Supporting Information

Carbon Dioxide Reduction by Multimetallic Uranium(IV) Complexes Supported by Redox-Active Schiff Base Ligands

Nadir Jori,[a] Marta Falcone,[a] Rosario Scopelliti[a] and Marinella Mazzanti*[a]

[a] Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland.

*Corresponding authors: E-mail: marinella.mazzanti@epfl.ch, ISIC/EPFL.

Table of Contents

1. NMR spectra

Figure S1: ^{1}H NMR spectrum (400 MHz, pyr-d_5, 298 K) of $K_3{}^{t}$BuTrensal

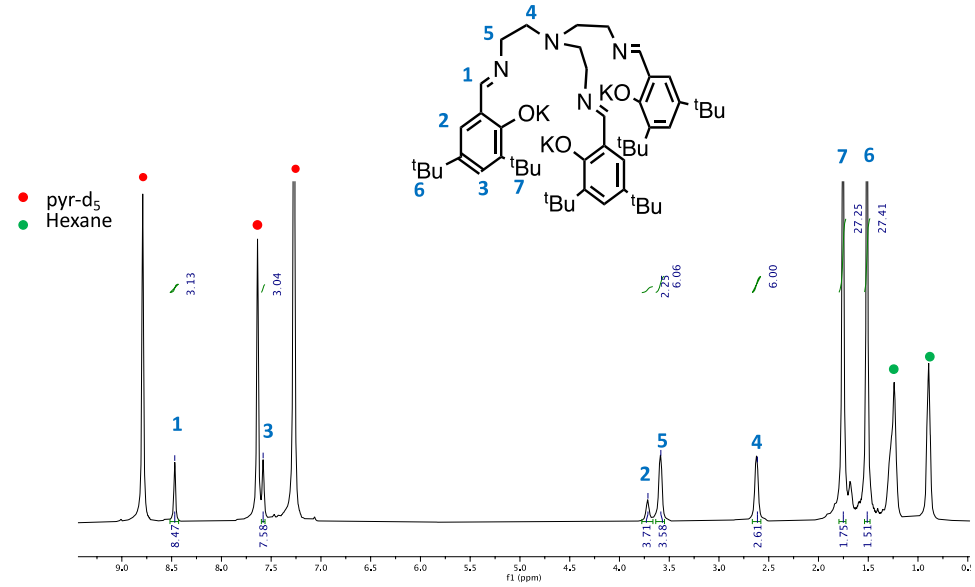


Figure S2: ^{13}C NMR spectrum (100 MHz, pyr-d_5, 298 K) of $K_3{}^{t}$BuTrensal

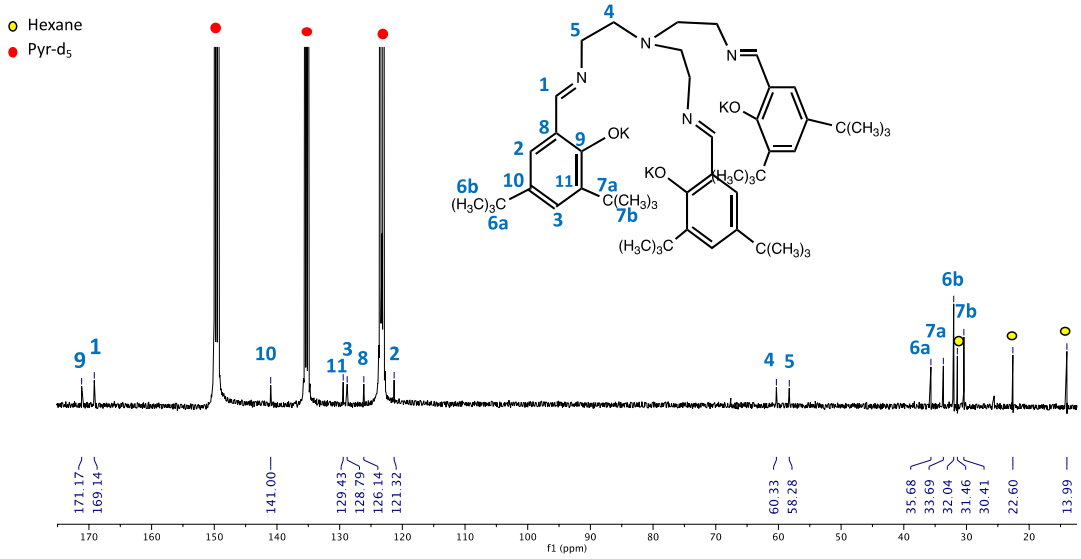


Figure S3: ^{1}H NMR spectrum (400 MHz, pyr-d_5, 298 K) of **1**

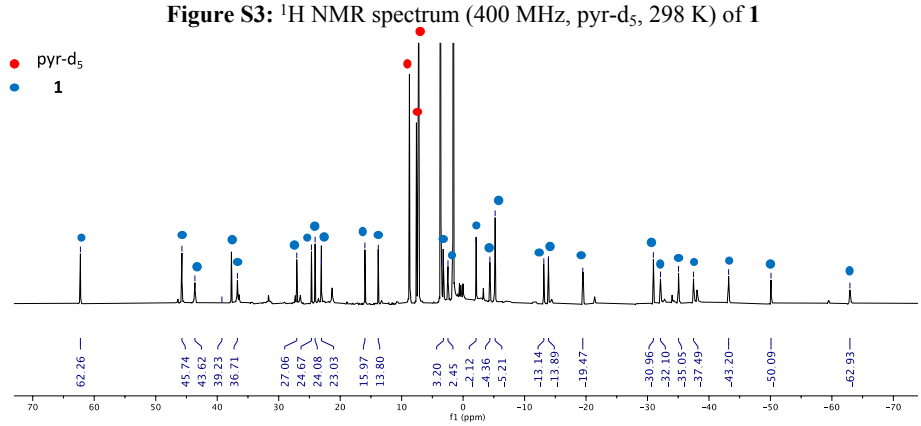


Figure S4: ^{1}H -NMR spectrum (400 MHz, THF-d_8, 298 K) of isolated compound of synthesis of [U_2-^{t}Bu-bis-trensal], complex **1a**

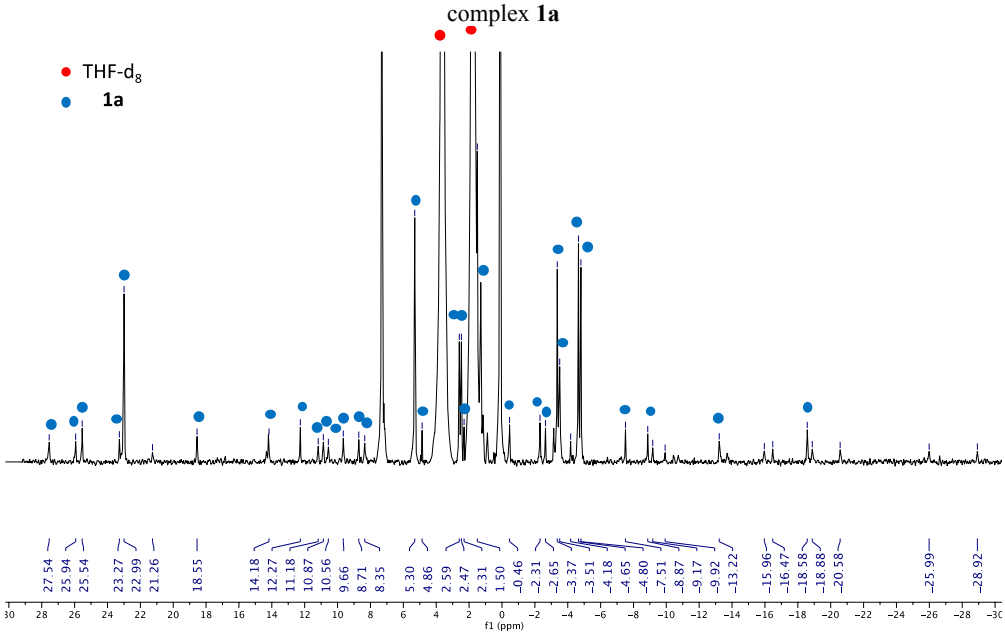


Figure S5: ^{1}H NMR spectrum (400MHz, THF-d_8, 298 K) of [U(trensal)][OTf], complex **2**

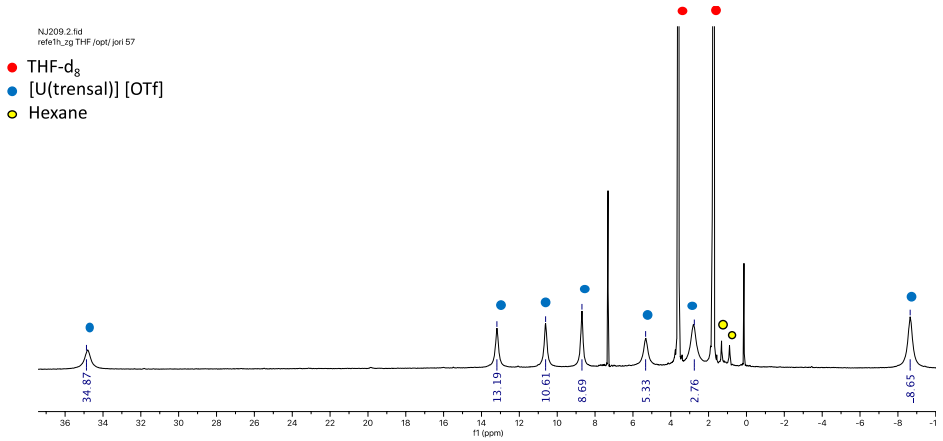


Figure S6: ^{1}H NMR (400 MHz, THF-d_8, 298K) spectrum of reaction mixture of **1** with 100 eq $^{13}CO_2$ after 6 days

