Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for the Manuscript

CS_2 activation at uranium(III) siloxide complexes: the effect of a Lewis acidic site

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A) **NMR Spectra**

Figure S1: ^{1}H NMR spectrum (200 MHz, toluene-d_8, 298K) of the crude reaction mixture of CS_2 and **1** after 30 minutes.

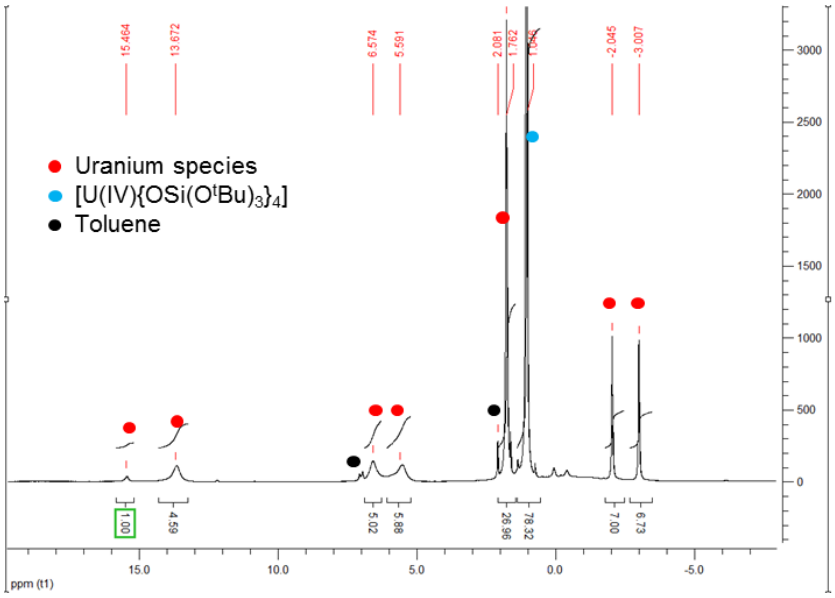


Figure S2: ^{1}H NMR spectrum (200 MHz, toluene-d_8, 298K) of the crude reaction mixture of CS_2 and **1** over the course of two days.

