Supporting Information for:

Reactivity of [U(*C*H_2SiMe_2*N*SiMe_3)(NR_2)$_2$] (R = SiMe_3) with elemental chalcogens: Towards a better understanding of chalcogen atom transfer in the actinides

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Experimental

General. All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions under an atmosphere of nitrogen. Hexanes, Et_2O, and toluene were dried using a Vacuum Atmospheres DRI-SOLV Solvent Purification system and stored over 3Å sieves for 24 h prior to use. Tetrahydrofuran (THF) was distilled twice, first from calcium hydride and then from sodium benzophenone ketyl, and stored over 3Å molecular sieves for 24 h prior to use. Pyridine, benzene-d_6, pyridine-d_5, and THF-d_8 were dried over 3Å molecular sieves for 24 h prior to use. $[U(\mathit{C}H_2SiMe_2\mathit{N}SiMe_3)(NR_2)_2]$ (R = $SiMe_3$) (**2**),[1] $[U(NR_2)_3]$,[2] $[U(Cl)(NR_2)_3]$.[3] and [K(18-crown-6)]$[U(S)(NR_2)_3]$,[4] were synthesized according to the previously reported procedures. All other reagents were purchased from commercial suppliers and used as received.

NMR spectra were recorded on a Varian UNITY INOVA 400, a Varian UNITY INOVA 500 spectrometer, a Varian UNITY INOVA 600 MHz spectrometer, or an Agilent Technologies 400-MR DD2 400 MHz Spectrometer. ^1H NMR spectra were referenced to external $SiMe_4$ using the residual protio solvent peaks as internal standards. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer with a NXR FT Raman Module. UV-Vis / NIR experiments were performed on a UV-3600 Shimadzu spectrophotometer. Elemental analyses were performed by the Micro-Analytical Facility at the University of California, Berkeley.

X-ray Crystallography. Data for **5** and **9·Et_2O** were collected on a Bruker KAPPA APEX II diffractometer equipped with an APEX II CCD detector using a TRIUMPH monochromator and a Mo Kα X-ray source (α = 0.71073 Å). The crystals were mounted on a cryoloop under Paratone-N oil, and all data were collected at 100(2) K using an Oxford nitrogen gas cryostream. Data were collected using ω scans with 0.5° frame widths. Frame exposures of 2 s (low angle) and 5 s (high angle) were used for **5**. Frame exposures of 10 s were used for **9·Et$_2$O**. Data collection and cell parameter determinations were conducted using the SMART program.[5] Integration of the data frames and final cell parameter refinement were performed using SAINT software.[6] Absorption correction of the data was carried out using the multi-scan method SADABS.[7] Subsequent calculations were carried out using SHELXTL.[8] Structure determinations were done using direct or Patterson methods and difference Fourier techniques. All hydrogen atom positions were idealized, and rode on the atom of attachment. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL.[8] Further crystallographic details can be found in Table S1. Complexes **5** and **9·Et$_2$O** have been deposited in the Cambridge Structural Database (**5**: CCDC 1050744; **9·Et$_2$O**: CCDC 1050745).

Synthesis of [U(*S*CH$_2$SiMe$_2$*N*SiMe$_3$)(NR$_2$)$_2$] (3). *Method A:* To a brown, cold (-25 °C), stirring solution of [U(*C*H$_2$SiMe$_2$*N*SiMe$_3$)(NR$_2$)$_2$] (**2**) (155.5 mg, 0.22 mmol) in hexanes (4 mL) was added S_8 (11.4 mg, 0.044 mmol). This mixture was allowed to stir for 30 min, whereupon the solvent was removed in vacuo to give a yellow-brown solid. This solid was extracted with hexanes (4 mL) and filtered through a Celite column supported on glass wool (0.5 cm × 2 cm) to provide a yellow-brown filtrate. The solvent was then removed in vacuo and the resulting yellow-brown solid was extracted with diethyl ether (4 mL) to provide a yellow-brown solution. This solution was filtered through a Celite column supported on glass wool (0.5 cm × 2 cm) to provide a yellow-brown filtrate. The volume of this filtrate was reduced in vacuo to 1 mL and the solution was transferred to a 4 mL scintillation vial that was placed inside a 20 mL scintillation vial. Toluene (6 mL) was then added to the outer vial. Storage of this two vial system at -25 °C for 72 h resulted in the deposition of yellow-brown crystals, which were isolated by decanting away the supernatant (101 mg, 62%). Anal. Calcd for $C_{18}H_{53}N_3SSi_6U$: C, 28.82; H, 7.12; N, 5.60. Found: C, 29.67; H, 7.03; N, 5.81. ^1H NMR (400 MHz, 25 °C, benzene-d_6): δ -11.44 (br s, 9H, Si(C*H*$_3$)$_3$), -9.97 (br s, 2H, C*H*$_2$), -4.22 (br s, 36H, N(Si(C*H*$_3$)$_3$)$_2$), 3.38 (br s, 6H, Si(C*H*$_3$)$_2$). IR (KBr Pellet, cm^{-1}): 615 (m), 662 (m), 683 (m), 757 (m), 818 (sh), 841 (s), 872 (sh), 933 (s), 1101 (w), 1182 (m), 1252 (s), 1404 (m). UV-Vis/NIR (C_4H_8O, 4.98 mM, 25 °C, L·mol^{-1}·cm^{-1}): 524 (ε = 31.0), 694 (ε = 25.5), 822 (ε = 7.1), 956 (ε = 7.9), 1069 (ε = 27.9), 1154 (sh) (ε = 17.3), 1406 (ε = 14.3), 1560 (ε = 10.9).

Method B: To a brown, cold (-25 °C), stirring solution of [U(*C*H$_2$SiMe$_2$*N*SiMe$_3$)(NR$_2$)$_2$] (**2**) (206.1 mg, 0.29 mmol) in hexanes (4 mL) was added ethylene sulfide (20 μL, 0.31 mmol). This solution was allowed to stir for 24 h, whereupon the color of the solution changed to yellow-brown. The solvent was removed in vacuo, and the resulting yellow-brown solid was extracted with hexanes (5 mL) to give a yellow-brown solution. This solution was then filtered through a Celite column supported on glass wool (0.5 cm × 2 cm) to provide a yellow-brown filtrate. The filtrate was then dried in vacuo to give a yellow-brown powder (200 mg, 93%). ^1H NMR (400 MHz, 25 °C, benzene-d_6): δ -11.40 (br s, 9H, Si(C*H*$_3$)$_3$), -10.06 (br s, 2H, C*H*$_2$), -4.18 (br s, 36H, N(Si(C*H*$_3$)$_3$)$_2$), 3.41 (br s, 6H, Si(C*H*$_3$)$_2$).

In Situ Reaction of [U(*C*H$_2$SiMe$_2$*N*SiMe$_3$)(NR$_2$)$_2$] (2) with Ethylene sulfide. To a brown solution of [U(*C*H$_2$SiMe$_2$*N*SiMe$_3$)(NR$_2$)$_2$] (**2**) (11.1 mg, 0.015 mmol) in benzene-d_6 (0.5 mL), in an NMR tube fitted with a J-Young valve, was added ethylene sulfide (1 μL, 0.016 mmol). This solution was allowed to stand for 24 h, whereupon a ^{1}H NMR spectrum was recorded, which revealed the complete consumption of **1** and the formation of **2** and ethylene. ^{1}H NMR (400 MHz, 25 °C, benzene-d_6): δ -11.40 (br s, 9H, Si(CH_3)$_3$), -9.90 (br s, 2H, CH_2), -4.20 (br s, 36H, N(Si(CH_3)$_3$)$_2$), 3.39 (br s, 6H, Si(CH_3)$_2$), 5.26 (s, 4H, ethylene CH_2).

Synthesis of [U(*Se*CH$_2$SiMe$_2$*N*SiMe$_3$)(NR$_2$)$_2$] (4). To a brown, cold (-25 °C), stirring solution of **2** (149.4 mg, 0.21 mmol) in hexanes (4 mL) was added Se powder (35.9 mg, 0.45 mmol). This mixture was allowed to stir for 18 h, whereupon the color changed to yellow-brown. This mixture was filtered through a Celite column supported on glass wool (0.5 cm × 2 cm) to provide a yellow-brown filtrate. The filtrate was then dried in vacuo and extracted with diethyl ether (3 mL). The volume of this solution was reduced to 1.5 mL in vacuo and the solution was transferred to a 4 mL scintillation vial that was placed inside a 20 mL scintillation vial. Toluene (5 mL) was then added to the outer vial. Storage of this two vial system at -25 °C for 48 h resulted in the deposition of yellow crystalline needles, which were isolated by decanting off the supernatant (99.8 mg, 60%). Anal. Calcd for $C_{18}H_{53}N_3SeSi_6U$: C, 27.12; H, 6.70; N, 5.27. Found: C, 27.83; H, 6.48; N, 5.63. ^{1}H NMR (400 MHz, 25 °C, benzene-d_6): δ -12.24 (br s, 9H, Si(CH_3)$_3$), -7.18 (br s, 2H, CH_2), -3.69 (br s, 36H, N(Si(CH_3)$_3$)$_2$), 4.67 (br s, 6H, Si(CH_3)$_2$). IR (KBr Pellet, cm^{-1}): 602 (sh), 617 (m), 667 (m), 676 (m), 712 (m), 729 (m), 756 (m), 793 (sh), 818 (sh), 841 (s), 866 (sh), 935 (s), 1067 (w), 1182 (m), 1250 (s), 1379 (w), 1404 (m). UV-Vis/NIR (C_4H_8O, 5.36 mM, 25 °C, L·mol^{-1}·cm^{-1}): 694 (ε = 35.2), 804 (ε = 14.9), 952 (ε = 12.4), 1056 (ε = 27.5), 1152 (sh) (ε = 17.9), 1388 (ε = 14.6), 1540 (ε = 11.7).

Synthesis of [U(*Te*CH$_2$SiMe$_2$*N*SiMe$_3$)(NR$_2$)$_2$] (5). To a brown, cold (-25 °C), stirring solution of **2** (135.4 mg, 0.19 mmol) in hexanes (4 mL) was added Te powder (25.0 mg, 0.20 mmol). This mixture was allowed to stir for 48 h, whereupon the color changed to red. This mixture was filtered through a Celite column supported on glass wool (0.5 cm × 2 cm) to provide a dark-red filtrate. The volume of this filtrate was reduced in vacuo to 1 mL and the solution was transferred to a 4 mL scintillation vial that was placed inside a 20 mL scintillation vial. Toluene (6 mL) was then added to the outer vial. Storage of this two vial system at -25 °C for 72 h resulted in the deposition of red crystalline needles, which were isolated by decanting off the supernatant (80.6 mg, 51%). Anal. Calcd for $C_{18}H_{53}N_3TeSi_6U$: C, 25.56; H, 6.32; N, 4.97. Found: C, 25.21; H, 5.96; N, 4.80. ^{1}H NMR (400 MHz, 25 °C, benzene-d_6): δ -16.30 (br s, 9H, Si(C*H*$_3$)$_3$), -3.22 (br s, 36H, N(Si(C*H*$_3$)$_3$)$_2$), -0.32 (br s, 2H, C*H*$_2$), 7.21 (br s, 6H, Si(C*H*$_3$)$_2$). IR (KBr Pellet, cm^{-1}): 615 (m), 663 (m), 681 (m), 706 (sh), 756 (m), 784 (m), 841 (s), 874 (sh), 933 (s), 1182 (m), 1252 (s), 1404 (m). UV-Vis/NIR (C_4H_8O, 4.91 mM, 25 °C, L·mol^{-1}·cm^{-1}): 686 (ε = 20.7), 811 (ε = 5.9), 854 (ε = 8.7), 1062 (ε = 25.7), 1156 (ε = 15.3), 1348 (ε = 12.3), 1523 (ε = 11.4).

Reaction of [U(*S*CH$_2$SiMe$_2$*N*SiMe$_3$)(NR$_2$)$_2$] (3) with [U(NR$_2$)$_3$]. To a solution of **3** (23.6 mg, 0.031 mmol) in benzene-d_6 (0.75 mL), in an NMR tube fitted with a J-Young valve, was added a solution of [U(NR$_2$)$_3$] (23.2 mg, 0.032 mmol) in benzene-d_6 (0.5 mL). This solution was allowed to stand for 2 h during which time the color changed to orange.

A ^{1}H NMR spectrum was then recorded, which revealed the formation of **2** and [U(NR$_2$)$_3$](μ-S) (**6**), along with the presence of **3**.[9] ^{1}H NMR (400 MHz, 25 °C, benzene-*d*$_6$): δ -118.8 (br s, 2H, **2** C*H*$_2$), -13.44 (br s, 36H, **2** N(Si(C*H*$_3$)$_3$)$_2$), -11.45 (br s, 9H, **3** Si(C*H*$_3$)$_3$), -10.00 (br s, 2H, **3** C*H*$_2$), -6.82 (br s, 108H, **6** N(Si(C*H*$_3$)$_3$)$_2$), -4.22 (br s, 36H, **3** N(Si(C*H*$_3$)$_3$)$_2$), 3.38 (br s, 6H, **3** Si(C*H*$_3$)$_2$), 9.90 (br s, 9H, **2** Si(C*H*$_3$)$_3$), 11.61 (br s, 6H, **2** Si(C*H*$_3$)$_2$). Another aliquot of [U(NR$_2$)$_3$)] (26.7 mg, 0.037 mmol) in benzene-*d*$_6$ (0.5 mL) was added to the reaction mixture. This solution was allowed to stand for another 2 h, whereupon a ^{1}H NMR spectrum was recorded, which revealed the complete consumption of **3** and an increase in the intensities of the resonances attributable to **2** and **6**. ^{1}H NMR (400 MHz, 25 °C, benzene-*d*$_6$): δ -119.0 (br s, 2H, **2** C*H*$_2$), -13.38 (br s, 36H, **2** N(Si(C*H*$_3$)$_3$)$_2$), -6.78 (br s, 108H, **6** N(Si(C*H*$_3$)$_3$)$_2$), 9.87 (br s, 9H, **2** Si(C*H*$_3$)$_3$), 11.55 (br s, 6H, **2** Si(C*H*$_3$)$_2$).