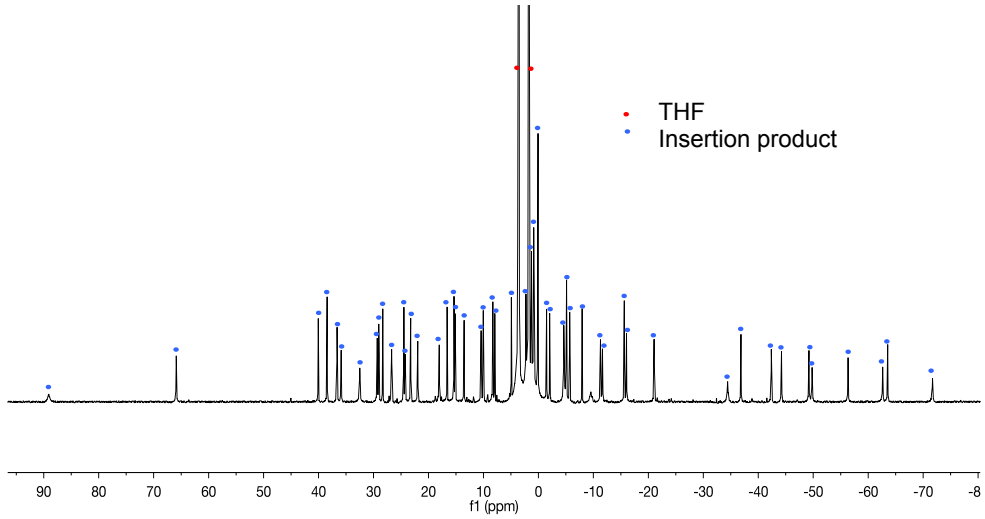


Figure S7: $^{13}C\{^{1}H\}$ NMR (151 MHz, THF-d_8, 298K) spectrum of reaction mixture of **1** with 100 eq $^{13}CO_2$ after 6 days.

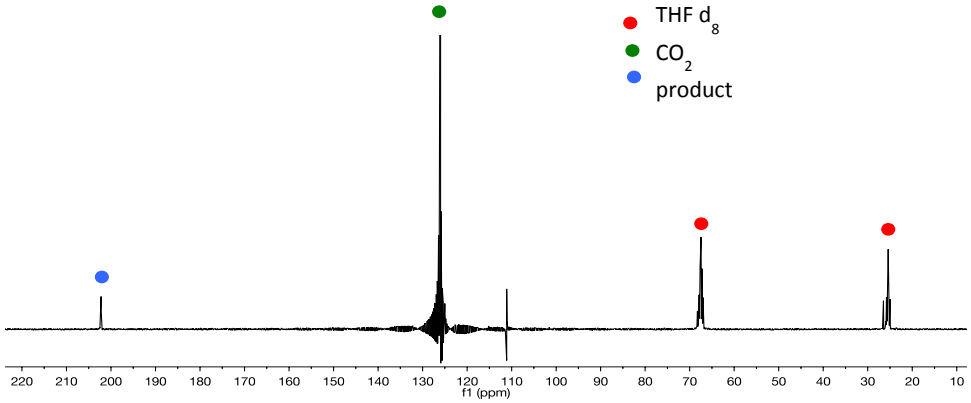


Figure S8: $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, DMSO-d_6, 298 K) powder from reaction **1** + 100 eq $^{13}CO_2$ after filtering and dissolving the powder in DMSO-d_6.

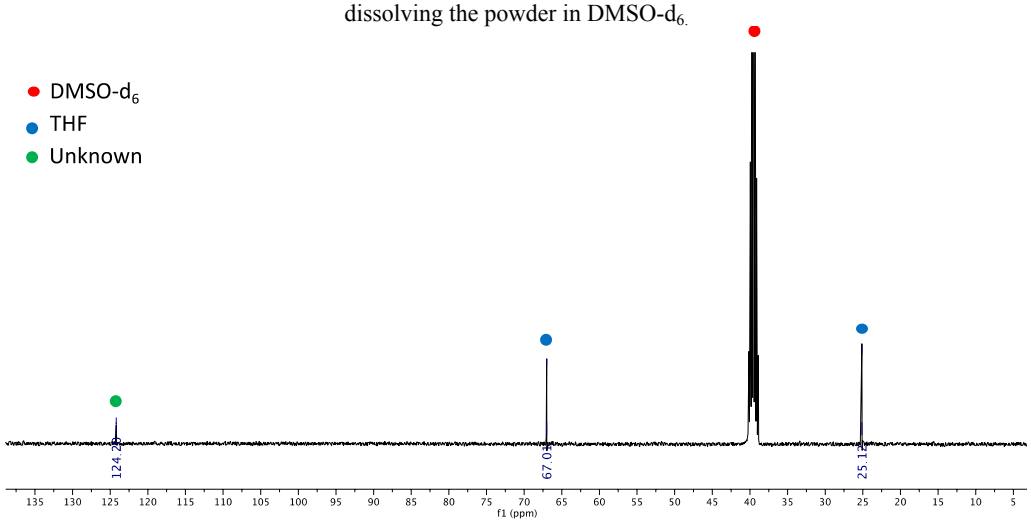


Figure S9: ^{1}H NMR spectrum (400MHz, THF-d_8, 298 K) evolution of **1** with 2 eq $^{13}CO_2$

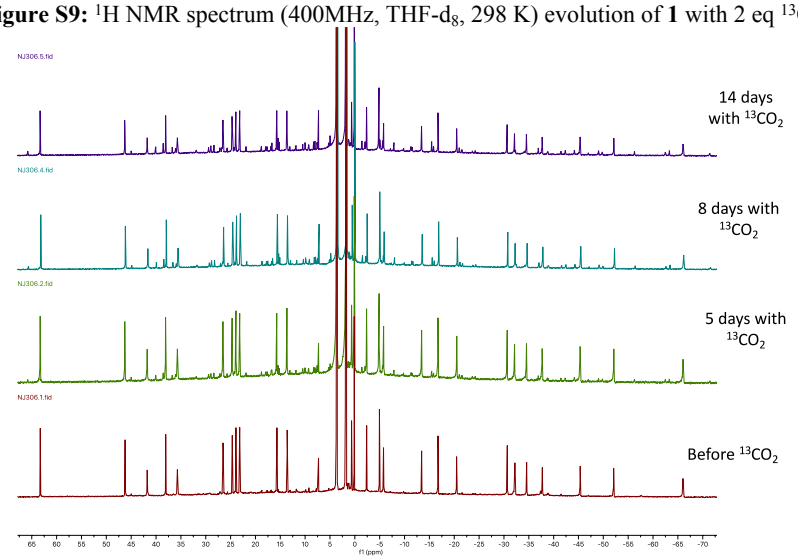


Figure S10: $^{13}C\{^{1}H\}$ NMR (151 MHz, D_2O, 298K) of the supernatant of reaction mixture of **1** with 2 eq of $^{13}CO_2$ after 20 days, after removing the solvent and dissolving in basic D_2O (pD= 12). CD_3CN was used as internal reference for the chemical shifts.

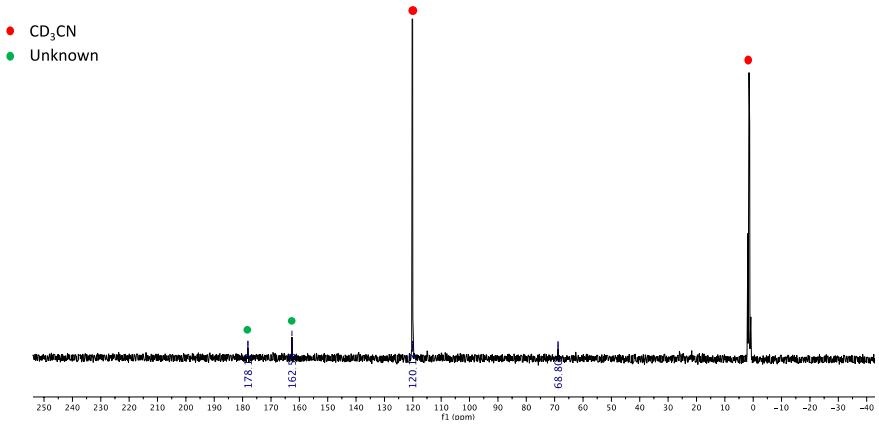


Figure S11: $^{13}C\{^{1}H\}$ NMR (151 MHz, D_2O, 298K) of the solid of reaction mixture of **1** with 2 eq of $^{13}CO_2$ after 20 days, dissolving in basic D_2O (pD= 12). CD_3CN was used as internal reference for the chemical shifts.

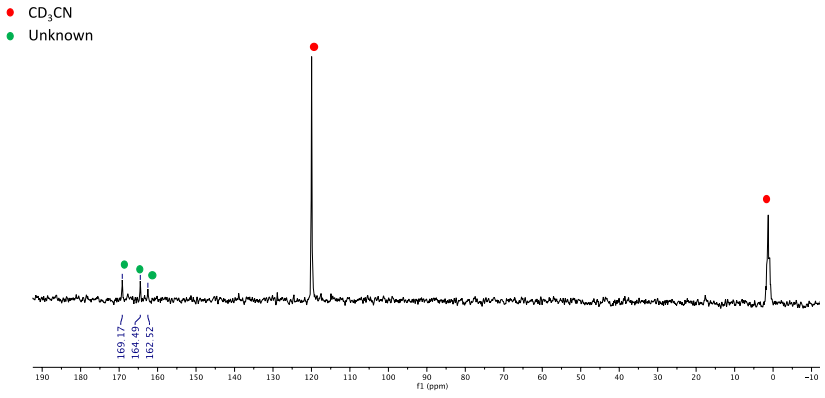


Figure S12: ^{1}H NMR spectrum (400MHz, THF-d_8, 298 K) evolution of **1** + 10 eq $^{13}CO_2$.

