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Supplementary Data: Multi-electron reduction of sulfur and carbon disulfide using binuclear uranium(III) borohydride complexes

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1. General Details

All manipulations were carried out under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques or in a glove box unless otherwise stated. Solvents (toluene, *n*-hexane, diethyl ether and tetrahydrofuran (THF)) were dried by passage through activated 4 Å molecular sieves or activated alumina towers and stored over activated 4 Å molecular sieves. Deuterated solvents were refluxed over potassium, freeze-pump-thaw degassed three times and vacuum transferred prior to use. ^{1}H NMR spectra were recorded at 298 K unless otherwise stated on a Bruker AVA400 or PRO500 spectrometers at 399.90 MHz, and 500.23 MHz respectively, were referenced internally to residual protio solvent (^{1}H) and are reported relative to external tetramethylsilane (δ = 0 ppm). ^{11}B NMR spectra were recorded at 298 K on a Bruker PRO500 at 160.49 MHz and were referenced to external $BF_3.OEt_2$. Chemical shifts are quoted in δ (ppm). Crystallographic data were collected at 150 K on an Oxford Diffraction Excalibur diffractometer using Cu-Kα radiation (λ = 1.5418 Å) or at 120 K on an Agilent Technologies SuperNova diffractometer with Cu-Kα radiation and X-ray mirror optics.

H_4L^A,[1] and $U(BH_4)_3(THF)_2$[2] were synthesised by published methods. NaN″ and KN″ (N″ = $N(SiMe_3)_2$) were synthesised by reaction of NaH or KH with $HN(SiMe_3)_2$ in toluene and recrystallisation. LiN″ was purchased from Alfa Aesar and recrystallised from hexane before use. M'OTtbp (M' =Na, K) was synthesised from treatment of HOTtbp with M'N" in THF.

2. Compound numbering scheme:

$[Na(THF)_4][\{U(BH_4)\}_2(\mu\text{-}BH_4)(L^A)(THF)_2]$ **1-Na** (previously reported)

$[Li(THF)_4][\{U(BH_4)\}_2(\mu\text{-}BH_4)(L^A)(THF)_2]$ **1-Li**

$[\{U(BH_4)\}_2(\textit{endo}\text{-}\mu\text{-}KBH_4)(L^A)(THF)_2]$ **1-K**

$[\{U(OAr)(THF)\}_2(\textit{endo}\text{-}\mu\text{-}KBH_4)(L^A)]$ **2-K**

$[\{U(OAr)(THF)\}_2(\textit{endo}\text{-}\mu\text{-}NaBH_4)(L^A)]$ **2-Na**

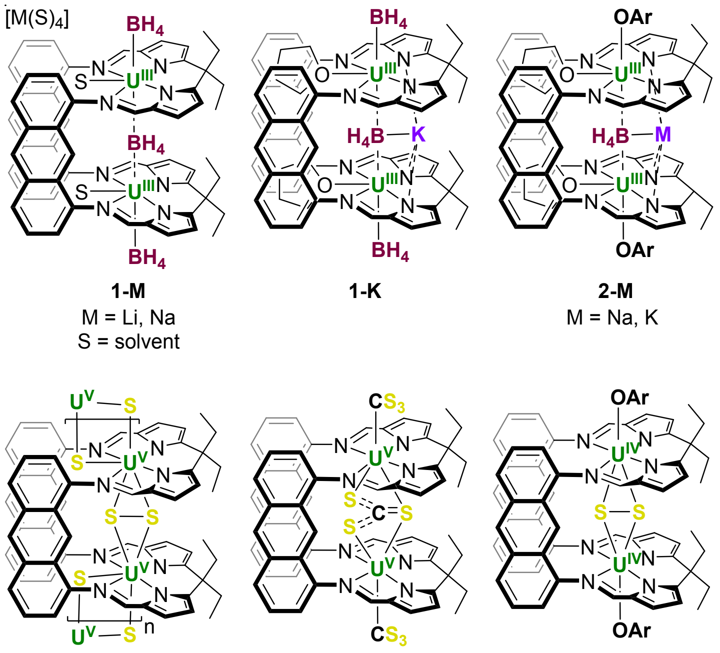
$[\{U(\mu\text{-}S)\}_2(\mu\text{-}\eta^2\text{:}\ \eta^2\text{-}S_2)(L^A)]_n$ **3**

$[\{U(CS_3)\}_2(\mu\text{-}\kappa^1\text{:}\kappa^1\text{:}\kappa^2\text{-}CS_3)(L^A)]$ **4**

$[\{U(OAr)\}_2(\mu\text{-}\eta^2\text{:}\ \eta^2\text{-}S_2)(L^A)]$ **5**

$[\{U(OAr)\}_2(\mu\text{-}CS_2)(L^A)]$ **6a**

$[\{U(OAr)\}_2(\mu\text{-}S)(L^A)]$ **6**



1-M
M = Li, Na
S = solvent

1-K

2-M
M = Na, K

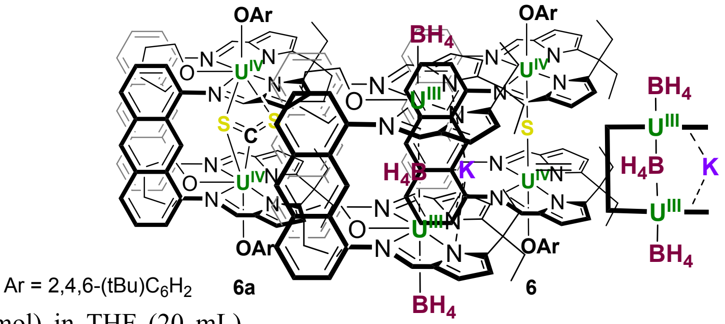
3

4

5

3. Syntheses of ion pairs and solvates

3.1. K analogue of 1: $[\{U(BH_4)\}_2(\mu\text{-}BH_4K)(L^A)(THF)_2]$, **1-K**



Ar = 2,4,6-(tBu)C_6H_2 **6a** **6** **1-K**

THF (50 mL) was added to a dry mix of H_4L^A (1 g, 1.16 mmol) and KN″ (927 mg, 4.65 mmol) forming an orange suspension, which was stirred for 15 min. It was then transferred onto a suspension of $[U(BH_4)_3(THF)_2]$ (991 mg, 2.32 mmol) in THF (20 mL) forming a green-brown mixture which was stirred for 2 h and then left to settle for 16 h. The mixture was filtered and the volatiles half removed from the filtrate resulting in the formation of dark green microcrystalline material (1.13 g, 62%) which was identified as **1-K**.

^{1}H NMR (*d_8*-THF): δ 38.28 (s, 4H), 31.8 (br, $W_{½}$ 441 Hz, terminal BH_4), 18.84 (s, 4H), 17.50 (s, 4H), 10.85 (d, $^3J_{HH}$ 8.70 Hz, 4H, pyrrole H), 10.69 (s, 4H), 9.77 (d, $^3J_{HH}$ 8.70 Hz, 4H, pyrrole H),9.65 (s, 4H), 6.11 (s, 6H, *meso* $CH_2C\underline{H}_3$), −0.13 (s, 6H, *meso* $CH_2C\underline{H}_3$), −18.40 (s, 2H, Ar-H) ppm. Two macrocycle resonances cannot be located. **^{1}H{^{11}B} NMR (*d_8*-THF):** resonance at δ 31.8 ppm sharpens to $W_{½}$ 376 Hz. **^{11}B NMR (*d_8*-THF):** δ 180 (s, terminal and bridging BH_4 overlapped) ppm; **Elemental Analysis** Found: C, 49.33; H, 4.16; N, 7.82 %, $C_{60}H_{60}B_3K_1N_8U_2$ requires: C, 49.17; H, 4.27; N, 7.91 %. **IR** (thin film, cm^{-1}) 2431 (m), 2359 (m), 1589 (s), 1554 (m, br.), 1455 (s), 1377 (s), 1312 (m), 1286 (m), 1168 (m), 1085 (m), 1053 (m), 1038 (m), 1011 (m), 964 (w), 864 (m), 740 (m), 722 (m).

