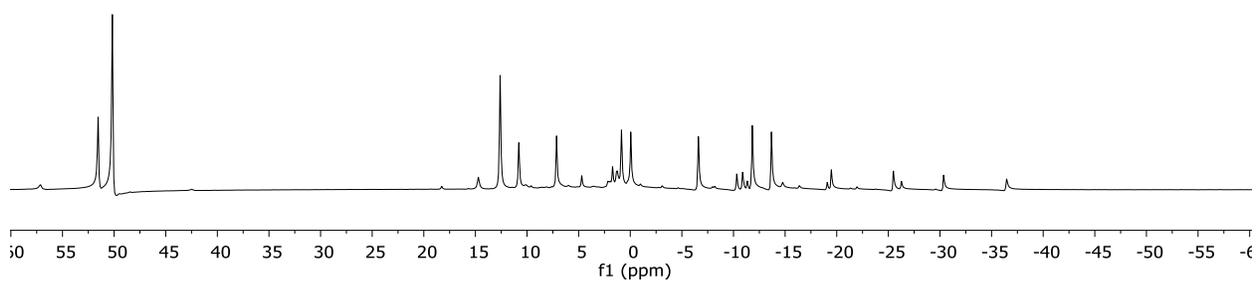
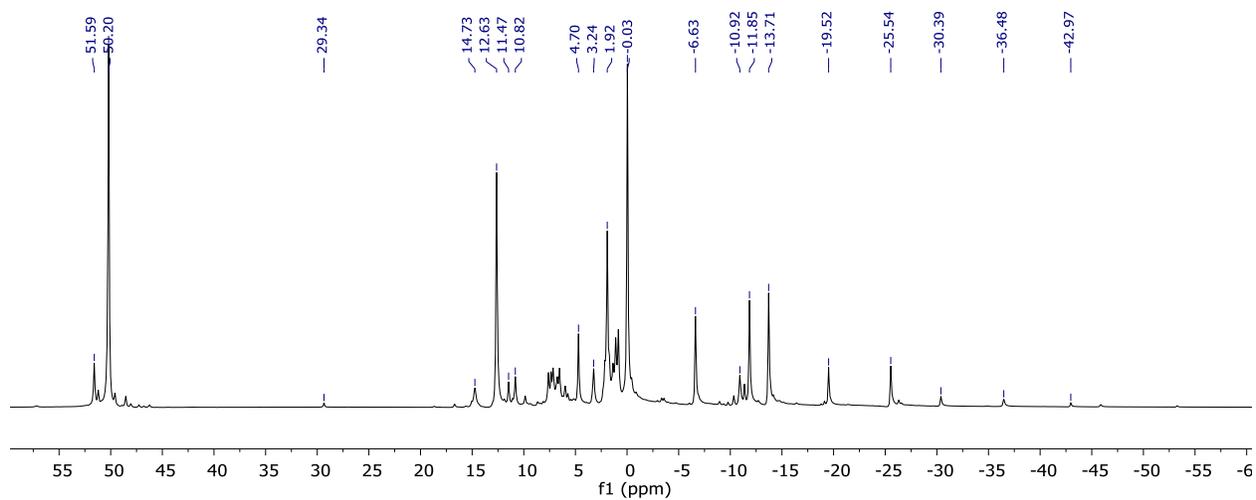


Figure S2. ^1H NMR spectra (400 MHz) in C_6D_6 of multiple attempts to silylate $^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{UO}_2(\text{THF})$ with $\text{Pyz}(\text{SiMe}_3)_2$ to form $^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{U}(\text{OSiMe}_3)_2(\text{THF})$. Inconsistencies in product formation and distribution from batch-to-batch are shown.

