MECHANISTIC STUDIES OF LITHIUM DIISOPROPYLAMIDE-MEDIATED ORTHOLITHIATIONS UNDER NONEQUILIBRIUM CONDITIONS

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Cornell University

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Jun Liang

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Lithium diisopropylamide (LDA) plays an integral role in organic synthesis. In a comprehensive survey of over 500 total syntheses conducted by Reich, LDA emerged as the most commonly used reagent attesting to its broad range of synthetic applications. Its widespread utility led Collum to investigate mechanisms of LDA-mediated lithiation; a survey of these studies was assembled into a review that paints a coherent picture of generalized LDA-mediated reactions conducted at or above –40 °C. Fast LDA aggregate exchange inherent at high temperatures precludes detailed mechanistic understanding of aggregation dynamics by rendering substrate lithiation rate-limiting. By lowering the temperature to –78 °C, the rate of aggregate exchange can become comparable to the rate of metalation in THF. Time dependent decays exhibit linear and sigmoidal curvatures under pseudo-first order conditions, foreshadowing mechanistic complexity. Under this non-limiting regime, aggregates are no longer in full equilibrium, causing the reaction to become sensitive to autocatalysis, exogenous salts, and trace impurities. Subtle changes to reaction conditions, including isotopic substitution, can shift the rate-limiting step unpredictably.

The work described herein presents two experimental accounts for elucidating mechanisms of lithiation: ortholithiation of 1,4-difluorobenzene and ortholithiation of 1,4-bis(trifluoromethyl)benzene. Given the highly substrate-dependent mechanisms, both substrates present different views of LDA deaggregation with internal consistency.

The third experimental account presents a fruitful collaboration with Zakarian aimed at understanding the underlying chemical basis for enantioselective alkylations of the enediolate of phenylacetic acid in the presence of a lithiated C_2-symmetric tetraamine ligand. The high facial selectivity was traced to the formation of a densely functionalized mixed aggregate.

BIOGRAPHICAL SKETCH

The author was born on October 30, 1987 in Fuzhou, China. At the age of eight, he immigrated to the United States and took up residence in Long Island, New York. After completing his secondary education at Central Islip Senior High School, he attended the State University of New York at Stony Brook where he developed an interest in chemical research. Under the guidance of Dr. Joseph W. Lauher and Dr. Frank W. Fowler, he investigated the synthesis and controlled polymerization of functionalized diacetylenes using host-guest macromolecular assembly. The author received a B.S. (in chemistry) summa cum laude with department honors in 2009. That year, he began graduate studies at Cornell University where he joined the research group of Dr. David B. Collum. His graduate research focused on elucidating the mechanisms of LDA-mediated ortholithiations under nonequilibrium conditions and the role of various LDA aggregates. He received a M.S. in 2011 and a Ph.D. in August 2014.

This work is dedicated to my parents,

Jing Guang Liang and Yan Lin

ACKNOWLEDGEMENTS

I would like to begin by thanking Dr. David B. Collum for providing me with a wonderful opportunity to carry out graduate research in his laboratory. He has been tremendously supportive while providing insightful guidance throughout my graduate career. He was always open for discussions on recent findings out of which new directions and experimental protocols grew. I am especially grateful for his hands-off approach that allowed me to explore ideas independently. I would also like to express my gratitude to Dr. William R. Dichtel and Dr. Hening Lin for serving on my special committee.

I would like to thank Dr. Alexander C. Hopker, who introduced me to the world of chemical kinetics. He is a very skilled experimentalist with extensive knowledge of nonequilibrium kinetics. I would also like to thank Dr. Yun Ma for bringing a lively, human element to the laboratory and her efforts in making the Zakarian collaboration a success. I am indebted to all the Collum group members who made my time at Cornell so enjoyable.

The faculty, staff, and administrative members of the department of Chemistry and Chemical Biology have been very supportive. I would like to thank Dr. Ivan Keresztes who has contributed immensely to the success of my nuclear magnetic resonance spectroscopy experiments. I owe Chemistry IT a big thank you for keeping Collum group clusters in operation. I would also like to acknowledge Pat Hine for her efforts in making administrative-related tasks a breeze.

I would like to express my deepest gratitude to my family. Both of my parents have been very supportive and without their encouragement, I would not have been

able to make it this far. I am very grateful to have a great sister who has made my life joyful and colorful.

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CHAPTER 1

LITHIUM DIISOPROPYLAMIDE-MEDIATED LITHIATION OF 1,4-DIFLUOROBENZENE UNDER NONEQUILIBRIUM CONDITIONS: ROLE OF MONOMER-, DIMER-, AND TETRAMER-BASED INTERMEDIATES AND LESSONS ABOUT RATE LIMITATION

Lithium Diisopropylamide-Mediated Lithiation of 1,4-Difluorobenzene Under Nonequilibrium Conditions: Role of Monomer-, Dimer-, and Tetramer-Based Intermediates and Lessons About Rate Limitation

Abstract

Lithiation of 1,4-difluorobenzene with lithium diisopropylamide (LDA) in THF at –78 °C joins the ranks of a growing number of metalations that occur under conditions in which the rates of aggregate exchanges are comparable to the rates of metalation. As such, a substantial number of barriers vie for rate limitation. Rate studies reveal that rate-limiting steps and even the choice of reaction coordinate depend on subtle variations in concentration. Deuteration shifts the rate-limiting step and markedly alters the concentration dependencies and overall rate law. This narrative is less about ortholithiation per se and more about rate limitation and the dynamics of LDA aggregate exchange.

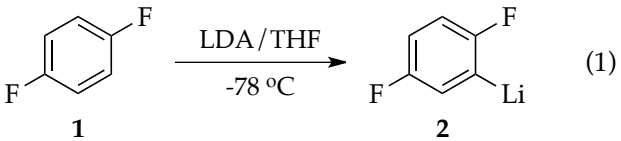
Introduction

A survey of more than 500 total syntheses shows that lithium diisopropyl-amide (LDA) is *the* most frequently used reagent in organic synthesis.[1,2] It is this prominence that piqued our interest in structural and mechanistic studies of LDA—studies that have now spanned more than 25 years.[3] For several practical reasons, we focused mechanistic studies on reactions that could be monitored at temperatures ranging from to –55 °C to 25 °C. Despite a large number of mechanistic variations arising from dozens

of substrate–solvent combinations, the aggregate equilibrations were rapid on the time scales of the rate-limiting substrate lithiation.

The opposite limiting behavior has been the focus of Reich and coworkers using rapid-injection NMR spectroscopy. LDA-mediated enolizations of reactive ketones that are observable on short time scales below –135 °C [4] are rapid on the time scales of aggregate exchanges.[5]

There is necessarily a window of substrate reactivity—a critical temperature range—in which readily observed lithiations and LDA aggregate exchanges occur at comparable rates. In this regime the chemistry would certainly become complex. In an irony that will be lost on few organic chemists, this twilight zone for LDA/tetrahydrofuran (THF)-mediated lithiations is centered at –78 °C:[6,7] *any LDA/THF-mediated lithiation that proceeds at observable rates at –78 °C is occurring under non-limiting conditions in which aggregation events and reactions with substrate vie to be rate limiting.* Under such non-limiting conditions, the rules governing reactivity change markedly: aggregates are no longer in full equilibrium; the rate-limiting step shifts unpredictably with subtle changes in reaction conditions; catalysis by traces of extraneous lithium salts (especially lithium chloride) and autocatalysis by the developing product become acute; and substituting deuterium for protium can change the rate, mechanism, and rate law. In short, LDA/THF-mediated lithiations observed at –78 °C are complex even by the standards of organolithium chemistry.

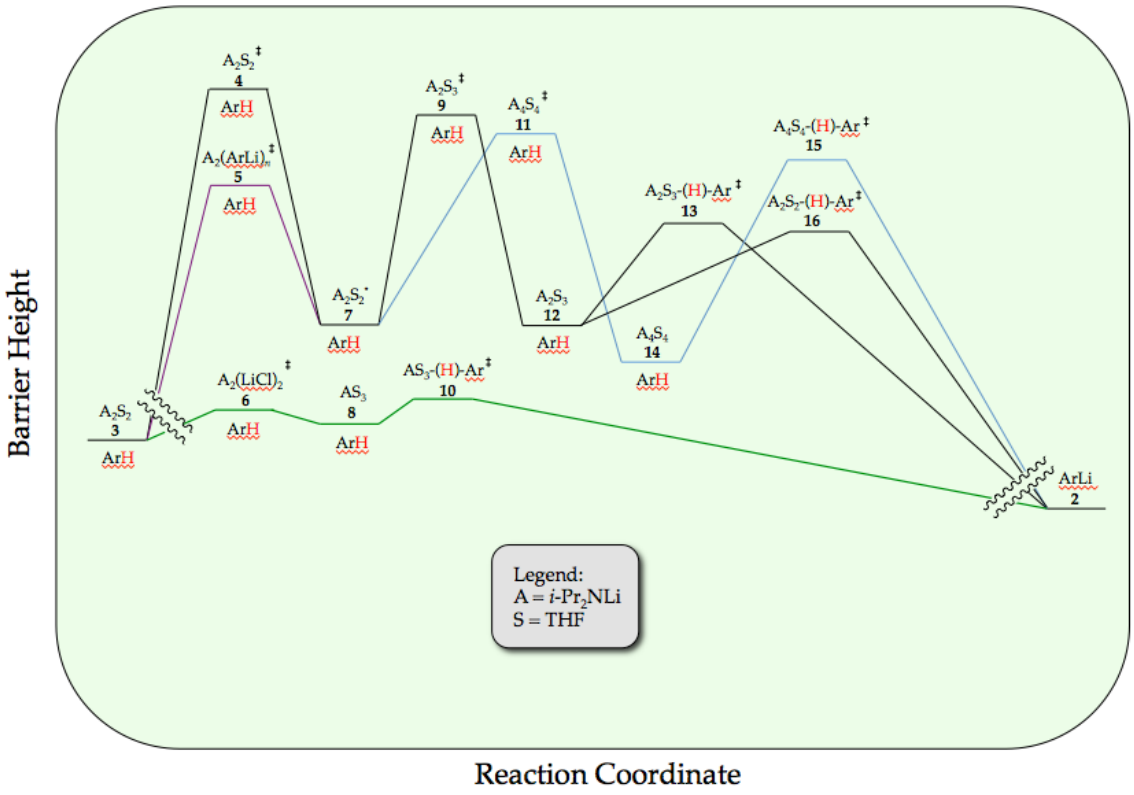


1 **2** (1)

We describe herein mechanistic studies of the LDA/THF-mediated lithiation of 1,4-difluorobenzene (**1**) (eq 1).[8] Spoiler alert: here is what we find. Lithiation of arene **1** by dimeric LDA occurs through the cascading deaggregation illustrated by the reaction coordinate diagram in Scheme 1. Note that Scheme 1 connotes qualitative relative barrier heights but lacks the implicit balancing to be called a free energy diagram. It is also a living, breathing diagram that changes consequentially with concentrations and, as we describe, isotopic substitution. In the absence of catalysis, rate-limiting deaggregation occurs via disolvated dimer transition state **4**. Autocatalysis[9,10] by the resulting aryllithium via mixed-aggregate-based transition structure **5** circumvents **4**, revealing LDA-tetramer-based transition state **11** lurking over the thermochemical horizon.[11] Perdeuteration of **1**, by virtue of the often large and highly variable isotope effects for LDA-mediated ortholithiations,[11] drops the zero-point energy (ZPE) of the barrier corresponding to **4** to reveal two competing dimer-based proton transfers (**13** and **16**) as the highest remaining barriers. Lithium chloride—the most efficient deaggregation catalyst reported to date—circumvents barriers corresponding to the aforementioned transition states altogether via a mixed-aggregate-based transition state **6** delineated previously,[6] affording trisolvated-monomer-based transition structure **10** for proton transfer.

These conclusions emanate from a series of spectroscopic, kinetic, and computational studies of the reaction cascade involved in the lithiation of **1** and its perdeuterated analog. The mechanistic changes accompanying subtle changes in conditions are legion, but we have not peered beyond rate-limiting steps with such clarity as described below. The discussion is written for the non-specialist wishing to skip the detailed results section.

Scheme 1



Results

To simplify the results and discussion, we introduce the following shorthand used in Scheme 1: A = an LDA subunit, S = THF, ArH = arene **1**, ArD = tetradeuterated arene **1-*d*$_4$**, and ArLi refers to aryllithiums **2** or **2-*d*$_3$**. By example, A_2S_2 corresponds to disolvated LDA dimer **3**. We will denote general structures and their more specific counterparts (ArLi **2** and **2a**, for example) interchangeably depending on the context. ArH and ArD are mechanistically so different that they demanded fully independent rate studies; they are presented in separate sections within the following subsections: uncatalyzed, autocatalyzed, and LiCl-catalyzed lithiations. The key to understanding the results is that changes in conditions—essentially *any* changes—shift the rate-limiting

steps and consequentially alter the mathematical form of the accompanying rate law. We begin with some foundational structural studies.

Reaction profile. Metalation of relatively high concentrations of ArH by LDA specifically at low THF concentrations promotes mixed aggregation. ^{19}F NMR spectroscopy shows the time dependence of a number of species: a downwardly curving decay of ArH, a nearly linear formation of ArLi, and sigmoidal growth of an LDA-ArLi mixed aggregate (Figure 1.1). The mixed aggregate is much less relevant than one might think, and the other decays are much more complex than most could imagine. The curves represent a best-fit numerical integration to a model described herein. We begin with the relatively simple task of characterizing the observable species.

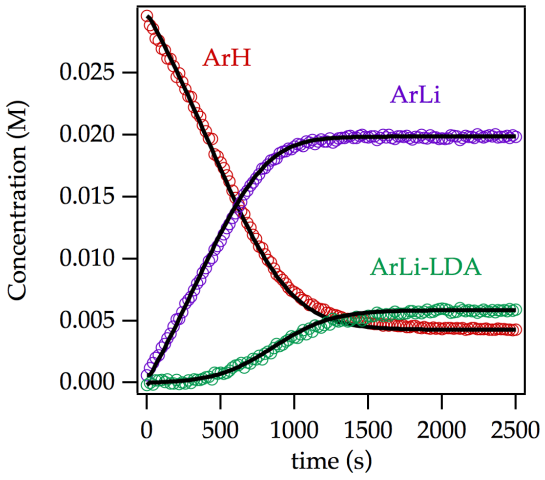
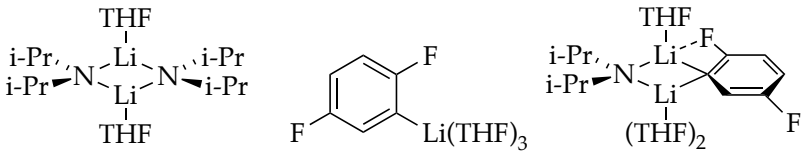


Figure 1.1. Time-dependent concentrations measured by ^{19}F NMR spectroscopy using 0.10 M LDA and 0.030 M ArH in 3.05 M THF/hexane at –65 °C. The curve represents a best fit numerical integration to the emergent model (*vide infra*).

Solution structures. Previous studies of [^{6}Li,^{15}N]LDA using ^{6}Li and ^{15}N NMR spectroscopies have revealed exclusively disolvated dimer **3**.[12] Aryllithium **2** is shown

to be trisolvated monomer **2a**. Trisolvated mixed dimer **17** is observed at low levels and only at high LDA *and* low THF concentrations.



3 **2a** **17**

^{19}F NMR spectroscopy of a sample prepared from 2:1 LDA:ArH in 3.5 M THF reveals a pair of doublets owing to five-bond ^{19}F–^{19}F coupling with additional ^{1}H–^{19}F coupling discernible using window functions,[6] consistent with **2a** (Figure 1.2). The ^{19}F–^{19}F coupling was confirmed with single-frequency ^{19}F decoupling.[13] A ^{13}C NMR spectrum shows the carbanionic carbon resonance of **2a** as a triplet ($J_{Li–C}$ = 6.0) further split by a large (130 Hz) two-bond ^{19}F–^{13}C coupling and a small (18.6 Hz) three-bond ^{19}F–^{13}C coupling (Figure 1.3).[14] The large two-bond coupling has been noted previously for ortholithiated fluoroarenes.[15]

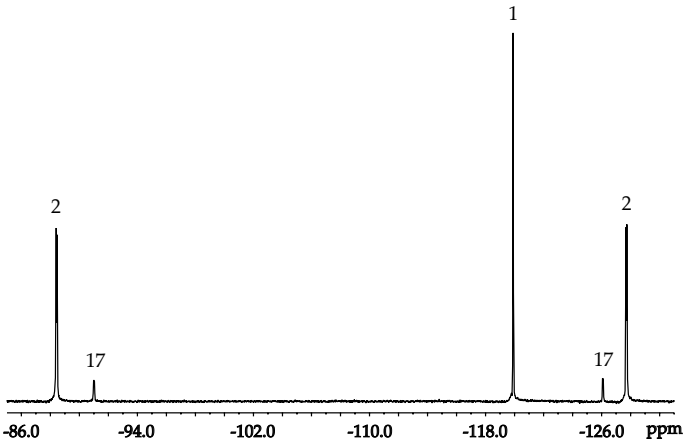


Figure 1.2. ^{19}F NMR spectrum of LDA (0.10 M) with ArH (0.050 M) and diisopropylamine (0.050 M) in 3.5 M THF/hexane at –78 °C. **1:** δ –119.90 (s). **2:** δ –127.71 (d, $^{5}J_{F–F}$ = 31.6 Hz), –88.43 (d, $^{5}J_{F–F}$ = 31.6 Hz). **17:** δ –126.09 (d, $^{5}J_{F–F}$ = 31.0 Hz), –91.01 (d, $^{5}J_{F–F}$ = 31.0 Hz). Excess amine was added to establish the balanced equilibrium.

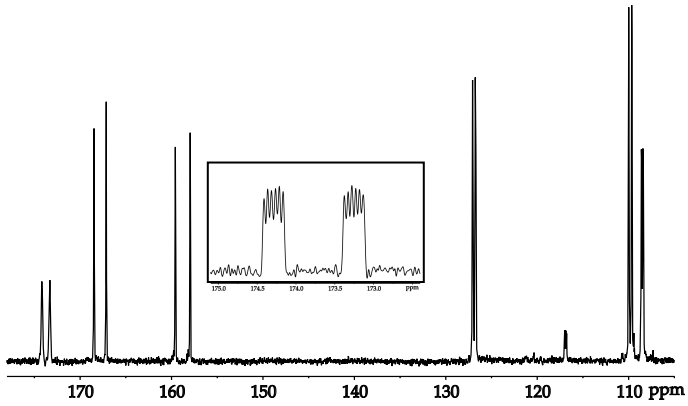
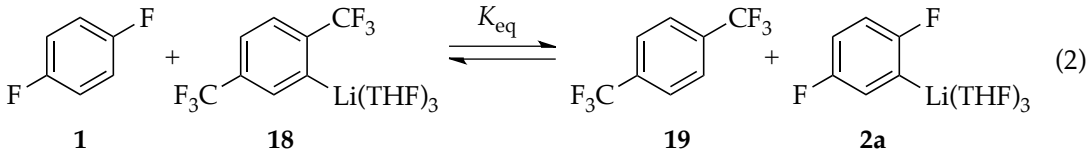


Figure 1.3. ^{13}C{^{1}H} NMR spectrum of ArLi generated from ArH (0.30 M) with [^{6}Li]LDA (0.40 M) in 12.2 M THF-d_8 at –105 °C: δ 173.75 (ddt, $^{2}J_{C-F}$ = 130.2 Hz, $^{3}J_{C-F}$ = 18.6 Hz, $^{1}J_{C-Li}$ = 6.0 Hz), 167.81 (d, $^{1}J_{C-F}$ = 201.7 Hz), 158.77 (d, $^{1}J_{C-F}$ = 244.7 Hz), 126.90 (dd, $^{2}J_{C-F}$ = 44.8 Hz, $^{3}J_{C-F}$ = 8.8 Hz), 109.82 (dd, $^{2}J_{C-F}$ = 49.3 Hz, $^{3}J_{C-F}$ = 3.7 Hz), 108.50 (dd, $^{2}J_{C-F}$ = 25.5 Hz, $^{3}J_{C-F}$ = 7.2 Hz).

We determined the solvation number of **2a** using three independent methods:

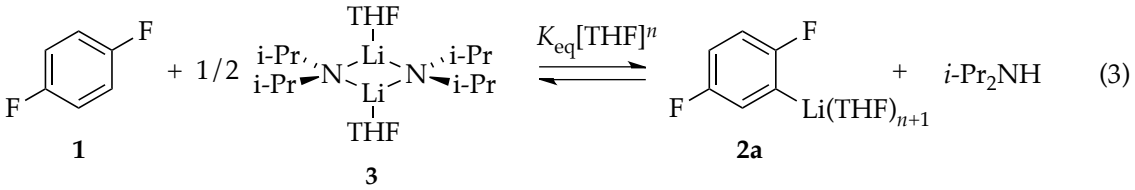
(1) We relied on the recently completed assignment of bis-trifluoromethylated aryllithium **18** as a trisolvated monomer.[16] Monitoring the equilibrium in eq 2 versus

THF concentration shows no dependence (±10%) over a tenfold THF concentration range, confirming **2a** as a trisolvate.



1 **18** **19** **2a** (2)

(2) Lithiation using excess *i*-Pr_2NH and variable THF concentrations (eq 3), conditions in which ArLi and ArH coexist at equilibrium, establishes the solvation number according to eq 4 (Figure 1.4). Monitoring the concentrations of ArH and ArLi with ^{19}F NMR spectroscopy and back calculating the concentrations of *i*–Pr_2NH and LDA affords the solvation number of 3.6 ± 0.2.



1 **3** **2a** (3)

$$y = [\mathrm{ArLiS}_{n+1}][i\text{-}\mathrm{Pr}_2\mathrm{NH}]/\{[\mathrm{ArH}][\mathrm{A}_2\mathrm{S}_2]^{1/2}\} = K_{eq}[\mathrm{S}]^n \quad (4)$$

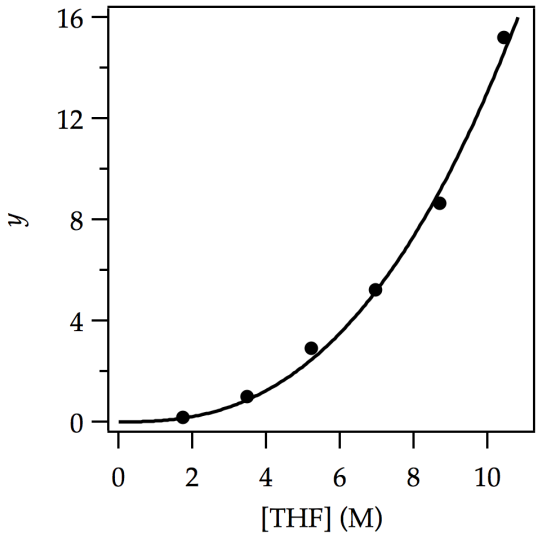
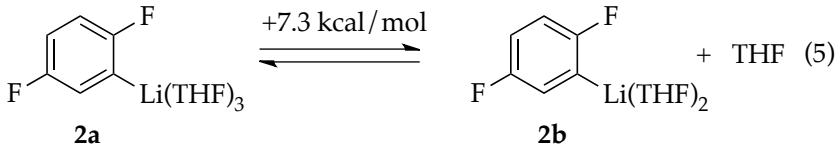


Figure 1.4. Plot of y from eq 4 versus [THF] in hexane cosolvent for the ortholithiation of ArH (0.050 M) with LDA (0.10 M) in the presence of added diisopropylamine (0.050 M) measured by ^{19}F NMR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to $y = a[\mathrm{THF}]^n$. [$a = (0.03 \pm 0.01) \times 10^{-2}$, $n = 2.6 \pm 0.2$]

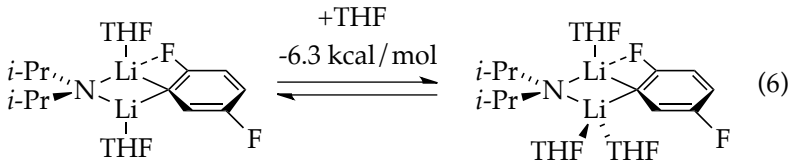
(3) Density functional theory (DFT) computations at the B3LYP/6–31G(d) level[17] with single-point calculations at the MP2 level of theory of the serial solvation revealed that trisolvate **2a** is 7.3 kcal more stable than the corresponding disolvate (eq 5); no minimum was found for the tetrasolvate.[18] Hereafter, we draw ArLi **2** as trisolvate **2a**.



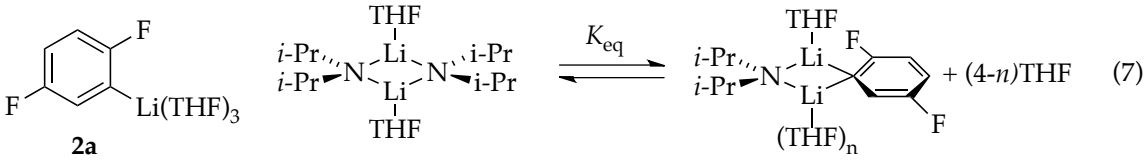
2a **2b**

In the presence of excess [^{6}Li,^{15}N]LDA[12] and low THF concentration, ^{19}F NMR spectroscopy shows the two doublets of **2a** along with two additional broad doublets corresponding to mixed dimer **17** that resolve into more complex multiplets owing to ^{1}H–^{19}F coupling with application of window functions.[6] Computations showed a 6.3

kcal/mol greater stability of trisolvated dimer **17b** than disolvate **17a** (eq 6). (The computations show a distinct F-Li interaction in **17a,b**). Monitoring the mixed dimer equilibrium versus THF concentration (eq 7 and Figure 1.5) and fitting according to eq 8 implicates trisolvated mixed dimer **17** (solvation number of 3.4 $\pm$ 0.1). The distinction is not germane to the rate and mechanistic studies.



17a **17b** (6)



2a **3** **17** (7)

$$y = [\mathrm{ArLiS_3}][\mathrm{A_2S_2}]^{1/2}/[\mathrm{A(ArLi)S}_{n+1}]\} = [\mathrm{S}]^{4-n}/K_{\mathrm{eq}} \qquad (8)$$

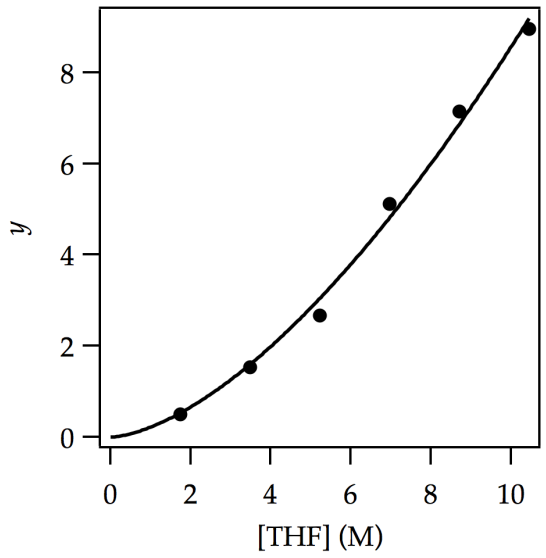
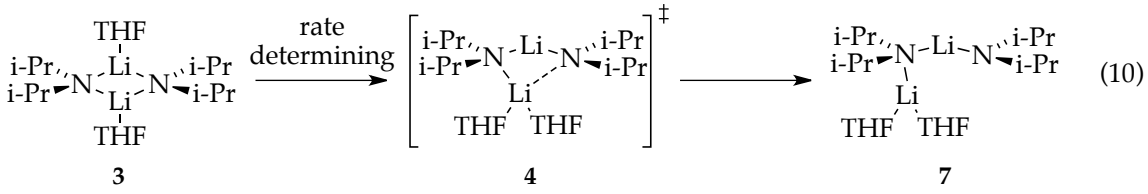


Figure 1.5. Plot of y (eq 8) versus [THF] in hexane cosolvent for the ortholithiation of ArH (0.050 M) with LDA (0.10 M) in the presence of diisopropylamine (0.050 M) measured with ^{19}F NMR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to $y = a[\text{THF}]^{4-n}$. [$a = 0.21 \pm 0.05$, $n = 2.4 \pm 0.1$]

Rate studies: general protocols. Lithiation of ArH using analytically pure (recrystallized) LDA[6d] was monitored using in situ IR spectroscopy[19] by following the disappearance of a strong arene stretch at 1510 cm^{-1}. The precise protocols were situation dependent, however. Reactions carried out at low ArH concentrations (0.0050 M ArH) *and* that were also clearly first order in ArH were followed to >5 half-lives, and the pseudo-first-order rate constants (k_{obsd}) were determined with standard nonlinear fits.[3] Under non-pseudo-first-order conditions in situations in which rate-limiting deaggregation dominates or under conditions in which autocatalysis caused deviation from a first-order decay, the initial rates[20] were determined by following the reaction to 5% conversion and extracting the rate at $t = 0$ from a polynomial fit as described.[6] Reaction orders in THF and LDA were determined by plotting either k_{obsd} or initial rate versus the respective concentrations.[21]

Uncatalyzed lithiation of ArH: rate-limiting deaggregation. Rate studies reveal a rate law described by eq 9 that is consistent with rate-limiting deaggregation of dimer **4** (eq 10).[22] Lithiation of ArH at low concentrations (0.0050 M) shows a linearity (Figure 1.6) that suggests either zeroth order in arene or an inherently upwardly curving decay being straightened by autocatalysis;[6] a plot of initial rate versus ArH concentration shows a clear ArH concentration independence consistent with a zeroth order in ArH (Figure 1.6 inset). The initial rates are also zeroth-order in THF (Figure 1.7); the cosolvent dependence illustrates a standard control experiment confirming that the downward slope derives from small medium effects.[3] An approximate first-order (1.12 $\pm$ 0.09 order) dependence on LDA concentration (Figure 1.8) is consistent with the dimer-based transition structure.[23] The slight upward curvature signifying an elevated LDA order foreshadows mechanistic complexity. Isotopic labeling studies confirm post-rate-limiting proton transfer, but their complexity demands that we describe perdeuterated arene in its own section. The overall idealized[24] rate law (eq 9) is consistent with a dominant disolvated-dimer-based rate-limiting deaggregation (eq 10) as noted in previous studies.[6]

$$-d[\mathrm{ArH}]/dt = k[\mathrm{A_2S_2}][\mathrm{S}]^0[\mathrm{ArH}]^0 \qquad (9)$$



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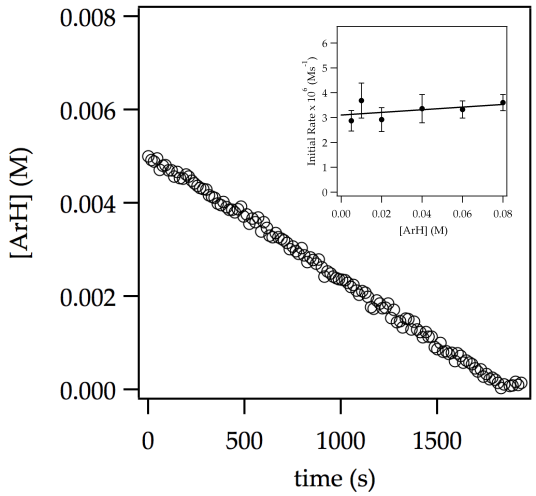


Figure 1.6. Representative plot showing linear decay for the ortholithiation of ArH (0.0050 M) with LDA (0.10 M) in 12.2 M THF monitored using IR spectroscopy at –78 °C. Inset shows a plot of initial rate versus [ArH] (initial arene concentration) for the ortholithiation of ArH with LDA (0.10 M) in THF (12.2 M) measured with IR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to $y = a$[ArH] + b. [$a = (5 \pm 5) \times 10^{-6}$, $b = (3.1 \pm 0.2) \times 10^{-6}$]

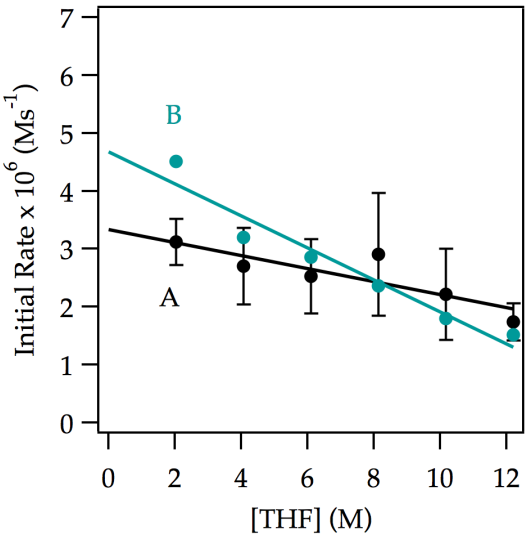


Figure 1.7. Plot of initial rate versus [THF] in Et_2O (curve A) and in hexanes (curve B) cosolvent for the ortholithiation of ArH (0.050 M) by LDA (0.10 M) at –78 °C. The data were measured with IR spectroscopy. The curves depict unweighted least-squares fits to $y = a$[THF] + b. Curve A: $a = (-1.1 \pm 0.3) \times 10^{-7}$, $b = (3.3 \pm 0.3) \times 10^{-6}$. Curve B: $a = (-2.8 \pm 0.3) \times 10^{-7}$, $b = (4.7 \pm 0.3) \times 10^{-6}$. The greater slope using hexane as cosolvent compared with that using Et_2O as cosolvent illustrates the influence of long-range medium effects.

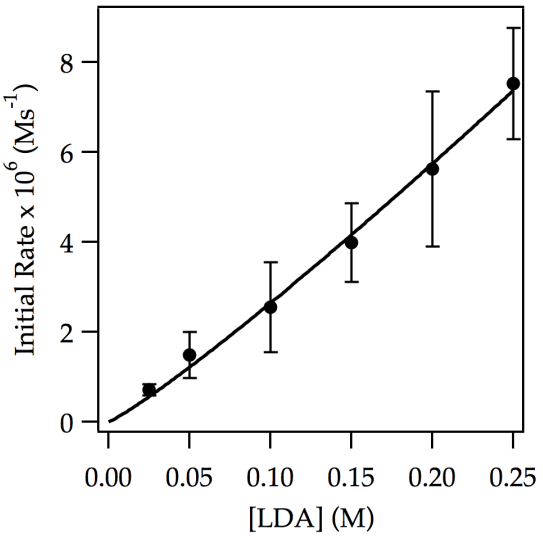


Figure 1.8. Plot of initial rate versus [LDA] in THF (12.2 M) for the ortholithiation of ArH (0.0050 M) measured with IR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to $y = a[\mathrm{LDA}]^n$. [$a = (3.5 \pm 0.3) \times 10^{-5}$, $n = 1.12 \pm 0.06$]

Autocatalyzed lithiation of ArH: rate-limiting aggregation. We suspected subtle upward curvature in Figure 1.6 is masked by downward curvature arising from autocatalysis.[6] Lithiations using larger concentrations of ArH—conditions allowing aryllithium **2** to build to appreciable concentrations—reveal the anticipated albeit subtle downward curvature (Figure 1.9). To tease out the underlying mechanistic changes, we carried out the lithiations under pseudo-first-order conditions with varying concentrations of ArLi. Figure 1.10 shows the rates versus ArLi concentration and reveals a sigmoid consistent with higher-order saturation kinetics but only a small (threefold) overall increase in rate. Fitting the data to eq 11 afforded a 3.0 ± 0.4 order in ArLi.[25] Previous studies are fully consistent with such higher-order catalysis but showed only *second*-order ArLi dependencies. The analogous second-order curve is included to show the similarity. We suspect that the disagreement is not about the mechanism per se but rather due to the sensitivity of such determinations.

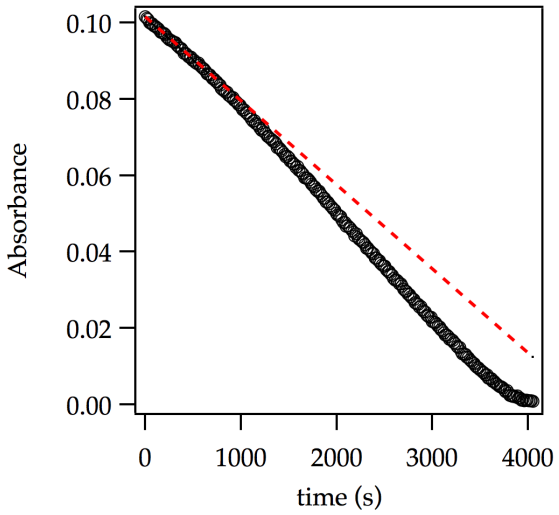


Figure 1.9. Representative plot showing sigmoidal decay for the ortholithiation of ArH (0.020 M) with LDA (0.10 M) in 12.2 M THF monitored with IR spectroscopy at –78 °C. The red dotted line depicts the time-dependent linear decay extrapolated from the initial rate in the absence of autocatalysis.

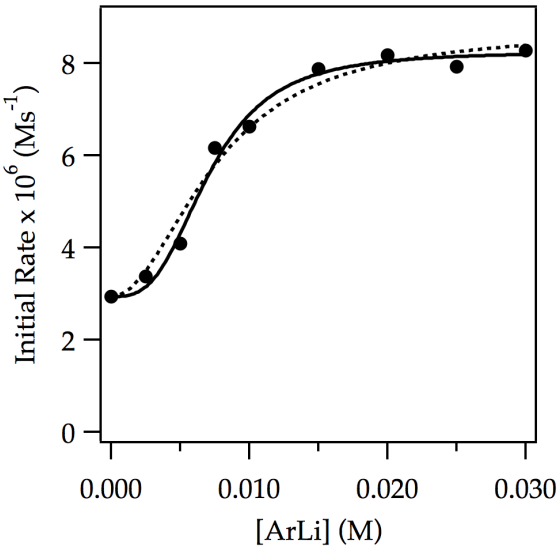


Figure 1.10. Plot of initial rate versus [ArLi] for the ortholithiation of ArH (0.0050 M) by 0.10 M LDA in 12.2 M THF monitored with IR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to eq 11. Solid curve: $a = 2 \pm 4$, $b = (3 \pm 8) \times 10^6$, $c = 2.94 \times 10^{-6}$, $n = 3.0 \pm 0.5$. Dotted curve: n is set at 2; $a = (9 \pm 2) \times 10^{-2}$), $b = (1.7 \pm 0.3) \times 10^4$, $c = 2.94 \times 10^{-6}$.

$$-d[\mathrm{ArH}]/dt = (a[\mathrm{ArLi}]^n)/(1 + b[\mathrm{ArLi}]^n) + c. \qquad (11)$$

For an alternative view of the autocatalysis, we applied the method of continuous variations (a Job plot).[6,26] Initial rates were monitored versus the mole fraction of ArLi while keeping the total normality of ArLi and LDA constant (Figure 1.11). The curve corresponds to a nonlinear least-squares fit to the generalized expression in eq 12. Eq 12 is an approximation because it corresponds to a fit for a *statistical* Job plot.[27] Moreover, in contrast to normal Job plots in which the curvature and position of the maximum provide insight into relative stoichiometries (via parameters *m* and *n* in eq 12), the shifting rate-limiting step precludes such a simple interpretation. Had ArLi been a highly efficient catalyst, for example, the maximum would have been pressed against the left-hand *y* axis irrespective of stoichiometry. Figure 1.11 does, however, offer a visually retrievable, qualitative view of the catalysis.

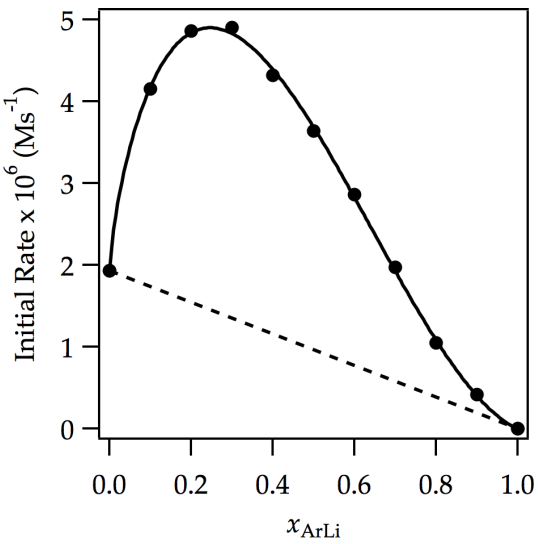


Figure 1.11. Plot of initial rates versus mole fraction of ArLi (X_{ArLi}) for the serial injection of 0.010 M aliquots of ArH to 0.10 M LDA in 12.2 M THF monitored with IR spectroscopy at –78 °C. The dotted curve depicts the theoretical initial rates in the absence of autocatalysis. The solid curve depicts an unweighted least-squares fit to eq 12. [$k = (1.67 \pm 0.09) \times 10^{-5}$, $k' = (1.93 \pm 0.05) \times 10^{-6}$, $n = 0.75 \pm 0.3$, $m = 1.87 \pm 0.05$]

$$-d[\mathrm{ArH}]/dt = k(X_{\mathrm{ArLi}})^n(1-X_{\mathrm{ArLi}})^m + k'(1-X_{\mathrm{ArLi}}) \qquad (12)$$

ArLi catalysis offers a remarkable mechanistic probe that requires some explaining. Although the saturation has the superficial appearance of Michaelis–Menten kinetics in which an intermediate becomes the dominant observable form,[28] no such form exists. Instead, saturation corresponds to a shift in the rate-limiting step as described by eqs 13 and 14.[6] Saturation occurs when rate-limiting deaggregation favored at zero or low ArLi concentration (k_{-1}[ArLi] << k_2) shifts to a new rate-limiting step at high ArLi concentration (k_{-1}[ArLi] >> k_2). As the evidence shows, the new rate-limiting step *still* does not involve proton transfer.

$$\underset{\mathbf{3}}{A_2S_2} \underset{k_{-1} + k_{-ArLi}[ArLi]}{\overset{k_1 + k_{ArLi}[ArLi]}{\rightleftharpoons}} \underset{\mathbf{7}}{A_2S_2{}^*} \xrightarrow{k_2} \underbrace{[A_mS_n]^{\ddagger}}_{\textit{rate determining}} \longrightarrow A_mS_n{}^* \qquad (13)$$

$$\underbrace{A_mS_n{}^*}_{\textit{post-rate determining}} \xrightarrow{ArH} ArLi \qquad (14)$$

To ascertain the nature of the new rate-limiting step, we simply added sufficient ArLi at the outset of the reaction (0.020 M ArLi) to establish full saturation (plateau in Figure 1.10) and determine a rate law. A zeroth-order in substrate, zeroth order in THF, and second order in LDA (Figure 1.12) affords the idealized rate law in eq 15 and implicates a *tetrasolvated tetramer-based LDA aggregation as the rate-limiting step* (eq 16). We had detected kinetic evidence of LDA tetramers previously[6] but without such clarity. The roles of ArLi catalysis and mixed tetramer intermediates remain shrouded in mystery despite considerable experimental and computational probing.[6] Nonetheless, catalyzing the aggregate exchange of dimer **3** has revealed a rate-limiting

tetramer pathway (labeled **11** in Scheme 1) lurking just beyond the first barrier. In theory, we could bring the proton transfer into view by slowing the trapping step in eq 14 through deuteration. In practice, it is not that simple.

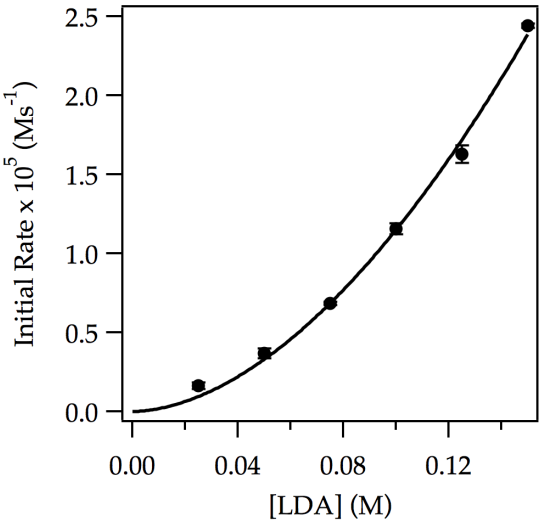


Figure 1.12. Plot of initial rate versus [LDA] in THF (12.2 M) for the ortholithiation of ArH (0.0050 M) in the presence of 0.020 M ArLi monitored with IR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to $y = a[\mathrm{LDA}]^n$. [$a = (7 \pm 1) \times 10^{-4}$, $n = 1.80 \pm 0.09$]

$$-d[\mathrm{ArH}]/dt = k[\mathrm{A_2S_2}]^2[\mathrm{S}]^0[\mathrm{ArH}]^0 \qquad (15)$$

$$\underset{\mathbf{3}}{\mathrm{A_2S_2}} \underset{k_{-1}+k_{-\mathrm{ArLi}}[\mathrm{ArLi}]}{\overset{k_1+k_{\mathrm{ArLi}}[\mathrm{ArLi}]}{\rightleftharpoons}} \underset{\mathbf{7}}{\mathrm{A_2S_2}^*} \xrightarrow{k_2[\mathrm{A_2S_2}]} \underbrace{\underset{\mathbf{11}}{[\mathrm{A_4S_4}]^{\ddagger}}}_{\textit{rate determining}} \longrightarrow \underset{\mathbf{14}}{\mathrm{A_4S_4}} \qquad (16)$$

LiCl-catalyzed lithiation of ArH. Previous studies have shown marked catalysis by traces of LiCl attributed in all instances to catalyzed deaggregations and monomer-based lithiations.[6] LiCl (0.0010 M) accelerates the lithiation of ArH by LDA/THF so much that rates can not be monitored at –78 °C with technology available to us.

Notably, at full saturation using ArLi as a catalyst (Figure 1.10), added LiCl causes a further rate spike (Figure 1.13), confirming that ArLi and LiCl catalyze distinctly different processes.[29] Lithiation of less reactive ArD under LiCl catalysis proves more revealing.

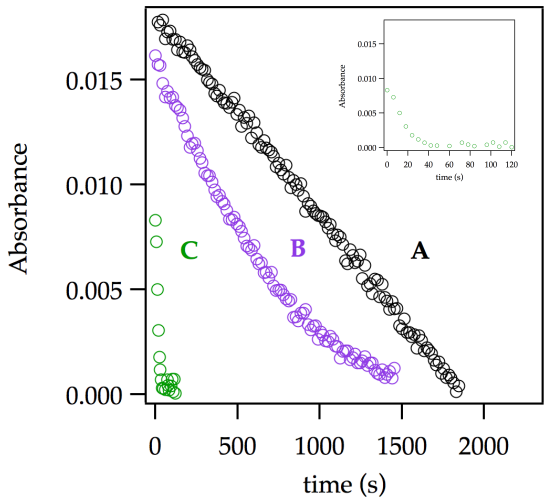
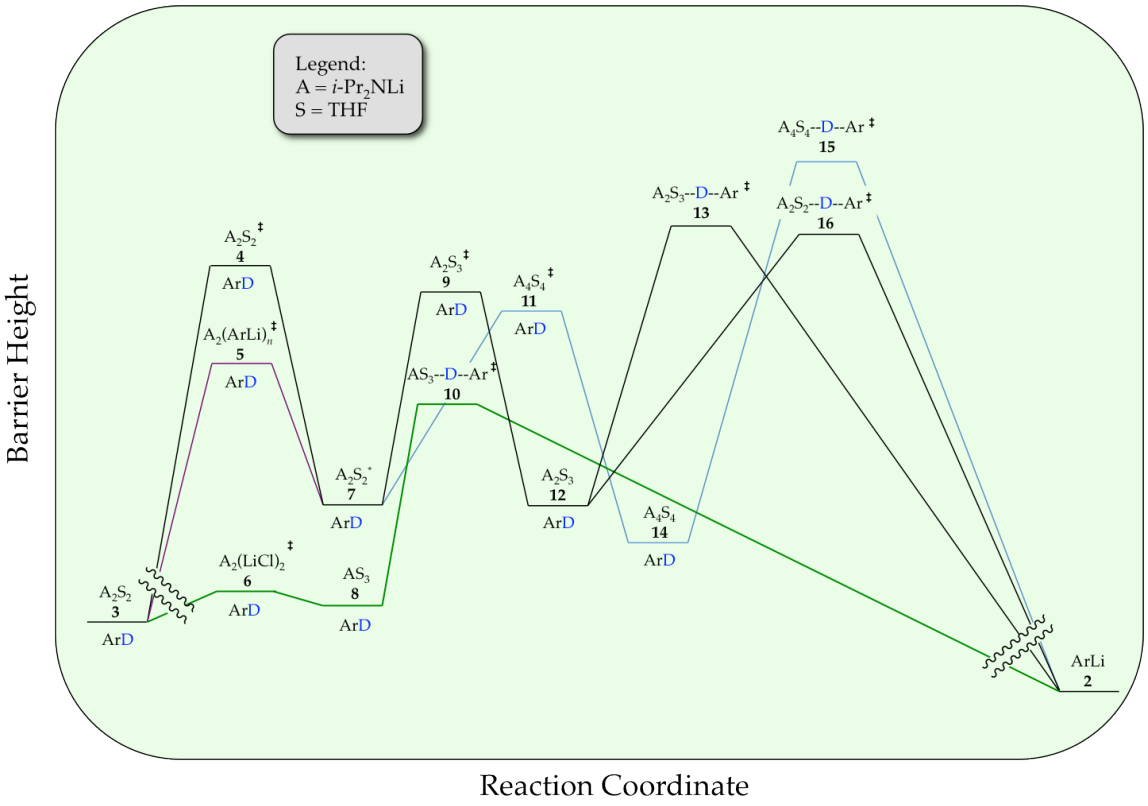


Figure 1.13. Representative plot showing the absorbance of ArH versus time for the ortholithiation of ArH (0.0050 M) with LDA (0.10 M) in THF (12.2 M) at –78 °C (curve A). Curve B shows the decay under the same conditions as in A but with 0.020 M ArLi. After the lithiation was complete, 0.0010 M LiCl was added and a second aliquot was injected into this mixture (curve C; see inset for expansion). Reactions were monitored with IR spectroscopy.

Uncatalyzed lithiation of ArD: rate-limiting deaggregation. As noted in the introduction, lithiations of the ArH and perdeuterated arene **1-d_4** (ArD) are markedly different. We offer the reaction coordinate diagram in Scheme 2 showing qualitative (relative) barrier heights for lithiation of ArD to aid the discussion. Of course, the ArH and ArD barriers in Schemes 1 and 2 can be placed on the *same* diagram to fully display the influence of isotopic substitution but the cost is a considerable increase in complexity; we will do so in the discussion. As a reminder to the reader, the diagram is

a static snapshot of a much more fluid picture in which the relative barriers vary markedly with changes in the concentrations of LDA, THF, and ArD.

Scheme 2



LDA-mediated lithiation of ArD at low concentration (0.0025 M ArD) affords a decay showing an upward curvature that is neither zeroth nor first order. The intermolecular kinetic isotope effect (KIE)—the isotope effect obtained from independently measured initial rates for ArH and ArD—is near unity ($k_H/k_D = 1.5$). The complementary *competitive* isotope effect, obtained by monitoring the relative rates within a single reaction vessel[6] reveals biphasic kinetics (Figure 1.14) from which $k_H/k_D = 40$ was determined from the initial rates. The biphasic kinetics and isotope effects are highly characteristic of a dominantly post-rate-limiting lithiation in which the less

reactive ArD does not react until ArH is consumed.[6] The fits in Figure 1.14 derive from a numerical integration using the simplified model in Scheme 3.[6]

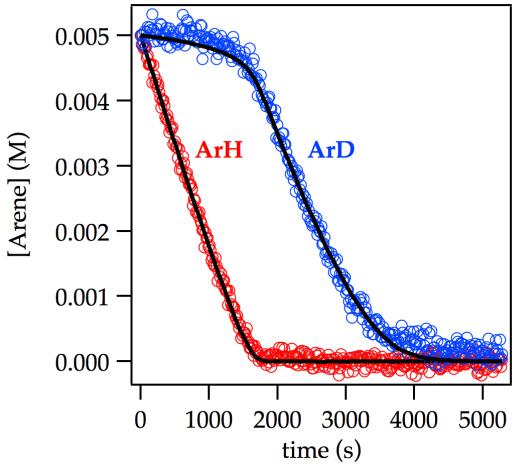
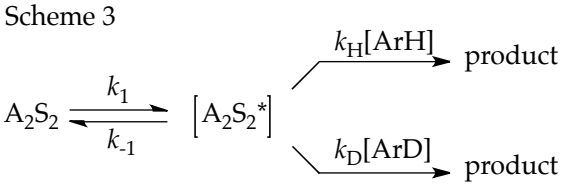


Figure 1.14. Competitive ortholithiation of ArH (0.0050 M) and ArD (0.0050 M) with LDA (0.10 M) in THF (12.2 M) at –78 °C. The curves result from a best-fit numerical integration to the highly simplified model in Scheme 3 and afford $k_H/k_D = 30$ (supporting information). By contrast, measuring the initial slopes directly affords $k_H/k_D = 40$.

Scheme 3



Detailed rate studies reveal the origins of these odd behaviors and present a new view of the ortholithiation. In contrast to ArH in which the lithiation occurs in a post-rate-limiting step, rate limitation for ArD depends on concentration (Figure 1.15). The rate studies are consistent with the rate law described by eq 17 and mechanisms described by eqs 18–20. The evidence is presented in the limits of high and low ArD concentration as follows.

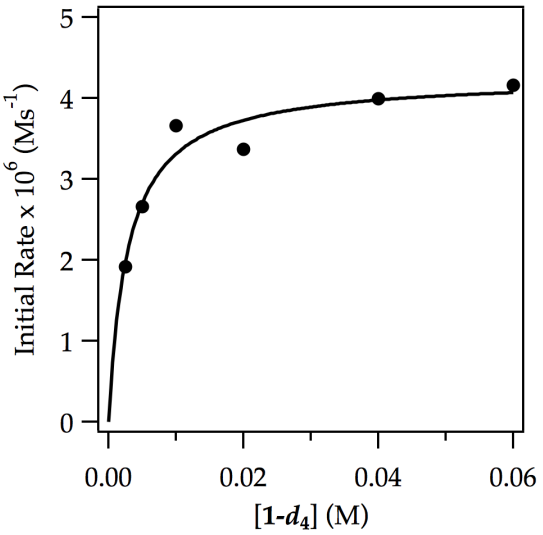


Figure 1.15. Plot of initial rate versus [ArD] for the ortholithiation of ArD with LDA (0.10 M) in THF (12.2 M) monitored with IR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to a first-order saturation function: $-d[\mathrm{ArD}]/dt = (a[\mathrm{ArD}])/(1 + b[\mathrm{ArD}])$. [$a = (1.5 \pm 0.3) \times 10^{-3}$, $b = (3.5 \pm 0.8) \times 10^{2}$]

$$-d[\mathrm{ArD}]/dt = k_1(k_2 + k_3[\mathrm{S}])[\mathrm{A_2S_2}][\mathrm{ArD}]/\{k_{-1} + (k_2 + k_3[\mathrm{S}])[\mathrm{ArD}]\} \quad (17)$$

$$\mathrm{A_2S_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{A_2S_2}^* \quad (18)$$

$$\mathrm{A_2S_2}^* + \mathrm{ArD} \xrightarrow{k_2} [\mathrm{A_2S_2(ArD)}]^{\ddagger} \quad (19)$$

$$\mathrm{A_2S_2}^* + \mathrm{S} + \mathrm{ArD} \xrightarrow{k_3} [\mathrm{A_2S_3(ArD)}]^{\ddagger} \quad (20)$$

High ArD concentration limit:

$$-d[\mathrm{ArD}]/dt = k_1[\mathrm{A_2S_2}] \quad (21)$$

$$\mathrm{A_2S_2} \xrightarrow{k_1} [\mathrm{A_2S_2}]^{\ddagger} \quad (22)$$

Low ArD concentration limit:

$$-d[\mathrm{ArD}]/d\mathrm{t} = (k_1/k_{-1})(k_2 + k_3[\mathrm{S}])[\mathrm{A_2S_2}][\mathrm{ArD}] \quad (23)$$

$$\mathrm{A_2S_2} + \mathrm{ArD} \xrightarrow{k_1k_2/k_{-1}} [\mathrm{A_2S_2(ArD)}]^{\ddagger} \quad (24)$$

$$\mathrm{A_2S_2} + \mathrm{S} + \mathrm{ArD} \xrightarrow{k_1k_3/k_{-1}} [\mathrm{A_2S_3(ArD)}]^{\ddagger} \quad (25)$$

(1) At high ArD concentration trapping of a fleeting (dimeric) intermediate A_2S_2* is efficient ($k_{-1} < k_2$[ArD] and $k_{-1} < k_3$[ArD][S] in eqs 18–20), rendering the reaction zeroth order in ArD (eq 21 and 22). The initial rates show a first-order dependence on LDA concentration and a zeroth-order dependence on THF concentration. The rate law in eq 17 reduces to the much simpler rate law in eq 21, which corresponds to the rate-limiting dimer fragmentation (via **4**) described by eq 10.

(2) At low ArD concentration the trapping is inefficient ($k_{-1} > k_2$[ArD] and $k_{-1} > k_3$[ArD][S] in eqs 17–20). A linear dependence on THF concentration with a significant non-zero intercept (Figure 1.16) and first-order LDA dependencies at both low and high THF concentrations (Figure 1.17) reduce the rate law to that in eq 23. The data are consistent with an A_2S_2–A_2S_2* dimer-based pre-equilibrium and an emergent superposition of rate-limiting di- and trisolvated-dimer-based lithiations (eqs 24 and 25). The failure to observe the saturation kinetics for ArH stemmed from the high reactivity and consequent efficient trapping at both low and high concentrations, which may have obscured the trisolvated-dimer-based mechanism made visible by ArD. Evidence exists, however, that the high isotopic sensitivity diverts proton and deuterium transfers through distinctly different pathways (*vide infra*).

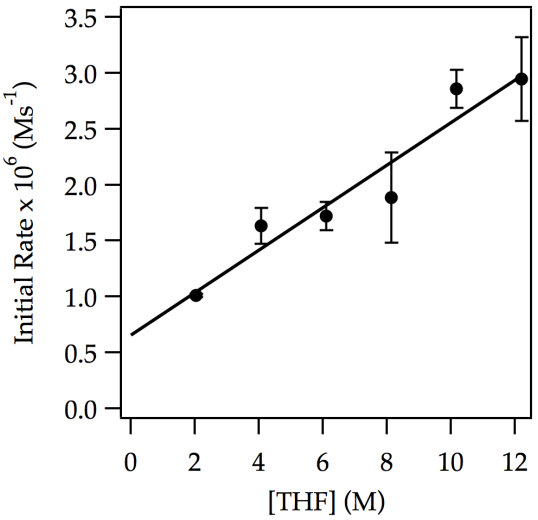


Figure 1.16. Plot of initial rate versus [THF] in Et_2O for the ortholithiation of ArD (0.0020 M) by LDA (0.10 M) monitored with IR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to $y = a[\text{THF}] + b$. [$a = (1.9 \pm 0.3) \times 10^{-7}$, $b = (7 \pm 2) \times 10^{-7}$]

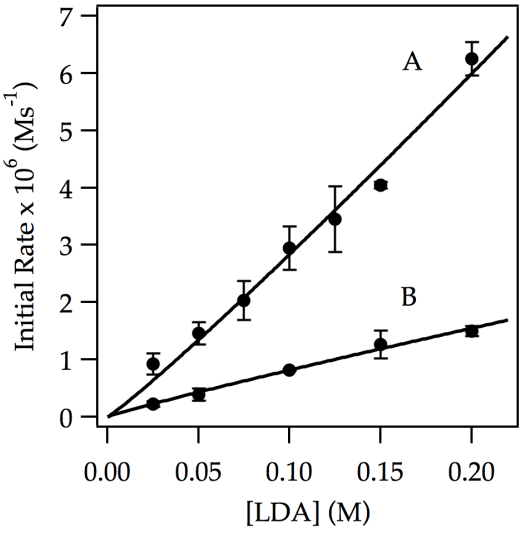
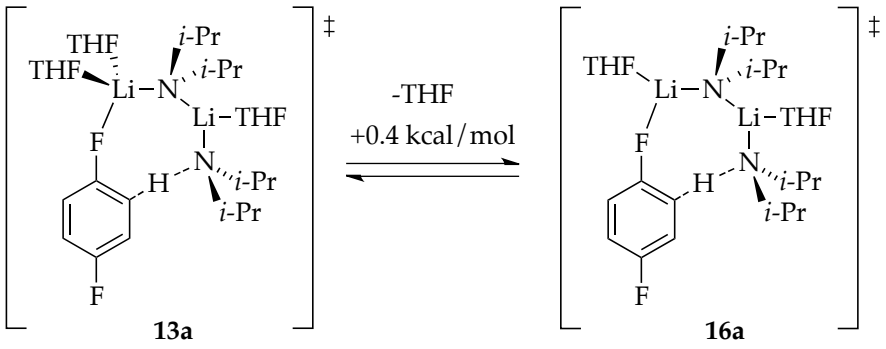


Figure 1.17. Plot of initial rate versus [LDA] in 12.2 M THF (Curve A: 12.2 M, Curve B: 2.03 M) for the ortholithiation of ArD (0.0020 M) monitored with IR spectroscopy at –78 °C. Curve A depicts an unweighted least-squares fit to $y = a[\text{LDA}]^n$. [$a = (3.4 \pm 5) \times 10^{-5}$, $n = 1.08 \pm 0.08$]. Curve B depicts an unweighted least-squares fit to $y = a[\text{LDA}]^n$. [$a = (6.8 \pm 0.9) \times 10^{-6}$, $n = 0.92 \pm 0.07$]

With stoichiometries of the rate-limiting transition structures in hand, we examined di- and trisolvated-dimer-based metalations computationally (eq 26).[30] The difference is negligible.



13a **16a** (26)

Autocatalyzed lithiation of ArD: dimer-based lithiation. Recall that metalations autocatalyzed by ArLi (Scheme 1) bypass the rate-limiting conversion of starting LDA dimer **3** to putative open dimer A_2S_2* **4**, revealing rate-limiting $[A_4S_4]^‡$ transition structure **11** and a kinetically invisible post-rate-limiting metalation of ArH. Guided by previous studies implicating analogous tetramer-based pathways, we surmised that suppressing the rate of metalation using ArD would bring either a tetramer- or a monomer-based metalation into view.[31,32]As stated, this idea contains embedded flaws, and the story is considerably more nuanced.

Monitoring the initial rates for the metalation of ArD versus ArLi concentration (perdeuterated aryllithium **2–*d*$_3$** to be more precise) showed saturation kinetics (Figure 1.18) analogous to that for ArH (Figure 1.10) with an attenuated acceleration but the same high-order dependence on ArLi concentration. (One could be excused for not detecting this saturation behavior.)

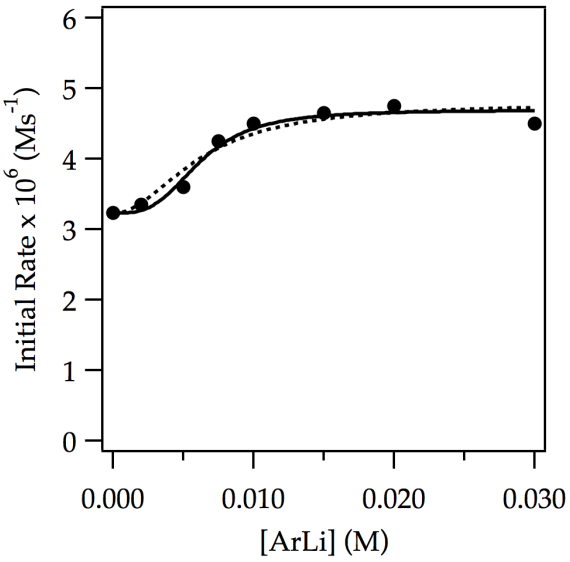


Figure 1.18. Plot of initial rate versus [ArLi] (specifically, **2–*d*$_3$**) for the ortholithiation of ArD (0.0020 M) by 0.10 M LDA in 12.2 M THF monitored with IR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to $-d[\mathrm{ArH}]/dt = (a[\mathrm{ArD}]^n)/(1 + b[\mathrm{ArD}]^n) + c$.[33] Solid curve: [$a = (6 \pm 2)$, $b = (4 \pm 1) \times 10^6$, $c = 2.94 \times 10^{-6}$, $n = 3$]. Dotted curve: [$a = (4 \pm 1) \times 10^{-2}$), $b = (2.5 \pm 0.9) \times 10^4$, $c = 3.23 \times 10^{-6}$, $n = 2$]

As already described, the mechanism in the limit of low (zero) ArLi concentration is via A_2S_2-based transition structure **4** using ArH. Ascertaining the concentration dependencies at saturation (0.020 M ArLi) gives unexpected results. A plot of rates versus ArD reveals saturation kinetics, indicating an ArD concentration dependence at low ArD and ArD concentration independence at high ArD (Figure 1.19). To be clear, this plot depicts saturation in substrate *superimposed on saturation in ArLi.* We treat the two limiting behaviors observed in the ArH saturation kinetics separately.

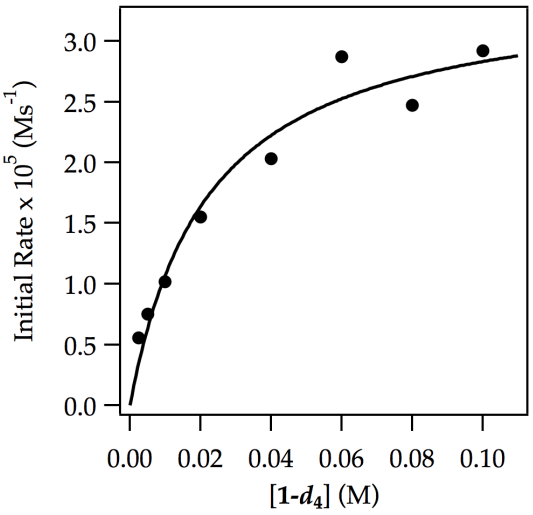


Figure 1.19. Plot of initial rate versus [ArD] for the ortholithiation of ArD in the presence of 0.020 M ArLi (**2-*d*$_3$**) with LDA (0.10 M) in 12.2 M THF monitored with IR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to a first-order saturation function: $-d[\mathrm{ArD}]/dt = (a[\mathrm{ArD}])/(1 + b[\mathrm{ArD}])$. [$a = (1.6 \pm 0.3) \times 10^{-3}$, $b = 40 \pm 10$]

(1) In the limit of low ArD with added ArLi, the dependence on ArD concentration attests to ArD participation in the rate-limiting step. The decays of ArD also show curvatures consistent with significant contributions from a first-order dependence as expected for at least a partially rate-limiting metalation. Plots of initial rates versus LDA and THF show nearly linear dependencies, implicating a transition structure of stoichiometry $[A_2S_3(\mathrm{ArD})]^{‡}$. Because the proton transfer for ArH under ArLi-catalyzed conditions was not kinetically visible, we could not measure the intermolecular isotope effect. An ArH/ArD competition shows biphasic behavior (Figure 1.20) consistent with the trapping of a common intermediate in a post-rate-limiting step and a substantial KIE ($k_H/k_D = 12$). This is consistent with the partial mechanism in Scheme 3 in which ArH is scavenging A_2S_2* (directly or via tetramer **14**, Scheme 1), largely precluding deuterium transfer.

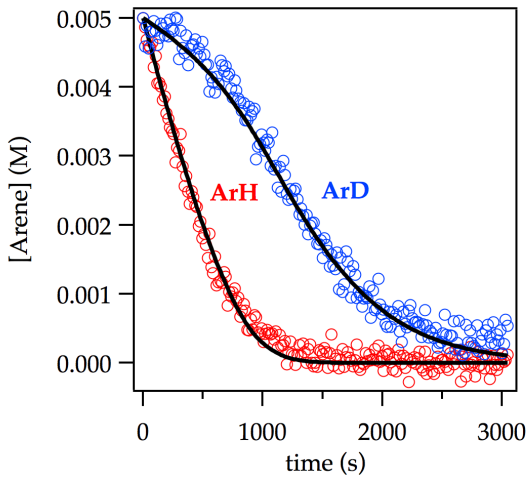


Figure 1.20. Competitive ortholithiation of ArH (0.0050 M) and ArD (0.0050 M) with LDA (0.10 M) in the presence of 0.020 M ArLi in 12.2 M THF at –78 °C. The curves result from a best-fit numerical integration to the highly simplified model in Scheme 3 and afford $k_H/k_D = 6.3$. Fitting the initial rates of both decays (linearly) directly affords $k_H/k_D = 12$.

(2) In the limit of high ArD with added ArLi, the decays of ArD are decidedly linear (zeroth order), and orders in LDA and THF are both unity. The rate-limiting transition state is of stoichiometry $[A_2S_3]^‡$ **9** (Scheme 2).

The most unexpected aspect of the rate studies using ArLi as the catalyst is that the metalation of ArH proceeds via a rate-limiting A_4S_4-tetramer-based aggregation event, whereas ArD diverts to A_2S_2- and A_2S_3-dimer-based mechanisms. Although one could infer the intermediacy of tetramer *en route from one dimer to another*, we believe there is a more rational explanation (*vide infra*).

LiCl-catalyzed lithiation of ArD: monomer-based lithiation. In previous studies of LDA/THF-mediated lithiations at –78 °C, the dramatic effects of LiCl on rates were traced to monomer-based lithiations without exception.[6] Metalations of ArH were too fast to test this thesis, but ArD metalations proved highly tractable. Monitoring the ArD metalation versus LiCl shows a second-order dependence that saturates at very low

(>0.0010 M) LiCl concentrations, as expected from previous studies (Figure 1.21).[6] The threefold acceleration is small owing to a very large isotope effect ($k_H/k_D > 50$). The lithiations of ArD at full saturation (0.0015 M LiCl) follow a clean exponential decay consistent with rate-limiting ortholithiation. A half-order LDA dependence and second-order THF dependence (Figure 1.22) are consistent with the rate law in eq 27 and the generic trisolvated-monomer-based mechanism described by eqs 28 and 29.

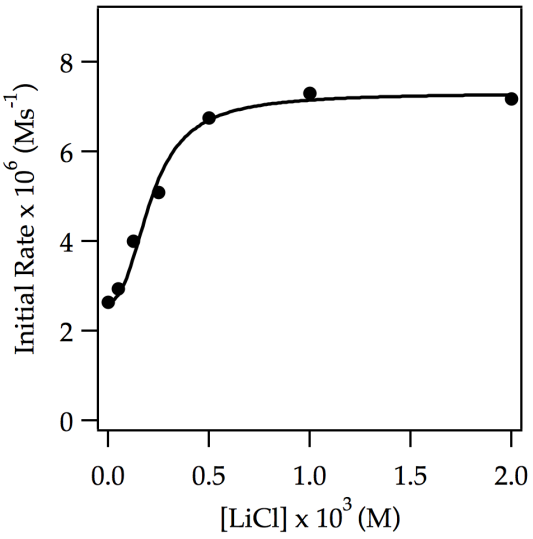


Figure 1.21. Plot of initial rate versus [LiCl] for the ortholithiation of ArD (0.0020 M) by 0.10 M LDA in 12.2 M THF monitored with IR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to eq 30.[33] [ArD] = 0.0020 M, $[A_2S_2]$ = 0.050 M, c = 2.63 x 10^{-6}. [k_1 = (5 ± 1) x 10^2, k_{-1} = (6 ± 2) x 10^7, k_2 = 4.06, n = 2.0]

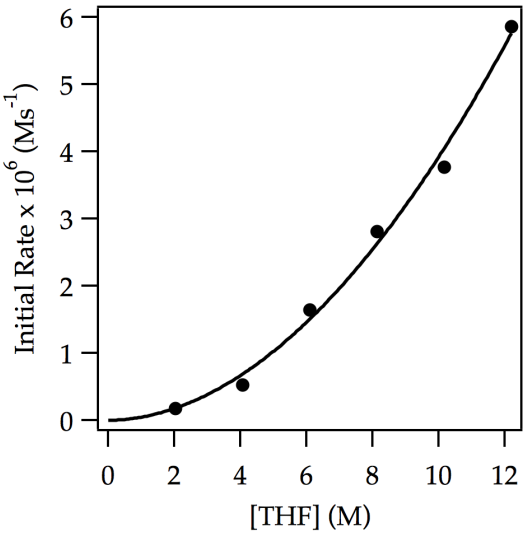


Figure 1.22. Plot of initial rate versus [THF] in Et_2O for the ortholithiation of ArD (0.0020 M) by LDA (0.10 M) in the presence of 1.5 mol% LiCl (1.5 mM) monitored with IR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to $y = a[\mathrm{THF}]^n$. [$a = (5 \pm 1) \times 10^{-8}$, $n = 1.9 \pm 0.1$]

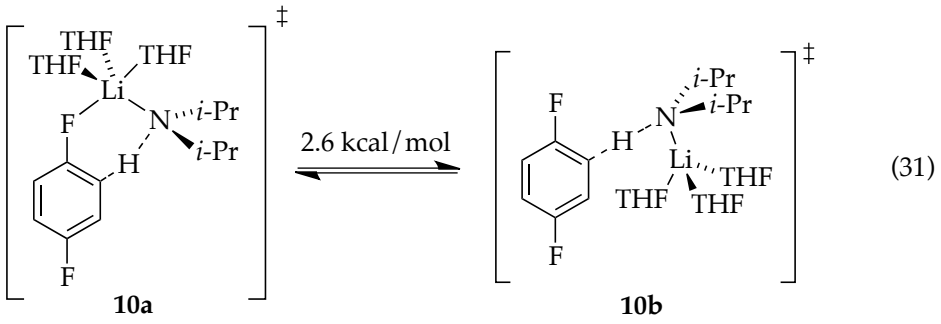
$$-d[\mathrm{ArD}]/d\mathrm{t} = k_2 K_{\mathrm{eq}}[\mathrm{A_2S_2}]^{1/2}[\mathrm{S}]^2[\mathrm{ArD}] \tag{27}$$

$$1/2\ \mathrm{A_2S_2} + 2\mathrm{S} \overset{K_{\mathrm{eq}}}{\rightleftharpoons} \mathrm{AS_3}^* \tag{28}$$

$$\mathrm{AS_3}^* + \mathrm{ArD} \xrightarrow{k_2} [\mathrm{AS_3(ArD)}]^{\ddagger} \tag{29}$$

$$-\Delta[\mathrm{ArH}]/\Delta t\big|_{t=0} = \frac{k_2[\mathrm{ArH}]}{4k_{-1}[\mathrm{LiCl}]^n}\left(\sqrt{k_2^2[\mathrm{ArH}]^2 + 16k_1k_{-1}[\mathrm{A_2S_2}][\mathrm{LiCl}]^{2n}} - k_2[\mathrm{ArH}]\right) + c \tag{30}$$

Computational studies probing the relative efficacies of the open and closed trisolvated-monomer-based transition structures support the closed form presumably owing to a strong Li–F interaction (eq 31).



10a **10b** (31)

Exchange studies of LDA. The rate studies of various metalations have suggested that several LDA aggregation events may be detectable using NMR spectroscopy: (a) LDA subunit exchange should be observable *on laboratory time scales* at low temperatures, and (b) the subunit exchange might occur via a dissociative dimer-derived deaggregation or a tetramer-based associative mechanism. We examined these suppositions using two distinctly different probes of LDA subunit exchange.

Let us first consider the two mechanisms:

Dissociative Subunit Exchange

$$A_2 + B_2 \rightleftharpoons 2A + 2B \rightleftharpoons 2AB \qquad (32)$$

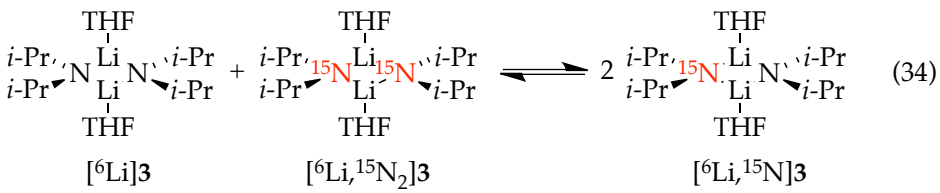
Associative Subunit Exchange

$$A_2 + B_2 \rightleftharpoons A_2B_2 \rightleftharpoons 2AB \qquad (33)$$

To facilitate the discussion, we use A_2 and B_2 as shorthand for [^{6}Li]LDA and [^{6}Li,^{15}N]LDA, respectively. The two mechanisms are highly simplified but easily distinguished nonetheless. In the dissociative mechanism (eq 32), the rate-limiting step for subunit exchange is necessarily dimer-based, affording an *overall* first-order

dependence; once a dimer dissociates it is committed to exchange albeit statistically weighted based on the probability of reaggregating in a mixed isotopic form. Although this statistical factor within unequal populations of A_2 and B_2 can be accounted for,[34] it is more expedient to eliminate it by maintaining equal relative proportions of A_2 and B_2. The associative mechanism in eq 33, by contrast, necessarily involves a tetramer-based rate-limiting step and would manifest an overall second-order dependence. We examined the concentration dependencies using two complementary experiments.

Experiment 1: Low-temperature exchange. We examined the time-dependent conversion of [^{6}Li]LDA and [^{6}Li,^{15}N]LDA to the mono-^{15}N-labeled isotopologue (eq 34) at fixed 1:1 stoichiometry. The exchange was easily followed using ^{6}Li NMR spectroscopy on laboratory time scales at –60 °C (Figure 1.23). This is satisfyingly consistent with the rate-limiting aggregation events detected in the ortholithiation rate studies. The extended timescales of the exchange when compared with the metalations stems from the second-order conditions. A plot of initial rate versus total LDA concentration in equimolar [^{6}Li]LDA and [^{6}Li,^{15}N]LDA mixtures (Figure 1.24) shows an upward curvature and an order of 1.7 consistent with a composite first- and second-order dependencies expected for competing dimer- and tetramer-based exchange. The rates are also independent of the THF concentration, implicating A_2S_2- and A_4S_4-based transition structures.



[^{6}Li]**3** [^{6}Li,^{15}N$_2$]**3** [^{6}Li,^{15}N]**3** (34)

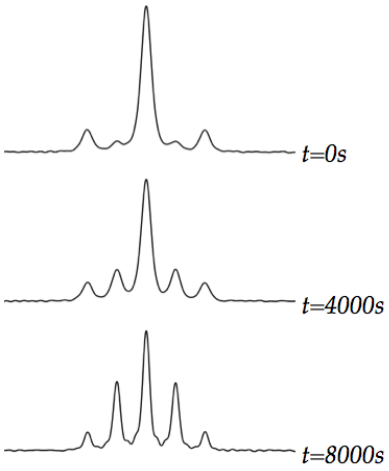


Figure 1.23. ^{6}Li NMR spectra showing the ^{6}Li nuclear exchange of [^{6}Li]LDA (0.10 M) and doubly ^{15}N labeled [^{6}Li,^{15}N]LDA (0.10 M) in 12.2 M THF at –60 °C (eq 34).

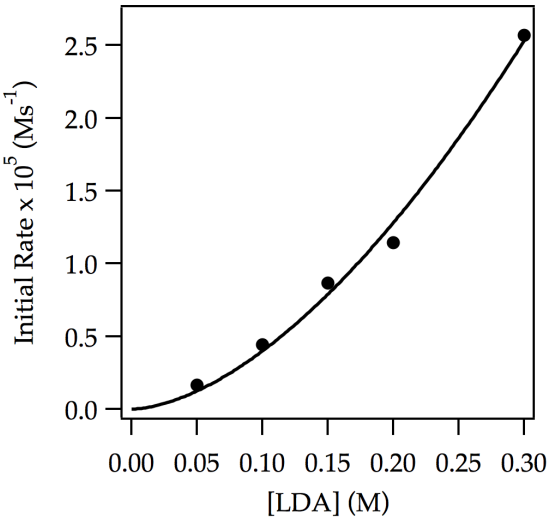


Figure 1.24. Plot of initial rate for the loss of [^{6}Li,^{15}N]LDA in 1:1 mixtures of [^{6}Li]LDA and [^{6}Li,^{15}N]LDA versus total [LDA] titer at –60 °C in 12.2 M THF. The curve depicts an unweighted least-squares fit to $y = a[\text{LDA}]^{n}$. [$a = (1.9 \pm 0.3)\ \text{x}10^{-4}$, $n = 1.7 \pm 0.1$]

Experiment 2. We examined LDA subunit exchange by monitoring the temperature-dependent coalescence of the ^{6}Li triplet of [^{6}Li,^{15}N]LDA. Lineshape analysis was carried out using *WinDNMR* software developed by Reich.[35] The ^{6}Li nuclear exchange rate was simulated by inspection. If exchange of monomer subunits

occurs by a unimolecular process the resulting rate constant, k_{exch}, would be independent of the LDA concentration. By contrast, an overall bimolecular exchange mechanism would manifest a linear dependence of k_{exch} on LDA concentration. In the event, k_{exch} shows a distinct linear dependence *and* a substantial non-zero y–intercept (eq 35) for all THF concentrations (Figure 1.25), implicating competing unimolecular and bimolecular pathways (eq 36). Moreover, the 12–fold range of THF concentrations shows minor slope and intercept variations at both low and high [^{6}Li,^{15}N]LDA consistent with zeroth-order THF dependencies as expected for A_2S_2- and A_4S_4-based rate-limiting transition structures.

$$k_{exch} = k'[\mathrm{LDA}] + k'' \tag{35}$$

$$[A_2S_2]^{\ddagger} \xleftarrow{k''} A_2S_2 \xrightarrow{k'[A_2S_2]} [A_4S_4]^{\ddagger} \tag{36}$$

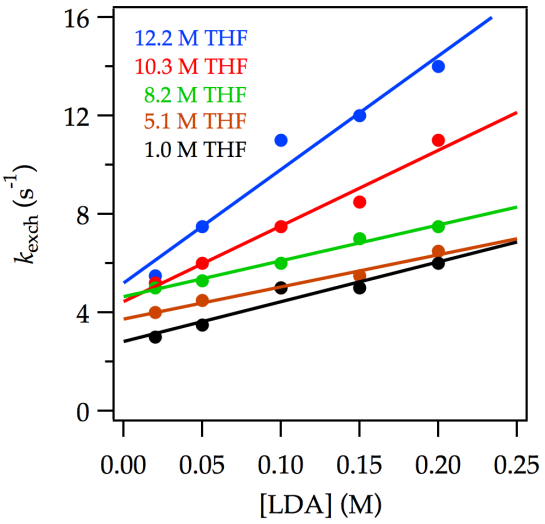
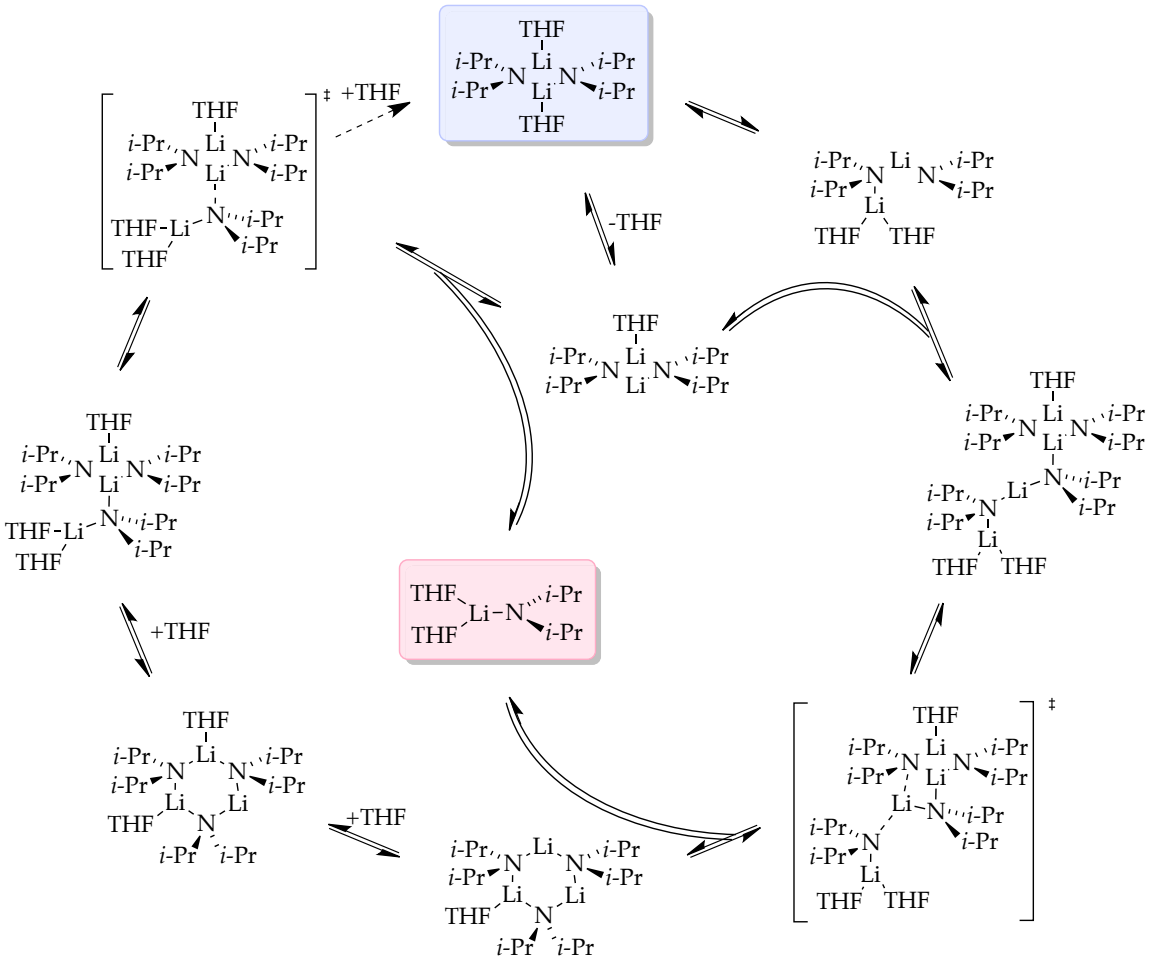


Figure 1.25. Plot of ^{6}Li nuclear exchange rate at 35 °C versus [LDA] at varying [^{6}Li,^{15}N]LDA and THF concentrations with hexanes as cosolvent. The curve depicts an unweighted least-squares fit to linear functions.

Tetramer formation: DFT computations. We had previously examined in considerable detail the dimer-based deaggregation of LDA to monomer.[7] We turned to DFT computations to examine how A_4S_4 tetramers might be formed and how they might be involved in a metalation. This computational problem is extremely difficult (in our hands); we offer the artist's rendition of a reaction coordinate in Scheme 4. The intermediates and transition structures drawn are viable by computational standards. They provide energies, but we do not take them seriously. The role of bridging THFs[36,37] as transitional substructures in critical deaggregation steps were detected in dimer-based deaggregation,[7] whereas the higher aggregates appear to be too congested for such THF bridging. The computed solvation numbers come up short by one (A_4S_3 rather than A_4S_4 observed kinetically). The most fundamental flaw and the origin of the highest energies (26 kcal/mol maximum) is that *two* high energy forms—monosolvated cyclic dimer and disolvated open dimer—condense to form tetramers. This scenario seems unlikely, but it was the best we could do.[38]

Scheme 4



Discussion

Ongoing studies of LDA-mediated metalations under non-equilibrium conditions are, in essence, a study of LDA deaggregation and rate limitation. Paradoxical behaviors abound under these conditions in which aggregation exchanges and reactions with substrates battle to determine the rate-limiting step. Studies of the ortholithiation of 1,4-difluorobenzene (**1**) and its perdeuterated analog (**1-*d*$_4$**) reveal the reaction coordinate illustrated in Schemes 1 and 2. For readers who bypassed the results section, we reiterate a shorthand introduced to simplify the presentation: (1) the various LDA-based fragments are reduced to A_mS_n notations in which A and S connote the LDA

subunits and coordinated THF ligands, respectively; (2) arene **1** and its perdeuterated analog **1–*d*$_4$** are represented as ArH and ArD, respectively; (3) aryllithium **2**, perdeuterated aryllithium **2-*d*$_3$** and structurally most accurate trisolvated monomer **2a** are collectively denoted as simply ArLi.

A staggering number of kinetically detectable minima and maxima cluster in an energetically *very* narrow window—a reaction coordinate approximating a metaphorical washboard. The resulting complexity is breathtaking. Changing concentrations of ArH, LDA, and THF alter the relative dominance of the barriers, resulting in wild swings in concentration dependencies and rate laws. Swapping ArD for ArH—a simple experiment in most settings—completely transforms the rate laws and observed mechanisms. Autocatalysis by ArLi accelerates the metalation and shifts the rate-limiting steps, markedly transforming the rate laws. Adding traces of LiCl similarly accelerates the reaction but does so via catalysis on an altogether different portion of the reaction coordinate. Saturation kinetics—simultaneously *superimposed* saturation kinetics—are legion owing to the relentlessly shifting rate-limiting steps.

In short, the rules governing rates and mechanisms under conditions in which aggregates are in full equilibrium falter badly for non-equilibrium conditions. Within this chaotic picture, however, are several critically important common denominators: (1) the complexity stems from coincident barriers to reaction with substrate and barriers corresponding to LDA aggregation and solvation steps; and (2) the conditions under which this coincidence occurs—LDA/THF/–78 °C —is the same for any substrate that reacts measurably. Although the different substrates[6] probe a single process—the deaggregation of LDA dimer **3**—each substrate provides a different perspective and different mechanistic insights.

We begin the analysis with an overview of the mechanism in the context of the reaction coordinate diagram depicted in Scheme 1. To reiterate, Scheme 1 was constructed from rate studies under many conditions. It represents a snapshot of a living, breathing reaction coordinate in which the relative barrier heights depend on many parameters. Because the equilibria are implicitly rather than explicitly balanced to minimize clutter—fragments of LDA and solvent molecules are inserted only where needed—we avoid labeling the *y* axis as "energy". We could balance all equilibria but at considerable pedagogic cost.

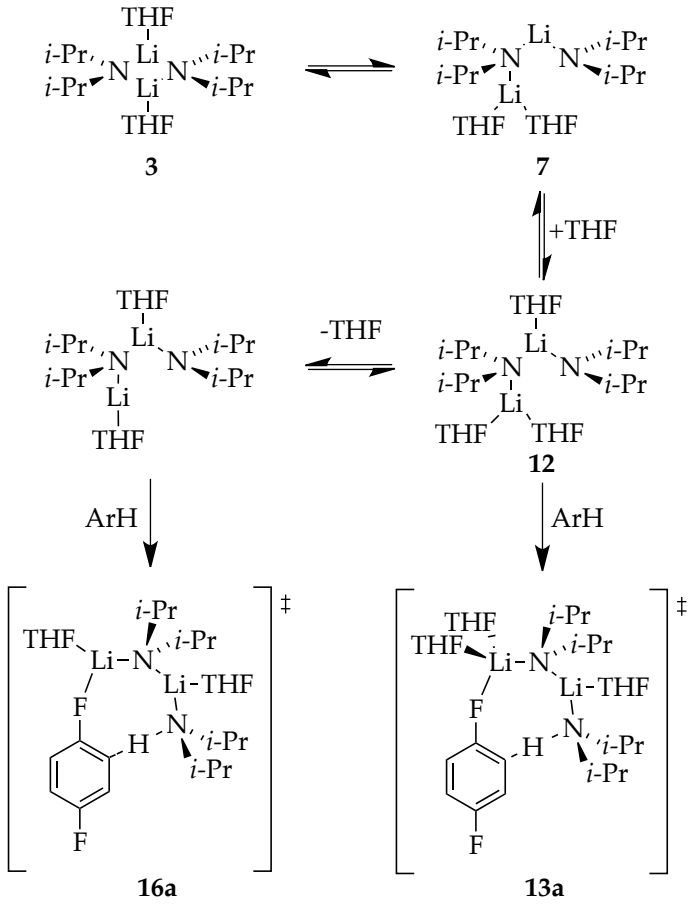
Summary. We opened the results with a reaction profile (Figure 1.1) showing the formation of ArLi and an LDA-ArLi mixed aggregate characterized as **2a** and **17**, respectively. Mixed aggregate **17** is only observable under highly specialized circumstances—low THF and high LDA concentrations—and is of little to no importance to our mechanistic thinking. Odd curvatures, however, are a consequence of a zeroth-order dependence in substrate overlayed with low levels of autocatalysis. The model used to generate the curves in Figure 1.1 stems from the rate studies.[39] We hasten to add that the quality of the fit is satisfying and consistent with the conclusions but should not be construed as confirmation.

The metalation of ArH by LDA dimer **3** (A_2S_2) proceeds via the $[A_2S_2]^‡$ rate-limiting transition structure **4** to give fleeting A_2S_2*-dimer-based intermediate **7**. A chemically tangible, computationally viable depiction of this dimer to open dimer conversion is shown in eq 10.[6,7] Ensuing autocatalysis accelerates the overall reaction via $A_2(ArLi)_n$ transition structure **5** (n = 2 or 3). Although the acceleration is moderate, it circumvents the $[A_2S_2]^‡$ barrier, revealing a well-defined tetramer-based $[A_4S_4]^‡$ barrier previously lurking over the horizon that does not formally include ArH in the transition structure. (We should clarify this statement by noting that we define "transition

structure" as the purely molecular depiction and the "transition state" as the energetically complete analog that includes all the necessary fragments including those not yet actively participating.[40]) The structures affiliated with $A_2(ArLi)_n$ and $[A_4S_4]^‡$ higher aggregates have been discussed previously in the context of $A_2(ArLi)_2$ ladder structures.[6] (If we are forced to accept an $A_2(ArLi)_3$ mixed-*pentamer*-based transition structure, we have no ideas worthy of sharing.) The role of A_4S_4 tetramers that we detected in the metalation rate studies was confirmed by NMR spectroscopic studies of LDA showing significant tetramer-based subunit exchange. We provided a calculated reaction coordinate for a tetramer-based *deaggregation* of LDA—dimer–to–tetramer–to–monomer—in Scheme 4. Although somewhat whimsical, the minima and maxima are legitimate by computational benchmarks.