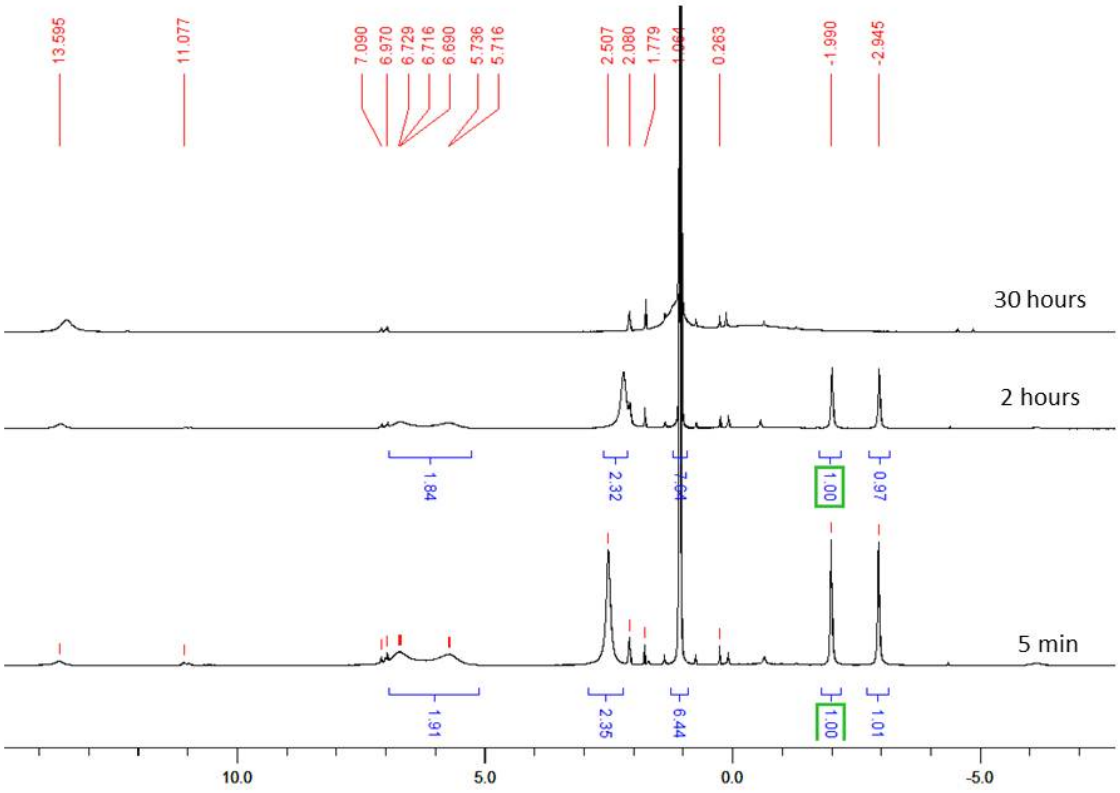


Figure S3: $^{13}C\{^{1}H\}$ NMR spectrum (400 MHz, pyridine-d_5, 298K) of the crystals of $[K(18\text{-c-}6)]C_2S_4$.Py **4 py** isolated from pyridine/hexane. (The same spectrum was measured for the solid obtained after washing with hexane of the crude obtained by evaporation of the toluene solution of **1** reacted with $^{13}CS_2$ for 30 minutes.)

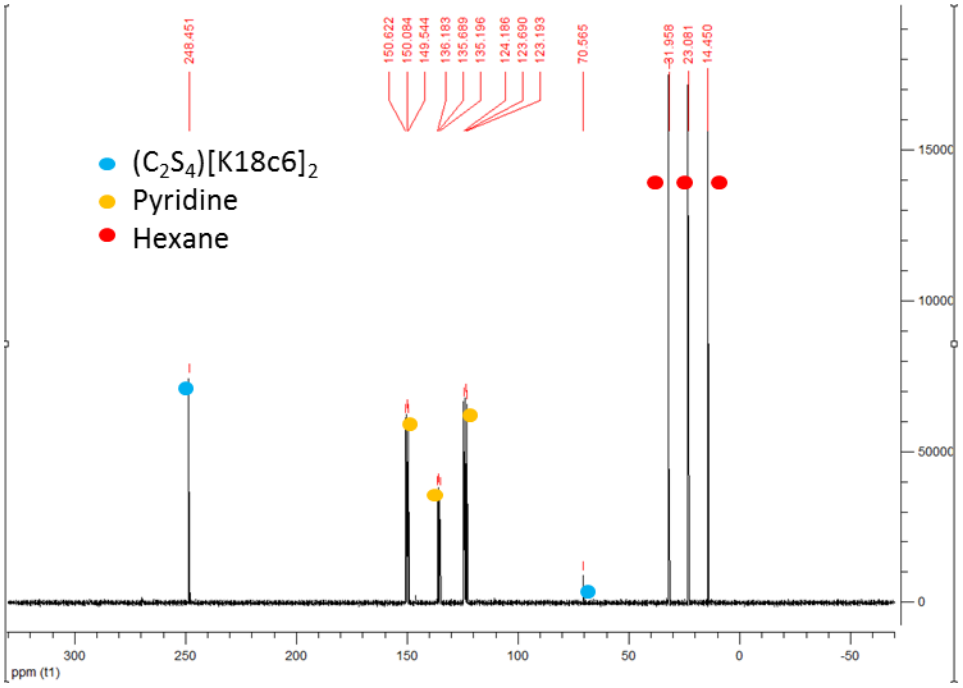


Figure S4: Quantitative ^{13}C NMR spectrum (400 MHz, DMSO-d_6, 298 K) of the reaction mixture between 1 eq. $^{13}CS_2$ and $[K(18c6)][U(OSi(O^tBu)_3)_4]$, **1** after 48 hours.

