Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for:

*Reductive Silylation of Cp*UO$_2$(^{Mes}PDI^{Me}) Promoted by Lewis Bases*

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General Synthesis of [$R_3POSiMe_3$][I] In a 20 mL scintillation vial, $R_3P{=}O$ was dissolved in in 10 mL of toluene. While stirring, iodotrimethylsilane was added *via* microsyringe resulting in immediate precipitation of a white solid. After ten min. of stirring, the solid was collected *via* vacuum filtration to afford the white powder, [$R_3POSiMe_3$][I], in quantitative yields.

R = Ph

^{1}H NMR (CD_2Cl_2, 25 °C) δ = 0.35 (s, 9H, Si(C*H*$_3$)$_3$), 7.69 (t, *J* =7.8, 6H, *o*-C*H*), 7.73-7.80 (m, 6H, *m*-C*H*), 7.92 (t, *J* = 7.2, 3H, *p*-C*H*).

^{31}P NMR (CD_2Cl_2, 25 °C) δ = 52.19.

^{29}Si NMR (CD_2Cl_2, 25 °C) δ = 37.22.

R = C_6H_4-*p*-CH_3

^{1}H NMR (CD_2Cl_2, 25 °C) δ = 0.31 (s, 9H, Si(C*H*$_3$)$_3$), 2.52 (s, 9H, C_6H_4-*p*-C*H*$_3$), 7.51-7.58 (m, 12H, *m*-C*H* & *o*-C*H*).

^{31}P NMR (CD_2Cl_2, 25 °C) δ = 53.03.

^{29}Si NMR (CD_2Cl_2, 25 °C) δ = 35.80.

R = $N(CH_3)_2$

^{1}H NMR (CD_2Cl_2, 25 °C) δ = 0.42 (s, 9H, Si(C*H*$_3$)$_3$), 2.77 (d, *J* = 10.5, 18H, N(C*H*$_3$)$_2$).

^{31}P NMR (CD_2Cl_2, 25 °C) δ = 26.57.

^{29}Si NMR (CD_2Cl_2, 25 °C) δ = 28.94.

Table S1 Equilibrium Determination of $[Ph_3POSiMe_3][Cl]$

Eq. TMS-X		$[OPPh_3]$	[TMS-Cl]	$[[Ph_3POSiMe_3][Cl]$	K_{eq}[a]
0.5	Initial	0.02984	0.01494	0	4.247
	End	0.02824	0.01334	0.0016	
1	Initial	0.02979	0.02983	0	4.099
	End	0.02683	0.02687	0.00296	
2	Initial	0.02967	0.05943	0	3.634
	End	0.02477	0.05452	0.00491	
5	Initial	0.02931	0.01544	0	3.583
	End	0.02791	0.01404	0.0014	
					K = 3.8908 +/- 0.3323

[a]Equilibrium Constants determined in CD_2Cl_2 (25 °C) by ^1H NMR spectroscopy.

Table S2 Equilibrium Determination of $[Ph_3POSiMe_3][SPh]$

Eq. TMS-X		$[OPPh_3]$	[TMS-SPh]	$[[Ph_3POSiMe_3][SPh]$	K_{eq}[a]
1	Initial	0.02574	0.02575	0	1.32
	End	0.02492	0.02493	0.00082	
2	Initial	0.02562	0.05124	0	1.36
	End	0.02399	0.04962	0.00163	
5	Initial	0.02525	0.12628	0	1.26
	End	0.02186	0.12289	0.00339	
10	Initial	0.02466	0.24667	0	1.27
	End	0.01888	0.24088	0.00578	
					K = 1.3025 +/- 0.0465

[a]Equilibrium Constants determined in CD_2Cl_2 (25 °C) by ^1H NMR spectroscopy.

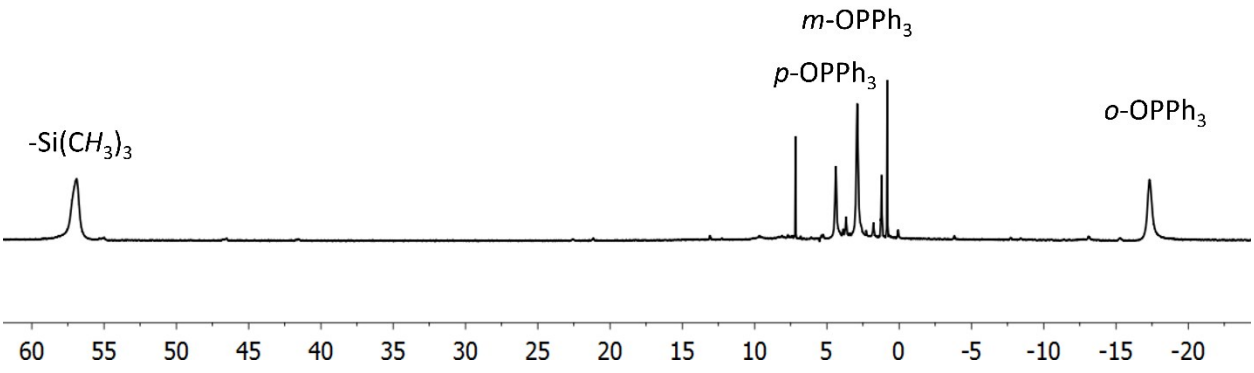

Figure S1 ^{1}H NMR spectrum of $(Me_3SiO)_2UI_2(OPPh_3)_2$ (**2-OPPh$_3$**)

