I. Preparations of [^{6}Li,^{15}N]*t*-BuNHLi, [^{6}Li]**6**, [^{6}Li,^{15}N]**6a**, [^{6}Li,^{15}N]**6b**, and [^{6}Li,^{13}C]LiCCPh

[^{15}N]Pivaloylamide.[1] A solution of pivaloyl chloride (6.0 mL, 48.7 mmol) in Et_2O (20 mL) was layered above an aqueous solution of $^{15}NH_4Cl$ (2.0 g, 36.7 mmol). The solution was cooled to 0 °C, and 10 M NaOH (20 mL) was added to the aqueous layer. The biphasic mixture was gently stirred at rt for 15 min taking care not to mix the layers together. The mixture was cooled to 0 °C, Et_2O (15 mL) was added, and the flask was inverted several times. The resulting white precipitate was filtered off and pumped dry. Sublimation of the crude product afforded 2.58 g (69%) of [^{15}N]pivaloylamide. ^{1}H NMR ($CDCl_3$) δ 5.93 (d, $J_{^{15}N-^{1}H}$ = 88.8 Hz, 1H), 5.70 (d, $J_{^{15}N-^{1}H}$ = 88.8 Hz, 1H), 1.22 (d, $J_{^{15}N-^{1}H}$ = 18.3 Hz, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 181.5 (d, $J_{^{15}N-^{13}C}$ = 13.7 Hz), 38.6 (d, $J_{^{15}N-^{13}C}$ = 6.9 Hz), 27.6.

[^{15}N]*t*-Butylamine hydrochloride.[1] A 250 mL rb flask was placed in an ice bath and charged with 20% KOH (70 mL), Br_2 (1.92 mL, 37.3 mmol), and [^{15}N]pivaloylamide (2.58 g, 25.3 mmol). The solution was stirred at 0 °C for 80 min and rt for 20 min. The flask was cooled in an ice bath, and Et_2O (10 mL) was added. Concentrated HCl was added (maintaining an internal temperature <15 °C) until the solution was distinctly acidic. The solution was stirred at 50 °C for 20 min to complete hydrolysis of the isocyanate. The flask was cooled to 0 °C, Et_2O (80 mL) was added, and KOH pellets were added until the aqueous layer was basic. The aqueous and ethereal layers were separated and gaseous HCl was passed through the ethereal layer to precipitate [^{15}N]*t*-butylamine hydrochloride. The ppt was washed with 10 mL of cold Et_2O and dried in vacuo to give 2.03 g (73%) of [^{15}N]*t*-BuNH$_3$Cl. ^{1}H NMR (D_2O) δ 1.35 (d, $J_{^{15}N-^{1}H}$ = 2.7 Hz). ^{13}C{^{1}H} NMR (D_2O, referenced to added dioxane at 67.4) δ 52.8 (d, $J_{^{15}N-^{13}C}$ = 3.8 Hz), 27.4.

[^{6}Li,^{15}N]Lithium *t*-Butylamide.[1,2] [^{15}N]*t*-butylamine hydrochloride (1.87 g, 17.0 mmol) and CaH_2 (1 g) were added to a 50 mL rb flask containing a high boiling amine (*N,N*-dibutylethylenediamine, 18 mL). Short-path distillation from a 120 °C oil bath into a collecting flask cooled to -78 °C afforded 1.2 mL (66%) of [^{15}N]*t*-butylamine. The amine was dissolved in 60 mL pentane, cooled to -78 °C, and treated with [^{6}Li]*n*-BuLi (1.42 M solution in pentane, 10.3 mmol), affording immediate precipitation of [^{6}Li]lithium *t*-butylamide. Following stirring at rt for 30 min, the resulting precipitate could be isolated by filtration. Alternatively, removal of the pentane in vacuo afforded 770 mg (94%) of crude lithium amide. Sublimation under vacuum in a 130-150 °C bath yielded 575 mg (71%).[3]

[^{15}N]Benzamide. A solution of benzoyl chloride (15.0 mL, 129 mmol) in Et_2O (25 mL) was layered upon an aqueous solution of $^{15}NH_4Cl$ (3.0 g, 56 mmol), cooled to 0 °C, and treated with 10 M NaOH (20 mL). The biphasic mixture was stirred at 0 °C for 5 minutes, at which point the reaction became quite vigorous. The resulting white precipitate was filtered off. The white solid was partitioned between EtOAc and 10% $NaHCO_3$. The EtOAc layer was dried over Na_2SO_4, filtered, and concentrated in vacuo to afford 5.46 g (80%) of [^{15}N]benzamide. ^{1}H NMR ($CDCl_3$) δ 7.84 (m, 2H), 7.43-7.53 (m, 3H), 6.37 (s, 1H), 6.15 (s, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 169.6 (d, $J_{^{15}N-^{13}C}$ = 15.3 Hz), 133.4 (d, $J_{^{15}N-^{13}C}$ = 8.4 Hz), 132.0, 128.6, 127.3.

[^{15}N]*N*-benzoylpyrrolidine.[4] A 250 mL rb flask was charged with [^{15}N]benzamide (4.5 g, 36.8 mmol), K_2CO_3 (7.2 g, 52 mmol), *t*-Bu_4NHSO_4 (1.2 g, 3.53 mmol), finely powdered NaOH (7.4 g, 185 mmol), and dry toluene (120 mL). Following dropwise addition of 1,4-Dibromobutane (6.6 mL, 55.3 mmol) in dry toluene (30 mL), the reaction was heated at 100 °C for 13 hours. The reaction mixture was cooled, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography (70:30 EtOAc/hexane followed by 95:5 EtOAc/Et_3N), yielding 6.03 g (93%) of [^{15}N]*N*-benzoylpyrrolidine. ^{1}H NMR ($CDCl_3$) δ

7.33-7.48 (m, 5H), 3.3-3.6 (m, 4H), 1.7-1.9 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 169.0 (d, $J_{^{15}N-^{13}C}$ = 16.0 Hz), 136.7 (d, $J_{^{15}N-^{13}C}$ = 7.6 Hz), 129.2, 127.7, 126.5, 49.5 (d, $J_{^{15}N-^{13}C}$ = 9.2 Hz), 45.6 (d, $J_{^{15}N-^{13}C}$ = 9.9 Hz), 25.8, 23.9 (d, $J_{^{15}N-^{13}C}$ = 1.5 Hz).

[^{15}N]Pyrrolidine hydrochloride.[5] A 100 mL pear-shaped flask cooled to 0 °C was charged with dry THF (15 mL), Dibal (1.0 M solution in heptane, 50 mL, 50 mmol), and a 1.28 M hexane solution of *n*-BuLi (37 mL, 47.3 mmol). The solution was stirred for 90 min at 0 °C and then transferred via cannula to a solution of [^{15}N]*N*-benzoylpyrolidine (5.915 g, 33.6 mmol) in THF (100 mL). The solution was stirred at 0 °C for 60 min at which point GC analysis indicated complete conversion of the benzamide to benzaldehyde. 4 N KOH (90 mL) was added to the reaction, and the volatiles were distilled in vacuo. Additional THF (4 x 100 mL) was added to the reaction flask and volatiles were again distilled in vacuo. The combined distillate treated with concentrated HCl and concentrated in vacuo, yielding 1.68 g of [^{15}N]pyrrolidine hydrochloride (46%). ^1H NMR (D_2O) δ 3.27 (m, 4H), 1.99 (m, 4H) $^{13}C\{^1H\}$ NMR (D_2O, referenced to added dioxane at δ 67.4 ppm) δ 46.3 (d, $J_{^{15}N-^{13}C}$ = 4.6 Hz), 24.5.

[^{15}N-Pyrrolidino] (R)-1-amino-1-phenyl-2-pyrrolidinoethane.[6] A solution of [^{15}N]pyrrolidine hydrochloride (1.68 g, 15.5 mmol) in EtOH (125 mL) was treated with Et_3N (10.8 mL, 77 mmol) and (R)-styrene oxide (1.95 mL, 17.1 mmol). The solution was refluxed for 12 hours and then concentrated in vacuo. The residue was partitioned between EtOAc and 10% $NaHCO_3$, and the aqueous phase was extracted with EtOAc. The combined organics were dried over Na_2SO_4, filtered, and concentrated in vacuo to afford the crude amino alcohols corresponding to a regioisomeric mixture of epoxide cleavage products. Flash chromatography (EtOAc with 5% Et_3N followed by 1:1:1 Et_3N/EtOAc/MeOH) afforded 1.68 g (57%) of an unseparated mixture of [^{15}N-pyrrolidino] (R)-1-hydroxy-1-phenyl-2-

pyrrolidinoethane and [^{15}N-pyrrolidino] (S)-2-hydroxy-1-phenyl-1-pyrrolidinoethane. ^{1}H NMR ($CDCl_3$) δ 7.24-7.39 (m), 4.71 (dd, J = 10.7 Hz, 3.0 Hz), 3.84 (m), 3.47 (t, J = 6.1 Hz), 2.76 (m), 2.48 (m), 1.77 (m). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 142.4, 139.0, 128.6, 128.30, 128.27, 127.6, 127.4, 125.8, 70.7, 69.7, 64.2 (d, $J_{^{15}N-^{13}C}$ = 3.1 Hz), 64.1 (d, $J_{^{15}N-^{13}C}$ = 3.8 Hz), 53.8 (d, $J_{^{15}N-^{13}C}$ = 4.6 Hz), 51.1 (d, $J_{^{15}N-^{13}C}$ = 4.6 Hz), 23.7 (d, $J_{^{15}N-^{13}C}$ = 2.3 Hz), 23.1 (d, $J_{^{15}N-^{13}C}$ = 3.1 Hz). The mixture of amino alcohols (1.50 g, 7.8 mmol) was dissolved in dry Et_2O (50 mL) and Et_3N (2.2 mL), cooled to 0 °C, treated with MsCl (0.66 mL, 8.5 mmol) dropwise, and stirred at 0 °C for 50 min. Following addition of Et_3N (3.3 mL) and NH_4OH (30% aq solution, 25 mL), the biphasic mixture was stirred at rt for 13 hours. The layers were separated, and the aqueous layer was extracted with Et_2O. The combined organics were dried over Na_2SO_4, filtered, and concentrated in vacuo. Flash chromatography (1:1 EtOAc/hexane with 5% Et_3N followed by 1:1:1 Et_3N/EtOAc/MeOH) afforded 820 mg (66%) of amine. ^{1}H NMR ($CDCl_3$) δ 7.22-7.39 (m, 5H), 4.08 (dd, J = 3.4, 10.4 Hz, 1H), 2.77 (m, 1H), 2.64 (m, 2H), 2.49 (m, 2H), 2.37 (dd, J = 12.0, 3.5 Hz, 1H), 2.04 (bs, 2H), 1.76-1.99 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 144.6 (d, $J_{^{15}N-C}$ = 1.5 Hz), 128.3, 127.0, 126.6, 65.0 (d, $J_{^{15}N-C}$ = 3.8 Hz), 54.5, 54.2 (d, $J_{^{15}N-^{13}C}$ = 3.8 Hz), 23.5 (d, $J_{^{15}N-^{13}C}$ = 3.1 Hz).

[^{15}N](R)-1-amino-1-phenyl-2-pyrrolidinoethane.[6] The $^{15}NH_2$-labelled amine was prepared as follows. To a solution of (R)-1-hydroxy-1-phenyl-2-pyrrolidinoethane and (S)-2-hydroxy-1-phenyl-1-pyrrolidinoethane (5.2 g, 27.7 mmol) in dry Et_2O (150 mL) and Et_3N (7.7 mL) at 0 °C was added MsCl (2.15 mL, 27.8 mmol) dropwise. After stirring at 0 °C for 1 hr and warming to rt, Et_3N (11.6 mL), and $^{15}NH_4Cl$ (1.7 g, 31.2 mmol) in H_2O (20 mL) were added sequentially. The flask was sealed and the reaction was stirred at rt for 16 hours. The layers were separated, the aqueous layer was extracted with Et_2O, and the combined organics were dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by

flash chromatography (1:1 EtOAc/hexane with 5% Et_3N followed by 1:1:1 Et_3N/EtOAc/MeOH), yielding 1.97 g (37%) of amine. ^1H NMR ($CDCl_3$) δ 7.20-7.38 (m, 5H), 4.05 (dd, J = 3.4, 10.5, 1H), 2.78 (m, 1H), 2.65 (m, 2H), 2.48 (m, 2H), 2.36 (m, 1H), 2.21 (s, 2H), 1.75 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 144.37 (d, $J_{^{15}N-^{13}C}$ = 1.5 Hz), 128.22, 126.95, 126.49, 64.79 (d, $J_{^{15}N-^{13}C}$ = 1.5 Hz) 54.38 (d, $J_{^{15}N-^{13}C}$ = 4.6 Hz), 54.11, 23.43.

