Supporting Information for:

Uranium(III) complexes supported by hydrobis(mercaptoimidazolyl)borates: synthesis and oxidation chemistry

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1- UV-vis-NIR

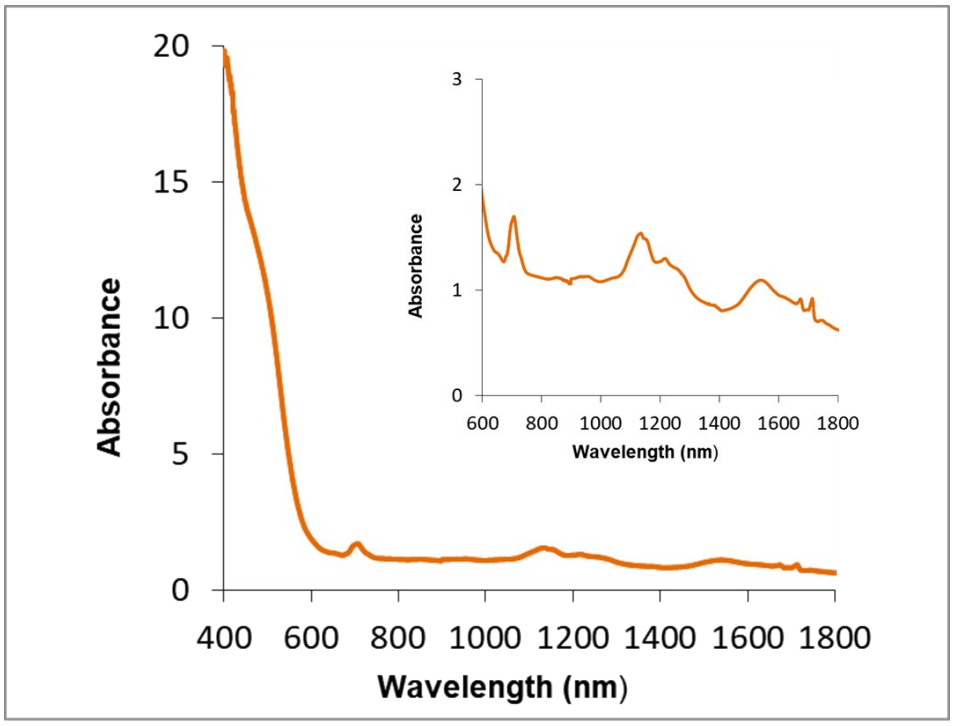

Figure S1. Room temperature UV-vis-NIR absorption spectra for complex [U{κ^3-H(R)B(tim^{Me})$_2$}$_3$][I] **6-I** in acetonitrile.

2. IR spectra

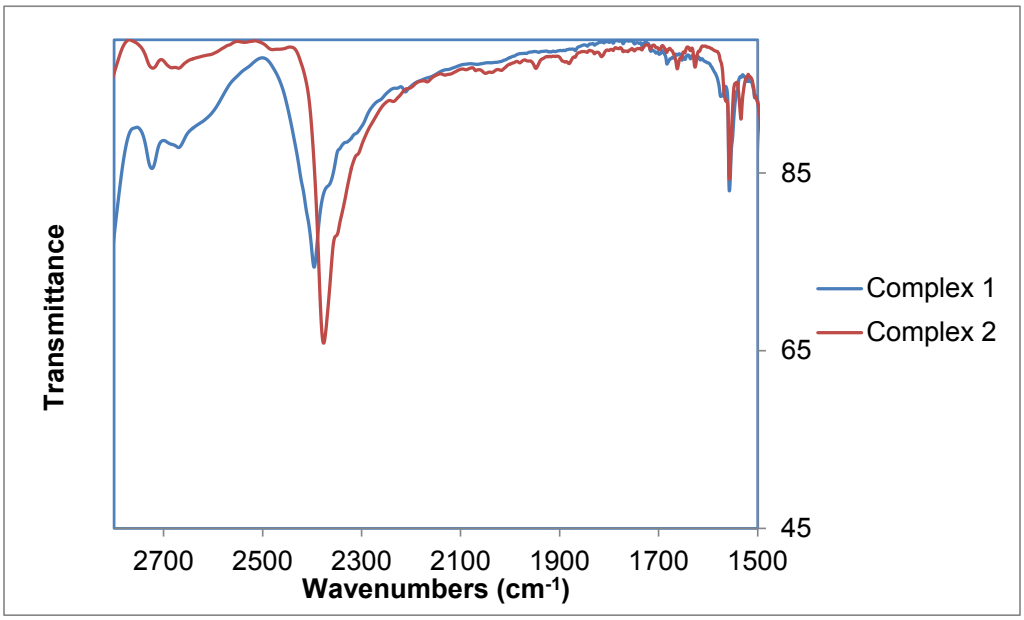

Figure S2. IR spectra of [UI{κ^3-H(R)B(tim^{Me})$_2$}$_2$(thf)$_2$] (R = H (**1**), Ph (**2**))

