

**Lithium confinement and dynamics in hexagonal and monoclinic tungsten oxide
nanocrystals: ^7Li solid state NMR study**

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Table S1. Fit data for deconvoluted ¹H-MAS-NMR spectra.

Sample	Position / ppm	Intensity a.u.	Area a.u.	FWHM / Hz	Ratio L/G	gof ^a
h-LiATB@RT	6.83	58.56	107.70	590.27	0.00	99.9 %
	5.25	319.99	655.59	629.52	0.40	
	2.13	45.44	158.08	1153.27	0.20	
	0.91	120.46	217.60	580.93	0.01	
h-LiATB@300	6.64	181.96	225.38	342.91	0.89	98.0 %
	3.69	17.73	41.66	750.00	0.08	
	0.99	1.55	1.96	398.39	0.00	
m-LiTB@500	4.28	88.25	166.80	594.00	0.10	92.6 %
	1.11	4.10	2.98	224.00	0.00	

a. Overlap of fit profile and real spectra

Table S2. Fit data for deconvoluted ^7Li -MAS-NMR spectra.

Sample	Position / ppm	Intensity a.u.	Area a.u.	FWHM / Hz	Ratio L/G	gof ^a
h-LiATB@RT	-0.46	1204.31	2861.52	263.38	1.00	85 %
	-2.18	757.01	2041.71	315.60	1.00	
h-LiATB@300	-0.36	1140.38	3199.60	330.90	0.82	92 %
	-2.41	563.36	1190.91	258.50	0.54	
m-LiTB@500	-0.45	327.40	830.93	283.93	1.00	91 %
	-1.44	261.98	788.98	351.88	1.00	
	-2.20	371.64	908.90	314.57	0.12	

a. Overlap of fit profile and real spectra

$$V(x) = u * L(x) + (u - 1) * G(x)$$

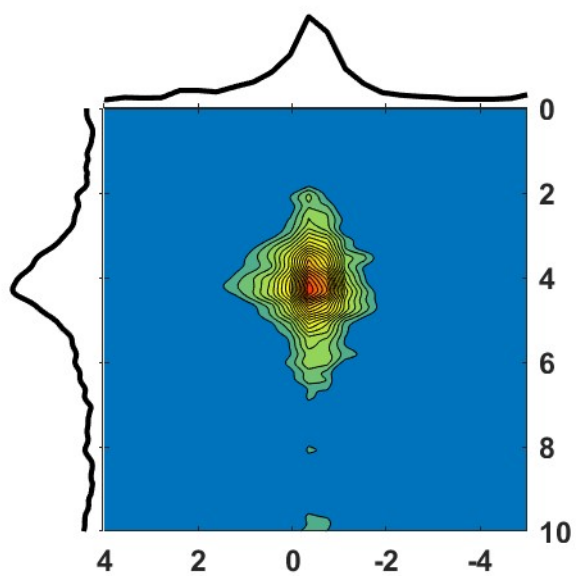


Fig. S1. HETCOR experiment of m-LiTB@500 with $t_{CP} = 1$ ms.

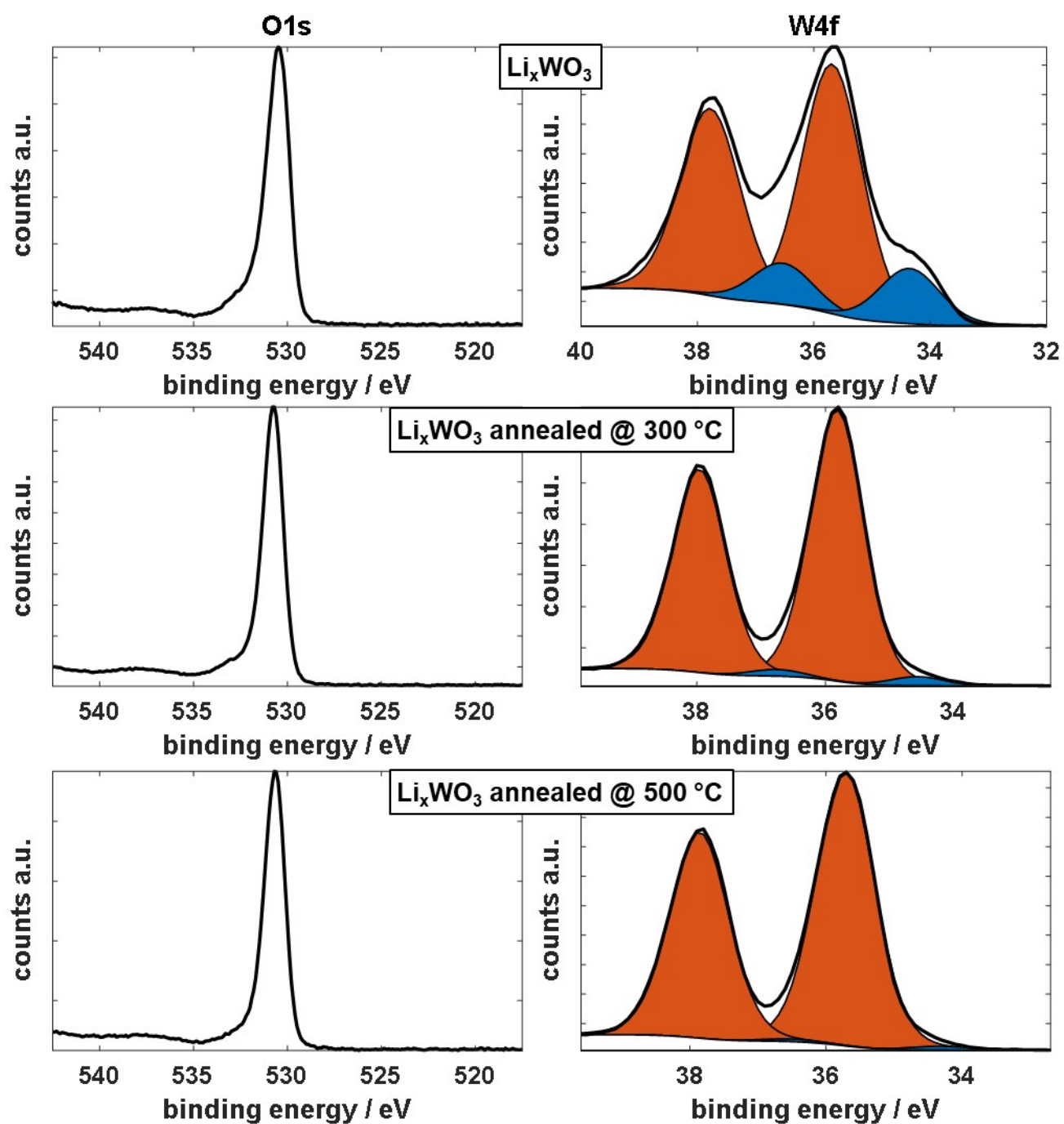


Fig. S2. XPS spectra for O1s and W4f of Li_xWO_3 nanocrystals; not annealed (top), annealed at 300 °C (middle) and annealed at 500 °C (bottom).

