

Ketone Enolization by Lithium Hexamethyldisilazide:  
Structural and Rate Studies  
of the  
Accelerating Effects of Trialkylamines

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**Supporting Information**

**Part I. NMR Structural Studies**

**Procedure for Sample Preparation**

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- Figure 2** Plot of  $^6\text{Li}$  chemical shift vs toluene mole fraction in the mixtures of [ $^6\text{Li}$ ,  $^{15}\text{N}$ ]LiHMDS in toluene/pentane.
- Figure 3**  $^6\text{Li}$  NMR spectra recorded on [ $^6\text{Li}$ ,  $^{15}\text{N}$ ]LiHMDS with  $\text{Me}_2\text{NEt}$  in 50% toluene/pentane.
- Figure 4**  $^6\text{Li}$  NMR spectra recorded on [ $^6\text{Li}$ ,  $^{15}\text{N}$ ]LiHMDS in toluene with *N,N*-dimethyl-1-ethylpropylamine, *N,N*-dimethyl-*s*-butylamine, *N,N*-dimethyl-*t*-butylamine and *N,N*-dimethyl-*t*-amylamine.
- Figure 5**  $^6\text{Li}$  NMR spectra recorded in [ $^6\text{Li}$ ,  $^{15}\text{N}$ ]LiHMDS in  $\text{Et}_3\text{N}$ /pentane.
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**Part II. *in situ* IR Kinetic Studies**

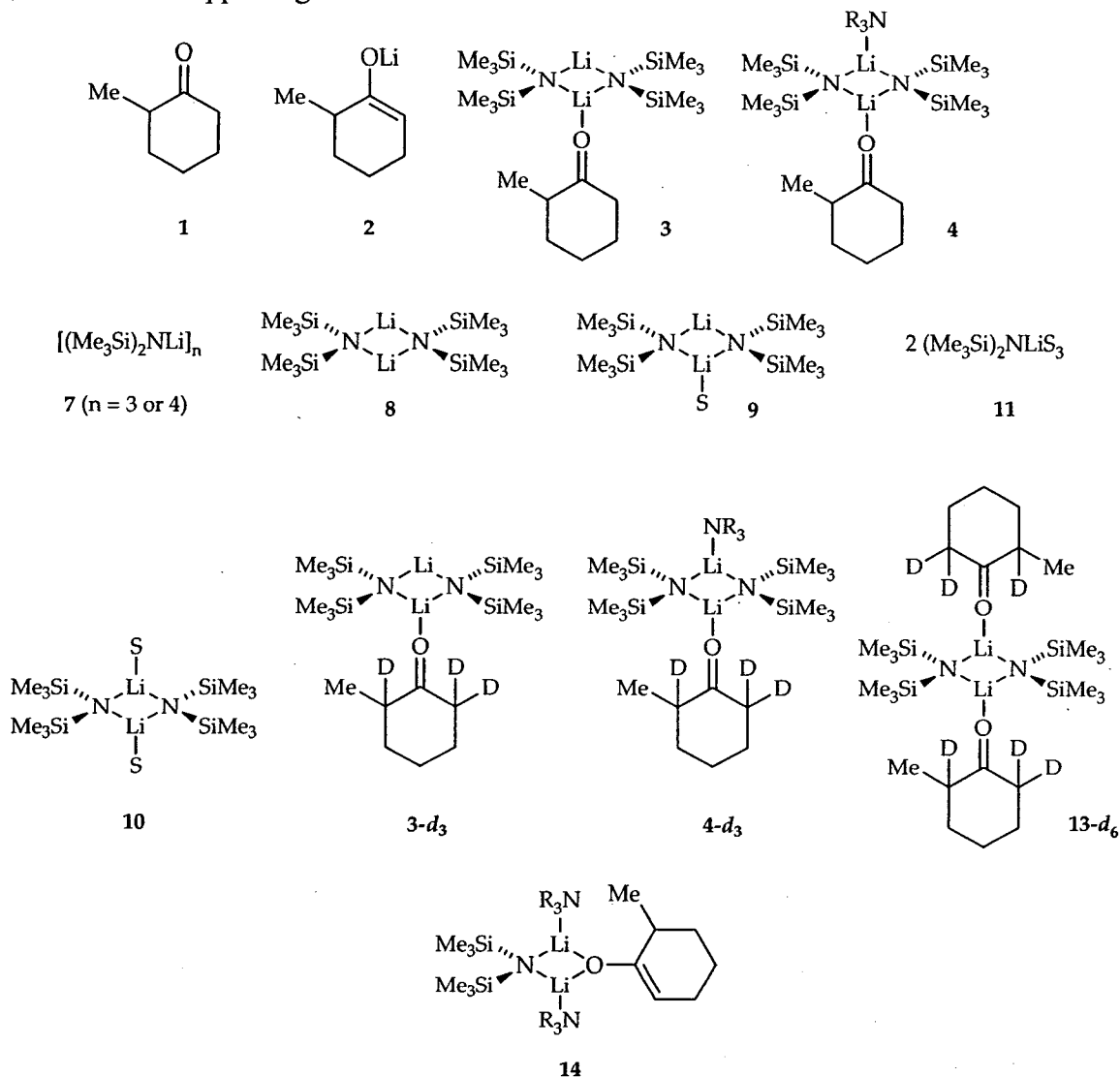
- I** Table of rate constants of the enolizations of 2-methylcyclohexanone (**1**) by LiHMDS in hydrocarbon solvents.
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- XXI Table of data for plot in section XX.

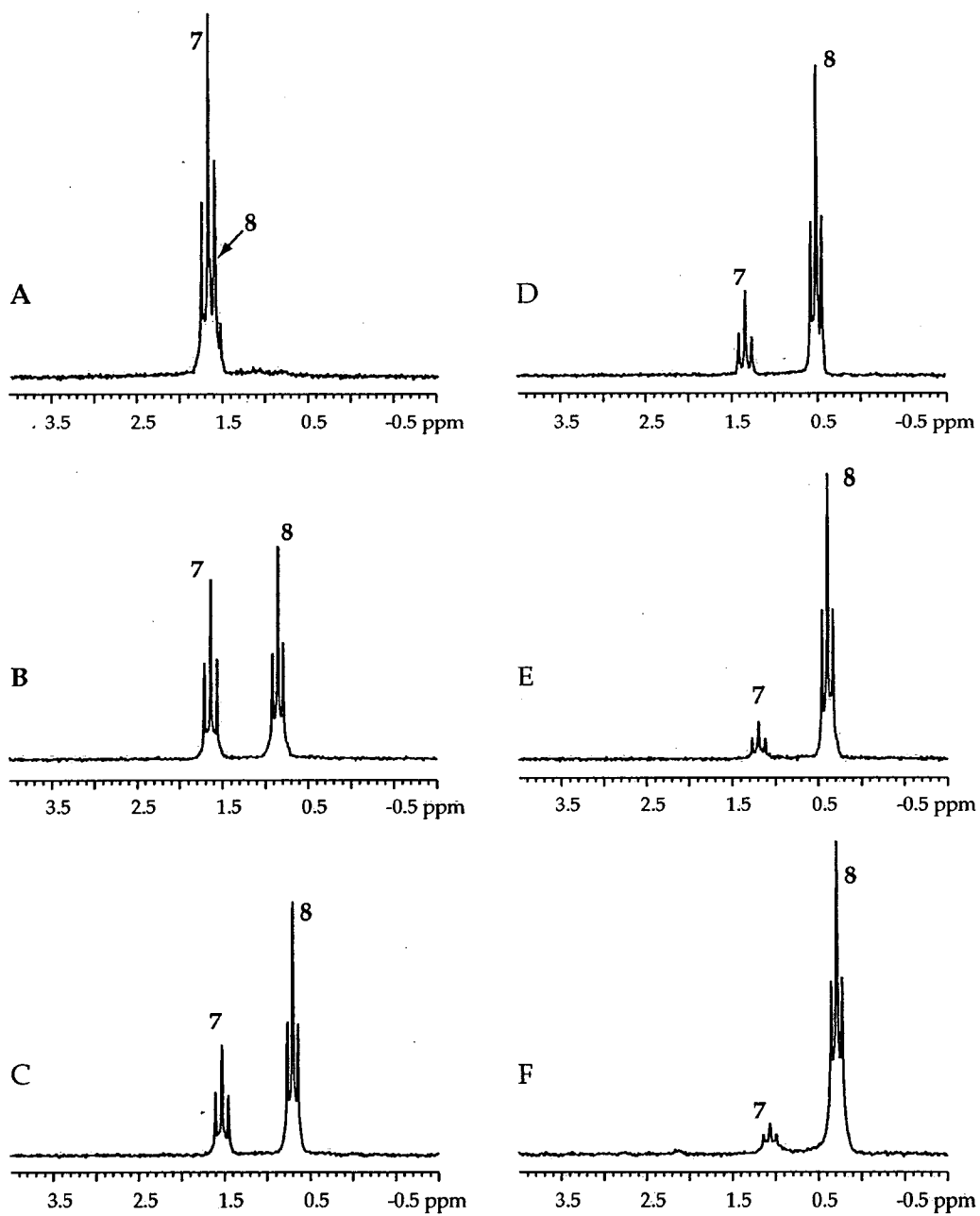
- XXVI** Plot of  $k_{\text{obsd}}$  vs  $X_{\text{MeNEt}_2}$  ( $X$  = mole fraction) for the enolization of **1** by LiHMDS in  $\text{Me}_2\text{NEt}/\text{MeNEt}_2/\text{toluene}$ .
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- XXXI** Table of data for plot in section **XXX**.
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- XXXVII** Table of data for plot in section **XXXVI**.
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- XXXIX** Table of data for plot in section **XXXVIII**.
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- XLI** Table of data for plot in section **XL**.
- XLII** Table of amine-dependent isotope effects.
- XLIII** Derivation of equation to establish ligand binding constants.

## Structures in Supporting Information

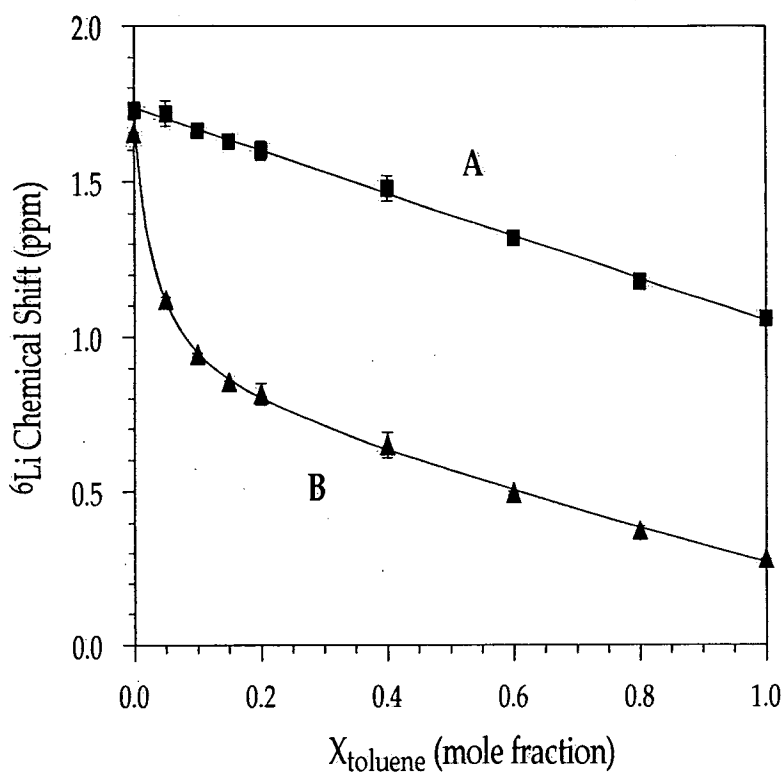


## Part I. NMR Structural Studies

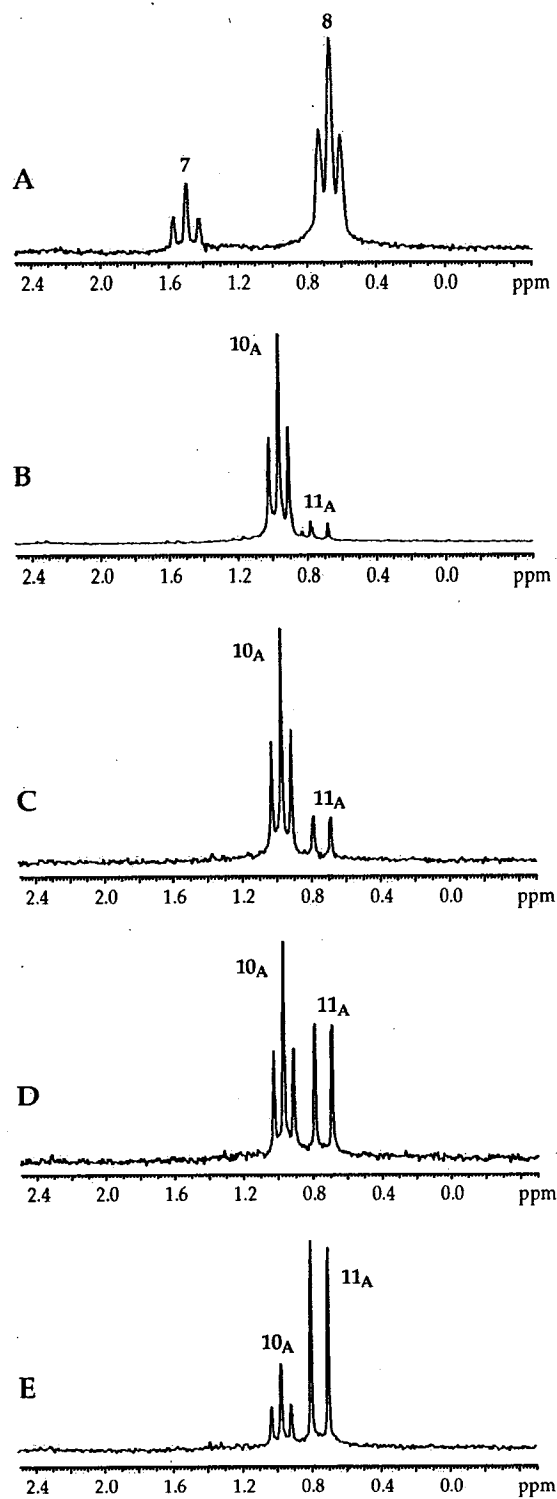
**Procedure for Sample Preparation** The stock solutions of [ $^6\text{Li}$ ,  $^{15}\text{N}$ ]LiHMDS (0.30 M in toluene),  $1-d_3$  (1.2 M in toluene), and  $\text{Me}_2\text{NEt}$  (6.0 M in toluene) were prepared. The NMR tubes were capped with a serum stopper and flushed with Ar, charged with 200  $\mu\text{L}$  of the LiHMDS solution, and submerged below the sample level in liquid nitrogen. The solution of ketone (100  $\mu\text{L}$ ) was layered and frozen sample to afford two separate frozen layers. The tube was placed in a dry ice/acetone bath to allow the solutions melt and mix. (In the absence of amine, the ketone enolization is very slow.) The sample was frozen in liquid nitrogen and layered with the solution of  $\text{Me}_2\text{NEt}$  (300  $\mu\text{L}$ ). The sample was allowed to warm and mix inside the NMR probe at  $-100\text{ }^\circ\text{C}$ .



