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Electronic Supplementary Information for:

"Single-Shot Titrations and Reaction Monitoring by Slice-Selective NMR Spectroscopy"

T. Niklas, D. Stalke and M. John

Georg-August Universität Göttingen

Institut für Anorganische Chemie

Tammannstraße 4

37077 Göttingen

Technical Setup

All NMR-spectra were measured on a Bruker Avance III 400 spectrometer with a standard BBFOplus probe with z gradient coil. The pulse programme written in Bruker Avance syntax is given below. Further detailed information for this experiment is given in ref [1].

```
;zg-slice.iacgoe
;avance-version
;selective excitation using a shaped pulse
;$CLASS=HighRes
;$DIM=1D
;$TYPE=
;$SUBTYPE=
;$COMMENT=

#include <Avance.incl>
#include <Grad.incl>

1 ze
2 30m
  d1
  3u UNBLKGRAD
  3u gron1
  (p11:sp1 ph1):f1
  3u groff
  3u BLKGRAD
  go=2 ph31
  30m mc #0 to 2 F0(zd)
exit

ph1=0 2 2 0 1 3 3 1
ph31=0 2 2 0 1 3 3 1

;sp1: f1 channel - shaped pulse
;p11: f1 channel -  90 degree shaped pulse
;d1 : relaxation delay; 1-5 * T1
;ns: 1 * n, total number of scans: NS * TD0
;choose p11 according to desired selectivity i.e. slice-width
;for a given gradient strength
;the flip-angle is determined by the amplitude
;choose frequency offsets according to desired slice distance
;for a given gradient strength
```

Slice-selective ^{1}H experiments were performed at 400.13 MHz with a gradient strength of 27.9 G/cm. Gauss-Cascade (G4) shaped pules were used to excite a bandwidth of 11850 Hz which corresponds to 1 mm thick slices. Frequency offsets for these pulses ranged between 106350 Hz and -106350 Hz with steps of 11850 Hz. This resulted in 19 slices with 1 mm distance between each slice.

Slice-selective ^{7}Li experiments were performed at 155 MHz with a gradient strength of 55.7 G/cm. Gauss-Cascade (G4) shaped pules were used to excite a bandwidth of 9220 Hz which corresponds to 1 mm thick slices. Frequency offsets for these pulses ranged between 82980 Hz and -82980 Hz with steps of 9220 Hz. This resulted in 19 slices with 1 mm distance between each slice.

The Bruker Topspin AU *poptau* offers a simple method to vary different parameters, among them are frequency offsets. Additionally, results obtained by *poptau* can be saved as pseudo-2D spectra. Further customization of this AU can easily achieve a standardized and fast acquisition procedure.

Spectrometer-dependent Inverse Sensitivity Profiles

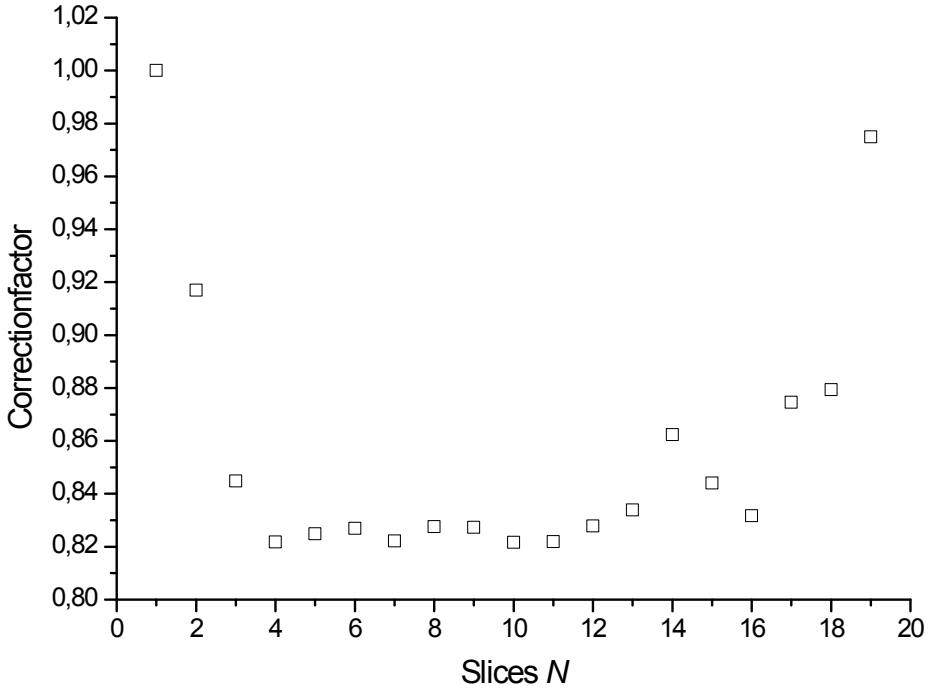

Figure S1: Averaged inverse sensitivity profile of the probe for ^{7}Li. To obtain this curve, three homogenous samples with different concentrations of $LiClO_4$ were investigated via slice-selective ^{7}Li experiments. For each sample the single ^{7}Li signal of each slice was integrated and normalized to slice 1. Finally the results were averaged over all three samples. To compare integrals between different slices, integrals have to be multiplied by the corresponding correctionfactor.

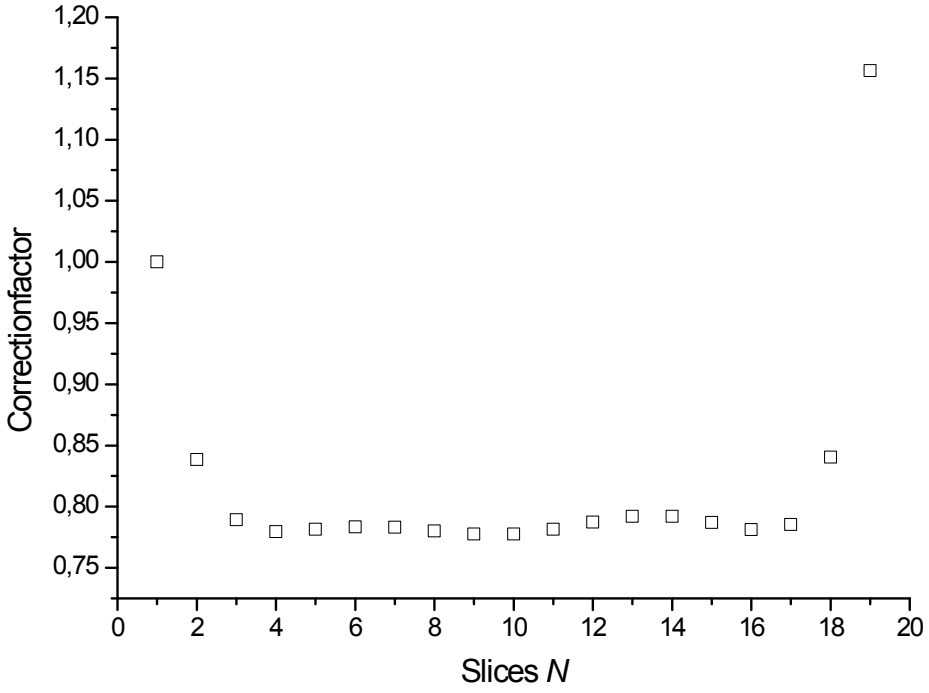

Figure S2: Averaged inverse sensitivity profile of the probe for ^{1}H. To obtain this curve, three homogenous samples with different concentrations of acetone were investigated via slice-selective ^{1}H experiments. For each sample the single ^{1}H signal of each slice was integrated and normalized to slice 1. Finally the results were averaged over all three samples. To compare integrals between different slices, integrals have to be multiplied by the corresponding correctionfactor.

