

## Amine- and Ether-Chelated Aryllithium Reagents - Structure and Dynamics

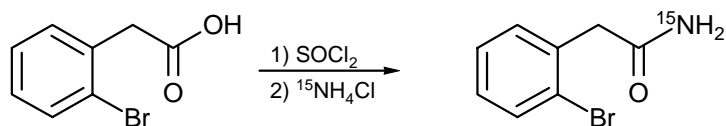
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### Supporting Materials

#### Experimental Section

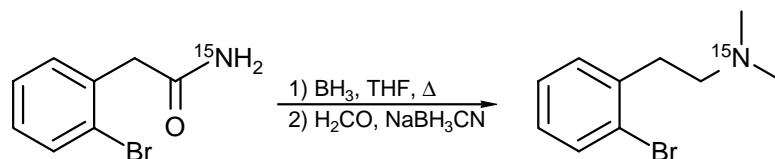
**General.** All reported reaction temperatures are those of the bath. Melting and boiling points are reported uncorrected. Kugelrohr distillation temperatures represent the pot temperature. Thin-layer chromatography (TLC) was performed on silica gel 60 F<sub>256</sub> plates and visualized under ultraviolet light. Mass spectrometry data were obtained using a Micromass AutoSpec™ with electron impact ionization.

**Routine NMR Spectroscopy.** Routine <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) data were obtained on Bruker-250, Bruker-300, AVANCE or AM-360 instruments. All spectra were acquired in CDCl<sub>3</sub> or C<sub>6</sub>D<sub>6</sub> using tetramethylsilane (TMS, δ 0.00) as an internal standard for <sup>1</sup>H NMR and CDCl<sub>3</sub> (δ 77.0) or C<sub>6</sub>D<sub>6</sub> (δ 128.0) for <sup>13</sup>C NMR spectra. Routine <sup>119</sup>Sn NMR spectra were acquired on a Bruker AM-360 spectrometer (unlocked) in protio-THF using Me<sub>4</sub>Sn (δ 0.00) as an internal standard.



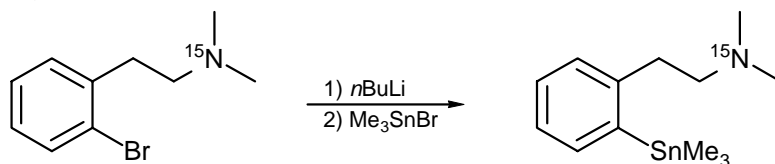
**[<sup>15</sup>N]2-Bromophenylacetamide.** A solution of 2.04 g of 2-bromophenylacetic acid (9.50 mmol), 740 μL of SOCl<sub>2</sub> (10.2 mmol, 1.07 equiv), and a catalytic amount of dimethylformamide (3 μL) in 40 mL of CH<sub>2</sub>Cl<sub>2</sub> was heated to reflux for 24 h. The CH<sub>2</sub>Cl<sub>2</sub> was removed by simple distillation with gentle heating to avoid decomposition of the 2-bromophenylacetyl chloride, which was used further without purification.

A solution of 99% isotopically-enriched <sup>15</sup>NH<sub>4</sub>Cl (0.556 g, 10.2 mmol, 1.07 equiv) in 7 mL of distilled water was covered with a thin layer of benzene (4 mL) and cooled to 0 °C. A solution of NaOH (0.843 g, 21.1 mmol, 2.22 equiv) in 5 mL of water was added directly to the aqueous layer via a Pasteur pipette inserted through the benzene layer followed immediately by the addition of the 2-bromophenylacetyl chloride in 40 mL of benzene. The biphasic solution was stirred vigorously at rt overnight and a white solid precipitated. The solution was cooled to 0 °C, the precipitate was filtered, washed with cold water (100 mL) and cold benzene (40 mL), and allowed to air dry overnight to yield 1.36 g (6.34 mmol, 67%) of a white crystalline solid; m.p. 183–185 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 3.75 (s, 2H), 5.36 (dd, <sup>1</sup>J<sub>H-15N</sub> = 89.6 Hz, J = 3.0 Hz, 1H), 5.42 (dd, <sup>1</sup>J<sub>H-15N</sub> = 90.0 Hz, J = 2.5 Hz, 1H), 7.14–7.20 (m, 1H), 7.29–7.40 (m, 2H), 7.58–7.64 (m, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (75.4 MHz, CDCl<sub>3</sub>): δ 43.54 (CH<sub>2</sub>; d, <sup>2</sup>J<sub>13C-15N</sub> = 8.97 Hz), 124.89 (C), 128.03 (CH), 129.22 (CH), 131.60 (CH), 133.15 (CH), 134.74 (C), 171.70 (C; d, <sup>1</sup>J<sub>13C-15N</sub> = 15.26 Hz). IR (KBr): 3378, 3288, 3184, 1658, 1616 cm<sup>-1</sup>. MS (EI): M<sup>+</sup> = 170.9648 (calc. for C<sub>8</sub>H<sub>8</sub>Br<sup>15</sup>N<sup>15</sup>O – C(O)<sup>15</sup>NH<sub>2</sub> = 170.9634).



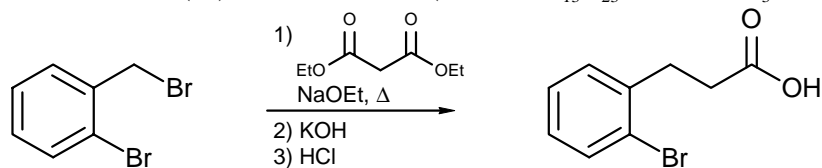
**[<sup>15</sup>N]N,N-Dimethyl-2-(2-bromophenyl)ethylamine.** [<sup>15</sup>N]2-Bromophenylacetamide (1.33 g, 6.17 mmol) was added to a dried and N<sub>2</sub>-flushed 50 mL conical flask fitted with a septum. The flask was cooled to 0 °C under positive N<sub>2</sub> pressure. The amide was dissolved in a 1.0 M solution of BH<sub>3</sub> in THF (9.0 mL, 9.0 mmol, 1.5 equiv). Gas evolution was observed due to H<sub>2</sub> formation. The solution was transferred via a cannula to a dried and N<sub>2</sub>-flushed 100 mL round-bottom flask equipped with a reflux condenser and fitted with a septum. Additional BH<sub>3</sub> was added (11.0 mL, 11.0 mmol, 1.8 equiv), and the solution was heated to reflux for 3 h. The solution was cooled to 0 °C and 20 mL of 6 M HCl<sub>(aq)</sub> (120 mmol, 19 equiv) was added dropwise over a period of 1 h. *Caution: Addition of the 6M HCl too quickly will cause rapid H<sub>2</sub> gas evolution resulting in eruption of the solution and loss of material.* The acidified solution was heated to reflux for 1 h (required to cleave the borane-amine complex), cooled to 0 °C and basified to pH 9 with NaOH pellets. The aqueous solution was extracted with 1:1 Et<sub>2</sub>O/hexanes (60 mL) and partitioned. The organic fraction was washed with water (2 x 200 mL) and brine (100 mL), dried over MgSO<sub>4</sub>, filtered and concentrated *in vacuo* to give a clear, yellow oil. The [<sup>15</sup>N]2-(2-bromophenyl)ethylamine- was used immediately and without purification before adsorption of atmospheric CO<sub>2</sub> would give the undesired carbonate.

A solution of 402 mg of NaBH<sub>3</sub>CN (6.39 mmol, 1.04 equiv) and 439 mg of ZnCl<sub>2</sub> (3.22 mmol, 0.52 equiv) in 15 mL of MeOH was added to a solution of [<sup>15</sup>N]2-(2-bromophenyl)ethylamine and 2.0 mL of 37% aqueous formaldehyde (24.6 mmol, 4.0 equiv) in 15 mL of MeOH. The solution was stirred at rt for 4 h. The reaction mixture was extracted with 1:1 Et<sub>2</sub>O/hexanes (50 mL), the organic fraction was washed with 0.5 M NaOH<sub>(aq)</sub> (100 mL), water (200 mL), and brine (100 mL), dried over MgSO<sub>4</sub>, filtered, and concentrated *in vacuo* to give a clear, yellow oil. The crude product was purified by a Kugelrohr distillation (80–90 °C @ 0.02 mm Hg) to give 565 mg (2.47 mmol, 40%) of a clear, colorless oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 2.33 (d, <sup>2</sup>J<sub>H-15N</sub> = 0.73 Hz, 6H), 2.48–2.56 (m, 2H), 2.89–2.96 (m, 2H), 7.01–7.11 (m, 1H), 7.19–7.27 (m, 2H), 7.50–7.55 (m, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (75.4 MHz, CDCl<sub>3</sub>): δ 34.35 (CH<sub>2</sub>; d, <sup>2</sup>J<sub>13C-15N</sub> = 2.54 Hz), 45.33 (CH<sub>3</sub>; d, <sup>1</sup>J<sub>13C-15N</sub> = 4.45 Hz), 59.52 (CH<sub>2</sub>; d, <sup>1</sup>J<sub>13C-15N</sub> = 3.81 Hz), 124.49 (C), 127.45 (CH), 127.74 (CH), 130.63 (CH), 132.78 (CH), 139.65 (C, <sup>3</sup>J<sub>13C-15N</sub> = 2.55 Hz). MS (EI): M<sup>+</sup> = 230.0238 (calc. for C<sub>10</sub>H<sub>14</sub>Br<sup>15</sup>N = 230.0261).

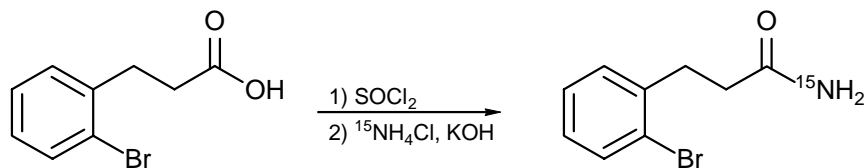


**[<sup>15</sup>N]N,N-Dimethyl-2-(2-Trimethylstannylphenyl)ethylamine.** [<sup>15</sup>N]N,N-Dimethyl-2-(2-bromophenyl)ethylamine (565 mg, 2.47 mmol) and 20 mL of THF were added to a dried and N<sub>2</sub>-flushed 50 mL round-bottom flask fitted with a septum. The flask was cooled to –78 °C under positive N<sub>2</sub> pressure, and 0.80 mL of 3.43 M *n*-BuLi in hexanes (2.75 mmol, 1.11 equiv) was added slowly down the inside of the flask. After stirring at –78 °C for 5 min, the aryllithium reagent was quenched by the addition of 681 mg of Me<sub>3</sub>SnBr (2.80 mmol, 1.13 equiv) in 10 mL of THF. The solution was diluted with 1:1 Et<sub>2</sub>O/ hexanes (50 mL), washed with water (2 x 200 mL) and brine (100 mL). The organic fraction was dried over MgSO<sub>4</sub>, filtered, and concentrated *in vacuo* to give a clear, colorless oil. The crude product was purified by a Kugelrohr distillation (110–120 °C @ 0.03 mm Hg) to give 627 mg (2.00 mmol, 81%) of a clear, colorless oil. Density = 1.21 g/mL. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.34 (s, <sup>2</sup>J<sub>H-119Sn</sub> = 54.2 Hz, 9H), 2.31 (d, <sup>2</sup>J<sub>H-15N</sub> = 0.74 Hz, 6H), 2.45–2.54 and 2.74–2.86 (AA'BB', 4H), 7.13–7.32 (m, 3H), 7.33–7.53 (m, <sup>3</sup>J<sub>H-119Sn</sub> = 56.1 Hz,

1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  -8.15 ( $\text{CH}_3$ ,  $^1J_{^{13}\text{C}-^{119}\text{Sn}} = 347.8$  Hz), 37.43 ( $\text{CH}_2$ ; d,  $^2J_{^{13}\text{C}-^{15}\text{N}} = 3.18$  Hz,  $^3J_{^{13}\text{C}-^{119}\text{Sn}} = 29.3$  Hz), 45.56 ( $\text{CH}_3$ ; d,  $^1J_{^{13}\text{C}-^{15}\text{N}} = 3.82$  Hz), 62.23 ( $\text{CH}_2$ ; d,  $^1J_{^{13}\text{C}-^{15}\text{N}} = 3.82$  Hz), 125.56 (CH,  $J_{^{13}\text{C}-\text{Sn}} = 46.4$  Hz), 128.55 (CH,  $J_{^{13}\text{C}-\text{Sn}} = 38.1$  Hz), 128.68 (CH,  $J_{^{13}\text{C}-\text{Sn}} = 10.2$  Hz), 136.17 (CH,  $J_{^{13}\text{C}-\text{Sn}} = 36.9$  Hz), 141.97 (C), 146.85 (C; d,  $^3J_{^{13}\text{C}-^{15}\text{N}} = 2.54$  Hz,  $J_{^{13}\text{C}-\text{Sn}} = 31.2$  Hz).  $^{119}\text{Sn}\{^1\text{H}\}$  NMR (THF, 134.3 MHz,  $-78$  °C):  $\delta$  -33.4. MS (EI):  $M^+ = 299.0580$  (calc. for  $\text{C}_{13}\text{H}_{23}^{15}\text{NSn} - \text{CH}_3 = 299.0587$ ).



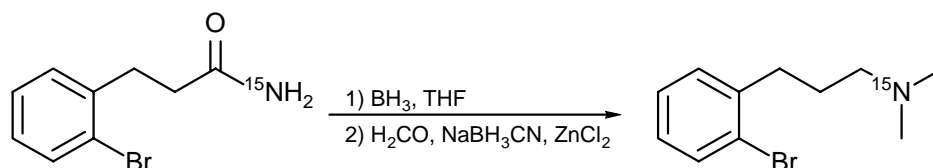
**3-(2-Bromophenyl)propionic Acid.**<sup>[S-1]</sup> A 0.77 M solution of NaOEt, made from 5.32 g of  $\text{Na}^0$  (231 mmol, 5.43 equiv) in 300 mL of EtOH, was added to 34 mL of diethyl malonate (224 mmol, 5.25 equiv) in 50 mL of EtOH. 2-Bromobenzyl bromide (10.66 g, 42.65 mmol) in 50 mL of EtOH was added to the NaOEt solution and heated to reflux for 19 h. The EtOH was removed by distillation. The remaining solution was cooled to 0 °C, diluted with 150 mL of distilled water, and acidified to pH 2 with 12 M  $\text{HCl}_{(\text{aq})}$ . The aqueous solution was extracted with 1:1  $\text{Et}_2\text{O}$ /hexanes (3 x 60 mL). The organic fraction was washed with water (2 x 200 mL) and brine (150 mL), dried over  $\text{MgSO}_4$ , filtered, and concentrated *in vacuo* to give a clear, colorless oil. The oil was taken up in 70 mL of EtOH and 200 mL of a 3.25 M  $\text{NaOH}_{(\text{aq})}$  was added; the solution was heated to reflux for 3 h. The EtOH was removed by distillation. The solution was cooled to 0 °C, acidified with 30 mL of 12 M  $\text{HCl}_{(\text{aq})}$ , and then heated to reflux for 12 h. The solution was reacidified to pH 2 with 12 M  $\text{HCl}_{(\text{aq})}$  and extracted with  $\text{Et}_2\text{O}$  (4 x 60 mL). The organic fraction was washed with brine (150 mL), dried over  $\text{MgSO}_4$ , filtered, and concentrated *in vacuo* to give 9.17 g of a light brown solid. The crude product was purified in a sublimation apparatus (100–120 °C @ 0.02–0.05 mm Hg) by melting, vaporization, and then deposition on the cold finger to yield 5.017 g (21.90 mmol, 51%) of a white powder. m.p. 92–96 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.68–2.75 and 3.03–3.11 (AA'BB', 4H), 7.04–7.14 (m, 1H), 7.21–7.30 (m, 2H), 7.51–7.56 (m, 1H),  $-\text{CO}_2\text{H}$   $^1\text{H}$  NMR signal not observed.  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  31.08 (CH), 33.82 (CH), 124.34 (C), 127.62 (CH), 128.21 (CH), 130.42 (CH), 132.94 (CH), 139.34 (C), 178.87 (C). IR (KBr):  $1701\text{ cm}^{-1}$ . MS (EI):  $M^+ = 229.9755$  (calc. for  $\text{C}_9\text{H}_9\text{BrO}_2 = 229.9767$ ).



**[ $^{15}\text{N}$ ]3-(2-Bromophenyl)propamide.** A solution of 3.22 g of 3-(2-bromophenyl)propionic acid (14.04 mmol), 1.09 mL of  $\text{SOCl}_2$  (15.0 mmol, 1.06 equiv), and a catalytic amount of dimethylformamide (5  $\mu\text{L}$ ) in 40 mL of  $\text{CH}_2\text{Cl}_2$  was heated to reflux for 22 h. The  $\text{CH}_2\text{Cl}_2$  was removed by distillation with gentle heating to avoid decomposition of the 3-(2-bromophenyl)propionyl chloride, which was used without purification.

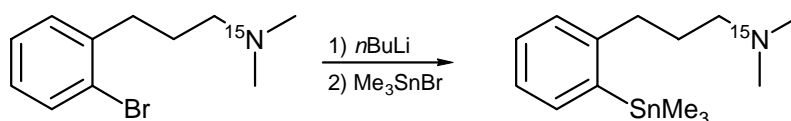
A solution of 99% isotopically-enriched  $^{15}\text{NH}_4\text{Cl}$  (0.842 g, 15.5 mmol, 1.10 equiv) in 8 mL of water was covered with a thin layer of benzene (6 mL) and cooled to 0 °C. A solution of 1.271 g of NaOH (31.76 mmol, 2.26 equiv) in 7 mL of distilled water was added directly to the aqueous layer via a Pasteur pipette inserted through the benzene layer followed immediately by the addition of the 3-(2-bromophenyl)propionyl chloride in 30 mL of benzene. The biphasic solution was stirred vigorously at rt overnight and a white solid precipitated. The solution was cooled to 0 °C. The precipitate was filtered, washed with cold distilled water (2 x 30 mL) and cold benzene (20 mL), and allowed to air dry overnight to yield 2.572 g (11.23 mmol, 80%) of a white crystalline solid; m.p. 108–109 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.50–2.56 and 3.05–3.12 (AA'BB', 4H), 5.63 (dd,  $^3J_{\text{H}-^{15}\text{N}} = 89.0$  Hz,  $J = 2.6$  Hz, 1H), 5.86 (dd,  $^3J_{\text{H}-^{15}\text{N}} = 88.3$  Hz,  $J = 2.6$  Hz, 1H), 7.08 (ddd,  $J = 7.73, 6.99, 2.21$  Hz, 1H), 7.24 (td,  $J = 7.72, 1.10$  Hz, 1H), 7.28 (dd,  $J = 7.72, 2.21$

Hz, 1H), 7.53 (dd,  $J = 8.08, 1.10$  Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  31.89 ( $\text{CH}_2$ ), 35.64 ( $\text{CH}_2$ ; d,  $^2J_{^{13}\text{C}-^{15}\text{N}} = 8.72$  Hz), 124.24 (C), 127.67 (CH), 128.11 (CH), 130.65 (CH), 132.86 (CH), 139.88 (C), 174.13 (C; d,  $^1J_{^{13}\text{C}-^{15}\text{N}} = 13.8$  Hz). IR (KBr): 3328, 3162, 1663, 1628  $\text{cm}^{-1}$ . MS (EI):  $M^+ = 149.0705$  (calc. for  $\text{C}_9\text{H}_{10}\text{Br}^{15}\text{NO} - \text{Br} = 149.0733$ ).



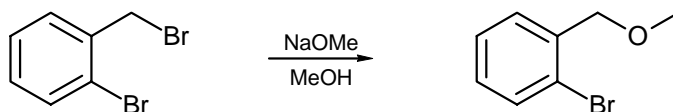
**[ $^{15}\text{N}$ ]N,N-Dimethyl-3-(2-Bromophenyl)propylamine.** To a dried and  $\text{N}_2$ -flushed 100 mL round-bottom flask equipped with a reflux condenser fitted with a septum, 2.357 g of 3-(2-bromophenyl)propionamide- $^{15}\text{N}$  (10.29 mmol) was added. The flask was cooled to  $0^\circ\text{C}$  while maintaining positive  $\text{N}_2$  pressure. The amide was dissolved in 27.0 mL of a 1.0 M solution of  $\text{BH}_3$  in THF (27.0 mmol, 2.62 equiv). The reaction mixture was stirred at  $0^\circ\text{C}$  for 15 minutes while gas evolution was observed due to  $\text{H}_2$  formation. The solution was heated to reflux for 4 h. The solution was cooled to  $0^\circ\text{C}$  and 20 mL of 6 M  $\text{HCl}_{(\text{aq})}$  (120 mmol, 11.7 equiv) was added dropwise over a period of 30 minutes. *Caution: Addition of the 6M  $\text{HCl}_{(\text{aq})}$  too quickly will cause rapid  $\text{H}_2$  gas evolution resulting in eruption of the solution and loss of material.* The acidified solution was heated to reflux for 90 min, required to cleave the borane-amine complex. The solution was then cooled to  $0^\circ\text{C}$  and basified to pH 9 with NaOH pellets. The aqueous solution was diluted with 1:1  $\text{Et}_2\text{O}$ /hexanes (60 mL) and partitioned. The organic fraction was washed with water (2 x 200 mL) and brine (100 mL), dried over  $\text{MgSO}_4$ , filtered, and concentrated *in vacuo* to give a clear, yellow oil. The [ $^{15}\text{N}$ ]3-(2-bromophenyl)propylamine was used immediately and without purification.

A solution of 1.42 g of  $\text{NaBH}_3\text{CN}$  (22.6 mmol, 1.10 equiv) and 1.55 g of  $\text{ZnCl}_2$  (11.35 mmol, 1.10 equiv) in 20 mL of MeOH was added to a solution of [ $^{15}\text{N}$ ]3-(2-bromophenyl)propylamine and 3.6 mL of 37% aqueous formaldehyde (44.3 mmol, 4.3 equiv) in 20 mL of MeOH and allowed to stir at room temperature overnight. The solution was cooled to  $0^\circ\text{C}$  and 20 mL of 6 M  $\text{HCl}_{(\text{aq})}$  (120 mmol, 11.7 equiv). *Note: Caution is required due to the formation of  $\text{HCN}_{(\text{g})}$ . This step must be performed in a well-ventilated hood.* The solution was heated to reflux for 1 h, required to cleave the borane-amine bond. The solution was then cooled to  $0^\circ\text{C}$  and basified to pH 9 with NaOH pellets. The aqueous solution was diluted with 1:1  $\text{Et}_2\text{O}$ /hexanes (60 mL) and partitioned. The organic fraction was washed with distilled water (2 x 200 mL) and brine (100 mL), dried over  $\text{MgSO}_4$ , filtered, and concentrated *in vacuo* to give a clear, pale yellow oil. The crude product was purified by a Kugelrohr distillation ( $105\text{--}120^\circ\text{C}$  @ 0.02 mm Hg) to give 1.548 g (6.37 mmol, 62%) of a clear, colorless oil.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.72–1.86 (m, 2H), 2.24 (d,  $^2J_{\text{H}-^{15}\text{N}} = 0.74$  Hz, 6H), 2.30–2.37 (m, 2H), 2.71–2.79 (m, 2H), 7.00–7.09 (m, 1H), 7.18–7.25 (m, 2H), 7.50–7.54 (m, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  27.90 ( $\text{CH}_2$ ; d,  $^2J_{^{13}\text{C}-^{15}\text{N}} = 1.91$  Hz), 34.00 ( $\text{CH}_2$ ; d,  $^3J_{^{13}\text{C}-^{15}\text{N}} = 2.54$  Hz), 45.43 ( $\text{CH}_3$ ; d,  $^1J_{^{13}\text{C}-^{15}\text{N}} = 3.82$  Hz), 59.18 ( $\text{CH}_2$ ; d,  $^1J_{^{13}\text{C}-^{15}\text{N}} = 3.82$  Hz), 124.41 (C), 127.35 (CH), 127.47 (CH), 130.32 (CH), 132.75 (CH), 141.56 (C). MS (EI):  $M^+ = 244.0395$  (calc. for  $\text{C}_{11}\text{H}_{16}\text{Br}^{15}\text{N} = 244.0417$ ).

