Supporting Information for

In situ generation of uranium alkyl complexes

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Experimental

All experiments were performed under a dry nitrogen atmosphere using standard Schlenk techniques or an MBraun inert-gas glove box. Solvents were purified using a two-column solid-state purification system by the method of Grubbs[1] and transferred to the glove box without exposure to air. NMR solvents were obtained from Cambridge Isotope Laboratories, degassed, and stored over activated molecular sieves prior to use. Uranium turnings were purchased from Argonne National Laboratories. $LiCH_2SiMe_3$ was purchased from Acros as an *n*-pentane solution (1 M), which was filtered through Celite; the volatiles were removed to leave a white solid, which was used without further purification. Compounds $UI_3(THF)_4$,[2-4] $LiCH_2CMe_3$,[5] $H_2(NN^{fc})$,[6] $H_2(NN^{fc'})$,[7] KCH_2Ph,[8] 2,6-bis(chloromethyl)pyridine,[9] $\mathbf{1^{fc}\text{-}(CH_2Ph)_2}$ and $\mathbf{1^{fc}\text{-}(CH_2{}^tBu)_2}$[10] were prepared following published procedures. Syntheses of $H_2(NN^{py})$[11] and $[Li(OEt_2)_2]_2[NN^{py}]$[12] were slightly modified from reported procedures. ^nBuLi was purchased from Alfa Aesar as a hexanes solution (2.88 M); all other chemicals were purchased and used as received. ^1H NMR spectra were recorded on Bruker300 or Bruker500 spectrometers (the spectrometers are supported by the NSF grant CHE-9974928) at room temperature in C_6D_6 unless otherwise specified. Chemical shifts are reported with respect to solvent residual peak, 7.16 ppm (C_6D_6). CHN analyses were performed by UC Berkeley Micro-Mass facility, 8 Lewis Hall, College of Chemistry, University of California, Berkeley, CA 94720.

Synthesis of $\mathbf{H_2(NN^{py})}$. A cold THF solution of 2,6-diisopropylaniline (1.4615 g, 7.986 mmol) was added to a stirring THF solution of 2,6-bis(chloromethyl)pyridine (0.6605 g, 3.803 mmol) at -78 °C. The mixture was warmed to room temperature and stirred for 19 h. The reaction was quenched with a saturated solution of Na_2CO_3 and extracted into diethyl ether three times. The fractions were combined and dried with $MgSO_4$. Volatiles were removed under reduced pressure and a small amount of hexanes was added to the resulting dark yellow oil to yield a sticky white precipitate, which was collected on a medium-porosity frit and dried. The off-white solid was dissolved in diethyl ether, filtered through alumina, and crystallized at room temperature by slow evaporation. Yellow needle crystals formed in a 91% yield (1.58 g, 3.461 mmol).

Synthesis of $\mathbf{[Li(OEt_2)_2]_2[NN^{py}]}$. In a 20-mL scintillation vial charged with a stir bar, $H_2(NN^{py})$ (0.2140 g, 0.467 mmol) was dissolved in toluene, then cooled for 30 min. To this white suspension, a cold hexanes solution of ^nBuLi (35 mL, 0.2360 g, 0.981 mmol) was added slowly and the resulting dark-orange mixture was stirred at room temperature for 10 min. The volatiles were removed under reduced pressure and the orange gel was washed with cold hexanes. The yellow solid was collected on a medium-porosity frit, washed with a small amount of cold hexanes, and dried. Yield: 90% (0.1930 g, 0.4203 mmol).

Synthesis of $\mathbf{1^{py}{}_2\text{-}U}$. A 5-mL THF solution of $[Li(OEt_2)_2]_2[NN^{py}]$ (0.1420 g, 0.3 mmol) was added to a THF solution of $UI_3(THF)_4$ (0.3670 g, 0.4 mmol). The mixture was stirred for 16 h, filtered through Celite, and dried. The crude product was extracted into toluene, the solution was filtered through Celite and dried; the extraction was repeated one more time. After washing with hexanes, the brown-yellow product was dissolved in Et_2O, the solution was filtered through Celite, and set to crystallize at -35 °C. Large, black icosahedra formed after 48 h. The mother liquor was decanted and the crystals were dried. Further recrystallization attempts were unsuccessful due to the compound's insolubility in organic solvents. Yield (based on $[Li(OEt_2)_2]_2[NN^{py}]$): 49% (169 mg, 0.147 mmol).

***Note*: The yields of the following compounds were calculated with respect to their proligands.**

Synthesis of 1^{py}-U(CH$_2$Ph)$_2$. In a 20-mL scintillation vial, $UI_3(THF)_4$ (0.6262 g, 0.691 mmol) was dissolved in 6 mL of THF and cooled to -78 °C for 1 h. KCH_2Ph (0.2700 g, 2.074 mmol) was added to the cold dark-purple solution and stirred until it warmed to room temperature. A cold diethyl ether solution of $H_2(NN^{py})$ (0.2360 g, 0.518 mmol) was added the reaction mixture, which was then allowed to stir at room temperature for 3 h. The final mixture was filtered through Celite, washed with toluene, and dried. The product was extracted into toluene, the solution was filtered through Celite and dried; the extraction was repeated one more time. After washing with hexanes, the product was extracted into diethyl ether, filtered through Celite, and set to crystallize at -35 °C. Large, red needles formed overnight that were recrystallized one more time. Yield: 62% (282 mg, 0.322 mmol).