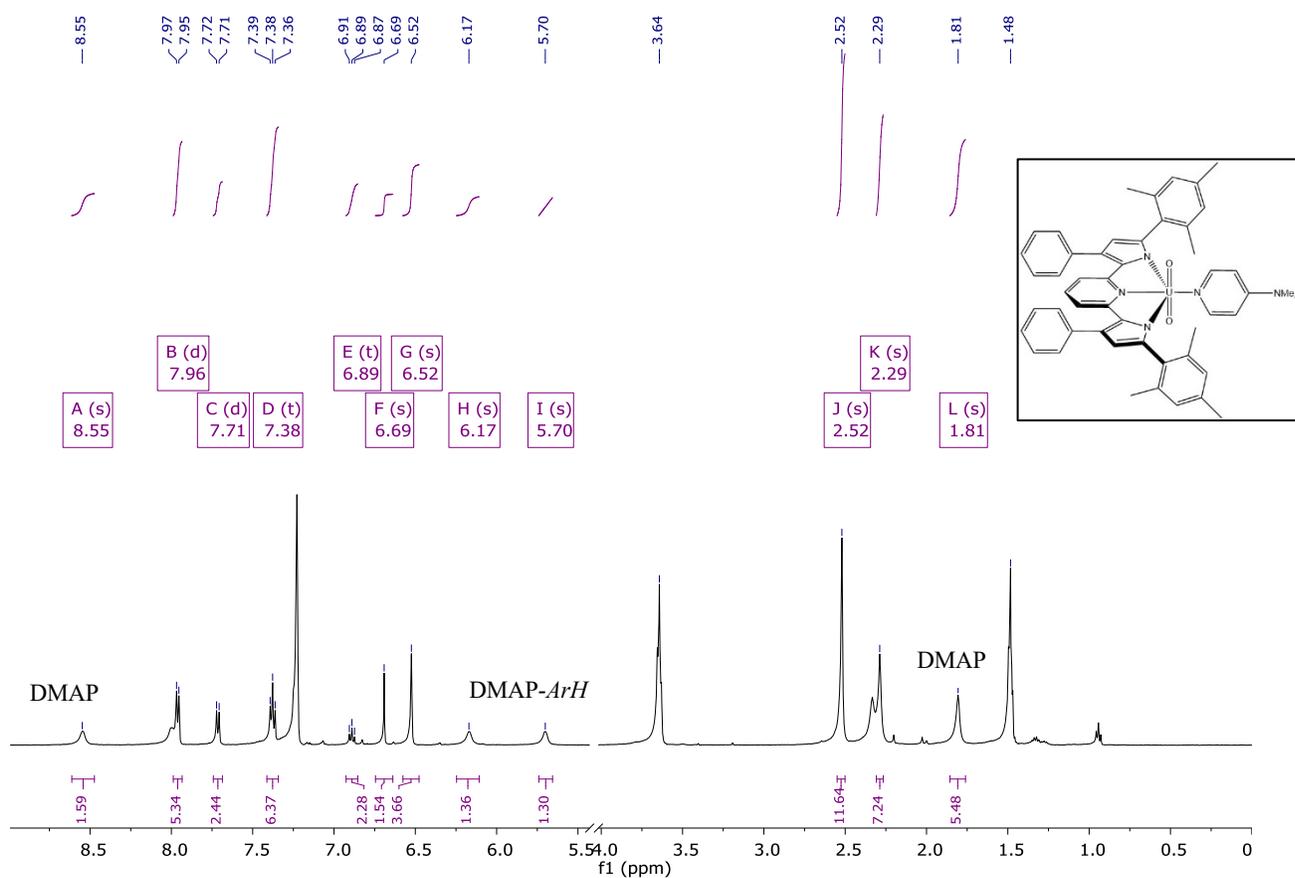


Figure S3. ¹H NMR spectrum (500 MHz) of ^{Mes}PDP^{Ph}UO₂(DMAP) (**1**) (DMAP = 4-dimethylaminopyridine) in C₆D₆. A singlet resonance corresponding to trace unreacted (^{Mes}PDP^{Ph})UO₂(THF) is observed at 2.39 ppm. The resonances at 3.65 and 1.48 ppm correspond to free THF generated as a product of the reaction. Resonances at 3.64, 1.35, and 0.97 indicate the presence of pentane and diethyl ether solvents.

