2D ^{7}Li Ultrafast CT-COSY: a new tool for the rapid measurement of tiny homonuclear lithium scalar couplings.

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Supporting Information

Experimental Section

General Remarks

All synthetic and spectroscopic manipulations were carried out under an atmosphere of anhydrous and deoxygenated argon in flame- or oven-dried glassware. The glassware was previously cooled in a vacuum system and, then, filled with argon. Argon was dried and deoxygenated by bubbling through a commercial solution of *n*-BuLi in hexanes. Tetrahydrofuran-d_8 (THF-d_8) was distilled over sodium and benzophenone and, then, degassed prior the use. The commercially available solutions of *n*-BuLi (1.6 M in hexanes) and MeLi (1.6 M in diethyl ether) and the corresponding solutions in THF-d_8 were titrated using a procedure reported by Duhamel.[1]

Preparation of *n*-BuLi and MeLi solutions in THF-d_8

A solution of commercially available *n*-BuLi (1.6 M in hexanes) or MeLi (1.6 M in diethyl ether) (2 mL) was syringed in a tube fitted with a septum and flushed under dry argon. The tube was then placed under vacuum (20 mmHg) for 2 h to remove the main part of the solvent (hexanes or diethyl ether). Then, a second aliquot of THF-d_8 was added (1 mL) and concentrated again under vacuum to evaporate the last traces of the solvent (hexanes or ether). THF-d_8 was finally added (2 mL) at −78 °C to the residual R-Li, and the resulting solution was titrated.

Preparation of *n*-BuLi / MeLi (1:1) mixed-aggregate solution in THF-d_8

An equivalent of MeLi (~1.6 M solution in THF-d_8) was added at –78°C into a dry 5-mm NMR tube, fitted with a septum and flushed under argon, containing a solution of *n*-BuLi (0.3 mL, ~1.6 M solution in THF-d_8). The tube was vigorously shaken and, after 10 minutes, it was dropped in the pre-cooled (–78°C) NMR probe.

NMR parameters and conditions

NMR spectra were recorded at 185 K on a Bruker AVIII 500 spectrometer operating at 500.13 MHz for ^{1}H, 194 MHz for ^{7}Li, with a 5 mm BBFO probe equipped with z-axis gradients. Conventional 1D and 2D experiments were recorded with routine pulse sequences available within the commercial software Bruker Topspin 3.2.

1D ^{7}Li experiment was acquired with the standard Bruker “zg” program using 16 scans. The acquisition time was 3 s and the relaxation delay was 10 s (D1).

2D ^{7}Li COSY spectra were acquired with 1024 data points in f2 and 128 increments in f1, using four scans for each FID for a total acquisition time of 1 h 35 min. The recycling delay was 10 s; the acquisition mode was QF; the data were zero-filled once in f1 and pure sine bell window functions were applied in both dimensions before Fourier Transformation.

2D ^{7}Li UF CT-COSY spectra were recorded with the pulse sequence of Figure 1. All the UF spectra presented in this article were recorded with the following parameters. The spatial encoding was

performed via smoothed chirp pulses sweeping a band-width of 1 kHz in a duration of Tp and applied together with excitation gradients Ge fixed at 0,47 % of the maximum gradient strength available. During the acquisition, 128 pairs of bipolar gradient pulses Ga were applied (952.4 µs each, separated by a 20 µs delay). For each experiment the value of Ga was fixed at 12,65 % of the maximum value to record a spectral width of 1000 Hz (i.e., 5.2 ppm) along the ultrafast dimension. The coherence-selection is achieved thanks to sine-shape gradients pulses flanking the second chirp pulse and the last 90° pulse. The UF spectrum in the Figure. 3a was recorded with a chirp pulse duration of Tp = 50 ms, (i.e., TE = 100 ms). Then, spectra were recorded with variable Tp values as described in the text.

Once acquired, the resulting data were processed using a homewritten routine in Topspin 3.2, including an optimized Gaussian apodization in the spatially-encoded dimension[2] and a sine-bell apodization in the FT dimension. In all the spectra, the indirect domain is refereed as “ultrafast dimension” since it results from spatial-encoding without FT, whereas the direct dimension - arising from a conventional evolution during the detection period- is called “conventional dimension”.

