# Supporting Information

## Aggregation of Donor Base stabilized 2-Thienyllithium in the Single Crystal and in Solution – Distances from X-ray and NOE

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Content:

Experimental Details, Physical and Spectroscopic data for componds **1-5**

**Synthesis and Characterization of 1-5** S2

**$^{1}$H,$^{7}$Li HOESY spectra** S4

**Build-up curves** S5

**Calculation *vs.* Experiments** S6

**Reactivity of 4 and 5 (temporary lithiation of toluene-$d_8$)** S6

**Stacked plots ($^{1}$H and $^{7}$Li)** S7

**Selected bond length and angles from the X-ray analysis** S7

**References** S8

**Experimental details and physical data**

***General Consideration***

All experimental manipulations were performed either in an inert gas atmosphere of purified dry nitrogen with standard Schlenk techniques.[S1] or in an argon glove box. The glassware's were dried at 140 °C, assembled hot and cooled down under vacuum. All solvents were dried over sodium-potassium alloy, distilled and degassed prior to use. The chemicals and solvents were commercially purchased, dried, freshly distilled before use and stored under inert atmosphere. The *n*-butyllithium, which was kindly contributed by the CHEMETALL GMBH, was filtered through Celite© before use and the concentration determined.[S2] All NMR spectra were recorded on a BRUKER Avance III 400 Microbay and BRUKER DPX 500 spectrometer using the protons of $C_7D_8$ as internal standard. Elemental analyses were carried out on a VARIO EL3 device at the Analytisches Labor, Institut für Anorganische Chemie, University of Göttingen.

***Synthesis and Characterization***

To a solution of thiophene (2.0 mL, 27.6 mmol) in 20 mL diethyl ether a solution of one equivalent of *n*-BuLi (1.51 M in *n*-hexane) over 30 minutes at 0 °C was added. An excess of donor base (2.5 eq.) was added followed by constant stirring for another 30 minutes. The solution was then cooled to -78° C. The crystals thus formed were filtered, washed twice with pre cooled *n*-hexane (-78° C) and finally dried in *vacuo*.

This general method was applied for the synthesis of all presented compounds (**1-5**).

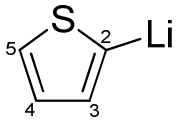



**Figure S1.** Assignment of 2-thienyllithium.

**[2-Thienyllithium · $Et_2O$]$_4$ (1):** Colorless crystals were obtained in a yield of 2.4 g (3.6 mmol, 52 %). $C_{32}H_{52}Li_4O_4S_4$ (656.74 g/mol); $\delta^1$H ($C_7D_8$): 7.80 (d, $^3J_{HH}$ = 4.3 Hz, 1 H, $H_5$), 7.63 (d, $^3J_{HH}$ = 2.7 Hz, 1 H, $H_3$), 7.33 (dd, $^3J_{HH}$ = 4.3 Hz, $^3J_{HH}$ = 2.8 Hz, 1H, $H_4$), 3.19 (q, $^3J_{HH}$ = 7.0 Hz 6 H, C$H_3$), 0.96 (t, $^3J_{HH}$ = 7.0 Hz 4 H, C$H_2$); $\delta^{13}$C{$^1$H}($C_7D_8$): 166.9 ($C_2$), 137.5 ($C_5$), 133.1 ($C_3$), 128.1 ($C_4$), 65.7 (*C*H$_3$), 15.1 (*C*H$_2$); $\delta^7$Li{$^1$H}: 2.1 (s).

**[2-Thienyllithium · 2 THF]$_2$ (2):** Colorless crystals were obtained in a yield of 1.2 g (2.6 mmol, 18.5 %). $C_{24}H_{38}Li_2O_4S_2$ (468.54 g/mol); $\delta^1$H ($C_7D_8$): 7.88 (d, $^3J_{HH}$ = 4.3 Hz, 1 H, $H_5$), 7.70 (dd, $^3J_{HH}$ = 2.7 Hz, $^4J_{HH}$ = 2.4 Hz, 1 H, $H_3$), 7.430 (dd, $^3J_{HH}$ = 4.28 Hz, $^3J_{HH}$ = 2.76 Hz, 1H, $H_4$), 3.41 (m, 8 H, OC$H_2$), 1.39 (m, 8 H, C$H_2$); $\delta^{13}$C{$^1$H} ($C_7D_8$): 170.9 ($C_2$), 137.2 ($C_5$), 131.6 ($C_3$), 127.7 ($C_4$), 65.7 (O*C*H$_2$), 25.7 (*C*H$_2$); $\delta^1$Li{$^1$H}: 1.9 (s).

