Autocatalysis in Lithium Diisopropylamide-Mediated Ortholithiations

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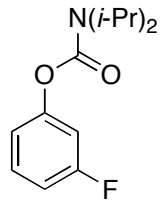
Supporting Information

Part I: Structural Studies

Part II: Rate Studies

Part IV: Computational Studies

Chart 1



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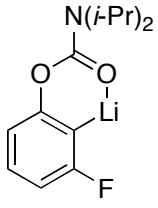

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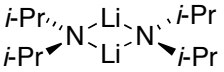

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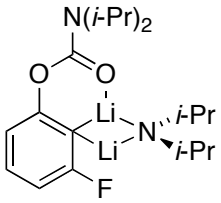

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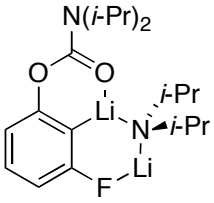


5

≡ mixed aggregates

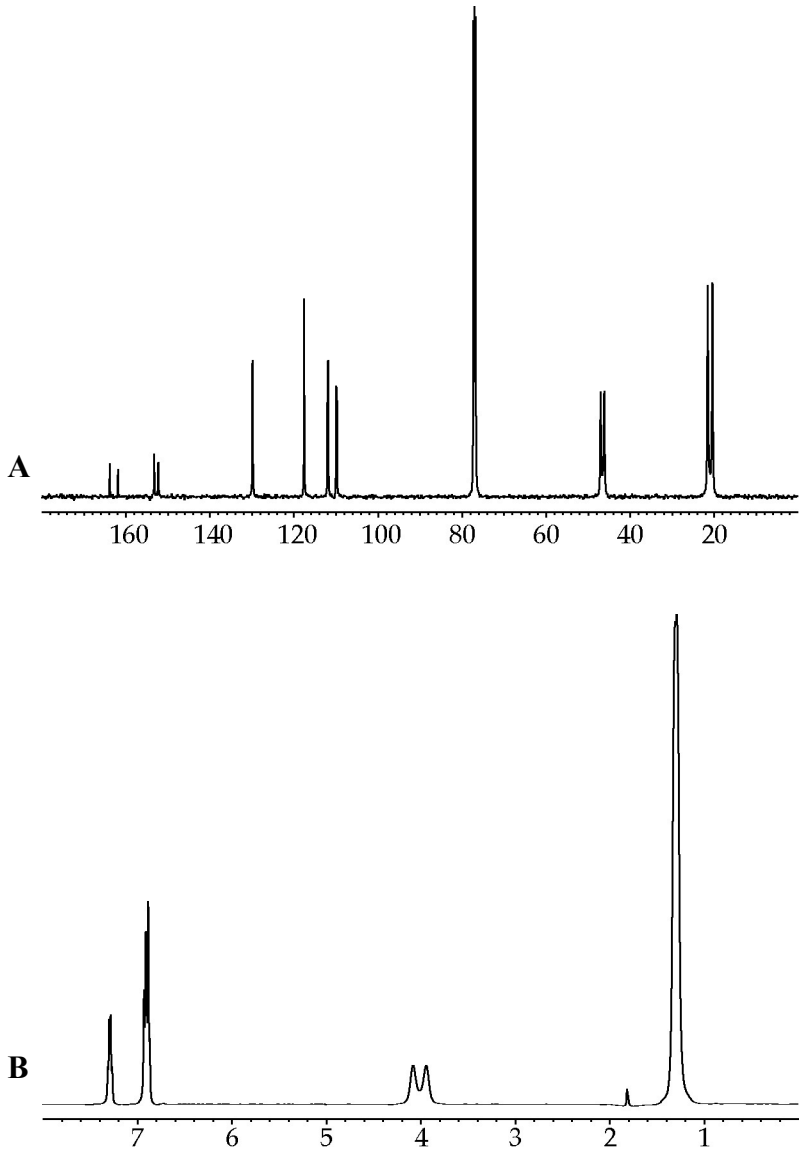


Figure 1. ^{13}C and ^{1}H NMR spectra of **1**. (**A**) ^{13}C NMR spectrum, 125 MHz, $CDCl_3$: δ 163.1 (d, *J* = 246.3 Hz), 153.5, 152.5 (d, *J* = 11.1 Hz), 130.1 (d, *J* = 9.6 Hz), 117.8 (d, *J* = 3.0 Hz), 112.1 (d, *J* = 21.2 Hz), 110.1 (d, *J* = 24.2 Hz), 47.2, 46.3, 21.8, 20.6; (**B**) ^{1}H NMR spectrum, 500 MHz, $CDCl_3$: δ 7.28 (m, 1H), 6.89 (m, 3H), 4.07 (s, 1H), 3.92 (s, 1H), 1.30 (br s, 6H), 1.27 (br s, 6H).

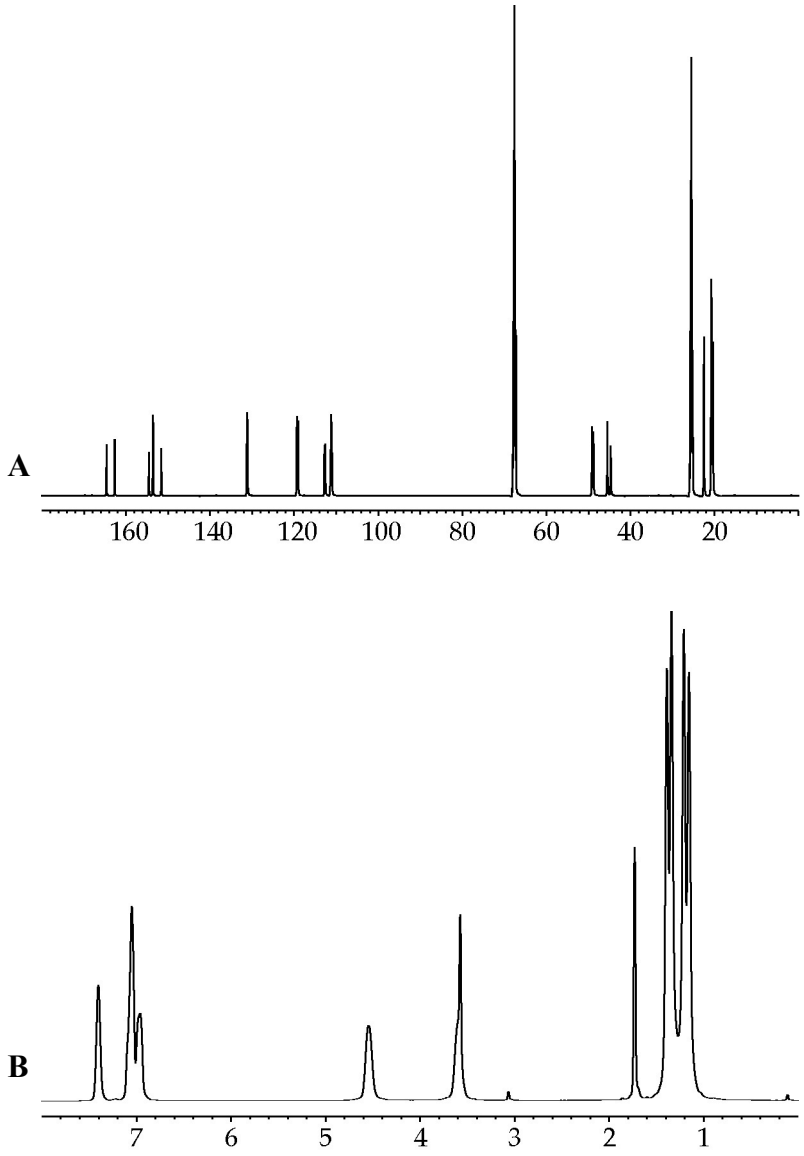


Figure 2. ^{13}C and ^{1}H NMR spectra of **1** at -90 °C. (**A**) ^{13}C NMR spectrum, 125 MHz, THF-d_8: δ 163.6 (d, J = 244.7 Hz), 154.5, 153.5 (d, J = 11.3 Hz), 151.5, 131.2 (d, J = 10.1 Hz), 131.0 (d, J = 10,1 Hz), 119.1 (d, J = 37.9 Hz), 112.6 (d, J = 20.2 Hz), 112.5 (d, J = 19.3 Hz), 111.2 (d, J = 24.9 Hz), 111.0 (d, J = 26.1 Hz), 49.1, 48.7, 45.4, 44.6, 22.4, 20.7, 20.6, 20.3; (**B**) ^{1}H NMR spectrum, 500 MHz, THF-d_8: δ 7.40 (br s, 1H), 7.05 (br s, 2H), 6.97 (br s, 1H), 4.54 (s, 1H), 3.59 (s, 1H), 1.39 (s, 3H), 1.34 (s, 3H), 1.21 (s, 3H), 1.16 (s, 3H), (Reference: 1H (CH_2O, THF, 3.58 ppm); ^{13}C (CH_2O, THF, 67.57 ppm).

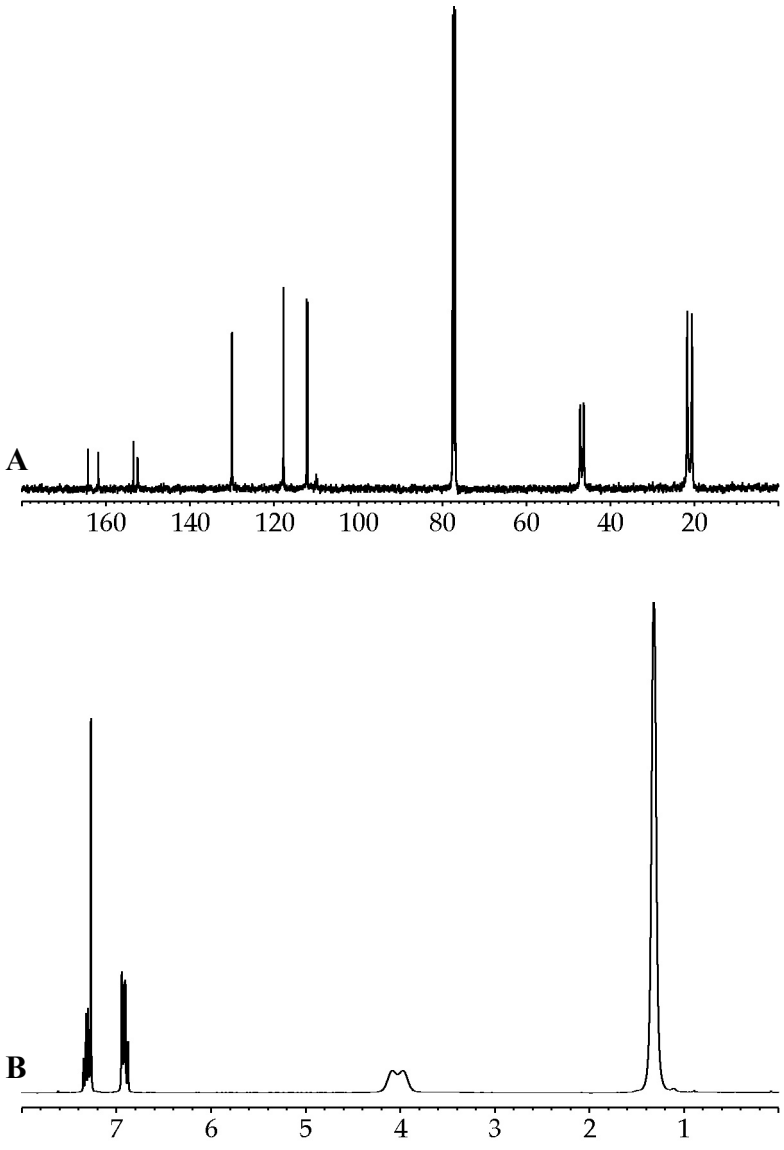


Figure 3. ^{13}C and ^{1}H NMR spectra of **1-*d*$_1$**. (**A**) ^{13}C NMR spectrum, 125 MHz, $CDCl_3$: δ 163.0 (d, *J* = 246.4 Hz), 153.5, 152.4 (d, *J* = 10.9 Hz), 130.0 (d, *J* = 9.4 Hz), 117.8 (d, *J* = 2.4 Hz), 112.1 (d, *J* = 21.0 Hz), 109.9 (t, *J* = 24.3 Hz), 47.2, 46.3, 21.7, 20.6; (**B**) ^{1}H NMR spectrum, 500 MHz, $CDCl_3$: δ 7.30 (m, 1H), 6.91 (m, 2H), 4.09 (s, 1H), 3.95 (s, 1H), 1.31 (br s, 12H).

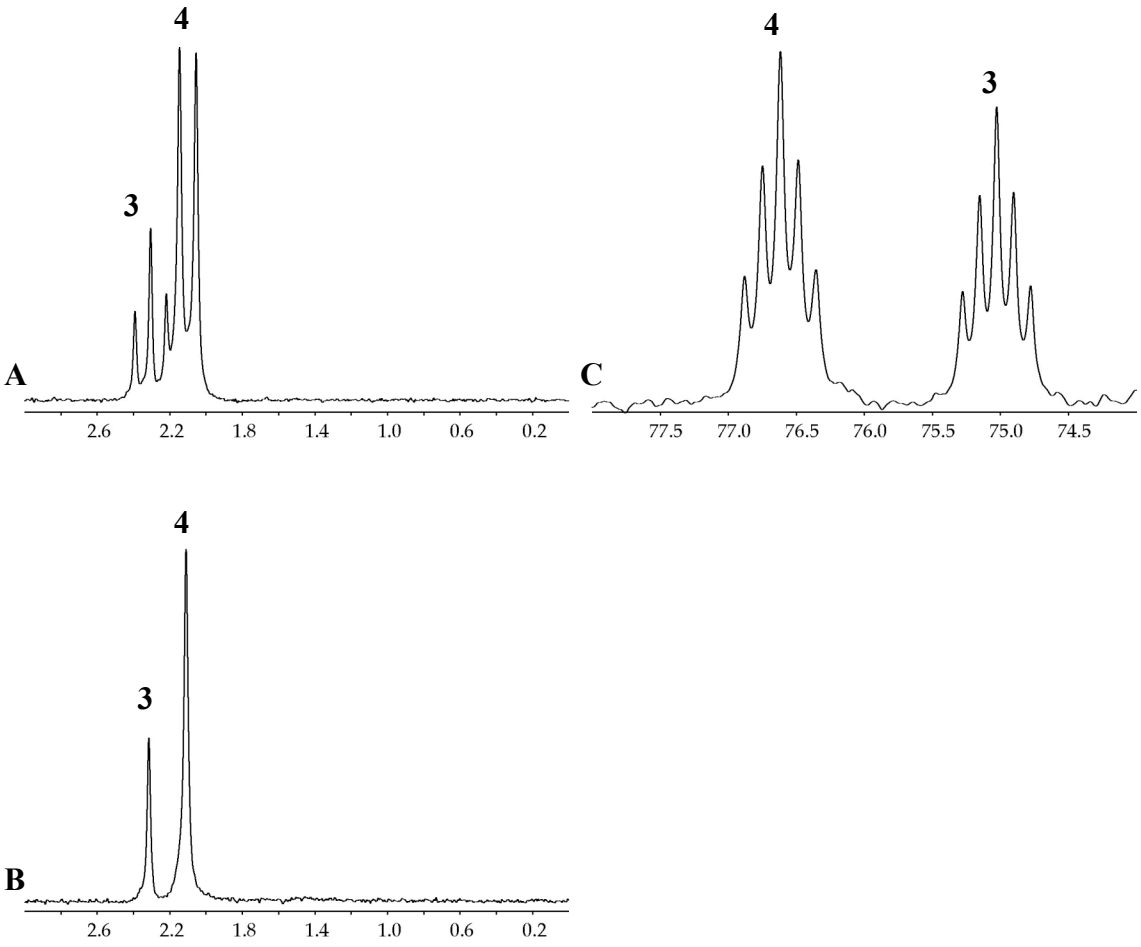


Figure 4. ^{6}Li and ^{15}N NMR spectra of 0.10 M [^{6}Li,^{15}N]LDA with 0.033 M **1** in 0.62 M THF/pentane at -90 °C after aging at -78 °C for 60 min: **(A)** ^{6}Li spectrum; **(B)** ^{6}Li{^{15}N} spectrum; **(C)** ^{15}N spectrum.

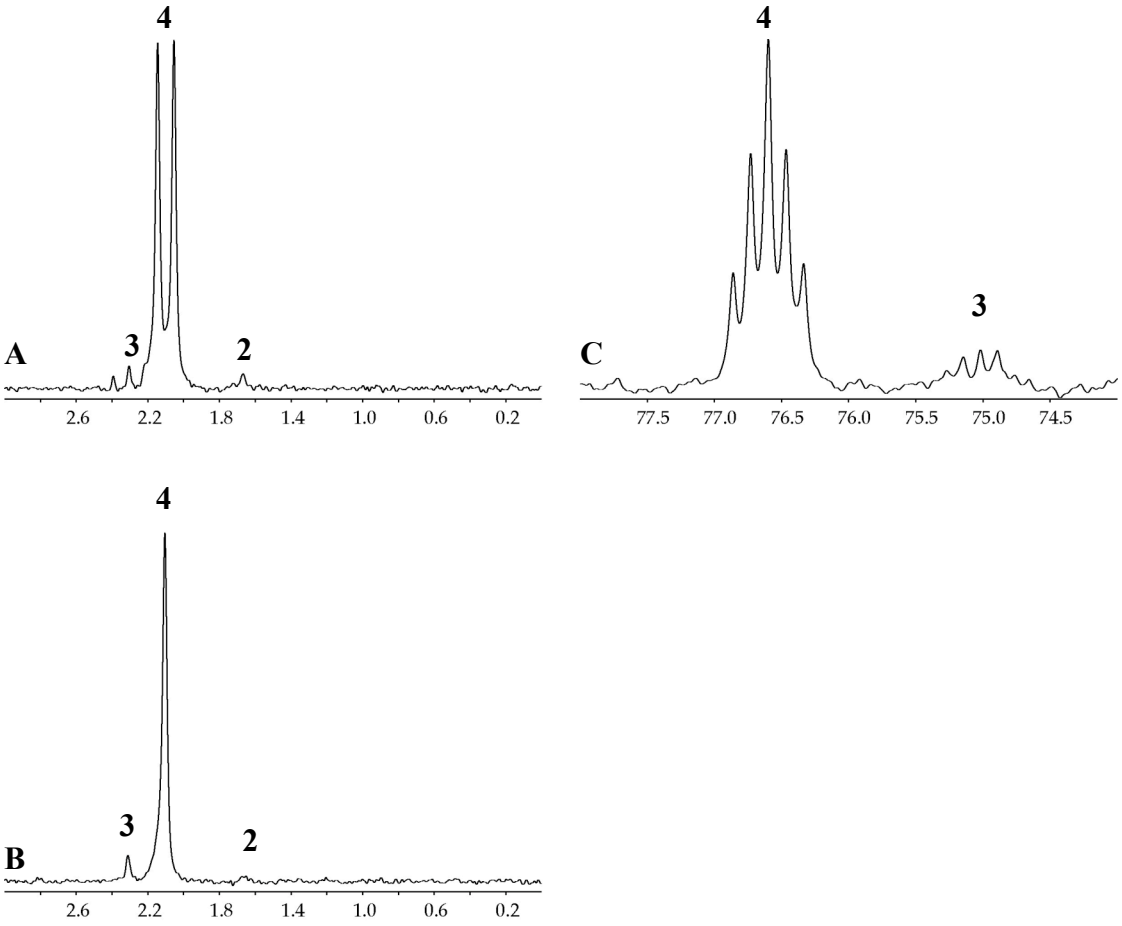


Figure 5. ^{6}Li and ^{15}N NMR spectra of 0.10 M [^{6}Li,^{15}N]LDA with 0.05 M **1** in 0.62 M THF/pentane at -90 ºC after aging at -78 ºC for 60 min: **(A)** ^{6}Li spectrum; **(B)** ^{6}Li{^{15}N} spectrum; **(C)** ^{15}N spectrum.

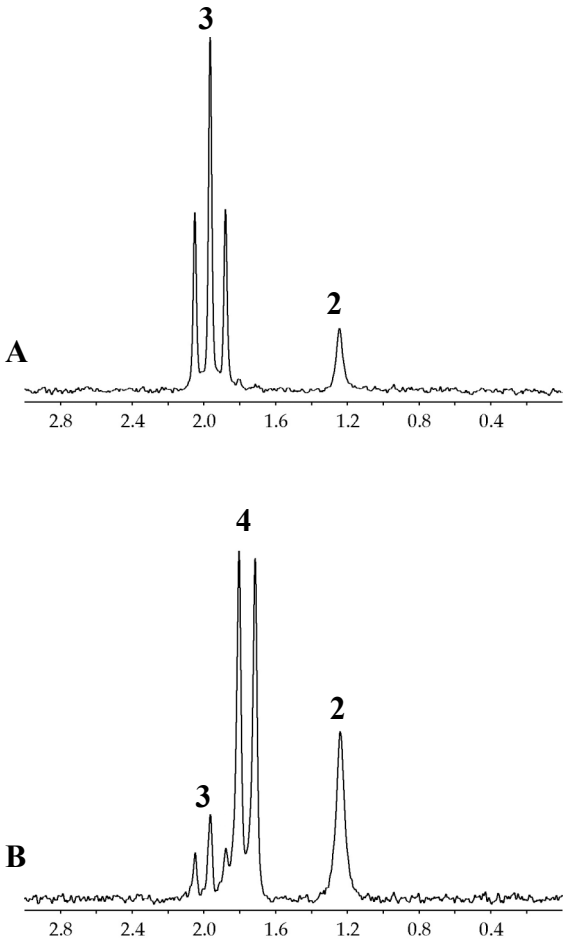


Figure 6. ^{6}Li NMR spectra of 0.10 M [^{6}Li,^{15}N]LDA with 0.05 M **1** in 11.1 M THF/pentane at -90 °C: **(A)** ^{6}Li spectrum after aging at -78 °C for 5 min; **(B)** ^{6}Li spectrum after aging at -78 °C for 30 min.

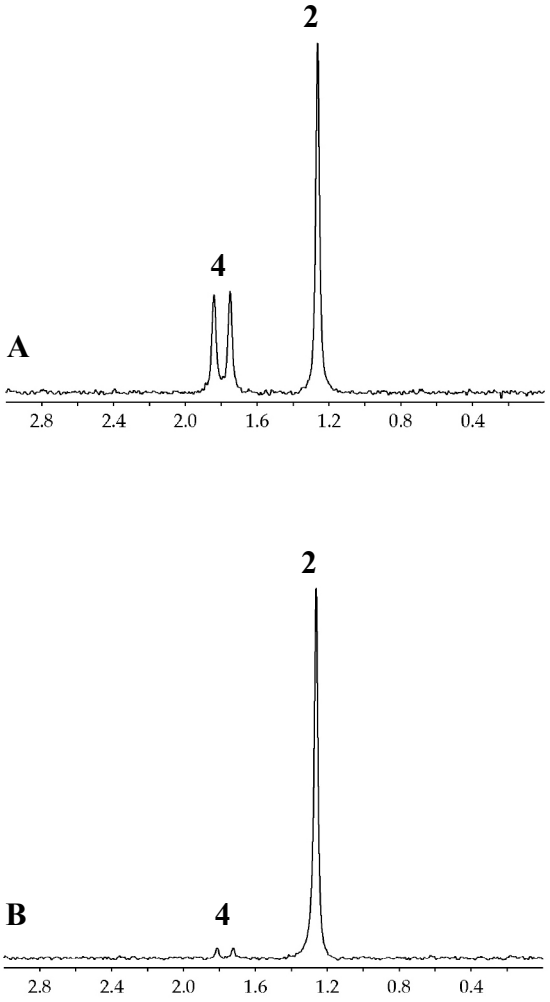


Figure 7. ^{6}Li NMR spectra of 0.10 M [^{6}Li,^{15}N]LDA with 0.10 M **1** in 11.1 M THF/pentane at -90 °C: **(A)** ^{6}Li spectrum after aging at -78 °C for 60 min; **(B)** ^{6}Li spectrum after aging at -40 °C for 60 min.

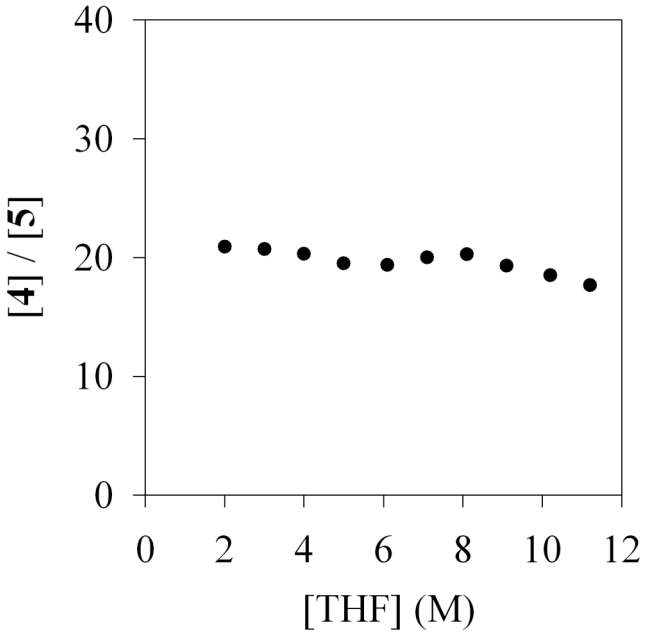


Figure 8. Plot of [**4**]/[**5**] versus [LDA] in 12.2 M THF at -90 °C.

[LDA] (M)	[**4**]/[**5**]
0.010	17.85
0.015	17.86
0.020	17.48
0.025	17.73
0.030	17.07
0.035	17.47
0.040	15.40

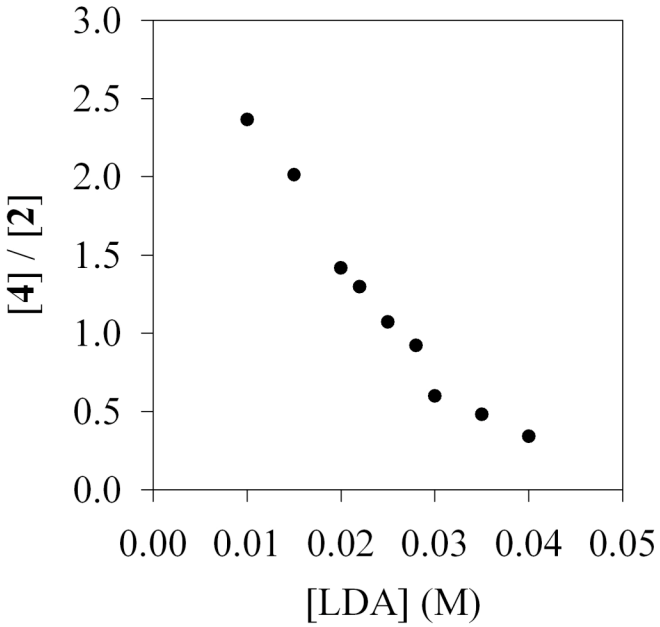


Figure 9. Plot of [**4**]/[**2**] versus [LDA] in 12.2 M THF at -90 ºC.

