Electronic Supplementary Material (ESI) for Dalton Transactions.

Oxidation of Uranium(IV) Imido/Amido complexes with PhEEPh and the generation of Uranium(VI) bis(imido) di-chalcogenides $U(NR)_2(EPh)_2(L)_2$

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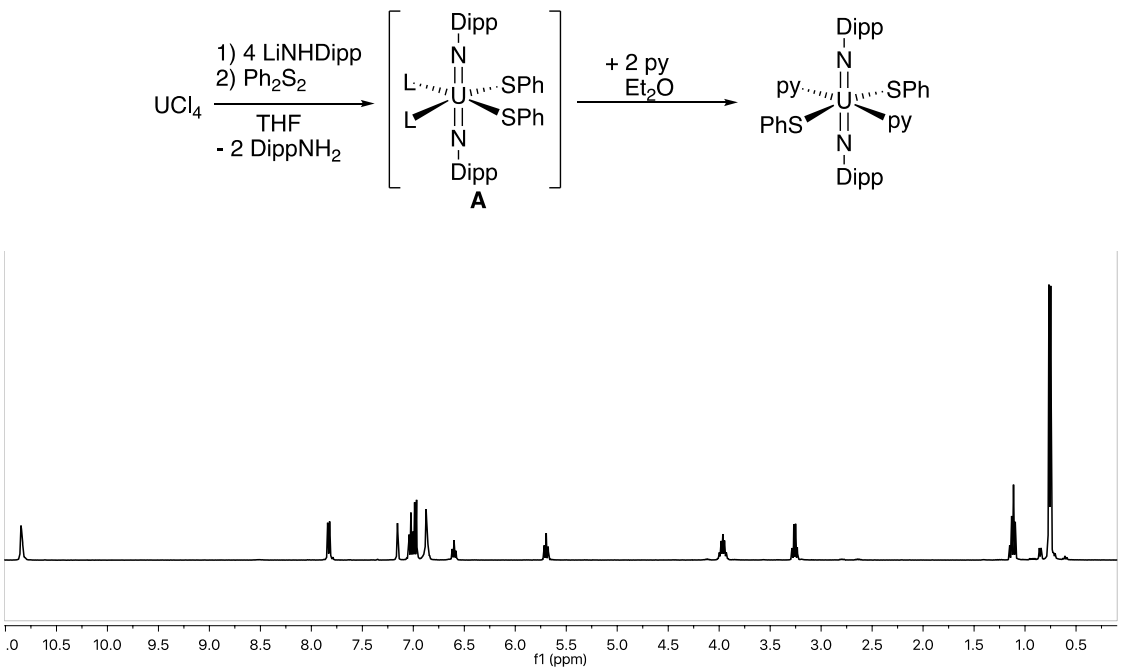


Figure S1. ^{1}H NMR Spectrum of **1-S.** Superfluous diethyl ether in solution is noted by resonances at 3.26 and 1.11 ppm.

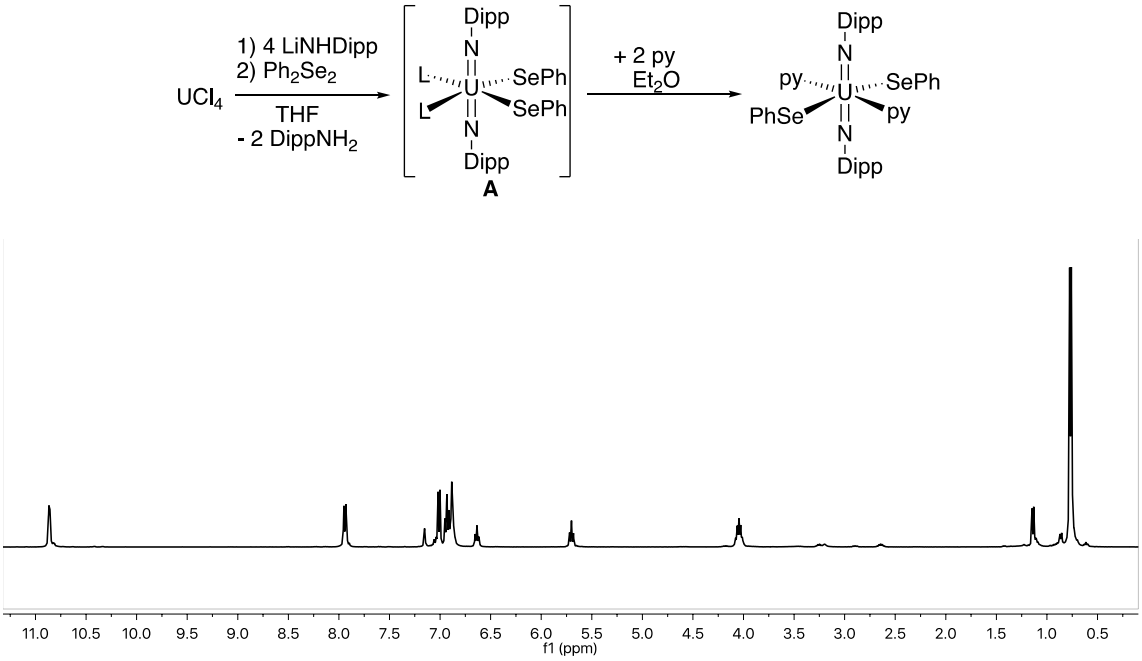


Figure S2. ^{1}H NMR Spectrum of **1-Se**. Superfluous NH_2DIPP in solution is noted by resonances at 3.26 and 1.11 ppm.

