Lithium Hexamethyldisilazide-Mediated Enolizations: Influence of Chelating Ligands and Hydrocarbon Cosolvents on the Rates and Mechanisms

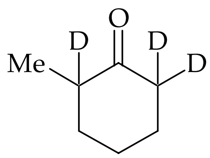
Peter F. Godenschwager and David B. Collum
Department of Chemistry and Chemical Biology
Baker Laboratory, Cornell University
Ithaca, New York 14853-1301

## Supporting Information

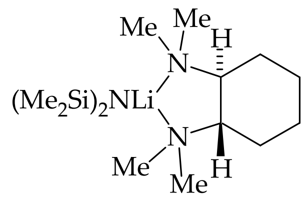
### Part I. NMR / in situ IR Structural Studies

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

## Structures in Supporting Information



**1**-$d_3$



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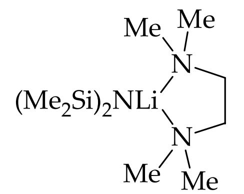

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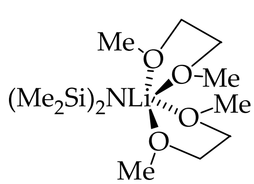

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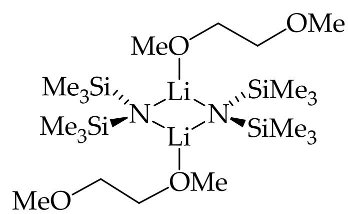

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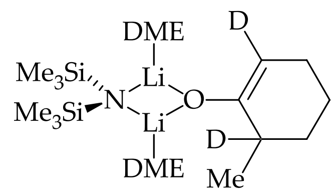
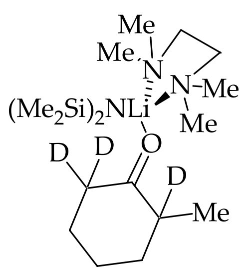
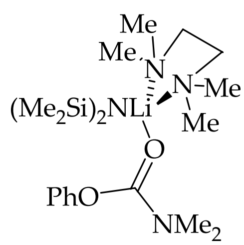


**11**-$d_2$



**13**-$d_3$



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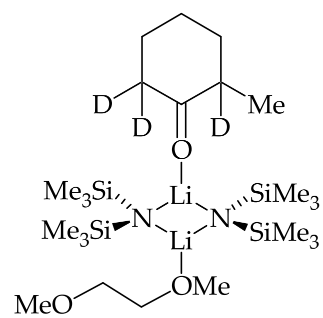
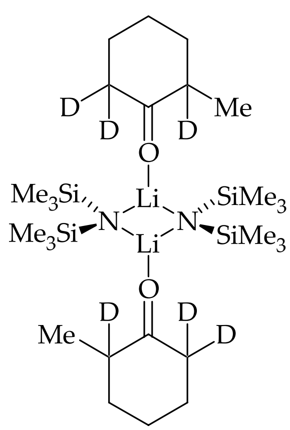
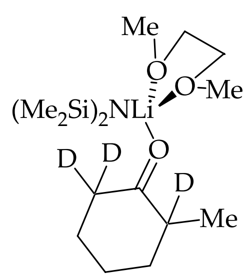


