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Structural and Rate Studies of the 1,2-Additions of
Lithium Phenylacetylide to Lithiated Quinazolinones:
Influence of Mixed Aggregates on the Reaction Mechanism

Timothy F. Briggs,[†] Mark D. Winemiller,[†] David B. Collum^{†*}
Rodney L. Parsons, Jr.,^{*} Akin H. Davulcu,^{*} Gregory D. Harris,^{*}
Joseph M. Fortunak^{*} and Pat N. Confalone^{*}

Contribution from the Department of Chemistry and Chemical Biology
Baker Laboratory, Cornell University, Ithaca, New York 14853-1301
Bristol Myers-Squibb Co., Process Research and Development
One Squibb Dr., New Brunswick, New Jersey 08903

[†]Cornell University

^{*}Bristol Myers-Squibb Co.

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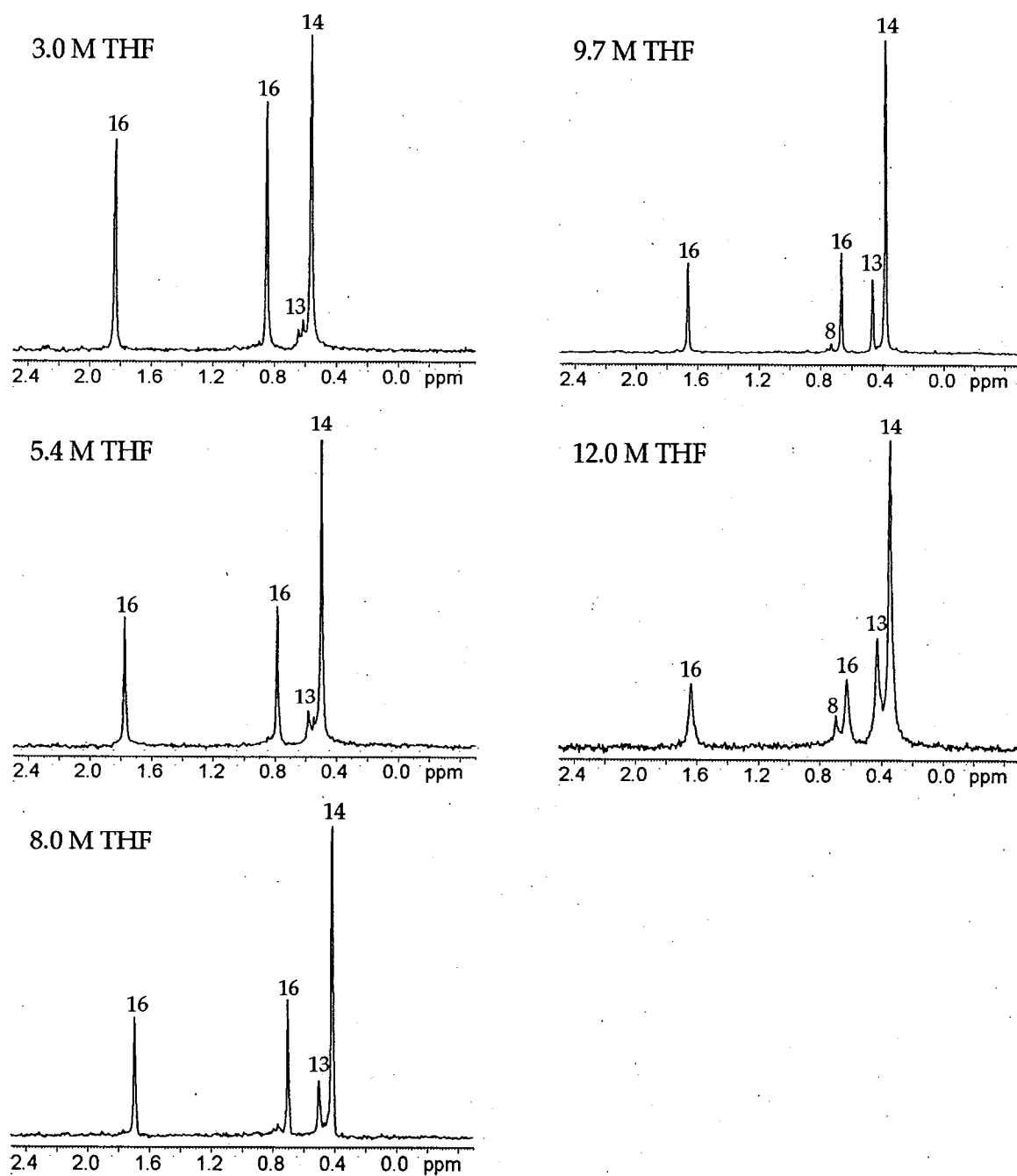


Figure 1. ^6Li NMR spectra recorded at $-120\text{ }^\circ\text{C}$ of solutions of 0.067 N $[\text{}^6\text{Li}]\text{PhCClLi}$ and 0.033 N $[\text{}^6\text{Li}]\text{8}$ at the THF concentrations indicated (pentane cosolvent).

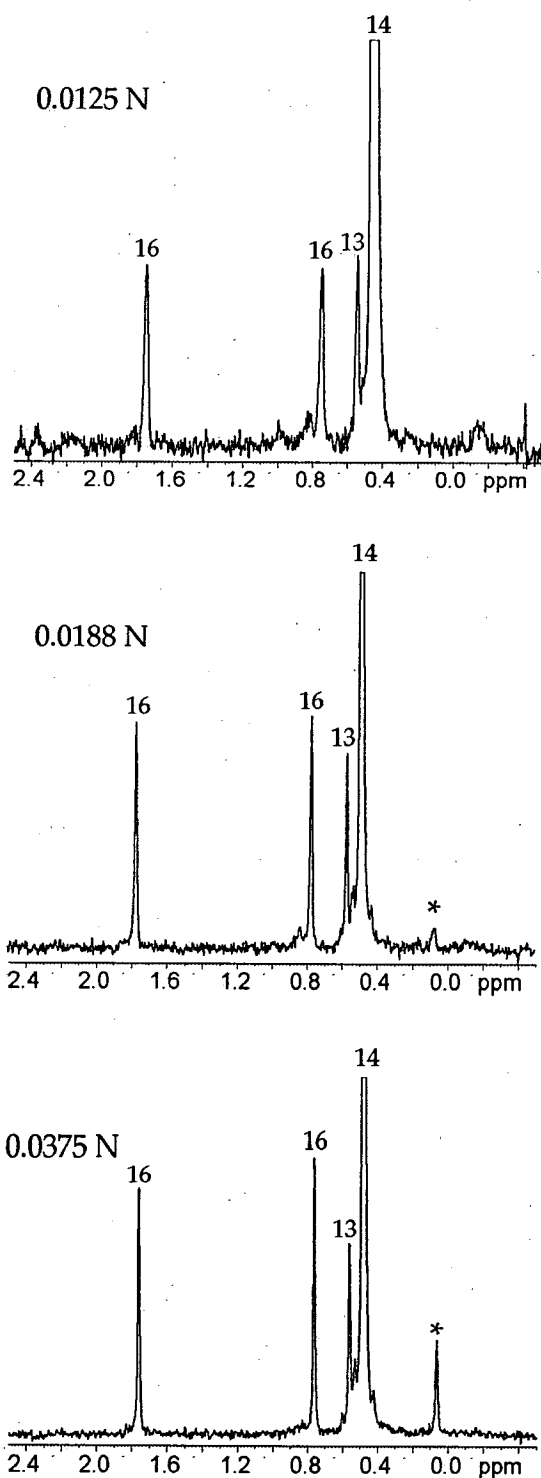


Figure 2. ^6Li NMR spectra recorded at -115°C of 9 M THF/pentane solutions containing ^6Li 8 at the concentrations labelled on each spectrum and excess ^6Li PhCCl. ^6Li LiHMDS is indicated by an asterisk (*).

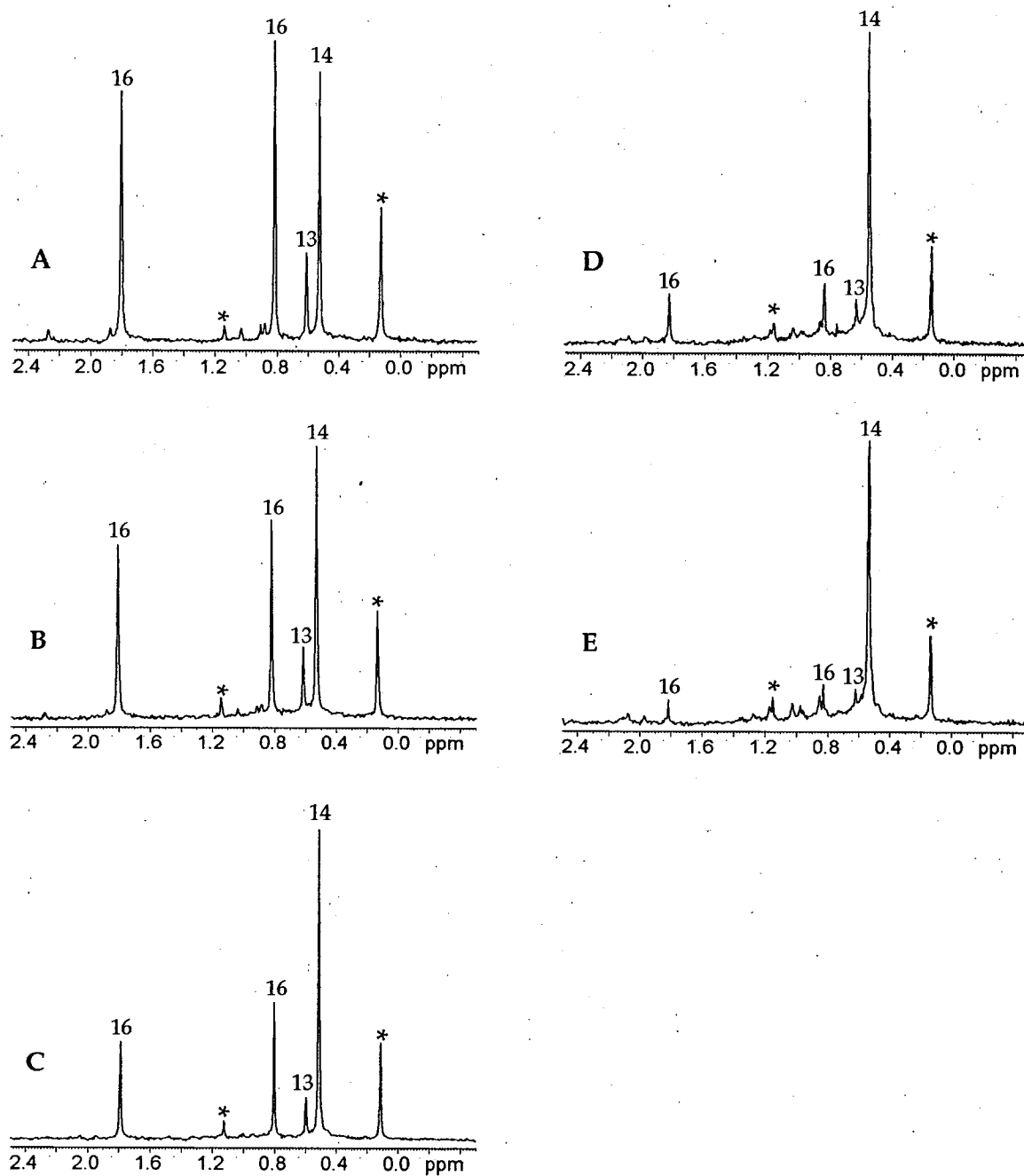


Figure 3. ^6Li NMR spectra recorded at $-120\text{ }^\circ\text{C}$ on $0.067\text{ N } [^6\text{Li}]\text{PhCClLi}$ and $0.033\text{ N } [^6\text{Li}]\text{8}$ in 6.0 M THF/pentane containing residual $[^6\text{Li}]\text{LiHMDS}$ (marked by *) after being warmed at $0\text{ }^\circ\text{C}$ for the following time intervals: (A) 0 min ; (B) 10 min ; (C) 30 min ; (D) 60 min ; (E) $>90\text{ min}$.