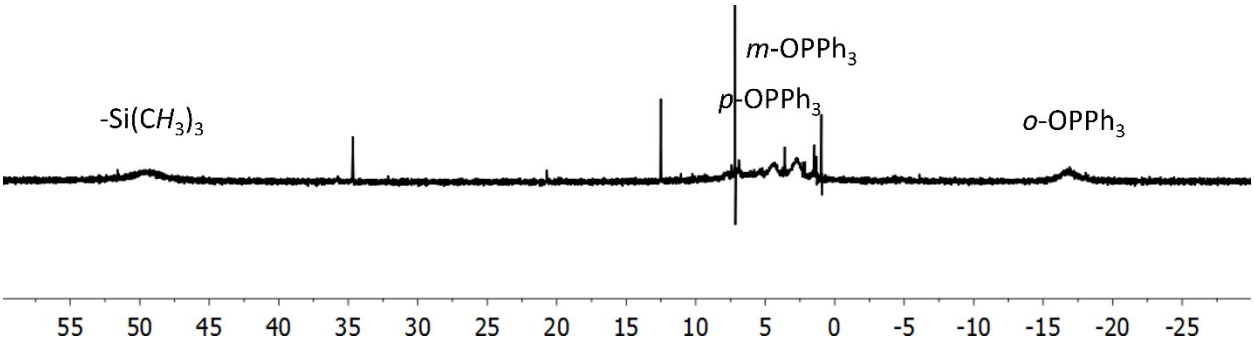

Figure S2 ^{1}H NMR spectrum of $(Me_3SiO)_2UCl_2(OPPh_3)_2$ (**3-OPPh$_3$**)

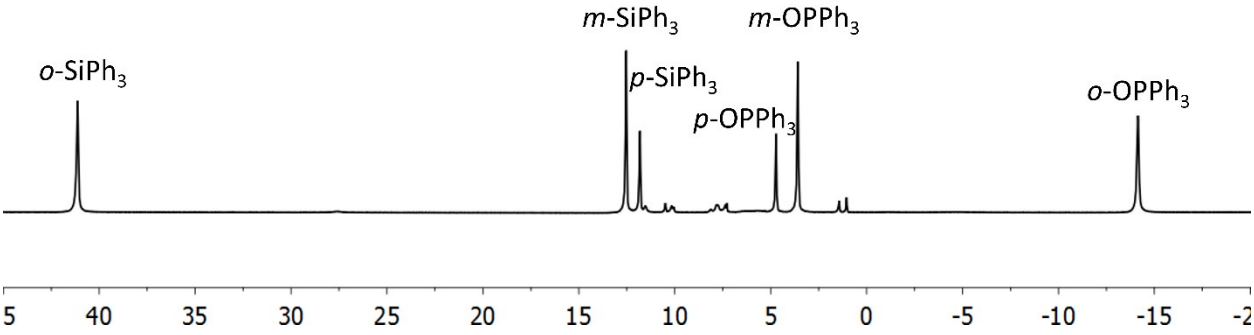

Figure S3 ^{1}H NMR spectrum of $(Ph_3SiO)_2UCl_2(OPPh_3)_2$ (**4-OPPh$_3$**)

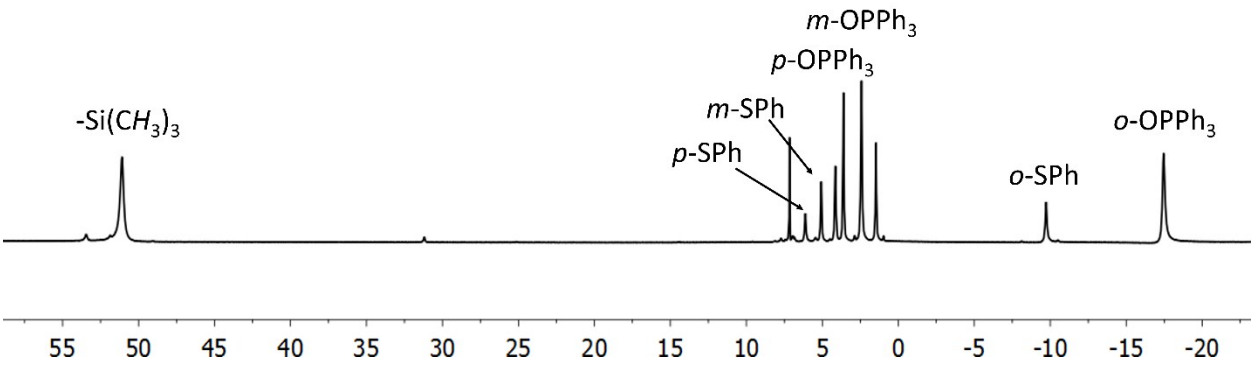

Figure S4 ^{1}H NMR spectrum of $(Me_3SiO)_2U(SPh)_2(OPPh_3)_2$ (**5-OPPh$_3$**)