3.2. Synthesis of $[Li(THF)_4][\{U(BH_4)\}_2(\mu\text{-}BH_4)(L^A)(THF)_2]$, **1-Li**

THF (15 mL) was added to a dry mix of UI_3 (458 mg, 0.74 mmol) and $LiBH_4$ (50 mg, 2.30 mmol) forming a dark red solution and a red microcrystalline solid. The mixture was stirred for 30 mins before being transferred onto an orange solution of Li_4L^A in THF (15 mL), formed in situ from H_4L^A (318 mg, 0.37 mmol) and LiN″ (250 mg, 1.49 mmol). The resultant green-brown solution was stirred for 16 h before the volatiles were removed under reduced pressure to yield an oily dark green residue. This was extracted with toluene (10 mL) and the extract was stored at −30 °C for 1 week to afford dark green microcrystals (293 mg, 44%).

^{1}H NMR (THF/C_6D_6): δ 35.51 (s, 4H), 18.80 (s, 4H), 15.88 (s, 4H), 10.88 (s, 2H, Ar-H), 10.03 (s, 4H), 9.89 (s, 4H), 8.99 (s, 4H), 8.72 (s, 4H), 5.12 (s, 6H, *meso* $CH_2C\underline{H}_3$), 4.49 (s, 4H), −0.09 (s, 6H, *meso* $CH_2C\underline{H}_3$), −12.70 (s, 2H, Ar-H), −69.4 (br, $W_{½}$ 527 Hz, terminal BH_4).

4. Reactions of $[M(THF)_4][\{U(BH_4)\}_2(\mu\text{-}BH_4)(L^A)(THF)_2]$, 1-M:

4.1. Reaction of **1-Na** with KN″

Solid $[Na(THF)_4][\{U(BH_4)\}_2(\mu\text{-}BH_4)(L^A)(THF)_2]$ (14 mg, 0.007 mmol) and KN″ (4 mg, 0.020 mmol) were combined in *d_8*-THF (0.5 mL) in a Teflon-tapped NMR tube forming a dark brown solution containing a pale brown precipitate. The ^{1}H NMR spectrum acquired after 2 h showed a mixture of paramagnetic and diamagnetic compounds. After 16 h a different set of low intensity paramagnetic resonances were observed which could not be assigned to a single product. No resonance corresponding to $NaBH_4$ or KBH_4 could be identified.

4.2. Reaction of **1-K** with NaO^{t}Bu

Excess Na^{t}OBu (4 mg, 0.042 mmol) was combined with **1-K** (14 mg, 0.09 mmol) in *d_8*-THF (0.5 mL) in a Teflon-tapped NMR tube. The mixture turned brown. **^{1}H NMR (*d_8*-THF):** δ 13.33 (s, 1H), 7.20 (s, 1H), 2.55 (s, 1H), 1.32 (s, 12H), 1.08 (s, 280H, excess NaO^{t}Bu), −0.41 (1:1:1:1 q, $^1J_{BH}$ 85 Hz, 44H, $NaBH_4$), −8.67 (s, 2H) ppm. These resonances cannot be assigned to a complex of L^A. Other very low intensity resonances were observed over the range δ 98 to −33 ppm so it is likely that decomposition has occurred.

4.3. Reaction of **1-K** with KCp*

Solid **1-K** (15 mg, 0.010 mmol) and KCp* (5 mg, 0.029 mmol) were combined in *d_8*-THF (0.5 mL) in a Teflon-tapped NMR tube. The mixture turned pale orange and an orange precipitate formed over 1 h. The ^{1}H NMR spectrum showed multiple low intensity paramagnetic resonances that could not be assigned to one product.

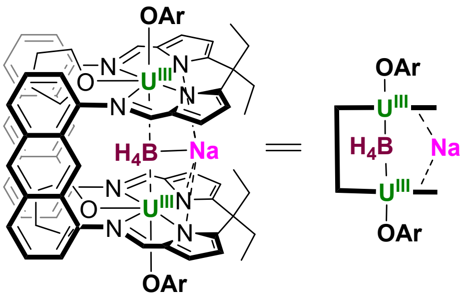
4.4. Reaction of **1-K** with potassium benzyl

Solid **1-K** (14 mg, 0.009 mmol) and KCH_2Ph (2.3 mg, 0.018 mmol) were combined in *d*$_8$-THF (0.5 mL) in a Teflon-tapped NMR tube. The ^{1}H NMR spectrum showed multiple low intensity paramagnetic resonances that could not be assigned to one product, along with toluene (δ 7.24 (m, 2H, *meta*-H), 7.18 (d, $^3J_{HH}$ 7.3 Hz, 2H, *ortho*-H), 7.13 (t, $^3J_{HH}$ 7.4 Hz, 1H, *para*-H), 2.36 (s, 3H, Me) ppm), and KN″ (δ 0.17 (s, 8H) ppm).

4.5. Reaction of **1-K** with lithium methylallyl

Solid **1-K** (15 mg, 0.010 mmol) and LiC_4H_7 (2 mg, 0.032 mmol) were combined in *d*$_8$-THF (0.5 mL) in a Teflon-tapped NMR tube. The ^{1}H NMR spectrum showed multiple, very low intensity paramagnetic resonances that could not be assigned to one product. $LiBH_4$ was observed at δ −0.51 (1:1:1:1 q, $^1J_{BH}$ 80 Hz) ppm.

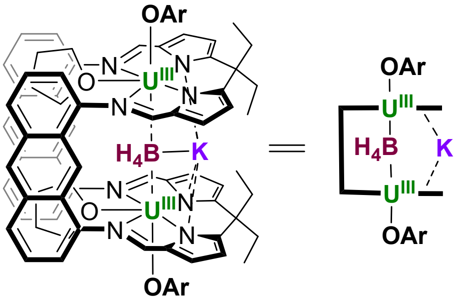
4.6. Synthesis of [{U(OAr)}$_2$(endo-BH$_4$Na)(L^A)(THF)$_2$], **2-Na**



2-Na

[Na(THF)$_4$][{U(BH$_4$)}$_2$(μ-BH$_4$)(L^A)(THF)$_2$] (205 mg, 0.13 mmol) and NaOAr (83 mg, 0.29 mmol) were combined in THF (10 mL) forming a dark green solution and a light green precipitate. After stirring for 2h the solvent was removed under reduced pressure and the product extracted into THF. The solvent was removed from the THF solution and the dark green powder washed with hexanes. Yield: 110 mg, 35%. Dark green crystals of [{U(OAr)}$_2$(*endo*-BH$_4$Na)(L^A)(THF)$_2$] (**2-Na**) formed upon standing of a NMR sample in *d*$_8$-THF at room temperature for 3 weeks. Analytically pure material was obtained by crystallisation of the bulk material from toluene. These crystals exhibited further broadened resonances when redissolved in C_6D_6 solvent presumably due to fluxionality in the Na coordination. **^{1}H NMR (*d*$_8$-THF):** δ 45.9 (br, 4H), 38.5 (br, 4H), 24.0 (br, 4H), 23.0 (br, 4H), 20.1 (br, 6H), 18.2 (br, 2H), 16.9 (br, 2H), 15.5 (br, 4H), 8.58 (br, 4H), 6.1 (br, 36H), −5.9 (br, 4H), −7.3 (br, 18H), −13.9 (br, 6H, *meso* $CH_2C\underline{H}_3$), −24.7 (br, 4H) ppm; **Elemental Analysis** Found: C, 59.58; H, 5.71; N, 6.01 %, $C_{94}H_{110}N_8O_2BNaU_2$ requires: C, 59.62; H, 5.85; N, 5.92 %

5. Synthesis of [{U(OAr)}$_2$(endo-BH$_4$K)(L^A)(THF)$_2$], 2-K



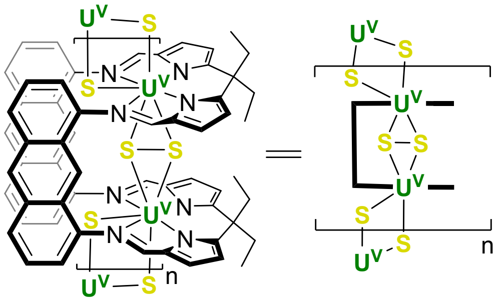
2-K

THF (15 mL) was added to a dry mix of [Na(THF)$_4$][{U(BH$_4$)}$_2$(μ-BH$_4$)(L^A)(THF)$_2$] (385 mg, 0.210 mmol) and KOAr (127 mg, 0.423 mmol, Ar = 2,4,6-$C_6H_2(^tBu)_3$) and the mixture was stirred for 16 h. Dark green crystals of [{U(OAr)}$_2$(endo-BH$_4$K)(L^A)(THF)$_2$], **2** formed that were isolated by filtration and dried under reduced pressure. Yield: 253 mg, 59 %. Single crystals suitable for X-ray diffraction and EA were grown from an NMR scale reaction solution in *d*$_8$-THF.

