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Lithium 2,2,6,6-Tetramethylpiperidide (LiTMP) and Lithium 2,2,4,6,6-Pentamethylpiperidide (LiPMP): Influence of TMEDA and Related Chelating Ligands on the Solution Structures. Characterization of Higher Cyclic Oligomers, Cyclic Dimers, Open Dimers, and Monomers.

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- Figure I. NMR spectra of samples containing 0.10 M LiPMP and TMEDA (**A**).
- Figure II. NMR spectra of samples containing 0.10 M LiPMP and TEEDA (**B**).
- Figure III. NMR spectra of samples containing 0.10 M LiPMP and Et(Me)NCH₂CH₂N(Me)Et (**C**).
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- Figure XVII. NMR spectra of samples containing 0.10 M LiPMP with THF and either TMEDA

(A), TMEDA (P), or dipyrrolidinoethane (F).

Figure XVIII. NMR spectra of samples containing 0.10 M LiPMP with THF and either Et(Me)CH₂CH₂NMe₂ (E), Me₂NCH₂CH₂N(CH₂)₄ (H), or Et₂CH₂CH₂NMe₂ (D).

Figure XIX. NMR spectra of samples containing 0.10 M LiPMP with THF and either *trans*-2-(dimethylamino)methoxycyclohexane (Q), MeOCH₂CH₂N(CH₂)₄ (L), MeOCH₂CH₂N(CH₂)₅ (M), or EtOCH₂CH₂N(CH₂)₄ (N).

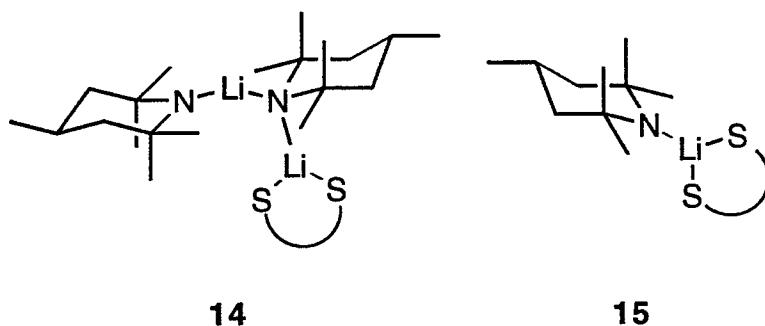
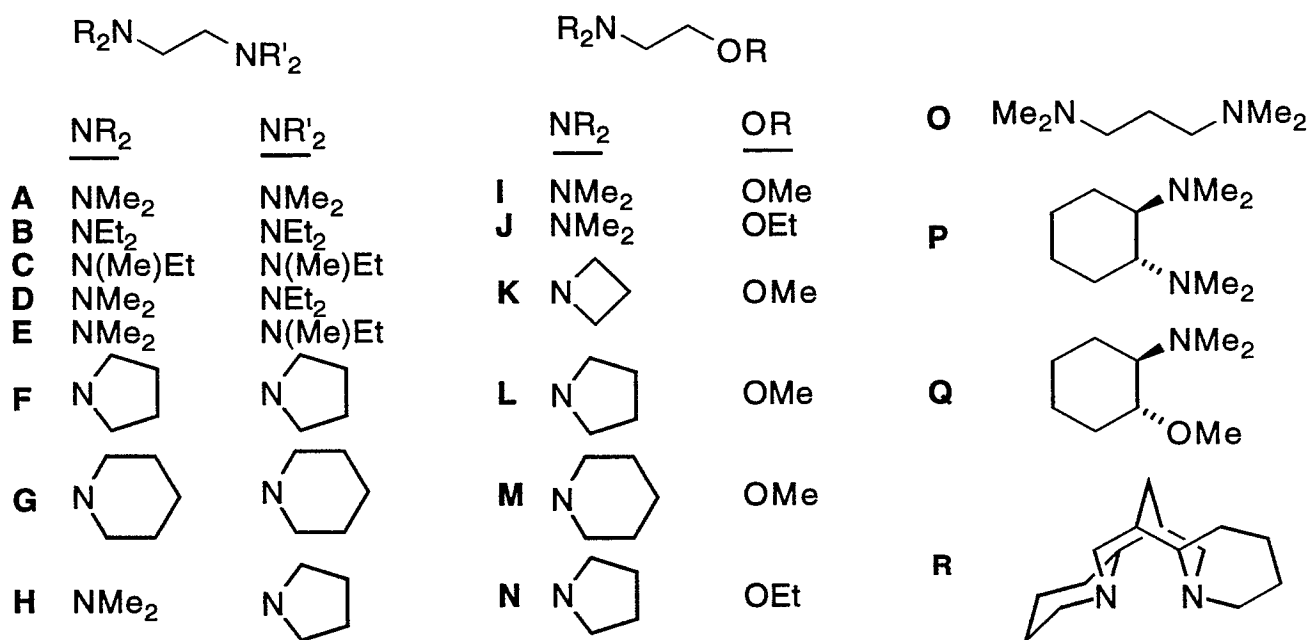


Chart 2



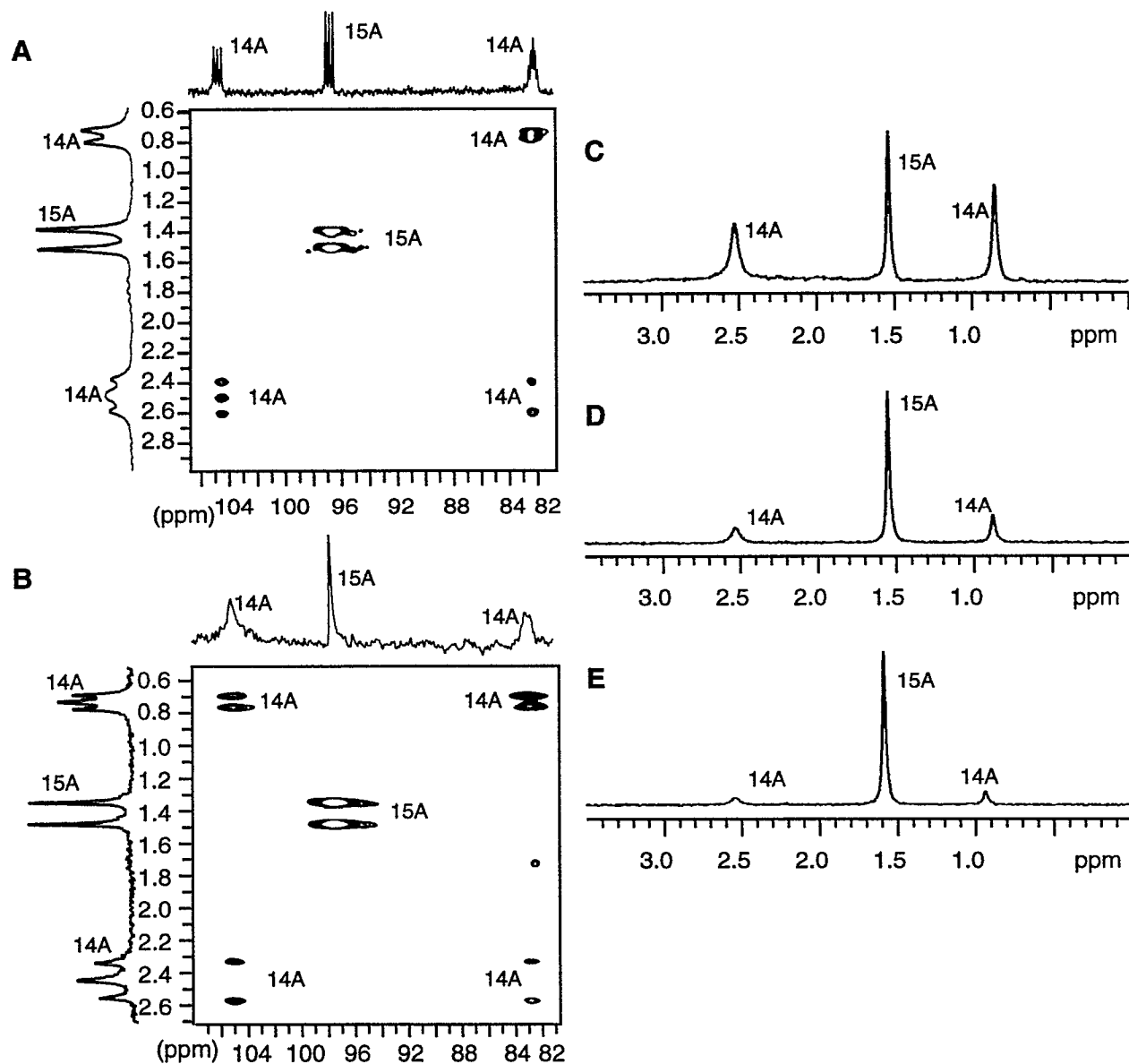


Figure I. NMR spectra of samples containing 0.10 M LiPMP varying amounts of TMEDA in 2:1 toluene:pentane. (A) ${}^6\text{Li}$ - ${}^{15}\text{N}$ HMQC spectrum of $[{}^6\text{Li}, {}^{15}\text{N}]$ LiPMP with 0.75 equiv of TMEDA at $-105\text{ }^\circ\text{C}$. The top and left hand traces are the ${}^{15}\text{N}\{^1\text{H}\}$ and ${}^6\text{Li}$ NMR spectra; (B) ${}^6\text{Li}$ - ${}^{15}\text{N}$ HMQC spectrum of $[{}^6\text{Li}, {}^{15}\text{N}]$ LiPMP with 0.75 equiv of TMEDA at $-95\text{ }^\circ\text{C}$. The top and left hand traces are the ${}^{15}\text{N}\{^1\text{H}\}$ and ${}^6\text{Li}$ NMR spectra; (C) ${}^6\text{Li}$ spectrum of $[{}^6\text{Li}]$ LiPMP with 0.50 equiv of TMEDA at $-105\text{ }^\circ\text{C}$; (D) ${}^6\text{Li}$ spectrum of $[{}^6\text{Li}]$ LiPMP with 2.0 equiv of TMEDA at $-105\text{ }^\circ\text{C}$; (E) ${}^6\text{Li}$ spectrum of $[{}^6\text{Li}]$ LiPMP with 5.0 equiv of TMEDA at $-105\text{ }^\circ\text{C}$.