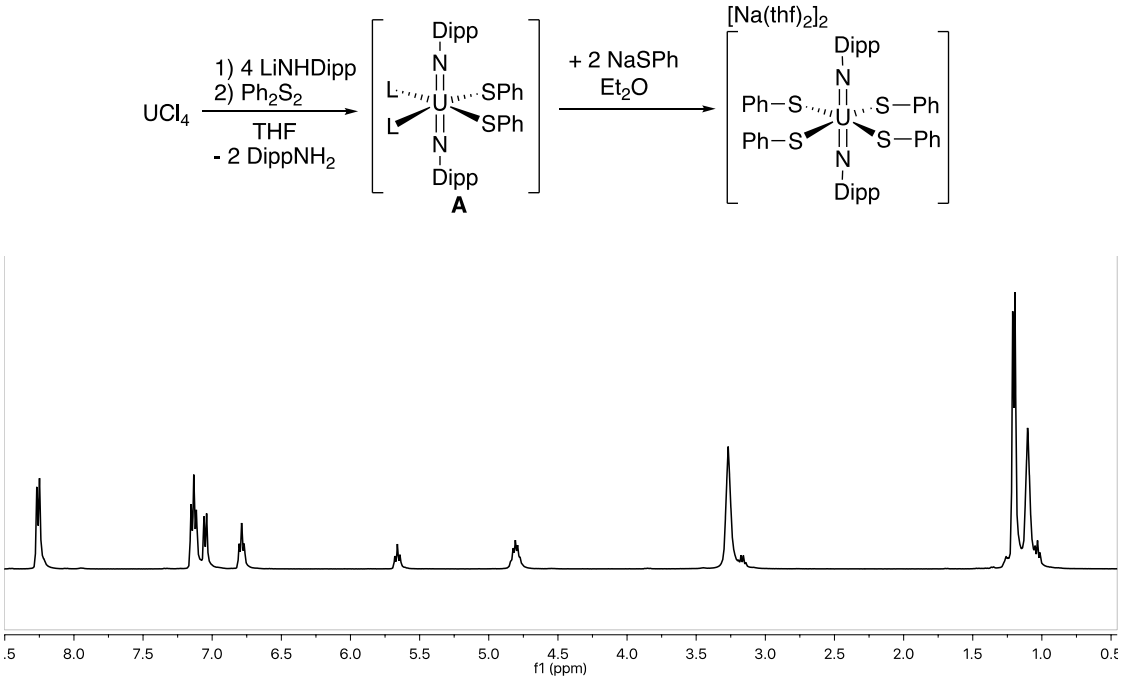


Figure S3. ^{1}H NMR Spectrum of **2-S**. Superfluous diethyl ether in solution is noted by resonances at 3.26 and 1.11 ppm.

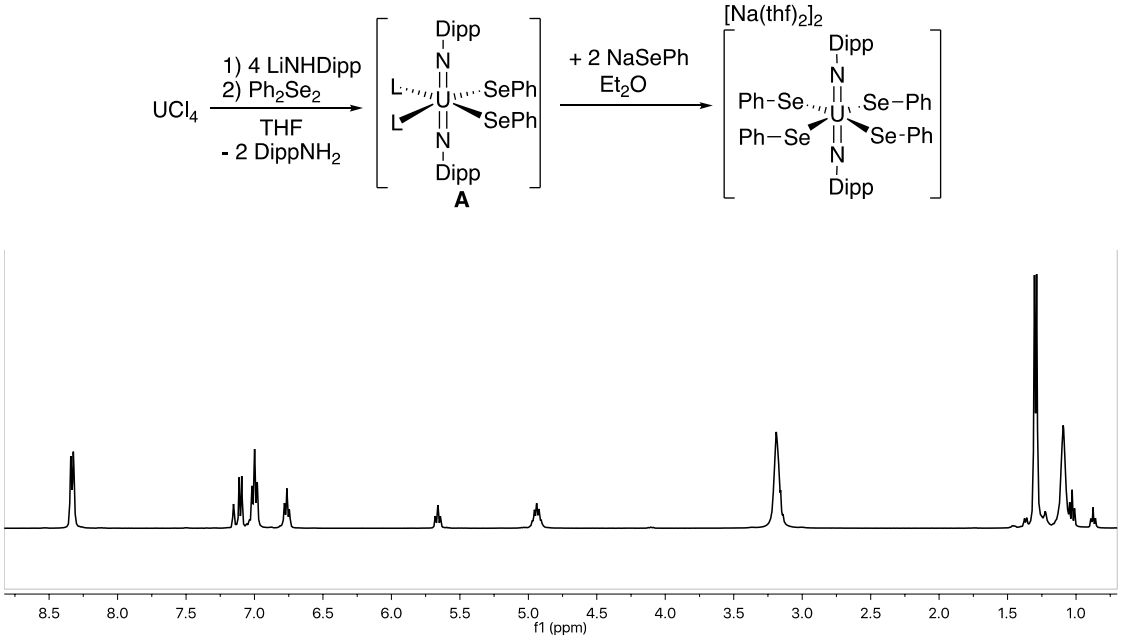


Figure S4. ^{1}H NMR Spectrum of **2-Se**. Superfluous hexane in solution is noted by resonances at 1.19 and 0.89 ppm.

