Consequences of Correlated Solvation on the Structures and Reactivities of RLi-Diamine Complexes: 1,2-Addition and α-Lithiation Reactions of Imines by TMEDA-Solvated *n*-Butyllithium and Phenyllithium

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Supporting Information

NMR Spectroscopy

I. ^{6}Li NMR spectra of PhLi with ligands **A-G**.

II. ^{6}Li NMR spectra of PhLi with combinations of ligands **A-G** at low ligand concentrations.

III. ^{6}Li and ^{1}H NMR spectra of PhLi with combinations of ligands **A-G** at high ligand concentrations.

IV. Partial ^{13}C NMR spectra of PhLi with ligands **A-G** showing the $\underline{C}H_2Li$ resonance.

V. ^{13}C spectra of PhLi with ligands **A-G** in the limit of slow solvent exchange.

VI. ^{13}C spectra of PhLi with combinations of ligands **A-G** at high ligand concentrations.

Table 1. ^{6}Li NMR spectroscopic data of diamine-solvated PhLi dimers, $(PhLi)_2SS'$.

Table 2. ^{13}C NMR spectroscopic data of diamine-solvated PhLi dimers, $(PhLi)_2S_2$.

Notes:

(1) Supporting information for *n*-BuLi NMR spectroscopy can be found in Hoffmann, D.; Collum, D. B. *J. Am. Chem. Soc.* **1998**, *120*, 5810.

(2) Broadening of ^{6}Li resonances coordinated by **D** (see 1D, 2C, 2H, 2L, 2P, 2Q, 2R), as well as the extra resonances (see 2C), are associated with conformation effects within the piperidine ring as discussed in a reference of the manuscript.

(3) The homosolvated dimer containing two (-)-sparteine ligands consists of two isomers with a peak integration ratio of 1:2.4. (see 2F, 2K, 2O, 2R, 2T, 2U, 2V)

IR Spectroscopy

VII. Plot of k_{obsd} vs. [*n*-BuLi] for the 1,2-addition to imine **1** (0.01 M) in TMEDA (0.5 M excess) and pentane at -40 °C.

VIII. Plot of k_{obsd} vs. [TMEDA] for the 1,2-addition of *n*-BuLi (0.3 M) to imine **1** (0.01 M) in pentane at -40 °C.

IX. Plot of k_{obsd} vs. [*n*-BuLi] for the α-lithiation of imine **6** (0.01 M) in TMEDA (0.5 M excess) and pentane at -40 °C.

X. Plot of k_{obsd} vs. [TMEDA] for the α-lithiation of imine **6** (0.01 M) with *n*-BuLi (0.3 M) in pentane at -40 °C.

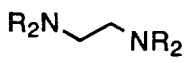
XI. Plot of k_{obsd} vs. [PhLi] for the 1,2-addition to imine **1** (0.01 M) in neat TMEDA at 19 °C .

XII. Plot of k_{obsd} vs. [TMEDA] for the 1,2-addition of PhLi (0.2 M) to imine **1** (0.01 M) in pentane at 19 °C.

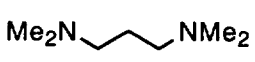
XIII. Plot of k_{obsd} vs. [PhLi] for the α-lithiation of imine **6** (0.01 M) in neat TMEDA at 19 °C.

XIV. Plot of k_{obsd} vs. [TMEDA] for the α-lithiation of imine **6** (0.01 M) with PhLi (0.2 M) in pentane at 19 °C.

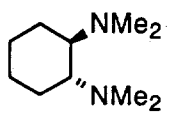
Table 3. k_{obsd} (s^{-1}) for the 1,2-addition and α-lithiation of imine **1** and imine **6**, respectively, with *n*-BuLi and PhLi in pentane and diamines **A-G**.



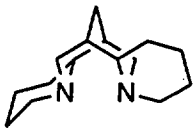
A; $NR_2 = NMe_2$ (TMEDA)
B; $NR_2 = NEt_2$ (TEEDA)
C; $NR_2 = N(CH_2)_4$
D; $NR_2 = N(CH_2)_5$



E (TMPDA)



F ((*R*,*R*)-TMCDA)



G ((-)-sparteine)

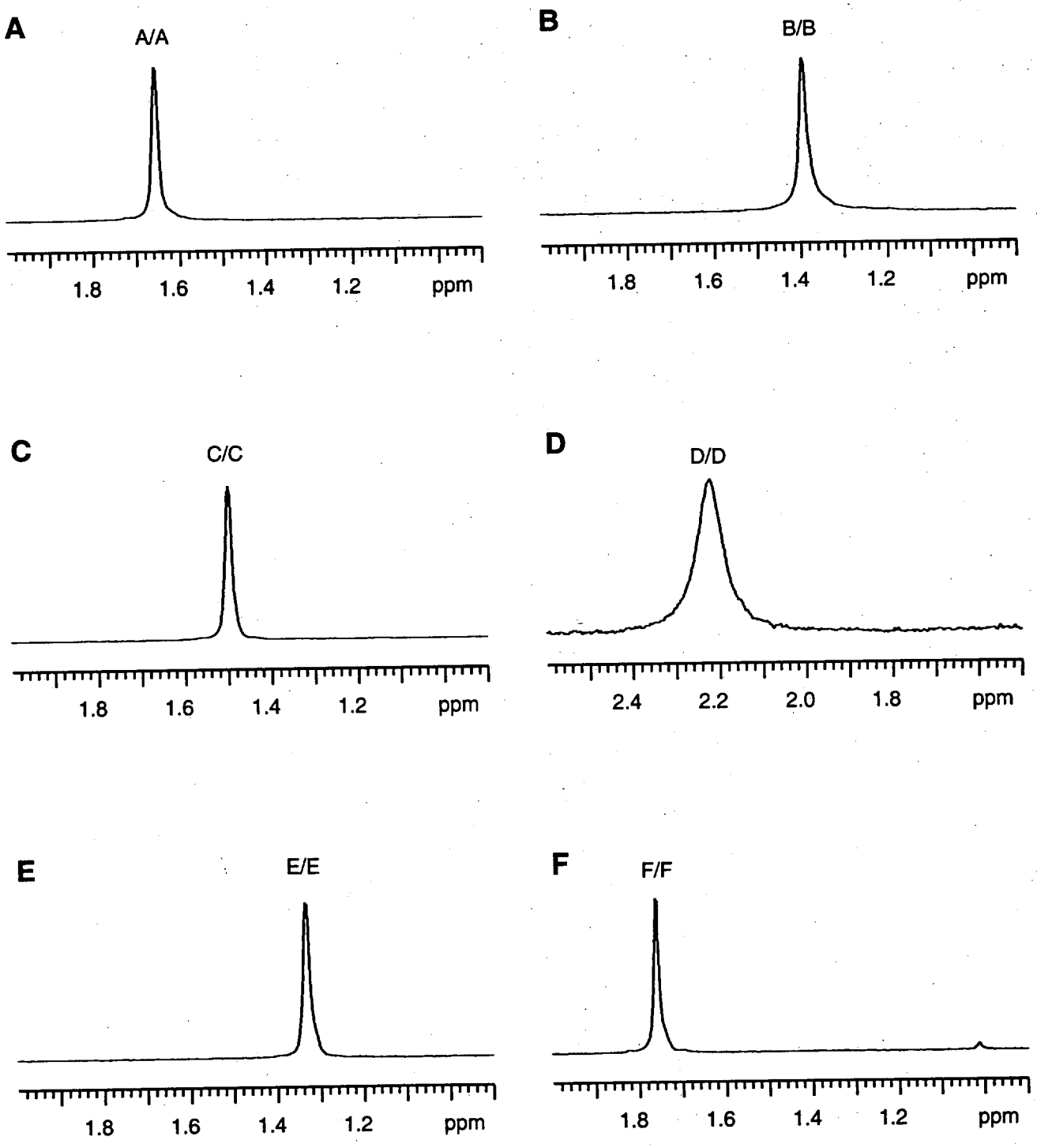


Figure I. ^{6}Li NMR spectra of 0.1 M [^{6}Li]PhLi in toluene-d_8 at -100 °C containing the following ligands: (A) 1.1 equiv of TMEDA (**A**); (B) 1.1 equiv of TEEDA (**B**); (C) 1.2 equiv of 1,2-dipyrrolidinoethane (**C**); (D) 1.5 equiv of 1,2-dipiperidinoethane (**D**); (E) 1.1 equiv of TMPDA (**E**); (F) 1.2 equiv of *trans-(R,R)*-TMCDA (**F**). PhLi does not dissolve with (-)-sparteine (**G**) alone. However, combinations of (-)-sparteine and other ligands dissolve PhLi (see Figure II).

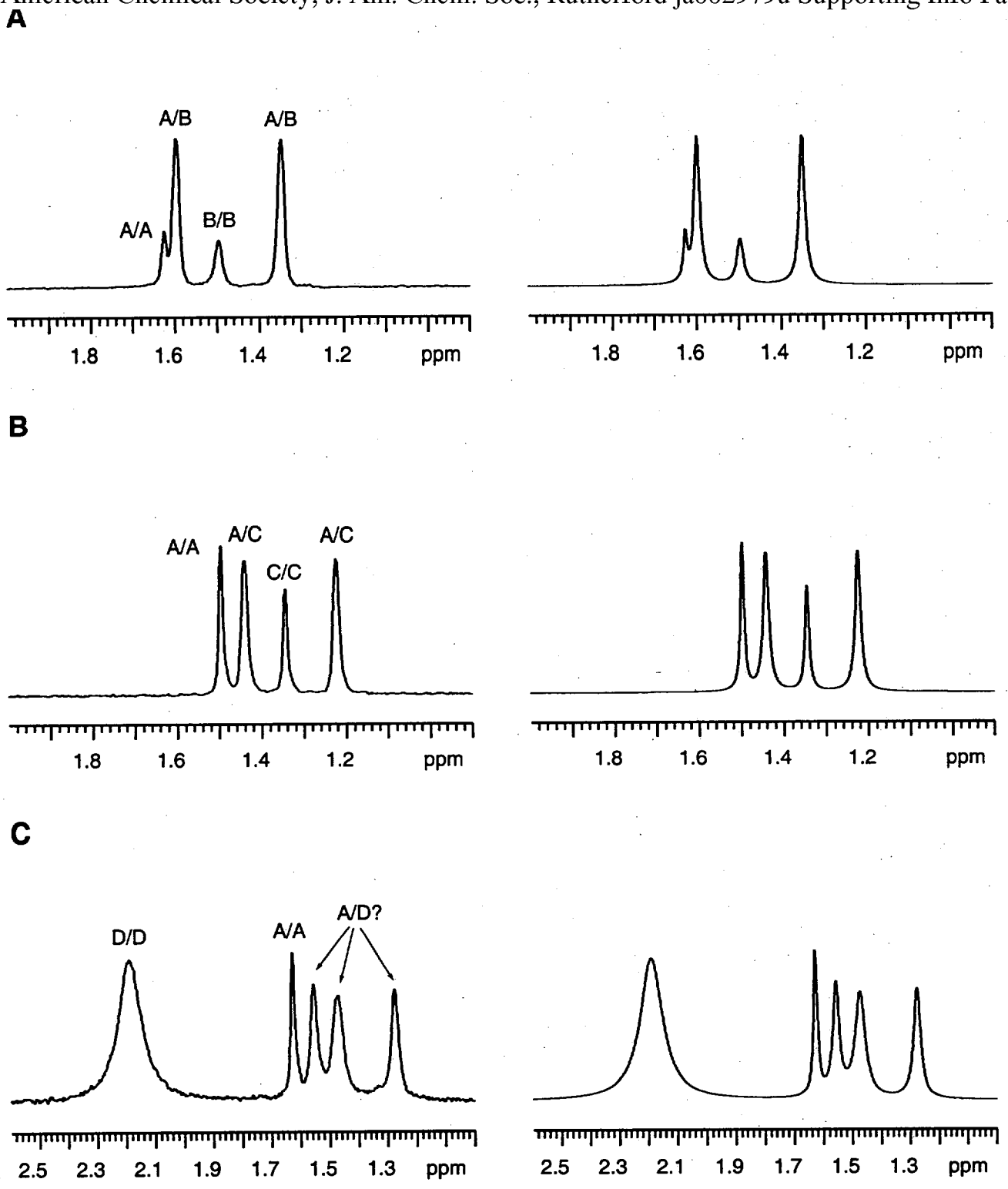


Figure II. ^{6}Li NMR spectra (*left*: before deconvolution; *right*: theoretical spectra after deconvolution) of 0.1 M [^{6}Li]PhLi in toluene-d_8 containing the following ligands: (A) 0.4 equiv of TMEDA (**A**) and 3.6 equiv of TEEDA (**B**) at -100 °C; (B) 0.5 equiv of TMEDA (**A**) and 1.5 equiv of 1,2-dipyrrolidinoethane (**C**) at -100 °C; (C) 0.4 equiv of TMEDA (**A**) and 1.2 equiv of 1,2-dipiperidinoethane (**D**) at -110 °C.

