

# SUPPORTING INFORMATION

## Binding of Diamines to *n*-Butyllithium Dimers: Relative Solvation Energies and Evidence of Correlated Solvation.

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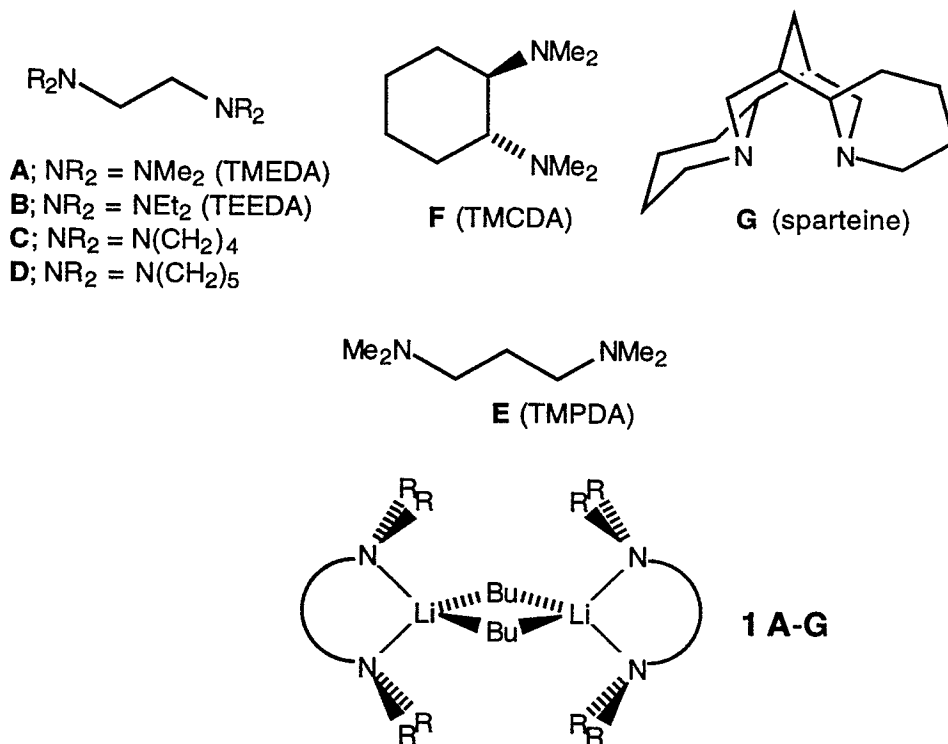
### Supporting Information

#### Experimental Procedure

Table 1.  $^6\text{Li}$  NMR spectroscopic data of diamine-solvated *n*-BuLi dimers,  $(n\text{-BuLi})_2\text{SS}'$ .

Table 2.  $^{13}\text{C}$  NMR spectroscopic data of diamine-solvated *n*-BuLi dimers,  $(n\text{-BuLi})_2\text{SS}'$ .

- I.  $^6\text{Li}$  NMR spectra of *n*-BuLi with ligands **A-G**.
- II.  $^6\text{Li}$  NMR spectra of *n*-BuLi with combinations of ligands **A-G** at low ligand concentrations.
- III.  $^6\text{Li}$  NMR spectra of *n*-BuLi with combinations of ligands **A-G** at high ligand concentrations.
- IV. Partial  $^{13}\text{C}$  NMR spectra of *n*-BuLi with ligands **A-G** showing the  $\text{C}\text{H}_2\text{Li}$  resonance.
- V.  $^{13}\text{C}$  NMR spectra of *n*-BuLi with ligands **A-G** in the limit of slow solvent exchange.
- VI.  $^{13}\text{C}$  NMR spectra of *n*-BuLi with combinations of ligands **A-G** at high ligand concentrations.



## Experimental Section

**Reagents and Solvents.** Hydrocarbons were distilled by vacuum transfer from blue or purple solutions containing sodium benzophenone ketyl. Diamines **A**, **B**, **C**, and **G** were obtained from Aldrich. Ligands **D**, **E**, **F**, and **H** were prepared according to literature procedures.<sup>1</sup> **A-G** were initially dried by refluxing them over CaH<sub>2</sub> for several days, purified by fractional distillation, stored over Na/Pb alloy, and freshly distilled before use. <sup>6</sup>Li metal (95.5% enriched) was obtained from Oak Ridge National Laboratory. The [<sup>6</sup>Li]butyllithium was prepared and multiply recrystallized from pentane at -95 °C.<sup>2</sup> The diphenylacetic acid used to check solution titers<sup>3</sup> was recrystallized from methanol and sublimed at 120 °C under full vacuum. Air and moisture sensitive materials were manipulated under argon or nitrogen using standard glove box, vacuum line, and syringe techniques.

**NMR Spectroscopic Analyses.** Samples for spectroscopic analyses were prepared and sealed under full vacuum. Standard <sup>6</sup>Li, <sup>1</sup>H, and <sup>13</sup>C NMR spectra were recorded on a Varian XL-400 spectrometer operating at 58.84 MHz, 399.83 MHz, and 100.58 MHz (respectively). The <sup>6</sup>Li, <sup>1</sup>H, and <sup>13</sup>C resonances are referenced to 0.3 M [<sup>6</sup>Li]LiCl/MeOH at -100 °C (0.0 ppm), toluene d<sub>8</sub> at -70 °C (7.09 ppm), and the toluene-d<sub>8</sub> methyl resonance at -100 °C (20.4 ppm), respectively. Integrations were obtained from <sup>6</sup>Li and <sup>13</sup>C NMR spectra (inverse-gated) recorded with appropriate delays based upon T<sub>1</sub> measurements to exclude saturation effects. The relevant resonances of each spectrum were integrated 3-5 times to ensure reproducibility. Each combination of ligands was investigated with a minimum of three independently prepared samples to determine the binding constant. The deconvolution routine available from Varian was used to integrate overlapping resonances. The reported values stem from an average of all measurements with standard deviations of <10% in each case.

1. For leading references, see: Lucht, B. L.; Bernstein, M. P.; Remenar, J. F.; Collum, D. B. *J. Am. Chem. Soc.* **1996**, *118*, 10707.
2. Kottke, T.; Stalke, D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 580.
3. Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879.

Table 1.  $^6\text{Li}$  NMR spectroscopic data of diamine-solvated  $n\text{-BuLi}$  dimers,  $(n\text{-BuLi})_2\text{SS}'$ .

S	S'	$\delta$ $^6\text{Li}$	S	S'	$\delta$ $^6\text{Li}$	S	S'	$\delta$ $^6\text{Li}$
A	A	2.06	A	E	1.97, 1.74	C	F	2.05, 1.95
B	B	1.79	A	F	2.20, 2.09	C	G	1.92, 1.63
C	C	1.79	A	G	2.03, 1.73	D	E	1.84, 1.67
D	D	1.71	B	C	1.88, 1.62	D	F	2.06, 1.86
E	E	1.67	B	D	1.80, 1.71	D	G	1.94, 1.63
F	F	2.24	B	E	1.75, 1.73	E	F	2.12, 1.77
G	G	1.77, 1.74 <sup>b</sup>	B	F	2.11, 1.92	E	G	1.79, 1.70
A	B	1.99, 1.93	B	G	1.92, 1.69	F	G	2.04, 1.80
A	C	1.94, 1.89	C	D	1.77, 1.76			
A	D	1.94, 1.87	C	E	1.87, 1.60			

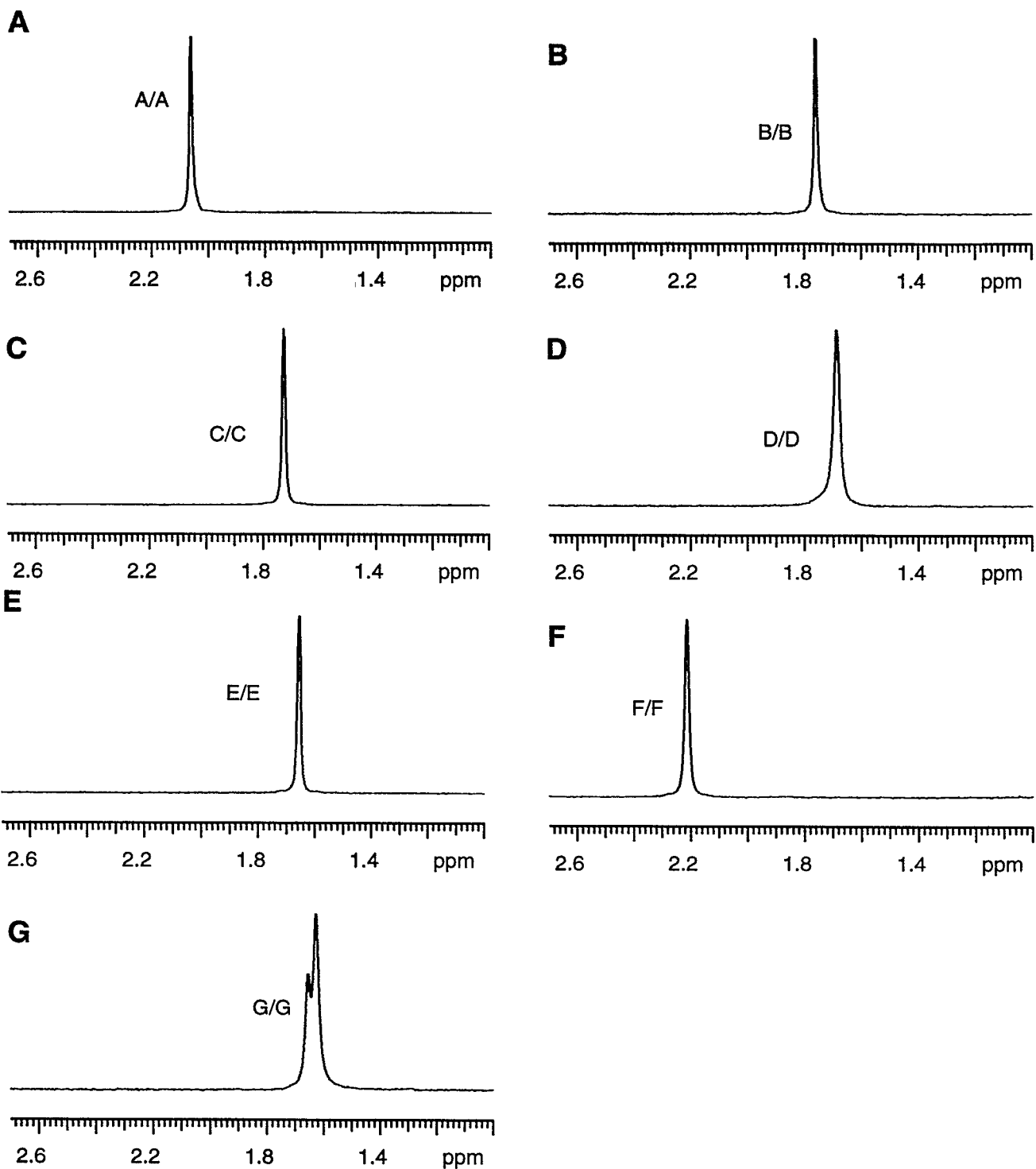
<sup>a</sup>Spectra were recorded on 0.1 M solutions of [ $^6\text{Li}$ ] $n\text{-BuLi}$  in toluene- $d_8$  at  $-100$  °C. Samples contain a single diamine (**A-G**;  $S = S'$ ) or mixtures of two diamines ( $S \neq S'$ ).  $^6\text{Li}$  chemical shifts are reported relative to 0.3 M  $^6\text{LiCl}/\text{MeOH}$  at  $-100$  °C (0.0 ppm). The shifts are temperature and concentration dependent. <sup>b</sup>The two resonances (1.83:1 ratio) may stem from two sparteine orientations.