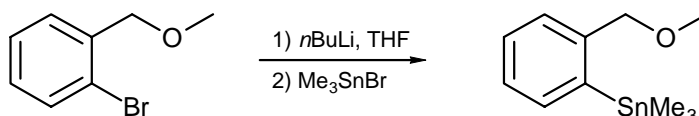


**[ $^{15}\text{N}$ ]N,N-Dimethyl-3-(2-Trimethylstannylphenyl)propylamine.** [ $^{15}\text{N}$ ]N,N-Dimethyl-3-(2-bromophenyl)propylamine (1.46 g, 6.00 mmol) and 10 mL of THF were added to a dried and  $\text{N}_2$ -flushed 100 mL round-bottom flask fitted with a septum. The flask was cooled to  $-78^\circ\text{C}$   $\text{N}_2$ , and 2.00 mL of 3.24 M  $n\text{-BuLi}$  in hexanes (6.48 mmol, 1.08 equiv) was added down the inside of the flask. After stirring at  $-78^\circ\text{C}$  for 5 min, 1.66 g of  $\text{Me}_3\text{SnBr}$  (6.82 mmol, 1.14 equiv) in 10 mL of THF was added. The solution was

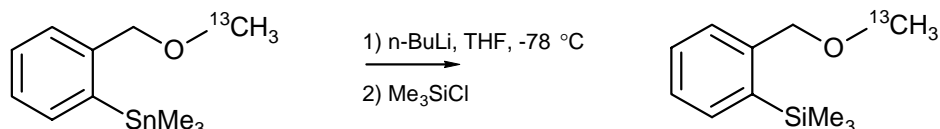
diluted with 1:1 Et<sub>2</sub>O/hexanes (40 mL), washed with water (2 x 200 mL) and brine (100 mL). The organic fraction was dried over MgSO<sub>4</sub>, filtered, and concentrated *in vacuo* to give a clear, colorless oil. The crude product was purified by a Kugelrohr distillation (145–160 °C @ 0.03 mm Hg) to give 1.612 g (4.93 mmol, 82% yield) of a clear, colorless oil. Density = 1.18 g/mL. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.31 (s, <sup>2</sup>J<sub>H-119Sn</sub> = 54.1 Hz, 9H), 1.70–1.83 (m, 2H), 2.23 (d, <sup>2</sup>J<sub>H-15N</sub> = 0.73 Hz, 6H), 2.30–2.37 (m, 2H), 2.58–2.67 (m, 2H), 7.12–7.32 (m, 3H), 7.32–7.53 (m, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (75.4 MHz, CDCl<sub>3</sub>): δ -8.19 (CH<sub>3</sub>), 30.54 (CH<sub>2</sub>; d, <sup>2</sup>J<sub>13C-15N</sub> = 1.90 Hz), 36.84 (CH<sub>2</sub>; d, <sup>3</sup>J<sub>13C-15N</sub> = 1.90 Hz), 45.47 (CH<sub>3</sub>; d, <sup>1</sup>J<sub>13C-15N</sub> = 4.45 Hz), 59.57 (CH<sub>2</sub>; d, <sup>1</sup>J<sub>13C-15N</sub> = 3.81 Hz), 125.37 (CH), 128.10 (CH), 128.68 (CH), 136.17 (CH), 141.57 (C), 148.93 (C). <sup>119</sup>Sn{<sup>1</sup>H} NMR (THF, 134.3 MHz, -78 °C): δ -34.4. MS (EI): M<sup>+</sup> = 313.0716 (calc. for C<sub>14</sub>H<sub>25</sub><sup>15</sup>NSn = 313.0743).



**2-Bromobenzyl Methyl Ether**<sup>[S-2]</sup> A 2.0 M solution of NaOMe, from 1.15 g of Na<sup>0</sup> (50.0 mmol, 1.20 equiv) in 25 mL of MeOH, was added to 10.44 g of 2-bromobenzyl bromide (41.8 mmol) and heated to reflux for 3 h. The solution was cooled to 0 °C and taken up in 1:1 Et<sub>2</sub>O/hexanes (80 mL). The organic fraction was washed with distilled water (2 x 200 mL) and brine (80 mL), dried over MgSO<sub>4</sub>, filtered, and concentrated *in vacuo* to give a clear, colorless oil. The crude product was purified by a Kugelrohr distillation (50–70 °C @ 0.25 mm Hg) to yield 7.10 g (35.3 mmol, 85%) of the Et<sub>2</sub>O. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 3.47 (m, 3H), 4.53 (m, 2H), 7.15 (td, *J* = 7.8, 2.0 Hz, 1H), 7.32 (td, *J* = 7.5, 1.2 Hz, 1H), 7.46 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.54 (dd, *J* = 7.8, 1.2 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75.4 MHz): δ 58.55 (CH<sub>3</sub>), 73.85 (CH<sub>2</sub>), 122.65 (C), 127.33 (CH), 128.84 (CH), 128.90 (CH), 132.47 (CH), 137.54 (C). MS (EI): M<sup>+</sup> = 201.9827 (calc. for C<sub>8</sub>H<sub>9</sub>BrO = 201.9818).

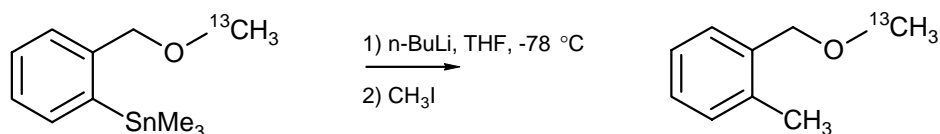


**2-Trimethylstannylbenzyl Methyl Ether.** 2-Bromobenzyl methyl ether (2.050 g, 10.20 mmol) and 20 mL of THF were added to a dried and N<sub>2</sub>-flushed 100 mL round-bottom flask fitted with a septum. The flask was cooled to -78 °C under positive N<sub>2</sub> pressure and 3.70 mL of 2.87 M *n*-BuLi in hexanes (10.62 mmol, 1.04 equiv) was added. The solution was initially homogenous with a yellow color but became heterogenous and cloudy white within 2 min. After stirring at -78 °C for 18 min, the lithium reagent was quenched by the addition of 2.594 g of Me<sub>3</sub>SnBr (10.64 mmol, 1.04 equiv) in 7 mL of THF. The solution was taken up in 1:1 Et<sub>2</sub>O/hexanes (60 mL), washed with water (2 x 200 mL) and brine (100 mL). The organic fraction was dried over MgSO<sub>4</sub>, filtered, and concentrated *in vacuo* to give a clear, yellow oil. The crude product was purified by a Kugelrohr distillation (103–112 °C @ 0.03 mm Hg) to yield 2.443 g (8.57 mmol, 84%) of a clear, colorless oil. Density = 1.31 g/mL. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.27 (s, <sup>2</sup>J<sub>H-119Sn-H</sub> = 54.6 Hz, 9H), 3.35 (s, 3H), 4.45 (s, <sup>4</sup>J<sub>H-119Sn</sub> = 4.4 Hz, 2H), 7.19–7.35 (m, 3H), 7.43–7.65 (m, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (75.4 MHz, CDCl<sub>3</sub>): δ -8.06 (CH<sub>3</sub>), 57.80 (CH<sub>3</sub>), 76.29 (CH<sub>2</sub>), 127.12 (CH), 127.66 (CH), 128.19 (CH), 136.56 (CH), 141.49 (C), 144.50 (C). <sup>119</sup>Sn{<sup>1</sup>H} NMR (THF, 134.3 MHz, -78 °C): δ -38.2. MS (EI): M<sup>+</sup> = 271.0155 (calc. for C<sub>11</sub>H<sub>18</sub>OSn - CH<sub>3</sub> = 271.0145).

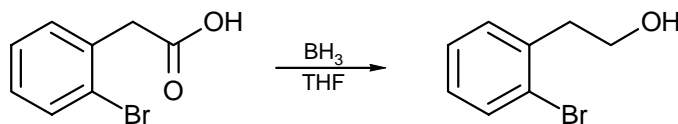


**[<sup>13</sup>C]2-Trimethylsilylbenzyl Methyl Ether.** A solution of [<sup>13</sup>C]-2-trimethylstannylbenzyl methyl ether

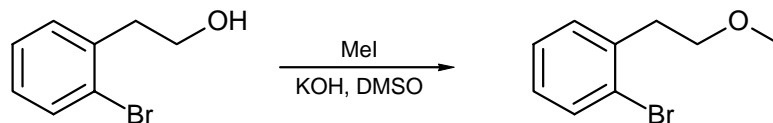
(276 mg, 0.96 mmol) and THF (3 mL) was cooled to  $-78\text{ }^{\circ}\text{C}$  under a  $\text{N}_2$  atmosphere and 382  $\mu\text{L}$  of 2.62 M *n*-BuLi in hexane (1.0 mmol) was added slowly. After 15 min, TMSCl (200  $\mu\text{L}$ , 1.57 mmol) was added. The solution was stirred for 15 min and warmed to rt for an additional 1 h. The solution was diluted with 1:1  $\text{Et}_2\text{O}$ /hexane and washed with water and brine, and then dried over  $\text{MgSO}_4$ . The solution was concentrated *in vacuo* to give an oil. Kugelrohr distillation ( $50 - 54\text{ }^{\circ}\text{C}$  @ 0.03 mm Hg) afforded 110 mg (59 %) of a clear, colorless oil.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.33 (s, 9H), 3.39 (d,  $^1J_{\text{HC}} = 141\text{ Hz}$ , 3H), 4.52 (d,  $^3J_{\text{HC}} = 3.7\text{ Hz}$ , 2H), 7.23 - 7.42 (m, 3H), 7.54 - 7.56 (m, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (90.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.22 ( $\text{CH}_3$ ), 57.9 ( $\text{CH}_3$ ), 74.9 (d,  $^2J = 1.9\text{ Hz}$ ,  $\text{CH}_2$ ), 126.9 (CH), 128.3 (CH), 129.1 (CH), 134.6 (CH), 138.4 (C), 143.5 (d,  $^3J = 3.4\text{ Hz}$ , C). MS (EI):  $M^+ = 180.0929$  (calc. for  $\text{C}_{11}\text{H}_{18}\text{OSi} - \text{CH}_3 = 180.0926$ ).



**[ $^{13}\text{C}$ ]2-Methylbenzyl Methyl Ether.** A solution of [ $^{13}\text{C}$ ]2-trimethylstannylbenzyl methyl ether (281 mg, 0.98 mmol) and THF (5 mL) was cooled to  $-78\text{ }^{\circ}\text{C}$  under a  $\text{N}_2$  atmosphere and 393  $\mu\text{L}$  of 2.62 M *n*-BuLi in hexane (1.03 mmol) was added slowly. After 15 minutes, MeI (181  $\mu\text{L}$ , 1.28 mmol) was added. The solution was stirred for 15 min and warmed to rt for an additional 1h. The solution was diluted with 1:1  $\text{Et}_2\text{O}$ /hexane, washed with water and brine, dried over  $\text{MgSO}_4$  and concentrated *in vacuo* to give an oil. Purification by column chromatography (5%  $\text{EtOAc}$ /hexane) yielded 32 mg (0.23 mmol, 23%) of a clear, colorless oil.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.33 (s, 3H), 3.40 (d,  $^1J_{\text{HC}} = 139\text{ Hz}$ , 3H), 4.45 (d,  $^3J_{\text{HC}} = 3.8\text{ Hz}$ , 2H), 7.13-7.34 (m, 4H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (90.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  18.7 ( $\text{CH}_3$ ), 58.1 ( $\text{CH}_3$ ), 73.0 (d,  $^2J_{\text{CC}} = 1.8\text{ Hz}$ ,  $\text{CH}_2$ ), 125.7 (CH), 127.8 (CH), 128.5 (CH), 130.2 (CH), 136.0 (d,  $^3J_{\text{CC}} = 3.2\text{ Hz}$ , C), 136.6 (C). MS (EI):  $M^+ = 137.0918$  (calc. for  $\text{C}_9\text{H}_{12}\text{O} = 137.0922$ ).

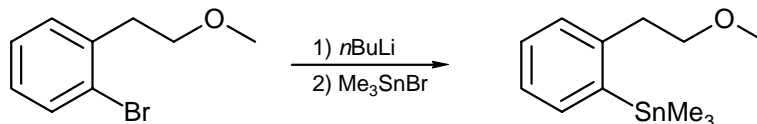


**2-(2-Bromophenyl)ethanol.**<sup>[S-3]</sup> 2-Bromophenylacetic acid (1.002 g, 4.66 mmol) was added to a dried and  $\text{N}_2$ -flushed 25 mL round-bottom flask and cooled to  $0\text{ }^{\circ}\text{C}$  under positive  $\text{N}_2$  pressure. A 1.0 M solution of  $\text{BH}_3$  in THF (10.0 mL, 10.0 mmol, 2.15 equiv) was added. Upon addition, gas evolution was observed due to  $\text{H}_2$  formation. The solution was stirred at  $0\text{ }^{\circ}\text{C}$  for 3 h, then quenched slowly with drops of distilled water until no more gas evolved. The reaction mixture was taken up in 1:1  $\text{Et}_2\text{O}$ /hexanes (40 mL), washed with saturated  $\text{Na}_2\text{CO}_3$  (100 mL), water (100 mL), and brine (100 mL), dried over  $\text{MgSO}_4$ , filtered, and concentrated *in vacuo* to give a cloudy, colorless oil. The crude product was purified by a Kugelrohr distillation ( $125 - 135\text{ }^{\circ}\text{C}$  @ 0.02 mm Hg) to give 758 mg (3.77 mmol, 81%) of a clear, colorless oil.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.63 (broad s, 1H), 3.03 (t,  $J = 6.62\text{ Hz}$ , 2H), 3.88 (t,  $J = 6.62\text{ Hz}$ , 2H), 7.04-7.15 (m, 1H), 7.19-7.30 (m, 2H), 7.52-7.58 (m, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  39.30 ( $\text{CH}_2$ ), 62.02 ( $\text{CH}_2$ ), 124.66 (C), 127.44 (CH), 128.18 (CH), 131.25 (CH), 132.94 (CH), 137.78 (C). IR ( $\text{CCl}_4$ ): 3631, 3941, 1040  $\text{cm}^{-1}$ . MS (EI):  $M^+ = 201.9825$  (calc. for  $\text{C}_8\text{H}_9\text{BrO} = 201.9818$ ).

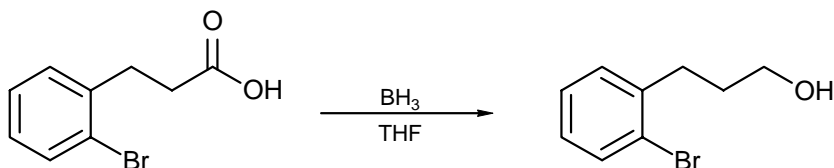


**2-(2-Bromophenyl)ethyl Methyl Ether.**<sup>[S-4]</sup> Powdered KOH (0.888 g, 15.82 mmol, 4.20 equiv) was added to 5 mL of DMSO in a 25 mL round-bottom flask and stirred at rt for 15 min. A solution of 0.50 mL of MeI (8.03 mmol, 2.13 equiv) and 0.758 g of 2-(2-bromophenyl)ethanol (3.77 mmol) in 4 mL of DMSO was added to the KOH solution. *This reaction is very exothermic!* Before the addition, the 25 mL flask was

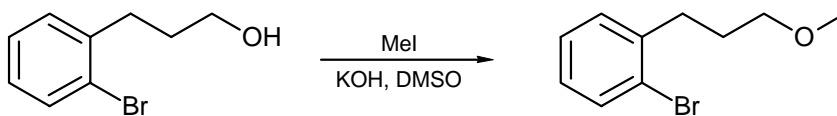
placed in a room temperature bath to absorb excess heat. The reaction mixture was poured into 80 mL of water and extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 20 mL). The organic extract was washed with water (2 x 50 mL) and brine (50 mL), dried over  $\text{MgSO}_4$ , filtered, and concentrated *in vacuo* to give a cloudy, colorless oil. The crude product was purified by Kugelrohr distillation (75–85 °C @ 0.04 mm Hg) to yield 0.713 g (3.31 mmol, 88%) of a clear, colorless oil.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.03 (t,  $J = 6.99$  Hz, 2H), 3.37 (s, 3H), 3.61 (t,  $J = 6.99$  Hz, 2H), 7.04–7.11 (m, 1H), 7.20–7.30 (m, 2H), 7.51–7.56 (m, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  39.29 ( $\text{CH}_2$ ), 58.64 ( $\text{CH}_3$ ), 71.72 ( $\text{CH}_2$ ), 124.59 (C), 127.37 (CH), 127.97 (CH), 131.02 (CH), 132.76 (CH), 138.15 (C). MS (EI):  $M^+ = 215.9968$  (calc. for  $\text{C}_9\text{H}_{11}\text{BrO} = 215.9974$ ).



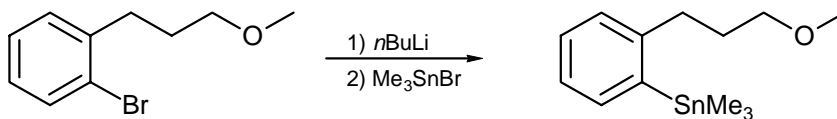
**(2-Trimethylstannylphenyl)ethyl Methyl Ether.** 2-(2-Bromophenyl)ethyl methyl ether (0.689 g, 3.20 mmol) and 10 mL of THF were added to a dried and  $\text{N}_2$ -flushed 50 mL round-bottom flask fitted with a septum. The flask was cooled to  $-78$  °C under positive  $\text{N}_2$  pressure and 1.80 mL of 1.91 M *n*-BuLi in hexanes (3.44 mmol, 1.07 equiv) was added. The solution turned yellow then became white and heterogenous within 10 min. After stirring at  $-78$  °C for 10 min, the aryllithium reagent was quenched by the addition of 0.875 g of  $\text{Me}_3\text{SnBr}$  (3.59 mmol, 1.12 equiv) in 5 mL of THF. The solution became homogenous and turned a pale yellow color. The solution was taken up in 1:1  $\text{Et}_2\text{O}$ /hexanes (40 mL), washed with distilled water (2 x 200 mL) and brine (150 mL). The organic fraction was dried over  $\text{MgSO}_4$ , filtered, and concentrated *in vacuo* to give a clear, pale yellow oil. The crude product was purified by a Kugelrohr distillation (107–118 °C @ 0.035 mm Hg) to yield 0.8623 g (2.88 mmol, 90%) of a clear, colorless oil. Density = 1.27 g/mL.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.32 (s,  $^2J_{\text{H}-^{119}\text{Sn}} = 54.4$  Hz, 9H), 2.88–2.96 and 3.51–3.58 (AA'BB', 4H), 3.36 (s, 3H), 7.15–7.32 (m, 3H), 7.33–7.54 (m, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  -8.19 ( $\text{CH}_3$ ), 39.14 ( $\text{CH}_2$ ), 58.74 ( $\text{CH}_3$ ), 74.20 ( $\text{CH}_2$ ), 125.81 (CH), 128.63 (CH), 128.70 (CH), 136.26 (CH), 142.50 (C), 145.22 (C).  $^{119}\text{Sn}\{^1\text{H}\}$  NMR (THF, 134.3 MHz,  $-78$  °C):  $\delta$  -34.1. MS (EI):  $M^+ = 285.0313$  (calc. for  $\text{C}_{12}\text{H}_{20}\text{OSn} - \text{CH}_3 = 285.0301$ ).



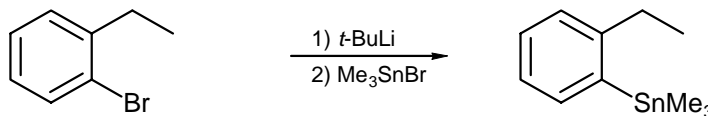
**3-(2-Bromophenyl)propanol.**<sup>[S-5]</sup> To a dried and  $\text{N}_2$ -flushed 25 mL round-bottom flask, 2.405 g of 3-(2-bromophenyl)propanoic acid (10.50 mmol) was added. The flask was cooled to 0 °C under positive  $\text{N}_2$  pressure. A 1.0 M solution of  $\text{BH}_3$  in THF (11.0 mL, 11.0 mmol, 1.05 equiv) was added. Upon addition, gas evolution was observed due to  $\text{H}_2$  formation. The solution was stirred at 0 °C for 3 h, then quenched slowly with drops of water until no more gas evolved. The reaction mixture was taken up in 1:1  $\text{Et}_2\text{O}$ /hexanes (40 mL), washed with saturated  $\text{Na}_2\text{CO}_3$  (150 mL), water (150 mL), and brine (150 mL), dried over  $\text{MgSO}_4$ , filtered, and concentrated *in vacuo* to give a cloudy, colorless oil. The crude product was purified by a Kugelrohr distillation (135–145 °C @ 0.05 mm Hg) to give 1.6943 g (7.88 mmol, 75%) of a clear, colorless oil.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.82–1.94 and 2.78–2.85 (AA'BB', 4H), 2.16 (s, 1H), 3.68 (t,  $J = 6.62$  Hz, 2H), 3.68 (t,  $J = 6.62$  Hz, 2H), 6.99–7.09 (m, 1H), 7.18–7.26 (m, 2H), 7.49–7.54 (m, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ):  $\delta$  32.31 ( $\text{CH}_2$ ), 32.61 ( $\text{CH}_2$ ), 61.95 ( $\text{CH}_2$ ), 124.36 (C), 127.39 (CH), 127.56 (CH), 130.33 (CH), 132.72 (CH), 141.03 (C). IR ( $\text{CCl}_4$ ): 3638, 3502, 1051, 1020  $\text{cm}^{-1}$ . MS (EI):  $M^+ = 215.9989$  (calc. for  $\text{C}_9\text{H}_{11}\text{BrO} = 215.9974$ ).



**3-(2-Bromophenyl)propyl Methyl Ether.**<sup>[S-6]</sup> Powdered KOH (2.50 g, 44.6 mmol, 5.66 equiv) was added to 9 mL of DMSO in a 25 mL round-bottom flask and stirred at rt for 20 min. A solution of 1.00 mL of MeI (16.1 mmol, 2.04 equiv) and 1.694 g of 3-(2-bromophenyl)propanol (7.88 mmol) in 4 mL of DMSO was added to the KOH solution. *This reaction is very exothermic!* Before the addition, the 25 mL flask was placed in a rt bath to absorb excess heat. The reaction mixture was poured into 80 mL of water and extracted with CH<sub>2</sub>Cl<sub>2</sub> (4 x 20 mL). The organic extract was washed with water (2 x 50 mL) and brine (50 mL), dried over MgSO<sub>4</sub>, filtered, and concentrated *in vacuo* to give a cloudy, colorless oil. The crude product was purified by Kugelrohr distillation (75–85 °C @ 0.04 mm Hg) to yield 1.65 g (7.19 mmol, 91%) of a clear, colorless oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.84–1.95 (m, 2H), 2.78–2.85 (m, 2H), 3.36 (s, 3H), 3.42 (t, *J* = 6.62 Hz, 2H), 7.00–7.10 (m, 1H), 7.19–7.25 (m, 2H), 7.53 (d, *J* = 7.35 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (75.4 MHz, CDCl<sub>3</sub>): δ 29.57 (CH<sub>2</sub>), 32.69 (CH<sub>2</sub>), 58.53 (CH<sub>3</sub>), 71.79 (CH<sub>2</sub>), 124.44 (C), 127.35 (CH), 127.54 (CH), 130.45 (CH), 132.77 (CH), 141.20 (C). MS (EI): M<sup>+</sup> = 230.0138 (calc. for C<sub>10</sub>H<sub>13</sub>BrO = 230.0131).



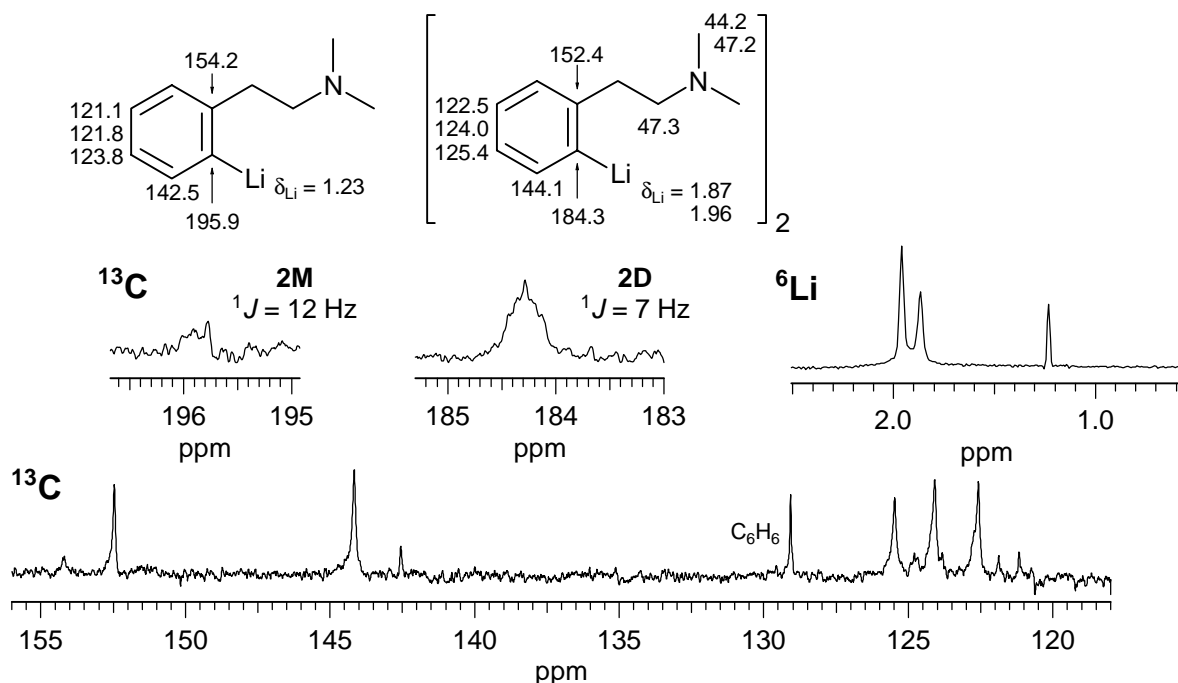
**3-(*o*-Trimethylstannylphenyl)propyl Methyl Ether.** To a dried and N<sub>2</sub>-flushed 100 mL round-bottom flask fitted with a septum, 1.306 g of 3-(2-bromophenyl)propyl methyl ether (5.70 mmol) and 10 mL of THF were added. The flask was cooled to –78 °C under positive N<sub>2</sub> pressure, then 2.00 mL of 3.24 M *n*-BuLi in hexanes (6.48 mmol, 1.14 equiv) was added slowly down the inside of the flask. After stirring at –78 °C for 5 min, the aryllithium reagent was quenched by the addition of 1.64 g of Me<sub>3</sub>SnBr (6.74 mmol, 1.18 equiv) in 7 mL of THF. The reaction mixture was taken up in 1:1 Et<sub>2</sub>O/hexanes (40 mL), washed with distilled water (2 x 200 mL) and brine (100 mL). The organic fraction was dried over MgSO<sub>4</sub>, filtered, and concentrated *in vacuo* to give a clear, colorless oil. The crude product was purified by a Kugelrohr distillation (120–130 °C @ 0.03 mm Hg) to yield 1.4251 g (4.55 mmol, 80%) of a clear, colorless oil. Density = 1.21 g/mL. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.32 (s, <sup>2</sup>*J*<sub>H-<sup>119</sup>Sn</sub> = 54.4 Hz, 9H), 1.81–1.95 (m, 2H), 2.65–2.74 (m, 2H), 3.36 (s, 3H), 3.43 (t, *J* = 6.62 Hz, 2H), 7.12–7.32 (m, 3H), 7.32–7.53 (m, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (75.4 MHz, CDCl<sub>3</sub>): δ –8.20 (CH<sub>3</sub>), 32.20 (CH<sub>2</sub>), 35.44 (CH<sub>2</sub>), 58.59 (CH<sub>3</sub>), 72.15 (CH<sub>2</sub>), 125.40 (CH), 128.16 (CH), 128.65 (CH), 136.22 (CH), 141.73 (C), 148.69 (C). <sup>119</sup>Sn{<sup>1</sup>H} NMR (THF, 134.3 MHz, –78 °C): δ –33.5. MS (EI): M<sup>+</sup> = 299.0449 (calc. for C<sub>13</sub>H<sub>22</sub>OSn – CH<sub>3</sub> = 299.0458).