Reaction of [U(*Se*CH$_2$SiMe$_2$*N*SiMe$_3$)(NR$_2$)$_2$] (4) with [U(NR$_2$)$_3$]. To a solution of **4** (25.3 mg, 0.032 mmol), in benzene-*d*$_6$ (0.75 mL), in an NMR tube fitted with a J-Young valve, was added a solution of [U(NR$_2$)$_3$] (22.6 mg, 0.031 mmol) in benzene-*d*$_6$ (0.75 mL). This solution was allowed to stand for 30 min during time which the color changed to orange. A ^{1}H NMR spectrum was then recorded, which revealed the formation of **2** and [U(NR$_2$)$_3$](μ-Se) (**7**), along with the presence of **4**.[9] ^{1}H NMR (400 MHz, 25 °C, benzene-*d*$_6$): δ -118.8 (br s, 2H, **2** C*H*$_2$), -13.40 (br s, 36H, **2** N(Si(C*H*$_3$)$_3$)$_2$), -12.29 (br s, 9H, **4** Si(C*H*$_3$)$_3$), -7.21 (br s, 2H, **4** C*H*$_2$), -6.62 (br s, 108H, **7** N(Si(C*H*$_3$)$_3$)$_2$), -3.70 (br s, 36H, **4** N(Si(C*H*$_3$)$_3$)$_2$), 4.68 (br s, 6H, **4** Si(C*H*$_3$)$_2$), 9.87 (br s, 9H, **2** Si(C*H*$_3$)$_3$), 11.58 (br s, 6H, **2** Si(C*H*$_3$)$_2$). Another aliquot of [U(NR$_2$)$_3$] (23.0 mg, 0.032 mmol) in benzene-*d*$_6$ (0.5 mL) was then added to the reaction mixture. This solution was allowed to stand for 15 min whereupon a ^{1}H NMR spectrum was recorded, which revealed complete consumption of **4** and an increase in the intensities of the resonances attributable to **2** and **7**. ^{1}H NMR (400 MHz, 25 °C, benzene-d_6): δ -119.0 (br s, 2H, **2** CH_2), -13.42 (br s, 36H, **2** N(Si(CH_3)$_3$)$_2$), -6.62 (br s, 108H, **7** N(Si(CH_3)$_3$)$_2$), 9.89 (br s, 9H, **2** Si(CH_3)$_3$), 11.59 (br s, 6H, **2** Si(CH_3)$_2$).

Reaction of [U(*Te*CH$_2$SiMe$_2$*N*SiMe$_3$)(NR$_2$)$_2$] (5) with [U(NR$_2$)$_3$]. To a solution of **5** (24.3 mg, 0.029 mmol) in benzene-d_6 (0.75 mL), in an NMR tube fitted with a J-Young valve, was added a solution of [U(NR$_2$)$_3$] (20.7 mg, 0.029 mmol) in benzene-d_6 (0.5 mL). The solution was allowed to stand for 5 min, whereupon a ^{1}H NMR spectrum was recorded, which revealed the formation of **2** and [U(NR$_2$)$_3$](μ-Te) (**8**), along with the presence of **5**.[9] ^{1}H NMR (400 MHz, 25 °C, benzene-d_6): δ -118.9 (br s, 2H, **2** CH_2), -16.50 (br s, 9H, **5** Si(CH_3)$_3$), -13.40 (br s, 36H, **2** N(Si(CH_3)$_3$)$_2$), -6.13 (br s, 108H, **8** N(Si(CH_3)$_3$)$_2$), -3.25 (br s, 36H, **5** N(Si(CH_3)$_3$)$_2$), -0.27 (br s, 2H, **5** CH_2), 7.27 (br s, 6H, **5** Si(CH_3)$_2$), 9.88 (br s, 9H, **2** Si(CH_3)$_3$), 11.59 (br s, 6H, **2** Si(CH_3)$_2$). After 30 min, another aliquot of [U(NR$_2$)$_3$] (20.2 mg, 0.028 mmol) in benzene-d_6 (0.5 mL) was added to the reaction mixture. This solution was then allowed to stand for 15 min, whereupon a ^{1}H NMR spectrum was recorded, which revealed complete consumption of **5** and an increase in the intensities of the resonances attributable to **2** and **8**. ^{1}H NMR (400 MHz, 25 °C, benzene-d_6): δ -119.0 (br s, 2H, **2** CH_2), -13.42 (br s, 36H, **2** N(Si(CH_3)$_3$)$_2$), -6.13 (br s, 108H, **8** N(Si(CH_3)$_3$)$_2$), 9.91 (br s, 9H, **2** Si(CH_3)$_3$), 11.61 (br s, 6H, **2** Si(CH_3)$_2$).

NMR scale reaction of [U(Cl)(NR$_2$)$_3$] with KSCPh$_3$. To a solution of [U(Cl)(NR$_2$)$_3$] (13.6 mg, 0.018 mmol) in tetrahydrofuran-d_8 (0.5 mL), in an NMR tube fitted with a J-Young valve, was added a solution of KSCPh$_3$ (5.8 mg, 0.018 mmol) in tetrahydrofuran-d_8 (0.5 mL). The solution was allowed to stand for 2 h, whereupon a ^{1}H NMR spectrum was recorded, which revealed the formation of complex **9**, Gomberg's dimer, and unreacted [U(Cl)(NR$_2$)$_3$]. A resonance tentatively assigned to a U(IV) terminal sulfide, [K(THF)$_x$][U(S)(NR$_2$)$_3$], was also observed. ^{1}H NMR (400 MHz, 25 °C, tetrahydrofuran-d_8): δ -8.13 (br s, 54H, **9**), -2.47 (br, s, 54H, [U(Cl)(NR$_2$)$_3$]), -2.06 (br, s, 54H, [U(S)(NR$_2$)$_3$]), 5.19 (m, 1H, allylic), 5.96 (m, 2H, vinylic), 6.22 (m, 2H, vinylic), 7.03-7.28 (m, 25H, aryl C*H*). The solution was allowed to stand for 6 d, whereupon another ^{1}H NMR spectrum was recorded, which revealed the presence of **9**, Gomberg's dimer, [U(Cl)(NR$_2$)$_3$], and the disappearance of the resonance assigned to [U(S)(NR$_2$)$_3$]. ^{1}H NMR (400 MHz, 25 °C, tetrahydrofuran-d_8): δ -8.14 (br s, 54H, **9**), -2.49 (br, s, 54H, [U(Cl)(NR$_2$)$_3$]), 5.19 (m, 1H, allylic), 5.96 (m, 2H, vinylic), 6.22 (m, 2H, vinylic), 7.03-7.28 (m, 25H, aryl C*H*).

Preparative scale reaction of [U(Cl)(NR$_2$)$_3$] with KSCPh$_3$. To a cold (-25 °C), stirring solution of [U(Cl)(NR$_2$)$_3$] (147.5 mg, 0.20 mmol) in THF (3 mL) was added a cold (-25 °C) solution of KSCPh$_3$ (137.1 mg, 0.44 mmol) in THF (3 mL). This mixture was allowed to stir for 24 h, whereupon the solvent was removed in vacuo and the resulting orange solid was triturated with hexanes (4 mL) and Et$_2$O (4 mL). The orange powder was then extracted with hexanes (8 mL) and filtered through a Celite column supported on glass wool (0.5 cm × 3 cm), to provide an orange solution. The filtrate was then dried in vacuo, extracted with Et$_2$O (6 mL), and filtered again through a Celite column supported on glass wool (0.5 cm × 3 cm) to afford a orange solution. The volume of the filtrate was reduced in vacuo to 2 mL. Storage of this solution at -25 °C for 24 h resulted in the deposition of orange crystals where were isolated by decanting off the supernatant (83.7 mg, 44%). ^{1}H NMR (400 MHz, 25 °C, benzene-d_6): δ -7.08 (br s, 108H, N(Si(CH_3)$_3$)$_2$), 1.08 (t, 24H, CH$_2$CH_3, J_{HH} = 8.0 Hz), 3.21 (q, 16H, CH_2CH$_3$, J_{HH} = 8.0 Hz). X-ray quality crystals were grown from a concentrated diethyl ether solution.

Reaction of [K(Et$_2$O)$_2$][U(S$_2$)(NR$_2$)$_3$] with 18-crown-6. To a solution of **9·Et$_2$O** (6.6 mg, 0.0034 mmol) in benzene-d_6 (0.5 mL), in an NMR tube fitted with a J-Young valve, was added a solution 18-crown-6 (1.9 mg, 0.0072 mmol). A ^{1}H NMR spectrum was then recorded, which revealed the formation of **9·18-crown-6**. The identity of **9·18-crown-6** was confirmed by comparison of the ^{1}H NMR spectrum with that of authentic material.[10] ^{1}H NMR (400 MHz, 25 °C, benzene-d_6): δ -7.41 (br s, 54H, N(Si(CH_3)$_3$)$_2$), 2.53 (br s, 24H, 18-crown-6).

Synthesis of Ph$_3$CSSCPh$_3$. To a stirring solution of Ph$_3$CSH (338.0 mg, 1.22 mmol) in THF (4 mL) was added NaN(SiMe$_3$)$_2$ (228.0 mg, 1.24 mmol). After 5 min, I$_2$ (156.2 mg, 0.62 mmol) in THF (3 mL) was added to this solution. This mixture was allowed to stir for a further 10 min. The solvent was then removed in vacuo and the resulting yellow solid was triturated with diethyl ether (5 mL). The resulting powder was extracted with diethyl ether (6 mL) and filtered through a Celite column supported on glass wool (0.5 cm × 3 cm) to provide a pale yellow filtrate. The volume of the filtrate was reduced in vacuo to 2 mL. Storage of this solution at -25 °C for 24 h resulted in the deposition of yellow solid which was isolated by decanting off the supernatant (124.7 mg, 18%). Melting point: 150-153 °C (lit. value = 153-155 °C).[11] ^{1}H NMR (500 MHz, 25 °C, benzene-d_6): δ 6.93-7.0 (m, 18H, *m*-, *p*-C*H*), 7.30-7.36 (m, 12H, *o*-C*H*). Pale yellow crystals suitable for X-ray crystallographic analysis were grown from a concentrated CH$_2$Cl$_2$ solution layered with hexanes (Unit Cell: a = 13.89 Å, b = 12.06 Å, c = 17.23 Å,

$\alpha = 90°$, $\beta = 103.56°$, $\gamma = 90°$). These unit cell parameters matched those previously reported for this material.[12]

Reaction of [U(NR$_2$)$_3$] with Ph$_3$CSSCCPh$_3$. To a purple solution of [U(NR$_2$)$_3$] (13.3 mg, 0.018 mmol) in benzene-*d*$_6$ (0.5 mL) was added a solution of Ph$_3$CSSCCPh$_3$ (5.2 mg, 0.009 mmol) in benzene-*d*$_6$ (0.5 mL). A color change to orange was observed immediately upon addition. After 5 min, a ^{1}H NMR spectrum was obtained, revealing the formation of [U(NR$_2$)$_3$]$_2$(μ-S) (**6**) and Gomberg's dimer, along with unreacted Ph$_3$CSSCCPh$_3$. ^{1}H NMR (400 MHz, 25 °C, benzene-*d*$_6$): δ -6.83 (br s, 54H, **6** N(Si(C*H*$_3$)$_3$)$_2$,), 4.92 (m, 1H, allylic, Gomberg's dimer), 5.93 (m, 2H, vinylic, Gomberg's dimer), 6.44 (m, 2H, vinylic, Gomberg's dimer), 6.96-7.4 (m, aryl C*H*, overlapping signals for Gomberg's dimer and Ph$_3$CSSCCPh$_3$).

Reaction of [K(18-crown-6)][U(S)(NR$_2$)$_3$] with Ph$_3$CSSCPh$_3$. To a orange solution of [K(18-crown-6)][U(S)(NR$_2$)$_3$] (10.6 mg, 0.01 mmol) in tetrahydrofuran-*d*$_8$ (0.5 mL), in an NMR tube fitted with a J-Young valve, was added a solution of Ph$_3$CSSCCPh$_3$ (3.0 mg, 0.005 mmol) in tetrahydrofuran-*d*$_8$ (0.5 mL). This solution was allowed to stand for 3 d, whereupon a ^{1}H NMR spectrum was recorded, which revealed the formation of **9·18-crown-6**, Gomberg's dimer, and triphenylmethane. ^{1}H NMR (400 MHz, 25 °C, tetrahydrofuran-*d*$_8$): δ -8.56 (br s, 54H, **9·18-crown-6** N(Si(C*H*$_3$)$_3$)$_2$), -2.64 (br s, 54H, [K(18-crown-6)][U(S)(NR$_2$)$_3$], N(Si(C*H*$_3$)$_3$)$_2$)), 3.15 (br s, 24H, **9·18-crown-6** 18-crown-6), 5.18 (m, 1H, allylic, Gomberg's dimer), 5.57 (s, 1H, *H*CPh$_3$), 5.94 (m, 2H, vinylic, Gomberg's dimer), 6.21-6.23 (m, 2H, vinylic, Gomberg's dimer), 6.9-7.4 (m, aryl C*H*, overlapping signals for Gomberg's dimer and triphenylmethane).