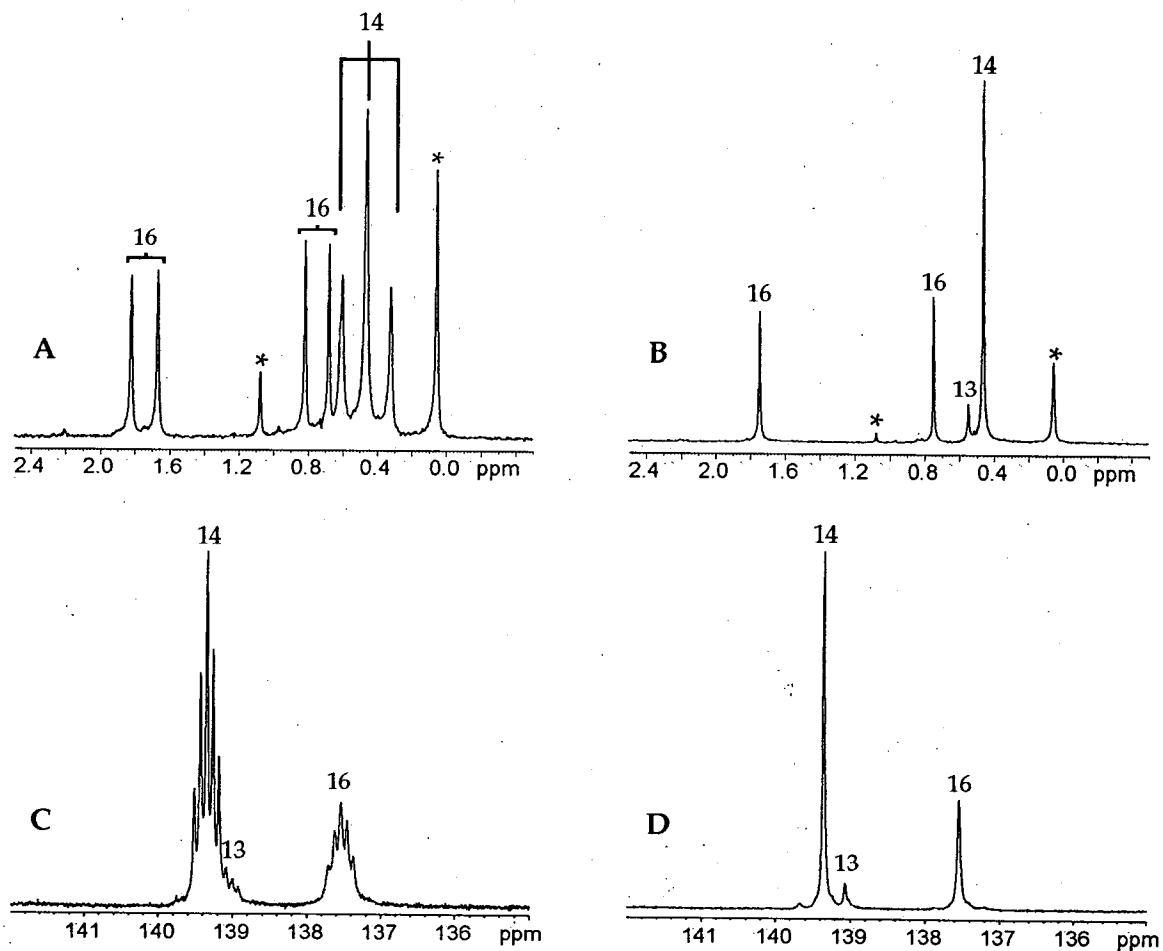


Figure 4. ^6Li and ^{13}C NMR spectra recorded at $-115\text{ }^\circ\text{C}$ on 0.133 N $[\text{}^6\text{Li}, \text{}^{13}\text{C}]\text{PhCCLi}$ and 0.067 N $[\text{}^6\text{Li}]\mathbf{8}$ in 7.6 M THF/pentane containing residual $[\text{}^6\text{Li}]\text{LiHMDS}$ (marked by *): (A) ^6Li spectrum; (B) ^6Li spectrum (^{13}C decoupled); (C) ^{13}C spectrum; (D) ^{13}C spectrum (^6Li decoupled).

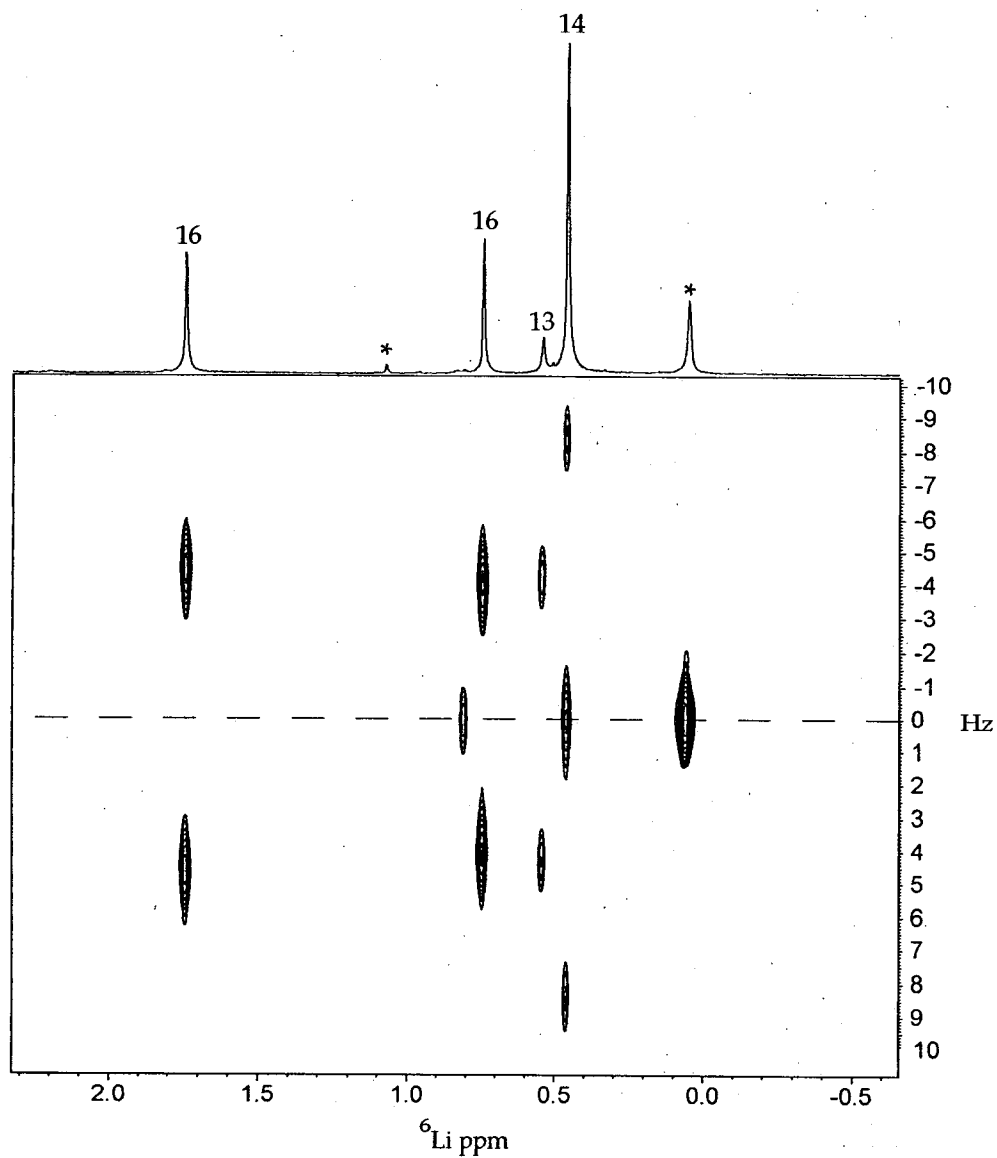


Figure 5. *J*-Resolved spectrum recorded on 0.133 N [^6Li , ^{13}C]PhCCLi and 0.067 N [^6Li]8 in 7.6 M THF/pentane at $-115\text{ }^\circ\text{C}$. [^6Li]LiHMDS is indicated by an asterisk (*).

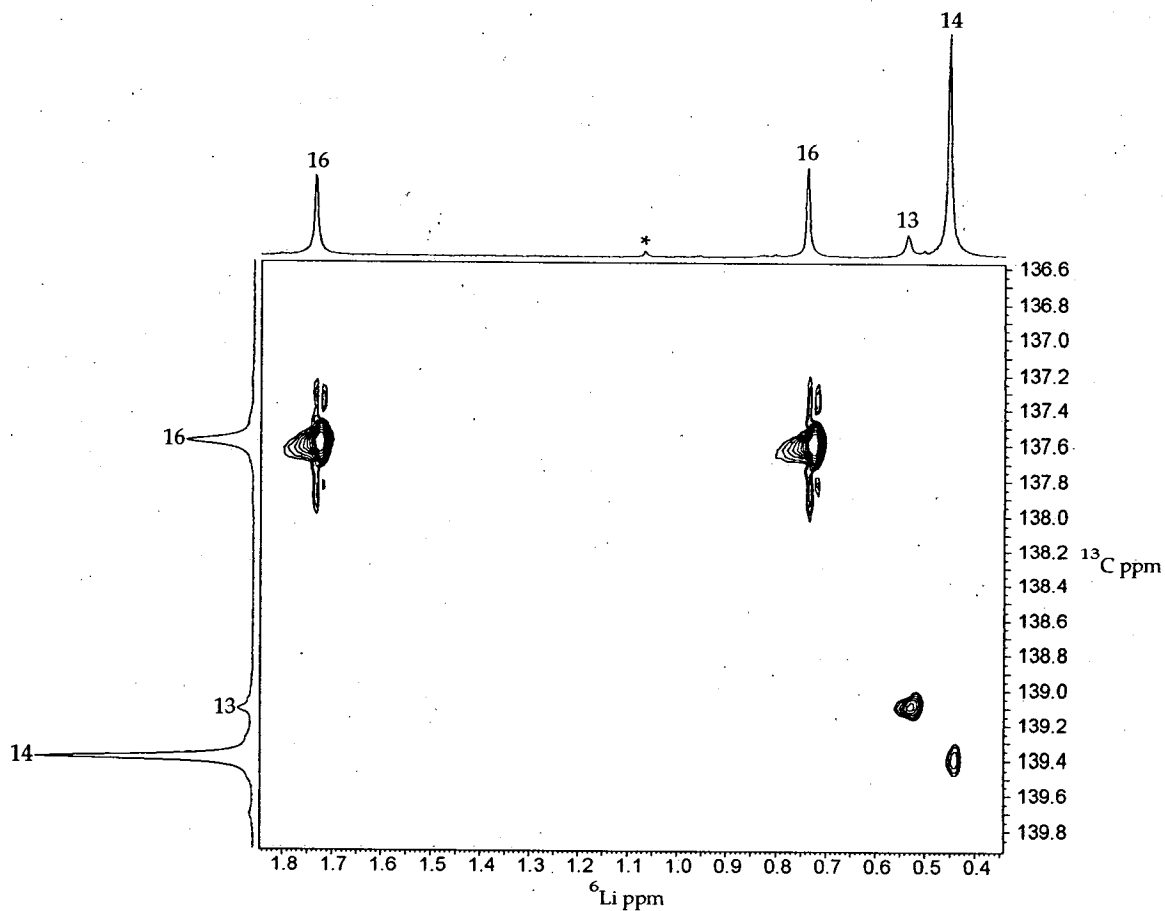


Figure 6. ^6Li , ^{13}C -HMQC spectrum recorded on 0.133 N [^6Li , ^{13}C]PhCClLi and 0.067 N [^6Li]8 in 7.6 M THF/pentane at $-115\text{ }^\circ\text{C}$. [^6Li]LiHMDS is indicated by an asterisk (*).

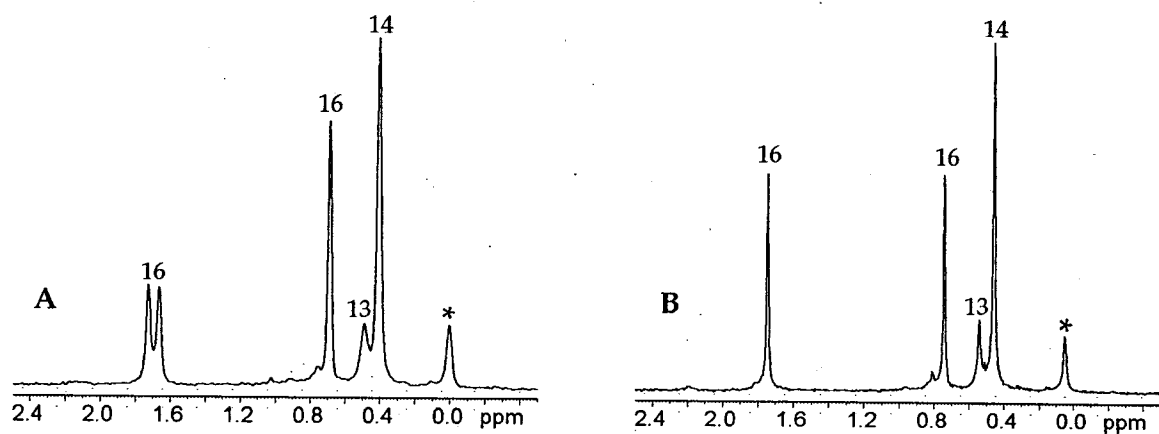


Figure 7. ${}^6\text{Li}$ NMR spectra recorded at $-110\text{ }^\circ\text{C}$ of 9.5 M THF/pentane solutions containing the following: (A) 0.20 N $[{}^6\text{Li}]\text{PhCCLi}$ and 0.10 N $[{}^6\text{Li},1\text{-}^{15}\text{N}]\mathbf{8}$; (B) 0.10 N $[{}^6\text{Li}]\text{PhCCLi}$ and 0.10 N $[{}^6\text{Li},3\text{-}^{15}\text{N}]\mathbf{8}$.