**2-Ethyltrimethylstannylbenzene.** 2-Bromoethylbenzene (692 uL, 5.0 mmol) and THF (5 mL) were added to a dry round-bottom flask under a N<sub>2</sub> atmosphere. The solution was cooled to –78 °C and 5.6 mL of 1.8 M *t*-BuLi (10.0 mmol) was slowly added. After 10 min, a solution of Me<sub>3</sub>SnBr (1.47 g, 5.5 mmol) in 5 mL of THF added slowly, the solution was stirred for 10 min, the cold bath was removed and the solution allowed to warm for 5 min before saturated NH<sub>4</sub>Cl (aq.) was added. The solution was diluted with Et<sub>2</sub>O (50 mL) and hexane (25 mL) and washed with water (200 mL) and brine (100 mL). The organic fraction was dried over MgSO<sub>4</sub>, filtered, and concentrated *in vacuo* to give an oil. Kugelrohr distillation (33–46 °C @ 0.014 mm Hg) afforded 821 mg (61 %) of a clear, colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 360 MHz): δ 0.31 (s, <sup>2</sup>*J*<sub>H-<sup>119</sup>Sn</sub> = 54.3 Hz, 9H), 1.23 (t, *J* = 7.6 Hz, 3H), 2.66 (q, *J* = 7.6 Hz, <sup>4</sup>*J*<sub>H-<sup>119</sup>Sn</sub> = 6.2 Hz, 2H), 7.11–7.5 (m, 4H).

$^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 90.56 MHz):  $\delta$  -8.3 ( $\text{CH}_3$ ,  $^1J_{^{13}\text{C}-^{119}\text{Sn}} = 347.8$  Hz), 16.5 ( $\text{CH}_3$ ), 32.0 ( $\text{CH}_2$ ,  $^3J_{^{13}\text{C}-\text{Sn}} = 28.2$  Hz), 125.3 ( $\text{CH}$ ,  $J_{^{13}\text{C}-\text{Sn}} = 48.1$  Hz), 127.4 ( $\text{CH}$ ,  $J_{^{13}\text{C}-\text{Sn}} = 38.5$  Hz), 128.8 ( $\text{CH}$ ,  $J_{^{13}\text{C}-\text{Sn}} = 10.3$  Hz), 136.1 ( $\text{CH}$ ,  $J_{^{13}\text{C}-\text{Sn}} = 38.1$  Hz), 141.3 (C), 150.8 (C). MS (EI):  $M^+ = 255.0188$  (calc. for  $\text{C}_{11}\text{H}_{18}\text{Sn}-\text{CH}_3 = 255.0196$ ).

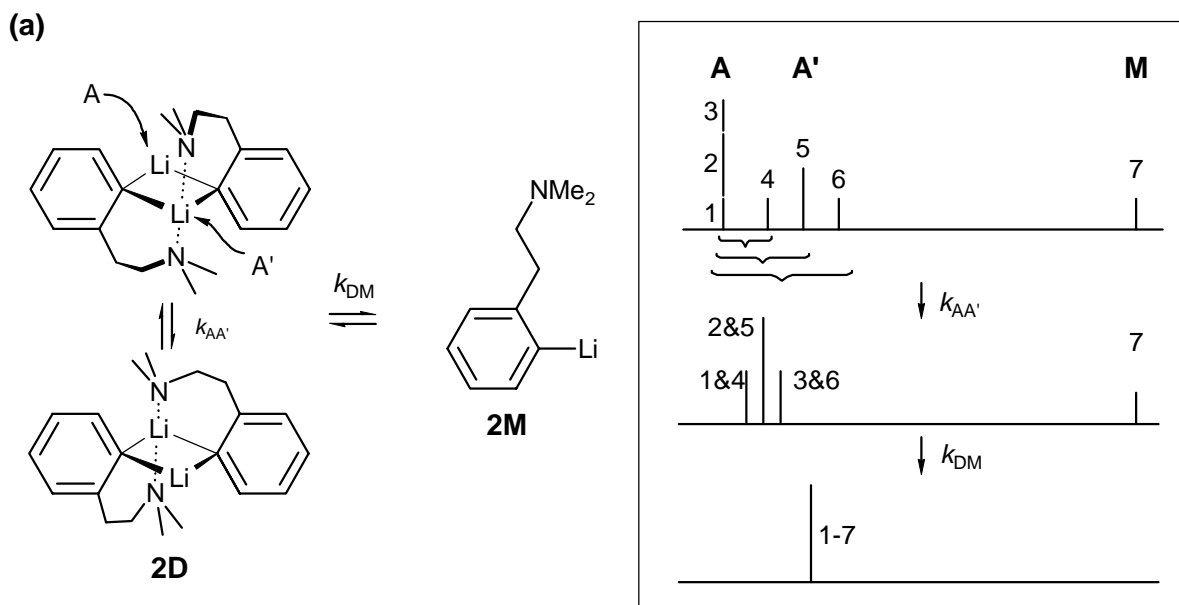
## NMR Experiments Conducted on 2-(2-Dimethylaminoethyl)phenyllithium (2)



**Figure S-1.**  $^6\text{Li}$  and  $^{13}\text{C}$  NMR spectra of 0.12 M 2-(2-dimethylaminoethyl)phenyllithium (2) in 3:2:1 THF/Me<sub>2</sub>O/Et<sub>2</sub>O at -130 to -145 °C.

**Variable-Temperature  $^6\text{Li}$  NMR Experiment of [ $^6\text{Li}$ ,  $^{15}\text{N}$ ]2.** [ $^{15}\text{N}$ ]N,N-Dimethyl-2-(2-trimethylstannylphenyl)ethylamine (0.163 g, 0.520 mmol) was added to a dried and N<sub>2</sub>-flushed 10 mm NMR tube. The NMR tube was cooled to -78 °C and 1.0 mL of Me<sub>2</sub>O and 0.32 mL of 1.54 M *n*-Bu $^6\text{Li}$ <sup>[16c]</sup> in pentane (0.49 mmol, 0.95 equiv) were added. The sample was stored at -78 °C for 22 h while the aryllithium reagent crystallized. The supernatant was removed by cannula transfer, and the crystals were washed with Et<sub>2</sub>O (2 x 0.5 mL). The aryllithium crystals were dissolved in 1.8 mL of THF and 1.2 mL of Et<sub>2</sub>O to give a clear, colorless 0.10 M solution of [ $^6\text{Li}$ ,  $^{15}\text{N}$ ]2. The variable temperature experiment was monitored by  $^6\text{Li}$  NMR spectroscopy with spectra acquired at the following probe temperatures: -137, -132, -128, -124, -122, -119, -115, -110, -107, -103, and -87 °C. Spectra are shown in Fig. 4 and Fig S-3b. The  $^6\text{Li}$  NMR spectra were simulated using the exchange matrix shown in Fig. S-2.<sup>[1k]</sup> This simulation has the usual problem of  $^6\text{Li}$  simulations in that there is no realistic way to estimate line width in the absence of exchange, since there are no other peaks in the spectra. Rate data is shown in Fig. 5. A similar experiment on a sample with  $^{15}\text{N}$  at natural abundance is shown in Fig. S-3a.

After the variable temperature experiment was completed, a TMEDA titration was performed on the sample (spectra are shown in Fig. 6).

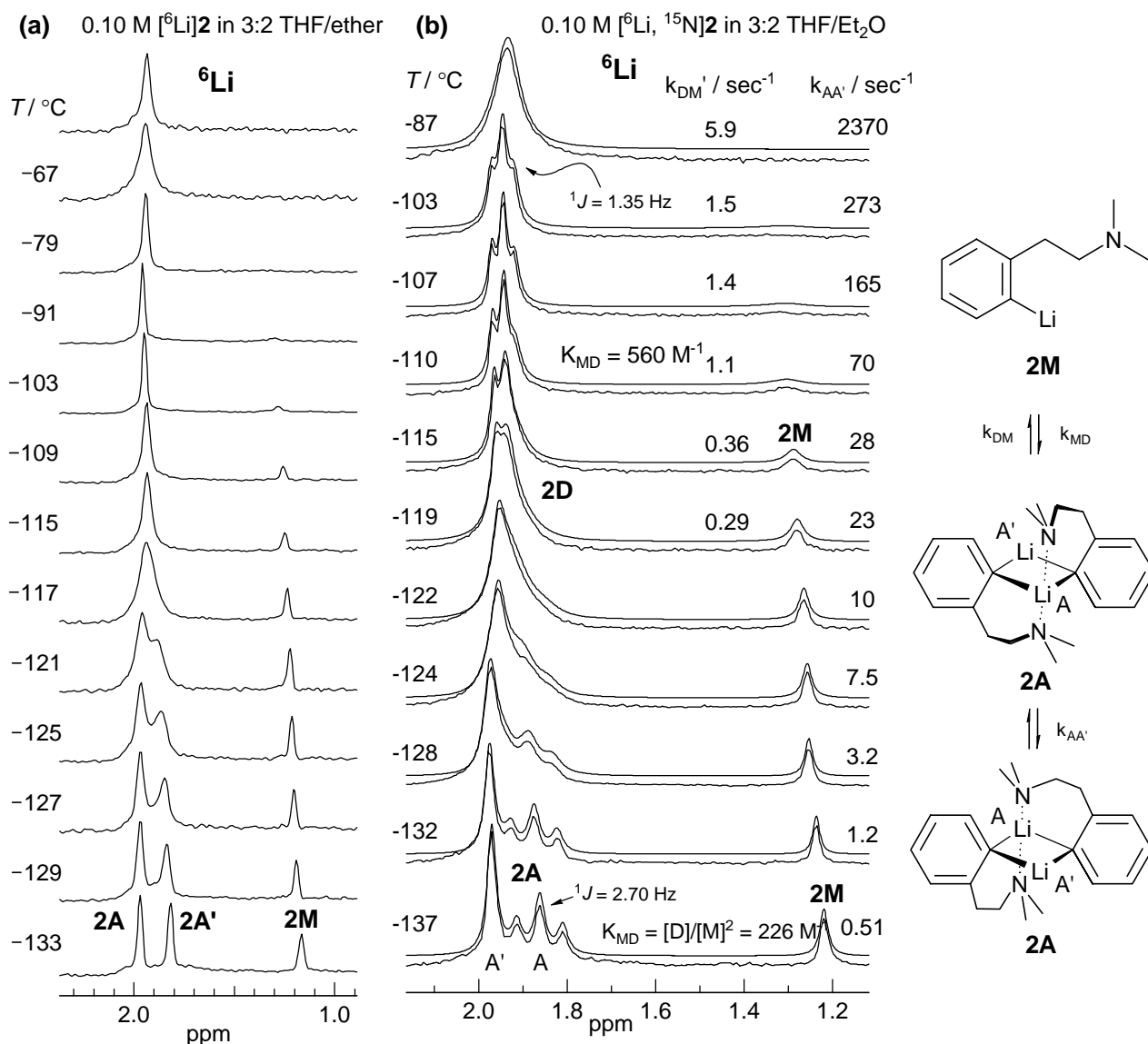


(b)

	A			A'			M
	1	2	3	4	5	6	7
1	$i2\pi(\Delta v_A)$	0	0	$k_{AA'}$	0	0	$k_{DM}$
2	$-1/T - k_{AA'} - k_{DM}$	$i2\pi(\Delta v_A)$	0	0	$k_{AA'}$	0	$k_{DM}$
3	0	$-1/T - k_{AA'} - k_{DM}$	$i2\pi(\Delta v_A)$	0	0	$k_{AA'}$	$k_{DM}$
4	$k_{AA'}$	0	0	$i2\pi(\Delta v_{A'} + J)$	0	0	$k_{DM}$
5	0	$k_{AA'}$	0	0	$-1/T - k_{AA'} - k_{DM}$	0	$k_{DM}$
6	0	0	$k_{AA'}$	0	0	$i2\pi(\Delta v_{A'} - J)$	$k_{DM}$
7	$k_{MD}/8$	$k_{MD}/4$	$k_{MD}/8$	$k_{MD}/8$	$k_{MD}/4$	$k_{MD}/8$	$i2\pi(\Delta v_M)$
							$-1/T - k_{MD}$

= E

**Figure S-2.** (a) Exchange processes in **2**. (b) Exchange matrix used to simulate the variable temperature NMR experiment on [ $^6\text{Li}$ ,  $^{15}\text{N}$ ]**2**.



**Figure S-3.**  $^6\text{Li}$  NMR spectra of a variable temperature experiment of 0.10 M **2** in 3:2 THF/Et<sub>2</sub>O. (a)  $[^6\text{Li}]_2$ . (b)  $[^6\text{Li}, ^{15}\text{N}]_2$ . The upper trace of each pair is a simulated spectrum using the rate constants shown and the exchange matrix of Fig. S-2.

**Estimation of Fractions of Chelated and Unchelated Forms of 2 (Scheme 3).** Scheme 3 presents a scenario for the effect of chelation on the monomer-dimer equilibrium. The estimates for the fractions of the two species in brackets that are not observable were made as follows.

*Dimer:* The presence of mono-chelated dimers in fast intramolecular exchange would only result in a diminution of the Li-N coupling. The coupling is not reduced by much, since, at 2.70 Hz, it is similar to those found for **1** and its analogs (2.5-2.8 Hz).<sup>[1h]</sup> The bis-unchelated form, if present, must be in slow exchange, otherwise only one Li signal would have been observed. There are no signals in the  $^6\text{Li}$  NMR spectra greater than about 4% of the intensity of the A-dimer, so this provides our best estimate of the maximum fraction of unchelated dimers in slow exchange,  $K_{\text{chel}}$  ( $[\text{chelated dimer}]/[\text{unchelated dimer}] \geq 25$ ).

*Monomer:* There are two limiting possibilities. If the chelated and unchelated forms of the monomer are in rapid equilibrium on the NMR time scale, the maximum size of the coupling ( $J < 0.3 \text{ Hz}$ , determined by line-shape simulation) means that less than 11% of the monomer can be chelated, assuming that the coupling was at least as large as in the dimer (2.7 Hz). Since chelation/dechelation in the dimer is in slow

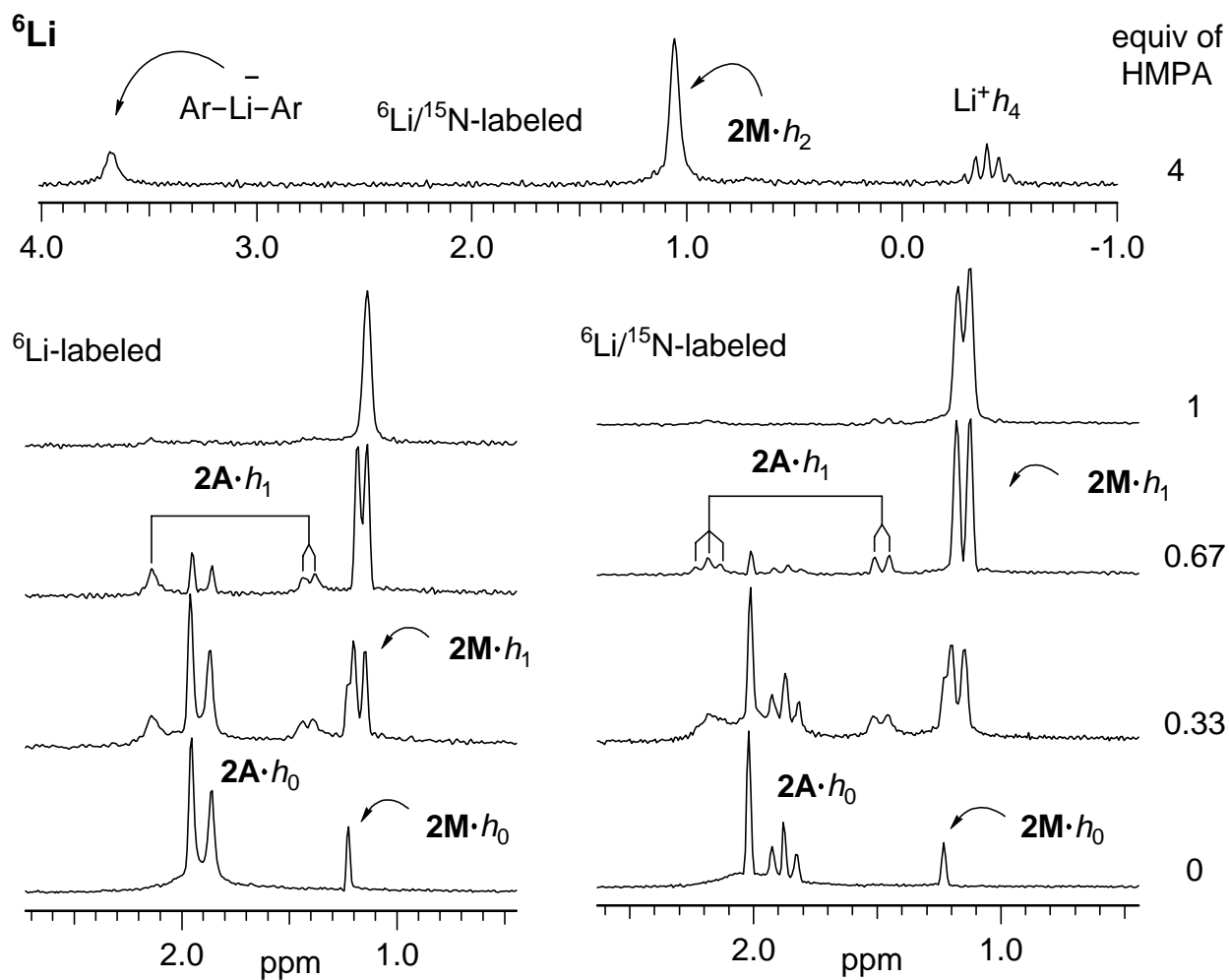
exchange on the NMR time scale, a more likely scenario is that the chelated and unchelated forms of the monomer are also slow exchange. In this case the absence of other signals attributable to the chelated monomer (a doublet) would be the deciding factor. If such a signal is not obscured by other signals, we estimate that <15% of the monomer is chelated by this criterion. Thus for the monomer  $K_{\text{eq}}$  (chelated/unchelated) = 0.18 and the dimer has >140 times propensity to chelate as does the monomer.

**Variable Temperature experiment on [<sup>6</sup>Li, <sup>15</sup>N]2 with 2 equiv of TMEDA.** A 0.13 M sample of [<sup>6</sup>Li, <sup>15</sup>N]2 in 1.5 mL of THF, 0.5 mL of Et<sub>2</sub>O, and 1.0 mL of Me<sub>2</sub>O was prepared from [<sup>15</sup>N]N,N-dimethyl-2-(2-trimethylstannylphenyl)ethylamine (0.137 g, 0.436 mmol) and 0.59 mL of 0.79 M *n*-Bu<sup>6</sup>Li in hexanes (0.47 mmol, 1.06 equiv) using the general procedure for crystallization from Me<sub>2</sub>O (clear, colorless solution). TMEDA (126 μL, 2 equiv) was added, and a series of <sup>6</sup>Li NMR spectra were acquired at -153, -150, -147, -140, and -134 °C to decoalesce the signal for the TMEDA-complexed monomer and the monomer. Spectra are shown in Fig. 6.

**PMDTA Titration of [<sup>6</sup>Li, <sup>15</sup>N]2.** A 0.13 M solution of [<sup>6</sup>Li, <sup>15</sup>N]2 prepared as for the TMEDA experiment above was used for a PMDTA titration experiment monitored by <sup>13</sup>C and <sup>6</sup>Li NMR spectroscopy. The <sup>13</sup>C NMR spectra were acquired at 0 and 1 equiv of PMDTA. The <sup>6</sup>Li NMR spectra were acquired at 0, 0.17, 0.33, 0.5, 0.67, 0.83, and 1 equiv of PMDTA. The probe temperature was -145 °C during the experiment. Spectra are shown in Fig. 7.

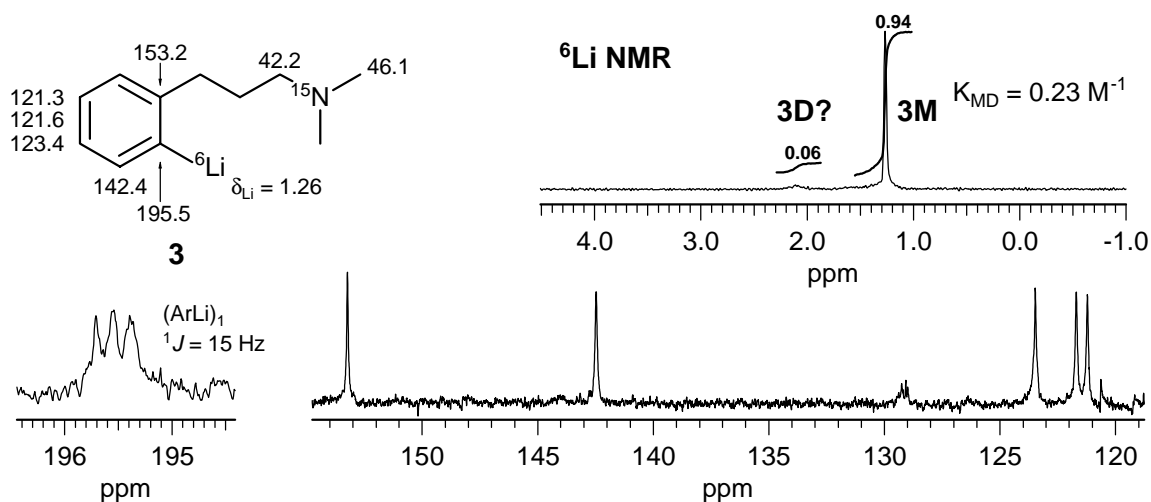
**HMPA Titration of [<sup>6</sup>Li, <sup>15</sup>N]2.** A sample like the one above (0.15 M) was used for an HMPA titration monitored by <sup>6</sup>Li and <sup>31</sup>P NMR spectroscopy. The NMR spectra were acquired at 0, 0.17, 0.33, 0.5, 0.673, 1, 2, 3, and 4 equiv of HMPA (1 equiv = 76 μL). The probe temperature ranged from -140 to -150 °C during the experiment. Selected spectra are shown in Fig. S-4. Samples of 2 containing HMPA were not stable to storage at -78 °C. After a few hours decomposition occurred to form lithium dimethylamide and, presumably, styrene (which was not detected).

*Interpretation of HMPA titration of 2.* Both the A-dimer 2A and the monomer 2M complex on HMPA at fractional equivalents, but by one equiv only the mono-HMPA complex of the monomer can be seen. This structure is not chelated, since only the doublet splitting ( $J_{\text{Li-P}} = 3.1$  Hz) from coupling to <sup>31</sup>P is seen. Past one equiv of HMPA the ArLi·(HMPA)<sub>2</sub> complex appears to be formed (Li-P coupling not resolved), as well as some of the triple ion Ar<sub>2</sub>Li<sup>-</sup> Li<sup>+</sup>(HMPA)<sub>4</sub> (top spectrum in Fig. S-4). No clear Li-N or Li-P coupling was detected for the central Li, but the signal was quite broad, and resolution enhancement sometimes gave triplet-like peak shapes, so it is probable that the triple ion is chelated, as demonstrated for 6-methoxy-2-dimethylaminomethylphenyllithium.<sup>[1h]</sup>



**Figure S-4.**  ${}^6\text{Li}$  NMR spectra of an HMPA titration of **2**. Left panel: 0.13 M  $[{}^6\text{Li}]\mathbf{2}$  in 3:2 THF/Et<sub>2</sub>O at -133 to -139 °C. Top spectrum and right panel: 0.15 M  $[{}^6\text{Li}, {}^{15}\text{N}]\mathbf{2}$  in 3:2:1 THF/Me<sub>2</sub>O/Et<sub>2</sub>O at -140 to -150 °C ( $h$  = HMPA).

