

**Supporting Information for:**  
**Tuning the Oxidation State, Nuclearity, and Chemistry of Uranium Hydrides**  
**with Phenylsilane and Temperature: the Case of the Classic Uranium(III)**  
**Hydride Complex, [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U( $\mu$ -H)]<sub>2</sub>**

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## Experimental

### General Considerations

Unless otherwise noted, all reactions and manipulations were performed at ambient temperature in a recirculating Vacuum Atmospheres NEXUS model inert atmosphere (Ar or  $\text{N}_2$ ) drybox equipped with a 40CFM Dual Purifier NI-Train. Glassware was dried overnight at 150 °C before use. All NMR spectra were obtained using a Bruker Avance 400 MHz spectrometer. Chemical shifts for  $^1\text{H}$  NMR spectra are reported in parts per million (ppm) were referenced to proteo solvent impurities ( $\delta = 7.16$  for  $\text{C}_6\text{D}_6$ ).<sup>1</sup> IR spectra were obtained using a Thermo Scientific Nicolet iS5 FT-IR spectrometer with a Golden Gate Diamond ATR (ZnSe lenses) with a reaction anvil. UV/Vis-NIR spectra were collected with a Perkin Elmer Lambda 1050 spectrometer using 1 mm pathlength cuvettes; two sample concentrations were measured to optimize absorbance between 0.1–1 mM in the NIR and UV/Vis regions. Melting points were measured with a Barnstead Thermolyne MEL-TEMP<sup>®</sup> Capillary Melting Point Apparatus using capillary tubes flame-sealed under nitrogen; values are uncorrected. Elemental analyses were performed by Atlantic Microlab, Inc. (Atlanta, GA). All samples for elemental analyses were dried under reduced pressure for at least 12 h before analysis to ensure the complete removal of solvent.

### Materials

Unless otherwise noted, reagents were purchased from commercial suppliers and were used without further purification. Benzene- $d_6$  (Cambridge Isotope Laboratories) was purified by storage over activated 3 Å molecular sieves for at least 48 h prior to use. 3 Å molecular sieves (Aldrich)

were dried under dynamic vacuum at 250 °C for 48 h before use. All solvents (Aldrich) were purchased anhydrous and were dried over KH for at least 24 h, passed through a column of activated alumina, and were stored over activated 3 Å molecular sieves prior to use.  $(\text{C}_5\text{Me}_5)_2\text{UMe}_2$  was prepared according to a previous literature report.<sup>2</sup>

*Caution: Depleted uranium (primary isotope  $^{238}\text{U}$ ) is a weak  $\alpha$ -emitter (4.197 MeV) with a half-life of  $4.47 \times 10^9$  years; manipulations should be carried out in a monitored fume hood or in an inert atmosphere drybox in a radiation laboratory equipped with  $\alpha$ - and  $\beta$ - counting equipment.*

**Synthesis and isolation of  $[(C_5Me_5)_2UH]_x$  (5):** A 20-mL scintillation vial equipped with a stir bar was charged with  $(C_5Me_5)_2UMe_2$  (0.140 g, 0.260 mmol) and toluene (2 mL). The reaction mixture was heated to 50 °C and  $PhSiH_3$  (0.064 mL, 0.520 mmol) was added by microsyringe, which resulted in a color change from orange-red to dark brown. The reaction was stirred at 50 °C for 10 minutes (until gas evolution had ceased), after which volatiles were removed under reduced pressure at 50 °C to give a dark brown powder identified as pure  $[(C_5Me_5)_2UH]_x$  (0.132 g, 0.260 mmol, 100%).  $^1H$  NMR ( $C_6D_6$ , 296 K, 400 MHz):  $\delta$  3.03 (s,  $C_5Me_5$ ,  $\nu_{1/2}$  = 10 Hz), -9.37 (s,  $C_5Me_5$ ,  $\nu_{1/2}$  = 20 Hz). Some  $[(C_5Me_5)_2U(H)(\mu-H)]_2$  was also observed at ambient temperature:  $^1H$  NMR ( $C_6D_6$ , 296 K, 400 MHz):  $\delta$  = -2.59 (s,  $C_5Me_5$ ,  $\nu_{1/2}$  = 6 Hz). IR (ATR-IR, 296 K, Neat,  $cm^{-1}$ ): 2965, 2880, 2360, 2342, 1426, 1378, 1099, 719, 695, 688.

