

Solution Structures and Reactivities of the Mixed Aggregates Derived from  
*n*-Butyllithium and Vicinal Amino Alkoxides

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Supporting Information

- I.  $^6\text{Li}$  NMR spectra of 1:2 mixture of *n*-BuLi and (1*R*,2*S*)-LiOCH(Ph)CH(Me)N(CH<sub>2</sub>)<sub>4</sub> in THF/pentane at -110 °C showing aging effects.
- II.  $^6\text{Li}$  NMR spectra of solutions containing *n*-BuLi and (1*R*,2*S*)-LiOCH(Ph)CH(Me)N(CH<sub>2</sub>)<sub>4</sub> (**5b**)
- III.  $^6\text{Li}$  and  $^{13}\text{C}$  NMR spectra of 1:2 mixtures of *n*-BuLi and (1*R*,2*S*)-LiOCH(Ph)CH(Me)N(CH<sub>2</sub>)<sub>4</sub> (**5b**)
- IV.  $^6\text{Li}$ ,  $^{13}\text{C}$ , and  $^{15}\text{N}$  NMR spectra of 2:1 mixtures of *n*-BuLi and (1*R*,2*S*)-LiOCH(Ph)CH(Me)N(CH<sub>2</sub>)<sub>4</sub> (**5b**)
- V.  $^6\text{Li}$ ,  $^{15}\text{N}$ -HMQC spectrum of a 2:1 mixture of *n*-BuLi and (1*R*,2*S*)-LiOCH(Ph)CH(Me)N(CH<sub>2</sub>)<sub>4</sub> (**5b**) showing Li-N connectivities
- VI.  $^6\text{Li}$  NMR spectra of mixtures of *n*-BuLi and (1*R*,2*S*)-LiOCH(Ph)CH(Ph)NMe<sub>2</sub> (**7b**)
- VII.  $^1\text{J}(^6\text{Li}, ^{13}\text{C})$ -resolved  $^6\text{Li}$  NMR spectrum of a 2:1 mixture of *n*-BuLi and (1*R*,2*S*)-LiOCH(Ph)CH(Ph)NMe<sub>2</sub> (**7b**)
- VIII.  $^6\text{Li}$ ,  $^{13}\text{C}$ -HMQC spectrum of a 2:1 mixture of *n*-BuLi and (1*R*,2*S*)-LiOCH(Ph)CH(Ph)NMe<sub>2</sub> (**7b**)
- IX.  $^6\text{Li}$  NMR spectra of mixtures of *n*-BuLi and (1*R*,2*S*)-LiOCH(Ph)CH(Ph)N(CH<sub>2</sub>)<sub>4</sub> (**6b**)
- X.  $^1\text{J}(^6\text{Li}, ^{13}\text{C})$ -resolved  $^6\text{Li}$  spectrum of a 2:1 mixture of *n*-BuLi and (1*R*,2*S*)-LiOCH(Ph)CH(Ph)N(CH<sub>2</sub>)<sub>4</sub> (**6b**)
- XI.  $^6\text{Li}$ ,  $^{13}\text{C}$ -HMQC spectrum of a 2:1 mixture of *n*-BuLi and (1*R*,2*S*)-LiOCH(Ph)CH(Ph)N(CH<sub>2</sub>)<sub>4</sub> (**6b**)



Table A3.1.  ${}^6\text{Li}$ ,  ${}^{13}\text{C}$  and  ${}^{15}\text{N}$  NMR spectral data<sup>a</sup>

Compound	$\delta {}^6\text{Li}$ (mult, $J_{\text{Li-C}}$ ) (mult, $J_{\text{Li-N}}$ )	$\delta {}^{13}\text{C}$ (mult, $J_{\text{C-Li}}$ )	$\delta {}^{15}\text{N}$ (mult, $J_{\text{Li-N}}$ )
<b>8</b>	2.11 (t, 8.2)	12.32 (qn, 7.9)	
<b>9</b>	1.66 (qt, 5.4)	10.02 (br m)	
<b>10</b>	1.74 (qt, 6.2)	10.21 (br m)	
	0.94 (t, 6.0)		
<b>12</b>	2.25 (t, 6.1) (d, 2.6)	9.82 (br m)	51.47 <sup>b</sup>
	0.96 (d, 4.8) (s)		
<b>15</b>	2.03 (qt, 6.2) (s)	9.16 (br m)	51.34 <sup>b</sup>
	1.97 (t, 6.0) (d, 2.7)	10.01 (br m)	
	1.15 (t, 5.5) (s)	10.06 (br m)	
	1.13 (t, 5.5) (s)		
<b>20a</b>	2.19 (t, 6.1)	9.79 (br m)	
	2.13 (qt, 5.4)	10.11 (br m)	
	1.17 (t, 6.0)	10.39 (br m)	
	1.01 (t, 5.6)		
<b>21a</b>	2.51 (t, 6.1)	10.33 (br m)	
	1.00 (d, 5.0)		
<b>20b</b>	2.13 (t, 6.1)	9.59 (br m)	
	2.07 (qt, 5.6)	10.13 (br m)	
	1.15 (t, 6.2)	10.13 (br m)	
	0.92 (t, 5.9)		
<b>21b</b>	2.45 (t, 6.2)	10.27 (br m)	
	0.89 (d, 4.9)		

<sup>a</sup> The  $J_{\text{C-Li}}$  coupling constants were routinely measured from the  ${}^1J({}^6\text{Li}, {}^{13}\text{C})$ -resolved spectrum. The multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, qt = quartet, qn = quintet, br m = broad multiplet. The  ${}^6\text{Li}$ ,  ${}^{13}\text{C}$  and  ${}^{15}\text{N}$  chemical shifts are reported relative to 0.3 M  ${}^6\text{LiCl}/\text{MeOH}$  ( $\delta {}^6\text{Li} = 0.0$  ppm), neat dimethylethylamine ( $\delta {}^{15}\text{N} = 25.7$  ppm), and the methyl group of neat toluene ( $\delta {}^{13}\text{C} = 20.4$  ppm) at  $-90$  °C, respectively. All  $J$  values are reported in Hertz. <sup>b</sup>Poor resolution stemmed from overlapping resonances.