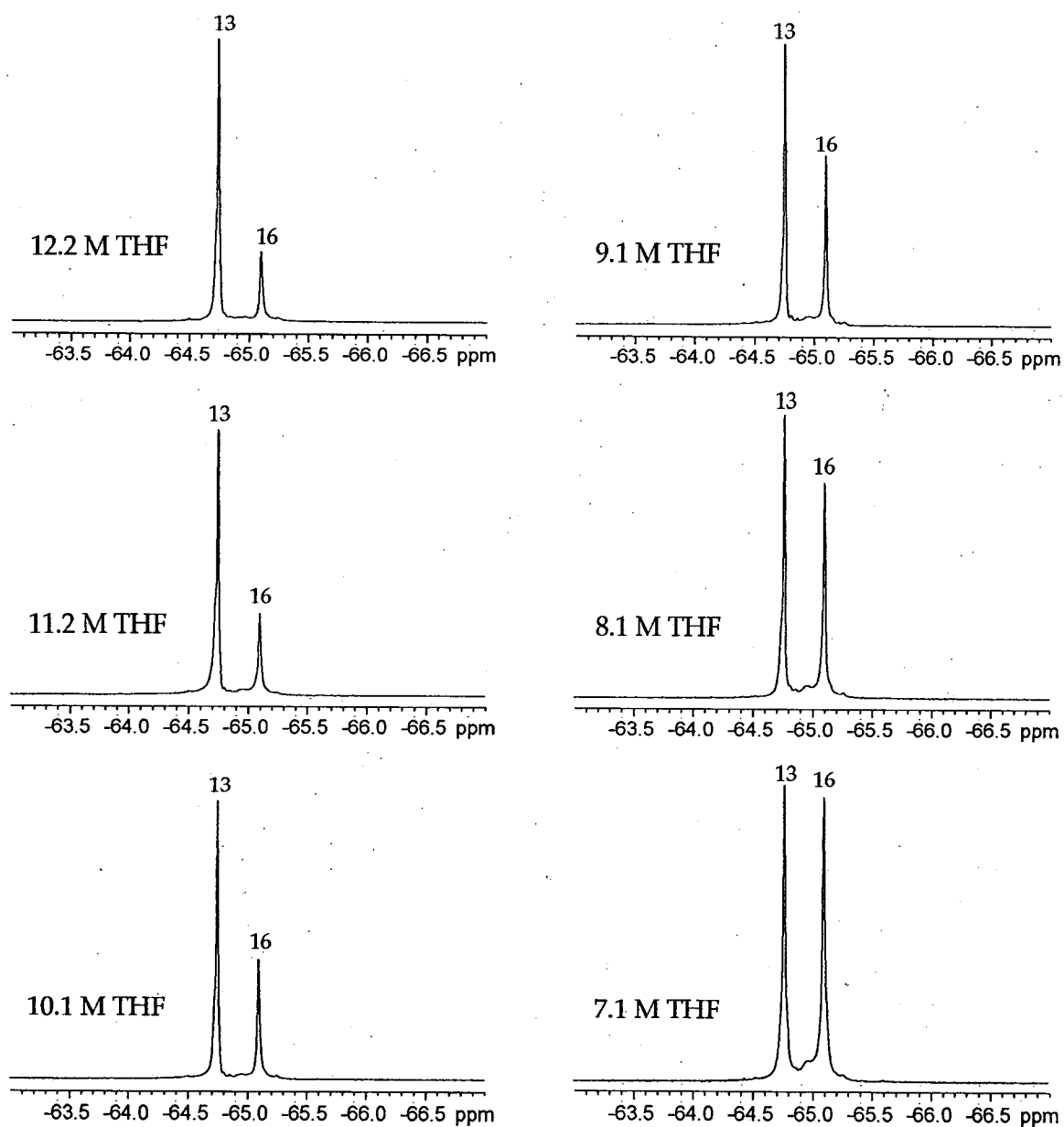
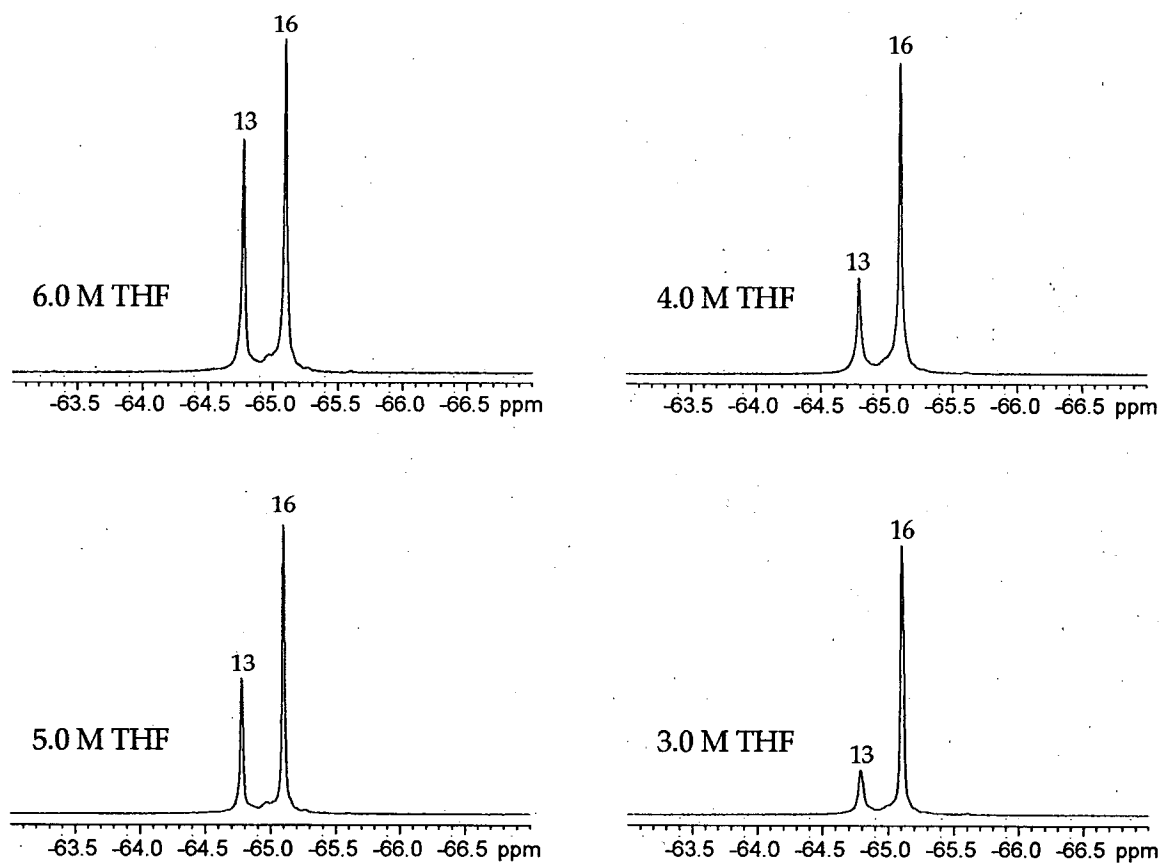


Figure 8. ^{19}F NMR spectra recorded at $-80\text{ }^\circ\text{C}$ of 0.04 N PhCCLi and 0.01 N **8** at the THF concentrations indicated (pentane cosolvent).

Figure 8. (Continued)



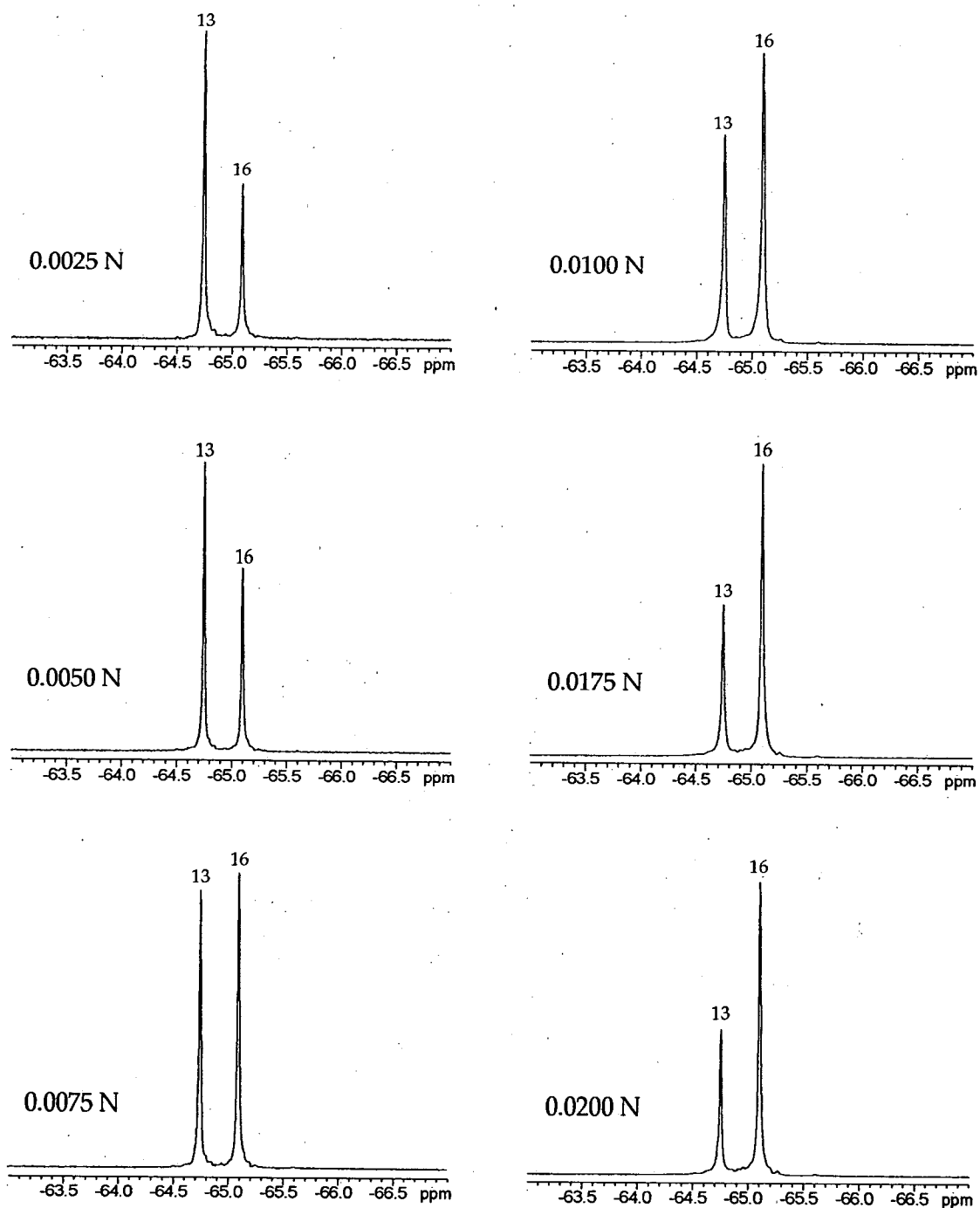


Figure 9. ^{19}F NMR spectra recorded at $-100\text{ }^\circ\text{C}$ of 7.6 M THF/pentane solutions of 0.10 N PhCCl₂ and 8 at the concentrations labelled on each spectrum.

