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Lithium Diisopropylamide-Mediated Enolizations: Solvent-Dependent Mixed Aggregation Effects

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Supporting Information

I. ^{6}Li and ^{15}N NMR spectra of [^{6}Li,^{15}N]LDA with ester **1-*d*$_1$** in t-BuOMe.
II. ^{6}Li and ^{15}N NMR spectra of [^{6}Li,^{15}N]LDA with ester **1-*d*$_1$** in t-BuOMe after aging.
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XIII. ^{6}Li spectra of the reaction of [^{6}Li]LDA with ester **1-*d*$_1$** in *t*-BuOMe.
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XVI. ^{6}Li spectra of the reaction of [^{6}Li]LDA with ester **1-*d*$_1$** and 1 M HMPA in THF.
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XVIII. ^{6}Li spectra of the reaction of [^{6}Li]LDA with ester **1-*d*$_1$** and 1 M DMPU in THF.
XIX. Concentration of homo- and mixed aggregates vs. time in the reaction of [^{6}Li]LDA with ester **1-*d*$_1$**.
XX. ^{6}Li and ^{15}N NMR spectra of [^{6}Li,^{15}N]LDA with cyclohexylpyrrolidin-1-yl-methanone in *t*-BuOMe.

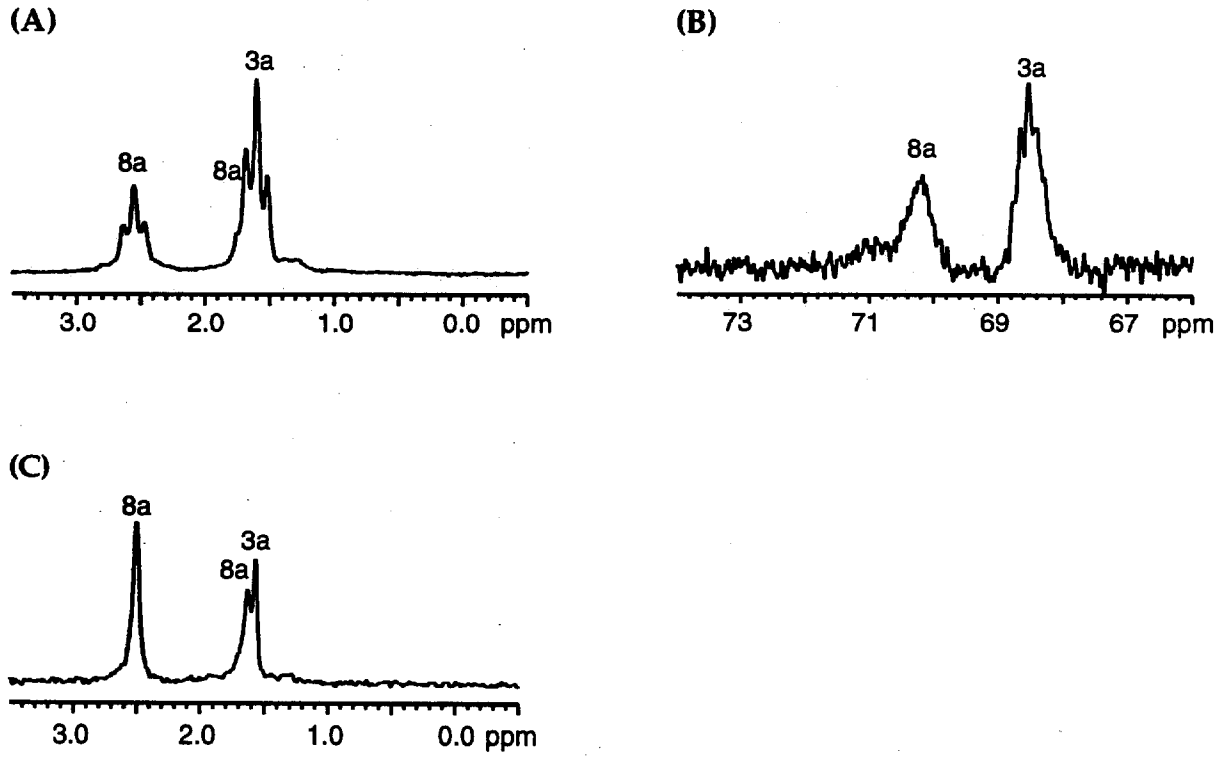


Figure I. ^{6}Li and ^{15}N NMR spectra of 0.13 M [^{6}Li,^{15}N]LDA with 0.13 M ester **1-*d*$_1$** in *t*-BuOMe at -125 °C. **(A)** ^{6}Li spectrum; **(B)** ^{15}N spectrum; **(C)** ^{6}Li spectrum with ^{15}N broad-band decoupling. The greater intensity of the ^{6}Li resonance at 2.5 ppm is likely due to contributions from (*i*-$Pr_2NLi)_2$(**1-*d*$_1$**)$_2$.

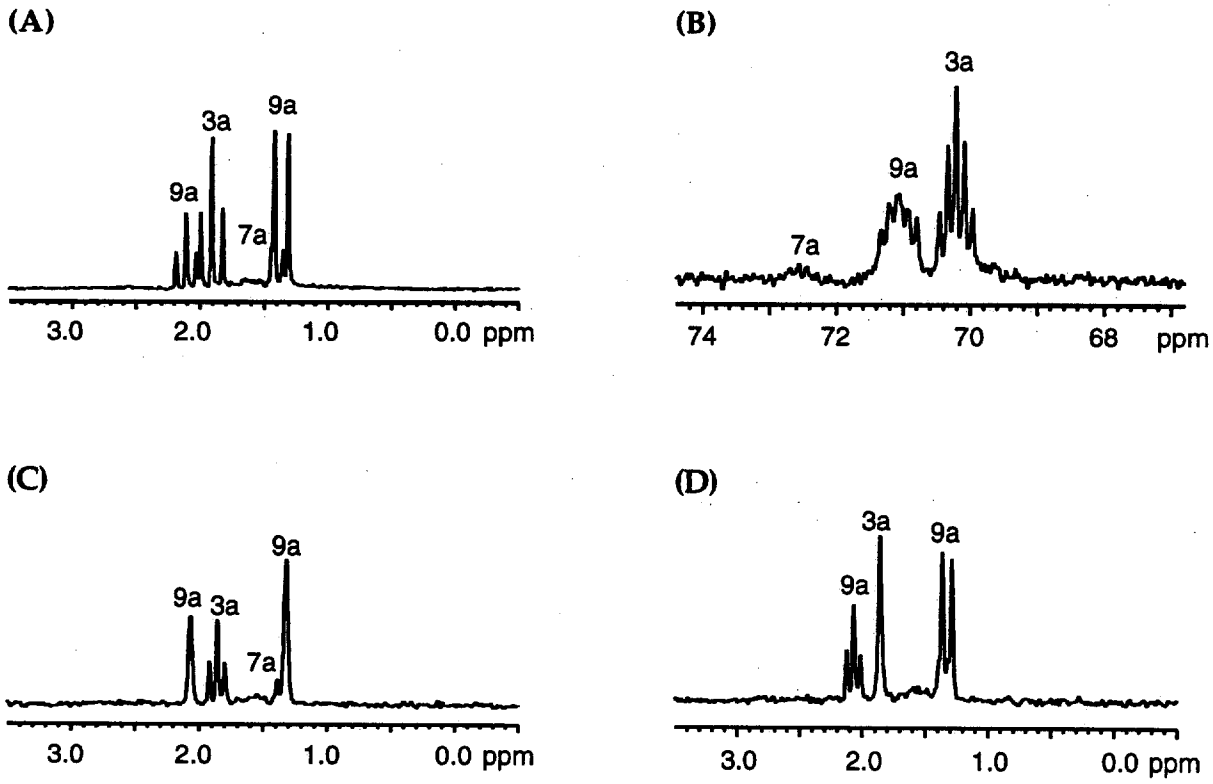


Figure II ^{6}Li and ^{15}N NMR spectra of 0.13 M [^{6}Li,^{15}N]LDA with 0.2 equiv/Li of ester **1**-d_1 in *t*-BuOMe at -60 °C after the sample reacted completely at -30 °C. **(A)** ^{6}Li spectrum; **(B)** ^{15}N spectrum. **(C)** ^{6}Li spectrum with ^{15}N single frequency decoupling at 71.1 ppm; **(D)** ^{6}Li spectrum with ^{15}N single frequency decoupling at 70.2 ppm.