^{1}H NMR (C_6D_6): δ 27.0 (br, 4H), 24.9 (br, 4H), 17.7 (br, 4H), 14.6 (br, 2H, ArH), 13.9 (br, 4H), 12.4 (br, 4H), 10.5 (br, 4H), 8.6 (br, 2H ArH), 7.7 (br, 6H, *meso* $CH_2C\underline{H}_3$ + 4H), 6.0 (br, 4H), 4.1 (br, 18H, *para* ^{t}Bu), 3.60 (br, 24H, THF), 1.42 (br, 24H, THF), −0.1 (br, 36 H, *ortho* ^{t}Bu), −10.0 (br, 4H), −12.8 (br, 6H, *meso* $CH_2C\underline{H}_3$) ppm. **^{11}B NMR (C_6D_6):** δ 188 (br, $W_{½}$ 1161 Hz, (μ-BH$_4$K)) ppm; IR (THF, cm^{-1}) 2280 (m); **Elemental Analysis** Found: C, 59.46; H, 5.91; N, 5.36 %, $C_{102}H_{126}B_1K_1N_8O_4U_2$ requires: C, 59.64; H, 6.18; N, 5.46 %.

6. Small molecule reactivity of 1-Na

6.1. Synthesis of $[\{US\}_2(S_2)(L^A)]_n$ (3)



3

S_8 (12 mg, 0.047 mmol) was added to a dark green solution of $[Na(THF)_4][\{U(BH_4)\}_2(\mu\text{-}BH_4)(L^A)(THF)_2]$ **1-Na** (114 mg, 0.062 mmol) in THF (ca. 5 mL) resulting in a dark red/orange solution. Upon standing at room temperature for 12h, a dark precipitate formed which was filtered, washed with cold THF (2 x 5mL) and dried under reduced pressure to yield an analytically pure reddish solid of **3**. Yield: 46 mg, 51 %. **Elemental Analysis** Found: C, 47.80; H, 3.43; N, 7.81 %, $C_{58}H_{48}N_8S_4U_2$ requires: C, 47.67; H, 3.31; N, 7.67 %.

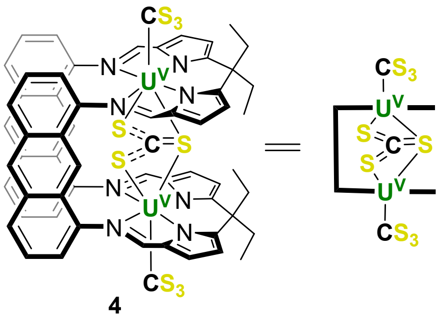
*Characterisation of the reaction mixture formed immediately on addition of S_8 to **1-Na**.*

^{1}H NMR (THF-d_8): δ 33.59 (s, 6H), 27.83 (s, 4H), 27.12 (s, 4H), 17.34 (s, 2H), 12.48 (s, 4H), 6.80 (s, 4H), 5.62 (s, 2H), 4.38 (s, 4H), -3.36 (s, 6H), -18.95 (s, 4H), -22.57 (s, 4H).

*Characterisation of the mother liquor from synthesis of **3**.*

^{11}B NMR (THF-d_8): two sharp triplets at -6.2 (t, J = 120 Hz) and -16.5 (t, J = 120 Hz) ppm the latter of which can be characterised as $Na_2[(BH_2)_6S_4]$.[3]

6.2. Synthesis of $[\{U(CS_3)\}_2(\mu\text{-}\kappa^1\text{:}\kappa^1\text{:}\kappa^2\text{-}CS_3)(L^A)]$ 4



4

CS_2 (287 mg, 3.769 mmol) was added to a dark green/brown solution of $[Na(THF)_4][\{U(BH_4)\}_2(\mu\text{-}BH_4)(L^A)(THF)_2]$ **1-Na** (200 mg, 0.109 mmol) in THF resulting in a dark orange solution. Upon sitting at room temperature for 30 min., an orange precipitate formed which was filtered and washed with THF yielding an orange, analytically pure solid. Yield: 166 mg, 92 %. Small single crystals were grown from the filtered THF solution however poor quality data meant that whilst the structure could be solved to identify the product as $[\{U(CS_3)\}_2(\mu\text{-}\kappa^1\text{:}\kappa^1\text{:}\kappa^2\text{-}CS_3)(L^A)]$ **4**, in-keeping with microanalysis and NMR of the precipitate; adequate refinement of the ligand was not possible.

^{1}H NMR (THF-d_8): δ 25.23 (s, 4H), 21.64 (s, 4H), 17.59 (s, 6H), 15.97 (s, 4H), 12.49 (s, 2H), 11.61 (s, 4H), 10.43 (s, 4H), 9.25 (s, 4H), 8.56 (s, 6H), -43.46 (s, 2H). **Elemental Analysis** Found C, 44.31; H 2.82; N 6.72, $C_{61}H_{48}N_8S_9U_2$ requires: C 44.20; H 2.92; N 6.76%. **IR** (thin film, cm^{-1}) 1592 (s), 1576 (m), 1554 (m), 1457 (s), 1377 (s), 1313 (w), 1274 (m), 1169 (w), 1085 (w), 1056 (m), 1013(m), 978 (w), 875 (m, CS_3 endocyclic), 864 (m), 739 (m), 721 (m).

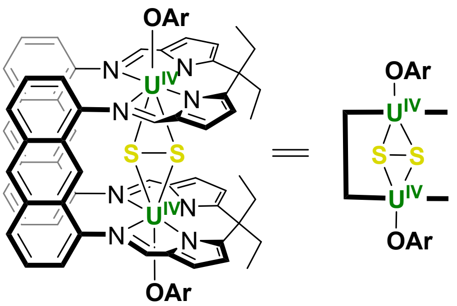
Characterisation of the mother liquor from synthesis of 4.

^{1}H NMR (THF-d_8): 3.97 (q, J = 3.4 Hz, *H*-C-S-B); **^{11}B NMR (THF-d_8):** two sharp resonances at 2.9 and 0.5 ppm and several smaller resonances including one broad one at 60 ppm (vs. 63 ppm for $B(SMe)_3$)[4]; **GC-MS** shows peaks at RT 3.2 (5.4%), 10.0 (3.1%) and 10.2 (5.3%) assigned to 1,2,4-trithiolane, at 5.0 (2.8%) assigned to tetrahydrothiophene and at 16.3 (1.2%) for 1,2,4,6 tetrathiepane which may form from degradation of boron-containing products in the GC oven.

7. Small molecule reactivity of 2-K

7.1. Synthesis of $[\{U(OAr)\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}S_2)(L^A)$, **5**

Toluene (10 mL) was added to a dry mix of $[\{U(OAr)\}_2$(*endo*-$BH_4K)(L^A)(THF)_2]$ (250 mg, 0.005 mmol) and S_8 (15 mg, 0.002 mmol) forming a pale orange solution. The mixture was left to stand for 2 h before being filtered. Hexane (50 mL) was added and the mixture left to stand. Dark orange crystals formed after 10 days which were filtered and dried under vacuum. Yield: 99 mg, 41 %. Single crystals for XRD and microanalysis were grown by vapour diffusion of hexane into a benzene solution at ambient temperature.