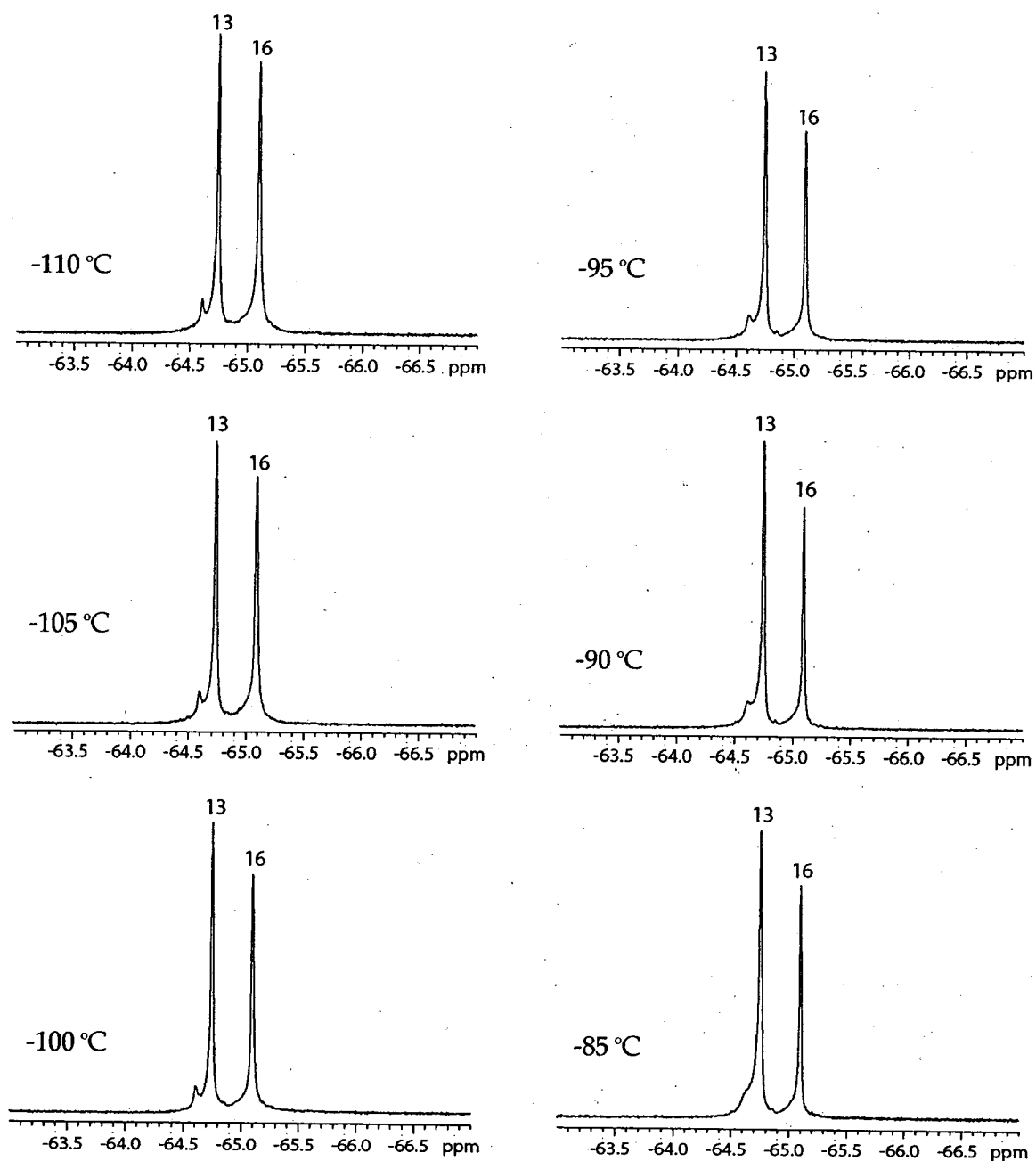
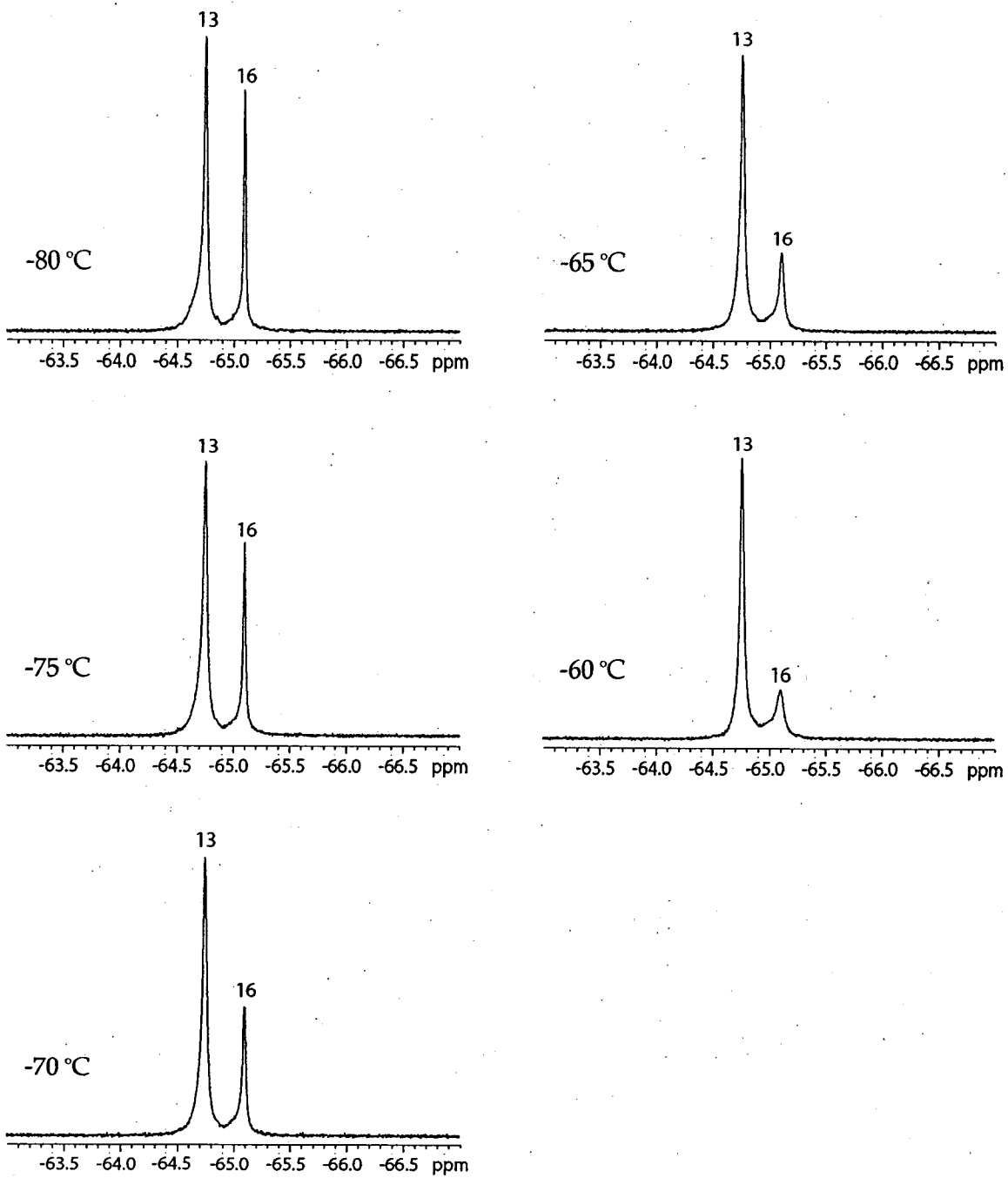


Figure 10. ^{19}F NMR spectra recorded on a solution containing 0.1 N PhCClLi and 0.005 N **8** in 8.0 M THF/pentane at the temperatures indicated.

Figure 10. (Continued)



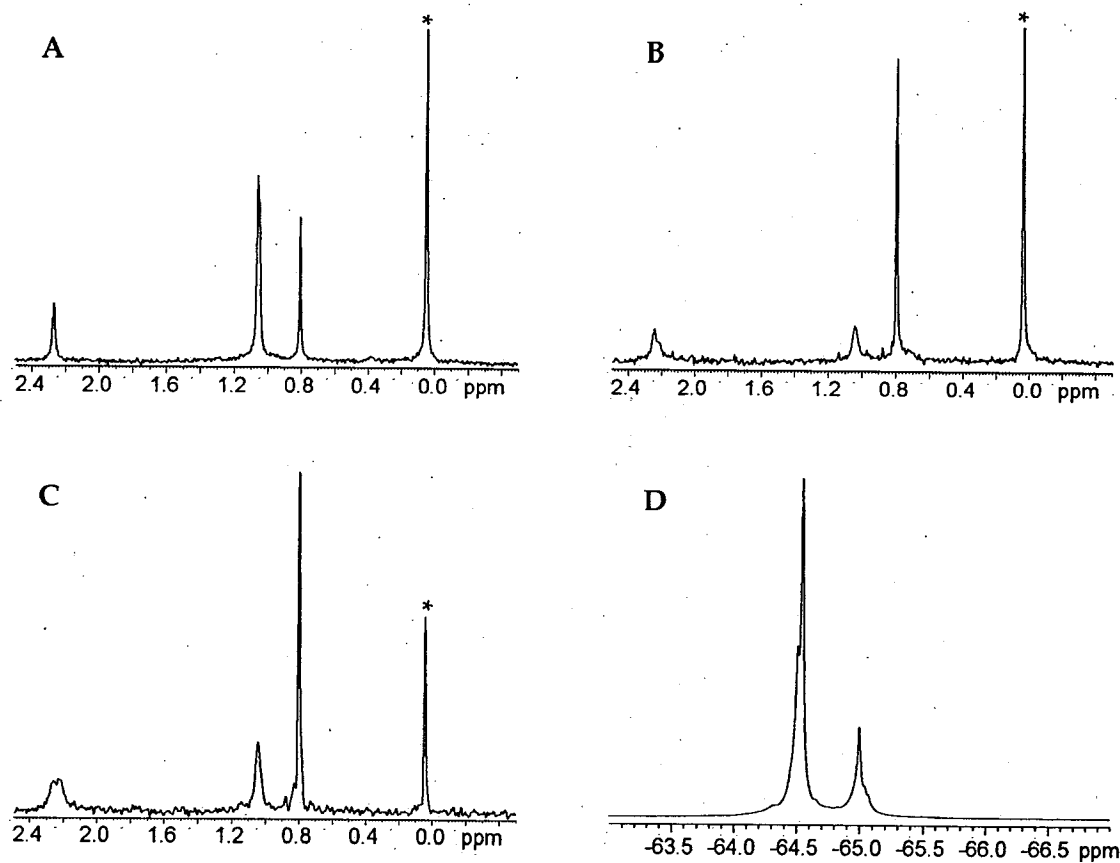


Figure 11. Selected NMR spectra of **8**; (A) ${}^6\text{Li}$ Spectrum of 0.1 N $[{}^6\text{Li}]\mathbf{8}$ in 5.6 M THF/pentane at $-125\text{ }^\circ\text{C}$; (B) ${}^6\text{Li}$ Spectrum of 0.1 N $[{}^6\text{Li}]\mathbf{8}$ in 8.6 M THF/pentane at $-115\text{ }^\circ\text{C}$; (C) ${}^6\text{Li}$ Spectrum of 0.1 N $[{}^6\text{Li},1\text{-}^{15}\text{N}]\mathbf{8}$ in 8.0 M THF/pentane at $-120\text{ }^\circ\text{C}$; (D) ${}^{19}\text{F}$ NMR spectrum of 0.1 N **8** in 9.1 M THF/pentane at $-120\text{ }^\circ\text{C}$. $[{}^6\text{Li}]\text{LiHMDS}$ is indicated by an asterisk (*).

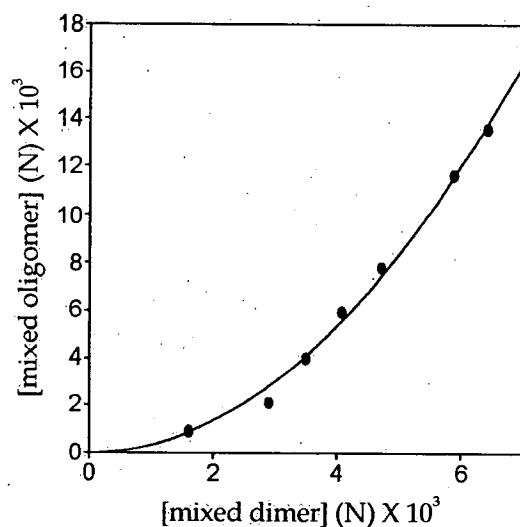


Figure 12. Plot of [mixed dimer] vs [mixed oligomer] (measured in normality of subunit 8) in 8.0 M THF/pentane solutions containing 0.20 N PhCClLi and a range of concentrations of 8 at -100 °C. The curve depicts an unweighted least-squares fit to $[\text{mixed oligomer}] = K'[\text{mixed dimer}]^m$ ($K' = 3 \pm 2 \times 10^2$, $m = 2.0 \pm 0.1$).