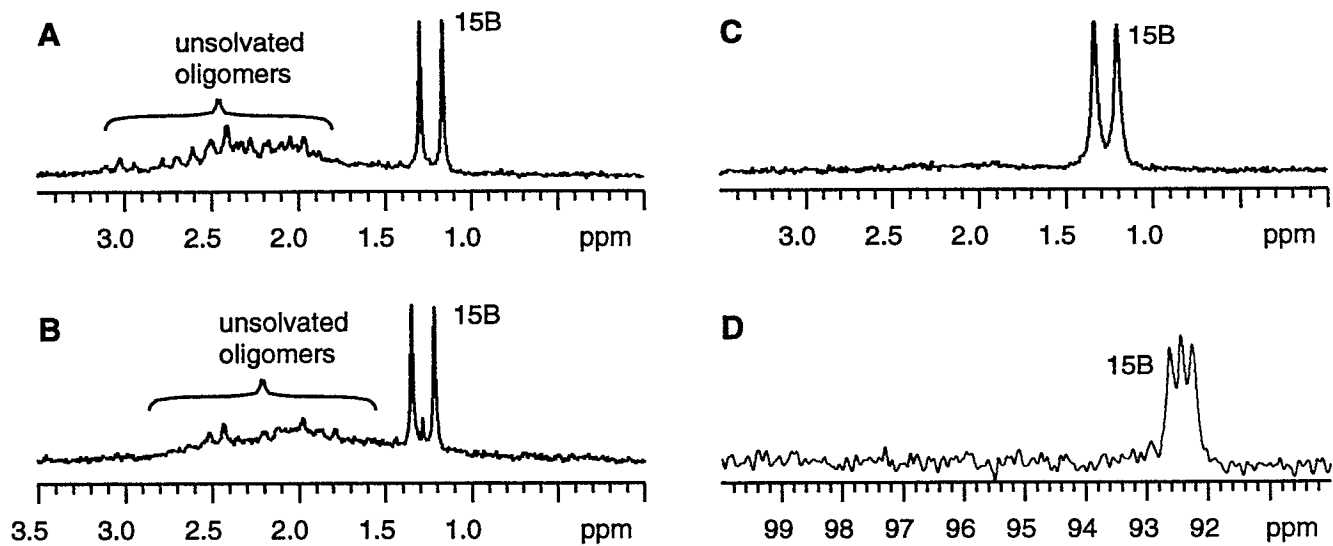


Figure II. NMR spectra of samples containing $0.10 \text{ M } [^6\text{Li}, ^{15}\text{N}]\text{LiPMP}$ and $\text{Et}_2\text{NCH}_2\text{CH}_2\text{NEt}_2$ in 2:1 toluene:pentane at -90°C . (A) ^6Li NMR spectrum with 5 equiv $\text{Et}_2\text{NCH}_2\text{CH}_2\text{NEt}_2$; (B) ^6Li NMR spectrum with 10 equiv $\text{Et}_2\text{NCH}_2\text{CH}_2\text{NEt}_2$; (C) ^6Li NMR spectrum with 20 equiv $\text{Et}_2\text{NCH}_2\text{CH}_2\text{NEt}_2$; (D) ^{15}N NMR spectrum with 20 equiv $\text{Et}_2\text{NCH}_2\text{CH}_2\text{NEt}_2$.

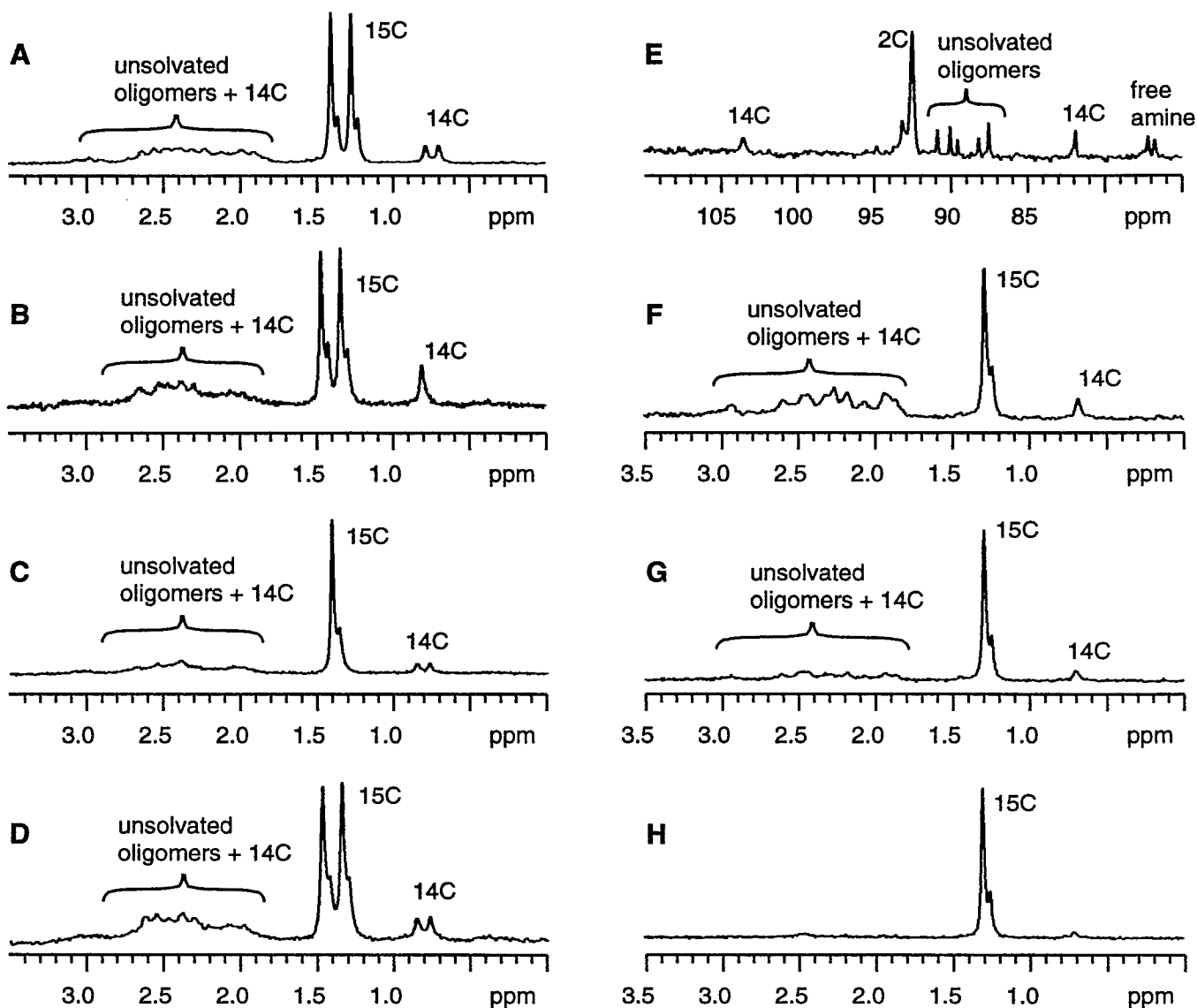


Figure III. NMR spectra of samples containing 0.10 M LiPMP and EtMeNCH₂CH₂NEtMe in 2:1 toluene:pentane at -100 °C. Samples (A)-(E) contain [⁶Li,¹⁵N]LiPMP and 0.75 equiv of EtMeNCH₂CH₂NEtMe: (A) ⁶Li NMR spectrum; (B) ⁶Li NMR spectrum with ¹⁵N single-frequency decoupled at 81.9 ppm; (C) ⁶Li NMR spectrum with ¹⁵N single-frequency decoupled at 92.5 ppm; (D) ⁶Li NMR spectrum with ¹⁵N single-frequency decoupled at 103.5 ppm; (E) ¹⁵N NMR spectrum with ⁶Li broad-band decoupled. Samples (F)-(H) contain [⁶Li]LiPMP and : (F) 0.5 equiv of EtMeNCH₂CH₂NEtMe; (G) 1.0 equiv of EtMeNCH₂CH₂NEtMe; (H) 2.0 equiv of EtMeNCH₂CH₂NEtMe.