[LDA] (M)	[**4**]/[**2**]
0.010	2.36
0.015	2.01
0.020	1.41
0.022	1.30
0.025	1.07
0.028	0.92
0.030	0.60
0.035	0.48
0.040	0.34

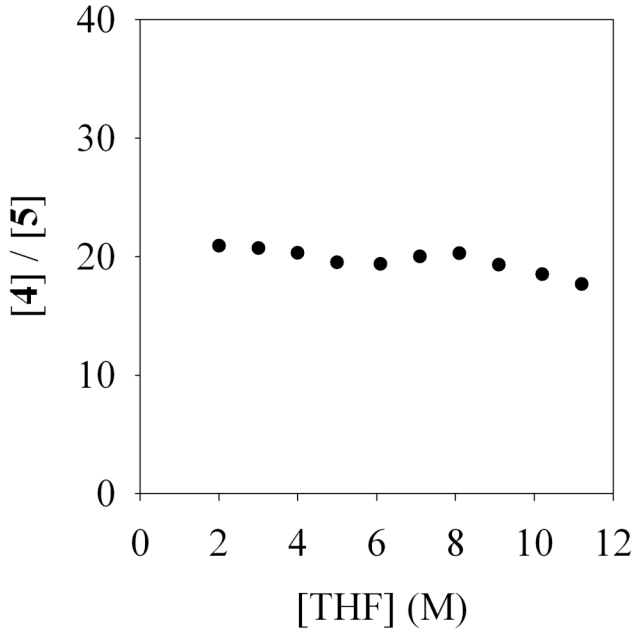


Figure 10. Plot of [**4**]/[**5**] versus [THF] in hexanes and 0.05 M LDA at -90 °C.

[THF] (M)	[**4**]/[**5**]
2.0	20.89
3.0	20.69
4.0	20.29
5.0	19.48
6.1	19.35
7.1	19.99
8.1	20.24
9.1	19.26
10.2	18.49
11.2	17.64

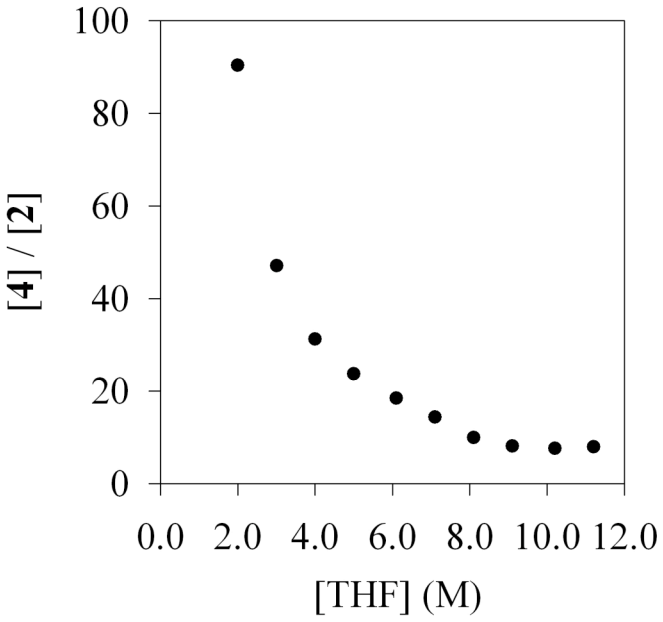


Figure 11. Plot of [**4**]/[**2**] versus [THF] in hexanes and 0.05 M LDA at -90 °C.

[THF] (M)	[**4**]/[**2**]
2.0	90.32
3.0	47.01
4.0	31.22
5.0	23.68
6.1	18.41
7.1	14.39
8.1	9.92
9.1	8.09
10.2	7.58
11.2	7.94

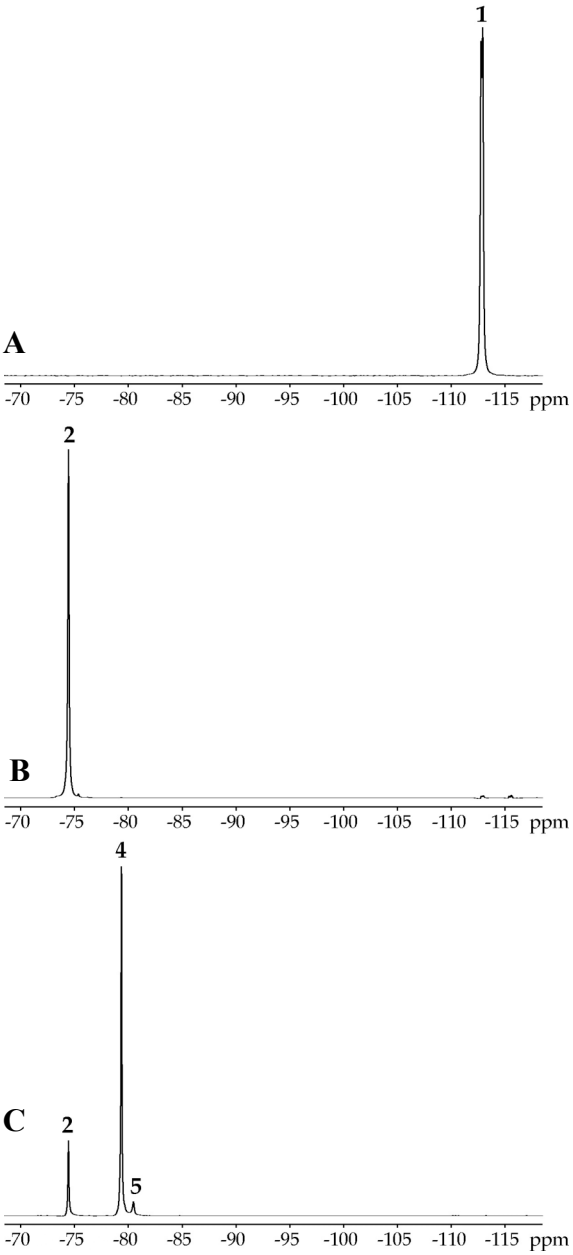


Figure 12. ^{19}F NMR spectra of 0.01 M **1** in 11.1 M THF/pentane at various LDA concentrations at -78 °C: **(A)** 0.010 M **1**, 0.0 M LDA; **(B)** 0.10 M **1**, 0.10 M LDA, after aging at -40 °C for 60 min; **(C)** 0.025 M **1**, 0.10 M LDA, after aging at -78 °C for 60 min.

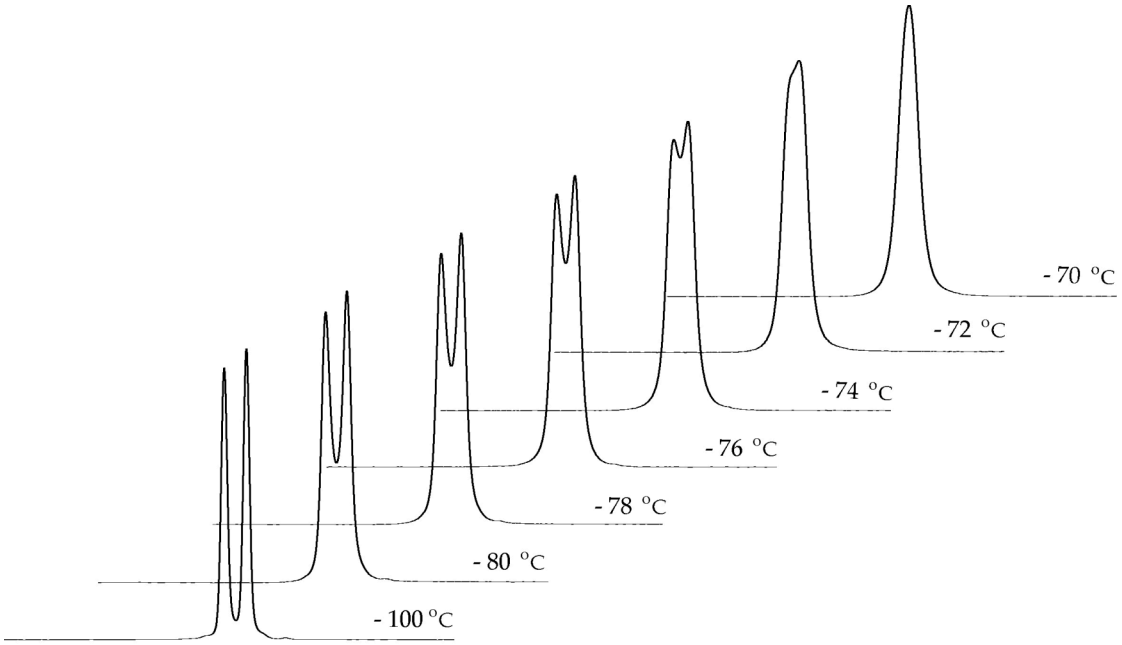


Figure 13. ^{19}F NMR spectra of 0.010 M **1** in 11.1 M THF/pentane at various temperatures using the approximation that $k_{exchange} = 2.22\ (\Delta\nu)$ at the coalescence temperature (T_c = -72 °C) where $\Delta\nu$ = 93.3 Hz (at -100 °C in the slow exchange limit), $\Delta G^{\neq}$ = 9.5 kcal/mol as calculated using the Eyring equation[1]).

Carbamate **1** and structurally related diisopropylamine-derived carbamates and carboxamides[2] display distinct conformational properties that are not observed in less sterically congested analogues. Carbamate **1** affords normal NMR spectra at ambient temperature. On cooling the sample below -70 °C, the single ^{19}F resonance (-113.1 ppm) appears as a pair of resonances in equal proportions. Similarly in the ^{13}C NMR spectrum, two methyne resonances of the diisopropyl moiety are observed at ambient temperatures whereas four are observed at <-90 °C. One can explain these results by a assuming a slow conformer exchange.

[1] (a) Jackman, L. M.; Cotton, F. A. eds. "Dynamic Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, NY, 1975. (b) Gasparro, F. P.; Kolodny, N. H. *J. Chem. Educ.* **1977**, *54*, 258.
[2] For leading references to conformational studies of acylated diisopropylamido framgments, see (a) Stewart, W. E.; Siddall, T. H. III. *Chem. Rev.* **1970**, *70*, 517. (b) Lidén, A.; Roussel, C.; Liljefors, T.; Chano, M.; Carter, R. E.; Metzger, J.; Sandström, J. *J. Am. Chem. Soc.* **1976**, *98*, 2853.

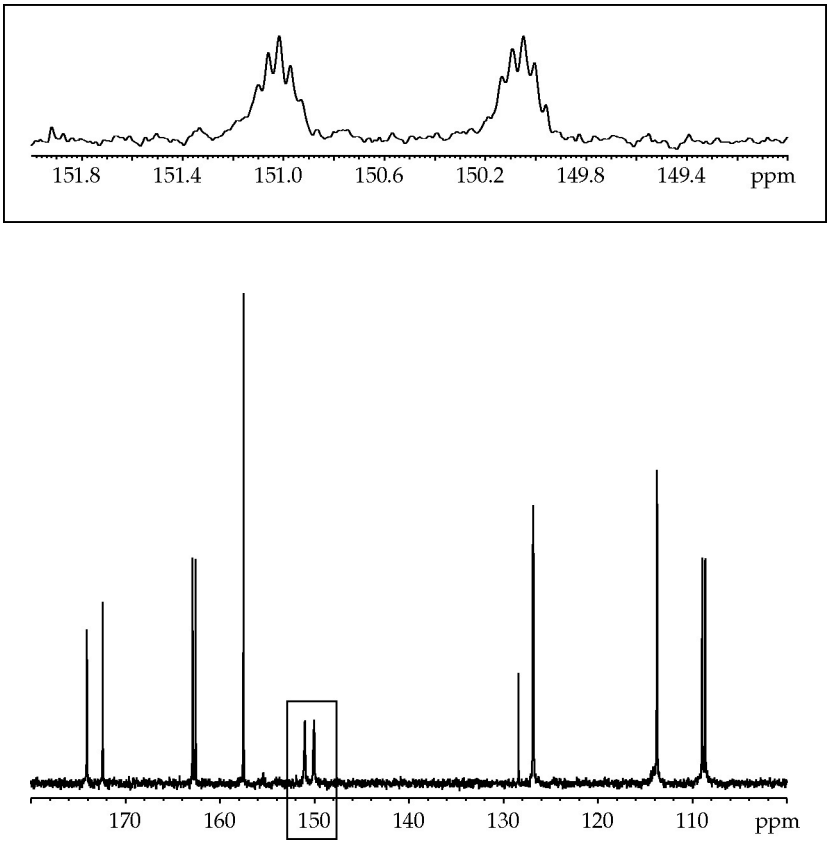


Figure 14. ^{13}C NMR spectrum of 0.40 M [^{6}Li]LDA with 0.33 equiv **1** in 3.1 M THF/pentane at -90 °C (δ ^{13}C = 150.5 ppm, $J_{C\text{-}F}$ = 121.7 Hz, $J_{C\text{-}Li}$ = 5.6 Hz).

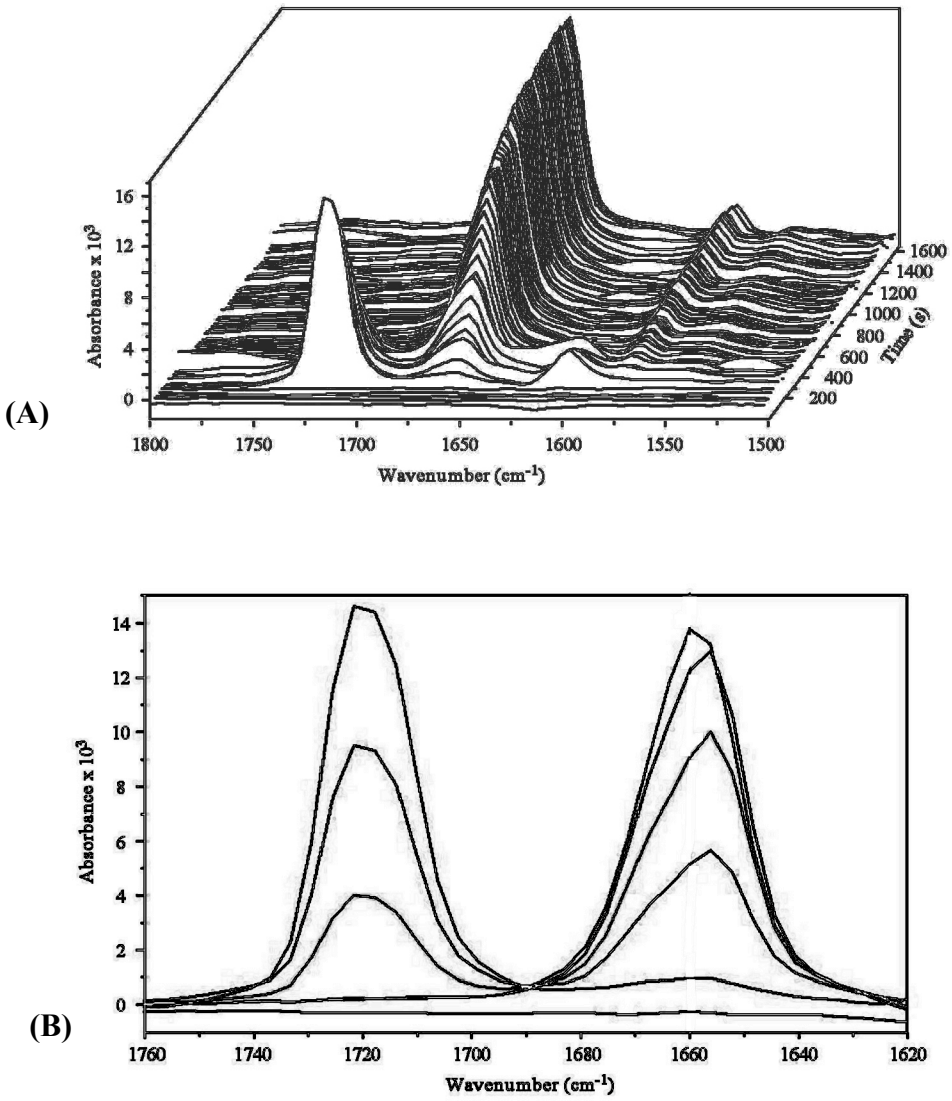


Figure 15. **(A)** Representative IR plot for the ortholithiation of **1** (0.004 M) by 0.10 M LDA in 12.2 M THF at -78 °C (**1**: 1721 cm^{-1}, **2 + 4**: 1660 cm^{-1}); **(B)** Cross-section of the plot in Figure 15A. The peak shift around 1660 cm^{-1} indicates product equilibration between **2** and **4**, as independently determined by ^{19}F NMR spectroscopy.

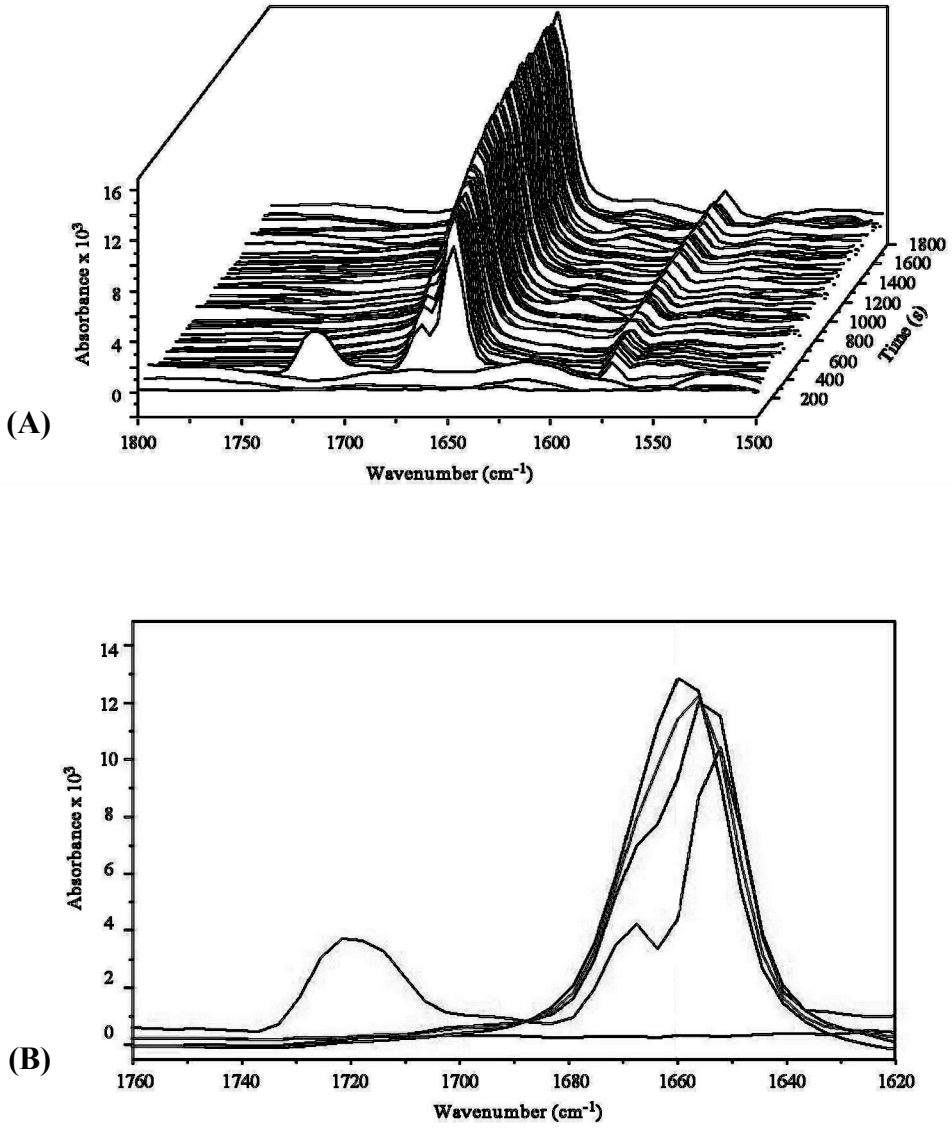


Figure 16. **(A)** Representative IR plot for the second injection of **1** (0.004 M) by 0.10 M LDA in 12.2 M THF/hexanes at -78 °C after zeroing the baseline of the reaction in Figure 16A. Note nearly instantaneous consumption of **1**. (**1**: 1721 cm^{-1}, **2 + 4**: 1660 cm^{-1}); **(B)** Cross-section of the plot in Figure 16A.

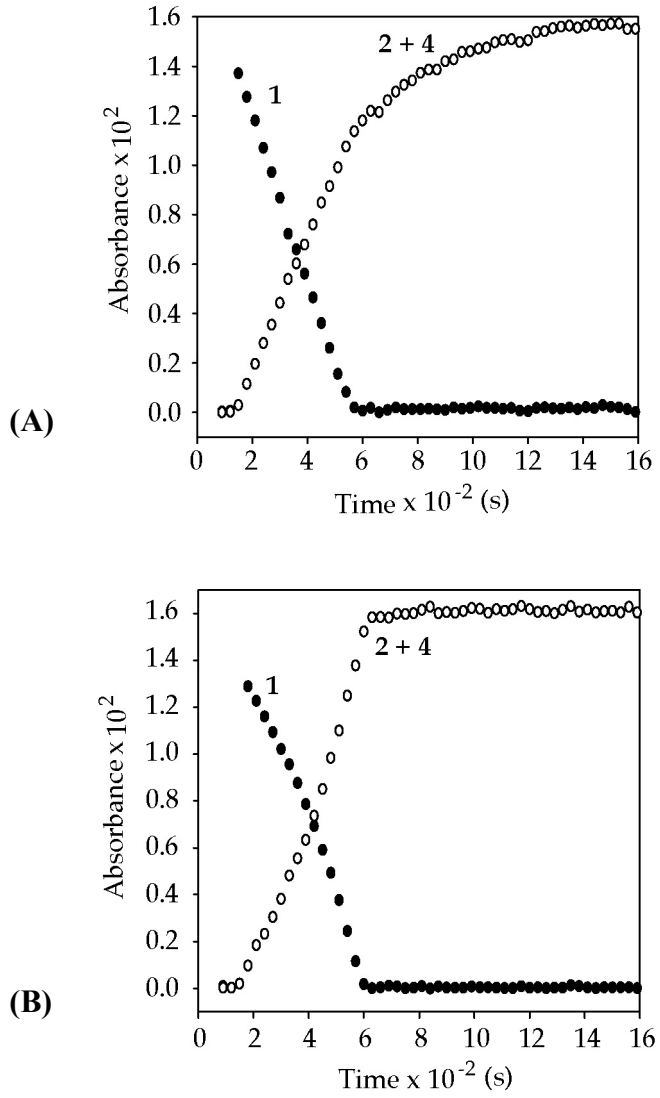


Figure 17. Plot of absorbance versus time for the ortholithiation of **1** (0.004 M) by 0.10 M LDA in THF/hexane at -78 °C: (**A**) 12.2 M THF; (**B**) 1.23 M THF. (**1**: 1721 cm^{-1}, **2 + 4**: 1660 cm^{-1}. Product (**2** + **4**) growth continues after consumption of **1** in Figure 17A and not in 17B.

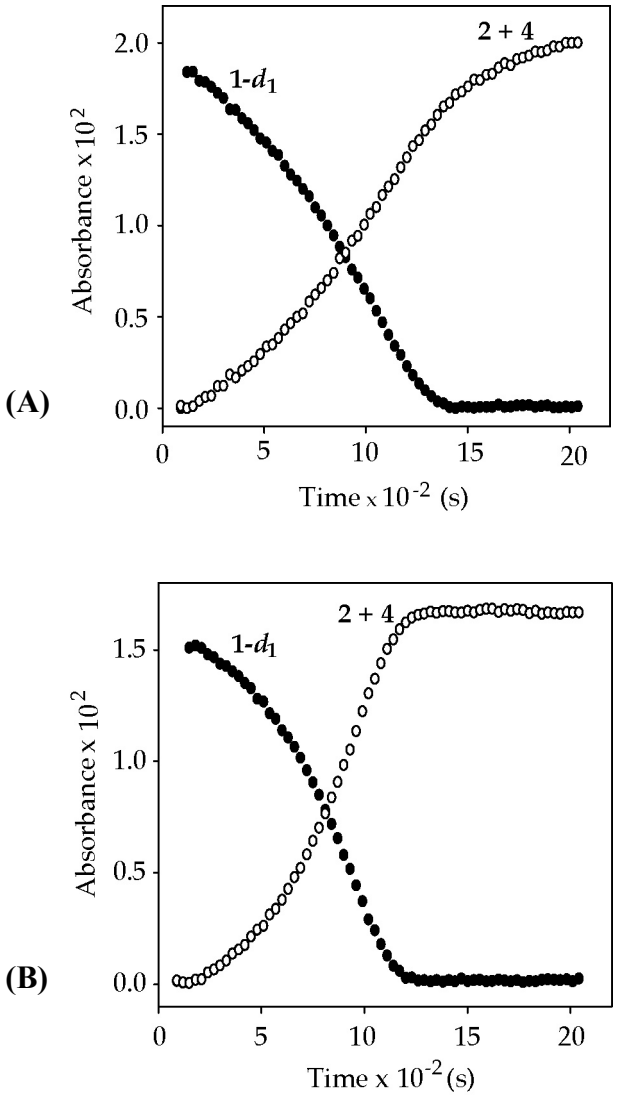


Figure 18. Plot of absorbance versus time for the ortholithiation of **1-d_1** (0.004 M) by 0.10 M LDA in THF/hexane at -78 °C: (**A**) 12.2 M THF (**B**) 1.23 M THF. (**1-d_1**: 1721 cm^{-1}, **2 + 4**: 1660 cm^{-1}).

