Lithiated Imines:
Solvent-Dependent Aggregate Structures and
Mechanisms of Alkylation

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Supporting Information

Part 1: Experimental Procedures

[^{15}N]Cyclohexylcarboxamide.[S-1] A 250 mL round bottom flask containing a small stir bar was charged with $^{15}NH_4Cl$ (3.01 g, 55.2 mmol) and 15 mL of distilled water. Cyclohexylcarbonyl chloride (11.0 g, 77.1 mmol) in 30 mL anhydrous Et_2O was layered on to the aqueous solution. The reaction mixture was cooled in an ice bath and 50 % aq NaOH (30 mL) was added via syringe with slow stirring to avoid mixing the layers. The reaction mixture was warmed to room temperature and stirred slowly for an additional 15 min. The reaction mixture was then stirred vigorously for 5 min, capped with a glass stopper, and shaken with frequent venting. The white solid that formed was extracted with 3 x 500 mL CH_2Cl_2, washed with 200 mL brine, dried over Na_2SO_4, filtered, and dried in vacuo. The resulting solid was dissolved in hot CH_3CN, filtered, and crystallized at -20 °C to yield 5.65 g of [^{15}N]cyclohexylcarboxamide (44.4 mmol, 80 %) as white flakes (see S7 for spectral data).

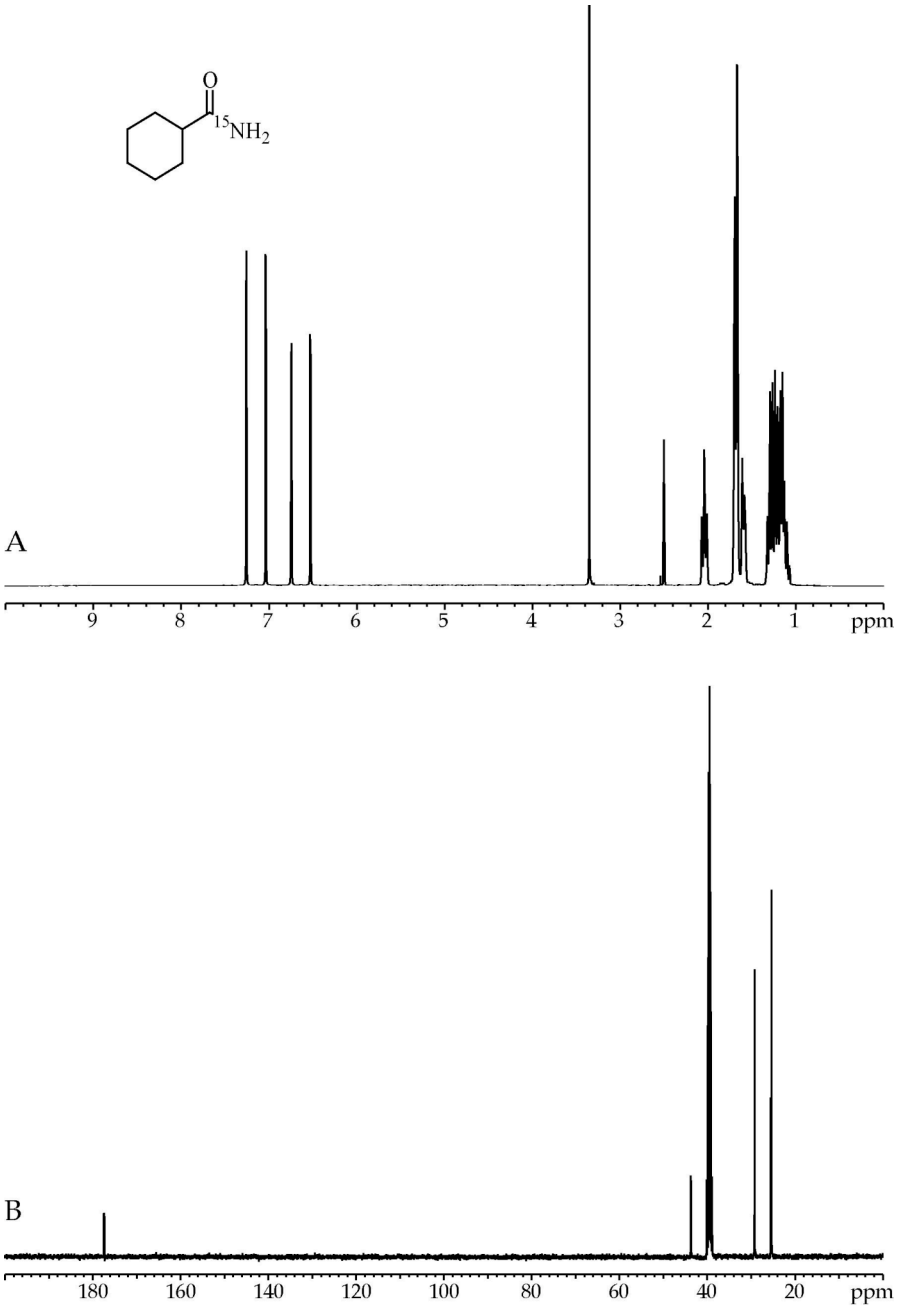
[^{15}N]Cyclohexylammonium tosylate.[S-2] A 500 mL round bottom flask was charged with [hydroxyl(tosyloxy)iodo]benzene[S-3] (18.5 g, 47.6 mmol) and 50 mL CH_3CN. [^{15}N]cyclohexylcarboxamide (5.55 g, 43.6 mmol) was added dissolved in hot CH_3CN (150 mL), and the reaction mixture was heated at reflux for 1 h to give a yellow solution that yielded a white precipitate upon standing at room temperature. The reaction mixture was cooled to -20 °C to complete precipitation. Filtration, drying, and recrystallization from 10:1 THF/EtOH yielded 10.1 g of [^{15}N]cyclohexylammonium tosylate (37.1 mmol, 85 %) as white needles (see S8 for spectral data).

[^{15}N]Cyclohexanone cyclohexylimine ([^{15}N]5). A flame dried 50 mL round bottom flask was charged with [^{15}N]cyclohexylammonium tosylate (3.05 g, 11.2 mmol) and 3 Å molecular sieves (3.5 g). The flask was evacuated, and freshly distilled Et_3N (25 mL) and cyclohexanone (2.50 mL, 2.37 g, 24.2 mmol) were added under an argon purge. The reaction mixture was stirred for 40 h under argon and filtered to remove the molecular sieves. Distillation (0.1 torr, b.p. 70-72 °C) yielded 1.72 g of [^{15}N]cyclohexanone cyclohexylimine (9.6 mmol, 86 %) as

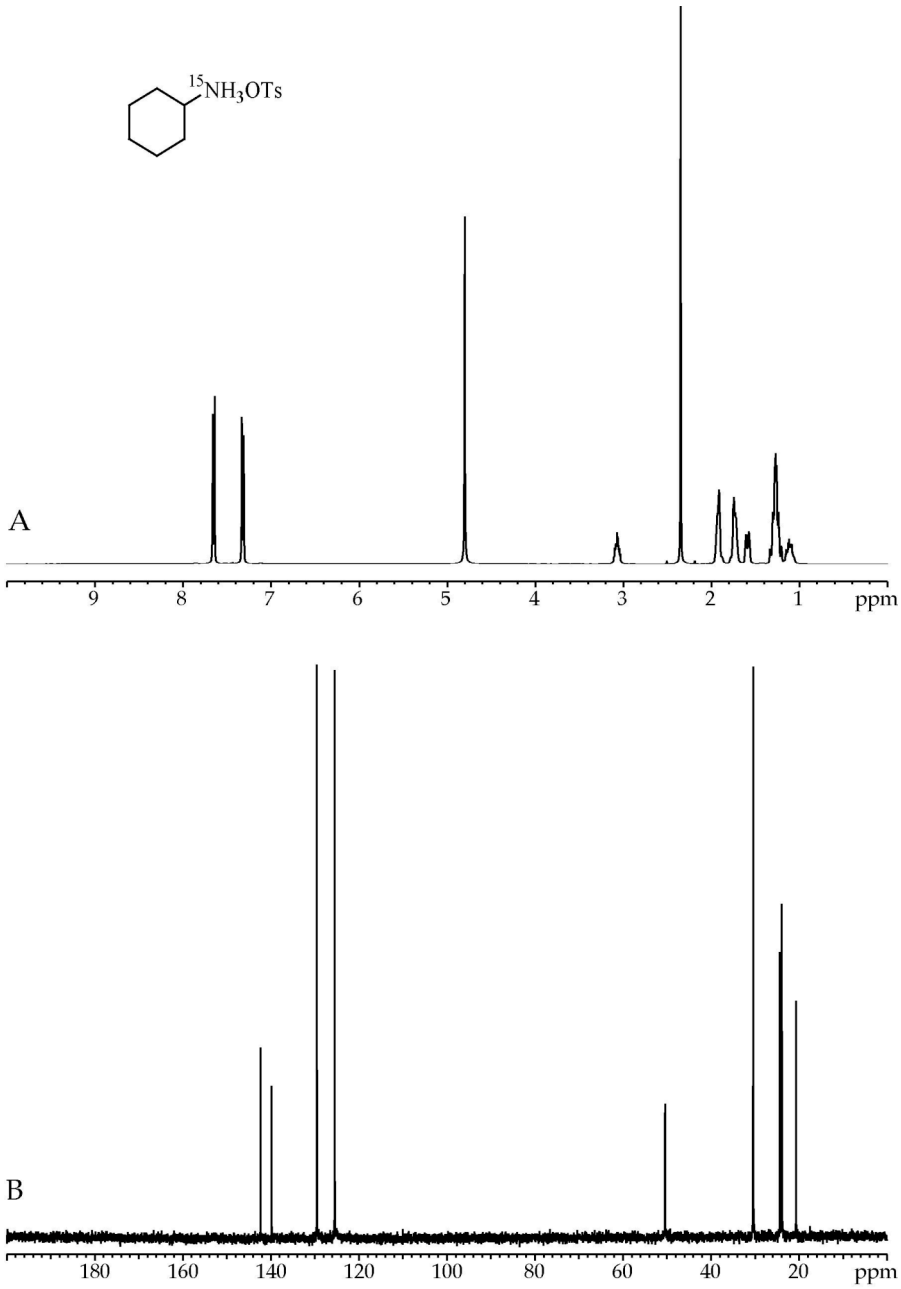
a colorless oil (see S9 for spectral data). Unlabelled **5** was prepared by methods described previously.[5a]

[^{6}Li,^{15}N]Lithiated cyclohexanone cyclohexylimine ([^{6}Li,^{15}N]3). A flame dried 100 mL round bottom flask was charged with recrystallized [^{6}Li]LDA[S-4] (0.50 g, 4.7 mmol) and 20 mL of freshly distilled hexanes under argon. After heating to dissolve the LDA and cooling to room temperature, [^{15}N]**3** (1.0 g, 5.6 mmol) was added neat. The solution immediately turned yellow and a precipitate was observed after ~ 5 min. Stirring for 1 h led to significant formation of a white solid. Further precipitation was achieved by cooling the reaction mixture to -78 °C for 2 h. Filtration, washing with 2 x 10 mL fresh hexanes, and drying in vacuo yielded 0.73 g of [^{6}Li,^{15}N]**3** (3.9 mmol, 84 %) as a white powder which was stored in a dry box. Unlabelled **3** for use in rate studies was prepared on multigram scales (5.0 g LDA) using the method described above with a 250 mL round bottom flask and 200 mL hexanes.

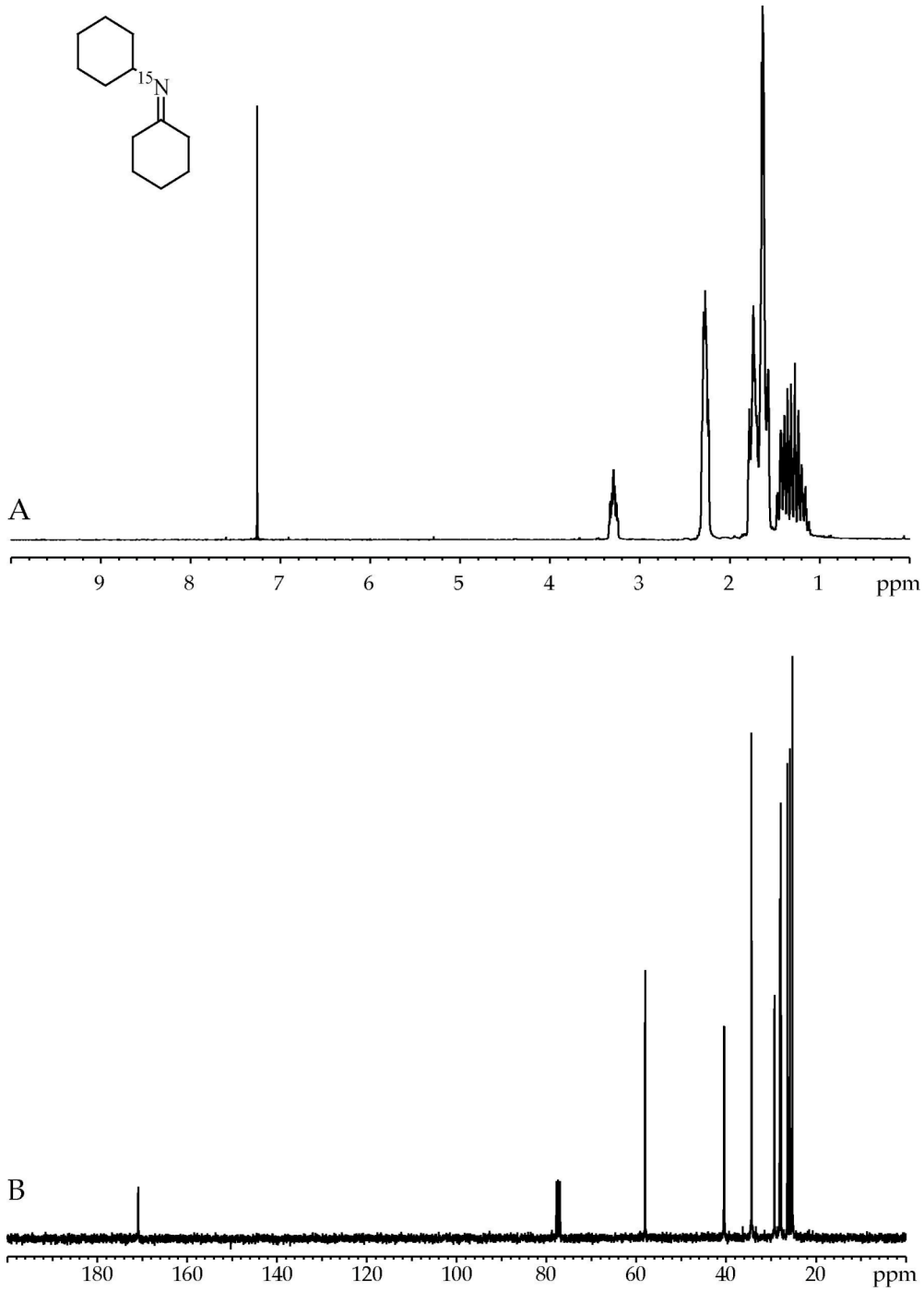
Part 2: NMR Spectroscopic Studies



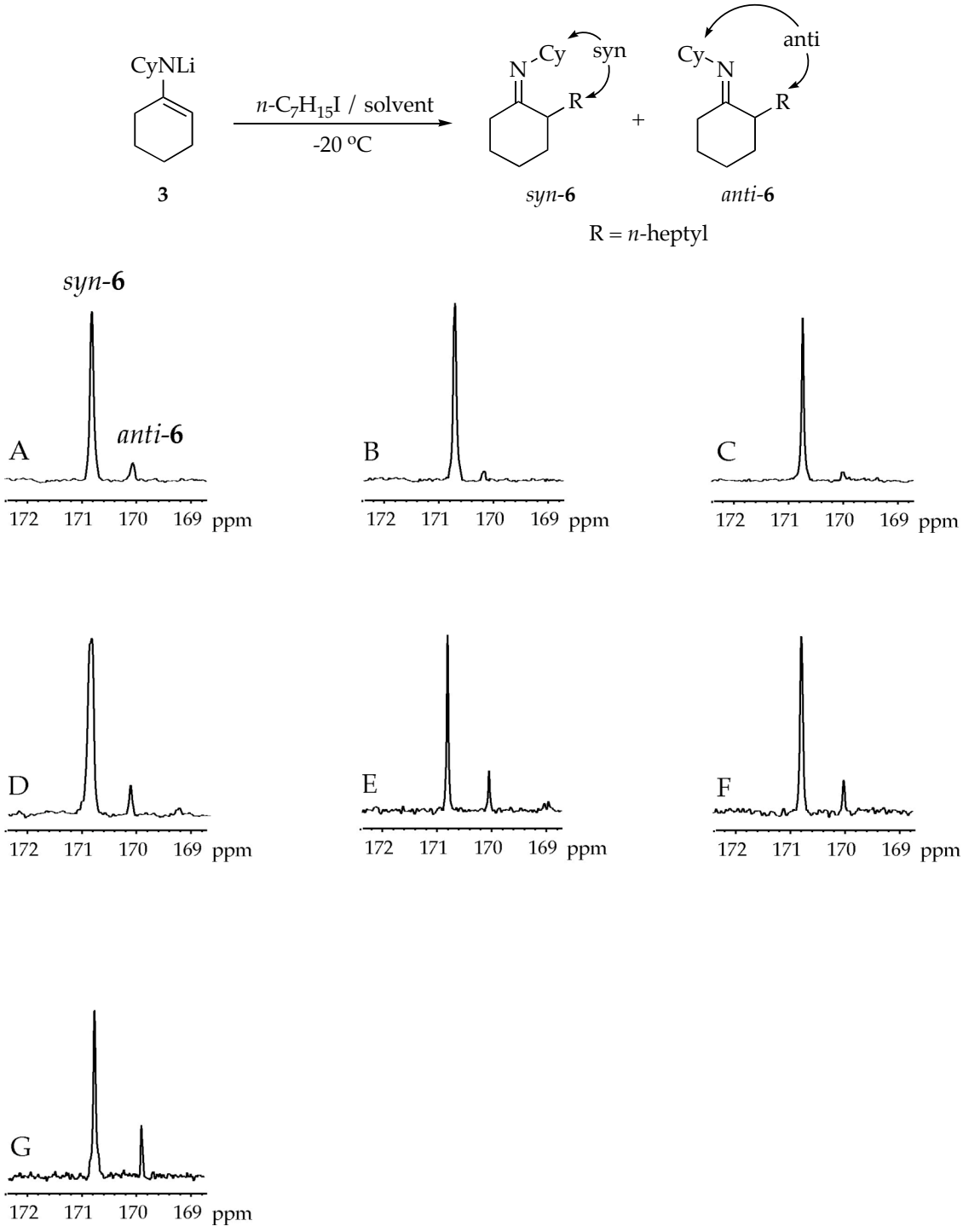
I. NMR spectra of [^{15}N]cyclohexylcarboxamide. (A) ^{1}H NMR (400 MHz, DMSO-d_6, 20 °C) δ 1.06-1.33 (m, 5H), 1.56-1.62 (m, 2H), 1.64-1.71 (m, 3H), 2.04 (tt, J = 11.4, 3.1 Hz, 1H), 6.64 (dd, J = 87.3, 2.4 Hz, 1H), 7.15 (dd, J = 89.2, 2.4 Hz, 1H). (B) ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 20 °C) δ 25.4, 25.6, 29.2, 43.7 (d, J = 7.5 Hz), 177.4 (d, J = 13.9 Hz).



II. NMR spectra of [^{15}N]cyclohexylammonium tosylate. (A) ^{1}H NMR (400 MHz, D_2O, 20 °C) δ 1.05-1.16 (m, 1H), 1.19-1.34 (m, 4H), 1.55-1.63 (m, 1H), 1.68-1.77 (m, 2H), 1.87-1.96 (m, 2H), 2.35 (s, 3H), 3.03-3.11 (m, 1H), 7.32 (d, J = 8.3 Hz, 2H), 7.65 (d, J = 8.3 Hz, 2H). (B) $^{13}C\{^{1}H\}$ NMR (75 MHz, D_2O, 20 °C) δ 20.7, 23.9, 24.4, 50.4 (d, J = 4.6 Hz), 125.5, 129.5, 139.8, 142.3.



III. NMR spectra of [^{15}N]**5**. (A) ^{1}H NMR (400 MHz, $CDCl_3$, 20 ^{o}C) δ 1.30-1.47 (m, 6H), 1.56-1.81 (m, 11H), 2.22-2.31 (m, 4H), 3.23-3.34 (m, 1H). (B) $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$, 20 ^{o}C) δ 25.3, 25.8, 26.4, 27.8, 28.1, 29.2 (d, J = 2.9 Hz), 34.3 (d, J = 2.9 Hz), 58.0, 170.9 (d, J = 7.0 Hz).

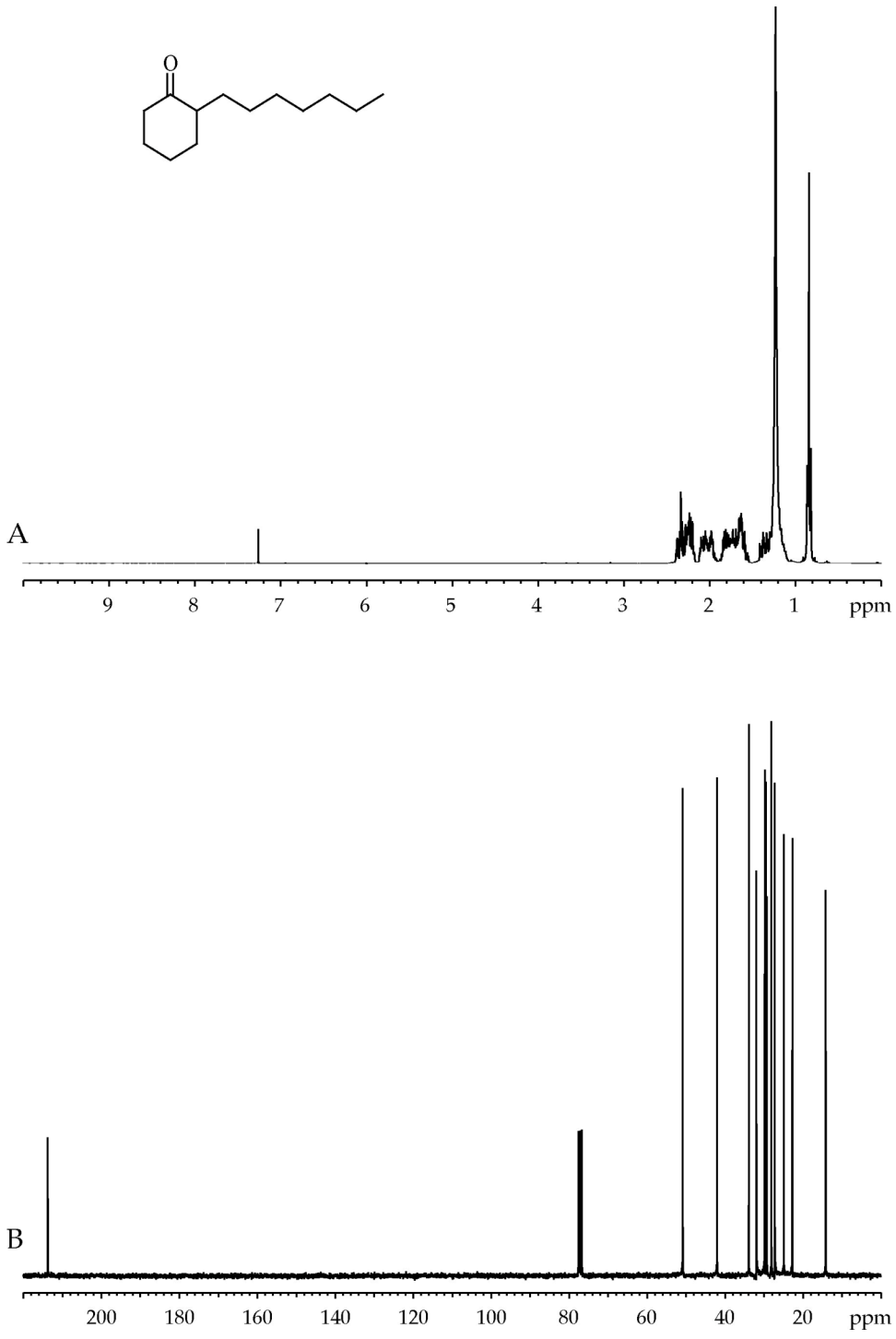


IV. C=N region of the ^{13}C spectra of syn/anti mixtures of imine **6** resulting from the alkylation of **3** with 1.1 equiv of *n*-$C_7H_{15}I$ in: (A) THF; (B) THP; (C) 2-MeTHF; (D) *n*-BuOMe; (E) 2,2-Me_2THF; (F) Et_2O; (G) *t*-BuOMe.

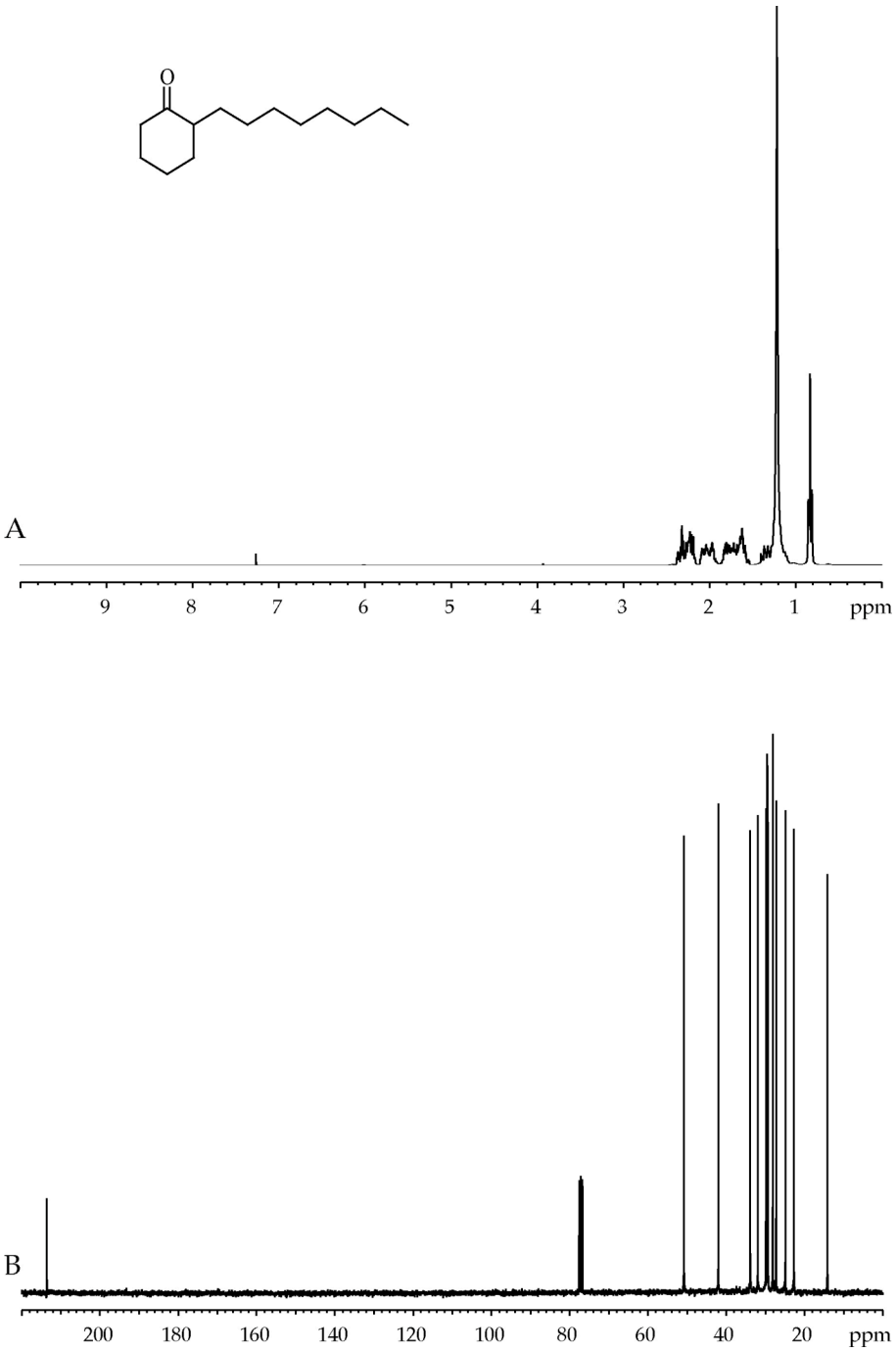
IV. (*Continued*) Syn/anti stereoselectivity of the alkylation of lithiated *N*-alkylimine **3** with *n*-$C_7H_{15}I$[a]

entry	solvent	syn/anti[b]
1	THF	10:1
2	THP	>20:1
3	2-MeTHF	>20:1
4	*n*-BuOMe	8:1
5	2,2-Me_2THF	6:1
6	Et_2O	6:1
7	*t*-BuOMe	5:1