Table 2.  $^{13}\text{C}$  NMR spectroscopic data of diamine-solvated  $n\text{-BuLi}$  dimers,  $(n\text{-BuLi})_2\text{S}_2$ .<sup>a</sup>

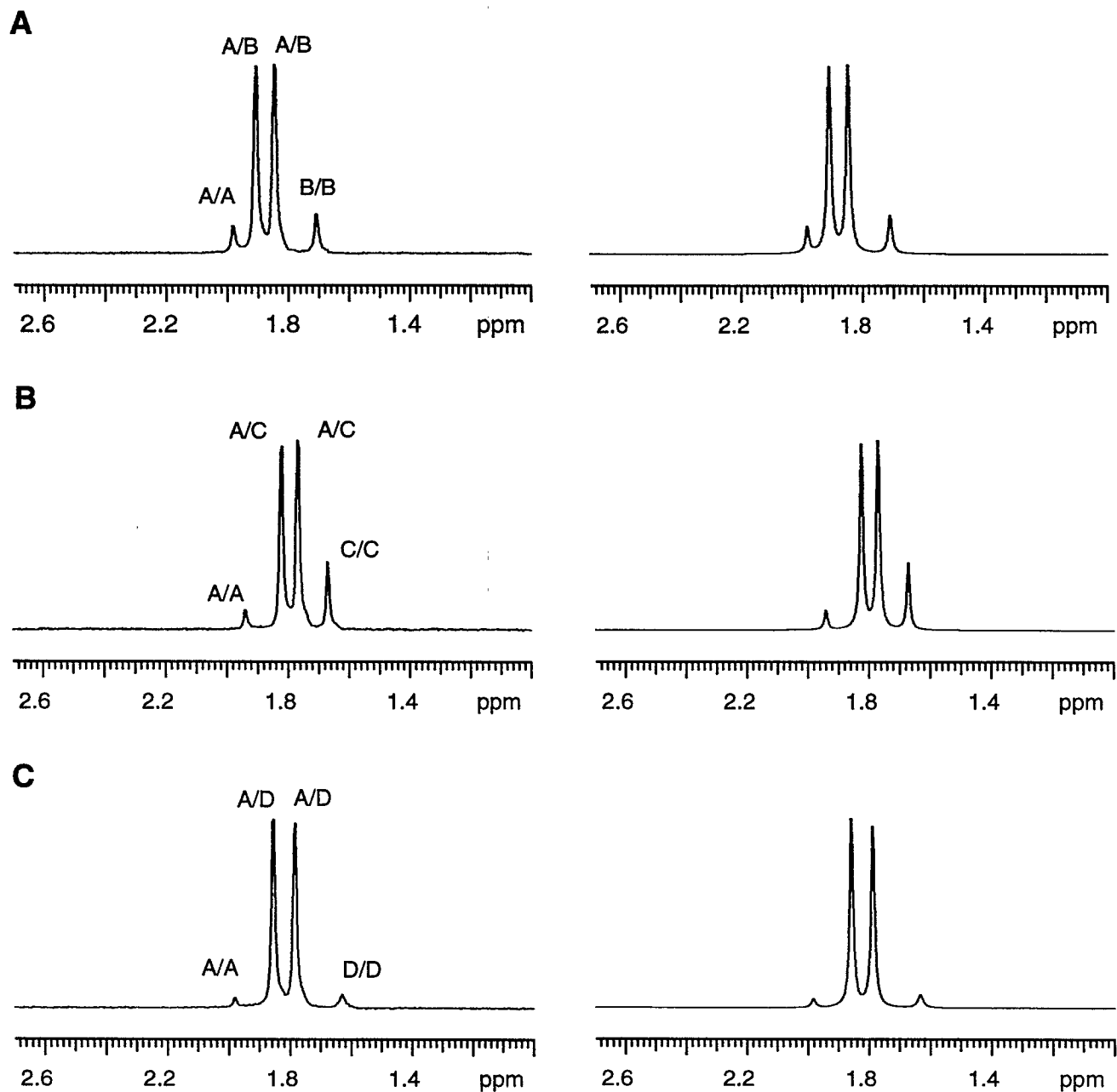
cmpd	ligand	$^{13}\text{C}\{^1\text{H}\}$ : bound ligand	$^{13}\text{C}\{^1\text{H}\}$ (Butyl)	$^{13}\text{C}\{^1\text{H}\}$ : free ligand
1A	A	56.13, 46.05 <sup>b</sup>	37.72, 36.24, 15.06, 13.32	58.09, 46.05 <sup>b</sup>
1B	B	50.45, 43.96, 8.53	36.92, 35.77, 14.66, 13.46	51.47, 47.32, 12.16
1C	C	55.33, 54.60, <sup>b</sup> 23.51	37.48, 36.15, 14.70, 11.76	55.90, 54.60, <sup>b</sup> 23.39
1D	D	56.24, 56.02, 25.04 24.53	36.38, 35.14, 14.17, 12.99	57.56, 55.23, 26.24 24.67
1E	E	60.42, 45.66, <sup>b</sup> 22.90	37.71, 36.31, 14.98, 13.27	57.52, 45.66, <sup>b</sup> 26.36
1F	F	62.95, 44.69, 37.81, 24.77, 21.24	37.81, 36.61, 15.41, 15.06	63.58, 40.46, 25.68, 25.07

<sup>a</sup>Spectra were recorded on 0.1 M solutions of [ $^6\text{Li}$ ]  $n\text{-BuLi}$  (containing diamines **A-G**) in toluene- $d_8$  at  $-100\text{ }^\circ\text{C}$ .  $^{13}\text{C}$  chemical shifts are reported relative to toluene- $d_8$  at  $-100\text{ }^\circ\text{C}$  (20.4 ppm). The coupling of the  $\alpha$ -carbon of the butyl moiety to lithium is no longer resolved at  $-100\text{ }^\circ\text{C}$ . The  $^{13}\text{C}$  NMR spectrum of  $n\text{-BuLi}/(-)\text{-sparteine}$  (**G**) was not assigned; see Figure V(G). <sup>b</sup>Average of free and bound ligand resonance.

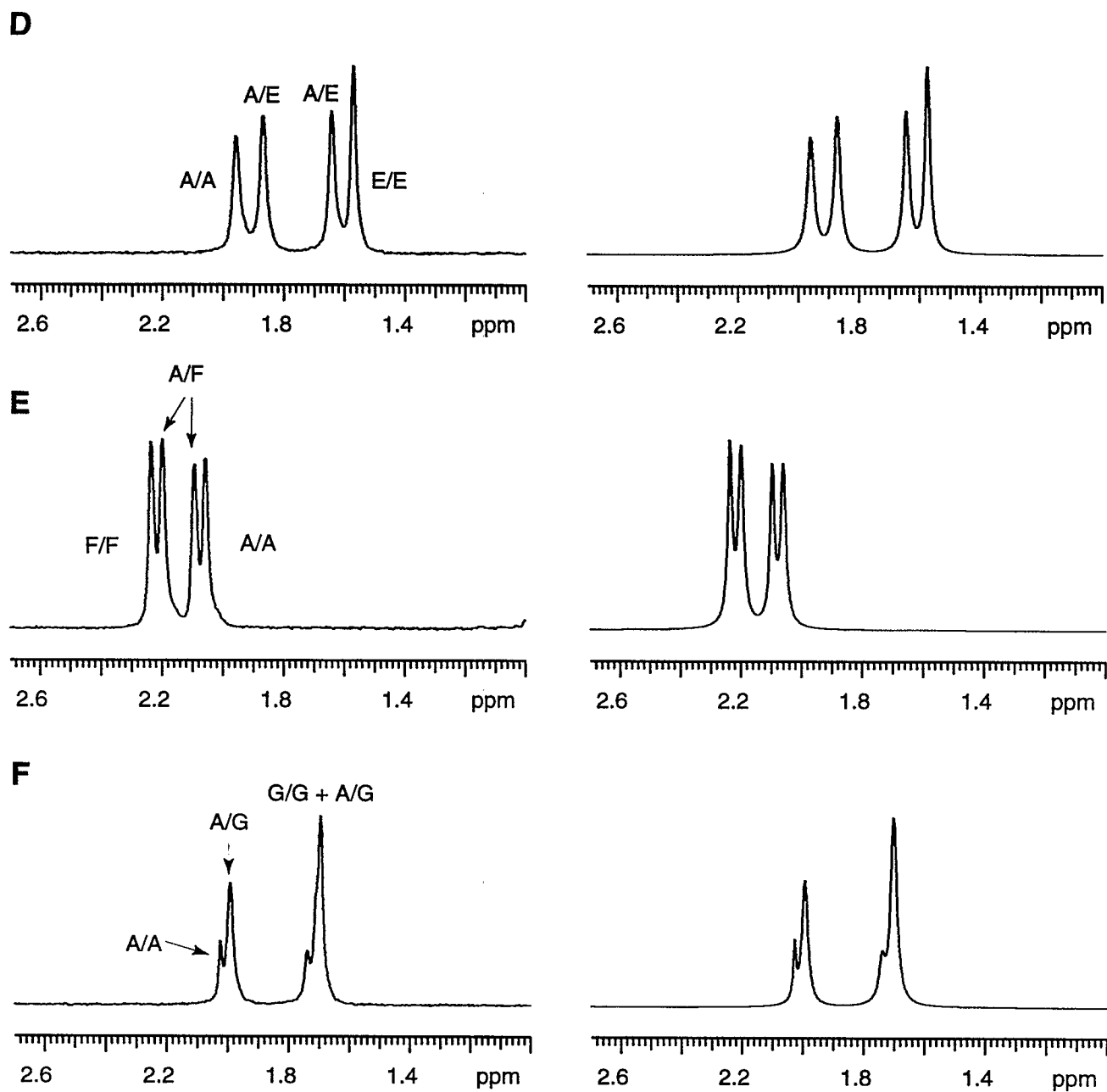
(I)



