

## Solution and Chelation Properties of 2-Thienyllithium Reagents

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### Supporting Materials

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## Experimental Section

**General.** All reactions requiring a dry atmosphere were performed in glassware flame-dried or dried overnight in a 110 °C oven, sealed with septa and flushed with dry N<sub>2</sub>. 3-Methylthiophene, 2-bromo-3-methylthiophene and selenophene were commercially available. 3-(Bromomethyl)thiophene was prepared as reported by Slocum and Gierer.<sup>[S-1]</sup> Thiophene was distilled from KOH and stored over 4Å molecular sieves under N<sub>2</sub>. Tetrahydrofuran (THF) and Et<sub>2</sub>O were freshly distilled from sodium benzophenone ketyl under N<sub>2</sub>. Me<sub>2</sub>O was purified by condensing several mL in a graduated conical flask at -78 °C from a pressurized gas cylinder, adding a small portion (0.5 mL) of *n*-BuLi and distilling the dry Me<sub>2</sub>O via cannula into the desired vessel at -78 °C. *N,N,N',N'*-Tetramethylethylenediamine (TMEDA), *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDTA) and hexamethylphosphoric triamide (HMPA) were distilled from CaH<sub>2</sub> under reduced pressure (if necessary) and stored over 4Å molecular sieves under N<sub>2</sub>. Common lithium reagents were handled with septum and syringe-based techniques and titrated against dry *n*-propanol in THF using 1,10-phenanthroline as indicator.<sup>[S-2]</sup> [<sup>6</sup>Li]BuLi was prepared by literature methods.<sup>[9c]</sup>

**3-Methyl-2-trimethylstannyl-thiophene.** 1.7 M *t*-BuLi in pentane (6.3 mL, 10.8 mmol) was added slowly to a -78 °C solution of 2-bromo-3-methyl-thiophene (0.91 g, 5.1 mmol) in THF (20 mL). After 5 min at -78 °C, Me<sub>3</sub>SnCl (1.2 g, 6.1 mmol) in THF (10 mL) was added slowly to the yellow solution. After stirring for 0.5 h, the clear, colorless solution was poured into aq. NH<sub>4</sub>Cl and the product extracted with 1:1 Et<sub>2</sub>O/hexane. The organic layer was washed with brine, dried with MgSO<sub>4</sub>, filtered and the solvent removed *in vacuo*. The clear, yellow oil was purified by distillation (130-137 °C at 10 mm Hg) giving 0.84 g of a clear, colorless oil (3.2 mmol, 63 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 360 MHz): δ 0.41 (s, <sup>2</sup>J<sub>IH-119Sn</sub> = 57.2 Hz, 9H), 2.37 (s, <sup>4</sup>J<sub>IH-119Sn</sub> = 5.7 Hz, 3H), 7.08 (d, *J* = 4.6 Hz, <sup>4</sup>J<sub>IH-119Sn</sub> = 7.0 Hz, 1H), 7.54 (d, *J* = 4.6 Hz, <sup>4</sup>J<sub>IH-119Sn</sub> = 13.6 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 90.56 MHz): δ -8.3 (*J*<sub>13C-119Sn</sub> = 370.9 Hz, CH<sub>3</sub>), 17.3 (<sup>3</sup>J<sub>13C-119Sn</sub> = 15.9 Hz, CH<sub>3</sub>), 130.4 (<sup>3</sup>J<sub>13C-119Sn</sub> = 21.9 Hz, CH), 130.6 (<sup>3</sup>J<sub>13C-119Sn</sub> = 40.4 Hz, CH). MS (EI): M<sup>+</sup> = 246.9614 (calcd for C<sub>8</sub>H<sub>14</sub>SSn-CH<sub>3</sub> = 246.9603).

**2-Methylselenophene.** Prepared by a modification of a literature preparation<sup>[S-3]</sup> using the metalation with *t*-butyllithium of a solution of selenophene in THF (-78 °C, 10 min) followed by quenching with MeI. A 1:37:1 ratio of selenophene, 2-methylselenophene and 2,5-dimethylselenophene was obtained.

**3-(Methoxymethyl)thiophene.** NaOMe (6.04 g, 112 mmol) was added to a flask containing CH<sub>3</sub>CN (50 mL) and cooled to 0 °C. 3-Bromomethylthiophene (6.8 g, 53 mmol) in CH<sub>3</sub>CN (5 mL) was added slowly and the reaction stirred at rt for 24 h. The mixture was filtered, diluted with H<sub>2</sub>O, and the product extracted with 1:1 Et<sub>2</sub>O/hexane. The aqueous layer was acidified and extracted with 1:1 Et<sub>2</sub>O/hexane. The combined organic layers were washed with brine, dried with MgSO<sub>4</sub>, filtered and the solvent removed *in vacuo*. The resulting oil was distilled (30-35 °C @ 0.04 mm Hg) to give 2.15 g (32 %) of a clear, colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 3.34 (s, 3H), 4.43 (s, 2H), 7.04 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.17 (m, 1H), 7.26 (dd, *J* = 5.0, 2.9 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ 57.7 (CH<sub>3</sub>), 69.6 (CH<sub>2</sub>), 122.6 (CH), 125.7 (CH), 127.1 (CH), 139.2 (C). MS (EI): M<sup>+</sup> = 128.0301 (calcd for C<sub>6</sub>H<sub>8</sub>OS = 128.0296).

**3-(*N,N*-Dimethylaminomethyl)thiophene.** 3-(Bromomethyl)thiophene (4.4 g, 25 mmol) was added dropwise to a solution of 40 % HNMe<sub>2</sub> in H<sub>2</sub>O. The solution was warmed to 50 °C for 3 h then allowed to stand at rt overnight. The product was extracted with 1:1 Et<sub>2</sub>O/hexane and washed with brine. The organic layer was dried with MgSO<sub>4</sub> and the solvent removed *in vacuo*. The resulting oil was distilled (27-29 °C @ 0.04 mm Hg) to give 280 mg (8%) of a clear oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.24 (s, 6H), 3.46 (s, 2H), 7.05 (dd, *J* = 5.1, 1.5 Hz, 1H), 7.11 (m, 1H), 7.27 (dd, *J* = 5.1, 2.9 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ 45.2 (CH<sub>3</sub>), 58.8 (CH<sub>2</sub>), 122.6 (CH), 125.3 (CH), 128.4 (CH), 139.8 (C). MS (EI): M<sup>+</sup> = 141.0609 (calcd for C<sub>7</sub>H<sub>11</sub>NS = 141.0612).

**[<sup>15</sup>N]-Thiophene-3-carboxylic acid amide.** Thionyl chloride (4.8 mL, 66 mmol) was added dropwise to 3-thiophenecarboxylic acid in a water bath. A catalytic amount of DMF (5 μL) was added. After 16 h, the

product mixture was heated to 50 °C and the thionyl chloride was evaporated under a stream of N<sub>2</sub>. Benzene (5 mL) was added and evaporated in the same fashion to ensure all of the thionyl chloride had evaporated. [<sup>15</sup>N]-Ammonium chloride (420 mg, 7.8 mmol) was dissolved in H<sub>2</sub>O (6 mL), benzene (5 mL) was added and the biphasic solution cooled to 0 °C. A solution of NaOH (820 mg, 21 mmol) in H<sub>2</sub>O (6 mL) was added directly to the aqueous layer via pipette. Immediately, thiophene-3-carbonyl chloride in 20 mL benzene was added. A white precipitate formed within minutes. The reaction was stirred for 18 h, cooled to 0 °C and filtered. The white precipitate was washed with cold H<sub>2</sub>O (50 mL) and benzene (30 mL). The light tan solid was allowed to dry giving 820 mg (6.4 mmol, 82 %) of [<sup>15</sup>N]-thiophene-3-carboxylic acid amide. mp 179-181 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 5.61 (br, 1H), 6.85 (br, 1H), 7.36 and 7.40 (AB of ABX,  $J_{AX} = 1.3$  Hz,  $J_{BX} = 2.9$  Hz,  $J_{AB} = 5.0$  Hz, 2H), 7.92 (X of ABX, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 126.4 (CH), 126.9 (CH), 129.3 (CH), 136.5 (d,  $^2J_{13C-15N} = 8.9$  Hz, (C)), 164.6 (d,  $J_{13C-15N} = 15.5$  Hz, (C)). MS (ESI): [M+Na]<sup>+</sup> = 150.9958 (calcd for [C<sub>5</sub>H<sub>5</sub><sup>15</sup>NOS + Na]<sup>+</sup> = 150.9960).