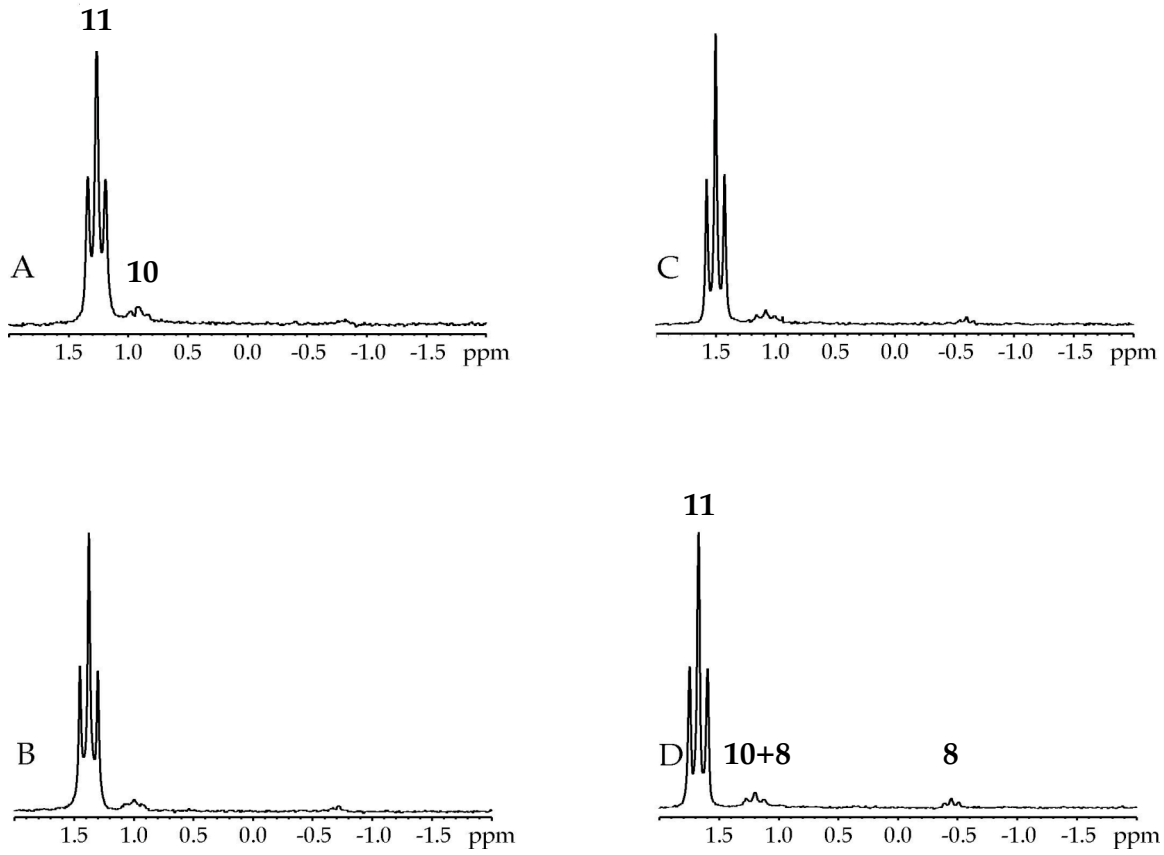
[a] Reactions were carried out at -20 °C using 0.1 M solutions of **3** in neat solvent and 1.1 equiv of *n*-$C_7H_{15}I$. The sample was sealed in an NMR tube under Ar and kept at -78 °C until the spectra were recorded. Under these conditions, the isomerizations ($t_{1/2}$ > 6 h at 40 °C) proved to be slower than the alkylations. [b] Numerical ratios were obtained from ^{13}C NMR spectra. The syn and anti orientations in 2-heptyl imine **6** (R = *n*-C_7H_{15}) were assigned following protocols described elsewhere.[5a]



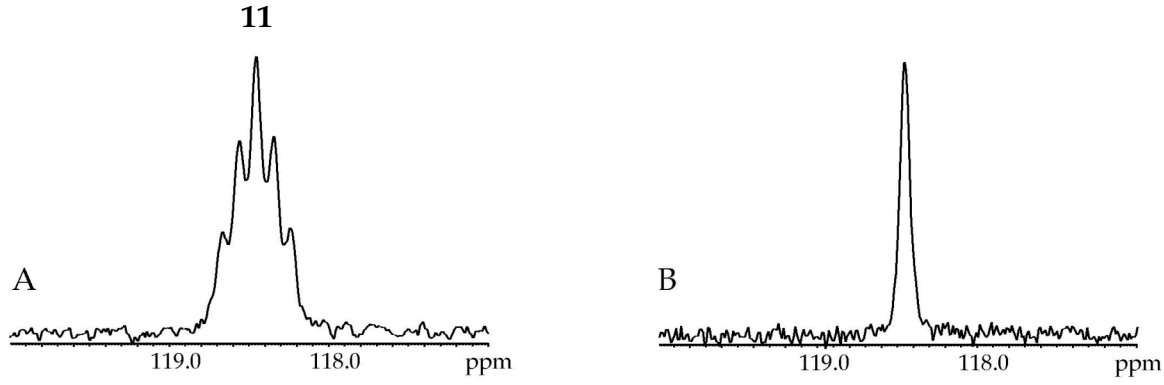
V. NMR spectra of 2-heptyl cyclohexanone. (A) ^{1}H NMR (300 MHz, $CDCl_3$, 20 ^{o}C) δ 0.84 (t, J = 6.6 Hz, 3H), 1.16-1.42 (m, 12H), 1.55-1.87 (m, 4H), 1.94-2.12 (m, 2H), 2.17-2.40 (m, 3H). (B) ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 20 ^{o}C) δ 14.2, 22.8, 24.9, 27.3, 28.1, 29.3, 29.5, 29.8, 31.9, 33.9, 42.0, 50.9, 213.7.



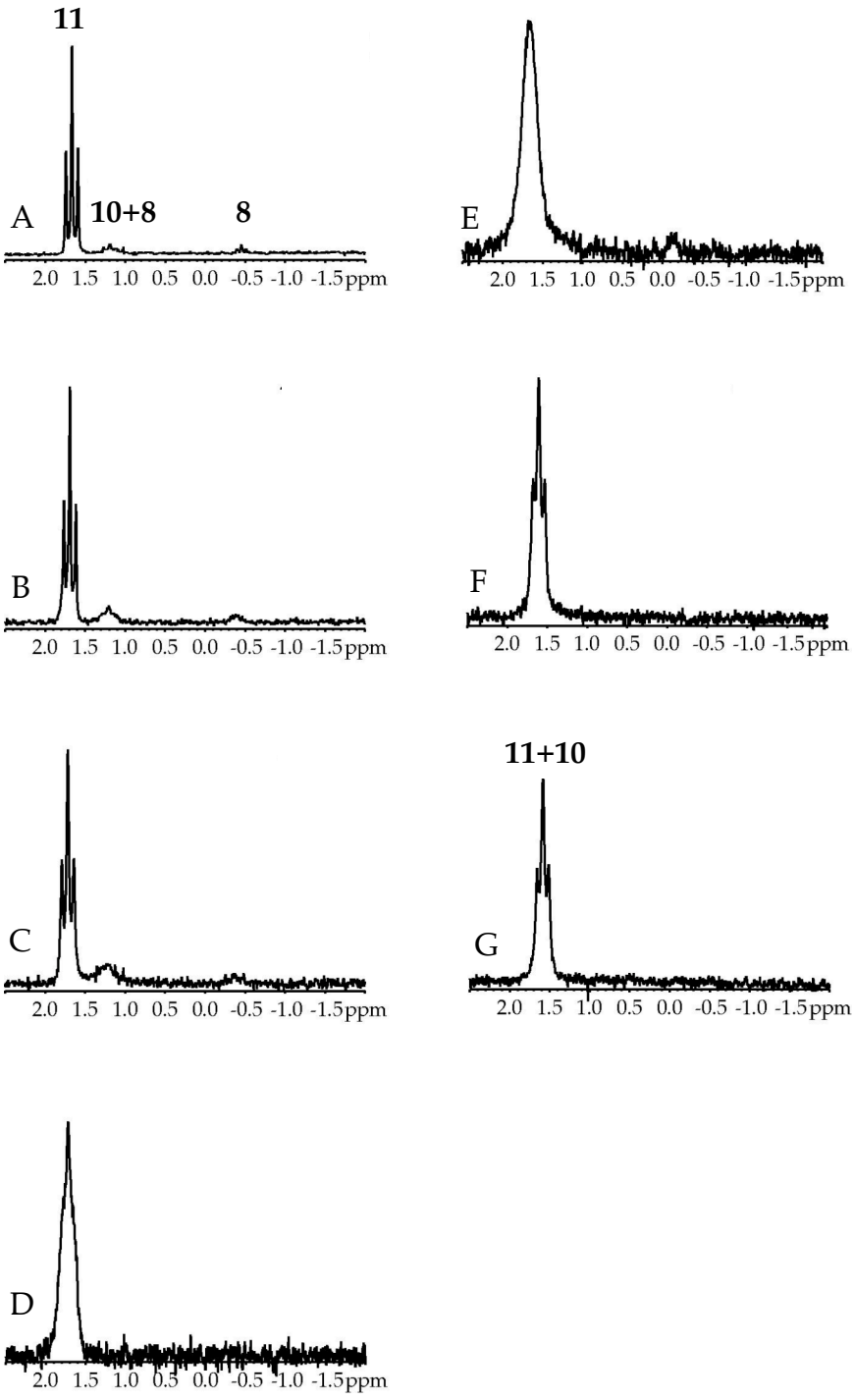
VI. NMR spectra of 2-octyl cyclohexanone. (A) ^{1}H NMR (300 MHz, $CDCl_3$, 20 ^{o}C) δ 0.83 (t, J = 6.5 Hz, 3H), 1.16-1.41 (m, 14H), 1.54-1.84 (m, 4H), 1.93-2.11 (m, 2H), 2.17-2.38 (m, 3H). (B) ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 20 ^{o}C) δ 14.2, 22.7, 24.9, 27.3, 28.1, 29.4, 29.5, 29.6, 29.9, 32.0, 33.9, 42.0, 50.8, 213.6.



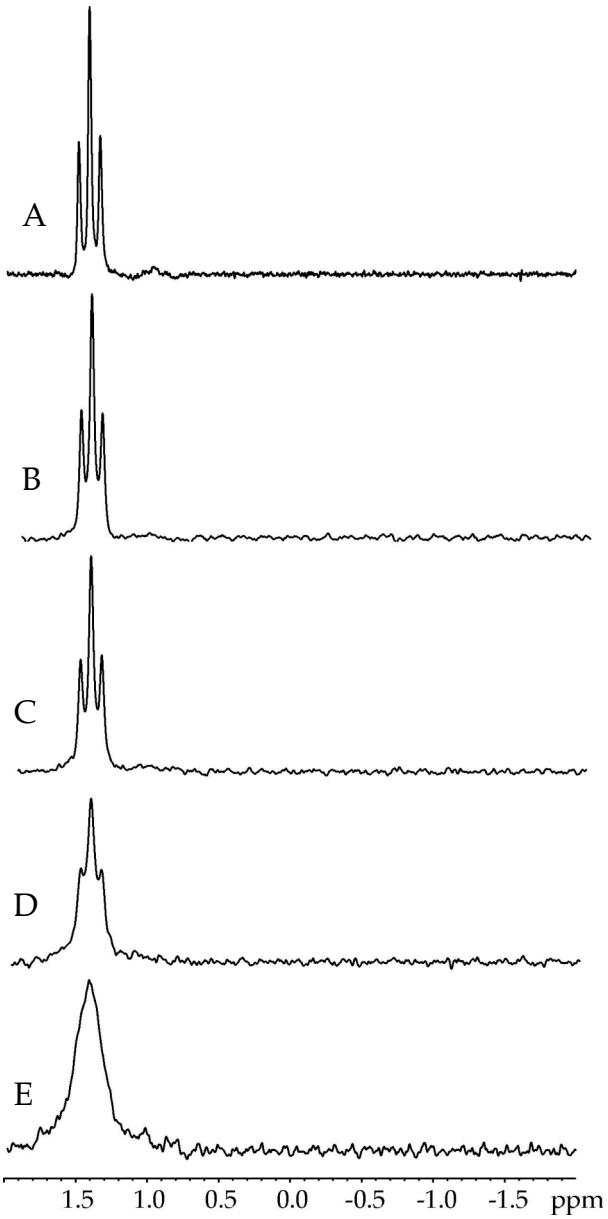
VII. ^{6}Li NMR spectra of 0.10 M [^{6}Li,^{15}N]**3** in *n*-BuOMe/toluene recorded at -90 ^{o}C: (A) 2.0 M *n*-BuOMe; (B) 4.0 M *n*-BuOMe; (C) 6.0 M *n*-BuOMe; (D) 8.1 M *n*-BuOMe.



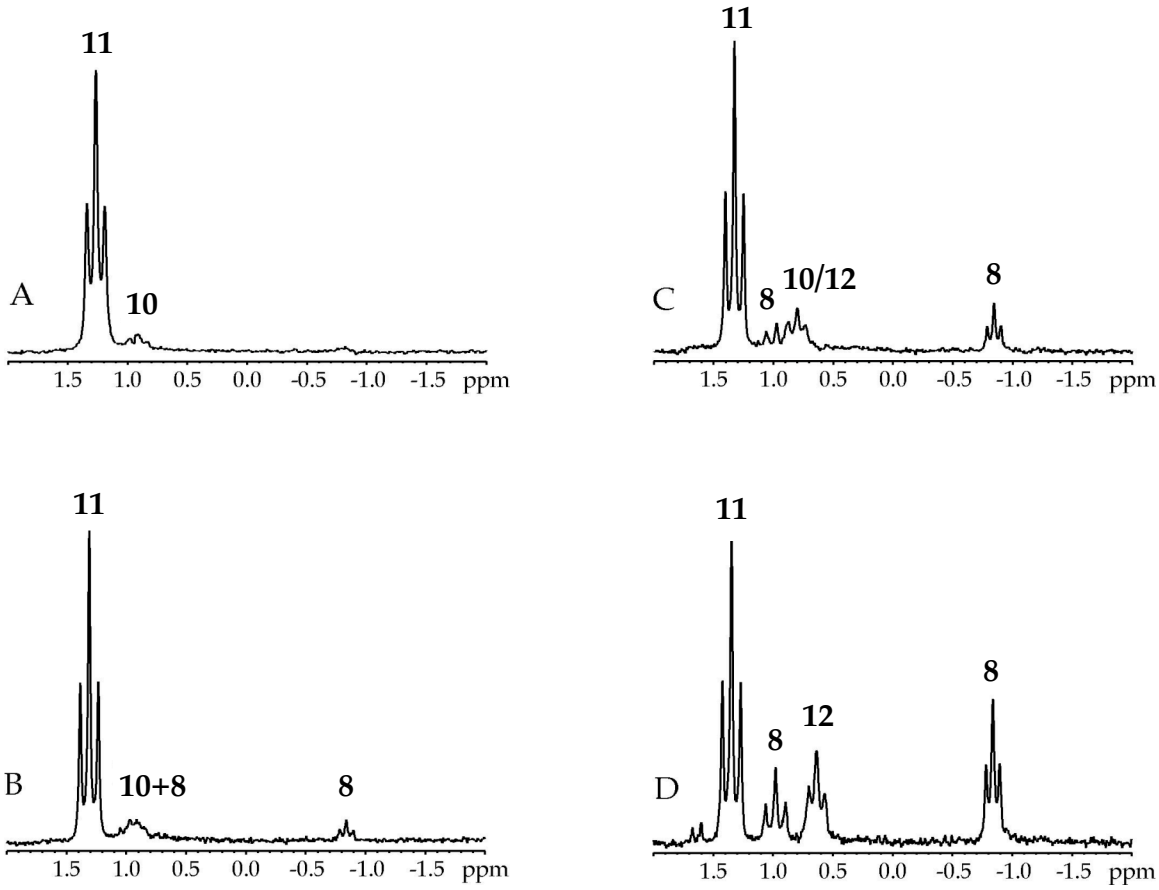
VIII. ^{15}N NMR spectra of 0.10 M [^{6}Li,^{15}N]**3** in *n*-BuOMe recorded at -90 ^{o}C: (A) ^{6}Li coupled; (B) ^{6}Li decoupled.



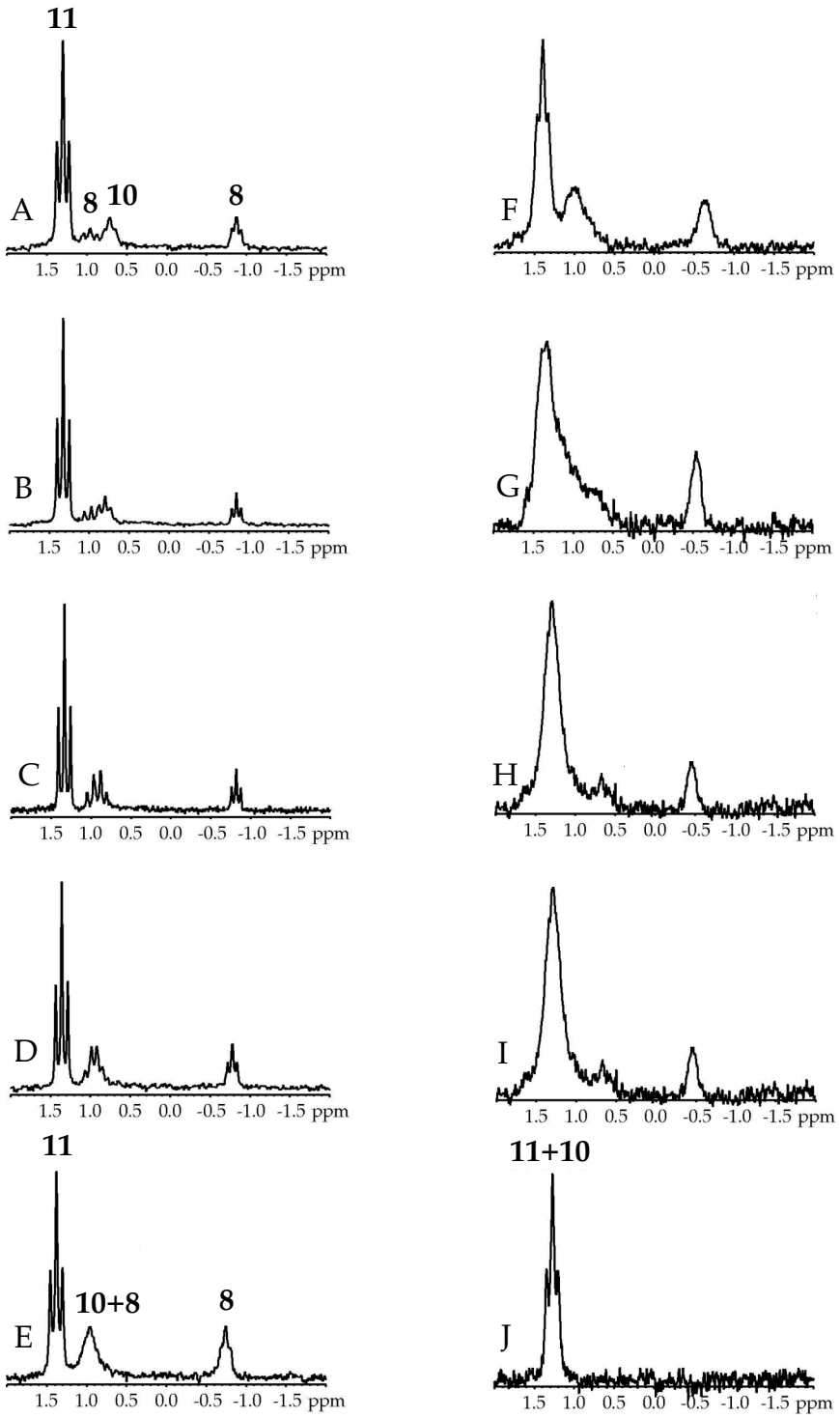
IX. ^{6}Li NMR spectra of 0.10 M [^{6}Li,^{15}N]**3** in *n*-BuOMe recorded at: (A) -90 °C; (B) -70 °C; (C) -60 °C; (D) -50 °C; (E) -40 °C; (F) -20 °C; (G) 0 °C.



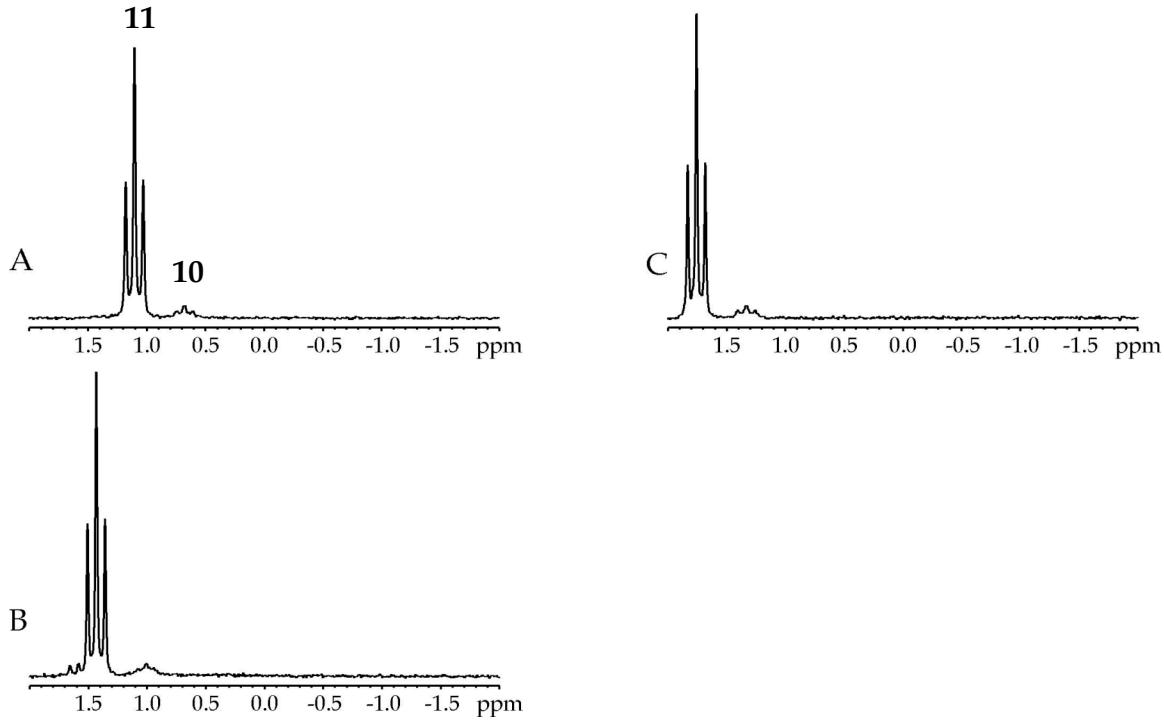
IX. (*Continued*) ^{6}Li NMR spectra of 0.10 M [^{6}Li,^{15}N]**3** in 4.0 M *n*-BuOMe/toluene recorded at: (A) -90 °C; (B) -100 °C; (C) -110 °C; (D) -120 °C; (E) -130 °C.



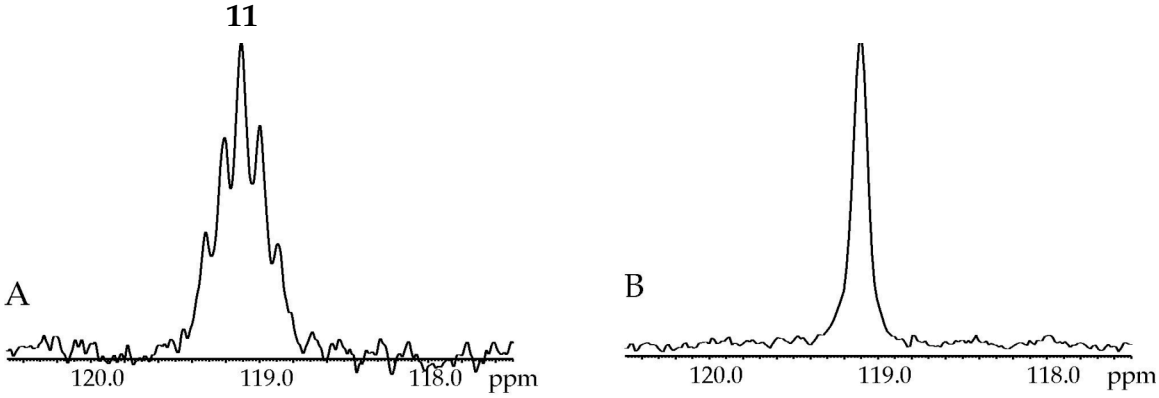
X. ^{6}Li NMR spectra of 0.10 M [^{6}Li,^{15}N]**3** in 2.0 M *n*-BuOMe/THP/toluene recorded at -90 °C: (A) 0.00 M THP; (B) 0.10 M THP; (C) 0.20 M THP; (D) 0.50 M THP.



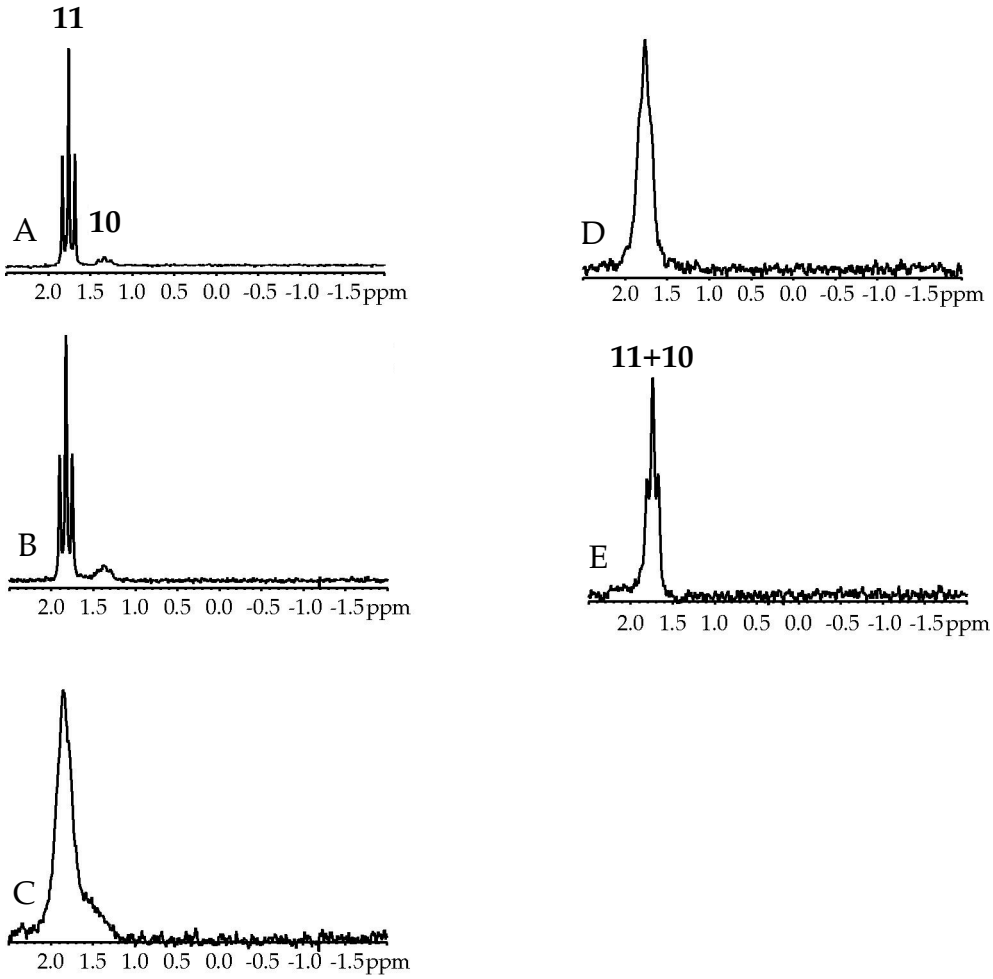
XI. ^{6}Li NMR spectra of 0.10 M [^{6}Li,^{15}N]**3** in 2.0 M *n*-BuOMe/0.20 M THP/toluene recorded at: (A) -100 °C; (B) -90 °C; (C) -80 °C; (D) -70 °C; (E) -60 °C; (F) -50 °C; (G) -40 °C; (H) -30 °C; (I) -20 °C; (J) 0 °C.



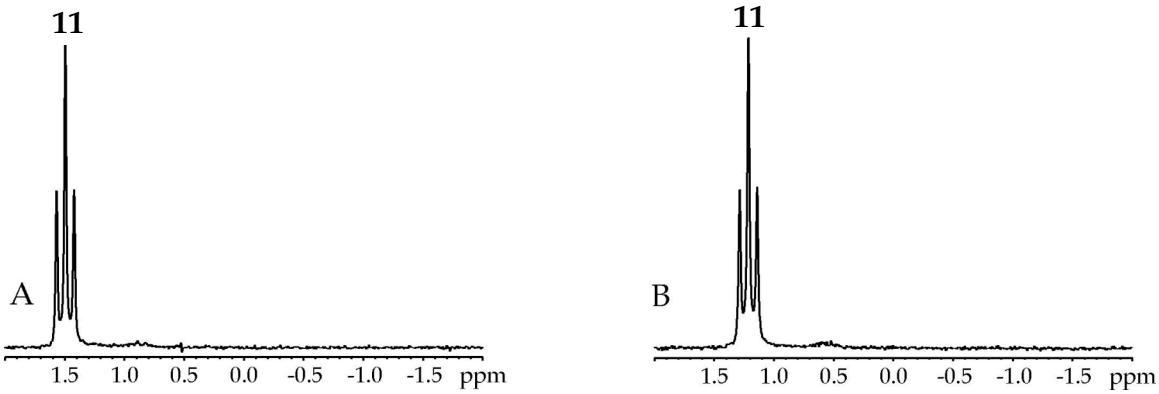
XII. ^{6}Li NMR spectra of 0.10 M [^{6}Li,^{15}N]**3** in Et_2O/toluene recorded at -90 °C: (A) 2.3 M Et_2O; (B) 4.7 M Et_2O; (C) 9.4 M Et_2O.