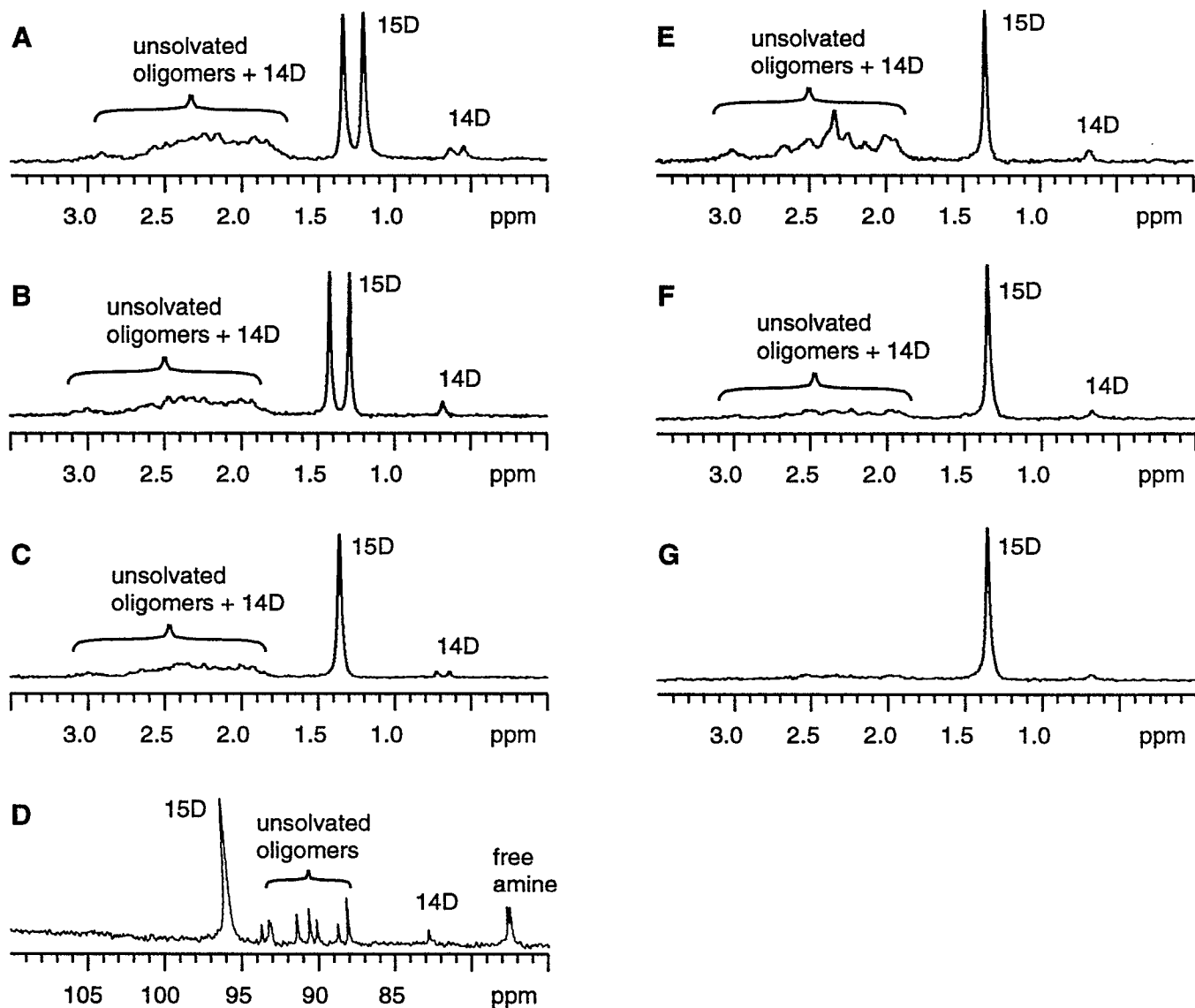


Figure IV. NMR spectra of samples containing 0.10 M LiPMP and $\text{Et}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$ in 2:1 toluene:pentane at $-100\text{ }^\circ\text{C}$. Samples (A)-(E) contain $[\text{}^6\text{Li},\text{}^{15}\text{N}]\text{LiPMP}$ and 0.75 equiv of $\text{Et}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$: (A) ${}^6\text{Li}$ NMR spectrum; (B) ${}^6\text{Li}$ NMR spectrum with ${}^{15}\text{N}$ single-frequency decoupled at 81.9 ppm; (C) ${}^6\text{Li}$ NMR spectrum with ${}^{15}\text{N}$ single-frequency decoupled at 95.4 ppm; (D) ${}^6\text{Li}$ NMR spectrum with ${}^{15}\text{N}$ single-frequency decoupled at 104.0 ppm; (E) ${}^{15}\text{N}$ NMR spectrum with ${}^6\text{Li}$ broad-band decoupled. Samples (F)-(H) contain $[\text{}^6\text{Li}]\text{LiPMP}$ and : (F) 0.5 equiv of $\text{Et}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$; (G) 1.0 equiv of $\text{Et}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$; (H) 2.0 equiv of $\text{Et}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$.

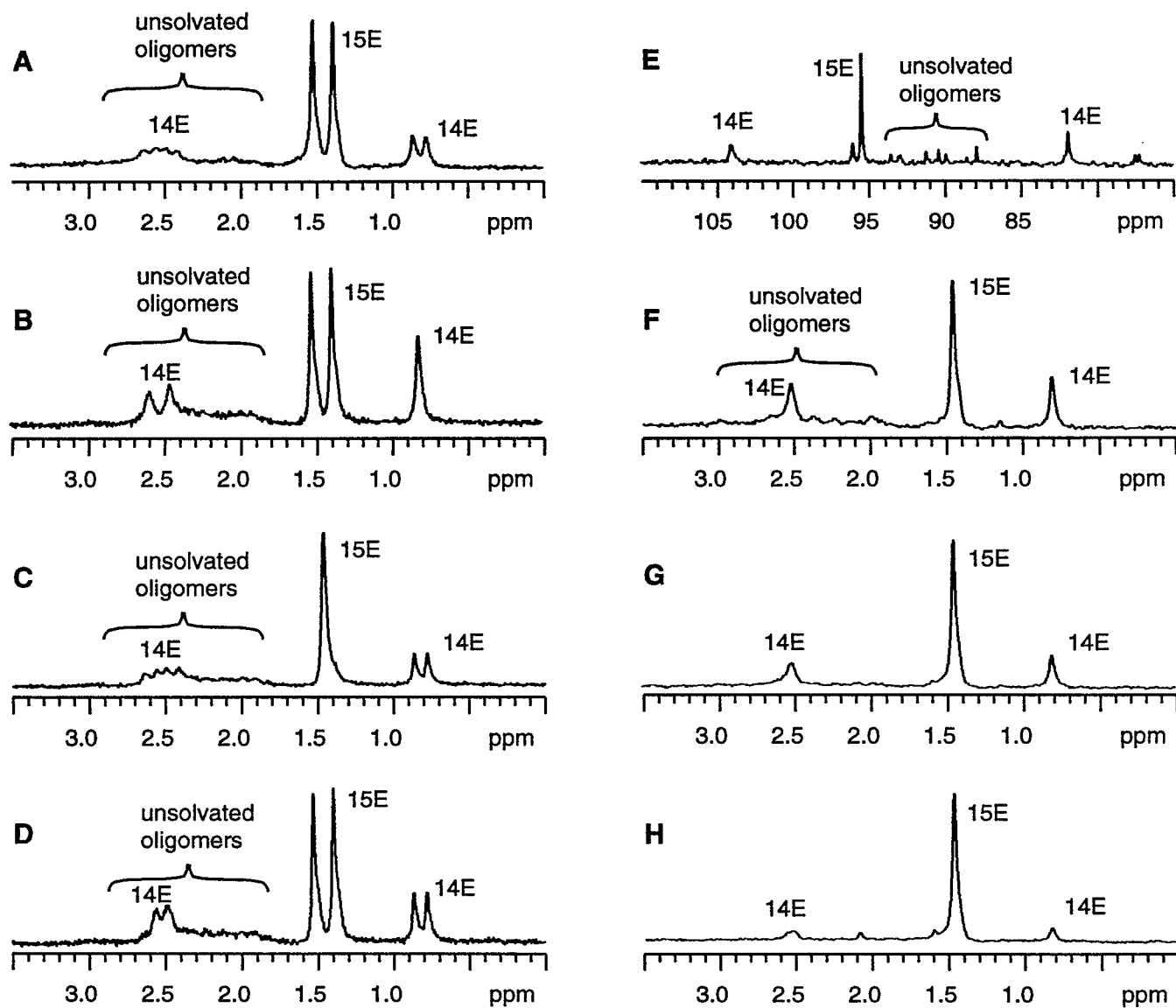


Figure V. NMR spectra of samples containing 0.10 M LiPMP and EtMeNCH₂CH₂NMe₂ in 2:1 toluene:pentane at -100 °C. Samples (A)-(E) contain [⁶Li,¹⁵N]LiPMP and 0.75 equiv of EtMeNCH₂CH₂NMe₂: (A) ⁶Li NMR spectrum; (B) ⁶Li NMR spectrum with ¹⁵N single-frequency decoupled at 81.9 ppm; (C) ⁶Li NMR spectrum with ¹⁵N single-frequency decoupled at 95.4 ppm; (D) ⁶Li NMR spectrum with ¹⁵N single-frequency decoupled at 104.0 ppm; (E) ¹⁵N NMR spectrum with ⁶Li broad-band decoupled. Samples (F)-(H) contain [⁶Li]LiPMP and : (F) 0.5 equiv of EtMeNCH₂CH₂NMe₂; (G) 1.0 equiv of EtMeNCH₂CH₂Nme₂; (F) 2.0 equiv of EtMeNCH₂CH₂NMe₂.

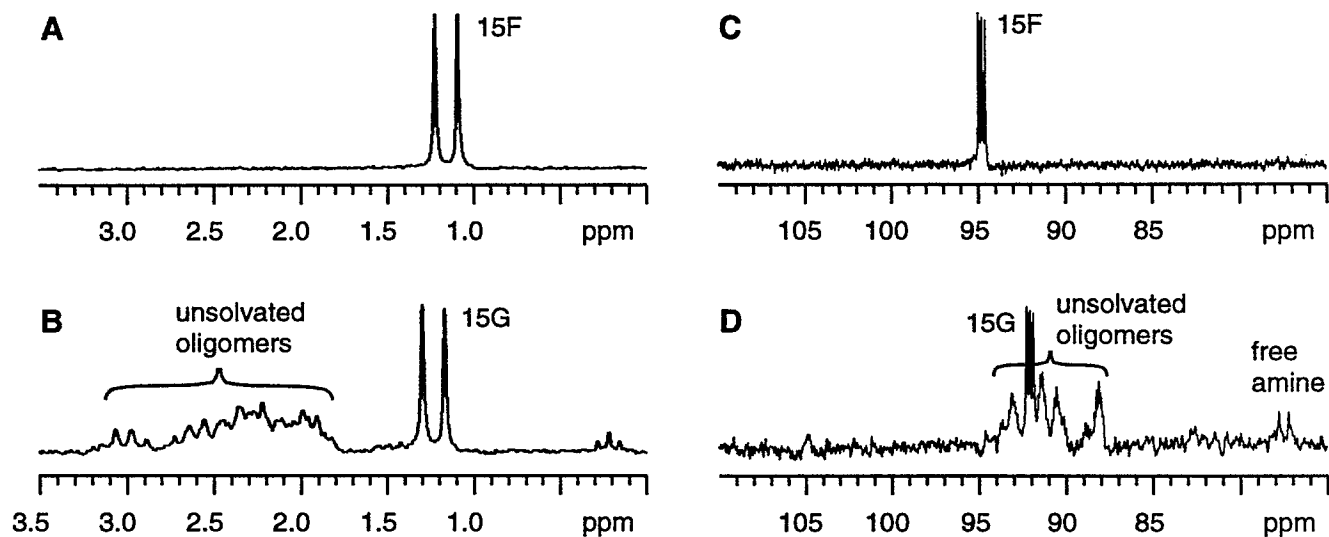


Figure VI. NMR spectra of samples containing 0.10 M $[^6\text{Li},^{15}\text{N}]$ LiPMP in 2:1 toluene:pentane at $-100\text{ }^\circ\text{C}$. (A) ^6Li NMR spectrum with 2 equiv of dipyrrolidinoethane; (B) ^6Li NMR spectrum with 2 equiv of dipiperidinoethane; (C) ^{15}N NMR spectrum with 2 equiv of dipyrrolidinoethane; (D) ^{15}N NMR spectrum with 2 equiv of dipiperidinoethane.