3. NMR Data

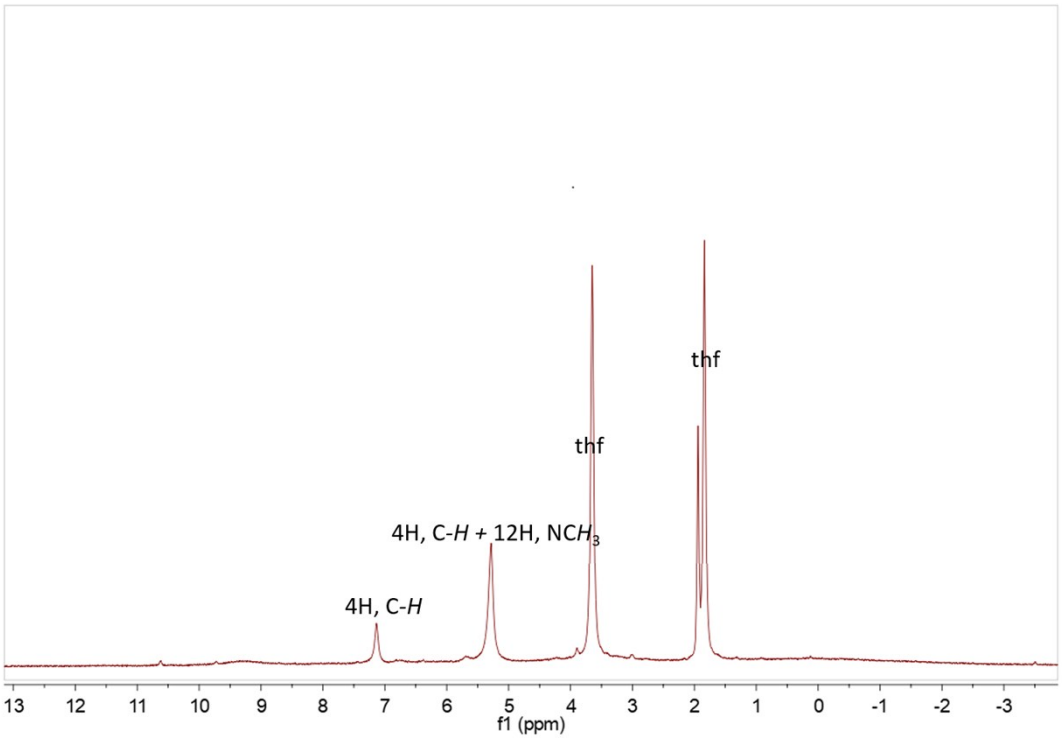

Figure S3. ^{1}H NMR of [UI{κ^{3}-H$_2$B(tim^{Me})$_2$}$_2$(thf)$_2$] (**1**) in acetonitrile-d_3 at 21ºC.

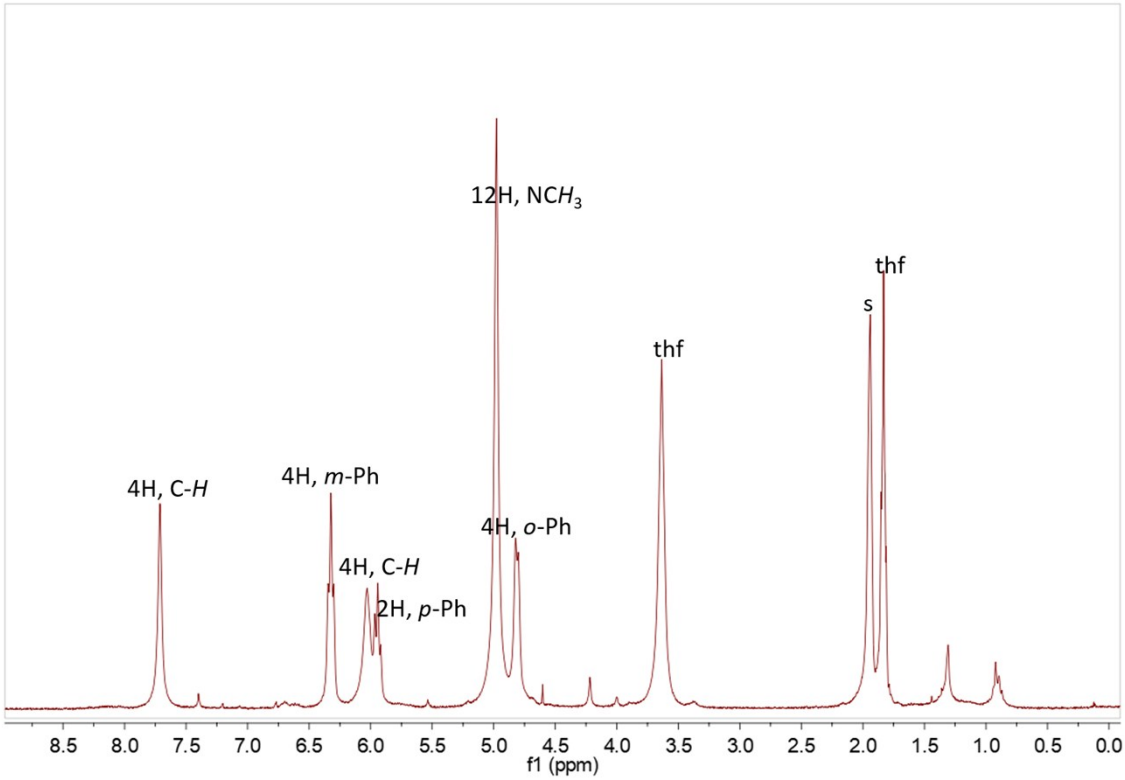

Figure S4. ^{1}H NMR of [UI{κ^{3}-H(Ph)B(tim^{Me})$_2$}$_2$(thf)$_2$] (**2**) in acetonitrile-d_3 at 21ºC (from 9 ppm to 0 ppm).