**[2-Thienyllithium · DME]$_2$ (3)**: Colorless crystals were obtained in a yield of 3.6 g (10.0 mmol, 79 %). $C_{16}H_{26}Li_2O_4S_2$ (360.39 g/mol); $\delta^1$H ($C_7D_8$): 7.95 (dd, $^3J_{HH}$ = 4.3 Hz, $^4J_{HH}$ = 0.4 Hz, 1 H, $H_5$), 7.69 (dd, $^3J_{HH}$ = 2.8 Hz, $^4J_{HH}$ = 0.4 Hz, 1 H, $H_3$), 7.57 (dd, $^3J_{HH}$ = 4.4 Hz, $^3J_{HH}$ = 2.8 Hz, 1 H, $H_4$), 3.02 (s, 6 H, C$H_3$), 2.72 (s, 4 H, C$H_2$); $\delta^{13}$C{$^1$H} ($C_7D_8$): 172.1 ($C_2$), 136.5 ($C_5$), 130.7 ($C_3$), 127.5 ($C_4$), 70.1 ($C$H$_3$), 58.8 ($C$H$_2$); $\delta^7$Li{$^1$H}: 1.7 (s).

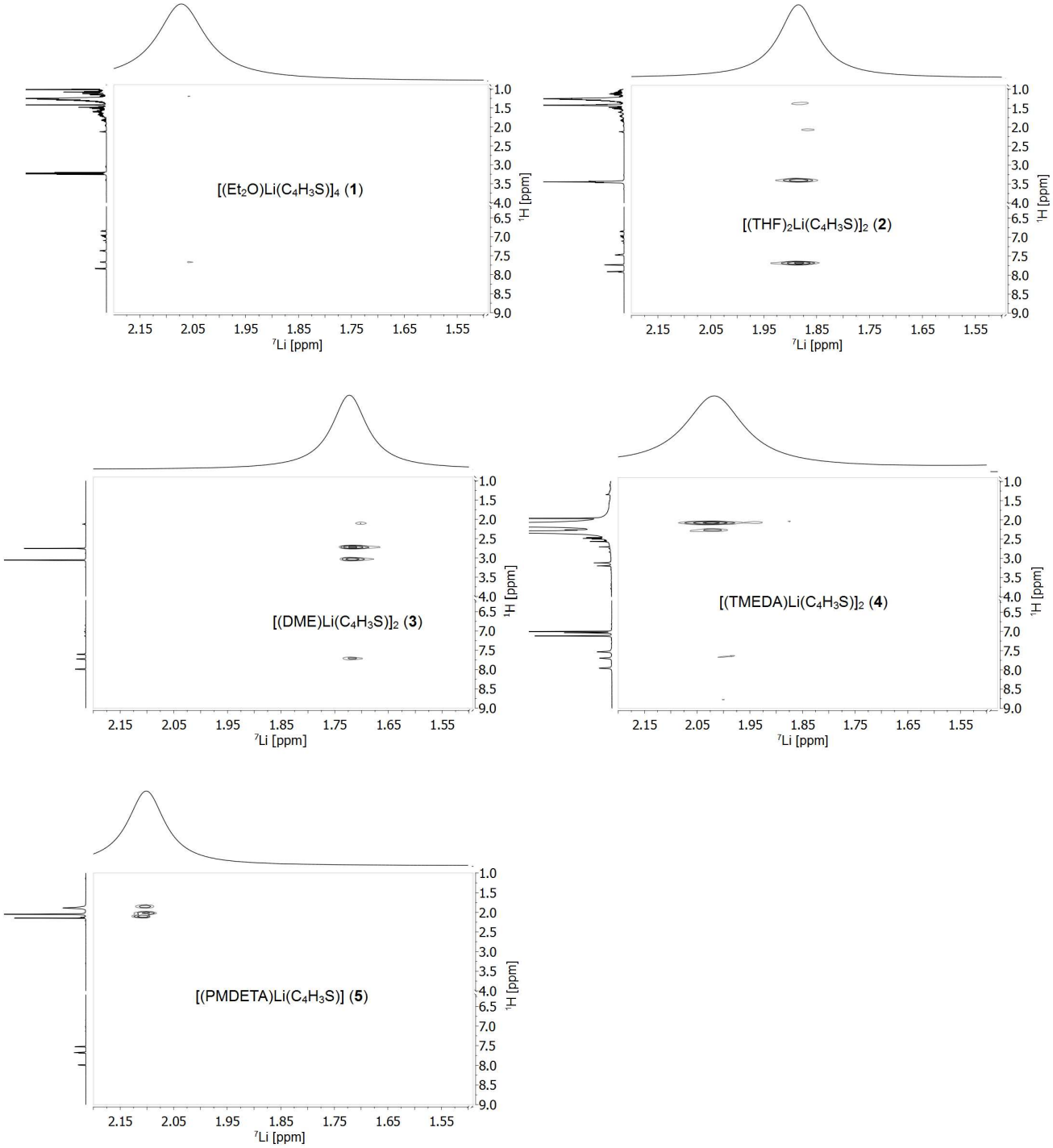
**[2-Thienyllithium · TMEDA]$_2$ (4)** Yellow crystals were obtained in a yield of 2.8 g (6.8 mmol, 49 %). $C_{20}H_{38}Li_2N_4S_2$ (412.55 g/mol); $\delta^1$H ($C_7D_8$): 7.92 (d, $^3J_{HH}$ = 5.0 Hz, 1 H, $H_5$), 7.66 ($s_{br}$, 1 H, $H_3$), 7.50 (d, $^3J_{HH}$ = 4.8 Hz, 1 H, $H_4$), 2.28 (s, 12 H, C$H_3$), 2.09 (s, 4 H, C$H_2$); $\delta^{13}$C{$^1$H} ($C_7D_8$): 174.4 ($C_2$), 137.2 ($C_5$), 130.8 ($C_3$), 127.4 ($C_4$), 58.4 ($C$H$_2$), 46.0 ($C$H$_3$); $\delta^7$Li{$^1$H}: 2.0 (s).

**[2-Thienyllithium · PMDETA] (5)**: Light-red crystals were obtained in a yield of 3.4 g (12.9 mmol, 47 %). $C_{13}H_{26}LiN_3S$ (263.3 g/mol); $\delta^1$H ($C_7D_8$): 7.95 (dd, $^3J_{HH}$ = 4.2 Hz, $^4J_{HH}$ = 0.4 Hz, 1 H, $H_5$), 7.64 (dd, $^3J_{HH}$ = 4.2 Hz, $^3J_{HH}$ = 2.7 Hz, 1 H, $H_4$), 7.49 (dd, $^3J_{HH}$ = 2.7 Hz, $^4J_{HH}$ = 0.4 Hz, 1 H, $H_3$), 2.11 (s, 3 H, NC$H_3$), 2.01 (s, 12 H, N(C$H_3$)$_2$), 1.86 (br, 8 H, C$H_2$); $\delta^{13}$C{$^1$H} ($C_7D_8$): 180.1 ($C_2$), 137.5 ($C_5$), 133.3 ($C_3$) 126.8 ($C_4$), 57.3 ($Me_2NCH_2$), 53.9 ($CH_2$NMe), 45.9 (N($C$H$_3$)$_2$), 44.6 (N$C$H$_3$); $\delta^7$Li{$^1$H}: 2.1 (s).