Synthesis of 1^{py}-UI(CH$_2$Ph). In a 20-mL scintillation vial, $UI_3(THF)_4$ (0.403 g, 0.444 mmol) was dissolved in approximately 4 mL of THF and cooled to -78 °C for 1 h. KCH_2Ph (0.1290 g, 0.933 mmol) was added to the dark-purple solution and stirred until it warmed to room temperature. A cold diethyl ether solution of $H_2(NN^{py})$ (0.1526 g, 0.3330 mmol) was added the final reaction mixture, which was allowed to stir at room temperature for 3 h. The final mixture was filtered through Celite, washed with toluene, and dried. The product was extracted into toluene, the solution was filtered through Celite and dried; the extraction was repeated one more time. After washing with hexanes, the product was extracted into diethyl ether, filtered through Celite, and set to crystallize at -35 °C. Small, pale-orange crystals formed overnight and were recrystallized one more time. Yield: 76% (231 mg, 0.253 mmol).

Synthesis of $1^{fc'}$-U(CH$_2$Ph)$_2$. A THF solution of $UI_3(THF)_4$ (0.5183 g, 0.5720 mmol) was cooled to -78 °C for 1 h and KCH_2Ph (0.2401 g, 1.830 mmol) was added to this slurry. The mixture was allowed to stir at -78 °C for 1 h, at which point a cold diethyl ether solution of $H_2(NN^{fc'})$ (0.1547 g, 0.4291 mmol) was added drop wise. After an additional hour of stirring at -40 °C, the volatiles were removed under reduced pressure and the resulting solid was dissolved in toluene, filtered through Celite, and dried. The dark red solid was extracted into hexanes, filtered through Celite, and set to crystallize at -35 °C. Dark-red needle crystals formed after 1 d. Yield: 77% (257 mg, 0.330 mmol).

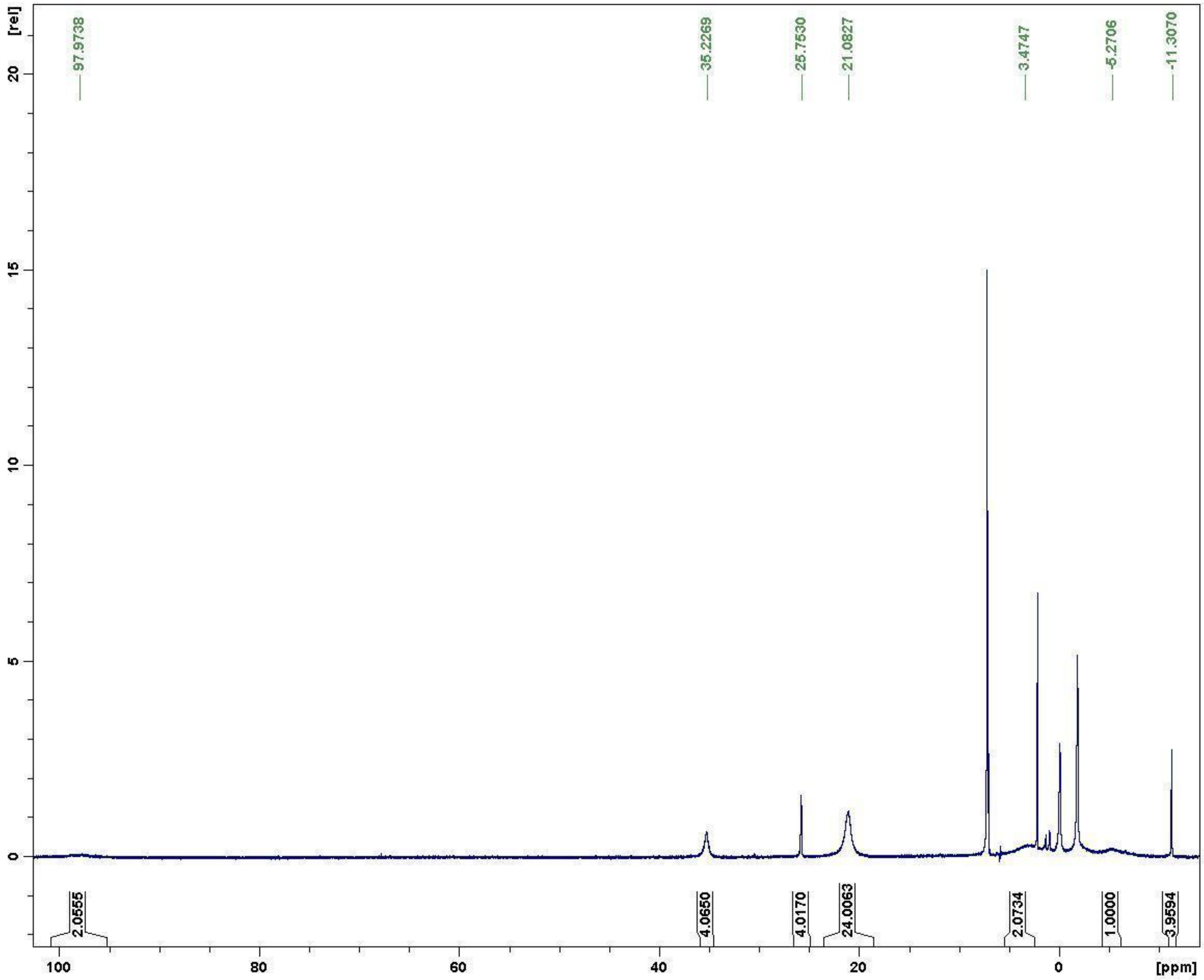
Synthesis of $1^{fc'}$-U(CH$_2$SiMe$_3$)$_2$. A THF solution of $UI_3(THF)_4$ (0.5136 g, 0.5670 mmol) was cooled to -78 °C for 1.5 h and $LiCH_2SiMe_3$ (0.1698 g, 1.814 mmol) was added to this slurry. The mixture was allowed to stir at -78 °C for 1 h, at which point a cold diethyl ether solution of $H_2(NN^{fc'})$ (0.1523 g, 0.4250 mmol) was added drop wise. After an additional hour of stirring at -40 °C, the volatiles were removed under reduced pressure and the resulting solid was dissolved in toluene, filtered through Celite, and dried. The yellow-brown solid was washed with hexanes, extracted into diethyl ether, filtered through Celite, and set to crystallize at -35 °C. Large, brown, hexagonal crystals formed after 2 d. Yield: 80% (262 mg, 0.340 mmol).

