SUPPORTING INFORMATION

A Case for Lithium Tetramethylpiperidide-Mediated Ortholithiations: Reactivity and Mechanisms

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I. NMR Spectroscopic Studies

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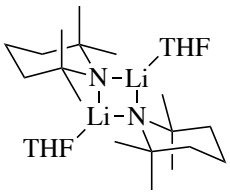
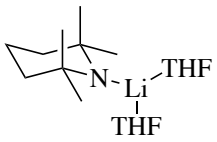
I. NMR Spectroscopic Studies

Table 1. ^{6}Li NMR chemical shifts and coupling constants for the different species in neat THF at –80 °C.

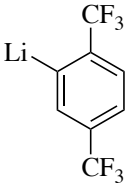
Species	^{6}Li δ (ppm)	^{19}F δ (ppm)	$J_{\text{Li-N}}$ (Hz)
A_2S_2	1.51	–	4.8
AS_2	0.90	–	8.9
1-Li	0.88	–63.64, –64.02	–
2-Li	0.84	–63.46, –63.94	–
3-Li Mixed Aggregate	2.19	–	5.1
4-Li Mixed Aggregate	2.11	–	5.1



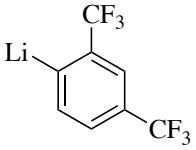
A_2S_2



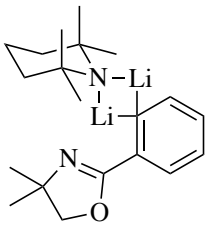
AS_3



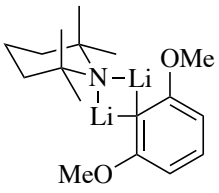
1-Li



2-Li



3-Li
Mixed Aggregate



4-Li
Mixed Aggregate

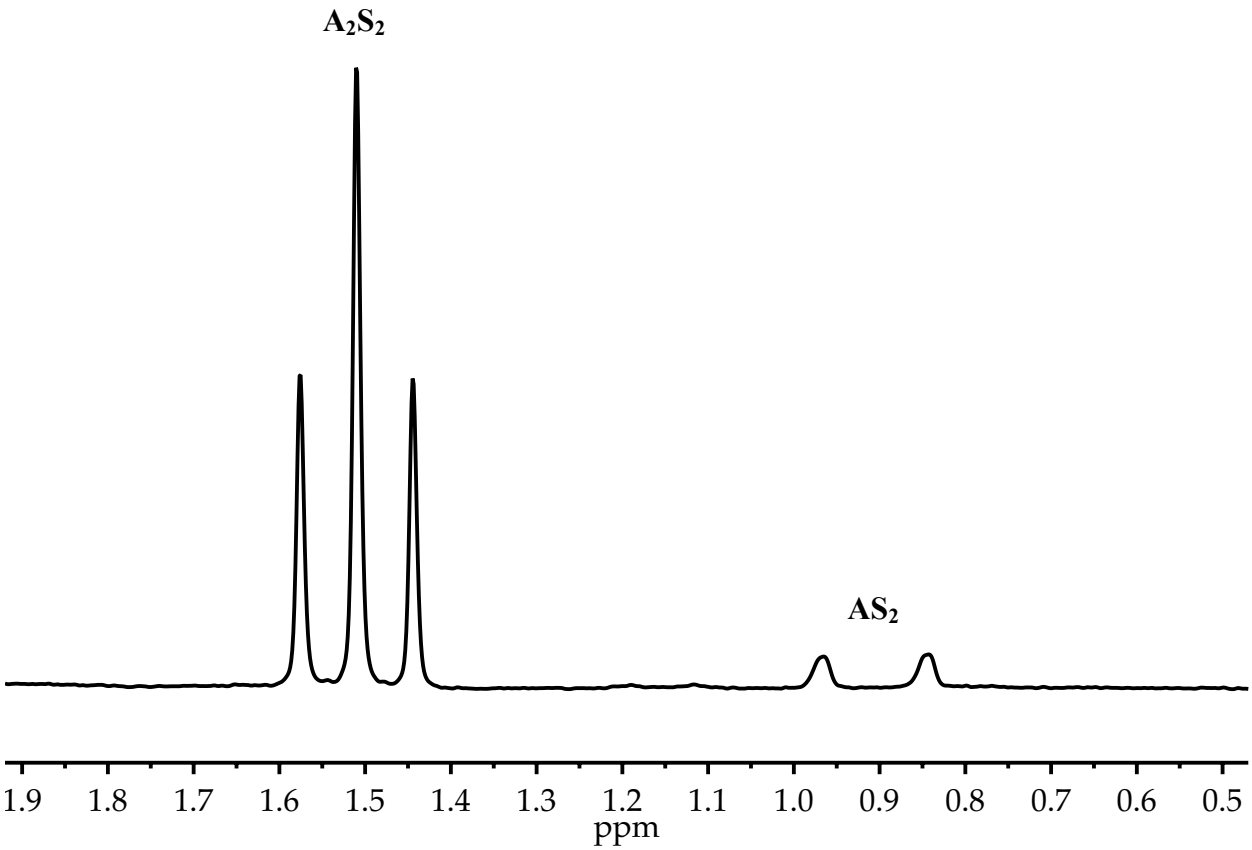


Figure 1. ^{6}Li spectrum of 0.10 M [^{6}Li,^{15}N]LiTMP in neat THF at –80 °C.

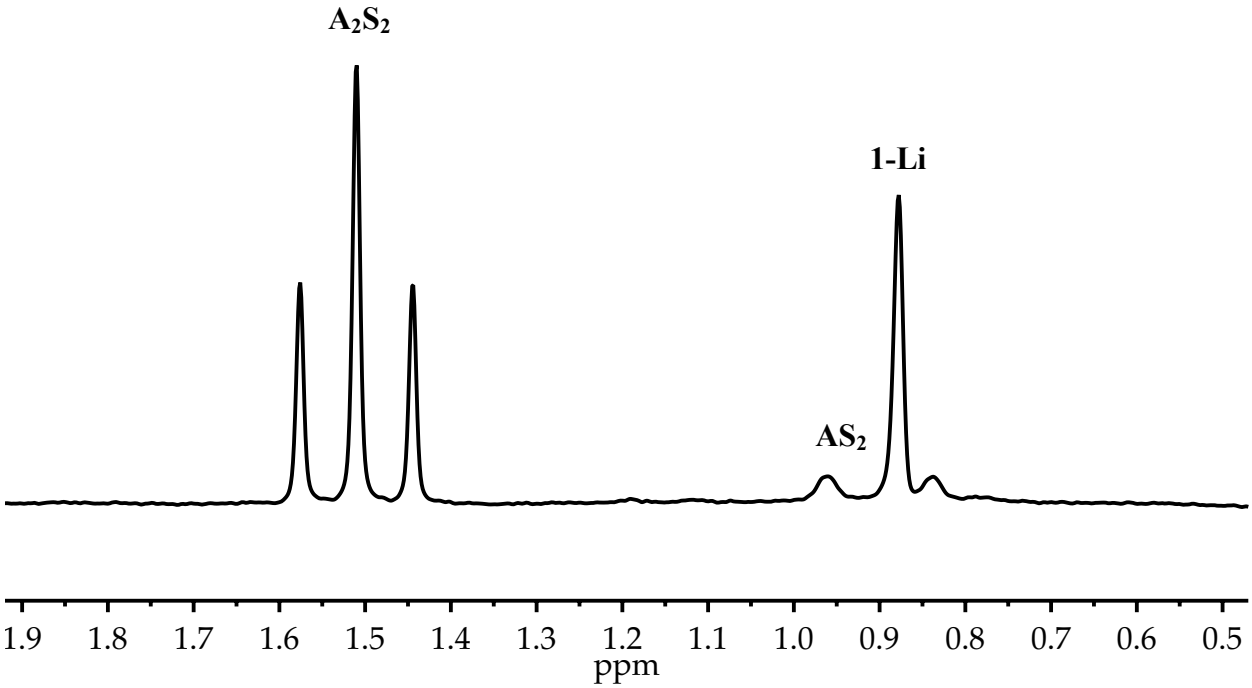


Figure 2. ^{6}Li spectrum of 0.10 M [^{6}Li,^{15}N]LiTMP and 0.030 M **1** in neat THF at –80 °C after aging at –80 °C for 2 hours. The lithiated product (**1-Li**) shows no mixed aggregation with free LiTMP as evidenced by the singlet.

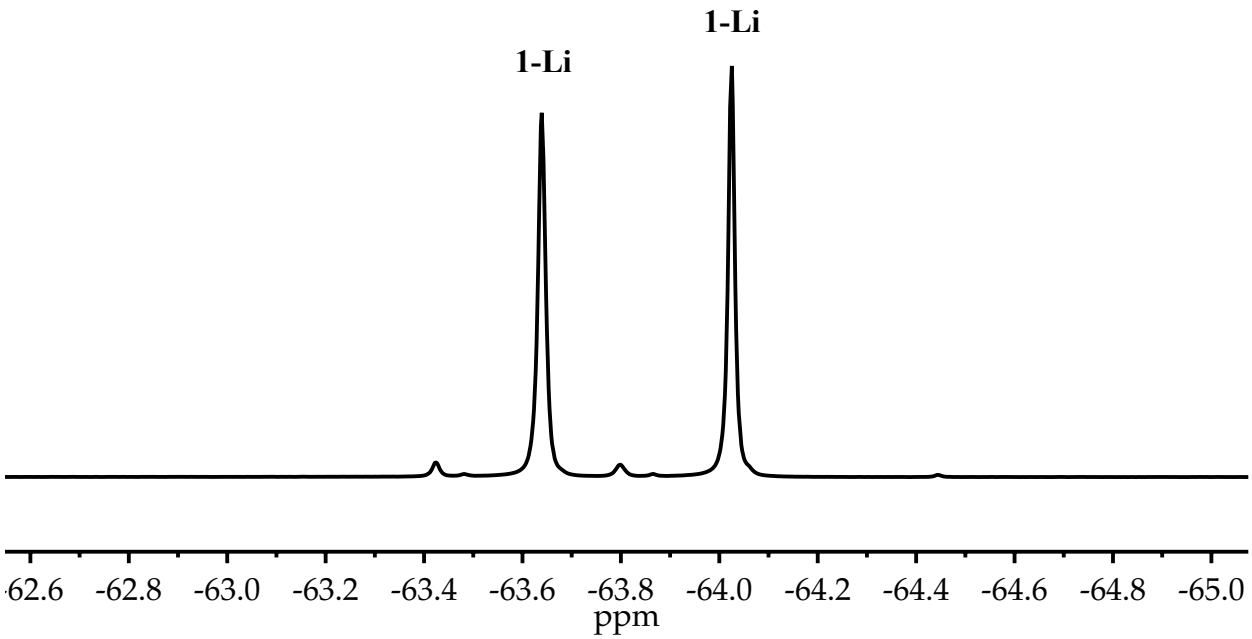


Figure 3. ^{19}F spectrum of 0.10 M [^{6}Li,^{15}N]LiTMP and 0.030 M **1** in neat THF at –80 °C after aging at –80 °C for 2 h.

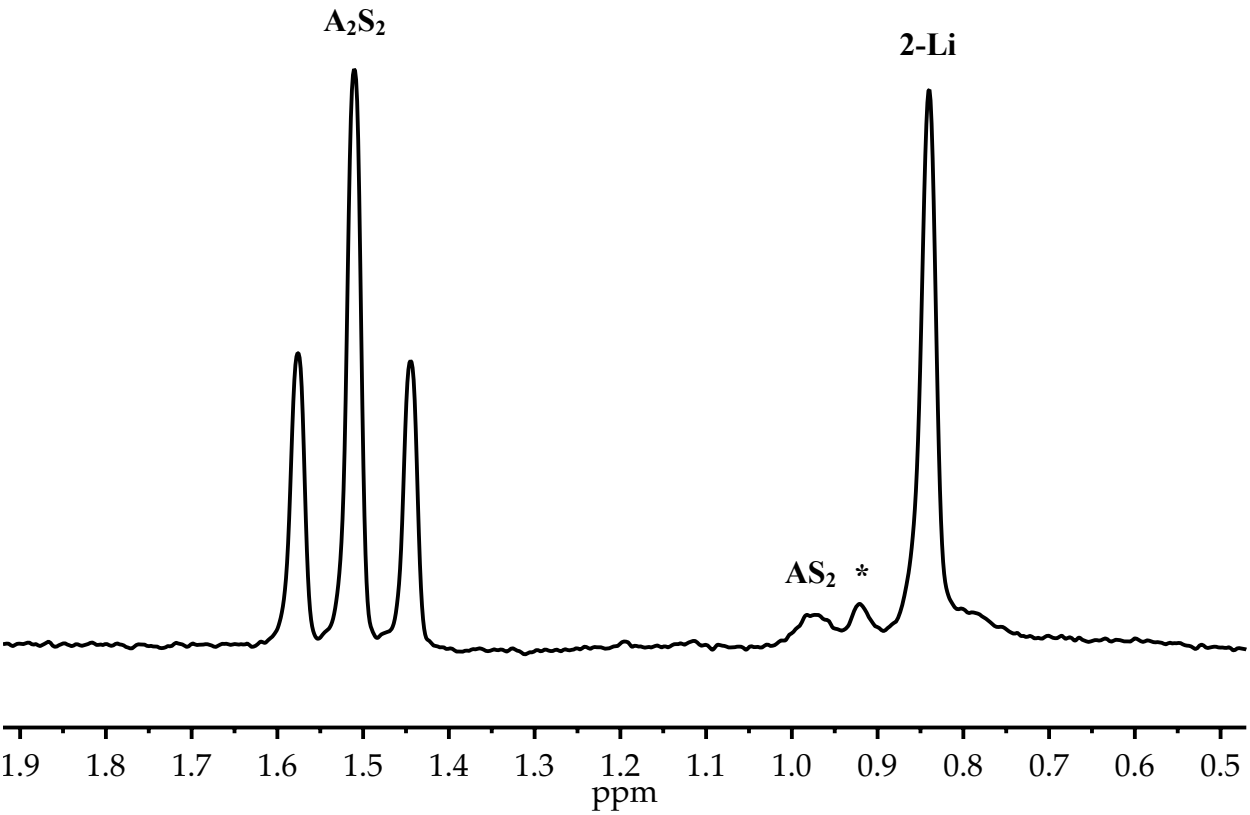


Figure 4. ^{6}Li spectrum of 0.10 M [^{6}Li,^{15}N]LiTMP and 0.030 M **2** in neat THF at –80 °C after aging at –80 °C for 2 hours. The lithiated product (**2-Li**) shows no mixed aggregation with free LiTMP as evidenced by the singlet. (Note: the * indicates a minor contribution of the internally metalated product.)