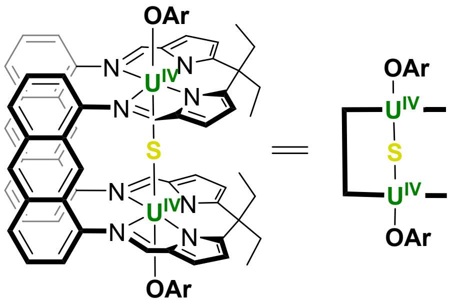


5

^{1}H NMR (C_6D_6): δ 65.54 (s, 4H), 48.45 (s, 2H), 36.97 (s, 2H), 35.67 (2, 6H, *meso* $CH_2C\underline{H}_3$), 29.51 (s, 18H, *ortho*-^{t}Bu), 15.09 (s, 18H, *para*-^{t}Bu), 13.94 (s, 4H), 4.30 (s, 4H), −4.04 (s, 4H), −6.96 (s, 4H), −10.95 (s, 4H), −11.55 (s, 4H), −12.13 (s, 2H), −13.19 (s, 4H), −31.15 (s, 4H), −31.72 (s, 18H, *ortho*-^{t}Bu), −56.12 (s, 2H) ppm. **Elemental Analysis** Found: C, 59.02; H, 5.63; N, 5.76 %, $C_{94}H_{106}N_8O_2S_2U_2$ requires: C, 58.80; H, 5.56; N, 5.84 %

7.2. Synthesis of $[\{U(OAr)\}_2(\mu\text{-}S)(L^A)]$, **6**

CS_2 (45 μL, 0.74 mmol) were added to a green suspension of $[\{U(OAr)\}_2$(*endo*-$BH_4K)(L^A)(THF)_2]$ (**2-K**) (110 mg, 0.058 mmol) in toluene (5 mL) in a teflon-tapped ampoule. The reaction mixture was heated at 80 °C for 2.5 h forming an orange solution containing a brown precipitate. The solution was filtered and orange crystals of $[U(OAr)\}_2(\mu\text{-}S)(L^A)]$ (**6**) formed from the filtrate upon standing at room temperature for 5 days. Analytically pure material was isolated after two vapour diffusion crystallisations from toluene/hexane. Yield: 70mg, 64%.

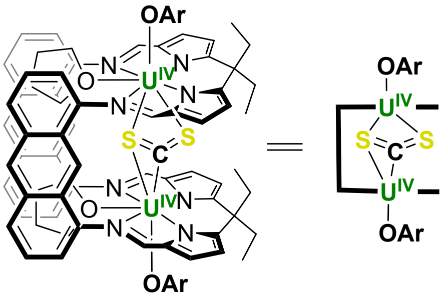


6

^{1}H NMR (C_6D_6): δ 72.40 (br, 4H), 39.49 (br, $W_{½}$ 140 Hz, 18H, *ortho*-^{t}Bu), 29.00 (br. s, 2H), 15.78 (br, 4H), 15.20 (s, 2H), 13.59 (s, 18H, *para*-^{t}Bu), 9.02 (s, 4H), 6.15 (br, 2H), 5.24 (s, 4H), −6.31 (s, 4H), −7.60 (s, 4H), −11.39 (s, 4H), −15.42 (br, 2H), −18.03 (s, 6H, *meso* $CH_2C\underline{H}_3$), -32.40 (br. S, 4H), −55.00 (br, $W_{½}$ 278 Hz, 18H, *ortho*-^{t}Bu) ppm; **Elemental Analysis** Found: C, 59.66; H, 5.20; N, 6.26 %, $C_{94}H_{106}N_8O_2SU_2$ requires: C, 59.80; H, 5.66; N, 5.94 %

7.3. Reaction of **2** with CS_2 to afford putative intermediate $[\{U(OAr)\}_2(\mu\text{-}CS_2)(L^A)(THF)_2]$, **6a**

CS_2 (45 μL, 0.74 mmol) was added to a green suspension of $[\{U(OAr)\}_2$(*endo*-$BH_4K)(L^A)(THF)_2]$ (**2-K**) (100 mg, 0.05 mmol) in toluene (5 mL) in a teflon-tapped ampoule at room temperature. The NMR spectrum showed two sets of resonances, the major product was assigned as **6a** which slowly converted to the minor product (**6**) over time. Isolation of **6a** was not possible due to spontaneous, slow loss of CS forming **6**.



6a

^{1}H NMR (d_8-toluene, 1 h): δ 77.54 (s, 2H), 45.38 (s, 1H, OAr *meta*-H), 42.67 (s, 1H, OAr *meta*-H), 41.87 (s, 2H), 40.05 (s, 1H, OAr *meta*-H), 36.51 (s, 9H, ^{t}Bu), 31.31 (s, 1H, OAr *meta*-H), 26.94 (s, 3H, *meso* $CH_2C\underline{H}_3$), 20.82 (s, 3H, *meso* $CH_2C\underline{H}_3$), 17.18 (s, 9H, ^{t}Bu), 15.01 (s, 9H, ^{t}Bu), 13.40 (s, 9H, ^{t}Bu), 12.67 (s, 2H), 5.35 (s, 2H), 5.27 (s, 2H), 3.59 (br, 30H, THF), 3.06 (s, 2H), 2.78 (s, 2H), 1.45 (br, 30H, THF), −5.05 (s, 2H), −5.94 (s, 2H), −7.28 (s, 2H), −7.95 (s, 2H), −8.15 (s, 2H), −9.90 (s, 3H, *meso* $CH_2C\underline{H}_3$),

−10.36 (s, 2H), −10.63 (s, 3H, *meso* $CH_2C\underline{H}_3$), −15.45 (s, 2H), −18.75 (s, 2H), −27.13 (s, 2H), −27.51 (s, 2H), −35.20 (s, 9H, ^{t}Bu), −36.25 (s, 2H) ppm. One of the aryloxide ^{t}Bu resonances is missing but is likely concealed by a THF resonance.

7.4. NMR scale reaction of $[\{U(OAr)\}_2(\mu\text{-}S)(L^A)]$, **6** with S_8 to form $[\{U(OAr)\}_2(\mu\text{-}S_2)(L^A)]$, **5**

Excess S_8 (9 mg, 0.012 mmol) was added to a solution of **6** (30 mg, 0.0053 mmol) in C_6D_6 and the mixture was heated for 12 h at 80°C yielding an orange solution and yellow precipitate. The ^{1}H NMR spectrum showed resonances corresponding to complex **5**.

7.5. NMR scale reaction of $[\{U(OAr)\}_2(\mu\text{-}CS_2)(L^A)]$, **6a** with S_8 to form $[\{U(OAr)\}_2(\mu\text{-}S_2)(L^A)]$, **5**

CS_2 (15 µL, 0.24 mmol) was added to a green suspension of $[\{U(OAr)\}_2(\textit{endo}\text{-}BH_4K)(L^A)(THF)_2]$ (**2-K**) (10 mg, 0.005 mmol) in C_6D_6 (1 mL) in a Teflon-tapped ampoule at room temperature. The ^{1}H NMR spectrum recorded after 6h showed clean formation of **6a** with no evidence of **6**. S_8 (1.3 mg, 0.005 mmol) was added subsequently and, after 16h, the ^{1}H NMR spectrum showed only resonances corresponding to complex **5**.

8. Crystallographic Details

8.1. Experimental details

Crystallographic X-ray data were collected using Mo-Kα radiation (λ = 0.71073) at 150 K on an Oxford Diffraction Excalibur diffractometer or Cu-Kα radiation (λ = 1.5418 Å) on a SuperNova X-ray Source and an Oxford Diffraction Excalibur CCD area detector diffractometer using ω scans. Structure solution and refinement was carried out using the WinGX32[5] suite of programs using Sir-92[6] or ShelXL 2014[7].