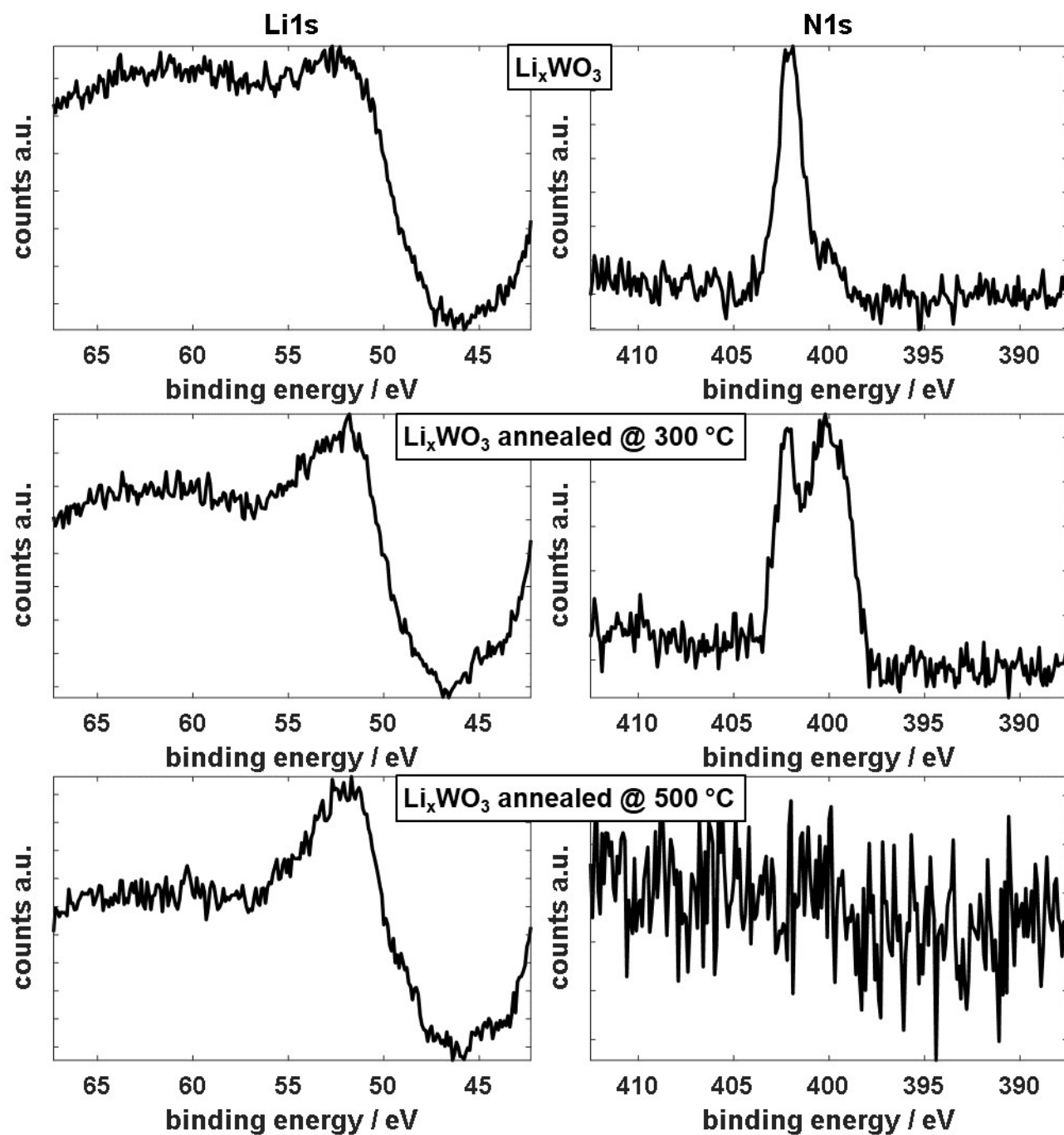


Fig. S3. XPS spectra for Li1s and N1s of Li_xWO₃ nanocrystals; not annealed (top), annealed at 300 °C (middle) and annealed at 500 °C (bottom).

Table S3. T_1 data for the separate signals of h-LiATB@RT, h-LiATB@300 and m-LiTB@500 measured at RT, 40 °C and 60 °C, as well as activation energy.

sample	Shift / ppm	T_1 / s (RT)	T_1 / s (40 °C)	T_1 / s (60 °C)	E_A / kJ/mol
h-LiATB@RT	-0.46	0.60	0.48	0.40	8.27
	-2.20	6.25	5.85	3.44	11.90
h-LiATB@300	-0.36	3.07	2.41	1.89	11.09
	-2.44	14.95	14.26	12.85	3.47
m-LiTB@500	-0.45	2.38	2.06	1.77	6.73
	-1.44	6.82	5.79	4.85	7.75
	-2.20	4.79	4.28	3.54	6.89

Table S4. T_2 data for the separate signals of h-LiATB@RT, h-LiATB@300 and m-LiTB@500 measured at RT, 40 °C and 60 °C.

sample	Shift / ppm	T_2 / ms (RT)	T_2 / ms (40 °C)	T_2 / ms (60 °C)
h-LiATB@RT	-0.46	2.04	2.32	2.65
	-2.20	5.50	6.14	5.75
h-LiATB@300	-0.36	2.36	2.51	2.57
	-2.44	3.54	3.38	3.48
m-LiTB@500	-0.45	1.60	1.63	1.84
	-1.44	0.64	0.56	0.58
	-2.20	0.79	0.91	0.88