We exploited large KIEs to detect or infer the existence of additional components of the reaction coordinate in Scheme 1. A higher $[A_2S_3]^‡$ barrier **9** is inferred from direct detection of $[A_2S_2(ArH)]^‡$ *and* $[A_2S_3(ArH)]^‡$ transition structures **13** and **16**, which correspond to the ortholithiations (proton/deuterium transfers) as shown in Scheme 5. We include the computationally viable A_2S_2*–$[A_2S_3]^‡$–A_2S_3* (**7**–**9**–**12**) transformation implicit in Scheme 1.

Scheme 5



The tetramer-based metalation of **15** could be inferred from the kinetically detectable $[A_4S_4]^‡$ aggregation event, yet $[A_4S_4(ArH)]^‡$-based lithiation was not kinetically visible and could be questioned in light of the previously[6] noted tetramer-based deaggregation to monomers.

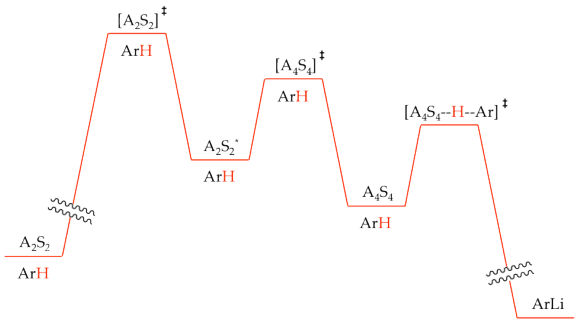
All reactions of LDA under non-equilibrium conditions studied to date have been accelerated by LiCl *at ppm levels* owing to the catalysis of dimer-monomer exchange.[6] Adding LiCl causes metalations of ArH to be immeasurably fast. The efficacy of LiCl relative to ArLi, in conjunction with saturation kinetics for both showing different rates at saturation, confirms that ArLi and LiCl catalyze different steps. Indeed, in contrast to

the ArLi-catalyzed dimer–dimer equilibration, LiCl diverts the ortholithiation of the less reactive ArD form through $[AS_3(ArD)]^‡$-based transition structure **10**. Open- and closed-monomer-based transition structures (eq 31) are computationally viable.

Direct detection of slow LDA subunit exchange. We have described NMR spectroscopic studies of the exchange of [^{6}Li]LDA and [^{6}Li,^{15}N]LDA. The most important finding is that LDA subunits exchange slowly *on laboratory time scales* at –78 °C consistent with the ortholithiation results. Direct rate studies of the subunit exchanges as well as complementary LDA coalescence studies implicated both dissociative (dimer-based) and associative (tetramer-based) exchange mechanisms—a satisfying result given that both are prominent in the lithiation rate studies. Extensive computational studies of the dissociative pathways had been published.[7] Scheme 4 provides insight to the tetramer-based events, although the computational studies were difficult as noted above. Overall, evidence that LDA associates to tetramer en route to monomers is both convincing and provocative.

What dictates rate limitation? This work calls out for a discussion of the basic principles underlying rate limitation.[41] Imagine the simplified scenario illustrated in Scheme 6 in which an A_2S_2 partial deaggregation is followed by an A_4S_4 tetramer and subsequent post-rate-limiting lithiation of ArH. We have chosen this particular sequence owing to its pedagogic value rather than its central importance. (The tetramer-based metalation was a minor contributor at best.) We further imposed the restriction that the relative barrier heights are similar and follow the order $[A_2S_2]^‡ > [A_4S_4]^‡ > [A_4S_4(ArH)]^‡$, which is consistent with a subset of the experimental results. We now present some concepts using a series of questions and answers.

Scheme 6



(1) How does the $[A_4S_4]^‡$ barrier influence the reaction rate and rate law? Conventional wisdom suggests that $[A_2S_2]^‡$ is the rate-limiting barrier, and $[A_4S_4]^‡$ is irrelevant, but that is not altogether correct. The existence of seemingly post-rate-limiting intermediate A_2S_2* imposes a barrier-weighted statistical factor on the rate. Once formed, A_2S_2* has <100% probability of proceeding to product. In the limit that $[A_2S_2]^‡$ and $[A_4S_4]^‡$ present barriers of equal height, that probability reduces to 50%. The rate law would also reflect barrier-weighted contributions from $[A_2S_2]^‡$ and $[A_4S_4]^‡$, including reaction orders that would be intermediate values rather than tidy integers. As the rate-limiting step shifts, so does the rate law.

(2) How do you peer beyond a rate-limiting step? There are isotopic labeling studies to probe post-rate-limiting steps through competition experiments (see part 6 for example).[30,42] More direct approaches either lower the obstructing barrier or elevate the subsequent barrier. Let's explore these latter strategies further. Recall that the energy diagrams are not static, but rather shift with changing concentrations of all participating species.

(3) How does substrate concentration influence reaction rates and mechanism? At high ArH concentration, the barrier height for metalation is low as drawn in Scheme 6,

and the metalation is post rate limiting. At lower concentrations, however, all minima and maxima drop relative to the $[A_4S_4\text{--H--Ar}]^{‡}$ barrier, rendering the metalation rate limiting. Using eq 37 as an alternative perspective, post-rate-limiting metalation occurs when $k_{-1} << k_2[\text{ArH}]$, and the intermediate denoted generically as A_mS_n is efficiently converted to ArLi with high fidelity. At low ArH concentrations, however, the trapping becomes inefficient, $k_{-1} >> k_2[\text{ArH}]$, and A_mS_n is in a fully established equilibrium with A_2S_2. A plot of rate versus [ArH] over a wide concentration range would display saturation kinetics. Although the rate-limiting metalations of ArH were too fast to observe, we noted saturation behavior under several circumstances with ArD (Figures 1.15 and 1.19). Deuteration, however, introduces enormous complexities (see part 6).

$$A_2S_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A_mS_n \xrightarrow{k_2[\text{ArH}]} \text{ArLi} \qquad (37)$$

(4) How would changing the concentration of LDA influence the rates? Elevated LDA concentration would promote the higher-order step by lowering the $[A_4S_4]^{‡}$ height relative to that of $[A_2S_2]^{‡}$, with the ironic effect of eliminating residual contributions of the tetramer-based step from the rate law. Viewed from the alternative perspective in eq 38, elevated LDA concentration imposes $k_2[A_2S_2] >> k_{-1}$ and renders the step corresponding to k_1 rate-limiting. By contrast, lowering the LDA concentration would raise $[A_4S_4]^{‡}$, causing $[A_4S_4]^{‡}$ to come into parity and eventually dominate $[A_2S_2]^{‡}$. Varying LDA concentration over the full range would afford a rate law that reflects the shifting rate-limiting step by showing a shift from second-order LDA dependence at low LDA concentrations to a first-order dependence at elevated concentrations.

Although we detected dimer- and tetramer-based metalations in the experiments above, the concentration range is too narrow to observe such a shift.[43] As a final note, the *relative* heights of the $[A_4S_4]^‡$ and $[A_4S_4(ArH)]^‡$ barriers do *not* change with LDA concentration. Consequently, changing the LDA concentration cannot bring the tetramer-based metalation into view.

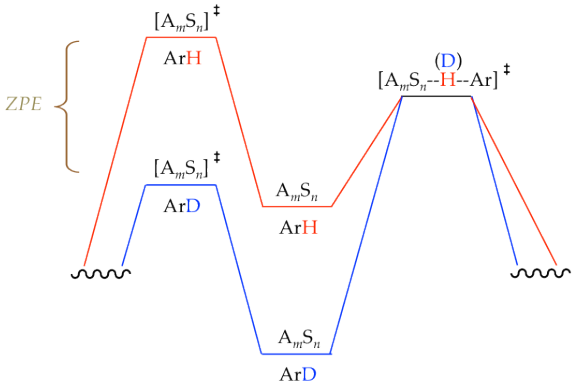
$$A_2S_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A_2S_2^* \xrightarrow{k_2[A_2S_2]} [A_4S_4]^‡ \qquad (38)$$

(5) What are the consequences of catalyzing the dimer-to-dimer conversion, circumventing $[A_2S_2]^‡$ in Scheme 6? This is precisely the effect of autocatalysis by ArLi. The short answer is that the rate-limiting step is shifted to transition structure $[A_4S_4]^‡$. To understand the role of catalysis let us consider the alternative perspective in eq 39. When $[A_2S_2]^‡$ is rate-limiting, catalysis of the forward step accelerates the formation of $A_2S_2^*$ and the overall reaction. At elevated catalyst loading, catalysis of the back reaction makes $k_{-cat}[cat] >> k_2[A_2S_2]$ with a consequent shift of the rate-limiting step to $[A_4S_4]^‡$. The kinetics would show saturation in catalyst (as in Figures 1.10 and 1.18) and an accompanying shift from first to second order in LDA. Here is the curious part: catalysis of the forward step is the source of acceleration whereas catalysis of the back reaction shifts the rate-limiting step.

$$A_2S_2 \underset{k_{-cat}[cat]}{\overset{k_{cat}[cat]}{\rightleftharpoons}} A_2S_2^* \xrightarrow{k_2[A_2S_2]} [A_4S_4]^‡ \qquad (39)$$

(6) How does isotopic substitution shift the rate-limiting step? Recall that the isotope effects are quite large, and the relative barrier heights for the different transition states cluster in a narrow energetic range. Scheme 7 shows barriers for the highly simplified and generic reaction coordinate with barriers for ArD superimposed on those for ArH. Of course, the core principle is that the rate depression through deuteration stems from a lower zero point energy (ZPE) in the ground state that is eliminated at the transition state. (Although tunneling in the transition structure is certainly possible—even probable—it does not change the model.[44]) When applied to sequential barriers in Scheme 7, ZPE also stabilizes the *preceding* transition state that includes both the $[A_mS_n]^‡$ and ArD components owing to net stabilization of ArD with the consequent shift to rate-limiting metalation, $[A_mS_n$--H(D)--Ar$]^‡$. Thus, the passive role of the arene ZPE in the non-metalation-based aggregation step shifts the rate-limiting step.

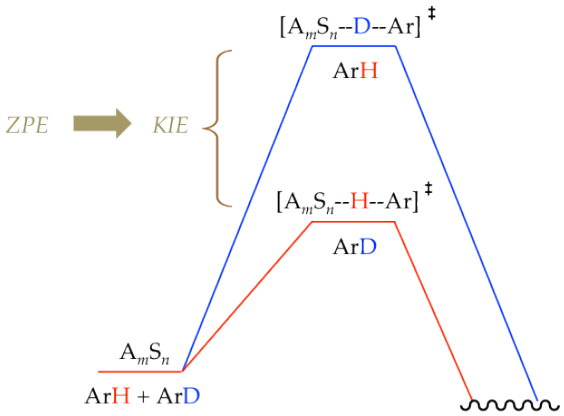
Scheme 7



(7) What are the origins of the competitive isotope effects and biphasic kinetics? Measurement of kinetic isotopes through competition of deuterated and protonated substrates necessarily leads to biphasic kinetics (Figures 1.14 and 1.20) if the metalation

step is post rate limiting. We are unaware of clean examples of such biphasic kinetics. A highly simplified model in Scheme 3 adequately fit the data using numerical integration. Biphasic kinetics ostensibly stem from efficient trapping by the more reactive protio form (ArH) first and by the deuterio form (ArD) only after the ArH is consumed, but this outcome is misleading as written. Imagine the competition of ArH and ArD represented in the idealized reaction coordinate diagram in Scheme 8. Note that ArH and ArD are both included in a single thermochemical depiction of the ground state. To a first approximation, the C–H and C–D stretches are lost in the transition state. The competitive isotope effect—preferential proton versus deuterium transfer—stems from the lower ZPE of ArD in the transition state. By using an ArH–ArD mixture not only in the vessel but also in the thermochemical diagram, we have arithmetically shifted the isotopic contribution of ZPE to the transition state. We return to this concept below.

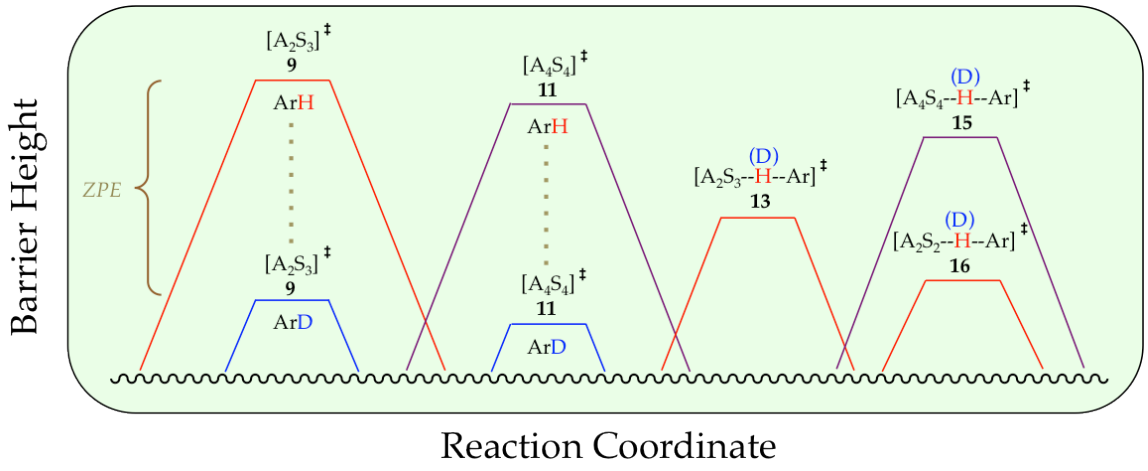
Scheme 8



(8) How does isotopic labeling divert a reaction through an entirely different reaction coordinate? Using catalyzed conditions we observed a tetramer-based $[A_4S_4]^‡$

rate-limiting step. Anticipating that deuteration would suppress the metalation rate and bring a tetramer-based metalation ($[A_4S_n(ArD)]^‡$) into view—an assertion that should feel charged with intellectual risk at this point—we were surprised to detect $[A_2S_2(ArD)]^‡$ and $[A_2S_3(ArD)]^‡$ (dimer-based) metalations. Let's strip away the inordinate complexities of Schemes 1 and 2 by gazing at just the relative barrier heights (Scheme 9). In short, the relative energies of $[A_2S_2]^‡$ and $[A_4S_4]^‡$ aggregation events do not correlate with the relative energies of the $[A_2S_2(ArD)]^‡$, $[A_2S_3(ArD)]^‡$, and $[A_4S_n(ArD)]^‡$ metalations. In fact, there is no reason whatsoever to expect such a correlation of the two fundamentally different processes such as aggregation and metalation. This is easy to say in retrospect. By shifting the rate-limiting step, fleeting intermediates A_2S_2*, A_2S_3, and A_4S_4 are all formed at equilibrium with starting LDA dimer A_2S_2, causing the choice of pathway to derive exclusively from the relative facilities of the proton transfers.

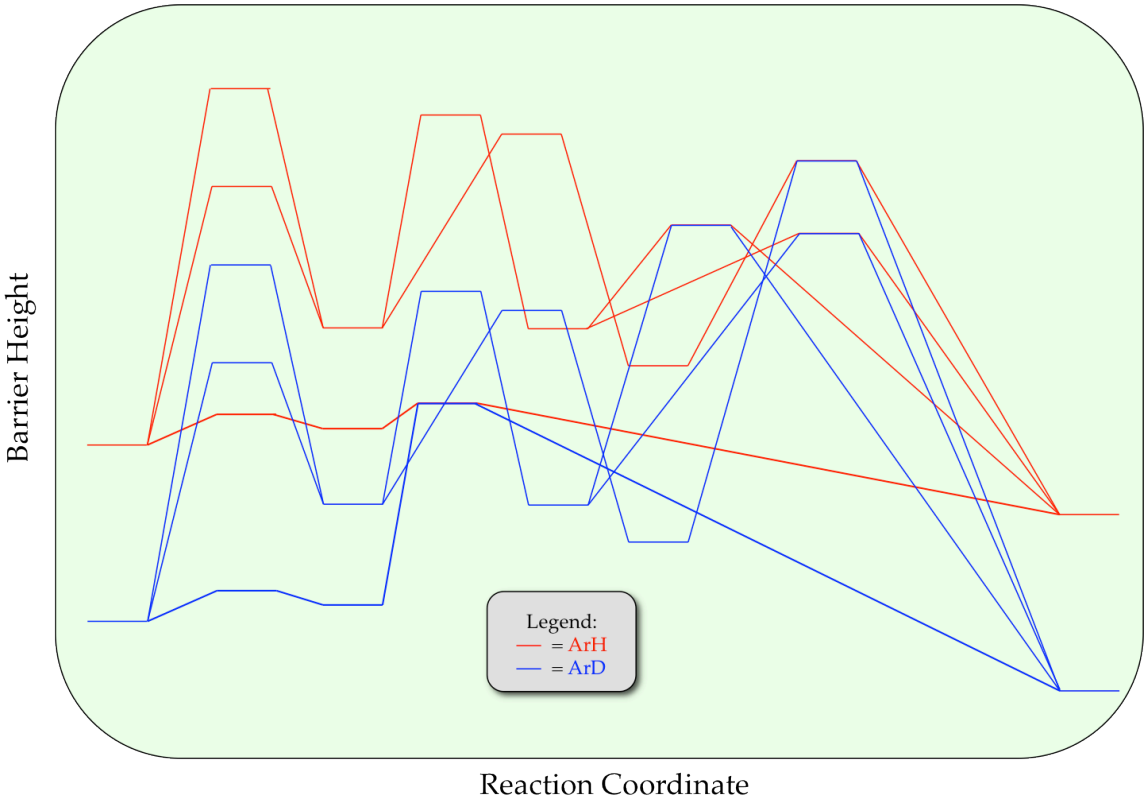
Scheme 9



(9) Can the reaction coordinate diagrams corresponding to reaction of ArH (Scheme 1) and ArD (Scheme 2) be presented as a single, self-consistent, coherent

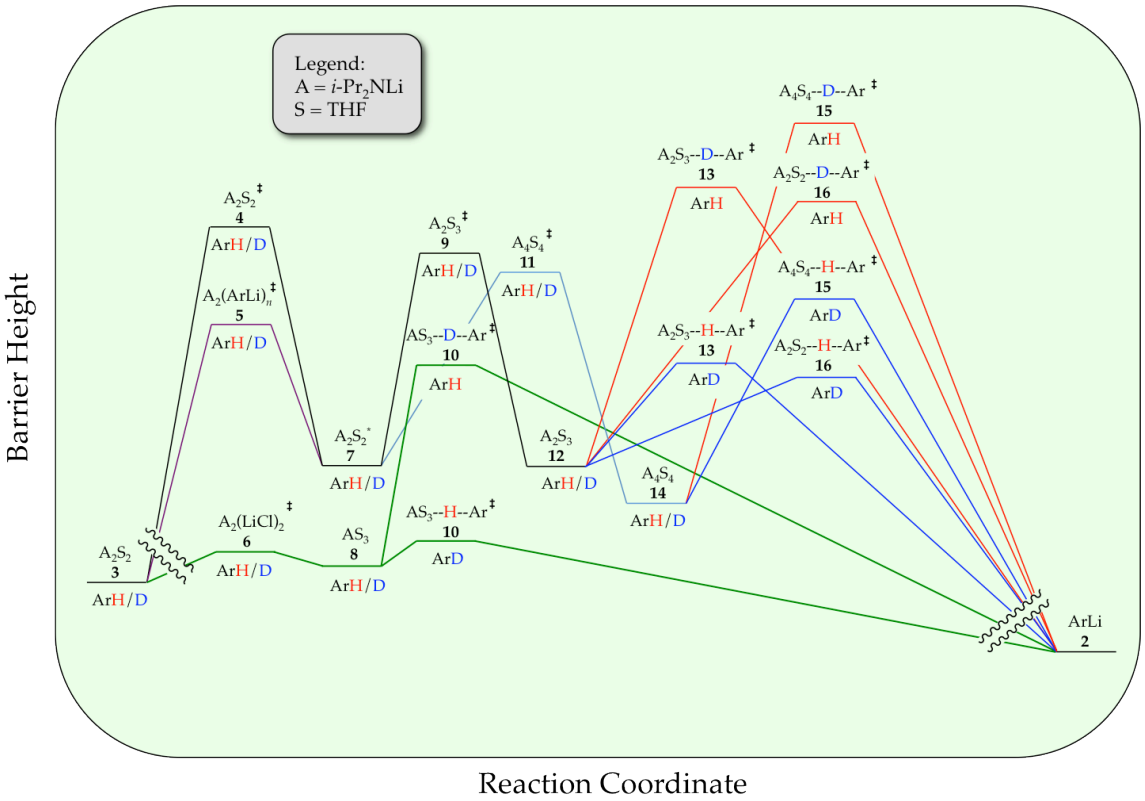
reaction coordinate diagram? In short, they sure better be superimposable, and indeed such a depiction is self-consistent (Scheme 10). As to whether the picture is *coherent*, we have our doubts, and adding labels to Scheme 10 would likely not help.

Scheme 10



A unified depiction, however, is not impossible. The problem with superimposing Schemes 1 and 2 to create Scheme 10 is that there are *six* distinct minima and *five* maxima in which contributions from ZPE create different energies corresponding to ArH (red) and ArD (blue)—12 minima and 14 maxima in total. Taking a cue from the discussion of the competitive isotopic studies (part 7) and from shifting the ZPEs to only *four* transition states, we offer a fully labeled variant as Scheme 11 with no further comment except to marvel at the finished product.

Scheme 11



Conclusions

Metalations of many substrates, including 1,4-difluorobenzene, using LDA/THF at –78 °C exhibit remarkable rate behaviors owing to the coincidence of barrier heights for aggregation events and metalations. Complexity aside, there are real consequences. Trace impurities such as LiCl can accelerate metalations moderately or massively (up to 100-fold), depending on the substrate. Commercial LDA and LDA generated in situ are *very* different—a difference that can be completely eliminated by adding traces of Et_3NHCl as a LiCl precursor to commercial LDA.[6,45] But the consequences are more subtle than that. Given the hypersensitivity of the choice of substrate to the ensuing mechanism, non-equilibrating aggregates cause erratic regio- and stereoselectivities. Autocatalysis by products (such as aryllithium **2**) alter the mechanisms. Such feedback

loops cause regioselectivities to vary with percent conversion and with the number of equivalents of LDA used.[6,46]

The metalation of ArH has provided the best view to date of how rate-limiting aggregation and solvation events involved in LDA deaggregation can dictate rates and mechanisms. We found, for example, that lithium salts can catalyze different steps involved in the deaggregation. Aryllithium **2** catalyzes LDA closed-to-open dimer conversion, whereas LiCl catalyzes dimer-to-monomer conversion. LDA-tetramer-based chemistry keeps surfacing and continues to baffle us.

This work offered a plethora of examples of saturation kinetics arising from shifting rate-limiting steps, often superimposing saturation behaviors. The plotline that emerged in many ways is more about understanding rate limitation and how to probe specific steps along a reaction coordinate than about organolithium chemistry per se.

We also have made some noteworthy observations that received scant attention. The Job plots to study autocatalysis represent exceedingly rare examples of Job plots used to study reaction kinetics.[26] There are a multitude of opportunities being overlooked by the chemistry community. Although measured competitive KIEs reveal highly characteristic biphasic kinetics, we must confess to being unaware of others exploiting such diagnostic behavior. Overall, the methodological developments required to study this remarkably complex organometallic problem are as poignant as the chemistry itself.

Experimental Section

Reagents and solvents. THF, Et_2O, and hexane were distilled from blue or purple solutions containing sodium benzophenone ketyl. The hexane contained 1% tetraglyme to dissolve the ketyl. $Et_3N{\cdot}HCl$ was recrystallized from THF/2-propanol.[45] Literature procedures[47] were modified to prepare LDA as a LiCl- and ligand-free solid.[6d] Solutions of LDA were titrated using a literature method.[48]

IR spectroscopic analyses. IR spectra were recorded using an in situ IR spectrometer fitted with a 30-bounce, silicon-tipped probe. The spectra were acquired in 16 scans at a gain of 1 and a resolution of 4 cm^{-1}. A representative reaction was carried out as follows: The IR probe was inserted through a nylon adapter and O-ring seal into an oven-dried, cylindrical flask fitted with a magnetic stir bar and a T-joint. The T-joint was capped by a septum for injections and a nitrogen line. After evacuation under full vacuum, heating, and flushing with nitrogen, the flask was charged with LDA (108 mg, 1.01 mmol) in THF and cooled in a dry ice–acetone bath prepared with fresh acetone. LiCl was added via a THF stock solution prepared from $Et_3N{\cdot}HCl$ and LDA. After recording a background spectrum, we added arene **1** (0.76 mmol) with stirring. For the most rapid reactions, IR spectra were recorded every 3 s with monitoring of the absorbance at 1510 cm^{-1} over the course of the reaction.

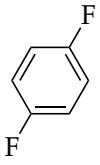
NMR spectroscopic analyses. All NMR samples were prepared using stock solutions and sealed under partial vacuum. Standard ^{6}Li, ^{13}C, ^{15}N, and ^{19}F NMR spectra were recorded on a 500 MHz spectrometer at 73.57, 125.79, 50.66, and 470.35 MHz, respectively. The ^{6}Li, ^{13}C, and ^{15}N resonances are referenced to 0.30 M [^{6}Li]LiCl/MeOH at –90 °C (0.0 ppm), the CH_2O resonance of THF at –90 °C (67.57 ppm), and neat Me_2NEt at –90 °C (25.7 ppm), respectively.

2,3,5,6-tetradeutero-1,4-difluorobenzene (1–d_4, ArD). A 10.6 M solution of *n*-BuLi in hexane (4.8 mL, 50.1 mmol) was added via syringe pump to a solution of 1,4-difluorobenzene (**1**, ArH, 5.0 mL, 48.6 mmol) in 150 mL of dry THF at –78 °C under argon over 20 min. The solution was stirred for an additional 25 min. MeOD (2.05 mL, 50.1 mmol) was added via syringe pump over a period of 20 min. The mixture was allowed to stir for 30 min. *Without any intervening workups* sequential additions of 1.1 equiv *n*-BuLi and 1.1 equiv MeOD were repeated five additional times. A final aliquot of MeOD (10 mL, 5.0 equiv) was added to quench the reaction fully. After the mixture was allowed to warm to room temperature, the pH was adjusted to 1.0 with 4.0 M aq HCl to dissolve all lithium salts. Organic and aqueous layers were separated, and the organic layer was extracted with additional cold 0.020 M HCl to remove excess THF. Extraction was stopped when the total organic volume was approximately 10 mL. The organic layer was dried over Na_2SO_4 and distilled. The product was collected as a colorless liquid (1.75 g, 15.3 mmol) via distillation at 88 °C in 31.5% yield. ^{13}C NMR δ 158.8 (dqn, $^1J_{C–F}$ = 243.0 Hz, $^2J_{C–D}$ = 1.7 Hz), 116.10 (tdd, $^1J_{C–D}$ = 25.2 Hz, $^2J_{C–F}$ = 19.4 Hz, $^3J_{C–F}$ = 13.2 Hz); LRMS: 118.1 *m*/*z* shows 98% **1-d_4**.

Numeric integrations. The time-dependent concentration plots obtained using IR spectroscopy were fit to mechanistic models expressed by a set of differential equations. The curve-fitting operation minimizes chi-square in searching for the coefficient values (rate constants). The Levenberg–Marquardt algorithm[49] was used for the chi-square minimization and is a form of nonlinear, least-squares fitting. The fitting procedure implements numeric integration based on the backward differentiation formula[50] to solve the differential equations, yielding functions describing concentration versus time.

Chapter 1 Appendix

Structures



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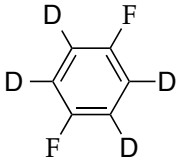
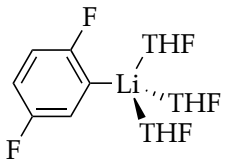


1-d_4



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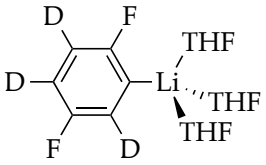
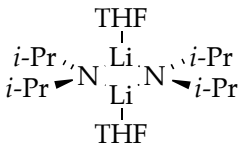


2-d_3



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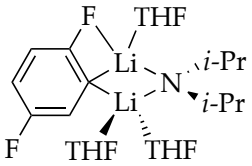


17

Part 1: Experimental Procedures

2,3,5,6-tetradeutero-1,4-difluorobenzene (1-d_4) A 10.6 M solution of *n*-BuLi in hexane (4.8 mL, 50.1 mmol) was added via syringe pump to a solution of 1,4-difluorobenzene (5.0 mL, 48.6 mmol) in 150 mL of dry THF at –78 °C under argon over a period of 20 min. The solution was stirred for an additional 25 min. MeOD (2.05 mL, 50.1 mmol) was added via syringe pump over a period of 20 min. The mixture was allowed to stir for 30 min. The process of sequential addition of 1.1 equiv *n*-BuLi and 1.1 equiv MeOD was repeated 5 more times. A final aliquot of MeOD (10 mL, 5.0 equiv) was added to fully quench the reaction. After the mixture was allowed to warm to room temperature, the pH was adjusted to 1.0 with 4.0 M aq HCl to dissolve all lithium salts. Organic and aqueous layers were separated, and the organic layer was extracted with more cold 0.02 M HCl to remove excess THF. Extraction was stopped when the total organic volume was approximately 10 mL. The organic later was dried over Na_2SO_4 and distilled. The product was collected by distillation at 88 ºC as a colorless liquid (1.75 g, 15.3 mmol) in 31.5% yield. ^{13}C NMR δ 158.83 (dqn, $^1J_{C\text{-}F}$ = 243.0 Hz, $^2J_{C\text{-}D}$ = 1.7 Hz), 116.10 (tdd, $^1J_{C\text{-}D}$ = 25.2 Hz, $^2J_{C\text{-}F}$ = 19.4 Hz, $^3J_{C\text{-}F}$ = 13.2 Hz); LRMS: 118.1 *m*/*z*.

Part 2: NMR Spectroscopic Studies

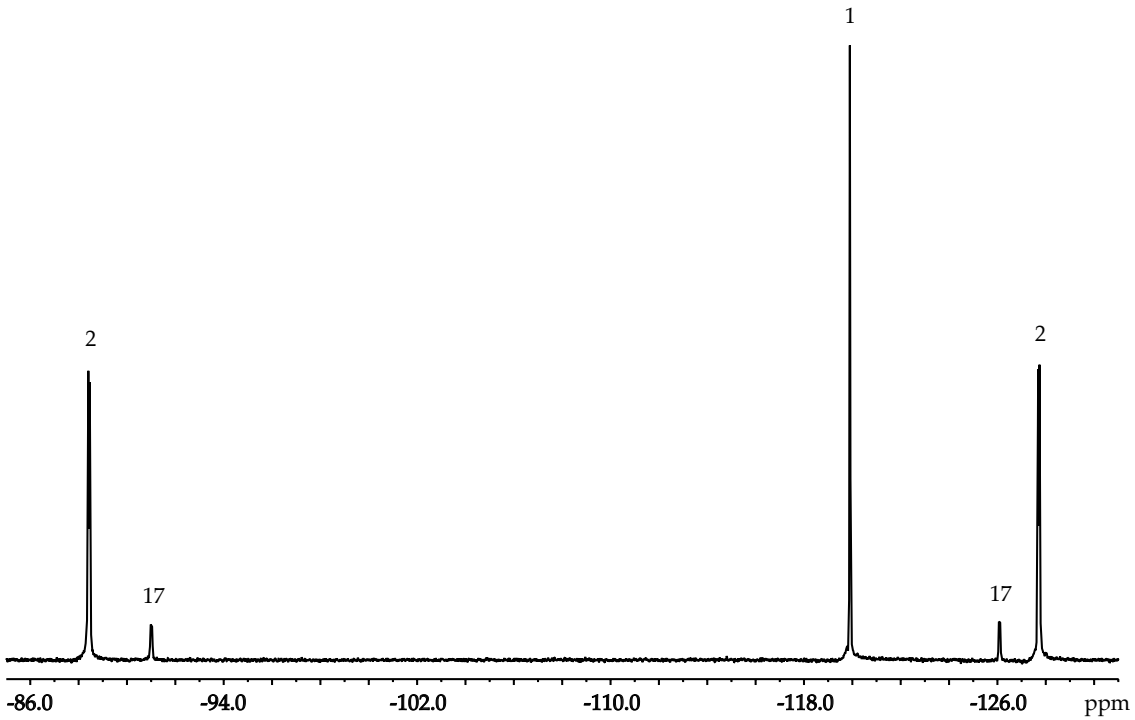


Figure A1.1. ^{19}F NMR spectrum of LDA (0.10 M) with **1** (0.050 M) and diisopropylamine (0.050 M) in 3.49 M THF/hexanes at –78 °C. **1:** δ -119.90 (s). **2:** δ -127.71 (d, $^{5}J_{F\text{-}F}$ = 31.6 Hz), -88.43 (d, $^{5}J_{F\text{-}F}$ = 31.6 Hz). **17:** δ -126.09 (d, $^{5}J_{F\text{-}F}$ = 31.0 Hz), -91.01 (d, $^{5}J_{F\text{-}F}$ = 31.0 Hz).

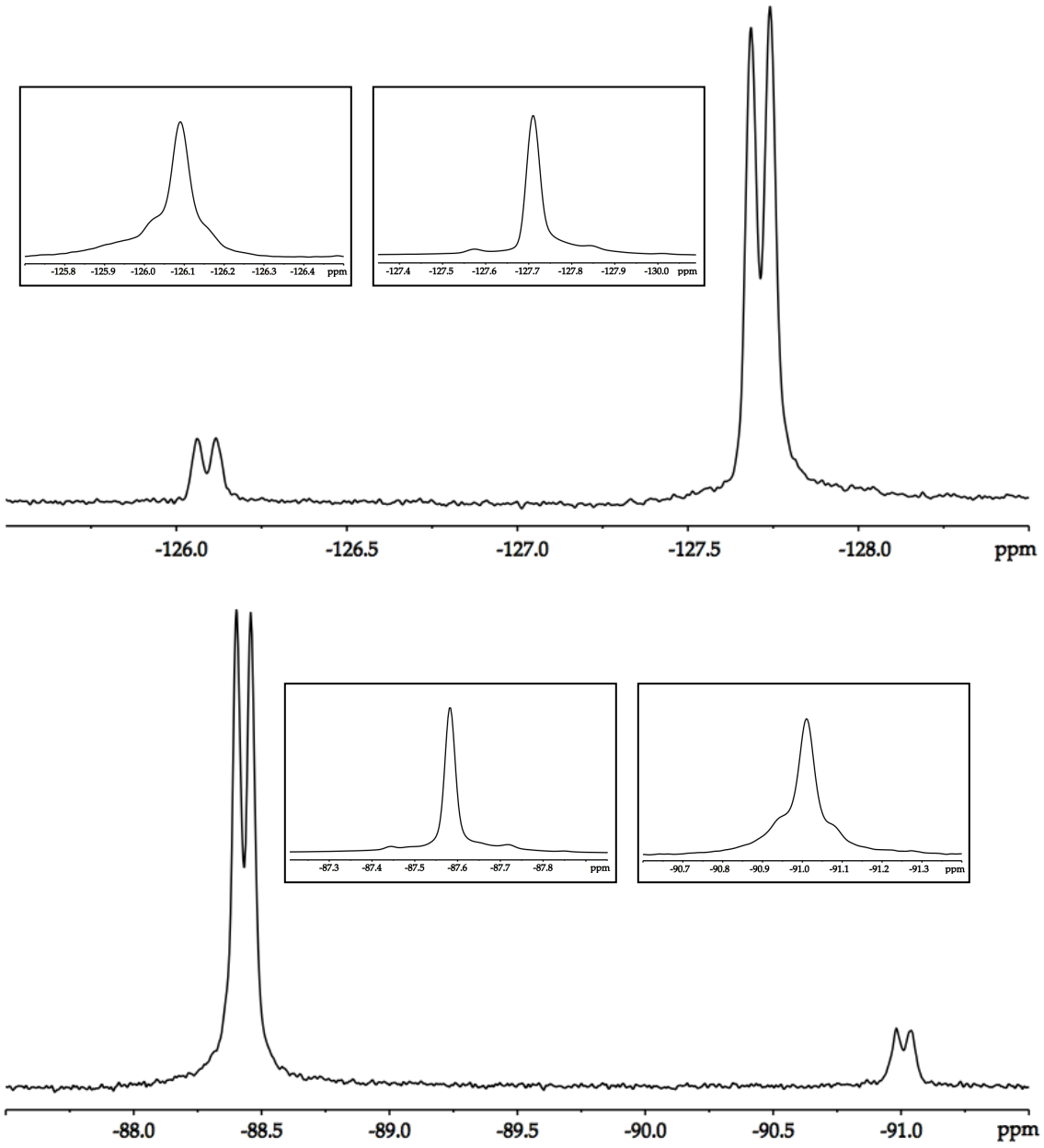


Figure A1.2. Expansion of ^{19}F NMR spectrum showing four sets of doublets for **2** and **17.** The five-bond ^{19}F –^{19}F coupling was confirmed by single-frequency ^{19}F decoupling (inserts).

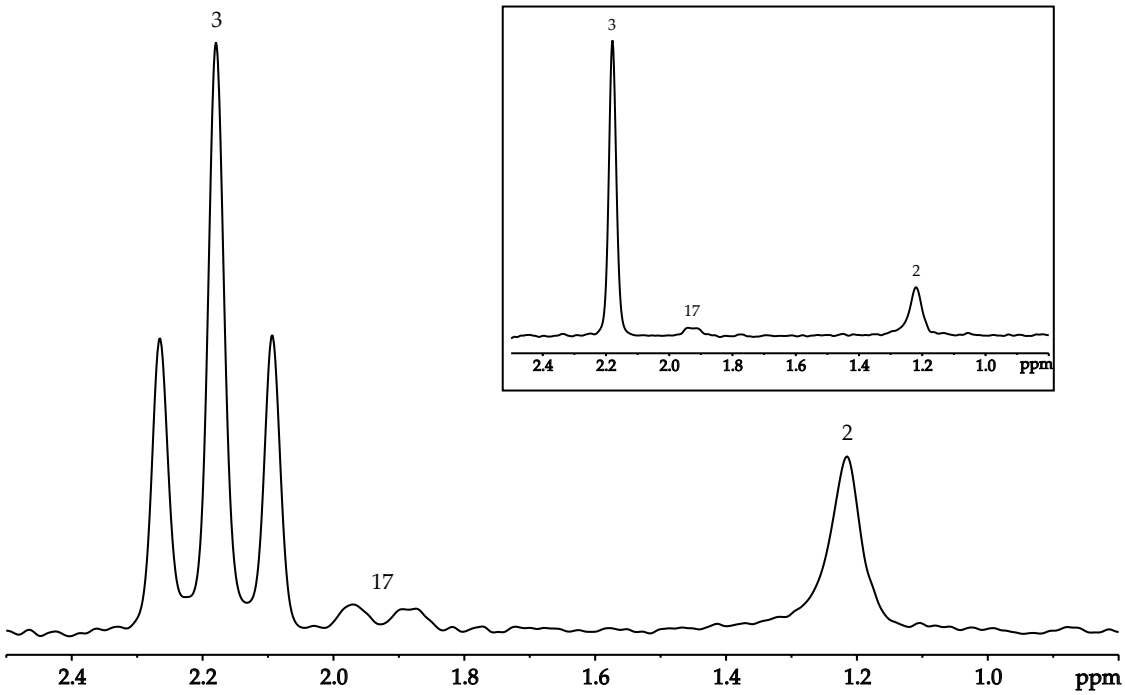


Figure A1.3. ^{6}Li NMR spectrum of [^{6}Li,^{15}N]LDA (0.10 M) and **1** (0.02 M) in 2.37 M THF/hexanes recorded at –78 °C. **2**: δ 1.22 (s). **17**: δ 1.93 (d, $^{1}J_{\text{Li-N}}$ = 5.1 Hz). **3**: δ 2.18 (t, $^{1}J_{\text{Li-N}}$ = 5.0 Hz). The insert shows ^{15}N decoupled ^{6}Li NMR spectrum. Resonances of **3** and **17** are reduced to singlets.

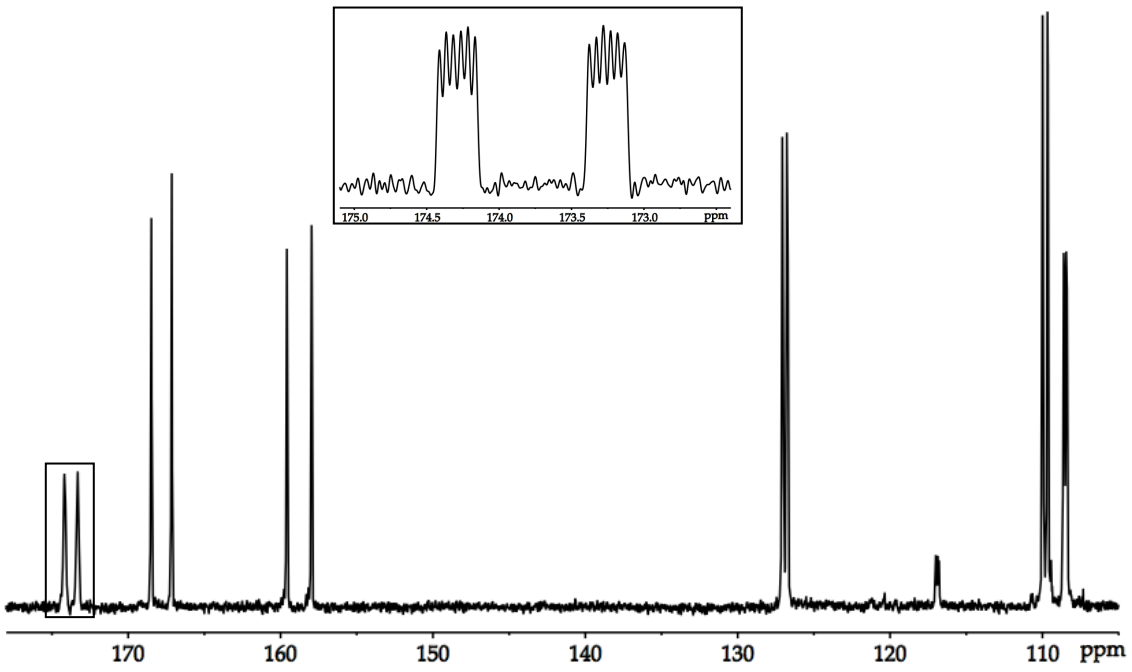


Figure A1.4. $^{13}C\{^{1}H\}$ NMR spectrum of **2** generated from **1** (0.30 M) with [^{6}Li]LDA (0.40 M) in 12.2 M THF-d_8 at –105 °C: δ 173.75 (ddt, $^{2}J_{C\text{-}F}$ = 130.2 Hz, $^{3}J_{C\text{-}F}$ = 18.6 Hz, $^{1}J_{C\text{-}Li}$ = 6.0 Hz,), 167.81 (d, $^{1}J_{C\text{-}F}$ = 201.7 Hz), 158.77 (d, $^{1}J_{C\text{-}F}$ = 244.7 Hz), 126.90 (dd, $^{2}J_{C\text{-}F}$ = 44.8 Hz, $^{3}J_{C\text{-}F}$ = 8.8 Hz), 109.82 (dd, $^{2}J_{C\text{-}F}$ = 49.3 Hz, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 108.50 (dd, $^{2}J_{C\text{-}F}$ = 25.5 Hz, $^{3}J_{C\text{-}F}$ = 7.2 Hz).

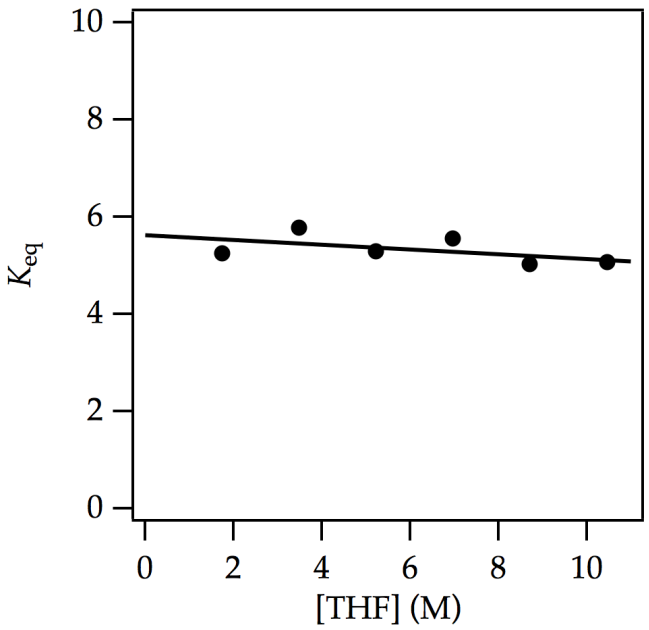


Figure A1.5. Plot of K_{eq} (derivation 2) versus [THF] in hexanes cosolvent for the equilibration of aryllithium **18** (0.025 M) and arene **1** (0.025 M) measured by ^{19}F NMR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to $y = a$[ArH] + b. [a = 5.6± 0.2, b = (-5 ± 4) x 10^{-2}]

[THF] (M)	y_1
1.74	5.26
3.48	5.78
5.23	5.29
6.97	5.55
8.71	5.02
10.46	5.06

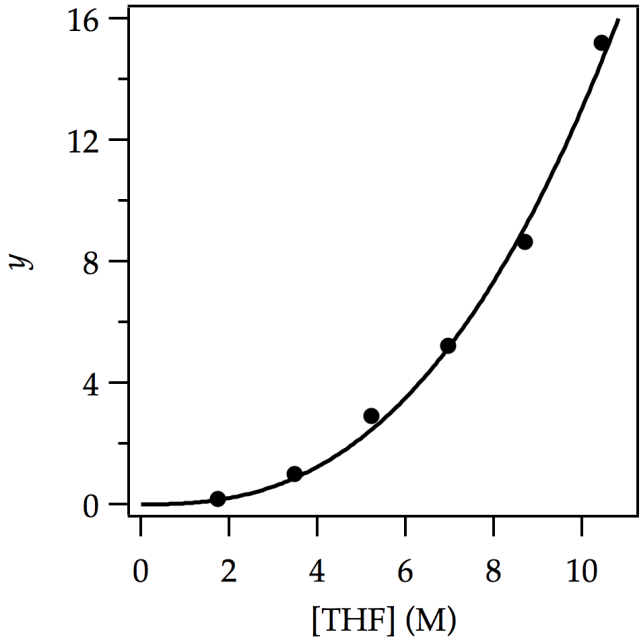


Figure A1.6. Plot of y (derivation 1) versus [THF] in hexanes cosolvent for the ortholithation of **1** (0.05 M) with LDA (0.10 M) in the presence of added diisopropylamine (0.050 M) measured by ^{19}F NMR at –78 °C. The curve depicts an unweighted least-squares fit to $y = a[\text{THF}]^n$. [$a = (0.03 \pm 0.01) \times 10^{-2}$, $n = 2.6 \pm 0.2$]

[THF] (M)	y_1 (M)
1.74	0.176
3.48	1.01
5.23	2.91
6.97	5.22
8.71	8.65
10.46	15.2

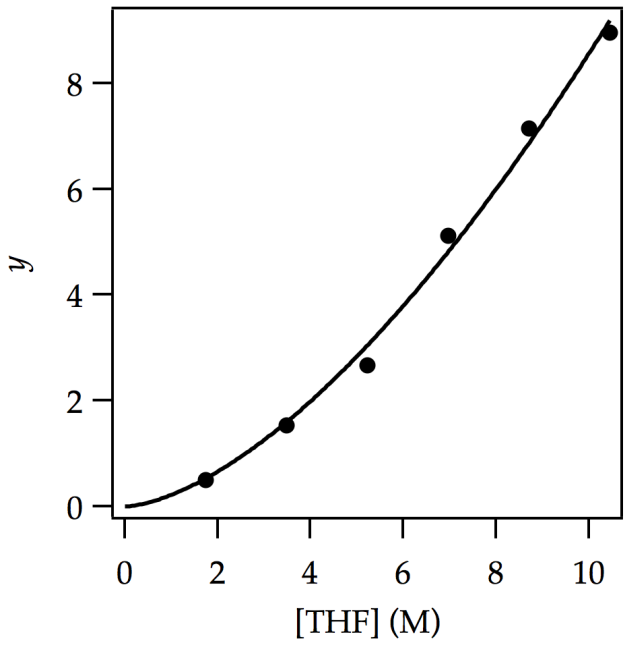


Figure A1.7. Plot of y (eq 8 in manuscript) versus [THF] in hexanes cosolvent for the ortholithation of **1** (0.050 M) with LDA (0.10 M) in the presence of diisopropylamine (0.05 M) measured by ^{19}F NMR at –78 °C. The curve depicts an unweighted least-squares fit to $y = a[\mathrm{THF}]^{4-n}$. [$a = 0.21 \pm 0.05$, $n = 2.4 \pm 0.1$]

[THF] (M)	y_1 (M)
1.74	0.499
3.48	1.52
5.23	2.67
6.97	5.12
8.71	7.14
10.46	8.96

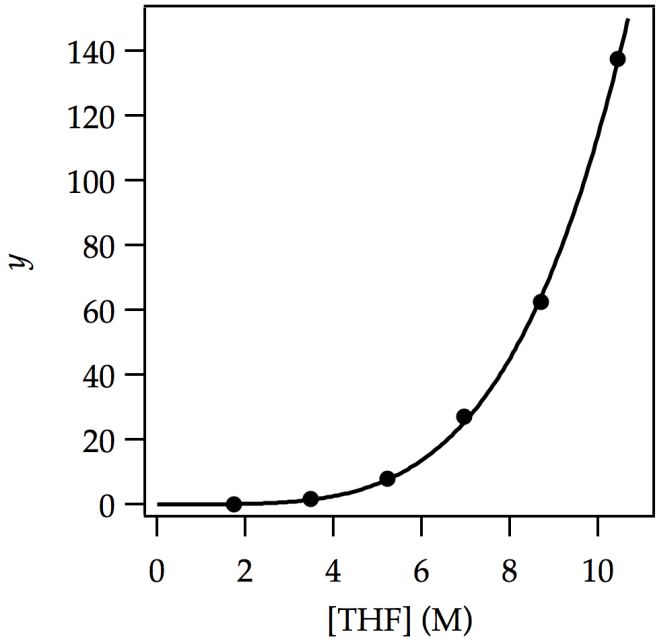


Figure A1.8. Plot of y (derivation 3) versus [THF] in hexanes cosolvent for the ortholithation of **1** (0.05 M) with LDA (0.10 M) in the presence of diisopropylamine (0.05 M) measured by ^{19}F NMR at –78 °C. The curve depicts an unweighted least-squares fit to $y = a[\text{THF}]^z$. [$a = (8 \pm 1) \times 10^{-3}$, $z = 4.16 \pm 0.08$]

[THF] (M)	y_1 (M)
1.74	9.584
3.48	1.606
5.23	7.976
6.97	27.10
8.71	62.43
10.46	137.4

Part 3: Rate Studies

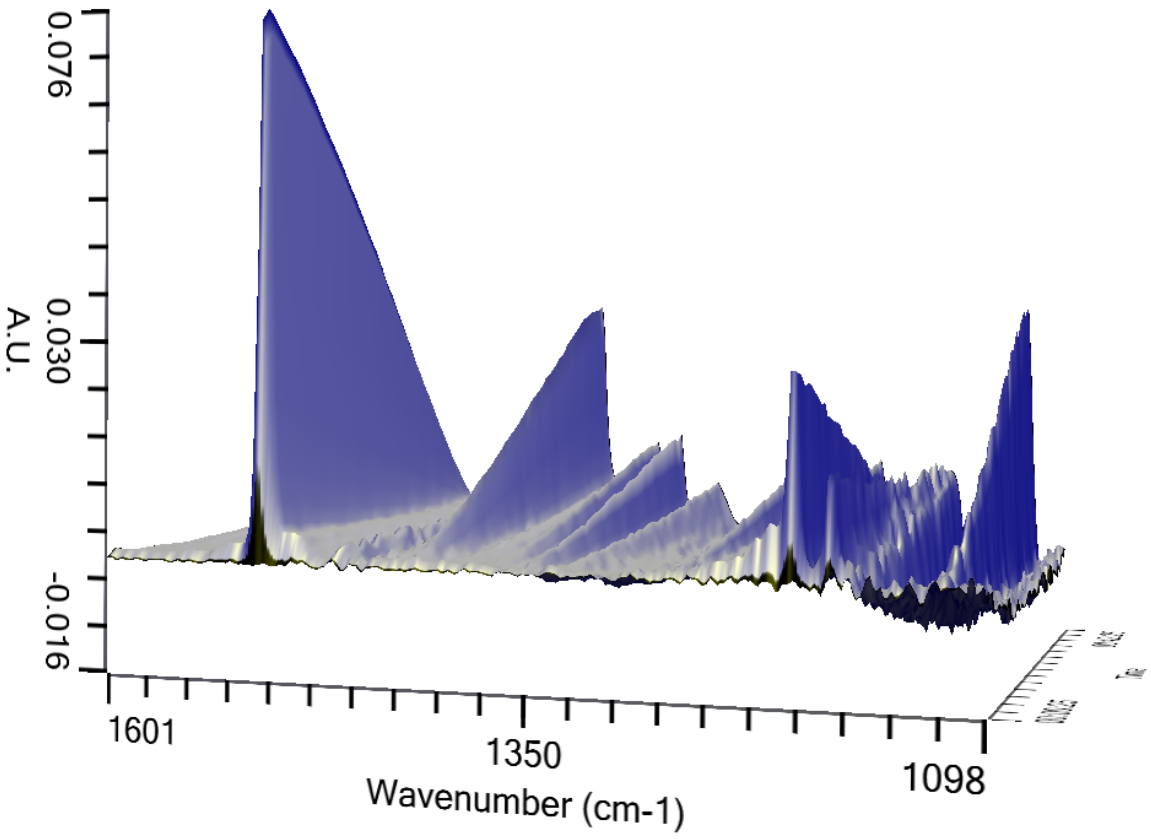


Figure A1.9. Representative in situ IR traces for the ortholithiation of **1** (0.020 M) by LDA (0.12 M) in THF at –78 °C. IR absorptions for compounds **1** and **2** and their associated isotopomers are listed below. The IR spectra were deconvoluted using ConcIRT®.

1: 1510 cm^{-1}, 1461 cm^{-1}, 1203 cm^{-1}, 1184 cm^{-1}
2: 1586 cm^{-1}, 1551 cm^{-1}, 1421 cm^{-1}, 1380 cm^{-1}, 1363 cm^{-1}, 1279 cm^{-1}, 1223 cm^{-1}, 1125 cm^{-1}

1-d_4: 1428 cm^{-1}, 1136 cm^{-1}, 1121 cm^{-1}
2-d_3: 1381 cm^{-1}, 1342 cm^{-1}, 1318 cm^{-1}, 1257 cm^{-1}, 1218 cm^{-1}, 1186 cm^{-1}

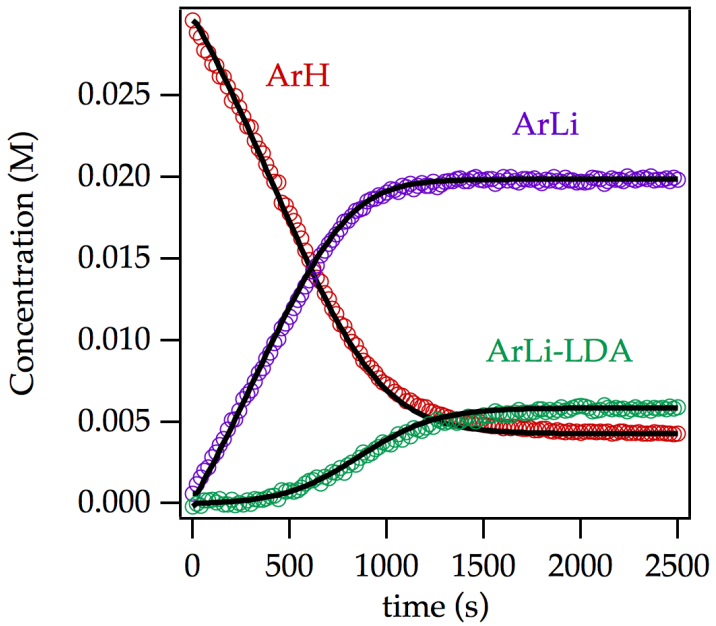


Figure A1.10. Time-dependent concentrations measured by ^{19}F NMR spectroscopy using 0.10 M LDA and **1** in 3.05 M THF at –65 °C. Legend: ArH = **1**; ArLi = **2**; ArLi-LDA = **17**. The curves represent a parametric fit to reference 39 in the manuscript.

Numerical best-fit parameters:

$k_1 = (2.08 \pm 0.02) \times 10^{-4}$
$k_{-1} = 0.2$
$k_2 = 5 \times 10^{-6}$
$k_{-2} = 90$
$k_3 = (1.5 \pm 0.8) \times 10^{4}$
$k_{-3} = (8 \pm 6) \times 10^{2}$
$k_4 = 16.8 \pm 0.8$
$k_{-4} = (8.7 \pm 0.6) \times 10^{-2}$
$k_5 = (8 \pm 3) \times 10^{3}$
$k_{-5} = 11 \pm 4$
$k_6 = (1.18 \pm 0.04) \times 10^{-2}$
$k_{-6} = (k_{-1}k_6)/k_1$

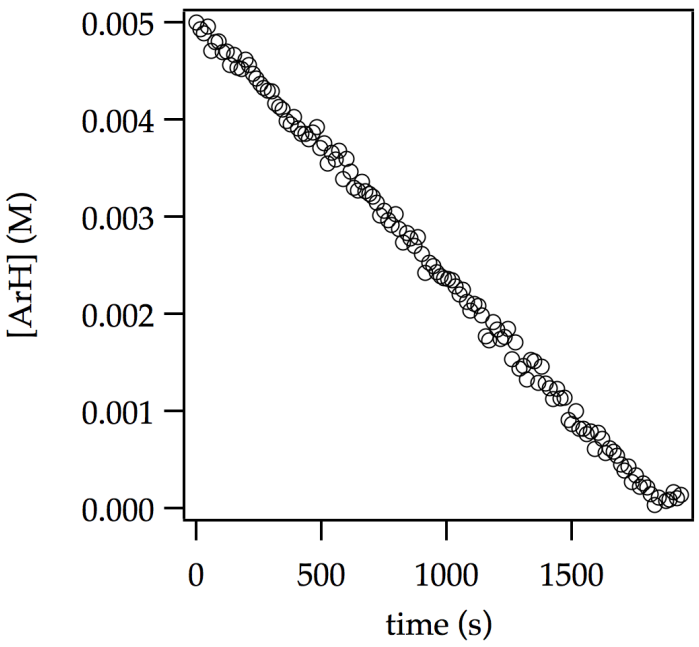


Figure A1.11. Representative plot showing linear decay for the ortholithiation of **1** (0.005 M) with LDA (0.10 M) in 12.2 M THF monitored using IR spectroscopy at –78 °C.

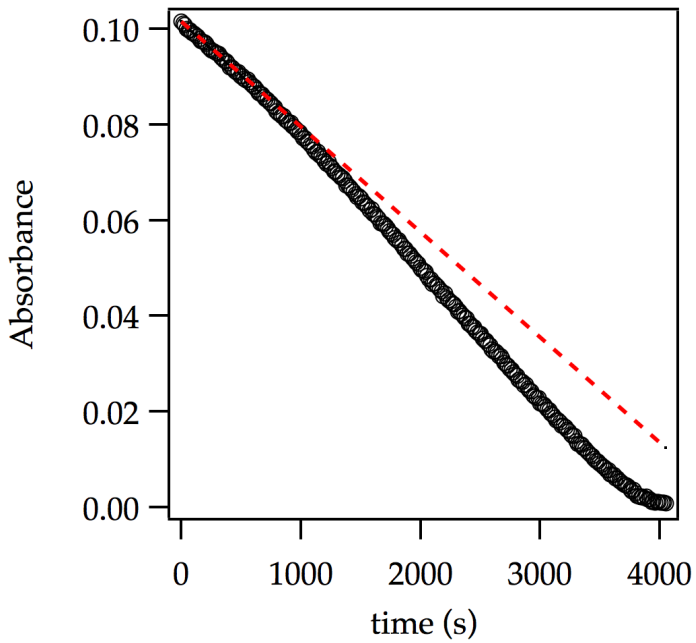


Figure A1.12. Representative plot showing sigmoidal decay for the ortholithiation of **1** (0.020 M) with LDA (0.10 M) in 12.2 M THF monitored with IR spectroscopy at –78 °C. The red dotted line depicts the time-dependent linear decay extrapolated from initial rate in the absence of autocatalysis.

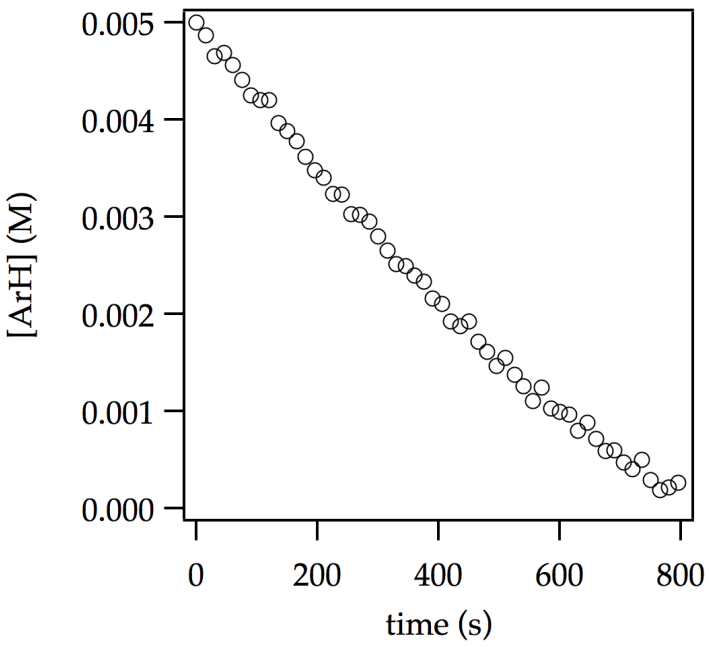


Figure A1.13. Representative plot showing [**1**] vs time for the ortholiation of **1** (0.005 M) with LDA (0.10 M) and ArLi (0.02 M) in THF (12.2 M) monitored with IR spectroscopy at –78 °C.

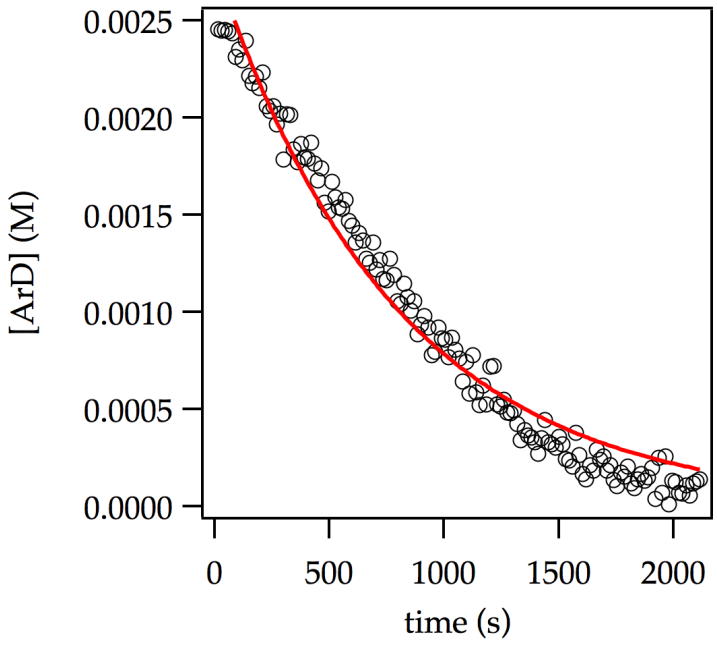


Figure A1.14. Representative plot showing poor exponential fit (red curve) to the decay for ortholithiation of **1-d_4** (0.0025 M) with LDA (0.10 M) in THF (12.2 M) monitored with IR spectroscopy at –78 °C.

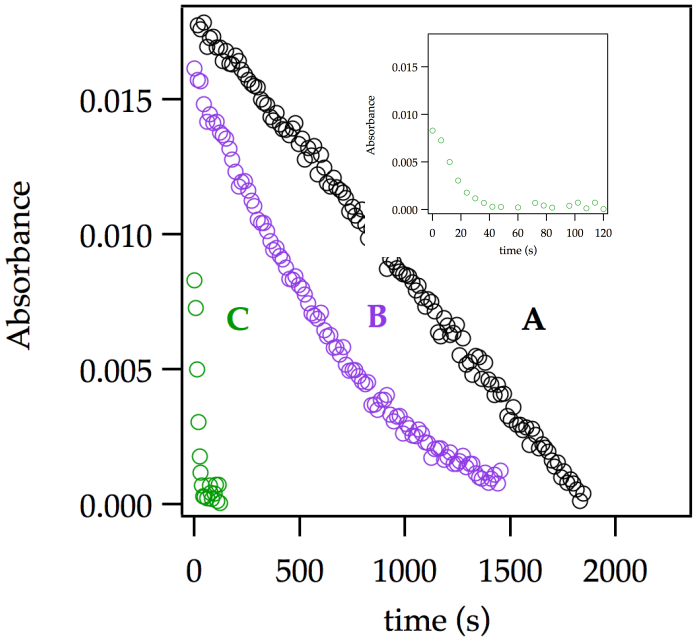


Figure A1.15. Representative plot showing the absorbance of **1** versus time for the ortholithiation of **1** (0.0050 M) with LDA (0.10 M) in THF (12.2 M) at –78 °C (curve A). Curve B shows the decay under the same conditions as in A but with 0.020 M ArLi. After the lithiation was complete, 0.0010 M LiCl was added and a second aliquot was injected into this mixture (curve C; see inset for expansion). Reactions were monitored with IR spectroscopy.

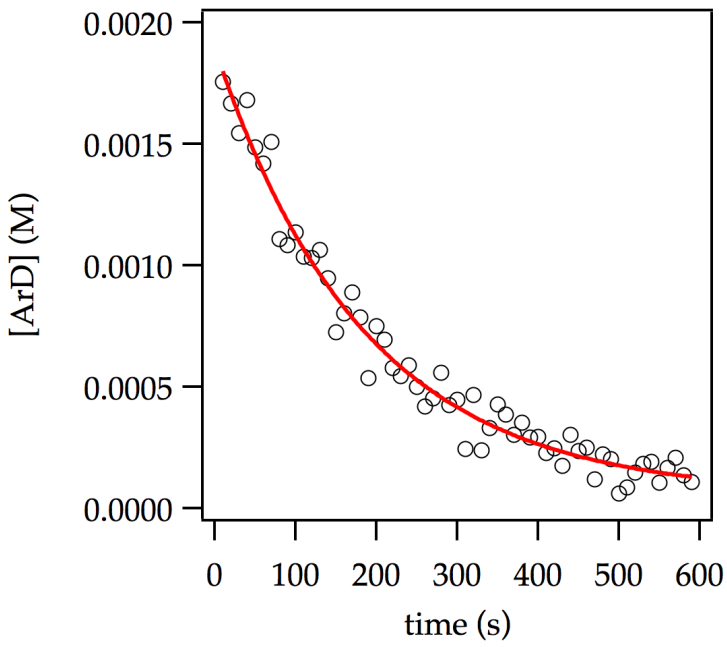


Figure A1.16. Representative plot showing exponential decay for the ortholithiation of **1**-d_4 (0.002 M) with LDA (0.25 M) in 12.2 M THF monitored with IR spectroscopy at –78 °C.

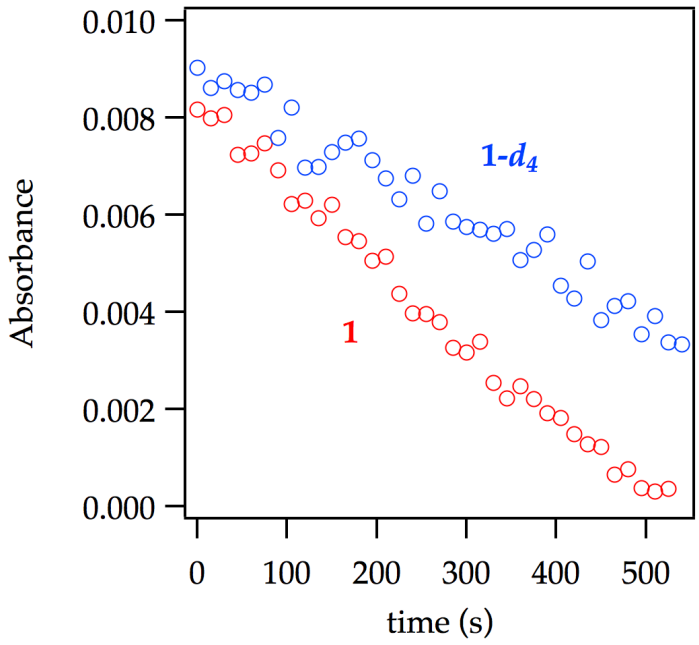


Figure A1.17. Ortholithiation of **1** (0.0025 M) and **1**-d_4 (0.0025 M) with LDA (0.10 M) in THF (12.2 M) at –78 °C (measured separately). Monitoring the initial rates of both decays by IR spectroscopy afford $k_H/k_D = 1.5$.

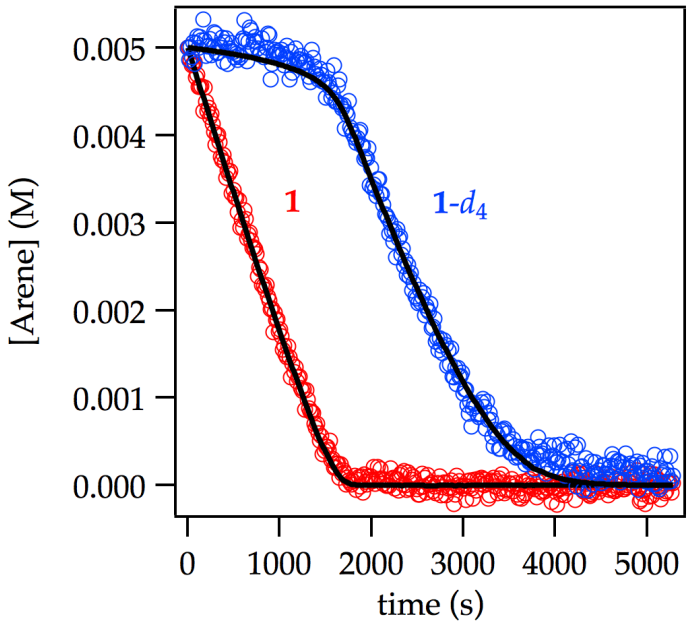


Figure A1.18. Competitive ortholithiation of **1** (0.005 M) and **1-*d*$_4$** (0.005 M) with LDA (0.10 M) in THF (12.2 M) at –78 °C. The curves result from a best-fit numerical integration to the highly simplified model in Scheme 3 (manuscript) and afford k_H/k_D = 29. By contrast, measuring the initial slopes directly affords k_H/k_D = 40.

Numerical best-fit parameters:

$k_1 = (3.53 \pm 0.01) \times 10^{-5}$
$k_2 = 0.41 \pm 0.03$
$k_3 = (1.3 \pm 0.1) \times 10^{4}$
$k_4 = (4.4 \pm 0.3) \times 10^{2}$

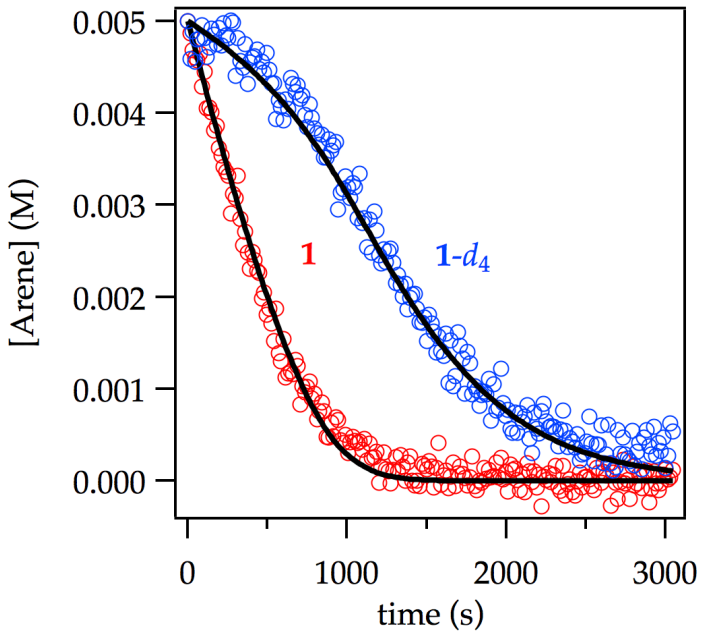


Figure A1.19. Competitive ortholithiation of **1** (0.0050 M) and **1-d_4** (0.0050 M) with LDA (0.10 M) in the presence of 0.020 M ArLi in THF (12.2 M) at –78 °C. The curves result from a best-fit numerical integration to the highly simplified model in Scheme 3 (manuscript) and afford $k_H/k_D = 6.3$. Fitting the initial rates of both decays directly affords $k_H/k_D = 40$.

Numerical best-fit parameters:

$k_1 = (8.7 \pm 0.1) \times 10^{-5}$
$k_2 = 24.0 \pm 0.9$
$k_3 = (3.8 \pm 0.2) \times 10^{4}$
$k_4 = (6.0 \pm 0.2) \times 10^{3}$

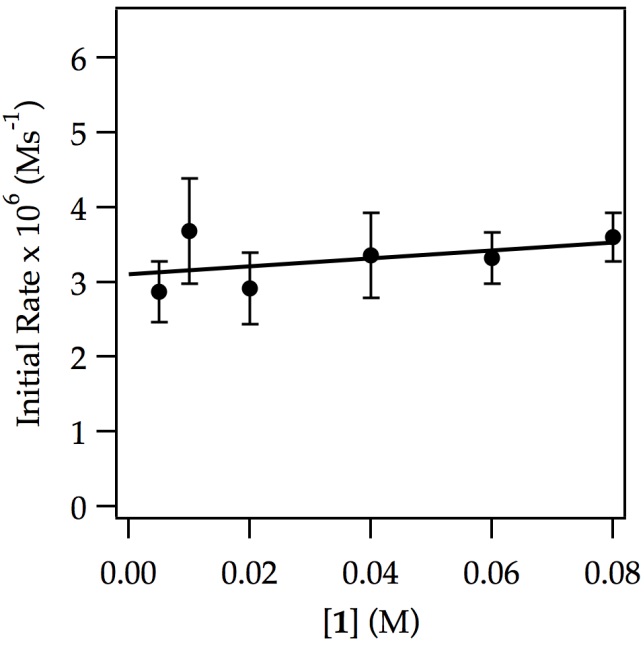


Figure A1.20. Plot of initial rate vs [ArH] (initial arene concentration) for the ortholithiation of **1** with LDA (0.10 M) in THF (12.2 M) monitored with IR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to $y = a$[ArH] + b. [a = (5 ± 5) x 10^{-6}, b = (3.1 ± 0.2) x 10^{-6}]

[**1**] (M)	y_1 (M·s^{-1})	y_2 (M·s^{-1})
0.005	3.16e-06	2.58e-06
0.01	4.18e-06	3.18e-06
0.02	3.26e-06	2.58e-06
0.04	3.76e-06	2.96e-06
0.06	3.57e-06	3.08e-06
0.08	3.83e-06	3.37e-06

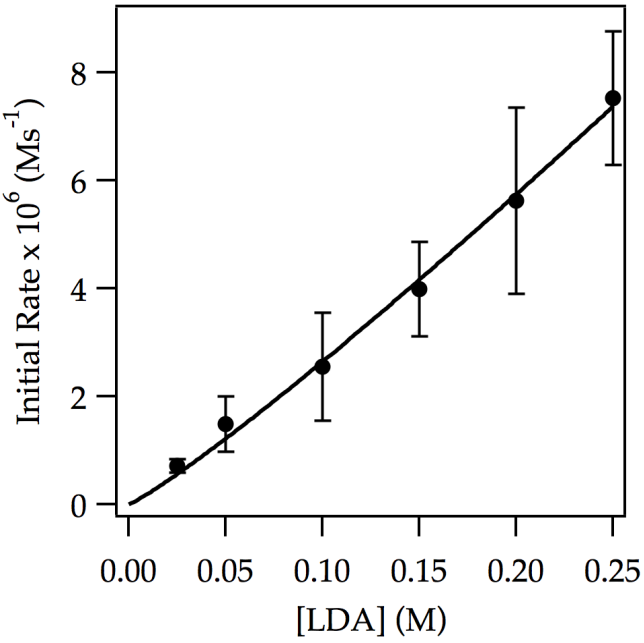


Figure A1.21. Plot of initial rate versus [LDA] in THF (12.2 M) for the ortholithiation of **1** (0.005 M) monitored with IR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to $y = a[\text{LDA}]^n$. [$a = (3.5 \pm 0.3) \times 10^{-5}$, $n = 1.12 \pm 0.06$]

[LDA] (M)	y_1 (M·s^{-1})	y_2 (M·s^{-1})	y_3 (M·s^{-1})	y_4 (M·s^{-1})
0.025	5.43e-07	8.21e-07	6.83e-07	7.82e-07
0.05	1.07e-06	1.03e-06	1.89e-06	1.96e-06
0.10	1.34e-06	2.10e-06	3.39e-06	3.36e-06
0.15	2.94e-06	3.83e-06	4.11e-06	5.06e-06
0.20	4.30e-06	6.69e-06	7.51e-06	4.03e-06
0.25	6.18e-06	8.19e-06	8.90e-06	6.85e-06

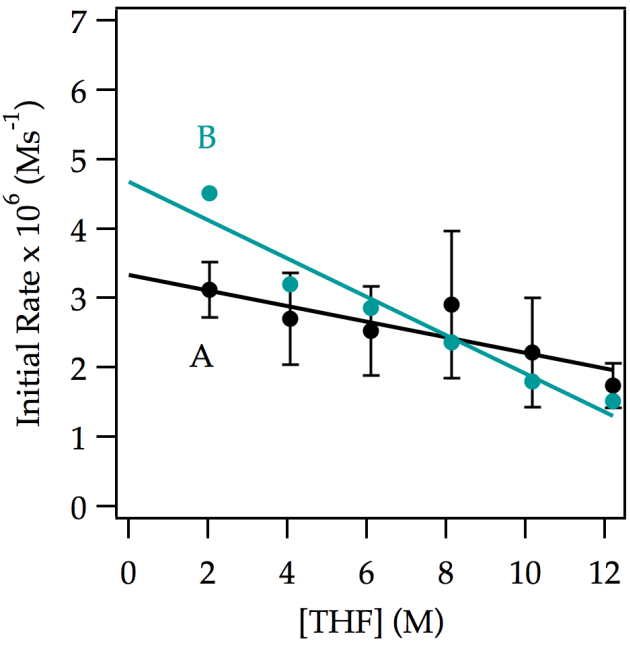


Figure A1.22. Plot of initial rate versus [THF] in Et_2O (curve A) and in hexanes (curve B) as cosolvent for the ortholithiation of **1** (0.050 M) by LDA (0.10 M) at –78 °C. The data was measured with IR spectroscopy. The curves depict unweighted least-squares fits to $y = a$[THF] + b. Curve A: a = (-1.1 ± 0.3) x 10^{-7}, b = (3.3 ± 0.3) x 10^{-6}. Curve B: a = (-2.8 ± 0.3) x 10^{-7}, b = (4.7 ± 0.3) x 10^{-6}. The greater slope using hexane as cosolvent compared with that using Et_2O as cosolvent illustrates the influence of long-range medium effects.

[THF] (M)	y_1-A (M·s^{-1})	y_2-A (M·s^{-1})	y_3-B (M·s^{-1})
2.03	2.84e-06	3.40e-06	4.51e-06
4.07	3.17e-06	2.23e-06	3.20e-06
6.00	2.98e-06	2.07e-06	2.86e-06
8.13	3.66e-05	2.16e-05	2.36e-05
10.17	2.77e-05	1.66e-05	1.80e-05
12.2	1.97e-05	1.51e-05	1.52e-05

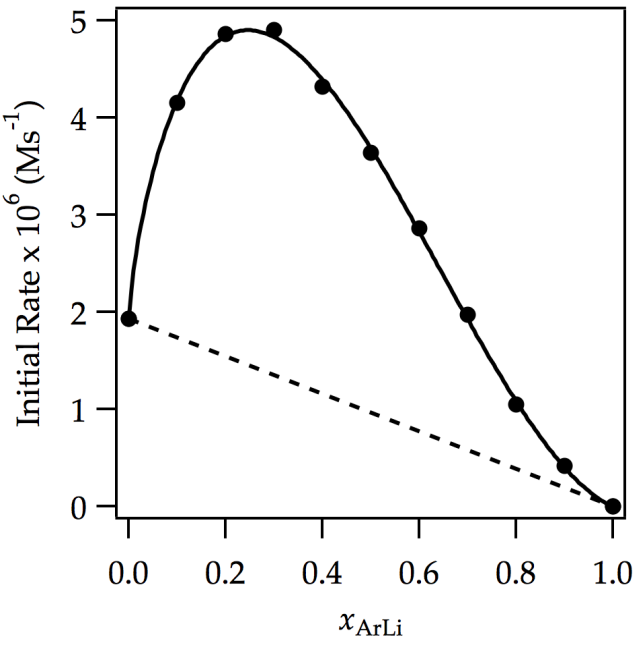


Figure A1.23. Plot of initial rates versus mole fraction of 2-lithio-1,4-difluorobenzene (X_{ArLi}) for the serial injection of 0.01M aliquots of **1** to 0.10 M LDA in 12.2 M THF monitored with IR spectroscopy at –78 °C. The dotted line depicts the theoretical initial rates in the absence of autocatalysis. The solid line depicts an unweighted least-squares fit to $-d[\mathrm{ArH}]/dt = k(X_{ArLi})^n(1-X_{ArLi})^m + k'(1-X_{ArLi})$. [$k = (1.67 \pm 0.09) \times 10^{-5}$, $k' = (1.93 \pm 0.05) \times 10^{-6}$, $n = 0.75 \pm 0.3$, $m = 1.87 \pm 0.05$]

X_{ArLi}	y_1 ($M \cdot s^{-1}$)
0.00	1.93e-06
0.10	4.15e-06
0.20	4.86e-06
0.30	4.90e-06
0.40	4.32e-06
0.50	3.64e-06
0.60	2.86e-06
0.70	1.97e-06
0.80	1.05e-06
0.90	4.14e-07
1.00	0

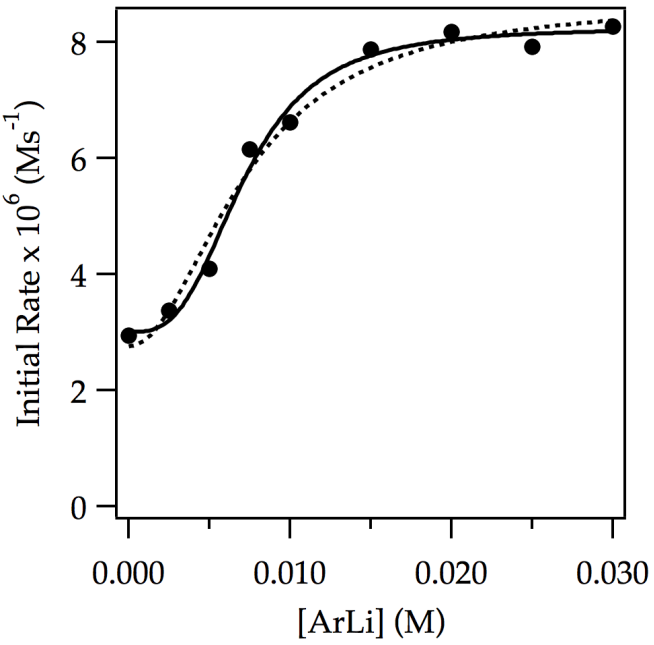


Figure A1.24. Plot of initial rate versus [ArLi] for the ortholithiation of **1** (0.005 M) by 0.10 M LDA in 12.2 M THF monitored with IR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to eq 4 in derivation 6. Solid curve: [$k_1 = (1.0 \pm 0.1) \times 10^{-4}$, $k_{-1} = 1000k_1$, $k_c = (2 \pm 5) \times 10^3$, $k_{-c} = 1000k_c$, $k_2 = 3.29 \pm 0.08$, $n = 3.2 \pm 0.6$]. Dotted curve: [$k_1 = (8 \pm 1) \times 10^{-5}$, $k_{-1} = 1000k_1$, $k_c = 4.8 \pm 0.9$, $k_{-c} = 1000k_c$, $k_2 = 3.5 \pm 0.1$, $n = 2$].

