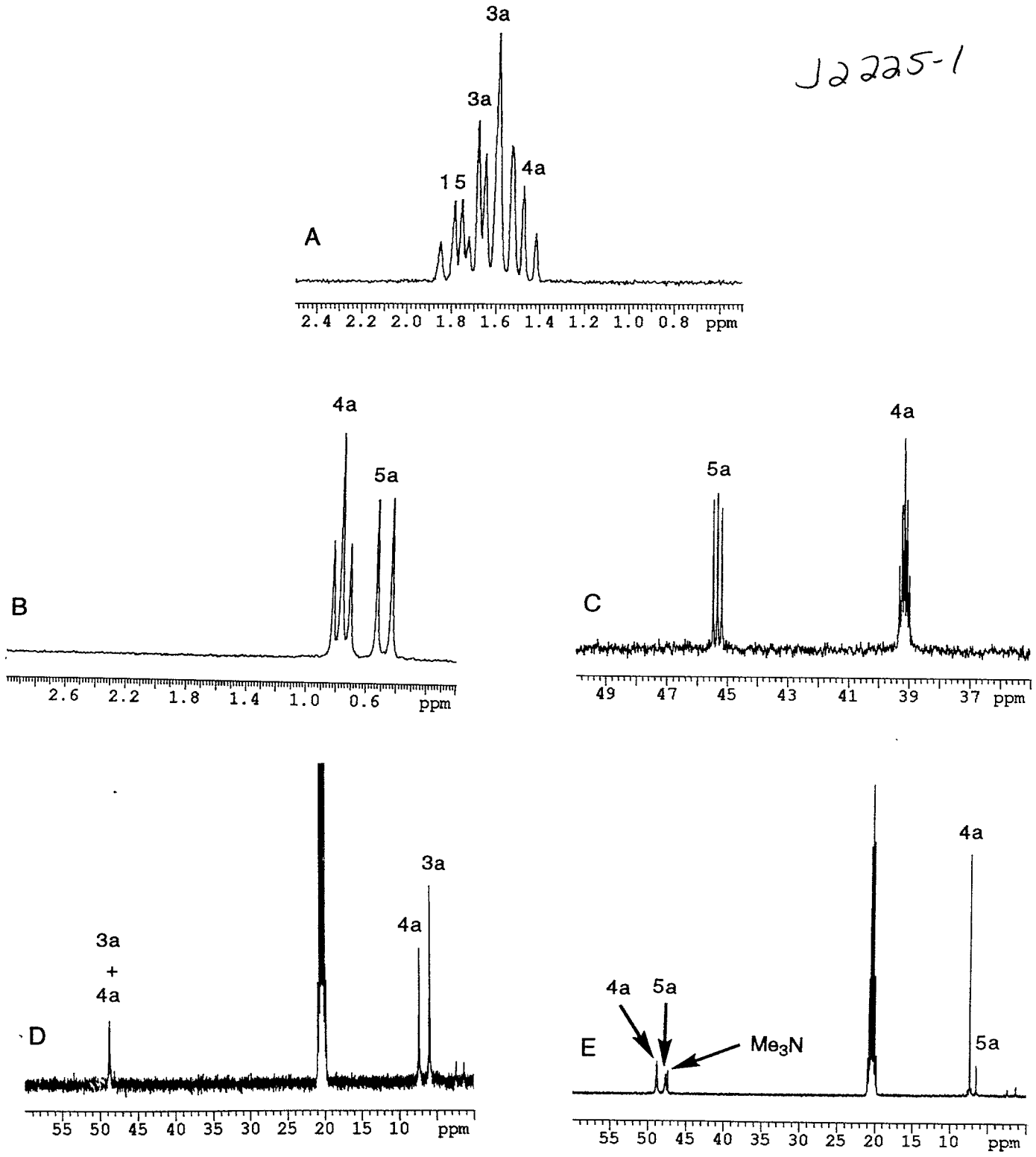
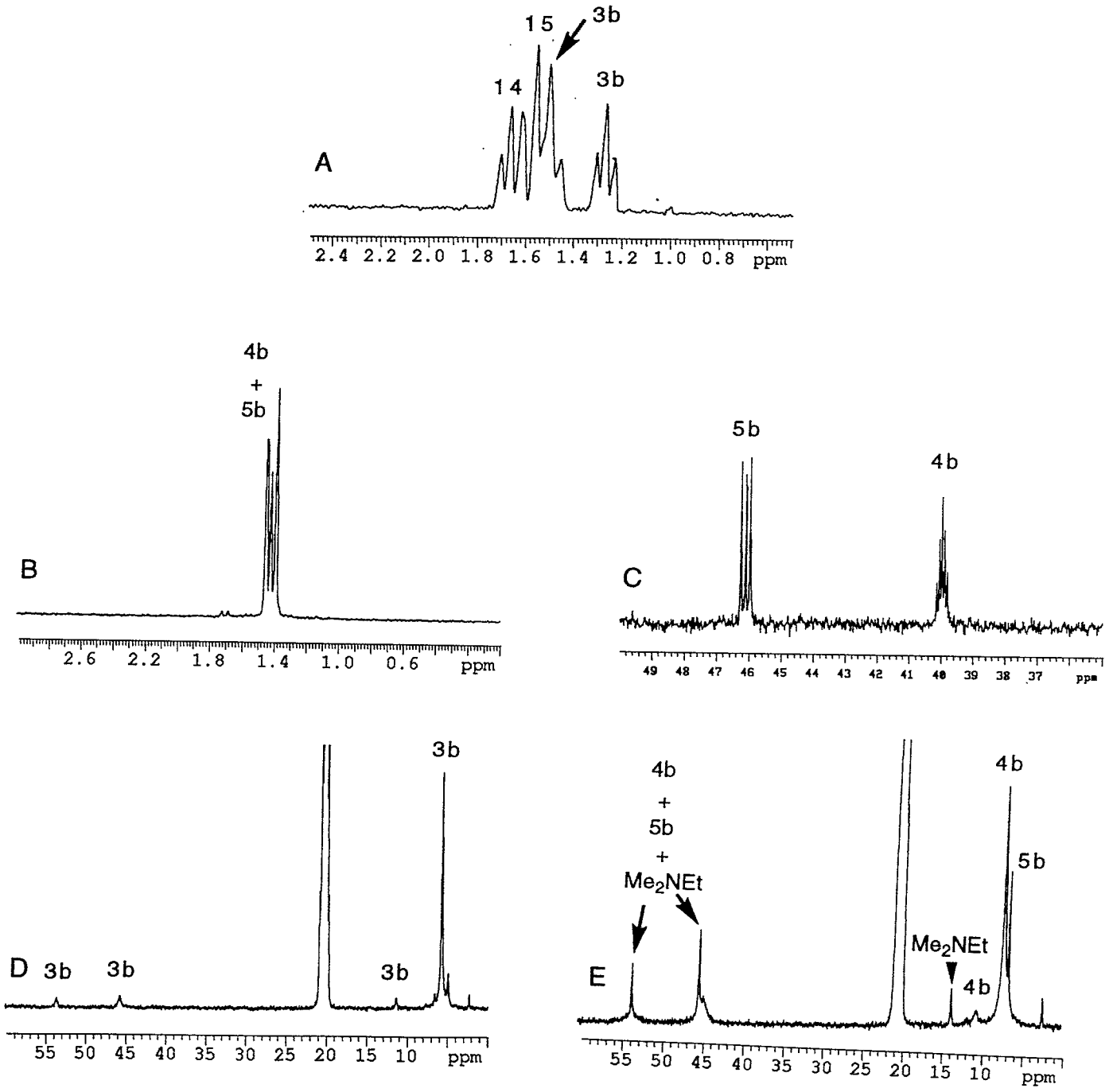
J2225-1



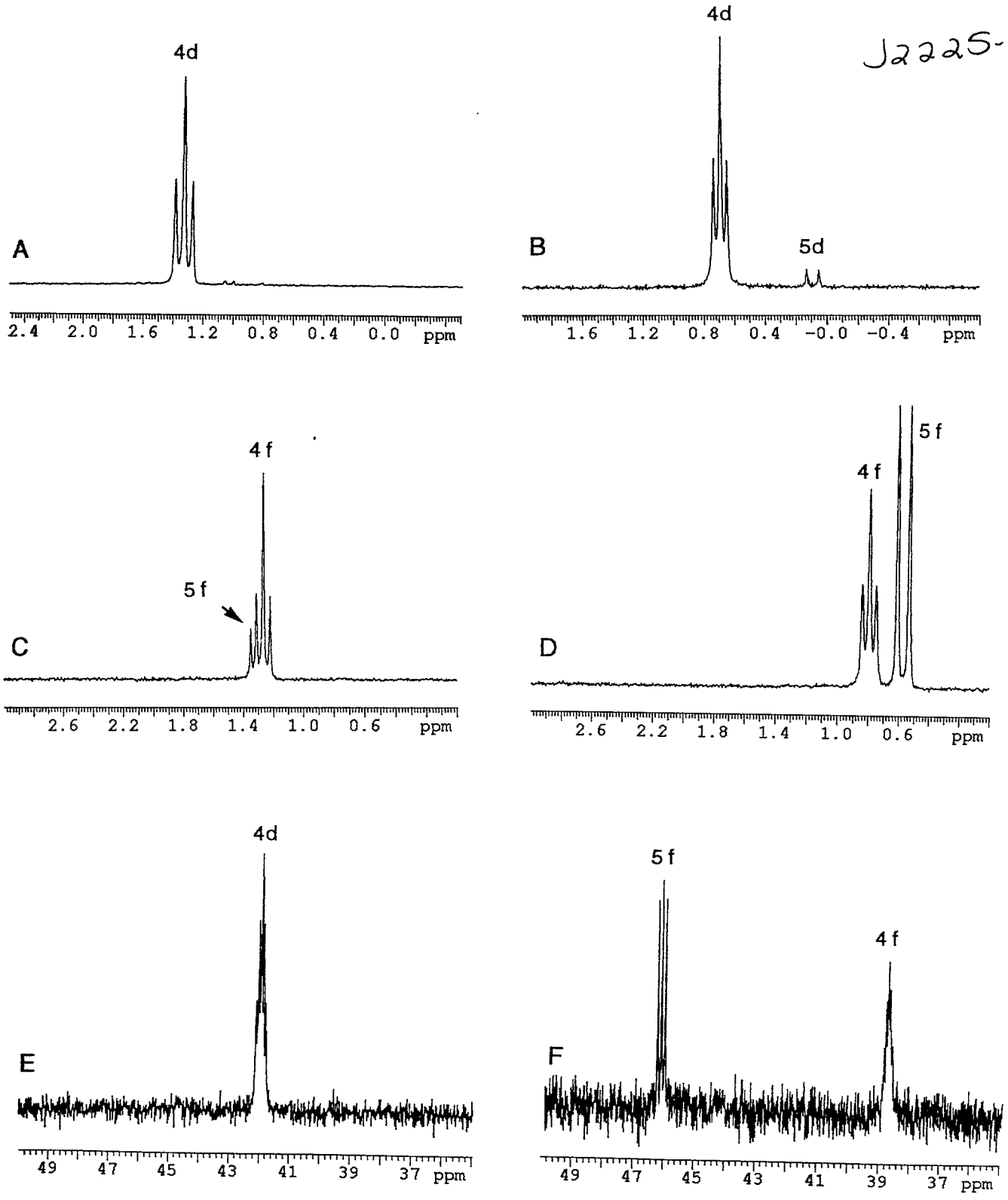
I. ^{6}Li, ^{15}N, and ^{13}C NMR spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS with added Me_3N: (A) ^{6}Li NMR spectrum with 0.3 equiv. of added Me_3N in pentane at -115 °C; (B) ^{6}Li NMR spectrum with 5.0 equiv. of added Me_3N in toluene-d_8 at -100 °C; (C) $^{15}N\{^{1}H\}$ NMR spectrum with 5.0 equiv. of added Me_3N in toluene-d_8 at -100 °C; (D) $^{13}C\{^{1}H\}$ NMR spectrum with 0.7 equiv. of added Me_3N in toluene-d_8 at -100 °C; (E) $^{13}C\{^{1}H\}$ NMR spectrum with 2.0 equiv. of added Me_3N in toluene-d_8 at -100 °C.

J2225-2



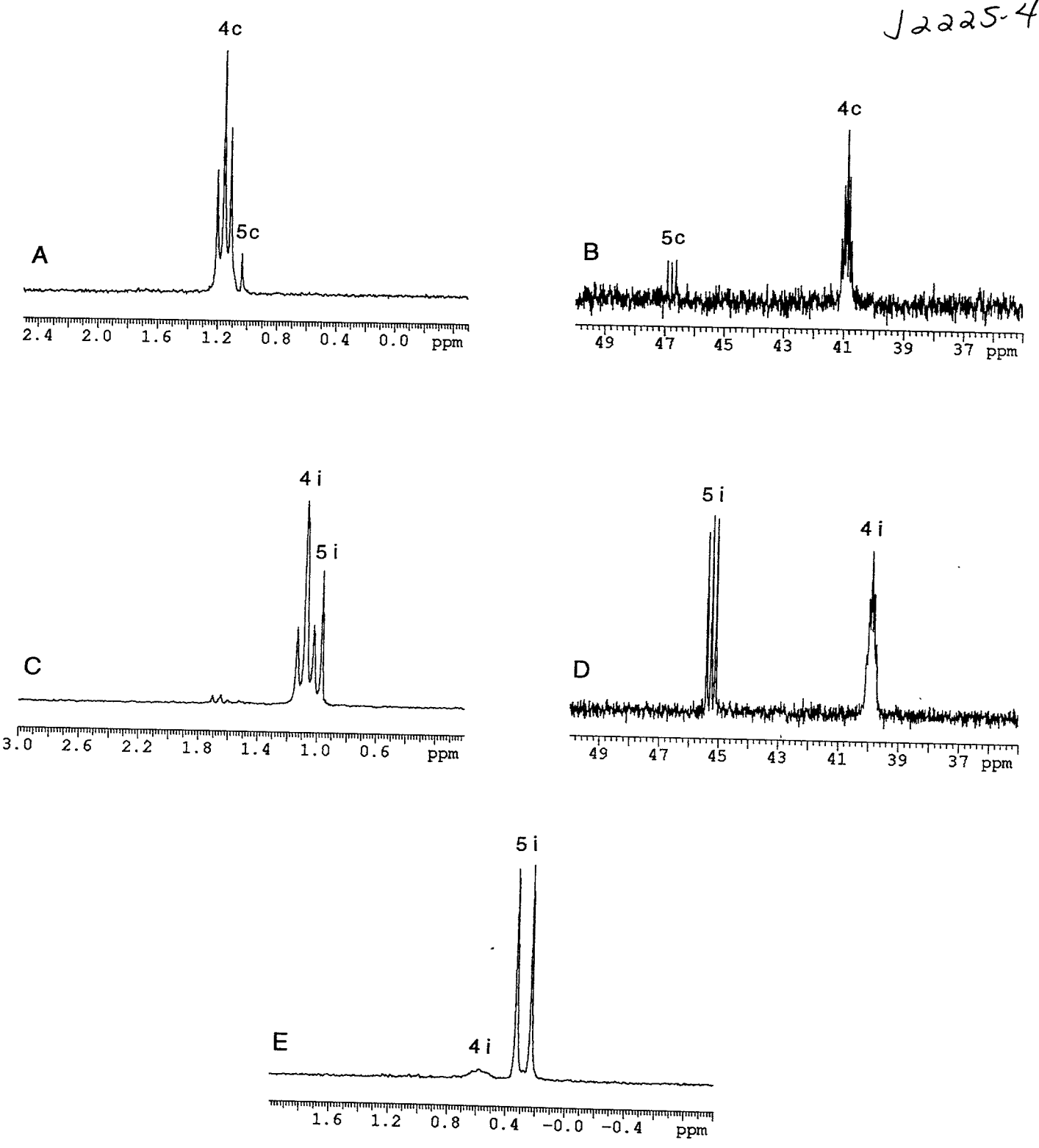
II. ^{6}Li, ^{15}N, and ^{13}C NMR spectra of 0.10 M $[^{6}Li,^{15}N]$LiHMDS with added Me_2NEt: (A) ^{6}Li NMR spectrum with 0.3 equiv. of added Me_2NEt in pentane at -115 °C; (B) ^{6}Li NMR spectrum with 20 equiv. of added Me_2NEt in pentane at -80 °C; (C) $^{15}N\{^{1}H\}$ NMR spectrum with 20 equiv. of added Me_2NEt in pentane at -80 °C; (D) $^{13}C\{^{1}H\}$ NMR spectrum with 0.7 equiv. of added Me_2NEt in toluene-d_8 at -100 °C; (E) $^{13}C\{^{1}H\}$ NMR spectrum with 2.0 equiv. of added Me_2NEt in toluene-d_8 at -100 °C.