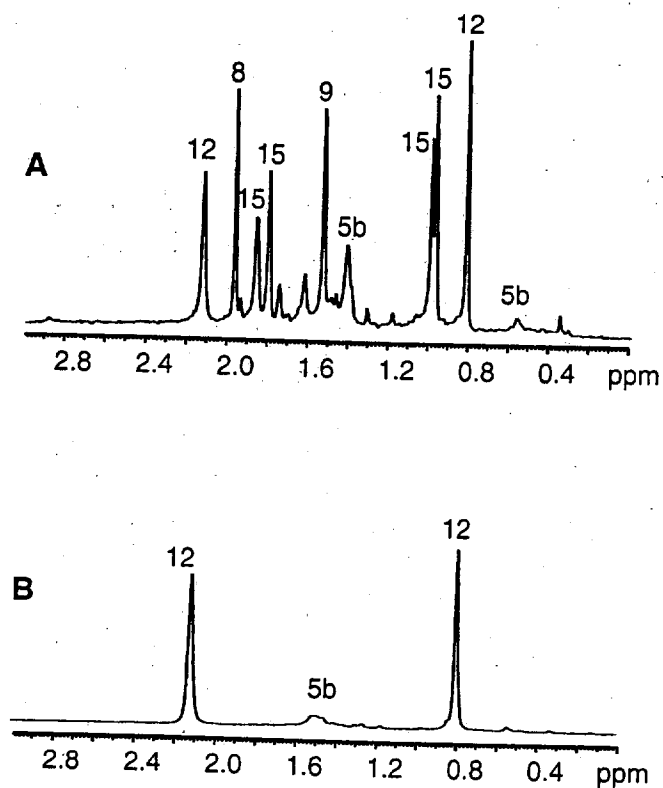


Figure I.  $^6\text{Li}$  NMR spectra of a solution containing 1:2  $[\text{}^6\text{Li}]n\text{-BuLi}$  and  $[\text{}^6\text{Li}](1R,2S)\text{-LiOCH(Ph)CH(Me)N(CH}_2)_4$  ( $\text{R}^*\text{OLi}$ ; **5b**) (0.15 M total lithium titer) in 1:1 THF/pentane at  $-110\text{ }^\circ\text{C}$  showing the oligomers of **5b**,  $n\text{-BuLi}$  dimer and tetramer (**8** and **9**), 2:2  $n\text{-BuLi}/\text{R}^*\text{OLi}$  mixed tetramer **12**, and 3:1  $n\text{-BuLi}/\text{R}^*\text{OLi}$  tetramer **15**: (A) spectrum taken without sample warming; (B) spectrum of the same sample recorded at  $-110\text{ }^\circ\text{C}$  after warming to  $0\text{ }^\circ\text{C}$  for 5 min.

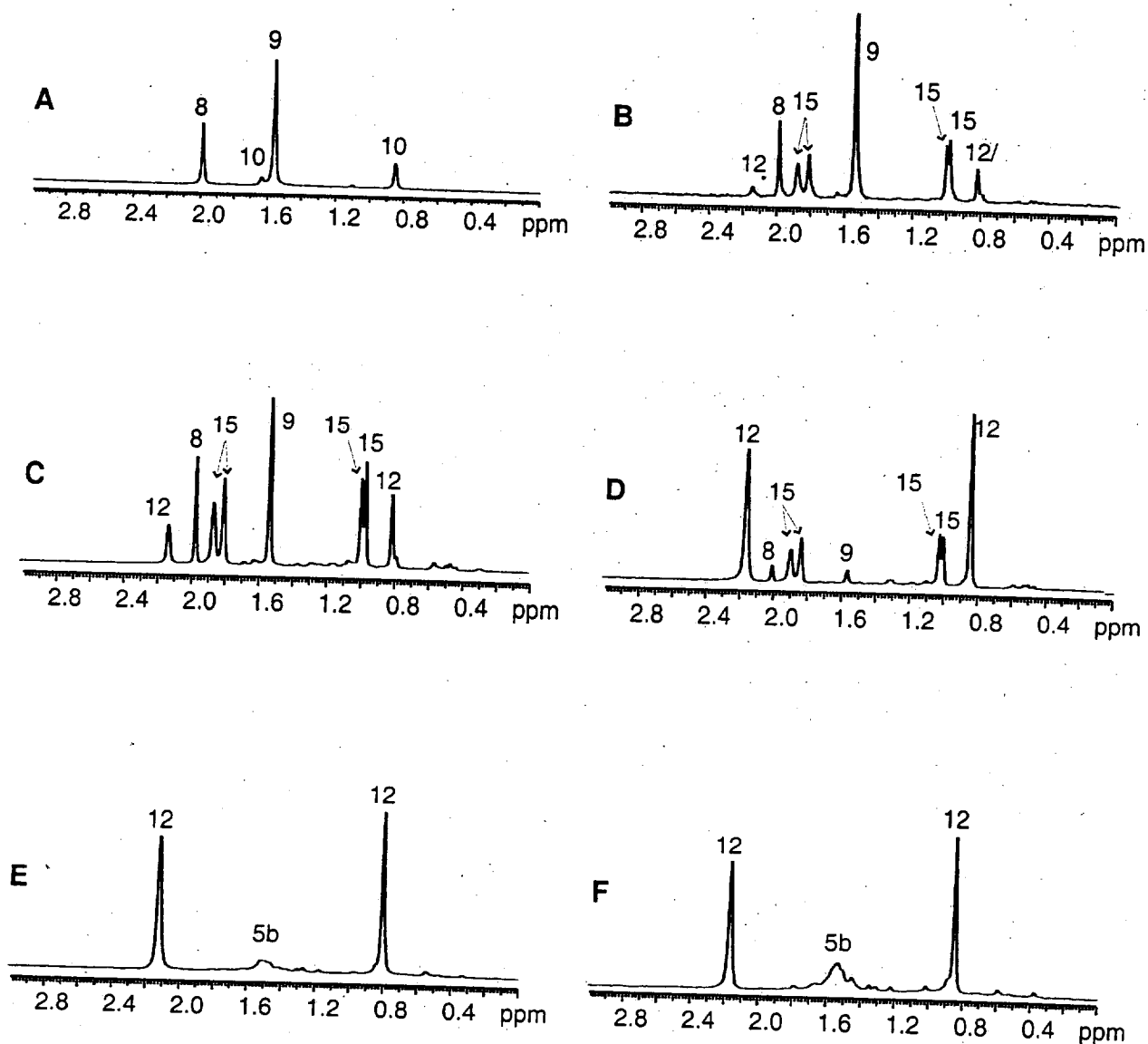


Figure II.  ${}^6\text{Li}$  NMR spectra recorded on solutions containing  $[\text{}^6\text{Li}]n\text{-BuLi}$  and  $[\text{}^6\text{Li}](1R,2S)\text{-LiOCH(Ph)CH(Me)N(CH}_2)_4$  ( $\text{R}^*\text{OLi}$ ; 5b) in 1:1 THF:pentane (0.15 M total lithium titer) at  $-110\text{ }^\circ\text{C}$  showing  $n\text{-BuLi}$  dimer and tetramer (8 and 9), 3:1  $n\text{-BuLi}/\text{R}^*\text{OLi}$  mixed tetramer 15, and 2:2  $n\text{-BuLi}/\text{R}^*\text{OLi}$  tetramer 12. (A)  $n\text{-BuLi}$ ; (B) 5:1  $n\text{-BuLi}/\text{R}^*\text{OLi}$ ; (C) 3:1  $n\text{-BuLi}/\text{R}^*\text{OLi}$ ; (D) 1:1  $n\text{-BuLi}/\text{R}^*\text{OLi}$ ; (E) 1:2  $n\text{-BuLi}/\text{R}^*\text{OLi}$ ; (F) 1:5  $n\text{-BuLi}/\text{R}^*\text{OLi}$ .