**[<sup>15</sup>N]-Thiophene-3-carboxylic acid dimethylamide.** A solution of [<sup>15</sup>N]-thiophene-3-carboxylic acid amide (820 mg, 6.4 mmol) and MeI (1.6 mL, 25 mmol) in DMSO (7 mL) was slowly added to a 0 °C mixture of KOH (2.8 g, 50 mmol) and DMSO (8 mL). The mixture was stirred for 3.5 h at rt, then added to H<sub>2</sub>O (130 mL). The product was extracted using CH<sub>2</sub>Cl<sub>2</sub> (4 x 40 mL). The combined organic layers were washed with H<sub>2</sub>O (4 x 80 mL) and brine (120 mL), dried with MgSO<sub>4</sub> and filtered. The solvent was removed *in vacuo* to give 930 mg of [<sup>15</sup>N]-thiophene-3-carboxylic acid dimethylamide (6.0 mmol, 93 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 3.09 (d,  $^2J_{1H-15N} = 1.1$  Hz, 6H), 7.22 (dd,  $J = 5.0, 1.4$  Hz, 1H), 7.32 (dd,  $J = 5.0, 3.0$  Hz, 1H), 7.53 (dd,  $J = 3.0, 1.4$  Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 35.6 (CH<sub>3</sub>), 39.3 (CH<sub>3</sub>), 125.5 (CH), 126.4 (CH), 127.3 (CH), 136.8 (d,  $^2J_{13C-15N} = 8.7$  Hz, (C)), 166.9 (d,  $J_{13C-15N} = 16.3$  Hz, (C)). MS (ESI): [M+Na]<sup>+</sup> = 179.0279 (calcd for [C<sub>7</sub>H<sub>9</sub><sup>15</sup>NOS + Na]<sup>+</sup> = 179.0273).

**[<sup>15</sup>N]-3-(*N,N*-Dimethylaminomethyl)thiophene.** Borane in THF (1.0 M, 26 mL, 26 mmol) was added at 0 °C to [<sup>15</sup>N]-thiophene-3-carboxylic acid dimethylamide (820 mg, 6.4 mmol). The solution was refluxed for 5 h, cooled to 0 °C and 6 M HCl (21 mL) was slowly added and heated to reflux for 2.5 h to hydrolyze the amine borane adduct. The solution was cooled to 0 °C and basified with NaOH until pH 10 and stirred for 1h. The solution was extracted with 1:1 Et<sub>2</sub>O/hexane (2 x 75 mL). The combined organic layers were washed with H<sub>2</sub>O (2 x 100 mL) and brine (100 mL). The organic layer was dried with MgSO<sub>4</sub>, filtered and the solvent removed *in vacuo*. Unfortunately, boronate esters were still present so the product was stirred for 4 h in 1 M NaOH (100 mL) and extracted. The product was purified by Kugelrohr distillation (84-91 °C @ 30 mm Hg) to give 340 mg of [<sup>15</sup>N]-3-(*N,N*-dimethylaminomethyl)thiophene (2.36 mmol, 40 %) as a clear, colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.23 (d,  $^2J_{1H-15N} = 0.9$  Hz, 6H), 3.45 (br, 2H), 7.05 (dd,  $J = 5.0, 1.3$  Hz, 1H), 7.11 (m, 1H), 7.27 (dd,  $J = 5.0, 2.9$  Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 45.2 (d,  $J_{13C-15N} = 4.1$  Hz, CH<sub>3</sub>), 58.8 (d,  $J_{13C-15N} = 3.8$  Hz, CH<sub>2</sub>), 122.7 (CH), 125.4 (CH), 128.4 (CH), 139.8 (C). MS (EI): M<sup>+</sup> = 142.0589 (calcd for C<sub>7</sub>H<sub>11</sub><sup>15</sup>NS = 142.0583).

**Table S-1.** Data for Simulation of the <sup>13</sup>C Spectra of Dimer (D) and Monomer (M) interconversion of **1** (Fig. 2).<sup>a</sup>

Temp °C:	-131	-119	-113	-109	-96
v <sub>D</sub> / Hz	14204.7	14204.7	14204.7	14204.7	14204.7
v <sub>M</sub> / Hz	13836.1	13836.1	13836.1	13836.1	13836.1
W <sub>D</sub> <sup>b</sup> / Hz	6.1	5.5	5.3	5.2	5.2
W <sub>M</sub> <sup>b</sup> / Hz	6.1	5.5	5.3	5.2	5.2
% D	33.1	39.1	42.1	44.3	48.1
k <sub>DM</sub> +k <sub>MD</sub> / sec <sup>-1</sup>	102	444	921	1485	5535
k <sub>DM</sub> <sup>c</sup> / sec <sup>-1</sup>	68	270	533	827	2872
ΔG <sub>DM</sub> <sup>‡</sup> / sec <sup>-1</sup>	6.94	7.12	7.17	7.23	7.39

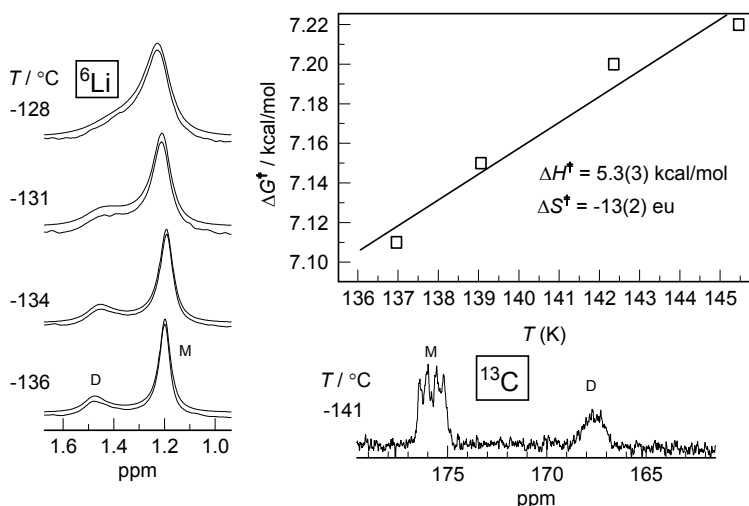
<sup>a</sup> Two spin mutual exchange in WINDNMR.<sup>[3k]</sup> <sup>b</sup> Line width in the absence of exchange. <sup>c</sup> Pseudo-first order approach to equilibrium gives the sum of the forward and backward rate constants:  $k_{DM} = (k_{DM} + k_{MD}) / (1 + [D]/[M])$ .

**Table S-2.** Data for Simulation of the  $^6\text{Li}$  Spectra of Dimer (D) and Monomer (M) interconversion of **1** (Fig. 2).<sup>a</sup>

Temp °C:	-140	-136	-133	-131
$\nu_{\text{D}}$ / Hz	236.7	237.7	238.0	237.9
$\nu_{\text{M}}$ / Hz	220.0	221.0	221.4	221.2
$W_{\text{D}}^{\text{b}}$ / Hz	1.6	1.1	1.1	1.1
$W_{\text{M}}^{\text{b}}$ / Hz	1.6	1.1	1.1	1.1
% D	26.7	31	32.7	33.5
$k_{\text{DM}}+k_{\text{MD}}^{\text{c}}$ / sec <sup>-1</sup>	21.7	42.2	65.7	95.7
$k_{\text{DM}}^{\text{c}}$ / sec <sup>-1</sup>	15.9	29.2	44.2	63.6
$\Delta G_{\text{DM}}^{\ddagger}$ / sec <sup>-1</sup>	6.84	6.9	6.91	6.96

<sup>a</sup> Two spin mutual exchange in WINDNMR.<sup>[3k]</sup> <sup>b</sup> Line width in the absence of exchange. <sup>c</sup> Pseudo-first order approach to equilibrium gives the sum of the forward and backward rate constants:  $k_{\text{DM}} = (k_{\text{DM}}+k_{\text{MD}}) / (1 + [\text{D}]/[\text{M}])$ .

**Figure S-1.** Variable temperature  $^{13}\text{C}$  and  $^6\text{Li}$  NMR experiment of 0.14 M 3-methyl-2-thienyllithium (**2**) in 3:2:1 THF/Me<sub>2</sub>O/Et<sub>2</sub>O.



**Table S-3.** Data for Simulation of the  $^6\text{Li}$  Spectra of Dimer (D) and Monomer (M) interconversion of **2**.<sup>a</sup>

Temp °C:	-136.2	-134.1	-130.8	-127.7
$\nu_{\text{D}}$ / Hz	351.3	350.5	350.8	350.3
$\nu_{\text{M}}$ / Hz	336.0	335.6	336.1	335.9
% D	24.8	26.8	28.2	30.2
% M	75.2	73.2	71.8	69.8
$W_{\text{D}}$ / Hz	1.5	1.5	1.5	1.6
$W_{\text{M}}$ / Hz	1.5	1.5	1.5	1.6
$k_{\text{DM}}$ / sec <sup>-1</sup>	12.7	16.7	26.2	42.2
$\Delta G^{\ddagger}$ / kcal/mol	7.11	7.15	7.2	7.22

<sup>a</sup> Three spin simulation in WINDNMR.<sup>[3k]</sup>

**Table S-4.** Data for Simulation of the  $^{13}\text{C}$  Spectra of the Loss of C-Li Coupling (Intermolecular exchange) of the Dimers of **4** (Fig. 6a).<sup>a</sup>

Temp °C:	-30.2	-24.5	-19.3	-8.4	9
$\nu_{\text{A}}$ / Hz	17050.2	17053.1	17056.5	16926.7	16933
$J_{\text{C-Li}}$ / Hz	20.5	20.5	20.5	20.5	20.5
$W_{\text{A}}^{\text{b}}$ / Hz	4	4.3	4.1	4	4
$k$ / sec <sup>-1</sup>	73	112	160	400	1160
$\Delta G^{\ddagger}$ / kcal/mol	12.05	12.13	12.22	12.28	12.53

<sup>a</sup> The exchange matrix has been reported;<sup>[3d]</sup> in WINDNMR it is the Custom-Septet simulation type. <sup>b</sup> Line width in the absence of exchange.