Comparison between non-selective and slice-selective Intensities

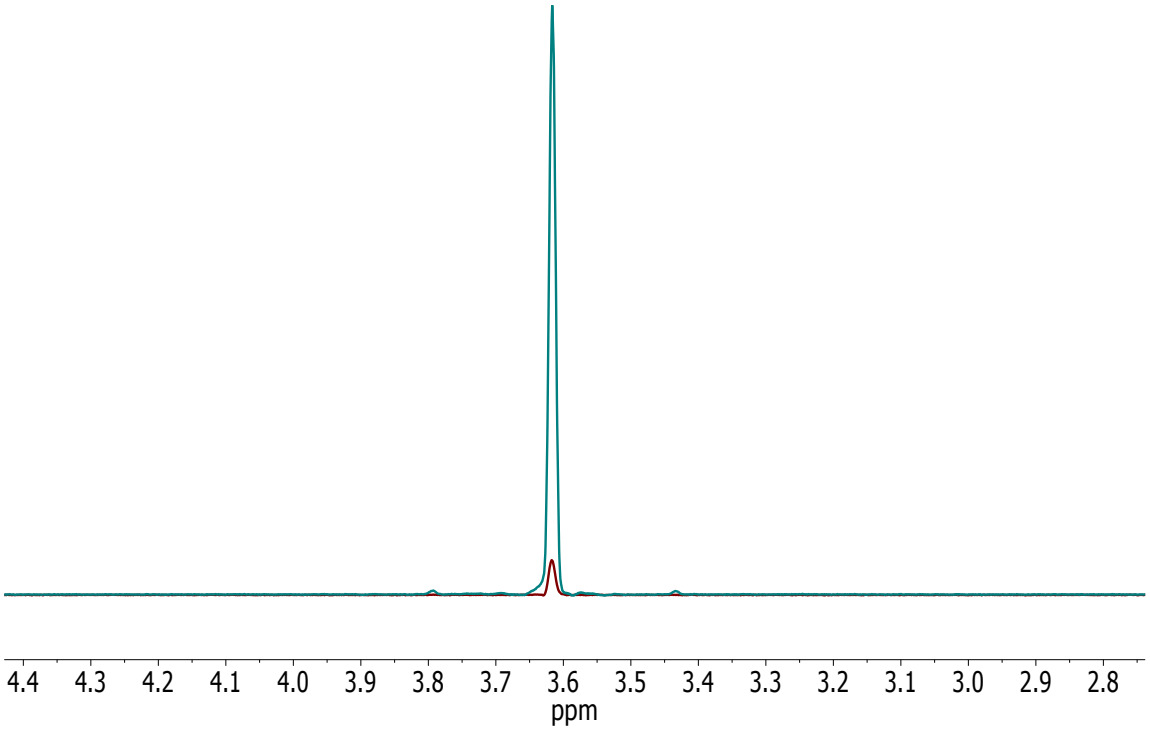

Figure S3: Comparison between a non-selective NMR spectrum (green) and a slice-selective NMR spectrum (red). Both spectra are taken with unchanged acquisition parameters apart from the gradient dependent parameters. The selective spectrum is from slice 10 (1 mm width). Its intensity is roughly 1/20 of the non-selective intensity, which in turn matches an active volume of 2 cm.

Calibration Curves for the Concentration Determination

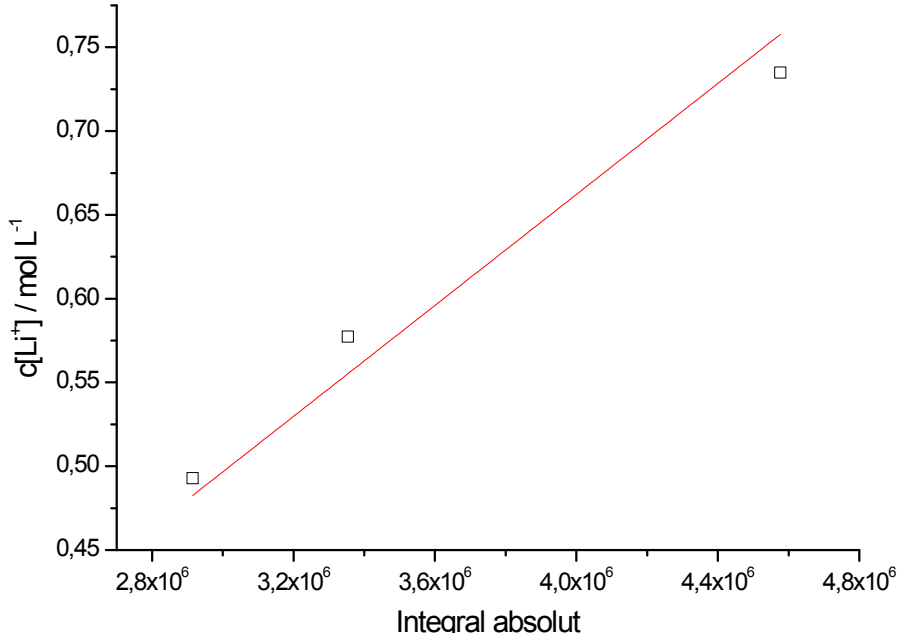

Figure S4: Calibration curve for the concentration determination of lithium-containing molecules. Three samples of $LiClO_4$ containing solutions with known concentration were prepared and measured via SSE. The signals were integrated and corrected according to the sensitivity profile. Then *c*[Li^+] *vs* absolute integral could be linearly fitted through (0,0). This gives the slope *m*=1.66E-7 mol L^{-1}.

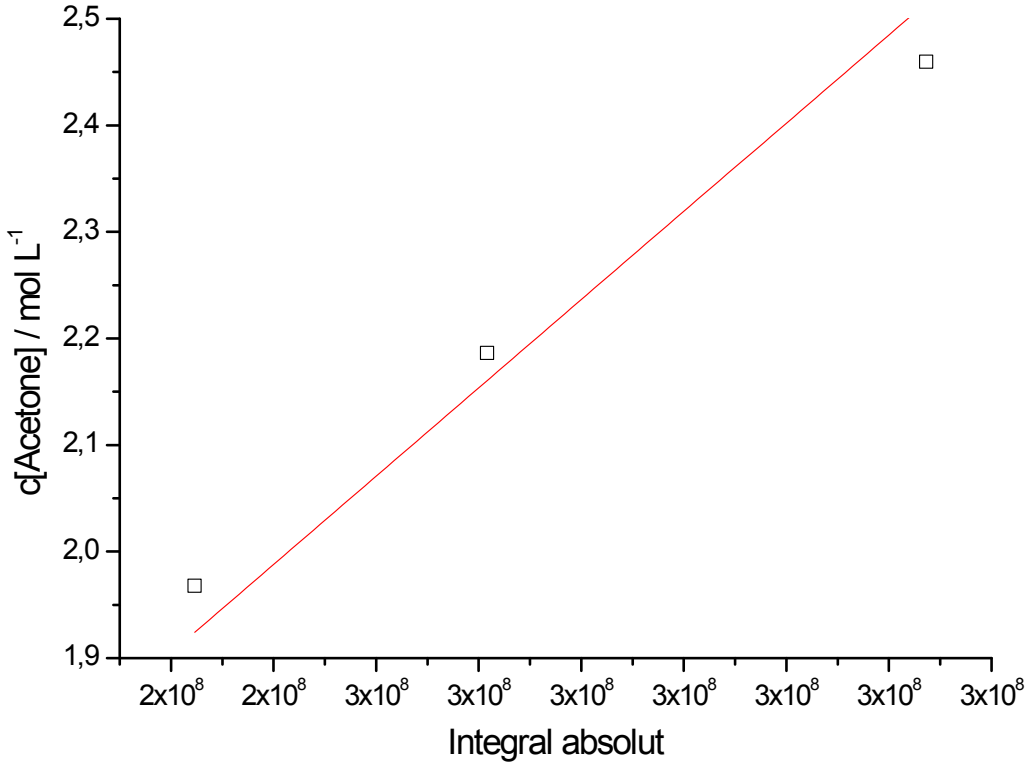

Figure S5: Calibration curve for the concentration determination of hydrogen-containing molecules. Three samples of acetone containing solutions with known concentration were prepared and measured via SSE. The signals were integrated and corrected according to the sensitivity profile. Then *c*[acetone] (*i.e.* 8 hydrogen-atoms) *vs* absolute integral could be linearly fitted through (0,0). This gives the slope *m*=8.28E-9 mol L^{-1}.