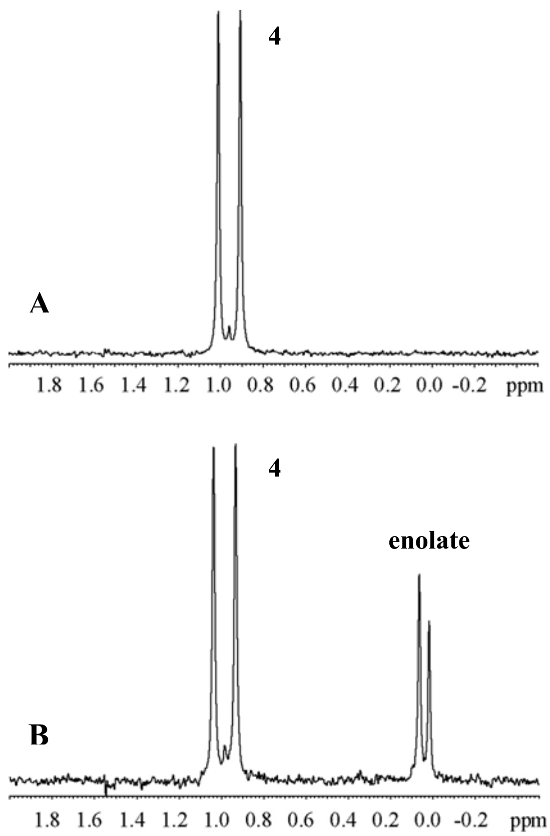
**18**-$d_3$



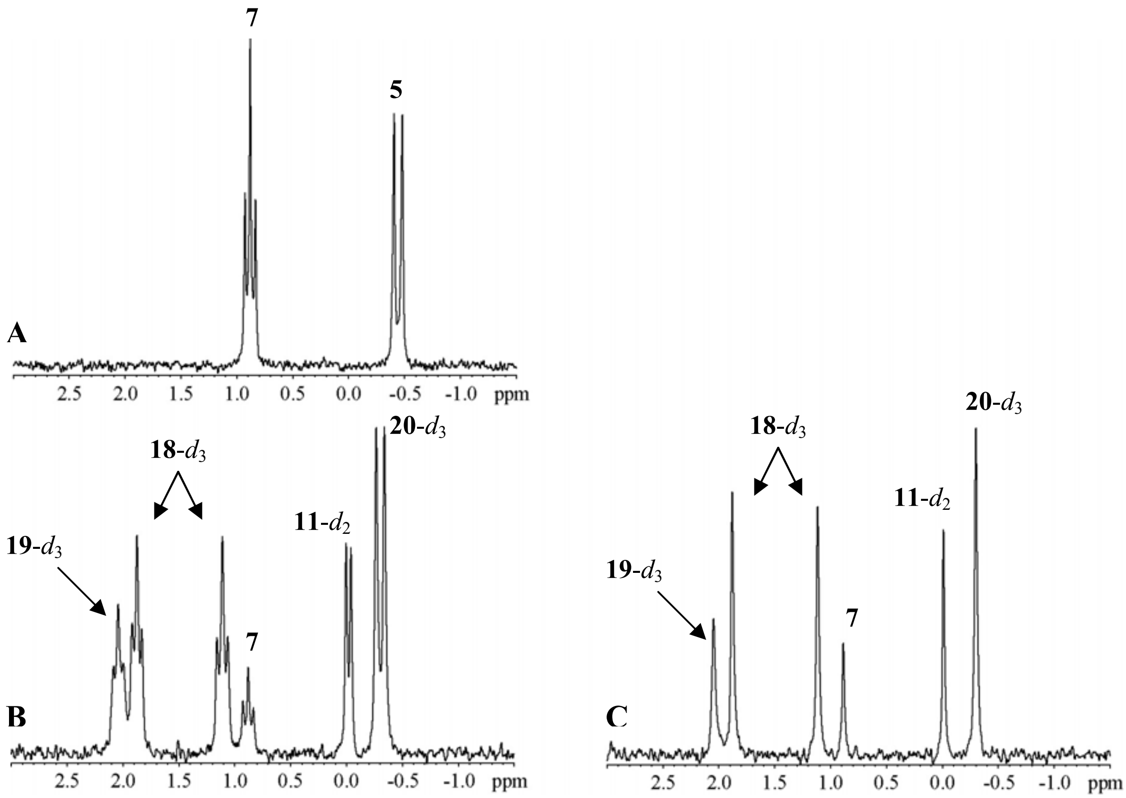
**19**-$d_3$



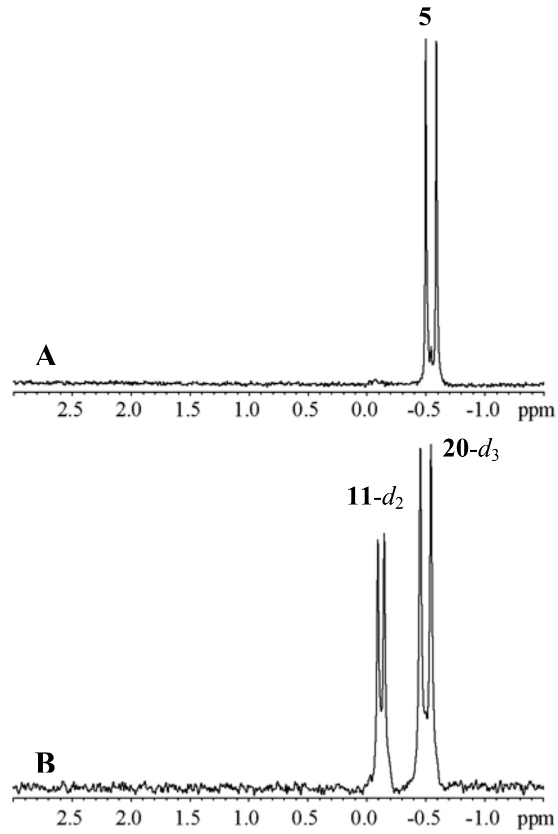
**20**-$d_3$



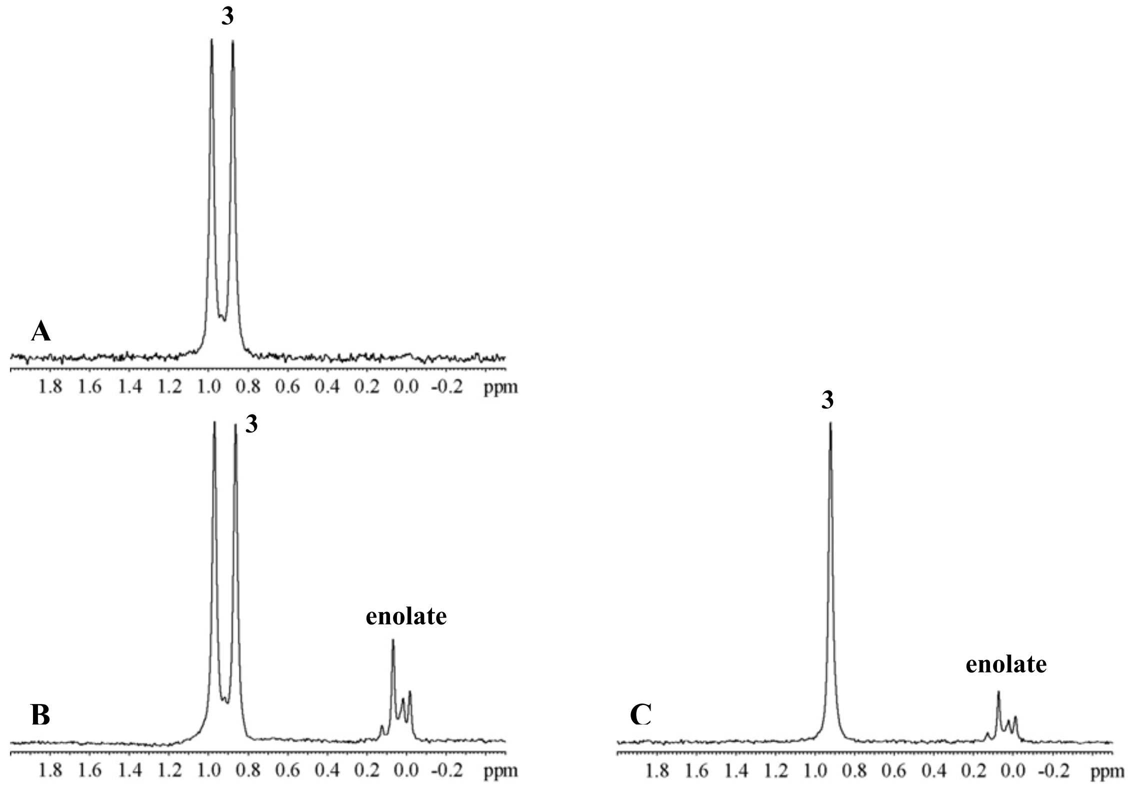

**I.** $^{6}$Li NMR spectra of 0.10 M [$^{6}$Li,$^{15}$N]LiHMDS with added TMEDA and **1**-$d_3$ in 2:1 toluene/pentane at -100 °C: A) $^{6}$Li NMR spectrum with 5.0 equiv of added TMEDA; B) $^{6}$Li NMR spectrum with 5.0 equiv of added TMEDA and 0.2 equiv of added **1**-$d_3$.



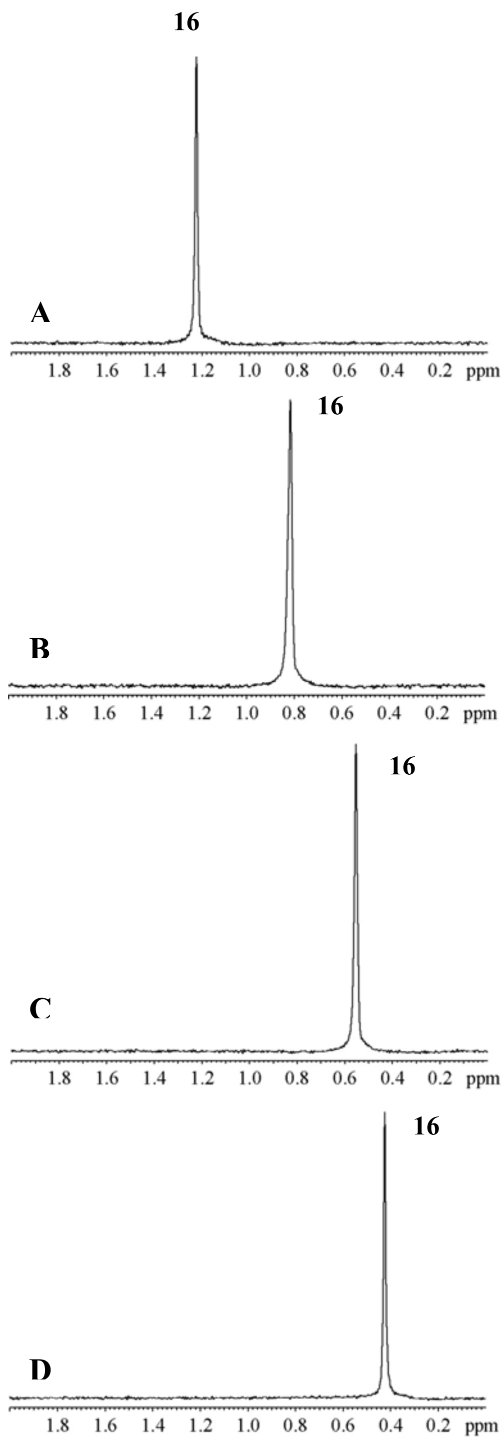

**II.** $^6$Li NMR spectra of 0.10 M [$^6$Li,$^{15}$N]LiHMDS with added DME and **1**-$d_3$ in 2:1 toluene/pentane at -100 °C: (A) $^6$Li NMR spectrum with 2.0 equiv of added DME; (B) $^6$Li NMR spectrum with 2.0 equiv of added DME and 0.50 equiv of added **1**-$d_3$; (C) $^6$Li{$^{15}$N} NMR spectrum of B.



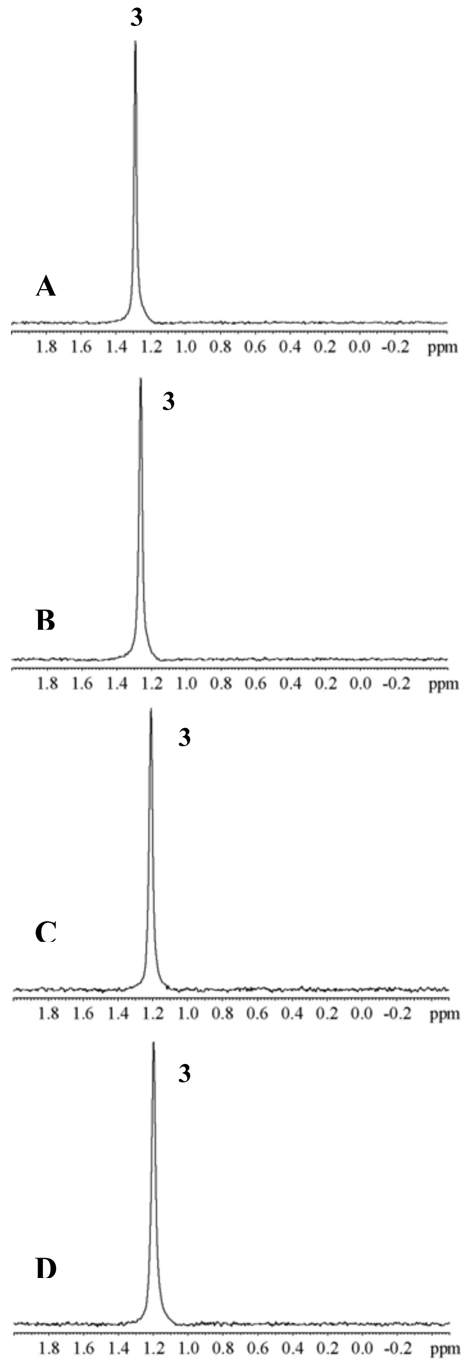

**III.** $^{6}$Li NMR spectra of 0.10 M [$^{6}$Li,$^{15}$N]LiHMDS with added DME and **1**-$d_3$ in toluene at -90 °C: (A) $^{6}$Li NMR spectrum with 10 equiv of added DME; (B) $^{6}$Li NMR spectrum with 10 equiv of added DME and 0.50 equiv of added **1**-$d_3$ (showing enolate peaks).