**Table S-5.** Data for Simulation of the  $^{13}\text{C}$  Spectra of the Interconversion of the A/B/C Dimers of **4** (Fig. 6b).<sup>a</sup>

Temp °C:	-142	-131	-127	-122	-111
$\nu_{\text{A}}$ / Hz	14785.2	14787.5	14789.5	14783.9	14784.6
$\nu_{\text{B}}$ / Hz	14727.4	14733.2	14736.5	14732.5	14736.8
$\nu_{\text{C}}$ / Hz	14682.9	14685.2	14687.2	14681.6	14682.3
% A	12.8	12.8	12.8	12.8	12.8
% B	62.1	62.1	62.1	62.1	62.1
% C	25.1	25.1	25.1	25.1	25.1
$W_{\text{A}}^{\text{b}}$ / Hz	5.7	3.5	3.3	2.8	2.4
$W_{\text{B}}^{\text{b}}$ / Hz	5.7	3.5	3.3	2.8	2.4
$W_{\text{C}}^{\text{b}}$ / Hz	5.7	3.5	3.3	2.8	2.4
$k_{\text{AB}}$ / sec <sup>-1</sup>	150	592	1175	2275	8695
$\Delta G_{\text{AB}}^{\ddagger}$ / kcal/mol	6.16	6.31	6.3	6.32	6.37
$k_{\text{BC}}$ / sec <sup>-1</sup>	3.362	13.232	26.25	50.82	194.25
$\Delta G_{\text{BC}}^{\ddagger}$ / kcal/mol	7.15	7.38	7.4	7.46	7.6
$k_{\text{AC}}$ / sec <sup>-1</sup>	0	0	0	0	0

<sup>a</sup> Three spin simulation in WINDNMR.<sup>[3k]</sup> <sup>b</sup> Line width in the absence of exchange.

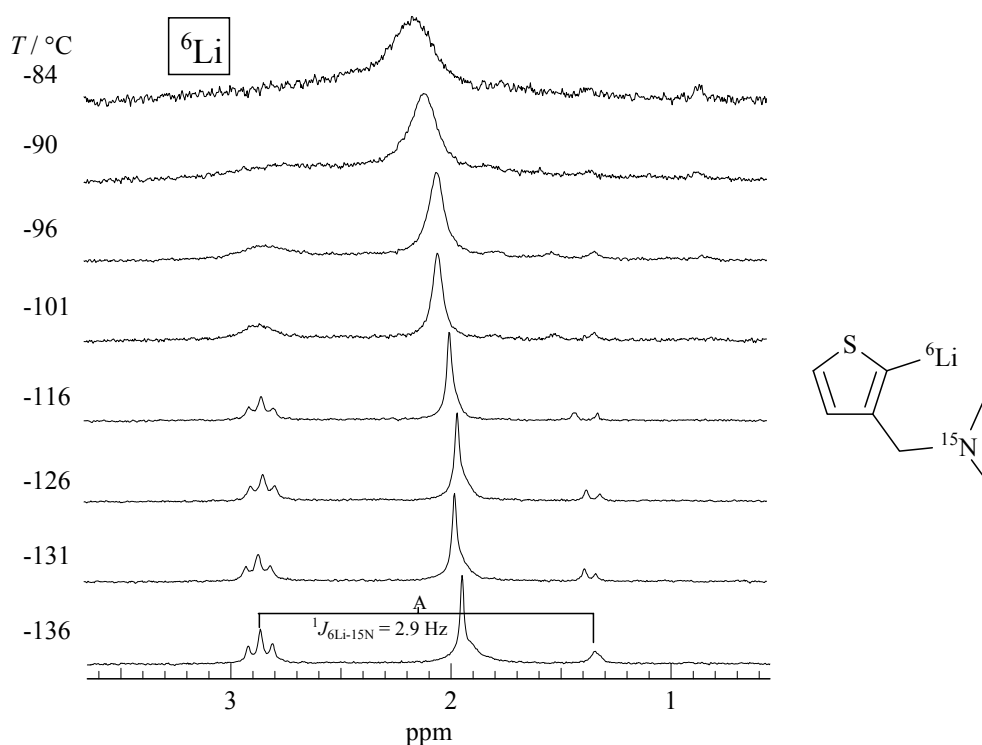
**Table S-6.** Data for Simulation of the  ${}^6\text{Li}$  Spectra of the Interconversion of the A/B/C Dimers of **4** (Fig. 6c).<sup>a</sup>

Temp °C:	-141.0	-143.5	-146.0	-149.0	-152.0
$\nu_A$ / Hz	463.7	462.3	462.1	461.1	460.6
$\nu_{A'}$ / Hz	386.1	384.8	384.6	383.6	383.0
$\nu_B$ / Hz	418.1	416.5	416.4	415.3	414.8
$\nu_C$ / Hz	423.4	422.0	421.9	420.7	420.2
% A	6.8	6.8	6.8	6.8	6.8
% A'	6.8	6.8	6.8	6.8	6.8
% B	61.9	61.9	61.9	61.9	61.9
% C	24.9	24.5	24.5	24.5	24.5
$W_A^b$ / Hz	0.75	0.85	0.85	1.25	1.35
$W_{A'}^b$ / Hz	0.75	0.85	0.85	1.25	1.35
$W_B^b$ / Hz	0.75	0.85	0.85	1.25	1.35
$W_C^b$ / Hz	0.75	0.85	0.85	1.25	1.35
$k_{AB}$ / sec <sup>-1</sup>	94	58.28	50.76	30.08	22.56
$\Delta G_{AB}^\ddagger$ / kcal/mol	6.33	6.33	6.24	6.21	6.12
$k_{BC}$ / sec <sup>-1</sup>	2.1	1.3	1.13	0.67	0.50
$\Delta G_{BC}^\ddagger$ / kcal/mol	7.3	7.3	7.2	7.2	7.0
$k_{BA'}$ / sec <sup>-1</sup>	9.7	6.0	5.2	3.1	2.3
$\Delta G_{BA'}^\ddagger$ / kcal/mol	6.93	6.91	6.81	6.77	6.67
$k_{AC}$ / sec <sup>-1</sup>	0	0	0	0	0
$k_{AA'}$ / sec <sup>-1</sup>	0	0	0	0	0
$k_{CA'}$ / sec <sup>-1</sup>	0	0	0	0	0

<sup>a</sup> This is a four spin simulation, defined in WINDNMR (Custom 4-AA'BC).<sup>[3k]</sup> <sup>b</sup> Line width in the absence of exchange.

**TMEDA titration of 4.** 3-(*N,N*-Dimethylaminomethyl)thiophene (59 mg, 0.42 mmol) was added to a dry, N<sub>2</sub>-purged 10 mm NMR tube sealed with a septum. THF (1.5 mL) was added, the solution was cooled to -78 °C and 2.0 M *n*-BuLi (0.21 mL, 0.42 mmol) was added slowly and the sample was mixed by shaking the NMR tube. The sample was stored at -78 °C overnight. Me<sub>2</sub>O (1.0 mL), Et<sub>2</sub>O (0.5 mL) and (Me<sub>3</sub>Si)<sub>3</sub>CH (2 μL) were added. <sup>13</sup>C and <sup>6</sup>Li NMR spectra were acquired at -140 °C and -93 °C. TMEDA (32 μL, 0.21 mmol, 0.50 equiv) was added and <sup>13</sup>C and <sup>6</sup>Li spectra were acquired at -140 °C. Addition quantities of TMEDA were added (32 μL and 63 μL) with <sup>13</sup>C and <sup>6</sup>Li spectra acquired at -140 °C after each addition.