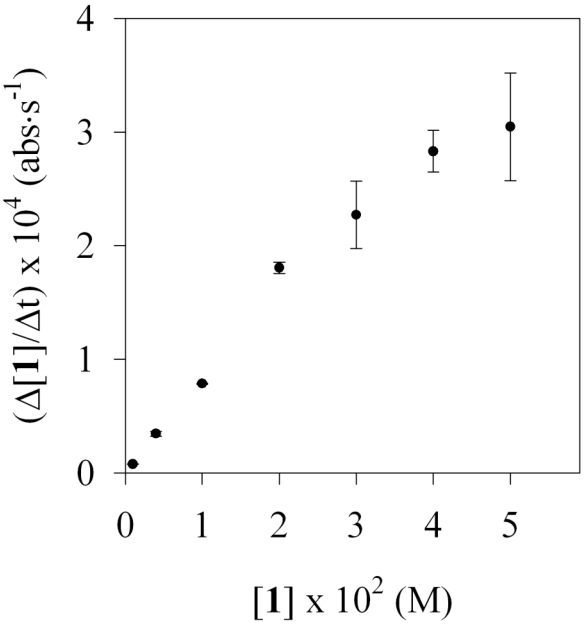


Figure 19. Plot of Δ[**1**]/Δt versus [**1**] for the ortholithiation of **1** by 0.10 M LDA in 12.2 M THF /hexanes at -78 °C.

[**1a**] (M)	(Δ[**1**]/Δt) 1 (abs·s^{-1})	(Δ[**1**]/Δt) 2 (abs·s^{-1})
0.001	0.0000079 ± 1E-7	0.0000075 ± 1E-7
0.004	0.000036 ± 1E-6	0.000033 ± 1E-6
0.010	0.0000789 ± 9E-7	0.000078 ± 1E-6
0.020	0.000184 ± 3E-6	0.000177 ± 2E-6
0.030	0.000248 ± 4E-6	0.000206 ± 2E-6
0.040	0.000270 ± 3E-6	0.000296 ± 6E-6
0.050	0.000338 ± 4E-6	0.000271 ± 3E-6

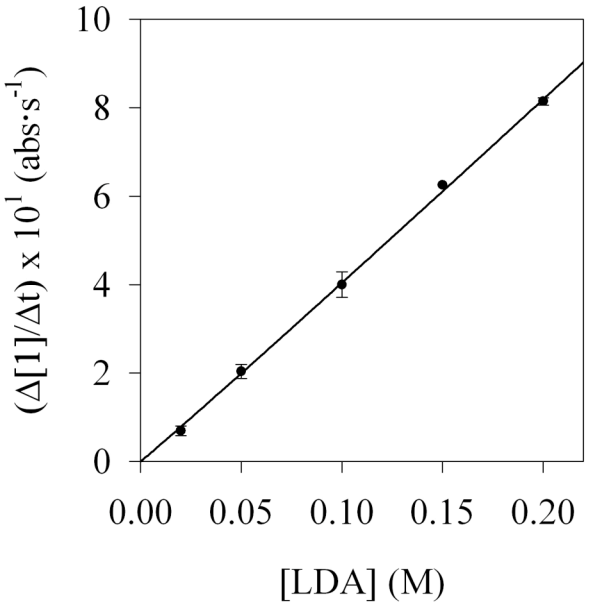


Figure 20. Plot of k_{obsd} versus [LDA] for the ortholithiation of **1** (0.0074 M) in 12.2 M THF at -78 °C. The curve depicts an unweighted least-squares fit to $k_{obsd} = k[\text{LDA}]^n$. ($k = (4.2 \pm 0.2) \times 10^1$, $n = (1.02 \pm 0.03)$.

[LDA] (M)	k_{obsd} 1 (abs·s^{-1})	k_{obsd} 2 (abs·s^{-1})
0.02	0.6160 E-5± 5E-8	0.7714E-5 ± 2E-8
0.05	1.921E-5 ± 1E-7	2.148E-5 ± 7E-8
0.10	6.796E-5 ± 5E-7	4.198E-5 ± 3E-7
0.15	6.252E-5 ± 6E-7	--
0.20	8.082E-5 ± 3E-7	8.205E-5 ± 5E-7

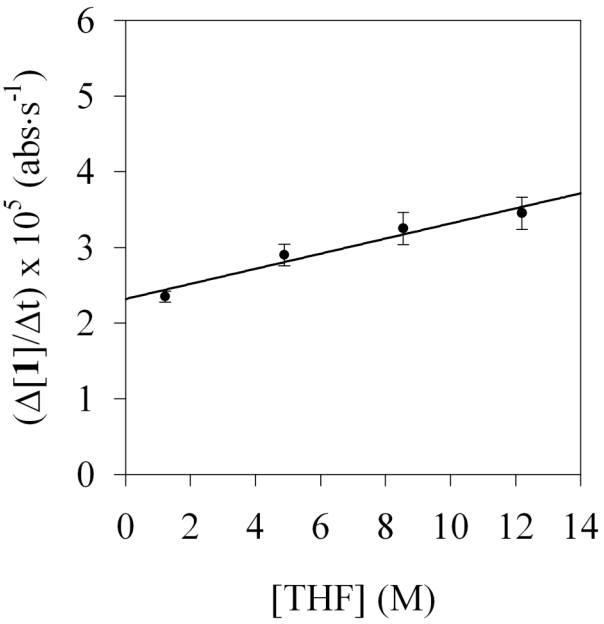


Figure 21. Plot of $\Delta[\mathbf{1}]/\Delta t$ versus [THF] in hexanes for the ortholithiation of **1** (0.004 M) by 0.10 M LDA at -78 °C. The curve depicts an unweighted least-squares fit to $\Delta[\mathbf{1}]/\Delta t = k[\text{THF}] + k'$ ($k = (1.0 \pm 0.2) \times 10^{-6}$, $k' = (2.3 \pm 0.1) \times 10^{-5}$).

[THF] (M)	$(\Delta[\mathbf{1}]/\Delta t)$ 1 (abs·s^{-1})	$(\Delta[\mathbf{1}]/\Delta t)$ 2 (abs·s^{-1})
1.22	0.000024 ± 1E-6	0.000023 ± 1E-6
4.88	0.000028 ± 2E-6	0.000030 ± 2E-6
8.54	0.000031 ± 1E-6	0.000034 ± 2E-6
12.2	0.000036 ± 1E-6	0.000033 ± 1E-6

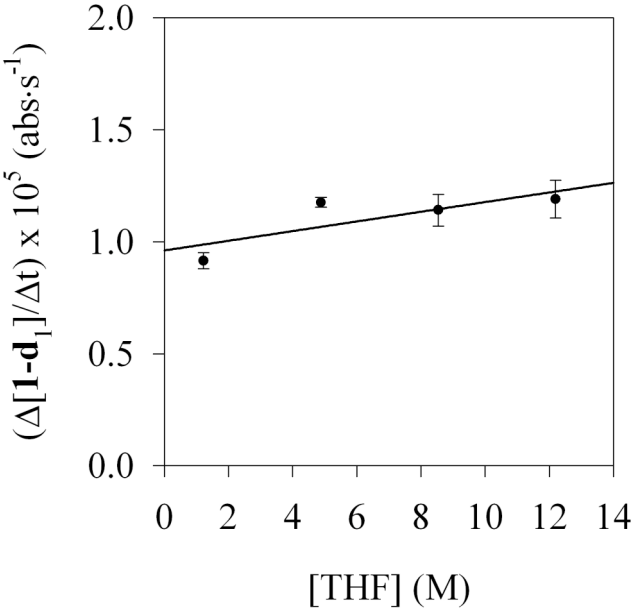


Figure 22. Plot of $\Delta[\mathbf{1}\text{-}\boldsymbol{d}_1]/\Delta t$ versus [THF] in hexanes for the ortholithiation of **1-*d*$_1$** (0.004 M) by 0.10 M LDA at -78 °C. The curve depicts an unweighted least-squares fit to $\Delta[\mathbf{1}\text{-}\boldsymbol{d}_1]/\Delta t = k[\text{THF}] + k'$ ($k = (2.2 \pm 0.8) \times 10^{-7}$, $k' = (9.6 \pm 0.6) \times 10^{-6}$).

[THF] (M)	$(\Delta[\mathbf{1}\text{-}\boldsymbol{d}_1]/\Delta t)$ 1 (abs·s^{-1})	$(\Delta[\mathbf{1}\text{-}\boldsymbol{d}_1]/\Delta t)$ 2 (abs·s^{-1})
1.22	0.0000089 ± 5E-7	0.0000094 ± 4E-7
4.88	0.0000119 ± 2E-7	0.0000116 ± 1E-7
8.54	0.0000109 ± 3E-7	0.0000119 ± 1E-7
12.2	0.0000113 ± 1E-7	0.0000125 ± 2E-7

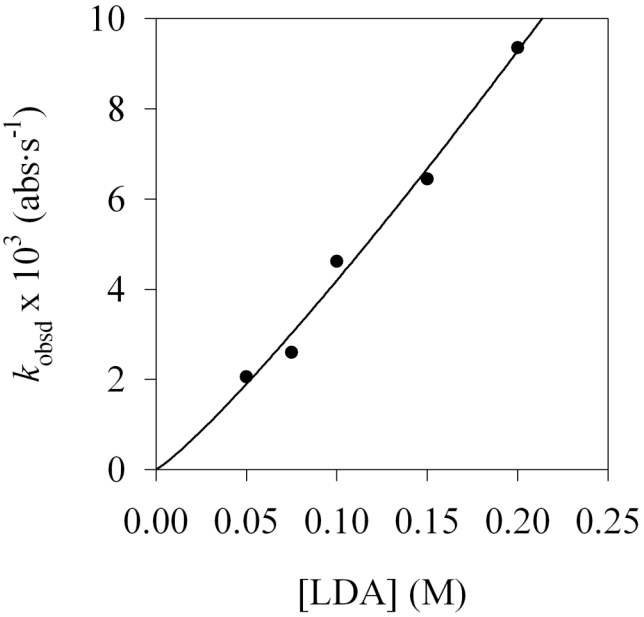


Figure 23. Plot of k_{obsd} versus [LDA] for the condensation of ArLi (**2**) with LDA (**3**) in 12.2 M THF at -78 °C. The curve depicts an unweighted least-squares fit to $k_{obsd} = k[\text{LDA}]^n$ (k = (60 ± 10), n = (1.1 ± 0.1). Individual rates were obtained by fitting the exponential decay to the expression: $y = y_0 + ae^{-kt}$.

[LDA] (M)	k_{obsd} (abs·s^{-1})
0.05	0.002055 ± 5E-5
0.075	0.002598 ± 6E-5
0.10	0.004614 ± 9E-5
0.15	0.006440 ± 1E-4
0.20	0.009347 ± 3E-4

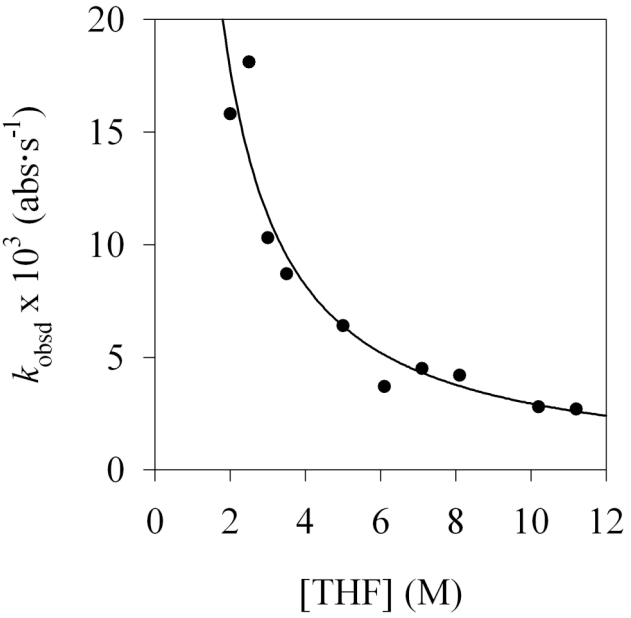


Figure 24. Plot of k_{obsd} versus [THF] for the condensation of ArLi (**2**) with LDA (**3**) (0.10 M) at -78 °C. The curve depicts an unweighted least-squares fit to $k_{obsd} = k[\text{THF}]^n$ ($k = (39 \pm 7)$, $n = (-1.1 \pm 0.2)$. Individual rates were obtained by fitting the exponential decay to the expression: $y = y_0 + ae^{-kt}$.

[THF] (M)	k_{obsd} (abs·s^{-1})
2.0	0.01584 ± 3.34E-3
2.5	0.01812 ± 2.85E-3
3.0	0.01031 ± 8.2E-4
3.5	0.008737 ± 5.6E-4
5.0	0.006421 ± 2.3E-4
6.1	0.003681 ± 2.8E-4
7.1	0.004487 ± 1.1E-4
8.1	0.004163 ± 7E-5
10.2	0.002809 ± 7E-5
11.2	0.002683 ± 1.4E-4

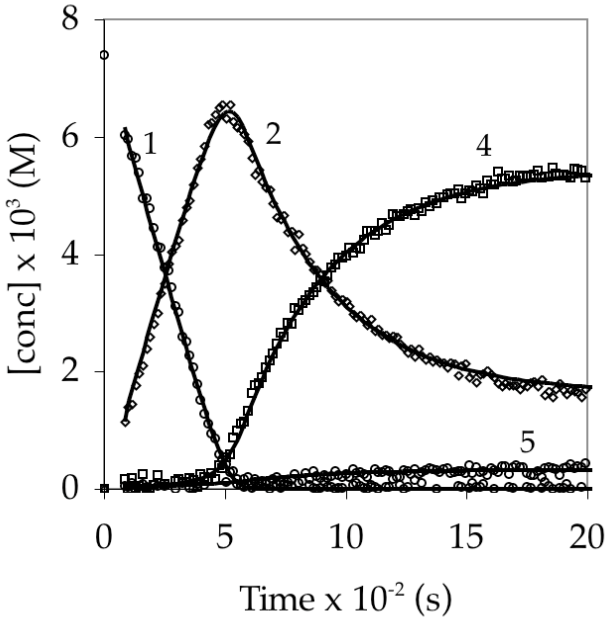


Figure 25. Parametric fit to the ^{19}F NMR spectroscopy derived concentration versus time profile of 0.10 M LDA, 0.0074 M **1**, 12.2 M THF at -78 °C.

		k_1	k_2	k_{-2}	k_3	k_4	k_{-4}
$k_1 = 0.020495 \pm 0.000728$	k_1	1.00	-0.76	-0.74	0.11	-0.87	-0.63
$k_2 = 0.09695 \pm 0.0275$	k_2	-0.76	1.00	0.99	-0.41	0.58	0.41
$k_{-2} = 1.4131 \pm 0.456$	k_{-2}	-0.74	0.99	1.00	-0.37	0.55	0.41
$k_3 = 828.12 \pm 86.4$	k_3	0.11	-0.41	-0.37	1.00	-0.20	-0.15
$k_4 = 0.0461 \pm 0.000664$	k_4	-0.87	0.58	0.55	-0.20	1.00	0.82
$k_{-4} = 0.0027294 \pm 9.36e\text{-}005$	k_{-4}	-0.63	0.41	0.41	-0.15	0.82	1.00

Shown are best estimates of rate constants with 95% confidence intervals and a covariance matrix describing the magnitude of correlation between the parameters. The parameters exhibit low correlations except for the rate constants describing mixed aggregate equilibration (k_2, k_{-2}). The values of k_2 and k_{-2} are lower bounds and can be higher provided that their ratio remains constant.

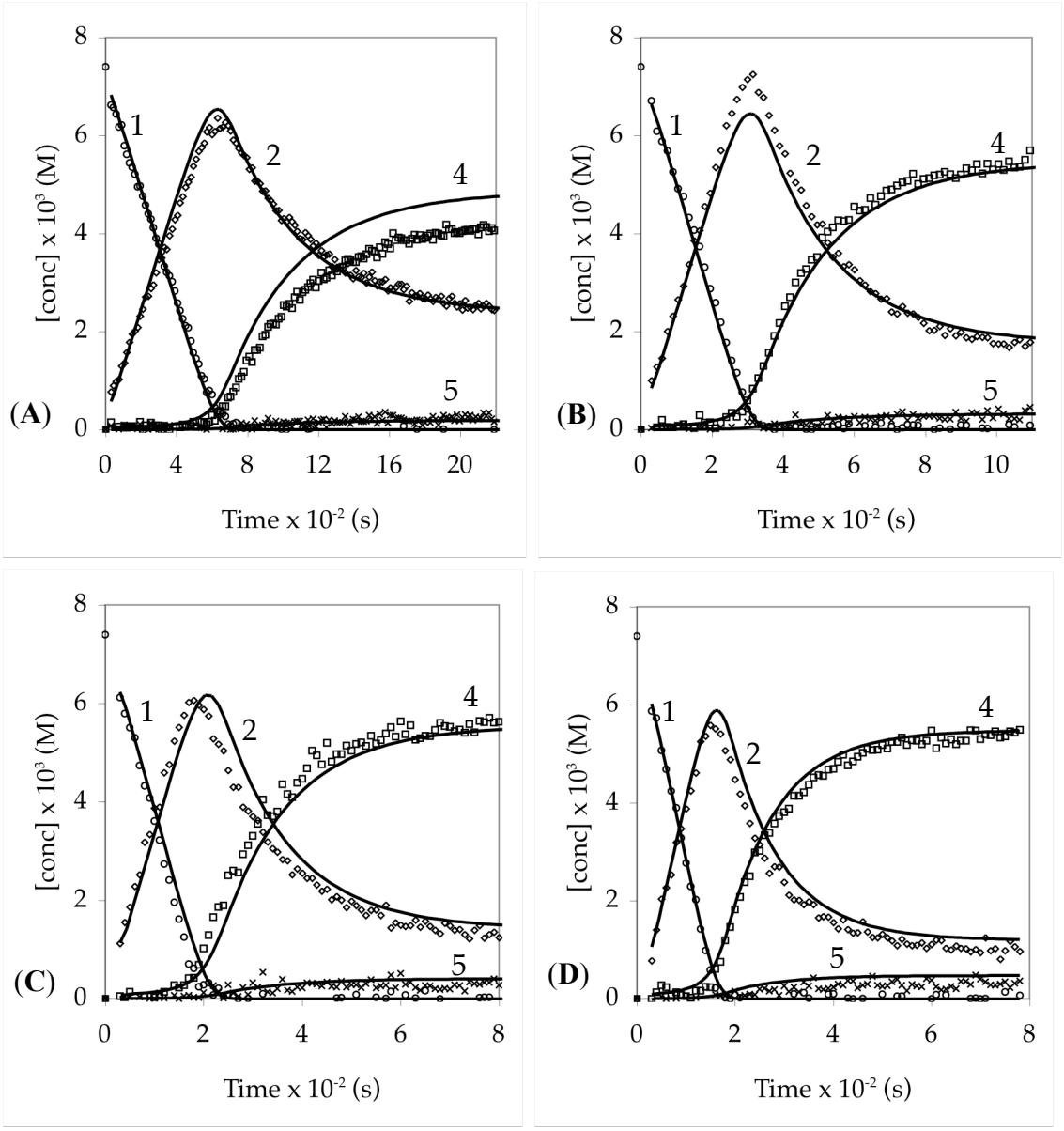


Figure 26. Global parametric fit to the ^{19}F NMR spectroscopy derived concentration versus time profile of 0.0074 M **1** in 12.2 M THF at -78 °C with **(A)** 0.05 M LDA, **(B)** 0.10 M LDA, **(C)** 0.15 M LDA and **(D)** 0.20 M LDA. The four traces are fit simultaneously with a global fitting routine.

$k_1 = 0.021785 \pm 0.000869$
$k_2 = 0.47672 \pm 0.0898$
$k_{-2} = 7.7405 \pm 1.5$
$k_3 = 584.99 \pm 69.9$
$k_4 = 0.056128 \pm 0.00101$
$k_{-4} = 0.0037294 \pm 0.000165$

	k_1	k_2	k_{-2}	k_3	k_4	k_{-4}
k_1	1.00	0.03	0.07	-0.21	-0.81	-0.55
k_2	0.03	1.00	0.92	-0.44	0.03	-0.08
k_{-2}	0.07	0.92	1.00	-0.25	0.00	-0.02
k_3	-0.21	-0.44	-0.25	1.00	0.09	0.21
k_4	-0.81	0.03	0.00	0.09	1.00	0.78
k_{-4}	-0.55	-0.08	-0.02	0.21	0.78	1.00

Shown are best estimates of rate constants with 95% confidence intervals and a covariance matrix describing the magnitude of correlation between the parameters. All parameters exhibit low correlations except for the rate constants describing mixed aggregate equilibration (k_2, k_{-2}). The global fit does not yield an improvement in the magnitude of the correlations as compared to individual fits. However, the global fit to a series of LDA concentrations does support the model and indicates that it correctly predicts the LDA dependence of the proposed mechanism.

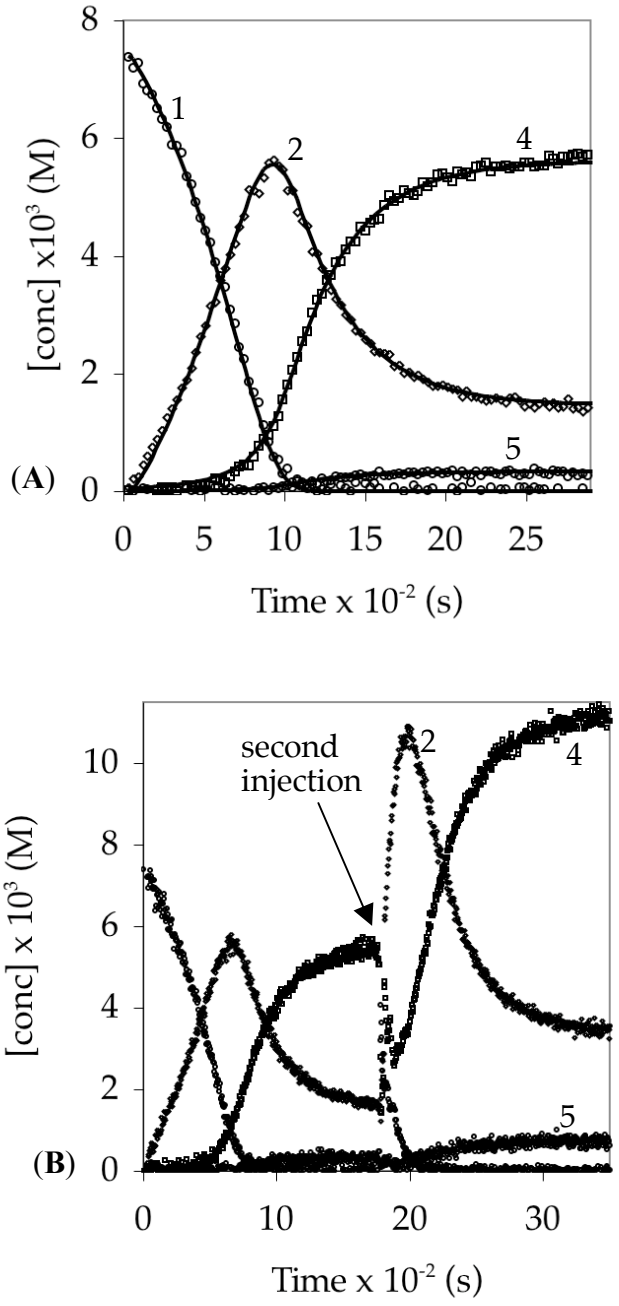


Figure 27. Parametric fit to the ^{19}F NMR spectroscopy derived concentration versus time profile of 0.10 M LDA, 0.0074 M **1**-d_1, 12.2 M THF at -78 °C. (**A**) first injection; (**B**) second injection.

		k_1	k_2	k_{-2}	k_3	k_4	k_{-4}
$k_1 = 0.0066199 \pm 0.000119$	k_1	1.00	-0.51	-0.52	0.03	-0.42	-0.04
$k_2 = 0.34666 \pm 0.0503$	k_2	-0.51	1.00	0.95	-0.60	-0.26	-0.57
$k_{-2} = 6.0123 \pm 0.914$	k_{-2}	-0.52	0.95	1.00	-0.40	-0.30	-0.54
$k_3 = 152.01 \pm 9.48$	k_3	0.03	-0.60	-0.40	1.00	0.01	0.34
$k_4 = 0.049395 \pm 0.000435$	k_4	-0.42	-0.26	-0.30	0.01	1.00	0.72
$k_{-4} = 0.002603 \pm 6.82e\text{-}005$	k_{-4}	-0.04	-0.57	-0.54	0.34	0.72	1.00

Shown are best estimates of rate constants with 95% confidence intervals and a covariance matrix describing the magnitude of correlation between the parameters. All parameters exhibit low correlations except for the rate constants describing mixed aggregate equilibration (k_2, k_{-2}). The kinetic isotope effect is calculated as KIE = k_{1h}/k_{1d}= 3.0. The value matches the kinetic isotope effect measured by in situ IR by an initial rates method.

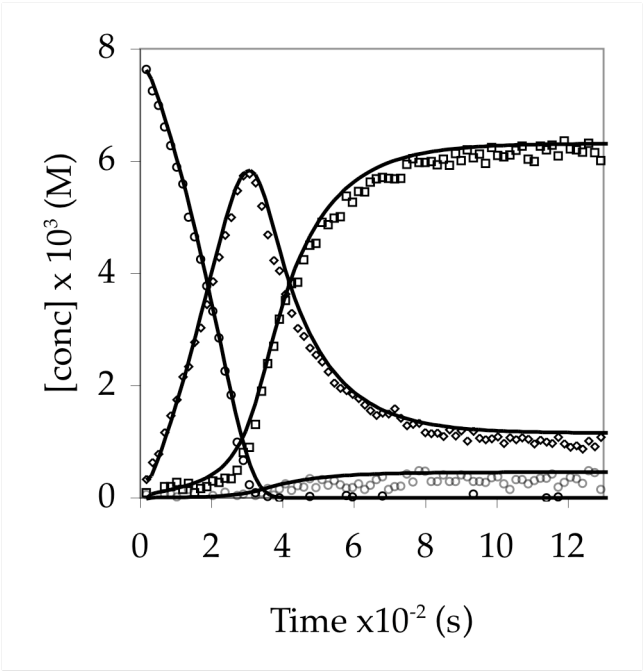


Figure 28. Parametric fit to the ^{19}F NMR spectroscopy derived concentration versus time profile of 0.10 M LDA, 0.0074 M **1**, 7.4 M THF/pentane at -78 °C.