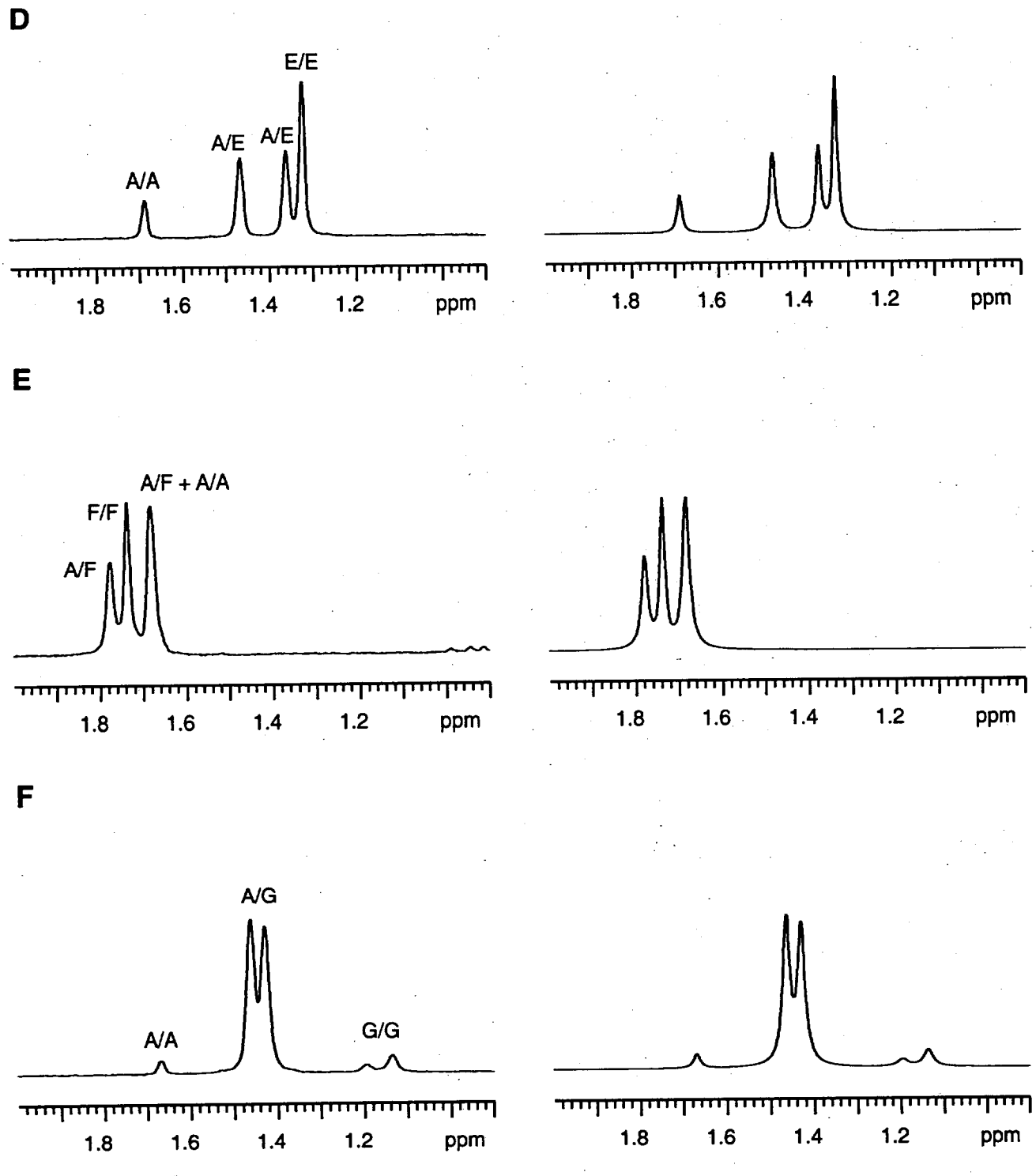


Figure II. (cont.) ^{6}Li NMR spectra (*left*: before deconvolution; *right*: theoretical spectra after deconvolution) of 0.1 M [^{6}Li]PhLi in toluene-d_8 at -100 °C containing the following ligands: (D) 0.3 equiv of TMEDA (**A**) and 1.5 equiv of TMPDA (**E**); (E) 1.2 equiv of TMEDA (**A**) and 1.2 equiv of *trans-(R,R)*-TMCDA (**F**); (F) 0.7 equiv of TMEDA (**A**) and 1.9 equiv of (-)-sparteine (**G**).

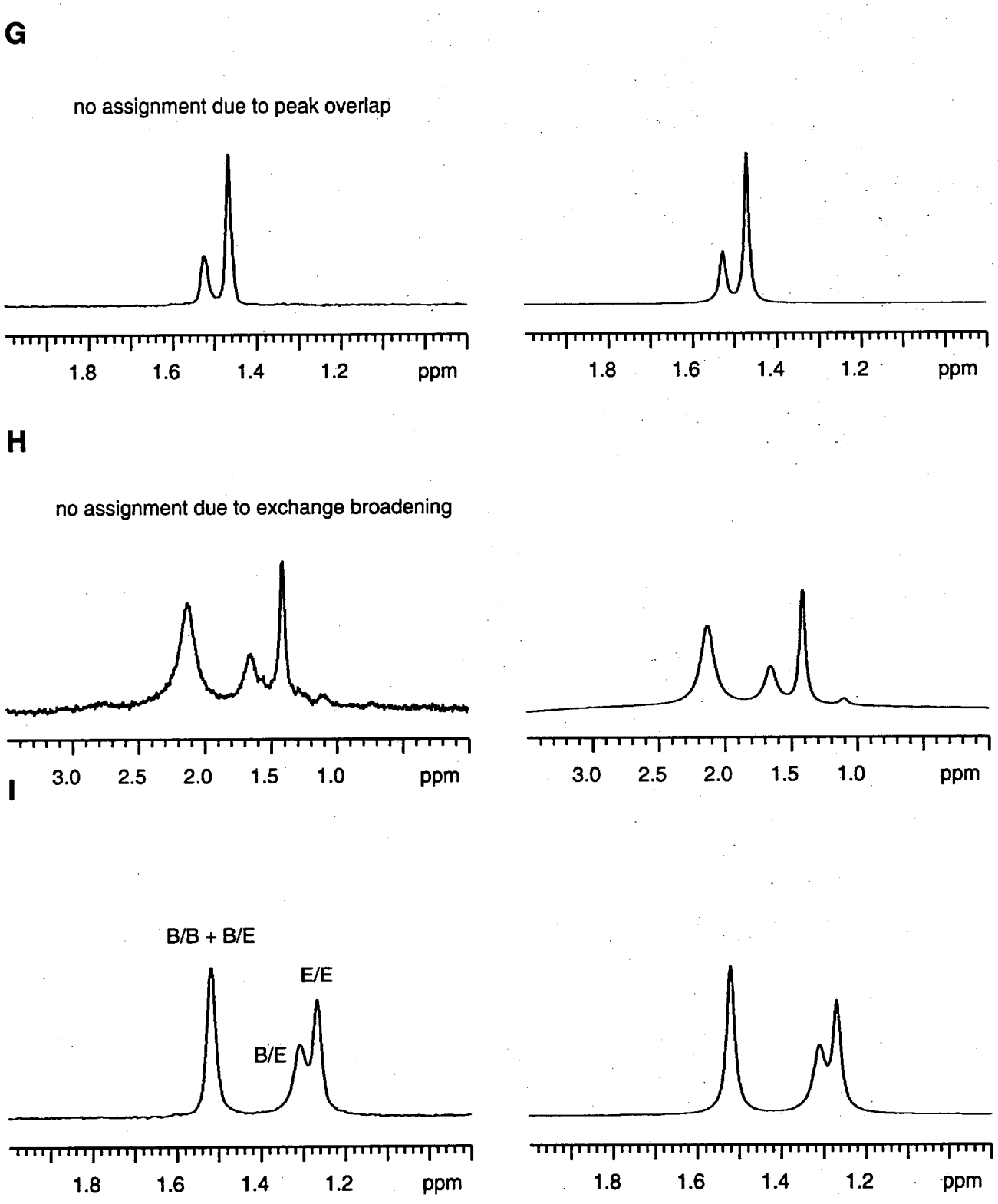


Figure II. (cont.) ^{6}Li NMR spectra (*left*: before deconvolution; *right*: theoretical spectra after deconvolution) of 0.1 M [^{6}Li]PhLi in toluene-d_8 at -100 °C containing the following ligands: (G) 0.6 equiv of TEEDA (**B**) and 0.6 equiv of 1,2-dipyrrolidinoethane (**C**); (H) 0.4 equiv of TEEDA (**B**) and 0.8 equiv of 1,2-dipiperidinoethane (**D**); (I) 0.6 equiv of TEEDA (**B**) and 0.6 equiv of TMPDA (**E**).

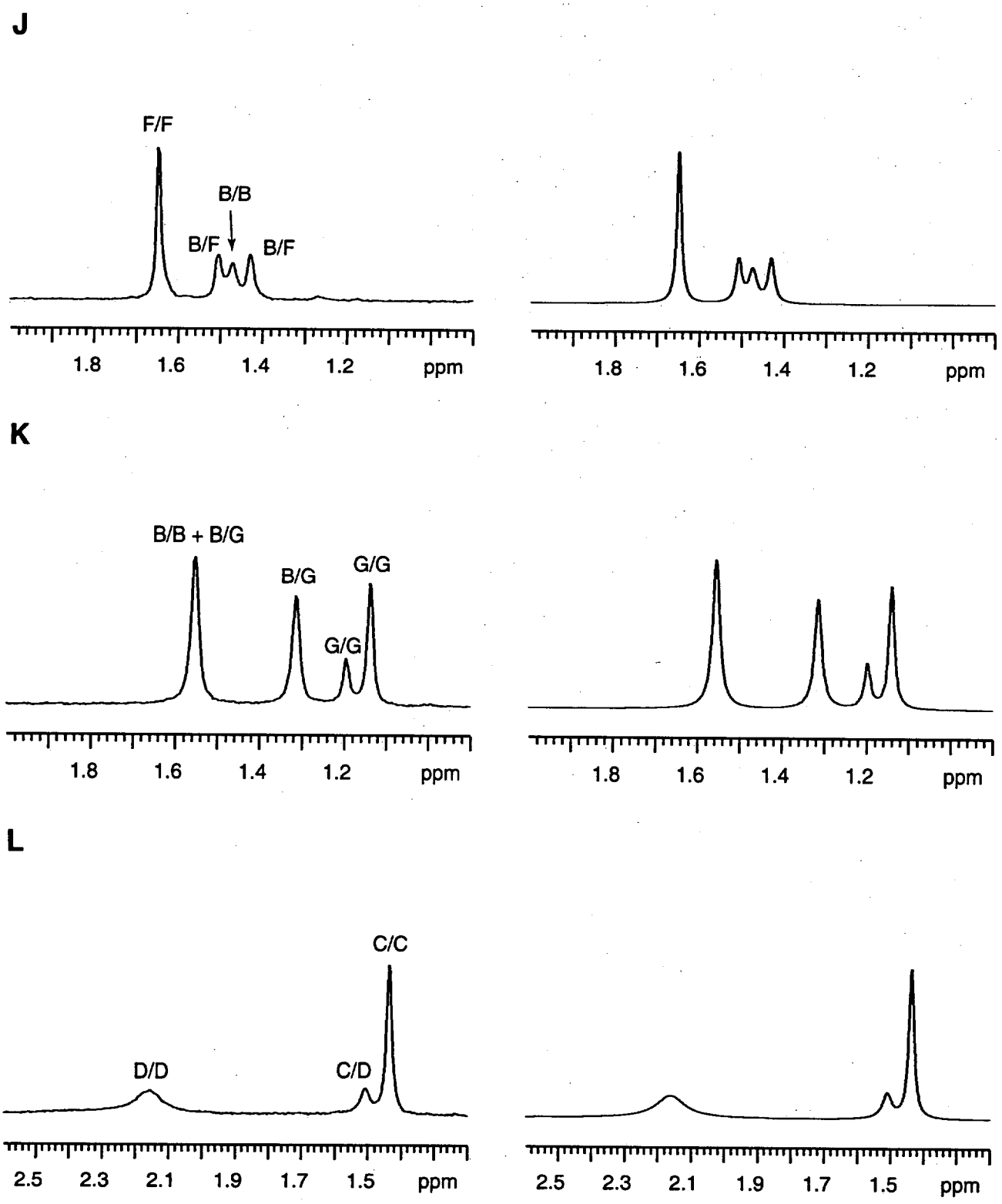


Figure II. (cont.) ^{6}Li NMR spectra (*left*: before deconvolution; *right*: theoretical spectra after deconvolution) of 0.1 M [^{6}Li]PhLi in toluene-d_8 at -100 °C containing the following ligands: (J) 0.6 equiv of TEEDA (**B**) and 0.6 equiv of *trans-(R,R)*-TMCDA (**F**); (K) 0.6 equiv of TEEDA (**B**) and 0.6 equiv of (-)-sparteine (**G**); (L) 0.5 equiv of 1,2-dipyrrolidinoethane (**C**) and 1.2 equiv of 1,2-dipiperidinoethane (**D**).