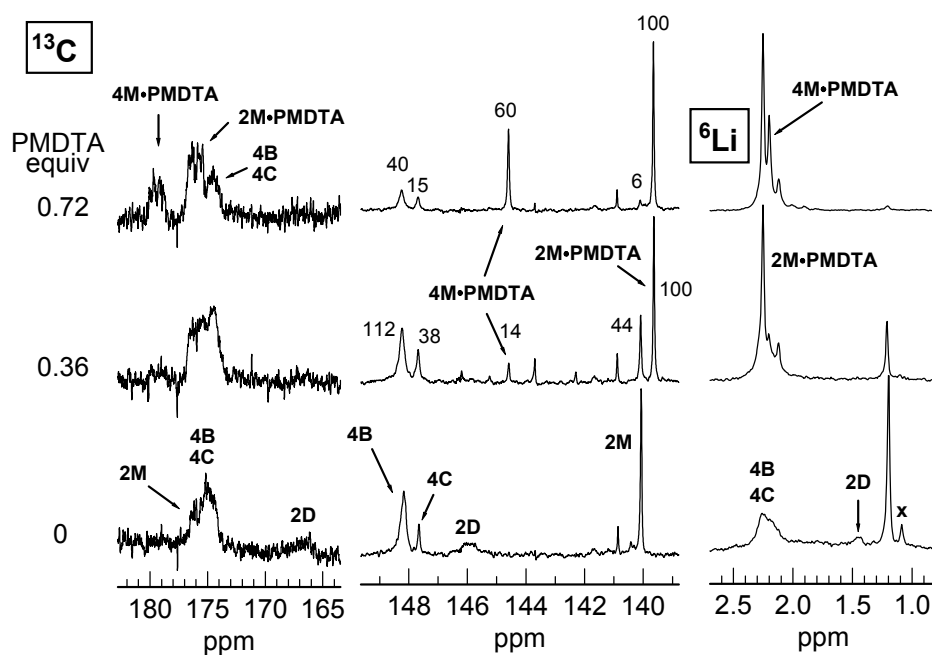
**TMEDA titration of [<sup>6</sup>Li,<sup>15</sup>N]-4.** [<sup>15</sup>N]-3-(*N,N*-Dimethylaminomethyl)thiophene (32 mg, 0.23 mmol) was added to a dry, N<sub>2</sub>-purged 10 mm NMR tube sealed with a septum. THF (1.5 mL) was added, the solution was cooled to -78 °C and 1.6 M *n*-BuLi (0.14 mL, 0.23 mmol) was added slowly and the sample was mixed by shaking the NMR tube. Me<sub>2</sub>O (1.0 mL), Et<sub>2</sub>O (0.5 mL) and (Me<sub>3</sub>Si)<sub>3</sub>CH (2 μL) were later added. <sup>6</sup>Li NMR spectra were acquired between -144 °C and -134 °C. TMEDA (20 μL, 0.10 mmol, 0.58 equiv) was added and <sup>15</sup>N and <sup>6</sup>Li spectra were acquired at -144 °C. Addition quantities of TMEDA were added (20 μL, 28 μL and 68 μL) with <sup>6</sup>Li spectra acquired at -144 °C after each addition. A variable temperature experiment was performed on the sample after the last addition. Spectra are shown in Figs. 7 and S-2.



**Figure S-2.** Variable temperature experiment of a 0.07 M [ $^6\text{Li}$ ,  $^{15}\text{N}$ ]3-(*N,N*-dimethylaminomethyl)thien-2-yllithium (**4**) in 3:2:1 THF/Me<sub>2</sub>O/Et<sub>2</sub>O with 4 equiv TMEDA.

**PMDTA titration of 4.** (*N,N*-Dimethylaminomethyl)thiophene (66 mg, 0.47 mmol) was added to a dry, N<sub>2</sub>-purged 10 mm NMR tube sealed with a septum. THF (1.5 mL) was added, the solution was cooled to -78 °C and 2.0 M *n*-BuLi (0.23 mL, 0.47 mmol) was added slowly and the sample was mixed by shaking the NMR tube. The sample was stored at -78 °C for several days. Me<sub>2</sub>O (1.0 mL), Et<sub>2</sub>O (0.5 mL) and (Me<sub>3</sub>Si)<sub>3</sub>CH (2 μL)<sup>[3j]</sup> were added. <sup>13</sup>C and <sup>6</sup>Li NMR spectra were acquired at -141 °C and -88 °C. PMDTA (24 μL, 0.11 mmol, 0.25 equiv) was added and <sup>13</sup>C and <sup>6</sup>Li NMR spectra were acquired at -141 °C. Additional quantities of PMDTA were added (24 μL, 49 μL, 98 μL, and 196 μL) and <sup>13</sup>C and <sup>6</sup>Li NMR spectra were acquired at -141 °C after each addition. Spectra are shown in Fig. 8, chemical shifts in Table S-8.

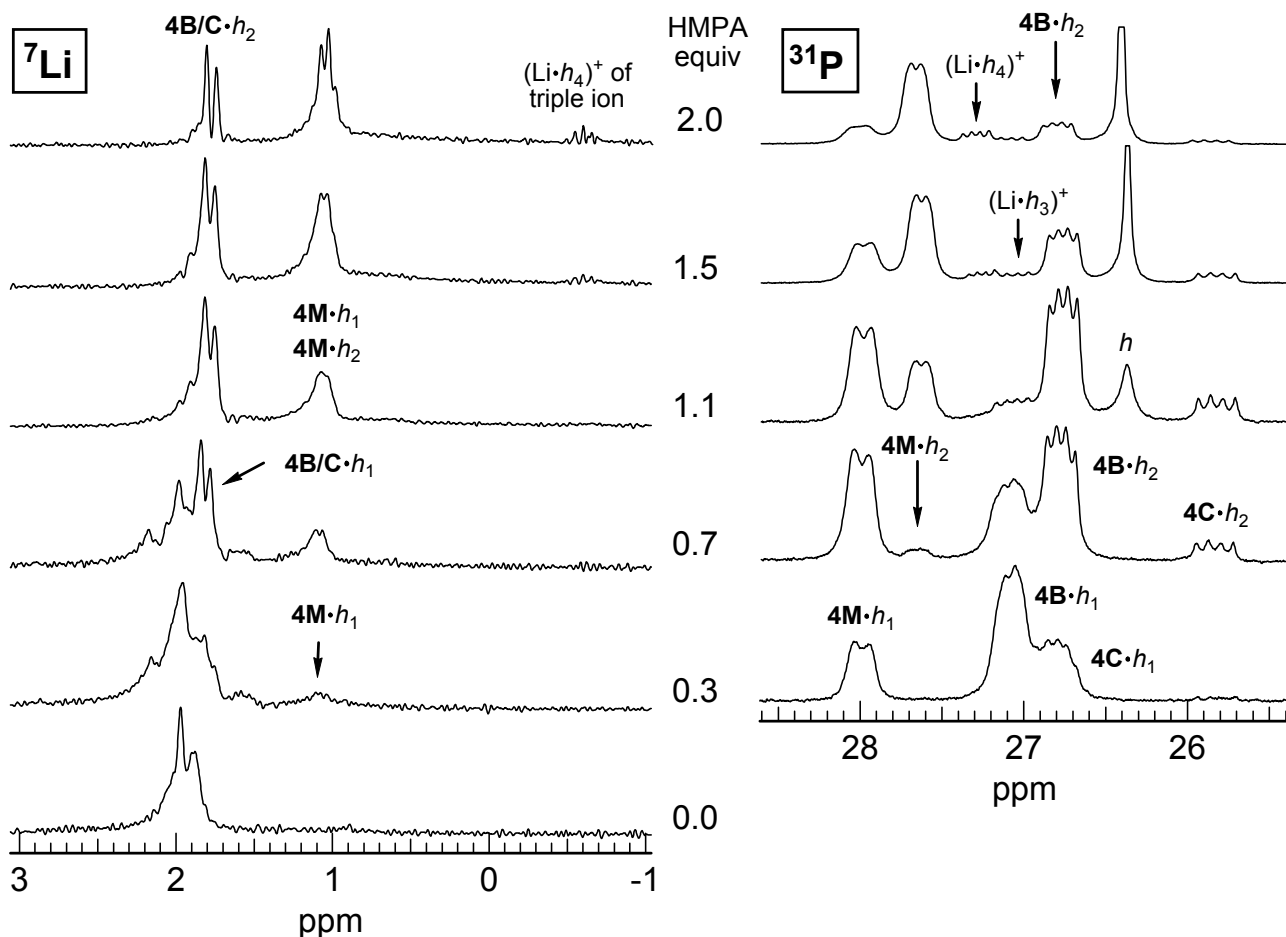
**Competitive PMDTA titration of 2 and 4.** 3-Methyl-2-trimethylstannyl-thiophene (60 mg, 0.23 mmol) and 3-(*N,N*-dimethylaminomethyl)thiophene (33 mg, 0.24 mmol) were added to a dry, N<sub>2</sub>-purged 10 mm NMR tube sealed with a septum. THF (1.5 mL) was added, the solution was cooled to -78 °C and 2.6 M *n*-BuLi (0.18 mL, 0.47 mmol) was added slowly and the sample was mixed by shaking the NMR tube. The sample was stored at -78 °C for several days. Me<sub>2</sub>O (1.0 mL), Et<sub>2</sub>O (0.5 mL) and (Me<sub>3</sub>Si)<sub>3</sub>CH (2 μL)<sup>[3j]</sup> were added. <sup>13</sup>C NMR spectra were acquired at -143 °C, -112 °C and -79 °C. A <sup>6</sup>Li NMR spectrum was acquired at -143 °C. PMDTA (30 μL, 0.14 mmol, 0.31 equiv (0.36 based on integration of the complexed and non-complexed <sup>13</sup>C NMR signals)) was added and <sup>13</sup>C and <sup>6</sup>Li NMR spectra were acquired at -143 °C. PMDTA (30 μL, 0.14 mmol, 0.31 equiv (0.36 based on quench data)) was added and <sup>13</sup>C and <sup>6</sup>Li NMR spectra were acquired at -143 °C. The sample was quenched with MeSSMe (70 μL), concentrated and pentachloroethane (30 μL, 0.25 mmol) was added. The quantity of the product sulfide derived from **2** (0.20 mmol) and **4** (0.23 mmol) was determined by integration relative to the pentachloroethane <sup>1</sup>H NMR signal. Spectra are shown in Fig. S-3.



