

^6Li Diffusion-Ordered NMR Spectroscopy (DOSY) and Applications to Organometallic Complexes

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Supporting Information

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Experimental Section

1. Procedures for NMR Experiments

NMR samples were prepared in tubes sealed with serum septa and Parafilm[®]. Tubes were evacuated *in vacuo*, flame dried, and filled with argon. Samples were prepared as about 50 mg of compound in 600 μ L toluene-*d*₈. NMR experiments were performed at 25 °C. ¹H chemical shifts were referenced to toluene-*d*₈ at 7.09 ppm. ⁶Li chemical shifts were calibrated to saturated LiBr in D₂O as an external reference at 0 ppm. DOSY experiments were performed on a Bruker DRX400 spectrometer equipped with an Accustar z-axis gradient amplifier and an ATMA BBO probe with a z-axis gradient coil. Maximum gradient strength was 0.214 T/m. A program for ⁶Li DOSY was adapted from the standard Bruker dstebpgp3s program, using double stimulated echo, LED, with bipolar gradient pulses and 3 spoil gradients. Diffusion time was 50 ms and rectangular gradient pulse duration was 2000 μ s. Gradient recovery delays were 200 μ s. Individual rows of the quasi-2-D diffusion databases were phased and baseline corrected.

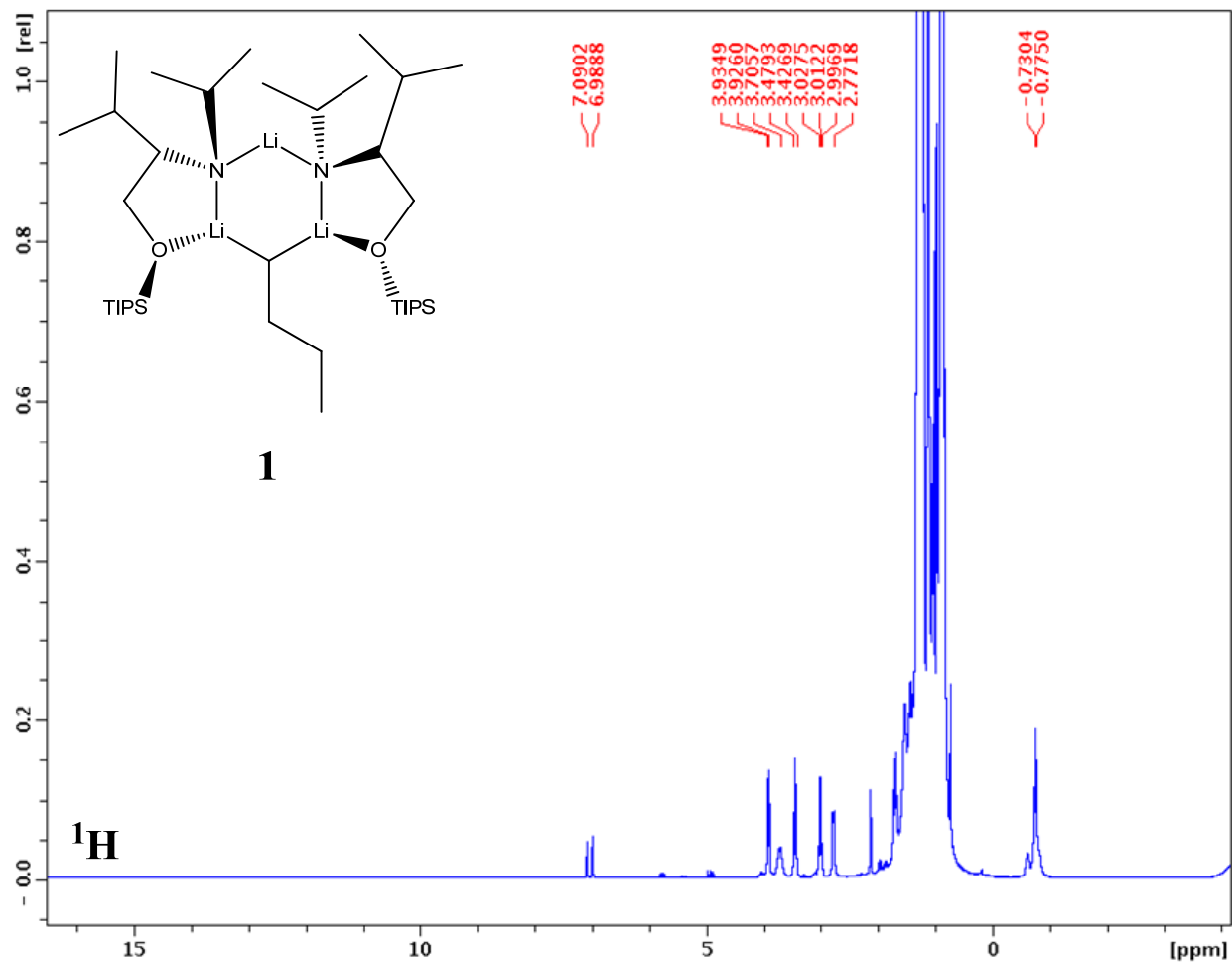
2. Synthesis of *n*-Bu⁶Li

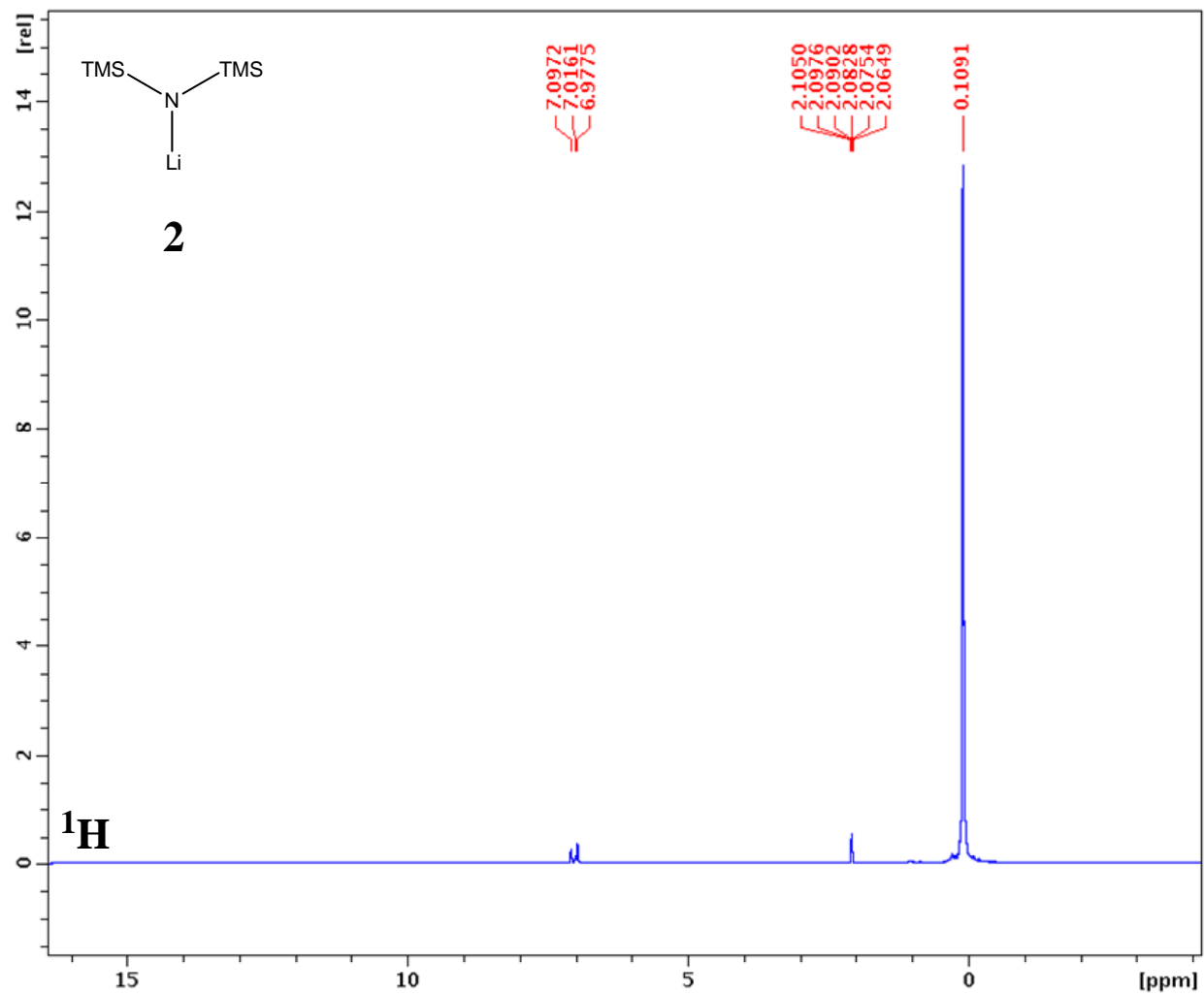
About 1.0 g (166 mmol) of finely cut ⁶Li metal was placed into a flame dried flask flushed with argon. The flask was fitted with a serum septum and sealed with Parafilm[®]. The metal was washed with dry pentane by adding 10 mL of pentane to the flask via syringe. The flask was then placed in ultrasound for 5 minutes. Pentane was then removed via syringe. This was repeated until the washings were clear, with no white solid suspended in the wash (3 times). Dry heptane (15 mL) was added to the flask, followed by 9.6 g (10.9 mL, 104 mmol) of 1-chlorobutane, dropwise. This mixture was kept under ultrasound overnight at room temperature, after which a purple slurry was obtained. The suspension was transferred via syringe to a clean, flame dried vial flushed with argon and fitted with a serum septum. The vial was centrifuged until the solid was separated. The supernatant was transferred to a second identical vial and centrifuged again. The supernatant was transferred to a third identical vial. This *n*-Bu⁶Li solution in heptane was titrated using 2,2-diphenylacetic acid in tetrahydrofuran and found to be 1.04 M.