Synthesis of 1^{fc}-U(CH$_2$SiMe$_3$)$_2$. A THF solution of $UI_3(THF)_4$ (0.2110 g, 0.2328 mmol) was cooled to -78 °C for 1.5 h and $LiCH_2SiMe_3$ (0.0695 g, 0.7450 mmol) was added to this slurry. The mixture was allowed to stir at -78 °C for 1 h, at which point a cold diethyl ether solution of

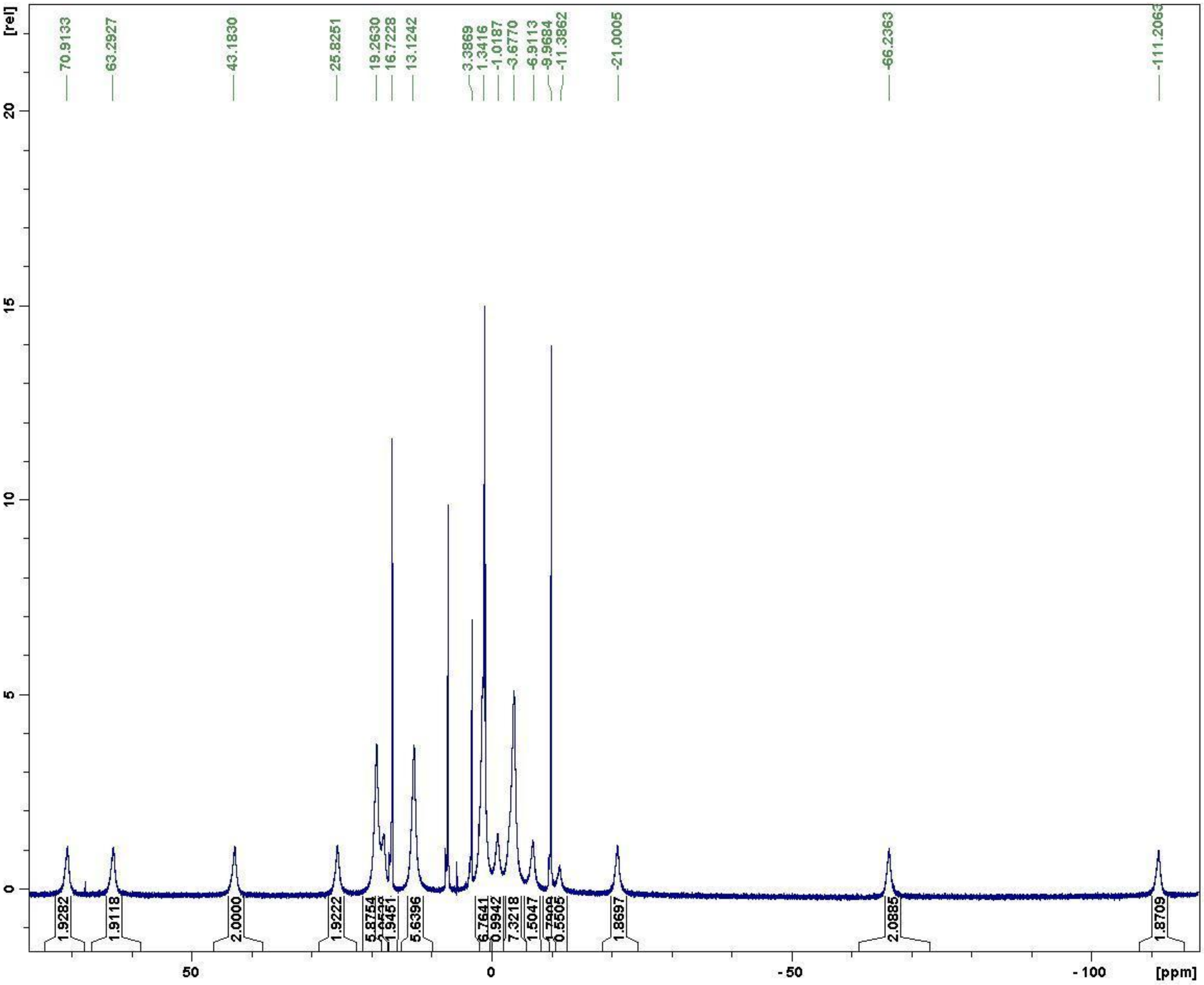
$H_2(NN^{fc})$ (0.0776 g, 0.1746 mmol) was added dropwise. After an additional hour of stirring at -40 °C, the volatiles were removed under reduced pressure and the resulting solid was dissolved in toluene, filtered through Celite, and dried. The yellow-brown solid was washed with hexanes, extracted into diethyl ether, filtered through Celite, and set to crystallize at -35 °C. Large, brown, hexagonal crystals formed after 2 d. Yield: 87% (130 mg, 0.152 mmol).