[^{6}Li,^{15}N] (R)-1-Li-amido-1-phenyl-2-pyrrolidinoethane. The $^{15}NH_2$-labelled lithium amide was prepared as follows. [^{15}N-NH_2] (R)-1-amino-1-phenyl-2-pyrrolidinoethane (1.78 g, 9.3 mmol) was vacuum distilled from CaH_2 into a tared Schlenk flask, affording 1.39 g (7.27 mmol). After the Schlenk tube was evacuated and backfilled with Ar several times, pentane (10 mL) was added via syringe. The solution was cooled to -78 °C and [^{6}Li]*n*-BuLi (6.94 mmol, solution in pentane) was added over several minutes, affording a white precipitate and a pale yellow filtrate. After storing the suspension in a -95 °C freezer for several days, the filtrate was removed via syringe and the remaining solid was dried in vacuo to obtain 1.05 g (77%) of **6a** as an off-white solid. Lithium amides **6** and **6b** were similarly prepared from the corresponding amine and [^{6}Li]*n*-BuLi.

[^{6}Li,^{13}C] Lithium phenylacetylide.[7] A solution of [^{13}C] phenylacetylene (1.87 g, 18.1 mmol) in dry pentane (20 mL) was dried by addition of freshly recrystallized *n*-BuLi in pentane (0.34 mmol in total) until a white precipitate began to form. The turbid mixture was vacuum transferred into a Schlenk tube. The residue was rinsed with dry pentane (2 x 10 mL) and the volatiles were also vacuum transferred into the Schlenk tube. The resulting distillate was cooled to -78 °C and treated with a pentane solution of [^{6}Li]*n*-BuLi (17.0 mmol). Although some lithium phenylacetylide precipitated immediately, the suspension was stirred at rt for 15 min and then stored at -95 °C for 4 days. Following removal of the peach colored filtrate via syringe, the off-white solid was rinsed with pentane (20 mL). After the solid had

settled to the bottom of the Schlenk tube and the filtrate was removed via syringe, the resulting solid was dried in vacuo to give 1.23 g (69%) of [^{6}Li,^{13}C]lithium phenylacetylide.

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3. Sublimation of [^{6}Li,^{15}N]*t*-BuNHLi was sometimes, but not always, an effective means of purification.

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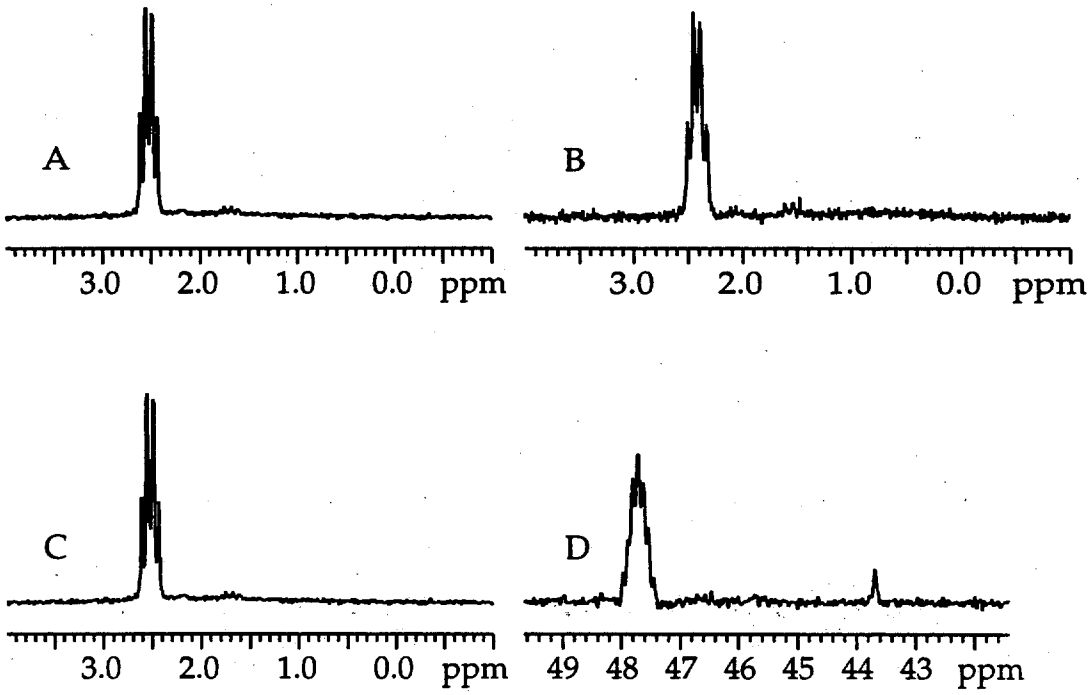
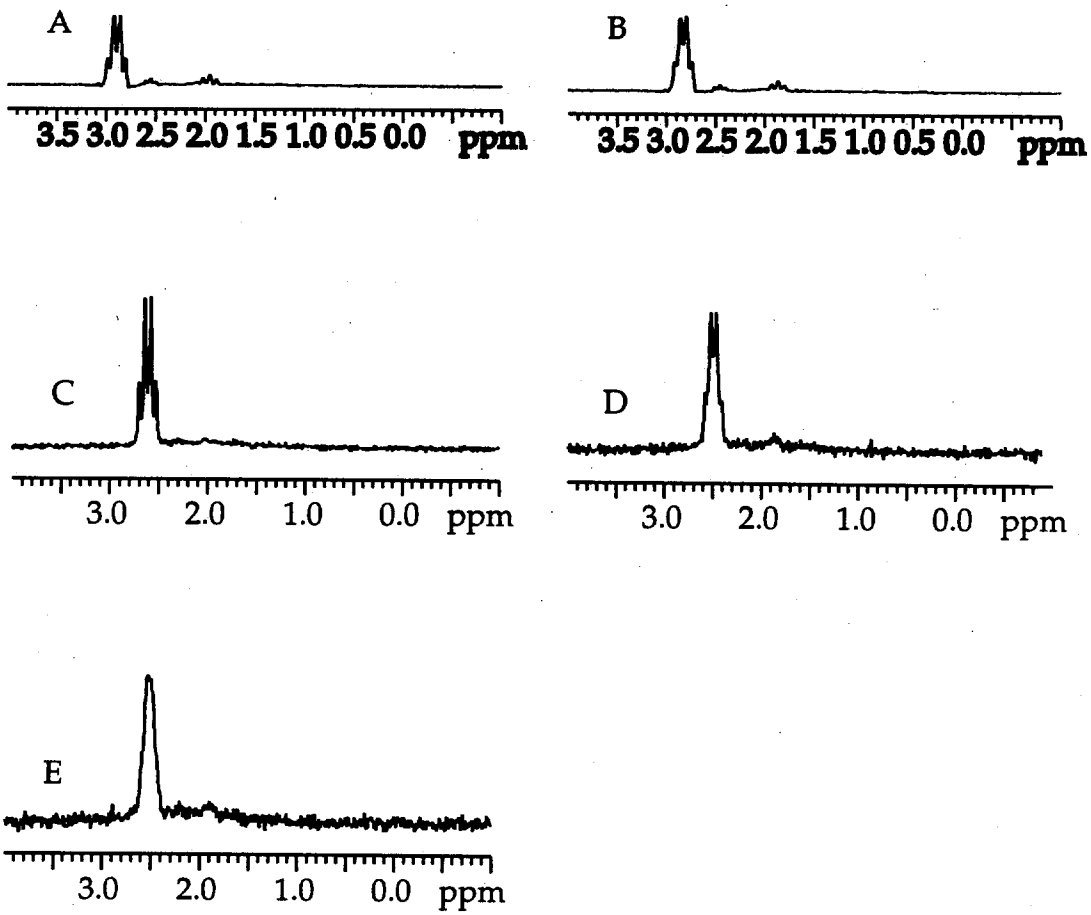
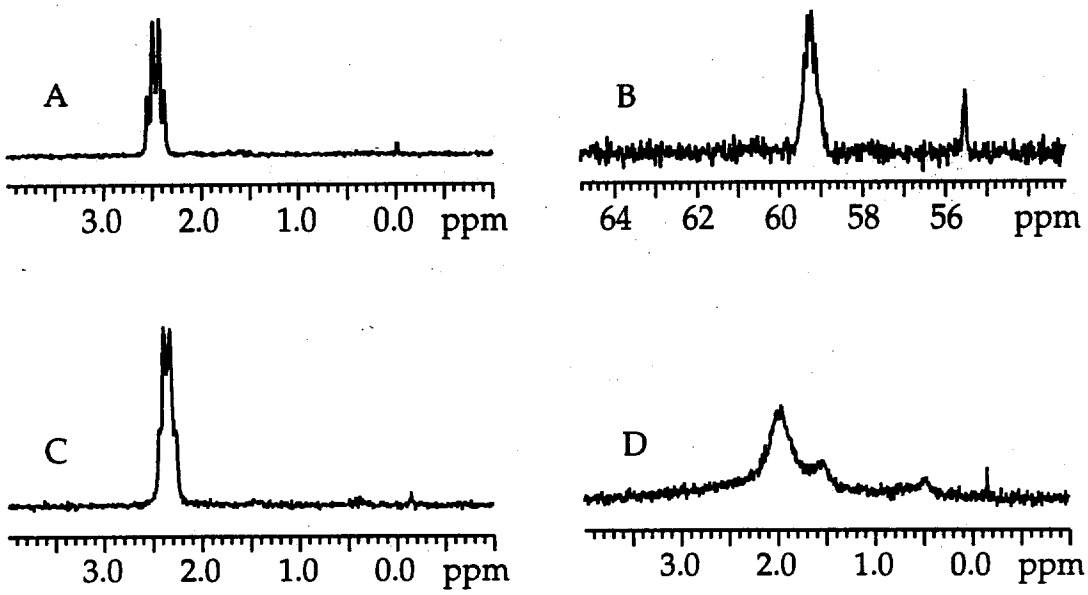


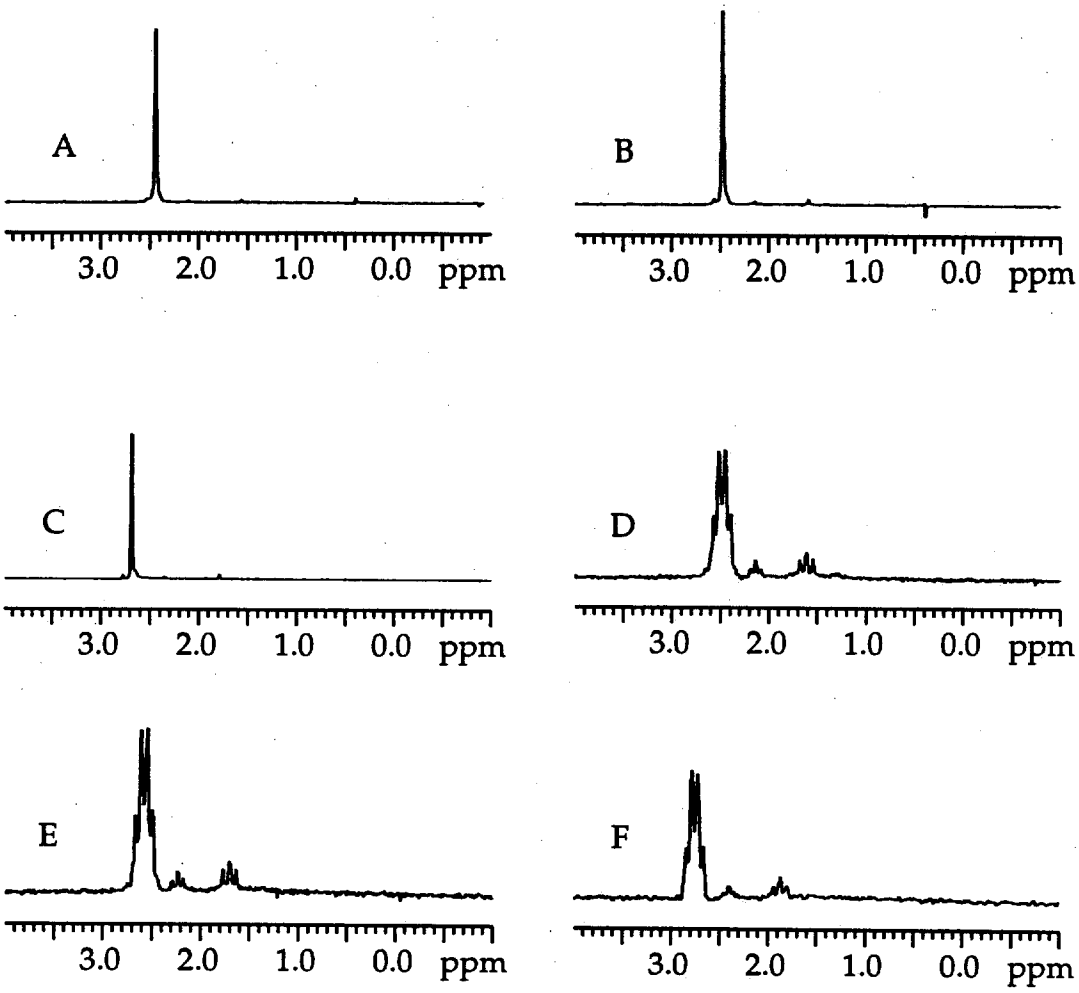
II. ^{6}Li and ^{15}N NMR spectra of 0.1 M [^{6}Li,^{15}N]*t*-BuNHLi in toluene solution: (A) ^{6}Li NMR spectrum at -90 °C; (B) ^{6}Li NMR spectrum at -60 °C; (C) ^{6}Li NMR spectrum at -30 °C; (D) ^{15}N NMR spectrum at -30 °C.