## NMR Experiments Conducted on 2-(3-Dimethylaminopropyl)phenyllithium (3)



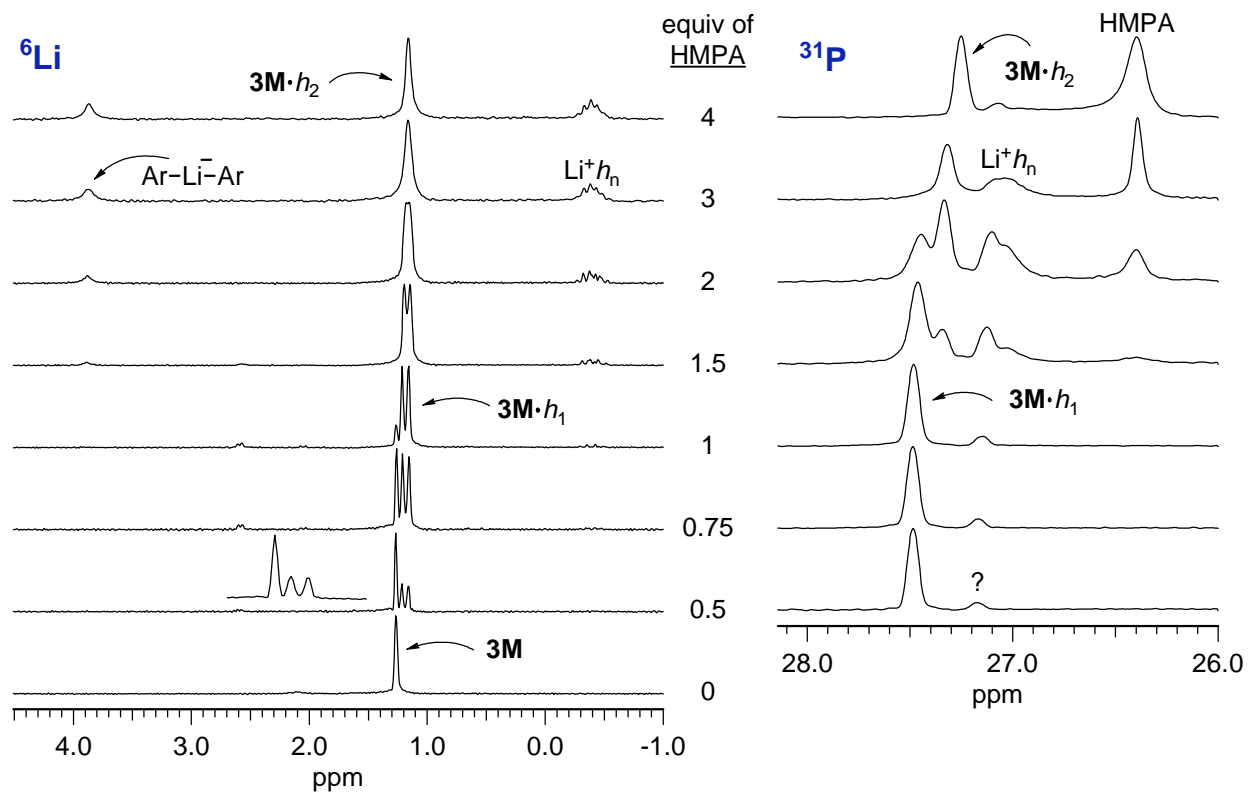
**Figure S-5.**  $^{13}\text{C}$  and  $^6\text{Li}$  NMR spectra of 0.15 M  $[^6\text{Li}, ^{15}\text{N}]\mathbf{3}$  in 3:2 THF/Et<sub>2</sub>O at  $-127\text{ }^\circ\text{C}$ .

**TMEDA Titration of  $[^6\text{Li}, ^{15}\text{N}]\mathbf{3}$ .**  $[^{15}\text{N}]\text{N,N}$ -Dimethyl-3-(2-trimethylstannylphenyl)propylamine- (0.166 g, 0.509 mmol), 1.5 mL of THF and 0.5 mL of Et<sub>2</sub>O were added to a dried and N<sub>2</sub>-flushed 10 mm NMR tube. The NMR tube was cooled to  $-78\text{ }^\circ\text{C}$  and 0.64 mL of 0.79 M *n*-Bu<sup>6</sup>Li in hexanes (0.51 mmol, 1.00 equiv) was added to give a yellow solution. Addition of 1.0 mL of Me<sub>2</sub>O gave an initial aryllithium concentration of 0.14 M. The sample was stored overnight at  $-78\text{ }^\circ\text{C}$  to insure complete the lithium-tin exchange before beginning the NMR experiment. The TMEDA titration experiment was monitored by  $^6\text{Li}$  NMR spectroscopy. The NMR spectra were acquired at 0, 1, 2, 4 and 6 equiv of TMEDA (1 equiv = 76  $\mu\text{L}$ ) at probe temperatures between  $-140$  to  $-145\text{ }^\circ\text{C}$ . After the experiment was completed, the sample was quenched with 100  $\mu\text{L}$  of Me<sub>3</sub>SiCl (0.788 mmol, 1.55 equiv) to give a 93 % yield of  $[^{15}\text{N}]\text{N,N}$ -dimethyl-3-(2-trimethylsilylphenyl)propylamine- by  $^1\text{H}$  NMR integration against pentachloroethane (30.0  $\mu\text{L}$ , 0.249 mmol, 0.490 equiv) as a standard.

**PMDTA Titration of  $[^6\text{Li}, ^{15}\text{N}]\mathbf{3}$ .**  $[^{15}\text{N}]\text{N,N}$ -Dimethyl-3-(2-trimethylstannylphenyl)propylamine (0.163 g, 0.498 mmol), 1.8 mL of THF and 1.2 mL of Et<sub>2</sub>O were added to a dried and N<sub>2</sub>-flushed 10 mm NMR tube. The NMR tube was cooled to  $-78\text{ }^\circ\text{C}$  and 0.63 mL of 0.79 M *n*-Bu<sup>6</sup>Li in hexanes (0.50 mmol, 1.00 equiv) was added to give a yellow solution with an initial aryllithium concentration of 0.14 M. The sample was stored for 30 min at  $-20\text{ }^\circ\text{C}$  to complete the lithium-tin exchange. The PMDTA titration experiment was monitored by  $^6\text{Li}$  NMR spectroscopy. The NMR spectra were acquired at 0, 0.25, 0.5, 0.75 and 1 equiv of PMDTA (1 equiv = 104  $\mu\text{L}$ ). The probe temperature was  $-127\text{ }^\circ\text{C}$  during the experiment. The spectra are shown in Fig. 8. After the experiment was completed, the sample was quenched with 100  $\mu\text{L}$  of Me<sub>3</sub>SiCl (0.788 mmol, 1.58 equiv) to give a 93 % yield of  $[^{15}\text{N}]\text{N,N}$ -dimethyl-3-(2-trimethylsilylphenyl)propylamine by  $^1\text{H}$  NMR integration against pentachloroethane (30.0  $\mu\text{L}$ , 0.249 mmol, 0.500 equiv) as a standard.

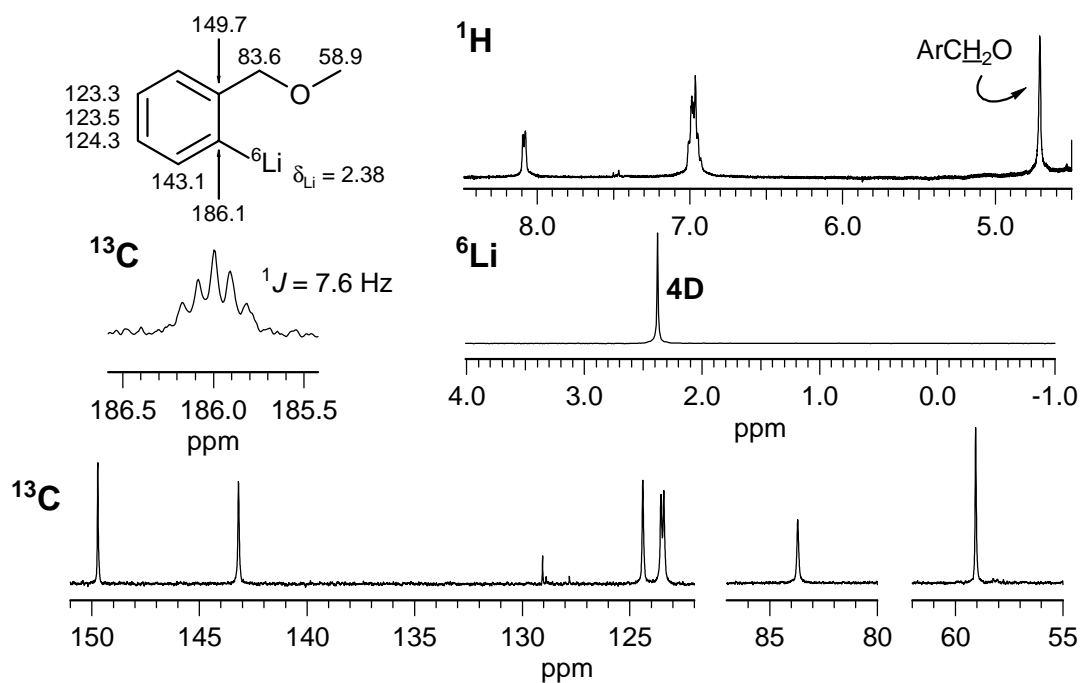
**HMPA Titration of  $[^6\text{Li}, ^{15}\text{N}]\mathbf{3}$ .** A sample of  $[^6\text{Li}, ^{15}\text{N}]\mathbf{3}$  in 1.8 mL of THF and 1.2 mL of Et<sub>2</sub>O was prepared from  $[^{15}\text{N}]\text{N,N}$ -dimethyl-3-(2-trimethylstannylphenyl)propylamine (0.168 g, 0.513 mmol) and 0.65 mL of 0.79 M *n*-Bu<sup>6</sup>Li in hexanes (0.513 mmol, 1.00 equiv) using the general procedure for crystallization from Me<sub>2</sub>O (0.15 M solution).  $^6\text{Li}$  and  $^{31}\text{P}$  NMR spectra were acquired at 0, 0.25, 0.5, 0.75, 1, 1.5, 2, 3, and 4 equiv of HMPA (1 equiv = 80  $\mu\text{L}$ ). The probe temperature ranged from  $-127$  to  $-137\text{ }^\circ\text{C}$ . Spectra are shown in Fig. S-6. After the experiment was completed, the sample was quenched with 100  $\mu\text{L}$  of Me<sub>3</sub>SiCl

(0.788 mmol, 1.53 equiv) to give 91 % of  $[^{15}\text{N}]N,N$ -dimethyl-3-(2-trimethylsilylphenyl)propylamine by  $^1\text{H}$  NMR integration against pentachloroethane (30.0  $\mu\text{L}$ , 0.249 mmol, 0.485 equiv) as a standard.



**Figure S-6.**  $^6\text{Li}$  and  $^{31}\text{P}$  NMR spectra of an HMPA titration experiment of 0.15 M  $[^{15}\text{N}, ^6\text{Li}]\mathbf{3}$  in 3:2 THF/Et<sub>2</sub>O at -127 to -137 °C ( $h = \text{HMPA}$ ).

## NMR Experiments Conducted on 2-(Methoxymethyl)phenyllithium (**4**)

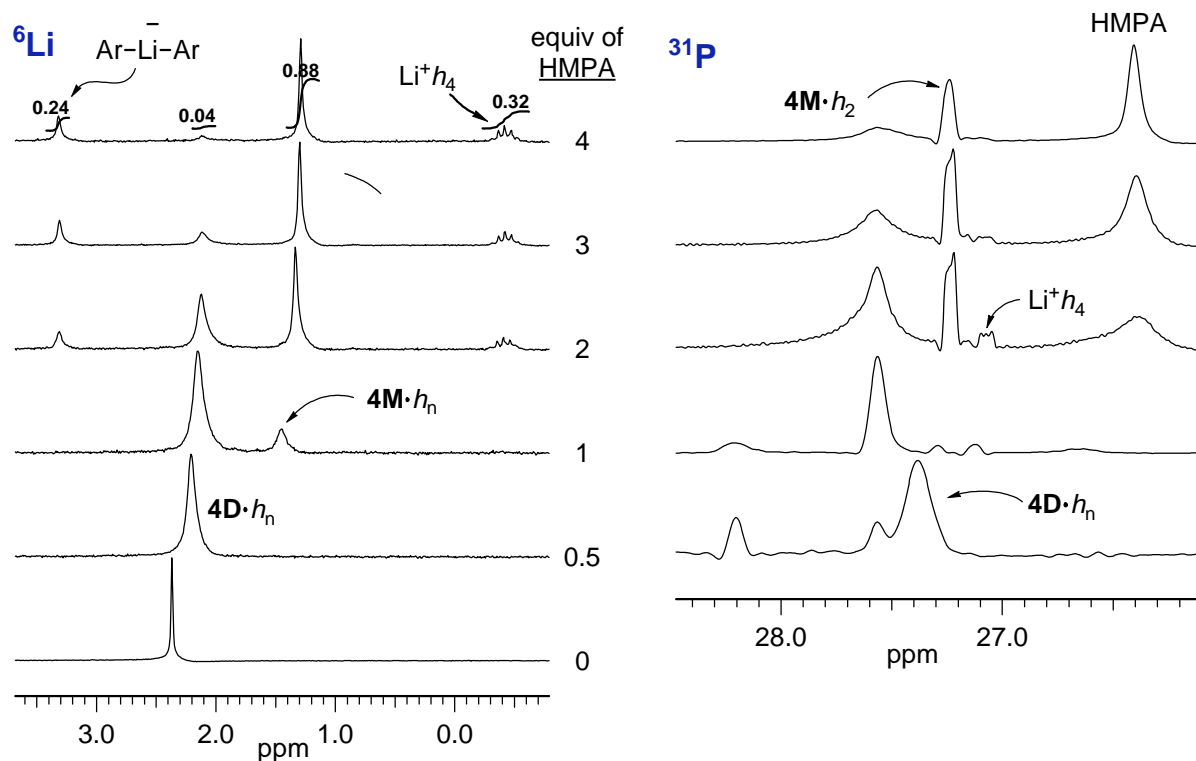


**Figure S-7.**  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^6\text{Li}$  NMR spectra of a 0.15 M solution of  $[\text{}^6\text{Li}]\mathbf{4}$  at  $-127\text{ }^\circ\text{C}$  in 3:2:1  $\text{Me}_2\text{O}/\text{THF}/\text{Et}_2\text{O}$ .

**Variable-Temperature  $^1\text{H}$  and  $^{13}\text{C}$  NMR Experiments on  $[\text{}^6\text{Li}]\mathbf{4}$ .** A sample of  $[\text{}^6\text{Li}]\mathbf{4}$  in 1.0 mL of THF, 0.5 mL of  $\text{Et}_2\text{O}$ , and 1.5 mL of  $\text{Me}_2\text{O}$  was prepared from 2-trimethylstannylbenzyl methyl ether (0.290 g, 1.02 mmol) and 0.68 mL of 1.54 M *n*-Bu $^6\text{Li}$  in hexanes (1.05 mmol, 1.03 equiv) using the general procedure for crystallization from  $\text{Me}_2\text{O}$  (0.15 M solution).  $^1\text{H}$  spectra were acquired at  $-140$ ,  $-126$  and  $-75\text{ }^\circ\text{C}$ , and  $^{13}\text{C}$  NMR at:  $-127$ ,  $-116$ ,  $-110$ ,  $-106$ ,  $-104$ ,  $-98$ ,  $-88$ ,  $-81$ ,  $-64$  and  $-52\text{ }^\circ\text{C}$ . Selected spectra and rate data are reported in Fig. 9.

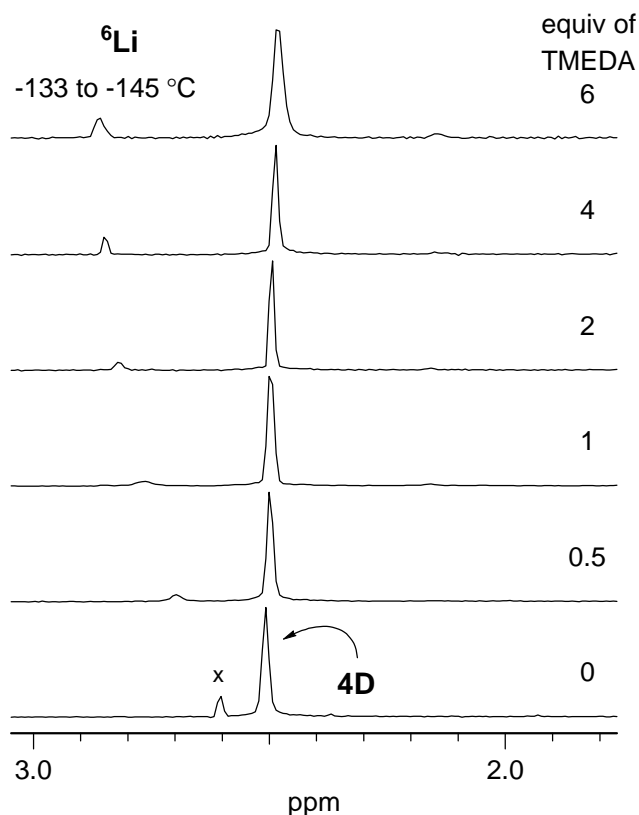
**HMPA Titration of  $[\text{}^6\text{Li}]\mathbf{4}$ .** A sample of  $[\text{}^6\text{Li}]\mathbf{4}$  in 2.1 mL of THF and 1.4 mL of  $\text{Et}_2\text{O}$  was prepared from 2-trimethylstannylbenzyl methyl ether (0.290 g, 1.02 mmol) and 0.68 mL of 1.54 M *n*-Bu $^6\text{Li}$  in hexanes (1.05 mmol, 1.03 equiv) using the general procedure for crystallization from  $\text{Me}_2\text{O}$  (0.15 M solution).  $^6\text{Li}$  and  $^{31}\text{P}$  NMR spectra were acquired at 0, 0.5, 1, 2, 3 and 4 equiv of HMPA (1 equiv = 88  $\mu\text{L}$ ). The probe temperature ranged from  $-133$  to  $-140\text{ }^\circ\text{C}$ . Spectra are shown in Fig. S-8.

**Interpretation of HMPA Titration of **4**.** In contrast to all other lithium reagents studied, no Li-P couplings could be detected for either the dimer or monomer HMPA complexes of **4** even at  $-140\text{ }^\circ\text{C}$ , so assignment of the NMR spectra cannot be done unambiguously. Up to one equiv of HMPA mono- and bis-HMPA complexes of the dimer appear to be formed. At higher equivalents monomer HMPA complexes predominate, but there is a significant fraction of triple ion formed (38%) at 4 equiv of HMPA.



**Figure S-8.**  $^6\text{Li}$  and  $^{31}\text{P}$  NMR spectra of an HMPA titration of  $[\text{}^6\text{Li}]\mathbf{4}$  in 3:2 THF/Et<sub>2</sub>O at -133 to -140 °C. Firm assignment could not be made for most of the signals because of the absence of detectable Li-P coupling ( $h$  = HMPA).

**TMEDA Titration of  $[\text{}^6\text{Li}]\mathbf{4}$ .** 2-Trimethylstannylbenzyl methyl ether (0.169 g, 0.593 mmol), 1.5 mL of THF and 0.5 mL of Et<sub>2</sub>O were added to a dried and N<sub>2</sub>-flushed 10 mm NMR tube. The NMR tube was cooled to -78 °C and 0.75 mL of 0.79 M *n*-Bu $^6\text{Li}$  in hexanes (0.59 mmol, 0.99 equiv) was added to give a yellow solution. Addition of 1.0 mL of Me<sub>2</sub>O gave an initial aryllithium concentration of 0.16 M.  $^{13}\text{C}$  NMR spectra were acquired at 0 and 6 equiv of TMEDA,  $^6\text{Li}$  NMR spectra at 0, 0.5, 1, 2, 4 and 6 equiv of TMEDA (1 equiv = 89  $\mu\text{L}$ ). The probe temperature ranged from -133 to -145 °C. Spectra are reported in Fig. S-9. After the experiment was completed, the sample was quenched with 100  $\mu\text{L}$  of Me<sub>3</sub>SiCl (0.788 mmol, 1.33 equiv) to give a 96 % yield of 2-trimethylsilylbenzyl methyl ether by  $^1\text{H}$  NMR integration against pentachloroethane (15.0  $\mu\text{L}$ , 0.125 mmol, 0.211 equiv) as a standard.



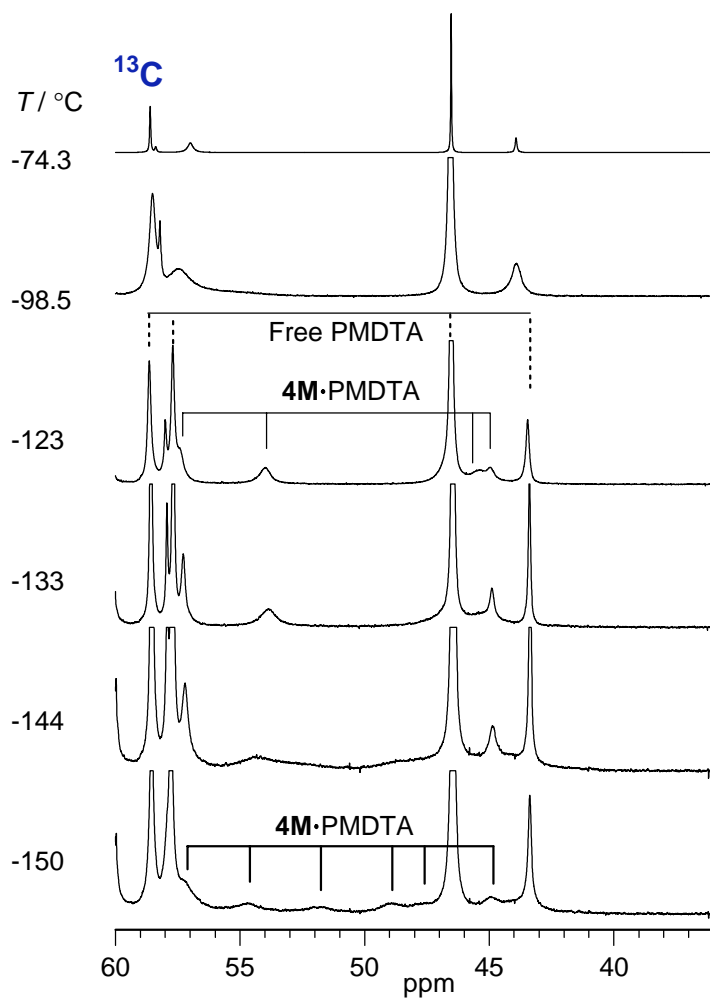
**Figure S-9.**  ${}^6\text{Li}$  NMR spectra of a TMEDA titration of 0.16 M  $[\text{}^6\text{Li}]\mathbf{4}$  in 3:2:1 THF/ $\text{Me}_2\text{O}$ / $\text{Et}_2\text{O}$  at -133 to -145  $^\circ\text{C}$ .

**Spectra of  $[\text{}^6\text{Li}]\mathbf{4}$  with PMDTA Cosolvent. Titration.** A sample of  $[\text{}^6\text{Li}]\mathbf{4}$  in 1.5 mL of THF, 0.5 mL of  $\text{Et}_2\text{O}$  and 1.0 mL of  $\text{Me}_2\text{O}$  was prepared from 2-trimethylstannylbenzyl methyl ether (0.144 g, 0.507 mmol) and 0.64 mL of 0.79 M  $n\text{-Bu}^6\text{Li}$  in hexanes (0.51 mmol, 1.01 equiv) using the general procedure for crystallization from  $\text{Me}_2\text{O}$  (0.14 M solution).  ${}^{13}\text{C}$  NMR spectra were acquired at 0 and 1.52 equiv of PMDTA,  ${}^6\text{Li}$  NMR spectra at 0, 0.25, 0.5, 0.75, 1, 1.25 and 1.5 equiv of PMDTA (1 equiv = 106  $\mu\text{L}$ ). The probe temperature ranged from -137 to -150  $^\circ\text{C}$ .  ${}^6\text{Li}$  NMR spectra are reported in Fig. 8. After the experiment was completed, the sample was quenched with 100  $\mu\text{L}$  of  $\text{Me}_3\text{SiCl}$  (0.788 mmol, 1.56 equiv) to give a 87 % yield of 2-trimethylsilylbenzyl methyl ether by  ${}^1\text{H}$  NMR integration against pentachloroethane (15.0  $\mu\text{L}$ , 0.125 mmol, 0.246 equiv) as a standard.

**Titration and Variable Temperature Study in 2:1  $\text{Me}_2\text{O}/\text{Et}_2\text{O}$ .**  $\text{Et}^6\text{Li}^{[22\text{f}]}$  (35.0 mg, 1.0 mmol) was weighed into a 10 mm NMR in a  $\text{N}_2$  filled dry box. The tube was sealed with a septum, removed from the box, cooled to -78  $^\circ\text{C}$  and  $\text{Et}_2\text{O}$  (2.0 mL) and 2-trimethylstannylbenzyl methyl ether (217  $\mu\text{L}$ , 1.0 mmol) were added. Addition of  $\text{Me}_2\text{O}$  (1.0 mL) gave an initial aryllithium concentration of 0.33 M.  ${}^6\text{Li}$  and  ${}^{13}\text{C}$  NMR spectra were acquired at 0, 0.25, 0.5, 0.75, 1, 1.5 and 2.5 equiv of PMDTA at a probe temperature of -135  $^\circ\text{C}$ . Spectra are shown in Fig. 10a. At 0.75 equiv of PMDTA a variable temperature  ${}^6\text{Li}$  NMR study was performed, with spectra acquired at -151, -148, -145, -142, -139, -136, -133, -128, -125, -122, -119, -116 and -111  $^\circ\text{C}$ . Selected spectra are shown in Fig. 10b.