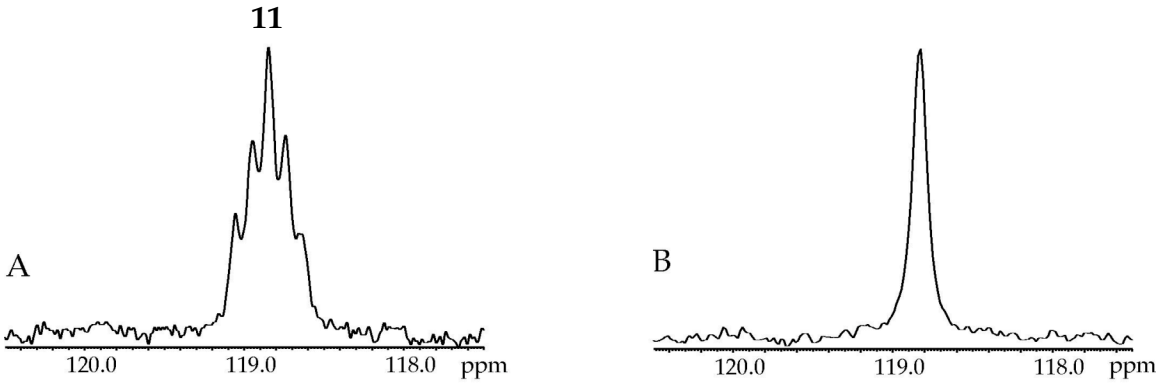
XIII. ^{15}N NMR spectra of 0.10 M [^{6}Li,^{15}N]**3** in Et_2O recorded at -90 °C: (A) ^{6}Li coupled; (B) ^{6}Li decoupled.



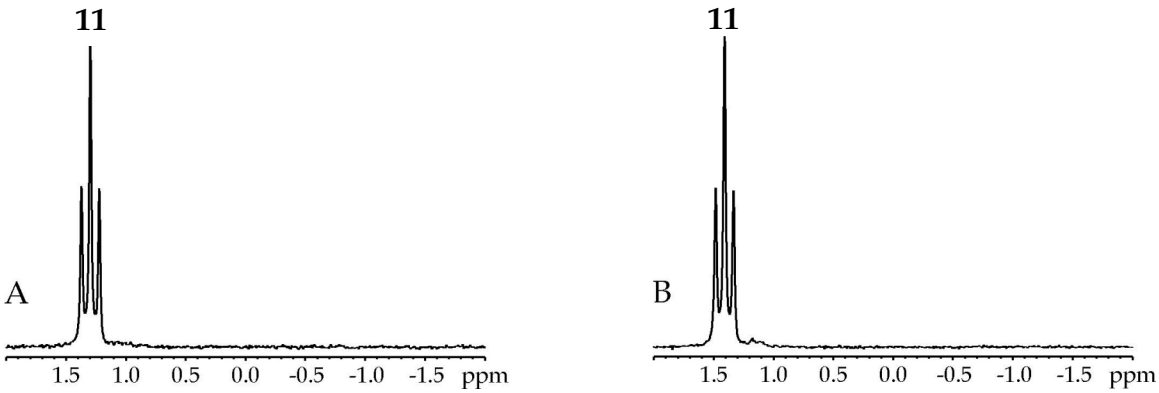
XIV. ^{6}Li NMR spectra of 0.10 M [^{6}Li,^{15}N]**3** in Et_2O recorded at: (A) -90 °C; (B) -75 °C; (C) -50 °C; (D) -30 °C; (E) 0 °C.



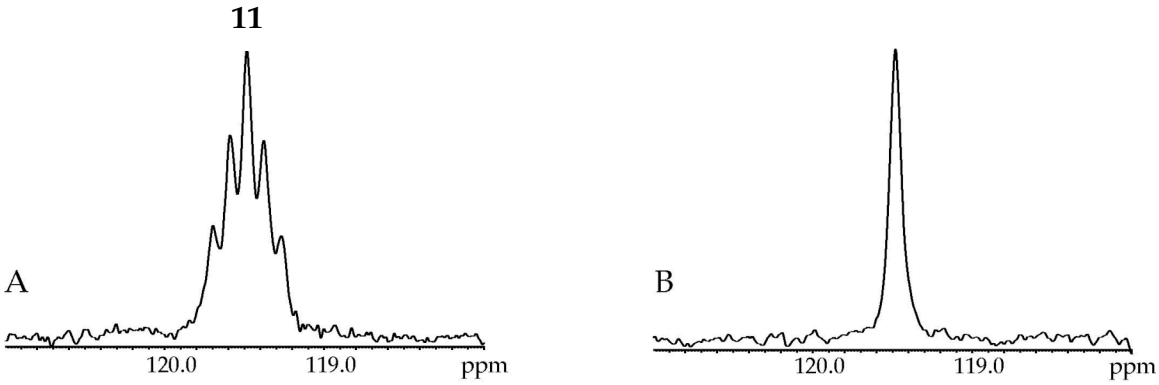
XV. ^{6}Li NMR spectra of 0.10 M [^{6}Li,^{15}N]**3** in *t*-BuOMe/toluene recorded at -90 °C: (A) 2.0 M *t*-BuOMe; (B) 8.1 M *t*-BuOMe.



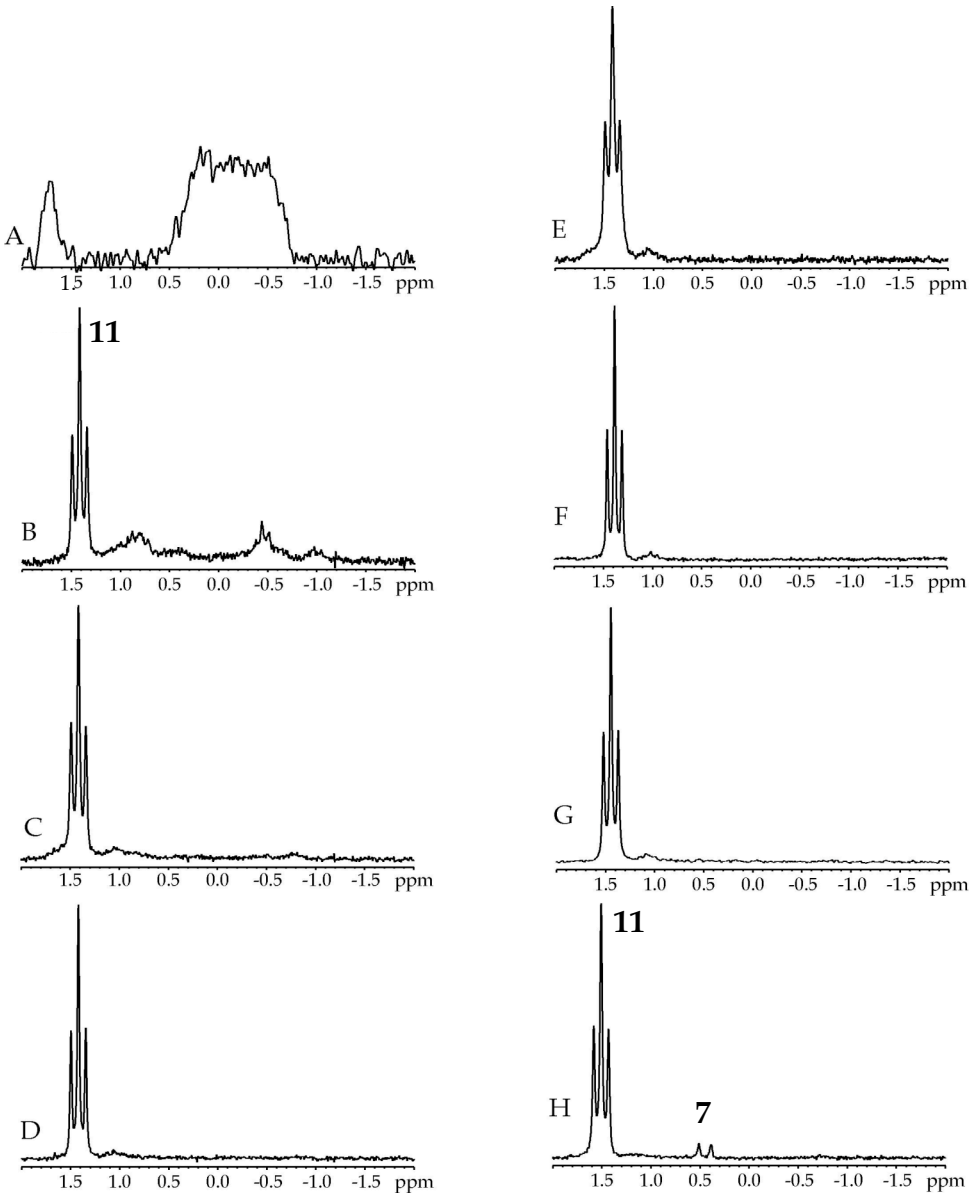
XVI. ^{15}N NMR spectra of 0.10 M [^{6}Li,^{15}N]**3** in *t*-BuOMe recorded at -90 °C: (A) ^{6}Li coupled; (B) ^{6}Li decoupled.



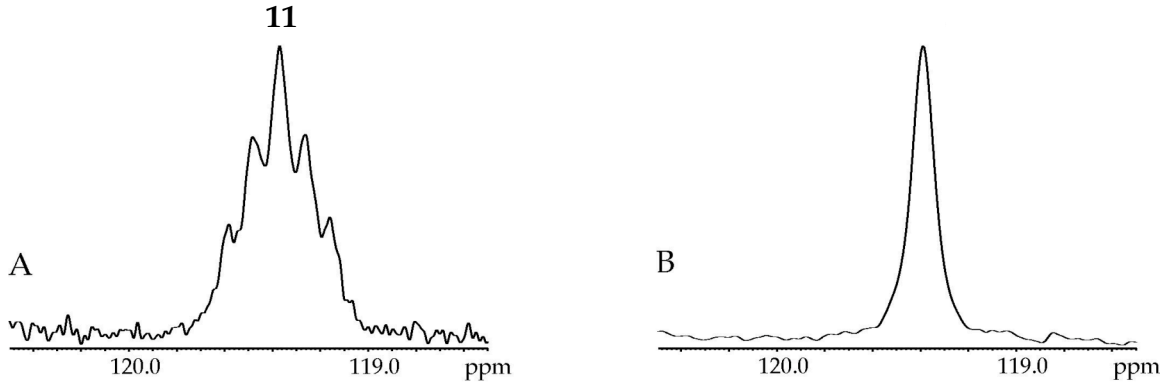
XVII. ^{6}Li NMR spectra of 0.10 M [^{6}Li,^{15}N]**3** in 2,2-Me_2THF/toluene recorded at -90 °C: (A) 2.1 M 2,2-Me_2THF; (B) 8.4 M 2,2-Me_2THF.



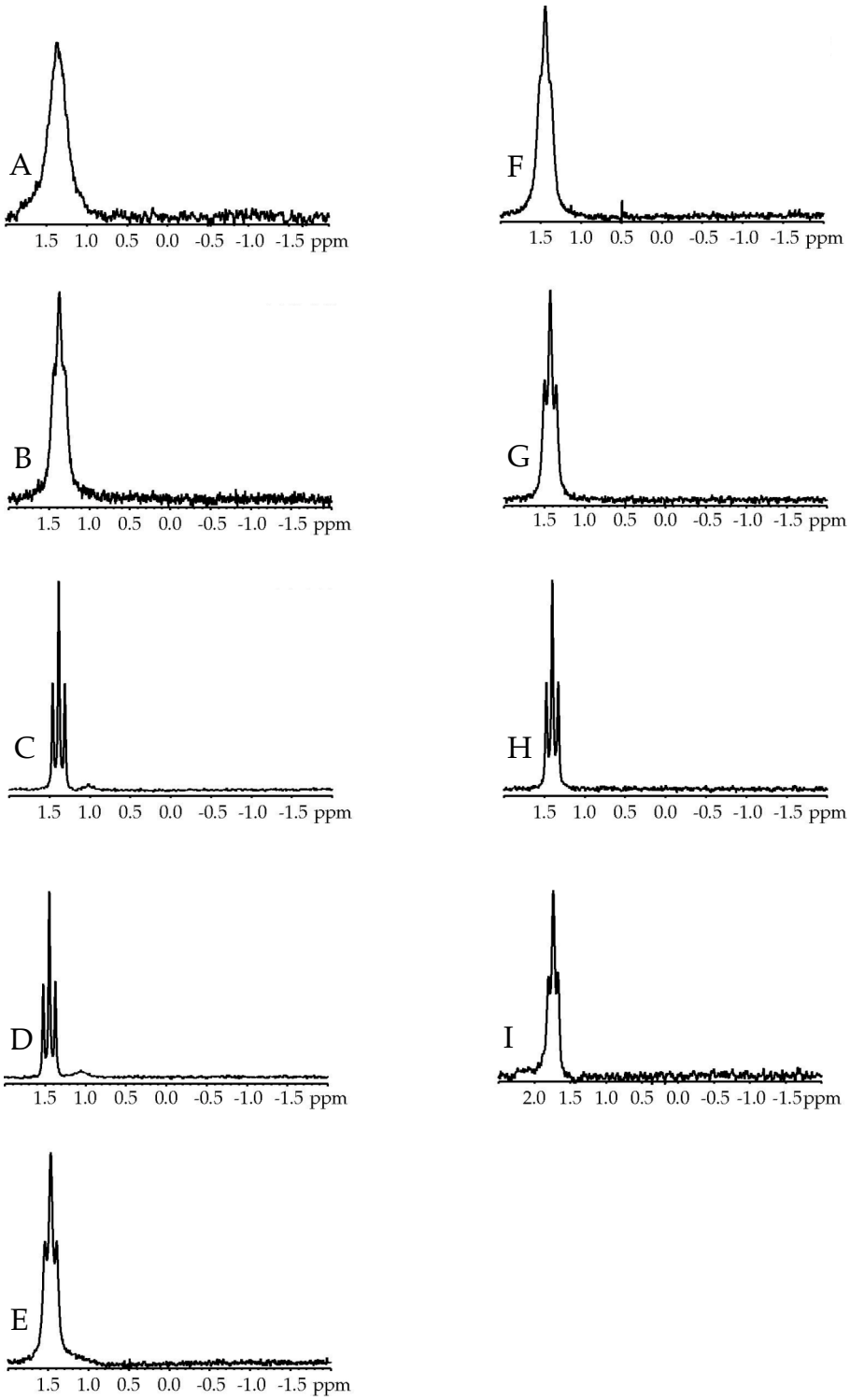
XVIII. ^{15}N NMR spectra of 0.10 M [^{6}Li,^{15}N]**3** in 2,2-Me_2THF recorded at -90 °C: (A) ^{6}Li coupled; (B) ^{6}Li decoupled.



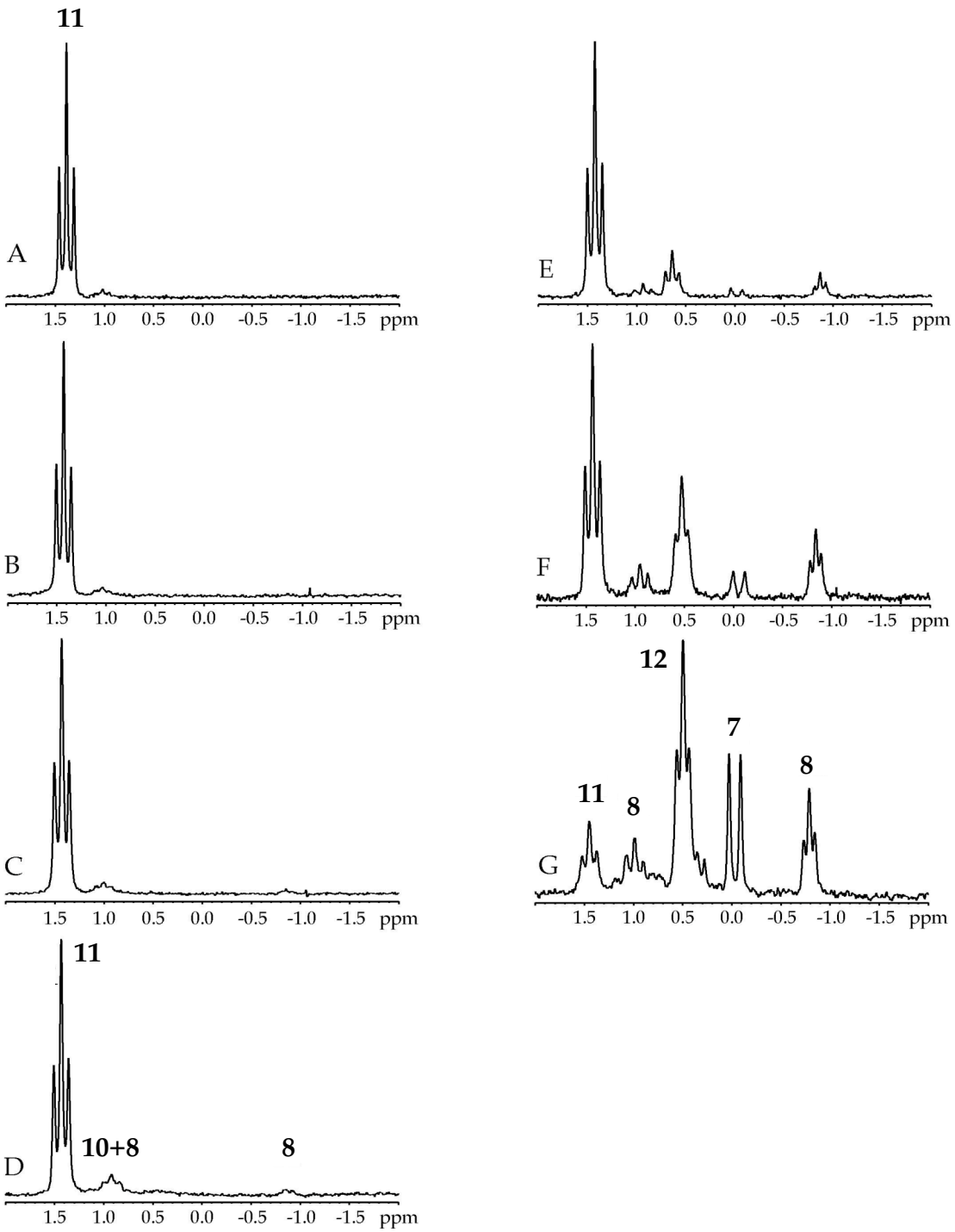
XIX. (A) ^{6}Li NMR spectra of 0.10 M [^{6}Li,^{15}N]**3** in toluene recorded at -60 °C. ^{6}Li NMR spectra of 0.10 M [^{6}Li,^{15}N]**3** in 2-MeTHF/toluene recorded at -90 °C: (B) 0.05 M 2-MeTHF; (C) 0.075 M 2-MeTHF; (D) 0.10 M 2-MeTHF; (E) 0.20 M 2-MeTHF; (F) 2.40 M 2-MeTHF; (G) 4.90 M 2-MeTHF; (H) 9.90 M 2-MeTHF.



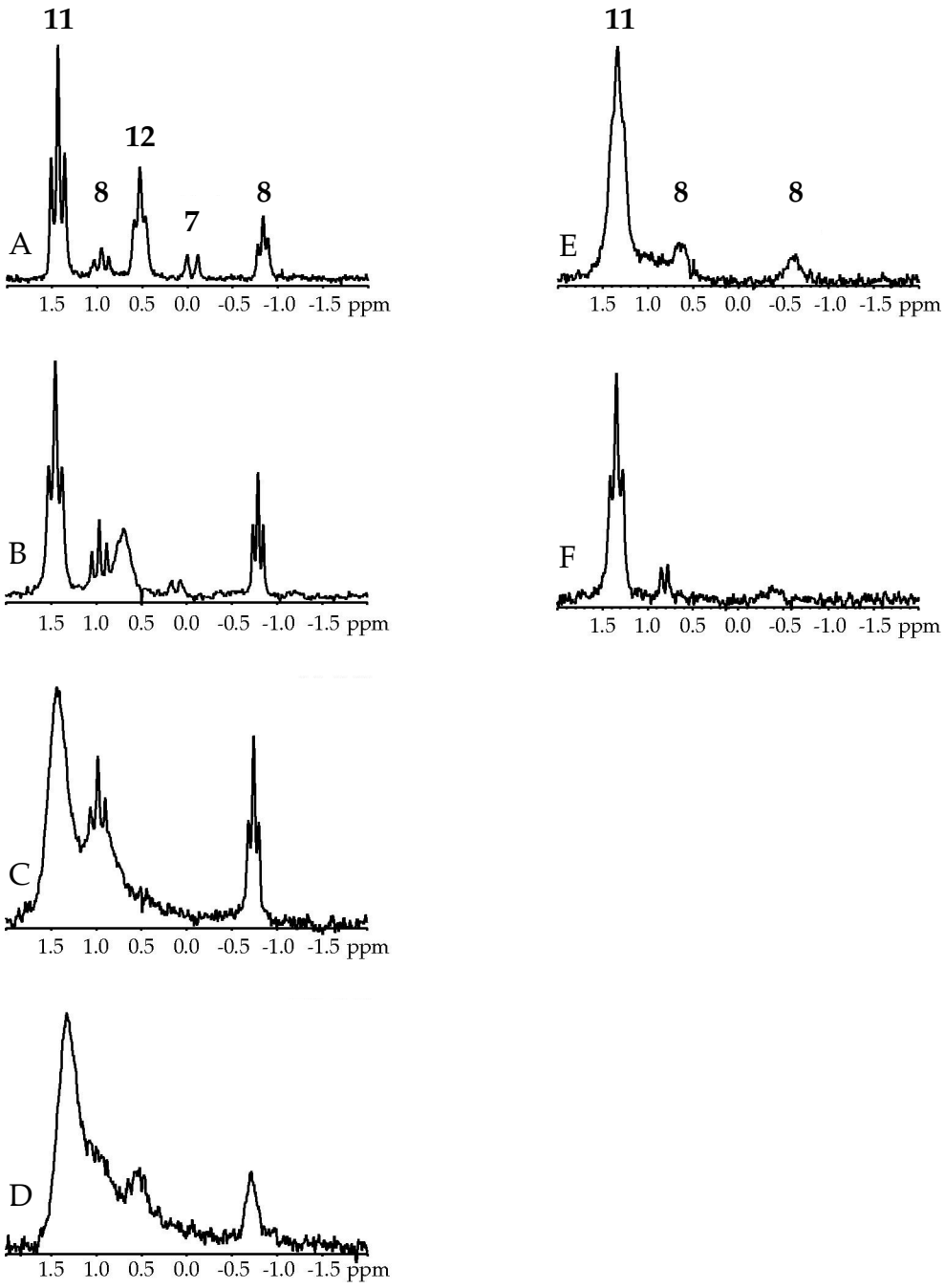
XX. ^{15}N NMR spectra of 0.10 M [^{6}Li,^{15}N]**3** in 2-MeTHF recorded at -90 ^{o}C: (A) ^{6}Li coupled; (B) ^{6}Li decoupled.



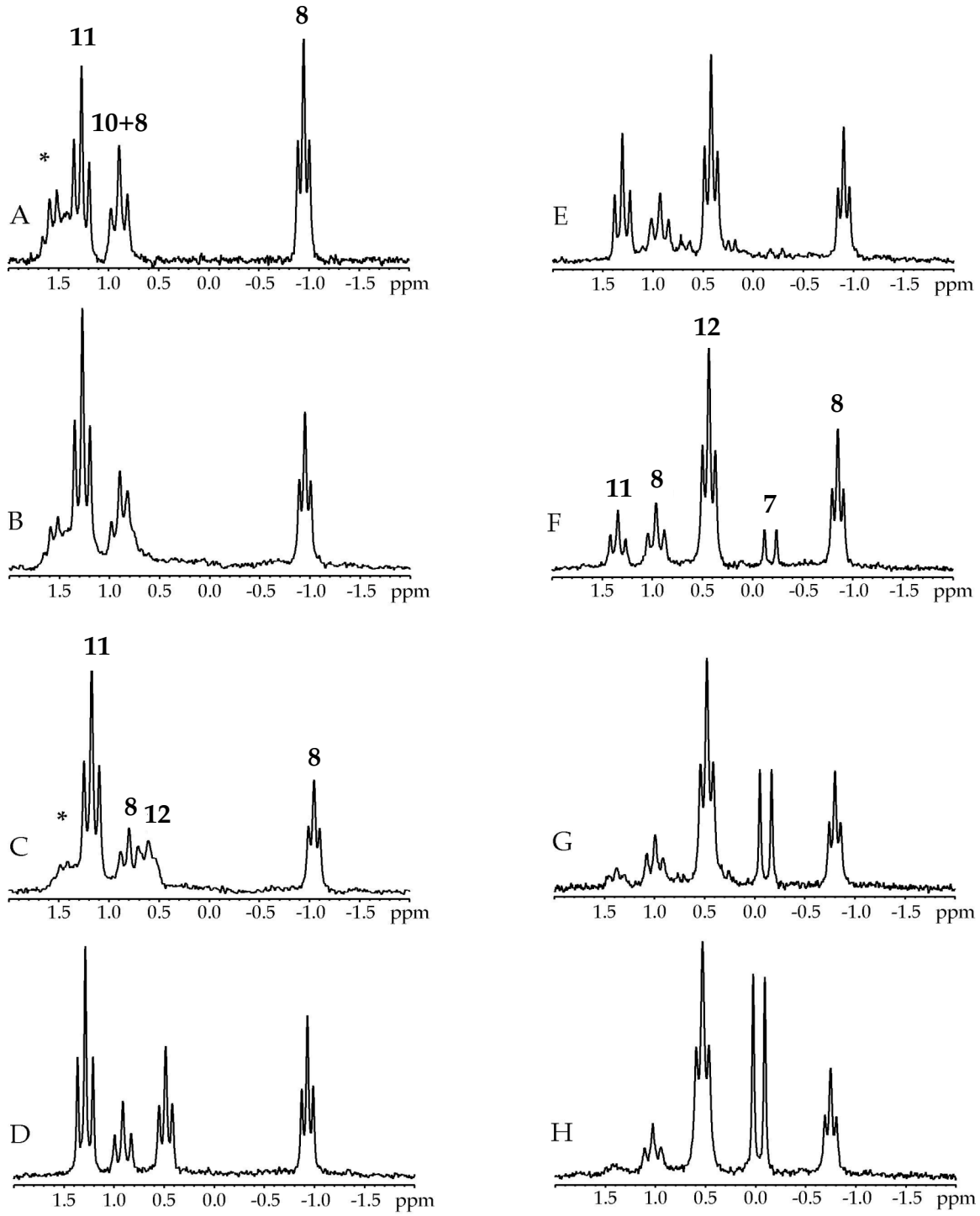
XXI. ^{6}Li NMR spectra of 0.10 M [^{6}Li,^{15}N]**3** in 2.4 M 2-MeTHF/toluene recorded at: (A) -115 °C; (B) -110 °C; (C) -90 °C; (D) -75 °C; (E) -60 °C; (F) -50 °C; (G) -40 °C; (H) -20 °C; (I) 0 °C.



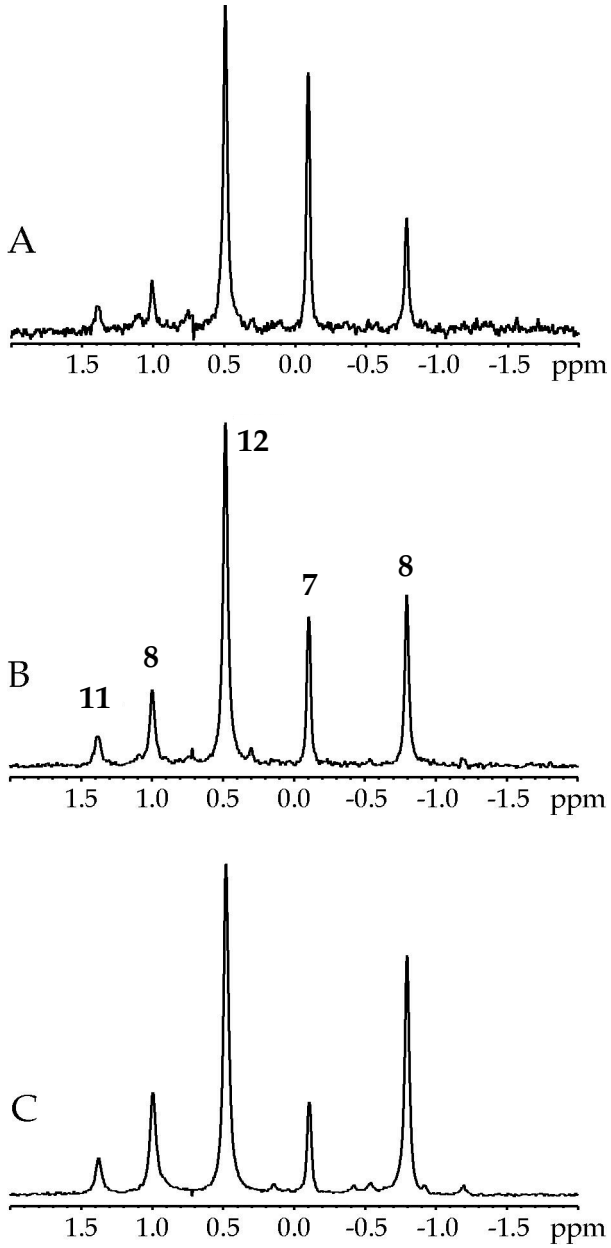
XXII. ^{6}Li NMR spectra of 0.10 M [^{6}Li,^{15}N]**3** in 2.0 M 2-MeTHF / THP / toluene recorded at -90 °C: (A) 0.00 M THP; (B) 0.10 M THP; (C) 0.20 M THP; (D) 0.50 M THP; (E) 1.0 M THP; (F) 2.0 M THP; (G) 4.0 M THP.



