Supplementary Material (ESI) for Dalton Transactions

Supporting Information For:

Isolation of a uranyl amide by "ate" complex formation

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Experimental

General. All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions either under high vacuum or an atmosphere of nitrogen or argon. Hexanes, diethyl ether, THF and toluene were dried by passage over activated molecular sieves using a Vacuum Atmospheres solvent purification system. DME was distilled from of Na/benzophenone before use, while C_6D_6 and THF-d_8 were dried over activated 4Å molecular sieves for 24 h. $UO_2Cl_2(THF)_3$ and LiS^tBu were prepared by the published procedures.[1, 2] All other reagents were purchased from commercial suppliers and used as received.

NMR spectra were recorded on either a Varian UNITY INOVA 400 MHz or 500 MHz spectrometer. ^1H NMR and $^{13}C\{^1H\}$ NMR spectra are referenced to external $SiMe_4$ using the residual protio solvent peaks as internal standards. $^7Li\{^1H\}$ NMR spectra referenced to an external saturated solution of LiCl in deuterium oxide. Elemental analyses were performed by the Microanalytical Laboratory at UC Berkeley. IR spectra were recorded on a Mattson Genesis FTIR spectrometer.

$Li(NC_5H_{10})$. To a solution of piperidine (3.0 mL, 30.4 mmol) in hexanes (20 mL) at 0 °C was added *n*-BuLi (1.6 M in hexanes, 19 mL, 30.4 mmol) dropwise via syringe. An off-white solid formed immediately. The reaction was stirred 24 hours and the solvent was decanted by means of a filter cannula. The solid was dried in vacuo to give 2.48 g of pale yellow powder. Yield 90%. ^1H NMR (500 MHz, 25 °C, C_6D_6): δ 3.20 (m, 6H, CH_2), 1.82 (m, 4H, CH_2). $^7Li\{^1H\}$ NMR (194 MHz, 25 °C, C_6D_6): δ -1.71 (s).

$Li(NH\text{-}2,6\text{-}Me_2C_6H_3)$. To a solution of 2,6-dimethylaniline (0.20 mL, 1.62 mmol) in hexanes (10 mL) was added *n*-BuLi (1.6 M in hexanes, 1.01 mL, 1.64 mmol) dropwise via syringe. A pale yellow solid formed immediately. The reaction was stirred 20 minutes and cooled to -25° C for 24 hours. The supernatant was then decanted and the remaining solid was dried in vacuo to give 179 mg of pale yellow solid. Yield 87 %. ^1H NMR (500 MHz, 25 °C, C_6D_6): δ 7.06 (m, 2H, *m*-H), 6.47 (m, 1H, *p*-H), 2.81 (s, 1H, NH), 2.27 (s, 6H, CH_3). $^7Li\{^1H\}$ NMR (194 MHz, 25 °C, C_6D_6): δ -0.978 (s).

$[Li(DME)][\{Li(DME)\}_2Cl][UO_2(NC_5H_{10})_3]_2$ (1). To a DME solution (2 mL) of $LiNC_5H_{10}$ (90 mg, 0.99 mmol) was added a THF solution (2 mL) of $UO_2Cl_2(THF)_3$ (138 mg, 0.25 mmol). An immediate color change from pale-yellow to dark-brown was observed. After stirring for 10 minutes the solution was filtered through a Celite column (2 cm × 0.5 cm) supported on glass wool. The solution was then layered with hexanes (3 ml) and cooled to -25˚ C for 24 hours resulting in the deposition of clear crystals. The mixture was filtered through a Celite column (2 cm × 0.5 cm) supported on glass wool. The supernatant was then concentrated and layered with hexanes (3 mL) and cooled to -25° C for 24 hours resulting in the deposition of a black crystalline solid. 82 mg, 48% yield. Anal. Calcd for $C_{42}H_{90}ClLi_3N_6O_{10}U_2$: C, 36.78; H, 6.61; N, 6.13. Found: C, 36.71; H, 6.62; N, 5.63. ^1H NMR (500 MHz, 25° C, C_6D_6): δ 7.81 (br s, 16H, terminal α CH_2), 7.00 (br s, 8H, bridging α CH_2), 3.18 (s, CH_3 DME), 2.99 (s, CH_2 DME), 2.38 (br s, 4H, bridging CH_2), 2.20 (br s, 8H, bridging CH_2), 2.12 (br s, 16H, terminal CH_2), 2.04 (s, 8H, terminal CH_2). $^7Li\{^1H\}$ NMR (194 MHz, 25° C, C_6D_6): δ -3.39 (s). IR (KBr pellet, cm^{-1}): 1645(w), 1587(w), 1548(w), 1530(w), 1465(sh), 1448(s), 1439(s), 1354(s), 1332(m), 1317(sh), 1283(sh), 1268(m), 1243(m), 1192(s), 1152(sh), 1133(sh), 1109(s), 1100(s), 1021(s), 978(w), 955(w), 923(w), 896(s), 868(s), 848(s), 805(s), 709(m), 667(w), 603(m), 582(m).