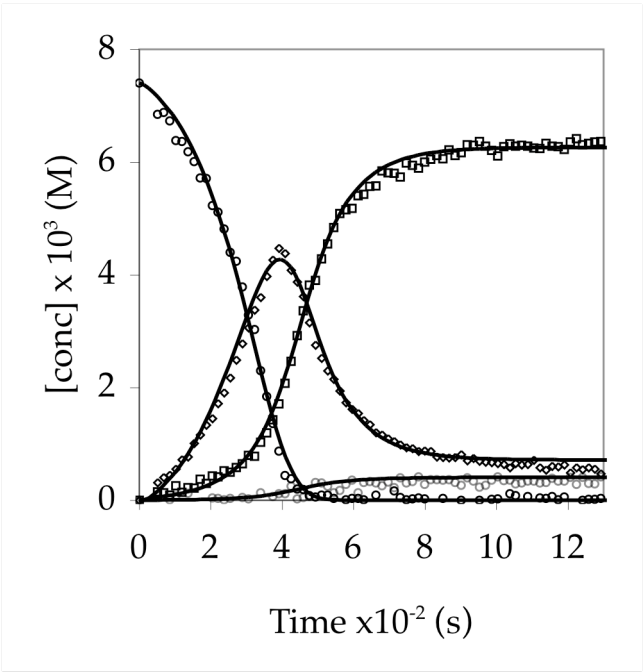


Figure 29. Parametric fit to the ^{19}F NMR spectroscopy derived concentration versus time profile of 0.10 M LDA, 0.0074 M **1**, 4.9 M THF/pentane at -78 °C.

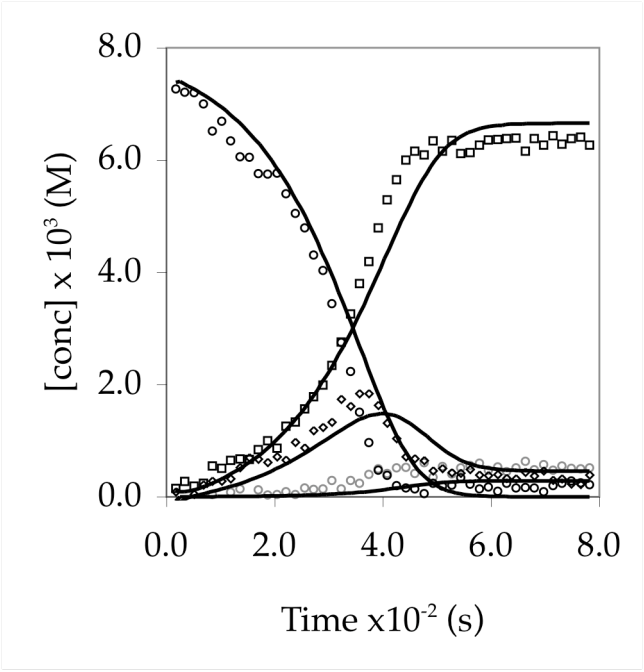


Figure 30. Parametric fit to the ^{19}F NMR spectroscopy derived concentration versus time profile of 0.10 M LDA, 0.0074 M **1**, 2.5 M THF/pentane at -78 °C.

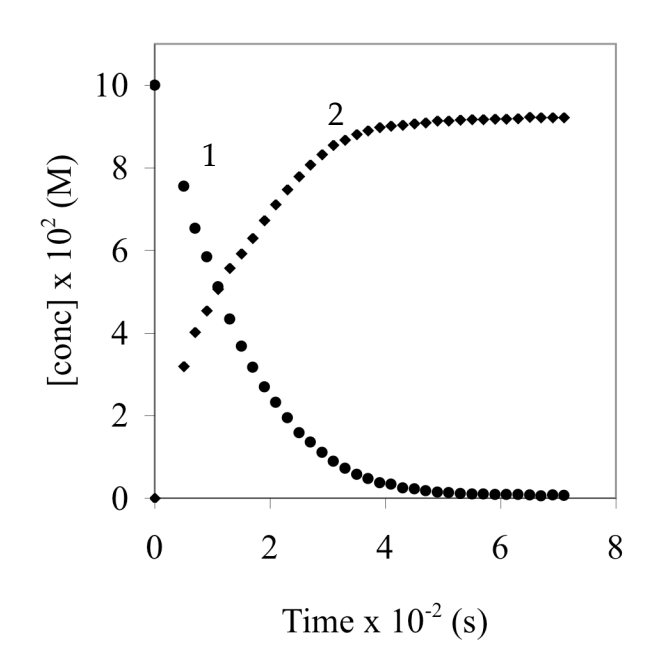


Figure 31. Plot of concentration versus time by ^{19}F NMR spectroscopy of 0.10 M **1**, 0.10 M LDA, 12.2 M THF at -78 °C.

Under stoichiometric conditions, **1** is converted quantitatively to aryllithium monomer **2.** No mixed aggregates are observed because they are rapidly consumed by **1**. Once the starting material has reacted there is no excess LDA and **2** cannot form mixed aggregates **4** and **5**. The decay in **1** fits a first order exponential function and does not fit a second order function.

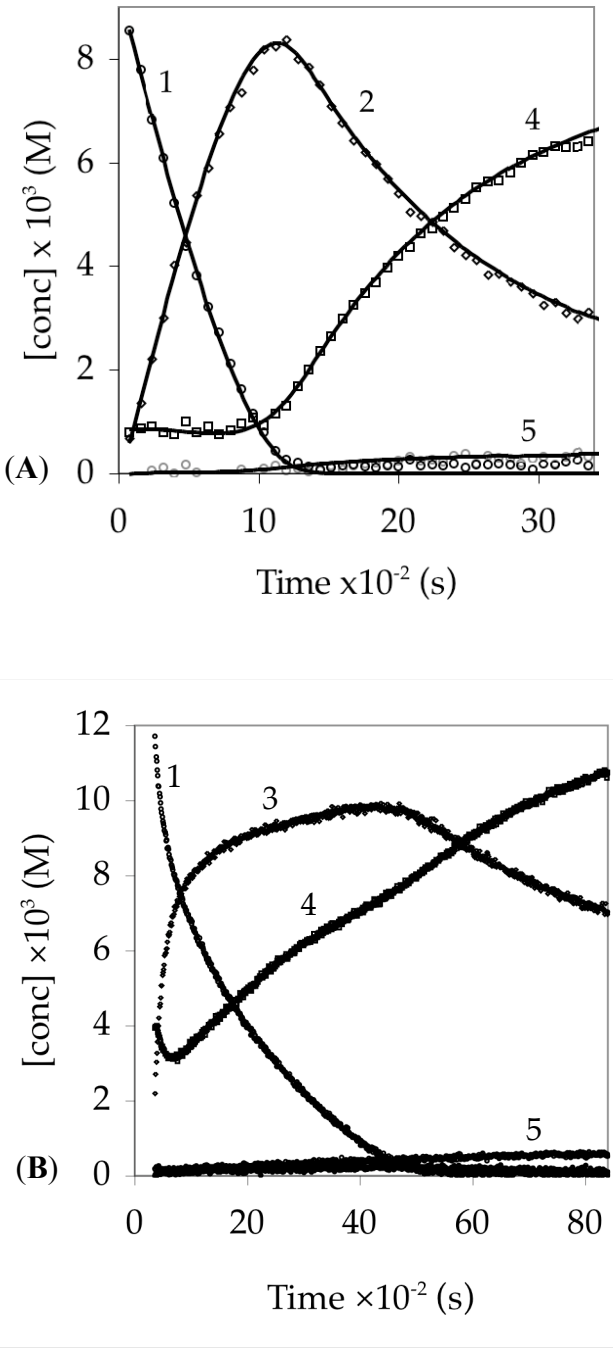


Figure 32. Parametric fit to the ^{19}F NMR spectroscopy derived concentration versus time profile of 0.40 M LDA, 0.010 M carbamate in 12.2 M THF at -100 °C. (**A**) First injection; (**B**) Second injection of 0.010 M carbamate.

		k_1	k_2	k_{-2}	k_3	k_4	k_{-4}
$k_1 = 0.0032963 \pm 6.09e\text{-}005$	k_1	1.00	-0.64	-0.33	0.17	-0.81	-0.59
$k_2 = 0.0080387 \pm 0.000479$	k_2	-0.64	1.00	0.79	-0.57	0.48	0.38
$k_{-2} = 0.13174 \pm 0.0129$	k_{-2}	-0.33	0.79	1.00	-0.41	0.22	0.22
$k_3 = 159.4 \pm 12.4$	k_3	0.17	-0.57	-0.41	1.00	-0.05	-0.08
$k_4 = 0.0033048 \pm 5.55e\text{-}005$	k_4	-0.81	0.48	0.22	-0.05	1.00	0.90
$k_{-4} = 0.00032168 \pm 3.11e\text{-}005$	k_{-4}	-0.59	0.38	0.22	-0.08	0.90	1.00

Shown are best estimates of rate constants with 95% confidence intervals and a covariance matrix describing the magnitude of correlation between the parameters. The correlation between k_2 and k_{-2} has decreased and now allows one to determine their values individually. This permits one to distinguish the reactivity of mixed dimers **4** and **5** (vide infra). The distinct reactivity at -100 °C also allows to exclude the possibility of forming aryllithium monomer **2** in the initiation step.

Solvent effects on the ortholithiation of carbamate **1**

Interesting solvent effects were observed and are summarized in the following figures (Figures 33 – 42). Systems in 2-methyltetrahydrofuran, tetrahydropyran and oxetane behaved similarly to the reaction in THF. These concentration versus time profiles were fit to the established model in THF. Structural assignments were made based on a ^{19}F NMR chemical shift analogy to the parent system in THF. The assignments are therefore tentative.

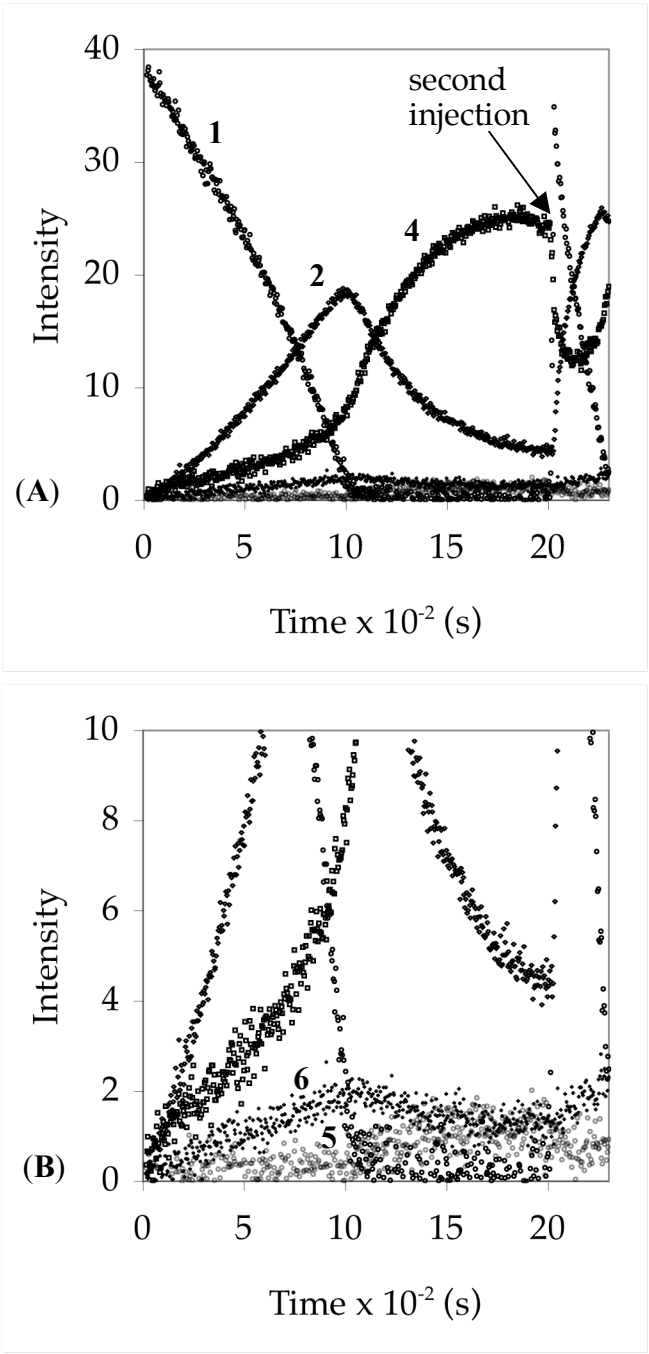


Figure 33. Plot of intensity versus time by ^{19}F NMR spectroscopy of 0.20 M LDA, 0.01 M **1**, 5.0 M THF/pentane at -90 °C. (**A**) trace including double injection; (**B**) expansion of Figure 33A.

Pentane cosolvent at < 8.0 M THF gives rise to an additional lithium aggregate (**6**) (hexanes were used in all kinetic experiments). It appears as two 1:1 resonances at -77.5 and -77.7 ppm in the ^{19}F NMR spectrum. Species **6** exhibits no delayed onset and therefore is not a reactive form involved in autocatalysis. It is not observable with hexanes as cosolvent down to 1.0 M THF.

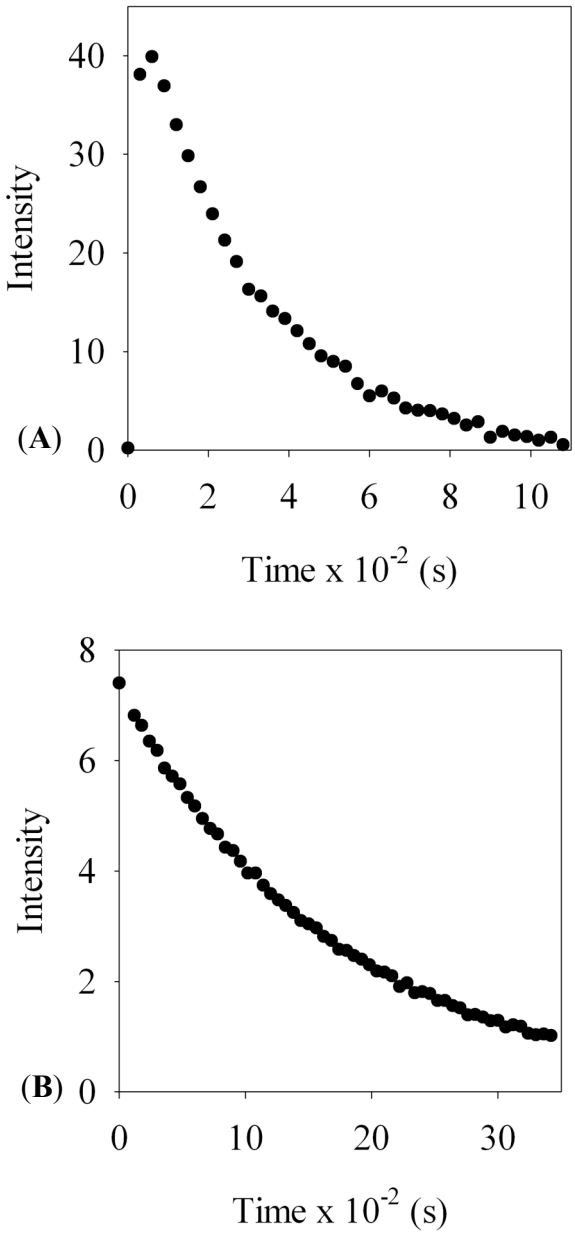


Figure 34. Plot of intensity versus time by ^{19}F NMR spectroscopy of 0.10 M LDA, 1.9 M *t*-BuOMe/cyclopentane at -78 °C. (**A**) 0.0074 M **1**, k_{obsd}= 3.4 ±0.1 (10^{-3}) s^{-1}; (**B**) 0.0074 M **1**-***d*$_1$**, k_{obsd}= 0.56 ±0.02 (10^{-3}) s^{-1}; KIE=6.1.

Studies by ReactIR show that **1** in 1.9 M *t*-BuOMe/cyclopentane appears as a precomplex indicative by a 30 cm^{-1} downward shift in the IR spectrum. In addition, the reaction is zeroth order in LDA further supporting the structural assignment as a precomplex. The ^{19}F NMR resonance of **1** (-113.1 ppm) shifts by 2.4 ppm upfield to -110.7 ppm upon complexation with LDA.

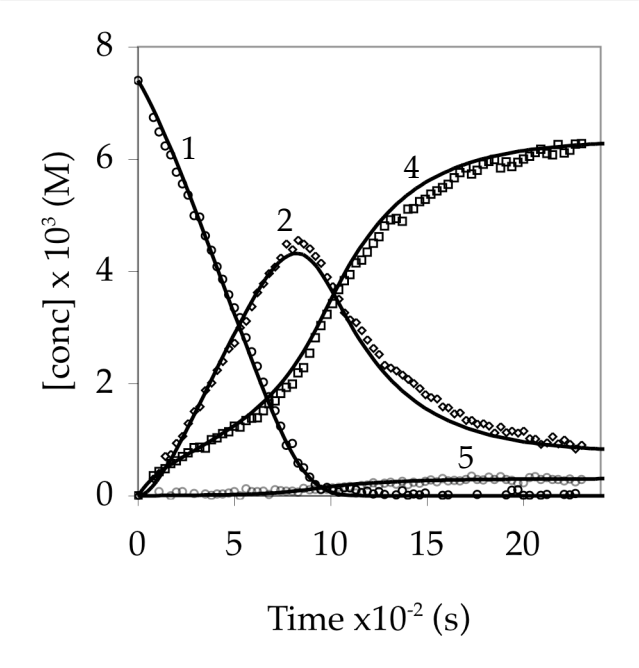


Figure 35. Parametric fit to the ^{19}F NMR spectroscopy derived concentration versus time profile of 0.0074 M **1**, 0.10 M LDA, 5.0 M 2-methyltetrahydrofuran/hexanes at -78 °C.

The reaction in 2-Me-THF (2-methyltetrahydrofuran) is similar to the parent system in THF. Strikingly though, mixed dimer **4** does not exhibit a delayed onset whereas mixed dimer **5** does. Species **4** does not maintain a steady state concentration but instead builds up as **1** is decaying. The following chemical shifts were observed: **1** (-113.1 ppm), **2** (-74.5 ppm), **4** (-79.8 ppm), **5** (-80.1 ppm).

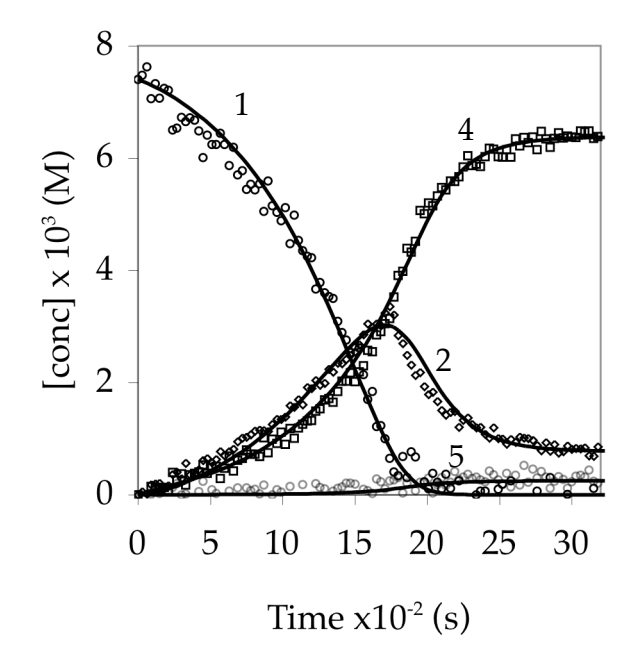


Figure 36. Parametric fit to the ^{19}F NMR spectroscopy derived concentration versus time profile of 0.0074 M **1**, 0.10 M LDA, 5.0 M tetrahydropyran/pentane at -78 °C.

The reaction in THP (tetrahydropyran) is similar to the reaction in THF. Strikingly as in the case of 2-Me-THF, mixed dimer **4** does not exhibit a delayed onset whereas mixed dimer **5** does. In addition, the decay in **1** is sigmoidal. This is an indication that the rate of the autocatalytic step has been accelerated relative to the initiation rate when switching from THF to THP.

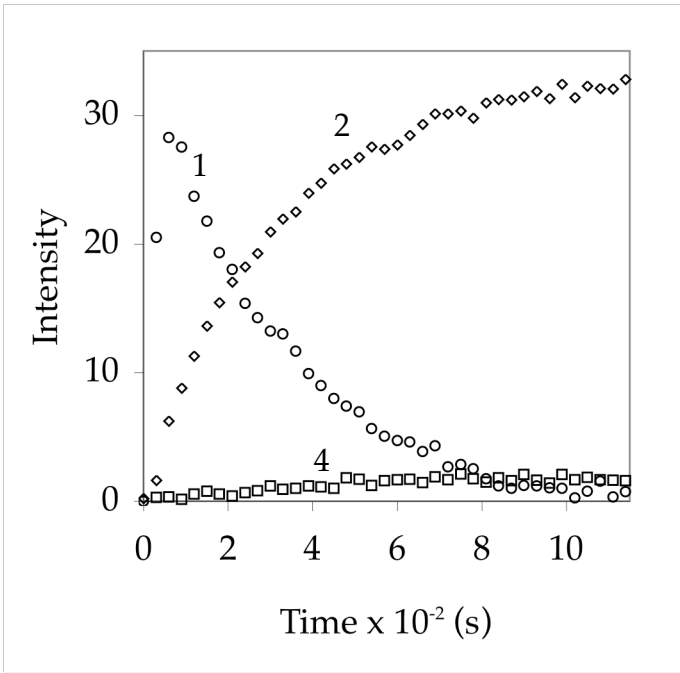


Figure 37. Plot of intensity versus time by ^{19}F NMR spectroscopy of 0.0074 M **1**, 0.10 M LDA, 4.1 M 2,2-dimethyltetrahydrofuran/pentane at -78 °C. The following chemical shifts were observed: **1** (-113.1 ppm), **2** (-74.9 ppm), **4** (-79.1 ppm). Small amounts of a supposed precomplex was observed at -112.0 ppm.

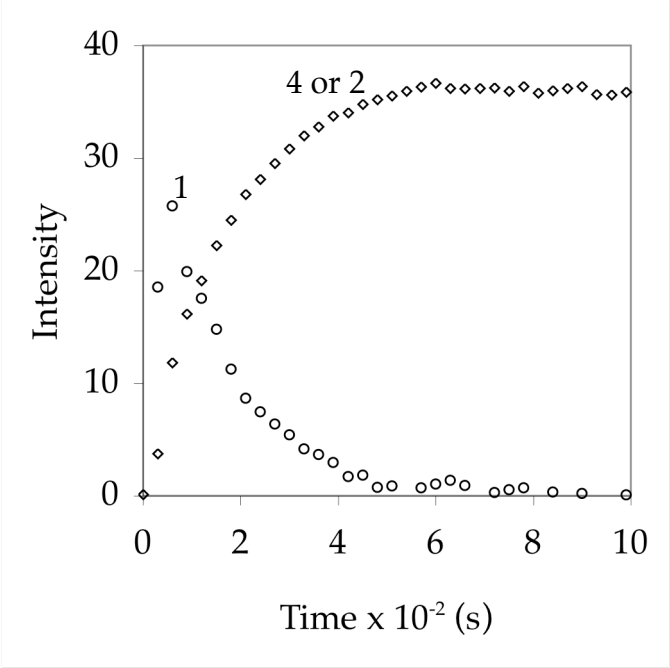


Figure 38. Plot of intensity versus time by ^{19}F NMR spectroscopy of 0.0074 M **1**, 0.10 M LDA, 4.1 M 2,5-dimethyltetrahydrofuran/pentane at -78 °C. The following chemical shifts were observed: **1** (-113.1 ppm), **4** or **2** (-80.4 ppm). It is unclear whether the product is **2** or **4**.

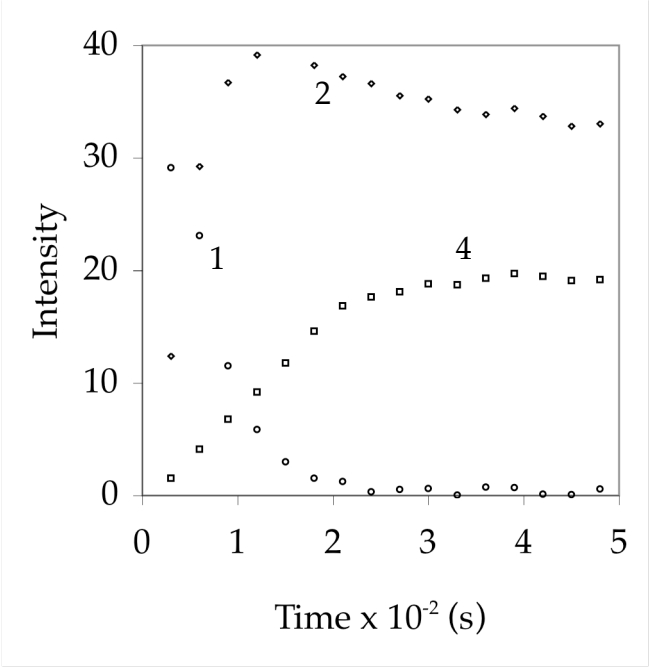


Figure 39 Plot of intensity versus time by ^{19}F NMR spectroscopy of 0.0074 M **1**-d_1, 0.10 M LDA, 0.5 M DMPU/THF at -78 °C. (DMPU = 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone)

The reaction with >0.50 M DMPU is intractably fast at -78 °C. It was also necessary to use the deuterated starting material to further slow down the rate. It is noteworthy that addition of 0.50 M DMPU will stabilize the ground state.[3] The rate increase must therefore derive either from a relative transition state stabilization or an enhancement of mixed aggregate reactivity. The following chemical shifts were observed: **1**-d_1 (-114.1 ppm), **2** (-75.1 ppm), **4** (-78.3 ppm).