**Synthesis of  $(C_5Me_5)_2U(dmpe)(H)$  (6):** A 20-mL scintillation vial equipped with a stir bar was charged with  $(C_5Me_5)_2UMe_2$  (0.102 g, 0.190 mmol) and toluene (3 mL). The reaction mixture was heated to 50 °C and  $PhSiH_3$  (0.047 mL, 0.380 mmol) was added by microsyringe, which resulted in a color change from orange-red to dark brown. The reaction was stirred at 50 °C for 10 minutes (until gas evolution had ceased). The reaction mixture was cooled to ambient temperature and  $dmpe$  (0.032 mL, 0.190 mmol) was added by microsyringe. After stirring at 50 °C for 15 minutes, volatiles were removed under reduced pressure to give an oily brown residue. This residue was quickly washed with pentane (2 mL), and the volatiles were removed under reduced pressure to give  $(C_5Me_5)_2U(dmpe)(H)$  (6) as a dark brown powder (0.118 g, 0.179 mmol, 94%). The  $^1H$  NMR spectrum collected in  $C_6D_6$  was consistent with data previously reported for complex 6.<sup>3</sup>  $^1H$  NMR ( $C_6D_6$ , 296 K, 400 MHz):  $\delta$  = -6.08 (s, 30H,  $C_5Me_5$ ).

**Synthesis of  $(C_5Me_5)_2U(terpy)$  (7):** A 20-mL scintillation vial equipped with a stir bar was charged with  $(C_5Me_5)_2UMe_2$  (0.051 g, 0.095 mmol) and toluene (2 mL). The reaction mixture was heated to 50 °C and  $PhSiH_3$  (0.023 mL, 0.186 mmol) was added by microsyringe, which resulted in a color change from orange-red to dark brown. The reaction was stirred at 50 °C until gas evolution had ceased (10 minutes). Then 2,2':6',2''-terpyridine (0.022 g, 0.094 mmol) was added and the reaction stirred at 50 °C for 24 h, resulting in a gradual color change from dark brown to dark teal. Volatiles were removed under reduced pressure to give  $(C_5Me_5)_2U(terpy)$  (7) as a dark teal waxy solid (0.066 g, 0.089 mmol, 94%). The  $^1H$  NMR spectrum collected in  $C_6D_6$  was consistent with data previously reported for complex 7.<sup>4</sup>  $^1H$  NMR ( $C_6D_6$ , 296 K, 400 MHz):  $\delta$  = 15.56 (s, 30H,  $C_5Me_5$ ), -8.14 (s, 2H, terpy), -19.64 (s, 2H, terpy), -28.48 (s, 2H, terpy), -40.51 (s, 2H, terpy), -46.83 ppm (s, 1H, terpy).

**Synthesis of  $(C_5Me_5)_2U(-N=CPh_2)_2$  (**8**):** A 20-mL scintillation vial equipped with a stir bar was charged with  $(C_5Me_5)_2UMe_2$  (0.048 g, 0.090 mmol) and toluene (2 mL). The reaction mixture was heated to 50 °C and  $PhSiH_3$  (0.023 mL, 0.186 mmol) was added by microsyringe, which resulted in a color change from orange-red to dark brown. The reaction was stirred at 50 °C until gas evolution had ceased (10 minutes). Benzophenone azine (0.033 g, 0.091 mmol) was added to the reaction mixture at 50 °C, which resulted in vigorous gas evolution, and the reaction was stirred at 50 °C for 24 h. The volatiles were removed under reduced pressure to give  $(C_5Me_5)_2U(-N=CPh_2)_2$  (**8**) as a brown, waxy solid (0.064 g, 0.074 mmol, 83%). The  $^1H$  NMR spectrum collected in  $C_6D_6$  was consistent with data previously reported for complex **8**.<sup>5</sup>  $^1H$  NMR ( $C_6D_6$ , 296 K, 400 MHz):  $\delta$  = -1.87 (s, 30H,  $C_5Me_5$ ).

