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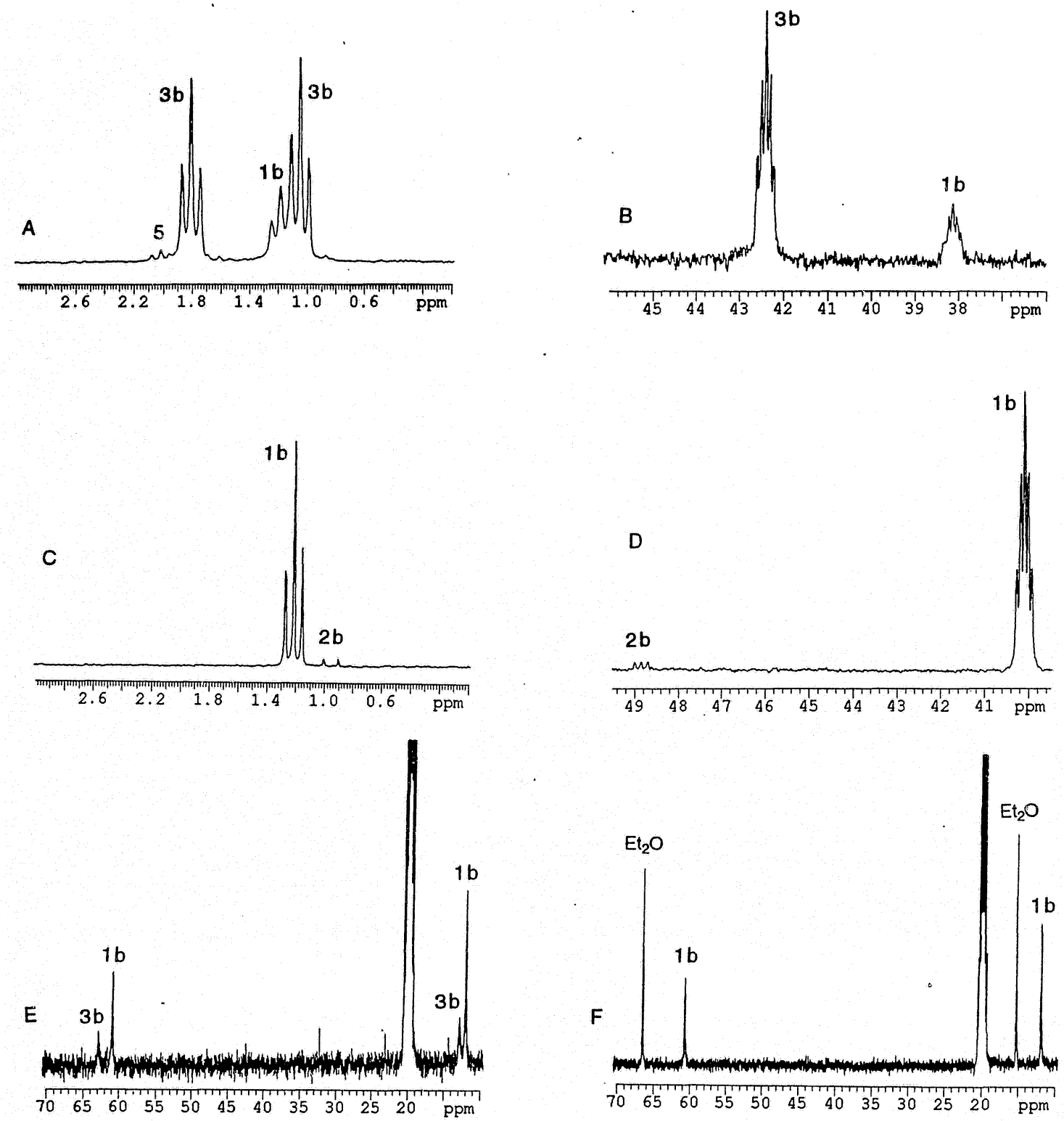

I. ^{6}Li, ^{15}N, and ^{13}C NMR spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS with added Et_2O at -100 °C: (A) ^{6}Li NMR spectrum with 0.7 equiv. of added Et_2O in pentane; (B) $^{15}N\{^{1}H\}$ NMR spectrum with 0.7 equiv. of added Et_2O in pentane; (C) ^{6}Li NMR spectrum with 40 equiv. of added Et_2O in pentane; (D) $^{15}N\{^{1}H\}$ NMR spectrum with 40 equiv. of added Et_2O in pentane; (E) ^{13}C NMR spectrum with 0.5 equiv. of added Et_2O in toluene-d_8 ; (F) ^{13}C NMR spectrum with 2.0 equiv. of added Et_2O in toluene-d_8.

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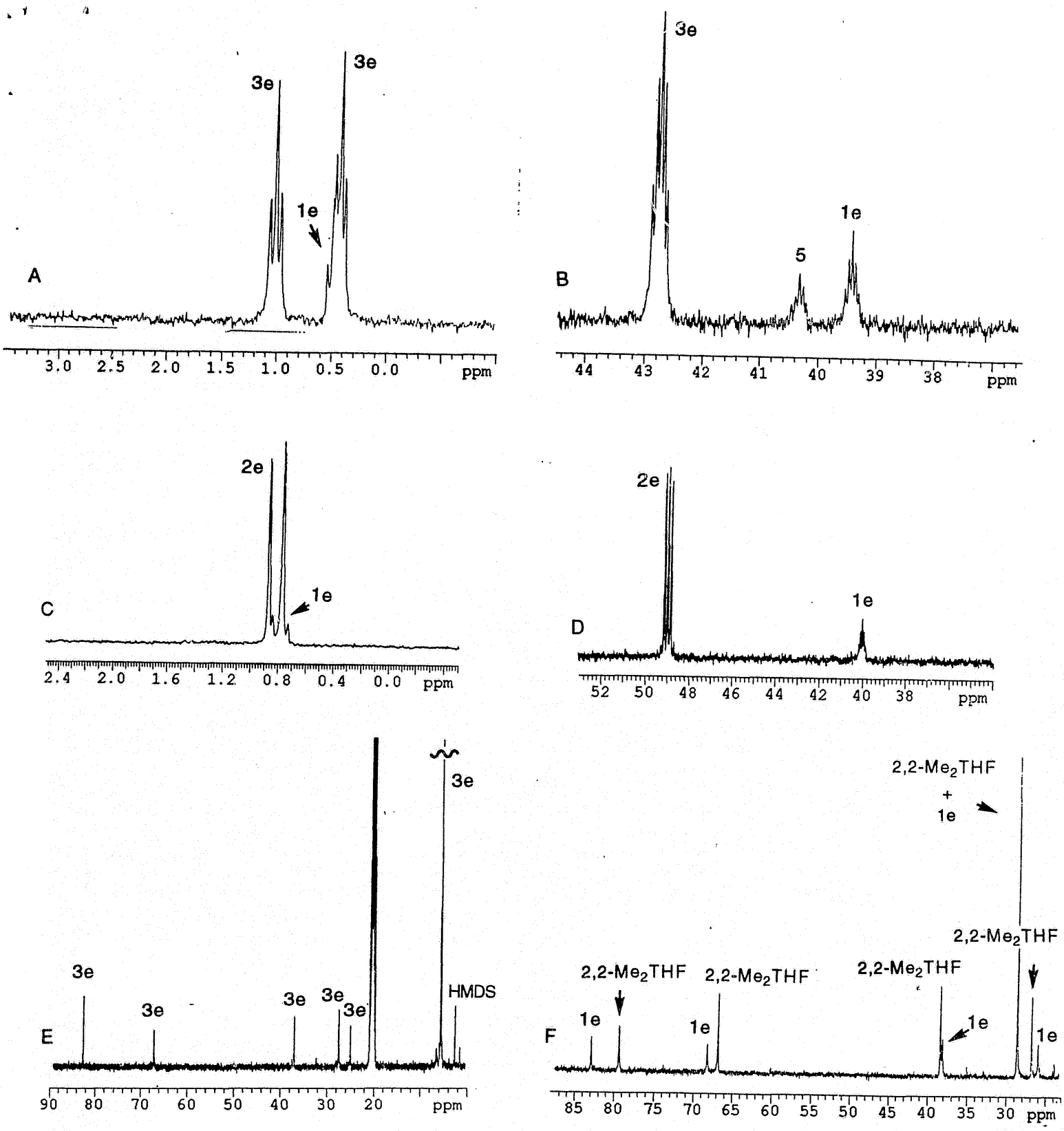
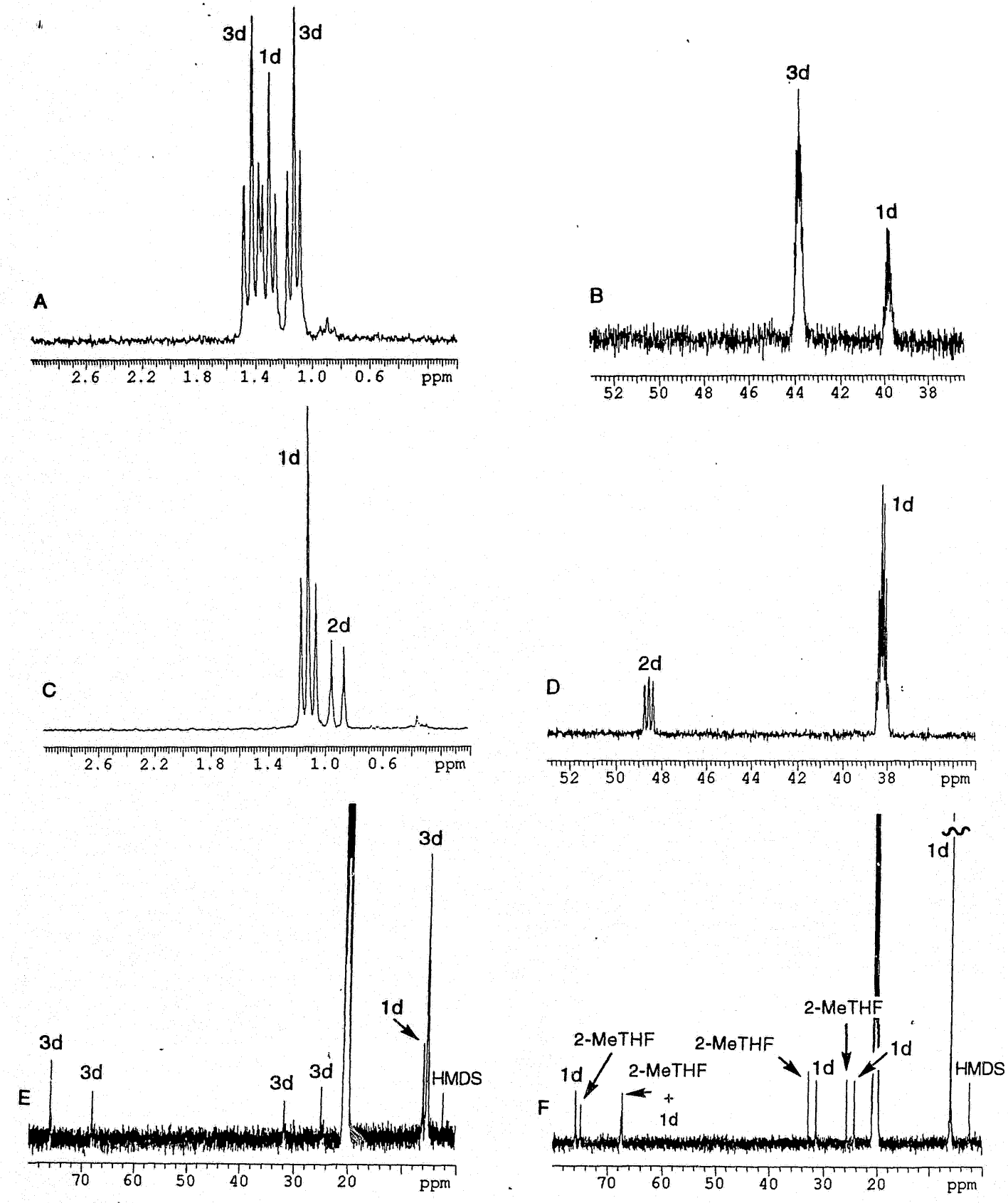


II. ^{6}Li, ^{15}N, and ^{13}C NMR spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS with added 2,2-Me_2THF at -100 °C: (A) ^{6}Li NMR spectrum with 0.7 equiv. of added 2,2-Me_2THF in pentane; (B) $^{15}N\{^{1}H\}$ NMR spectrum with 0.7 equiv. of added 2,2-Me_2THF in pentane; (C) ^{6}Li NMR spectrum with 40 equiv. of added 2,2-Me_2THF in pentane; (D) $^{15}N\{^{1}H\}$ NMR spectrum with 40 equiv. of added 2,2-Me_2THF in pentane; (E) ^{13}C NMR spectrum with 0.5 equiv. of added 2,2-Me_2THF in toluene-d_8; (F) ^{13}C NMR spectrum with 2.0 equiv. of added 2,2-Me_2THF in toluene-d_8.



III. ^{6}Li, ^{15}N, and ^{13}C NMR spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS with added 2-MeTHF at -100 °C: (A) ^{6}Li NMR spectrum with 0.7 equiv. of added 2-MeTHF in pentane; (B) $^{15}N\{^{1}H\}$ NMR spectrum with 0.7 equiv. of added 2-MeTHF in pentane; (C) ^{6}Li NMR spectrum with 40 equiv. of added 2-MeTHF in pentane; (D) $^{15}N\{^{1}H\}$ NMR spectrum with 40 equiv. of added 2-MeTHF in pentane; (E) ^{13}C NMR spectrum with 0.5 equiv. of added 2-MeTHF in toluene-d_8 ; (F) ^{13}C NMR spectrum with 2.0 equiv. of added 2-MeTHF in toluene-d_8.