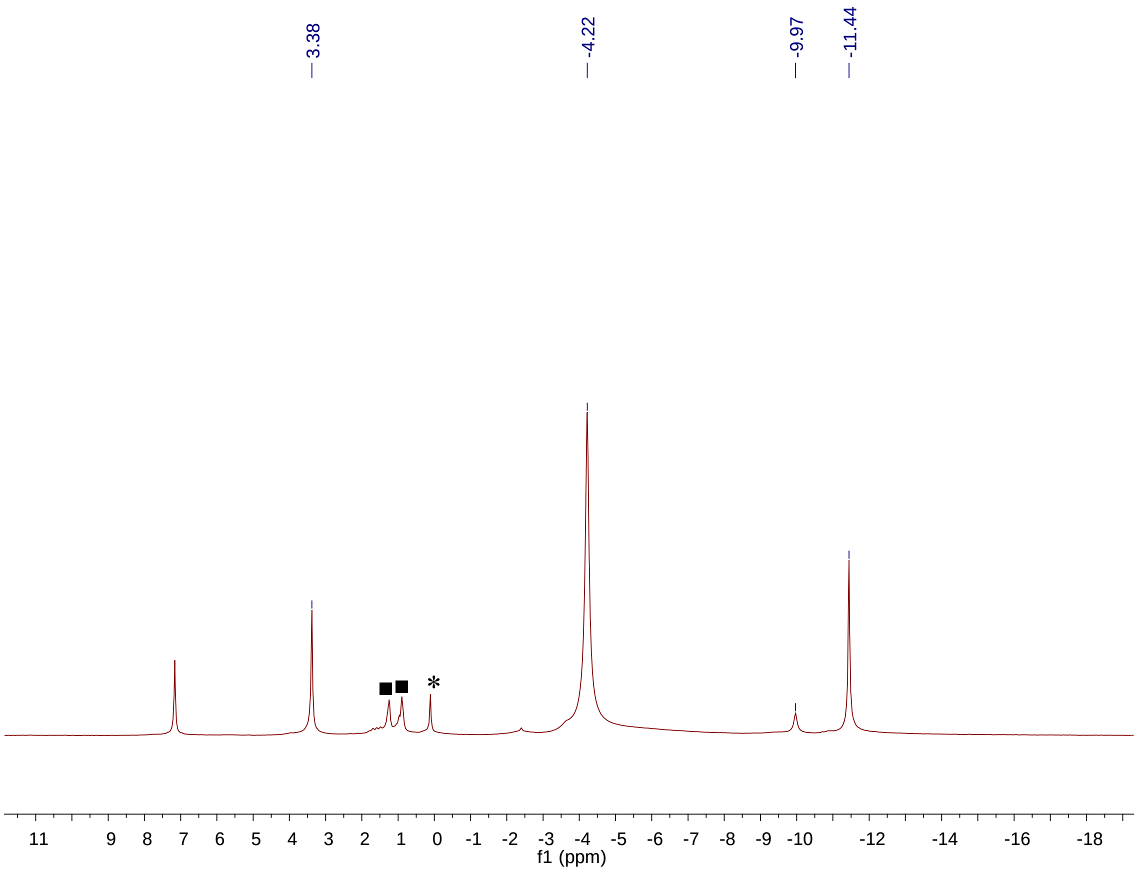

Figure S1. ^{1}H NMR spectrum of **3**, in benzene-d_6, isolated from the reaction of **2** with S_8. (*) indicates the presence of $HN(SiMe_3)_2$ and (■) indicates the presence of hexanes.

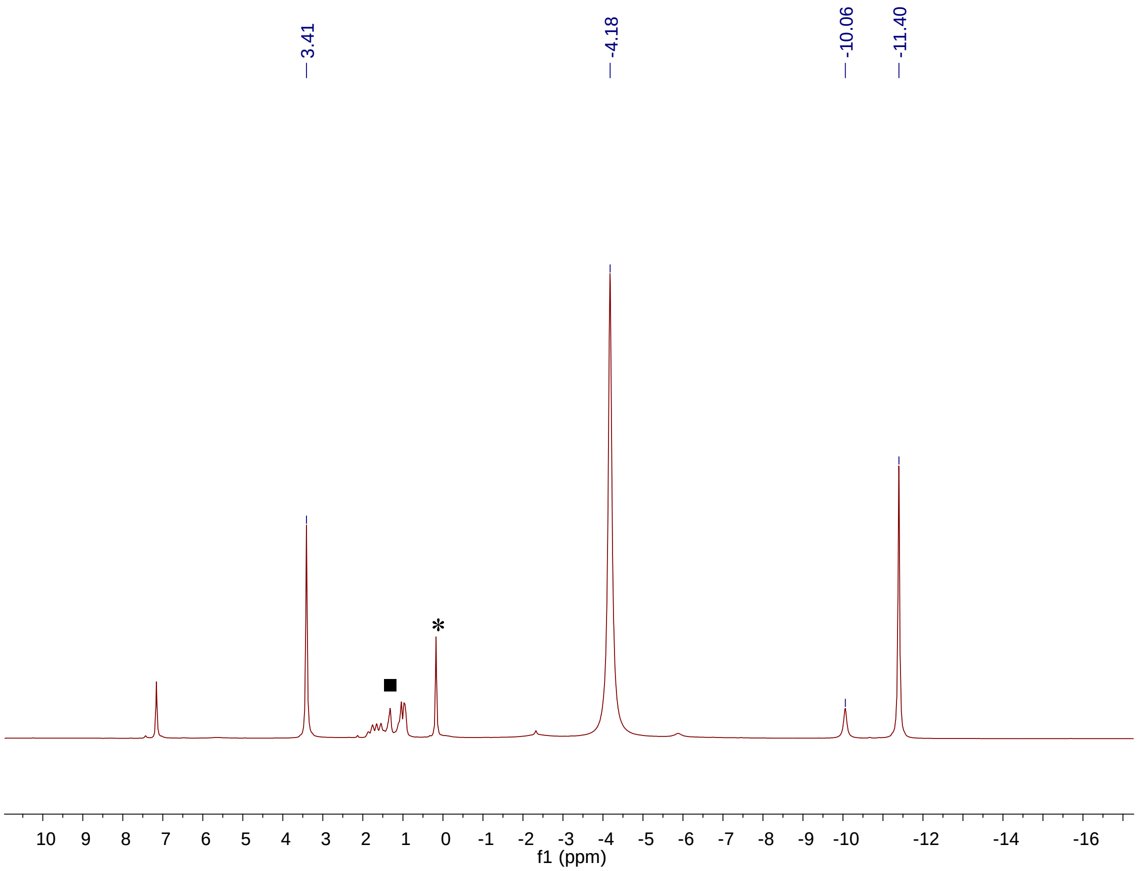

Figure S2. ^{1}H NMR spectrum of **3**, in benzene-d_6, isolated from the reaction of **2** with ethylene sulfide. (*) indicates the presence of $HN(SiMe_3)_2$ and (■) indicates the presence of hexanes.

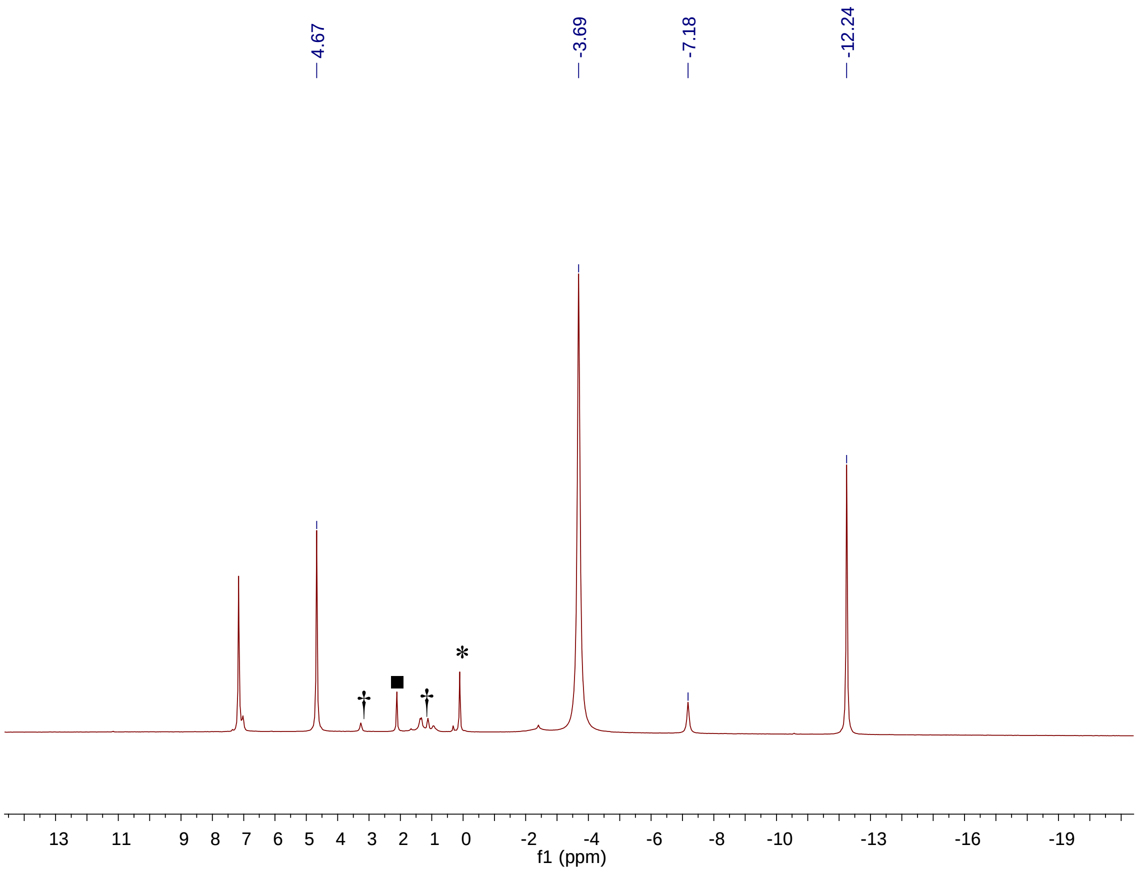

Figure S3. ^{1}H NMR spectrum of **4** in benzene-d_6. (*) indicates the presence of $HN(SiMe_3)_2$, (■) indicates the presence of toluene, and (†) indicates the presence of diethyl ether.

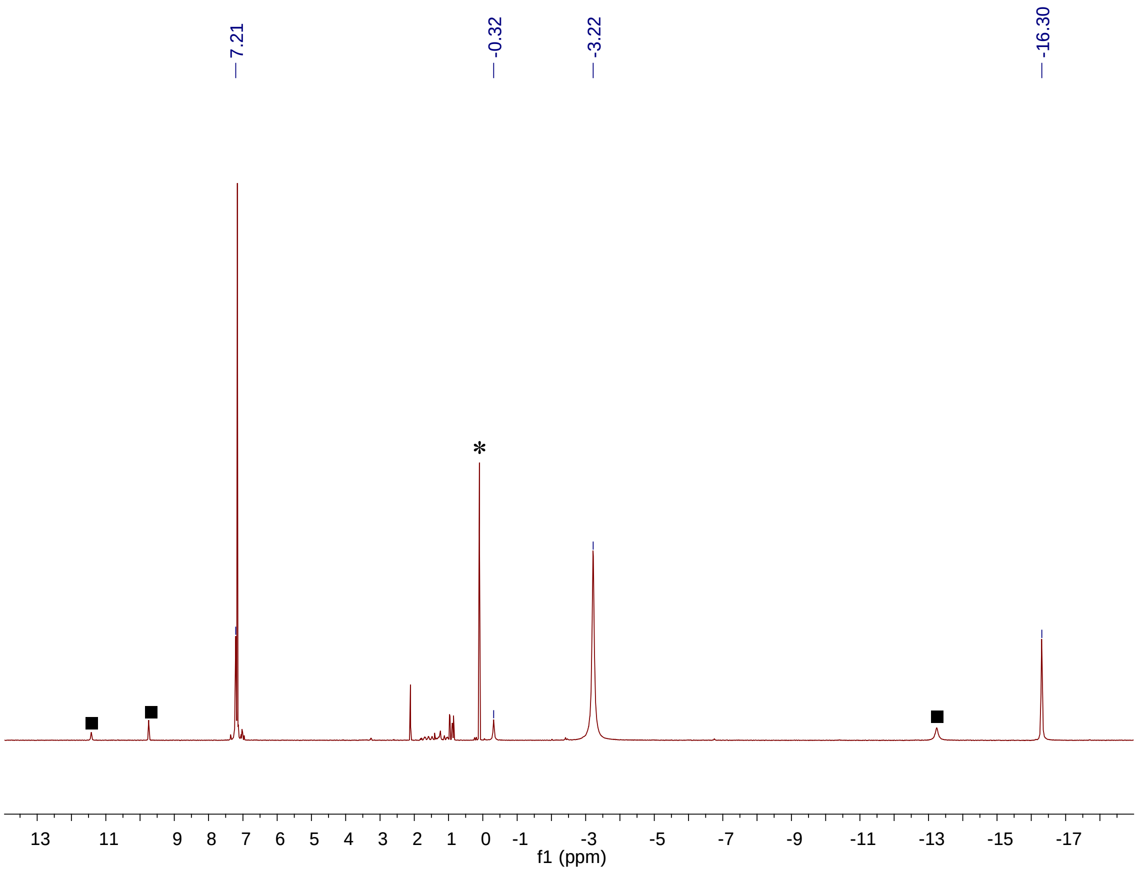

Figure S4. ^{1}H NMR spectrum of **5** in benzene-d_6. (*) indicates the presence of $HN(SiMe_3)_2$, (■) indicates the presence of unreacted **2**.