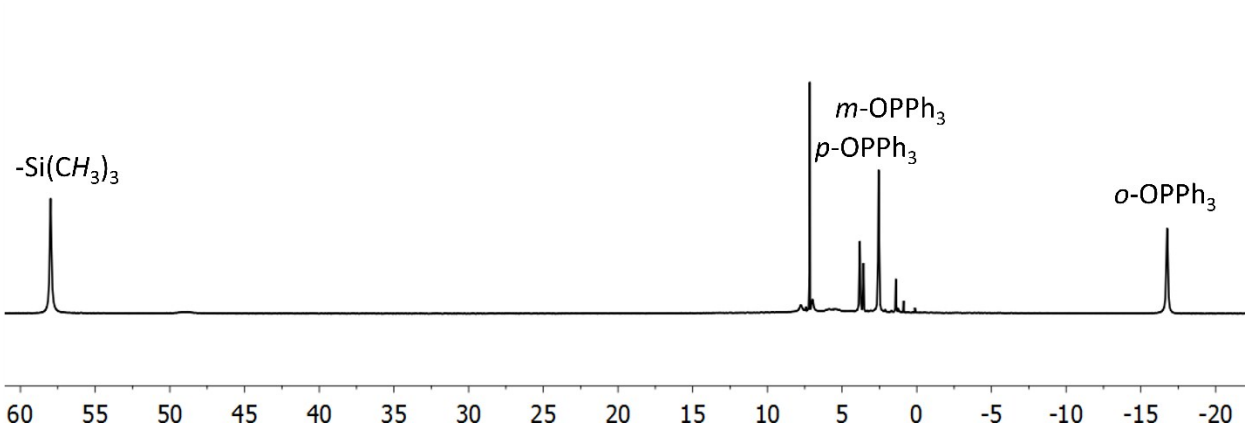

Figure S5 ^{1}H NMR spectrum of $(Me_3SiO)_2U(OTf)_2(OPPh_3)_2$ (**6-OPPh$_3$**)

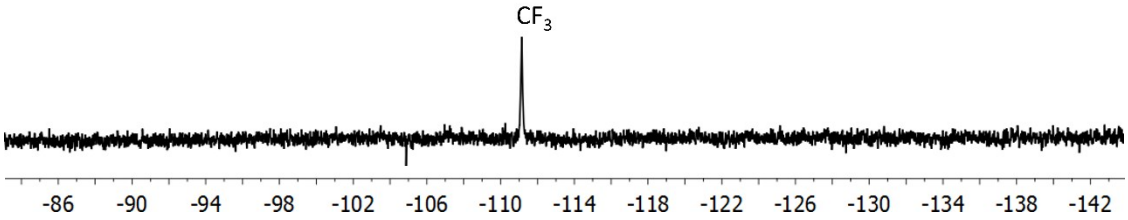

Figure S6 ^{19}F NMR spectrum of $(Me_3SiO)_2U(OTf)_2(OPPh_3)_2$ (**6-OPPh$_3$**)

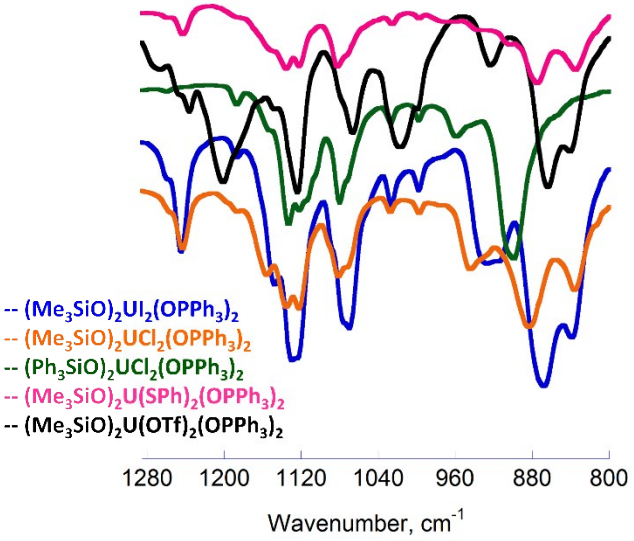

Figure S7 IR Spectra (KBr Salt Plate) of complexes **2-OPPh$_3$**, **3-OPPh$_3$**, **4-OPPh$_3$**, **5-OPPh$_3$**, and **6-OPPh$_3$**,