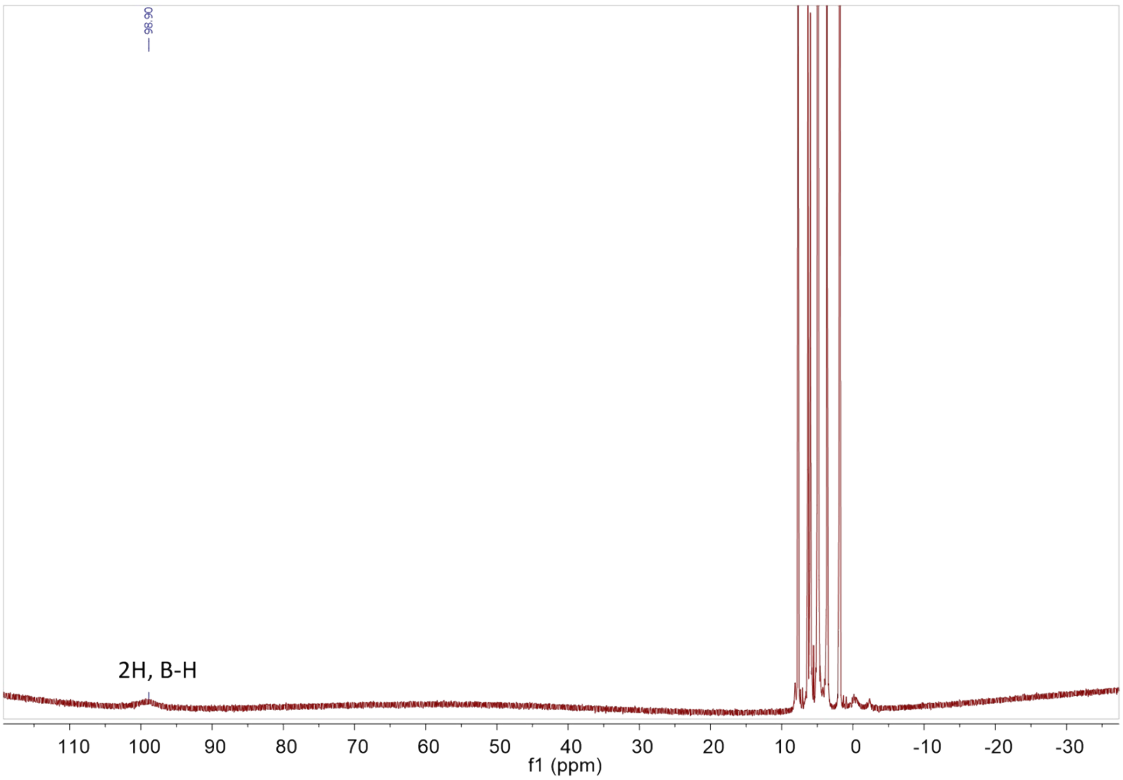

Figure S5. ^{1}H NMR of [UI{κ^{3}-H(Ph)B(tim^{Me})$_2$}$_2$(thf)$_2$] (**2**) in acetonitrile-d_3 at 21ºC (full spectrum).