J2225-3

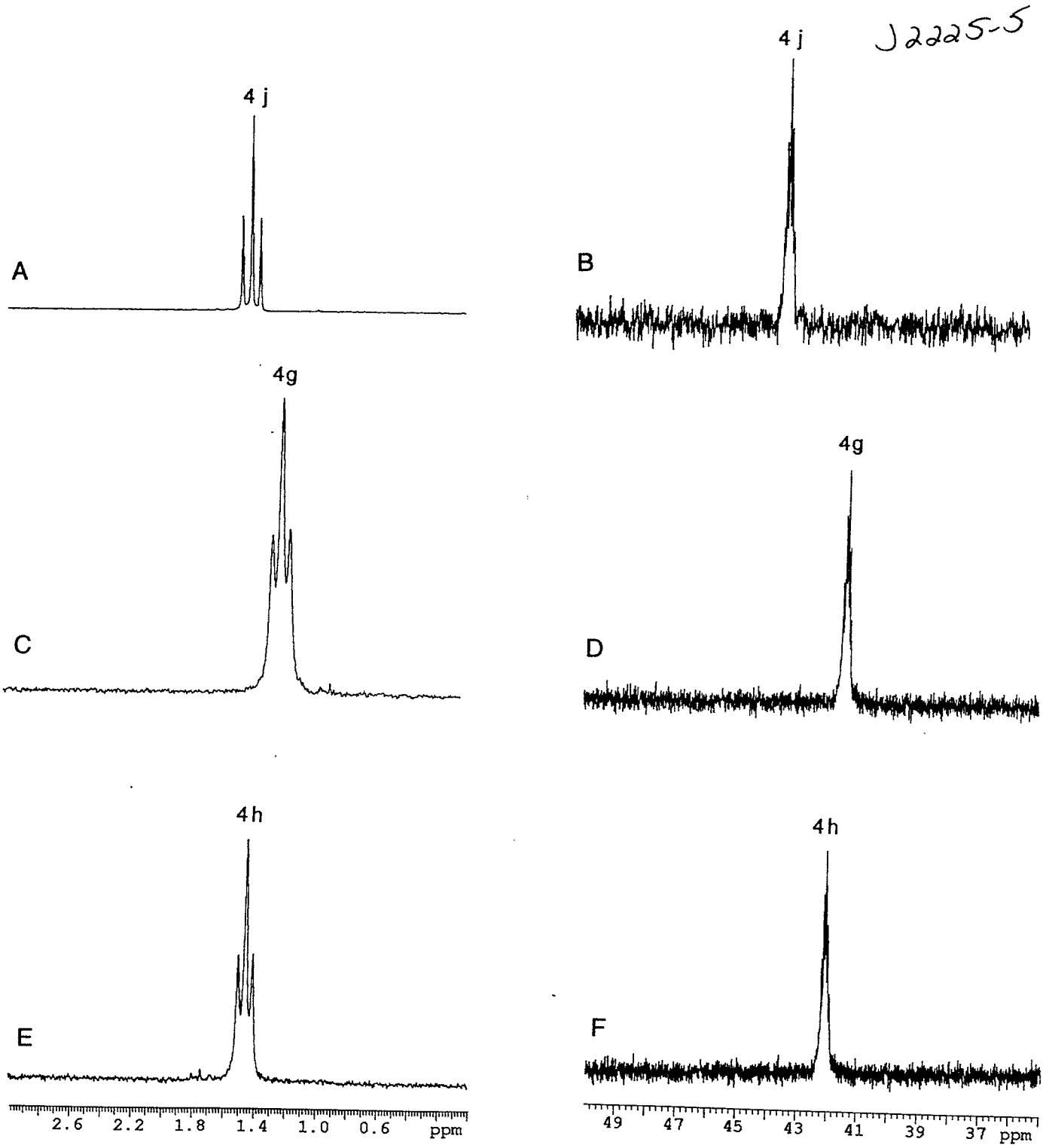


III. ^{6}Li and ^{15}N NMR spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS at -80 °C: (A) ^{6}Li NMR spectrum with 20 equiv. of added Et_3N in pentane; (B) ^{6}Li NMR spectrum with 20 equiv. of added Et_3N in toluene; (C) ^{6}Li NMR spectrum with 20 equiv. of added Me_2N-*n*-Pr in pentane; (D) ^{6}Li NMR spectrum with 20 equiv. of added Me_2N-*n*-Pr in toluene; (E) $^{15}N\{^{1}H\}$ NMR spectrum with 20 equiv. of added Et_3N in pentane; (F) $^{15}N\{^{1}H\}$ NMR spectrum with 20 equiv. of added Me_2N-*n*-Pr in toluene.

J2225-4

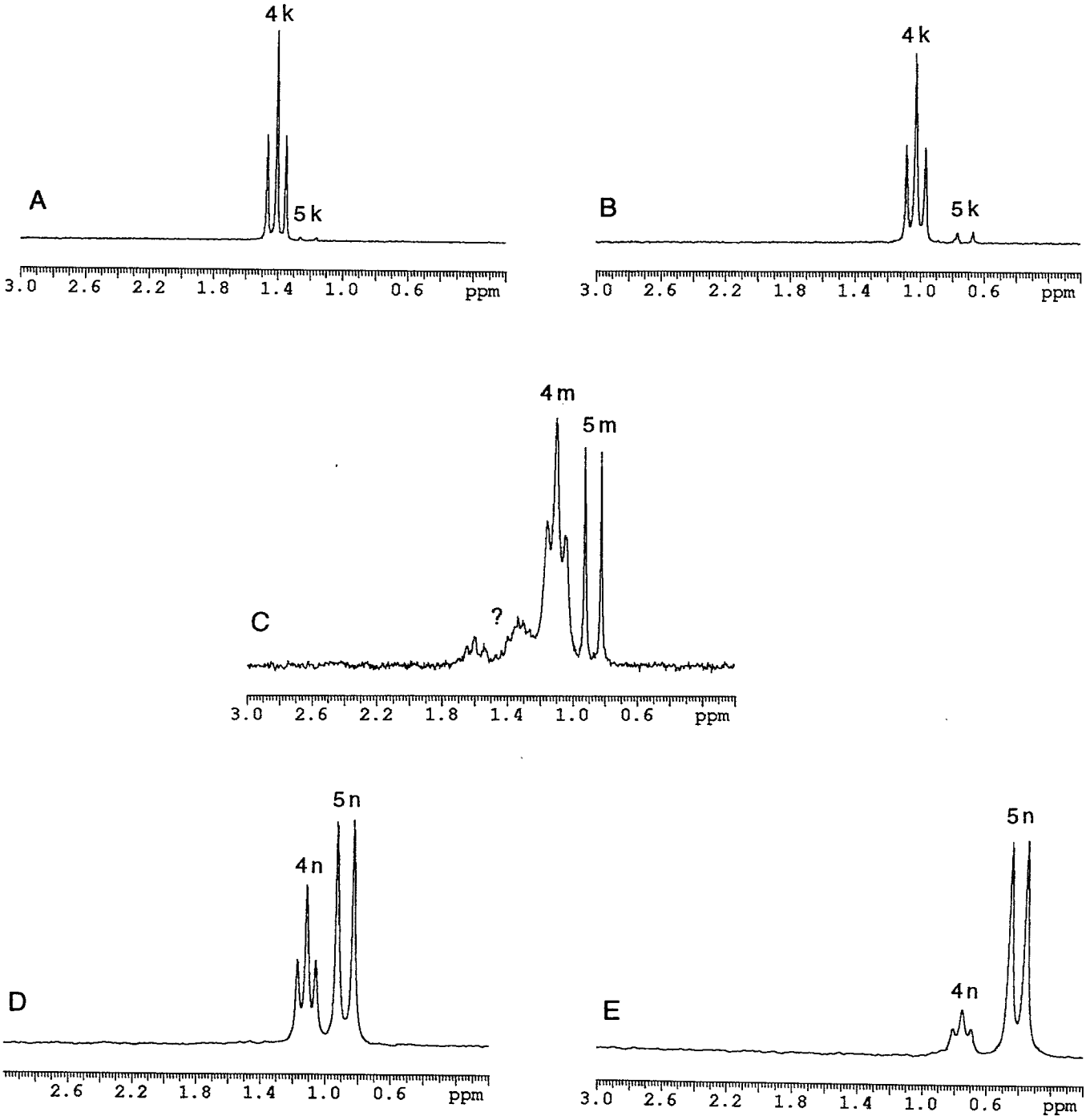


IV. ^{6}Li and ^{15}N NMR spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS at -80 °C: (A) ^{6}Li NMR spectrum with 20 equiv. of added $MeNEt_2$ in pentane; (B) $^{15}N\{^{1}H\}$ NMR spectrum with 20 equiv. of added $MeNEt_2$ in pentane; (C) ^{6}Li NMR spectrum with 20 equiv. of added Me_2N-*i*-Pr in pentane; (D) $^{15}N\{^{1}H\}$ NMR spectrum with 20 equiv. of added Me_2N-*i*-Pr in pentane; (E) ^{6}Li NMR spectrum with 20 equiv. of added Me_2N-*i*-Pr in toluene.



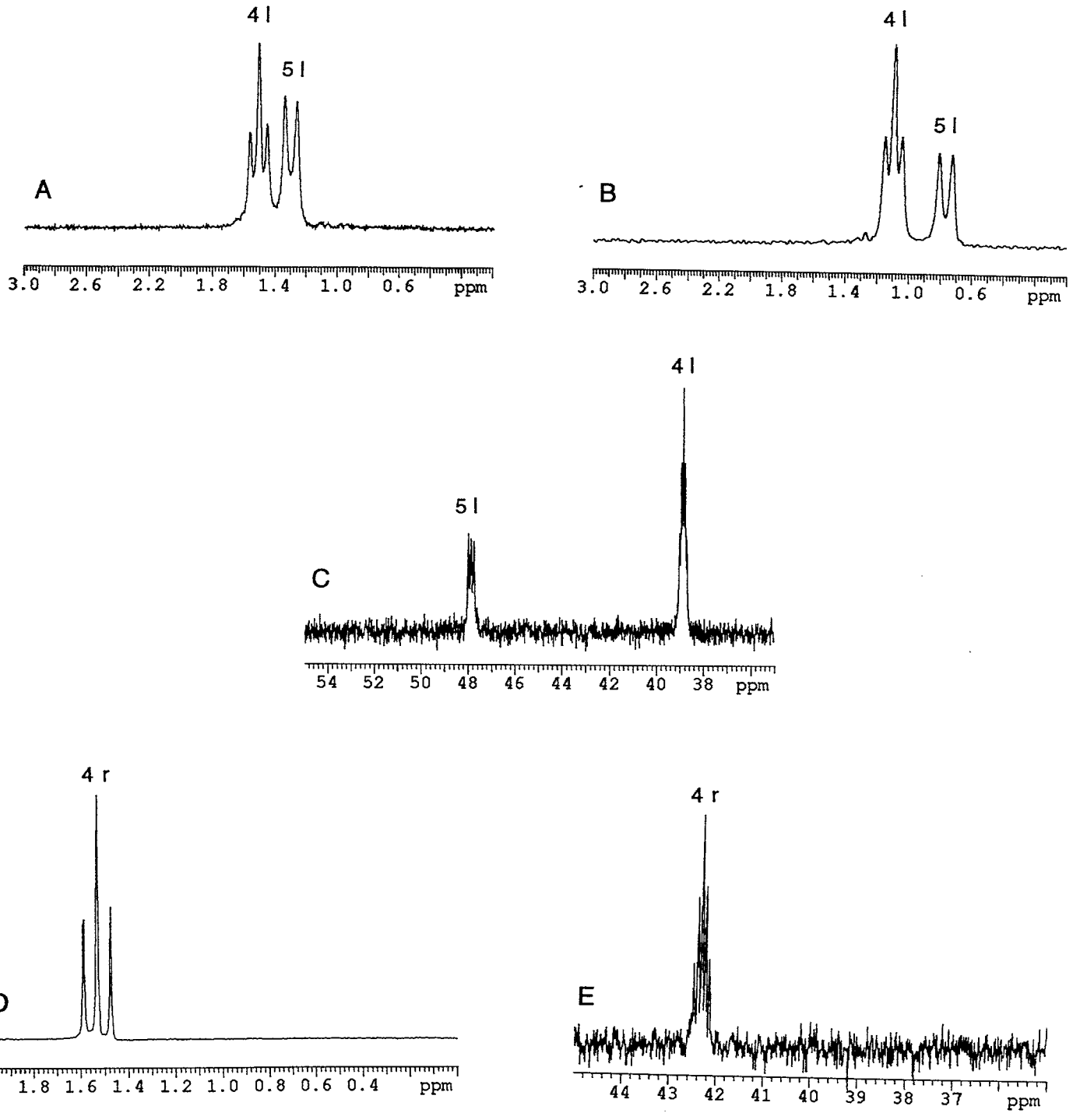
V. ^{6}Li and ^{15}N NMR spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS at -80 °C: (A) ^{6}Li NMR spectrum with 20 equiv. of added Me_2N-*t*-Bu in pentane; (B) $^{15}N\{^{1}H\}$ NMR spectrum with 20 equiv. of added Me_2N-*t*-Bu in pentane; (C) ^{6}Li NMR spectrum with 20 equiv. of added Me_2NCH_2-*i*-Pr in pentane; (D) $^{15}N\{^{1}H\}$ NMR spectrum with 20 equiv. of added Me_2NCH_2-*i*-Pr in pentane; (E) ^{6}Li NMR spectrum with 20 equiv. of added Me_2NCH_2-*t*-Bu in pentane; (F) $^{15}N\{^{1}H\}$ NMR spectrum with 20 equiv. of added Me_2NCH_2-*t*-Bu in pentane.