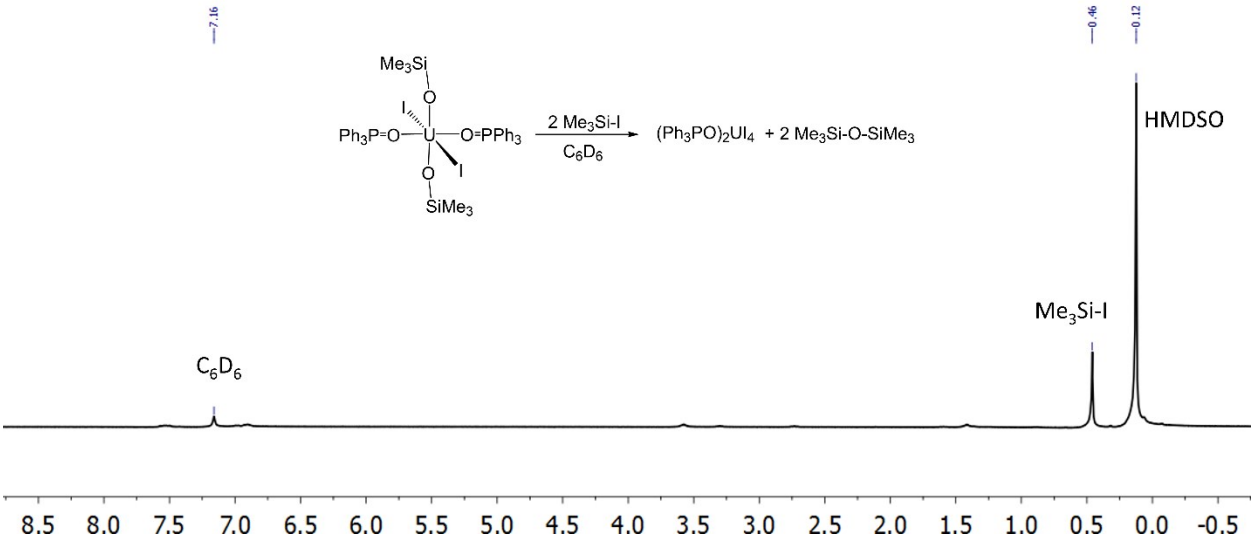

Figure S8 NMR tube experiment (C_6D_6, 25 °C) between **2-OPPh$_3$** and 2 Me_3Si-I.

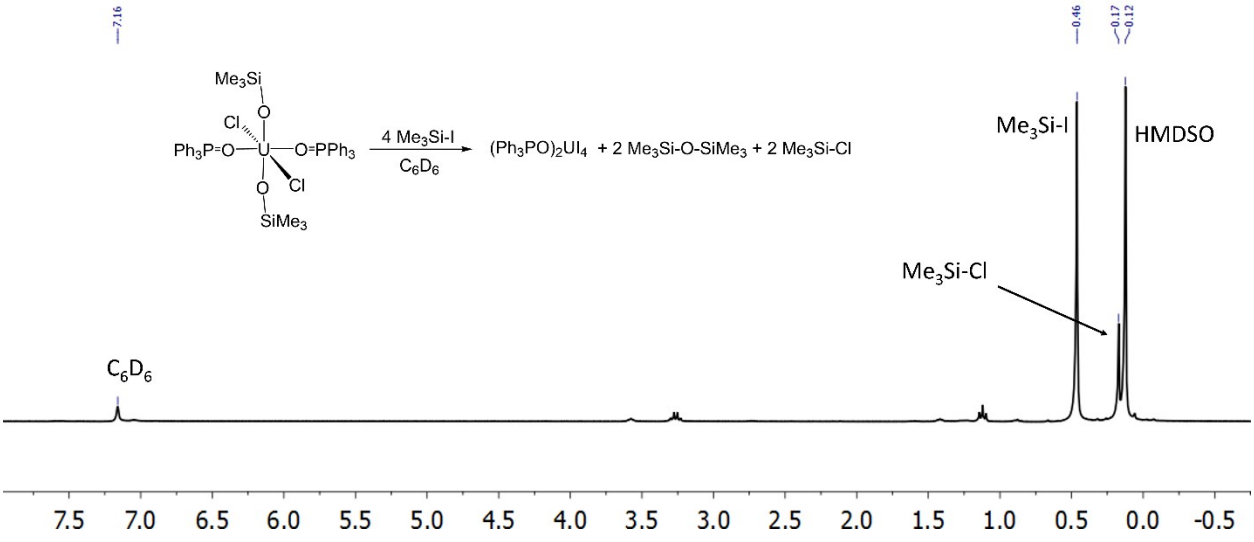

Figure S9 NMR tube experiment (C_6D_6, 25 °C) between **3-OPPh$_3$** and 4 Me_3Si-I.