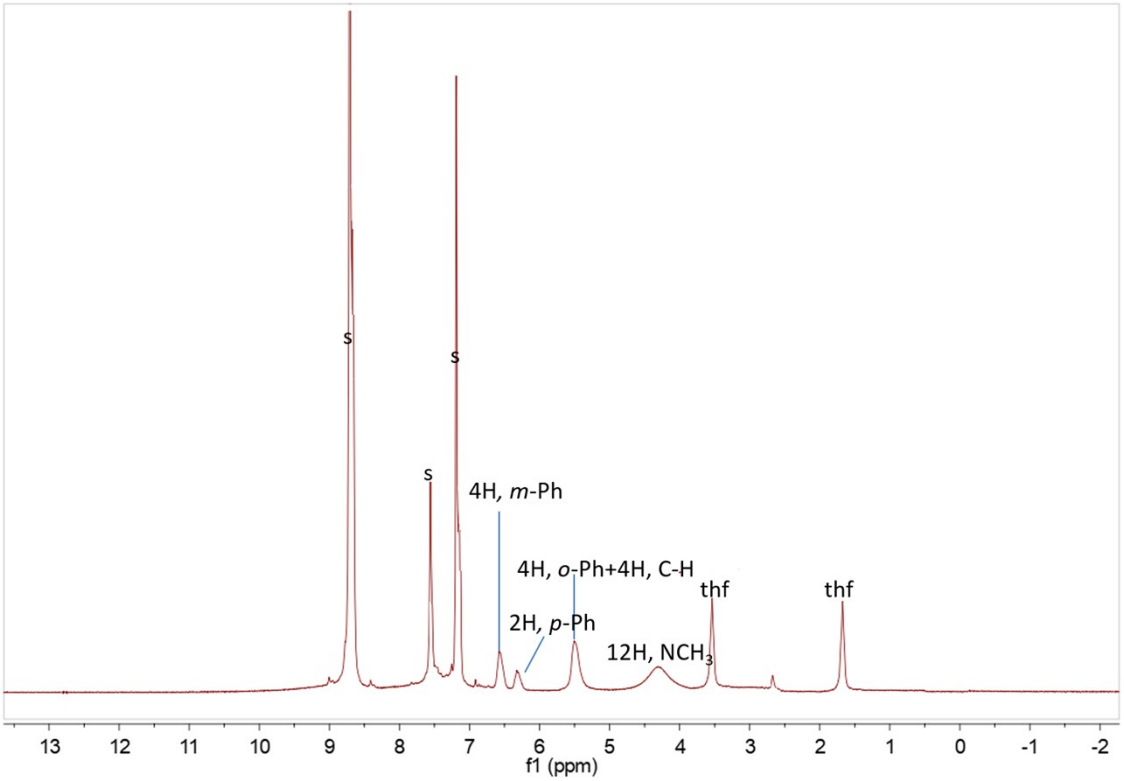

Figure S6. ^{1}H NMR of [UI{κ^{3}-H(Ph)B(tim^{Me})$_2$}$_2$(thf)$_2$] (**2**) in pyridine-d_5 at 20ºC.

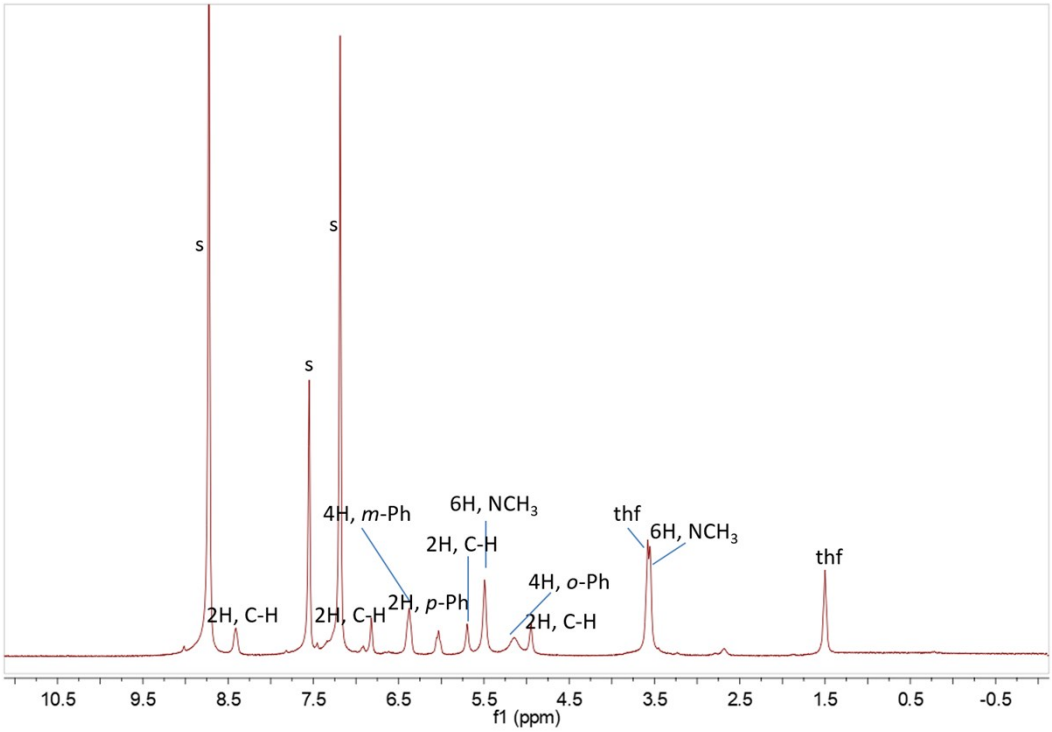

Figure S7. ^{1}H NMR of [UI{κ^{3}-H(Ph)B(tim^{Me})$_2$}$_2$(thf)$_2$] (**2**) in pyridine-d_5 at -25ºC.

