Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supplemental Materials for Tuning lithium-yttrium chloride local dynamics through coordination control and mixing during synthesis

*Teerth Brahmbhatt[a,b], Cheng Li[c], Mounesha N. Garaga[d], Wan-Yu Tsai[a], Steve G. Greenbaum[d], Jagjit Nanda[e], Robert L. Sacci[a]**

[a.] *Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 38712 USA. E-mail: saccirl@ornl.gov*
[b.] *Bredesen Center for Interdisciplinary Research and Education, University of Tennessee, Knoxville, TN, 37996*
[c.] *Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, TN 38712*
[d.] *Department of Physics and Astronomy, Hunter College, City University of New York, New York, NY 10065*
[e.] *Applied Energy Division, SLAC National Laboratory, Menlo Park, CA 94025*

Larger high resolution images from manuscript are provided for the reader.

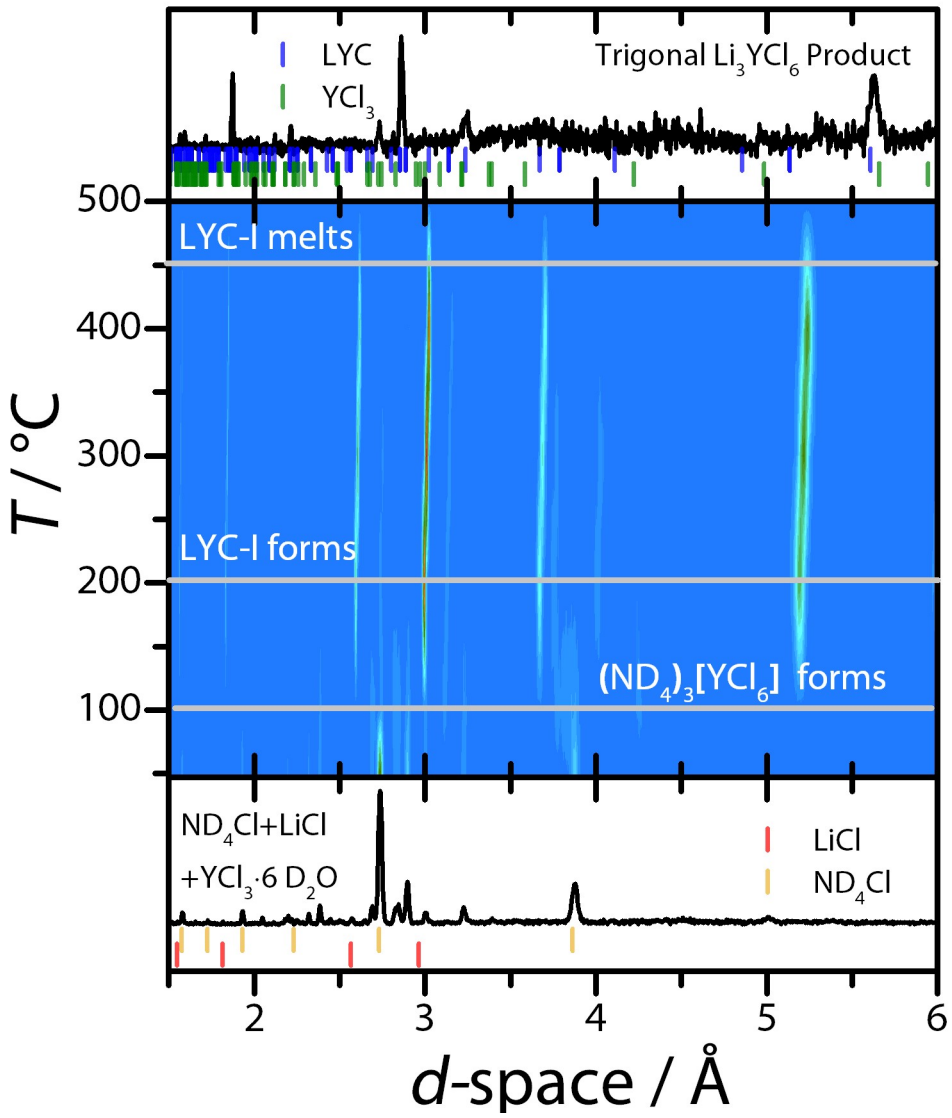

Figure S1: Visualization of the synthesis pathways using *in situ* neutron diffraction of the ammonium chloride-assisted synthesis from aqueous solution, heating from 47 to 500 °C. The initial NPD pattern is the precursors after dissolution and vacuum drying prior to ramping, the final NPD pattern is the RT product obtained after ramping and cooling.

