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

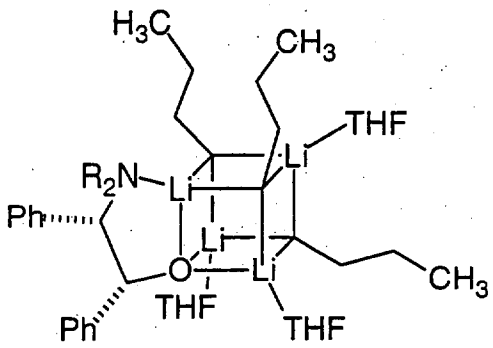
Xiufeng Sun, Mark D. Winemiller, Bosong Xiang, and David B. Collum*
Department of Chemistry and Chemical Biology
Baker Laboratory, Cornell University
Ithaca, New York, 14853-1301

Supporting Information

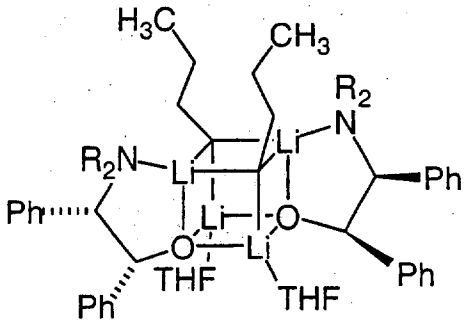
XII. ^{6}Li and ^{13}C NMR spectra of 1:1.5 mixtures of *n*-BuLi and (*1R,2S*)-LiOCH(Ph)CH(Me)N$(CH_2)_4$ (**5b**) with added PhCHO.

XIII. Enantiomeric ratios (er) of 1-phenyl-1-pentanol vs. equiv of PhCHO for the addition of *n*-BuLi to PhCHO.

XIV. Structures that do not appear in the primary text are numbered as follows:



20a: NR2 = NMe_2
20b: NR2 = $N(CH_2)_4$



21a: NR2 = NMe_2
21b: NR2 = $N(CH_2)_4$

Table A3.1. ^{6}Li, ^{13}C and ^{15}N NMR spectral data[a]

Compound	δ ^{6}Li (mult, J_{Li-C}) (mult, J_{Li-N}))	δ ^{13}C (mult, J_{C-Li})	δ ^{15}N (mult, J_{Li-N})
8	2.11 (t, 8.2)	12.32 (qn, 7.9)	
9	1.66 (qt, 5.4)	10.02 (br m)	
10	1.74 (qt, 6.2)	10.21 (br m)	
	0.94 (t, 6.0)		
12	2.25 (t, 6.1) (d, 2.6)	9.82 (br m)	51.47[b]
	0.96 (d, 4.8) (s)		
15	2.03 (qt, 6.2) (s)	9.16 (br m)	51.34[b]
	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)		
20a	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)		
21a	2.51 (t, 6.1)	10.33 (br m)	
	1.00 (d, 5.0)		
20b	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)		
21b	2.45 (t, 6.2)	10.27 (br m)	
	0.89 (d, 4.9)		

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

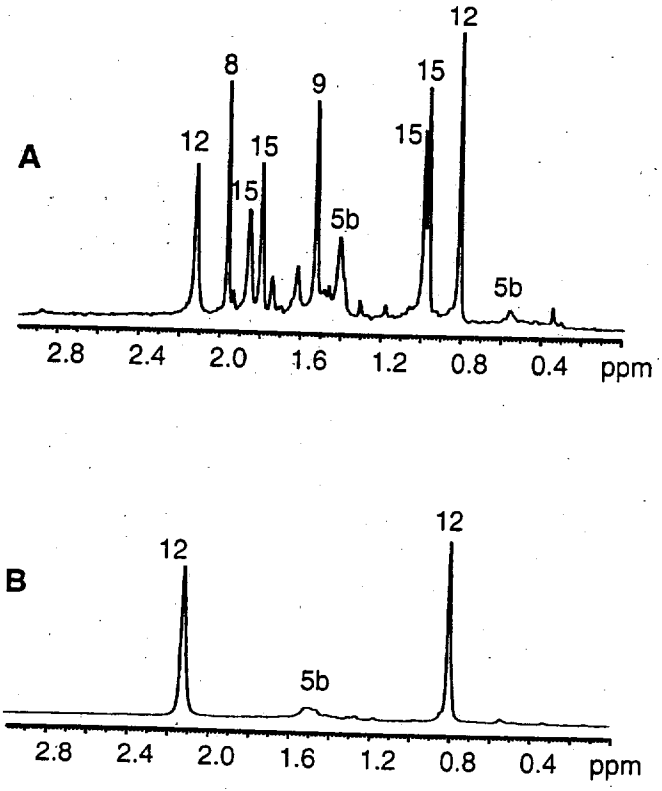


Figure I. ^{6}Li NMR spectra of a solution containing 1:2 [^{6}Li]*n*-BuLi and [^{6}Li](*1R,2S*)-LiOCH(Ph)CH(Me)N(CH_2)$_4$ (R*OLi; **5b**) (0.15 M total lithium titer) in 1:1 THF/pentane at -110 °C showing the oligomers of **5b**, *n*-BuLi dimer and tetramer (**8** and **9**), 2:2 *n*-BuLi/R*OLi mixed tetramer **12**, and 3:1 *n*-BuLi/R*OLi tetramer **15**: (**A**) spectrum taken without sample warming; (**B**) spectrum of the same sample recorded at -110 °C after warming to 0 °C for 5 min.