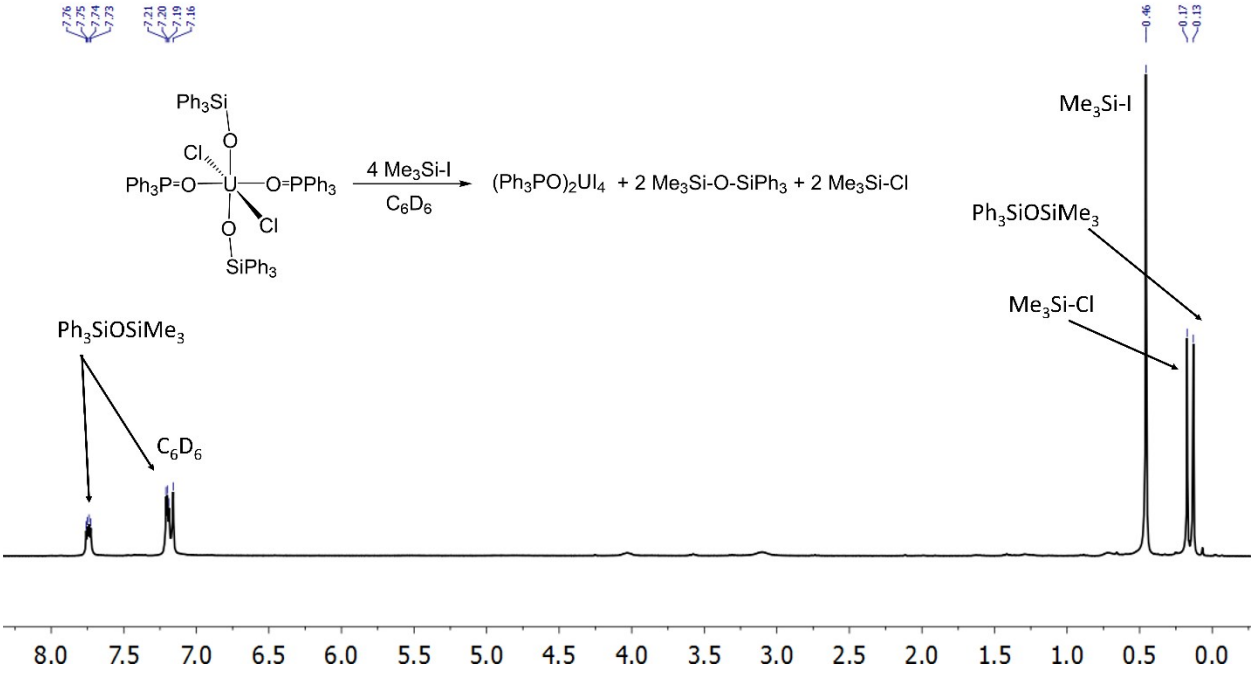

Figure S10 NMR tube experiment (C_6D_6, 25 °C) between **4-OPPh$_3$** and 4 Me_3Si-I.

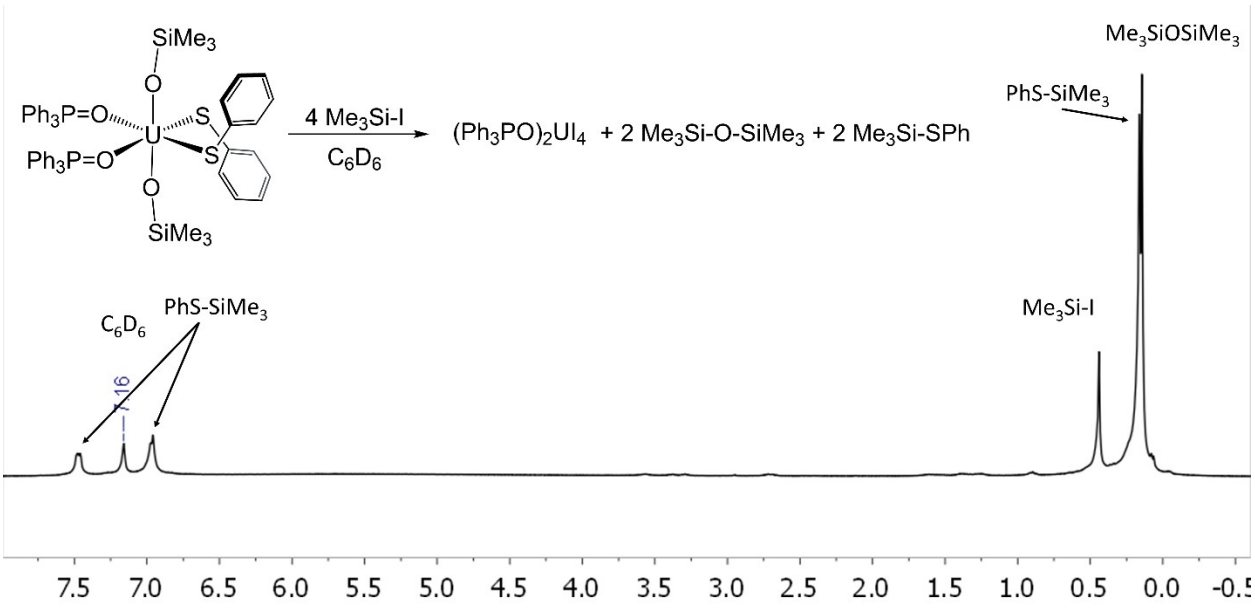

Figure S11 NMR tube experiment (C_6D_6, 25 °C) between **5-OPPh$_3$** and 4 Me_3Si-I.