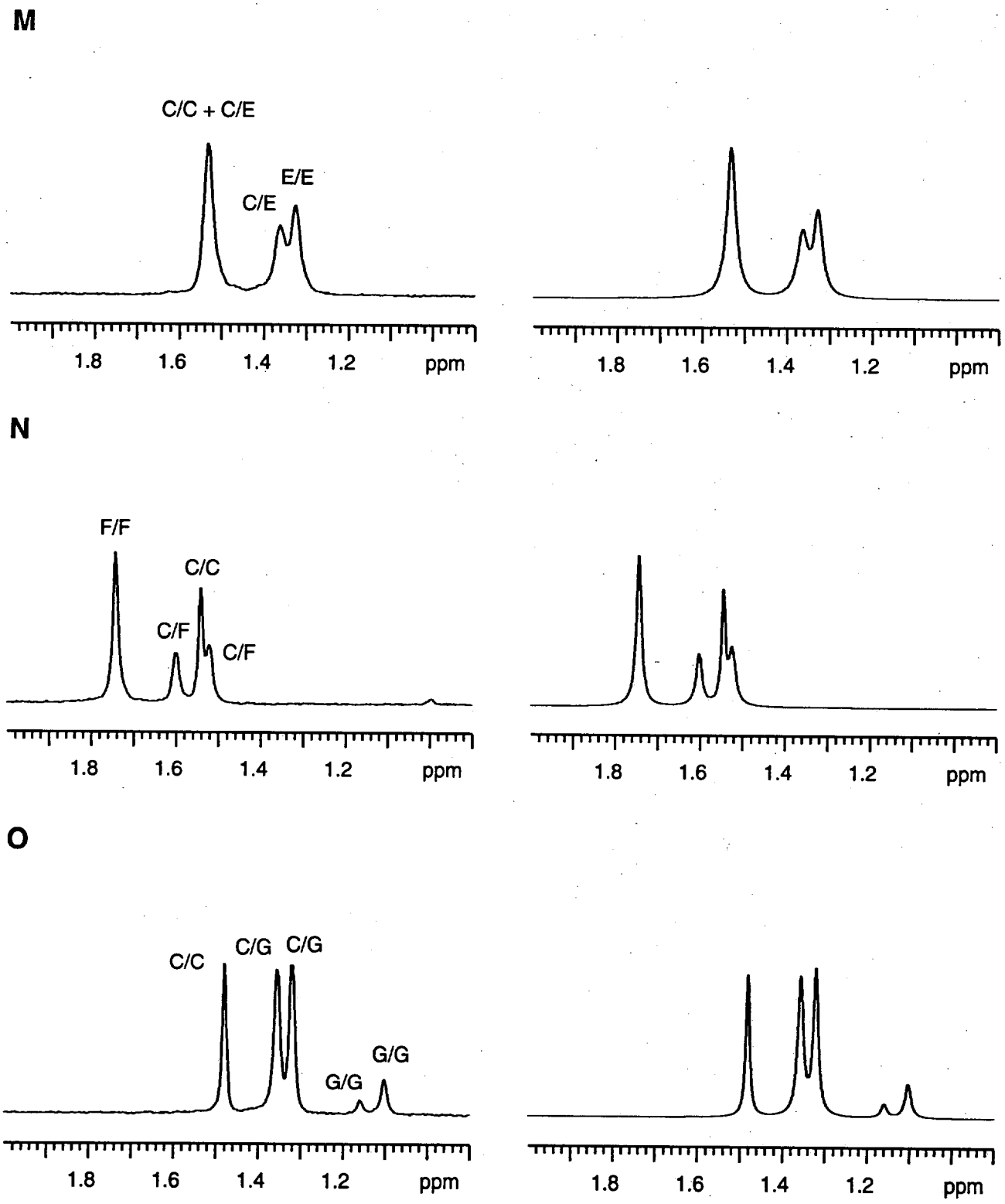


Figure II. (cont.) ^{6}Li NMR spectra (*left*: before deconvolution; *right*: theoretical spectra after deconvolution) of 0.1 M [^{6}Li]PhLi in toluene-d_8 at -100 °C containing the following ligands: (M) 0.7 equiv of 1,2-dipyrrolidinoethane (**C**) and 5.7 equiv of TMPDA (**E**); (N) 2.6 equiv of 1,2-dipyrrolidinoethane (**C**) and 0.6 equiv of *trans-(R,R)*-TMCDA (**F**); (O) 0.6 equiv of 1,2-dipyrrolidinoethane (**C**) and 0.6 equiv of (-)-sparteine (**G**).

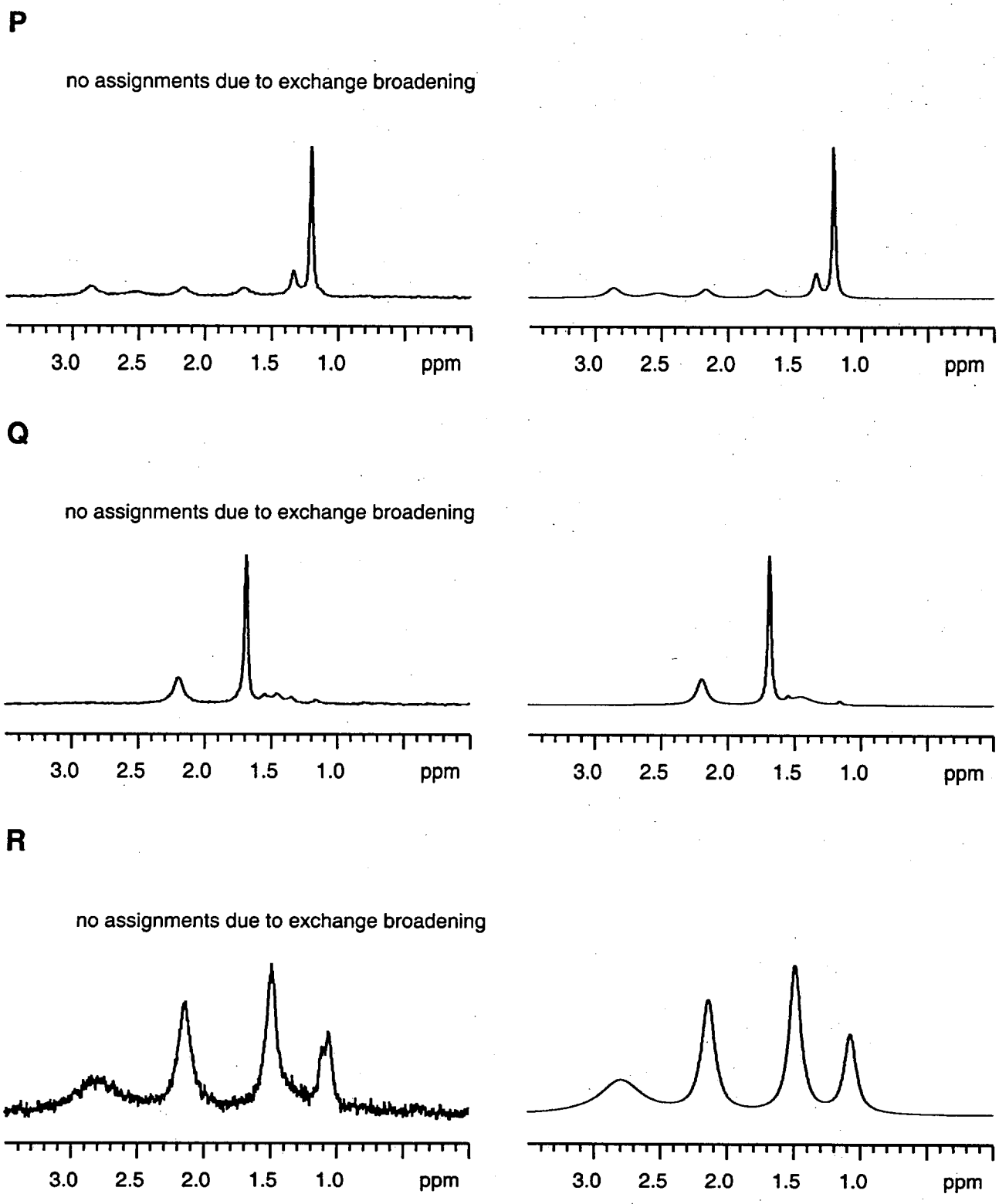


Figure II. (cont.) ^{6}Li NMR spectra (*left*: before deconvolution; *right*: theoretical spectra after deconvolution) of 0.1 M [^{6}Li]PhLi in toluene-d_8 at -100 °C containing the following ligands: (P) 0.6 equiv of 1,2-dipiperidinoethane (**D**) and 0.6 equiv of TMPDA (**E**); (Q) 0.6 equiv of 1,2-dipiperidinoethane (**D**) and 0.6 equiv of *trans-(R,R)*-TMCDA (**F**); (R) 1.2 equiv 1,2-dipiperidinoethane (**D**) and 0.4 equiv of (-)-sparteine (**G**).

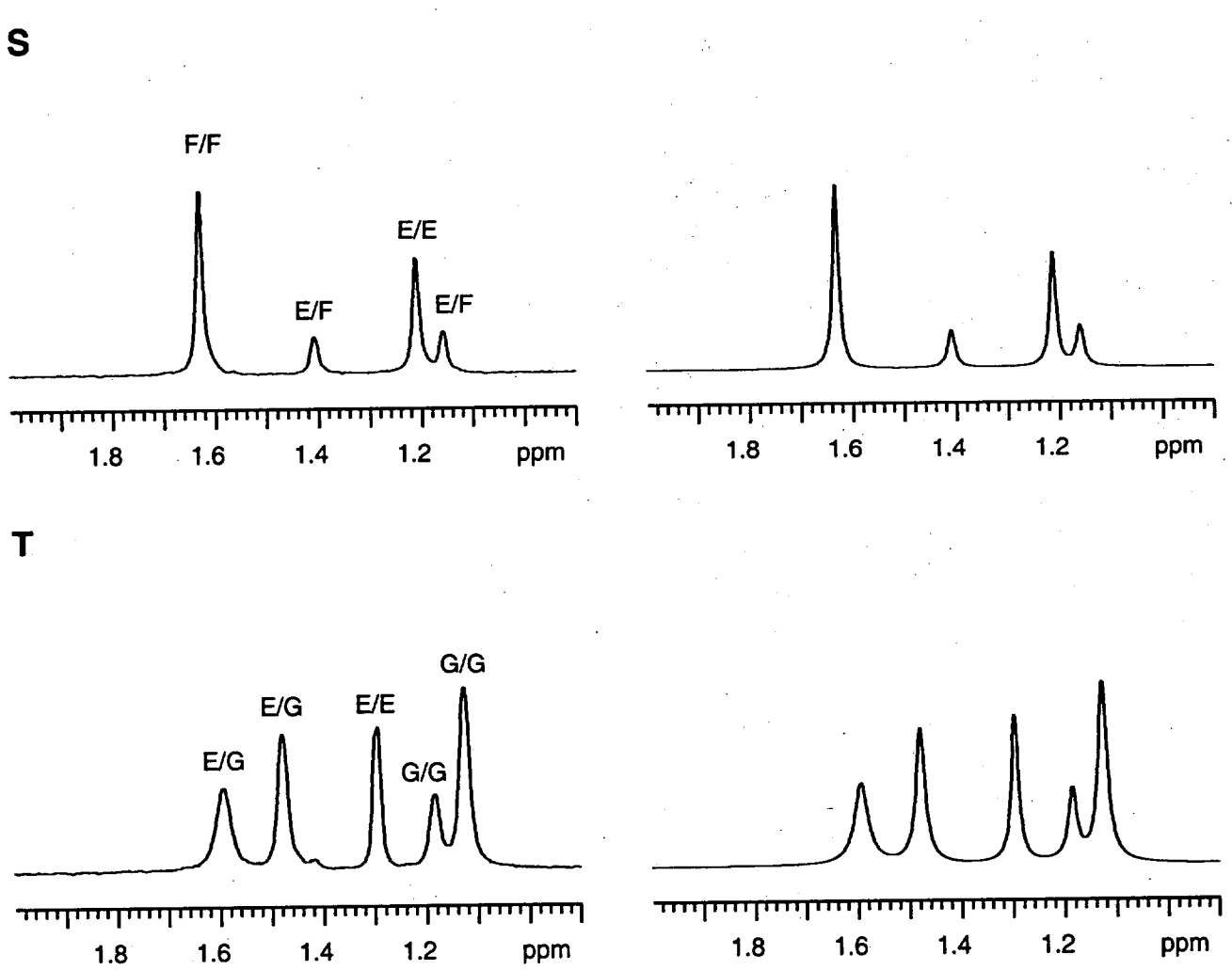


Figure II. (cont.) ^{6}Li NMR spectra (*left*: before deconvolution; *right*: theoretical spectra after deconvolution) of 0.1 M [^{6}Li]PhLi in toluene-d_8 at -100 °C containing the following ligands: (S) 0.6 equiv of TMPDA (**E**) and 0.6 equiv of *trans-(R,R)*-TMCDA (**F**); (T) 1.2 equiv of TMPDA (**E**) and 1.2 equiv of (-)-sparteine (**G**).