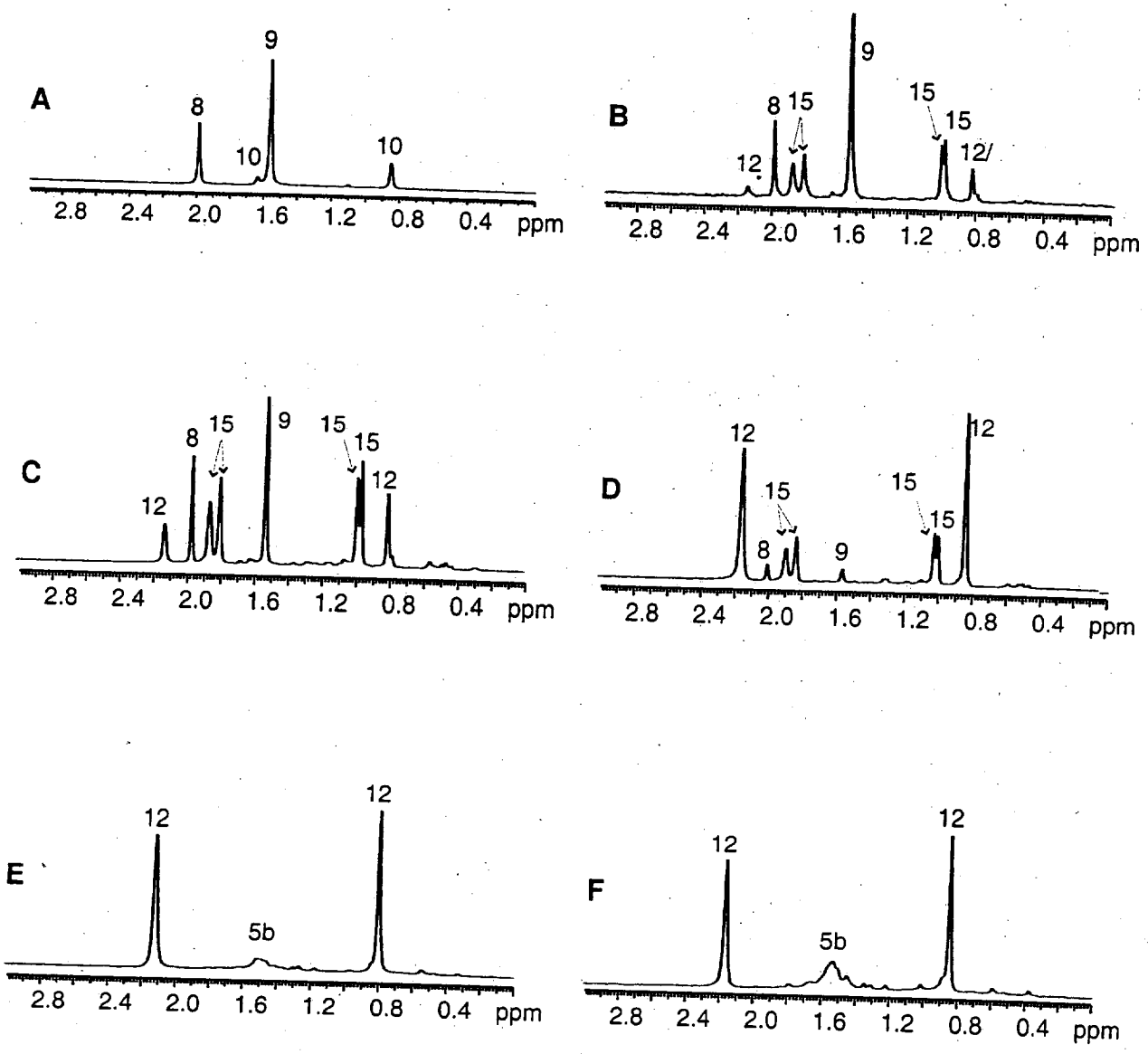


Figure II. ^{6}Li NMR spectra recorded on solutions containing [^{6}Li]*n*-BuLi and [^{6}Li](*1R,2S*)-LiOCH(Ph)CH(Me)N(CH_2)$_4$ (R*OLi; **5b**) in 1:1 THF:pentane (0.15 M total lithium titer) at -110 °C showing *n*-BuLi dimer and tetramer (**8** and **9**), 3:1 *n*-BuLi/R*OLi mixed tetramer **15**, and 2:2 *n*-BuLi/R*OLi tetramer **12**. (**A**) *n*-BuLi; (**B**) 5:1 *n*-BuLi/R*OLi; (**C**) 3:1 *n*-BuLi/R*OLi; (**D**) 1:1 *n*-BuLi/R*OLi; (**E**) 1:2 *n*-BuLi/R*OLi; (**F**) 1:5 *n*-BuLi/R*OLi.