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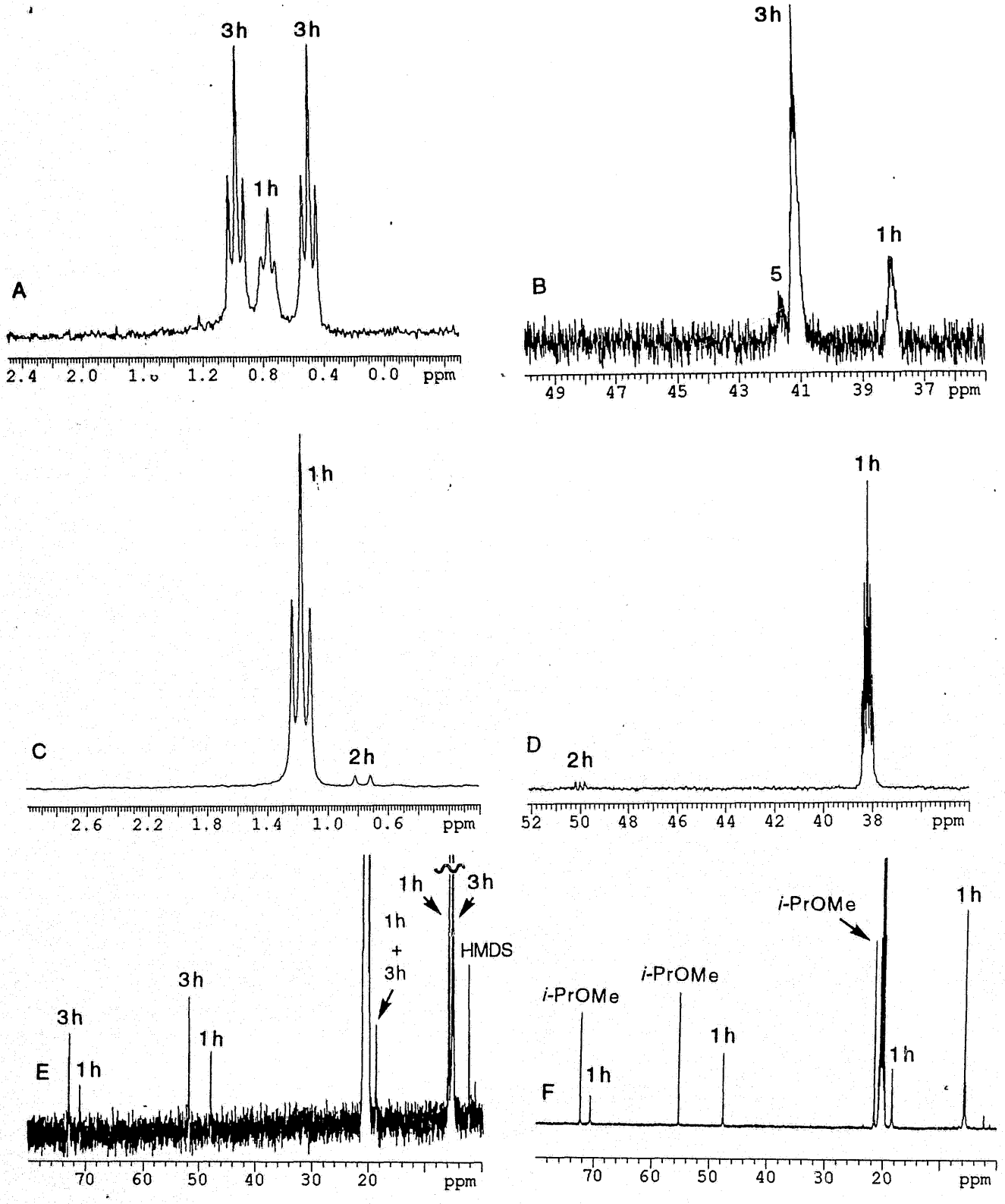
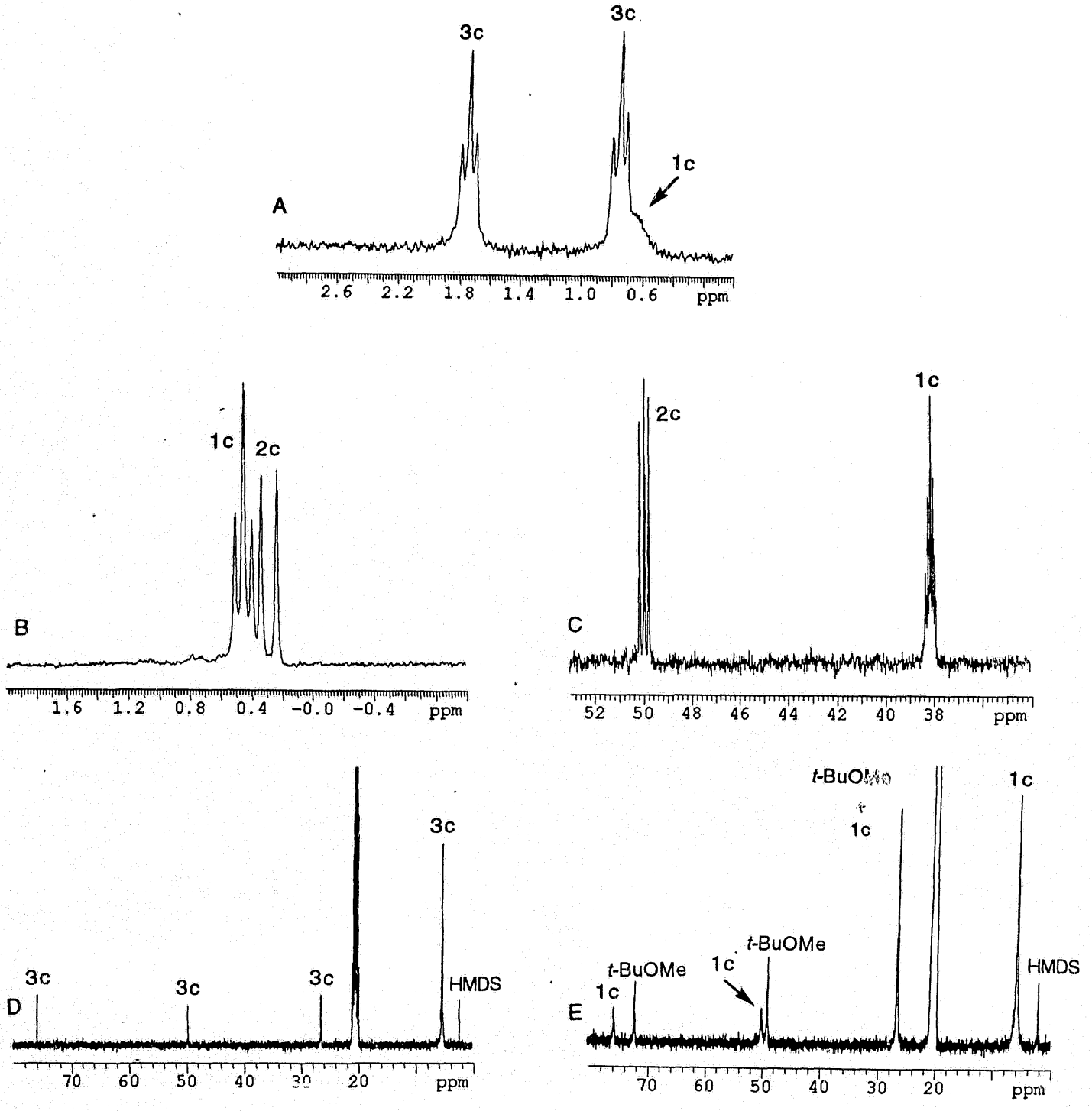
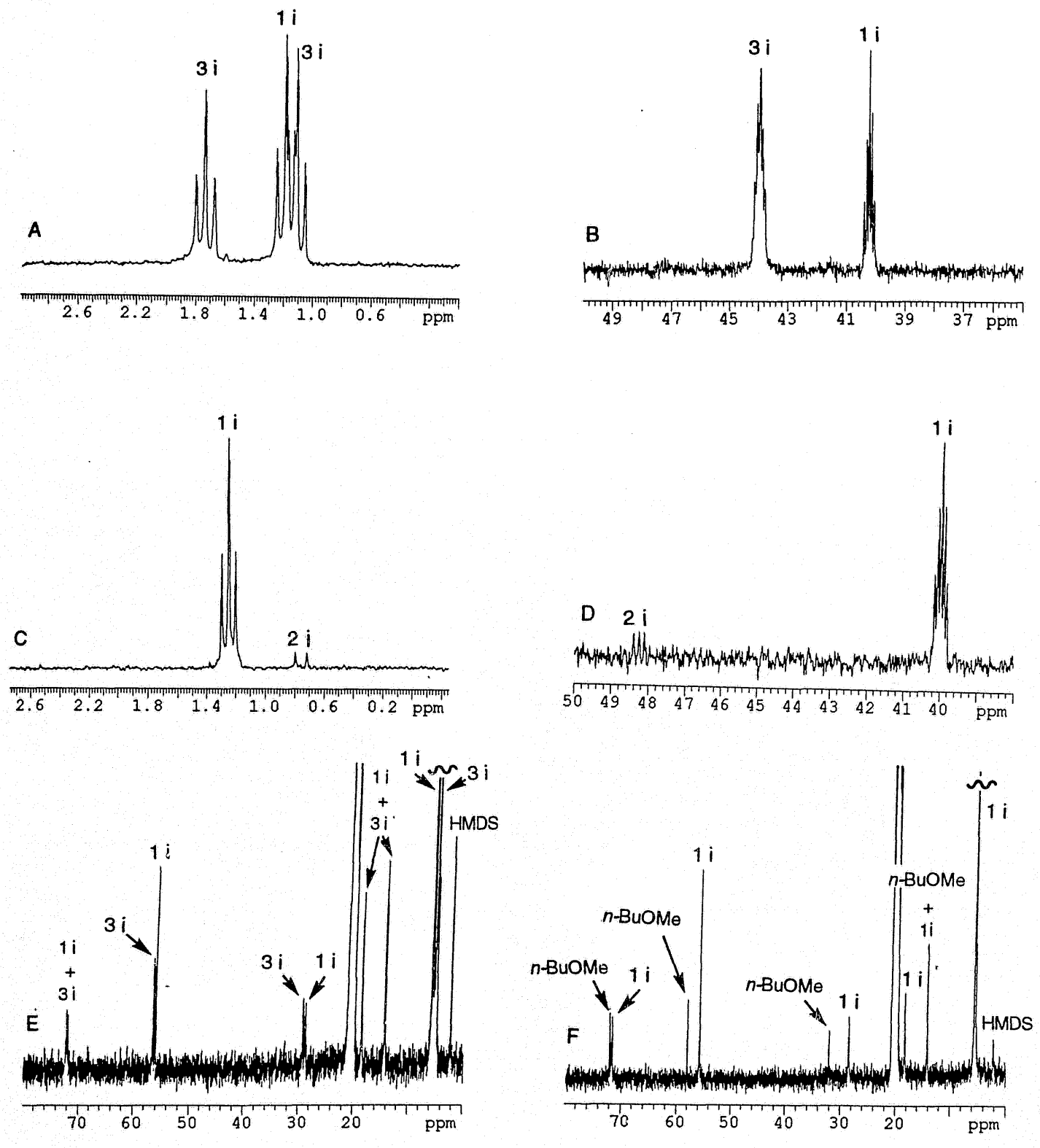


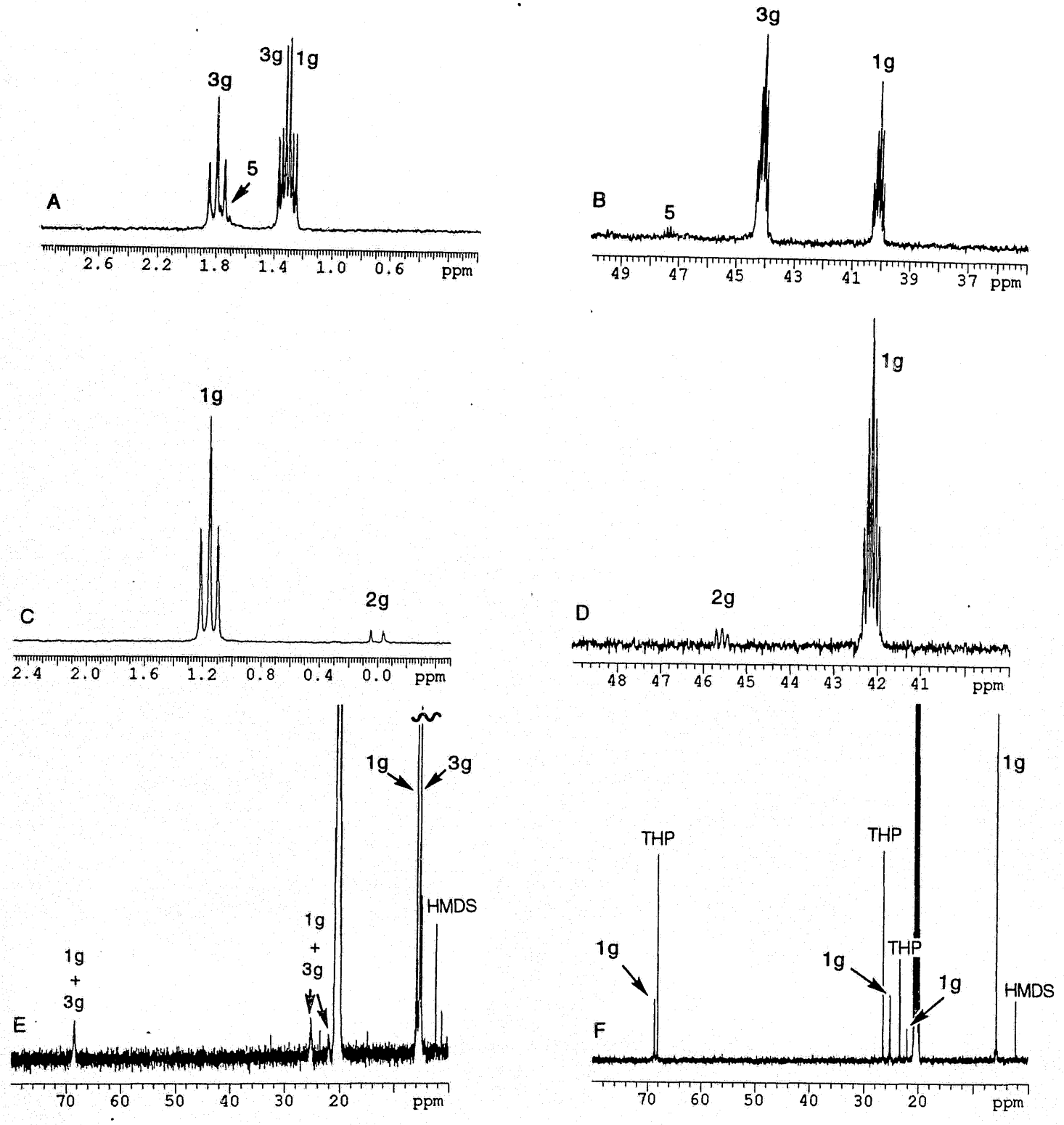
IV. ^{6}Li, ^{15}N, and ^{13}C NMR spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS with added *i*-PrOMe at -100 °C: (A) ^{6}Li NMR spectrum with 0.7 equiv. of added *i*-PrOMe in pentane; (B) $^{15}N\{^{1}H\}$ NMR spectrum with 0.7 equiv. of added *i*-PrOMe in pentane; (C) ^{6}Li NMR spectrum with 40 equiv. of added *i*-PrOMe in pentane; (D) $^{15}N\{^{1}H\}$ NMR spectrum with 40 equiv. of added *i*-PrOMe in pentane; (E) ^{13}C NMR spectrum with 0.5 equiv. of added *i*-PrOMe in toluene-d_8 ; (F) ^{13}C NMR spectrum with 2.0 equiv. of added *i*-PrOMe in toluene-d_8.