[3] Sun, X.; Collum, D. B. *J. Am. Chem. Soc.* **2000**, *122*, 2452

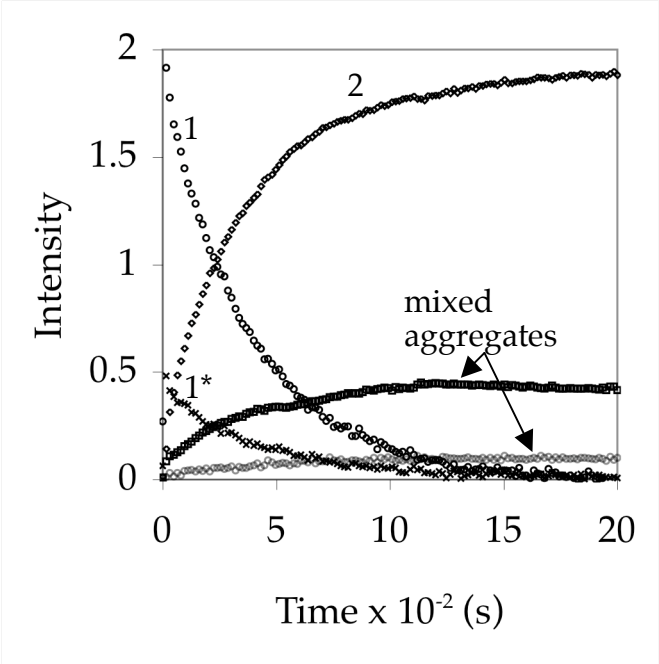


Figure 40. Plot of intensity versus time by ^{19}F NMR spectroscopy of 0.0074 M **1**, 0.10 M LDA, 5.1 M DMEA/toluene at -78 °C (DMEA = dimethylethylamine).

At 5.1 M DMEA, carbamate **1** is a mixture of its free and precomplexed form (**1**/**1***= 4:1 ratio, respectively). Three lithiated products are observed. The major species in solution is an aryllithium monomer or a homoaggregate (**2**) as evident from its singlet in the ^{6}Li NMR spectrum. The other products are likely to be mixed aggregates. The following chemical shifts were observed: **1** (-112.3 ppm), **1*** (-112.3 ppm), **2** (-73.6 ppm) and mixed aggregates at -76.1 ppm (major) and -76.7 ppm (minor).

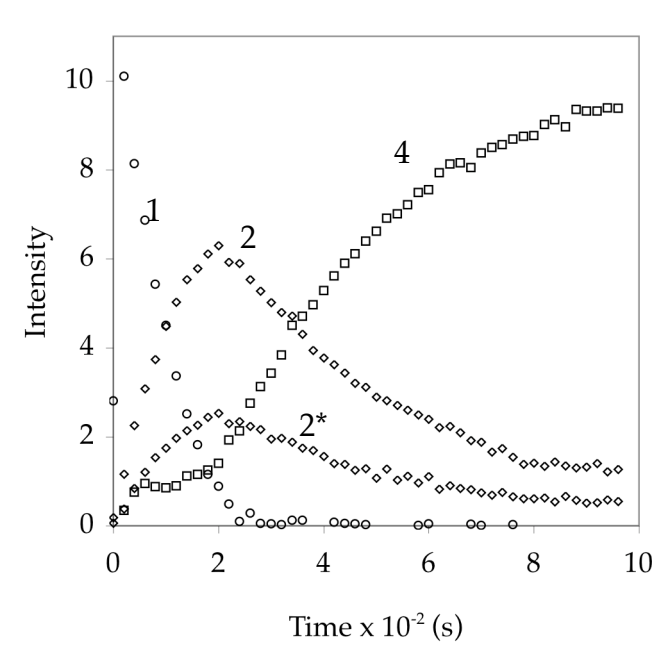


Figure 41. Plot of intensity versus time by ^{19}F NMR spectroscopy of 0.0074 M **1**, 0.10 M LDA, 5.0 M oxetane/hexanes at -100 °C.

The reaction is too fast to monitor at -78 °C and needed to be cooled to -100 °C. There are three other mixed aggregates at low concentrations that are not shown in the above plot. It is not clear whether these are distinct lithium aggregates or conformers. In THF at -100 °C, mixed dimer **4** initially grows in to a steady concentration until **1** is consumed. It appears that this 'plateau' arises from a delicate balance between the rates of consumption and formation of **4**. If the rate of consumption is greater we arrive at cases as in THF at -78 °C where **4** never appears observably. On the contrary, if the rate of formation is greater, we arrive at cases as in Me-THF and THP where **4** increases steadily. Only in oxetane and THF at -100 °C is this balance ('plateau') satisfied. The following chemical shifts were observed: **1** (doublet at -112.6 ppm), **2** (-74.7 ppm), **2*** (-75.1 ppm), **4** (-76.8 ppm) and minor peaks at -75.6, -77.5 and -77.9 ppm. Species **2** and **2*** preserve a constant ratio and are therefore either conformers of the same aryllithium or rapidly equilibrating lithium aggregates.

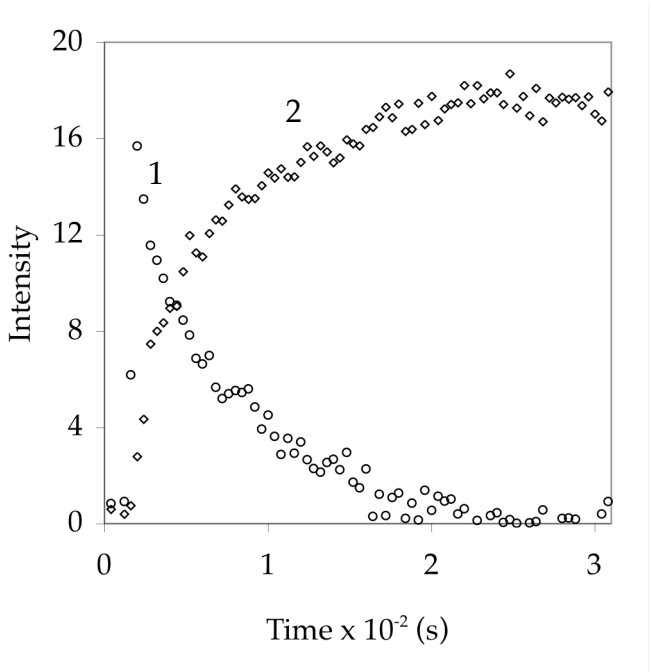


Figure 42. Plot of intensity versus time by ^{19}F NMR spectroscopy of 0.0074 M **1**, 0.10 M LDA, 1.4 M TMEDA/THF at -78 °C (TMEDA = tetramethylethylenediamine).

The reaction is too fast to monitor at >2.0 M TMEDA in THF. As THF concentration is increased the reaction gradually shifts to the profile shown in Figure 25. It is striking that a small amount of TMEDA in THF so dramatically alters the course of the reaction. Because LDA remains solvated by THF [4] and because there are no detectable mixed aggregates present it is likely that TMEDA selectively stabilizes the transition state. The initial rate of decay in **1** is accelerated 300 fold relative to the parent system in THF. The following chemical shifts were observed: **1** (-113.1 ppm) and two peaks with a 10:7 ratio at -74.7 and -75.0 ppm. It is likley that the peaks represent two conformations of the of an aryllithium monomer **2**. Even though conformer of the diisopropyl moiety have only been seen in THF at -78 °C for **1**, such conformers may arise for the lithiated species in different solvents as well.

[4] Bernstein, M. P.; Romesberg, F. E.; Fuller, D. J.; Harrison, A. T.; Liu, Q. Y.; Williard, P. G; Collum, D. B. *J. Am. Chem. Soc.* **1992**, *114*, 5100.

Model:

Initiation

$$\underset{\mathbf{3}}{(i\text{-}Pr_2NLi)_2} + \underset{\mathbf{1}}{ArH} \xrightarrow{k_1} \underset{\mathbf{4}}{(i\text{-}Pr_2NLi)(ArLi)} + i\text{-}Pr_2NH \quad (1)$$

Mixed Aggregate Exchange

$$\underset{\mathbf{4}}{(i\text{-}Pr_2NLi)(ArLi)} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\mathbf{5}}{(i\text{-}Pr_2NLi)(ArLi)^*} \quad (2)$$

Autocatalysis

$$\underset{\mathbf{5}}{(i\text{-}Pr_2NLi)(ArLi)^*} + \underset{\mathbf{1}}{ArH} \xrightarrow{k_3} \underset{\mathbf{2}}{2\ ArLi} + i\text{-}Pr_2NH \quad (3)$$

$$\underset{\mathbf{3}}{(i\text{-}Pr_2NLi)_2} + \underset{\mathbf{2}}{ArLi} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \underset{\mathbf{4}}{(i\text{-}Pr_2NLi)(ArLi)} + 0.5\underset{\mathbf{3}}{(i\text{-}Pr_2NLi)_2} \quad (4)$$

The model is described by the following differential equations [5]

$$d[ArH]/dt = -k_1[ArH][A_2] - k_3[A{\cdot}ArLi^*][ArH]$$

$$d[ArLi]/dt = -k_4[ArLi][A_2] + k_{-4}[A{\cdot}ArLi][A_2]^{0.5} + 2k_3[A{\cdot}ArLi^*][ArH]$$

$$d[A{\cdot}ArLi^*]/dt = k_2[A{\cdot}ArLi] - k_{-2}[A{\cdot}ArLi^*] - k_3[A{\cdot}ArLi^*][ArH]$$

$$d[A{\cdot}ArLi]/dt = k_1[ArH][A_2] - k_2[A{\cdot}ArLi] + k_{-2}[A{\cdot}ArLi^*] + k_4[ArLi][A_2] - k_{-4}[A{\cdot}ArLi][A_2]^{0.5}$$

$$A_2 = [A_2(init)] - 0.5[ArLi] - [A_2{\cdot}ArLi] - [A_2{\cdot}ArLi^*]$$

where,

ArH = **1**	A·ArLi = **4**
ArLi = **2**	A·ArLi* = **5**
A_2 = **3**	$[A_2(init)]$ = initial concentration of LDA

[5] (a) Toby, S. *J. Chem. Educ.* **2000**, *77*, 188. (b) Alberty, R. A. *J. Chem. Educ.* **2004**, *81*, 12006. (c) Francl, M. M. *J. Chem. Educ.* **2004**, *81*, 1535.

Mathematica 6.0 code for modeling of above mechanism [6]

```
Manipulate[
 Plot[
  Evaluate[{b[t], c[t], ac[t], ach[t], a2[t]} /.
    NDSolve[
     {b'[t] == - k1 b[t] a2[t] – k3 ach[t] b[t],
      c'[t] == 2 k3 ach[t] b[t] – k4 c[t] a2[t] + k4b ac[t] a2[t]^0.5 ,
      ac'[t] == k1 b[t] a2[t] + k4 c[t] a2[t] – k4b ac[t] a2[t]^0.5 – k2 ac[t] + k2b ach[t] ,
      ach'[t] == - k3 ach[t] b[t] + k2 ac[t] – k2b ach[t] ,
      a2'[t] == - k1 a2[t] b[t] - 0.5 k4 c[t] a2[t] + 0.5 k4b ac[t] a2[t]^0.5 ,
      b[0] == 0.0074,
      c[0] == 0.0,
      ac[0] == 0.0,
      ach[0] == 0.0,
      a2[0] == 0.1},
     {b, c, ac, ach, a2}, {t, 0, 800}, MaxSteps -> 5000, AccuracyGoal -> 10]],
  {t, 0, 800}, PlotRange -> {{0, 800}, {0, 0.008}},
  PlotStyle -> {{Red, Thickness[0.008]}, {Blue, Thickness[0.008]}, {Green,
Thickness[0.008]}, {Yellow, Thickness[0.008]}}],
 {{k1, 0.02, "initiation"}, 0, 0.04},
 {{k2, 1.42, "closed to open dimer"}, 0, 5},
 {{k2b, 25, "open to closed dimer"}, 0, 50},
 {{k3, 650, "fast catalytic step"}, 0, 1000},
 {{k4, 0.058, "condensation forward"}, 0, 1},
 {{k4b, 0.0035, "condensation reverse"}, 0, 0.05}]
```

where,

b = **1** ac = **4**
c = **2** ach = **5**
a_2 = **3**

NDSolve is an algorithm that numerically solves differential equations. A closed analytical solution to this set of differential equations could not be found. *b[0], c[0]* etc. represent the initial concentrations of species *b* and *c*, respectively, at time zero. The time derivative is expressed by an apostrophe (*b'[t], c'[t]* etc.). The *Manipulate* command allows one to manually adjust the values of rate constants with a slider. The default value for each parameter, a description of each parameter and the slider range is listed in the last six lines of the code. The *slider* feature is convenient and allows for a rough but fast manual curve fit to the experimental data. With reasonable initial guesses at hand the data can then be fit rigorously in *Igor Pro*. The *Manipulate* command conveniently illustrates the principle of autocatalysis by varying either k_1 (initiation) or k_4 (condensation forward) and thereby shifting the linear decay in starting material towards a more exponential or sigmoidal form.

Because LDA is dimeric in solution, the concentration of LDA in the model must represent its dimeric concentration which is one half of the monomeric LDA concentration weighed out in solid form.
Note: *Mathematica* is very sensitive to the choice of variables. For example, k_{-2} is not a viable variable and instead is written as k_{2b}. Numbers and symbols are poor choices for variables and will cause errors during the excecution of the macro.

[6] *Mathematica 6.0*, Wolfram Research Inc., http://www.wolfram.com/

Mathematica 6.0 – Superposition of experimental data with theoretical model [6]

The following code superimposes experimental data with the numerical solution of a set of differential equations describing the model.

```
data = Import["/Users/davidcollum/Documents/Mathematica files/data to fit/nb91i.txt", "Table"];
```

The data set has now been uploaded from the particular directory. The textfile must be in a tabular format.

```
ext = Map[#[[1]] &, data];
exc = Map[#[[2]] &, data];
exd = Map[#[[3]] &, data];
exe = Map[#[[4]] &, data];
exb = Map[#[[5]] &, data];
```

Each column in the textfile is mapped in row format and given a name (*ext*, *exc* etc.).

```
p1 = ListPlot[Transpose[{ext, exc}], PlotStyle -> {Blue, Thickness[0.1]},
  PlotRange -> {{0, 1700}, {0, 0.008}}];
p2 = ListPlot[Transpose[{ext, exd}], PlotStyle -> {Green, Thickness[0.1]},
  PlotRange -> {{0, 1700}, {0, 0.008}}];
p3 = ListPlot[Transpose[{ext, exb}], PlotStyle -> {Red, Thickness[0.1]},
  PlotRange -> {{0, 1700}, {0, 0.008}}];
p4 = ListPlot[Transpose[{ext, exe}], PlotStyle -> {Yellow, Thickness[0.1]},
  PlotRange -> {{0, 1700}, {0, 0.08}}];
```

The five rows (*ext, exc, exd, exe* and *exb*) are paired to give concentration versus time plots (*ext* paired with *exc*, *ext* paired with *exd* etc.). In addition, the rows are transposed to yield columns. Plots *p1* through *p4* now represent concentration versus time plots for each species with a given range in the time and concentration domain. The color and line thickness are also specified here. The semi-colon suppresses the output at this point.

```
solution = NDSolve[
  {b'[t] == - k1 b[t] a2[t] – k3 ach[t] b[t],
     c'[t] == 2 k3 ach[t] b[t] – k4 c[t] a2[t] + k4b ac[t] a2[t]^0.5 ,
     ac'[t] == k1 b[t] a2[t] + k4 c[t] a2[t] – k4b ac[t] a2[t]^0.5 – k2 ac[t] + k2b ach[t] ,
     ach'[t] == - k3 ach[t] b[t] + k2 ac[t] – k2b ach[t] ,
     a2'[t] == - k1 a2[t] b[t] - 0.5 k4 c[t] a2[t] + 0.5 k4b ac[t] a2[t]^0.5 ,
     b[0] == 0.0074,
     c[0] == 0.0,
     ac[0] == 0.0,
     ach[0] == 0.0,
     a2[0] == 0.1},
```

/. {k1 -> 0.02, k2 -> 1.42, k2b -> 25, k3 -> 650, k4 -> 0.058, k4b -> 0.0035}, {b, c, ach, ac, a2}, {t, 0, 1700}]

This set of commands is similar to the ones presented previously. It numerically differentiates the equations without yet plotting the solution.

```
fn[t_] = c[t] /. solution
p5 = Plot[fn[t], {t, 0, 1700}, PlotPoints -> 2000, PlotStyle -> {Blue,
Thickness[0.008]}, PlotRange -> {{0, 1700}, {0, 0.008}}, DisplayFunction ->
Identity];

fn[t_] = ac[t] /.solution
p6 = Plot[fn[t], {t, 0, 1700}, PlotPoints -> 2000, PlotStyle -> {Green,
Thickness[0.008]}, PlotRange -> {{0, 1700}, {0, 0.008}}, DisplayFunction ->
Identity];

fn[t_] = b[t] /. solution
p7 = Plot[fn[t], {t, 0, 1700}, PlotPoints -> 2000, PlotStyle -> {Red,
Thickness[0.008]}, PlotRange -> {{0, 1700}, {0, 0.008}}, DisplayFunction ->
Identity];

fn[t_] = ach[t] /. solution
p8 = Plot[fn[t], {t, 0, 1700}, PlotPoints -> 2000, PlotStyle -> {Yellow,
Thickness[0.008]}, PlotRange -> {{0, 1700}, {0, 0.008}}, DisplayFunction ->
Identity];
```

The last set of commands plot each of the four interpolated functions (*c[t], ac[t], b[t]* and *ach[t]*). These plots are named *p5* through *p8*. The plotting is again suppressed with a semicolon.

```
Show[p1, p2, p3, p4, p5, p6, p7, p8]
```

Finally, all eight plots (*p1* through *p8*) are plotted together.

The *Igor Pro* macro: The curve fitting protocol [7]

```
// Use modern global access method.
#pragma rtGlobals=1

Menu "Collum"
	"Set Up Fit"
	"Normalize Data"
	"-"
	"Display Current Fit"
End

Proc SetUpFit(stTime)
variable stTime
Prompt stTime, "Enter the initial time point to fit:"

	Silent(1); PauseUpdate
	string  theWaveList,curWave, curTwave, tmpWave
	string/G curSuffix, msg1
	variable waveCnt = 0, cnt = 0, startPnt
	variable/G a2_init, startTime

	startTime = stTime

	// Make a multidimensional wave corresponding to each entered data set
	theWaveList = wavelist("a2c_*", ";", "")
	curWave = StringFromList(waveCnt, theWaveList)
	make/n=0/o initial_a2_concs
	do
		// Get the suffix of the next data set
		curSuffix = curWave[4,100]

		// Make the multidimensional wave that will describe this data set
		msg1 = "Enter the initial concentration of a2_" + curSuffix + ":"
//		msg2 = "Enter the initial concentration of b_" + curSuffix + ":"
		CreateMultidimWave()

		waveCnt += 1
		curWave = StringFromList(waveCnt, theWaveList)
	while(strlen(curWave) > 4)

	// Make the waves to hold the data for the fit. 'allDataY' will contain the experimental data; 'fitDataY' will contain the fits; 'fitDataX' contains the corresponding x values
	// The total number of points should be 400 * # of experiments to fit
	make/D/O/N=(400 *waveCnt) allDataY, fitDataY, fitDataX
```

```
	do
		startPnt = 400 * cnt
		curWave = StringFromList(cnt, theWaveList)
		curSuffix = curWave[4,100]
		curTwave = "t_" + curSuffix
		tmpWave = "ChemKin_" + curSuffix; fitDataX[startPnt,
startPnt+399] = pnt2x($tmpWave, mod(p,100))//pnt2X($tmpwave, mod(p,100))
	// Setup the xdata
		tmpWave = "b_" + curSuffix; allDataY[startPnt, startPnt + 99] =
interp(fitDataX[p], $curTwave, $tmpwave)	// First goes [b]
		tmpWave = "c_" + curSuffix; allDataY[startPnt + 100, startPnt + 199]
= interp(fitDataX[p], $curTwave, $tmpwave) // . . . then [c]
		tmpWave = "a2c_" + curSuffix; allDataY[startPnt + 200, startPnt +
299] = interp(fitDataX[p], $curTwave, $tmpwave)	// . . . then [a2c]
		tmpWave = "ac_" + curSuffix; allDataY[startPnt + 300, startPnt +
399] = interp(fitDataX[p], $curTwave, $tmpwave)	// . . . then [ac]
		cnt += 1
	while(cnt < waveCnt)

	// Make the wave to hold the kinetic parameters and initialize the
	values
	make/n=6/o/D   KK={0.02,600,0.046,0.045,6,0.36}

	// Make an epsilon wave for the fit
	duplicate/o KK, KK_epsilon
	KK_epsilon = 0.1*KK

	// Do the forward integration with the starting kinetic parameters
	cnt = 0
	do
		curWave = StringFromList(cnt, theWaveList)
		curSuffix = curWave[4,100]
		tmpWave = "ChemKin_" + curSuffix
		a2_init = initial_a2_concs[cnt]
		IntegrateODE/M=3 ChemKinetic, KK, $tmpWave

		// Copy the data from the forward integration into the fit wave
		startPnt = 400 * cnt
		fitDataY[startPnt, startPnt + 399] = $tmpWave[mod((p-
startPnt),100)][floor((p-startPnt)/100)]
		cnt += 1
	 while(cnt < waveCnt)

	// Make a graph so the user can follow the fitting procedure.
	display allDataY, fitDataY
	ModifyGraph mode(allDataY)=2,lsize(allDataY)=2,rgb(allDataY)=(0,0,0)
End

Proc NormalizeData()
```

```
	Silent(1); PauseUpdate
	string theWaveList,curWave, tmpWave,tWave, curSuffix
	variable waveCnt = 0, tmp

	// Make a multidimensional wave corresponding to each entered data
	set
	theWaveList = wavelist("a2c_*", ";", "")
	curWave = StringFromList(waveCnt, theWaveList)
	do
		// Get the suffix of the next data set
		curSuffix = curWave[4,100]

		tmpWave = "b_"+ curSuffix; tWave = "t_" + curSuffix
		duplicate/o $tmpWave, tempSum
		tmpWave = "c_" + curSuffix;tempSum += $tmpWave
		tmpWave = "ac_" + curSuffix;tempSum += $tmpWave
		tmpWave = "a2c_" + curSuffix;tempSum += $tmpWave
		tmp = tempSum[0]
		tempSum /= tmp

		// Do a 9th order polynomial curve fit to the data
		CurveFit/NTHR=1/Q poly 9,  tempSum /X=$tWave
		tmpWave = "b_"+ curSuffix; $tmpWave /= poly(W_coef,$tWave)
		tmpWave = "c_" + curSuffix; $tmpWave /= poly(W_coef,$tWave)
		tmpWave = "ac_" + curSuffix; $tmpWave /= poly(W_coef,$tWave)
		tmpWave = "a2c_" + curSuffix; $tmpWave /= poly(W_coef,$tWave)

		waveCnt += 1
		curWave = StringFromList(waveCnt, theWaveList)
	while(strlen(curWave) > 4)
	KillWaves tempSum
end
Proc CreateMultidimWave(a2conc)
variable a2Conc
Prompt a2Conc, msg1

//"Enter the initial concentration of a2:"
	string newWave = "ChemKin_" + curSuffix,timeWave = "t_" + curSuffix,
cw
	variable endPnt,startFitPnt, endFitPnt

	make/D/O/N=(100,4) $newWave
	SetScale/I x startTime, $timeWave[numpnts($timeWave)-1], $newWave
	SetDimLabel 1, 0, Y0,$newWave;SetDimLabel 1, 1,
Y1,$newWave;SetDimLabel 1, 2, Y2,$newWave;SetDimLabel 1, 3, Y3,$newWave;

	// To get initial conditions, fit 9 points of data around the desired start
	time and use a linear interpolation
```

```
	FindLevel/P/Q $timeWave, startTime
	startFitPnt = V_LevelX - 4
	endFitPnt = V_LevelX + 4
	if(startFitPnt < 0)
		startFitPnt = 0
	endif
	cw = "b_" + curSuffix; CurveFit/NTHR=1/Q line  $cw[startFitPnt,
endFitPnt]/X=$timeWave;$newWave[0][%Y0] = W_coef[0]+W_coef[1]*startTime
	cw = "c_" + curSuffix; CurveFit/NTHR=1/Q line  $cw[startFitPnt,
endFitPnt]/X=$timeWave;$newWave[0][%Y1] = W_coef[0]+W_coef[1]*startTime
	cw = "a2c_" + curSuffix; CurveFit/NTHR=1/Q line  $cw[startFitPnt,
endFitPnt]/X=$timeWave;$newWave[0][%Y2] = W_coef[0]+W_coef[1]*startTime
	cw = "ac_" + curSuffix; CurveFit/NTHR=1/Q line  $cw[startFitPnt,
endFitPnt]/X=$timeWave;$newWave[0][%Y3] = W_coef[0]+W_coef[1]*startTime

	// Increase length of initial_a2_concs wave by 1, and store the new a2
	concentration in last point
	endPnt = numpnts(initial_a2_concs)
	Redimension/N=(endPnt+1) initial_a2_concs
	initial_a2_concs[endPnt] = a2conc

End
Proc DisplayCurrentFit(timeWave)
string timeWave
Prompt timeWave,"Select the dataset to be
displayed",popup,WaveList("t_*",";","")

	string curSuffix,fit_b, fit_c, fit_a2c, fit_ac, data_b, data_c, data_a2c,
data_ac,multidimWave, labelStr
	string bWinName, cWinName, a2cWinName, acWinName, command

	curSuffix = timeWave[2,100]
	fit_b = "fit_b_" + curSuffix;fit_c = "fit_c_" + curSuffix;fit_a2c = "fit_a2c_" +
curSuffix;fit_ac = "fit_ac_" + curSuffix;
	data_b = "b_" + curSuffix; data_c = "c_" + curSuffix; data_a2c = "a2c_" +
curSuffix; data_ac = "ac_" + curSuffix;
	multidimWave = "ChemKin_" + curSuffix
	make/D/O/n=100 $fit_b, $fit_c, $fit_a2c, $fit_ac
	SetScale/P x DimOffset($multiDimWave, 0),
DimDelta($multiDimWave,0), $fit_b, $fit_c, $fit_a2c, $fit_ac

	// Make the individual graphs
	$fit_b = $multidimWave[p][0]
	display /W=(5,44,266,211) $data_b vs $timeWave;append
$fit_b;ModifyGraph rgb($fit_b)=(0,0,0)
	labelStr = "b_"+ curSuffix + "\r\\s(b_" + curSuffix + ") Data\r\\s(fit_b_"
+ curSuffix + ") Fit"
	TextBox/C/N=text0/F=0/M/H=25 labelStr
	ModifyGraph mirror=2,btLen=3;DelayUpdate
```

```
	Label left "Concentration (M\\E)";DelayUpdate
	Label bottom "Time (s)"
	bWinName = "Result_b_" + curSuffix
	DoWindow/C $bWinName

	$fit_c = $multidimWave[p][1]
	display /W=(5,44,266,211) $data_c vs $timeWave;append
$fit_c;ModifyGraph rgb($fit_c)=(0,0,0)
	labelStr = "c_"+ curSuffix + "\r\\s(c_" + curSuffix + ") Data\r\\s(fit_c_" +
curSuffix + ") Fit"
	TextBox/C/N=text0/F=0/M/H=25 labelStr
	ModifyGraph mirror=2,btLen=3;DelayUpdate
	Label left "Concentration (M\\E)";DelayUpdate
	Label bottom "Time (s)"
	cWinName = "Result_c_" + curSuffix
	DoWindow/C $cWinName

	$fit_a2c = $multidimWave[p][2]
	display /W=(5,44,266,211) $data_a2c vs $timeWave;append
$fit_a2c;ModifyGraph rgb($fit_a2c)=(0,0,0)
	labelStr = "a2c_"+ curSuffix + "\r\\s(a2c_" + curSuffix + ")
Data\r\\s(fit_a2c_" + curSuffix + ") Fit"
	TextBox/C/N=text0/F=0/M/H=25 labelStr
	ModifyGraph mirror=2,btLen=3;DelayUpdate
	Label left "Concentration (M\\E)";DelayUpdate
	Label bottom "Time (s)"
	a2cWinName = "Result_a2c_" + curSuffix
	DoWindow/C $a2cWinName

	$fit_ac = $multidimWave[p][3]
	display /W=(5,44,266,211) $data_ac vs $timeWave;append
$fit_ac;ModifyGraph rgb($fit_ac)=(0,0,0)
	labelStr = "ac_"+ curSuffix + "\r\\s(ac_" + curSuffix + ")
Data\r\\s(fit_ac_" + curSuffix + ") Fit"
	TextBox/C/N=text0/F=0/M/H=25 labelStr
	ModifyGraph mirror=2,btLen=3;DelayUpdate
	Label left "Concentration (M\\E)";DelayUpdate
	Label bottom "Time (s)"
	acWinName = "Result_ac_" + curSuffix
	DoWindow/C $acWinName

	// Make the layout
	command = "Layout/C=1/W=(5,44,662,623)
"+acWinName+"(27,257,290,426)/O=1/F=0,"+a2cWinName+
"(291,257,554,426)/O=1/F=0"
	Execute(command)
	command ="Append
"+cWinName+"(293,71,556,240)/O=1/F=0,"+bWinName+"(27,69,290,238)/O=1/
F=0"
```

```
	Execute(command)
	ModifyLayout mag=1, units=1

	// Add the annotation
	labelStr = "\\f01\\Z12Fit Parameters:\\f00\\Z10\rk1 = "+
num2str(KK[0]) + " ± " + num2str(W_sigma[0])+ "\rk2 = " + num2str(KK[1]) + " ±
" + num2str(W_sigma[1])
	labelStr += " \rk4 = " + num2str(KK[2])+  " ± " + num2str(W_sigma[2])+
"\rk4b = " + num2str(KK[3]) + " ± " + num2str(W_sigma[3])
	labelStr += "\rk5 = " + num2str(KK[4])+ " ± " + num2str(W_sigma[4])+ "
\rk5b = " + num2str(KK[5]) + " ± " + num2str(W_sigma[5])
	TextBox/N=text0/F=0/M/H=25/A=LB/X=6.27/Y=25.27  labelStr
End

Function myFitFunc(pw, yw, xw) : FitFunc
Wave pw, yw, xw

	variable waveCnt = 0
	string theWaveList, curWave
	NVAR a2_init
	WAVE initial_a2_concs

	theWaveList = wavelist("ChemKin_*", ";", "")
	curWave = StringFromList(waveCnt, theWaveList)

	// For every experiment, do the forward integration from the starting
	concentrations
	// 'ChemKinetic' is the model function, 'KK' holds the kinetic
	parameters, and 'ChemKin_XXX' contains the various experiments
	do
		// Do the forward integration
		a2_init = initial_a2_concs[waveCnt]
		IntegrateODE/M=3 ChemKinetic, KK, $curWave

		// Copy the results of the forward integration into the output
		wave
		wave tempWave = $curWave
		yw[400*waveCnt, 400*waveCnt+399] = tempWave[mod((p-
400*waveCnt),100)][floor((p-400*waveCnt)/100)]

		// Iterate the counter and get the next wave
		waveCnt += 1
		curWave = StringFromList(waveCnt, theWaveList)
	while(strlen(curWave) > 8)
End

// This function describes the kinetic model and calculates the derivatives
Function ChemKinetic(pw, tt, yw, dydt)
Wave pw
```

```
variable tt
Wave yw
Wave dydt

        variable a2
        NVARa2_init

        a2 = a2_init- 0.5*yw[1] - yw[3] - yw[2]
        dydt[0] = -pw[0]*yw[0]*a2 - pw[1]*yw[2]*yw[0]
        dydt[1] = -pw[2]*yw[1]*a2 + pw[3]*yw[2]*a2^0.5 + 2*pw[1]*yw[2]*yw[0]
        dydt[2] =  pw[2]*yw[1]*a2 - pw[3]*yw[2]*a2^0.5 - pw[4]*yw[2]
                  + pw[5]*yw[3] - pw[1]*yw[2]*yw[0]
        dydt[3] = pw[0]*yw[0]*a2 + pw[4]*yw[2] - pw[5]*yw[3]

//      Legend of variables and parameters:
//      a2  = 3
//      yw[0] = 1
//      yw[1] = 2
//      yw[2] = 5
//      yw[3] = 4
//      pw[0] = k1
//      pw[1] = k3
//      pw[2] = k4
//      pw[3] = k4b
//      pw[4] = k2
//      pw[5] = k2b
End
```