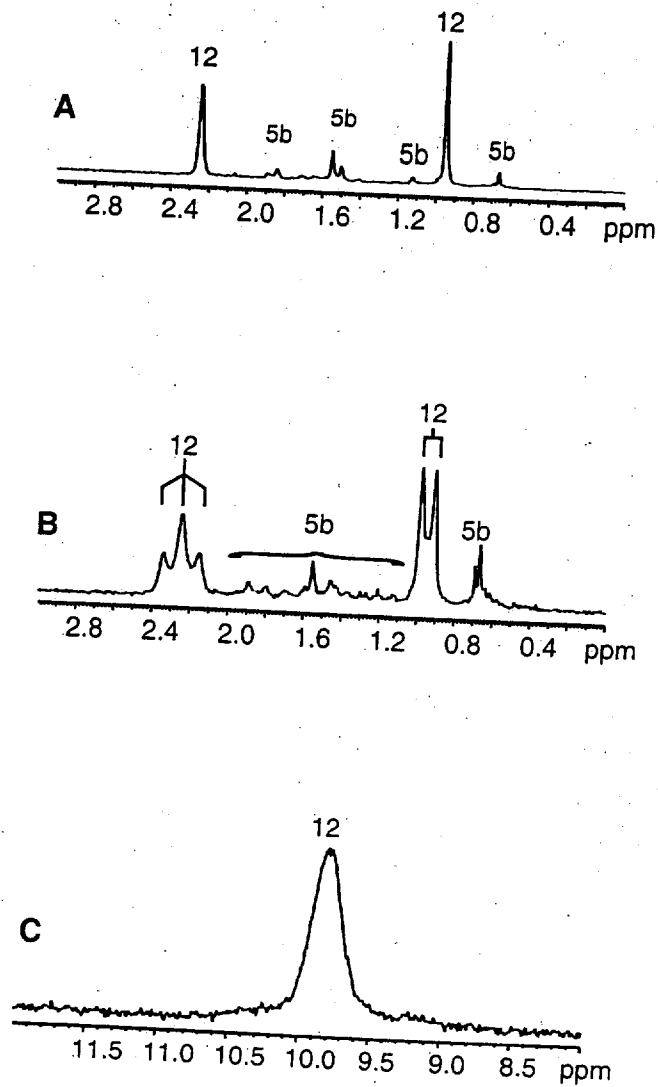


Figure III.  $^6\text{Li}$  and  $^{13}\text{C}$  NMR spectra recorded on solutions containing 1:2 *n*-BuLi and (1*R*,2*S*)-LiOCH(Ph)CH(Me)N(CH<sub>2</sub>)<sub>4</sub> (R\*OLi; 5b) (0.15 M total lithium titer) in 1:5 THF/pentane at -110 °C showing 2:2 mixed tetramer 12 and oligomers of 5b. (A)  $^6\text{Li}$  NMR spectrum of 1:2 [ $^6\text{Li}$ ]*n*-BuLi/[ $^6\text{Li}$ ]5b; (B)  $^6\text{Li}$  NMR spectrum of 1:2 [ $^6\text{Li}$ , $^{13}\text{C}$ ]*n*-BuLi/[ $^6\text{Li}$ ]5b; (C)  $^{13}\text{C}$  NMR spectrum of [ $^6\text{Li}$ ]*n*-BuLi/[ $^6\text{Li}$ ]5b.