8.2. Refinement details

For **2**, the *para* tert-butyl group of the aryloxide ligand was found to be rotationally disordered over two sites in the ratio 0.42(2):0.58(2). All atoms were successfully refined anisotropically with distance restraints of 1.53(2) Å applied to the 1,2 CCH_3 distances, 2.44(4) Å to the 1,3 $CH_3\cdots CH_3$ distances and 2.50(4) Å to the 1,3 *ipso*- $C\cdots CH_3$ distances. The atomic displacement parameters of the three carbon atoms in each orientation were constrained to be equal. For **2-Na**, the CH_3 groups of the *meso* ethyl groups were found to be disordered over two sites in the ratio 0.51(1):0.49(1). All disordered atoms were refined anisotropically. In the initial solution Na1 lay on the crystallographic C_2 rotational axis. However, its thermal ellipsoid was severely elongated so the position of Na1 was perturbed creating two half-occupied Na sites related by rotation about the C_2 axis. The data were treated with SQUEEZE[8, 9] to remove residual electron density equating to three molecules of THF per unit cell. For **6**, one meso carbon atom of the macrocycle and the two ethyl groups bound to it appeared to be disordered. However, this disorder could not be modelled successfully so instead distance restraints were applied to the 1,2 C-C distances of 1.56(1) Å ($C\textit{meso}\text{-}CH_2$) and 1.52(1) Å ($CH_2\text{-}CH_3$). The magnitude and direction of the atomic displacement parameters of these five C atoms were normalised using the SIMU (su 0.04 Å^2) and DELU (su 0.01 Å^2) commands. The six ring carbon atoms of the molecule of toluene lattice solvent were refined as a perfect hexagon and the methyl carbon was constrained to lie in the plane of the ring with distance restraints placed on the 1,3 $CH_3\text{-}C\textit{ortho}$ distances of 2.55(2) Å. The SIMU (su 0.04 Å^2) and DELU (su 0.01 Å^2) commands were applied to all the toluene carbon atoms. The maximum residual electron density peak appears 0.8 Å from U2.

8.3. CCDC

X-ray crystallographic coordinates for the complexes have been deposited at the Cambridge Crystallographic Database, numbers CCDC 1480072-1480076.

Table SI1. Experimental details

	2-K	**2-Na**	**4**
Crystal data			
Chemical formula	$C_{102}H_{122}BKN_8O_4U_2\cdot C_4H_8O$	$C_{102}H_{122}BN_8NaO_4U_2\cdot 2(C_4H_8O)$	$3(C_{61}H_{48}N_8S_9U_2)$
M_r	2122.15	2178.14	4973.01
Crystal system, space group	Orthorhombic, *Pnma*	Monoclinic, *C*2/*c*	Orthorhombic, $P2_12_12_1$
Temperature (K)	120	170	125
a, *b*, *c* (Å)	29.6933 (4), 29.9161 (4), 10.8656 (1)	15.5798 (8), 33.7862 (17), 20.7334 (12)	28.579 (8), 28.912 (8), 33.323 (8)
Β(°)	-	105.543 (6)	-
V (Å^3)	9652.0 (2)	10514.6 (10)	27534 (13)
Z	4	4	4
Radiation type	Cu *K*α	Mo *K*α	Cu *K*α
μ (mm^{-1})	10.19	3.14	12.01
Crystal size (mm)	0.14 × 0.10 × 0.03	0.25 × 0.11 × 0.04	0.12 × 0.03 × 0.03
Data collection			
Diffractometer	SuperNova, Dual, Cu at zero, Atlas	Xcalibur, Eos	Rigaku Pilatus 200K
Absorption correction	Gaussian	Analytical	Multi-scan
$T_{\min}$, $T_{\max}$	0.789, 0.952	0.867, 0.976	0.268, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	159878, 10302, 8057	49850, 7555, 5446	231223, 49276, 34052
R_{int}	0.067	0.119	0.221
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.632	0.556	0.601
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.047, 0.131, 1.06	0.059, 0.108, 1.08	0.168, 0.447, 1.46
No. of reflections	10302	7555	49276
No. of parameters	575	602	1150
No. of restraints	130	104	275
H-atom treatment	Riding	Constrained	Constrained
	$w = 1/[\sigma^2(F_o^2) + (0.0541P)^2 + 53.4926P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.027P)^2 + 78.9178P]$ where $P = (F_o^2 + 2F_c^2)/3$	1.410
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	2.44, -2.11	0.83, -1.44	3.29, -5.05

	5	**6**
Chemical formula	$C_{94}H_{106}N_8O_2S_2U_2\cdot C_6H_6$	$C_{94}H_{97}N_8O_2SU_2\cdot C_7H_8$
M_r	1998.15	1971.05
Crystal system, space group	Monoclinic, $C2/c$	Triclinic, $P\bar{1}$
Temperature (K)	170	170
a, b, c (Å)	17.3745 (5), 34.2240 (8), 17.0130 (5)	15.9605 (3), 16.6905 (3), 18.0699 (4)
β (°)	112.037 (3)	67.132 (2), 86.551 (2), 82.450 (2)
V (Å^3)	9377.3 (5)	4396.61 (15)
Z	4	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	3.55	3.76
Crystal size (mm)	0.47 × 0.06 × 0.03	0.41 × 0.23 × 0.07
Diffractometer	Xcalibur, Eos	Xcalibur, Eos
Absorption correction	Multi-scan	Analytical
$T_{\min}$, $T_{\max}$	0.570, 1.000	0.035, 0.356
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	57840, 9563, 7001	108077, 17944, 14244
R_{int}	0.069	0.058
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.625	0.625
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.102, 0.80	0.058, 0.141, 1.05
No. of reflections	9563	17944
No. of parameters	519	1015
No. of restraints	24	98
H-atom treatment	H-atom parameters constrained	Riding
	$w = 1/[\sigma^2(F_o^2) + (0.0605P)^2 + 81.8008P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0399P)^2 + 47.5089P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	2.59, -1.04	7.56, -4.45

9. ^{1}H-NMR Spectra[1]