This macro has a number of automated features that allow for a fast and expedient curve fitting protocol. It allows one to either fit one (single fit) or multiple (global fit) data traces. The macro automatically recognizes how many data traces were added and then subsequently asks for the initial concentration of *a2* (LDA) of each data trace. Furthermore, the initial time point is found by an additional parametric fit for each data set. This circumvents the problem of an ill-defined time-zero point due to the timing of the injection and the thermal turbulance during injection. To expedite the curve fitting protocol the concentration of *a2* was expressed by the linear equation,

$$[a2] = [a2(init)] - 0.5\,[\mathbf{2}] - [\mathbf{4}] - [\mathbf{5}]$$

This equation simply derives from the principle of mass balance. For every aryllithium monomer unit (**1**) generated, one half of an LDA dimer has been consumed and for every mixed dimer unit (**4** or **5**) generated, one LDA dimer has been consumed. The substitution of the differential equation associated with *a2* with a linear equation greatly simplifies the numerical integration problem. The solutions to the original and simplified equations have been shown to be identical by plotting the residuals of their solutions.

[7] *Igor Pro 6.0*, Wavemetrics, http://www.wavemetrics.com/

The 'simplified' *Igor Pro* macro[7]

The following macro is a simplified version of the macro listed above. Initial conditions for all species must be entered manually and the procedure does not conduct a parametric fit to establish the time-zero point. Additionally, the time range must be specified for each reaction. In its current form, the macro only allows to perform fits to one data set. It can however be modified to do global fits. Because this simplified macro is less intricate and more overseeable, models and corresponding differential equations can be more easily modified.

```
// Use modern global access method.
#pragma rtGlobals=1

// This function describes the kinetic model and calculates the derivatives
Function ChemKinetic(pw, tt, yw, dydt)
Wave pw
variable tt
Wave yw
Wave dydt

dydt[0] = -pw[0]*yw[1]*yw[0] - 0.5*pw[2]*yw[0]*yw[2] +
0.5*pw[3]*yw[4]*yw[0]^0.5
dydt[1] = -pw[0]*yw[1]*yw[0] - pw[1]*yw[3]*yw[1]
dydt[2] = -pw[2]*yw[2]*yw[0] + pw[3]*yw[4]*yw[0]^0.5 + 2*pw[1]*yw[3]*yw[1]
dydt[3] =  -pw[1]*yw[1]*yw[3] + pw[4]*yw[4] - pw[5]*yw[3]
dydt[4] = pw[0]*yw[1]*yw[0] + pw[2]*yw[2]*yw[0] - pw[3]*yw[4]*yw[0]^0.5 -
pw[4]*yw[4] + pw[5]*yw[3]

//      Legend of variables and parameters
//      yw[0] == 3
//      yw[1] == 1
//      yw[2] == 2
//      yw[3] == 5
//      yw[4] == 4
//      pw[0] = k1
//      pw[1] = k3
//      pw[2] = k4
//      pw[3] = k4b
//      pw[4] = k2
//      pw[5] = k2b

End

Function mySingleFitFunc(pw, yw, xw) : FitFunc
Wave pw, yw, xw
        wave ChemKin_01
        IntegrateODE/M=3 ChemKinetic, KK, ChemKin_01
        yw = ChemKin_01[mod(p,100)][1+floor(p/100)]
```

```
End

Macro SetUpFit()
	Silent(1); PauseUpdate

// Generate the multidimensional waves that will describe the first experiment
	make/D/O/N=(100,5) ChemKin_01;SetScale/I x 0,2020,"", ChemKin_01

// The parameters in SetScale (0,2788) describe the first and last time point

	SetDimLabel 1, 0, Y0,ChemKin_01;SetDimLabel 1, 1,
Y1,ChemKin_01;SetDimLabel 1, 2, Y2,ChemKin_01;SetDimLabel 1, 3,
Y3,ChemKin_01;SetDimLabel 1, 4, Y4,ChemKin_01

// The next line contains the initial conditions. The definition of the columns
(e.g., Y0) is given in ChemKinetic

	ChemKin_01[0][%Y0] = 0.05; ChemKin_01[0][%Y1] = 0.0074;
ChemKin_01[0][%Y2] = 0.0; ChemKin_01[0][%Y3] = 0.0; ChemKin_01[0][%Y4] =
0.0;

// Make the waves to hold the data for the fit. allDataY will contain the
experimental data; fitDataY will contain the fits; fitDataX contains the
corresponding x valuesThe total number of points should be 400 * # of
experiments to fit.

	make/D/O/N=400 allDataY, fitDataY, fitDataX

// Change 800 to 4 * 100 * number of experiments, The first 400 points contain
the data for expt #1.
	fitDataX[0,399] = pnt2X(ChemKin_01, mod(p,100)) // Set up the xdata
	allDataY[0,99] = interp(fitDataX[p], t_01, b_01)  // First goes [b]
	allDataY[100,199] = interp(fitDataX[p], t_01, c_01) // . . . then [c]
	allDataY[200,299] = interp(fitDataX[p], t_01, a2c_01)    // . . . then [a2c]
	allDataY[300,399] = interp(fitDataX[p], t_01, ac_01)      // . . . then [ac]

	// Make the wave to hold the kinetic parameters and initialize the values
	make/n=6/o/D   KK={0.02,800,0.046,0.0027,0.1,1.4}
	// Make an epsilon wave for the fit
	duplicate/o KK, KK_epsilon
	KK_epsilon = 0.1*KK
	// Do the forward integration with the starting kinetic parameters
	IntegrateODE/M=3 ChemKinetic, KK, ChemKin_01
	// Copy the data from the forward integration into the fit wave
	fitDataY[0,399] = ChemKin_01[mod(p,100)][1+floor(p/100)]
	// Make a graph so the user can follow the fitting procedure.
	display allDataY, fitDataY

End
```

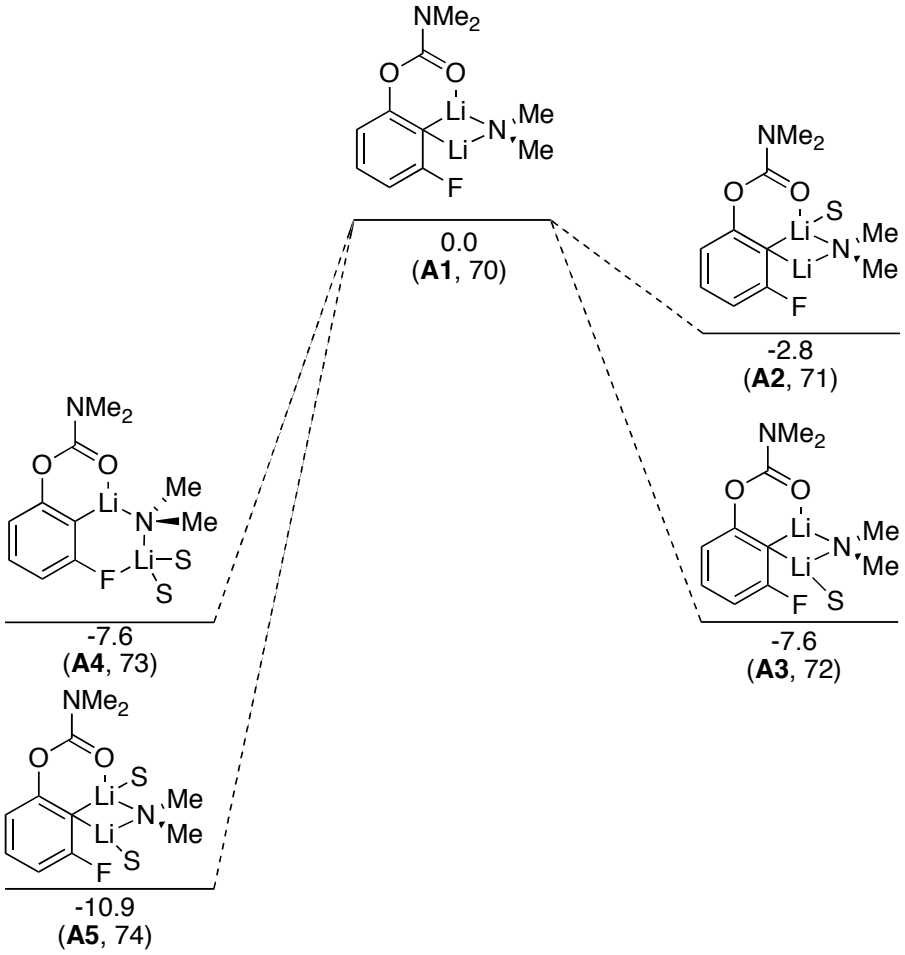


Figure 43. Relative free energies of solvation (! G, kcal/mol) at -78 °C. S = Me_2O.

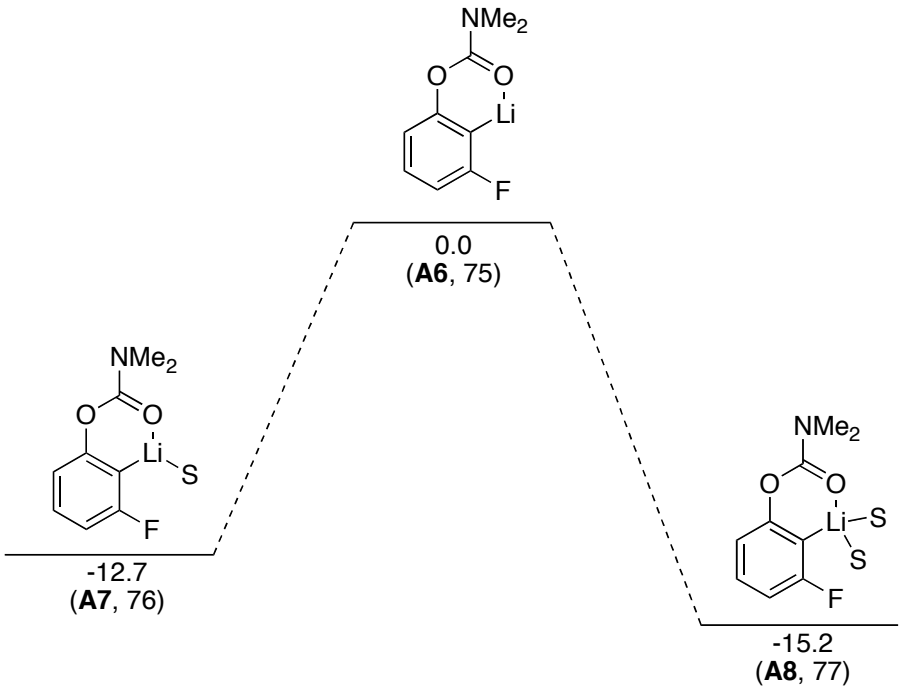


Figure 44. Relative free energies of solvation (! G, kcal/mol) at -78 °C. S = Me_2O.

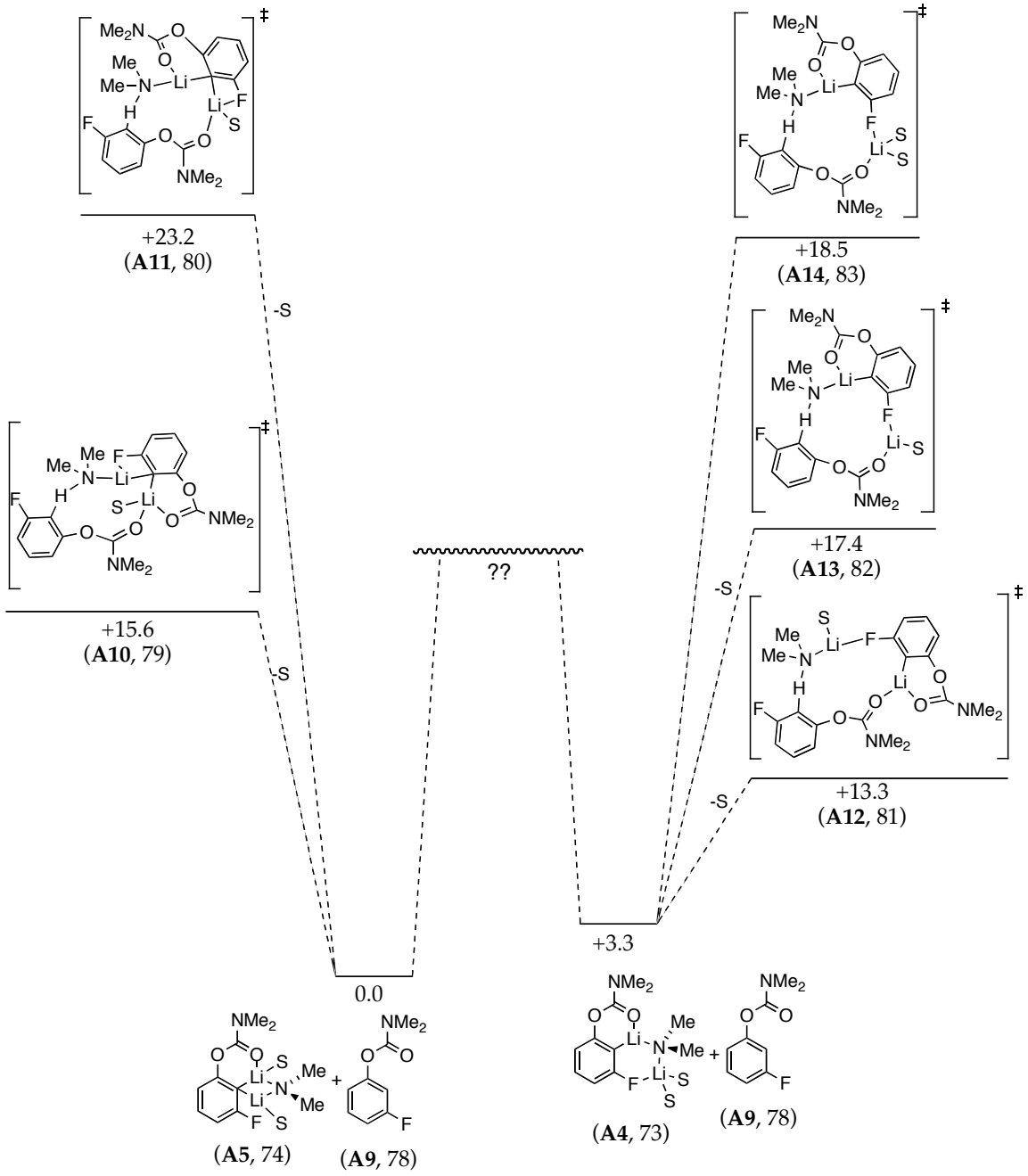


Figure 45. Relative free energies (! G, kcal/mol) at -78 °C. S = Me_2O. Transition structures for the post-rate-limiting deprotonation of arene **A9** by mixed dimers **A4** and **A5**. Free energies of activation are reported relative to the ground state energy of closed mixed dimer **A5** and arene **A9**. The left-hand transition structures exhibit a closed mixed dimer motif akin to **A5** whereas the right-hand transition structures exhibit an open dimer motif akin to **A4**.

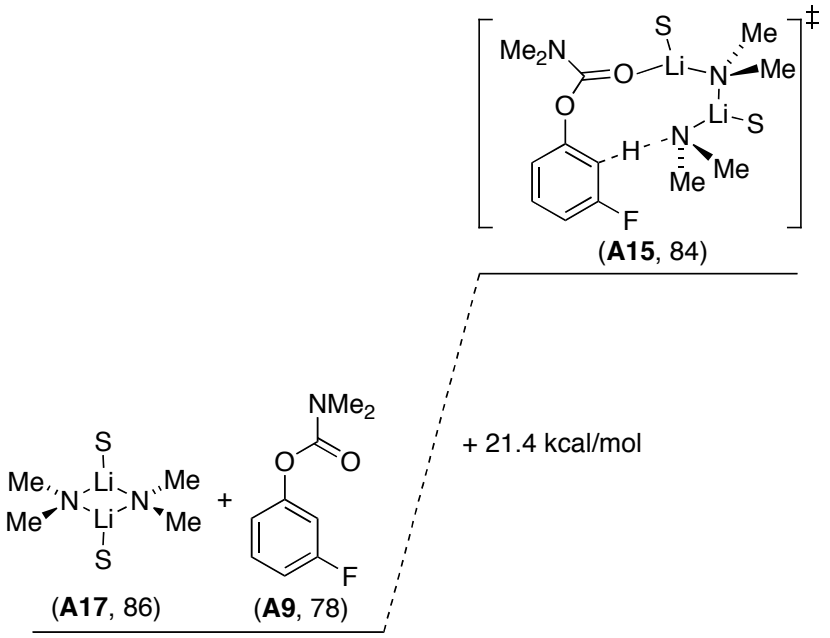
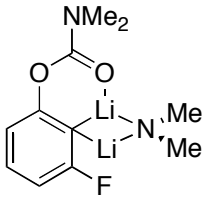
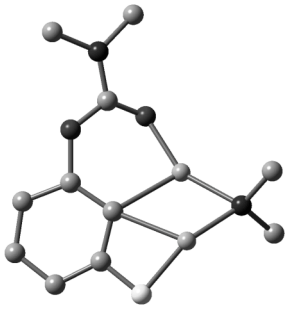


Figure 46. Relative free energy (! G, kcal/mol) at -78 °C. S = Me_2O. Free energy of activation for the deprotonation of arene **A9** leading to disolvated open dimer transition state **A15**.

Table A1. Optimized geometry at B3LYP level of theory with 6-31G(d) basis set, free energy (G, Hartrees), and cartesian coordinates (X, Y, Z).

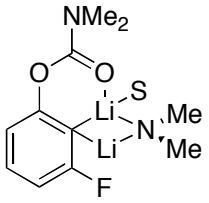


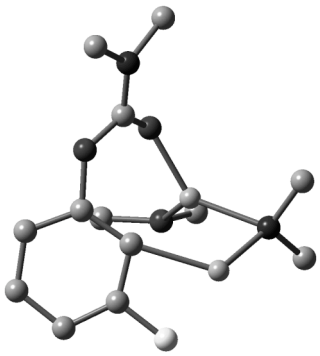


A1
G = -802.924566
(-78 °C)
See pg S66

Atom	X	Y	Z	Atom	X	Y	Z
Li	-0.624833	-1.264982	-0.498977	C	0.323528	1.510318	0.050073
C	-0.871734	0.820380	0.261375	O	1.604128	0.905222	0.218154
C	-1.948328	1.680260	0.159169	C	1.932116	-0.310103	-0.245768
F	-3.227229	1.079954	0.386587	O	1.177363	-1.056834	-0.886935
Li	-2.475195	-0.610438	0.852900	N	3.210726	-0.649116	0.058405
N	-2.164200	-2.336329	0.106435	C	3.753728	-1.913370	-0.420900
C	-3.129199	-2.808543	-0.874934	H	2.954214	-2.505743	-0.861142
H	-2.717933	-3.584660	-1.555059	H	4.531028	-1.736518	-1.175921
H	-4.032987	-3.262983	-0.417669	H	4.200352	-2.464817	0.414746
H	-3.475326	-1.979021	-1.510521	C	4.146801	0.238888	0.736967
C	-1.742229	-3.456690	0.933123	H	3.617760	1.084263	1.169355
H	-2.577592	-3.933625	1.487666	H	4.654790	-0.313205	1.535995
H	-1.266463	-4.275838	0.352241	H	4.907404	0.608949	0.036174
H	-1.007531	-3.130346	1.686519	H	1.408924	3.321532	-0.390750
C	-1.973935	3.038956	-0.108881	H	-0.669660	4.702647	-0.540916
C	-0.731081	3.641031	-0.320638	H	-2.904311	3.595664	-0.150377
C	0.431142	2.874105	-0.240424				

Table A1 (Continued).