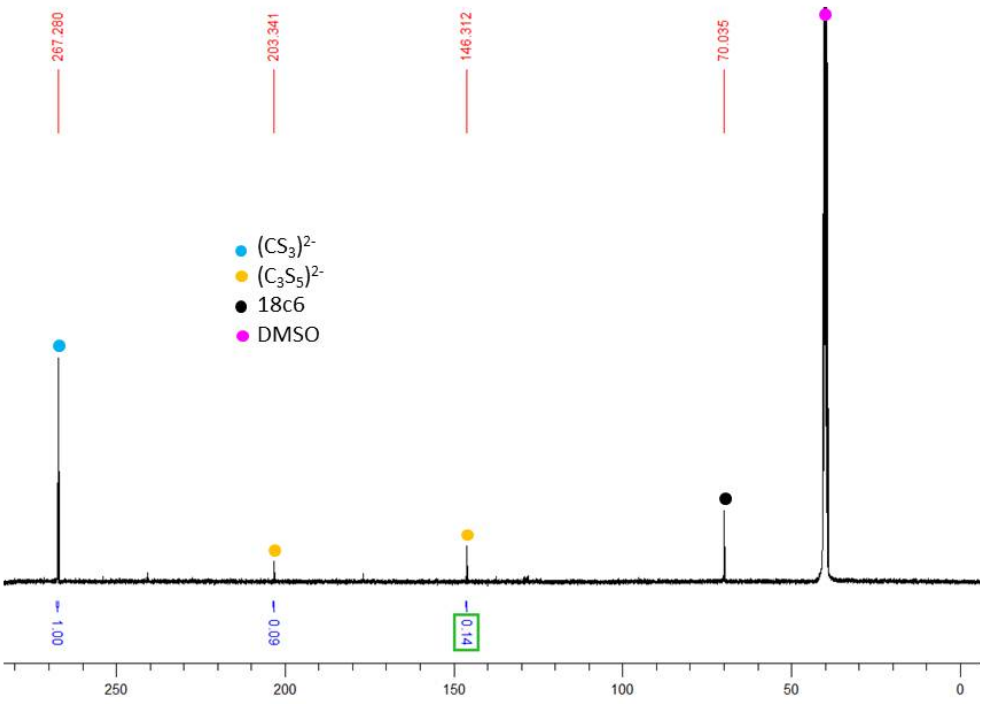


Figure S5: ^{1}H NMR spectrum (200 MHz, toluene-d_8, 298 K) of the crude reaction mixture between 1 equiv. CS_2 and **2** over time.