**Variable Temperature  ${}^6\text{Li}$  NMR Study in 3:2:1 THF/ $\text{Me}_2\text{O}/\text{Et}_2\text{O}$ .** A solution of  $[\text{}^6\text{Li}]\mathbf{4}$  was prepared in a  $\text{N}_2$  filled dry box by addition of  $\text{Et}^6\text{Li}$  (37.0 mg, 1.06 mmol) to a solution of 2-trimethylstannylbenzyl methyl ether (230  $\mu\text{L}$ , 1.06 mmol) in  $\text{Et}_2\text{O}$  (0.5 mL) at -78  $^\circ\text{C}$  in a 10 mm NMR tube. The tube was sealed with a septum, removed from the box, and warmed briefly to dissolve the  $\text{Et}^6\text{Li}$ . Addition of THF (1.0 mL),  $\text{Me}_2\text{O}$  (1.5 mL) and 5  $\mu\text{L}$  of  $(\text{Me}_3\text{Si})_3\text{CH}^{[1\text{j}]}$  gave an initial aryllithium concentration of 0.33 M. An initial  ${}^{13}\text{C}$

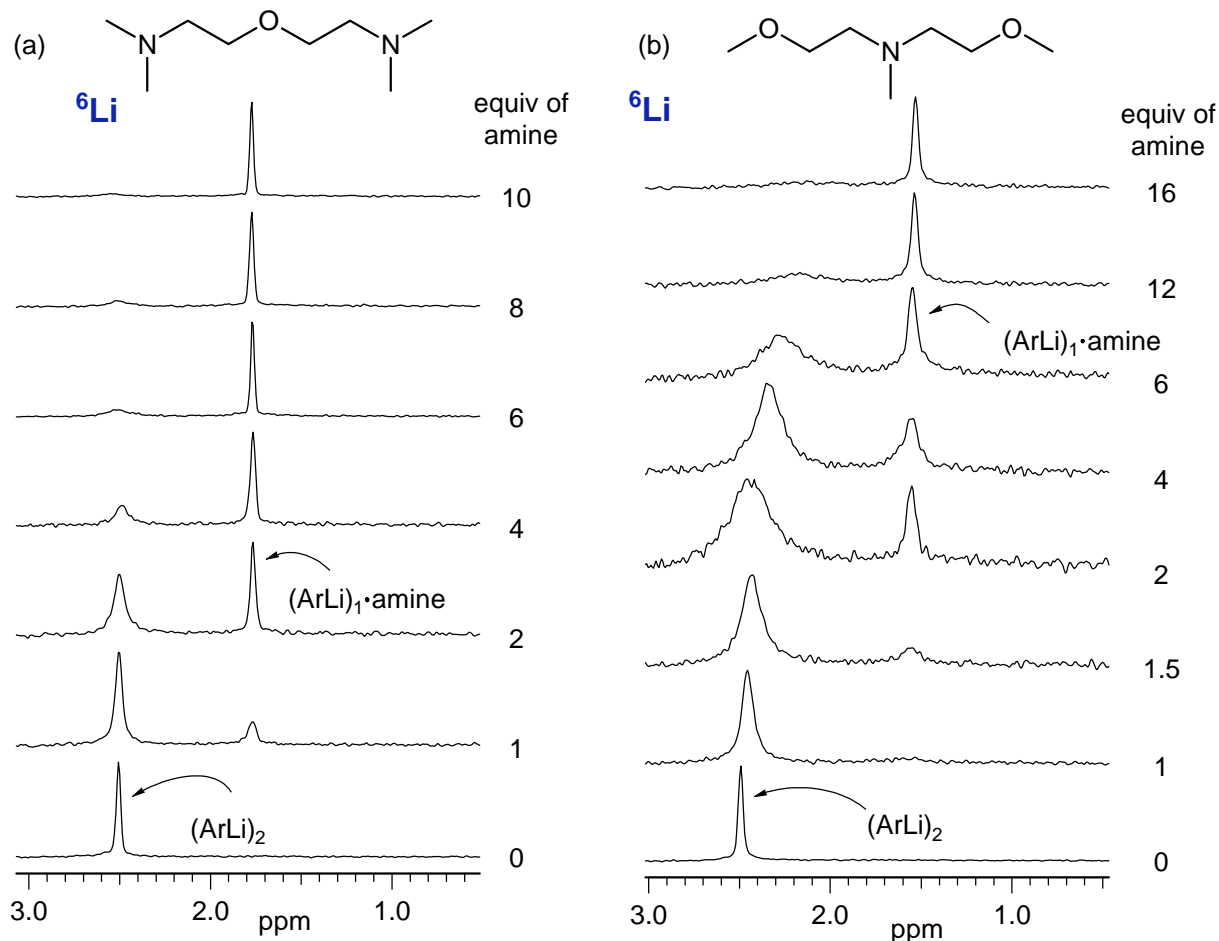
NMR spectrum was acquired and PMDTA (630  $\mu$ L, 3.0 mmol, 3 equiv) was added. The variable temperature experiment was monitored by  $^{13}\text{C}$  NMR spectroscopy with spectra acquired at -150, -144, -133, -123, -99, and -74  $^{\circ}\text{C}$ . Spectra shown in Fig. S-10 and Fig. 11. Activation parameters are shown in Table S-2.



**Figure S-10.** Variable temperature  $^{13}\text{C}$  NMR study of 0.33 M  $[\text{}^6\text{Li}]\mathbf{4}$  containing 3.0 equiv of PMDTA in 3:2:1 THF/Me<sub>2</sub>O/Et<sub>2</sub>O.

***N*-Methylbis-(2-methoxyethyl)amine Titration of [<sup>6</sup>Li]4.** A 0.05 M solution of [<sup>6</sup>Li]4 was prepared from 2-trimethylstannylbenzyl methyl ether (42 mg, 0.146 mmol), and 0.19 mL of 0.79 M *n*-Bu<sup>6</sup>Li. Increments of bis(2-dimethylaminoethyl)ether and methylbis(methoxyethyl)amine were added and <sup>6</sup>Li spectra acquired at -142 °C (Fig. S-11).

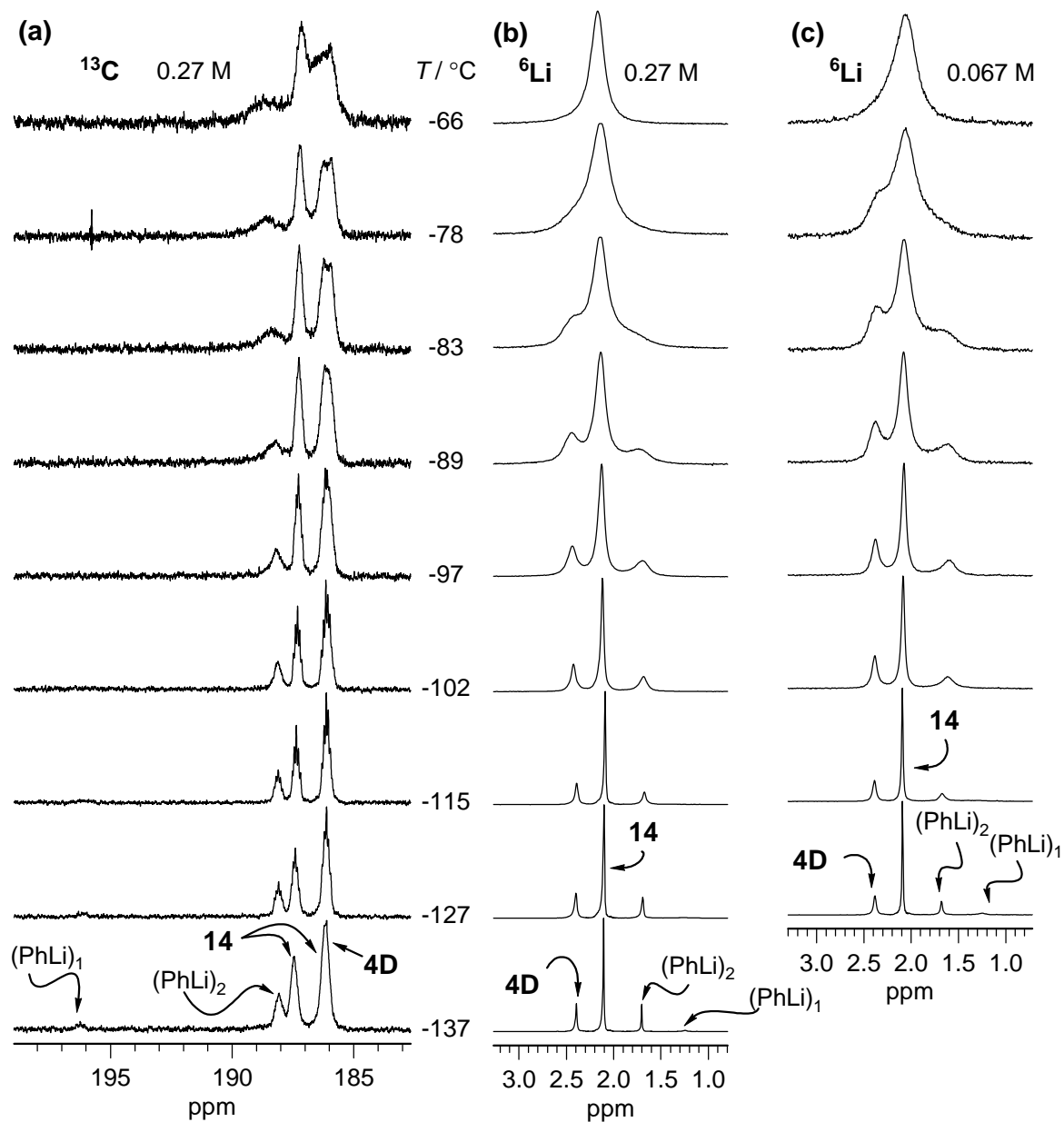
Both of the tridentate cosolvents break up the dimer of 4, but the complexation in each case is weaker than with PMDTA, with less than 20% conversion to monomer for the former and ca 2% conversion to monomer for the latter at 1 equiv of the cosolvent. In comparison, PMDTA converts >90% of 4 to the complexes 12 and 13 at 1 equiv of PMDTA. The only indication of dimeric complexes analogous to 12 was significant broadening of the dimer signal with methylbis(2-methoxyethyl)amine at -142 °C.



**Figure S-11.** <sup>6</sup>Li NMR spectra of the titration of 0.05 M [<sup>6</sup>Li]4 with: (a) bis(2-dimethylaminoethyl) ether in 3:2 THF/Et<sub>2</sub>O and (b) methylbis(2-methoxyethyl)amine in 3:2:1 THF/Me<sub>2</sub>O/Et<sub>2</sub>O at -142 to -147 °C.

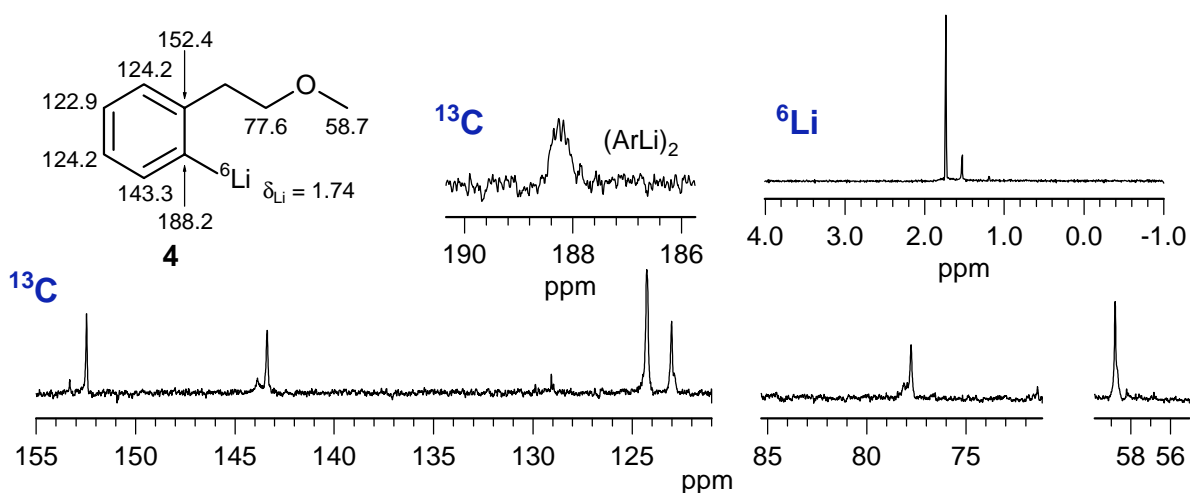
**Variable Temperature Study 4-PhLi mixtures.** Et<sup>6</sup>Li (56.0 mg, 1.6 mmol) was weighed into a 10 mm NMR tube in a N<sub>2</sub> filled dry box. The tube was sealed with a septum, removed from the box, cooled to -78 °C and Et<sub>2</sub>O (1.2 mL), PhSnMe<sub>3</sub> (146 μL, 0.80 mmol), 2-trimethylstannylbenzyl methyl ether (176 μL, 0.81 mmol) and 4 μL of (Me<sub>3</sub>Si)<sub>3</sub>CH<sup>[1j]</sup> were added. Addition of THF (1.8 mL) gave an initial aryllithium concentration of 0.27 M [<sup>6</sup>Li]4 and 0.27 M [<sup>6</sup>Li]PhLi. <sup>6</sup>Li and <sup>13</sup>C NMR were acquired at -137, -127, -115, -102, -97, -89, -83, -78 and -66 °C. A 3-spin line shape simulation of the spectra was done using WINDNMR.<sup>[1k]</sup> The spectra, DNMR line shape simulations and kinetic analysis are shown in Fig. 12 and Fig. S-12. The sample was diluted by a factor of 4 (1.0 mL of solution with 1.2 mL of Et<sub>2</sub>O and 1.8 mL of THF) and <sup>13</sup>C and <sup>6</sup>Li NMR spectra were acquired at -137, -127, -115, -102, -97, -89, -83, -78 and -66 °C.

Spectra are shown in Fig. S-12c.



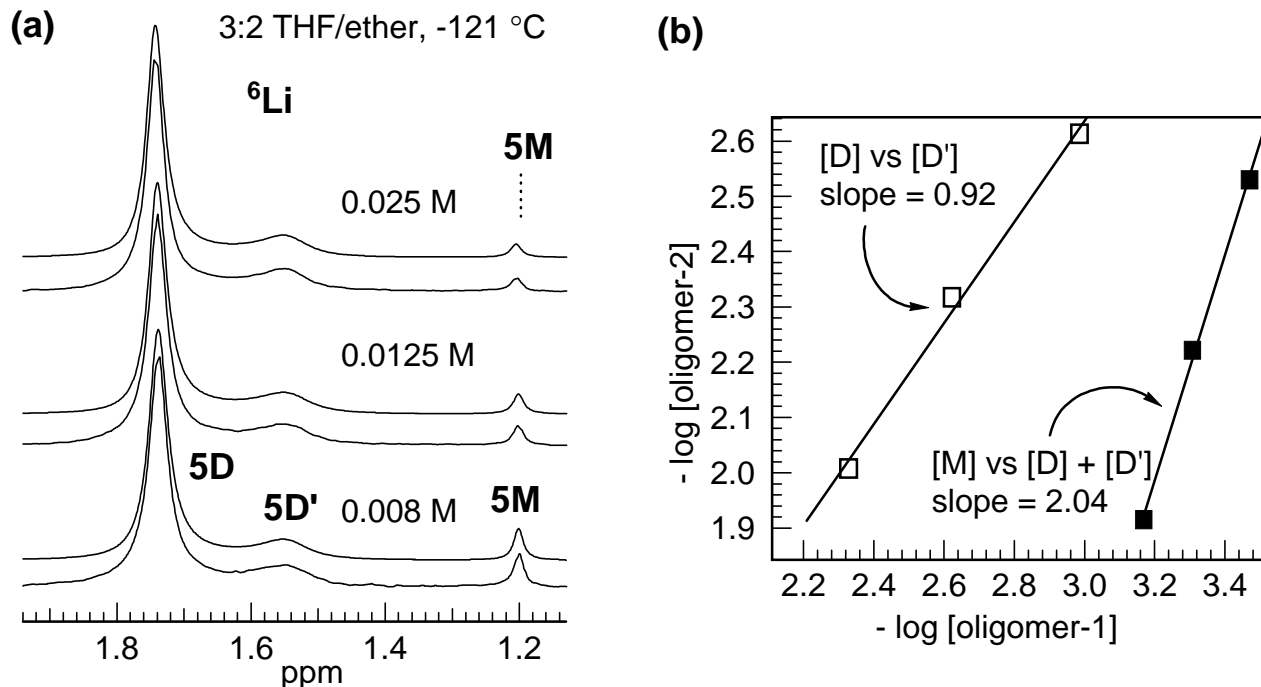
**Figure S-12.** Variable temperature NMR spectroscopic studies of 1:1 mixture of  $[\text{}^6\text{Li}]\mathbf{4}$  and  $[\text{}^6\text{Li}]\text{PhLi}$  in 3:2 THF/Et<sub>2</sub>O. (a) and (b)  $^{13}\text{C}$  and  $^6\text{Li}$  NMR spectra of a solution 0.27 M in each ArLi. (c)  $^6\text{Li}$  NMR spectra of a solution 0.07 M in each ArLi.

## NMR Experiments Conducted on 2-(2-Methoxyethyl)phenyllithium (**5**)



**Figure S-13.**  $^{13}\text{C}$  and  $^6\text{Li}$  NMR spectra of 0.08 M  $[\text{}^6\text{Li}] \mathbf{5}$  in 3:2 THF/Et<sub>2</sub>O solvent at -125 to -130 °C.

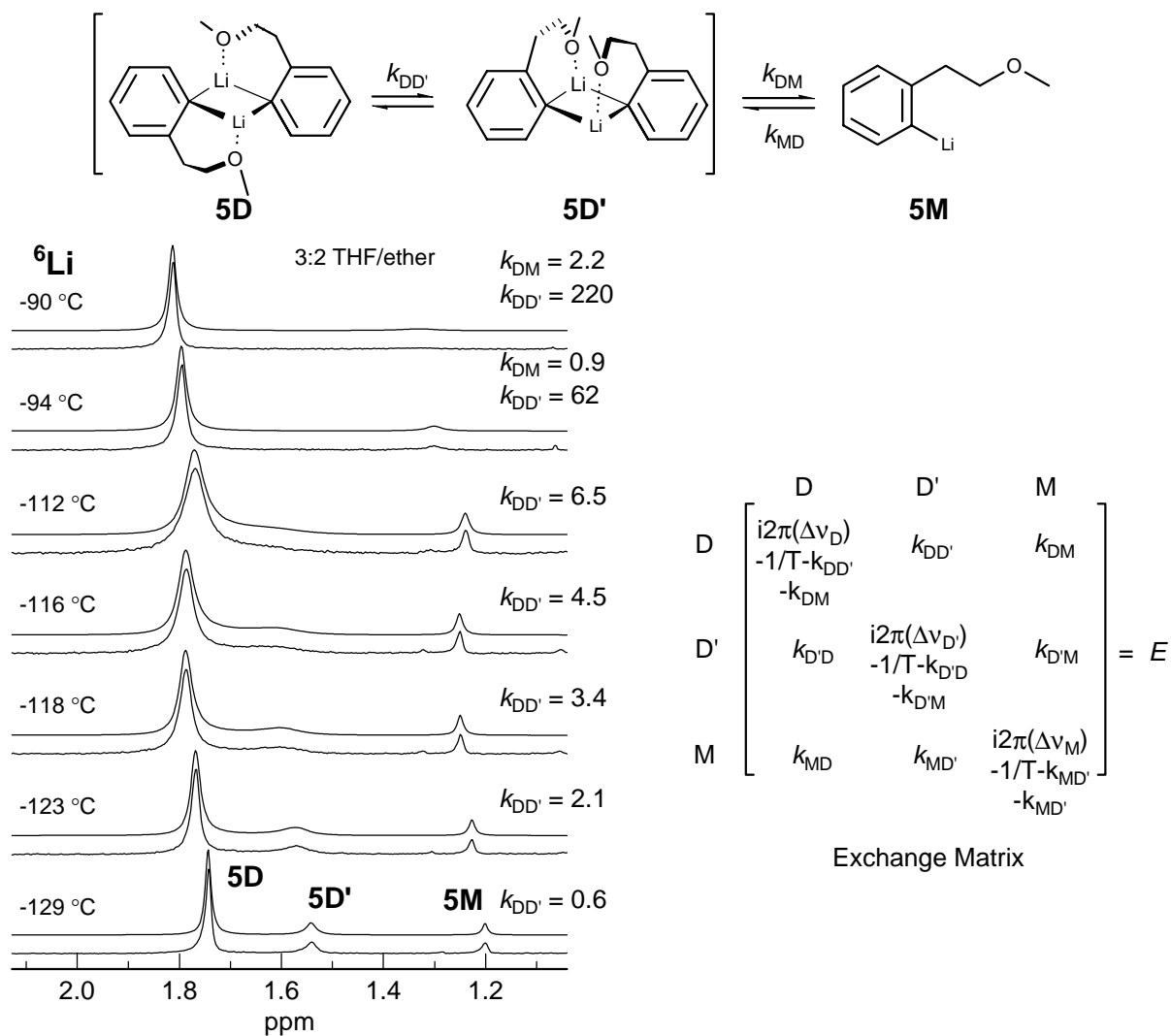
**Variable Concentration Experiment of  $[\text{}^6\text{Li}] \mathbf{5}$ .** A sample of 2-(2-trimethylstannylphenyl)ethyl methyl ether (164 mg, 0.55 mmol) in 1.2 mL of Et<sub>2</sub>O was cooled to -78 °C in a dry, N<sub>2</sub>-purged 10 mm NMR tube and 344  $\mu\text{L}$  of 1.60 M *n*-Bu<sup>6</sup>Li in pentane (0.55 mmol) was slowly added. Precipitation of a white solid occurred within minutes. The sample was stored overnight and the solvent removed by cannula. The solid was washed with 3 mL of Et<sub>2</sub>O and then dissolved in 1.8 mL of THF, 1.2 mL of Et<sub>2</sub>O and 2.5  $\mu\text{L}$  of (Me<sub>3</sub>Si)<sub>3</sub>CH.<sup>[1j]</sup>  $^{13}\text{C}$  and  $^6\text{Li}$  spectra were acquired at -121 °C. The sample was diluted (1:1) by addition of 1.8 mL of THF and 1.2 mL of Et<sub>2</sub>O at -78 °C and  $^{13}\text{C}$  and  $^6\text{Li}$  spectra were acquired at -121 °C. The final dilution (1:1) was accomplished by removing half of the solution via syringe and then adding 1.8 mL of THF and 1.2 mL of Et<sub>2</sub>O. Spectra and analysis are reported in Fig. S-14. The ratio of the two  $^6\text{Li}$  NMR peaks of the two dimers **5D** and **5D'** are concentration independent ( $D/D' = 4.19, 4.03, 4.73$ , top to bottom), whereas the ratio of **5M**/(**5D**+**5D'**) varied as expected for dimer and monomer (0.028, 0.041, 0.057). Our best value for  $K_{\text{MD}}$  is 11,000 M<sup>-1</sup> at -121 °C in 3:2 THF/Et<sub>2</sub>O.



**Figure S-14.** (a) Variable concentration experiment of  $[{}^6\text{Li}]\mathbf{5}$  in 3:2 THF/Et<sub>2</sub>O at -121 °C. The ratio of the two  ${}^6\text{Li}$  NMR peaks marked **5D** and **5D'** are concentration independent, whereas the ratio of **5M**/**(5D+5D')** varied as expected for dimer and monomer. The upper trace at each concentration is a DNMR 3-spin simulation used to integrate the spectra. (b) Log/log plot of the aggregates, showing that D and D' have the same molecularity, whereas M is a factor of two lower.

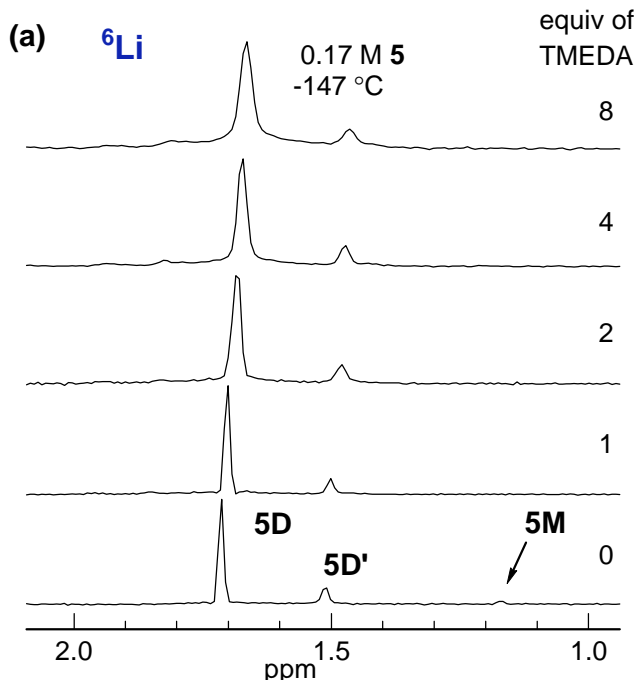
**Variable-Temperature  ${}^6\text{Li}$  NMR Experiment of  $[{}^6\text{Li}]\mathbf{5}$  in 3:2 THF/Et<sub>2</sub>O.** Et ${}^6\text{Li}$  (9.8 mg, 0.28 mmol) was weighed into a 10 mm NMR tube in a N<sub>2</sub> filled dry box. The tube was sealed with a septum and removed from the box. The tube was cooled to -78 °C and Et<sub>2</sub>O (2.0 mL), 2-(2-trimethylstannylphenyl)ethyl methyl ether (66  $\mu\text{L}$ , 0.28 mmol), and 5  $\mu\text{L}$  of (Me<sub>3</sub>Si)<sub>3</sub>CH<sup>[1j]</sup> were added. Addition of THF (3.0 mL) gave an initial aryllithium concentration of 0.056 M.  ${}^6\text{Li}$  and  ${}^{13}\text{C}$  NMR spectra were acquired at -123, -120, -114, -108, -101, -91, -84, -64 and -42 °C.

After this experiment 1.0 mL of the solution was diluted with Et<sub>2</sub>O (1.2 mL) and THF (1.8 mL) in a second dried and N<sub>2</sub>-flushed 10 mm NMR tube to give a clear, pale yellow 0.014 M solution (higher dilution was needed to observe the monomer signal). Results of the variable temperature experiment ( ${}^{13}\text{C}$  and  ${}^6\text{Li}$  NMR spectroscopy) as well as a 3-spin line shape simulation,<sup>[1k]</sup> the kinetic scheme and exchange matrix are shown in Fig. S-15, excerpts are shown in Fig. 13.



**Figure S-15.** Variable temperature  $^6\text{Li}$  DNMR experiment on 0.014 M  $[\text{}^6\text{Li}]\mathbf{5}$  in 3:2 THF/ $\text{Et}_2\text{O}$ . The upper spectrum in each pair is the simulation using the rate constants shown<sup>[1k]</sup> ( $k_{D'M}$  was set equal to  $k_{DM}$ ).