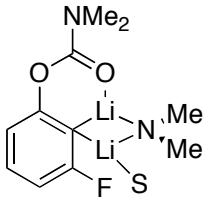


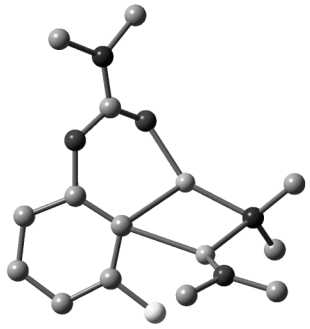


A2
G = -957.888979
(-78 °C)
S=Me_2O
See pg S66

Atom	X	Y	Z	Atom	X	Y	Z
Li	1.538805	-0.183019	-1.981520	C	-4.415377	-0.094867	-0.575358
N	1.666073	-1.961363	-1.314191	H	-4.064784	0.842440	-1.000513
Li	0.703742	-0.995534	0.177978	H	-4.904155	-0.684352	-1.359537
O	-1.138232	-0.959785	0.707347	H	-5.156415	0.119532	0.207124
C	-2.070747	-0.314963	0.213174	O	1.727461	-0.704333	1.875039
O	-2.017298	0.993112	-0.100623	C	2.378951	-1.794743	2.515117
C	-0.781402	1.691704	-0.201734	H	3.275037	-1.449512	3.049625
C	0.309780	1.141830	-0.868215	H	1.704690	-2.289451	3.229341
C	1.346826	2.046645	-0.956040	H	2.670543	-2.498200	1.734073
C	1.418322	3.346949	-0.478971	C	1.311681	0.302851	2.790907
C	0.281950	3.812040	0.190776	H	0.834292	1.091164	2.207850
C	-0.833047	2.982323	0.334515	H	0.595122	-0.101965	3.519418
H	-1.729852	3.330268	0.838847	H	2.178490	0.713942	3.326925
H	0.263044	4.821124	0.592492	C	2.976393	-2.540671	-1.090115
H	2.300014	3.963745	-0.620978	H	2.961902	-3.416003	-0.400280
F	2.492102	1.564152	-1.650048	H	3.460281	-2.916666	-2.017237
N	-3.293393	-0.852451	-0.036562	H	3.660271	-1.798557	-0.651468
C	-3.571078	-2.224216	0.364554	C	0.799713	-2.970133	-1.901016
H	-2.652128	-2.686367	0.719573	H	-0.201730	-2.555497	-2.095025
H	-4.323585	-2.247190	1.164337	H	0.658437	-3.861545	-1.249703
H	-3.957052	-2.791467	-0.490700	H	1.175032	-3.370897	-2.867507

Table A1 (Continued).

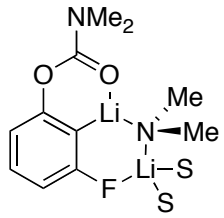


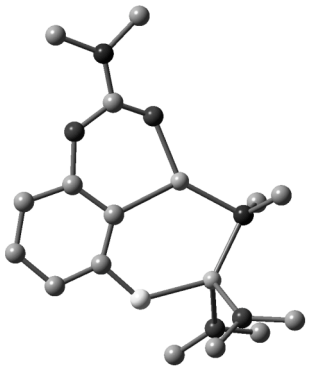


A3
G = -957.896696
(-78 °C)
S=Me_2O
See pg S66

Atom	X	Y	Z	Atom	X	Y	Z
Li	0.101372	-1.069732	-1.126766	H	-5.071450	-0.597213	1.431387
C	-0.067547	0.949959	-0.298910	H	-3.994617	-1.967080	1.012527
C	-0.962323	1.924352	-0.700360	C	-0.739622	3.275286	-0.926535
F	-2.296339	1.484919	-0.886546	C	0.570625	3.724325	-0.741736
Li	-1.957887	-0.336946	-0.057821	C	1.561041	2.825436	-0.344469
N	-1.637778	-1.958306	-1.104837	C	1.208406	1.488275	-0.138102
C	-2.376859	-2.044231	-2.352318	O	2.301321	0.716700	0.362837
H	-1.955034	-2.783345	-3.067929	C	2.579751	-0.526964	-0.057088
H	-3.439949	-2.344589	-2.215530	O	1.961910	-1.138995	-0.940209
H	-2.386504	-1.071217	-2.866779	N	3.645219	-1.063596	0.594456
C	-1.649870	-3.256977	-0.459562	C	4.132258	-2.381291	0.210338
H	-2.673954	-3.626942	-0.220716	H	3.422147	-2.842007	-0.473437
H	-1.190973	-4.063088	-1.072976	H	5.110677	-2.303663	-0.282643
H	-1.096350	-3.225813	0.492188	H	4.242432	-3.009494	1.102142
O	-3.015895	-0.282617	1.583646	C	4.448271	-0.337308	1.569538
C	-3.073652	0.854766	2.437046	H	3.930954	0.565434	1.884495
H	-2.159467	1.426907	2.268708	H	4.621068	-0.975677	2.443750
H	-3.947295	1.478026	2.201503	H	5.423988	-0.064186	1.144575
H	-3.124546	0.543563	3.489486	H	2.586099	3.150245	-0.192576
C	-4.151413	-1.134775	1.700562	H	0.817529	4.769231	-0.906273
H	-4.242596	-1.515850	2.726833	H	-1.540735	3.940030	-1.234024

Table A1 (Continued).

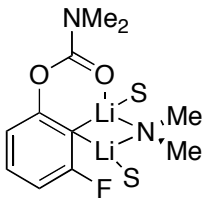


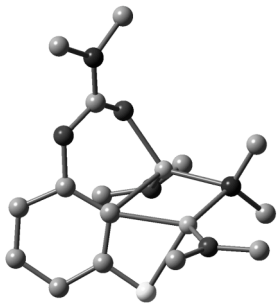


A4
G = -1112.856618
(-78 °C)
S=Me_2O
See pg S66

Atom	X	Y	Z
Li	-2.139629	-0.301924	0.033013
F	-1.481740	1.619872	0.001697
C	-0.103922	2.004807	-0.025467
C	0.820035	0.989392	0.013171
Li	0.545906	-1.050824	-0.148863
N	-1.184801	-2.018456	-0.153130
C	-1.302077	-2.762453	-1.393663
H	-0.457756	-3.465817	-1.574411
H	-2.217109	-3.396255	-1.450311
H	-1.335686	-2.078389	-2.254973
C	-1.146525	-2.961173	0.949221
H	-2.058432	-3.598725	1.026152
H	-0.301656	-3.684792	0.890167
H	-1.045767	-2.432710	1.909231
O	2.389800	-1.423671	-0.278066
C	3.338872	-0.659673	-0.066605
O	3.287705	0.676127	0.024453
C	2.115517	1.493254	-0.030195
C	2.460280	2.849150	-0.099839
C	1.436953	3.795195	-0.128479
C	0.103280	3.375289	-0.090083
H	-0.721894	4.081137	-0.111191
H	1.674813	4.853975	-0.180496
H	3.503352	3.151244	-0.129209
N	4.612814	-1.123212	0.105286
C	4.885353	-2.541472	-0.072794
H	3.943651	-3.084066	-0.125256
H	5.454959	-2.717069	-0.996261
H	5.475737	-2.914383	0.772766
C	5.774750	-0.260664	0.263276
H	5.464729	0.736568	0.565154
H	6.431878	-0.680084	1.034027
H	6.346569	-0.189807	-0.673200
O	-3.176023	-0.088777	1.770866
C	-3.950951	-1.158419	2.294568
H	-3.741396	-2.035709	1.681426
H	-3.670111	-1.370138	3.335854
H	-5.024011	-0.919919	2.255564
C	-3.319876	1.114060	2.515572
H	-2.682931	1.857673	2.037918
H	-3.000642	0.966159	3.556866
H	-4.364825	1.457056	2.507209
O	-3.497466	0.035579	-1.469338
C	-4.346249	-1.018961	-1.901243
H	-4.155775	-1.871370	-1.247788
H	-5.403009	-0.721948	-1.832841
H	-4.120032	-1.304461	-2.937874
C	-3.604399	1.197834	-2.281176
H	-3.339743	0.970491	-3.323607
H	-4.626711	1.602205	-2.252465
H	-2.905828	1.929159	-1.876166

Table A1 (Continued).

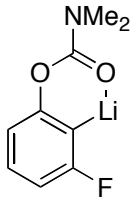


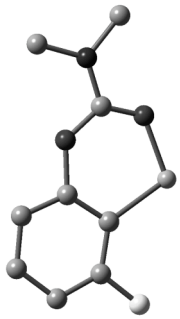


A5
G = -1112.861835
(-78 °C)
S=Me_2O
See pg S66

Atom	X	Y	Z
Li	1.880224	-0.378052	0.092888
Li	-0.121979	0.612900	1.175384
N	1.528840	-0.139946	2.000493
C	2.423041	0.720832	2.744092
H	2.609775	1.655555	2.195340
H	2.035917	1.009056	3.749945
H	3.418817	0.262848	2.950252
C	1.297489	-1.349824	2.762249
H	2.225575	-1.927677	2.984604
H	0.831068	-1.168328	3.757821
H	0.625493	-2.030802	2.216756
O	-1.881990	-0.174026	0.971351
C	-2.255949	-0.928194	0.066676
O	-2.005866	-0.741818	-1.242436
C	-1.061093	0.233434	-1.681736
C	0.206961	0.306319	-1.113323
C	0.991496	1.248137	-1.753254
F	2.295085	1.386249	-1.249614
C	0.656929	2.060362	-2.830646
C	-0.639587	1.920394	-3.335894
C	-1.516850	0.998362	-2.759331
H	-2.526348	0.868512	-3.138788
H	-0.963582	2.525553	-4.178133
H	1.367771	2.763246	-3.254508
N	-3.007202	-2.039870	0.294560
C	-3.459998	-2.332414	1.646478
H	-2.951639	-1.671113	2.345498
H	-4.545777	-2.187230	1.733220
H	-3.229455	-3.374511	1.897291
C	-3.525743	-2.896978	-0.762376
H	-3.038115	-2.664343	-1.705940
H	-3.334168	-3.946183	-0.507849
H	-4.610754	-2.763969	-0.875965
O	-0.475268	2.549401	1.583356
C	-0.675914	2.863779	2.955436
H	-0.433151	3.918068	3.150321
H	-1.717579	2.674995	3.254265
H	-0.004606	2.224331	3.530613
C	-1.290620	3.325546	0.713865
H	-1.049467	3.024524	-0.306421
H	-2.356856	3.144174	0.909661
H	-1.076529	4.396224	0.841607
O	3.129770	-1.701620	-0.605805
C	3.111519	-2.231079	-1.924558
H	2.284756	-1.748247	-2.448751
H	4.055255	-2.015960	-2.444811
H	2.950382	-3.318370	-1.904191
C	4.152799	-2.250694	0.216376
H	4.025866	-3.337295	0.320958
H	5.145301	-2.042117	-0.207126
H	4.060030	-1.776399	1.194627

Table A1 (Continued).

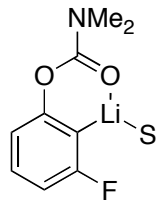


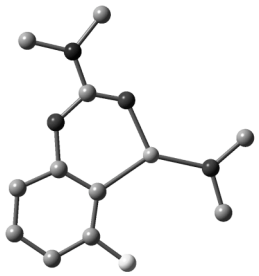


A6
G = -660.832717
(-78 °C)
See pg S67

Atom	X	Y	Z	Atom	X	Y	Z
C	-4.050422	-0.810708	0.018894	C	1.292784	1.728781	0.018752
N	-2.916883	0.100402	-0.039833	H	0.681193	2.626149	0.030590
C	-1.646760	-0.389793	0.001582	H	3.177638	2.766977	0.022533
O	-0.735550	0.577240	0.012614	H	4.528269	0.646987	-0.003890
C	0.702804	0.459376	0.007660	C	-3.239146	1.521228	-0.028479
C	1.378924	-0.751982	-0.006539	H	-2.343606	2.110964	-0.204772
Li	0.220158	-2.346082	0.009898	H	-3.971356	1.733765	-0.816522
O	-1.433154	-1.619433	0.023610	H	-3.677429	1.811749	0.935945
C	2.758669	-0.586646	-0.009757	H	-3.691487	-1.836878	-0.018726
F	3.533728	-1.718387	-0.022388	H	-4.617623	-0.658480	0.946897
C	3.442592	0.624793	-0.000278	H	-4.721258	-0.627605	-0.829397
C	2.683796	1.799088	0.014527				

Table A1 (Continued).

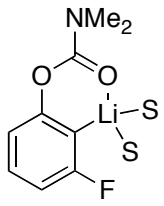


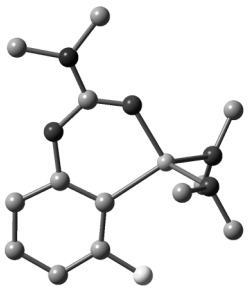


A7
G = -815.812997
(-78 °C)
S=Me_2O
See pg S67

Atom	X	Y	Z	Atom	X	Y	Z
C	3.665407	2.087935	0.010268	H	-2.371550	4.347358	0.960941
N	3.196836	0.713732	-0.072842	C	-1.945166	-1.759068	-0.041667
C	1.858108	0.448421	-0.001814	F	-3.223054	-1.229492	-0.094658
O	1.616280	-0.859669	0.021783	C	-1.877662	-3.147277	0.009208
C	0.340245	-1.531991	0.016297	C	-0.607433	-3.728926	0.067420
C	-0.878161	-0.871934	-0.042226	C	0.525681	-2.918842	0.071701
Li	-0.808469	1.135769	-0.022358	H	1.524027	-3.344600	0.116503
O	1.020616	1.366856	0.032510	H	-0.503079	-4.809827	0.108628
O	-2.137813	2.512625	0.005879	H	-2.781987	-3.748757	0.004145
C	-3.517188	2.134131	0.003650	C	4.225882	-0.316391	-0.047703
H	-4.023883	2.550039	-0.877589	H	3.795670	-1.282663	-0.298280
H	-3.544198	1.044156	-0.026981	H	5.001671	-0.067516	-0.781195
H	-4.012560	2.499290	0.913372	H	4.697649	-0.380473	0.943083
C	-1.932189	3.917832	0.050132	H	2.814222	2.762224	-0.056342
H	-0.853131	4.086842	0.051719	H	4.192388	2.263886	0.958563
H	-2.378233	4.404748	-0.827966	H	4.360241	2.295476	-0.812685

Table A1 (Continued).

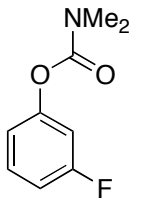


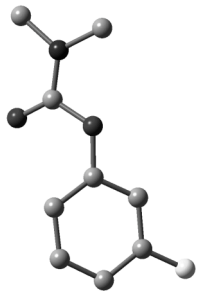


A8
G = -970.776834
(-78 °C)
S=Me_2O
See pg S67

Atom	X	Y	Z	Atom	X	Y	Z
Li	-0.679154	-0.966331	0.065571	H	-0.079640	5.001265	-0.343325
C	-0.583232	1.086798	-0.000816	H	-2.393411	4.022512	-0.179768
C	-1.615081	2.010361	-0.041095	O	-1.742115	-1.876755	-1.373794
F	-2.914226	1.515068	0.033591	C	-1.235574	-3.027579	-2.032935
C	-1.509014	3.392014	-0.159487	H	-2.056753	-3.656572	-2.405615
C	-0.220054	3.927614	-0.250246	H	-0.588518	-2.747454	-2.876369
C	0.885292	3.079426	-0.222582	H	-0.651684	-3.588689	-1.300137
C	0.654712	1.703212	-0.099819	C	-2.517227	-1.037504	-2.229675
O	1.904578	0.986015	-0.081619	H	-2.833119	-0.182319	-1.632139
C	2.081855	-0.333696	-0.020423	H	-1.915463	-0.688961	-3.080227
O	1.203993	-1.208978	-0.007913	H	-3.393092	-1.584839	-2.606602
N	3.411608	-0.657794	0.040554	O	-1.488737	-1.753750	1.743068
C	3.809766	-2.055204	-0.007990	C	-0.832385	-1.225949	2.892809
H	2.935430	-2.683056	0.152061	H	-1.210551	-1.708686	3.805190
H	4.258848	-2.304571	-0.980317	H	0.231184	-1.443435	2.777479
H	4.551997	-2.256954	0.773869	H	-0.976777	-0.139780	2.961147
C	4.485356	0.319119	-0.068485	C	-2.897122	-1.521137	1.772008
H	4.111635	1.313964	0.160265	H	-3.315597	-2.027099	0.900290
H	5.279300	0.062021	0.642543	H	-3.336153	-1.942182	2.687301
H	4.918866	0.323910	-1.079101	H	-3.114680	-0.447537	1.709269
H	1.896913	3.469293	-0.294248				

Table A1 (Continued).

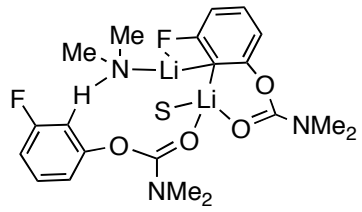


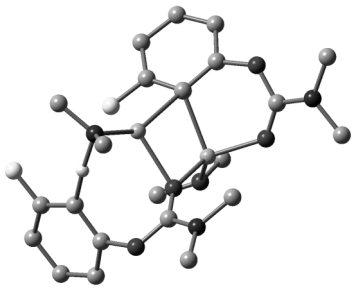


A9
G = -653.870377
(-78 °C)
See pg S68,69

Atom	X	Y	Z
C	-2.385163	1.644281	0.480605
C	-1.028254	1.322421	0.528044
C	-0.636544	0.022115	0.203143
C	-1.572098	-0.948119	-0.154763
C	-2.913428	-0.588360	-0.182096
C	-3.346010	0.695231	0.127355
F	-3.823469	-1.524927	-0.524631
O	0.675330	-0.423564	0.300089
C	1.709565	0.344587	-0.199865
O	1.551540	1.404106	-0.774601
N	2.910978	-0.253860	0.044331
C	3.084100	-1.544887	0.693488
C	4.117312	0.380955	-0.464035
H	-2.698880	2.654655	0.726342
H	-0.287744	2.065132	0.792055
H	-1.262163	-1.956625	-0.402632
H	-4.403688	0.932154	0.089851
H	3.464906	-2.289277	-0.019611
H	3.810881	-1.452879	1.510586
H	2.138108	-1.893876	1.099536
H	3.851159	1.336011	-0.914046
H	4.830631	0.547011	0.353261
H	4.599332	-0.254619	-1.219142

Table A1 (Continued).

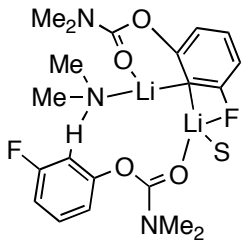


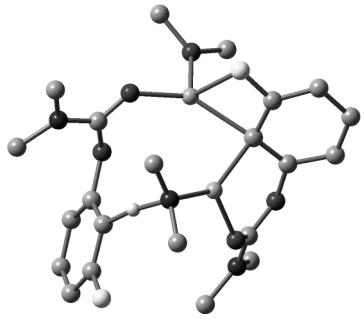


A10
G = -1611.747433
(-78 °C)
S=Me_2O
See pg S68

Atom	X	Y	Z
Li	-0.982916	0.069237	-1.045221
O	0.489335	1.094149	-0.303090
C	1.167285	2.140222	-0.220919
O	2.484168	2.190700	-0.412807
C	3.243811	0.988811	-0.613460
C	3.315935	0.051995	0.404318
C	4.146759	-1.019038	0.099569
C	4.873028	-1.162321	-1.081779
C	4.761590	-0.163858	-2.052148
C	3.932276	0.936752	-1.825653
H	3.829106	1.732004	-2.558386
H	5.320459	-0.241612	-2.980696
H	5.508614	-2.030629	-1.228485
F	4.272257	-2.019059	1.018312
N	0.623375	3.349872	0.049115
C	1.431999	4.543598	0.285026
H	0.967679	5.396456	-0.221699
H	1.491655	4.762908	1.358965
H	2.436532	4.397212	-0.103305
C	-0.790147	3.453478	0.391170
H	-1.342247	2.614191	-0.027855
H	-0.929629	3.467039	1.480501
H	-1.185875	4.386143	-0.024163
Li	0.445000	-0.396247	1.137625
C	-1.452778	-1.403123	0.471651
C	-2.826653	-1.620972	0.499568
O	-3.764125	-0.540378	0.508188
C	-3.638204	0.550203	-0.256134
O	-2.770558	0.722877	-1.127447
N	-4.598592	1.476166	0.012213
C	-4.722500	2.654810	-0.833381
H	-3.880399	2.694898	-1.521528
H	-5.656726	2.618316	-1.409915
H	-4.735432	3.560401	-0.214930
C	-5.662755	1.267694	0.987459
H	-6.601569	0.982466	0.492960
H	-5.379760	0.488533	1.691110
H	-5.831511	2.201438	1.535088
C	-3.454331	-2.865359	0.607454
C	-2.655180	-4.005693	0.703373
C	-1.262771	-3.883878	0.687125
C	-0.757531	-2.596213	0.565368
F	0.638519	-2.471838	0.551559
H	-0.606307	-4.744406	0.769214
H	-3.115260	-4.985299	0.796402
H	-4.537968	-2.934383	0.625098
N	1.658072	0.052566	2.579456
C	2.066884	-1.032191	3.459743
H	2.158348	-1.963092	2.886679
H	3.048260	-0.846936	3.940787
H	1.343884	-1.211664	4.276978
C	1.677539	1.313113	3.293850
H	0.938103	1.354822	4.116110
H	2.663216	1.538756	3.750935
H	1.442889	2.145695	2.612598
O	-0.431937	-0.810187	-2.729097
C	-1.422625	-1.651002	-3.314486
H	-1.193739	-1.831659	-4.373604
H	-1.480166	-2.610927	-2.783911
H	-2.377086	-1.128548	-3.229141
C	0.876028	-1.387455	-2.787776
H	0.907055	-2.332419	-2.231145
H	1.162739	-1.564934	-3.832906
H	1.565331	-0.676218	-2.332802
H	2.565551	0.095598	1.543904

Table A1 (Continued).

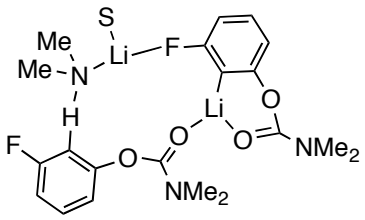


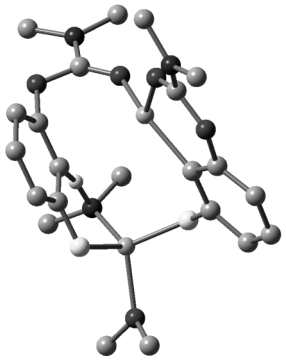


A11
G = -1611.735290
(-78 °C)
S=Me_2O
See pg S68

Atom	X	Y	Z	Atom	X	Y	Z
Li	-1.321363	-1.747387	-0.313956	C	-1.535831	4.021621	-2.193091
O	0.320680	-2.663494	-0.176337	H	-4.846744	2.404403	0.558302
C	1.443795	-2.232624	-0.490336	H	-6.122799	0.592058	1.719466
O	1.502108	-1.127200	-1.266912	H	-5.030233	-1.652158	2.063418
C	2.385697	-0.032233	-1.012581	H	0.877064	3.897978	0.189259
C	2.624460	0.393034	0.288261	H	1.177278	3.842269	-1.561596
C	3.482769	1.487743	0.348433	H	0.444613	5.297183	-0.832532
C	4.055742	2.131027	-0.747278	H	-1.562601	5.114912	-2.273585
C	3.745019	1.658560	-2.024411	H	-1.014883	3.624056	-3.074526
C	2.900535	0.557472	-2.169736	H	-2.554042	3.640291	-2.178833
F	3.793475	1.995586	1.575033	H	4.461005	-1.915372	0.031261
N	2.583870	-2.878952	-0.169988	H	4.457752	-3.472773	-0.844074
C	2.537259	-3.999168	0.766401	H	3.834442	-2.008400	-1.626936
C	3.909342	-2.539178	-0.680075	H	1.514695	-4.145720	1.105342
O	-2.205063	-2.459423	-1.920809	H	2.892966	-4.912604	0.273865
C	-1.882846	-3.750620	-2.425102	H	3.179834	-3.787643	1.628526
C	-3.346593	-1.882030	-2.544861	H	1.886211	0.075857	1.370988
C	-2.411794	-0.035663	0.478884	H	2.647758	0.159098	-3.148349
Li	-0.514306	0.579214	1.483723	H	4.169566	2.138460	-2.902173
N	1.022255	-0.041176	2.479385	H	4.719951	2.976660	-0.595626
C	1.183552	-1.370806	3.039028	H	0.651088	-1.493614	4.000528
C	1.505833	0.950873	3.434510	H	0.781305	-2.124915	2.352431
O	-0.683010	2.372066	0.916285	H	2.245783	-1.629650	3.242680
C	-1.300121	2.716090	-0.097724	H	1.407889	1.959831	3.014848
O	-2.514910	2.234503	-0.438542	H	0.939469	0.926449	4.383749
C	-3.093644	1.171596	0.307647	H	2.572742	0.812666	3.696364
C	-4.398456	1.431096	0.733805	H	-0.999066	-4.088424	-1.882223
C	-5.107015	0.414243	1.378087	H	-2.713107	-4.451365	-2.259721
C	-4.510241	-0.833112	1.576668	H	-1.661616	-3.701699	-3.500352
C	-3.206705	-0.971479	1.117863	H	-4.234312	-2.511077	-2.391647
F	-2.628117	-2.245819	1.263227	H	-3.503885	-0.908244	-2.079379
N	-0.839571	3.644045	-0.971141	H	-3.173966	-1.757689	-3.622915
C	0.494294	4.203017	-0.782307				

Table A1 (Continued).