[ArLi] (M)	y_1 (M·s^{-1})
0.00	2.94e-06
0.0025	3.37e-06
0.005	4.09e-06
0.075	6.16e-06
0.01	6.62e-06
0.015	7.88e-06
0.02	8.18e-06
0.025	7.92e-06
0.03	8.27e-06

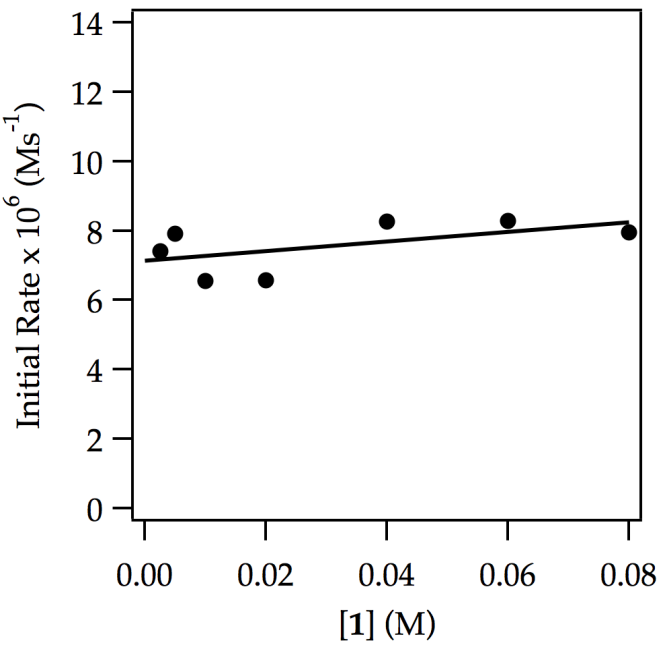


Figure A1.25. Plot of initial rate vs [ArH] (initial arene concentration) for the ortholithiation of **1** with LDA (0.10 M) in THF (12.2 M) with 0.02 M ArLi monitored with IR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to $y = a[\mathrm{ArH}] + b$. [$a = (14 \pm 9) \times 10^{-5}$, $b = (7.1 \pm 0.4) \times 10^{-6}$]

[**1**] (M)	y_1 (M·s^{-1})
0.0025	7.95e-06
0.005	8.29e-06
0.01	8.27e-06
0.02	6.57e-06
0.04	6.56e-06
0.06	7.91e-06
0.08	7.41e-06

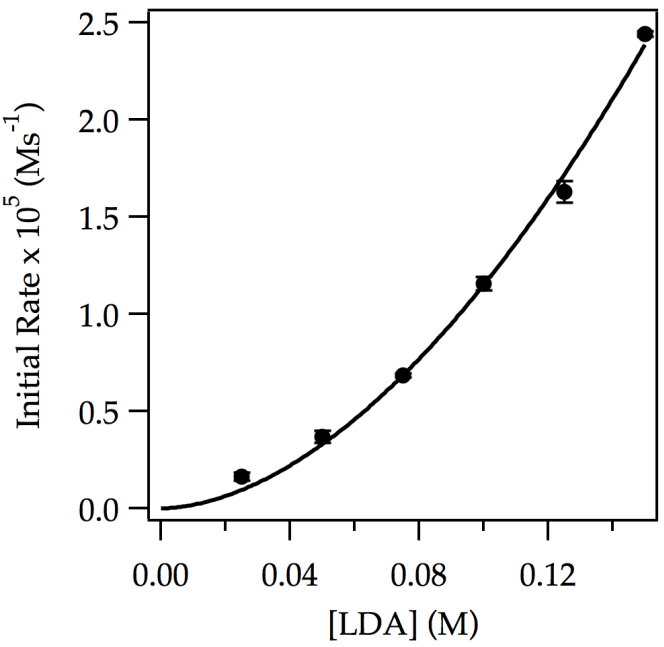


Figure A1.26. Plot of initial rate versus [LDA] in THF (12.2 M) for the ortholithiation of **1** (0.005 M) in the presence of 0.020 M ArLi monitored with IR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to $y = a[\text{LDA}]^n$. [$a = (7 \pm 1) \times 10^{-4}$, $n = 1.80 \pm 0.09$]

[LDA] (M)	y_1 ($M \cdot s^{-1}$)	y_2 ($M \cdot s^{-1}$)
0.025	1.77e-06	1.48e-06
0.05	3.48e-06	3.90e-06
0.075	6.77e-06	6.90e-06
0.10	1.13e-05	1.18e-05
0.125	1.59e-05	1.67e-05
0.150	2.45e-05	2.43e-05

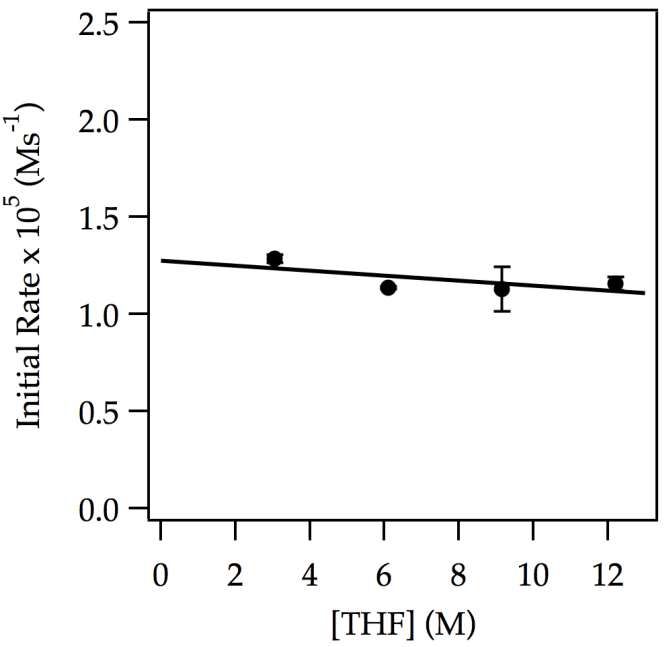


Figure A1.27. Plot of initial rate versus [THF] in Et_2O for the ortholithiation of **1** (0.005 M) by LDA (0.10 M) with 0.020 M ArLi monitored with IR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to $y = a$[THF] + b. [a = (-1.3 $\pm$ 0.9) x 10^{-7}, b = (1.28 $\pm$ 0.08) x 10^{-5}]

[THF] (M)	y_1 ($M \cdot s^{-1}$)	y_2 ($M \cdot s^{-1}$)
3.05	1.30e-05	1.27e-05
6.10	1.14e-05	1.13e-05
9.15	1.05e-05	1.21e-05
12.2	1.13e-05	1.18e-05

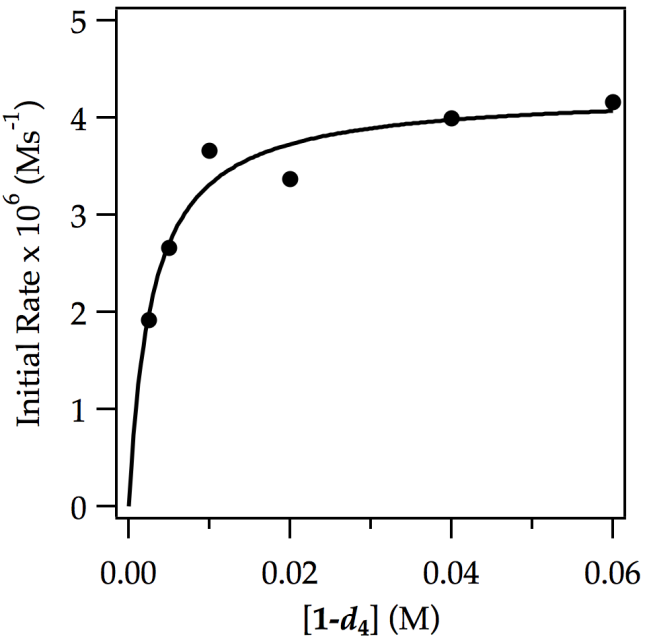


Figure A1.28. Plot of initial rate vs [ArD] (initial arene concentration) for the ortholithiation of **1-d_4** with LDA (0.10 M) in THF (12.2 M) monitored with IR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to a first-order saturation function: $-d[\mathrm{ArD}]/dt = (a[\mathrm{ArD}])/(1 + b[\mathrm{ArD}])$. [$a = (1.5 \pm 0.3) \times 10^{-3}$, $b = (3.5 \pm 0.8) \times 10^{2}$]

[**1-d_4**] (M)	y_1 (M·s^{-1})
0.0025	1.92e-06
0.005	2.66e-06
0.01	3.66e-06
0.02	3.37e-06
0.04	3.99e-06
0.06	4.16e-06

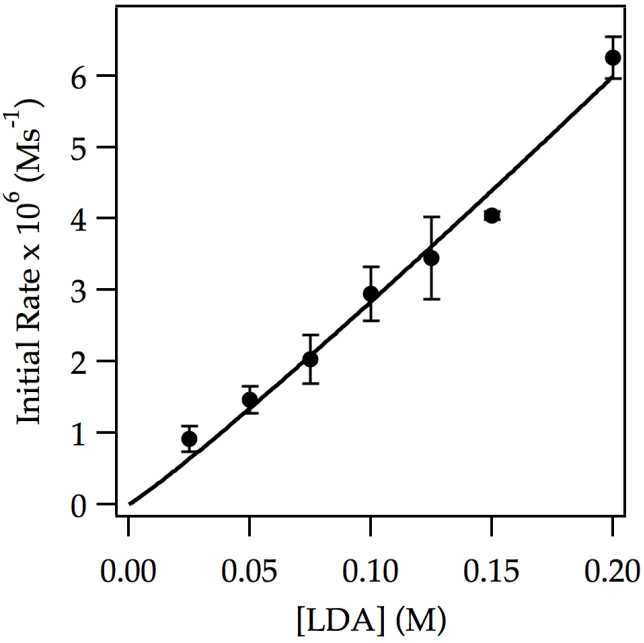


Figure A1.29. Plot of initial rate versus [LDA] in THF (12.2 M) for the ortholithiation of **1-*d*$_4$** (0.002 M) monitored with IR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to $y = a[\text{LDA}]^n$. [$a = (3.4 \pm 5) \times 10^{-5}$, $n = 1.08 \pm 0.08$]

[LDA] (M)	y_1 (M·s^{-1})	y_2 (M·s^{-1})
0.025	1.05e-06	9.20e-06
0.05	1.32e-06	1.59e-06
0.075	1.79e-06	2.27e-06
0.10	3.21e-06	2.68e-06
0.125	3.04e-06	3.85e-06
0.150	4.08e-06	4.00e-06
0.20	6.04e-06	6.45e-06

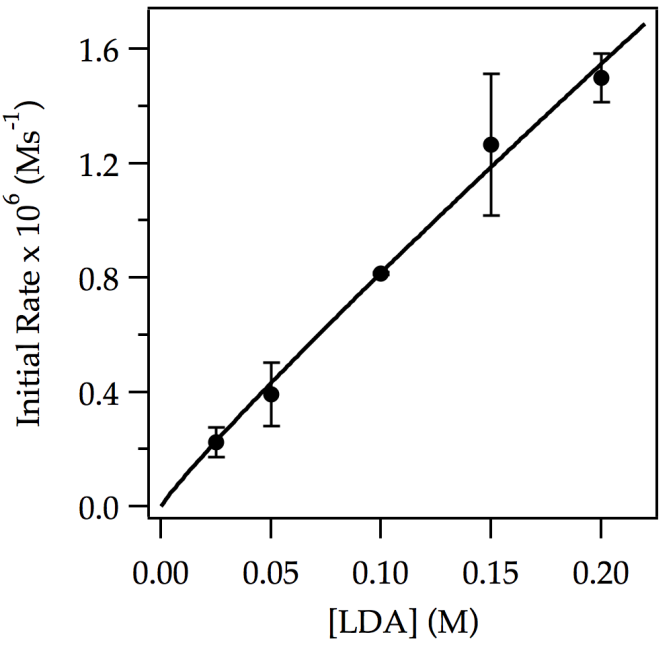


Figure A1.30. Plot of initial rate versus [LDA] in THF (2.03 M) for the ortholithiation of **1-d_4** (0.002 M) monitored with IR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to $y = a[\text{LDA}]^n$. [$a = (6.8 \pm 0.9) \times 10^{-6}$, $n = 0.92 \pm 0.07$]

[LDA] (M)	y_1 (M·s^{-1})	y_2 (M·s^{-1})
0.025	1.88e-07	2.61e-07
0.05	4.70e-07	3.13e-07
0.10	8.11e-07	8.19e-07
0.15	1.09e-06	1.44e-06
0.20	1.44e-06	1.56e-06

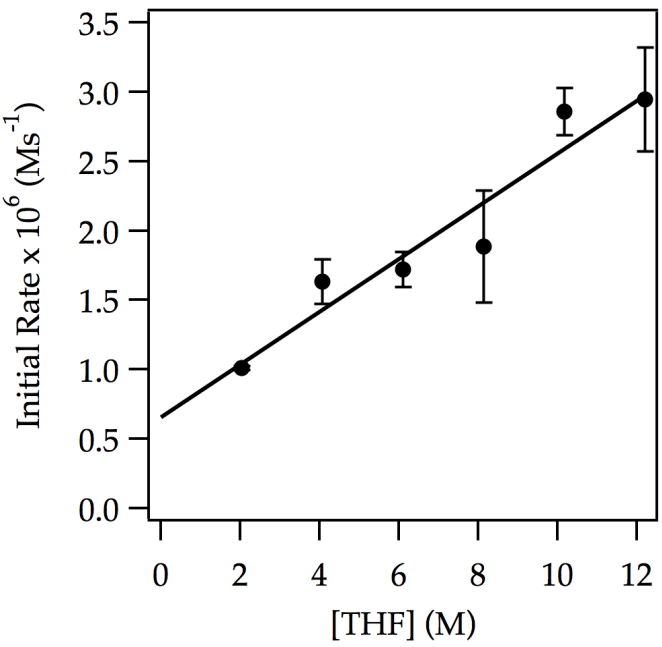


Figure A1.31. Plot of initial rate versus [THF] in Et_2O for the ortholithiation of **1-d_4** (0.002 M) by LDA (0.10 M) monitored with IR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to $y = a[\text{THF}] + b$. [$a = (1.9 \pm 0.3) \times 10^{-7}$, $b = (7 \pm 2) \times 10^{-7}$]

[THF] (M)	y_1 ($M \cdot s^{-1}$)	y_2 ($M \cdot s^{-1}$)
2.03	1.02e-06	1.00e-06
4.07	1.75e-06	1.52e-06
6.10	1.81e-06	1.63e-06
8.13	2.17e-06	1.60e-06
10.17	2.98e-06	2.74e-06
12.2	3.21e-06	2.68e-06

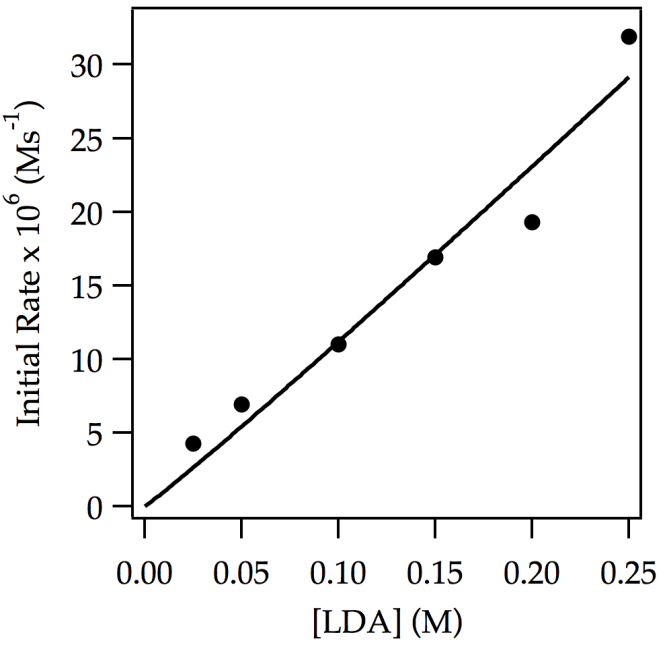


Figure A1.32. Plot of initial rate versus [LDA] in THF (12.2 M) for the ortholithiation of **1-*d*$_4$** (0.060 M) monitored with IR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to $y = a[\text{LDA}]^n$. [$a = (1.2 \pm 0.4) \times 10^{-4}$, $n = 1.0 \pm 0.2$]

[LDA] (M)	y_1 (M·s^{-1})
0.025	4.27e-06
0.05	6.94e-06
0.01	1.10e-05
0.15	1.69e-05
0.20	1.93e-05
0.25	3.19e-05

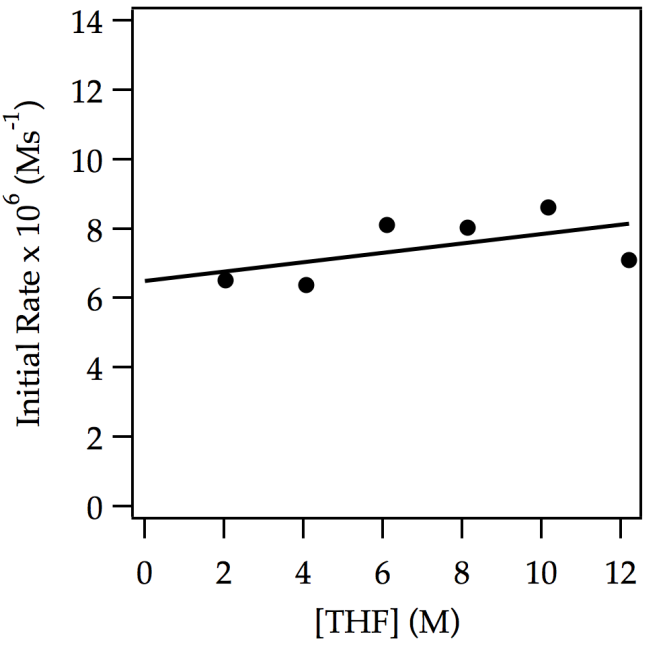


Figure A1.33. Plot of initial rate versus [THF] in Et_2O for the ortholithiation of **1-*d*$_4$** (0.060 M) by LDA (0.10 M) monitored with IR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to $y = a[\text{THF}] + b$. [$a = (1 \pm 1) \times 10^{-7}$, $b = (6.5 \pm 0.8) \times 10^{-6}$]

[THF] (M)	y_1 (M·s^{-1})
2.03	6.51e-06
4.07	6.37e-06
6.10	8.11e-06
8.13	8.04e-06
10.17	8.62e-06
12.2	7.09e-06

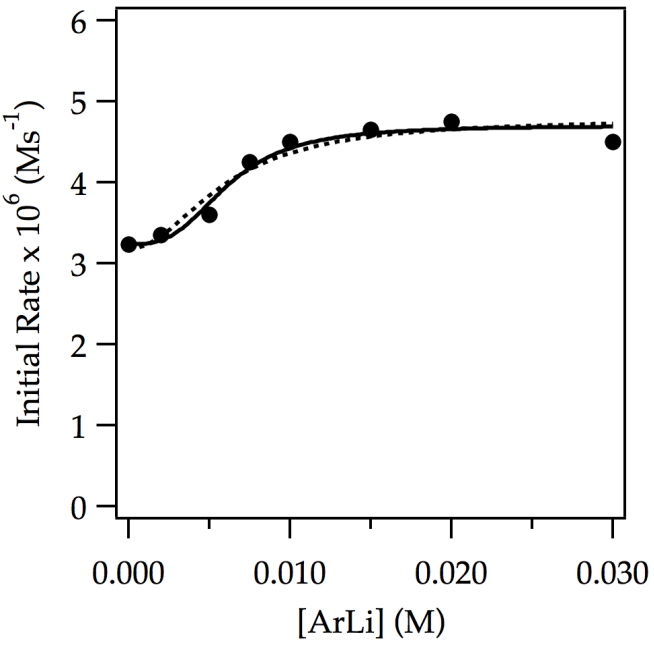


Figure A1.34. Plot of initial rate versus [ArLi] (specifically, **2–*d*$_3$**) for the ortholithiation of **1-*d*$_4$** (0.002 M) by 0.10 M LDA in 12.2 M THF monitored with IR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to eq 4 in derivation 6. Solid line: [k_1 = (2.1 ± 0.2) x 10^{-4}, $k_{-1} = 1000k_1$, k_c = (1.3 ± 0.4) x 10^3, $k_{-c} = 1000k_c$, k_2 = 47.0 ± 0.8, n = 3]. Dotted line: [k_1 = (1.9 ± 0.2) x 10^{-4}, $k_2 = 1000k_1$, k_c = 8 ± 3, $k_{-c} = 1000k_c$, k_2 = 47 ± 1, n = 2].

[$ArLiD_3$] (M)	y_1 ($M \cdot s^{-1}$)
0	3.23e-06
0.002	3.35e-06
0.005	3.60e-06
0.0075	4.25e-06
0.01	4.50e-06
0.015	4.65e-06
0.02	4.75e-06
0.03	4.50e-06

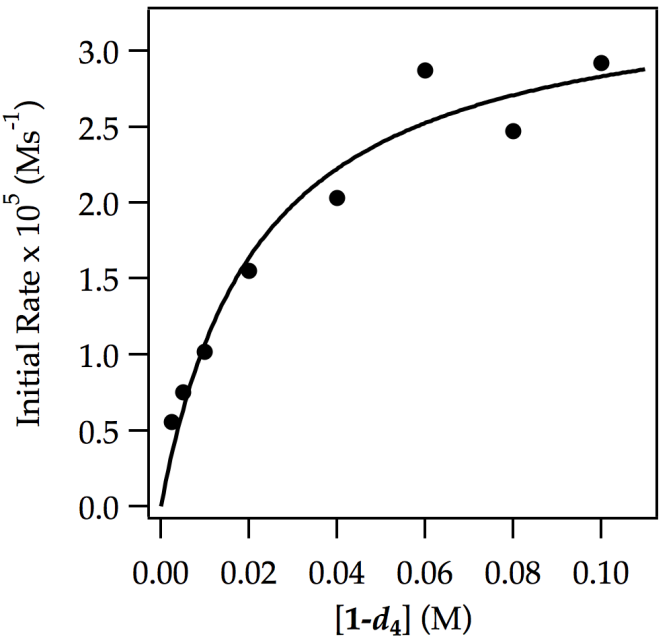


Figure A1.35. Plot of initial rate vs [ArD] (initial arene concentration) for the ortholithiation of **1-d_4** in the presence of 0.020 M ArLi (**2-d_3**) with LDA (0.10 M) in THF (12.2 M) monitored with IR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to a first-order saturation function: $-d[\mathrm{ArD}]/dt = (a[\mathrm{ArD}])/(1 + b[\mathrm{ArD}])$. [$a = (1.6 \pm 0.3) \times 10^{-3}$, $b = 40 \pm 10$]

[**1-d_4**] (M)	y_1 (M·s^{-1})
0.0025	5.56e-06
0.005	7.50e-06
0.01	1.02e-05
0.02	1.55e-05
0.04	2.03e-05
0.06	2.87e-05
0.08	2.47e-05
0.10	2.92e-05

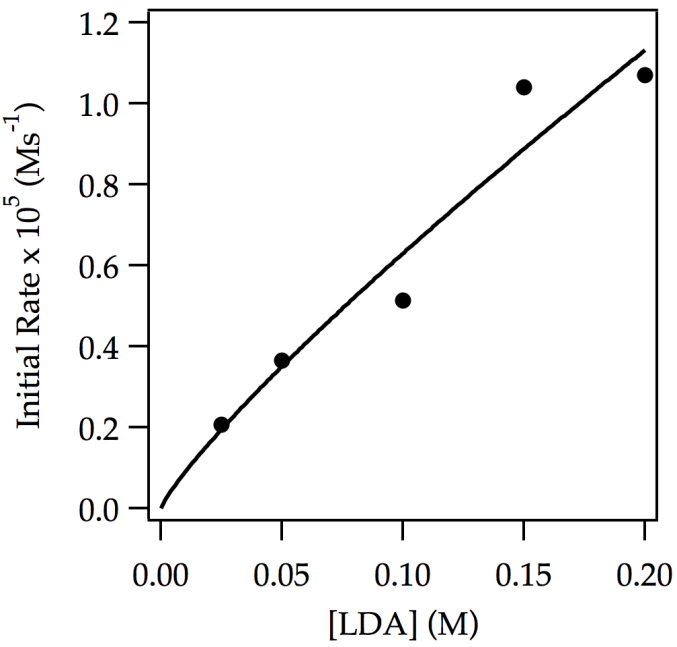


Figure A1.36. Plot of initial rate versus [LDA] in THF (12.2 M) for the ortholithiation of **1-*d*$_4$** (0.002 M) in the presence of 0.020 M ArLi (**2-*d*$_3$**) monitored with IR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to $y = a[\text{LDA}]^n$. [$a = (4 \pm 1) \times 10^{-5}$, $n = 0.9 \pm 0.2$]

[LDA] (M)	y_1 (M·s^{-1})
0.025	2.06e-06
0.05	3.65e-06
0.01	5.14e-06
0.15	1.04e-05
0.20	1.07e-05

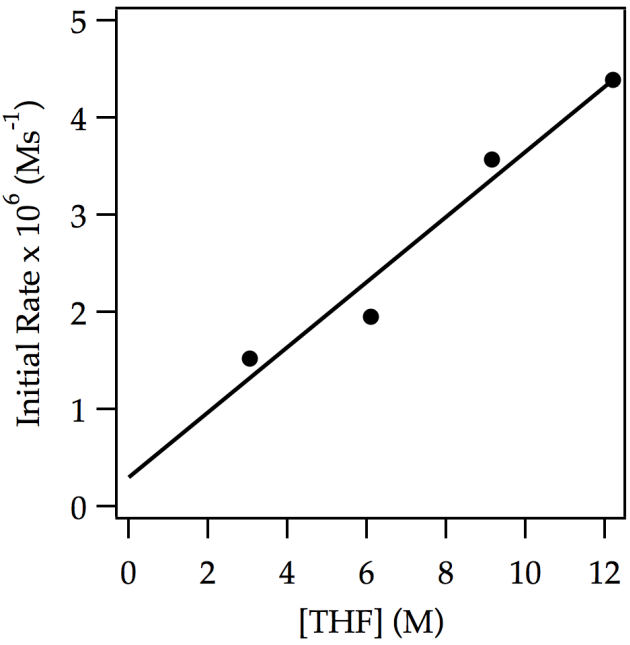


Figure A1.37. Plot of initial rate versus [THF] in Et_2O for the ortholithiation of **1-*d*$_4$** (0.002 M) in the presence of 0.020 M ArLi (**2-*d*$_3$**) by LDA (0.10 M) monitored with IR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to $y = a$[THF] + b. [$a = (3.4 \pm 0.5) \times 10^{-7}$, $b = (3 \pm 4) \times 10^{-7}$]

[THF] (M)	y_1 (M·s^{-1})
3.05	1.52e-06
6.10	1.95e-06
9.15	3.57e-06
12.2	4.39e-06

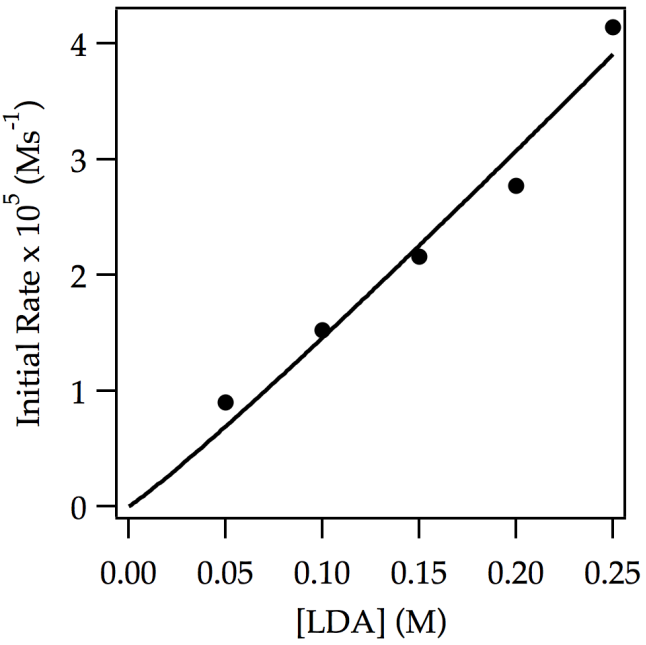


Figure A1.38. Plot of initial rate versus [LDA] in THF (12.2 M) for the ortholithiation of **1-*d*$_4$** (0.08 M) in the presence of 0.020 M ArLi (**2-*d*$_3$**) monitored with IR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to $y = a[\text{LDA}]^n$. [$a = (1.7 \pm 0.4) \times 10^{-4}$, $n = 1.1 \pm 0.1$]

[LDA] (M)	y_1 (M·s^{-1})
0.05	9.80e-06
0.01	1.52e-06
0.15	2.16e-05
0.20	2.77e-05
0.25	4.14e-05

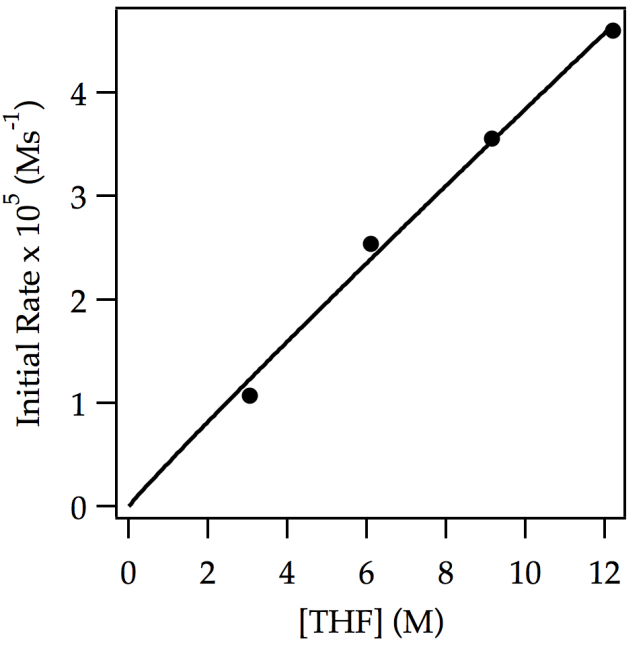


Figure A1.39. Plot of initial rate versus [THF] in Et_2O for the ortholithiation of **1-*d*$_4$** (0.08 M) in the presence of 0.020 M ArLi (**2-*d*$_3$**) by LDA (0.10 M) monitored with IR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to $y = a[\text{THF}]^n$. [$a = (4.2 \pm 0.7) \times 10^{-6}$, $n = 0.96 \pm 0.08$]

[THF] (M)	y_1 (M·s^{-1})
3.05	1.07e-05
6.10	2.54e-05
9.15	3.56e-05
12.2	4.60e-05

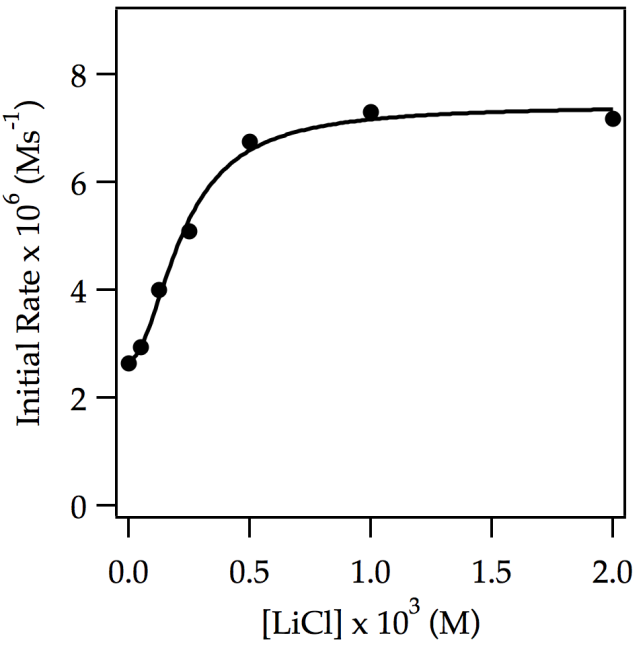


Figure A1.40. Plot of initial rate versus [LiCl] for the ortholithiation of **1-*d*$_4$** (0.002 M) by 0.10 M LDA in 12.2 M THF monitored with IR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to eq 4 in derivation 4. [ArD_4] = 0.002 M, [A_2S_2] = 0.05 M. [$k_1 = (3.1 \pm 0.3) \times 10^{-5}$, $k_{-1} = 1000k_1$, $k_c = (3 \pm 7) \times 10^2$, $k_{-c} = 1000k_c$, $k_2 = (5.3 \pm 0.2) \times 10^{-1}$, $n = 1.8 \pm 0.4$]

[LiCl] x 10^3 (M)	y_1 (M·s^{-1})
0	2.64e-06
0.05	2.94e-06
0.125	4.00e-06
0.25	5.08e-06
0.50	6.75e-06
1.0	7.29e-06
2.0	7.18e-06

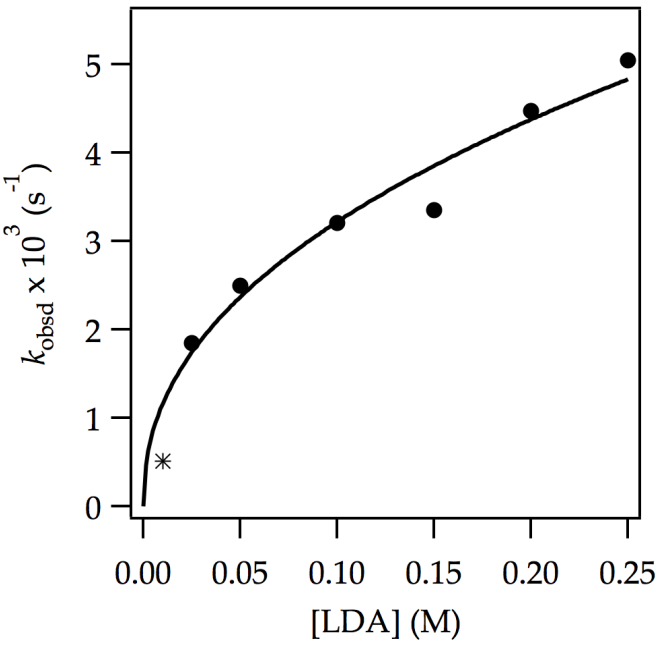


Figure A1.41. Plot of k_{obsd} versus [LDA] in THF (12.2 M) for the ortholithiation of **1-d_4** (0.002 M) in the presence of 1.5 mol% LiCl (1.5 mM) monitored with IR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to $y = a[\text{LDA}]^n$. [$a = (2.1 \pm 0.2) \times 10^{-2}$, $n = 0.47 \pm 0.04$]. Asterisk is not included in the fit.

[LDA] (M)	y_1 (s^{-1})
0.010*	5.10e-04
0.025	1.85e-03
0.05	2.50e-03
0.01	3.21e-03
0.15	3.35e-03
0.20	4.48e-03
0.25	5.05e-03

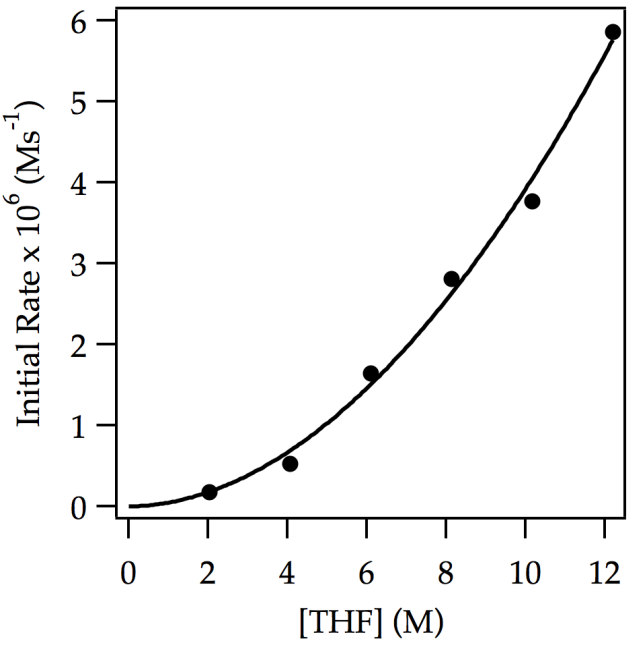


Figure A1.42. Plot of initial rate versus [THF] in Et_2O for the ortholithiation of **1-*d*$_4$** (0.002 M) by LDA (0.10 M) in the presence of 1.5 mol% LiCl (1.5 mM) monitored with IR spectroscopy at –78 °C. The curve depicts an unweighted least-squares fit to $y = a[\text{THF}]^n$. [$a = (5 \pm 1) \times 10^{-8}$, $n = 1.9 \pm 0.1$]

[THF] (M)	y_1 (M·s^{-1})
2.03	1.74e-07
4.07	5.26e-07
6.10	1.64e-06
8.13	2.81e-06
10.17	3.77e-06
12.2	5.86e-06

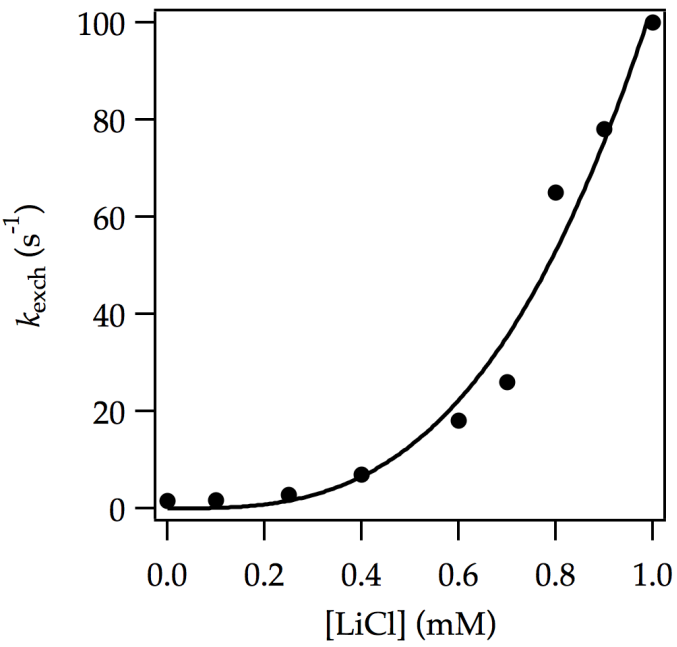


Figure A1.43. Plot of ^{6}Li nuclear exchange rate versus [LiCl] of [^{6}Li,^{15}N] LDA (0.10 M) at 10 °C in 12.2 M THF. The curve depicts an unweighted least-squares fit to $y = a[\text{LiCl}]^n$. [$a = 104 \pm 6$, $n = 3.0 \pm 0.3$]

[LiCl] (mM)	y (s^{-1})
0.00	1.5
0.10	1.7
0.25	2.8
0.40	7.0
0.60	18
0.70	26
0.80	65
0.90	78
1.00	100

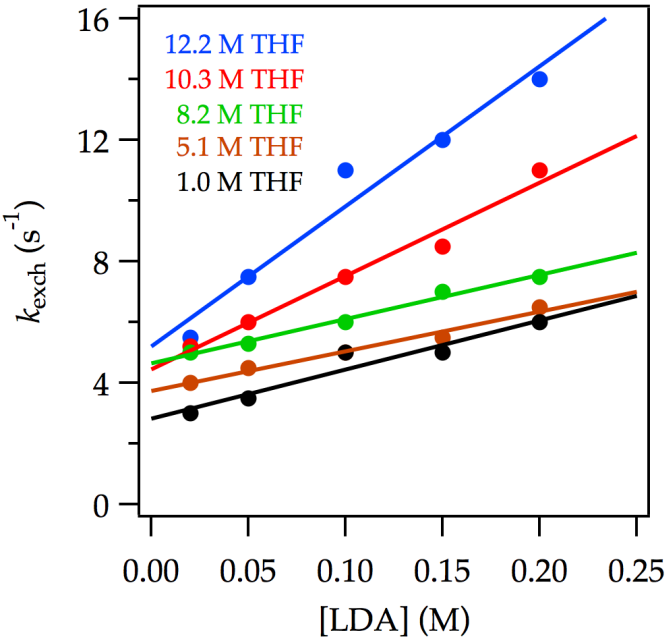


Figure A1.44. Plot of ^{6}Li nuclear exchange rate at 35 °C versus [LDA] at varying [^{6}Li,^{15}N] LDA and THF concentrations with hexanes as cosolvent. The curve depicts an unweighted least-squares fit to linear functions.

		y_1 (s^{-1})	y_2 (s^{-1})	y_3 (s^{-1})	y_4 (s^{-1})	y_5 (s^{-1})
[LDA] (M)	[THF]	12.2 M	10.3 M	8.2 M	5.1 M	1.0 M
0.02		5.5	5.2	5.0	4.0	3.0
0.05		7.5	6.0	5.3	4.5	3.5
0.10		11	7.5	6.0	5.0	5.0
0.15		12	8.5	7.0	5.5	5.0
0.20		14	11	7.5	6.5	6.0

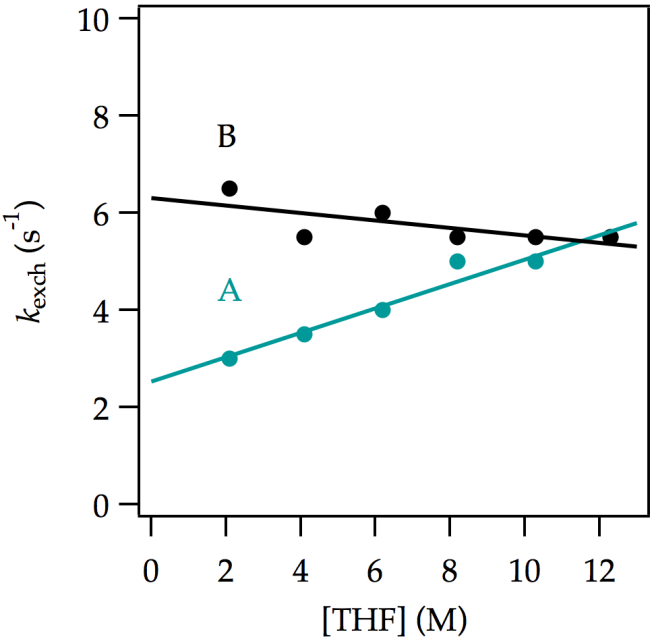
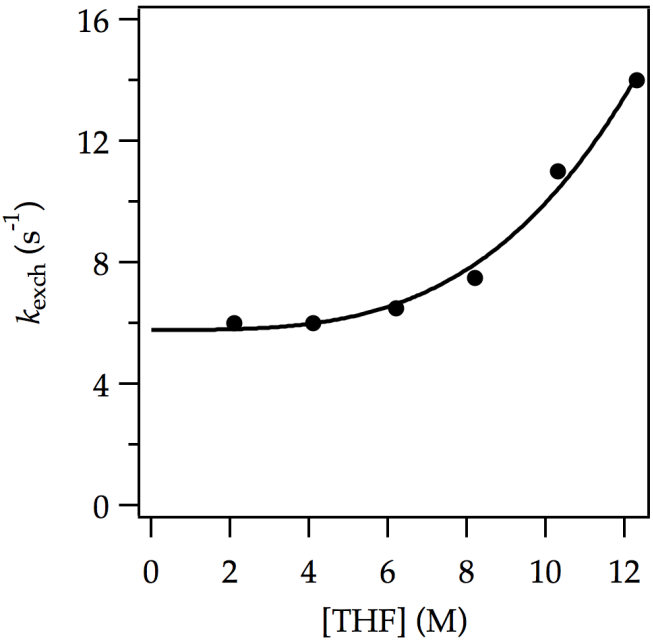


Figure A1.45. Plot of ^{6}Li nuclear exchange rate of [^{6}Li,^{15}N] LDA (0.02 M) at varying THF concentrations with (A) hexanes (y_1), and (B) 2,5-Me_2THF (y_2), as the cosolvent at 35 °C. The curve depicts an unweighted least-squares fit to (A) $y = a$[THF]+b. [a = 0.25± 0.03, b = 2.5 ± 0.2], (B) $y = a$[THF]+b. [a = -0.08± 0.04, b = 6.3 ± 0.3]

[THF] (M)	y_1 (s^{-1})	y_2 (s^{-1})
2.1	3.0	6.5
4.1	3.5	5.5
6.2	4.0	6.0
8.2	5.0	5.5
10.3	5.0	5.5
12.3	5.5	-

(A)



(B)

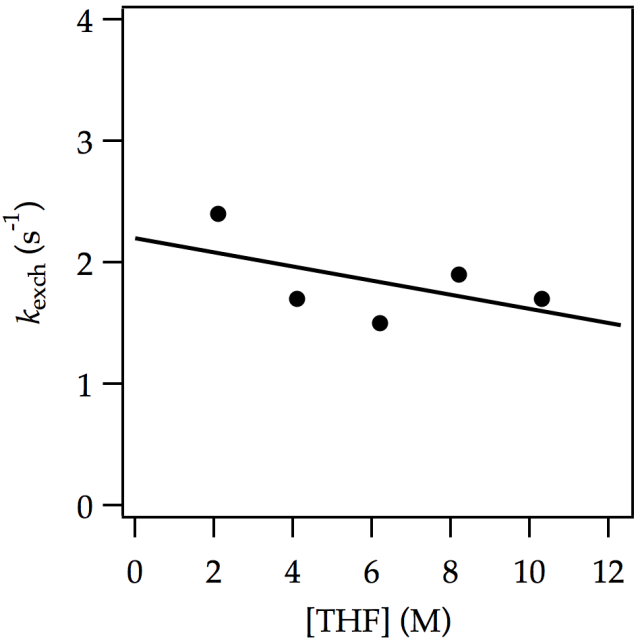
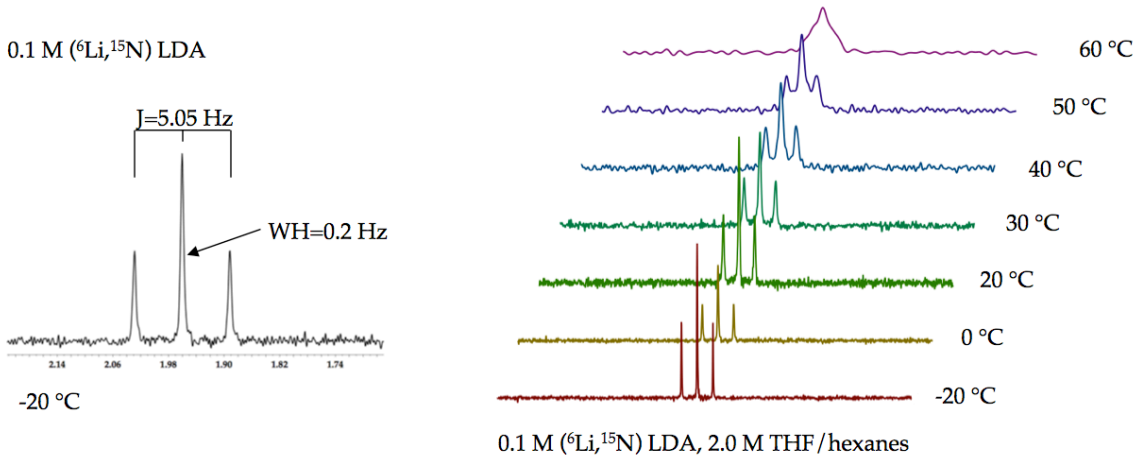


Figure A1.46. Plot of ^{6}Li nuclear exchange rate of [^{6}Li,^{15}N] LDA (0.20 M) at varying THF concentrations with (A) hexanes, and (B) 2,5-Me_2THF, as the cosolvent at 35 °C. The curve depicts an unweighted least-squares fit to (A) $y = a[\text{THF}]^n+b$. [$a = (2 \pm 3)\ x10^{-3}$, $n = 3.3 \pm 0.5$, $b = 5.8 \pm 0.4$] (B) $y = a[\text{THF}]+b$. [$a = -0.06 \pm 0.05$, $b = 2.2 \pm 0.4$]

Figure A1.46 cont.

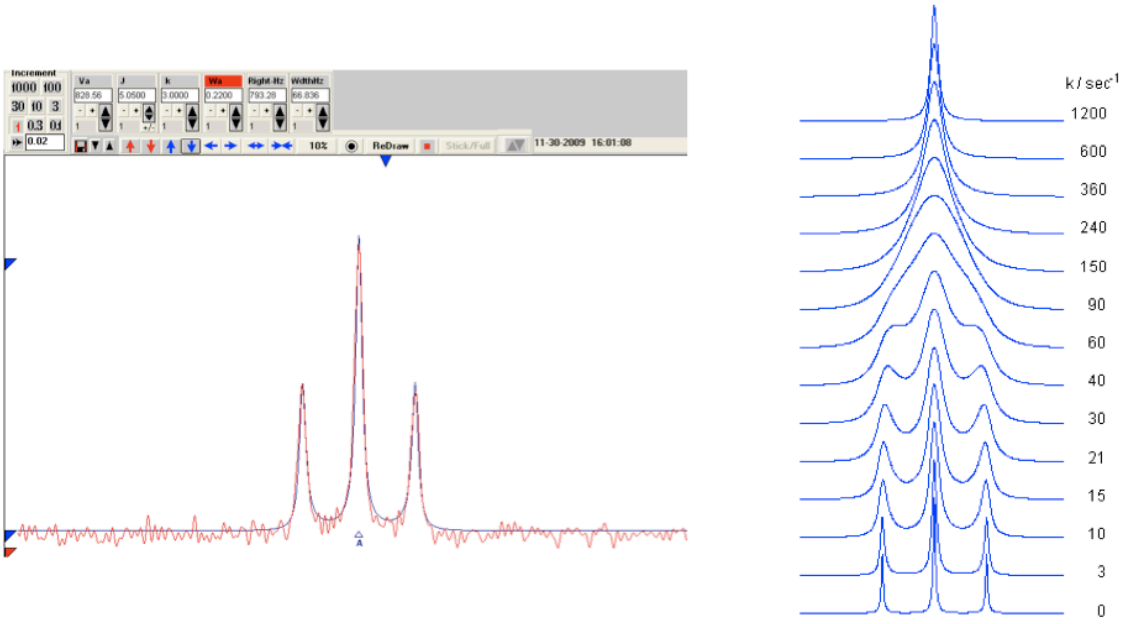
[THF] (M)	y_1 (s^{-1})	y_2 (s^{-1})
2.1	6.0	2.4
4.1	6.0	1.7
6.2	6.5	1.5
8.2	7.5	1.9
10.3	11	1.7
12.3	14	-

(A) (B)

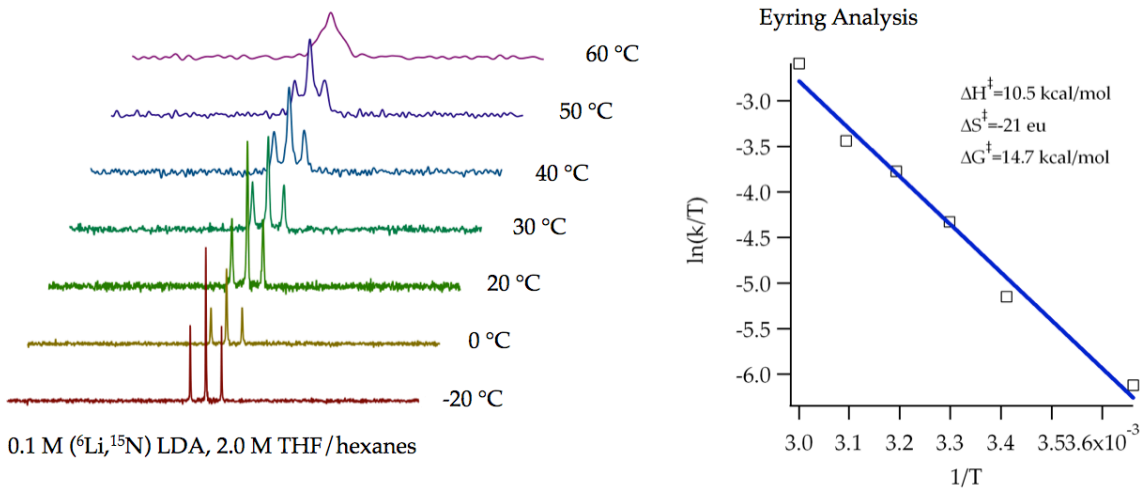


Scheme A1.1. ^{6}Li NMR spectra of [^{6}Li,^{15}N] LDA (0.10 M) in 12.2 M THF at (A) –20 °C, (B) –20 to +60 °C. The coupling constant by ^{15}N and the width at half height are indicated.

(A) (B)

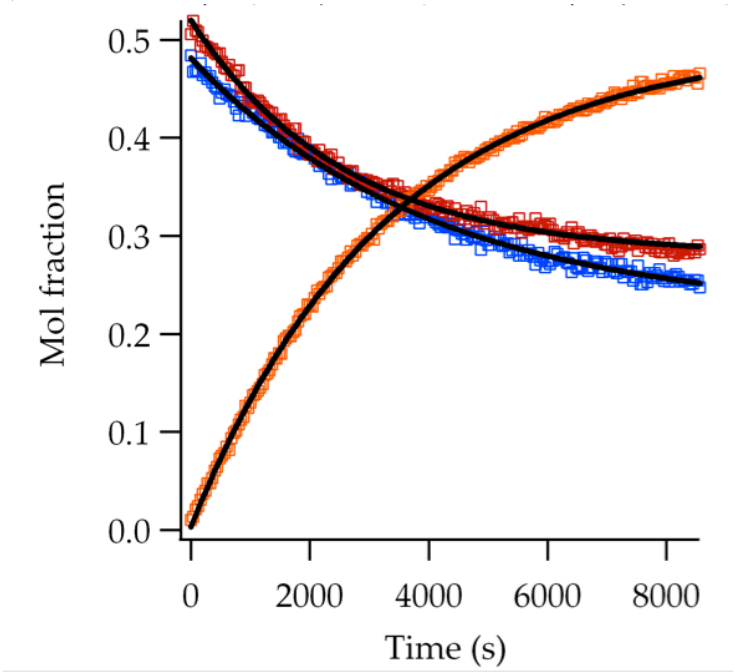


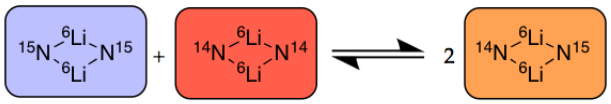
Scheme A1.2. (A) Screenshot of the NMR line shape analysis software *WinDNMR* by Hans Reich. The spectra are handfitted by adjusting the peak frequency (Va), the coupling frequency (*J*), the exchange rate (*k*), and the width at half height (Wa). Wa and *J* are determined at the low exchange limit for which *k* is effectively zero. (B) Simulation of a triplet exchange at varying exchange rates.



Scheme A1.3. ^{6}Li NMR spectra of [^{6}Li,^{15}N] LDA (0.10 M) in 12.2 M THF at varying temperatures, and the corresponding Eyring plot.

(A)





(B)

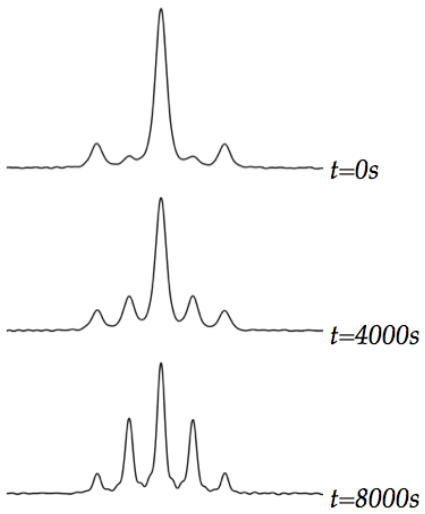


Figure A1.47. (A) Representative ^{6}Li NMR time trace of the ^{6}Li nuclear exchange of [^{6}Li] LDA (0.10 M) and [^{6}Li,^{15}N] LDA (0.10 M) in 12.2 M THF at –60 °C. (B) Select ^{6}Li NMR spectra at the indicated time point of the time trace in (A).

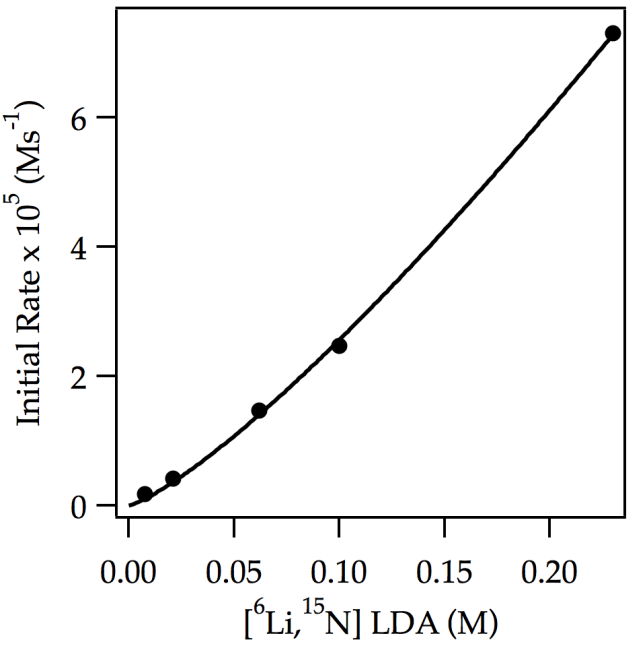


Figure A1.48. Plot of initial rate versus [^{6}Li,^{15}N] LDA for the subunit exchange in the presence of 0.10M [^{6}Li] LDA at –60 °C in 12.2 M THF. The curve depicts an unweighted least-squares fit to $y = a[\text{LDA}]^{n}$. [$a = (4.6 \pm 0.2)\ \text{x}10^{-4}$, $n = 1.25 \pm 0.03$]

[^{6}Li,^{15}N] LDA (M)	y (M·s^{-1})
0.0076	1.80e-06
0.021	4.20e-06
0.062	1.47e-05
0.10	2.47e-05
0.23	7.30e-05

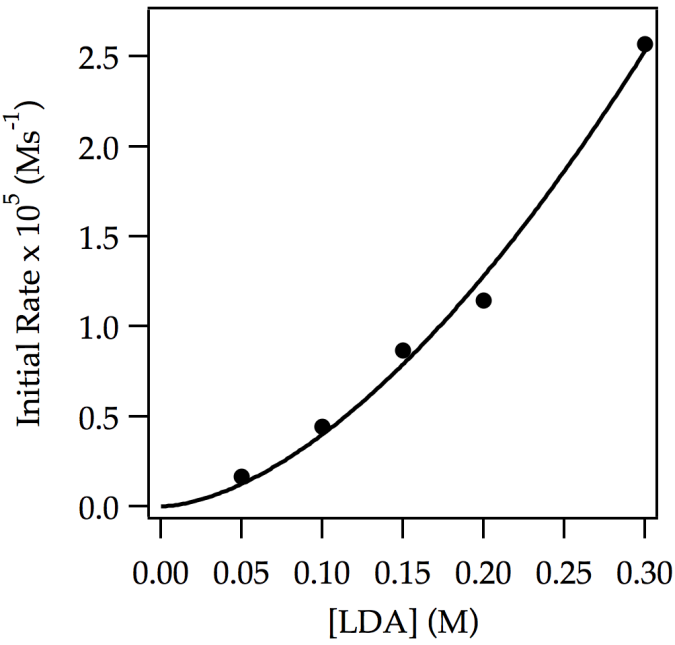
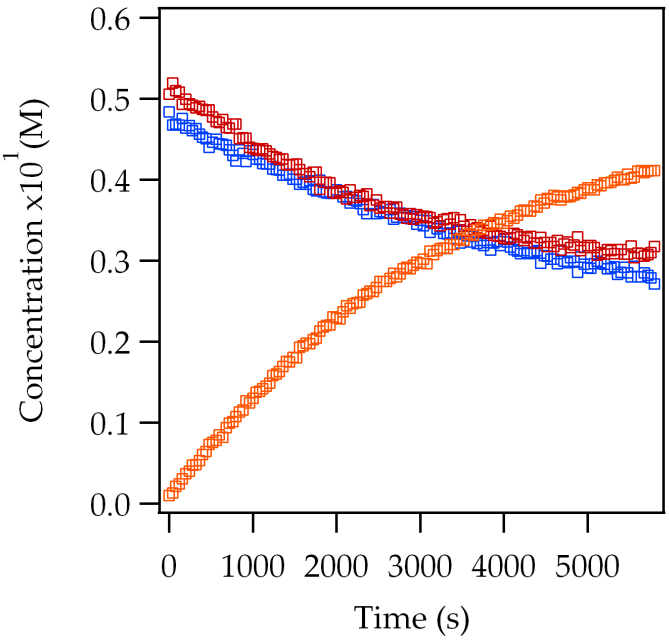


Figure A1.49. Plot of initial rate for the loss of [^{6}Li,^{15}N] LDA in 1:1 mixtures of [^{6}Li]LDA and [^{6}Li,^{15}N]LDA versus total [LDA] titer at –60 °C in 12.2 M THF. The curve depicts an unweighted least-squares fit to $y = a[\text{LDA}]^n$. [$a = (1.9 \pm 0.3)\ \text{x}10^{-4}$, $n = 1.7 \pm 0.1$]

[LDA] (M)	y ($\text{M}\cdot\text{s}^{-1}$)
0.05	1.64e-06
0.10	4.43e-06
0.15	8.68e-06
0.20	1.14e-05
0.30	2.57e-05

(A)



(B)

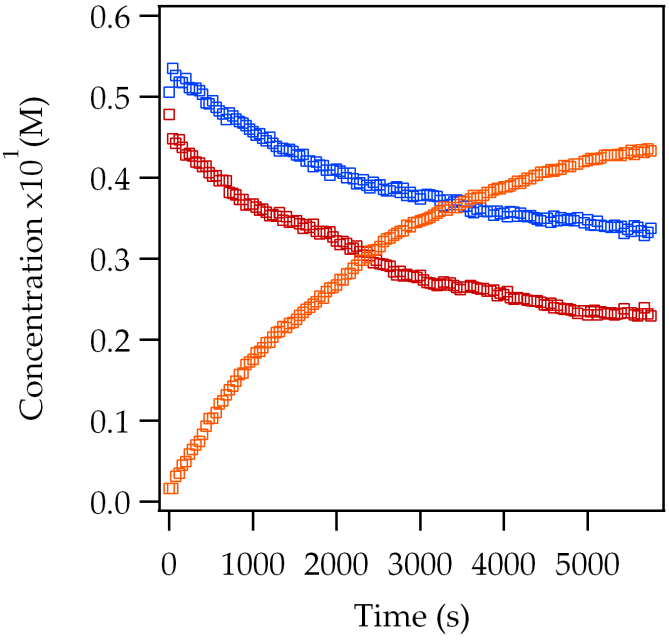


Figure A1.50. Concentration vs time for the exchange of [^{6}Li]LDA (0.05 M) with [^{6}Li,^{15}N]LDA (0.05 M) at –60 °C in (A) 12.2 M THF and (B) 1.5 M THF/hexanes. The initial rate is measured to be 2.7e-6 M·s^{-1} at 12.2 M THF and 3.2e-6 M·s^{-1} at 1.5 M THF/hexanes indicating a zeroth order dependence on THF.

Part 4: Derivations

Derivation A1.1. Derivation of fit function for aryllithium solvation.

$$0.5\ A_2S_2 + ArH + nS \underset{}{\overset{K_{eq}}{\rightleftharpoons}} AH + ArLiS_{n+1}$$

The equilibrium expression is defined as:

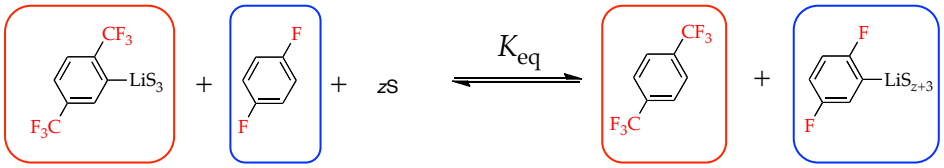
$$K_{eq} = \frac{[AH]\,[ArLiS_{n+1}]}{[A_2S_2]^{0.5}\,[ArH]\,[S]^n} \tag{1}$$

Rearranging the equation gives

$$\frac{[AH]\,[ArLiS_{n+1}]}{[A_2S_2]^{0.5}\,[ArH]} = K_{eq}\,[S]^n \tag{2}$$

Note: Concentrations of [ArH] and [$ArLi_{n+1}$] at equilibrium can be measured by ^{19}F NMR spectroscopy. [AH] and [A_2S_2] are calculated based on the extent of lithiation. K_{eq} and n are the two fitting parameters.

Derivation A1.2. Derivation of fit function for aryllithium **2** solvation by equilibration with other aryllithium of known solvation number.



$$ArLiS_3(CF_3) + ArH(F) + zS \underset{}{\overset{K_{eq}}{\rightleftharpoons}} ArH(CF_3) + ArLiS_{z+3}(F)$$

The equilibrium expression is defined as:

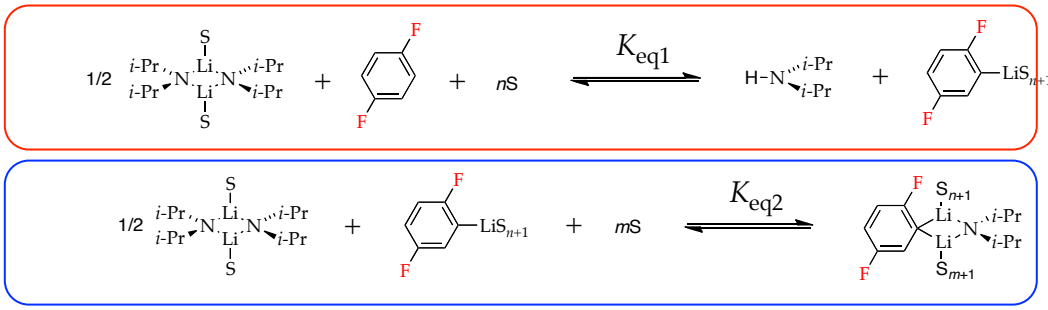
$$K_{eq} = \frac{[ArH(CF_3)]\,[ArLiS_{z+3}(F)]}{[ArLiS_3(CF_3)]\,[ArH(F)]\,[S]^z} \tag{1}$$

Rearranging the equation gives

$$\frac{[ArH(CF_3)]\,[ArLiS_{z+3}(F)]}{[ArLiS_3(CF_3)]\,[ArH(F)]} = K_{eq}\,[S]^z \tag{2}$$

Note: Concentrations of all species at equilibrium can be measured by ^{19}F NMR spectroscopy. K_{eq} and z are the two fitting parameters.

Derivation A1.3. Derivation of fit function for mixed dimer **3** solvation.



$$0.5\ A_2S_2 + ArH + nS \rightleftharpoons[K_{eq1}] AH + ArLiS_{n+1}$$

$$0.5\ A_2S_2 + ArLiS_{n+1} + mS \rightleftharpoons[K_{eq2}] ArLiS_{n+1} * AS_{m+1}$$

The equilibrium expressions are defined as:

$$K_{eq1} = \frac{[AH]\,[ArLiS_{n+1}]}{[A_2S_2]^{0.5}\,[ArH]\,[S]^n} \qquad K_{eq2} = \frac{[ArLiS_{n+1} * AS_{m+1}]}{[A_2S_2]^{0.5}\,[ArLiS_{n+1}]\,[S]^m} \tag{1}$$

Rearranging the equations to give

$$[A_2S_2]^{0.5} = \frac{[AH]\,[ArLiS_{n+1}]}{K_{eq1}\,[ArH]\,[S]^n} \qquad [A_2S_2]^{0.5} = \frac{[ArLiS_{n+1} * AS_{m+1}]}{K_{eq2}\,[ArLiS_{n+1}]\,[S]^m} \tag{2}$$

Combining both equations to give

$$\frac{[AH]\,[ArLiS_{n+1}]}{K_{eq1}\,[ArH]\,[S]^n} = \frac{[ArLiS_{n+1} * AS_{m+1}]}{K_{eq2}\,[ArLiS_{n+1}]\,[S]^m} \tag{3}$$

Further rearrangement gives

$$\frac{[AH]\,[ArLiS_{n+1}]}{[ArH]} * \frac{[ArLiS_{n+1}]}{[ArLiS_{n+1} * AS_{m+1}]} = \frac{K_{eq1}\,[S]^n}{K_{eq2}\,[S]^m} \tag{4}$$

Note: Concentrations of all fluorinated species at equilibrium can be measured by ^{19}F NMR spectroscopy. [AH] is calculated based on the extend of lithiation. K_{eq1}/K_{eq2} and (n-m) are the two fitting parameters.

Derivation A1.4. Derivation of LiCl saturation curve.

$$A_2 \underset{k_{-1}+k_{-c}[LiCl]^n}{\overset{k_1+k_c[LiCl]^n}{\rightleftharpoons}} 2A$$

$$A + ArH \xrightarrow{k_2} \text{product}$$

The initial rate of consumption of ArH is defined as:

$$\frac{-d[ArH]}{dt} = k_2[A][ArH] \quad (1)$$

Applying the steady-state approximation to monomer A while denoting $a = (k_1 + k_c[LiCl]^n)$ and $b = (k_{-1} + k_{-c}[LiCl]^n)$

$$\frac{d[A]}{dt} = 2(a)[A_2] - 2(b)[A]^2 - k_2[ArH][A] = 0 \quad (2)$$

solving for $[AS_2]$ using the quadratic equation gives

$$[A] = \frac{1}{4(b)}(\sqrt{k_2^2[ArH]^2 + 16(a)(b)[A_2]} - k_2[ArH]) \quad (3)$$

Substituting eq 3 into eq 1 gives

$$\frac{-d[ArH]}{dt} = \frac{k_2[ArH]}{4(b)}(\sqrt{k_2^2[ArH]^2 + 16(a)(b)[A_2]} - k_2[ArH]) \quad (4)$$

where [ArH] and $[A_2]$ are evaluated at t=0.

In the limit of no catalyst, the equation reduces to

$$\frac{-d[ArH]}{dt} = 2k_1[A_2] \quad (5)$$

In the limit of catalyst saturation, the equation becomes

$$\frac{-d[ArH]}{dt} = k_2\sqrt{\frac{k_1}{k_{-1}}}[ArH][A_2]^{1/2} \quad (6)$$

Derivation A1.5. Derivation of expression for fitting incremental addition curve (eq 12).

In a serial injection experiment, the amount of [ArH] injected remains constant, but the concentration of LDA and ArLi varies with each successive injection.

Hence, the rate of consumption of arene and its initial rate ($rate_{init}$) are defined as:

$$-d[\mathrm{ArH}]/d\mathrm{t} = k'[\mathrm{ArLi}]^n[\mathrm{LDA}]^m \quad (1)$$

Writing the concentrations in terms of mole fractions:

$$-d[\mathrm{ArH}]/d\mathrm{t} = k[X_{\mathrm{ArLi}}]^n[X_{\mathrm{LDA}}]^m \quad (2)$$

where $X_{\mathrm{ArLi}} = \mathrm{N}_{\mathrm{ArLi}}/(\mathrm{N}_{\mathrm{ArLi}} + \mathrm{N}_{\mathrm{LDA}})$ (N stands for normality)

Also, $X_{\mathrm{LDA}} = 1 - X_{\mathrm{ArLi}}$ (3)

Substituting eq 3 into eq 2 gives

$$-d[\mathrm{ArH}]/d\mathrm{t} = k[X_{\mathrm{ArLi}}]^n[1 - X_{\mathrm{ArLi}}]^m \quad (4)$$

The initial rate in the absence of autocatalysis, assuming an LDA order of 1 is given by:

$$-d[\mathrm{ArH}]/d\mathrm{t} = k'[X_{\mathrm{LDA}}]^1 \quad (5)$$
$$-d[\mathrm{ArH}]/d\mathrm{t} = k'[1 - X_{\mathrm{ArLi}}]^1 \quad (6)$$

To account for the rate in the presence of autocatalysis, we add eq 6 to eq 4. Hence, eq 4 becomes

$$-d[\mathrm{ArH}]/d\mathrm{t} = k[X_{\mathrm{ArLi}}]^n[1 - X_{\mathrm{ArLi}}]^m + k'[1 - X_{\mathrm{ArLi}}]^1 \quad (7)$$

Derivation A1.6. Derivation of ArLi saturation curve.

$$A_2 \underset{k_{-1} + k_{-c}[\mathrm{ArLi}]^n}{\overset{k_1 + k_c[\mathrm{ArLi}]^n}{\rightleftharpoons}} A_2^*$$

$$A_2 + A_2^* \xrightarrow{k_2} A_4$$

The consumption rate of the reaction is defined as

$$\frac{-d[\mathrm{ArH}]}{dt} = k_2[\mathrm{A}_2][\mathrm{A}_2^*] \tag{1}$$

Applying steady state approximation to A_2^* gives

$$\frac{d[\mathrm{A}_2^*]}{dt} = (k_1 + k_c[\mathrm{ArLi}]^n)[\mathrm{A}_2] - (k_{-1} + k_{-c}[\mathrm{ArLi}]^n)[\mathrm{A}_2^*] - k_2[\mathrm{A}_2][\mathrm{A}_2^*] = 0 \tag{2}$$

Solving for A_2^* gives

$$[\mathrm{A}_2^*] = \frac{(k_1 + k_c[\mathrm{ArLi}]^n)[\mathrm{A}_2]}{(k_{-1} + k_{-c}[\mathrm{ArLi}]^n) + k_2[\mathrm{A}_2]} \tag{3}$$

Combining equations 1 and 3 gives

$$\frac{-d[\mathrm{ArH}]}{dt} = \frac{(k_1 + k_c[\mathrm{ArLi}]^n)k_2[\mathrm{A}_2]^2}{(k_{-1} + k_{-c}[\mathrm{ArLi}]^n) + k_2[\mathrm{A}_2]} \tag{4}$$

In the absence of catalyst and $k_2[\mathrm{A}] >> k_{-1}$, the equation reduces to

$$\frac{-d[\mathrm{ArH}]}{dt} = k_1[\mathrm{A}_2] \tag{5}$$

In the limit of catalyst saturation, the equation becomes

$$\frac{-d[\mathrm{ArH}]}{dt} = \frac{k_1}{k_{-1}}k_2[\mathrm{A}_2]^2 \tag{6}$$

Derivation A1.7. Saturation equation for dimer based subunit exchange.

$$A_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2A \qquad B_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2B \qquad AB \underset{2k_{-1}}{\overset{k_1}{\rightleftharpoons}} A + B$$

The consumption rate of the reaction is defined as:

$$\frac{d[AB]}{dt} = 2k_{-1}[A][B] - k_1[AB] \tag{1}$$

Applying the steady state approximation to [A] and [B] and set [AB] to 0

$$\frac{d[A]}{dt} = 2k_1[A_2] - 2k_{-1}[A]^2 - 2k_{-1}[A][B] + k_1[AB] = 0 \tag{2}$$

$$\frac{d[B]}{dt} = 2k_1[B_2] - 2k_{-1}[B]^2 - 2k_{-1}[A][B] + k_1[AB] = 0 \tag{3}$$

Solving for [A] and [B] using the quadratic equation gives

$$[A] = \sqrt{\frac{[B]^2}{4} + \frac{k_1}{k_{-1}}[A_2]} - \frac{1}{2}[B] \qquad [B] = \sqrt{\frac{[A]^2}{4} + \frac{k_1}{k_{-1}}[B_2]} - \frac{1}{2}[A] \qquad (4) + (5)$$

Adding eq 2 to eq 3 and solving for [A] and [B] gives

$$[A] = \sqrt{\frac{k_1}{k_{-1}}([A_2]+[B_2])} - [B] \qquad [B] = \sqrt{\frac{k_1}{k_{-1}}([A_2]+[B_2])} - [A] \qquad (6) + (7)$$

Substituting eq 7 into eq 4 and eq 6 into eq 5 and solving for [A] and [B]

$$[A] = \frac{[A_2]\sqrt{k_1}}{\sqrt{k_{-1}([A_2]+[B_2])}} \qquad [B] = \frac{[B_2]\sqrt{k_1}}{\sqrt{k_{-1}([A_2]+[B_2])}} \qquad (8) + (9)$$

Substituting eq 8 and 9 into eq 1 and set [AB] to 0 gives

$$\frac{d[AB]}{dt} = \frac{2k_1[A_2][B_2]}{[A_2]+[B_2]} \tag{10}$$

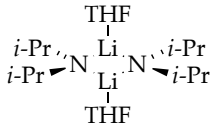
Divide top and bottom by $[A_2]$ and denote $a = 2k_1$ and $b = 1/[A_2]$ produces

$$\frac{d[AB]}{dt} = \frac{a[B_2]}{1+b[B_2]} \tag{11}$$

Part 5: DFT Computation

Chart 1

A



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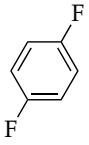

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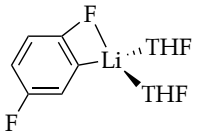

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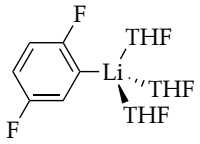

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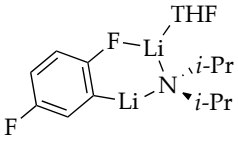

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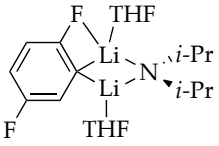

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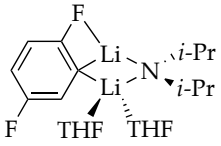

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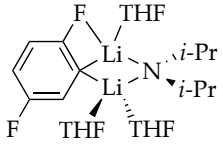
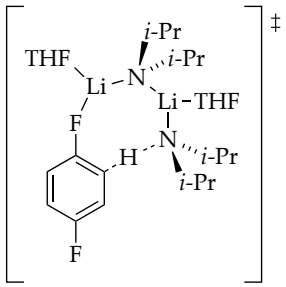


E-4

Chart 2



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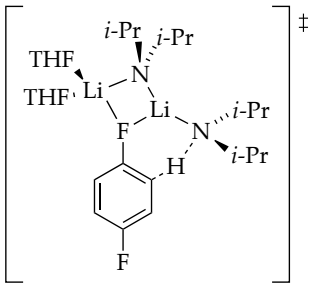

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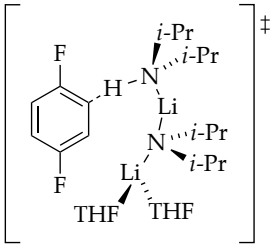

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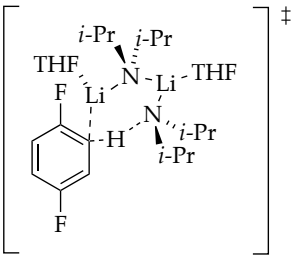

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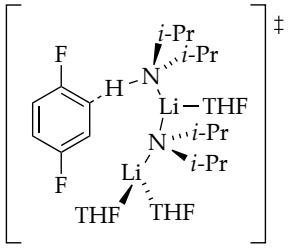

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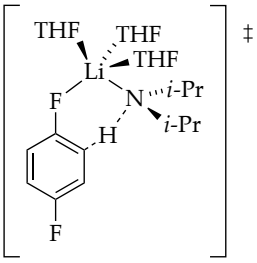

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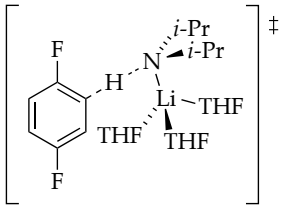

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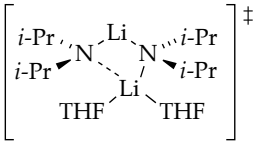

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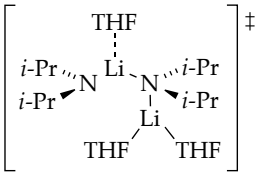
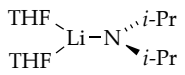


N

Chart 3



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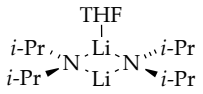

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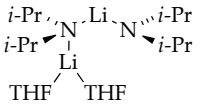

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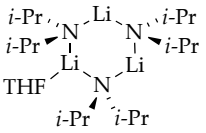

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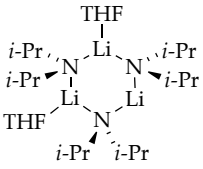

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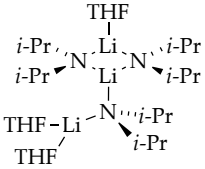

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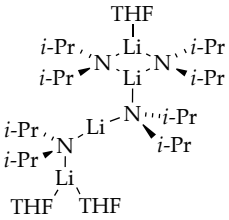

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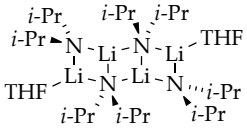

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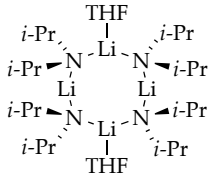

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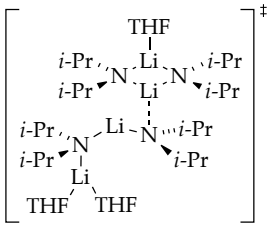

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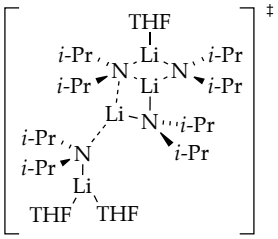

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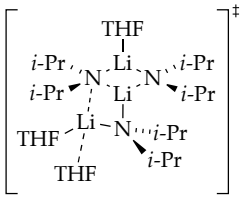

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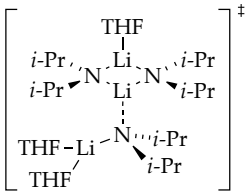
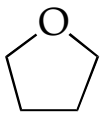
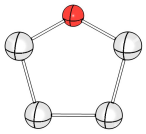


Y

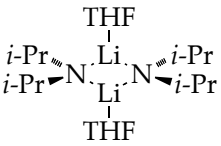
Table A1.1. Optimized geometries at B3LYP level of theory with 6-31G(d) basis set for the reactants at –78 °C with free energies (Hartrees) and cartesian coordinates (X,Y,Z) (Note: G_{MP2} includes single point MP2 corrections to B3LYP/6-31G(d) optimized structures).

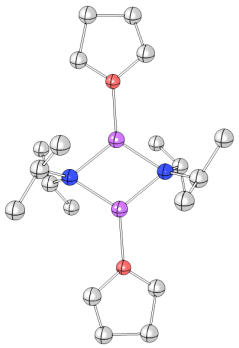




A
G = -232.349367
G_{MP2} = -231.6694404

Atom	X	Y	Z
C	0	0	0
O	1.132807	-0.739653	-0.442032
C	2.264796	-0.012388	0.019216
C	1.92285	1.47444	-0.210686
C	0.368847	1.489728	-0.185167
H	-0.032338	2.108191	0.623792
H	2.365524	2.11958	0.5546
H	2.296315	1.80941	-1.183111
H	2.436349	-0.210295	1.091379
H	3.13745	-0.361827	-0.539569
H	-0.860576	-0.323589	-0.591979
H	-0.206691	-0.218661	1.061467
H	-0.031366	1.878296	-1.126381





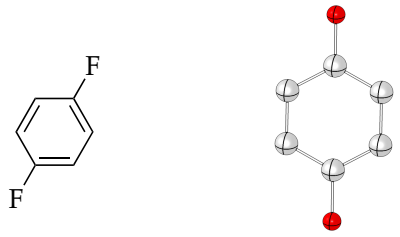
B
G = -1063.135501
G_{MP2} = -1059.937725

Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	H	2.342273	-2.489712	-3.066295
N	1.208636	1.651497	0.054512	H	1.459639	-1.024712	-2.61925
C	1.39116	2.418143	1.296121	H	2.197266	-3.327267	-0.744239
C	2.354157	1.715455	2.267998	O	4.377659	-0.007833	-0.149374

Table A1.1 (Continued).

H	3.35351	1.612369	1.827423	C	5.226931	-1.136002	0.177639
H	2.45675	2.272938	3.207825	C	6.632699	-0.75042	-0.292196
H	1.996407	0.710457	2.527911	C	6.60642	0.781703	-0.175985
C	0.062992	2.727638	2.025475	C	5.17888	1.10291	-0.614951
H	-0.404588	1.799198	2.381707	H	5.097869	1.165111	-1.708138
H	0.210938	3.384896	2.894533	H	4.76747	2.017259	-0.182359
H	-0.643891	3.225258	1.35117	H	7.356982	1.27767	-0.79854
H	1.853057	3.400278	1.081215	H	6.765393	1.090722	0.863961
Li	2.389288	0.015575	0.000151	H	6.785755	-1.049705	-1.335767
N	1.18061	-1.635948	0.054545	H	7.414534	-1.219315	0.312467
C	0.997712	-2.402508	1.296154	H	5.185927	-1.29307	1.261339
C	2.325627	-2.711789	2.026056	H	4.82494	-2.023405	-0.318518
H	2.793014	-1.783266	2.382324	C	0.916955	2.561647	-1.058533
H	2.177402	-3.368931	2.895154	C	0.262689	1.821865	-2.23548
H	3.032798	-3.209463	1.352093	H	-0.681409	1.346346	-1.94212
C	0.034251	-1.699838	2.267586	H	0.048061	2.505124	-3.066774
H	-0.96495	-1.596941	1.826616	H	0.930465	1.040099	-2.61936
H	-0.06863	-2.257225	3.207438	C	2.156626	3.319383	-1.592437
H	0.39177	-0.694765	2.527528	H	2.851123	2.61614	-2.071628
H	0.536005	-3.384713	1.081164	H	1.88059	4.081234	-2.33552
C	1.472737	-2.546163	-1.058327	H	2.695608	3.828048	-0.785076
C	0.23331	-3.304044	-1.592589	H	0.192386	3.342833	-0.744747
H	-0.461095	-2.6009	-2.072056	O	-1.988352	0.02346	-0.150036
H	0.509659	-4.065925	-2.335526	C	-2.789454	-1.087285	-0.615741
H	-0.305885	-3.812705	-0.785366	C	-4.216803	-0.766713	-0.175751
C	2.127338	-1.806416	-2.235112	C	-4.24375	0.765406	-0.291896
H	3.071325	-1.330832	-1.941487	C	-2.837739	1.151607	0.176811
H	-4.374893	-1.075857	0.864293	H	-2.796006	1.309332	1.260376
H	-4.967616	-1.262934	-0.7978	H	-2.436368	2.038844	-0.320162
H	-2.709131	-1.148906	-1.709022	H	-5.025285	1.233986	0.313398
H	-2.377444	-2.001694	-0.183863	H	-4.397782	1.064636	-1.335336

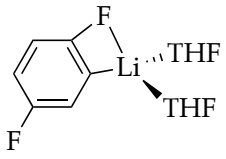
Table A1.1 (Continued).

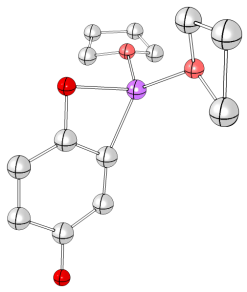


C
G = -430.647552
G_{MP2} = -429.4940576

Atom	X	Y	Z
C	0	0	0
C	0.673675	1.216576	0.000039
C	0.000262	2.433404	0.000081
C	1.395373	2.433304	0.000022
C	2.069264	1.216414	0.000165
C	1.395472	0.000144	0.000152
F	3.419751	1.216878	0.000055
H	1.960835	3.359105	0.000057
H	0.564798	3.359418	0.000189
F	2.024163	1.216878	0.000145
H	0.564873	0.926144	0.000082
H	1.959954	0.926528	-0.00016

Table A1.2. Optimized geometries at B3LYP level of theory with 6-31G(d) basis set for the serial solvation of products at –78 °C with free energies (Hartrees) and cartesian coordinates (X,Y,Z) (Note: G_{MP2} includes single point MP2 corrections to B3LYP/6-31G(d) optimized structures).

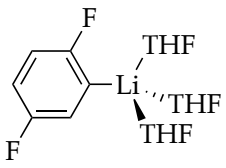


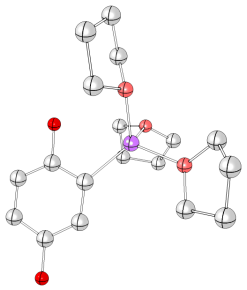


D-1
G = -902.315871
G_{MP2} = -899.7819475

Atom	X	Y	Z	Atom	X	Y	Z
C	0	0	0	H	3.89103	3.029114	-0.521797
O	0.831409	0.268012	1.142115	H	2.797179	4.385512	-0.947988
Li	2.484909	1.297424	0.956078	H	4.717384	4.196871	1.435122
C	4.357348	0.452916	0.665251	H	4.522866	5.573346	0.328766
C	5.473645	-0.062437	-0.023137	H	3.167966	5.625345	2.704464
C	6.618244	-0.476831	0.656577	H	2.303496	6.08275	1.227792
C	6.737111	-0.410682	2.042639	H	0.87188	4.263878	1.842338
C	5.655473	0.09362	2.771309	H	2.173948	3.430242	2.729556
C	4.550118	0.486557	2.031641	C	0.996743	-1.001248	1.811583
F	3.442187	1.006065	2.785818	C	-0.381401	-1.679723	1.721305
H	5.684286	0.170834	3.854916	C	-1.064484	-0.988123	0.506897
H	7.648452	-0.74539	2.527376	H	-1.354302	-1.697512	-0.273564
F	7.671275	-0.967585	-0.052757	H	-1.965987	-0.455405	0.823054
H	5.480733	-0.155223	-1.109504	H	-0.281609	-2.760323	1.584875
O	2.22798	3.208292	0.673585	H	-0.958888	-1.513258	2.635093
C	1.94035	4.025538	1.839579	H	1.773028	-1.576466	1.29001
C	2.838052	5.265385	1.725648	H	1.338894	-0.787665	2.824945
C	3.992617	4.765594	0.84189	H	-0.399648	0.955352	-0.347234
C	3.268133	3.833237	-0.123392	H	0.613239	-0.444486	-0.797456

Table A1.2 (Continued).

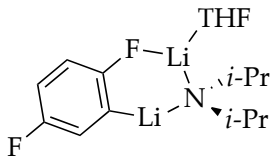


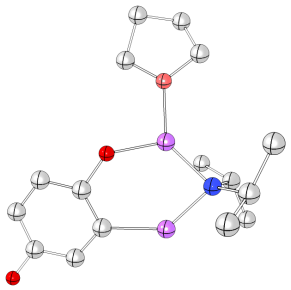


D-2
G = -1134.665978
G_{MP2} = -1131.478216

Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	C	-1.066228	1.266228	3.468569
C	-1.977909	-0.201321	-0.728057	C	-1.879143	-0.00683	3.119493
C	-2.987446	0.670318	-1.193713	C	-0.804927	-0.994998	2.662446
C	-4.24425	0.213724	-1.588177	H	-1.145597	-1.72271	1.925942
C	-4.593724	-1.130726	-1.549237	H	-0.339182	-1.515225	3.513826
C	-3.632819	-2.036155	-1.089978	H	-2.56203	0.188237	2.288331
C	-2.3976	-1.524164	-0.709516	H	-2.460156	-0.384773	3.966263
F	-1.477042	-2.485918	-0.24566	H	-1.544248	2.163509	3.065532
H	-3.842716	-3.101242	-1.032087	H	-0.967902	1.40299	4.550253
H	-5.581532	-1.450236	-1.8655	H	1.089798	0.846098	3.586058
F	-5.170841	1.111509	-2.02897	H	0.649898	1.815163	2.154685
H	-2.820971	1.747117	-1.260492	O	0.910116	1.78117	-0.406082
O	1.428339	-1.293335	-0.685155	C	2.306047	1.876526	-0.754643
C	1.854424	-2.366972	0.171392	C	2.326434	2.515664	-2.141569
C	2.821456	-3.177497	-0.69618	C	1.153516	3.504725	-2.045212
C	2.227992	-3.027042	-2.121611	C	0.140696	2.74308	-1.177823
C	1.187904	-1.890347	-1.979253	H	-0.585521	2.180422	-1.770385
H	0.163209	-2.271723	-1.999772	H	-0.402772	3.392156	-0.483389
H	1.291431	-1.096929	-2.723161	H	0.737862	3.777642	-3.019479
H	1.744598	-3.948757	-2.458736	H	1.476263	4.426548	-1.54726
H	3.005649	-2.779532	-2.850037	H	2.128463	1.757821	-2.908895
H	2.892497	-4.220261	-0.372693	H	3.281822	2.996631	-2.372632
H	3.825004	-2.742023	-0.648502	H	2.823889	2.507783	-0.017616
H	2.30134	-1.919103	1.060743	H	2.71872	0.866274	-0.71855
H	0.980095	-2.961945	0.466448	C	0.318224	1.017759	2.822223
O	0.186711	-0.16958	2.017715				

Table A1.2 (Continued).

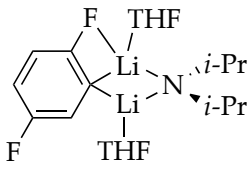


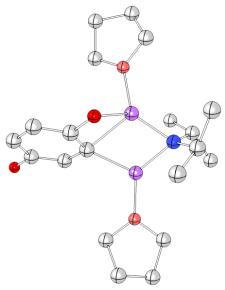


E-1
G = -969.185475
G_{MP2} = -966.3761757

Atom	X	Y	Z	Atom	X	Y	Z
N	0	0	0	H	-2.288946	5.869997	-1.041841
Li	0.127581	1.961569	-0.215594	H	-1.865965	6.59197	0.521089
Li	1.945511	-0.029353	-0.032954	H	-0.132279	4.939275	0.924211
C	3.469387	1.333381	-0.026367	H	-0.022073	5.03788	-0.849023
C	4.857577	1.202549	0.205354	C	-0.608796	-0.727766	-1.122499
C	5.718012	2.296741	0.153528	C	0.367712	-0.780076	-2.307923
C	5.274382	3.585281	-0.129005	H	1.275392	-1.348456	-2.05758
C	3.909916	3.767229	-0.365021	H	-0.08059	-1.258807	-3.186809
C	3.110693	2.63604	-0.295605	H	0.677543	0.232166	-2.606011
F	1.710531	2.903168	-0.550168	H	-0.820597	-1.776523	-0.842947
H	3.500115	4.746547	-0.5954	C	-1.952555	-0.124538	-1.590373
H	5.9776	4.410711	-0.162703	H	-2.653221	-0.02573	-0.753011
F	7.043257	2.110463	0.38463	H	-1.795914	0.875077	-2.022117
H	5.30294	0.23456	0.432862	H	-2.437032	-0.745469	-2.356073
O	-1.116161	3.436717	-0.118979	C	-0.592005	-0.363359	1.295817
C	-0.690195	4.822258	-0.012505	H	-1.695657	-0.430192	1.222757
C	-1.978575	5.645192	-0.014789	C	-0.104505	-1.728569	1.830876
C	-2.978045	4.68538	0.649478	H	-0.254485	-2.523256	1.091761
C	-2.549782	3.334626	0.076884	H	0.969385	-1.685718	2.066296
H	-3.020748	3.134817	-0.892997	H	-0.633947	-2.023124	2.747091
H	-2.740823	2.487873	0.741288	C	-0.282879	0.723555	2.339064
H	-4.021846	4.920182	0.422355	H	-0.730701	1.68942	2.065094
H	-2.854537	4.697022	1.738656	H	-0.66785	0.455309	3.330137
H	0.802094	0.872748	2.436432				

Table A1.2 (Continued).

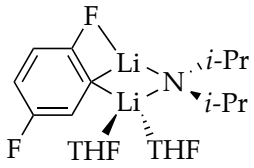


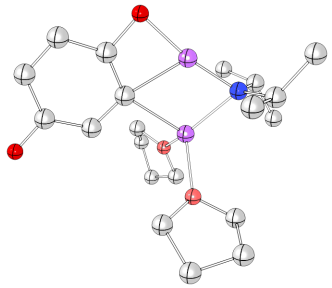


E-2
G = -1201.545187
G_{MP2} = -1198.084676

Atom	X	Y	Z	Atom	X	Y	Z
N	0	0	0	H	4.365325	0.526541	1.200296
Li	1.305203	1.49154	0.274532	H	3.775428	-0.386323	-0.211698
Li	-1.05799	1.642072	-0.33966	H	6.367023	0.598973	-0.175658
C	0.117779	3.465408	-0.072906	H	5.418401	0.626579	-1.67407
C	-0.230083	4.581967	-0.86814	H	5.694108	2.90312	0.367305
C	0.112954	5.8831	-0.505492	H	5.944103	3.011416	-1.38523
C	0.82473	6.171846	0.655293	H	3.564906	2.774231	-1.832741
C	1.205946	5.103508	1.471052	H	3.481313	3.651076	-0.285106
C	0.826525	3.832166	1.059183	C	-0.309479	-0.747005	1.224229
F	1.267876	2.766485	1.887357	C	-1.076668	0.141393	2.218064
H	1.767522	5.260105	2.387715	H	-2.037414	0.467862	1.796672
H	1.070981	7.199127	0.903123	H	-1.289294	-0.390242	3.154181
F	-0.25938	6.916049	-1.306336	H	-0.498306	1.039384	2.470473
H	-0.783411	4.460217	-1.80006	H	-0.966371	-1.612661	1.010924
O	-2.963357	1.942	-0.638989	C	0.943077	-1.326462	1.924561
C	-3.946362	0.874573	-0.69592	H	1.53427	-1.938336	1.233166
C	-5.283892	1.495254	-0.254748	H	1.586611	-0.514709	2.293848
C	-4.850443	2.772213	0.48537	H	0.679088	-1.960182	2.782876
C	-3.620463	3.188673	-0.314412	C	0.258976	-0.884887	-1.139162
H	-2.900466	3.804144	0.22759	H	0.952346	-1.705717	-0.860903
H	-3.900927	3.704062	-1.243531	C	-1.007813	-1.568817	-1.707015
H	-4.568328	2.546307	1.520177	H	-1.569862	-2.093533	-0.926622
H	-5.625336	3.544309	0.500526	H	-1.674266	-0.818815	-2.155869
H	-5.866951	0.81326	0.370718	H	-0.757161	-2.304352	-2.484098
H	-5.894385	1.752798	-1.127527	C	0.943275	-0.107627	-2.275047
H	-3.977993	0.477227	-1.71523	H	1.905931	0.307406	-1.954593
H	-3.605264	0.08154	-0.024035	H	1.121833	-0.747094	-3.148517
O	3.219077	1.603421	-0.154354	H	0.314087	0.731794	-2.606353
C	3.854804	2.748935	-0.77482	C	5.455631	0.987331	-0.639536
C	5.356943	2.520803	-0.603397	C	4.193593	0.568976	0.117307

Table A1.2 (Continued).

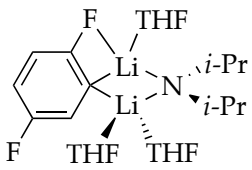


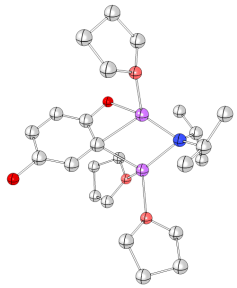


E-3
G = -1201.534585
G_{MP2} = -1198.076993

Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	H	-2.554855	1.214013	-1.201208
N	-1.451067	-1.344955	-0.799489	H	-3.719616	0.703986	-2.444832
Li	0.259201	-2.171783	-1.025234	C	-1.241543	-0.376367	-3.051579
F	1.765657	-3.284262	-1.285997	H	-0.614855	-1.216489	-3.382904
C	2.6186	-2.367018	-0.575295	H	-1.785865	-0.005529	-3.929122
C	2.010025	-1.206407	-0.13467	H	-0.581582	0.426644	-2.702355
C	2.92433	-0.370451	0.545458	O	0.600807	1.762469	-0.866527
C	4.260663	-0.722739	0.725776	C	-0.009275	3.042074	-0.588524
C	4.791659	-1.916558	0.24865	C	0.918886	4.091096	-1.205571
C	3.933501	-2.78143	-0.43505	C	1.510692	3.326401	-2.399223
H	4.278473	-3.729098	-0.837412	C	1.678822	1.92026	-1.823128
H	5.83813	-2.153784	0.408122	H	2.632107	1.802306	-1.296661
F	5.083541	0.131478	1.390389	H	1.592505	1.124051	-2.566143
H	2.614091	0.593248	0.949743	H	2.455922	3.744618	-2.757668
C	-2.287708	-2.072339	0.161025	H	0.801929	3.316807	-3.235673
C	-1.408075	-2.625444	1.294877	H	1.710359	4.367273	-0.498816
H	-0.804023	-1.836986	1.755885	H	0.385855	5.002479	-1.492552
H	-2.016133	-3.095018	2.077973	H	-1.004368	3.064172	-1.052204
H	-0.718989	-3.398893	0.921535	H	-0.123727	3.134558	0.494711
H	-3.035041	-1.406444	0.646615	O	-0.393996	0.762175	1.867801
C	-3.104973	-3.244699	-0.42996	C	-1.748889	1.021434	2.297688
H	-3.851457	-2.91159	-1.15786	C	-1.801514	0.559383	3.751247
H	-2.437792	-3.955981	-0.937439	C	-0.398287	0.94085	4.249874
H	-3.64216	-3.784004	0.361158	C	0.482023	0.672079	3.021122
C	-2.204118	-0.813681	-1.938522	H	0.919602	-0.331363	3.031405
H	-2.849936	-1.588945	-2.390148	H	1.290221	1.401157	2.906162
C	-3.139533	0.362605	-1.576617	H	-0.076852	0.362751	5.120982
H	-3.855052	0.078873	-0.796117	H	-0.36763	2.002607	4.521192
H	-1.954157	2.098609	2.213951	H	-1.947155	-0.525447	3.796766
H	-2.416104	0.478512	1.625811	H	-2.606156	1.039159	4.316448

Table A1.2 (Continued).