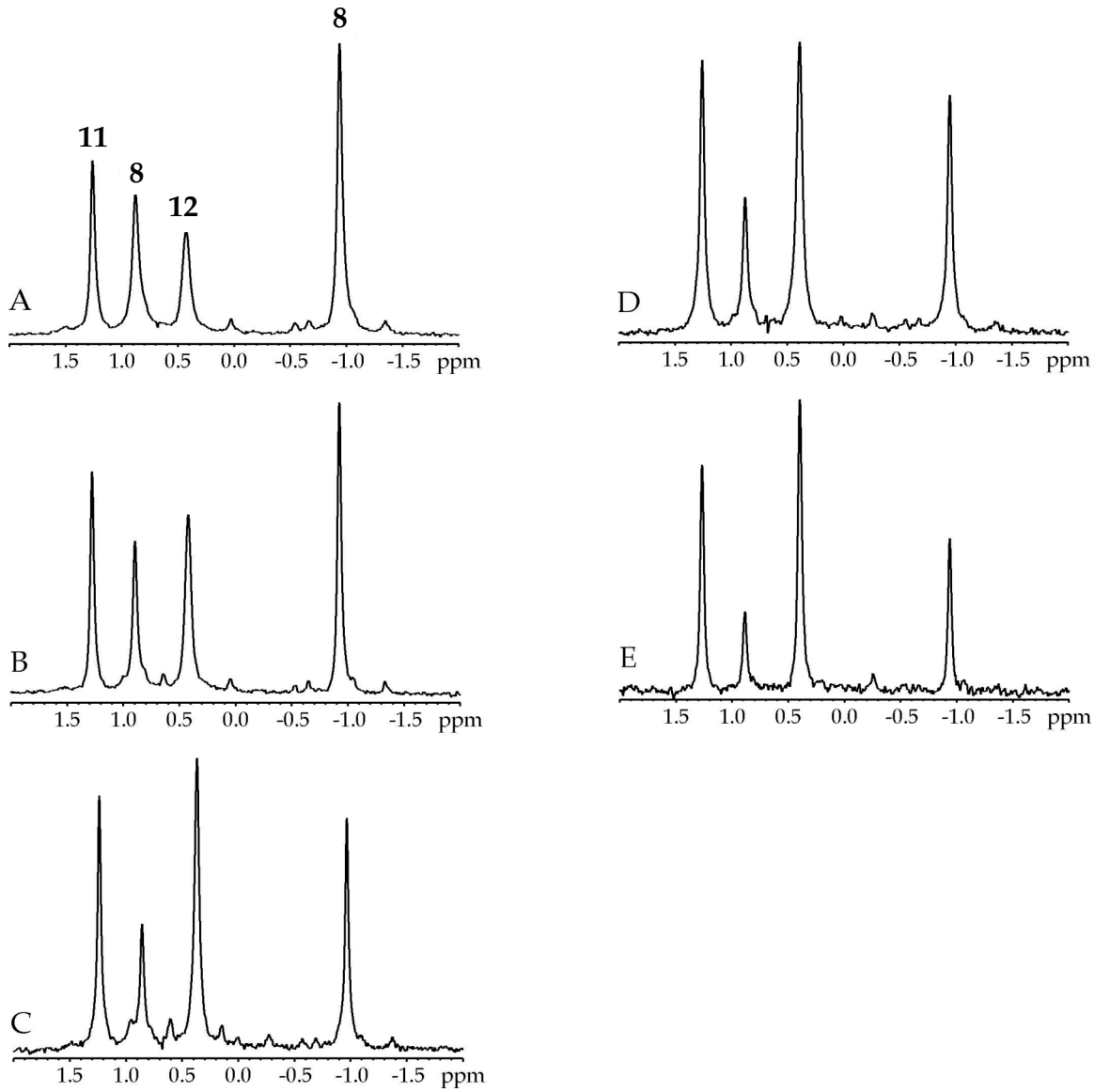
XXIII. ^{6}Li NMR spectra of 0.10 M [^{6}Li,^{15}N]**3** in 2.0 M 2-MeTHF/2.0 M THP/toluene recorded at: (A) -90 °C; (B) -75 °C; (C) -60 °C; (D) -50 °C; (E) -40 °C; (F) -20 °C.



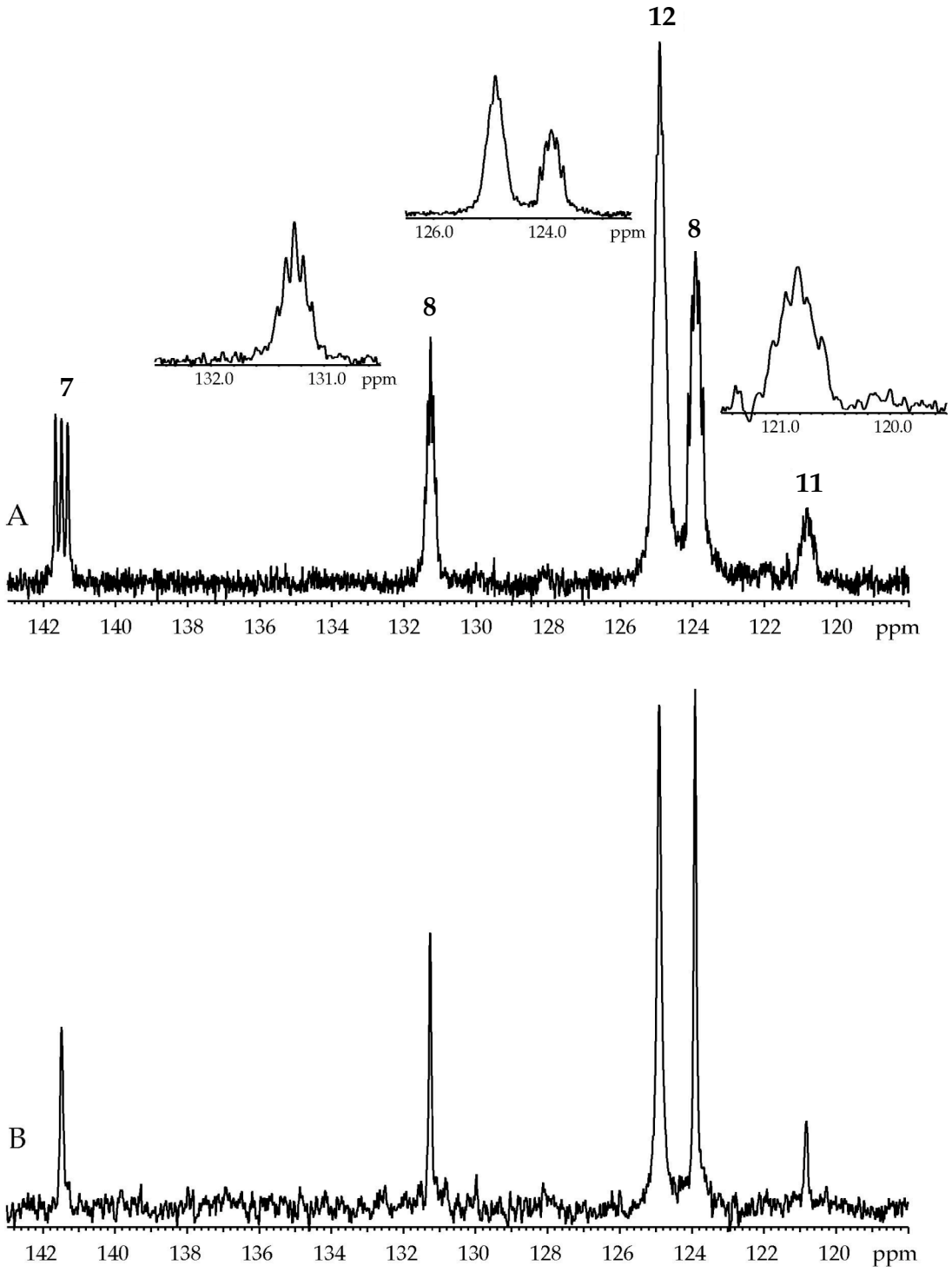
XXIV. ^{6}Li NMR spectra of 0.10 M [^{6}Li,^{15}N]**3** in THP/toluene recorded at -90 °C: (A) 0.075 M; (B) 0.10 M THP; (C) 0.20 M THP; (D) 0.80 M THP; (E) 1.60 M THP; (F) 3.30 M THP; (G) 5.0 M THP; (H) 6.70 M THP. * Unassigned.



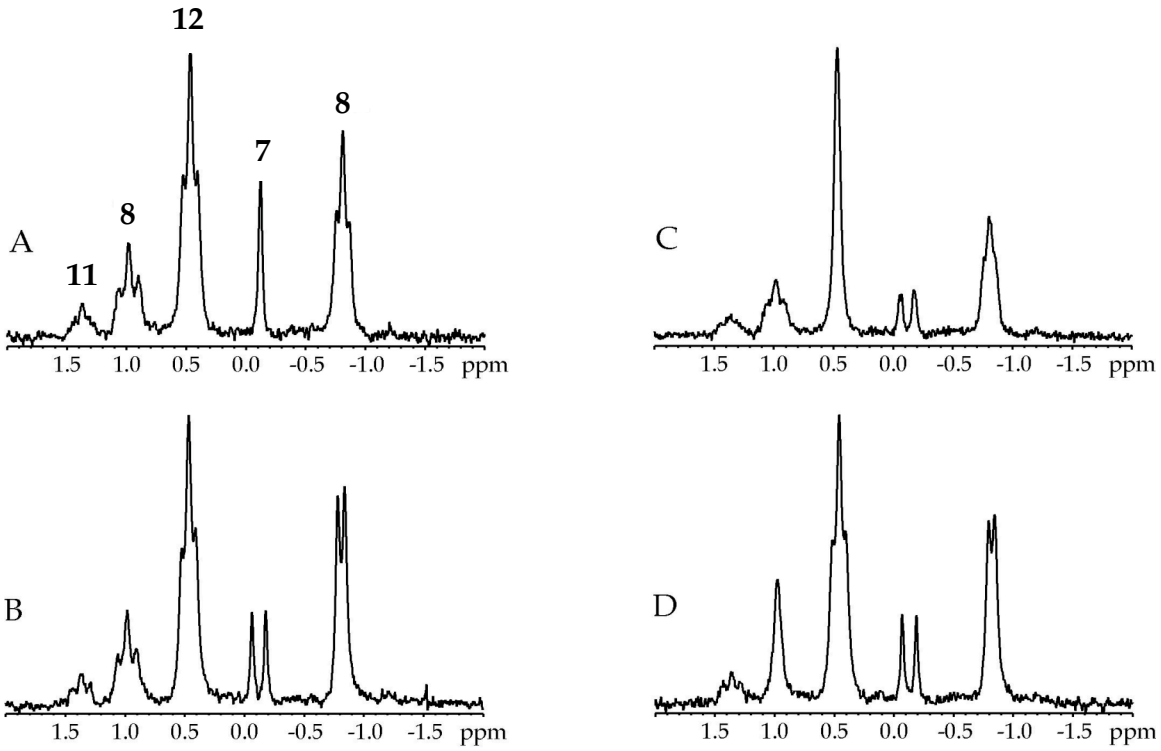
XXV. ^{6}Li{^{15}N} NMR spectra of [^{6}Li,^{15}N]**3** in 5.0 M THP/toluene recorded at -90 ^{o}C: (A) 0.030 M [^{6}Li,^{15}N]**3**; (B) 0.10 M [^{6}Li,^{15}N]**3**; (C) 0.20 M [^{6}Li,^{15}N]**3**.



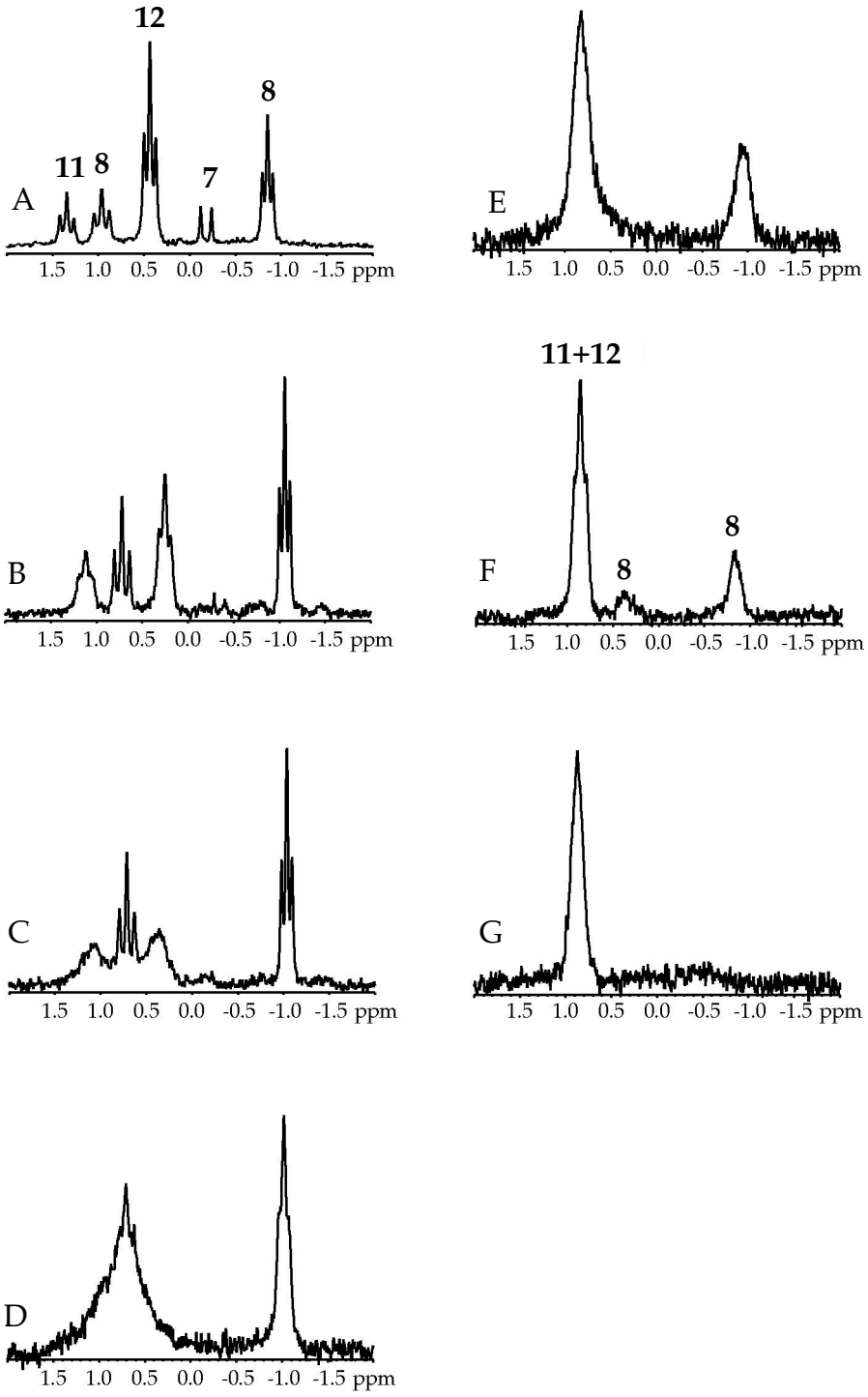
XXVI. ^{6}Li{^{15}N} NMR spectra of [^{6}Li,^{15}N]**3** in 1.6 M THP/toluene recorded at -90 ^{o}C: (A) 0.40 M [^{6}Li,^{15}N]**3**; (B) 0.20 M [^{6}Li,^{15}N]**3**; (C) 0.10 M [^{6}Li,^{15}N]**3**; (D) 0.050 M [^{6}Li,^{15}N]**3**; (E) 0.025 M [^{6}Li,^{15}N]**3**.



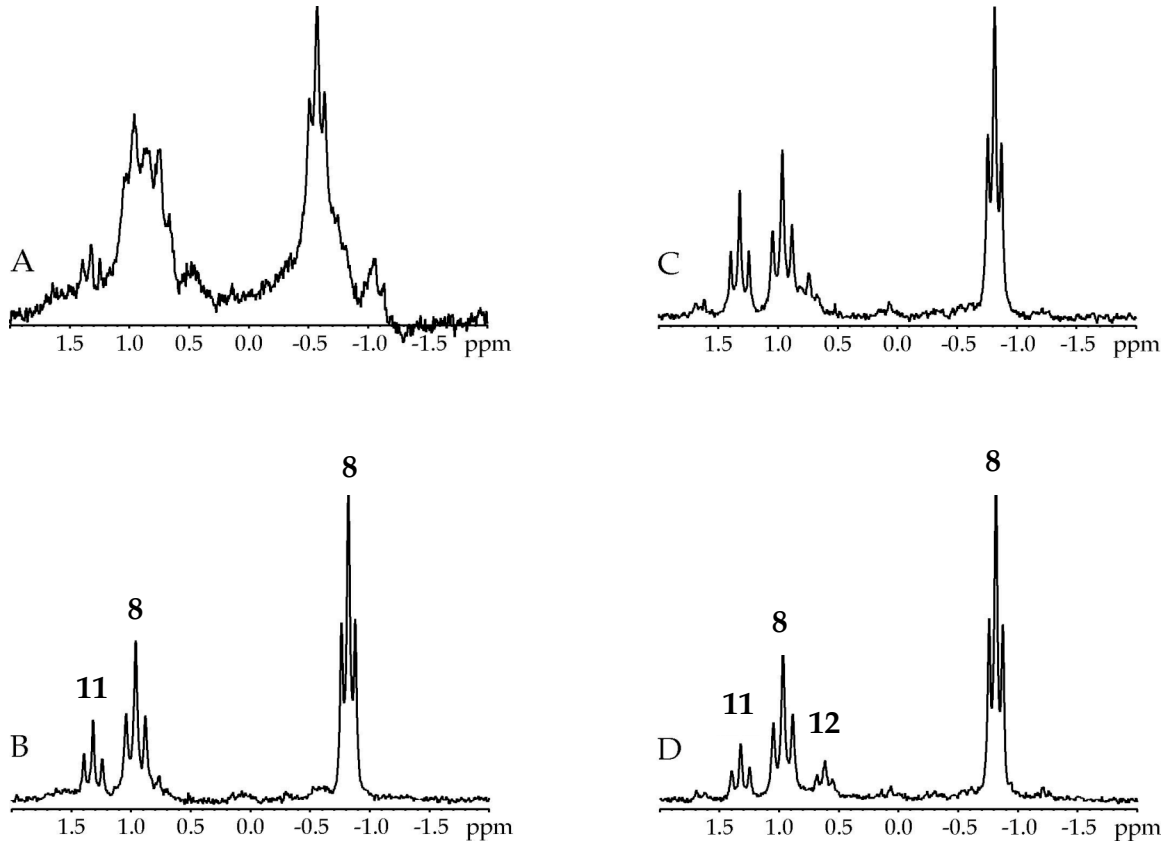
XXVII. ^{15}N NMR spectra of 0.20 M [^{6}Li,^{15}N]**3** in 5.0 M THP/toluene recorded at -90 °C: (A) ^{6}Li coupled; (B) ^{6}Li decoupled.



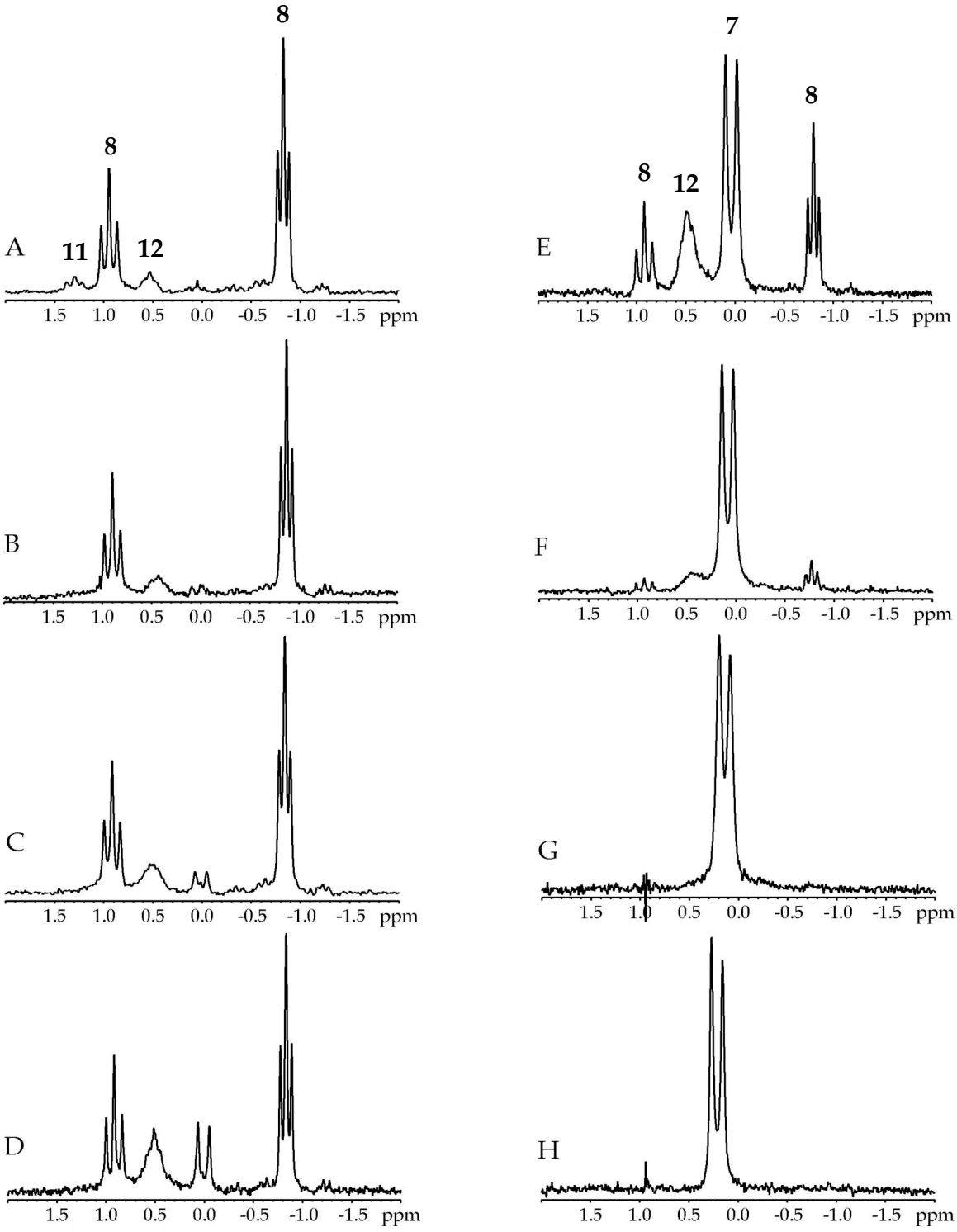
XXVIII. Selective ^{15}N decoupled ^{6}Li NMR spectra of 0.20 M [^{6}Li,^{15}N]**3** in 5.0 M THP/toluene recorded at -90 °C: (A) 142 ppm; (B) 131 ppm; (C) 125 ppm; (D) 124 ppm.



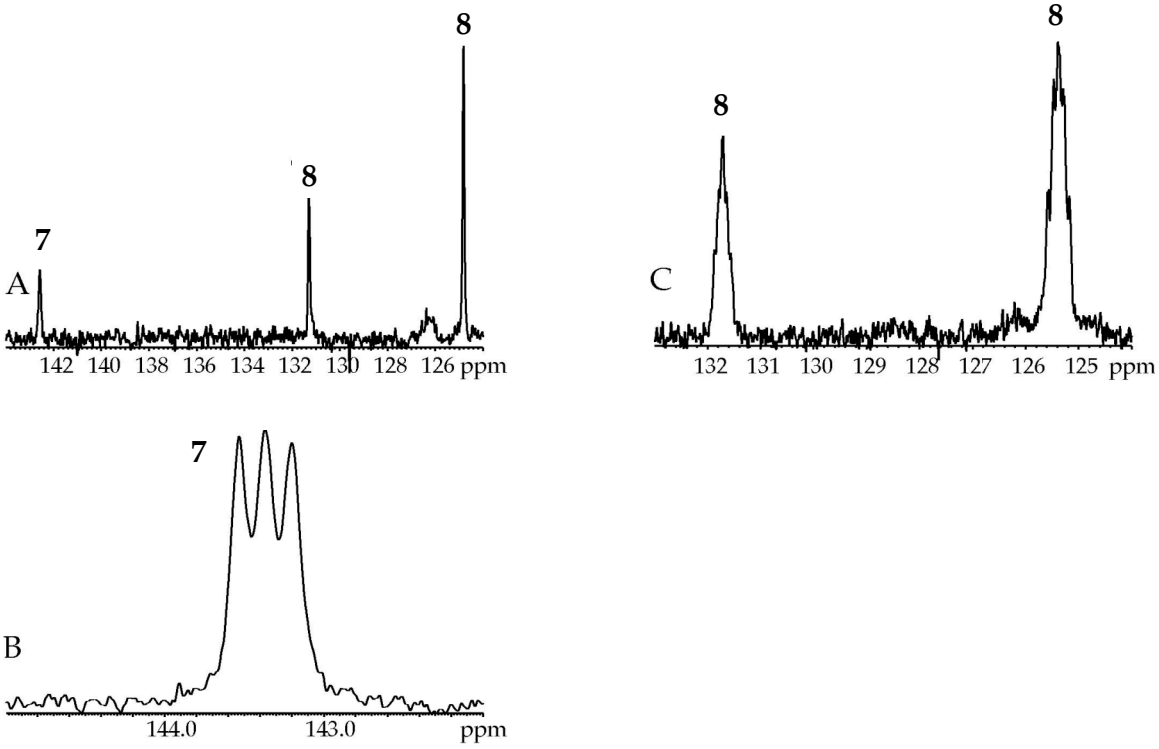
XXIX. ^{6}Li NMR spectra of 0.10 M [^{6}Li,^{15}N]**3** in 5.0 M THP/toluene recorded at: (A) -90 °C; (B) -75 °C; (C) -60 °C; (D) -50 °C; (E) -35 °C; (F) -20 °C; (G) 0 °C.



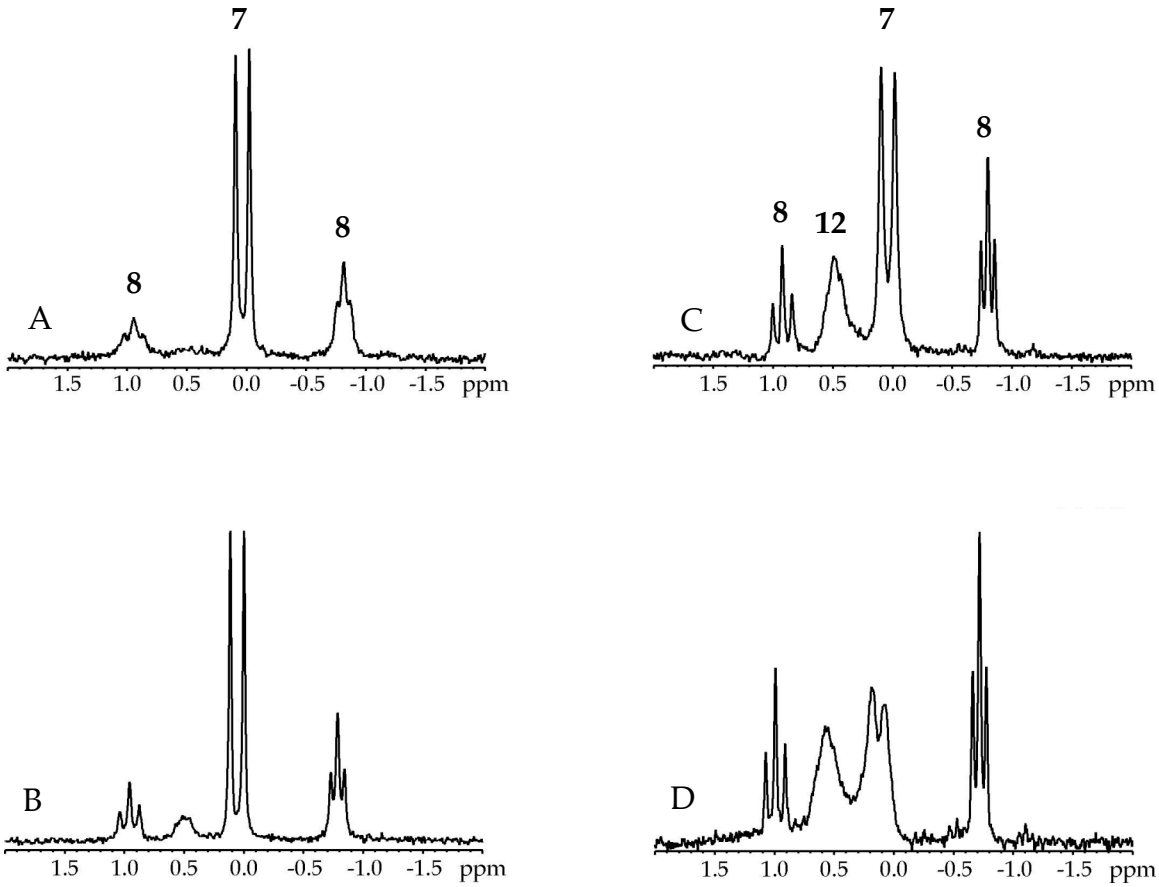
XXX. ^{6}Li NMR spectra of 0.10 M [^{6}Li,^{15}N]**3** in THF/toluene recorded at -90 °C: (A) 0.050 M THF; (B) 0.075 M THF; (C) 0.10 M THF; (D) 0.20 M THF.