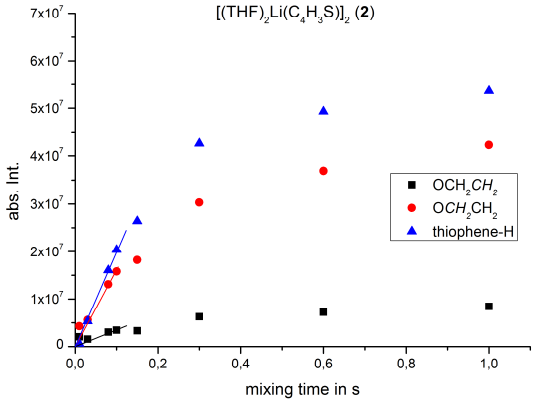
**Further NMR data (COSY, of 1-5**

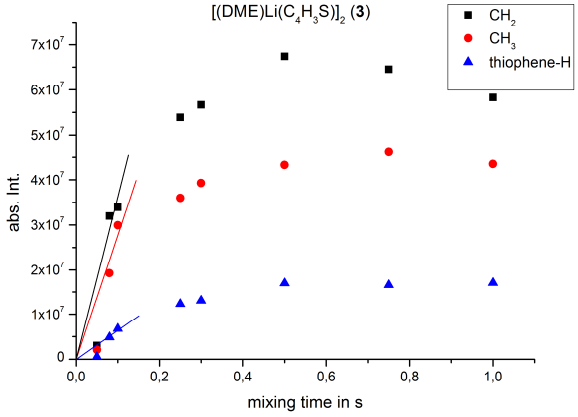
All NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer (Bruker Biospin, Rheinstetten ) with a broadband-observe-probe, z-gradient and temperature unit. The spectra were measured at RT in toluene$d_8$ if not indicated otherwise. All spectra were processes with Topspin 2.1 (Bruker Biospin, Rheinstetten) and further plotted with MestreNova, Version 7.0 (Mestrelab Research, Santiago de Compostela, Spain).