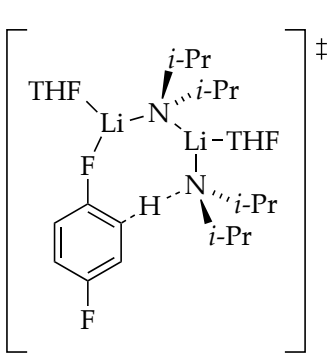


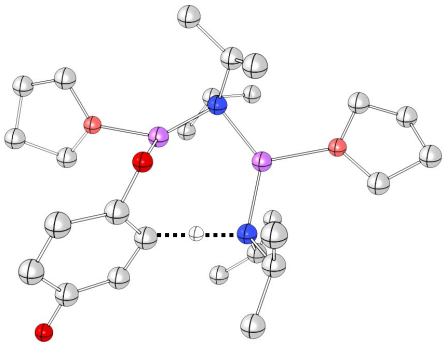


E-4
G = -1433.88825
G_{MP2} = -1429.779748

Atom	X	Y	Z	Atom	X	Y	Z
N	0	0	0	C	-5.594927	1.63566	-0.729663
Li	1.036157	1.765313	-0.379037	C	-4.961515	2.614248	-1.732088
Li	-1.41945	1.328559	-0.340139	C	-3.726271	1.839671	-2.183445
C	-0.576225	3.309926	-0.995372	H	-2.900484	2.470684	-2.519548
C	-0.198628	4.21489	-2.012518	H	-3.97055	1.110438	-2.968086
C	-0.647644	5.535523	-2.034046	H	-4.658972	3.541347	-1.232355
C	-1.506153	6.048814	-1.067174	H	-5.624984	2.870217	-2.563676
C	-1.927728	5.189322	-0.047295	H	-6.254454	2.124269	-0.006435
C	-1.437161	3.889989	-0.078754	H	-6.179864	0.874548	-1.259062
F	-1.902014	3.035819	0.954954	H	-4.503001	-0.057826	0.177095
H	-2.605095	5.524822	0.733574	H	-4.081084	1.53559	0.855089
H	-1.834924	7.081527	-1.120283	O	1.996561	2.98596	1.057099
F	-0.234661	6.360618	-3.033509	C	2.874683	4.012778	0.546807
H	0.459476	3.907655	-2.825462	C	3.058414	5.006437	1.693091
C	0.209479	-0.602523	1.323408	C	1.682912	4.95019	2.372984
C	-0.623813	0.104901	2.403645	C	1.318353	3.468051	2.244994
H	-1.695555	0.007024	2.186454	H	0.247191	3.301137	2.12141
H	-0.441636	-0.315765	3.401719	H	1.676299	2.882707	3.10098
H	-0.390762	1.175047	2.447789	H	0.961624	5.565713	1.823909
H	-0.12873	-1.653673	1.330904	H	1.697558	5.286228	3.414232
C	1.697018	-0.643986	1.746479	H	3.3279	6.006421	1.339485
H	2.29525	-1.170343	0.992492	H	3.842223	4.662162	2.378602
H	2.101071	0.371808	1.84875	H	3.802051	3.534637	0.221681
H	1.840893	-1.16633	2.703556	H	2.395981	4.489427	-0.318659
C	0.04112	-1.022671	-1.052728	O	2.728985	1.705286	-1.587862
H	0.943766	-1.666188	-0.951259	C	3.658222	0.612857	-1.386878
C	-1.173893	-1.985291	-1.051618	C	4.378343	0.431083	-2.72427
H	-1.309519	-2.473688	-0.080754	C	4.379379	1.861489	-3.285337
H	-2.091983	-1.42689	-1.277651	C	3.012039	2.379697	-2.833126
H	-1.05925	-2.778582	-1.804135	H	2.225994	2.12702	-3.556503
C	0.125115	-0.374593	-2.444414	H	2.986976	3.458054	-2.652974
H	1.011224	0.26042	-2.537516	H	4.501881	1.903146	-4.371695
H	0.159412	-1.135256	-3.234785	H	5.183729	2.451288	-2.829564
H	-0.754481	0.255812	-2.63586	H	3.805103	-0.23522	-3.3791
O	-3.278452	1.130147	-1.005579	H	5.381272	0.010701	-2.604426
C	-4.36828	1.002568	-0.057729	H	4.35468	0.890742	-0.584914
H	3.085468	-0.260587	-1.067717				

Table A1.3. Optimized geometries of dimer-based transition state structures at B3LYP level of theory with 6-31G(d) basis set for the ortholithiation of **1** at –78 °C with free energies (Hartrees), and cartesian coordinates (X,Y,Z). (Note: G_{MP2} includes single point MP2 corrections to B3LYP/6-31G(d) optimized structures)



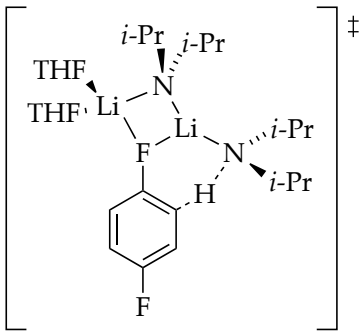


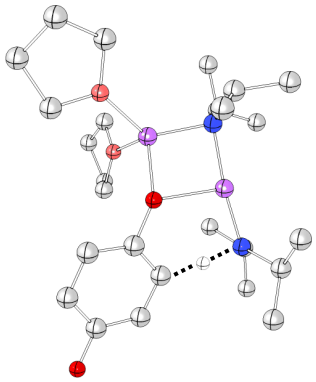
F
G = -1493.742385
G_{MP2} = -1489.417062

Atom	X	Y	Z	Atom	X	Y	Z
N	0	0	0	C	-2.989629	2.812244	-1.35154
Li	0.964914	1.835393	0.016495	C	-4.232279	2.980886	-1.947721
N	0.219992	3.741485	0.264427	C	-5.11067	3.88612	-1.350356
C	0.614788	4.681116	-0.807611	C	-4.684942	4.542655	-0.197288
H	1.675811	4.9622	-0.660878	C	-3.423556	4.342246	0.354429
C	0.519773	4.00604	-2.183357	C	-2.500837	3.44665	-0.223606
H	-0.501795	3.680102	-2.398466	H	-3.164189	4.910877	1.243946
H	0.824537	4.697498	-2.978963	F	-5.536816	5.414102	0.396817
H	1.166832	3.122808	-2.244294	H	-6.096258	4.083718	-1.758478
C	-0.167533	6.014765	-0.834707	H	-4.505373	2.429092	-2.842584
H	-0.086254	6.546997	0.119241	O	-3.594654	0.021812	0.076442
H	0.227664	6.679935	-1.614282	C	-4.07997	-1.218062	-0.497848
H	-1.230406	5.847622	-1.039041	C	-5.447217	-1.473736	0.145282
C	0.570396	4.287275	1.598175	C	-5.919983	-0.052946	0.489674
H	1.218222	5.170717	1.463244	C	-4.616826	0.616919	0.915588
C	-0.640216	4.757416	2.429981	H	-4.377902	0.401682	1.965954
H	-1.334329	3.927694	2.612469	H	-4.594406	1.695775	0.757683
H	-0.321882	5.14664	3.406106	H	-6.679015	-0.028288	1.277069
H	-1.189375	5.551182	1.915541	H	-6.327898	0.445507	-0.397145
C	1.389206	3.287087	2.437606	H	-5.336483	-2.070146	1.058362
H	2.296247	2.971433	1.909627	H	-6.125934	-2.007316	-0.526508
H	1.694442	3.724408	3.397503	H	-4.160093	-1.082309	-1.583224
H	0.80141	2.389562	2.66555	H	-3.346985	-2.003367	-0.295802
O	3.035009	1.847221	-0.365037	C	0.00732	-0.740568	1.274688
C	3.897226	0.688324	-0.413083	H	-0.37228	-1.771142	1.13376
C	5.299917	1.222209	-0.139409	C	1.406066	-0.903795	1.913651
C	5.257894	2.578163	-0.860545	H	1.836446	0.073494	2.170256
C	3.816654	3.044572	-0.612675	H	1.359097	-1.502477	2.833673

Table A1.3 (Continued).

H	3.384768	3.576208	-1.464217	H	2.096483	-1.413861	1.232377
H	3.737548	3.685237	0.271919	C	-0.941255	-0.084036	2.2916
H	5.440078	2.442107	-1.932901	H	-1.984674	-0.162681	1.965876
H	5.993639	3.294349	-0.483111	H	-0.866617	-0.560565	3.276937
H	6.083409	0.556194	-0.51328	H	-0.707903	0.980097	2.420888
H	5.451723	1.360505	0.937663	C	0.485783	-0.836797	-1.111045
H	3.534749	-0.02396	0.327897	H	1.429056	-1.35114	-0.837749
H	3.831737	0.228913	-1.408935	C	0.801105	0.024789	-2.343808
Li	-1.782541	0.781681	-0.31937	H	-0.085129	0.584767	-2.666841
F	-2.160478	1.829222	-1.943975	H	1.596612	0.749024	-2.137506
H	-0.040528	-2.614375	-2.298574	H	1.128151	-0.595537	-3.187846
H	-0.79744	-2.585252	-0.701861	C	-0.493256	-1.955336	-1.545292
H	-1.169434	3.5204	0.098493	H	-1.399792	-1.519603	-1.989019



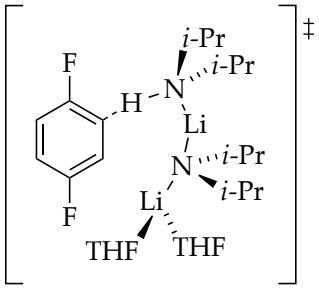


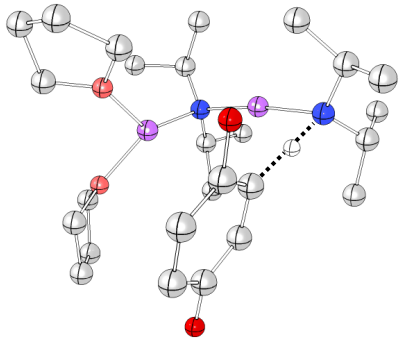
G
G = -1493.745707
G_{MP2} = -1489.410302

Atom	X	Y	Z	Atom	X	Y	Z
N	0	0	0	C	0.740486	3.819534	2.397735
Li	1.928702	0.436552	-0.210132	H	1.68339	3.414819	2.029016
N	3.890328	0.52216	0.159332	H	0.648183	4.85952	2.056904
C	4.694988	-0.143385	-0.884847	H	0.9727	2.761078	4.269824
H	5.192748	-1.026248	-0.446294	H	1.017652	4.525949	4.452922
C	3.784738	-0.667898	-2.00984	H	-1.344148	3.235271	4.951881
H	3.2365	0.160657	-2.482151	H	-1.375519	4.716262	3.981955
H	4.358748	-1.164584	-2.802611	H	-2.336819	3.269248	2.331638
H	3.055714	-1.391726	-1.623595	H	-1.531788	1.830641	3.001766
C	5.793135	0.748369	-1.505799	O	-1.992051	2.828526	-0.692906
H	6.470183	1.145763	-0.744502	C	-2.06788	4.242618	-0.985464
H	6.393277	0.185091	-2.232837	C	-3.541072	4.524791	-1.284451
H	5.347327	1.60277	-2.028307	C	-3.998209	3.195957	-1.906142
C	4.325846	0.199113	1.526116	C	-3.225982	2.170498	-1.074777
H	4.242111	-0.894968	1.683422	H	-2.970809	1.258009	-1.617629
C	5.785849	0.571356	1.869119	H	-3.770659	1.896621	-0.162171
H	5.952383	1.650109	1.75438	H	-3.695758	3.142478	-2.958385

Table A1.3 (Continued).

H	6.020765	0.299916	2.90688	H	-5.080035	3.042639	-1.855277
H	6.500445	0.04759	1.226568	H	-3.674102	5.383808	-1.948416
C	3.392595	0.879293	2.539558	H	-4.09074	4.723632	-0.356622
H	2.342988	0.612838	2.36469	H	-1.676067	4.788779	-0.122914
H	3.643227	0.581907	3.564978	H	-1.434346	4.454155	-1.856675
H	3.486265	1.969753	2.473604	C	-0.308195	-0.584741	1.320533
Li	-0.373356	1.965856	0.113398	C	0.555553	-1.799124	1.752088
F	1.365218	2.577261	-0.791525	H	0.416927	-2.014764	2.821168
C	2.375639	3.600205	-0.736105	H	0.305957	-2.709295	1.198722
C	1.976421	4.861449	-1.150924	H	1.620211	-1.594619	1.589155
C	2.938169	5.874255	-1.091253	H	-0.051728	0.205291	2.050096
C	4.210942	5.546364	-0.629859	C	-1.79936	-0.905913	1.568633
C	4.554617	4.254641	-0.238272	H	-2.146312	-1.749962	0.961436
C	3.613506	3.212466	-0.281344	H	-1.970988	-1.171682	2.619659
H	5.575915	4.075054	0.096217	H	-2.436449	-0.043866	1.329202
F	5.142684	6.530614	-0.570027	C	-0.644782	-0.637355	-1.155565
H	2.71698	6.890987	-1.398376	C	-0.317623	0.167904	-2.426676
H	0.97168	5.057522	-1.514882	H	-0.606765	1.220876	-2.329782
O	-0.335875	3.037128	1.822904	H	0.758063	0.138033	-2.646071
C	-1.411707	2.89746	2.784616	H	-0.837783	-0.245432	-3.299673
C	-0.984659	3.69302	4.025819	H	-1.751133	-0.618097	-1.056195
C	0.547731	3.703394	3.905961	C	-0.28983	-2.119584	-1.425526
H	0.796958	-2.252231	-1.504039	H	-0.650347	-2.780641	-0.632743
H	3.847704	1.860382	-0.01825	H	-0.742945	-2.463282	-2.365704





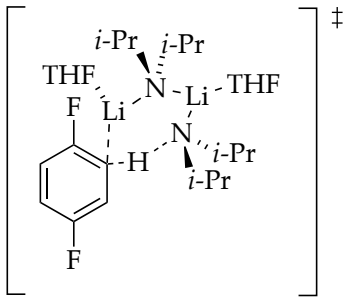
H
G = -1493.738102
G_{MP2} = -1489.408464

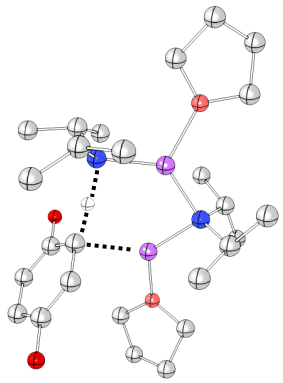
Atom	X	Y	Z	Atom	X	Y	Z
N	0	0	0	H	3.833656	1.705623	3.25059
Li	-1.656097	0.905947	0.633139	O	2.971787	2.029818	0.313192
N	-3.205031	2.023551	1.157528	C	3.767692	1.654598	-0.827177
C	-3.888418	1.740974	2.439449	C	4.011676	2.961542	-1.601117
H	-4.78652	1.132596	2.236317	C	3.821907	4.07548	-0.533232
C	-2.994219	0.908374	3.367347	C	3.482416	3.305411	0.75419
H	-2.071568	1.450095	3.598852	H	2.711763	3.777206	1.365201

Table A1.3 (Continued).

H	-3.500198	0.699869	4.318604	H	4.379105	3.133313	1.367118
H	-2.738215	-0.056306	2.912498	H	3.003151	4.745463	-0.804161
C	-4.363224	3.011001	3.180618	H	4.722074	4.683204	-0.401813
H	-4.959951	3.658697	2.528966	H	3.281249	3.073497	-2.406764
H	-4.989203	2.747735	4.043805	H	5.00862	2.974959	-2.051101
H	-3.508265	3.587636	3.544671	H	4.710637	1.21418	-0.47214
C	-4.190889	2.360935	0.111621	H	3.208777	0.898778	-1.381961
H	-5.028245	2.928294	0.55364	C	0.17785	0.128423	-1.460491
C	-3.592133	3.263615	-0.973699	C	-0.931709	-0.544109	-2.303195
H	-2.74114	2.778802	-1.470467	H	-1.898101	-0.052511	-2.126464
H	-4.337493	3.481165	-1.748248	H	-0.711001	-0.472177	-3.376492
H	-3.245462	4.212829	-0.555776	H	-1.051161	-1.606041	-2.066216
C	-4.803675	1.101725	-0.534212	H	1.131348	-0.343902	-1.780271
H	-5.230851	0.431691	0.220471	C	0.256684	1.604119	-1.87205
H	-5.603143	1.360155	-1.241776	H	1.04241	2.142033	-1.332915
H	-4.036782	0.53961	-1.085101	H	0.44813	1.704847	-2.947544
Li	1.339759	1.134307	1.0169	H	-0.689906	2.116508	-1.66314
O	1.869871	1.092149	2.944122	C	0.201819	-1.400542	0.424457
C	3.233953	0.790232	3.326116	C	-0.564925	-1.7065	1.71608
C	3.154369	0.294565	4.76839	H	-0.281404	-1.009948	2.515696
C	1.991341	1.130622	5.321432	H	-1.647613	-1.620544	1.560925
C	1.029476	1.173171	4.133402	H	-0.362539	-2.723152	2.0758
H	0.436397	2.085695	4.076582	H	-0.194616	-2.095682	-0.333987
H	0.355525	0.309202	4.132076	C	1.691542	-1.780334	0.604557
H	2.332963	2.140411	5.577118	H	2.124156	-1.254424	1.467322
H	1.527659	0.694755	6.210953	H	1.820802	-2.856927	0.780237
H	4.093721	0.439783	5.310136	H	2.277598	-1.520338	-0.285267
H	2.90579	-0.772903	4.792761	C	0.294281	5.296512	2.917768
H	3.630634	0.050944	2.62495	C	0.840091	5.922389	1.793258
F	-1.122443	3.697829	3.88036	C	0.404918	5.492735	0.5457
H	-0.847689	4.240549	-0.625158	C	-0.548432	4.490222	0.390763
F	0.954009	6.067689	-0.566142	C	-1.12355	3.83405	1.49671
H	1.569761	6.721475	1.876875	C	-0.645288	4.288031	2.72136
H	0.582194	5.591834	3.923231	H	-2.242381	2.950164	1.347369

Table A1.3 (Continued).



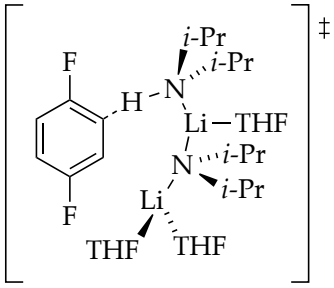


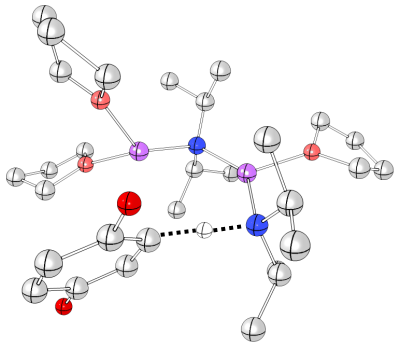
I
G = -1493.734144
G_{MP2} = -1489.410234

Atom	X	Y	Z	Atom	X	Y	Z
N	0	0	0	H	5.403198	0.466256	1.038726
Li	-1.192693	-1.695058	-0.063952	H	5.743783	2.019033	0.24517
N	-0.675301	-3.675555	-0.137412	H	3.562048	2.00221	-0.878403
C	-1.148543	-4.376495	-1.350143	H	3.131317	1.336763	0.713322
H	-2.22586	-4.605173	-1.220472	C	0.140186	0.620646	1.329106
C	-1.037033	-3.466724	-2.581355	C	-1.197586	0.879091	2.061197
H	0.002476	-3.183786	-2.767809	H	-1.702578	-0.068544	2.292019
H	-1.405538	-3.980097	-3.478343	H	-1.040196	1.415054	3.007181
H	-1.629062	-2.553358	-2.459959	H	-1.875896	1.485654	1.452126
C	-0.479822	-5.735454	-1.661976	H	0.632356	1.610421	1.252378
H	-0.615862	-6.451724	-0.84627	C	1.041618	-0.224649	2.242108
H	-0.926545	-6.179908	-2.561775	H	2.058563	-0.327537	1.840363
H	0.592109	-5.616726	-1.846255	H	1.133636	0.223763	3.238821
C	-1.045372	-4.425753	1.083509	H	0.632435	-1.233338	2.372176
H	-1.907134	-5.075219	0.839933	C	-0.468786	0.9808	-0.994582
C	0.045503	-5.352308	1.669429	C	-0.929603	0.274657	-2.276728
H	0.866831	-4.771015	2.10151	H	-0.123408	-0.345235	-2.692892
H	-0.37121	-5.978265	2.470086	H	-1.791818	-0.375469	-2.093508
H	0.476594	-6.012039	0.912729	H	-1.218613	0.99939	-3.048041
C	-1.52163	-3.481228	2.203366	H	-1.34855	1.538031	-0.612968
H	-2.369148	-2.864223	1.881319	C	0.566878	2.060824	-1.389999
H	-1.833198	-4.041369	3.09461	H	1.406673	1.605415	-1.931031
H	-0.712591	-2.808496	2.51381	H	0.115237	2.818401	-2.044714
O	-3.229971	-1.436471	-0.186793	H	0.96957	2.58574	-0.517296
C	-3.988817	-0.213087	-0.024911	C	4.125078	-4.314803	-1.276906
C	-5.391026	-0.521364	-0.551294	C	4.795021	-4.242968	-0.053098
C	-5.5325	-2.014431	-0.220202	C	4.116755	-3.693858	1.029947
C	-4.122861	-2.533664	-0.503311	C	2.798877	-3.257338	0.931631
H	-3.994481	-2.795269	-1.560657	C	2.084295	-3.319733	-0.283016
H	-3.833222	-3.392965	0.104776	C	2.819115	-3.839196	-1.350422
H	-6.291575	-2.52393	-0.821096	F	2.229974	-3.898686	-2.58718
H	-5.787847	-2.149322	0.837646	H	2.322372	-2.886587	1.836971

Table A1.3 (Continued).

H	-5.438256	-0.365205	-1.63555	F	4.762831	-3.591272	2.219033
H	-6.157453	0.10391	-0.083718	H	5.813249	-4.599367	0.06442
H	-4.005621	0.048921	1.039538	H	4.605266	-4.726264	-2.160084
H	-3.47543	0.581401	-0.571856	H	0.74717	-3.411744	-0.251461
Li	1.662541	-0.996964	-0.434338	C	4.554852	-0.679694	-1.386618
O	3.384134	-0.072406	-0.768623	H	4.697438	-1.658461	-0.925902
C	3.758271	1.189332	-0.167906	H	4.3555	-0.813792	-2.454713
C	5.247885	1.0512	0.124789	H	6.66286	-0.271745	-0.939426
C	5.728541	0.271017	-1.108837	H	5.883853	0.954586	-1.951406





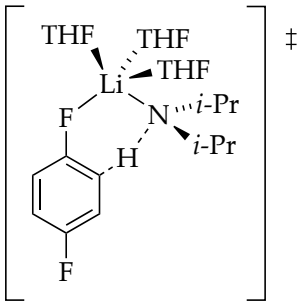
J
G = -1726.079261
G_{MP2} = -1721.100781

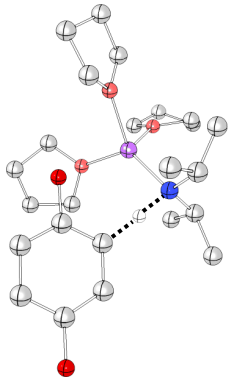
Atom	X	Y	Z	Atom	X	Y	Z
N	0	0	0	C	3.548958	1.837012	4.353121
Li	-1.37906	1.57084	0.246915	C	2.374992	1.956319	3.382055
N	-1.384291	3.647861	0.289643	H	2.196647	2.970224	3.027833
C	-1.864966	4.161012	1.591151	H	1.451211	1.561629	3.821883
H	-2.964498	4.034964	1.635217	H	4.327934	2.567721	4.105483
C	-1.271671	3.330209	2.736971	H	3.245967	2.00207	5.391228
H	-0.184518	3.437948	2.762106	H	5.078561	0.237589	4.393276
H	-1.664251	3.666276	3.704952	H	3.406539	-0.320247	4.593835
H	-1.516149	2.266438	2.636767	H	3.671801	-0.717007	2.221386
C	-1.613379	5.659952	1.878931	H	4.747955	0.687593	2.034924
H	-2.107774	6.303605	1.145058	O	3.481877	0.407254	-0.573112
H	-2.01796	5.925474	2.865166	C	3.752938	-0.919797	-1.088087
H	-0.543813	5.889079	1.881086	C	5.049733	-0.804915	-1.895466
C	-2.062364	4.324953	-0.839545	C	5.758097	0.374803	-1.211692
H	-3.032247	4.714078	-0.476535	C	4.58231	1.295564	-0.896128
C	-1.303305	5.527719	-1.448673	H	4.308735	1.907593	-1.760978
H	-0.396029	5.19613	-1.964419	H	4.739716	1.955388	-0.03964
H	-1.933369	6.048434	-2.182524	H	6.506475	0.857769	-1.84674
H	-0.99922	6.250886	-0.688903	H	6.251765	0.045062	-0.289217
C	-2.385806	3.342703	-1.979872	H	4.830794	-0.55974	-2.94105
H	-2.982318	2.491531	-1.630278	H	5.630644	-1.731877	-1.879579
H	-2.945241	3.836937	-2.784953	H	3.864631	-1.601055	-0.23595

Table A1.3 (Continued).

H	-1.463824	2.949553	-2.424055	H	2.89481	-1.243453	-1.682408
O	-3.366057	0.943296	0.61015	C	-0.022899	-0.49092	-1.391829
C	-4.486801	1.831111	0.772088	C	-1.417735	-0.915778	-1.913327
C	-5.68336	1.104499	0.127392	H	-2.109281	-0.062726	-1.921175
C	-5.251584	-0.387903	0.119355	H	-1.352446	-1.304116	-2.938601
C	-3.893977	-0.373229	0.83848	H	-1.861731	-1.706879	-1.299487
H	-3.171642	-1.091531	0.45445	H	0.615069	-1.3912	-1.504896
H	-4.015826	-0.530468	1.920948	C	0.553971	0.557929	-2.351992
H	-5.135732	-0.751655	-0.905962	H	1.592641	0.802085	-2.107609
H	-5.969547	-1.040369	0.625271	H	0.525598	0.202992	-3.389919
H	-5.85676	1.464666	-0.890785	H	-0.025679	1.486284	-2.306112
H	-6.601837	1.271853	0.697832	C	-0.241095	-1.102366	0.947269
H	-4.655207	2.002979	1.844929	C	-0.5552	-0.560337	2.347923
H	-4.225949	2.777452	0.301652	H	0.275324	0.051751	2.718576
Li	1.76139	0.940398	0.430647	H	-1.456816	0.061447	2.346234
O	2.727065	1.126447	2.238892	H	-0.714977	-1.376236	3.064476
C	3.869135	0.301546	2.566097	H	-1.121468	-1.703679	0.646327
C	4.043965	0.409804	4.081194	C	0.917912	-2.123174	1.069041
C	1.349096	4.022723	0.074704	H	1.808698	-1.643572	1.496155
C	2.148475	4.736903	0.9615	H	0.643699	-2.960246	1.725436
F	1.676903	4.961161	2.245097	H	1.195159	-2.548686	0.098915
H	1.399141	3.322832	-1.984171	C	3.407917	5.264278	0.693704
F	3.730643	4.105577	-2.729802	C	3.953997	5.064741	-0.577819
H	4.929716	5.452524	-0.852396	C	3.196469	4.350596	-1.496367
H	3.942941	5.824648	1.455855	C	1.934572	3.846207	-1.19369
H	-0.037327	3.804473	0.232869				

Table A1.4. Optimized geometries of monomer-based transition state structures at B3LYP level of theory with 6-31G(d) basis set for the ortholithiation of **1** at –78 °C with free energies (Hartrees), and cartesian coordinates (X,Y,Z). (Note: G_{MP2} includes single point MP2 corrections to B3LYP/6-31G(d) optimized structures)



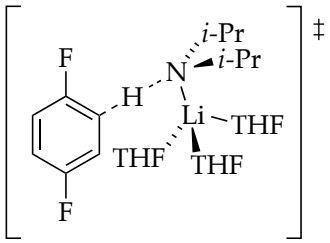


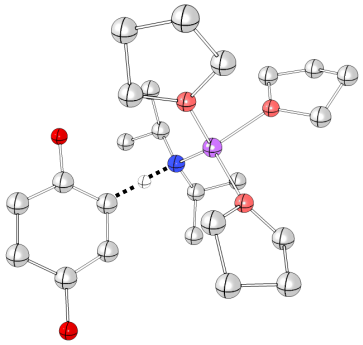
K
G = -1426.871146
G_{MP2} = -1422.815045

Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	C	-2.492091	0.310904	-1.991576
N	1.160162	1.522202	0.85362	H	-1.780564	0.58542	-2.77892
C	1.06774	1.622684	2.327489	H	-2.618481	-0.77569	-2.00617
H	1.479617	2.585934	2.672278	H	-4.081046	1.270281	-3.16178
C	-0.390283	1.580151	2.827681	H	-4.628858	0.52218	-1.651037
H	-0.850367	0.613347	2.586684	H	-2.931233	3.062451	-1.932302
H	-0.44448	1.722318	3.915981	H	-4.407923	2.872561	-0.969473
H	-0.993629	2.369047	2.363556	H	-3.275767	1.478062	0.664299
C	1.899144	0.533126	3.021507	H	-1.922299	2.537111	0.204099
H	1.64837	-0.461171	2.638303	O	-0.882126	-1.582113	1.127516
H	2.968491	0.681258	2.850024	C	-0.221883	-2.469859	2.061275
H	1.718775	0.5405	4.104056	C	-1.153532	-3.671285	2.176462
C	1.060379	2.852823	0.221592	C	-2.531435	-2.991613	2.140137
H	0.183689	3.38898	0.634182	C	-2.309282	-1.818584	1.169423
C	0.840785	2.719562	-1.292175	H	-2.815636	-0.902456	1.487988
H	0.730584	3.705509	-1.761607	H	-2.637162	-2.059276	0.152019
H	1.700648	2.225867	-1.758168	H	-2.793701	-2.619781	3.137088
H	-0.054571	2.130624	-1.51741	H	-3.335561	-3.655723	1.809273
C	2.283434	3.770674	0.457394	H	-0.982805	-4.251145	3.088394
H	3.167309	3.37212	-0.052428	H	-1.025182	-4.339774	1.316551
H	2.094251	4.779035	0.065783	H	0.768318	-2.684309	1.660988
H	2.527579	3.87268	1.519545	H	-0.111563	-1.960955	3.02796
O	0.372403	-0.946668	-1.811034	C	5.937692	-1.259109	-0.140916
C	0.097566	-2.349342	-1.98339	C	5.952136	0.131053	-0.164366
C	1.399805	-2.954984	-2.498369	C	4.795252	0.891121	-0.005485
C	1.922939	-1.834715	-3.412279	C	3.53859	0.289191	0.180843
C	1.461386	-0.55601	-2.694521	C	3.582041	-1.095326	0.197282
H	1.090153	0.206004	-3.388374	C	4.707536	-1.896484	0.04604
H	2.246185	-0.122527	-2.070535	H	4.634674	-2.980822	0.07864

Table A1.4 (Continued).

H	1.468626	-1.90891	-4.407445	F	2.370238	-1.781612	0.364709
H	3.009265	-1.860111	-3.534719	H	4.902821	1.975977	-0.025881
H	1.246157	-3.903162	-3.023212	F	7.144191	0.761642	-0.346484
H	2.083652	-3.116027	-1.661657	H	6.860412	-1.817036	-0.263215
H	-0.229165	-2.736218	-1.016485	H	2.309823	0.983985	0.512862
H	-0.717119	-2.475724	-2.714252	C	-3.509155	2.358362	-1.322587
O	-1.93465	0.688083	-0.712732	C	-3.80897	1.07998	-2.119269
C	-2.653825	1.82069	-0.174033				





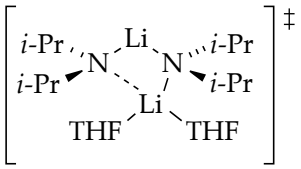
L
G = -1426.867251
G_{MP2} = -1422.810814

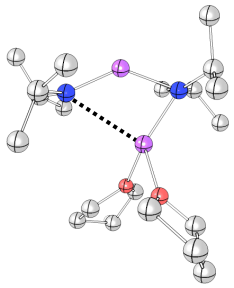
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	H	2.499832	4.408857	1.024973
N	0.886732	-1.219237	-1.411148	H	1.062254	2.660908	1.916424
C	0.741567	-0.757156	-2.807456	H	2.183354	1.672558	0.935369
H	1.04291	-1.556136	-3.506369	O	0.266204	-0.205678	2.054772
C	-0.717125	-0.406743	-3.168102	C	-0.770897	0.198991	2.974926
H	-1.070377	0.451224	-2.580739	C	-0.276676	-0.165701	4.386357
H	-0.815497	-0.15194	-4.232426	C	0.818808	-1.207366	4.10672
H	-1.389264	-1.24959	-2.968915	C	1.408403	-0.688791	2.799702
C	1.655592	0.43657	-3.111846	H	1.912378	-1.440029	2.19499
H	1.50236	1.239306	-2.381011	H	2.103277	0.143511	2.980441
H	2.707914	0.145856	-3.069367	H	0.382955	-2.201689	3.955547
H	1.450614	0.840816	-4.111154	H	1.561658	-1.276165	4.906911
C	0.613558	-2.673274	-1.330923	H	-1.083411	-0.543826	5.021504
H	-0.289521	-2.898221	-1.929267	H	0.154295	0.711659	4.882175
C	0.315617	-3.118965	0.107766	H	-0.954917	1.273944	2.85881
H	0.038305	-4.180849	0.132706	H	-1.684605	-0.337433	2.701083
H	1.202033	-2.993756	0.733472	C	6.012699	-0.019506	0.705583
H	-0.506404	-2.546678	0.551923	C	5.368652	0.82875	-0.185629
C	1.755135	-3.553182	-1.892383	C	4.110418	0.539643	-0.709362
H	2.639956	-3.479205	-1.253691	C	3.400462	-0.62603	-0.361198
H	1.450637	-4.607711	-1.933715	C	4.088176	-1.434906	0.536103
H	2.041605	-3.254858	-2.906669	C	5.346351	-1.189892	1.077602
O	-2.095467	0.005678	0.053985	H	5.793972	-1.898093	1.770046
C	-2.949032	1.166788	0.028053	F	3.480364	-2.604224	0.976438

Table A1.4 (Continued).

C	-4.368431	0.641716	0.240516	H	3.694849	1.257474	-1.415994
C	-4.301898	-0.720108	-0.467291	F	5.992023	1.983671	-0.554835
C	-2.888472	-1.194916	-0.118305	H	6.996331	0.230231	1.090033
H	-2.423645	-1.804983	-0.895282	H	2.100962	-0.97171	-0.941954
H	-2.872675	-1.755565	0.82517	C	0.741836	4.400572	-0.314714
H	-4.406883	-0.591969	-1.550792	C	-0.024314	3.17266	-0.816364
H	-5.070738	-1.422607	-0.132666	H	0.249013	2.918773	-1.846844
H	-5.128997	1.311117	-0.172266	H	-1.110683	3.293262	-0.764358
H	-4.573	0.509887	1.309762	H	0.951438	5.11387	-1.117291
H	-2.608265	1.856796	0.804995	H	0.16812	4.922361	0.460851
H	-2.852779	1.660251	-0.94856	H	2.733138	3.528759	-0.495001
O	0.359799	2.076675	0.046218	C	2.005543	3.769385	0.287668
C	1.456669	2.485876	0.906324				

Table A1.5. Optimized geometries of dimer-based deaggregation transition state structures of LDA at B3LYP level of theory with 6-31G(d) basis set for the ortholithiation of **1** at –78 °C with free energies (Hartrees), and cartesian coordinates (X,Y,Z). (Note: G_{MP2} includes single point MP2 corrections to B3LYP/6-31G(d) optimized structures)



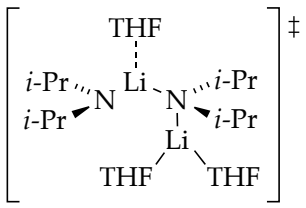


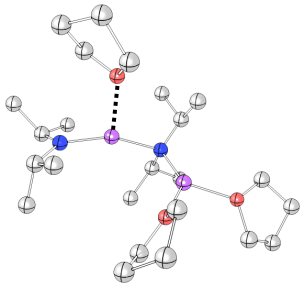
M
G = -1063.113138
G_{MP2} = -1059.914778

Atom	X	Y	Z	Atom	X	Y	Z
C	0	0	0	C	3.321573	-0.562069	5.874681
N	-0.086375	0.248713	1.43741	H	4.194396	-1.159861	5.587908
Li	0.476016	-1.014773	2.724545	H	3.269569	-0.552599	6.972743
N	2.138128	-1.279129	3.772572	H	3.497472	0.467446	5.534423
Li	2.503654	0.456333	2.713605	H	1.864103	-2.113578	5.707163
O	4.188355	0.779148	1.581	C	2.815518	-2.559001	3.486633
C	5.37711	1.142108	2.32174	C	1.83041	-3.751466	3.449856
C	6.463722	1.370813	1.270717	H	1.222611	-3.784152	4.361881
C	6.063604	0.366196	0.179428	H	2.346175	-4.717753	3.356511
C	4.535377	0.440423	0.216395	H	1.147073	-3.659353	2.59187
H	4.1503	1.226979	-0.443671	H	3.541764	-2.786577	4.288659
H	4.045636	-0.501902	-0.039364	C	3.631923	-2.532551	2.189454
H	6.467125	0.612726	-0.807057	H	4.401326	-1.755005	2.232552
H	6.405074	-0.641	0.444514	H	2.991672	-2.331203	1.322646
H	6.416126	2.396203	0.884895	H	4.124597	-3.497449	2.01308
H	7.469242	1.20287	1.667689	C	-1.166122	1.190216	1.736546
H	5.635506	0.316928	2.998032	C	-2.585773	0.5927	1.568951
H	5.140613	2.025672	2.919472	H	-2.739853	0.17485	0.568726
O	2.52989	2.437526	3.310016	H	-3.366342	1.349284	1.73273
C	2.5151	3.159012	4.564058	H	-2.737295	-0.218396	2.294919
C	2.576658	4.641315	4.19128	C	-1.049528	1.737147	3.164053
C	1.835537	4.661018	2.845345	H	-1.196206	0.936463	3.901054
C	2.301532	3.353513	2.205813	H	-1.811408	2.501877	3.362518
H	1.568674	2.891354	1.540712	H	-0.060742	2.172735	3.33861
H	3.246961	3.482046	1.663679	H	-1.125068	2.073656	1.063815
H	0.751896	4.642554	3.005453	C	0.706389	1.130825	-0.787323
H	2.075568	5.53355	2.23051	H	0.233109	2.101165	-0.596934
H	2.11638	5.279458	4.951366	H	0.675249	0.958044	-1.87267
H	3.616919	4.963587	4.061334	H	1.758879	1.205665	-0.483494
H	3.363344	2.819745	5.165453	C	0.702643	-1.330503	-0.292682
H	1.588768	2.917666	5.098605	H	1.728104	-1.318927	0.097898

Table A1.5 (Continued).

C	2.032262	-1.127061	5.234221	H	0.764447	-1.532404	-1.369675
C	0.833133	-0.262547	5.639443	H	0.169187	-2.166927	0.178112
H	0.883335	0.729323	5.175844	H	-1.007396	-0.090339	-0.449933
H	0.788757	-0.119683	6.7266	H	-0.112084	-0.728423	5.329526





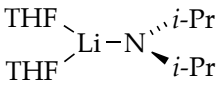
N
G = -1295.456439
G_{MP2} = -1291.595118

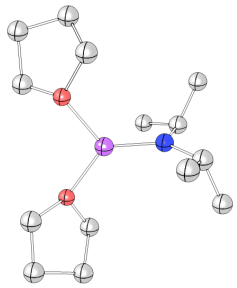
Atom	X	Y	Z	Atom	X	Y	Z
C	0	0	0	C	5.948311	1.07573	-0.249706
N	0.231281	0.82555	1.200346	H	6.381895	2.075788	-0.364667
Li	-0.922353	2.39411	1.193924	H	5.992563	0.812125	0.815805
O	-2.836904	2.454698	1.733351	H	6.591337	0.372991	-0.799418
C	-3.835183	3.161251	0.963905	C	3.920643	-0.375683	-0.48896
C	-5.039848	2.224737	0.912707	H	2.928644	-0.493957	-0.939725
C	-4.979343	1.563123	2.298333	H	4.57409	-1.160099	-0.892517
C	-3.471485	1.417498	2.534541	H	3.825177	-0.550987	0.592848
H	-3.086167	0.453066	2.192427	C	3.888033	3.370072	-0.674588
H	-3.181138	1.563292	3.578578	H	4.975295	3.604372	-0.676727
H	-5.496625	0.600429	2.338467	C	3.23914	4.423153	0.237295
H	-5.428394	2.2191	3.053055	H	2.15554	4.243156	0.308104
H	-4.906139	1.477232	0.122415	H	3.644763	4.365684	1.251926
H	-5.977244	2.757208	0.726878	H	3.38791	5.443225	-0.144194
H	-4.080578	4.105027	1.470072	C	3.413412	3.611135	-2.132062
H	-3.406096	3.389509	-0.015	H	3.709192	4.603743	-2.504017
O	-0.696455	4.264401	0.614359	H	3.833857	2.865637	-2.815663
C	-0.583776	5.336419	1.581899	H	2.318841	3.530384	-2.195563
C	-0.810647	6.621968	0.787926	H	0.759785	-0.800508	-0.093641
C	-0.193601	6.264339	-0.57357	C	0.144669	0.872946	-1.256104
C	-0.574671	4.79072	-0.734881	H	0.028735	0.276434	-2.169583
H	0.175498	4.201998	-1.267183	H	-0.634577	1.653196	-1.281191
H	-1.545095	4.672384	-1.234544	H	1.12503	1.363707	-1.290141
H	0.895318	6.36944	-0.53795	C	-1.369598	-0.71722	-0.056047
H	-0.571308	6.880438	-1.394592	H	-1.466524	-1.299134	-0.981684
H	-0.340981	7.489772	1.259947	H	-1.51548	-1.410877	0.779002
H	-1.883279	6.826629	0.686757	H	-2.19013	0.016056	-0.033712
H	-1.326579	5.159712	2.365695	O	3.022723	2.770745	3.337815

Table A1.5 (Continued).

H	0.419403	5.305933	2.024023	C	2.869218	3.894967	4.215297
C	0.14168	0.063213	2.454972	C	4.198653	4.046127	4.967658
H	-0.805735	-0.510356	2.510513	C	5.201225	3.463821	3.958303
C	1.270788	-0.972044	2.658101	C	4.396085	2.320315	3.340244
H	1.322205	-1.68204	1.825913	H	4.471449	1.407573	3.950363
H	2.246531	-0.472337	2.73202	H	4.654086	2.091623	2.302323
H	1.12096	-1.551614	3.579255	H	6.132831	3.122801	4.420448
C	0.12859	1.026131	3.653192	H	5.452386	4.20876	3.193948
H	-0.707581	1.738934	3.589445	H	4.190105	3.445691	5.885312
H	0.014746	0.480622	4.598927	H	4.407531	5.084327	5.245296
H	1.061439	1.59813	3.698923	H	2.651776	4.789838	3.612973
Li	2.123565	1.626121	0.935432	H	2.016314	3.713229	4.88081
N	3.614951	2.037711	-0.170474	H	4.546263	1.124202	-1.861082
C	4.483007	1.027814	-0.754776				

Table A1.6. Optimized geometries of LDA Monomer and Dimer intermediates at B3LYP level of theory with 6-31G(d) basis set at –78 °C with free energies (Hartrees), and cartesian coordinates (X,Y,Z). (Note: G_{MP2} includes single point MP2 corrections to B3LYP/6-31G(d) optimized structures)

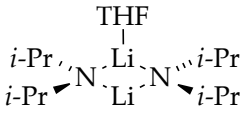


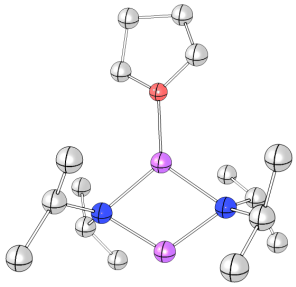


O
G = -763.909491
G_{MP2} = -761.6322164

Atom	X	Y	Z	Atom	X	Y	Z
C	0	0	0	H	-4.600416	-5.275712	-2.065516
N	-0.552097	-0.791733	-1.08216	H	-2.277069	-4.73069	-2.421557
C	-1.100726	0.003952	-2.163167	H	-2.054509	-5.85731	-1.062374
H	-0.42462	0.838047	-2.452483	O	0.928677	-3.84446	-1.600313
C	-1.261764	-0.861954	-3.422722	C	1.430248	-4.933118	-0.788525
H	-1.922259	-1.719434	-3.214761	C	2.950846	-4.9556	-0.995241
H	-1.708423	-0.303457	-4.255299	C	3.255616	-3.502185	-1.393799
H	-0.292451	-1.254225	-3.754666	C	2.032631	-3.142063	-2.231704
C	-2.463159	0.663803	-1.830387	H	2.13068	-3.498223	-3.266133
H	-2.802676	1.338115	-2.630223	H	1.769306	-2.081255	-2.227245
H	-3.232374	-0.1078	-1.684469	H	4.191584	-3.396235	-1.950228
H	-2.403086	1.250892	-0.90701	H	3.308556	-2.859385	-0.507448
Li	-0.554552	-2.660513	-1.083367	H	3.216417	-5.6368	-1.811959
O	-2.040768	-3.840775	-0.566936	H	3.485002	-5.28118	-0.097692
C	-2.544624	-4.929889	-1.376656	H	1.162279	-4.731873	0.255882
C	-4.065111	-4.949637	-1.168831	H	0.938866	-5.86023	-1.101727
C	-4.367295	-3.495144	-0.772206	H	-0.672433	0.836632	0.290479
C	-3.14313	-3.135747	0.064289	C	1.365347	0.654309	-0.33183
H	-3.241005	-3.490326	1.099282	H	1.707479	1.326654	0.468548
H	-2.878003	-2.075394	0.058276	H	2.131354	-0.120443	-0.477981
H	-5.302683	-3.386912	-0.215241	H	1.308012	1.242189	-1.254875
H	-4.419918	-2.853576	-1.659473	C	0.157181	-0.868367	1.258346
H	-4.331203	-5.629195	-0.350914	H	0.814037	-1.728384	1.049267
H	-0.813839	-1.256932	1.58963	H	0.606163	-0.312969	2.091742

Table A1.6 (Continued).

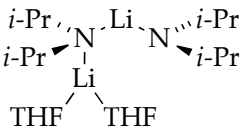


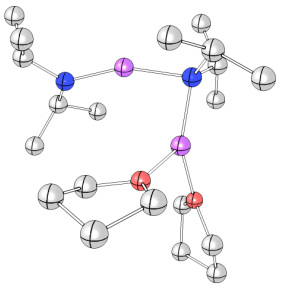


P
G = -830.781351
G_{MP2} = -828.2368513

Atom	X	Y	Z	Atom	X	Y	Z
N	0	0	0	H	1.629998	5.253231	-0.973867
Li	1.055816	1.628316	0.006298	C	-1.107815	3.490471	-2.194308
N	-0.000752	3.256107	0.012202	H	-2.079779	3.153228	-1.812989
Li	-1.263992	1.627801	0.006004	H	-1.296414	4.16856	-3.035649
O	-3.236325	1.627449	0.005869	H	-0.580032	2.614526	-2.595291
C	-4.064991	2.727409	0.458429	H	-0.885496	5.034735	-0.743763
C	-5.480265	2.394865	-0.01548	C	-0.277878	-0.919445	1.108398
C	-5.479759	0.858724	0.027435	C	-1.10751	-0.23505	2.206206
C	-4.064418	0.527156	-0.446904	H	-2.079514	0.101731	1.824586
H	-4.003634	0.47322	-1.540595	H	-1.296043	-0.913309	3.047426
H	-3.658459	-0.396839	-0.027697	H	-0.580321	0.641135	2.607453
H	-6.247246	0.406149	-0.607121	C	0.999641	-1.516298	1.742168
H	-5.633406	0.505027	1.053705	H	1.591091	-0.721205	2.216957
H	-5.634469	2.748446	-1.041706	H	0.766335	-2.270459	2.507056
H	-6.247854	2.846945	0.619302	H	1.631579	-1.996288	0.986427
H	-4.003956	2.781752	1.552079	H	-0.883908	-1.779154	0.755706
H	-3.659702	3.651517	0.038814	C	0.320874	-0.742282	-1.226831
C	0.319438	3.998626	1.239077	C	1.341495	0.023724	-2.088242
C	-0.928935	4.336924	2.082978	H	2.296429	0.137595	-1.553096
H	-1.399739	3.416616	2.455837	H	1.55771	-0.493165	-3.031326
H	-0.690261	4.97018	2.949206	H	0.969794	1.024158	-2.354464
H	-1.667621	4.870725	1.473441	C	-0.927114	-1.080946	-2.07116
C	1.340049	3.233067	2.100901	H	-1.398145	-0.160766	-2.444047
H	2.295242	3.119556	1.566136	H	-0.687948	-1.714016	-2.937388
H	1.555695	3.750092	3.044041	H	-1.665774	-1.615086	-1.46189
H	0.968653	2.232497	2.367031	H	0.800445	-1.707153	-0.981465
H	0.798758	4.963636	0.993772	H	1.590422	3.97816	-2.204443
C	-0.278877	4.175379	-1.09629	H	0.764923	5.526996	-2.494661
C	0.998465	4.772931	-1.729749				

Table A1.6 (Continued).

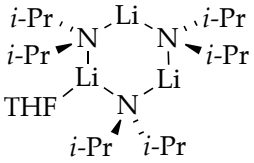


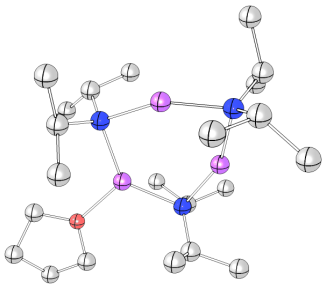


Q
G = -1063.11763
G_{MP2} = -1059.913141

Atom	X	Y	Z	Atom	X	Y	Z
N	0	0	0	H	1.013566	-4.608918	-1.607685
Li	-1.524323	-0.913264	-0.958264	O	2.824175	-1.567241	-1.79498
N	-2.416496	-2.13582	-2.069113	C	2.918494	-1.274852	-3.213947
C	-3.633338	-2.83569	-1.677259	C	4.044204	-2.164986	-3.737922
C	-3.613251	-3.182217	-0.182693	C	4.98415	-2.236533	-2.524837
H	-2.748355	-3.808297	0.066417	C	3.994712	-2.301189	-1.359861
H	-3.553507	-2.268271	0.425102	H	4.370024	-1.836363	-0.442485
H	-4.523129	-3.714816	0.122135	H	3.692782	-3.331319	-1.137198
H	-3.73242	-3.803458	-2.213703	H	5.59461	-1.328534	-2.460122
C	-4.929971	-2.044	-1.980975	H	5.657361	-3.09843	-2.545751
H	-4.965162	-1.133002	-1.367765	H	4.519924	-1.749311	-4.630738
H	-4.974767	-1.73781	-3.031912	H	3.66211	-3.161716	-3.987492
H	-5.832504	-2.63605	-1.769976	H	1.945387	-1.477376	-3.667045
C	-2.214651	-2.180273	-3.510086	H	3.150101	-0.210574	-3.336437
H	-3.165775	-2.019714	-4.057977	C	0.197785	1.383	-0.475737
C	-1.279283	-1.051514	-3.960533	C	1.020782	1.431286	-1.769051
H	-1.707075	-0.069215	-3.725346	H	2.027774	1.030111	-1.602891
H	-0.313853	-1.133122	-3.437843	H	0.541908	0.842581	-2.561944
H	-1.073874	-1.087992	-5.038427	H	1.123113	2.45882	-2.140228
C	-1.655756	-3.530509	-4.02786	H	0.77277	1.960827	0.272188
H	-1.640221	-3.573856	-5.126686	C	-1.133852	2.141058	-0.679612
H	-0.628128	-3.683432	-3.668953	H	-0.972209	3.19906	-0.92884
H	-2.261657	-4.371834	-3.672843	H	-1.713566	1.692133	-1.499193
Li	1.255858	-1.41748	-0.572615	H	-1.750834	2.103971	0.226192
O	1.176476	-3.319601	0.022002	C	-0.151937	0.002689	1.467792
C	0.386848	-4.250039	-0.779451	C	-1.026873	-1.162473	1.948467
C	0.02824	-5.383739	0.175908	H	-2.061476	-1.045761	1.603947
C	1.267678	-5.448704	1.081976	H	-0.654589	-2.119093	1.561376
C	1.6414	-3.970464	1.229048	H	-1.051854	-1.227437	3.043799
H	2.719871	-3.802948	1.323528	H	-0.664971	0.925587	1.79546
H	1.139029	-3.507909	2.086093	C	1.206244	-0.013721	2.208878
H	2.074179	-6.002702	0.586929	H	1.855435	0.793374	1.849308
H	1.076299	-5.922778	2.049142	H	1.090071	0.108304	3.294981
H	-0.172411	-6.321525	-0.350081	H	1.730769	-0.966692	2.039234
H	-0.862534	-5.121649	0.757788	H	-0.474491	-3.703127	-1.18328

Table A1.7. Optimized geometries of LDA Trimer intermediates at B3LYP level of theory with 6-31G(d) basis set at –78 °C with free energies (Hartrees), and cartesian coordinates (X,Y,Z). (Note: G_{MP2} includes single point MP2 corrections to B3LYP/6-31G(d) optimized structures)



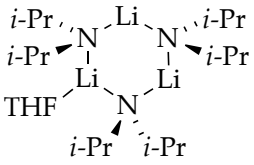


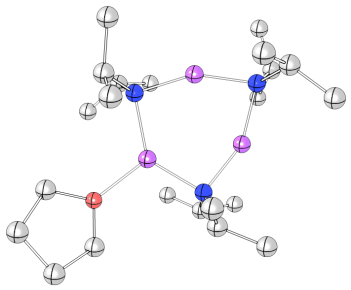
R-1$_a$
G = -1129.995901
G_{MP2} = -1126.529703

Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	H	-3.387124	-1.826488	3.168147
Li	-2.705154	1.333703	0.301623	H	-3.588751	-0.186344	2.520526
N	-1.842967	3.235262	0.410489	H	-4.112525	-1.593059	1.573184
C	-2.17202	4.105492	-0.731863	C	-0.885997	-0.791009	2.587209
H	-3.220116	4.460131	-0.644646	H	-0.972938	0.292686	2.738092
C	-2.082663	3.327978	-2.051792	H	-0.99117	-1.267871	3.569325
H	-2.367682	3.958351	-2.902891	H	0.132857	-1.00247	2.235153
H	-1.058946	2.978299	-2.238906	O	-4.747745	1.451446	0.011674
H	-2.737688	2.449276	-2.052352	C	-5.427603	2.696396	-0.29375
C	-1.323203	5.393769	-0.858178	C	-6.925244	2.385248	-0.232039
H	-0.255479	5.153629	-0.973252	C	-6.9622	0.90038	-0.621893
H	-1.626929	5.985486	-1.732467	C	-5.708733	0.369345	0.069804
H	-1.428698	6.034015	0.022817	H	-5.264242	-0.501831	-0.416064
C	-2.191141	3.890284	1.689365	H	-5.903848	0.12485	1.12115
H	-2.914977	4.704505	1.495473	H	-6.878476	0.786157	-1.709209
C	-0.995774	4.532915	2.433305	H	-7.870006	0.386081	-0.29282
H	-0.438365	5.218836	1.787227	H	-7.509027	3.026333	-0.899036
H	-1.322201	5.095625	3.31895	H	-7.305267	2.520357	0.787476
H	-0.30084	3.757982	2.784581	H	-5.103584	3.450479	0.427236
C	-2.885164	2.91525	2.658963	H	-5.120969	3.017698	-1.295695
H	-2.225442	2.070123	2.895891	N	1.444339	1.338627	-0.138644
H	-3.13962	3.400321	3.610204	Li	0.034882	2.667266	0.261845
H	-3.810974	2.513235	2.230761	C	2.512914	1.325012	0.879686
N	-1.846894	-0.588857	0.302932	C	2.03328	1.928415	2.206611
C	-2.380519	-1.433335	-0.781579	H	1.791619	2.99376	2.093066
H	-3.329367	-1.915352	-0.469279	H	1.140291	1.410552	2.580831
C	-2.706426	-0.596595	-2.026788	H	2.802128	1.853449	2.985285
H	-3.07492	-1.227052	-2.84565	H	3.357146	1.956644	0.546164
H	-3.471841	0.159195	-1.816713	C	3.098076	-0.083675	1.123659
H	-1.812063	-0.076518	-2.392259	H	2.345245	-0.743176	1.577401
C	-1.434739	-2.587103	-1.196122	H	3.420782	-0.542554	0.18182

Table A1.7 (Continued).

H	-1.135103	-3.195747	-0.335869	H	3.966411	-0.057204	1.796227
H	-1.907634	-3.258626	-1.925629	C	2.04363	1.389518	-1.487174
H	-0.520868	-2.187644	-1.659863	H	3.002169	0.840268	-1.491836
C	-1.942425	-1.297983	1.595745	C	1.155594	0.696282	-2.529265
H	-1.73422	-2.375147	1.460144	H	1.044864	-0.374334	-2.30799
C	-3.338385	-1.2214	2.252523	H	0.153506	1.1436	-2.559969
H	1.442336	3.408715	-2.083277	H	1.576812	0.778112	-3.53876
H	2.979431	3.346879	-1.199022	C	2.366179	2.828665	-1.945738
H	2.913799	2.84694	-2.898097				



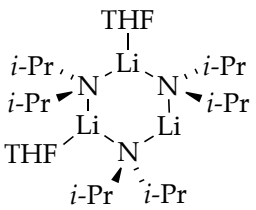


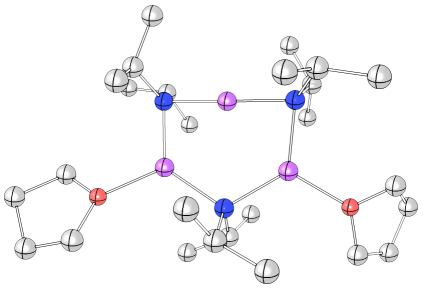
R-1$_b$
G = -1129.995057
G_{MP2} = -1126.528457

Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	C	-6.804798	0.899427	-0.849272
Li	-2.695004	1.340324	0.368957	C	-5.698552	0.351589	0.068995
N	-1.830083	3.247066	0.426154	H	-5.16707	-0.512618	-0.32871
C	-2.226756	4.090102	-0.713337	H	-6.091835	0.100305	1.064169
H	-3.270649	4.446813	-0.574224	H	-6.616815	0.619239	-1.889849
C	-2.216099	3.282211	-2.01737	H	-7.786128	0.503618	-0.571701
H	-2.550055	3.8933	-2.864537	H	-6.473774	2.927916	-1.619257
H	-1.205395	2.925256	-2.254996	H	-7.632858	2.880023	-0.287845
H	-2.873984	2.408397	-1.957183	H	-5.923692	2.682642	1.363275
C	-1.39692	5.380537	-0.923188	H	-4.903882	3.471216	0.131646
H	-0.334401	5.144767	-1.085219	N	1.439408	1.338618	-0.191178
H	-1.751092	5.938984	-1.800203	Li	0.043649	2.677686	0.218128
H	-1.463288	6.051207	-0.061179	C	2.530911	1.303673	0.802071
C	-2.098866	3.92854	1.709769	C	2.088886	1.896294	2.146541
H	-2.861057	4.715393	1.551749	H	1.858665	2.965681	2.051048
C	-0.871281	4.626949	2.345174	H	1.197434	1.385698	2.534187
H	-0.376917	5.30387	1.641594	H	2.87384	1.801318	2.906787
H	-1.151033	5.211198	3.232814	H	3.373808	1.930099	0.455654
H	-0.133951	3.881601	2.673517	C	3.1063	-0.113973	1.016942
C	-2.681084	2.959663	2.754927	H	2.356645	-0.770722	1.480363
H	-1.97853	2.140555	2.956171	H	3.402888	-0.565851	0.06319
H	-2.872652	3.461902	3.71186	H	3.989596	-0.104815	1.670156

Table A1.7 (Continued).

H	-3.626056	2.520277	2.415306	C	2.008764	1.395017	-1.552638
N	-1.840205	-0.586245	0.339429	H	2.963912	0.840854	-1.582042
C	-2.385208	-1.435876	-0.735054	C	1.094655	0.714963	-2.580406
H	-3.332222	-1.914236	-0.410785	H	0.978409	-0.35555	-2.362157
C	-2.718431	-0.608635	-1.984339	H	0.09619	1.171246	-2.588946
H	-3.101079	-1.243769	-2.792991	H	1.49681	0.798805	-3.597514
H	-3.474856	0.156573	-1.775827	C	2.328278	2.836007	-2.00753
H	-1.824972	-0.0984	-2.364639	H	2.855935	2.859331	-2.970955
C	-1.446091	-2.5953	-1.149483	H	1.403815	3.420516	-2.122398
H	-1.140913	-3.198188	-0.287216	H	2.958667	3.346506	-1.269841
H	-1.926508	-3.270797	-1.870341	H	-4.108168	-1.531281	1.649703
H	-0.534975	-2.201405	-1.623429	C	-0.846213	-0.803692	2.608762
C	-1.931031	-1.288082	1.637036	H	-0.905125	0.282102	2.756922
H	-1.750678	-2.370007	1.501439	H	-0.945593	-1.274156	3.594603
C	-3.314506	-1.176602	2.315606	H	0.160747	-1.040562	2.238972
H	-3.362629	-1.778336	3.233445	O	-4.75129	1.42708	0.197769
H	-3.537785	-0.135767	2.584678	C	-5.549769	2.617043	0.330742
C	-6.706372	2.440126	-0.66829				





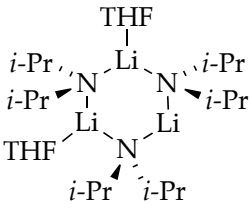
R-2$_a$
G = -1362.338194
G_{MP2} = -1358.219791

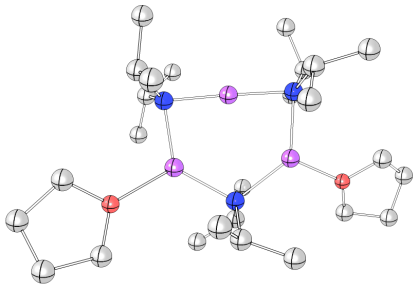
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	C	5.281677	-4.310928	-1.174317
Li	1.844654	-1.982372	0.165167	C	5.828197	-2.864555	-1.044757
N	0.060237	-3.128876	0.010099	C	4.972559	-2.258477	0.073007
C	0.264497	-4.053587	-1.126559	H	4.785455	-1.190263	-0.021639
H	0.887121	-4.915826	-0.813934	H	5.405736	-2.458632	1.064217
C	1.01404	-3.385756	-2.288456	H	5.67699	-2.31075	-1.976497
H	1.151454	-4.087128	-3.121642	H	6.895341	-2.832203	-0.806057
H	0.454099	-2.527789	-2.672516	H	5.0384	-4.548135	-2.213866
H	2.008163	-3.03359	-1.991511	H	6.00268	-5.057166	-0.827249
C	-1.036969	-4.675064	-1.690509	H	4.205433	-4.816366	0.672814
H	-1.672053	-3.902648	-2.145979	H	3.1447	-4.766988	-0.755711
H	-0.820807	-5.424894	-2.464058	N	-1.928025	-0.002237	-0.495715
H	-1.618915	-5.171865	-0.907618	Li	-1.750905	-2.02915	-0.251418

Table A1.7 (Continued).

C	-0.154139	-3.916884	1.244113	O	-3.585426	-2.97447	-0.025763
H	-0.81065	-4.78651	1.040081	C	-4.759028	-2.365995	-0.624135
C	-0.86168	-3.092645	2.326642	C	-5.963265	-3.087055	-0.014089
H	-1.858936	-2.768632	2.013569	C	-5.389549	-4.480984	0.278904
H	-0.983168	-3.671886	3.250809	C	-3.97252	-4.140904	0.737141
H	-0.285519	-2.19534	2.573958	H	-3.242655	-4.930471	0.547639
C	1.135878	-4.512214	1.858179	H	-3.948868	-3.889931	1.805791
H	1.812364	-3.713933	2.195245	H	-5.361918	-5.085717	-0.635376
H	0.910281	-5.14434	2.728056	H	-5.951993	-5.03368	1.037409
H	1.678354	-5.13233	1.138142	H	-6.823366	-3.10234	-0.689901
N	1.951566	0.065123	0.334348	H	-6.271732	-2.59881	0.917832
C	2.640155	0.818467	-0.731718	H	-4.72965	-1.295002	-0.417118
H	3.670009	1.077498	-0.420372	H	-4.706992	-2.516356	-1.709629
C	2.784719	-0.010849	-2.014725	C	-2.735349	0.756388	0.47387
H	3.300288	0.558844	-2.798034	C	-2.834907	0.011912	1.811479
H	3.350465	-0.931961	-1.838382	H	-3.303564	-0.969878	1.68129
H	1.804858	-0.296445	-2.41557	H	-1.847045	-0.145884	2.261615
C	1.954438	2.162201	-1.082541	H	-3.435559	0.579513	2.533084
H	1.80097	2.779801	-0.19071	H	-3.779113	0.860645	0.121363
H	2.551695	2.75059	-1.792806	C	-2.233966	2.197521	0.731009
H	0.971092	1.988927	-1.543427	H	-1.229234	2.187008	1.178504
C	2.270985	0.650915	1.650233	H	-2.175982	2.779732	-0.195131
H	2.189051	1.755081	1.613651	H	-2.898627	2.736879	1.419207
C	3.698979	0.350932	2.163074	C	-2.0227	0.568029	-1.854193
H	3.900525	0.879782	3.104532	H	-1.526566	1.561179	-1.913124
H	3.821145	-0.724738	2.347192	C	-1.282648	-0.333367	-2.848012
H	4.467967	0.662663	1.447921	H	-0.248765	-0.512502	-2.535881
C	1.280799	0.187383	2.724344	H	-1.778942	-1.310363	-2.93444
H	1.336375	-0.899892	2.863279	H	-1.249985	0.114079	-3.848848
H	1.499583	0.651614	3.693678	C	-3.450335	0.799292	-2.400767
H	0.245909	0.445465	2.467576	H	-3.402618	1.17896	-3.429212
O	3.704849	-2.930629	-0.035239	H	-4.018142	-0.13965	-2.414266
C	4.017859	-4.313882	-0.28568	H	-4.017153	1.529266	-1.814468

Table A1.7 (Continued).



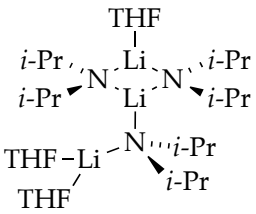


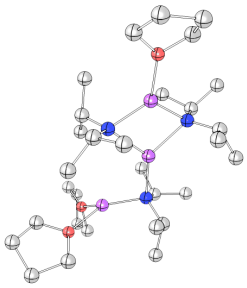
R-2$_b$
G = -1362.337705
G_{MP2} = -1358.220942

Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	C	-3.9043	2.408759	-2.000251
Li	-1.855196	2.023135	-0.085893	H	-3.365144	3.371629	-2.140417
N	0.076333	2.039418	0.280808	C	-3.259375	1.413734	-2.971587
C	0.793414	2.829097	-0.732567	H	-2.235332	1.171655	-2.673482
H	1.890334	2.739316	-0.57738	H	-3.829385	0.473893	-3.002471
C	0.508834	2.30599	-2.146518	H	-3.222555	1.812954	-3.992752
H	1.124071	2.827229	-2.890226	C	-5.344179	2.6801	-2.492952
H	0.712444	1.232414	-2.235339	H	-5.326749	2.994517	-3.544046
H	-0.539031	2.471906	-2.428022	H	-5.958064	1.772993	-2.424192
C	0.50186	4.348843	-0.710288	H	-5.846409	3.471181	-1.927489
H	0.755014	4.795484	0.25653	N	-1.708027	-1.209978	-0.142575
H	1.083471	4.876954	-1.478564	C	-1.519533	-2.15048	-1.267846
H	-0.563768	4.541611	-0.900448	H	-0.90153	-3.013511	-0.950877
C	0.529652	2.410453	1.638328	C	-0.76653	-1.505206	-2.441581
H	1.4531	3.012338	1.559941	H	-0.635293	-2.220345	-3.264098
C	0.902033	1.18281	2.49337	H	-1.316736	-0.647355	-2.839842
H	1.266837	1.477384	3.48629	H	0.230304	-1.159753	-2.144274
H	0.03083	0.535356	2.652463	C	-2.831578	-2.765994	-1.812766
H	1.682124	0.582937	2.011384	H	-3.466972	-1.992172	-2.265313
C	-0.484209	3.268262	2.427094	H	-2.631103	-3.522812	-2.583747
H	-1.401728	2.696617	2.625569	H	-3.406926	-3.253438	-1.018889
H	-0.084707	3.585672	3.400782	C	-1.913953	-1.966961	1.109672
H	-0.765284	4.165719	1.86677	H	-2.633078	-2.797004	0.954093
N	-3.768139	1.908628	-0.617512	C	-2.522211	-1.071887	2.197845
Li	-3.528159	-0.112575	-0.366463	H	-3.521591	-0.716611	1.928074
O	-5.334494	-1.064892	-0.021417	H	-2.612704	-1.605871	3.152144
C	-6.543447	-0.460239	-0.548982	H	-1.896309	-0.188908	2.372184
C	-7.705774	-1.166795	0.151698	C	-0.640454	-2.635336	1.684278
C	-7.1212	-2.562003	0.41613	H	0.096034	-1.879516	1.988701
C	-5.671615	-2.229576	0.766884	H	-0.875881	-3.244532	2.567775
H	-4.964255	-3.024575	0.522738	H	-0.164725	-3.296338	0.952973
H	-5.565249	-1.980044	1.83073	O	1.890809	-0.808571	-0.291674
H	-7.164898	-3.175054	-0.49196	C	2.273595	-2.203497	-0.357361
H	-7.630587	-3.10388	1.218652	C	3.646645	-2.223725	-1.027738

Table A1.7 (Continued).

H	-8.611657	-1.182636	-0.461476	C	4.255825	-0.903792	-0.532809
H	-7.945056	-0.667626	1.098188	C	3.045319	0.031569	-0.547774
H	-6.494692	0.613191	-0.360341	H	2.91524	0.509294	-1.525614
H	-6.566388	-0.627231	-1.633153	H	3.078479	0.810072	0.21713
C	-4.568843	2.689632	0.338214	H	5.070984	-0.536421	-1.163231
C	-4.545362	2.03694	1.726153	H	4.641144	-1.020284	0.487145
H	-4.958989	1.023102	1.690391	H	3.54144	-2.211874	-2.119134
H	-3.523698	1.968179	2.123071	H	4.232519	-3.105412	-0.751208
H	-5.135343	2.618113	2.445642	H	2.317568	-2.605381	0.662187
H	-5.635787	2.707308	0.040823	H	1.501431	-2.74046	-0.912953
C	-4.147689	4.173297	0.466071	H	-4.179108	4.689259	-0.499711
H	-3.122733	4.257943	0.854119	H	-4.808668	4.718334	1.153257





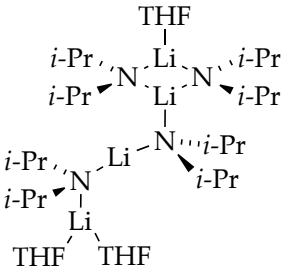
R-3
G = -1362.337705
G_{MP2} = -1358.220942

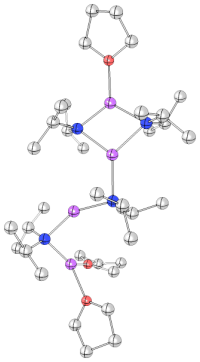
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	H	-4.694872	-2.07748	-1.142442
Li	-2.215681	-0.899809	0.79248	H	-3.219149	-3.013107	-0.857054
N	-0.226963	-1.826001	0.725784	H	-4.754863	-3.849279	-1.120164
C	0.387552	-2.208656	2.001063	H	-5.657164	-3.097955	0.977188
H	1.407294	-2.614525	1.841639	C	-3.916162	-4.214322	1.469687
C	0.585241	-0.991113	2.912196	H	-2.824371	-4.162396	1.401296
H	1.097095	-1.27508	3.840642	H	-4.181491	-4.35819	2.522358
H	1.187086	-0.217041	2.420725	H	-4.252509	-5.107589	0.926898
H	-0.373649	-0.539615	3.191843	C	-4.20845	-1.662469	2.903098
C	-0.371965	-3.298735	2.791711	H	-3.608889	-2.485824	3.332614
H	-0.507477	-4.209428	2.197948	C	-3.602818	-0.374407	3.472091
H	0.170583	-3.580119	3.705435	H	-2.541269	-0.291051	3.216423
H	-1.367621	-2.94069	3.080672	H	-4.105505	0.51517	3.0743
C	-0.23111	-2.937369	-0.236212	H	-3.679402	-0.345007	4.566448
H	-1.003674	-3.696736	0.01487	C	-5.636984	-1.84849	3.473048
C	1.088283	-3.736752	-0.369925	H	-5.633372	-1.866201	4.571245
H	1.003845	-4.47399	-1.179	H	-6.296452	-1.026366	3.154636
H	1.924464	-3.065807	-0.611408	H	-6.090654	-2.785623	3.132245
H	1.349473	-4.285317	0.540434	N	-1.699095	1.105979	-0.157718
C	-0.581409	-2.415816	-1.637186	C	-1.581111	2.362457	0.588782

Table A1.7 (Continued).

H	0.237166	-1.798891	-2.034526	H	-1.049139	3.128518	-0.022197
H	-0.74843	-3.239541	-2.343216	C	-0.758133	2.20534	1.87308
H	-1.486458	-1.800316	-1.628284	H	-0.663622	3.164045	2.399269
N	-4.131111	-1.657844	1.434259	H	-1.233875	1.498034	2.561166
Li	-5.322796	-0.257581	0.699089	H	0.253855	1.840148	1.665302
O	-6.214851	1.460352	1.311934	C	-2.938279	3.009662	0.965373
C	-6.680901	2.370655	0.283005	H	-3.482178	2.350897	1.652456
C	-6.931425	3.704395	0.987108	H	-2.804294	3.988094	1.450566
C	-7.326668	3.250076	2.400231	H	-3.564399	3.164381	0.078607
C	-6.388176	2.064424	2.618585	C	-2.14901	1.412709	-1.52705
H	-6.782942	1.301387	3.293843	H	-2.489222	2.461619	-1.587065
H	-5.410179	2.392821	2.98754	C	-3.361185	0.574235	-1.967875
H	-8.373658	2.924356	2.422184	H	-4.209615	0.765509	-1.297208
H	-7.195503	4.027376	3.158582	H	-3.679258	0.815537	-2.992879
H	-7.70283	4.298567	0.488255	H	-3.142671	-0.498277	-1.932697
H	-6.009593	4.295312	1.021362	C	-1.025617	1.30043	-2.584401
H	-5.916432	2.427911	-0.496676	H	-0.643795	0.275122	-2.652111
H	-7.59914	1.958567	-0.151275	H	-1.369883	1.593092	-3.587218
O	-6.864359	-0.65038	-0.598883	H	-0.188389	1.954986	-2.31589
C	-6.986948	-0.670627	-2.036848	O	1.833371	0.726389	-0.316822
C	-7.8976	-1.856669	-2.338208	C	2.260824	2.065527	-0.608559
C	-8.887694	-1.795016	-1.163696	C	3.444233	2.337093	0.343747
C	-8.005441	-1.319088	0.000604	C	3.91347	0.918455	0.77344
H	-7.622013	-2.152016	0.598373	C	3.029526	-0.026346	-0.055993
H	-8.516715	-0.612866	0.663529	H	2.728224	-0.941846	0.453601
H	-9.364329	-2.756144	-0.951503	H	3.507422	-0.285692	-1.012439
H	-9.679285	-1.065736	-1.371495	H	3.737928	0.762708	1.841928
H	-7.321466	-2.787941	-2.311265	H	4.97733	0.749029	0.58249
H	-8.382431	-1.777578	-3.315714	H	3.121992	2.919096	1.211901
H	-7.433904	0.275289	-2.375935	H	4.233629	2.903794	-0.159182
H	-5.983119	-0.756691	-2.457082	H	2.574072	2.121614	-1.661071
C	-4.558582	-2.948756	0.859631	H	1.40205	2.722281	-0.45986
C	-4.294032	-2.969523	-0.651568				

Table A1.8. Optimized geometries of LDA tetramer intermediates at B3LYP level of theory with 6-31G(d) basis set at –78 °C with free energies (Hartrees), and cartesian coordinates (X,Y,Z). (Note: G_{MP2} includes single point MP2 corrections to B3LYP/6-31G(d) optimized structures)





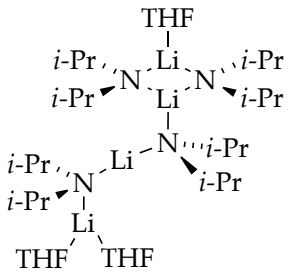
S_a
G = -1893.879194
G_{MP2} = -1888.176857

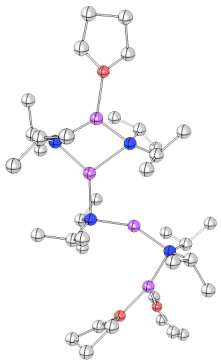
Atom	X	Y	Z	Atom	X	Y	Z
N	0	0	0	H	-9.529513	0.018572	2.228396
Li	-1.646691	-1.202396	-0.044941	H	-9.070793	0.470815	0.5736
Li	-4.606241	-2.519729	0.555657	N	-2.497481	-2.979743	-0.077115
Li	-7.01109	-1.962917	0.995127	C	-1.909569	-3.972755	0.831058
N	-5.520134	-0.575957	1.031807	C	-1.787879	-3.389111	2.244689
C	-5.691837	0.463661	0.005311	H	-1.201468	-2.461387	2.253487
H	-6.275001	1.315467	0.413993	H	-2.772963	-3.159354	2.662697
C	-6.482507	-0.026831	-1.215115	H	-1.301645	-4.10127	2.92474
H	-6.607498	0.776691	-1.952486	H	-0.868664	-4.234291	0.522994
H	-5.967548	-0.852464	-1.717986	C	-2.660463	-5.320452	0.919819
H	-7.482732	-0.37907	-0.934313	H	-3.698429	-5.166118	1.233553
C	-4.359917	1.073651	-0.496276	H	-2.686067	-5.840129	-0.043295
H	-3.784682	0.31899	-1.047041	H	-2.174049	-5.991826	1.64112
H	-4.524809	1.925607	-1.172145	C	-2.643481	-3.499119	-1.449156
H	-3.743179	1.431807	0.335493	H	-3.425644	-4.281103	-1.499466
C	-5.258114	0.103471	2.314711	C	-3.102211	-2.371924	-2.383817
H	-4.674492	1.027899	2.141854	H	-3.976238	-1.848256	-1.983923
C	-4.41673	-0.72849	3.288803	H	-2.306409	-1.626761	-2.527167
H	-3.479586	-1.044501	2.821567	H	-3.366908	-2.756585	-3.376385
H	-4.16808	-0.14759	4.1873	C	-1.377047	-4.141951	-2.0627
H	-4.950744	-1.623683	3.618442	H	-1.561519	-4.443692	-3.101896
C	-6.547155	0.558909	3.041984	H	-0.542681	-3.426957	-2.062456
H	-7.138442	-0.314502	3.35262	H	-1.054601	-5.035229	-1.517346
H	-6.326511	1.15056	3.942569	Li	1.233581	-1.392872	0.7309
H	-7.172518	1.176895	2.387651	O	1.661564	-2.08719	2.586325
N	-6.37457	-3.847862	0.703611	C	1.844734	-3.522032	2.737488
C	-6.854834	-4.534447	-0.503406	C	1.730326	-3.802374	4.235696
H	-7.921723	-4.830949	-0.397773	C	2.249912	-2.494422	4.849805
C	-6.818895	-3.604186	-1.720827	C	1.678938	-1.451001	3.891583

Table A1.8 (Continued).

H	-7.223261	-4.104616	-2.610098	H	2.280934	-0.542043	3.81705
H	-7.410459	-2.697501	-1.553635	H	0.654108	-1.173836	4.162319
H	-5.792355	-3.298067	-1.955053	H	3.346177	-2.47078	4.838427
C	-6.115759	-5.844039	-0.8702	H	1.916555	-2.336271	5.879396
H	-6.191498	-6.599015	-0.080801	H	2.305468	-4.682932	4.536554
H	-6.538896	-6.284859	-1.783095	H	0.683796	-3.966014	4.514993
H	-5.050982	-5.6505	-1.044888	H	1.082671	-4.029493	2.140431
C	-6.478463	-4.72978	1.874629	H	2.835881	-3.784497	2.349887
H	-5.858546	-5.641064	1.749952	O	2.625595	-2.550042	-0.126762
C	-7.904064	-5.244653	2.19812	C	2.463645	-3.679451	-1.023319
H	-7.889498	-5.905636	3.075245	C	3.86147	-4.276469	-1.171813
H	-8.573644	-4.402515	2.421356	C	4.751735	-3.026904	-1.079707
H	-8.343245	-5.813354	1.372065	C	4.024616	-2.186354	-0.026421
C	-5.941018	-4.040619	3.131094	H	4.114572	-1.107923	-0.19165
H	-6.536408	-3.151351	3.381324	H	4.368257	-2.416727	0.989983
H	-5.976095	-4.712964	3.997799	H	4.771837	-2.501774	-2.041209
H	-4.901335	-3.724925	2.998887	H	5.783513	-3.248551	-0.792344
O	-8.980292	-1.550477	0.97882	H	3.981277	-4.82333	-2.111243
C	-9.616956	-0.262695	1.175183	H	4.077167	-4.965106	-0.346339
C	-11.075876	-0.426167	0.716456	H	1.729497	-4.357368	-0.580384
C	-11.011188	-1.657925	-0.201461	H	2.072933	-3.314515	-1.979715
C	-9.952735	-2.504567	0.498967	C	0.361387	0.559399	-1.321739
H	-9.430351	-3.212346	-0.146228	C	0.975793	-0.505332	-2.238679
H	-10.378488	-3.052762	1.350436	H	1.910657	-0.898542	-1.825028
H	-10.669306	-1.377197	-1.2046	H	0.285518	-1.348107	-2.374852
H	-11.970282	-2.1759	-0.297545	H	1.191632	-0.093144	-3.232082
H	-11.452477	0.46913	0.21305	H	1.134452	1.343179	-1.203888
H	-11.728565	-0.627995	1.57368	C	-0.815348	1.232776	-2.064103
H	-0.658159	-0.227774	2.631707	H	-0.468401	1.756799	-2.965173
H	-1.096327	1.463712	2.915206	H	-1.556354	0.487491	-2.379863
H	-0.645165	1.966907	0.50878	H	-1.331238	1.964975	-1.435074
C	1.206329	1.63209	1.509714	C	-0.145407	1.100035	0.975884
H	1.872623	1.923417	0.689695	C	-1.039003	0.681195	2.148464
H	1.073662	2.511729	2.154285	H	-2.06394	0.478101	1.817546
H	1.722315	0.863624	2.103335				

Table A1.8 (Continued).





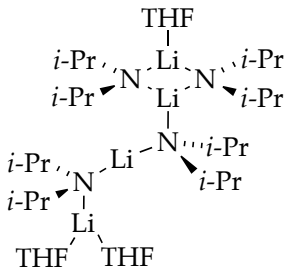
S_b
G = -1893.879904
G_{MP2} = -1888.178118

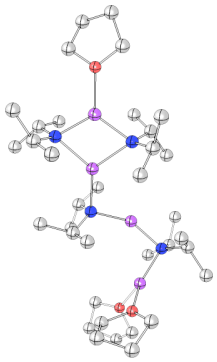
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	H	2.491297	0.703447	-2.426719
N	2.136146	0.49095	0.253539	H	0.973212	1.52789	-2.039328
Li	2.901182	-1.169983	-0.561624	H	2.386394	2.466629	-2.535457
N	4.447644	-2.291539	-1.237319	H	3.591073	1.875154	-0.499771
Li	5.90121	-0.988896	-0.787894	C	1.890627	3.026839	0.081937
O	6.417709	0.843787	-1.306811	H	0.800472	2.945324	0.154007
C	7.028784	1.720877	-0.323757	H	2.280739	3.270152	1.076106
C	6.776925	3.141869	-0.826207	H	2.12747	3.874912	-0.574648
C	6.778773	2.948232	-2.349874	C	2.452644	0.625868	1.684154
C	6.070623	1.601995	-2.498509	H	1.914226	1.482165	2.131205
H	6.395022	1.027403	-3.370271	C	1.98941	-0.60422	2.470063
H	4.98295	1.718948	-2.527608	H	0.926842	-0.801185	2.305902
H	7.805585	2.890032	-2.730204	H	2.540635	-1.502998	2.17278
H	6.260614	3.747193	-2.887546	H	2.144129	-0.464372	3.547586
H	7.537484	3.846159	-0.476486	C	3.948176	0.883127	2.001312
H	5.796904	3.495933	-0.488321	H	4.116522	0.969357	3.083197
H	6.573526	1.515216	0.647905	H	4.567895	0.05253	1.62938
H	8.100742	1.492245	-0.272752	H	4.309322	1.807772	1.537414
O	7.596432	-1.443928	0.174087	Li	-2.296363	-0.84021	-0.503682
C	7.806281	-1.88397	1.539993	N	-0.745445	-2.089665	-0.329662
C	9.321308	-1.990402	1.700945	C	-1.015678	-3.090896	0.709647
C	9.754657	-2.438075	0.296485	H	-1.716989	-3.86799	0.338171
C	8.805164	-1.643684	-0.603513	C	-1.719718	-2.466356	1.922512
H	8.538354	-2.166004	-1.526394	H	-2.035464	-3.242965	2.631149
H	9.215237	-0.658925	-0.859969	H	-1.056237	-1.781412	2.460799
H	9.590127	-3.514301	0.171927	H	-2.616543	-1.901774	1.63552
H	10.805433	-2.22732	0.077972	C	0.216519	-3.875436	1.220874
H	9.607144	-2.694787	2.487229	H	0.943553	-3.194758	1.678265
H	9.752935	-1.012373	1.944099	H	-0.076604	-4.617096	1.976682
H	7.337822	-1.152783	2.204522	H	0.72299	-4.416222	0.41435
H	7.315681	-2.853938	1.676568	C	-0.127122	-2.700293	-1.50966
C	4.794716	-3.482786	-0.432718	H	0.907314	-3.057818	-1.292769
C	4.48116	-3.219513	1.045389	C	0.008202	-1.671551	-2.637684

Table A1.8 (Continued).

H	4.87684	-2.25439	1.38646	H	0.527034	-0.765272	-2.305329
H	3.397944	-3.212969	1.214253	H	0.568929	-2.083444	-3.486315
H	4.904172	-4.001107	1.689238	H	-0.978397	-1.36987	-3.007481
H	5.885525	-3.701831	-0.486159	C	-0.856471	-3.93218	-2.104497
C	4.089714	-4.796042	-0.838774	H	-1.877228	-3.65907	-2.407066
H	4.297502	-5.582116	-0.101823	H	-0.328687	-4.299176	-2.994749
H	3.003173	-4.648707	-0.884679	H	-0.92562	-4.767743	-1.400838
H	4.420946	-5.172183	-1.812037	N	-1.846608	1.107456	-0.170982
C	4.532541	-2.568637	-2.683274	C	-2.26024	1.720446	1.102229
C	3.907769	-1.434895	-3.500292	H	-2.237057	2.823478	1.028797
H	2.842711	-1.325713	-3.272869	C	-3.707073	1.365535	1.527315
H	4.398216	-0.475066	-3.29641	H	-4.012987	1.90703	2.434191
H	3.994643	-1.628224	-4.576821	H	-4.424382	1.622942	0.738771
H	3.953904	-3.471079	-2.940772	H	-3.796617	0.289806	1.732154
C	5.97241	-2.825197	-3.194745	C	-1.30179	1.371501	2.247576
H	6.467231	-3.626751	-2.634059	H	-0.285596	1.712058	2.022305
H	5.978968	-3.11192	-4.254461	H	-1.61421	1.84265	3.189064
H	6.589445	-1.916559	-3.102349	H	-1.272708	0.290359	2.423526
C	2.487755	1.717618	-0.484631	C	-2.366433	1.914102	-1.28459
C	2.063497	1.593123	-1.953332	H	-3.440954	2.153349	-1.123321
C	-6.497041	-1.5911	-0.891755	C	-2.304953	1.156239	-2.619061
C	-5.28191	-0.772084	-1.323584	H	-2.737739	1.754383	-3.431226
H	-5.208126	0.20609	-0.84524	H	-1.268467	0.930045	-2.892639
H	-5.257201	-0.636946	-2.413328	H	-2.856014	0.207254	-2.584708
H	-6.727057	-1.404868	0.164057	C	-1.671769	3.283473	-1.492737
H	-7.388964	-1.360063	-1.482066	H	-0.636771	3.145532	-1.824702
H	-6.544568	-3.768648	-0.502704	H	-2.196149	3.880071	-2.253131
H	-6.052594	-3.313911	-2.143635	H	-1.648671	3.876475	-0.572558
H	-3.85117	-3.588065	-1.177585	O	-4.131637	-1.551175	-0.923008
H	-4.416698	-3.093453	0.432538	C	-4.52793	-2.917293	-0.64389
C	-5.989801	-3.028228	-1.086748				

Table A1.8 (Continued).





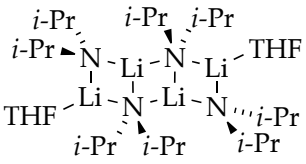
S$_c$
G = -1893.877324
G_{MP2} = -1888.176843

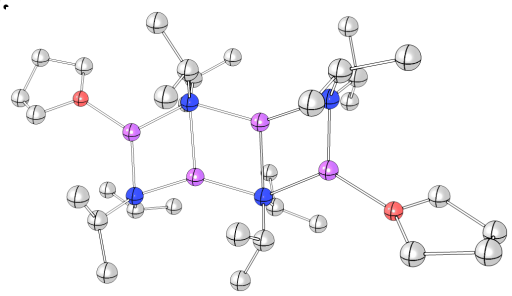
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	C	2.817179	-0.862614	1.694185
Li	-2.404951	0.559818	0.434599	H	3.403213	0.065378	1.699081
N	-0.913285	1.946068	0.467474	H	1.831958	-0.631333	2.11106
C	-1.084211	2.981893	-0.562941	H	3.303431	-1.57174	2.377393
H	-1.667114	3.835477	-0.157618	H	3.73678	-1.71549	-0.023572
C	-1.874819	2.487145	-1.781674	C	1.944694	-2.79961	0.377635
H	-1.999438	3.28794	-2.522078	H	0.906778	-2.643773	0.690827
H	-1.360098	1.659448	-2.281397	H	1.918923	-3.323429	-0.583231
H	-2.875211	2.136354	-1.499643	H	2.43106	-3.467934	1.101783
C	0.24815	3.589352	-1.066421	C	1.962618	-0.988938	-1.999477
H	0.823245	2.832247	-1.613976	H	1.180418	-1.771053	-2.046476
H	0.083921	4.438712	-1.745711	C	1.504367	0.134107	-2.939325
H	0.864732	3.950472	-0.235812	H	0.630452	0.659906	-2.542001
C	-0.651733	2.63013	1.74801	H	2.30047	0.878308	-3.086018
H	-0.068131	3.553987	1.572033	H	1.239728	-0.254969	-3.930181
C	0.189418	1.801705	2.725325	C	3.229213	-1.634455	-2.609833
H	1.127003	1.484638	2.259716	H	3.045	-1.941051	-3.647658
H	0.437182	2.38554	3.622165	H	4.063401	-0.919247	-2.61276
H	-0.344388	0.9073	3.05741	H	3.551773	-2.525137	-2.060315
C	-1.941063	3.08807	2.473152	N	4.606747	2.516764	-0.570802
H	-2.532438	2.215756	2.786686	Li	5.841682	1.127973	0.164795
H	-1.720818	3.682969	3.371695	O	6.274794	0.447599	2.023722
H	-2.566186	3.703667	1.816338	C	6.449539	-0.986898	2.186346
N	-1.769517	-1.326704	0.151319	C	6.334308	-1.253535	3.686739
C	-2.249176	-2.017979	-1.053261	C	6.869758	0.053679	4.288666
H	-3.316322	-2.313401	-0.947318	C	6.309435	1.09608	3.322717
C	-2.211618	-1.092797	-2.274495	H	6.925106	1.994867	3.23651
H	-2.615252	-1.596742	-3.162109	H	5.290485	1.391948	3.595614
H	-2.803023	-0.185197	-2.1117	H	7.966196	0.0643	4.275478
H	-1.184738	-0.788015	-2.508884	H	6.540111	0.224404	5.317436
C	-1.51065	-3.329577	-1.41403	H	6.900141	-2.137836	3.994211
H	-1.586888	-4.080977	-0.621279	H	5.286416	-1.40316	3.968806

Table A1.8 (Continued).