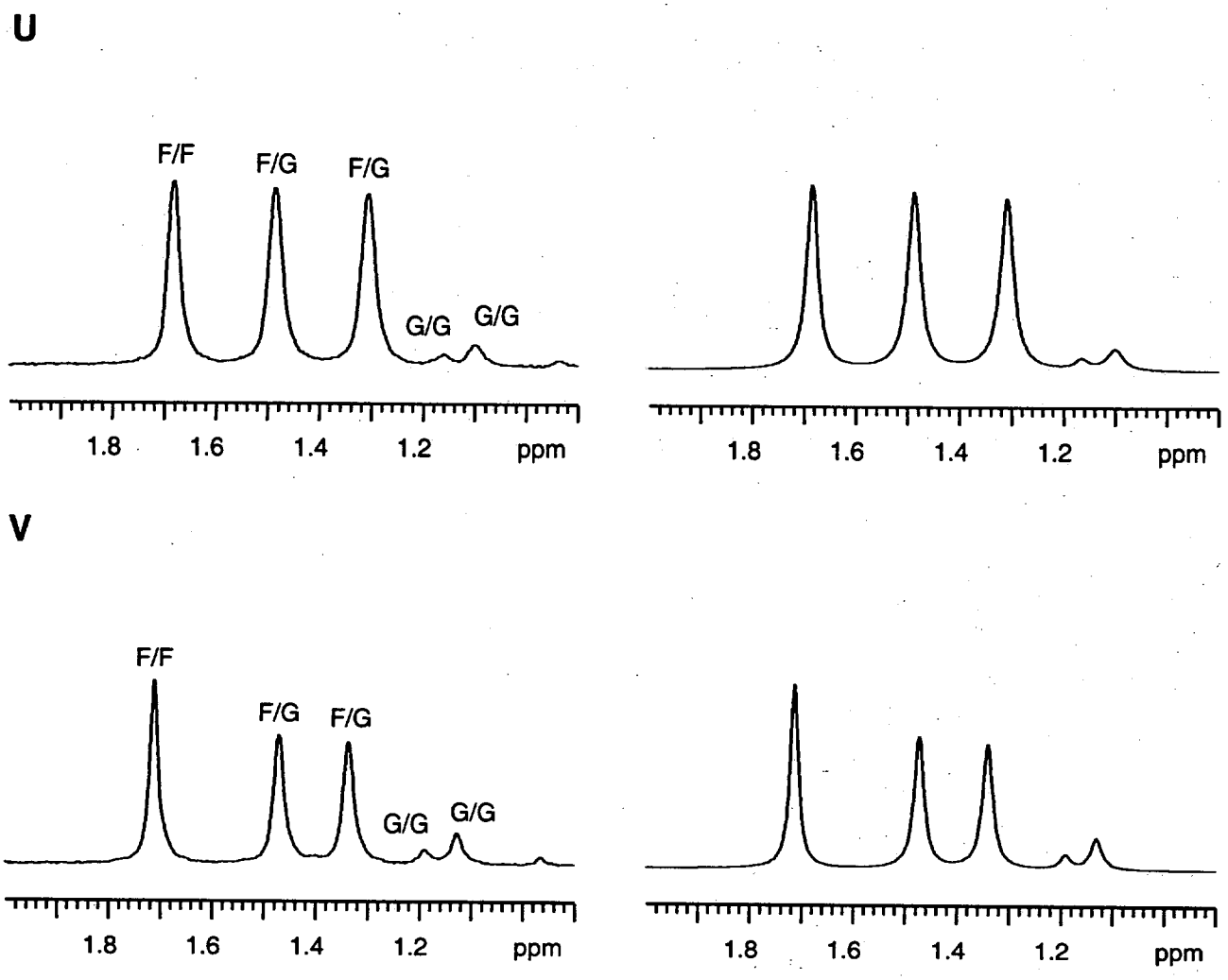


Figure II. (cont.) ^{6}Li NMR spectra (*left*: before deconvolution; *right*: theoretical spectrum after deconvolution) of 0.1 M [^{6}Li]PhLi in toluene-d_8 at -100 °C containing the following ligands: (U) 1.3 equiv of *trans-(R,R)*-TMCDA (**F**) and 5.6 equiv of (-)-sparteine (**G**); (V) 0.7 equiv of *trans-(S,S)*-TMCDA (**F**) and 3.7 equiv of (-)-sparteine (**G**).

W

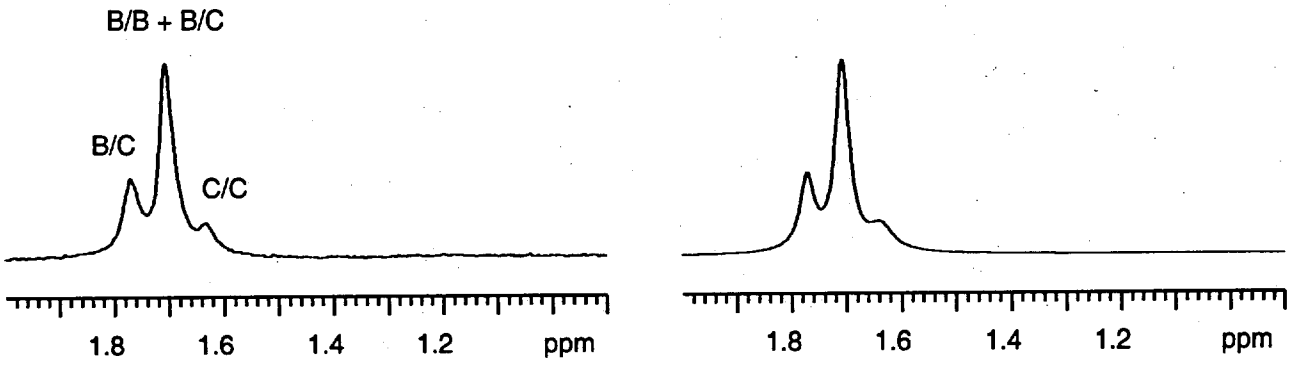


Figure II. (cont.) ^{6}Li NMR spectra (*left*: before deconvolution; *right*: theoretical spectrum after deconvolution) of 0.1 M [^{6}Li]PhLi in pentane/toluene-d_8 (2:1) at -135 °C containing the following ligands: (W) 0.6 equiv of 1,2-dipyrrolidinoethane (**C**) and 0.6 equiv of TEEDA (**B**).

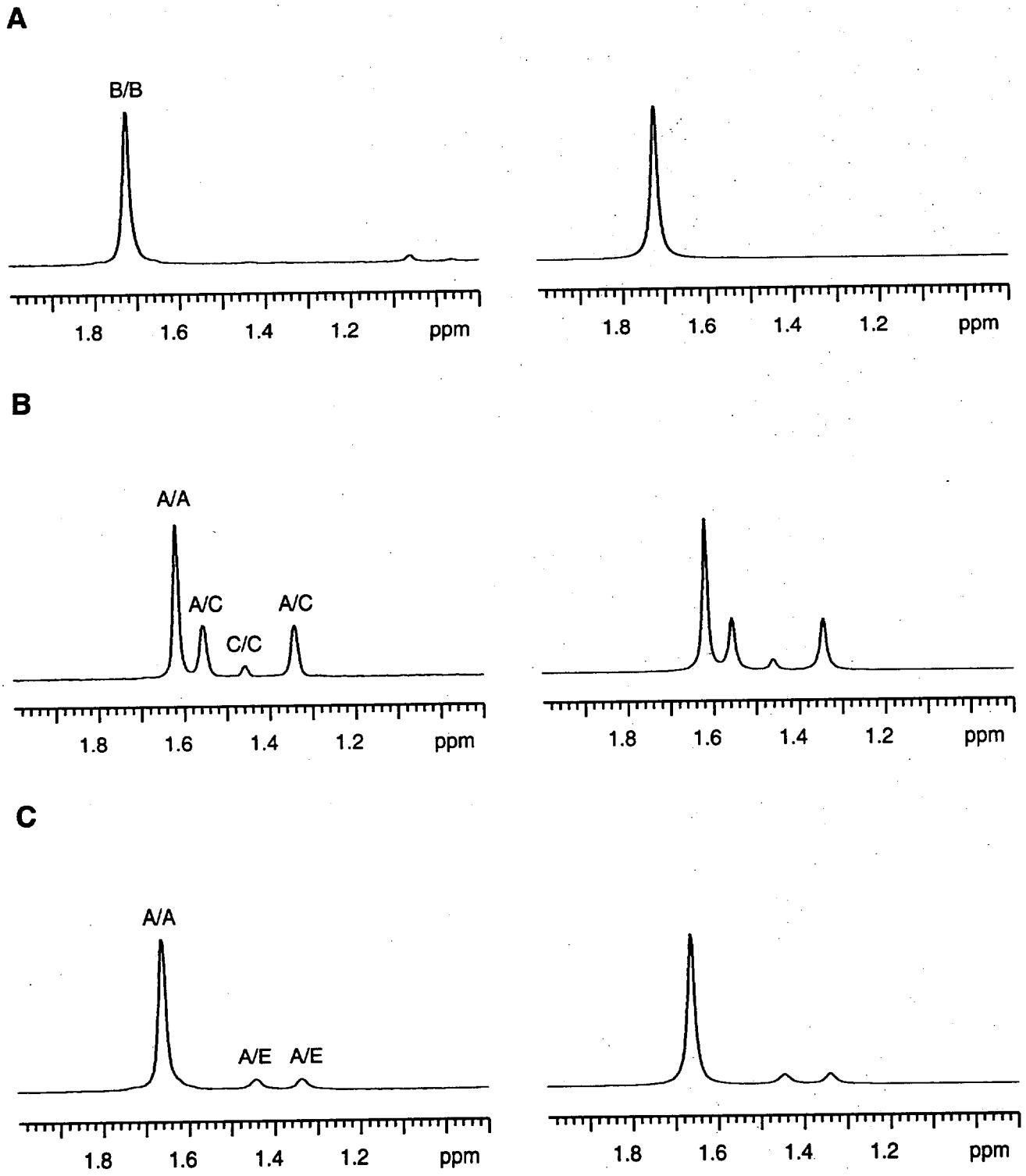


Figure III. ^{6}Li NMR spectra (*left*: before deconvolution; *right*: theoretical spectra after deconvolution) of 0.1 M [^{6}Li]PhLi in toluene-d_8 at -100 °C containing the following ligands: (A) 1.5 equiv of TMEDA (**A**) and 15.0 equiv of TEEDA (**B**); (B) 1.5 equiv of TMEDA (**A**) and 9.0 equiv of 1,2-dipyrrolidinoethane (**C**); (C) 1.5 equiv of TMEDA (**A**) and 10.0 equiv of TMPDA (**E**). Note: The combination of TMEDA and **D** was not investigated at high ligand concentrations due to unassignable peaks in the spectrum (see Figure II (C)).