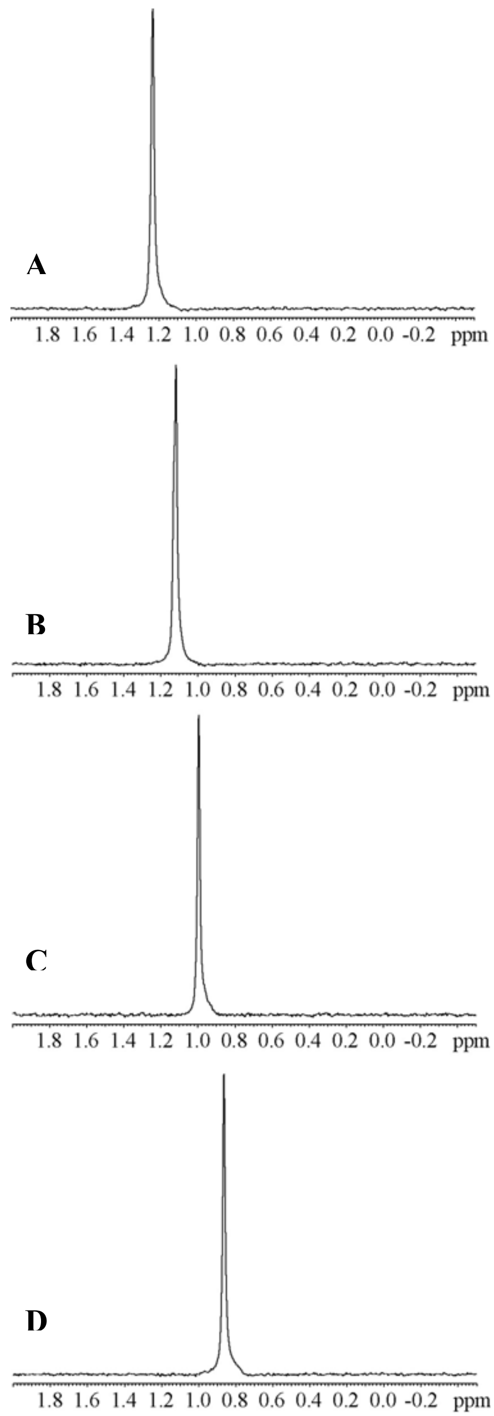

**IV.** $^{6}$Li NMR spectra of 0.10 M [$^{6}$Li,$^{15}$N]LiHMDS with added *trans*-TMCDA and **1**-$d_3$ in toluene at -90 °C: (A) $^{6}$Li NMR spectrum with 5.0 equiv added *trans*-TMCDA and 0.2 equiv of added **1**-$d_3$ (before reaction); (B) $^{6}$Li NMR spectrum of A after warming of tube (showing enolate peaks); (C) $^{6}$Li{$^{15}$N} NMR spectrum of B.



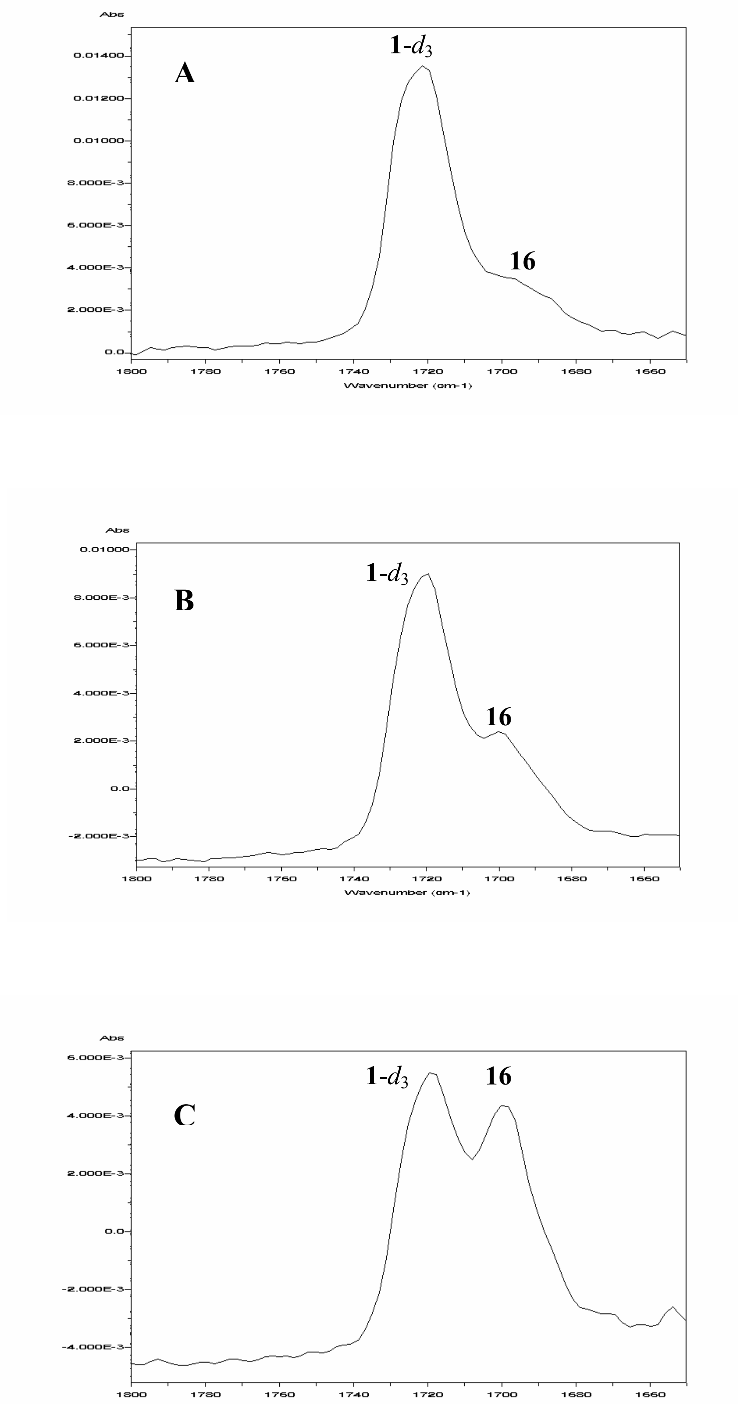

**V.** $^{6}Li$ NMR spectra of 0.10 M [$^{6}Li$,$^{15}N$]LiHMDS with added TMEDA and carbamate **15** in 3.0 M toluene/pentane at -90 °C: (A) $^{6}Li\{^{15}N\}$ NMR spectrum with 5.0 equiv of added TMEDA; (B) $^{6}Li\{^{15}N\}$ NMR spectrum with 5.0 equiv of added TMEDA and 0.5 equiv of added **15**; (C) $^{6}Li\{^{15}N\}$ NMR spectrum with 5.0 equiv of added TMEDA and 1.0 equiv of added **15**; (D) $^{6}Li\{^{15}N\}$ NMR spectrum with 5.0 equiv of added TMEDA and 2.0 equiv of added **15**.