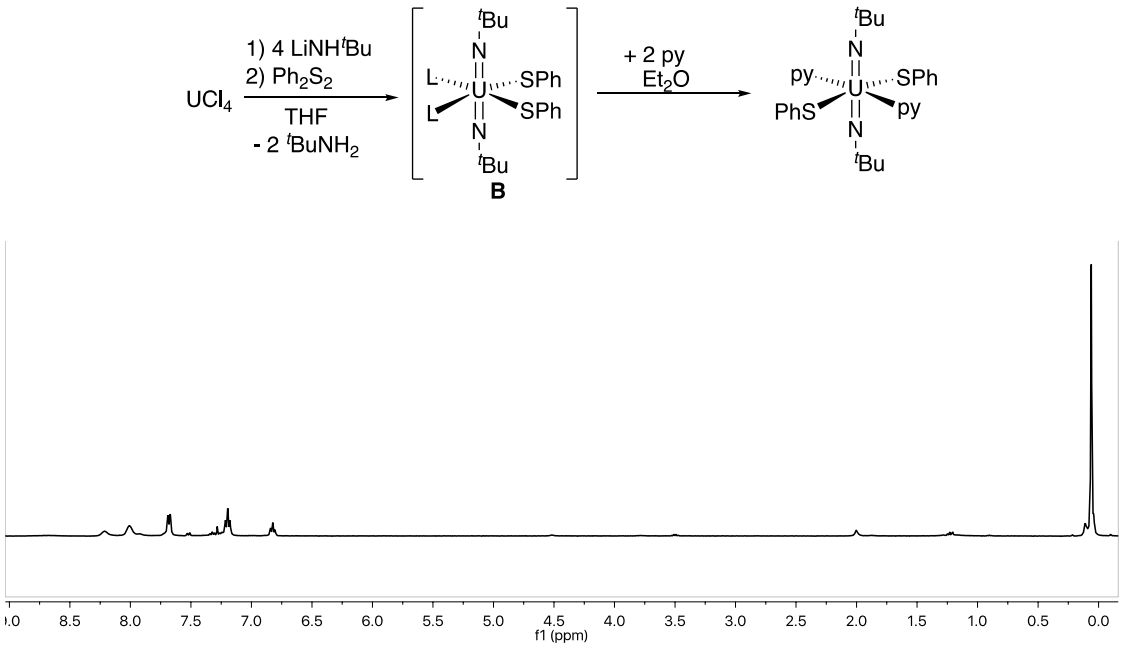


Figure S5. ^{1}H NMR Spectrum of **3-S**.

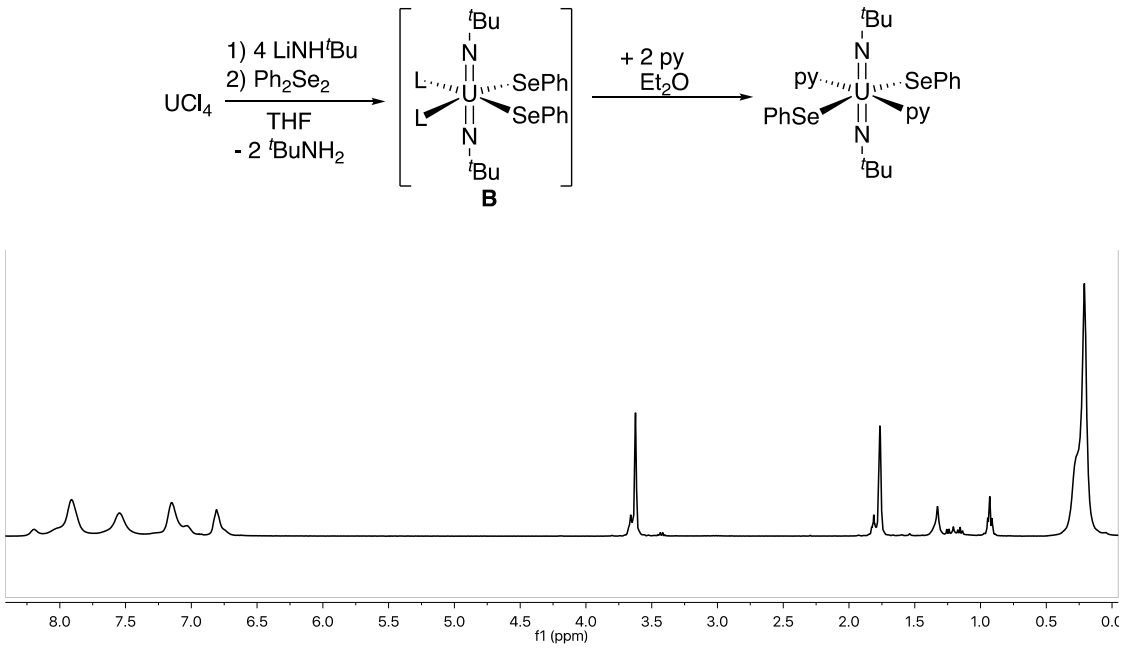


Figure S6. ^{1}H NMR Spectrum of **3-Se**. Superfluous hexane in solution is noted by resonances at 1.19 and 0.89 ppm.