J2225-6



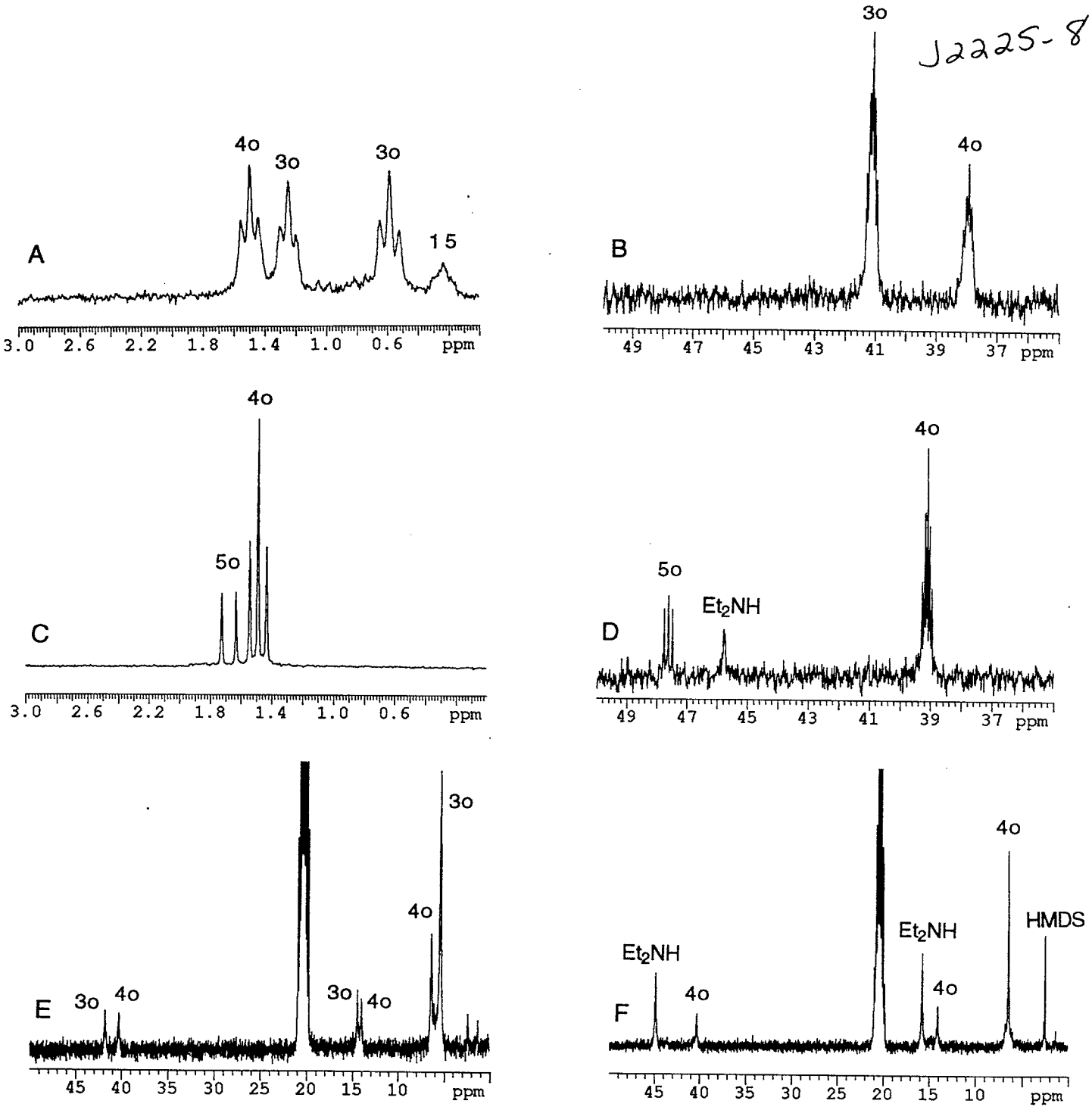
VI. ^{6}Li NMR spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS at -80 °C: (A) ^{6}Li NMR spectrum with 20 equiv. of added Me_2NCH_2Ph in pentane; (B) ^{6}Li NMR spectrum with 20 equiv. of added Me_2NCH_2Ph in toluene; (C) ^{6}Li NMR spectrum with 20 equiv. of added $Me_2N(CH_2)_3Ph$ in pentane; (D) ^{6}Li NMR spectrum with 20 equiv. of added $Me_2N(CH_2)_4Ph$ in pentane; (E) ^{6}Li NMR spectrum with 20 equiv. of added $Me_2N(CH_2)_4Ph$ in toluene.

J2225-7



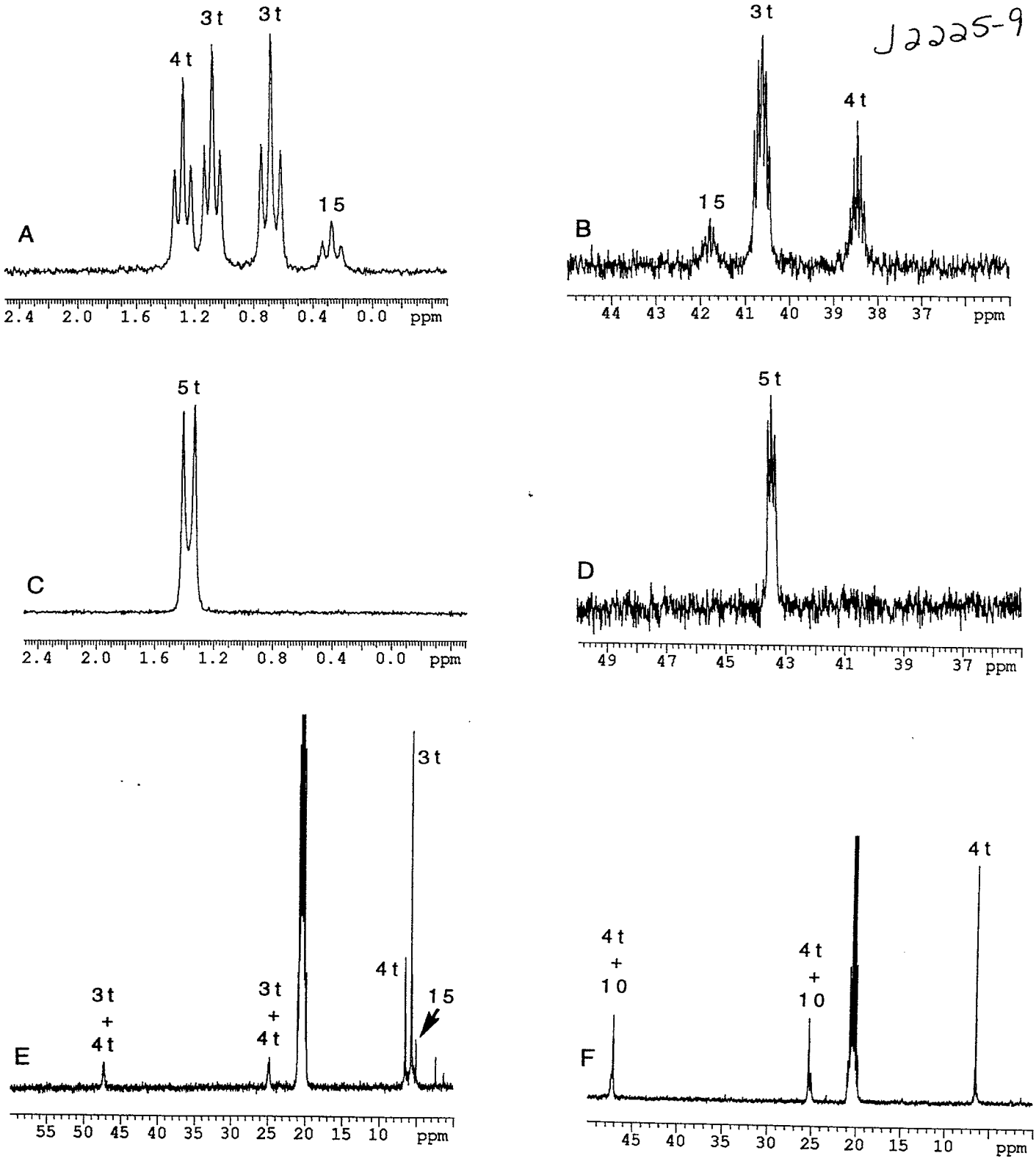
VII. ^{6}Li and ^{15}N NMR spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS at -80 °C: (A) ^{6}Li NMR spectrum with 20 equiv. of added $Me_2N(CH_2)_2Ph$ in pentane; (B) ^{6}Li NMR spectrum with 20 equiv. of added $Me_2N(CH_2)_2Ph$ in toluene; (C) $^{15}N\{^{1}H\}$ NMR spectrum with 20 equiv. of added $Me_2N(CH_2)_2Ph$ in pentane; (D) ^{6}Li NMR spectrum with 10 equiv. of added $(i\text{-}Pr)_2NH$ in pentane; (E) $^{15}N\{^{1}H\}$ NMR spectrum with 10 equiv. of added $(i\text{-}Pr)_2NH$ in pentane.

J2225-8



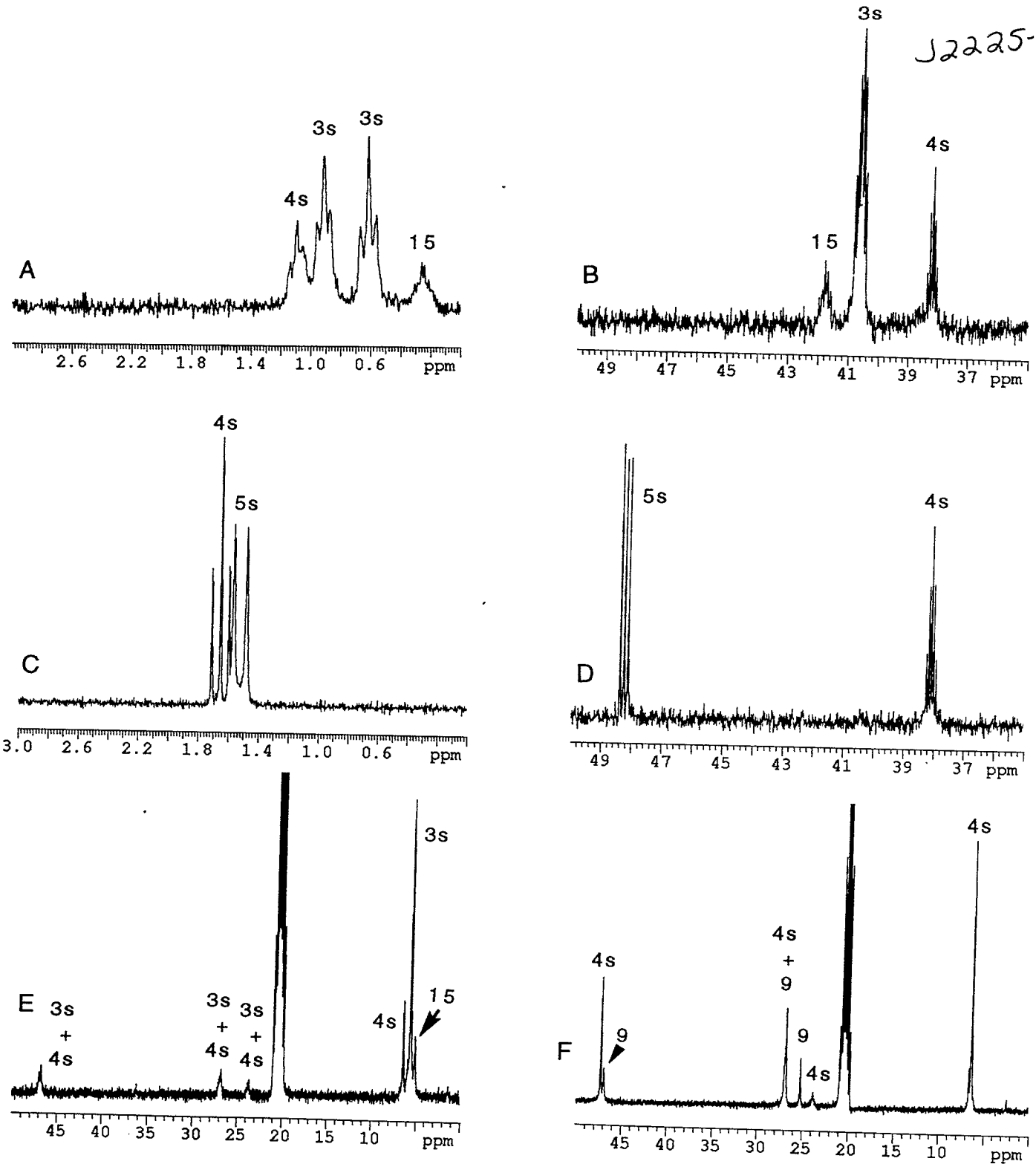
VIII. ^{6}Li, ^{15}N, and ^{13}C NMR spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS with added Et_2NH at -100 °C: (A) ^{6}Li NMR spectrum with 0.5 equiv. of added Et_2NH in toluene-d_8; (B) $^{15}N\{^{1}H\}$ NMR spectrum with 0.5 equiv. of added Et_2NH in toluene-d_8; (C) ^{6}Li NMR spectrum with 10 equiv. of added Et_2NH in pentane; (D) $^{15}N\{^{1}H\}$ NMR spectrum with 10 equiv. of added Et_2NH in pentane; (E) $^{13}C\{^{1}H\}$ NMR spectrum with 0.5 equiv. of added Et_2NH in toluene-d_8; (F) $^{13}C\{^{1}H\}$ NMR spectrum with 2.0 equiv. of added Et_2NH in toluene-d_8.

J2225-9



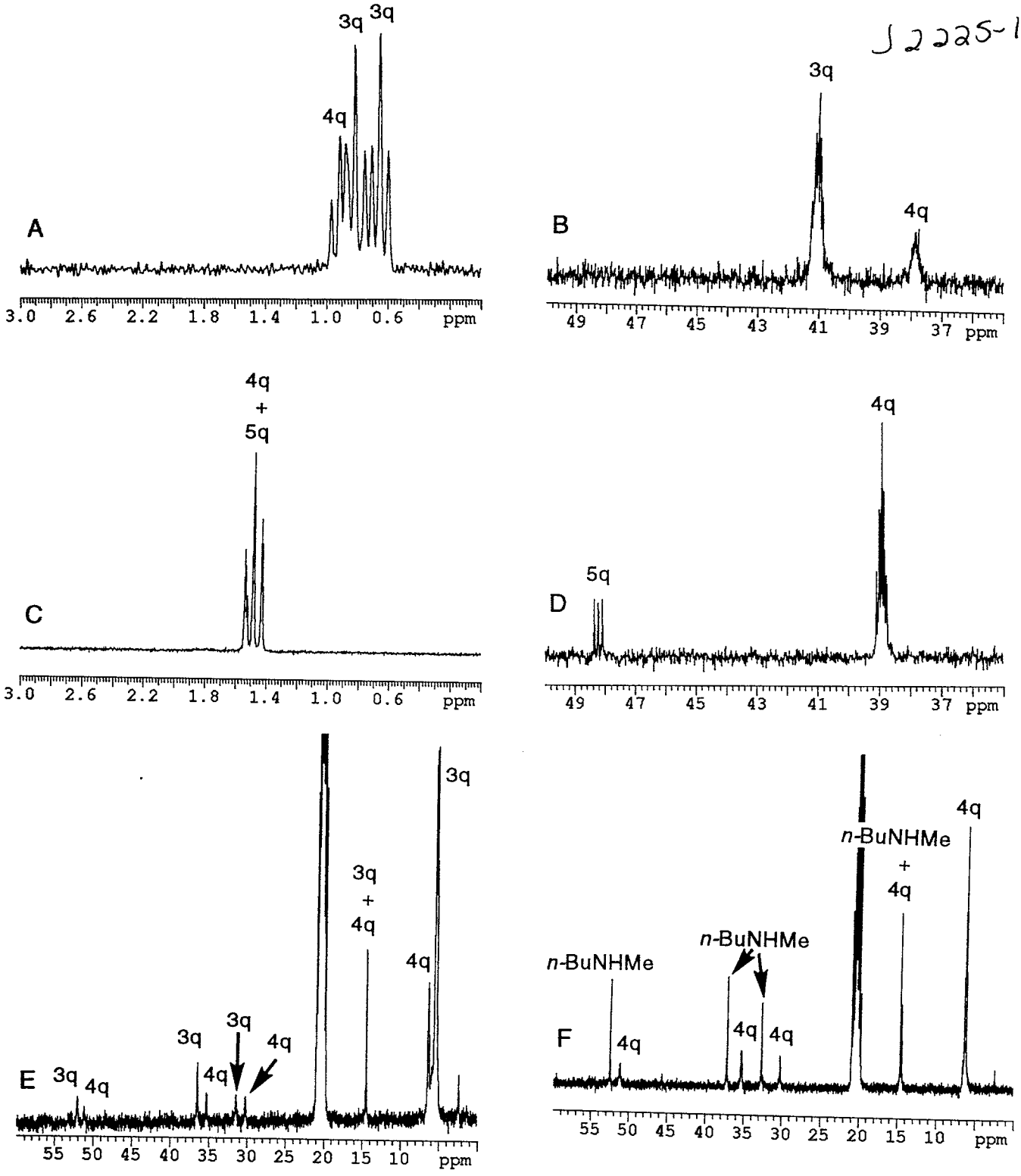
IX. ^{6}Li, ^{15}N, and ^{13}C NMR spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS with added pyrrolidine at -100 °C: (A) ^{6}Li NMR spectrum with 0.5 equiv. of added pyrrolidine in toluene-d_8; (B) $^{15}N\{^{1}H\}$ NMR spectrum with 0.5 equiv. of added pyrrolidine in toluene-d_8; (C) ^{6}Li NMR spectrum with 10 equiv. of added pyrrolidine in pentane; (D) $^{15}N\{^{1}H\}$ NMR spectrum with 10 equiv. of added pyrrolidine in pentane; (E) $^{13}C\{^{1}H\}$ NMR spectrum with 0.5 equiv. of added pyrrolidine in toluene-d_8; (F) $^{13}C\{^{1}H\}$ NMR spectrum with 2.0 equiv. of added pyrrolidine in toluene-d_8.