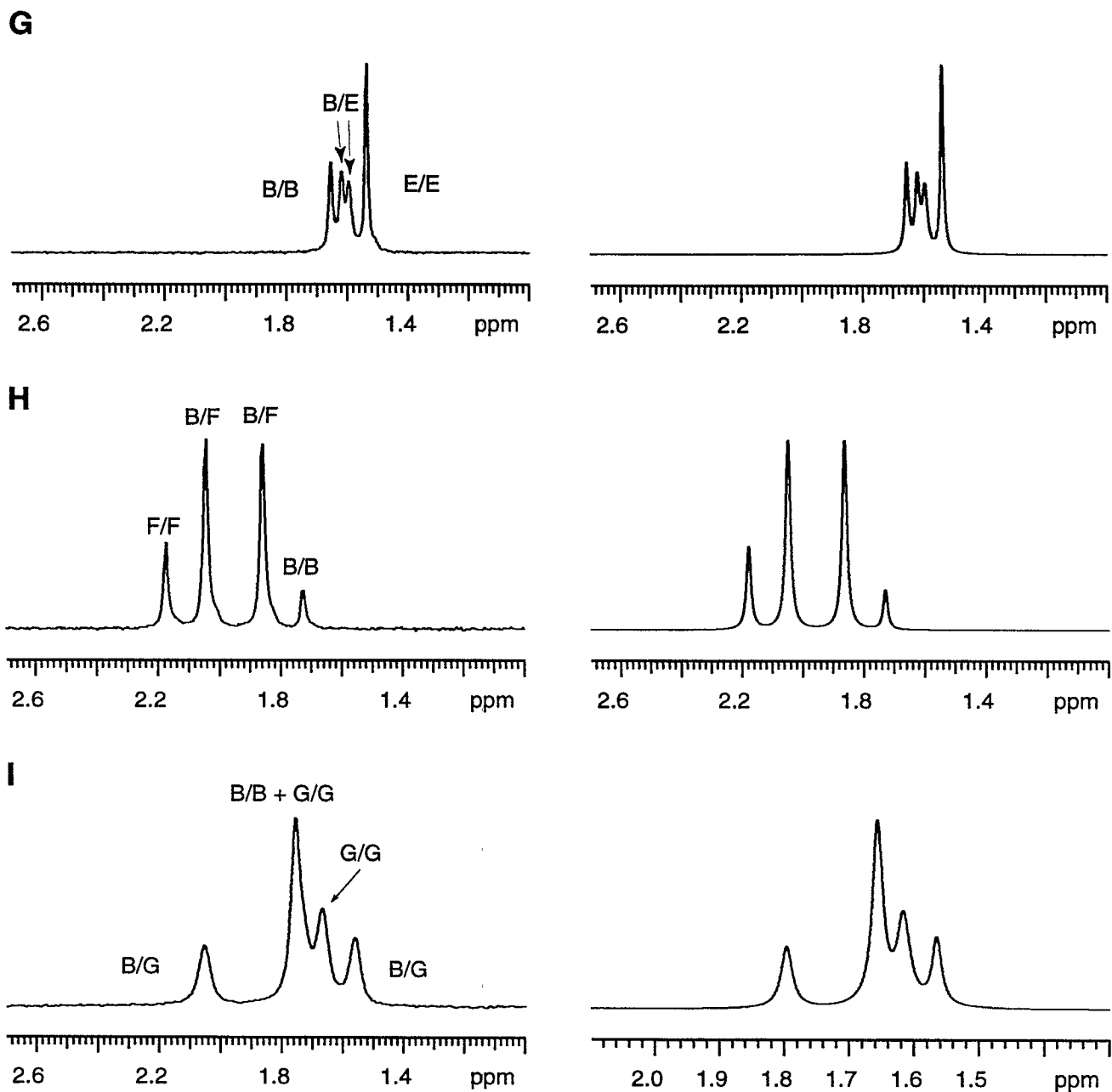
I.  $^6\text{Li}$  NMR spectra of 0.1 M  $[\text{}^6\text{Li}]n\text{-BuLi}$  in toluene- $d_8$  at  $-100\text{ }^\circ\text{C}$  containing the following ligands: (A) 1.5 equiv. of TMEDA (A); (B) 1.5 equiv. of TEEDA (B); (C) 1.5 equiv. of 1,2-dipyrrolidinoethane (C); (D) 1.5 equiv. of 1,2-dipiperidinoethane (D); (E) 1.5 equiv. of TMPDA (E); (F) 1.5 equiv. of *trans*-(*R,R*)-TMCDA (F); (G) 1.5 equiv. of (-)-sparteine (G) (peak ratio = 1:1.83).



II.  ${}^6\text{Li}$  NMR spectra (*left*: before deconvolution; *right*: theoretical spectra after deconvolution) of 0.1 M  ${}^6\text{Li}$   $n\text{-BuLi}$  in toluene- $d_8$  at  $-100\text{ }^\circ\text{C}$  containing the following ligands: (A) 0.5 equiv. of TMEDA (A) and 2.0 equiv. of TEEDA (B); (B) 0.7 equiv. of TMEDA (A) and 0.8 equiv. of 1,2-dipyrrolidinoethane (C); (C) 0.6 equiv. of TMEDA (A) and 3.0 equiv. of 1,2-dipiperidinoethane (D).

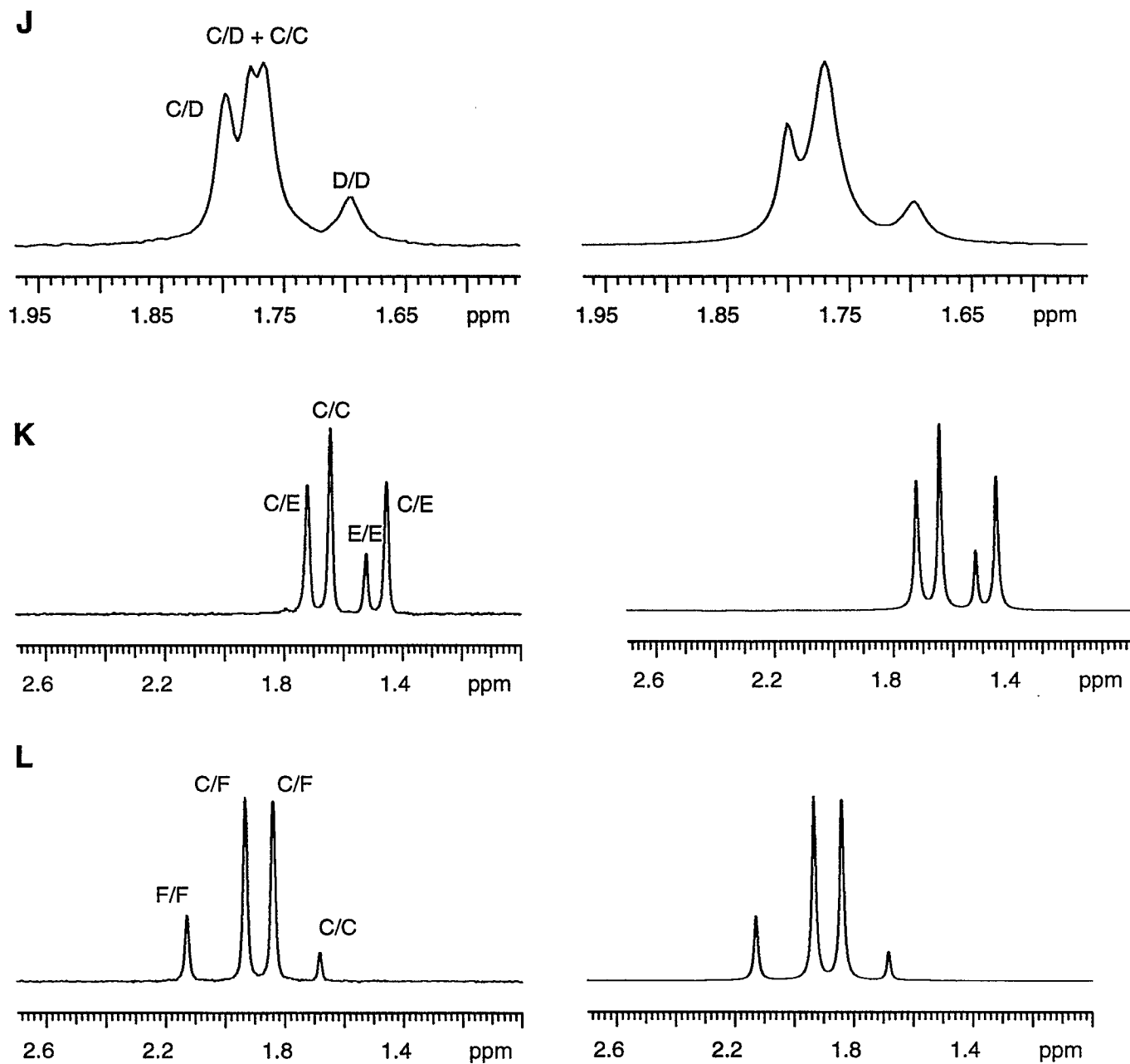


II. (cont.)  $^6\text{Li}$  NMR spectra (*left*: before deconvolution; *right*: theoretical spectra after deconvolution) of 0.1 M  $[\text{}^6\text{Li}]n\text{-BuLi}$  in toluene- $\text{d}_8$  at  $-100^\circ\text{C}$  containing the following ligands: (D) 0.5 equiv. of TMEDA (A) and 0.7 equiv. of TMPDA (E); (E) 0.6 equiv. of TMEDA (A) and 0.6 equiv. of *trans*-(*R,R*)-TMEDA (F); (F) 0.4 equiv. of TMEDA (A) and 0.8 equiv. of (-)-sparteine (G).