[8] (N)	[mixed dimer] (N)	[mixed oligomer] (N)
0.0025	0.0016	0.0009
0.0050	0.0029	0.0021
0.0075	0.0035	0.0040
0.0100	0.0041	0.0059
0.0125	0.0047	0.0078
0.0175	0.0059	0.0116
0.0200	0.0064	0.0136

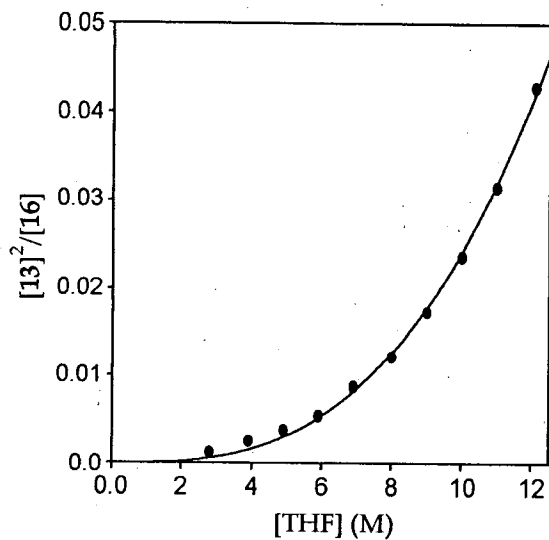


Figure 13. Plot of [mixed dimer]²/[mixed tetramer] (i.e., [13]²/[16]) vs [THF] of solutions containing 0.04 N PhCClLi and 0.009 N **8** in pentane cosolvent at -80 °C. The curve depicts an unweighted least-squares fit to [13]²/[16] = K_{eq} [THF]^{*n*} ($K_{eq} = 3.0 \pm 0.5 \times 10^{-5}$, $n = 2.91 \pm 0.07$).

[THF] (M)	[13] (M)	[16] (M)	[13] ² /[16]
12.1	0.0068	0.0011	0.0427
11.0	0.0064	0.0013	0.0315
10.0	0.0060	0.0015	0.0237
9.0	0.0055	0.0018	0.0173
8.0	0.0050	0.0020	0.0122
6.9	0.0045	0.0023	0.0088
5.9	0.0038	0.0026	0.0055
4.9	0.0033	0.0029	0.0038
3.9	0.0028	0.0031	0.0026
2.8	0.0021	0.0035	0.0012

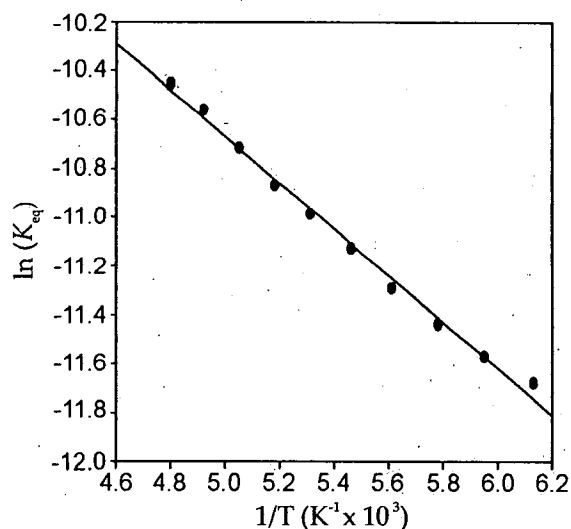


Figure 14. Plot of $\ln(K_{eq})$ vs $(1/T)$ of a solution containing 0.10 N PhCClLi and 0.005 N **8** in neat THF. The curve depicts an unweighted least-squares fit to $\ln(K_{eq}) = (-\Delta H/R)(1/T) + \Delta S/R$ ($\Delta H = 1.89 \pm 0.05$ kcal/mol, $\Delta S = -11.7 \pm 0.2$ cal/molK).

Temperature	[13] (M)	[16] (M)	$\ln(K_{eq})$
-110 °C, 163 K, 0.00613 1/K	0.00326	0.000871	-11.68
-105 °C, 168 K, 0.00595 1/K	0.00335	0.000825	-11.57
-100 °C, 173 K, 0.00578 1/K	0.00346	0.000769	-11.44
-95 °C, 178 K, 0.00561 1/K	0.00358	0.000712	-11.29
-90 °C, 183 K, 0.00546 1/K	0.00371	0.000647	-11.12
-85 °C, 188 K, 0.00531 1/K	0.00381	0.000594	-10.99
-80 °C, 193 K, 0.00518 1/K	0.00390	0.000552	-10.87
-75 °C, 198 K, 0.00505 1/K	0.00400	0.000499	-10.71
-70 °C, 203 K, 0.00492 1/K	0.00410	0.000449	-10.56
-65 °C, 208 K, 0.00480 1/K	0.00417	0.000417	-10.45

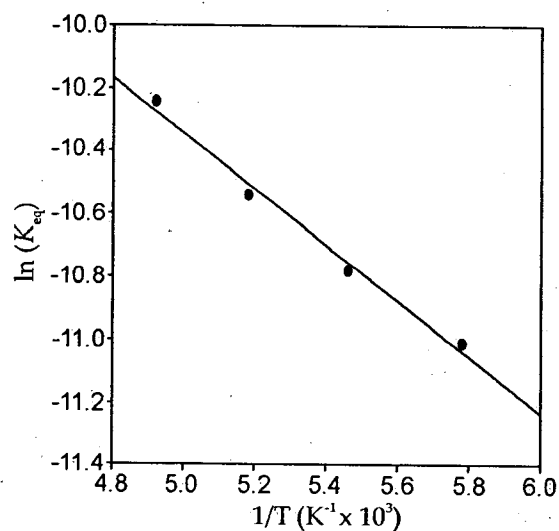


Figure 15. Plot of $\ln(K_{eq})$ vs $(1/T)$ of a solution containing 0.083 N PhCClLi and 0.016 N **8** in 9.5 M THF/pentane. The curve depicts an unweighted least-squares fit to $\ln(K_{eq}) = (-\Delta H/R)(1/T) + \Delta S/R$ ($\Delta H = 1.8 \pm 0.1$ kcal/mol, $\Delta S = -12.0 \pm 0.7$ cal/mol·K).

Temperature	[13] (M)	[16] (M)	$\ln(K_{eq})$
-100 °C, 173 K, 0.00578 1/K	0.00766	0.00417	-11.01
-90 °C, 183 K, 0.00546 1/K	0.00829	0.00385	-10.78
-80 °C, 193 K, 0.00518 1/K	0.00894	0.00353	-10.54
-70 °C, 203 K, 0.00492 1/K	0.00976	0.00312	-10.24

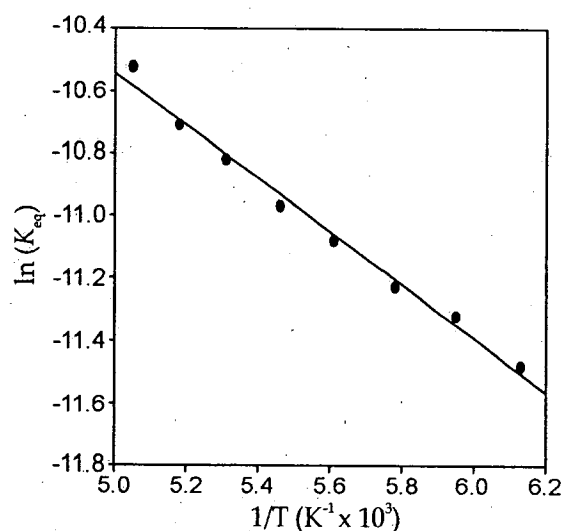


Figure 16. Plot of $\ln(K_{eq})$ vs $(1/T)$ of a solution containing 0.074 N PhCCl₂ and 0.018 N 8 in 10.5 M THF/pentane. The curve depicts an unweighted least-squares fit to $\ln(K_{eq}) = (-\Delta H/R)(1/T) + \Delta S/R$ ($\Delta H = 1.70 \pm 0.07$ kcal/mol, $\Delta S = -12.4 \pm 0.5$ cal/molK).

Temperature	[13] (M)	[16] (M)	$\ln(K_{eq})$
-110 °C, 163 K, 0.00613 1/K	0.0078	0.0051	-11.48
-105 °C, 168 K, 0.00595 1/K	0.0082	0.0049	-11.32
-100 °C, 173 K, 0.00578 1/K	0.0085	0.0047	-11.23
-95 °C, 178 K, 0.00561 1/K	0.0090	0.0045	-11.08
-90 °C, 183 K, 0.00546 1/K	0.0093	0.0044	-10.97
-85 °C, 188 K, 0.00531 1/K	0.0098	0.0041	-10.82
-80 °C, 193 K, 0.00518 1/K	0.0101	0.0040	-10.71
-75 °C, 198 K, 0.00505 1/K	0.0107	0.0037	-10.52

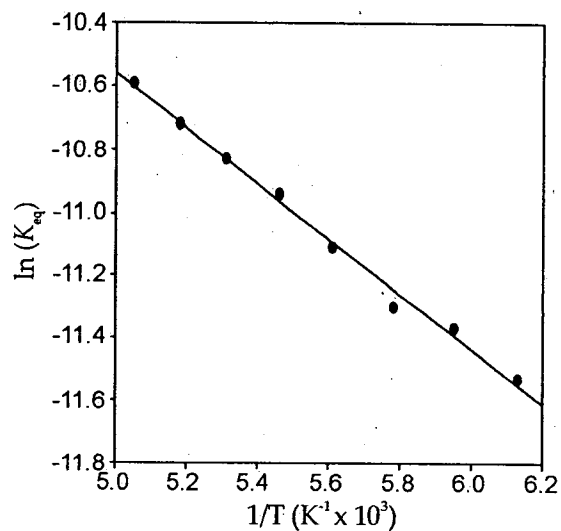


Figure 17. Plot of $\ln(K_{eq})$ vs $(1/T)$ of a solution containing 0.039 N PhCClLi and 0.009 N 8 in 7.15 M THF/pentane. The curve depicts an unweighted least-squares fit to $\ln(K_{eq}) = (-\Delta H/R)(1/T) + \Delta S/R$ ($\Delta H = 1.75 \pm 0.05$ kcal/mol, $\Delta S = -12.4 \pm 0.5$ cal/mol·K).

Temperature	[13] (M)	[16] (M)	$\ln(K_{eq})$
-110 °C, 163 K, 0.00613 1/K	0.0032	0.0029	-11.53
-105 °C, 168 K, 0.00595 1/K	0.0034	0.0028	-11.37
-100 °C, 173 K, 0.00578 1/K	0.0035	0.0027	-11.30
-95 °C, 178 K, 0.00561 1/K	0.0038	0.0026	-11.11
-90 °C, 183 K, 0.00546 1/K	0.0040	0.0025	-10.94
-85 °C, 188 K, 0.00531 1/K	0.0042	0.0024	-10.83
-80 °C, 193 K, 0.00518 1/K	0.0043	0.0023	-10.72
-75 °C, 198 K, 0.00505 1/K	0.0045	0.0022	-10.59

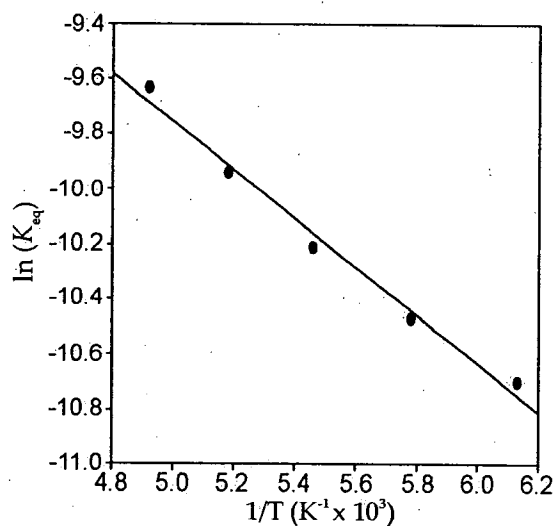


Figure 18. Plot of $\ln(K_{eq})$ vs $(1/T)$ of a solution containing 0.020 N PhCCLi and 0.0048 N **8** in 2.86 M THF/pentane. The curve depicts an unweighted least-squares fit to $\ln(K_{eq}) = (-\Delta H/R)(1/T) + \Delta S/R$ ($\Delta H = 1.7 \pm 0.1$ kcal/mol, $\Delta S = -10.8 \pm 0.5$ cal/molK).