[Li(THF)(Et_2O)][UO_2(NH-2,6-$Me_2C_6H_3$)$_4$] (2). To a cold (-25° C) Et_2O solution (2 mL) of $UO_2Cl_2(THF)_3$ (26 mg, 0.047 mmol) was added a cold Et_2O solution (2 mL) of LiNH-2,6-$Me_2C_6H_3$ (23 mg, 0.18 mmol). After stirring for 10 minutes the solution was filtered through a Celite column (2 cm × 0.5 cm) supported on glass wool. The resulting red-brown solution was layered with hexanes (3 ml) and cooled to -25° C for 24 hours resulting in the deposition of a small amount of dark red solid. Recrystallization of this solid by vapor diffusion of hexanes into an Et_2O solution provided a few dark red rods that were of X-ray quality (Yield: < 2%).

[Li(DME)]$_2$[UO_2(S^{t}Bu)$_4$] (3). A solution of LiS^{t}Bu (57 mg, 0.59 mmol) in Et_2O was added to a yellow solution of $UO_2Cl_2(THF)_3$ (54 mg, 0.096 mmol) in DME at -25 °C. Over the course of 5 minutes, the solution changed from orange to dark green to deep orange-red in colour. After stirring for 30 min the resulting solution was filtered though a Celite column supported on glass wool (0.5 cm × 2 cm). The filtrate was concentrated in vacuo, layered with hexanes (2 mL), and stored at -25 °C for 78 hours resulting in the deposition of bright orange crystals and a white powder (presumably LiCl). The white solid was removed by washing with DME (2 × 0.5 mL), providing 58 mg of orange crystals. A second batch of crystals was isolated from the supernatant in a similar fashion (18 mg). Total: 76 mg, 96% yield. Anal. Calcd for $UO_6S_4Li_2C_{24}H_{56}$: C, 35.12; H, 6.88. Found: C, 36.26; H, 6.97. ^{1}H NMR (THF-d_8, 25 °C, 400 MHz): δ 1.75 (s, 36H, CMe_3), 3.27 (s, 12H, CH_3), 3.43 (s, 8H, CH_2). ^{7}Li{^{1}H} NMR (THF-d_8, 25 °C, 155 MHz): δ 2.33 (s). IR (KBr pellet, cm^{-1}): 1514(w), 1504(sh w), 1470(vs), 1455(vs), 1409(m), 1386(m), 1324(w), 1308(w), 1279(m), 1244(m), 1210(m), 1194(s), 1157(vs), 1119(vs), 1111(sh s), 1080(vs), 1076(m), 1019(m), 990(w), 955(w), 940(w), 926(w), 891(vs, ν_{asym}(U=O)), 868(vs), 836(m), 827(sh m), 589(s), 576(sh m), 562(sh m), 535(sh m), 524(sh m), 515(sh m), 499(sh m), 460(s), 455(sh s), 445(sh s), 432(s), 417(sh s), 410(s).

X-ray Crystallography. Crystals of **1**·½C_6H_{14} or **2** were mounted on a glass fiber under Paratone-N oil. Data collection was carried out on a Bruker 3-axis platform diffractometer with SMART-1000 CCD detector. The instrument was equipped with graphite monochromatized MoKα X-ray source (λ = 0.71073 Å). All data were collected at 150(2) K using Oxford nitrogen gas cryostream system. A hemisphere of data was collected using ω scans, with 10-second (for **1**·½C_6H_{14}) or 20-second (for **2**) frame exposures, and 0.3° frame widths. SMART[3] was used to determine the cell parameters and data collection. The raw frame data were processed using SAINT.[4] The empirical absorption correction was applied based on Psi-scan. Subsequent calculations were carried out using SHELXTL.[5] The structures were solved using Direct methods and difference Fourier techniques. All hydrogen atom positions were idealized, and rode on the atom of attachment. The final refinement included anisotropic temperature factors on all non-hydrogen atoms. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL. A summary of relevant crystallographic data for **1**·½C_6H_{14} and **2** is presented in Table S1.