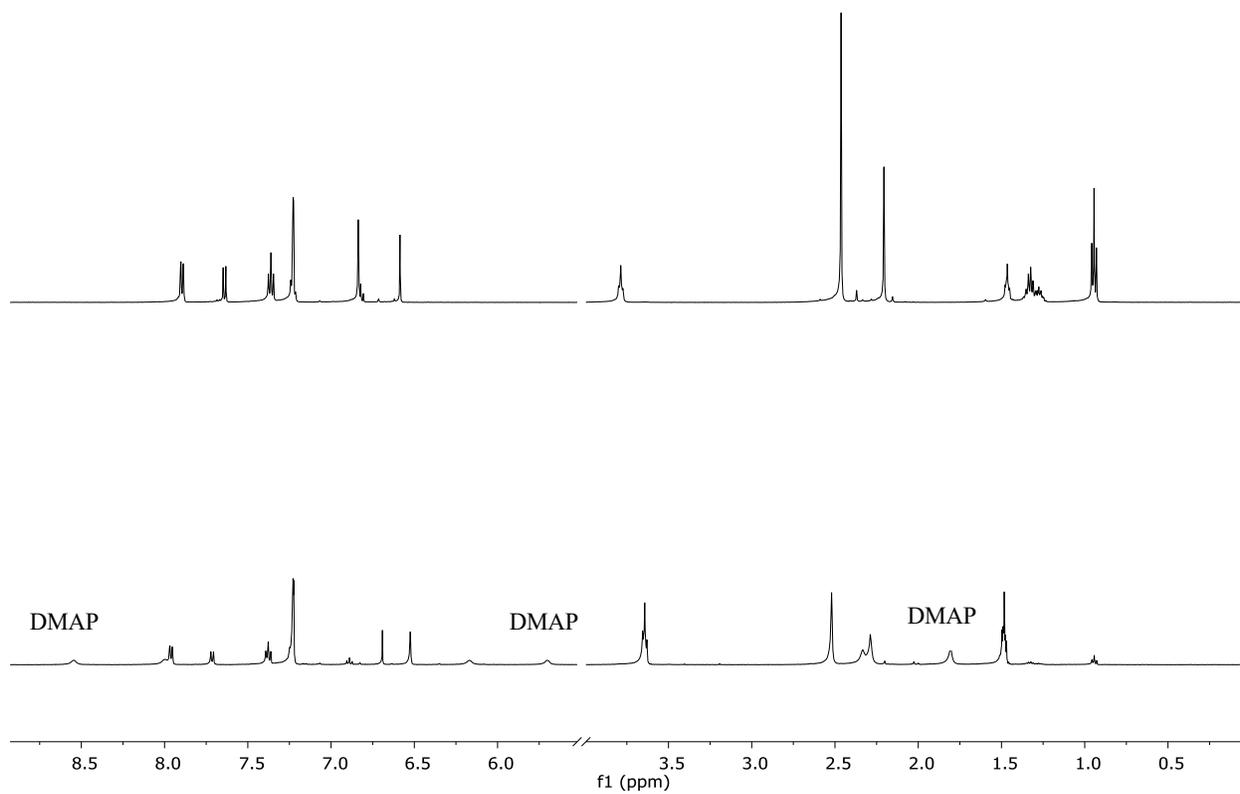


Figure S4. Comparison of the ^1H NMR spectra (400 MHz) of $^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{UO}_2(\text{THF})$ (top) and $^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{UO}_2(\text{DMAP})$ (bottom) in C_6D_6 .