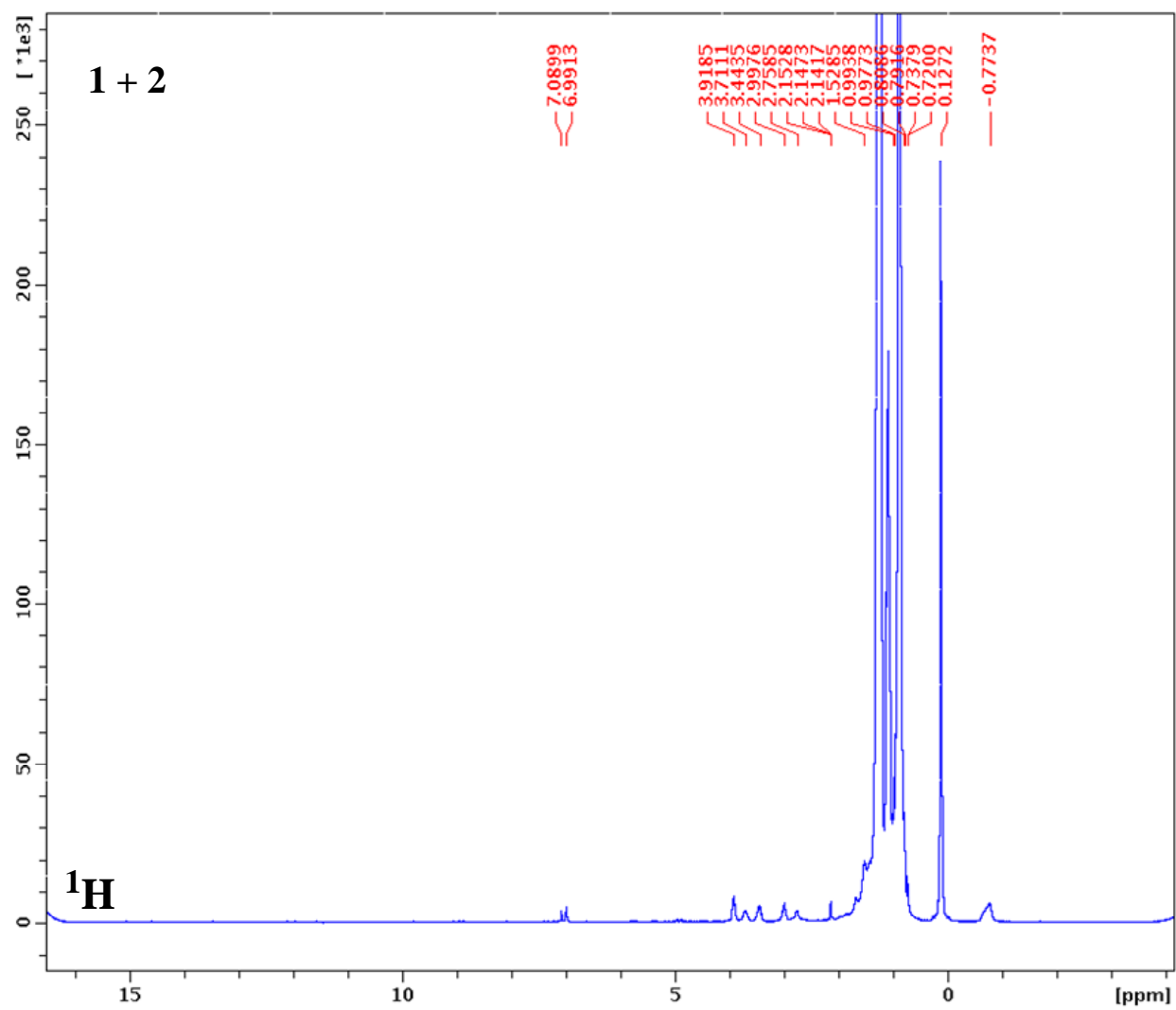
3. Synthesis of ⁶LiHMDS

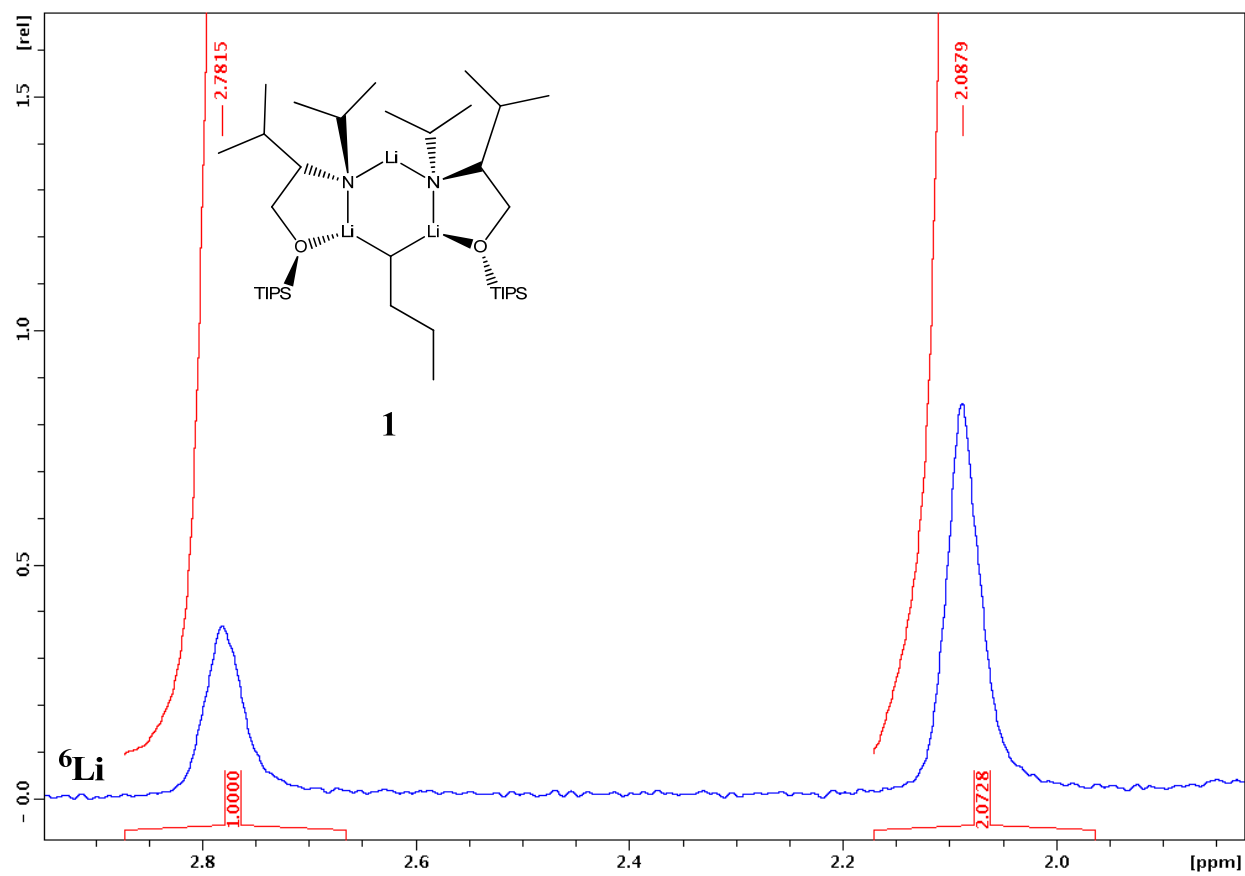
Crystals of ⁶LiHMDS were prepared from hexamethyldisilazane (HMDS) and *n*-Bu⁶Li by cooling a flame dried and argon filled microwave tube equipped with a stir bar to 0°C in an ice bath and adding 168 mg of HMDS (221 μ L, 1.04 mmol). To this was added dropwise 66 mg *n*-Bu⁶Li as a 1.04 M solution in heptane (1.00mL, 1.04 mmol). The solution became cloudy within minutes, then cleared. The solution was stirred for 5 minutes, then placed in a -50°C freezer for 4 hours, after which clear crystals were obtained.