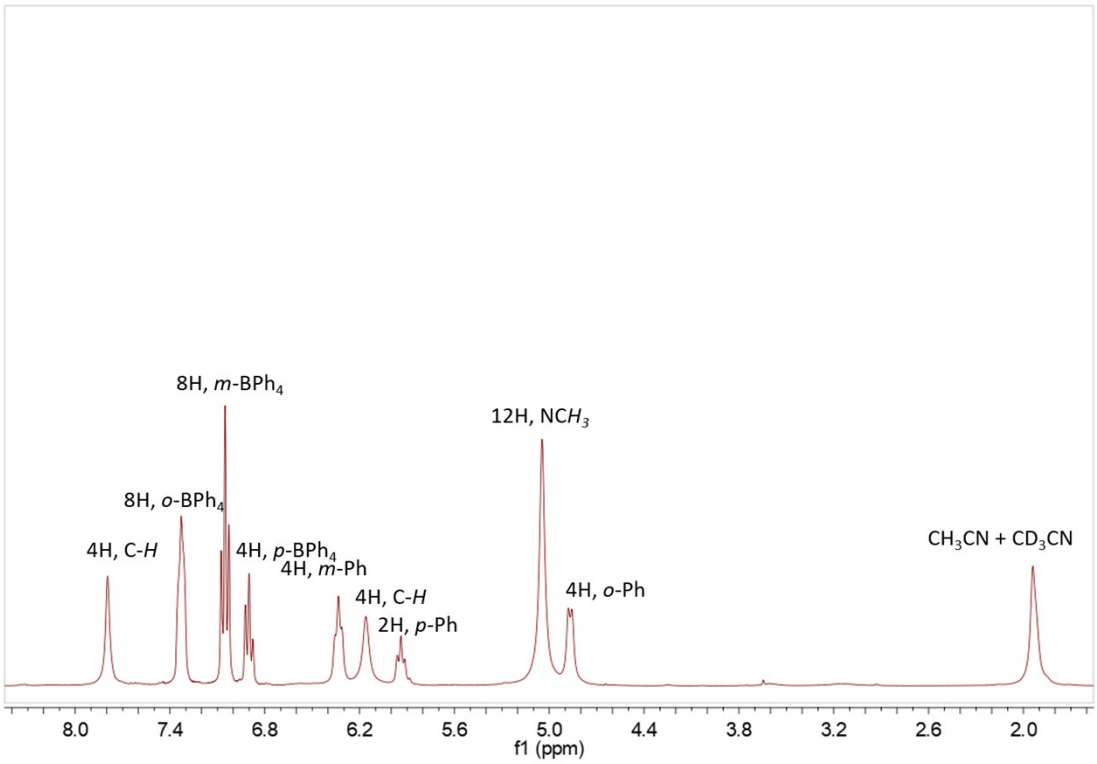

Figure S8. ^{1}H NMR of [U{κ^{3}-H(Ph)B(tim^{Me})$_2$}$_2$(CH$_3$CN)$_3$][BPh$_4$] (**3-BPh$_4$**) in acetonitrile-d_3 at 20ºC.

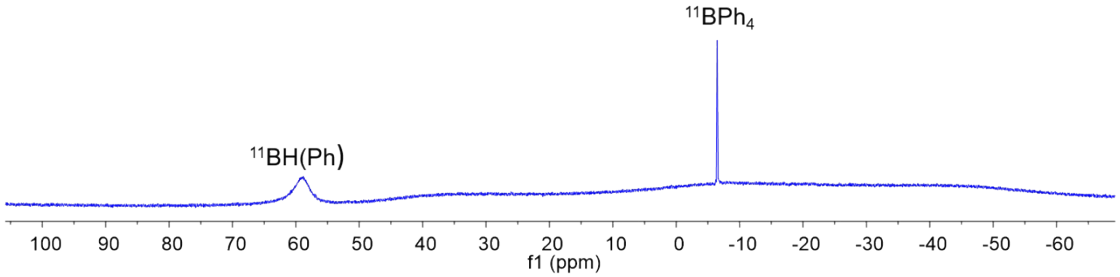

Figure S9. ^{11}B NMR of [U{κ^3-H(Ph)B(tim^{Me})$_2$}$_2$(CH$_3$CN)$_3$][BPh$_4$] (**3-BPh$_4$**) in acetonitrile-d_3 at 20ºC.

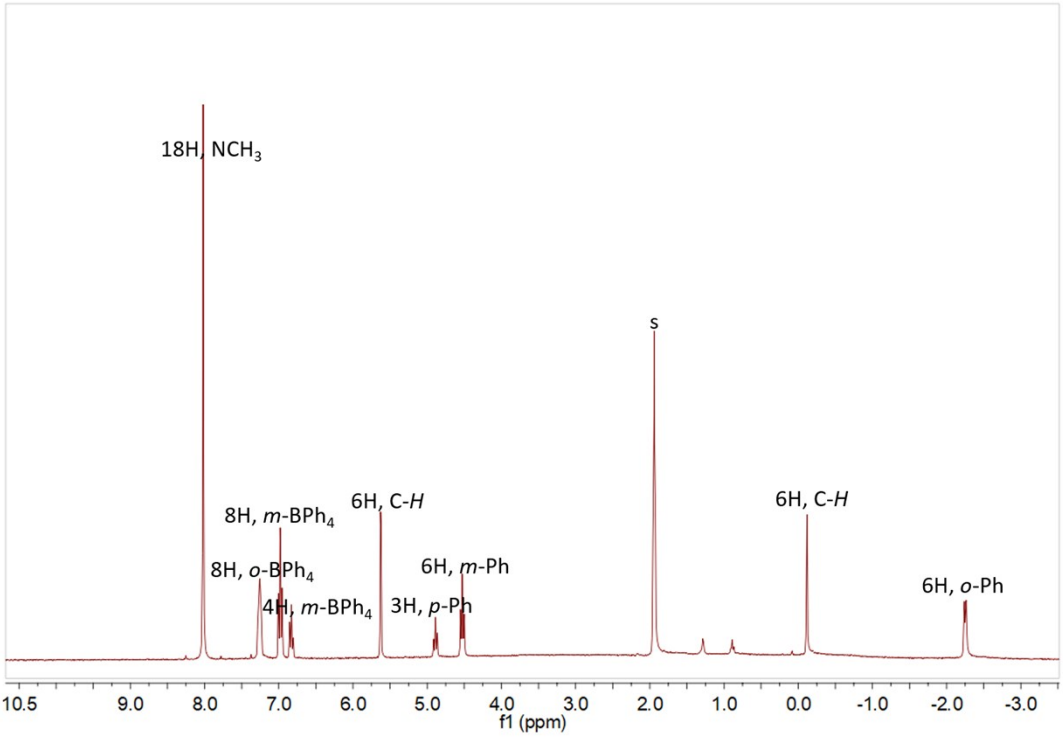

Figure S10. ^{1}H NMR of [U{κ^3-H(Ph)B(tim^{Me})$_2$}$_3$][BPh$_4$] (**6-BPh$_4$**) in acetonitrile-d_3 at 21ºC.