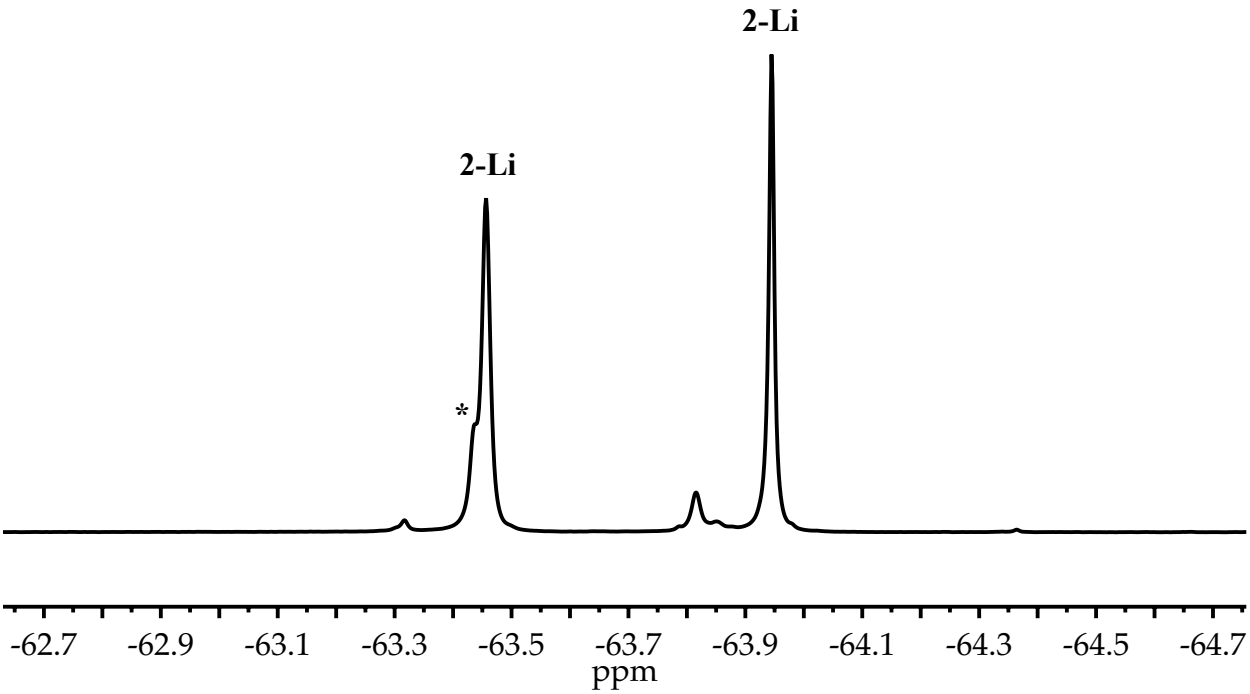


Figure 5. ^{19}F spectrum of 0.10 M [^{6}Li,^{15}N]LiTMP and 0.030 M **2** in neat THF at –80 °C after aging at –80 °C for 2 h. (Note: the * indicates a minor contribution of the internally metalated product.)

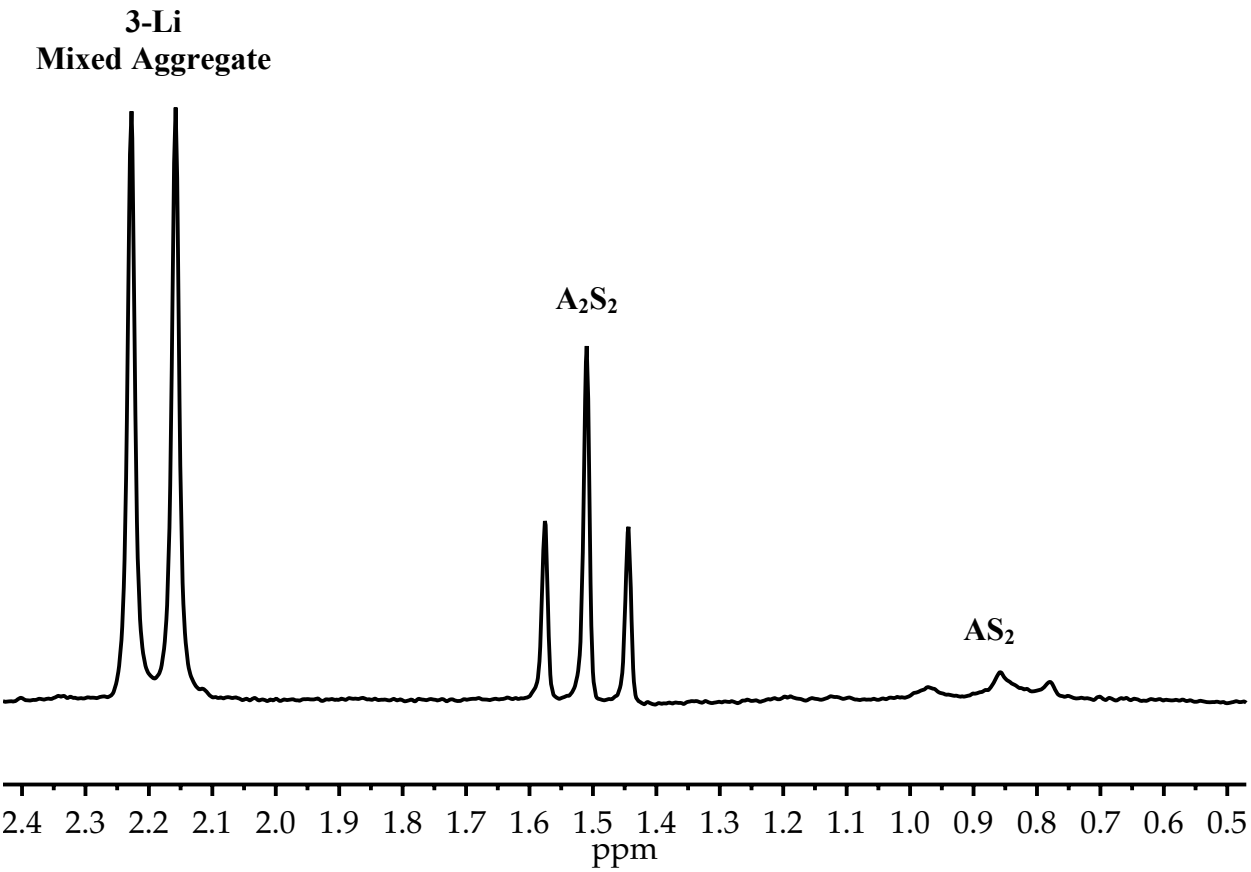


Figure 6. ^{6}Li spectrum of 0.10 M [^{6}Li,^{15}N]LiTMP and 0.030 M **3** in neat THF at –80 °C after aging at –40 °C for 2 hours. The lithiated product (**3-Li**) forms a dimeric mixed aggregate with free LiTMP as evidenced by the doublet and coupling constant.

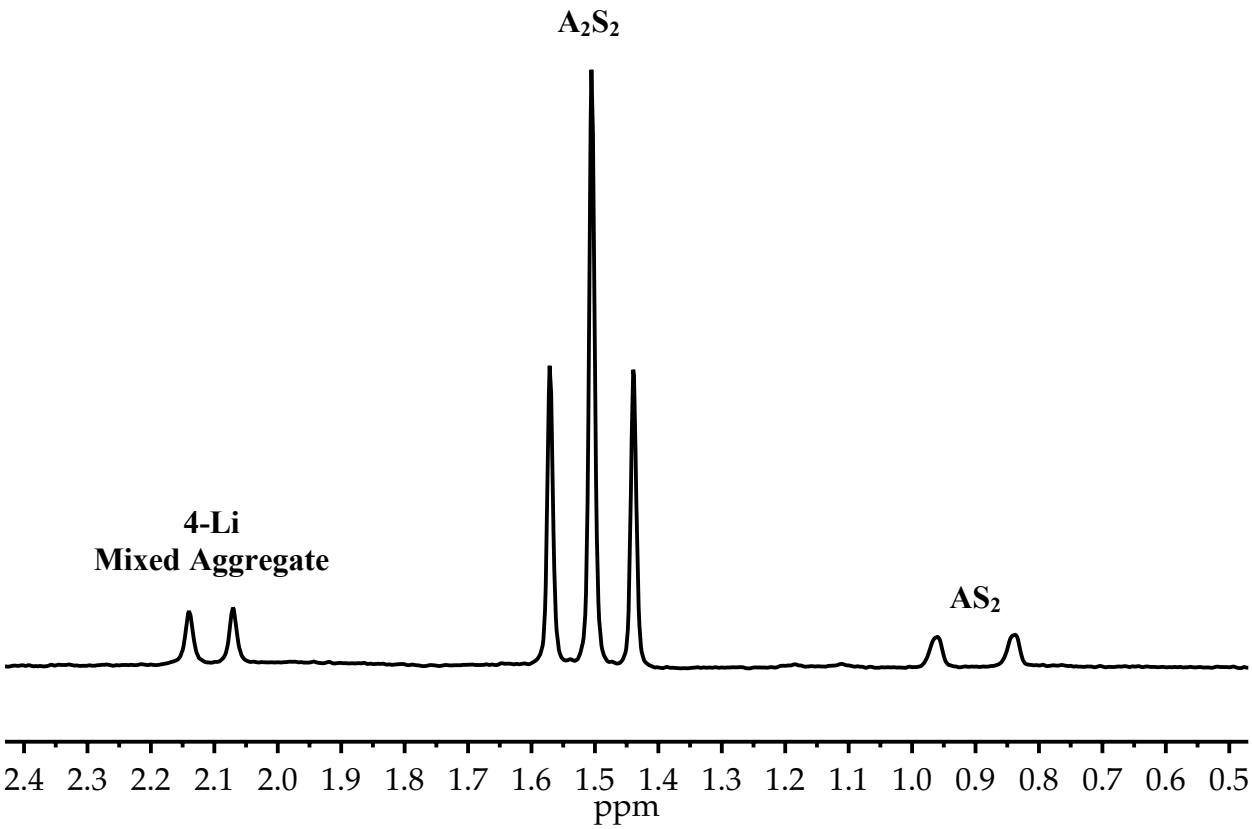
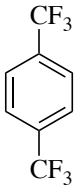


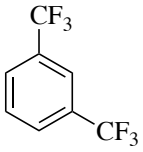
Figure 7. ^{6}Li spectrum of 0.10 M [^{6}Li,^{15}N]LiTMP and 0.030 M **4** in neat THF at –80 °C after aging at –40 °C for 2 hours. The lithiated product (**4-Li**) forms a dimeric mixed aggregate with free LiTMP as evidenced by the doublet and coupling constant.

II. IR Rate Studies

Chart 1. Substrates for Orthometalations



1



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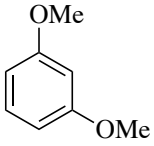

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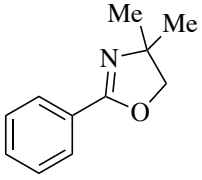

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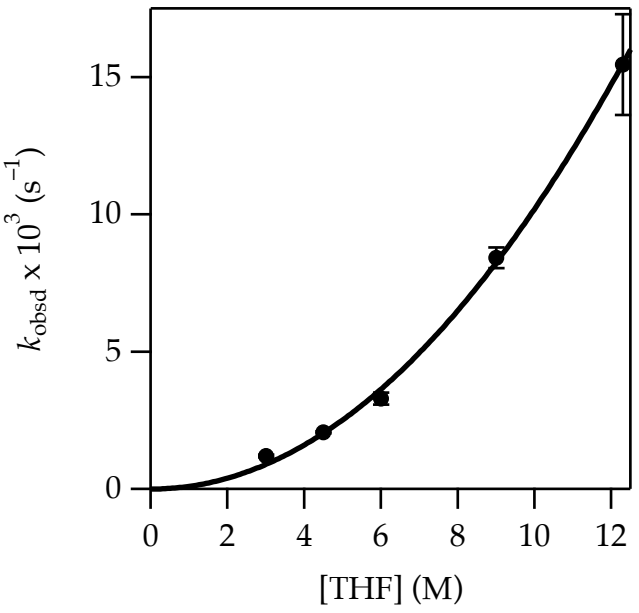


Figure 8. Plot of k_{obsd} vs. THF concentration in hexane for the metalation of **1** (0.010 M) by LiTMP (0.10 M) at –78 °C measured with IR spectroscopy (1323 cm^{-1}). The curve depicts the result of an unweighted least-squares fit to $y = ax^n$ ($a = 0.10 \pm 0.02$, $n = 2.02 \pm 0.07$).

[THF] (M)	$k_{obsd}^1 \times 10^3$ (s^{-1})	$k_{obsd}^2 \times 10^3$ (s^{-1})	$k_{obsd}^{avg} \times 10^3$ (s^{-1})
3.0	1.2349	1.1623	1.20 ± 0.05
4.5	2.0881	2.0391	2.06 ± 0.03
6.0	3.4505	3.1484	3.3 ± 0.2
9.0	8.1481	8.6858	8.4 ± 0.4
12.3	14.1630	16.7650	15 ± 2

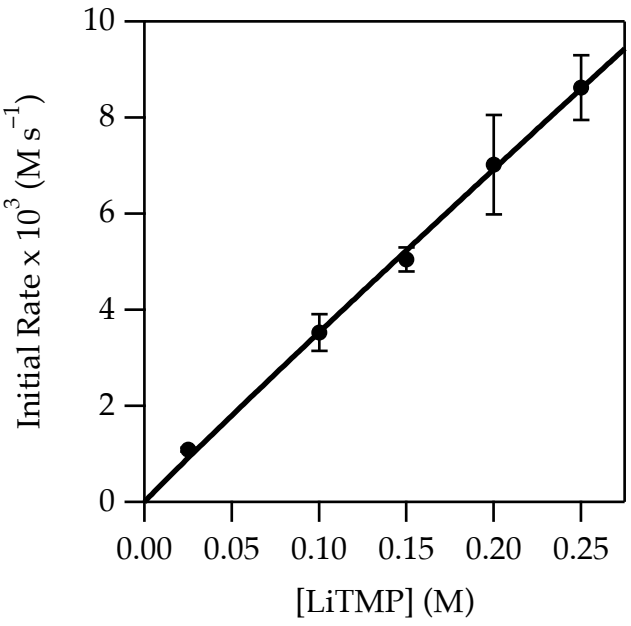


Figure 9. Plot of initial rate vs. LiTMP concentration in 6.0 M THF with hexane cosolvent for the metalation of **1** (0.010 M) at –78 °C measured with IR spectroscopy (1323 cm^{-1}). The curve depicts the result of an unweighted least-squares fit to $y = ax^n$ (a = 33.07 ± 2.19, n = 0.97 ± 0.04).