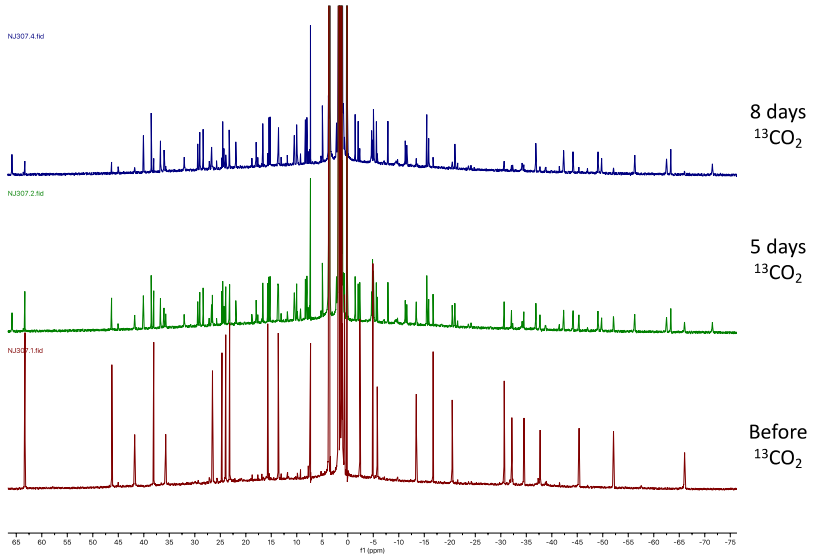


Figure S13: ^{1}H NMR spectrum (400 MHz, pyr-d_5, 298 K) of supernatant from reaction **1** + 10 eq $^{13}CO_2$ after centrifuging and removing the solvent in vacuo.

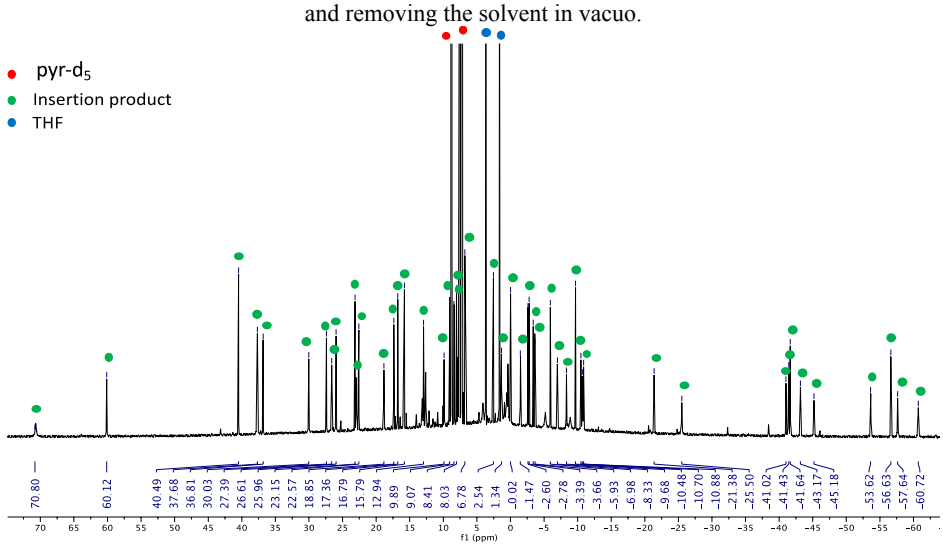


Figure S14: $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, pyr-d_5, 298 K) of supernatant from reaction **1** + 10 eq $^{13}CO_2$ after centrifuging and removing the solvent in vacuo.

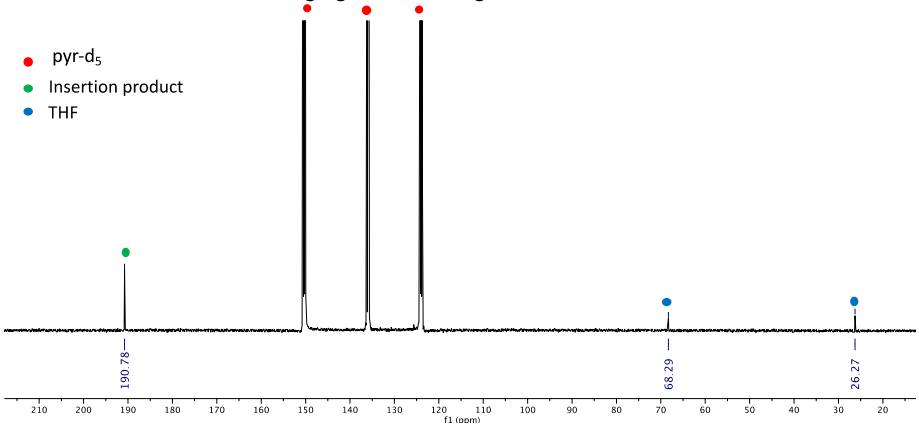


Figure S15: ^{1}H NMR spectrum (400 MHz, THF-d_8, 298 K) evolution of reaction mixture **3** + 4 eq AgOTf.

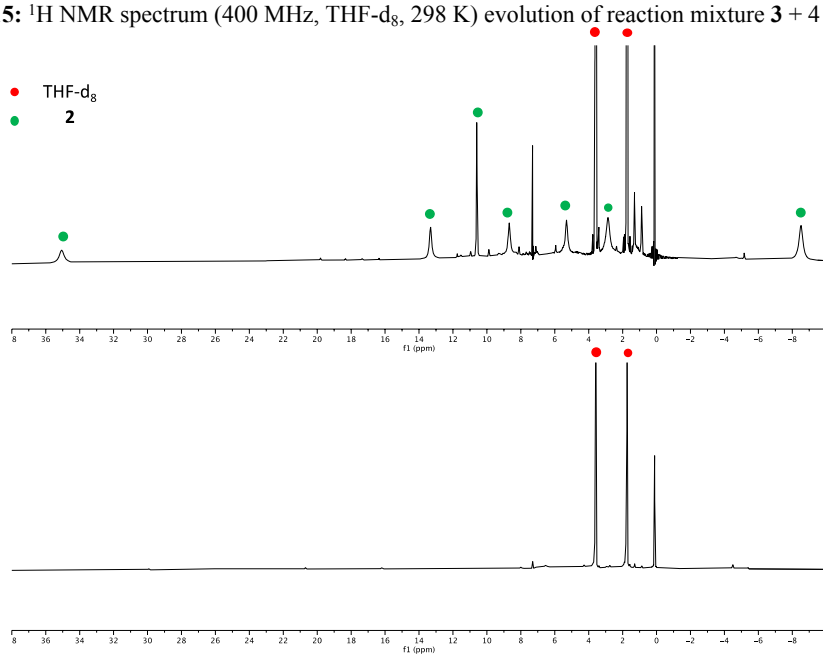


Figure S16: ^{1}H NMR spectrum (400 MHz, THF-d_8, 298 K) of reaction mixture **3** + 2 eq AgOTf after filtering.

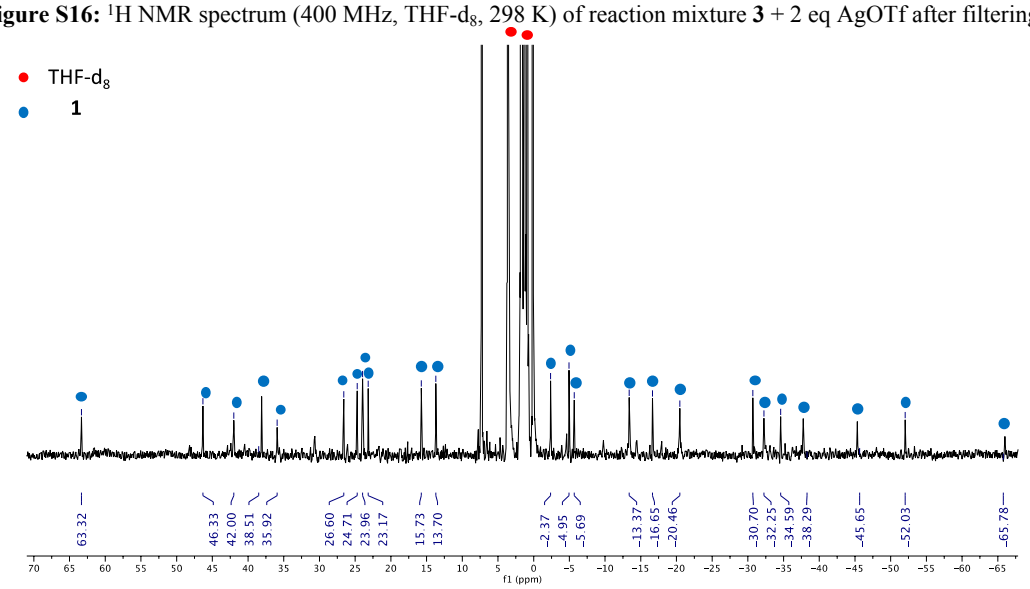


Figure S17: ^{1}H NMR spectrum (400 MHz, THF-d_8, 298 K) comparison of reaction mixture **3** + 4 eq $^{13}CS_2$. (After two days and before) .

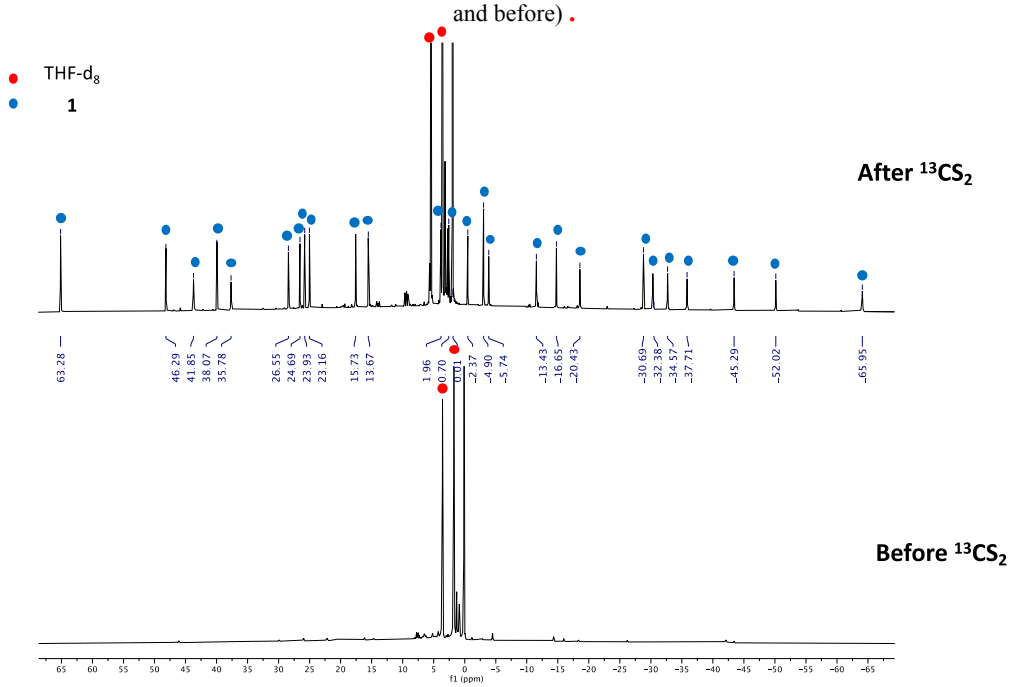


Figure S18: $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, THF-d_8, 298 K) of reaction mixture **3** + 4 eq $^{13}CS_2$ after two days.