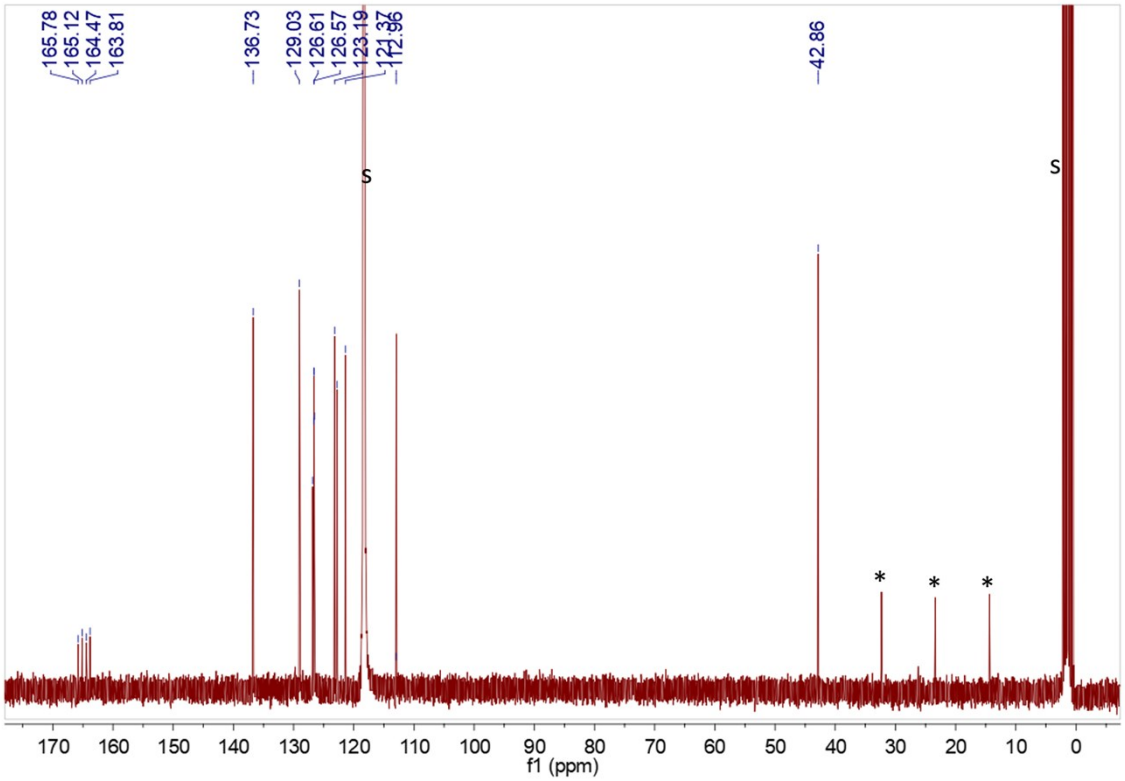

Figure S11. ^{13}C NMR of [U{κ^3-H(Ph)B(tim^{Me})$_2$}$_3$][BPh$_4$] (**6-BPh$_4$**) in acetonitrile-d_3 at 21ºC (* residual *n*-hexane resonances).

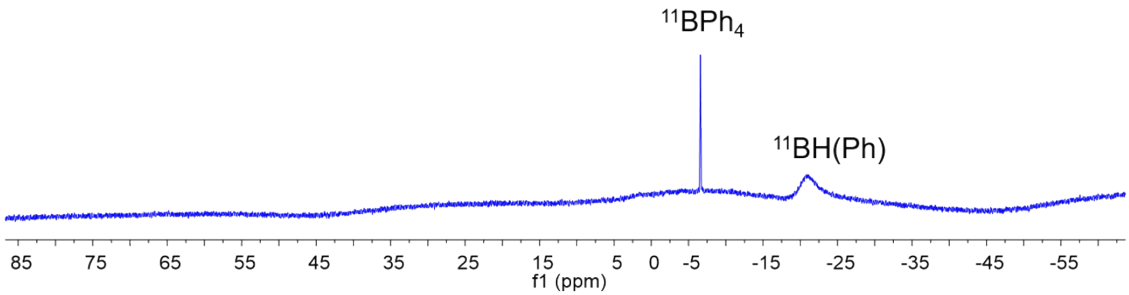

Figure S12. ^{11}B NMR of [U{κ^3-H(Ph)B(tim^{Me})$_2$}$_3$][BPh$_4$] (**6-BPh$_4$**) in acetonitrile-d_3 at 21ºC.