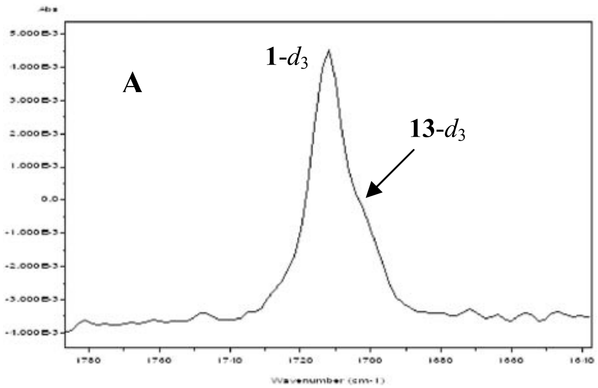

**VI.** $^{6}$Li NMR spectra of 0.10 M [$^{6}$Li,$^{15}$N]LiHMDS with added *trans*-TMCDA and carbamate **15** in 3.0 M toluene/pentane at -90 °C: (A) $^{6}$Li{$^{15}$N} NMR spectrum with 5.0 equiv of added *trans*-TMCDA; (B) $^{6}$Li{$^{15}$N} NMR spectrum with 5.0 equiv of added *trans*-TMCDA and 0.5 equiv of added **15**; (C) $^{6}$Li{$^{15}$N} NMR spectrum with 5.0 equiv of added *trans*-TMCDA and 1.0 equiv of added **15**; (D) $^{6}$Li{$^{15}$N} NMR spectrum with 5.0 equiv of added *trans*-TMCDA and 2.0 equiv of added **15**.

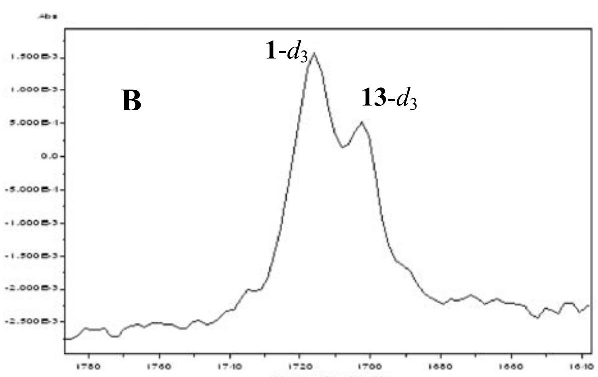



**VII.** $^{6}$Li NMR spectra of 0.10 M [$^{6}$Li,$^{15}$N]LiHMDS with added toluene in pentane at -90 °C showing LiHMDS dimer: (A) $^{6}$Li{$^{15}$N} NMR spectrum with 3.0 M added toluene; (B) $^{6}$Li{$^{15}$N} NMR spectrum with 4.0 M added toluene; (C) $^{6}$Li{$^{15}$N} NMR spectrum with 6.0 M added toluene; (D) $^{6}$Li{$^{15}$N} NMR spectrum with 8.0 M added toluene.

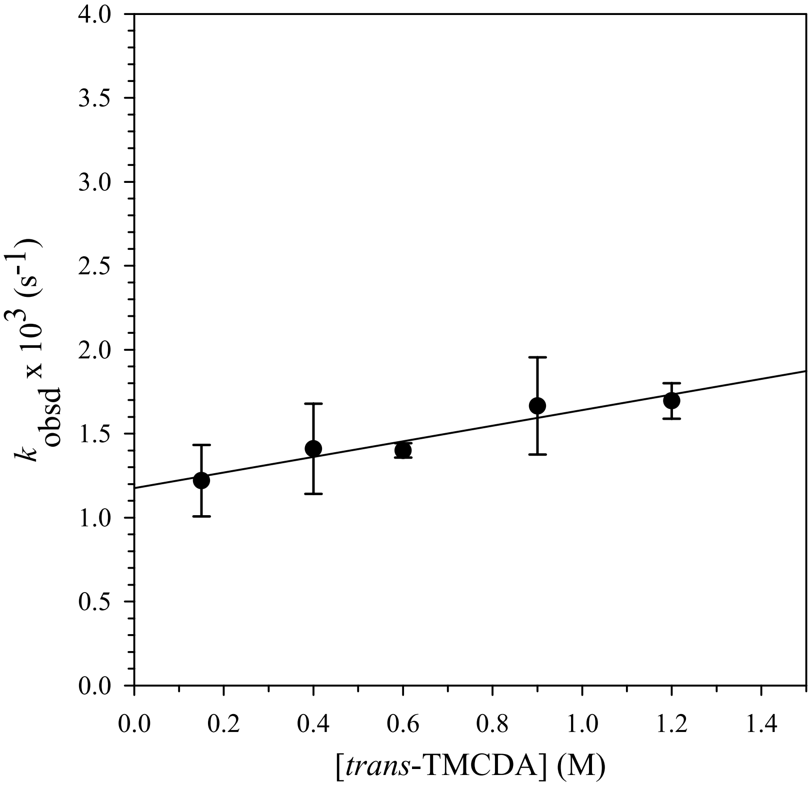



**VIII**. In situ IR spectra recorded on 0.005 M carbamate **15** in 3.0 M toluene/pentane with 0.10 M LiHMDS and 0.50 M TMEDA at (A) 0 °C; (B) -30 °C; (C) -60 °C showing free and complexed carbamate.



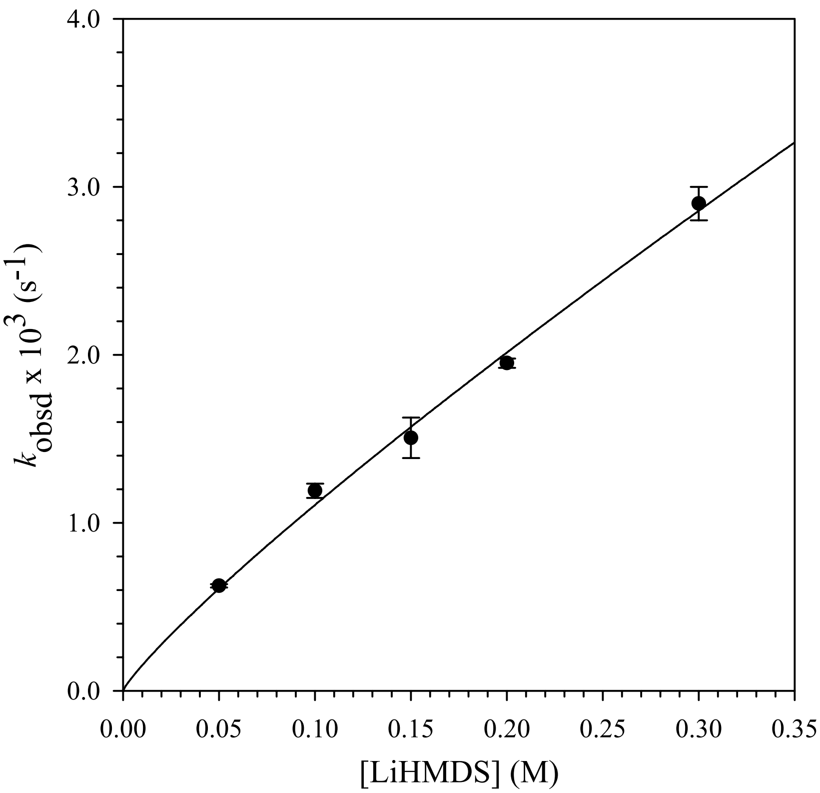

**IX.** In situ IR spectra of ketone **1**-$d_3$ with 0.10 M LiHMDS and 0.50 M TMEDA in A) neat toluene and B) 2.5 M toluene/pentane at -60 °C.




**X.** Plot of $k_{obsd}$ vs. [*trans*-TMCDA] for the enolization of **1** (0.005 M) by LiHMDS (0.10 M) in toluene at -55 ºC. The curve depicts an unweighted least-squares fit to $k_{obsd} = a[trans\text{-TMCDA}] + b$ ($a = 4.6 \pm 0.1 \times 10^{-1}$, $b = 1.17 \pm 0.02$).