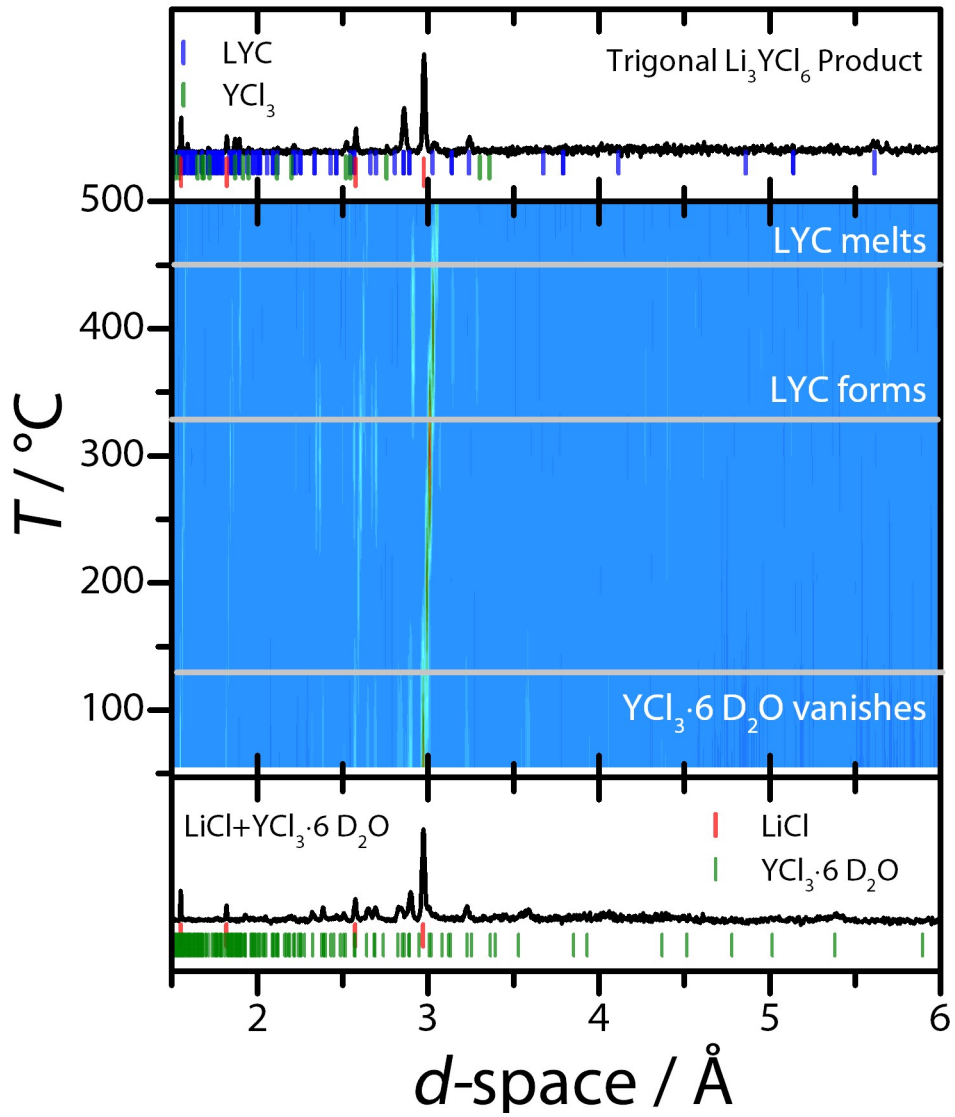

Figure S2: Visualization of the synthesis pathways using *in situ* neutron diffraction of the ammonium chloride-free synthesis from aqueous solution, heating from 45 to 500 °C. The initial NPD pattern is the precursors after dissolution and vacuum drying prior to ramping, the final NPD pattern is the RT product obtained after ramping and cooling.