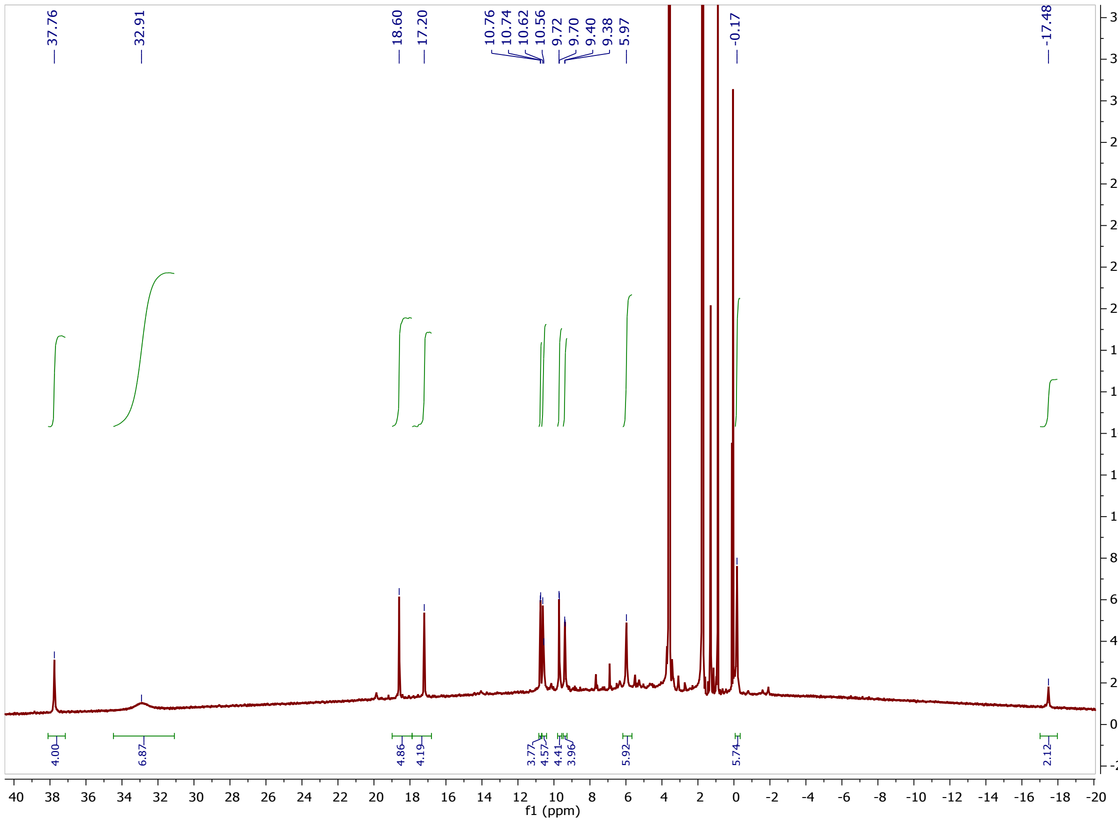
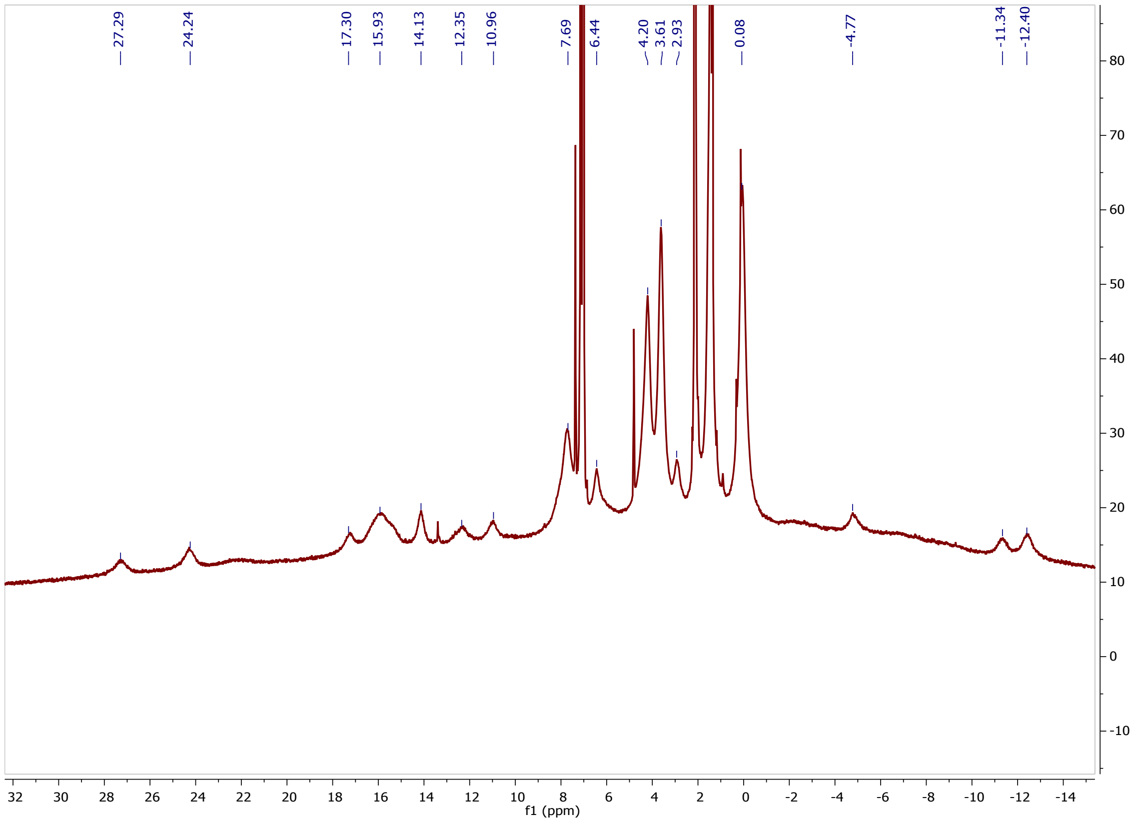


Figure 1: ^{1}H NMR spectrum of **1-K** in *d*$_8$-THF.



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[1] ^{1}H NMR spectra represent bulk isolated material.

Figure 2: ^{1}H NMR spectrum of **2-K** in d_8-toluene.

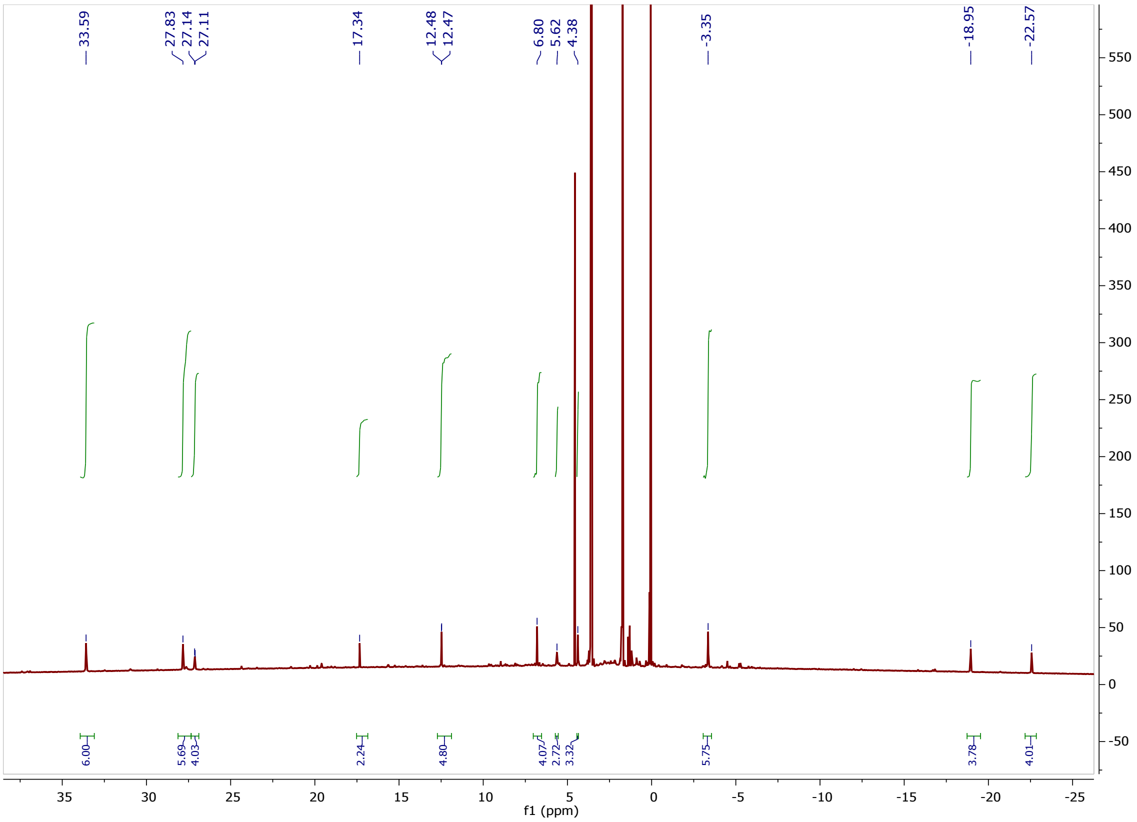

Figure 3: NMR spectrum of **3** in d_8-THF.