[LiTMP] (M)	Initial Rate[1] × 10^3 ($M\ s^{-1}$)	Initial Rate[2] × 10^3 ($M\ s^{-1}$)	Initial Rate[avg] × 10^3 ($M\ s^{-1}$)
0.025	1.0611	1.1226	1.09 ± 0.04
0.10	3.2593	3.7978	3.5 ± 0.4
0.15	4.8724	5.2261	5.0 ± 0.3
0.20	6.2916	7.756	7 ± 1
0.25	8.1469	9.0975	8.6 ± 0.7

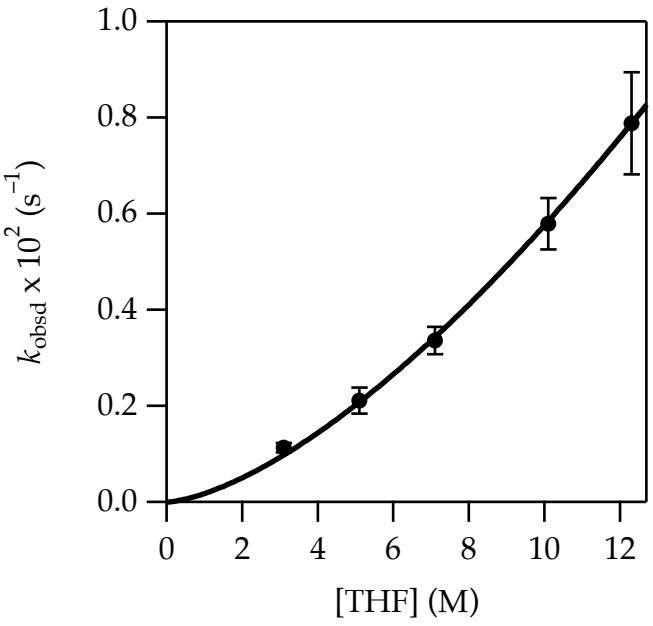


Figure 10. Plot of k_{obsd} vs. THF concentration in hexane for the metalation of **2** (0.0025 M) by LiTMP (0.10 M) at –78 °C measured with IR spectroscopy (1356 cm^{-1}). The curve depicts the result of an unweighted least-squares fit to $y = ax^n$ ($a = 0.018 \pm 0.002$, $n = 1.50 \pm 0.04$).

[THF] (M)	$k_{obsd}^{1} \times 10^2$ (s^{-1})	$k_{obsd}^{2} \times 10^2$ (s^{-1})	$k_{obsd}^{avg} \times 10^2$ (s^{-1})
3.0	0.10584	0.11988	0.11 ± 0.01
5.0	0.19222	0.23033	0.21 ± 0.03
7.0	0.35638	0.31640	0.34 ± 0.3
10.0	0.61657	0.54127	0.58 ± 0.5
12.3	0.86309	0.71293	0.8 ± 0.1

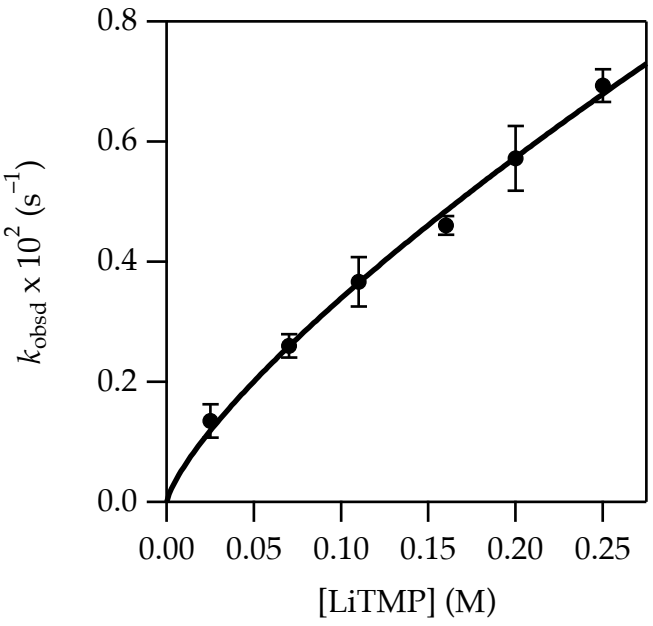


Figure 11. Plot of k_{obsd} vs. LiTMP concentration in 6.0 M THF with hexane cosolvent for the metalation of **2** (0.0025 M) at –78 °C measured with IR spectroscopy (1356 cm^{-1}). The curve depicts the result of an unweighted least-squares fit to $y = ax^n$ ($a = 1.9 \pm 0.1$, $n = 0.76 \pm 0.04$).

[THF] (M)	$k_{obsd}^{1} \times 10^2$ (s^{-1})	$k_{obsd}^{2} \times 10^2$ (s^{-1})	$k_{obsd}^{avg} \times 10^2$ (s^{-1})
0.025	0.11550	0.15455	0.14 ± 0.03
0.070	0.24632	0.27404	0.26 ± 0.02
0.11	0.33746	0.39563	0.37 ± 0.04
0.16	0.44992	0.47159	0.46 ± 0.02
0.20	0.61031	0.53383	0.57 ± 0.05
0.25	0.67421	0.71238	0.69 ± 0.03

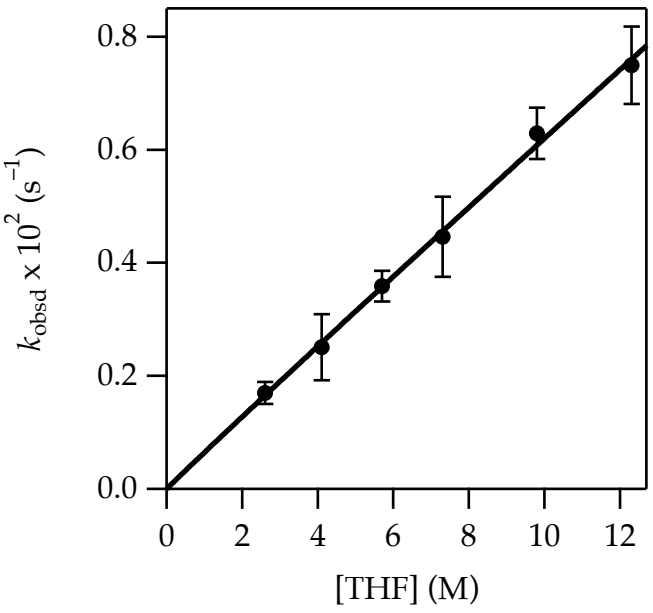


Figure 12. Plot of k_{obsd} vs. THF concentration in hexane for the metalation of **3** (0.0025 M) by LiTMP (0.10 M) at –40 °C measured with IR spectroscopy (1496 cm^{-1}). The curve depicts the result of an unweighted least-squares fit to $y = ax^n$ ($a = 0.065 \pm 0.005$, $n = 0.98 \pm 0.03$).

[THF] (M)	$k_{obsd}^{1} \times 10^2$ (s^{-1})	$k_{obsd}^{2} \times 10^2$ (s^{-1})	$k_{obsd}^{avg} \times 10^2$ (s^{-1})
2.5	0.18386	0.1563	0.17 ± 0.02
4.0	0.29205	0.20944	0.25 ± 0.06
5.6	0.33978	0.37821	0.36 ± 0.03
7.2	0.39605	0.49637	0.45 ± 0.07
9.7	0.59712	0.66112	0.63 ± 0.05
12.3	0.70152	0.79822	0.75 ± 0.07

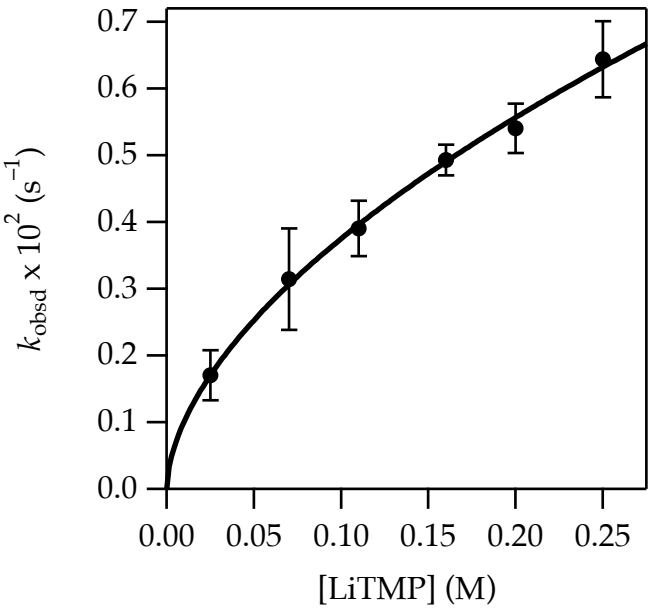


Figure 13. Plot of k_{obsd} vs. LiTMP concentration in 6.0 M THF with hexane cosolvent for the metalation of **3** (0.0025 M) at –40 °C measured with IR spectroscopy (1496 cm^{-1}). The curve depicts the result of an unweighted least-squares fit to $y = ax^n$ ($a = 1.39 \pm 0.05$, $n = 0.57 \pm 0.02$).

[THF] (M)	$k_{obsd}^{1} \times 10^2$ (s^{-1})	$k_{obsd}^{2} \times 10^2$ (s^{-1})	$k_{obsd}^{avg} \times 10^2$ (s^{-1})
0.025	0.19712	0.1438	0.17 ± 0.04
0.070	0.26101	0.36832	0.31 ± 0.08
0.11	0.4198	0.36122	0.39 ± 0.04
0.16	0.47688	0.50936	0.49 ± 0.02
0.20	0.56696	0.5143	0.54 ± 0.04
0.25	0.60363	0.68393	0.64 ± 0.06

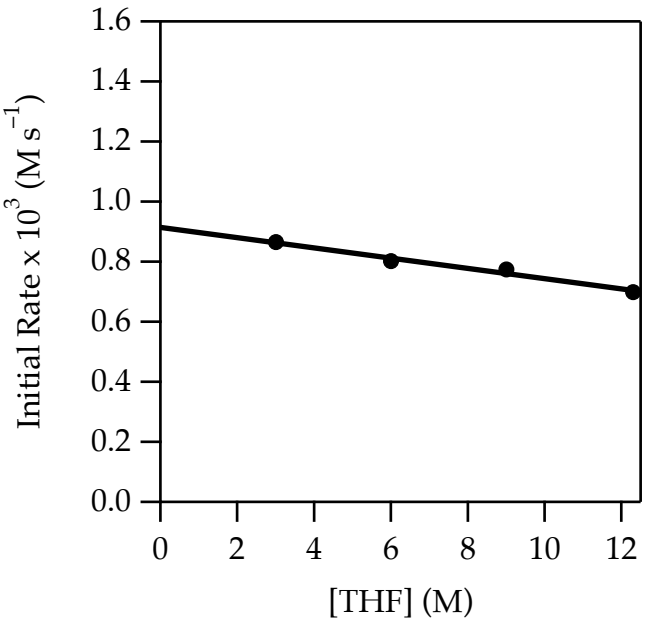


Figure 14. Plot of k_{obsd} vs. THF concentration in hexane for the metalation of **4** (0.010 M) by LiTMP (0.10 M) at –40 °C measured with IR spectroscopy (1655 cm^{-1}). The curve depicts the result of an unweighted least-squares fit to $y = ax + b$ ($a = 0.91 \pm 0.02$, $b = -0.017 \pm 0.002$).

[THF] (M)	Initial Rate × 10^3 (M s^{-1})
3.0	0.86543
6.0	0.80176
9.0	0.77434
12.3	0.69852

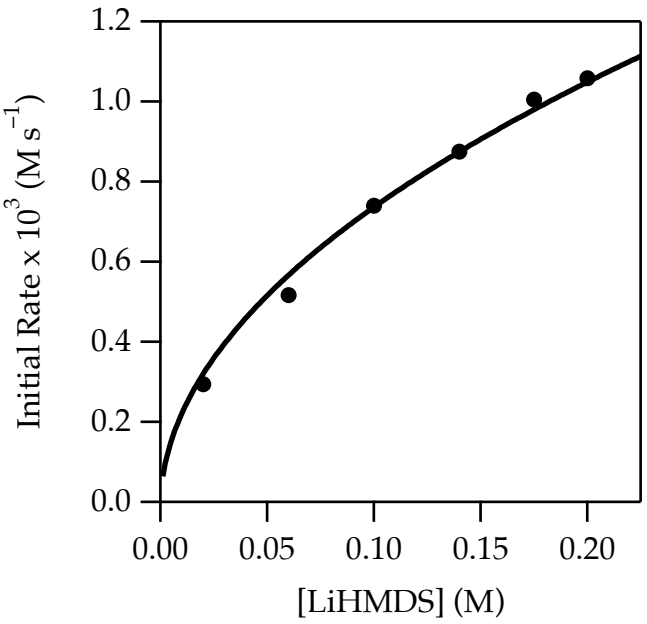


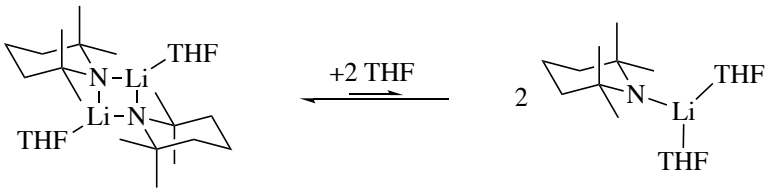
Figure 15. Plot of k_{obsd} vs. LiTMP concentration in 6.0 M THF with hexane cosolvent for the metalation of **4** (0.010 M) at –40 °C measured with IR spectroscopy (1655 cm^{-1}). The curve depicts the result of an unweighted least-squares fit to $y = ax^n$ ($a = 2.7 \pm 0.1$, $n = 0.57 \pm 0.02$).

[THF] (M)	Initial Rate × 10^3 ($M\ s^{-1}$)
0.025	0.29389
0.070	0.74015
0.11	0.87481
0.16	1.0051
0.20	1.058
0.25	0.51666

III. Derivations

i. LiTMP-meidated enolization: THF

To simplify the discussion of the mechanistic model, we introduce the following shorthand: A = a LiTMP subunit, and S = THF. As shown below, A_2S_2 corresponds to the disolvated LiTMP dimer, and AS_2 corresponds to disolvated LiTMP monomer.