H	-1.933871	-3.774266	-2.32501	H	5.684046	-1.494241	1.593675
H	-0.445747	-3.137404	-1.589449	H	7.438917	-1.259043	1.800633
C	-1.875482	-2.203435	1.32601	O	7.230885	-0.036608	-0.687223
H	-1.256596	-3.116033	1.205855	C	7.067775	-1.16869	-1.580199
C	-3.302021	-2.71508	1.650581	C	8.46447	-1.769377	-1.724317
H	-3.28893	-3.372734	2.530229	C	9.357322	-0.521422	-1.635594
H	-3.970534	-1.871142	1.870202	C	8.630511	0.324651	-0.586516
H	-3.741512	-3.286271	0.826407	H	8.722922	1.40225	-0.75586
C	-1.338189	-1.509543	2.579936	H	8.972347	0.097562	0.431215
H	-1.93223	-0.618051	2.825403	H	9.379973	0.00004	-2.599036
H	-1.375488	-2.177856	3.44966	H	10.388201	-0.744221	-1.3459
H	-0.297756	-1.196403	2.447483	H	8.584507	-2.320057	-2.661482
O	-4.374197	0.972852	0.415955	H	8.677376	-2.455319	-0.895885
C	-5.010692	2.261246	0.608799	H	6.331328	-1.843337	-1.136122
C	-6.469701	2.096503	0.151041	H	6.679513	-0.806145	-2.538511
C	-6.404774	0.863367	-0.764965	C	4.967371	3.070862	-1.894935
C	-5.346294	0.017932	-0.063095	C	5.583183	2.002745	-2.807006
H	-4.823544	-0.690551	-0.707226	H	6.518178	1.61205	-2.391187
H	-5.772132	-0.529319	0.788914	H	4.893697	1.158793	-2.939948
H	-6.062855	1.142638	-1.768502	H	5.799246	2.410842	-3.802048
H	-7.363774	0.345087	-0.860351	H	5.739445	3.856128	-1.780622
H	-6.846907	2.990874	-0.35356	C	3.789861	3.739449	-2.640363
H	-7.121907	1.895663	1.00887	H	4.136181	4.259599	-3.543911
H	-4.922794	2.545531	1.661155	H	3.049616	2.991907	-2.952561
H	-4.46481	2.993055	0.004855	H	3.273217	4.474065	-2.014773
N	2.108288	-0.463397	-0.629725	C	4.459376	3.620552	0.400538
Li	2.960125	1.313824	-0.608934	C	3.569055	3.203529	1.576268
C	2.695826	-1.452431	0.283076	H	2.544299	2.995256	1.247969
C	5.810083	4.159142	0.930303	H	3.954106	2.298052	2.062782
H	6.474333	4.449478	0.108301	H	3.51	3.989191	2.339644
H	5.675316	5.040844	1.57161	H	3.956031	4.483823	-0.069399
H	6.329277	3.394636	1.526148				

Table A1.8 (Continued).



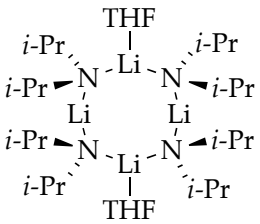


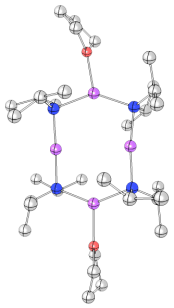
T
G = -1661.533838
G_{MP2} = -1656.500785

Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	H	-1.754553	-1.586992	1.965124
N	-2.156026	-0.271004	0.33449	C	-1.797294	0.389756	2.704235
Li	-1.77685	1.950746	0.035036	H	-0.733973	0.566034	2.530905
N	-3.705226	2.807429	-0.303196	H	-2.324546	1.340584	2.589766
Li	-3.964163	0.834629	-0.135468	H	-1.911417	0.076846	3.74948
O	-5.770511	0.042599	-0.463549	C	-3.792257	-1.020216	2.159044
C	-6.914841	0.58265	0.247996	H	-3.823833	-1.399838	3.188609
C	-8.150268	-0.066453	-0.386141	H	-4.440816	-0.133809	2.124519
C	-7.664227	-0.387406	-1.80835	H	-4.235395	-1.784016	1.511632
C	-6.212675	-0.790856	-1.558418	N	1.849696	-0.90347	-0.259117
H	-5.549401	-0.609665	-2.408541	Li	2.178555	1.090211	-0.463263
H	-6.12944	-1.845373	-1.264739	N	0.470916	2.272267	-0.200046
H	-7.706673	0.506837	-2.440633	C	0.901326	3.185781	0.883827
H	-8.240849	-1.179909	-2.294437	H	1.706419	3.847921	0.51996
H	-9.020184	0.596253	-0.366198	C	1.514067	2.435492	2.073493
H	-8.415319	-0.989271	0.142785	H	1.910471	3.146237	2.809552
H	-6.802765	0.346871	1.310699	H	0.773825	1.816121	2.586991
H	-6.904385	1.670077	0.122218	H	2.344	1.781672	1.776868
C	-4.344949	3.688258	0.690573	C	-0.198568	4.129693	1.411007
C	-4.20114	3.154871	2.11942	H	-0.990041	3.564999	1.920743
H	-4.533974	2.112815	2.201839	H	0.203469	4.8522	2.134443
H	-3.163533	3.207988	2.468571	H	-0.664464	4.698416	0.600397
H	-4.806128	3.749033	2.815697	C	0.168209	3.032594	-1.444498
H	-5.438646	3.732761	0.514763	H	-0.834241	3.512127	-1.392905
C	-3.866996	5.159619	0.675938	C	0.14361	2.077982	-2.644643
H	-4.417265	5.754493	1.417363	H	-0.431748	1.170096	-2.439993
H	-2.799765	5.223471	0.91515	H	-0.295377	2.558898	-3.526975
H	-4.017276	5.634979	-0.298722	H	1.161035	1.770112	-2.909916
C	-3.949604	3.323096	-1.665099	C	1.1315	4.185724	-1.813998
C	-3.487402	2.315466	-2.721406	H	2.166053	3.821278	-1.870425
H	-2.451991	2.008192	-2.563273	H	0.8632	4.583906	-2.800154
H	-4.119634	1.41551	-2.710381	H	1.098586	5.022701	-1.109753
H	-3.549677	2.741642	-3.7304	O	3.994149	1.915822	-0.768553
H	-3.36703	4.248115	-1.854223	C	4.539676	3.075456	-0.08641
C	-5.419565	3.682244	-1.999824	C	6.0145	3.151119	-0.492801

Table A1.8 (Continued).

H	-5.807796	4.511967	-1.402113	C	6.349462	1.681056	-0.78578
H	-5.507369	3.9749	-3.054064	C	5.058113	1.192122	-1.43578
H	-6.072957	2.814145	-1.835134	H	4.868887	0.125467	-1.30566
C	-2.515741	-1.396238	-0.571287	H	5.031205	1.43336	-2.506793
C	-2.089655	-1.088401	-2.011957	H	6.536643	1.134667	0.145933
H	-2.472517	-0.125475	-2.357223	H	7.218751	1.555908	-1.438107
H	-0.996499	-1.069312	-2.101804	H	6.636513	3.590304	0.292564
H	-2.455767	-1.859876	-2.701064	H	6.134192	3.757322	-1.398361
H	-3.617182	-1.542986	-0.603321	H	3.96065	3.954147	-0.380701
C	-1.943928	-2.781597	-0.190283	H	4.423057	2.922035	0.992579
H	-0.855955	-2.733184	-0.065486	C	2.372721	-1.565945	0.953604
H	-2.375515	-3.180912	0.732752	H	2.432477	-2.656511	0.792968
H	-2.158904	-3.506041	-0.985743	C	3.807492	-1.127533	1.335672
C	-2.338869	-0.676449	1.75058	H	4.198336	-1.708207	2.183132
H	3.410338	-1.886892	-1.318764	H	4.500107	-1.26874	0.497683
C	2.221313	-0.837698	-2.733172	H	3.829362	-0.066567	1.619939
H	2.625019	-1.402345	-3.582871	C	1.452328	-1.387139	2.166571
H	1.177086	-0.601741	-2.964571	H	0.455779	-1.79569	1.9652
H	2.774733	0.108755	-2.681345	H	1.852012	-1.903163	3.049168
C	1.632286	-3.010514	-1.675419	H	1.345599	-0.33087	2.436094
H	0.589711	-2.860673	-1.97765	C	2.331121	-1.649811	-1.436141
H	2.136216	-3.580008	-2.468997	H	1.630694	-3.634552	-0.77579





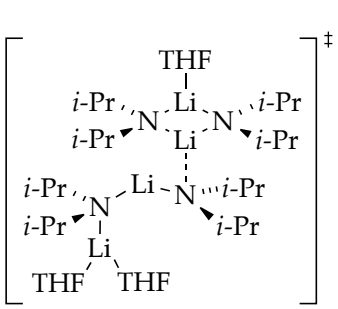
U
G = -1661.537728
G_{MP2} = -1656.49475

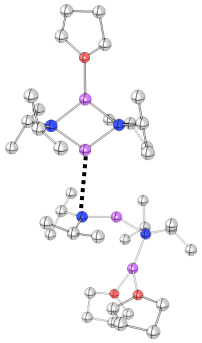
Atom	X	Y	Z	Atom	X	Y	Z
C	0	0	0	H	3.445614	-7.280682	-1.011027
Li	1.65886	-1.485071	-1.615402	C	5.505144	-6.885702	-1.37996
N	-0.28003	-1.285513	-2.12282	H	5.849863	-7.584127	-0.606884
Li	-1.046697	-3.16368	-1.711183	H	5.545618	-7.4172	-2.335896
N	-0.350376	-5.05736	-1.097101	H	6.209394	-6.047812	-1.42736
C	-1.106719	-6.019421	-1.921357	C	4.117676	-5.833686	0.39514
H	-2.188859	-5.922807	-1.696899	H	3.139814	-5.457744	0.711391
C	-0.948043	-5.686314	-3.411429	H	4.412902	-6.615841	1.105234
H	-1.307328	-4.676484	-3.639887	H	4.836097	-5.007917	0.491287
H	0.100647	-5.742152	-3.72889	C	3.684939	-5.751863	-3.369989
N	3.526754	-5.355326	-1.958677	C	4.086396	-6.372957	-1.039928

Table A1.8 (Continued).

H	-1.515364	-6.385908	-4.037295	H	4.75547	-5.870586	-3.628189
C	-0.780861	-7.518638	-1.710921	C	3.153637	-4.649556	-4.293229
H	0.286601	-7.722905	-1.873074	H	3.311976	-4.902786	-5.348703
H	-1.036009	-7.851225	-0.700451	H	2.077104	-4.493928	-4.151635
H	-1.352048	-8.143671	-2.411023	H	3.649842	-3.687812	-4.108935
C	-0.704644	-5.189326	0.329592	C	3.017848	-7.092229	-3.758333
H	-1.735107	-5.59118	0.411814	H	1.930894	-7.051507	-3.6094
C	0.19448	-6.132701	1.167144	H	3.199859	-7.330554	-4.814654
H	0.328327	-7.107451	0.692721	H	3.398642	-7.928302	-3.162748
H	1.188739	-5.689618	1.306472	O	6.390515	-3.573922	-1.951305
H	-0.225259	-6.298584	2.169315	C	7.381971	-3.372015	-0.91743
C	-0.700552	-3.818436	1.028196	C	8.709001	-3.840714	-1.517427
H	-0.911693	-3.906979	2.101591	C	8.516622	-3.518364	-3.007373
H	0.282994	-3.343852	0.9255	C	7.037756	-3.850141	-3.215857
H	-1.448043	-3.13288	0.609221	H	6.887291	-4.907986	-3.459829
O	-3.177549	-3.464438	-1.894409	H	6.558387	-3.238812	-3.986712
C	-4.075907	-3.682129	-0.795251	H	9.16956	-4.099561	-3.665148
C	-5.191807	-4.579748	-1.355444	H	8.700819	-2.454251	-3.194353
C	-5.172762	-4.283734	-2.880104	H	8.836402	-4.919718	-1.372318
C	-4.01407	-3.281884	-3.046652	H	9.568996	-3.332325	-1.071573
H	-4.381091	-2.245969	-3.069794	H	7.406553	-2.306697	-0.66087
H	-3.399863	-3.456684	-3.931907	H	7.075384	-3.942811	-0.03589
H	-6.116117	-3.860955	-3.238155	C	4.041225	-1.371624	0.104989
H	-4.981875	-5.197733	-3.449256	H	5.084924	-1.736569	0.240714
H	-6.15765	-4.355403	-0.893256	C	3.148599	-2.287616	0.955127
H	-4.965939	-5.632702	-1.165184	H	3.554616	-2.42735	1.964803
H	-3.503783	-4.139401	0.012808	H	2.144715	-1.857547	1.061285
H	-4.472654	-2.714575	-0.454341	H	3.042283	-3.278296	0.501323
C	-0.809788	-0.178282	-1.296288	C	4.024899	0.034717	0.74756
C	-2.303915	-0.301561	-0.917081	H	3.0297	0.490317	0.673876
H	-2.932666	-0.457713	-1.797424	H	4.281544	-0.036876	1.812184
H	-2.459791	-1.152725	-0.241316	H	4.739977	0.721869	0.285633
H	-2.658986	0.599423	-0.397061	C	4.202331	-0.381109	-2.135897
H	-0.704654	0.773659	-1.850842	H	3.874337	0.609681	-1.764078
C	-0.254151	-0.8979	-3.546549	C	3.688458	-0.474318	-3.578035
C	0.351924	-2.021281	-4.394848	H	2.59692	-0.392411	-3.633974
H	1.322199	-2.350161	-4.008179	H	4.101638	0.333589	-4.194374
H	-0.308443	-2.897132	-4.416212	H	3.977452	-1.427544	-4.040142
H	0.50398	-1.699058	-5.432085	C	5.745984	-0.317149	-2.17627
H	0.399518	-0.005271	-3.681754	H	6.156025	-1.211135	-2.657229
C	-1.601673	-0.486488	-4.182825	H	6.081649	0.56276	-2.740867
H	-2.047514	0.376721	-3.679763	H	6.181485	-0.247237	-1.17373
H	-1.458295	-0.211171	-5.236383	H	-0.414063	0.796131	0.631981
H	-2.32312	-1.311544	-4.144129	H	-0.002215	-0.923052	0.593726
N	3.623594	-1.459738	-1.309647	H	1.042645	0.270963	-0.210687
Li	4.313422	-3.431602	-1.731915	Li	1.593528	-5.155649	-1.497991

Table A1.9. Optimized geometries of LDA aggregation transition structures at B3LYP level of theory with 6-31G(d) basis set at –78 °C with free energies (Hartrees), and cartesian coordinates (X,Y,Z). (Note: G_{MP2} includes single point MP2 corrections to B3LYP/6-31G(d) optimized structures)





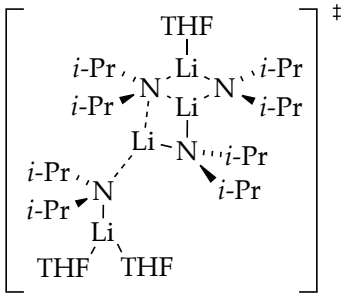
V
G = -1893.880012
G_{MP2} = -1888.161058

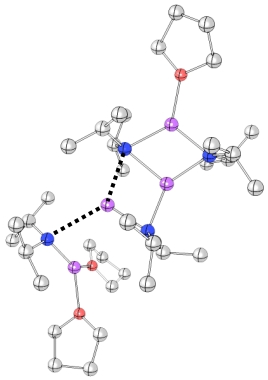
Atom	X	Y	Z	Atom	X	Y	Z
N	0	0	0	C	-1.13489	1.260205	-1.879603
Li	-1.464073	-1.397256	-0.142253	H	-0.945244	1.887159	-2.761813
N	-2.074315	-3.180441	-0.317334	H	-1.788694	0.435811	-2.19433
C	-1.804487	-4.203705	0.680899	H	-1.690993	1.867261	-1.157741
C	-1.75191	-3.557368	2.072808	C	-0.212536	0.96659	1.093929
H	-1.004723	-2.754347	2.109943	C	-0.977097	0.325611	2.258243
H	-2.722945	-3.115077	2.330078	H	-1.978737	0.004542	1.947548
H	-1.496075	-4.289999	2.850437	H	-0.448578	-0.556936	2.639299
H	-0.804857	-4.686558	0.531036	H	-1.102147	1.025737	3.093805
C	-2.801189	-5.385237	0.723255	H	-0.836595	1.809925	0.747841
H	-3.829437	-5.019372	0.835698	C	1.100778	1.597601	1.614698
H	-2.769575	-5.988373	-0.190037	H	1.678058	2.041861	0.795561
H	-2.577654	-6.05434	1.564956	H	0.912722	2.388665	2.353786
C	-2.292427	-3.713251	-1.657308	H	1.732796	0.83691	2.095656
H	-3.106134	-4.464236	-1.669462	Li	-5.530291	-2.588074	0.598535
C	-2.747725	-2.595083	-2.603757	Li	-7.835154	-2.010928	0.61328
H	-3.643084	-2.096861	-2.213156	N	-6.287801	-0.771632	1.042997
H	-1.963965	-1.83331	-2.725505	C	-6.018093	0.34642	0.135665
H	-2.980422	-2.981295	-3.604048	H	-6.718632	1.186836	0.342547
C	-1.060823	-4.420687	-2.274852	C	-6.250634	-0.056235	-1.325388
H	-1.289074	-4.850372	-3.260188	H	-6.083585	0.790947	-2.002043
H	-0.237256	-3.703337	-2.39818	H	-5.559171	-0.85426	-1.62854
H	-0.703057	-5.236901	-1.635669	H	-7.271866	-0.42039	-1.488034
Li	1.332345	-1.399458	0.4531	C	-4.599794	0.950615	0.257951
O	1.856329	-2.254662	2.198878	H	-3.84665	0.195195	-0.005921
C	1.959325	-3.704493	2.203399	H	-4.467883	1.812904	-0.410747
C	1.948075	-4.111376	3.675622	H	-4.391783	1.288624	1.278616
C	2.638757	-2.913136	4.343629	C	-6.312533	-0.305968	2.442829
C	2.087991	-1.738177	3.534785	H	-6.266759	0.797748	2.465049
H	2.778059	-0.893078	3.459578	C	-5.115641	-0.800247	3.283682

Table A1.9 (Continued).

H	1.136208	-1.378743	3.940659	H	-4.170168	-0.496254	2.82334
H	3.72713	-2.984192	4.229742	H	-5.139838	-0.403793	4.309204
H	2.41419	-2.821423	5.410161	H	-5.11243	-1.895432	3.356178
H	2.462752	-5.061168	3.847794	C	-7.632559	-0.670628	3.157109
H	0.917482	-4.209794	4.033709	H	-7.790011	-1.757435	3.180348
H	1.120011	-4.108704	1.631393	H	-7.645869	-0.322591	4.199021
H	2.898278	-3.986235	1.711038	H	-8.488528	-0.219414	2.640548
O	2.809243	-2.314709	-0.5501	N	-7.044127	-3.878132	0.366664
C	2.763101	-3.253168	-1.655776	C	-7.363334	-4.501117	-0.927135
C	4.212933	-3.679301	-1.883093	H	-8.287815	-5.109824	-0.845756
C	4.981673	-2.402791	-1.507051	C	-7.645008	-3.44728	-2.007592
C	4.170367	-1.878008	-0.320473	H	-7.898635	-3.919534	-2.965115
H	4.173656	-0.786354	-0.237694	H	-8.479219	-2.791375	-1.72709
H	4.516134	-2.303855	0.63011	H	-6.764066	-2.816583	-2.179017
H	4.956458	-1.685178	-2.334854	C	-6.265747	-5.456081	-1.45061
H	6.028189	-2.585064	-1.246234	H	-6.003885	-6.21719	-0.707869
H	4.393152	-4.005366	-2.911309	H	-6.587665	-5.980233	-2.361888
H	4.483127	-4.50296	-1.211672	H	-5.352695	-4.894057	-1.68522
H	2.092892	-4.069766	-1.377463	C	-7.245074	-4.855789	1.447938
H	2.348429	-2.740788	-2.531109	H	-6.93639	-5.865166	1.118815
C	0.182443	0.719444	-1.277454	C	-8.723588	-4.983972	1.888063
C	0.883858	-0.161866	-2.319108	H	-8.871691	-5.804028	2.605224
H	1.897805	-0.42439	-1.996668	H	-9.062456	-4.054624	2.368476
H	0.327703	-1.095949	-2.478358	H	-9.375378	-5.175962	1.027872
H	0.956683	0.347889	-3.287742	C	-6.385648	-4.537615	2.679173
H	0.836283	1.600761	-1.131017	H	-6.636711	-3.554647	3.094291
H	-11.134582	-2.579438	1.157889	H	-6.540947	-5.27499	3.477358
H	-11.831625	-1.51119	-1.627012	H	-5.317311	-4.541644	2.430278
H	-12.929745	-1.755251	-0.256195	O	-9.679761	-1.416404	0.242205
H	-11.975747	0.765035	-0.708073	C	-10.041365	-0.051249	-0.075998
H	-11.943067	0.147176	0.95414	C	-11.570131	-0.02022	-0.063321
H	-9.574081	0.604365	0.662792	C	-11.920372	-1.439909	-0.536509
H	-9.640457	0.195448	-1.067039	C	-10.838813	-2.280022	0.145214
H	-10.550006	-3.17339	-0.414				

Table A1.9 (Continued).





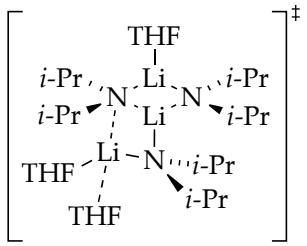
W
G = -1893.865927
G_{MP2} = -1888.166029

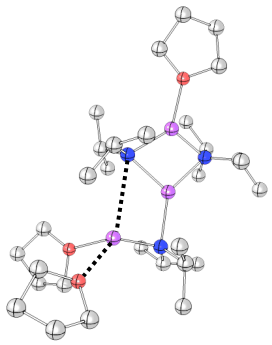
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	H	-6.135808	4.092197	-0.260542
Li	-2.077429	1.150198	0.588834	H	-6.566688	3.297665	1.258704
N	-0.244757	2.249699	0.284575	H	-4.303991	3.603858	1.869617
C	-0.66182	3.293797	-0.689882	H	-3.789281	3.855032	0.186679
H	-1.195573	4.105595	-0.159647	N	1.925404	-0.394507	-0.678198
C	-1.645738	2.782303	-1.751921	Li	1.98306	1.583058	-0.431058
H	-1.88902	3.578781	-2.466922	C	2.605965	-1.392978	0.152695
H	-1.225713	1.949813	-2.323793	C	2.875943	-0.850019	1.559901
H	-2.590508	2.443004	-1.312145	H	3.472675	0.069844	1.532305
C	0.522601	3.969164	-1.409266	H	1.943624	-0.623396	2.087348
H	1.000567	3.268482	-2.104744	H	3.41872	-1.588839	2.164466
H	0.203157	4.83865	-2.001003	H	3.604402	-1.637937	-0.264489
H	1.283363	4.31754	-0.702968	C	1.860957	-2.74274	0.284188
C	0.101694	2.945169	1.549251	H	0.881367	-2.599603	0.756901
H	0.617722	3.896495	1.323519	H	1.68705	-3.208035	-0.691592
C	1.068535	2.142431	2.424122	H	2.435261	-3.456348	0.891673
H	2.00897	1.9281	1.90506	C	1.774938	-0.851277	-2.073408
H	1.326073	2.701919	3.332603	H	0.977052	-1.619569	-2.162806
H	0.629854	1.190836	2.735806	C	1.336739	0.326211	-2.954468
C	-1.122077	3.34073	2.411659	H	0.466485	0.839238	-2.531942
H	-1.644344	2.450434	2.790151	H	2.147715	1.06066	-3.054206
H	-0.823699	3.939262	3.283374	H	1.06379	-0.003786	-3.964479
H	-1.838047	3.938013	1.838077	C	3.023213	-1.489782	-2.724742
N	-1.843598	-0.836457	0.440545	H	2.826765	-1.705008	-3.78276
C	-2.494074	-1.559406	-0.66335	H	3.88027	-0.806941	-2.672278
H	-3.566237	-1.747937	-0.441454	H	3.311043	-2.433417	-2.250206
C	-2.486718	-0.724449	-1.949501	N	4.681424	3.029085	-0.548121
H	-3.003221	-1.25069	-2.76176	Li	5.502983	1.526575	0.36703
H	-2.98626	0.240566	-1.809922	O	5.830263	1.056991	2.35133
H	-1.46221	-0.527524	-2.290047	C	6.321075	-0.25865	2.715699
C	-1.896016	-2.94883	-0.988091	C	6.02993	-0.414933	4.208324
H	-1.935485	-3.63014	-0.132106	C	6.135668	1.033088	4.706405
H	-2.447358	-3.426972	-1.80889	C	5.50271	1.805541	3.550194

Table A1.9 (Continued).

H	-0.846191	-2.853531	-1.290974	H	5.88737	2.820817	3.431616
C	-1.960449	-1.585147	1.701887	H	4.411623	1.850106	3.648648
H	-1.525944	-2.599452	1.604917	H	7.185946	1.321376	4.834004
C	-3.405807	-1.794818	2.214995	H	5.617326	1.206789	5.653888
H	-3.411419	-2.403525	3.129079	H	6.729932	-1.098147	4.698504
H	-3.871588	-0.828379	2.450927	H	5.014232	-0.797211	4.361207
H	-4.040401	-2.305292	1.483208	H	5.813692	-0.998977	2.093735
C	-1.162484	-0.906125	2.819078	H	7.39683	-0.298949	2.507725
H	-1.539068	0.106258	3.022089	O	6.940416	0.215232	-0.224535
H	-1.231315	-1.472959	3.755873	C	6.817204	-1.02799	-0.95922
H	-0.102017	-0.829981	2.558799	C	8.250116	-1.467488	-1.264179
O	-3.959362	1.881648	0.75105	C	8.977187	-0.119913	-1.396638
C	-4.426322	3.251874	0.840404	C	8.294197	0.720842	-0.316738
C	-5.90077	3.245153	0.390262	H	8.243625	1.78764	-0.55352
C	-6.050043	1.884845	-0.313223	H	8.779731	0.598846	0.660779
C	-5.08753	1.016458	0.489158	H	8.798428	0.314241	-2.386655
H	-4.710133	0.136864	-0.032275	H	10.058189	-0.192535	-1.24554
H	-5.534077	0.6989	1.441436	H	8.31143	-2.081865	-2.166944
H	-5.721822	1.946713	-1.357139	H	8.663188	-2.04627	-0.429484
H	-7.075638	1.504055	-0.297552	H	6.258564	-1.734947	-0.339034
H	3.499553	4.82031	-2.282194	H	6.245153	-0.836898	-1.873451
C	4.76309	4.297377	0.188604	C	5.02719	3.269295	-1.954981
C	3.815316	4.322437	1.391748	C	5.442852	1.976932	-2.667207
H	2.771962	4.292777	1.063632	H	6.363725	1.56503	-2.242072
H	3.979002	3.452901	2.038023	H	4.65455	1.220597	-2.565813
H	3.953674	5.224724	2.002907	H	5.609779	2.144175	-3.738914
H	4.455079	5.14513	-0.451584	H	5.900594	3.952991	-2.027056
C	6.205092	4.630414	0.653583	C	3.907371	3.937578	-2.785209
H	6.903015	4.594458	-0.191656	H	4.273455	4.254933	-3.772286
H	6.281375	5.630526	1.104971	H	3.081468	3.234019	-2.944789
H	6.548515	3.89942	1.401231				

Table A1.9 (Continued).



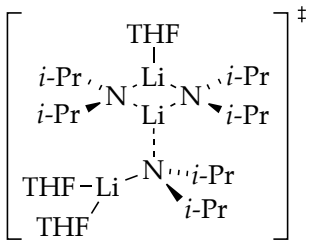


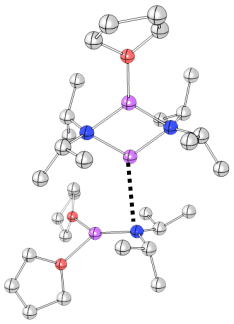
X
G = -1594.669023
G_{MP2} = -1589.893992

Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	C	-1.45471	-1.767731	-1.858058
Li	-2.024694	1.474731	-0.067723	H	-1.698854	-2.624505	-2.499796
N	0.061697	1.977493	-0.139925	H	-1.769609	-0.861855	-2.386773
C	0.536344	2.543577	-1.407042	H	-0.364748	-1.731872	-1.750534
H	1.650669	2.511854	-1.442528	C	-3.65841	-2.134228	-0.725595
C	0.054047	1.716234	-2.605621	H	-4.085904	-1.344295	-1.356647
H	0.478562	2.095736	-3.543682	H	-3.845664	-3.092351	-1.233114
H	0.340068	0.661398	-2.512318	H	-4.205086	-2.159994	0.22513
H	-1.036716	1.762908	-2.703144	C	-2.069117	-1.135613	1.781315
C	0.164533	4.024492	-1.652769	H	-2.968324	-1.779222	1.882262
H	0.541107	4.670248	-0.852442	C	-2.317822	0.078143	2.682697
H	0.588697	4.392044	-2.598461	H	-3.224738	0.611208	2.384448
H	-0.925287	4.142972	-1.695039	H	-2.424671	-0.214966	3.735723
C	0.782707	2.597103	0.988278	H	-1.486335	0.789871	2.627241
H	1.645595	3.169101	0.598025	C	-0.904656	-1.968795	2.375052
C	1.393483	1.551446	1.948466	H	0.004428	-1.358046	2.458155
H	1.952613	2.027715	2.765387	H	-1.144829	-2.344066	3.380161
H	0.614243	0.934161	2.413709	H	-0.672742	-2.837462	1.748644
H	2.080008	0.880907	1.417851	O	1.651436	-1.082744	-0.409917
C	-0.048553	3.597641	1.819632	C	1.975841	-2.430267	0.008605
H	-0.893567	3.092148	2.304593	C	3.34079	-2.74713	-0.612169
H	0.553065	4.067466	2.611682	C	3.977224	-1.353433	-0.732564
H	-0.457692	4.391208	1.188558	C	2.772777	-0.494194	-1.110986
N	-3.976788	2.321603	-0.490666	H	2.576281	-0.531197	-2.190569
Li	-4.771122	0.603956	-0.011167	H	2.844287	0.550908	-0.80384
O	-6.020936	0.128996	1.464475	H	4.776553	-1.304687	-1.478007
C	-7.251435	0.899455	1.516103	H	4.388359	-1.032993	0.232102
C	-7.81826	0.675225	2.918946	H	3.217147	-3.19459	-1.605388
C	-7.316126	-0.738853	3.24894	H	3.923762	-3.440615	0.001115
C	-5.920288	-0.730376	2.626344	H	2.010677	-2.45034	1.103765
H	-5.57521	-1.71279	2.293233	H	1.177766	-3.09903	-0.32719
H	-5.175022	-0.31059	3.310725	C	-7.564988	0.039435	-2.550613
H	-7.949742	-1.493518	2.767393	O	-6.786987	-0.457183	-1.439682
H	-7.290365	-0.951277	4.321688	C	-7.18509	-1.8072	-1.129793

Table A1.9 (Continued).

H	-8.908127	0.766504	2.945391	C	-8.503904	-2.041614	-1.870755
H	-7.398181	1.402473	3.623008	C	-8.316049	-1.167989	-3.119465
H	-7.006443	1.942986	1.300289	H	-7.698014	-1.689866	-3.859433
H	-7.917157	0.522556	0.732601	H	-9.257019	-0.886665	-3.601697
C	-4.331349	3.492052	0.331504	H	-8.675345	-3.098018	-2.098659
C	-4.202653	3.173807	1.827031	H	-9.351361	-1.680427	-1.275158
H	-4.785427	2.287935	2.104377	H	-6.404997	-2.499068	-1.472047
H	-3.158727	2.987315	2.103036	H	-7.269374	-1.895228	-0.042279
H	-4.558384	4.014976	2.435688	H	-8.259265	0.806531	-2.180757
H	-5.39493	3.772976	0.176052	H	-6.887137	0.508387	-3.268164
C	-3.513708	4.770208	0.038921	H	-4.698669	0.627455	-2.588266
H	-2.446555	4.585868	0.20135	H	-3.837143	1.559821	-3.824716
H	-3.636948	5.116086	-0.992645	C	-5.431292	3.257948	-2.367642
H	-3.825671	5.591573	0.698132	H	-5.477101	3.352494	-3.460826
C	-4.090304	2.621425	-1.929145	H	-6.2769	2.636995	-2.041748
H	-3.301812	3.32921	-2.256785	H	-5.578419	4.259049	-1.950772
C	-3.880743	1.342216	-2.75006	N	-1.870759	-0.734119	0.379587
H	-2.947847	0.841166	-2.47694	C	-2.149155	-1.883677	-0.492918
H	-1.762841	-2.819465	-0.040099				





Y
G = -1594.667347
G_{MP2} = -1589.877074

Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	H	3.556206	0.133741	0.858635
Li	-2.228386	0.72715	-0.431385	H	3.824858	-0.556578	-2.086223
N	-0.591668	1.8635	-0.553922	H	4.964998	-0.870567	-0.775107
C	-0.006441	2.332485	-1.818591	H	2.844422	-2.650543	-1.826728
H	0.940358	2.879556	-1.62734	H	4.012566	-3.059837	-0.566343
C	0.35952	1.160773	-2.740147	H	2.561458	-2.313213	1.188025
H	0.818702	1.51829	-3.670357	H	1.276475	-2.687226	0.008305
H	1.067105	0.470732	-2.263102	N	-5.472771	1.873344	-1.487137
H	-0.533505	0.587198	-3.01691	Li	-6.453414	0.499521	-0.620606
C	-0.911443	3.303605	-2.610574	O	-7.512539	-1.043663	-1.396178
H	-1.224994	4.15726	-2.001354	C	-7.334756	-2.410008	-0.950824
H	-0.395801	3.70067	-3.496606	C	-7.885316	-3.285857	-2.077483

Table A1.9 (Continued).

H	-1.820089	2.787315	-2.946133	C	-8.99293	-2.396372	-2.663021
C	-0.523655	2.931392	0.456476	C	-8.366208	-1.004361	-2.565676
H	-0.691029	3.918834	-0.010717	H	-9.094311	-0.199652	-2.428737
C	0.850677	3.019918	1.161998	H	-7.749325	-0.772121	-3.440911
H	0.912425	3.884028	1.838886	H	-9.898104	-2.456243	-2.046789
H	1.036378	2.113631	1.756206	H	-9.263225	-2.659164	-3.689854
H	1.662826	3.116282	0.431692	H	-8.249123	-4.251559	-1.714347
C	-1.62364	2.782257	1.51759	H	-7.109352	-3.474155	-2.82811
H	-1.523052	1.835814	2.062765	H	-6.27233	-2.570881	-0.749768
H	-1.576408	3.588262	2.260986	H	-7.895293	-2.549022	-0.017177
H	-2.621212	2.813833	1.06053	O	-7.24418	0.20329	1.223702
N	-1.677958	-1.120189	0.250652	C	-6.622395	0.478235	2.505069
C	-1.806919	-2.318387	-0.581661	C	-7.718617	1.101883	3.367301
H	-1.213255	-3.153259	-0.143249	C	-8.976588	0.394026	2.840992
C	-1.242567	-2.088215	-1.98904	C	-8.683838	0.296598	1.342007
H	-1.308837	-2.999867	-2.59582	H	-9.019343	1.195892	0.808408
H	-1.799682	-1.30366	-2.516086	H	-9.125935	-0.57993	0.860961
H	-0.189741	-1.783644	-1.955401	H	-9.901962	0.93946	3.048221
C	-3.249331	-2.869058	-0.710101	H	-9.065104	-0.606405	3.280966
H	-3.891071	-2.128328	-1.204771	H	-7.78023	2.180511	3.184176
H	-3.275077	-3.797306	-1.298934	H	-7.547689	0.94469	4.436312
H	-3.679663	-3.090449	0.273195	H	-6.262404	-0.467855	2.926781
C	-1.956442	-1.448916	1.661081	H	-5.767879	1.133856	2.329606
H	-2.070244	-2.542408	1.771314	C	-5.692487	3.272527	-1.133791
C	-3.268659	-0.830225	2.187322	C	-6.178774	3.380835	0.317633
H	-4.110964	-1.134737	1.556858	H	-7.094734	2.795952	0.473137
H	-3.482698	-1.133439	3.223061	H	-5.410571	3.002931	1.006082
H	-3.219915	0.266481	2.169668	H	-6.396259	4.420736	0.591528
C	-0.788716	-1.066638	2.595651	H	-6.49821	3.728844	-1.751105
H	-0.571876	0.00853	2.54767	C	-4.470153	4.204544	-1.305412
H	-1.006556	-1.305227	3.645794	H	-3.62164	3.838688	-0.714163
H	0.122755	-1.604865	2.310461	H	-4.140788	4.26649	-2.347449
O	1.832452	-0.717361	0.079354	H	-4.70706	5.22631	-0.978217
C	2.185442	-2.106975	0.175259	C	-5.041512	1.69876	-2.868656
C	3.281887	-2.310145	-0.88373	H	-4.13742	2.299171	-3.09606
C	3.906398	-0.895606	-1.04975	C	-4.633255	0.2404	-3.113557
C	3.06599	-0.003859	-0.115493	H	-3.833478	-0.057508	-2.424477
H	2.813743	0.974571	-0.526409	H	-5.476926	-0.442341	-2.943674
H	-7.009311	1.523467	-3.814542	H	-4.27553	0.082981	-4.139098
H	-6.367554	3.170802	-3.828909	C	-6.090691	2.115706	-3.930164
				H	-5.713372	1.972421	-4.952401

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21. The concentration of LDA, although expressed in units of molarity, refers to the concentration of the monomer unit (normality).

22. Open dimers were first proposed for the isomerization of oxiranes to allylic alcohols by mixed metal bases. See: Mordini, A.; Rayana, E. B.; Margot, C.; Schlosser, M. *Tetrahedron* **1990**, *46*, 2401. For a bibliography of lithium amide open dimers, see Ramírez, A.; Sun, X.; Collum, D. B. *J. Am. Chem. Soc.* **2006**, *128*, 10326 and references cited therein.

23. The rate law provides the stoichiometry of the transition structure relative to that of the reactants: Edwards, J. O.; Greene, E. F.; Ross, J. *J. Chem. Educ.* **1968**, *45*, 381.

24. We define the idealized rate law as that obtained by rounding the observed reaction orders to the nearest rational order.

25. Equations 11 and 30 are approximations, good ones but approximations nonetheless. The non-zero intercept is conveniently addressed with an added constant. We have derived the rigorous and decidedly more complex counterparts (supporting information). They require additional fitting parameters yet offer no additional significant difference nor added insights in comparison to the simple versions.

26. Renny, J. S.; Tomasevich, L. L.; Tallmadge, E. H.; Collum, D. B. *Angew. Chem., Int. Ed.* **2013**, *52*, 11998.

27. The mathematical function described by eq 12 includes no provision for the build up of intermediate mixed aggregate, which is an imperfect approximation under such stoichiometric conditions. The shifting rate-limiting step adds additional imprecisions to the model.

28. Frey, P. A.; Hegeman, A. D. *Enzymatic Reaction Mechanisms*; Oxford University Press: New York, 2007; Chapter 2.

29. ArLi- and LiCl-catalyzed metalations of 2-fluoropyridines showed saturation kinetics that afforded saturation plateaus at very close but not identical rates. We suspect, in retrospect, that the ArLi and LiCl may have been operating on two different parts of the reaction coordinate in that case as well.

30. Selected examples of fully-characterized through-space Li–F interactions: (a) Armstrong, D. R.; Khandelwal, A. H.; Kerr, L. C.; Peasey, S.; Raithby, P. R.; Shields, G. P.; Snaith, R.; Wright, D. S. *Chem. Commun.* **1998**, 1011. (b) Plenio, H.; Diodone, R. *J. Am. Chem. Soc.* **1996**, *118*, 356. (c) Henderson, K. W.; Dorigo, A. E.; Liu, Q.-Y.; Williard, P. G. *J. Am. Chem. Soc.* **1997**, *119*, 11855. (d) Kessar, S. V.; Singh, P.; Singh. K. N.; Bharatam, P. V.; Sharma, A. K.; Lata, S.; Kaur, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 4703. (e) Lee, W.-Y.; Liang, L.-C. *Inorg. Chem.* **2008**, *47*, 3298. (f) Stalke, D.; Klingebiel, U.; Sheldrick, G. M. *Chem. Ber.* **1988**, *121*, 1457. (g) Sini, G.; Tessier, A.; Pytkowicz, J.; Brigaud, T. *Chem. Eur. J.* **2008**, *14*, 3363 and references cited therein.

31. Cyclic tetramers of lithium 2,2,6,6–tetramethylpiperidide were shown to react by dissociation to dimers: Wiedemann, S. H.; Ramírez, A.; Collum, D. B. *J. Am. Chem. Soc.* **2003**, *125*, 15893.

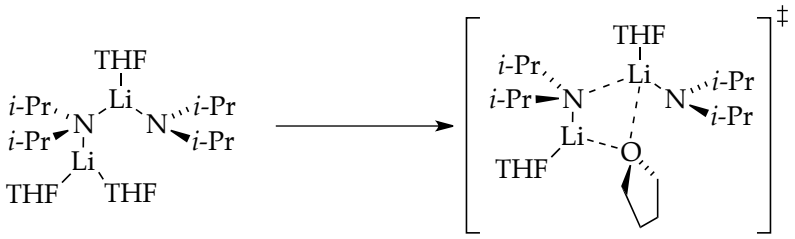
32. Lithium amide tetramers: (a) Cyclic: Lucht, B. L.; Collum, D. B. *J. Am. Chem. Soc.* **1994**, *116*, 7949. (b) Ladders: Armstrong, D. R.; Barr, D.; Clegg, W.; Mulvey, R. E.; Reed, D.; Snaith, R.; Wade, K. *J. Chem. Soc., Chem. Commun.* **1986**, 869. (c) Ladders: Gardiner, M. G.; Raston, C. L. *Inorg. Chem.* **1996**, *35*, 4047. (d) Ladders: Vestergren, M.; Eriksson, J.; Hilmersson, G.; Hakansson, M. *J. Organomet. Chem.* **2003**, *682*, 172. (e) Ladders: Boche, G.; Langlotz, I.; Marsch, M.; Harms, K.; Nudelman, N. E. S. *Angew. Chem.* **1992**, *104*, 1239. (f) Cubic: Gardiner, M. G.; Raston, C. L. *Inorg. Chem.* **1995**, *34*, 4206.

33. The equation as written using adjustable parameter *c* is an approximation. The more rigorous analog described in the supporting information fits the data but provides no net changes in the conclusion despite the marked increase in complexity.

34. Holding the concentration of A_2 constant and varying B_2, for example, will afford a saturation behavior displaying a first-order dependence on B_2 in the limit of low B_2 limit and zeroth order dependence in the limit of a large excess of B_2. (A derivation is provided in supporting information.) This behavior originates purely from the statistical probabilities of reaggregation.

35. Reich, H. J. unpublished.

36. We have asserted that bridging THF ligands may play an important role in deaggregations. Studies of direct dimer-based dissociation supported this notion:



Computations akin to those shown in Scheme 4 using Me_2NLi as a less demanding model uncovered possible transition structures with bridging THF ligands. Analogous attempts using the more hindered *i*-Pr_2NLi fragment, however, provided no support.

37. Representative examples of structurally characterized bridging THF ligands: (a) Pratt, L. M.; Merry, A.; Nguyen, S. C.; Quanb, P.; Thanh, B. T. *Tetrahedron* **2006**, *62*, 10821. (b) Clegg, W.; Liddle, S. T.; Mulvey, R. E.; Robertson, A. *Chem. Commun.* **1999**, 511. (c) Boche, G.; Boie, C.; Bosold, F.; Harms, K.; Marsch, M. *Angew. Chem., Int. Ed.*

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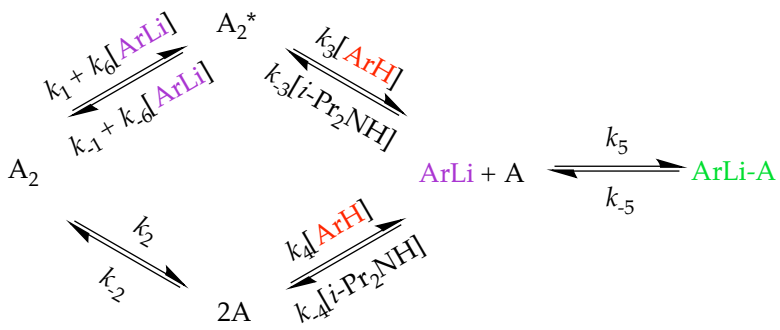
38. We also computationally examined the possible intermediacy of four-rung LDA ladders as key intermediates, possibly dissociating to a monomer and trimer. (For Lithium amide ladders showing open-dimer-like subunits, see Armstrong, D. R.; Barr, D.; Clegg, W.; Hodgson, S. M.; Mulvey, R. E.; Reed, D.; Snaith, R.; Wright, D. S. *J. Am. Chem. Soc.* **1989**, *111*, 4719.) Although minima were found, we obtained no evidence ladders that were on, rather than tangential to, the reaction coordinate en route to monomers.

39. The model used to numerically integrate the curves in Figure 1.1 is as follows (with appropriate color coding):



The role of A_2 (**3**) A_2* (**7**), A (**8**), ArLi-A (**17**), and their interconversions are founded in the structural and rate studies. The model is underdetermined (such as the magnitudes of k_2 and k_{-2}), but not profoundly so.

40. We infer that "reactant" and "transition structure" (often awkwardly referred to as a "transition state structure") have structural connotations whereas "ground state" and "transition state" have energetic connotations: Bauer, S. H.; Wilcox, C. F., Jr. *J. Chem. Educ.* **1995**, *72*, 13-16.

41. (a) Stegelmann, C.; Andreasen, A.; Campbell, C. T. *J. Am. Chem. Soc.* **2009**, *131*, 8077. (b) Maniscalco, S. J.; Tally, J. F.; Fisher, H. F. *Arch. Biochem. Biophys.* **2004**, *425* 165.

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43. We are unaware of a clean example of an upwardly curving second-order dependence giving way to a linear first-order dependence.

44. We have kept a distance from any debate about the role of tunnelling despite routinely observed isotope effects that exceed 40. The use of reaction coordinate diagrams with affiliated zero point energies argue for bringing tunnelling into the discussion. One could, for example, invoke a normal isotope effect that is magnified by an contributions in the transition structure owing to the reluctance of deuteria to tunnel.

Apportioning the ArH–ArD energy gap in this way, however, does not change the qualitative model presented.

45. Snaith and co-workers underscored the merits of R_3NHX salts as precursors to anhydrous LiX salts. See: Barr, D.; Snaith, R.; Wright, D. S.; Mulvey, R. E.; Wade, K. *J. Am. Chem. Soc.* **1987**, *109*, 7891. Also see: Hall, P. L.; Gilchrist, J. H.; Collum, D. B. *J. Am. Chem. Soc.* **1991**, *113*, 9571.

46. Galiano-Roth, A. S.; Kim, Y.-J.; Gilchrist, J. H.; Harrison, A. T.; Fuller, D. J.; Collum, D. B. *J. Am. Chem. Soc.* **1991**, *113*, 5053.

47. (a) Marck, W.; Huisgen, R. *Chem. Ber.* **1960**, *93*, 608. (b) Gaudemar-Bardone, F.; Gaudemar M. *Synthesis* **1979**, 463. (c) Reetz, M. T.; Maier, W. F. *Liebigs Ann. Chem.* **1980**, 1471. (d) Williard, P. G.; Carpenter, G. B. *J. Am. Chem. Soc.* **1986**, *108*, 462. Williard, P. G.; Salvino, J. M. *J. Org. Chem.* **1993**, *58*, 1. (e) Morrison, R. C.; Hall, R. W.; Rathman, T. L. Stable Lithium Diisopropylamide and Method of Preparation. U.S. Patent 4,595,779, June 17, 1986.

48. Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879.

49. For an explanation of Levenberg-Marquardt nonlinear least-squares optimization, see: Press, W. H.; Flannery, B. P.; Teukolsky, S. A.; Vetterling, V. T. *Numerical Recipes in C*; Cambridge University Press: London, 1988; Chapter 14.4.

50. Brown, P. N.; Byrne, G. D.; Hindmarsh, A. C. *J. Sci. Stat. Comput.* **1989**, *10*, 1038.

CHAPTER 2

MECHANISM OF LITHIUM DIISOPROPYLAMIDE-MEDIATED ORTHOLITHIATION OF 1,4-BIS(TRIFLUOROMETHYL)BENZENE UNDER NONEQUILIBRIUM CONDITIONS: CONDITION-DEPENDENT RATE LIMITATION AND LITHIUM CHLORIDE-CATALYZED INHIBITION

Mechanism of Lithium Diisopropylamide-Mediated Ortholithiation of 1,4-bis(Trifluoromethyl)benzene under Nonequilibrium Conditions: Condition-Dependent Rate Limitation and Lithium Chloride-Catalyzed Inhibition

Abstract

Lithiation of 1,4-bis(trifluoromethyl)benzene with lithium diisopropylamide (LDA) in tetrahydrofuran at –78 °C occurs under conditions in which the rates of aggregate exchanges are comparable to the rates of metalation. Under such nonequilibrium conditions, a substantial number of barriers compete to be rate limiting, making the reaction sensitive to trace impurities (LiCl), reactant concentrations, and isotopic substitution. Rate studies using the perdeuterated arene reveal odd effects of LiCl, including catalyzed rate acceleration at lower temperature and catalyzed rate inhibition at higher temperatures. The catalytic effects are accompanied by corresponding changes in the rate law. A kinetic model captures the critical features of the LiCl catalysis.

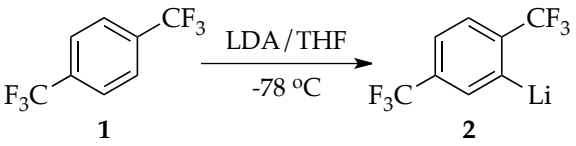
Introduction

Decades of studying lithium diisopropylamide (LDA)-mediated metalations have revealed that the large, rapidly equilibrating ensemble of transiently accessible aggregation and solvation states quite rationally leads to an equally diverse array of mechanisms.[1] The dominant pathways depend on substrate, solvent, temperature, and reagent concentrations. The rates are dictated by the barrier height of the proton transfer for each substrate–solvent combination.

We only recently began studying metalations carried out using LDA/tetrahydrofuran (THF)/–78 °C—one of the most commonly chosen reagent, solvent, and temperature combinations in all of organic synthesis.[2,3] Although a fear of poor temperature control proved misplaced, a far more challenging problem lurked beneath the surface. We discovered that under these conditions, the activation barriers for the large number of aggregate and solvent exchanges are remarkably similar and comparable to those for lithiation of the substrates, leading to a chaotic mechanistic scenario.[4] Reaction coordinates are often dictated by the barriers of aggregate exchanges rather than the barriers in the metalation step. The resulting paradoxical behaviors include dependencies of rate on the choice of substrate but not necessarily on substrate concentration. Simple deuteration to measure a kinetic isotope effect can cause profound changes in the mechanism and accompanying rate law.[2d,e] Autocatalysis and catalysis by trace impurities—parts per million of LiCl—are rampant owing to deep-seated changes accelerated deaggregation steps. The *source* of the LDA (commercial versus *n*-BuLi-derived) can be the single most important variable, imparting up to 100-fold differences in rates.

We continued these studies by examining the ortholithiation of 1,4-bis(trifluoromethyl)benzene (**1**, eq 1)[5] in which rate-limiting dimer- and tetramer-based aggregation events dominate. This metalation is an outlier in the series in that autocatalysis by aryllithium **2** is *not* important. The most striking observation is that traces of LiCl can accelerate or inhibit the metalation, depending on subtle changes in conditions. The seemingly paradoxical notion of catalyzed inhibition is a consequence of nonequilibrium kinetics.[6] Although this paper ostensibly describes the study of an ortholithiation,[7] it is primarily about using ortholithiation as a tool to investigate the underlying dynamics of LDA aggregate and solvent exchanges under nonequilibrium

conditions.[8] The nonspecialists will find a synopsis at the outset of the discussion section; cursory perusal of the results is adequate.

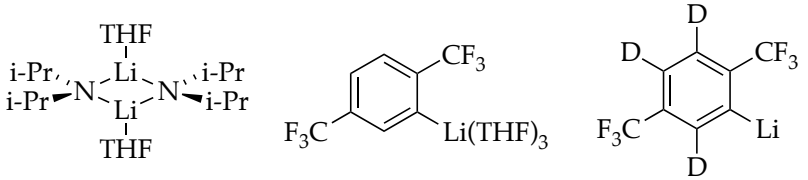


1 **2** (1)

Results

The results are presented sequentially in three categories: structural studies that are foundational for understanding the metalation, rate studies of uncatalyzed metalations, and rate studies of catalyzed metalations. The markedly different metalations of arene **1** and its perdeuterated analog demanded complete rate studies for each; these studies are discussed within their own subsections. To facilitate the complex presentation, we introduce the following shorthand: A = an LDA subunit, S = THF, ArH = arene **1**, ArD = **1-*d*$_4$**, and ArLi = aryllithium **2** or its perdeuterated analog **2-*d*$_3$**.

Solution structures. Studies of [^{6}Li,^{15}N]LDA using ^{6}Li and ^{15}N NMR spectroscopies have revealed exclusively disolvated dimer **3** in THF and THF/hydrocarbon mixtures.[2b,9] The resulting aryllithium **2** is characterized as trisolvated monomer **2a** as follows.



3 **2a** **2-*d*$_3$**

The ^{19}F NMR spectrum of aryllithium **2** displays a pair of singlets (1:1).[10,11] The ^{13}C NMR spectrum of **2** shows a multiplet resulting from a composite of one-bond ^{6}Li–^{13}C coupling[12] and three-bond ^{19}F–^{13}C coupling. Removing the requisite ^{1}H decoupling using perdeuterated **1-*d*$_4$** frees up the second probe channel for ^{19}F decoupling, revealing a 1:1:1 triplet ($J_{Li–C}$ = 13.2 Hz) consistent with monomeric **2** (Figure 2.1). Generating **2** with excess [^{6}Li,^{15}N]LDA reveals no additional species and no ^{6}Li–^{15}N splitting in the resonance corresponding to **2**, confirming the absence of detectable mixed aggregates that are often observed in LDA–ArLi mixtures.[2a]

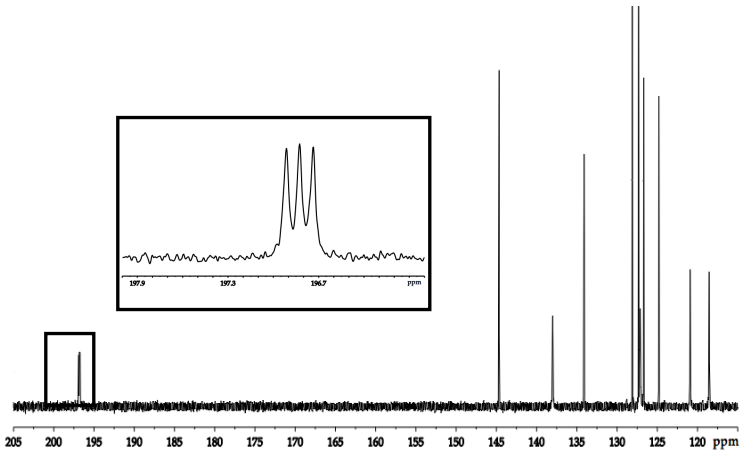
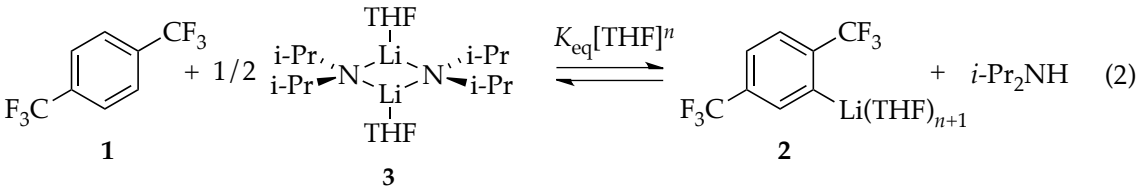


Figure 2.1. $^{13}C\{^{19}F\}$ NMR spectrum of **2-*d*$_3$** generated from ArD (0.15 M) with [^{6}Li]LDA (0.30 M) in neat (12.2 M) THF-d_8 at –100 °C. Resonances of ArD remaining at equilibrium are noted. **2-*d*$_3$**: δ 196.8 (t, $^{1}J_{C–Li}$ = 13.2 Hz), 144.7 (s), 138.0 (s), 128.1 (s), 127.1 (s), 126.7 (s), 120.9 (s), 118.6 (s). ArD: δ 134.1 (s), 127.3 (s), 124.8 (s).

Solvation numbers of **2** were determined using two methods:

(1) Metalation with added *i*-Pr_2NH and monitoring with ^{19}F NMR spectroscopy (eq 2) revealed a THF-concentration-dependent equilibrium population of **1** and **2** (Figure 2.2). Least squares fit to eq 3 afforded a solvation number (n + 1) of 3.1 ± 0.3.



$$y = [\mathrm{ArLiS}_{n+1}][i\text{-}\mathrm{Pr}_2\mathrm{NH}]/\{[\mathrm{ArH}][\mathrm{A}_2\mathrm{S}_2]^{1/2}\} = K_{\mathrm{eq}}[\mathrm{S}]^n \qquad (3)$$

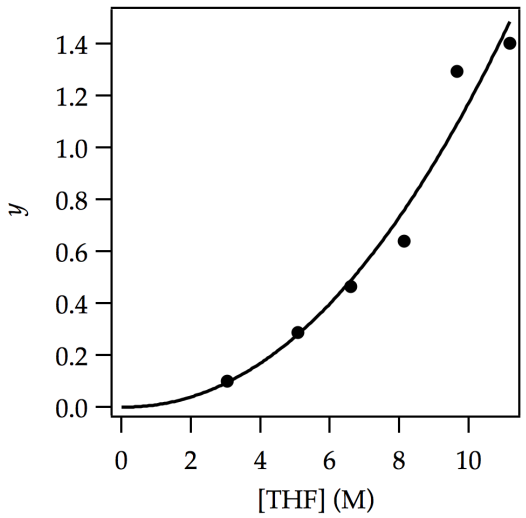
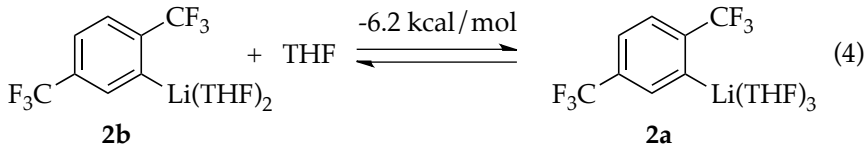


Figure 2.2. Plot of $[\mathrm{ArLiS}_{n+1}][i\text{-}\mathrm{Pr}_2\mathrm{NH}]/\{[\mathrm{ArH}][\mathrm{A}_2\mathrm{S}_2]^{1/2}\}$ (y, eq 3) vs THF concentration for the ortholithiation of ArH (0.0050 M) with LDA (0.10 M) containing added diisopropylamine (0.025 M) at –78 °C measured with ^{19}F NMR spectroscopy. The curve depicts an unweighted least-squares fit to $y = K_{\mathrm{eq}}[\mathrm{THF}]^n$. [$K_{\mathrm{eq}} = (9 \pm 7) \times 10^{-3}$, $n = (2.1 \pm 0.3)$].

(2) Density functional theory (DFT) computations at the B3LYP/6–31G(d) level with single-point calculations at the MP2 level of theory[13] showed trisolvate **2a** to be 6.2 kcal/mol more stable than disolvate **2b** (eq 4). No minimum for the tetrasolvate was found.[14]



2b **2a** (4)

Rate studies: general protocol. Lithiations of ArH and ArD using analytically pure LDA[9] were followed by monitoring the loss of arene using in situ IR spectroscopy (1323 cm^{-1})[15] or ^{19}F NMR spectroscopy (–65.7 ppm). Metalations under most conditions, whether ostensibly pseudo-first-order (low substrate concentration) or not, fail to display first-order decays (Figure 2.3) owing to partially or completely rate-limiting deaggregations. Accordingly, initial rates were extracted from the first derivative (slope) of a polynomial fit to data within 5% conversion.[2c,16] Reaction orders were obtained by independently varying the concentrations of ArH, LDA, and THF and monitoring the initial rates. ArH and ArD metalations are mechanistically different owing to the retention of zero-point energy differences in rate-limiting transition states involving deaggregations and even metalations. We have expounded on this difference[2e] and return to it briefly in the discussion. ArH and ArD demanded independently determined rate laws.

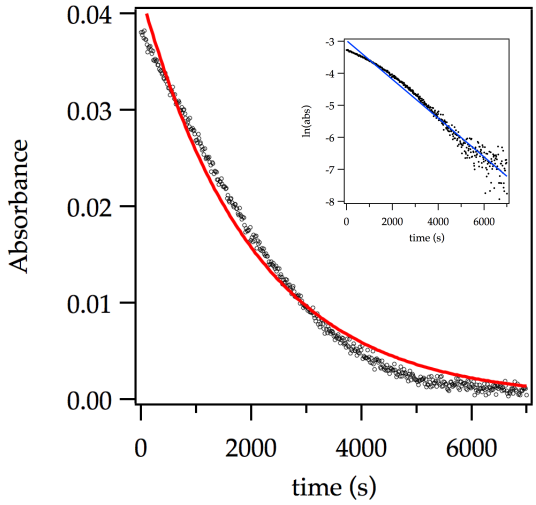


Figure 2.3. Representative plot showing poor exponential fit (red curve) to the decay of ArH (0.0050 M) with LDA (0.10 M) in THF (12.2 M) at –78 °C monitored with IR spectroscopy. The natural log plot (inset) shows the deviation from a linear first-order decay.

Autocatalysis. We always begin detailed rate studies by addressing the role of autocatalysis,[17] which has been prevalent in previous studies of LDA-mediated metalations under nonequilibrium conditions.[2] Using a standard protocol in which a second aliquot of substrate is added and monitored at the completion of a decay, we found that the first and second aliquots of ArH (or ArD) afforded indistinguishable rates under a variety of conditions. Thus, autocatalysis is *not* important.

Uncatalyzed ortholithiation: ArD. We introduce the detailed rate studies of ArD somewhat unconventionally with investigations of the deuterated substrate because the results, although limited in scope, are simple compared with those of ArH. The results are interpreted in the context of the mechanism and rate law described by eqs 5-7.[18]

$$-d[\mathrm{ArD}]/d\mathrm{t} = k_1k_2[\mathrm{ArD}][\mathrm{A_2S_2}][\mathrm{S}]/(k_{-1} + k_2[\mathrm{ArD}]) \quad (5)$$

$$-d[\mathrm{ArD}]/d\mathrm{t} = (k_1k_2/k_{-1})[\mathrm{ArD}][\mathrm{A_2S_2}][\mathrm{S}] \quad (6)$$

$$A_2S_2 \underset{k_{-1}}{\overset{k_1[S]}{\rightleftharpoons}} [A_2S_3] \xrightarrow{k_2[ArD]} ArLi \qquad (7)$$

Plotting initial rates versus ArD concentration revealed saturation kinetics (Figure 2.4) consistent with a shift from rate-limiting metalation at low ArD concentration (eq 5; $k_{-1} >> k_2[ArD]$) to rate-limiting deaggregation at high ArD concentration ($k_{-1} << k_2[ArD]$).

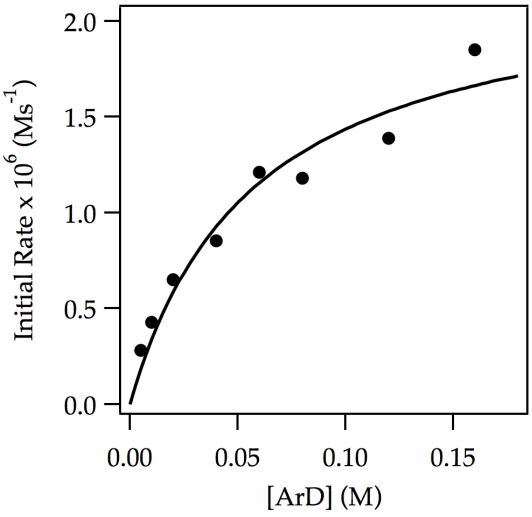


Figure 2.4. Plot of initial rate vs ArD concentration for the ortholithiation of ArD with LDA (0.10 M) in THF (12.2 M) at –78 °C measured with IR spectroscopy. The curve depicts an unweighted least-squares fit to a first-order saturation function: $y = (a[ArD])/(1 + b[ArD])$. [$a = (3.9 \pm 0.8) \times 10^{-5}$, $b = (17 \pm 5)$].

Monitoring the initial rates versus the LDA and THF concentrations[19] in the limit of low ArD concentration revealed first-order dependencies in each (Figures 2.5 and 2.6). Because the trapping of a fleeting A_2S_3 intermediate is slow at these relatively low ArD concentrations ($k_{-1} >> k_2[ArD]$), the generalized rate law in eq 5 reduces to the

simpler form in eq 6. Computational studies showed that the conventional open-dimer-based **4** is more stable than the surprisingly viable 10-membered analog **5** (eq 8).[20]

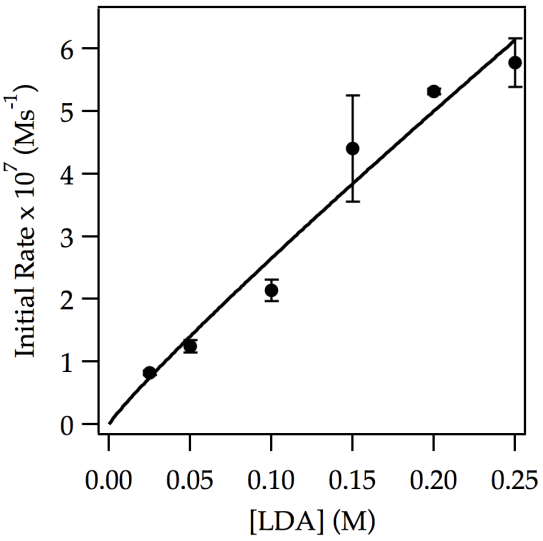


Figure 2.5. Plot of initial rate vs LDA concentration in THF (12.2 M) for the ortholithiation of ArD (0.0050 M) at –78 °C measured with IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\mathrm{LDA}]^n$. [$a = (2.2 \pm 0.5) \times 10^{-6}$, $n = 0.9 \pm 0.1$].

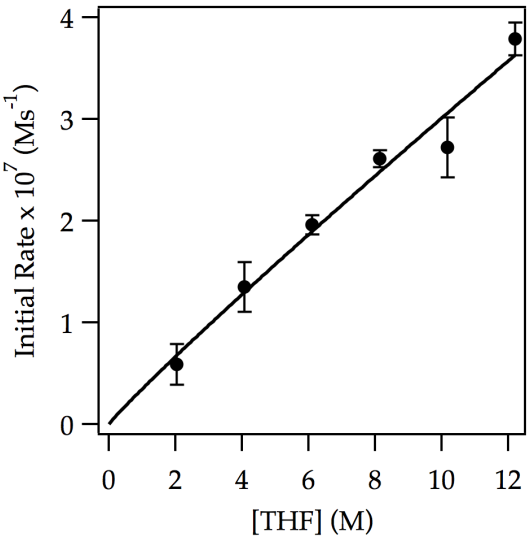
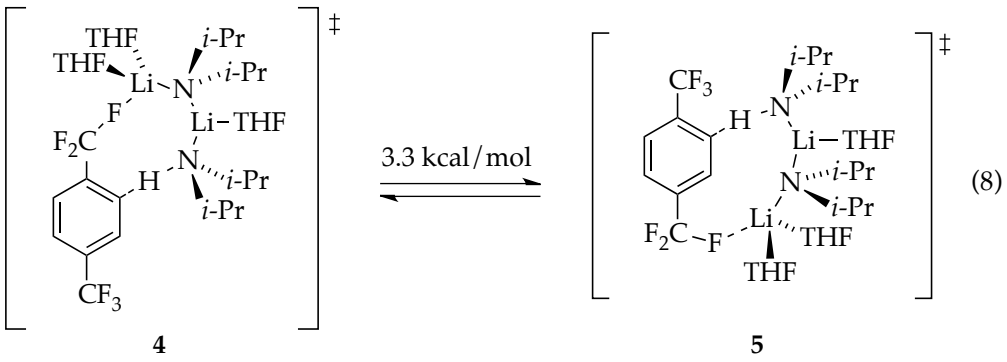


Figure 2.6. Plot of initial rate vs THF concentration in hexanes for the ortholithiation of ArD (0.0050 M) by LDA (0.10 M) at –78 °C measured with IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\mathrm{THF}]^n$. [$a = (3.5 \pm 0.8) \times 10^{-8}$, $n = (0.94 \pm 0.09)$].



The zeroth-order dependence on ArD at high ArD concentration stems from the efficient trapping of a fleeting intermediate ($k_{-1} << k_2[\mathrm{ArD}]$), precluding its return to starting A_2S_2 dimer **3**.[2] Although the domination of a transition structure of stoichiometry $[A_2S_3]^‡$ on the saturation plateau seems rational, it is presumptuous; previous studies of LDA-mediated metalations under nonequilibrium conditions have revealed that deuteration can markedly change the reaction mechanism and affiliated

rate law.[2c,e] Normally we would determine the rate law at high ArD concentration to confirm the stoichiometry of the rate-limiting aggregation event and complete the story, but the high concentrations of ArD required to effect efficient trapping presented technical challenges.[21] Nevertheless, this example provided a brief introduction to nonequilibrium kinetics and the more complex ArH metalations.

Uncatalyzed ortholithiation: ArH. Metalations of ArH (0.0050 M), ostensibly under pseudo-first-order conditions, deviate from clean exponential decays akin to that shown in Figure 2.3. Metalations at high LDA and low THF concentrations afford a noisy zeroth-order dependence on arene concentration (Figure 2.7). By contrast, metalation at low LDA and high THF concentrations display an ArH dependence manifesting clear saturation behavior (Figure 2.8) consistent with rate-limiting ortholithiation at low ArH concentration and rate-limiting deaggregation at high ArH concentration. The isotope effect measured from two independent metalations of ArH and ArD is large at low arene concentrations ($k_H/k_D = 14$) while approaching unity at high arene concentrations (consistent with a rate-limiting deaggregation.) The competitive isotope measured by competing ArH and ArD approximates 20 at all arene concentrations.

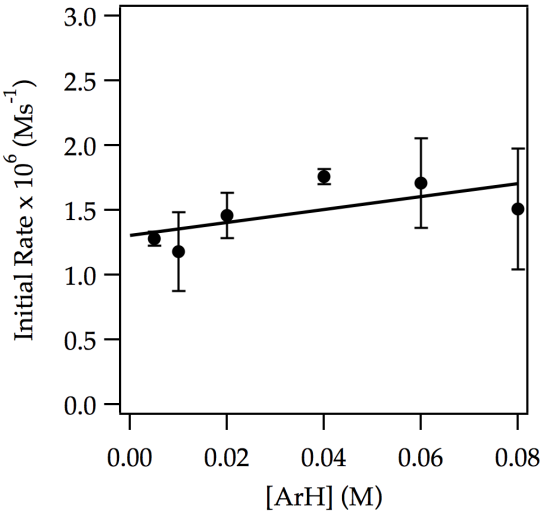


Figure 2.7. Plot of initial rate vs initial ArH concentration for the ortholithiation of ArH with LDA (0.20 M) in THF (3.05 M) at –78 °C measured with IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\mathrm{ArH}] + b$. [$a = (5 \pm 3) \times 10^{-6}$, $b = (1.3 \pm 0.1) \times 10^{-6}$].

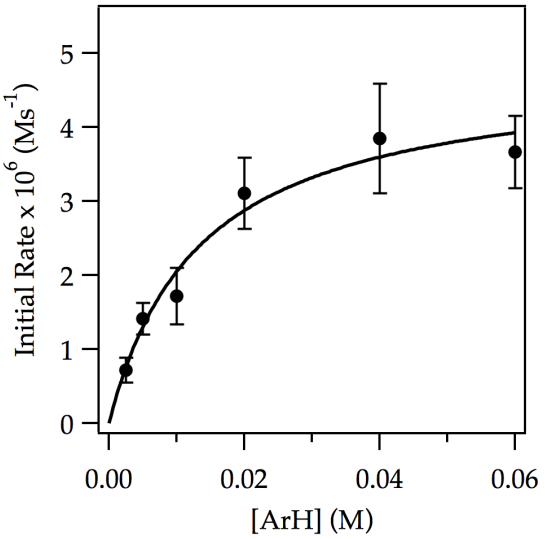


Figure 2.8. Plot of initial rate vs initial ArH concentration for the ortholithiation of ArH with LDA (0.050 M) in THF (12.2 M) at –78 °C measured with IR spectroscopy. The curve depicts an unweighted least-squares fit to a first-order saturation function: $y = (a[\mathrm{ArH}])/(1 + b[\mathrm{ArH}])$. [$a = (3.6 \pm 0.7) \times 10^{-4}$, $b = (74 \pm 20)$].

The saturation showed that we were probing the cusp of a shifting rate-limiting step. Detailed rate studies, however, revealed even greater complexity in which dimer- and tetramer-based pathways compete for dominance.

We now consider both low ArH concentrations—the left sides of Figures 2.7 and 2.8—and high ArH concentrations—the plateau in Figure 2.8—and explore the roles of THF and LDA.

(1) Low ArH concentrations. In neat THF, a first-order LDA dependence (Figure 2.9, curve A) implicates a dimer-based mechanism. At low THF concentration (3.05 M), a markedly elevated LDA dependence is consistent with a tetramer-based mechanism (Figure 2.9, curve B). Similarly, at high LDA concentration (0.20 M) the THF order is reduced to unity (Figure 2.10, curve A), whereas at low LDA concentration (0.050 M), the THF order approaches 2 (Figure 2.10, curve B).

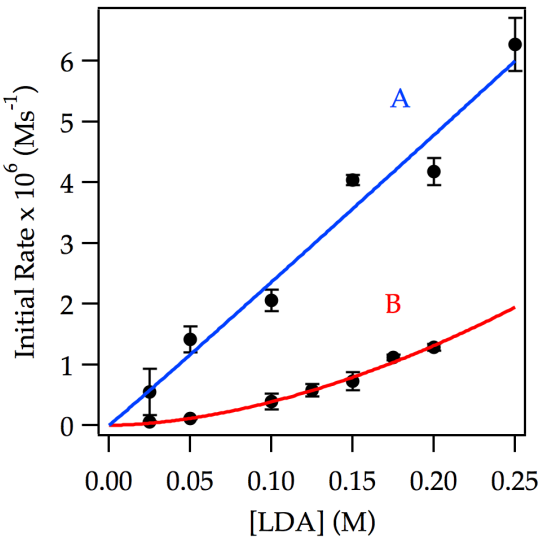


Figure 2.9. Plot of initial rate vs LDA concentration in 12.2 M THF (curve A) and 3.05 M THF (curve B) for the ortholithiation of ArH (0.0050 M) at –78 °C measured with IR spectroscopy. The curves depict unweighted least-squares fits to $y = a[\mathrm{LDA}]^n$. Curve A: [$a = (2.5 \pm 0.6) \times 10^{-5}$, $n = (1.0 \pm 0.1)$]. Curve B: [$a = (2.3 \pm 0.5) \times 10^{-5}$, $n = (1.8 \pm 0.1)$].

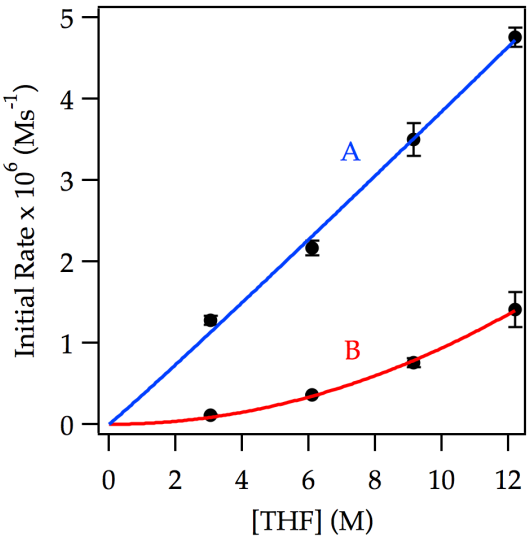


Figure 2.10. Plot of initial rate vs THF concentration in hexanes for the ortholithiation of ArH (0.0050 M) by 0.20 M LDA (curve A) and 0.050 M LDA (curve B) at –78 °C measured with IR spectroscopy. The curves depict unweighted least-squares fits to $y = a[\text{THF}]^n$. Curve A: [$a = (3.6 \pm 0.6) \times 10^{-7}$, $n = (1.03 \pm 0.07)$]. Curve B: [$a = (9 \pm 2) \times 10^{-9}$, $n = (2.0 \pm 0.1)$].

(2) High ArH concentration. Conditions under which the ArH concentration is sufficiently high to establish the zeroth-order plateau in Figure 2.8 afford a first-order THF dependence (Figure 2.11). The LDA dependence also appears to follow a first-order dependence up to 0.20 M that gives way to what is unscientifically referred to as a "glitch" (Figure 2.12). No number of replications brought adequate reproducibility. Some points measured at 0.20 and 0.25 M LDA fell within normal error on the curve, and others fell far below. The erratic behavior resembled a phase change (a random nucleation), but we found no visual evidence for this hypothesis nor have we observed it in other rate studies. We are unable to determine why it occurs with this very specific set of otherwise quite ordinary conditions.

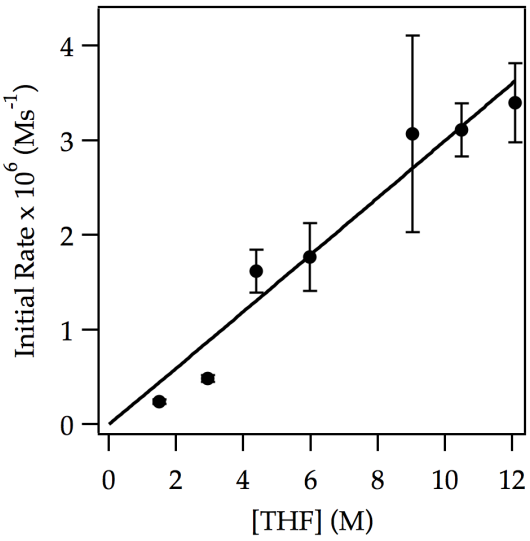


Figure 2.11. Plot of initial rate vs THF concentration in hexanes for the ortholithiation of ArH (0.060 M) by LDA (0.20 M) at –78 °C measured with IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\text{THF}]^n$. [$a = (3 \pm 1) \times 10^{-7}$, $n = (1.0 \pm 0.1)$].

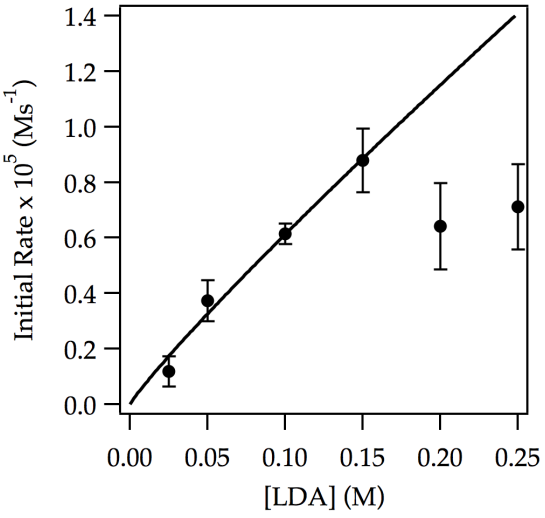


Figure 2.12. Plot of initial rate vs LDA concentration in THF (12.2 M) for the ortholithiation of ArH (0.060 M) at –78 °C measured with IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\text{LDA}]^n$. [$a = (4 \pm 1) \times 10^{-5}$, $n = (0.9 \pm 0.1)$]. Large deviations at 0.20 and 0.25 M LDA were recurring and not understood. These two points are excluded from the fit.

Altogether (excluding the glitch), the rate data afforded the idealized rate law[22] described by eq 9 and are consistent with the combination of dimer- and tetramer-based

mechanisms depicted collectively in eqs 9–17. At low LDA concentration, the dimer-based mechanism in eqs 10 and 11 dominates, reducing the rate law in eq 9 to the simpler form in eq 12, which retains the mathematical form corresponding to the saturation kinetics shown in Figure 2.8. The rate law further reduces to eqs 13 and 14 at low and high ArH concentrations, respectively. The tetramer-based pathway (eqs 15 and 16) shows only a zeroth-order ArH dependence (eq 17) owing to the high efficiency of subsequent steps including the proton transfer.

$$-d[\mathrm{ArH}]/dt = \underbrace{k_1k_2[\mathrm{A_2S_2}][\mathrm{S}]^2[\mathrm{ArH}]/\{k_{-1}+k_2[\mathrm{ArH}][\mathrm{S}]\}}_{\text{dimer based}} + \underbrace{k_3[\mathrm{A_2S_2}]^2[\mathrm{S}]}_{\text{tetramer based}} \quad (9)$$

Dimer-based mechanism

$$\underset{\mathbf{3}}{\mathrm{A_2S_2}} + \mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{A_2S_3}] \quad (10)$$

$$[\mathrm{A_2S_3}] + \mathrm{S} \xrightarrow{k_2[\mathrm{ArH}]} \mathrm{ArLi} \quad (11)$$

$$-d[\mathrm{ArH}]/dt = k_1k_2[\mathrm{A_2S_2}][\mathrm{S}]^2[\mathrm{ArH}]/\{k_{-1}+k_2[\mathrm{ArH}][\mathrm{S}]\} \quad (12)$$

$$-d[\mathrm{ArH}]/dt = (k_1k_2/k_{-1})[\mathrm{A_2S_2}][\mathrm{S}]^2[\mathrm{ArH}] \quad (13)$$

$$-d[\mathrm{ArH}]/dt = k_1[\mathrm{A_2S_2}][\mathrm{S}] \quad (14)$$

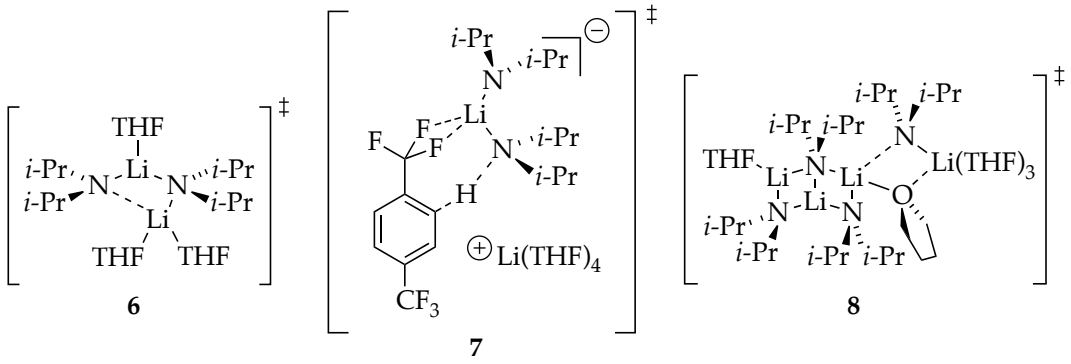
Tetramer-based mechanism

$$2\underset{\mathbf{3}}{A_2S_2} + S \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [A_4S_5] \tag{15}$$

$$[A_4S_5] \xrightarrow[fast]{k_4[ArH]} ArLi \tag{16}$$

$$-d[ArH]/dt = k_3[A_2S_2]^2[S] \tag{17}$$

Trisolvated dimer-based rate-limiting steps can be attributed to one of several computationally viable transition structures; open dimer **6** is emblematic.[20] The tetrasolvated dimers have occasionally been implicated[1,2,23] and attributed to triple ions.[24] Although triple ion computations are of no quantitative value because of their ionic bonds,[25] the cationic and anionic fragments of transition structure **7** are both computationally viable. The $[A_4S_5]^‡$ aggregation event is the most computationally intractable. We have successfully computed tetramer-based aggregation events (including some based on LDA ladder structures[2e]), but a pentasolvate is elusive. We offer transition structure **8** with a ladder motif,[26] a high per-lithium coordination number,[27] and a bridging THF[4,28] simply to provoke thought. Such tetramers have been implicated in LDA subunit exchanges[2e] and their possible intermediacy en route to monomers have been noted.[2d,e]



LiCl-catalysis: ArH. Traces of LiCl elicit marked rate accelerations accompanied by an upwardly curving decay (Figure 2.13). This dramatic effect has been traced to monomer-based lithiations in previous studies without exception.[2] Indeed, first-order decays were observed at >1.0 mol% LiCl. Plotting initial rates versus LiCl concentration shows first-order saturation behavior (Figure 2.14) consistent with shifting the rate-limiting step from LDA deaggregation to ArH-dependent lithiation. Monitoring initial rates at the saturation limit in Figure 2.14 (1.0 mol % LiCl) revealed a half-order dependence on LDA (Figure 2.15) and first-order dependence on ArH (Figure 2.16). The second-order THF dependence shows a modest medium effect (Figure 2.17).[29] The idealized rate law (eq 18) is consistent with a trisolvated-monomer-based proton transfer described by eqs 19 and 20. Both $[AS_2(ArH)]^‡$ and $[AS_3(ArH)]^‡$ stoichiometries have been noted in ortholithiations.[2]

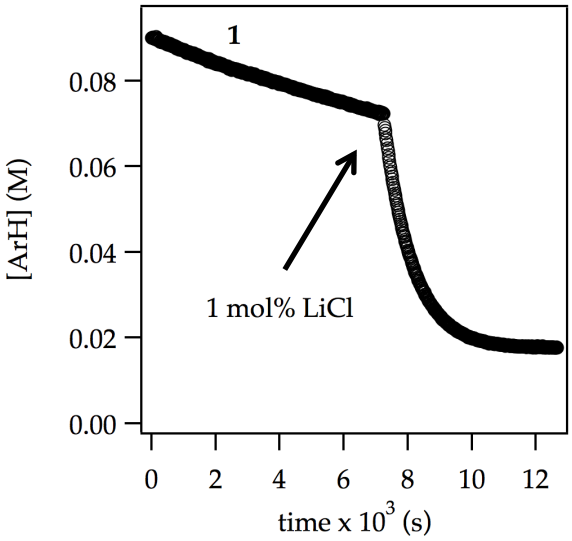


Figure 2.13. Ortholithiation of ArH (0.090 M) with LDA (0.10 M) in 12.2 M THF at –78 °C monitored using IR spectroscopy (1323 cm^{-1}) with injection of 1.0 mol % LiCl.

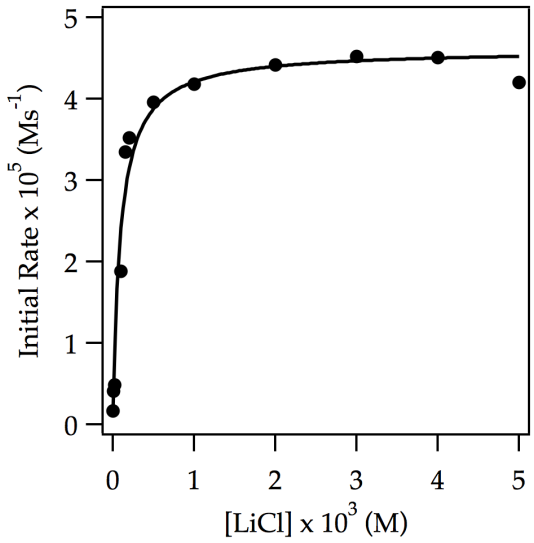


Figure 2.14. Plot of initial rate vs LiCl concentration for the ortholithiation of ArH (0.050 M) by 0.10 M LDA in 12.2 M THF at –78 °C measured with IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = (a[\text{LiCl}])/(1 + b[\text{LiCl}]) + c$. [$a = (4.5 \pm 0.8) \times 10^{-1}$, $b = (1.0 \pm 0.20) \times 10^{4}$, $c = (1.70) \times 10^{-6}$].

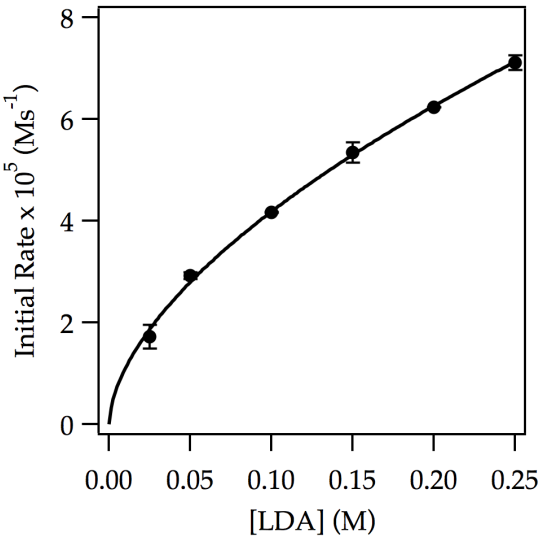


Figure 2.15. Plot of initial rate vs LDA concentration in THF (12.2 M) for the ortholithiation of ArH (0.050 M) with 2.0 mol% LiCl at –78 °C measured with IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\text{LDA}]^n$. [a = (1.60 ± 0.05) x 10^{-4}, n = 0.58 ± 0.02].

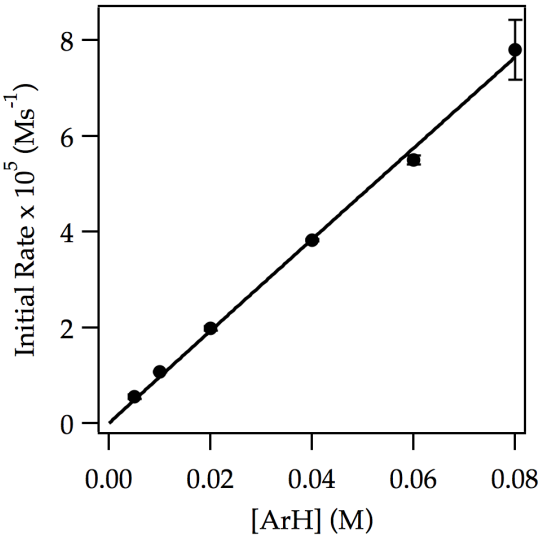


Figure 2.16. Plot of initial rate vs initial ArH concentration for the ortholithiation with LDA (0.10 M) in THF (12.2 M) with 1.0 mol% LiCl at –78 °C measured with IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\text{ArH}]^n$. [a = (9 ± 1) x 10^{-4}, n = (0.99 ± 0.04)].