**XI.** Table of data for the plot in section **I**.

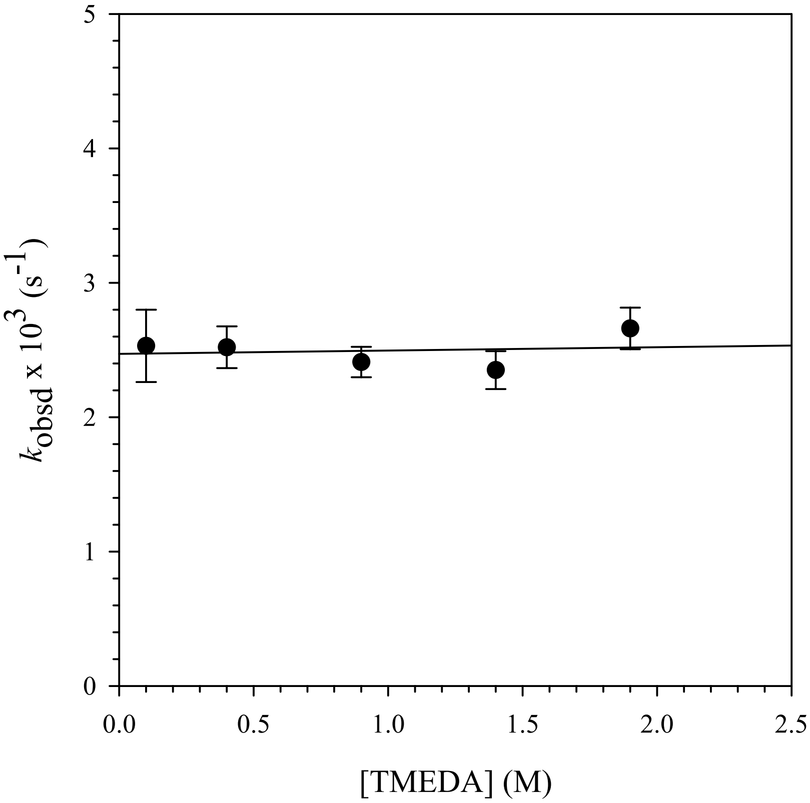
| [*trans*-TMCDA] (M) | $k_{obsd}1$ ($s^{-1}$) | $k_{obsd}2$ ($s^{-1}$) | $k_{obsd}$ (avg) ($s^{-1}$) |
|---|---|---|---|
| 0.15 | 1.37 ± 0.01E-3 | 1.07 ± 0.01E-3 | 1.2 ±0.2E-3 |
| 0.4 | 1.60 ± 0.01E-3 | 1.22 ± 0.01E-3 | 1.4 ± 0.3E-3 |
| 0.6 | 1.43 ± 0.01E-3 | 1.30 ± 0.01E-3 | 1.40 ± 0.04E-3 |
| 0.9 | 1.87 ± 0.02E-3 | 1.46 ± 0.02E-3 | 1.6 ± 0.3E-3 |
| 1.2 | 1.77 ± 0.02E-3 | 1.62 ± 0.03E-3 | 1.7 ± 0.1E-3 |




**XII.** Plot of $k_{obsd}$ vs. [LiHMDS] for the enolization of **1** (0.005 M) in *trans*-TMCDA (0.40 M) and toluene at -55 ºC. The curve depicts an unweighted least-squares fit to $k_{obsd} = a[\text{LiHMDS}]^b$ ($a = 8.0 \pm 0.5$, $b = 0.86 \pm 0.04$).

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

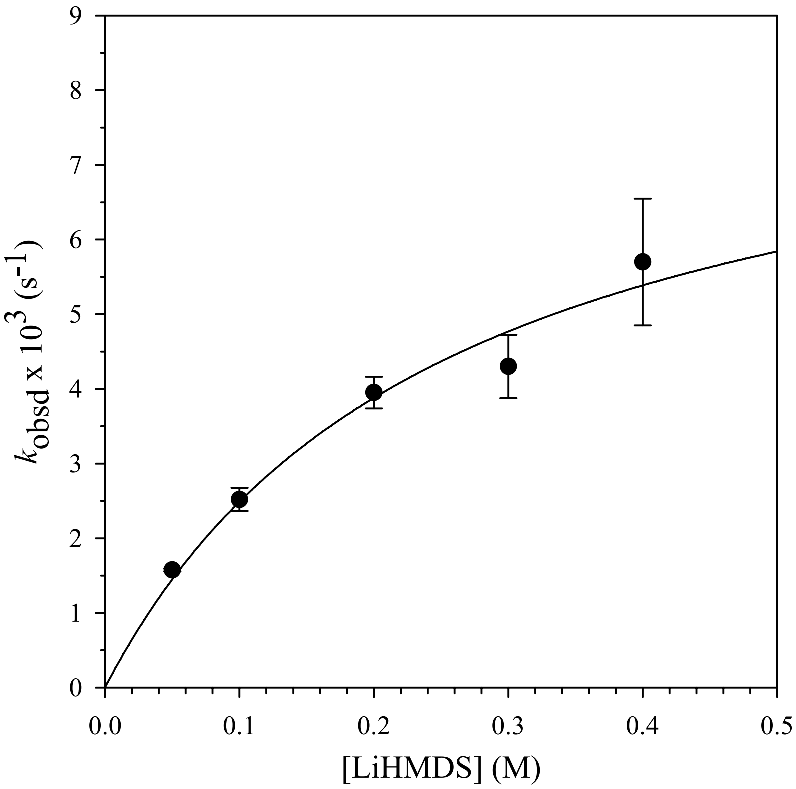
| [LiHMDS] (M) | $k_{obsd}1$ ($s^{-1}$) | $k_{obsd}2$ ($s^{-1}$) | $k_{obsd}$ (avg) ($s^{-1}$) |
|---|---|---|---|
| 0.05 | 6.17 ± 0.04E-4 | 6.32 ± 0.03E-4 | 6.2 ± 0.1E-4 |
| 0.10 | 1.16 ± 0.01E-3 | 1.22 ± 0.01E-3 | 1.19 ± 0.04E-3 |
| 0.15 | 1.42 ± 0.02E-3 | 1.59 ± 0.03E-3 | 1.5 ± 0.1E-3 |
| 0.20 | 1.93 ± 0.04E-3 | 1.97 ± 0.03E-3 | 1.95 ± 0.02E-3 |
| 0.30 | 2.83 ± 0.08E-3 | 2.97 ± 0.05E-3 | 2.90 ± 0.09E-3 |




**XIV.** Plot of $k_{obsd}$ vs. [TMEDA] for the enolization of **1**-$d_3$ (0.005 M) by LiHMDS (0.10 M) in toluene at -60 ºC. The curve depicts an unweighted least-squares fit to $k_{obsd} = a[\text{TMEDA}] + b$ ($a = 2 \pm 9 \times 10^{-2}$, $b = 2.4 \pm 0.1$).

**XV.** Table of data for plot in section **XIV**.

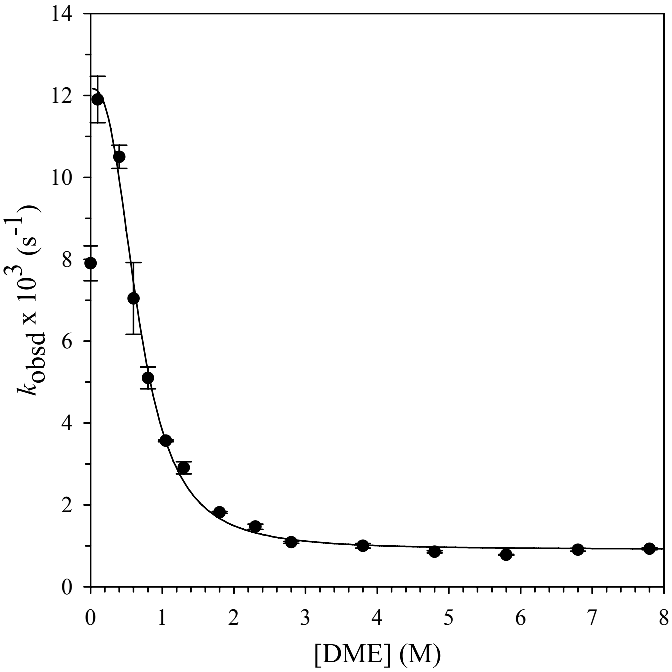
| [TMEDA] (M) | $k_{obsd}$1 ($s^{-1}$) | $k_{obsd}$2 ($s^{-1}$) | $k_{obsd}$ (avg) ($s^{-1}$) |
|---|---|---|---|
| 0.1 | 2.34 ± 0.05E-3 | 2.72 ± 0.04E-3 | 2.5 ± 0.1E-3 |
| 0.4 | 2.41 ± 0.05E-3 | 2.63 ± 0.05E-3 | 2.5 ± 0.1E-3 |
| 0.9 | 2.49 ± 0.04E-3 | 2.33 ± 0.05E-3 | 2.4 ± 0.1E-3 |
| 1.4 | 2.25 ± 0.05E-3 | 2.45 ± 0.04E-3 | 2.3 ± 0.1E-3 |
| 1.9 | 2.77 ± 0.05E-3 | 2.55 ± 0.06E-3 | 2.6 ± 0.1E-3 |




**XVI.** Plot of $k_{obsd}$ vs [LiHMDS] for the enolization of **1**-$d_3$ (0.005 M) in TMEDA (0.40 M) and toluene at -60 ºC. The curve depicts an unweighted least-squares fit to $k_{obsd} = a$[LiHMDS]/(1 + $b$[LiHMDS]) ($a = 3.4 \pm 0.6 \times 10^1$, $b = 3.9 \pm 0.1$).