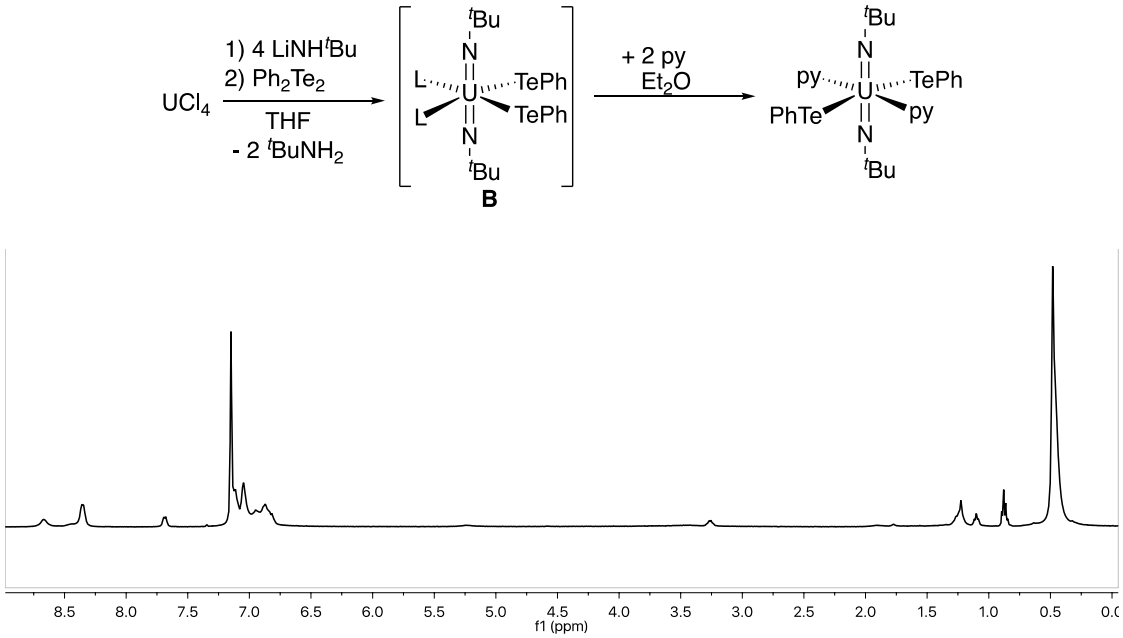


Figure S7. ^{1}H NMR Spectrum of **3-Te.** Superfluous hexane in solution is noted by resonances at 1.19 and 0.89 ppm.