Temperature	[13] (M)	[16] (M)	$\ln(K_{eq})$
-110 °C, 163 K, 0.00613 1/K	0.00100	0.00190	-10.70
-100 °C, 173 K, 0.00578 1/K	0.00111	0.00185	-10.47
-90 °C, 183 K, 0.00546 1/K	0.00124	0.00178	-10.21
-80 °C, 193 K, 0.00518 1/K	0.00139	0.00171	-9.94
-70 °C, 203 K, 0.00493 1/K	0.00157	0.00161	-9.63

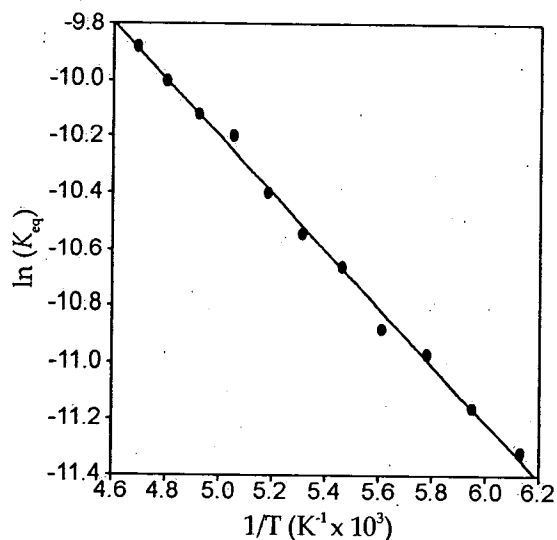


Figure 19. Plot of $\ln(K_{eq})$ vs $(1/T)$ of a solution containing 0.099 N PhCCl₂ and 0.049 N **8** in 7.5 M THF/pentane. The curve depicts an unweighted least-squares fit to $\ln(K_{eq}) = (-\Delta H/R)(1/T) + \Delta S/R$ ($\Delta H = 2.01 \pm 0.05$ kcal/mol, $\Delta S = -10.2 \pm 0.2$ cal/molK).

Temperature	[13] (M)	[16] (M)	$\ln(K_{eq})$
-110 °C, 163 K, 0.00613 1/K	0.00248	0.00120	-11.32
-105 °C, 168 K, 0.00595 1/K	0.00261	0.00114	-11.16
-100 °C, 173 K, 0.00578 1/K	0.00277	0.00106	-10.97
-95 °C, 178 K, 0.00561 1/K	0.00284	0.00102	-10.88
-90 °C, 183 K, 0.00546 1/K	0.00303	0.00093	-10.66
-85 °C, 188 K, 0.00531 1/K	0.00314	0.00088	-10.54
-80 °C, 193 K, 0.00518 1/K	0.00325	0.00082	-10.40
-75 °C, 198 K, 0.00505 1/K	0.00341	0.00074	-10.20
-70 °C, 203 K, 0.00492 1/K	0.00347	0.00071	-10.12
-65 °C, 208 K, 0.00480 1/K	0.00356	0.00066	-10.00
-60 °C, 213 K, 0.00469 1/K	0.00365	0.00062	-9.88

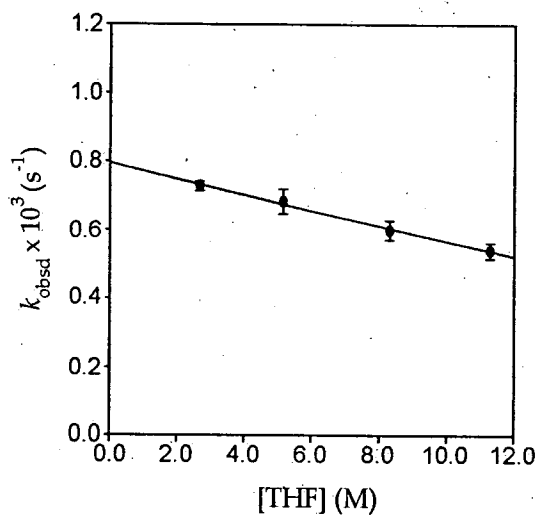


Figure 20. Plot of k_{obsd} vs [THF] (M) in pentane cosolvent for the 1,2-addition of PhCCLi (0.20 N) to mixed dimer 13 (0.005 N in subunit 8) at 10 °C. The curve depicts an unweighted least-squares fit to $k_{\text{obsd}} = k[\text{THF}] + k'$ ($k = -2.29 \pm 0.02 \times 10^{-5}$, $k' = 8.0 \pm 0.1 \times 10^{-4}$). Rate constants were acquired using ^{19}F NMR spectroscopy.

[THF] (M)	$k_{\text{obsd}1} \times 10^4$	$k_{\text{obsd}2} \times 10^4$	$k_{\text{obsd}}(\text{avg}) \times 10^4$
2.7	7.2 ± 0.2	7.4 ± 0.3	7.3 ± 0.1
5.2	6.6 ± 0.1	7.1 ± 0.2	6.9 ± 0.4
8.3	5.78 ± 0.07	6.2 ± 0.1	6.0 ± 0.3
11.3	5.54 ± 0.07	5.20 ± 0.07	5.4 ± 0.2

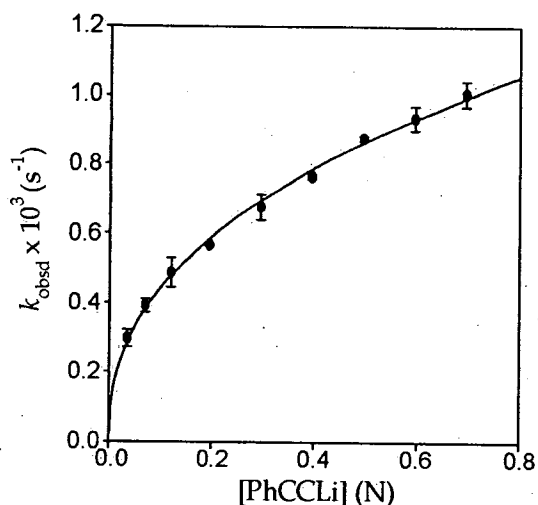


Figure 21. Plot of k_{obsd} vs $[\text{PhCCLi}]$ in 7.75 M THF/pentane for the 1,2-addition of PhCCLi to mixed dimer **13** (0.005 M) at 10 °C. The curve depicts an unweighted least-squares fit to $k_{\text{obsd}} = a[\text{PhCCLi}]^b$ ($a = 1.16 \pm 0.01 \times 10^{-3}$, $b = 0.42 \pm 0.01$). Rate constants were acquired using ^{19}F NMR spectroscopy.

$[\text{PhCCLi}]$ (N)	$k_{\text{obsd}1} \times 10^4$	$k_{\text{obsd}2} \times 10^4$	$k_{\text{obsd}}(\text{avg}) \times 10^4$
0.035	2.81 ± 0.09	3.14 ± 0.04	3.0 ± 0.2
0.070	4.05 ± 0.07	3.77 ± 0.06	3.9 ± 0.2
0.120	4.57 ± 0.07	5.18 ± 0.08	4.9 ± 0.4
0.195	5.65 ± 0.09	5.7 ± 0.1	5.68 ± 0.04
0.295	6.5 ± 0.2	7.03 ± 0.09	6.8 ± 0.4
0.395	7.6 ± 0.1	7.7 ± 0.1	7.65 ± 0.07
0.495	8.8 ± 0.1	8.7 ± 0.1	8.75 ± 0.07
0.595	9.6 ± 0.2	9.1 ± 0.1	9.4 ± 0.4
0.695	10.3 ± 0.1	9.8 ± 0.1	10.1 ± 0.4

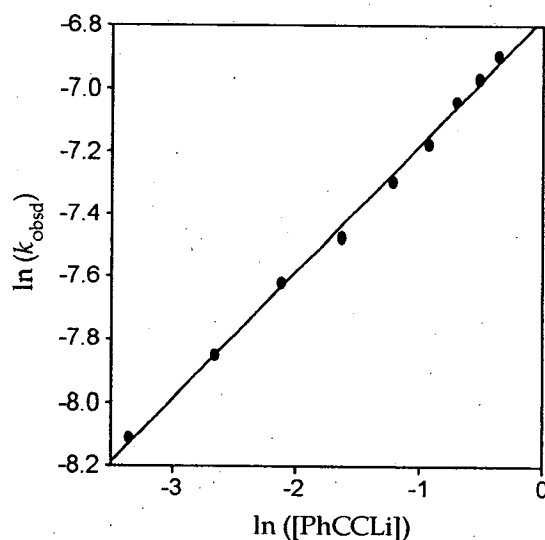


Figure 22. Plot of $\ln(k_{\text{obsd}})$ vs $\ln[\text{PhCCLi}]$ in 7.75 M THF/pentane solutions for the 1,2-addition of PhCCLi to mixed dimer 13 (0.005 N of subunit 8) at 10 °C. The curve depicts an unweighted least-squares fit to $\ln(k_{\text{obsd}}) = b(\ln[\text{PhCCLi}]) + \ln a$ ($a = -6.78 \pm 0.02$, $b = 0.404 \pm 0.008$). Rate constants were acquired using ^{19}F NMR spectroscopy.

$\ln([\text{PhCCLi}])$	$\ln(k_{\text{obsd}})$
-3.352	-8.112
-2.659	-7.849
-2.120	-7.621
-1.635	-7.473
-1.221	-7.293
-0.929	-7.176
-0.703	-7.041
-0.519	-6.970
-0.364	-6.898

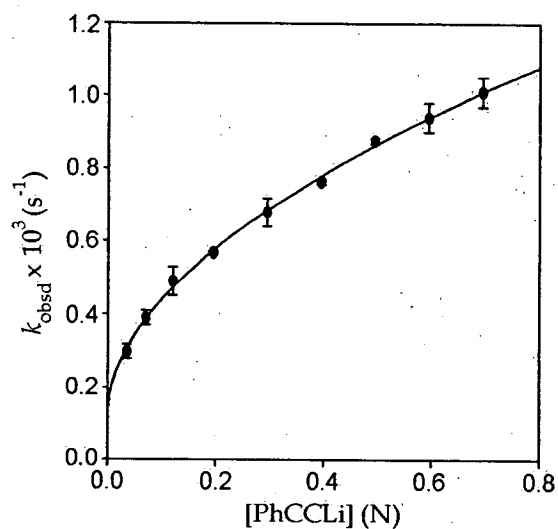


Figure 23. Plot of k_{obsd} vs $[\text{PhCCLi}]$ in 7.75 M THF/pentane for the 1,2-addition of PhCCLi to mixed dimer **13** (0.005 M) at 10 °C. The curve depicts an unweighted least-squares fit to $k_{\text{obsd}} = a[\text{PhCCLi}]^b + c$ ($a = 1.1 \pm 0.3 \times 10^{-3}$, $b = 0.54 \pm 0.04$, $c = 1.3 \pm 0.4 \times 10^{-4}$). Rate constants were acquired using ^{19}F NMR spectroscopy.

$[\text{PhCCLi}]$ (N)	$k_{\text{obsd}1} \times 10^4$	$k_{\text{obsd}2} \times 10^4$	$k_{\text{obsd}}(\text{avg}) \times 10^4$
0.035	2.81 ± 0.09	3.14 ± 0.04	3.0 ± 0.2
0.070	4.05 ± 0.07	3.77 ± 0.06	3.9 ± 0.2
0.120	4.57 ± 0.07	5.18 ± 0.08	4.9 ± 0.4
0.195	5.65 ± 0.09	5.7 ± 0.1	5.68 ± 0.04
0.295	6.5 ± 0.2	7.03 ± 0.09	6.8 ± 0.4
0.395	7.6 ± 0.1	7.7 ± 0.1	7.65 ± 0.07
0.495	8.8 ± 0.1	8.7 ± 0.1	8.75 ± 0.07
0.595	9.6 ± 0.2	9.1 ± 0.1	9.4 ± 0.4
0.695	10.3 ± 0.1	9.8 ± 0.1	10.1 ± 0.4

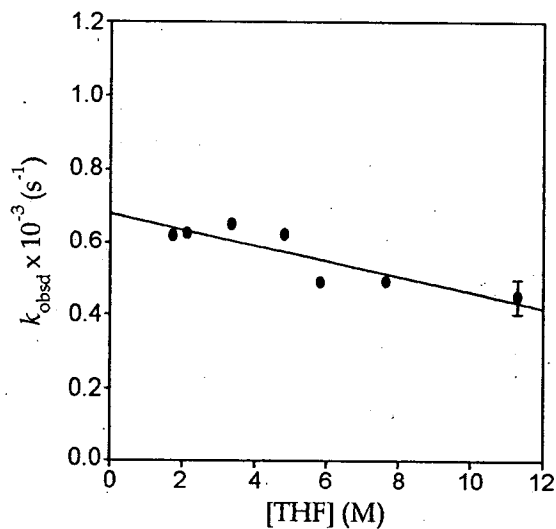


Figure 24. Plot of k_{obsd} vs [THF] in THF/pentane solutions for the 1,2-addition of PhCCLi (0.20 N) to mixed dimer **13** (0.005 N of subunit **8**) at 10 °C. The curve depicts an unweighted least-squares fit to $k_{\text{obsd}} = k[\text{THF}] + k'$ ($k = -2.2 \pm 5 \times 10^{-5}$, $k' = 6.8 \pm 0.3 \times 10^{-4}$). Rate constants were acquired using in situ IR spectroscopy.