**Synthesis of  $(C_5Me_5)_2U(=NPh)_2$  (**9**):** A 20-mL scintillation vial equipped with a stir bar was charged with  $(C_5Me_5)_2UMe_2$  (0.050 g, 0.093 mmol) and toluene (2 mL). The reaction mixture was heated to 50 °C and  $PhSiH_3$  (0.023 mL, 0.186 mmol) was added by microsyringe, which resulted in a color change from orange-red to dark brown. The reaction was stirred at 50 °C until gas evolution had ceased (10 minutes). Azobenzene (0.016 g, 0.088 mmol) was added to the reaction mixture at 50 °C, which resulted in vigorous gas evolution, and the reaction was stirred at 50 °C for 1 hour. The volatiles were removed under reduced pressure to give  $(C_5Me_5)_2U(=NPh)_2$  (**9**) as a waxy, dark brown solid (0.061 g, 0.089 mmol, 95%). The  $^1H$  NMR spectrum collected in  $C_6D_6$  was consistent with data previously reported for complex **9**.<sup>6</sup>  $^1H$  NMR ( $C_6D_6$ , 296 K, 400 MHz):  $\delta$  = 9.27 (t, 4H,  $J$  = 7.8 Hz, *m*-Ar-*H*), 4.14 (s, 30H,  $C_5Me_5$ ), 2.92 (d, 4H,  $J$  = 7.4 Hz, *o*-Ar-*H*), 0.87 (t, 2H,  $J$  = 8.0 Hz, *p*-Ar-*H*).

**Synthesis of  $(C_5Me_5)_2U(C_4Ph_4)$  (**10**):** A 20-mL scintillation vial equipped with a stir bar was charged with  $(C_5Me_5)_2UMe_2$  (0.058 g, 0.107 mmol) and toluene (2 mL). The reaction mixture was heated to 50 °C and  $PhSiH_3$  (0.026 mL, 0.214 mmol) was added by microsyringe, which resulted in a color change from orange-red to dark brown. The reaction was stirred at 50 °C until gas evolution ceased (10 minutes). Diphenylacetylene (0.038 g, 0.214 mmol) was added to the reaction mixture, which resulted in vigorous gas evolution, and the reaction stirred at 50 °C for 30 minutes. The volatiles were removed under reduced pressure to give  $(C_5Me_5)_2U(C_4Ph_4)$  (**10**) as a dark brown powder (0.092 g, 0.107 mmol, 100%). The  $^1H$  NMR spectrum collected in  $C_6D_6$  was consistent with data previously reported for complex **10**.<sup>7</sup>  $^1H$  NMR ( $C_6D_6$ , 296 K, 400 MHz):  $\delta$  6.15 (s, 30H,  $C_5Me_5$ ), 5.68 (m, 4H, *m*-Ar-*H*), 4.47 (m, 4H, *o*-Ar-*H*), -0.66 (t,  $J$  = 6.8 Hz, 2H, *p*-Ar-*H*), -1.42 (t,  $J$  = 6.8 Hz, *m*-Ar-*H*), -37.32 (t,  $J$  = 6.9 Hz, *o*-Ar-*H*). One *p*-Ar-*H* resonance is located under the  $C_5Me_5$  resonance.

**Synthesis of  $(C_5Me_5)_2U(C_4Me_4)$  (**11**):** A 20-mL scintillation vial equipped with a stir bar was charged with  $(C_5Me_5)_2UMe_2$  (0.028 g, 0.052 mmol) and toluene (2 mL). The reaction mixture was heated to 50 °C and  $PhSiH_3$  (0.013 mL, 0.104 mmol) was added by microsyringe, which resulted in a color change from orange-red to dark brown. The reaction was stirred at 50 °C until gas evolution ceased (10 minutes). 2-Butyne (0.006 g, 0.104 mmol) was added to the reaction mixture, which resulted in vigorous gas evolution, and the reaction stirred at 50 °C for 30 minutes. The volatiles were removed under reduced pressure to give  $(C_5Me_5)_2U(C_4Me_4)$  (**11**) as a bright red powder (0.032 g, 0.052 mmol, 100%).  $^1H$  NMR ( $C_6D_6$ , 296 K, 400 MHz):  $\delta$  0.45 (s, 30H,  $C_5Me_5$ ), -3.61 (s, 6H,  $C_4Me_4$ ), -4.55 (s, 6H,  $C_4Me_4$ ). IR (ATR-IR, Neat, 296 K,  $cm^{-1}$ ): 3569, 2967, 2888, 2822, 2722, 1488, 1436, 1375, 1219, 1063, 1019, 735. UV/Vis (Toluene, 296 K, 0.2 mM,  $cm^{-1}$  ( $cm^{-1}M^{-1}$ )): 32895 (12525), 22300 (3200). NIR (Toluene, 296 K, 20 mM,  $cm^{-1}$  ( $cm^{-1}M^{-1}$ )): 13700 (87), 12950 (40), 10700 (35), 10275 (25), 8800 (90), 8500 (75), 8150 (125), 7800 (70), 6600 (20), 6300 (25), 5875 (50). mp: 198–199 °C. Anal. Calcd. for  $C_{28}H_{42}U$  (mol. wt. 616.66): C, 54.54; H, 6.86. Found: C, 54.22; H, 6.83.