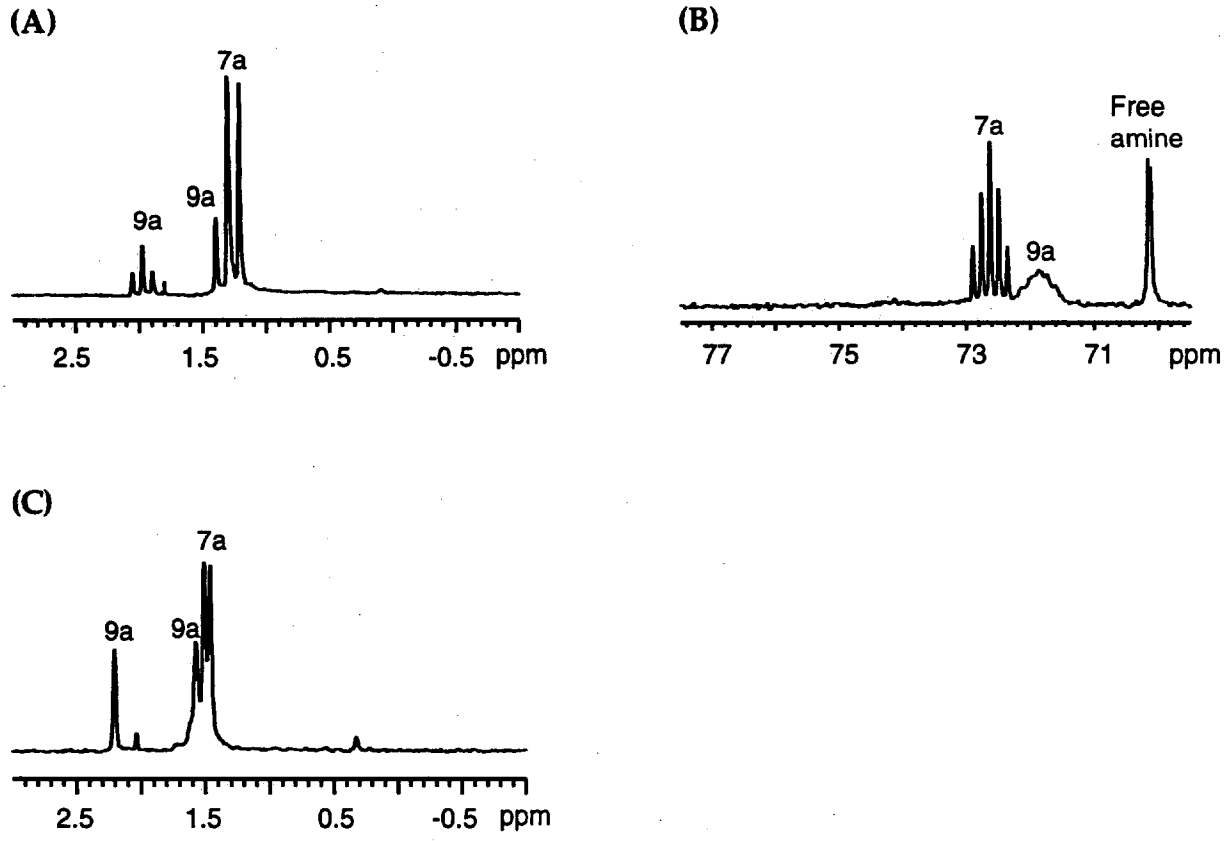


Figure III. ^{6}Li and ^{15}N NMR spectra of 0.13 M [^{6}Li,^{15}N]LDA with 0.13 M ester **1-d_1** in *t*-BuOMe at -60 °C after the sample was aged at -50 °C for 15 min. **(A)** ^{6}Li spectrum; **(B)** ^{15}N spectrum; **(C)** ^{6}Li spectrum with ^{15}N single frequency decoupling at 71.8 ppm.

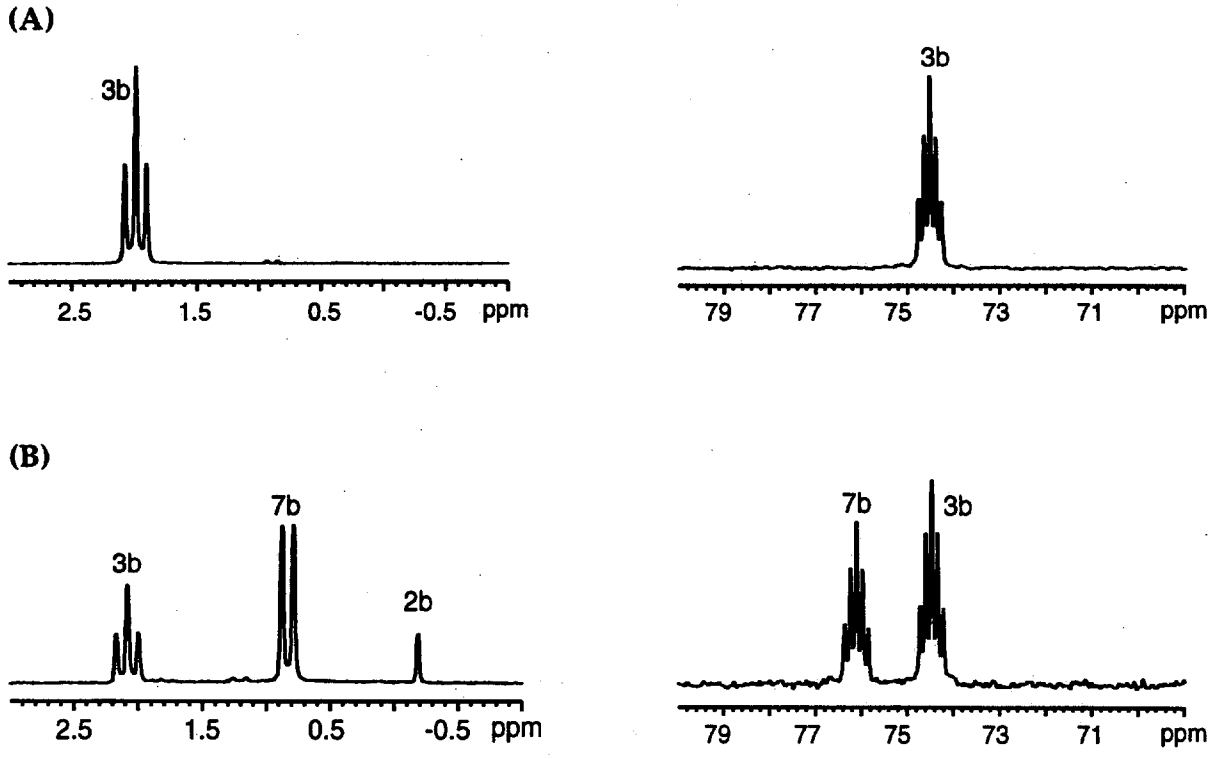


Figure IV. ^{6}Li and ^{15}N NMR spectra of 0.13 M [^{6}Li,^{15}N]LDA with 0.13 M ester **1-d_1** in THF at -90 °C . **(A)** ^{6}Li and ^{15}N spectra before the sample was aged. **(B)** ^{6}Li and ^{15}N spectra after the sample was aged at -50 °C for 2 min.