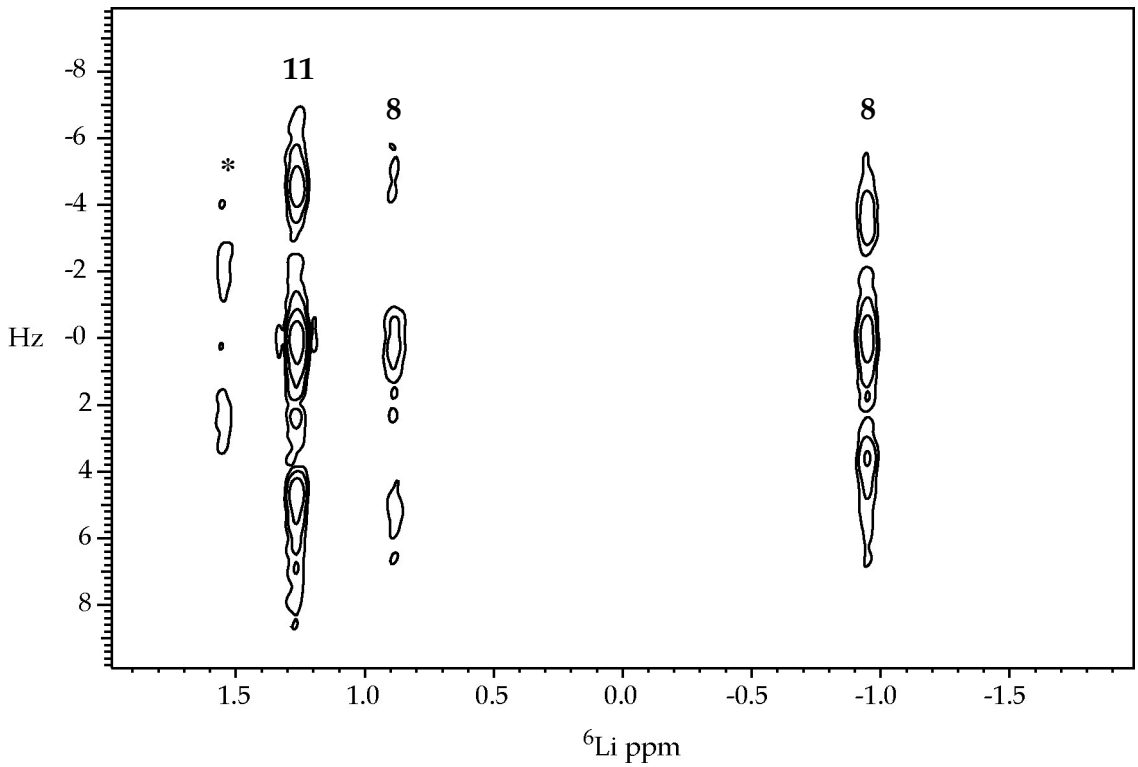
XXXI. ^{6}Li NMR spectra of 0.10 M [^{6}Li,^{15}N]**3** in THF/toluene recorded at -90 °C: (A) 0.50 M THF; (B) 1.0 M THF; (C) 2.0 M THF; (D) 3.0 M THF; (E) 5.0 M THF; (F) 7.0 M THF; (G) 9.0 M THF.



XXXII. ^{15}N NMR spectra of 0.10 M [^{6}Li,^{15}N]**3** in THF/toluene recorded at -90 ^{o}C: (A) 2.0 M THF, ^{6}Li decoupled; (B) 9.0 M THF, ^{6}Li coupled; (C) 0.50 M THF, ^{6}Li coupled.

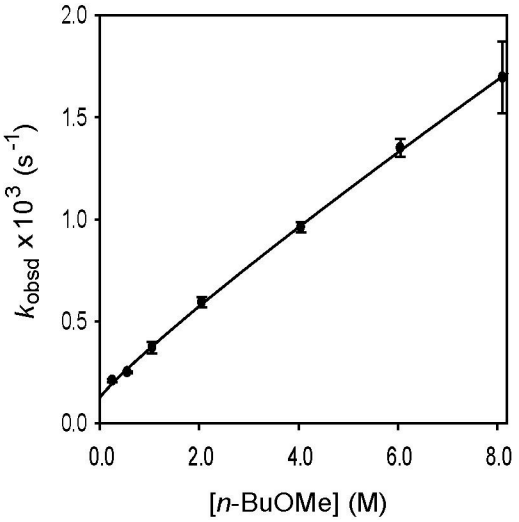


XXXIII. ^{6}Li NMR spectra of 0.10 M [^{6}Li,^{15}N]**3** in 5.0 M THF/toluene recorded at: (A) -110 °C; (B) -100 °C; (C) -90 °C; (D) -80 °C.



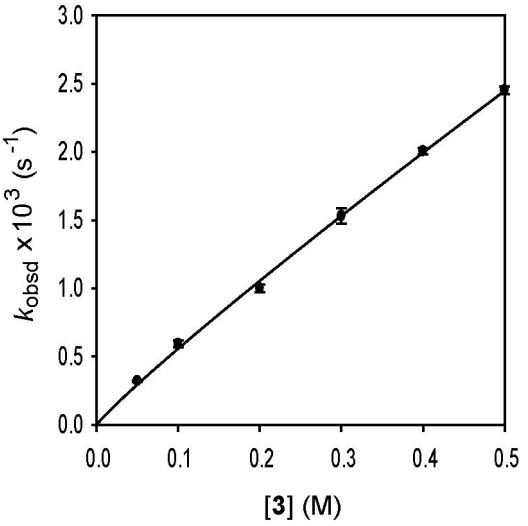
XXXIV. *J*(^{6}Li,^{15}N)-resolved NMR spectrum of 0.10 M [^{6}Li,^{15}N]**3** in 0.075 M THP/toluene recorded at -90 °C. * Unassigned.

Part 3: Rate Studies



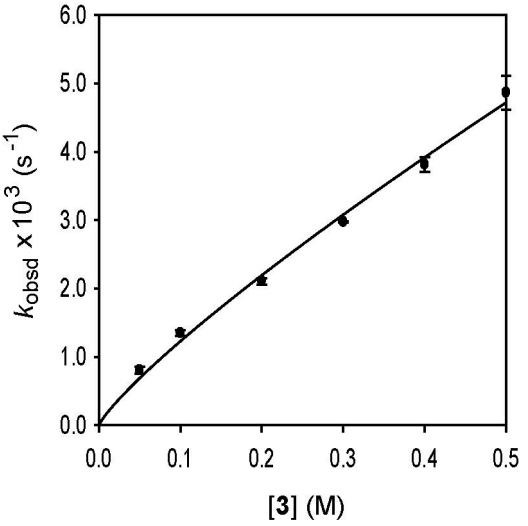
XXXV. Plot of k_{obsd} vs [*n*-BuOMe] in toluene cosolvent for the alkylation of **3** (0.10 M) with *n*-$C_7H_{15}I$ (0.005 M) at 0 °C. The curve depicts an unweighted least-squares fit to $k_{obsd} = a + b[n\text{-BuOMe}]^c$ ($a = 0.13 \pm 0.05$, $b = 0.24 \pm 0.05$, $c = 0.90 \pm 0.09$).

[*n*-BuOMe] (M)	$k_{obsd}1$ x 10^3 (s^{-1})	$k_{obsd}2$ x 10^3 (s^{-1})	k_{obsd}av x 10^3 (s^{-1})
0.25	0.214 ± 6E-3	0.204 ± 3E-3	0.209 ± 7E-3
0.55	0.254 ± 5E-3	0.247 ± 5E-3	0.251 ± 5E-3
1.05	0.352 ± 9E-3	0.392 ± 6E-3	0.372 ± 3E-2
2.05	0.57 ± 2E-2	0.61 ± 2E-2	0.59 ± 3E-2
4.05	0.94 ± 2E-2	0.98 ± 1E-2	0.96 ± 3E-2
6.05	1.33 ± 3E-2	1.38 ± 3E-2	1.35 ± 3E-2
8.05	1.57 ± 3E-2	1.82 ± 2E-3	1.69 ± 2E-1



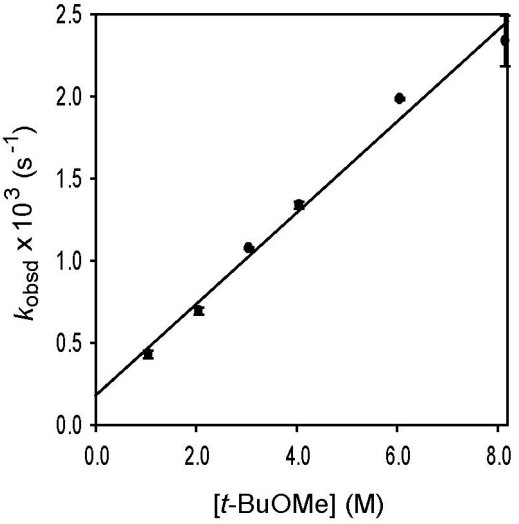
XXXVI. Plot of k_{obsd} vs [**3**] in 2.10 M *n*-BuOMe and toluene cosolvent for the alkylation of **3** with *n*-$C_7H_{15}I$ (0.005 M) at 0 °C. The curve depicts an unweighted least-squares fit to $k_{obsd} = a[\mathbf{3}]^b$ ($a = 4.6 \pm 0.1$, $b = 0.92 \pm 0.02$).

[**3**] (M)	$k_{obsd}1$ x 10^3 (s^{-1})	$k_{obsd}2$ x 10^3 (s^{-1})	k_{obsd}av x 10^3 (s^{-1})
0.050	0.315 ± 4E-3	0.327 ± 9E-3	0.321 ± 8E-3
0.10	0.57 ± 2E-2	0.61 ± 2E-2	0.59 ± 3E-2
0.20	0.98 ± 4E-2	1.02 ± 2E-2	1.00 ± 3E-2
0.30	1.49 ± 4E-3	1.57 ± 2E-2	1.53 ± 6E-2
0.40	2.02 ± 4E-2	1.99 ± 2E-2	2.00 ± 2E-2
0.50	2.4 ± 1E-1	2.47 ± 5E-2	2.45 ± 6E-2



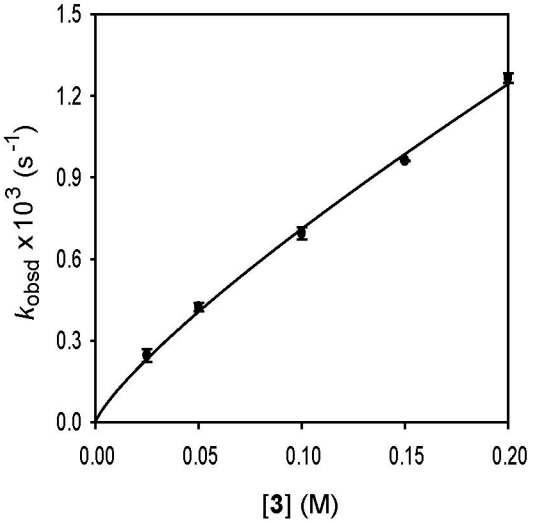
XXXVII. Plot of k_{obsd} vs [**3**] in 6.10 M *n*-BuOMe and toluene cosolvent for the alkylation of **3** with *n*-$C_7H_{15}I$ (0.005 M) at 0 °C. The curve depicts an unweighted least-squares fit to $k_{obsd} = a[\mathbf{3}]^b$ ($a = 8.4 \pm 0.3$, $b = 0.84 \pm 0.04$).

[**3**] (M)	$k_{obsd}1$ x 10^3 (s^{-1})	$k_{obsd}2$ x 10^3 (s^{-1})	k_{obsd}av x 10^3 (s^{-1})
0.050	0.77 ± 2E-2	0.84 ± 1E-2	0.80 ± 5E-2
0.10	1.38 ± 3E-2	1.32 ± 2E-2	1.35 ± 4E-2
0.20	2.14 ± 3E-2	2.07 ± 2E-2	2.11 ± 5E-2
0.30	2.97 ± 5E-2	2.98 ± 1E-2	2.98 ± 1E-2
0.40	3.9 ± 2E-1	3.74 ± 9E-2	3.8 ± 1E-1
0.50	5.04 ± 7E-2	4.69 ± 5E-2	4.9 ± 2E-1



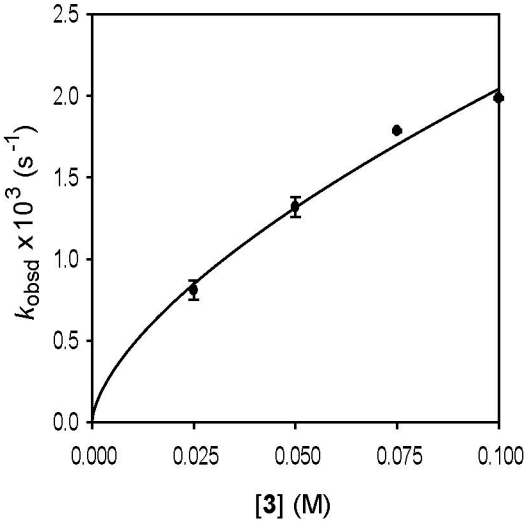
XXXVIII. Plot of k_{obsd} vs [*t*-BuOMe] in toluene cosolvent for the alkylation of **3** (0.10 M) with *n*-$C_7H_{15}I$ (0.005 M) at 0 °C. The curve depicts an unweighted least-squares fit to $k_{obsd} = a + b$[*t*-BuOMe] ($a = 0.18 \pm 0.06$, $b = 0.28 \pm 0.01$).

[*t*-BuOMe] (M)	$k_{obsd}1$ x 10^3 (s^{-1})	$k_{obsd}2$ x 10^3 (s^{-1})	k_{obsd}av x 10^3 (s^{-1})
1.05	0.45 ± 2E-2	0.413 ± 4E-3	0.44 ± 3E-2
2.05	0.711 ± 6E-3	0.68 ± 1E-2	0.69 ± 2E-2
3.05	1.07 ± 2E-2	1.08 ± 2E-2	1.08 ± 1E-2
4.05	1.36 ± 2E-2	1.325 ± 8E-3	1.34 ± 2E-2
6.05	1.99 ± 5E-2	1.98 ± 2E-2	1.99 ± 1E-2
8.05	2.22 ± 1E-2	2.45 ± 2E-2	2.34 ± 2E-1



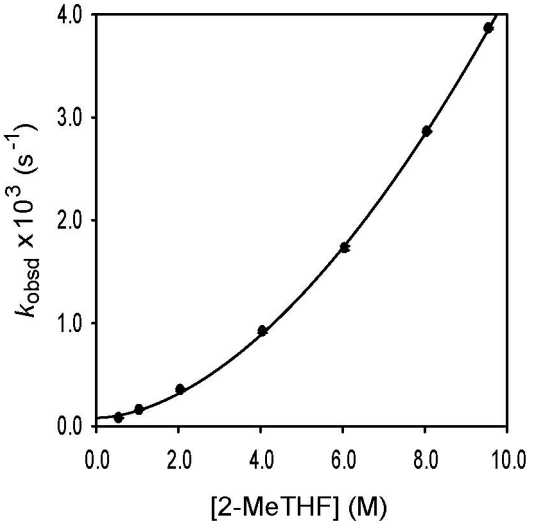
XXXIX. Plot of k_{obsd} vs [**3**] in 2.10 M *t*-BuOMe and toluene cosolvent for the alkylation of **3** with *n*-$C_7H_{15}I$ (0.005 M) at 0 °C. The curve depicts an unweighted least-squares fit to $k_{obsd} = a[\mathbf{3}]^b$ ($a = 4.5 \pm 0.2$, $b = 0.81 \pm 0.02$).

[**3**] (M)	$k_{obsd}1$ x 10^3 (s^{-1})	$k_{obsd}2$ x 10^3 (s^{-1})	k_{obsd}av x 10^3 (s^{-1})
0.025	0.262 ± 6E-3	0.228 ± 5E-3	0.24 ± 2E-2
0.05	0.412 ± 5E-3	0.433 ± 3E-3	0.42 ± 1E-2
0.10	0.711± 6E-3	0.68 ± 1E-2	0.69 ± 2E-2
0.15	0.96 ± 2E-2	0.96 ± 1E-2	0.96 ± 1E-2
0.20	1.28 ± 2E-2	1.25 ± 1E-2	1.26 ± 2E-2



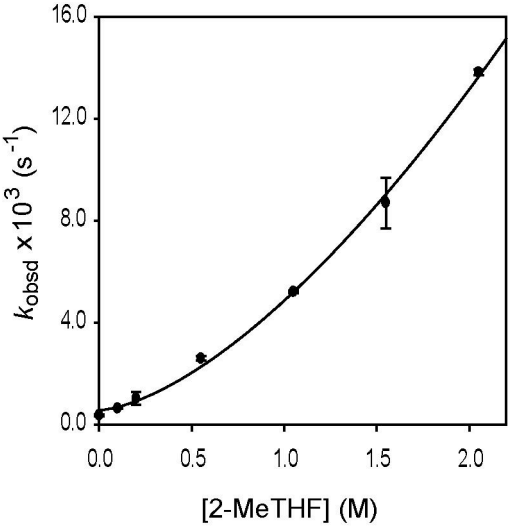
XL. Plot of k_{obsd} vs [**3**] in 6.10 M *t*-BuOMe and toluene cosolvent for the alkylation of **3** with *n*-$C_7H_{15}I$ (0.005 M) at 0 °C. The curve depicts an unweighted least-squares fit to $k_{obsd} = a[\mathbf{3}]^b$ ($a = 9 \pm 1$, $b = 0.64 \pm 0.04$).

[**3**] (M)	$k_{obsd}1$ x 10^3 (s^{-1})	$k_{obsd}2$ x 10^3 (s^{-1})	k_{obsd}av x 10^3 (s^{-1})
0.025	0.77 $\pm$ 2E-2	0.85 $\pm$ 1E-2	0.81 $\pm$ 6E-2
0.05	1.28 $\pm$ 1E-2	1.36 $\pm$ 2E-2	1.32 $\pm$ 6E-2
0.075	1.78 $\pm$ 1E-2	1.79 $\pm$ 2E-2	1.78 $\pm$ 1E-2
0.10	1.99 $\pm$ 5E-2	1.98 $\pm$ 2E-2	1.99 $\pm$ 1E-2



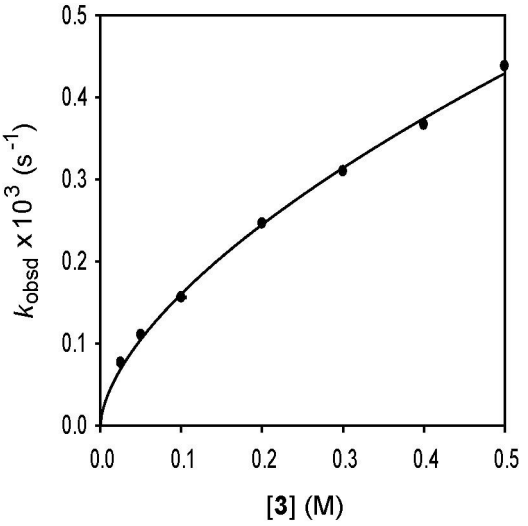
XLI. Plot of k_{obsd} vs [2-MeTHF] in toluene cosolvent for the alkylation of **3** (0.10 M) with *n*-$C_8H_{17}Br$ (0.005 M) at 0 °C. The curve depicts an unweighted least-squares fit to $k_{obsd} = a + b[\text{2-MeTHF}]^c$ ($a = 0.08 \pm 0.01$, $b = 0.068 \pm 0.003$, $c = 1.78 \pm 0.02$).

[2-MeTHF] (M)	$k_{obsd}1$ x 10^3 (s^{-1})	$k_{obsd}2$ x 10^3 (s^{-1})	k_{obsd}av x 10^3 (s^{-1})
0.55	0.0759 ± 5E-4	0.0788 ± 3E-4	0.077 ± 2E-3
1.05	0.157 ± 1E-3	0.156 ± 1E-3	0.156 ± 1E-3
2.05	0.342 ± 2E-3	0.358 ± 2E-3	0.35 ± 1E-2
4.05	0.909 ± 1E-3	0.929 ± 6E-3	0.92 ± 1E-2
6.05	1.71 ± 3E-2	1.744 ± 6E-3	1.73 ± 2E-2
8.05	2.864 ± 7E-3	2.857 ± 7E-3	2.861 ± 5E-3
9.55	3.87 ± 4E-2	3.86 ± 2E-2	3.86 ± 1E-2



XLII. Plot of k_{obsd} vs [2-MeTHF] in toluene cosolvent for the alkylation of **3** (0.10 M) with *n*-$C_7H_{15}I$ (0.005 M) at 0 °C. The curve depicts an unweighted least-squares fit to $k_{obsd} = a + b[\text{2-MeTHF}]^c$ ($a = 0.6 \pm 0.2$, $b = 4.0 \pm 0.3$, $c = 1.5 \pm 0.1$).

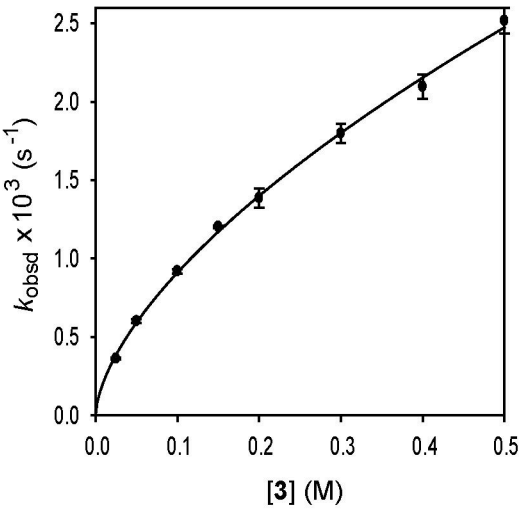
[2-MeTHF] (M)	$k_{obsd}1$ x 10^3 (s^{-1})	$k_{obsd}2$ x 10^3 (s^{-1})	k_{obsd}av x 10^3 (s^{-1})
0.00	0.341 ± 5E-3	0.395 ± 7E-3	0.37 ± 4E-2
0.10	0.65 ± 2E-2	0.626 ± 7E-3	0.64 ± 2E-2
0.20	0.844 ± 5E-3	1.21 ± 2E-2	1.0 ± 3E-1
0.55	2.66 ± 1E-2	2.533 ± 9E-3	2.60 ± 9E-2
1.05	5.2 ± 1E-1	5.25 ± 3E-2	5.22 ± 3E-2
1.55	8.00 ± 8E-2	9.40 ± 6E-2	8.70 ± 6E-2
2.05	13.9 ± 4E-1	13.7 ± 1E-1	13.8 ± 1E-1



XLIII. Plot of k_{obsd} vs [**3**] in 1.10 M 2-MeTHF and toluene cosolvent for the alkylation of **3** with *n*-$C_8H_{17}Br$ (0.005 M) at 0 °C. The curve depicts an unweighted least-squares fit to $k_{obsd} = a[\mathbf{3}]^b$ ($a = 0.66 \pm 0.01$, $b = 0.61 \pm 0.02$).

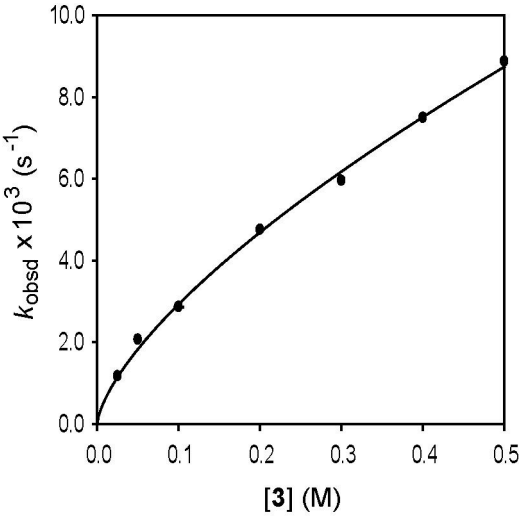
[**3**] (M)	k_{obsd} x 10^3 (s^{-1})
0.025	0.076 ± 1E-3
0.05	0.110 ± 1E-3
0.10	0.156 ± 1E-3[a]
0.20	0.246 ± 2E-3
0.30	0.310 ± 6E-3
0.40	0.367 ± 3E-1
0.50	0.44 ± 2E-2

[a]Average of two measurements.



XLIV. Plot of k_{obsd} vs [**3**] in 4.10 M 2-MeTHF and toluene cosolvent for the alkylation of **3** with n-$C_8H_{17}Br$ (0.005 M) at 0 °C. The curve depicts an unweighted least-squares fit to $k_{obsd} = a[\mathbf{3}]^b$ ($a = 3.8 \pm 0.1$, $b = 0.62 \pm 0.01$).

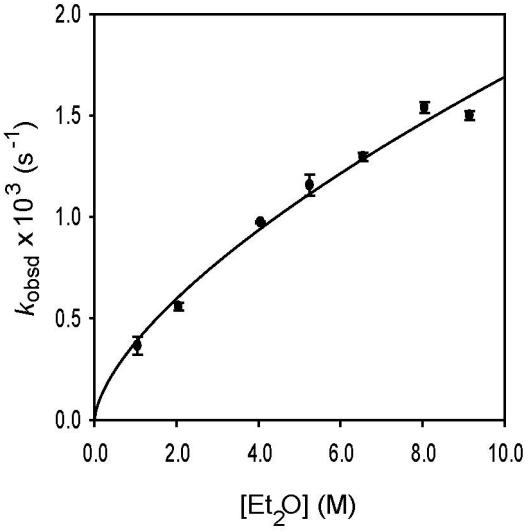
[**3**] (M)	$k_{obsd}1$ x 10^3 (s^{-1})	$k_{obsd}2$ x 10^3 (s^{-1})	k_{obsd}av x 10^3 (s^{-1})
0.025	0.368 ± 4E-3	0.357 ± 5E-3	0.363 ± 8E-3
0.05	0.610 ± 3E-3	0.591 ± 3E-3	0.60 ± 1E-2
0.10	0.909 ± 1E-3	0.929 ± 6E-3	0.92 ± 1E-2
0.15	1.20 ± 1E-2	1.21 ± 1E-2	1.20 ± 1E-2
0.20	1.34 ± 2E-2	1.43 ± 1E-2	1.39 ± 6E-2
0.30	1.84 ± 3E-2	1.75 ± 2E-2	1.80 ± 6E-2
0.40	2.0 ± 1E-1	2.15 ± 3E-2	2.10 ± 1E-1
0.50	2.57 ± 1E-2	2.46 ± 5E-2	2.52 ± 8E-2



XLV. Plot of k_{obsd} vs [**3**] in 8.10 M 2-MeTHF and toluene cosolvent for the alkylation of **3** with *n*-$C_8H_{17}Br$ (0.005 M) at 0 °C. The curve depicts an unweighted least-squares fit to $k_{obsd} = a[\mathbf{3}]^b$ ($a = 14.0 \pm 0.3$, $b = 0.68 \pm 0.02$).

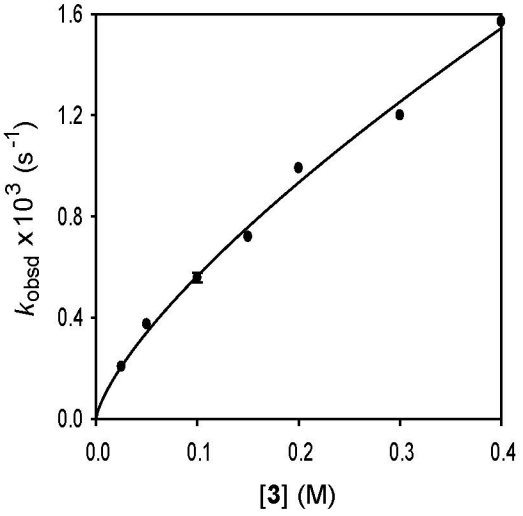
[**3**] (M)	k_{obsd} x 10^3 (s^{-1})
0.025	1.17 $\pm$ 2E-2
0.05	2.061 $\pm$ 9E-3
0.10	2.861 $\pm$ 5E-3[a]
0.20	4.75 $\pm$ 4E-2
0.30	5.95 $\pm$ 9E-2
0.40	7.49 $\pm$ 5E-2
0.50	8.9 $\pm$ 1E-1

[a]Average of two measurements.



XLVI. Plot of k_{obsd} vs [Et_2O] in toluene cosolvent for the alkylation of **3** (0.10 M) with *n*-$C_7H_{15}I$ (0.005 M) at 0 °C. The curve depicts an unweighted least-squares fit to $k_{obsd} = a[Et_2O]^b$ ($a = 0.38 \pm 0.03$, $b = 0.65 \pm 0.03$).

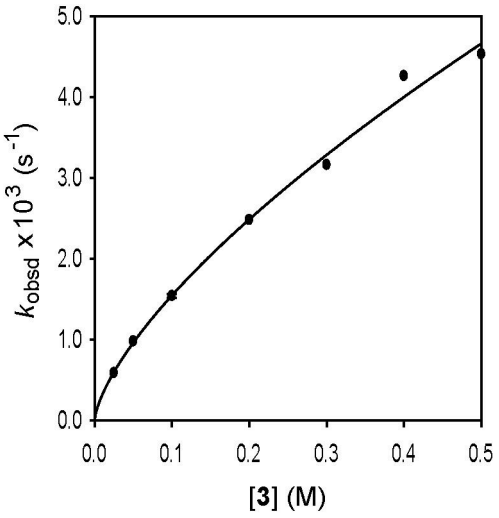
[Et_2O] (M)	$k_{obsd}1$ x 10^3 (s^{-1})	$k_{obsd}2$ x 10^3 (s^{-1})	k_{obsd}av x 10^3 (s^{-1})
1.05	0.333 ± 5E-3	0.397 ± 4E-3	0.365 ± 4E-2
2.05	0.57 ± 1E-2	0.554 ± 5E-3	0.563 ± 1E-2
4.05	0.97 ± 2E-2	0.977 ± 9E-3	0.974 ± 5E-3
5.25	1.19 ± 2E-2	1.12 ± 2E-2	1.157 ± 5E-3
6.55	1.28 ± 2E-2	1.31 ± 3E-2	1.30 ± 2E-2
8.05	1.52 ± 4E-2	1.56 ± 2E-2	1.54 ± 3E-2
9.15	1.51 ± 2E-2	1.48 ± 2E-2	1.50 ± 2E-2



XLVII. Plot of k_{obsd} vs [**3**] in 2.10 M Et_2O and toluene cosolvent for the alkylation of **3** with *n*-$C_7H_{15}I$ (0.005 M) at 0 °C. The curve depicts an unweighted least-squares fit to $k_{obsd} = a[\mathbf{3}]^b$ ($a = 3.0 \pm 0.1$, $b = 0.73 \pm 0.03$).

[**3**] (M)	k_{obsd} x 10^3 (s^{-1})
0.025	0.206 ± 3E-3
0.05	0.374 ± 7E-3
0.10	0.563 ± 1E-2[a]
0.15	0.72 ± 1E-2
0.20	0.99 ± 1E-2
0.30	1.20 ± 3E-2
0.40	1.57 ± 5E-2

[a]Average of two measurements.



XLVIII. Plot of k_{obsd} vs [**3**] in 8.10 M Et_2O and toluene cosolvent for the alkylation of **3** with *n*-$C_7H_{15}I$ (0.005 M) at 0 °C. The curve depicts an unweighted least-squares fit to $k_{obsd} = a[\mathbf{3}]^b$ ($a = 7.5 \pm 0.3$, $b = 0.69 \pm 0.03$).