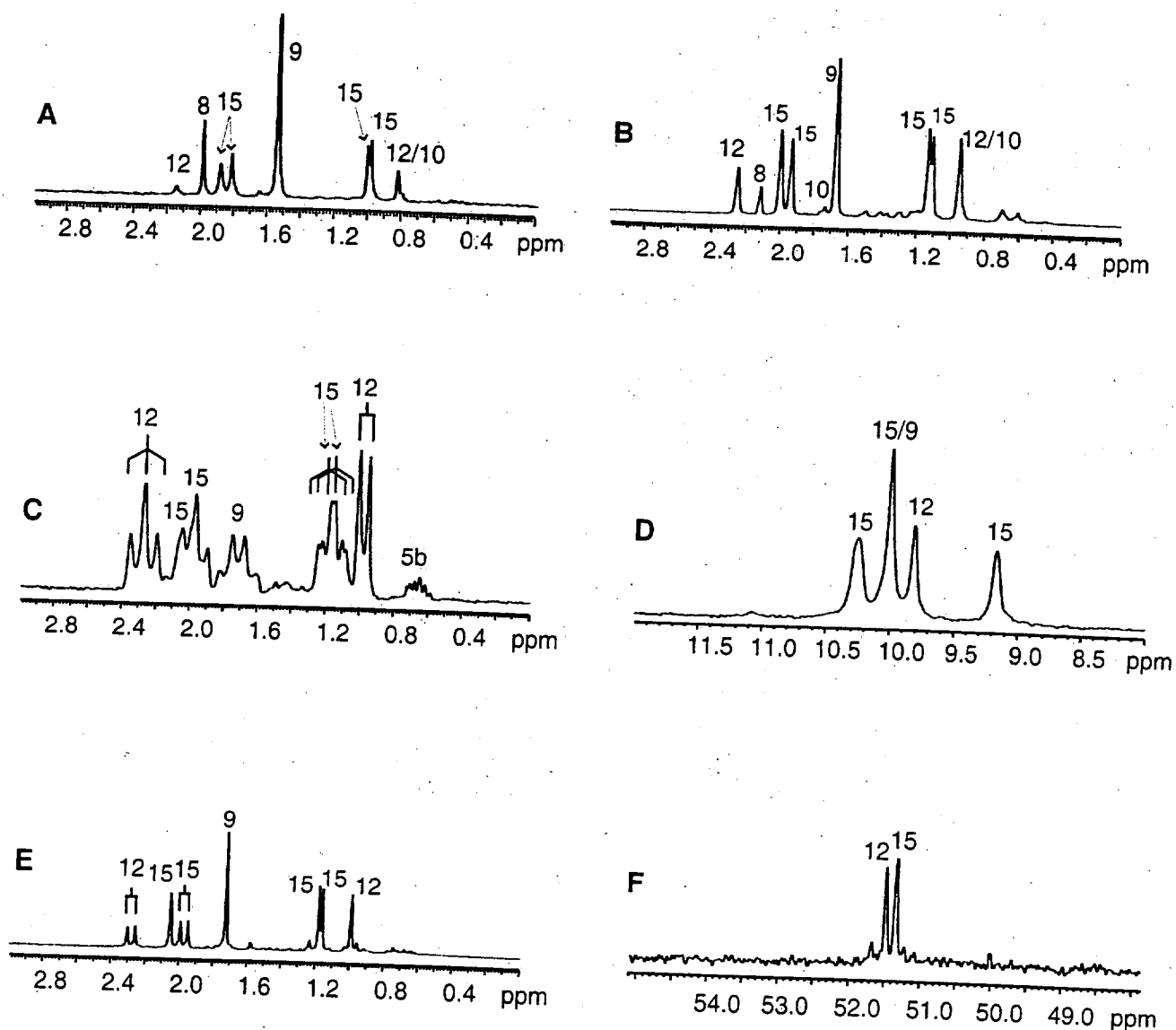


Figure IV.  $^6\text{Li}$ ,  $^{13}\text{C}$ , and  $^{15}\text{N}$  NMR spectra recorded on solutions containing  $n\text{-BuLi}$  and  $(1R,2S)\text{-LiOCH(Ph)CH(Me)N(CH}_2)_4$  ( $\text{R}^*\text{OLi}$ ; **5b**) (0.15 M total lithium titer) in 1:5 THF/pentane at  $-110\text{ }^\circ\text{C}$  showing  $n\text{-BuLi}$  tetramer **9**, 3:1  $n\text{-BuLi}/\text{R}^*\text{OLi}$  mixed tetramer **15**, and 2:2  $n\text{-BuLi}/\text{R}^*\text{OLi}$  tetramer **12**. (A)  $^6\text{Li}$  NMR spectrum of 5:1 [ $^6\text{Li}$ ] $n\text{-BuLi}$  and [ $^6\text{Li}$ ]**5b**; (B)  $^6\text{Li}$  NMR spectrum of 2:1 [ $^6\text{Li}$ ] $n\text{-BuLi}$  and [ $^6\text{Li}$ ]**5b**; (C)  $^6\text{Li}$  NMR spectrum of 2:1 [ $^6\text{Li},^{13}\text{C}$ ] $n\text{-BuLi}$  and [ $^6\text{Li}$ ]**5b**; (D)  $^{13}\text{C}$ [ $^6\text{Li}$ ] NMR spectrum of 2:1 [ $^6\text{Li},^{13}\text{C}$ ] $n\text{-BuLi}$  and [ $^6\text{Li}$ ]**5b**; (E)  $^6\text{Li}$  NMR spectrum of 2:1 [ $^6\text{Li}$ ] $n\text{-BuLi}$  and [ $^6\text{Li},^{15}\text{N}$ ]**5b**; (F)  $^{15}\text{N}$ [ $^6\text{Li}$ ] NMR spectrum of 2:1 [ $^6\text{Li}$ ] $n\text{-BuLi}$  and [ $^6\text{Li}$ ]**5b**.

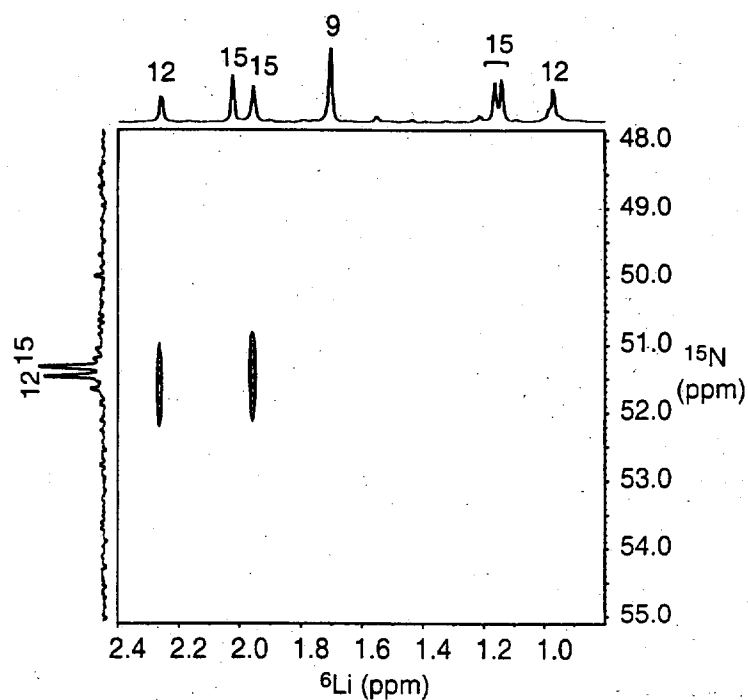


Figure V.  ${}^6\text{Li}$ ,  ${}^{15}\text{N}$ -HMQC spectrum recorded on a solution containing 2:1  $[{}^6\text{Li}]n\text{-BuLi}$  and  $[{}^6\text{Li}, {}^{15}\text{N}](1R,2S)\text{-LiOCH(Ph)CH(Me)N(CH}_2)_4$  (**5b**) (0.15 total lithium titer) in 1:5 THF/pentane at  $-110\text{ }^\circ\text{C}$