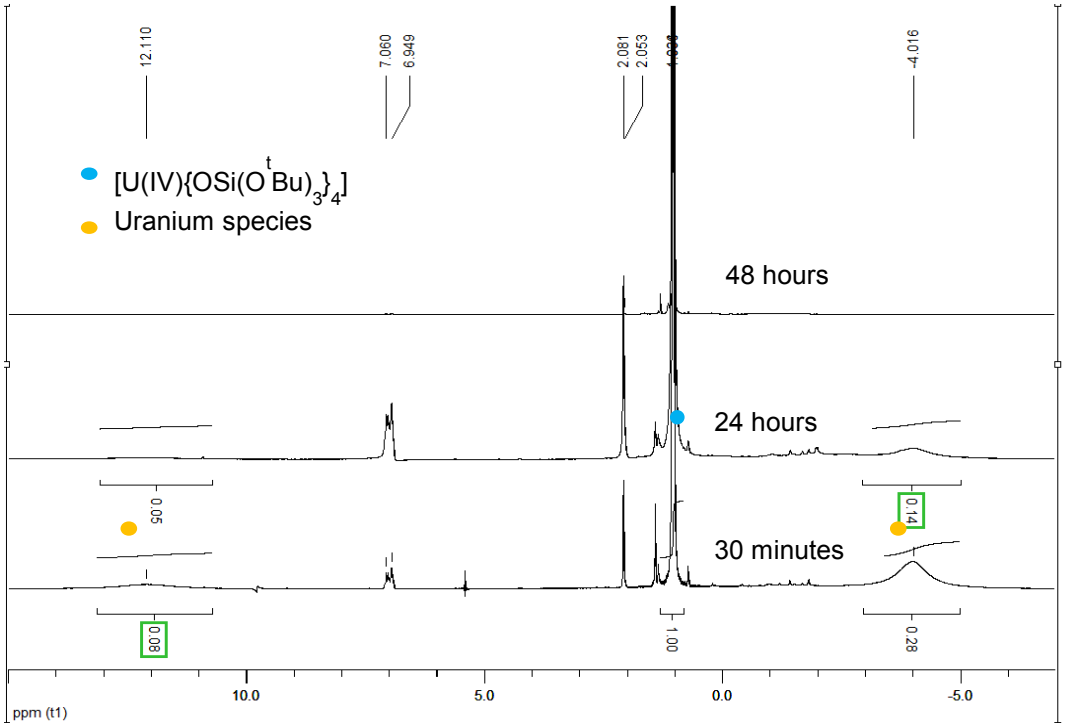


Figure S6: ^{13}C{^{1}H} NMR spectrum (400 MHz, DMSO-d_6, 298K) of crystals of $(C_2S_4)[K(DMSO)_{1.5}]$.

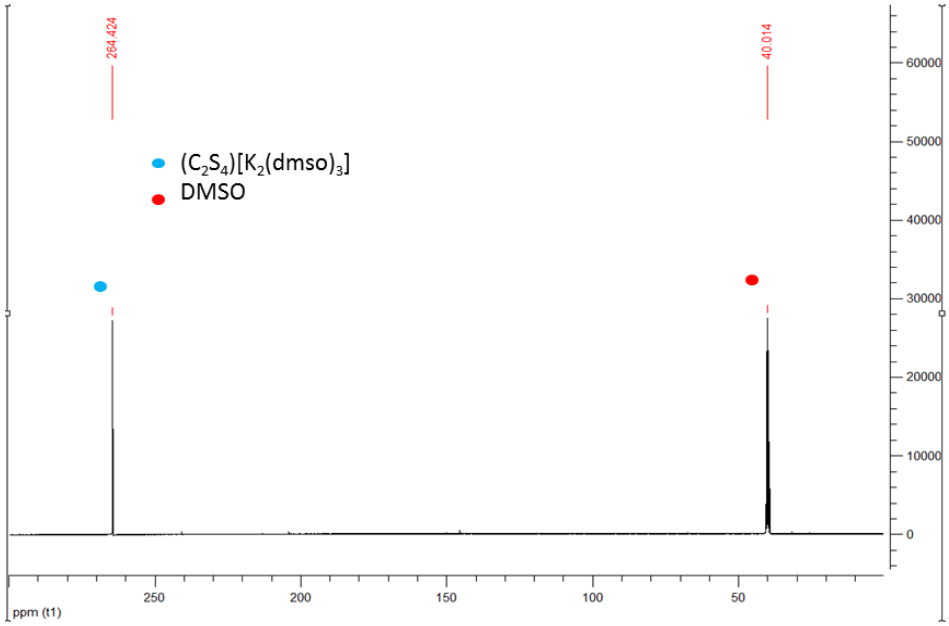


Figure S7: ^{13}C NMR spectrum (400 MHz, DMSO-d_6, 298 K) of the crude reaction mixture between 4 equiv. of $^{13}CS_2$ and **2** after 48 hours.