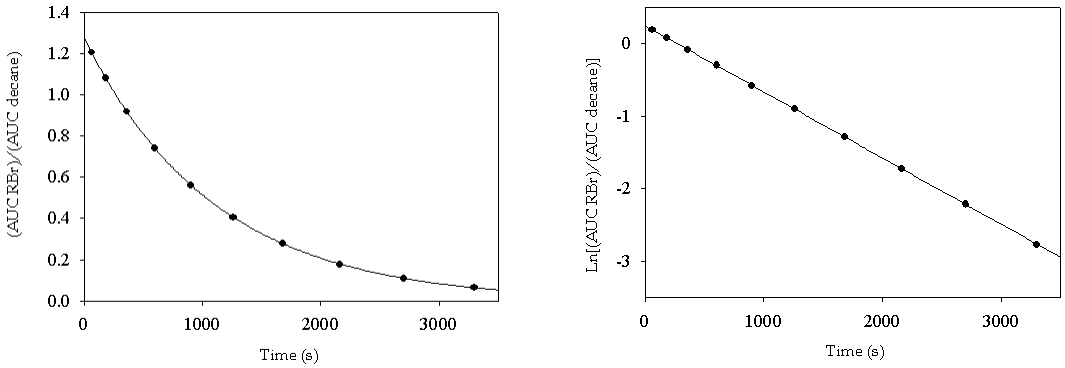
[**3**] (M)	k_{obsd} x 10^3 (s^{-1})
0.025	0.59 ± 2E-2
0.05	0.98 ± 3E-2
0.10	1.54 ± 3E-2[a]
0.20	2.48 ± 8E-2
0.30	3.2 ± 1E-1
0.40	4.3 ± 1E-1
0.50	4.53 ± 9E-2

[a]Average of two measurements.

XLIX. Table of data for k_{obsd} in various ethereal solvents (1.10 M) and toluene cosolvent for the alkylation of **3** (0.10 M) with *n*-$C_7H_{15}I$ (0.005 M) at 0 °C.

Solvent	$k_{obsd}1$ x 10^3 (s^{-1})	$k_{obsd}2$ x 10^3 (s^{-1})	k_{obsd}av x 10^3 (s^{-1})	k_{rel}
Et_2O	0.333 ± 5E-3	0.397 ± 4E-3	0.36 ± 4E-2	1.0
n-BuOMe	0.352 ± 9E-3	0.392 ± 6E-3	0.37 ± 3E-2	1.0
t-BuOMe	0.45 ± 2E-2	0.41 ± 4E-2	0.43 ± 3E-2	1.2
THP	3.42 ± 8E-2	3.68 ± 6E-2	3.55 ± 2E-1	10
2-MeTHF	5.2 ± 1E-1	5.25 ± 3E-2	5.22 ± 4E-2	14
THF	23.3 ± 4E-1	20.8 ± 4E-1	22 ± 2	61

L. Representative plots of the time-dependent decay of *n*-$C_8H_{17}Br$ relative to an *n*-C_8H_{18} internal standard (relative area under the curve, AUC).



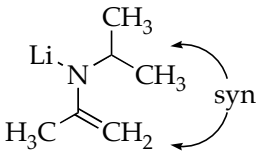
A B

(A) Plot of the GC integration of *n*-$C_8H_{17}Br$ vs time (s) for sequentially quenched samples of a reaction mixture containing **3** (0.1 M), 2-MeTHF (4.10 M), *n*-$C_8H_{17}Br$ (0.005 M), and toluene cosolvent at 0 °C. The curve depicts a least squares fit to $f(x) = ae^{-bx}$ ($a = 1.273 \pm 0.001$, $b = k_{obsd} = (0.909 \pm 0.001) \times 10^{-3}$. (B) Plot of the natural logarithm of the data plotted in A vs time (s). The curve depicts a least squares fit to $f(x) = ax + b$ ($a = (-9.128 \pm 0.008) \times 10^{-3}$, $b = 0.24 \pm 0.01$).

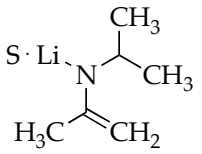
Part 4: DFT Computational Studies

LI. Optimized geometries and free energies (*G*, Hartrees) of monomers $\mathbf{AS_n}$.[a]

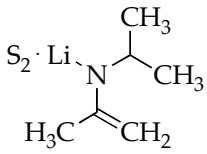
A. Syn isomers $\mathbf{AS_n}$. n = 0-3, S = Me_2O (ΔG = -154.97011 Hartrees).



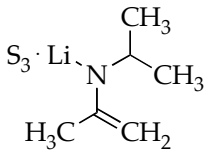
I



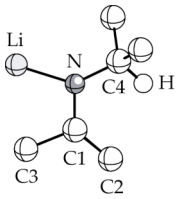
II



III

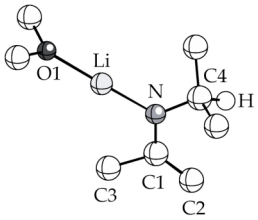


IV



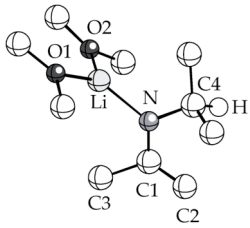
η^1

-298.00126



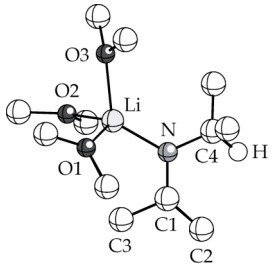
η^1

-452.99219



η^1

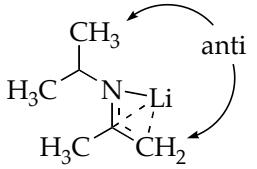
-607.96733



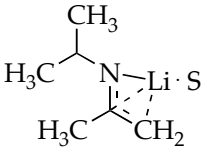
η^1

-762.92543

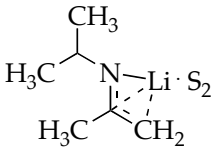
B. Anti isomers $\mathbf{AS_n}$.



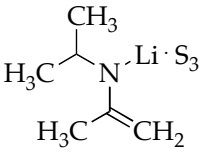
V



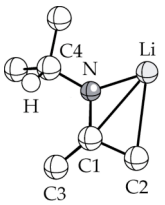
VI



VII

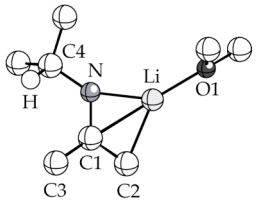


VIII



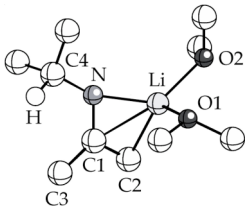
η^3

-298.01488



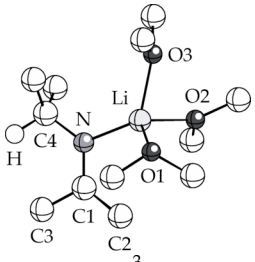
η^3

-452.99797



η^3

-607.96860



η^3

-762.92552

[a] Only selected hydrogens shown for clarity.

LII. Selected bond lengths (Å) and angles (deg) of monomers $\mathbf{AS_n}$.[a, b]

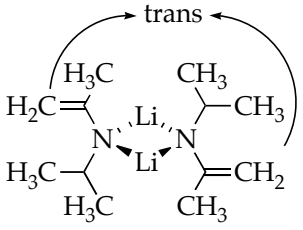
	I	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**
Li-N[b]	1.80	1.83	1.89	1.95	1.85	1.88	1.92	1.96
Li-C1[b]	2.60	2.77	2.83	2.86	2.09	2.16	2.25	2.83
Li-C2[b]	---	---	---	---	2.11	2.15	2.22	3.03
Li-O1	---	1.89	1.95	2.10	---	1.93	2.02	2.09
Li-O2	---	---	1.96	2.07	---	---	1.99	2.07
Li-O3	---	---	---	2.06	---	---	---	2.05
N-C1	1.38	1.37	1.37	1.37	1.35	1.35	1.35	1.37
C1-C2	1.36	1.36	1.36	1.37	1.41	1.40	1.39	1.38
Li-N-C1	109.0	119.1	119.5	117.4	80.9	81.7	83.6	115.4
N-Li-C2	---	---	---	---	73.4	71.5	69.0	52.8
N-C1-C2	129.8	129.2	129.4	129.4	118.6	119.2	119.9	123.5
Li-N-C1-C2	182.9	184.9	206.8	216.6	39.6	41.7	42.2	179.5

[a]See 3D representations in Section **LI** for atom numbering.

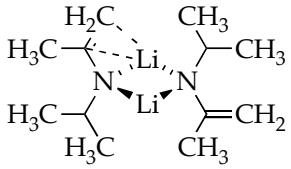
[b]N-C1-C2 constitute the azaallylic moiety.

LIII. Optimized geometries and free energies (*G*, Hartrees) of dimers $\mathbf{A_2S_n}$.[a]

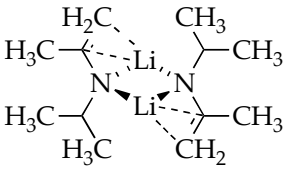
A. Unsolvated trans isomers $\mathbf{A_2S_n}$. n = 0.



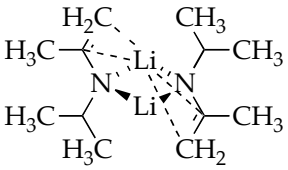
IX



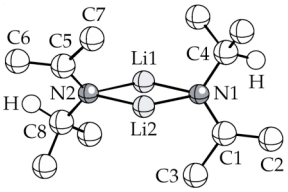
X



XI

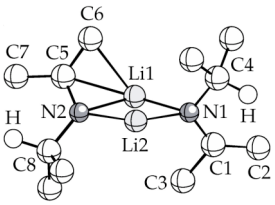


XII



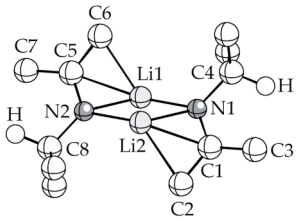
η^1-syn,η^1-syn

-596.05679



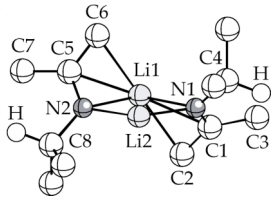
η^3-syn,η^1-anti

-596.06571



vic(η^3-anti,η^3-anti)

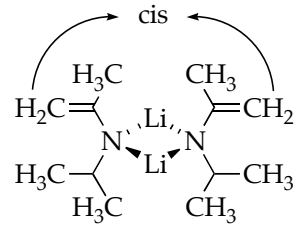
-596.06927



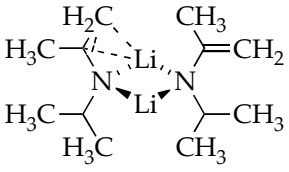
gem(η^3-anti,η^3-anti)

-596.07295

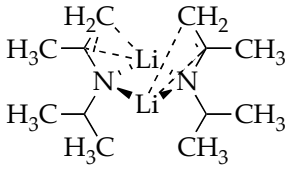
B. Unsolvated cis isomers $\mathbf{A_2S_n}$



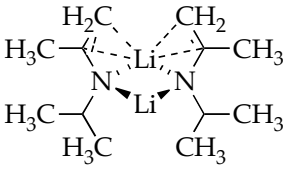
XIII



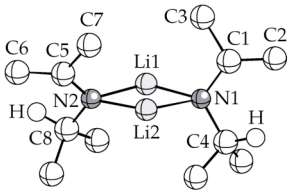
XIV



XV

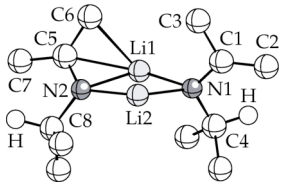


XVI



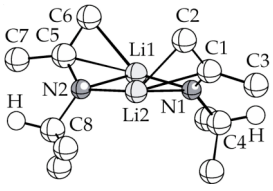
η^1-syn,η^1-syn

-596.05573



η^3-syn,η^1-anti

-596.06523



vic(η^3-anti,η^3-anti)

-596.07295

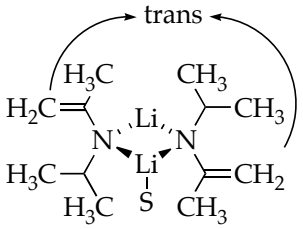
gem(η^3-anti,η^3-anti)

not found

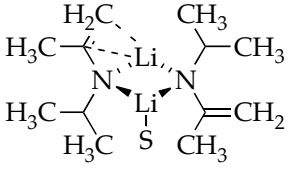
[a] Only selected hydrogens shown for clarity.

LIII (*Continued*)**.**

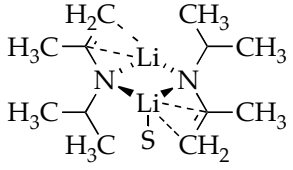
C. Monosolvated trans isomers $\mathbf{A_2S_n}$. n = 1, S = Me_2O (*G* = -154.97011 Hartrees).



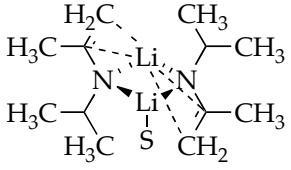
XVII



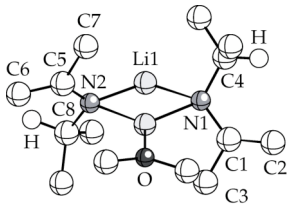
XVIII



XIX

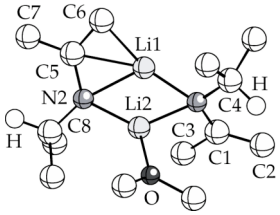


XX



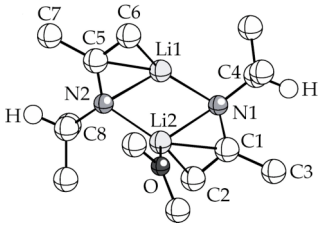
η¹-syn,η¹-syn

-751.03903



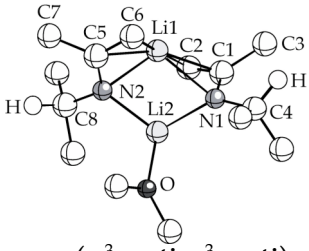
η³-syn,η¹-anti

-751.04081



vic(η³-anti,η³-anti)

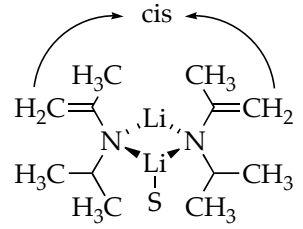
-751.04587



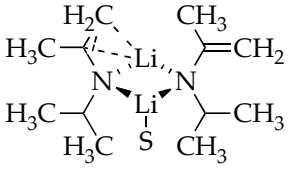
gem(η³-anti,η³-anti)

-751.04601

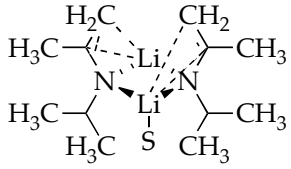
D. Monosolvated cis isomers $\mathbf{A_2S_n}$. n = 1, S = Me_2O



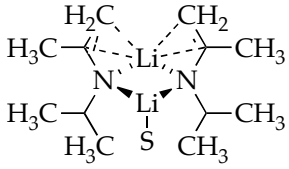
XXI



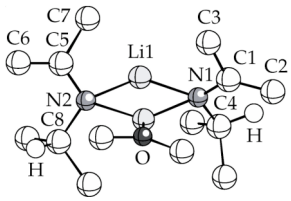
XXII



XXIII

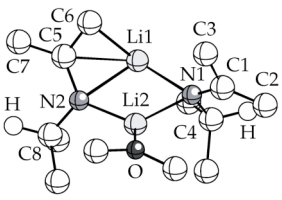


XXIV



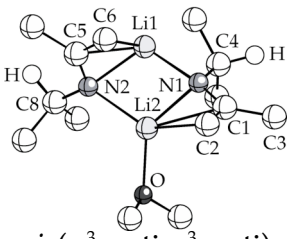
η¹-syn,η¹-syn

-751.03671



η³-syn,η¹-anti

-751.04143



vic(η³-anti,η³-anti)

-751.04347

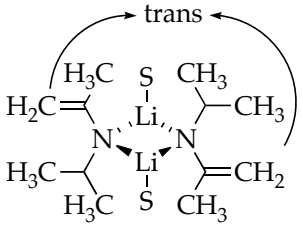
gem(η³-anti,η³-anti)

not found

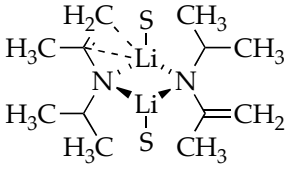
[a] Only selected hydrogens shown for clarity.

LIII (*Continued*).

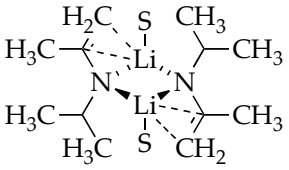
E. Disolvated trans isomers $\mathbf{A_2S_n}$. n = 2, S = Me_2O (*G* = -154.97011 Hartrees).



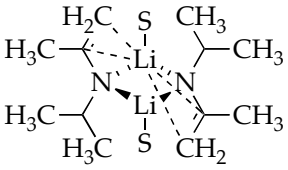
XXV



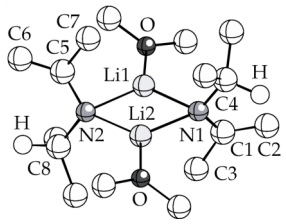
XXVI

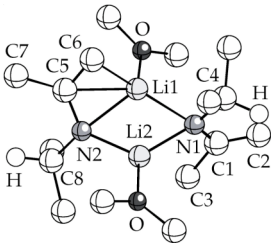


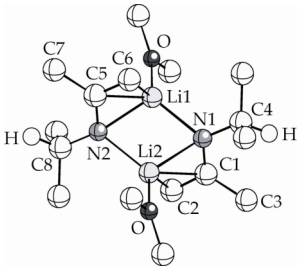
XXVII



XXVIII

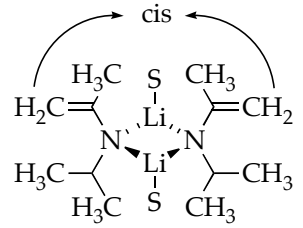




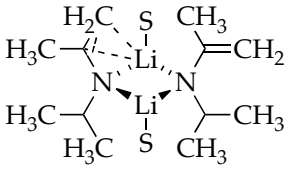


η^1-syn,η^1-syn	η^3-syn,η^1-anti	*vic*(η^3-anti,η^3-anti)	*gem*(η^3-anti,η^3-anti)
-906.01273	-906.01459	-906.02107	not found

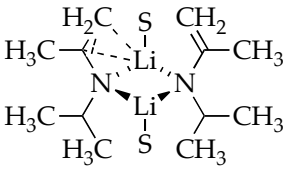
F. Disolvated cis isomers $\mathbf{A_2S_n}$. n = 2, S = Me_2O



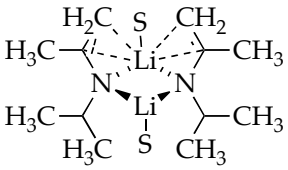
XXIX



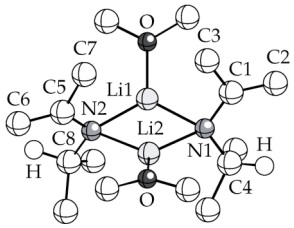
XXX

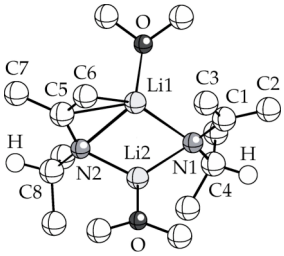


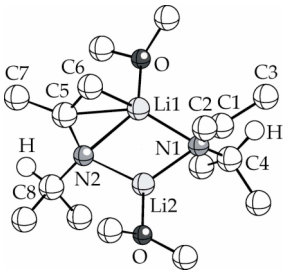
XXXI



XXXII







η^1-syn,η^1-syn	η^3-syn,η^1-anti	η^3-anti,η^1-anti [b]	*gem*(η^3-anti,η^3-anti)
-906.01500	-906.01371	-906.01069	not found

[a] Only selected hydrogens shown for clarity.
[b] Li2 and the azaallyl moiety N1-C1-C2 show no evidence of π complexation.

LIV. Selected bond lengths (Å) and angles (deg) calculated for unsolvated dimers $\mathbf{A_2}$.[a, b]

	IX	X	XI	XII	XIII	XIV	XV
Li1-N1[b]	1.98	1.94	2.07	1.93	1.97	1.96	2.05
Li1-N2[b]	1.98	1.97	2.01	1.93	1.99	1.95	2.01
Li2-N1[b]	1.97	2.03	2.01	2.18	1.99	2.01	2.01
Li2-N2[b]	1.98	2.11	2.07	2.18	1.98	2.17	2.05
Li1-C1[b]	---	---	2.22	---	---	---	2.23
Li1-C2[b]	---	---	2.19	---	---	---	2.17
Li2-C1[b]	---	---	---	2.28	---	---	---
Li2-C2[b]	---	---	---	2.19	---	---	---
Li2-C5[b]	---	2.25	2.22	2.28	---	2.26	2.23
Li2-C6[b]	---	2.16	2.19	2.19	---	2.15	2.16
N1-C1	1.39	1.39	1.37	1.37	1.39	1.39	1.37
N2-C5	1.39	1.37	1.37	1.37	1.40	1.36	1.37
C1-C2	1.36	1.36	1.38	1.38	1.36	1.36	1.39
C5-C6	1.36	1.39	1.38	1.38	1.36	1.39	1.39
Li1-N1-C1-C2	150.0	144.0	46.0	45.0	149.7	136.1	42.1
Li2-N2-C5-C6	136.2	42.5	46.0	6.5	150.4	44.0	42.1

[a]See 3D representations in Section **LIII** for atom numbering.

[b]N1-C1-C2, and N2-C5-C6 constitute the azaallylic moieties.

LIV (*Continued*)**.** Selected bond lengths (Å) and angles (deg) calculated for monosolvated dimers $\mathbf{A_2S}$.[a, b]

	XVII	**XVIII**	**XIX**	**XX**	**XXI**	**XXII**	**XXIII**
Li1-N1[b]	2.08	2.04	2.20	2.02	2.05	2.06	2.05
Li1-N2[b]	2.06	2.07	2.09	2.02	2.07	2.03	2.11
Li2-N1[b]	1.95	2.00	1.97	2.05	1.97	1.98	1.98
Li2-N2[b]	1.94	2.10	2.02	2.20	1.96	2.13	2.03
Li1-C1[b]	---	---	2.30	---	---	---	2.43
Li1-C2[b]	---	---	2.24	---	---	---	2.46
Li2-C1[b]	---	---	---	2.29	---	---	---
Li2-C2[b]	---	---	---	2.26	---	---	---
Li2-C5[b]	---	2.23	2.22	2.23	---	2.45	2.18
Li2-C6[b]	---	2.17	2.23	2.21	---	2.17	2.18
Li1-O	1.92	1.95	1.95	1.97	1.91	1.94	2.00
N1-C1	1.39	1.39	1.35	1.37	1.39	1.39	1.37
N2-C5	1.39	1.37	1.37	1.37	1.39	1.37	1.37
C1-C2	1.36	1.36	1.38	1.38	1.36	1.36	1.37
C5-C6	1.36	1.38	1.39	1.38	1.36	1.39	1.39
Li1-N1-C1-C2	126.3	133.2	47.2	38.5	116.0	117.4	40.3
Li2-N2-C5-C6	159.1	43.9	46.4	51.7	161.1	44.7	45.8

[a]See 3D representations in Section **LIII** for atom numbering.

[b]N1-C1-C2, and N2-C5-C6 constitute the azaallylic moieties.

LIV (*Continued*)**.** Selected bond lengths (Å) and angles (deg) calculated for disolvated dimers $\mathbf{A_2S_2}$.[a, b]

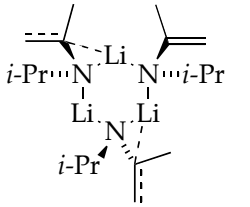
	XXV	**XXVI**	**XXVII**	**XXIX**	**XXX**	**XXXI**
Li1-N1[b]	2.04	2.00	2.12	2.02	2.01	2.10
Li1-N2[b]	2.03	2.03	2.05	2.07	2.03	2.08
Li2-N1[b]	2.06	2.13	2.05	2.07	2.10	2.03
Li2-N2[b]	2.06	2.13	2.12	2.01	2.08	2.01
Li1-C1[b]	---	---	2.29	---	---	2.30
Li1-C2[b]	---	---	2.30	---	---	2.32
Li2-C5[b]	---	2.36	2.29	---	2.30	2.83
Li2-C6[b]	---	2.33	2.29	---	2.32	2.97
Li1-O	1.95	1.95	1.96	1.93	1.97	1.99
Li2-O	1.92	1.96	1.96	1.93	2.00	1.97
N1-C1	1.39	1.39	1.36	1.39	1.40	1.38
N2-C5	1.39	1.37	1.36	1.39	1.38	1.39
C1-C2	1.36	1.37	1.38	1.36	1.36	1.38
C5-C6	1.36	1.38	1.38	1.36	1.38	1.36
Li1-N1-C1-C2	136.1	162.6	47.7	157.5	154.8	47.6
Li2-N2-C5-C6	150.0	44.1	47.7	156.9	52.9	6.5

[a]See 3D representations in Section **LIII** for atom numbering.

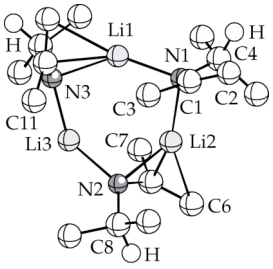
[b]N1-C1- C2, and N2-C5-C6 constitute the azaallylic moieties.

LV. Optimized geometries and free energies (*G*, Hartrees) of trimers $\mathbf{A_3S_n}$.[a]

A. Unsolvated cis,trans isomers $\mathbf{A_3S_n}$. n = 0.

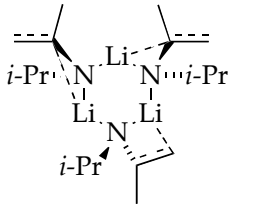


XXXIII

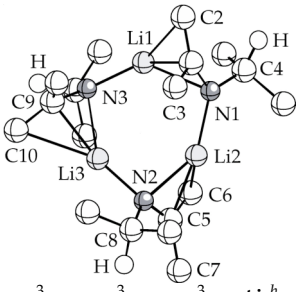


η^3-syn,η^3-syn,η^1-syn [b,c]

-894.10477

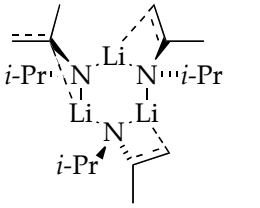


XXXIV

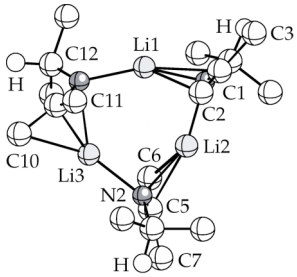


η^3-syn,η^3-syn,η^3-anti [b]

-894.11213

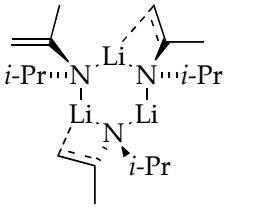


XXXV

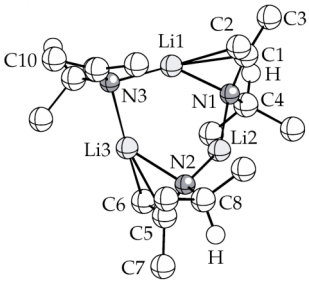


η^3-syn,η^3-anti,η^3-anti [b]

-894.11550

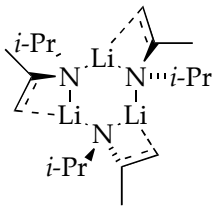


XXXVI

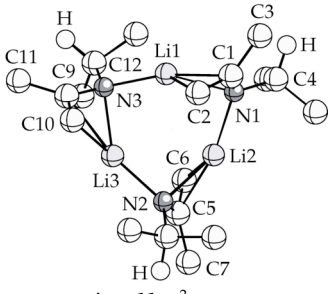


η^1-syn,η^3-anti,η^3-anti

-894.11224

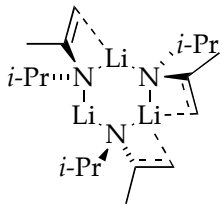


XXXVII

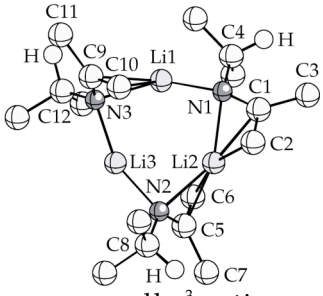


vic-all η^3-anti

-894.11834

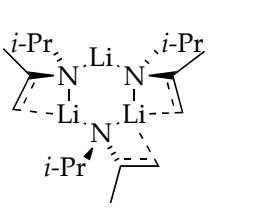


XXXVIII

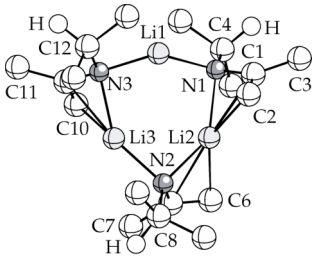


gem-all η^3-anti

-894.11906



XXXIX



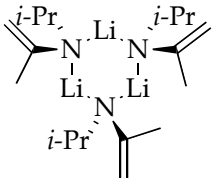
gem-all η^3-anti

-894.10971

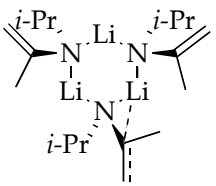
[a] Only selected hydrogens shown for clarity.
[b] η^1-Syn azaallyl moieties turned into η^3-syn upon geometry optimization.
[c] All η^3-syn not found.