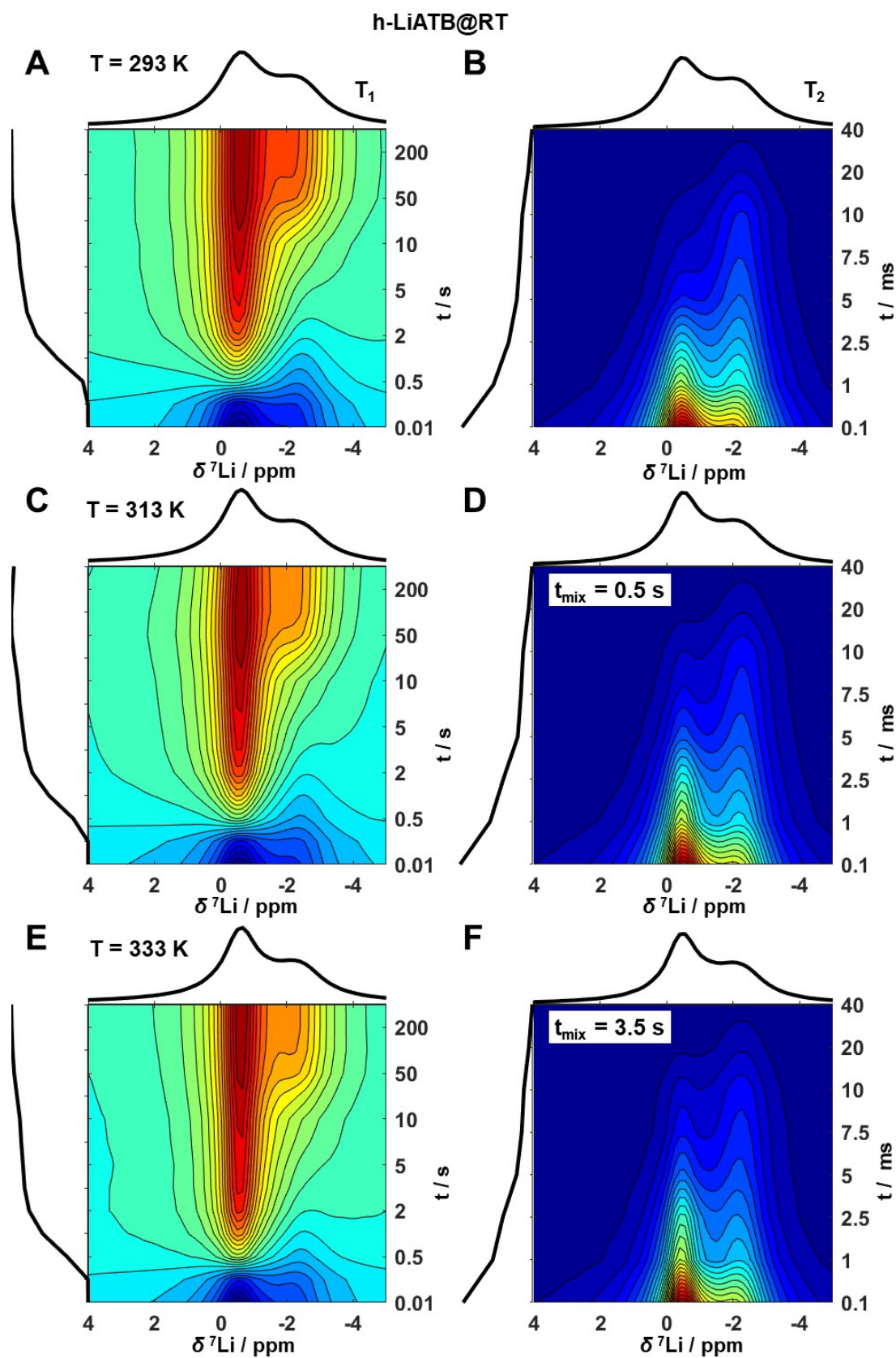


Fig. S4. T_1 (A, C, E) and T_2 (B, D, F) contour plots of h-LiATB@300 measured at RT (A & B), at 40 °C (C & D) and at 60 °C (E & F)