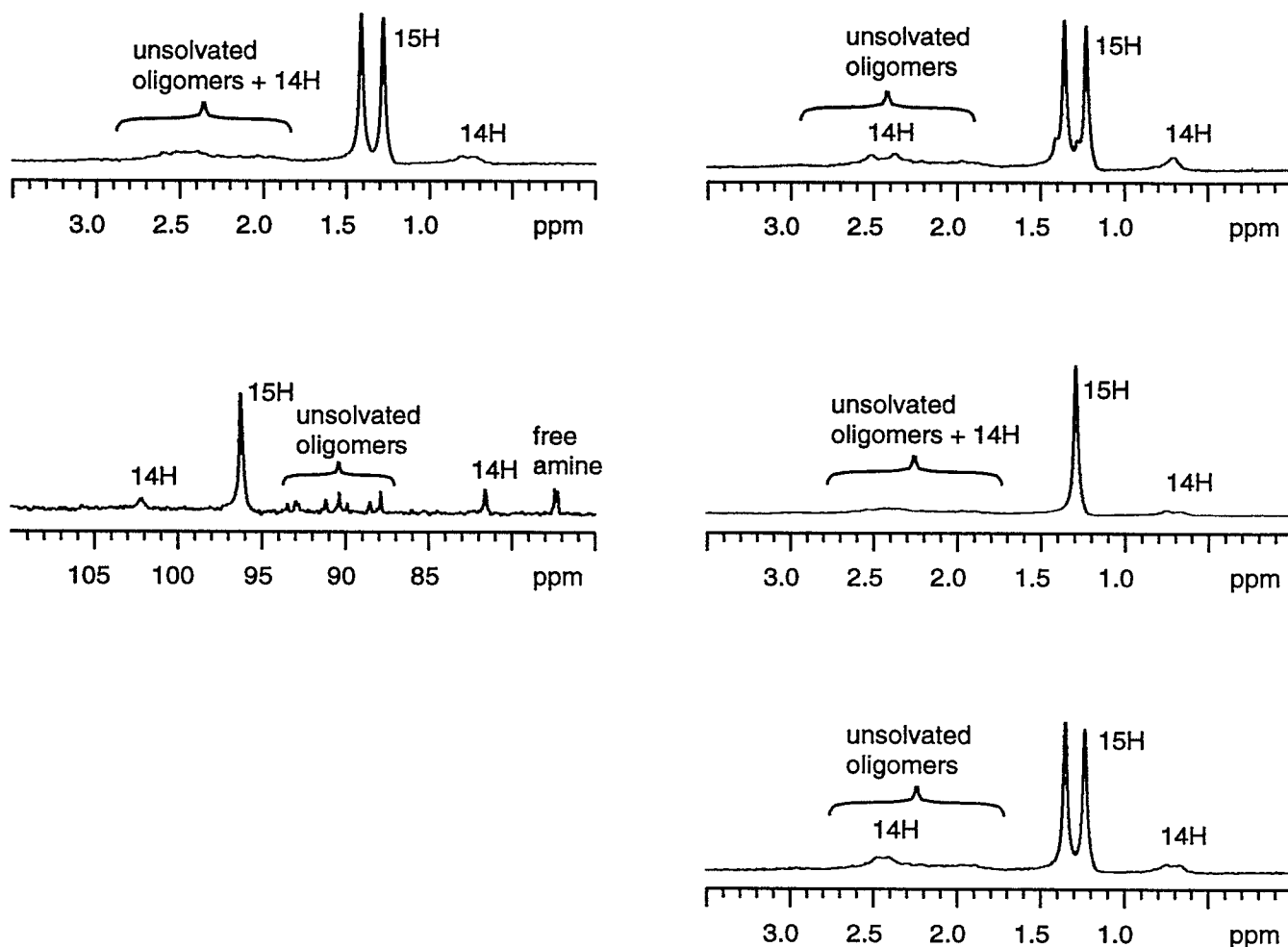


Figure VII. NMR spectra of samples containing 0.10 M $[^6\text{Li},^{15}\text{N}]$ LiPMP and 0.75 equiv of $\text{Me}_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2)_4$ in 2:1 toluene:pentane at -100°C . (A) ^6Li NMR spectrum; (B) ^{15}N NMR spectrum with ^6Li broad-band decoupled; (C) ^6Li NMR spectrum with ^{15}N single-frequency decoupled at 81.7 ppm; (D) ^6Li NMR spectrum with ^{15}N single-frequency decoupled at 96.2 ppm; (E) ^6Li NMR spectrum with ^{15}N single-frequency decoupled at 102.2 ppm.

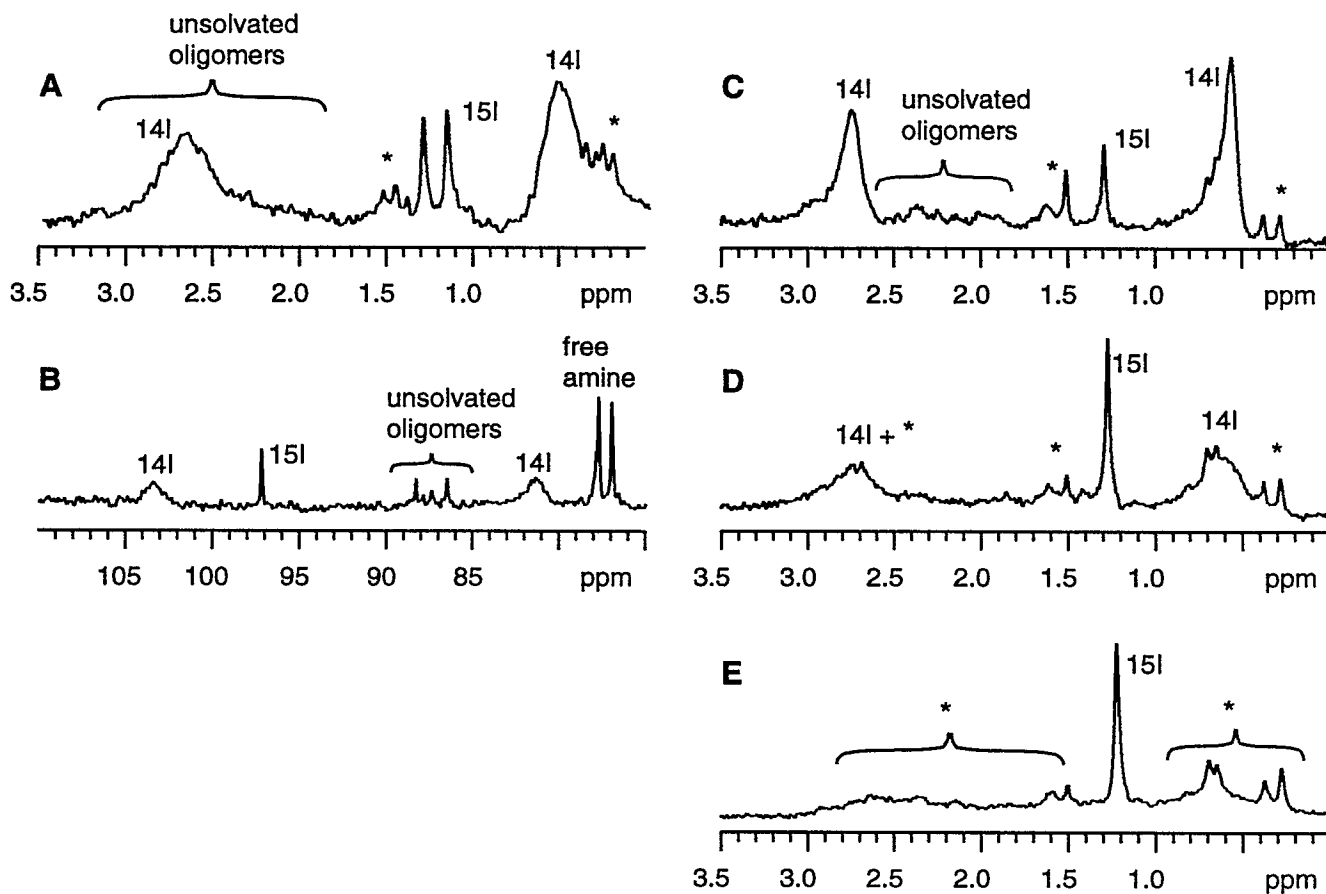


Figure VIII. NMR spectra of samples containing 0.10 M LiPMP in 2:1 toluene:pentane at -100°C . (A) ${}^6\text{Li}$ NMR spectrum of $[{}^6\text{Li}, {}^{15}\text{N}]$ LiPMP and 0.5 equiv of $\text{MeOCH}_2\text{CH}_2\text{NMe}_2$; (B) ${}^6\text{Li}$ decoupled ${}^{15}\text{N}$ NMR spectrum of $[{}^6\text{Li}, {}^{15}\text{N}]$ LiPMP and 0.5 equiv of $\text{MeOCH}_2\text{CH}_2\text{NMe}_2$; (C) ${}^6\text{Li}$ NMR spectrum of $[{}^6\text{Li}]$ LiPMP and 0.5 equiv of $\text{MeOCH}_2\text{CH}_2\text{NMe}_2$; (D) ${}^6\text{Li}$ NMR spectrum of $[{}^6\text{Li}]$ LiPMP and 1.0 equiv of $\text{MeOCH}_2\text{CH}_2\text{NMe}_2$; (E) ${}^6\text{Li}$ NMR spectrum of $[{}^6\text{Li}]$ LiPMP and 2.0 equiv of $\text{MeOCH}_2\text{CH}_2\text{NMe}_2$.