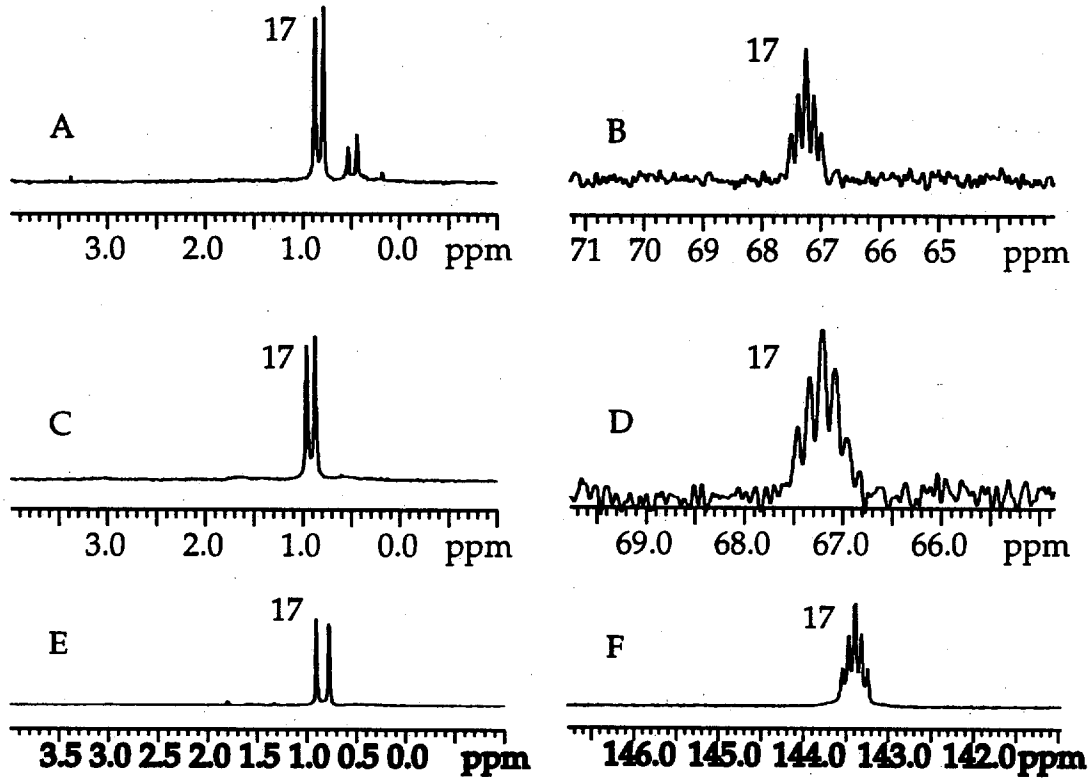
III. ^{6}Li NMR spectra of 0.1 M [^{6}Li,^{15}N]*t*-BuNHLi: (A) 1:1 pentane/Et_2O solution at -100 °C; (B) 1:1 pentane/Et_2O solution at -128 °C; (C) toluene solution at 15 °C; (D) toluene solution at 30 °C; (E) toluene solution at 40 °C.



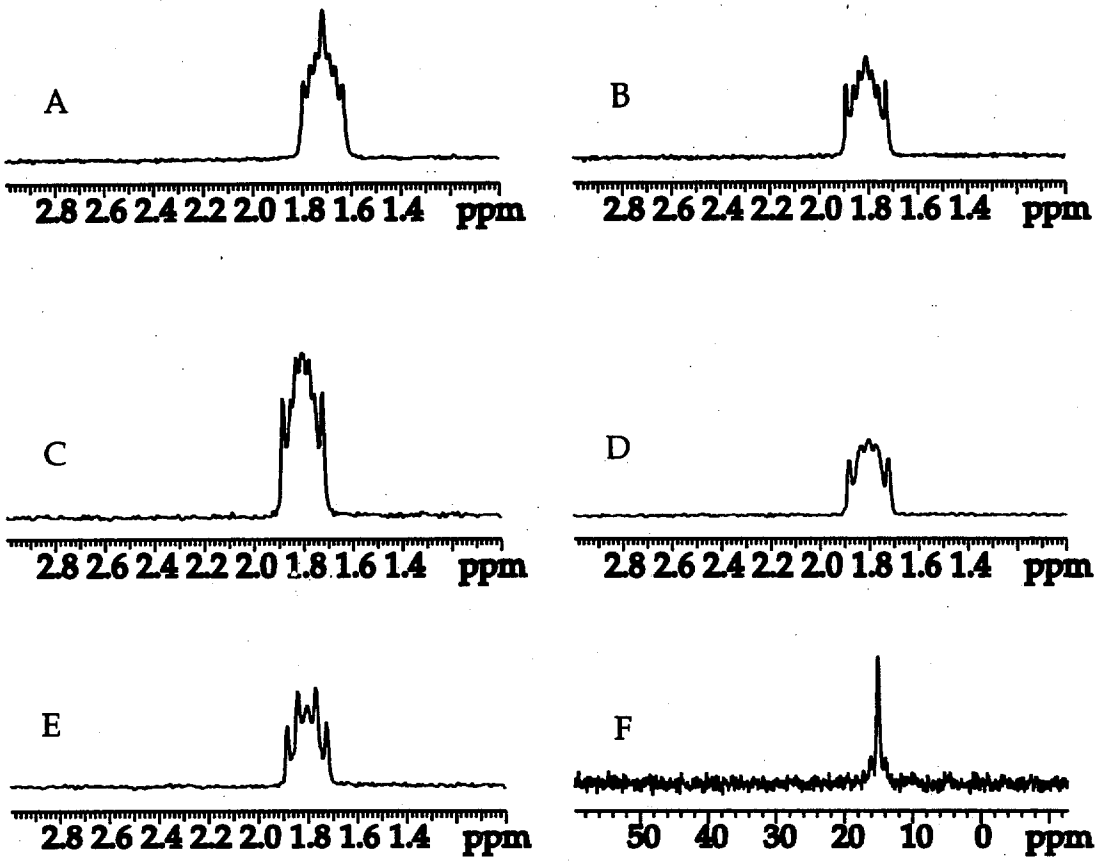
IV. ^{6}Li and ^{15}N NMR spectra of 0.1 M [^{6}Li,^{15}N]*t*-BuNHLi in toluene solution with THF: (A) ^{6}Li NMR spectrum at -80 °C with 1.0 equiv THF; (B) ^{15}N NMR spectrum at -60 °C with 1.0 equiv THF; (C) ^{6}Li NMR spectrum at -80 °C with 2.0 equiv THF; (D) ^{6}Li NMR spectrum at -80 °C with 50 equiv THF.



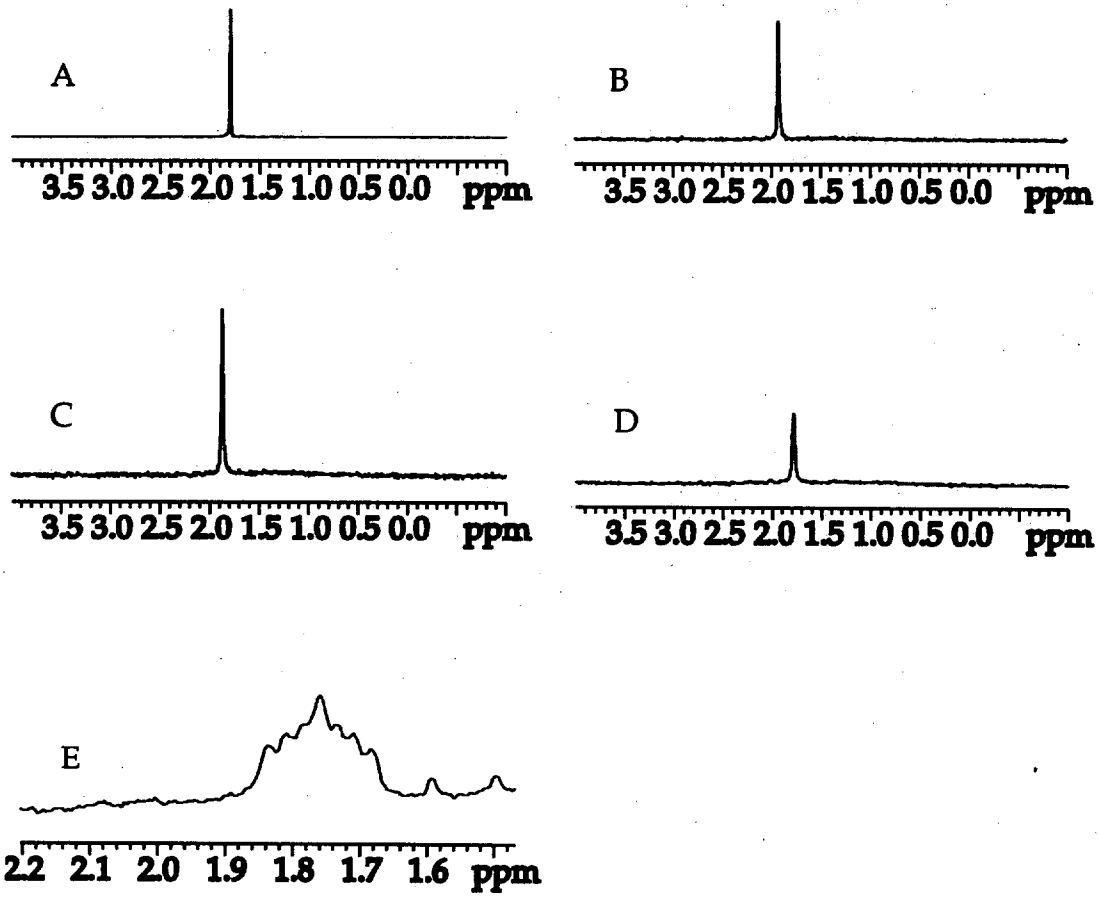
V. ^{6}Li NMR spectra in toluene solution: (A) 0.1 M [^{6}Li]*t*-BuNHLi with 2.0 equiv Et_2O at -80 °C; (B) 0.1 M [^{6}Li]*t*-BuNHLi with 10 equiv Et_2O at -80 °C; (C) 0.1 M [^{6}Li]*t*-BuNHLi with 50 equiv Et_2O at -80 °C; (D) 0.1 M [^{6}Li,^{15}N]*t*-BuNHLi with 5.0 equiv Et_2O at -60 °C; (E) 0.1 M [^{6}Li,^{15}N]*t*-BuNHLi with 25 equiv Et_2O at -60 °C; (F) 0.1 M [^{6}Li,^{15}N]*t*-BuNHLi with 50 equiv Et_2O at -60 °C.