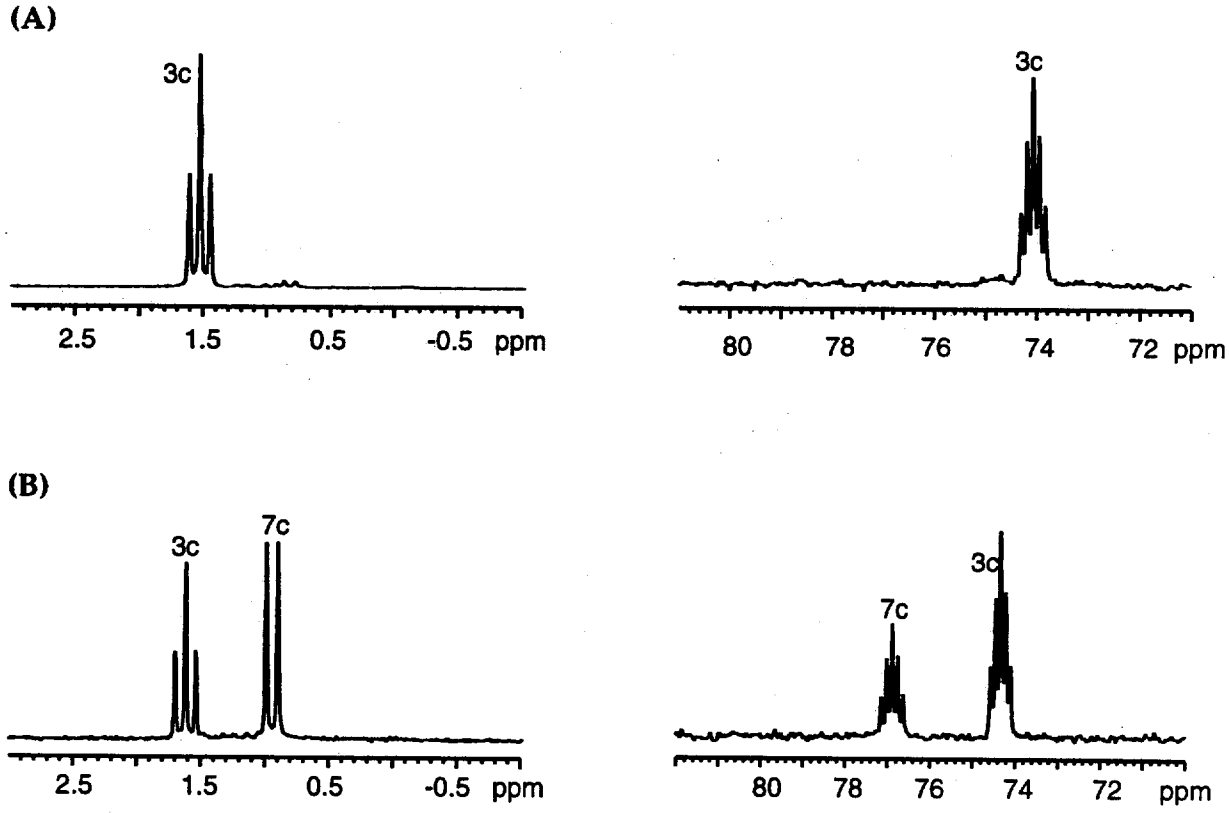


Figure V. ^{6}Li and ^{15}N NMR spectra of 0.13 M [^{6}Li,^{15}N]LDA with 0.13 M ester **1**-d_1 and 0.2 M HMPA in THF at -90 °C. **(A)** ^{6}Li and ^{15}N spectra recorded before the sample was aged. **(B)** ^{6}Li and ^{15}N spectra recorded after the sample was aged at -50 °C for 3 min.

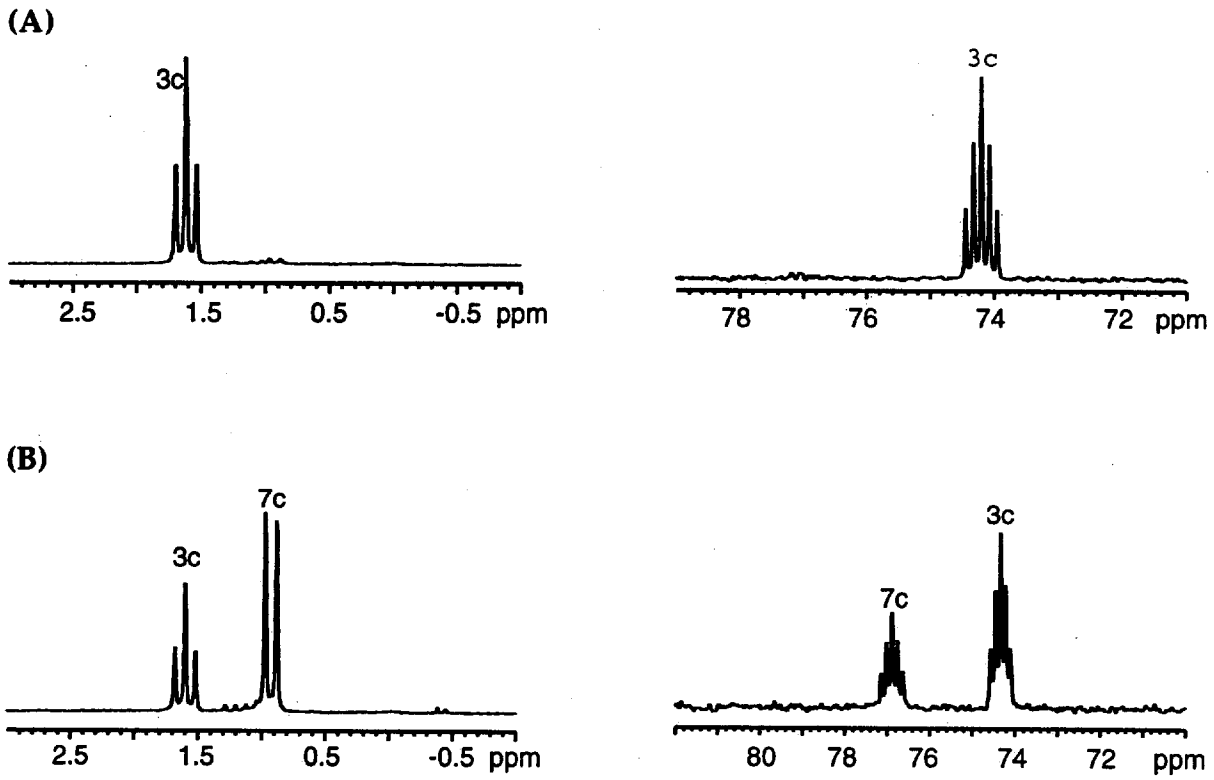


Figure VI. ^{6}Li and ^{15}N NMR spectra of 0.13 M [^{6}Li,^{15}N]LDA with 0.13 M ester **1-*d*$_1$** and 1 M HMPA in THF at -90 °C. **(A)** ^{6}Li and ^{15}N spectra recorded before the sample was aged. **(B)** ^{6}Li and ^{15}N spectra recorded after the sample was aged at -50 °C for 2 min.