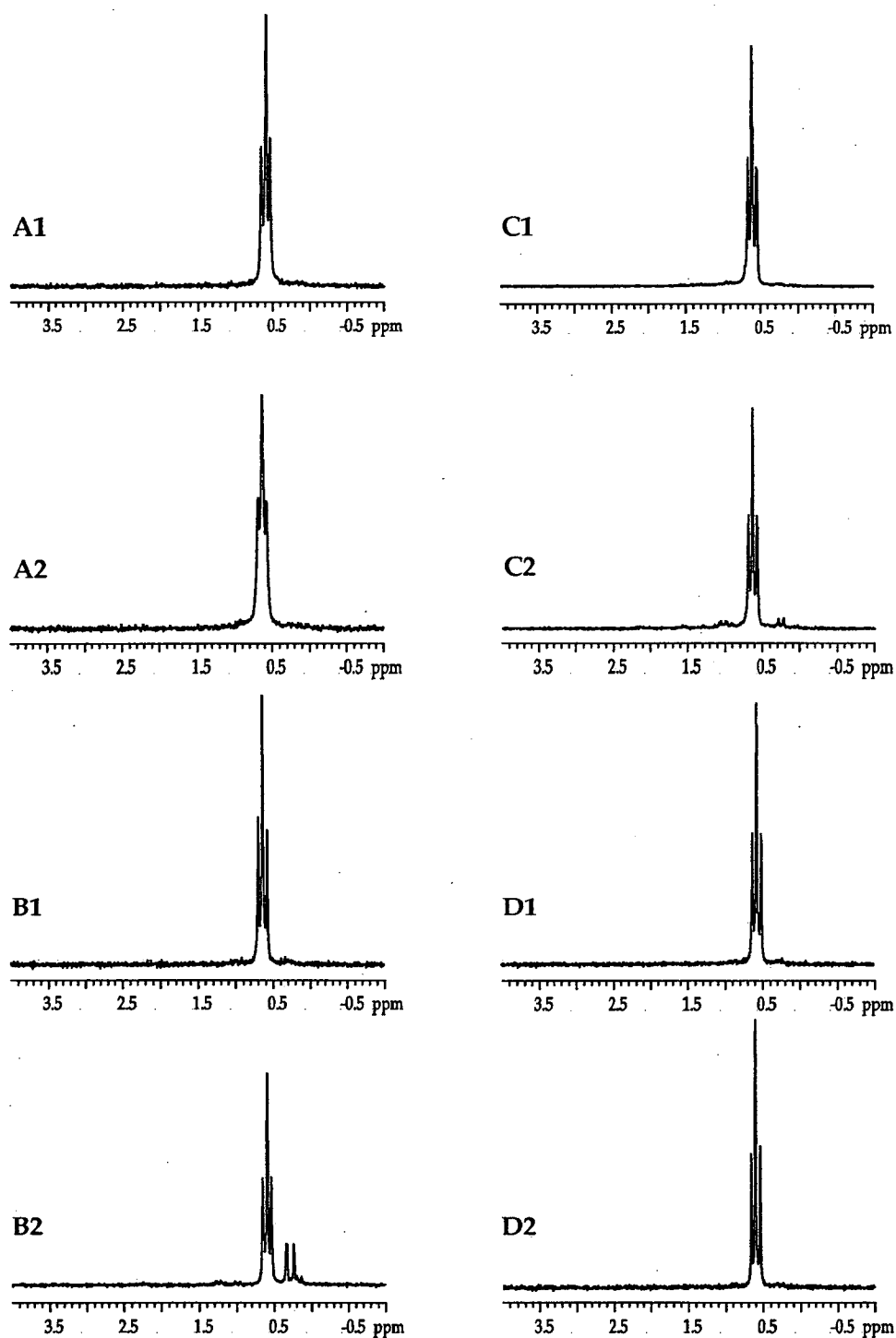
**Figure 1.**  $^6\text{Li}$  NMR spectra recorded on 0.1 M [ $^6\text{Li}$ ,  $^{15}\text{N}$ ]LiHMDS in toluene/pentane mixtures at  $-100\text{ }^\circ\text{C}$ . Higher oligomer **7** and dimer **8** were monitored at different toluene volume contents: (A) neat pentane; (B) 20% toluene; (C) 40% toluene; (D) 60% toluene; (E) 80% toluene; (F) neat toluene.



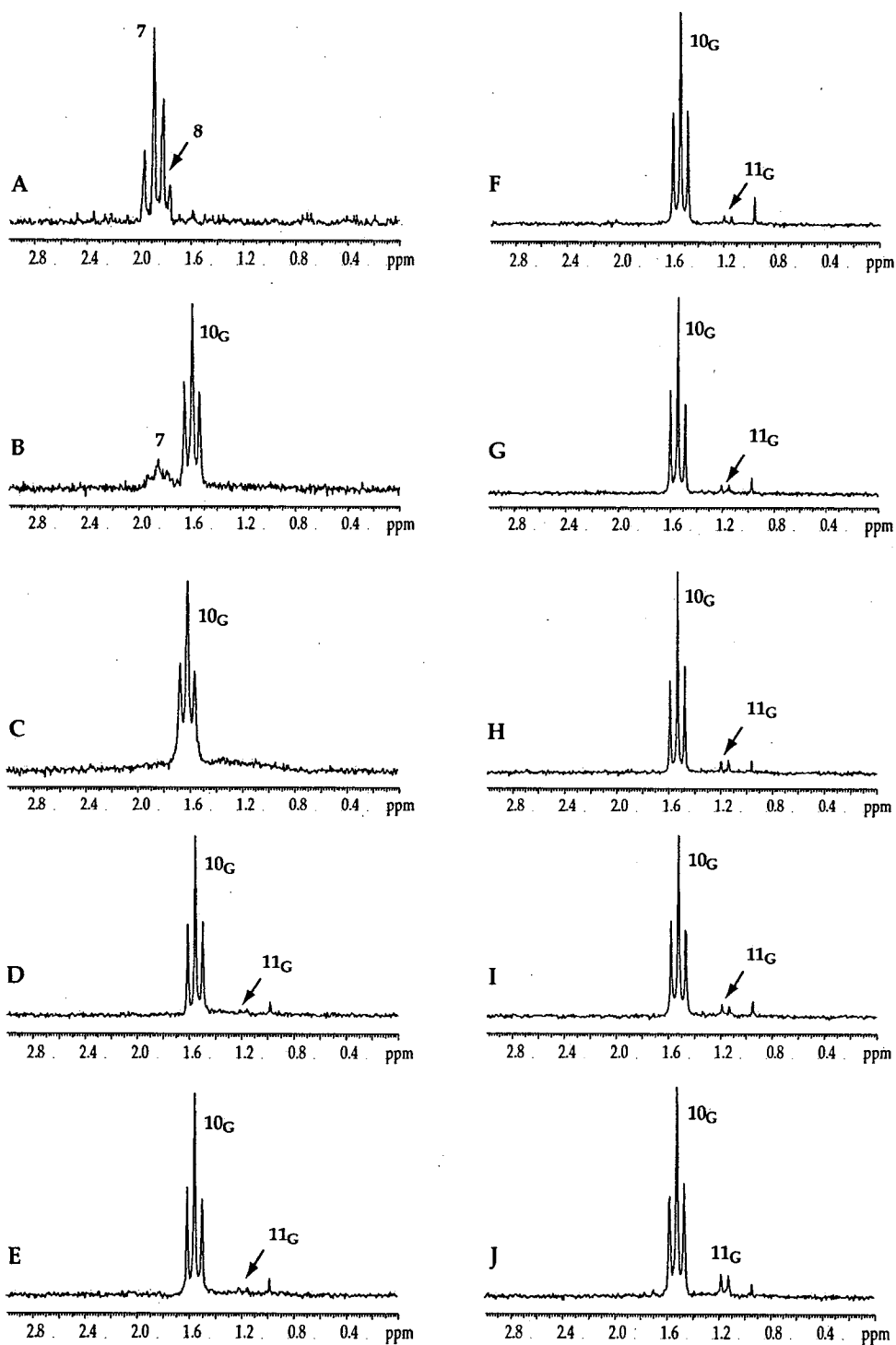
**Figure 2.** Plot of  ${}^6\text{Li}$  chemical shift vs toluene mole fraction in the solution of 0.1 M  $[{}^6\text{Li}, {}^{15}\text{N}]\text{LiHMDS}$  in toluene/pentane at  $-100\text{ }^\circ\text{C}$ . **Curve A** (correlating to higher oligomer **7**) depicts the results of an unweighted least-squares fit to  $y = ax + b$ , where  $a = 1.736 \pm 0.008$ ,  $b = -0.68 \pm 0.01$ ; **Curve B** (correlating to dimer **8**) depicts the results of an unweighted least-squares fit to  $y = (a + bx)/(1 + cx) + dx$ , where  $a = 1.66 \pm 0.01$ ,  $b = 22 \pm 3$ ,  $c = 29 \pm 3$ ,  $d = -0.54 \pm 0.03$ .



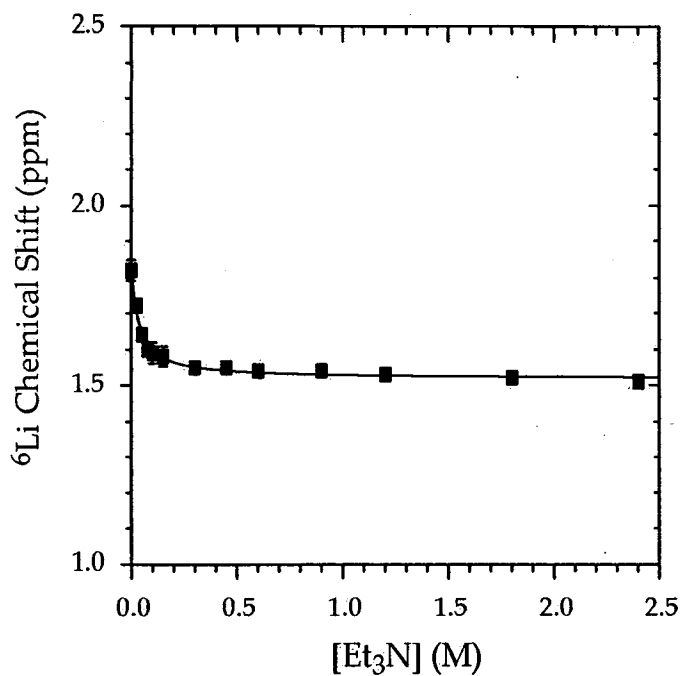
**Figure 3.**  ${}^6\text{Li}$  NMR spectra recorded on 0.1 M  $[{}^6\text{Li}, {}^{15}\text{N}]\text{LiHMDS}$  with  $\text{Me}_2\text{NEt}$  (A) in 50% toluene/pentane at  $-100\text{ }^\circ\text{C}$ . Dimer  $10_{\text{A}}$  and monomer  $11_{\text{A}}$  were monitored at different  $\text{Me}_2\text{NEt}$  concentrations: (A) 0 M (showing higher oligomer 7 and dimer 8); (B) 0.15 M; (C) 0.30 M; (D) 0.60 M; (E) 1.2 M.



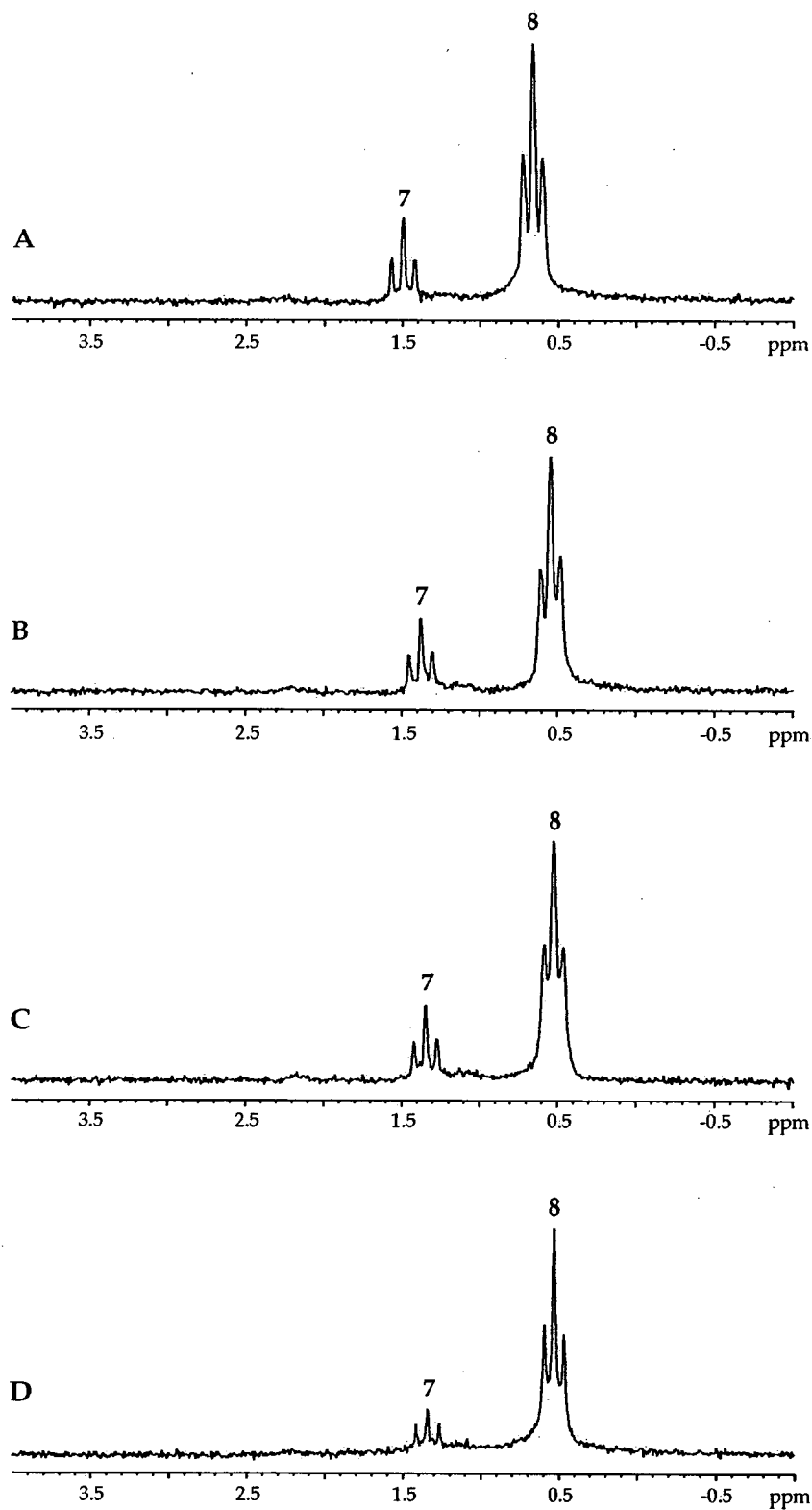
**Figure 4.**  ${}^6\text{Li}$  NMR spectra recorded on 0.1 M [ ${}^6\text{Li}$ ,  ${}^{15}\text{N}$ ]LiHMDS in toluene at  $-100\text{ }^\circ\text{C}$  with (1) 0.15 M and (2) 0.60 M dimethylamines: (A) *N,N*-dimethyl-1-ethylpropylamine; (B) *N,N*-dimethyl-*s*-butylamine; (C) *N,N*-dimethyl-*t*-butylamine; (D) *N,N*-dimethyl-*t*-amylamine.