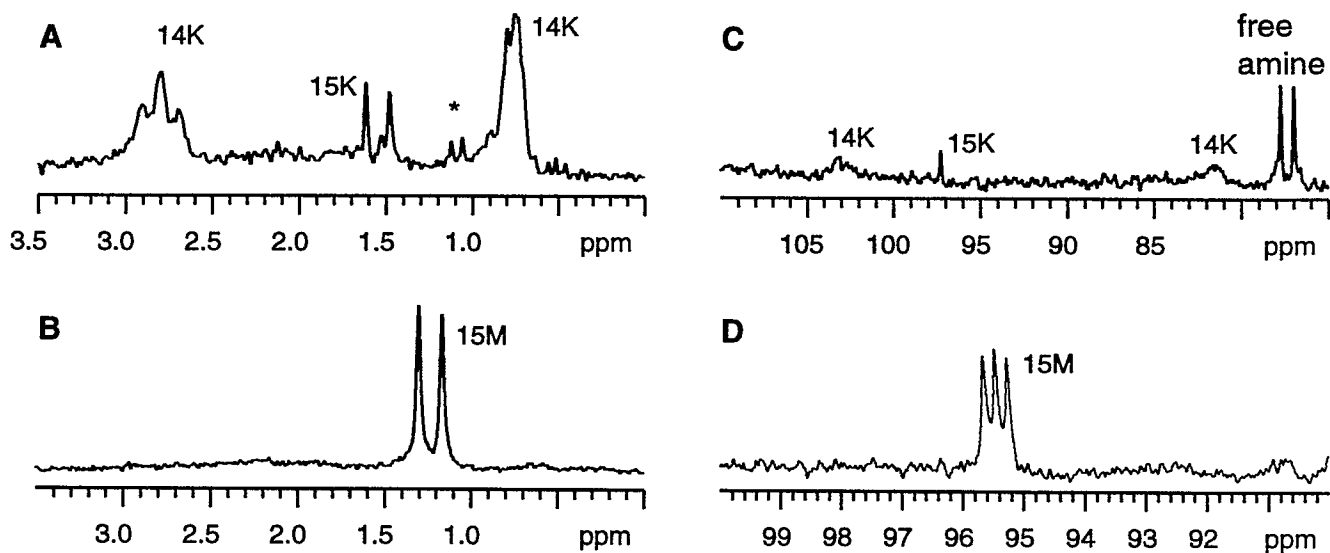


Figure IX. NMR spectra of samples containing 0.10 M $[\text{}^6\text{Li},\text{}^{15}\text{N}]\text{LiPMP}$ in 2:1 toluene:pentane at $-100\text{ }^\circ\text{C}$. (A) ^6Li NMR spectrum containing 0.5 equiv of 2-azetidino-methoxyethane; (B) ^6Li NMR spectrum containing 0.75 equiv of 2-piperidino-methoxyethane; (C) ^{15}N NMR spectrum containing 0.5 equiv of 2-azetidino-methoxyethane; (D) ^{15}N NMR spectrum containing 0.75 equiv of 2-piperidino-methoxyethane.

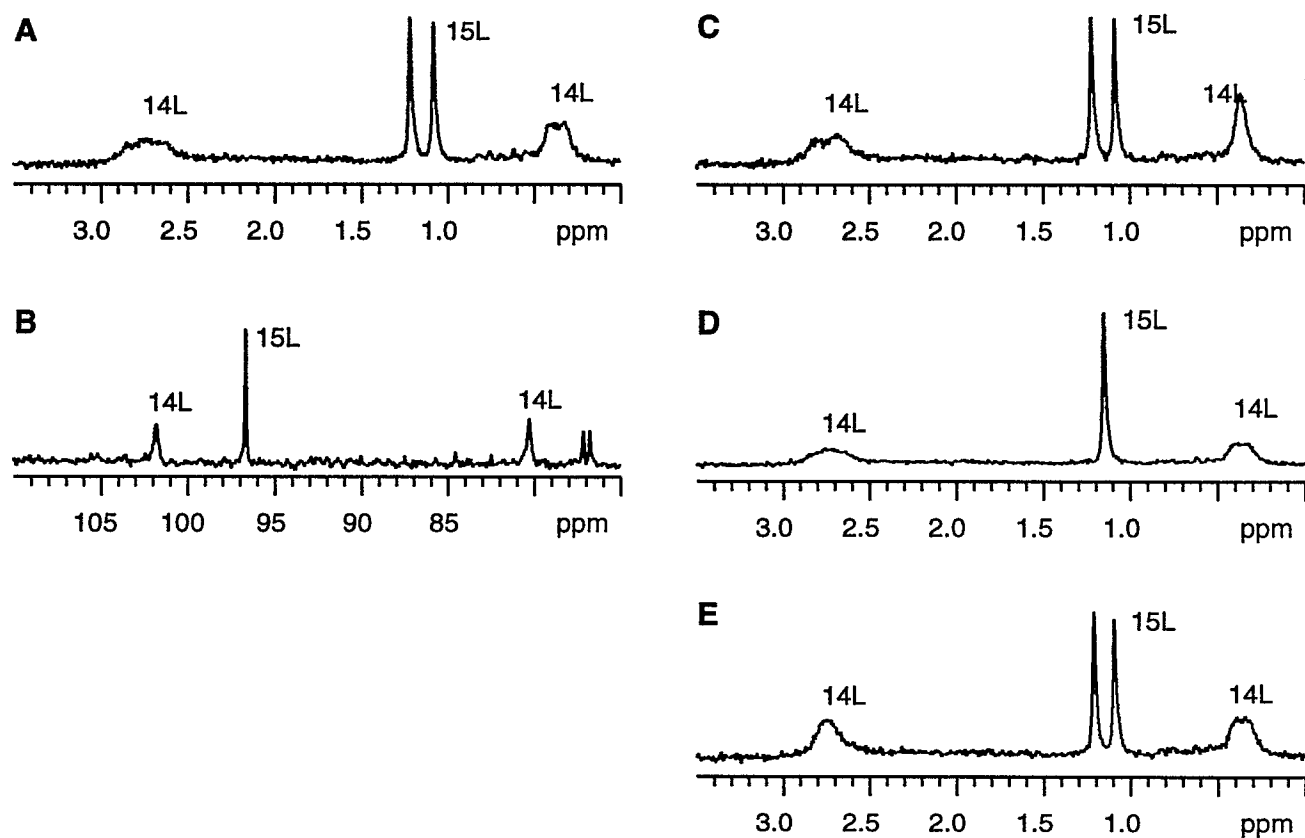


Figure X. NMR spectra of samples containing 0.10 M $[^6\text{Li},^{15}\text{N}]\text{LiPMP}$ and 0.75 equiv of 2-pyrrolidino-methoxyethane in 2:1 toluene:pentane at $-100\text{ }^\circ\text{C}$. (A) ^6Li NMR spectrum; (B) ^6Li decoupled ^{15}N NMR spectrum; (C) ^6Li NMR spectrum with ^{15}N single frequency decoupling at 80.3 ppm; (D) ^6Li NMR spectrum with ^{15}N single frequency decoupling at 96.7 ppm; (E) ^6Li NMR spectrum with ^{15}N single frequency decoupling at 101.8 ppm.

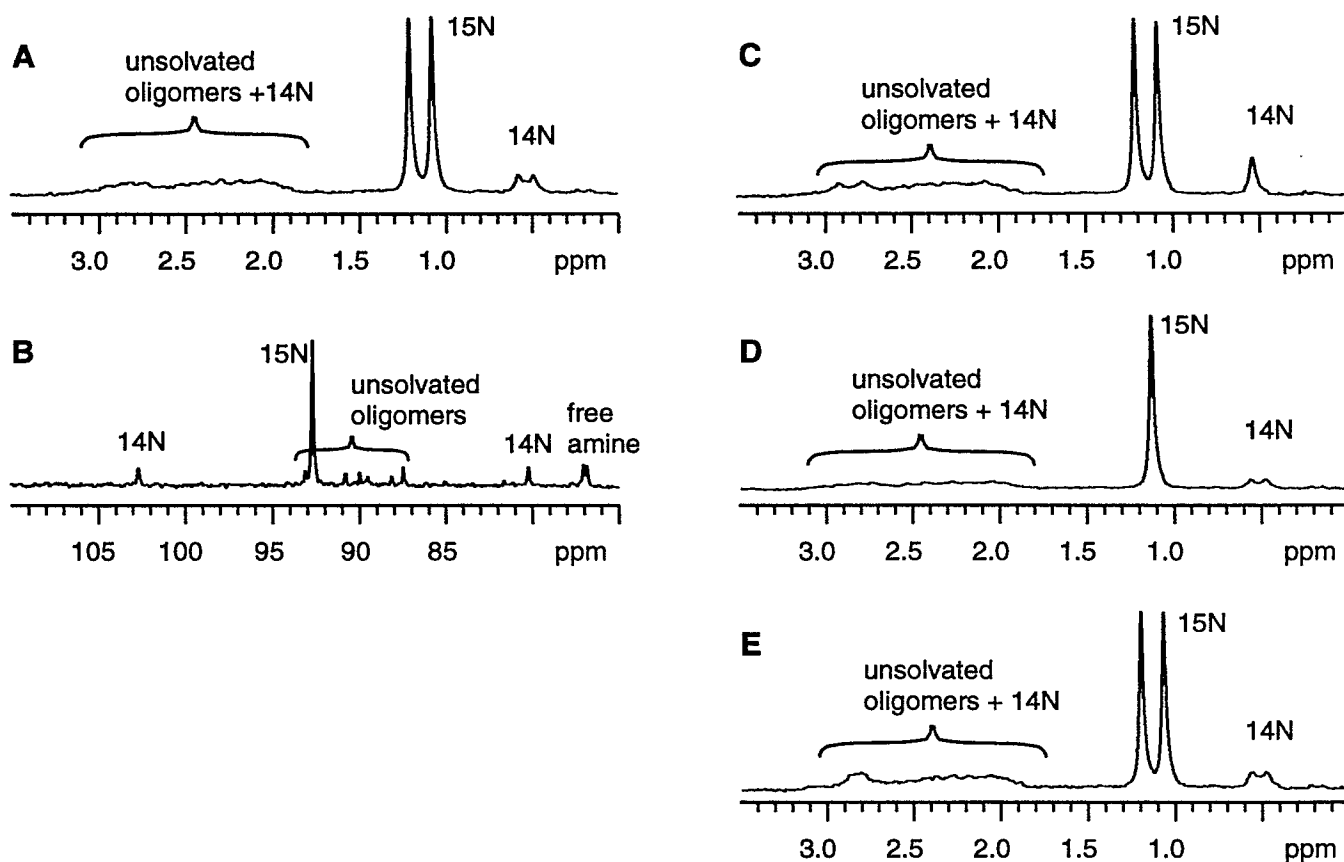


Figure XI. NMR spectra of samples containing $0.10\text{ M } [^6\text{Li},^{15}\text{N}]\text{LiPMP}$ and 0.75 equiv of 2-pyrrolidino-ethoxyethane in $2:1$ toluene:pentane at $-100\text{ }^\circ\text{C}$. (A) ^6Li NMR spectrum; (B) ^6Li decoupled ^{15}N NMR spectrum; (C) ^6Li NMR spectrum with ^{15}N single frequency decoupling at 80.3 ppm ; (D) ^6Li NMR spectrum with ^{15}N single frequency decoupling at 92.7 ppm ; (E) ^6Li NMR spectrum with ^{15}N single frequency decoupling at 102.7 ppm .