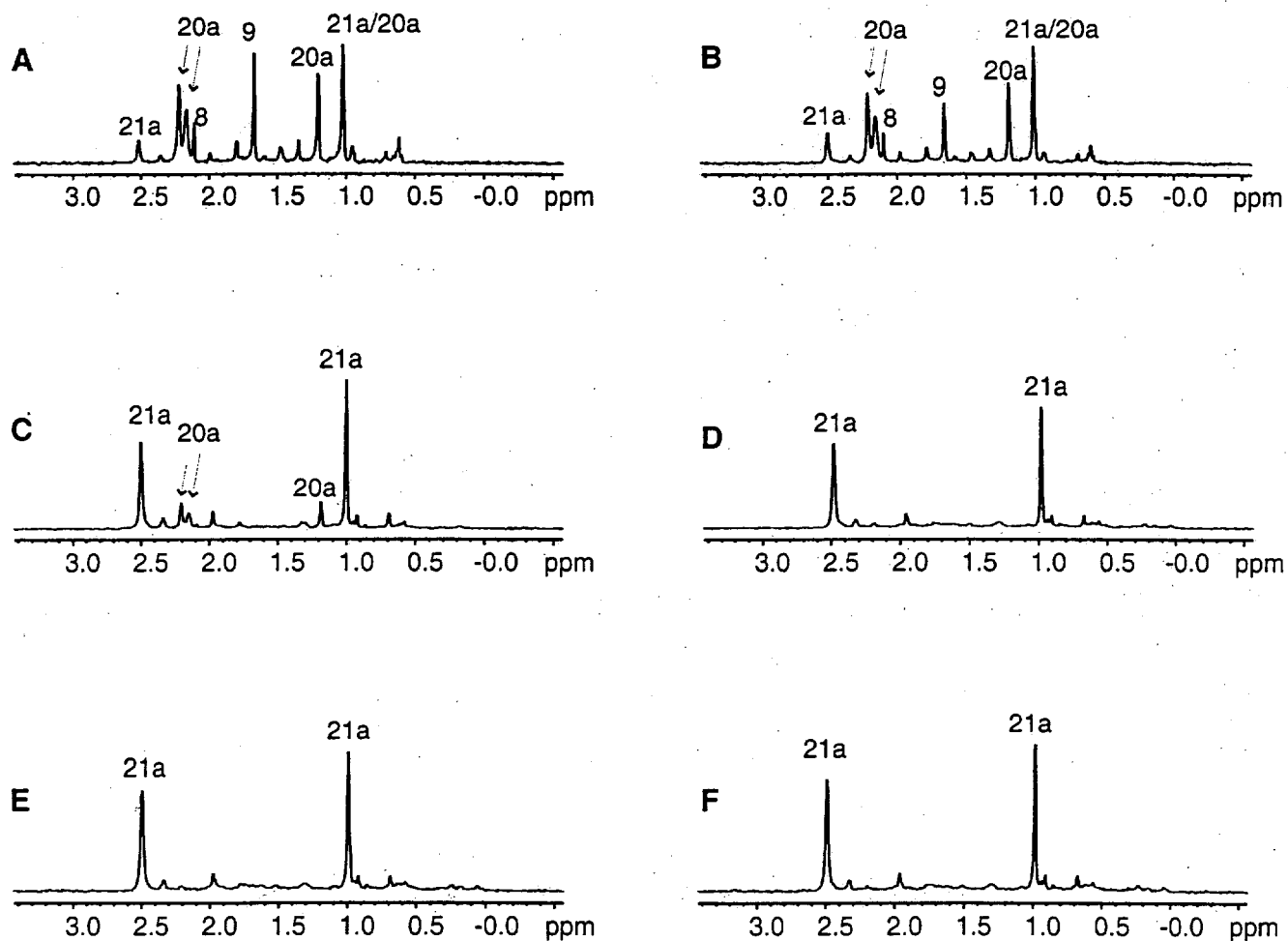


Figure VI.  $^6\text{Li}$  NMR spectra recorded on solutions containing  $[\text{}^6\text{Li}]n\text{-BuLi}$  and  $[\text{}^6\text{Li}](1R,2S)\text{-LiOCH(Ph)CH(Ph)NMe}_2$  (**7b**) (0.15 M total lithium titer) in 1:2 THF/pentane at  $-110\text{ }^\circ\text{C}$  showing  $n\text{-BuLi}$  dimer and tetramer (**8** and **9**), 2:2  $n\text{-BuLi}/\text{R}^*\text{OLi}$  mixed tetramer (**21a**), and 3:1  $n\text{-BuLi}/\text{ROLi}$  tetramer (**20a**). (A) 5:1  $[\text{}^6\text{Li}]n\text{-BuLi}/[\text{}^6\text{Li}]\text{7b}$ ; (B) 3:1  $[\text{}^6\text{Li}]n\text{-BuLi}/[\text{}^6\text{Li}]\text{7b}$ ; (C) 2:1  $[\text{}^6\text{Li}]n\text{-BuLi}/[\text{}^6\text{Li}]\text{7b}$ ; (D) 1:2  $[\text{}^6\text{Li}]n\text{-BuLi}/[\text{}^6\text{Li}]\text{7b}$ . (E) 1:2  $[\text{}^6\text{Li}]n\text{-BuLi}/[\text{}^6\text{Li}]\text{7b}$ . (F) 1:5  $[\text{}^6\text{Li}]n\text{-BuLi}/[\text{}^6\text{Li}]\text{7b}$ .

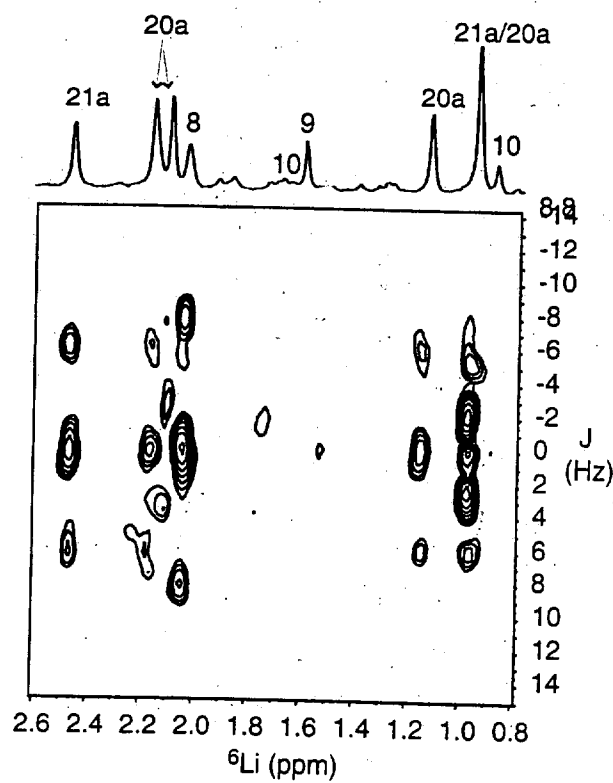


Figure VII.  $1J(^6\text{Li},^{13}\text{C})$ -resolved  $^6\text{Li}$  NMR spectrum recorded on a solution containing 2:1  $[^6\text{Li},^{13}\text{C}]n\text{-BuLi}$  and  $[^6\text{Li}] (1R,2S)\text{-LiOCH(Ph)CH(Ph)NMe}_2$  (**7b**) (0.15 M total lithium titer) in 1:2 THF/pentane at  $-110^\circ\text{C}$ .