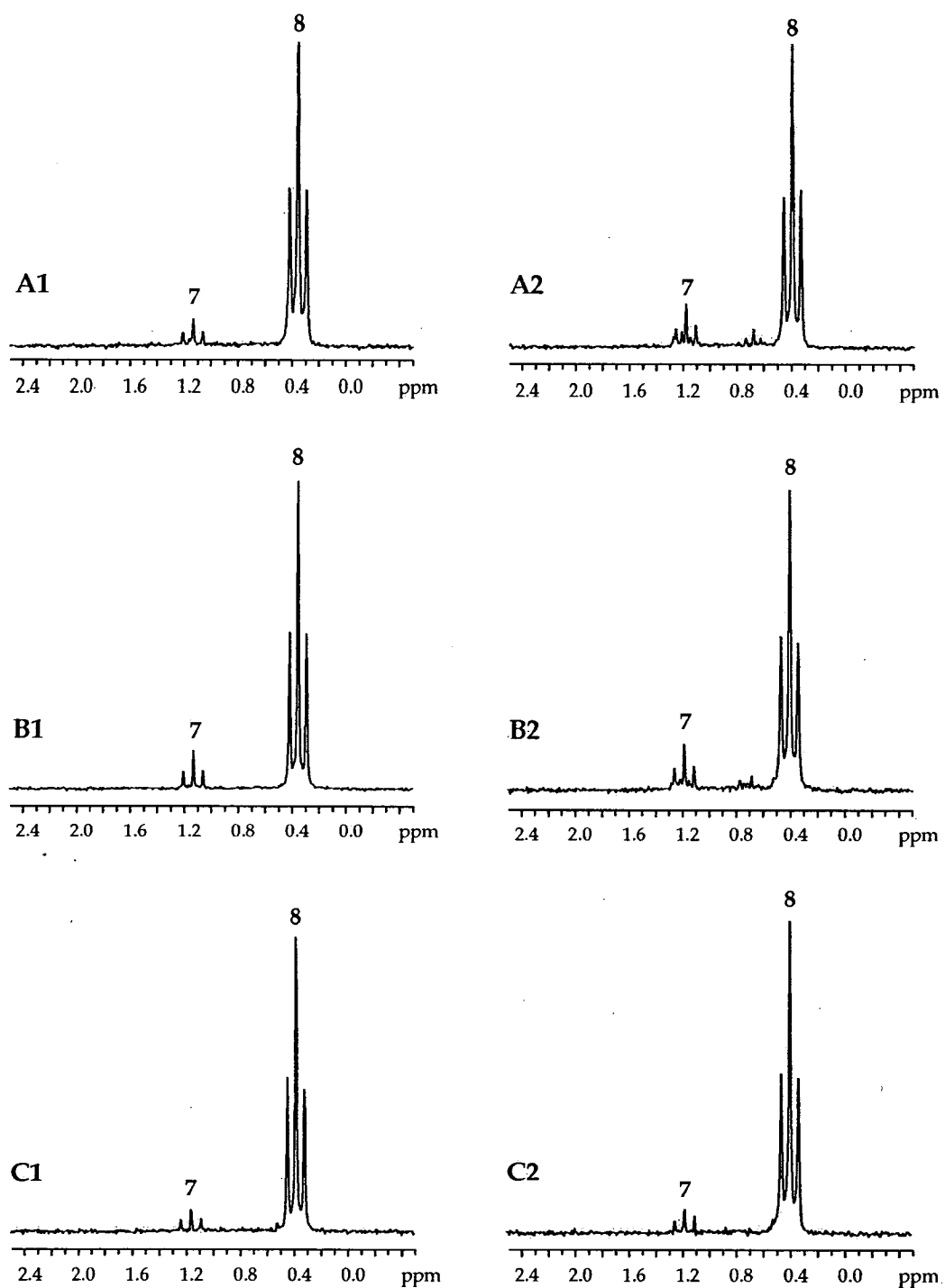
**Figure 5.**  ${}^6\text{Li}$  NMR spectra recorded on 0.1 M  $[{}^6\text{Li}, {}^{15}\text{N}]\text{LiHMDS}$  in  $\text{Et}_3\text{N}$  (G)/pentane mixtures at  $-60\text{ }^\circ\text{C}$ . Dimer  $10_{\text{G}}$  and monomer  $11_{\text{G}}$  were monitored at different  $\text{Et}_3\text{N}$  concentrations: (A) 0 M (showing higher oligomer 7 and dimer 8); (B) 0.05 M; (C) 0.10 M; (D) 0.15 M; (E) 0.30 M; (F) 0.45 M; (G) 0.60 M; (H) 0.90 M; (I) 1.2 M; (J) 1.8 M.



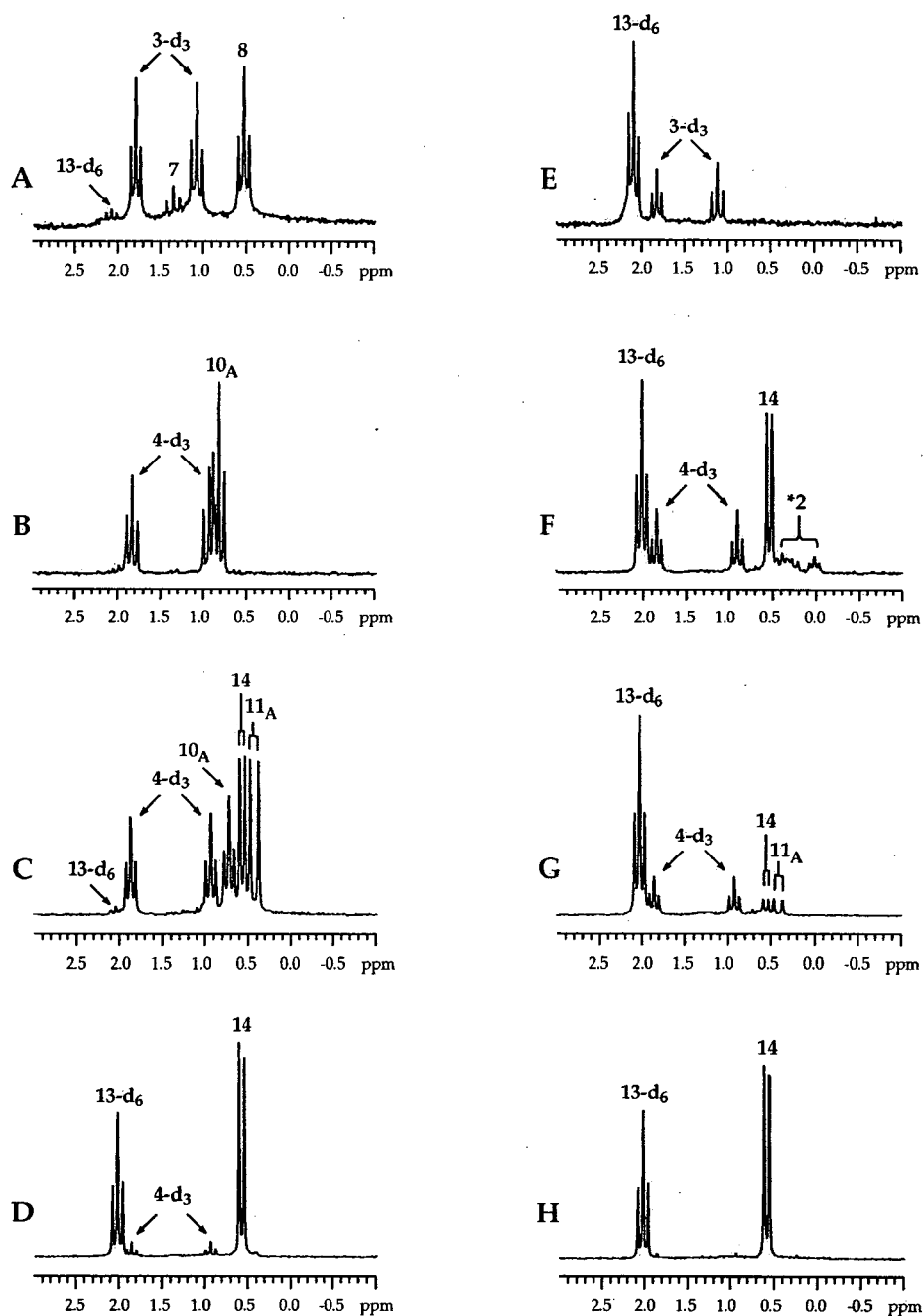
**Figure 6.** Plot of <sup>6</sup>Li chemical shift vs [Et<sub>3</sub>N] for 0.1 M [<sup>6</sup>Li, <sup>15</sup>N]LiHMDS in pentane at -60 °C. The curve depicts the results of an unweighted least-squares fit to  $y = ax/(1 + bx) + c$ . The values of the parameters are as follows:  $a = -9 \pm 1$  (ppm·M<sup>-1</sup>),  $b = K_{eq} = 28 \pm 3$  (M<sup>-1</sup>),  $c = 2 \pm 1$  (ppm).



**Figure 7.**  ${}^6\text{Li}$  NMR spectra recorded on 0.1 M  $[{}^6\text{Li}, {}^{15}\text{N}]\text{LiHMDS}$  in  $\text{EtNi-Pr}_2$ /toluene mixtures at  $-78^\circ\text{C}$ . Higher oligomer **7** and dimer **8** were monitored at different  $\text{EtNi-Pr}_2$  concentrations: (A) 0 M; (B) 0.15 M; (C) 0.60 M; (D) 1.2 M.



**Figure 8.**  ${}^6\text{Li}$  NMR spectra recorded on 0.1 M  $[{}^6\text{Li}, {}^{15}\text{N}]\text{LiHMDS}$  in different amine/toluene mixtures at  $-78\text{ }^\circ\text{C}$ : (A)  $i\text{-Bu}_3\text{N}$  (O); (B)  $n\text{-BuNi-Bu}_2$  (T); (C)  $\text{MeNi-Bu}_2$  (J). Higher oligomer 7 and dimer 8 were monitored at two amine concentrations: (1) 0.15 M; (2) 0.60 M.

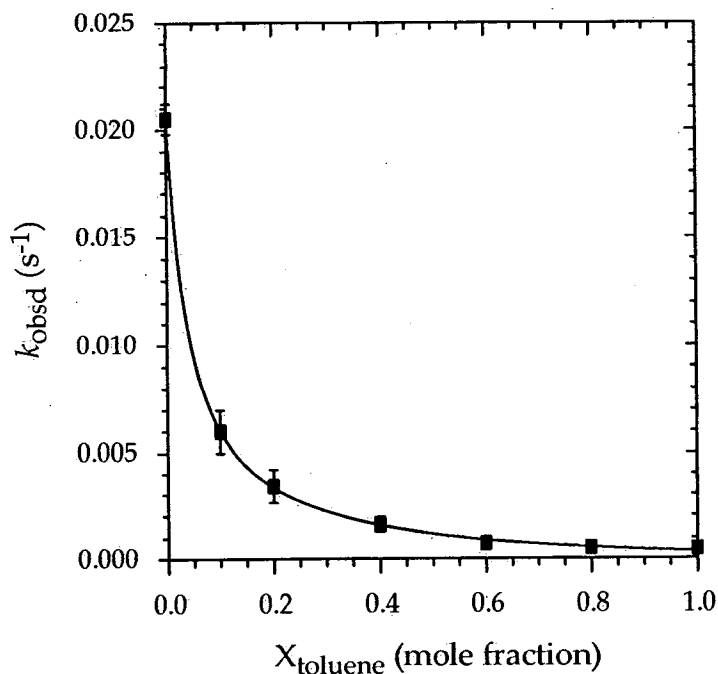


**Figure 9.**  ${}^6\text{Li}$  NMR spectra of  $[{}^6\text{Li}, {}^{15}\text{N}]\text{LiHMDS}$ ,  $\text{Me}_2\text{NEt}$  (A), and  $1\text{-}d_3$  in toluene at  $-100\text{ }^\circ\text{C}$  with: (A) 0.2 equiv of  $1\text{-}d_3$ ; (B) 0.2 equiv of  $1\text{-}d_3$  and 6.0 equiv of  $\text{Me}_2\text{NEt}$ ; (C) 0.2 equiv of  $1\text{-}d_3$  and 12 equiv of  $\text{Me}_2\text{NEt}$ ; (D) 0.5 equiv of  $1\text{-}d_3$  and 12 equiv of  $\text{Me}_2\text{NEt}$ ; (E) 0.8 equiv of  $1\text{-}d_3$ ; (F) 0.8 equiv of  $1\text{-}d_3$  and 1.5 equiv of  $\text{Me}_2\text{NEt}$ ; (G) 0.8 equiv of  $1\text{-}d_3$  and 6.0 equiv of  $\text{Me}_2\text{NEt}$ ; (H) 0.8 equiv of  $1\text{-}d_3$  and 12 equiv of  $\text{Me}_2\text{NEt}$ .

**Part II. *in situ* IR Kinetic Studies**

**I.** Table of rate constants for the enolizations of **1** (0.004M) by LiHMDS (0.10 M) in hydrocarbon solvents at  $-40\text{ }^{\circ}\text{C}$ .