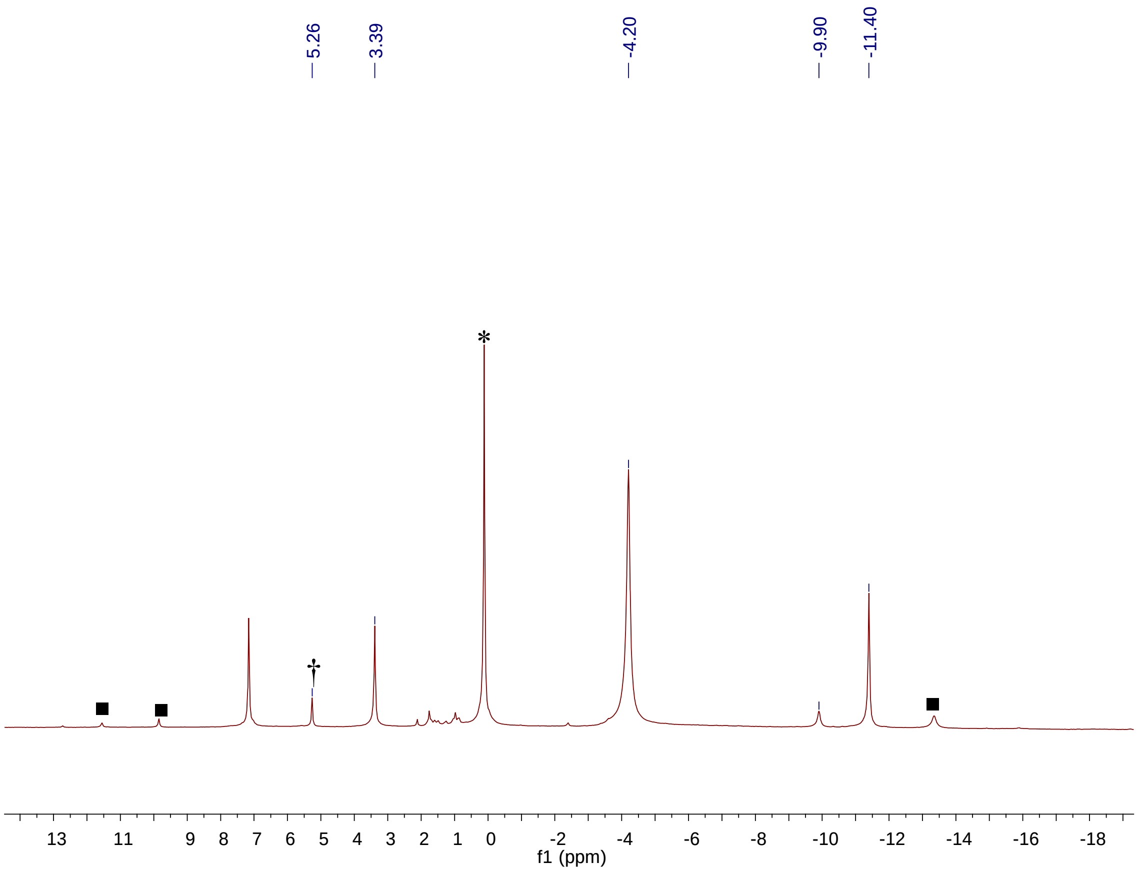

Figure S5. In-situ ^{1}H NMR spectrum of the reaction of **2** with ethylene sulfide, in benzene-d_6, after 24 h. (*) indicates the presence of $HN(SiMe_3)_2$, (■) indicates the presence of unreacted **2**, and (†) indicates the presence of ethylene.

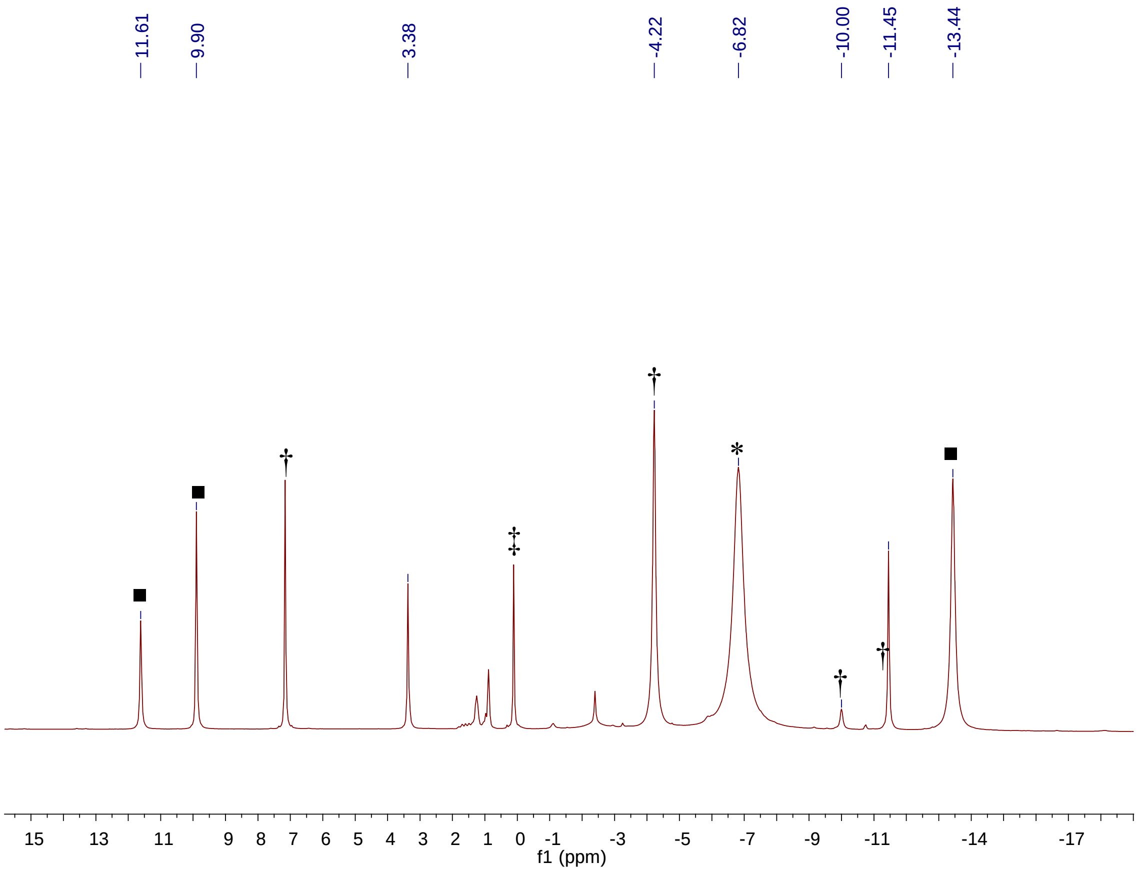

Figure S6. Portion of the in situ ^{1}H NMR spectrum of the reaction of **3** with 1 equiv of [U(NR$_2$)$_3$] in benzene-d_6, after 2 h. (*) indicates the presence of **6**, (■) indicates the presence of **2**, (†) indicates the presence of unreacted **3**, and (‡) indicates the presence of HN(SiMe$_3$)$_2$. (Not shown: resonance assignable to CH_2 of **2** at -118.8 ppm).

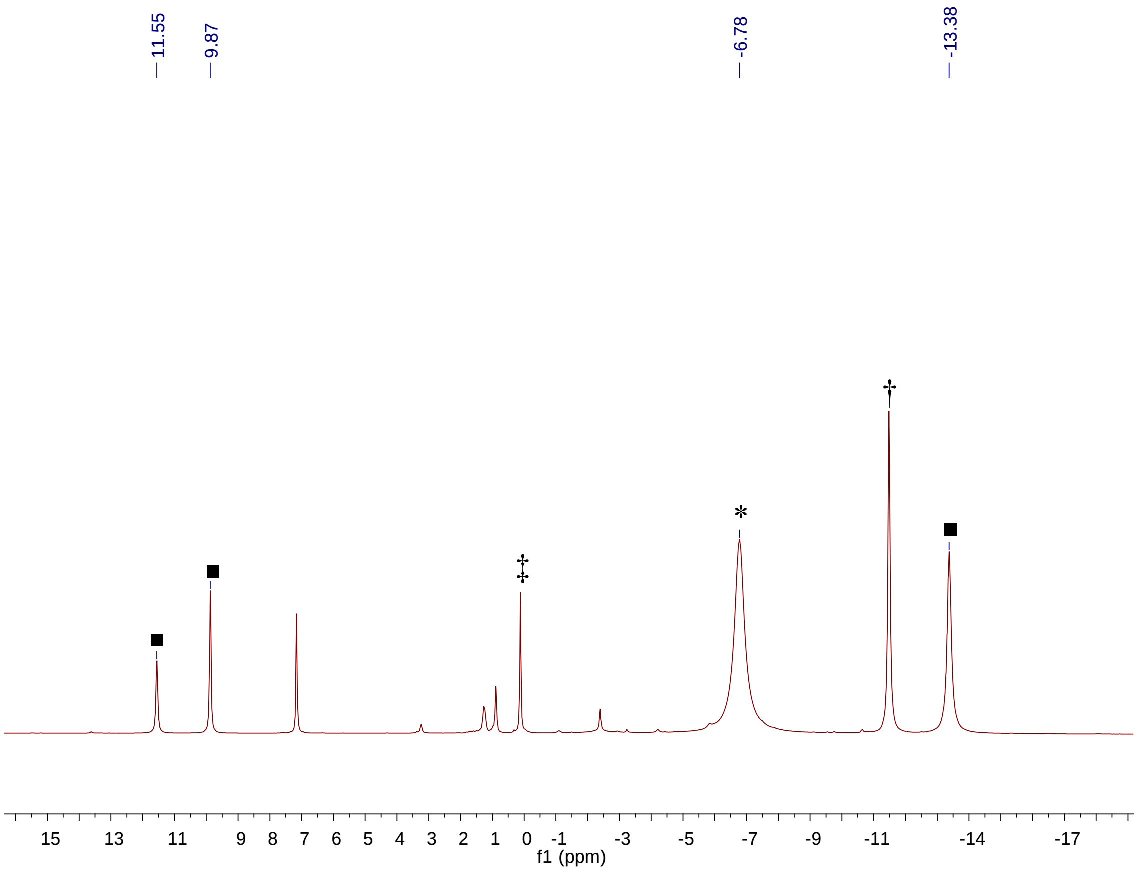

Figure S7. Portion of the in situ ^{1}H NMR spectrum of the reaction of **3** with 2 equiv of [U(NR$_2$)$_3$] in benzene-d_6, after 4 h. (*) indicates the presence of **6**, (■) indicates the presence of **2**, (†) indicates the presence of unreacted [U(NR$_2$)$_3$], and (‡) indicates the presence of HN(SiMe$_3$)$_2$. (Not shown: resonance assignable to CH_2 of **2** at -119.0 ppm).

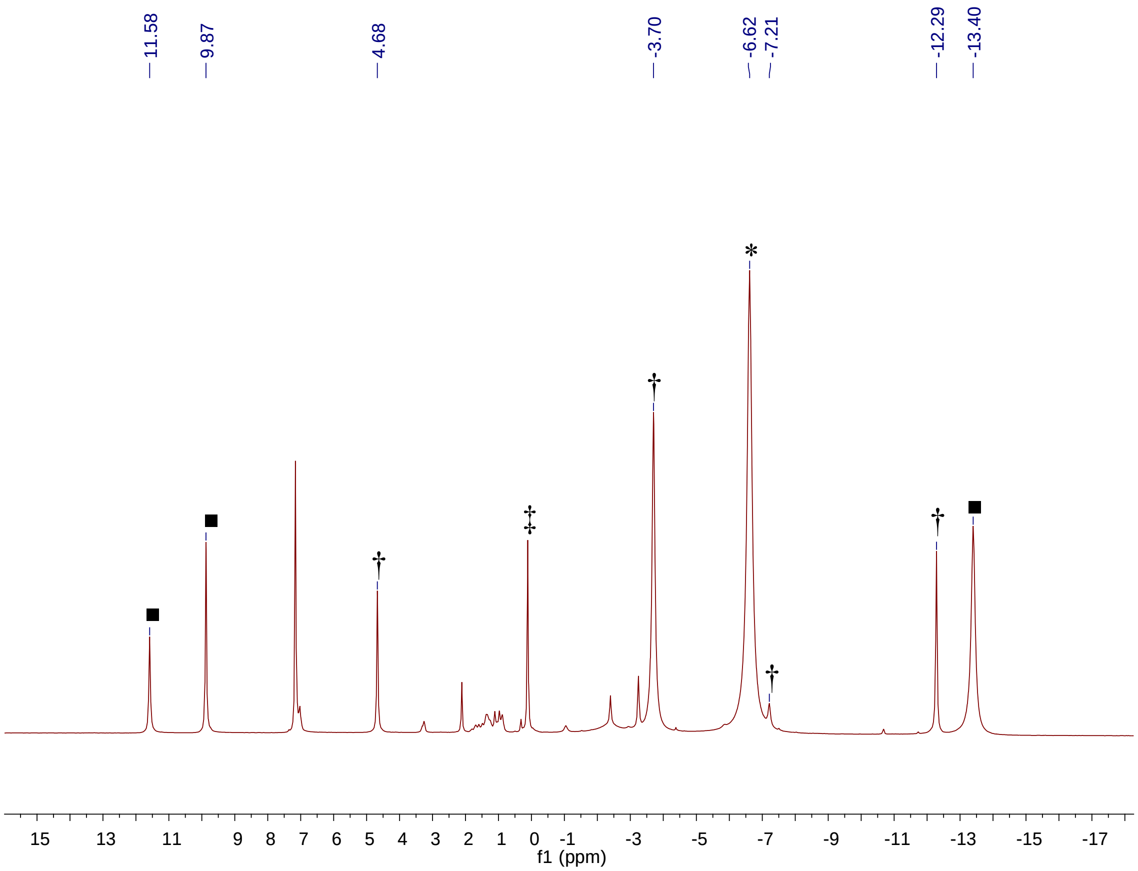

Figure S8. Portion of the in situ ^{1}H NMR spectrum of the reaction of **4** with 1 equiv of [U(NR$_2$)$_3$] in benzene-d_6, after 30 min. (*) indicates the presence of **7**, (■) indicates the presence of **2**, (†) indicates the presence of unreacted **4**, and (‡) indicates the presence of HN(SiMe$_3$)$_2$. (Not shown: resonance assignable to CH_2 of **2** at -118.8 ppm).