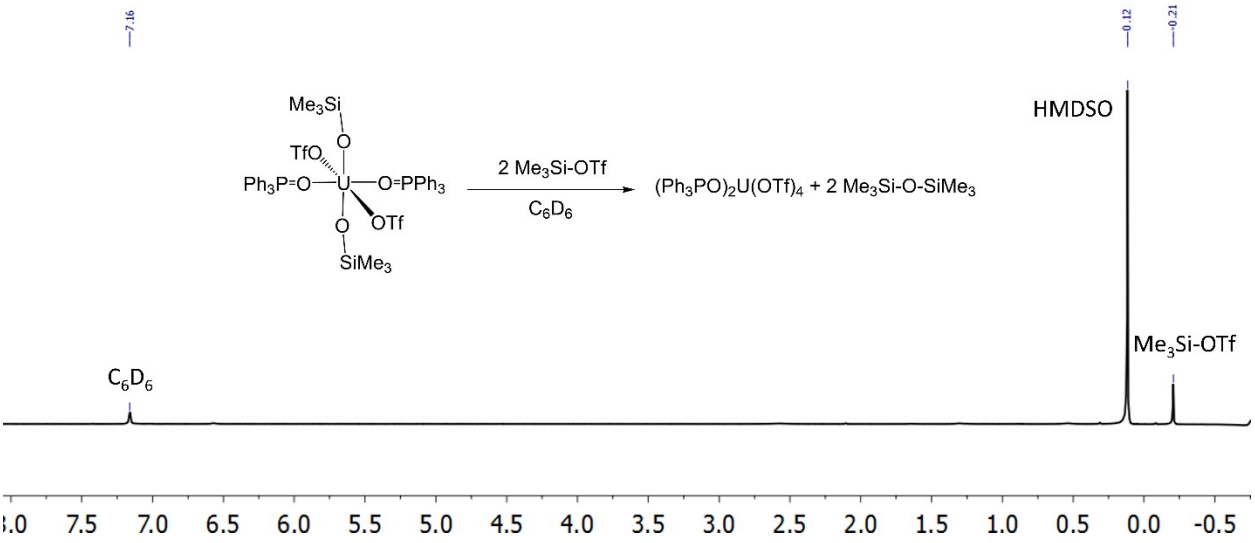

Figure S12 NMR tube experiment (C_6D_6, 25 °C) between **6-OPPh$_3$** and 2 Me_3Si-OTf.

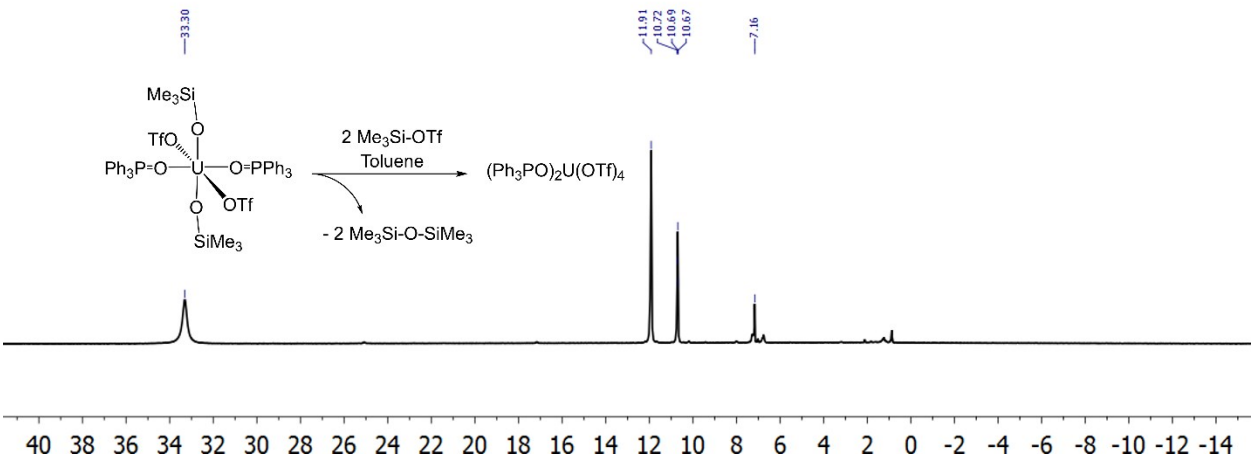

Figure S13 ^{1}H NMR (C_6D_6, 25 °C) of $(Ph_3PO)_2U(OTf)_4$ (**7-OTf**)

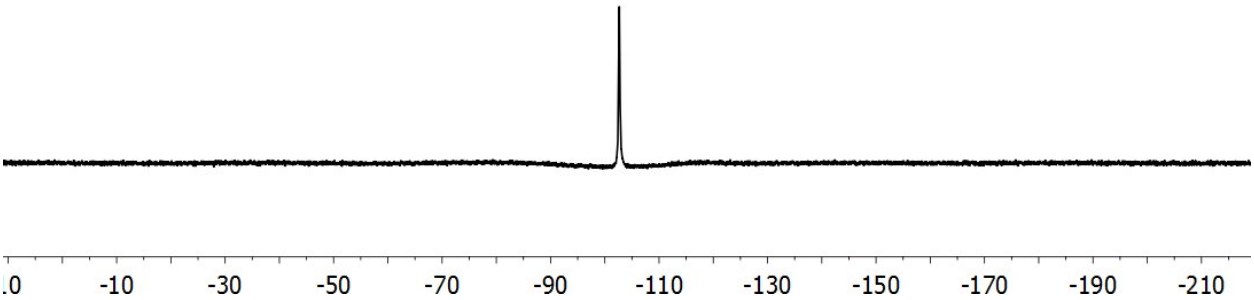

Figure S14 ^{19}F NMR (C_6D_6, 25 °C) of $(Ph_3PO)_2U(OTf)_4$ (**7-OTf**) referenced externally to C_6H_5F