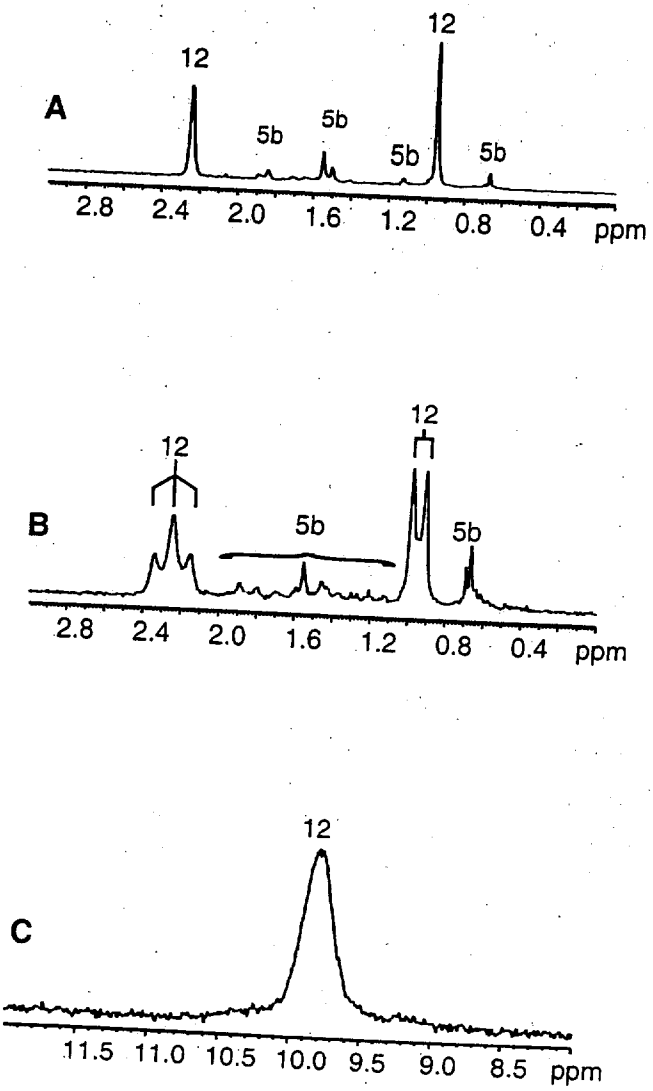


Figure III. ^{6}Li and ^{13}C NMR spectra recorded on solutions containing 1:2 *n*-BuLi and (*1R,2S*)-LiOCH(Ph)CH(Me)N$(CH_2)_4$ (R*OLi; **5b**) (0.15 M total lithium titer) in 1:5 THF/pentane at -110 °C showing 2:2 mixed tetramer **12** and oligomers of **5b**. (**A**) ^{6}Li NMR spectrum of 1:2 [^{6}Li]*n*-BuLi/[^{6}Li]**5b**; (**B**) ^{6}Li NMR spectrum of 1:2 [^{6}Li,^{13}C]*n*-BuLi/[^{6}Li]**5b**; (**C**) ^{13}C NMR spectrum of [^{6}Li]*n*-BuLi/[^{6}Li]**5b**.

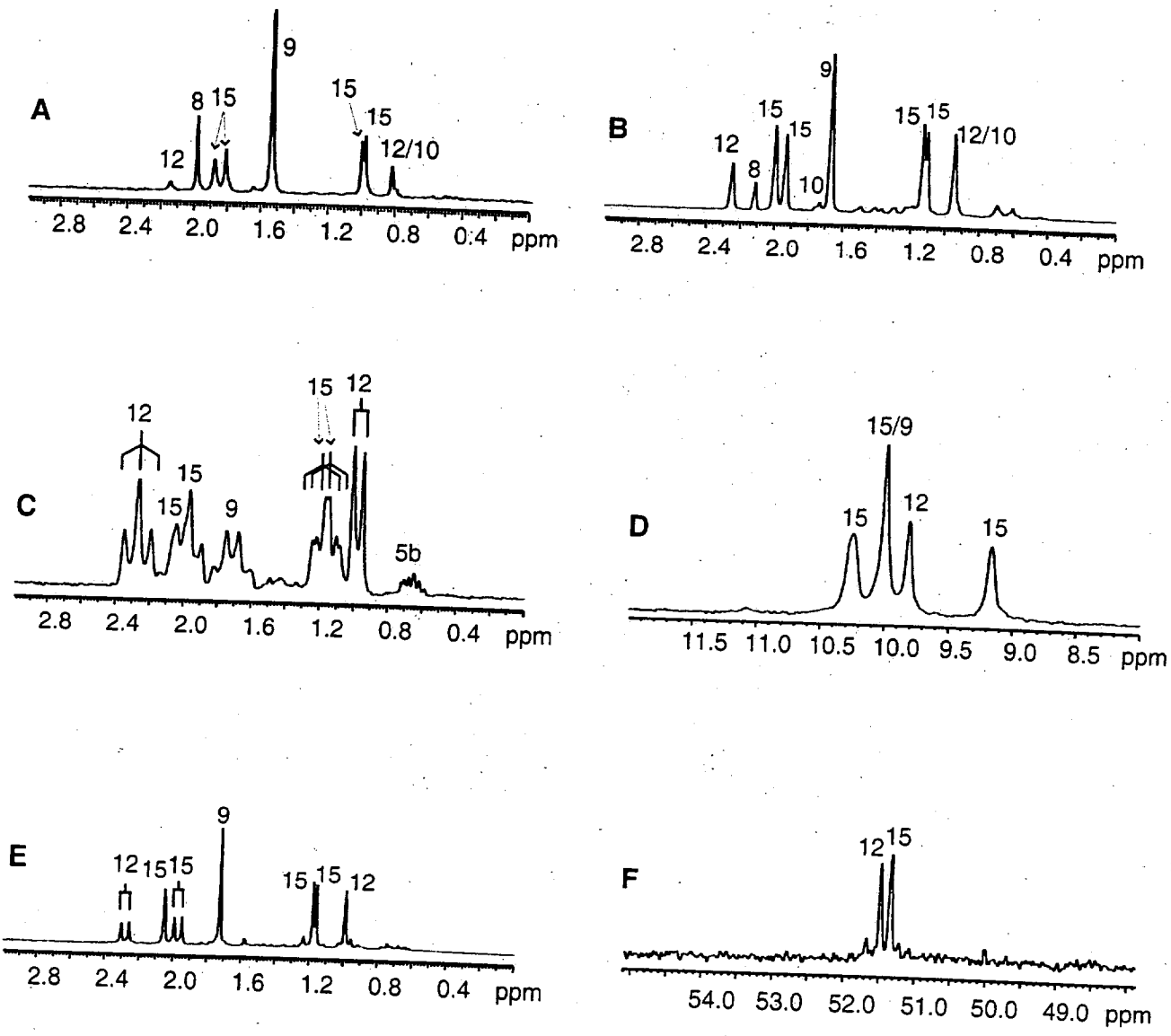


Figure IV. ^{6}Li, ^{13}C, and ^{15}N NMR spectra recorded on solutions containing *n*-BuLi and (*1R,2S*)-LiOCH(Ph)CH(Me)N$(CH_2)_4$ (R*OLi; **5b**) (0.15 M total lithium titer) in 1:5 THF/pentane at -110 °C showing *n*-BuLi tetramer **9**, 3:1 *n*-BuLi/R*OLi mixed tetramer **15**, and 2:2 *n*-BuLi/R*OLi tetramer **12**. (**A**) ^{6}Li NMR spectrum of 5:1 [^{6}Li]*n*-BuLi and [^{6}Li]**5b**; (**B**) ^{6}Li NMR spectrum of 2:1 [^{6}Li]*n*-BuLi and [^{6}Li]**5b**; (**C**) ^{6}Li NMR spectrum of 2:1 [^{6}Li,^{13}C]*n*-BuLi and [^{6}Li]**5b**; (**D**) $^{13}C\{^{6}Li\}$ NMR spectrum of 2:1 [^{6}Li,^{13}C]*n*-BuLi and [^{6}Li]**5b**; (**E**) ^{6}Li NMR spectrum of 2:1 [^{6}Li]*n*-BuLi and [^{6}Li,^{15}N]**5b**; (**F**) $^{15}N\{^{6}Li\}$ NMR spectrum of 2:1 [^{6}Li]*n*-BuLi and [^{6}Li]**5b**.