**Figure S-3.** Addition of PMDTA to a solution of **2** and **4** in 3:2:1 THF/Me<sub>2</sub>O/Et<sub>2</sub>O at -143 °C. Numbers are areas of the marked peaks determined by integration.

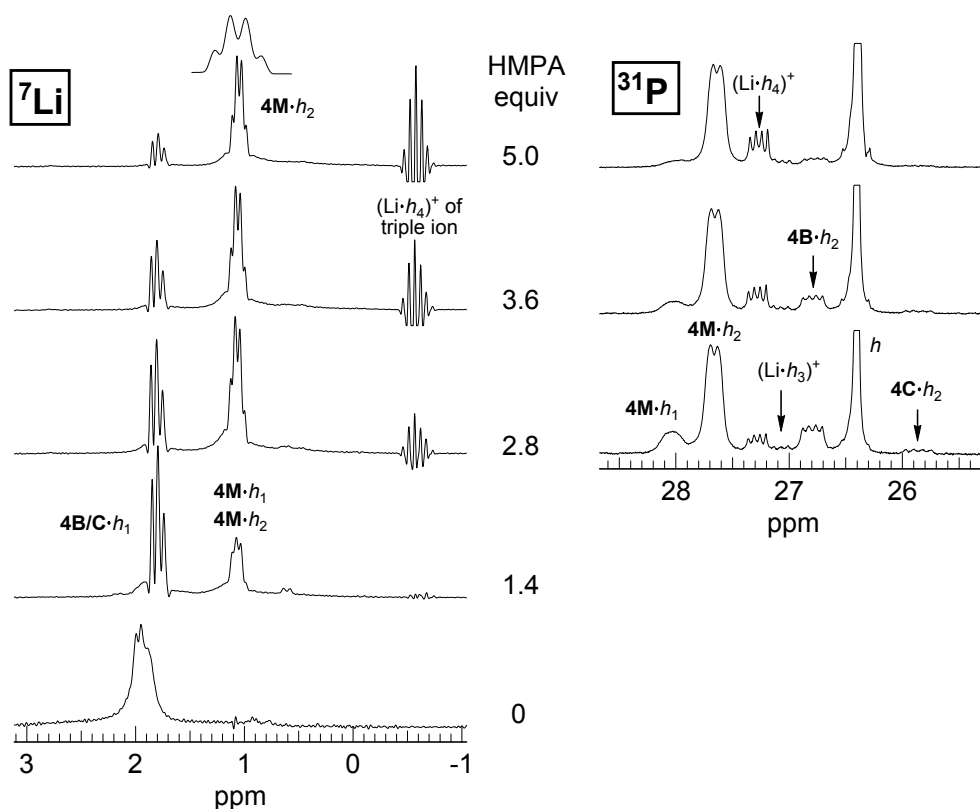
**HMPA Titration of 4.** 3-(*N,N*-Dimethylaminomethyl)thiophene (18 mg, 0.13 mmol) was added to a dry, N<sub>2</sub>-purged 10 mm NMR tube sealed with a septum. THF (1.8 mL) was added, the solution was cooled to -78 °C and 2.0 M *n*-BuLi (0.064 mL, 0.13 mmol) was added slowly and the sample was mixed by shaking the NMR tube. The sample was stored at -78 °C for 2 h. Me<sub>2</sub>O (1.2 mL), Et<sub>2</sub>O (0.6 mL) and (Me<sub>3</sub>Si)<sub>3</sub>CH (2 μL)<sup>[3j]</sup> were added. <sup>13</sup>C, <sup>6</sup>Li and <sup>7</sup>Li NMR spectra were acquired at -143 °C. HMPA (4 μL, 0.02 mmol, 0.2 equiv) was added and <sup>31</sup>P and <sup>7</sup>Li spectra were acquired at -143 °C. Addition quantities of HMPA were added (4, 8, 8, 10 and 11 μL) with <sup>13</sup>C and <sup>7</sup>Li spectra acquired at -143 °C after each addition. Spectra are shown in Figs. 9 and S-4.





**Figure S-4.**  $^7\text{Li}$  and  $^{31}\text{P}$  NMR spectra of the  $-143\text{ }^\circ\text{C}$  HMPA titration of  $0.04\text{ M } \mathbf{3}$  in  $3:2:1$  THF/Me<sub>2</sub>O/Et<sub>2</sub>O. The assignments for **4B** and **4C** could be reversed ( $h = \text{HMPA}$ ).

**HMPA Titration of [ $^{15}\text{N}$ ]-**4**.** 3-(*N,N*-Dimethylaminomethyl)thiophene (14 mg, 0.10 mmol) was added to a dry, N<sub>2</sub>-purged 10 mm NMR tube sealed with a septum. THF (1.5 mL) was added, the solution was cooled to  $-78\text{ }^\circ\text{C}$  and  $2.6\text{ M } n\text{-BuLi}$  (0.038 mL, 0.10 mmol) was added slowly and the sample was mixed by shaking the NMR tube. The sample was stored at  $-78\text{ }^\circ\text{C}$  for 48 h. Me<sub>2</sub>O (1.0 mL), Et<sub>2</sub>O (0.5 mL) and (Me<sub>3</sub>Si)<sub>3</sub>CH (2  $\mu\text{L}$ )<sup>[3j]</sup> were added.  $^{13}\text{C}$ ,  $^6\text{Li}$  and  $^7\text{Li}$  NMR spectra were acquired at  $-141\text{ }^\circ\text{C}$ . HMPA (17  $\mu\text{L}$ , 0.10 mmol, 1.0 equiv (1.4 equiv based on quenched product)) was added and  $^{13}\text{C}$  and  $^7\text{Li}$  spectra were acquired at  $-141\text{ }^\circ\text{C}$ . Addition quantities of HMPA were added (17, 10 and 17  $\mu\text{L}$ ) with  $^{13}\text{C}$ ,  $^7\text{Li}$  and  $^{31}\text{P}$  spectra acquired at  $-141\text{ }^\circ\text{C}$  after each addition. Spectra are shown in Figs. 9 and S-5. The sample was quenched with MeSSMe (13  $\mu\text{L}$ ), concentrated and pentachloroethane (30  $\mu\text{L}$ , 0.25 mmol) was added. The quantity of the product sulfide (0.07 mmol) derived from **4** was determined by integration relative to the pentachloroethane  $^1\text{H}$  NMR signal.



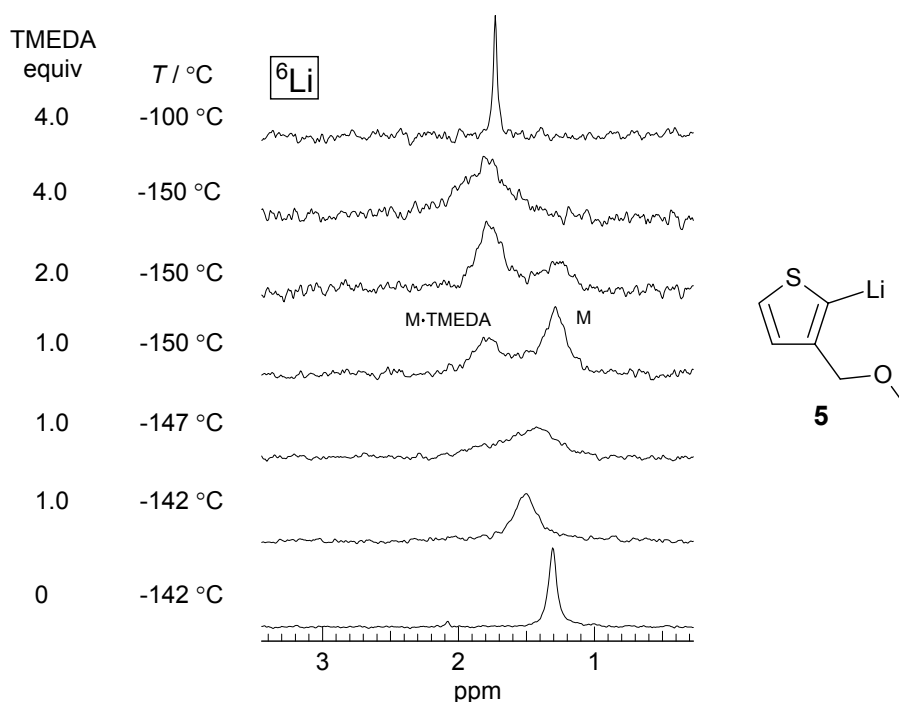
**Figure S-5.** HMPA titration of 0.023 M [<sup>15</sup>N]-**4** at -141 °C in 3:2:1 THF/Me<sub>2</sub>O/Et<sub>2</sub>O. The assignments for **4B** and **4C** could be reversed.