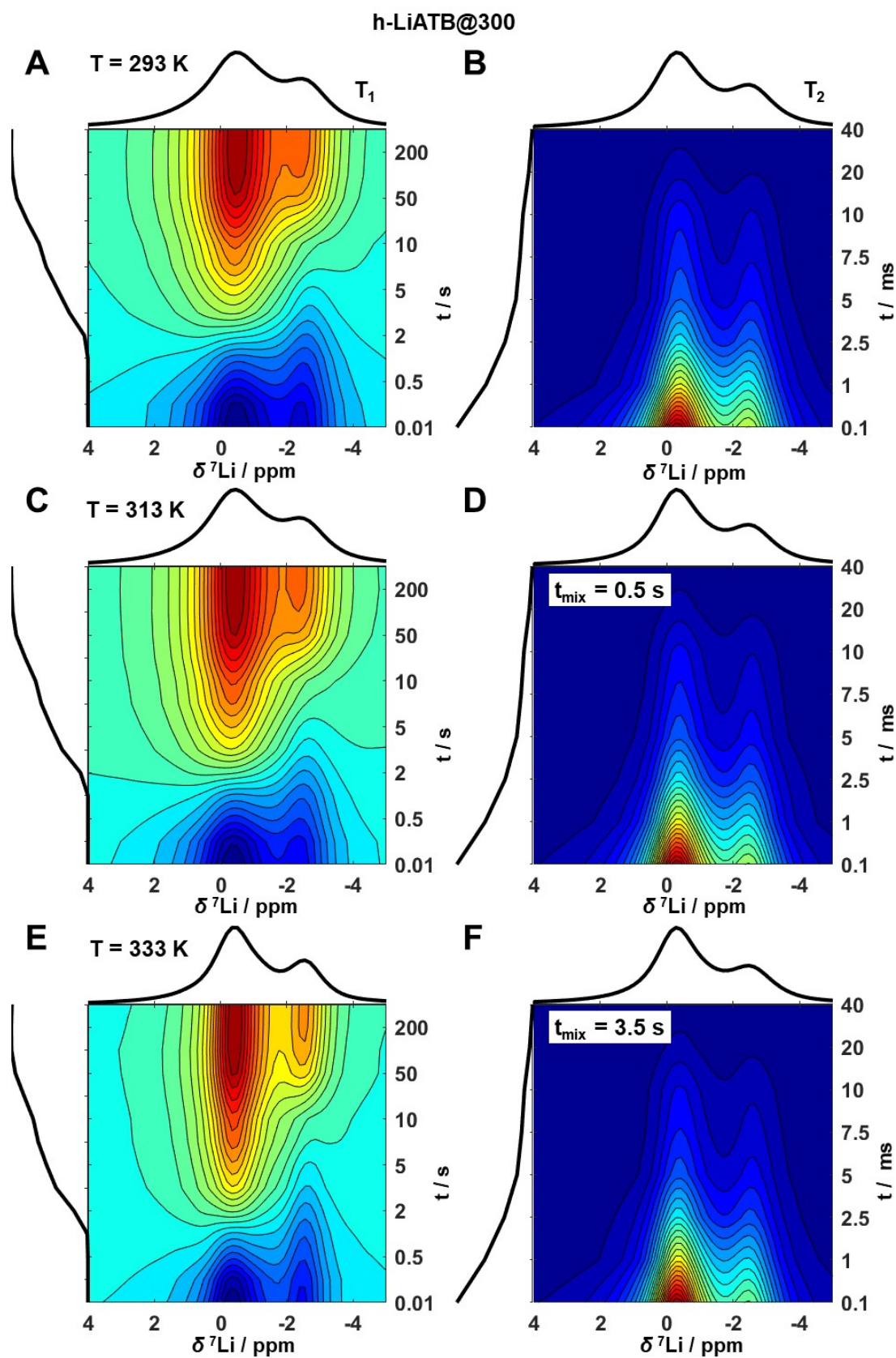


Fig. S

5. T_1 (A, C, D) and T_2 (B, D, F) contour plots of h-LiATB@300 measured at RT (A & B), at 40 °C (C & D) and at 60 °C (E & F)

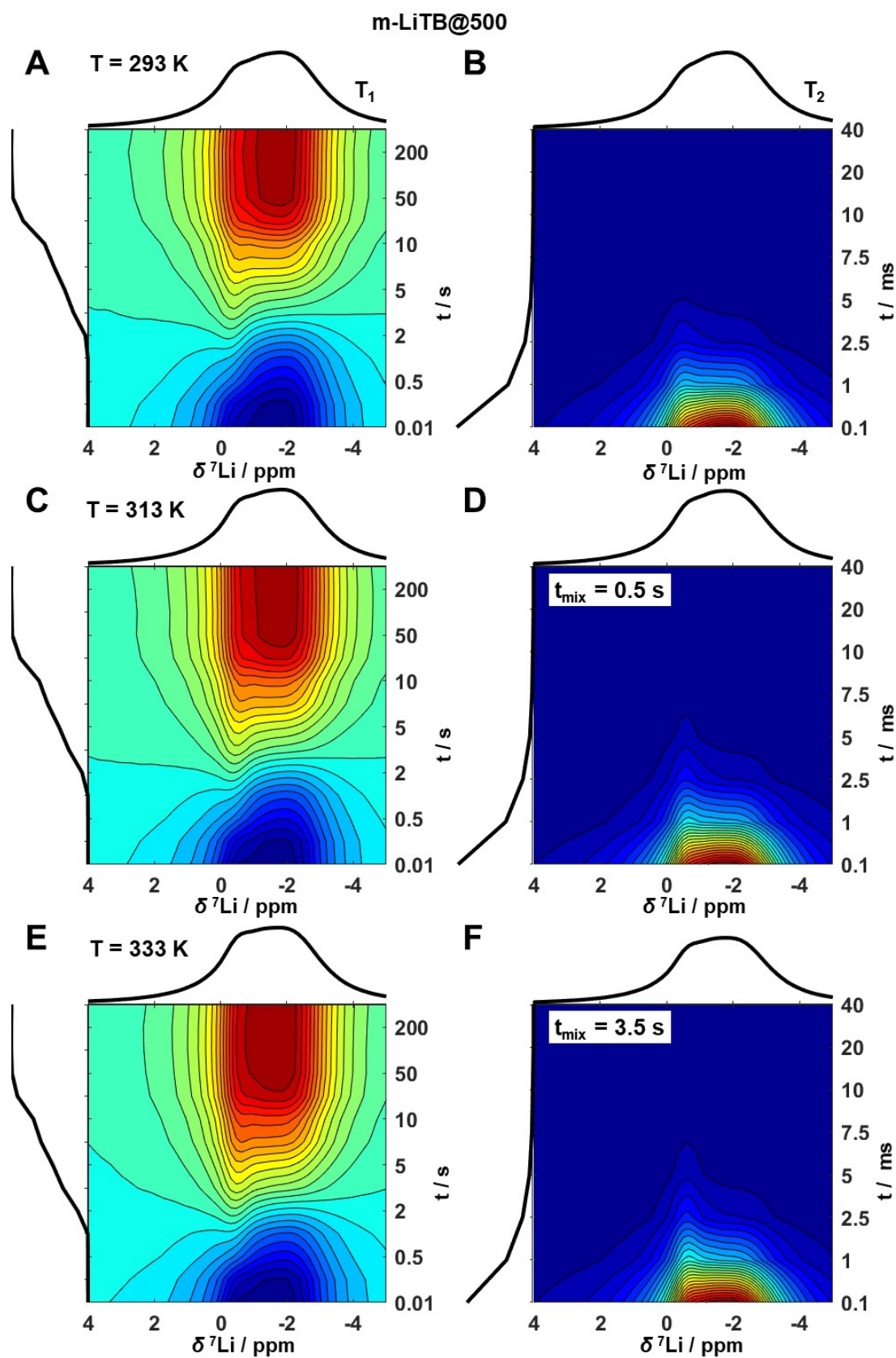


Fig. S6. T_1 (A, C, E) and T_2 (B, D, F) contour plots of h-LiATB@300 measured at RT (A & B), at 40 °C (C & D) and at 60 °C (E & F)