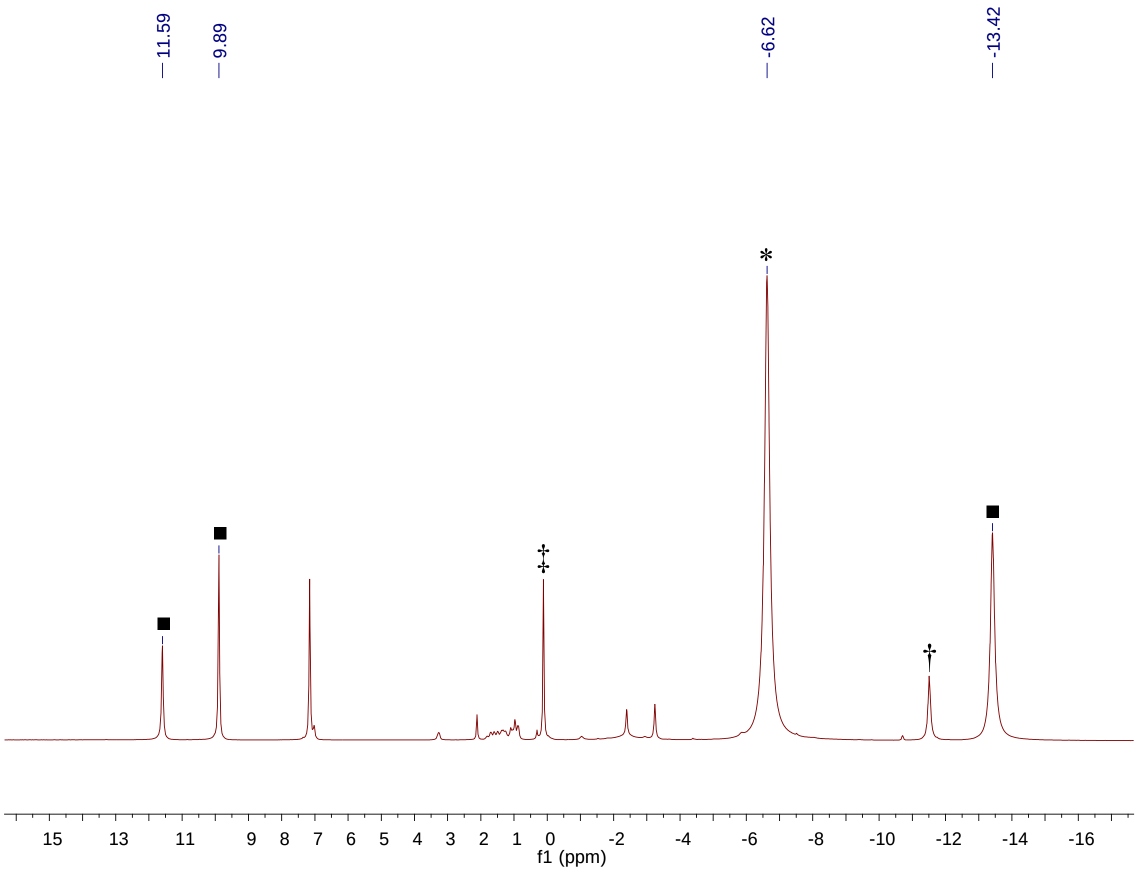

Figure S9. Portion of the in situ ^{1}H NMR spectrum of the reaction of **4** with 2 equiv of $[U(NR_2)_3]$ in benzene-d_6, after 1h. (*) the presence of **7**, (■) indicates the presence of **2**, (†) indicates unreacted $[U(NR_2)_3]$, and (‡) indicates the presence of $HN(SiMe_3)_2$. (Not shown: resonance assignable to CH_2 of **2** at -119.0 ppm).

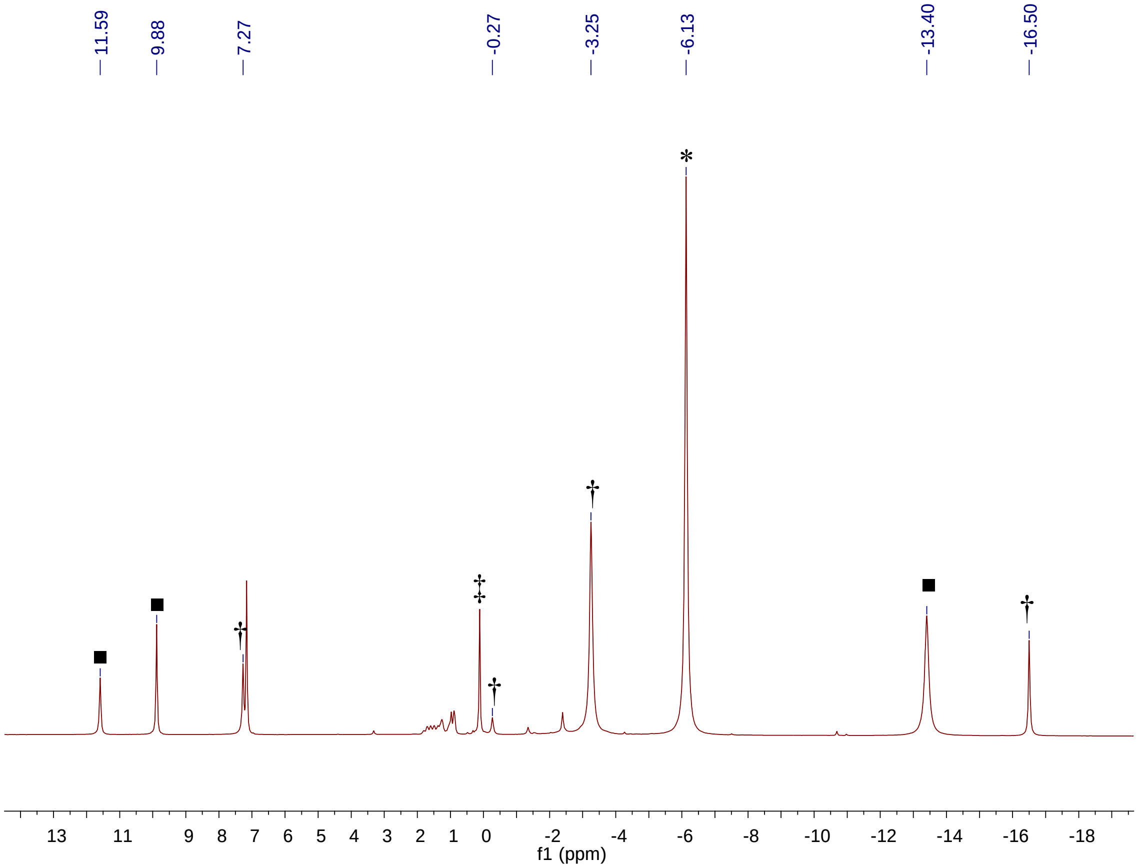

Figure S10. Portion of the in situ ^{1}H NMR spectrum of the reaction of **5** with 1 equiv of [U(NR$_2$)$_3$] in benzene-d_6, after 5 min. (*) indicates the presence of **8**, (■) indicates the presence of **2**, (†) indicates the presence of unreacted **5**, and (‡) indicates the presence of HN(SiMe$_3$)$_2$. (Not shown: resonance assignable to CH_2 of **2** at -118.9 ppm).

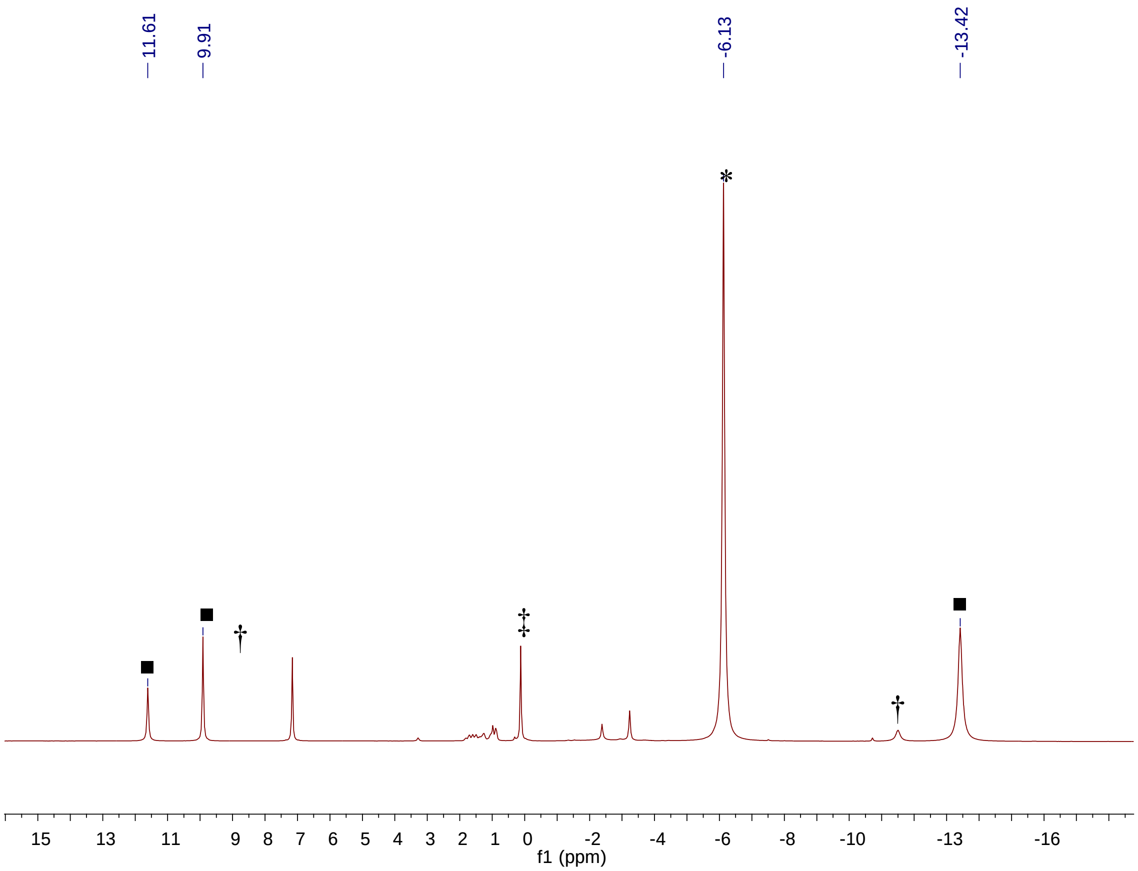

Figure S11. Portion of the in situ ^{1}H NMR spectrum of the reaction of **5** with 2 equiv of [U(NR$_2$)$_3$] in benzene-d_6, after 45 min. (*) indicates the presence of **8**, (■) indicates the presence of **2**, (†) indicates the presence of unreacted [U(NR$_2$)$_3$], and (‡) indicates the presence of HN(SiMe$_3$)$_2$. (Not shown: resonance assignable to CH_2 of **2** at -119.0 ppm).

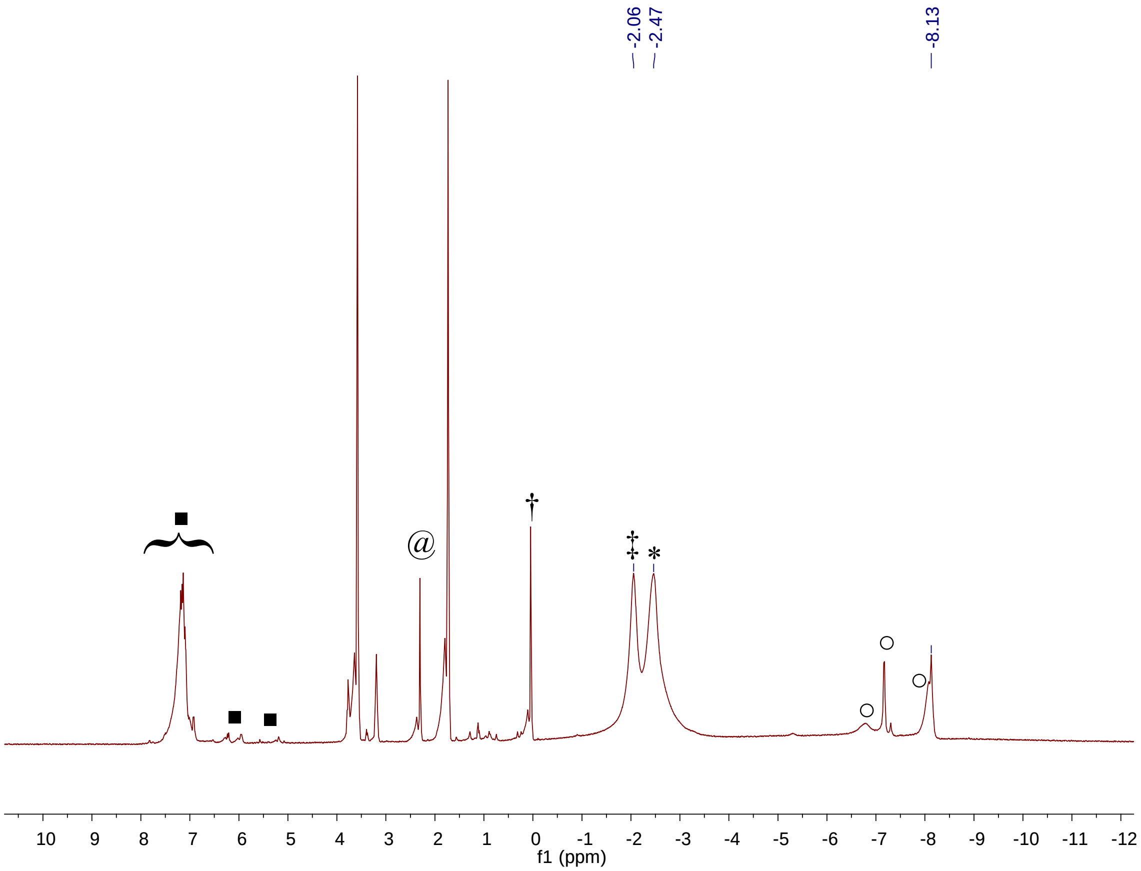

Figure S12. In situ ^{1}H NMR spectrum of the reaction of $[U(Cl)(NR_2)_3]$ with 1 equiv of $KSCPh_3$ in tetrahydrofuran-d_8, after 2 h. (*) indicates the presence of unreacted $[U(Cl)(NR_2)_3]$, (■) indicates the presence of Gomberg's dimer, (†) indicates the presence of $HN(SiMe_3)_2$, (‡) indicates the presence of a complex tentatively assigned as $[K(THF)_x][U(S)(NR_2)_3]$, (@) indicates the presence of toluene, and (○) indicates the presence of as-yet-unidentified intermediates.