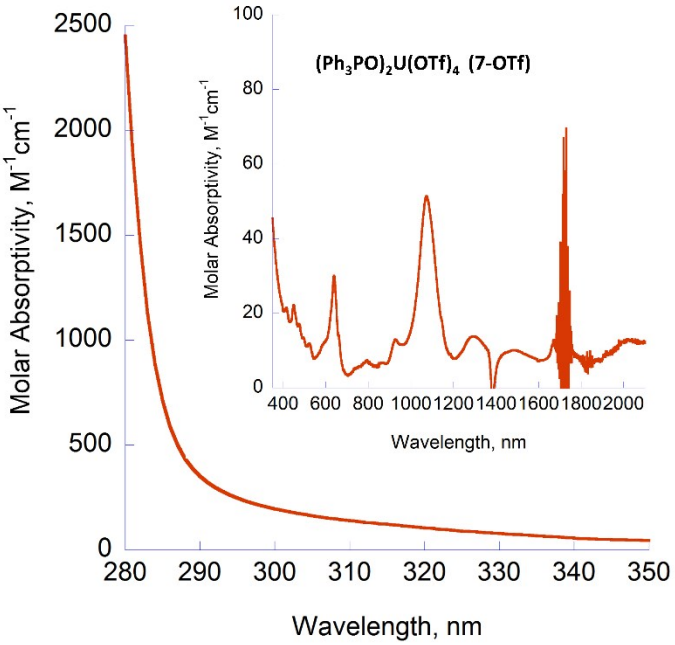

Figure S15 Electronic absorption spectrum of $(Ph_3PO)_2U(OTf)_4$ (**7-OTf**) recorded in THF at 25 °C.

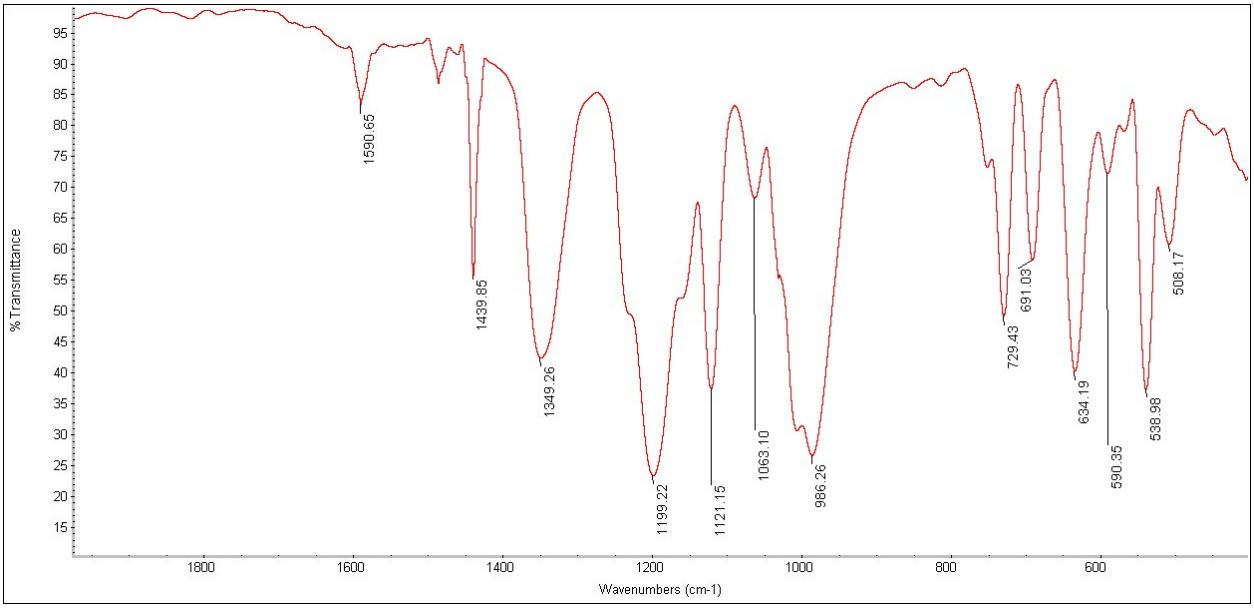

Figure S16 IR spectrum (KBr Salt Plate) of $(Ph_3PO)_2U(OTf)_4$ (**7-OTf**) recorded at 25 °C.

Complex: **2-OPPh$_3$** $(Me_3SiO)_2UI_2(OPPh_3)_2$

ID: jk6202

CCDC 1436229

Table S2. Experimental details

Crystal data	
Chemical formula	$C_{42}H_{48}I_2O_4P_2Si_2U \cdot C_7H_8$
M_r	1318.88
Crystal system, space group	Triclinic, *P*1
Temperature (K)	200
a, *b*, *c* (Å)	10.3801 (7), 11.9238 (9), 12.6051 (12)
α, β, γ (°)	76.394 (6), 67.826 (6), 67.689 (5)
V (Å^3)	1328.9 (2)
Z	1
Radiation type	Cu *K*α
μ (mm^{-1})	19.02
Crystal size (mm)	0.15 × 0.15 × 0.04
Data collection	
Diffractometer	Rigaku Rapid II diffractometer
Absorption correction	Multi-scan *SCALEPACK* (Otwinowski & Minor, 1997)
T_{min}, T_{max}	0.001, 0.467
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	180581, 4519, 4270
R_{int}	0.092
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.601
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.052, 0.150, 1.13
No. of reflections	4519
No. of parameters	276
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.58, −1.34

Computer programs: Crystal Clear(Rigaku 2001), *HKL-3000* (Otwinowski & Minor, 1997), *SHELXT* (Sheldrick), *SHELXL2014*/6 (Sheldrick, 2014), local programs.