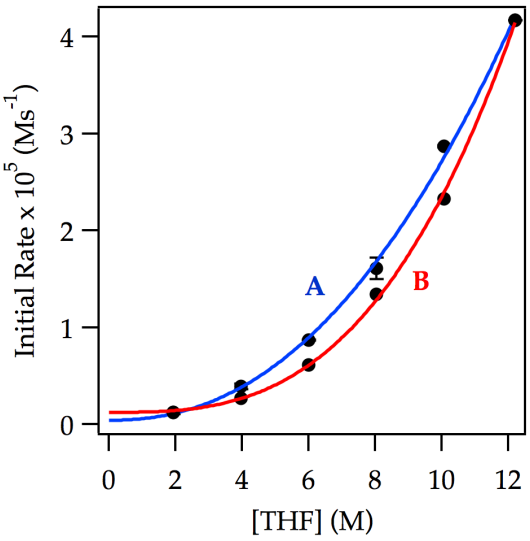


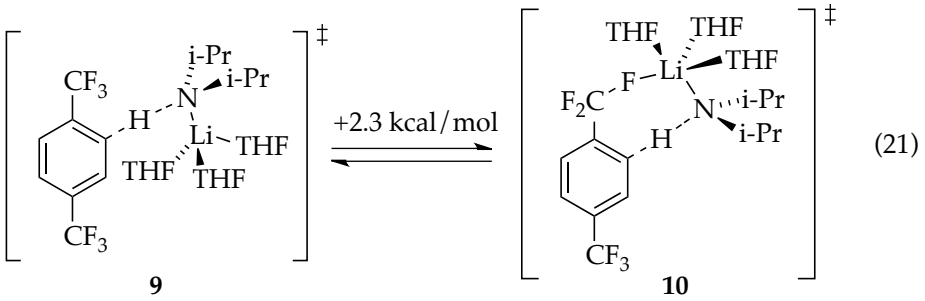
Figure 2.17. Plot of initial rate vs THF concentration with cosolvents Et_2O (curve A) and hexanes (curve B) for the ortholithiation of ArH (0.050 M) by LDA (0.10 M) with 1.0 mol% LiCl at –78 °C measured with IR spectroscopy. The curves depict unweighted least-squares fits to $y = a[\text{THF}]^n + b$. Curve A: $a = (1.8 \pm 0.3) \times 10^{-7}$, $n = 2.18 \pm 0.08$, $b = (0.0 \pm 0.1) \times 10^{-7}$. Curve B: $a = (2.3 \pm 0.7) \times 10^{-8}$, $n = 3.0 \pm 0.1$, $b = (1.2 \pm 0.4) \times 10^{-6}$.

$$-d[\text{ArH}]/dt = k_2 K_{eq}[A_2S_2]^{1/2}[S]^2[\text{ArH}] \quad (18)$$

$$1/2\ A_2S_2 + 2S \overset{K_{eq}}{\rightleftharpoons} AS_3^* \quad (19)$$

$$AS_3^* + \text{ArH} \xrightarrow{k_2} \text{ArLi} \quad (20)$$

Computational studies of trisolvated monomer-based metalation afforded **9** and **10** as the two most plausible transition structures (eq 21). Although Li–F are crystallographically[30] well-precedented and can dominate computational studies of ortholithiation of fluorobenzenes,[31] trisolvation state and Li–F interaction are not synergistic in this case.



9 **10** (21)

LiCl catalysis: ArD. As noted for ArH and other substrates explored to date, traces of LiCl have never failed to accelerate metalations, and the acceleration has invariably been traded to LiCl-catalyzed deaggregation to monomer. LiCl has no effect on the metalation rate of ArD in neat THF at –78 °C, however (Figure 2.18). Of note, the point to the far left in Figure 2.18 was recorded *without* added LiCl. Given that the uncatalyzed metalation of ArD occurs via dimer-based metalation as described by eqs 6 and 7, we wondered whether the monomer played any role whatsoever. The answer proved to be definitive and baffling. Rate studies revealed a first order in ArD (Figure 2.19), half order in LDA (Figure 2.20), and second order in THF (Figure 2.21), consistent with the ArD analog of the rate law in eq 18 and the generic monomer-based mechanism described by eqs 19 and 20. *Despite no detectable change in rate, LiCl catalysis diverts a dimer-dominated metalation of ArD to a monomer-dominated metalation.*

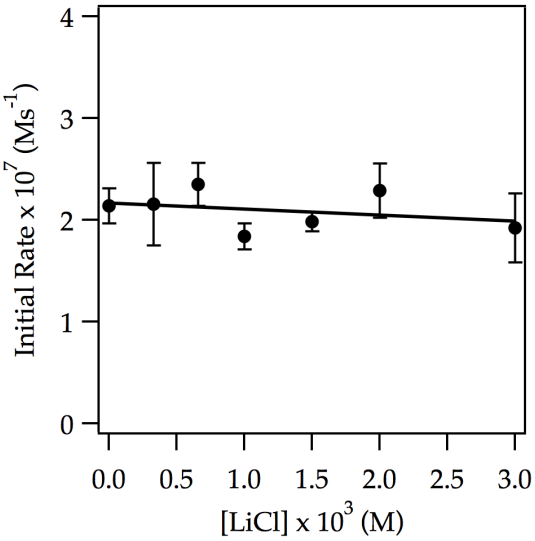


Figure 2.18. Plot of initial rate vs LiCl concentration for the ortholithiation of ArD (0.0050 M) by 0.10 M LDA in 12.2 M THF at –78 °C measured with IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\text{LiCl}] + b$. [$a = (6 \pm 8) \times 10^{-9}$, $b = (2.2 \pm 0.1) \times 10^{-7}$].

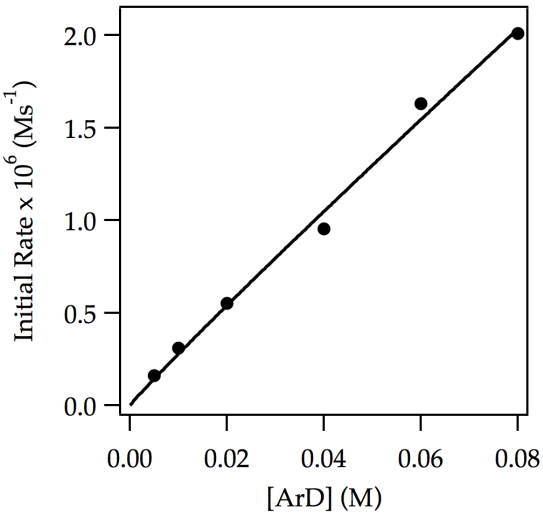


Figure 2.19. Plot of initial rate vs ArD concentration for the ortholithiation of ArD (0.0050 M) by LDA (0.10 M) with 2.0 mol% LiCl at –78 °C measured with IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\text{ArD}_4]^n$. [$a = (2.3 \pm 0.4) \times 10^{-5}$, $n = (0.96 \pm 0.06)$].

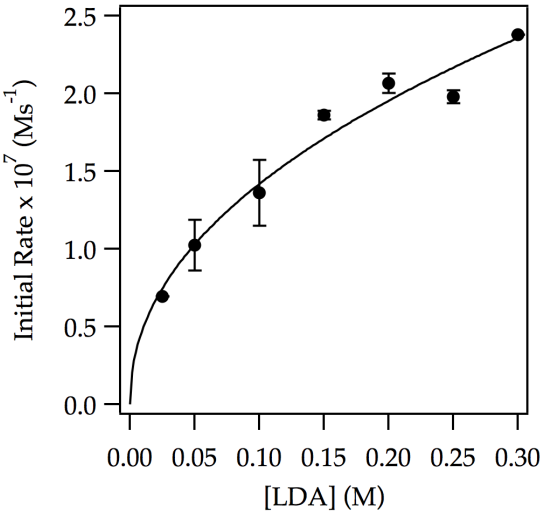


Figure 2.20. Plot of initial rate vs LDA concentration in THF (12.2 M) for the ortholithiation of ArD (0.0050 M) with 2.0 mol% LiCl at –78 °C measured with IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\text{LDA}]^n$. [a = (4.1 ± 0.4) x 10^{-7}, n = 0.46 ± 0.05].

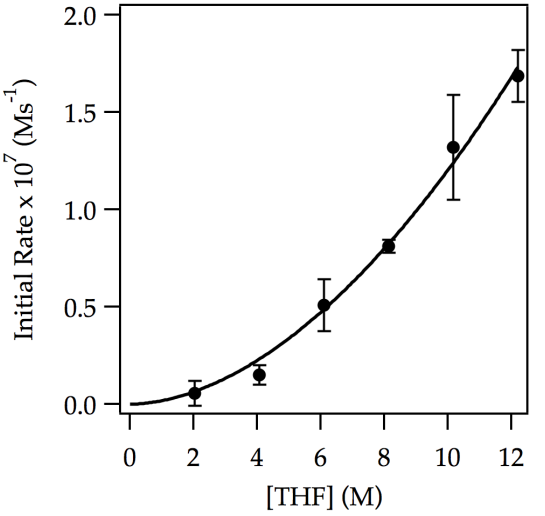


Figure 2.21. Plot of initial rate vs THF concentration in Et_2O for the ortholithiation of ArD (0.0050 M) by LDA (0.10 M) with 2.0 mol% LiCl at –78 °C measured with IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\text{THF}]^n$. [a = (1.8 ± 0.5) x 10^{-9}, n = (1.8 ± 0.1)].

The story gets even more strange. For reasons that are not germane, we examined the catalysis at –42 °C and found that traces of LiCl *inhibit the metalation of ArD* (Figure 2.22). This inhibition is unlike enzyme inhibition: it is *catalytic* in inhibitor.[6] Rate studies in the absence of catalyst showed what appears to be partial saturation in ArD (Figure 2.23), an intermediate 0.77 order in LDA (Figure 2.24), and a 1.5 order in THF (Figure 2.25), implicating contributions from both dimer- and monomer-based mechanisms. At full inhibition (3.0% LiCl), clean first-order dependence on ArD (Figure 2.26), half-order dependence on LDA (Figure 2.27), and second-order dependence on THF (Figure 2.28) are consistent with the monomer-based metalation described by eqs 18–20. This finding proved to be important (vide infra).

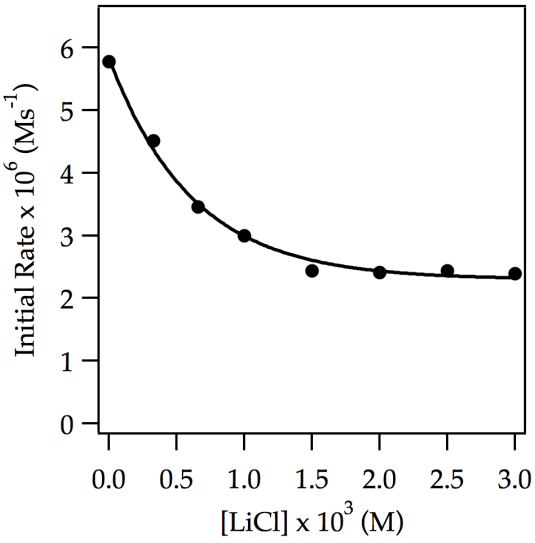


Figure 2.22. Plot of initial rate vs LiCl concentration for the ortholithiation of ArD (0.0050 M) by 0.30 M LDA in 12.2 M THF at –42 °C measured with ^{19}F NMR spectroscopy. The curve has no particular physical meaning.

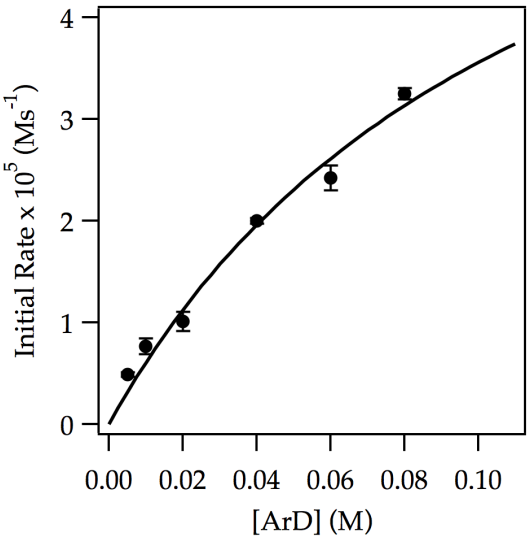


Figure 2.23. Plot of initial rate vs initial ArD concentration for the ortholithiation of ArD with LDA (0.10 M) in THF (12.2 M) at –42 °C measured with ^{19}F NMR spectroscopy. The curve depicts an unweighted least-squares fit to a first-order saturation function: : $y = (a[\text{ArD}])/(1 + b[\text{ArD}])$. [$a = (6 \pm 1) \times 10^{-4}$, $b = (8 \pm 4)$].

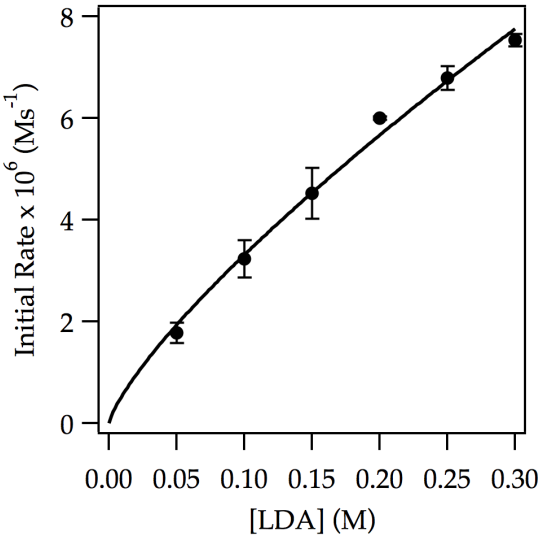


Figure 2.24. Plot of initial rate vs LDA concentration in THF (12.2 M) for the ortholithiation of ArD (0.0050 M) at –42 °C measured with ^{19}F NMR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\text{LDA}]^n$. [$a = (2.0 \pm 0.1) \times 10^{-5}$, $n = 0.77 \pm 0.04$].

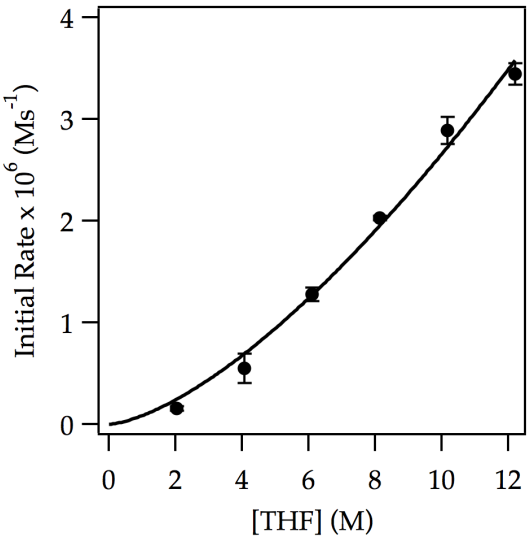


Figure 2.25. Plot of initial rate vs THF concentration in Et_2O cosolvent for the ortholithiation of ArD (0.0050 M) by LDA (0.10 M) at –42 °C measured with ^{19}F NMR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\text{THF}]^n$. [a = (8 ± 2) x 10^{-5}, n = (1.5 ± 0.1)].

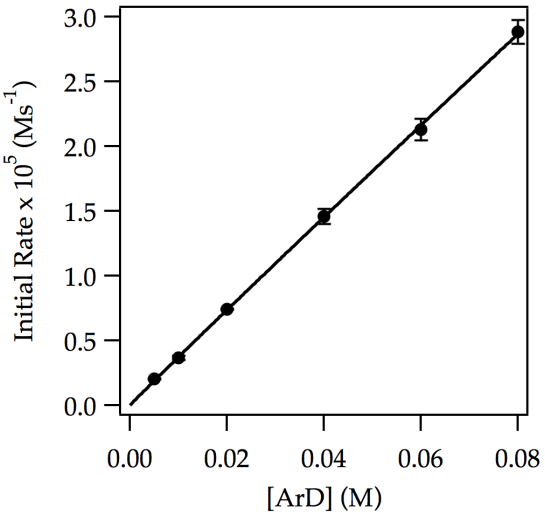


Figure 2.26. Plot of initial rate vs ArD concentration for the ortholithiation of **1-d_4** (0.0050 M) by LDA (0.10 M) with 3.0 mol % LiCl at –42 °C measured with ^{19}F NMR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\text{ArD}_4]^n$. [a = (3.4 ± 0.1) x 10^{-4}, n = (0.98 ± 0.01

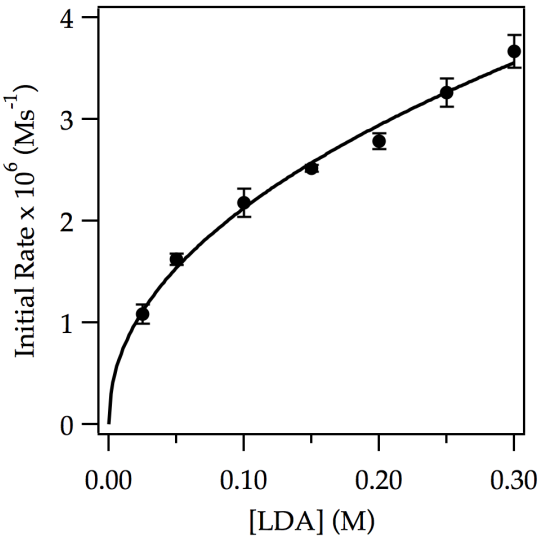


Figure 2.27. Plot of initial rate vs LDA concentration in THF (12.2 M) for the ortholithiation of ArD (0.0050 M) with 3.0 mol % LiCl at –42 °C measured with ^{19}F NMR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\text{LDA}]^n$. [$a = (6.2 \pm 0.3) \times 10^{-6}$, $n = 0.46 \pm 0.03$].

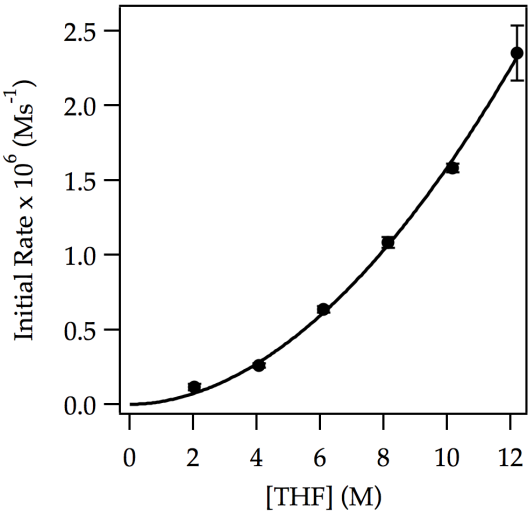


Figure 2.28. Plot of initial rate vs THF concentration in Et_2O cosolvent for the ortholithiation of ArD (0.0050 M) by LDA (0.10 M) with 3.0 mol % LiCl at –42 °C measured with ^{19}F NMR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\text{THF}]^n$. [$a = (1.9 \pm 0.3) \times 10^{-8}$, $n = (1.92 \pm 0.07$

Given the LiCl-catalyzed inhibition at –42 °C and no change in rate with added LiCl at –78 °C, we wondered whether we would observe acceleration at lower temperatures. Technical challenges made a full rate study difficult, but several spot checks showed that our supposition was correct: metalations at –90 °C showed modest (twofold) acceleration by LiCl (Figure 2.29).

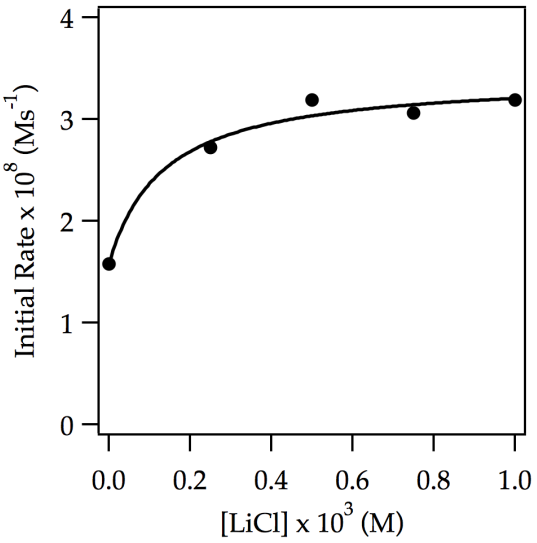
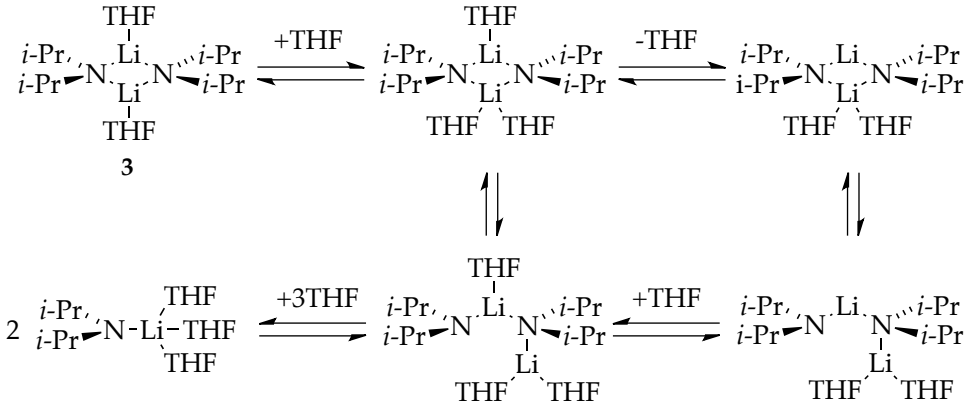


Figure 2.29. Plot of initial rate vs LiCl concentration for the ortholithiation of ArD (0.0050 M) by 0.10 M LDA in 12.2 M THF at –90 °C measured with IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = (a[\mathrm{LiCl}])/(1 + b[\mathrm{LiCl}]) + c$. [$a = (1.4 \pm 0.5) \times 10^{-7}$, $b = 7 \pm 3$, $c = 1.58 \times 10^{-8}$].

Discussion

The deaggregation of LDA dimer **3** proceeds through a variety of forms with variable solvation numbers and placements, as illustrated simplistically in Scheme 1. The barriers to aggregate and solvent exchange reside within a very narrow energetic range,[4] resulting in a washboard-like reaction coordinate that wreaks mechanistic havoc when the barriers to the reactions with substrates also fall within this range. Metalations of arene **1** (denoted as ArH) by LDA in THF at –78 °C —conditions under which aggregate exchanges occur with half-lives of minutes[2e]—produce anomalies similar to those found in several preceding case studies of metalations under such nonequilibrium conditions. Linear decays signifying zeroth-order substrate dependencies and rate-limiting aggregation events are prevalent. (In some instances the rate-limiting step—the maximum along the reaction coordinate—may be a solvation event, but we will not belabor this point and simply call it generically "aggregation" to distinguish it from a "metalation".) Saturation kinetics often result from rate-limiting metalations at low substrate concentrations that give way to rate-limiting aggregation events at high substrate concentrations. Perdeuterating the substrate to measure isotope effects often causes marked mechanistic changes, routinely forcing us to determine full rate laws for each. (We elaborate on this oddity shortly.)

Scheme 1

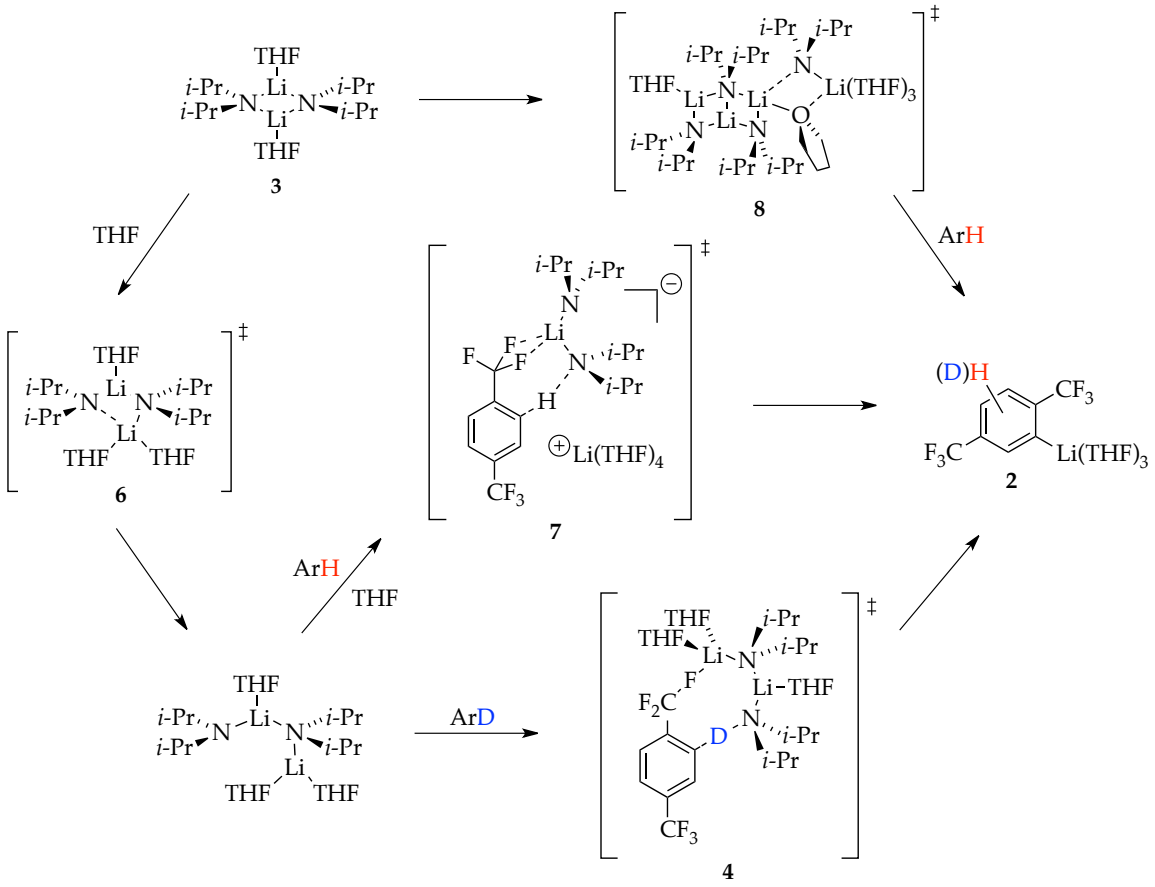


The work poses as many questions as it answers. Following a brief summary of the results (Scheme 2), we focus on insights and new questions emanating from the metalation in eq 1, followed by more explicit discussions of the particularly odd role of LiCl catalysis.

Summary. Using NMR spectroscopic and computational methods, we showed that metalation of ArH with LDA in THF affords trisolvated aryllithium monomer **2** (denoted as ArLi). Rate studies showed that the *uncatalyzed* metalation of the perdeuterated substrate (ArD) is relatively simple, affording a rate law consistent with a trisolvated dimer-based rate-limiting metalation. Transition structure **4** is emblematic but is not the only computationally viable candidate.[4] By contrast, metalation of ArH differing only in the substitution of protium for deuterium reveals two competing pathways corresponding to rate-limiting tetramer-based transition structure $[A_4S_5]^‡$ and dimer-based transition structures $[A_2S_3]^‡$ (open dimer **6**) and $[A_2S_4(ArH)]^‡$. The dimer-based mechanism shifts from a rate-limiting aggregation event at high ArH to rate-limiting metalation—$[A_2S_4(ArH)]^‡$—at low ArH. Confronted by evidence of highly solvated dimers,[1,2,23] we have routinely invoked triple ions similar to **7**. Although triple

ions are difficult to examine computationally because of electron correlation problems associated with ionic bonds,[25] they are amply documented in the structural lithium amide and organolithium literature.[24] Similarly, tetramer-based transition structure **8** also defies density functional theory computational methods in our hands as congested aggregates often do; previous studies could only place three solvents on a ladder without fracturing the ladder. Ladder **8** derives support from structurally well-characterized lithium amide ladders[23] and well-documented bridging THF ligands.[3,28] LDA tetramers have been documented during rate studies of LDA-mediated metalations under nonequilibrium conditions[2c,d,e] and implicated as being central to subunit exchanges within dimeric LDA.[2e] Monomer-based chemistry just outside our detection limits at –78 °C (and not shown in Scheme 2) comes into view at elevated temperatures and through LiCl catalysis (vide infra).

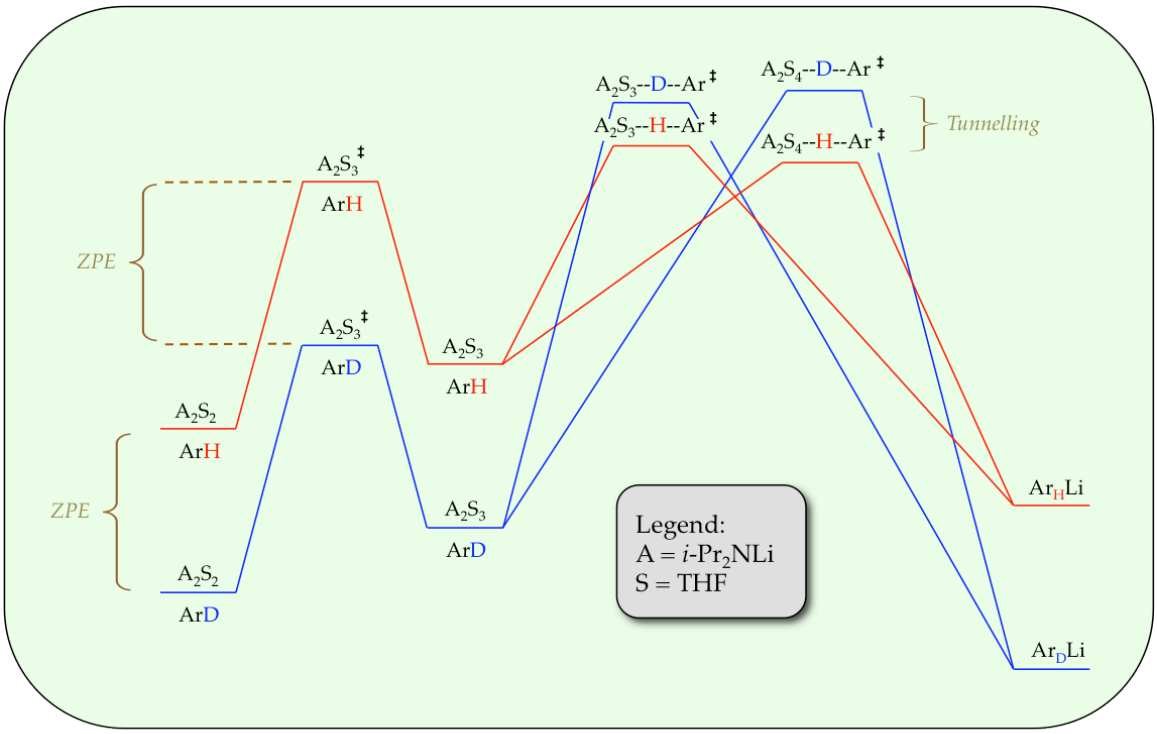
Scheme 2



Reaction coordinate diagram. Readers who have not followed the papers in the series may find the notion that ArH and ArD proceed via different mechanisms is counterintuitive, maybe even disconcerting. Scheme 3 illustrates how isotopically sensitive changes in mechanism can occur. To clarify an important point, we first refer to Scheme 3 as a reaction coordinate diagram rather than a free energy diagram because it connotes relative barrier heights but lacks the implicit balancing and fixed concentrations. As is always true but often overlooked, the positions of peaks and troughs depend consequentially on concentrations and isotopic substitution. The depiction in Scheme 3 represents a single snapshot of a highly fluctional reaction

coordinate. Higher LDA and THF concentrations stabilize intermediates and transition states of higher aggregates and higher solvates, respectively. Of special note, the zero-point energies are retained in the barriers corresponding to aggregation events that precede metalation. The transition states may also retain inherent isotopic sensitivities. A simple (two-body) analysis assumes that the isotopic sensitivities are lost in the transition state as the key stretch becomes the reaction coordinate.[32] Ortholithiations, however, display very large isotope effects in the range of 20–60,[2,33] forcing us to consider contributions from tunnelling.[34] Tunnelling *inverts* the isotopic sensitivity relative to the zero-point energy in the ground states. When we consider the roles of close barrier heights, zero-point energies, and tunneling together, we begin to see how changes in concentration and isotopic substitution can cause considerable reordering of the barrier heights if they reside within a narrow energetic window.

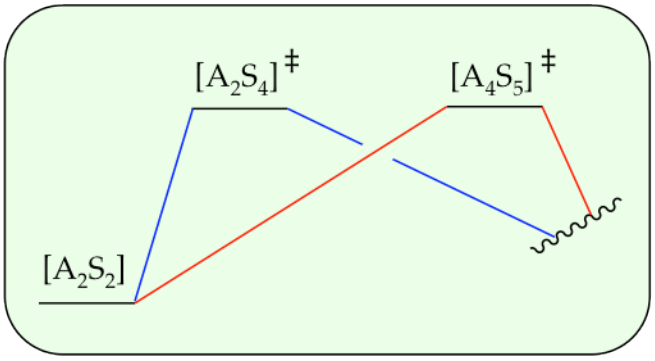
Scheme 3



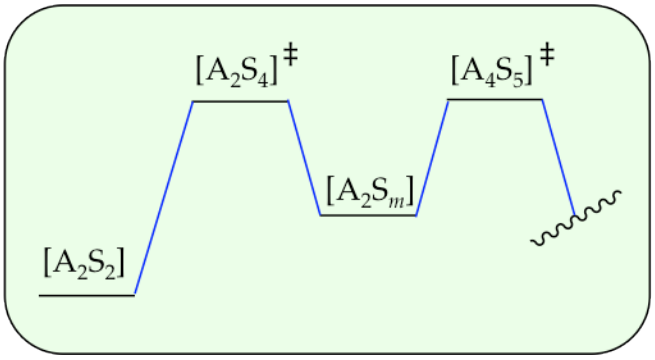
Rate limitation: barriers in parallel versus in series. The rate law for metalation of ArH was suggested to reflect the operation of A_2S_4- and A_4S_5-based transition structures in parallel as depicted simplistically in Scheme 4. Low LDA and high THF concentrations favor the highly solvated dimer-based pathway, whereas high LDA and low THF concentrations favor the more aggregated but lower-per-lithium-solvated tetramer-based pathway. How do we know that the two barriers are not aligned sequentially as depicted in Scheme 5? In short, serially aligned barriers have the opposite concentration dependencies on the rate-limiting step and affiliated rate law. In the parallel sequence (Scheme 4), dimer stabilization would shift the rate-limiting step toward the dimer and make the rate law dimer-like mathematically (first order in LDA and second order in THF). By contrast, stabilizing the dimer-based transition state in the serial sequence (Scheme 5) shifts the rate-limiting step to the tetramer, making the

rate law tetramer-like (second order in LDA and first order in THF). Similarly, stabilizing the tetramer-based transition state in the serial sequence (Scheme 5) shifts the rate-limiting step to the dimer, making the rate law dimer-like. However, modest ambiguity stems from the possibility of other serially aligned transition structures such as those shown in Scheme 6. Although Scheme 6 is distinguishable from the parallel pathways in Scheme 4 in theory, such a distinction might be difficult in the impure world of experimental kinetics. We present this ambiguity more as a point of interest than as a pressing problem. Additional data—a new view with a different substrate—could abruptly resurrect this debate, however.

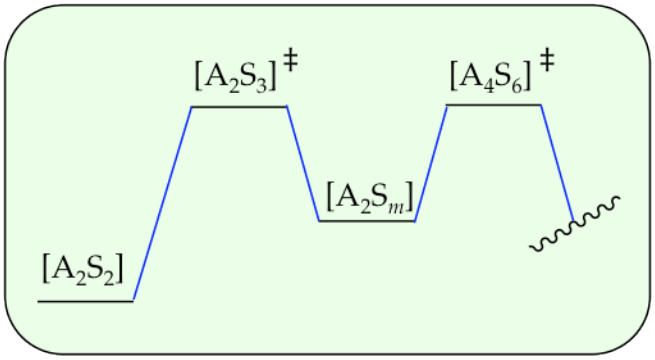
Scheme 4



Scheme 5



Scheme 6



Autocatalysis. The metalation of ArH offers a rare example of an LDA-mediated metalation under nonequilibrium conditions that does *not* display autocatalysis.[2] In previous studies, pronounced autocatalysis by aryllithiums was initially believed to arise from catalyzed dimer-to-monomer conversion,[2d] although a recent study of 1,4-difluorobenzene traced weak autocatalysis to a catalyzed LDA dimer-to-dimer conversion.[2e] We wondered whether autocatalysis was absent in the metalation of ArH because the metalation is marginally susceptible to such catalysis or because aryllithium **2** is a poor catalyst. The answer turns out to be both. We found that the metalation of the 1,4-difluorobenzene studied previously[2e] is only marginally catalyzed by ArLi *and* the metalation of ArH is only marginally catalyzed by ortholithiated 1,4-difluorobenzene. These observations serve as a segue to the discussion of some very odd catalytic effects of LiCl.

LiCl catalysis. Ortholithiation of ArH in the presence of traces (<2 mol %) of LiCl showed a marked acceleration. Rate studies revealed the LiCl-catalyzed LDA dimer-to-monomer conversion noted for *all* LDA-mediated metalations in THF at –78 °C studied to date.[2] The solvent order and computations supported transition structure **9** (eq 21). A minor oddity occurred, however. If LiCl is catalyzing the same deaggregation, the order

in LiCl should be the same in all cases, but it is not. A first-order dependence on LiCl concentration (Figure 2.14 and eqs 17–19) was observed rather than the more frequently observed second-order LiCl dependence. We have seen the variation before and could easily imagine variation from investigator to investigator—these kinetics are technically quite difficult. However, one of the second-order LiCl dependencies[2c,d,e] and the first-order LiCl dependence noted herein were measured by the same researcher (JL). We cannot explain this minor incongruence. As has happened so many times in this series of studies, an explanation may be forthcoming in a subsequent study. Regardless, far more interesting oddities showed up in studies of LiCl-catalyzed ArD metalations.

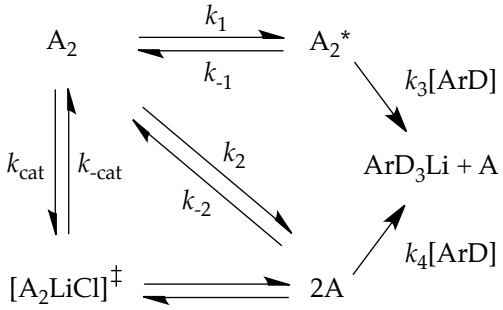
Metalation of ArD with LDA in THF at –78 °C in the presence of varying quantities of LiCl showed no change in rate whatsoever (Figure 2.18). When the rate law was determined with added LiCl, however, the mechanism had shifted from an $[A_2S_3]^‡$-based rate-limiting step in the absence of LiCl to $[AS_3(ArD)]^‡$-based rate limiting step with added LiCl. *The rate law changed with no discernible change in the rate.*

The plot thickened when we changed the temperature of the metalation. Uncatalyzed metalations at –42 °C showed mixed orders consistent with a composite of $[A_2S_3(ArD)]^‡$ and $[AS_3(ArD)]^‡$, suggesting that a monomer-based metalation had been lurking just below the surface. The fact that changes in temperature brought it into view is not surprising, and why raising the temperature did so is not really of interest to us. However, rate studies at –42 °C with added LiCl revealed LiCl-catalyzed *inhibition* and an accompanying shift in the rate law toward $[AS_3(ArD)]^‡$. On a hunch that the LiCl-independent rates at –78 °C might result from a cancellation or coincidence of factors, we investigated the effect of LiCl at –90 °C and found that, indeed, LiCl *accelerates* the metalation.

The temperature-dependent acceleration by LiCl at the lowest temperatures and deceleration at the highest temperatures is unique and unexpected but not altogether irrational. The principle of detailed balance and the accumulated wisdom of enzyme kineticists suggest that the inhibition of systems at equilibrium requires the *stoichiometric* binding of the active species. Analogy with photochemical desensitizers and other complex systems,[6] however, shows that nonequilibrium systems can be susceptible to catalyzed inhibition.

The simplified model in Scheme 7 in conjunction with numerical integration captures much (but not all) of what is needed to explain LiCl-catalyzed inhibition. The differential equations and underlying calculations are not particularly germane to the discussion and are relegated to the supporting information.

Scheme 7



The rate studies told us that the dimer-based mechanism ($A_2 \rightarrow A_2^* \rightarrow$product) proceeds with rate limitation shared by the dimer-based deaggregation and dimer-based metalation ($k_{-1} \sim k_3$[ArD]).[35] Dimer-based metalation affords ArLi and *releases an equivalent of monomer A*. At equilibrium, the population of A is defined by k_2/k_{-2}, but under nonequilibrium conditions the exchange is slow. If monomer A is trapped

efficiently relative to a much slower reaggregation to dimer (k_4[ArD] >> k_{-2}[A]), each rate-limiting dimer-based metalation affords 2 equiv of ArLi product. Now imagine that we introduce catalytic LiCl to hasten the A_2–2A exchange and bring it to equilibrium. Both k_{cat} and k_{-cat} implicitly include LiCl, but the LiCl concentrations cancel in k_{cat}/k_{-cat}, which is necessarily equivalent to k_2/k_{-2}. (We've included $[A_2LiCl]^{‡}$ transition structure to underscore the nature of this catalysis and symmetrize the scheme but it is not mathematically germane.)

We discuss below three limiting scenarios describing the influence of catalysis on the steady state concentration of monomer A and, consequently, the rate of metalation (Figure 2.30). The three behaviors in Figure 2.30 qualitatively correspond to metalations at –42 °C (Scenario 1), –78 °C (Scenario 2), and –90 °C (Scenario 3). The initial rates are normalized to the same initial rate of the LiCl-free metalation although experimentally they were obviously quite different. Simulations in Figure 2.30 as well as in Figures 2.31-2.34 were generated from the model in Scheme 7 via numerical integration. The numerical debris—numbering and units on axes—has been omitted for clarity but is retained in a more detailed analysis in the supporting information.

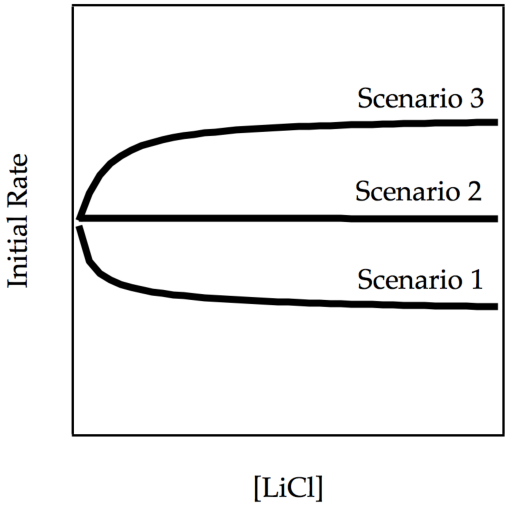


Figure 2.30. Plot of initial rate vs [LiCl] showing catalyzed inhibition (Scenario 1), no change in rate (Scenario 2), and catalyzed acceleration (Scenario 3). The curves result from numerical integrations (simulations) of the model in Scheme 7.

Scenario 1. The steady-state concentration of A delivered exclusively by the dimer-based pathway ($A_2 \rightarrow A_2^* \rightarrow A+ArLi$) is *higher* than the equilibrium population of A. Simulations derived from Scheme 7 reveal catalytic inhibition akin to that seen at –42 °C (Figure 2.22). Introducing the catalyst and establishing equilibrium causes a net *decrease* in the steady-state concentration of A available for conversion to product and an affiliated decrease in the measured reaction rate (Figure 2.30, Scenario 1). To the extent that the decrease in the concentration of A is pronounced, the inhibition approaches a factor of two in the limit: each dimer-based deaggregation event produces one rather than two molecules of ArLi.

Simulations of the LDA dependence show that catalyzed inhibition will cause changes in the law (Figure 2.31). Curve A shows a first-order LDA dependence of an uninhibited metalation owing to exclusively the dimer-based pathway. Curve C shows the case in which the catalysis causes a marked depletion of the monomer concentration and retains the linearity associated with dimer reactivity but a factor of two loss in rate.

Curve B shows the most interesting case in which reduction of monomer concentration is less pronounced. The A_2–2A preequilibrium contributes appreciably to monomer-based metalation (Scheme 7). A fractional LDA order—less than one and greater than one half—reflects the funneling of the metalation through the dimer-based pathway *and* via the dimer–monomer pre-equilibrium. Thus, when catalysis establishes the dimer–monomer equilibration *and* reduces the concentration of monomer, the model predicts a rate decrease and intermediate LDA order.

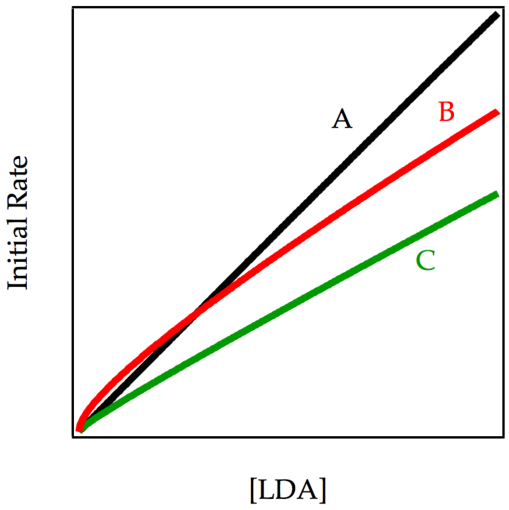


Figure 2.31. Plot of initial rate vs [LDA] concentration reflecting changing LDA dependencies with catalysis within scenario 1 (inhibition): curve A (black) corresponds to dimer-based metalation without any added LiCl; curve B (blue) corresponds to partial inhibition retaining both dimer and monomer reactivity at saturation. curve C (green) corresponds to full inhibition retaining only dimer-based reactivity at saturation. The curves result from numerical integrations (simulations) of the model in Scheme 7.

Scenario 2. The steady-state concentration of A delivered exclusively by the dimer-based-metalation is *identical* to the population of A at equilibrium as depicted experimentally in Figure 2.18 and simulated in Figure 2.30 (Scenario 2). Because restoring the A_2–2A equilibrium results in no change in the concentration of A

(confirmed by simulation), the metalation rate is unchanged. The rate law will, however, show an intermediate fractional order because the rate of reaction reflects balanced contributions from dimer-based and *fully equilibrated* monomer-based metalations. Anticipated LDA dependencies in Figure 2.32 show nominally different rates with measurably different LDA orders.

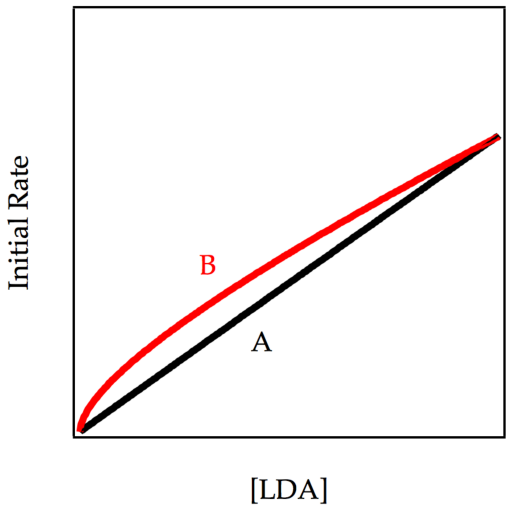


Figure 2.32. Plot of initial rate vs [LDA] for the two circumstances depicted in Figure 2.30 (Scenario 2). Curve A (black) reflects the LDA order of the uncatalyzed metalation (corresponding to the *y* intercept in Figure 2.30). Curve B reflects the fully LiCl catalyzed metalation (high LiCl portion of Scenario 2 in Figure 2.30). The curves result from numerical integrations (simulations) of the model in Scheme 7.

Scenario 3. The steady-state concentration of A delivered by the dimer-based metalation is *below* the equilibrium population of A. Establishing the A_2–2A equilibrium through catalysis increases the steady state concentration of A with a consequent increase in the observable rate (Figure 2.30, Scenario 3). The LDA dependence (Figure 2.33, curve B) shows acceleration and curvature consistent with a monomer-dominated metalation.

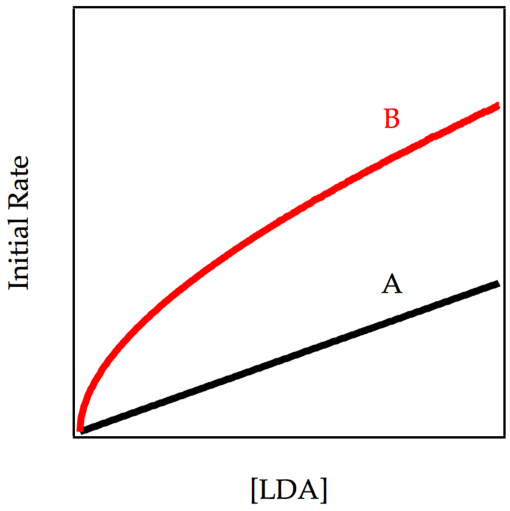


Figure 2.33. Plot of initial rate vs [LDA] for Scenario 3 (Figure 2.30). Curve A (black) reflects the LDA order of the uncatalyzed (dimer-dominated) metalation; Curve B reflects the fully LiCl-catalyzed metalation (high LiCl portion of Scenario 2 in Figure 2.30). The curves result from numerical integrations (simulations) of the model in Scheme 7.

It is satisfying that the simple model in Scheme 7 replicates the experimentally observed LiCl-catalyzed acceleration and inhibition. Catalyzed inhibition was a notion that we would have declared impossible before completing these rate studies, and it is uniquely characteristic of nonequilibrium conditions.[6] The model also qualitatively reflects observed changes in the rate laws affiliated with the catalysis. Despite the qualitative successes, however, quantitative inconsistencies remain. Although changes in the rates and the rate laws are nicely reflected by simulations using the model in Scheme 7, there are discrepancies in the experimentally determined LDA orders with the predicted values from the simulations. Nonetheless, given the simplifications in the model, we find this study to be an excellent beginning, and the implications of the model, even in isolation, are provocative.

Conclusion

This paper is the latest in a series describing metalations using LDA under nonequilibrium conditions, all contributing to a single chapter in narrative about LDA structure-reactivity relationships. Understanding how different substrates could be subjected to different rate-limiting deaggregations of widely varying stoichiometries took considerable effort. Variations in the catalytic effects of LiX salts stem from the catalysis of various steps along a complex cascade of fleeting intermediates that are *not* in fully established equilibria. Each substrate and even isotopologues of a single substrate provide different views of the cascade. The present study underscored some familiar paths and principles yet also ventured into uncharted territory. The apparent change in mechanism of the LiCl-catalyzed deaggregation seems illogical—a minor annoyance—but we are loathe to summarily dismiss it as user error. Similarly baffling oddities have tended to resolve with further scrutiny. The LiCl-catalyzed inhibition of the metalation and the mathematical model showing its plausibility through numerical simulation constitute the cornerstone of this work. Residual quantitative discrepancies trouble us, but not very much. We reiterate: oddities rearing their ugly heads throughout these studies often resolve in a subsequent case studies. With that said, we may be nearing the logical completion of the study of LDA metalations under nonequilibrium conditions, which has been an eye-opening exposure to the role of rate limitation in complex reaction mechanisms. Given the prevalence of LDA-mediated metalations in THF at –78 °C, the irony that these same conditions generate such complexity is difficult to overlook.

Experimental Section

Reagents and solvents. THF, Et_2O, and hexane were distilled from blue or purple solutions containing sodium benzophenone ketyl. The hexane contained 1% tetraglyme to dissolve the ketyl. Et_3N–HCl was recrystallized from THF/2-propanol.[36] Literature procedures[9] were modified to prepare LDA as a LiCl- and ligand-free solid.[2b] Solutions of LDA were titrated using a literature method.[37]

IR spectroscopic analyses. IR spectra were recorded using an in situ IR spectrometer fitted with a 30-bounce, silicon-tipped probe. The spectra were acquired in 16 scans at a gain of 1 and a resolution of 4 cm^{-1}. A representative reaction was carried out as follows: The IR probe was inserted through a nylon adapter and O-ring seal into an oven-dried, cylindrical flask fitted with a magnetic stir bar and a T-joint. The T-joint was capped with a septum for injections and a nitrogen line. After evacuation under full vacuum, heating, and flushing with nitrogen, the flask was charged with LDA (108 mg, 1.01 mmol) in THF and cooled in a dry ice–acetone bath prepared with fresh acetone. LiCl was added via a THF stock solution prepared from $Et_3N{\cdot}HCl$ and LDA. After recording a background spectrum, we added ArH (0.76 mmol) with stirring. For the most rapid reactions, IR spectra were recorded every 3 s with monitoring of the absorbance at 1323 cm^{-1} over the course of the reaction.

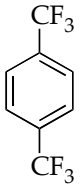
NMR spectroscopic analyses. All NMR samples were prepared using stock solutions and sealed under partial vacuum. Standard ^6Li, ^{13}C, ^{15}N, and ^{19}F NMR spectra were recorded on a 500 MHz spectrometer at 73.57, 125.79, 50.66, and 470.35 MHz, respectively. The ^6Li, ^{13}C, and ^{15}N resonances are referenced to 0.30 M [^{6}Li]LiCl/MeOH at –90 °C (0.0 ppm), the CH_2O resonance of THF at –90 °C (67.57 ppm), and neat Me_2NEt at –90 °C (25.7 ppm).

2,3,5,6-Tetradeutero-1,4-bis(trifluoromethyl)benzene (1-d_4). A 10.6 M solution of *n*-BuLi in hexane (4.70 mL, 50.0 mmol) was added via syringe pump to a solution of 1,4-bis(trifluoromethyl)benzene (7.0 mL, 45.2 mmol) in 150 mL of dry THF at –78 °C under argon over 20 min. The solution was stirred for an additional 25 min. MeOD (2.03 mL, 50.0 mmol) was added via syringe pump over 20 min. The mixture was allowed to stir for 1 hr. The process of sequential addition of 1.1 equiv *n*-BuLi and 1.1 equiv MeOD was repeated five additional times. A final aliquot of MeOD (10 mL, 5.0 equiv) was added to quench the reaction fully. After the mixture was allowed to warm to room temperature, the pH was adjusted to 1.0 with 4.0 M aqueous HCl to dissolve all lithium salts. The organic and aqueous layers were separated, and the organic layer was extracted with additional cold 0.20 M HCl to remove excess THF. The extraction was stopped when the total organic volume was approximately 10–15 mL. The organic layer was dried over Na_2SO_4 and distilled. The product was collected as a colorless liquid (2.26 g, 10.4 mmol) in 23% yield via distillation at 116 °C. ^{13}C NMR δ 134.20 (q, $^2J_{C–F}$ = 33.2 Hz), 125.75 (tq, $^1J_{C–D}$ = 25.5 Hz, $^3J_{C–F}$ = 3.3 Hz), 123.80 (q, $^1J_{C–F}$ = 272.1 Hz); LRMS: 218.2 *m*/*z* shows 98% **1-d_4**.

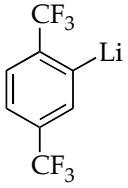
Numeric integrations. The time-dependent concentration plots obtained using IR spectroscopy were fit to mechanistic models expressed by a set of differential equations. The curve-fitting operation minimizes chi-square in searching for the coefficient values (rate constants). The Levenberg–Marquardt algorithm[38] was used for the chi-square minimization and is a form of nonlinear, least-squares fitting. The fitting procedure implements numeric integration based on the backward differentiation formula[39] to solve the differential equations, yielding functions describing concentration versus time.

Chapter 2 Appendix

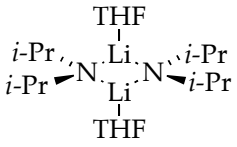
Chart 1



1



2



3

Part 1: Experimental Procedures:

2,3,5,6-Deutero-1,4-Bis(trifluoromethyl)benzene (1-d_4) A 10.6 M solution of *n*-BuLi in hexane (4.70 mL, 50.0 mmol) was added via syringe pump to a solution of 1,4-bis(trifluoromethyl)benzene (7.0 mL, 45.2 mmol) in 150 mL of dry THF at -78 °C under Argon over a period of 20 min. The solution was stirred for an additional 25 min. MeOD (2.03 mL, 50.0 mmol) was added via syringe pump over a period of 20 min. The mixture was allowed to stir for 1 hr. The process of sequential addition of 1.1 equiv *n*-BuLi and 1.1 equiv *d*-MeOH was repeated 5 more times. A final aliquot of MeOD (10 mL, 5.0 equiv) was added to fully quench the reaction. After the mixture was allowed to warm to room temperature, the pH was adjusted to 1.0 with 4.0 M aq HCl to dissolve all lithium salts. Organic and aqueous layers were separated, and the organic layer was extracted with more cold 0.2 M HCL to remove excess THF. Extraction was stopped when the total organic vol was approximately 10-15 mL. The organic later was dried over Na_2SO_4 and distilled. The product was collected by distillation at 116 ºC as a colorless liquid (2.26 g, 10.4 mmol) in 23% yield. ^{13}C NMR δ 134.20 (q, $^2J_{C\text{-}F}$ = 33.2 Hz), 125.75 (tq, $^1J_{C\text{-}D}$ = 25.5 Hz, $^3J_{C\text{-}F}$ = 3.3 Hz), 123.80 (q, $^1J_{C\text{-}F}$ = 272.1 Hz); LRMS: 218.2 *m*/*z*.

Part 2: NMR Spectroscopic Studies

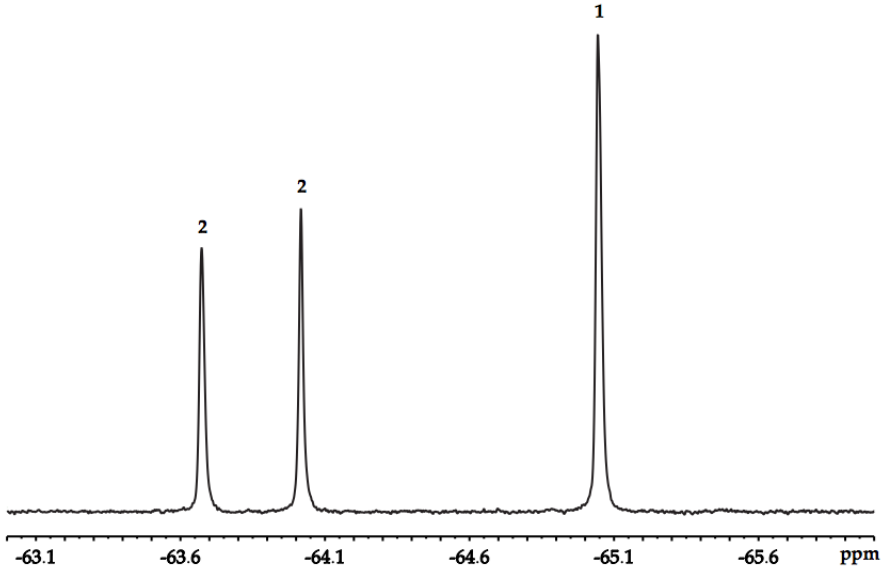


Figure A2.1. ^{19}F NMR spectrum of LDA (0.10 M) with **1** (0.005 M) in 12.2 M THF after aging for 10 min at –78 °C: δ -65.05 (s), -64.02 (s), -63.67 (s).

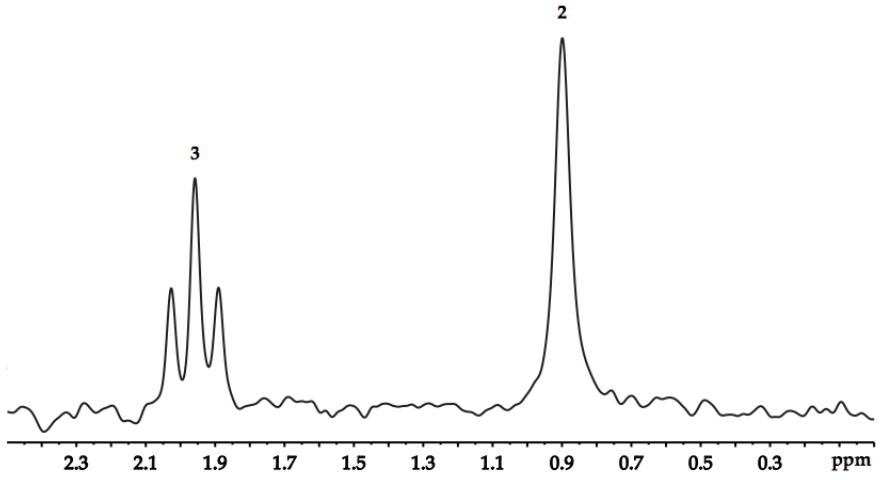


Figure A2.2. ^{6}Li NMR Spectrum of [^{6}Li,^{15}N]LDA (0.10 M) and **1** (0.05 M) in 12.2 M THF recorded at –78 °C: δ 1.96 (t, $^{1}J_{\text{Li-N}}$ = 5.0 Hz), 0.90 (s).

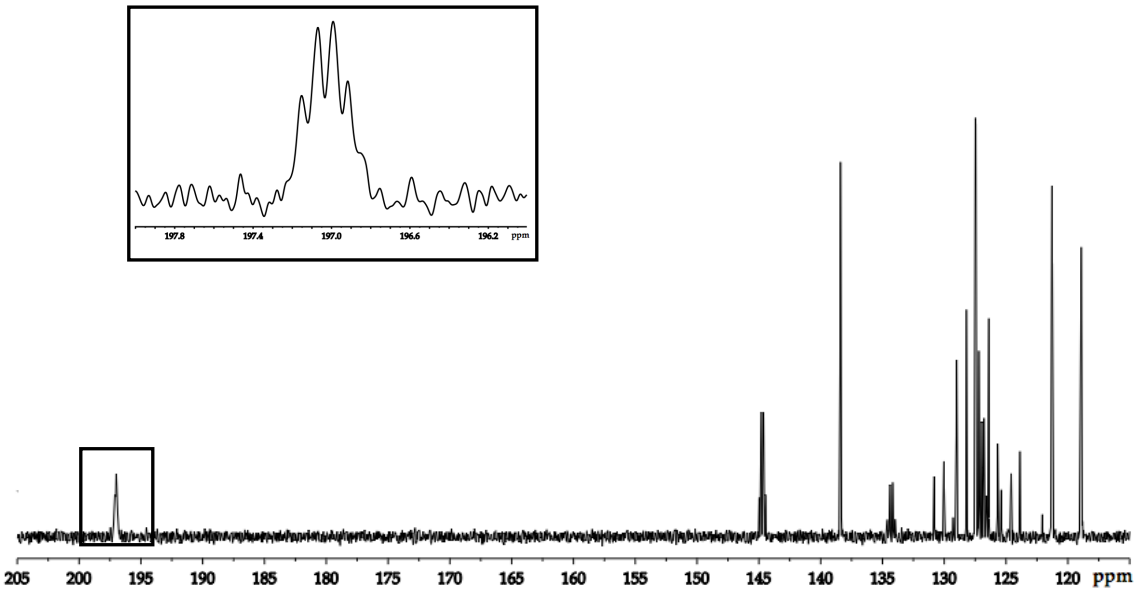


Figure A2.3. $^{13}C\{^{1}H\}$ NMR spectrum of **2** generated from **1** (0.15 M) with [^{6}Li]LDA (0.30 M, 2.0 equiv) in 12.2 M THF-d_8 at –100 °C. Resonances of **1** remain at equilibrium. **2**: δ 197.02 (m), 144.72 (q, $^{2}J_{C\text{-}F}$ = 25.2 Hz), 138.40 (s), 128.11 (q, $^{1}J_{C\text{-}F}$ = 273.3 Hz), 127.31 (q, $^{1}J_{C\text{-}F}$ = 273.0 Hz), 126.88 (q, $^{2}J_{C\text{-}F}$ = 28.5 Hz), 121.29 (s), 118.93 (s). **1**: δ 134.28 (q, $^{2}J_{C\text{-}F}$ = 32.8 Hz), 127.48 (s), 124.79 (q, $^{1}J_{C\text{-}F}$ = 272.3 Hz).

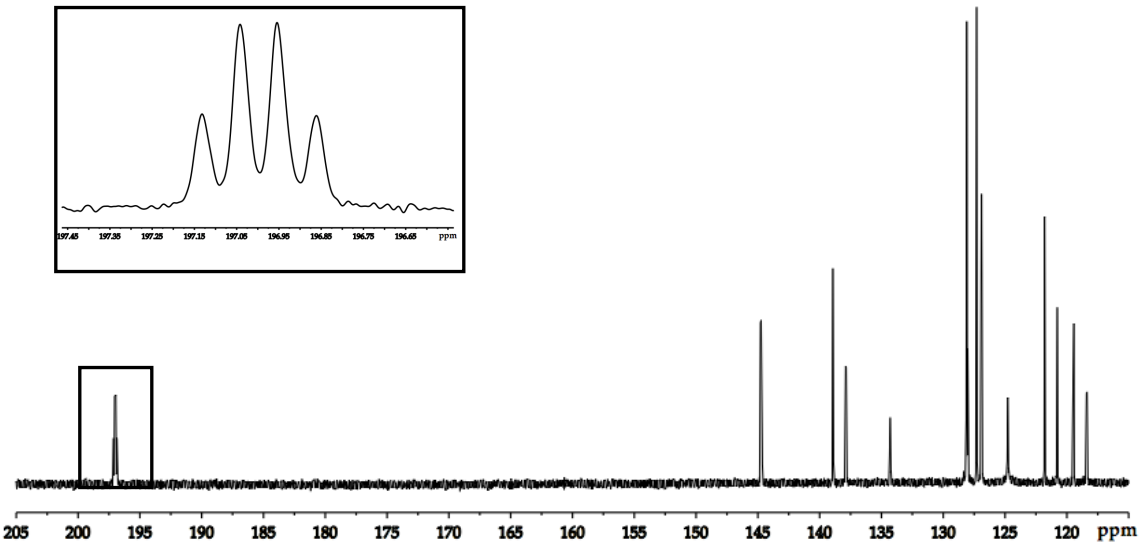


Figure A2.4. $^{13}C\{^{19}F\}$ NMR spectrum of **2** generated from **1** (0.15 M) with [^{6}Li]LDA (0.30 M, 2.0 equiv) in 12.2 M THF-d_8 at –100 °C. Resonances of **1** remain at equilibrium. **2**: δ 197.00 (td, $^{1}J_{C\text{-}Li}$ = 13.2 Hz, $^{2}J_{C\text{-}H}$ = 6.6 Hz), 144.72 (dd, $^{2}J_{C\text{-}H}$ = 12.6 Hz, $^{3}J_{C\text{-}H}$ = 7.2 Hz), 138.40 (dd, $^{1}J_{C\text{-}H}$ = 156.5 Hz, $^{2}J_{C\text{-}H}$ = 5.3 Hz), 128.11 (m), 127.31 (t, $^{2}J_{C\text{-}H}$ = 3.8 Hz), 126.88 (m), 121.29 (d, $^{1}J_{C\text{-}H}$ = 155.3 Hz), 118.93 (dd, $^{1}J_{C\text{-}H}$ = 160.2 Hz, $^{2}J_{C\text{-}H}$ = 5.8 Hz). **1**: δ 134.29 (m), 127.47 (dm, $^{1}J_{C\text{-}H}$ = 168.0 Hz), 124.79 (m).

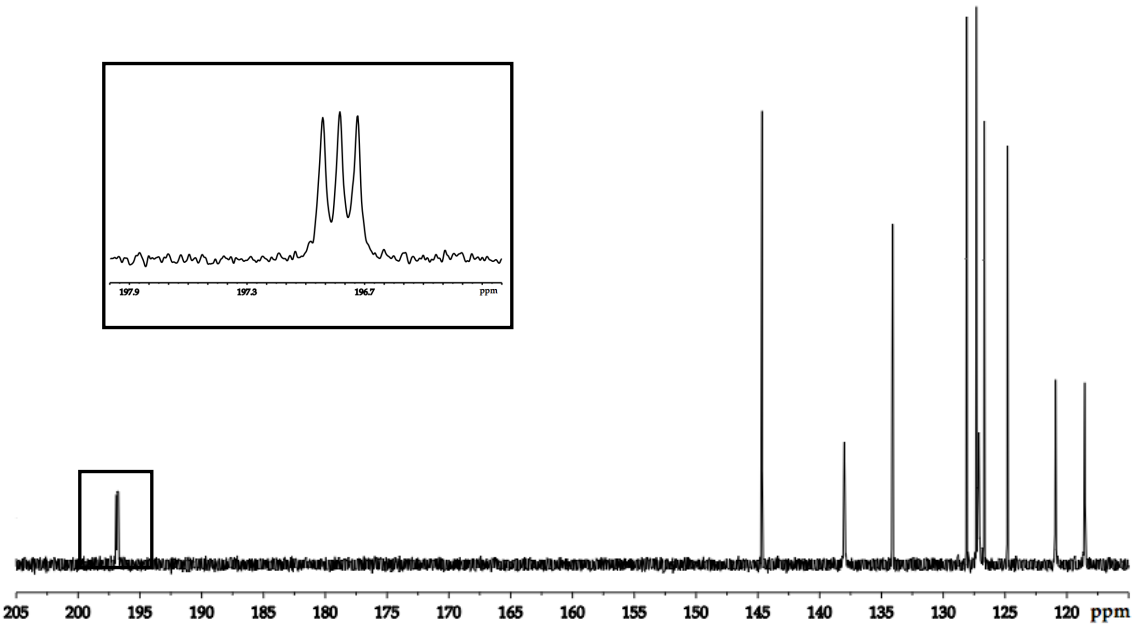


Figure A2.5. $^{13}C\{^{19}F,^{2}H\}$ NMR spectrum of **2-***d*$_3$ generated from **1-*d*$_4$** (0.15 M) with [^{6}Li]LDA (0.30 M) in 12.2 M THF-*d*$_8$ at –100 °C. Resonances of **1-*d*$_4$** remain at equilibrium. **2-***d*$_3$: δ 196.83 (t, $^{1}J_{C\text{-}Li}$ = 13.2 Hz) 144.66 (s),138.00 (s), 128.11 (s), 127.12 (s), 126.68 (s), 120.92 (s), 118.55 (s). **1-*d*$_4$**: δ 134.10 (s), 127.33 (s), 124.80 (s).

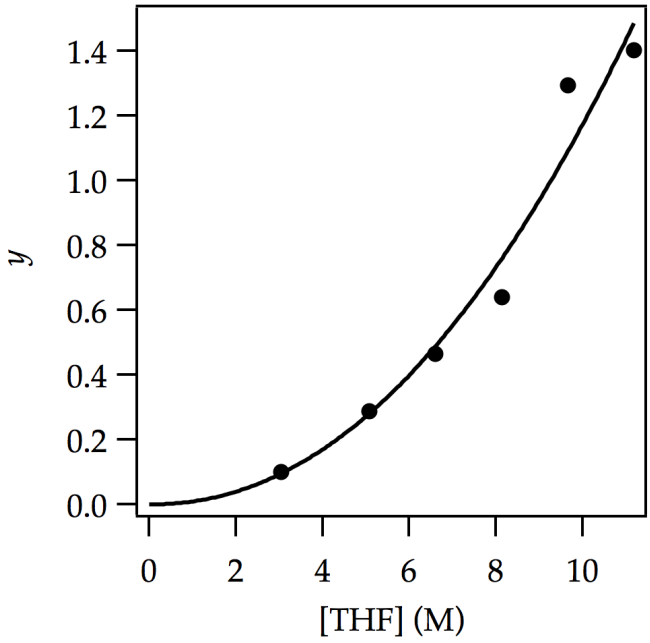


Figure A2.6. Plot of {[*i*-Pr_2NH][ArLi]} / {[LDA]$^{(1/2)}$[ArH]} vs [THF] for the ortholithiation of **1** (0.005 M) with LDA (0.10 M) and diisopropylamine (0.025 M) at –78 °C measured by ^{19}F NMR spectroscopy. The curve depicts an unweighted least-squares fit to $y = K_{eq}[THF]^n$. [$K_{eq} = (9 \pm 7) \times 10^{-3}$, $n = (2.1 \pm 0.3)$]

[THF] (M)	y
11.18	1.40
9.66	1.29
8.13	0.64
6.61	0.46
5.08	0.29
3.05	0.10

Part 3: Rate Studies

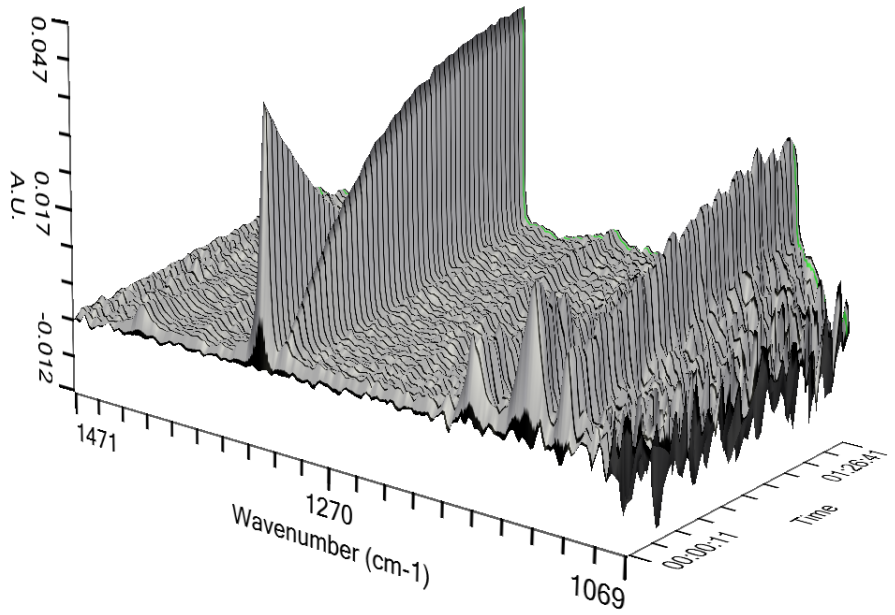


Figure A2.7. Representative in situ IR traces for the ortholithiation of **1** (0.005 M) by LDA (0.10 M) in THF at –78 °C. IR absorptions for compounds **1** and **2** and their associated isotopomers are listed below. The IR spectra were deconvoluted using ConcIRT®.

1: 1421 cm^{-1}, 1323 cm^{-1}, 1173 cm^{-1}, 1138 cm^{-1}, 1115 cm^{-1}
2: 1378 cm^{-1}, 1307 cm^{-1}, 1160 cm^{-1}, 1111 cm^{-1}

1-d_4: 1448 cm^{-1}, 1348 cm^{-1}, 1253 cm^{-1}, 1156 cm^{-1}, 1136 cm^{-1}, 1026 cm^{-1}
2-d_3: 1391 cm^{-1}, 1212 cm^{-1}, 1015 cm^{-1}

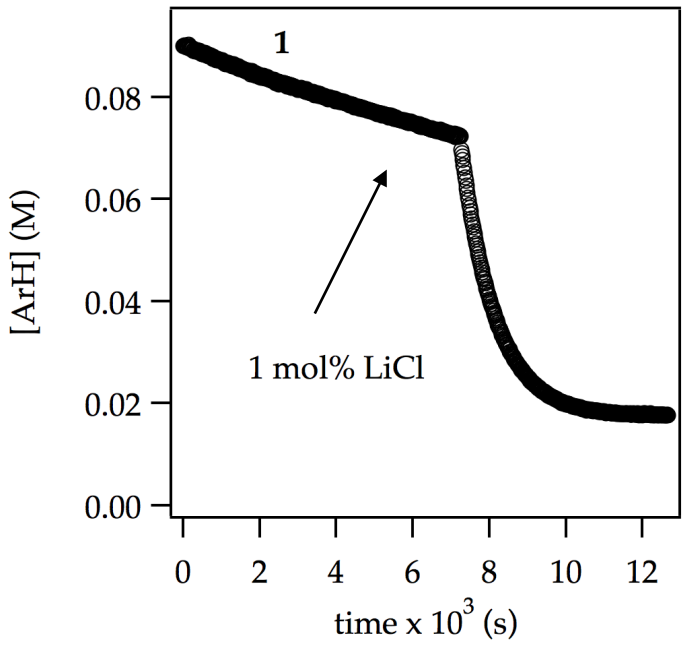


Figure A2.8. Ortholithiation of **1** (0.09 M) with LDA (0.10 M) in 12.2 M THF at –78 °C monitored by IR spectroscopy (1323 cm^{-1}) with injection of 1.0 mol % LiCl.

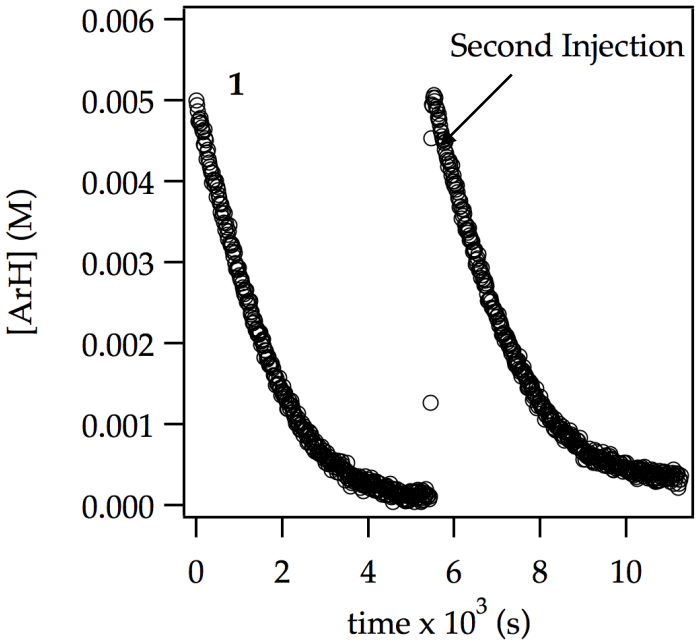


Figure A2.9. Representative plot showing concentration of arene **1** vs time for the ortholithiation of **1** (0.005 M) with LDA (0.10 M) in 12.2 M THF at –78 °C. After the completion of the reaction, a second aliquot of **1** (0.005 M) was injected, showing no evidence of autocatalysis (catalysis by ArLi).

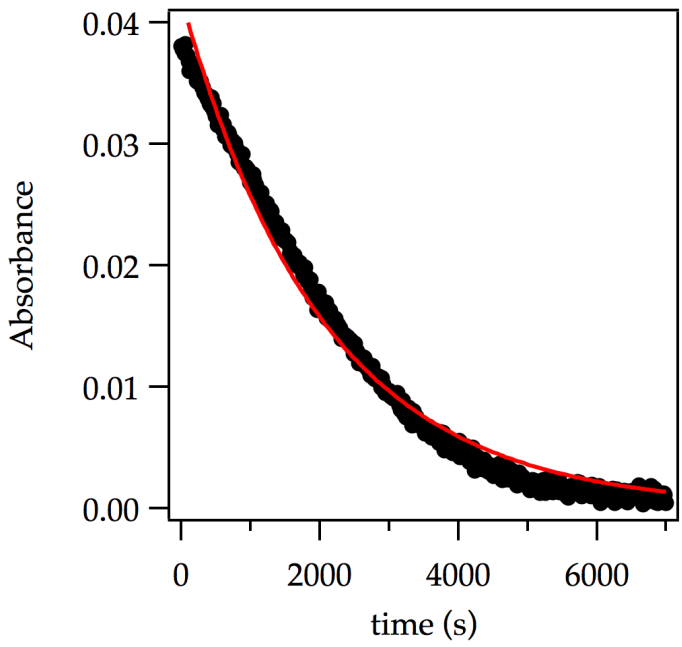


Figure A2.10. Representative plot showing poor exponential fit (red curve) to the decay of ortholithiation of **1** (0.005 M) with LDA (0.10 M) in THF (12.2 M) at –78 °C monitored by IR spectroscopy.

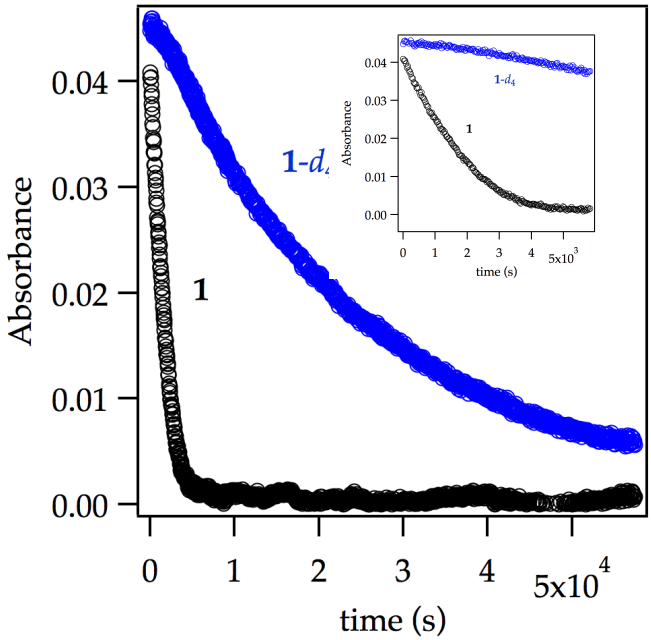


Figure A2.11. Competitive ortholithiation of **1** (0.005 M) and **1-d_4** (0.005 M) with LDA (0.10 M) in THF (12.2 M) at –78 °C. Monitoring absorbances of **1** and **1-d_4** at 1322 cm^{-1} and 1253 cm^{-1}, respectively, by IR Spectroscopy affords $k_H/k_D = 21$.

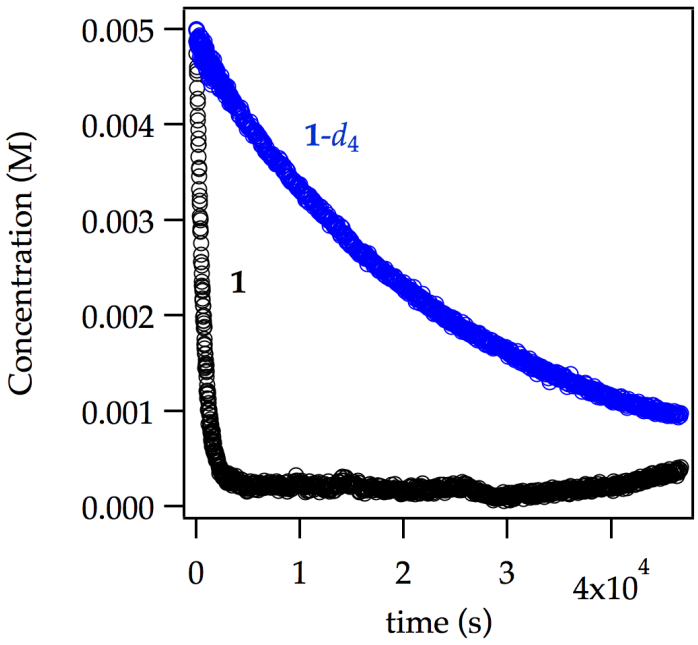


Figure A2.12. Competitive ortholithiation of **1** (0.005 M) and **1-d_4** (0.005 M) with LDA (0.10 M) in the presence of 1 mol % LiCl in THF (12.2 M) at –78 °C. Monitoring absorbances of **1** and **1-d_4** at 1322 cm^{-1} and 1253 cm^{-1}, respectively, by IR Spectroscopy affords $k_H/k_D = 36$.

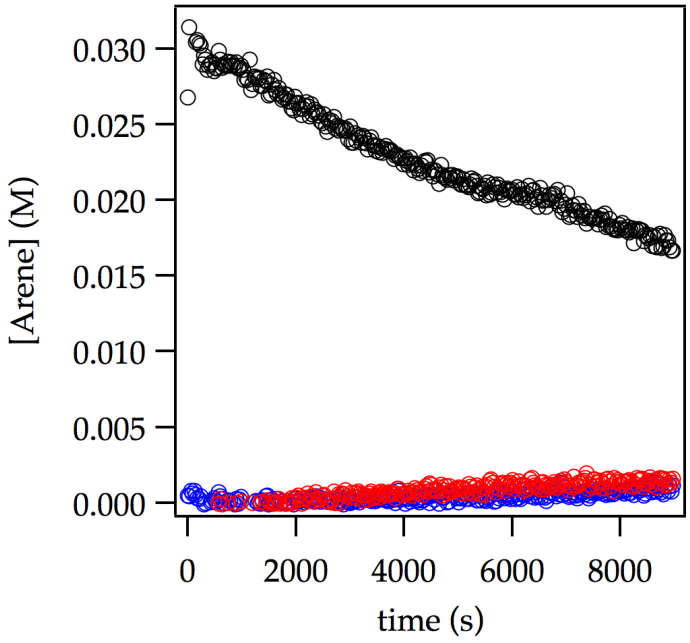
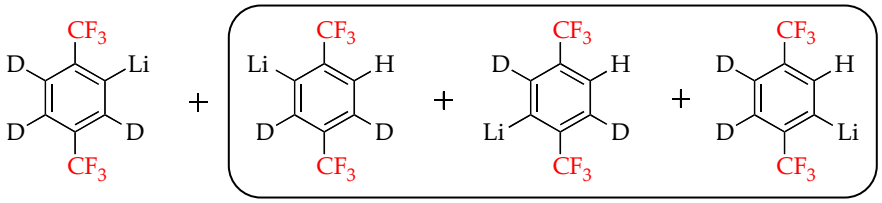


Figure A2.13. Ortholithiation of **1-*d*$_3$** (0.032 M) with LDA (0.10 M) in 12.2 M d_8-THF monitored by ^{1}H NMR. Percentages of regio-isomers were determined based on the initial rates of reactant decay (8.08 ppm) and products formation (7.11, 7.33, and 8.16 ppm). Theoretical percentages for the reversible and non-reversible mechanisms were derived from intramolecular (competitive) KIE.