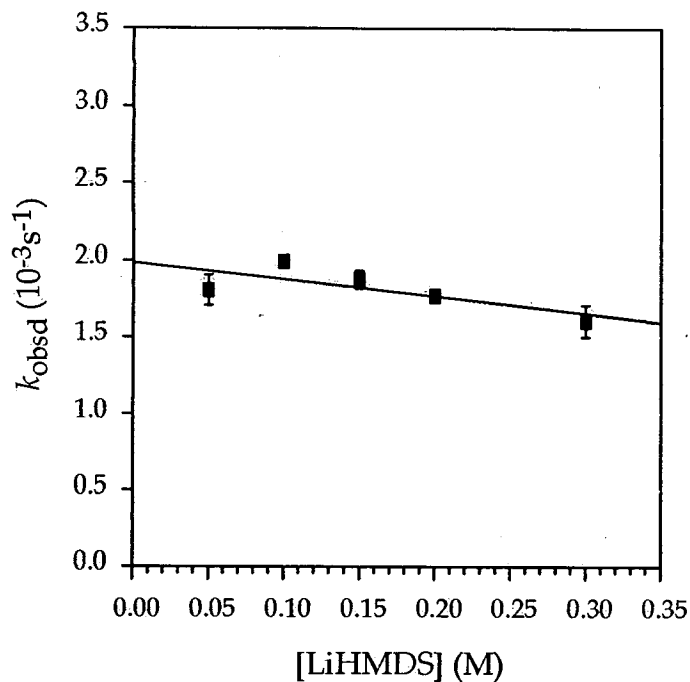
Solvent	$k_{\text{obsd1}}\text{ (s}^{-1}\text{)}$	$k_{\text{obsd2}}\text{ (s}^{-1}\text{)}$	$k_{\text{obsd}}\text{ (avg) (s}^{-1}\text{)}$	$k_{\text{rel}}$
Toluene	$2.22 \pm 0.05\text{E-3}$	$1.80 \pm 0.04\text{E-3}$	$2.0 \pm 0.1\text{E-3}$	1
Mesitylene	$3.84 \pm 0.08\text{E-3}$	$4.0 \pm 0.1\text{E-3}$	$3.9 \pm 0.1\text{E-3}$	2
1-Pentene	$5.5 \pm 0.2\text{E-3}$	$5.5 \pm 0.1\text{E-3}$	$5.5 \pm 0.2\text{E-3}$	3
1-Hexene	$5.5 \pm 0.1\text{E-3}$	$5.9 \pm 0.2\text{E-3}$	$5.7 \pm 0.2\text{E-3}$	3
3-Hexyne	$6.0 \pm 0.3\text{E-3}$	$6.6 \pm 0.4\text{E-3}$	$6.3 \pm 0.4\text{E-3}$	3
Pentane	$1.32 \pm 0.03\text{E-2}$	$1.28 \pm 0.04\text{E-2}$	$1.3 \pm 0.1\text{E-2}$	6
Cyclopentane	$1.34 \pm 0.05\text{E-2}$	$1.27 \pm 0.05\text{E-2}$	$1.3 \pm 0.1\text{E-2}$	6
Hexane	$1.348 \pm 0.009\text{E-2}$	$1.34 \pm 0.02\text{E-2}$	$1.34 \pm 0.01\text{E-2}$	7
Hexanes	$1.87 \pm 0.01\text{E-2}$	$1.925 \pm 0.006\text{E-2}$	$1.90 \pm 0.01\text{E-2}$	10



II. Plot of  $k_{\text{obsd}}$  vs  $X_{\text{toluene}}$  ( $X$  = mole fraction) in hexane for the enolization of **1-d<sub>3</sub>** (0.004 M) by LiHMDS (0.10 M) at  $-60$  °C. The curve depicts the results of an unweighted least-squares fit to  $k_{\text{obsd}} = (a + bx)/(1 + cx)$  ( $a = 2.05 \pm 0.01 \times 10^{-2}$ ,  $b = -1.3 \pm 0.2 \times 10^{-2}$ ,  $c = 21.9 \pm 0.7$ ,  $K_{\text{eq}} = 1 + c = 22.9 \pm 0.7$ ).

III. Table of data for plot in section II.

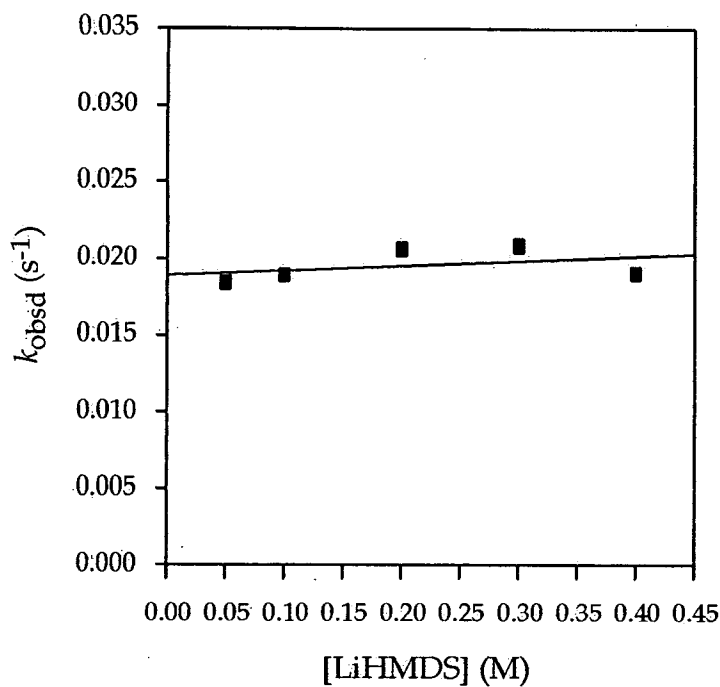
$X_{\text{toluene}}$	$k_{\text{obsd1}}$ ( $\text{s}^{-1}$ )	$k_{\text{obsd2}}$ ( $\text{s}^{-1}$ )	$k_{\text{obsd}}$ (avg) ( $\text{s}^{-1}$ )
0	$2.00 \pm 0.02\text{E-}2$	$2.1 \pm 0.8\text{E-}2$	$2.1 \pm 0.8\text{E-}2$
0.1	$6.70 \pm 0.07\text{E-}3$	$5.2 \pm 0.1\text{E-}3$	$6 \pm 1\text{E-}3$
0.2	$2.7 \pm 0.1\text{E-}3$	$4.0 \pm 0.2\text{E-}3$	$3.4 \pm 0.2\text{E-}3$
0.4	$1.8 \pm 0.2\text{E-}3$	$1.3 \pm 0.1\text{E-}3$	$1.6 \pm 0.2\text{E-}3$
0.6	$7.3 \pm 0.1\text{E-}4$	--	--
0.8	$5.33 \pm 0.09\text{E-}4$	--	--
1.0	$4.79 \pm 0.03\text{E-}4$	--	--



IV. Plot of  $k_{\text{obsd}}$  vs [LiHMDS] in toluene for the enolization of **1** (0.004 M) by 0.10 M LiHMDS at  $-40$  °C. The curve depicts the results of an unweighted least-squares fit to  $k_{\text{obsd}} = a[\text{LiHMDS}] + b$  ( $a = -1.1 \pm 0.6 \times 10^{-3}$ ,  $b = 2.0 \pm 0.1 \times 10^{-3}$ ).

V. Table of data for plot in section IV.

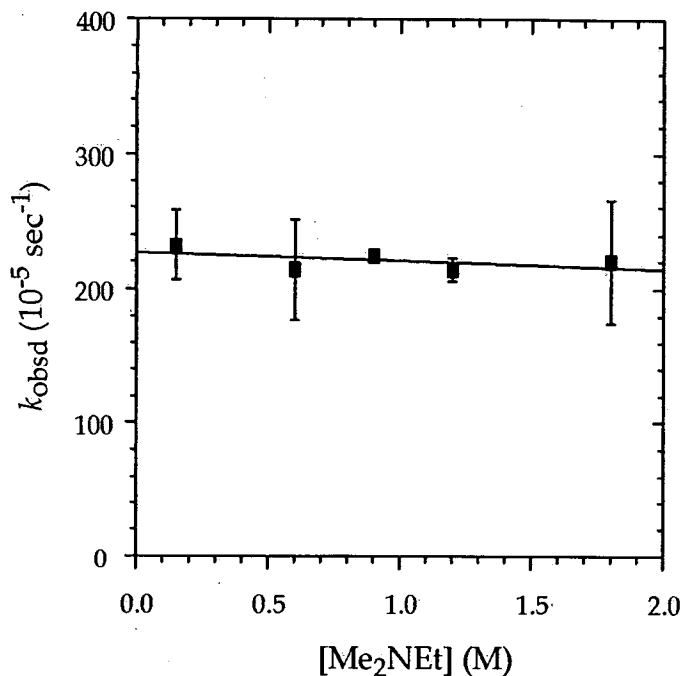
[LiHMDS] (M)	$k_{\text{obsd}1} (\text{s}^{-1})$	$k_{\text{obsd}2} (\text{s}^{-1})$	$k_{\text{obsd}} (\text{avg}) (\text{s}^{-1})$
0.05	$1.76 \pm 0.03\text{E-}3$	$1.95 \pm 0.05\text{E-}3$	$1.8 \pm 0.1\text{E-}3$
0.10	$2.00 \pm 0.03\text{E-}3$	$1.98 \pm 0.02\text{E-}3$	$1.99 \pm 0.03\text{E-}3$
0.15	$1.81 \pm 0.04\text{E-}3$	$1.93 \pm 0.04\text{E-}3$	$1.87 \pm 0.04\text{E-}3$
0.20	$1.81 \pm 0.04\text{E-}3$	$1.72 \pm 0.03\text{E-}3$	$1.76 \pm 0.04\text{E-}3$
0.30	$1.72 \pm 0.03\text{E-}3$	$1.46 \pm 0.03\text{E-}3$	$1.6 \pm 0.1\text{E-}3$



VI. Plot of  $k_{\text{obsd}}$  vs [LiHMDS] in hexane for the enolization of **1** (0.004 M) by 0.10 M LiHMDS at  $-40$  °C. The curve depicts the results of an unweighted least-squares fit to  $k_{\text{obsd}} = a[\text{LiHMDS}] + b$  ( $a = 3 \pm 4 \times 10^{-3}$ ,  $b = 1.9 \pm 0.1 \times 10^{-2}$ ).

VII. Table of data for plot in section VI.

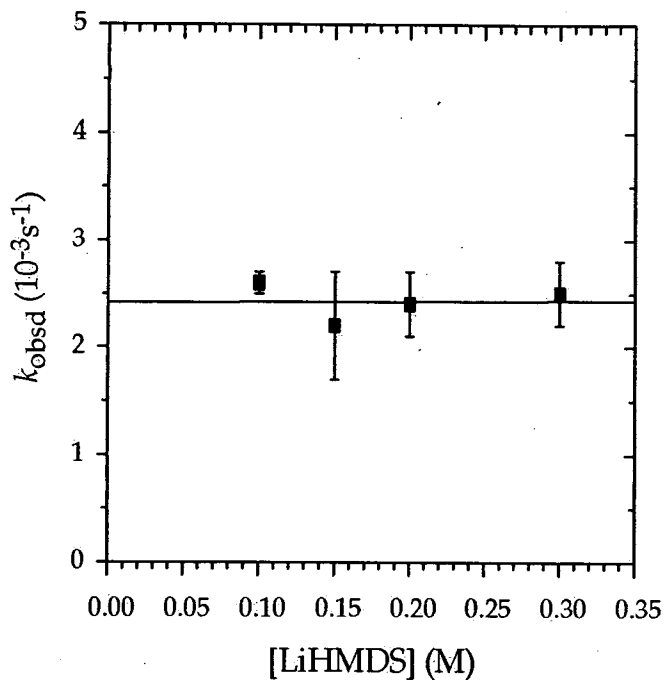
[LiHMDS] (M)	$k_{\text{obsd}}$ ( $\text{s}^{-1}$ )
0.05	$1.84 \pm 0.08\text{E-}2$
0.10	$1.89 \pm 0.06\text{E-}2$
0.20	$2.06 \pm 0.06\text{E-}2$
0.30	$2.08 \pm 0.06\text{E-}2$
0.40	$1.9 \pm 0.1\text{E-}2$



**VIII.** Plot of  $k_{\text{obsd}}$  vs  $[\text{Me}_2\text{NEt}]$  in toluene for the enolization of **1** (0.004 M) by LiHMDS (0.10 M) at  $-78\text{ }^\circ\text{C}$ . The curve depicts the results of an unweighted least-squares fit to  $k_{\text{obsd}} = a[\text{Me}_2\text{NEt}] + b$  where  $a = 6 \pm 6 \times 10^5 \text{ (s}^{-1}\cdot\text{M}^{-1})$ ,  $b = 2.26 \pm 0.07 \times 10^{-3} \text{ (s}^{-1})$ .

**IX.** Table of data for plot in section **VIII**.

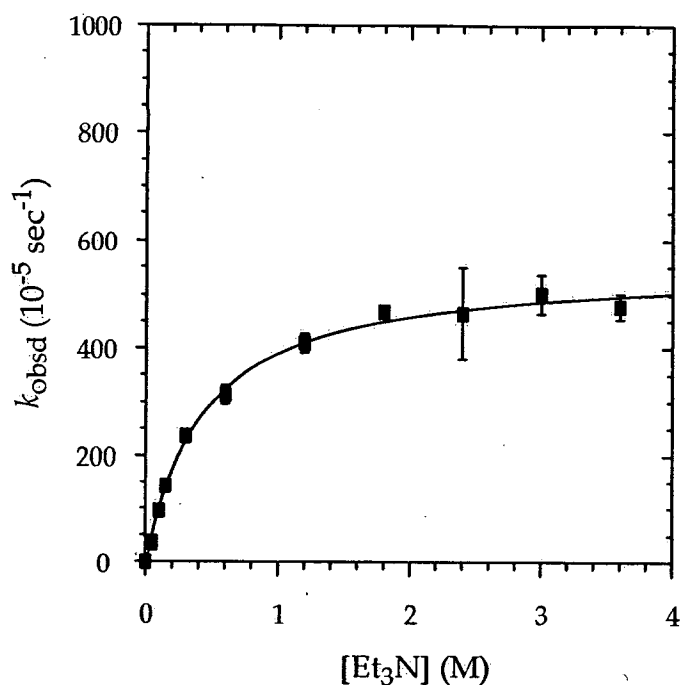
$[\text{Me}_2\text{NEt}] \text{ (M)}$	$k_{\text{obsd}1} \text{ (s}^{-1})$	$k_{\text{obsd}2} \text{ (s}^{-1})$	$k_{\text{obsd}3} \text{ (s}^{-1})$	$k_{\text{obsd}} \text{ (avg) (s}^{-1})$
0.15	$2.14 \pm 0.02\text{E-}3$	$2.50 \pm 0.03\text{E-}3$	$1.85 \pm 0.01\text{E-}3$	$2.3 \pm 0.1\text{E-}3$
0.60	$1.87 \pm 0.07\text{E-}3$	$2.40 \pm 0.04\text{E-}3$	$1.80 \pm 0.02\text{E-}3$	$2.1 \pm 0.1\text{E-}3$
0.90	$2.2 \pm 0.1\text{E-}3$	$2.2 \pm 0.2\text{E-}3$	--	$2.2 \pm 0.2\text{E-}3$
1.2	$2.07 \pm 0.08\text{E-}3$	$2.2 \pm 0.4\text{E-}3$	--	$2.1 \pm 0.4\text{E-}3$
1.8	$1.89 \pm 0.03\text{E-}3$	$2.52 \pm 0.07\text{E-}3$	--	$2.2 \pm 0.1\text{E-}3$



X. Plot of  $k_{\text{obsd}}$  vs [LiHMDS] for the enolization of 1 (0.004 M) by 0.10 M LiHMDS in  $\text{Me}_2\text{NEt}$ /toluene at  $-78^\circ\text{C}$ . The curve depicts the results of an unweighted least-squares fit to  $k_{\text{obsd}} = a[\text{LiHMDS}] + b$  ( $a = 0 \pm 2 \times 10^{-4}$ ,  $b = 2.4 \pm 0.3 \times 10^{-3}$ ).