V. ^{6}Li, ^{15}N, and ^{13}C NMR spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS with added *t*-BuOMe: (A) ^{6}Li NMR spectrum with 0.7 equiv. of added *t*-BuOMe in pentane at -120 °C; (B) ^{6}Li NMR spectrum with 40 equiv. of added *t*-BuOMe in pentane at -100 °C; (C) $^{15}N\{^{1}H\}$ NMR spectrum with 40 equiv. of added *t*-BuOMe in pentane at -100 °C; (D) ^{13}C NMR spectrum with 0.5 equiv. of added *t*-BuOMe in toluene-d_8 at -110 °C (E) ^{13}C NMR spectrum with 2.0 equiv. of added *t*-BuOMe in toluene-d_8 at -110 °C. (An ^{15}N NMR spectrum of 0.7 equiv. of added *t*-BuOMe was not recorded due to solubility problems.)



VI. ^{6}Li, ^{15}N, and ^{13}C NMR spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS with added *n*-BuOMe at -100 °C: (A) ^{6}Li NMR spectrum with 0.7 equiv. of added *n*-BuOMe in pentane; (B) $^{15}N\{^{1}H\}$ NMR spectrum with 0.7 equiv. of added *n*-BuOMe in pentane; (C) ^{6}Li NMR spectrum with neat *n*-BuOMe; (D) $^{15}N\{^{1}H\}$ NMR spectrum with neat *n*-BuOMe in pentane; (E) ^{13}C NMR spectrum with 0.5 equiv. of added *n*-BuOMe in toluene-d_8 ; (F) ^{13}C NMR spectrum with 2.0 equiv. of added *n*-BuOMe in toluene-d_8.



VII. ^{6}Li, ^{15}N, and ^{13}C NMR spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS with added THP at -100 °C: (A) ^{6}Li NMR spectrum with 0.7 equiv. of added THP in pentane; (B) $^{15}N\{^{1}H\}$ NMR spectrum with 0.7 equiv. of added THP in pentane; (C) ^{6}Li NMR spectrum with 40 equiv. of added THP in pentane; (D) $^{15}N\{^{1}H\}$ NMR spectrum with 40 equiv. of added THP in pentane; (E) ^{13}C NMR spectrum with 0.5 equiv. of added THP in toluene-d_8; (F) ^{13}C NMR spectrum with 2.0 equiv. of added THP in toluene-d_8.

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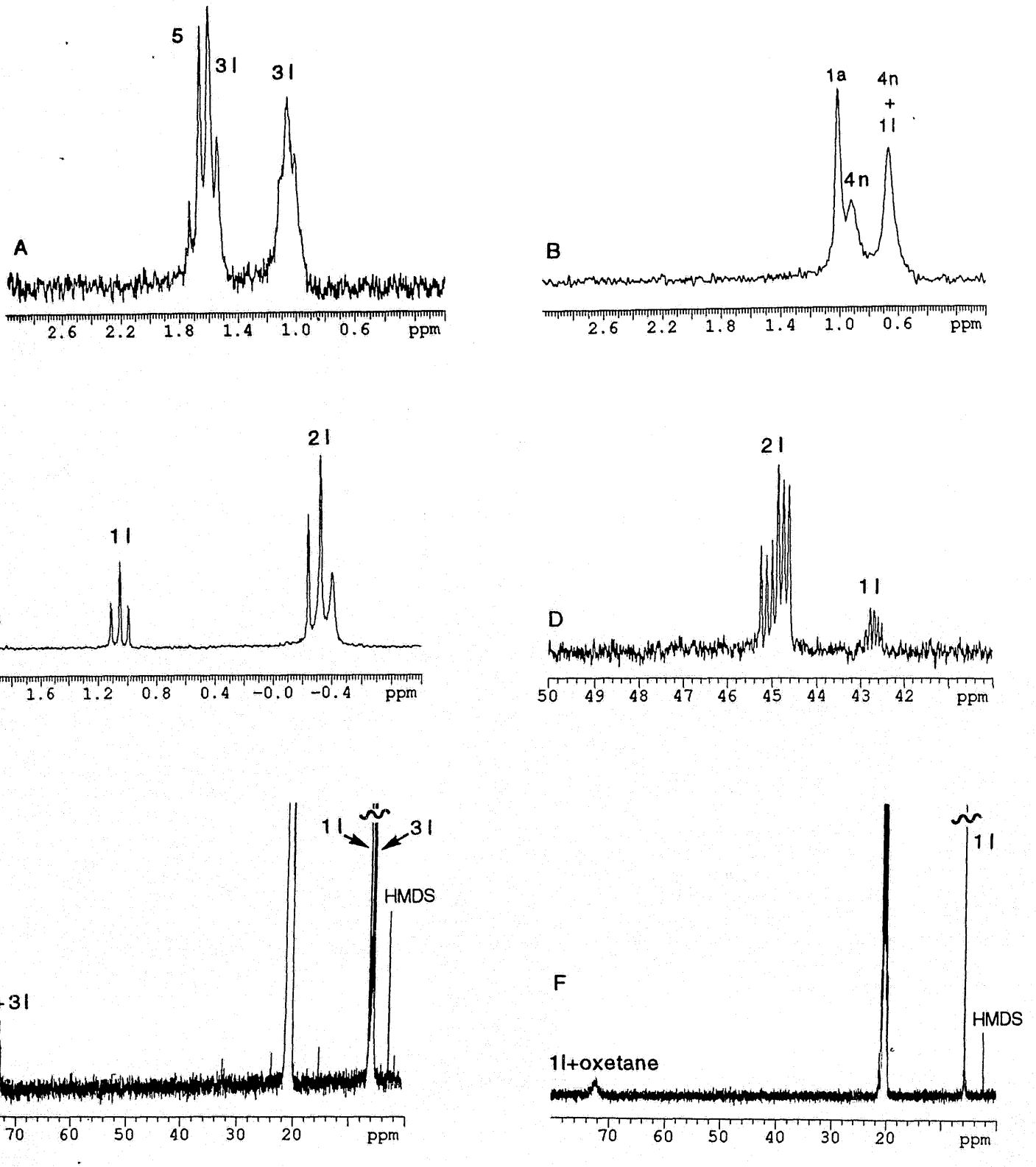
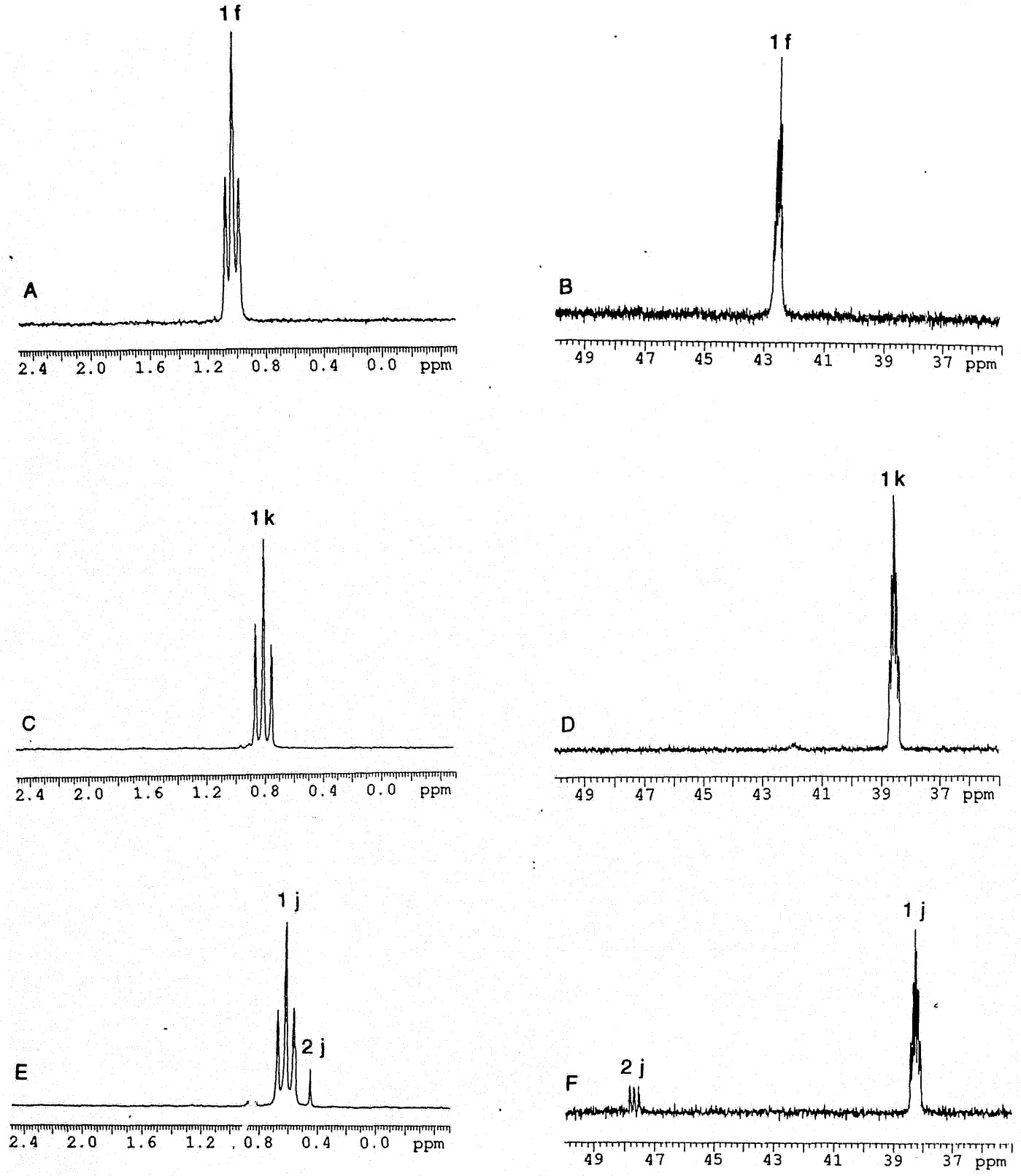
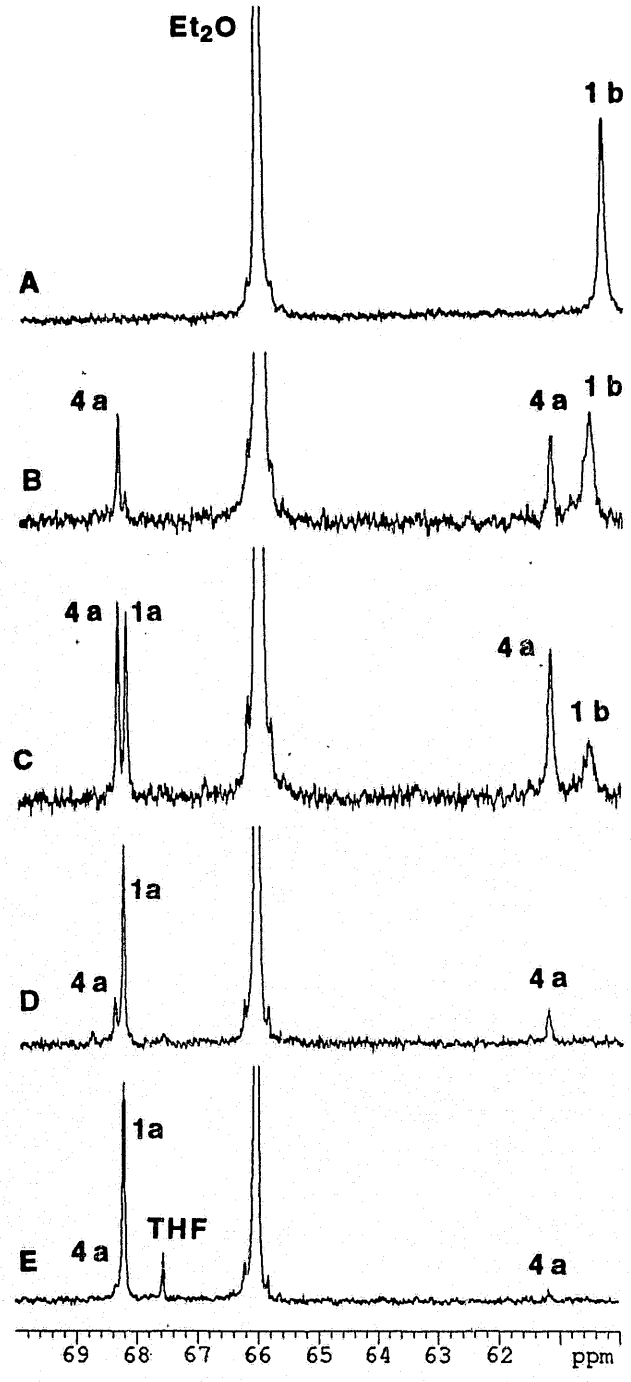


VIII. ^{6}Li, ^{15}N, and ^{13}C NMR spectra of 0.10 M LiHMDS with added oxetane at -100 °C: (A) ^{6}Li NMR spectrum of [^{6}Li,^{15}N]LiHMDS with 0.7 equiv. of added oxetane in pentane; (B) ^{6}Li NMR spectrum of [^{6}Li]LiHMDS with 1.1 equiv. of added oxetane and 2.0 equiv. of added THF in toluene-d_8; (C) ^{6}Li NMR spectrum of [^{6}Li,^{15}N]LiHMDS with 13 equiv. of added oxetane in pentane; (D) $^{15}N\{^{1}H\}$ NMR spectrum of [^{6}Li,^{15}N]LiHMDS with 13 equiv. of added oxetane in pentane; (E) ^{13}C NMR spectrum of [^{6}Li]LiHMDS with 0.5 equiv. of added oxetane in toluene-d_8; (F) ^{13}C NMR spectrum of [^{6}Li]LiHMDS with 2.0 equiv. of added oxetane in toluene-d_8.



IX. ^{6}Li, and ^{15}N NMR spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS at -100 °C in pentane: (A) ^{6}Li NMR spectrum with 40 equiv. of added 2,2,5,5-Me_4THF; (B) $^{15}N\{^{1}H\}$ NMR spectrum with 40 equiv. of added 2,2,5,5,-Me_4THF; (C) ^{6}Li NMR spectrum with 40 equiv. of added *i*-Pr_2O; (D) $^{15}N\{^{1}H\}$ NMR spectrum with 40 equiv. of added *i*-Pr_2O; (E) ^{6}Li NMR spectrum with 40 equiv. of added Me_2(Et)COMe; (F) $^{15}N\{^{1}H\}$ NMR spectrum with 40 equiv. of added Me_2(Et)COMe.