**TMEDA Titration of  $[\text{}^6\text{Li}]\mathbf{5}$ .** A pure sample of  $[\text{}^6\text{Li}]\mathbf{2}$ -(2-methoxyethyl)phenyllithium was prepared by the general procedure for the crystallization and purification of aryllithium reagents for NMR in  $\text{Me}_2\text{O}$ , using 0.151 g (0.51 mmol) of 2-trimethylstannylphenethyl methyl ether and 0.65 mL of 0.79 M  $n\text{-Bu}^6\text{Li}$  in hexanes (0.51 mmol, 1.03 equiv). The white powder was dissolved in 1.5 mL of THF, 0.8 mL of  $\text{Et}_2\text{O}$ , and 1.0 mL of  $\text{Me}_2\text{O}$  to give a clear, pale yellow 0.17 M solution. A TMEDA titration of the  $^6\text{Li}$ -labeled ArLi was conducted on the sample, monitored by  $^6\text{Li}$  NMR spectroscopy with spectra acquired at 0, 0.5, 1, 2, 3, 4, 6 and 8 equiv of TMEDA (1 equiv = 40  $\mu\text{L}$ ) at a probe temperature of  $-147\text{ }^\circ\text{C}$ . Spectra are shown in Fig. S-16. After the experiment was completed, the sample was quenched with 130  $\mu\text{L}$  of  $\text{Me}_3\text{SiCl}$  (1.02 mmol, 2.03 equiv) to give a 90 % yield of 2-(2-trimethylsilylphenyl)ethyl methyl ether by  $^1\text{H}$  NMR integration against pentachloroethane (30.5  $\mu\text{L}$ , 0.253 mmol, 0.501 equiv) as a standard.

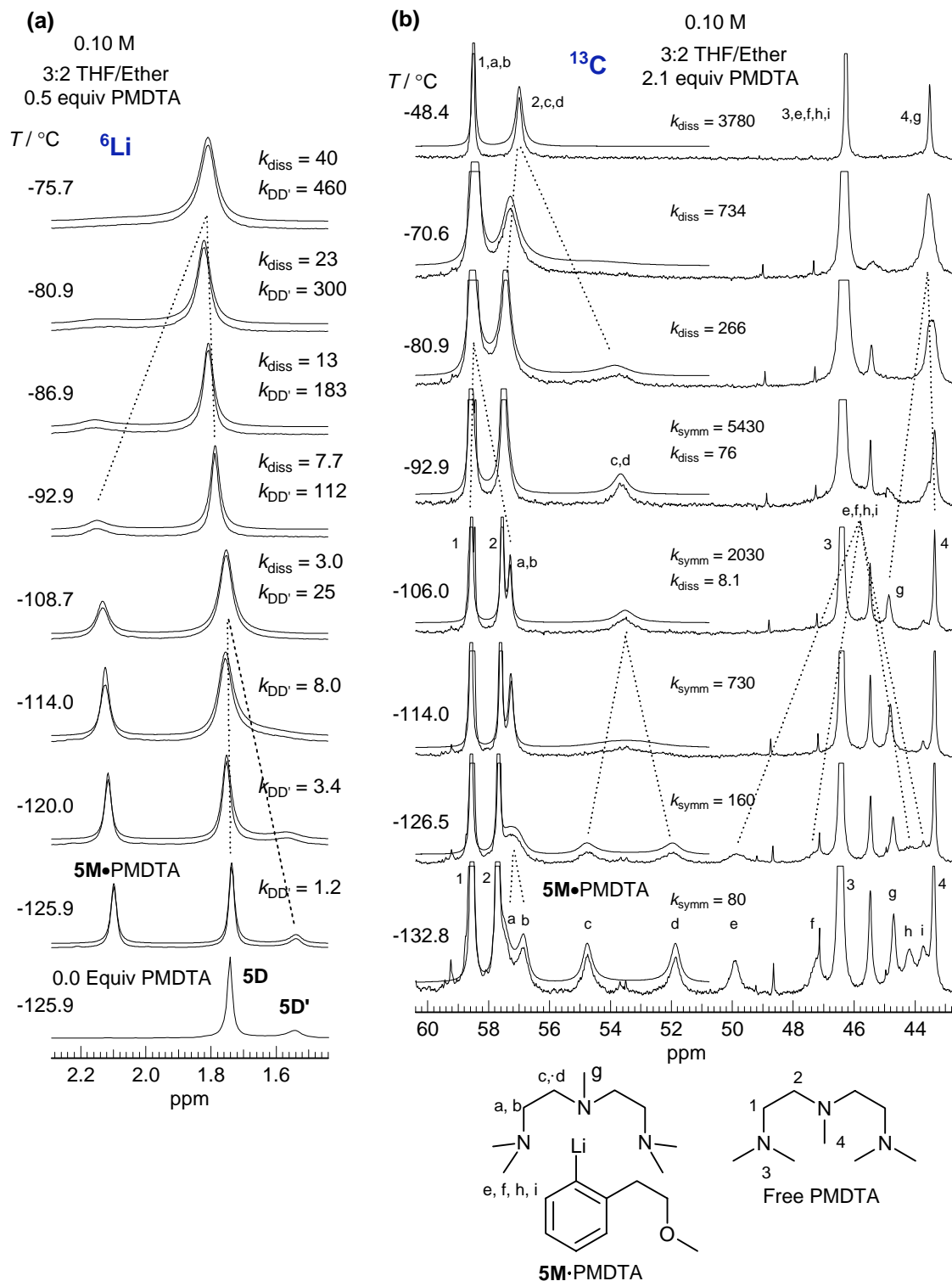


**Figure S-16.**  ${}^6\text{Li}$  NMR study of the effect of treating a solution of  $[\text{}^6\text{Li}]\mathbf{5}$  in 3:2:1 THF/Me<sub>2</sub>O/Et<sub>2</sub>O with (a) TMEDA

**PMDTA Titration of  $[\text{}^6\text{Li}]\mathbf{5}$ .** A sample identical to the one above was used for a PMDTA titration experiment, monitored by  ${}^6\text{Li}$  NMR spectroscopy with spectra acquired at 0, 0.25, 0.5, 0.75, 1, 1.25, 1.5, 1.75 and 2 equiv of PMDTA (1 equiv = 105  $\mu\text{L}$ ) at a probe temperature of  $-147\text{ }^\circ\text{C}$ . Spectra are shown in Fig. 8c. After the experiment was completed, the sample was quenched with 130  $\mu\text{L}$  of Me<sub>3</sub>SiCl (1.02 mmol, 2.03 equiv) to give an 88% yield of 2-(2-trimethylsilylphenyl)ethyl methyl ether by  ${}^1\text{H}$  NMR integration against pentachloroethane (30.0  $\mu\text{L}$ , 0.249 mmol, 0.497 equiv) as a standard.

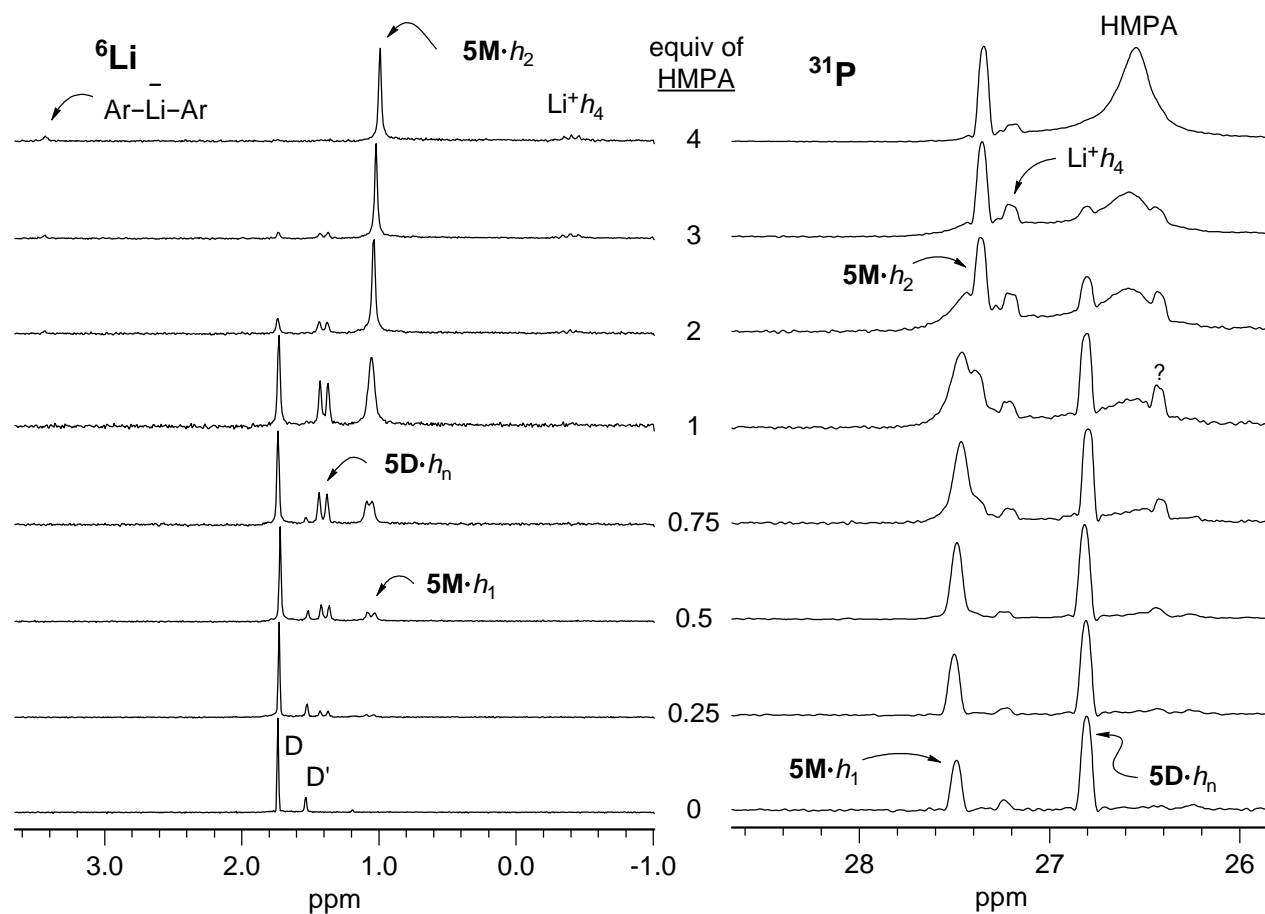
**Variable Temperature PMDTA Titration of  $[\text{}^6\text{Li}]\mathbf{5}$ .** A sample of (2-trimethylstannylphenyl)ethyl methyl ether (132 mg, 0.44 mmol), THF (1.8 mL), Et<sub>2</sub>O (1.2 mL) and (Me<sub>3</sub>Si)<sub>3</sub>CH (4  $\mu\text{L}$ )<sup>[1j]</sup> was cooled to  $-78\text{ }^\circ\text{C}$  in a dry, N<sub>2</sub>-purged 10 mm NMR tube and 276  $\mu\text{L}$  of 1.6 M *n*-Bu<sup>6</sup>Li (0.44 mmol) were added. The 0.10 M sample was monitored by  ${}^6\text{Li}$  and  ${}^{13}\text{C}$  NMR spectroscopy at 0.5 and 2.1 equivalents of PMDTA (addition of 46 and 92  $\mu\text{L}$  of PMDTA) at temperatures from  $-132.8$  to  $-48.4\text{ }^\circ\text{C}$ . The ArLi concentration was determined by assuming that the PMDTA concentration was accurate, and measuring the fraction of  $\mathbf{5M}\cdot\text{PMDTA}$  and  $\mathbf{5D}$  by line shape simulation of the  ${}^{13}\text{C}$  NMR spectrum. The concentration of free PMDTA was determined by measuring the ratio of free to complexed PMDTA by simulation of the  ${}^{13}\text{C}$  NMR spectrum. Spectra are shown in Fig. S-17. The PMDTA dynamics of Fig. S-17a were determined by a 3-spin DNMR simulation. The rate  $k_{\text{diss}}$  in Fig. S-17a is the rate of conversion of  $\mathbf{5}\cdot\text{PMDTA}$  to  $\mathbf{5D}$ . Since this process probably involves dissociation of  $\mathbf{5}\cdot\text{PMDTA}$  to  $\mathbf{5M}$ , which then forms  $\mathbf{5D}$  and  $\mathbf{5D}'$ ,  $k_{\text{diss}}$  does not correspond to a physically real rate, but is a composite and thus cannot be directly compared to the rate  $k_{\text{diss}}$  determined in Fig. S-17b (6-spin DNMR simulation<sup>[1k]</sup> of the CH<sub>2</sub> carbons of the PMDTA ligand) which is a physically real rate. Activation parameters are shown in Table S-2.

The data in Scheme 4 was obtained from a sample which was 0.10 M in total ArLi containing 2.1 equiv of PMDTA. This sample showed a 88/12 ratio of  $\mathbf{5M}\cdot\text{PMDTA}$  to  $\mathbf{5D}$ , and a 58/42 ratio of free to complexed PMDTA (0.085 M  $\mathbf{5M}\cdot\text{PMDTA}$ , 0.0057 M  $\mathbf{5D}$  and 0.12 M free PMDTA).



**Figure S-17.** Variable temperature study of a 0.10 M solution of **5** in 3:2 THF/Et<sub>2</sub>O in the presence of PMDTA. The upper trace at each temperature is an appropriate DNMR simulation using the rate constants shown in sec<sup>-1</sup> for interconversion of isomeric dimers ( $k_{\text{DD}'}$ ), ligand symmetrization ( $k_{\text{symm}}$ ) and ligand dissociation ( $k_{\text{diss}}$  conversion of **5**•PMDTA to **5** in the left panel, and conversion of complexed to free PMDTA for the right panel).<sup>[1k]</sup> (a) 0.5 equiv of PMDTA; (b) 2.1 equiv of PMDTA.

**HMPA Titration of  $[^6\text{Li}]\mathbf{5}$ .** A pure sample of  $[^6\text{Li}]\mathbf{5}$  was prepared by the general procedure for the crystallization and purification of aryllithium reagents for NMR using 1.0 mL of  $\text{Me}_2\text{O}$ , 0.197 g of 2-(2-trimethylstannylphenyl)ethyl methyl ether (0.66 mmol) and 0.85 mL of 0.79 M *n*-Bu $^6\text{Li}$  in hexanes (0.67 mmol, 1.02 equiv). The white powder was dissolved in 1.8 mL of THF and 1.2 mL of  $\text{Et}_2\text{O}$  to give a clear, colorless 0.08 M solution.  $^6\text{Li}$  and  $^{31}\text{P}$  NMR spectra were acquired at 0, 0.25, 0.5, 0.75, 1, 1.5, 2, 3, and 4 equiv of HMPA (1 equiv = 40  $\mu\text{L}$ ) at a probe temperature of  $-125$  to  $-130$   $^\circ\text{C}$ . Spectra are shown in Fig. S-18.

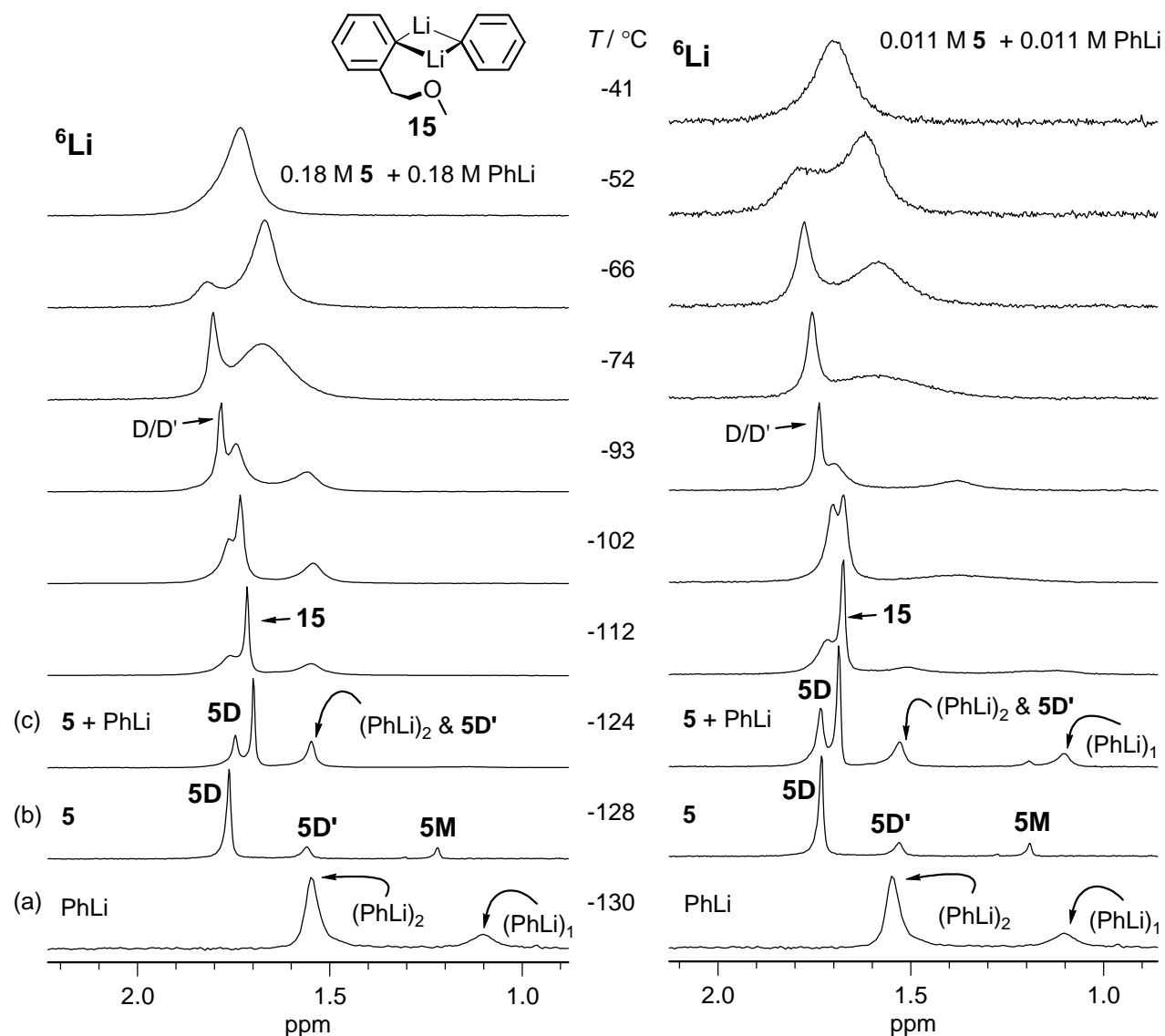


**Figure S-18.**  $^6\text{Li}$  NMR spectra of an HMPA titration of 0.08 M  $[^6\text{Li}]\mathbf{5}$  in 3:2 THF/ $\text{Et}_2\text{O}$  at  $-125$  to  $-130$   $^\circ\text{C}$  ( $h$  = HMPA).

**Variable Temperature Study of 5-PhLi Mixtures.**  $\text{Et}^6\text{Li}$  (38.0 mg, 1.09 mmol) was weighed into a 10 mm NMR tube in a  $\text{N}_2$  filled dry box. The tube was sealed with a septum and removed from the box. The tube was cooled to  $-78$   $^\circ\text{C}$  and  $\text{Et}_2\text{O}$  (1.2 mL),  $\text{PhSnMe}_3$  (98  $\mu\text{L}$ , 0.54 mmol), 2-(2-trimethylstannylphenyl)ethyl methyl ether (128  $\mu\text{L}$ , 0.54 mmol) and 4  $\mu\text{L}$  of  $(\text{Me}_3\text{Si})_3\text{CH}^{[11]}$  were added. Addition of THF (1.8 mL) gave an initial aryllithium concentration of 0.18 M in  $[^6\text{Li}]\text{PhLi}$  and 0.18 M in  $[^6\text{Li}]\mathbf{5}$ . The variable temperature experiment was monitored by  $^6\text{Li}$  and  $^{13}\text{C}$  NMR spectroscopy with spectra acquired at  $-129$ ,  $-124$ ,  $-118$ ,  $-112$ ,  $-107$ ,  $-102$ ,  $-96$ ,  $-91$ ,  $-79$  and  $-74$   $^\circ\text{C}$ . Spectra are shown in Fig. S-19.

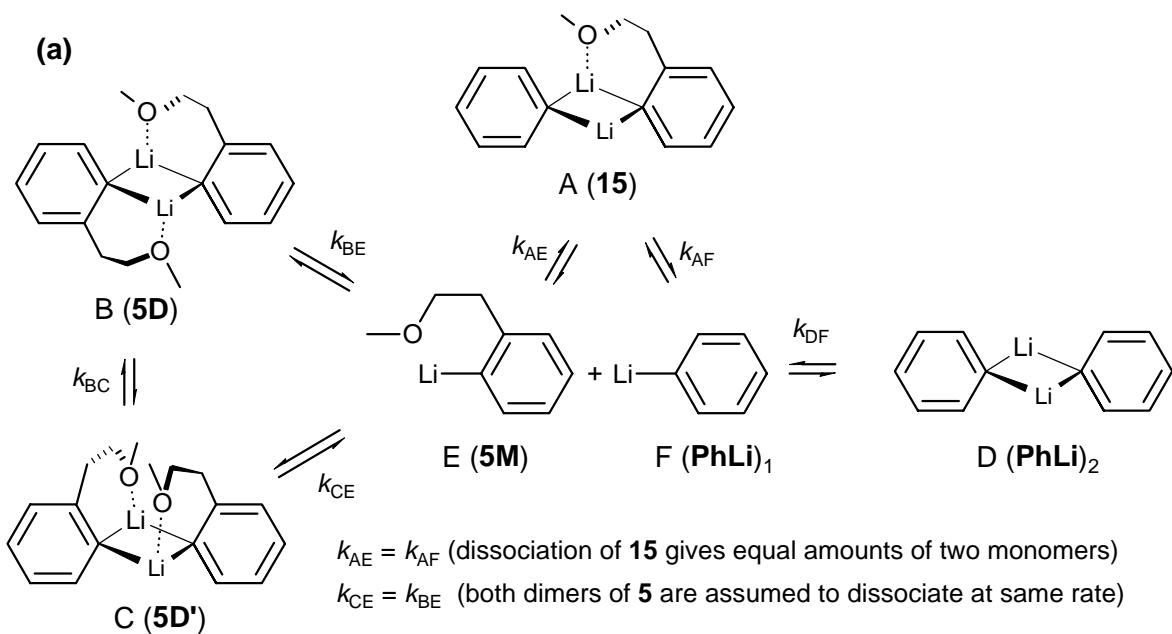
The sample was diluted by a factor of 16 by mixing 0.25 mL of the solution with  $\text{Et}_2\text{O}$  (1.5 mL) and THF (2.25 mL) in a second dried and  $\text{N}_2$ -flushed 10 mm NMR tube to give a clear, pale yellow solution of 0.011 M in  $[^6\text{Li}]\text{PhLi}$  and 0.011 M in  $[^6\text{Li}]\mathbf{5}$ . A second variable temperature experiment was monitored by  $^{13}\text{C}$  and  $^6\text{Li}$  NMR spectroscopy with spectra acquired  $-124$ ,  $-118$ ,  $-112$ ,  $-107$ ,  $-102$ ,  $-96$ ,  $-91$ ,  $-79$  and  $-74$   $^\circ\text{C}$ .

Spectra are shown in Fig. S-19 and Fig. 14, line shape simulations and data analysis are shown in Fig. 15.



**Figure S-19.**  $^6\text{Li}$  NMR spectra of variable temperature study of **5** + PhLi in 3:2 THF/Et<sub>2</sub>O. The spectra on the left have a concentration of 0.18 M **5** and 0.18 M PhLi. The spectra on the right have a concentration of 0.011 M **5** and 0.011 M PhLi. The  $^6\text{Li}$  NMR of 0.2 M PhLi in 4:1 THF/Et<sub>2</sub>O at -130 °C (a), and 0.014 M **5** in 3:2 THF/Et<sub>2</sub>O at -128 °C (b) are shown for comparison. **5D** and **5D'** are the two isomeric dimers of **5**, **5M** is the monomer of **5**.

**Line shape simulations of the 5-PhLi System.** Because all of the reacting partners were detectable in the 0.011 M mixed dimer solution, it was possible to do a mechanistically correct simulation of the spectra. The proposed exchange scheme is shown in Fig. S-20a and involves only dissociation of the three dimers (**5**, **15**, (PhLi)<sub>2</sub>) to the two monomers, and reassociation of these to form the dimers. The exchange matrix used for the simulation using WINDNMR<sup>[1k]</sup> is shown in Fig. S-20b. A complete set of output data for simulation obtained from the program is given in Table S-1.