**Table S-7.** Data for Simulation of the <sup>13</sup>C Spectra of Dimer (D) and Monomer (M) Interconversion of **5** (Fig. 10).<sup>a</sup>

Temp °C:	-146	-139	-132	-126	-121
$\nu_D$ / Hz	14706.7	15052.1	14704.4	14704.4	14704.4
$\nu_M$ / Hz	14488.8	14834.2	14486.5	14486.5	14486.5
$W_D^b$ / Hz	5.8	6.1	5.8	5.5	5.6
$W_M^b$ / Hz	5.8	6.1	5.8	5.5	5.6
% D	22	30.5	41.4	50.4	59.4
$k_{DM}+k_{MD}$ / sec <sup>-1</sup>	206	500	1016	1656	2706
$k_{DM}$ / sec <sup>-1</sup>	161	348	595	821	1114
$\Delta G_{DM}^\ddagger$ / kcal/mol	5.93	6.09	6.27	6.43	6.58

<sup>a</sup> Two spin mutual exchange in WINDNMR.<sup>[3k]</sup> <sup>b</sup> Line width in the absence of exchange. <sup>c</sup> Pseudo-first order approach to equilibrium gives the sum of the forward and backward rate constants:  $k_{DM} = (k_{DM}+k_{MD}) / (1 + [D]/[M])$ .

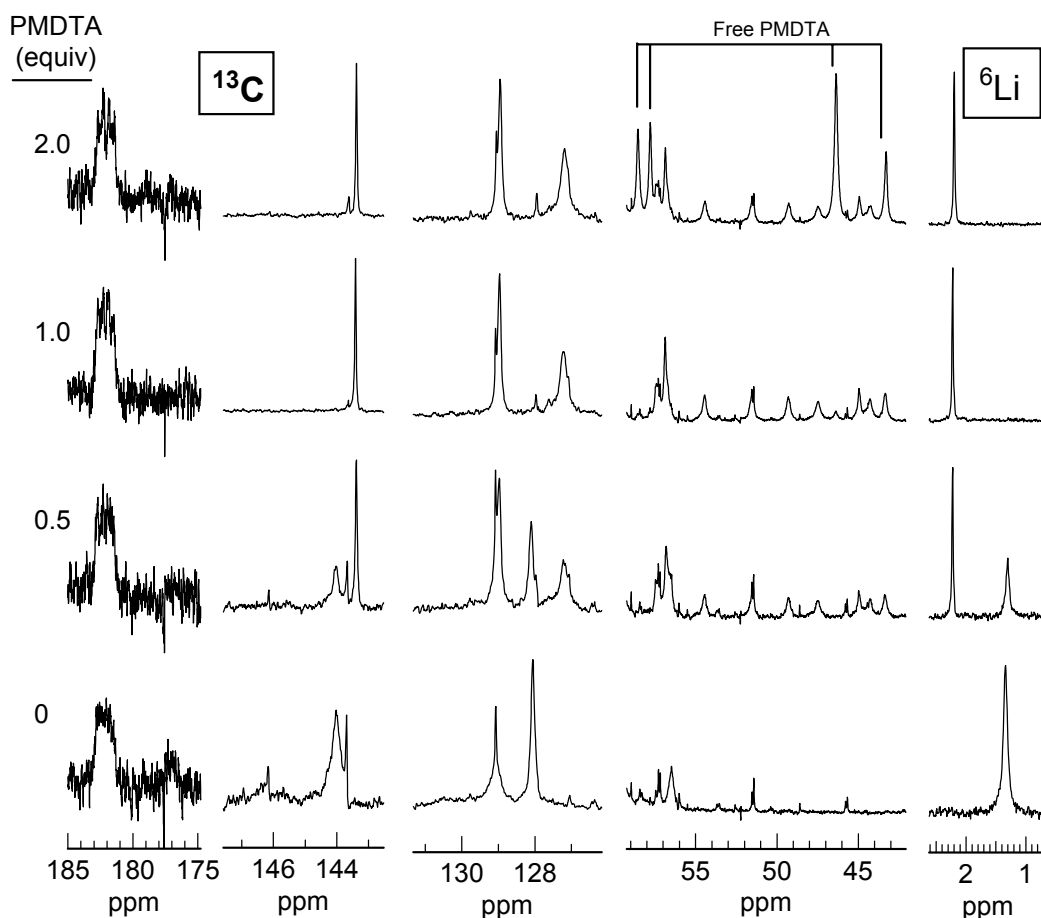
**TMEDA titration of 5.** 3-(Methoxymethyl)thiophene (54 mg, 0.42 mmol) was added to a dry, N<sub>2</sub>-purged 10 mm NMR tube sealed with a septum. THF (1.5 mL) was added, the solution was cooled to -78 °C and 2.0 M *n*-BuLi (0.21 mL, 0.42 mmol) was added slowly and the sample was mixed by shaking the NMR tube. The sample was stored at -78 °C overnight. Me<sub>2</sub>O (1.0 mL), Et<sub>2</sub>O (0.5 mL) and (Me<sub>3</sub>Si)<sub>3</sub>CH (2 μL) were added. <sup>13</sup>C and <sup>6</sup>Li NMR spectra were acquired at -138 °C. TMEDA (32 μL, 0.21 mmol, 0.50 equiv) was added and <sup>13</sup>C and <sup>6</sup>Li NMR spectra were acquired at -138 °C. Additional quantities of TMEDA (32 μL and 63 μL) were added and <sup>13</sup>C and <sup>6</sup>Li NMR spectra were acquired at -138 °C after each addition. Spectra are shown in Figs. 12 and S-6.



**Figure S-6.**  $^6\text{Li}$  NMR spectra of the variable temperature TMEDA titration of 0.06 M **5** in 3:2:1 THF/Me<sub>2</sub>O/Et<sub>2</sub>O.

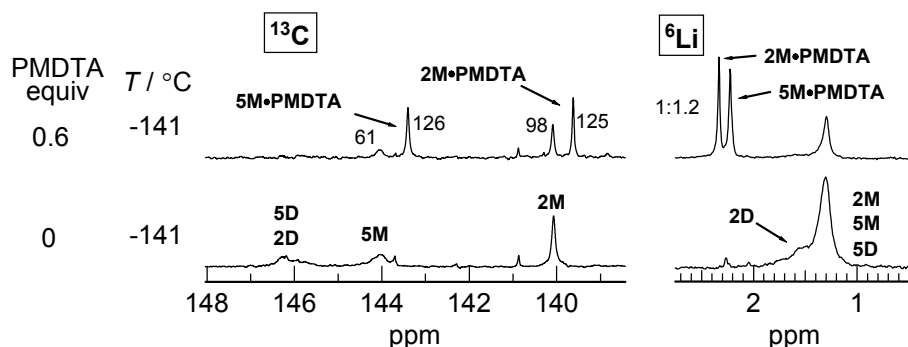
**Variable temperature TMEDA titration of 5.** 3-(Methoxymethyl)thiophene (25 mg, 0.19 mmol) was added to a dry, N<sub>2</sub>-purged 10 mm NMR tube sealed with a septum. THF (1.5 mL) was added, the solution was cooled to -78 °C and 2.0 M *n*-BuLi (0.096 mL, 0.19 mmol) was added slowly and the sample was mixed by shaking the NMR tube. The sample was stored at -78 °C overnight. Me<sub>2</sub>O (1.0 mL), Et<sub>2</sub>O (0.5 mL) and (Me<sub>3</sub>Si)<sub>3</sub>CH (2 μL) were added. <sup>13</sup>C and <sup>6</sup>Li NMR spectra were acquired at -142 °C. TMEDA (14 μL, 0.09 mmol, 0.5 equiv) was added and a <sup>6</sup>Li NMR spectrum was acquired at -142 °C. TMEDA (14 μL, 0.09 mmol, 0.5 equiv) was added and <sup>6</sup>Li NMR spectra were acquired at -142, -147 and -150 °C. Another portion of TMEDA (29 μL, 0.19 mmol, 1.0 equiv) was added and <sup>6</sup>Li NMR spectra were acquired at -142 °C, -147 °C and -150 °C. Finally, another portion of TMEDA (58 μL, 0.38 mmol, 2.0 equiv) was added and a <sup>6</sup>Li NMR spectrum was acquired at -150 °C. A <sup>13</sup>C NMR spectrum was acquired at -100 °C.