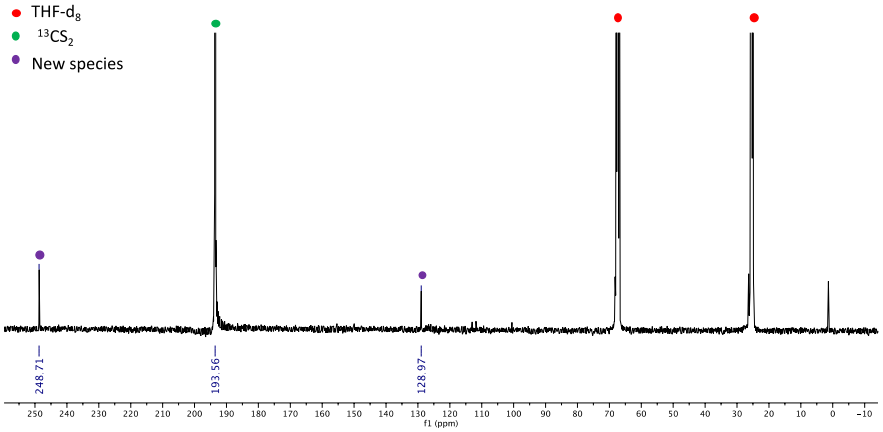


Figure S19: ^{1}H NMR spectrum (DMSO-d_6, 400 MHz, 298K). of the reaction mixture after 2 days addition of 4 eq $^{13}CS_2$ to a THF solution of **3** at room temperature, removal of the solvent and dissolution in DMSO-d_6.

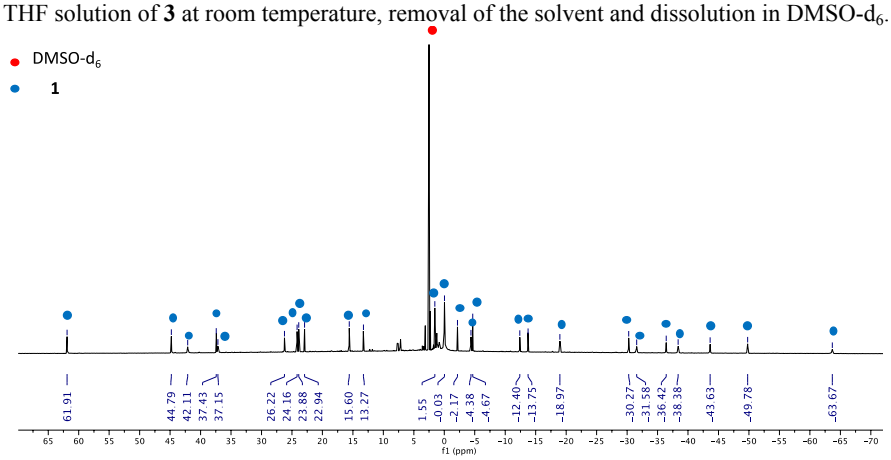


Figure S20: $^{13}C\{^{1}H\}$ NMR spectrum (DMSO-d_6, 100 MHz, 298K) of the reaction mixture after 2 days addition of 4 eq $^{13}CS_2$ to a THF solution of **3** at room temperature, removal of the solvent and dissolution in DMSO-d_6.

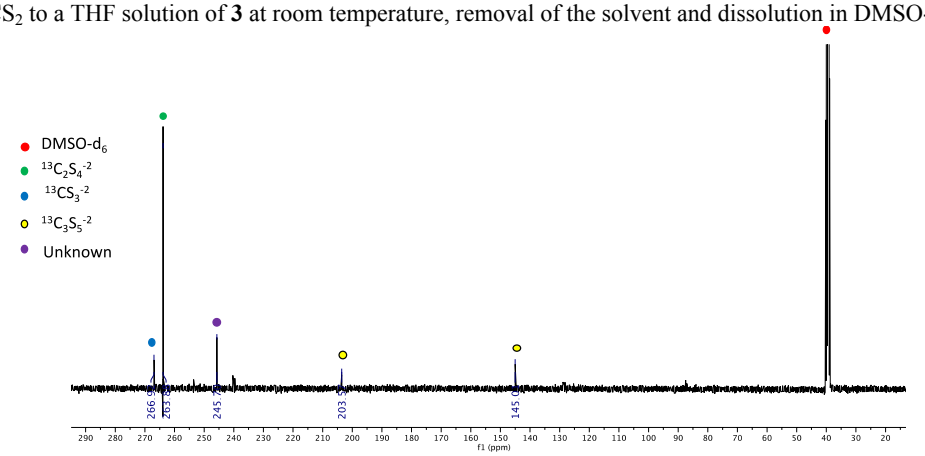


Figure S21: $^{13}C\{^{1}H\}$ NMR (THF-d_8, 151 MHz, 298K) spectrum of the reaction mixture after 6 days addition of 1 equivalent $^{13}CO_2$ to a THF solution of **3** at room temperature.

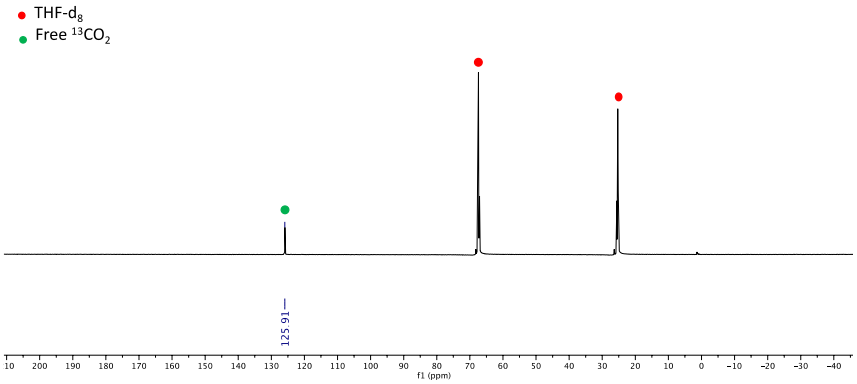


Figure S22: Quantitative $^{13}C\{^{1}H\}$ NMR (D_2O, 151 MHz, 298K) spectrum of the reaction mixture after addition of 1 equivalent $^{13}CO_2$ to a THF solution of **3** at room temperature, removal of the solvent and dissolution in basic D_2O (pD=12) using ^{13}C-labelled sodium acetate as internal standard.

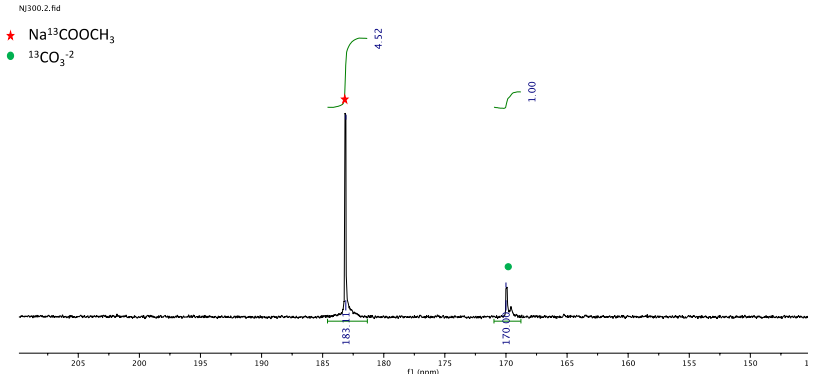


Figure S23: ^{1}H NMR spectrum (THF-d_8, 400 MHz, 298K) of the reaction mixture, after addition of 2 eq $^{13}CO_2$ to a THF solution of **3** at room temperature

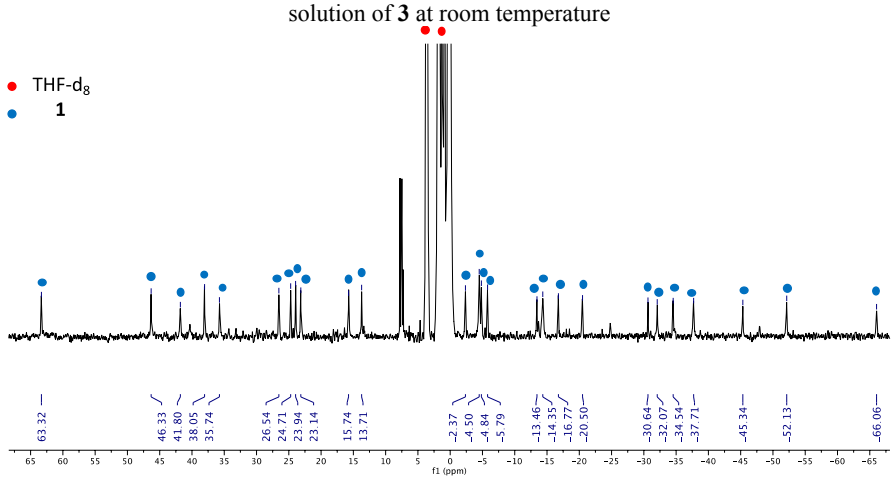


Figure S24: Quantitative $^{13}C\{^{1}H\}$ NMR (D_2O, 151 MHz, 298K) spectrum of the reaction mixture after addition of 2 equivalent $^{13}CO_2$ to a THF solution of **3** at room temperature, removal of the solvent and dissolution in basic D_2O (pD=12) using ^{13}C-labelled sodium acetate as internal standard..