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

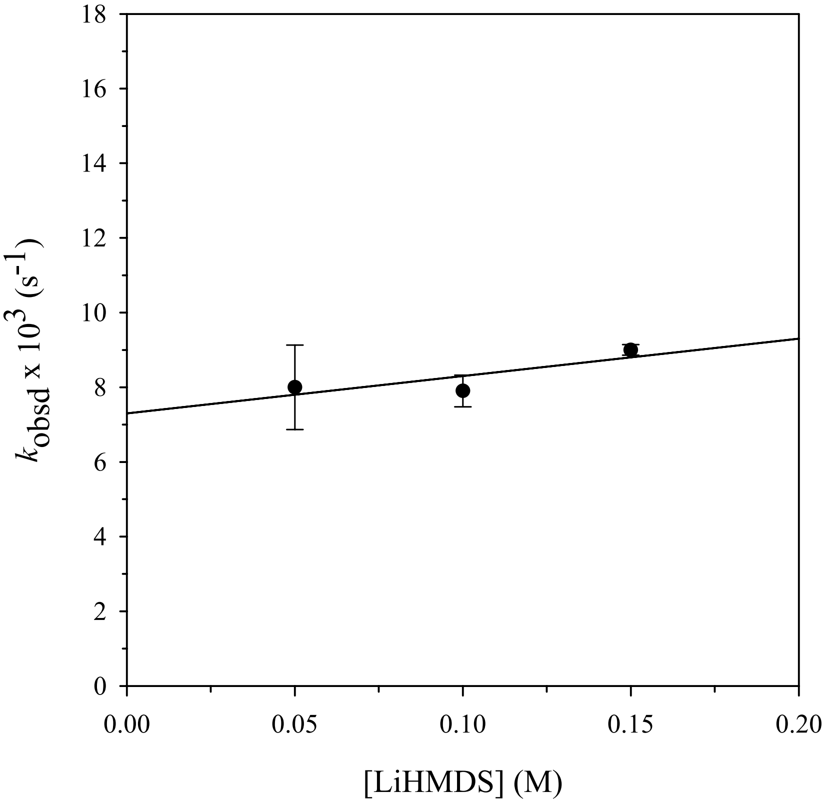
| [LiHMDS] (M) | $k_{obsd}1$ ($s^{-1}$) | $k_{obsd}2$ ($s^{-1}$) | $k_{obsd}$ (avg) ($s^{-1}$) |
|---|---|---|---|
| 0.05 | 1.59 ± 0.01E-3 | 1.56 ± 0.01E-3 | 1.57 ± 0.02E-3 |
| 0.10 | 2.41 ± 0.05E-3 | 2.63 ± 0.05E-3 | 2.5 ± 0.1E-3 |
| 0.20 | 3.8 ± 0.1E-3 | 4.1 ± 0.1E-3 | 3.9 ± 0.2E-3 |
| 0.30 | 4.0 ± 0.1E-3 | 4.6 ± 0.1E-3 | 4.3 ± 0.4E-3 |
| 0.40 | 5.1 ± 0.3E-3 | 6.3 ± 0.4E-3 | 5.7 ± 0.8E-3 |




**XVIII.** Plot of $k_{obsd}$ vs [DME] for the enolization of **1** (0.005 M) by LiHMDS (0.10 M) in toluene at -78 ºC. The curve depicts an unweighted least-squares fit to $k_{obsd} = a[\text{DME}]^b/(1 + c[\text{DME}]^b) + d$ ($a = 3.9 \pm 0.3$, $b = -2.6 \pm 0.1$, $c = 3.4 \pm 0.3 \times 10^{-1}$, $d = 9 \pm 1 \times 10^{-1}$.

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

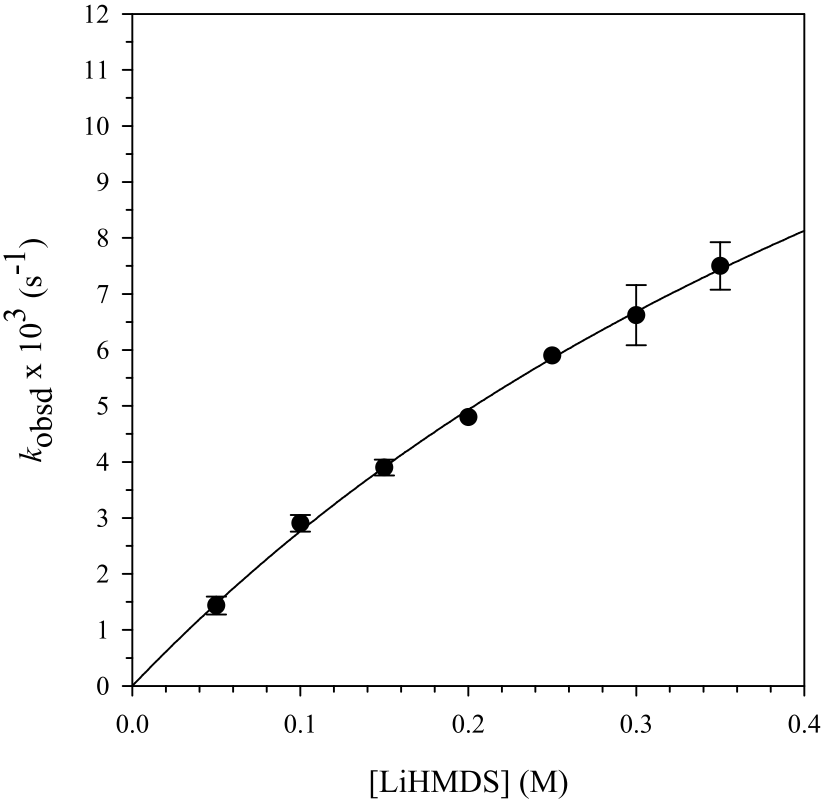
| [DME] (M) | $k_{obsd}1$ ($s^{-1}$) | $k_{obsd}2$ ($s^{-1}$) | $k_{obsd}$ (avg) ($s^{-1}$) |
|---|---|---|---|
| 0.0 | 8.2 ± 0.1E-3 | 7.6 ± 0.2E-3 | 8 ± 1E-3 |
| 0.1 | 1.15 ± 0.01E-2 | 1.23 ± 0.03E-2 | 1.19 ± 0.05E-2 |
| 0.4 | 1.07 ± 0.01E-2 | 1.03 ± 0.01E-2 | 1.05 ± 0.02E-2 |
| 0.6 | 6.42 ± 0.08E-3 | 7.66 ± 0.07E-3 | 7.0 ± 0.8E-3 |
| 0.8 | 5.2 ± 0.1E-3 | 4.8 ± 0.1E-3 | 5.0 ± 0.2E-3 |
| 1.05 | 3.58 ± 0.05E-3 | 3.55 ± 0.04E-3 | 3.56 ± 0.02E-3 |
| 1.3 | 3.01 ± 0.05E-3 | 2.80 ± 0.06E-3 | 2.9 ± 0.1E-3 |
| 1.8 | 1.83 ± 0.02E-3 | 1.80 ± 0.02E-3 | 1.81 ± 0.02E-3 |
| 2.3 | 1.42 ± 0.01E-3 | 1.51 ± 0.01E-3 | 1.46 ± 0.06E-3 |
| 2.8 | 1.07 ± 0.01E-3 | 1.100±0.009E-3 | 1.08 ± 0.02E-3 |
| 3.8 | 9.6 ± 0.1E-4 | 1.04 ± 0.01E-3 | 1.00 ± 0.05E-3 |
| 4.8 | 8.75 ± 0.08E-4 | 8.35 ± 0.07E-4 | 8.5 ± 0.2E-4 |
| 5.8 | 7.69 ± 0.08E-4 | 7.85 ± 0.06E-4 | 7.7 ± 0.1E-4 |
| 6.8 | 9.27 ± 0.06E-4 | 8.79 ± 0.09E-4 | 9.0 ± 0.3E-4 |
| 7.8 | 9.4 ± 0.1E-4 | 9.1 ± 0.1E-4 | 9.2 ± 0.2E-4 |




**XX.** Plot of $k_{obsd}$ vs. [LiHMDS] for the enolization of **1** (0.005 M) in DME (1.0 equiv) and toluene at -78 ºC. The curve depicts an unweighted least-squares fit to $k_{obsd}$ = $a$[LiHMDS] + $b$ ($a = 1.0 \pm 0.6 \times 10^1$, $b = 7.3 \pm 0.7$).