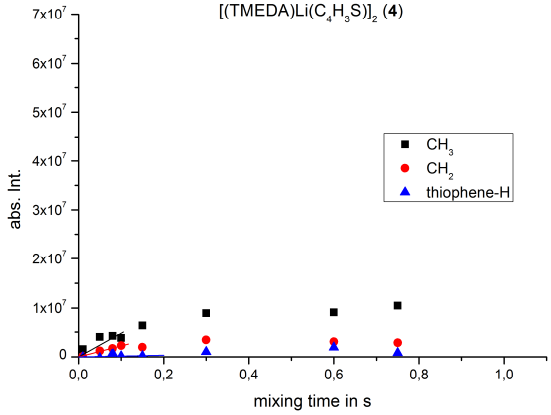
**$^1$H,$^7$Li HOESY spectra**

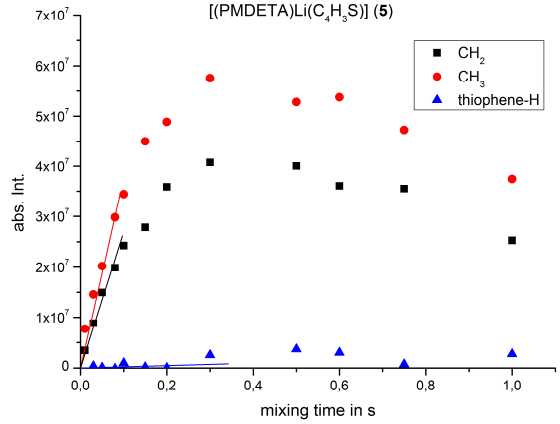


## Build-up curves

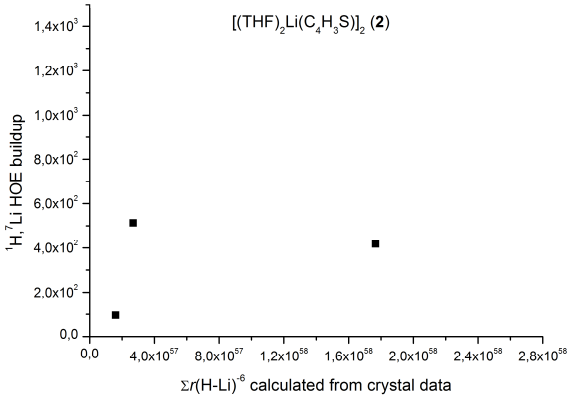


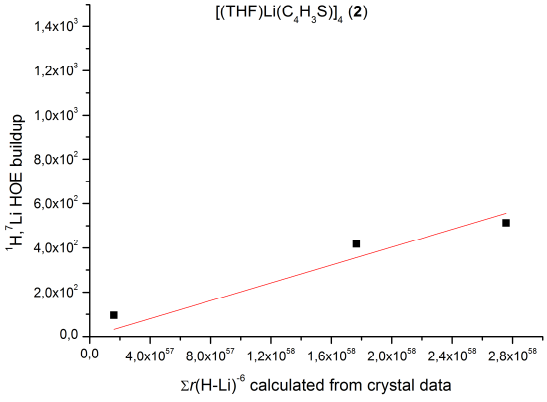



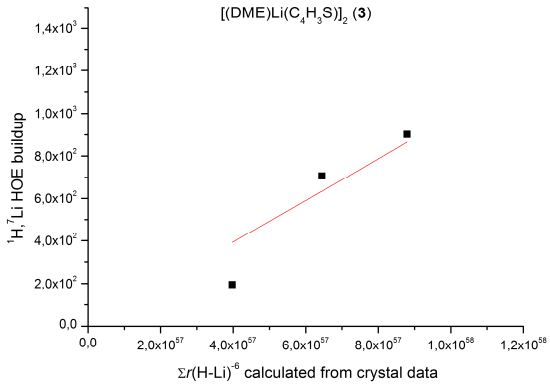



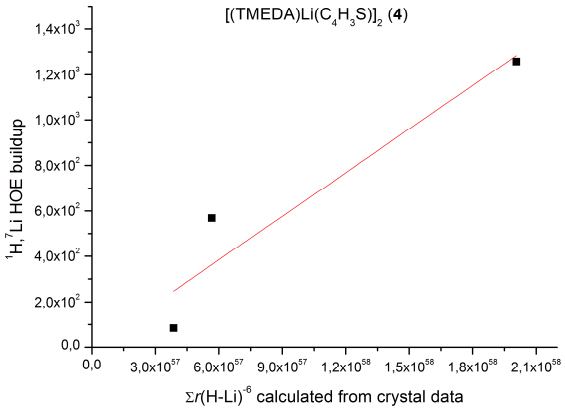



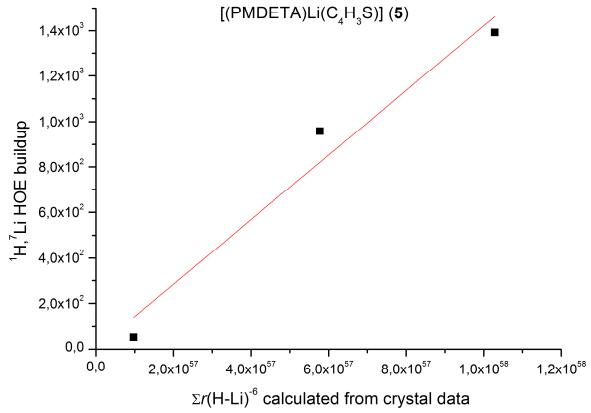

## Calculation *vs.* Experiments



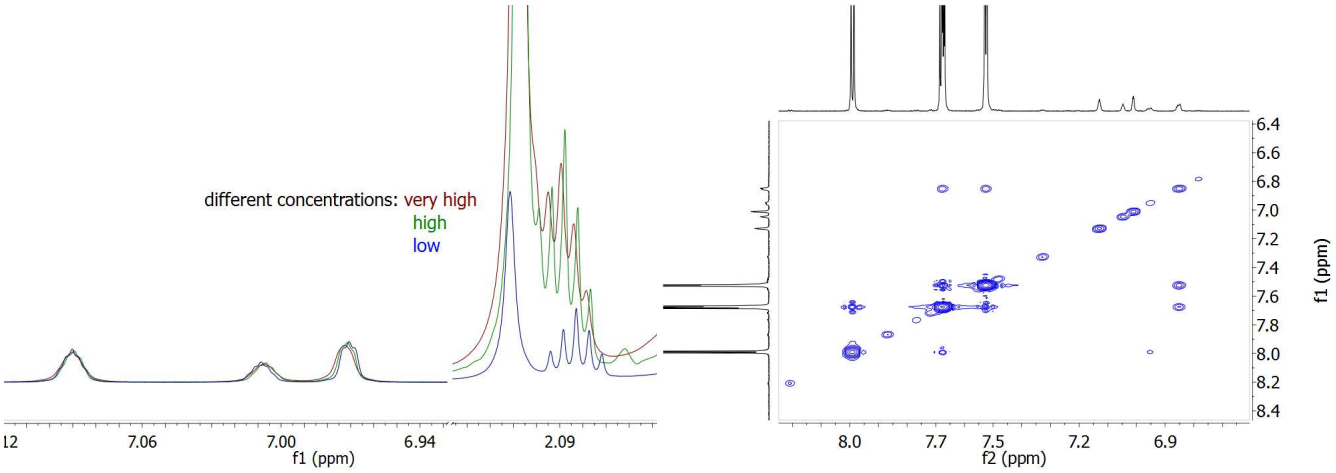





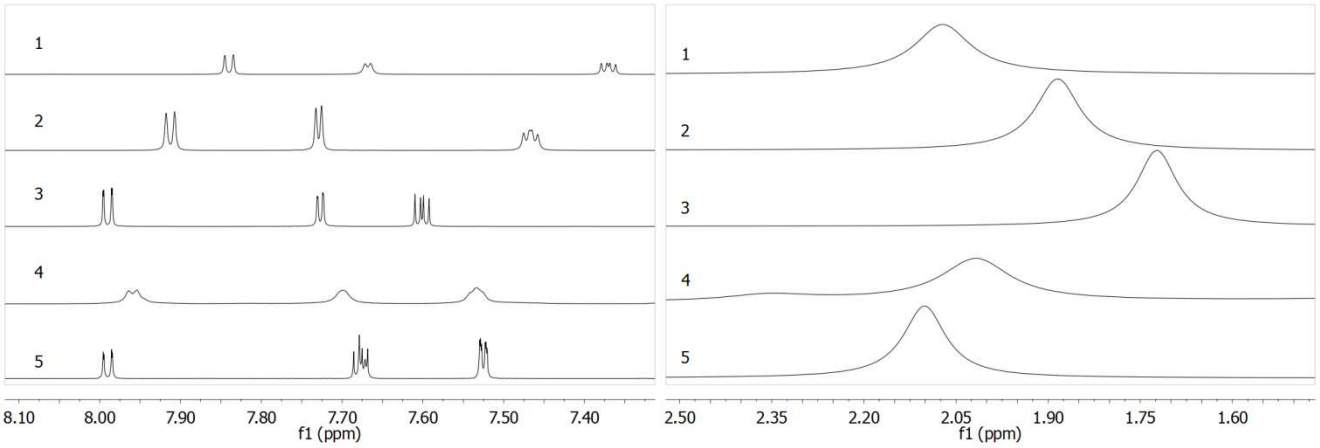




## Reactivity of 4 and 5 (temporary lithiation of toluene-$d_8$)




Left: $^1$H NMR spectra of solutions containing different concentrations of **5.** The aromatic protons of toluene are superimposed adequately and a different intensity for the methyl group becomes obvious (due to protonation). Right: Aromatic region from the $^1$H-EXSY spectrum of **5** in toluene-$d_8$. (traces do not match 2D spectrum, less numbers on f1 axis)

## Stacked plots ([1]




Left: $^{1}$H NMR spectra of **1**-**5**, right: $^{7}$Li{$^{1}$H} NMR spectra of **1**-**5**. All spectra were recorded in toluene-$d_8$ at 25 °C.