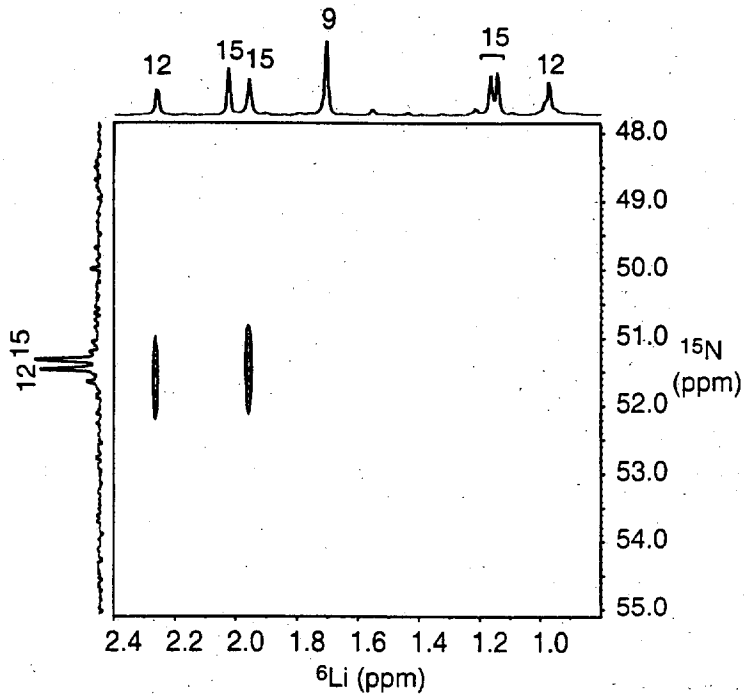


Figure V. ^{6}Li,^{15}N-HMQC spectrum recorded on a solution containing 2:1 [^{6}Li]*n*-BuLi and [^{6}Li,^{15}N](*1R,2S*)-LiOCH(Ph)CH(Me)N(CH_2)$_4$ (**5b**) (0.15 total lithium titer) in 1:5 THF/pentane at -110 °C