J2225-10

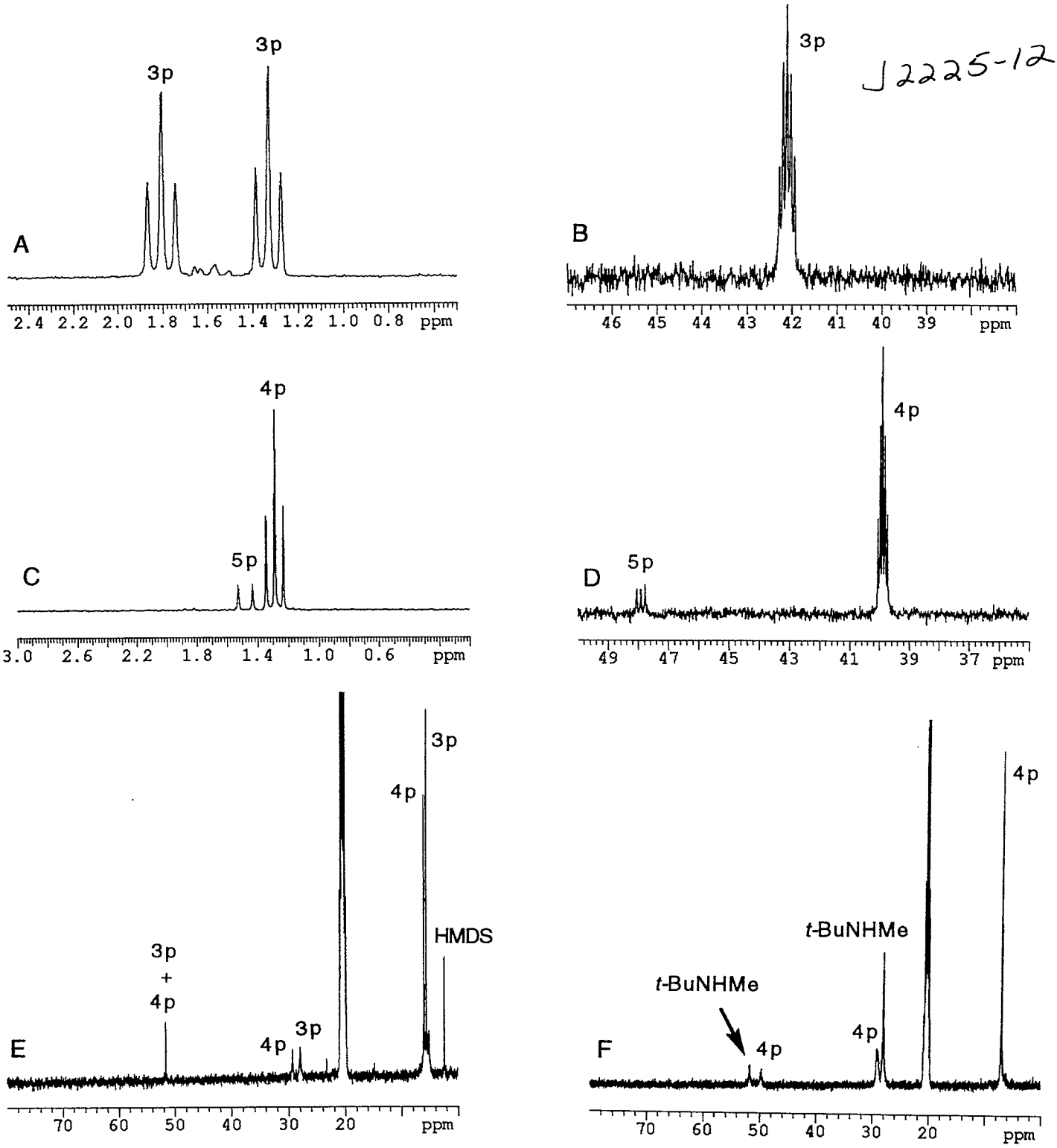


X. ^{6}Li, ^{15}N, and ^{13}C NMR spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS with added piperidine at -100 °C: (A) ^{6}Li NMR spectrum with 0.5 equiv. of added piperidine in toluene-d_8; (B) $^{15}N\{^{1}H\}$ NMR spectrum with 0.5 equiv. of added piperidine in toluene-d_8; (C) ^{6}Li NMR spectrum with 10 equiv. of added piperidine in pentane; (D) $^{15}N\{^{1}H\}$ NMR spectrum with 10 equiv. of added piperidine in pentane; (E) $^{13}C\{^{1}H\}$ NMR spectrum with 0.5 equiv. of added piperidine in toluene-d_8; (F) $^{13}C\{^{1}H\}$ NMR spectrum with 2.0 equiv. of added piperidine in toluene-d_8.

J2225-11



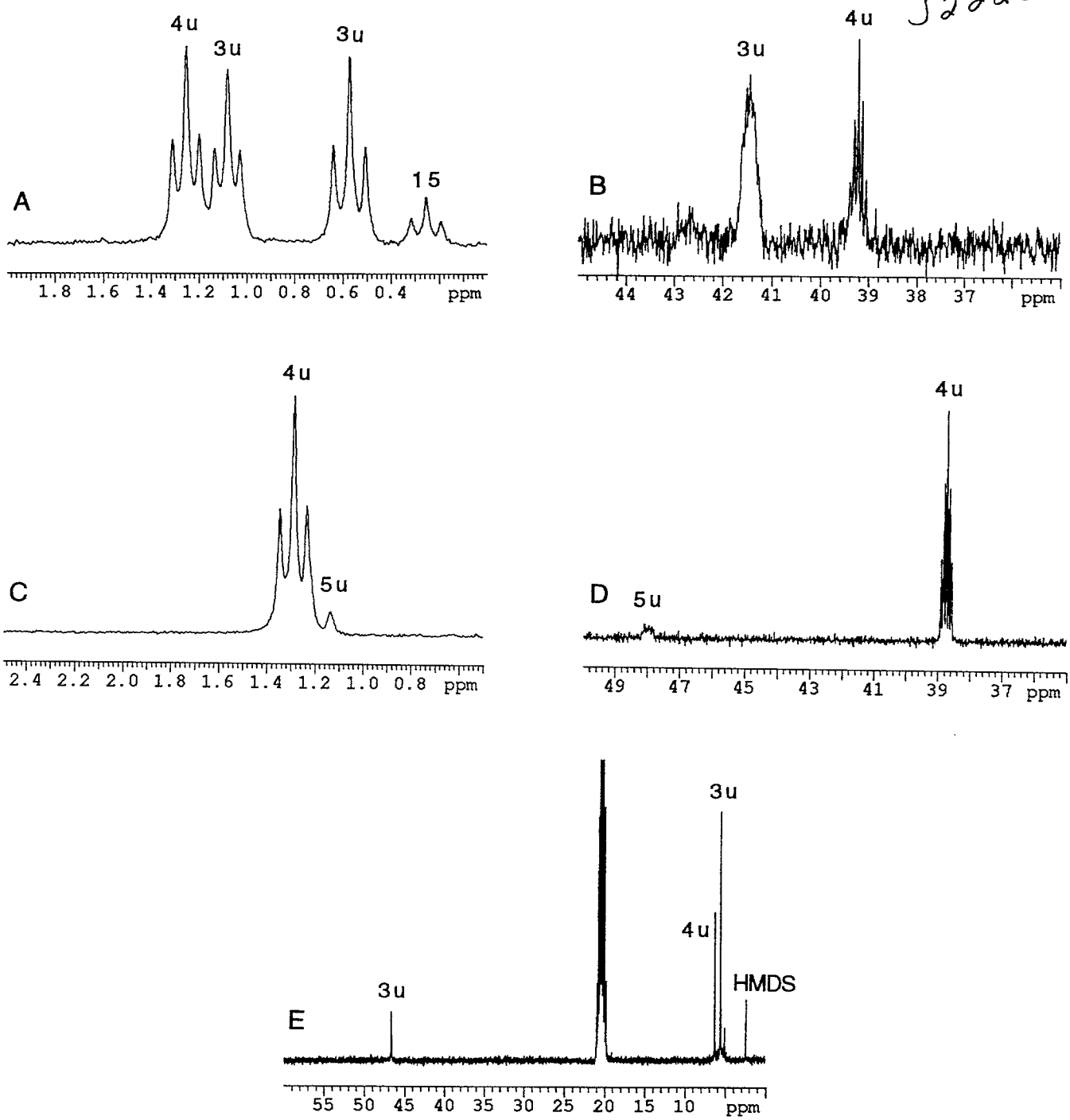
XI. ^{6}Li, ^{15}N, and ^{13}C NMR spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS with added *n*-BuNHMe at -100 °C: (A) ^{6}Li NMR spectrum with 0.5 equiv. of added *n*-BuNHMe in toluene-d_8; (B) $^{15}N\{^{1}H\}$ NMR spectrum with 0.5 equiv. of added *n*-BuNHMe in toluene-d_8; (C) ^{6}Li NMR spectrum with 10 equiv. of added *n*-BuNHMe in pentane; (D) $^{15}N\{^{1}H\}$ NMR spectrum with 10 equiv. of added *n*-BuNHMe in pentane; (E) $^{13}C\{^{1}H\}$ NMR spectrum with 0.5 equiv. of added *n*-BuNHMe in toluene-d_8; (F) $^{13}C\{^{1}H\}$ NMR spectrum with 2.0 equiv. of added *n*-BuNHMe in toluene-d_8.



J2225-12

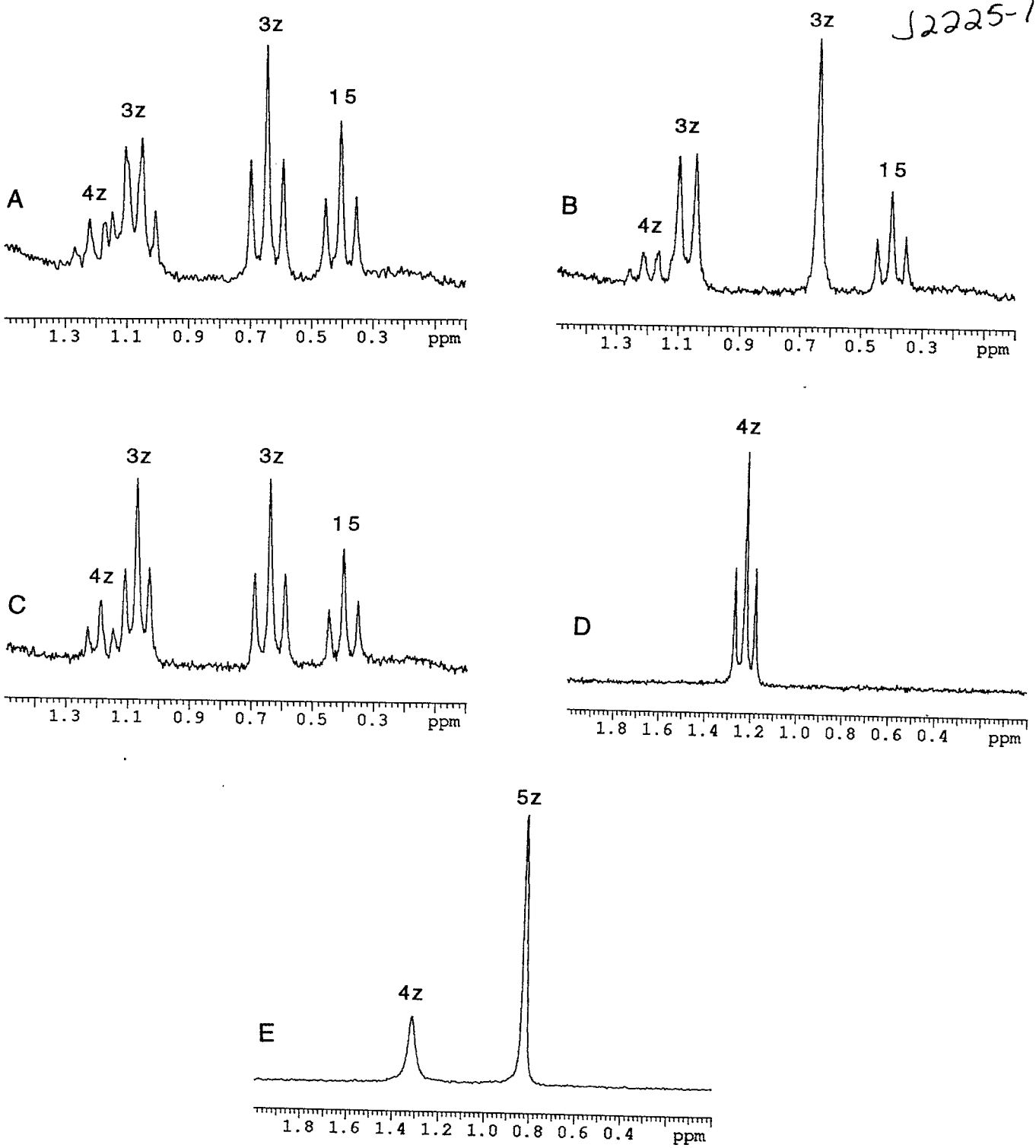
XII. ^{6}Li, ^{15}N, and ^{13}C NMR spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS with added *t*-BuNHMe: (A) ^{6}Li NMR spectrum with 0.5 equiv. of added *t*-BuNHMe in pentane at -115 °C; (B) $^{15}N\{^{1}H\}$ NMR spectrum with 0.5 equiv. of added *t*-BuNHMe in pentane at -115 °C; (C) ^{6}Li NMR spectrum with 10 equiv. of added *t*-BuNHMe in pentane at -100 °C; (D) $^{15}N\{^{1}H\}$ NMR spectrum with 10 equiv. of added *t*-BuNHMe in pentane at -100 °C; (E) $^{13}C\{^{1}H\}$ NMR spectrum with 0.5 equiv. of added *t*-BuNHMe in toluene-d_8 at -100 °C; (F) $^{13}C\{^{1}H\}$ NMR spectrum with 2.0 equiv. of added *t*-BuNHMe in toluene-d_8 at -100 °C.