(b)

		<b>15</b>	<b>5D</b>	<b>5D'</b>	<b>(PhLi)<sub>2</sub></b>	<b>5M</b>	<b>(PhLi)<sub>1</sub></b>
		A	B	C	D	E	F
<b>15</b>	A	$i2\pi(\Delta v_A)$ $-1/T-\Sigma k$	0	0	0	$k_{AE}$	$k_{AF}$
<b>5D</b>	B	0	$i2\pi(\Delta v_B)$ $-1/T-\Sigma k$	$k_{BC}$	0	$k_{BE}$	0
<b>5D'</b>	C	0	$k_{CB}$	$i2\pi(\Delta v_C)$ $-1/T-\Sigma k$	0	$k_{BE}$	0
<b>(PhLi)<sub>2</sub></b>	D	0	0	0	$i2\pi(\Delta v_D)$ $-1/T-\Sigma k$	0	$k_{DF}$
<b>5M</b>	E	$k_{EA}$	$k_{EB}$	$k_{EB}$	0	$i2\pi(\Delta v_E)$ $-1/T-\Sigma k$	0
<b>(PhLi)<sub>1</sub></b>	F	$k_{FA}$	0	0	$k_{FD}$	0	$i2\pi(\Delta v_F)$ $-1/T-\Sigma k$

= E

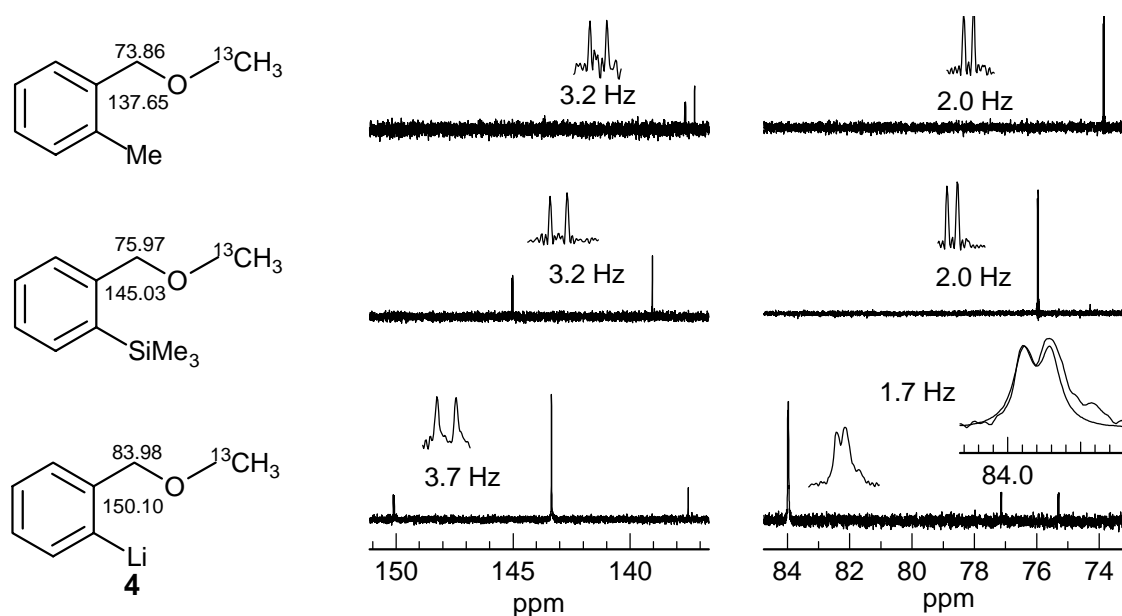
$\Sigma k$  is the sum of the rate constants in that row  
 $1/T$  is the line width in the absence of exchange

**Figure S-20.** (a) Kinetic scheme assumed for the simulations of the mixed dimer DNMR spectra. The rate constants shown are the ones directly manipulated during the simulation (top-right half of the exchange matrix), the reverse rates are automatically determined by the program from the forward rates and the populations. (b) Exchange matrix used to implement the exchange scheme, and which produced the line shape simulations shown in Fig. 15.

**Table S-1.** Output Data from the Simulation of Mixed dimer **15** exchange (0.011 M **5**, 0.011 M PhLi).

SimNum:	1	2	3	4	5	6	7	8
Filename:	4209.009	4209.006	4209.004	4209.002	4209.011	4209.013	4209.015	4209.016
Temp K:	149.0	161.0	171.0	180.0	199.0	207.0	221.0	232.0
Temp C:	-124.2	-112.2	-102.2	-93.2	-74.2	-66.2	-52.2	-41.2
Va	379.680	381.280	383.030	384.220	384.600	385.880	387.350	388.926
Vb	382.250	384.118	385.550	387.642	388.530	389.812	391.292	392.869
Vc	371.700	373.300	374.900	375.692	376.580	377.862	379.342	380.919
Vd	371.330	372.930	374.530	376.232	377.120	378.402	379.882	381.459
Ve	353.560	355.160	356.760	357.862	358.750	360.032	361.512	363.089
Vf	348.518	350.340	351.940	353.642	354.530	355.812	357.292	358.869
k	0.030	0.250	1.030	5.810	43.710	78.010	350.310	909.010
kab/k	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
kac/k	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
kad/k	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
kae/k	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
kaf/k	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
kbc/k	21.000	33.000	23.200	30.600	22.700	23.000	26.000	26.000
kbd/k	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
kbe/k	0.200	0.200	0.120	0.130	0.100	0.090	0.058	0.060
kbf/k	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
kcd/k	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
kce/k	0.200	0.200	0.120	0.130	0.100	0.090	0.058	0.060
kcf/k	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
kde/k	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
kdf/k	74.000	62.000	53.640	31.400	63.000	63.000	48.000	63.000
kef/k	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
% a	42.041	40.710	39.070	33.010	32.300	32.430	32.322	32.328
% b	25.310	26.010	29.270	33.280	34.030	33.470	33.522	33.408
% c	3.715	3.815	3.455	4.046	4.137	4.068	4.086	4.061
% d	15.940	16.375	14.817	16.690	17.069	16.781	16.857	16.753
% e	1.954	1.530	1.668	0.568	0.584	0.780	0.682	0.980
% f	11.040	11.550	11.720	12.410	11.870	12.480	12.531	12.469
Wa	0.700	0.700	0.700	0.700	0.700	0.700	0.700	0.700
Wb	0.700	0.700	0.700	0.700	0.700	0.700	0.700	0.700
Wc	0.700	0.700	0.700	0.700	0.700	0.700	0.700	0.700
Wd	0.700	0.700	0.700	0.700	0.700	0.700	0.700	0.700
We	0.700	0.700	0.700	0.700	0.700	0.700	0.700	0.700
Wf	0.700	0.700	0.700	0.700	0.700	0.700	0.700	0.700
Right-Hz	313.765	313.765	313.765	313.765	313.765	313.765	313.561	313.765
WdthHz	102.008	102.008	102.008	102.008	102.008	102.008	102.008	102.008

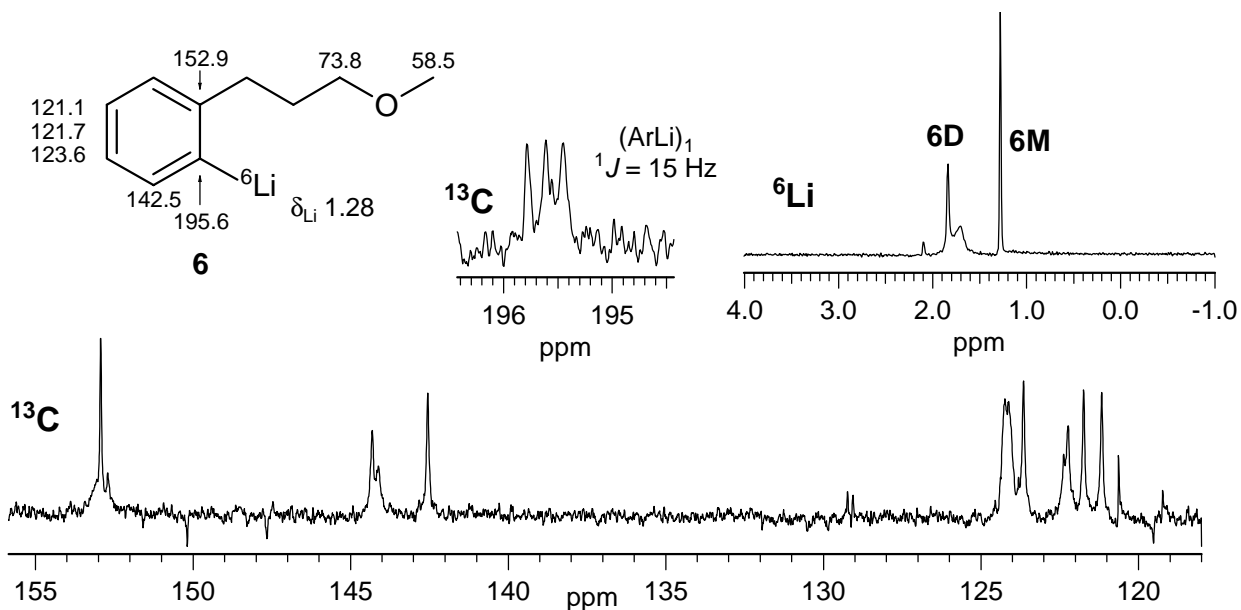
**Determination of  $^{13}\text{C}$  Coupling Constants ( $J_{\text{COC}}$  and  $J_{\text{COCC}}$ ) of **4** and Analogs.** A sample of 2-trimethylstannylbenzyl methyl- $^{13}\text{C}$  ether (38.0 mg, 0.13 mmol) in 0.45 mL THF and 0.30 mL Et<sub>2</sub>O was cooled to -78 °C in a dry, N<sub>2</sub>-purged 5 mm NMR tube and 2.58 M *n*-BuLi in hexane (62  $\mu\text{L}$ , 0.16 mmol) was slowly added. A proton decoupled  $^{13}\text{C}$  NMR spectrum was acquired at 11 °C. Sample spectra are shown in Fig. S-21. The sample was then quenched with Me<sub>3</sub>SiCl (20.3  $\mu\text{L}$ , 0.16 mmol) and a  $^{13}\text{C}$  NMR spectrum was acquired at 11 °C. The coupling constants were determined using natural line widths (no Lorentzian line broadening) and two zero fills. The  $J_{\text{COC}}$  of **4** was determined by line shape simulation of the NMR spectrum. Data is shown in Fig. 16.



**Figure S-21.** Sample  $^{13}\text{C}$  NMR spectra of  $^{13}\text{CH}_3\text{-O}$  labeled **4** and analogs.

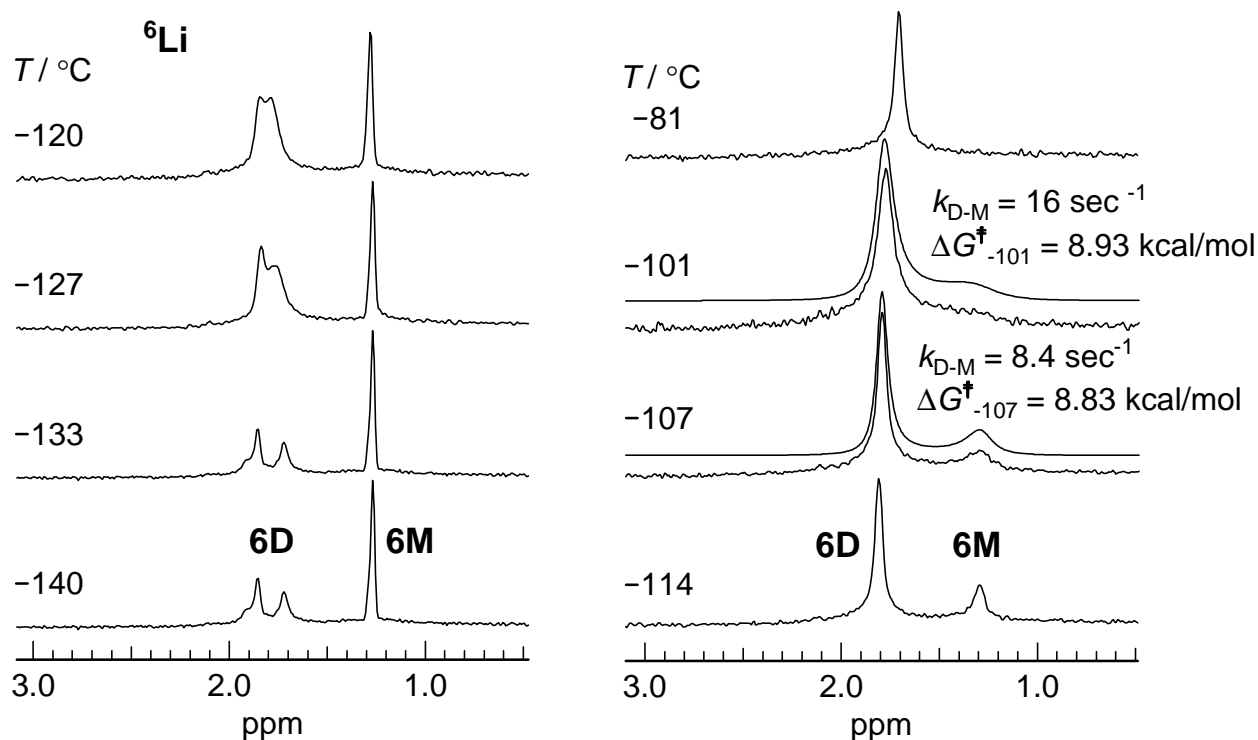
**Determination of  $^{13}\text{C}$  Coupling Constants ( $J_{\text{COC}}$  and  $J_{\text{COCC}}$ ) **5** and its Analogs.** A sample of 2-(2-bromophenyl)ethyl methyl- $^{13}\text{C}$  ether<sup>[S-4]</sup> (26.4 mg, 0.12 mmol) in 0.45 mL THF and 0.30 mL  $\text{Et}_2\text{O}$  was cooled to  $-78\text{ }^\circ\text{C}$  in a dry,  $\text{N}_2$ -purged 5 mm NMR tube and 1.8 M *t*-BuLi in hexane (150  $\mu\text{L}$ , 0.27 mmol) was slowly added. A  $^{13}\text{C}$  NMR spectrum was acquired at  $11\text{ }^\circ\text{C}$ . The sample was quenched with MeI (9.0  $\mu\text{L}$ , 0.14 mmol) and a  $^{13}\text{C}$  NMR spectrum was acquired at  $11\text{ }^\circ\text{C}$ . The coupling constants were determined using natural line widths (no Lorentzian line broadening) and two zero fills. The  $J_{\text{COC}}$  of **5** was determined by line shape simulation of the NMR spectrum.

## NMR Experiments Conducted on 2-(3-Methoxypropyl)phenyllithium (**6**)



**Figure S-22.**  $^{13}\text{C}$  and  $^6\text{Li}$  NMR spectra of 0.08 M **6** in 3:2 THF/Et<sub>2</sub>O solvent at -125 °C.

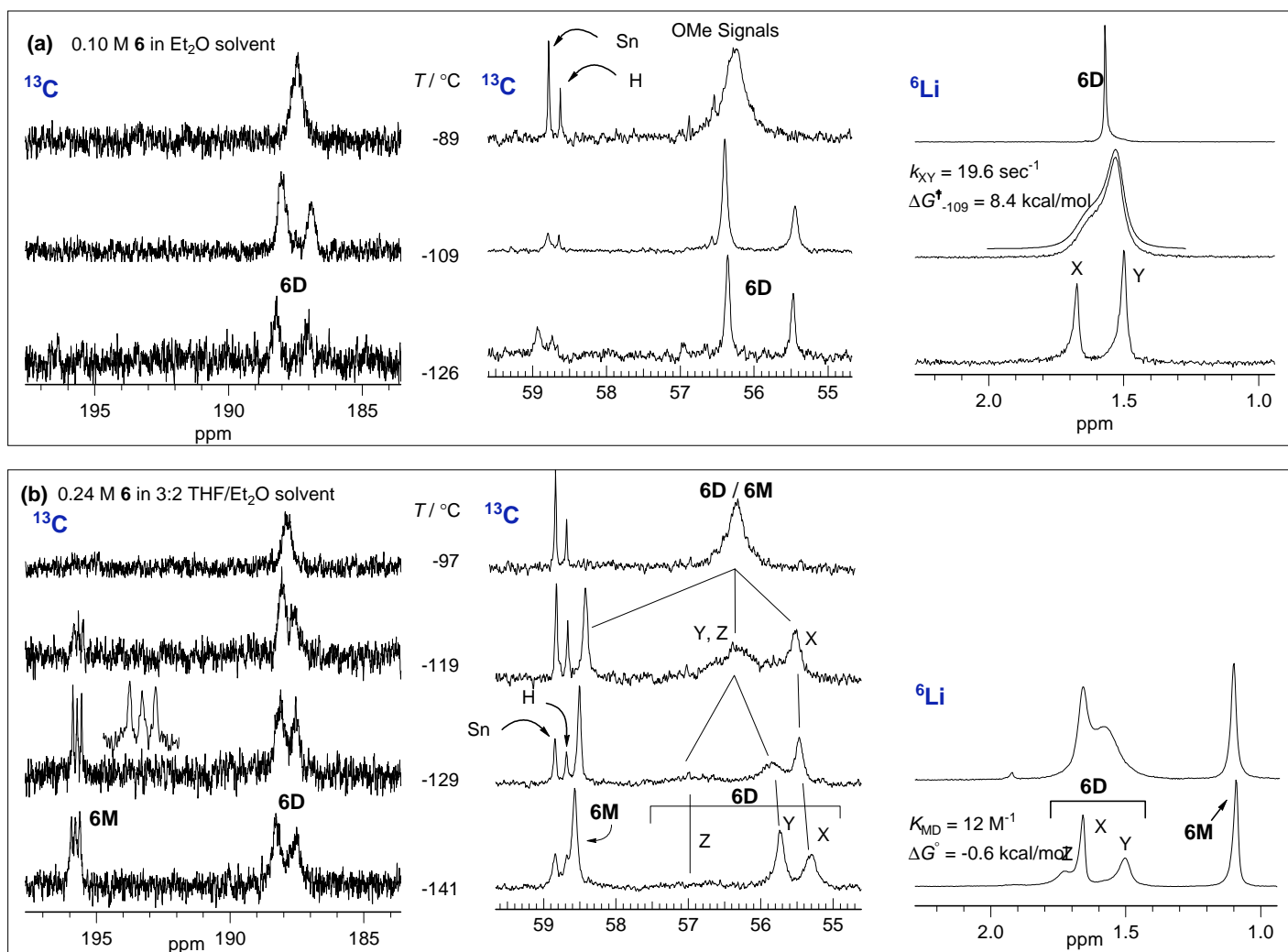
**Variable Temperature  $^6\text{Li}$  NMR Study of [ $^6\text{Li}$ ]**6**.** A sample of 3-(2-trimethylstannylphenyl)propyl methyl ether (155 mg, 0.496 mmol), THF (1.5 mL) and Et<sub>2</sub>O (0.5 mL) in a dry, N<sub>2</sub>-purged 10 mm NMR tube was cooled to -78 °C and 0.62 mL of 0.79 M *n*-Bu $^6\text{Li}$  in hexanes (0.49 mmol) was added. Me<sub>2</sub>O (1.0 mL) was added and the sample was stored overnight at -78 °C.  $^6\text{Li}$  NMR spectra were acquired at -140, -133, -127, -120, -114, -107, -101, -88 and -81 °C. Selected spectra and 2-spin line shape simulations are shown in Fig. S-23.



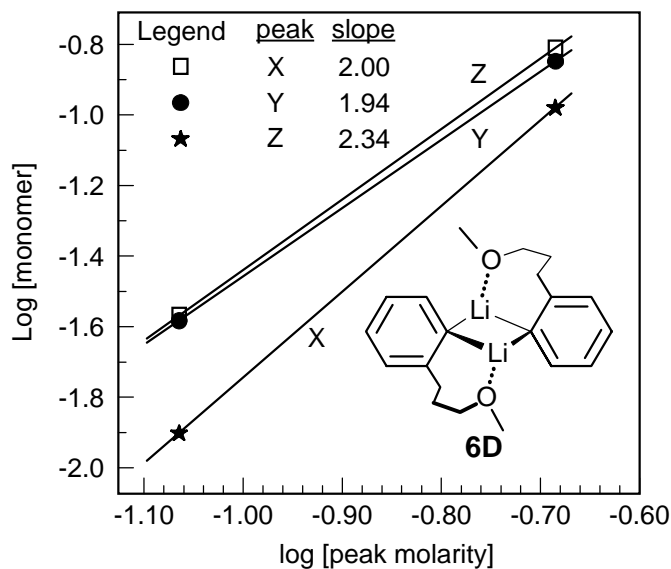
**Figure S-23.** Variable temperature  ${}^6\text{Li}$  NMR study of 0.135 M **6** in 3:2:1 THF/Me<sub>2</sub>O/Et<sub>2</sub>O. The second trace at -101 and -107 °C are 2-spin DNMR simulations to determine the dimer dissociation rate. The rate constants are the NMR rates, the physical rate constants for dimer dissociation are 0.5 times the values shown.

**Variable Temperature and Concentration Study of [ ${}^6\text{Li}$ ]**6** in Et<sub>2</sub>O and 3:2 THF/Et<sub>2</sub>O.** Five samples of **6** were prepared as follows: Sample 1 (0.61 M [ ${}^6\text{Li}$ ]**6** in Et<sub>2</sub>O) To a 10 mL round bottom flask under N<sub>2</sub> was added 63.9 mg of Et<sup>6</sup>Li, 3.0 mL of Et<sub>2</sub>O, 5 μL of (Me<sub>3</sub>Si)<sub>3</sub>CH<sup>[1]</sup> and 472 μL (1.83 mmol) of 3-(2-trimethylstannylphenyl)propyl methyl ether. Sample 2: (0.10 M in Et<sub>2</sub>O) 0.5 mL of Sample 1 and 2.5 mL of Et<sub>2</sub>O. Sample 3 (0.24 M in 3:2 THF/Et<sub>2</sub>O): 1.2 mL of Sample 1 and 1.8 mL of THF. Sample 4 (0.08 M in 3:2 THF/Et<sub>2</sub>O): 1.0 mL of Sample 3, 1.8 mL of THF, 1.2 mL of Et<sub>2</sub>O and 2 μL of (Me<sub>3</sub>Si)<sub>3</sub>CH.<sup>[1]</sup> Sample 5 (0.2 M in 3:2 THF/Et<sub>2</sub>O): 1.0 mL of Sample 1 and 1.5 mL of THF.

${}^6\text{Li}$  and  ${}^{13}\text{C}$  spectra were taken of Samples 2-4 between -141 and -89 °C. Partial spectra are presented in Fig. S-24 and Fig. 17. The  ${}^6\text{Li}$  spectra of the 0.25 M and 0.08 M (Samples 3 and 4) at -141 °C were integrated by line shape fitting, and used to determine the concentration dependence of the three signals (X, Y, Z and monomer). The graphed results, shown in Fig. S-25, demonstrate that the X, Y, Z peaks are dimeric relative to the peak at  $\delta$  1.1 (the monomer).



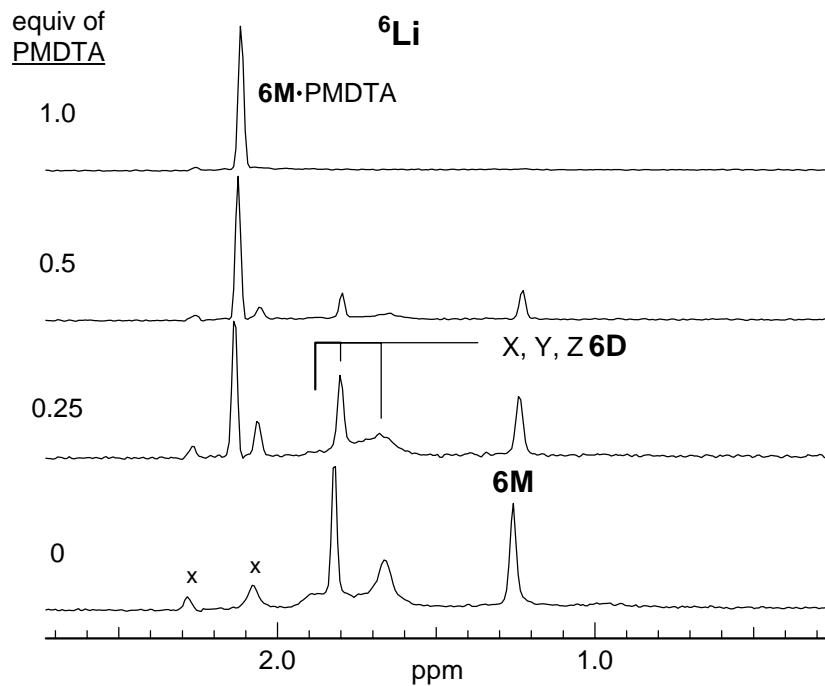
**Figure S-24.**  ${}^6\text{Li}$  and  ${}^{13}\text{C}$  NMR spectra (C-Li region) of a variable temperature study of  $[\text{}^6\text{Li}]\mathbf{6}$ . (a) Spectra of a 0.10 M solution in  $\text{Et}_2\text{O}$  (Sample 2). The inset for the  ${}^6\text{Li}$  NMR spectrum at  $-109\text{ }^\circ\text{C}$  is a 2-spin simulation to estimate the rate of interconversion of the X and Y dimers. (b) Spectra of Sample 3 (of 0.24 M in 3:2 THF/ $\text{Et}_2\text{O}$ ). The inset shows an expansion of the monomer 1:1:1 triplet ( $J_{\text{CLi}} = 15\text{ Hz}$ ). The value for  $K_{\text{MD}}$  ( $[\text{D}] / [\text{M}]^2$ ) was obtained by line-shape simulation of the  ${}^6\text{Li}$  spectrum at  $-141\text{ }^\circ\text{C}$ .



**Figure S-25.** Logarithmic plot of the areas of the  ${}^6\text{Li}$  signal at  $\delta$  1.1 (**6M**) versus the X, Y, Z signals of **6D** at  $\delta$  1.4-1.7.