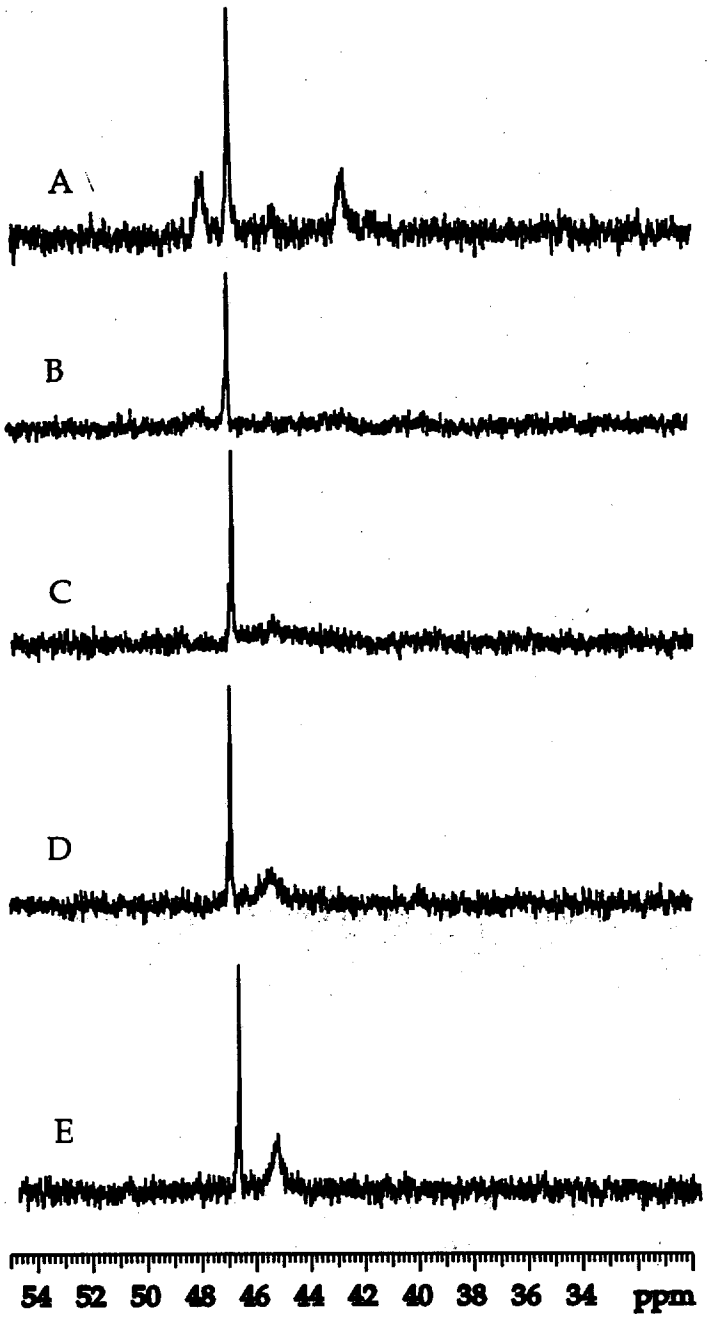
VI. ^{6}Li, ^{15}N, and ^{13}C NMR spectra in 1:1:1 THF/toluene/pentane solutions at -115 °C, 0.1 M total ^{6}Li concentration: (A) ^{6}Li NMR spectrum of 0.1 M [^{6}Li,^{15}N]*t*-BuNHLi with 2.0 equiv [^{6}Li]lithium phenylacetylide; (B) ^{15}N NMR spectrum of 0.1 M [^{6}Li,^{15}N]*t*-BuNHLi with 2.0 equiv [^{6}Li]lithium phenylacetylide; (C) ^{6}Li NMR spectrum of 0.1 M [^{6}Li,^{15}N]*t*-BuNHLi with 0.50 equiv [^{6}Li]lithium phenylacetylide; (D) ^{15}N NMR spectrum of 0.1 M [^{6}Li,^{15}N]*t*-BuNHLi with 0.50 equiv [^{6}Li]lithium phenylacetylide; (E) ^{6}Li NMR spectrum of 0.1 M [^{6}Li]*t*-BuNHLi with 1.0 equiv [^{6}Li,^{13}C]lithium phenylacetylide; (F) $^{13}C\{^{1}H\}$ NMR spectrum of 0.1 M [^{6}Li]*t*-BuNHLi with 1.0 equiv [^{6}Li,^{13}C]lithium phenylacetylide.



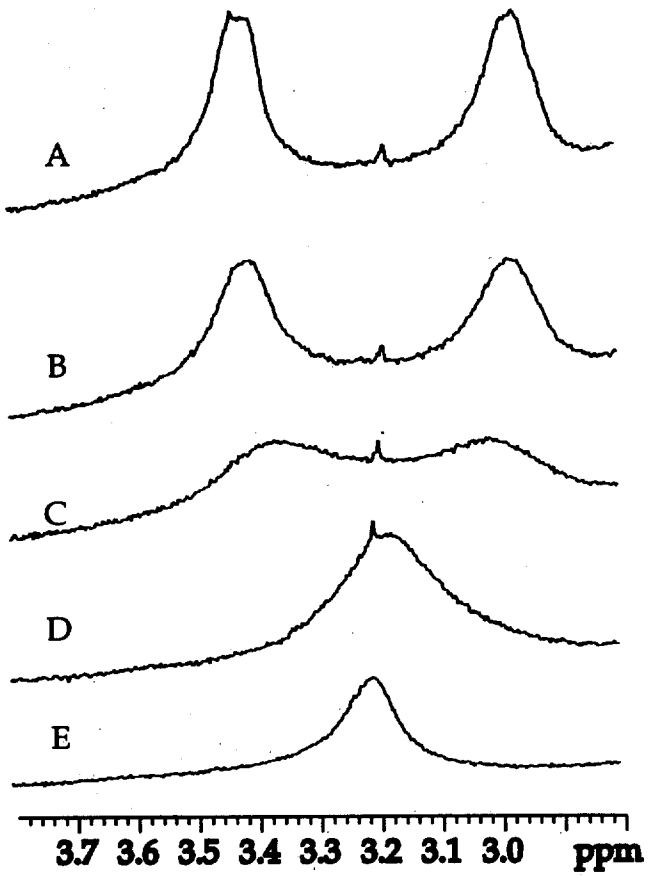
VII. ^{6}Li and ^{15}N NMR spectra of 0.1 M [^{6}Li,^{15}N]LiDMEDA in 2:1 pentane/toluene: (A) $^{6}Li\{^{1}H\}$ NMR spectrum at -90 °C; (B) $^{6}Li\{^{1}H\}$ NMR spectrum at -50 °C; (C) $^{6}Li\{^{1}H\}$ NMR spectrum at -20 °C; (D) $^{6}Li\{^{1}H\}$ NMR spectrum at 10 °C; (E) $^{6}Li\{^{1}H\}$ NMR spectrum at 30 °C; (F) $^{15}N\{^{1}H\}$ NMR spectrum at -115 °C.



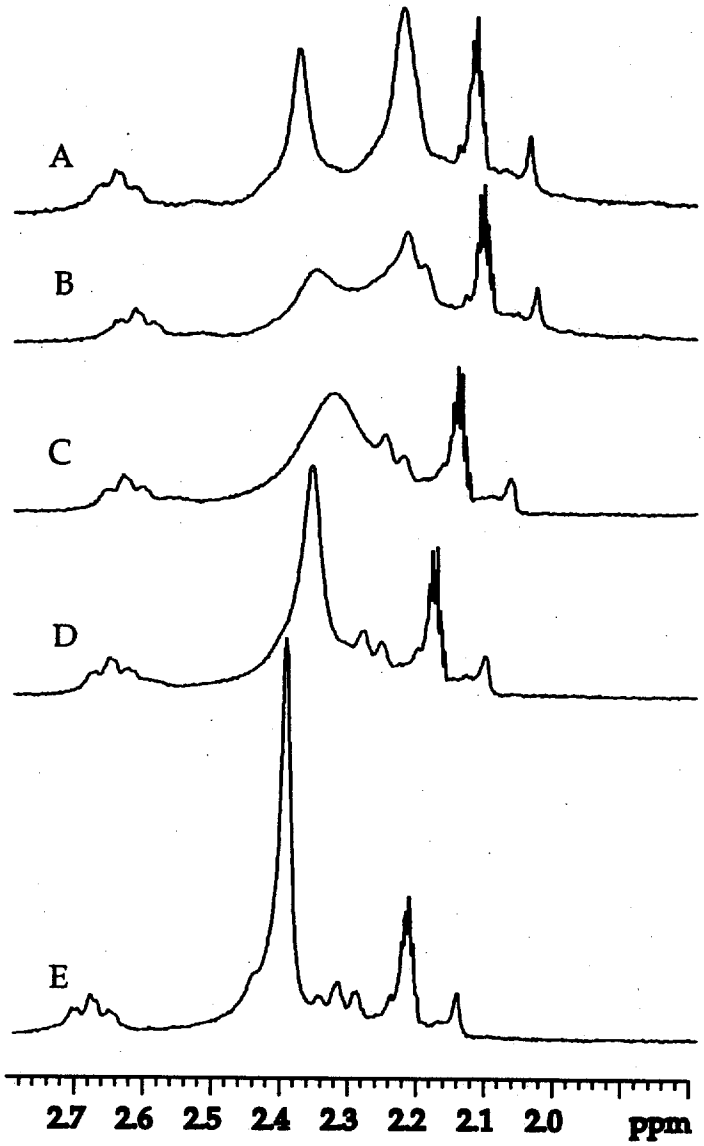
VIII. ^{6}Li NMR spectra of 0.1 M solutions: (A) [^{6}Li]LiDMEDA in toluene at -50 °C; (B) [^{6}Li]LiDMEDA in toluene with 10 equiv THF at -100 °C; (C) [^{6}Li]LiDMEDA in toluene with 50 equiv THF at -100 °C; (D) [^{6}Li]LiDMEDA in THF at -100 °C; (E) [^{6}Li,^{15}N]LiDMEDA in THF at -90 °C.



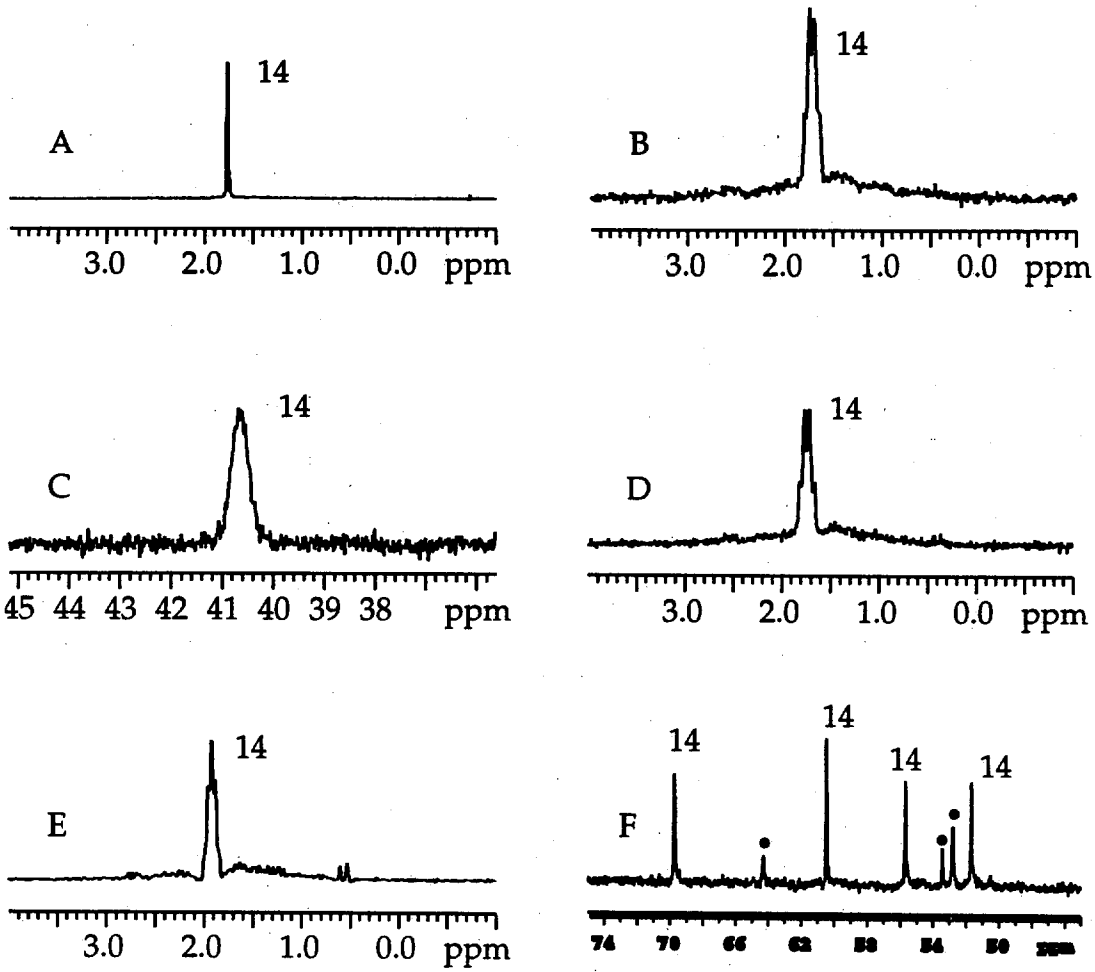
IX. ^{13}C NMR spectra of 0.1 M [^{6}Li]LiDMEDA in d_8 toluene: (A) -40 °C; (B) -20 °C; (C) 0 °C; (D) 10 °C; (E) 20 °C.