J2225-13



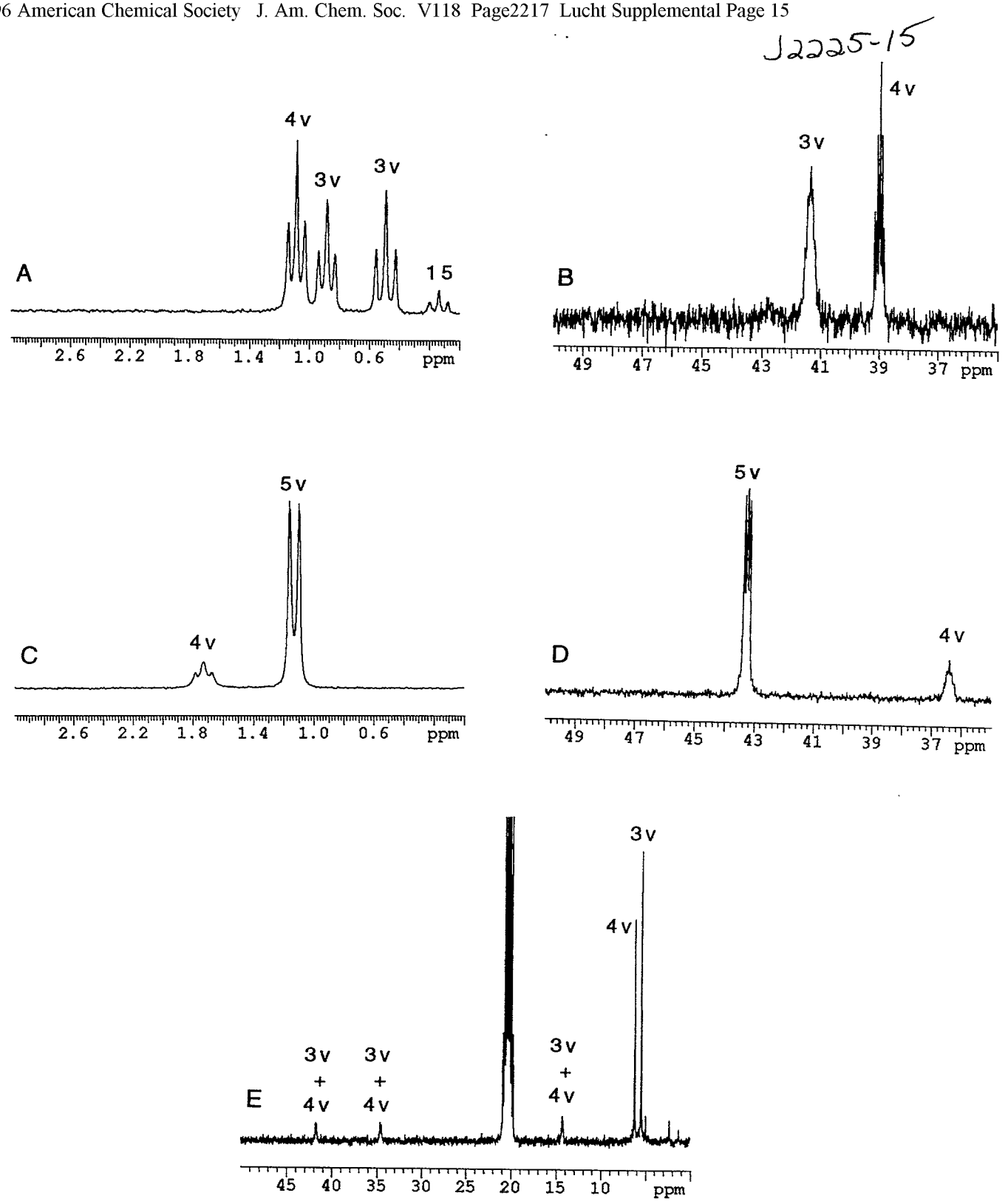
XIII. ^{6}Li, ^{15}N, and ^{13}C NMR spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS with added azetidine at -100 °C: (A) ^{6}Li NMR spectrum with 0.5 equiv. of added azetidine in toluene-d_8; (B) $^{15}N\{^{1}H\}$ NMR spectrum with 0.5 equiv. of added azetidine in toluene-d_8; (C) ^{6}Li NMR spectrum with 2.0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

J2225-14



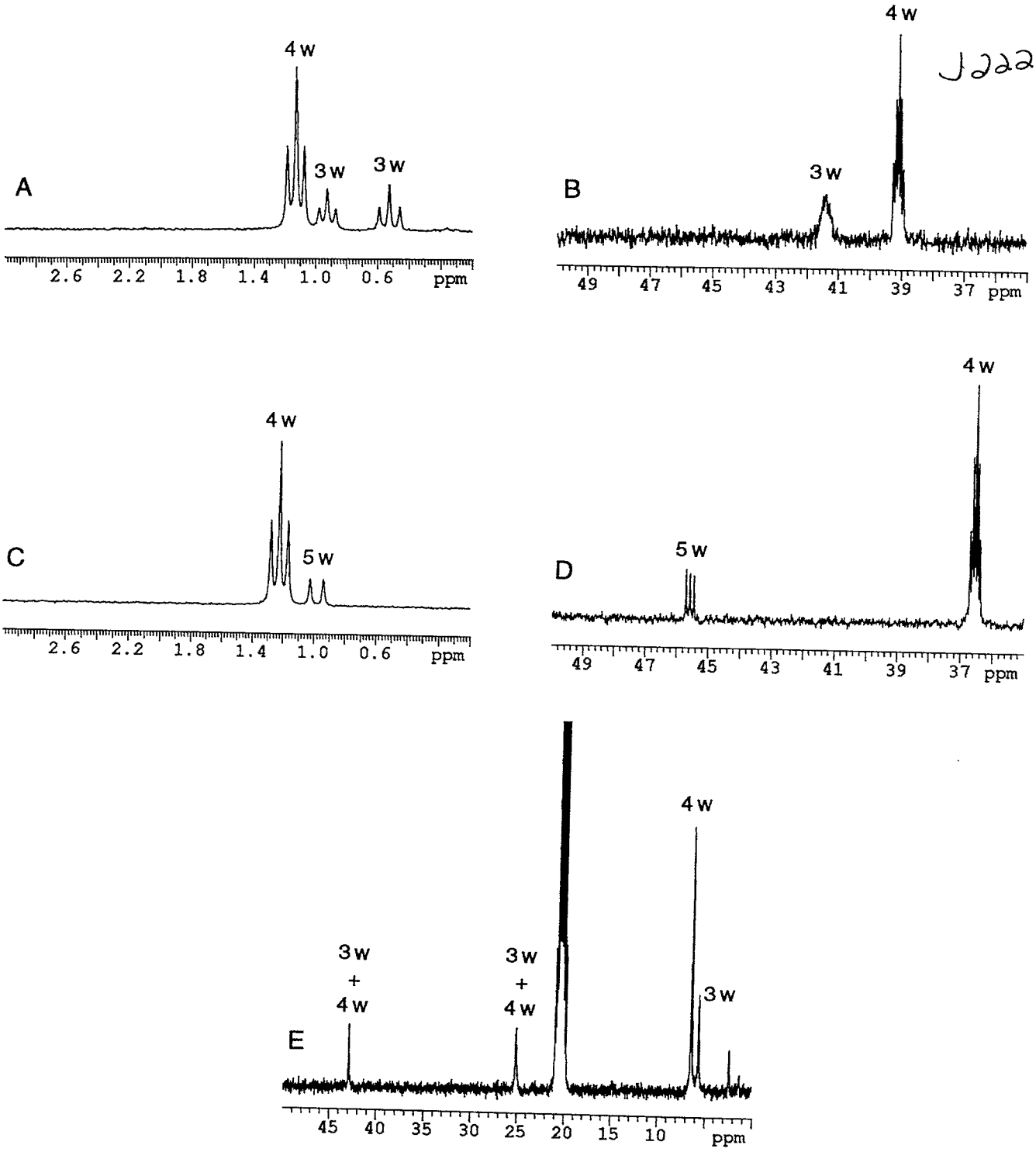
XIV. ^{6}Li NMR spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS with added NH_3 in 2:1 pentane/toluene at -100 °C: (A) ^{6}Li NMR spectrum with 0.5 equiv. of added $^{15}NH_3$; (B) ^{6}Li NMR spectrum with 0.5 equiv. of added $^{15}NH_3$ with single frequency ^{15}N decoupling at 39.9 ppm.(**3z**); (C) ^{6}Li NMR spectrum with 0.5 equiv. of added $^{15}NH_3$ with single frequency ^{15}N decoupling at 18.3 ppm. ($^{15}NH_3$); (D) ^{6}Li NMR spectrum with 1.2 equiv. of added $^{15}NH_3$; (E) ^{6}Li NMR spectrum with 3 equiv. of added NH_3.

J2225-15



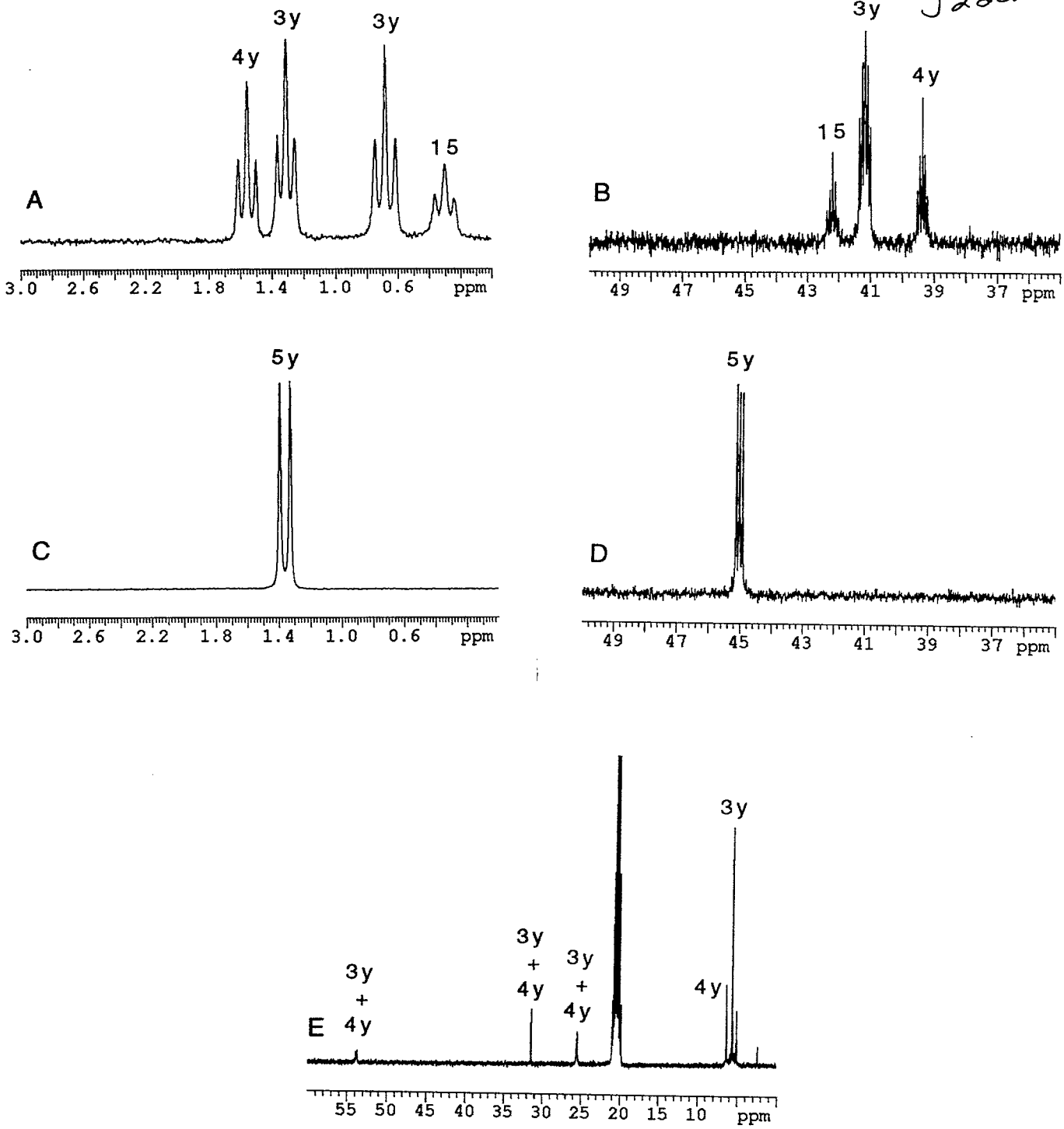
XV. ^{6}Li, ^{15}N, and ^{13}C NMR spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS with added *n*-$BuNH_2$ at -100 °C: (A) ^{6}Li NMR spectrum with 0.5 equiv. of added *n*-$BuNH_2$ in toluene-d_8; (B) $^{15}N\{^{1}H\}$ NMR spectrum with 0.5 equiv. of added *n*-$BuNH_2$ in toluene-d_8; (C) ^{6}Li NMR spectrum with 5.0 equiv. of added *n*-$BuNH_2$ in pentane; (D) $^{15}N\{^{1}H\}$ NMR spectrum with 5.0 equiv. of added *n*-$BuNH_2$ in pentane; (E) $^{13}C\{^{1}H\}$ NMR spectrum with 0.5 equiv. of added *n*-$BuNH_2$ in toluene-d_8.

J2225-16



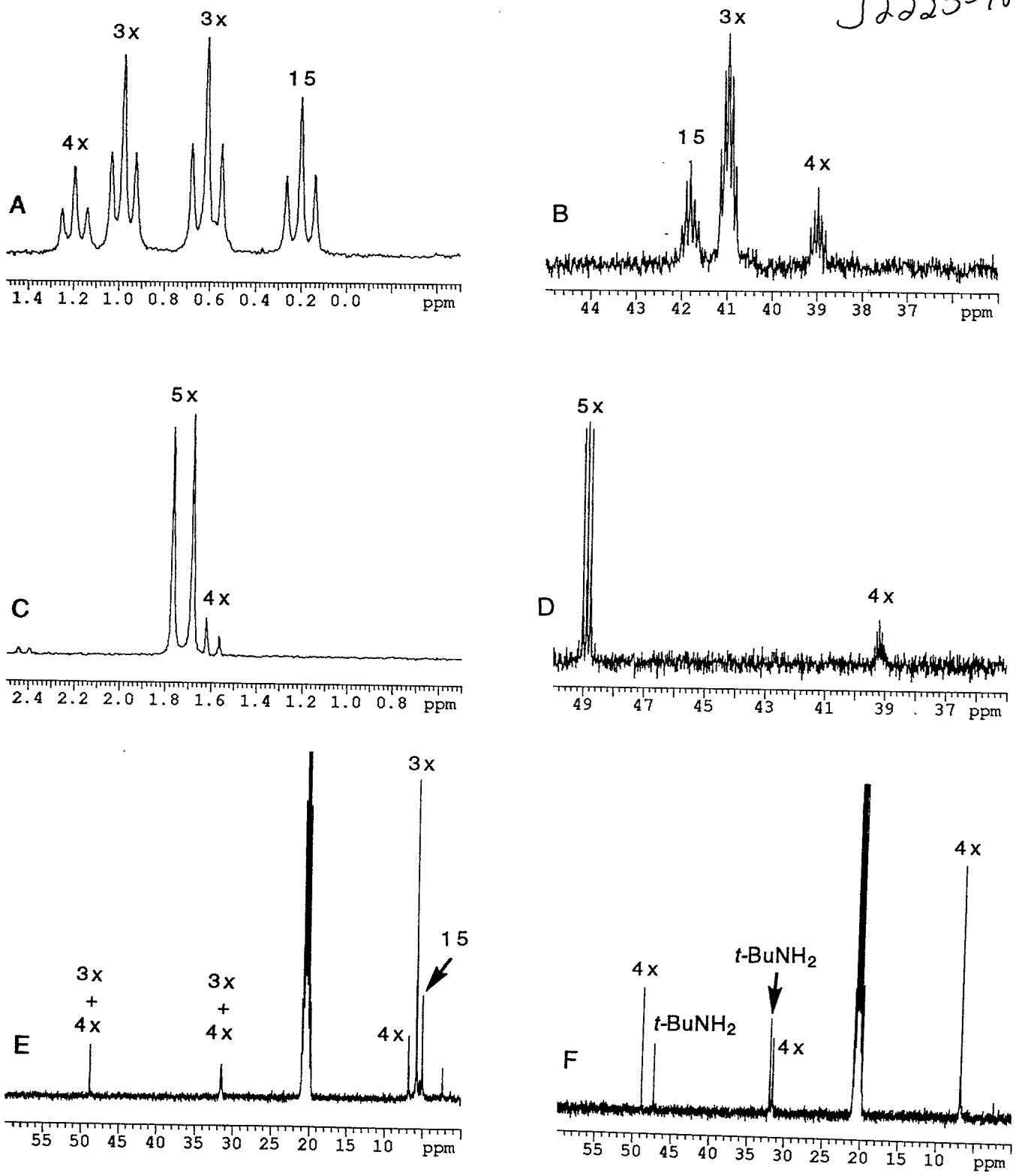
XVI. ^{6}Li, ^{15}N, and ^{13}C NMR spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS with added *i*-$PrNH_2$ at -100 °C: (A) ^{6}Li NMR spectrum with 0.7 equiv. of added *i*-$PrNH_2$ in toluene-d_8; (B) $^{15}N\{^{1}H\}$ NMR spectrum with 0.7 equiv. of added *i*-$PrNH_2$ in toluene-d_8; (C) ^{6}Li NMR spectrum with 5.0 equiv. of added *i*-$PrNH_2$ in toluene-d_8; (D) $^{15}N\{^{1}H\}$ NMR spectrum with 5.0 equiv. of added *i*-$PrNH_2$ in toluene-d_8; (E) $^{13}C\{^{1}H\}$ NMR spectrum with 0.7 equiv. of added *i*-$PrNH_2$ in toluene-d_8.