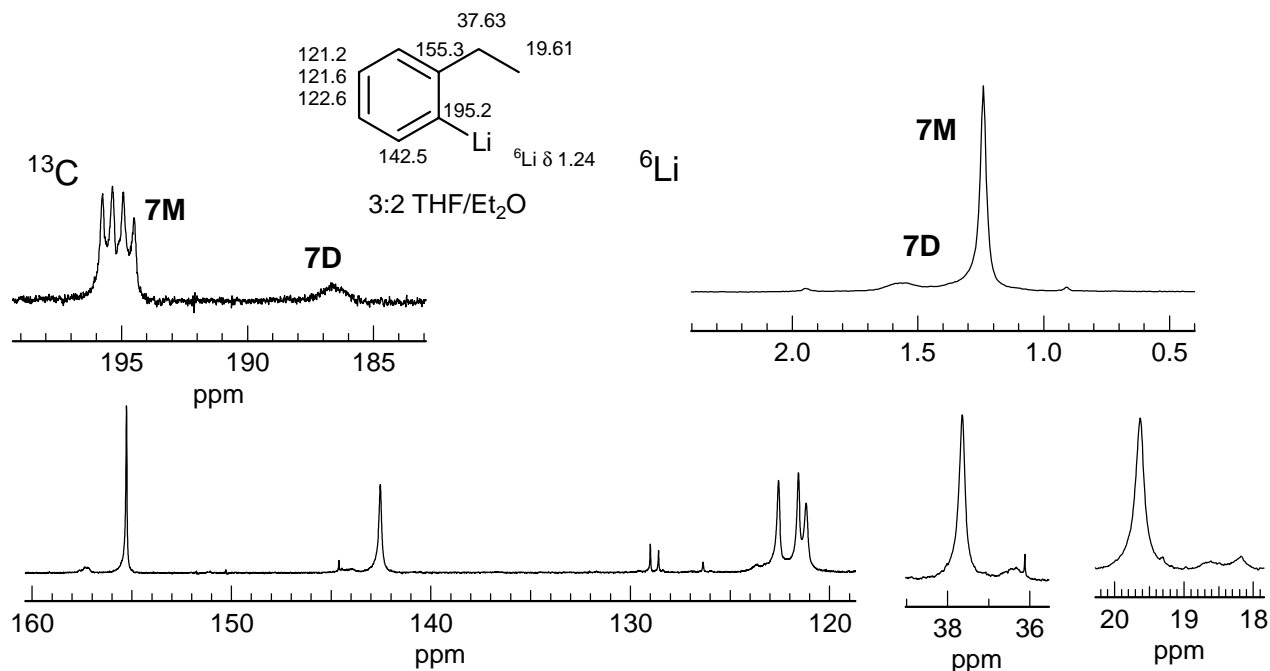
**TMEDA Titration of [ ${}^6\text{Li}$ ]6 in 3:2 THF/Et<sub>2</sub>O.** Increments of TMEDA (30  $\mu\text{L}$ /0.25 equiv) were added to Sample 5 from the above experiment and  ${}^6\text{Li}$  and  ${}^{13}\text{C}$  NMR spectra were taken. Data, simulations and analysis are reported in Fig. 18.

**PMDTA Titration of [ ${}^6\text{Li}$ ]6.** A 0.14 M solution of [ ${}^6\text{Li}$ ]6 in 3:2 THF/Et<sub>2</sub>O was prepared from 0.158 g (0.505 mmol) of 3-(2-trimethylstannylphenyl)propyl methyl ether, 0.79 M *n*-Bu ${}^6\text{Li}$  in hexanes (0.51 mmol, 1.00 equiv), 1.8 mL of THF and 1.2 mL of Et<sub>2</sub>O at  $-78$  °C. The sample was stored overnight at  $-78$  °C. The PMDTA titration experiment (0, 0.25, 0.5, 0.75 and 1 equiv, 105  $\mu\text{L}$  PMDTA per equiv ) was monitored by  ${}^6\text{Li}$  NMR spectroscopy at  $-125$  °C (Fig. S-26). After the experiment was completed, the sample was quenched with 100  $\mu\text{L}$  of Me<sub>3</sub>SiCl (0.788 mmol, 1.56 equiv) to give a 92 % yield of 3-(2-trimethylsilylphenyl)propyl methyl ether by  ${}^1\text{H}$  NMR integration against pentachloroethane (30.0  $\mu\text{L}$ , 0.249 mmol, 0.494 equiv) as a standard.



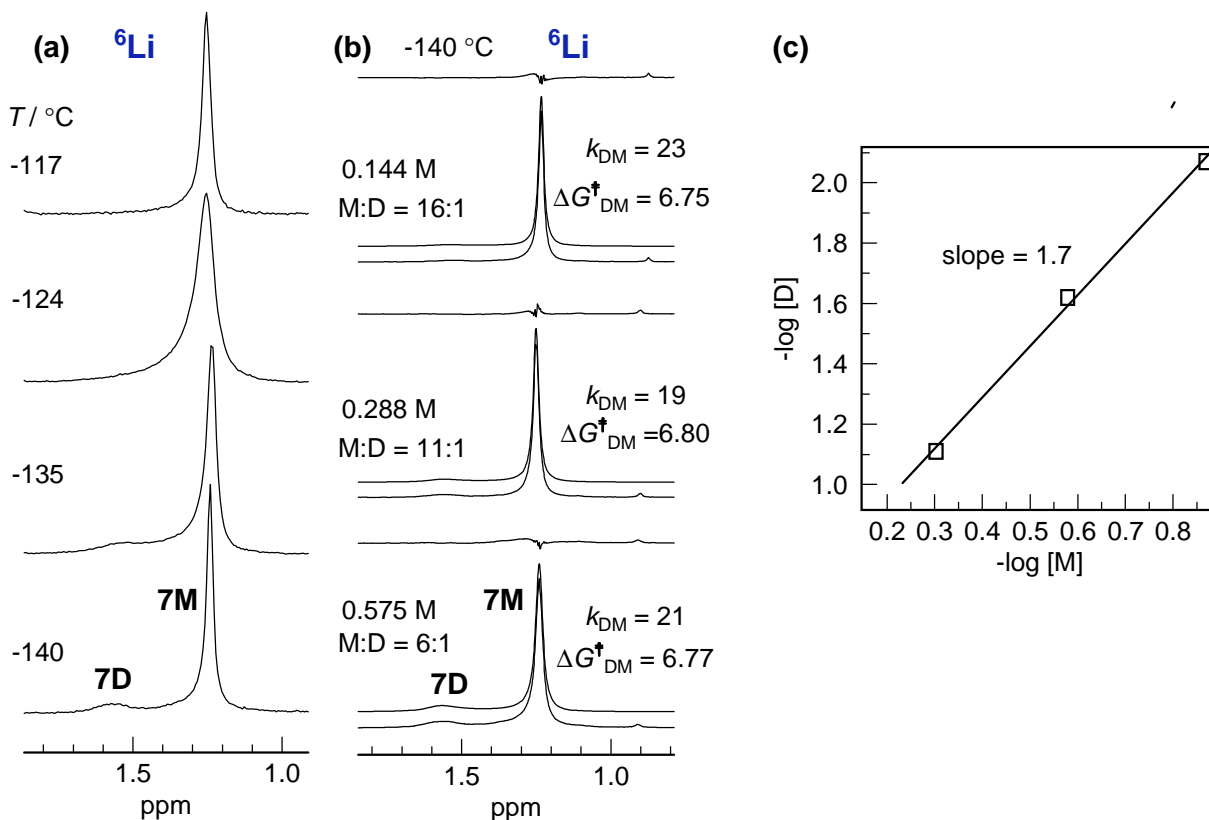
**Figure S-26.**  ${}^6\text{Li}$  NMR spectra of a PMDTA titration experiment of 0.14 M **6** in 3:2 THF/Et<sub>2</sub>O at -125 °C).

## NMR Experiments Conducted on 2-Ethylphenyllithium (7)



**Figure S-27.**  $^{13}\text{C}$  and  $^6\text{Li}$  NMR spectra of 0.57 M **7** in 3:2 THF/Et<sub>2</sub>O solvent at -140 °C.

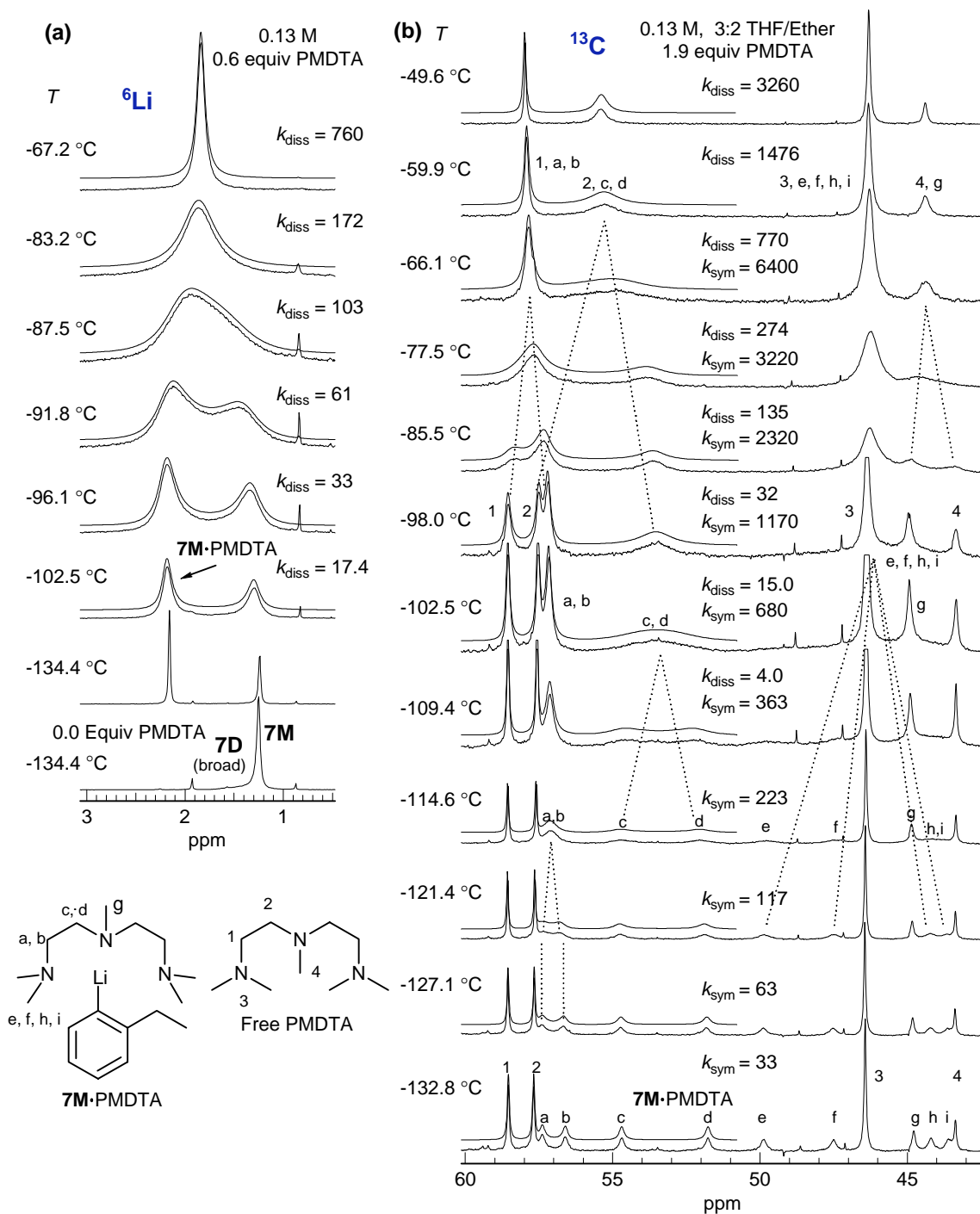
**Variable Concentration Experiment of 2-Ethylphenyllithium (7).** A sample of 2-ethyltrimethylstannybenzene (333 mg, 1.24 mmol) in 1.0 mL of Et<sub>2</sub>O was cooled to -78 °C in a dry, N<sub>2</sub>-purged 10 mm NMR tube and 474  $\mu\text{L}$  of 2.62 M *n*-BuLi in hexane (1.24 mmol) was slowly added. The lithium reagent proved to be soluble in Et<sub>2</sub>O. However, upon addition of 1.5 mL of THF, crystals formed overnight. The solvent was removed via cannula and the crystals were dissolved in 1.2 mL of THF and 0.8 mL of Et<sub>2</sub>O after warming slightly. The temperature of the various spectra were determined using 2.5  $\mu\text{L}$  of the internal chemical shift thermometer, (Me<sub>3</sub>Si)<sub>3</sub>CH.<sup>[1j]</sup>  $^{13}\text{C}$  and  $^6\text{Li}$  NMR spectra were acquired at -140 °C. The sample was diluted (1:1) with 1.2 mL of THF and 0.8 mL of Et<sub>2</sub>O. The final dilution (1:1) was accomplished by removing half of the sample by syringe followed by the addition of 1.2 mL of THF and 0.8 mL of Et<sub>2</sub>O. The final sample concentration (0.14 M) was determined by benzaldehyde quench (130  $\mu\text{L}$ , 1.3 mmol) and  $^1\text{H}$  NMR integration relative to an internal pentachloroethane standard (30  $\mu\text{L}$ , 0.25 mmol). Spectra are shown in Fig. S-28. The aggregation difference between **7M** and **7D** was measured as 1.7.



**Figure S-28.** (a) Variable temperature  ${}^6\text{Li}$  NMR spectra of 0.57 M **7** in 3:2 THF/Et<sub>2</sub>O showing coalescence of **7D** and **7M**. (b) Variable concentration study of **7** in 3:2 THF/Et<sub>2</sub>O. The 2-spin DNMR simulation (second trace of each set) also gave the rates for interconversion of **7M** and **7D**, the free energies of activation (kcal/mol) are shown on the spectra. The upper trace of each set is the difference spectrum (spectrum-simulation). (c) Log-log plot of the concentrations of the two oligomers.

**Variable Temperature PMDTA Titration of [ ${}^6\text{Li}$ ]-**7**.** A sample of 2-ethyltrimethylstannylbenzene (131 mg, 0.49 mmol), THF (1.8 mL), Et<sub>2</sub>O (1.2 mL) and (Me<sub>3</sub>Si)<sub>3</sub>CH (4  $\mu\text{L}$ ) was cooled to -78 °C in a dry, N<sub>2</sub>-purged 10 mm NMR tube and 304  $\mu\text{L}$  of 1.6 M *n*-Bu ${}^6\text{Li}$  (0.49 mmol) were added. 51, 42, and 56  $\mu\text{L}$  of PMDTA were added (0.6, 1.06 and 1.9), and  ${}^6\text{Li}$  and  ${}^{13}\text{C}$  NMR spectra were measured at temperatures from -134.4 to -67.2 °C after each addition. The concentration of **7** was determined by assuming that the PMDTA concentrations were accurate, and determining the fraction of **7M**·PMDTA and **7M** by line shape simulation of the  ${}^{13}\text{C}$  and/or  ${}^6\text{Li}$  spectra. Spectra are shown in Fig. S-29. The PMDTA dynamics were determined by a 2-spin DNMR simulation of the  ${}^6\text{Li}$  NMR spectra at 0.6 equiv of PMDTA (Fig. S-29a) and a 6-spin DNMR simulation<sup>[1k]</sup> of the CH<sub>2</sub> carbons of the PMDTA ligand with 1.9 equiv of PMDTA (Fig. S-29b). Activation parameters are shown in Table S-2.

The data in Scheme 4 was obtained from a sample which was 0.13 M in total ArLi containing 1.06 equiv of PMDTA. This sample showed a 96/4 ratio of **7M**·PMDTA to **7M**, and a 9.5/90.5 ratio free to complexed PMDTA (0.122 M **7M**·PMDTA, 0.0051 M **7M** and 0.012 M free PMDTA).



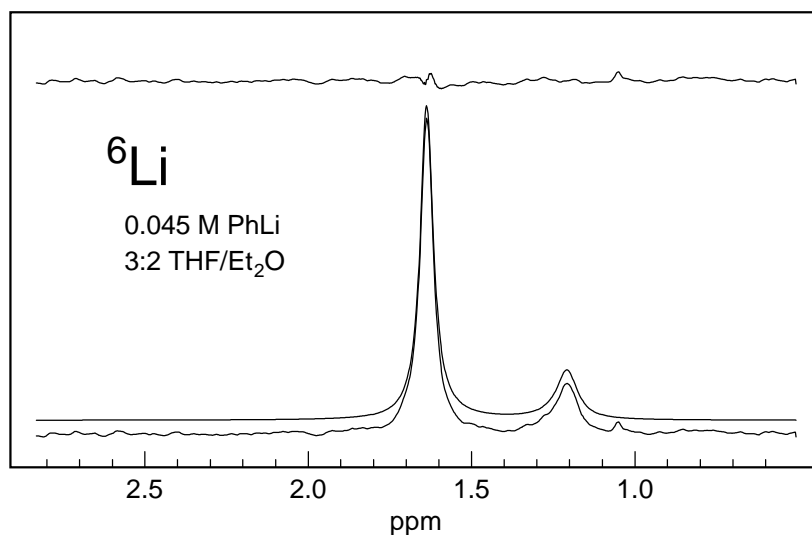
**Figure S-29.** Variable temperature  ${}^6\text{Li}$  and  ${}^{13}\text{C}$  NMR study of a 0.13 M solution of  $[\text{}^6\text{Li}]\mathbf{7}$  in 3:2 THF/Et $_2$ O in the presence of PMDTA. The upper trace at each temperature is an appropriate DNMR simulation using the rate constants shown in sec $^{-1}$  for ligand symmetrization ( $k_{\text{sym}}$ ) and ligand dissociation ( $k_{\text{diss}}$ , conversion of  $\mathbf{7M}\cdot\text{PMDTA}$  to  $\mathbf{7M}$  in the left panel, and conversion of complexed to free PMDTA for the right panel).<sup>[1k]</sup> (a) 0.6 equiv of PMDTA; (b) 1.9 equiv of PMDTA.

**Table S-2.** Rates and Activation Parameters for the Dynamics of the PMDTA Complexes of **4**, **5** and **7**.

<b>Symmetrization</b>	<b>4M·PMDTA<sup>[a]</sup></b>	<b>5M·PMDTA<sup>[b]</sup></b>	<b>7M·PMDTA<sup>[c]</sup></b>
$k_{\text{symm}}$ (sec <sup>-1</sup> )	52,100	3490	820
$\Delta G^\ddagger_{-100}$ (kcal/mol)	6.21	7.14	7.64
$\Delta H^\ddagger$ (kcal/mol)	4.03±0.36	5.42±0.26	4.43±0.04
$\Delta S^\ddagger$ (eu)	-12.6±2.6	-10.0±1.6	-18.54±2.4
<b>Dissociation</b>			
$k_{\text{diss}}$ (sec <sup>-1</sup> )	710	34	23.8
$\Delta G^\ddagger_{-100}$ (kcal/mol)	7.69	8.74	8.86
$\Delta H^\ddagger$ (kcal/mol)		6.66±0.14	7.06±0.1
$\Delta S^\ddagger$ (eu)		-12.0±0.7	-10.38±1

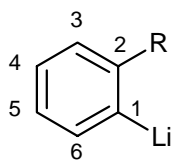
<sup>[a]</sup> For spectra see Fig. S-10. <sup>[b]</sup> For spectra see Fig. S-17. <sup>[c]</sup> For spectra see Fig. S-29.

**Preparation of PhLi and Determination of  $K_{\text{MD}}$  in 3:2 THF/Et<sub>2</sub>O.** PhLi was prepared as previously reported.<sup>[S-7]</sup> 100  $\mu\text{L}$  of 1.35 M PhLi in Et<sub>2</sub>O (0.135 mmol) was added to a dry, N<sub>2</sub>-purged 10 mm NMR tube at -78 °C. THF (1.8 mL) and Et<sub>2</sub>O (1.1 mL) were added along with 2.5  $\mu\text{L}$  of (Me<sub>3</sub>Si)<sub>3</sub>CH<sup>[1]</sup> to give a final concentration of 0.045 M PhLi. <sup>13</sup>C and <sup>6</sup>Li NMR spectra were acquired at -129 °C.  $K_{\text{MD}}$  (210 M<sup>-1</sup>) was determined by line shape simulation of the <sup>6</sup>Li NMR spectrum (Fig. S-30).



**Figure S-30.** <sup>6</sup>Li NMR spectrum of 0.045 M PhLi at -129 °C. The second trace is a simulation, the third trace a difference spectrum (spectrum-simulation).

**Table S-3.**  $^{13}\text{C}$  NMR chemical Shifts of 2-Alkylphenyllithium Reagents.



	Solv.	$T$	C-1	C-2	C-3	C-4	C-5	C-6	$\text{XCH}_3$	$\text{CH}_2\text{X}$	$\delta_{\text{Li}}^{[\text{a}]}$	$J_{\text{CLi}} (^6\text{Li})$
<b>Monomers:</b>												
$(\text{PhLi})_1^{[\text{b}]}$	THF	-111	196.4	143.2	124.1	120.7	124.1	143.2	---	---	1.15	15.3 <sup>[c]</sup>
$(\text{PhLi})_1 \cdot \text{PMDTA}^{[\text{b}][\text{d}]}$		-125	196.5	143.8	124.0	120.7	124.0	143.8	---	---	1.95	15.6
$(\mathbf{9})_1$		-126	195.2	153.6	121.1	121.6	123.4	142.5	---	---	1.20	15.2 <sup>[c]</sup>
$(\mathbf{7})_1$		-141	195.2	155.3	121.2*	121.6*	122.6*	142.5	---	---	1.24	14.6 <sup>[g]</sup>
$(\mathbf{2})_1$		-130	195.9	154.3	121.1*	121.8*	123.8*	142.6	46.3	<sup>[i]</sup>	1.23	12 <sup>[c]</sup>
$(\mathbf{2})_1 \cdot \text{PMDTA}$		-145	196.7	150.5	121.1*	121.9*	124.0*	142.3	<sup>[i]</sup>	<sup>[i]</sup>	2.06	15.5 <sup>[c]</sup>
$(\mathbf{3})_1$		-127	195.5	153.2	121.3*	121.6*	123.4*	142.4	46.1	61.1	1.26	15 <sup>[c]</sup>
$(\mathbf{3})_1 \cdot \text{PMDTA}$		-127	195.8	152.5	121.0*	121.8*	123.7*	142.2	<sup>[i]</sup>	61.1	2.05	13.3 <sup>[c]</sup>
$(\mathbf{4})_1 \cdot \text{PMDTA}$		-127	195.8	148.4	120.8*	121.7*	122.9*	142.6	58.6	83.0	2.1	17 <sup>[c]</sup>
$(\mathbf{5})_1 \cdot \text{PMDTA}$		-147	197.0	148.0	121.3*	122.2*	124.3*	142.1	58.6	78.3	2.05	14.8 <sup>[c]</sup>
$(\mathbf{6})_1$		-125	195.6	152.9	121.1*	121.7*	123.6*	142.5	58.5	73.8	1.28	15
$(\mathbf{6})_1 \cdot \text{PMDTA}$		-125	195.7	152.2	121.0*	121.8*	123.7*	142.3	58.6	73.9	2.1	<sup>[k]</sup>
<b>Dimers</b>												
$(\text{PhLi})_2^{[\text{b}]}$	THF	-111	188.2	144.5	124.6	123.0	124.6	144.5	---	---	1.59	7.9 <sup>[j]</sup>
$(\mathbf{7})_2$		-141	186.6	157.3	123.7*	<sup>[i]</sup>	<sup>[i]</sup>	144.0	---	---	1.57	<sup>[k]</sup>
$(\mathbf{1})_2 (\mathbf{A})^{[\text{h}]}$		-132	188.8	152.2	123.9*	123.4*	125.0*	143.5	44.0, 48.1	72.0	1.81, 3.84	7.0 <sup>[j]</sup>
$(\mathbf{1})_2 (\mathbf{B})^{[\text{h}]}$		-132	188.4	151.9	123.9*	123.5*	125.1*	143.2	43.0, 47.3	71.8	2.61	7.0 <sup>[j]</sup>
$(\mathbf{1})_2 (\mathbf{C})^{[\text{h}]}$		-132	<sup>[i]</sup>	151.2	124.0*	123.2*	125.3*	143.0	<sup>[i]</sup>	72.4	2.90	<sup>[i]</sup>
$(\mathbf{2})_2 (\mathbf{A})$		-130	184.3	152.4	122.5*	124.0*	125.4*	144.1	44.2, 47.2	58.8	1.87, 1.96	7 <sup>[j]</sup>
$(\mathbf{4})_2 (\mathbf{B/C})$		-127	186.1	149.7	123.3*	123.5*	124.3*	143.1	58.9	83.6	2.38	8.1 <sup>[j]</sup>
$(\mathbf{5})_2 (\mathbf{B/C})$		-127	188.2	152.4	124.2*	122.9*	124.2*	143.2	58.7	77.7	1.74	8.1 <sup>[j]</sup>
$(\mathbf{6})_2 (\mathbf{X})^{[\text{m}]}$	$\text{Et}_2\text{O}$	-126	188.0	152.8	122.6*	124.9*	124.5*	144.0	55.5	<sup>[i]</sup>	1.67	<sup>[k]</sup>
$(\mathbf{6})_2 (\mathbf{Y})^{[\text{m}]}$	$\text{Et}_2\text{O}$	-126	186.8	153.7	122.4*	124.9*	124.5*	144.2	56.4	<sup>[i]</sup>	1.50	<sup>[k]</sup>
<b>Tetramers:</b>												
$(\text{PhLi})_4^{[\text{b}]}$	$\text{Et}_2\text{O}$	-106	174.0	143.8	126.3	125.5	126.3	143.8	---	---	2.39	5.1

\* Assignments not done <sup>[a]</sup> Reference: 0.3 M LiCl in methanol. <sup>[b]</sup> Ref. 1i. <sup>[c]</sup> 1:1:1 Triplet. <sup>[d]</sup> 2:1 THF/ $\text{Me}_2\text{O}$ . <sup>[e]</sup> 45:25:30 THF/ $\text{Me}_2\text{O}$ / $\text{Et}_2\text{O}$ . <sup>[f]</sup> 3:2 THF/ $\text{Et}_2\text{O}$ . <sup>[g]</sup> Calculated from a measured  $J_{\text{C-7Li}}$  coupling of 38.5 Hz. <sup>[h]</sup> 3:2:1 THF/ $\text{Me}_2\text{O}$ / $\text{Et}_2\text{O}$ . <sup>[i]</sup> Signal not found. <sup>[j]</sup> 1:2:3:2:1 quintet. <sup>[k]</sup> Splitting not resolved, coupling estimated from simulated spectra.

## Supplementary Materials References

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