Table S1. X-ray Crystallographic Data for Complexes **1**·½C_6H_{14} and **2**.

	1·½C_6H_{14}	**2**
Empirical formula	$C_{45}H_{97}ClLi_3N_6O_{10}U_2$	$C_{48}H_{76}Li_2N_4O_6U$
Crystal Habit, color	irregular, black	sheet, red
Crystal size (mm)	0.6 × 0.4 × 0.3	0.5 × 0.25 × 0.2
Crystal system	triclinic	triclinic
Space group	P-1	P-1
Volume (Å^3)	2931.8(5)	1220.0(6)
a (Å)	12.5313(12)	9.001(3)
b (Å)	12.7238(13)	11.766(4)
c (Å)	19.6221(19)	12.875(4)
α (°)	83.505(2)	115.047(4)
β (°)	73.948(2)	92.432(4)
γ (°)	77.607(2)	96.819(4)
Z	2	1
Formula weight (g/mol)	1414.62	1057.04
Density (calculated) (Mg/m^3)	1.602	1.439
Absorption coefficient (mm^{-1})	5.615	3.375
F_{000}	1398.0	538
Total no. reflections	25453	10192
Unique reflections	11708	4843
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0441	R1 = 0.0303
	wR2 = 0.1106	wR2 = 0.0752
Largest diff. peak and hole (e$^-$Å^{-3})	3.568 and -1.460	2.255 and -1.516
GOF	1.009	1.047

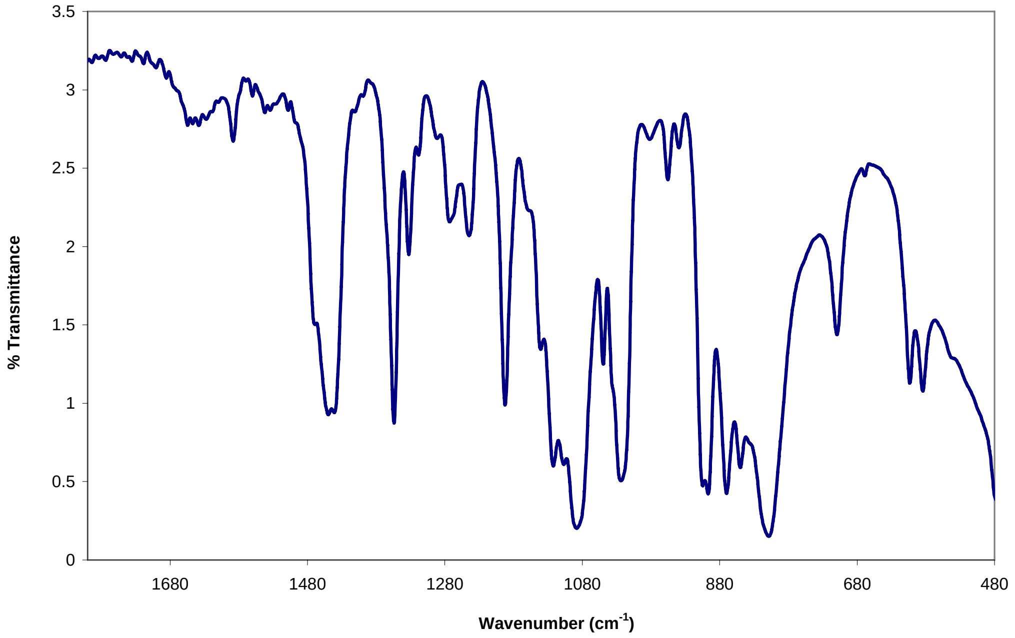

Figure S1. IR spectrum (KBr pellet) of **1**.