X. Partial ^{13}C NMR spectra of 0.10 M [^{6}Li]LiHMDS in toluene-d_8 with 5.0 equiv. of Et_2O per Li recorded at -100 °C: (A) 0.0 equiv. THF; (B) 0.25 equiv. THF; (C) 0.5 equiv. THF; (D) 0.75 equiv. THF; (E) 1.0 equiv. THF.

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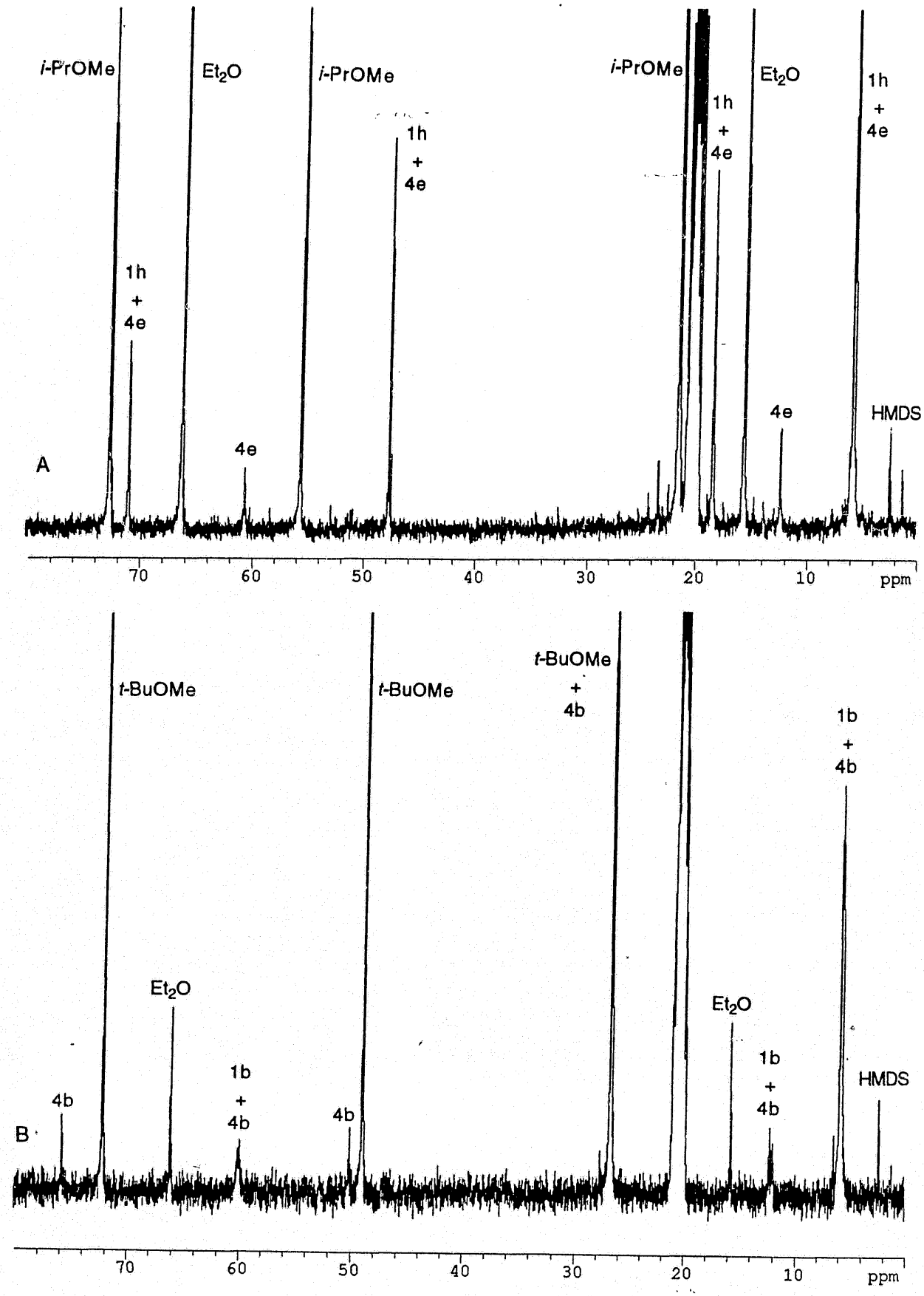
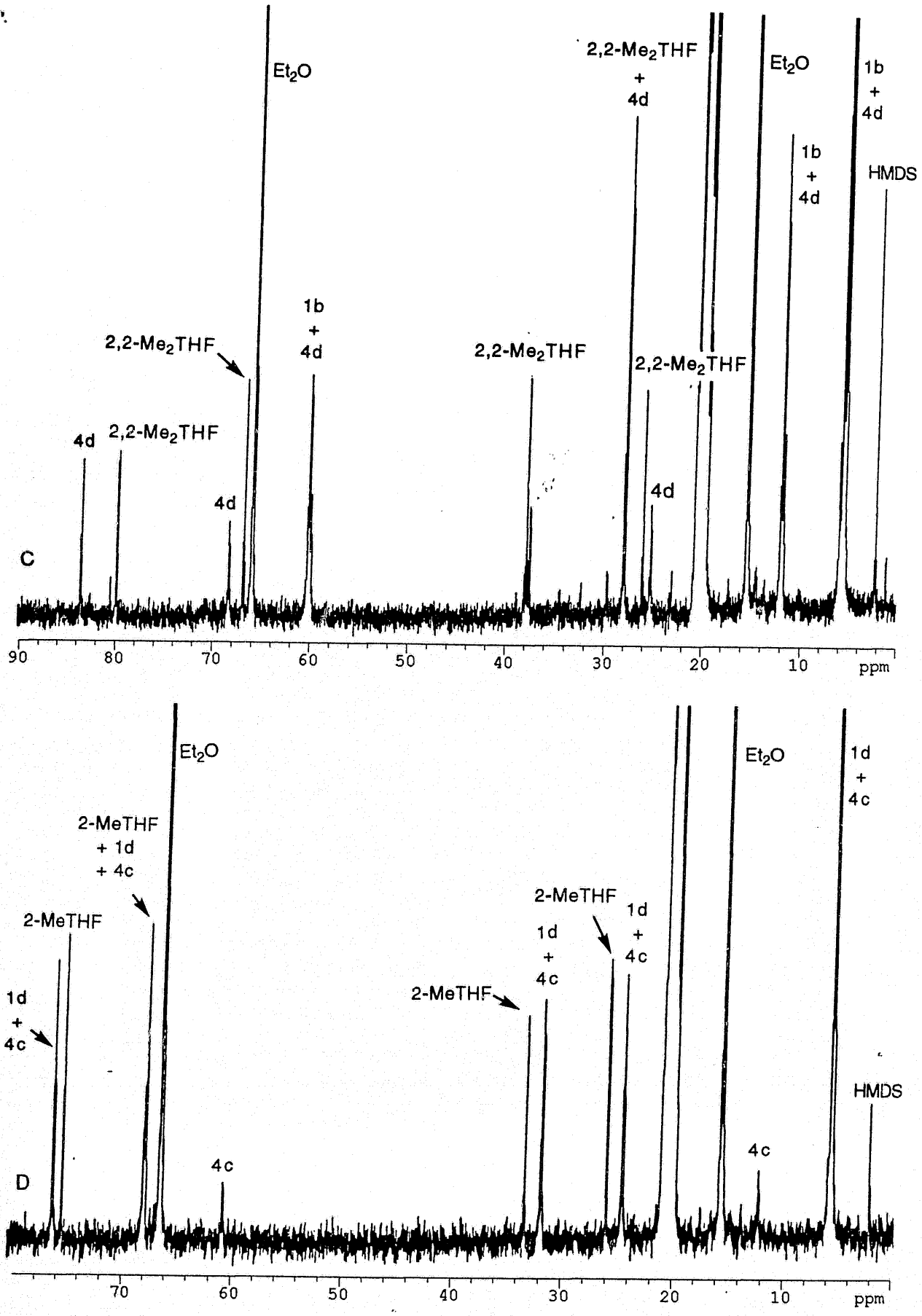
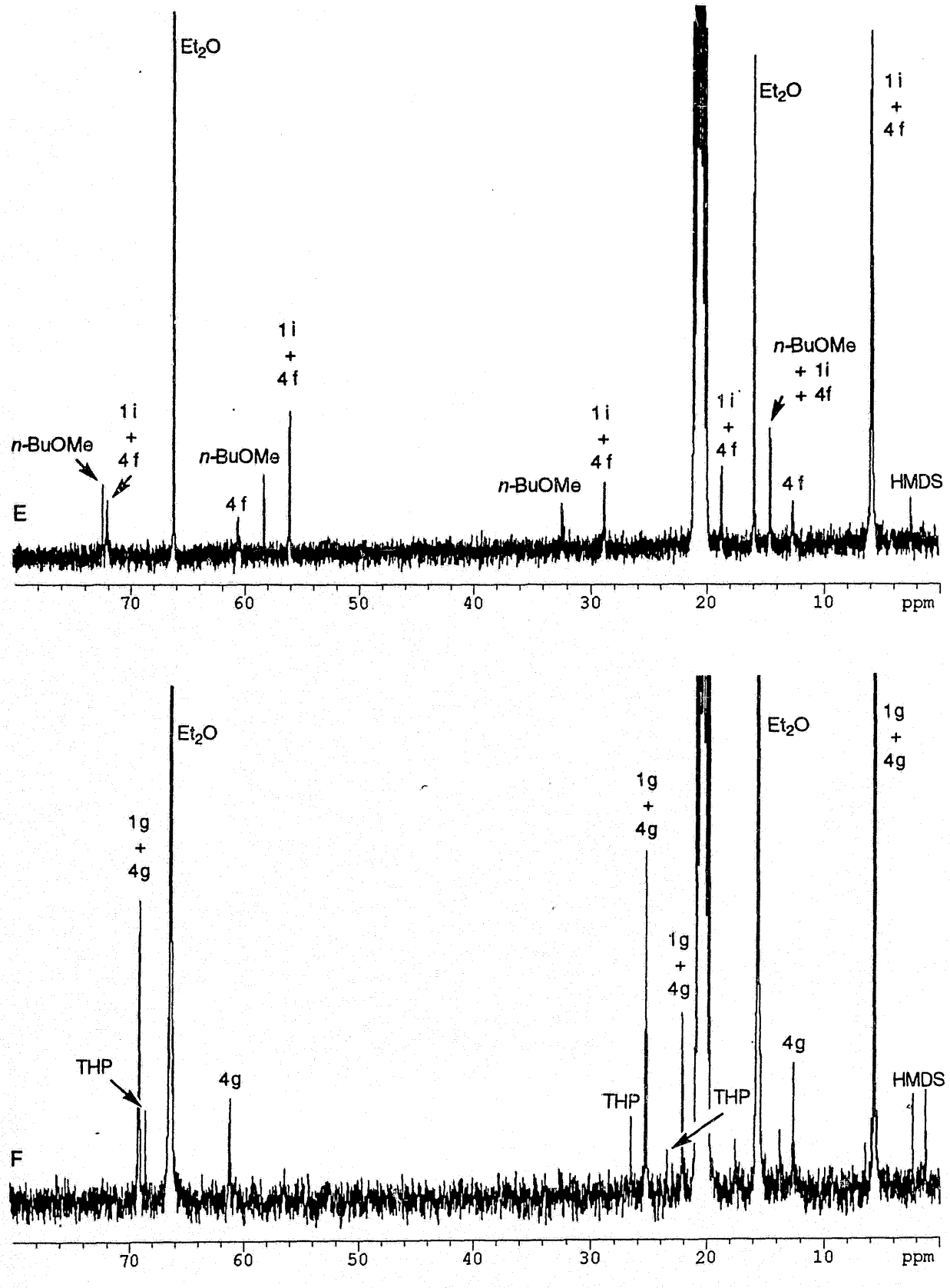


XI. $^{13}C\{^1H\}$ NMR spectra of 0.10M [^{6}Li]LiHMDS with Et_2O and added ethereal solvent in toluene-d_8 at -100 °C: (A) 1.1 equiv. of added *i*-PrOMe and 3.0 equiv of added Et_2O; (B) 4.0 equiv. of added *t*-BuOMe and 1.1 equiv of added Et_2O;



XI.(cont) (C) 1.1 equiv. of added 2,2-Me_2THF and 5.0 equiv. of added Et_2O; (D) 1.1 equiv of added 2-MeTHF and 5.0 equiv. of added Et_2O;

J-9874-13



XI.(cont) (E) 1.1 equiv of added *n*-BuOMe and 3.0 equiv. of added Et_2O; (F)1.1 equiv of added THP and 5.0 equiv. of added Et_2O.