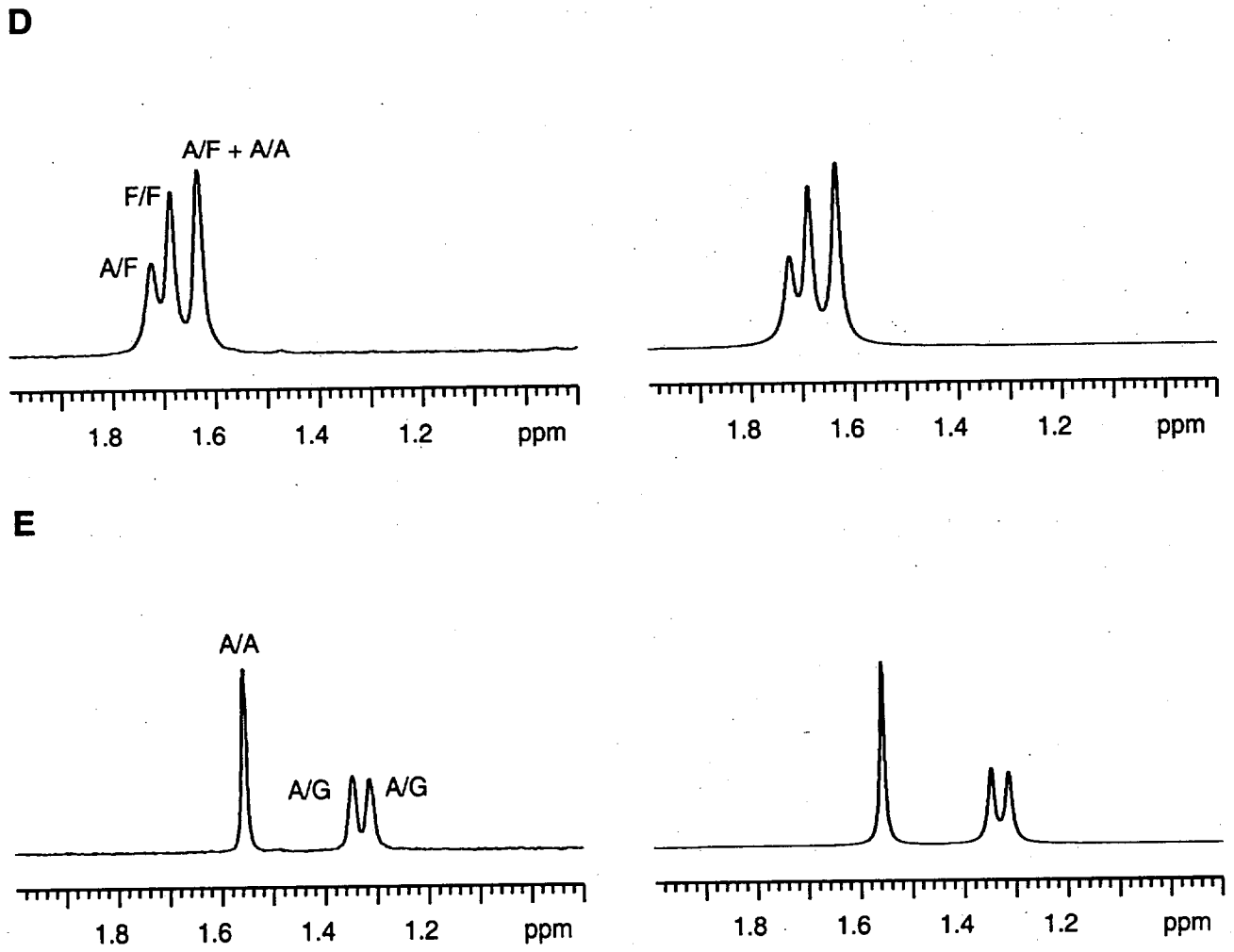


Figure III. (cont.) ^{6}Li NMR spectra (*left*: before deconvolution; *right*: theoretical spectra after deconvolution) of 0.1 M [^{6}Li]PhLi in toluene-d_8 at -100° C containing the following ligands: (D) 1.5 equiv of TMEDA (**A**) and 1.5 equiv of *trans-(R,R)*-TMCDA (**F**); (E) 1.3 equiv of TMEDA (**A**) and 1.3 equiv of (-)-sparteine (**G**).

F

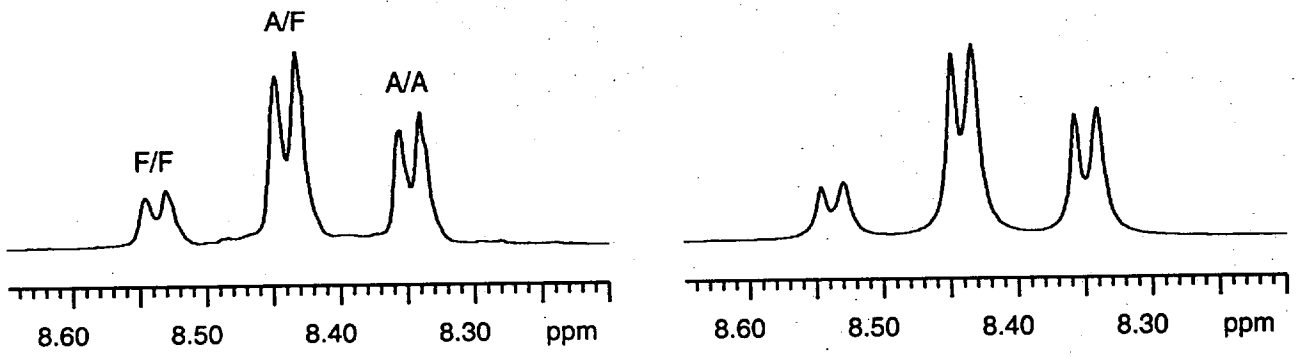


Figure III. (cont.) Partial ^{1}H NMR spectra (*left*: before deconvolution; *right*: theoretical spectrum after deconvolution) depicting the *ortho*-proton region of 0.1 M [^{6}Li]PhLi in toluene-d_8 at -70 °C containing the following ligands: (F) 2.4 equiv of TMEDA (**A**) and 1.2 equiv of *trans-(R,R)*-TMCDA (**F**). Note: The *ortho*-protons of the two homosolvates and the mixed solvate are well resolved in the ^{1}H NMR spectrum for all TMCDA/diamine combinations.

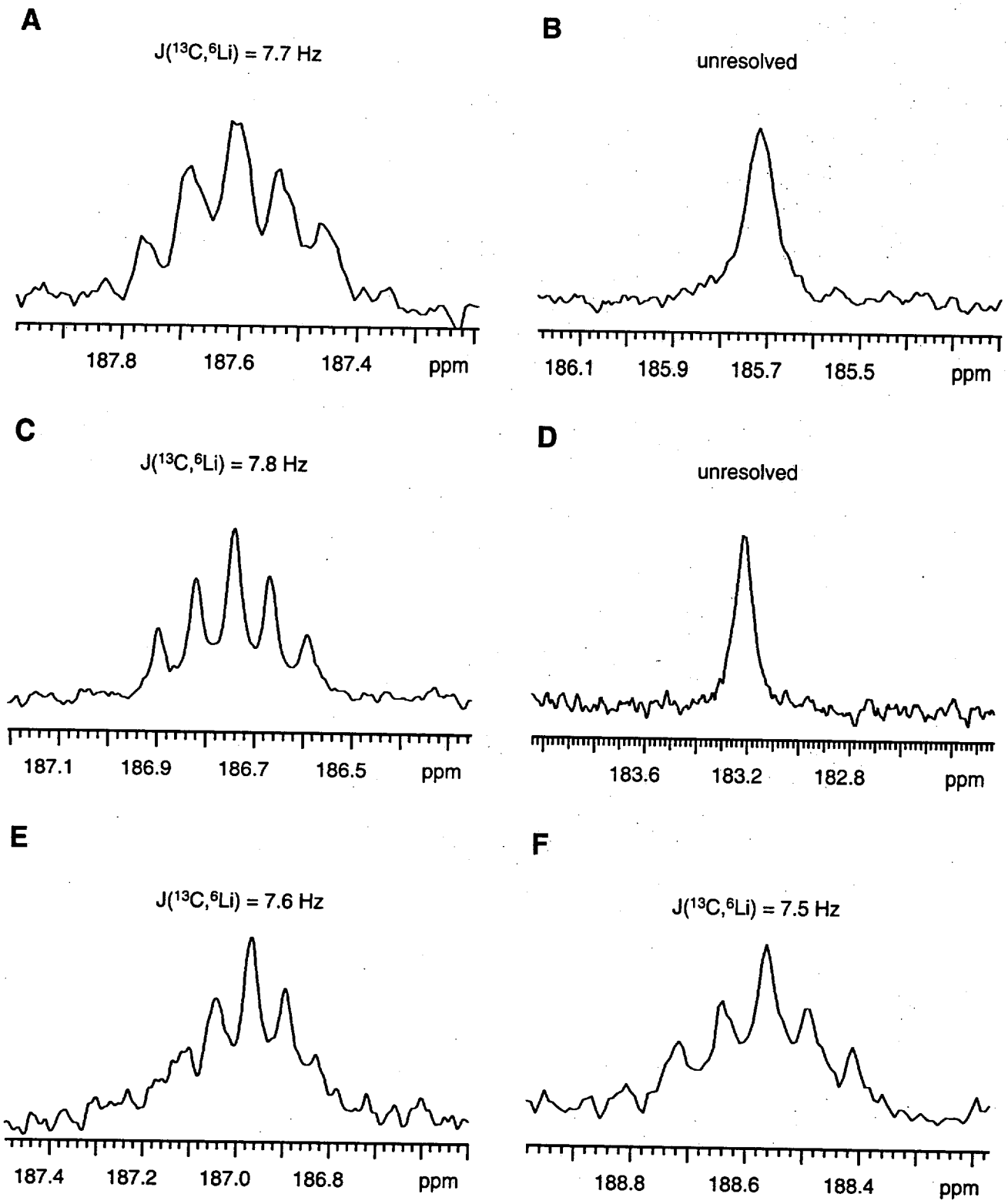


Figure IV. Partial $^{13}C\{^1H\}$ NMR spectra of 0.1 M [^{6}Li]PhLi in toluene-d_8 at -70 °C showing the PhLi *ipso*-carbon resonances ($\underline{C}H_2Li$). The samples contained the following ligands: (A) 1.0 equiv of TMEDA (**A**); (B) 3.0 equiv of TEEDA (**B**); (C) 1.2 equiv of 1,2-dipyrrolidinoethane (**C**); (D) 1.5 equiv of 1,2-dipiperidinoethane (**D**); (E) 2.1 equiv of TMPDA (**E**); (F) 1.2 equiv of *trans-(R,R)*-TMCDA (**F**). Note: PhLi does not dissolve with(-)-sparteine (**G**).