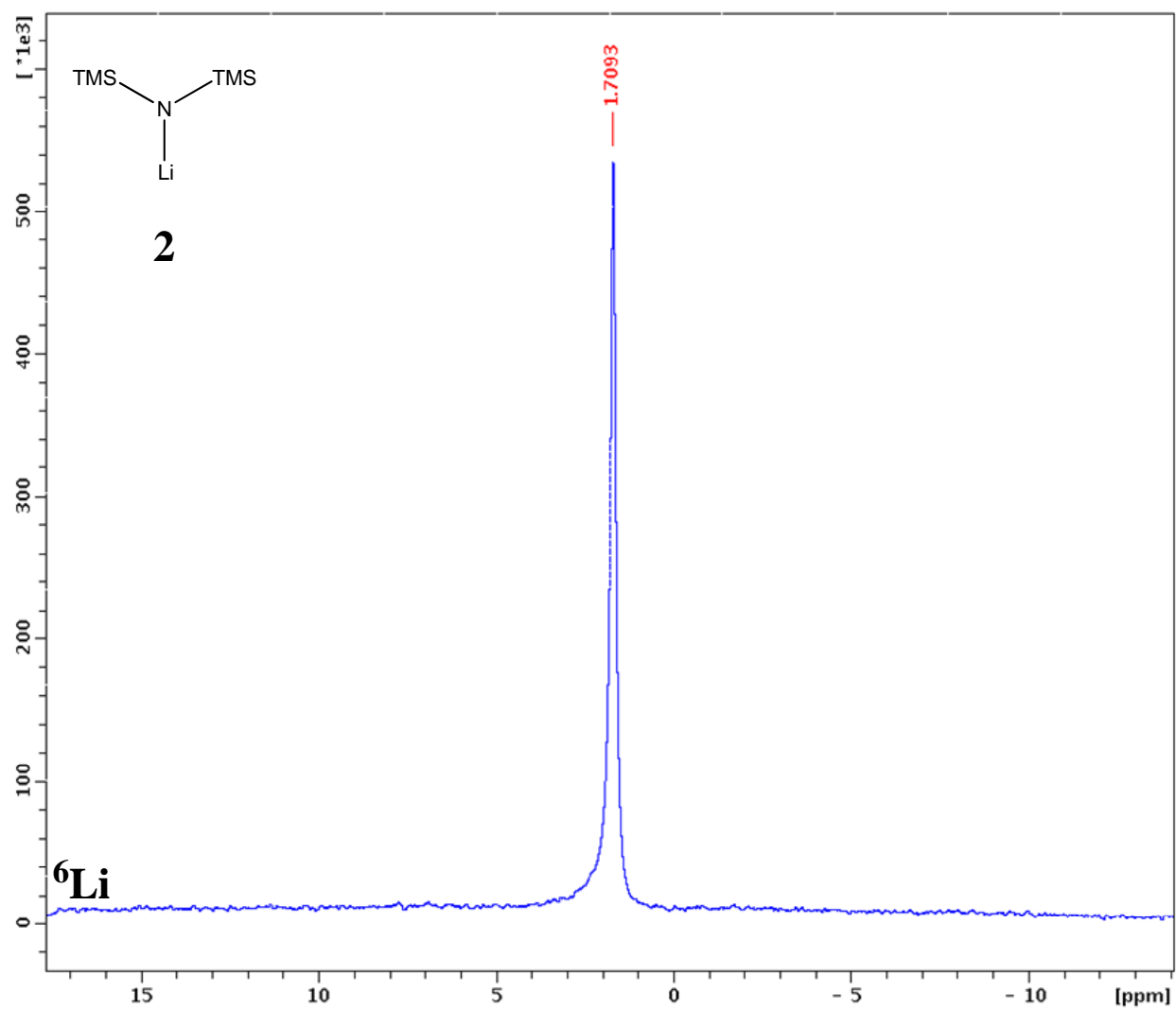
These were washed twice with dry -50°C pentane, and then dissolved in 800 μL of toluene- d_8 . A fraction of this solution was required for NMR experiments.