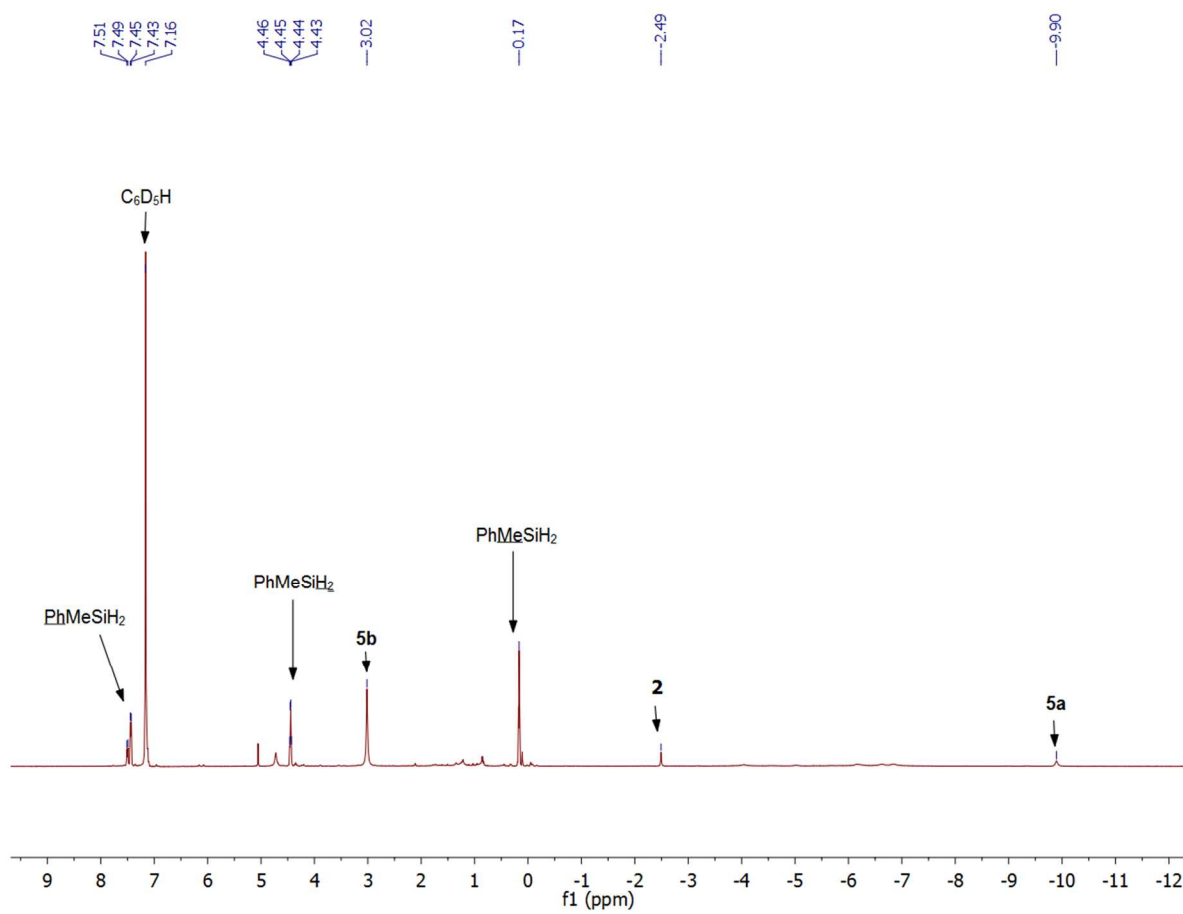
## X-ray Crystallography

Data for **11** were collected on a Bruker D8 APEX II diffractometer, with CCD detector. The crystal was cooled with a KRYO-FLEX liquid nitrogen vapor-cooling device. Hemispheres of data were collected with  $\omega$  scans. Data collection, initial indexing, and cell refinement were handled with APEX II software. Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out with SAINT+ software. The data were corrected for absorption with the SADABS program. The structure was solved with direct methods and difference Fourier techniques. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as idealized contributions. Structure solution and refinement were performed with SHELXTL. Additional details of data collection and structure refinement are shown below.