Reversible	85%	5%	5%	5%
Non-reversible	47.5%	2.5%	25%	25%
Result	-------*	-------**	5.3%	6.5%

* Product not observed because no protons are present for detection
** Product not observed due to chemical shift overlap with benzene (d_8-THF impurity)

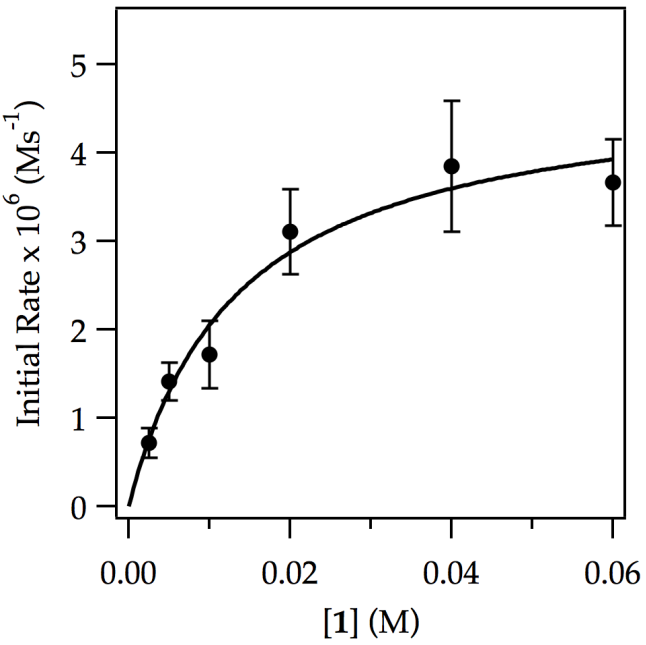


Figure A2.14. Plot of initial rate vs [ArH] (initial arene concentration) for the ortholithiation of **1** with LDA (0.050 M) in THF (12.2 M) at –78 °C as measured by IR spectroscopy. The curve depicts an unweighted least-squares fit to a first-order saturation function: $-\Delta[\mathrm{ArH}]/\Delta t\,|_{t=0} = (a[\mathrm{ArH}])/(1 + b[\mathrm{ArH}])$. [$a = (3.6 \pm 0.7) \times 10^{-4}$, $b = (74 \pm 20)$]

[1] (M)	y_1 (M·s^{-1})	y_2 (M·s^{-1})
0.0025	8.37e-07	5.95e-07
0.005	1.56e-06	1.26e-06
0.01	1.45e-06	1.99e-06
0.02	2.77e-06	3.45e-06
0.04	3.32e-06	4.37e-06
0.06	4.01e-06	3.32e-06

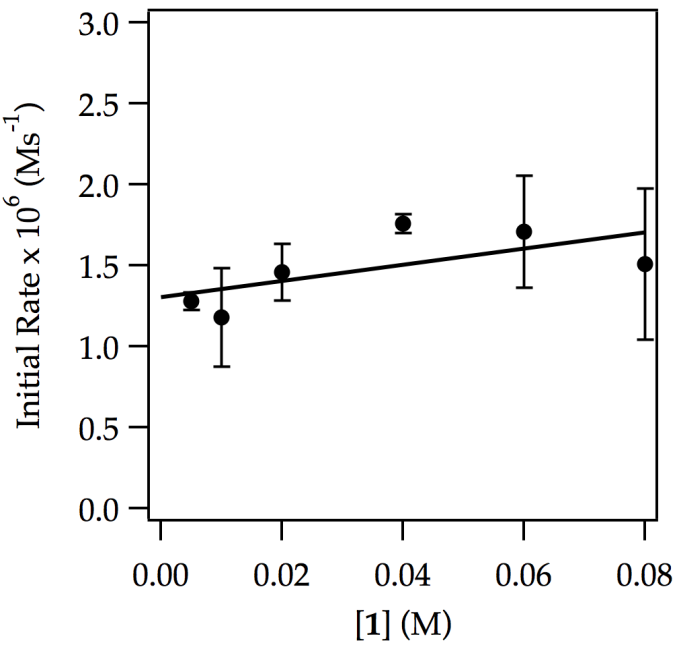


Figure A2.15. Plot of initial rate vs [ArH] (initial arene concentration) for the ortholithiation of **1** with LDA (0.20 M) in THF (3.05 M) at –78 °C as measured by IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\mathrm{ArH}] + b$. [$a = (5 \pm 3) \times 10^{-6}$, $b = (1.3 \pm 0.1) \times 10^{-6}$]

[1] (M)	y_1 ($M \cdot s^{-1}$)	y_2 ($M \cdot s^{-1}$)	y_3 ($M \cdot s^{-1}$)
0.005	1.30e-06	1.33e-06	1.22e-06
0.01	1.40e-06	9.67e-07	----------
0.02	1.58e-06	1.33e-06	----------
0.04	1.80e-06	1.72e-06	----------
0.06	1.95e-06	1.46e-06	----------
0.08	1.18e-06	1.84e-06	----------

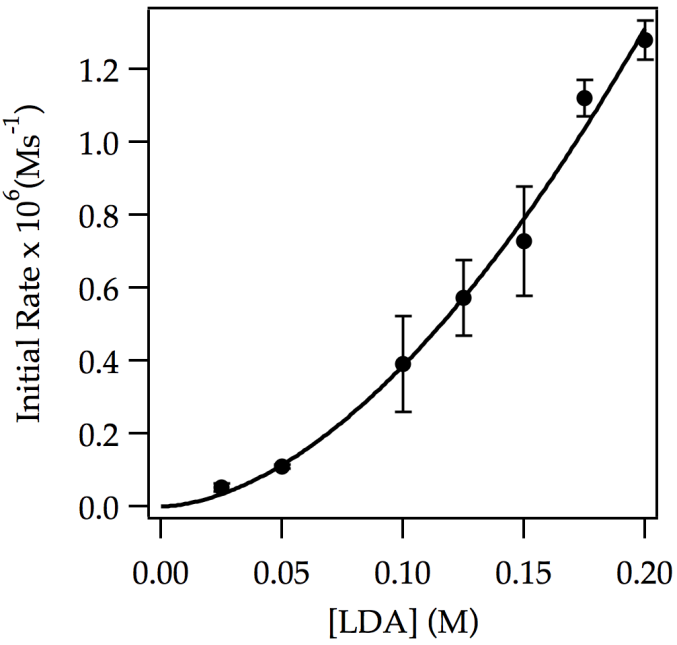


Figure A2.16. Plot of initial rate versus [LDA] in THF (3.05 M) for the ortholithiation of **1** (0.005 M) at –78 °C measured by IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\text{LDA}]^n$. [$a = (2.3 \pm 0.5) \times 10^{-5}$, $n = (1.8 \pm 0.1)$]

[LDA] (M)	y_1 ($M \cdot s^{-1}$)	y_2 ($M \cdot s^{-1}$)	y_3 ($M \cdot s^{-1}$)
0.025	5.99e-08	----------	4.31e-08
0.05	1.13e-07	----------	1.06e-07
0.10	3.04e-07	5.43e-07	3.27e-97
0.125	4.99e-07	----------	6.46e-07
0.150	5.60e-07	8.46e-07	7.76e-07
0.175	1.13e-06	1.17e-06	1.07e-06
0.20	1.30e-06	1.32e-06	1.22e-06

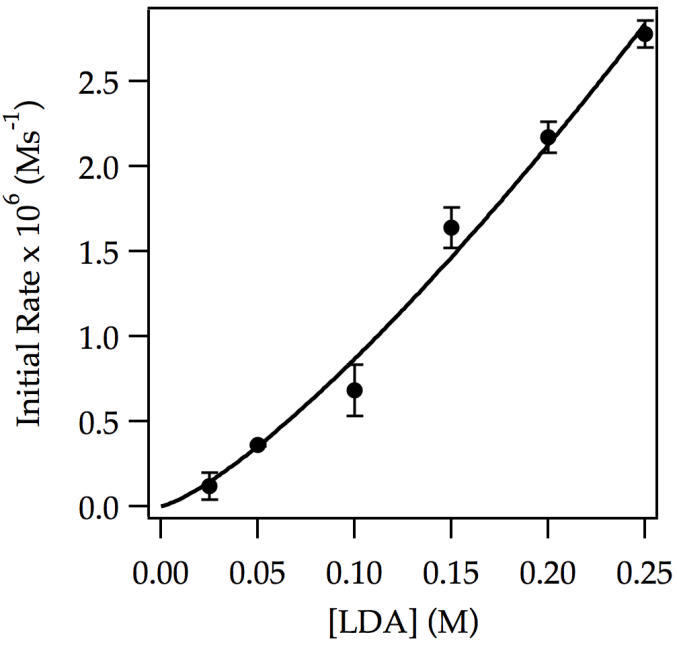


Figure A2.17. Plot of initial rate versus [LDA] in THF (6.10 M) for the ortholithiation of **1** (0.005 M) at –78 °C measured by IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\text{LDA}]^n$. [$a = (1.7 \pm 0.3) \times 10^{-5}$, $n = (1.3 \pm 0.1)$]

[LDA] (M)	y_1 (M·s^{-1})	y_2 (M·s^{-1})
0.025	1.76e-07	6.48e-08
0.05	3.53e-07	3.66e-07
0.10	7.87e-07	5.74e-07
0.15	1.72e-06	1.58e-06
0.20	2.23e-06	2.10e-06
0.25	2.83e-06	2.70e-06

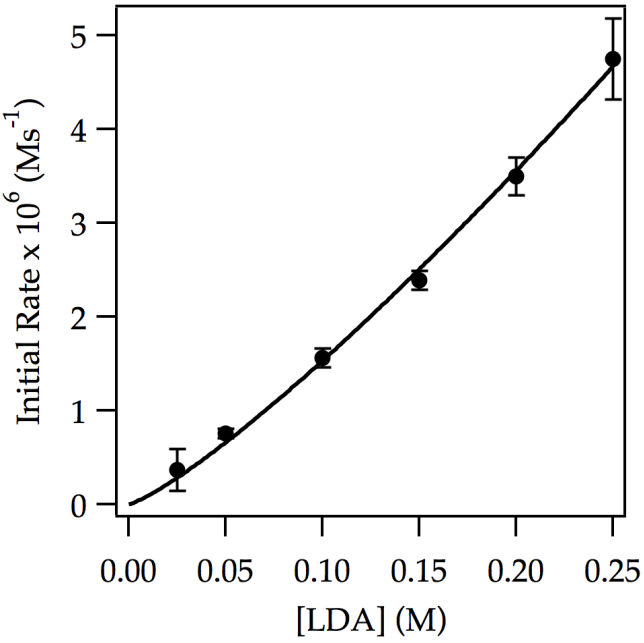


Figure A2.18. Plot of initial rate versus [LDA] in THF (9.15 M) for the ortholithiation of **1** (0.005 M) at –78 °C measured by IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\text{LDA}]^n$. [$a = (2.5 \pm 0.2) \times 10^{-5}$, $n = (1.22 \pm 0.05)$]

[LDA] (M)	y_1 (M·s^{-1})	y_2 (M·s^{-1})
0.025	5.27e-07	2.14e-07
0.05	7.17e-07	7.93e-07
0.10	1.64e-06	1.49e-06
0.15	2.47e-06	2.32e-06
0.20	3.65e-06	3.36e-06
0.25	5.06e-06	4.45e-06

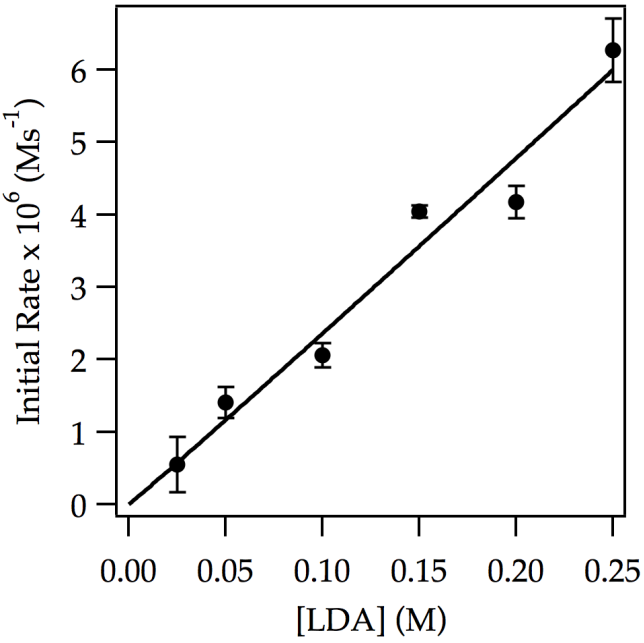


Figure A2.19. Plot of initial rate versus [LDA] in THF (12.2 M) for the ortholithiation of **1** (0.005 M) at –78 °C measured by IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\mathrm{LDA}]^n$. [$a = (2.5 \pm 0.6) \times 10^{-5}$, $n = (1.0 \pm 0.1)$]

[LDA] (M)	y_1 (M·s^{-1})	y_2 (M·s^{-1})
0.025	8.16e-07	2.75e-07
0.05	1.56e-06	1.26e-06
0.10	2.18e-06	1.94e-06
0.15	3.98e-06	4.10e-06
0.20	4.02e-06	4.33e-06
0.25	6.58e-06	5.96e-06

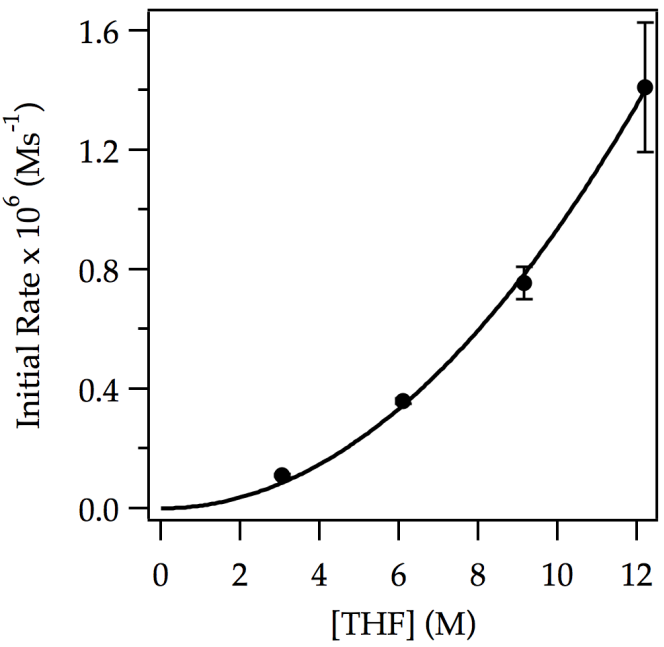


Figure A2.20. Plot of initial rate versus [THF] in hexanes for the ortholithiation of **1** (0.005 M) by LDA (0.050 M) at –78 °C measured by IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\mathrm{THF}]^n$. [$a = (9 \pm 2) \times 10^{-9}$, $n = (2.0 \pm 0.1)$]

[THF] (M)	y_1 (M·s^{-1})	y_2 (M·s^{-1})
12.2	1.56e-06	1.26e-06
9.15	7.17e-07	7.93e-07
6.10	3.53e-07	3.66e-07
3.05	1.13e-07	1.06e-07

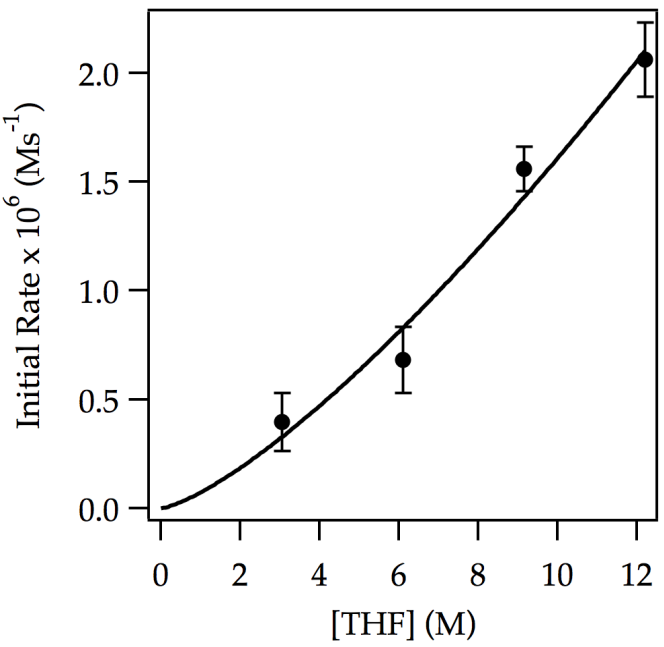


Figure A2.21. Plot of initial rate versus [THF] in hexanes for the ortholithiation of **1** (0.005 M) by LDA (0.10 M) at –78 °C measured by IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\mathrm{THF}]^n$. [$a = (7 \pm 4) \times 10^{-8}$, $n = (1.3 \pm 0.2)$]

[THF] (M)	y_1 (M·s^{-1})	y_2 (M·s^{-1})	y_3 (M·s^{-1})
12.2	2.18e-06	1.94e-06	----------
9.15	1.64e-06	1.49e-06	----------
6.10	7.87e-07	5.74e-07	----------
3.05	3.04e-07	5.43e-07	3.27e-07

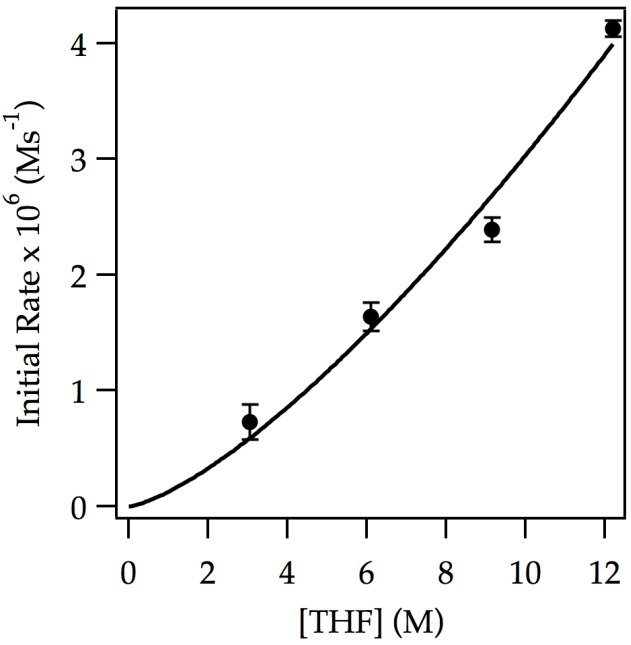


Figure A2.22. Plot of initial rate versus [THF] in hexanes for the ortholithiation of **1** (0.050 M) by LDA (0.15 M) at –78 °C measured by IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\mathrm{THF}]^n$. [$a = (1.3 \pm 0.6) \times 10^{-7}$, $n = (1.4 \pm 0.2)$]

[THF] (M)	y_1 ($M \cdot s^{-1}$)	y_2 ($M \cdot s^{-1}$)	y_3 ($M \cdot s^{-1}$)
12.2	3.98e-06	4.10e-06	----------
9.15	2.47e-06	2.32e-06	----------
6.10	1.72e-06	1.55e-06	----------
3.05	5.60e-07	8.46e-07	7.76e-07

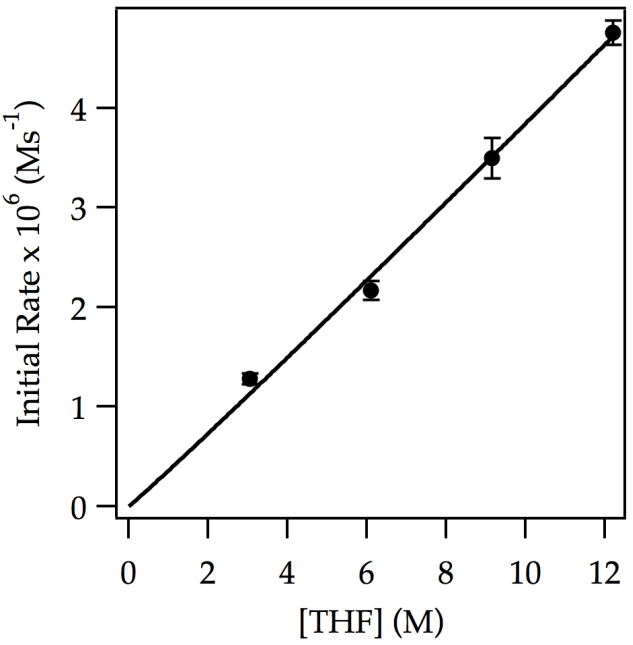


Figure A2.23. Plot of initial rate versus [THF] in hexanes for the ortholithiation of **1** (0.005 M) by LDA (0.20 M) at –78 °C measured by IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\mathrm{THF}]^n$. [$a = (3.58 \pm 0.60) \times 10^{-7}$, $n = (1.03 \pm 0.07)$]

[THF] (M)	y_1 (M·s^{-1})	y_2 (M·s^{-1})	y_3 (M·s^{-1})
12.2	4.02e-06	4.33e-06	----------
9.15	3.65e-06	3.36e-06	----------
6.10	2.23e-06	2.10e-06	----------
3.05	1.30e-06	1.33e-06	1.22e-06

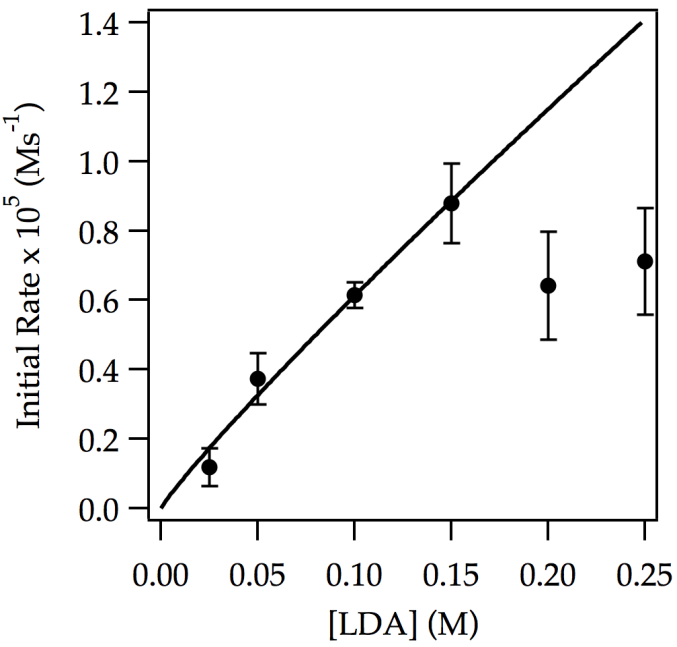


Figure A2.24. Plot of initial rate versus [LDA] in THF (12.2 M) for the ortholithiation of **1** (0.060 M) at –78 °C measured by IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\text{LDA}]^n$. [$a = (4 \pm 1) \times 10^{-5}$, $n = (0.9 \pm 0.1)$]
*The deviation at 0.20 and 0.25 was recurring and not understood. It has the appearance of a phase change (precipitation), but we don't visually see evidence for this hypothesis nor have we observed it previously.

[LDA] (M)	y_1 (M·s^{-1})	y_2 (M·s^{-1})
0.025	8.00e-07	1.56e-06
0.05	3.32e-06	4.37e-06
0.10	6.40e-06	5.88e-06
0.15	9.59e-06	7.96e-06
0.20	7.50e-06	5.31e-06
0.25	8.21e-06	6.03e-06

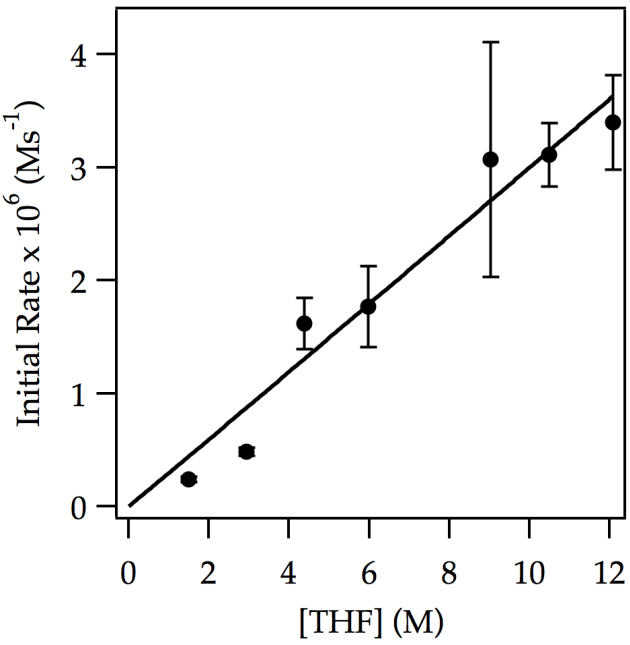


Figure A2.25. Plot of initial rate versus [THF] in hexanes for the ortholithiation of **1** (0.005 M) by LDA (0.20 M) at –78 °C measured by IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\mathrm{THF}]^n$. [$a = (3 \pm 1) \times 10^{-7}$, $n = (1.0 \pm 0.1)$]

[THF] (M)	y_1 (M·s^{-1})	y_2 (M·s^{-1})	y_3 (M·s^{-1})	y_4(M·s^{-1})
12.08	3.07e-06	3.21e-06	3.32e-06	4.01e-06
10.48	2.91e-06	3.31e-06	---------	---------
9.03	3.80e-06	2.33e-06	---------	---------
5.98	2.02e-06	1.51e-06	---------	---------
4.38	1.78e-06	1.46e-06	---------	---------
2.93	4.57e-07	5.05e-07	---------	---------
1.50	2.17e-07	2.54e-07	---------	---------

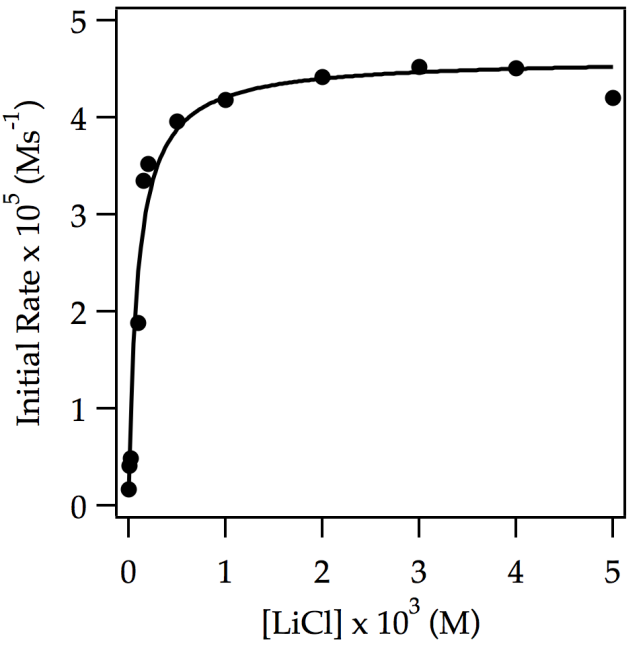


Figure A2.26. Plot of initial rate versus [LiCl] for the ortholithiation of **1** (0.05 M) by 0.10 M LDA in 12.2 M THF at –78 °C measured by IR spectroscopy. The curve depicts an unweighted least-squares fit to $-\Delta[ArH]/\Delta t\,|_{t=0} = (a[LiCl])/(1 + b[LiCl]) + c$. [$a = (4.5 \pm 0.8) \times 10^{-1}$, $b = (1.0 \pm 0.20) \times 10^{4}$, $c = (1.70) \times 10^{-6}$]

[LiCl x 10^3] (M)	y_1 ($M \cdot s^{-1}$)
0.00	1.70e-07
0.01	4.08e-06
0.02	4.87e-06
0.10	1.88e-06
0.15	3.35e-06
0.20	3.52e-06
0.50	3.96e-06
1.00	4.18e-05
2.00	4.42e-05
3.00	4.52e-05
4.00	4.51e-05
5.00	4.20e-05

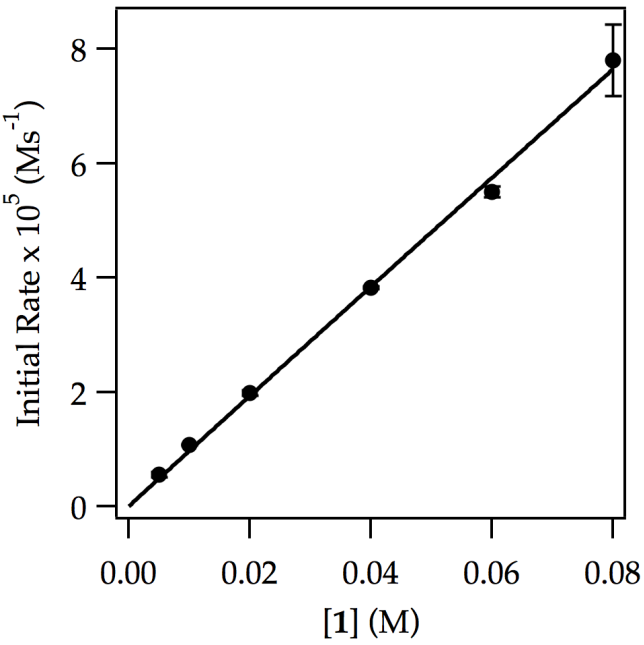


Figure A2.27. Plot of initial rate vs [ArH] (initial arene concentration) for the ortholithiation of **1** with LDA (0.10 M) in THF (12.2 M) with 1.0 mol% LiCl at –78 °C measured by IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\mathrm{ArH}]^n$. [$a = (9 \pm 1) \times 10^{-4}$, $n = (0.99 \pm 0.04)$]

[1] (M)	y_1 ($M \cdot s^{-1}$)	y_2 ($M \cdot s^{-1}$)
0.005	5.19e-06	5.89e-06
0.01	1.06e-05	1.08e-05
0.02	2.02e-05	1.95e-05
0.04	3.85e-05	3.81e-05
0.06	5.57e-05	5.44e-05
0.08	8.25e-05	7.36e-05

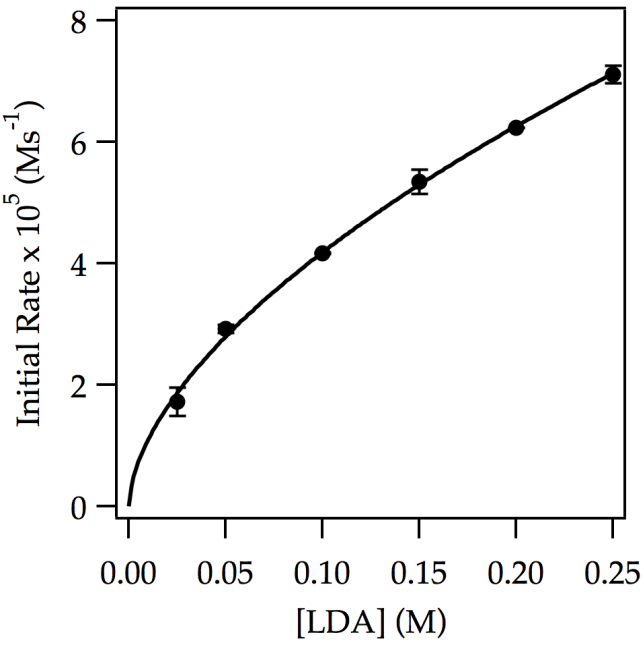


Figure A2.28. Plot of initial rate versus [LDA] in THF (12.2 M) for the ortholithiation of **1** (0.050 M) in the presence of 1.0 mol% LiCl at –78 °C measured by IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\text{LDA}]^n$. [$a = (1.60 \pm 0.05) \times 10^{-4}$, $n = 0.58 \pm 0.02$]

[LDA] (M)	y_1 ($M \cdot s^{-1}$)	y_2 ($M \cdot s^{-1}$)
0.025	1.88e-05	1.55e-05
0.05	2.96e-05	2.87e-05
0.10	4.17e-05	4.16e-05
0.15	5.49e-05	5.20e-05
0.20	6.23e-05	6.23e-05
0.25	7.00e-05	7.21e-05

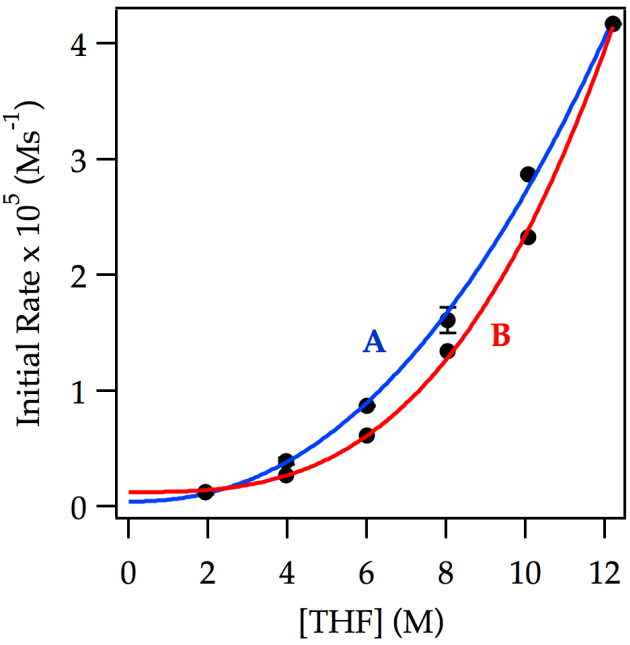


Figure A2.29. Plot of initial rate versus [THF] in Et_2O (curve A) and in hexanes (curve B) cosolvent for the ortholithiation of **1** (0.05 M) by LDA (0.10 M) in the presence of 1.0 mol% LiCl at –78 °C. The data was measured by IR spectroscopy. The curves depict unweighted least-squares fits to $y = a[\text{THF}]^n + b$. Curve A: $a = (1.8 \pm 0.3) \times 10^{-7}$, $n = 2.18 \pm 0.08$, $b = (0.0 \pm 0.1) \times 10^{-7}$. Curve B: $a = (2.3 \pm 0.7) \times 10^{-8}$, $n = 3.0 \pm 0.1$, $b = (1.2 \pm 0.4) \times 10^{-6}$.

[THF] (M)	y_1-A ($M \cdot s^{-1}$)	y_2-A ($M \cdot s^{-1}$)	y_3-B ($M \cdot s^{-1}$)
12.2	4.17e-05	4.17e-05	4.17e-05
10.07	2.88e-05	2.86e-05	2.33e-05
8.03	1.53e-05	1.69e-05	1.34e-05
6.00	8.74e-06	8.64e-06	6.15e-06
3.97	3.71e-06	4.15e-06	2.66e-06
1.93	1.12e-06	1.38e-06	1.24e-06

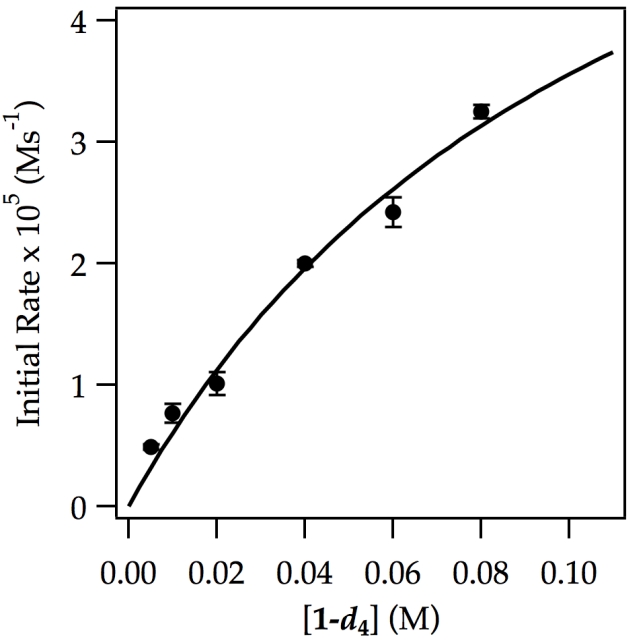


Figure A2.30. Plot of initial rate vs [ArD_4] (initial arene concentration) for the ortholithiation of **1-d_4** with LDA (0.10 M) in THF (12.2 M) with at –42 °C measured by ^{19}F NMR spectroscopy. The curve depicts an unweighted least-squares fit to a first-order saturation function: $-\Delta[ArD_4]/\Delta t\,|_{t=0} = (a[ArD_4])/(1 + b[ArD_4])$. [$a = (6 \pm 1) \times 10^{-4}$, $b = (8 \pm 4)$]

[**1-d_4**] (M)	y_1 ($M \cdot s^{-1}$)	y_2 ($M \cdot s^{-1}$)
0.005	4.74e-06	5.09e-06
0.01	7.10e-06	8.20e-06
0.02	1.08e-05	9.47e-06
0.04	2.02e-05	1.98e-05
0.06	2.51e-05	2.34e-05
0.08	3.21e-05	3.29e-05

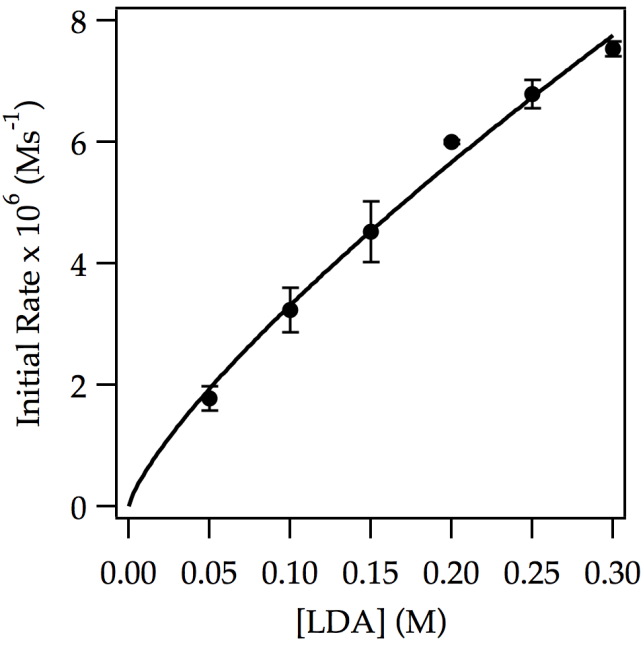


Figure A2.31. Plot of initial rate versus [LDA] in THF (12.2 M) for the ortholithiation of **1-*d*$_4$** (0.005 M) at –42 °C measured by ^{19}F NMR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\text{LDA}]^n$. [$a = (2.0 \pm 0.1) \times 10^{-5}$, $n = 0.77 \pm 0.04$]

[LDA] (M)	y_1 (M·s^{-1})	y_2 (M·s^{-1})
0.05	1.64e-06	1.92e-06
0.10	2.98e-06	3.50e-06
0.15	4.18e-06	4.88e-06
0.20	5.98e-06	6.03e-06
0.25	6.63e-06	6.95e-06
0.30	7.45e-06	7.63e-06

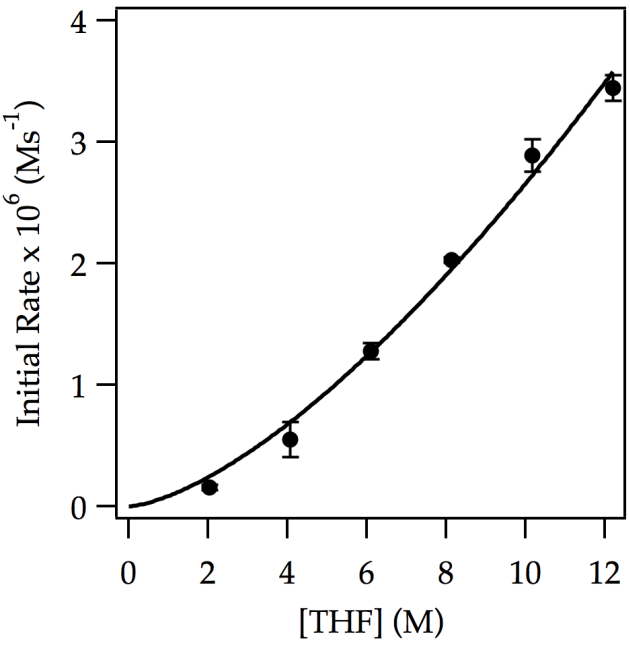


Figure A2.32. Plot of initial rate versus [THF] in Et_2O cosolvent for the ortholithiation of **1-*d*$_4$** (0.005 M) by LDA (0.10 M) at –42 °C measured by ^{19}F NMR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[THF]^n$. [$a = (8 \pm 2) \times 10^{-5}$, $n = (1.5 \pm 0.1)$]

[THF] (M)	y_1 (M·s^{-1})	y_2 (M·s^{-1})
12.2	3.52e-06	3.37e-06
10.17	2.99e-06	2.80e-06
8.13	2.04e-06	2.03e-06
6.10	1.23e-06	1.33e-06
4.07	0.45e-06	0.66e-06
2.03	0.17e-06	0.14e-06

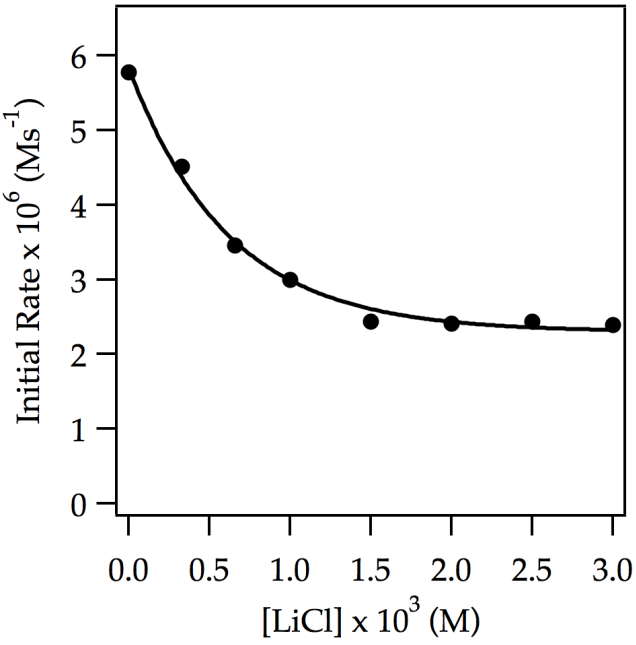


Figure A2.33. Plot of initial rate versus [LiCl] for the ortholithiation of **1-*d*$_4$** (0.005 M) by 0.30 M LDA in 12.2 M THF at –42 °C measured by ^{19}F NMR spectroscopy. The curve has no physical meaning.

[LiCl x 10^3] (M)	y_1 (M·s^{-1})
0.00	5.78e-06
0.33	4.51e-06
0.66	3.46e-06
1.00	3.00e-06
1.50	2.44e-06
2.00	2.41e-06
2.50	2.44e-06
3.00	2.39e-06

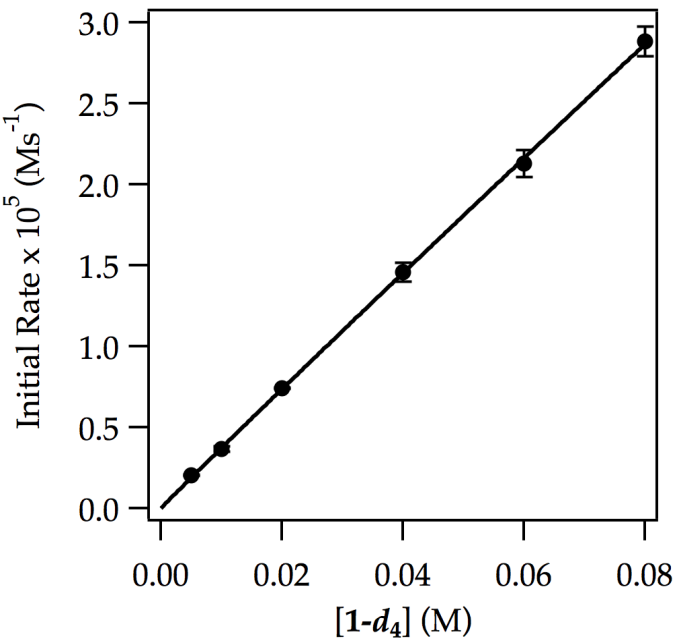


Figure A2.34. Plot of initial rate versus [ArD_4] for the ortholithiation of **1-d_4** (0.005 M) by LDA (0.10 M) in the presence of 3.0 mol% LiCl at –42 °C measured by ^{19}F NMR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[ArD_4]^n$. [a = (3.4 $\pm$ 0.1) x 10^{-4}, n = (0.98 $\pm$ 0.01)]

[**1-d_4**] (M)	y_1 ($M \cdot s^{-1}$)	y_2 ($M \cdot s^{-1}$)
0.005	2.03e-06	2.08e-06
0.01	3.79e-06	3.58e-06
0.02	7.46e-06	7.41e-06
0.04	1.50e-05	1.42e-05
0.06	2.19e-05	2.07e-05
0.08	2.82e-05	2.95e-05

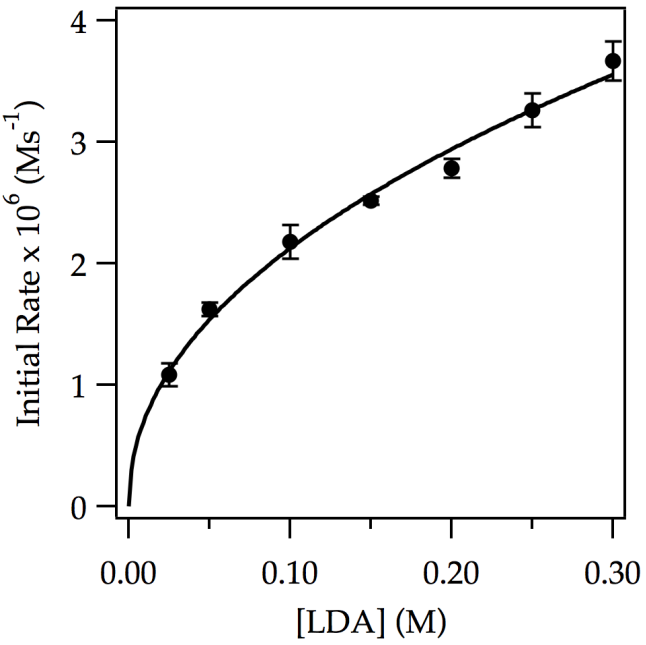


Figure A2.35. Plot of initial rate versus [LDA] in THF (12.2 M) for the ortholithiation of **1-*d*$_4$** (0.005 M) in the presence of 3.0 mol% LiCl at –42 °C measured by ^{19}F NMR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\text{LDA}]^n$. [a = (6.2 ± 0.3) x 10^{-6}, n = 0.46 ± 0.03]

[LDA] (M)	y_1 (M·s^{-1})	y_2 (M·s^{-1})
0.025	1.02e-06	1.15e-06
0.05	1.58e-06	1.66e-06
0.10	2.08e-06	2.28e-06
0.15	2.54e-06	2.49e-06
0.20	2.73e-06	2.84e-06
0.25	3.16e-06	3.36e-06
0.30	3.55e-06	3.78e-06

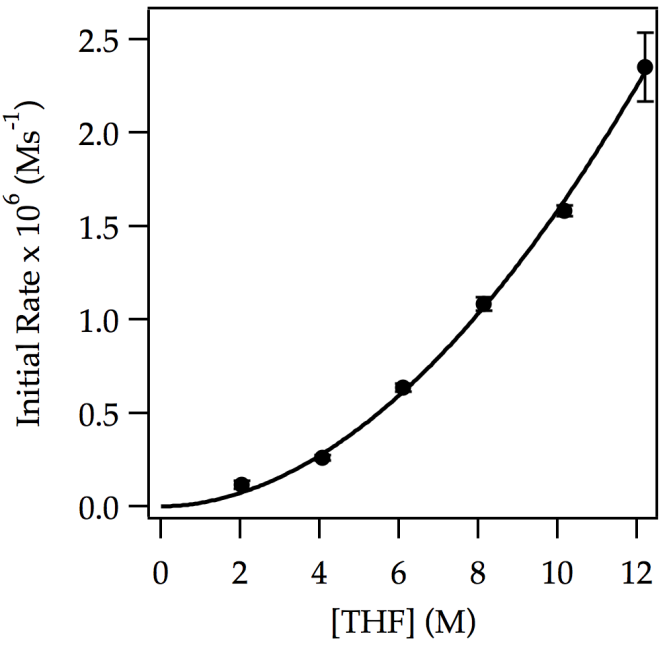


Figure A2.36. Plot of initial rate versus [THF] in Et_2O cosolvent for the ortholithiation of **1-*d*$_4$** (0.005 M) by LDA (0.10 M) in the presence of 3.0 mol% LiCl at –42 °C measured by ^{19}F NMR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[THF]^n$. [$a = (1.9 \pm 0.3) \times 10^{-8}$, $n = (1.92 \pm 0.07)$]

[THF] (M)	y_1 (M·s^{-1})	y_2 (M·s^{-1})
12.2	2.48e-06	2.22e-06
10.17	1.56e-06	1.60e-06
8.13	1.06e-06	1.11e-06
6.10	6.20e-07	6.50e-07
4.07	2.50e-07	2.70e-07
2.03	1.30e-07	1.00e-07

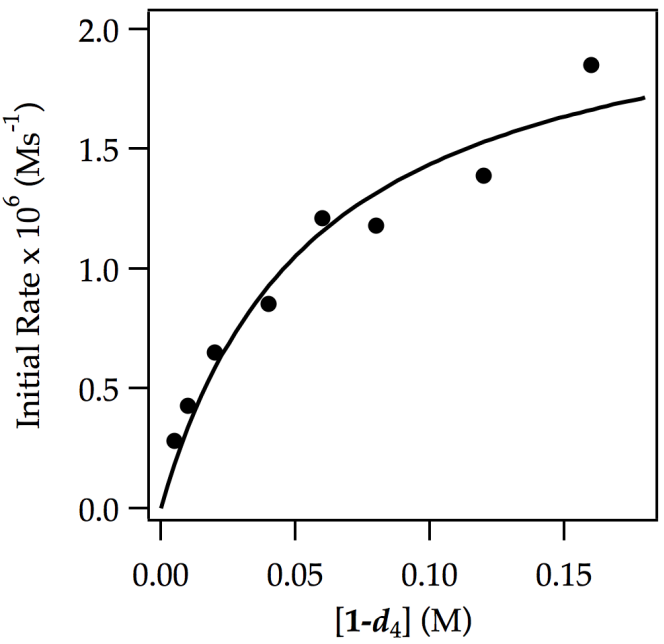


Figure A2.37. Plot of initial rate vs [ArD_4] (initial arene concentration) for the ortholithiation of **1-d_4** with LDA (0.10 M) in THF (12.2 M) with at –78 °C measured by IR spectroscopy. The curve depicts an unweighted least-squares fit to a first-order saturation function: $-\Delta[ArD_4]/\Delta t\,|_{t=0} = (a[ArD_4])/(1 + b[ArD_4])$. [$a = (3.9 \pm 0.8) \times 10^{-5}$, $b = (17 \pm 5)$]

[**1-d_4**] (M)	y_1 ($M \cdot s^{-1}$)
0.005	2.81e-07
0.01	4.28e-07
0.02	6.51e-07
0.04	8.53e-07
0.06	1.21e-06
0.08	1.18e-06
0.12	1.39e-06
0.16	1.85e-06

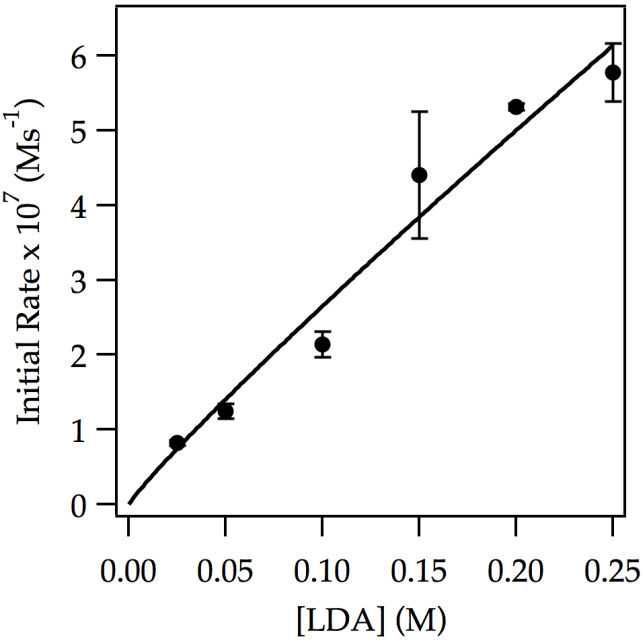


Figure A2.38. Plot of initial rate versus [LDA] in THF (12.2 M) for the ortholithiation of **1-*d*$_4$** (0.005 M) at –78 °C measured by IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\text{LDA}]^n$. [$a = (2.2 \pm 0.5) \times 10^{-6}$, $n = 0.9 \pm 0.1$]

[LDA] (M)	y_1 (M·s^{-1})	y_2 (M·s^{-1})
0.025	8.43e-06	7.98e-06
0.05	1.18e-06	1.32e-06
0.10	2.02e-06	2.26e-06
0.15	5.01e-06	3.81e-06
0.20	5.28e-06	5.35e-06
0.25	6.05e-06	5.50e-06

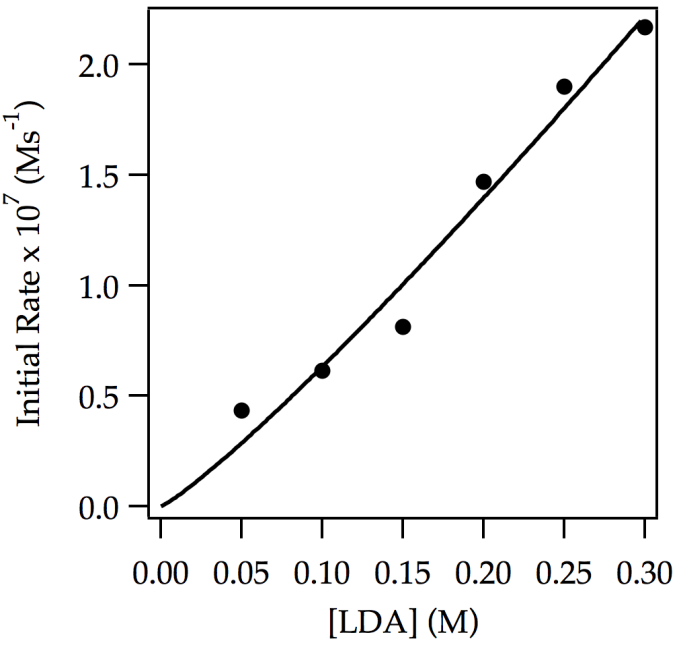


Figure A2.39. Plot of initial rate versus [LDA] in THF (3.05 M) for the ortholithiation of **1-*d*$_4$** (0.005 M) at –78 °C measured by IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\text{LDA}]^n$. [$a = (9 \pm 2) \times 10^{-7}$, $n = 1.1 \pm 0.1$]

[LDA] (M)	y_1 (M·s^{-1})
0.025	4.33e-08
0.05	6.13e-08
0.10	8.12e-08
0.15	1.47e-07
0.20	1.90e-07
0.25	2.17e-07

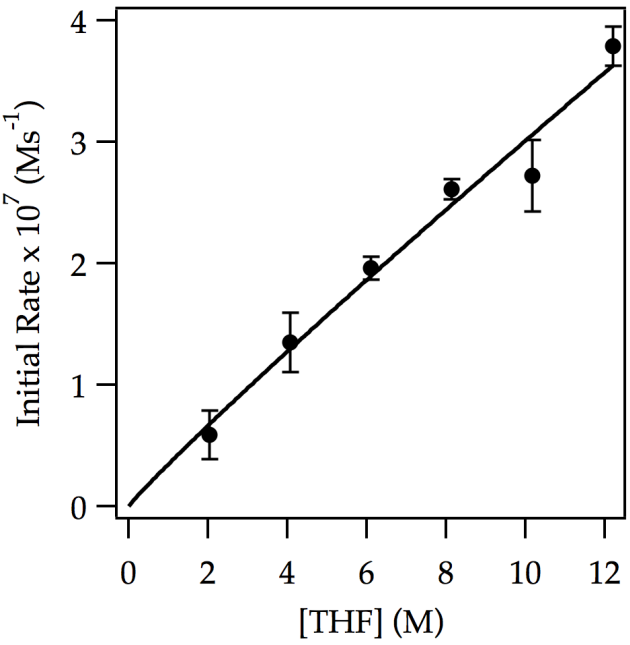


Figure A2.40. Plot of initial rate versus [THF] in hexanes for the ortholithiation of **1-d_4** (0.005 M) by LDA (0.10 M) at –78 °C measured by IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\text{THF}]^n$. [$a = (3.5 \pm 0.8) \times 10^{-8}$, $n = (0.94 \pm 0.09)$]

[THF] (M)	y_1 (M·s^{-1})	y_2 (M·s^{-1})
12.2	3.90e-07	3.67e-07
10.17	2.93e-07	2.51e-07
8.13	2.55e-07	2.67e-07
6.10	2.02e-07	1.89e-07
4.07	1.52e-07	1.17e-07
2.03	4.50e-08	7.31e-08

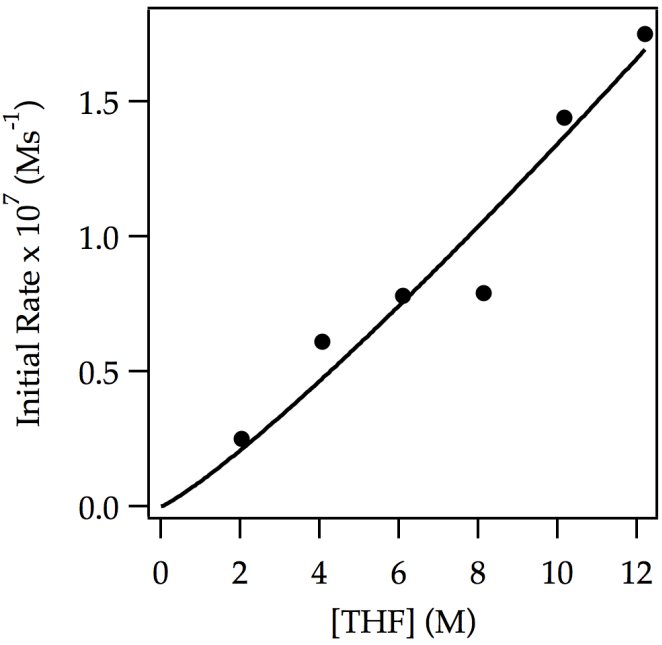


Figure A2.41. Plot of initial rate versus [THF] in hexanes for the ortholithiation of **1-d_4** (0.005 M) by LDA (0.10 M) at –78 °C measured by IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\text{THF}]^n$. [$a = (9 \pm 4) \times 10^{-9}$, $n = (1.2 \pm 0.2)$]

[THF] (M)	y_1 (M·s^{-1})
12.2	1.75e-07
10.17	1.44e-07
8.13	7.91e-08
6.10	7.79e-08
4.07	6.10e-08
2.03	2.51e-08

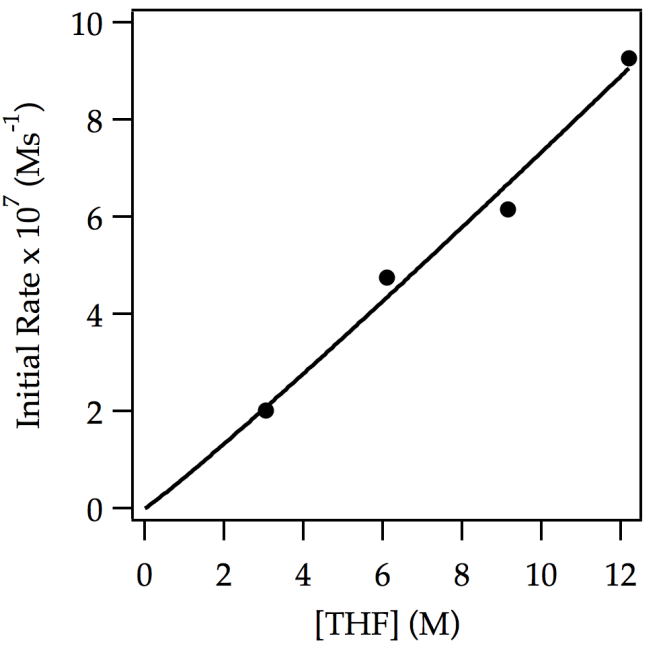


Figure A2.42. Plot of initial rate versus [THF] in hexanes for the ortholithiation of **1-d_4** (0.005 M) by LDA (0.10 M) at –78 °C measured by IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\text{THF}]^n$. [$a = (6 \pm 2) \times 10^{-8}$, $n = (1.1 \pm 0.1)$]

[THF] (M)	y_1 (M·s^{-1})
12.2	9.27e-07
9.15	6.15e-07
6.10	4.75e-07
3.05	2.01e-07

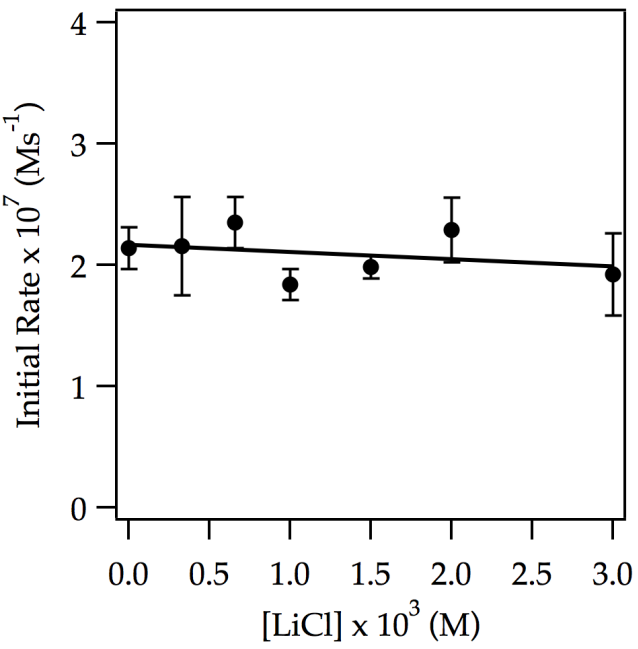


Figure A2.43. Plot of initial rate versus [LiCl] for the ortholithiation of **1-*d*$_4$** (0.005 M) by 0.10 M LDA in 12.2 M THF at –78 °C measured by IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a$[LiCl] + b. [$a = (6 \pm 8) \times 10^{-9}$, $b = (2.2 \pm 0.1) \times 10^{-7}$]

[LiCl] x 10^3 (M)	y_1 (M·s^{-1})	y_2 (M·s^{-1})
0.00	2.02e-07	2.26e-07
0.33	2.44e-07	1.87e-07
0.66	2.20e-07	2.50e-07
1.00	1.93e-07	1.75e-07
1.50	2.05e-07	1.92e-07
2.00	2.48e-07	2.10e-07
3.00	2.16e-07	1.68e-07

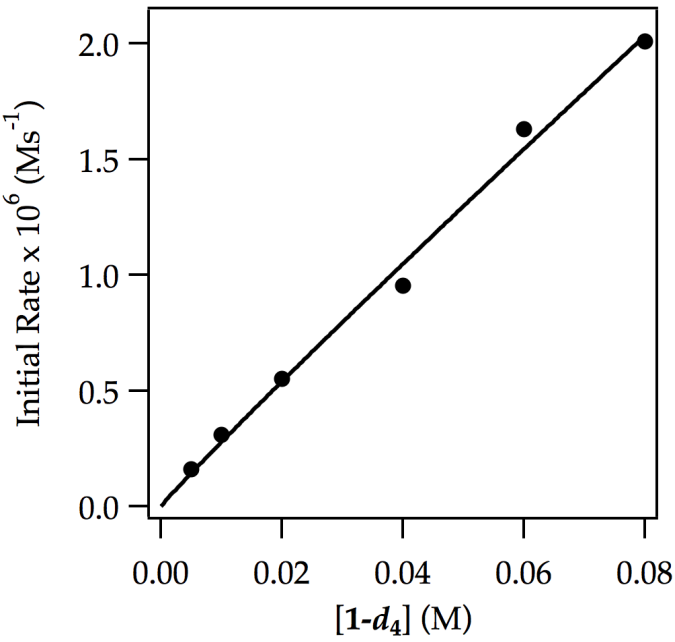


Figure A2.44. Plot of initial rate versus [ArD_4] for the ortholithiation of **1-d_4** (0.005 M) by LDA (0.10 M) in the presence of 2.0 mol% LiCl at –78 °C measured by IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[ArD_4]^n$. [$a = (2.3 \pm 0.4) \times 10^{-5}$, $n = (0.96 \pm 0.06)$]

[**1-d_4**] (M)	y_1 ($M \cdot s^{-1}$)
0.005	1.59e-07
0.01	3.08e-07
0.02	5.50e-07
0.04	9.53e-07
0.06	1.63e-06
0.08	2.01e-06

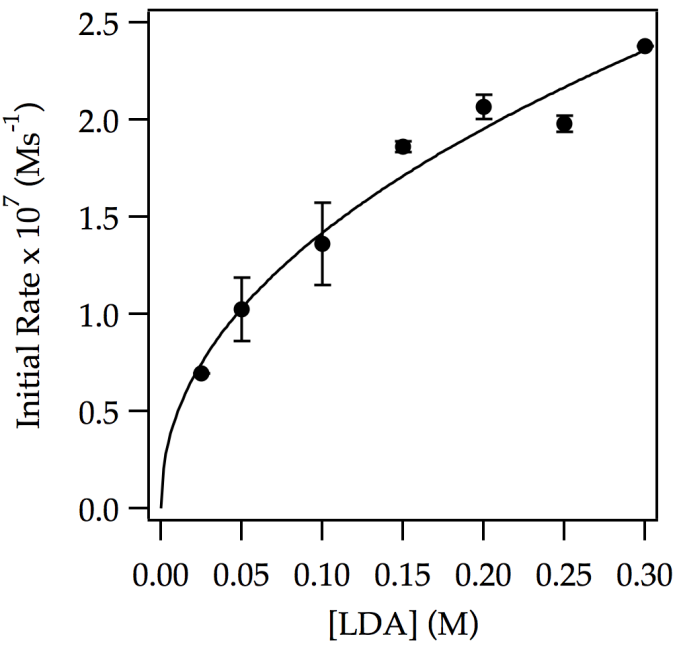


Figure A2.45. Plot of initial rate versus [LDA] in THF (12.2 M) for the ortholithiation of **1-d_4** (0.005 M) in the presence of 2.0 mol% LiCl at –78 °C measured by IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\text{LDA}]^n$. [$a = (4.1 \pm 0.4) \times 10^{-7}$, $n = 0.46 \pm 0.05$]

[LDA] (M)	y_1 (M·s^{-1})	y_2 (M·s^{-1})
0.025	6.96e-08	7.11e-06
0.05	9.08e-08	1.14e-07
0.10	1.51e-07	1.21e-07
0.15	1.84e-07	1.88e-07
0.20	2.02e-07	2.11e-07
0.25	2.01e-07	1.95e-07
0.30	2.38e-07	2.38e-07

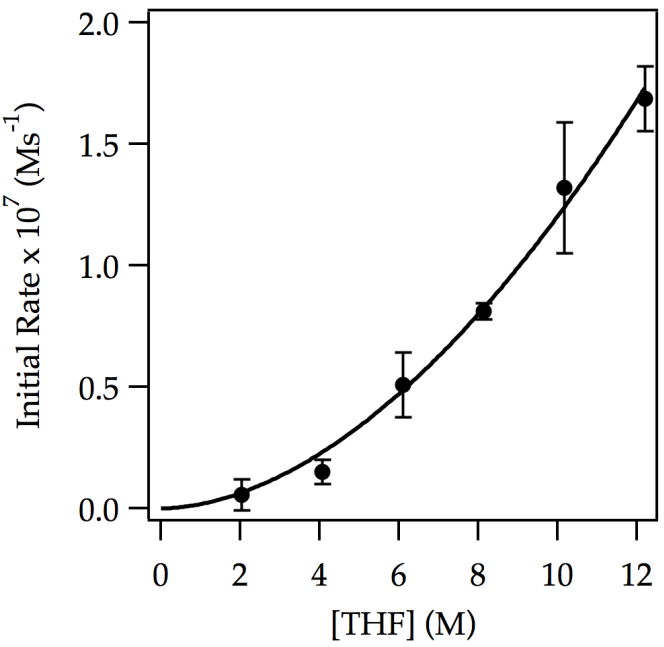


Figure A2.46. Plot of initial rate versus [THF] in Et_2O for the ortholithiation of **1-*d*$_4$** (0.005 M) by LDA (0.10 M) in the presence of 2.0 mol% LiCl at –78 °C measured by IR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a[\text{THF}]^n$. [a = (1.8 $\pm$ 0.5) x 10^{-9}, n = (1.8 $\pm$ 0.1)]

[THF] (M)	y_1 (M·s^{-1})	y_2 (M·s^{-1})
12.2	1.78e-07	1.59e-07
10.17	1.51e-07	1.13e-07
8.13	7.88e-08	8.36e-08
6.10	6.03e-08	4.16e-08
4.07	1.85e-08	1.16e-08
2.03	1.01e-08	9.20e-09

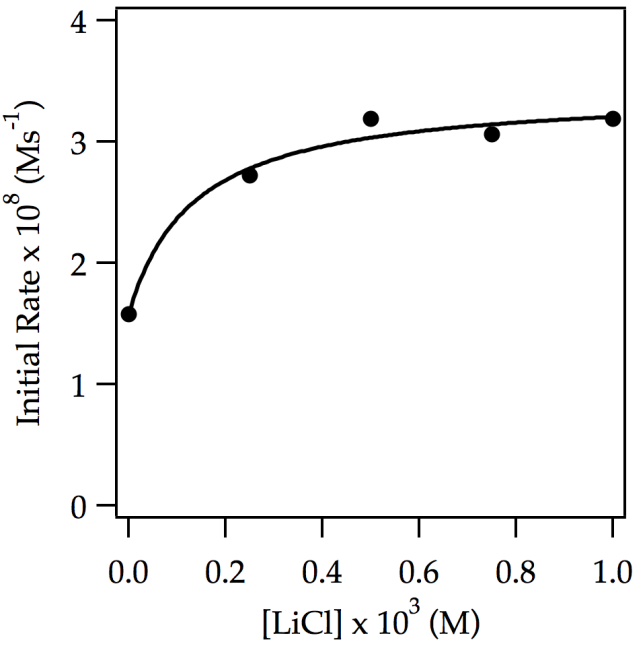


Figure A2.47. Plot of initial rate versus [LiCl] for the ortholithiation of **1-*d*$_4$** (0.005 M) by 0.10 M LDA in 12.2 M THF at –90 °C measured by IR spectroscopy. The curve depicts an unweighted least-squares fit to $-\Delta[\mathrm{ArD}]/\Delta t\,|_{t=0} = (a[\mathrm{LiCl}])/(1 + b[\mathrm{LiCl}]) + c$. [$a = (1.4 \pm 0.5) \times 10^{-7}$, $b = 7 \pm 3$, $c = 1.58 \times 10^{-8}$]

[LiCl x 10^3] (M)	y_1 (M·s^{-1})
0.00	1.58e-06
0.33	2.72e-06
0.66	3.19e-06
1.00	3.06e-06
1.50	3.19e-06

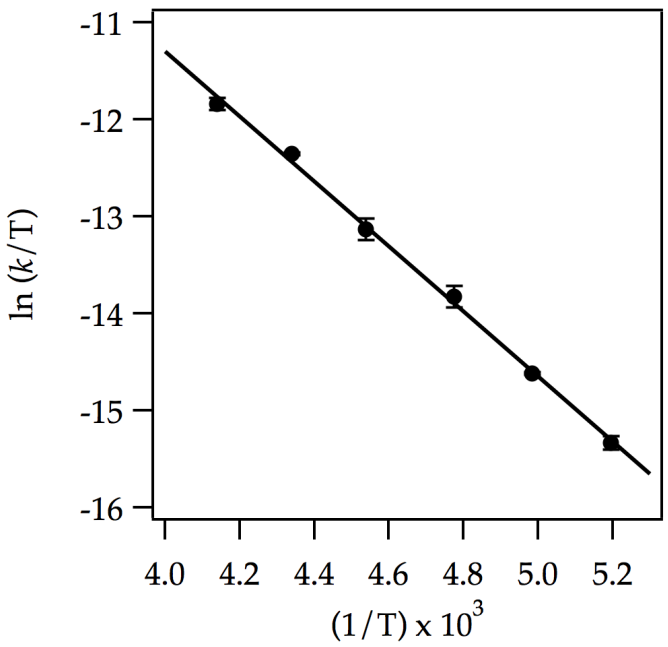
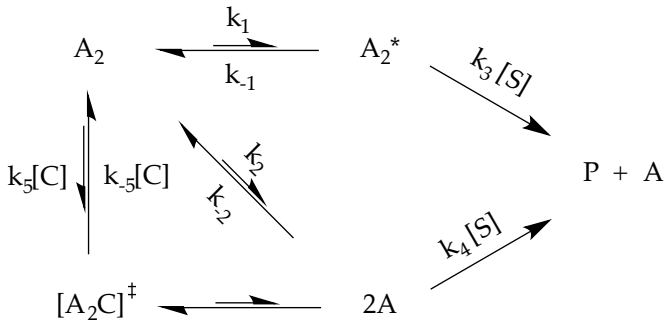


Figure A2.48. Plot of ln(k/T) versus (1/T) for the ortholithiation of **1-d_4** (0.005 M) by LDA (0.10 M) in THF (12.2 M) at various temperatures measured by ^{19}F NMR spectroscopy. The curve depicts an unweighted least-squares fit to $y = a(1/T) + b$. [a = -(3.35 $\pm$ 0.08) x 10^3, b = (2.1 $\pm$ 0.4)]. Fit corresponds to $\Delta H^{\ddagger}$ = (6.6 $\pm$ 0.2) kcal/mol and $\Delta S^{\ddagger}$ = (-43 $\pm$ 8) cal/(mol·K).

Temperature (K)	k_1(M^{-2}·s^{-1})	k_2 (M^{-2}·s^{-1})
241.55	1.82e-03	1.67e-03
230.45	1.01e-03	9.85e-03
220.35	4.03e-04	4.74e-04
209.45	2.14e-04	1.92e-04
200.65	8.92e-05	9.08e-05
192.45	4.44e-05	4.03e-05

Scheme A2.1. Scheme of dimer- and monomer-based lithations.



The system of differential equations that describes this mechanism follows.

$$\frac{d[\mathrm{A}_2]}{dt} = -k_1[\mathrm{A}_2] + k_{-1}[\mathrm{A}_2^*] - (k_2 + k_5[\mathrm{C}])[\mathrm{A}_2] + (k_{-2} + k_{-5}[\mathrm{C}])[\mathrm{A}]^2$$

$$\frac{d[\mathrm{A}_2^*]}{dt} = k_1[\mathrm{A}_2] - k_{-1}[\mathrm{A}_2^*] - k_3[\mathrm{A}_2^*][\mathrm{S}]$$

$$\frac{d[\mathrm{A}]}{dt} = 2(k_2 + k_5[\mathrm{C}])[\mathrm{A}_2] - 2(k_{-2} + k_{-5}[\mathrm{C}])[\mathrm{A}]^2 - k_4[\mathrm{A}][\mathrm{S}] + k_3[\mathrm{A}_2^*][\mathrm{S}]$$

$$\frac{d[\mathrm{S}]}{dt} = -k_3[\mathrm{A}_2^*][\mathrm{S}] - k_4[\mathrm{A}][\mathrm{S}]$$

$$\frac{d[\mathrm{P}]}{dt} = k_3[\mathrm{A}_2^*][\mathrm{S}] + k_4[\mathrm{A}][\mathrm{S}]$$

In order that the system conforms to mass balance both in the absence and presence of catalyst C, it must be that

$$k_{-5} = k_5 \frac{k_{-2}}{k_2}$$

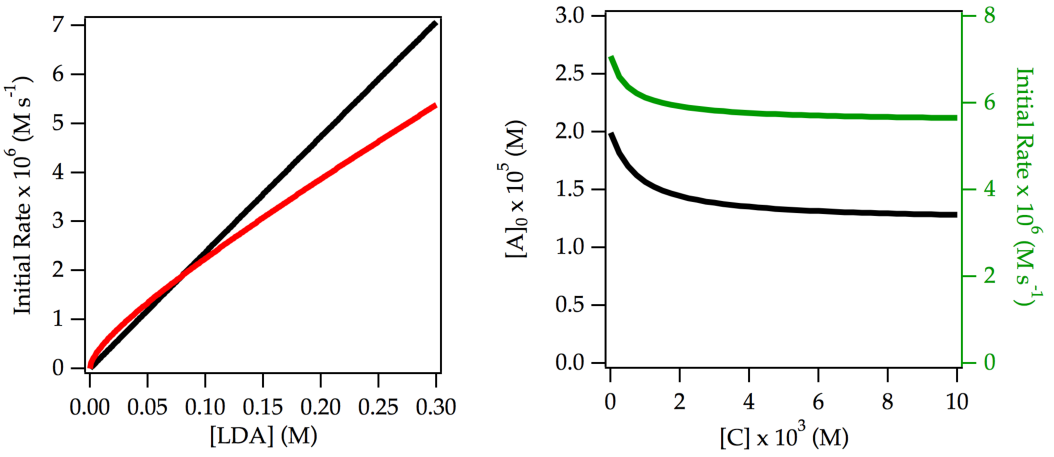


Figure A2.49. (a) Plot of initial rate vs [LDA]; (b) Plot of steady state $[A]_0$ and initial rate vs [C] at [LDA] = 0.30 M. The traces are produced by numerical integration of the differential equations described in Scheme 1 with $k_1 = 0.0005$, $k_{-1} = 0.5$, $k_2 = 1 \times 10^{-10}$, $k_{-2} = 0.1$, $k_3 = 5$, $k_4 = 30$, $k_5 = 0.005$, and $[S]_0 = 0.005$ M. In plot (a), the black trace corresponds to [C] = 0, and the red trace corresponds to saturation in catalyst. Fitting the traces in plot (a) to $y = a[\text{LDA}]^n$ provides observed orders (black trace: $a = 2.34 \times 10^{-5}$, $n = 0.99$; red trace: $a = 1.37 \times 10^{-5}$, $n = 0.78$).

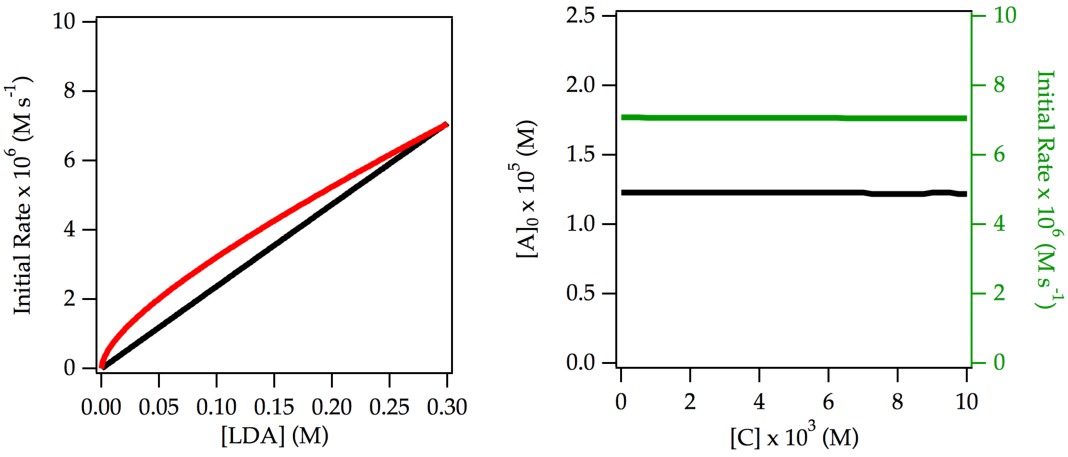


Figure A2.50. (a) Plot of initial rate vs [LDA]; (b) Plot of steady state $[A]_0$ and initial rate vs [C] at [LDA] = 0.30 M. The traces are produced by numerical integration of the differential equations described in Scheme 1 with $k_1 = 0.0005$, $k_{-1} = 0.5$, $k_2 = 1 \times 10^{-10}$, $k_{-2} = 0.1$, $k_3 = 5$, $k_4 = 58$, $k_5 = 0.005$, and $[S]_0 = 0.005$ M. In plot (a), the black trace corresponds to [C] = 0, and the red trace corresponds to saturation in catalyst. Fitting the traces in plot (a) to $y = a[\text{LDA}]^n$ provides observed orders (black trace: $a = 2.35 \times 10^{-5}$, $n = 1.00$; red trace: $a = 1.63 \times 10^{-5}$, $n = 0.70$).

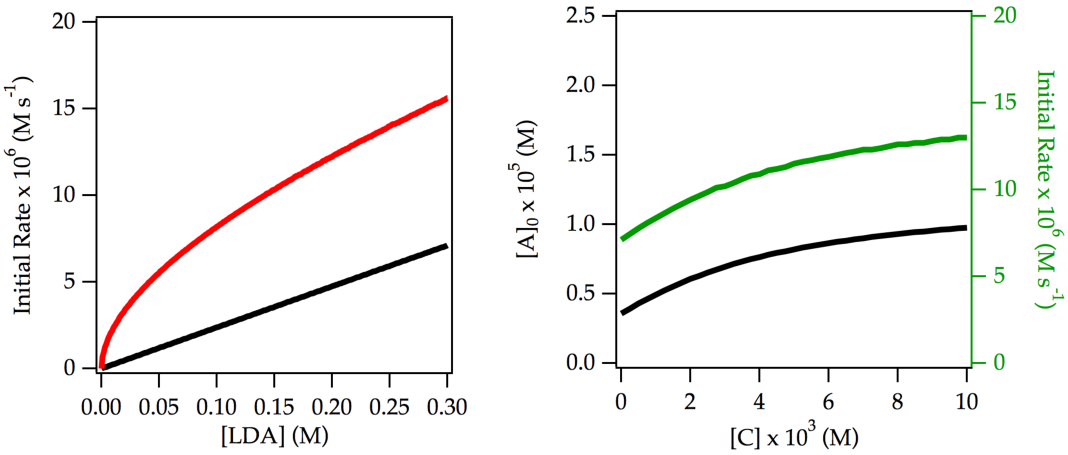


Figure A2.51. (a) Plot of initial rate vs [LDA]; (b) Plot of steady state $[A]_0$ and initial rate vs [C] at [LDA] = 0.30 M. The traces are produced by numerical integration of the differential equations described in Scheme 1 with $k_1 = 0.0005$, $k_{-1} = 0.5$, $k_2 = 1 \times 10^{-10}$, $k_{-2} = 0.1$, $k_3 = 5$, $k_4 = 200$, $k_5 = 0.005$, and $[S]_0 = 0.005$ M. In plot (a), the black trace corresponds to [C] = 0, and the red trace corresponds to saturation in catalyst. Fitting the traces in plot (a) to $y = a[\text{LDA}]^n$ provides observed orders (black trace: $a = 2.36 \times 10^{-5}$, $n = 1.00$; red trace: $a = 3.11 \times 10^{-5}$, $n = 0.58$).

Derivations

Derivation A2.1. Derivation of steady-state rate expressions**:**

Considering the mechanism depicted in Scheme 1, the rate of consumption of substrate is given by

$$-\frac{d[\mathrm{S}]}{dt} = k_3[\mathrm{A}_2^*][\mathrm{S}] + k_4[\mathrm{A}][\mathrm{S}] \tag{1}$$

Use the mechanism to derive steady-state concentrations of A_2^* and A.

For open dimer A_2^*,

$$\frac{d[\mathrm{A}_2^*]}{dt} = k_1[\mathrm{A}_2] - k_{-1}[\mathrm{A}_2^*] - k_3[\mathrm{A}_2^*][\mathrm{S}] = 0$$

$$[\mathrm{A}_2^*] = \frac{k_1[\mathrm{A}_2]}{k_{-1} + k_3[\mathrm{S}]} \tag{2}$$

For monomer A,

$$\frac{d[\mathrm{A}]}{dt} = 2(k_2 + k_5[\mathrm{C}])[\mathrm{A}_2] - 2(k_{-2} + k_5\frac{k_{-2}}{k_2}[\mathrm{C}])[\mathrm{A}]^2 - k_4[\mathrm{A}][\mathrm{S}] + k_3[\mathrm{A}_2^*][\mathrm{S}] = 0 \tag{3}$$

Let $(k_2 + k_5[\mathrm{C}]) = x$ and $(k_{-2} + k_5\frac{k_{-2}}{k_2}[\mathrm{C}]) = y$ so that

$$[\mathrm{A}] = \frac{-k_4[\mathrm{S}] + \sqrt{(k_4[\mathrm{S}])^2 + 8y(2x[\mathrm{A}_2] + k_3[A_2^*][\mathrm{S}])}}{4y} \tag{4}$$

Insert equations (2) and (4) into (1) to give the rate of consumption of substrate as a function of the observables and microscopic rate constants:

$$-\frac{d[\mathrm{S}]}{dt} = \frac{k_1k_3[\mathrm{A}_2][\mathrm{S}]}{k_{-1} + k_3[\mathrm{S}]} + k_4\left(\frac{-k_4[\mathrm{S}] + \sqrt{(k_4[\mathrm{S}])^2 + 8y\left(2x[\mathrm{A}_2] + \frac{k_1k_3[\mathrm{A}_2][\mathrm{S}]}{k_{-1} + k_3[\mathrm{S}]}\right)}}{4y}\right)[\mathrm{S}] \tag{5}$$

Analysis of limiting cases:

No catalyst:

In the absence of catalyst, $x = k_2$ and $y = k_{-2}$, so equation (5) becomes

$$-\frac{d[\mathrm{S}]}{dt} = \frac{k_1 k_3 [\mathrm{A}_2][\mathrm{S}]}{k_{-1} + k_3[\mathrm{S}]} + k_4 \left(\frac{-k_4[\mathrm{S}] + \sqrt{(k_4[\mathrm{S}])^2 + 8k_{-2}\left(2k_2[\mathrm{A}_2] + \frac{k_1 k_3 [\mathrm{A}_2][\mathrm{S}]}{k_{-1} + k_3[\mathrm{S}]}\right)}}{4k_{-2}} \right) [\mathrm{S}]$$

Assume that the basal deaggregation to monomer is negligible relative to the contribution from dimer metalation, i.e. $2k_2[\mathrm{A}_2] << \frac{k_1 k_3 [\mathrm{A}_2][\mathrm{S}]}{k_{-1} + k_3[\mathrm{S}]}$, so that

$$-\frac{d[\mathrm{S}]}{dt} = \frac{k_1 k_3 [\mathrm{A}_2][\mathrm{S}]}{k_{-1} + k_3[\mathrm{S}]} + k_4 \left(\frac{-k_4[\mathrm{S}] + \sqrt{(k_4[\mathrm{S}])^2 + 8k_{-2}\frac{k_1 k_3 [\mathrm{A}_2][\mathrm{S}]}{k_{-1} + k_3[\mathrm{S}]}}}{4k_{-2}} \right) [\mathrm{S}] \qquad (6)$$

An altogether different route to a similar end is to assume that the contribution of basal deaggregation to the monomer is negligible in equation (3) by way of $2(k_2 + k_5[\mathrm{C}])[\mathrm{A}_2] - 2(k_{-2} + k_5 \frac{k_{-2}}{k_2}[\mathrm{C}])[\mathrm{A}]^2 << -k_4[\mathrm{A}][\mathrm{S}] + k_3[\mathrm{A}_2^*][\mathrm{S}]$, so that equation (3) becomes

$$[\mathrm{A}] = \frac{k_3}{k_4}[\mathrm{A}_2^*]$$

and therefore the rate law for consumption of substrate, equation (1), becomes

$$-\frac{d[\mathrm{S}]}{dt} = 2\frac{k_1 k_3 [\mathrm{A}_2][\mathrm{S}]}{k_{-1} + k_3[\mathrm{S}]} \qquad (7)$$

Full catalyst saturation:

With [C]>>0, $x \approx k_5[\mathrm{C}]$ and $y \approx k_5 \frac{k_{-2}}{k_2}[\mathrm{C}]$, so equation (5) becomes

$$-\frac{d[\mathrm{S}]}{dt} = \frac{k_1 k_3[\mathrm{A}_2][\mathrm{S}]}{k_{-1} + k_3[\mathrm{S}]} + k_4 \left(\frac{-k_4[\mathrm{S}] + \sqrt{(k_4[\mathrm{S}])^2 + 8k_5 \frac{k_{-2}}{k_2}[\mathrm{C}]\left(2k_5[\mathrm{C}][\mathrm{A}_2] + \frac{k_1 k_3[\mathrm{A}_2][\mathrm{S}]}{k_{-1} + k_3[\mathrm{S}]}\right)}}{4k_5 \frac{k_{-2}}{k_2}[\mathrm{C}]} \right)[\mathrm{S}]$$

Noting that $2k_5[\mathrm{C}][\mathrm{A}_2] >> \frac{k_1 k_3[\mathrm{A}_2][\mathrm{S}]}{k_{-1} + k_3[\mathrm{S}]}$ gives

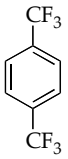
$$-\frac{d[\mathrm{S}]}{dt} = \frac{k_1 k_3[\mathrm{A}_2][\mathrm{S}]}{k_{-1} + k_3[\mathrm{S}]} + k_4 \left(\frac{-k_4[\mathrm{S}] + \sqrt{(k_4[\mathrm{S}])^2 + 16(k_5[\mathrm{C}])^2 \frac{k_{-2}}{k_2}[\mathrm{A}_2]}}{4k_5 \frac{k_{-2}}{k_2}[\mathrm{C}]} \right)[\mathrm{S}]$$

Given that the second term under the radical can grow indefinitely, i.e. $(k_4[\mathrm{S}])^2 << 16(k_5[\mathrm{C}])^2 \frac{k_{-2}}{k_2}[\mathrm{A}_2]$, one has

$$-\frac{d[\mathrm{S}]}{dt} = \frac{k_1 k_3[\mathrm{A}_2][\mathrm{S}]}{k_{-1} + k_3[\mathrm{S}]} + k_4 \left(\sqrt{\frac{k_2}{k_{-2}}[\mathrm{A}_2]} \right)[\mathrm{S}] \qquad (8)$$

Part 4: Computational Studies

A



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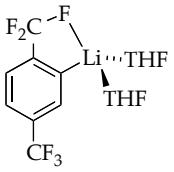

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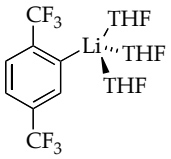

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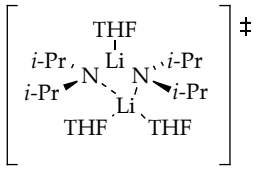

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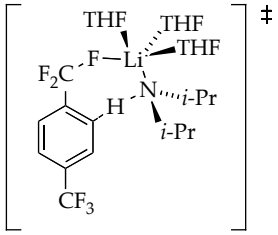

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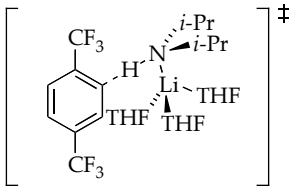

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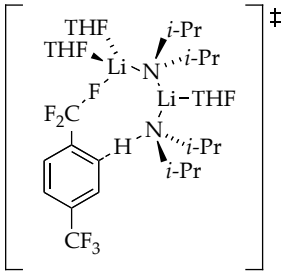

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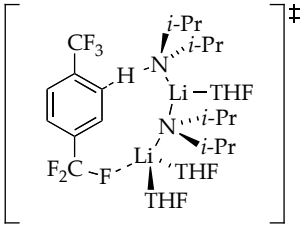

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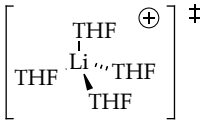

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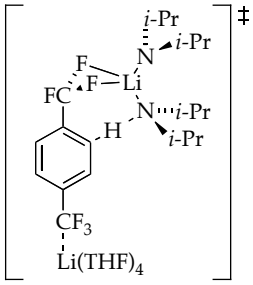
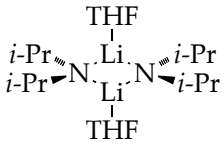
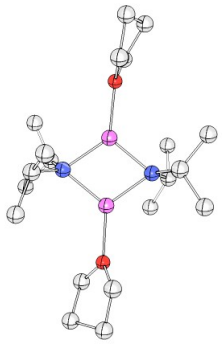


K

Table A2.1. Optimized geometries at B3LYP level of theory with 6-31G(d) basis set for the reactants at -78 °C with free energies (Hartrees) and cartesian coordinates (X, Y, Z) (Note: G_{MP2} includes single point MP2 corrections to B3LYP/6-31G(d) optimized structures).



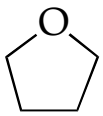


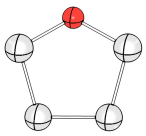
3
G = -1063.135501
G_{MP2} = -1059.937725

Atom	X	Y	Z	Atom	X	Y	Z
N	0	0	0	H	-0.940577	-3.291008	-1.825271
C	-0.215739	0.612452	1.318612	C	-2.275223	-4.680069	-0.904214
C	0.984066	1.381887	1.921761	H	-2.504256	-5.19534	-1.84738
H	1.212505	2.284952	1.34251	H	-2.310069	-5.431695	-0.105932
H	0.778689	1.697923	2.953722	H	-3.068237	-3.948858	-0.708955
H	1.882702	0.753584	1.932942	C	0.182248	-5.031842	-1.330903
C	-1.475882	1.513412	1.414833	H	0.292339	-5.788992	-0.544657
H	-1.662511	1.833942	2.448825	H	-0.066363	-5.560021	-2.261741
H	-1.371101	2.42064	0.807577	H	1.156355	-4.547171	-1.460089
H	-2.362674	0.977827	1.055352	O	2.890094	-2.114628	-0.276836
H	-0.400482	-0.231238	2.010144	C	3.52909	-2.599416	-1.47886
C	0.294364	0.950027	-1.075375	C	5.02417	-2.634817	-1.16185
H	-0.088612	1.959024	-0.838431	C	5.17113	-1.444535	-0.201398
C	1.804497	1.126678	-1.373756	C	3.871831	-1.516212	0.604784
H	1.981395	1.865835	-2.168777	H	3.498476	-0.537145	0.916021
H	2.34994	1.453509	-0.48314	H	3.974185	-2.15728	1.489104
H	2.239835	0.172163	-1.698457	H	5.220904	-0.505023	-0.763636
C	-0.411394	0.5173	-2.373716	H	6.058482	-1.507597	0.435346
H	-0.126925	-0.512599	-2.63791	H	5.642686	-2.546191	-2.059904
H	-1.500227	0.542654	-2.246722	H	5.286266	-3.571958	-0.656761
H	-0.152964	1.159869	-3.226138	H	3.104737	-3.577461	-1.718479
Li	-1.462938	-1.378687	-0.078227	H	3.309896	-1.905896	-2.301885
Li	0.922415	-1.791464	0.023104	O	-3.431996	-1.14847	-0.425881
N	-0.560416	-3.145972	0.199308	C	-4.064444	-1.141073	-1.728456
C	-0.522816	-3.873798	1.472891	C	-5.569847	-1.045588	-1.463002
H	-0.46329	-4.963706	1.307703	C	-5.702828	-1.732285	-0.094683
C	0.733203	-3.499287	2.286203	C	-4.431019	-1.269572	0.614429
H	0.750947	-2.417347	2.490329	H	-4.055787	-1.97603	1.358533
H	0.766551	-4.00792	3.259096	H	-4.566131	-0.288873	1.089082
H	1.643109	-3.758699	1.732093	H	-5.700242	-2.822319	-0.210242

Table A2.1 (Continued).

C	-1.771806	-3.638553	2.355096	H	-6.60968	-1.447449	0.44699
H	-1.728216	-4.20067	3.299517	H	-6.159851	-1.526531	-2.248671
H	-1.859018	-2.571836	2.60852	H	-5.883179	0.002828	-1.396109
H	-2.683407	-3.937095	1.82658	H	-3.667369	-0.297566	-2.299805
C	-0.893909	-3.980504	-0.960233	H	-3.802081	-2.073238	-2.243737

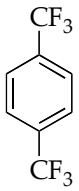


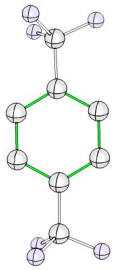


A
G = -232.349367
G_{MP2} = -231.6694404

Atom	X	Y	Z
C	0	0	0
O	1.132807	-0.739653	-0.442032
C	2.264796	-0.012388	0.019216
C	1.92285	1.47444	-0.210686
C	0.368847	1.489728	-0.185167
H	-0.032338	2.108191	0.623792
H	2.365524	2.11958	0.5546
H	2.296315	1.80941	-1.183111
H	2.436349	-0.210295	1.091379
H	3.13745	-0.361827	-0.539569
H	-0.860576	-0.323589	-0.591979
H	-0.206691	-0.218661	1.061467
H	-0.031366	1.878296	-1.126381

Table A2.1 (Continued).

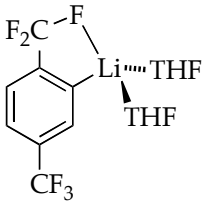


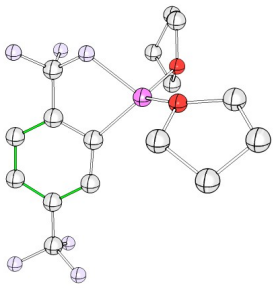


B
G = -906.232925
G_{MP2} = -903.9700518

Atom	X	Y	Z
C	0	0	0
C	-1.505925	0.032078	-0.000082
C	-2.199386	1.240823	-0.000053
C	-3.59506	1.240823	-0.000003
C	-4.288522	0.032078	0.000028
C	-3.591787	-1.182468	0.000001
C	-2.202658	-1.182468	-0.000058
H	-1.656905	-2.120819	-0.00011
H	-4.137541	-2.120819	0.000027
C	-5.794446	0	0.000016
F	-6.272325	-0.650206	-1.08545
F	-6.333334	1.236442	0.000523
F	-6.272317	-0.651108	1.084947
H	-4.139698	2.178082	0.000014
H	-1.654749	2.178082	-0.000084
F	0.477838	-0.649702	1.085789
F	0.477912	-0.651611	-1.084607
F	0.538888	1.236442	-0.001049

Table A2.2. Optimized geometries at B3LYP level of theory with 6-31G(d) basis set for the serial solvation of **C** and **D** at -78 °C with free energies (Hartrees) and cartesian coordinates (X, Y, Z) (Note: G_{MP2} includes single point MP2 corrections to B3LYP/6-31G(d) optimized structures).

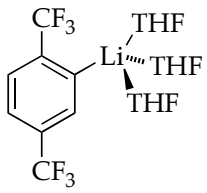


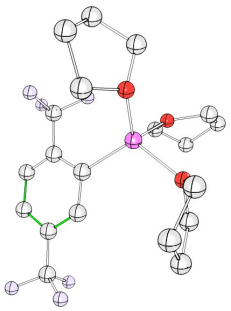


C
G = -1377.907053
G_{MP2} = -1374.2644

Atom	X	Y	Z	Atom	X	Y	Z
C	0	0	0	H	-1.946008	-1.583823	-4.733239
C	1.201259	0.624969	-0.64827	H	-1.398545	-1.427745	-3.047946
C	0.980986	1.589795	-1.657516	H	-4.160658	-0.69365	-4.167982
C	2.174286	2.061903	-2.244922	H	-3.82412	-1.701574	-2.750382
C	3.44926	1.621147	-1.867383	H	-3.207441	0.203343	-1.412113
C	3.598932	0.666126	-0.856026	H	-4.308539	1.049445	-2.530166
C	2.460508	0.162205	-0.237549	O	-1.722611	3.803523	-1.16997
H	2.556523	-0.573166	0.557457	C	-2.691462	4.589891	-1.906131
H	4.586649	0.333843	-0.55483	C	-2.320081	6.062253	-1.668289
C	4.659727	2.143818	-2.588016	C	-0.835645	5.981499	-1.273899
F	5.801042	1.981985	-1.876064	C	-0.794145	4.678078	-0.482661
F	4.55392	3.465363	-2.870052	H	-1.135534	4.819212	0.551779
F	4.853472	1.515995	-3.776067	H	0.17629	4.176653	-0.480051
H	2.122353	2.817238	-3.029464	H	-0.49899	6.841469	-0.687676
Li	-1.039707	2.071383	-1.723567	H	-0.200497	5.901973	-2.163628
O	-2.282102	1.202371	-2.969336	H	-2.909378	6.477916	-0.843113
C	-3.406388	0.432491	-2.464248	H	-2.498726	6.680851	-2.552494
C	-3.476708	-0.837133	-3.323411	H	-2.618841	4.306236	-2.961904
C	-2.030186	-0.982434	-3.823317	H	-3.69479	4.339	-1.546078
C	-1.629531	0.472492	-4.042277	F	-0.418987	-1.137038	-0.621207
H	-1.994585	0.85701	-5.004514	F	0.17366	-0.320477	1.297214
H	-0.557482	0.662991	-3.952826	F	-1.109484	0.839294	-0.033341

Table A2.2 (Continued).