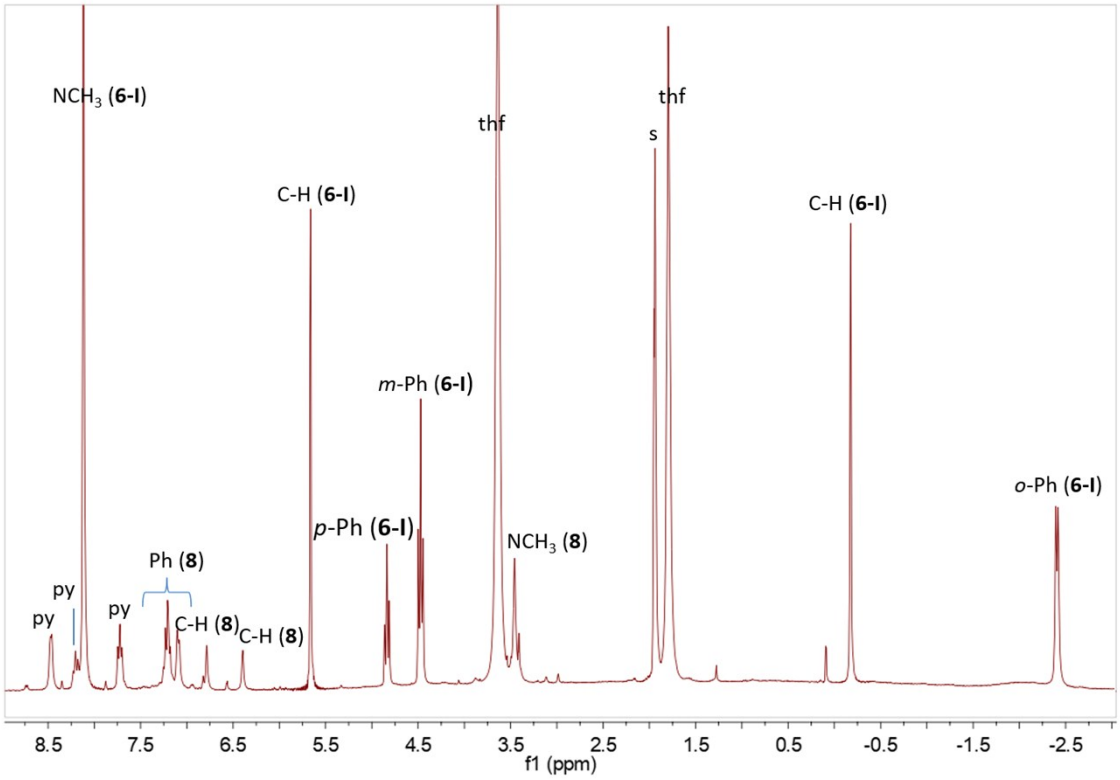

Figure S13. ^{1}H NMR of the reaction mixture of [UI{κ^{3}-H(Ph)B(tim^{Me})$_2$}$_2$(thf)$_2$] (**2**) with 1 equiv. pyNO in acetonitrile-d_3 at 21ºC.

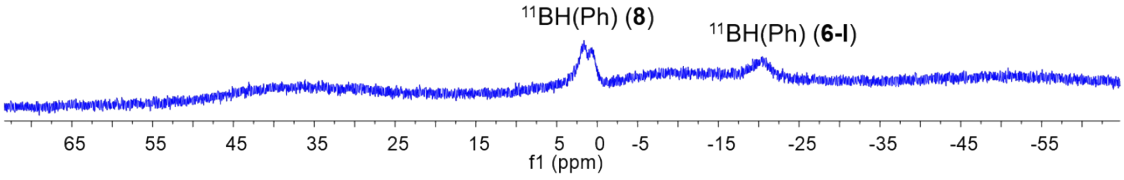

Figure S14. ^{11}B NMR of the reaction mixture of [UI{κ^{3}-H(Ph)B(tim^{Me})$_2$}$_2$(thf)$_2$] (**2**) with 1 equiv. pyNO in acetonitrile-d_3 at 21ºC.

4 X-ray crystallography data

Table S1. Selected Crystal Data and Data Collection Parameters for **2** and **3-I.**2.5(CH_3CN).

	2	**3-I**.2.5(CH_3CN)
Empirical formula	$C_{36}H_{48}B_2IN_8O_2S_4U$	$C_{78}H_{97}B_4I_2N_{27}S_8U_2$
Crystal size (mm)	0.60 x 0.40 x 0.10	0.60 x 0.60 x 0.20
Formula weight	1139.61	2442.41
Cryst. System	Monoclinic	Monoclinic
Space group	C2/c	P21/n
a [Å]	21.492(3)	12.0828(7)
b[Å]	12.195(4)	21.5636(10)
c [Å]	22.050(2)	19.5689(10)
α [º]	90	90
β [º]	105.35(5)	95.239(2)
γ [º]	90	90
V[Å^3]	5573(2)	5077.4(5)
Z	4	2
Calculated density (mg/m^{-3})	1.358	1.598
μ (mm^{-1})	3.649	4.011
T_{min}/T_{max}	0.2181/0.7117	0.197/0.501
F(000)	2392	2384.0
θ_{max} (º)	25.02	25.03
Reflections collected	3057	38203
Unique refl. (R_{int})	2872 (0.1065)	8958 (0.1657)
R_1[I>2σ(I)]	0.0870	0.0723
wR2 (all data)	0.2408	0.1793
Parameters	246	554
GOF on F^2	1.089	0.956
Largest diff. peak , hole/e Å^{-3}	2.280, -4.105	2.795, -3.689

Table S2 : Selected Crystal Data and Data Collection Parameters for compounds **6-9**