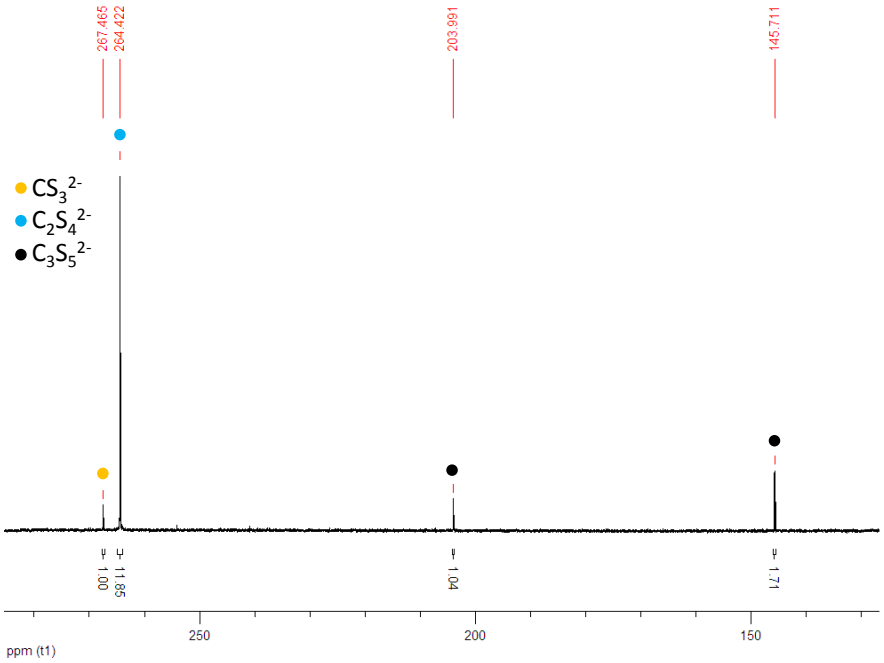
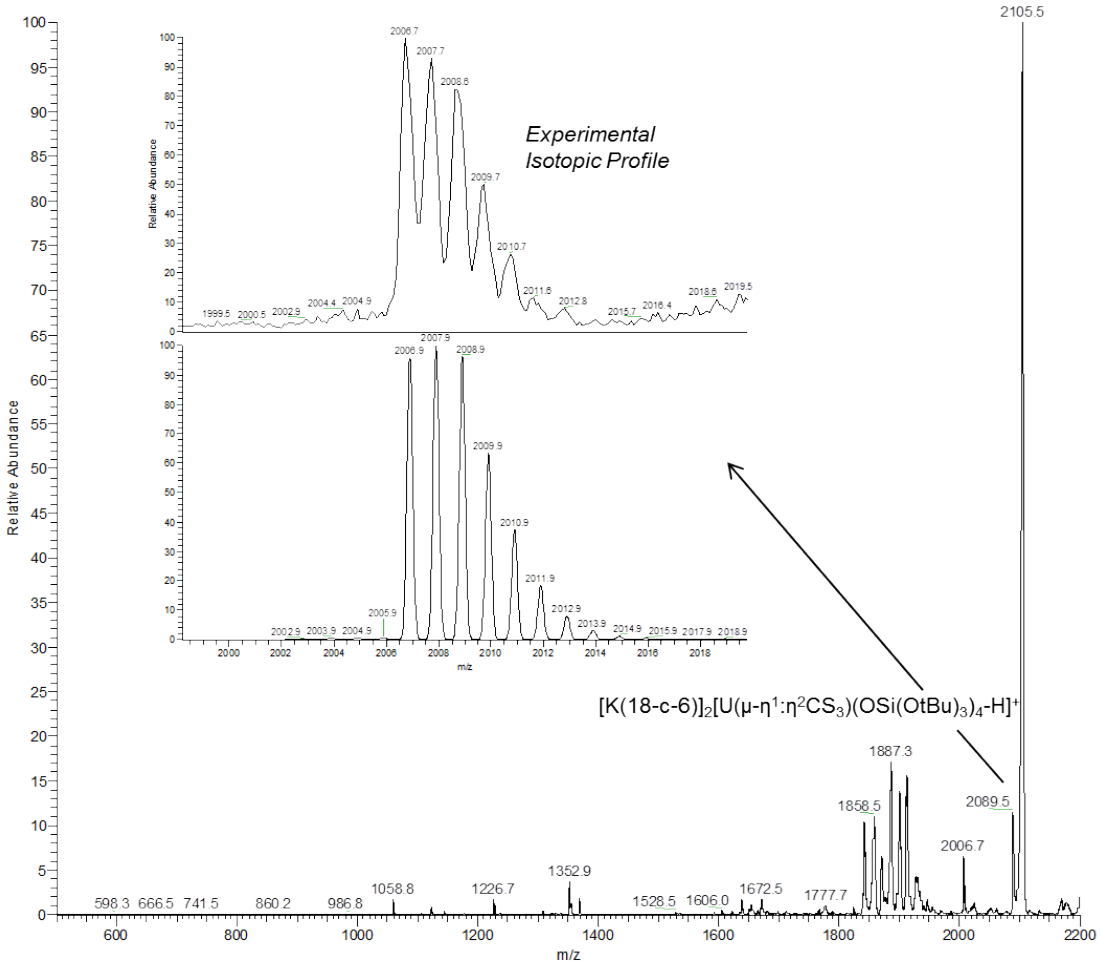