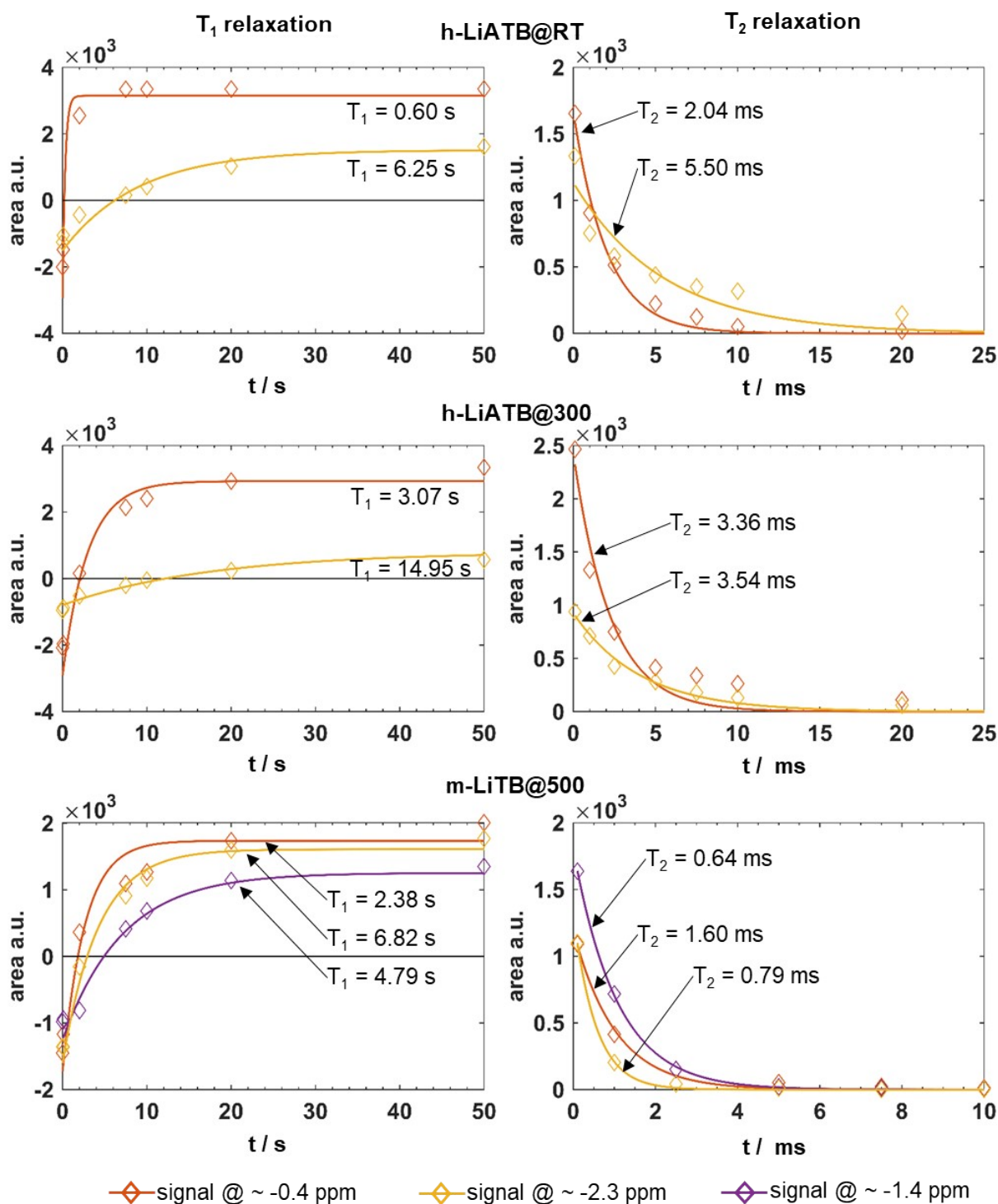


Fig. S7. T_1 and T_2 Fit curves for samples h-LiATB@RT (top), h-LiATB@300 (middle) and m-LiTB@500 (bottom) measured at RT.

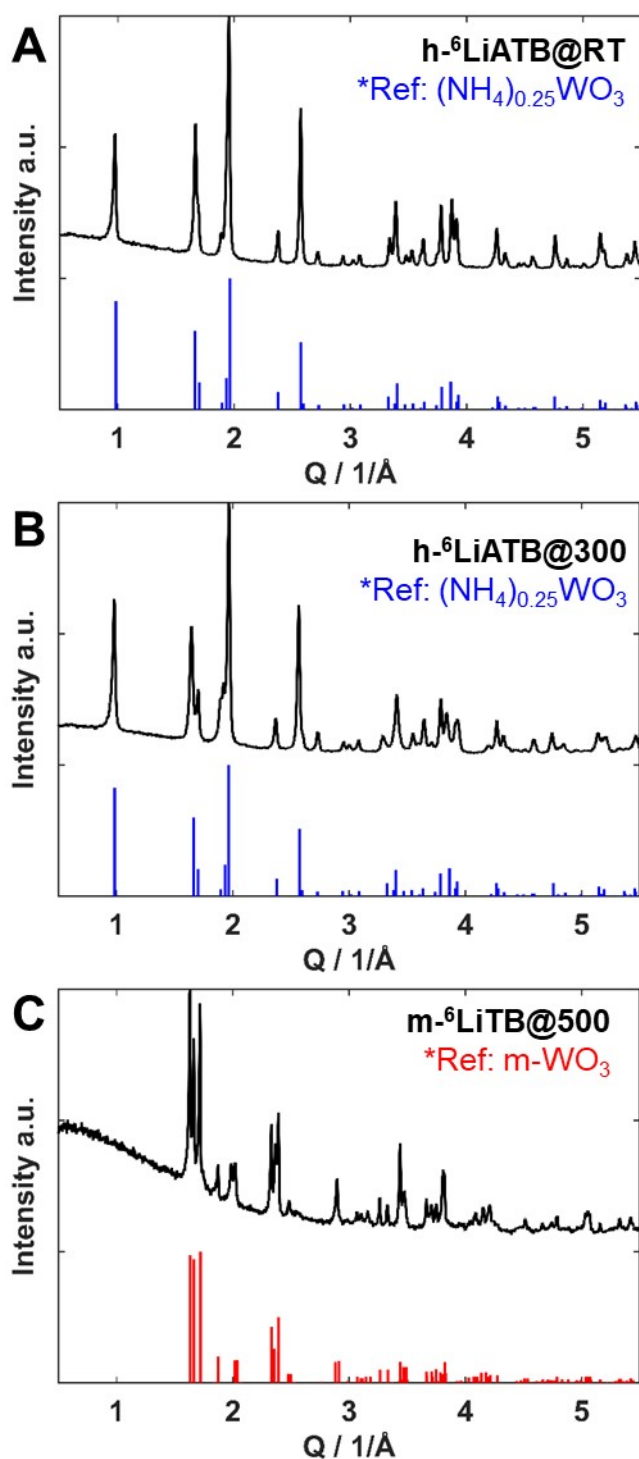


Fig. S8. PXRd patterns of (a) sample A-500 with references for monoclinic WO₃ (space group P12₁/n1, ICSD no. 99-500-3824), trigonal Li₂WO₄ and (space group $R\bar{3}$, ICSD no. 99-500-4151) and triclinic Li₂W₂O₇ and (space group $P\bar{1}$, ICSD no. 99-500-1186).and (b) sample A-300W with references for hexagonal WO₃ (space group P6₃/mcm, ICSD no. 99-503-1860) and trigonal Li₂WO₄ and (space group $R\bar{3}$, ICSD no. 99-500-4151).