A_2S_2 **AS_2**

Given $K_{eq} = [AS_2]^2/\{[A_2S_2][S]^2\}$, and $2[A_2S_2] + [AS_2] = [A_{total}]$, one can solve for $[A_2S_2]$ as a function of $[A_{total}]$ and [S]:

$$K_{eq} = \frac{\left[AS_2\right]^2}{\left[A_2S_2\right]\left[S\right]^2} = \frac{\left(\left[A_{total}\right] - 2\left[A_2S_2\right]\right)^2}{\left[A_2S_2\right]\left[S\right]^2}$$

Rearranging,

$$4\left[A_2S_2\right]^2 - \left(4\left[A_{total}\right] + K_{eq}\left[S\right]^2\right)\left[A_2S_2\right] + \left[A_{total}\right]^2 = 0$$

Applying the quadratic equation to $[A_2S_2]$ gives:

$$\left[A_2S_2\right] = \frac{\left(4\left[A_{total}\right] + K_{eq}\left[S\right]^2\right) - \sqrt{\left(4\left[A_{total}\right] + K_{eq}\left[S\right]^2\right)^2 - 16\left[A_{total}\right]}}{8} = \frac{4\left[A_{total}\right] + K_{eq}\left[S\right]^2 - \sqrt{K_{eq}}\left[S\right]\sqrt{K_{eq}\left[S\right]^2 + 8\left[A_{total}\right]}}{8}$$

ii. Mathematica simulation of LiTMP order vs. percent monomer

Knowing that LiTMP exists as a dimer-monomer equilibrium we sought to develop a simulation that illustrated how the order in LiTMP (base order) varied with percent monomer relative to the total base titer. Consider the following equation:

$$1/2\ A_2 + 2S \underset{}{\overset{K_{eq}}{\rightleftharpoons}} AS_2 \xrightarrow{k} [AS_2]^{\ddagger}$$

for which $K_{eq} = [A]^2/\{[A_2][S]^2\}$. For simplicity, the model assumes reactivity funnels exclusively through a monomer-based transition state. Within this section, text within boxes contains executable code that can be directly pasted into *Mathematica*, and images beneath the code are screenshots of the actual input/output. We first solve for $[A_2]$ and [A]:

```
Solve[{keq == a^2/(a2*s^2), a0 == 2*a2 + a}, {a2, a}]
```

```
Solve[{keq == a^2 / (a2 * s^2), a0 == 2 a2 + a}, {a2, a}]
{{a2 → 1/8 (4 a0 + keq s^2 - Sqrt[keq] s Sqrt[8 a0 + keq s^2]), a → 1/4 (-keq s^2 + Sqrt[keq] s Sqrt[8 a0 + keq s^2])},
 {a2 → 1/8 (4 a0 + keq s^2 + Sqrt[keq] s Sqrt[8 a0 + keq s^2]), a → 1/4 (-keq s^2 - Sqrt[keq] s Sqrt[8 a0 + keq s^2])}}
```

We chose the first set of roots, which correspond to the realistic case of all concentrations being positive. We then solve for the concentration of dimer (d) and monomer (m) as a function of the fraction of monomer (r) by normality:

```
Solve[{2 d + m == 0.1, m/(2 d + m) == r/100}, {d, m}]
```

```
Solve[{2 d + m == 0.1, m / (2 d + m) == r / 100}, {d, m}]
{{d → 0.05 - 0.0005 r, m → 0.001 r}}
```

We can then use the equilibrium expression to solve for the equilibrium constant (K_{eq}) as a function of r by substituting in the previous result:

```
m^2/(d*s^2) /. {d -> 0.05` - 0.0005` r, m -> 0.001` r}
```

```
m^2 / (d*s^2) /. {d → 0.05` - 0.0005` r, m → 0.001` r}
```

$$\frac{1.\times 10^{-6}\, r^2}{(0.05 - 0.0005\, r)\, s^2}$$

With this is hand, we replace all instances of the equilibrium constant (K_{eq}) in the rate expression with the solution above:

```
Simplify[k*1/4 (-keq s^2 + Sqrt[keq] s Sqrt[8 a0 + keq s^2])
/.   keq -> (1.`*^-6 r^2)/((0.05` - 0.0005` r) s^2)]
```

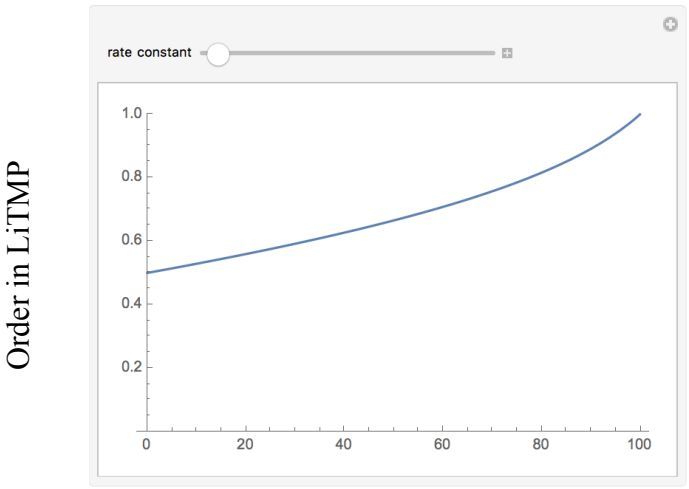
```
Simplify[k * 1/4 (-keq s^2 + Sqrt[keq] s Sqrt[8 a0 + keq s^2]) /. keq → 1.`*^-6 r^2/((0.05` - 0.0005` r) s^2)]
```

$$k\left(-\frac{2.5`*^{-7}\, r^2}{0.05` - 0.0005` r} + 0.00025` \sqrt{8\, a0 + \frac{1.`*^{-6}\, r^2}{0.05` - 0.0005` r}}\ \sqrt{\frac{r^2}{(0.05` - 0.0005` r)}}\right)$$

The output from this substitution provides us with the necessary equation to describe LiTMP order as a function of percent monomer (observable). If one looks closely at the previous input/output, it becomes apparent that the change in solvation has no effect on the contribution of the aggregates to the total measured order—all *s* terms cancel. Therefore, only the change in aggregation state in conjunction with the shifting ground state influences the measured order.

We can now plot the LiTMP order as a function of percent monomer for 0.1 N LiTMP as follows:

```
Manipulate[Plot[n /.FindFit[Flatten[Table[{k (-((2.5`*^-7 r^2)/(0.05` -
0.0005` r)) + 0.00025` Sqrt[8 a0 + (1.`*^-6 r^2)/(0.05` - 0.0005` r)]
Sqrt[r^2/(0.05` - 0.0005` r) ] )}, {a0, 0, 0.25,0.0001}]], a*x^n, {a, n}, x],
{r, 0, 100}, PlotRange -> {0, 1}], {{k, 1, "rate constant"}, 0, 100}]
```

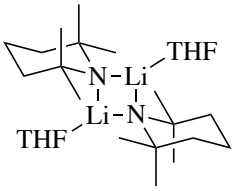


We first generate a table of data, which corresponds to rate vs. base concentration (a0) at a given percent monomer (r). We then fit to a simple power function to obtain the LiTMP order. We repeat this calculation incrementally from r=0 (no observable monomer) to r=100 (100% observable monomer). We include a provision to adjust the rate constant, *k*, but add there is no effect on the plot shape.

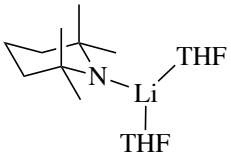
IV: Ground State Computations

Chart 2.

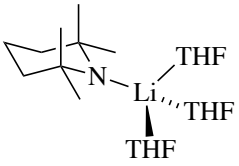
THF



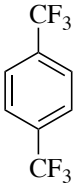
A_2S_2



AS_2



AS_3



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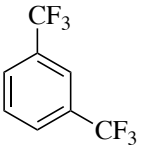

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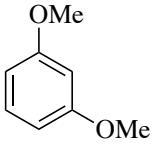

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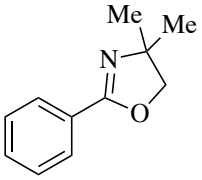
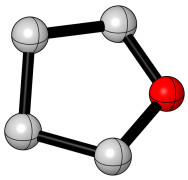


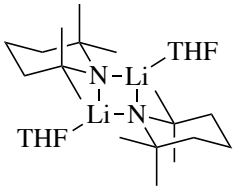
4

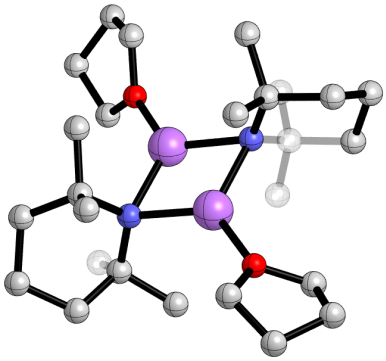
Table 2. Optimized geometries at the B3LYP level of theory with 6-31G(d) basis set for relevant ground states of LiTMP/THF-mediated ortholithiations with free energies (Hartrees), corrected MP2 energies (kcal), and cartesian coordinates (X, Y, Z). (Note: G_{MP2} includes single-point MP2 corrections to B3LYP/6-31G(d) optimized structures at the given temperature.)



THF (–78 °C)
G = –232.357946
G_{MP2} = –145317.665

Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
H	0.36944100	0.05245400	1.03607400
H	0.78366900	0.39304900	-0.65835500
C	-0.43145400	-1.42747100	-0.35907500
H	-0.36819400	-1.58569300	-1.44243900
H	0.17898100	-2.19202000	0.13156300
C	-1.89873200	-1.42780000	0.09478400
H	-2.50889400	-2.19240900	-0.39610500
H	-1.96191900	-1.58645800	1.17808700
C	-2.33082600	-0.00036200	-0.26378100
H	-2.70107000	0.05220800	-1.29954200
H	-3.11413200	0.39228800	0.39526100
O	-1.16547600	0.82075200	-0.13234900

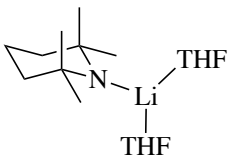


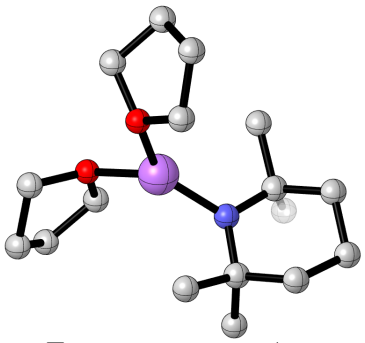


A_2S_2 (–78 °C)
G = –1296.456254
G_{MP2} = –810668.178

Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
H	-0.93184200	-0.53199300	0.23483900
H	0.76398100	-0.77620000	-0.14547200
C	0.39424400	0.92553200	1.14842500
H	0.49607000	0.36089700	2.08628100
H	1.38887300	1.34097900	0.92492200
C	-0.59074100	2.11271100	1.35418200
N	-0.91199800	2.83953700	0.09804500
C	-1.19052500	1.98766800	-1.08691600
C	-0.16564200	0.83494700	-1.26810400
H	-0.45998600	0.20130700	-2.11701800
H	0.81030200	1.27422700	-1.52577600
C	-1.08637200	2.87248700	-2.34340400
H	-1.79871500	3.70871300	-2.31125000
H	-1.30222600	2.30033800	-3.25475200
H	-0.07780800	3.29034000	-2.44162400
C	-2.62305200	1.36871800	-1.12858100
H	-2.79315800	0.63944800	-0.33295700

H	-3.37448500	2.15846400	-1.02721200
H	-2.80163800	0.85238300	-2.08231700
Li	-2.25521100	4.44387100	0.05504500
N	-1.19582100	6.20192000	0.06674400
Li	0.12525800	4.60742000	0.03482700
O	2.14443600	4.71693200	-0.01996500
C	2.97341700	5.69906500	0.64722800
H	2.96245800	5.48369100	1.72274300
H	2.53422300	6.68673900	0.48466300
C	4.37364000	5.53987700	0.04790300
H	4.48536500	6.17263000	-0.84048100
H	5.16138300	5.81013700	0.75725600
C	4.39211600	4.05525800	-0.34844200
H	5.13367500	3.82062000	-1.11779600
H	4.59556500	3.42668700	0.52654300
C	2.95899300	3.84315600	-0.83461300
H	2.84399100	4.13309200	-1.88793300
H	2.58703200	2.82411300	-0.70653300
C	-1.51248300	6.91137100	1.33743700
C	-2.19060500	8.28866000	1.12592900
H	-2.39609300	8.74930200	2.10188500
H	-3.17014000	8.11030700	0.66525000
C	-1.37269200	9.25280300	0.24696800
H	-0.75413400	9.90898000	0.87221100
H	-2.05791500	9.91730600	-0.29441300
C	-0.47097800	8.49160900	-0.74285800
C	-1.00294300	7.08496600	-1.11492600
C	0.04511900	6.46065700	-2.06170100
H	1.02262300	6.38951900	-1.57161700
H	0.16783400	7.06012200	-2.97358200
H	-0.25566900	5.45642400	-2.37671800
C	-2.30066600	7.24477900	-1.96151400
H	-3.11595500	7.68660200	-1.38074200
H	-2.14117100	7.87703700	-2.84736700
H	-2.63602900	6.26131600	-2.31489200
H	0.52788500	8.36079900	-0.30704200
H	-0.32722200	9.08572700	-1.65578600
C	-2.51416500	6.06962900	2.16250100
H	-2.70071200	6.51421800	3.14897600
H	-3.47395000	5.99497500	1.63874700
H	-2.14234600	5.05280800	2.34241100
C	-0.25234100	7.11367500	2.22986300
H	-0.49842100	7.58407100	3.19331600
H	0.49303800	7.74281700	1.73434500
H	0.22031400	6.14783200	2.44367100
O	-4.27873200	4.23550500	-0.07206100
C	-5.07033400	3.48555900	0.88149200
H	-5.05101100	4.01470100	1.84329900
H	-4.60715000	2.50477100	1.00733000
C	-6.48110600	3.43531000	0.29520700
H	-6.57563300	2.59519300	-0.40277000
H	-7.24839400	3.32535800	1.06727300
C	-6.56056000	4.77152500	-0.45832500
H	-7.32228100	4.78344600	-1.24346600
H	-6.77610600	5.59046100	0.23810900
C	-5.14427300	4.90660200	-1.02073300
H	-5.04615000	4.40613300	-1.99267800
H	-4.80406300	5.93919200	-1.11987800
C	0.12507800	3.08648500	2.31574000
H	-0.50846500	3.94147300	2.57203800
H	0.38902100	2.58793400	3.25712600
H	1.05517200	3.46312700	1.87324500
C	-1.83783500	1.59687500	2.13255700
H	-1.55797100	1.19091500	3.11479700
H	-2.53868200	2.42308100	2.30241500
H	-2.37512700	0.80835700	1.59934000

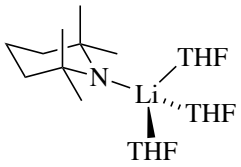


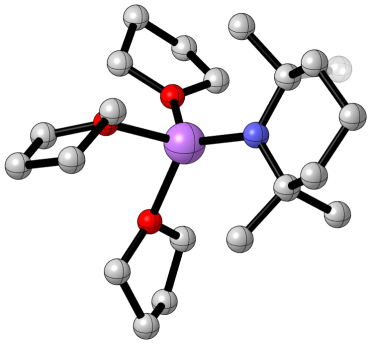


AS_2 (–78 °C)
G = –880.575136
G_{MP2} = –550642.897

Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
H	0.75391800	-0.74172200	-0.29845100