Titration of Li^+ with 12-crown-4

Figure S6: Schematic description of experiment 1: Titration. First 12-crown-4 is filled in the NMR tube. The solution is then frozen at 5°C. Then a solution of $LiClO_4$is added. As soon as the ether melts SSE can be performed.

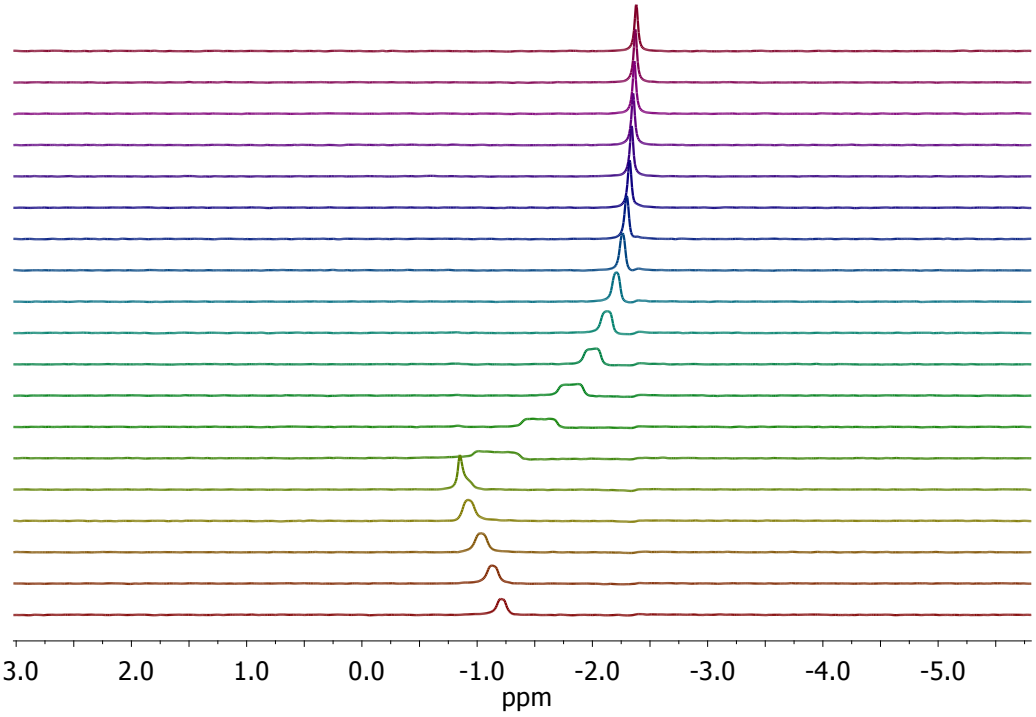

Figure S7: Slice-selective ^7Li spectra for the titration of Li^+ by 12-crown-4. Spectra were taken approximately 3 h after preparation of the sample.

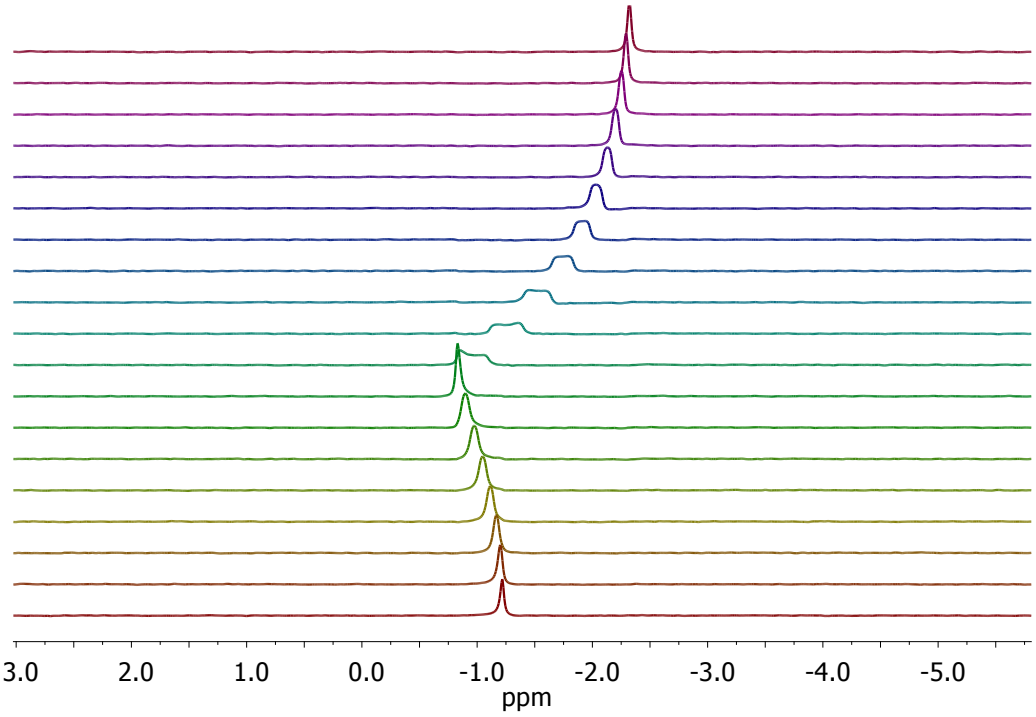

Figure S8: Slice-selective ^{7}Li spectra for the titration of Li^{+} by 12-crown-4. Spectra were taken approximately 6 h after preparation of the sample.