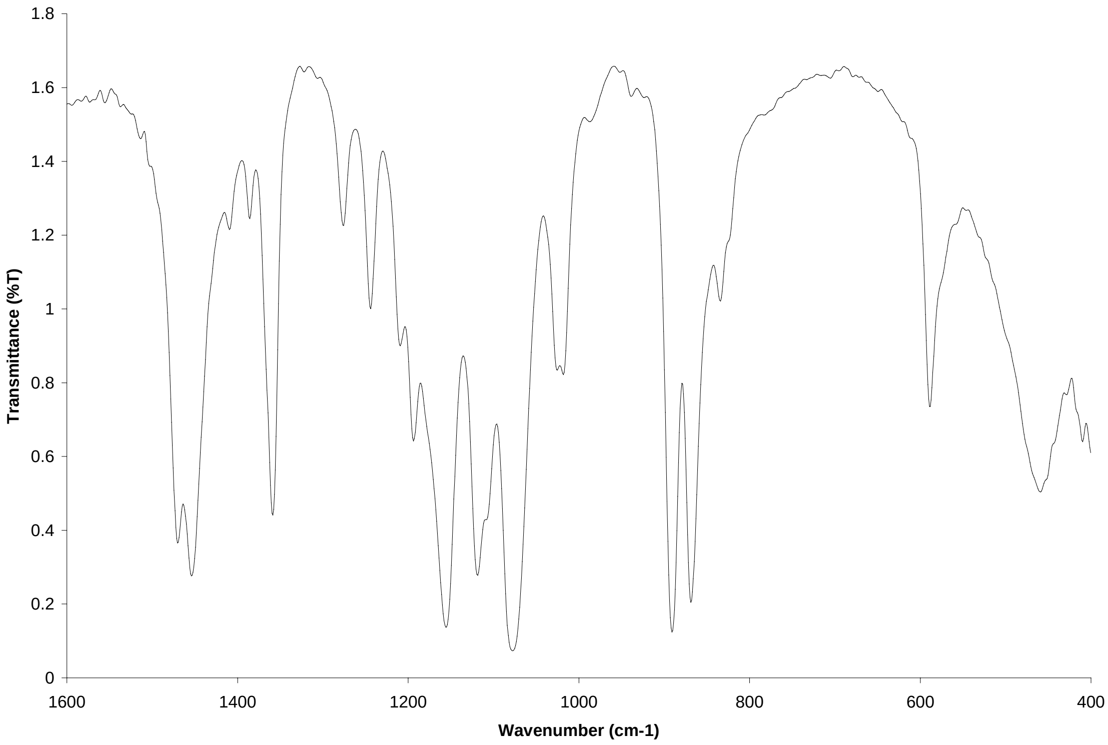

Figure S2. IR spectrum of complex **3** (as KBr mull).

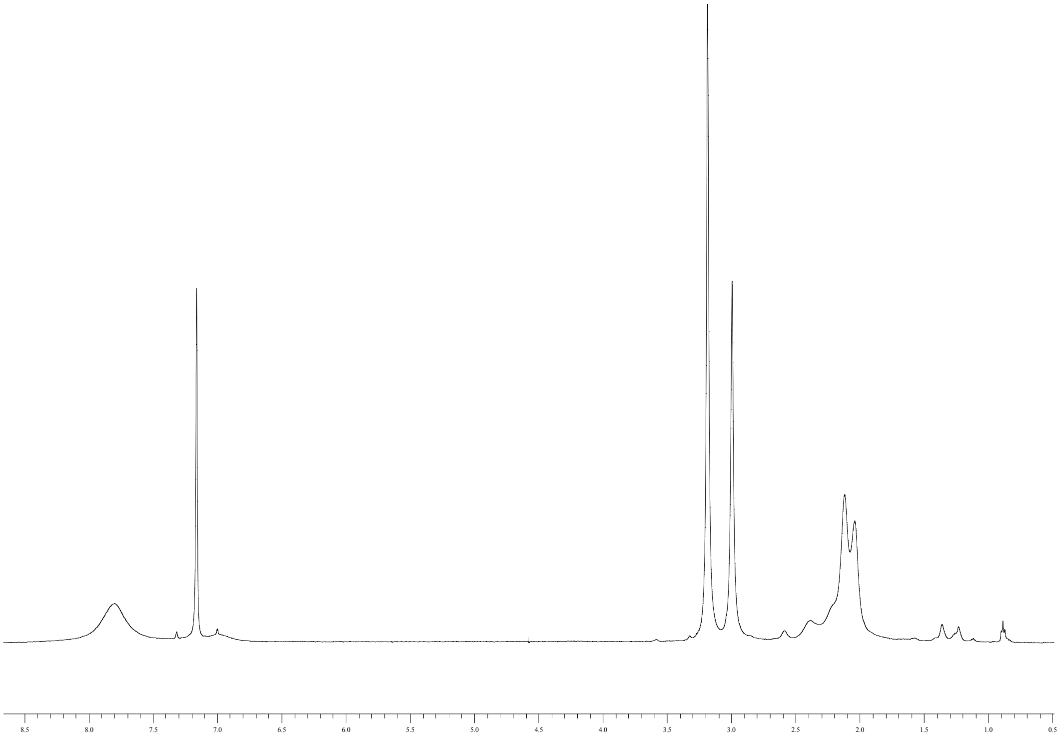

Figure S3. ^{1}H NMR spectrum (C_6D_6) of **1**.