	(C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> U(C <sub>4</sub> Me <sub>4</sub> ) ( <b>11</b> )
Empirical formula	C <sub>28</sub> H <sub>42</sub> U
Formula weight	616.66
Crystal system	Monoclinic
<i>a</i> [Å]	12.024(2)
<i>b</i> [Å]	14.635(2)
<i>c</i> [Å]	13.996(2)
$\beta$ [°]	95.19(2)
<i>V</i> [Å <sup>3</sup> ]	2456.6(6)
Space group	C2/c
<i>Z</i>	4
$\rho$ [g/cm <sup>3</sup> ]	1.667
$\mu$ (MoK $\alpha$ )	6.619
<i>T</i> [K]	100
$2\theta_{\text{max}}$ [°]	57.24
min/max trans.	0.2874/0.6263
Total reflns	14162
Unique reflns	2990
Parameters	139
R <sub>1</sub> (wR <sub>2</sub> ) (all data)	0.0171 (0.0411)

Table S1: Crystallographic collection details for (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>U(C<sub>4</sub>Me<sub>4</sub>)<sub>2</sub> (**11**).





**Figure S1:**  $^1H$  NMR of  $[(C_5Me_5)_2UH]_x$  (**5**) at 20 °C.

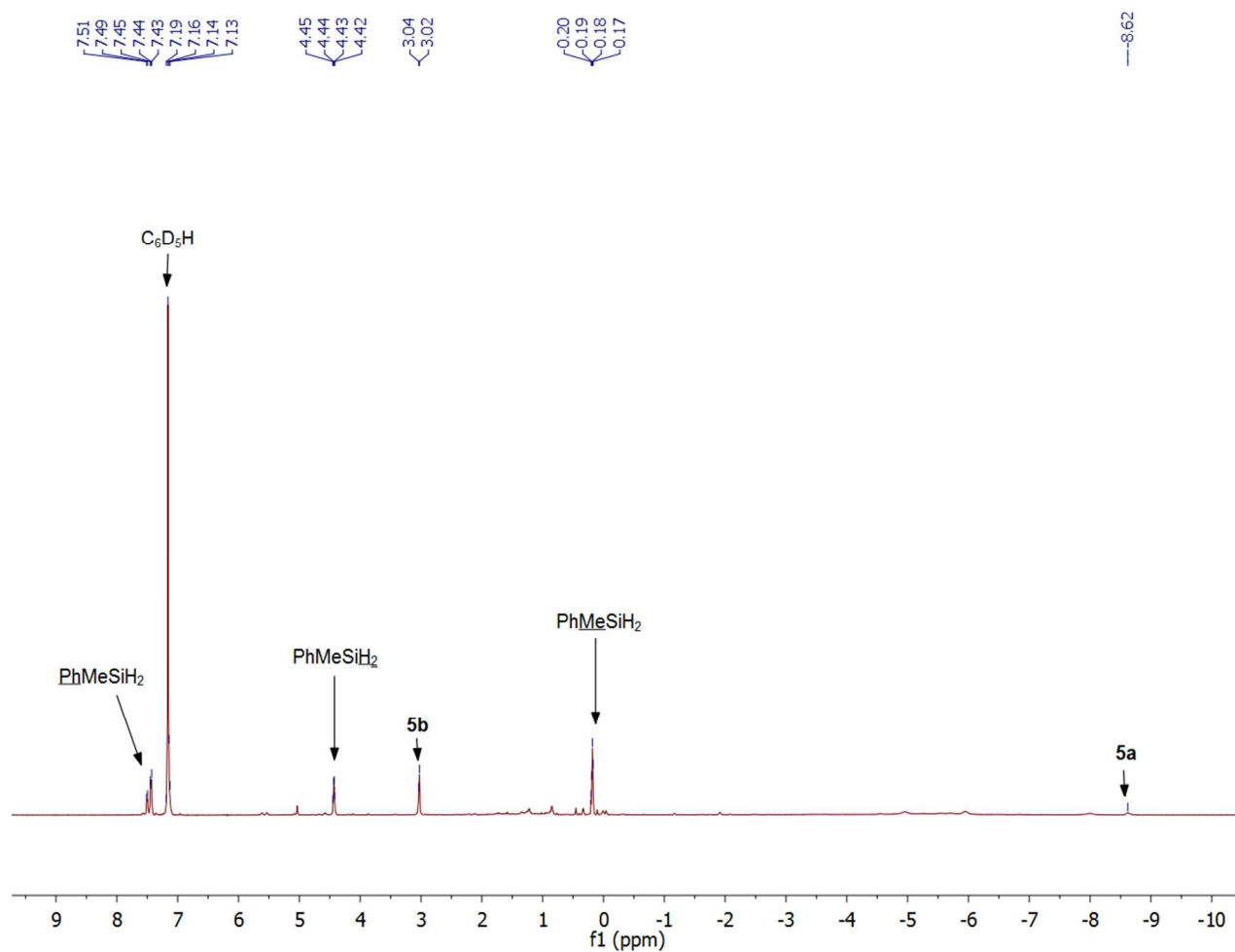
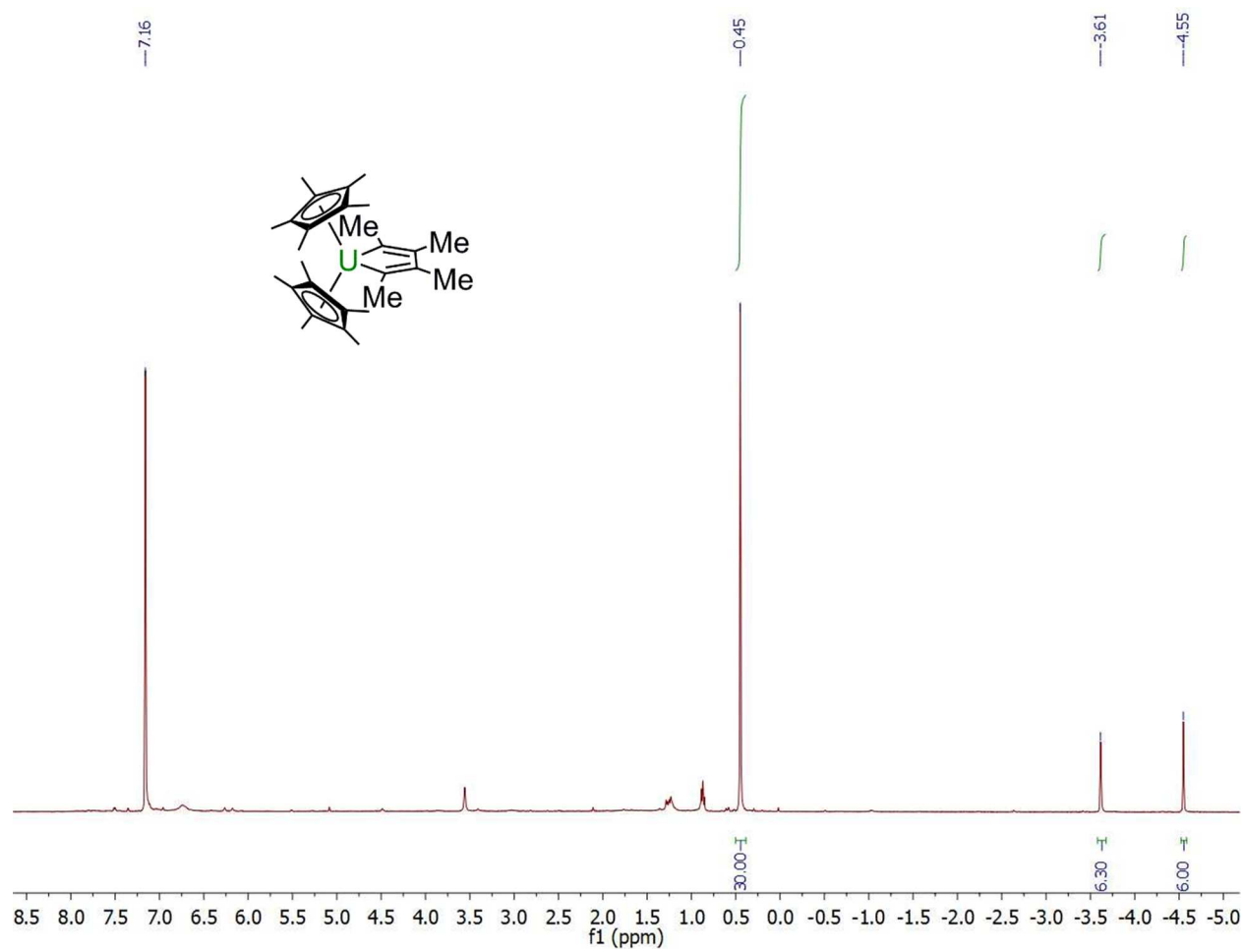