LV (*Continued*)**.**

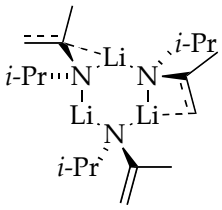
B. Unsolvated cis,cis isomers $\mathbf{A_3S_n}$. n = 0.[a]



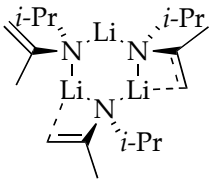
XL



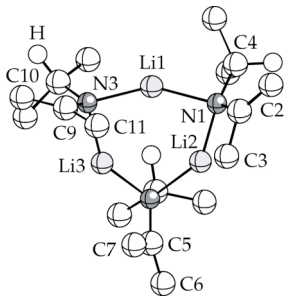
XLI



XLII

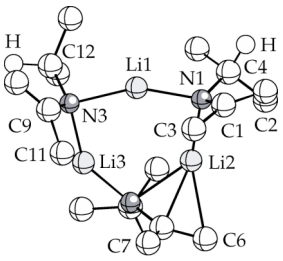


XLIII



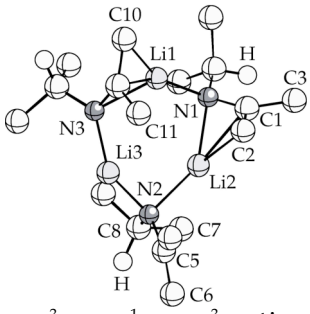
All η^1-syn

-894.09950



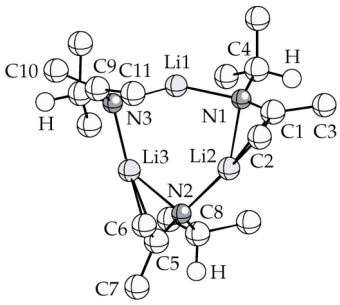
η^3-syn,η^1-syn,η^1-syn

-894.10146



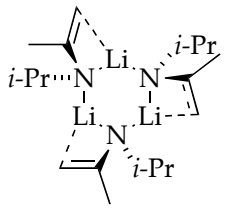
η^3-syn,η^1-syn,η^3-anti

-894.10871

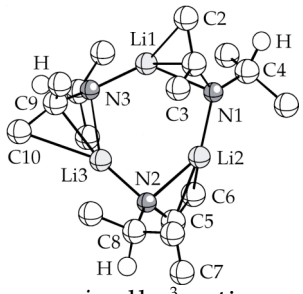


η^1-syn,η^3-anti,η^3-anti [b]

-894.11475



XLIV



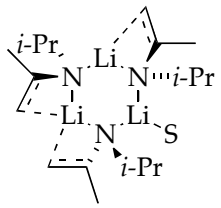
vic-all η^3-anti

-894.11328

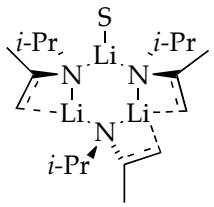
[a] Only selected hydrogens shown for clarity.
[b] η^3-Syn isomer not found.

LV (*Continued*)**.**

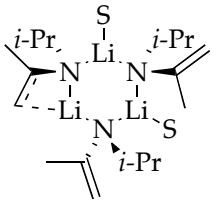
C. Solvated cis,trans isomers $\mathbf{A_3S_n}$. n = 1-3, S = Me_2O (*G* = -154.97011 Hartrees).



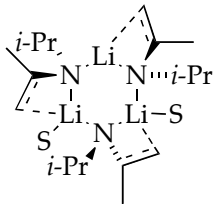
XLV



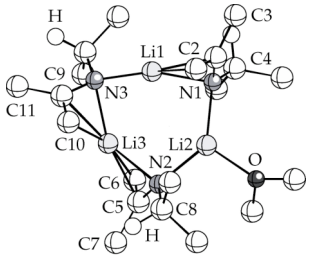
XLVI



XLVII

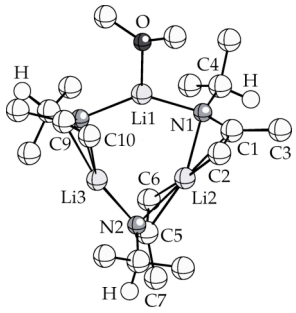


XLVIII



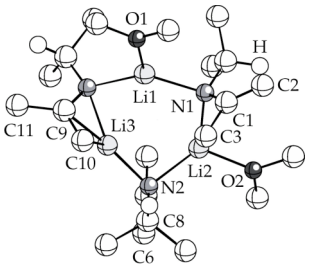
cis,trans
gem-all η^3-anti

-1049.08338



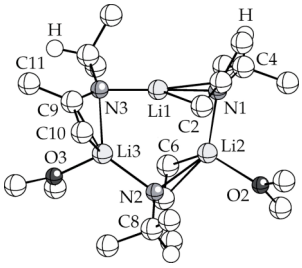
cis,trans
gem-all η^3-anti

-1049.08577



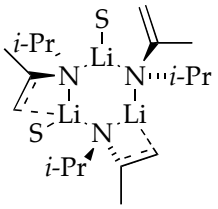
cis,trans
η^1-syn,η^1-syn,η^3-anti [b]

-1204.04735

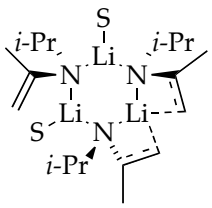


cis,trans
vic-all η^3-anti

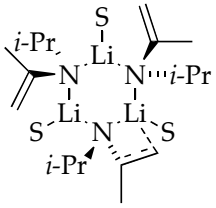
-1204.05556



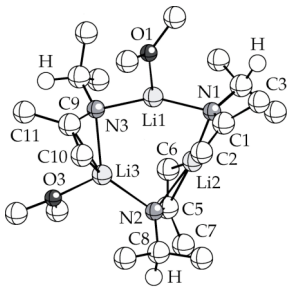
XLIX



L



LI

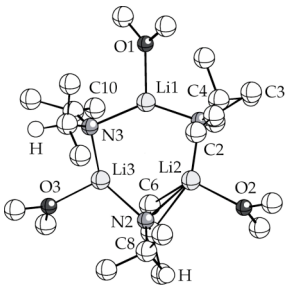


cis,trans
η^1-anti,η^3-anti,η^3-anti [c]

-1204.05369

cis,trans
η^1-anti,η^3-anti,η^3-anti

not found [d]

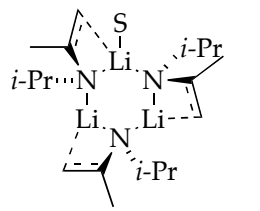


cis,cis
η^1-anti, η^1-anti,η^3-anti [c]

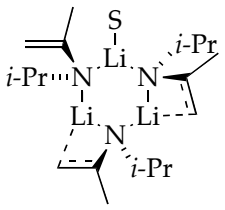
-1359.01423

LV (*Continued*)**.**

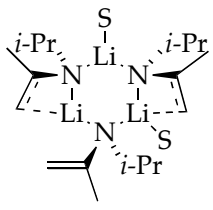
D. Solvated cis,cis isomers $\mathbf{A_3S_n}$. n = 1-3, S = Me_2O (*G* = -154.97011 Hartrees).



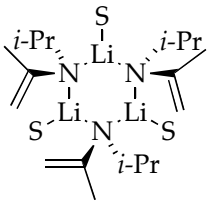
LII



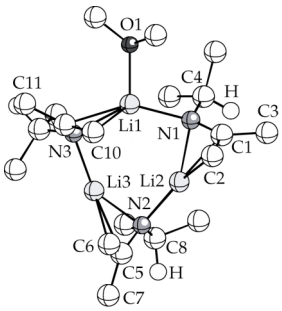
LIII



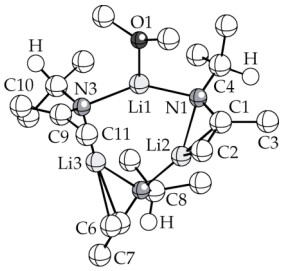
LIV



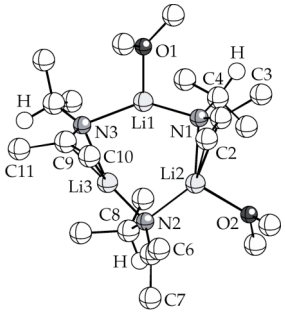
LV



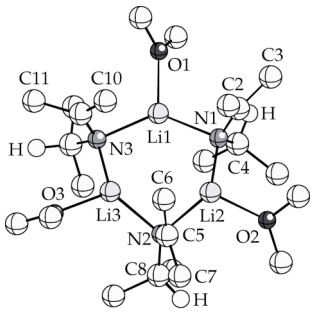
all η^3-anti



η^1-syn,η^3-anti,η^3-anti[b]



η^1-anti,η^3-anti,η^3-anti



All η^3-anti[c]

-1049.08304 -1049.08545 -1204.04653 -1359.01043

[a] Only selected hydrogens shown for clarity.
[b] η^3-Syn azaallyl moiety not found.
[c] η^3-Anti azaallyl moiety turned into η^1-anti upon geometry optimization.
[d] Optimization of **XLX** converges to its isomer **XLIX**.

LVI. Selected bond lengths (Å) and angles (deg) calculated for unsolvated trimers $\mathbf{A_3S}$.[a, b]

	XXXIII	XXXIV	XXXV	XXXVI	XXXVII	XXXVIII
Li1-N1[b]	2.00	1.96	2.28	2.21	2.29	1.98
Li1-N3[b]	2.21	2.05	1.96	2.00	1.96	2.05
Li2-N1[b]	2.01	2.00	1.94	1.93	1.95	2.11
Li2-N2[b]	2.13	2.04	2.04	1.93	2.04	2.16
Li3-N3[b]	1.93	2.18	2.13	2.01	2.13	1.95
Li3-N2[b]	1.93	1.99	1.98	2.13	1.98	1.92
Li1-N1-N3	140.9	141.5	134.4	140.9	134.3	138.4
Li2-N1-N2	140.3	144.0	143.7	144.6	143.2	135.7
Li3-N2-N3	144.6	136.3	141.2	140.3	141.1	152.6

	XXXIX	XL	XLI	XLII	XLIII	XLIV
Li1-N1[b]	1.96	1.99	1.97	1.98	1.95	2.03
Li1-N3[b]	2.07	1.95	2.02	2.07	1.96	1.98
Li2-N1[b]	2.12	1.96	2.02	2.10	2.22	2.00
Li2-N2[b]	2.16	2.01	2.16	2.02	2.00	2.05
Li3-N3[b]	1.95	1.98	1.96	1.96	2.03	2.02
Li3-N2[b]	1.93	1.95	1.91	1.95	2.05	1.99
Li1-N1-N3	138.3	144.1	153.0	138.7	147.6	137.7
Li2-N1-N2	137.7	147.3	134.8	141.3	136.5	140.0
Li3-N2-N3	156.1	145.5	145.7	152.6	143.2	139.7

[a]See 3D representations in Section **LV** for atom numbering.

[b] N1-C3-C2, N2-C5-C6, and N3-C9-C10 constitute the azaallylic moieties.

LVI (*Continued*)**.** Selected bond lengths (Å) and angles (deg) calculated for solvated trimers $\mathbf{A_3S_n}$.[a, b]

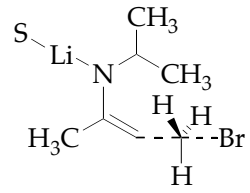
	XLV	XLVI	XLVII	XLVIII	XLIX	LI	LII	LIII	LIV	LV
Li1-N1[b]	2.02	2.05	2.06	2.02	2.05	2.05	2.07	2.10	2.06	2.06
Li1-N3[b]	1.95	2.06	2.08	1.96	2.09	2.07	2.14	2.05	2.12	2.08
Li2-N1[b]	2.07	2.16	2.07	2.10	1.99	2.09	2.07	2.04	2.13	2.08
Li2-N2[b]	2.07	2.09	2.06	2.14	2.03	2.15	1.98	1.99	2.06	2.06
Li3-N3[b]	2.13	2.08	2.03	2.11	2.14	2.09	2.00	2.01	1.99	2.07
Li3-N2[b]	2.12	1.97	1.97	2.11	2.11	2.07	2.04	2.07	2.04	2.08
Li1-N1-N3	142.7	134.8	132.4	147.1	131.0	136.0	132.2	135.8	136.9	135.3
Li2-N1-N2	137.2	140.1	133.0	131.2	150.8	99.8	141.7	144.8	129.6	98.9
Li3-N2-N3	148.1	92.6	154.2	128.2	131.1	137.2	142.3	86.2	144.0	99.8
Li-O (av)	1.97	2.00	2.00	2.01	2.02	2.05	2.00	1.98	2.01	2.06

[a]See 3D representations in Section **LV** for atom numbering.

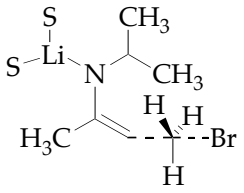
[b] N1-C3-C2, N2-C5-C6, and N3-C9-C10 constitute the azaallylic moieties.

LVII. Optimized geometries and free energies (*G*, Hartrees) of monomer-based transition structures $[AS_n{\cdot}CH_3Br]^{‡}$.[a,b]

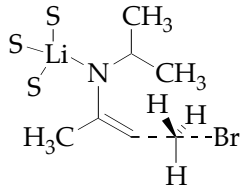
A. Syn alkylations $[AS_n{\cdot}CH_3Br]^{‡}$. n = 1-3. S = Me_2O, *G* = -154.97011 Hartrees. MeBr, *G* = -2613.76945 Hartrees.



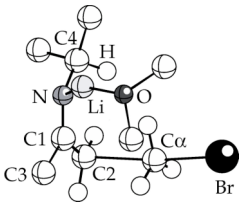
A



B

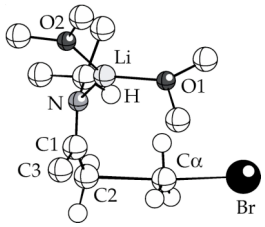


C



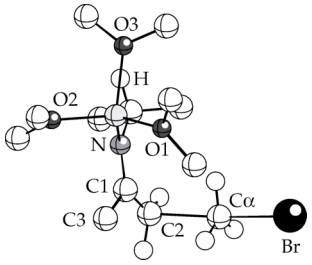
$[AS{\cdot}CH_3Br]^{‡}$

-3066.71919



$[AS_2{\cdot}CH_3Br]^{‡}$

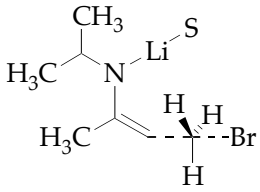
-3221.69655



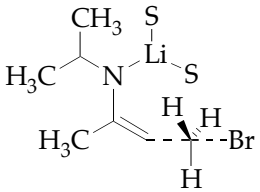
$[AS_3{\cdot}CH_3Br]^{‡}$

-3376.64811

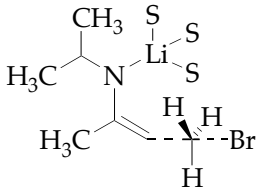
B. Anti alkylations $[AS_n{\cdot}CH_3Br]^{‡}$.



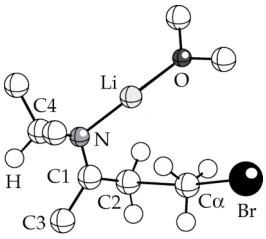
D



E

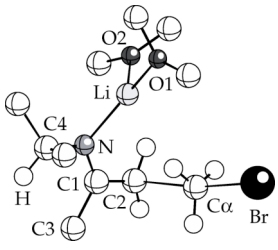


F



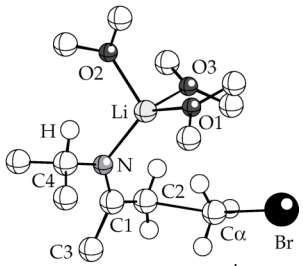
$[AS{\cdot}CH_3Br]^{‡}$

-3066.72378



$[AS_2{\cdot}CH_3Br]^{‡}$

-3221.69413



$[AS_3{\cdot}CH_3Br]^{‡}$

-3376.64535

[a] Only selected hydrogens shown for clarity.
[b] Only most stable conformers shown.

LVIII. Selected bond lengths (Å) and angles (deg) calculated for monomer-based transition structures **A**-**F**.[a, b]

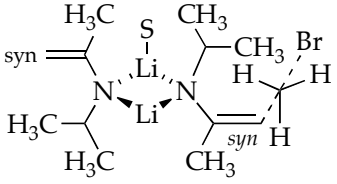
	A	**B**	**C**	**D**	**E**	**F**
Li-N[b]	1.89	1.94	1.99	1.91	1.94	2.02
Li-C1[b]	2.64	2.80	2.95	2.33	2.80	2.92
Li-C2[b]	---	---	---	2.24	2.97	3.13
Li-O1	1.88	1.95	2.06	1.89	1.95	2.04
Li-O2	---	1.93	2.03	---	1.94	2.05
Li-O3	---	---	2.03	---	---	2.12
N-C1	1.34	1.34	1.34	1.33	1.34	1.34
C1-C2	1.40	1.40	1.40	1.43	1.41	1.40
C2-Cα	2.33	2.34	2.31	2.35	2.34	2.36
Cα-Br	2.42	2.40	2.41	2.40	2.37	2.35
C2-Cα-Br	172.8	175.5	175.5	177.3	172.3	171.5
Li-N-C1	108.4	116.0	123.4	90.2	115.7	119.3

[a]See 3D representations in Section **LVII** for atom numbering.

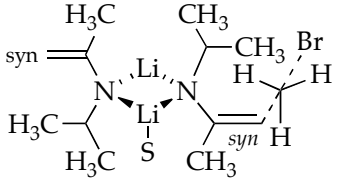
[b]N-C1-C2 constitutes the azaallylic moiety.

LIX. Optimized geometries and free energies (*G*, Hartrees) of dimer-based transition structures $[A_2S_n{\cdot}CH_3Br]^{\ddagger}$.[a,b]

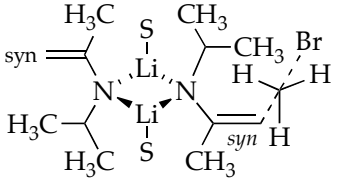
A. Exo alkylations $[A_2S_n{\cdot}CH_3Br]^{\ddagger}$.
n = 1-2. S = Me_2O, *G* = -154.97011 Hartrees. MeBr, *G* = -2613.76945 Hartrees.



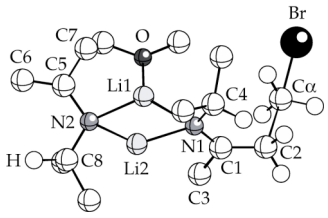
G



H

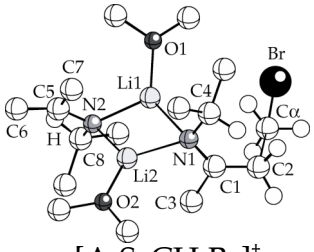


I

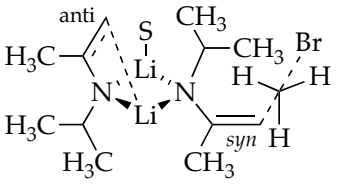


$[A_2S{\cdot}CH_3Br]^{\ddagger}$
trans,syn,*syn*
-3364.74847

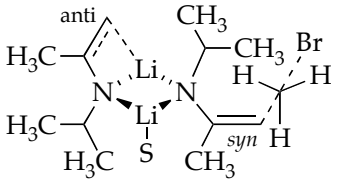
$[A_2S{\cdot}CH_3Br]^{\ddagger}$
trans,syn,*syn*
not found[c]



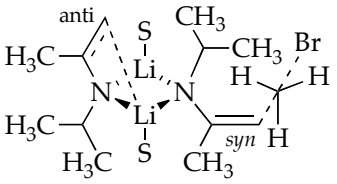
$[A_2S_2{\cdot}CH_3Br]^{\ddagger}$
trans,syn,*syn*
-3519.72375



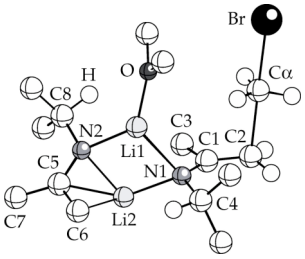
J



K

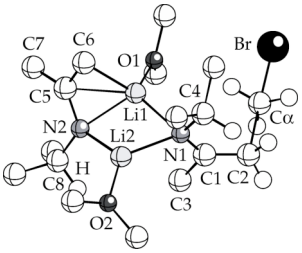


L



$[A_2S{\cdot}CH_3Br]^{\ddagger}$
trans,anti,*syn*
-3364.74785

$[A_2S{\cdot}CH_3Br]^{\ddagger}$
trans,anti,*syn*
not found[c]

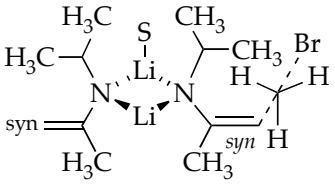


$[A_2S_2{\cdot}CH_3Br]^{\ddagger}$
trans,anti,*syn*
-3519.72658

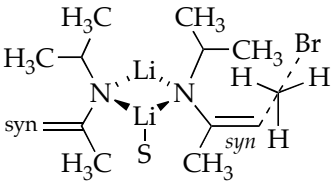
[a] Only selected hydrogens shown for clarity.
[b] Only most stable conformers shown.
[c] TS optimization collapsed into an endo isomer following a Li-Br interaction (see below).

LIX (*Continued*).

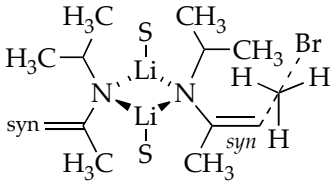
A. Exo alkylations $[A_2S_n{\cdot}CH_3Br]^{‡}$



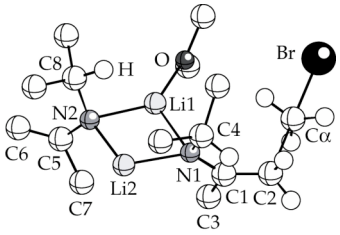
M



N

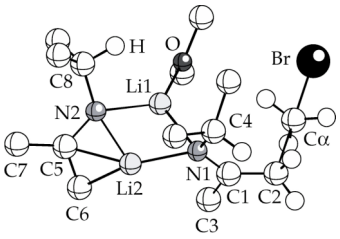


O

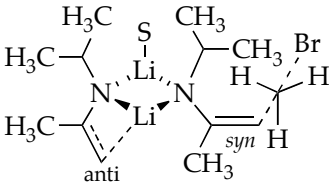


$[A_2S{\cdot}CH_3Br]^{‡}$
cis,syn,*syn*
-3364.74500

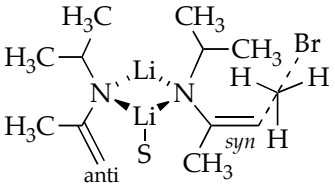
$[A_2S{\cdot}CH_3Br]^{‡}$
cis,syn,*syn*
not found[c]



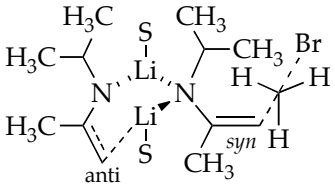
$[A_2S_2{\cdot}CH_3Br]^{‡}$
cis,syn,*syn*
-3519.72146



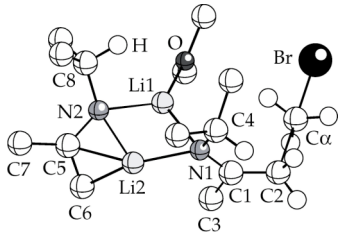
P



Q

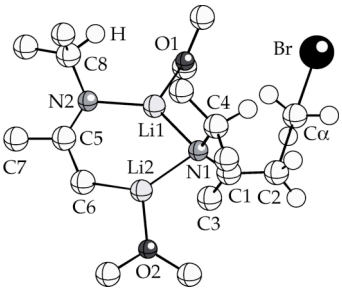


R



$[A_2S{\cdot}CH_3Br]^{‡}$
cis,anti,*syn*
-3364.75455

$[A_2S{\cdot}CH_3Br]^{‡}$
cis,anti,*syn*
not found[c]

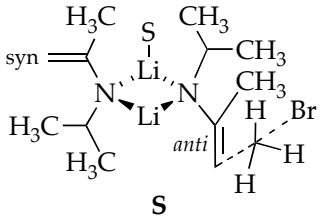


$[A_2S_2{\cdot}CH_3Br]^{‡}$
cis,anti,*syn*
-3519.72033[d]

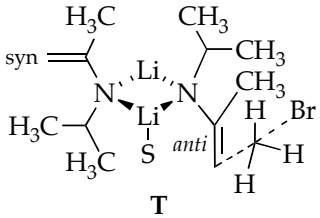
[c] TS optimization collapsed into an endo isomer following a Li-Br interaction (see below).
[d] The isomer with an intact Li_2N_2 core couldn't be located.

LIX (*Continued*).

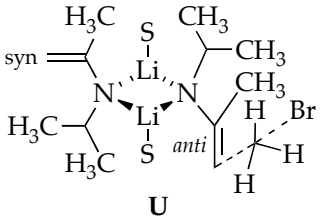
A. Exo alkylations $[A_2S_n{\cdot}CH_3Br]^{‡}$



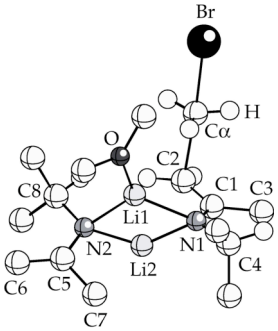
S



T

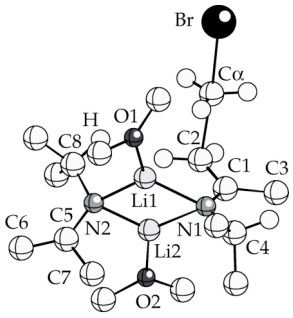


U

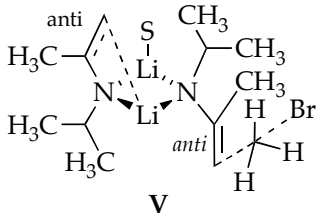


$[A_2S{\cdot}CH_3Br]^{‡}$
trans,syn,*anti*
-3364.74039

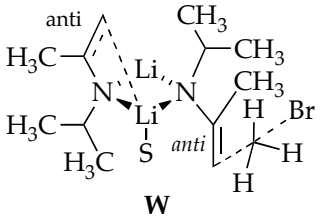
$[A_2S{\cdot}CH_3Br]^{‡}$
trans,syn,*anti*
not found[c]



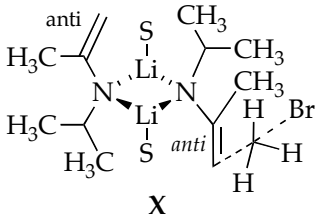
$[A_2S_2{\cdot}CH_3Br]^{‡}$
trans,syn,*anti*
-3519.72313



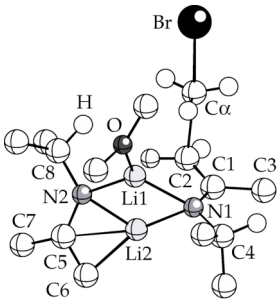
V



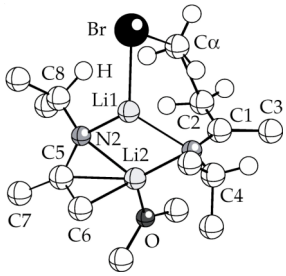
W



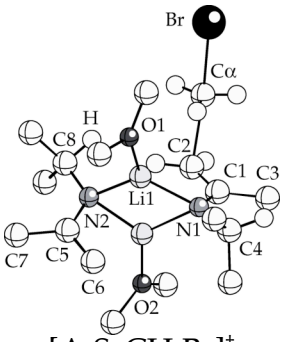
X



$[A_2S{\cdot}CH_3Br]^{‡}$
trans,anti,*anti*
-3364.75287



$[A_2S{\cdot}CH_3Br]^{‡}$
trans,anti,*anti*
-3364.75307

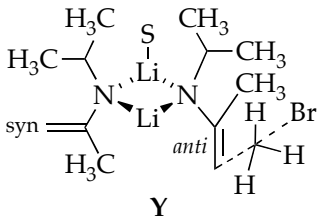


$[A_2S_2{\cdot}CH_3Br]^{‡}$
trans,anti,*anti*
-3519.72486

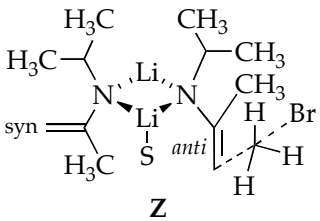
[c] TS optimization collapsed into an endo isomer following a Li-Br interaction (see below).

LIX (*Continued*).