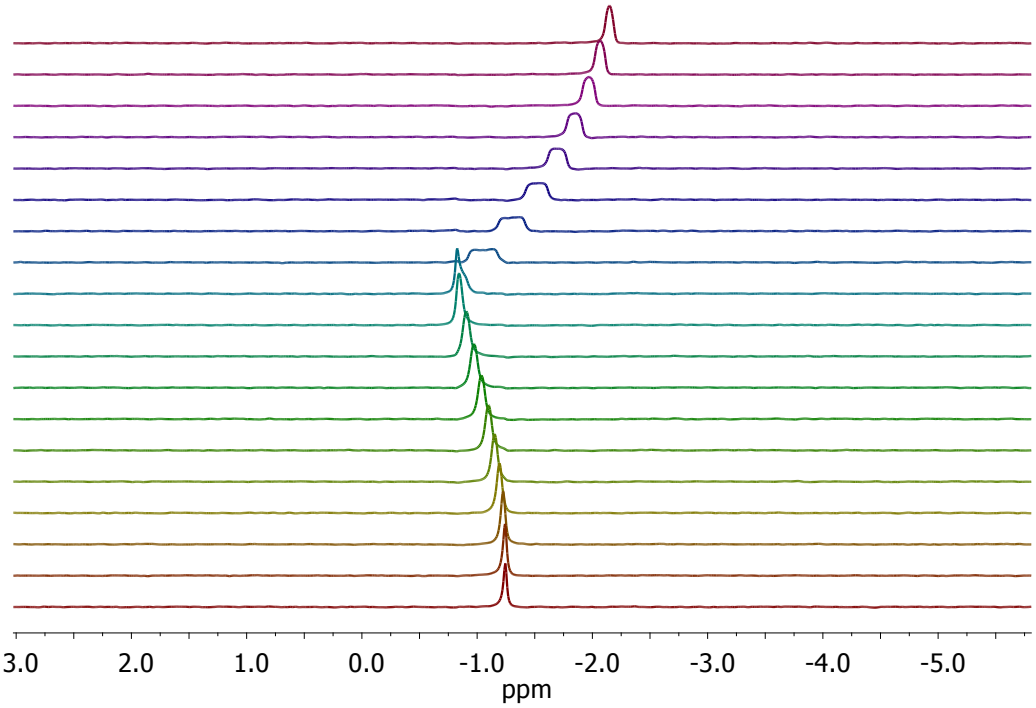

Figure S9: Slice-selective ^{7}Li spectra for the titration of Li^{+} by 12-crown-4. Spectra were taken approximately 9 h after preparation of the sample.

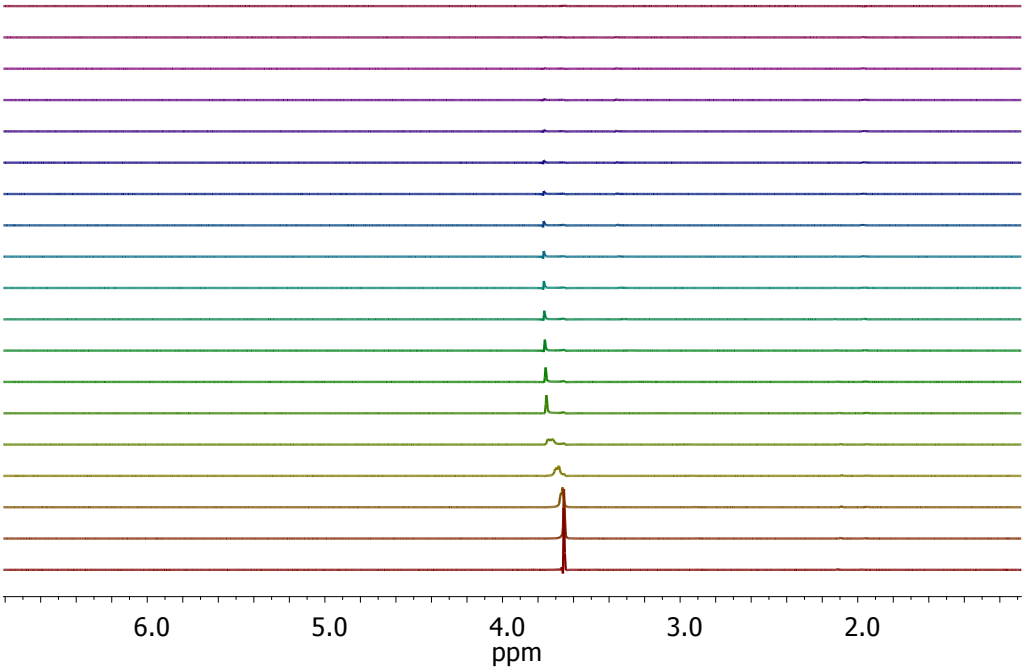

Figure S10: Slice-selective ^{1}H spectra for the titration of Li^{+} by 12-crown-4. Spectra were taken approximately 3 h after preparation of the sample.

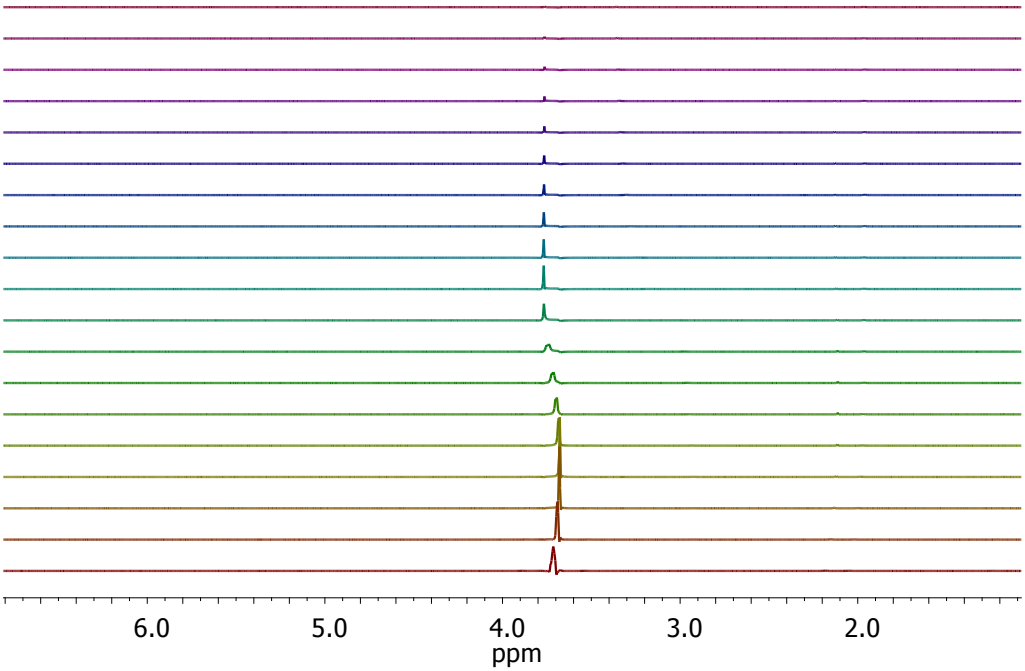

Figure S11: Slice-selective ^{1}H spectra for the titration of Li^{+} by 12-crown-4. Spectra were taken approximately 6 h after preparation of the sample.

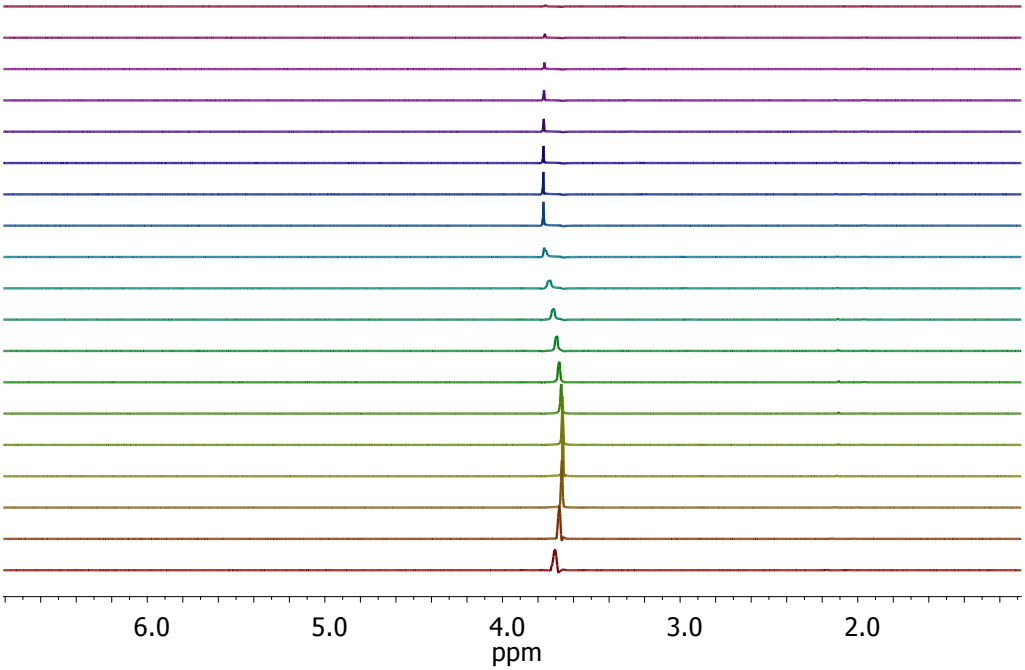

Figure S12: Slice-selective ^{1}H spectra for the titration of Li^{+} by 12-crown-4. Spectra were taken approximately 9 h after preparation of the sample.