^{1}H NMR Spectra

$1^{py}{}_2$-U (500 MHz, 25 °C, C_6D_6)

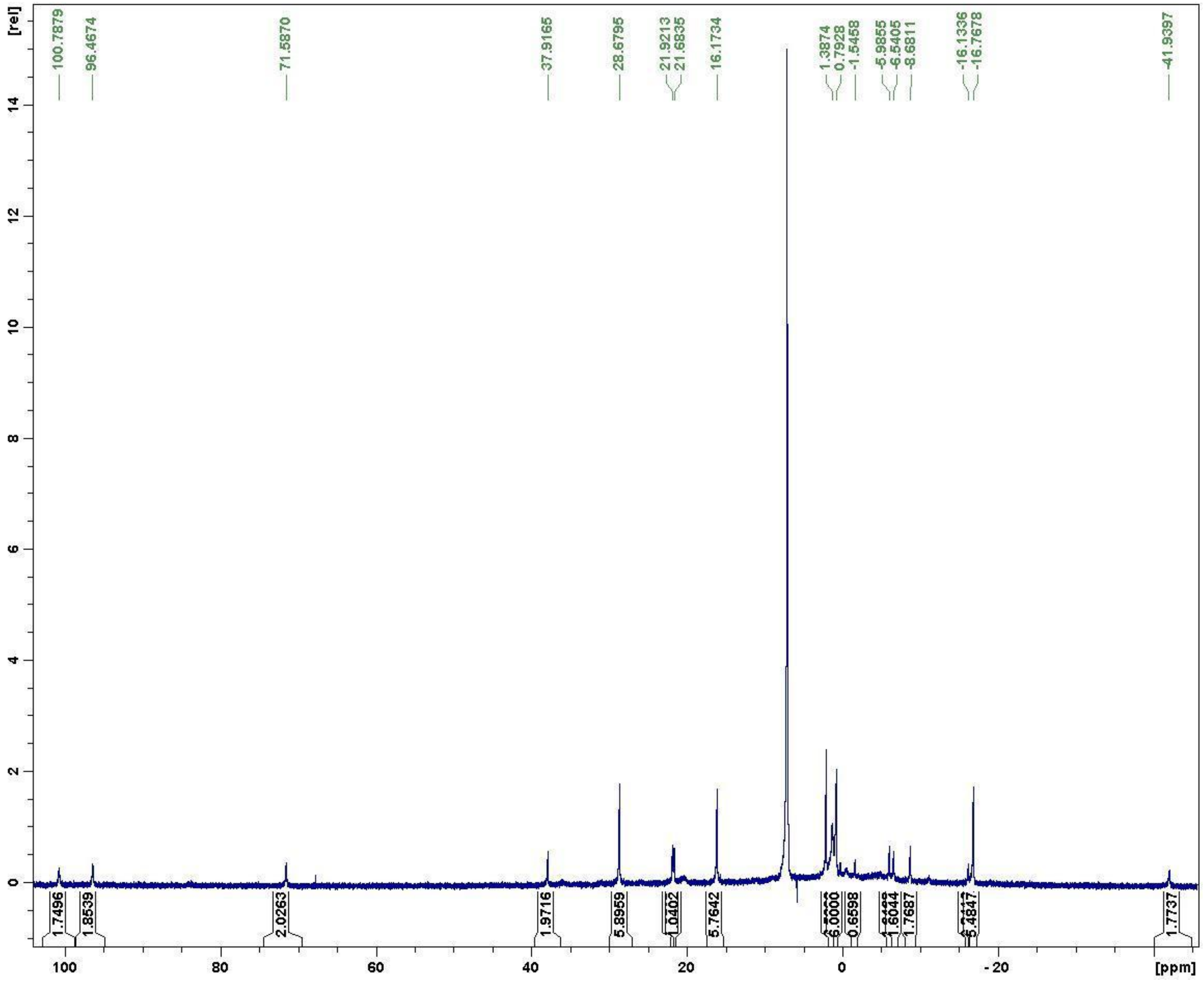


1^{py}-U(CH_2Ph)$_2$ (500 MHz, 25 °C, C_6D_6)