[THF] (M)	$k_{\text{obsd}1} \times 10^4$	$k_{\text{obsd}2} \times 10^4$	$k_{\text{obsd}}(\text{avg}) \times 10^4$
1.73	6.21 ± 0.04		
2.12	6.26 ± 0.09		
3.35	6.52 ± 0.07		
4.81	6.24 ± 0.04		
5.81	4.89 ± 0.05		
7.64	4.91 ± 0.01		
11.3	4.79 ± 0.01	4.13 ± 0.07	4.5 ± 0.5

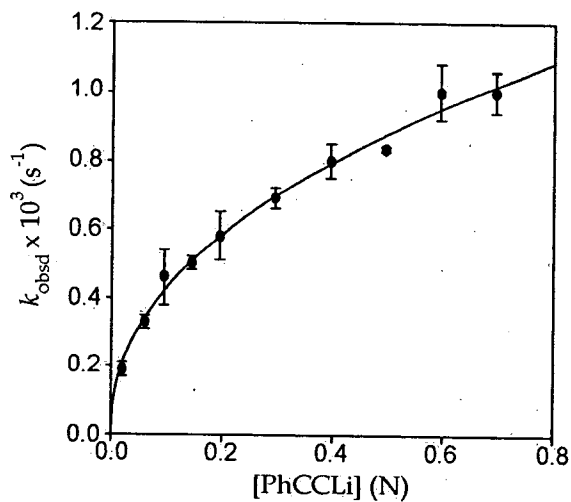


Figure 25. Plot of k_{obsd} vs $[\text{PhCCLi}]$ in 4.5 M THF/pentane solutions for the 1,2-addition of PhCCLi to mixed dimer 13 (0.005 N of subunit 8) at 10 °C. The curve depicts an unweighted least-squares fit to $k_{\text{obsd}} = a[\text{PhCCLi}]^b$ ($a = 12.0 \pm 0.03$, $b = 0.45 \pm 0.02$). Rate constants were acquired using in situ IR spectroscopy.

$[\text{PhCCLi}]$ (N)	$k_{\text{obsd}1} \times 10^4$	$k_{\text{obsd}2} \times 10^4$	$k_{\text{obsd}}(\text{avg}) \times 10^4$
0.020	1.740 ± 0.007	1.978 ± 0.007	1.9 ± 0.2
0.060	3.16 ± 0.02	3.39 ± 0.01	3.3 ± 0.2
0.095	4.01 ± 0.02	5.16 ± 0.04	4.6 ± 0.8
0.145	4.84 ± 0.02	5.13 ± 0.02	5.0 ± 0.2
0.195	5.36 ± 0.04	6.32 ± 0.04	5.8 ± 0.7
0.295	7.12 ± 0.04	6.71 ± 0.03	6.9 ± 0.3
0.395	7.63 ± 0.05	8.40 ± 0.06	8.0 ± 0.5
0.495	8.41 ± 0.04	8.29 ± 0.05	8.35 ± 0.08
0.595	9.44 ± 0.05	10.51 ± 0.06	10.0 ± 0.8
0.695	9.60 ± 0.05	10.43 ± 0.05	10.0 ± 0.6

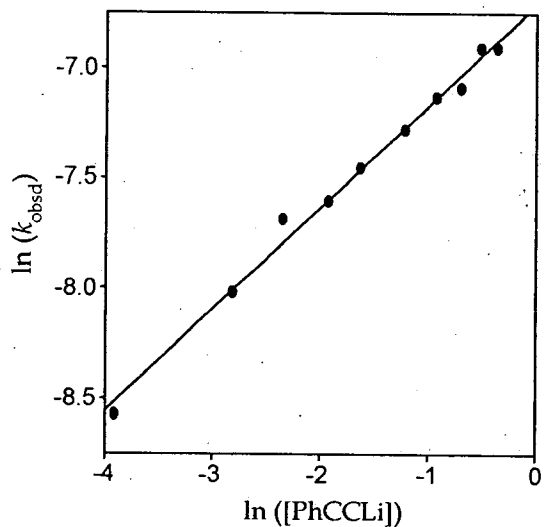


Figure 26. Plot of $\ln(k_{\text{obsd}})$ vs $\ln([\text{PhCCLi}])$ in 4.5 M THF/pentane solutions for the 1,2-addition of PhCCLi to mixed dimer **13** (0.005 N of subunit **8**) at 10 °C. The curve depicts an unweighted least-squares fit to $\ln(k_{\text{obsd}}) = b(\ln[\text{PhCCLi}]) + \ln a$. ($a = -6.71 \pm 0.03$, $b = 0.46 \pm 0.02$). Rate constants were acquired using in situ IR spectroscopy.

$\ln([\text{PhCCLi}])$	$\ln(k_{\text{obsd}})$
-3.912	-8.568
-2.813	-8.016
-2.354	-7.684
-1.931	-7.601
-1.635	-7.452
-1.221	-7.278
-0.929	-7.131
-0.703	-7.088
-0.519	-6.907
-0.364	-6.907

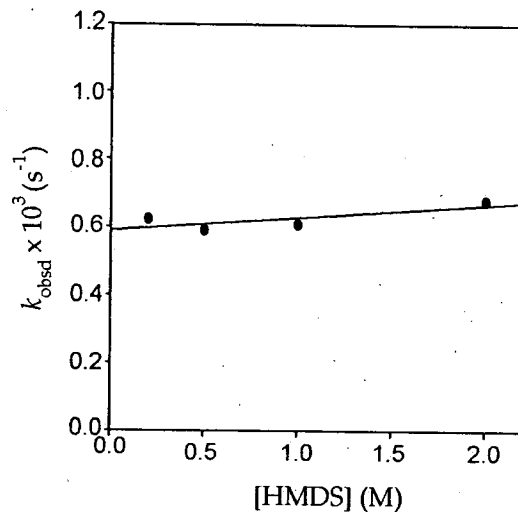


Figure 27. Plot of k_{obsd} vs [HMDS] in 5.3 M THF/pentane for the 1,2-addition of PhCCLi (0.20 N) to mixed dimer **13** (0.005 N of subunit **8**) at 10 °C. The curve depicts an unweighted least-squares fit to $k_{\text{obsd}} = k[\text{HMDS}] + k'$ ($k = 4 \pm 2 \times 10^{-5}$, $k' = 5.9 \pm 0.2 \times 10^{-4}$). Rate constants were acquired using in situ IR spectroscopy.

[HMDS] (M)	$k_{\text{obsd}} \times 10^4$
0.20	6.24 ± 0.04
0.50	5.90 ± 0.03
1.00	6.08 ± 0.04
2.00	6.78 ± 0.04

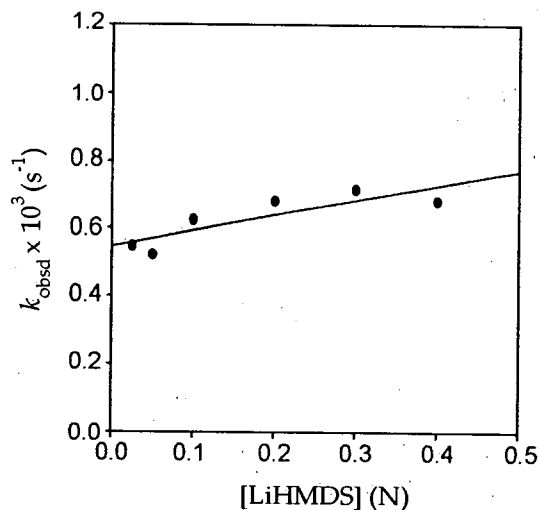


Figure 28. Plot of k_{obsd} vs $[\text{LiHMDS}]$ in 5.2 M THF/pentane for the 1,2-addition of PhCClLi (0.20 N) to mixed dimer 13 (0.005 N of subunit 8) at 10 °C. The curve depicts an unweighted least-squares fit to $k_{\text{obsd}} = k[\text{LiHMDS}] + k'$ ($k = 4 \pm 1 \times 10^{-4}$, $k' = 5.5 \pm 0.3 \times 10^{-4}$). Rate constants were acquired using in situ IR spectroscopy.

$[\text{LiHMDS}]$ (N)	$k_{\text{obsd}1} \times 10^4$	$k_{\text{obsd}2} \times 10^4$	$k_{\text{obsd}}(\text{avg}) \times 10^4$
0.025	5.50 ± 0.03		
0.050	5.21 ± 0.04		
0.100	6.24 ± 0.04		
0.200	6.81 ± 0.04		
0.300	7.17 ± 0.04		
0.400	6.81 ± 0.04		
		5.26 ± 0.03	5.24 ± 0.04

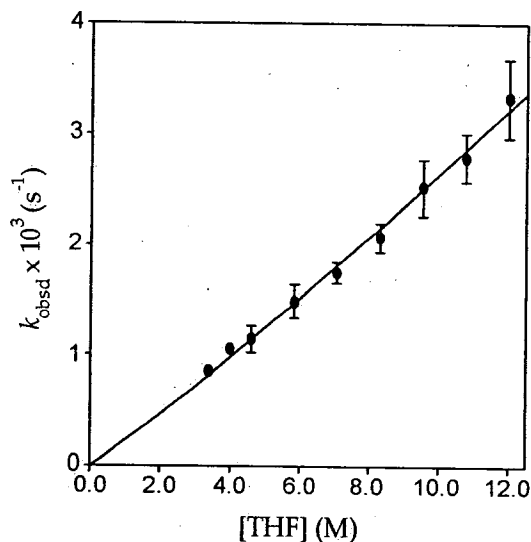


Figure 29. Plot of k_{obsd} vs [THF] in pentane cosolvent for the 1,2-addition of PhCClLi (0.05 N) to **11** (0.005 M) at $-40\text{ }^{\circ}\text{C}$. The curve depicts an unweighted least-squares fit to $k_{\text{obsd}} = a[\text{THF}]^b$ ($a = 2.1 \pm 0.2 \times 10^4$, $b = 1.09 \pm 0.04$). Rate constants were acquired using ^{19}F NMR spectroscopy.

[THF]	$k_{\text{obsd}1} \times 10^3$	$k_{\text{obsd}2} \times 10^3$	$k_{\text{obsd}3} \times 10^3$	$k_{\text{obsd}4} \times 10^3$	$k_{\text{obsd}}(\text{avg}) \times 10^3$
3.38	0.853 ± 0.003				0.853
4.00	1.053 ± 0.003				1.053
4.61	1.11 ± 0.03	1.160 ± 0.009	1.000 ± 0.005	1.29 ± 0.01	1.1 ± 0.1
5.84	1.35 ± 0.02	1.47 ± 0.01	1.42 ± 0.01	1.70 ± 0.02	1.5 ± 0.2
7.07	1.61 ± 0.02	1.83 ± 0.03	1.8 ± 0.1	1.74 ± 0.01	1.7 ± 0.1
8.30	1.92 ± 0.02	2.05 ± 0.03	2.07 ± 0.03	2.25 ± 0.02	2.1 ± 0.1
9.53	2.37 ± 0.04	2.39 ± 0.03	2.82 ± 0.03		2.5 ± 0.3
10.76	2.74 ± 0.06	2.84 ± 0.08	2.53 ± 0.03	3.05 ± 0.04	2.8 ± 0.2
11.99	3.24 ± 0.06	3.34 ± 0.05	2.94 ± 0.07	3.81 ± 0.07	3.3 ± 0.4

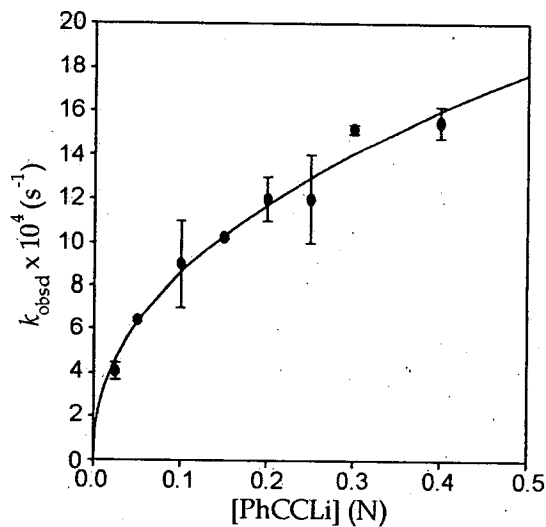


Figure 30. Plot of k_{obsd} vs $[\text{PhCCLi}]$ in 8.64 M THF/pentane for the 1,2-addition of PhCCLi to **11** (0.005 M) at $-55\text{ }^{\circ}\text{C}$. The curve depicts an unweighted least-squares fit to $k_{\text{obsd}} = a[\text{PhCCLi}]^b$ ($a = 2.4 \pm 0.1 \times 10^{-3}$, $b = 0.45 \pm 0.04$). Rate constants were acquired using ^{19}F NMR spectroscopy.