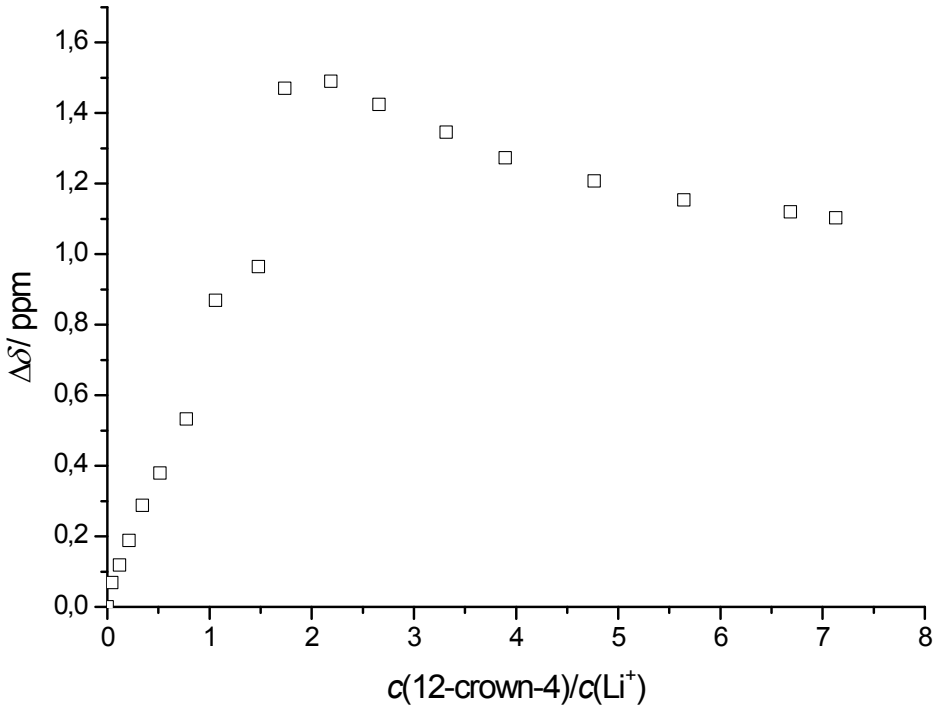

Figure S13: Chemical shift difference between pure Li^{+} in acetonitrile and varying amounts of 12-crown-4 as measured 6 h after the diffusion started.

Observation of the Lithiation of PMDTA by *n*BuLi

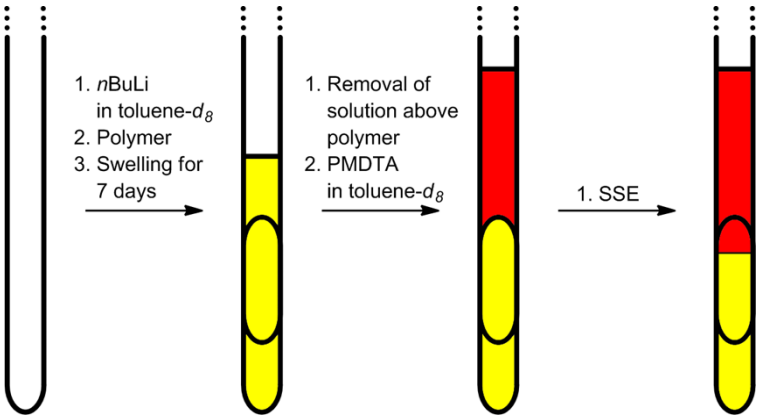

Figure S14: Schematic description of experiment 2: Observation of a lithiumorganic reaction. First *n*BuLi solution is filled in the NMR tube and a polymer is induced at approximately 1 cm above the bottom of the tube. After 7 days of swelling the remaining solution above the polymer is removed and PMDTA solution is added instead. As soon as PMDTA diffuses into the polymer SSE can be performed.

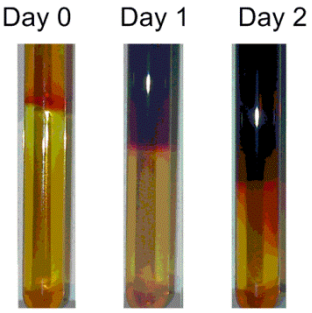

Figure S15: Pictures of the samples as PMDTA diffuses into the polymer and reacts with *n*BuLi.

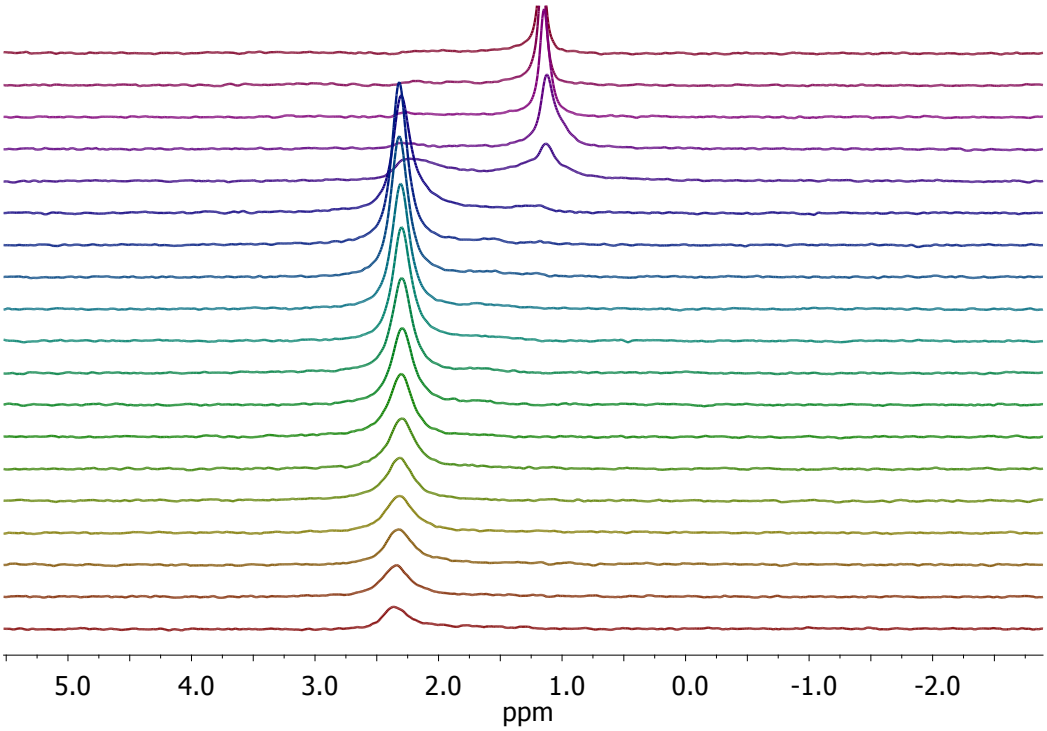

Figure S16: Slice-selective ^{7}Li spectra for the lithiation of PMDTA by *n*BuLi. Spectra were taken approximately 3 h after addition of PMDTA.