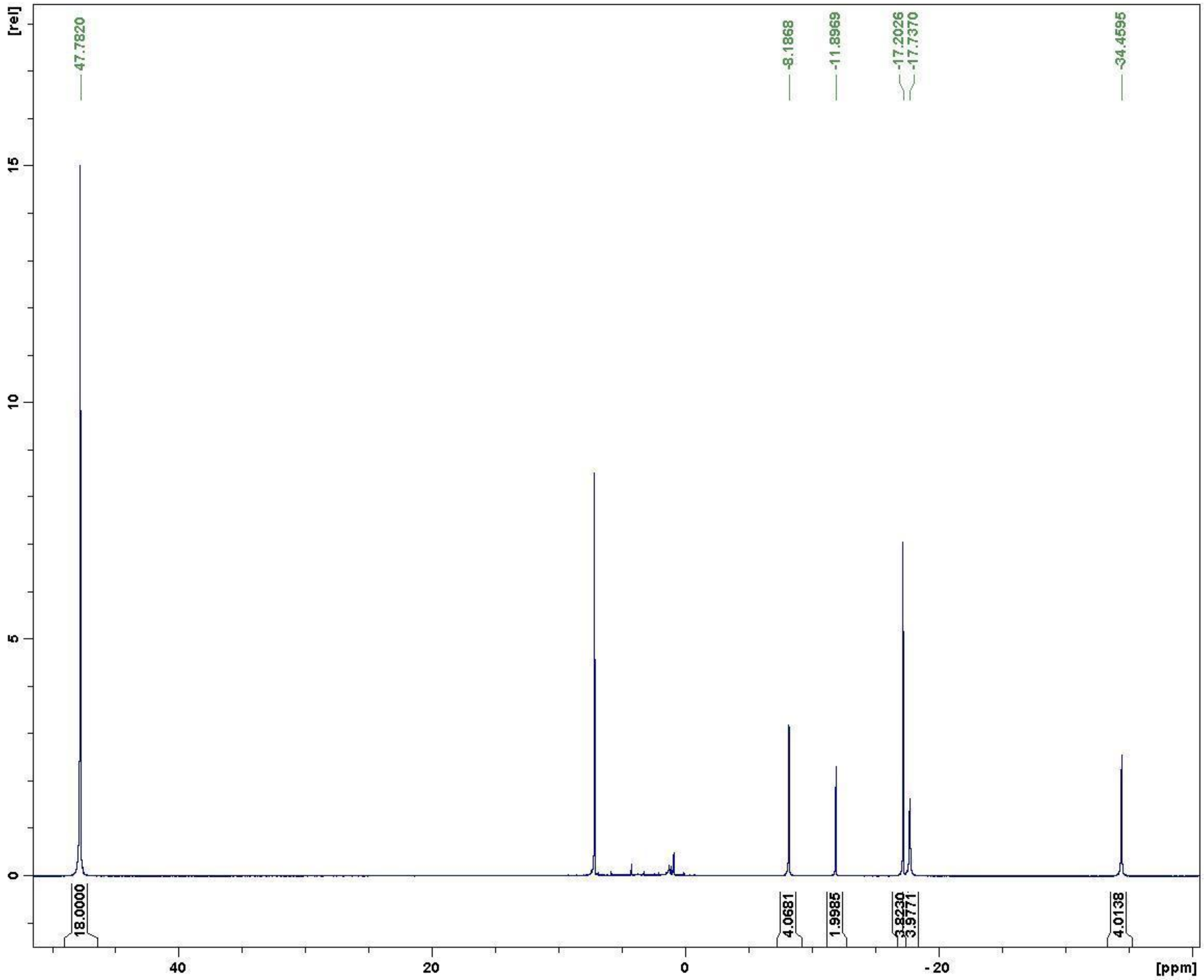
Note: U−CH_2 protons are likely not observed.

$\mathbf{1}^{\mathrm{py}}$-UI(CH$_2$Ph) (500 MHz, 25 °C, C_6D_6)



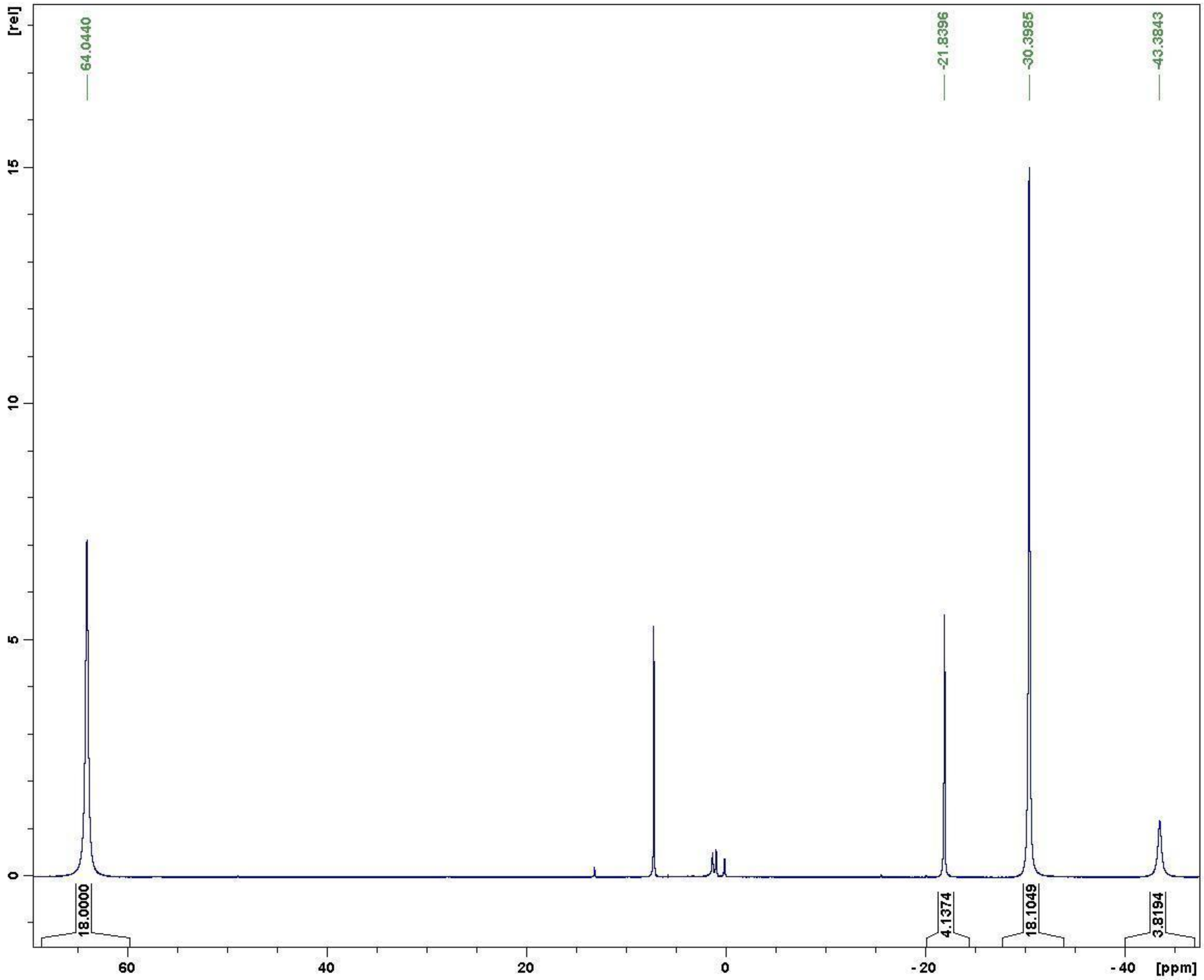
Note: U−CH$_2$ protons are likely not observed.