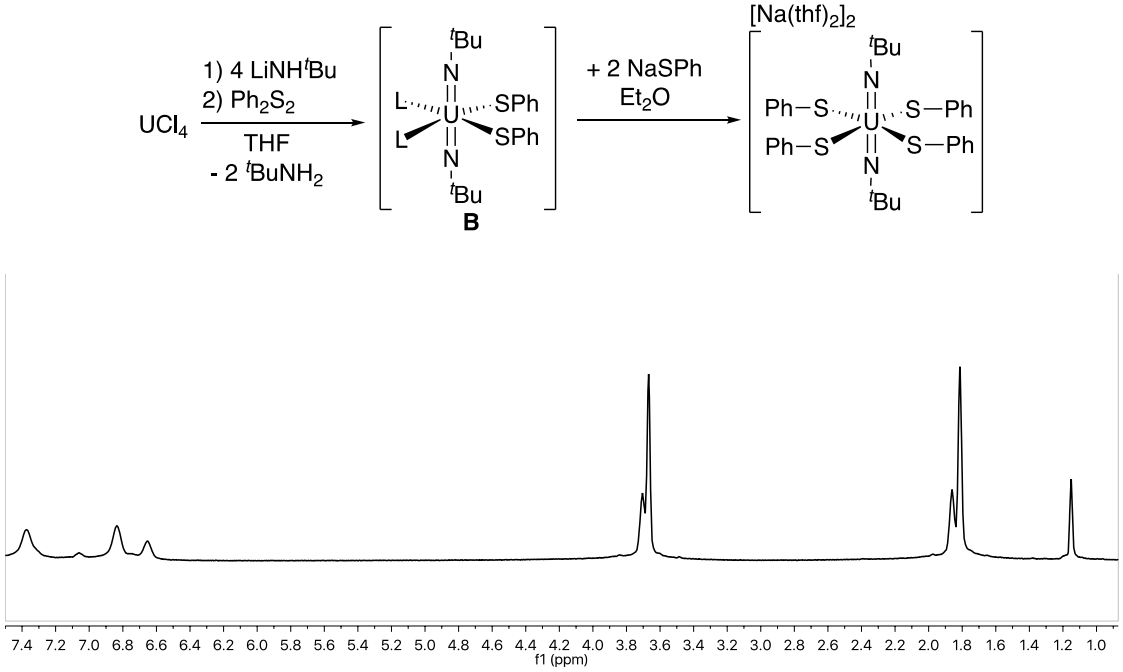


Figure S8. ^{1}H NMR Spectrum of **4-S.**

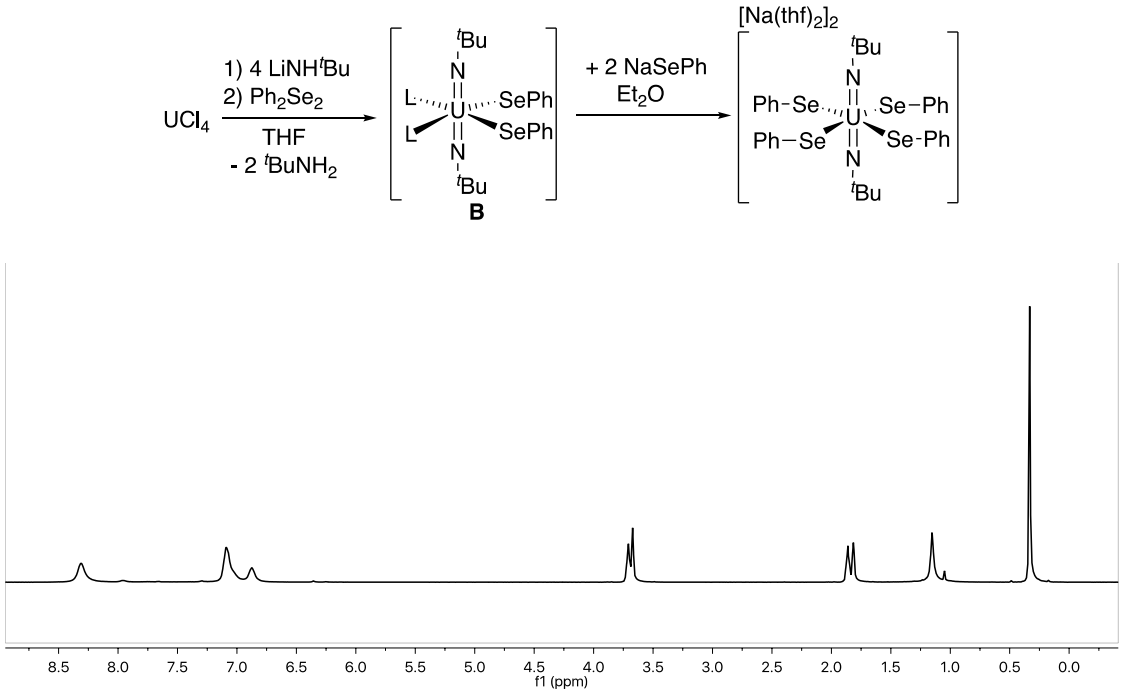


Figure S9. ^{1}H NMR Spectrum of **4-Se.**

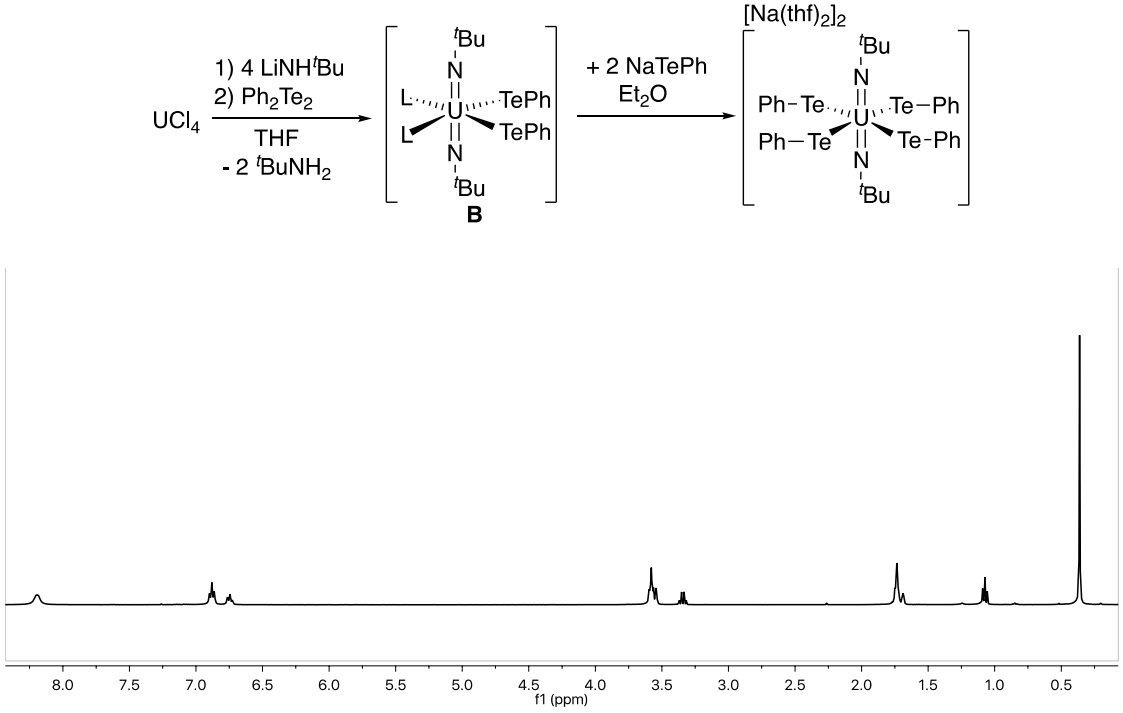
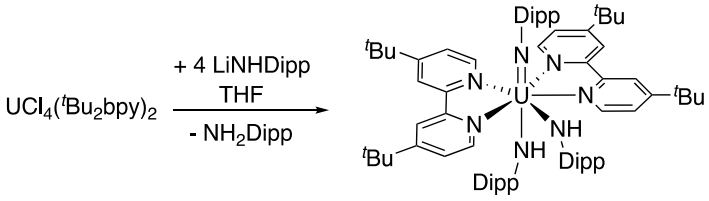


Figure S10. ^{1}H NMR Spectrum of **4-Te.** Superfluous diethyl ether in solution is noted by resonances at 3.26 and 1.11 ppm.