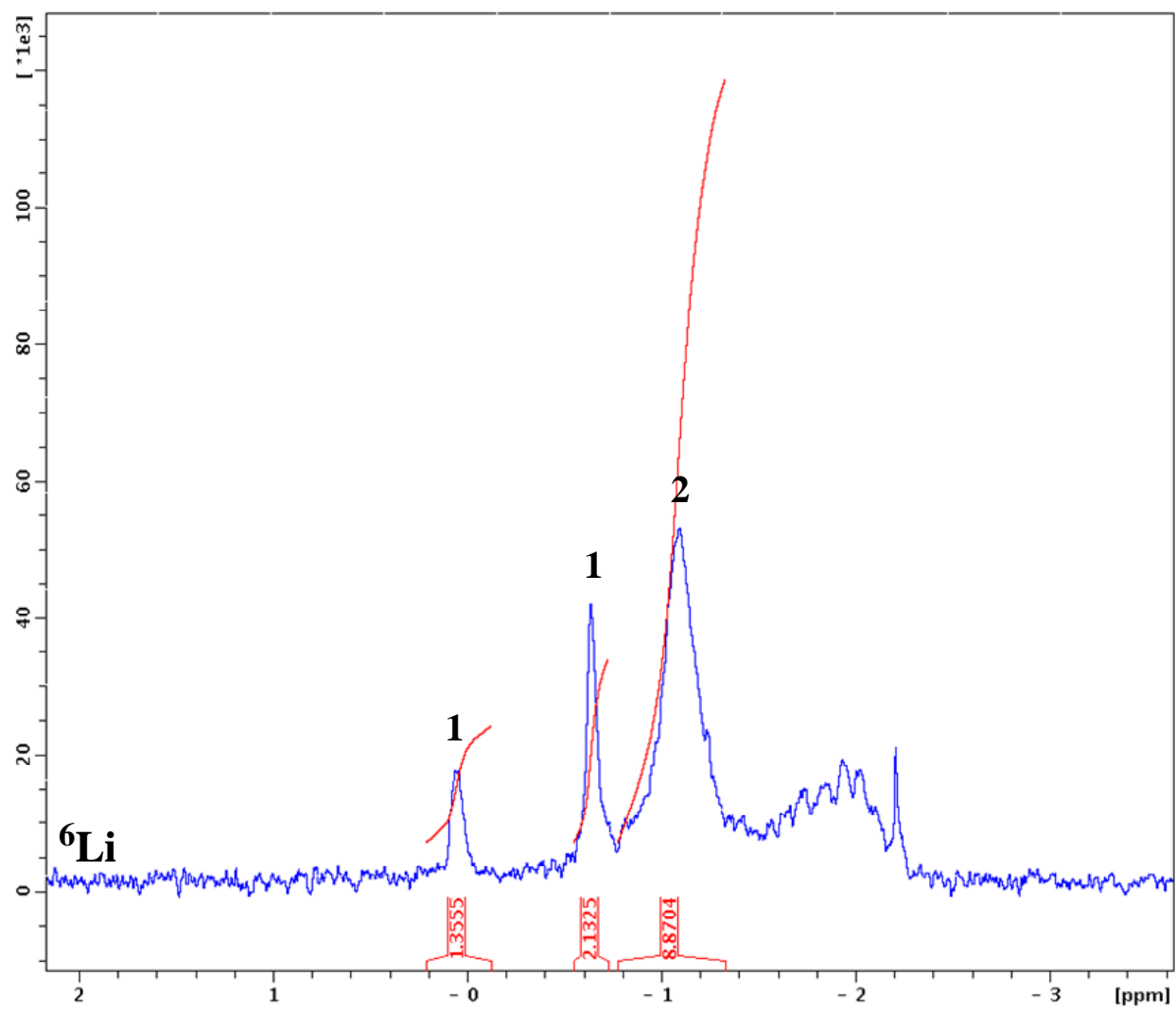


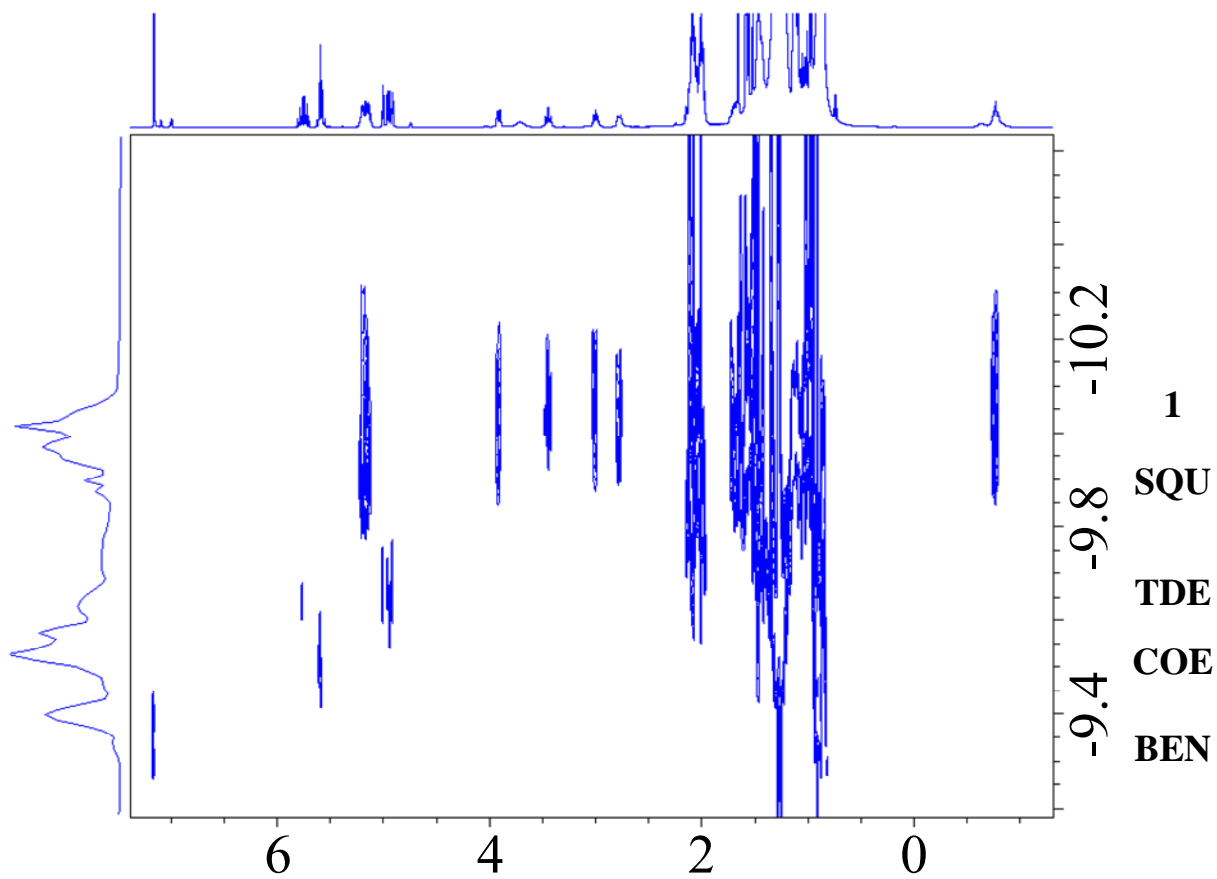






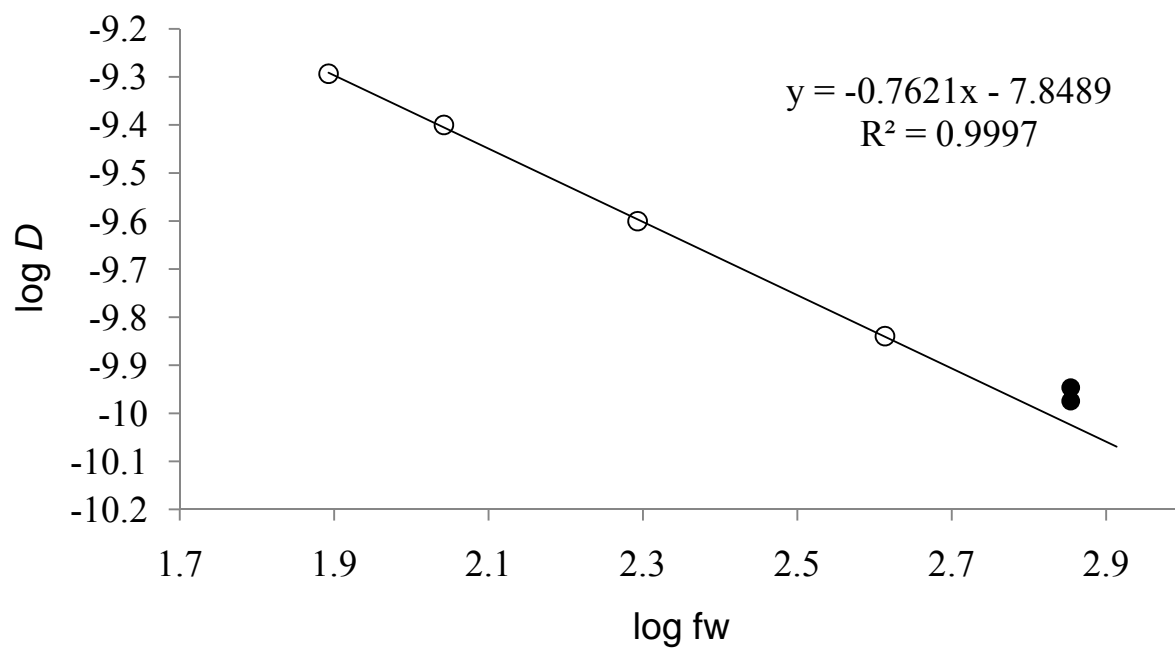


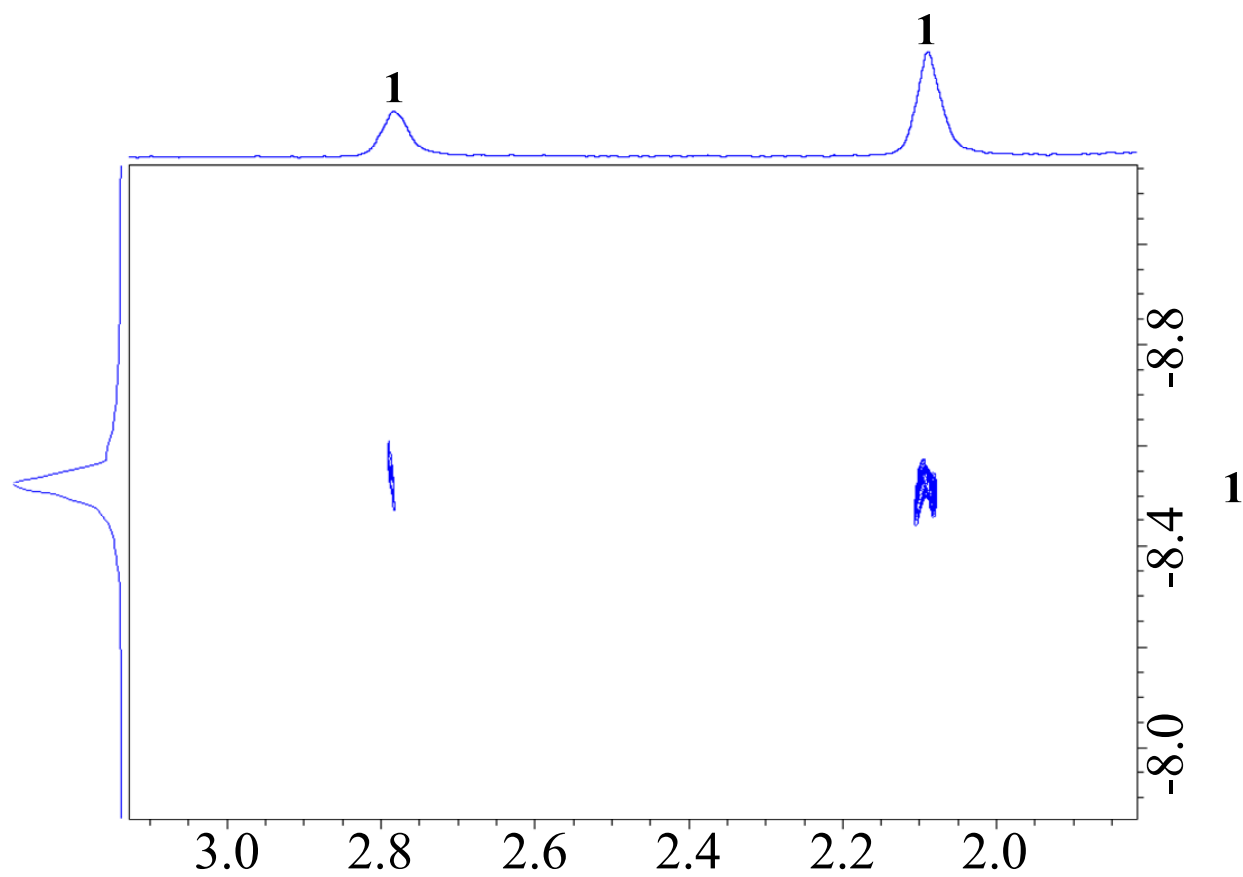


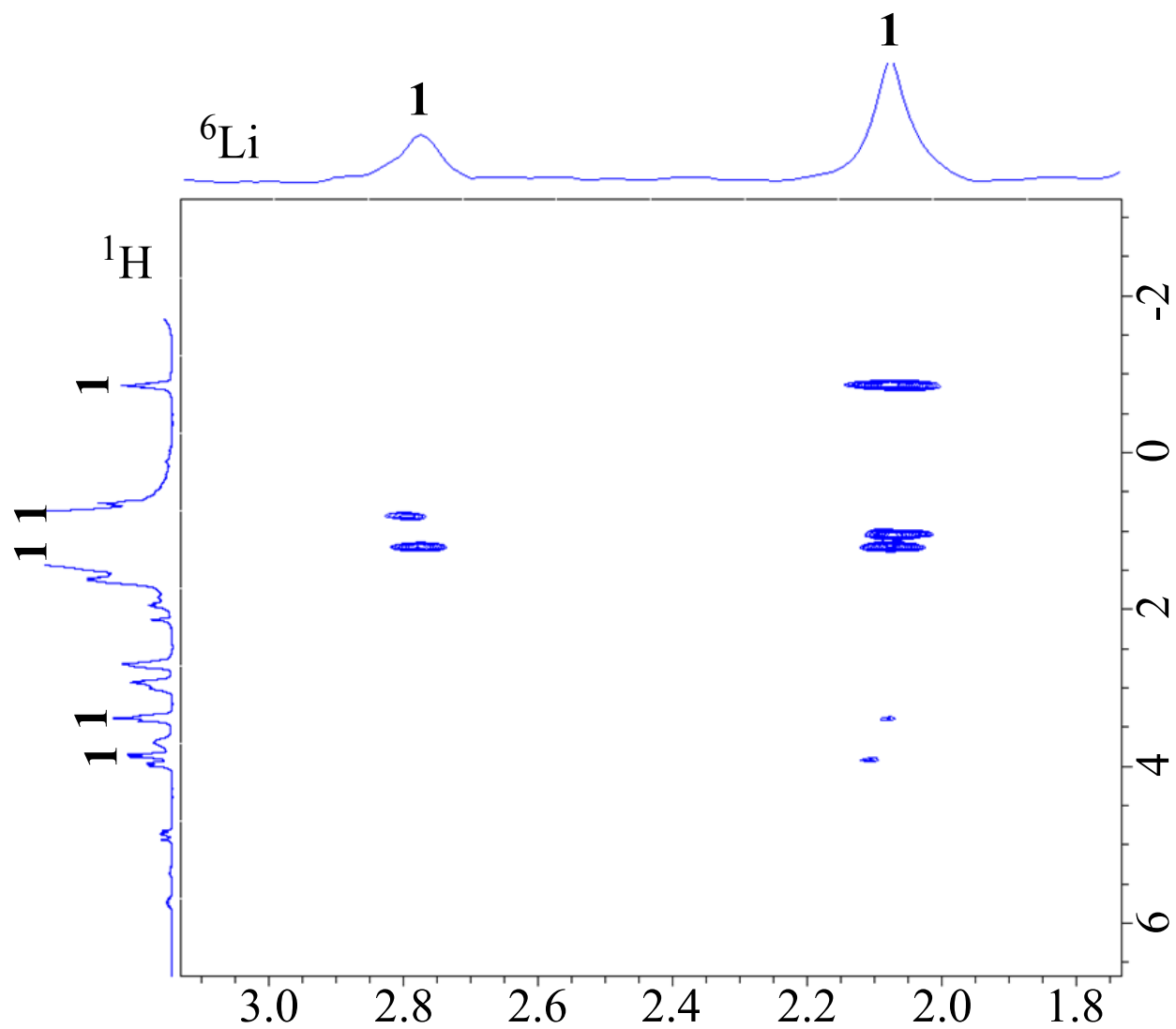