Table S1: Ratio of the reaction products from the reactions of **1** and **2** with CS_2.

Compound	**Eq. of CS_2**	**Ratio of CS_3**	**Ratio of C_2S_4**	**Ratio of C_3S_5**
[U(OSi(O^{t}Bu)$_3$)$_4$][K18c6] **1**	1	10	0	1
[U(OSi(O^{t}Bu)$_3$)$_4$][K18c6] **1**	4	5	0	1
[U(OSi(O^{t}Bu)$_3$)$_4$K] **2**	1	1	1.2	1
[U(OSi(O^{t}Bu)$_3$)$_4$K] **2**	2	1	3.7	1
[U(OSi(O^{t}Bu)$_3$)$_4$K] **2**	4	1	5.9	1

B) **Mass Spectrometry**

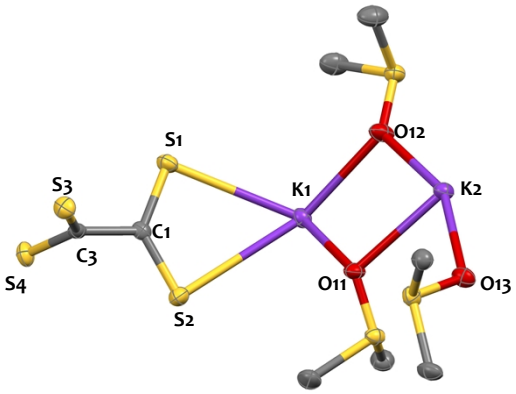
Figure S8: ESI-MS spectrum of the reaction mixture between **1** and CS_2 in THF (positive ionization mode). Insert: zoom on the molecular peak compared with the theoretical isotopic profile calculated for **$[K(18\text{-c-}6)]_2[U(\mu\text{-}\eta^1\text{:}\eta^2CS_3)(OSi(O^tBu)_3)_4\text{-}H]^+$ (3-H)$^+$.**



C) **Crystallographic Data**

Figure S9: Ellipsoid plot for of $[K_2C_2S_4(DMSO)_3]_n$, **5**; probability 50%. Hydrogen atoms are omitted for clarity. (a) Asymetric unit ; (b) View of the 2-D coordination polymer.