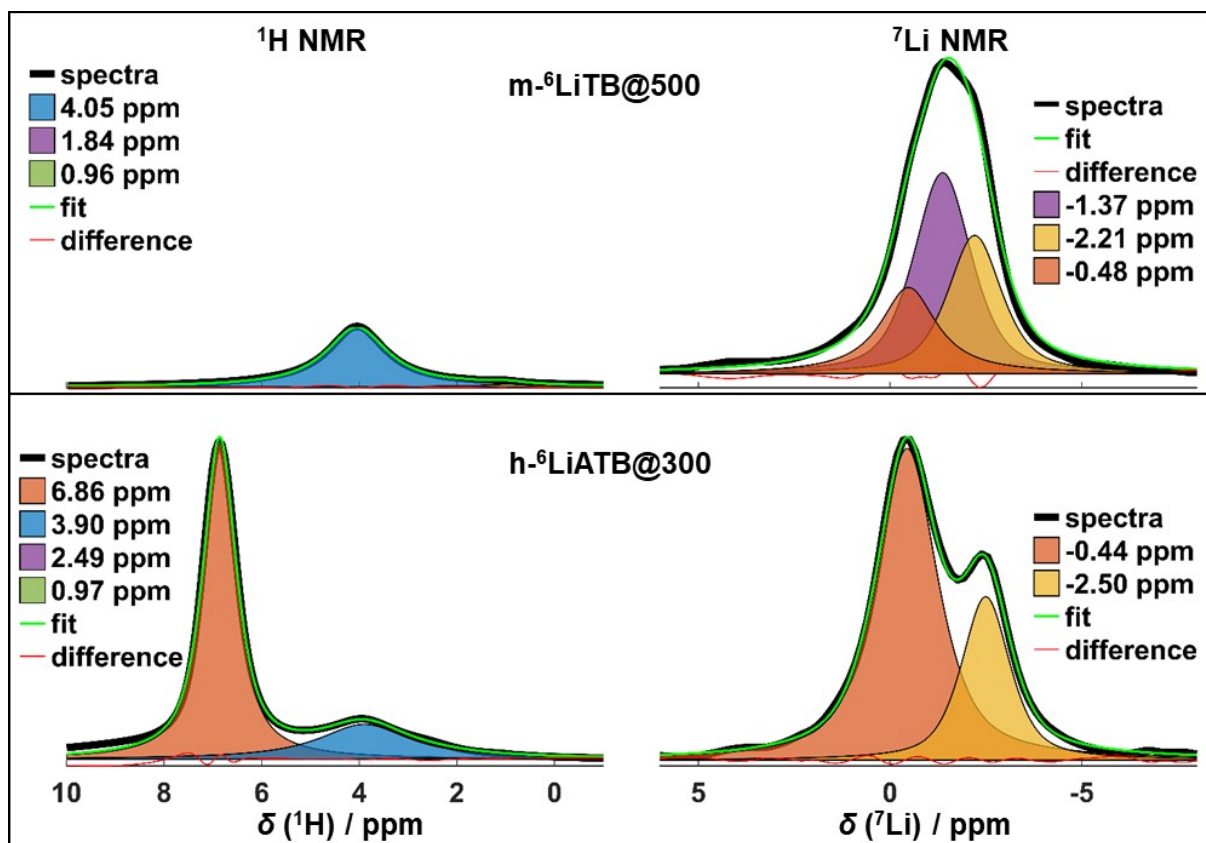


Fig. S9. Solid state MAS-NMR spectra (^1H , right and ^7Li , left) of (a) and (b) sample B, (c) and (d) sample C-300, (e) and (f) sample C-500. Peaks fitted by pseudo-Voigt profile.