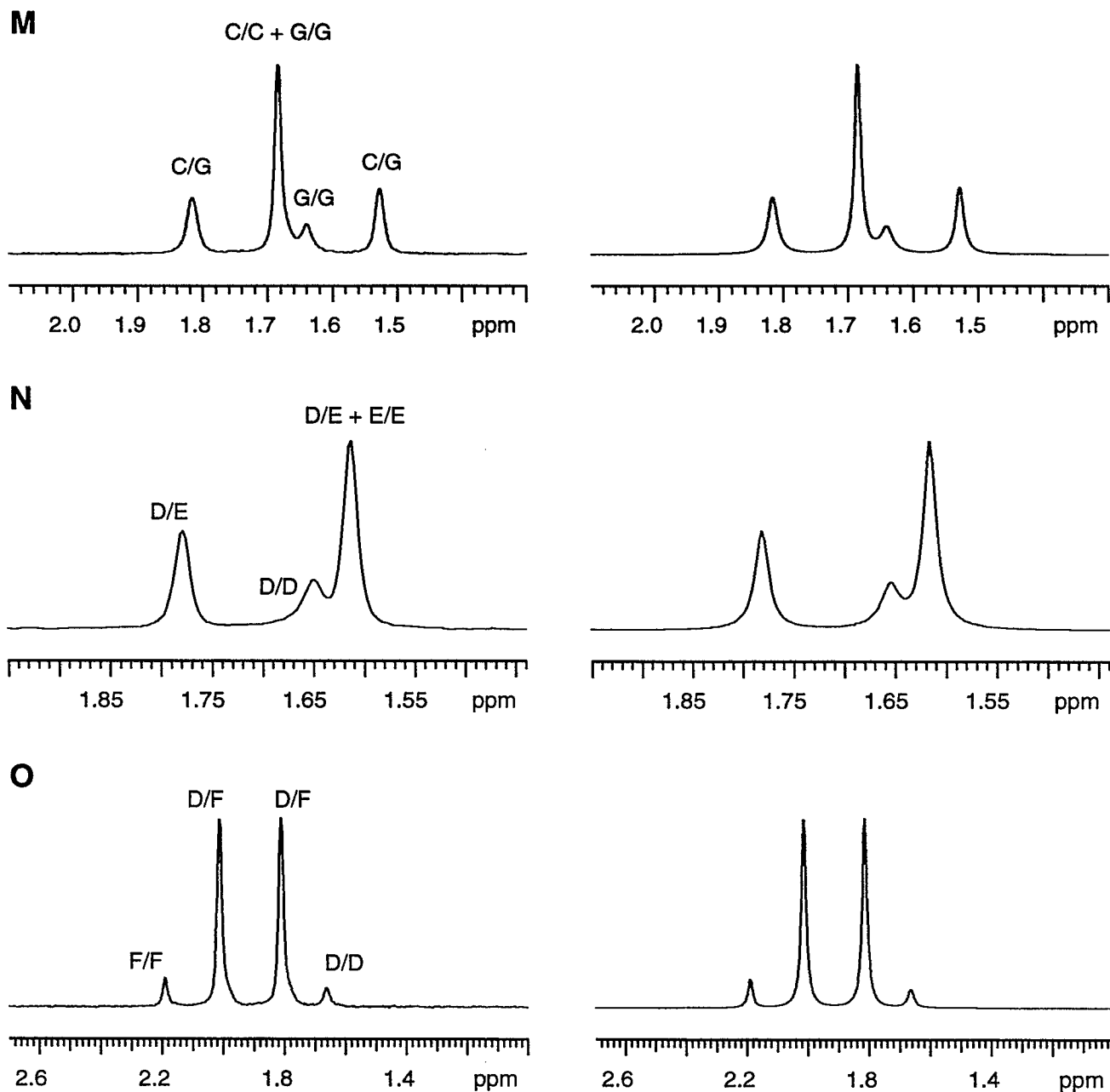


II. (cont.)  ${}^6\text{Li}$  NMR spectra (*left*: before deconvolution; *right*: theoretical spectra after deconvolution) of 0.1 M  $[\text{}^6\text{Li}]n\text{-BuLi}$  in toluene- $d_8$  at  $-100\text{ }^\circ\text{C}$  containing the following ligands: (G) 0.6 equiv. of TEEDA (B) and 0.6 equiv. of TMPDA (E); (H) 0.7 equiv. of TEEDA (B) and 0.5 equiv. of *trans*-(*R,R*)-TMCD (F); (I) 0.7 equiv. of TEEDA (B) and 0.5 equiv. of (-)-sparteine (G).

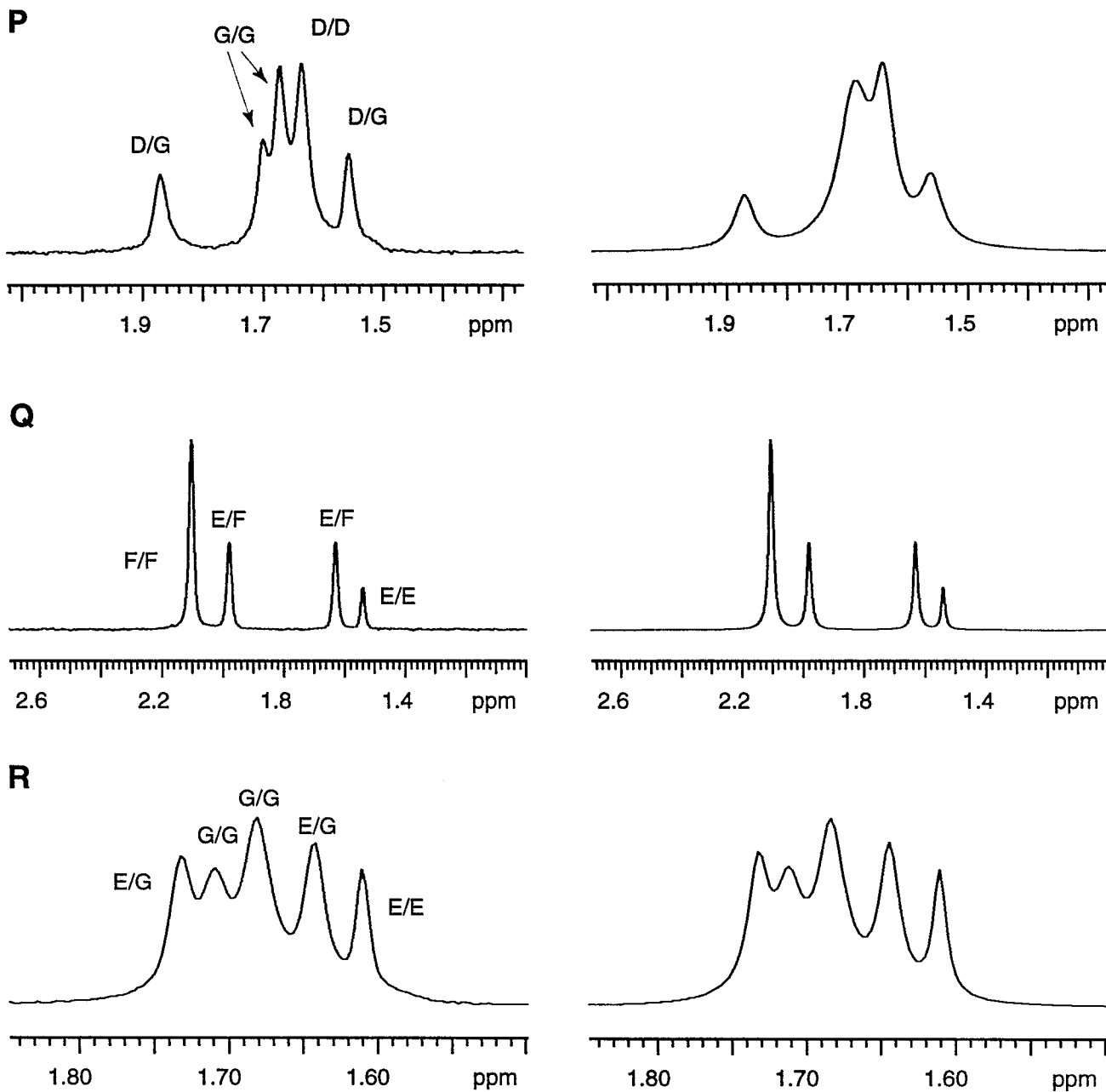




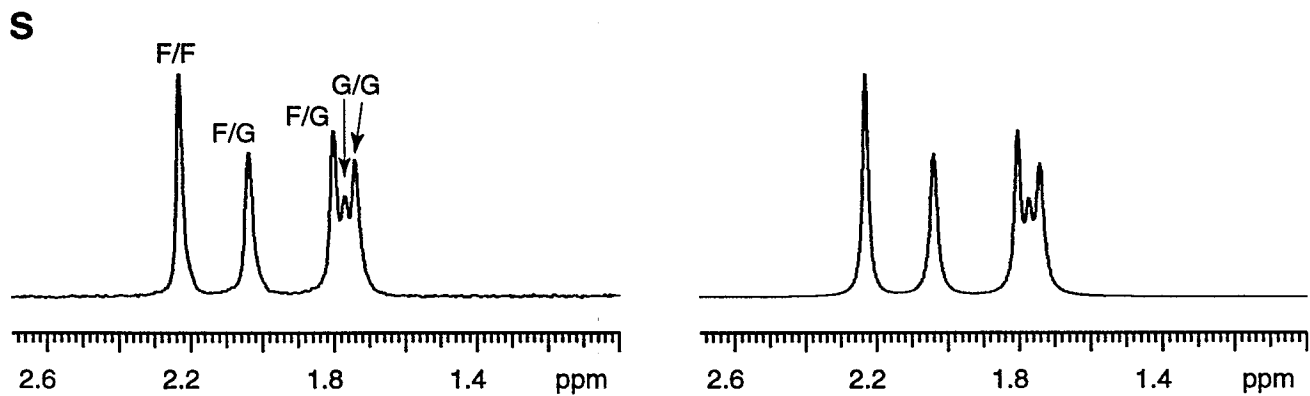
II. (cont.)  $^6\text{Li}$  NMR spectra (*left*: before deconvolution; *right*: theoretical spectra after deconvolution) of 0.1 M  $[\text{}^6\text{Li}]n\text{-BuLi}$  in toluene- $d_8$  at  $-100\text{ }^\circ\text{C}$  containing the following ligands: (J) 0.5 equiv. of 1,2-dipyrrolidinoethane (C) and 0.7 equiv. of 1,2-dipiperidinoethane (D); (K) 0.6 equiv. of 1,2-dipyrrolidinoethane (C) and 0.6 equiv. of TMPDA (E); (L) 0.6 equiv. of 1,2-dipyrrolidinoethane (C) and 0.6 equiv. of *trans*-(*R,R*)-TMCDA (F).