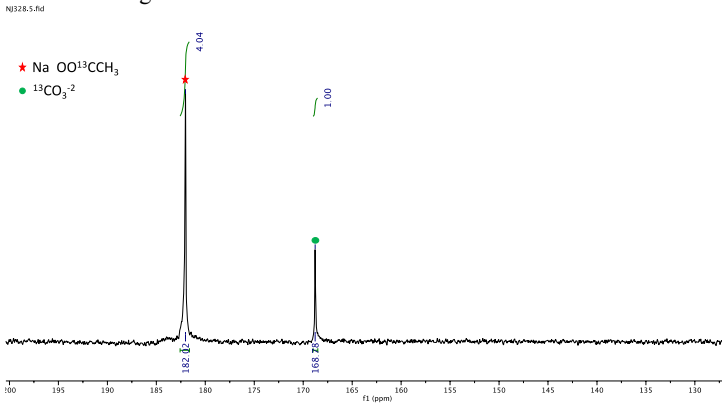


Figure S25: ^{1}H NMR (THF-d_8, 400 MHz, 298K) spectra comparison of the evolution of the reaction mixture of the addition 4 equivalents $^{13}CO_2$ to a THF solution of **3** at room temperature.

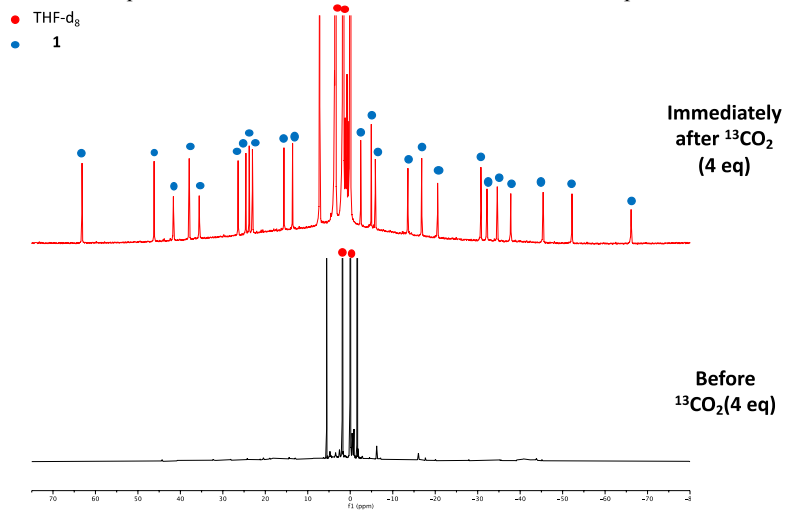


Figure S26: $^{13}C\{^{1}H\}$ NMR (THF-d_8, 151 MHz, 298K) spectrum of the reaction mixture after 6 days addition of 4 equivalents $^{13}CO_2$ to a THF solution of **3** at room temperature.

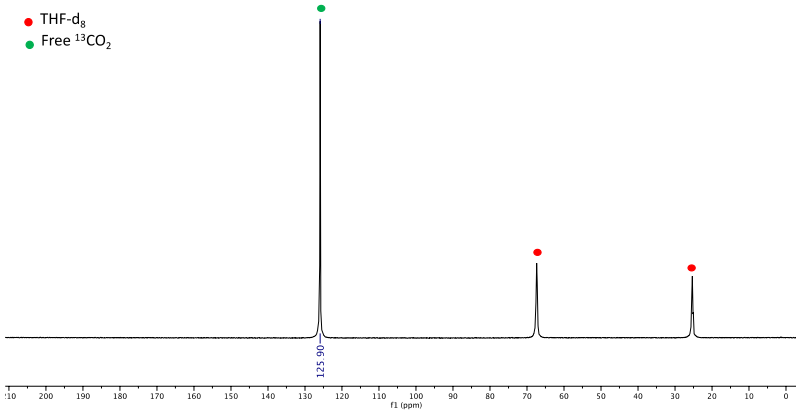


Figure S27: Quantitative $^{13}C\{^{1}H\}$ NMR (D_2O, 151 MHz, 298K) spectrum of the reaction mixture after 6 days addition of 4 equivalents $^{13}CO_2$ to a THF solution of **3** at room temperature, removal of the solvent and dissolution in basic D_2O (pD=12) using ^{13}C-labelled sodium acetate as internal standard.

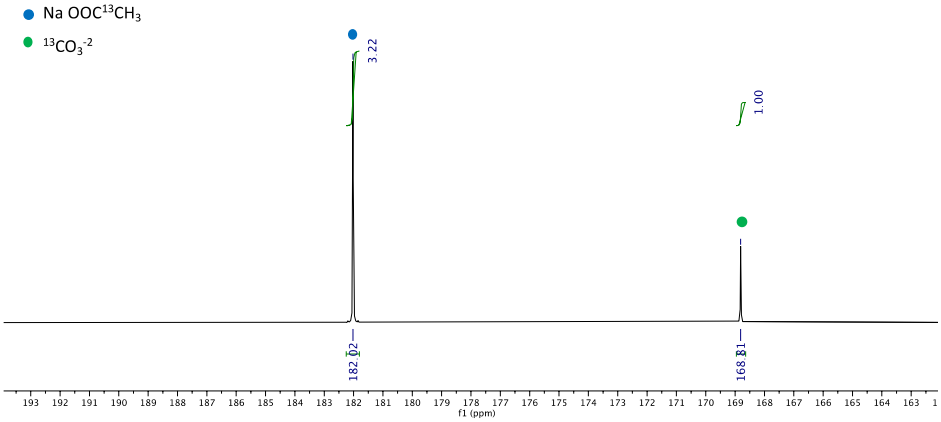


Figure S28: ^{1}H NMR (DMSO-d_6, 400 MHz, 298K) spectrum of the powder of the reaction mixture after addition of 100 equivalents $^{13}CO_2$ to a THF solution of **3** at room temperature.

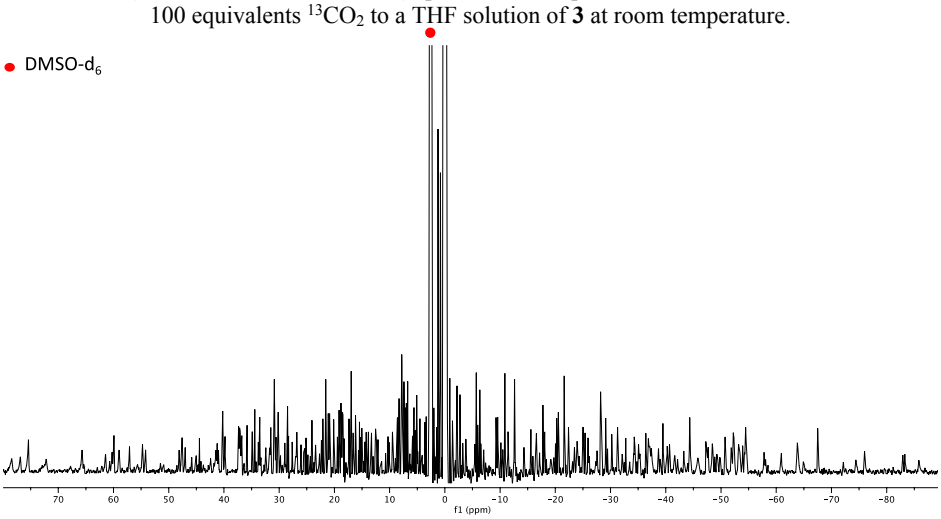


Figure S29: $^{13}C\{^{1}H\}$ NMR (THF-d_8, 151 MHz, 298K) spectrum of the reaction mixture after 6 days addition of 100 equivalents $^{13}CO_2$ to a THF solution of **3** at room temperature.

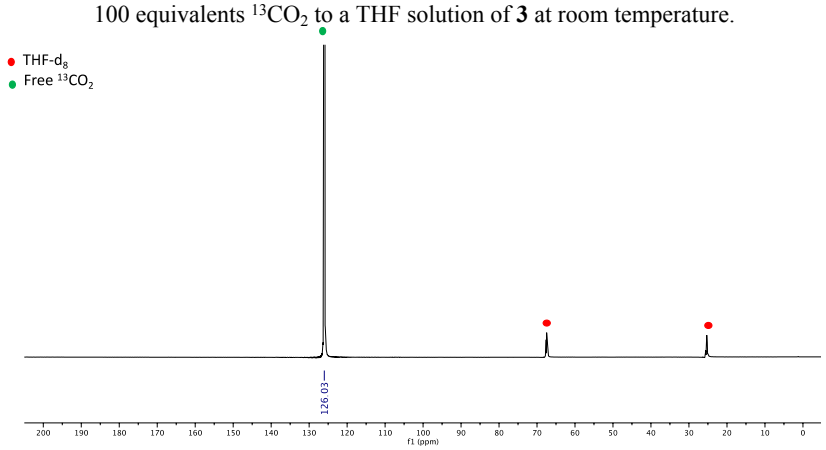
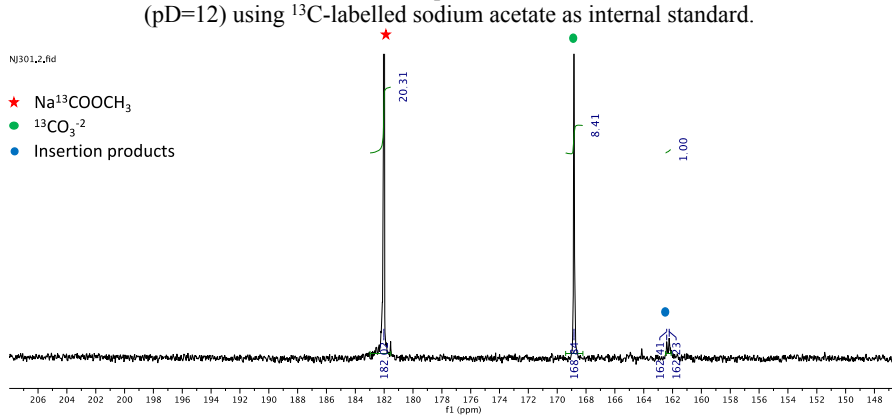


Figure S30: Quantitative $^{13}C\{^{1}H\}$ NMR (D_2O, 151 MHz, 298K) spectrum of the reaction mixture after 6 days addition of 100 equivalents $^{13}CO_2$ to a THF solution of **3** at room temperature, removal of the solvent and dissolution in basic D_2O (pD=12) using ^{13}C-labelled sodium acetate as internal standard.