XI. Table of data for plot in section X.

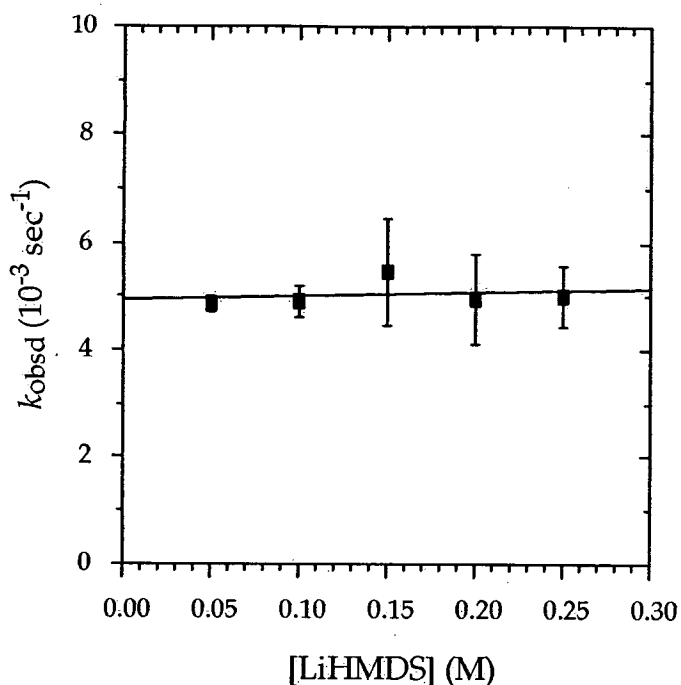
[LiHMDS] (M)	$k_{\text{obsd}1} (\text{s}^{-1})$	$k_{\text{obsd}2} (\text{s}^{-1})$	$k_{\text{obsd}} (\text{avg}) (\text{s}^{-1})$
0.10	$2.5 \pm 0.2\text{E-}3$	$2.7 \pm 0.2\text{E-}3$	$2.6 \pm 0.2\text{E-}3$
0.15	$2.5 \pm 0.3\text{E-}3$	$1.8 \pm 0.3\text{E-}3$	$2.2 \pm 0.3\text{E-}3$
0.20	$2.6 \pm 0.4\text{E-}3$	$2.0 \pm 0.1\text{E-}3$	$2.4 \pm 0.4\text{E-}3$
0.30	$2.7 \pm 0.3\text{E-}3$	$2.3 \pm 0.4\text{E-}3$	$2.5 \pm 0.4\text{E-}3$



**XII.** Plot of  $k_{\text{obsd}}$  vs  $[\text{Et}_3\text{N}]$  in toluene for the enolization of **1-d<sub>3</sub>** (0.004 M) by LiHMDS (0.10 M) at  $-78\text{ }^\circ\text{C}$ . The curve depicts the results of an unweighted least-squares fit to  $k_{\text{obsd}} = a[\text{Et}_3\text{N}]/(1 + b[\text{Et}_3\text{N}])$  ( $a = 1.25 \pm 0.08 \times 10^{-2}$ ,  $K_{\text{eq}} = b = 2.2 \pm 0.2$ ,  $k_2 = a/b = 5.7 \times 10^{-3}$ ).

**XIII.** Table of data for plot in section XII.

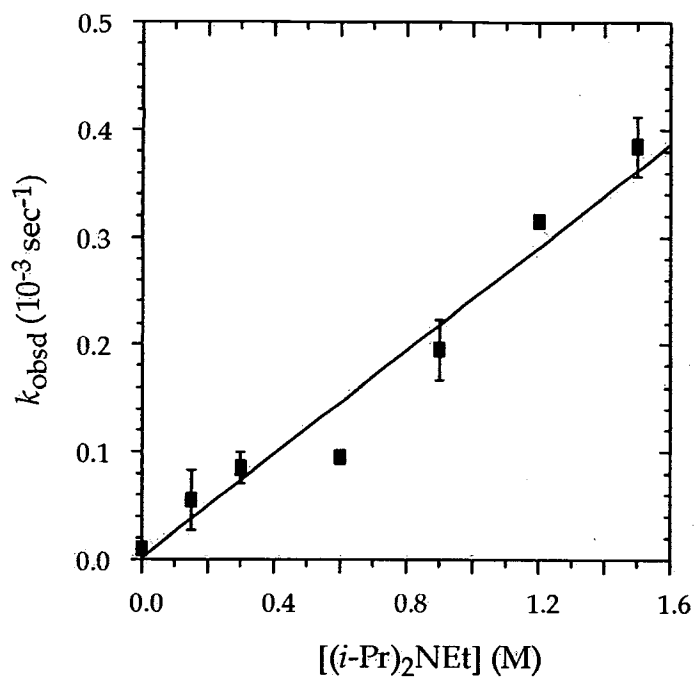
$[\text{Et}_3\text{N}]$ (M)	$k_{\text{obsd}1}$ ( $\text{s}^{-1}$ )	$k_{\text{obsd}2}$ ( $\text{s}^{-1}$ )	$k_{\text{obsd}}(\text{avg})$ ( $\text{s}^{-1}$ )
0.15	$1.46 \pm 0.02\text{E-}3$	$1.40 \pm 0.02\text{E-}3$	$1.43 \pm 0.02\text{E-}3$
0.30	$2.32 \pm 0.04\text{E-}3$	$2.39 \pm 0.03\text{E-}3$	$2.36 \pm 0.04\text{E-}3$
0.60	$3.02 \pm 0.07\text{E-}3$	$3.2 \pm 0.1\text{E-}3$	$3.1 \pm 0.1\text{E-}3$
1.2	$4.0 \pm 0.2\text{E-}3$	$4.2 \pm 0.1\text{E-}3$	$4.1 \pm 0.2\text{E-}3$
1.8	$4.7 \pm 0.1\text{E-}3$	$4.7 \pm 0.2\text{E-}3$	$4.7 \pm 0.2\text{E-}3$
2.4	$5.0 \pm 0.4\text{E-}3$	$4.2 \pm 0.1\text{E-}3$	$4.6 \pm 0.4\text{E-}3$
3.0	$4.9 \pm 0.2\text{E-}3$	$5.3 \pm 0.2\text{E-}3$	$5.0 \pm 0.2\text{E-}3$
3.6	$4.6 \pm 0.2\text{E-}3$	$5.0 \pm 0.1\text{E-}3$	$4.8 \pm 0.2\text{E-}3$



XIV. Plot of  $k_{\text{obsd}}$  vs [LiHMDS] for the enolization of **1-d<sub>3</sub>** (0.004 M) by 0.10 M LiHMDS in Et<sub>3</sub>N/toluene at -78 °C. The curve depicts the results of an unweighted least-squares fit to  $k_{\text{obsd}} = a[\text{LiHMDS}] + b$  ( $a = 2 \pm 3 \times 10^{-3}$ ,  $b = 4.8 \pm 0.4 \times 10^{-4}$ ).

XV. Table of data for plot in section XIV.

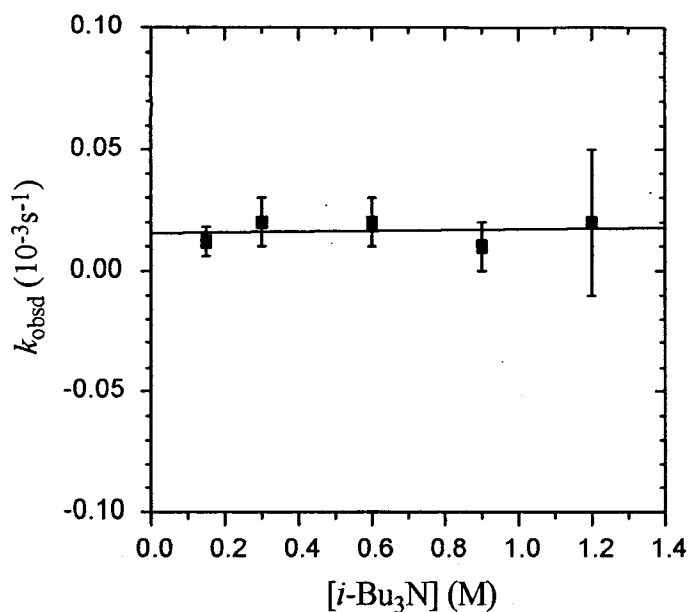
[LiHMDS] (M)	$k_{\text{obsd}1} (\text{s}^{-1})$	$k_{\text{obsd}2} (\text{s}^{-1})$	$k_{\text{obsd}} (\text{avg}) (\text{s}^{-1})$
0.05	$4.7 \pm 0.1\text{E-}3$	$4.9 \pm 0.2\text{E-}3$	$4.8 \pm 0.2\text{E-}3$
0.10	$4.8 \pm 0.2\text{E-}3$	$5.3 \pm 0.3\text{E-}3$	$5.0 \pm 0.3\text{E-}3$
0.15	$5.8 \pm 0.4\text{E-}3$	$4.4 \pm 0.3\text{E-}3$	$5 \pm 1\text{E-}3$
0.20	$5.3 \pm 0.2\text{E-}3$	$4.0 \pm 0.2\text{E-}3$	$4.6 \pm 0.2\text{E-}3$
0.25	$5.2 \pm 0.7\text{E-}3$	$4.4 \pm 0.2\text{E-}3$	$4.8 \pm 0.7\text{E-}3$



**XVI.** Plot of  $k_{\text{obsd}}$  vs  $[i\text{-Pr}_2\text{NEt}]$  in toluene for the enolization of **1** (0.004 M) by LiHMDS (0.10 M) at  $-78\text{ }^\circ\text{C}$ . The curve depicts the results of an unweighted least-squares fit to  $k_{\text{obsd}} = a[i\text{-Pr}_2\text{NEt}] + b$  ( $a = 2.4 \pm 0.2 \times 10^{-4}$ ,  $b = 0 \pm 2 \times 10^{-5}$ ).

**XVII.** Table of data for plot in section **XVI**.

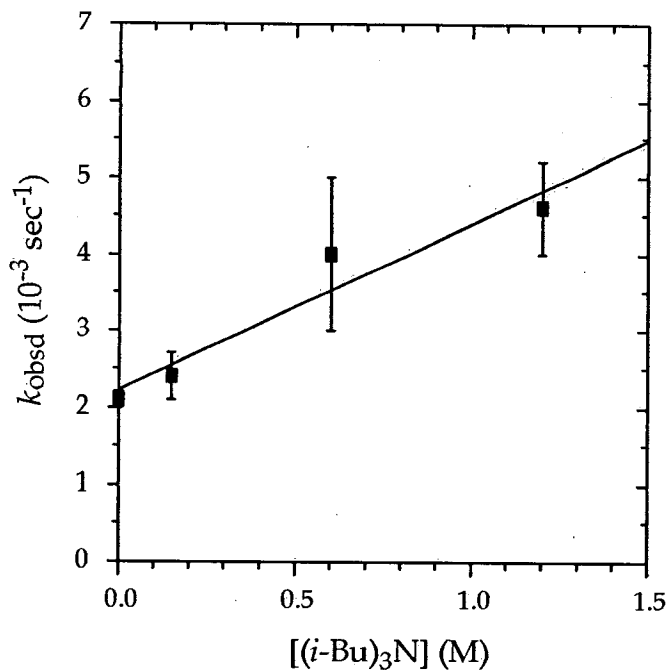
$[i\text{-Pr}_2\text{NEt}]$ (M)	$k_{\text{obsd}1}$ ( $\text{s}^{-1}$ )	$k_{\text{obsd}2}$ ( $\text{s}^{-1}$ )	$k_{\text{obsd}}(\text{avg})$ ( $\text{s}^{-1}$ )
0.15	$7 \pm 1\text{E-}5$	$4 \pm 1\text{E-}5$	$6 \pm 1\text{E-}5$
0.30	$9 \pm 7\text{E-}5$	$7.9 \pm 0.7\text{E-}5$	$8 \pm 7\text{E-}5$
0.60	$9.3 \pm 0.2\text{E-}5$	$1.0 \pm 0.1\text{E-}4$	$1.0 \pm 0.1\text{E-}4$
0.90	$2.1 \pm 0.2\text{E-}4$	$1.8 \pm 0.1\text{E-}4$	$2.0 \pm 0.2\text{E-}4$
1.2	$3.1 \pm 0.3\text{E-}4$	$3.2 \pm 0.0\text{E-}4$	$3.2 \pm 0.3\text{E-}4$
1.5	$4.0 \pm 0.1\text{E-}4$	$3.7 \pm 0.0\text{E-}4$	$3.8 \pm 0.1\text{E-}4$



**XVIII** Plot of  $k_{\text{obsd}}$  vs.  $[(i\text{-Bu})_3\text{N}]$  (O) in toluene for the enolization of **1** (0.004 M) by LiHMDS (0.10 M) at  $-78^\circ\text{C}$ . The curve depicts the results of an unweighted least-square fit to  $k_{\text{obsd}} = a[(i\text{-Bu})_3\text{N}] + b$ , where  $a = 2 \pm 7 \times 10^{-6} \text{ (s}^{-1}\cdot\text{M}^{-1}\text{)}$ ,  $b = 1.5 \pm 0.5 \times 10^{-5} \text{ (s}^{-1}\text{)}$ .