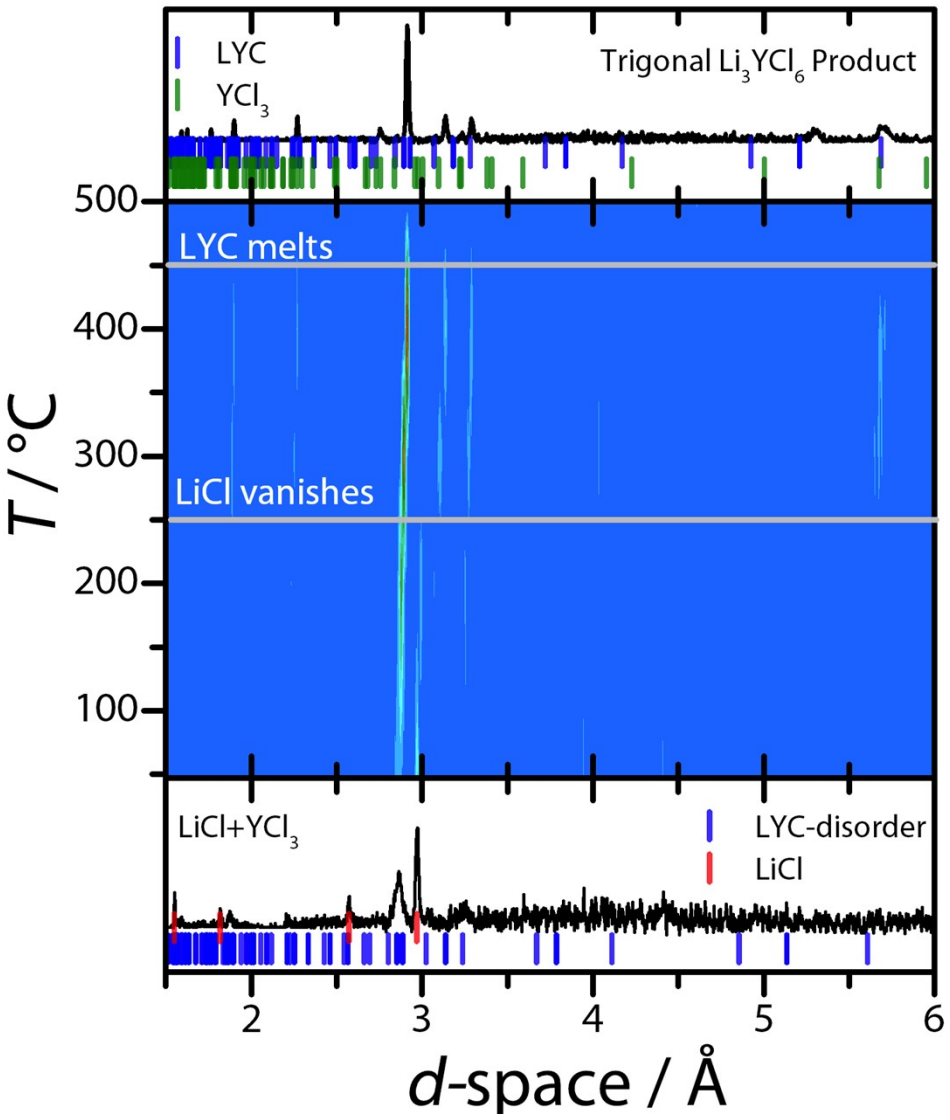

Figure S3: Visualization of the synthesis pathways using *in situ* neutron diffraction of the mechanochemical LYC synthesis, heating from 45 to 500 °C. The initial NPD pattern is the precursors after dissolution and vacuum drying prior to ramping, the final NPD pattern is the RT product obtained after ramping and cooling.