2. Mass spectra

Figure S31: MS spectra of complex **1:** experimental (up) and theoretical (down) profiles of the peak at m/z 1387

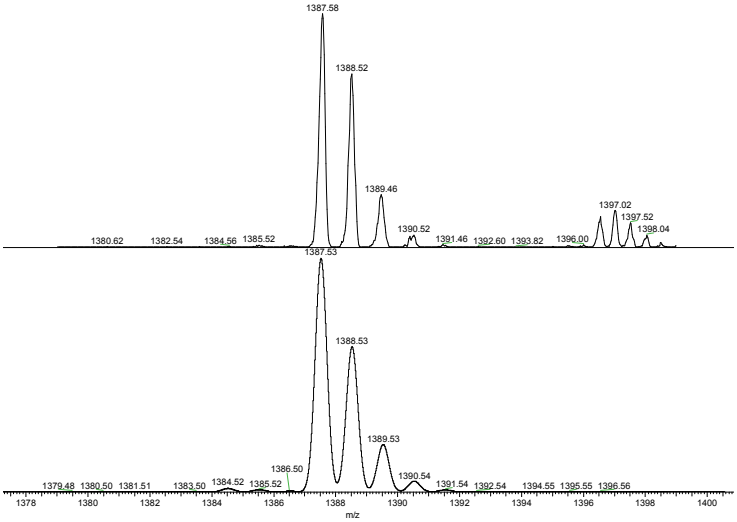
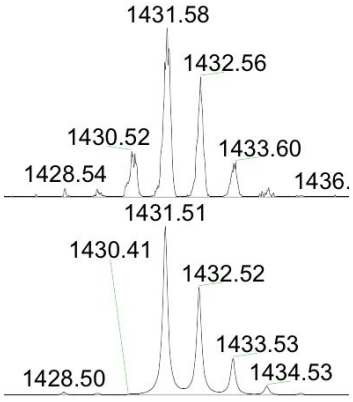


Figure S32: MS spectra of reaction mixture of **1** with CO_2 after 6 days**:** experimental (up) and theoretical (down) profiles of the peak at m/z 1431



3. Electrochemistry

Figure S33 Room temperature cyclic voltammogram of complex $[U_2(\text{bis-trensal})]$ **1** recorded in 0.1 M $[NBu_4][PF_6]$ in 4 mM pyridine solution at 100 mV/sec scan rate, referenced against $[Fe(C_5H_5)_2]^+/[Fe(C_5H_5)_2]$.

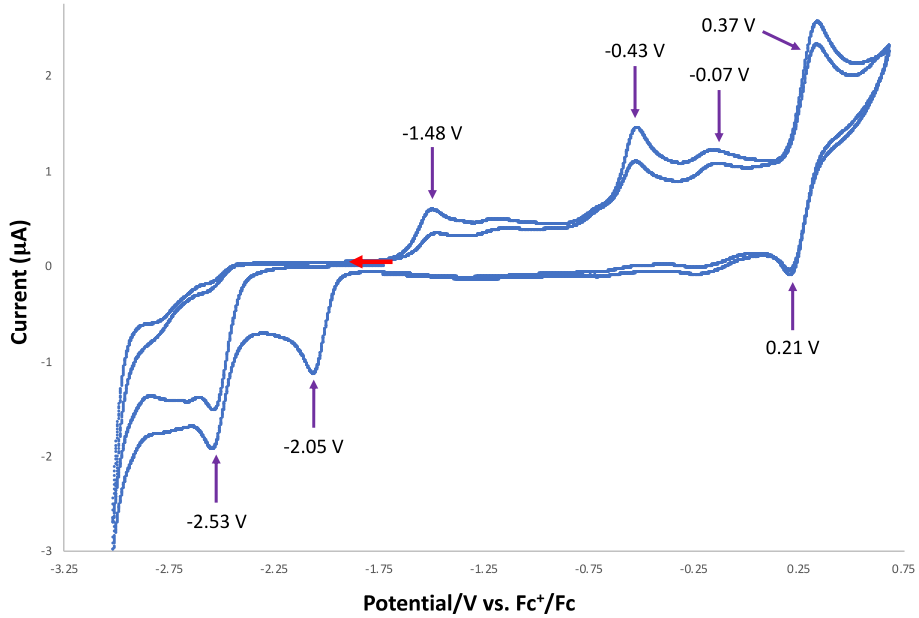


Figure S34 Room temperature cyclic voltammogram of complex $[U_2(\text{bis-trensal})]$ **1** recorded in 0.1 M $[NBu_4][PF_6]$ in 4 mM pyridine solution, referenced against $[Fe(C_5H_5)_2]^+/[Fe(C_5H_5)_2]$, at different scan rates 50 mV/sec (blue), 100 mV/sec (orange), 500 mV/sec (grey) and 1000 mV/sec (yellow).

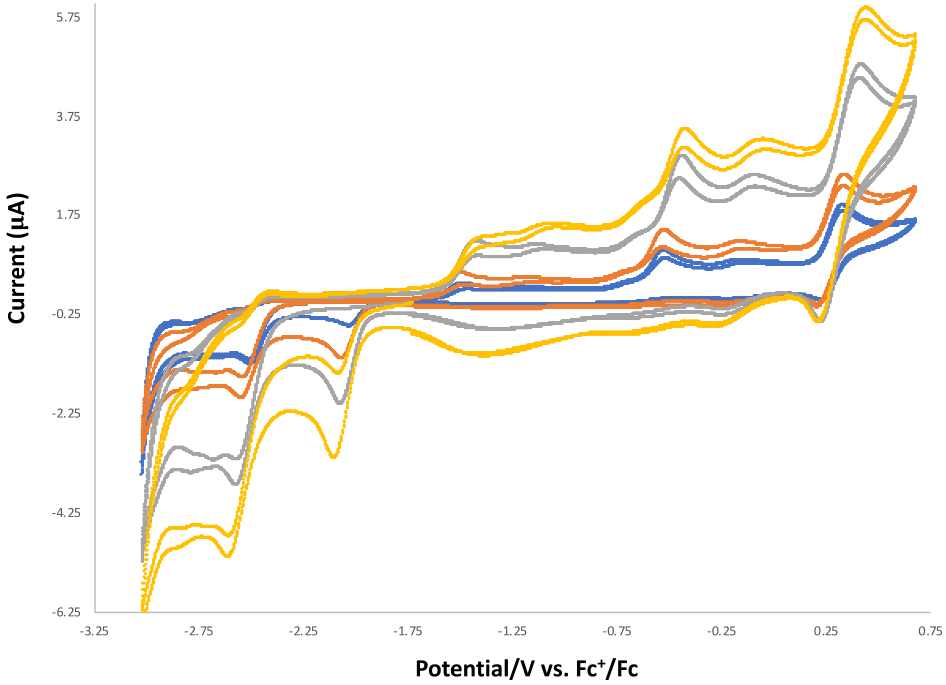


Figure S35 Room temperature cyclic voltammogram of complex [U(trensal)][OTf] **2** recorded in 0.1 M $[NBu_4][PF_6]$ in 4 mM pyridine solution at 100 mV/sec scan rate, referenced against $[Fe(C_5H_5)_2]^+/[Fe(C_5H_5)_2]$.

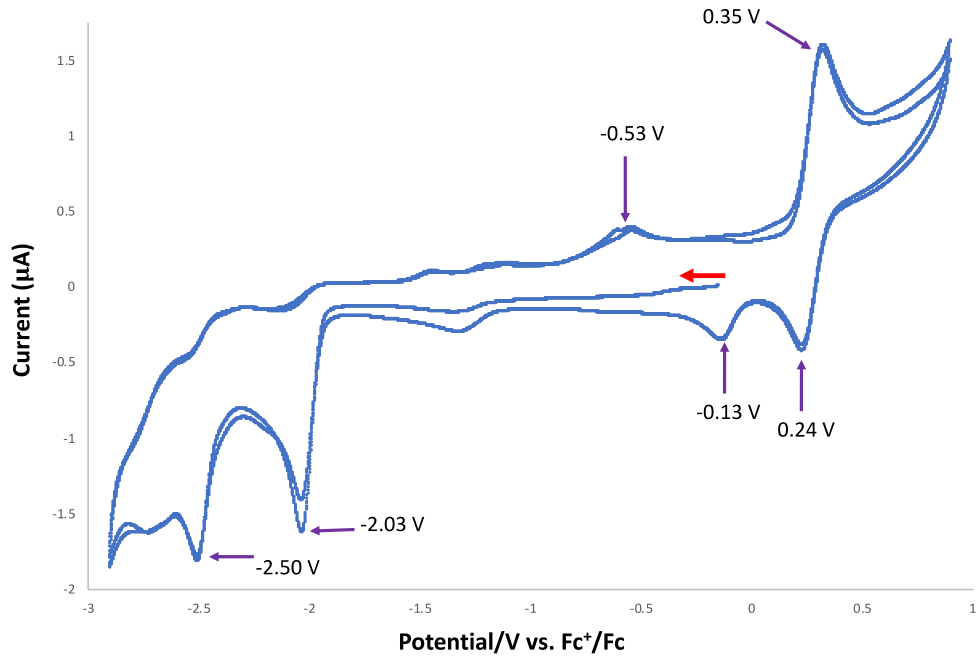


Figure S36 Room temperature cyclic voltammogram of complex [U(trensal)][OTf] **2** recorded in 0.1 M $[NBu_4][PF_6]$ in 4 mM pyridine solution, referenced against $[Fe(C_5H_5)_2]^+/[Fe(C_5H_5)_2]$, at different scan rates 50 mV/sec (blue), 100 mV/sec (orange), 500 mV/sec (grey) and 1000 mV/sec (yellow).