II. (cont.)  $^6\text{Li}$  NMR spectra (*left*: before deconvolution; *right*: theoretical spectra after deconvolution) of 0.1 M  $[^6\text{Li}]n\text{-BuLi}$  in toluene- $d_8$  at  $-100^\circ\text{C}$  containing the following ligands: (M) 0.6 equiv. of 1,2-dipyrrolidinoethane (**C**) and 0.6 equiv. of (-)-sparteine (**G**); (N) 0.6 equiv. of 1,2-dipiperidinoethane (**D**) and 0.6 equiv. of TMPDA (**E**); (O) 0.7 equiv. of 1,2-dipiperidinoethane (**D**) and 0.5 equiv. of *trans*-(*R,R*)-TMCDA (**F**). (Note: The homosolvated dimer containing two sparteine ligands exists as two isomers.)

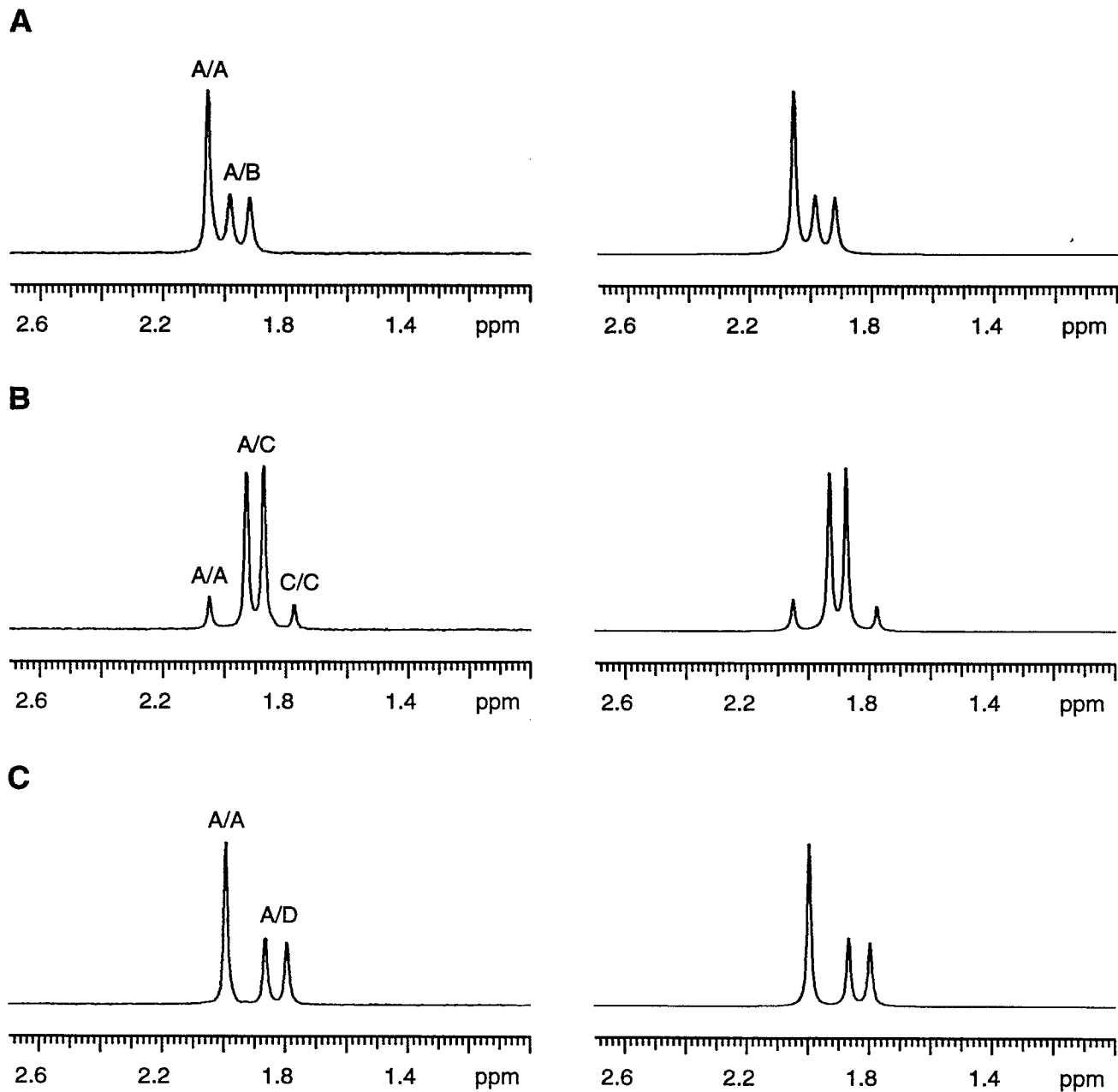


II. (cont.)  ${}^6\text{Li}$  NMR spectra (*left*: before deconvolution; *right*: theoretical spectra after deconvolution) of 0.1 M  ${}^6\text{Li}n\text{-BuLi}$  in toluene- $d_8$  at  $-100\text{ }^\circ\text{C}$  containing the following ligands: (P) 0.6 equiv. of 1,2-dipiperidinoethane (D) and 0.6 equiv. of (-)-sparteine (G); (Q) 0.6 equiv. of TMPDA (E) and 0.6 equiv. of *trans*-(*R,R*)-TMCDA (F); (R) 1.2 equiv. of TMPDA (E) and 2.0 equiv. of (-)-sparteine (G). (Note: The homosolvated dimer containing two sparteine ligands exists as two isomers.)



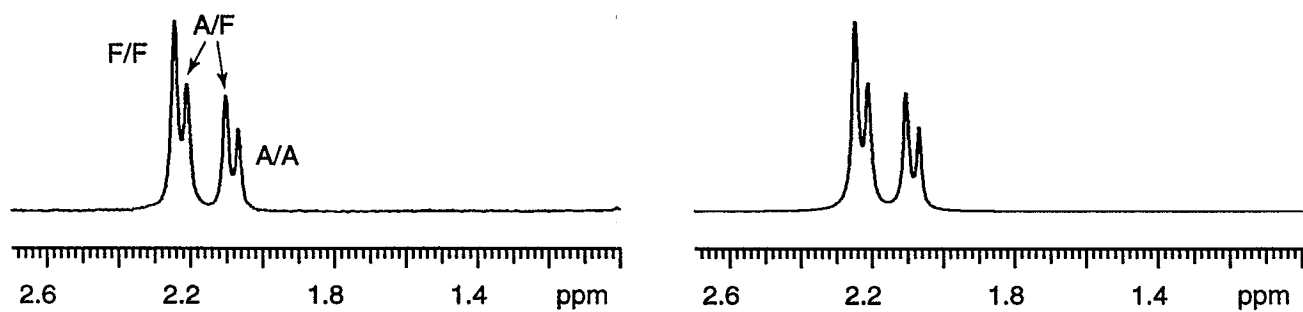
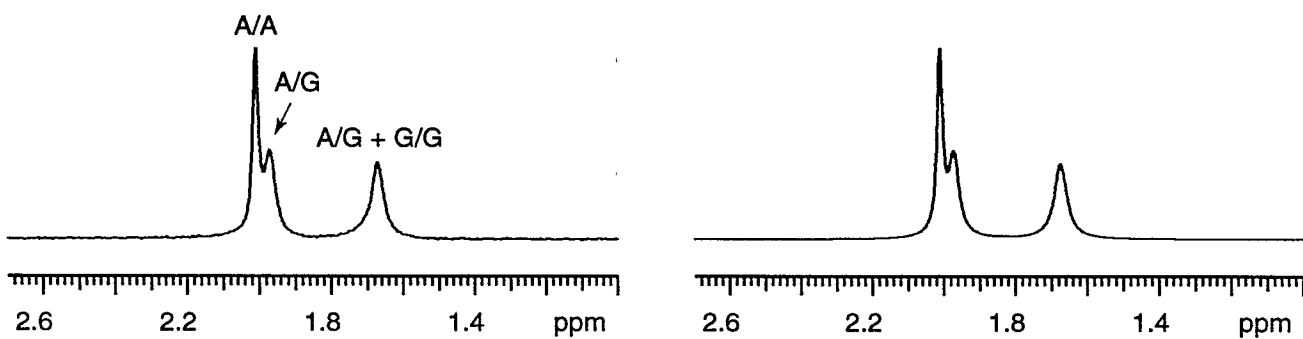
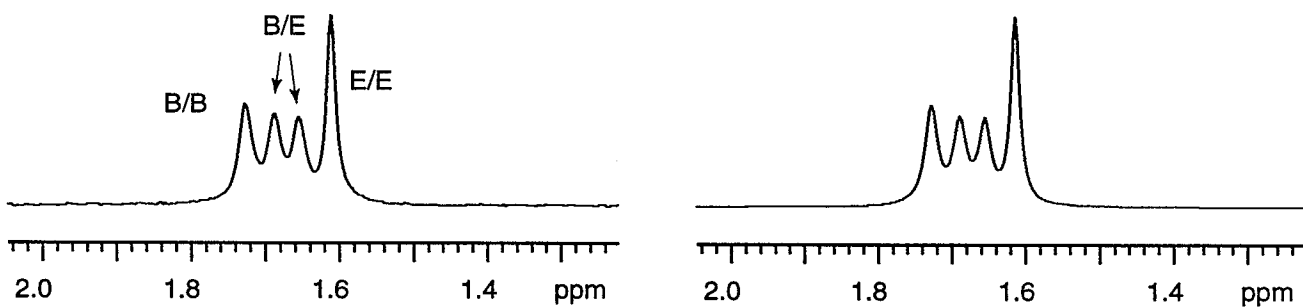
II. (cont.)  ${}^6\text{Li}$  NMR spectra (*left*: before deconvolution; *right*: theoretical spectrum after deconvolution) of 0.1  $\text{M}$   $[{}^6\text{Li}]n\text{-BuLi}$  in toluene- $\text{d}_8$  at  $-100\text{ }^\circ\text{C}$  containing 0.5 equiv. of *trans*-(*R,R*)-TMCDA (**F**) and 1.0 equiv. of (-)-sparteine (**G**). (Note: The homosolvated dimer containing two sparteine ligands exists as two isomers.)