J2225-17

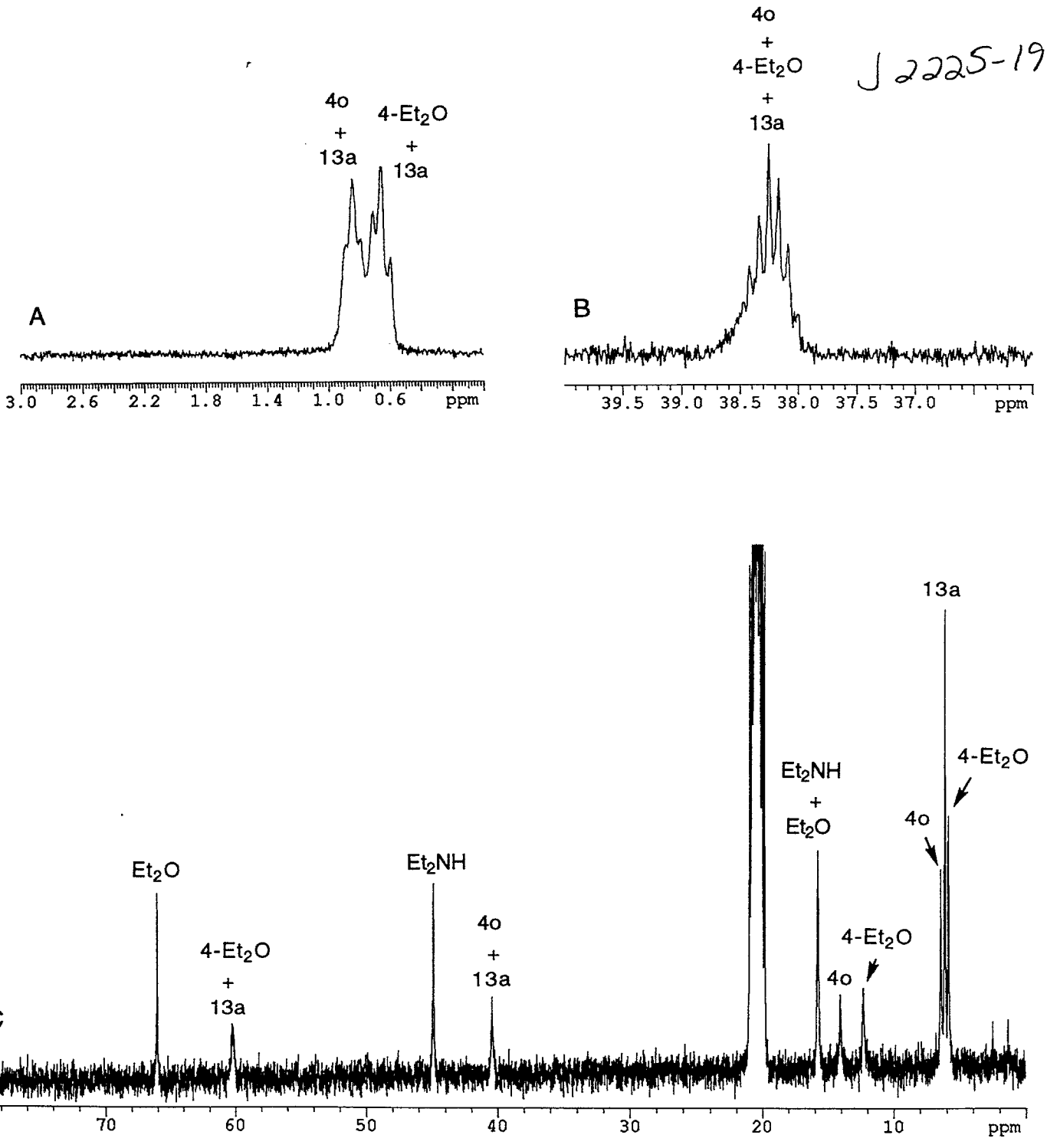


XVII. ^{6}Li, ^{15}N, and ^{13}C NMR spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS with added *t*-$BuCH_2NH_2$ at -100 °C: (A) ^{6}Li NMR spectrum with 0.5 equiv. of added *t*-$BuCH_2NH_2$ in toluene-d_8; (B) $^{15}N\{^{1}H\}$ NMR spectrum with 0.5 equiv. of added *t*-$BuCH_2NH_2$ in toluene-d_8; (C) ^{6}Li NMR spectrum with 10 equiv. of added *t*-$BuCH_2NH_2$ in pentane; (D) $^{15}N\{^{1}H\}$ NMR spectrum with 10 equiv. of added *t*-$BuCH_2NH_2$ pentane; (E) $^{13}C\{^{1}H\}$ NMR spectrum with 0.5 equiv. of added *t*-$BuCH_2NH_2$ in toluene-d_8.

J2225-18

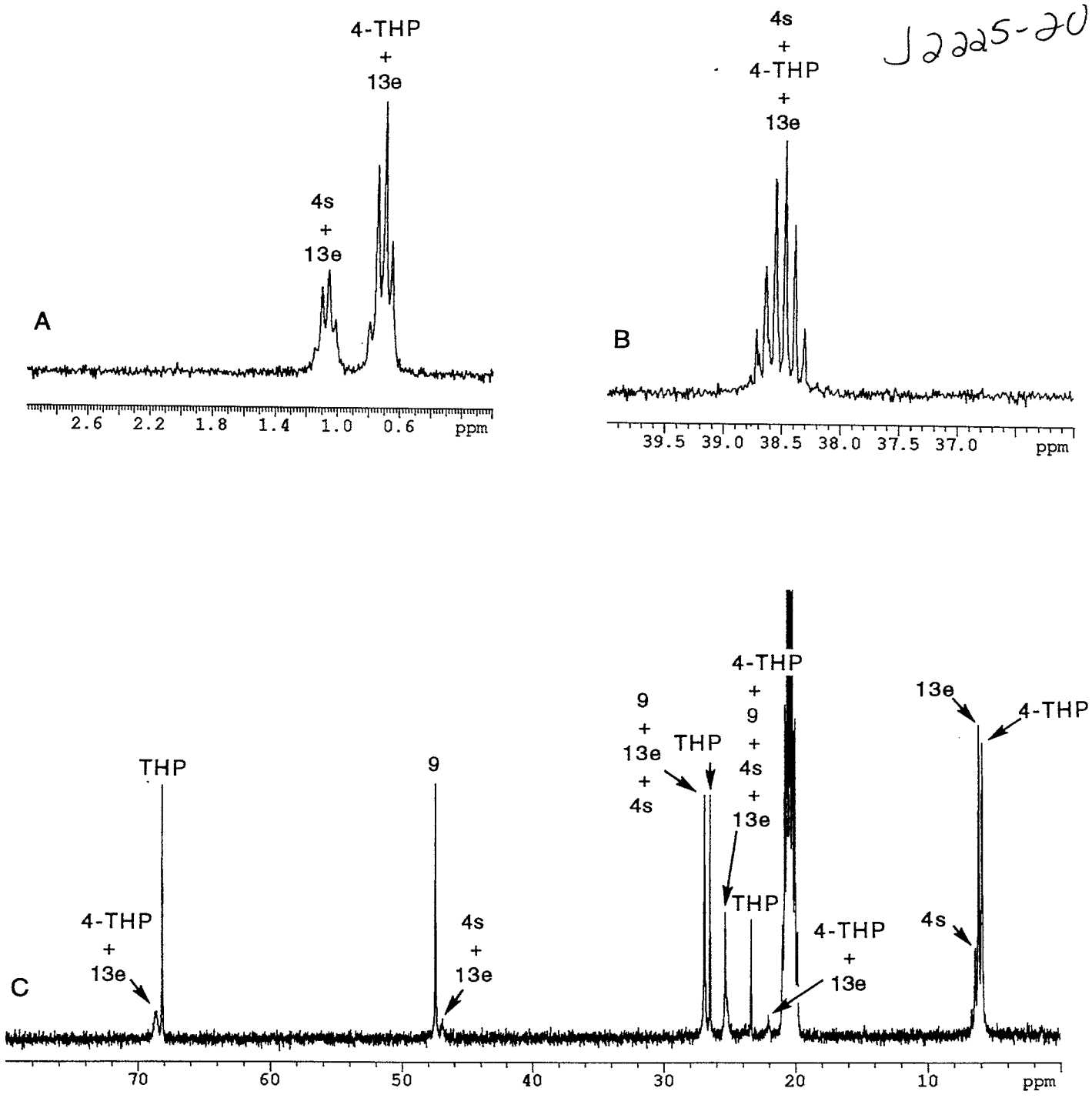


XVIII. ^{6}Li, ^{15}N, and ^{13}C NMR spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS with added *t*-$BuNH_2$ at -100 °C: (A) ^{6}Li NMR spectrum with 0.5 equiv. of added *t*-$BuNH_2$ in toluene-d_8; (B) $^{15}N\{^{1}H\}$ NMR spectrum with 0.5 equiv. of added *t*-$BuNH_2$ in toluene-d_8; (C) ^{6}Li NMR spectrum with 10 equiv. of added *t*-$BuNH_2$ in pentane; (D) $^{15}N\{^{1}H\}$ NMR spectrum with 10 equiv. of added *t*-$BuNH_2$ pentane; (E) $^{13}C\{^{1}H\}$ NMR spectrum with 0.5 equiv. of added *t*-$BuNH_2$ in toluene-d_8; (F) $^{13}C\{^{1}H\}$ NMR spectrum with 2.0 equiv. of added *t*-$BuNH_2$ in toluene-d_8.

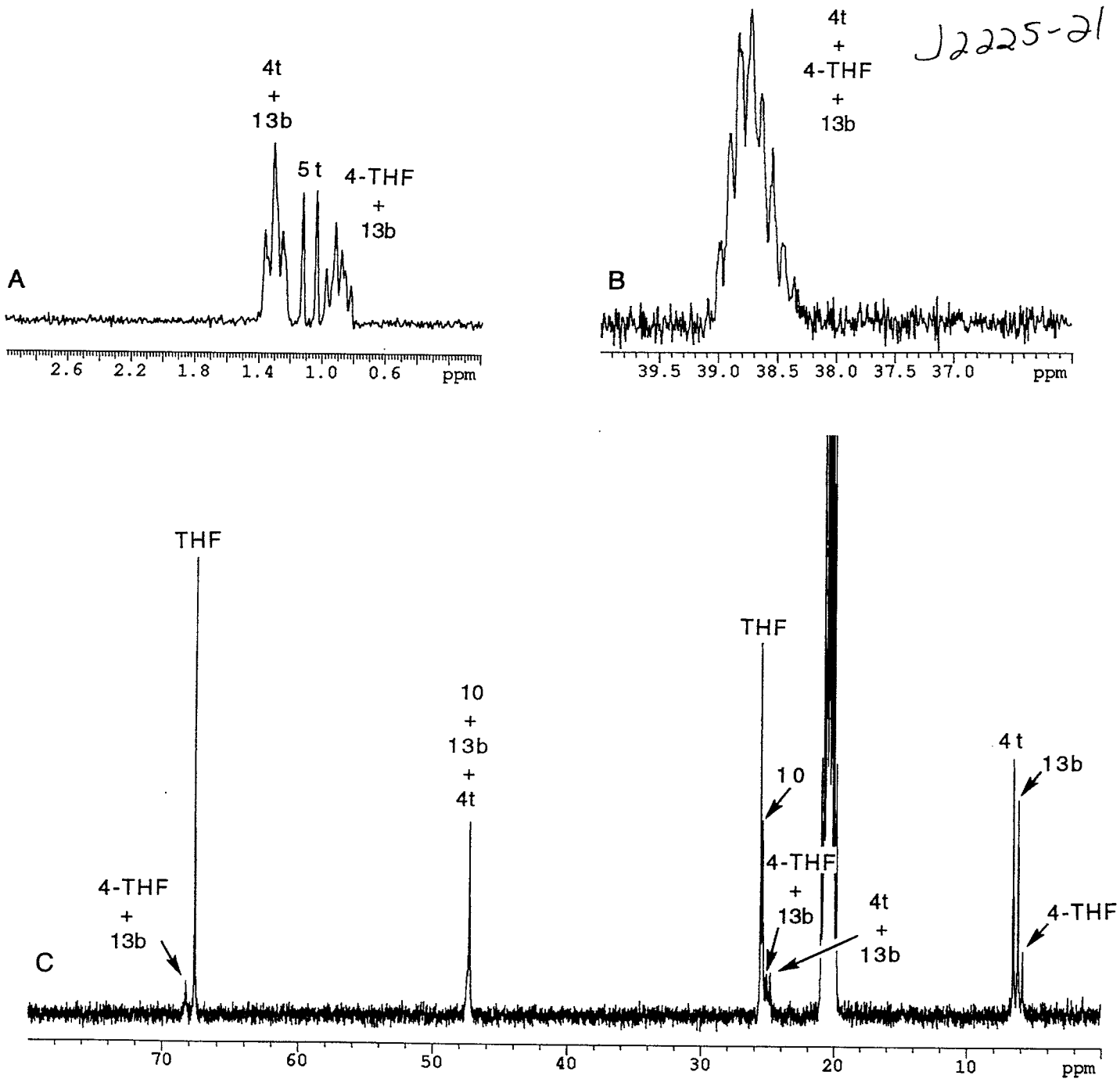


XIX. ^{6}Li, ^{15}N, and ^{13}C NMR spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS with 1.1 equiv. of added Et_2NH and 1.1 equiv. of added Et_2O at -100 °C in toluene-d_8: (A) ^{6}Li NMR spectrum; (B) $^{15}N\{^{1}H\}$ NMR spectrum; (C) $^{13}C\{^{1}H\}$ NMR spectrum.