Figure S2:  $^1\text{H}$  NMR spectrum of  $[(\text{C}_5\text{Me}_5)_2\text{UH}]_x$  (**5**) at  $50\text{ }^\circ\text{C}$ .



**Figure S3:**  $^1\text{H}$  NMR spectrum of  $(\text{C}_5\text{Me}_5)_2\text{U}(\text{C}_4\text{Me}_4)$  in  $\text{C}_6\text{D}_6$  (**11**).

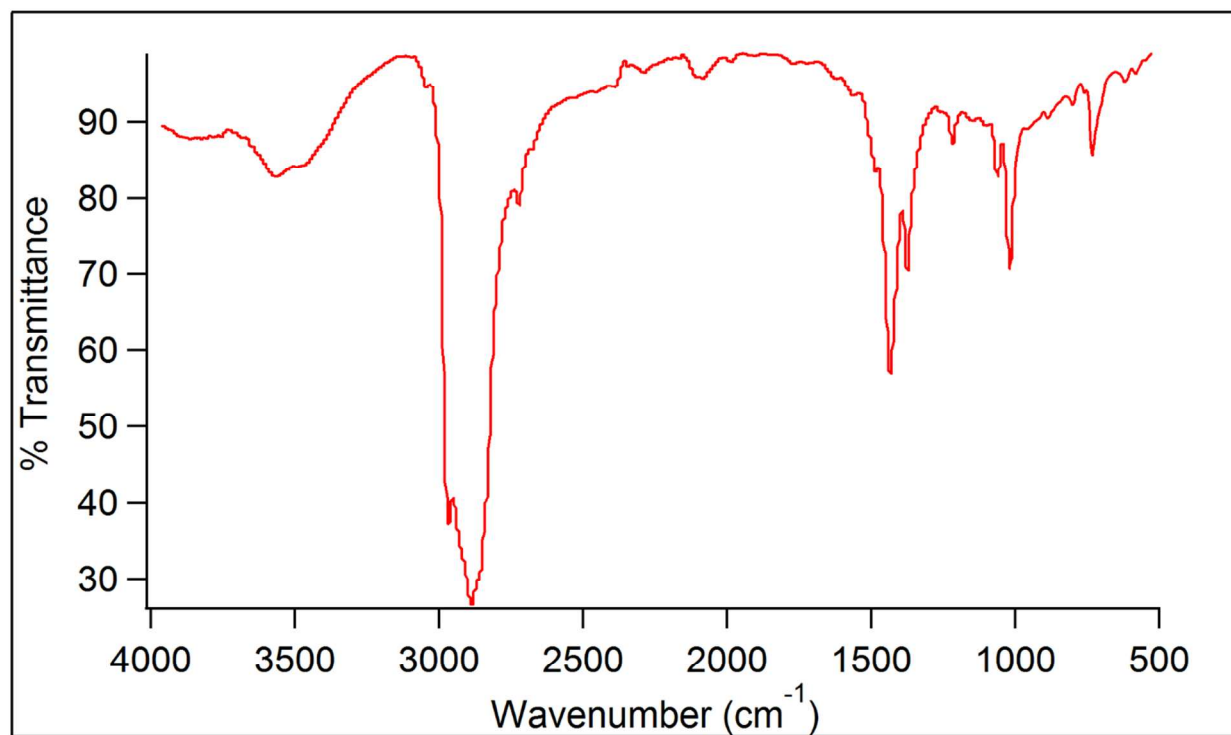