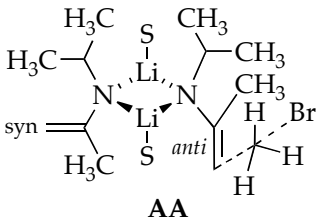
A. Exo alkylations $[A_2S_n{\cdot}CH_3Br]^{‡}$



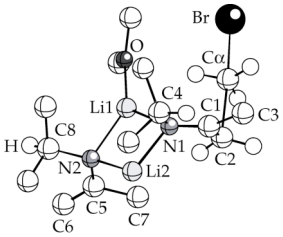
Y



Z

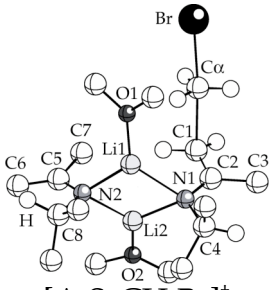


AA

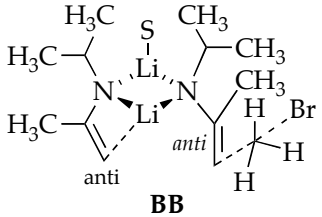


$[A_2S{\cdot}CH_3Br]^{‡}$
cis,syn,*anti*
-3364.74707

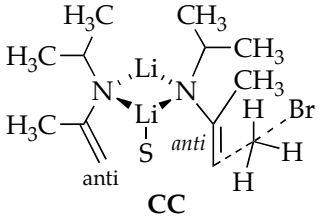
$[A_2S{\cdot}CH_3Br]^{‡}$
cis,syn,*anti*
not found[c]



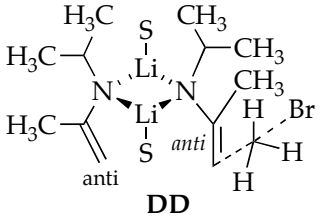
$[A_2S_2{\cdot}CH_3Br]^{‡}$
cis,syn,*anti*
-3519.72518



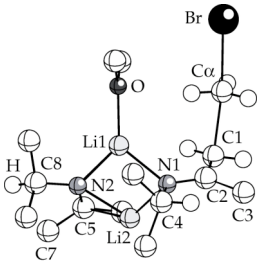
BB



CC

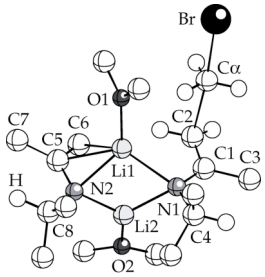


DD



$[A_2S{\cdot}CH_3Br]^{‡}$
cis,anti,*anti*
-3364.75528

$[A_2S{\cdot}CH_3Br]^{‡}$
cis,anti,*anti*
not found[c]

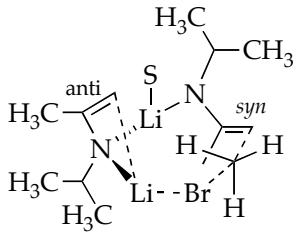


$[A_2S_2{\cdot}CH_3Br]^{‡}$
cis,anti,*anti*
-3519.72609

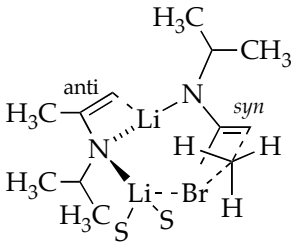
[c] TS optimization collapsed into an endo isomer following a Li-Br interaction (see below).

LIX (*Continued*)**.**

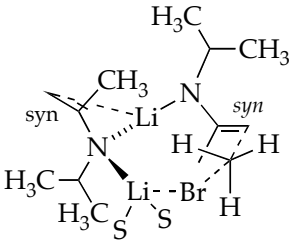
B. Endo alkylations $[A_2S_n{\cdot}CH_3Br]^{‡}$.
n = 1-2. S = Me_2O, *G* = -154.97011 Hartrees. MeBr, *G* = -2613.76945 Hartrees.



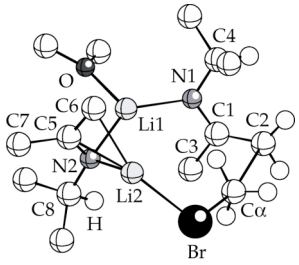
EE



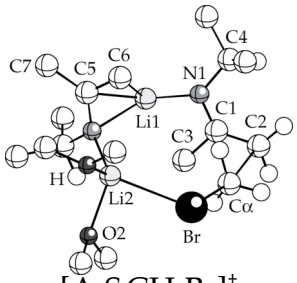
FF



GG

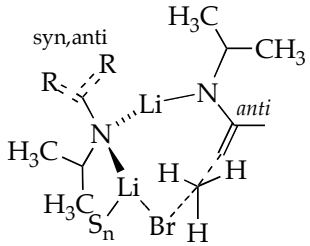


$[A_2S{\cdot}CH_3Br]^{‡}$
anti,*syn*
-3364.76278



$[A_2S{\cdot}CH_3Br]^{‡}$
anti,*syn*
-3519.72627[c]

$[A_2S_2{\cdot}CH_3Br]^{‡}$
syn,*syn*
not found



HH

$[A_2S_n{\cdot}CH_3Br]^{‡}$
syn or anti,*anti*
not found[c]

[c]Isomers, including species with different solvation numbers, couldn't be located.
[e]Endo alkylations of anti lithioimine subunits collapsed into their exo isomers or couldn't be located.

LX. Selected bond lengths (Å) and angles (deg) calculated for dimer-based transition structures **G**-**FF**.[a, b]

	G	**I**	**J**	**L**	**M**	**O**	**P**	**R**	**S**	**U**
Li1-N1	2.16	2.27	2.15	2.34	2.23	2.16	2.15	2.15	2.15	2.13
Li1-N2	2.08	2.00	2.02	2.08	2.01	1.98	2.00	1.96	2.06	1.99
Li2-N1	1.97	2.05	2.00	2.03	1.97	2.02	2.01	2.05	2.03	2.09
Li2-N2	1.91	2.03	1.99	1.98	1.93	2.00	2.01	3.32	1.93	2.02
C2-Cα	2.18	2.23	2.25	2.26	2.26	2.24	2.25	2.22	2.20	2.20
Cα-Br	2.48	2.44	2.45	2.45	2.47	2.46	2.45	2.47	2.46	2.46
Li1-N1-N2	100.6	103.1	103.1	100.0	100.4	101.5	103.6	127.0	102.7	105.6
Li2-N1-N2	114.0	110.4	110.3	111.3	113.6	105.9	108.3	82.7	112.3	106.0
C2-Cα-Br	178.3	176.6	177.5	178.2	179.5	138.3	179.3	178.9	172.5	174.7
Li-O (av)	1.91	1.94	1.92	1.94	1.91	1.92	1.93	1.95	1.91	1.93

	V	**W**	**X**	**Y**	**AA**	**BB**	**DD**	**EE**	**FF**
Li1-N1	2.12	2.28	2.10	2.15	2.20	2.13	2.23	1.91	1.94
Li1-N2	2.00	2.00	2.00	2.00	2.02	2.05	2.09	2.05	2.04
Li2-N1	2.03	2.16	2.14	2.01	2.07	2.04	2.07	---	---
Li2-N2	2.02	2.07	2.02	2.01	2.03	2.03	2.01	1.98	2.05
C2-Cα	2.21	2.42	2.24	2.25	2.25	2.24	2.26	2.60	2.51
Cα-Br	2.45	2.43	2.43	2.45	2.43	2.43	2.04	2.31	2.36
Li-Br	---	---	---	---	---	---	---	2.59	2.78
Li1-N1-N2	105.5	102.7	106.4	103.6	105.4	104.3	101.6	145.2	152.5
Li2-N1-N2	108.2	106.0	104.4	108.3	109.8	108.8	110.7	---	---
C2-Cα-Br	173.9	101.2	175.3	179.3	175.1	172.5	175.2	167.8	167.9
Li-O (av)	1.93	1.98	1.95	1.91	1.92	1.93	1.94	1.94	2.04

[a]See 3D representations in Section **LIX** for atom numbering.

[b]N-C1-C2, and N2-C5-C6 constitutes the azaallylic moieties.

Part 5: GIAO Computational Studies

LXI. Calculated chemical shifts (δ, ppm)[a] and coupling constants (*J*, Hz) for monomers $\mathbf{AS_n}$.[b, c]

Structure	no π / no S		no π / S		π / no S		π / S	
	$J_{Li\text{-}N}$	δ_{Li}	$J_{Li\text{-}N}$	δ_{Li}	$J_{Li\text{-}N}$	δ_{Li}	$J_{Li\text{-}N}$	δ_{Li}
I	6.6	0.0	---	---	---	---	---	---
II	---	---	3.6	-0.7	---	---	---	---
III	---	---	6.9	-0.5	---	---	---	---
IV	---	---	6.8	-0.4	---	---	---	---
V	---	---	---	---	3.2	0.8	---	---
VI	---	----	---	---	---	---	2.9	-0.5
VII	---	----	---	---	---	---	2.0	-1.1
VIII	---	---	6.4	0.1	---	---	---	---

[a]Chemical shifts are referenced to the calculated shielding value of monomer **I**.
[b]See Chart 2 for atom numbering.
[c]N, C(1) and C(2) constitute the azaallylic moiety.

LXII. Calculated chemical shifts (δ, ppm) and coupling constants (*J*, Hz) for dimers $\mathbf{A_2S_n}$.[a, b]

Structure	no π / no S		no π / S		π / no S		π / S	
	$J_{Li\text{-}N}$	δ_{Li}	$J_{Li\text{-}N}$	δ_{Li}	$J_{Li\text{-}N}$	δ_{Li}	$J_{Li\text{-}N}$	δ_{Li}
IX	4.0	0.0	---	---	---	---	---	---
X	3.7	-0.2	---	---	1.7	0.1	---	---
XI	---	---	---	---	2.1	-0.7	---	---
XII	---	---	---	---	3.4	-0.7	---	---
XIII	4.1	0.0	---	---	---	---	---	---
XIV	3.4	0.6	---	---	1.6	-0.7	---	---
XV	---	---	---	---	1.7	-0.2	---	---
XVII	5.1	0.0	3.3	0.0	---	---	---	---
XVIII	---	---	4.6	0.0	1.9	0.1	---	---
XIX	---	---	---	---	2.5	-0.6	1.4	-1.5
XX	---	---	5.2	0.2	1.9	-0.9	---	---
XXI	5.4	0.4	3.2	0.3	---	---	---	---
XXII	---	---	3.2	0.2	1.8	-0.5	---	---
XXIII	---	---	---	---	2.1	-0.5	---	---
XXV	---	---	4.3	0.2	---	---	2.1	-1.1
XXVI	---	---	5.4	0.1	---	---	1.8	-1.0
XXVII	---	---	---	---	---	---	1.9	-1.5
XXIX	---	---	4.4	0.3	---	---	---	---
XXX	---	---	5.3	0.4	---	---	2.1	-1.1
XXXI	---	---	---	---	---	---	3.3	0.2
av	4.3	0.1	4.3	0.1	2.1	-0.5	2.1	-1.0
σ	0.7	0.3	0.9	0.2	0.5	0.3	0.6	0.6

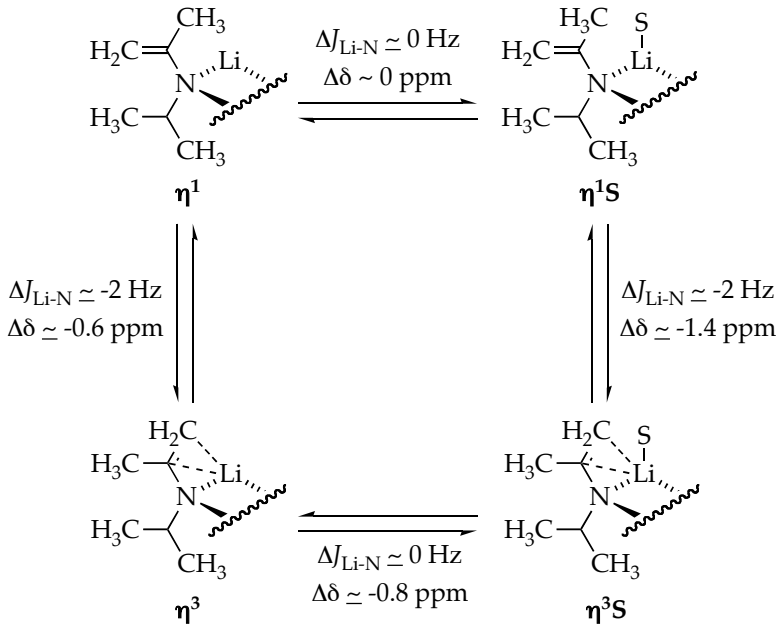
[a]Chemical shifts are referenced to the calculated shielding value of dimer **IX**. [a]See Chart 2 for atom numbering. [b]N, C(1) and C(2) constitute the azaallylic moiety. [c]Double π complexation not included.

LXIII. Calculated chemical shifts (δ, ppm) and coupling constants (*J*, Hz) for trimers $\mathbf{A_3S_n}$.[a, b]

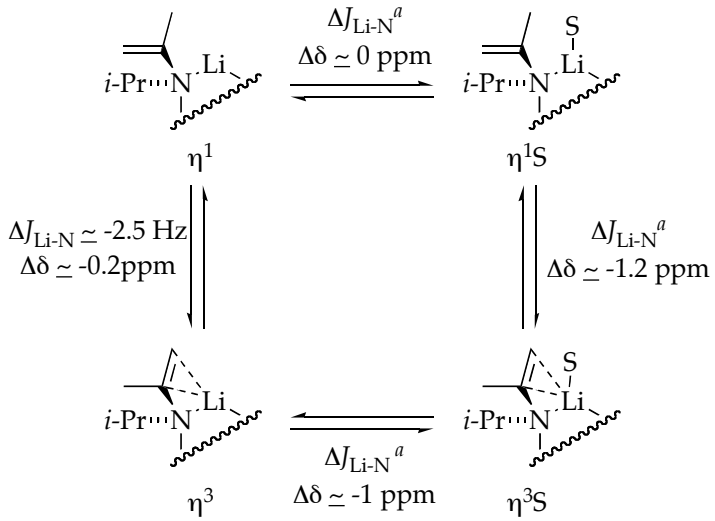
Structure	no π / no S		no π / S		π / no S		π / S	
	$J_{Li\text{-}N}$	δ_{Li}	$J_{Li\text{-}N}$	δ_{Li}	$J_{Li\text{-}N}$	δ_{Li}	$J_{Li\text{-}N}$	δ_{Li}
XXXIII	---	0.0	---	---	1.0[c]	-1.1[c]	---	---
XXXIV	---	---	---	---	1.1[c]	-1.2[c]	---	---
XXXV	---	---	---	---	1.7[c]	-0.8[c]	---	---
XXXVI	---	0.0	---	---	2.2[c]	-0.7[c]	---	---
XXXVII	---	0.0	---	---	2.2[c]	-1.2[c]	---	---
XXXVIII	---	0.1	---	---	1.9[d]	-0.7[d]	---	---
XXXIX	---	0.1	---	---	2.0[d]	-0.7[d]	---	---
XL	4.7[c]	0.6[c]	---	---	---	---	---	---
XLI	4.5[c]	0.5[c]	---	---	0.6	-0.3	---	---
XLII	4.6	0.3	---	---	1.4[c]	-0.8[c]	---	---
XLIII	3.8	1.3	---	---	1.9[c]	-0.5[c]	---	---
XLIV	---	---	---	---	1.9[c]	-0.5[c]	---	---
XLV	---	---	---	0.2	2.2[d]	-0.3[d]	---	---
XLVI	---	---	---	-0.1	2.1[d]	-0.6[d]	---	---
XLVII	---	---	---[e]	-0.1	---[e]	-0.7[c]	---	---
XLVIII	---	---	---[e]	---	---[e]	-0.2[c]	---[e]	-1.7
XLIX	---	---	---[e]	-0.2	---[e]	-0.1[c]	---[e]	-1.5
LI	---	---	---[e]	-0.7[c]	---	---	---[e]	-1.6
LII	---	---	---	---	1.9[c]	-0.3[c]	2.7	-1.4
LIII	---	---	4.6	-0.2	2.0[c]	-0.2[c]	---	---
LIV	---	---	---[e]	-0.7	---[e]	-0.1	---[e]	-1.1
LV	---	---	---	-0.5[c]	---	---	---	---
av	4.4	0.3	4.6	-0.3	1.7	-0.6	2.7	-1.5
σ	0.4	0.4	---	0.3	0.5	0.3	---	0.2

[a]Chemical shifts are referenced to the calculated shielding value (90.2) for the no π / no S Li atom in trimer **XXXIII**. [b]N1-C1-C2, N2-C5-C6, and N3-C9-C10 constitute the azaallylic moieties. [c]Average values. [d]Double π complexation not included. [e]The size of the system precluded the calculation of coupling constants.

LXIV. Effect of solvation and π-complexation upon calculated chemical shifts (δ, ppm) and coupling constants (*J*, Hz) for dimers $\mathbf{A_2S_n}$.



LXV. Effect of solvation and π-complexation upon calculated chemical shifts (δ, ppm) and coupling constants (*J*, Hz) for trimers $\mathbf{A_3S_n}$ [a]



[a] $\Delta J_{\text{Li-N}}$ values of statistical significance not calculated due to low populations.

Part 6: X-Ray Crystal Data

LXVI. X-ray crystal data for lithioimine *trans*-**12** (**A_2S_2**, S = Me_2EtN, Figure 5).

Table 1. Crystal data and structure refinement.

Identification code	ar4	
Empirical formula	C16 H31 Li N2	
Formula weight	258.37	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.2212(11) Å	α = 82.311(5)°.
	b = 9.3182(11) Å	β = 72.770(5)°.
	c = 10.5245(13) Å	γ = 70.616(6)°.
Volume	814.14(17) $Å^3$	
Z	2	
Density (calculated)	1.054 Mg/m^3	
Absorption coefficient	0.060 mm^{-1}	
F(000)	288	
Crystal size	0.40 x 0.30 x 0.20 mm^3	
Theta range for data collection	2.03 to 30.59°.	
Index ranges	-13<=h<=12, -13<=k<=13, -15<=l<=13	
Reflections collected	18562	
Independent reflections	4910 [R(int) = 0.0398]	
Completeness to theta = 30.59°	98.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9881 and 0.9763	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4910 / 0 / 283	
Goodness-of-fit on F^2	1.076	
Final R indices [I>2sigma(I)]	R1 = 0.0494, wR2 = 0.1447	
R indices (all data)	R1 = 0.0710, wR2 = 0.1576	
Largest diff. peak and hole	0.312 and -0.225 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Li(1)	4059(2)	4681(2)	996(2)	24(1)
N(1)	3937(1)	6862(1)	159(1)	19(1)
N(2)	1918(1)	4119(1)	1933(1)	27(1)
C(1)	2891(1)	8110(1)	-473(1)	20(1)
C(2)	2561(1)	7566(1)	-1635(1)	22(1)
C(3)	1469(1)	8863(1)	-2303(1)	26(1)
C(4)	2136(1)	10195(1)	-2765(1)	29(1)
C(5)	2452(1)	10753(1)	-1608(1)	29(1)
C(6)	3566(1)	9442(1)	-976(1)	27(1)
C(7)	3948(1)	7127(1)	1423(1)	21(1)
C(8)	2601(1)	8355(1)	2277(1)	30(1)
C(9)	3049(5)	8653(3)	3538(3)	32(1)
C(10)	3670(4)	7151(4)	4272(3)	36(1)
C(9')	2444(3)	8134(4)	3758(2)	36(1)
C(10')	4079(3)	7797(4)	3984(2)	37(1)
C(11)	5215(1)	6261(1)	3368(1)	32(1)
C(12)	5120(1)	6194(1)	1972(1)	24(1)
C(13)	1744(2)	3370(2)	845(2)	40(1)
C(14)	589(2)	5473(2)	2278(2)	42(1)
C(15)	1984(2)	3000(2)	3079(1)	35(1)
C(13')	1987(8)	2814(8)	1445(8)	43(2)
C(14')	583(9)	5465(9)	1535(10)	51(2)
C(15')	1373(7)	4150(8)	3460(5)	43(2)
C(16)	2543(2)	3395(2)	4121(1)	59(1)

Table 3. Bond lengths [Å] and angles [°].

Li(1)-N(1)#1	2.0821(17)
Li(1)-N(1)	2.0850(17)
Li(1)-N(2)	2.1306(18)
Li(1)-C(7)	2.3452(18)
Li(1)-C(12)	2.4285(19)
Li(1)-Li(1)#1	2.441(3)
N(1)-C(7)	1.3883(11)
N(1)-C(1)	1.4672(11)
N(1)-Li(1)#1	2.0821(17)
N(2)-C(13')	1.357(6)
N(2)-C(14)	1.4346(18)
N(2)-C(15)	1.4867(15)
N(2)-C(13)	1.4898(18)
N(2)-C(15')	1.537(5)
N(2)-C(14')	1.551(7)
C(1)-C(2)	1.5281(13)
C(1)-C(6)	1.5329(13)
C(2)-C(3)	1.5338(12)
C(3)-C(4)	1.5239(15)
C(4)-C(5)	1.5223(15)
C(5)-C(6)	1.5312(13)
C(7)-C(12)	1.3674(12)
C(7)-C(8)	1.5268(14)
C(8)-C(9')	1.514(2)
C(8)-C(9)	1.584(3)
C(9)-C(10)	1.524(5)
C(10)-C(11)	1.499(3)
C(9')-C(10')	1.518(4)
C(10')-C(11)	1.555(3)
C(11)-C(12)	1.5076(13)
C(15)-C(16)	1.474(2)
C(15')-C(16)	1.396(6)
N(1)#1-Li(1)-N(1)	108.30(7)
N(1)#1-Li(1)-N(2)	121.65(8)

N(1)-Li(1)-N(2)	119.85(8)
N(1)#1-Li(1)-C(7)	124.12(8)
N(1)-Li(1)-C(7)	35.92(4)
N(2)-Li(1)-C(7)	114.21(7)
N(1)#1-Li(1)-C(12)	104.74(7)
N(1)-Li(1)-C(12)	63.24(5)
N(2)-Li(1)-C(12)	124.78(8)
C(7)-Li(1)-C(12)	33.23(4)
N(1)#1-Li(1)-Li(1)#1	54.20(6)
N(1)-Li(1)-Li(1)#1	54.09(6)
N(2)-Li(1)-Li(1)#1	150.79(12)
C(7)-Li(1)-Li(1)#1	77.69(8)
C(12)-Li(1)-Li(1)#1	80.35(8)
C(7)-N(1)-C(1)	115.59(7)
C(7)-N(1)-Li(1)#1	118.44(7)
C(1)-N(1)-Li(1)#1	120.51(7)
C(7)-N(1)-Li(1)	82.31(7)
C(1)-N(1)-Li(1)	139.30(7)
Li(1)#1-N(1)-Li(1)	71.70(7)
C(13')-N(2)-C(14)	129.2(3)
C(13')-N(2)-C(15)	75.8(4)
C(14)-N(2)-C(15)	111.48(12)
C(13')-N(2)-C(13)	32.1(4)
C(14)-N(2)-C(13)	109.48(13)
C(15)-N(2)-C(13)	107.15(11)
C(13')-N(2)-C(15')	113.9(4)
C(14)-N(2)-C(15')	72.9(3)
C(15)-N(2)-C(15')	42.6(3)
C(13)-N(2)-C(15')	138.9(3)
C(13')-N(2)-C(14')	109.6(5)
C(14)-N(2)-C(14')	30.2(3)
C(15)-N(2)-C(14')	134.8(3)
C(13)-N(2)-C(14')	82.4(4)
C(15')-N(2)-C(14')	102.0(4)
C(13')-N(2)-Li(1)	109.9(3)
C(14)-N(2)-Li(1)	110.53(10)

C(15)-N(2)-Li(1)	115.78(9)
C(13)-N(2)-Li(1)	101.79(9)
C(15')-N(2)-Li(1)	116.0(2)
C(14')-N(2)-Li(1)	104.6(3)
N(1)-C(1)-C(2)	111.64(7)
N(1)-C(1)-C(6)	112.86(8)
C(2)-C(1)-C(6)	108.56(7)
C(1)-C(2)-C(3)	112.03(8)
C(4)-C(3)-C(2)	112.00(8)
C(5)-C(4)-C(3)	110.36(8)
C(4)-C(5)-C(6)	110.27(8)
C(5)-C(6)-C(1)	112.55(8)
C(12)-C(7)-N(1)	119.81(8)
C(12)-C(7)-C(8)	118.27(8)
N(1)-C(7)-C(8)	121.71(8)
C(12)-C(7)-Li(1)	76.73(7)
N(1)-C(7)-Li(1)	61.77(6)
C(8)-C(7)-Li(1)	130.18(8)
C(9')-C(8)-C(7)	115.04(11)
C(9')-C(8)-C(9)	30.58(11)
C(7)-C(8)-C(9)	111.83(13)
C(10)-C(9)-C(8)	110.2(3)
C(11)-C(10)-C(9)	107.3(3)
C(8)-C(9')-C(10')	108.8(2)
C(9')-C(10')-C(11)	110.2(2)
C(10)-C(11)-C(12)	113.31(13)
C(10)-C(11)-C(10')	30.05(12)
C(12)-C(11)-C(10')	110.44(11)
C(7)-C(12)-C(11)	125.81(9)
C(7)-C(12)-Li(1)	70.04(7)
C(11)-C(12)-Li(1)	132.72(8)
C(16)-C(15)-N(2)	114.53(12)
C(16)-C(15')-N(2)	116.1(4)
C(15')-C(16)-C(15)	44.9(3)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + \ldots + 2 h k a^* b^* U^{12}]$

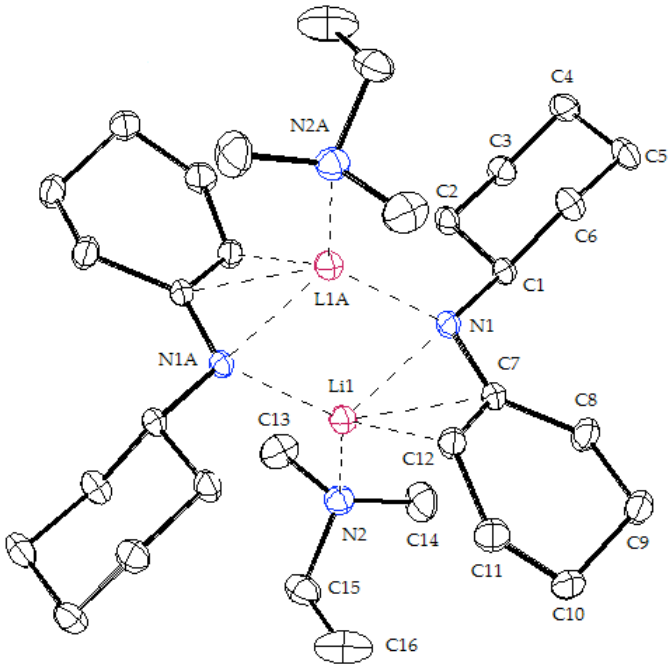
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Li(1)	24(1)	21(1)	24(1)	0(1)	-4(1)	-4(1)
N(1)	21(1)	16(1)	19(1)	0(1)	-7(1)	0(1)
N(2)	25(1)	28(1)	27(1)	0(1)	-5(1)	-9(1)
C(1)	20(1)	15(1)	21(1)	0(1)	-7(1)	-1(1)
C(2)	24(1)	17(1)	25(1)	0(1)	-10(1)	-2(1)
C(3)	27(1)	25(1)	27(1)	2(1)	-13(1)	-3(1)
C(4)	32(1)	24(1)	26(1)	7(1)	-9(1)	-2(1)
C(5)	32(1)	18(1)	35(1)	5(1)	-11(1)	-5(1)
C(6)	29(1)	20(1)	34(1)	3(1)	-14(1)	-7(1)
C(7)	24(1)	16(1)	20(1)	-1(1)	-6(1)	-3(1)
C(8)	35(1)	25(1)	25(1)	-7(1)	-9(1)	3(1)
C(9)	43(2)	24(1)	25(1)	-7(1)	-11(1)	0(1)
C(10)	52(2)	29(2)	20(1)	-1(1)	-11(1)	-5(1)
C(9')	36(1)	40(1)	24(1)	-11(1)	-2(1)	-5(1)
C(10')	48(1)	38(2)	25(1)	-9(1)	-13(1)	-9(1)
C(11)	42(1)	30(1)	25(1)	0(1)	-17(1)	-7(1)
C(12)	28(1)	20(1)	22(1)	-3(1)	-10(1)	-2(1)
C(13)	40(1)	50(1)	37(1)	-6(1)	-8(1)	-24(1)
C(14)	27(1)	35(1)	54(1)	-4(1)	-5(1)	1(1)
C(15)	35(1)	34(1)	36(1)	8(1)	-7(1)	-15(1)
C(13')	42(4)	42(4)	48(4)	-9(3)	-6(3)	-21(3)
C(14')	39(4)	47(4)	63(5)	6(4)	-25(4)	-1(3)
C(15')	43(4)	63(5)	24(2)	-2(3)	-4(2)	-22(3)
C(16)	57(1)	90(1)	37(1)	19(1)	-18(1)	-36(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3)

	x	y	z	U(eq)
H(9A)	3877	9174	3252	39
H(9B)	2095	9324	4144	39
H(10A)	3842	7342	5110	43
H(10B)	2890	6578	4491	43
H(9'A)	2013	7278	4124	43
H(9'B)	1699	9066	4218	43
H(10C)	3977	7743	4951	44
H(10D)	4531	8628	3571	44
H(13A)	783	3049	1164	60
H(13B)	2682	2478	573	60
H(13C)	1653	4091	82	60
H(14A)	-384	5195	2710	63
H(14B)	460	6101	1470	63
H(14C)	785	6049	2890	63
H(15A)	904	2902	3485	42
H(15B)	2702	1994	2742	42
H(13D)	998	2563	1880	65
H(13E)	2897	1983	1621	65
H(13F)	2114	2953	483	65
H(14D)	-451	5287	1932	76
H(14E)	793	5547	563	76
H(14F)	561	6413	1859	76
H(16A)	2554	2605	4836	89
H(16B)	1823	4376	4482	89
H(16C)	3624	3469	3737	89
H(2B)	2072(14)	6747(14)	-1307(11)	32(3)
H(12)	5991(14)	5505(13)	1421(11)	26(3)
H(3A)	380(14)	9218(13)	-1597(11)	29(3)
H(6B)	4598(15)	9035(15)	-1662(12)	34(3)
H(1)	1851(14)	8524(13)	191(11)	29(3)
H(4A)	3139(14)	9891(14)	-3474(12)	30(3)

H(2A)	3617(14)	7097(13)	-2307(11)	28(3)
H(5A)	1425(15)	11157(14)	-906(12)	37(3)
H(6A)	3787(14)	9826(14)	-239(13)	38(3)
H(4B)	1409(16)	11043(16)	-3115(13)	47(4)
H(3A)	1262(15)	8471(14)	-3042(13)	36(3)
H(5B)	2879(16)	11620(16)	-1897(13)	46(4)
H(8B)	2593(16)	9382(16)	1837(14)	48(4)
H(11B)	5258(19)	5275(19)	3847(15)	65(4)
H(11A)	6262(17)	6404(15)	3330(13)	45(4)
H(8A)	1566(18)	8239(16)	2297(14)	53(4)

LXVII. Ortep drawing of lithioimine *trans*-**12** (**A_2S_2**, S = Me_2EtN)



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