**PMDTA titration of 5.** 3-(Methoxymethyl)thiophene (59 mg, 0.46 mmol) was added to a dry, N<sub>2</sub>-purged 10 mm NMR tube sealed with a septum. THF (1.5 mL) was added, the solution was cooled to -78 °C and 2.0 M *n*-BuLi (0.23 mL, 0.46 mmol) was added slowly and the sample was mixed by shaking the NMR tube. The sample was stored at -78 °C overnight. Me<sub>2</sub>O (1.0 mL), Et<sub>2</sub>O (0.5 mL) and (Me<sub>3</sub>Si)<sub>3</sub>CH (2 μL)<sup>[3]</sup> were added. <sup>13</sup>C and <sup>6</sup>Li NMR spectra were acquired between -143 and -110 °C. PMDTA (48 μL, 0.23 mmol, 0.50 equiv) was added and <sup>13</sup>C and <sup>6</sup>Li spectra were acquired at -143 °C. Additional quantities of PMDTA were added (48 μL and 95 μL) with <sup>13</sup>C and <sup>6</sup>Li NMR spectra acquired after each addition. Spectra are shown in Figs. 12 and S-7, chemical shifts in Table S-8.



**Figure S-7.** PMDTA titration of 3-(methoxymethyl)thien-2-yl lithium (**5**) in 3:2:1 THF/Me<sub>2</sub>O/Et<sub>2</sub>O at -143 °C.

**Competitive PMDTA titration of **2** and **5**.** 3-Methyl-2-trimethylstannyl-thiophene (58 mg, 0.22 mmol) and 3-(methoxymethyl)thiophene (28 mg, 0.22 mmol) were added to a dry, N<sub>2</sub>-purged 10 mm NMR tube sealed with a septum. THF (1.5 mL) was added, the solution was cooled to -78 °C and 2.6 M *n*-BuLi (0.17 mL, 0.44 mmol) was added slowly and the sample was mixed by shaking the NMR tube. The sample was stored at -78 °C for several days then Me<sub>2</sub>O (1.0 mL), Et<sub>2</sub>O (0.5 mL) and (Me<sub>3</sub>Si)<sub>3</sub>CH (2 μL)<sup>[3j]</sup> were added. <sup>13</sup>C and <sup>6</sup>Li NMR spectra were acquired between -141 °C and -79 °C. PMDTA (46 μL, 0.22 mmol, 0.50 equiv) was added and <sup>13</sup>C and <sup>6</sup>Li spectra were acquired at -141 °C. Spectra are shown in Fig. S-8. The sample was quenched with MeSSMe (50 μL), concentrated and pentachloroethane (30 μL, 0.25 mmol) was added. The quantity of the product sulfide derived from **2** and **5** was determined by integration relative to the pentachloroethane <sup>1</sup>H NMR signal to be 0.40 mmol indicating >90% formation of **2** and **5**.



**Figure S-8.** Addition of PMDTA to a solution of **2** and **5** in 3:2:1 THF/Me<sub>2</sub>O/Et<sub>2</sub>O at -141 °C.

**HMPA titration of 5.** 3-(Methoxymethyl)thiophene (54 mg, 0.42 mmol) was added to a dry, N<sub>2</sub>-purged 10 mm NMR tube sealed with a septum. THF (1.5 mL) was added, the solution was cooled to -78 °C and 2.0 M *n*-BuLi (0.21 mL, 0.42 mmol) was added slowly and the sample was mixed by shaking the NMR tube. The sample was stored at -78 °C overnight. Me<sub>2</sub>O (1.0 mL), Et<sub>2</sub>O (0.5 mL) and (Me<sub>3</sub>Si)<sub>3</sub>CH (2 μL)<sup>[3]</sup> were added. <sup>13</sup>C NMR spectra were acquired at -141 °C and -100 °C. <sup>6</sup>Li NMR spectra were acquired at -145 °C and -100 °C. A <sup>7</sup>Li spectrum was acquired at -145 °C. HMPA (18 μL, 0.10 mmol, 0.25 equiv) was added and <sup>7</sup>Li and <sup>31</sup>P NMR spectra were acquired. Additional quantities of HMPA (18, 18, 18, 37, 37, 73 and 73 μL) were added with <sup>7</sup>Li and <sup>31</sup>P NMR spectra acquired after each addition. <sup>6</sup>Li NMR spectra were taken occasionally. Spectra are shown in Fig. 13.

**Table S-8.** <sup>13</sup>C and <sup>6</sup>Li NMR chemical Shifts of 2-Thienyllithium Reagents in 3:2:1 THF/Me<sub>2</sub>O/Et<sub>2</sub>O.

RLi	<i>T</i> / °C	C-2	C-3	C-4	C-5	δ <sub>Li</sub> <sup>[a]</sup>	<i>J</i> <sub>CLi</sub> ( <sup>7</sup> Li)
<b>Monomers (<i>p</i> = PMDTA):</b>							
<b>1</b>	-140	181.3	132.8	126.8	126.5	1.15	37.4
<b>2</b>	-141	175.8	140.0	129.0	128.3	1.20 <sup>[b]</sup>	37.3
<b>4</b>	-141	[c]	[c]	[c]	[c]	0.97	[d]
<b>4·<i>p</i></b>	-141	179.4	144.6	128.5	127.6	1.87	36.3
<b>5</b>	-146	182.3	144.1	129.1	128.1	1.30 <sup>[c]</sup>	37.6
<b>5·<i>p</i></b>	-143	182.1	143.3	129.0	127.2	2.22	35.1
<b>Dimers</b>							
<b>1</b>	-140	173.9	136.9	129.9	127.1	1.43	19.2
<b>2</b>	-141	167.6	145.9	131.2	[c]	1.48 <sup>[b]</sup>	[d]
<b>4 (B)</b>	-141	174.5	148.1	131.2	129.2	1.91	[d]
<b>4 (C)</b>	-141	174.5	147.6	130.4	129.5	1.98	[d]
<b>5</b>	-146	177.1	146.3	130.5	[c]	[f]	[d]

<sup>[a]</sup> Reference: 0.3 M LiCl in methanol. <sup>[b]</sup> -136 °C. <sup>[c]</sup> Signal not observed. <sup>[d]</sup> Splitting not resolved.

<sup>[e]</sup> Coalesced with dimer. <sup>[f]</sup> Coalesced with monomer.

**X-Ray Structure of 5.** X-ray quality crystals of **5B**·(THF)<sub>2</sub> were grown from a 3:2 THF/Et<sub>2</sub>O solution at -78 °C in a 10 mm NMR tube under a N<sub>2</sub> atmosphere. A colorless crystal with approximate dimensions 0.45 x 0.43 x 0.37 mm<sup>3</sup> was selected under an Ar atmosphere and attached to the tip of a glass capillary. The crystal was mounted in a stream of cold nitrogen at 100(2) K and centered in the X-ray beam by using a video camera.

**Data Collection.** The crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo K<sub>α</sub> (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 4.9 cm. The initial cell constants were obtained from three series of *w* scans at different starting angles. Each series consisted of 20 frames collected at intervals of 0.3° in a 6° range about *w* with the exposure time of 10 seconds per frame. A total of 63 reflections was obtained. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 3687 strong reflections from the actual data collection.

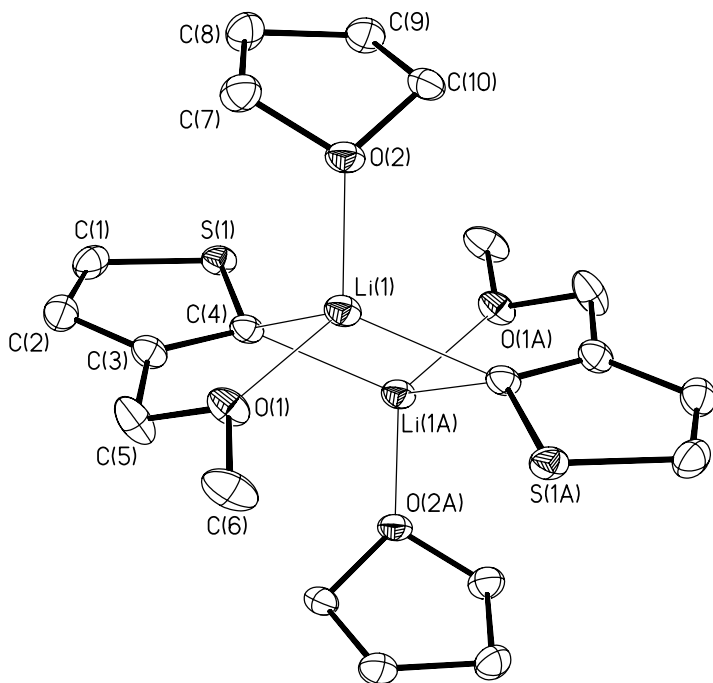
The data were collected by using the hemisphere data collection routine. The reciprocal space was surveyed to the extent of a full sphere to a resolution of 0.80 Å. A total of 4126 data were harvested by collecting three sets of frames with 0.3° scans in  $\omega$  with an exposure time 30 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.<sup>[S-4]</sup>

*Structure Solution and Refinement.* The systematic absences in the diffraction data were consistent for the space groups  $P$  and  $P1$ . The  $E$ -statistics strongly suggested the centrosymmetric space group  $P$  that yielded chemically reasonable and computationally stable results of refinement.<sup>[S-5]</sup> A successful solution by the direct methods provided most non-hydrogen atoms from the  $E$ -map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The dinuclear complex occupies a crystallographic inversion center. The final least-squares refinement of 128 parameters against 2145 data resulted in residuals  $R$  (based on  $F^2$  for  $I \geq 2\sigma$ ) and  $wR$  (based on  $F^2$  for all data) of 0.0462 and 0.1340, respectively. The final difference Fourier map was featureless. The ORTEP diagram is drawn with 40% probability ellipsoids.