H	0.56133000	0.88448500	0.33118600
C	-0.89292400	0.35723200	-1.19268800
H	-0.29118200	0.78020100	-2.01091300
H	-1.34502100	-0.57012800	-1.57584200
C	-2.04274800	1.32709400	-0.79672700
N	-2.77693400	0.86481800	0.38098700
C	-2.00128400	0.42878100	1.54168400
C	-0.85389600	-0.54473100	1.15022800
H	-0.22342800	-0.77560400	2.02190500
H	-1.30823300	-1.49291600	0.82429600
C	-1.41100100	1.58316700	2.41116100
H	-2.19795300	2.30976900	2.64572100
H	-1.00083700	1.20555400	3.35896600
H	-0.60619700	2.12364800	1.90638000
C	-2.96902700	-0.33856100	2.46966100
H	-3.79424100	0.31442400	2.79169700
H	-2.47000700	-0.70442100	3.37624200
H	-3.39550700	-1.20455800	1.94623000
Li	-4.62479000	0.59603900	0.31422200
C	-1.46847600	2.77415100	-0.68467700
H	-2.25527000	3.45606400	-0.34049600
H	-0.63992300	2.84571700	0.02462300
H	-1.09693700	3.13798000	-1.65356400
C	-3.04656700	1.36567000	-1.97021400
H	-3.87216700	2.05878000	-1.74701100
H	-3.47130100	0.36959300	-2.15077800
H	-2.57892100	1.70606500	-2.90303400
C	-7.09920100	2.31019900	0.00498000
H	-8.03925300	2.33551800	0.57610300
H	-7.18987700	1.56883800	-0.79333000
C	-6.69360500	3.70457300	-0.46459500
H	-5.95408500	3.62509200	-1.26912300
H	-7.54058300	4.29230100	-0.83154600
C	-6.05377200	4.29445700	0.80676700
H	-5.29068400	5.04454400	0.58120500
H	-6.81689800	4.77261800	1.43066900
C	-5.45828800	3.06384300	1.52118300
H	-4.37361100	2.97283700	1.41490800
H	-5.72523400	3.02820000	2.58331000
O	-6.02206400	1.89162800	0.86177300
C	-6.76867200	-1.52092800	0.53848900
H	-7.65807700	-1.66175100	-0.09358400
H	-7.00230700	-0.79778500	1.32375200
C	-6.22446400	-2.85541500	1.04057800
H	-5.55814500	-2.68799400	1.89365800
H	-7.01453300	-3.54623700	1.35014300
C	-5.43131400	-3.35502500	-0.18213100
H	-4.59847200	-4.00704100	0.09542700
H	-6.08546800	-3.91939000	-0.85573300
C	-4.94725800	-2.05587900	-0.85914600
H	-3.89089900	-1.83517200	-0.68368300
H	-5.13904400	-2.05178300	-1.93783200
O	-5.69768200	-0.96863900	-0.24894500

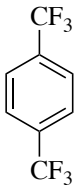


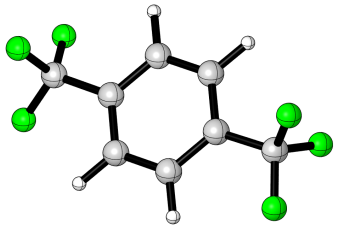


AS_3 (–78 °C)
G = –1112.914623
G_{MP2} = –695956.399

Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
H	-0.93184200	-0.53199300	0.23483900
H	0.76398100	-0.77620000	-0.14547200
C	0.39424400	0.92553200	1.14842500
H	0.49607000	0.36089700	2.08628100
H	1.38887300	1.34097900	0.92492200
C	-0.59074100	2.11271100	1.35418200
N	-0.91199800	2.83953700	0.09804500
C	-1.19052500	1.98766800	-1.08691600
C	-0.16564200	0.83494700	-1.26810400
H	-0.45998600	0.20130700	-2.11701800
H	0.81030200	1.27422700	-1.52577600

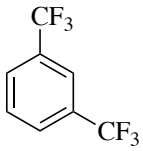
C	-1.08637200	2.87248700	-2.34340400
H	-1.79871500	3.70871300	-2.31125000
H	-1.30222600	2.30033800	-3.25475200
H	-0.07780800	3.29034000	-2.44162400
C	-2.62305200	1.36871800	-1.12858100
H	-2.79315800	0.63944800	-0.33295700
H	-3.37448500	2.15846400	-1.02721200
H	-2.80163800	0.85238300	-2.08231700
Li	-2.25521100	4.44387100	0.05504500
N	-1.19582100	6.20192000	0.06674400
Li	0.12525800	4.60742000	0.03482700
O	2.14443600	4.71693200	-0.01996500
C	2.97341700	5.69906500	0.64722800
H	2.96245800	5.48369100	1.72274300
H	2.53422300	6.68673900	0.48466300
C	4.37364000	5.53987700	0.04790300
H	4.48536500	6.17263000	-0.84048100
H	5.16138300	5.81013700	0.75725600
C	4.39211600	4.05525800	-0.34844200
H	5.13367500	3.82062000	-1.11779600
H	4.59556500	3.42668700	0.52654300
C	2.95899300	3.84315600	-0.83461300
H	2.84399100	4.13309200	-1.88793300
H	2.58703200	2.82411300	-0.70653300
C	-1.51248300	6.91137100	1.33743700
C	-2.19060500	8.28866000	1.12592900
H	-2.39609300	8.74930200	2.10188500
H	-3.17014000	8.11030700	0.66525000
C	-1.37269200	9.25280300	0.24696800
H	-0.75413400	9.90898000	0.87221100
H	-2.05791500	9.91730600	-0.29441300
C	-0.47097800	8.49160900	-0.74285800
C	-1.00294300	7.08496600	-1.11492600
C	0.04511900	6.46065700	-2.06170100
H	1.02262300	6.38951900	-1.57161700
H	0.16783400	7.06012200	-2.97358200
H	-0.25566900	5.45642400	-2.37671800
C	-2.30066600	7.24477900	-1.96151400
H	-3.11595500	7.68660200	-1.38074200
H	-2.14117100	7.87703700	-2.84736700
H	-2.63602900	6.26131600	-2.31489200
H	0.52788500	8.36079900	-0.30704200
H	-0.32722200	9.08572700	-1.65578600
C	-2.51416500	6.06962900	2.16250100
H	-2.70071200	6.51421800	3.14897600
H	-3.47395000	5.99497500	1.63874700
H	-2.14234600	5.05280800	2.34241100
C	-0.25234100	7.11367500	2.22986300
H	-0.49842100	7.58407100	3.19331600
H	0.49303800	7.74281700	1.73434500
H	0.22031400	6.14783200	2.44367100
O	-4.27873200	4.23550500	-0.07206100
C	-5.07033400	3.48555900	0.88149200
H	-5.05101100	4.01470100	1.84329900
H	-4.60715000	2.50477100	1.00733000
C	-6.48110600	3.43531000	0.29520700
H	-6.57563300	2.59519300	-0.40277000
H	-7.24839400	3.32535800	1.06727300
C	-6.56056000	4.77152500	-0.45832500
H	-7.32228100	4.78344600	-1.24346600
H	-6.77610600	5.59046100	0.23810900
C	-5.14427300	4.90660200	-1.02073300
H	-5.04615000	4.40613300	-1.99267800
H	-4.80406300	5.93919200	-1.11987800
C	0.12507800	3.08648500	2.31574000
H	-0.50846500	3.94147300	2.57203800
H	0.38902100	2.58793400	3.25712600
H	1.05517200	3.46312700	1.87324500
C	-1.83783500	1.59687500	2.13255700
H	-1.55797100	1.19091500	3.11479700
H	-2.53868200	2.42308100	2.30241500
H	-2.37512700	0.80835700	1.59934000

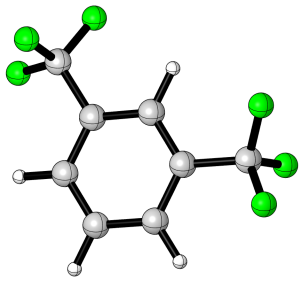




1 (–78 °C)
G = –906.234214
G_{MP2} = –567194.695

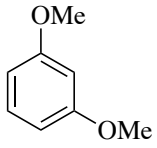
Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	-1.50628400	0.01470000	-0.04260800
C	-2.20922400	-1.19482000	-0.03627300
H	-1.66871600	-2.13528900	-0.05072600
C	-3.59950900	-1.18619100	-0.02081600
H	-4.15079200	-2.12131700	-0.01888900
C	-4.28918300	0.03108900	-0.01172600
C	-3.58864500	1.23692100	-0.02045500
H	-4.12890600	2.17661700	-0.01802000
C	-2.19431200	1.22845000	-0.03538000
H	-1.64406900	2.16292800	-0.04841500
C	-5.79572400	0.00760500	0.00414100
F	-6.32789500	1.24690200	0.01107900
F	-6.28810300	-0.64012600	-1.07605900
F	-6.26445900	-0.64218400	1.09352400
F	0.52971200	1.12319100	-0.53001300
F	0.50791700	-1.05178200	-0.67883200
F	0.45657300	-0.09336900	1.26974700

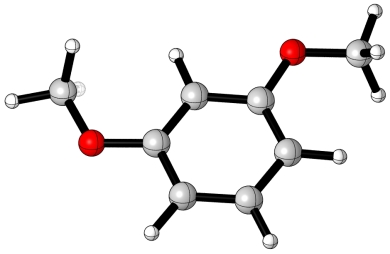




2 (–78 °C)
G = –906.235281
G_{MP2} = –567195.185

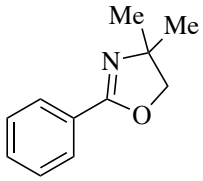
Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	1.30595600	0.75079400	0.02869900
C	2.51087200	0.04811000	-0.00223900
H	2.51087200	-1.03580500	-0.00223900
C	3.71578800	0.75079400	-0.03317700
C	3.71864200	2.14811600	-0.03447700
C	2.51087200	2.84347200	-0.00223900
H	2.51087200	3.92917900	-0.00223900
C	1.30310200	2.14811600	0.02999900
H	0.36063200	2.68457300	0.06144400
H	4.66111200	2.68457300	-0.06592200
C	5.02174400	0.00000000	-0.00447800
F	5.99786900	0.67456800	-0.65066100
F	4.91477200	-1.21641600	-0.58010000
F	5.45208700	-0.19861100	1.26252300
F	-0.97612500	0.67456800	0.64618300
F	0.10697200	-1.21641600	0.57562100
F	-0.43034300	-0.19861100	-1.26700100

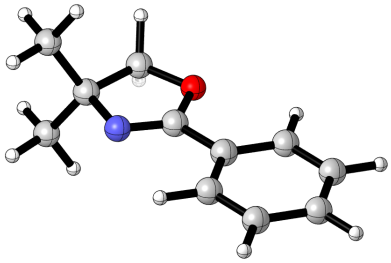




3 (–40 °C)
G = –461.153141
G_{MP2} = – 288461.342

Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
O	0.34817800	1.37452300	-0.00001500
C	1.67304100	1.70514300	-0.00001000
C	2.71155100	0.77588800	-0.00001100
C	4.04380600	1.22219100	-0.00000700
C	4.33789500	2.58732100	-0.00000500
C	3.27612800	3.50243100	-0.00000500
C	1.95495600	3.08278900	-0.00000700
H	1.12937800	3.78661700	-0.00000800
H	3.49779300	4.56650100	-0.00000100
H	5.36001400	2.94621900	0.00000100
O	4.97997100	0.22564000	-0.00000800
C	6.34872200	0.59497500	-0.00000700
H	6.61076600	1.17599000	-0.89434600
H	6.91223000	-0.34027600	-0.00001200
H	6.61076400	1.17598200	0.89433800
H	2.53636000	-0.29287000	-0.00001200
H	0.37882800	-0.51267300	0.89423200
H	0.37882100	-0.51269100	-0.89422300
H	-1.09131600	-0.03310600	0.00000500



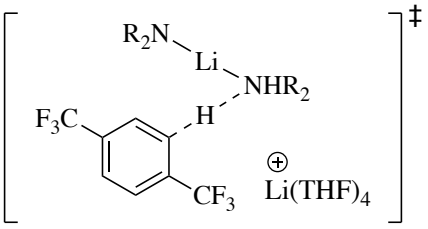


4 (–40 °C)
G = –556.788405
G_{MP2} = –348261.434

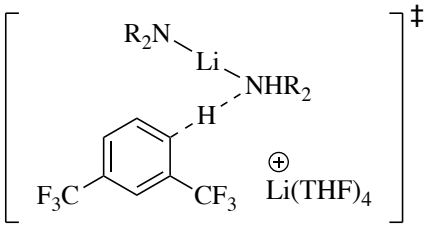
Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	0.27714300	-1.53802700	0.00004300
N	-1.07582200	-2.13027000	0.00005300
C	-1.91843800	-1.17072800	0.00003200
C	-3.38476300	-1.30798200	0.00003500
C	-3.95446200	-2.59038700	0.00002800
C	-5.33809000	-2.73875000	0.00003300
C	-6.16538700	-1.61134200	0.00004500
C	-5.60181600	-0.33425100	0.00005100
C	-4.21589600	-0.17930500	0.00004600
H	-3.77170300	0.81013500	0.00004900
H	-6.24192800	0.54387100	0.00006100
H	-7.24582300	-1.72923000	0.00004900
H	-5.77388500	-3.73418800	0.00002700
H	-3.29600600	-3.45277000	0.00002100
O	-1.43895000	0.11276300	0.00000300
C	1.02639500	-1.98728300	-1.26304900
H	2.03452800	-1.55554300	-1.29352100
H	1.11620500	-3.07792800	-1.28304900
H	0.48890800	-1.67411400	-2.16469100
C	1.02638000	-1.98721400	1.26317000
H	1.11618400	-3.07785800	1.28323400
H	2.03451400	-1.55547700	1.29362700
H	0.48888400	-1.67399000	2.16478800
H	0.38213400	0.50885700	-0.89132700
H	0.38214200	0.50890800	0.89129500

V. Transition State Computations

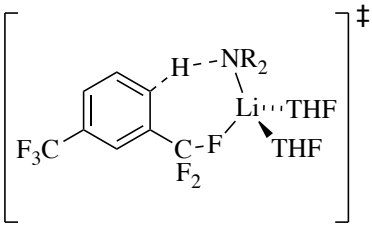
Chart 3.