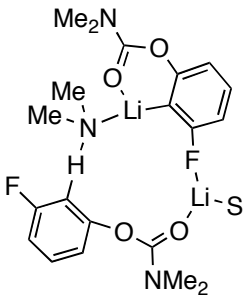


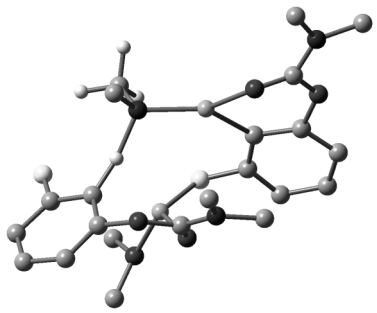


A12
G = -1611.750819
(-78 °C)
S=Me_2O
See pg S68

Atom	X	Y	Z
Li	0.999573	0.610510	-0.627879
O	0.191034	2.263591	-1.135255
C	-0.446730	3.173712	-0.599983
O	-0.704981	3.230254	0.728853
C	-0.470694	2.060544	1.491656
C	-1.194165	0.909200	1.205325
C	-0.891649	-0.150509	2.035097
C	0.003370	-0.143514	3.095139
C	0.676516	1.056732	3.344253
C	0.451630	2.172148	2.532629
H	0.975598	3.108006	2.702208
H	1.385179	1.118351	4.165034
H	0.172643	-1.031977	3.695218
F	-1.556018	-1.355760	1.772089
H	-2.194628	0.730250	0.353053
N	-0.929968	4.246015	-1.271827
C	-0.729385	4.338993	-2.711272
H	-0.052398	3.549117	-3.030861
H	-1.685778	4.230305	-3.238632
H	-0.299783	5.316064	-2.963575
C	-1.768001	5.272966	-0.667010
H	-1.827589	5.123614	0.408078
H	-1.344138	6.264029	-0.870977
H	-2.779775	5.234768	-1.091259
C	1.102368	-1.450780	-0.912555
C	2.354196	-2.059885	-0.870223
O	3.541000	-1.409902	-0.407221
C	3.695053	-0.102136	-0.167064
O	2.863673	0.788922	-0.372825
N	4.930181	0.168145	0.353200
C	5.328085	1.552075	0.558711
H	4.455268	2.193954	0.457210
H	5.755378	1.670030	1.561874
H	6.086156	1.855696	-0.177271
C	5.973882	-0.832972	0.519235
H	5.539042	-1.829227	0.541611
H	6.709444	-0.781731	-0.296551
H	6.498270	-0.650198	1.464312
C	2.635347	-3.384945	-1.228417
C	1.589727	-4.192009	-1.670837
C	0.295859	-3.665768	-1.739806
C	0.148629	-2.340345	-1.352743
F	-1.191709	-1.860382	-1.438850
Li	-2.468638	-1.446791	-0.101181
N	-3.325499	0.292769	-0.380637
C	-4.486162	0.757885	0.351986
H	-4.445547	0.403411	1.392756
H	-4.564429	1.865291	0.390511
H	-5.444795	0.403728	-0.076953
C	-3.304872	0.862491	-1.714541
H	-4.163501	0.540357	-2.335493
H	-3.333417	1.974725	-1.712379
H	-2.390791	0.559043	-2.240814
O	-3.441493	-3.133063	0.247004
C	-4.812763	-3.063456	0.622377
H	-5.206357	-2.132614	0.211828
H	-5.368618	-3.916988	0.210436
H	-4.918760	-3.057599	1.716486
C	-2.783875	-4.293840	0.742711
H	-2.798904	-4.313085	1.841388
H	-3.266850	-5.203061	0.358859
H	-1.751230	-4.254840	0.390860
H	-0.546895	-4.253044	-2.092571
H	1.778947	-5.221408	-1.962049
H	3.649933	-3.767276	-1.161922

Table A1 (Continued).



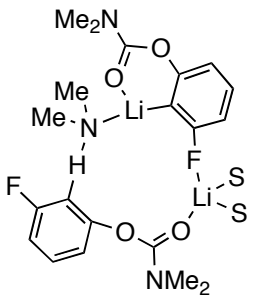


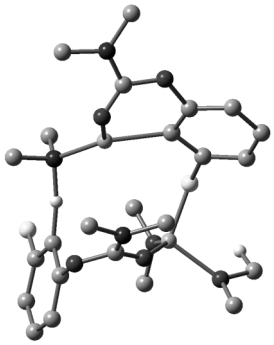
A13
G = -1611.744505
(-78 °C)
S=Me_2O
See pg S68

Atom	X	Y	Z	Atom	X	Y	Z
C	0.564709	-0.712537	-3.126678	H	6.191169	-2.042205	0.942146
N	0.305432	-1.310002	-1.822236	H	6.040651	-0.920723	-1.298575
Li	-1.322245	-0.545890	-1.066903	F	3.859559	-0.090618	-2.376807
C	-1.836095	1.392537	-0.525336	N	-0.273704	-1.316042	2.449133
C	-3.098557	1.623133	0.009376	C	-0.594145	-2.730306	2.609818
O	-4.183099	0.701077	-0.149614	H	-1.477394	-2.978981	2.009434
C	-4.045017	-0.608511	-0.400433	H	0.242424	-3.345825	2.289119
O	-2.983134	-1.247162	-0.380425	H	-0.815104	-2.939162	3.663710
N	-5.243651	-1.202445	-0.667666	C	-1.305906	-0.372669	2.868100
C	-5.298498	-2.636312	-0.907713	H	-2.220358	-0.547478	2.292140
H	-4.286746	-3.036577	-0.923444	H	-1.517556	-0.510280	3.935559
H	-5.876610	-3.137274	-0.119195	H	-0.963926	0.643807	2.687573
H	-5.784080	-2.837142	-1.870809	O	3.089978	2.417227	0.129795
C	-6.521185	-0.503964	-0.665619	C	4.145422	2.192943	1.061745
H	-7.048047	-0.695542	-1.608703	H	4.922654	1.554114	0.624094
H	-7.154262	-0.860748	0.158538	H	4.585021	3.149305	1.375259
H	-6.363811	0.565861	-0.557046	H	3.704110	1.690580	1.923981
C	-3.501090	2.773641	0.696293	C	3.525399	3.068766	-1.063189
C	-2.570186	3.798156	0.872832	H	3.997168	4.030517	-0.821777
C	-1.272971	3.650718	0.370642	H	4.231143	2.435980	-1.615278
C	-1.005425	2.457472	-0.285345	H	2.635412	3.243565	-1.670020
F	0.346210	2.338476	-0.761105	H	-0.519480	4.423878	0.486908
Li	1.584505	1.161305	0.040247	H	-2.852366	4.707095	1.396658
O	1.090511	0.338606	1.663404	H	-4.515336	2.865306	1.074870
C	0.846702	-0.862163	1.853206	C	0.402683	-2.757466	-1.927993
O	1.705175	-1.854340	1.516290	H	-0.327122	-3.189391	-2.641433
C	2.850684	-1.536617	0.754950	H	1.401715	-3.105953	-2.267008
C	2.703696	-0.923119	-0.489355	H	0.216131	-3.225084	-0.950680
C	3.900106	-0.725801	-1.169341	H	0.464384	0.380581	-3.068174
C	5.155095	-1.103195	-0.697451	H	1.582615	-0.929092	-3.510570
C	5.228390	-1.726681	0.550253	H	-0.139221	-1.060644	-3.909015
C	4.068499	-1.938515	1.298648	H	1.581696	-0.951520	-1.055359

H 4.100591 -2.414836 2.273597

Table A1 (Continued).

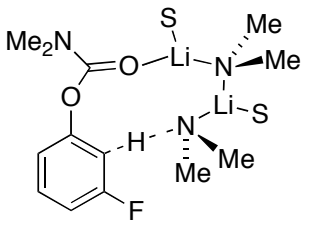


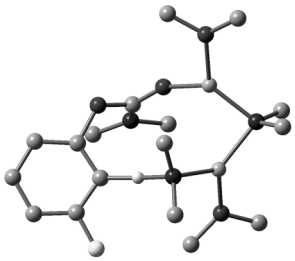


A14
G = -1766.702728
(-78 °C)
S=Me_2O
See pg S68

Atom	X	Y	Z
Li	1.743046	1.541289	-0.166678
O	1.274767	0.701012	1.443227
C	0.733729	-0.264780	2.007190
N	-0.457241	-0.186180	2.642251
C	-1.176857	1.079068	2.707714
H	-2.131270	0.996507	2.178449
H	-1.367856	1.340268	3.756687
H	-0.584347	1.860361	2.237725
C	-1.138895	-1.335730	3.230693
H	-0.514845	-2.221972	3.150045
H	-1.350280	-1.136991	4.289086
H	-2.083816	-1.508035	2.703043
O	1.292902	-1.481603	2.091977
C	2.440521	-1.778551	1.296649
C	2.256021	-2.044128	-0.053197
C	3.424671	-2.431636	-0.692594
C	4.675449	-2.558898	-0.090632
C	4.780078	-2.273948	1.273472
C	3.649195	-1.871184	1.986172
H	3.696276	-1.653524	3.049329
H	5.737616	-2.369444	1.778105
H	5.532429	-2.885778	-0.672878
F	3.370515	-2.701695	-2.039562
F	0.252872	1.989983	-1.282918
C	-1.121021	2.223169	-0.953976
C	-1.419145	3.560432	-0.723320
C	-2.742216	3.854291	-0.382074
C	-3.673685	2.819647	-0.297567
C	-3.245074	1.514736	-0.564889
C	-1.950798	1.128093	-0.910111
Li	-1.497674	-0.923391	-0.707180
O	-3.168247	-1.230075	0.245099
C	-4.209474	-0.696193	-0.159264
O	-4.335221	0.589332	-0.524596
N	-5.385562	-1.375649	-0.268931
C	-5.438674	-2.782313	0.100309
H	-4.434313	-3.130065	0.333750
H	-6.087829	-2.927402	0.974526
H	-5.843922	-3.371633	-0.731529
C	-6.642282	-0.774039	-0.691389
H	-7.053714	-1.331144	-1.542478
H	-7.375645	-0.806828	0.125931
H	-6.482489	0.259500	-0.986987
N	-0.234429	-2.354434	-1.142640
C	0.005525	-2.476815	-2.576115
H	0.197162	-1.486816	-3.012810
H	0.880220	-3.113564	-2.813812
H	-0.857416	-2.908794	-3.117820
C	-0.551607	-3.665567	-0.592420
H	-1.464975	-4.106648	-1.034270
H	0.259768	-4.406516	-0.746384
H	-0.716089	-3.590115	0.491266
H	-4.710623	3.016550	-0.040311
H	-3.044190	4.880127	-0.190424
H	-0.664716	4.336685	-0.813383
O	3.046982	1.240311	-1.631254
C	4.440209	1.131516	-1.350536
H	4.626001	1.702342	-0.438260
H	4.727896	0.085593	-1.194485
H	5.030371	1.556581	-2.174897
C	2.669996	0.552631	-2.830500
H	1.593056	0.682787	-2.938741
H	3.185717	0.996727	-3.693458
H	2.910193	-0.512353	-2.758864
O	2.523886	3.279566	0.482055
C	2.441199	3.699381	1.839865
H	2.232092	2.807243	2.430344
H	3.389464	4.151475	2.162383
H	1.631723	4.430931	1.973276
C	2.755801	4.353748	-0.420908
H	2.815592	3.919249	-1.419687
H	1.934728	5.083281	-0.381286
H	3.699294	4.864532	-0.182420
H	1.026204	-2.103495	-0.607138

Table A1 (Continued).

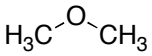


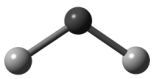


A15
G = -1247.905576
(-78 °C)
S=Me_2O
See pg S69

Atom	X	Y	Z	Atom	X	Y	Z
C	-4.597855	-0.432083	-1.063330	H	0.977044	0.414029	2.697038
C	-4.607581	-1.712094	-0.503362	H	-0.476131	1.256072	3.291076
C	-3.444745	-2.233715	0.065548	H	0.209083	-0.103771	4.217827
C	-2.290570	-1.449118	0.038822	H	-2.177145	-0.731798	4.020502
C	-2.189830	-0.190360	-0.542405	H	-2.834422	0.014311	2.537269
C	-3.394535	0.267480	-1.062174	H	-2.596922	-1.742981	2.624618
F	-3.404718	1.515593	-1.628318	H	-0.234598	-0.955136	-3.037196
O	-1.138714	-2.047064	0.638482	H	1.436825	-0.367651	-2.975350
C	-0.299246	-1.301118	1.394072	H	0.733064	-1.241939	-1.589765
N	-0.816326	-0.635148	2.451557	H	-0.774456	2.580302	-2.395152
C	-2.188667	-0.780672	2.926523	H	0.396242	1.894333	-3.538997
C	0.025476	0.284936	3.207981	H	-1.233650	1.207153	-3.413666
O	0.915560	-1.325007	1.151811	H	3.388022	1.074898	-2.062303
Li	2.398435	-0.820431	0.108489	H	4.104754	2.451035	-1.194784
N	3.049527	1.018122	0.019750	H	4.879649	0.869234	-1.114411
C	3.880547	1.363136	-1.122160	H	3.143936	1.174699	2.122574
Li	1.215913	1.628048	-0.434855	H	4.728570	0.915079	1.364548
N	0.059858	0.745951	-1.763305	H	3.969966	2.503963	1.281395
C	0.520455	-0.495161	-2.367862	H	5.248270	-3.196620	-0.493276
C	-0.404347	1.638027	-2.819280	H	4.521527	-2.808903	-2.083318
O	0.338493	3.139843	0.494997	H	5.004878	-1.489681	-0.976163
C	-1.040193	3.483761	0.365008	H	1.655848	-3.559420	0.007651
C	1.119894	4.193043	1.047021	H	2.503592	-4.066299	-1.486714
C	3.742314	1.414068	1.230221	H	3.199427	-4.464928	0.115214
O	3.302846	-2.458300	-0.431246	H	-1.471147	3.704603	1.352059
C	4.592742	-2.498526	-1.031841	H	-1.159045	4.364909	-0.280470
C	2.631447	-3.716011	-0.453468	H	-1.553895	2.632345	-0.081232
H	-1.062824	0.348254	-1.013596	H	2.147582	3.832115	1.108961
H	-5.523221	-2.296986	-0.499432	H	1.078074	5.086674	0.408313
H	-3.430168	-3.219523	0.522128	H	0.761447	4.457045	2.052231
H	-5.489490	0.009577	-1.497865				

Table A1 (Continued).

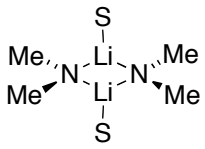


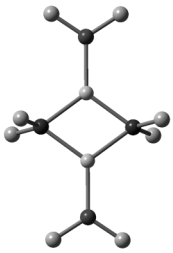


A16
G = -154.959965
(-78 °C)
See pg S66,67,68

Atom	X	Y	Z	Atom	X	Y	Z
O	-0.000002	-0.590096	0.000019	H	-1.231078	0.841249	-0.891928
C	1.170987	0.195373	-0.000004	H	1.232122	0.839832	0.892886
C	-1.170983	0.195373	0.000003	H	2.021832	-0.491270	0.000142
H	-2.021833	-0.491263	-0.002201	H	1.232128	0.839577	-0.893071
H	-1.233173	0.838164	0.894024				

Table A1 (Continued).





A17
G = -594.069311
(-78 °C)
S=Me_2O
See pg S69

Atom	X	Y	Z	Atom	X	Y	Z
N	-0.000649	1.589387	0.003319	H	4.444149	-1.235814	-0.932190
Li	-1.176636	-0.000012	-0.097348	H	-0.732842	-3.107130	-1.337374
Li	1.177294	0.000852	0.102285	H	1.020614	-3.108821	-1.132982
N	0.000692	-1.588611	0.003054	H	0.242525	-1.820982	-2.078905
O	-3.110978	-0.000835	-0.088970	H	-1.022193	3.107662	1.140457
O	3.111475	0.000403	0.084379	H	0.731236	3.107385	1.345242
C	3.885448	1.192440	0.011343	H	-0.243116	1.819717	2.085447
C	3.883735	-1.192812	0.012062	H	-0.734691	3.108634	-1.336048
C	0.134913	2.432935	-1.166776	H	0.242004	1.823917	-2.078285
C	-0.137300	2.430602	1.175038	H	1.018639	3.111461	-1.130712
C	-0.135087	-2.430971	1.173991	H	-4.585224	-1.252312	-0.863099
C	0.136335	-2.430962	-1.167926	H	-4.449062	-1.235266	0.922615
C	-3.884344	1.191814	-0.020739	H	-3.181288	-2.027104	-0.063311
C	-3.884231	-1.193467	-0.019058	H	-4.449252	1.234885	0.920844
H	3.183423	2.026686	0.058562	H	-3.181463	2.025447	-0.066048
H	4.446346	1.233824	-0.932697	H	-4.585319	1.249439	-0.864880
H	4.590033	1.250584	0.852423	H	-0.241535	-1.821014	2.084943
H	3.180515	-2.025986	0.060318	H	0.734114	-3.107076	1.343657
H	4.588608	-1.251189	0.852886	H	-1.019284	-3.108935	1.138825

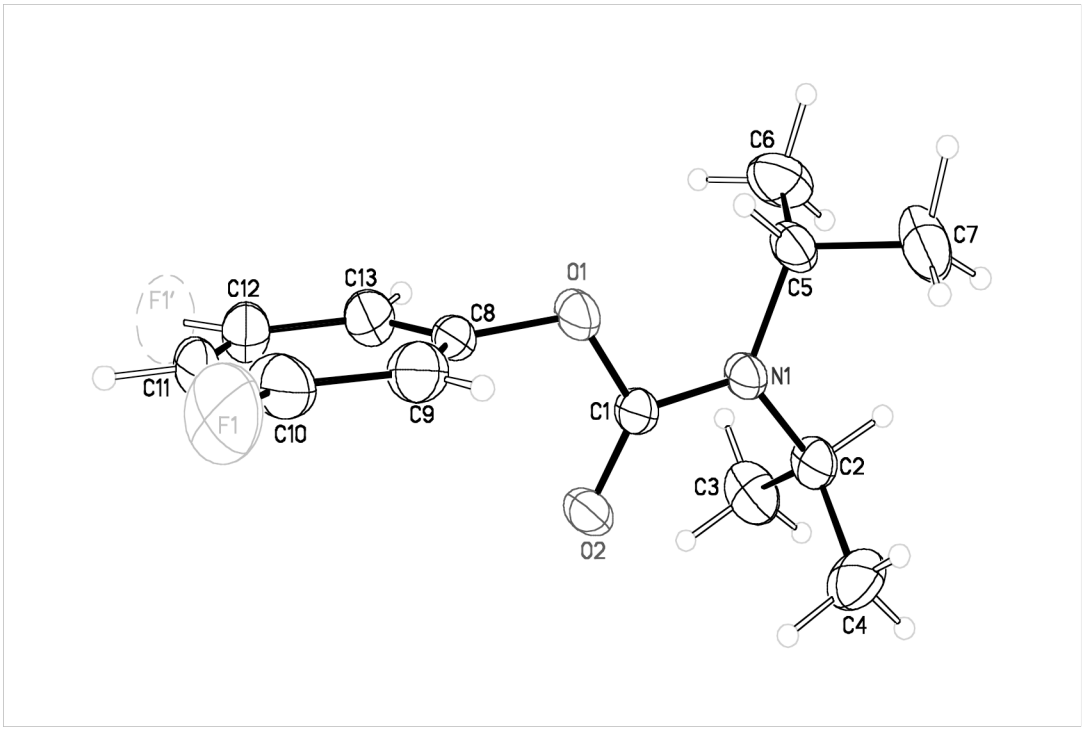


Figure 47. ORTEP of **1** revealing the orientation of the carbonyl group (C1-O2) relative to the *N,N*-diisopropyl groups (C2-C4 and C5-C7). The *meta* fluorine (F1) shows disorder between the two *meta* positions.

Figure 47 (Continued).

Crystal data and structure refinement for **1**.

Identification code	**1**
Empirical formula	C13 H17 F N O2
Formula weight	238.28
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 10.7977(4) Å # = 90°. b = 11.3149(5) Å = 116.2230(10)°. c = 11.9339(5) Å %= 90°.
Volume	1307.96(9) $Å^3$
Z	4
Density (calculated)	1.210 Mg/m^3
Absorption coefficient	0.091 mm^{-1}
F(000)	508
Crystal size	0.40 x 0.30 x 0.10 mm^3
Theta range for data collection	2.10 to 28.31°.
Index ranges	-14<=h<=11, -14<=k<=15, -15<=l<=15
Reflections collected	16281
Independent reflections	3231 [R(int) = 0.0298]
Completeness to theta = 28.31°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9910 and 0.9647
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3231 / 0 / 232
Goodness-of-fit on F^2	1.058
Final R indices [I>2sigma(I)]	R1 = 0.0415, wR2 = 0.1163
R indices (all data)	R1 = 0.0612, wR2 = 0.1267
Largest diff. peak and hole	0.184 and -0.233 $e.Å^{-3}$

Figure 47 (Continued).

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	1435(2)	317(1)	4340(2)	101(1)
F(1')	-433(4)	851(3)	463(3)	99(1)
O(1)	2238(1)	3971(1)	2884(1)	47(1)
O(2)	3982(1)	3358(1)	2471(1)	49(1)
N(1)	3750(1)	5307(1)	2820(1)	35(1)
C(1)	3398(1)	4167(1)	2698(1)	35(1)
C(2)	4960(1)	5677(1)	2626(1)	43(1)
C(3)	4806(2)	5384(1)	1335(2)	59(1)
C(4)	6297(2)	5214(2)	3645(2)	64(1)
C(5)	2902(1)	6241(1)	2996(1)	45(1)
C(6)	2073(2)	6884(2)	1780(2)	71(1)
C(7)	3752(2)	7083(2)	4039(2)	67(1)
C(8)	1722(1)	2825(1)	2694(1)	44(1)
C(9)	1974(2)	2129(1)	3709(2)	59(1)
C(10)	1349(2)	1022(1)	3470(2)	80(1)
C(11)	527(2)	618(1)	2292(2)	81(1)
C(12)	296(2)	1348(2)	1309(2)	76(1)
C(13)	880(2)	2458(1)	1492(2)	57(1)

Figure 47 (Continued).

Bond lengths [Å] and angles [°] for **1**.

F(1)-C(10)	1.279(2)
F(1')-C(12)	1.118(3)
O(1)-C(1)	1.3827(13)
O(1)-C(8)	1.3906(13)
O(2)-C(1)	1.2086(13)
N(1)-C(1)	1.3348(13)
N(1)-C(5)	1.4725(14)
N(1)-C(2)	1.4838(14)
C(2)-C(3)	1.512(2)
C(2)-C(4)	1.512(2)
C(5)-C(6)	1.513(2)
C(5)-C(7)	1.513(2)
C(8)-C(9)	1.367(2)
C(8)-C(13)	1.380(2)
C(9)-C(10)	1.391(2)
C(10)-C(11)	1.368(3)
C(11)-C(12)	1.365(3)
C(12)-C(13)	1.379(2)
C(1)-O(1)-C(8)	116.72(8)
C(1)-N(1)-C(5)	122.98(9)
C(1)-N(1)-C(2)	118.89(9)
C(5)-N(1)-C(2)	117.75(9)
O(2)-C(1)-N(1)	127.24(10)
O(2)-C(1)-O(1)	120.95(9)
N(1)-C(1)-O(1)	111.80(9)
N(1)-C(2)-C(3)	112.93(11)
N(1)-C(2)-C(4)	111.77(11)
C(3)-C(2)-C(4)	112.29(13)
N(1)-C(5)-C(6)	110.45(11)
N(1)-C(5)-C(7)	112.33(12)
C(6)-C(5)-C(7)	111.91(13)
C(9)-C(8)-C(13)	121.97(13)
C(9)-C(8)-O(1)	118.96(13)

Figure 47 (Continued).

C(13)-C(8)-O(1)	118.86(12)
C(8)-C(9)-C(10)	116.66(18)
F(1)-C(10)-C(11)	114.02(17)
F(1)-C(10)-C(9)	122.7(2)
C(11)-C(10)-C(9)	123.13(17)
C(12)-C(11)-C(10)	118.12(14)
F(1')-C(12)-C(11)	105.1(3)
F(1')-C(12)-C(13)	133.7(3)
C(11)-C(12)-C(13)	121.16(19)
C(12)-C(13)-C(8)	118.94(17)

Symmetry transformations used to generate equivalent atoms:

Figure 47 (Continued).

Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	101(1)	68(1)	126(1)	50(1)	43(1)	-8(1)
F(1')	92(2)	92(2)	99(2)	-59(2)	30(2)	-36(2)
O(1)	48(1)	27(1)	84(1)	-8(1)	45(1)	-7(1)
O(2)	48(1)	27(1)	88(1)	-1(1)	45(1)	1(1)
N(1)	38(1)	25(1)	50(1)	-1(1)	26(1)	-3(1)
C(1)	34(1)	28(1)	47(1)	1(1)	22(1)	-1(1)
C(2)	46(1)	31(1)	63(1)	1(1)	34(1)	-7(1)
C(3)	80(1)	45(1)	75(1)	0(1)	57(1)	-8(1)
C(4)	41(1)	61(1)	90(1)	6(1)	29(1)	-10(1)
C(5)	52(1)	27(1)	69(1)	-6(1)	39(1)	-3(1)
C(6)	70(1)	49(1)	93(1)	11(1)	35(1)	21(1)
C(7)	94(1)	46(1)	84(1)	-25(1)	60(1)	-21(1)
C(8)	36(1)	26(1)	81(1)	-3(1)	37(1)	-3(1)
C(9)	52(1)	44(1)	90(1)	12(1)	39(1)	1(1)
C(10)	75(1)	41(1)	151(2)	26(1)	76(1)	6(1)
C(11)	62(1)	35(1)	174(2)	-19(1)	78(1)	-14(1)
C(12)	58(1)	49(1)	138(2)	-33(1)	57(1)	-17(1)
C(13)	53(1)	43(1)	83(1)	-12(1)	38(1)	-6(1)

Figure 47 (Continued).

Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **1**.

	x	y	z	U(eq)
H(2)	4972(12)	6536(12)	2701(11)	35(3)
H(3C)	3870(20)	5670(17)	677(18)	88(6)
H(3B)	4817(17)	4537(15)	1219(15)	66(4)
H(3A)	5532(19)	5766(15)	1197(16)	75(5)
H(4C)	6360(17)	4350(17)	3581(15)	70(5)
H(4A)	6330(20)	5409(17)	4461(19)	84(6)
H(4A)	7070(20)	5530(16)	3517(17)	87(6)
H(5)	2289(14)	5838(12)	3237(12)	44(3)
H(6C)	1470(20)	6320(20)	1120(20)	107(7)
H(6B)	2681(17)	7291(14)	1509(14)	58(4)
H(6A)	1463(19)	7461(17)	1909(16)	82(5)
H(7C)	4322(19)	6665(16)	4820(17)	80(6)
H(7B)	3060(20)	7622(19)	4160(18)	94(6)
H(7A)	4374(18)	7609(15)	3808(15)	71(5)
H(9)	2560(20)	2386(16)	4537(17)	81(6)
H(11)	130(20)	-150(20)	2173(19)	98(6)
H(13)	704(19)	3027(17)	767(18)	91(6)

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