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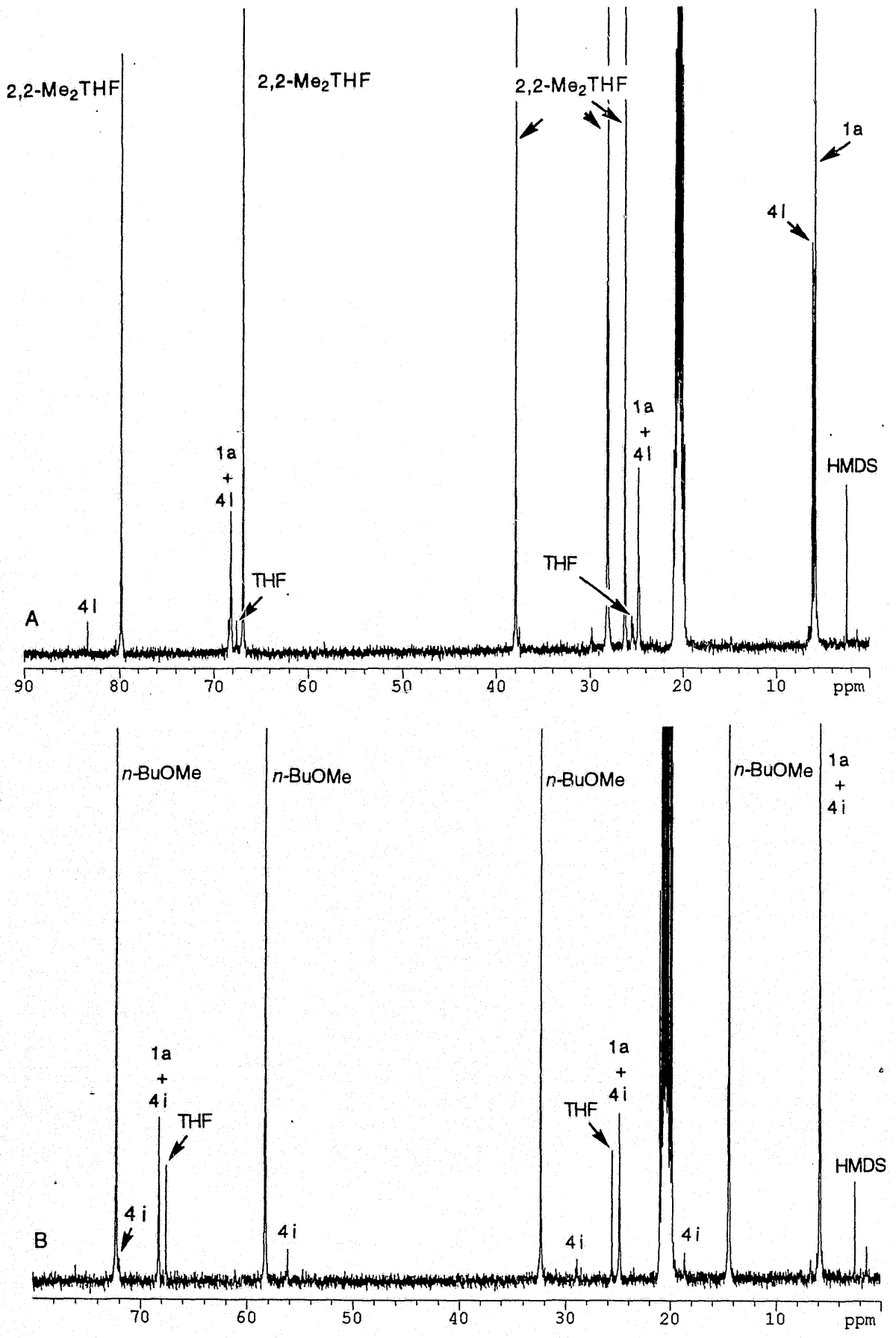

XII. $^{13}C\{^{1}H\}$ NMR spectra of 0.10M [^{6}Li]LiHMDS with THF and added ethereal solvent in toluene-d_8 at -100 °C: (A) 3.0 equiv. of added 2,2-Me_2THF and 1.1 equiv of added THF; (B) 4.0 equiv. of added *n*-BuOMe and 1.1 equiv of added THF;

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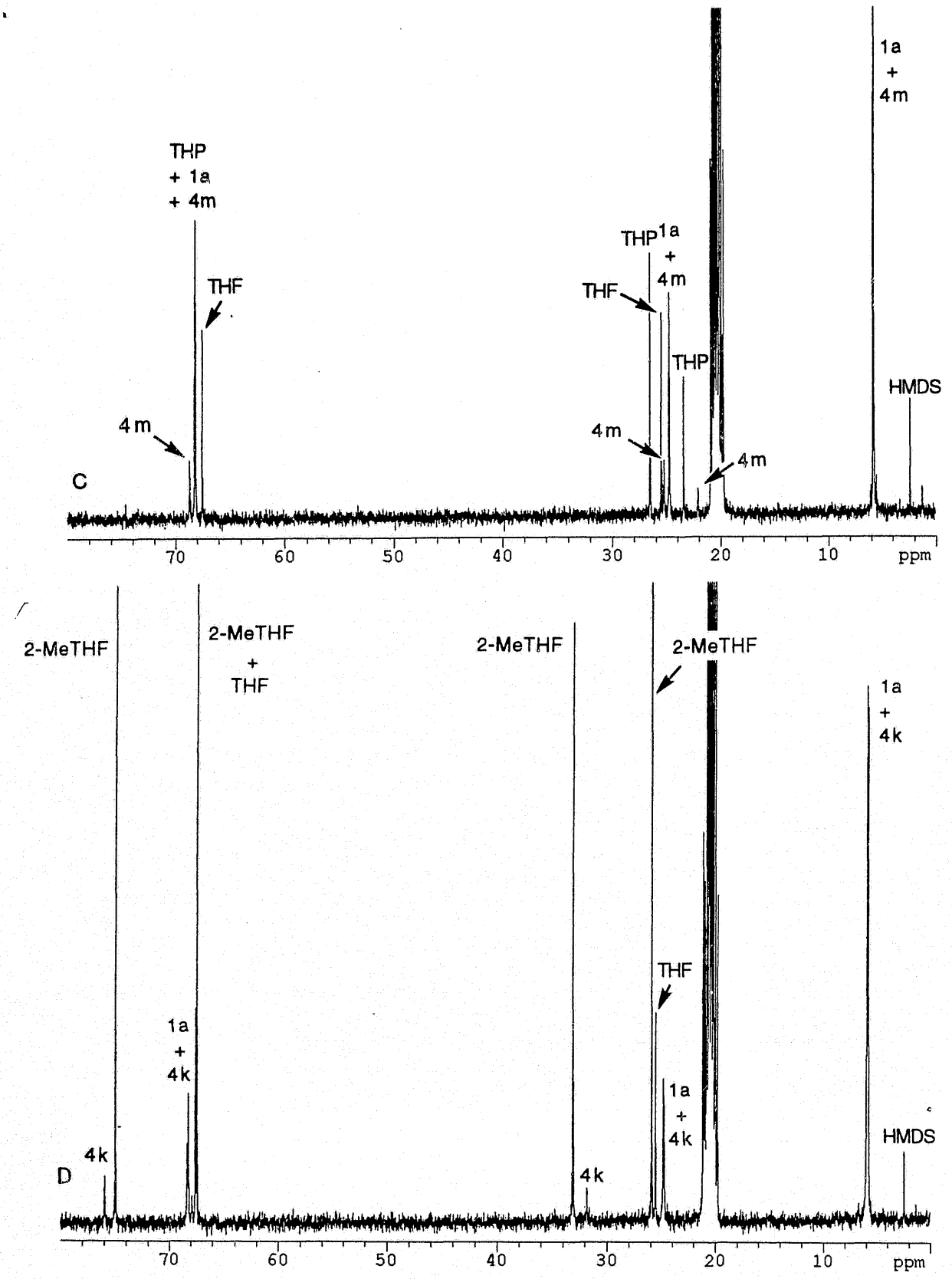

XII.(cont.) (C) 1.1 equiv. of added THP and 1.1 equiv. of added THF; (D) 2.0 equiv of added 2-MeTHF and 1.1 equiv. of added THF.

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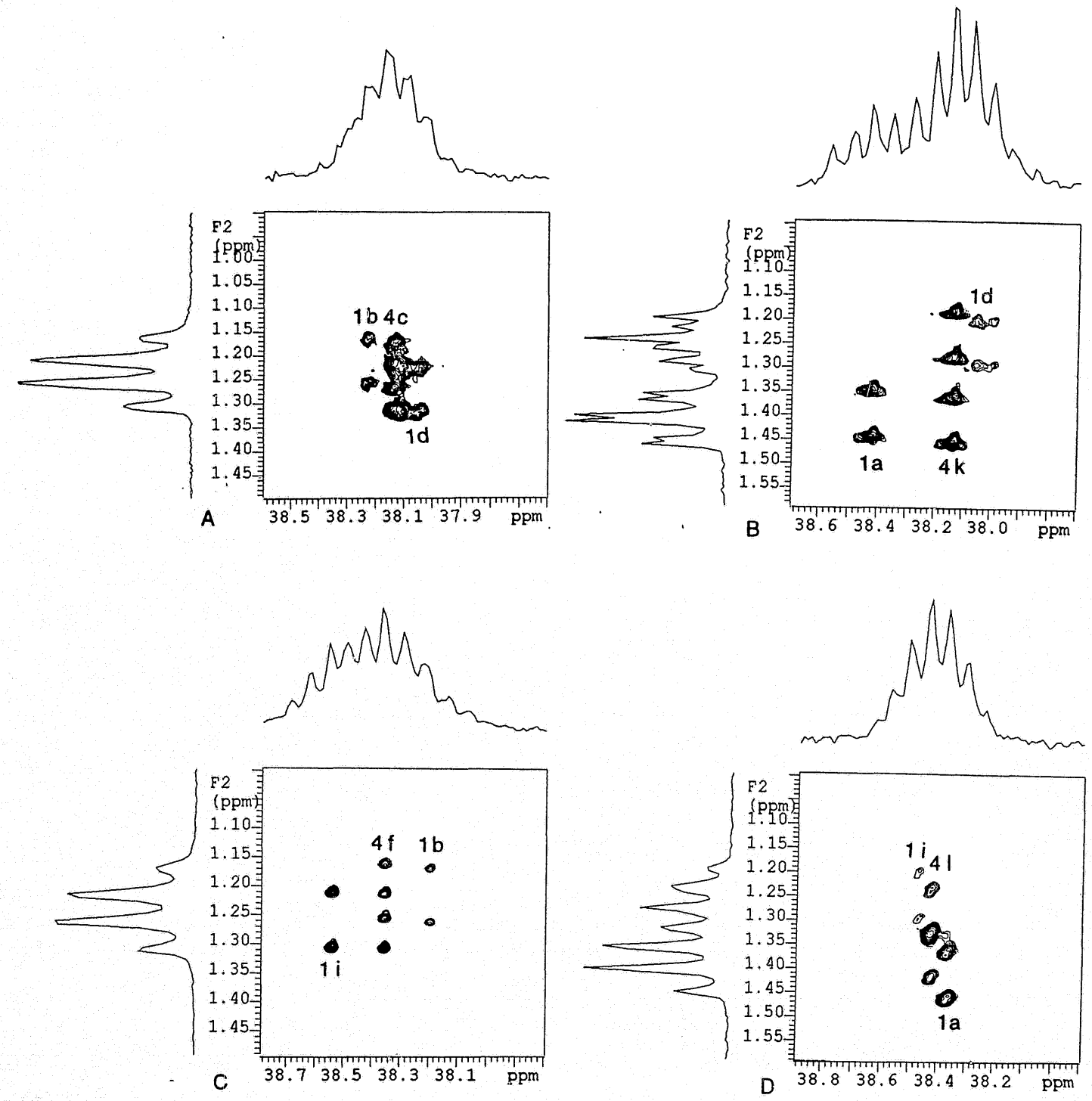

XIII. ^{6}Li-^{15}N HMQC spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS in pentane at -100 °C: (A) 0.5 equiv. of added 2-MeTHF and 1.0 equiv. of added Et_2O; (B) 0.5 equiv. of added THF and 1.0 equiv. of added 2-MeTHF; (C) 0.5 equiv. of added *n*-BuOMe and 1.0 equiv. of added Et_2O; (D) 0.5 equiv. of added THF and 1.0 equiv. of added *n*-BuOMe. The upper and left-hand traces are the corresponding $^{15}N\{^{1}H\}$ and ^{6}Li NMR spectra.