## Selected bond length and angles from the X-ray analysis

**Table S1.** Additional selected bond length [pm] and angle [°] of **1**-**5**.

| Bond length[pm] and angle[°] | **1** | **2** | **3** | **4**[S8] | **5** |
|---|---|---|---|---|---|
| C1–Li1 | 230.1(4) | 220.9(3) | 217.5(4) | 220.9 | 211.5(3) |
| C1–Li2 | 225.7(4) | 224.4(3) | 225.3(3) | 217.9 | – |
| C1–Li3 | 227.2(4) | – | – | – | – |
| C1'–Li1 | – | | 200(4) <10% | | 195.(2) <10% |
| C1'–Li2 | – | | 193(4) <10% | | – |
| C5–Li1 | 228.9(4) | 223.0(4) | 223.1(14) | 220.5 | – |
| C5–Li3 | 225.1(4) | 216.0(4) | 218.8(9) | 217.9 | – |
| C5–Li4 | 228.9(4) | | | – | – |
| C9–Li2 | 233.2(4) | | | – | – |
| C9–Li3 | 229.2(4) | | | – | – |
| C9–Li4 | 225.7(4) | | | – | – |
| C13–Li1 | 227.9(4) | | | – | – |
| C13–Li2 | 229.1(4) | | | – | – |
| C13–Li4 | 227.6(4) | | | – | – |
| | | | | | |
| C5'–Li1 | | 215.2.(14) | 215(2) <40% | – | – |
| C5'–Li2 | | 237.5(13) | 214.2(16) <40% | – | – |

| | | | | | |
|---|---|---|---|---|---|
| C1–S1 | 173.8(2) | 172.95(15) | 172.4(3) | 171.2 | 172.5(2) |
| C5–S2 | 173.9(2) | 174.5(3) | 172.0(9) | 171.1 | – |
| C1–C2 | 138.8(3) | 137.8(4) | 136.4(5) | 144.2 | 136.5(5) |
| C5–C6 | 139.3(3) | 139.5(6) | 136.4(12) | 149.6 | – |
| | | | | | |
| O1–L1 | 193.8(4) | 196.3(2) | | – | – |
| O1–Li2 | | | 199.2(3) | – | – |
| O2–Li1 | | 204.8(6) | | – | – |
| O2–Li2 | 198.3(4) | | 201.7(3) | – | – |
| O3–Li1 | 184.6(7) | 194.8(2) | 201.1(3) | – | – |
| O4–Li1 | | 195.9(3) | 198.8(3) | – | – |
| N1–Li1 | – | – | – | 215.5 | 212.1(2) |
| N2–Li1 | – | – | – | 213.9 | 213.7(2) |
| N3–Li1 | – | – | – | 216.8 | 214.5(2) |
| N4–Li2 | – | – | – | 219.2 | – |
| | | | | | |
| S1'–Li1 | ~300 | | 303.6(17) <10% | – | |
| S2'–Li1 | | | 303.9(6) <40% | – | |
| | | | | | |
| C2–C1–S1 | 105.06(15) | 104.9(2) | 104.22(14) | 107.53 | 103.6(2) |
| Li1–C1–Li2 | | 67.90(9) | 68.85(12) | 72.04 | – |
| Li1–C5–Li2 | | 68.98(12) | 69.0(2) | 70.80 | – |
| C1–Li1–C5 | 100.17(15) | 109.65(12) | 110.2(3) | 103.73 | – |
| C1–Li2–C5 | | 110.94(13) | 108.9(5) | 103.24 | – |
| | | | | | |
| Av. Li–Li | 271.4(5) | 248.7(3) | | 258.1 | – |
| Av. C–Li | 228.2(4) | 222.83(14) | 213.3(14) | 218.73 | 211.5(3) |

**References**


S1 a) Schlenk W. *Die Methoden der Organischen Chemie* **1924** J. Houben. Leipzig, G. Thieme, 720. b) Schlenk, W.; Holtz, J. *Berichte der Deutschen Chemischen Gesellschaft* **1917**, *50*, 262-274.

S2 Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*(10), 1879-1880.