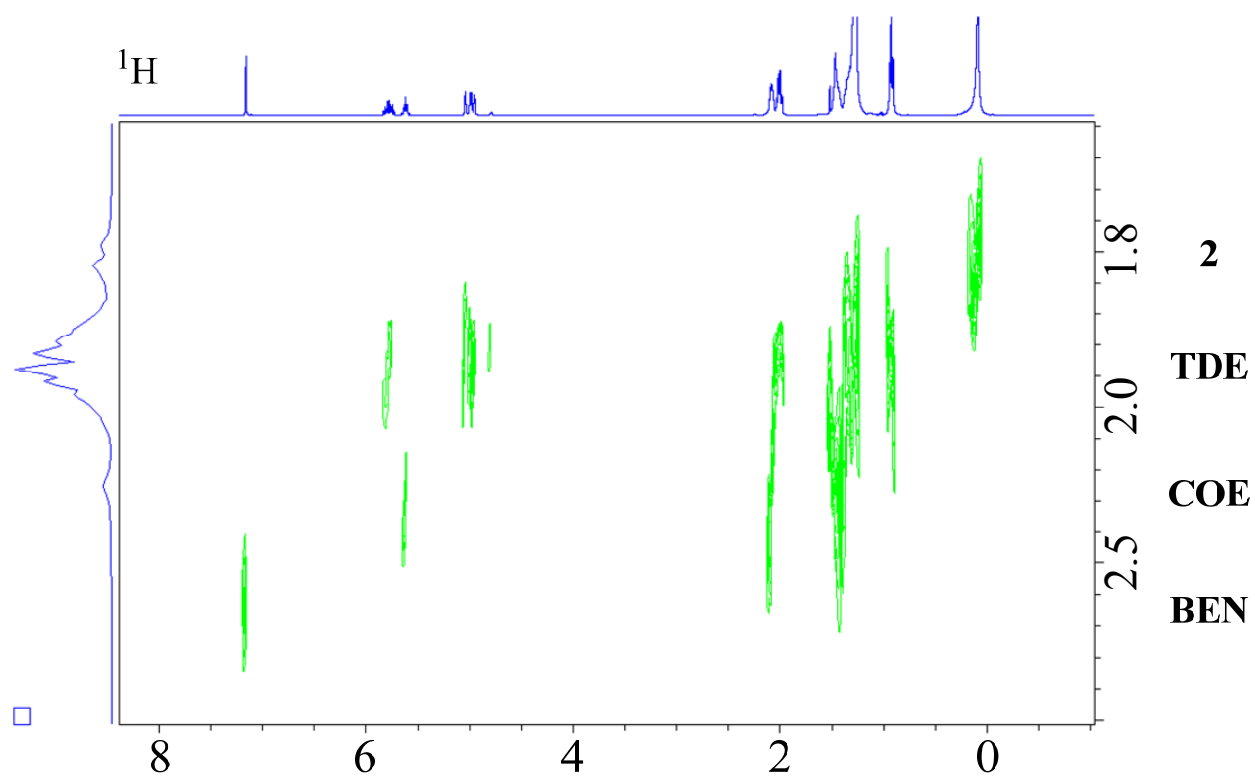
compound	fw	$D \times (10^{10})$	log fw	log D	fw*	% error
BEN	78.1	5.086	1.893	-9.294	79	-1
COE	110.2	3.980	2.042	-9.400	109	2
TDE	196.4	2.510	2.293	-9.600	199	-1
SQU	410.7	1.447	2.614	-9.840	409	<1
Ligand	714.7	1.131	2.854	-9.947	566	21
<i>n</i> -Bu ⁶ Li	714.7	1.060	2.854	-9.975	616	14

A = -0.7621, C = -7.8489









compound	fw	$D \times (10^{10})$	log fw	log D	fw*	% error
BEN	78.1	3.090	1.893	-10.510	76	2
COE	110.2	2.399	2.042	-10.620	115	-4
TDE	196.4	1.738	2.293	-10.760	193	1
LiHMDS (dimer)	334.7	1.230	2.525	-10.910	339	-1
A = -0.6175, C = -9.348						