$1^{fc'}$-U(CH_2Ph)$_2$ (300 MHz, 25 °C, C_6D_6)



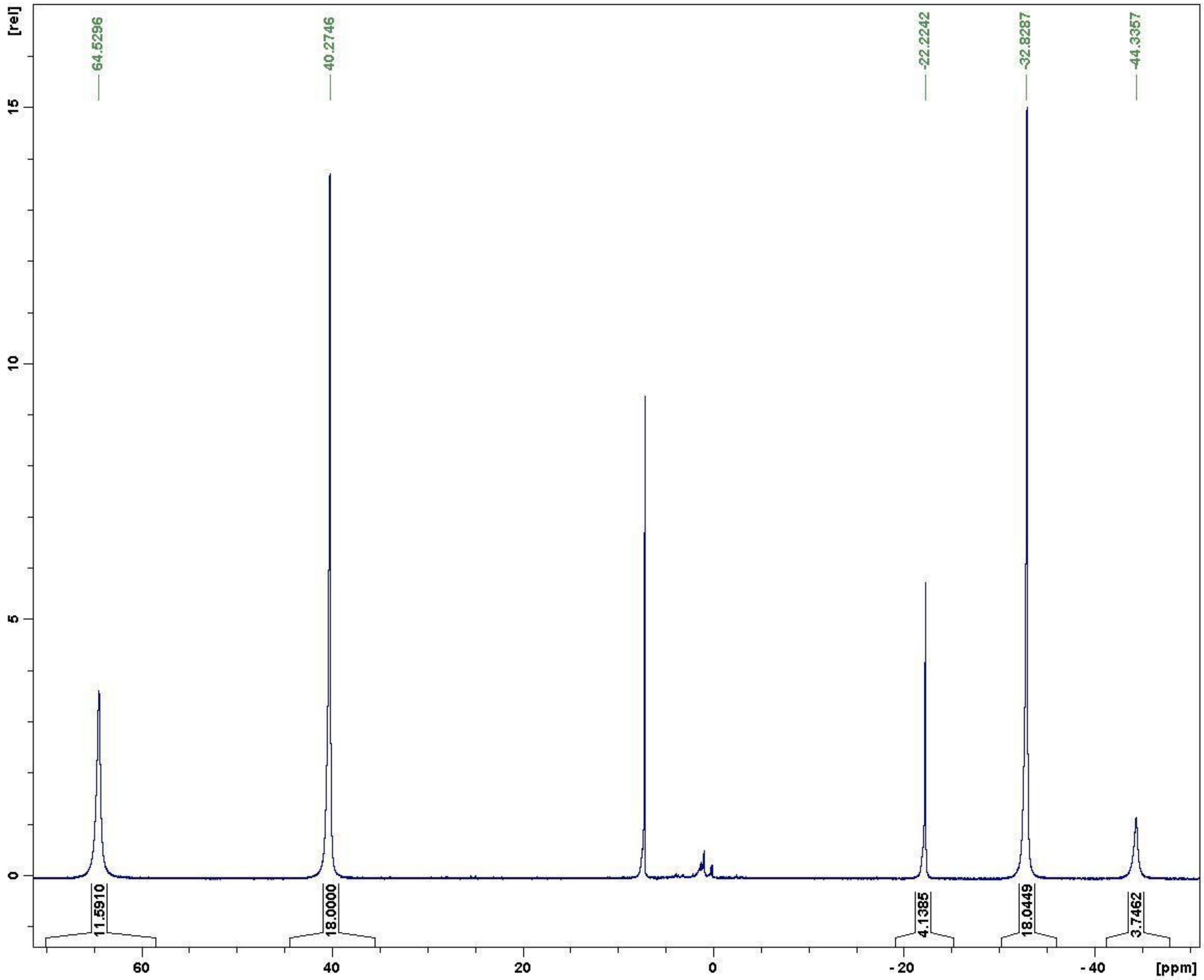
Note: U−CH_2 protons are likely not observed.

$1^{fc'}$-U(CH_2SiMe_3)$_2$ (300 MHz, 25 °C, C_6D_6)



Note: U−CH_2 protons are likely not observed.

1^{fc}-U(CH_2SiMe_3)$_2$ (300 MHz, 25 °C, C_6D_6)



Note: U−CH_2 protons are likely not observed.