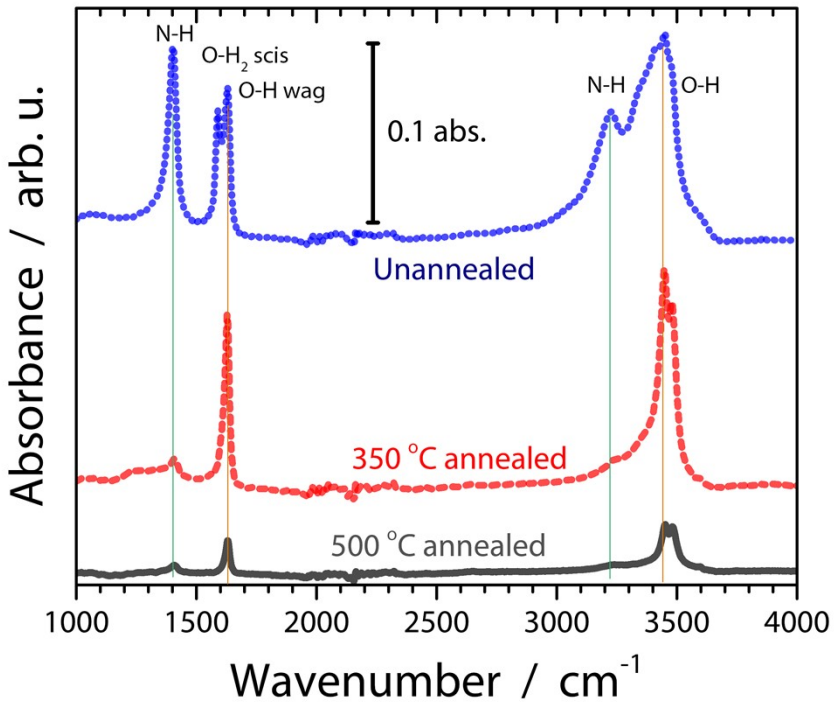

Figure S4: Infrared absorbance spectra of AC-LYC samples measured using a diamond crystal attenuated total reflection accessory at cut at a 45° angle. Absorbances are offset for clarity. Unannealed, as-dried, sample shows clear N-H bands, while annealing at 350°C leaves behind little N-H bands suggesting ammonium is removed. Further annealing at 500 °C reduces strongly adsorbed H_2O and hydroxyl groups.

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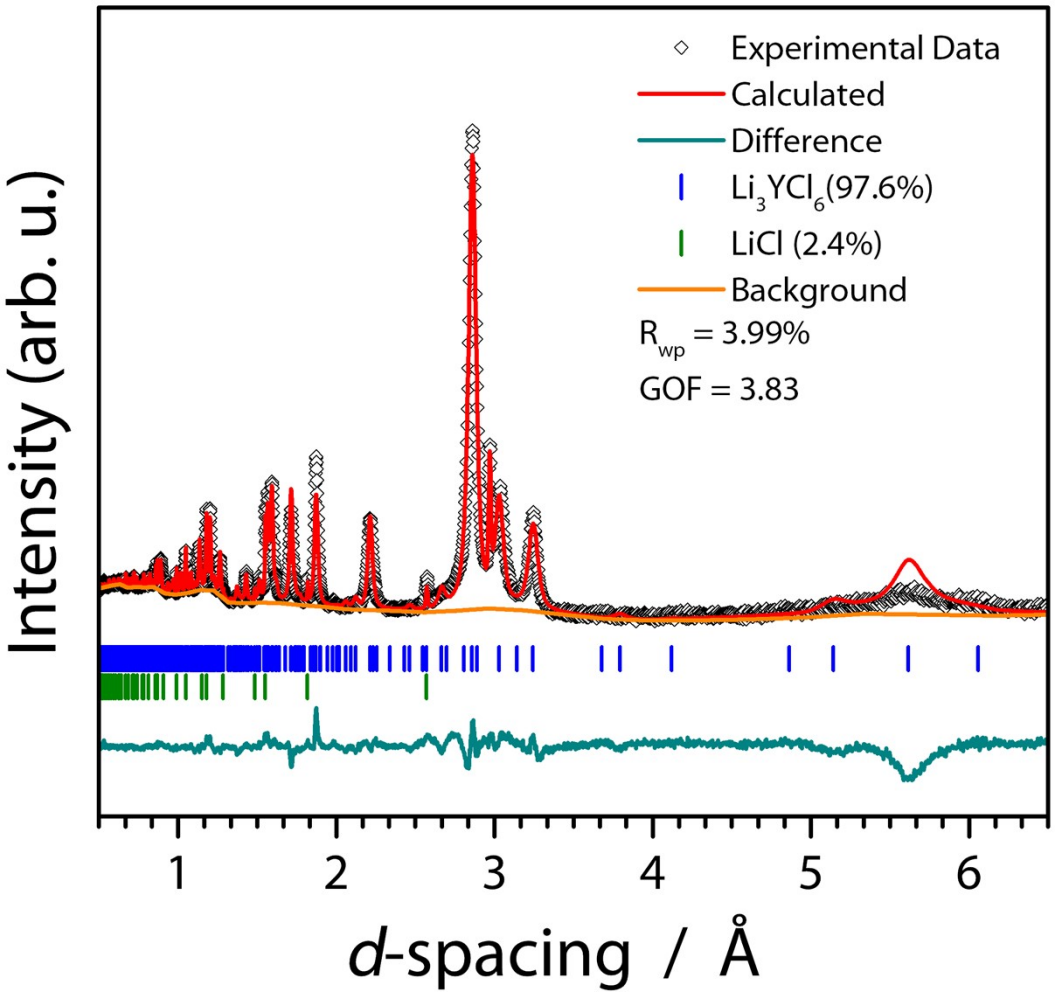