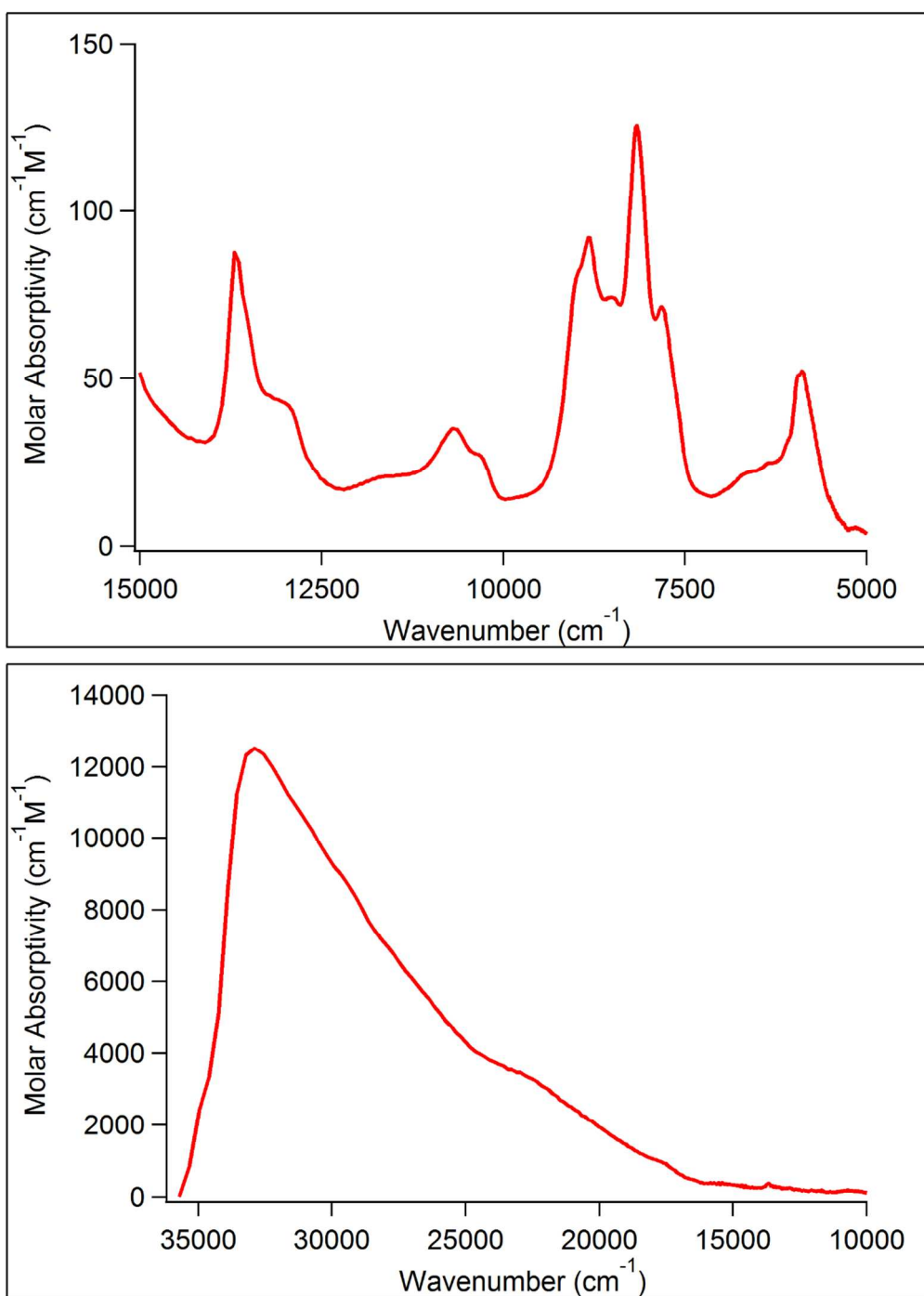


Figure S4: IR spectrum of  $(\text{C}_5\text{Me}_5)_2\text{U}(\text{C}_4\text{Me}_4)$  (**11**).



**Figure S5:** NIR (top) and UV/vis (bottom) spectra of  $(\text{C}_5\text{Me}_5)_2\text{U}(\text{C}_4\text{Me}_4)$  (**11**)

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