Complex: **4-OPPh$_3$** $(Ph_3SiO)_2UCl_2(OPPh_3)_2$

ID: jk725

CCDC 1436227

Table S3. Experimental details

Crystal data	
Chemical formula	$C_{12}H_{10}Cl_2P_2U·2(C_{18}H_{15}OSi)·2(H_2O)·4(C_4H_8O)·4(C_6H_5)$
M_r	1704.66
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	200
a, *b*, *c* (Å)	29.2654 (7), 18.0309 (4), 15.5926 (4)
β (°)	91.090 (2)
V (Å^3)	8226.4 (3)
Z	4
Radiation type	Cu *K*α
μ (mm^{-1})	7.23
Crystal size (mm)	0.28 × 0.000 × 0.000
Data collection	
Diffractometer	Rigaku Rapid II diffractometer
Absorption correction	Multi-scan *SCALEPACK* (Otwinowski & Minor, 1997)
T_{min}, T_{max}	0.013, 0.236
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	46906, 7812, 7255
R_{int}	0.073
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.618
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.057, 0.169, 1.16
No. of reflections	7812
No. of parameters	450
No. of restraints	6
H-atom treatment	H-atom parameters constrained $w = 1/[\sigma^2(F_o^2) + (0.1003P)^2 + 37.3361P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.54, −2.37

Computer programs: Crystal Clear(Rigaku 2001), *HKL-3000* (Otwinowski & Minor, 1997), *SHELXT* (Sheldrick), *SHELXL2014*/7 (Sheldrick, 2014), local programs.

Complex: **5-OPPh$_3$** $(Me_3SiO)_2U(SPh)_2(OPPh_3)_2$

ID: jk717

CCDC: 1436226

Table S4. Experimental details

Crystal data	
Chemical formula	$C_{54}H_{58}O_4Si_2P_2S_2U \cdot 3(C_6H_6)$
M_r	1425.59
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	200
a, *b*, *c* (Å)	22.9048 (7), 11.6124 (4), 25.6316 (8)
β (°)	95.099 (2)
V (Å^3)	6790.5 (4)
Z	4
Radiation type	Cu *K*α
μ (mm^{-1})	8.45
Crystal size (mm)	0.20 × 0.20 × 0.10
Data collection	
Diffractometer	Rigaku Rapid II
Absorption correction	Multi-scan *SCALEPACK* (Otwinowski & Minor, 1997)
T_{min}, T_{max}	0.017, 0.430
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	35035, 6290, 5831
R_{int}	0.057
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.610
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.055, 0.161, 1.13
No. of reflections	6290
No. of parameters	378
H-atom treatment	H-atom parameters constrained $w = 1/[\sigma^2(F_o^2) + (0.0969P)^2 + 20.1313P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	3.05, −1.24

Computer programs: Crystal Clear(Rigaku 2001), *HKL-3000* (Otwinowski & Minor, 1997), *SHELXT* (Sheldrick), *SHELXL2014*/7 (Sheldrick, 2014), local programs.

Complex: **6-OPPh$_3$** $(Me_3SiO)_2U(OTf)_2(OPPh_3)(THF)_2$

ID: jk755

CCDC 1436228

Table S5. Experimental details

Crystal data	
Chemical formula	$C_6H_5PS_2SiU \cdot C_3H_9OSi \cdot 2(CF_3) \cdot 8(H_2O) \cdot 2(C_4H_8O) \cdot 3(CH_3) \cdot 2(C_6H_5)$
M_r	1137.03
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	200
a, b, c (Å)	14.0951 (3), 18.5493 (4), 17.7595 (5)
β (°)	92.379 (1)
V (Å^3)	4639.29 (19)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	12.17
Crystal size (mm)	0.20 × 0.20 × 0.10
Data collection	
Diffractometer	Rigaku Rapid II
Absorption correction	Multi-scan *SCALEPACK* (Otwinowski & Minor, 1997)
T_{min}, T_{max}	0.003, 0.296
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	53002, 8289, 7883
R_{int}	0.069
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.601
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.125, 1.06
No. of reflections	8289
No. of parameters	520
H-atom treatment	H-atom parameters constrained $w = 1/[\sigma^2(F_o^2) + (0.0792P)^2 + 18.9372P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	4.06, −1.67

Computer programs: Crystal Clear(Rigaku 2001), *HKL-3000* (Otwinowski & Minor, 1997), *SHELXT* (Sheldrick), *SHELXL2014*/7 (Sheldrick, 2014), local programs.