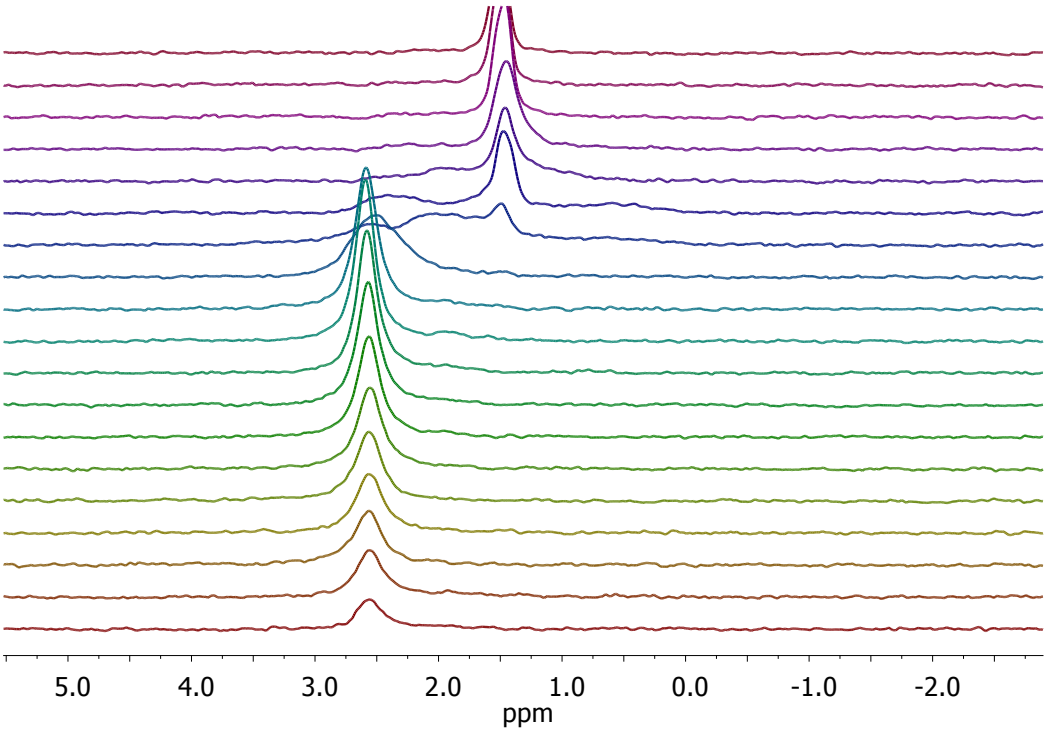

Figure S17: Slice-selective ^{7}Li spectra for the lithiation of PMDTA by *n*BuLi. Spectra were taken approximately 1 d after addition of PMDTA.

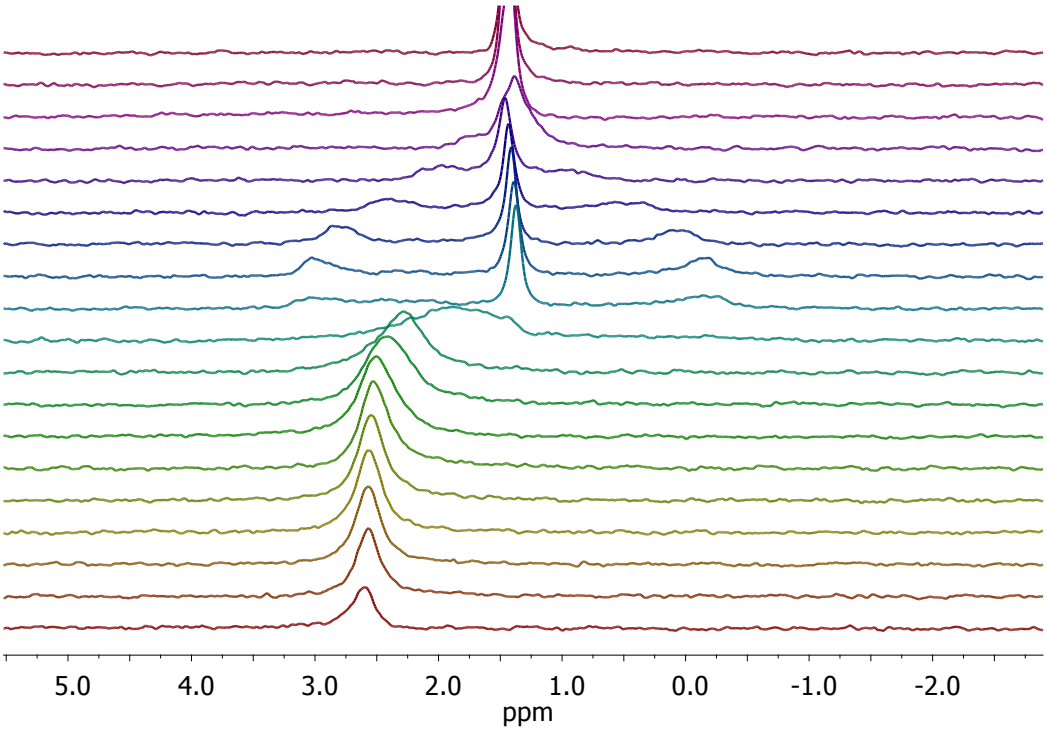

Figure S18: Slice-selective ^{7}Li spectra for the lithiation of PMDTA by *n*BuLi. Spectra were taken approximately 2 d after addition of PMDTA.

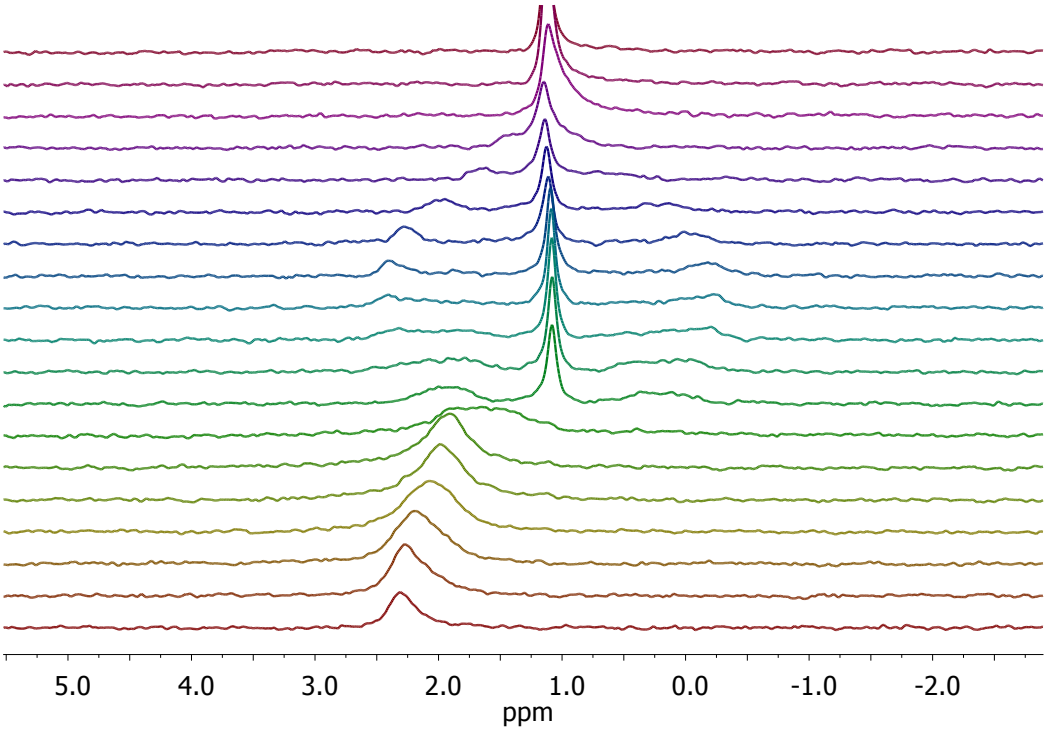

Figure S19: Slice-selective ^{7}Li spectra for the lithiation of PMDTA by *n*BuLi. Spectra were taken approximately 3 d after addition of PMDTA.