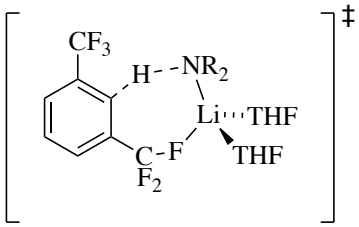
1-A_2S_4



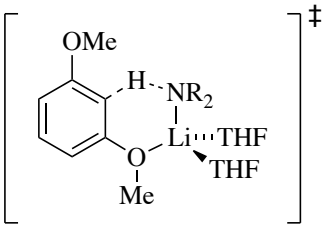
2-A_2S_4



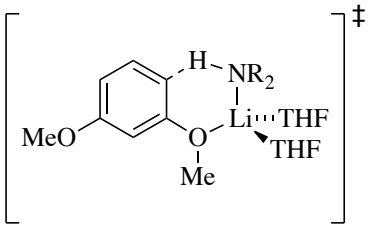
2-AS_2 (external)



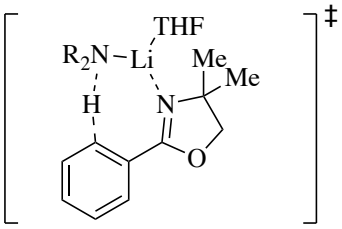
2-AS_2 (internal)



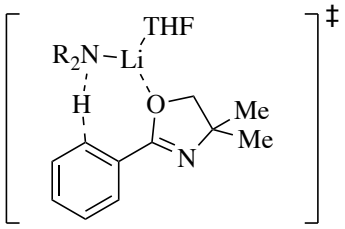
3-AS_2 (internal)



3-AS_2 (external)

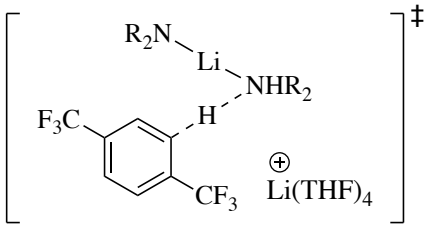


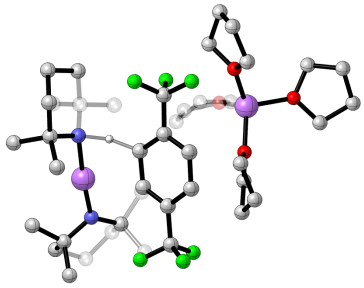
4-AS (N-bound)



4-AS(O-bound)

Table 3. Optimized geometries at the B3LYP level of theory with 6-31G(d) basis set for relevant transition states of LiTMP/THF-mediated ortholithiation of **1** at –78 °C with free energies (Hartrees), corrected MP2 energies (kcal), and cartesian coordinates (X, Y, Z). (Note: G_{MP2} includes single-point MP2 corrections to B3LYP/6-31G(d) optimized structures.)



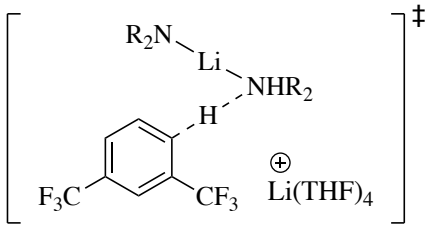


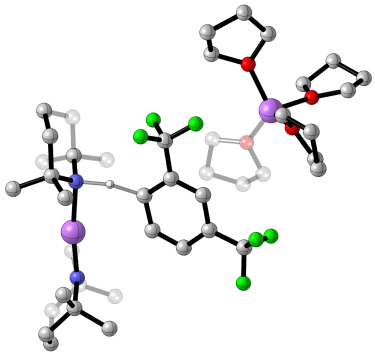
1-A_2S_4
G = –2667.335463
G_{MP2} = –1668467.937

Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	0.71694400	-1.14002400	-0.66933800
C	0.35965800	-1.44299000	-1.99328600
C	0.97976800	-2.49963900	-2.65080800
H	0.73063700	-2.73313800	-3.68102200
C	1.94507800	-3.24462900	-1.96537300
C	2.29549800	-2.90837600	-0.65300800
C	1.71231500	-1.83506600	0.04916800
H	3.07397000	-3.49913400	-0.16951800
C	2.57111100	-4.43194100	-2.63982500
F	1.84437300	-5.57196900	-2.41989900
F	3.81745700	-4.68722200	-2.20167900
F	2.63394200	-4.28645800	-3.98508800
H	-0.38831900	-0.85195000	-2.51270000
F	-1.04838700	0.47886100	-0.73456600
F	-0.55140900	-0.37012800	1.19845500
F	0.78962000	1.06218300	0.26431700
H	2.41346100	-1.54184300	1.25741800
Li	3.84453600	-3.41564000	2.25821200
N	3.29682200	-1.45086300	2.30397300
C	2.53241700	-1.10962600	3.53739700
C	2.05527500	0.36892400	3.54739100
C	3.17503100	1.36307600	3.22249700
H	2.76281300	2.37860900	3.14537800
H	3.90565000	1.39575300	4.04165600
C	3.86151000	0.97202800	1.90994700
C	4.37866600	-0.49034600	1.92207300
C	5.64472600	-0.56949200	2.81879600
H	5.96215500	-1.60712600	2.95776100
H	6.47384200	-0.02633900	2.34612900
H	5.50329100	-0.13077900	3.80876300
C	4.84404900	-0.84426200	0.49429100
H	5.21634200	-1.87571700	0.44083900
H	5.66237100	-0.18248200	0.18565400
H	4.03575400	-0.74207500	-0.23325800
H	4.69301800	1.65846600	1.69480800
H	3.13988400	1.07754000	1.09069800
H	1.60587400	0.60515500	4.52368100
H	1.26274700	0.48306200	2.79903600
C	3.29773900	-1.41334300	4.85526500
H	2.60940300	-1.37745500	5.71150000
H	4.10312600	-0.70608300	5.06229800
H	3.73722700	-2.41813300	4.82048000
C	1.28017800	-2.01071200	3.56208400
H	1.56137200	-3.06480500	3.66972700
H	0.69724100	-1.90211400	2.64500800
H	0.64242100	-1.74724400	4.41740000
N	4.21621200	-5.25737600	2.14349300
C	3.24032200	-6.34485000	2.14894600
C	3.54359800	-7.40944700	3.24400600
C	4.99310600	-7.89970600	3.19338700
H	5.19235000	-8.58724200	4.02778400
H	5.16592300	-8.47994500	2.27642700
C	5.94665000	-6.70262800	3.25066500
C	5.63238700	-5.64254700	2.15710000
C	6.18674000	-6.14238800	0.78626600
H	5.86260700	-5.46355600	-0.01009700
H	7.28572400	-6.17763900	0.78765700
H	5.83704900	-7.14540300	0.52745400
C	6.44771600	-4.38000900	2.50045200

H	6.32862300	-3.61506700	1.72030900
H	7.52128400	-4.59531500	2.57685200
H	6.11870300	-3.95924600	3.45974800
H	6.99101600	-7.04014400	3.17127500
H	5.83938900	-6.22005500	4.23343400
H	2.84723300	-8.25893600	3.16121800
H	3.36959500	-6.94513800	4.22629900
C	3.05178400	-7.07394900	0.78019200
H	2.92084900	-6.34182400	-0.02270000
H	3.90824700	-7.69782600	0.51330600
H	2.17147900	-7.73575100	0.79635000
C	1.86952100	-5.72603000	2.48886800
H	1.59186900	-4.96787300	1.74338800
H	1.91014200	-5.24482000	3.47345100
H	1.07793800	-6.49084400	2.51184400
C	-5.57785700	-5.70085500	0.58925800
H	-5.34665100	-6.69800000	0.97815500
H	-4.97842500	-5.52870900	-0.31005400
C	-7.08118700	-5.48968000	0.34961000
H	-7.66903600	-6.18135400	0.96303000
H	-7.35881600	-5.65113200	-0.69559600
C	-7.30585300	-4.04230400	0.81812900
H	-7.02789700	-3.33161500	0.03100200
H	-8.33984800	-3.84075000	1.11203800
C	-6.33044900	-3.94268500	1.98744300
H	-5.98164300	-2.93078900	2.20520000
H	-6.75405000	-4.38128900	2.90189200
O	-5.17999300	-4.71197600	1.57536800
Li	-3.31634000	-4.08714100	1.85427500
O	-2.22208200	-4.97016100	0.51356200
C	-1.78203100	-6.35297700	0.61466500
H	-2.68066200	-6.97992400	0.66267000
H	-1.21467300	-6.47695700	1.54178000
C	-0.93936100	-6.63137500	-0.63884400
H	-1.10137500	-7.64150200	-1.02562900
H	0.12693200	-6.52189400	-0.42130800
C	-1.38799200	-5.53177700	-1.61479400
H	-0.62776600	-5.31081700	-2.36523200
H	-2.32000400	-5.80909300	-2.12300000
C	-1.62649700	-4.36327000	-0.66733800
H	-0.69066200	-3.86844500	-0.38794100
H	-2.33169900	-3.61447900	-1.03765000
O	-3.41416600	-2.12183600	1.86439100
C	-3.72650000	-1.24286000	0.74971200
H	-4.66656000	-1.59985600	0.31362500
H	-2.93362500	-1.31324000	0.00085800
C	-3.83968800	0.17870400	1.33119500
H	-4.69392300	0.72445800	0.92065600
H	-2.93317700	0.74231900	1.10135700
C	-3.95539000	-0.05945000	2.84754800
H	-3.58293900	0.78196100	3.43859200
H	-4.99560100	-0.24951300	3.13910100
C	-3.11541000	-1.31811300	3.03321800
H	-2.04461800	-1.08961100	3.05299800
H	-3.37663900	-1.91821300	3.90801600
O	-2.74414200	-4.67316300	3.63630200
C	-1.36980500	-4.46456800	4.07961400
H	-1.30501800	-3.47299300	4.54066000
H	-0.72147100	-4.48709500	3.20143800
C	-1.09277500	-5.57962700	5.08501700
H	-0.33339800	-5.29332600	5.81722200
H	-0.74065800	-6.48107800	4.57169100
C	-2.48054000	-5.81019100	5.70302000
H	-2.59016800	-6.79363300	6.16903900
H	-2.69424100	-5.04846700	6.46189800
C	-3.40336100	-5.63458400	4.49583300
H	-3.52637000	-6.57528400	3.94350500
H	-4.39415500	-5.24581800	4.74977900

Table 4. Optimized geometries at the B3LYP level of theory with 6-31G(d) basis set for relevant transition states of LiTMP/THF-mediated ortholithiation of **2** at –78 °C with free energies (Hartrees), corrected MP2 energies (kcal), and cartesian coordinates (X, Y, Z). (Note: G_{MP2} includes single-point MP2 corrections to B3LYP/6-31G(d) optimized structures.)

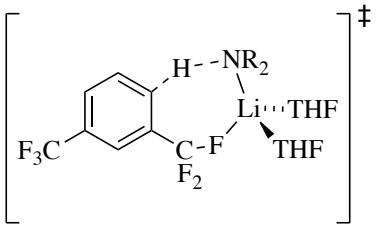


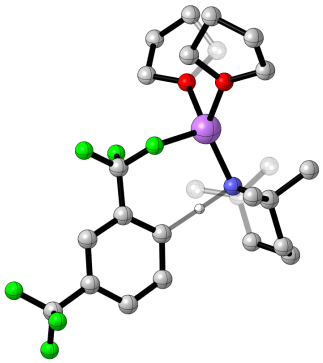


2-A_2S_4
G = –2667.337914
G_{MP2} = –1668467.049

Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	0.69713800	-1.30409400	0.25979700
C	0.04105700	-2.48219600	-0.11146300
C	0.66289100	-3.71149700	0.11412900
C	1.92769800	-3.74225400	0.71168100
C	2.55974900	-2.54531300	1.05485900
C	1.98468300	-1.27582900	0.83788600
H	3.55427700	-2.61857400	1.50207700
H	2.42024600	-4.69444800	0.88948000
C	-0.05901200	-4.97074600	-0.23677500
F	-0.74611300	-4.86637100	-1.40720000
F	-1.01021900	-5.30709900	0.70269900
F	0.74995200	-6.03854200	-0.34097600
H	-0.93918200	-2.45262500	-0.57579200
F	0.50948900	0.70112200	-1.03440300
F	-1.34016300	-0.15260400	-0.27817100
F	0.03750000	0.83242300	1.08207400
H	2.84316600	-0.18566100	1.12825200
C	-5.06674200	-1.64193700	4.78678200
H	-4.59557400	-0.65615000	4.75204600
H	-4.43789200	-2.31459600	5.38247200
C	-6.51082900	-1.62227100	5.28807200
H	-7.00631700	-0.68923600	4.99511400
H	-6.57579200	-1.71389700	6.37584900
C	-7.12496600	-2.81465400	4.53872000
H	-6.86318600	-3.75495800	5.03715200
H	-8.21457800	-2.76404600	4.46002200
C	-6.43695600	-2.72309600	3.17507400
H	-6.29816100	-3.69278900	2.68886500
H	-6.98345000	-2.06200800	2.48964700
O	-5.13304600	-2.15114200	3.43040700
Li	-3.67736200	-1.56436200	2.18042000
O	-2.09765900	-2.08184200	3.19050200
C	-1.03989200	-1.24389200	3.74290800
H	-1.48599500	-0.60926300	4.51954000
H	-0.64429300	-0.61467000	2.94486400
C	-0.00043500	-2.20785900	4.31609400
H	0.53493700	-1.77697900	5.16621400
H	0.73565800	-2.46780400	3.54909000
C	-0.85170200	-3.43130100	4.68807500
H	-0.26887800	-4.35380300	4.75965700
H	-1.36395100	-3.27376300	5.64534800
C	-1.85676700	-3.47212700	3.54005300
H	-1.44727000	-3.98847600	2.66680700
H	-2.82133700	-3.91627800	3.80618100
O	-4.10461600	-2.43129800	0.45439600
C	-4.12439600	-3.87295000	0.24599000
H	-5.02835800	-4.26793400	0.72535900
H	-3.24361700	-4.30880900	0.72141700
C	-4.14006000	-4.08336700	-1.27126900
H	-4.70139200	-4.97822300	-1.55486000
H	-3.11853700	-4.19448500	-1.64600800
C	-4.77595800	-2.78349800	-1.78720500
H	-4.52217100	-2.56480700	-2.82830900
H	-5.86847200	-2.82483800	-1.70208900
C	-4.20341300	-1.74858000	-0.82295000
H	-3.20633700	-1.41353500	-1.12569000
H	-4.84187200	-0.87177800	-0.68323000