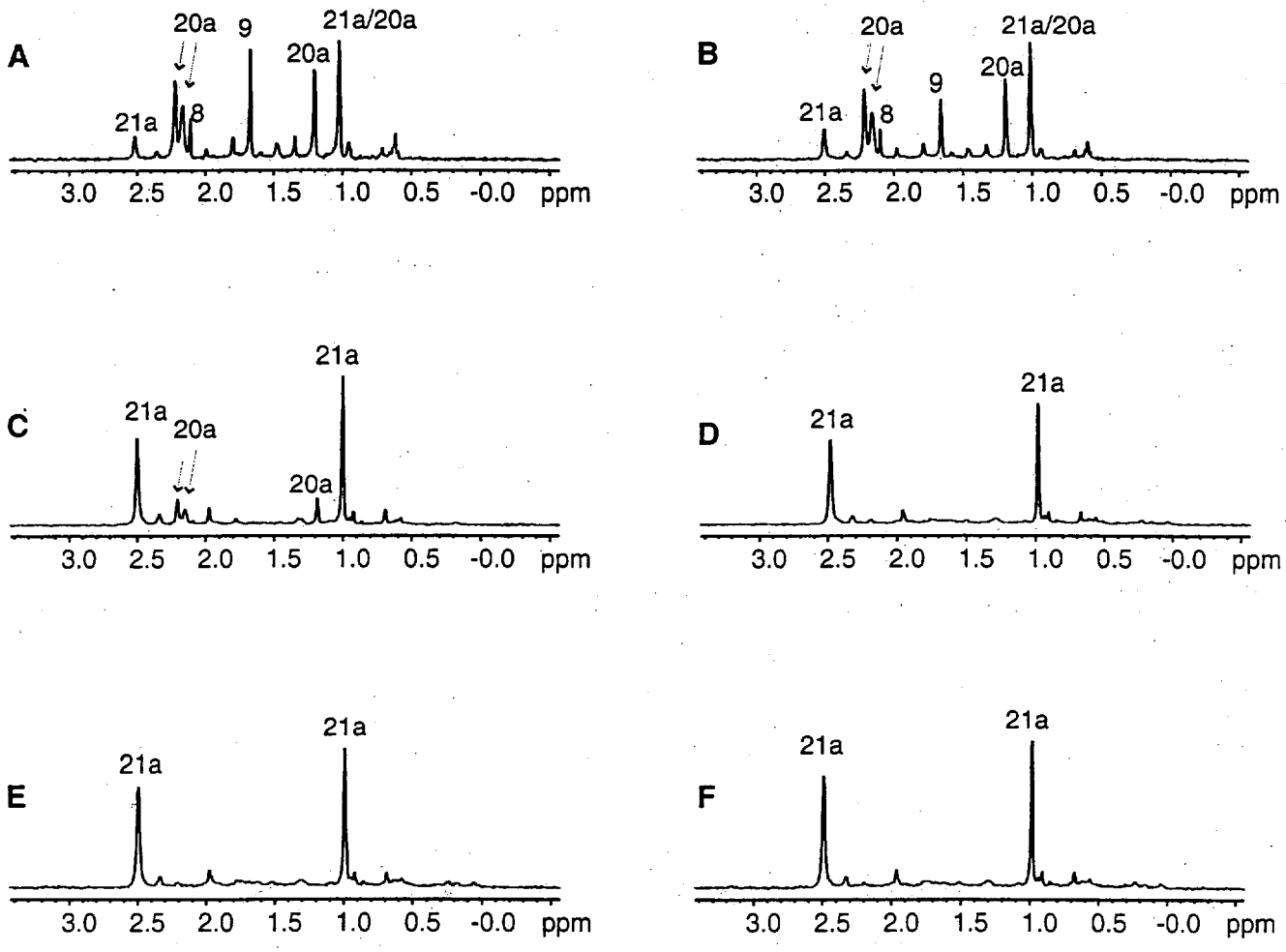


Figure VI. ^{6}Li NMR spectra recorded on solutions containing [^{6}Li]*n*-BuLi and [^{6}Li](*1R,2S*)-LiOCH(Ph)CH(Ph)NMe_2 (**7b**) (0.15 M total lithium titer) in 1:2 THF/pentane at -110 °C showing *n*-BuLi dimer and tetramer (**8** and **9**), 2:2 *n*-BuLi/R*OLi mixed tetramer (**21a**), and 3:1 *n*-BuLi/ROLi tetramer (**20a**). (**A**) 5:1 [^{6}Li]*n*-BuLi/[^{6}Li]**7b**; (**B**) 3:1 [^{6}Li]*n*-BuLi/[^{6}Li]**7b**; (**C**)2:1 [^{6}Li]*n*-BuLi/[^{6}Li]**7b**; (**D**) 1:2 [^{6}Li]*n*-BuLi/[^{6}Li]**7b**. (**E**) 1:2 [^{6}Li]*n*-BuLi/[^{6}Li]**7b**. (**F**) 1:5 [^{6}Li]*n*-BuLi/[^{6}Li]**7b**.

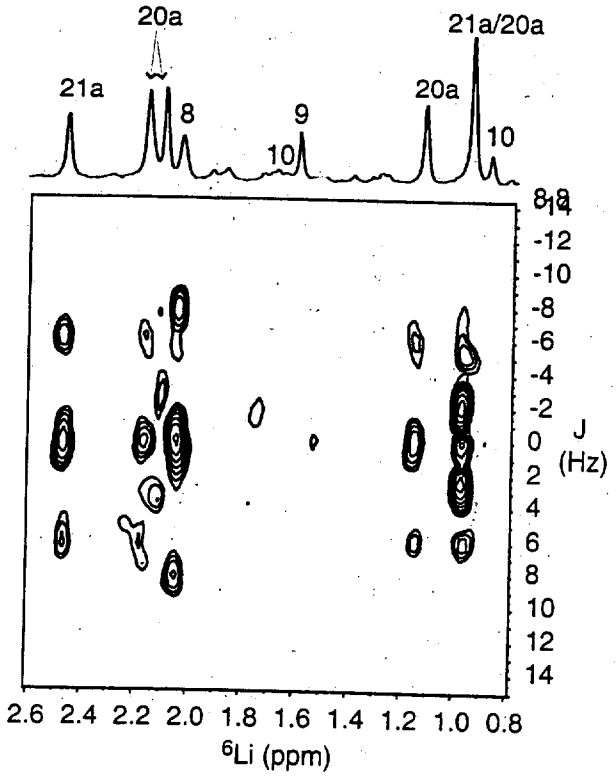


Figure VII. $^1J(^6Li,^{13}C)$-resolved ^6Li NMR spectrum recorded on a solution containing 2:1 [^6Li,^{13}C]*n*-BuLi and [^6Li] (*1R,2S*)-LiOCH(Ph)CH(Ph)NMe_2 (**7b**) (0.15 M total lithium titer) in 1:2 THF/pentane at -110 °C.

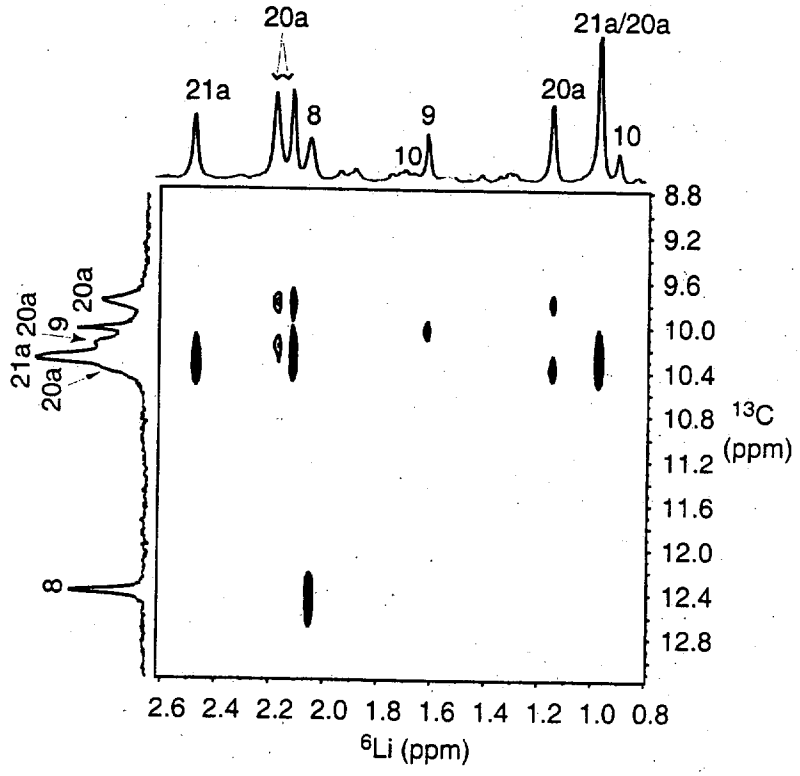


Figure VIII. $^{6}Li,^{13}C$-HMQC spectrum recorded on a solution containing 2:1 [$^{6}Li,^{13}C$]*n*-BuLi and [^{6}Li]**7b** (0.15 M total lithium titer) in 1:2 THF/pentane at -110 °C showing *n*-BuLi dimer **8** and tetramer **9**, 3:1 *n*-BuLi/R*OLi mixed tetramer **20a**, and 2:2 *n*-BuLi/R*OLi mixed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