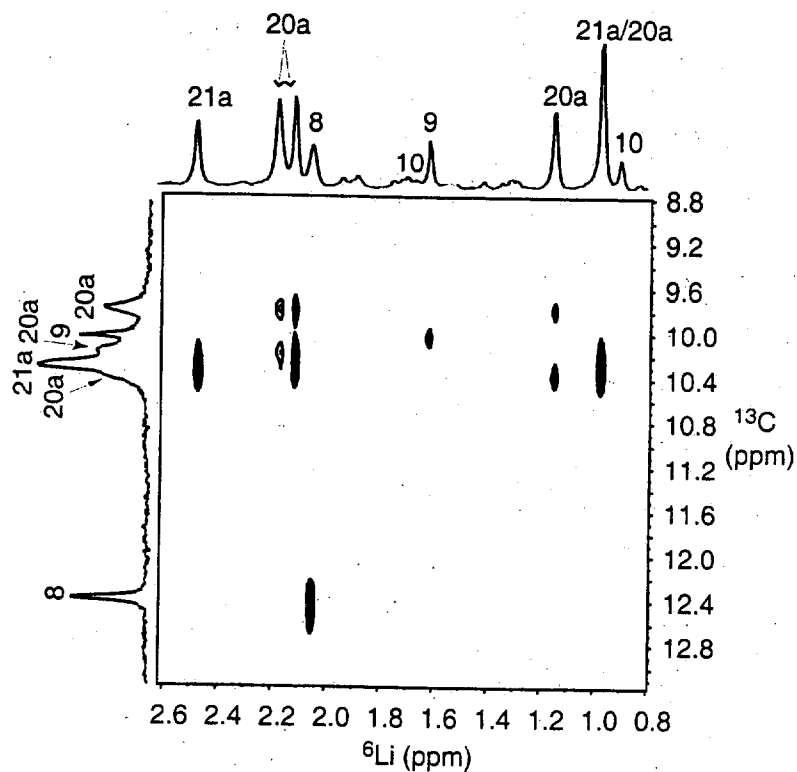


Figure VIII.  ${}^6\text{Li}, {}^{13}\text{C}$ -HMQC spectrum recorded on a solution containing 2:1  $[{}^6\text{Li}, {}^{13}\text{C}]n$ -BuLi and  $[{}^6\text{Li}]7b$  (0.15 M total lithium titer) in 1:2 THF/pentane at  $-110\text{ }^\circ\text{C}$  showing  $n$ -BuLi dimer 8 and tetramer 9, 3:1  $n$ -BuLi/ $R^*OLi$  mixed tetramer 20a, and 2:2  $n$ -BuLi/ $R^*OLi$  mixed tetramer 21a. The  ${}^6\text{Li}\{{}^{13}\text{C}\}$  and  ${}^{13}\text{C}\{{}^6\text{Li}\}$  NMR spectra are shown on top and left, respectively.

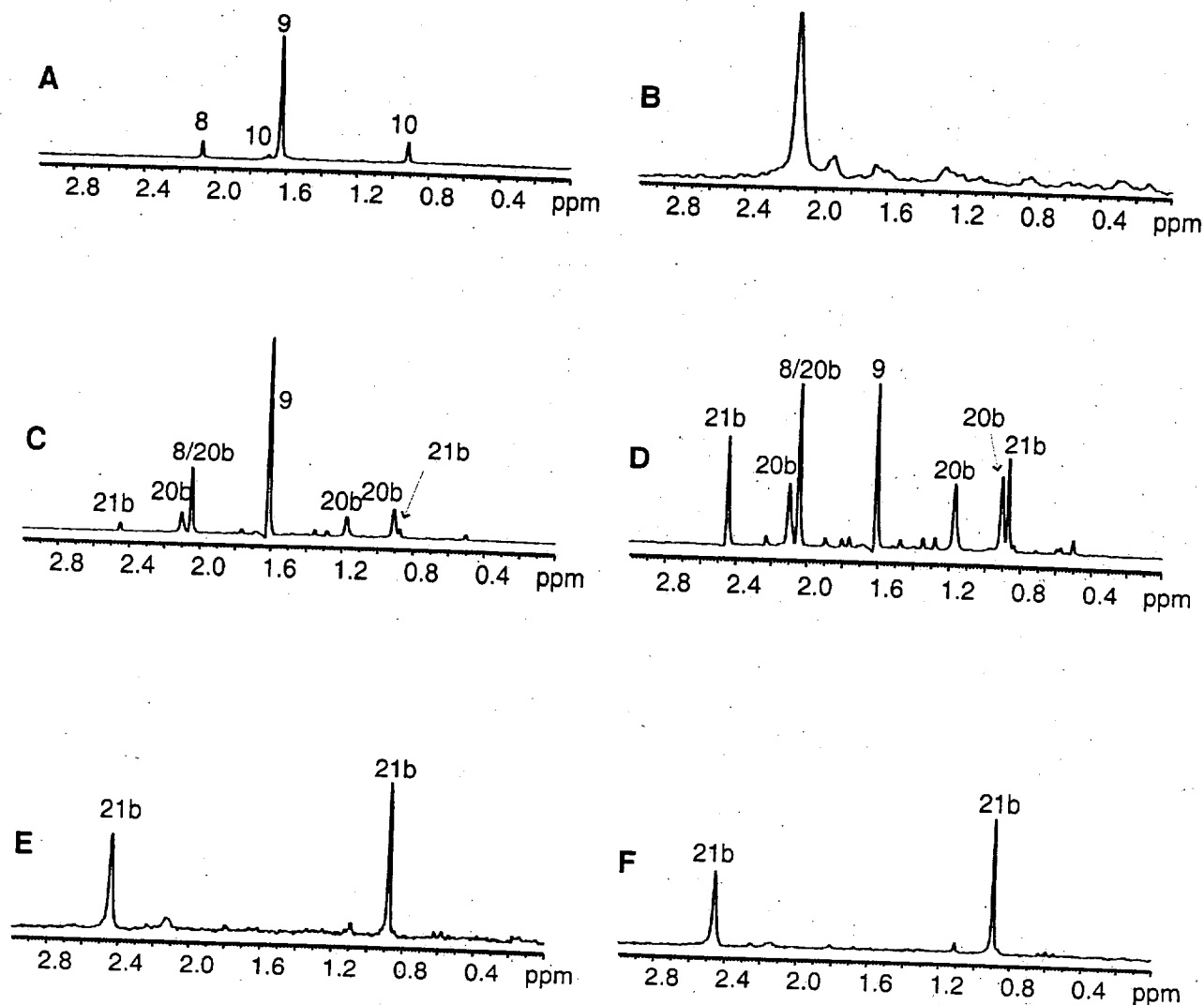


Figure IX.  $^6\text{Li}$  NMR spectra recorded on solutions containing  $[\text{}^6\text{Li}]n\text{-BuLi}$  and  $[\text{}^6\text{Li}](1R,2S)\text{-LiOCH(Ph)CH(Ph)N(CH}_2)_4$  (**6b**) (0.15 M total lithium titer) in 1:2 THF/pentane at  $-95^\circ\text{C}$  showing  $n\text{-BuLi}$  dimer **8** and tetramer **9**, 2:2  $n\text{-BuLi}/\text{ROLi}$  mixed tetramer **21b**, and 3:1  $n\text{-BuLi}/\text{ROLi}$  tetramer **20b**. (A) spectrum of  $[\text{}^6\text{Li}]n\text{-BuLi}$ ; (B) spectrum of  $[\text{}^6\text{Li}]\mathbf{6b}$ ; (C) spectrum of 5:1  $[\text{}^6\text{Li}]n\text{-BuLi}/[\text{}^6\text{Li}]\mathbf{6b}$ ; (D) spectrum of 3:1  $[\text{}^6\text{Li}]n\text{-BuLi}/[\text{}^6\text{Li}]\mathbf{6b}$ ; (E) spectrum of 1:1  $[\text{}^6\text{Li}]n\text{-BuLi}/[\text{}^6\text{Li}]\mathbf{6b}$ ; (F) spectrum of 1:3  $[\text{}^6\text{Li}]n\text{-BuLi}/[\text{}^6\text{Li}]\mathbf{6b}$ .