5

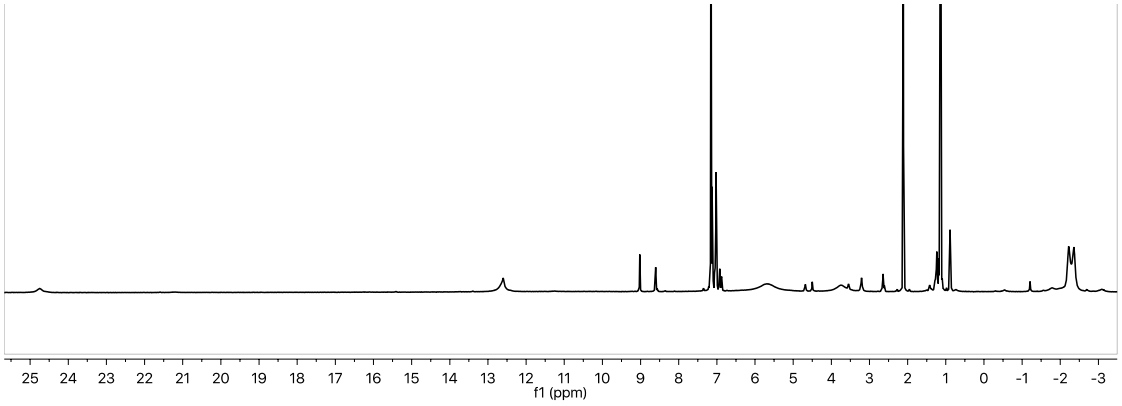


Figure S11. ^{1}H NMR Spectrum of **5.**

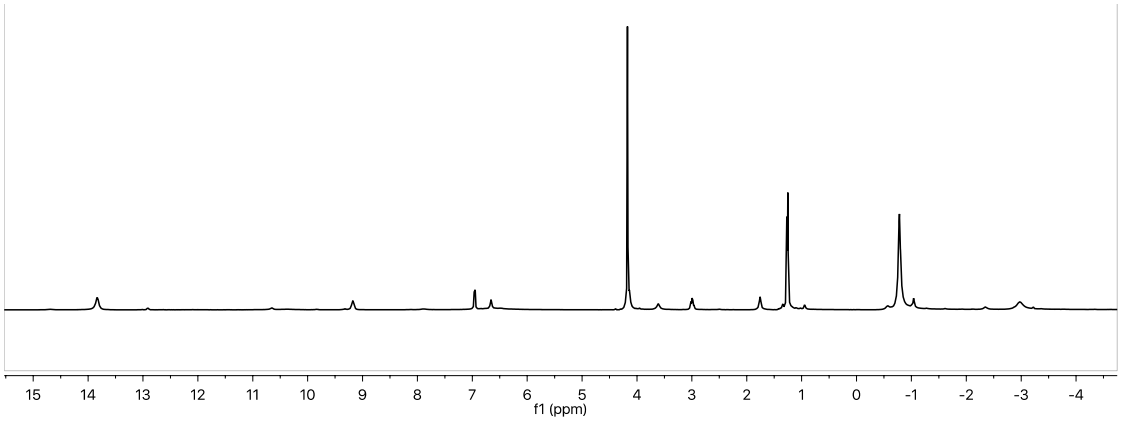


Figure S12. ^{1}H NMR spectrum of UCl_4 with 4 equivalents of $LiNH_2DIPP$.

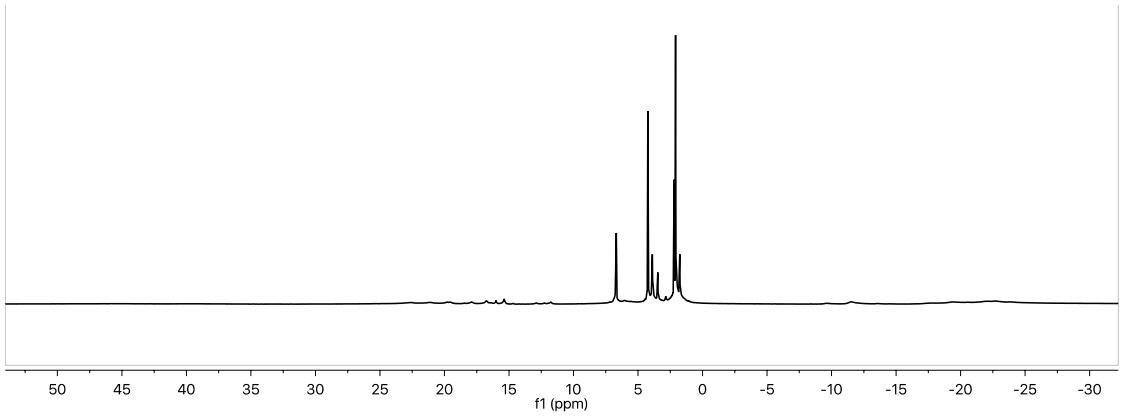


Figure S13. ^{1}H NMR spectrum of UCl_4 with 4 equivalents of $LiNH_2Mes$.