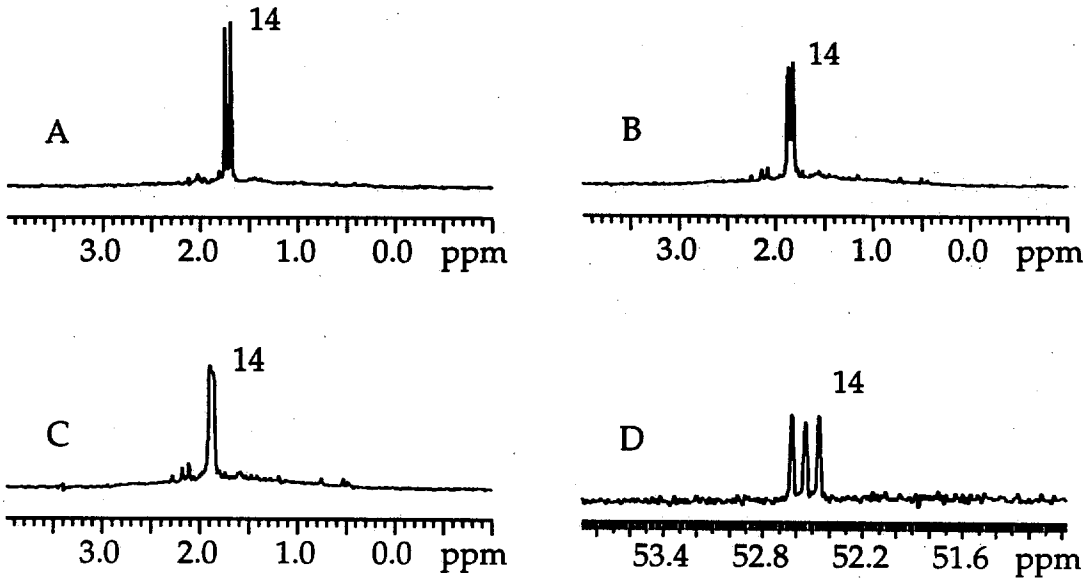
X. ^{1}H NMR spectra of 0.1 M [^{6}Li]LiDMEDA in d_8 toluene: (A) 30 °C; (B) 40 °C; (C) 50 °C; (D) 60 °C; (E) 70 °C.



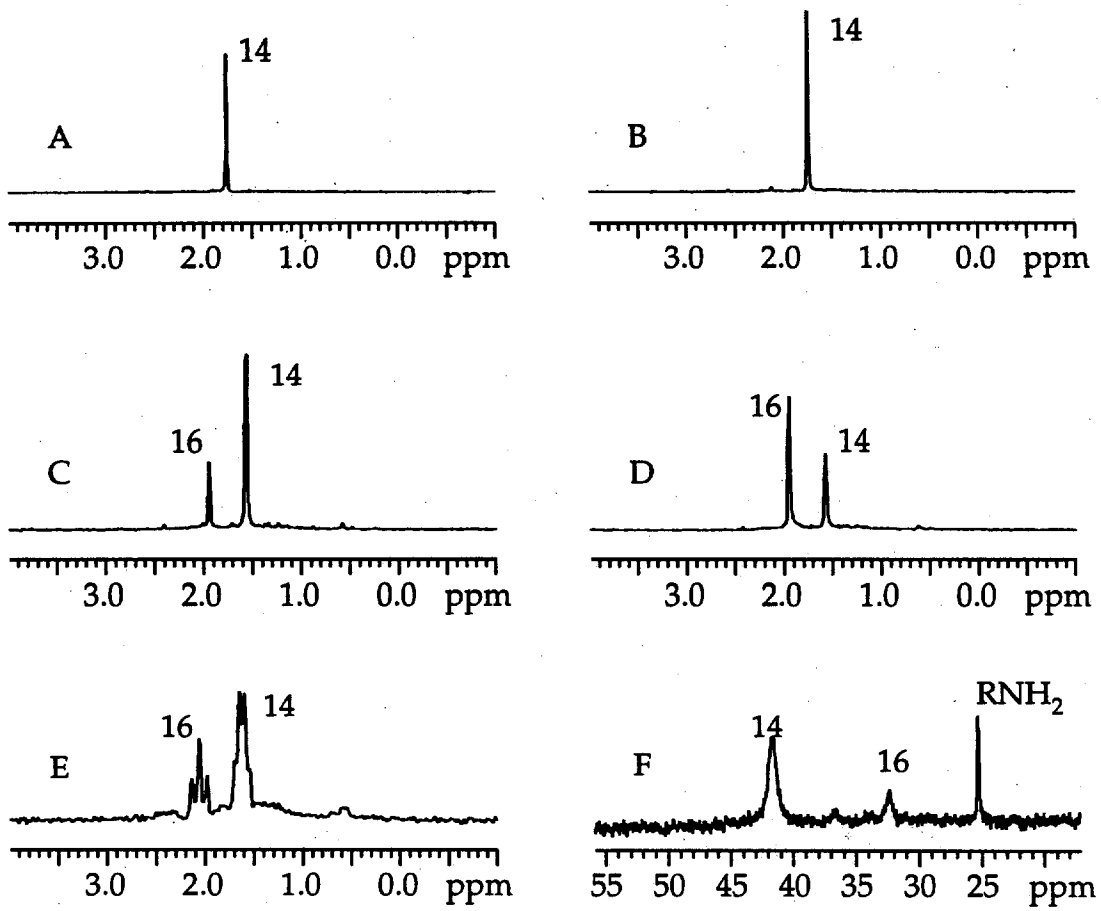
XI. ^{1}H NMR spectra of 0.1 M [^{6}Li]LiDMEDA in d_8 toluene: (A) -40 °C; (B) -30 °C; (C) -20 °C; (D) -10 °C; (E) 0 °C.



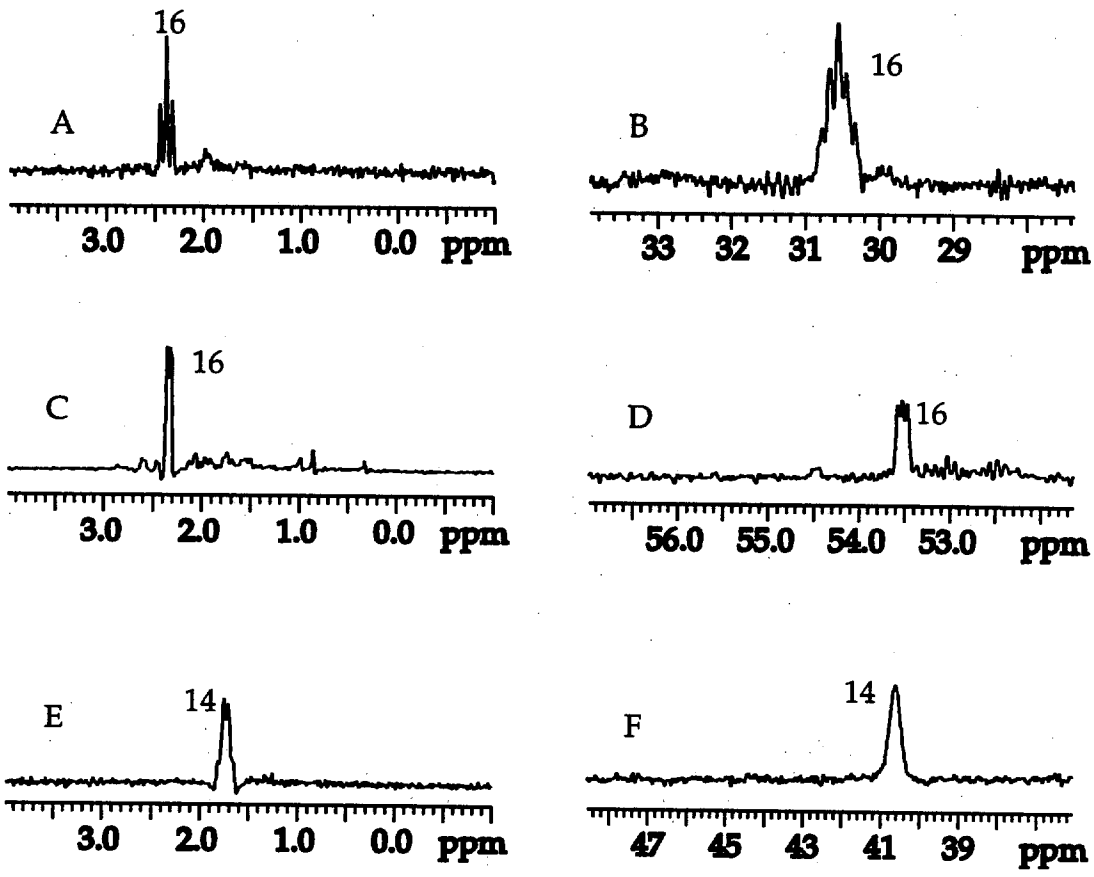
XII. ^{6}Li, ^{15}N, and ^{13}C NMR spectra of 0.1 M **6** in toluene: (A) ^{6}Li NMR spectrum of [^{6}Li]**6** at -80 °C; (B) ^{6}Li NMR spectrum of [^{6}Li,^{15}N]**6a** at -95 °C; (C) ^{15}N NMR spectrum of [^{6}Li,^{15}N]**6a** at -95 °C; (D) ^{6}Li NMR spectrum of [^{6}Li,^{15}N]**6a** at -60 °C; (E) ^{6}Li NMR spectrum of [^{6}Li,^{15}N]**6a** at -30 °C; (F) partial $^{13}C\{^{1}H\}$ NMR spectrum of [^{6}Li]**6** at -60 °C, free amine peaks are indicated with a dot.



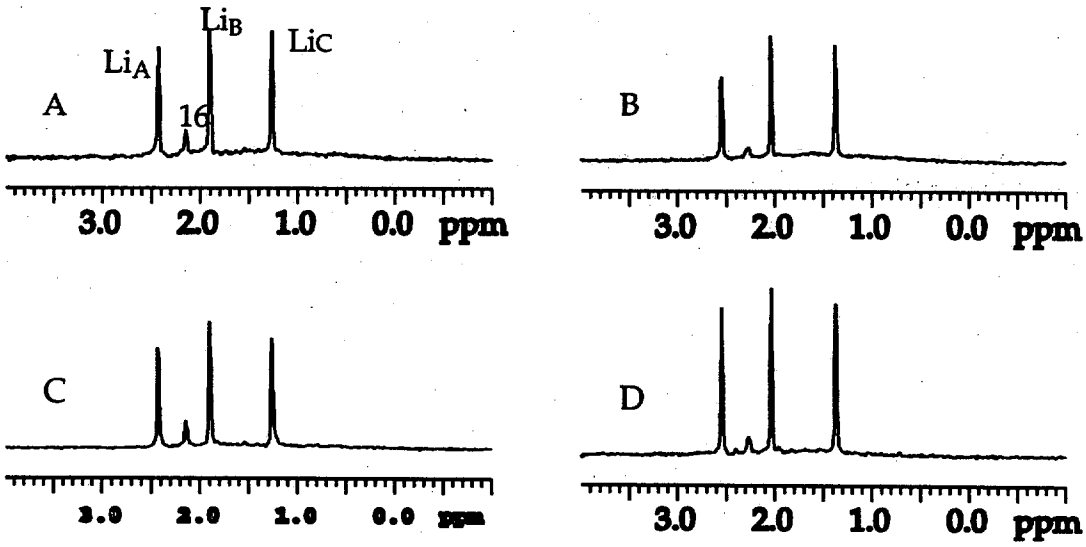
XIII. ^{6}Li and ^{15}N NMR spectra of 0.1 M [^{6}Li,^{15}N]**6b** in toluene solution: (A) ^{6}Li NMR spectrum at -90 °C; (B) ^{6}Li NMR spectrum at -50 °C; (C) ^{6}Li NMR spectrum at -40 °C; (D) ^{15}N NMR spectrum at -80 °C.



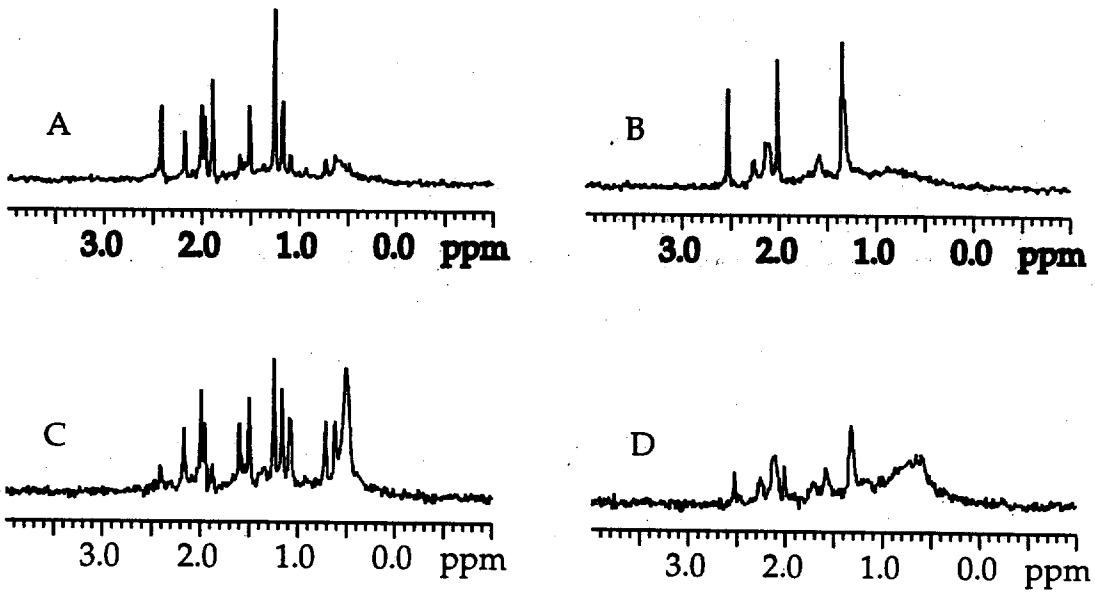
XIV. ^{6}Li and ^{15}N NMR spectra of 0.1 M **6** in toluene with THF: (A) ^{6}Li NMR spectrum of [^{6}Li]**6** with 5.0 equiv THF at -80 °C; (B) ^{6}Li NMR spectrum of [^{6}Li]**6** with 10 equiv THF at -80 °C; (C) ^{6}Li NMR spectrum of [^{6}Li]**6** with 25 equiv THF at -80 °C; (D) ^{6}Li NMR spectrum of [^{6}Li]**6** with 50 equiv THF at -80 °C; (E) ^{6}Li NMR spectrum of [^{6}Li,^{15}N]**6a** with 25 equiv THF at -110 °C; (F) ^{15}N NMR spectrum of [^{6}Li,^{15}N]**6a** with 25 equiv THF at -110 °C.