a



b

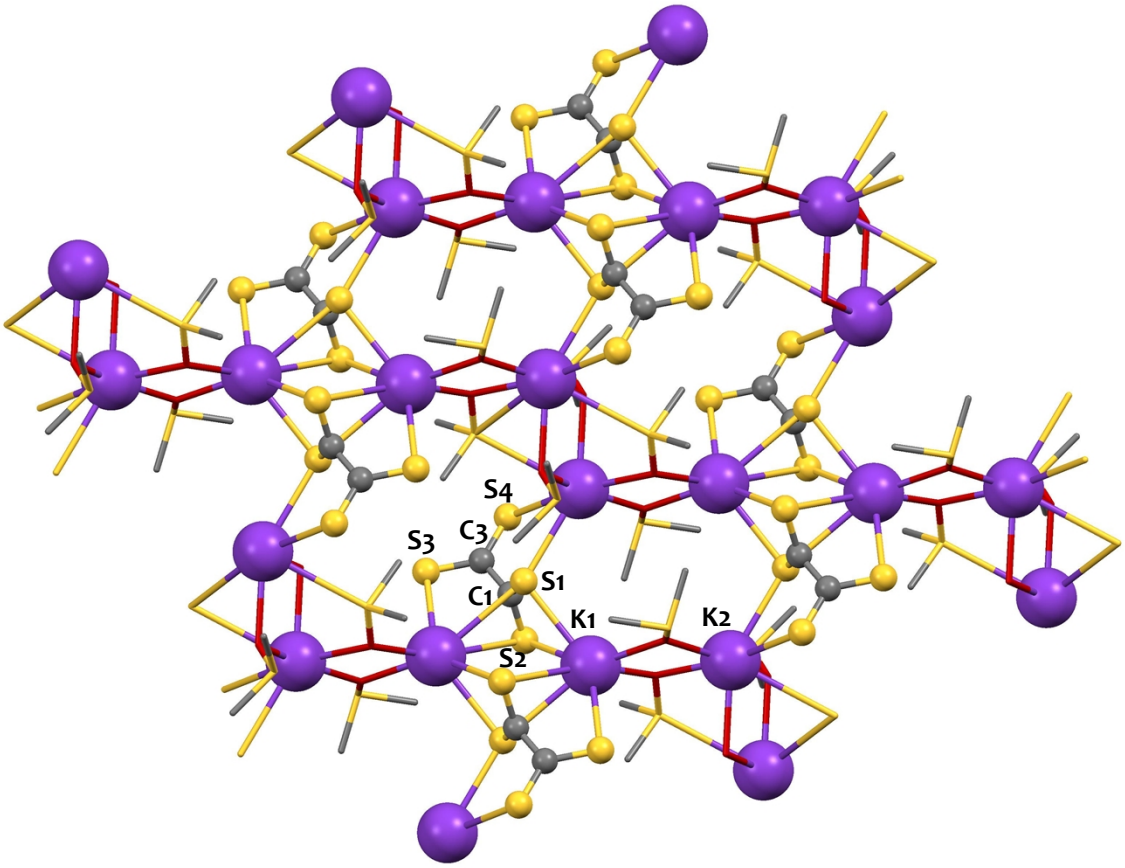


Figure S10: Solid-state structure of $[U(OSi(O^tBu)_3)_4K_2(C_3S_5)]_n$, **6** showing the 1D-coordination polymeric arrangement. Hydrogen atoms are omitted for clarity.