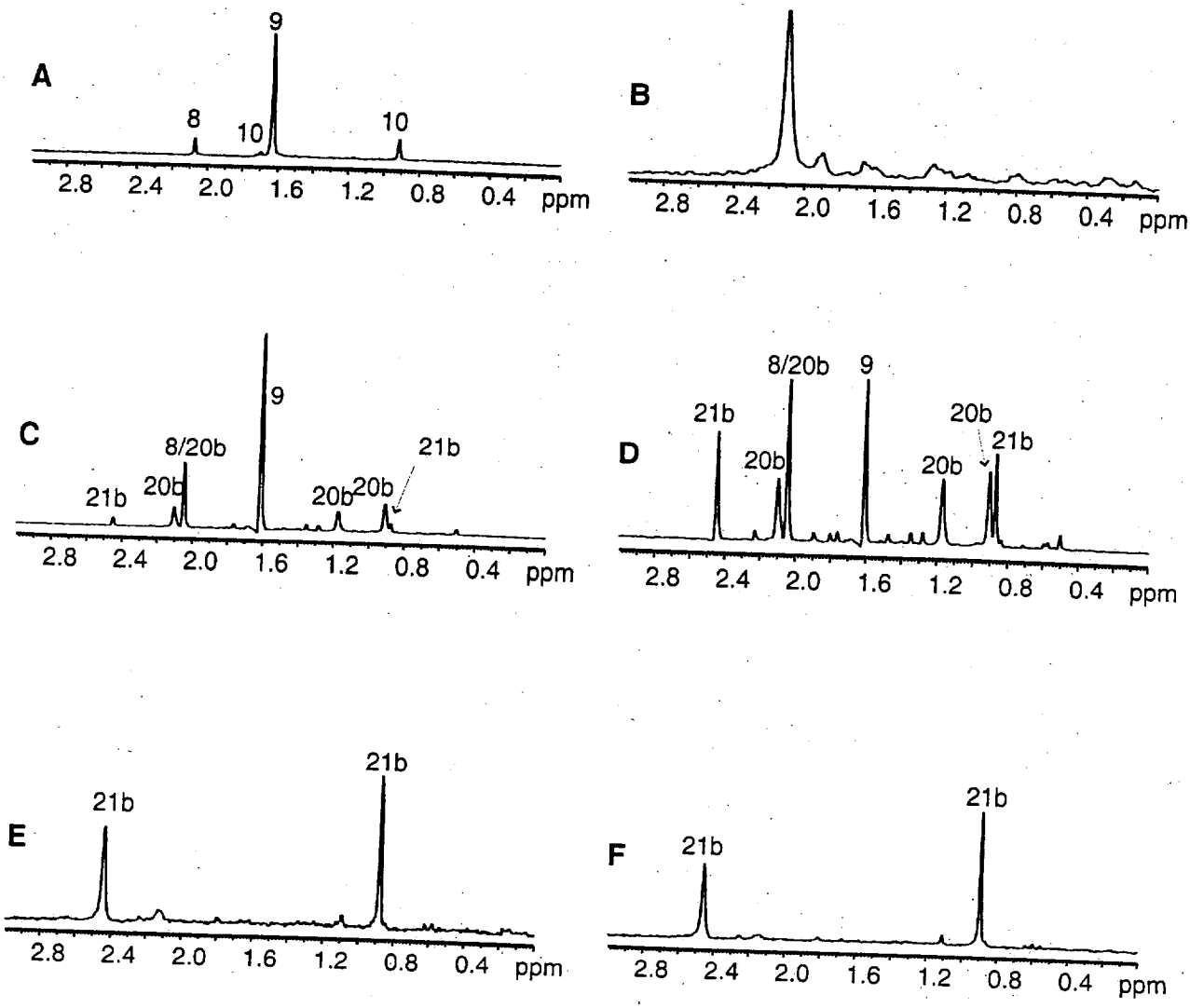


Figure IX. ^{6}Li NMR spectra recorded on solutions containing [^{6}Li]*n*-BuLi and [^{6}Li](*1R,2S*)-LiOCH(Ph)CH(Ph)N(CH_2)$_4$ (**6b**) (0.15 M total lithium titer) in 1:2 THF/pentane at -95 °C showing *n*-BuLi dimer **8** and tetramer **9**, 2:2 *n*-BuLi/ROLi mixed tetramer **21b**, and 3:1 *n*-BuLi/ROLi tetramer **20b**. (**A**) spectrum of [^{6}Li]*n*-BuLi; (**B**) spectrum of [^{6}Li]**6b**; (**C**) spectrum of 5:1 [^{6}Li]*n*-BuLi/[^{6}Li]**6b**; (**D**) spectrum of 3:1 [^{6}Li]*n*-BuLi/[^{6}Li]**6b**; (**E**) spectrum of 1:1 [^{6}Li]*n*-BuLi/[^{6}Li]**6b**; (**F**) spectrum of 1:3 [^{6}Li]*n*-BuLi/[^{6}Li]**6b**.