J2225-20

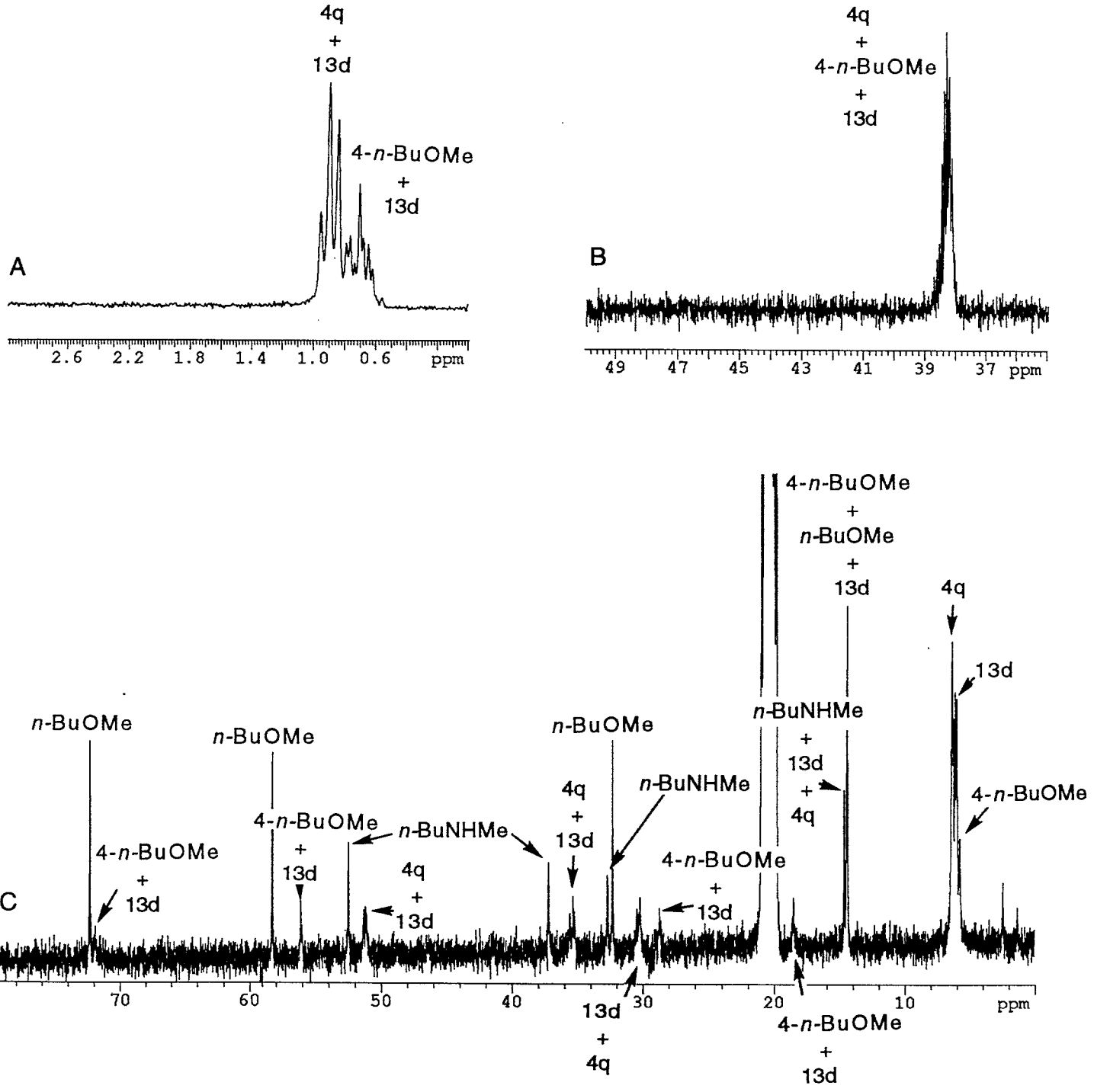


XX. ^{6}Li, ^{15}N, and ^{13}C NMR spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS with 1.1 equiv. of added tetrahydropyran and 1.1 equiv. of added piperidine at -100 °C in toluene-d_8: (A) ^{6}Li NMR spectrum; (B) $^{15}N\{^{1}H\}$ NMR spectrum; (C) $^{13}C\{^{1}H\}$ NMR spectrum.



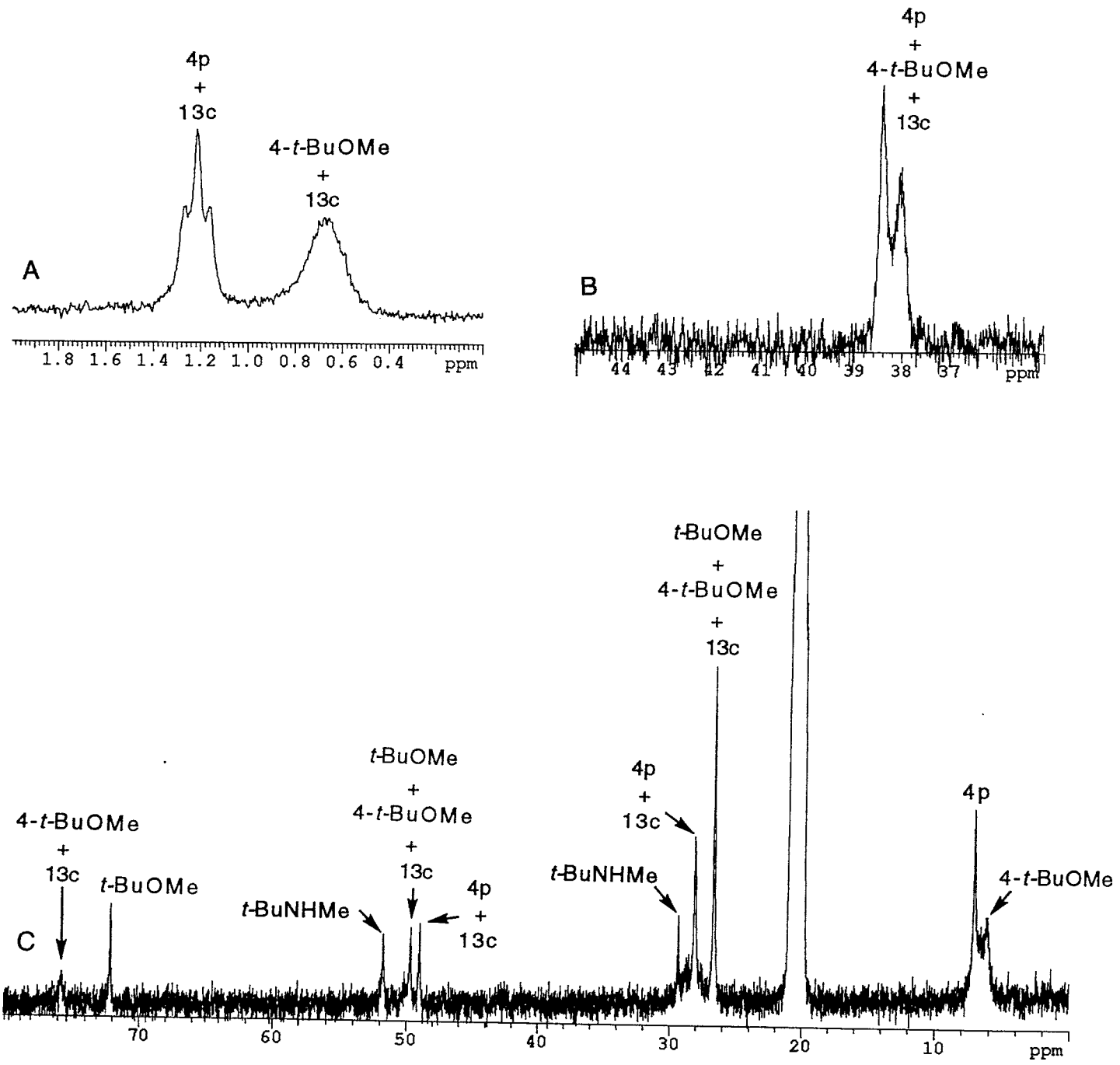
XXI. ^{6}Li, ^{15}N, and ^{13}C NMR spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS with 1.1 equiv. of added tetrahydrofuran and 1.1 equiv. of added pyrrolidine at -100 °C in toluene-d_8: (A) ^{6}Li NMR spectrum; (B) $^{15}N\{^{1}H\}$ NMR spectrum; (C) $^{13}C\{^{1}H\}$ NMR spectrum.

J2225-22



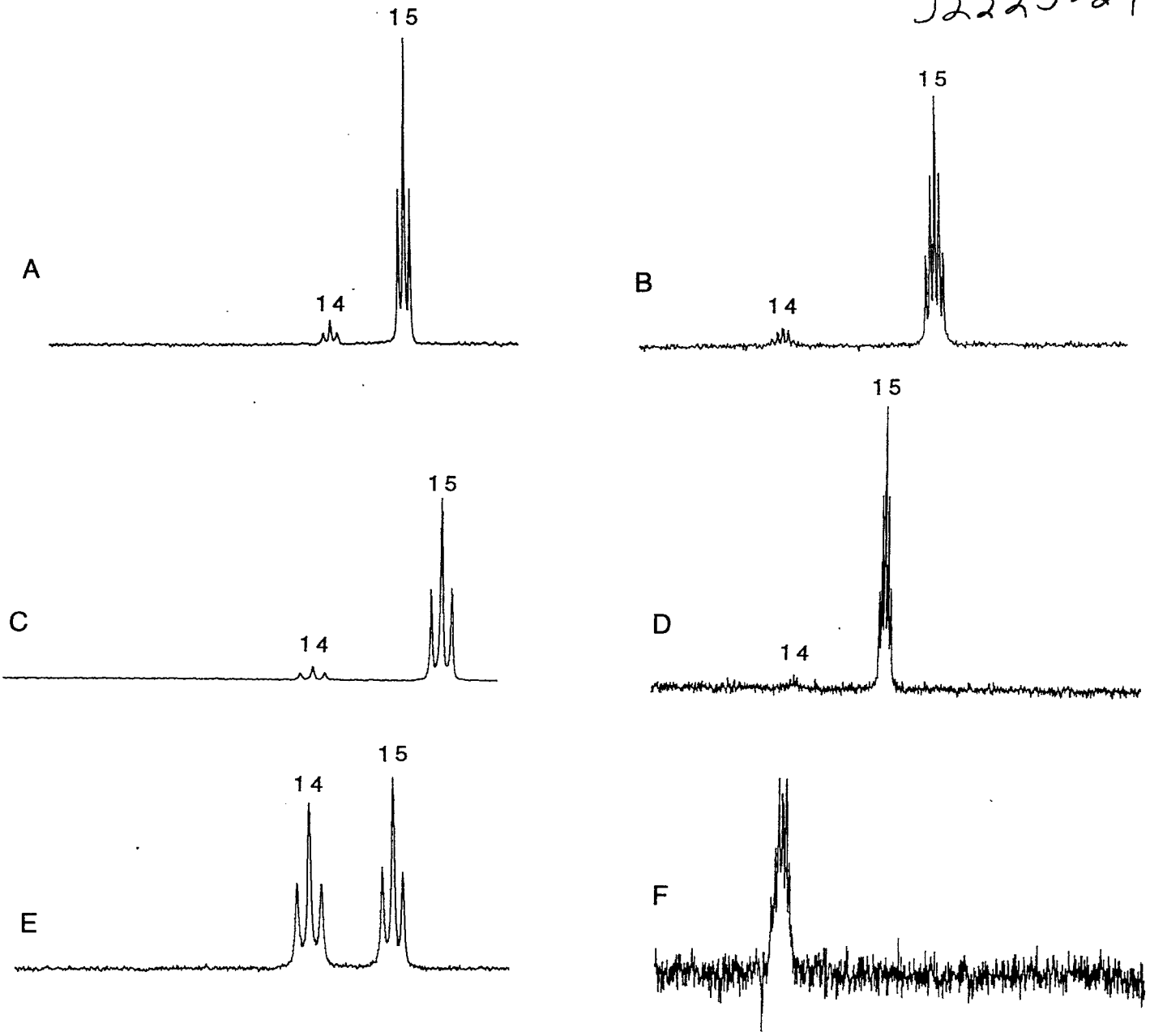
XXII. ^{6}Li, ^{15}N, and ^{13}C NMR spectra of 0.10 M $[^{6}Li,^{15}N]$LiHMDS with 1.1 equiv. of added *n*-BuOMe and 1.1 equiv. of added *n*-BuNHMe at -100 °C in toluene-d_8: (A) ^{6}Li NMR spectrum; (B) $^{15}N\{^{1}H\}$ NMR spectrum; (C) $^{13}C\{^{1}H\}$ NMR spectrum.

J2225-23



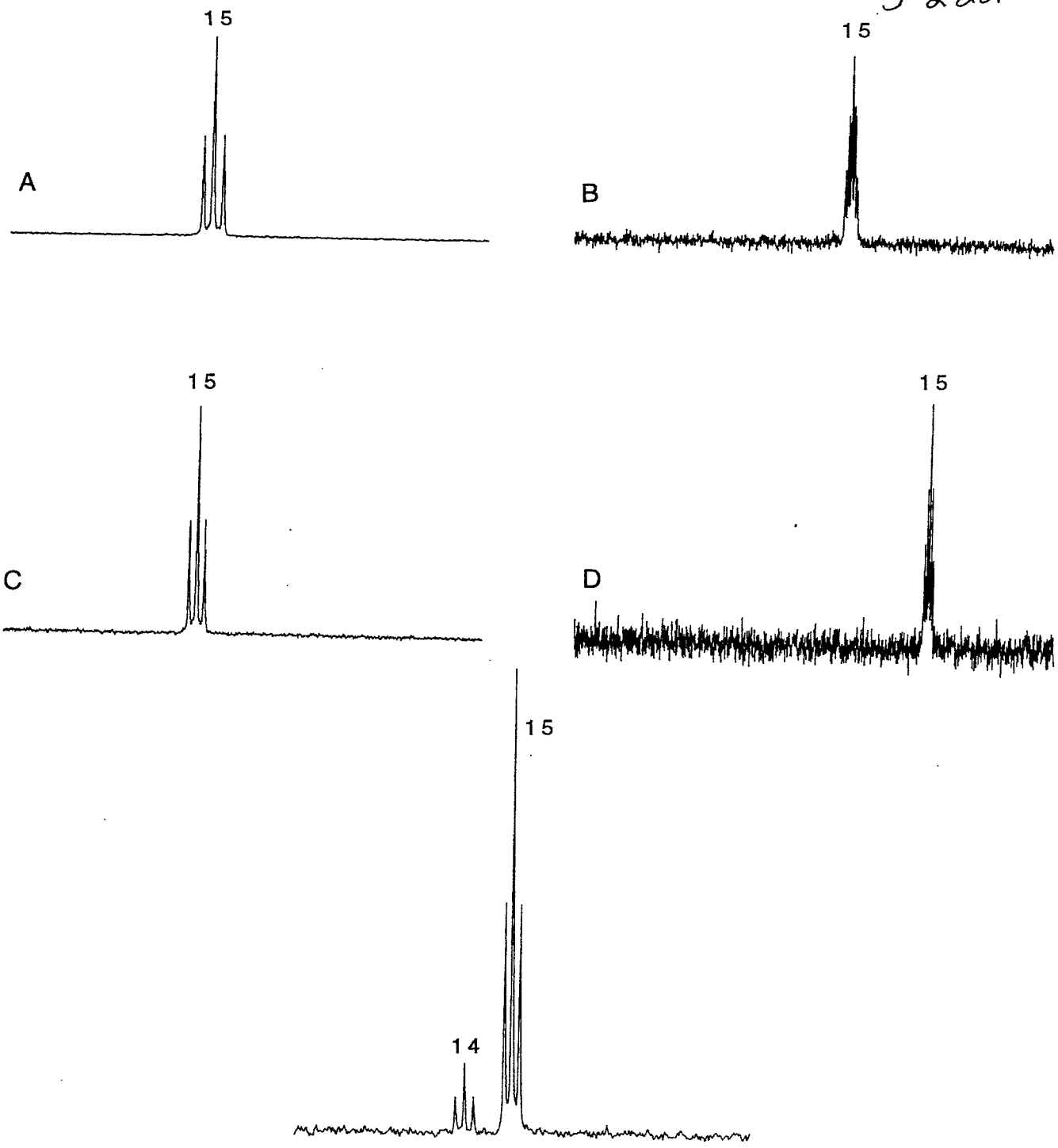
XXIII. ^{6}Li, ^{15}N, and ^{13}C NMR spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS with 1.1 equiv. of added *t*-BuOMe and 1.1 equiv. of added *t*-BuNHMe: (A) ^{6}Li NMR spectrum in pentane at -115 °C; (B) $^{15}N\{^{1}H\}$ NMR spectrum in pentane at -115 °C; (C) $^{13}C\{^{1}H\}$ NMR spectrum in toluene-d_8 at -100 °C.