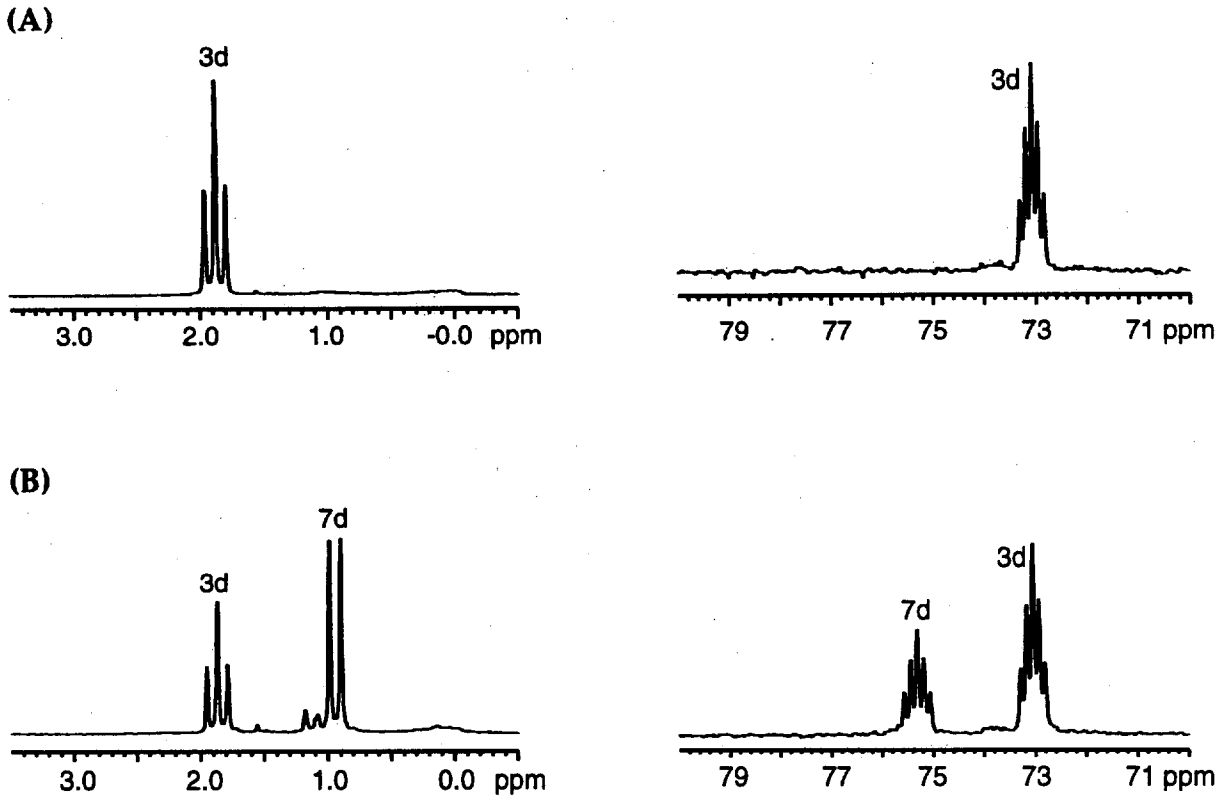


Figure VII. ^{6}Li and ^{15}N NMR spectra of 0.13 M [^{6}Li,^{15}N]LDA with 0.13 M ester **1-*d*$_1$** and 0.2 M DMPU in THF at -90 °C. **(A)** ^{6}Li and ^{15}N spectra before the sample was aged. **(B)** ^{6}Li and ^{15}N spectra after the sample was aged at -50 °C for 3 min.

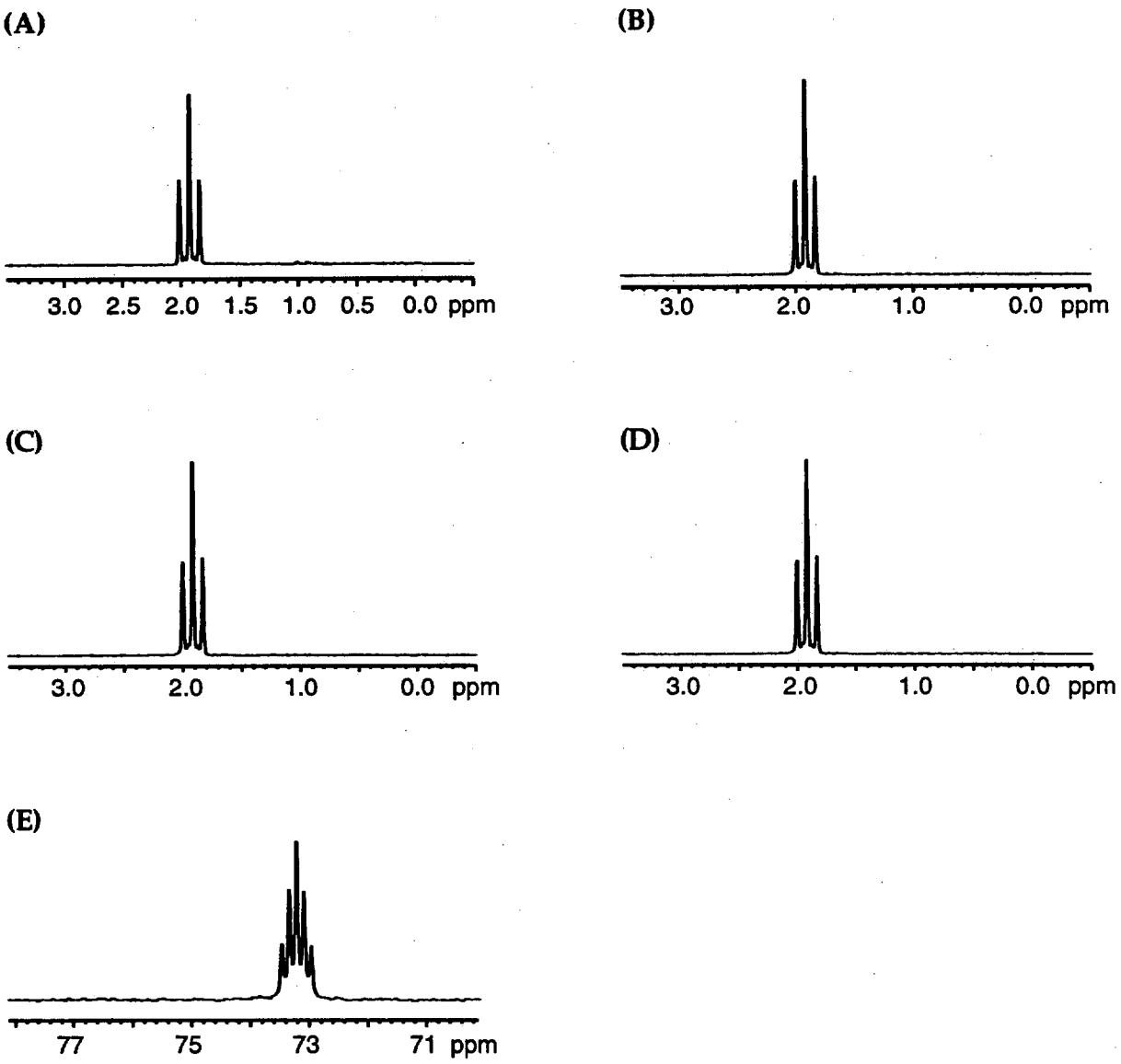


Figure VIII. ^{6}Li and ^{15}N NMR spectra of 0.1 M [^{6}Li,^{15}N]LDA in 2:1 THF/pentane at -90 °C. **(A)** ^{6}Li spectrum with no DMPU; **(B)** ^{6}Li spectrum with 0.5 eq DMPU; **(C)** ^{6}Li with 1 equiv DMPU; **(D)** ^{6}Li spectrum with 2 equiv DMPU; **(E)** ^{15}N spectrum with 2 equiv DMPU.