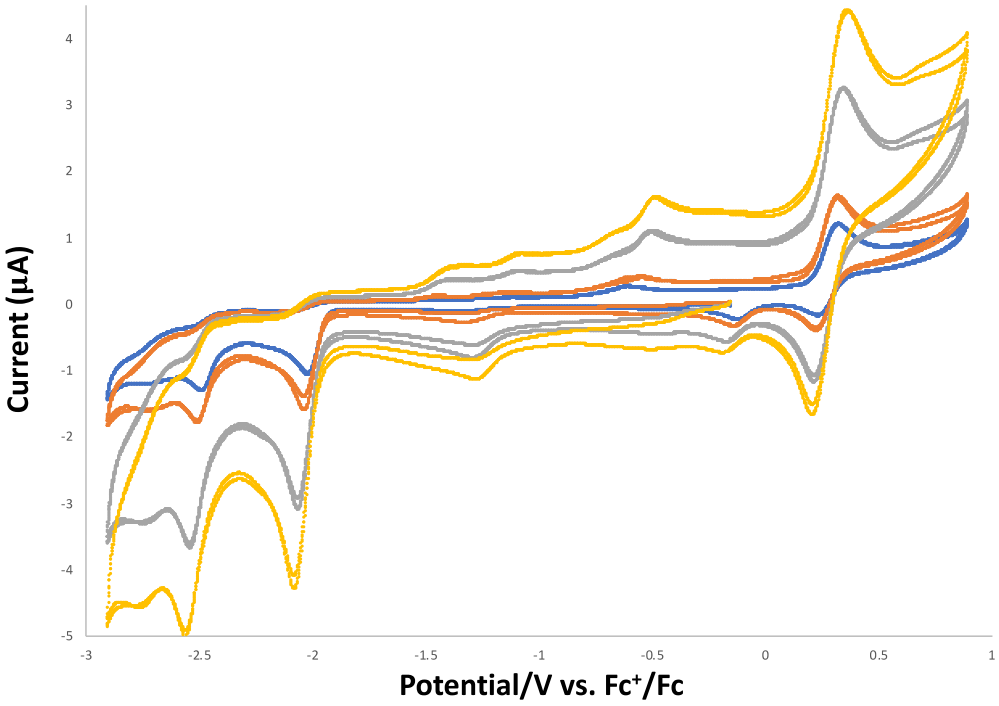


Figure S37 Room temperature cyclic voltammogram of complex [{K(THF)$_3$}$_2$U$_2$(cyclo-trensal)] **3-THF** recorded in 0.1 M [NBu$_4$][PF$_6$] in 4 mM pyridine solution in presence of excess cryptand, at 100 mV/sec scan rate, referenced against [Fe(C$_5$H$_5$)$_2$]$^+$/[Fe(C$_5$H$_5$)$_2$].

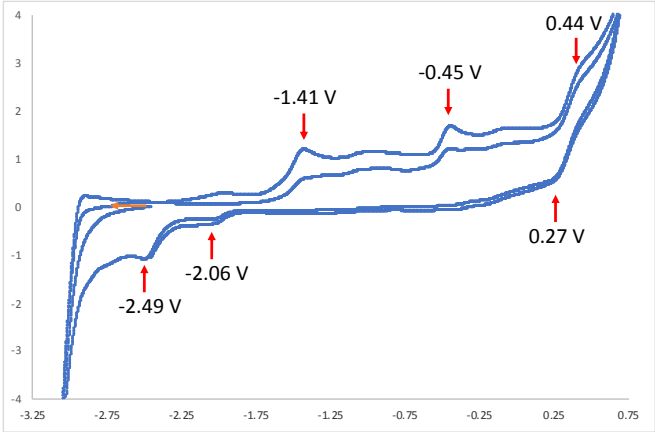


Figure S38 Room temperature cyclic voltammogram of complex [{K(THF)$_3$}$_2$U$_2$(cyclo-trensal)] **3-THF** recorded in 0.1 M [NBu$_4$][PF$_6$] in 4 mM pyridine solution in presence of excess cryptand, referenced against [Fe(C$_5$H$_5$)$_2$]$^+$/[Fe(C$_5$H$_5$)$_2$], at different scan rates 50 mV/sec (blue), 100 mV/sec (orange), 500 mV/sec (grey) and 1000 mV/sec (yellow).

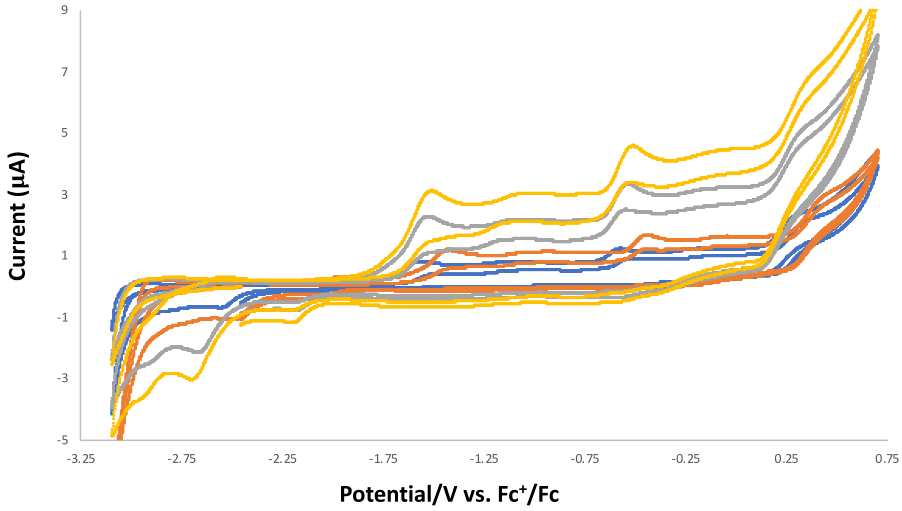


Figure S39 Room temperature cyclic voltammogram of complex $[U_2(\text{bis-trensal})]$ **1** recorded in 0.1 M $[NBu_4][PF_6]$ in 4 mM pyridine solution at 100 mV/sec scan rate, referenced against $[Fe(C_5H_5)_2]^+/[Fe(C_5H_5)_2]$.

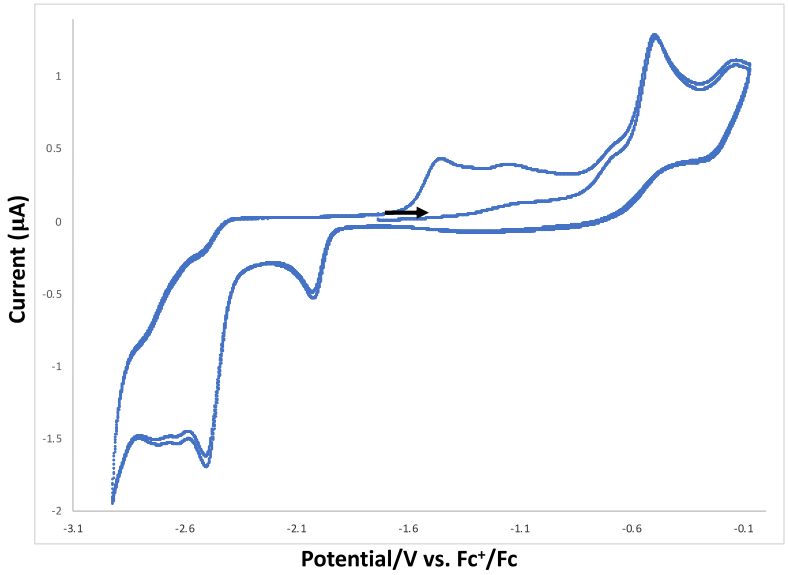


Figure S40 Room temperature cyclic voltammogram of complex $[U_2(\text{bis-trensal})]$ **1** recorded in 0.1 M $[NBu_4][PF_6]$ in 4 mM THF solution at 100 mV/sec scan rate, referenced against $[Fe(C_5H_5)_2]^+/[Fe(C_5H_5)_2]$.