J2225-24



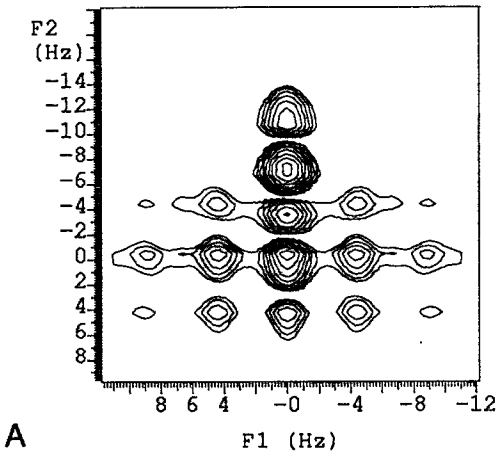
XXIV. ^{6}Li and ^{15}N NMR spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS: (A) ^{6}Li NMR spectrum in neat toluene at -80 °C; (B) $^{15}N\{^{1}H\}$ NMR spectrum in neat toluene at -80 °C; (C) ^{6}Li NMR spectrum in neat *m*-xylene at -60 °C; (D) $^{15}N\{^{1}H\}$ NMR spectrum in neat *m*-xylene at -60 °C; (E) ^{6}Li NMR spectrum in neat mesitylene at -60 °C; (F) $^{15}N\{^{1}H\}$ NMR spectrum in neat mesitylene at -60 °C.

J2225-25

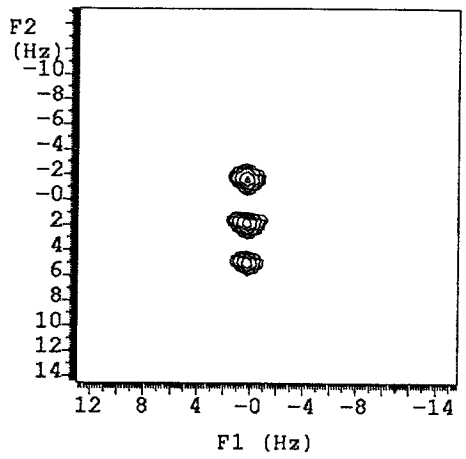


XXV. ^{6}Li and ^{15}N NMR spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS in pentane at -80 °C: (A) ^{6}Li NMR spectrum with 40 equiv. of ethylene; (B) $^{15}N\{^{1}H\}$ NMR spectrum with 40 equiv. of ethylene; (C) ^{6}Li NMR spectrum with 15 equiv. of butyne; (D) $^{15}N\{^{1}H\}$ NMR spectrum with 15 equiv. of butyne; (E) ^{6}Li NMR spectrum with 60 equiv. of 1-pentene.

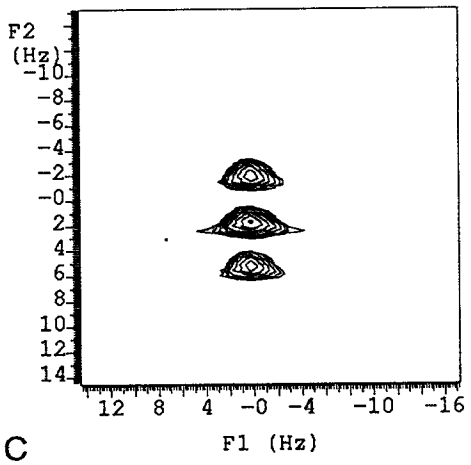
J2225-26



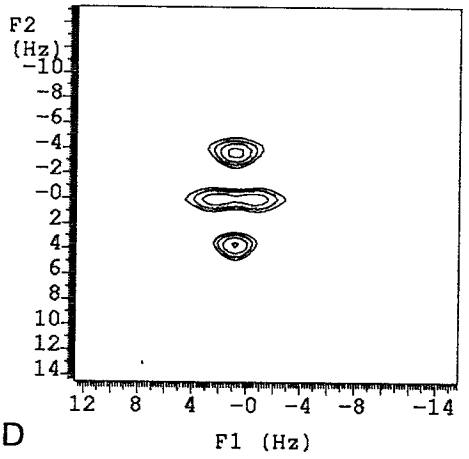
A



B



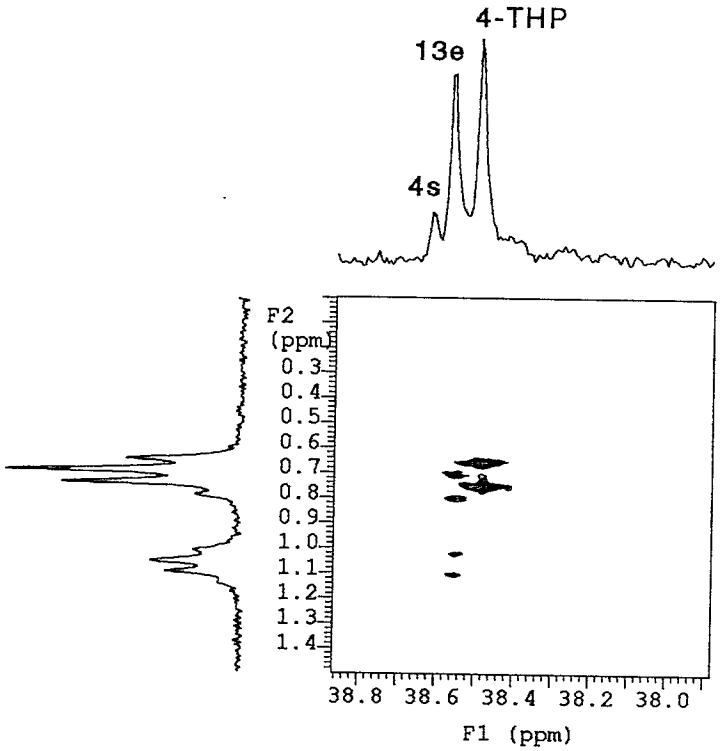
C



D

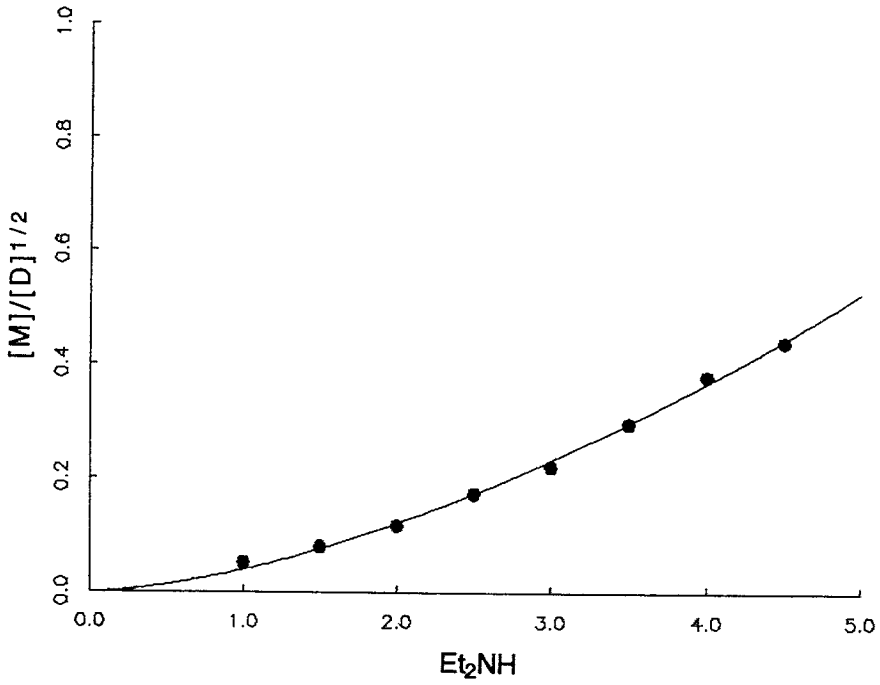
XXVI. ^{6}Li-detected ^{15}N zero-quantum NMR spectra of 0.1 M [^{6}Li,^{15}N]LiHMDS in pentane at -80 °C: (A) neat pentane; (B) 20 equiv. of Et_3N; (C) 15 equiv. of butyne; (D) 40 equiv. of ethylene.

J2225-27



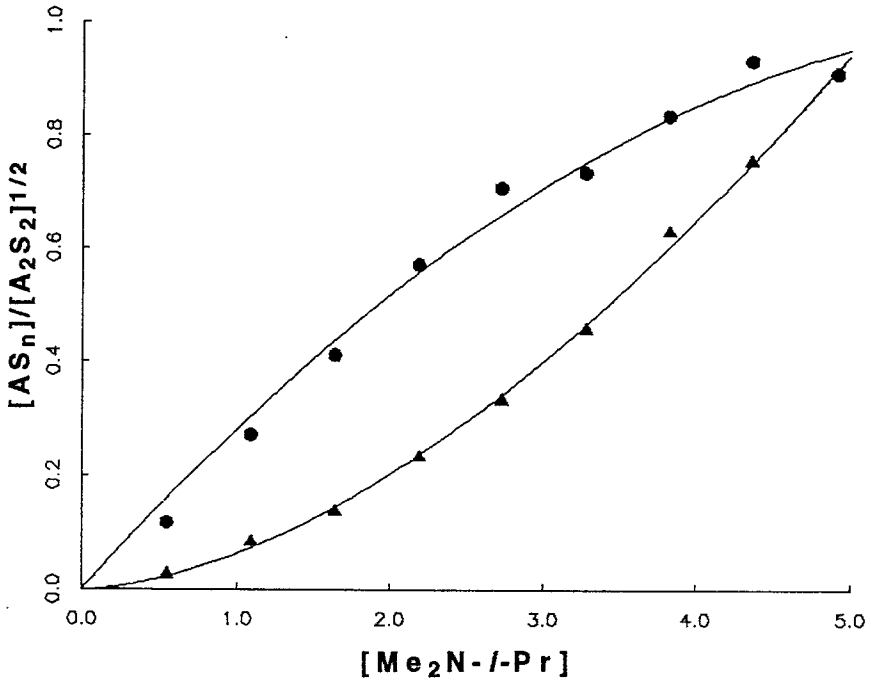
XXVII. ^{6}Li-^{15}N HMQC spectra of 0.10 M [^{6}Li,^{15}N]LiHMDS at -100 °C with 1.1 equiv. of added tetrahydropyran and 1.1 equiv. of added piperidine at -100 °C in toluene-d_8. The upper and left-hand traces are the corresponding $^{15}N\{^{1}H,^{6}Li\}$ and ^{6}Li NMR spectra.

J2225-28



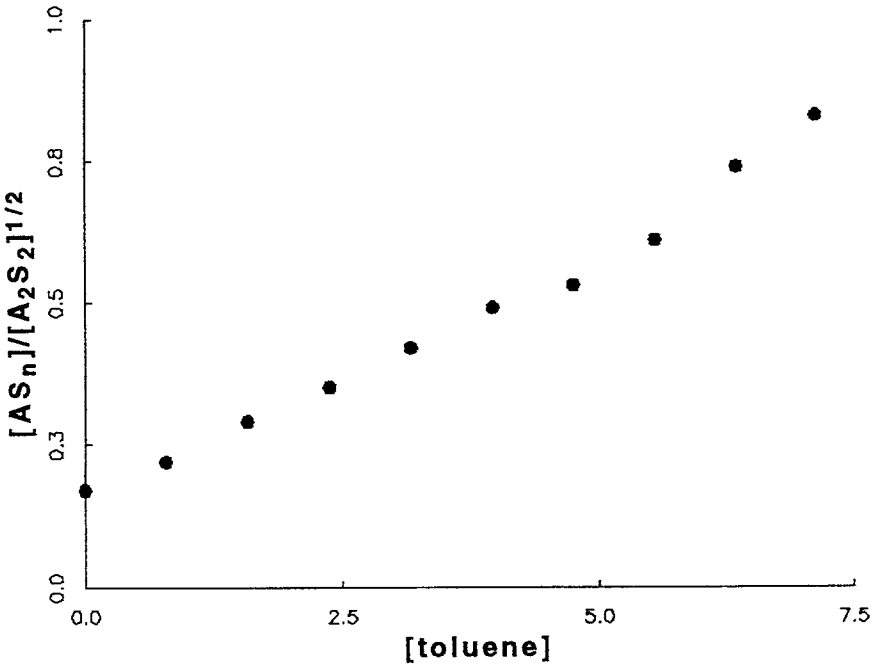
XXVIII. Plot of $[AS_n]/[A_2S_2]^{1/2}$ vs. $[Et_2NH]$ for 0.1 M LiHMDS in pentane at -80 °C. The data are fit by non-linear least squares methods to the function in equation 5 of the manusript. $K_{eq} = 4.0 \times 10^{-2}$, n = 2.6.

J2225-29



XXIX. Plot of $[AS_n]/[A_2S_2]^{1/2}$ vs. $[Me_2N\text{-}i\text{-}Pr]$ for 0.1 M LiHMDS at -80 °C in pentane (▲) and $[AS_n]/[A_2S_2]^{1/2}$ vs. $[Me_2N\text{-}i\text{-}Pr]$ in toluene (●). All samples contain 33% pentane by volume. The data are fit by non-linear least squares methods to the function in equation 5 (K_{eq} = 6.3 x10^{-2}, n = 2.7) or to the function in equation 8 ($K_{eq(1)}$ = 2.3 x10^{-3}, $K_{eq(2)}$ = 6.8 x 10^{-1}) of the manuscript.

J2225-30



XXX. Plot of $[AS_n]/[A_2S_2]^{1/2}$ vs. [toluene] for 0.1 M LiHMDS at -80 °C with 33% Me_2N-*i*-Pr by volume and a pentane cosolvent.

J2225-31

XXXI. **Derivation of equation 8 and equations for Least-Squares Figure 4.**

Given the equilibria

$$1/2\,A_2S_2 + 2S + T \overset{K_1}{\rightleftharpoons} AS_2T + S \overset{K_2}{\rightleftharpoons} AS_3 + T$$

such that

$$K_1 = \frac{[AS_2T]}{[A_2S_2]^{1/2}[S][T]} \qquad (1)$$

and

$$K_2 = \frac{[AS_3][T]}{[AS_2T][S]} \qquad (2)$$

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

$$[A_T] = [AS_2T] + [AS_3]$$

Substituting into equation 2 and rearranging affords

$$[AS_2T] = \frac{[A_T][T]}{(K_2)[S] + [T]}$$

Squaring equation 1, substituting for $[AS_2T]$, and rearranging affords

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

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

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

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

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