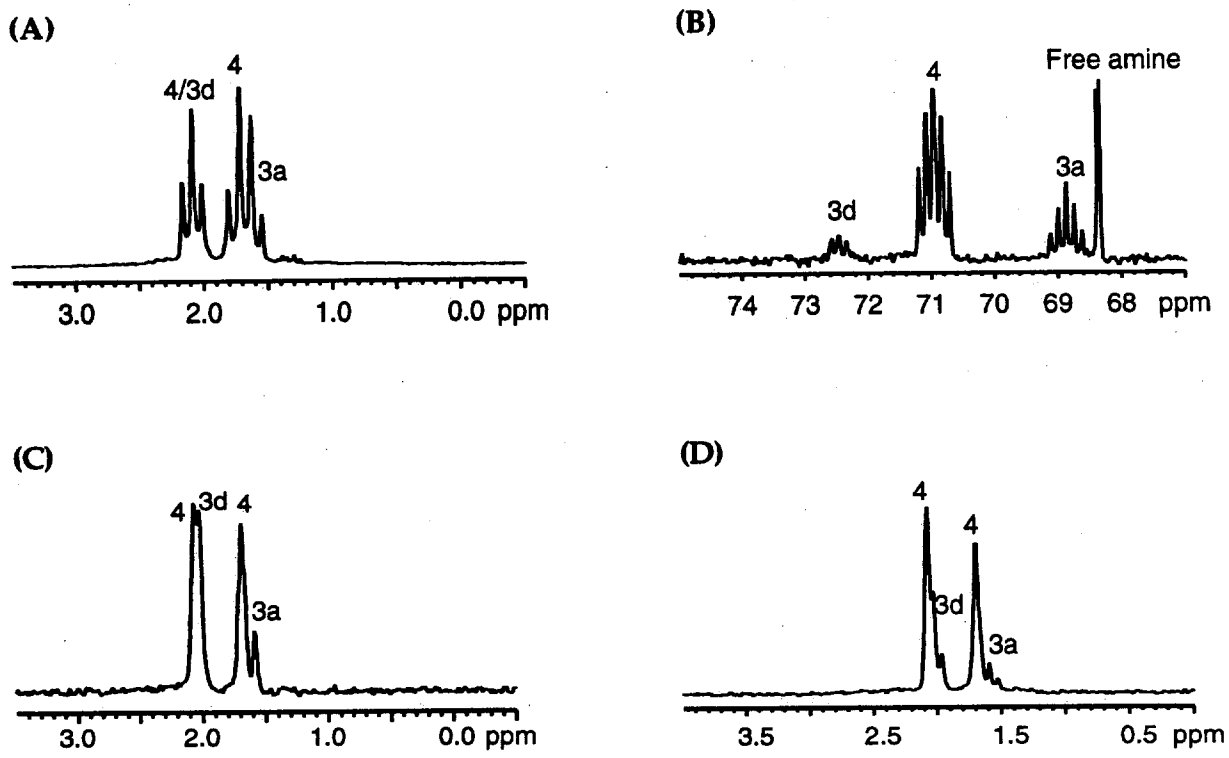


Figure IX. ^{6}Li and ^{15}N NMR spectra of 0.1 M [^{6}Li,^{15}N]LDA with 0.5 equiv DMPU in *t*-BuOMe at -90 °C. **(A)** ^{6}Li spectrum. **(B)** ^{15}N spectrum; **(C)** ^{6}Li spectrum with ^{15}N broad-band decoupling; **(D)** ^{6}Li spectrum with ^{15}N single frequency decoupling at 71.1 ppm.

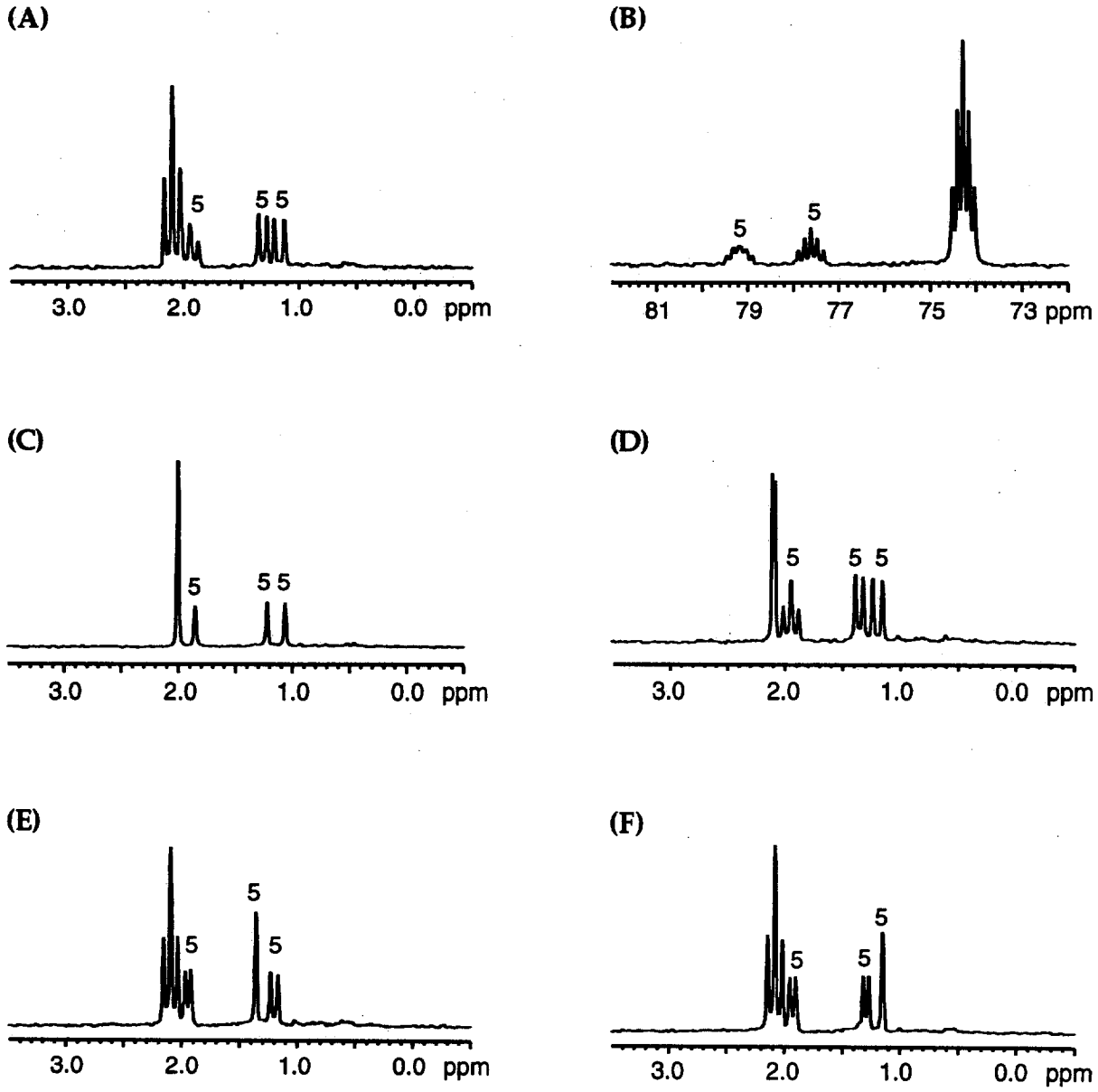


Figure X. ^{6}Li and ^{15}N NMR spectra of 0.1 M [^{6}Li,^{15}N]LDA with 0.5 equiv DMPU in 2:1 THF/pentane at -90 °C after the sample was aged at 0 °C for 8 h. **(A)** ^{6}Li spectrum; **(B)** ^{15}N spectrum; **(C)** ^{6}Li spectrum with ^{15}N broad-band decoupling; **(D)** ^{6}Li spectrum with ^{15}N single frequency decoupling at 74.3 ppm; **(E)** ^{6}Li spectrum with ^{15}N single frequency decoupling at 77.6 ppm; **(F)** ^{6}Li spectrum with ^{15}N single frequency decoupling at 79.1 ppm.