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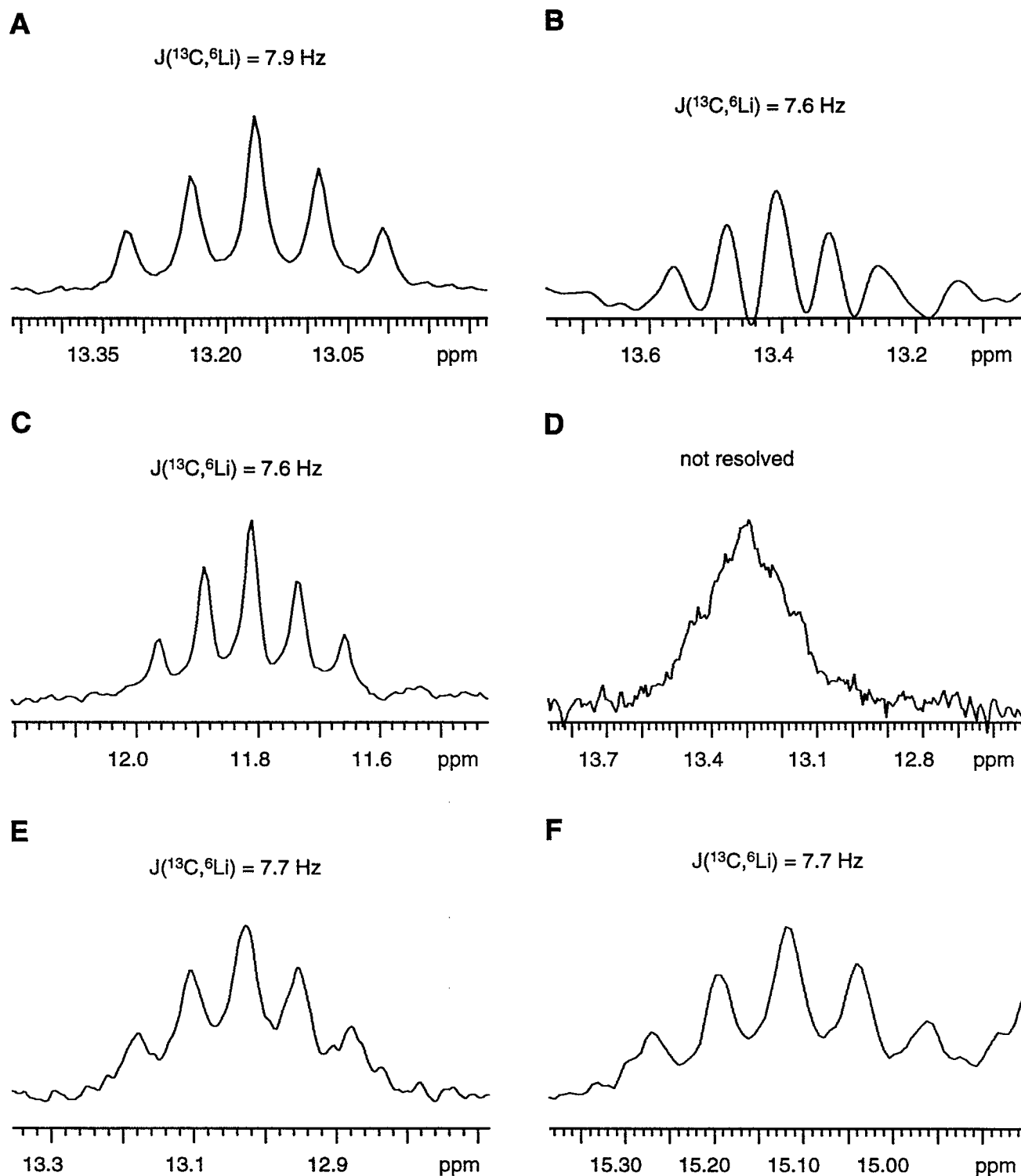
III.  ${}^6\text{Li}$  NMR spectra (*left*: before deconvolution; *right*: theoretical spectrum after deconvolution) of 0.1 M  $[\text{}^6\text{Li}]n\text{-BuLi}$  in toluene- $d_8$  at  $-100\text{ }^\circ\text{C}$  containing the following ligands: (A) 1.5 equiv. of TMEDA (A) and 4.5 equiv. of TEEDA (B); (B) 1.5 equiv. of TMEDA (A) and 1.5 equiv. of 1,2-dipyrrolidinoethane (C); (C) 1.5 equiv. of TMEDA (A) and 1.5 equiv. of 1,2-dipiperidinoethane (D).

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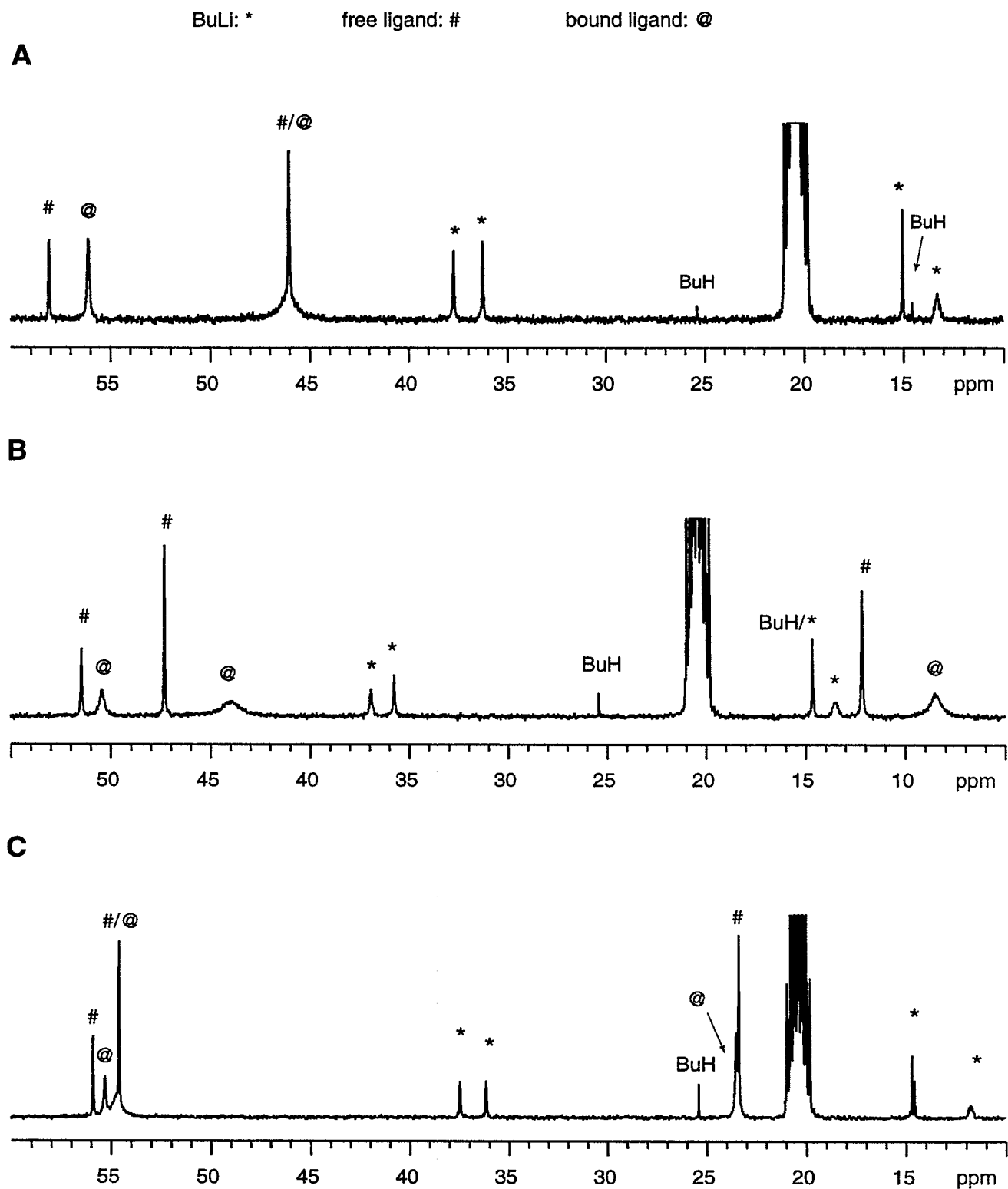
**D****E****F**

III. (cont.)  $^6\text{Li}$  NMR spectra (*left*: before deconvolution; *right*: theoretical spectra after deconvolution) of 0.1 M  $[\text{}^6\text{Li}]n\text{-BuLi}$  in toluene- $d_8$  at  $-100\text{ }^\circ\text{C}$  containing the following ligands: (D) 1.5 equiv. of TMEDA (A) and 1.5 equiv. of *trans*-(*R,R*)-TMEDA (F); (E) 1.5 equiv. of TMEDA (A) and 5.0 equiv. of (-)-sparteine (G); (F) 1.5 equiv. of TEEDA (B) and 1.0 equiv. of TMPDA (E).