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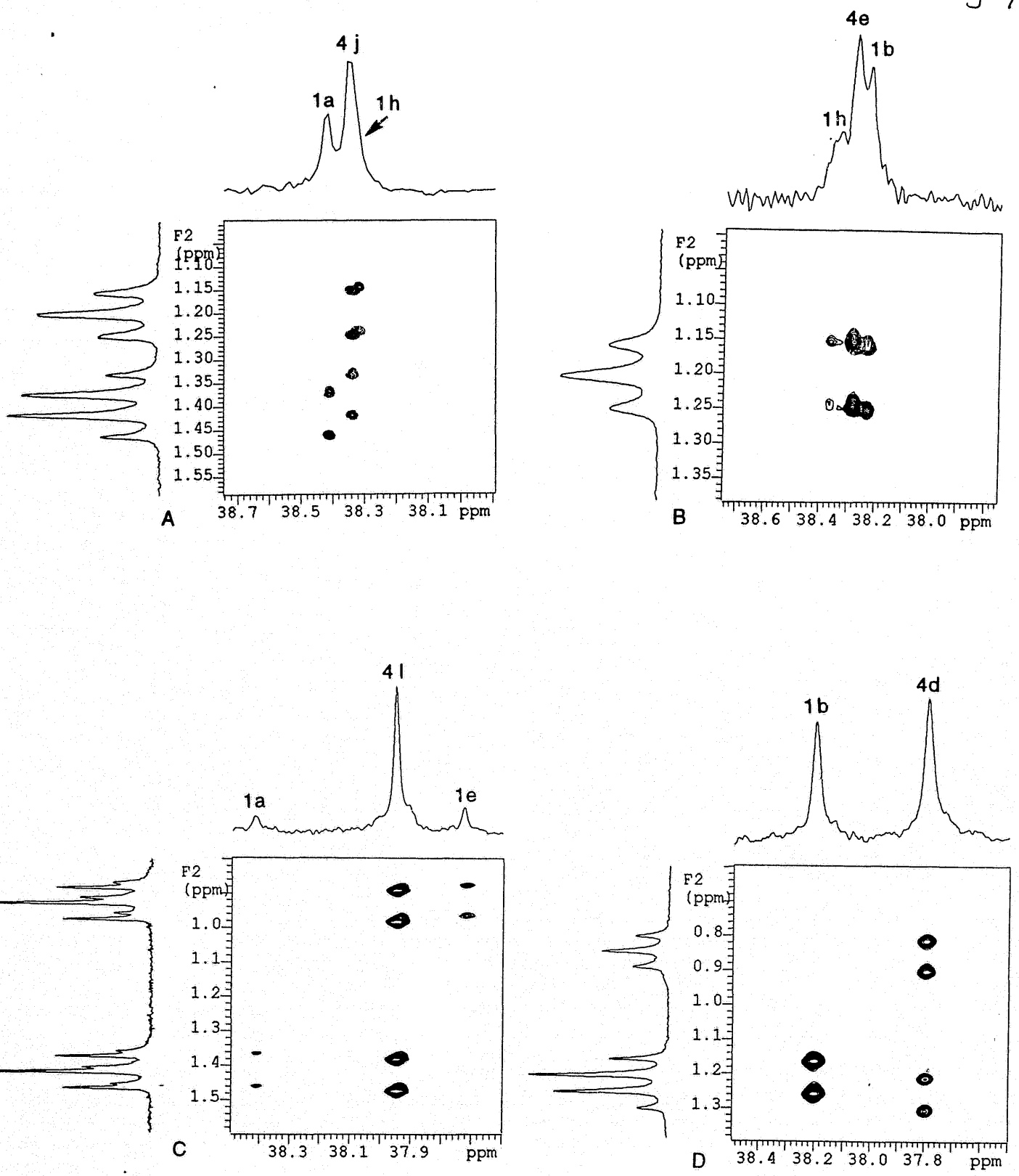
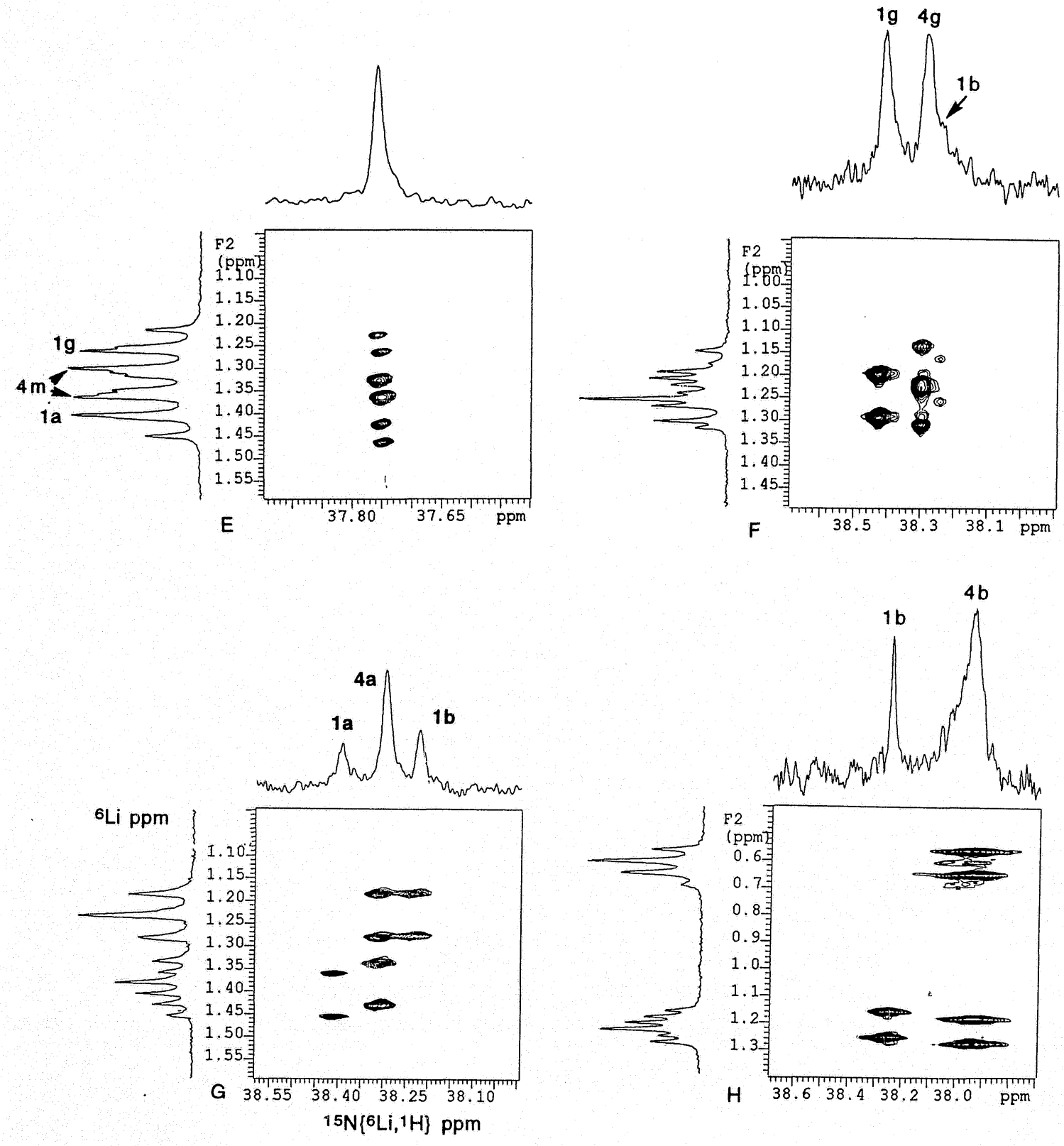
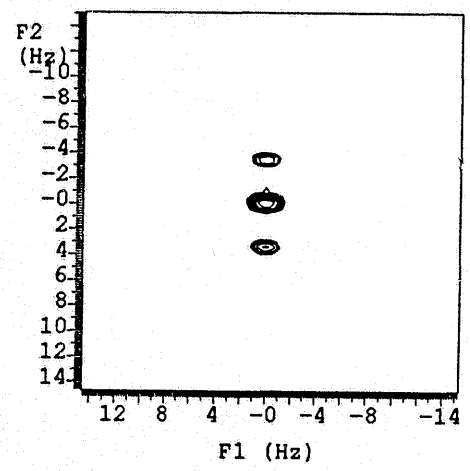


XIV. ^{6}Li-^{15}N HMQC spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS in pentane at -100 °C: (A) 0.5 equiv. of added THF and 1.0 equiv. of added *i*-PrOMe; (B) 0.5 equiv. of added *i*-PrOMe and 1.0 equiv. of added Et_2O; (C) 0.5 equiv. of added THF and 1.0 equiv. of added 2,2-Me_2THF; (D) 0.5 equiv. of added 2,2-Me_2THF and 1.0 equiv. of added Et_2O;

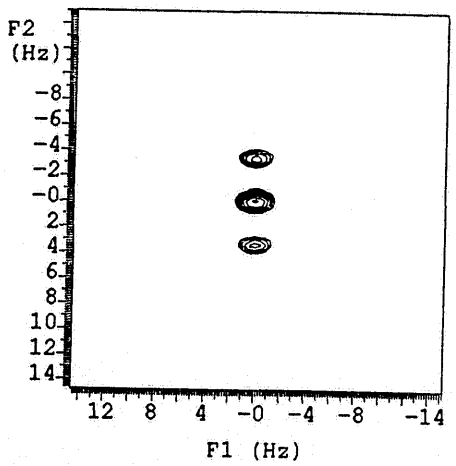
J-9874-18



XIV.(cont.) (E) 0.5 equiv. of added THF and 0.7 equiv. of added THP; (F) 0.5 equiv. of added THP and 1.0 equiv. of added Et_2O; (G) 0.5 equiv. of added THF and 1.0 equiv. of added Et_2O (H) 0.5 equiv. of added Et_2O and 1.0 equiv of added *t*-BuOMe at -120 °C. The upper and left-hand traces are the corresponding $^{15}N\{^1H,^6Li\}$ and ^6Li NMR spectra, respectively.



A



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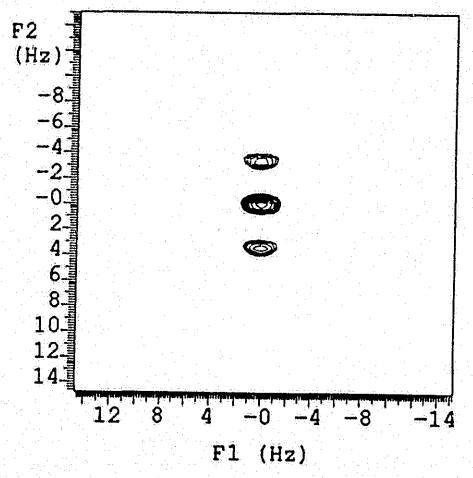

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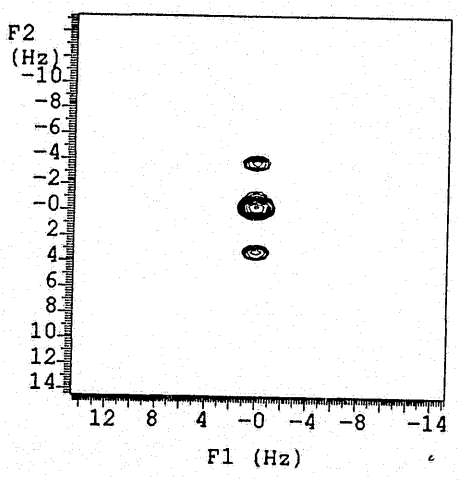
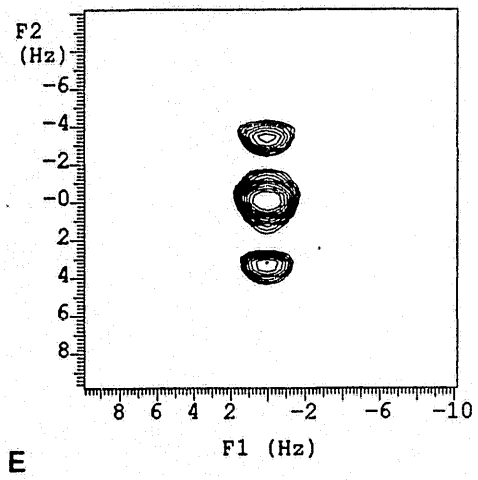
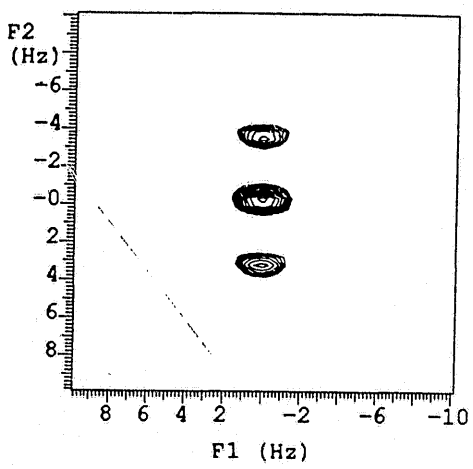


D

XV. ^{6}Li-detected ^{15}N zero-quantum NMR spectra of 0.1 M [^{6}Li,^{15}N]LiHMDS in pentane at -100 °C: (A) 5 equiv. of Et_2O ; (B) 5 equiv. of *t*-BuOMe; (C) 5 equiv. 2-MeTHF; (D) 5 equiv. 2,2-Me_2THF;



E



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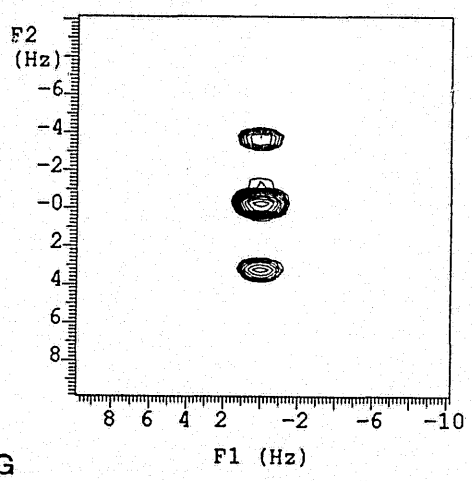
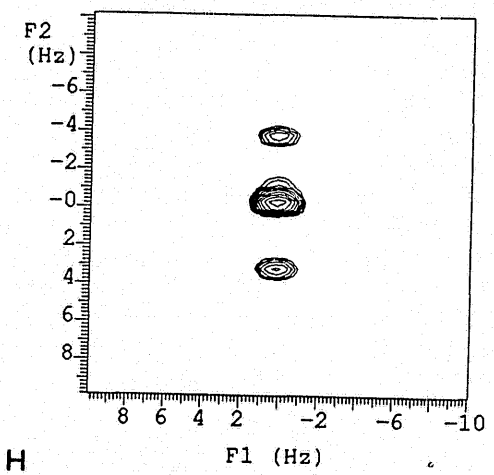
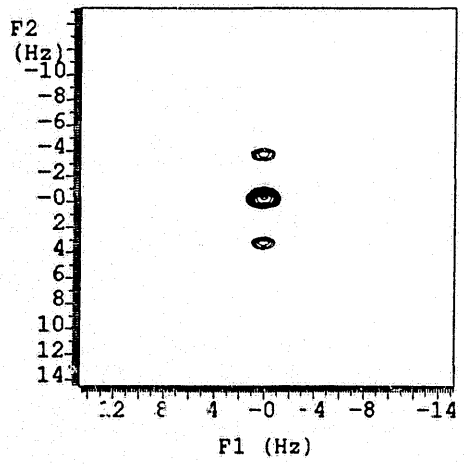


G



H

XV.(cont.) (E) 40 equiv. 2,2,5,5-Me_4THF; (F) 5 equiv. THP; (G) 5 equiv. *i*-PrOMe; (H) 5 equiv. *n*-BuOMe.



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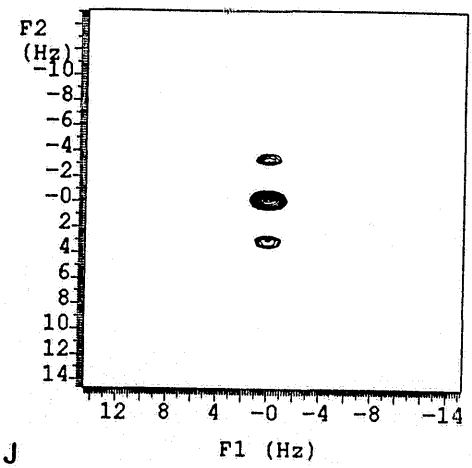

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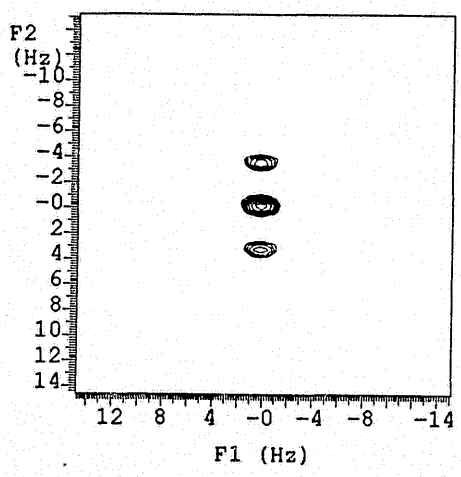
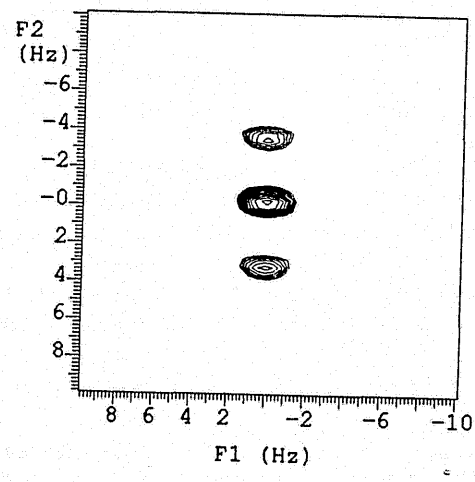
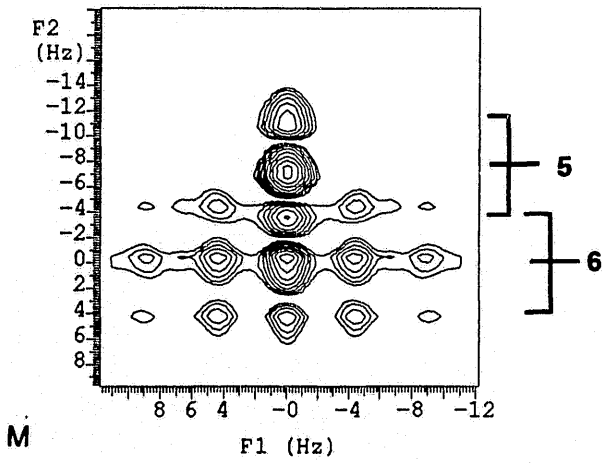