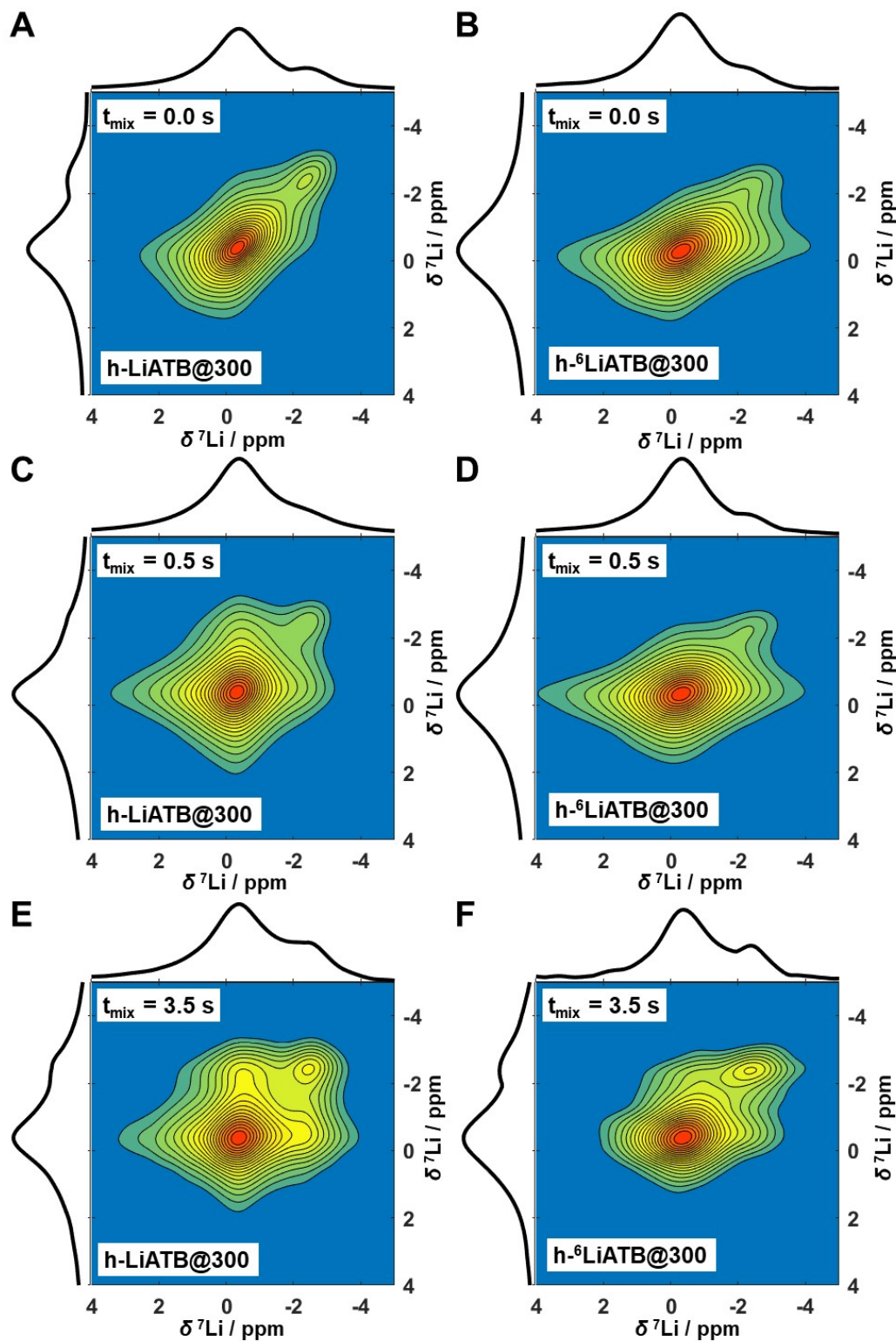


Fig. S10. EXSY spectra of h-LiATB@300 (A, C, E) and h- ${}^6\text{Li}$ ATB@300 (B, D, F) with mixing times of 0.0 s (A & B), 0.5 s (C & D) and 3.5 s (E & F).

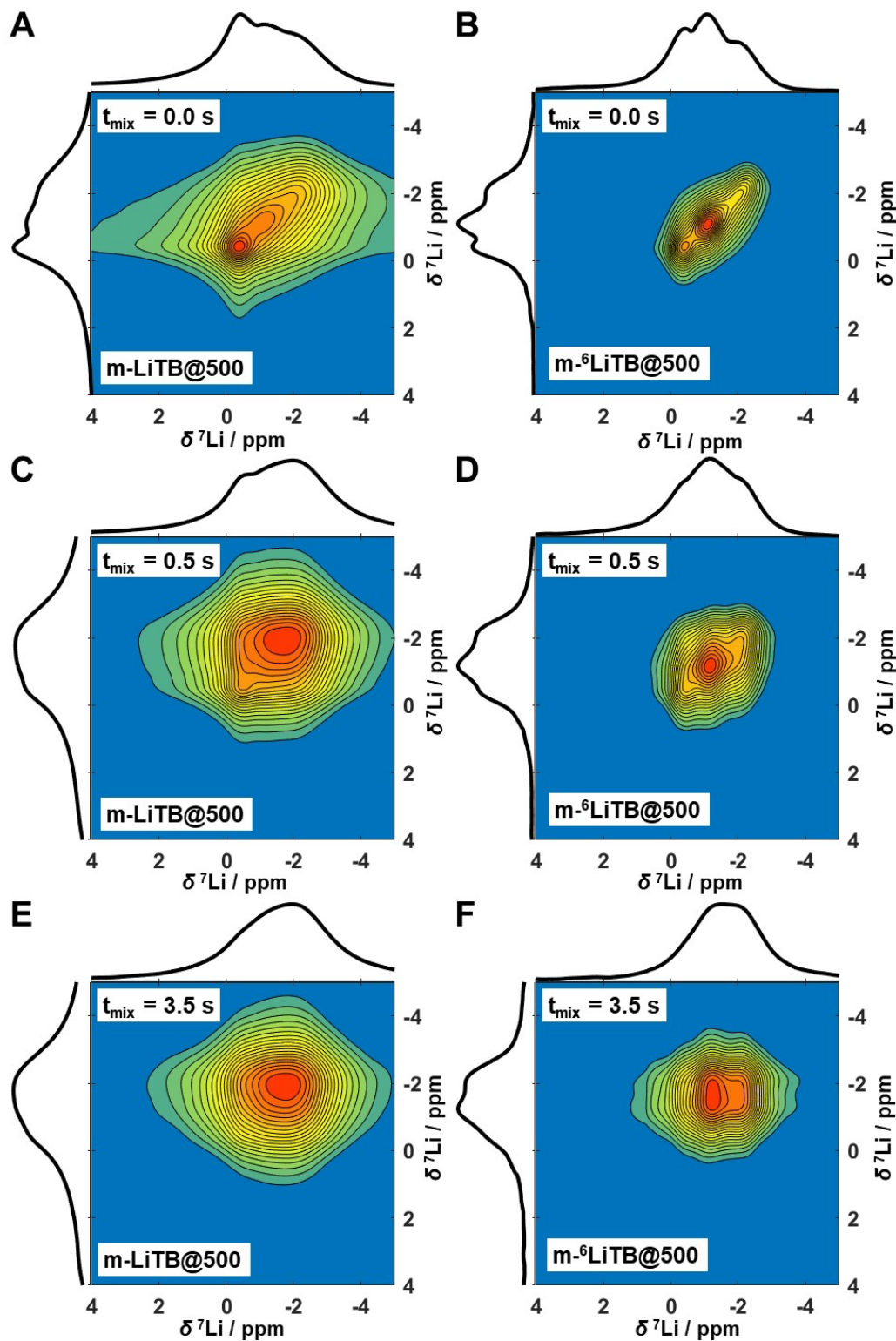


Fig. S11. EXSY spectra of m-LiTB@500 (A, C, E) and m-⁶LiTB@500 (B, D, F) with mixing times of 0.0 s (A & B), 0.5 s (C & D) and 3.5 s (E & F).