(14)



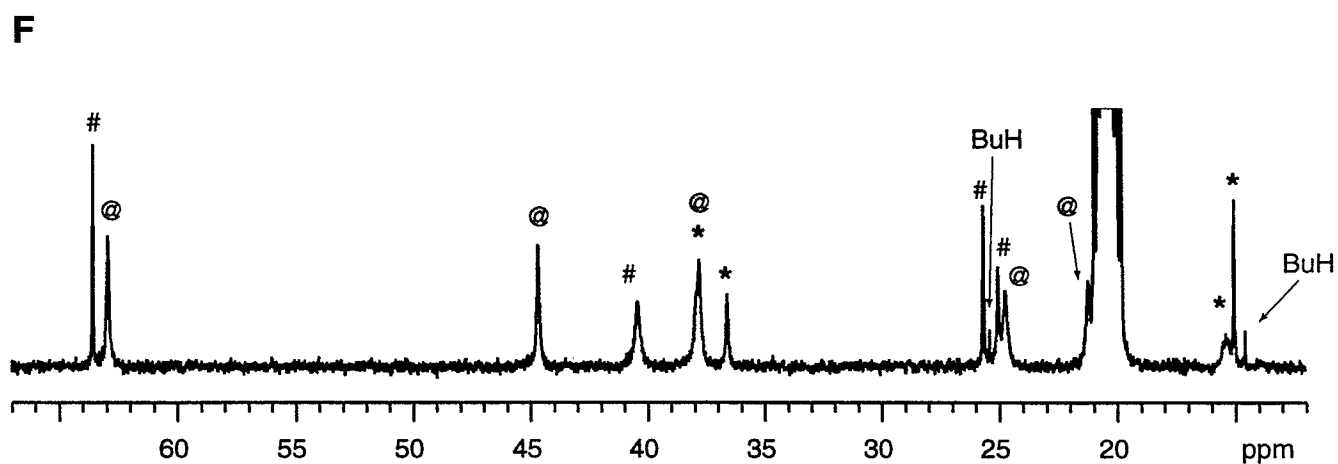
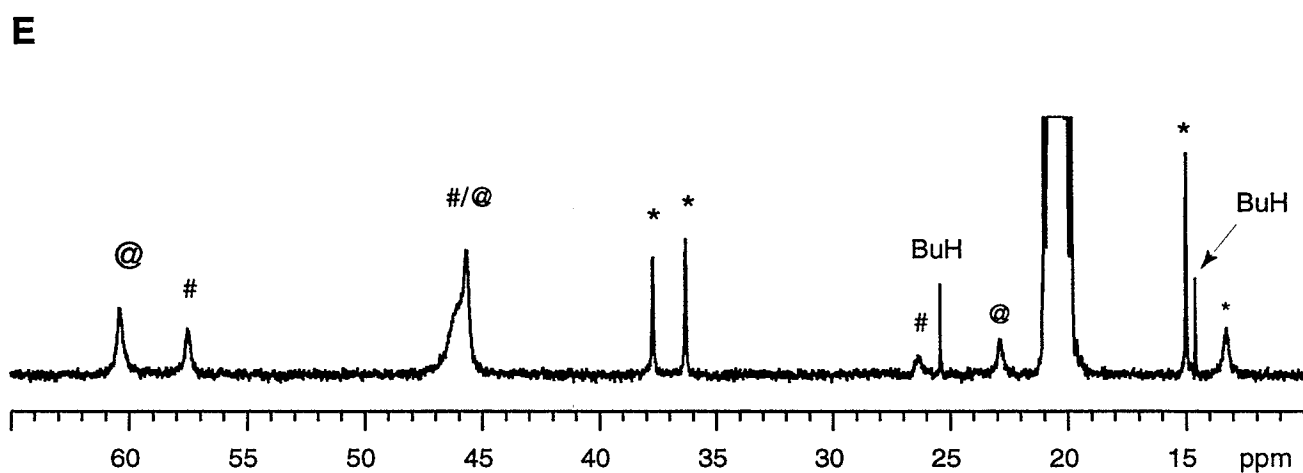
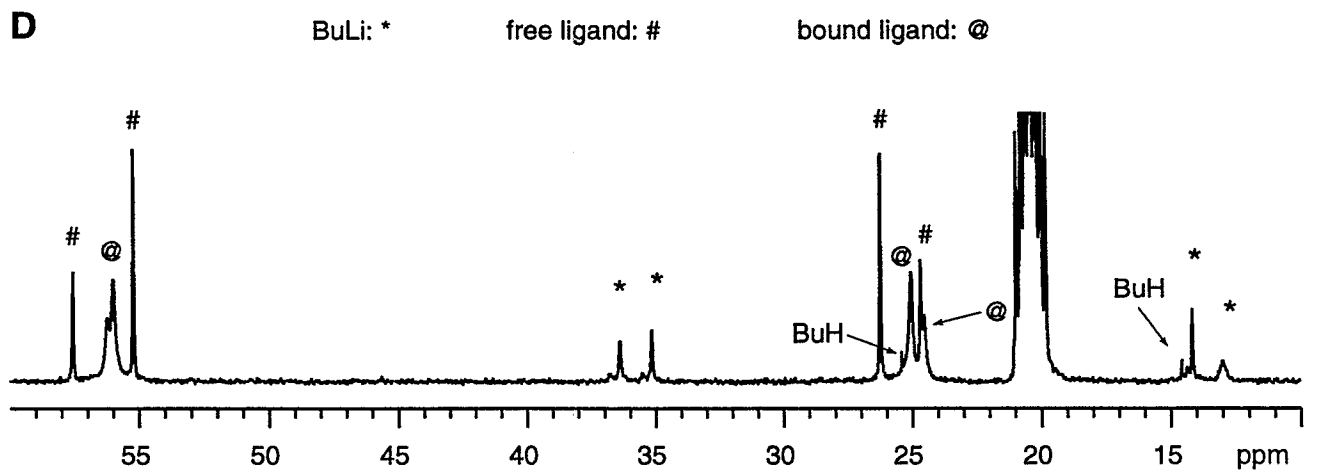
IV. Partial  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of 0.1 M  $[^6\text{Li}]n\text{-BuLi}$  in toluene- $d_8$  at  $-70^\circ\text{C}$  showing the  $n\text{-BuLi}$   $\alpha$ -carbon resonances ( $\text{CH}_2\text{Li}$ ). The samples contained the following ligands: (A) 1.5 equiv. of TMEDA (A); (B) 1.5 equiv. of TEEDA (B); (C) 1.5 equiv. of 1,2-dipyrrolidinoethane (C); (D) 1.5 equiv. of 1,2-dipiperidinoethane (D); (E) 1.5 equiv. of TMPDA (E); (F) 1.5 equiv. of *trans*-(*R,R*)-TMCDA (F); the  $\alpha$  carbon resonance for  $n\text{-BuLi}$  containing (-)-sparteine (G) could not be identified due to overlap with ligand resonances.



V. Inverse gated  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of 0.1 M  $[^6\text{Li}]n\text{-BuLi}$  in toluene- $d_8$  at  $-100^\circ\text{C}$  containing the following ligands: (A) 1.5 equiv. of TMEDA (A); (B) 1.5 equiv. of TEEDA (B); (C) 1.5 equiv. of 1,2-dipyrrolidinoethane (C).

(15)