L



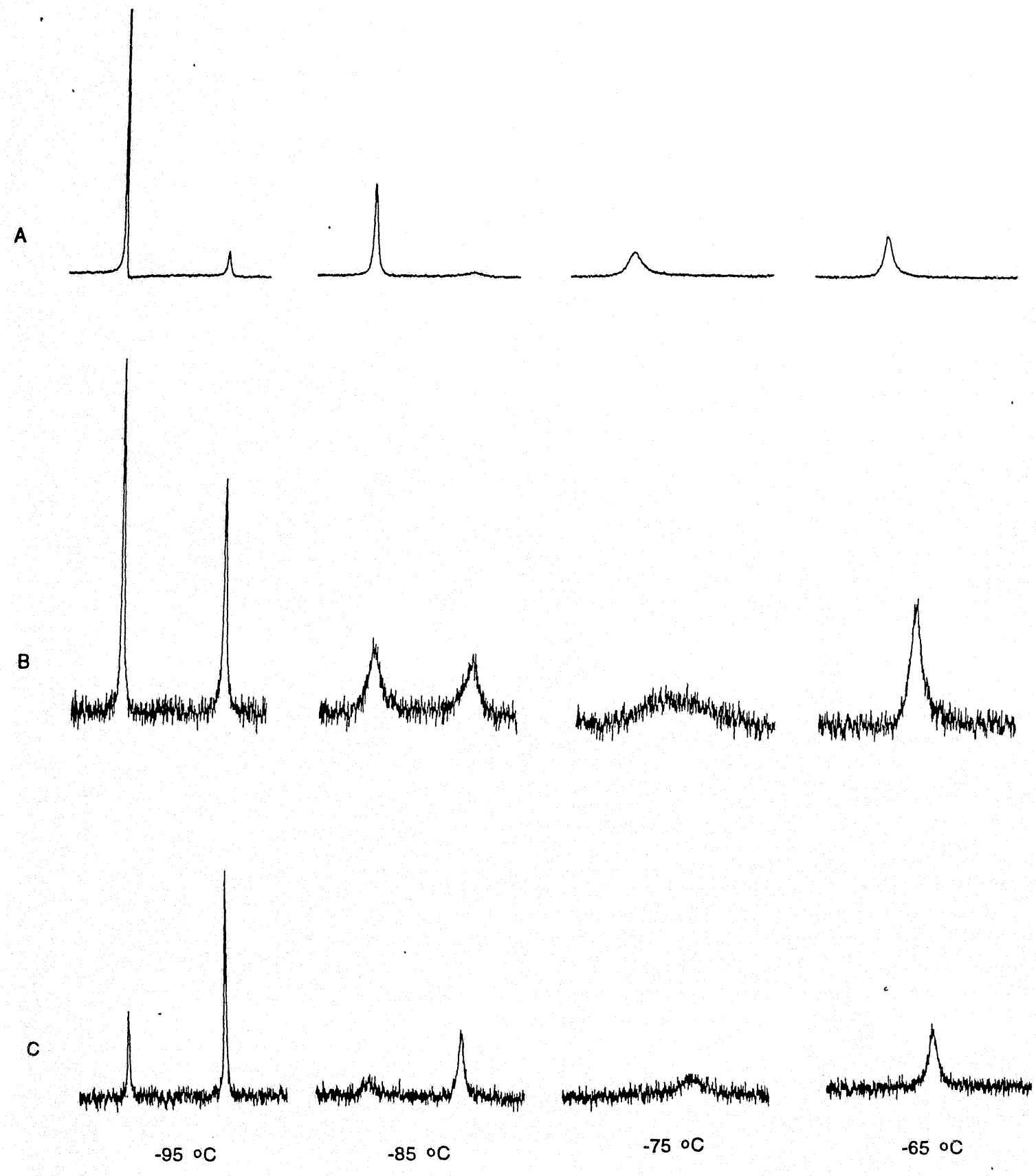
K

XV.(cont.) (I) 5 equiv. $Me_2(Et)COMe$; (J) 40 equiv. *i*-Pr_2O; (K) 5 equiv. oxetane; (L) 5 equiv. THF

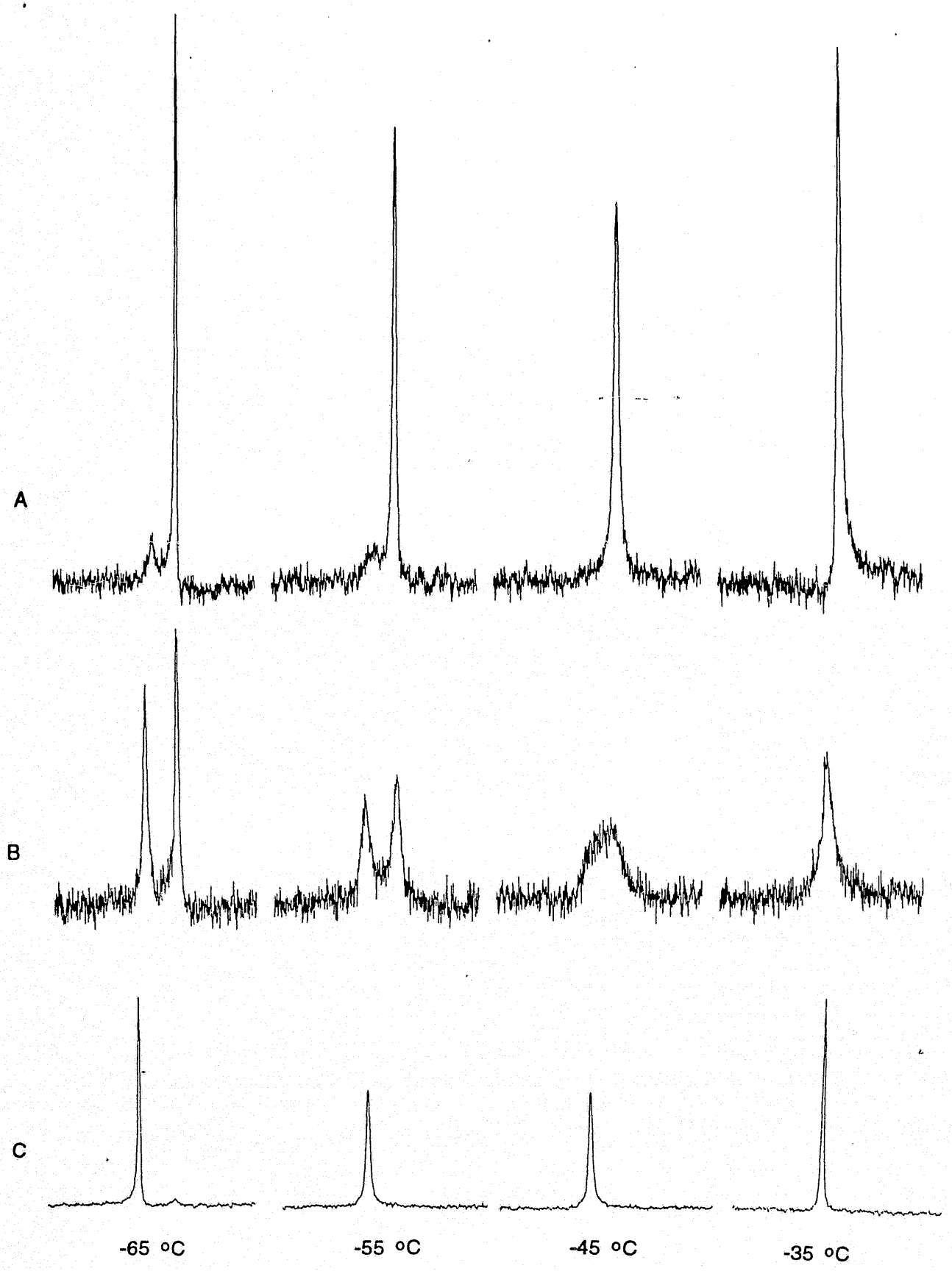


M

XV.(cont.) (M) neat pentane.

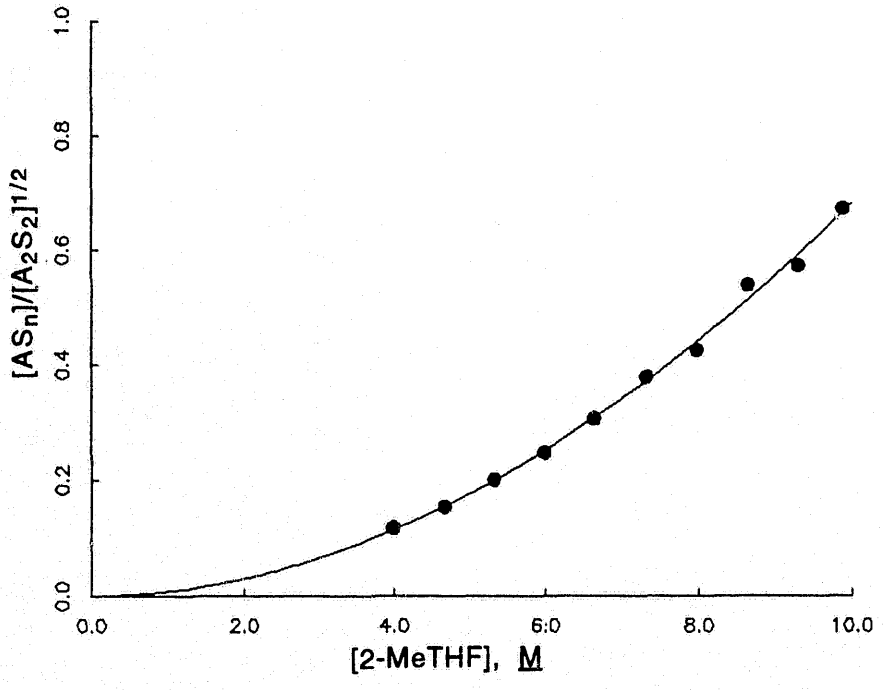


XVI. Variable temperature ^{13}C spectra of 0.1 M [^{6}Li]LiHMDS with added Et_2O: (A) 5.0 equiv. of added Et_2O; (B) 2.0 equiv. of added Et_2O (C) 1.2 equiv. of added Et_2O.

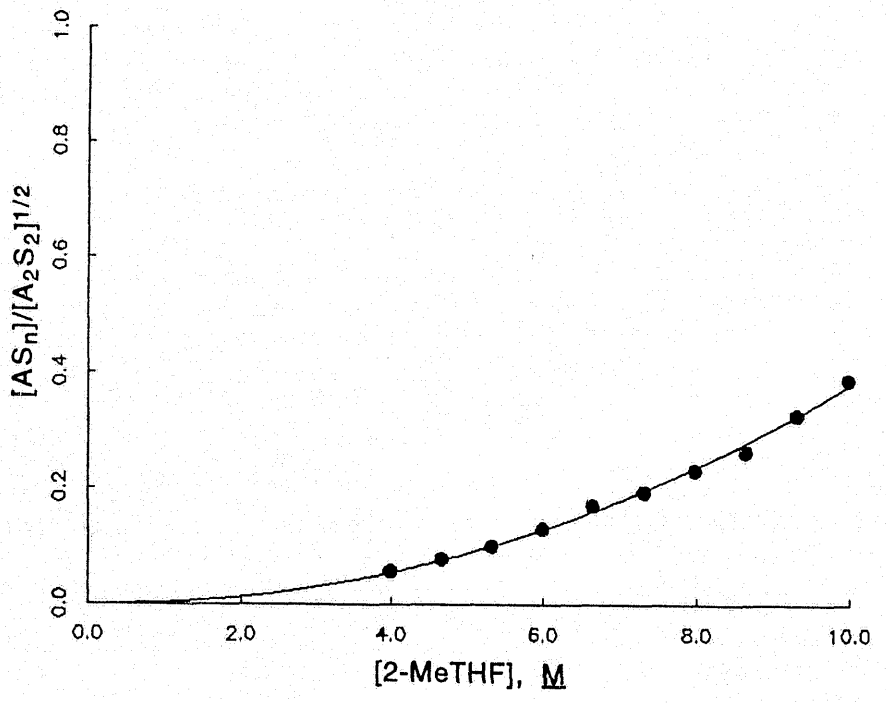


XVII. Variable temperature ^{13}C spectra of 0.1 M [^{6}Li]LiHMDS with added THF: (A) 5.0 equiv. of added THF; (B) 2.0 equiv. of added THF (C) 1.2 equiv. of added THF.