^{7}Li CPMG experiment was performed with the standard Bruker “CPMG” program. Ten spin-echo blocks between 0.02 s and 2 s were used with 4 scans and relaxation delay of 10 s (D1).

References

1. L. Duhamel and J.-C. Plaquevent, *J. Org. Chem.*, 1993, **448**, 1.
2. P. Giraudeau and S. Akoka, *Magn. Reson. Chem.*, 2011, **49**, 307.

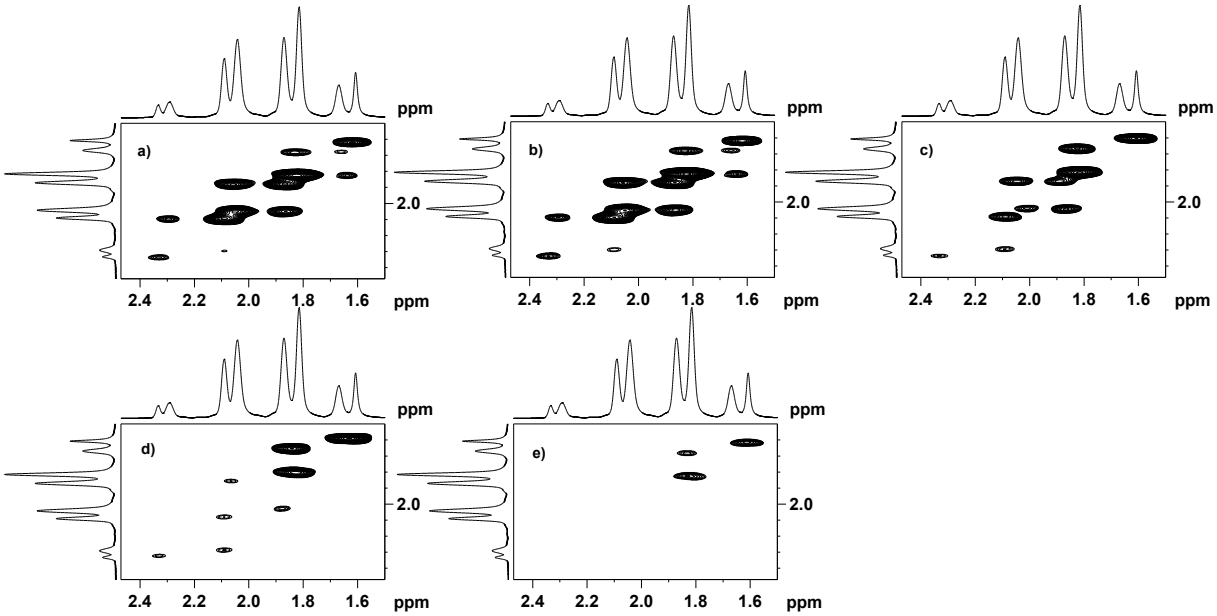

Fig. S1 2D ^{7}Li UF CT-COSY spectra of 1 : 1 *n*-BuLi / MeLi solution in THF-d_8 at 185 K, recorded with 4 scans at 194 MHz. Mixing time t_{mix} used was: (a) 0 s; (b) 0.05 s; (c) 0.10 s; (d) 0.15 s and (e) 0.16 s.