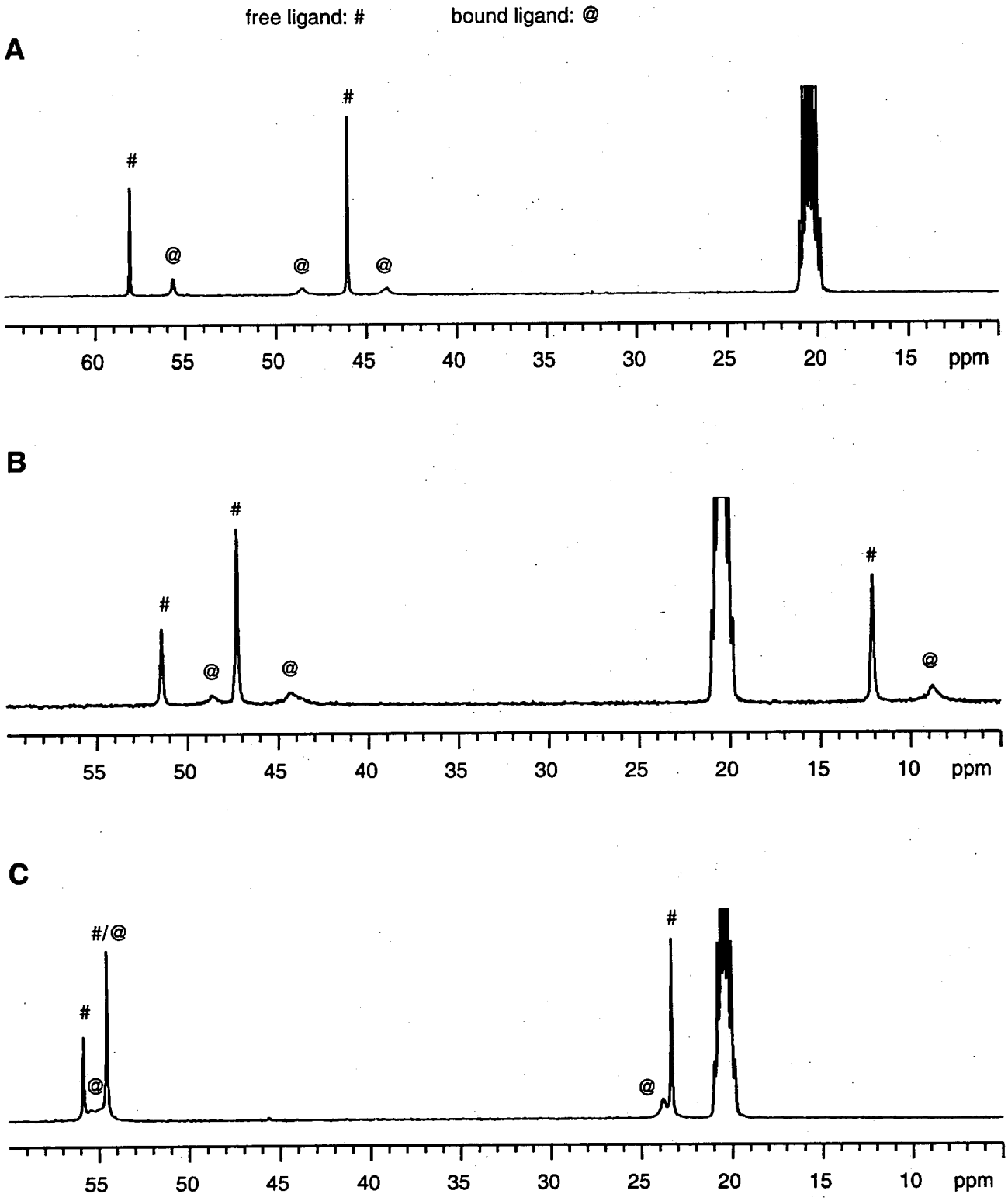


Figure V. Inverse gated $^{13}C\{^{1}H\}$ NMR spectra of 0.1 M [^{6}Li]PhLi in toluene-d_8 at -100 °C containing the following ligands: (A) 3.0 equiv of TMEDA (**A**); (B) 3.0 equiv of TEEDA (**B**); (C) 3.2 equiv of 1,2-dipyrrolidinoethane (**C**).

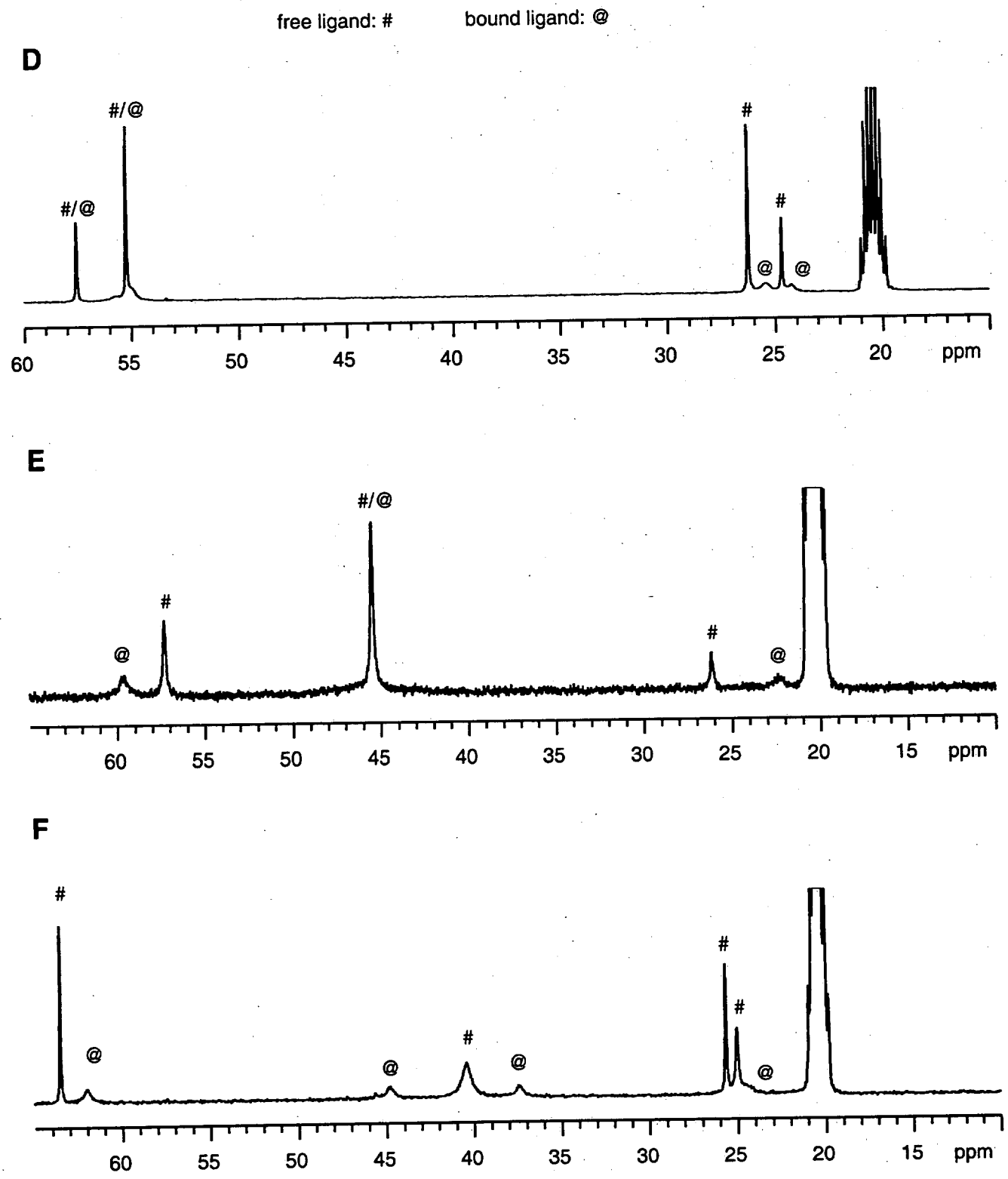


Figure V. (cont.) Inverse gated $^{13}C\{^{1}H\}$ NMR spectra of 0.1 M [^{6}Li]PhLi in toluene-d_8 at -100 °C containing the following ligands: (D) 3.0 equiv of 1,2-dipiperidinoethane (**D**); (E) 2.1 equiv of TMPDA (**E**); (F) 3.2 equiv of *trans*-(*R,R*)-TMCDA (**F**).

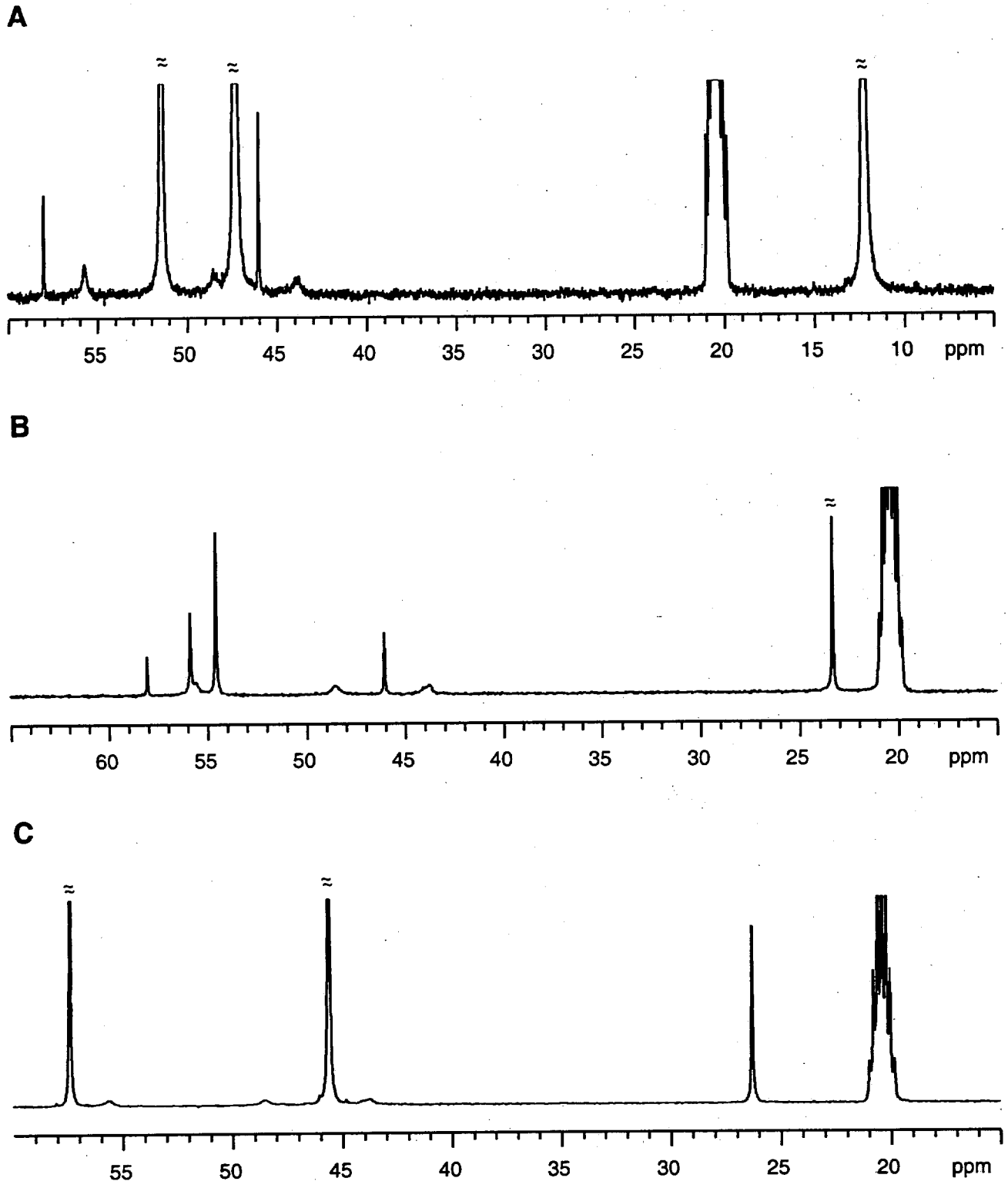


Figure VI. Inverse gated $^{13}C\{^{1}H\}$ NMR spectra of 0.1 M [^{6}Li]PhLi in toluene-d_8 at -100 °C containing molar excesses of each of the following ligands: (A) 1.5 equiv of TMEDA (**A**) and 15.0 equiv of TEEDA (**B**); (B) 1.5 equiv of TMEDA (**A**) and 1.5 equiv of 1,2-dipyrrolidinoethane (**C**); (C) 1.5 equiv of TMEDA (**A**) and 10.0 equiv of TMPDA (**E**).