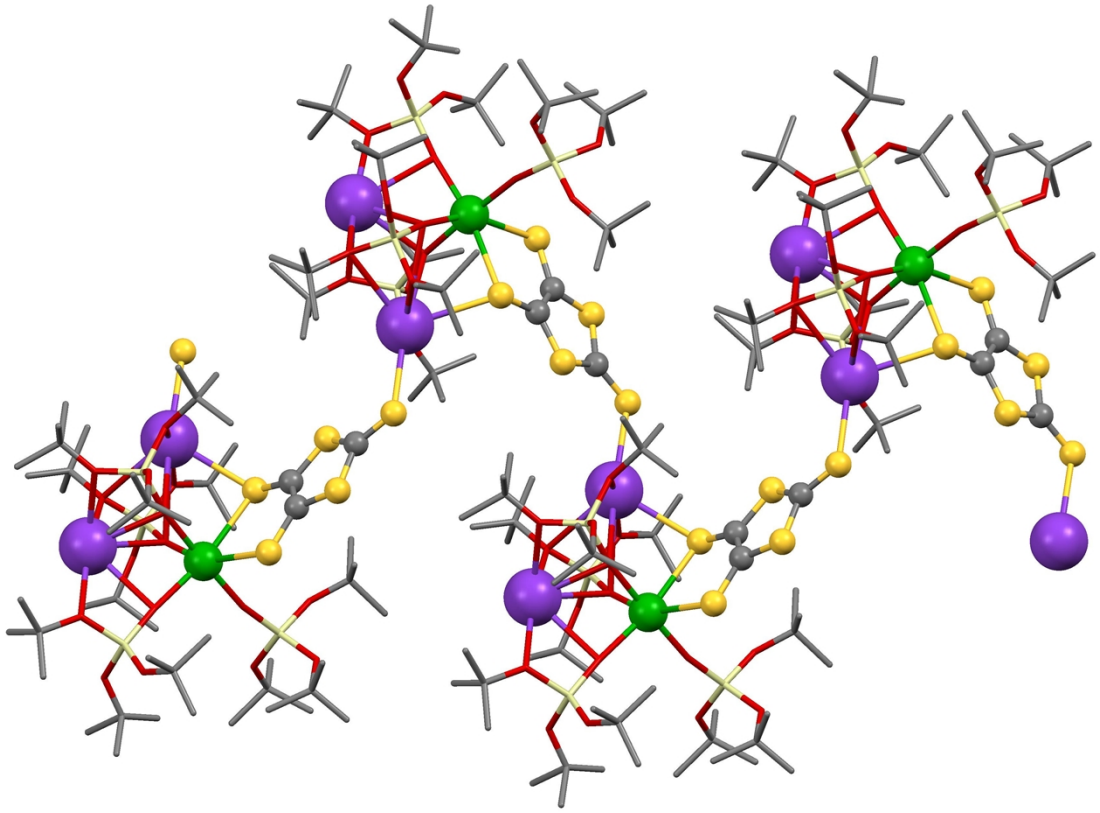


Table S2. Crystallographic Data for Compounds **3-5.**

	4.Py	**3. 4 toluene**	**5**
Formula	$C_{31}H_{53}K_2NO_{12}S_4$	$C_{101}H_{188}K_2O_{28}S_3Si_4U$	$C_8H_{18}K_2O_3S_7$
Crystal size (mm)	1.07 x 0.13 x 0.02	0.544 x 0.440 x 0.349	0.522 x 0.265 x 0.020
cryst syst	Monoclinic	Triclinic	Triclinic
space group	C 2/c	P -1	P-1
volume ($Å^3$)	4109.4(11)	6545.9(5)	1008.95(6)
a (Å)	23.321(3)	14.8483(6)	9.9182(3)
b (Å)	10.1497(5)	17.9359(8)	10.2993(4)
c (Å)	21.907(3)	25.5598(12)	10.3745(4)
α (deg)	90	81.725(4)	90.141(3)
β (deg)	127.579(19)	85.150(3)	107.571(3)
γ (deg)	90	76.692(4)	92.782(3)
Z	4	2	2
formula weight (g/mol)	838.18	2375.27	464.84
density (g cm^{-3})	1.355	1.205	1.530
absorption coefficient (mm^{-1})	0.489	1.449	1.194
F(000)	1776	2504	480
temp (K)	150.0(2)	150.0(2)	150.0(2)
total no. reflections	20966	59744	12179
unique reflections [R(int)]	5082 [R(int) = 0.0672]	26722 [R(int) = 0.0880]	6084 [R(int) = 0.0408]
Final R indices [I > 2σ(I)]	R1 = 0.0611, wR2 = 0.1339	R1 = 0.0919, wR2 = 0.2028	R1 = 0.0472, wR2 = 0.0708
Largest diff. peak and hole e.Å	0.967 and -0.471	3.509 and -1.881	0.459 and -0.400
GOF	1.034	1.070	1.023