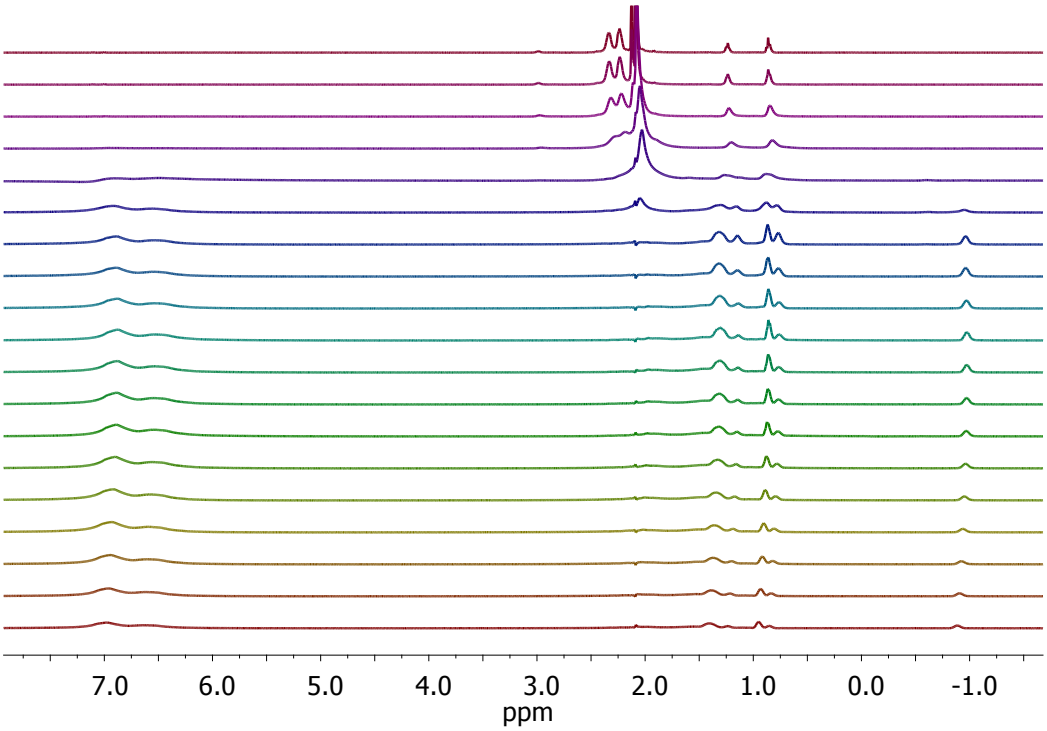

Figure S20: Slice-selective ^{1}H spectra for the lithiation of PMDTA by *n*BuLi. Spectra were taken approximately 3 h after addition of PMDTA.

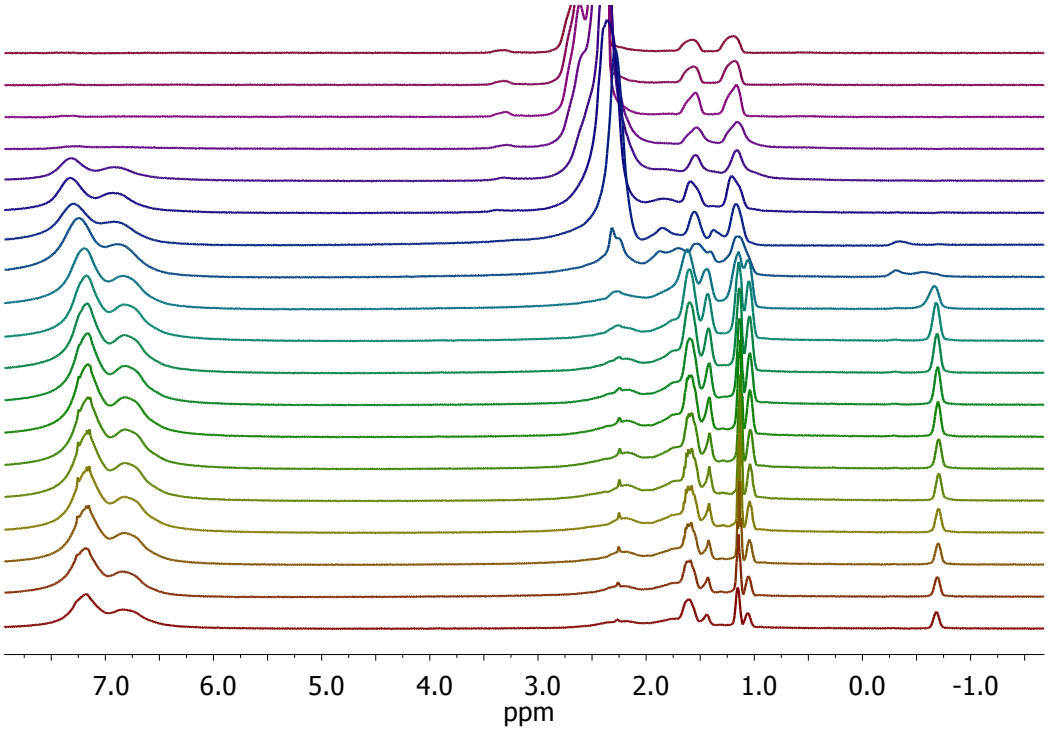

Figure S21: Slice-selective ^{1}H spectra for the lithiation of PMDTA by *n*BuLi. Spectra were taken approximately 1 d after addition of PMDTA.

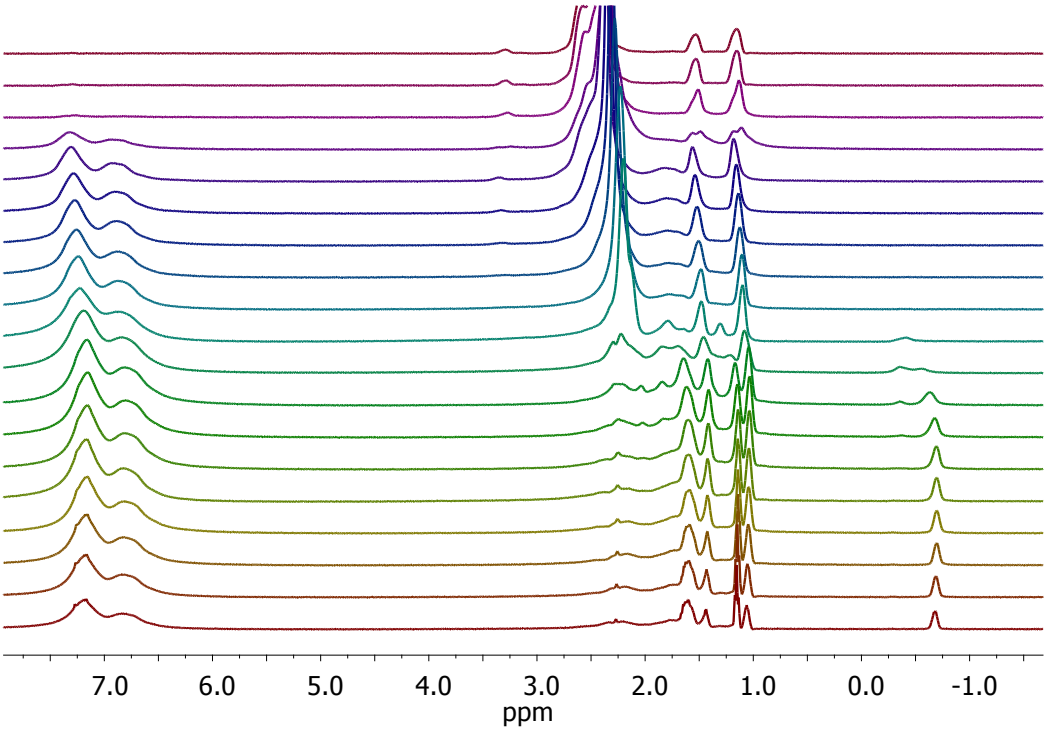

Figure S22: Slice-selective ^{1}H spectra for the lithiation of PMDTA by *n*BuLi. Spectra were taken approximately 2 d after addition of PMDTA.