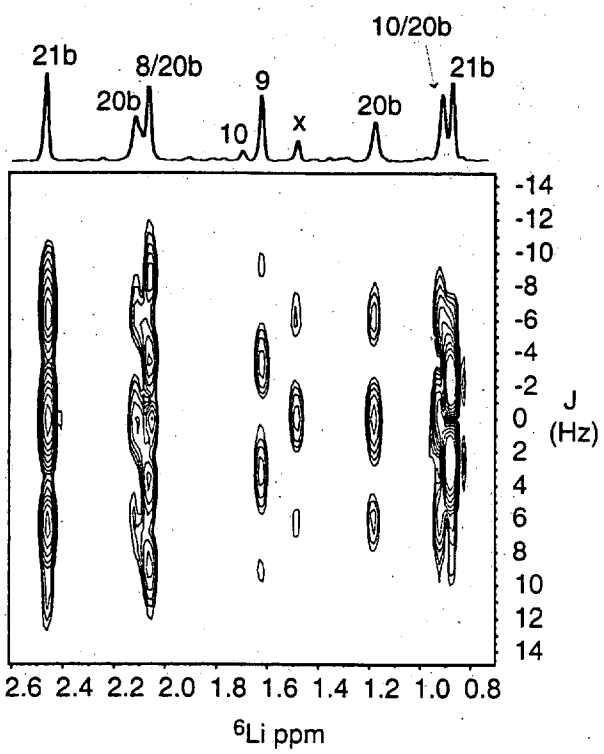


Figure X. $^{1}J(^{6}Li,^{13}C)$-resolved ^{6}Li spectrum recorded on a solution containing 2:1 [$^{6}Li,^{13}C$]*n*-BuLi and [^{6}Li](*1R,2S*)-LiOCH(Ph)CH(Ph)N(CH_2)$_4$ (**6b**) (0.15 M total lithium titer) in 1:2 THF/pentane at -95 °C.

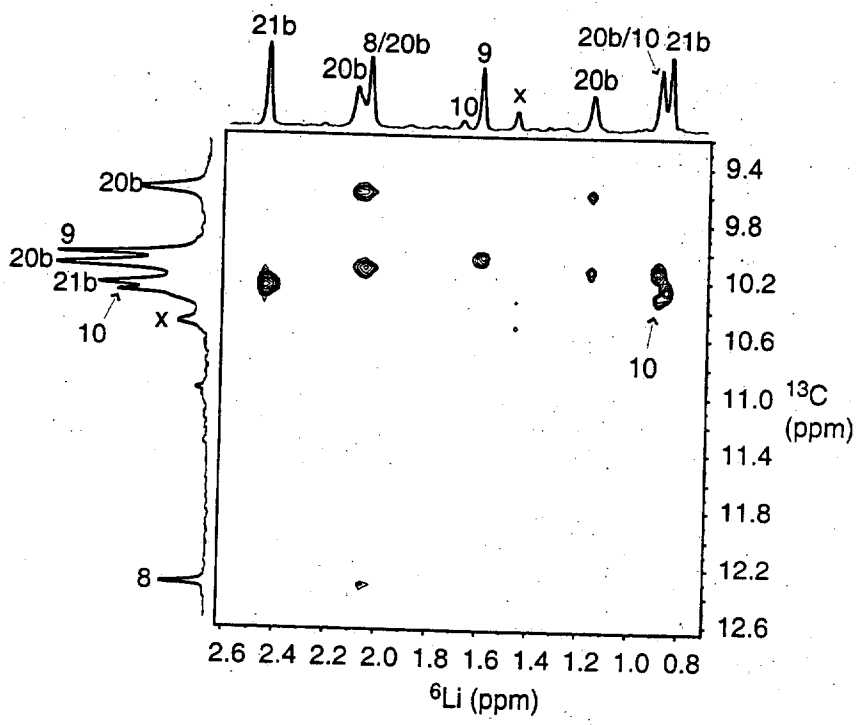


Figure XI. $^{6}Li,^{13}C$-HMQC spectrum recorded on a solution containing 2:1 [$^{6}Li,^{13}C$]*n*-BuLi and [^{6}Li](*1R,2S*)-LiOCH(Ph)CH(Ph)N(CH_2)$_4$ (**6b**) (0.15 M total lithium titer) in 1:2 THF/pentane at -95 °C showing *n*-BuLi dimer **8** and tetramer **9**, 3:1 *n*-BuLi/R*OLi mixed tetramer **20b**, and 2:2 *n*-BuLi/R*OLi mixed tetramer **21b**. The $^{6}Li\{^{13}C\}$ and $^{13}C\{^{6}Li\}$ NMR spectra are shown on top and left, respectively.

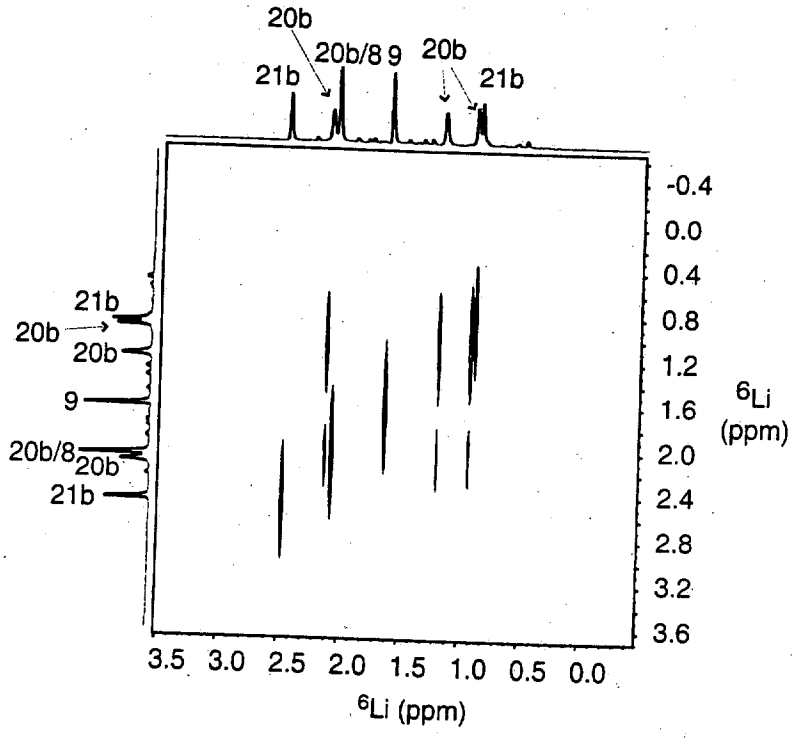


Figure XII. ^{6}Li,^{6}Li-EXSY spectrum recorded on a solution containing 2:1 [^{6}Li]*n*-BuLi and [^{6}Li](*1R,2S*)-LiOCH(Ph)CH(Ph)N(CH_2)$_4$ (**6b**) (0.15 M total lithium titer) in 1:2 THF/pentane at -95 °C. The spectrum was recorded with a mixing time of 2 seconds.