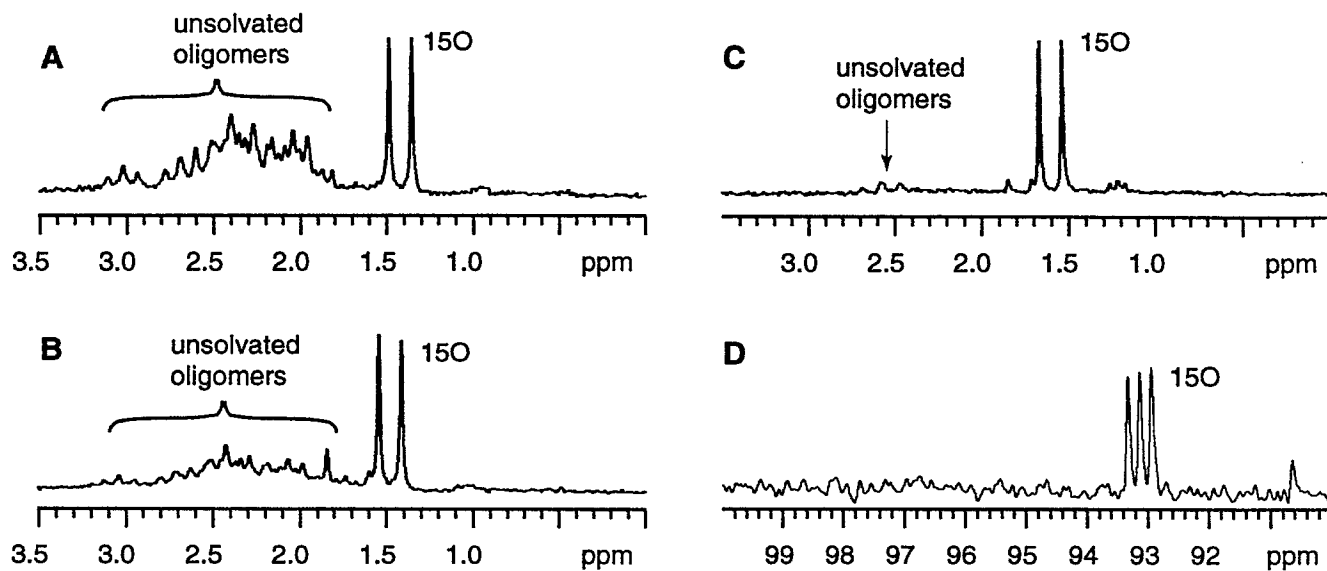


Figure XII. NMR spectra of samples containing 0.10 M $[^6\text{Li},^{15}\text{N}]\text{LiPMP}$ and varying amounts of TMPDA in 2:1 toluene:pentane at $-100\text{ }^\circ\text{C}$. (A) ^6Li NMR spectrum with 5 equiv of TMPDA; (B) ^6Li NMR spectrum with 10 equiv of TMPDA; (C) ^6Li NMR spectrum with 20 equiv of TMPDA; (D) ^{15}N NMR spectrum with 20 equiv of TMPDA.

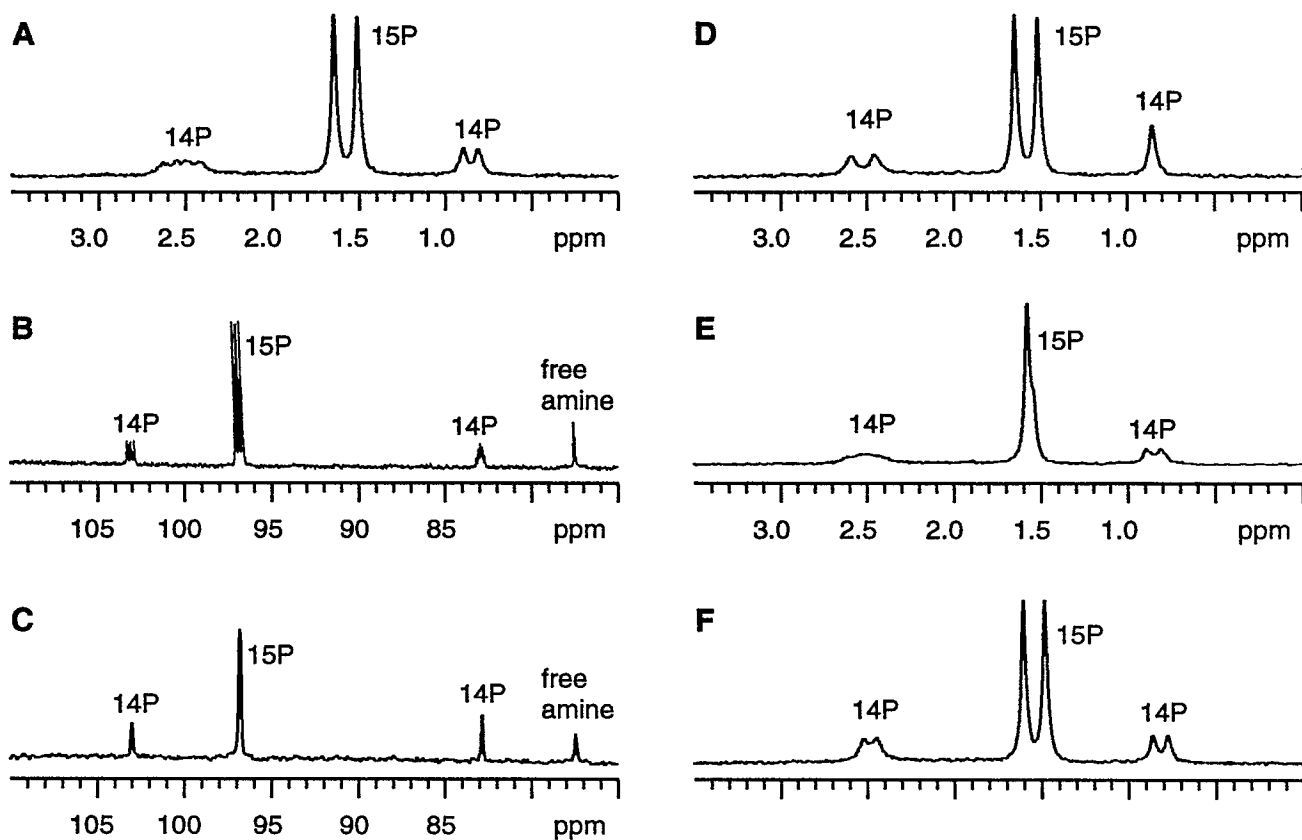


Figure XIII. NMR spectra of a sample containing $0.10\text{ M } [^6\text{Li}, ^{15}\text{N}]\text{LiPMP}$ and 0.75 equiv of TMEDA in $2:1$ toluene:pentane at $-100\text{ }^\circ\text{C}$. (A) ^6Li NMR spectrum; (B) ^{15}N NMR spectrum; (C) ^6Li broad-band decoupled ^{15}N NMR spectrum; (D) ^6Li NMR spectrum with ^{15}N single-frequency decoupling at 82.8 ppm ; (E) ^6Li NMR spectrum with ^{15}N single-frequency decoupling at 96.6 ppm ; (F) ^6Li NMR spectrum with ^{15}N single-frequency decoupling at 102.9 ppm .

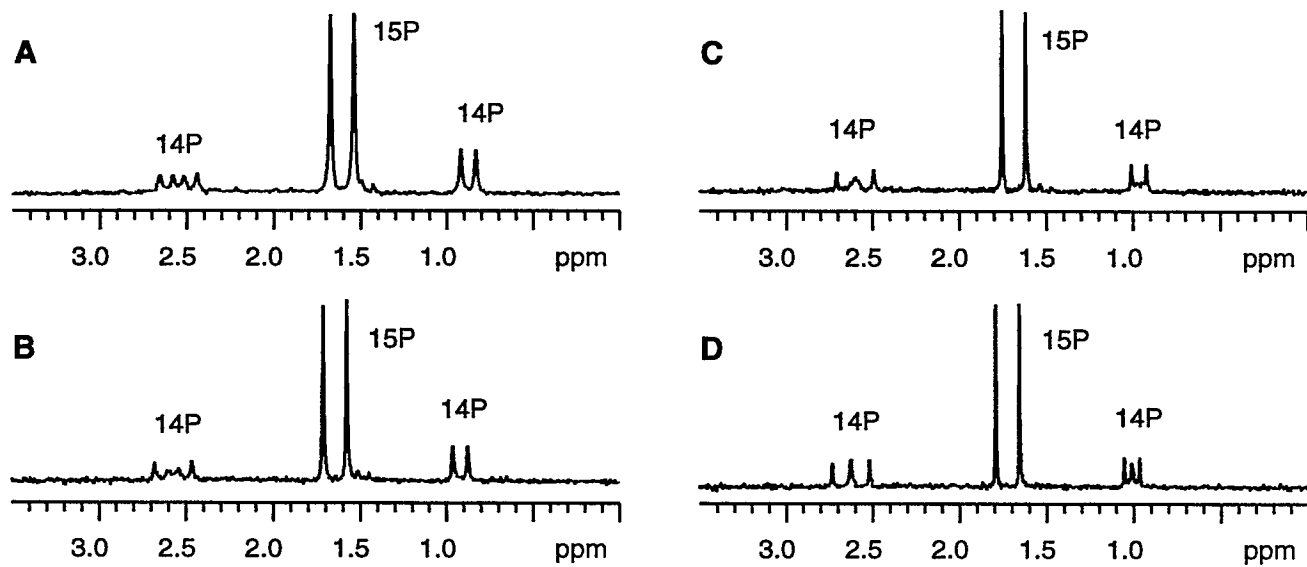


Figure XIV. ${}^6\text{Li}$ NMR spectra of a sample containing 0.10 M $[{}^6\text{Li}, {}^{15}\text{N}]\text{LiPMP}$ and 0.75 equiv of TMCDA in $2:1$ toluene:pentane at $-100\text{ }^\circ\text{C}$. The spectra were acquired at: (A) $-100\text{ }^\circ\text{C}$; (B) $-90\text{ }^\circ\text{C}$; (C) $-80\text{ }^\circ\text{C}$; (D) $-70\text{ }^\circ\text{C}$.