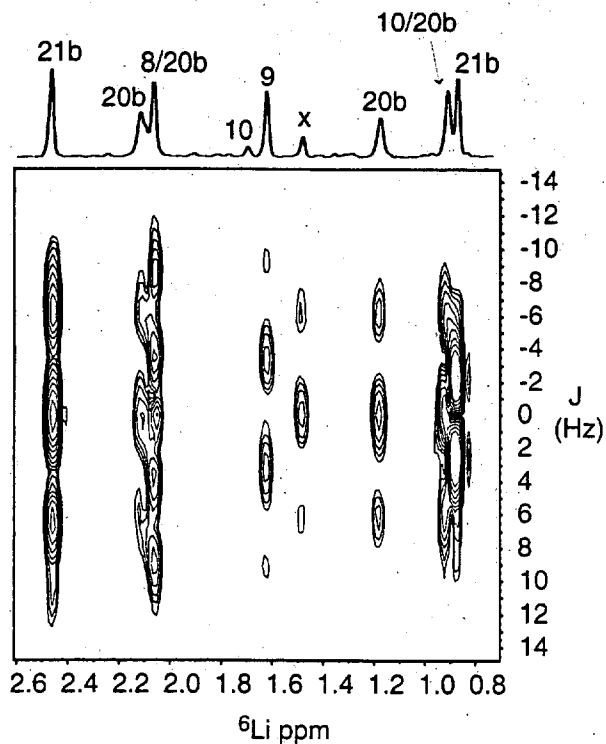


Figure X.  $1J(^6\text{Li},^{13}\text{C})$ -resolved  $^6\text{Li}$  spectrum recorded on a solution containing 2:1  $[^6\text{Li},^{13}\text{C}]n\text{-BuLi}$  and  $[^6\text{Li}](1R,2S)\text{-LiOCH(Ph)CH(Ph)N(CH}_2)_4$  (**6b**) (0.15 M total lithium titer) in 1:2 THF/pentane at  $-95\text{ }^\circ\text{C}$ .

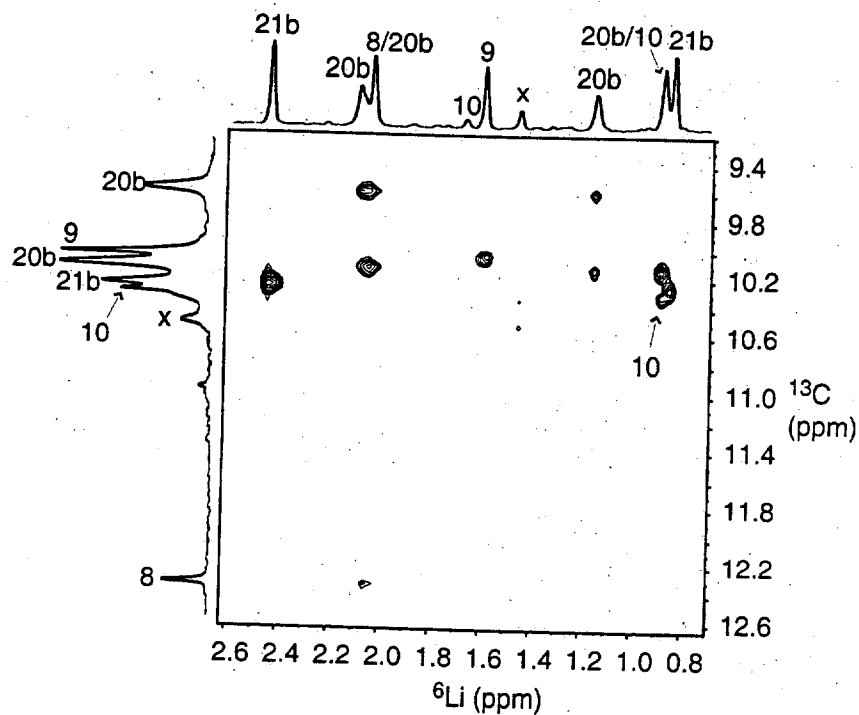


Figure XI.  ${}^6\text{Li}, {}^{13}\text{C}$ -HMQC spectrum recorded on a solution containing 2:1  $[{}^6\text{Li}, {}^{13}\text{C}]n\text{-BuLi}$  and  $[{}^6\text{Li}](1R,2S)\text{-LiOCH(Ph)CH(Ph)N(CH}_2)_4$  (**6b**) (0.15 M total lithium titer) in 1:2 THF/pentane at  $-95\text{ }^\circ\text{C}$  showing  $n\text{-BuLi}$  dimer **8** and tetramer **9**, 3:1  $n\text{-BuLi}/R^*\text{OLi}$  mixed tetramer **20b**, and 2:2  $n\text{-BuLi}/R^*\text{OLi}$  mixed tetramer **21b**. The  ${}^6\text{Li}\{{}^{13}\text{C}\}$  and  ${}^{13}\text{C}\{{}^6\text{Li}\}$  NMR spectra are shown on top and left, respectively.

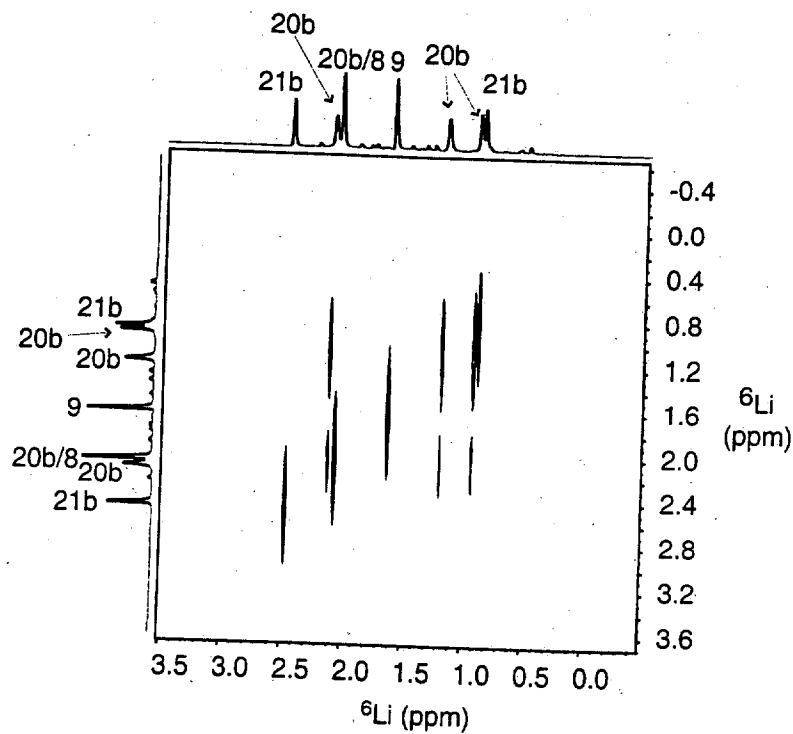


Figure XII.  ${}^6\text{Li}, {}^6\text{Li}$ -EXSY spectrum recorded on a solution containing 2:1  $[{}^6\text{Li}]n\text{-BuLi}$  and  $[{}^6\text{Li}](1R,2S)\text{-LiOCH(Ph)CH(Ph)N(CH}_2)_4$  (**6b**) (0.15 M total lithium titer) in 1:2 THF/pentane at  $-95\text{ }^\circ\text{C}$ . The spectrum was recorded with a mixing time of 2 seconds.