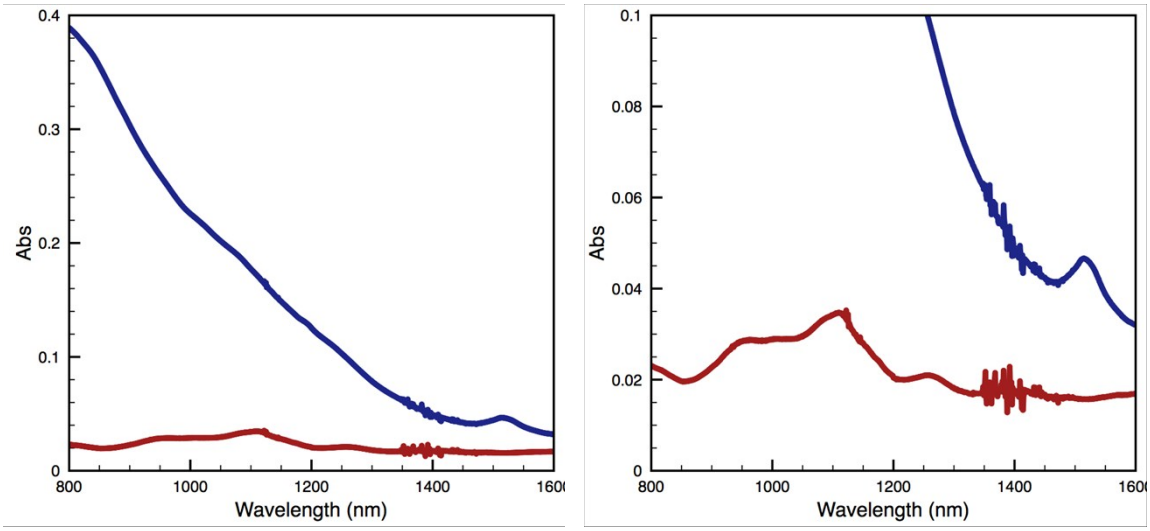


Figure S14. NIR spectrum (800 – 2100 nm) of **5** (blue trace) and "$UNHDIPP_4$" (red trace) recorded in THF at ambient temperature at 5 mmol concentration.

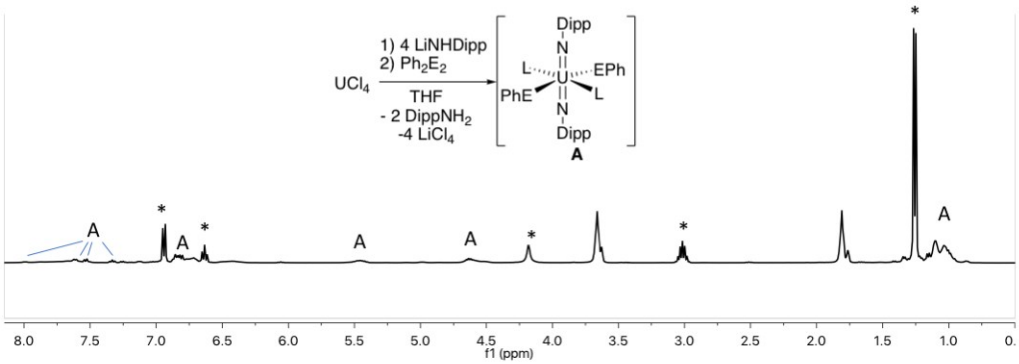


Figure S15. ^{1}H NMR spectrum of crude reaction mixture for the formation of intermediate **A**. resonances labeled with * are attributed to NH_2DIPP produced during the reaction.

Crystallographic data

Table S1: Crystallographic data for of **1-Se**.

Crystal data	
Chemical formula	$C_{46}H_{54}N_4Se_2U$
M_r	1058.88
Crystal system, space group	Monoclinic, $P2_{1/n}$
Temperature (K)	100
a, b, c (Å)	8.8361 (8), 16.7930 (14), 14.5778 (12)
α, β, γ (°)	90, 96.450 (3), 90
V (Å^3)	2149.4 (3)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	5.51
Crystal size (mm)	0.25 × 0.17 × 0.11
Data Collection	
Diffractometer	Bruker *APEX*-II CCD
Absorption correction	Empirical (using intensity measurements) *SADABS2014/2 - Bruker AXS area detector scaling and absorption correction*
Tmin, Tmax	0.429, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	48471, 5348, 5071
Rint	0.028
(sin θ/λ)$_{max}$ (Å^{-1})	0.667
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.013, 0.034, 1.08
No. of reflections	5348
No. of parameters	245
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.68, -0.45

Table S2: Crystallographic data for **2-S**.