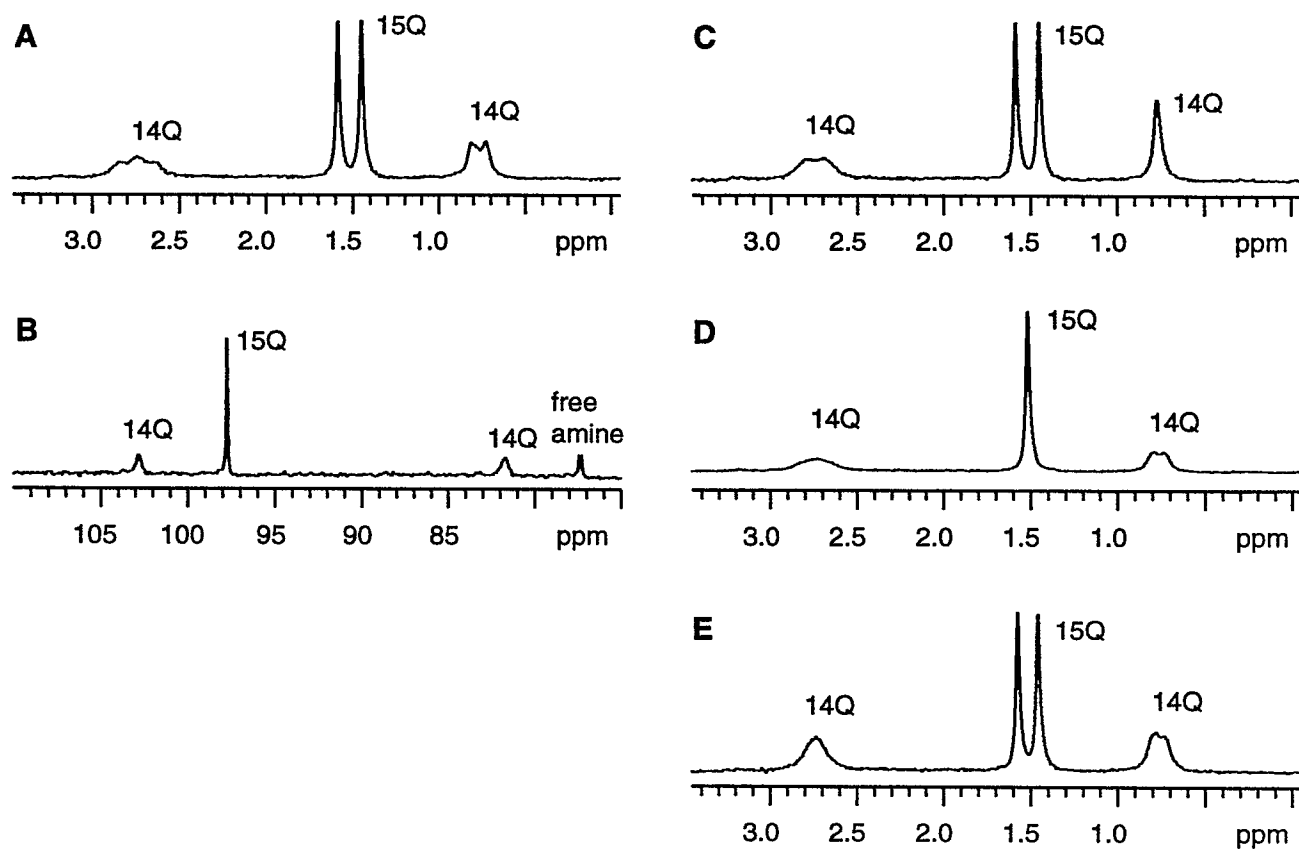


Figure XV. NMR spectra of a sample containing 0.10 M $[\text{}^6\text{Li},\text{}^{15}\text{N}]\text{LiPMP}$ and 0.75 equiv of *trans*-2-(*N,N*-dimethylamino)methoxycyclohexane in $2:1$ toluene:pentane at $-100\text{ }^\circ\text{C}$. (A) ^6Li NMR spectrum; (B) ^6Li broad-band decoupled ^{15}N NMR spectrum; (C) ^6Li NMR spectrum with ^{15}N single frequency decoupling at 81.6 ppm ; (D) ^6Li NMR spectrum with ^{15}N single-frequency decoupling at 97.8 ppm ; (E) ^6Li NMR spectrum with ^{15}N single-frequency decoupling at 102.8 ppm .

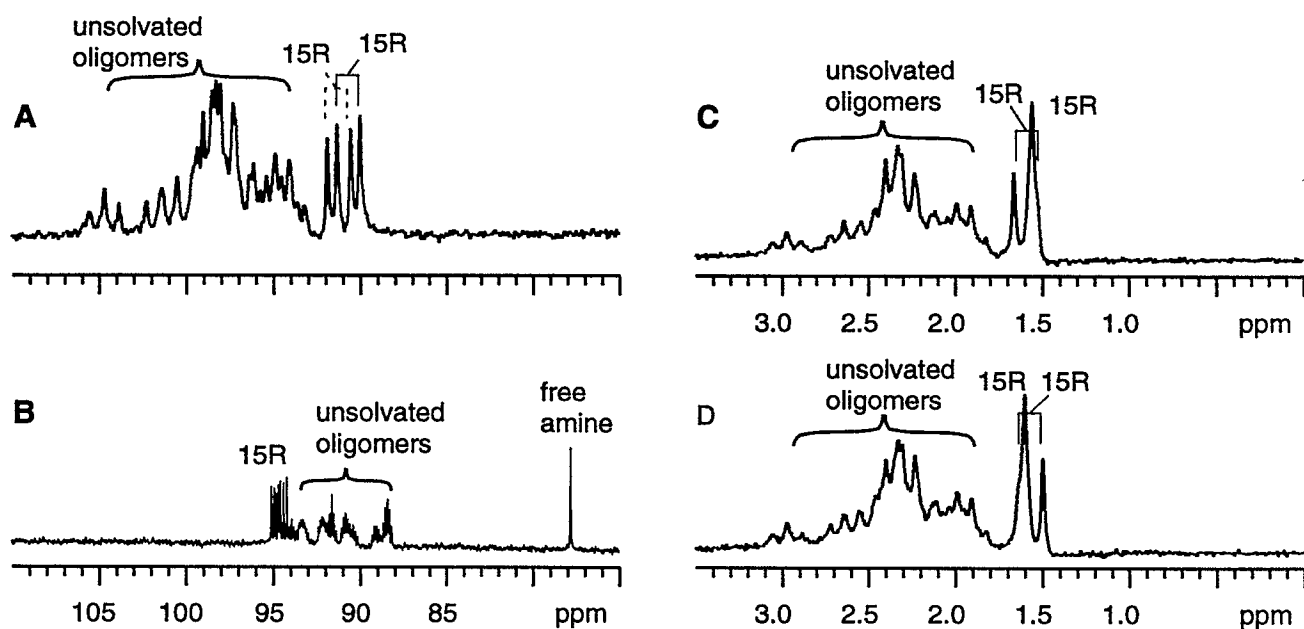


Figure XVI. NMR spectra of a sample containing 0.10 M $[^6\text{Li},^{15}\text{N}]\text{LiPMP}$ and 5 equiv of sparteine in 2:1 toluene:pentane at $-100\text{ }^\circ\text{C}$. (A) ^6Li NMR spectrum; (B) ^{15}N NMR spectrum; (C) ^6Li NMR spectrum with ^{15}N single-frequency decoupling at 94.4 ppm; (D) ^6Li NMR spectrum with ^{15}N single-frequency decoupling at 94.9 ppm.

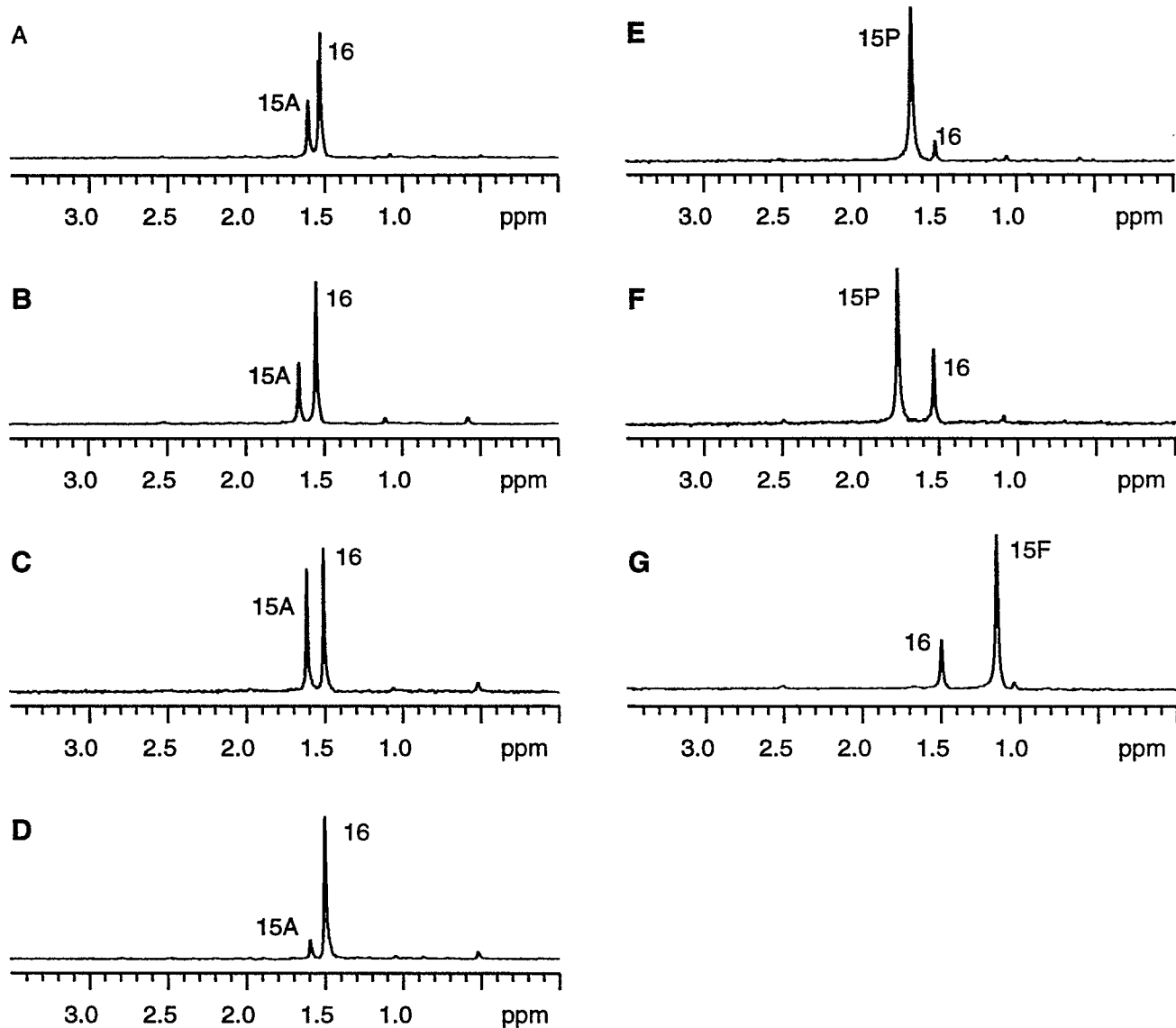


Figure XVII. ${}^6\text{Li}$ NMR spectra of samples containing 0.1 M ${}^6\text{Li}$ LDA in 2:1 toluene:pentane at $-100\text{ }^\circ\text{C}$. The samples also contain: (A) 2 equiv of THF and 2 equiv of TMEDA; (B) 5 equiv of THF and 5 equiv of TMEDA; (C) 2 equiv of THF and 5 equiv of TMEDA; (D) 5 equiv of THF and 2 equiv of TMEDA; (E) 2 equiv of TMCDA and 5 equiv of THF; (F) 2 equiv of TMCDA and 20 equiv of THF; (G) 2 equiv of dipyrrolidinoethane and 2 equiv of THF.