**XXI.** Table of data for the plot in section **XX**.

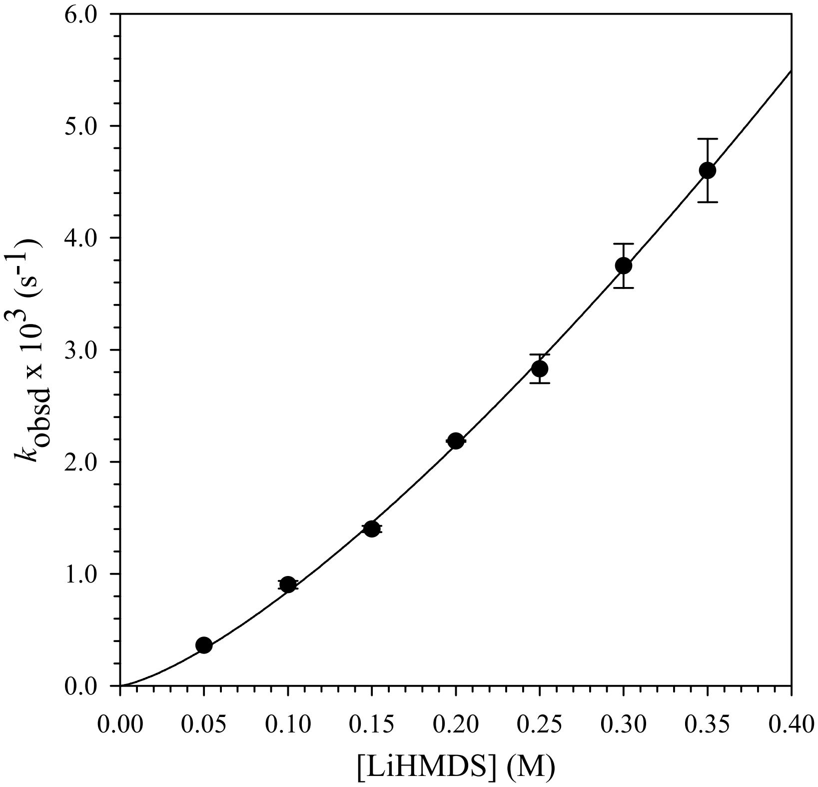
| [LiHMDS] (M) | $k_{obsd}1$ ($s^{-1}$) | $k_{obsd}2$ ($s^{-1}$) | $k_{obsd}$ (avg) ($s^{-1}$) |
|---|---|---|---|
| 0.05 | 7.2 ± 0.2E-3 | 8.80 ± 0.07E-3 | 8 ± 1E-3 |
| 0.10 | 8.2 ± 1E-3 | 7.6 ± 0.2E-3 | 7.9 ± 0.4E-3 |
| 0.15 | 9.1 ± 0.3E-3 | 8.9 ± 0.1E-3 | 9.0 ± 0.1E-3 |




**XXII.** Plot of $k_{obsd}$ vs. [LiHMDS] for the enolization of **1** (0.005 M) in DME (1.30 M) and toluene at -78 ºC. The curve depicts an unweighted least-squares fit to $k_{obsd} = a[\text{LiHMDS}]/(1 + b[\text{LiHMDS}])$ ($a = 3.1 \pm 0.1 \times 10^1$, $b = 1.3 \pm 0.2$).

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

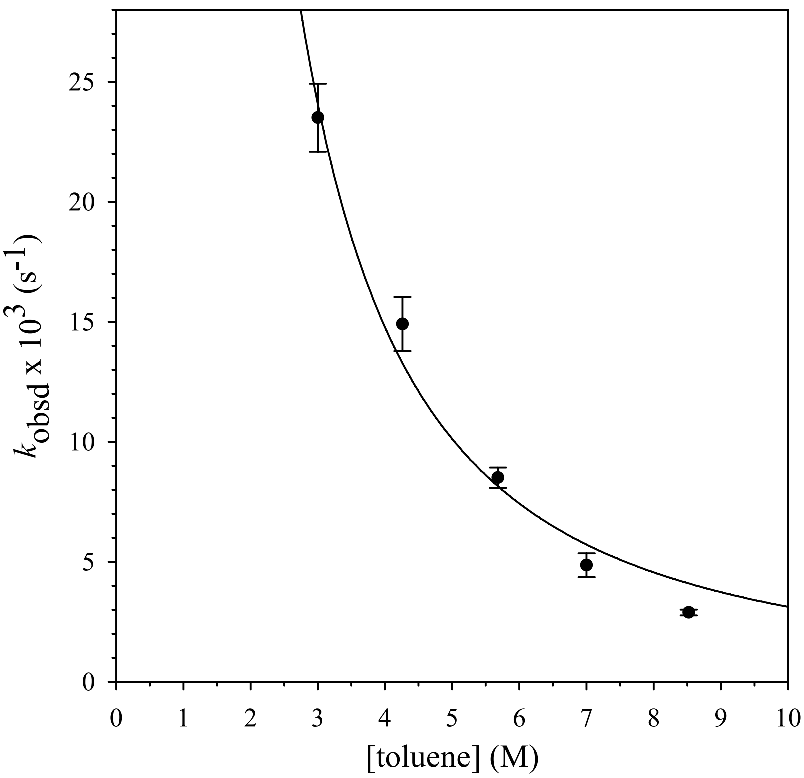
| [LiHMDS] (M) | $k_{obsd}$1 ($s^{-1}$) | $k_{obsd}$2 ($s^{-1}$) | $k_{obsd}$ (avg) ($s^{-1}$) |
|---|---|---|---|
| 0.05 | 1.32 ± 0.01E-3 | 1.55 ± 0.01E-3 | 1.4 ± 0.1E-3 |
| 0.10 | 3.01 ± 0.05E-3 | 2.80 ± 0.06E-3 | 2.9 ± 0.1E-3 |
| 0.20 | 4.8 ± 0.2E-3 | 4.8 ± 0.2E-3 | 4.8 ± 0.0E-3 |
| 0.30 | 6.24 ± 0.06E-3 | 7.0 ± 0.1E-3 | 6.6 ± 0.5E-3 |
| 0.35 | 7.2 ± 0.3E-3 | 7.8 ± 0.2E-3 | 7.5 ± 0.4E-3 |




**XXIV.** Plot of $k_{obsd}$ vs. [LiHMDS] for the enolization of **1** (0.005 M) in DME (6.80 M) and toluene at -78 ºC. The curve depicts an unweighted least-squares fit to $k_{obsd} = a[\mathrm{LiHMDS}]^b$ ($a = 1.90 \pm 0.07 \times 10^1$, $b = 1.35 \pm 0.2$).