X-ray crystal structures

$1^{py}{}_2$-U

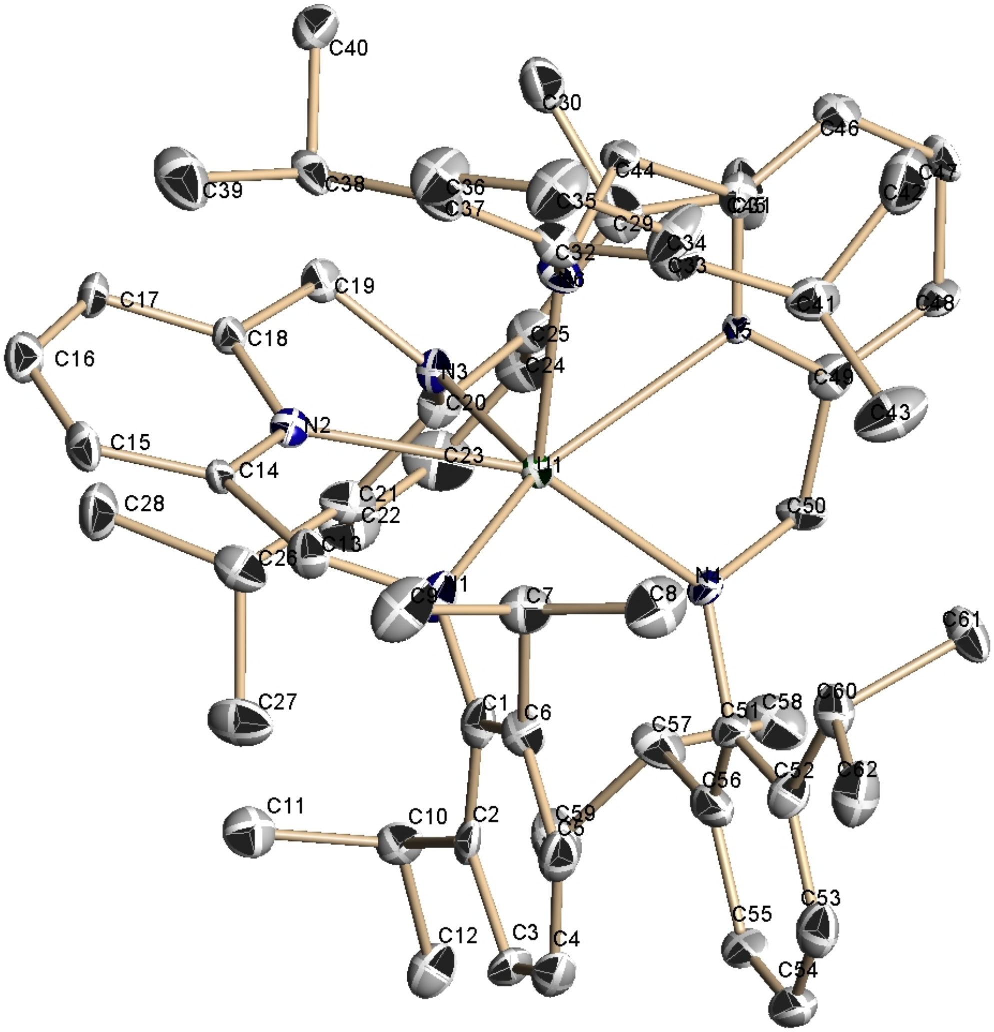


Figure SX1. Thermal-ellipsoid (50% probability) representation of **$1^{py}{}_2$-U**. Hydrogen atoms were omitted for clarity.