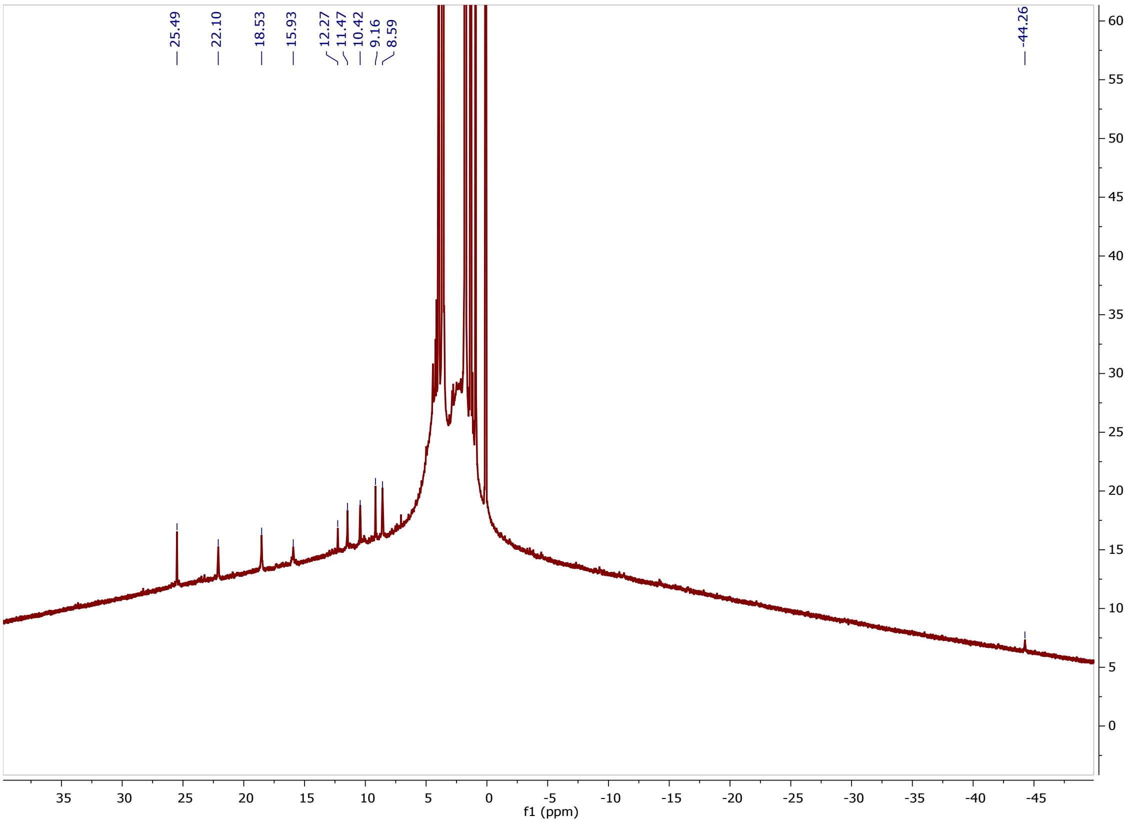

Figure 4: ^{1}H NMR spectrum of **4** in d_8-THF.

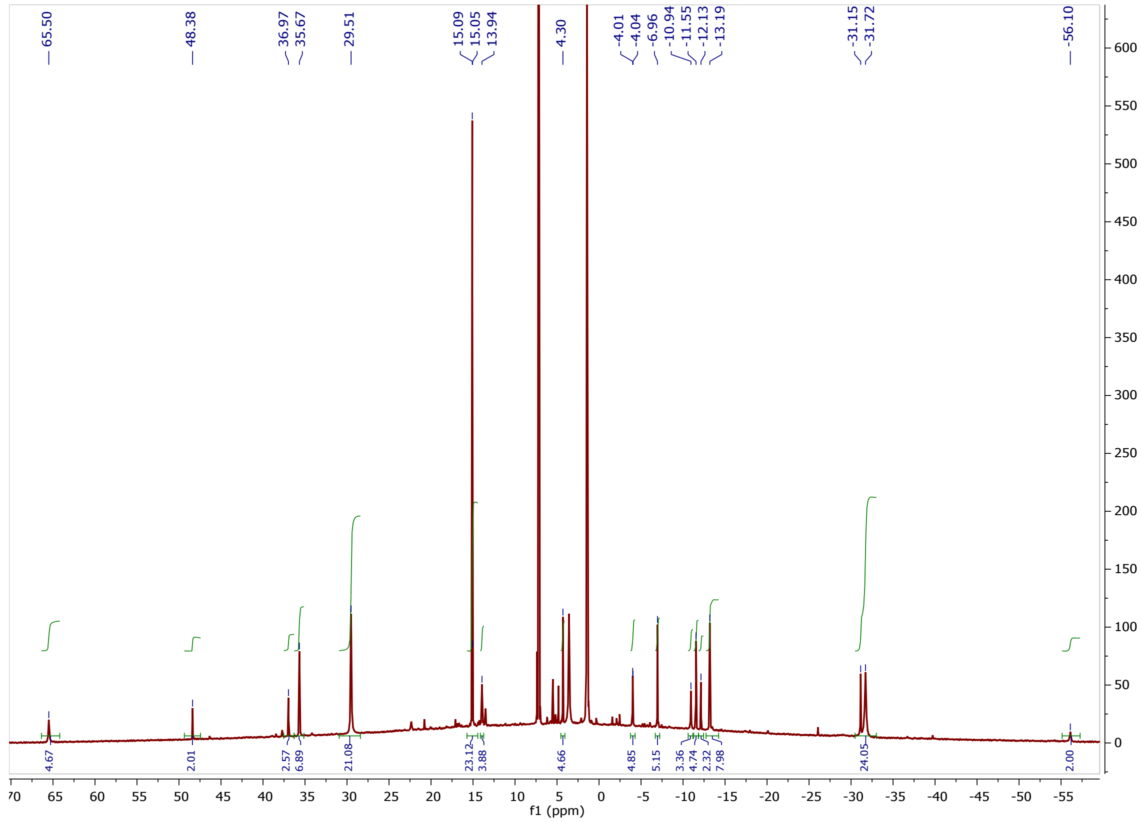

Figure 5: NMR spectrum of **5** in C_6D_6.

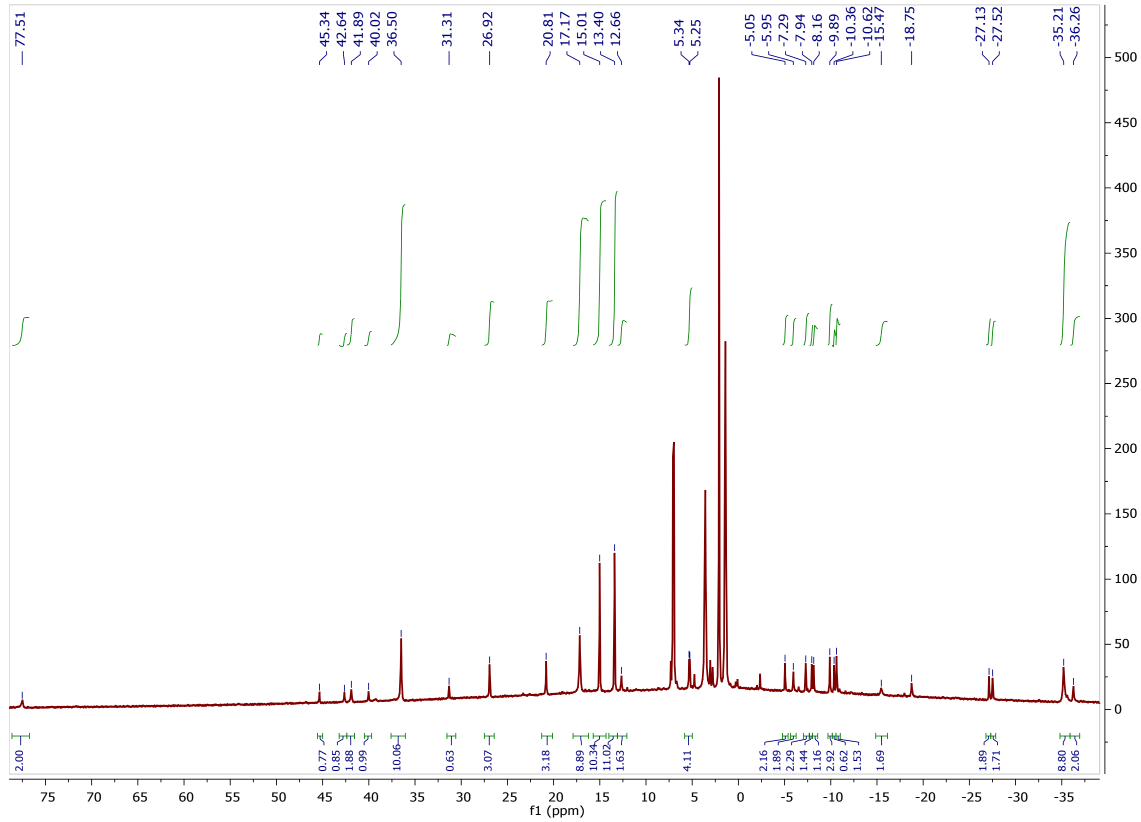

Figure 6: ^{1}H NMR spectrum of **6a** in d_8-toluene.