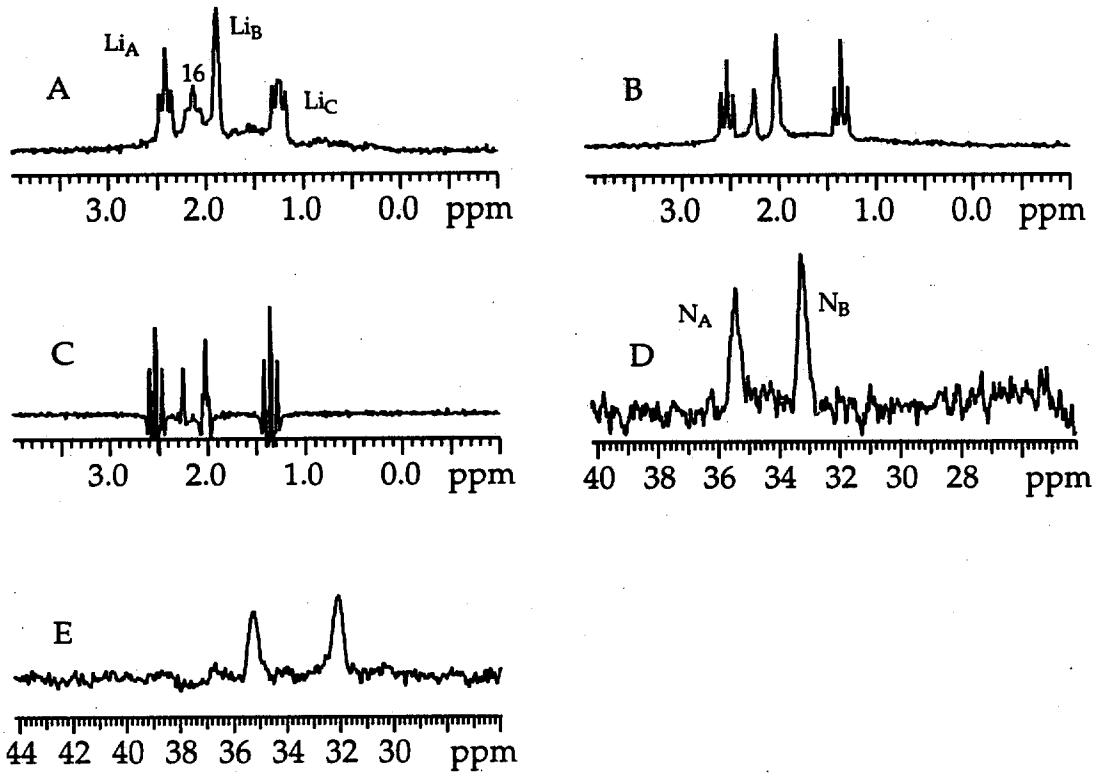
XV. ^{6}Li and ^{15}N NMR spectra of 0.1 M [^{6}Li,^{15}N]**6a** or [^{6}Li,^{15}N]**6b**: (A) ^{6}Li NMR spectrum of **6a** in 1:1 pentane/THF at -115 °C; (B) ^{15}N NMR spectrum of **6a** in 1:1 pentane/THF at -115 °C; (C) ^{6}Li NMR spectrum of **6b** in 1:1 pentane/THF at -115 °C; (D) ^{15}N NMR spectrum of **6b** in 1:1 pentane/THF at -115 °C; (E) ^{6}Li NMR spectrum of **6a** in toluene with 25 equiv Et_2O at -90 °C; (F) ^{15}N NMR spectrum of **6a** in toluene with 25 equiv Et_2O at -90 °C.



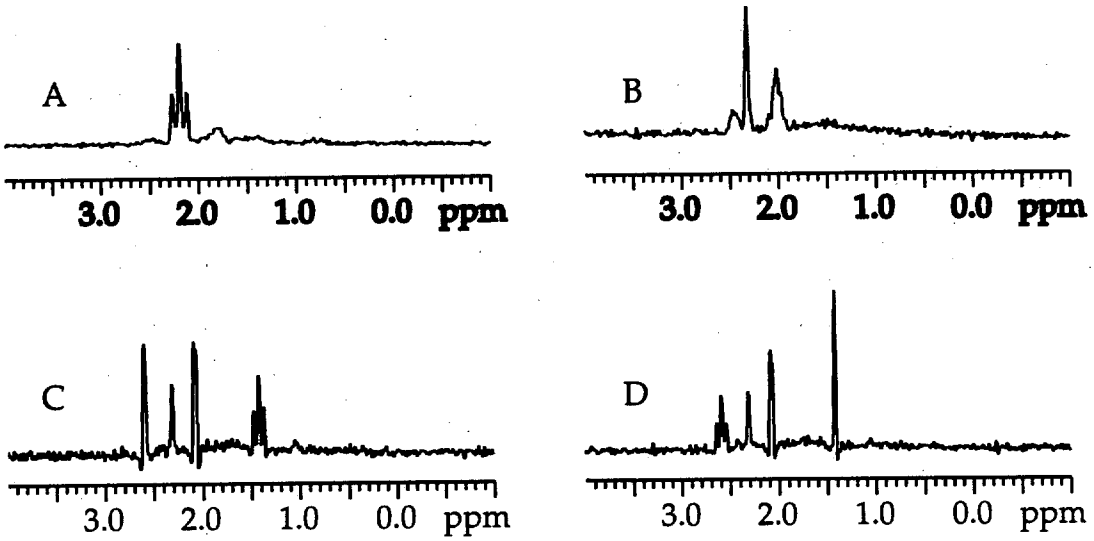
XVI. ^{6}Li NMR spectra of 1:1 toluene:THF solutions: (A) 0.08 M [^{6}Li]**6** and 0.02 M [^{6}Li]lithium phenylacetylide at -90 °C; (B) 0.08 M [^{6}Li]**6** and 0.02 M [^{6}Li]lithium phenylacetylide at -40 °C; (C) 0.075 M [^{6}Li]**6** and 0.025 M [^{6}Li]lithium phenylacetylide at -90 °C; (D) 0.075 M [^{6}Li]**6** and 0.025 M [^{6}Li]lithium phenylacetylide at -40 °C.



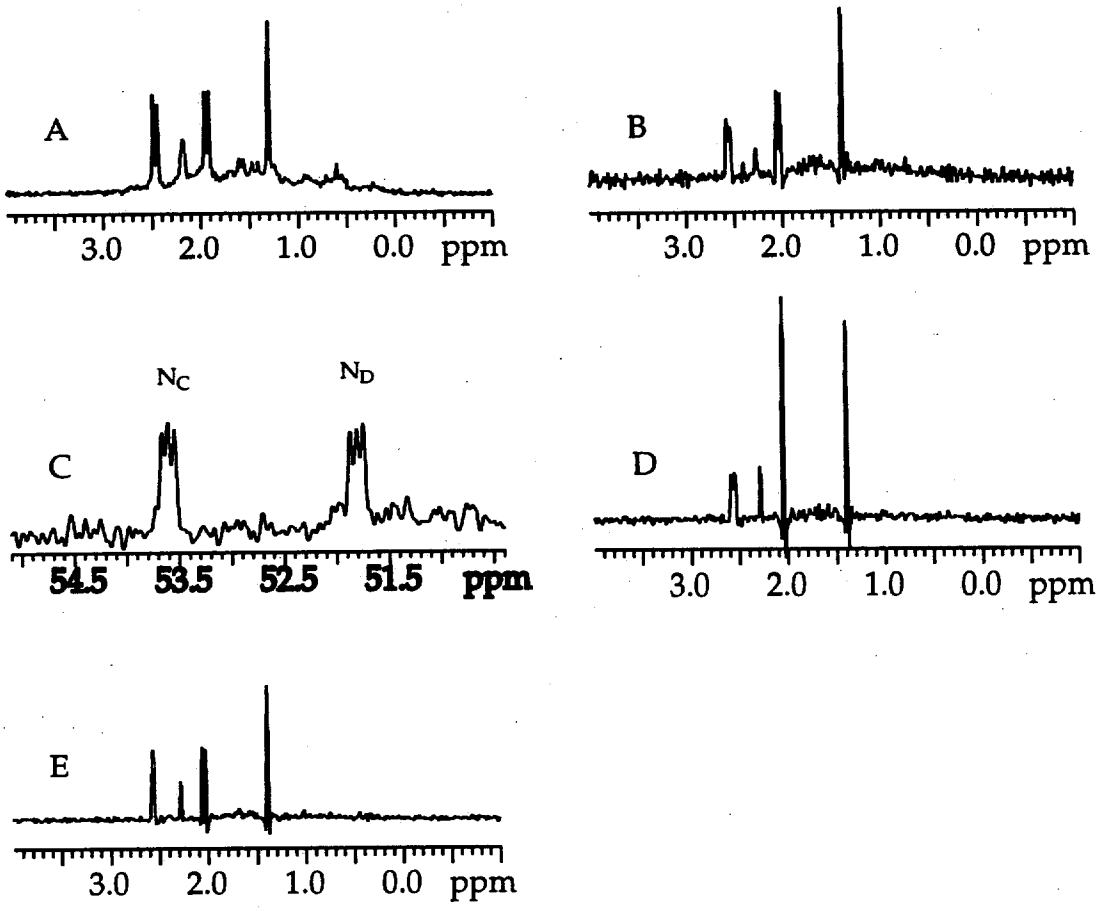
XVII. ^{6}Li NMR spectrum of 1:1 toluene/THF solutions: (A) 0.067 M [^{6}Li]**6** and 0.033 M [^{6}Li]lithium phenylacetylide at -90 °C; (B) 0.067 M [^{6}Li]**6** and 0.033 M [^{6}Li]lithium phenylacetylide at -40 °C; (C) 0.033 M [^{6}Li]**6** and 0.067 M [^{6}Li]lithium phenylacetylide at -90 °C; (D) 0.033 M [^{6}Li]**6** and 0.067 M [^{6}Li]lithium phenylacetylide at -40 °C.



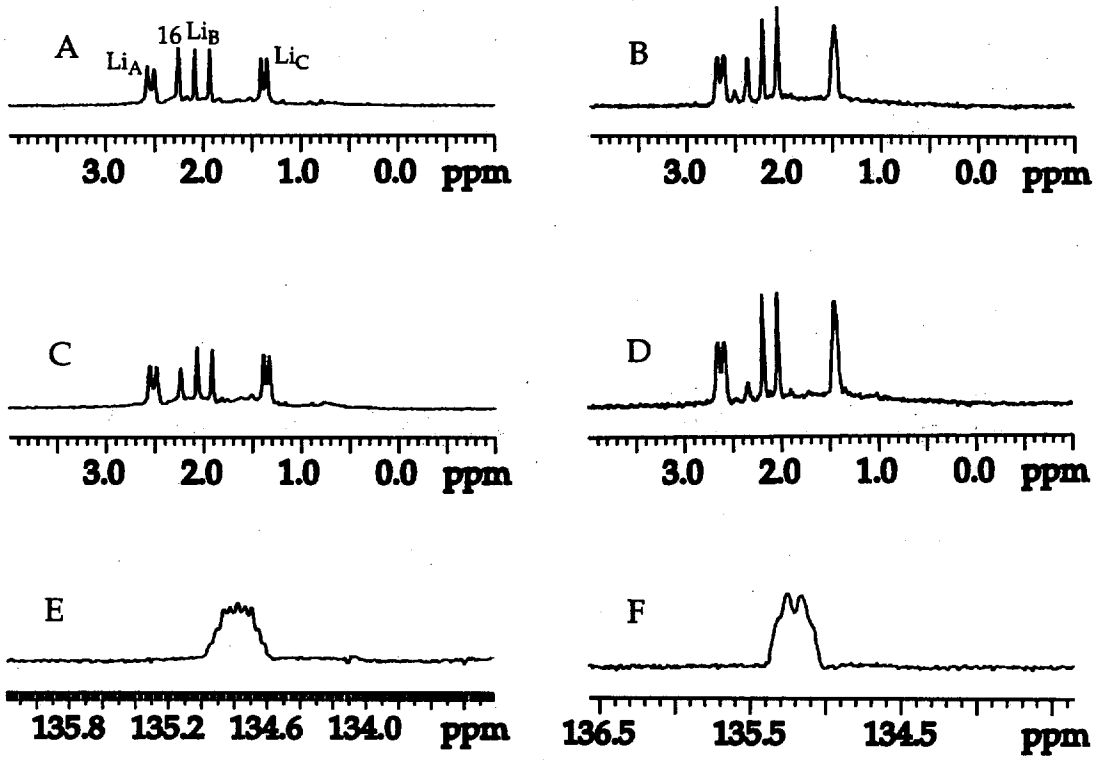
XVIII. ^{6}Li and ^{15}N NMR spectra 1:1 toluene/THF solutions of 0.08 M [^{6}Li,^{15}N]**6a** with 0.02 M [^{6}Li]lithium phenylacetylide: (A) ^{6}Li NMR spectrum at -85 °C; (B) ^{6}Li NMR spectrum at -40 °C; (C) ^{6}Li NMR spectrum at -40 °C, sine bell resolution enhancement function applied; (D)^{15}N NMR spectrum at -40 °C; (E) ^{15}N NMR spectrum at -95 °C.