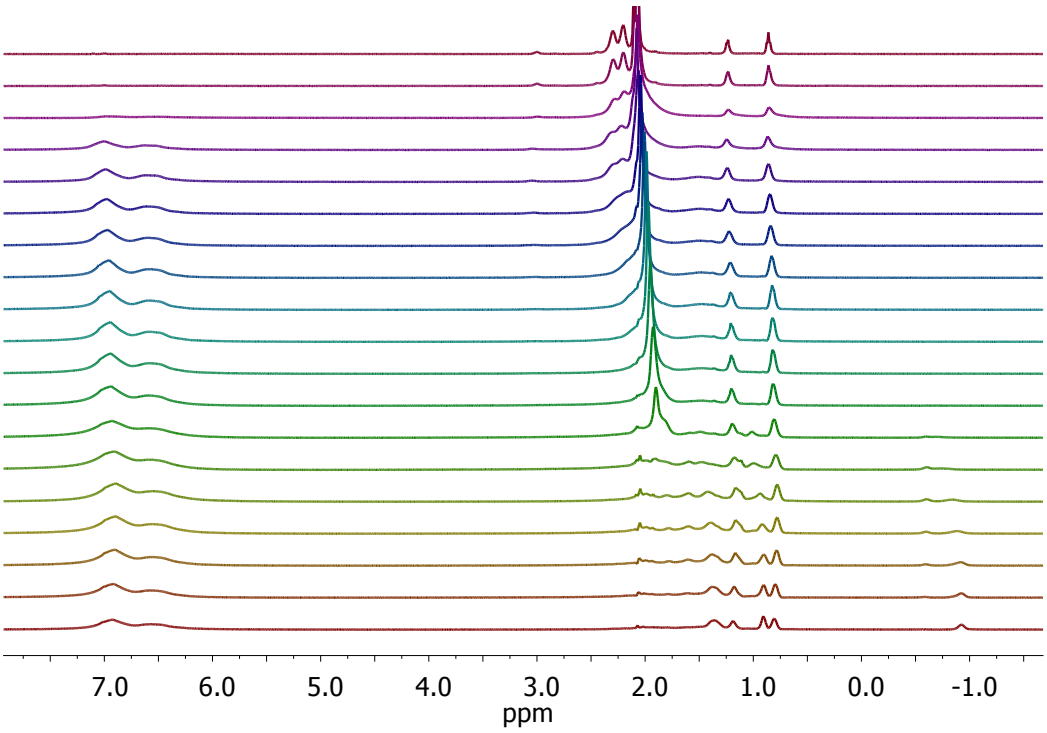

Figure S23: Slice-selective ^{1}H spectra for the lithiation of PMDTA by *n*BuLi. Spectra were taken approximately 3 d after addition of PMDTA.

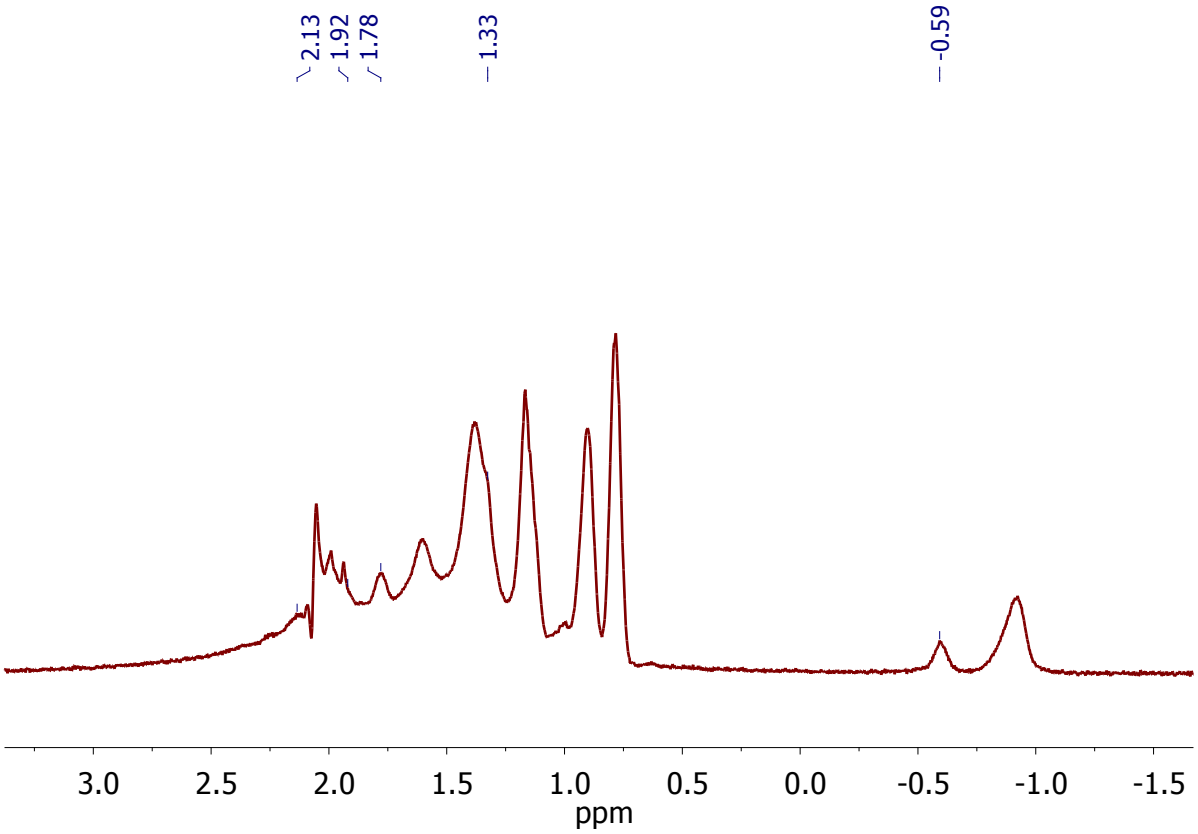

Figure S24: Slice 17 of SSE ^{1}H after 3 d with peaks marked that can be attributed to [(*n*BuLi)$_2$PMDTA]$_2$.

Peaks reported in ref. [2]: δ(ppm): -0.58 [br, 4 H, C*H*$_2$Li], 1.30 [br, 6 H, CH$_3$(C*H*$_2$)$_3$Li], 1.77 [br, 12 H, C*H*$_2$+NC*H*$_2$], 1.94 (br, 4 H, NC*H*$_2$], 2.14 [br, 15 H, NC*H*$_3$].

References

[1] A.-C. Pöppler, S. Frischkorn, D. Stalke, M. John, *ChemPhysChem* **2013**, *14*, 3103.
[2] C. Strohmann, V. H. Gessner, *Angew. Chem. Int. Ed.* **2007**, *46*, 4566.