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

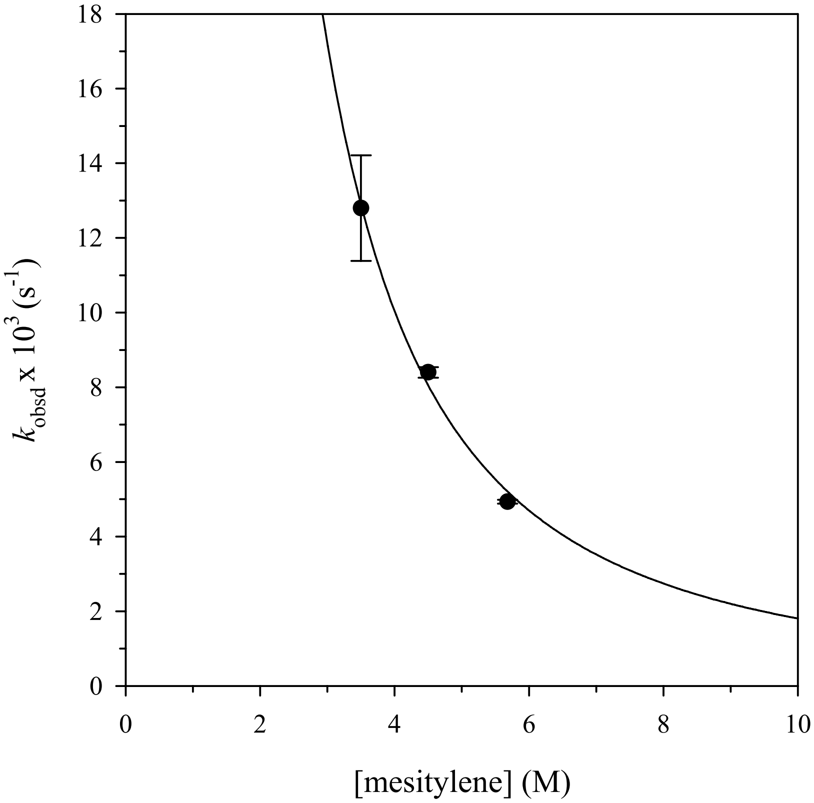
| [LiHMDS] (M) | $k_{obsd}$1 ($s^{-1}$) | $k_{obsd}$2 ($s^{-1}$) | $k_{obsd}$ (avg) ($s^{-1}$) |
|---|---|---|---|
| 0.05 | 3.61 ± 0.02E-4 | 3.61 ± 0.03E-4 | 3.61E-4 |
| 0.10 | 9.27 ± 0.06E-4 | 8.79 ± 0.09E-4 | 9.0 ± 0.3E-4 |
| 0.15 | 1.38 ± 0.01E-3 | 1.42 ± 0.02E-3 | 1.40 ± 0.02E-3 |
| 0.20 | 2.18 ± 0.04E-3 | 2.19 ± 0.03E-3 | 2.185 ± 0.007E-3 |
| 0.25 | 2.92 ± 0.09E-3 | 2.74 ± 0.04E-3 | 2.8 ± 0.1E-3 |
| 0.30 | 3.61 ± 0.09E-3 | 3.89 ± 0.08E-3 | 3.7 ± 0.1E-3 |
| 0.35 | 4.4 ± 0.1E-3 | 4.8 ± 0.1E-3 | 4.6 ± 0.2E-3 |




**XXVI.** Plot of $k_{obsd}$ vs. [toluene] for the enolization of **1**-$d_3$ (0.005 M) by LiHMDS (0.10 M) in TMEDA (0.50 M) and pentane at -60 ºC. The curve depicts an unweighted least-squares fit to $k_{obsd} = a[\text{toluene}]^b$ ($a = 1.5 \pm 0.3 \times 10^2$, $b = -1.6 \pm 0.1$).

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

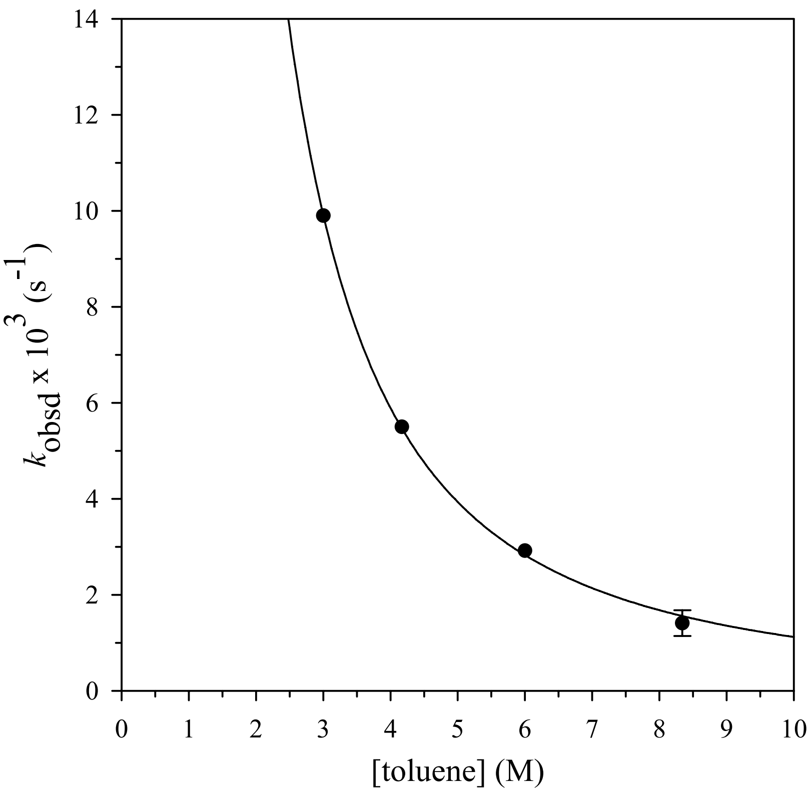
| [toluene] (M) | $k_{obsd}$1 ($s^{-1}$) | $k_{obsd}$2 ($s^{-1}$) | $k_{obsd}$ (avg) ($s^{-1}$) |
|---|---|---|---|
| 3.00 | 2.45 ± 0.03E-2 | 2.25 ± 0.06E-2 | 2.3 ± 0.1E-2 |
| 4.26 | 1.57 ± 0.03E-2 | 1.41 ± 0.02E-2 | 1.5 ± 0.1E-2 |
| 5.68 | 8.2 ± 0.1E-3 | 8.8 ± 0.1E-3 | 8.5 ± 0.4E-3 |
| 7.00 | 4.5 ± 0.1E-3 | 5.2 ± 0.2E-3 | 4.8 ± 0.4E-3 |
| 8.52 | 2.8 ± 0.1E-3 | 2.97 ± 0.06E-3 | 2.8 ± 0.1E-3 |




**XXVIII.** Plot of $k_{obsd}$ vs. [mesitylene] for the enolization of **1**-$d_3$ (0.005 M) by LiHMDS (0.10 M) in TMEDA (0.50 M) and pentane at -65 ºC. The curve depicts an unweighted least-squares fit to $k_{obsd} = a[\text{mesitylene}]^b$ ($a = 1.3 \pm 0.3 \times 10^2$, $b = -1.8 \pm 0.1$).

**XIX.** Table of data for the plot in section **XXVIII**.

| [mesitylene] (M) | $k_{obsd}$1 ($s^{-1}$) | $k_{obsd}$2 ($s^{-1}$) | $k_{obsd}$ (avg) ($s^{-1}$) |
|---|---|---|---|
| 3.50 | 1.38 ± 0.03E-2 | 1.18 ± 0.03E-2 | 1.2 ± 0.1E-2 |
| 4.50 | 8.5 ± 0.2E-3 | 8.3 ± 0.2E-3 | 8.4 ± 0.1E-3 |
| 5.68 | 4.97 ± 0.08E-3 | 4.9 ± 0.1E-3 | 4.93 ± 0.04E-3 |




**XXX.** Plot of $k_{obsd}$ vs [toluene] for the enolization of **1** (0.005 M) by LiHMDS (0.10 M) in TMCDA (0.50 M) and pentane at -55 °C. The curve depicts an unweighted least-squares fit to $k_{obsd} = a[\text{toluene}]^b$ ($a = 7.2 \pm 0.4 \times 10^1$, $b = -1.81 \pm 0.04$).

**XXXI.** Table of data for the plot in section **XXX**.

| [toluene] (M) | $k_{obsd}1$ ($s^{-1}$) | $k_{obsd}2$ ($s^{-1}$) | $k_{obsd}$ (avg) ($s^{-1}$) |
|---|---|---|---|
| 3.00 | 9.9 ± 0.6E-3 | - | 9.9 ± 0.6E-3 |
| 4.17 | 5.5 ± 0.2E-3 | - | 5.5 ± 0.2E-3 |
| 6.00 | 2.92 ± 0.05E-3 | - | 2.92 ± 0.05E-3 |
| 8.34 | 1.22 ± 0.01E-3 | 1.60 ± 0.01E-3 | 1.4 ± 0.3E-3 |