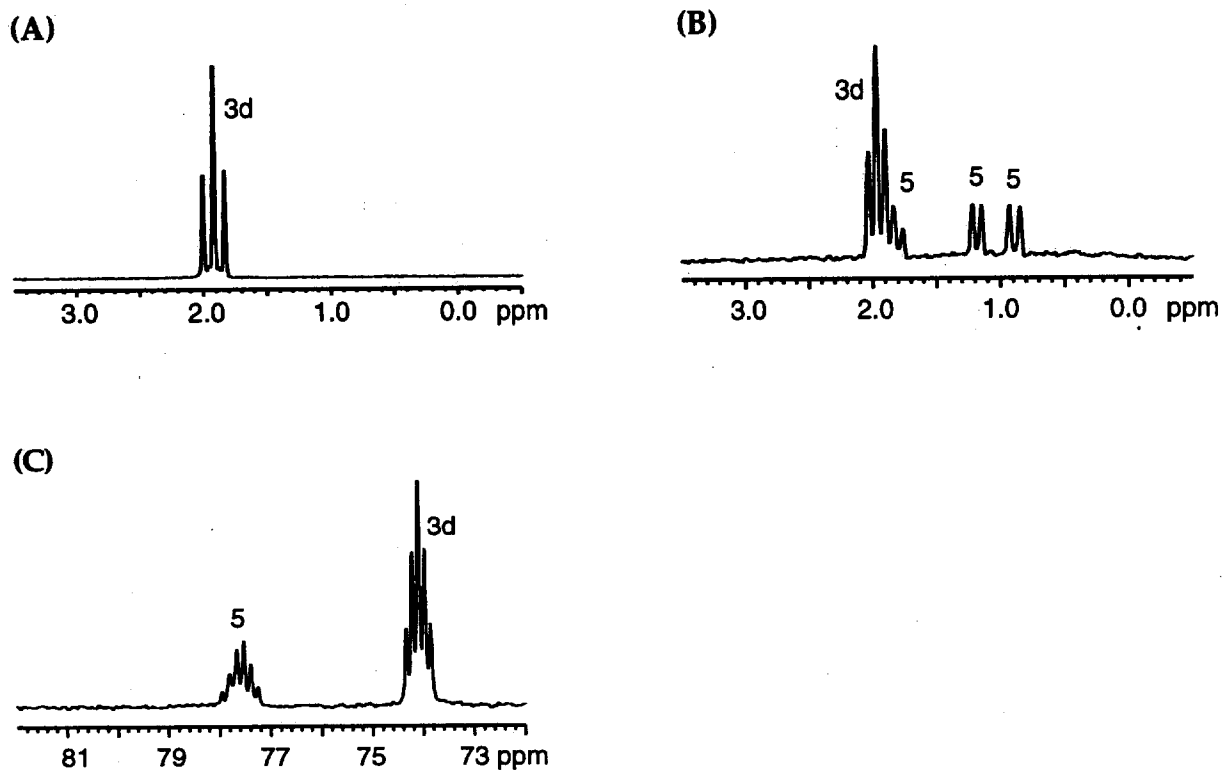


Figure XI. ^{6}Li and ^{15}N NMR spectra of 0.1 M [^{6}Li,^{15}N]LDA with 1.0 equiv/Li DMPU in 2:1 THF/pentane at -90 °C. **(A)** ^{6}Li spectrum; **(B)** ^{6}Li spectrum after the sample was aged at 0 °C for 3 h; **(C)** ^{15}N spectrum after the sample was aged. The two overlapping ^{15}N resonances of **5** are resolved at lower and higher DMPU concentration (**Figure X**, F and **Figure XII**, C.).

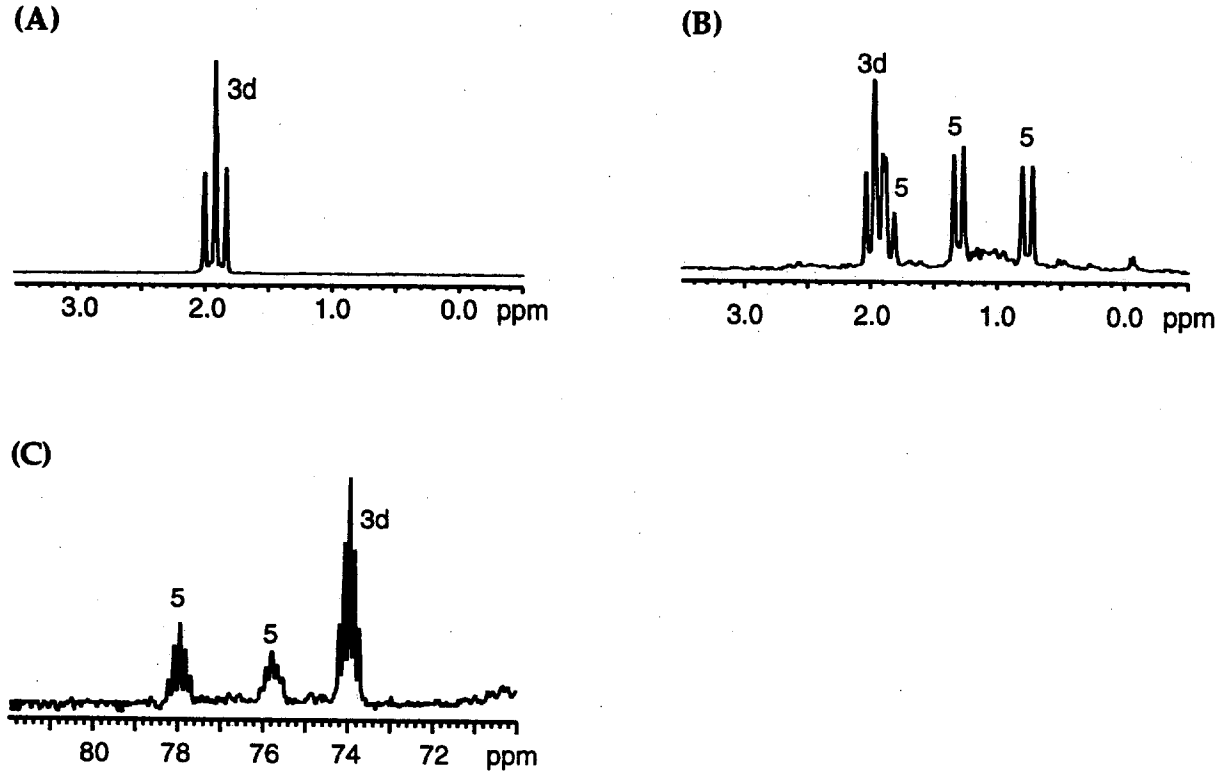


Figure XII. ^{6}Li and ^{15}N NMR spectra of 0.1 M [^{6}Li,^{15}N]LDA with 2.0 eq/Li DMPU in THF at -90 °C. **(A)** ^{6}Li spectrum; **(B)** ^{6}Li spectrum after the sample was aged at 0 °C for 2 h; **(C)** ^{15}N spectrum after the sample was aged.

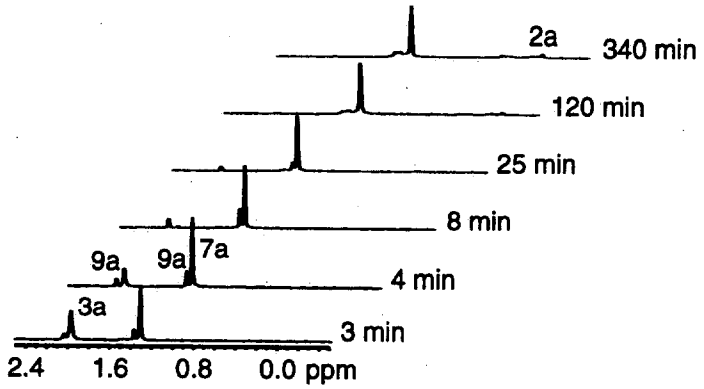


Figure XIII. ^{6}Li NMR spectra of the reaction of 0.1 M [^{6}Li]LDA with 0.1 M ester **1-d_1** in neat *t*-BuOMe at -50 °C.

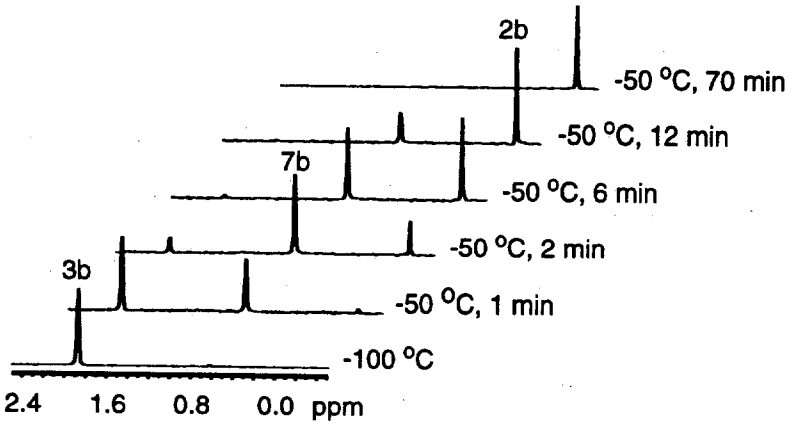


Figure XIV. ^{6}Li NMR spectra of the reaction of 0.1 M [^{6}Li]LDA with 0.1 M ester **1-d_1** in THF.