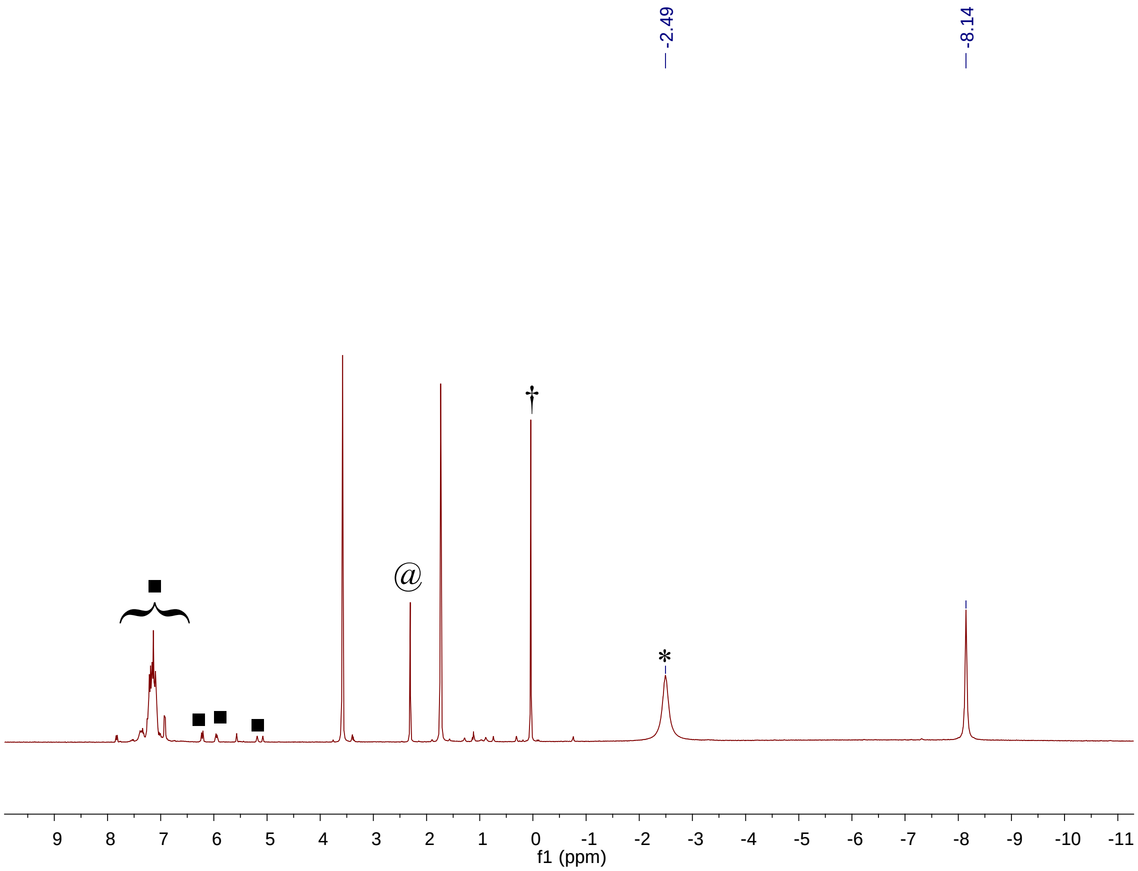

Figure S13. In situ ^{1}H NMR spectrum of the reaction of $[U(Cl)(NR_2)_3]$ with 1 equiv of $KSCPh_3$ in tetrahydrofuran-d_8, after 6 d. (*) indicates the presence of unreacted $[U(Cl)(NR_2)_3]$, (■) indicates the presence of Gomberg's dimer, (@) indicates the presence of toluene, and (†) indicates the presence of $HN(SiMe_3)_2$.

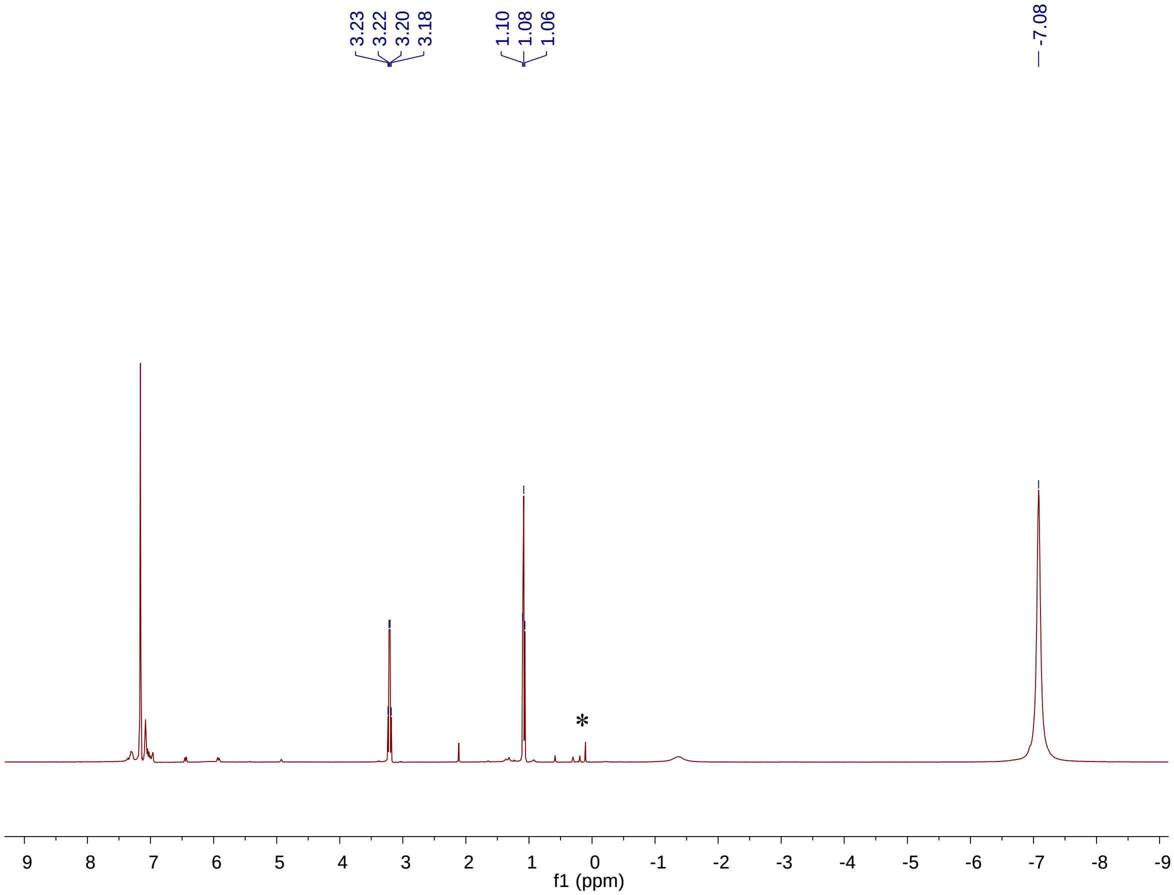

Figure S14. ^{1}H NMR spectrum of **9·Et$_2$O** in benzene-d_6. (*) indicates the presence of HN(SiMe$_3$)$_2$.

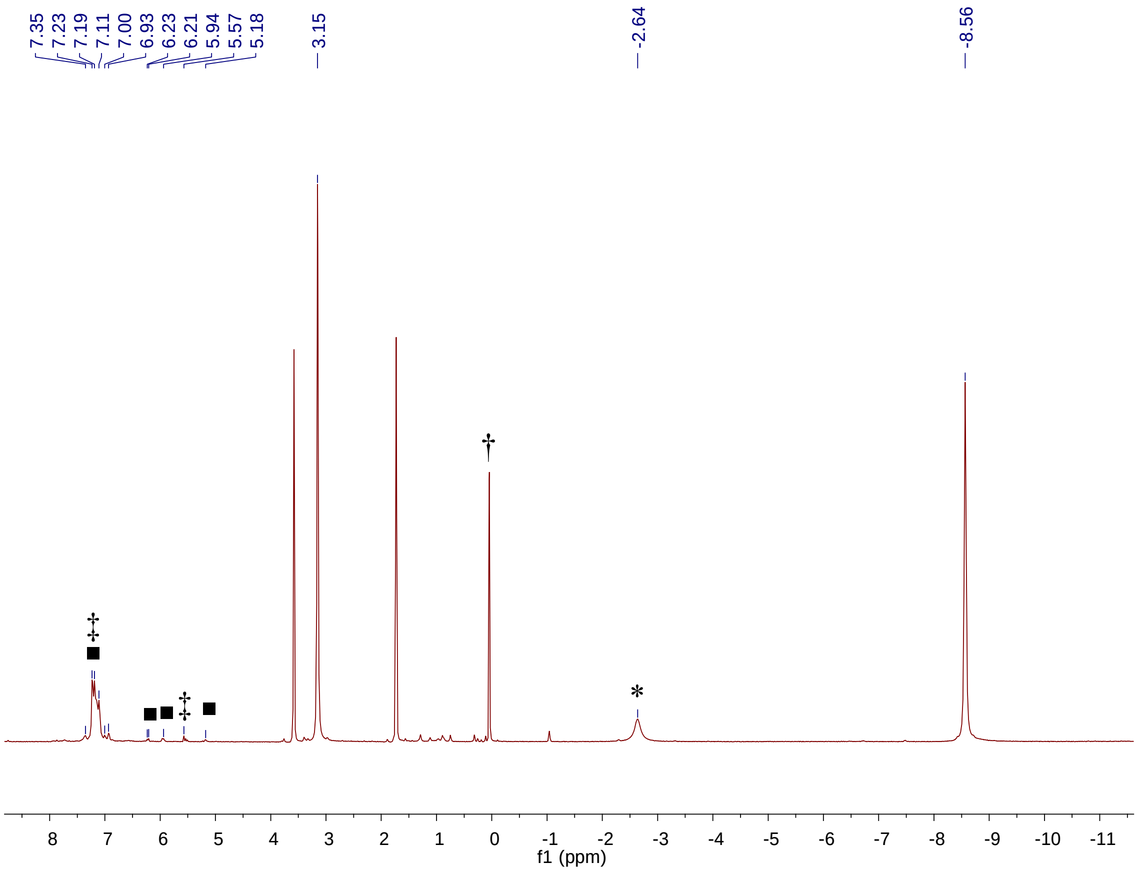

Figure S15. In situ ^{1}H NMR spectrum of the reaction of [K(18-crown-6)][U(S)(NR$_2$)$_3$] with 0.5 equiv of Ph$_3$CSSCPh$_3$ in tetrahydrofuran-d_8, after 3 d. (*) indicates the presence of unreacted [K(18-crown-6)][U(S)(NR$_2$)$_3$], (■) indicates the presence of Gomberg's dimer, (†) indicates the presence of HN(SiMe$_3$)$_2$, (‡) indicates the presence of triphenylmethane.