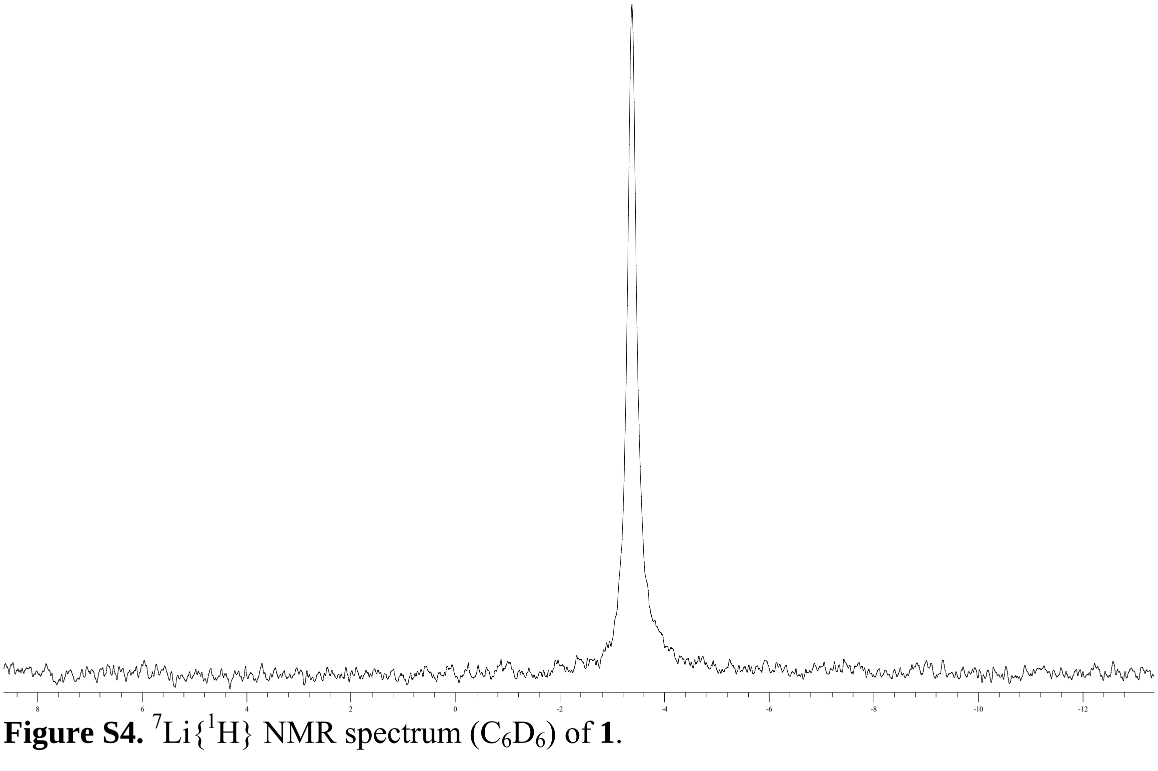

Figure S4. ^{7}Li{^{1}H} NMR spectrum (C_6D_6) of **1**.