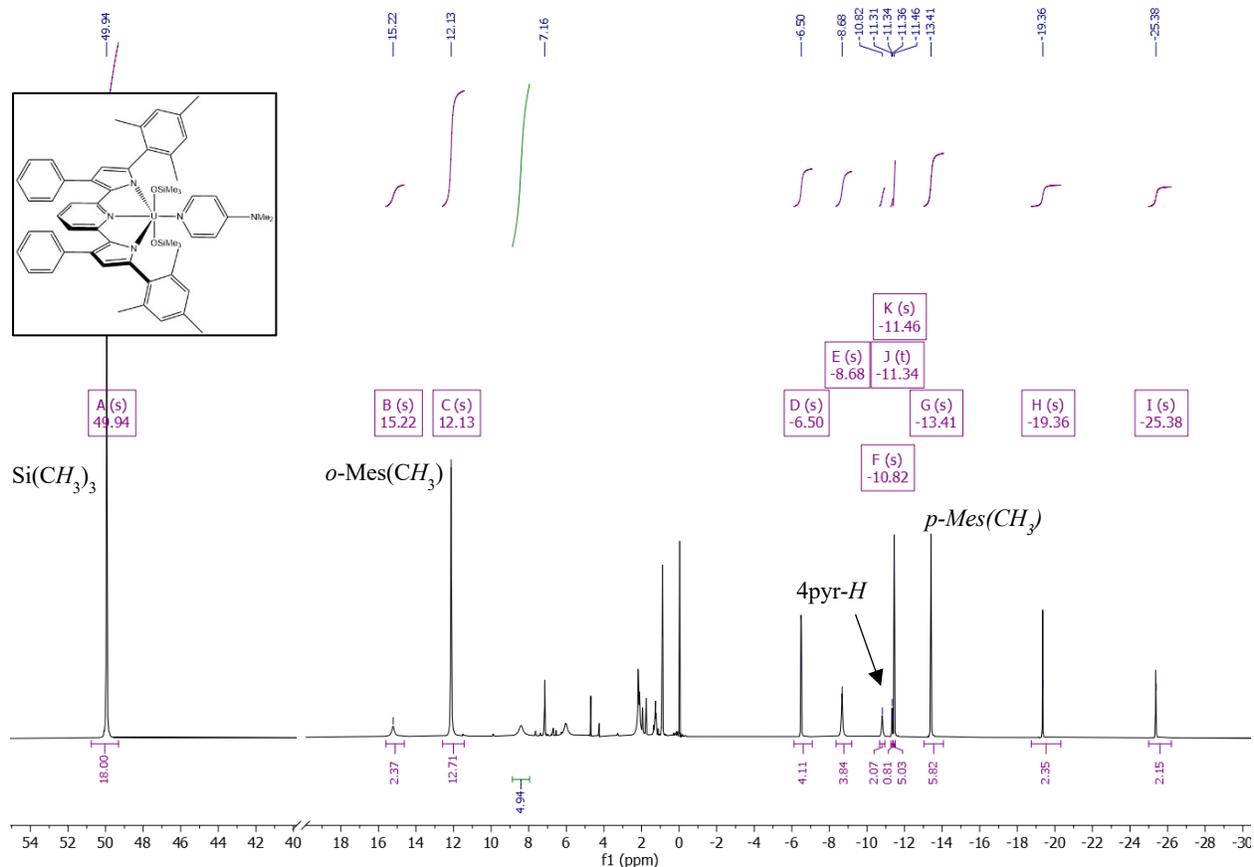


Figure S5. ^1H NMR spectrum (400 MHz) of $^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{U}(\text{OSiMe}_3)_2(\text{DMAP})$ collected in C_6D_6 . Unmarked resonances in the diamagnetic region correspond to small amounts of unreacted starting material and pentane in the sample. Identifiable peaks in the paramagnetic region with unique resonances are labeled; those that could not be formally assigned (2 and 4 H resonances) were left unlabeled. Formation of pyrazine from the release of SiMe_3 groups in $\text{Pyz}(\text{SiMe}_3)_2$ is evidenced by a peak at 8.5 ppm that integrates to ≈ 4 protons (labeled in blue).