**XIX.** Table of data for plot in section XVIII.

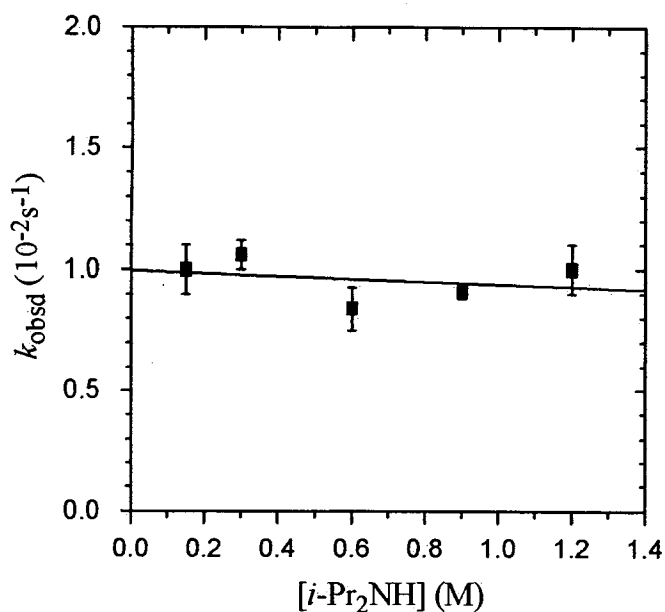
$[(i\text{-Bu})_3\text{N}] \text{ (M)}$	$k_{\text{obsd1}} \text{ (s}^{-1}\text{)}$	$k_{\text{obsd2}} \text{ (s}^{-1}\text{)}$	$k_{\text{obsd}} \text{ (avg) (s}^{-1}\text{)}$
0.15	$7 \pm 1\text{E-}6$	$1.6 \pm 0.3\text{E-}5$	$1.2 \pm 0.3\text{E-}5$
0.30	$1.5 \pm 0.7\text{E-}5$	$2.9 \pm 0.6\text{E-}5$	$2 \pm 1\text{E-}5$
0.60	$2 \pm 2\text{E-}6$	$2.8 \pm 0.7\text{E-}5$	$2 \pm 2\text{E-}5$
0.90	$2 \pm 0.1\text{E-}6$	$0.0 \pm 0.5\text{E-}5$	$1 \pm 1\text{E-}6$
1.2	$4 \pm 1\text{E-}6$	$4.4 \pm 0.2\text{E-}5$	$2 \pm 1\text{E-}5$



XX. Plot of  $k_{\text{obsd}}$  vs  $[(i\text{-Bu})_3\text{N}]$  in toluene for the enolization of **1** (0.004 M) by LiHMDS (0.10 M) at  $-40\text{ }^\circ\text{C}$ . The curve depicts the results of an unweighted least-squares fit to  $k_{\text{obsd}} = a[(i\text{-Bu})_3\text{N}] + b$  ( $a = 2.2 \pm 0.4 \times 10^{-3}$ ,  $b = 2.2 \pm 0.1 \times 10^{-3}$ ).

XXI. Table of data for plot in section XX.

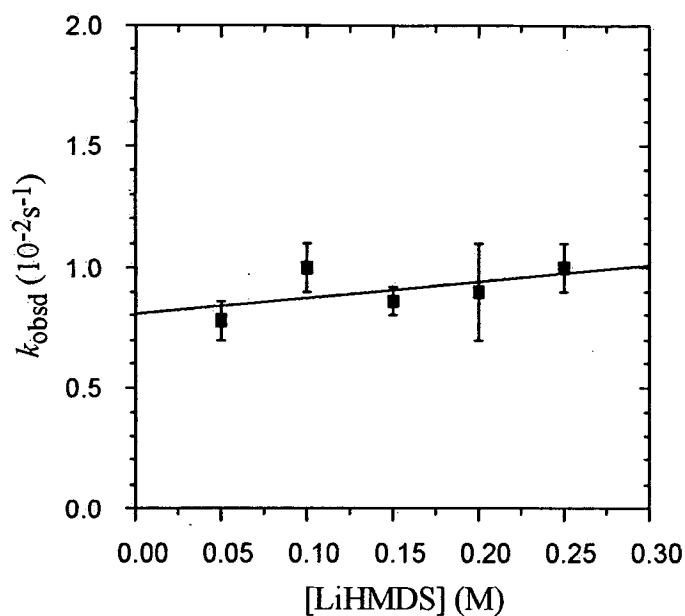
$[(i\text{-Bu})_3\text{N}]$ (M)	$k_{\text{obsd}1}$ ( $\text{s}^{-1}$ )	$k_{\text{obsd}2}$ ( $\text{s}^{-1}$ )	$k_{\text{obsd}3}$ ( $\text{s}^{-1}$ )	$k_{\text{obsd}}$ (avg) ( $\text{s}^{-1}$ )
0	$2.18 \pm 0.08\text{E-}3$	$2.0 \pm 0.1\text{E-}3$	$1.98 \pm 0.08\text{E-}3$	$2.1 \pm 0.1\text{E-}3$
0.15	$2.2 \pm 0.1\text{E-}3$	$2.5 \pm 0.1\text{E-}3$	$2.45 \pm 0.05\text{E-}3$	$2.4 \pm 0.1\text{E-}3$
0.60	$3.1 \pm 0.1\text{E-}3$	$2.5 \pm 0.1\text{E-}3$	$5.3 \pm 0.2\text{E-}3$	$4 \pm 1\text{E-}3$
1.2	$4.5 \pm 0.3\text{E-}3$	$5.2 \pm 0.2\text{E-}3$	$4.2 \pm 0.1\text{E-}3$	$4.6 \pm 0.3\text{E-}3$



**XXII.** Plot of  $k_{\text{obsd}}$  vs  $[i\text{-Pr}_2\text{NH}]$  in toluene for the enolization of **4** (0.004 M) by LiHMDS (0.10 M) at  $-78^\circ\text{C}$ . The curve depicts the results of an unweighted least-squares fit to  $k_{\text{obsd}} = ax + b$  ( $a = -1 \pm 1 \times 10^{-3}$ ,  $b = 1.00 \pm 0.08 \times 10^{-2}$ ).

**XXIII.** Table of data for plot in section **XXII**.

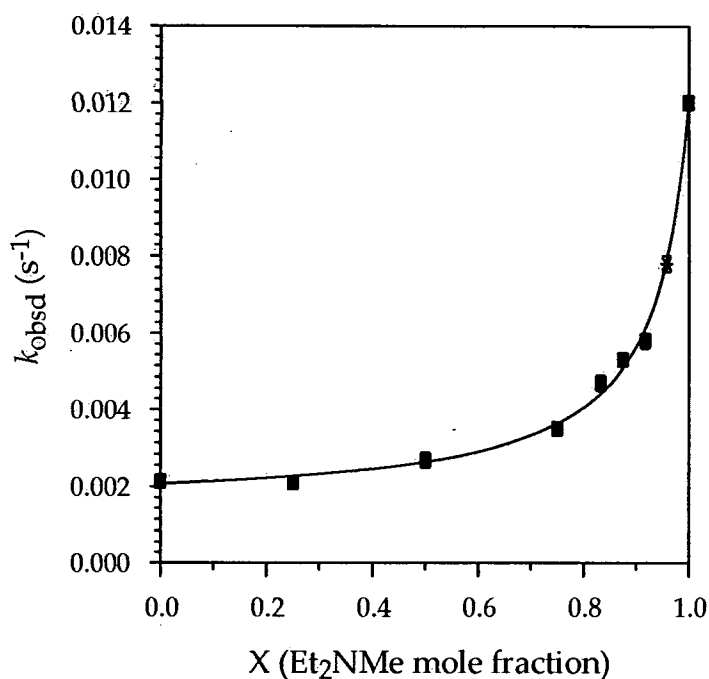
$[i\text{-Pr}_2\text{NH}]$ (M)	$k_{\text{obsd1}}$ ( $\text{s}^{-1}$ )	$k_{\text{obsd2}}$ ( $\text{s}^{-1}$ )	$k_{\text{obsd}}(\text{avg})$ ( $\text{s}^{-1}$ )
0.15	$1.1 \pm 0.1\text{E-}2$	$8.4 \pm 0.3\text{E-}3$	$1.0 \pm 0.3\text{E-}2$
0.30	$1.02 \pm 0.03\text{E-}2$	$1.1 \pm 0.1\text{E-}2$	$1.1 \pm 0.1\text{E-}2$
0.60	$9 \pm 1\text{E-}3$	$7.7 \pm 0.4\text{E-}3$	$8 \pm 1\text{E-}3$
0.90	$9.3 \pm 0.4\text{E-}3$	$8.9 \pm 0.5\text{E-}3$	$9.1 \pm 0.5\text{E-}3$
1.2	$1.1 \pm 0.1\text{E-}2$	$9.3 \pm 0.5\text{E-}3$	$1.0 \pm 0.1\text{E-}2$



**XXIV.** Plot of  $k_{\text{obsd}}$  vs [LiHMDS] in *i*-Pr<sub>2</sub>NH/toluene for the enolization of **4** (0.004 M) by LiHMDS at -78 °C. The curve depicts the results of an unweighted least-squares fit to  $k_{\text{obsd}} = ax + b$  ( $a = 7 \pm 6 \times 10^{-3}$ ,  $b = 8.1 \pm 0.9 \times 10^{-3}$ ).

**XXV.** Table of data for plot in section **XXIV**:

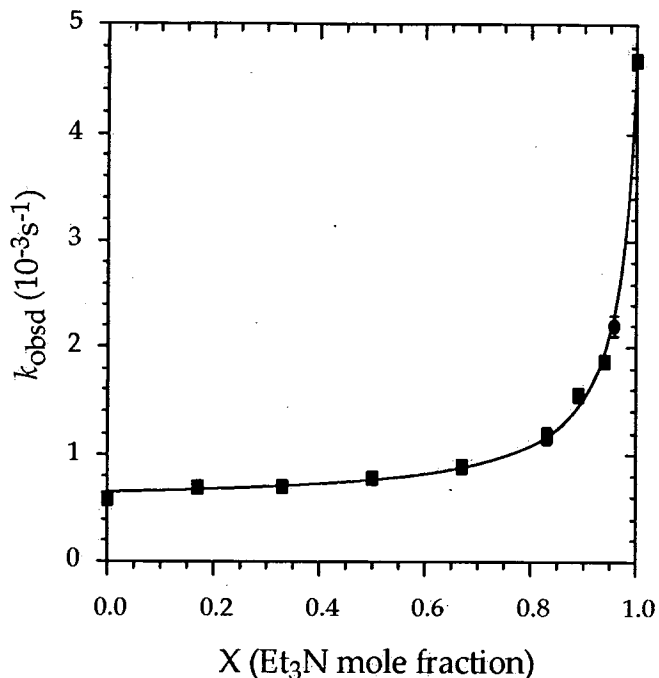
[LiHMDS] (M)	$k_{\text{obsd}1} (\text{s}^{-1})$	$k_{\text{obsd}2} (\text{s}^{-1})$	$k_{\text{obsd}} (\text{avg}) (\text{s}^{-1})$
0.05	$7.8 \pm 0.8\text{E-}3$	$7.8 \pm 0.3\text{E-}3$	$7.8 \pm 0.8\text{E-}3$
0.10	$1.1 \pm 0.1\text{E-}2$	$9.3 \pm 0.5\text{E-}3$	$1.0 \pm 0.1\text{E-}2$
0.15	$9 \pm 1\text{E-}3$	$8.2 \pm 0.3\text{E-}3$	$9 \pm 1\text{E-}3$
0.20	$7.4 \pm 0.3\text{E-}3$	$1.01 \pm 0.05\text{E-}2$	$9 \pm 1\text{E-}3$
0.25	$1.1 \pm 0.1\text{E-}2$	$9.1 \pm 0.4\text{E-}3$	$1.0 \pm 0.4\text{E-}2$



**XXVI.** Plot of  $k_{\text{obsd}}$  vs  $X_{\text{MeNEt}_2}$  ( $X$  = mole fraction) in  $\text{Me}_2\text{NEt}/\text{MeNEt}_2$  (1.2 M total)/toluene mixtures for the enolization of **1** (0.004 M) by LiHMDS (0.10 M) at  $-78$  °C. The curve depicts the results of an unweighted least-squares fit to  $k_{\text{obsd}} = (a + bx)/(1 + cx)$  ( $a = 2.1 \pm 0.1 \times 10^{-3}$ ,  $b = -1.3 \pm 0.2 \times 10^{-3}$ ,  $c = -0.938 \pm 0.006$ ). The point with \* is not included in the fit.

**XXVII.** Table of data for plot in section XXVI.

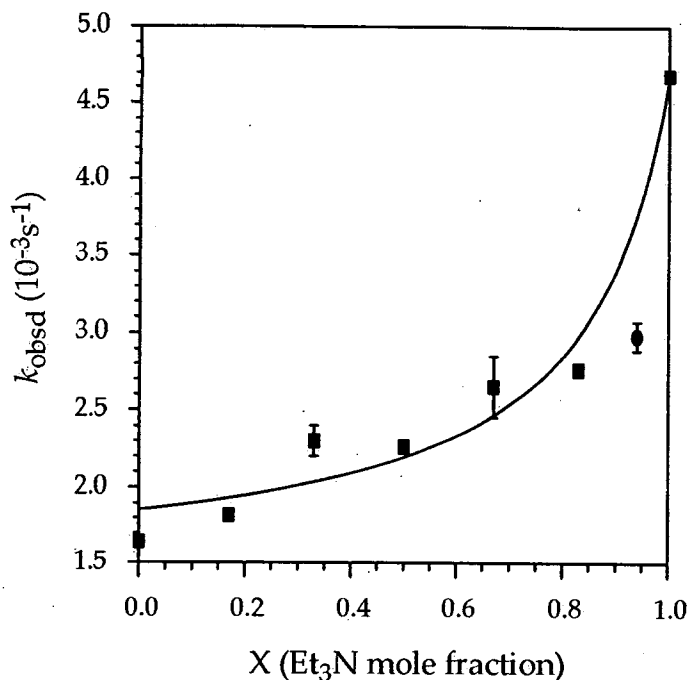
MeNEt <sub>2</sub> mol%	$k_{\text{obsd}1}$ (s <sup>-1</sup> )	$k_{\text{obsd}2}$ (s <sup>-1</sup> )	$k_{\text{obsd}}(\text{avg})$ (s <sup>-1</sup> )
0	$2.20 \pm 0.04\text{E-}3$	$2.07 \pm 0.03\text{E-}3$	$2.1 \pm 0.1\text{E-}3$
25	$2.03 \pm 0.03\text{E-}3$	$2.18 \pm 0.03\text{E-}3$	$2.1 \pm 0.1\text{E-}3$
50	$2.87 \pm 0.08\text{E-}3$	$2.44 \pm 0.05\text{E-}3$	$2.7 \pm 0.1\text{E-}3$
75	$3.6 \pm 0.1\text{E-}3$	$3.4 \pm 0.1\text{E-}3$	$3.5 \pm 0.1\text{E-}3$
83	$4.85 \pm 0.04\text{E-}3$	$4.5 \pm 0.9\text{E-}3$	$4.7 \pm 0.9\text{E-}3$
88	$5.4 \pm 0.5\text{E-}3$	$5.2 \pm 0.1\text{E-}3$	$5.3 \pm 0.5\text{E-}3$
92	$6.1 \pm 0.1\text{E-}3$	$5.6 \pm 0.2\text{E-}3$	$5.8 \pm 0.2\text{E-}3$
96*	$7.6 \pm 0.3\text{E-}3$	$7.9 \pm 0.1\text{E-}3$	$7.8 \pm 0.3\text{E-}3$
100	$1.2 \pm 0.1\text{E-}2$	$1.2 \pm 0.1\text{E-}2$	$1.2 \pm 0.1\text{E-}2$



**XXVIII.** Plot of  $k_{\text{obsd}}$  vs  $X_{\text{Et}_3\text{N}}$  ( $X$  = mole fraction) in MeNEt<sub>2</sub>/Et<sub>3</sub>N (1.8 M total)/toluene mixtures for the enolization of **1-d<sub>3</sub>** (0.004 M) by LiHMDS (0.10 M) at  $-78$  °C. The curve depicts the results of an unweighted least-squares fit to  $k_{\text{obsd}} = (a + bx)/(1 + cx)$  ( $a = 6.6 \pm 0.4 \times 10^{-5}$ ,  $b = -5.2 \pm 0.5 \times 10^{-4}$ ,  $c = -0.971 \pm 0.002$ ). The point with \* is not included in the fit.