$[\text{PhCCLi}]$ (N)	$k_{\text{obsd}1} \times 10^4$	$k_{\text{obsd}2} \times 10^4$	$k_{\text{obsd}3} \times 10^4$	$k_{\text{obsd}}(\text{avg}) \times 10^4$
0.025	4.35 ± 0.09	3.82 ± 0.06		4.1 ± 0.4
0.050	6.45 ± 0.07	6.31 ± 0.05		6.4 ± 0.1
0.100	7.7 ± 0.3	11.1 ± 0.4	7.52 ± 0.09	9 ± 2
0.150	10.3 ± 0.1	10.2 ± 0.5		10.25 ± 0.07
0.200	10.6 ± 0.2	12.0 ± 0.3	13.3 ± 0.2	12 ± 1
0.250	13.3 ± 0.4	10.6 ± 0.2		12 ± 2
0.300	15.0 ± 0.3	15.3 ± 0.3		15.2 ± 0.2
0.400	16.0 ± 0.8	15.0 ± 0.4		15.5 ± 0.7

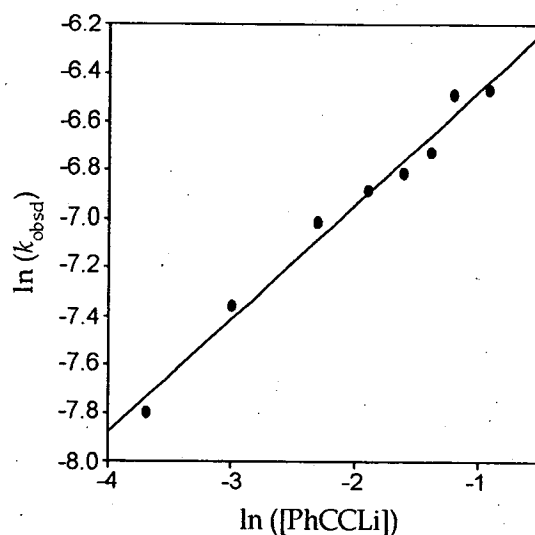


Figure 31. Plot of $\ln(k_{\text{obsd}})$ vs $\ln([\text{PhCCLi}])$ in 8.64 M THF/pentane solutions for the 1,2-addition of PhCCLi to 11 (0.005 M) at $-55\text{ }^{\circ}\text{C}$. The curve depicts an unweighted least-squares fit to $\ln(k_{\text{obsd}}) = b(\ln[\text{PhCCLi}]) + a$. ($a = -6.01 \pm 0.06$, $b = 0.47 \pm 0.03$). Rate constants were acquired using ^{19}F NMR spectroscopy.

$\ln([\text{PhCCLi}])$	$\ln(k_{\text{obsd}})$
-3.689	-7.799
-2.996	-7.354
-2.303	-7.013
-1.897	-6.883
-1.609	-6.812
-1.386	-6.725
-1.204	-6.489
-0.916	-6.470

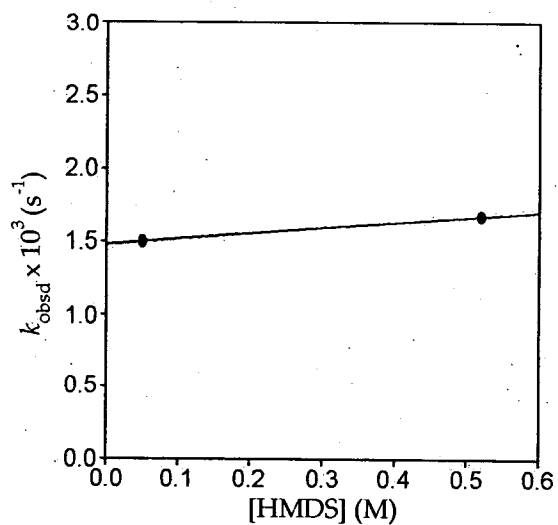


Figure 32. Plot of k_{obsd} vs [HMDS] in 5.84 M THF/pentane for the 1,2-addition of PhCCLi (0.05 N) to **11** (0.005 M) at $-40\text{ }^{\circ}\text{C}$. The curve depicts an unweighted least-squares fit to $k_{\text{obsd}} = k[\text{HMDS}] + k'$ ($k = 3.6 \times 10^{-4}$, $k' = 1.48 \times 10^{-3}$). Rate constants were acquired using ^{19}F NMR spectroscopy.

[HMDS] (M)	$k_{\text{obsd}} \times 10^3$
0.05	1.5 ± 0.2
0.52	1.67 ± 0.01

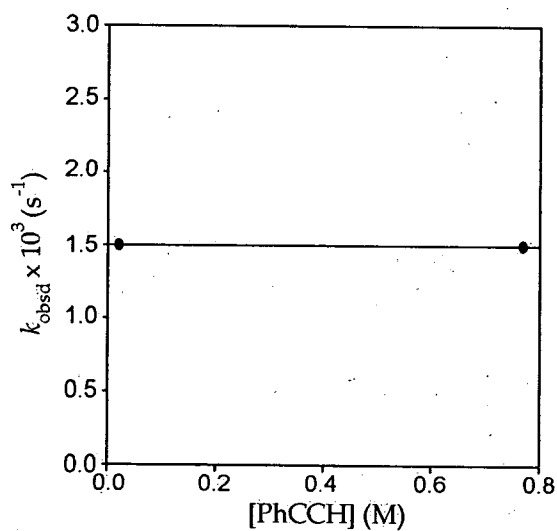


Figure 33. Plot of k_{obsd} vs [PhCCH] in 5.84 M THF/pentane for the 1,2-addition of PhCCLi (0.05 N) to 11 (0.005 M) at $-40\text{ }^{\circ}\text{C}$. The curve depicts an unweighted least-squares fit to $k_{\text{obsd}} = k[\text{PhCCH}] + k'$ ($k = 0$, $k' = 1.5 \times 10^{-3}$). Rate constants were acquired using ^{19}F NMR spectroscopy.

[PhCCH] (M)	$k_{\text{obsd}} \times 10^3$
0.02	1.5 ± 0.2
0.77	1.50 ± 0.03

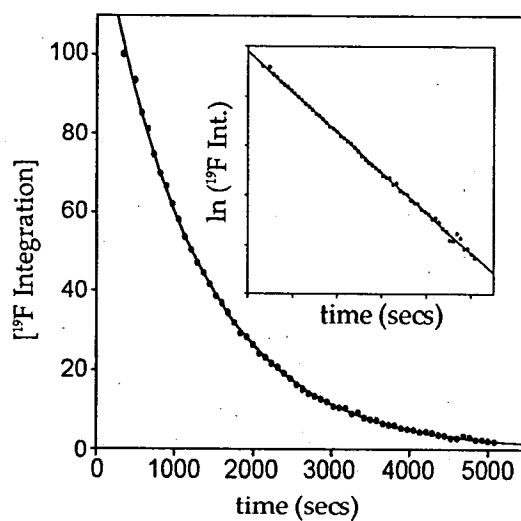
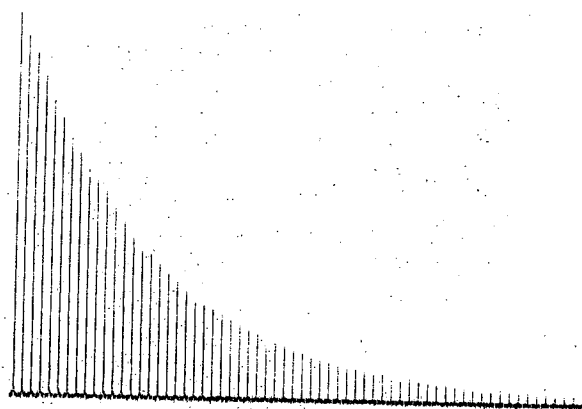


Figure 34. Series of ^{19}F spectra over time with a plot of the ^{19}F integration vs time for the 1,2-addition of PhCClLi (0.50 N) to mixed dimer **13** (0.005 N) at 10°C in a 7.75 M free THF/pentane. The curve depicts an unweighted least-squares fit to ^{19}F integration = ^{19}F integration $_0 e^{-k_{\text{obsd}}t} + c$ ($k_{\text{obsd}} = 8.19 \pm 0.07 \times 10^{-4}$; ^{19}F integration $_0 = 136.1 \pm 0.7$; $c = 0.0 \pm 0.2$). The insert depicts the $\ln(^{19}\text{F}$ integration) vs time.

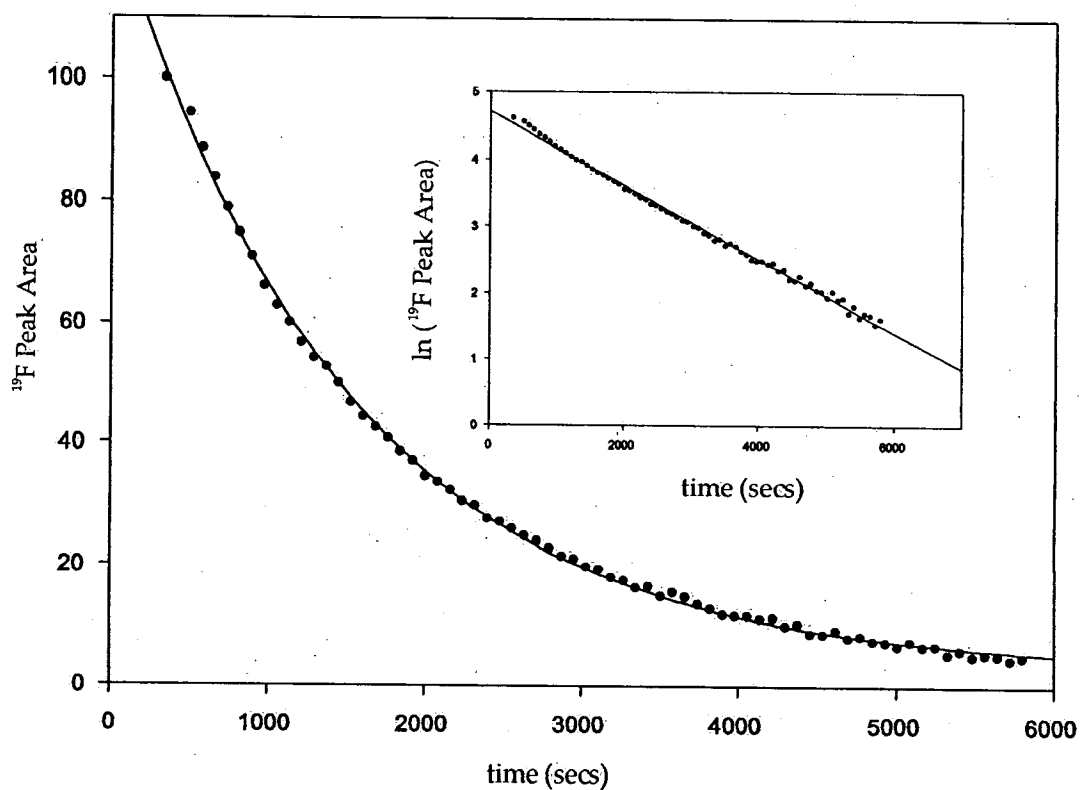


Figure 35. Plot of the ^{19}F integration vs time for the 1,2-addition of PhCClLi (0.50 N) to mixed dimer **13** (0.005 N of subunit **8**) at $10\text{ }^\circ\text{C}$ in 2.96 M free THF in pentane cosolvent. The curve depicts an unweighted least-squares fit to ^{19}F integration = ^{19}F integration $_0 e^{-k_{\text{obsd}} t} + c$ ($k_{\text{obsd}} = 6.68 \pm 0.07 \times 10^{-4}$; ^{19}F integration $_0 = 122.9 \pm 0.6$; $c = 3.2 \pm 0.3$). The insert depicts the $\ln(^{19}\text{F}$ integration) vs time showing a slight deviation from a first order decay.