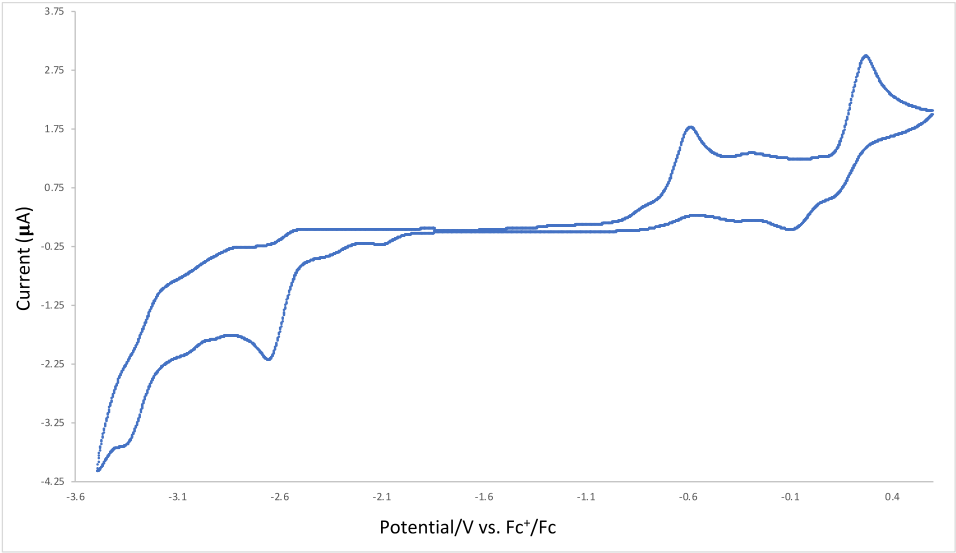
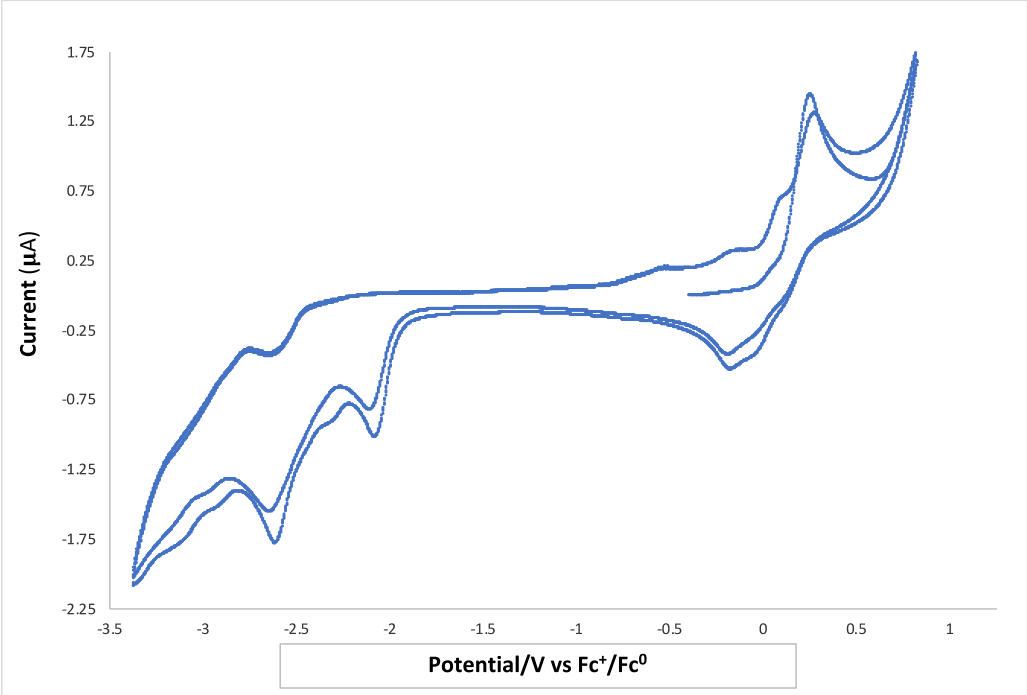


Figure S41 Room temperature cyclic voltammogram of complex [U(trensal)][OTf] **2** recorded in 0.1 M $[NBu_4][PF_6]$ in 4 mM solution THF solution at 100 mV/sec scan rate, referenced against $[Fe(C_5H_5)_2]^+/[Fe(C_5H_5)_2]$.



4. UV-vis spectroscopy

Figure S42 UV-vis spectrum at room temperature of a 5mM solution of [U(trensal)][OTf], **2** in THF.

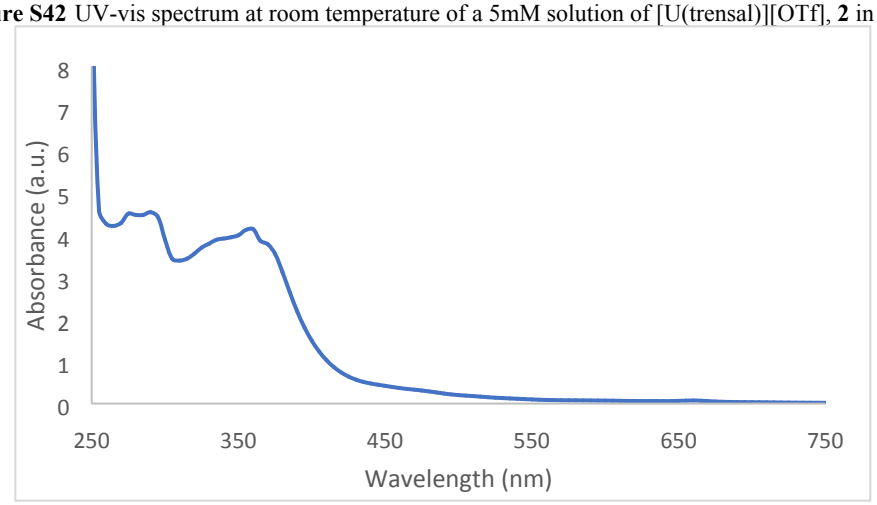


Figure S43 UV-vis spectrum at room temperature of a 5mM solution of [U(bis-trensal)], **1** in THF.

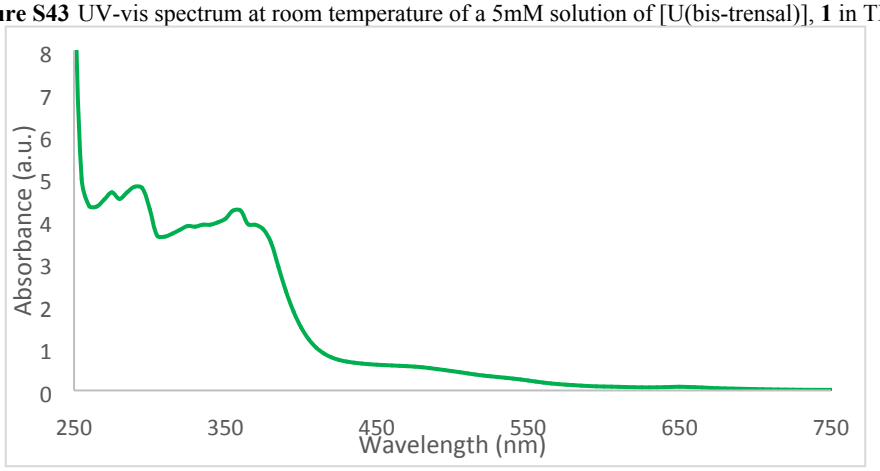
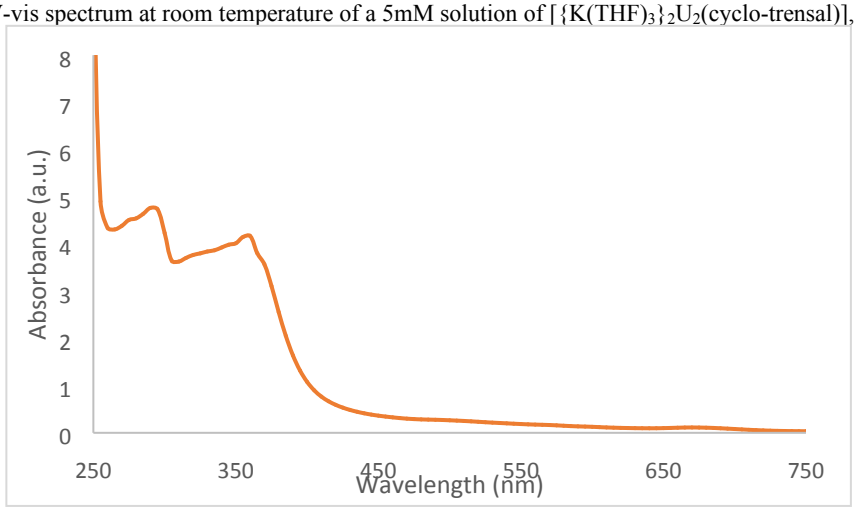


Figure S44 UV-vis spectrum at room temperature of a 5mM solution of $[\{K(THF)_3\}_2U_2$(cyclo-trensal)], **3-THF** in THF.



5. X-ray crystallographic data

Figure S45 Molecular structure of complex **4**. Hydrogen atoms and THF molecules were omitted for clarity. Color code: uranium (green), nitrogen (blue), oxygen (red), carbon (grey), C-C bond between imine (yellow).

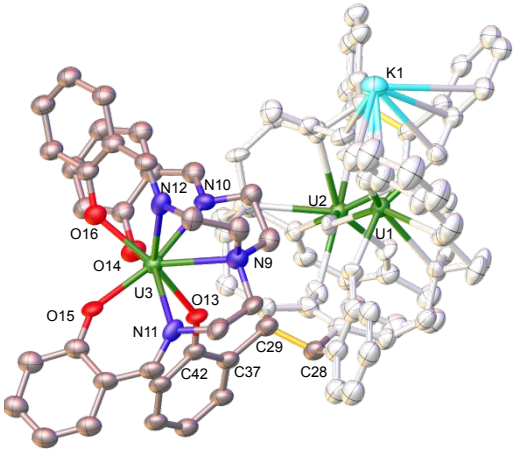


Table S1. X-ray crystallographic data.

Compound	**1a**	**2**	**3-Py.**(pyridine)	**4**
Formula	$C_{102}H_{150}N_8O_6U_2$	$C_{28}H_{27}F_3N_4O_6SU$	$C_{88}H_{88}K_2N_{14.8}O_6U_2$	$C_{95}H_{105}KN_{12}O_{16}U_3$
Crystal size [mm]	0.13×0.07×0.04	0.32×0.10×0.05	0.25×0.21×0.08	0.43×0.27×0.23
Crystal system	Triclinic	Trigonal	Triclinic	Triclinic
Space group	P -1	$P\bar{3}c1$	P -1	P -1
V [Å3]	2700.5(9)	3238.8(5)	2064.0(16)	4772.1(4)
a [Å]	11.0515(12)	15.2336(10)	11.872(3)	13.9739(7)
b [Å]	15.966(4)	15.2336(10)	12.416(6)	17.1424(5)
c [Å]	16.284(2)	16.1157(10)	15.141(8)	21.3152(9)
α [°]	70.59(2)	90	91.66(4)	84.872(3)
β [°]	85.304(12)	90	107.63(3)	82.993(4)
γ [°]	87.757(14)	120	102.69(3)	70.549(4)
Z	1	4	1	2
Absorption coefficient [mm-1]	4.287	4.324	4.324	4.941
F (000)	1050	1624	989.6	2364.0
T [K]	100(2)	100(2)	100(2)	140(10)
Total no. reflexions	30.886	39917	30691	31290
Unique reflexions [R(int)]	9511 [0.1473]	2488 [0.0942]	9446 [0.1031]	16858 [0.0473]
Final R indice [I>2σ(I)]	0.0812	0.0549	0.0766	0.0740
Largest diff. peak and hole [eA-3]	1.182 and -1.491	2.622 and -1.056	2.036 and -1.705	4.504 and -2.751
GOF	1.024	1.109	1.100	1.078