**XXIX.** Table of data for plot in section XXVIII.

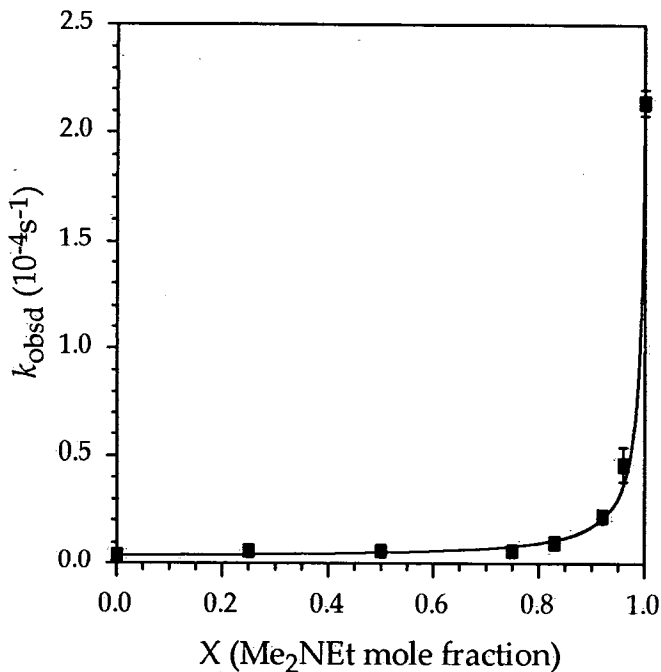
Et <sub>3</sub> N mol%	$k_{\text{obsd}1}$ (s <sup>-1</sup> )	$k_{\text{obsd}2}$ (s <sup>-1</sup> )	$k_{\text{obsd}}$ (avg) (s <sup>-1</sup> )
0	$5.5 \pm 0.2\text{E-}4$	$6.1 \pm 0.7\text{E-}4$	$5.8 \pm 0.7\text{E-}4$
17	$6.9 \pm 0.2\text{E-}4$	$6.9 \pm 0.2\text{E-}4$	$6.9 \pm 0.2\text{E-}4$
33	$7.2 \pm 0.1\text{E-}4$	$6.9 \pm 0.1\text{E-}4$	$7.0 \pm 0.1\text{E-}3$
50	$7.4 \pm 0.1\text{E-}4$	$8.1 \pm 0.1\text{E-}4$	$7.8 \pm 0.1\text{E-}4$
67	$8.8 \pm 0.1\text{E-}4$	$9.0 \pm 0.2\text{E-}4$	$8.9 \pm 0.2\text{E-}4$
83	$1.24 \pm 0.08\text{E-}3$	$1.12 \pm 0.02\text{E-}3$	$1.18 \pm 0.08\text{E-}3$
94	$1.51 \pm 0.07\text{E-}3$	$1.60 \pm 0.01\text{E-}3$	$1.55 \pm 0.07\text{E-}3$
96*	$1.88 \pm 0.06\text{E-}3$	$1.86 \pm 0.05\text{E-}3$	$1.87 \pm 0.06\text{E-}3$
100	$4.65 \pm 0.08\text{E-}2$	$4.71 \pm 0.06\text{E-}2$	$4.68 \pm 0.08\text{E-}2$



XXX. Plot of  $k_{\text{obsd}}$  vs  $X_{\text{Et}_3\text{N}}$  ( $X$  = mole fraction) in MeNEt<sub>2</sub>/2,2,6,6-tetramethylpiperidine (1.8 M total)/toluene mixtures for the enolization of **1-d<sub>3</sub>** (0.004 M) by LiHMDS (0.10 M) at  $-78$  °C. The curve depicts the results of an unweighted least-squares fit to  $k_{\text{obsd}} = (a + bx)/(1 + cx)$  ( $a = 1.9 \pm 0.1 \times 10^{-3}$ ,  $b = -1.2 \pm 0.3 \times 10^{-3}$ ,  $c = -0.86 \pm 0.05$ ). The point with \* is not included in the fit.

XXXI. Table of data for plot in section XXX.

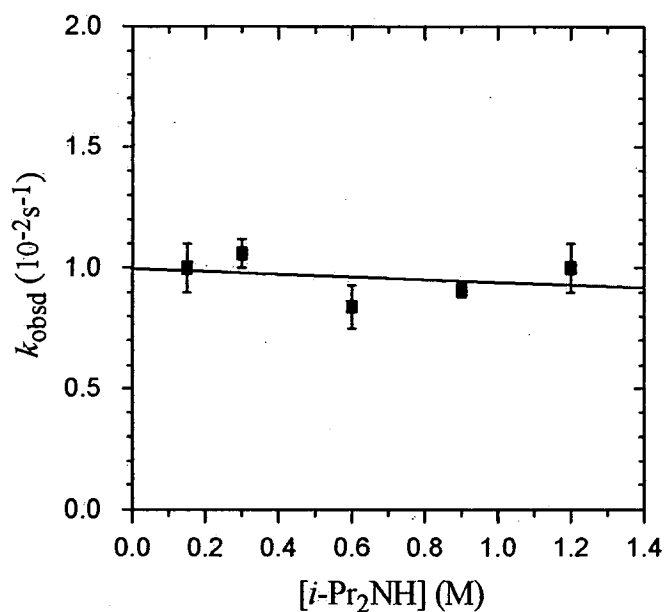
Et <sub>3</sub> N mol%	$k_{\text{obsd}1}$ (s <sup>-1</sup> )	$k_{\text{obsd}2}$ (s <sup>-1</sup> )	$k_{\text{obsd}}$ (avg) (s <sup>-1</sup> )
0	1.60 ± 0.01E-3	1.69 ± 0.01E-3	1.64 ± 0.01E-3
17	1.84 ± 0.06E-3	1.79 ± 0.03E-3	1.82 ± 0.06E-3
33	2.2 ± 0.3E-3	2.4 ± 0.2E-3	2.3 ± 0.3E-3
50	2.29 ± 0.01E-3	2.24 ± 0.01E-3	2.26 ± 0.01E-3
67	2.83 ± 0.02E-3	2.47 ± 0.02E-3	2.7 ± 0.1E-3
83	2.71 ± 0.03E-3	2.80 ± 0.03E-3	2.76 ± 0.03E-3
94*	3.07 ± 0.01E-3	2.89 ± 0.02E-3	3.0 ± 0.1E-3
100	4.65 ± 0.08E-2	4.71 ± 0.06E-2	4.68 ± 0.08E-3



**XXXII.** Plot of  $k_{\text{obsd}}$  vs  $X_{\text{Me}_2\text{NEt}}$  ( $X$  = mole fraction) in  $\text{Me}_2\text{NEt}/i\text{-Bu}_2\text{NH}$  (1.2 M total)/toluene mixtures for the enolization of **1** (0.004 M) by LiHMDS (0.10 M) at  $-78$  °C. The curve depicts the results of an unweighted least-squares fit to  $k_{\text{obsd}} = (a + bx)/(1 + cx)$  ( $a = 4 \pm 1 \times 10^{-5}$ ,  $b = -2 \pm 1 \times 10^{-5}$ ,  $c = -0.9925 \pm 0.0009$ ). The point with \* is not included in the fit.

**XXXIII.** Table of data for plot in section **XXXII**.

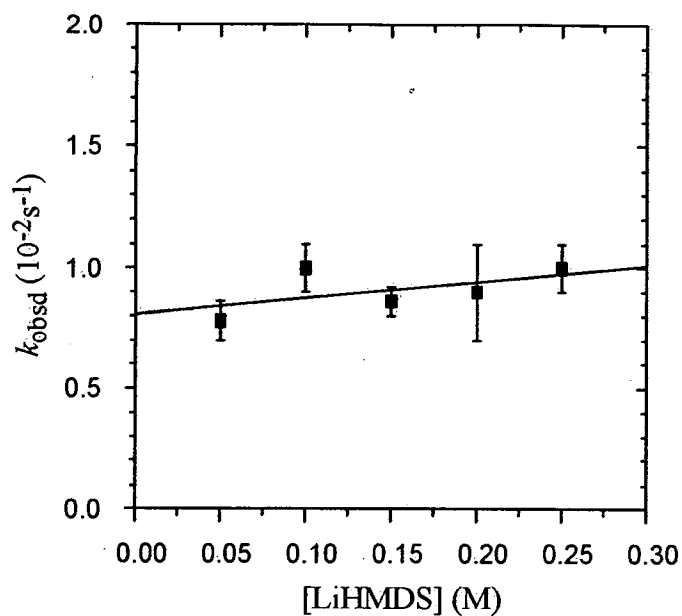
$\text{Me}_3\text{NEt}$ mol%	$k_{\text{obsd}1}$ ( $\text{s}^{-1}$ )	$k_{\text{obsd}2}$ ( $\text{s}^{-1}$ )	$k_{\text{obsd}}$ (avg) ( $\text{s}^{-1}$ )
0	$2.8 \pm 0.8\text{E-}5$	$6 \pm 1\text{E-}5$	$4 \pm 1\text{E-}5$
25	$3.9 \pm 0.9\text{E-}5$	$7 \pm 1\text{E-}5$	$6 \pm 1\text{E-}5$
50	$4 \pm 2\text{E-}5$	$8 \pm 2\text{E-}5$	$6 \pm 2\text{E-}5$
75	$6 \pm 1\text{E-}5$	$5 \pm 2\text{E-}5$	$6 \pm 2\text{E-}5$
83	$1.1 \pm 0.3\text{E-}4$	$1.0 \pm 0.1\text{E-}4$	$1.0 \pm 0.3\text{E-}4$
92	$1.9 \pm 0.3\text{E-}4$	$2.4 \pm 0.4\text{E-}4$	$2.2 \pm 0.4\text{E-}4$
96*	$5.4 \pm 0.8\text{E-}4$	$3.8 \pm 0.6\text{E-}4$	$5 \pm 1\text{E-}4$
100	$2.07 \pm 0.08\text{E-}3$	$2.20 \pm 0.04\text{E-}3$	$2.1 \pm 0.1\text{E-}3$



XXXIV. Plot of  $k_{\text{obsd}}$  vs  $[i\text{-Pr}_2\text{NH}]$  in toluene for the enolization of **4** (0.004 M) by LiHMDS (0.10 M) at  $-78\text{ }^\circ\text{C}$ . The curve depicts the results of an unweighted least-squares fit to  $k_{\text{obsd}} = ax + b$  ( $a = -1 \pm 1 \times 10^{-3}$ ,  $b = 1.00 \pm 0.08 \times 10^{-2}$ ).

XXXV. Table of data for plot in section XX1a.

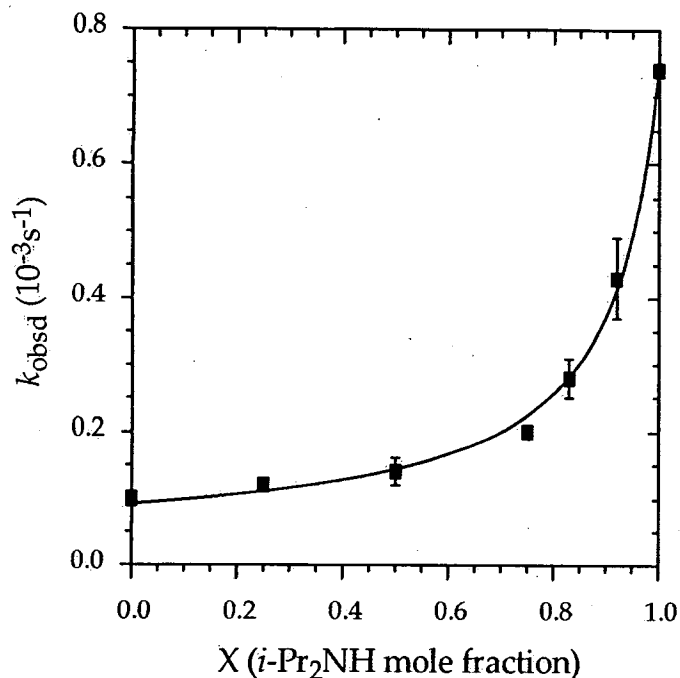
$[i\text{-Pr}_2\text{NH}]$ (M)	$k_{\text{obsd}1}$ ( $\text{s}^{-1}$ )	$k_{\text{obsd}2}$ ( $\text{s}^{-1}$ )	$k_{\text{obsd}}(\text{avg})$ ( $\text{s}^{-1}$ )
0.15	$1.1 \pm 0.1\text{E-}2$	$8.4 \pm 0.3\text{E-}3$	$1.0 \pm 0.3\text{E-}2$
0.30	$1.02 \pm 0.03\text{E-}2$	$1.1 \pm 0.1\text{E-}2$	$1.1 \pm 0.1\text{E-}2$
0.60	$9 \pm 1\text{E-}3$	$7.7 \pm 0.4\text{E-}3$	$8 \pm 1\text{E-}3$
0.90	$9.3 \pm 0.4\text{E-}3$	$8.9 \pm 0.5\text{E-}3$	$9.1 \pm 0.5\text{E-}3$
1.2	$1.1 \pm 0.1\text{E-}2$	$9.3 \pm 0.5\text{E-}3$	$1.0 \pm 0.1\text{E-}2$



XXXVI. Plot of  $k_{\text{obsd}}$  vs [LiHMDS] in *i*-Pr<sub>2</sub>NH/toluene for the enolization of **4** (0.004 M) by LiHMDS at  $-78$  °C. The curve depicts the results of an unweighted least-squares fit to  $k_{\text{obsd}} = ax + b$  ( $a = 7 \pm 6 \times 10^{-3}$ ,  $b = 8.1 \pm 0.9 \times 10^{-3}$ ).