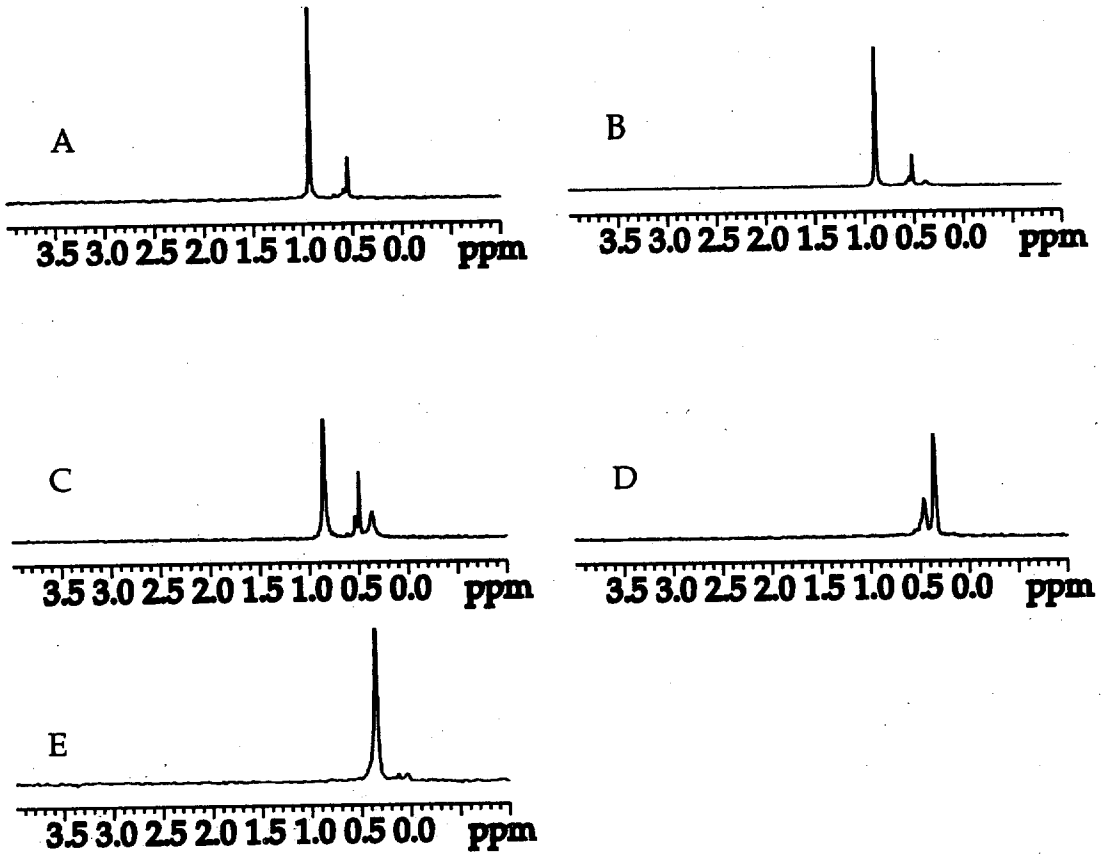
XIX. ^{6}Li NMR spectra in 1:1 toluene/THF solution: (A) 0.1 M [^{6}Li,^{15}N]**6a** at -90 °C; (B) 0.1 M [^{6}Li,^{15}N]**6a** at -40 °C; (C) $^{6}Li\{^{15}N\}$ spectrum of 0.08 M [^{6}Li,^{15}N]**6a** with 0.02 M [^{6}Li]lithium phenylacetylide at -40 °C, ^{15}N single frequency decoupled at 33.3 ppm; (D) $^{6}Li\{^{15}N\}$ spectrum of 0.08 M [^{6}Li,^{15}N]**6a** with 0.02 M [^{6}Li]lithium phenylacetylide at -40 °C, ^{15}N single frequency decoupled at 35.4 ppm.



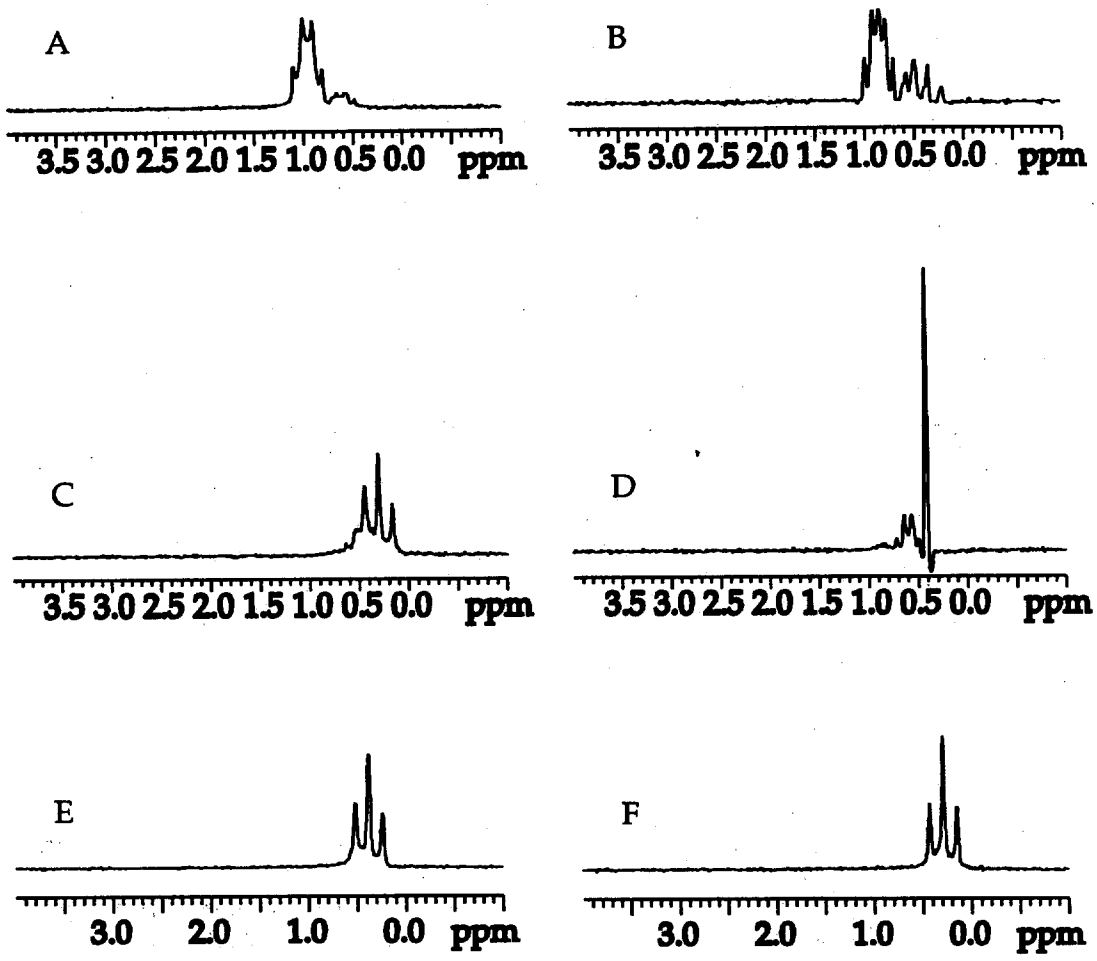
XX. ^{6}Li and ^{15}N NMR spectra of 0.08 M [^{6}Li,^{15}N]**6b** with 0.02 M [^{6}Li]lithium phenylacetylide in 1:1 toluene/THF solution: (A) ^{6}Li NMR spectrum at -90 °C; (B) ^{6}Li NMR spectrum at -40 °C; (C) ^{15}N NMR spectrum at -40 °C; (D) $^{6}Li\{^{15}N\}$ NMR spectrum at -40 °C, ^{15}N single frequency decoupled at 53.5 ppm; (E) $^{6}Li\{^{15}N\}$ NMR spectrum at -40 °C, ^{15}N single frequency decoupled at 51.7 ppm.



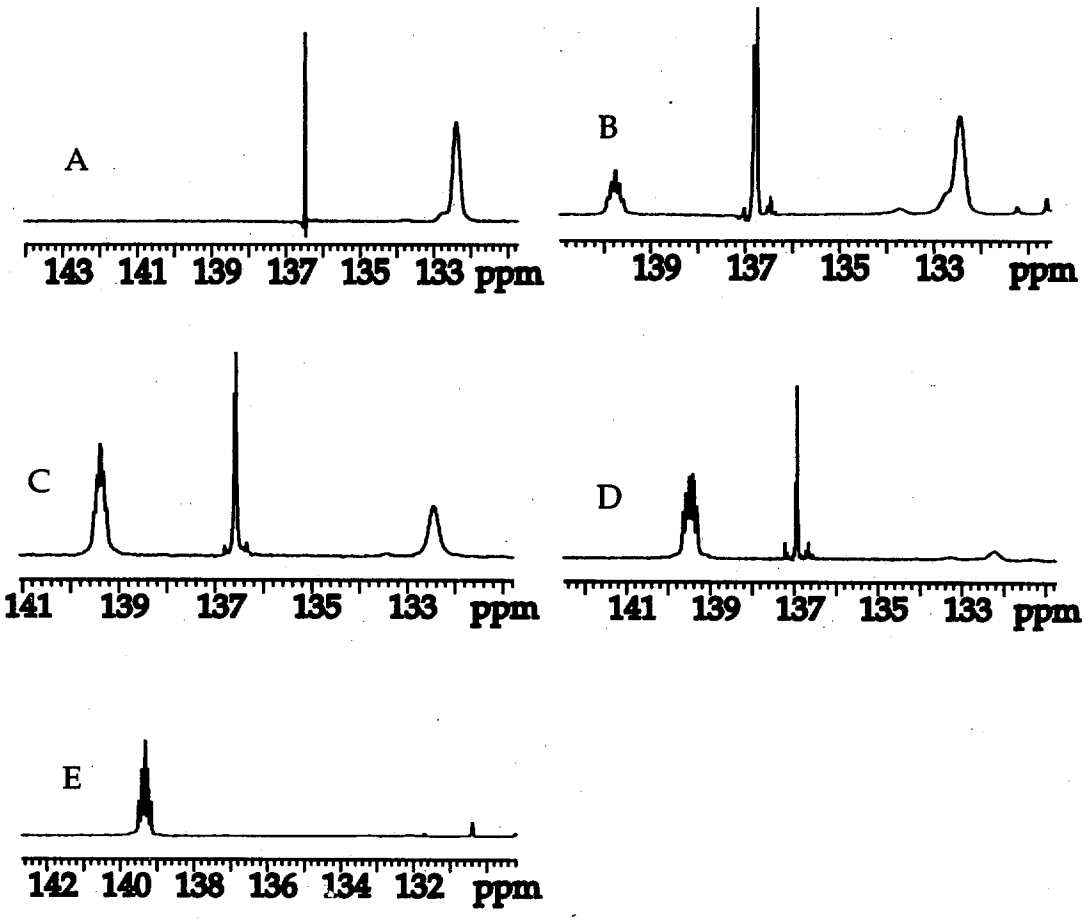
XXI. ^{6}Li and ^{13}C NMR spectra in 1:1 toluene/THF solution: (A) ^{6}Li NMR spectrum of 0.08 M [^{6}Li]**6** with 0.02 M [^{6}Li,^{13}C]lithium phenyl-acetylide at -90 °C; (B) ^{6}Li NMR spectrum of 0.08 M [^{6}Li]**6** with 0.02 M [^{6}Li,^{13}C]lithium phenylacetylide at -40 °C; (C) ^{6}Li NMR spectrum of 0.075 M [^{6}Li]**6** with 0.025 M [^{6}Li,^{13}C]lithium phenylacetylide at -90 °C; (D) ^{6}Li NMR spectrum of 0.075 M [^{6}Li]**6** with 0.025 M [^{6}Li,^{13}C]lithium phenylacetylide at -40 °C; (E) $^{13}C\{^{1}H\}$ NMR spectrum of 0.075 M [^{6}Li]**6** with 0.025 M [^{6}Li,^{13}C]lithium phenylacetylide at -90 °C; (F) $^{13}C\{^{1}H\}$ NMR spectrum of 0.075 M [^{6}Li]**6** with 0.025 M [^{6}Li,^{13}C]lithium phenylacetylide at -40 °C.