Crystal data	
Chemical formula	$C_{64}H_{86}Li_2N_2O_4S_4U$
M_r	1327.49
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, b, c (Å)	12.6118 (10), 18.0426 (15), 13.8368 (11) \
β (°)	98.635 (1)
V (Å^3)	3112.9 (4)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	2.79
Crystal size (mm)	0.2145 × 0.15 × 0.08
Data Collection	
Diffractometer	Bruker D8 Quest with CMOS detector
Absorption correction	Multi-scan*SADABS* v. 2014/3 (Bruker AXS, 2013)
T_{min}, T_{max}	0.592, 0.808
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	70503, 12400, 9692
R_{int}	0.038
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.781
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.024, 0.050, 1.37
No. of reflections	12400
No. of parameters	353
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.86, −0.96

Table S3: Crystallographic data for of **3-S**.

Crystal data	
Chemical formula	$C_{30}H_{38}N_4S_2U$
M_r	756.79
Crystal system, space group	Triclinic, P1-
Temperature (K)	100
a, *b*, *c* (Å)	8.1655 (8), 9.6294 (10), 11.0077 (11)
α, *β*, *γ* (°)	89.562 (2), 73.083 (1), 70.719 (1)
V (Å^3)	777.87 (14)
Z	1
Radiation type	Mo $K\alpha$
μ (mm^{-1})	5.38
Crystal size (mm)	0.22 × 0.12 × 0.08
Data Collection	
Diffractometer	Bruker *APEX*-II CCD
Absorption correction	Empirical (using intensity measurements)*SADABS2014*/3 - Bruker AXS area detector scaling and absorption correction 0.467, 0.746
T_{min}, T_{max}	0.467, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11426, 3851, 3851
R_{int}	0.029
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.667
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.016, 0.038, 1.08
No. of reflections	3851
No. of parameters	172
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.25, −1.21

Table S4: Crystallographic data for of **3-Te**.

Crystal data	
Chemical formula	$C_{15}H_{19}N_2TeU_{0.5}$
M_r	47.94
Crystal system, space group	Triclinic, P1-
Temperature (K)	100
a, *b*, *c* (Å)	8.3876 (11), 9.8459 (13), 11.1701 (14)
α, *β*, *γ* (°)	87.084 (6), 73.083 (6), 69.599 (6)
V (Å^3)	825.88 (19)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	6.67
Crystal size (mm)	0.05 × 0.05 × 0.01
Data Collection	
Diffractometer	Bruker *APEX*-II CCD
Absorption correction	Multi-scan *SADABS2014*/2 (Bruker,2014) was used for absorption correction. wR2(int) was 0.0982 before and 0.0391 after correction. The Ratio of minimum to maximum transmission is 0.7181. The $\lambda/2$ correction factor is 0.00150.
T_{min}, T_{max}	0.535, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11462, 3400, 3274
R_{int}	0.028
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.629
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.018, 0.043, 1.06
No. of reflections	3400
No. of parameters	173
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.90, −0.48

Table S5: Crystallographic data for of **4-S**.

Crystal data	
Chemical formula	$C_{48}H_{69}Li_2N_2O_4S_4U$
M_r	1118.21
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, b, c (Å)	10.790 (2), 22.803 (5), 21.399 (5)
β (°)	99.345 (2)
V (Å^3)	825.88 (19)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	3.33
Crystal size (mm)	0.25 × 0.20 × 0.11
Data Collection	
Diffractometer	Bruker *APEX*-II CCD
Absorption correction	Multi-scan *Empirical (using intensity measurements)* *SADABS2014/2 - Bruker AXS area detector scaling and absorption correction*
T_{min}, T_{max}	0.788, 0.865
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	47137, 8850, 5929
R_{int}	0.121
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.588
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.048, 0.109, 1.00
No. of reflections	8850
No. of parameters	643
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.12, −1.43

Table S6: Crystallographic data for of **4-Te**.

Crystal data	
Chemical formula	$C_{62}H_{86}N_2Na_2O_4Te_4U$
M_r	1717.73
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, b, c (Å)	12.2409 (16), 26.166 (3), 10.0543 (13)
β (°)	103.477 (1)
V (Å^3)	3131.6 (7)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	4.48
Crystal size (mm)	0.22 × 0.16 × 0.06
Data Collection	
Diffractometer	Bruker D8 Quest with CMOS detector
Absorption correction	Multi-scan *SADABS* v. 2014/3 (Bruker AXS, 2013)
T_{min}, T_{max}	0.439, 0.775
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	34388, 7332, 6491
R_{int}	0.031
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.667
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.037, 0.071, 1.95
No. of reflections	7332
No. of parameters	280
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.61, −1.83

Table S7: Crystallographic data for of **5**.

Crystal data	
Chemical formula	$C_{79}H_{107}N_7U$
M_r	1392.74
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	100
a, b, c (Å)	15.8483 (16), 20.707 (2), 26.010 (3)
V (Å^3)	8536.0 (15)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.94
Crystal size (mm)	0.28 × 0.25 × 0.22
Data Collection	
Diffractometer	Bruker *APEX*-II CCD
Absorption correction	Empirical (using intensity measurements) *SADABS2014*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.847, 1
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16191, 16191, 14322
R_{int}	0.116
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.611
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.044, 0.116, 105
No. of reflections	16191
No. of parameters	768
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.72, −0.81
Absolute structure	Refined as inversion twin
Absolute structure parameter	0.047 (9)