XXXVII. Table of data for plot in section XX2a.

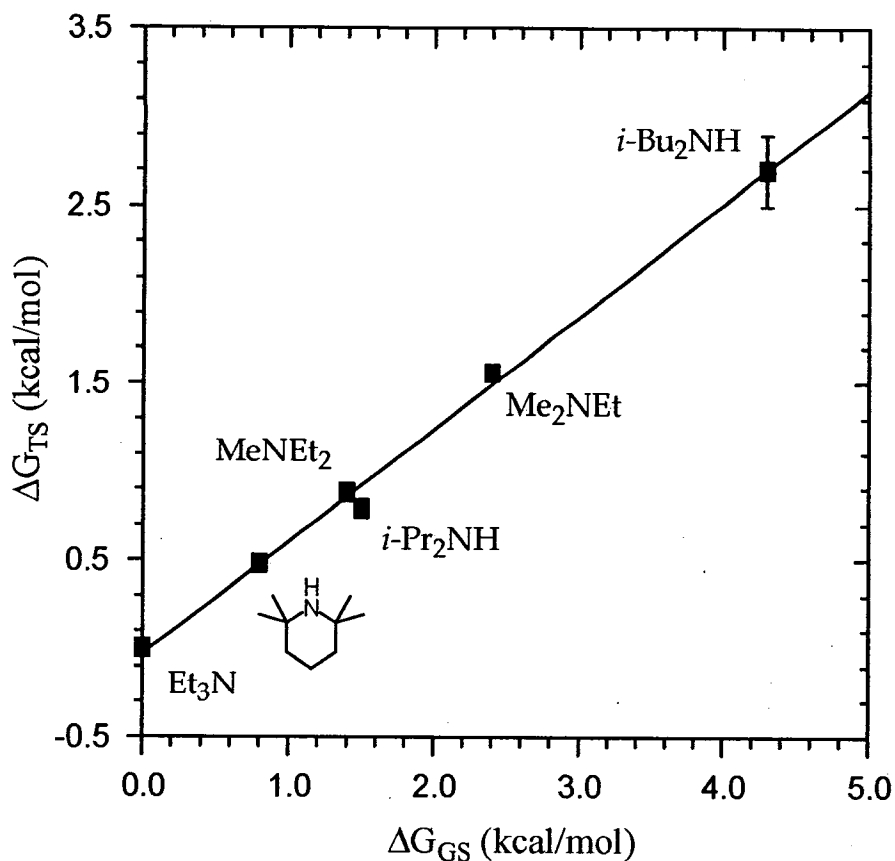
[LiHMDS] (M)	$k_{\text{obsd}1}$ (s <sup>-1</sup> )	$k_{\text{obsd}2}$ (s <sup>-1</sup> )	$k_{\text{obsd}}$ (avg) (s <sup>-1</sup> )
0.05	$7.8 \pm 0.8\text{E-}3$	$7.8 \pm 0.3\text{E-}3$	$7.8 \pm 0.8\text{E-}3$
0.10	$1.1 \pm 0.1\text{E-}2$	$9.3 \pm 0.5\text{E-}3$	$1.0 \pm 0.1\text{E-}2$
0.15	$9 \pm 1\text{E-}3$	$8.2 \pm 0.3\text{E-}3$	$9 \pm 1\text{E-}3$
0.20	$7.4 \pm 0.3\text{E-}3$	$1.01 \pm 0.05\text{E-}2$	$9 \pm 1\text{E-}3$
0.25	$1.1 \pm 0.1\text{E-}2$	$9.1 \pm 0.4\text{E-}3$	$1.0 \pm 0.1\text{E-}2$



**XXXVIII.** Plot of  $k_{\text{obsd}}$  vs  $X_{i\text{-Pr}_2\text{NH}}$  ( $X$  = mole fraction) in  $\text{Me}_2\text{NEt}/i\text{-Pr}_2\text{NH}$  (1.2 M total)/toluene mixtures for the enolization of  $1\text{-}d_3$  (0.004 M) by LiHMDS (0.10 M) at  $-78^\circ\text{C}$ . The curve depicts the results of an unweighted least-squares fit to  $k_{\text{obsd}} = (a + bx)/(1 + cx)$  ( $a = 9 \pm 1 \times 10^{-5}$ ,  $b = -3 \pm 1 \times 10^{-5}$ ,  $c = -0.916 \pm 0.008$ ;  $K_{\text{eq}} = 1 + c = 0.084 \pm 0.008$ ).

**XXXIX.** Table of data for plot in section XXXVIII.

$i\text{-Pr}_2\text{NH}$ mol%	$k_{\text{obsd}1}$ (s <sup>-1</sup> )	$k_{\text{obsd}2}$ (s <sup>-1</sup> )	$k_{\text{obsd}3}$ (s <sup>-1</sup> )	$k_{\text{obsd}}$ (avg) (s <sup>-1</sup> )
0	$1.0 \pm 0.1\text{E-}4$	$1.0 \pm 0.1\text{E-}4$	--	$1.0 \pm 0.1\text{E-}4$
25	$1.1 \pm 0.1\text{E-}4$	$1.3 \pm 0.1\text{E-}4$	--	$1.2 \pm 0.1\text{E-}4$
50	$1.5 \pm 0.1\text{E-}4$	$1.3 \pm 0.3\text{E-}4$	--	$1.4 \pm 0.3\text{E-}4$
75	$1.9 \pm 0.4\text{E-}4$	$2.0 \pm 0.4\text{E-}4$	--	$2.0 \pm 0.4\text{E-}4$
83	$3.1 \pm 0.2\text{E-}4$	$2.5 \pm 0.2\text{E-}4$	--	$2.8 \pm 0.2\text{E-}4$
92	$4.4 \pm 0.1\text{E-}4$	$3.5 \pm 0.2\text{E-}4$	$5.0 \pm 0.1\text{E-}4$	$4.3 \pm 0.2\text{E-}4$
100	$7.4 \pm 0.1\text{E-}3$	$7.4 \pm 0.2\text{E-}3$	--	$7.4 \pm 0.2\text{E-}4$



**XL.** Plot of  $\Delta G_{TS}^{\circ}$  vs  $\Delta G_{GS}^{\circ}$  for selected amine ligands at the enolization of **1-d<sub>3</sub>** (0.004 M) by LiHMDS (0.10 M) in R<sub>3</sub>N/toluene at -78 °C, using binary ligand systems listed in part **XXVI-XXXIX**. The curve depicts the results of an unweighted least-square fit to  $y = ax + b$ , where  $a = 0.64 \pm 0.02$ ,  $b = -0.03 \pm 0.05$  (kcal/mol).

**XLI.** Table of data for plot in section **XL**.

Ligand	$K_{eq}$	$\Delta G_{GS}^{\circ}$ (kcal/mol)	$k_2$ (s <sup>-1</sup> )	$\Delta G_{TS}^{\circ}$ (kcal/mol)
Et <sub>3</sub> N	$2.2 \pm 0.2$	0.00	$5.7 \pm 0.5E10^{-3}$	0.00
Me <sub>2</sub> NEt	$1.2 \pm 0.1E10^3$	$2.4 \pm 0.3$	$1.0 \pm 0.1E10^{-4}$	$1.56 \pm 0.04$
MeNEt <sub>2</sub>	$76 \pm 6$	$1.4 \pm 0.2$	$5.8 \pm 0.3E10^{-4}$	$0.88 \pm 0.02$
i-Bu <sub>2</sub> NH	$1.7 \pm 0.2E10^5$	$4.3 \pm 0.5$	$6 \pm 2E10^{-6}$	$2.7 \pm 0.2$
i-Pr <sub>2</sub> NH	$1.0 \pm 0.1E10^2$	$1.5 \pm 0.2$	$7.4 \pm 0.0E10^{-4}$	$0.79 \pm 0.01$
2,2,6,6-tetramethyl- piperidine	$16 \pm 6$	$0.8 \pm 0.4$	$1.64 \pm 0.04E10^{-3}$	$0.48 \pm 0.01$

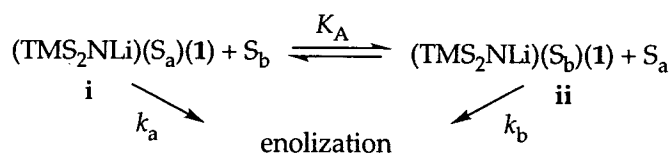
**XLII.** Isotope effects of ketone enolizations with LiHMDS and amine ligands (Chart 1 and 2 in text). Reactions were carried out using 0.1 M LiHMDS and 0.004 M 2-methylcyclohexanone (**1** or **1-*d*<sub>3</sub>**) in amine/toluene mixtures at  $-78$  °C.

Amine Ligand	$k_H$	$k_D$	KIE
None <sup>a</sup>	$2.0 \pm 0.1E-4$	$2.0 \pm 0.1E-5$	$10 \pm 1$
<b>A</b> <sup>b</sup>	$2.1 \pm 0.1E-3$	$1.0 \pm 0.1E-4$	$20 \pm 2$
<b>B</b> <sup>c</sup>	$8 \pm 1E-3$	$2.13 \pm 0.05E-4$	$40 \pm 5$
<b>D</b> <sup>b</sup>	$1.2 \pm 0.1E-2$	$6.28 \pm 0.09E-4$	$19 \pm 2$
<b>F</b> <sup>c</sup>	$3 \pm 1E-2$	$2.5 \pm 0.3E-3$	$12 \pm 4$
<b>G</b> <sup>d</sup>	$2.4 \pm 0.2E-2$	$7.4 \pm 0.3E-4$	$30 \pm 3$
<b>H</b> <sup>c</sup>	$2.5 \pm 0.1E-2$	$9 \pm 1E-4$	$26 \pm 3$
<b>I</b> <sup>c</sup>	$9.6 \pm 0.1E-3$	$5.1 \pm 0.1 E-4$	$19 \pm 1$
<b>N</b> <sup>b</sup>	$3.1 \pm 0.1E-4$	$3 \pm 1E-5$	$10 \pm 3$
<b>O</b> <sup>f</sup>	$4.6 \pm 0.5E-3$	$5.0 \pm 0.1E-4$	$9 \pm 1$
<b>P</b> <sup>e</sup>	$2.2 \pm 0.1E-2$	$1.3 \pm 0.1E-3$	$17 \pm 1$
<b>R</b> <sup>c</sup>	$7 \pm 1E-3$	$4.3 \pm 0.2E-4$	$16 \pm 2$
<b>U</b> <sup>c</sup>	$9.0 \pm 0.1E-3$	$3.9 \pm 0.1E-4$	$22 \pm 1$
<b>Z</b> <sup>c</sup>	$1.1 \pm 0.1E-2$	$7 \pm 1E-4$	$16 \pm 2$
<b>BB</b> <sup>c</sup>	$4.7 \pm 0.2E-3$	$2.6 \pm 0.2E-4$	$18 \pm 2$
<b>EE</b> <sup>b</sup>	$6 \pm 1E-3$	$3.7 \pm 0.1E-4$	$16 \pm 2$
<b>GG</b> <sup>b</sup>	$6.0 \pm 0.1E-3$	$5 \pm 1E-4$	$12 \pm 2$
<b>HH</b> <sup>c</sup>	$8 \pm 1E-3$	$6.0 \pm 0.3E-4$	$13 \pm 2$
<b>II</b> <sup>c</sup>	$2.8 \pm 0.1E-3$	$1.16 \pm 0.03E-4$	$23 \pm 1$
<b>NN</b> <sup>b</sup>	$7 \pm 2E-3$	$7.4 \pm 0.1E-4$	$10 \pm 3$
<b>OO</b> <sup>b</sup>	$4 \pm 2E-5$	$6 \pm 3E-6$	$7 \pm 3$
<b>PP</b> <sup>e</sup>	$1.2 \pm 0.1E-2$	$6.9 \pm 0.1E-4$	$17 \pm 1$

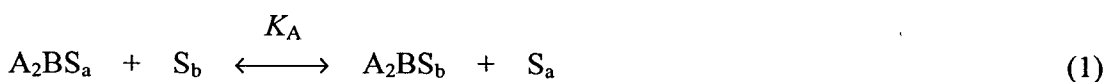
<sup>a</sup> Reactions were carried out in neat toluene at  $-40$  °C. <sup>b</sup> Reactions were carried out with 1.2 M amine ligand. <sup>c</sup> Reactions were carried out with 0.60 M amine ligand. <sup>d</sup> Reactions were carried out with 0.10 M Et<sub>3</sub>N. <sup>e</sup> Reactions were carried out with 0.15 M amine ligand. <sup>f</sup> Reactions were carried out with 1.2 M *i*-Bu<sub>3</sub>N at  $-40$  °C.

**XLIII.** Derivation of expression for solvent binding constant determination (eq 10 and 15 in manuscript):

Scheme 3



For convenience, we let  $A = \text{TMS}_2\text{NLi}$ ,  $B = \text{ketone substrate (1)}$  and describe Scheme 3 by eq 1-3.



$$[\text{B}]_{\text{total}} = [A_2\text{BS}_a] + [A_2\text{BS}_b] \quad (4)$$

$$d[\text{product}]/dt = k_{\text{obsd}}[\text{B}]_{\text{total}} = k_a[A_2\text{BS}_a] + k_b[A_2\text{BS}_b] \quad (5)$$

From eq 1 and 4,

$$[A_2\text{BS}_a] = [\text{B}]_{\text{total}}[\text{S}_a]/([\text{S}_a] + K_A[\text{S}_b]) \quad (6)$$

$$[A_2\text{BS}_b] = K_A[\text{B}]_{\text{total}}[\text{S}_b]/([\text{S}_a] + K_A[\text{S}_b]) \quad (7)$$

Substitution of  $[A_2\text{BS}_a]$  and  $[A_2\text{BS}_b]$  from eq 6 and 7 into eq 5 affords

$$k_{\text{obsd}} = (k_a[\text{S}_a] + k_b K_A [\text{S}_b])/([\text{S}_a] + K_A[\text{S}_b]) \quad (8)$$

Eliminating  $[\text{S}_a]$  from the right side of eq 8 affords

$$K_{\text{obsd}} = \{k_a + k_b K_A([\text{S}_b]/[\text{S}_a])\}/\{1 + K_A([\text{S}_b]/[\text{S}_a])\} \quad (9)$$

Defining  $[\text{S}_a]$  and  $[\text{S}_b]$  in terms of mole fractions  $X_a$  and  $X_b$  for  $\text{S}_a$  and  $\text{S}_b$  (eq 10 and 11) and substituting into eq 8 affords eq 12.

$$X_a = [S_a]/([S_a] + [S_b]) \quad (10)$$

$$X_b = 1 - X_a \quad (11)$$

$$k_{\text{obsd}} = [k_a X_a + k_b K_A (1 - X_a)]/[X_a + K_A (1 - X_a)] \quad (12)$$