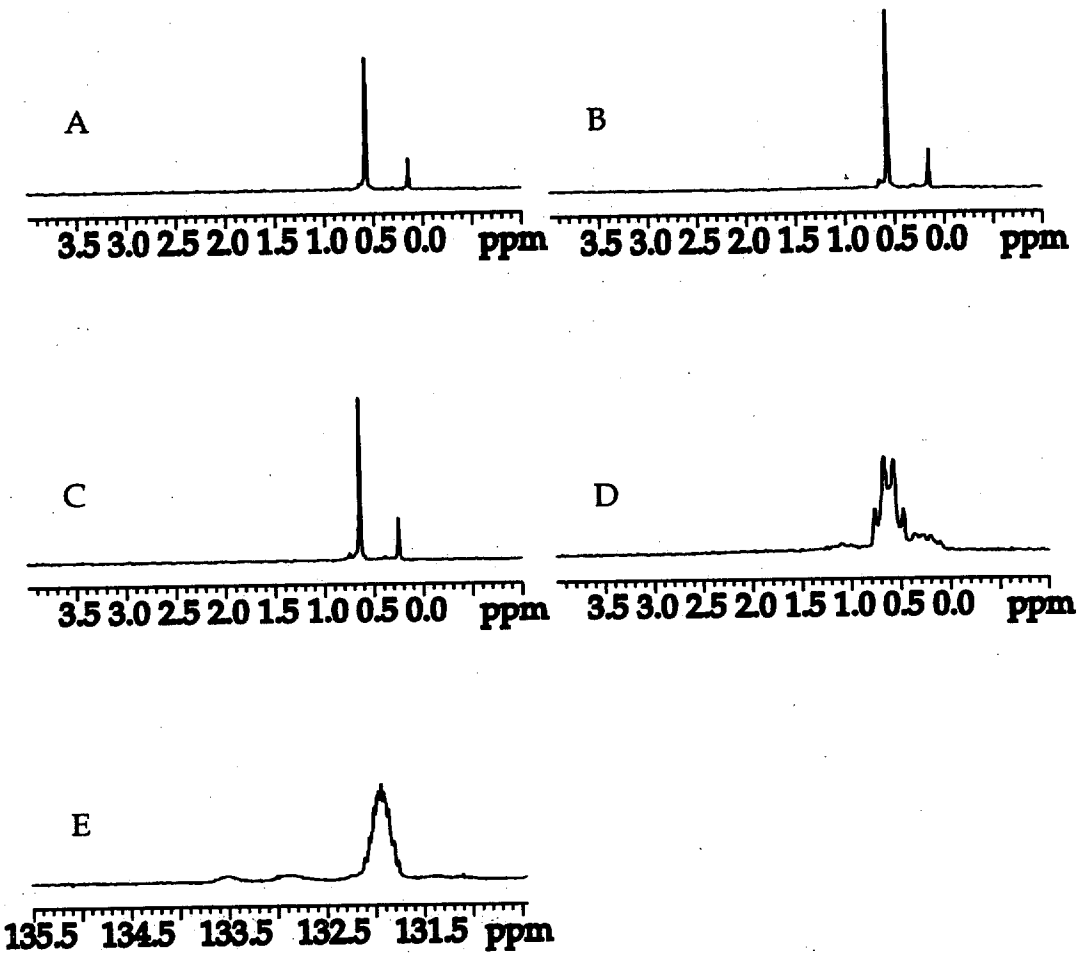
XXII. ^{6}Li NMR spectra of 0.1 M [^{6}Li]lithium phenylacetylide in toluene: (A) 2.0 equiv THF, spectrum recorded at -90 °C; (B) 10 equiv THF, spectrum recorded at -90 °C; (C) 20 equiv THF, spectrum recorded at -90 °C; (D) 61 equiv THF, spectrum recorded at -100 °C; (E) neat THF, spectrum recorded at -105 °C.



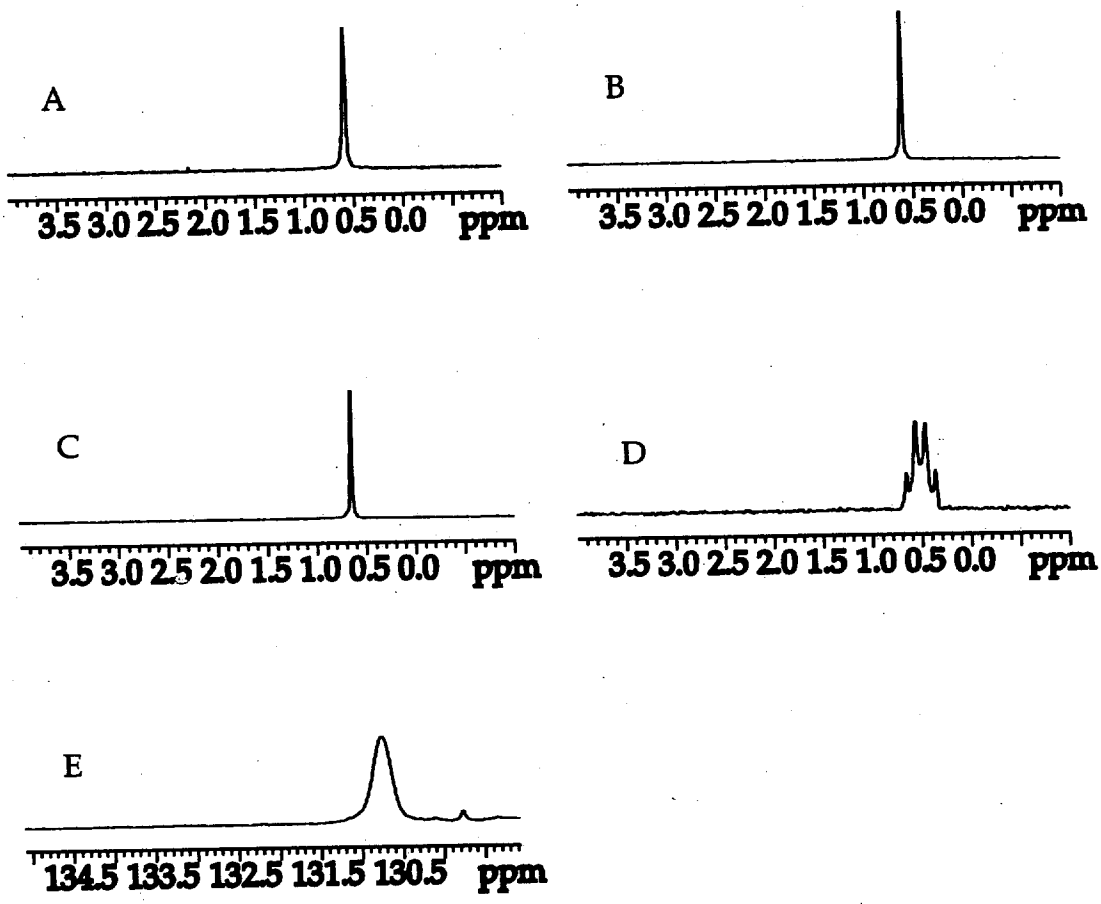
XXIII. ^{6}Li NMR spectra of 0.1 M [^{6}Li,^{13}C]lithium phenylacetylide: (A) toluene solution with 3.0 equiv THF, spectrum recorded at -90 °C; (B) toluene solution with 15 equiv THF, spectrum recorded at -90 °C; (C) 2:1 toluene/THF solution, spectrum recorded at -100 °C; (D) $^{6}Li\{^{13}C\}$ NMR spectrum of sample with 61 equiv THF, spectrum recorded at -100 °C, ^{13}C single frequency decoupled at 139.3 ppm; (E) 1:1 toluene/THF solution, spectrum recorded at -105 °C; (F) neat THF, spectrum recorded at -105 °C.



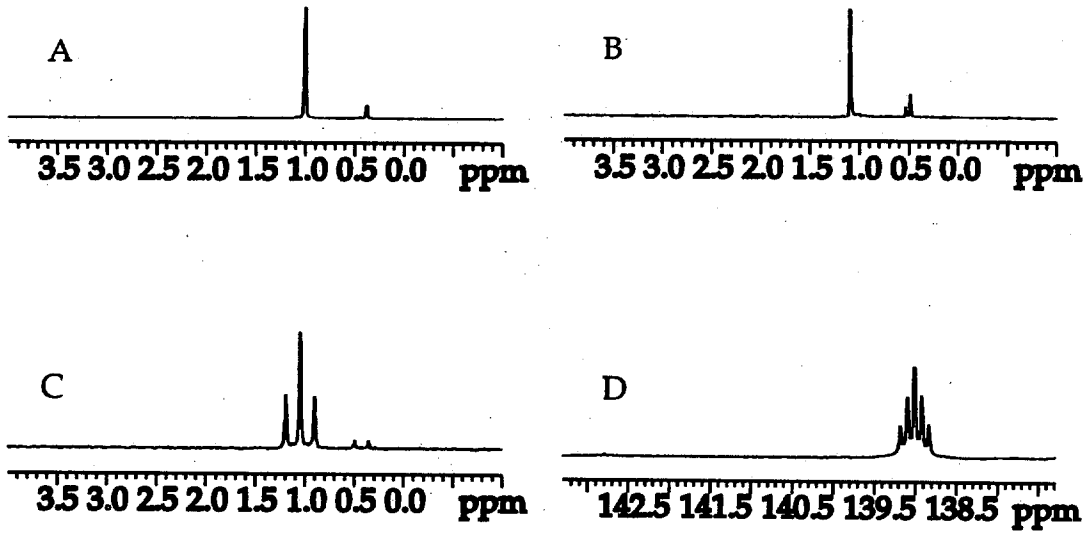
XXIV. $^{13}C\{^{1}H\}$ NMR spectra of 0.1 M [^{6}Li,^{13}C]lithium phenylacetylide, peak at 136.73 (toluene) is cropped: (A) 1:1 pentane /toluene solution with 3.0 equiv THF, spectrum recorded at -80 °C; (B) toluene solution with 20 equiv THF, spectrum recorded at -90 °C; (C) 1:1 pentane/toluene solution, 20 equiv THF, spectrum recorded at -120 °C; (D) 1:1 toluene/THF solution, spectrum recorded at -105 °C; (F) THF solution, spectrum recorded at -105 °C



XXV. ^{6}Li and ^{13}C NMR spectra of 0.1 M solutions in toluene at -90 °C; (A) ^{6}Li NMR spectrum of [^{6}Li]lithium phenylacetylide with 10 equiv Et_2O; (B) ^{6}Li NMR spectrum of [^{6}Li]lithium phenylacetylide with 25 equiv Et_2O; (C) ^{6}Li NMR spectrum of [^{6}Li]lithium phenylacetylide with 50 equiv Et_2O; (D) ^{6}Li NMR spectrum of [^{6}Li,^{13}C]lithium phenylacetylide with 25 equiv THF; (E) $^{13}C\{^{1}H\}$ NMR spectrum of [^{6}Li,^{13}C]lithium phenylacetylide with 25 equiv THF.



XXVI. ^{6}Li and ^{13}C NMR spectra of 0.1 M solutions in toluene:(A) ^{6}Li NMR spectrum at -90 °C of [^{6}Li]lithium phenylacetylide with 15 equiv Et_3N; (B) ^{6}Li NMR spectrum at -90 °C of [^{6}Li]lithium phenylacetylide with 25 equiv Et_3N; (C) ^{6}Li NMR spectrum at -90 °C of [^{6}Li]lithium phenyl-acetylide with 40 equiv Et_3N; (D) ^{6}Li NMR spectrum at -100 °C of [^{6}Li,^{13}C]lithium phenylacetylide with 20 equiv Et_3N; (E) $^{13}C\{^{1}H\}$ NMR spectrum at -100 °C of [^{6}Li,^{13}C]lithium phenylacetylide with 20 equiv Et_3N.



XXVII. ^{6}Li and ^{13}C NMR spectra of 0.1 M solutions in toluene at -90 °C: (A) ^{6}Li NMR spectrum of [^{6}Li]lithium phenylacetylide with 5.0 equiv TMEDA; (B) ^{6}Li NMR spectrum of [^{6}Li]lithium phenylacetylide with 15 equiv TMEDA; (C) ^{6}Li NMR spectrum of [^{6}Li,^{13}C]lithium phenylacetylide with 5.0 equiv TMEDA; (D) $^{13}C\{^{1}H\}$ NMR spectrum of [^{6}Li,^{13}C]lithium phenylacetylide with 5.0 equiv TMEDA.