C	-3.12889900	1.52106100	2.04457900
H	-2.11112600	1.14744700	1.95767000
H	-3.23219900	2.09912700	2.97428900
C	-3.60688100	2.30932100	0.82786400
H	-3.16402900	1.87876900	-0.07477400
H	-3.32122100	3.36352000	0.87675300
C	-5.14150300	2.09980700	0.85318800
H	-5.66144600	2.97812600	1.24695500
H	-5.53814400	1.90757600	-0.14773800
C	-5.34016400	0.88663200	1.79434900
H	-5.83430700	1.18142300	2.72996900
H	-5.90592400	0.06576900	1.34655900
O	-4.02226900	0.38527100	2.09645500
C	3.21145200	3.53971600	1.20024700
H	2.52167700	4.36746100	0.98304500
H	4.16289500	4.00661800	1.48800100
C	2.66477600	2.68279500	2.34401500
H	2.54894000	3.28397800	3.25781000
H	1.66363300	2.33239500	2.06397700
C	3.55578800	1.44699700	2.64608900
N	3.88191300	0.65208200	1.42690700
C	4.29164100	1.42176100	0.21489800
C	3.39466200	2.66467500	-0.04074700
H	3.81223300	3.25230100	-0.87075800
H	2.40606700	2.31627200	-0.36748200
C	5.77912700	1.86706300	0.25428400
H	6.43282000	1.01358400	0.47445100
H	6.08617800	2.27555900	-0.71814800
H	5.97815600	2.63475200	1.00593700
C	4.14523100	0.49850200	-1.01281400
H	4.76341600	-0.39928400	-0.91445400
H	4.46701700	1.02310900	-1.92126700
H	3.10885900	0.18296400	-1.15529100
Li	5.20361900	-0.87474500	1.84114800
N	6.20774600	-2.42742800	2.22986700
C	6.57112400	-2.79976300	3.60053000
C	8.10145500	-3.02306500	3.77651600
C	8.69090600	-3.94997800	2.71114600
H	9.78305400	-4.01100200	2.82162100
H	8.31637100	-4.97422600	2.84654400
C	8.32356100	-3.43069200	1.31921400
C	6.79077500	-3.23233500	1.15041400
C	6.12788600	-4.63138300	0.93566400
H	5.03855500	-4.52162400	0.88904200
H	6.46443900	-5.09263500	-0.00410600
H	6.35503900	-5.33826300	1.73786400
C	6.57081900	-2.46689100	-0.16911100
H	5.49849000	-2.37170000	-0.38513200
H	7.02973300	-2.98403400	-1.02217300
H	7.00815900	-1.46195900	-0.10885300
H	8.71205900	-4.10513300	0.54099100
H	8.81071500	-2.45549500	1.17138300
H	8.31964900	-3.40632300	4.78502000
H	8.59746400	-2.04485400	3.69300900
C	5.80622300	-4.04238800	4.15773300
H	4.73277200	-3.92363400	3.96793300
H	6.12169700	-4.97926500	3.69099200
H	5.95524000	-4.15604200	5.24182500
C	6.18674100	-1.62621800	4.52221300
H	5.10477800	-1.44150700	4.48709800
H	6.70604200	-0.71178300	4.21067400
H	6.44999900	-1.82603300	5.56952100
C	4.80812900	1.92616300	3.43030700
H	4.51718100	2.32585600	4.41175900
H	5.35899400	2.71507100	2.91269900
H	5.50280300	1.09802400	3.60420200
C	2.76262400	0.52583500	3.59751400
H	3.33968500	-0.36849800	3.86029100
H	1.83048000	0.19574500	3.13110200
H	2.51921400	1.05268100	4.52915500

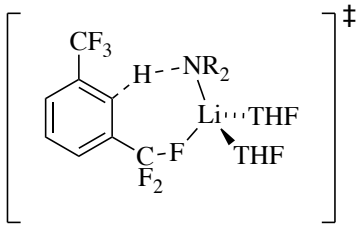


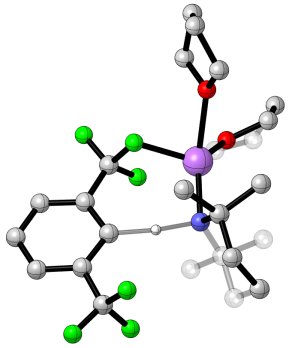


2-AS$_2$ (external)
G = –1786.784042
G_{MP2} = –1117830.948

Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	1.16963400	0.91262200	0.18214000
C	0.91832800	2.29930800	0.22772900
C	2.07774300	3.09102100	0.32734200
C	3.36761600	2.56142300	0.38064900
C	3.55475100	1.17550000	0.33678100
C	2.44477900	0.33887000	0.23440600
H	2.57991400	-0.73642700	0.18926500
C	4.93066400	0.59151700	0.45744400
F	5.30691200	0.42777400	1.75168200
F	5.87025700	1.38030500	-0.11580300
F	5.02138800	-0.62845100	-0.12445200
H	4.23309300	3.21573000	0.44954000
H	1.97950100	4.17661600	0.36226400
F	0.26476600	-1.30722900	0.18788900
F	-0.57562000	0.10554400	-1.22978900
F	-1.04081500	0.29159100	0.87998800
Li	-2.56878800	1.59534500	0.37815400
N	-1.64363500	3.40296700	0.31374400
C	-1.79263200	4.21078300	-0.93471700
C	-1.38871300	3.30715700	-2.11858700
H	-0.38354400	2.89892500	-1.98724400
H	-2.09039500	2.47126100	-2.22042100
H	-1.41037000	3.87569000	-3.05669300
C	-0.85409300	5.44576500	-0.93099900
C	-0.97878700	6.28666200	0.34428700
H	-0.23908100	7.09817600	0.33431800
H	-1.96109500	6.77685300	0.38195900
C	-0.77489500	5.40721300	1.58293500
C	-1.70066400	4.16185400	1.60027600
C	-3.13410200	4.60489700	1.99878000
H	-3.85102700	3.79219000	1.83553700
H	-3.16646200	4.87904600	3.06203000
H	-3.48949600	5.47190100	1.43722500
C	-1.19826200	3.21567800	2.71321100
H	-1.83615700	2.32793800	2.79991500
H	-1.20321400	3.72895000	3.68283100
H	-0.17977500	2.87300600	2.51360000
H	-0.92921900	5.99462700	2.49921900
H	0.26715300	5.06320100	1.60538900
H	-1.05247000	6.06440200	-1.81756700
H	0.18089000	5.09012400	-1.02179100
C	-3.24743700	4.66685300	-1.21743700
H	-3.93659700	3.82103400	-1.10940400
H	-3.59349900	5.46482000	-0.55713900
H	-3.33245400	5.04049600	-2.24670900
O	-3.73448200	0.70946100	1.90014900
C	-3.70944300	-0.73829800	1.95284400
H	-2.74388200	-1.06361800	2.35714100
H	-3.80459500	-1.10609200	0.92831500
C	-4.86370100	-1.13237600	2.87178600
H	-5.80911700	-1.15621100	2.31631100
H	-4.71414300	-2.11325900	3.33238900
C	-4.86125300	0.02280300	3.88358800
H	-5.81424200	0.14707800	4.40599400
H	-4.08007300	-0.13359200	4.63629000
C	-4.52039800	1.22821300	3.00263500
H	-5.42208900	1.69912100	2.59022600
H	-3.93485000	1.99172500	3.51912600
O	-3.75026000	0.72959400	-1.06897000
C	-3.42360200	-0.13585100	-2.18939300
H	-3.04881700	-1.08318400	-1.78634000
H	-2.62804300	0.33339000	-2.77118700
C	-4.72662200	-0.31930500	-2.97445900
H	-4.81821200	0.44866300	-3.75094200
H	-4.78230200	-1.29804800	-3.45964000
C	-5.79937100	-0.11192300	-1.89419400
H	-6.77477200	0.17286100	-2.29944600
H	-5.92864600	-1.02402900	-1.29909300
C	-5.17113200	0.99296400	-1.04832400

H	-5.35998300	1.98441500	-1.48067500	H	-0.43271200	2.89113000	0.25613600
H	-5.48870700	0.99543500	-0.00305700				



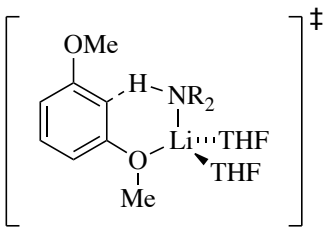


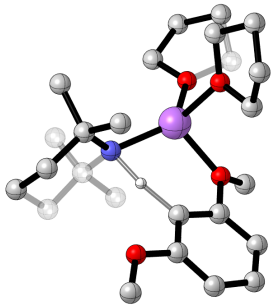
2-AS$_2$ (internal)
G = –1786.779685
G_{MP2} = –1117828.900

Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	H	-1.67800400	3.91892800	2.56276300
C	1.48855000	-0.02357800	0.11546500	H	-0.85836100	4.67546900	3.93325700
C	2.15079100	1.14893800	0.54228700	H	-0.97686500	5.52777700	2.39567200
C	3.55371600	0.99433400	0.61701800	C	0.74150700	2.66047500	3.32302900
C	4.22477200	-0.19256700	0.29663100	H	-0.03404700	1.90218700	3.16367400
C	3.51108100	-1.31132900	-0.12422600	H	0.71368600	2.95333800	4.38037400
C	2.12761500	-1.22749600	-0.21455000	H	1.70728900	2.18970700	3.12733100
H	1.54971000	-2.08849300	-0.53544000	H	1.51455200	5.30058800	3.75619100
H	4.02684900	-2.23391700	-0.37384800	H	2.61692000	4.37708900	2.73987100
H	5.30535900	-0.24223100	0.37756000	H	1.94276400	6.25724000	-0.42952700
C	4.40704300	2.15961400	1.04864600	H	2.85912600	4.93167600	0.27889100
F	4.35161800	3.19092000	0.16661700	C	-0.50310300	5.29029900	-0.39517000
F	4.03263400	2.65636700	2.25398000	H	-1.32933100	4.62368700	-0.66112200
F	5.71986000	1.83984900	1.16697400	H	-0.83678100	5.92839700	0.42732700
F	-0.56774800	-1.18808600	-0.28410600	H	-0.31122500	5.94643700	-1.25511400
F	-0.46718800	0.87593600	-0.94762400	O	-2.87419500	1.60839100	2.27761700
F	-0.61194500	0.43099000	1.16363700	C	-3.62352400	0.46116000	1.81192600
Li	-1.24601700	2.38451500	0.80250800	H	-2.92271000	-0.34932200	1.58138800
N	0.52600400	3.41928900	0.99740100	H	-4.13912900	0.74595600	0.89061100
C	0.76755100	4.46505300	-0.04925500	C	-4.56230700	0.08131500	2.95741000
C	1.19009200	3.75371500	-1.35139000	H	-5.48259100	0.67658200	2.91781200
H	2.12987700	3.21229600	-1.22231500	H	-4.84012900	-0.97664500	2.93537500
H	0.43123000	3.03453100	-1.67768000	C	-3.72538800	0.46868300	4.18535200
H	1.32953900	4.48655500	-2.15596600	H	-4.32220700	0.62610600	5.08863700
C	1.90109900	5.45818900	0.32430800	H	-2.98189200	-0.30780600	4.39959600
C	1.74218500	6.04864800	1.72551600	C	-3.03742800	1.74999000	3.70994600
H	2.59506300	6.69943700	1.96036600	H	-3.65634800	2.63610400	3.90427400
H	0.85017300	6.68782700	1.78097400	H	-2.05376300	1.90921800	4.15671800
C	1.66036000	4.90752200	2.73965000	O	-2.82445500	2.72323300	-0.45612200
C	0.52957000	3.89334600	2.41793500	C	-2.88923300	2.46444800	-1.88352300
C	-0.82054800	4.54315500	2.84323900	H	-3.06088000	1.39142100	-2.02386700

H	-1.92658400	2.72844500	-2.32808200
C	-4.05338000	3.30878100	-2.41217900
H	-3.69735300	4.29669900	-2.72538200
H	-4.54883600	2.84065800	-3.26771000
C	-4.95884000	3.43854100	-1.17741400
H	-5.63497200	4.29728300	-1.22409300
H	-5.56387100	2.53333900	-1.04535600
C	-3.93148000	3.56517100	-0.05481900
H	-3.57431400	4.59847200	0.04532400
H	-4.27153000	3.21188400	0.92043600
H	1.39714300	2.35829100	0.81646300

Table 5. Optimized geometries at the B3LYP level of theory with 6-31G(d) basis set for relevant transition states of LiTMP/THF-mediated ortholithiation of **3** at –40 °C with free energies (Hartrees), corrected MP2 energies (kcal), and cartesian coordinates (X, Y, Z). (Note: G_{MP2} includes single-point MP2 corrections to B3LYP/6-31G(d) optimized structures.)

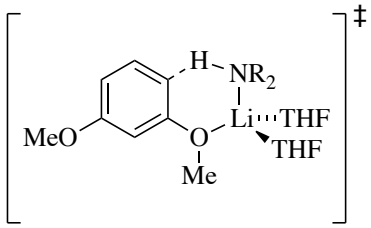


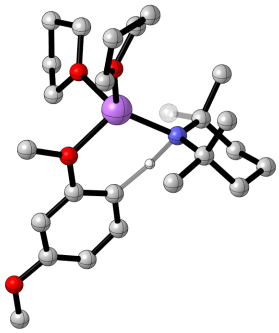


3-AS$_2$ (internal)
G = –1341.698652
G_{MP2} = –839100.800

Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	H	-0.65924100	5.84721000	1.13626100
H	0.33073000	-1.04645100	-0.04128400	H	-0.79078600	5.95810000	2.88760300
H	0.86927900	0.65417500	-0.08991200	C	-1.45528400	3.43665200	0.62601600
H	-0.68697800	0.18971400	-0.83256600	H	-0.42724800	3.07802600	0.48318300
O	-0.61668600	0.31135400	1.24268700	H	-1.66258300	4.16853600	-0.16463300
C	-1.96867300	-0.08412300	1.41021900	H	-2.13349300	2.58998900	0.49687500
C	-2.44560600	-1.24386100	0.78234000	H	-3.18405100	5.47446800	1.35457600
C	-3.77675500	-1.59146000	1.00225900	H	-3.77305500	3.87491100	1.82400200
C	-4.59141000	-0.81161700	1.82703800	H	-3.38008400	4.41803400	5.53694300
C	-4.04571400	0.33273200	2.43066700	H	-3.93726700	3.26695200	4.31758900
C	-2.71637100	0.73837800	2.24165500	C	-0.74593400	4.30576400	5.14883200
O	-4.79383600	1.15220300	3.25899500	H	0.26299600	3.89352800	5.01830900
C	-6.15370800	0.83568400	3.47600600	H	-0.73589500	5.33082400	4.77128800
H	-6.73019000	0.83914300	2.53992000	H	-0.95296700	4.36124300	6.22650000
H	-6.27652000	-0.14360800	3.96107000	C	-1.85932300	2.09641800	5.26804000
H	-6.54455700	1.61207000	4.13819100	H	-0.88639600	1.59511000	5.28844200
H	-5.62468500	-1.10518500	1.97991500	H	-2.59589500	1.40474100	4.85255500
H	-4.18687100	-2.48130300	0.53052200	H	-2.14511800	2.32089200	6.30351000
H	-1.81684000	-1.86415800	0.15030800	O	0.74766700	0.17614000	4.04653900
Li	0.06175100	1.62370000	2.67438000	C	1.61683800	0.35913500	5.18478300
N	-1.40288100	3.03777600	3.04736200	H	1.22661200	1.17801100	5.80232300
C	-1.78770200	3.39851800	4.44268100	H	2.60889500	0.64247200	4.81869000
C	-3.19730400	4.05120000	4.51622000	C	1.60171400	-0.97106200	5.94147500
C	-3.40693300	5.17477700	3.49846700	H	1.81128100	-0.84526900	7.00790600
H	-4.44973600	5.51918400	3.53175000	H	2.34923700	-1.65810100	5.52658300
H	-2.79350400	6.05024700	3.75296000	C	0.18235000	-1.48289000	5.65251000
C	-3.06443400	4.66945100	2.09441000	H	0.07908300	-2.56512800	5.77527000
C	-1.62738200	4.08972900	2.01388000	H	-0.54182500	-0.99411000	6.31374600
C	-0.61050800	5.26265200	2.06522600	C	-0.03435900	-1.03971900	4.20526200
H	0.40893400	4.88108400	2.17327400	H	0.34021900	-1.78357000	3.49110800