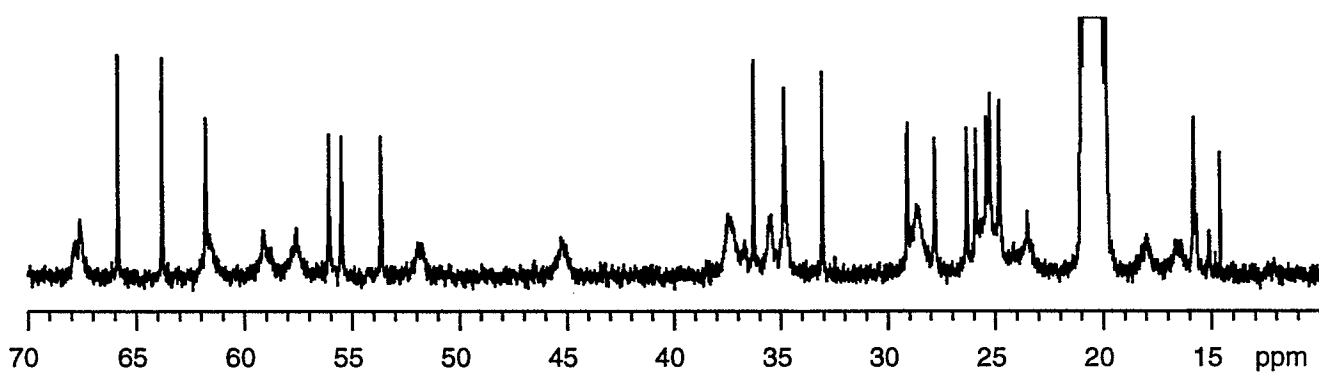




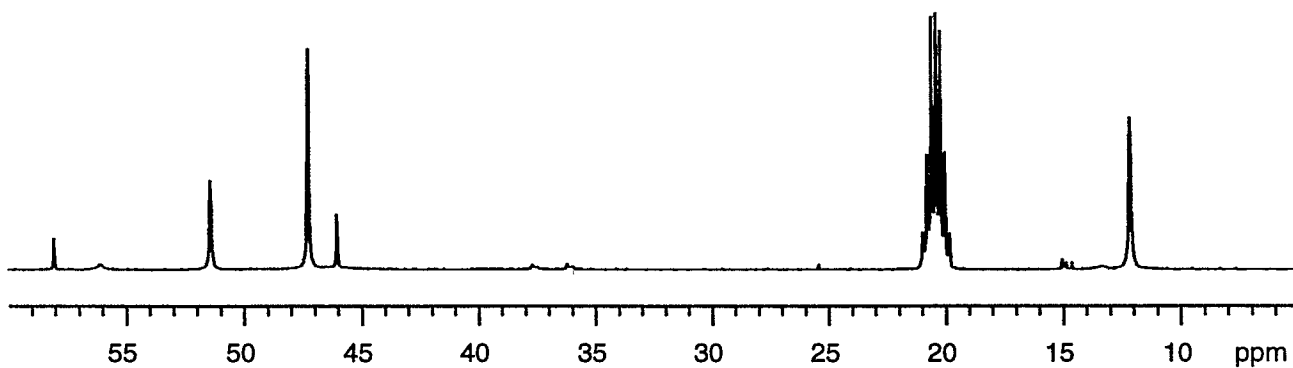
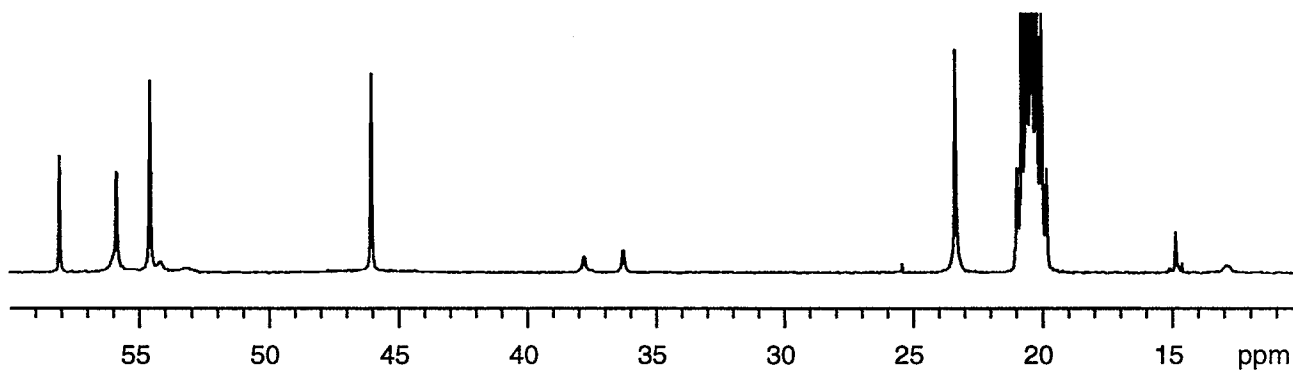
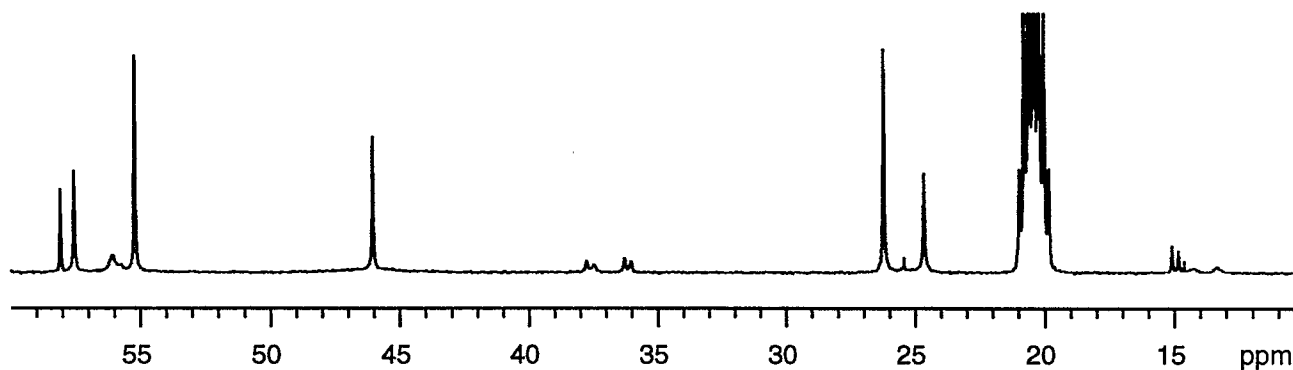
V. (cont.) Inverse gated  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of 0.1 M  $[^6\text{Li}]n\text{-BuLi}$  in toluene- $d_8$  at  $-100\text{ }^\circ\text{C}$  containing the following ligands: (D) 1.5 equiv. of 1,2-dipiperidinoethane (D); (E) 1.5 equiv. of TMPDA (E); (F) 1.5 equiv. of *trans*-(*R,R*)-TMCDA (F).

no assignments due to peak overlap

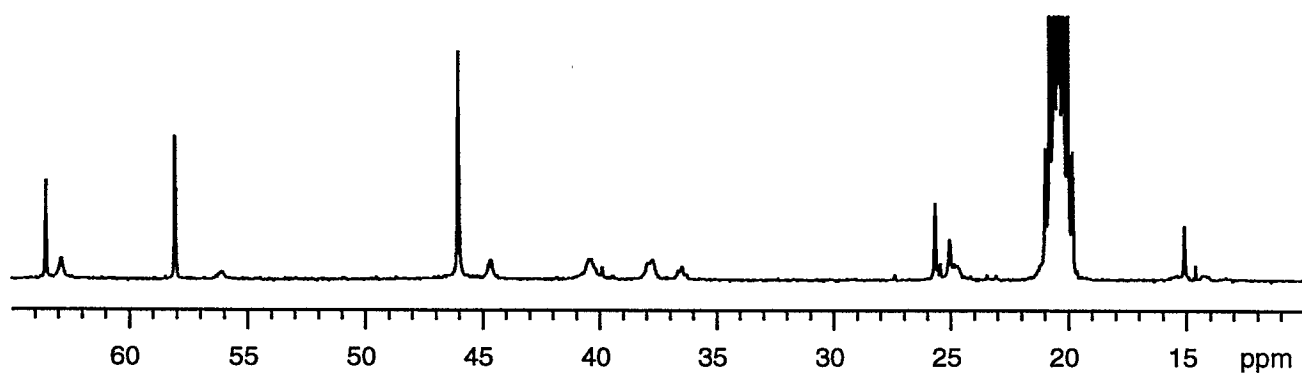
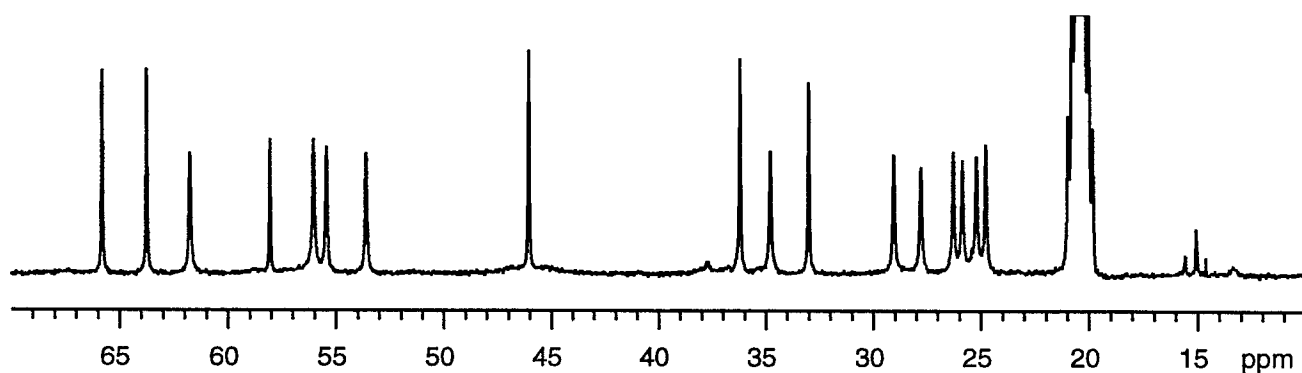
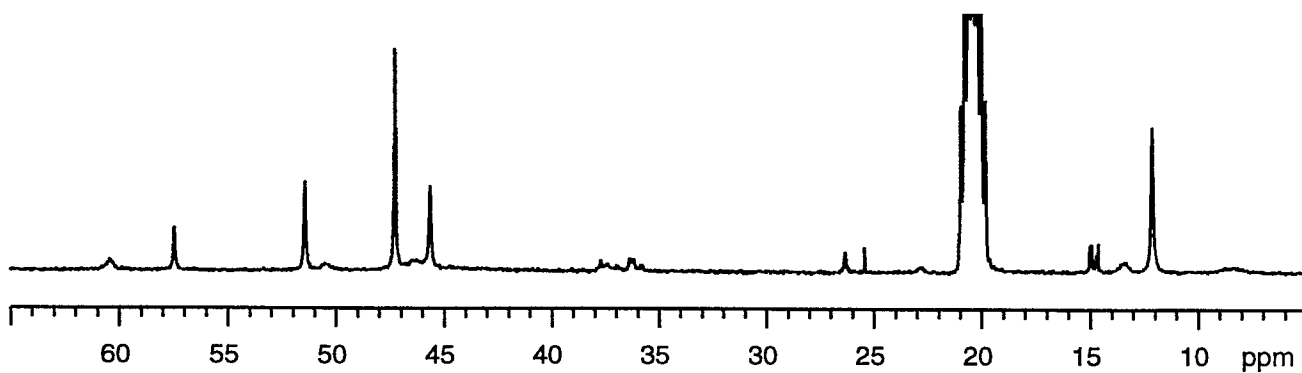
**G**



V. (cont.) Inverse gated  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (G) of 0.1 M [ $^6\text{Li}$ ]*n*-BuLi in toluene- $\text{d}_8$  at  $-100\text{ }^\circ\text{C}$  containing 1.5 equiv. of (-)-sparteine (G).

**A****B****C**

VI. Inverse gated  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of 0.1 M  $[\text{}^6\text{Li}]n\text{-BuLi}$  in toluene- $d_8$  at  $-100\text{ }^\circ\text{C}$  containing molar excesses of each of the following ligands: (A) 1.5 equiv. of TMEDA (A) and 4.5 equiv. of TEEDA (B); (B) 1.5 equiv. of TMEDA (A) and 1.5 equiv. of 1,2-dipyrrolidinoethane (C); (C) 1.5 equiv. of TMEDA (A) and 1.5 equiv. of 1,2-dipiperidinoethane (D).

**D****E****F**

VI. (cont.) Inverse gated  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of 0.1 M  $[\text{Li}]n\text{-BuLi}$  in toluene- $d_8$  at  $-100\text{ }^\circ\text{C}$  containing molar excesses of each of the following ligands: (D) 1.5 equiv. of TMEDA (A) and 1.5 equiv. of *trans*-(*R,R*)-TMCDA (F); (E) 1.5 equiv. of TMEDA (A) and 3.0 equiv. of (-)-sparteine (G); (F) 1.5 equiv. of TEEDA (B) and 1.0 equiv. of TMPDA (E).