1^{py}-U(CH_2Ph)$_2$

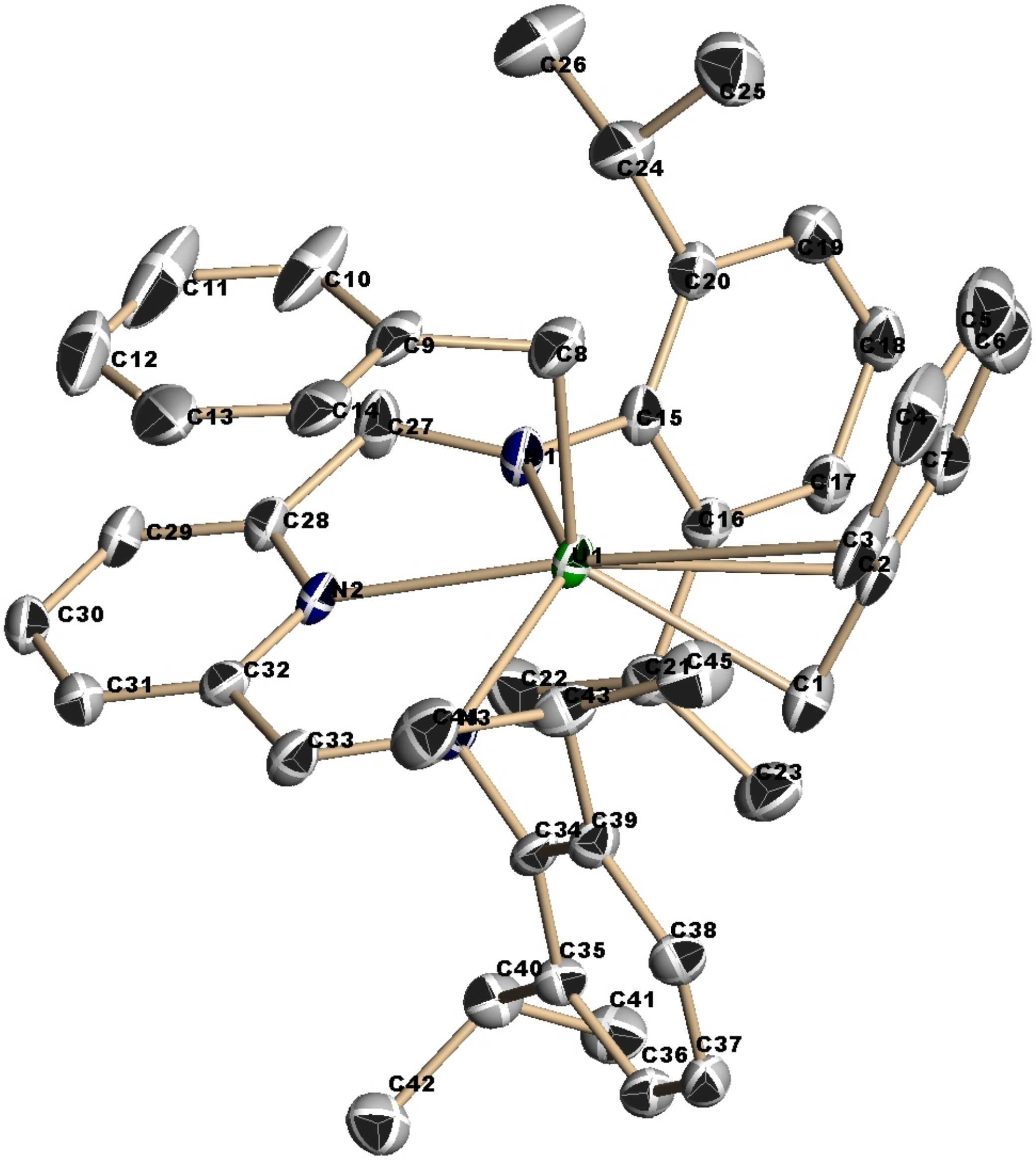


Figure SX2. Thermal-ellipsoid (50% probability) representation of **1^{py}-U(CH_2Ph)$_2$**. Hydrogen and solvent atoms were omitted for clarity.

1^{py}-UI(CH_2Ph)

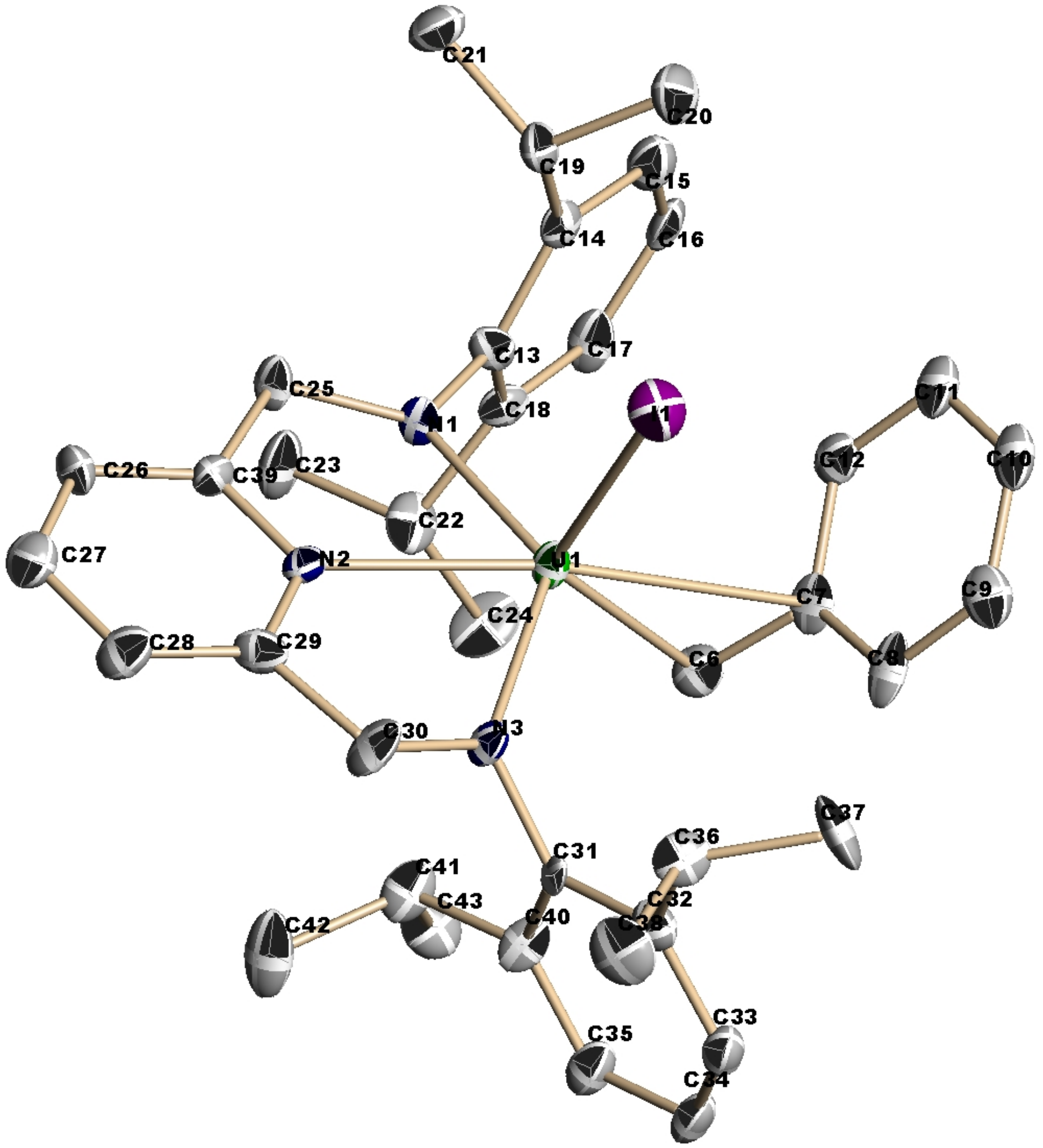


Figure SX3. Thermal-ellipsoid (50% probability) representation of **1^{py}-UI(CH_2Ph)**. Hydrogen and solvent atoms were omitted for clarity.

Note: The unit cell contains half a molecule of *trans*-stilbene, which is likely the result of accidental contamination.

References:

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