H	-1.07175700	-0.80679300	3.95909600
O	2.01169800	1.99862000	1.97772000
C	2.98942500	0.94830900	1.83463100
H	3.02196300	0.61460200	0.78726000
H	2.66341300	0.11582200	2.46009100
C	4.31659600	1.58182700	2.24287500
H	4.40828700	1.61031700	3.33531900
H	5.18176600	1.04572800	1.84117400
C	4.16360500	3.00144000	1.67438200
H	4.79653000	3.73952400	2.17537900
H	4.41814900	3.01037800	0.60840400
C	2.66731300	3.28882000	1.87534800
H	2.47084900	3.83589000	2.80312500
H	2.22416400	3.84588100	1.04493500
H	-2.12703400	1.97342000	2.70137000



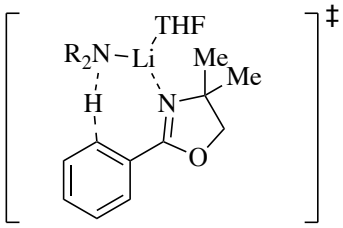


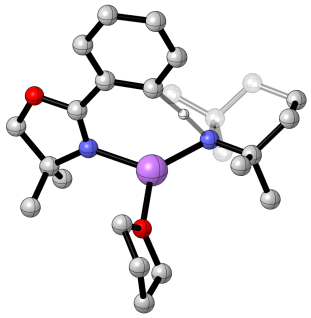
3-AS$_2$ (external)
G = –1341.69689
G_{MP2} = –839098.202

Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
H	-0.63351300	-0.71210700	0.54438100
H	1.00373400	-0.41795300	-0.09956400
H	-0.42977300	0.16596100	-0.99614900
O	0.13857800	1.21788000	0.71275200
C	-1.03829400	1.91611300	1.08300100
C	-2.29290200	1.46223200	0.68268000
C	-3.42325400	2.18825000	1.09316500
C	-3.27126500	3.32805800	1.88108600
C	-1.97190400	3.72884800	2.24342600
C	-0.80752500	3.05156800	1.86902300
H	-1.88665200	4.63105800	2.85393100
H	-4.13123800	3.90310900	2.20931100
O	-4.62631900	1.67956500	0.66013000
C	-5.80260000	2.37153900	1.03031000
H	-5.80894400	3.40061100	0.64475800
H	-6.63307700	1.81676300	0.58701200
H	-5.93149100	2.40317400	2.12139100
H	-2.45562100	0.58422600	0.06676800
Li	1.81374000	1.85259600	1.72337300
N	1.80639400	3.88619300	2.19074600
C	2.07693700	4.34930800	3.57988000
C	1.57936900	5.79930700	3.82858300
C	2.04402600	6.78577700	2.75592400
H	1.60909300	7.77738500	2.94012800
H	3.13358000	6.92023700	2.80109600
C	1.62289300	6.27195000	1.37828600
C	2.13500900	4.83506700	1.08808100
C	3.64957500	4.88578700	0.75732100
H	4.03298600	3.86915100	0.62088000
H	3.82077200	5.44350200	-0.17365100
H	4.24801100	5.36709000	1.53437400
C	1.42580400	4.34743700	-0.19354700
H	1.74742500	3.33556000	-0.46720000
H	1.66478000	5.01221100	-1.03292500
H	0.34107000	4.32554200	-0.06742500
H	1.96660600	6.95418800	0.58765700
H	0.52494200	6.25965400	1.33146200
H	1.89579900	6.13327000	4.82716300
H	0.47997600	5.78667700	3.83418400
C	3.57101300	4.24067000	3.98277900
H	3.95226300	3.24058300	3.74198800
H	4.21092200	4.97009100	3.48098200
H	3.69033400	4.39545700	5.06392800
C	1.30212300	3.43051200	4.54766800
H	1.66405700	2.39939100	4.47662400
H	0.23216100	3.42876800	4.32366200
H	1.44128100	3.76718500	5.58262000
O	1.70379100	0.29760900	3.12480800
C	2.72948700	-0.28680600	3.95640300

H	3.26517100	0.52238500	4.46957400
H	3.43582100	-0.82337500	3.31500200
C	2.00656500	-1.20224100	4.95094300
H	2.53666300	-1.27845500	5.90500600
H	1.90522100	-2.21306500	4.53839300
C	0.62945800	-0.53105900	5.06730100
H	-0.15465100	-1.21046300	5.41449500
H	0.67341600	0.32121900	5.75460500
C	0.39056600	-0.04914800	3.63821900
H	-0.03083800	-0.84666000	3.01244200
H	-0.24297300	0.83591600	3.55787100
O	3.45490400	1.12998100	0.60915500
C	4.76389800	1.11030800	1.22695200
H	4.89788200	0.14499100	1.73214100
H	4.79953600	1.90996400	1.97177800
C	5.77025600	1.28823400	0.08896100
H	5.93526300	2.35257900	-0.11208500
H	6.73752000	0.82892700	0.31342200
C	5.03876600	0.62741200	-1.08883500
H	5.39724900	0.96383300	-2.06608800
H	5.14458100	-0.46306600	-1.04372300
C	3.58855000	1.03838500	-0.82947400
H	3.36202100	2.01757700	-1.26693100
H	2.85727100	0.31364000	-1.19774300
H	0.56424700	3.57328900	2.09373200

Table 6. Optimized geometries at the B3LYP level of theory with 6-31G(d) basis set for relevant transition states of LiTMP/THF-mediated ortholithiation of **4** at –40 °C with free energies (Hartrees), corrected MP2 energies (kcal), and cartesian coordinates (X, Y, Z). (Note: G_{MP2} includes single-point MP2 corrections to B3LYP/6-31G(d) optimized structures.)

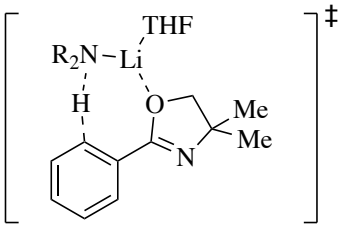


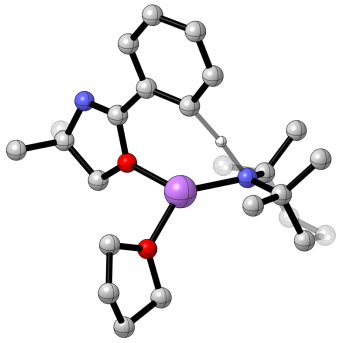


4-AS (N-bound)
G = –1204.987027
G_{MP2} = –753581.678

Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	-1.28983200	0.79866200	-0.33135500
C	-2.36802300	-0.04880000	-1.00974900
C	-1.78538700	-0.72464300	-2.25307600
C	-0.50582800	-1.54672500	-1.94308500
C	-0.91254600	-2.87205300	-1.24080600
H	-1.44440300	-3.53144900	-1.94031100
H	-0.02026600	-3.39866400	-0.88344500
H	-1.57028500	-2.72224700	-0.38193700
C	0.12233600	-1.95809400	-3.29251300
H	0.98914100	-2.61160400	-3.13948400
H	-0.60759600	-2.51258100	-3.89497400
H	0.45077100	-1.09251700	-3.87227500
N	0.49966700	-0.76378100	-1.17572900
Li	2.41167100	-1.36149100	-1.32399100
O	3.16402800	-3.09318200	-2.02727200
C	2.82236200	-4.47018700	-1.74235300
H	1.74643500	-4.60510100	-1.90375100
H	3.04731200	-4.66581200	-0.68959100
C	3.65002100	-5.31058300	-2.71674800
H	4.64504700	-5.51215100	-2.30292600
H	3.17560100	-6.26971100	-2.94380400
C	3.75235700	-4.37833200	-3.93448300
H	4.59397300	-4.61489500	-4.59195800
H	2.83218500	-4.42272600	-4.52800600
C	3.89805600	-3.00555700	-3.27647000
H	4.94368100	-2.77139800	-3.04645800
H	3.47357700	-2.18549200	-3.86234600
N	4.06993700	-0.29927000	-0.84156100
C	5.21179100	-0.49197200	0.08202500
C	5.96682000	0.86021100	-0.03725500
O	5.38353800	1.49795900	-1.18941200
C	4.26271900	0.79026800	-1.50804000
C	3.41748500	1.34233400	-2.57877900
C	2.10993000	0.83042600	-2.79153600
C	1.40093000	1.44422800	-3.83961300
C	1.92775300	2.46405800	-4.63607000
C	3.22101000	2.93574300	-4.39742100
C	3.96369600	2.38007100	-3.36204900
H	4.96685400	2.74198700	-3.15797500
H	3.64240800	3.73193400	-5.00583500
H	1.33132100	2.89893100	-5.43654500
H	0.37737100	1.12318500	-4.03904100
H	7.04116400	0.75392000	-0.21127100
H	5.80596200	1.51157600	0.82978000
C	6.07497900	-1.66390400	-0.41588400
H	6.92246400	-1.83704200	0.25864000
H	5.47782900	-2.57954800	-0.46718500
H	6.46997800	-1.45469200	-1.41650200
C	4.72284900	-0.75587200	1.51089300
H	4.14089200	-1.68315300	1.55551900
H	5.57167800	-0.85693600	2.19833900
H	4.08729400	0.06158600	1.86526000
H	-2.53570300	-1.37090800	-2.73056500
H	-1.52883700	0.05431300	-2.98534900
H	-2.76052800	-0.80173000	-0.31317200
H	-3.22418700	0.58040100	-1.28783900
H	-1.68327300	1.26289900	0.58396000
H	-1.01602300	1.61962400	-1.00933200
C	-0.23815900	-0.89105100	1.24831600

H	0.63784300	-1.52642600	1.42685700
H	-0.39363800	-0.26951700	2.14038200
H	-1.10882800	-1.54435900	1.15774300
C	1.07628100	1.02632300	0.40954900
H	0.72992700	1.61082000	1.27071900
H	2.00831100	0.52687300	0.69439400
H	1.30089300	1.72127300	-0.40404800
H	1.23767500	0.02455200	-1.96604100





4-AS (N-bound)
G = –1204.980404
G_{MP2} = –753577.231

Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	-1.11082700	-1.02996100	-0.33894500
C	-1.51290200	-1.88041200	0.86994100
C	-0.27520900	-2.53942600	1.48558600
C	0.83934500	-1.51932300	1.84449700
C	0.45206900	-0.74685200	3.13379300
H	1.17778100	0.05328000	3.32307200
H	-0.53979000	-0.29237900	3.08811600
H	0.45671500	-1.42250700	3.99941900
C	2.10733200	-2.32389200	2.19905600
H	2.91376400	-1.65886600	2.53089100
H	1.89345900	-3.01997200	3.01890500
H	2.47145800	-2.90438300	1.34738600
N	1.15251900	-0.63238200	0.69441100
Li	2.90225700	0.22244800	0.36523700
O	3.49779400	2.06661000	-0.02567700
C	4.34213700	2.28168900	-1.18730700
H	3.81609000	1.89951600	-2.07048500
H	5.26140000	1.70635900	-1.04970300
C	4.55945900	3.79401300	-1.26445400
H	5.42287800	4.09107000	-0.65768800
H	4.73132200	4.13548100	-2.28914900
C	3.25969800	4.33949000	-0.65162300
H	3.35317100	5.36198200	-0.27455800
H	2.45009300	4.31939600	-1.39009500
C	2.98616300	3.33024600	0.46313200
H	3.52045700	3.59062200	1.38603300
H	1.92575300	3.20030300	0.69263500
O	4.62822700	-0.55645600	0.82371000
C	5.55568300	-0.27613600	1.89639500
C	6.80238600	-1.13969600	1.54819700
N	6.30812200	-2.03904700	0.49083200
C	5.14622100	-1.65710200	0.13108000
C	4.30257000	-2.20705900	-0.94175600
C	2.93057700	-1.86466500	-1.06601800
C	2.26184400	-2.49476800	-2.13388700
C	2.88016800	-3.37733700	-3.02046500
C	4.23646800	-3.68136000	-2.86692000
C	4.94596700	-3.09773000	-1.82628700
H	5.99944400	-3.31778100	-1.67982700
H	4.73187900	-4.36686900	-3.54989500
H	2.30933200	-3.83397900	-3.82722800
H	1.19764100	-2.30129500	-2.27352100
C	7.94652000	-0.28648600	0.97442300
H	8.35890700	0.38396500	1.73870200
H	8.75031900	-0.93216300	0.60778200
H	7.59389600	0.32194200	0.13328500
C	7.28813000	-1.95916600	2.74966300
H	8.12141800	-2.60426600	2.45421200
H	7.62934500	-1.30411000	3.56090500
H	6.48522800	-2.59769800	3.13243500
H	5.74604500	0.80018600	1.90809600
H	5.08563300	-0.57483500	2.84008900
H	-0.55301500	-3.11877600	2.37742900
H	0.13807100	-3.25416100	0.75979700
H	-2.02861000	-1.26239400	1.61741700
H	-2.23586600	-2.64845800	0.56440300
H	-1.98703400	-0.51228000	-0.75458700

H	-0.73590900	-1.69853200	-1.12669500
C	-0.62542000	1.18162200	0.79266400
H	-1.26875000	1.78499000	0.13816500
H	-1.24016200	0.86088800	1.63586400
H	0.16464800	1.82953000	1.18981100
C	0.51066700	0.60721500	-1.32610500
H	-0.32351100	1.04250200	-1.88941300
H	1.23300700	1.41333900	-1.14008700
H	0.99340400	-0.13877600	-1.96159300
H	1.97086100	-1.27181700	-0.16422700

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2. GaussView, Version 5.0, Roy Dennington, Todd Keith, and John Millam, *Semichem Inc*., Shawnee Mission, KS, 2009.