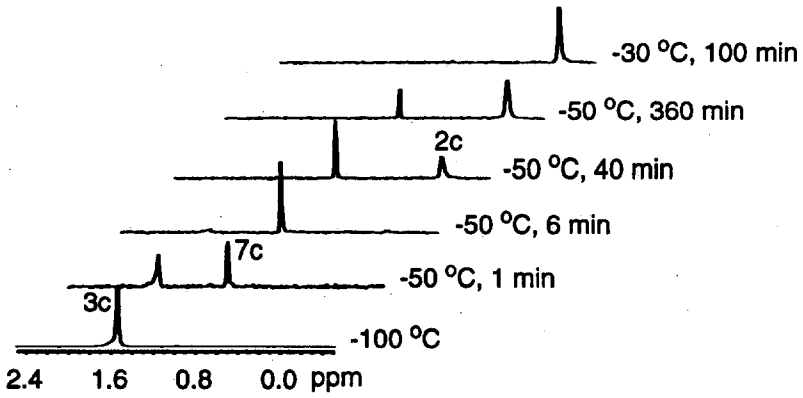


Figure XV. ^{6}Li NMR spectra of the reaction of 0.1 M [^{6}Li]LDA with 0.1 M ester **1-*d*$_1$** and 0.2 M HMPA in THF.

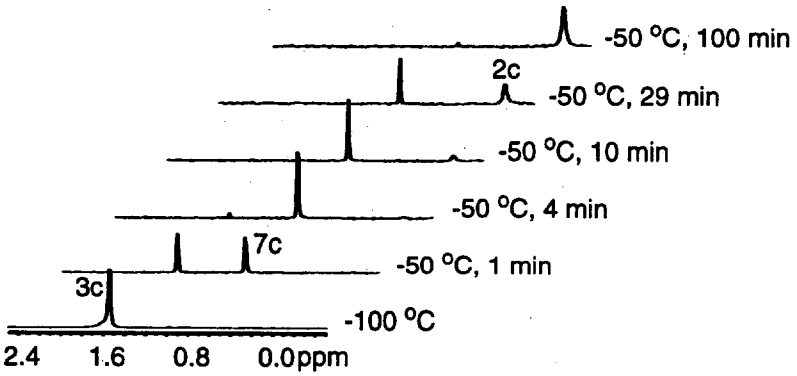


Figure XVI. ^{6}Li NMR spectra of the reaction of 0.1 M [^{6}Li]LDA with 0.1 M ester **1-*d*$_1$** and 1 M HMPA in THF.

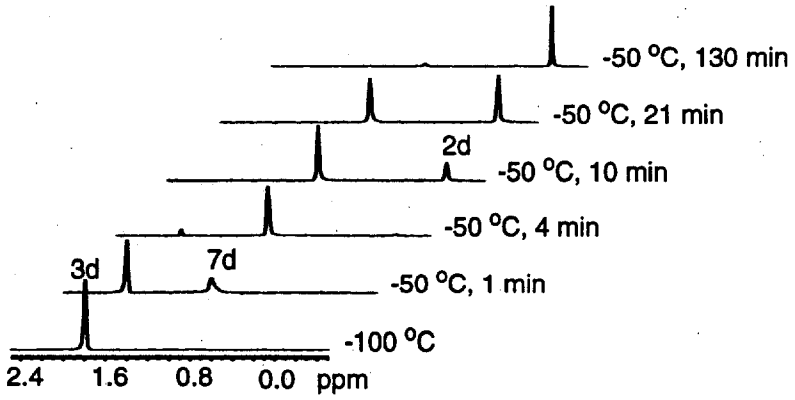


Figure XVII. ^{6}Li NMR spectra of the reaction of 0.1 M [^{6}Li]LDA with 0.1 M ester **1-*d*$_1$** and 0.2 M DMPU in THF.

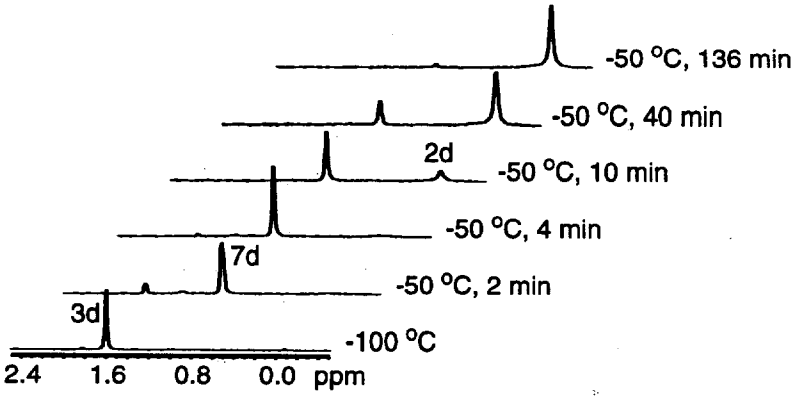
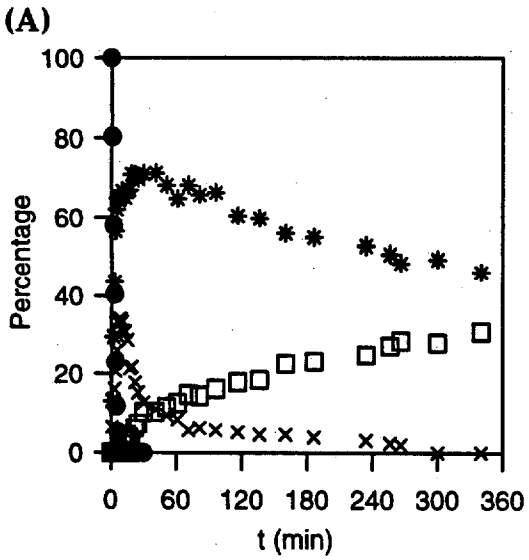
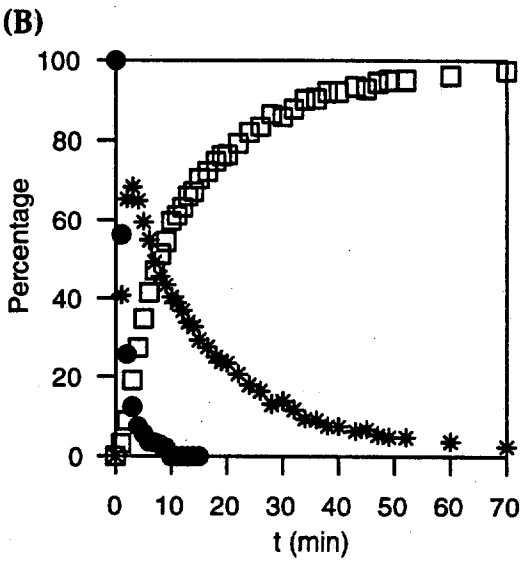
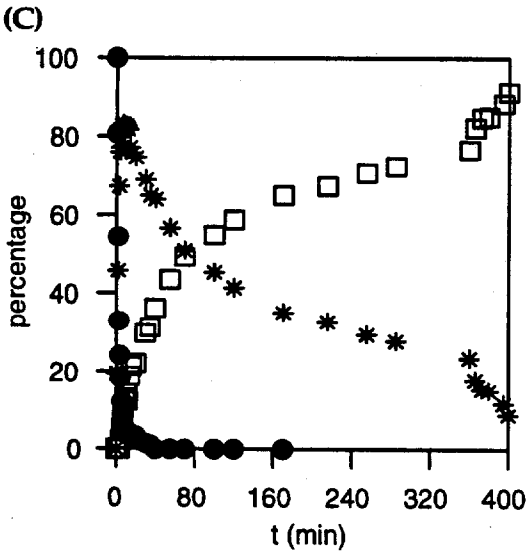
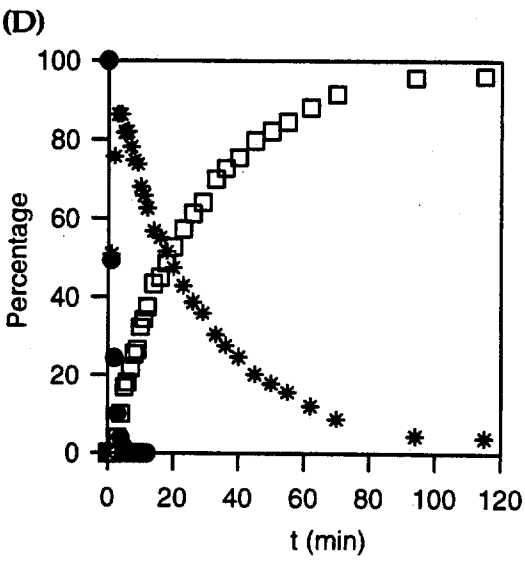


Figure XVIII. ^{6}Li NMR spectra of the reaction of 0.1M [^{6}Li]LDA with 0.1 M ester **1-*d*$_1$** and 1 M DMPU in THF.