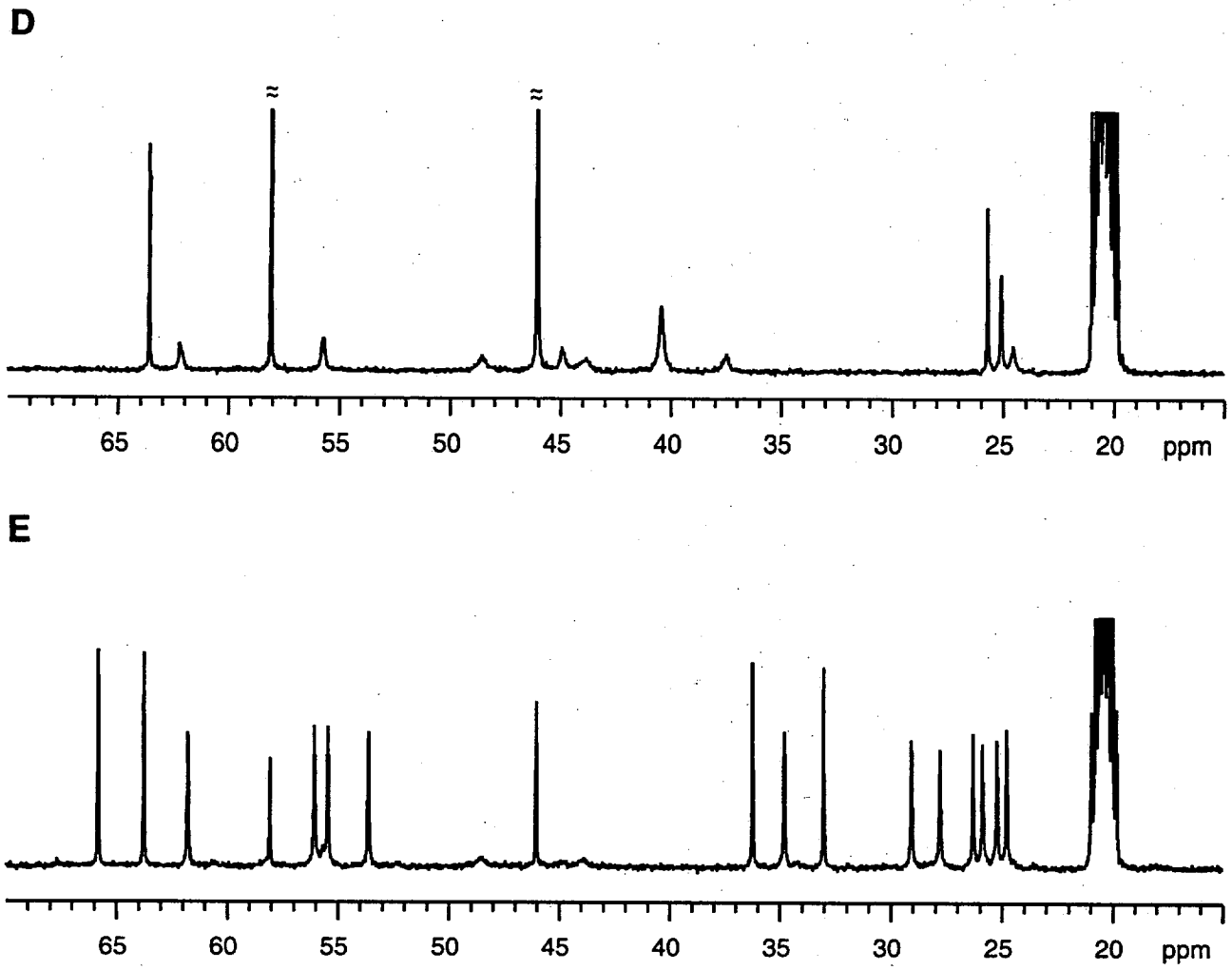


Figure VI. (cont.) Inverse gated $^{13}C\{^{1}H\}$ NMR spectra of 0.1 M [^{6}Li]PhLi in toluene-d_8 at -100 °C containing molar excesses of each of the following ligands: (D) 2.4 equiv of TMEDA (**A**) and 1.2 equiv of *trans-(R,R)*-TMCDA (**F**); (E) 1.3 equiv of TMEDA (**A**) and 3.1 equiv of (-)-sparteine (**G**).

Table 1. ^{6}Li NMR spectroscopic data of diamine-solvated PhLi dimers, $(PhLi)_2SS'$.[a]

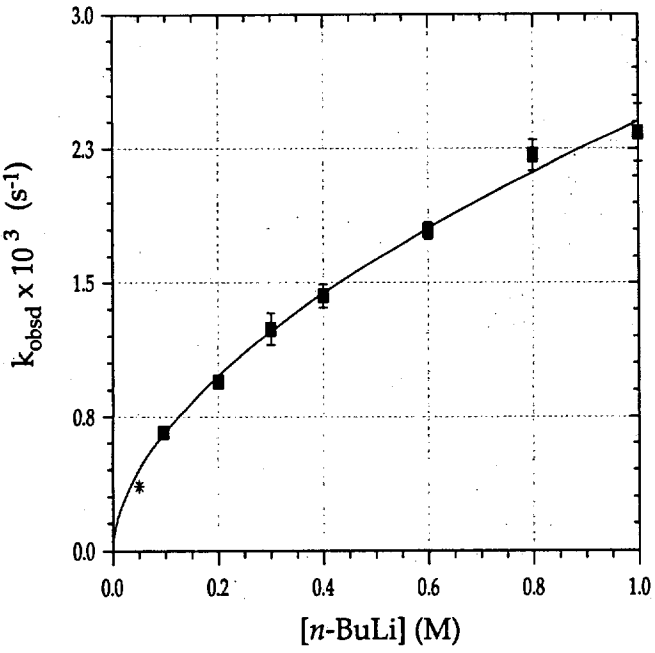
S	S′	δ ^{6}Li	S	S′	δ ^{6}Li	S	S′	δ ^{6}Li
A	**A**	1.68	**A**	**B**	1.64, 1.40	**G**	**B**	1.32, 1.56
B	**B**	1.55	**A**	**C**	1.65, 1.40	**G**	**C**	1.36, 1.39
C	**C**	1.53	**A**	**D**	1.60, 1.52, 1.32[b]	**G**	**D**	---[c], ---[c]
D	**D**	2.20	**A**	**E**	1.46, 1.35	**G**	**E**	1.49, 1.59
E	**E**	1.31	**A**	**F**	---[d], ---[d]	**G**	**F**	1.35, 1.52
F	**F**	1.69	**A**	**G**	1.47, 1.44			
G	**G**	1.20, 1.14[d]						

[a]Spectra were recorded on 0.1 M solutions of [^{6}Li]PhLi in toluene-d_8 at -100 °C. Samples contain a single diamine (**A**-**G**; S = S′) or mixtures of two diamines (S ≠ S′). ^{6}Li chemical shifts are reported relative to 0.3 M ^{6}LiCl/MeOH at -100 °C (0.0 ppm). The shifts are temperature and concentration dependent. [b]The additional resonance may stem from slow conformational exchange within the piperidine ring. See discussion of this topic in a footnote of the manuscript. [c]Rapid exchange at -100 °C causes severe (50-60 Hz) resonance broadening. [d]Complete overlap of resonances is observed. [e]The two resonances may stem from two possible sparteine orientations.

Table 2. ^{13}C NMR spectroscopic data of diamine-solvated PhLi dimers, $(PhLi)_2S_2$.[a]

cmpd	$^{13}C\{^1H\}$: bound ligand	$^{13}C\{^1H\}$ (δ, ppm) (*ipso*-carbon of phenyl)	$^{13}C\{^1H\}$: free ligand (δ, ppm)
$\mathbf{5_A}$	55.66, 48.57, 43.85	187.69	58.07, 46.05
$\mathbf{5_B}$	48.61, 44.20, 8.72	186.35	51.46, 47.30, 12.15
$\mathbf{5_C}$	55.46, 54.60,[b] 23.79	186.89	55.89, 54.60,[b] 23.35
$\mathbf{5_D}$	57.56,[b]55.23,[b] 25.40, 24.22	182.93	57.56,[b]55.23,[b]26.23, 24.67
$\mathbf{5_E}$	59.64, 45.47,[b] 22.39	187.65	57.28, 45.47,[b] 26.16
$\mathbf{5_F}$	62.01, 44.76, 37.46, ----[c]	188.80	63.54, 40.42, 25.66, 25.03

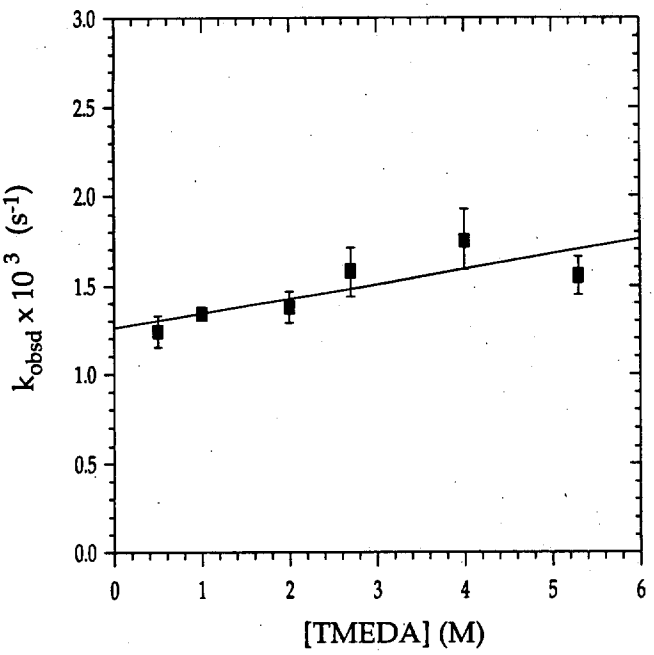
[a]Spectra were recorded on 0.1 M solutions of [^{6}Li]PhLi (containing diamines **A-G**) in toluene-d_8 at -100 °C. ^{13}C chemical shifts are reported relative to toluene-d_8 at -100 °C (δ 20.4 ppm). [b]Average of free and bound ligand resonance. [c]Peaks are too small to be observed above baseline.



[*n*-BuLi] (M)	k_{obsd} x10^3 (s^{-1})		Average k_{obsd} x10^3 (s^{-1})
0.05[a,b]	0.362(6)		
0.096[b]	0.67(2)	0.65(2)	0.66
0.2	0.91(2)	0.98(1)	0.95
0.3	1.33(2)	1.15(2)	1.24
0.4	1.36(2)	1.49(5)	1.43
0.6	1.75(5)	1.84(5)	1.80
0.8	2.13(9)	2.3(1)	2.22
1.0	2.18(7)	2.5(1)	2.34

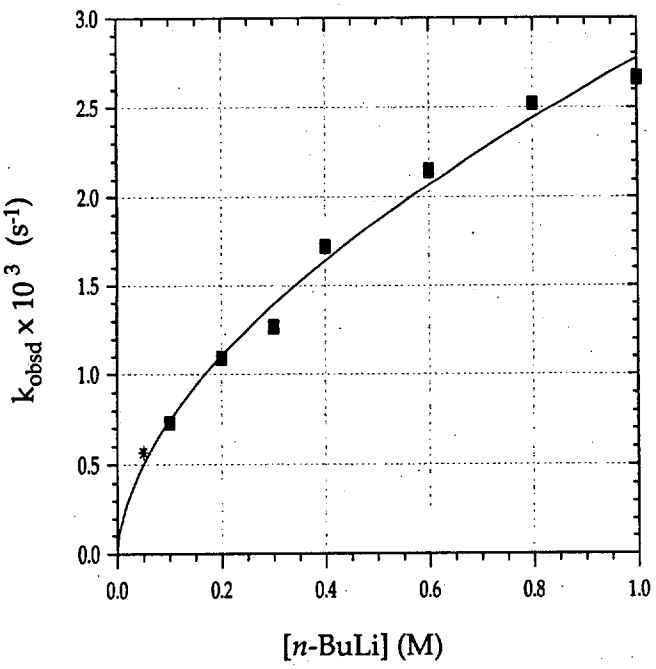
[a]Not included in fit. [b][1] = 0.004 M.

Figure VII. Plot of k_{obsd} vs. [*n*-BuLi] for the 1,2-addition to imine 1 (0.01 M) in TMEDA (0.5 M excess) and pentane at -40 °C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = a[n\text{-BuLi}]^b$ (a = 2.40(4) x 10^{-3}, b= 0.56(2)). (Asterisk (*) not included in fit.)



[TMEDA] (M)		k_{obsd} x10^3 (s^{-1})		Average k_{obsd} x10^3 (s^{-1})
0.5	1.33(2)	1.15(2)		1.24
1.0	1.31(2)	1.37(2)		1.34
2.0	1.29(3)	1.47(3)		1.38
2.7	1.71(4)	1.60(4)	1.44(3)	1.58
4.0	1.93(4)	1.73(4)	1.59(4)	1.75
5.3	1.45(3)	1.66(4)		1.56

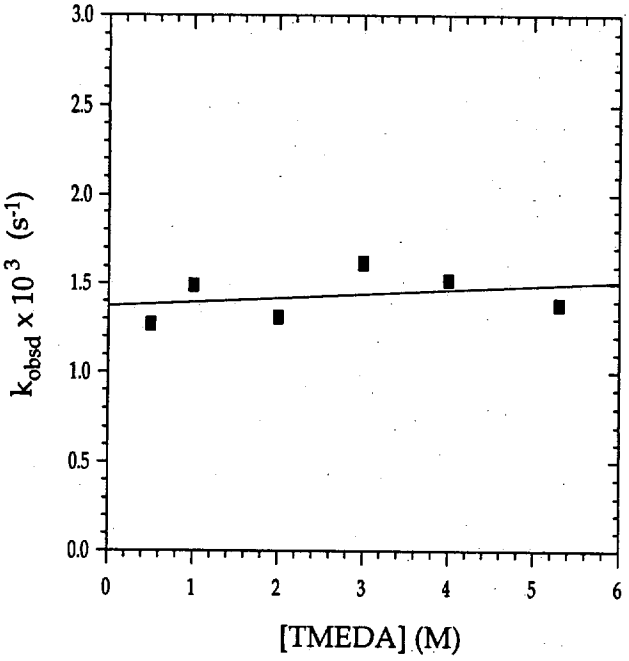
Figure VIII. Plot of k_{obsd} vs. [TMEDA] for the 1,2-addition of *n*-BuLi (0.3 M) to imine **1** (0.01 M) in pentane at -40 °C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = a[TMEDA] + b$ ($a = 8(3) \times 10^{-5}$, $b = 1.26(9) \times 10^{-3}$).