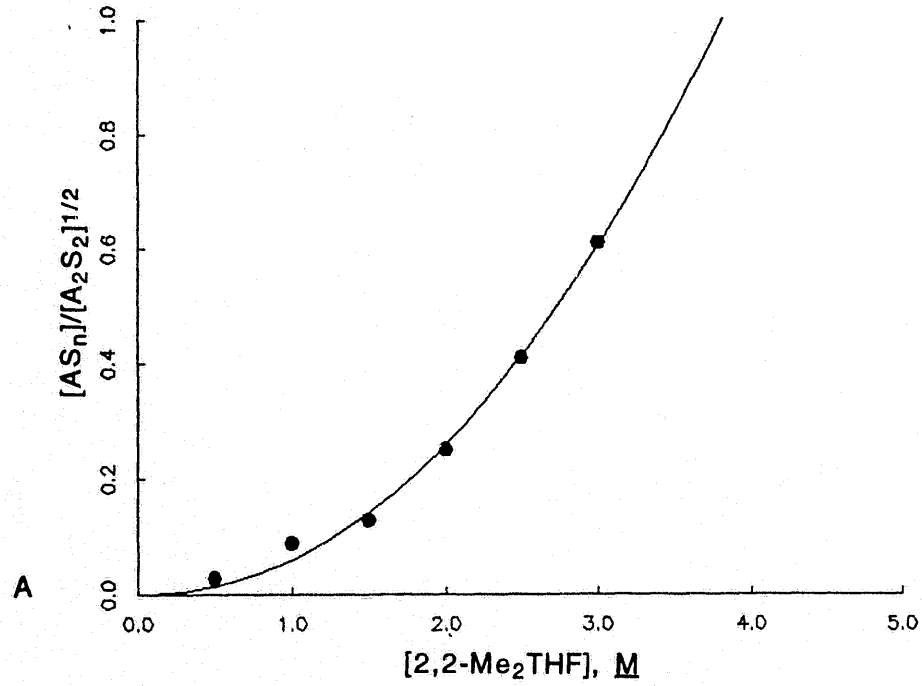
A

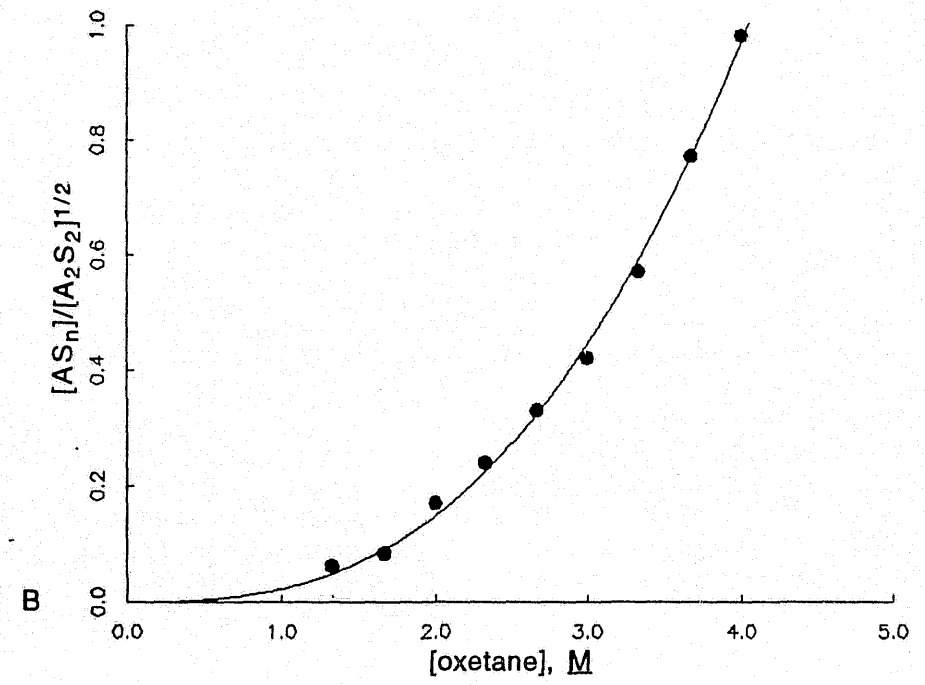


B

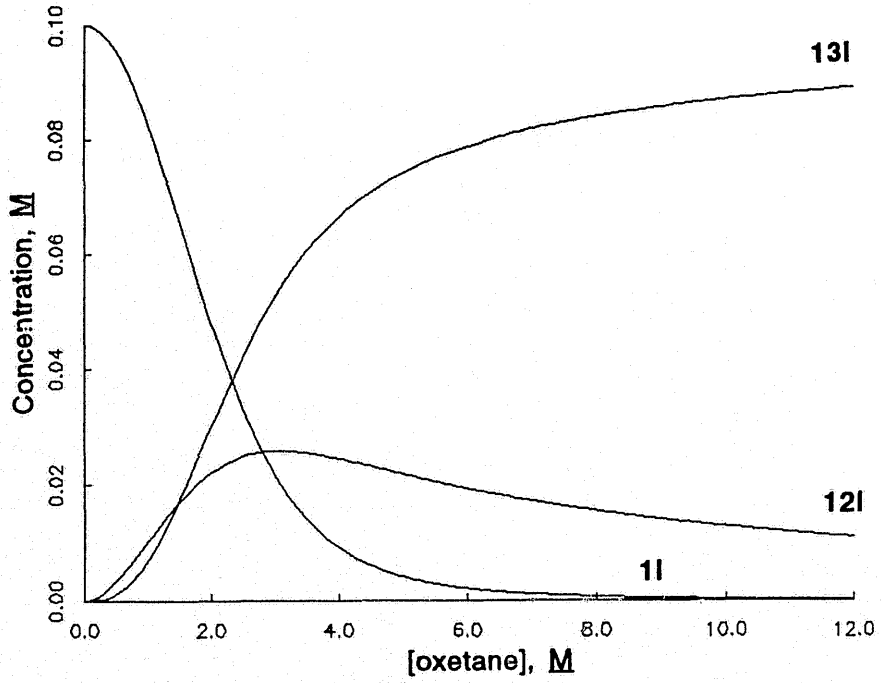


XVIII. Plot of $[AS_n]/[A_2S_2]^{1/2}$ vs. [2-MeTHF] for 0.1 M LiHMDS in pentane. The data are fit by non-linear least squares methods to the function in equation 10 of the manuscript: (A) at -20 °C $K_{eq} = 7.8 \times 10^{-3}$, n = 2.9; (B) at -80 °C, $K_{eq} = 2.9 \times 10^{-3}$, n = 3.1.





XIX. (A) Plot of $[AS_n]/[A_2S_2]^{1/2}$ vs. [2,2-Me_2THF] for 0.1 M LiHMDS in pentane at -80 °C. The data are fit by non-linear least squares methods to the function in equation 10 of the manusript. K_{eq} = 6.0 x 10^{-2}, n = 3.1. (B) Plot of $[AS_n]/[A_2S_2]^{1/2}$ vs. [oxetane] for 0.1 M LiHMDS in pentane at -20 °C. The data are fit by non-linear least squares methods to the function in equation 10 of the manuscript. K_{eq} = 2.3 x 10^{-2}, n = 3.7.

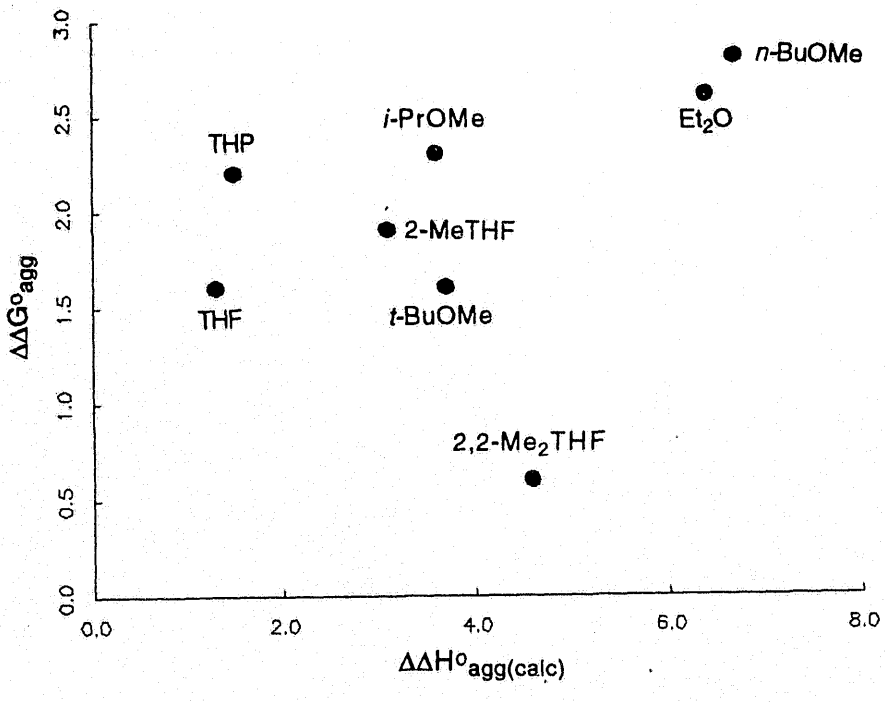


XX. Predicted concentrations of disolvated dimer **1I**, trisolvated monomer **12I** and tetrasolvated monomer **13I** at -80 °C in oxetane. The functions are calculated using adjustable parameters $K_{eq(1)} = 7.1 \times 10^{-3}$ and $K_{eq(2)} = 6.8 \times 10^{-1}$ derived from nonlinear least squares fit to equation 12.

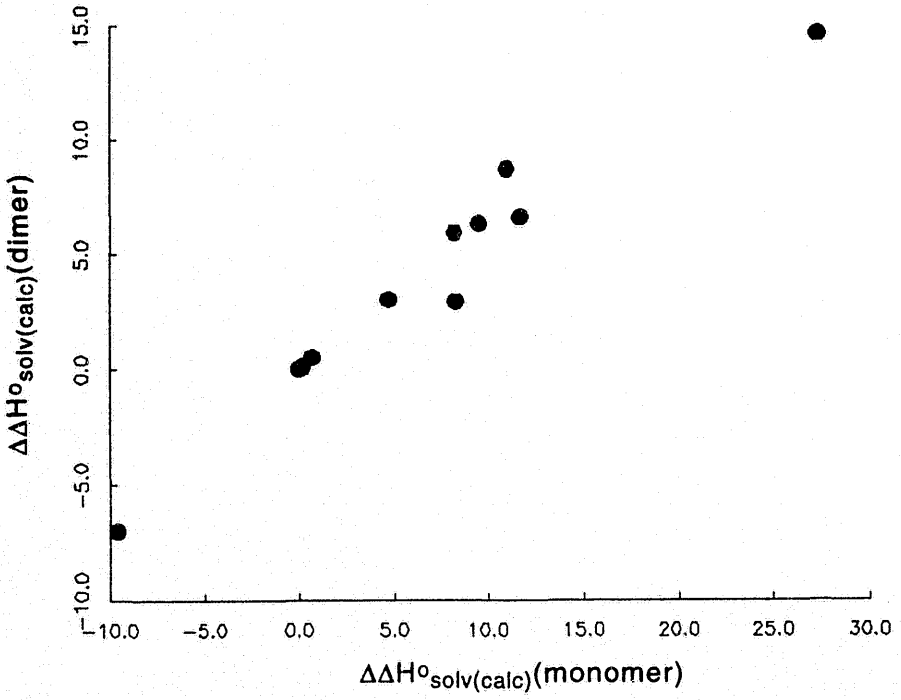
XXI. Tabulated thermodynamic data from MNDO semiempirical calculations on disolvated dimer (**11**) and disolvated monomer (**10**).[a]

Solvent	$\Delta H°_f$(**11**)	$\Delta H°_f$(**10**)	$\Delta H°_f$(**S**)
THF	-398.4	-257.2	-59.3
2-MeTHF	-398.9	-258.9	-62.5
2,2-Me_2THF	-390.9	-252.7	-61.8
Et_2O	-390.6	-250.9	-62.0
n-BuOMe	-406.0	-262.3	-66.0
i-PrOMe	-384.4	-246.8	-58.2
t-BuOme	-371.7	-236.8	-54.6
THP	-399.0	-258.1	-60.1
i-Pr_2O	-379.7	-240.3	-64.5
H_2O	-415.6	-270.0	-60.9
Me_2O	-382.0	-240.8	-51.2

[a]Enthalpies are reported in kcal/mol.



XXII. Plot of observed LiHMDS aggregation free energies ($\Delta\Delta G^{o}_{agg}$, equation 2 and 3, Table 3) vs LiHMDS aggregation enthalpies ($\Delta\Delta H^{o}_{agg(calc)}$, equation 6) calculated from MNDO.



XXIII. Plot of LiHMDS monomer solvation enthalpies ($\Delta\Delta H^{o}_{solv(calc)}$(monomer), equation 7) calculated from MNDO vs. calculated LiHMDS dimer solvation enthalpies ($\Delta\Delta H^{o}_{solv(calc)}$(dimer), equation 8).

XXIV. **Derivation of equation 12 and equations for Least-Squares Figure 14.**

Given the equilibria

$$1/2\,A_2S_2 + 3S \overset{K_1}{\rightleftharpoons} AS_3 + S \overset{K_2}{\rightleftharpoons} AS_4$$

such that

$$K_1 = \frac{[AS_3]}{[A_2S_2]^{1/2}[S]^2} \qquad (1)$$

and

$$K_2 = \frac{[AS_4]}{[AS_3][S]} \qquad (2)$$

we can derive the equations describing the equilibrium constants as a function of solvent and organolithium concentrations. We define the total monomer concentration, A_T, such that

$$[A_T] = [AS_3] + [AS_4]$$

Substituting into equation 2 and rearranging affords

$$[AS_3] = \frac{[A_T]}{(K_2)[S] + 1}$$

Squaring equation 1, substituting for $[AS_3]$, and rearranging affords

$$\frac{[A_T]}{[A_2S_2]} = K_1^2[S]^4((K_2)[S]+1)^2 \qquad (3)$$

Since the total LiHMDS concentration equals 0.10 M, then

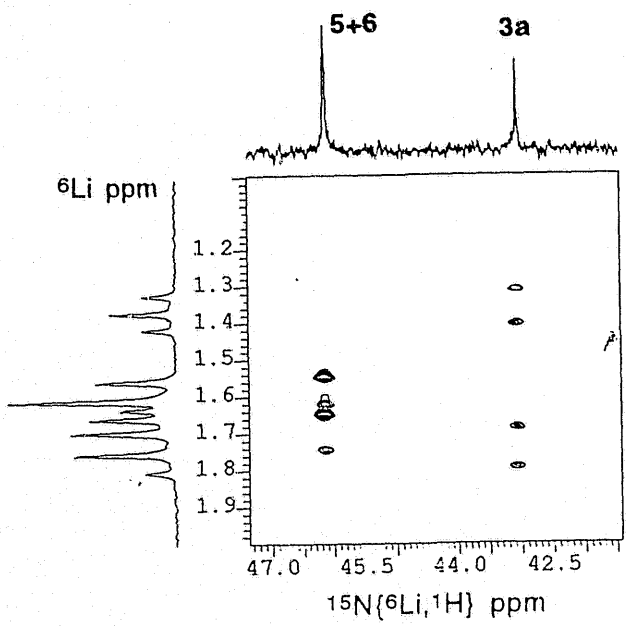
$$[A_2S_2] = \frac{0.10 - [A_T]}{2}$$

Substituting into equation 3 for $[A_2S_2]$ and rearranging affords

$$[A_T]^2 + \frac{K_1^2[S]^4((K_2)[S] + 1)^2[A_T]}{2} - \frac{(0.1)\,K_1^2[S]^4((K_2)[S] + 1)^2}{2} = 0$$

Solving for $[A_T]$ using the quadratic equation affords

$$[A_T] = \frac{K_1^2[S]^4((K_2)[S] + 1)^2}{4} + \frac{[S]^2((K_2)[S] + 1)}{2}\sqrt{\frac{K_1^4[S]^4((K_2)[S] + 1)^2}{2} + (0.2)K_1^2}$$



XXV. ^{6}Li-^{15}N HMQC spectrum of 0.10 M [^{6}Li,^{15}N]LiHMDS with 0.3 equiv. THF per Li. The left and upper traces are the corresponding one-dimensional ^{6}Li and $^{15}N\{^{6}Li,^{1}H\}$NMR spectra, respectively.