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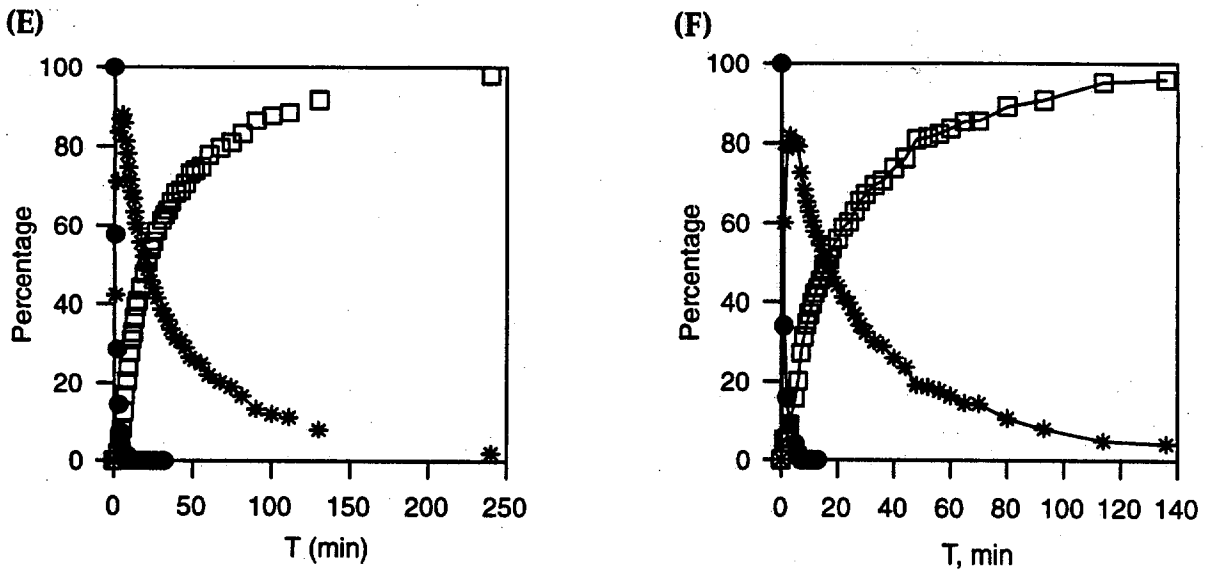

Figure XIX. Concentration of species vs. time for the reaction of 0.1 M [^{6}Li]LDA with 0.1 M ester **1-d_1** at -50 °C (as indicated by the percentage of integration in the ^{6}Li NMR spectra). Legend: • represents LDA dimers (**3a-d**); * represents LDA-enolate mixed dimers (**7a-d**); □ represents homonuclear enolate aggregates (**2a-d**); x represents mixed trimer (**9a**). **(A)** neat t-BuOMe; **(B)** neat THF; **(C)** 0.2 M HMPA in THF (The sample was warmed up to -30 °C in the last phase due to the slow rate of the reaction.); **(D)** 1.0 M HMPA in THF; **(E)** 0.2 M DMPU in THF; **(F)** 1.0 M DMPU in THF.

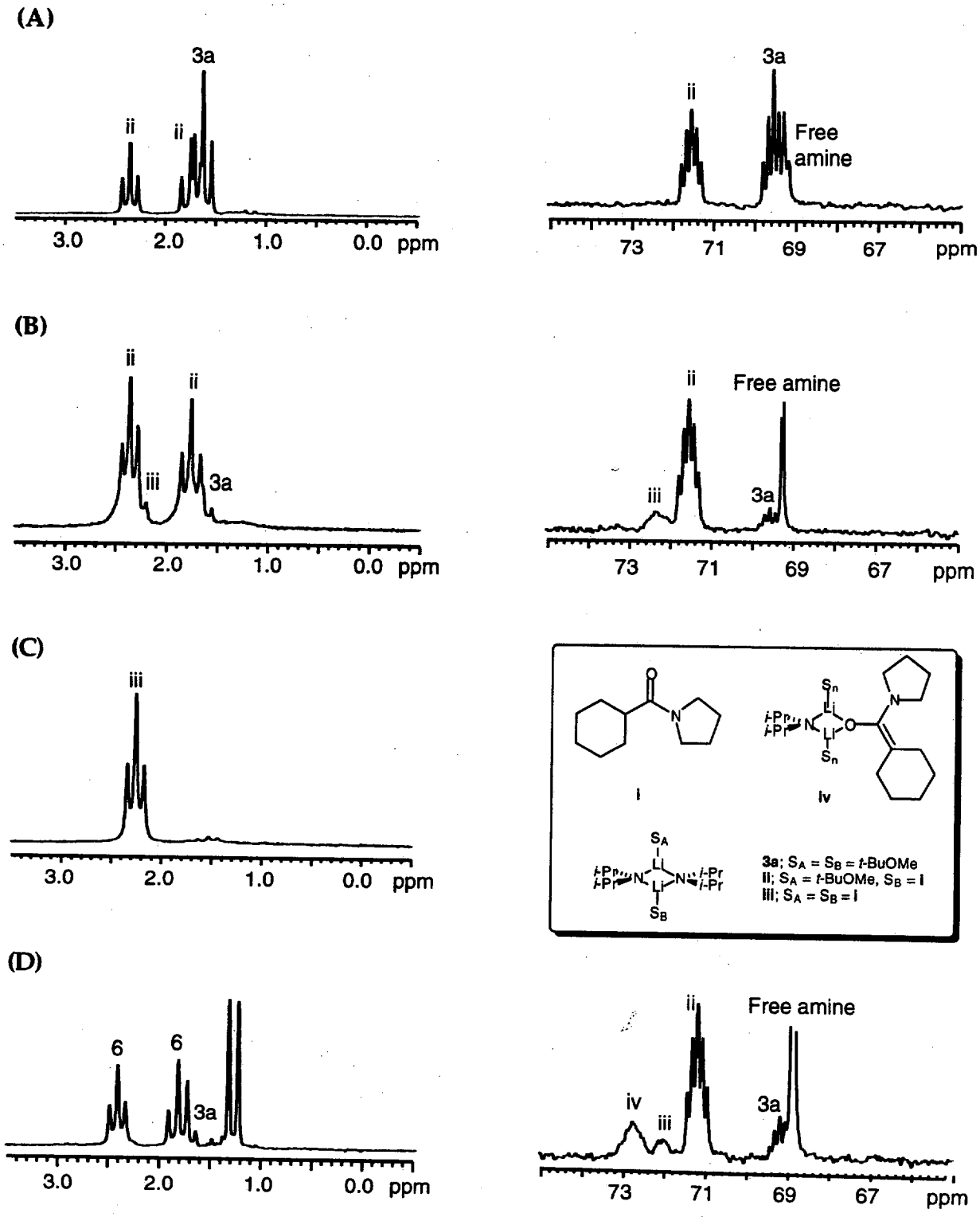

Figure XX. ^{6}Li and ^{15}N NMR spectra of 0.13 M [^{6}Li,^{15}N]LDA with carboxamide **i** in *t*-BuOMe at -100 °C. **(A)** ^{6}Li and ^{15}N spectra with 0.25 equiv/Li carboxamide **i**; **(B)** ^{6}Li and ^{15}N spectra with 0.5 equiv/Li carboxamide **i**; **(C)** ^{6}Li spectrum with 1 equiv/Li carboxamide **i**; **(D)** ^{6}Li and ^{15}N spectra with 0.5 equiv/Li carboxamide **i** after the sample was aged at -30 °C for 15 min.