[*n*-BuLi] (M)	k_{obsd} x10^3 (s^{-1})
0.05[a,b]	0.566(9)
0.1[b]	0.73(1)
0.2	1.09(1)
0.3	1.27(2)
0.4	1.72(3)
0.6	2.15(4)
0.8	2.52(5)
1.0	2.66(8)

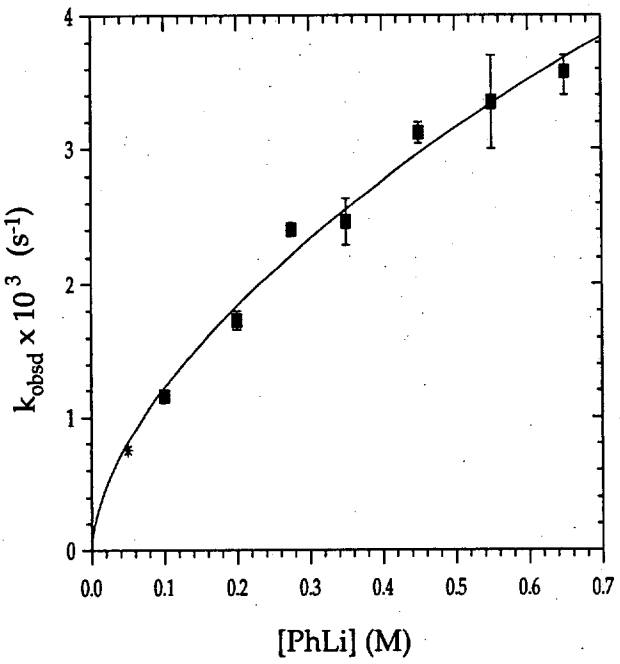
[a]Not included in fit. [b][**1**] = 0.004 M.

Figure IX. Plot of k_{obsd} vs. [*n*-BuLi] for the α-lithiation of **6** (0.01 M) in TMEDA (0.5 M excess) and pentane at -40 °C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = a[n\text{-BuLi}]^b$ (a = 2.77(7) x 10^{-3}, b= 0.57(4)). (Asterisk (*) not included in fit.)



[TMEDA] (M)	k_{obsd} x10^3 (s^{-1})
0.5	1.27(2)
1.0	1.49(2)
2.0	1.31(2)
3.0	1.62(5)
4.0	1.52(8)
5.3	1.38(2)

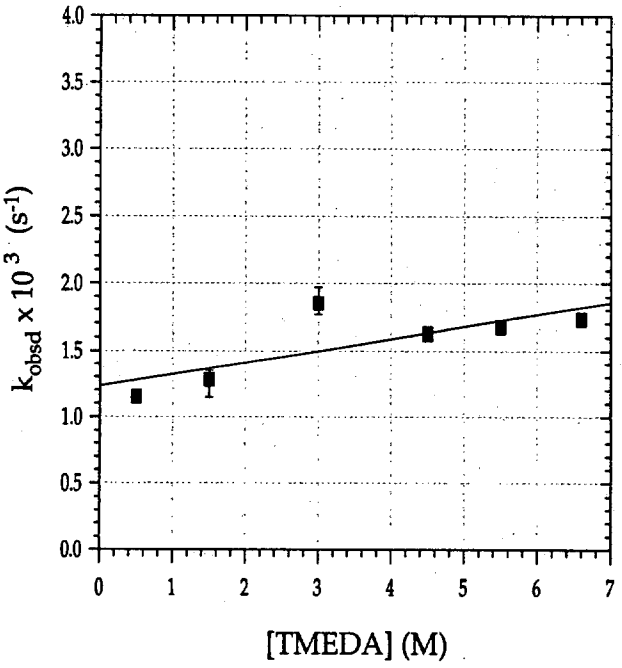
Figure X. Plot of k_{obsd} vs. [TMEDA] for the α-lithiation of imine **6** (0.01 M) with *n*-BuLi (0.3 M) in pentane at -40 °C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = a[TMEDA] + b$ ($a = 2(3) \times 10^{-5}$, $b = 1.4(1) \times 10^{-3}$).



[PhLi] (M)	k_{obsd} x10^3 (s^{-1})			Average k_{obsd} x10^3 (s^{-1})
0.05[a]	0.75(2)			
0.1	1.16(3)	1.15(4)		1.16
0.2	1.80(8)	1.66(6)		1.73
0.275	2.41(3)	2.40(4)		2.41
0.35	2.64(5)	2.29(3)		2.47
0.45	3.2(2)	3.04(4)		3.12
0.55	3.0(9)	3.7(1)		3.35
0.65	3.63(9)	3.4(2)	3.7(1)	3.58

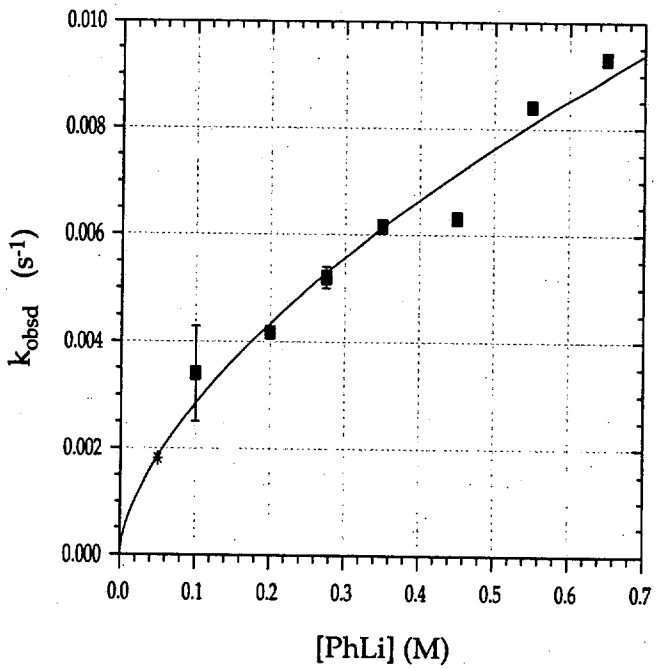
[a] Not included in fit. [b] **[1]** = 0.004 M

Figure XI. Plot of k_{obsd} vs. [PhLi] for the 1,2-addition to imine **1** (0.01 M) in neat TMEDA at 19 °C. The curve depicts the result of an unweighted least-squares fit to k_{obsd} = a[PhLi]^b (a = 4.8(2) x 10^{-3}, b= 0.59(4)). (Asterisk (*) not included in fit.)



[TMEDA] (M)		k_{obsd} x10^3 (s^{-1})		Average k_{obsd} x10^3 (s^{-1})
0.5	1.19(3)	1.11(5)		1.15
1.5	1.01(3)	1.42(5)	1.40(4)	1.28
3.0	1.68(5)	2.09(4)	1.77(6)	1.85
4.5	1.70(3)	1.55(4)		1.63
5.5	1.64(7)	1.71(5)		1.68
6.6	1.80(8)	1.66(6)		1.73

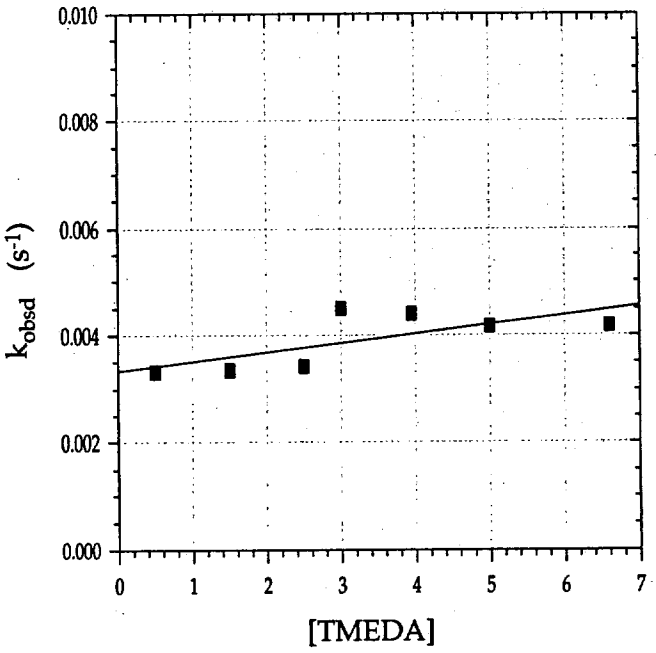
Figure XII. Plot of k_{obsd} vs. [TMEDA] for the 1,2-addition of PhLi (0.2 M) to imine **1** (0.01 M) in pentane at 19 °C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = a[TMEDA] + b$ ($a = 9(4) \times 10^{-5}$, $b = 1.2(2) \times 10^{-3}$).



[PhLi] (M)	k_{obsd} x10^3 (s^{-1})		Average k_{obsd} x10^3 (s^{-1})
0.05[a,b]	1.81(4)		
0.1[b]	4.3(2)	2.51(7)	3.41
0.2	4.22(7)	4.14(8)	4.18
0.275	5.4(2)	5.0(2)	5.20
0.35	6.2(2)	6.1(2)	6.15
0.45	6.3(2)		
0.55	8.4(4)		
0.65	9.3(3)		

[a]Not included in fit. [b][1] = 0.004 M.

Figure XIII. Plot of k_{obsd} vs. [PhLi] for the α-lithiation of **6** (0.01 M) in neat TMEDA at 19 °C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = a[PhLi]^b$ (a = 1.17(8) x 10^{-2}, b= 0.61(7)). (Asterisk (*) not included in fit.)



[TMEDA] (M)	k_{obsd} x10^3 (s^{-1})
0.5	3.32(5)
1.5	3.35(5)
2.5	3.42(7)
3.0	4.50(4)
3.95	4.4(1)
5.0	4.17(7)
6.6	4.18(7)

Figure XIV. Plot of k_{obsd} vs. [TMEDA] for the α-lithiation of **6** (0.01 M) with PhLi (0.2 M) in pentane at 19 °C. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = a[TMEDA] + b$ ($a = 1.7(8) \times 10^{-4}$, $b = 3.3(3) \times 10^{-3}$).

Table 3. k_{obsd} (s^{-1}) for the 1,2-addition and α-lithiation of imine **1** and imine **6**, respectively, with *n*-BuLi and PhLi in pentane and diamines **A**-**G**.

	BuLi[a]		PhLi[c]	
Ligand	1,2-addition	α-lithiation	1,2-addition	α-lithiation
A (TMEDA)	2.2(1)	3.2(4)	1.15(5)	3.3(3)
B (TEEDA)	1.23(2)	3.1(6)	1.62(8)	2.05(9)[d]
C	0.147(3)	0.273(4)	0.133(8)	2.1(1)
D	0.39(1)	0.96(5)[b]	0.54(2)	2.5(1)[d]
E (TMPDA)	0.77(2)	0.89(3)	0.95(2)	0.75(1)
F ((*R*,*R*)-TMCDA)	1.16(8)	1.16(5)	2.2(2)	3.6(3)
G (-)-sparteine	0.65(2)	2.4(2)	----[e]	----[e]

[a]Measured at -20 °C with 0.1 M *n*-BuLi and 0.6 M (0.5 M excess) diamine in pentane. [b][**D**] = 0.4 M (excess). [c]Measured at 19 °C. Solubility problems required variations in the PhLi molarities; scaling to 0.2 M assuming a 1/2 order dependence is not included in this table: **A**, [PhLi] = 0.2 M; **B**, [PhLi] = 0.2 M; **C**, [PhLi] = 0.07 M; **D**, [PhLi] = 0.2 M (addition), 0.1 M (α-lithiation); **E**, [PhLi] = 0.2 M; **F**, [PhLi] = 0.1 M. The diamines were maintained at 0.5 M excess in pentane. [d]Low concentrations of possible imine/PhLi pre-complexes appear to form (1645-1655 cm^{-1}). [e]PhLi is insoluble in (-)-sparteine/pentane.