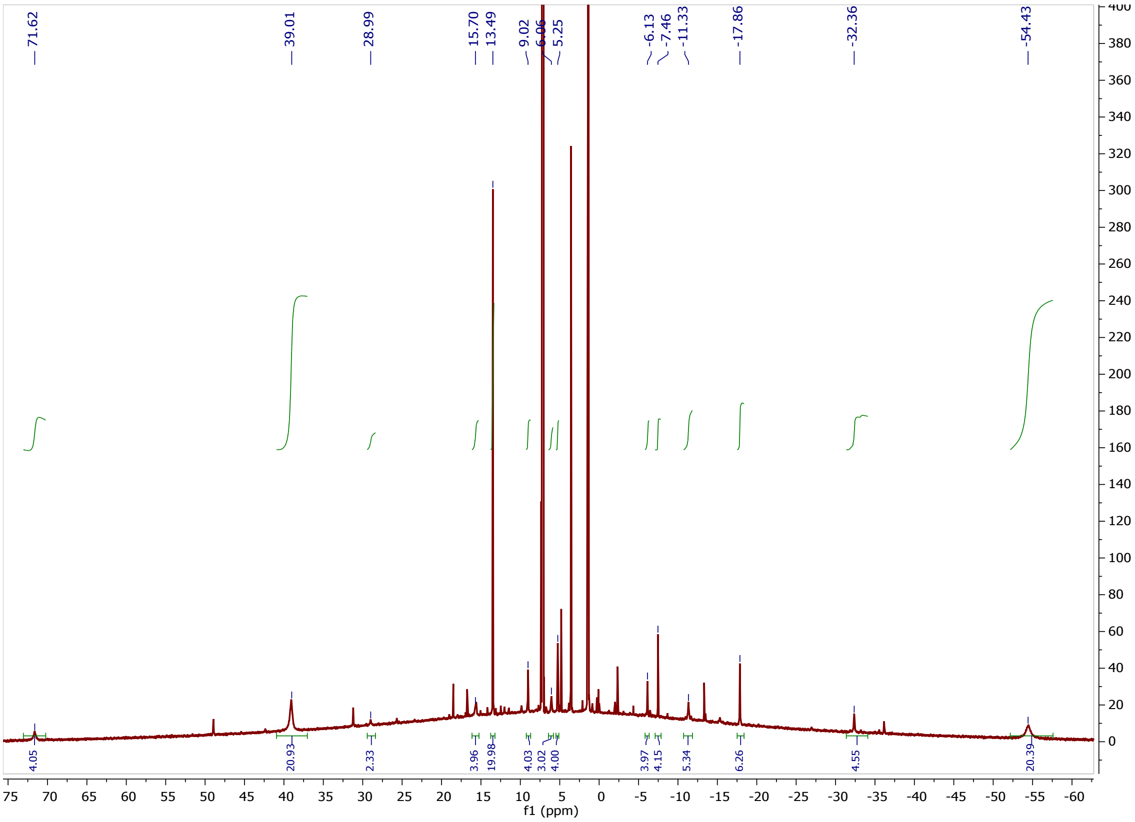

Figure 7: NMR spectrum of **6** in C_6D_6. Contains traces of **6a**.

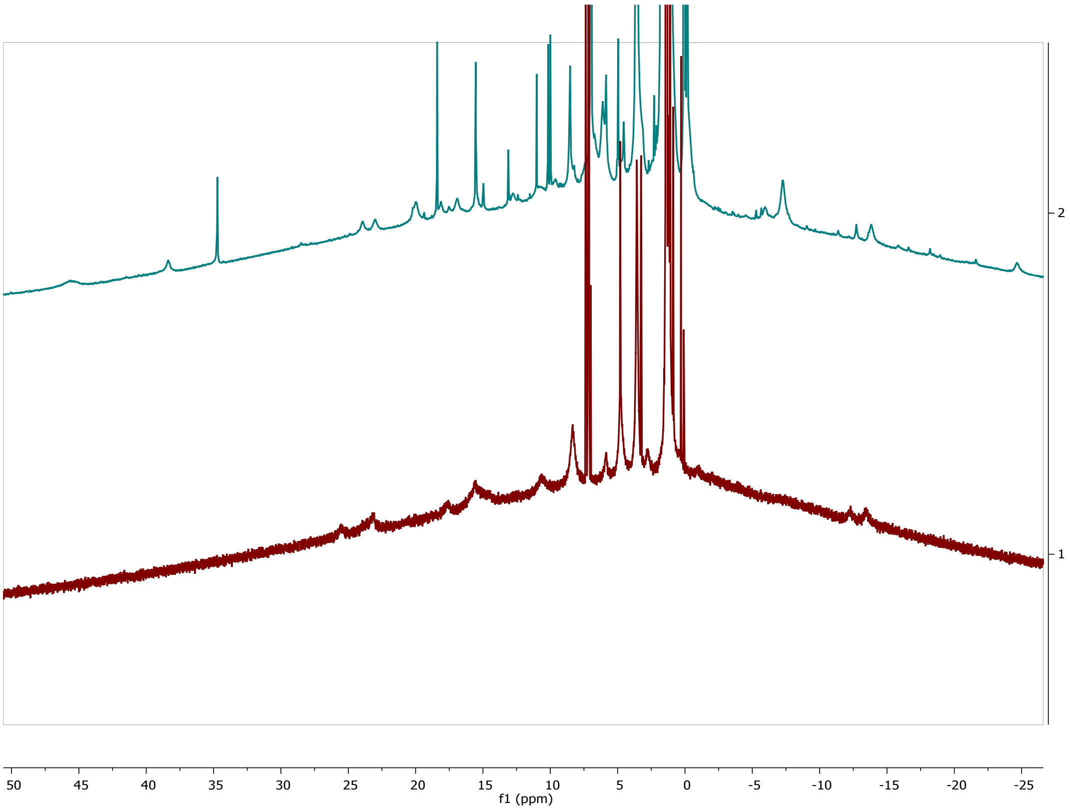

Figure 8: Stacked spectrum of reaction mixture from synthesis of **2-Na** (blue) in d_8-THF and isolated material (red) in C_6D_6 showing increased linewidths upon re-dissolution of isolated material in arene solvent.

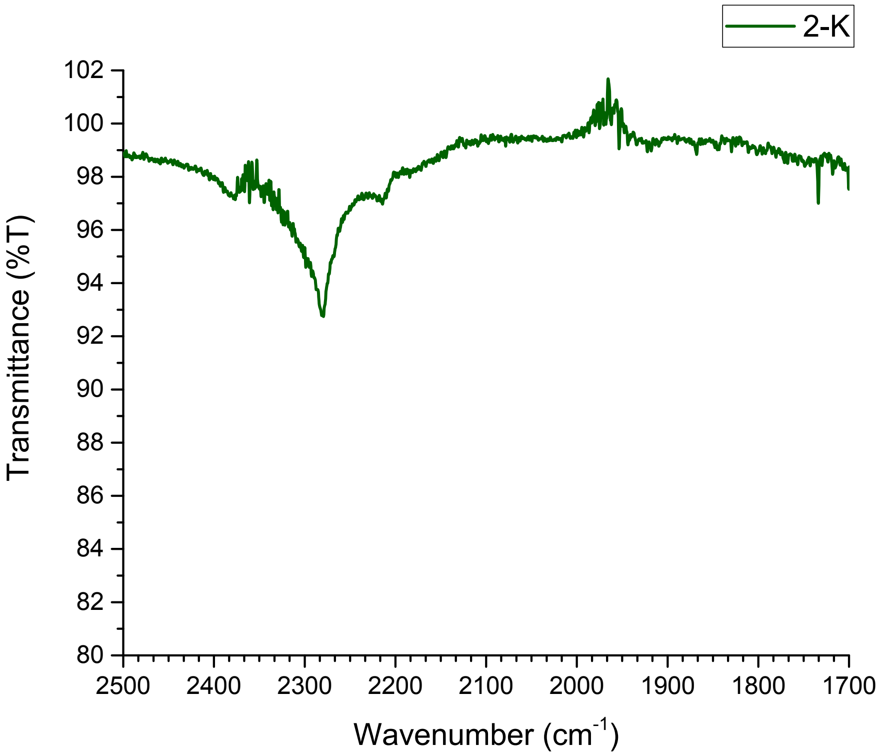

Figure 9: Solution state IR of 2-K in THF showing B-H stretching region.

10. References

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