Figure S6: Refinement of the neutron powder diffraction data of the tetragonal LYC product synthesized through the mechanochemical route before annealing. This sample was synthesized in parallel to the *in situ* diffraction samples. Note, the non-flat background is indicative of an amorphous phase, presumably YCl_3 as it is observed in the following figure.

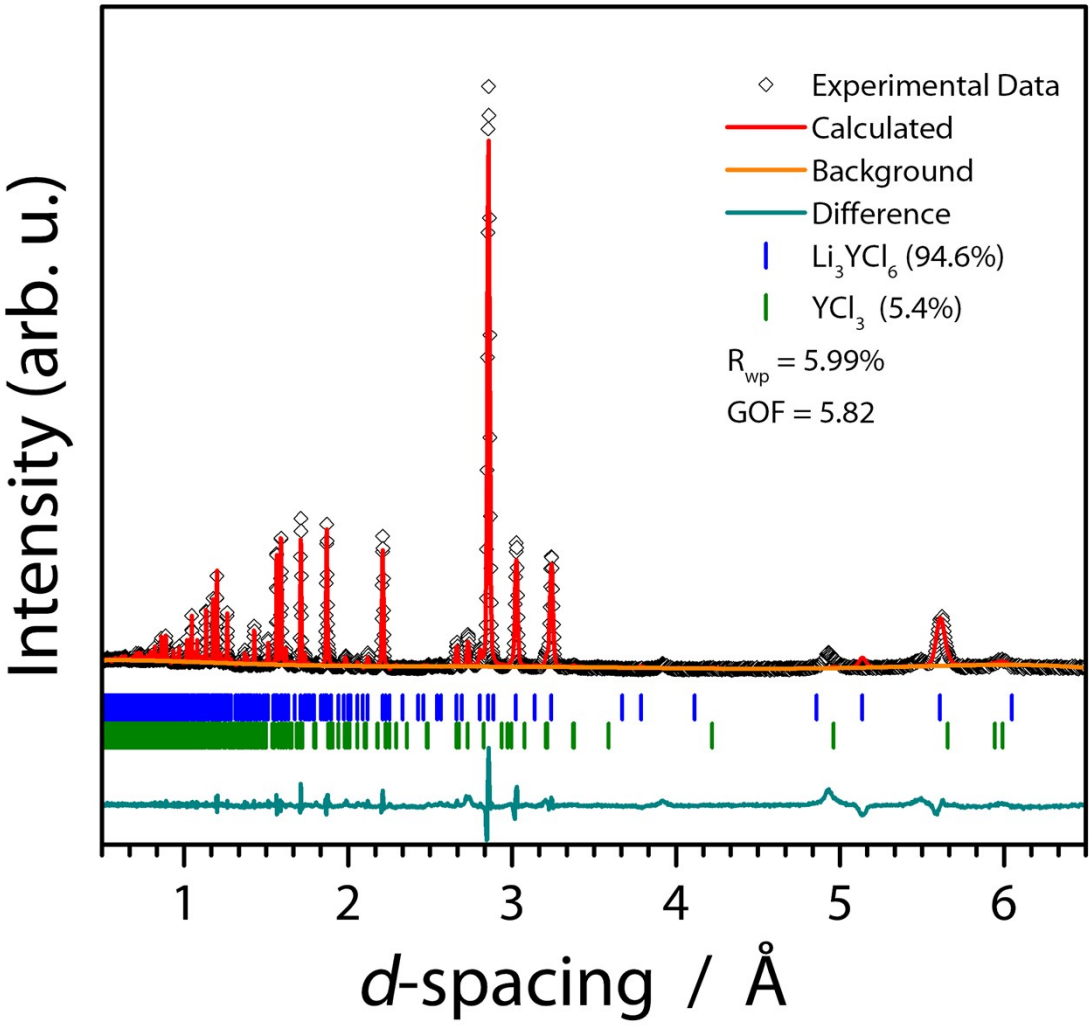

Figure S7: Refinement of the neutron powder diffraction data of the tetragonal LYC product synthesized by annealing the mechanochemical sample shown in Figure S5. This sample was synthesized in parallel to the *in situ* diffraction samples.