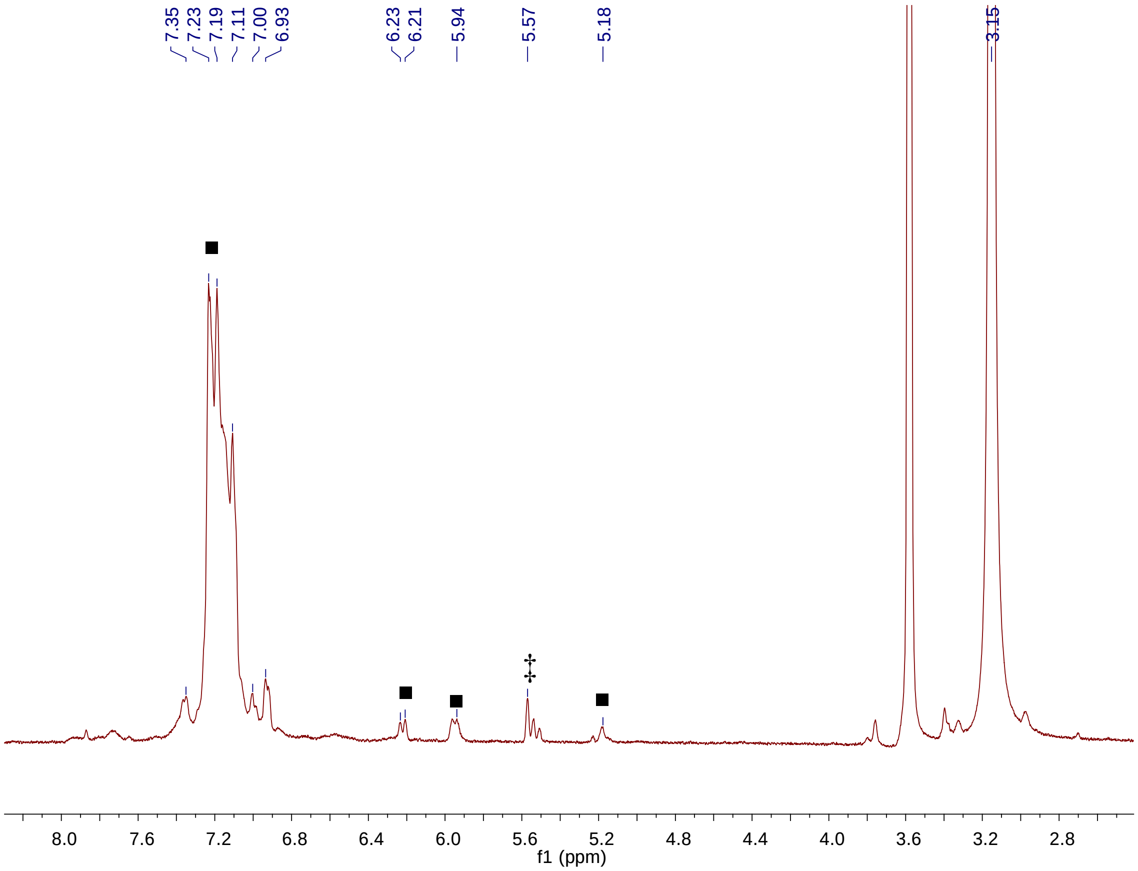

Figure S16. Partial in situ ^{1}H NMR spectrum of the reaction of [K(18-crown-6)][U(S)(NR$_2$)$_3$] with 0.5 equiv of Ph$_3$CSSCPh$_3$ in tetrahydrofuran-d_8, after 3 d. (■) indicates the presence of Gomberg's dimer, and (‡) indicates the presence of triphenylmethane.

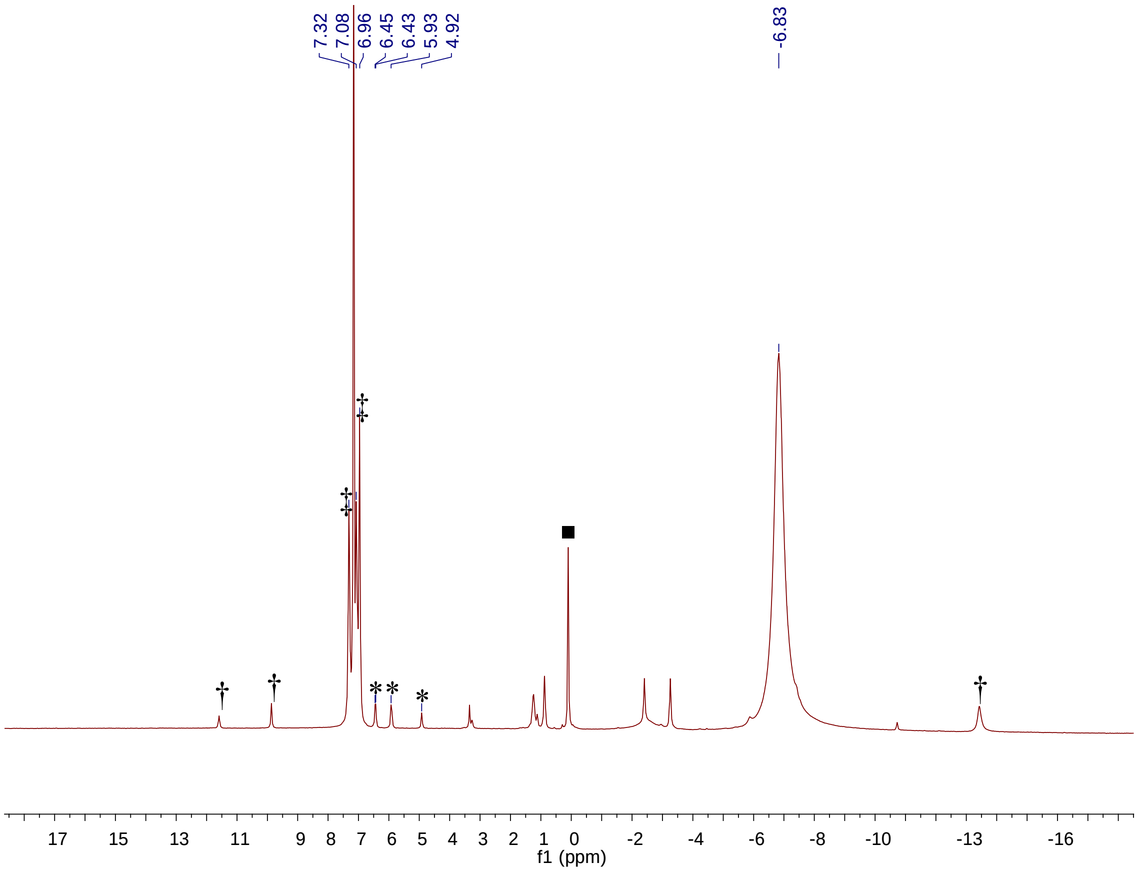

Figure S17. In situ ^{1}H NMR spectrum of the reaction of [U(NR$_2$)$_3$] and 0.5 equiv of Ph$_3$CSSCPh$_3$ in benzene-*d*$_6$ after 5 min. (*) indicates the presence of Gomberg's dimer. (■) indicates the presence of HN(SiMe$_3$)$_2$, (†) indicates the presence of [U(*C*H$_2$SiMe$_2$*N*SiMe$_3$)(NR$_2$)$_2$], an impurity in the starting material, and (‡) indicates the presence of unreacted Ph$_3$CSSCPh$_3$.

Table S1. X-ray Crystallographic Data for **5** and **9·Et$_2$O**

	5	**9·Et$_2$O**
empirical formula	$C_{18}H_{53}N_3TeSi_6U$	$C_{26}H_{74}KN_3O_2S_2Si_6U$
crystal habit, color	needle, orange-red	block, orange
crystal size (mm)	0.1 × 0.05 × 0.02	0.2 × 0.1 × 0.05
space group	$P\bar{1}$	$P2_1/c$
volume (Å^3)	1672.15(8)	4594.6(6)
a (Å)	8.3155(2)	15.629(1)
b (Å)	11.8276(3)	20.397(2)
c (Å)	17.5749(5)	14.649(1)
α (deg)	88.157(1)	90.00
β (deg)	89.051(1)	100.297(4)
γ (deg)	75.447(1)	90.00
Z	2	4
formula weight (g/mol)	845.78	970.67
density (calculated) (Mg/m^3)	1.680	1.403
absorption coefficient (mm^{-1})	5.935	3.895
F_{000}	820	1976
total no. reflections	38455	52766
unique reflections	16143	11508
R_{int}	0.0260	0.0298
final R indices (I >2σ(I)]	$R_1 = 0.0213$ $wR_2 = 0.0464$	$R_1 = 0.0174$ $wR_2 = 0.0385$
largest diff. peak and hole (e$^-$ A^{-3})	2.450 and -0.810	0.845 and -0.494
GOF	0.979	1.020

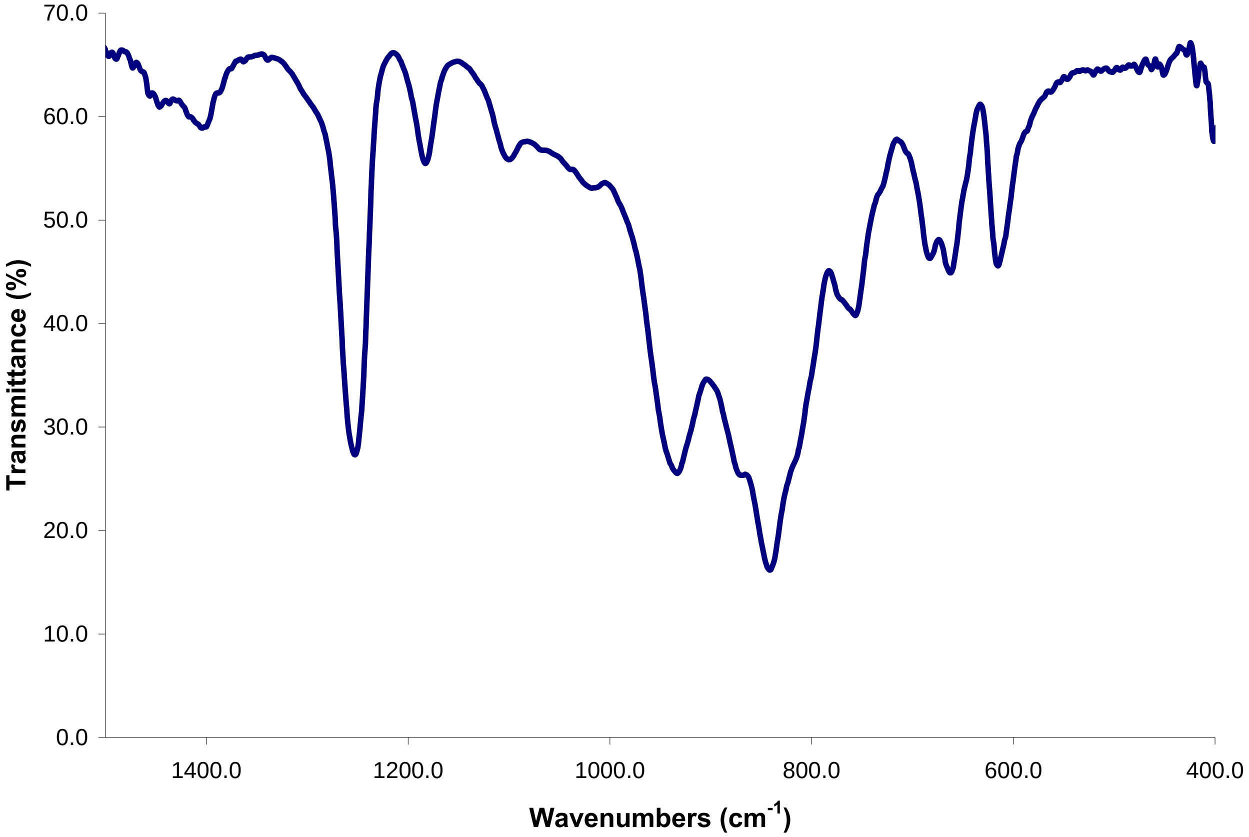

Figure S18. Partial IR spectrum of **3** (KBr pellet).

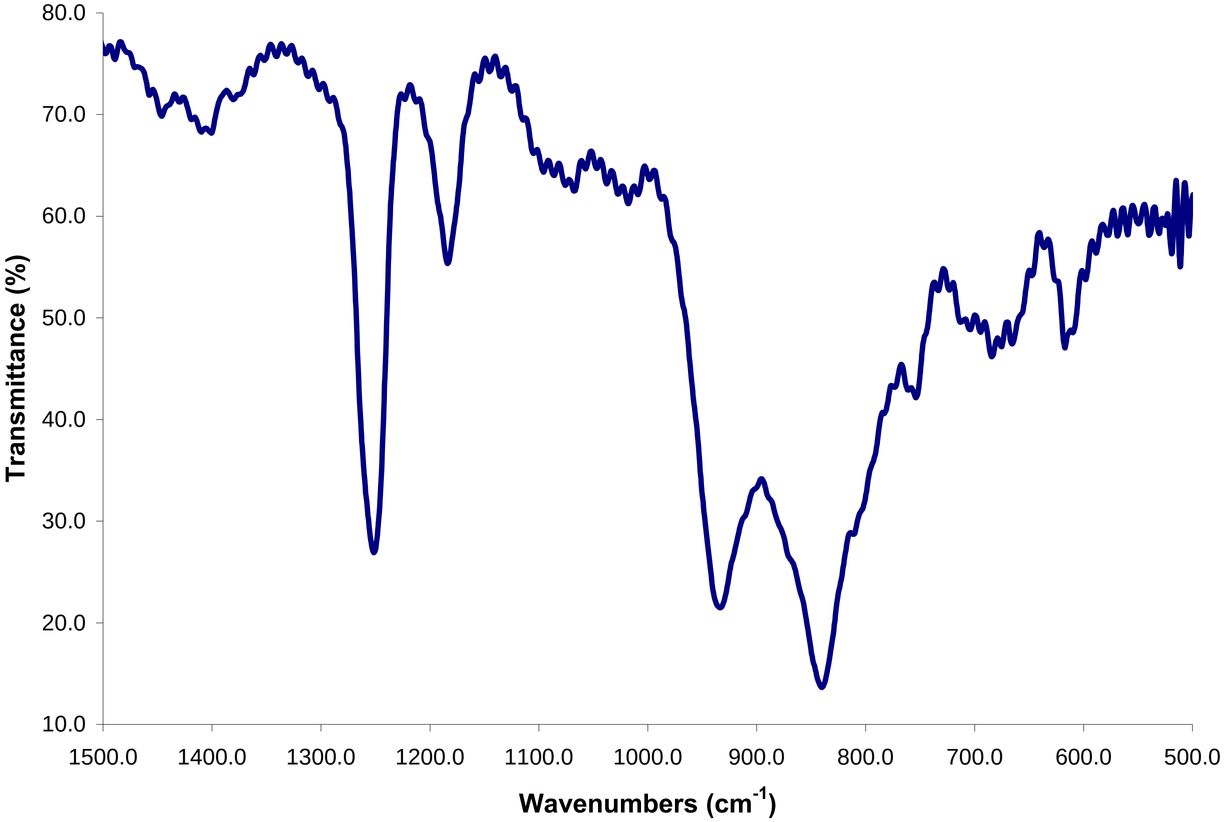

Figure S19. Partial IR spectrum of **4** (KBr pellet).