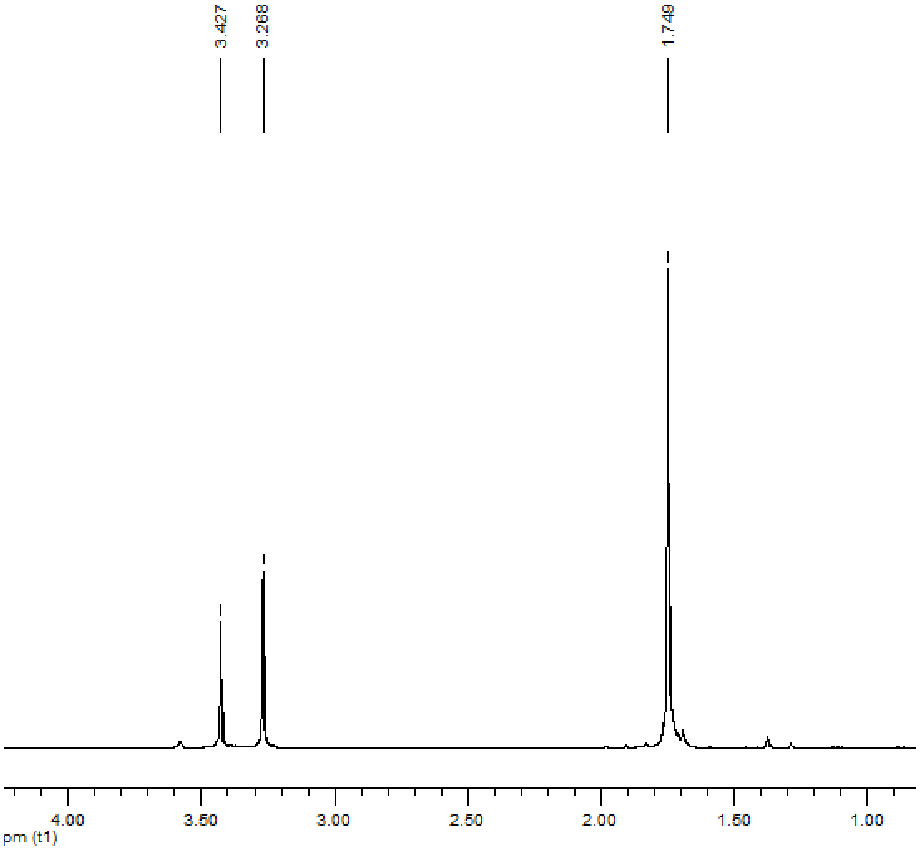

Figure S5. ^{1}H NMR spectrum of **3** in THF-d_8.

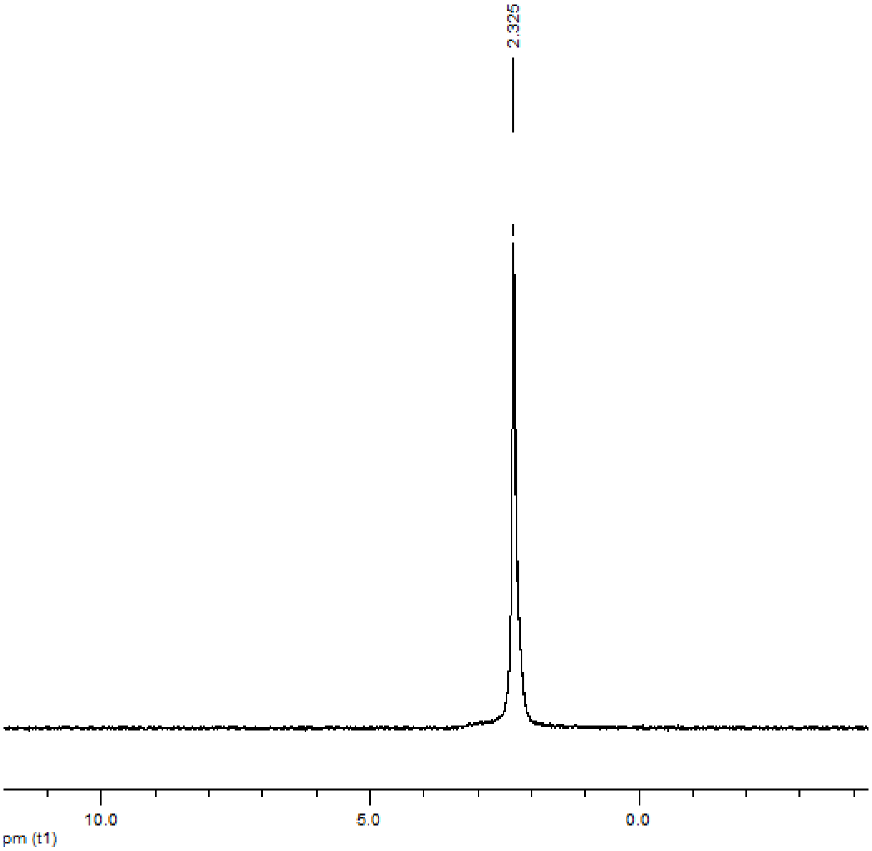

Figure S6. ^{7}Li{^{1}H} NMR spectrum of **3** in THF-d_8.

References

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3. SMART Software Users Guide, Bruker Analytical X-ray Systems Inc, Madison, WI, 1999.
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