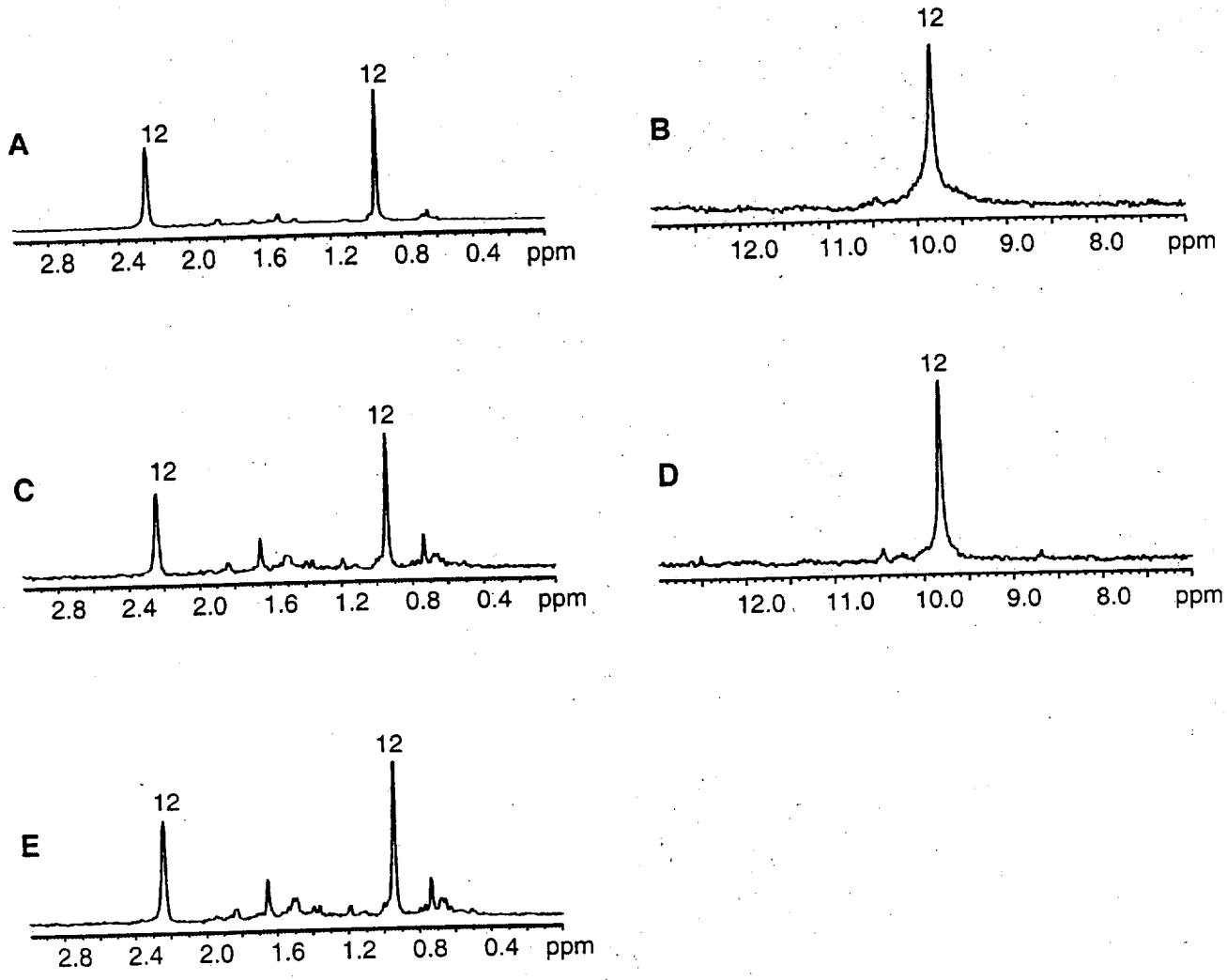


Figure XIII. ^{6}Li and ^{13}C NMR spectra of 1:1.5 mixtures of [^{6}Li,^{13}C]*n*-BuLi and [^{6}Li](*1R*,*2S*)-LiOCH(Ph)CH(Ph)N(CH_2)$_4$ (R*OLi; **5b**) (0.15 M total lithium titer) in 1:5 THF/pentane at -110 °C. (**A**) $^{6}Li\{^{13}C\}$ NMR spectrum; (**B**) $^{13}C\{^{6}Li\}$ NMR spectrum; (**C**) $^{6}Li\{13C\}$ NMR spectrum of a 1:1.5 mixture [^{6}Li,^{13}C]n-BuLi/[6Li]**5b** with added PhCHO (0.5 eq/*n*-BuLi); (**D**) ^{13}C NMR spectrum of the sample in C; (**E**) ^{6}Li NMR spectrum after aging at 0 °C for 3 min.

Table 2. Enantiomeric ratios (er) vs. equiv. of PhCHO for the (*1R,2S*)-LiOCH(Ph)CH(Me)N$(CH_2)_4$ (R*OLi; **5b**)-mediated addition of *n*-BuLi to PhCHO at -78 °C.[a]

PhCHO (equiv. per *n*-BuLi)	*n*-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

[a]Protocol used was the same as described in the Experimental section.

Table 3. Enantiomeric ratios (er) vs. equiv. of PhCHO for the (*1R,2S*)-LiOCH(Ph)CH(Ph)N$(CH_2)_4$ (R*OLi; **7b**)-mediated addition of *n*-BuLi to PhCHO at -78 °C.

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

[a]Protocol used was the same as described in the Experimental section.