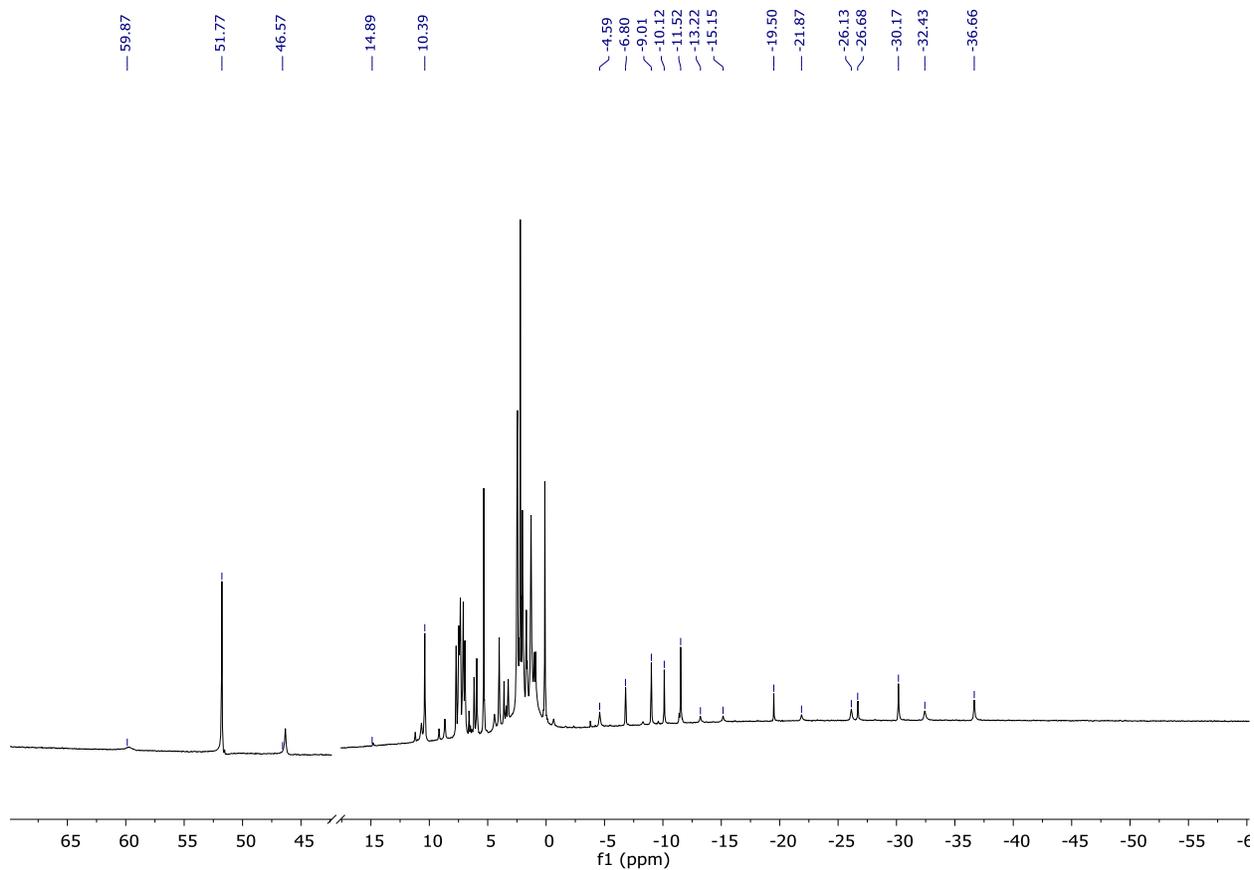


Figure S6. ^1H NMR spectrum (400 MHz) of reaction between $^{\text{Mes}}\text{PDP}^{\text{Ph}}\text{UO}_2(\text{THF})$ and excess TMSI collected in C_6D_6 . Multiple species are formed in solution as evidenced by NMR.