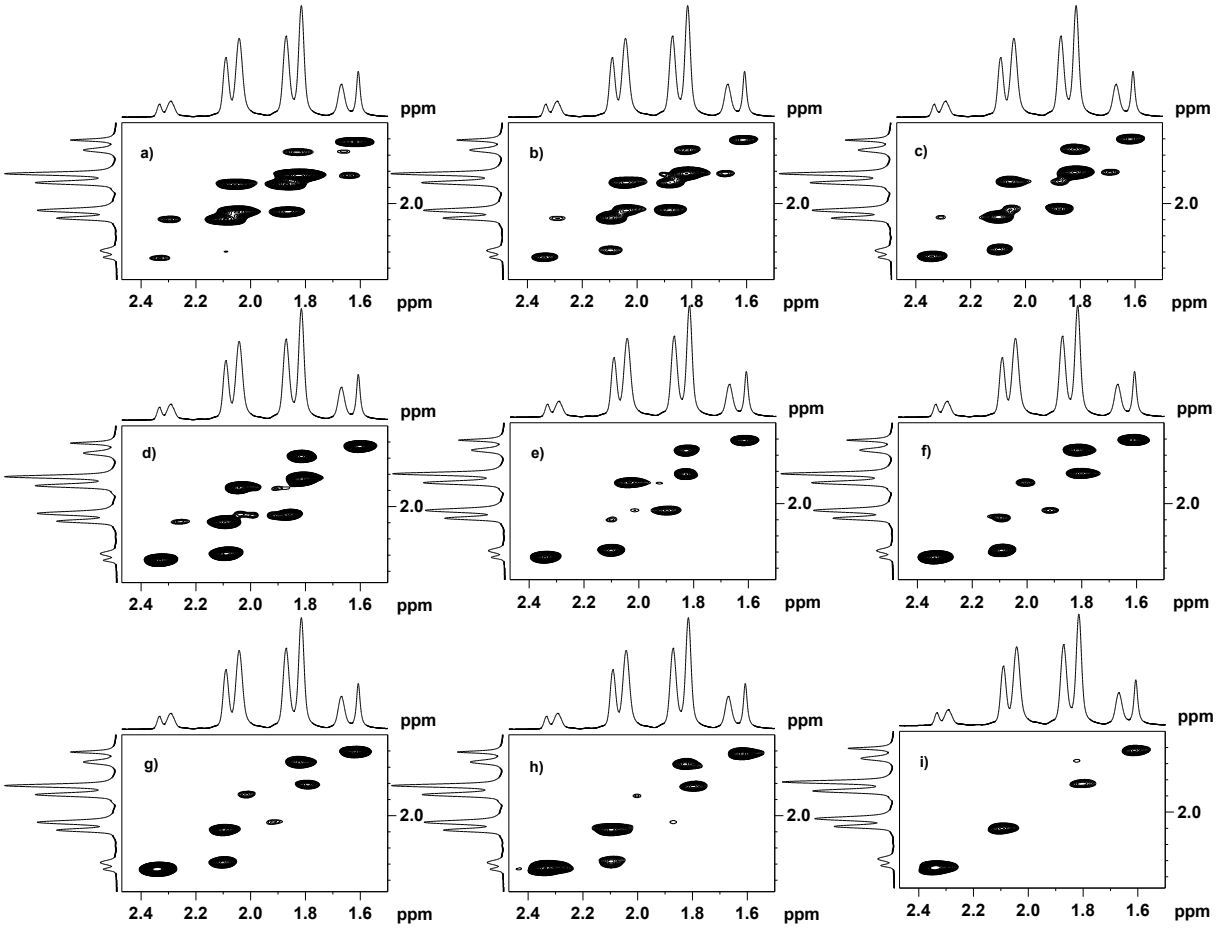

Fig. S2 2D ^{7}Li UF CT-COSY spectra of 1 : 1 *n*-BuLi / MeLi solution in THF-d_8 at 185 K, recorded with 64 scans at 194 MHz. Adiabatic pulse Tp and acquisition gradient Ga values were : (a) 50 ms and Ga of 12,6 %, (b) 80 ms and Ga of 20 %, (c) 100 ms and Ga of 25,3 %, (d) 120 ms and Ga of 30,36 %, (e) 135 ms and Ga of 32,89 %, (f) 160 ms, Ga of 40,48 % and (g) 180 ms and Ga of 45,54 % and (h) 195 ms and Ga of 49,33 %, (i) 215 ms and Ga of 54,39 %.

Aggregates	Lithium signal	T_2 (s)
$(MeLi)_4$	L_1	0.732
$(n\text{-BuLi})_1(MeLi)_3$	L_2	0.245
	L_3	0.203
$(n\text{-BuLi})_2(MeLi)_2$	L_4	0.208
	L_5	0.212
$(n\text{-BuLi})_3(MeLi)_1$	L_6	0.223
	L_7	0.227
$(n\text{-BuLi})_4$	L_8	0.208

Table S1. Mixed-aggregates $(n\text{-BuLi})_{4-n}(MeLi)_n$ lithium transverse relaxation T_2 values obtained at 185 K by a CPMG sequence at 194 MHz.