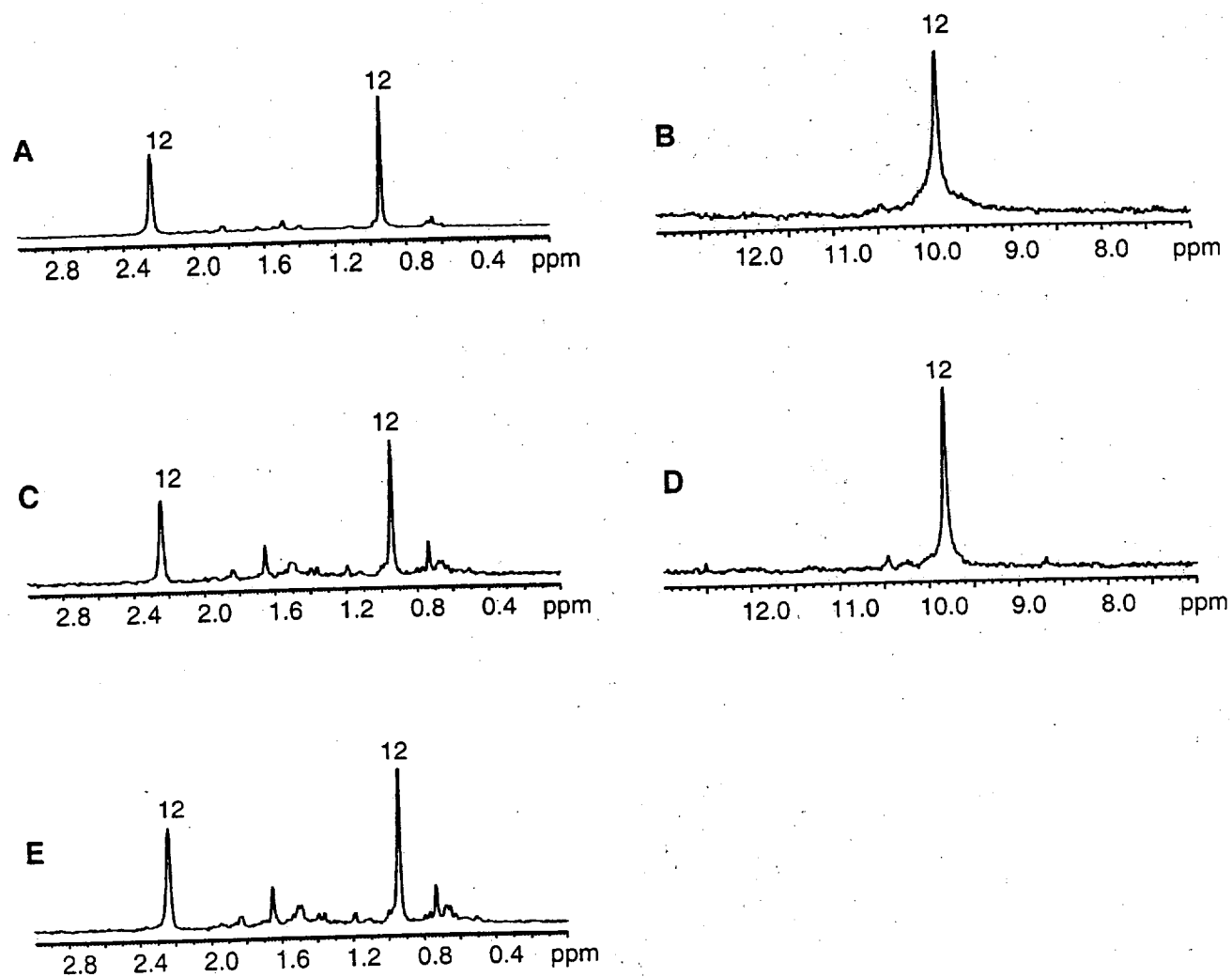


Figure XIII.  ${}^6\text{Li}$  and  ${}^{13}\text{C}$  NMR spectra of 1:1.5 mixtures of  $[{}^6\text{Li},{}^{13}\text{C}]n\text{-BuLi}$  and  $[{}^6\text{Li}](1R,2S)\text{-LiOCH(Ph)CH(Ph)N(CH}_2)_4$  ( $R^*\text{OLi}$ ; **5b**) (0.15 M total lithium titer) in 1:5 THF/pentane at  $-110\text{ }^\circ\text{C}$ . (A)  ${}^6\text{Li}\{{}^{13}\text{C}\}$  NMR spectrum; (B)  ${}^{13}\text{C}\{{}^6\text{Li}\}$  NMR spectrum; (C)  ${}^6\text{Li}\{{}^{13}\text{C}\}$  NMR spectrum of a 1:1.5 mixture  $[{}^6\text{Li},{}^{13}\text{C}]n\text{-BuLi}/[{}^6\text{Li}]\mathbf{5b}$  with added PhCHO (0.5 eq/ $n\text{-BuLi}$ ); (D)  ${}^{13}\text{C}$  NMR spectrum of the sample in C; (E)  ${}^6\text{Li}$  NMR spectrum after aging at  $0\text{ }^\circ\text{C}$  for 3 min.

Table 2. Enantiomeric ratios (er) vs. equiv. of PhCHO for the (1*R*,2*S*)-LiOCH(Ph)CH(Me)N(CH<sub>2</sub>)<sub>4</sub> (R\*OLi; **5b**)-mediated addition of *n*-BuLi to PhCHO at -78 °C.<sup>a</sup>

PhCHO (equiv. per <i>n</i> -BuLi)	<i>n</i> -BuLi/R*OLi	selectivity (er)
0.20	1 : 2	2.5
0.50	1 : 2	2.4
0.70	1 : 2	2.4
0.90	1 : 2	2.4

<sup>a</sup>Protocol used was the same as described in the Experimental section.

Table 3. Enantiomeric ratios (er) vs. equiv. of PhCHO for the (1*R*,2*S*)-LiOCH(Ph)CH(Ph)N(CH<sub>2</sub>)<sub>4</sub> (R\*OLi; **7b**)-mediated addition of *n*-BuLi to PhCHO at -78 °C.

PhCHO (equiv. per <i>n</i> -BuLi)	<i>n</i> -BuLi/R*OLi	selectivity (er)
0.20	1 : 1.5	10
0.45	1 : 1.5	8.5
0.90	1 : 1.5	10

<sup>a</sup>Protocol used was the same as described in the Experimental section.