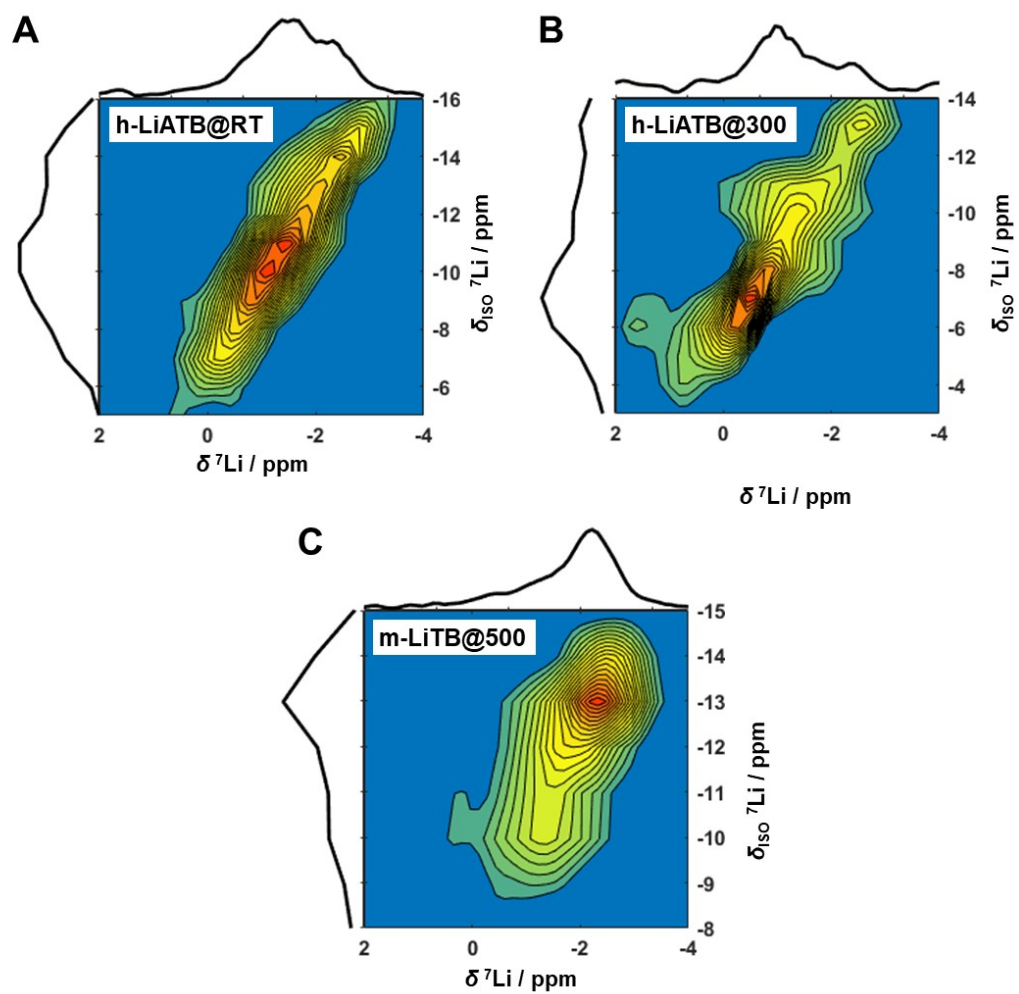


Fig. S12. Unsheared ^7Li MQMAS spectra of h-LiTB@RT, h-LiTB@300 and m-LiTB@500 samples.

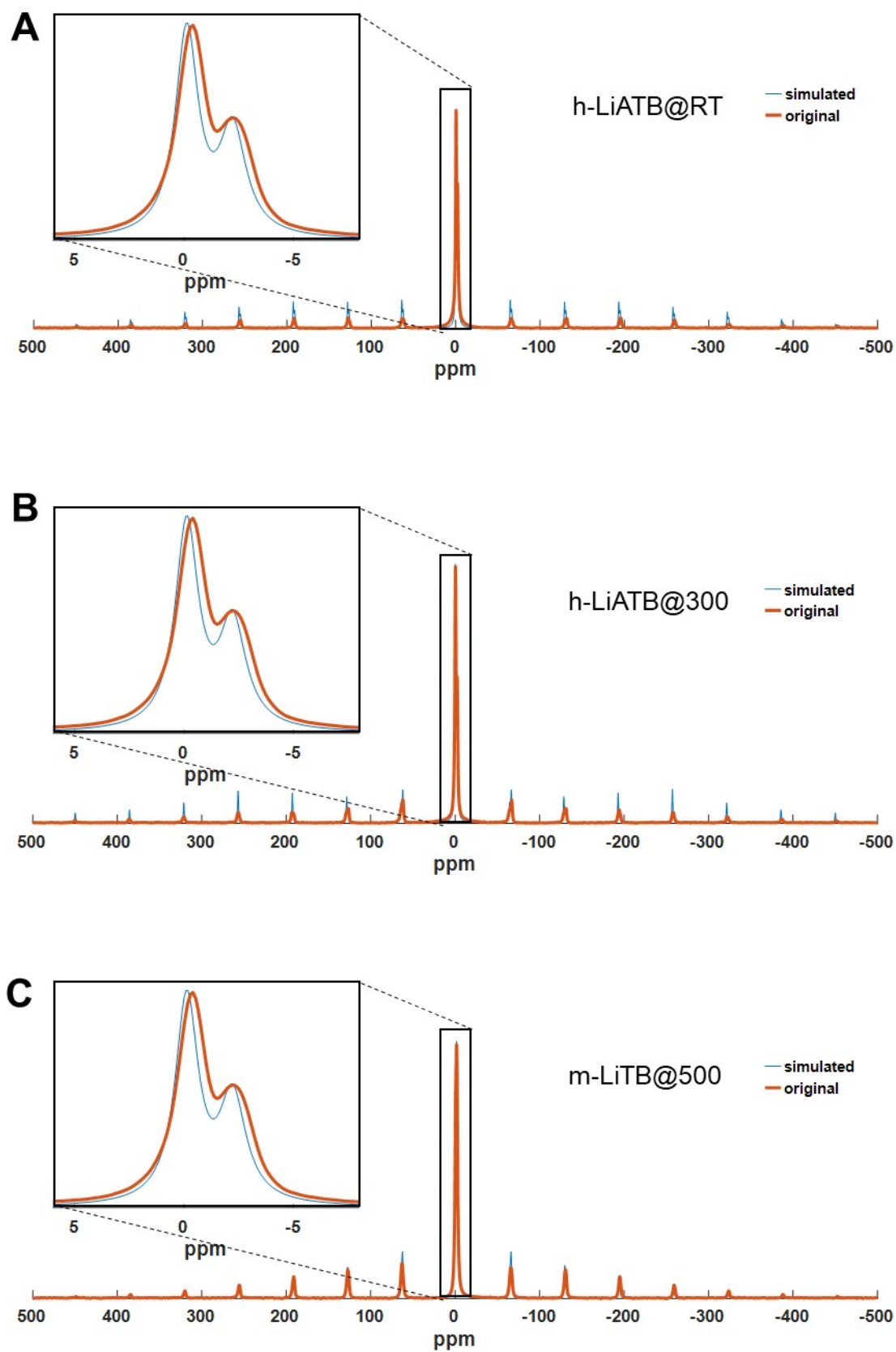


Fig. S13. Measured and simulated ^7Li NMR spectra of h-LiTB@RT (A), h-LiTB@300 (B) and m-LiTB@500 (C) samples.

Table S5. Estimated quadrupole coupling constants and asymmetry parameters from simulated spinning sideband patterns using the SIMPSON software.

sample	Shift / ppm	C _q / kHz	η
h-LiATB@RT	-0.46	150	0.5
	-2.20	120	0.3
h-LiATB@300	-0.51	160	0.7
	-2.57	90	0.7
m-LiTB@500	-0.50	30	0.2
	-1.44	110	0.7
	-2.16	60	0.1