	(6-BPh_4)$_2$(C_4H_8O)(C_6H1_4)	**6-I.**2(CH_3CN)	**7**	**8**	**9.**2(CH_3CN)
Empirical formula	$C_{139}H_{151}B_8N_{24}OS_{12}U_2$	$C_{46}H_{54}B_3I\ N_{14}S_6U$	$C_{90}H_{104}B_4I_2N_{29}S_{10}U_2$	$C_{28}H_{32}B_2N_8O_2S_4U$	$C_{118}H_{120}B_6N_{20}O_3S_8U_2$
Crystal size (mm)	0.15 x 0.06 x 0.02	0.12x0.10x0.03	0.40x0.10x0.02	0.22x0.16x0.02	0.50x0.40x0.10
Formula weight	3121.09	1392.75	2685.72	900.51	2663.74
Cryst. System	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	P-1	P-1	C2/c
a [Å]	17.9457(7)	14.2831(3)	10.7351(6)	7.6236(2)	36.9304(7)
b[Å]	20.3574(7)	14.6707(3)	16.1789(9)	8.5987(3)	15.7162(4)
c [Å]	23.3731(8)	14.6867(4)	17.9924(10)	13.1949(4)	26.9494(5)
α [º]	106.936(2)	84.0770(10	100.001(2)	83.5600(10)	90
β [º]	111.251(3)	65.3760(10)	105.549(2)	78.969(2)	131.5080(10
γ [º]	97.625(2)	85.0710(10)	103.819(2)	79.5510(10)	90
V[$Å^3$]	7336.2(5)	2779.56(11)	2827.5(3)	832.21(4)	11713.4(4)
Z	2	2	1	1	4
Calculated density (mg/m^{-3})	1.413	1.664	1.577	1.797	1.510
μ (mm^{-1})	2.433	3.747	3.645	5.168	2.965
T_{min}/T_{max}	0.712/ 0.953	0.6619/0.8959	0.3234/0.9307	0.3960/0.9037	
F(000)	3154	1368	1317	438	5336
θ_{max} (º)	25.68	25.68	25.68	25.02	25.68
Reflections collected	65595	37704	36066	5635	59233
Unique refl. (R_{int})	27673(0.1129)	10399 (0.0491)	10519 (0.0427)	2835 (0.0317)	11088 (0.0529)
R_1[I>2σ(I)]	0.0690	0.0319	0.0441	0.0230	0.0351
wR2 (all data)	0.1559	0.0624	0.1135	0.0566	0.0914
Parameters	1694	648	590	207	713
GOF on F^2	0.909	1.038	1.064	1.081	1.084
Largest diff. peak , hole/e $Å^{-3}$	1.780, -1.670	0.759, -0.664	2.429, -1.220	0.583, -0.568	3.025, -1.121

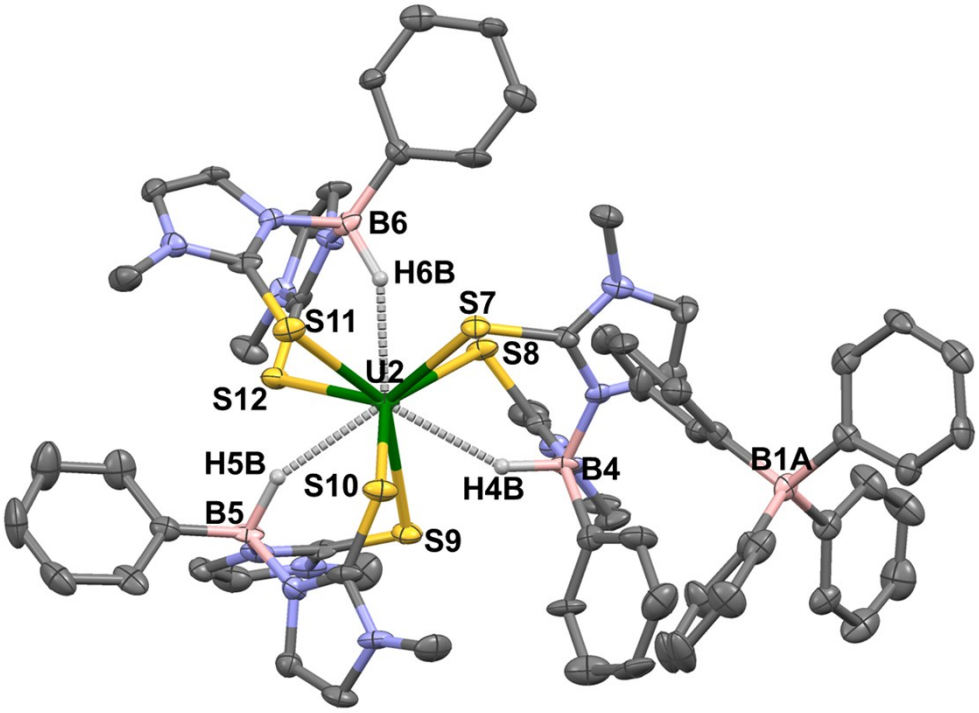

Figure S15. Molecular structure of [U{κ^3-H(Ph)B(tim^{Me})$_2$}$_3$][BPh$_4$] (**6-BPh4**) in **6-BPh$_4$**.(C$_4$H$_8$O)(C$_6$H$_{14}$) with thermal ellipsoids set a 40%. Hidrogen atoms, except B-H, and cocrystallized solvent molecules are omitted for clarity.

Table S3. Selected bond distances (Å) and angles (deg) of [U{κ^3-H(Ph)B(tim^{Me})$_2$}$_3$][BPh$_4$] (**6-BPh$_4$**)

	Cation 1 (U1)	**Cation 2 (U2)**
U-S$_{av.}$	2.806(11)	2.791(6)
	2.821(10)	2.798(25)
	2.798(4)	2.788(8)
S-U-S bite	85.18(7), 83.30(7), 85.61(8)	84.68(8), 86.91(8), 84.21(8)
U···H	2.46(9), 2.20(7), 2.43(7)	2.47(8), 2.41(10), 2.29(7)
U···B	3.40(1), 3.39(1), 3.42(1)	3.44(1), 3.45(1), 3.44(1)