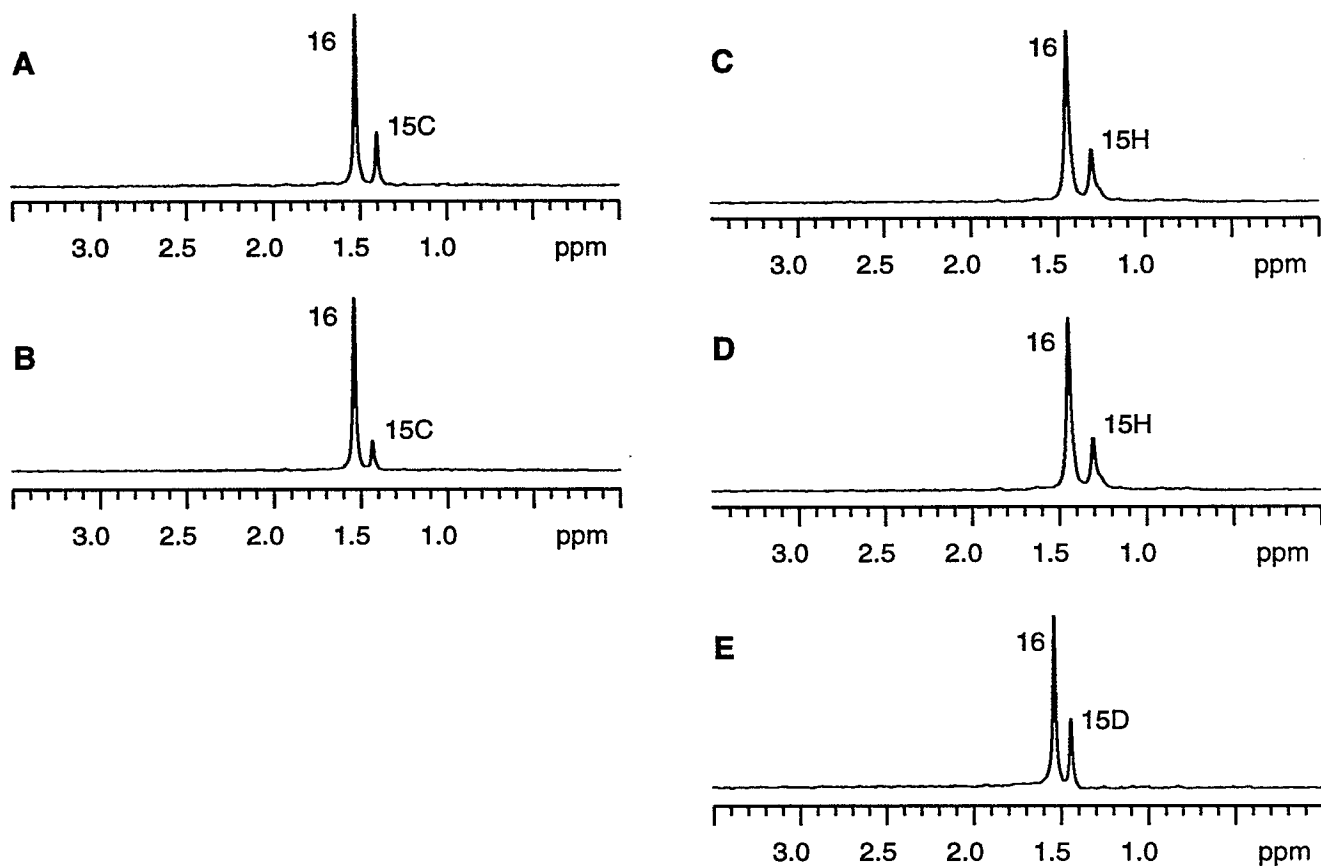


Figure XVIII. ${}^6\text{Li}$ NMR spectra of samples containing 0.1 M ${}^6\text{Li}$ LDA in 2:1 toluene:pentane at $-100 \text{ }^\circ\text{C}$. The samples also contain: (A) 2 equiv of THF and 2.1 equiv $\text{EtMeNCH}_2\text{CH}_2\text{NMe}_2$; (B) 2 equiv of THF and 5.3 equiv $\text{EtMeNCH}_2\text{CH}_2\text{NMe}_2$; (C) 5 equiv of THF and 2 equiv of $\text{Me}_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2)_4$; (D) 10 equiv of THF and 2 equiv of $\text{Me}_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2)_4$; (E) 2 equiv of THF and 2 equiv of $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NEt}_2$.

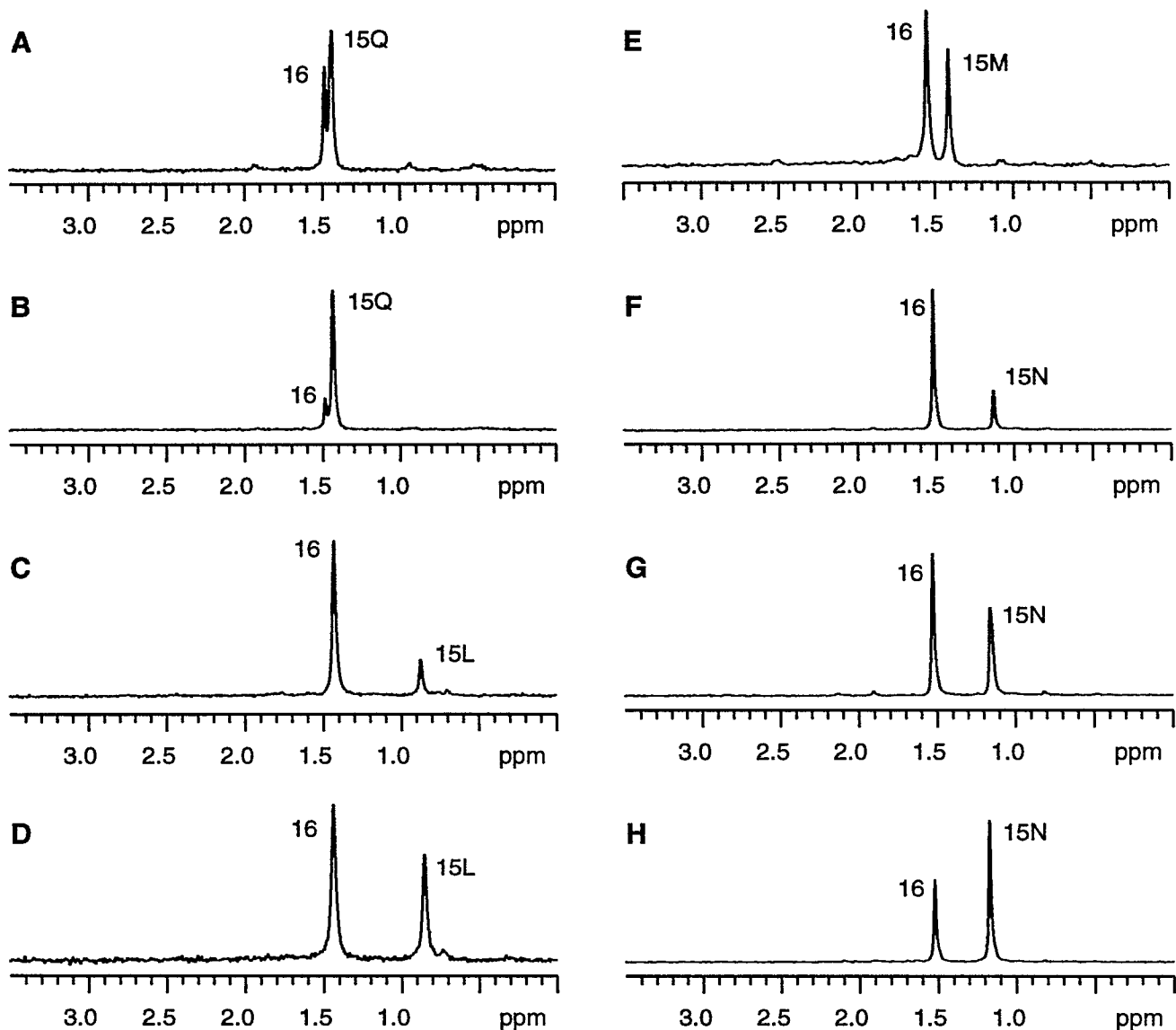


Figure XIX. ${}^6\text{Li}$ NMR spectra of samples containing 0.1 M $[{}^6\text{Li}]\text{LDA}$ in 2:1 toluene:pentane at $-100\text{ }^\circ\text{C}$. The samples also contain: (A) 2 equiv of THF and 2 equiv of *trans*-2-(dimethylamino)-methoxycyclohexane; (B) 2 equiv of THF and 5 equiv of *trans*-2-(dimethylamino)-methoxycyclohexane; (C) 2 equiv of THF and 3.4 equiv of $\text{MeOCH}_2\text{CH}_2\text{N}(\text{CH}_2)_4$; (D) 2 equiv of THF and 9 equiv of $\text{MeOCH}_2\text{CH}_2\text{N}(\text{CH}_2)_4$; (E) 2 equiv of THF and 10 equiv of $\text{MeOCH}_2\text{CH}_2\text{N}(\text{CH}_2)_5$; (F) 2 equiv of THF and 2 equiv of $\text{EtOCH}_2\text{CH}_2\text{N}(\text{CH}_2)_4$; (G) 2 equiv of THF and 5 equiv of $\text{EtOCH}_2\text{CH}_2\text{N}(\text{CH}_2)_4$; (H) 2 equiv of THF and 10 equiv of $\text{EtOCH}_2\text{CH}_2\text{N}(\text{CH}_2)_4$.