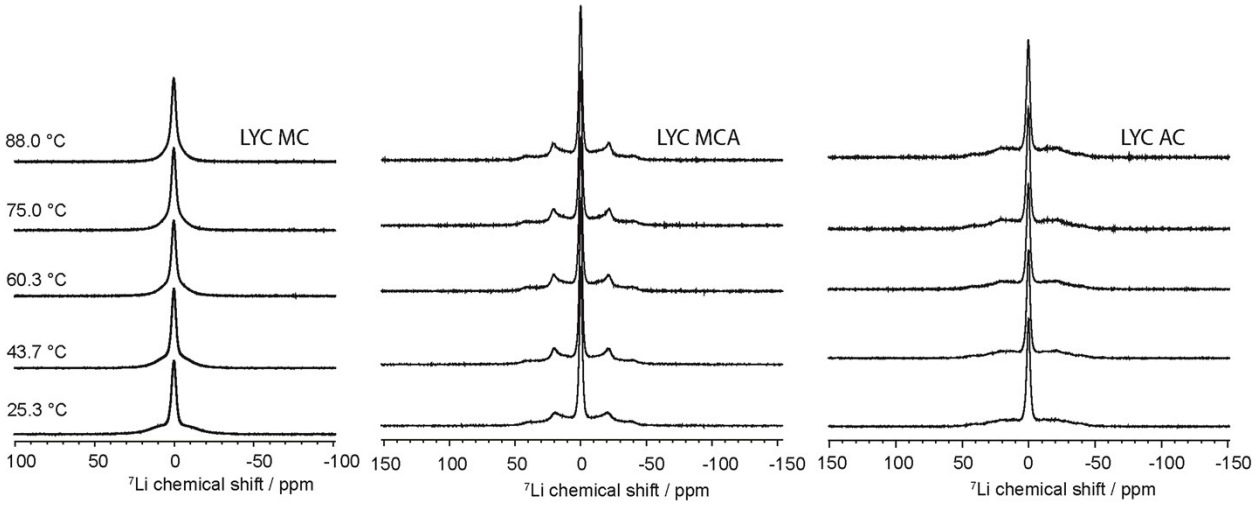

Figure S8: ^{7}Li static NMR spectra of MC, MCA and AC samples as a function of temperature.

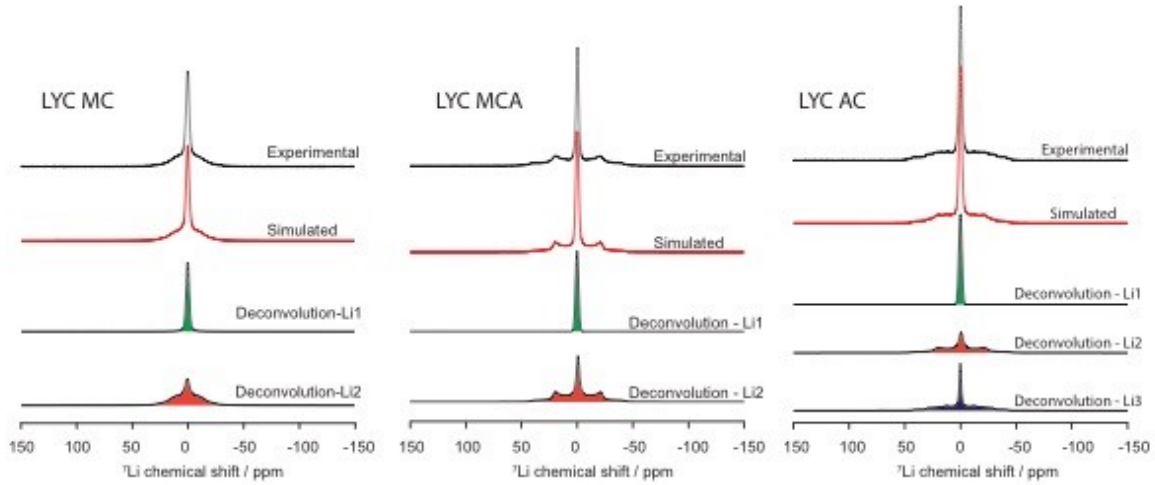

Figure S9: Representative deconvolution of the ^{7}Li static NMR spectra of MC, MCA and AC.