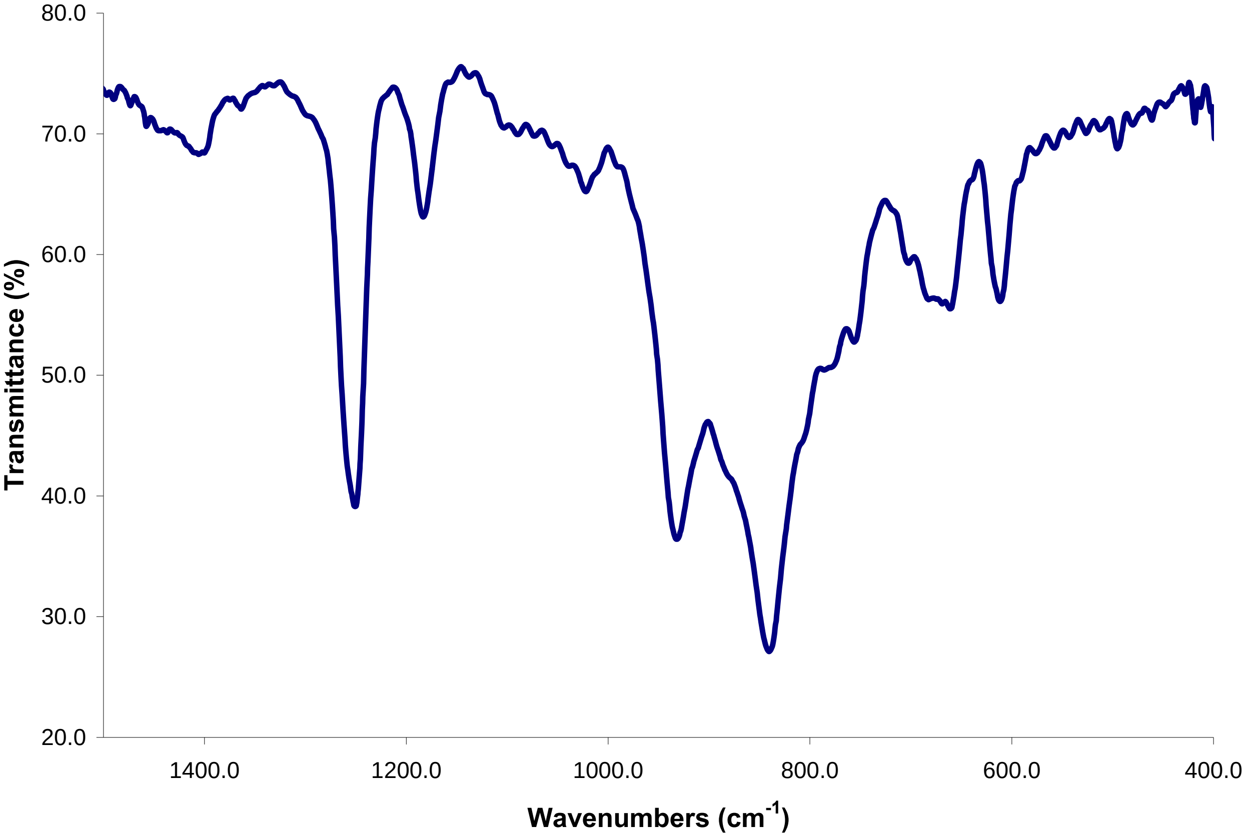

Figure S20. Partial IR spectrum of **5** (KBr pellet).

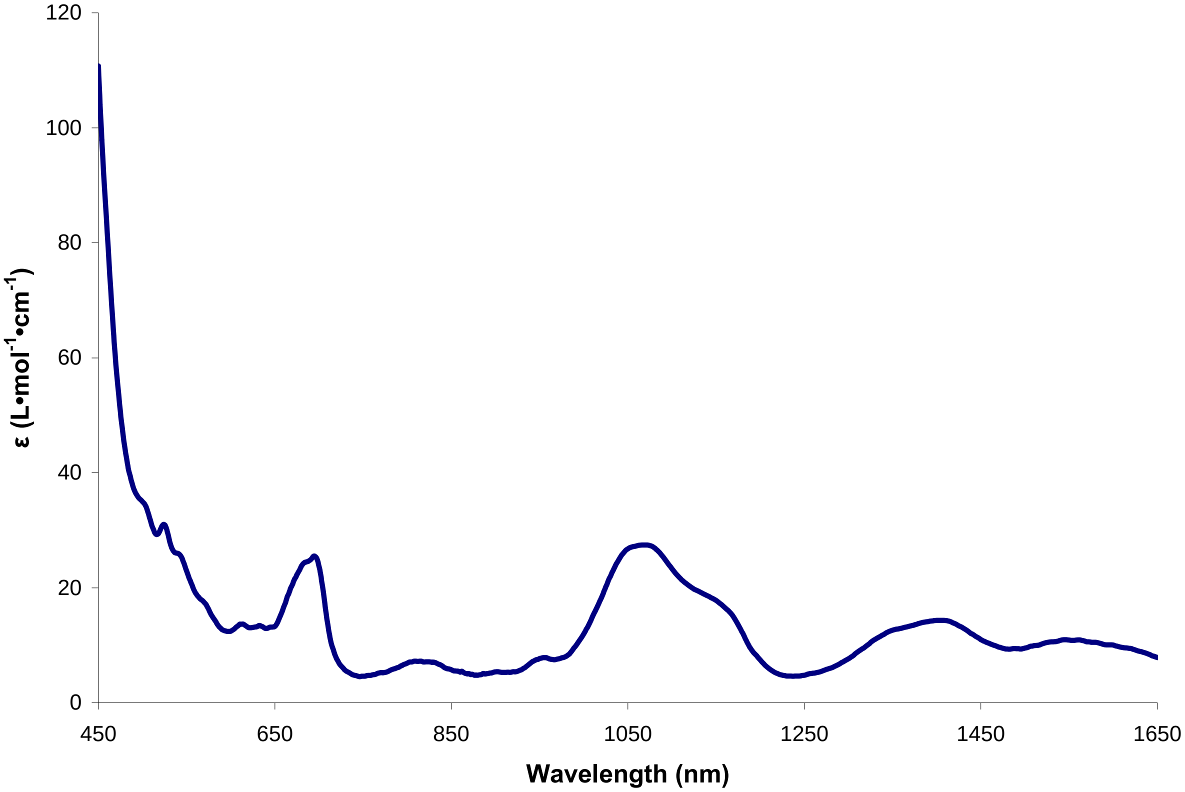

Figure S21. UV-Vis / NIR spectrum of **3** (4.98 mM, C_4H_8O).

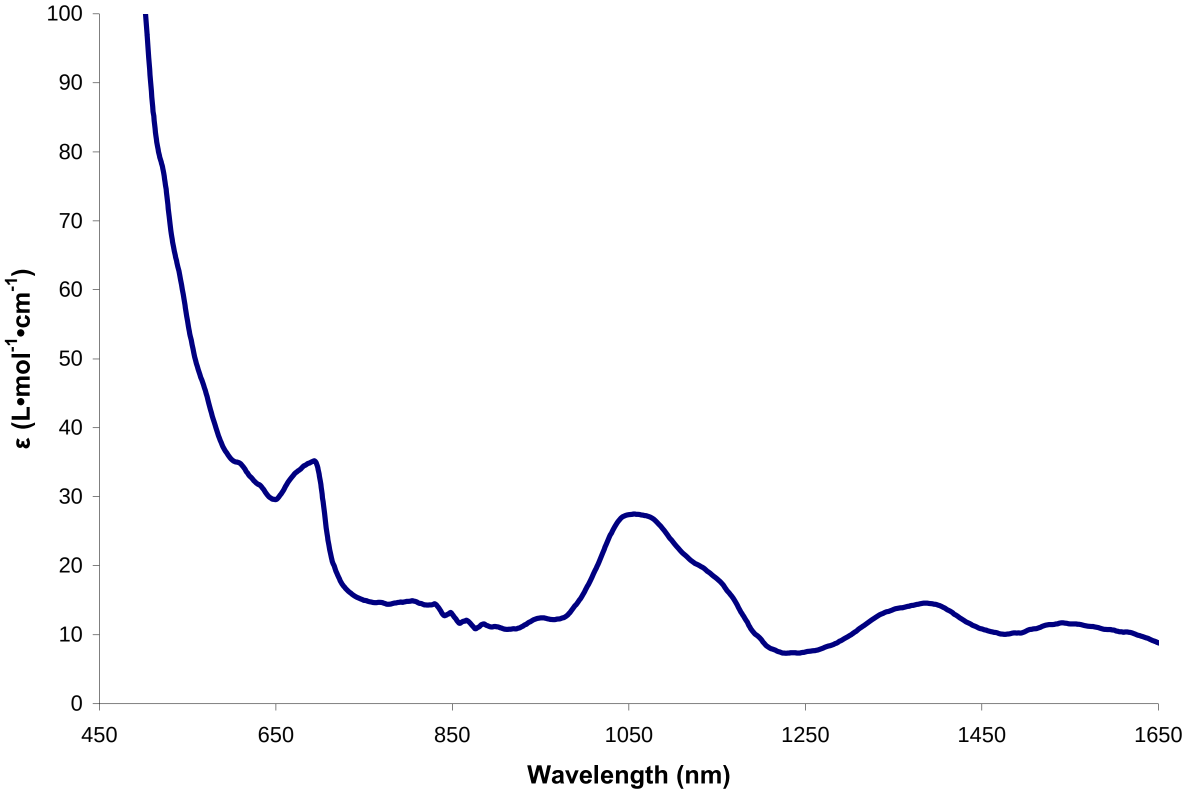

Figure S22. UV-Vis / NIR spectrum of **4** (5.36 mM, C_4H_8O).

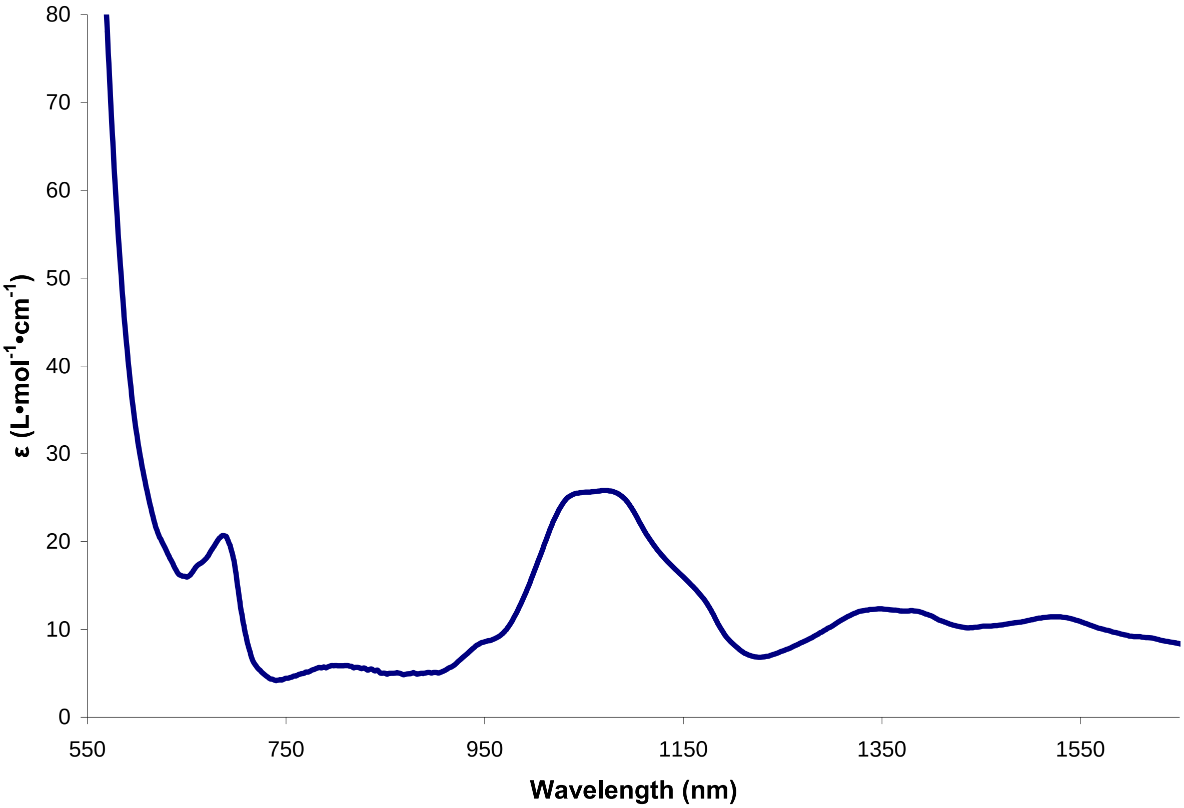

Figure S23. UV-Vis / NIR spectrum of **5** (4.91 mM, C_4H_8O).

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