The X-ray structure of **5** is shown in Figs. 11 and S-9, data is shown in Tables S-9 to S-13.

**Table S-9.** Crystal data and structure refinement for **5B**·(THF)<sub>2</sub>.

Identification code	rei05	
Empirical formula	C <sub>20</sub> H <sub>30</sub> Li <sub>2</sub> O <sub>4</sub> S <sub>2</sub>	
Formula weight	412.44	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.047(2) Å	$\alpha = 101.308(4)^\circ$
	b = 8.266(2) Å	$\beta = 106.610(4)^\circ$
	c = 10.044(3) Å	$\gamma = 113.598(4)^\circ$
Volume	548.8(3) Å <sup>3</sup>	
Z	1	
Density (calculated)	1.248 Mg/m <sup>3</sup>	
Absorption coefficient	0.264 mm <sup>-1</sup>	
F(000)	220	
Crystal size	0.45 x 0.43 x 0.37 mm <sup>3</sup>	
Theta range for data collection	2.26 to 26.42°.	
Index ranges	-10 ≤ h ≤ 9, -10 ≤ k ≤ 10, -12 ≤ l ≤ 12	
Reflections collected	4126	
Independent reflections	2145 [R(int) = 0.0334]	
Completeness to theta = 26.42°	94.9 %	
Absorption correction	Empirical with SADABS	
Max. and min. transmission	0.9087 and 0.8905	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	2145 / 0 / 128	
Goodness-of-fit on F <sup>2</sup>	1.117	
Final R indices [I > 2σ(I)]	R1 = 0.0462, wR2 = 0.1314	
R indices (all data)	R1 = 0.0483, wR2 = 0.1340	
Largest diff. peak and hole	0.425 and -0.350 e.Å <sup>-3</sup>	



**Figure S-9.** Ortep drawing of **5B**·(THF)<sub>2</sub>.

**Table S-10.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **5B**·(THF)<sub>2</sub>. U(eq) is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

	x	y	z	U(eq)
S(1)	1899(1)	4798(1)	7004(1)	24(1)
O(1)	8207(2)	6257(2)	9486(1)	26(1)
O(2)	5189(2)	1756(2)	8331(1)	25(1)
Li(1)	5873(4)	4276(4)	9520(3)	23(1)
C(1)	2706(3)	5631(3)	5741(2)	30(1)
C(2)	4723(3)	6438(2)	6289(2)	28(1)
C(3)	5556(2)	6381(2)	7729(2)	24(1)
C(4)	4225(2)	5531(2)	8332(2)	22(1)
C(5)	7759(3)	7236(3)	8545(2)	36(1)
C(6)	10265(3)	7182(3)	10443(2)	36(1)
C(7)	4934(3)	1370(3)	6804(2)	29(1)
C(8)	2707(3)	456(3)	5883(2)	30(1)
C(9)	1770(2)	-209(2)	6954(2)	29(1)
C(10)	3519(3)	170(2)	8307(2)	28(1)



**Table S-11.** Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for **5B**·(THF)<sub>2</sub>.

S(1)-C(1)	1.7208(19)	Li(1)-Li(1)#1	2.451(5)
S(1)-C(4)	1.7311(17)	C(1)-C(2)	1.364(3)
O(1)-C(5)	1.420(2)	C(2)-C(3)	1.429(2)
O(1)-C(6)	1.428(2)	C(3)-C(4)	1.394(2)
O(1)-Li(1)	1.951(3)	C(3)-C(5)	1.501(2)
O(2)-C(7)	1.439(2)	C(4)-Li(1)#1	2.158(3)
O(2)-C(10)	1.443(2)	C(7)-C(8)	1.527(2)
O(2)-Li(1)	1.949(3)	C(8)-C(9)	1.546(2)
Li(1)-C(4)#1	2.158(3)	C(9)-C(10)	1.520(2)
Li(1)-C(4)	2.223(3)		
<hr/>			
C(1)-S(1)-C(4)	96.37(9)	C(2)-C(1)-S(1)	109.21(14)
C(5)-O(1)-C(6)	112.55(13)	C(1)-C(2)-C(3)	112.44(15)
C(5)-O(1)-Li(1)	113.86(13)	C(4)-C(3)-C(2)	116.56(15)
C(6)-O(1)-Li(1)	132.02(14)	C(4)-C(3)-C(5)	122.53(16)
C(7)-O(2)-C(10)	104.89(12)	C(2)-C(3)-C(5)	120.90(15)
C(7)-O(2)-Li(1)	118.89(13)	C(3)-C(4)-S(1)	105.41(12)
C(10)-O(2)-Li(1)	117.81(12)	C(3)-C(4)-Li(1)#1	139.21(14)
O(2)-Li(1)-O(1)	112.79(14)	S(1)-C(4)-Li(1)#1	110.42(11)
O(2)-Li(1)-C(4)#1	113.30(14)	C(3)-C(4)-Li(1)	97.07(13)
O(1)-Li(1)-C(4)#1	116.51(14)	S(1)-C(4)-Li(1)	138.57(11)
O(2)-Li(1)-C(4)	114.10(14)	Li(1)#1-C(4)-Li(1)	68.00(12)
O(1)-Li(1)-C(4)	85.28(12)	O(1)-C(5)-C(3)	110.58(13)
C(4)#1-Li(1)-C(4)	112.00(12)	O(2)-C(7)-C(8)	106.13(13)
O(2)-Li(1)-Li(1)#1	135.95(18)	C(7)-C(8)-C(9)	103.71(14)
O(1)-Li(1)-Li(1)#1	108.58(17)	C(10)-C(9)-C(8)	104.11(14)
C(4)#1-Li(1)-Li(1)#1	57.25(12)	O(2)-C(10)-C(9)	104.39(14)
C(4)-Li(1)-Li(1)#1	54.75(12)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+2

**Table S-12.** Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **5B**·(THF)<sub>2</sub>. The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U <sup>11</sup>	U <sup>22</sup>	U <sup>33</sup>	U <sup>23</sup>	U <sup>13</sup>	U <sup>12</sup>
S(1)	19(1)	22(1)	23(1)	6(1)	1(1)	9(1)
O(1)	14(1)	23(1)	36(1)	12(1)	6(1)	8(1)
O(2)	21(1)	18(1)	24(1)	3(1)	4(1)	6(1)
Li(1)	19(1)	20(1)	24(1)	6(1)	6(1)	7(1)
C(1)	37(1)	30(1)	21(1)	8(1)	6(1)	19(1)
C(2)	37(1)	27(1)	29(1)	12(1)	16(1)	20(1)
C(3)	23(1)	20(1)	29(1)	10(1)	9(1)	11(1)
C(4)	18(1)	17(1)	23(1)	6(1)	3(1)	6(1)
C(5)	23(1)	34(1)	51(1)	28(1)	12(1)	10(1)
C(6)	16(1)	26(1)	53(1)	13(1)	3(1)	6(1)
C(7)	25(1)	29(1)	26(1)	5(1)	9(1)	10(1)
C(8)	25(1)	33(1)	23(1)	8(1)	5(1)	11(1)
C(9)	22(1)	27(1)	28(1)	6(1)	6(1)	6(1)
C(10)	29(1)	17(1)	27(1)	7(1)	7(1)	5(1)

**Table S-13.** Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **5B**·(THF)<sub>2</sub>.

	x	y	z	U(eq)
H(1)	1878	5543	4810	36
H(2)	5488	6979	5772	34
H(5A)	8368	7179	7821	43
H(5B)	8325	8579	9148	43
H(6A)	11051	7329	9845	54
H(6B)	10509	6425	11034	54
H(6C)	10647	8428	11108	54
H(7A)	5442	504	6525	35
H(7B)	5657	2553	6644	35
H(8A)	2268	-625	4989	36
H(8B)	2352	1380	5571	36
H(9A)	1116	515	7224	35
H(9B)	782	-1569	6500	35
H(10A)	3305	483	9225	34
H(10B)	3728	-942	8208	34

### Supporting Material References

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S-5. All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-Ray Systems, Madison, WI).