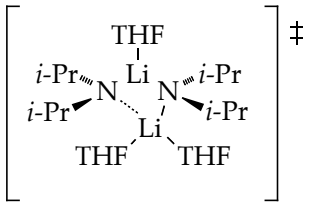


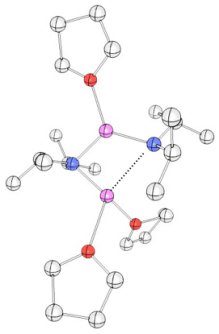


D
G = -1610.253454
G_{MP2} = -1605.959647

Atom	X	Y	Z	Atom	X	Y	Z
C	0	0	0	F	0.366552	-0.618982	-1.166369
C	-1.280095	0.777744	-0.143239	F	1.069917	0.775586	0.340894
C	-1.211102	2.128546	-0.55715	O	0.339579	5.194262	-1.423521
C	-2.487721	2.708636	-0.73307	C	0.484322	5.563751	-2.803596
C	-3.696557	2.035062	-0.5222	C	-0.952682	5.685554	-3.308691
C	-3.693431	0.699423	-0.108648	C	-1.683865	6.30284	-2.093728
C	-2.470381	0.065916	0.078315	C	-0.764444	5.959471	-0.894181
H	-2.445976	-0.973508	0.395015	H	-1.245802	5.339894	-0.135117
H	-4.625732	0.168675	0.055219	H	-0.372807	6.867756	-0.416392
C	-4.998456	2.766185	-0.673877	H	-2.6887	5.889505	-1.972686
F	-4.93928	3.734505	-1.624208	H	-1.782451	7.387841	-2.201678
F	-5.371621	3.388616	0.475155	H	-1.35118	4.690086	-3.529119
F	-6.020569	1.944214	-1.01272	H	-1.03504	6.297717	-4.211896
H	-2.561209	3.743069	-1.064474	H	1.018373	6.524513	-2.874874
Li	0.604902	3.210493	-0.794735	H	1.082182	4.786869	-3.282257
O	1.659833	3.649597	0.878832	O	1.894954	2.578484	-2.221931
C	2.521817	4.797625	1.052279	C	3.208522	2.118959	-1.831193
C	2.442569	5.183512	2.540536	C	3.303627	0.683006	-2.340909
C	1.139185	4.509933	3.002199	C	2.500775	0.761753	-3.649281
C	1.132275	3.237774	2.159703	C	1.373769	1.73643	-3.287983
H	0.144681	2.81136	1.977896	H	0.489671	1.222757	-2.903315
H	1.782908	2.464669	2.591001	H	1.078644	2.381732	-4.122472
H	0.270945	5.13138	2.7531	H	2.113188	-0.208441	-3.972625
H	1.117101	4.306236	4.076968	H	3.12186	1.167148	-4.457056
H	2.444167	6.267652	2.687552	H	2.812253	0.004767	-1.63832
H	3.295827	4.771253	3.091028	H	4.33791	0.356232	-2.485954
H	3.539066	4.529773	0.742782	H	3.966036	2.764486	-2.298782
H	2.151686	5.584336	0.388546	H	3.279844	2.212835	-0.745077
F	-0.065379	-0.982949	0.930582				

Table A2.3. Optimized geometries of trisolvated LDA open dimer transition state structures at B3LYP level of theory with 6-31G(d) basis set for the ortholithiation of **1** at -78 °C with free energies (Hartrees), and cartesian coordinates (X,Y,Z). (Note: G_{MP2} includes single point MP2 corrections to B3LYP/6-31G(d) optimized structures)





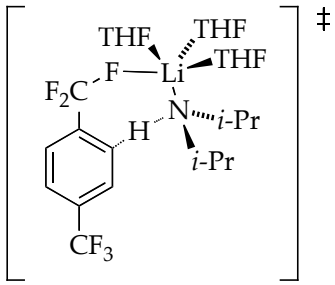
E
G = -1295.45861
G_{MP2} = -1291.60688

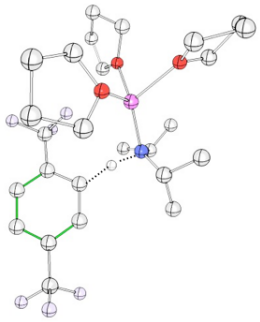
Atom	X	Y	Z	Atom	X	Y	Z
C	0	0	0	C	-0.297343	-2.91898	4.819492
N	0.330915	-0.051082	1.422569	C	1.039513	-3.303098	5.496281
Li	0.986676	-1.672013	2.368464	H	1.824191	-2.582994	5.228076
N	-0.282232	-2.951862	3.349522	H	0.942489	-3.302802	6.590401
Li	-1.64914	-1.778369	2.432447	H	1.383128	-4.300321	5.20026
O	-3.075329	-0.436062	2.943572	C	-0.708565	-1.534135	5.334881
C	-2.84135	0.979554	2.799132	H	-1.682181	-1.232428	4.935819
C	-3.092344	1.53698	4.198001	H	-0.777125	-1.528438	6.430134
C	-4.263684	0.664608	4.708739	H	0.02156	-0.770802	5.041526
C	-4.192193	-0.612199	3.833537	H	-1.051191	-3.623592	5.223685
H	-4.011404	-1.525555	4.405869	O	2.957949	-2.23587	2.144177
H	-5.108242	-0.747326	3.24293	C	3.839073	-1.579267	1.198093
H	-4.168411	0.434692	5.77365	C	5.260195	-1.938343	1.635383
H	-5.223512	1.171845	4.566428	C	5.060173	-3.329132	2.255506
H	-2.202051	1.391064	4.817817	C	3.712153	-3.165101	2.957009
H	-3.331755	2.60452	4.189773	H	3.13656	-4.089837	3.039553
H	-3.554451	1.39297	2.068543	H	3.834023	-2.738861	3.960801
H	-1.822166	1.077853	2.420136	H	4.995314	-4.092702	1.471043
O	-3.503113	-2.916608	1.39482	H	5.857543	-3.617842	2.947029
C	-4.012701	-4.255303	1.589486	H	5.966577	-1.930488	0.799832
C	-5.258243	-4.383549	0.701005	H	5.62115	-1.232105	2.392805
C	-5.715985	-2.924267	0.562604	H	3.624822	-0.508578	1.218396
C	-4.376772	-2.191292	0.507948	H	3.616782	-1.960727	0.195054
H	-3.959349	-2.201454	-0.508403	C	1.178976	1.079778	1.803019
H	-4.416882	-1.157824	0.857707	C	1.754242	0.887495	3.21633
H	-6.332889	-2.743613	-0.323031	H	2.356703	-0.026582	3.300152
H	-6.286983	-2.614417	1.446515	H	2.398485	1.728568	3.502729
H	-4.989408	-4.790007	-0.280963	H	0.941025	0.827574	3.950073
H	-6.016037	-5.03962	1.139706	C	0.502409	2.476781	1.767272
H	-4.255821	-4.377537	2.652162	H	-0.234466	2.572867	2.57531

Table A2.3 (Continued).

H	-3.230278	-4.974039	1.331682	H	1.243737	3.277433	1.899679
C	0.001158	-4.298846	2.83583	H	-0.011352	2.663144	0.818405
C	-0.899415	-5.428177	3.390368	H	2.059852	1.173151	1.125303
H	-1.959154	-5.177334	3.265482	C	-1.249688	-0.837808	-0.293613
H	-0.703634	-6.37467	2.869043	H	-2.109656	-0.454238	0.266453
H	-0.727917	-5.606058	4.457096	H	-1.511508	-0.825292	-1.360224
C	-0.071347	-4.303505	1.301159	H	-1.090417	-1.888183	-0.014883
H	0.615745	-3.568952	0.861903	C	1.138208	-0.456515	-0.947194
H	0.200404	-5.286148	0.894782	H	1.356435	-1.522714	-0.796038
H	-1.083814	-4.062232	0.954224	H	0.873604	-0.31234	-2.004863
H	1.037301	-4.618883	3.082845	H	2.059933	0.106639	-0.7627
H	-0.253896	1.030267	-0.31996				

Table A2.4. Optimized geometries of monomer-based transition state structures at B3LYP level of theory with 6-31G(d) basis set for the ortholithiation of **1** at -78 °C with free energies (Hartrees), and cartesian coordinates (X,Y,Z). (Note: G_{MP2} includes single point MP2 corrections to B3LYP/6-31G(d) optimized structures)



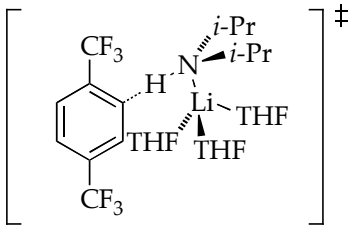


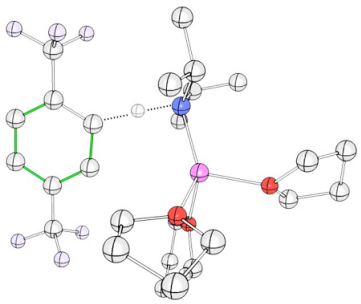
F
G = -1902.453745
G_{MP2} = -1897.287936

Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	H	-2.065919	-3.87235	0.249237
F	1.545013	-2.09467	-0.010064	H	-2.593875	-1.516035	0.69611
C	2.723025	-2.673943	-0.388153	H	-3.338613	-1.333845	-0.909359
C	3.906978	-1.770606	-0.195866	H	-1.050651	-1.817627	-2.908917
C	5.133265	-2.395836	0.077719	H	0.064761	-2.718598	-1.861065
C	6.276806	-1.624194	0.247653	H	1.636755	0.021042	-4.262057
C	6.171008	-0.236071	0.133428	C	1.84339	2.350617	-0.306742
C	4.936436	0.357531	-0.154422	H	2.327134	2.016377	0.626304
C	3.748312	-0.375753	-0.333723	C	2.87618	3.254637	-1.020872
H	4.912584	1.441363	-0.244333	H	2.421971	3.846778	-1.824528
C	7.372433	0.635132	0.37184	H	3.307515	3.965821	-0.305365
F	7.457279	1.642404	-0.528685	H	3.6956	2.675098	-1.456233
F	7.33528	1.220648	1.596325	C	0.651408	3.231442	0.121434
F	8.536185	-0.054922	0.307709	H	0.987217	4.053986	0.768433
H	7.232652	-2.088904	0.463375	H	0.157746	3.683874	-0.747932
H	5.195722	-3.476824	0.16629	H	-0.094603	2.647484	0.667591
F	2.810607	-3.82311	0.335151	O	0.324454	-0.524824	1.983782
F	2.540507	-3.05922	-1.680587	C	-0.268177	-1.710266	2.559288
N	1.487742	1.089421	-1.000472	C	0.590078	-2.06929	3.775015
C	1.297753	1.207803	-2.462595	C	1.973899	-1.555555	3.350874
H	1.880268	2.051607	-2.860747	C	1.621921	-0.276548	2.59299
C	-0.166418	1.465131	-2.874902	H	2.328146	-0.032984	1.797328
H	-0.550239	2.389694	-2.431494	H	1.523621	0.582052	3.270609
H	-0.26366	1.552554	-3.966217	H	2.460866	-2.272095	2.681522
H	-0.812579	0.640575	-2.545417	H	2.642942	-1.366444	4.195444
C	1.826433	-0.043229	-3.183113	H	0.571777	-3.141468	3.992304
H	2.903232	-0.160956	-3.031566	H	0.238197	-1.535417	4.665948
H	1.346088	-0.953502	-2.810677	H	-1.308448	-1.485874	2.818293
C	-0.965957	-2.386331	-1.976645	H	-0.253994	-2.507069	1.807293

Table A2.4 (Continued).

O	-1.258589	-1.505056	-0.859361	O	-1.915811	1.040077	0.64693
C	-2.551397	-1.85216	-0.339885	C	-2.251395	1.351956	2.017645
C	-2.645158	-3.362706	-0.529296	C	-3.246808	2.513593	1.959064
C	-1.985676	-3.544201	-1.908359	C	-3.944322	2.270102	0.612242
H	-2.73312	-3.448477	-2.703394	C	-2.783013	1.771554	-0.248234
H	-1.505688	-4.520148	-2.021936	H	-2.220461	2.606268	-0.682095
H	-3.673792	-3.734336	-0.491216	H	-3.083197	1.098015	-1.055564
H	-2.704385	0.462412	2.477073	H	-4.416227	3.166204	0.198499
H	-1.329398	1.585943	2.554625	H	-4.713757	1.494832	0.712145
H	2.538908	0.330746	-0.724475	H	-2.715507	3.472129	1.944093
H	-3.932756	2.518781	2.811489				





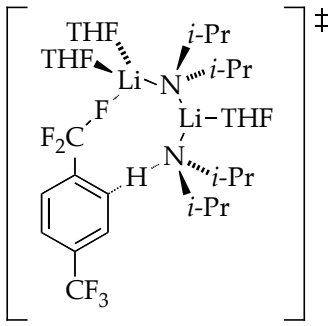
G
G = -1902.455318
G_{MP2} = -1897.293589

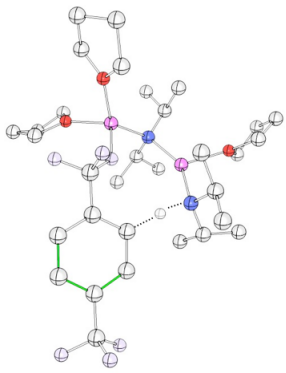
Atom	X	Y	Z	Atom	X	Y	Z
C	0	0	0	C	-3.876154	0.70273	-1.916701
C	0.299892	-1.463765	0.091404	C	-3.727669	-0.828191	-1.926217
C	1.61239	-1.918102	0.218953	H	-2.685986	-1.14084	-2.01999
C	1.838176	-3.29138	0.299153	H	-4.312059	-1.301821	-2.721891
C	0.757076	-4.179009	0.254859	H	-3.020908	1.19448	-2.387099
C	-0.587727	-3.76982	0.129538	H	-4.781677	1.007822	-2.453794
C	-0.761339	-2.380854	0.045402	H	-3.013453	1.099869	0.041254
H	-1.770573	-1.980281	-0.061676	H	-4.541185	1.966565	-0.230653
C	1.039161	-5.65517	0.357437	H	-5.828694	-0.105503	-0.087245
F	0.49165	-6.353938	-0.666461	H	-4.588237	-0.403013	1.159438
F	0.529871	-6.190681	1.501288	O	-3.980437	-2.428127	2.271635
F	2.363652	-5.949377	0.360663	C	-5.043221	-2.38179	3.246818
H	2.853442	-3.663817	0.392499	C	-4.489764	-1.571568	4.418367
H	2.440219	-1.218113	0.251439	C	-3.00529	-1.966497	4.396001
F	-0.669804	0.316756	-1.145341	C	-2.714079	-2.068574	2.89717
F	1.09754	0.782204	0.036763	H	-1.979431	-2.833065	2.639412
F	-0.81152	0.42245	1.018564	H	-2.385431	-1.113707	2.473685
H	-1.837801	-4.523642	0.028017	H	-2.862917	-2.938536	4.881931

Table A2.4 (Continued).

N	-3.060497	-4.991591	-0.1361	H	-2.356157	-1.240519	4.893923
Li	-4.152653	-3.271043	0.337674	H	-4.98974	-1.806802	5.362772
O	-6.221207	-3.47258	0.302631	H	-4.605115	-0.497467	4.229193
C	-7.017642	-2.991588	-0.807364	H	-5.920946	-1.937394	2.769265
C	-8.374835	-3.691416	-0.688942	H	-5.29178	-3.406774	3.555017
C	-8.002018	-5.010728	0.004644	C	-3.126924	-5.42712	-1.546554
C	-6.909467	-4.556565	0.971179	H	-2.341034	-6.175635	-1.748257
H	-6.173524	-5.329581	1.202617	C	-4.471962	-6.06225	-1.947182
H	-7.3379	-4.177402	1.909155	H	-4.460039	-6.36061	-3.003587
H	-7.594697	-5.724473	-0.719494	H	-4.71173	-6.953124	-1.35763
H	-8.844208	-5.484071	0.517978	H	-5.287907	-5.339995	-1.810399
H	-8.853807	-3.833704	-1.662058	C	-2.843254	-4.246362	-2.482095
H	-9.055571	-3.107342	-0.058211	H	-2.777546	-4.58577	-3.523432
H	-7.082745	-1.902486	-0.741097	H	-3.652461	-3.50707	-2.427902
H	-6.505035	-3.255885	-1.739625	H	-1.903486	-3.750518	-2.225313
O	-4.212397	-1.305235	-0.639795	C	-3.291935	-6.109047	0.812636
C	-4.747139	-0.190221	0.102434	C	-2.940285	-5.661986	2.239296
C	-4.001999	1.033193	-0.420801	H	-3.478314	-4.749375	2.512627
H	-1.464142	-7.28593	0.509809	H	-3.200524	-6.443564	2.963899
H	-2.785326	-8.167215	1.293849	H	-1.866419	-5.467211	2.325476
H	-2.833991	-7.870045	-0.4436	H	-4.368841	-6.370537	0.814995
C	-2.546347	-7.430239	0.51626				

Table A2.5. Optimized geometries of dimer-based transition state structures at B3LYP level of theory with 6-31G(d) basis set for the ortholithiation of **1** at -78 °C with free energies (Hartrees), and cartesian coordinates (X,Y,Z). (Note: G_{MP2} includes single point MP2 corrections to B3LYP/6-31G(d) optimized structures)



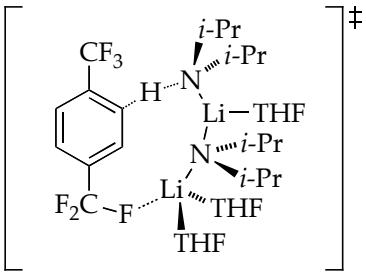


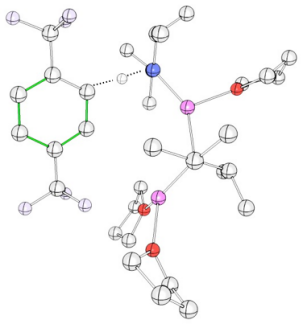
H
G = -2201.67344
G_{MP2} = -2201.67344

Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	H	-0.337915	5.205289	1.975749
F	1.919926	0.280235	0.70689	H	0.521493	6.564748	1.219138
C	2.950701	-0.393385	1.332851	H	-2.442735	6.30198	1.614743
F	2.683518	-1.713842	1.15399	H	-1.50894	7.735416	1.183915
F	2.77314	-0.161539	2.660499	C	-1.758212	2.20445	-0.758713
C	4.297248	0.024467	0.830434	H	-1.925654	3.201641	-1.213265
C	4.512826	1.379568	0.513877	C	-2.879533	1.302861	-1.328505
C	5.83323	1.671754	0.118908	H	-2.81603	1.193555	-2.416481
C	6.84356	0.706861	0.043477	H	-2.834204	0.29691	-0.886219
C	6.573635	-0.626014	0.367997	H	-3.869019	1.721781	-1.102662
C	5.287676	-0.968792	0.76603	C	-2.009906	2.380516	0.745909
H	5.058998	-2.00034	1.018838	H	-1.253383	3.02728	1.202409
H	7.352179	-1.378307	0.301316	H	-2.992203	2.832959	0.933631
C	8.241702	1.110901	-0.334923	H	-1.982595	1.411721	1.258729
F	8.955395	0.077797	-0.846497	O	-0.738235	-0.708529	1.762689
F	8.255977	2.098939	-1.259042	C	-1.72433	-1.764999	1.823858
F	8.941182	1.571404	0.732371	C	-1.906844	-2.081642	3.309658
H	6.091672	2.693014	-0.15301	C	-1.617936	-0.722536	3.965052
N	-0.382466	1.730717	-0.98615	C	-0.482606	-0.187676	3.093868
C	-0.083729	1.530185	-2.415489	H	0.495515	-0.547374	3.425938
H	-0.790095	0.810105	-2.878385	H	-0.451839	0.902339	3.027136
C	-0.185188	2.796865	-3.297275	H	-1.331984	-0.800893	5.017984
H	0.025924	2.561882	-4.348686	H	-2.496087	-0.069712	3.896264
H	-1.185988	3.241237	-3.258377	H	-1.170908	-2.825751	3.636145
H	0.537713	3.559702	-2.977991	H	-2.905172	-2.469368	3.533059
C	1.311802	0.910113	-2.586781	H	-2.655895	-1.397913	1.372806
H	2.089267	1.538515	-2.140167	H	-1.357971	-2.608023	1.233588
H	1.368502	-0.075823	-2.112993	O	-0.141257	-1.826551	-1.001426

Table A2.5 (Continued).

H	1.555495	0.780663	-3.648856	C	0.862532	-2.876649	-0.99454
Li	0.947642	3.177182	-0.211144	C	0.405973	-3.910349	-2.029645
N	2.845883	3.604032	0.517146	C	-0.440419	-3.064496	-2.992743
C	3.655473	4.494704	-0.345689	C	-1.120928	-2.093783	-2.031855
H	4.707417	4.502858	-0.005585	H	-2.011417	-2.54564	-1.571629
C	3.205543	5.967879	-0.368617	H	-1.400433	-1.140335	-2.482103
H	3.302806	6.451187	0.609603	H	-1.157437	-3.653197	-3.572607
H	3.818943	6.541246	-1.075339	H	0.201324	-2.516617	-3.691985
H	2.158101	6.044801	-0.682421	H	-0.213339	-4.682708	-1.558162
C	3.667296	3.947748	-1.778389	H	1.250707	-4.406953	-2.515575
H	3.981278	2.90039	-1.80043	H	1.824557	-2.426879	-1.25926
H	2.669491	4.014418	-2.233046	H	0.936851	-3.279688	0.018769
H	4.355326	4.52249	-2.410854	H	3.561778	2.48217	0.539386
C	2.776665	4.080999	1.915761	H	4.664267	3.257608	2.668744
H	2.309383	5.079827	1.944998	O	-0.183386	5.09359	-0.065337
C	1.870586	3.153951	2.738974	C	-0.747256	5.870739	-1.131911
H	0.874429	3.055764	2.285471	H	-0.040653	6.662914	-1.424589
H	2.298271	2.152028	2.822439	H	-0.905914	5.204723	-1.979833
H	1.731518	3.546969	3.754319	C	-2.029614	6.459946	-0.538128
C	4.140554	4.218392	2.631635	H	-2.845405	5.736285	-0.629988
H	4.796221	4.936589	2.128065	H	-2.335211	7.382299	-1.041091
H	3.999734	4.572122	3.66133	C	-1.658319	6.676632	0.951228
C	-0.337462	5.888207	1.124165				





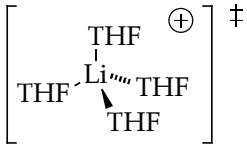
I
G = -2201.665013
G_{MP2} = -2195.577105

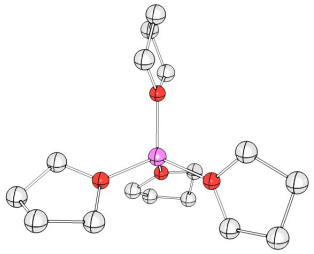
Atom	X	Y	Z	Atom	X	Y	Z
C	0	0	0	H	3.877434	9.389276	1.076968
C	1.45488	-0.106454	-0.314976	H	3.728451	7.130643	1.953243
C	2.283075	1.004956	-0.104262	H	5.410376	6.766986	1.493931
C	3.656507	1.004886	-0.37565	C	1.096047	4.878844	-2.392617
C	4.155455	-0.220953	-0.866264	H	0.058394	5.013884	-2.766662
C	3.356269	-1.351698	-1.07627	C	1.493029	3.436175	-2.738672

Table A2.5 (Continued).

C	1.991261	-1.298885	-0.802719	H	2.537983	3.236593	-2.479541
H	1.359245	-2.164531	-0.969415	H	0.893718	2.697974	-2.192503
H	3.791513	-2.270834	-1.455004	H	1.370486	3.238486	-3.811434
C	5.622704	-0.31785	-1.206594	C	1.960836	5.843186	-3.235463
F	6.417566	0.044824	-0.170401	H	1.833649	5.645928	-4.307913
F	5.959798	0.486542	-2.247455	H	1.699447	6.89244	-3.060703
F	6.002703	-1.573024	-1.55898	H	3.026555	5.718973	-3.002421
H	1.829702	1.921732	0.278045	C	0.805291	6.44371	-0.520689
F	-0.73192	-1.052509	-0.41364	H	1.565884	7.175689	-0.853084
F	-0.241246	0.142841	1.33454	C	0.779458	6.532147	1.012402
F	-0.567995	1.112685	-0.581934	H	0.652912	7.568618	1.350525
Li	-0.267534	3.807717	-0.268755	H	-0.049725	5.943129	1.427112
N	1.164378	5.073542	-0.931114	H	1.708878	6.148136	1.447619
Li	3.202842	4.834227	-0.342831	C	-0.541645	6.98541	-1.054374
N	4.721203	3.502482	0.147063	H	-1.37831	6.360687	-0.714347
C	5.031494	3.519378	1.592015	H	-0.719346	8.005258	-0.688899
C	3.723318	3.457083	2.392253	H	-0.575013	7.019117	-2.148218
H	3.042427	4.272061	2.111337	O	-0.856115	3.334818	1.569641
H	3.204041	2.508907	2.214483	C	-2.149335	2.743598	1.86469
H	3.914463	3.542602	3.469449	C	-2.031187	2.128458	3.263336
H	5.51577	4.475727	1.85977	C	-0.909468	2.962646	3.901455
C	5.977441	2.398971	2.079262	C	0.022239	3.185188	2.714645
H	5.558389	1.41035	1.87135	H	0.674707	2.321375	2.549948
H	6.955441	2.449383	1.590307	H	0.631067	4.087811	2.783559
H	6.144929	2.485145	3.161028	H	-0.410795	2.452589	4.730733
C	5.927866	3.56161	-0.708933	H	-1.297388	3.919965	4.269719
C	6.890857	4.723074	-0.403556	H	-1.727994	1.079935	3.188536
H	6.37445	5.686169	-0.489351	H	-2.974544	2.175944	3.815348
H	7.321169	4.658207	0.601661	H	-2.897534	3.544473	1.835556
H	7.726961	4.719023	-1.114616	H	-2.378503	2.011921	1.087935
C	5.494286	3.628712	-2.178311	O	-2.036453	3.591229	-1.312058
H	4.818395	2.805908	-2.423884	C	-2.213477	2.863092	-2.544546
H	4.981826	4.577115	-2.395678	C	-3.056461	3.784468	-3.445277
H	6.360883	3.560066	-2.847422	C	-3.749598	4.75372	-2.447786
H	6.512082	2.631992	-0.602417	C	-3.293688	4.243078	-1.07254
O	4.035292	6.813113	-0.063624	H	-4.00572	3.512283	-0.66098
C	4.505509	7.315642	1.206517	H	-3.128265	5.030418	-0.334497
C	4.79607	8.79885	0.97939	H	-4.839791	4.747815	-2.537648
C	5.285082	8.798712	-0.476696	H	-3.40506	5.779424	-2.604968
C	4.386795	7.73764	-1.120142	H	-3.774229	3.209344	-4.037402
H	4.883692	7.179064	-1.918709	H	-2.417974	4.336826	-4.139799
H	3.462627	8.172941	-1.518273	H	-1.223659	2.635447	-2.93814
H	6.336353	8.49223	-0.524254	H	-2.736364	1.922103	-2.326677
H	5.192882	9.772467	-0.967024	H	4.266891	2.291101	-0.111196
H	5.533457	9.193231	1.684997				

Table A2.5 (Continued).

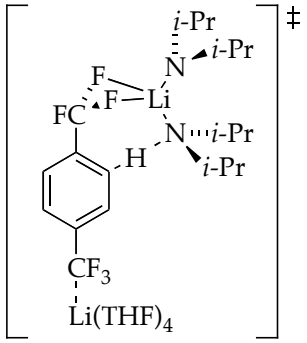


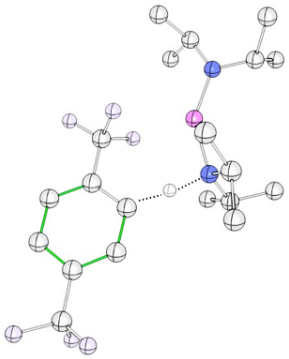


J
G = -936.851978
G_{MP2} = -934.1446904

Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	H	-2.149322	1.360014	1.952391
O	-1.144662	0.198341	-1.583784	H	-3.126007	0.082431	1.188036
C	-2.266027	-0.669753	-1.889826	H	-2.244754	0.281713	4.111398
C	-3.233358	0.194136	-2.694152	H	-3.817297	-0.240458	3.48664
C	-2.268198	1.082764	-3.494689	H	-2.023838	-2.161565	4.219983
C	-1.137065	1.33501	-2.49278	H	-2.868102	-2.359883	2.674355
H	-1.30352	2.242085	-1.901185	H	-0.574485	-2.37367	1.87507
H	-0.150424	1.395803	-2.96245	H	-0.061385	-1.22254	3.136545
H	-2.726206	2.012594	-3.841897	O	1.248352	-1.490122	-0.303631
H	-1.89292	0.543866	-4.371491	C	2.438788	-1.778754	0.478115
H	-3.853719	0.800389	-2.024102	C	2.9693	-3.112277	-0.049936
H	-3.89651	-0.40046	-3.328057	C	2.528907	-3.075513	-1.521572
H	-1.90499	-1.524549	-2.476451	C	1.157422	-2.409918	-1.426419
H	-2.66937	-1.036861	-0.942332	H	0.367328	-3.141381	-1.214007
O	1.004177	1.651159	0.331102	H	0.877839	-1.832653	-2.311274
C	2.164628	2.100408	-0.420458	H	2.478552	-4.066127	-1.981308
C	2.491539	3.495199	0.113757	H	3.214918	-2.459861	-2.114295
C	2.016898	3.403227	1.572368	H	2.493874	-3.95013	0.472418
C	0.753912	2.554012	1.442173	H	4.051254	-3.206039	0.075205
H	-0.122744	3.168683	1.200723	H	3.159331	-0.966262	0.324596
H	0.531655	1.947891	2.32427	H	2.156801	-1.804335	1.534784
H	1.816528	4.378903	2.022881	O	-1.139352	-0.408864	1.552755
H	2.762987	2.889887	2.189439	C	-0.883468	-1.508994	2.467919
H	1.921633	4.258314	-0.427999	C	-2.186969	-1.711595	3.237157
H	3.553779	3.735711	0.019551	C	-2.739125	-0.279391	3.310447
H	2.985022	1.394472	-0.243293	C	-2.355933	0.285873	1.942054
H	1.910857	2.08539	-1.48443				

Table A2.5 (Continued).





K
G = -1497.09314
G_{MP2} = -1493.001723
(calculation does not include $Li(THF)_4^+$ ion)

Atom	X	Y	Z	Atom	X	Y	Z
C	0	0	0	H	11.869147	0.149489	1.115158
C	1.37859	-0.58757	-0.073634	H	11.763527	1.878075	0.740327
C	2.502526	0.249372	-0.07264	H	10.596947	1.129298	1.862021
C	3.815766	-0.24614	-0.079696	C	10.991792	0.577622	-1.557262
C	3.920775	-1.648893	-0.08613	H	11.701643	-0.260434	-1.553977
C	2.818612	-2.513172	-0.094385	H	10.304347	0.428791	-2.39813
C	1.533936	-1.977789	-0.084975	H	11.570579	1.496359	-1.739515
H	0.664859	-2.627958	-0.093795	C	6.100362	2.141097	-1.280174
H	2.956811	-3.590439	-0.108066	H	6.951439	2.844865	-1.264132
C	5.305462	-2.236455	-0.111286	C	6.352763	1.178761	-2.451157
F	5.32963	-3.582354	0.019637	H	5.55363	0.432536	-2.522283
F	5.976209	-1.944282	-1.257829	H	6.397944	1.723023	-3.403969
F	6.093909	-1.740705	0.897038	H	7.30271	0.64581	-2.322263
H	4.96277	0.595538	-0.06902	C	4.836196	2.986227	-1.56524
H	2.338913	1.326666	-0.075554	H	3.953571	2.344291	-1.67179
F	-0.940054	-0.804523	-0.562904	H	4.634133	3.704031	-0.761625
F	-0.404406	0.208886	1.281758	H	4.95209	3.558953	-2.49573
F	-0.088015	1.198922	-0.623912	C	5.920008	2.193611	1.186005
N	6.055363	1.372312	-0.025767	H	4.955325	2.742634	1.192054
Li	7.48032	-0.073043	0.09975	C	7.026662	3.251654	1.360545
N	9.306302	-0.475242	0.022407	H	6.906699	3.782378	2.31517
C	9.965188	-1.766056	0.121444	H	8.015134	2.774941	1.35358
H	11.06769	-1.662229	0.147091	H	7.011244	4.00396	0.564005
C	9.578846	-2.497941	1.426328	C	5.897955	1.27057	2.414947
H	9.867157	-1.896318	2.295918	H	5.71417	1.845585	3.332358
H	8.491415	-2.640393	1.467823	H	5.114158	0.512818	2.322655
H	10.052734	-3.48879	1.511682	H	6.860573	0.753657	2.531229
C	9.649665	-2.683818	-1.086716	H	10.138918	-3.669072	-1.01235
H	8.566362	-2.844622	-1.158118	C	10.191982	0.648356	-0.227765
H	9.971194	-2.209695	-2.020718	H	9.542522	1.536408	-0.323471
C	11.165948	0.974363	0.938045				

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CHAPTER 3

ENEDIOLATE-DILITHIUM AMIDE MIXED AGGREGATES IN THE ENANTIOSELECTIVE ALKYLATION OF ARYLACETIC ACIDS: STRUCTURAL STUDIES AND A STEREOCHEMICAL MODEL

Enediolate-Dilithium Amide Mixed Aggregates in the Enantioselective Alkylation of Arylacetic Acids: Structural Studies and a Stereochemical Model

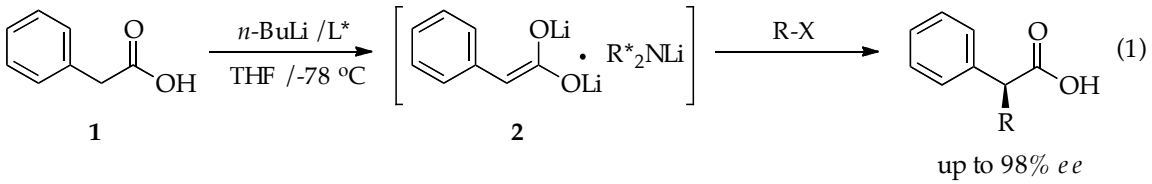
Abstract

A combination of X-ray crystallography, ^{6}Li, ^{15}N, and ^{13}C NMR spectroscopies, and density functional theory computations afford insight into the structures and reactivities of intervening aggregates underlying highly selective asymmetric alkylations of carboxylic acid dianions (enediolates) mediated by the dilithium salt of a C_2-symmetric chiral tetraamine. Crystallography shows a trilithiated *n*-butyllithium-dilithiated amide that has dimerized to a hexalithiated form. Spectroscopic studies implicate the non-dimerized trilithiated mixed aggregate. Reaction of the dilithiated amide with phenylacetic acid with excess *n*-butyllithium affords a tetralithio aggregate comprised of the two dianions in solution and the dimerized octalithio form in the solid state. Computational studies shed light on the details of the solution structures and afford a highly predictive stereochemical model.

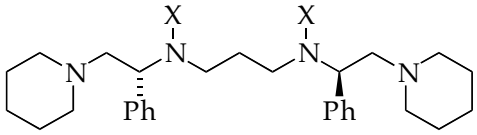
Introduction

Despite remarkable progress in the field of catalytic asymmetric synthesis,[1] asymmetric alkylations of lithium enolates are predominantly based on covalent chiral auxiliaries even in the simplest functionalizations.[2-5] Recently, we developed an alkylation of the dianions of aryl and heteroaryl acetic acids[6] (enediolates)[7] in which a dilithium amide derived from a C_2-symmetric chiral diamine[8,9] imparts high enantioselectivity (eq 1).[10,11] The enediolate-dilithiated amide complex is generated in situ, circumventing discrete steps to add and remove when covalently bound chiral

auxiliaries are used. The reaction shows considerable generality for activated, unactivated, and functionalized electrophiles.



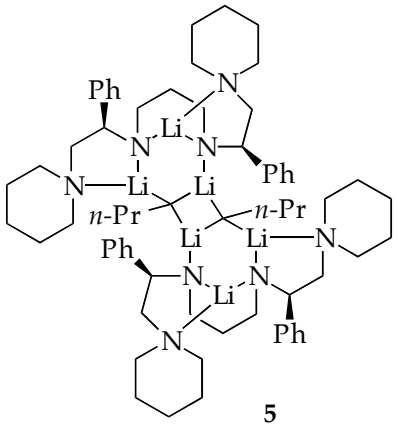
1 **2** up to 98% *ee*



3; X = H
4; X = Li (R^*_2NLi)

Evidence from a few enantioselective organolithium reactions scrutinized through structural and mechanistic studies[12] has demonstrated that high stereocontrol can correlate with high structural control of the aggregates.[13] Thus, we presumed that the enantioselectivity in eq 1 derives from a well-defined chiral aggregate, **2**, composed of the dilithium enediolate and the chiral dilithium amide.[11,14] The optimized conditions suggested a 1:1 stoichiometry, although that assertion lacked direct support. Nevertheless, a detailed understanding of the enantioselectivity clearly requires knowledge of the underlying coordination chemistry.

We describe herein a combination of X-ray crystallography, ^{6}Li, ^{13}C, and ^{15}N NMR spectroscopies, and density functional theory (DFT) computations that afford insight into the structures and reactivities of intervening aggregates **5**-**8**.[15-17] These studies suggest a mechanistic model affording remarkable agreement between observed and computed enantioselectivities.



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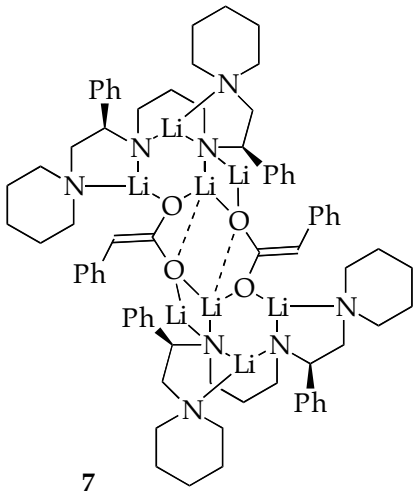

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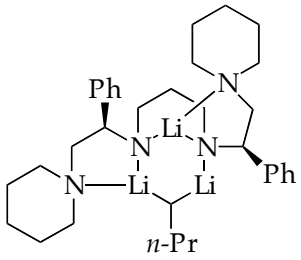

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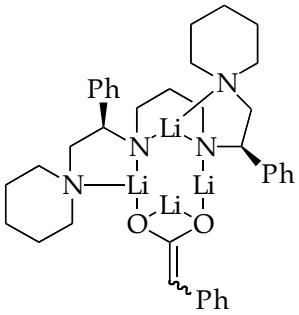

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To help guide the reader, we note that the detailed organolithium chemistry delineated in the results section is summarized for the generalists at the start of the discussion section. This summary is followed by a discussion of the possible implications and predictive capabilities of the seemingly robust stereochemical model.

Results

The structures of mixed aggregates **5**-**8** were determined using a combination of X-ray crystallography, multinuclear NMR spectroscopies, and density functional theory (DFT) computations as described below. In addition, COSY, TOCSY, HSQC, HMBC and

ROESY spectroscopies provided support to both the aggregate assignements and spatial orientations. These are archived in supporting information.

***n*-BuLi-dilithiated amide mixed aggregate: X-ray crystal structure.**[14,18]

Addition of 4.0 equiv of *n*-BuLi (2.5 M) to a hexane solution of amine **3** at –25 °C affords a pale yellow solution. Subsequent crystallization from a hexane/pentane mixture yields $[Li_3(\mathbf{1})(^n\text{Bu})]_2$ (**5**) as a colorless microcrystalline solid in 46% yield. The composition of **5** was confirmed with an X-ray diffraction study, and its solid-state structure is shown in Figure 3.1. Complex **5** crystallizes in the orthorhombic space group $P2_12_12_1$ as the pentane solvate **5**. Complex **5** displays overall C_2 symmetry and is assembled from two trilithio components each constituted from an *n*-BuLi and a doubly deprotonated diamine subunit.

The metrical parameters of each trilithiated form an *n*-Bu fragment coordinated to the three lithium cations as are similar to those found in alkyllithium aggregates.[7] Incorporation of *n*-BuLi into the structure of an organo- or amido-lithium reagent was reported previously.[19] The most interesting feature of the solid-state structure of **5** is the binding mode of the amine ligand. Each piperidine-derived nitrogen atom is coordinated to a single lithium cation, whereas each amide nitrogen atom is coordinated to two lithium cations. More specifically, Li2 is chelated by three nitrogen atoms, N2, N3, and N4, thereby generating a five-membered ring and a six-membered ring. Additionally, Li2, N2, N3, and N4 are all roughly co-planar. This orientation places both phenyl groups in the amine backbones pseudo-equatorially. Li1 is coordinated by two nitrogen atoms (N1 and N2), thereby generating a five-membered ring. Finally, Li3 is only coordinated by one nitrogen atom (N3) in addition to the carbon atom (C1 and C1A) of the *n*-Bu fragment. The Li-N(amide) bond lengths are 1.979(5) Å (Li2-N2), 1.923(4) Å (Li2-N3), 1.936(4) Å (Li1-N2), 1.953(4) Å (Li3-N3),

whereas the Li-N(amine) bond lengths are 2.089(4) Å (Li1-N1) and 2.167(4) Å (Li2-N4). Similar bond lengths are seen in the lithium salt of a related bidentate Koga base, *N*-neopentyl-1-phenyl-2-(1-piperidino)ethylamine.[20]

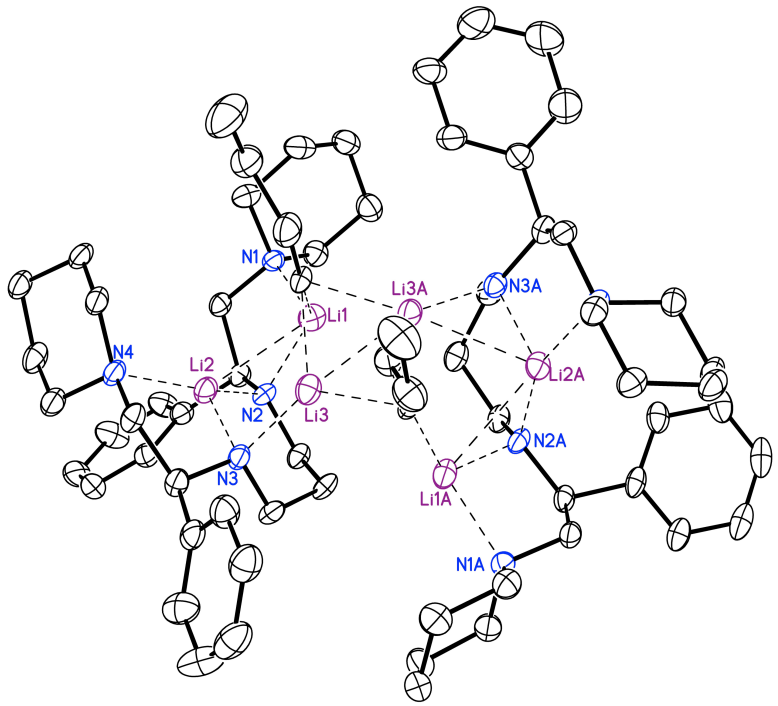
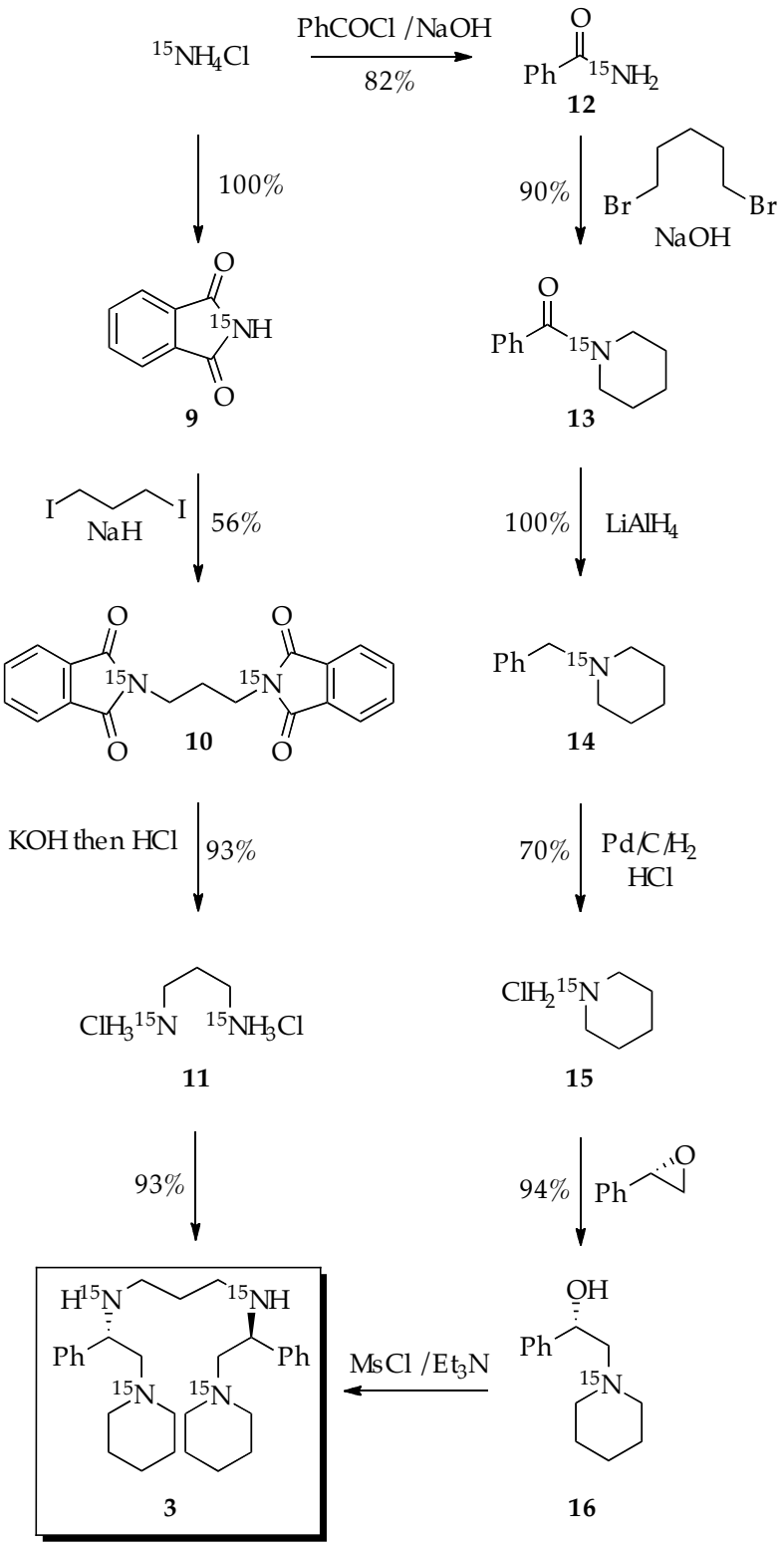


Figure 3.1. ORTEP of hexalithio *n*-BuLi-dilithiated amide mixed aggregate **5**.

***n*-BuLi-dilithiated amide mixed aggregate: solution structure.** The structural assignments used a tetra-^{15}N-labelled analog, [$^{15}N_4$]**3**, prepared using a modification of the original synthesis, as illustrated in Scheme 1. Metalation of [$^{15}N_4$]**3** with two equiv of recrystallized [^{6}Li]*n*-BuLi[21] in THF at –78 °C was incomplete, affording lithium amide-*n*-BuLi (see below) and unreacted diamine **3**.[22-24] Subsequent warming to –20 °C for 10 min caused complete consumption of **3**, affording dilithiated amide homoaggregate **4** as a complex mixture that was not investigated further.[25,26]

Scheme 1


$^{15}NH_4Cl$
PhCOCl /NaOH
82%
Ph
$^{15}NH_2$
12
100%
90%
Br
Br
NaOH
^{15}NH
9
Ph
^{15}N
13
I
NaH
I
56%
100%
$LiAlH_4$
^{15}N
^{15}N
10
Ph
^{15}N
14
KOH then HCl
93%
70%
Pd/C/H_2
HCl
$ClH_3{}^{15}N$
$^{15}NH_3Cl$
11
$ClH_2{}^{15}N$
15
93%
94%
Ph
O
$H^{15}N$
^{15}NH
Ph
Ph
^{15}N
^{15}N
3
MsCl /Et_3N
OH
Ph
^{15}N
16

Lithiation of [$^{15}N_4$]**3** with ≥3.0 equiv of [^{6}Li]BuLi[21] in 6.1 M THF/hexane affords a dilithium amide-*n*-BuLi mixed aggregate displaying three ^{6}Li resonances (1:1:1) along with resonances of residual *n*-BuLi dimer and tetramer[26] at elevated *n*-BuLi concentrations (Figures 3.2 and 3.3). The resonance count and intensities, most easily observed in the ^{15}N broadband decoupled spectrum (Figure 3.2A), are consistent with those of trilithiated mixed aggregate **6** or the corresponding dimerized hexalithiated **5** observed crystallographically. (The trace impurities noted by asterisks were initially believed to be *n*-BuOLi-derived mixed aggregates, but addition of *n*-BuOH incrementally reveals a distinctly different mixed aggregate.) The connectivities in the trilithio subunit were assigned from the splitting patterns in the coupled spectra (indicated in red in Figure 3.2A and Figure 3.3A) with the aid of single-frequency decoupling[27] and [^{6}Li,^{15}N]-HMQC spectroscopy[28,29] (supporting information). Spectroscopic data are compiled in Table 3.1. The primary Li-N linkages of the lithium amide moieties showed characteristically large (3.6-5.8 Hz) coupling constants[30] whereas the dative Li-N linkages deriving from chelation by the piperidino moieties displayed much smaller (1.9-2.2 Hz) coupling constants.[31] The assignment as trilithiated **6** rather than hexalithio **5** stems from a ^{13}C NMR spectrum showing that was tentatively assigned as a quintet corresponding to the Li-C-Li' and the heptet of the *n*-BuLi tetramer (Figure 3.4).[26,32]

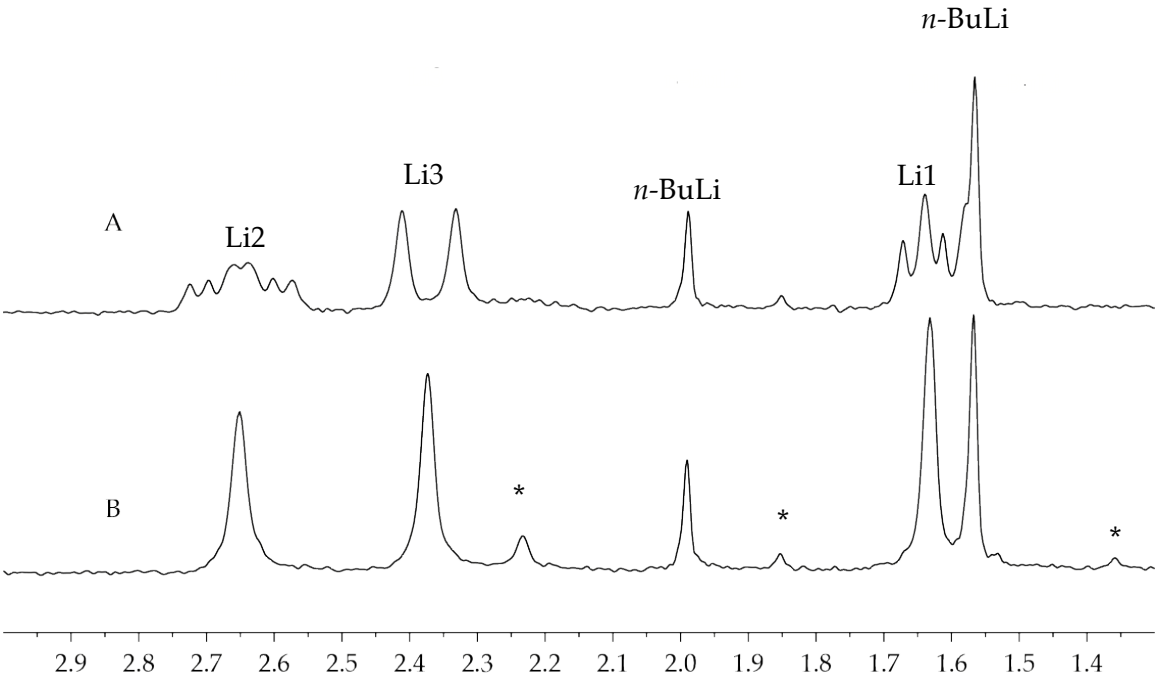


Figure 3.2. ^{6}Li NMR spectra of 0.10 M [^{6}Li,^{15}N]**6** prepared from [$^{15}N_4$]**3** with 4.0 equiv *n*-BuLi in 6.10 M THF-pentane recorded at –90 °C after aging at –78 °C for 2.0 hr: (A) fully coupled; (B) broadband ^{15}N decoupled. *Unknown impurities that appear sporadically

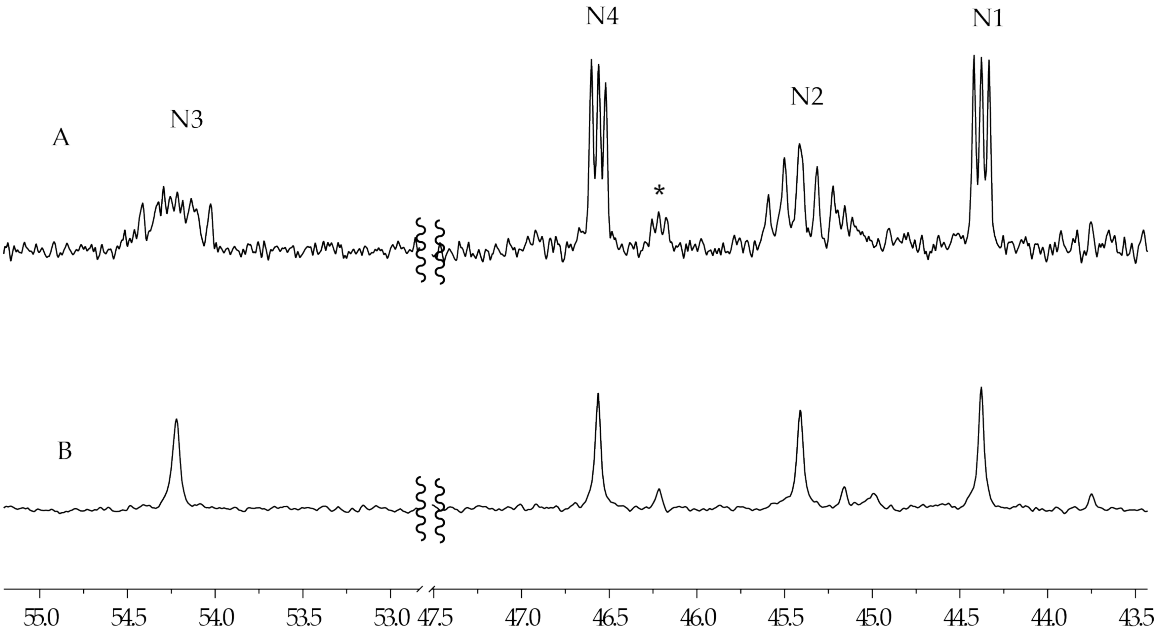


Figure 3.3. ^{15}N NMR spectra of 0.10 M [^{6}Li,^{15}N]**6** prepared from [$^{15}N_4$]**3** with 4.0 equiv *n*-BuLi in 6.10 M THF-pentane recorded at –90 °C after aging at –78 °C overnight: (A) fully coupled; (B) broadband ^{15}N decoupled. *Unknown impurities that appear sporadically.

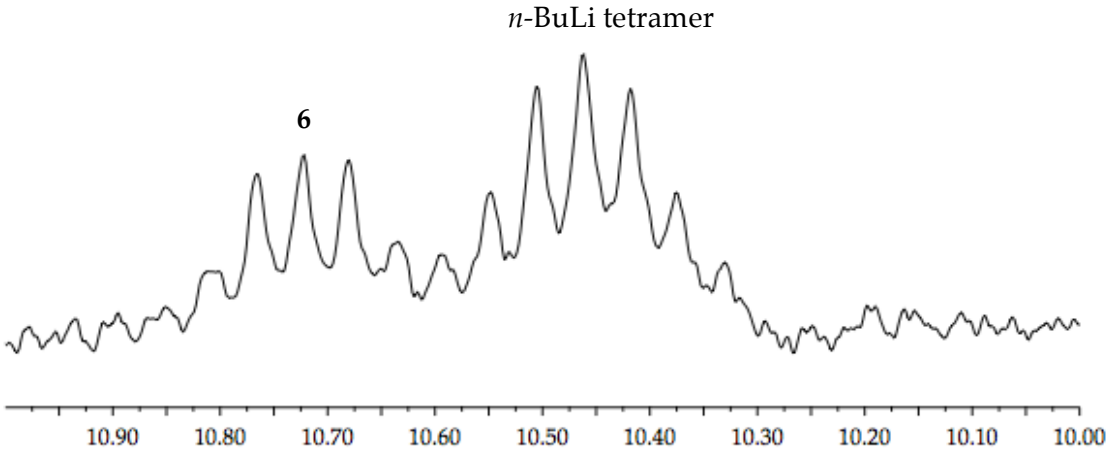
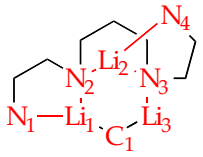


Figure 3.4. ^{13}C NMR spectra of 0.10 M [^{6}Li,^{15}N]**6** prepared from [$^{15}N_4$]**3** with 4.0 equiv *n*-BuLi in 6.10 M THF-pentane recorded at –90 °C after aging at –78 °C overnight. (^{13}C resonance of the *n*-BuLi dimer is not shown but appears as a 1:2:3:2:1 quintet at 12.6 ppm.)

Table 3.1. ^{6}Li and ^{15}N NMR spectroscopic data for mixed aggregates **6** and **8**.



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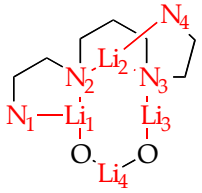

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	d (ppm)	mult	*J* (Hz)	d (ppm)	mult	*J* Hz)
Li_1	1.63	dd	Li_1-N_1 = 2.1	1.24	dd	Li_1-N_1 = 2.2
Li_2	2.65	ddd	Li_1-N_2 = 4.3	2.20	ddd	Li_1-N_2 = 4.3
Li_3	2.37	d	Li_2-N_2 = 4.9	2.06	d	Li_2-N_2 = 4.8
Li_4	---	---	Li_2-N_3 = 4.3	-0.26	s	Li_2-N_3 = 3.6
			Li_2-N_4 = 2.1			Li_2-N_4 = 1.9
			Li_3-N_3 = 5.8			Li_3-N_3 = 5.6
N_1	44.4	t		44.7	t	
N_2	45.4	tt		41.3	tt	
N_3	54.2	tt		45.8	tt	
N_4	46.4	t		46.4	t	

***n*-BuLi-dilithiated amide mixed aggregation: DFT computed structure.** DFT calculations were performed with the Gaussian 09 package using Gaussview 5.0 and WebMO as a graphical user interface.[33] Geometry optimizations and frequency calculations were performed at the B3LYP level of theory using the 6-31G(d) and 6-31+G(d) Pople basis sets. Free energies were calculated from an MP2-derived single-point energy [6–31G(d) basis set] and a B3LYP-derived thermal correction [6–31G(d)] at 195 K (–78 °C) and 1 atm. (MP2 corrections seem to provide superior correlations of theory and experiment, especially for highly congested structures.)

We followed a pedagogically interesting protocol by providing only the atomic connectivities—no detailed NMR or crystallographic data—to the coworker (JL) doing

computations. Comparing the computed structures to the crystal structure revealed remarkable similarities, but we had computationally missed the orientation of the three-carbon propanediamine bridge and one of the five-membered chelates. With this additional information in hand, the computations were repeated (supporting information).

Three important variables are summarized in Figure 3.5 and described below.

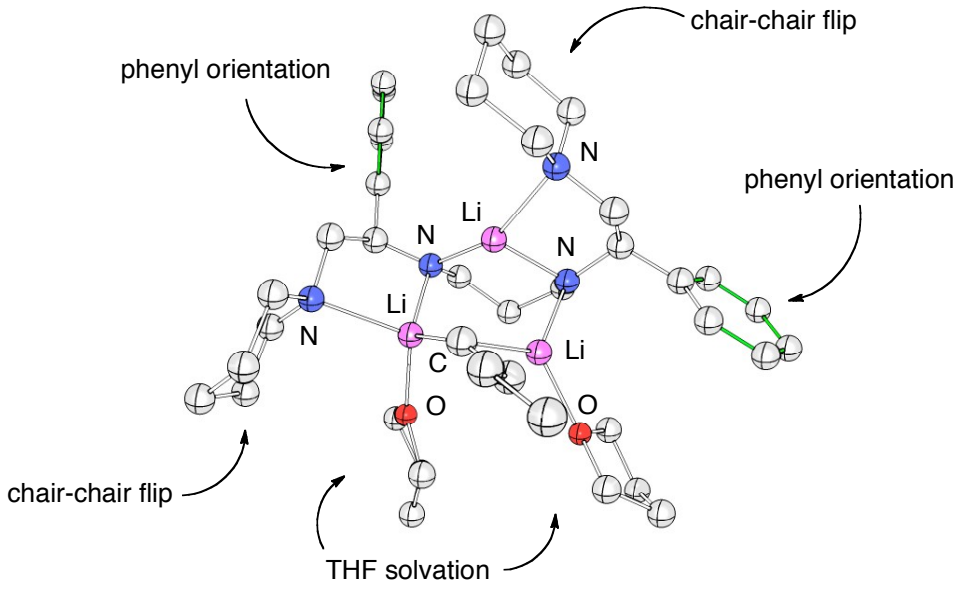
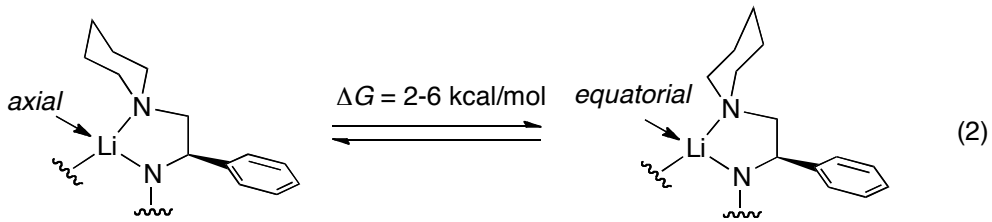


Figure 3.5. DFT computed structure of **6** as disolvate (**6a**) showing critical structural variables.

(1) Piperidine chair-chair flip. Each piperidine rings can exist in two chair conformers, which differ by 2.0-6.0 kcal/mol (for all solvates).[34] The preferred conformers have lithiums positioned axially as drawn in Figure 3.5. This proves to be the overwhelming preference found crystallographically for N-alkylpiperidine-lithium complexes.[35,36]



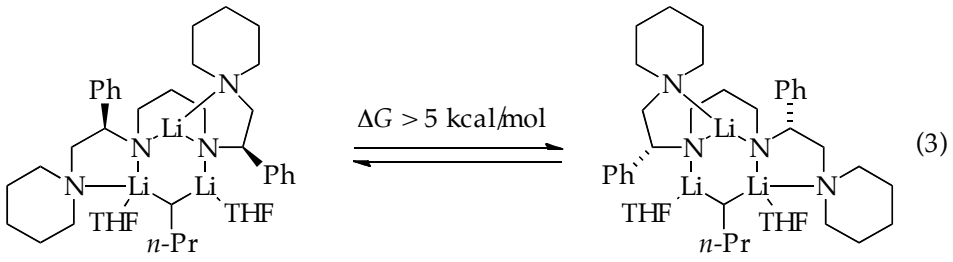
(2)

(2) *Chelate Conformation.* The five-membered chelate rings show two conformers orienting the phenyl in roughly the equatorial plane and substantially displaced from this plane. They are essentially of equal energy (± 0.2 kcal/mol).

(3) *n-Butyl orientation.* The *n*-butyl moiety always positions on the opposite face of the six-membered ring from the two THF ligands as drawn, regardless of starting geometry.

(4) *Solvation.* Serial solvation of solvent-free trilithiated fragment **6** shows a strong (8.3 kcal/mol) preference for the di-THF solvate over the monosolvate. Additional solvation was undetectable.[37]

(5) *Chelate orientation.* Reversing the role of the two chelating piperidines (eq 3)—inverting the absolute configuration of the backbone of the structure—revealed a pronounced preference for diastereomer **6a** relative to **6b**.



6a **6b**

(3)

(5) *Dimerization.* The association of **6** to give **5** proved to be very high energy owing largely to a loss of solvation energy. The crystal for X-ray determination of **5** was obtained from hydrocarbon solutions wherein solvation would not be an issue.

Enediolate-dilithiated amide mixed aggregate: X-ray crystal structure. Addition of 4.0 equiv of *n*-BuLi to a THF solution containing **3** and phenylacetic acid at –25 °C yields a light yellow solution. Crystallization from hexanes, with a small amount of added THF, affords $[Li_4(\mathbf{1})(PhCH{=}CO_2)(THF)_2]_2$ (**7**) as a light yellow powder in 48% yield. The composition of **7** was confirmed by X-ray diffraction (Figure 3.6). Although the data quality is poorer than that observed for **5**, the connectivity of the atoms in **7** is clearly defined. Complex **7** crystallizes in the orthorhombic space group $P2_12_12_1$ as the THF solvate **7**·THF. Complex **7** comprises two tetralithio subunits in the solid state—octalithio overall—with C_2 symmetry. It consists of two chiral dilithiated amides and two enediolates. Four of the eight lithium cations are ligated by THF molecules. The presence of the same dilithium amide core in both **5** and **7** suggests its central importance. Because the molecule is composed of two identical tetralithio subunits, the metrical parameters of only one half are discussed. As was observed for **5**, one lithium atom (Li2) is chelated by three nitrogen atoms from one tetra(amine) ligand: N2, N3, and N4, thereby generating a five membered ring and a six membered ring. One lithium atom (Li1) is coordinated by two nitrogen atoms (N1 and N2), generating a five membered ring. Additionally, two lithium atoms (Li3 and Li4) bridge the chiral amine moiety and the oxygen atoms of the enediolate ligands, $[PhCH{=}CO_2]^{2-}$. The Li-N(amide) and Li-N(amine) bond lengths in **7** are similar to those in **5**. Finally, the Li-Li distances in **7** range from 2.418 Å to 2.661 Å, in line with structurally related lithium aggregates.[38]

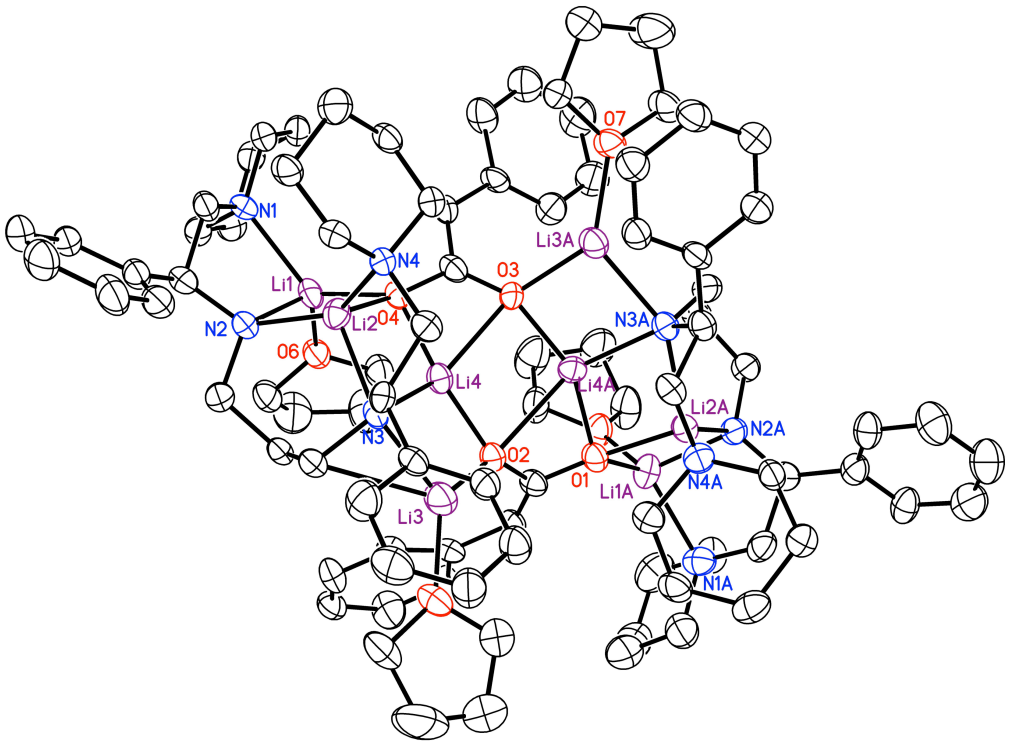


Figure 3.6. ORTEP of hexalithio enediolate-dilithiated amide mixed aggregate **7**.

The most interesting structural feature of **7** is the incorporation of the enediolate moiety, $[PhCH{=}CO_2]^{2-}$. The atoms within the enediolate ligand are all co-planar, suggesting strong π conjugation. Additionally, each oxygen atom of the endiolate is coordinated to three lithium cations. For instance, one oxygen atom (O4) is coordinated to a triangular face formed by three lithium cations (Li1, Li2, Li4), whereas the other oxygen atom (O2) is ligated by Li3, Li4, and Li4A. The Li-O bond lengths range from 1.857 Å to 2.245 Å; however, the average Li-O bond length of 1.96 Å is standard.[39] Additionally, there are two independent C=C bonds that exhibit somewhat different C-C bond lengths (C48–C49 = 1.408(8) Å, C40–C41 = 1.356(15) Å). The C–O bond lengths

of the two moieties are comparable [C48–O4 = 1.322(6) Å and C48–O3 = 1.283(7) Å versus C40–O1 = 1.312(7) and C40–O2 = 1.326(7) Å].

Enediolate-dilithiated amide mixed aggregate: solution structure. The structure of the centrally important mixed aggregate of dilithiated amide **3** with the dianionic enediolate of phenylacetic acid was studied using the protocols and spectroscopic methods described above. Figure 3.7 shows ^{6}Li NMR spectra recorded on a solution prepared from a 1:4:1 mixture of [$^{15}N_4$]**3**, *n*-BuLi, and phenylacetic acid (**1**) in THF-pentane. Residual *n*-BuLi-derived mixed aggregate **6** is observed along with a new mixed aggregate corresponding to tetralithio mixed aggregate **8** (The connectivities are highlighted in red in Figure 3.7). Despite differential broadening, the four resonances integrate to 1:1:1:1, consistent with a 1:1 mixed aggregate constituted from the two dianions. The corresponding fully coupled and broadband decoupled ^{15}N NMR spectra are illustrated in Figure 3.8. Single-frequency decoupling and [^{6}Li,^{15}N]-HMQC spectroscopy provided the connectivities and completed the assignments (Table 3.1). COSY, TOCSY, HSQC, HMBC and ROESY spectroscopies (supporting information) supported the spatial orientations observed computationally (below). Although tetralithio mixed aggregate **8** could have, in theory, dimerized into an octalithio form, neither the physical nor the computational models provided any support for such a severely congested aggregate.

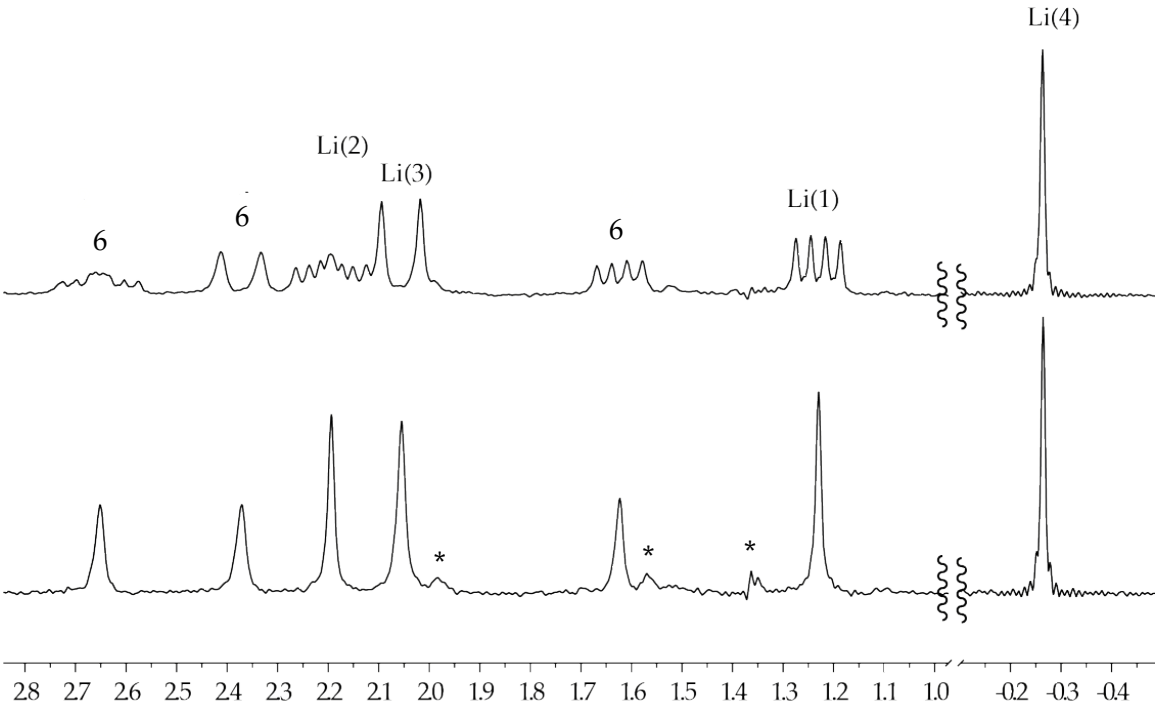


Figure 3.7. ^{6}Li NMR spectra of 0.10 M [^{6}Li,^{15}N]**8** and residual [^{6}Li,^{15}N]**6** prepared from [$^{15}N_4$]**3** with 4.0 equiv *n*-BuLi in 6.1 M THF-pentane recorded at –90 °C after aging at –78 °C for 2.0 hr: (A) fully ^{15}N coupled; (B) ^{15}N broadband decoupled. *Unassigned resonances.

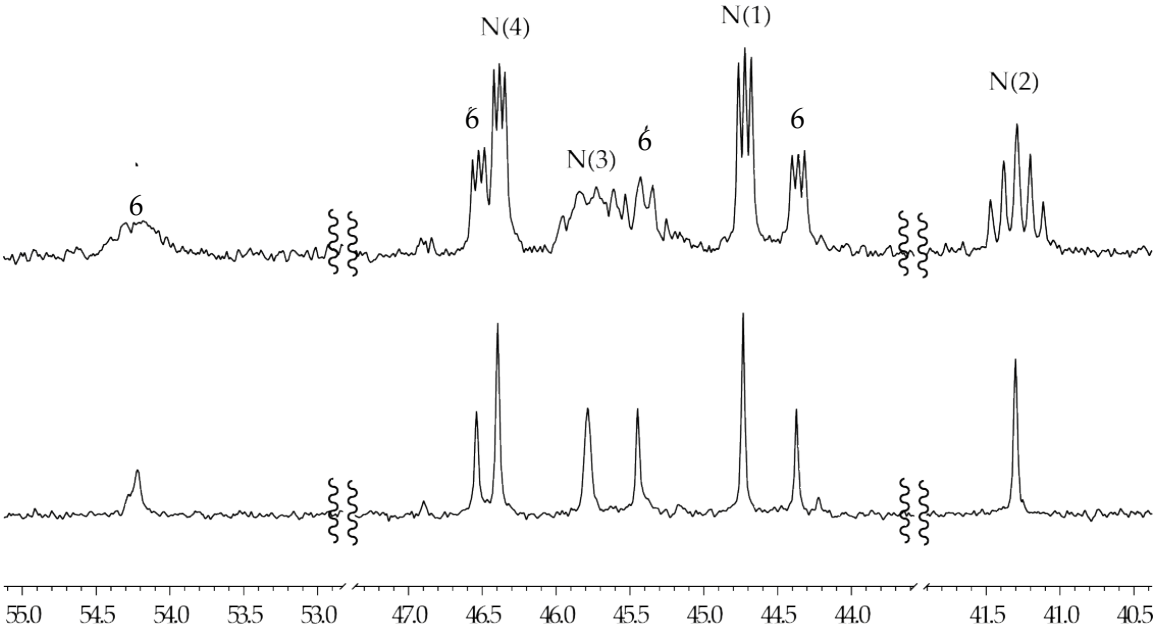
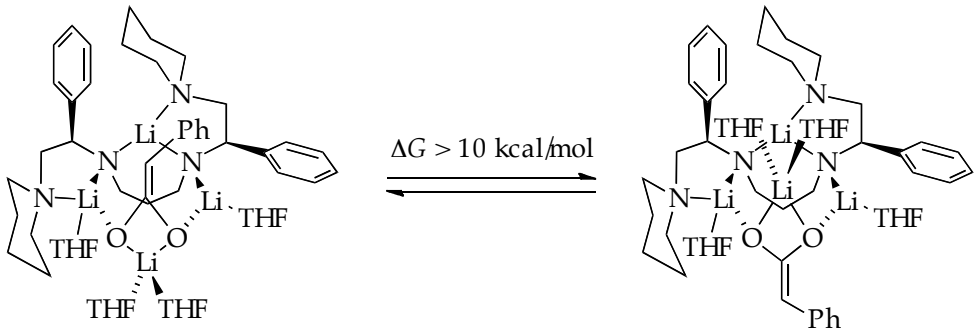


Figure 3.8. ^{15}N NMR spectra of 0.10 M [^{6}Li,^{15}N]**8** and residual [^{6}Li,^{15}N]**6** prepared from [$^{15}N_4$]**3**, 4.0 equiv *n*-BuLi, and phenylacetic acid in 0.10 M THF-pentane recorded at –90 °C after aging at –78 °C for 2.0 hr: (A) fully ^{15}N coupled; (B) ^{6}Li broadband decoupled.

Enediolate-dilithiated amide mixed aggregate: DFT computed structure. The structure of **8** was examined computationally.[40-42] Many of the structural details such as piperidino chair preferences and chelating side chain orientations were analogous to those outlined above (and provided in detail in supporting information), warranting no additional comment. We also observed no tendency of tetralithio **8** to form an octalithio (dimerized) form. The three significant variables are as follows:

(1) *Solvation.* The serial solvation of the core is exergonic to the tetrasolvation state (7.1 kcal/mol favored over the trisolvate). Additional solvation was undetected without significant structural disruptions.

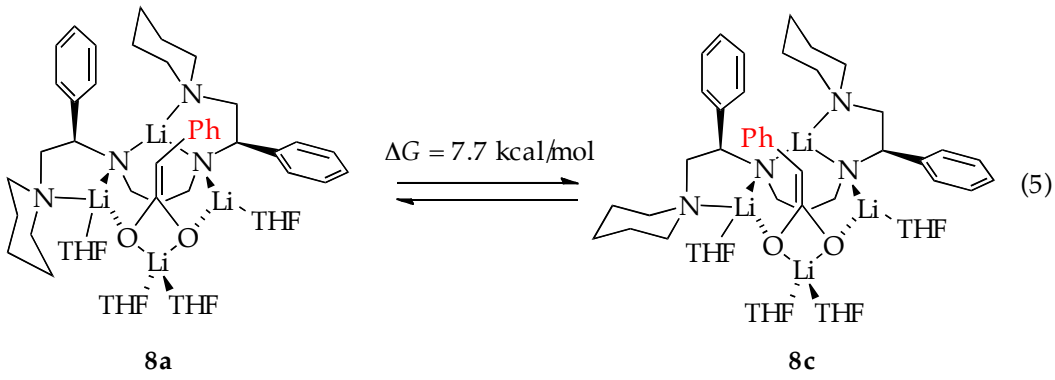
(2) *Enolate orientation.* The enolate orients favoring **8a** as shown in eq 4, presumably owing to the steric demands of the disolvated lithium nucleus.



(4)

8a **8b**

(3) *Phenyl orientation.* The orientation of the phenyl moiety on the enediolate fragment is the variable that we believe is at the heart of the enantioselectivity in eq 1. We observe a 7.7 kcal/mol preference for **8a** versus **8c** (eq 5).



(5)

Calculated transition structures and enantioselectivities. Aggregates **8a** and **8c** expose the *si* and *re* faces, respectively, of the enediolate to the sterically accessible exterior of the globular aggregate. All that remained was to examine the transition structures for the alkylation and predict the affiliated enantioselectivities. The calculations used methyl chloride. Transition structures **17a** and **17b** correspond to the alkylation of **8a** and **8c**, respectively (Figure 3.9). We explored cyclic transition structures bearing Li-Cl contacts and found they were only marginally viable.[43-47] The ≥20 kcal/mol barriers (referenced to common ground state **8a**) do not trouble us; barriers of alkylations are routinely over estimated.[48] More importantly, the 6.4 kcal/mol preference for **17a** suggests a >>99.9% ee. Although this value exceeds the experimental value of 98% ee for allyl bromide,[6] the model is impressively robust, especially given possible sources of erosion experimentally. Equilibration of the aggregates on the time scales of alkylation is by no means certain.

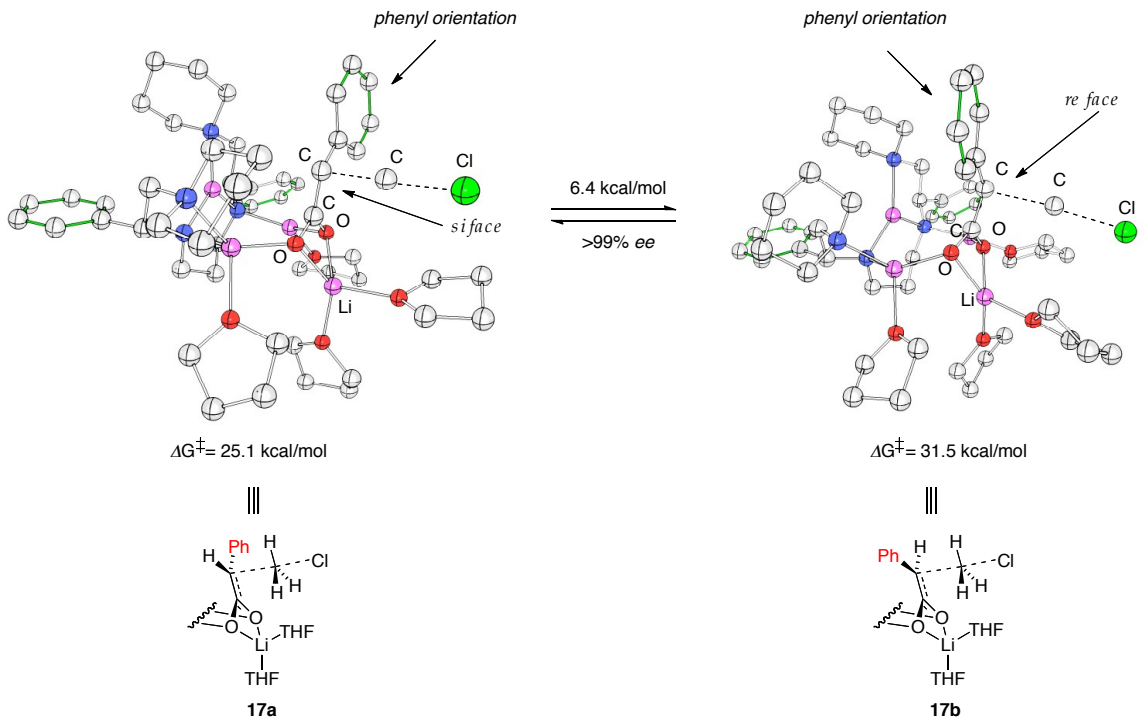
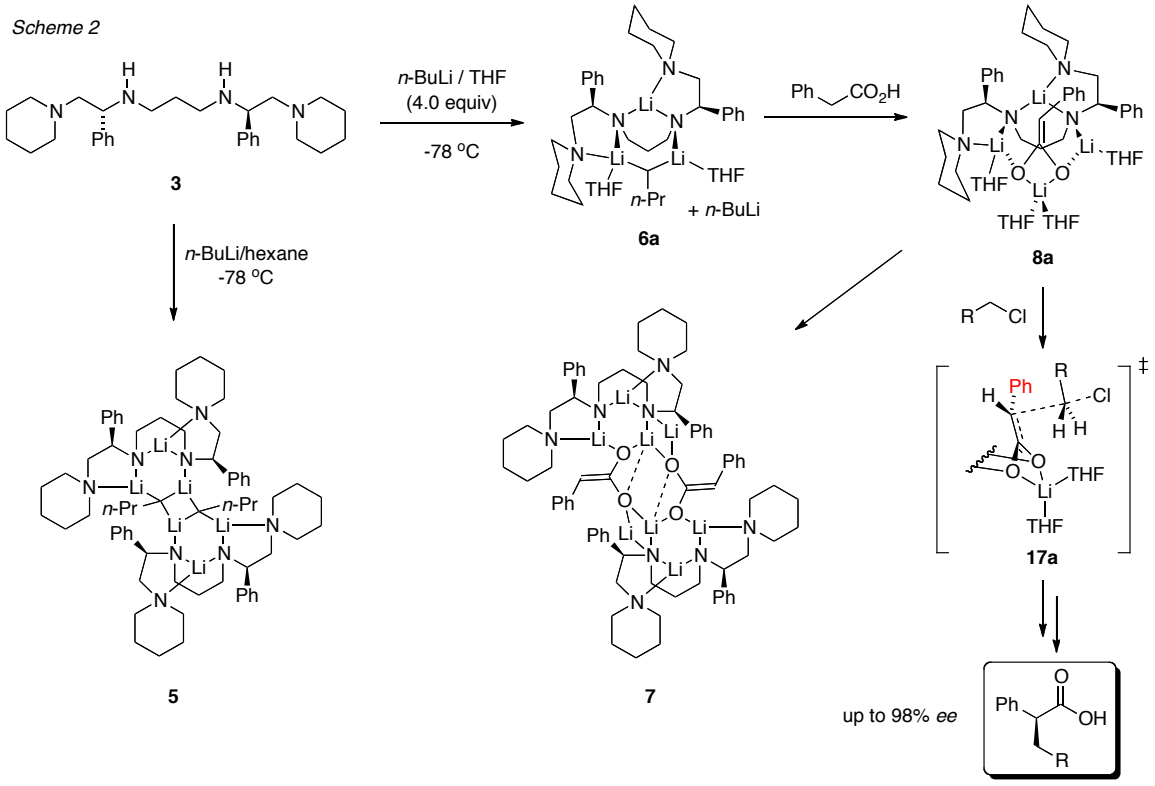


Figure 3.9. Calculated transition structures **17a** and **17b** showing selectivity for alkylation from the *si* and *re* enolate faces, respectively.

Discussion

Summary. The studies of the mixed aggregates derived from dilithiated amide **4** and the coordination chemistry underlying the enantioselective alkylation of carboxylic acid enediolates in eq 1[6] reveals a remarkably coherent picture (Scheme 2). In the absence of coordinating ligand, dilithiated amide **4** and *n*-BuLi affords a crystalline mixed aggregate shown by X-ray crystallography to be an exceedingly complex hexalithiated form, **5**, comprising two *n*-BuLi-dilithiated amide trilithio subunits. Analogous metalation in THF solution affords trilithio form **6** as a single diastereomer, suggested by computations to be disolvate **6a** (vide supra).[49]

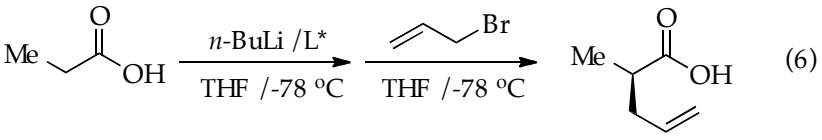


Mixing diamine **3**, 4.0 equiv *n*-BuLi, and phenylacetic acid (**1**) affords octalithio mixed aggregate **8** comprising two dilithiated amides and two enediolate dianions in a C_2-symmetric dimerized form. Analogous mixtures in THF solution afford the corresponding tetralithio mixed aggregate **8** composed of a dilithiated amide and enediolate dianions and suggested by computations to be tetrasolvated (**8a**). Once again, the structural and stereocontrol are predicted to be very high. Computations of **8a** also indicate a strong (7.7 kcal/mol) preference for a single orientation of the enediolate relative to the dilithium amide fragment.

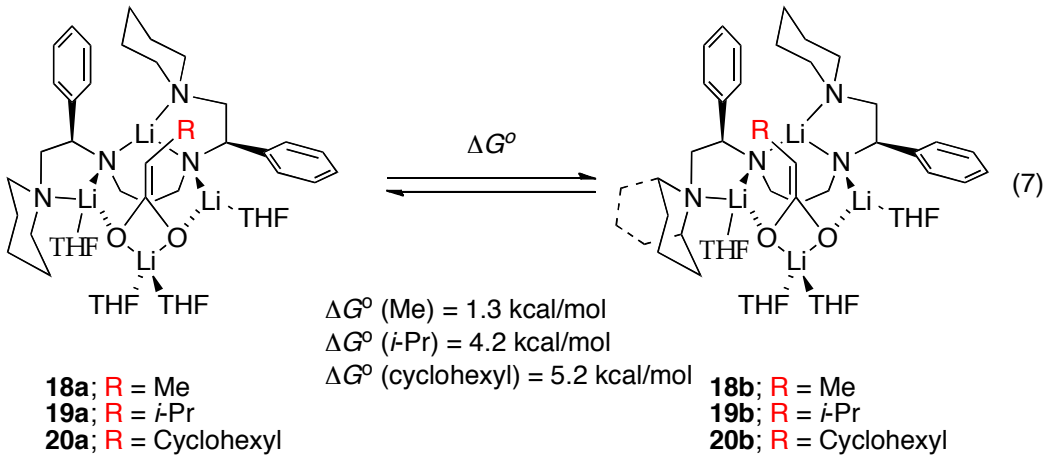
Stereochemical model: predictions. In essence, the dilithium amide fragment concurrently controls the orientation of the enediolate and blocks one of two enantiotopic enediolate faces, ensuring a highly enantioselective alkylation. Computed product-determining transition structures **17a** and **17b** (Figure 3.9) do not contain Li-Cl

interactions. Importantly, the computations predict the correct facial selectivity and an enantioselectivity of >99% ee compared with the experimental values of up to 98% ee. This satisfying theory-experiment correlation attests to a potentially robust stereochemical model. One should note, however, that the predicted selectivity based on reactant preference or transition structure preference will depend critically on whether the aggregates equilibrate on the time scale of the alkylation. Instantaneous alkylation could be construed as evidence of non-equilibrium kinetics. Given the enormous energetic bias, this would not measurably affect the observed selectivities.

Of course, many variables that had to be controlled to obtain the highly enantioselective alkylations. Ultimately, however, the orientation of the enediolate phenyl moiety appears to be the central variable (eq 5). The robustness of this model is easily tested. The data showed a priori that the propionate enediolate is poorly selective (eq 6). Computations confirmed the inferior (1.3 kcal/mol) selectivity of the enediolate geometry (eq 7). The corresponding computed transition structures for isopropyl and cyclohexyl-substituted enolates are akin to the 4.2 and 5.2 kcal/mol facial preference of the phenyl-substituted enediolate. The cyclohexyl- and isopropyl-substituted enolates force a conformational flip of the piperidine (dotted line in **19b** and **20b**).



(6)



(7)

Conclusions

Only in a few instances has stereocontrol been correlated with the underlying organolithium aggregation.[12,13] We suspect, however, that high stereocontrol is affiliated with high structural control.[13] To borrow a familiar phrase, what you see is what you get (WYSIWYG). The structural studies described herein certainly are supportive. The emergent model appears to be highly predictive. Ongoing studies may reveal why certain electrophiles are poorly selective owing to specific steric interactions. At this time we do not know the relative rates of alkylations and aggregate exchanges.[50] We suspect, however, that highly reactive electrophiles—those most likely to react directly with the mixed aggregate without intervening deaggregations and other structural changes—are amenable to computational prediction. For sluggish electrophiles, intervening deaggregations could cause stereochemical leakage. Of course, alkylations are a small subset of the reactions of lithium enolates, so this story may be only in its infancy.

Experimental Section

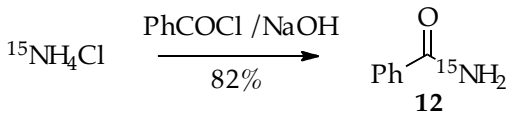
Reagents and solvents. THF and hexanes were distilled from blue or purple solutions containing sodium benzophenone ketyl. The hexane contained 1% tetraglyme to dissolve the ketyl. *n*-BuLi was prepared and recrystallized as described previously.[21] Solutions of *n*-BuLi were titrated using a literature method.[51] Amine **3** was prepared as described previously.[8] [$^{15}N_4$]**1** was prepared as described below.

NMR spectroscopic analyses. All NMR tubes were prepared using stock solutions and sealed under partial vacuum. Standard ^{6}Li, ^{13}C, and ^{15}N NMR spectra were recorded on a 500 MHz spectrometer at 73.57, 125.79, and 50.66 MHz, respectively. The ^{6}Li, ^{13}C, and ^{15}N resonances are referenced to 0.30 M [^{6}Li]LiCl/methanol at –90 °C (0.0 ppm), the CH_2O resonance of THF at –90 °C (67.57 ppm), and neat Me_2NEt at –90 °C (25.76 ppm), respectively.

Computations. DFT computations were optimized at B3LYP/6–31G(d) level[33] with single-point calculations at the MP2 level of theory.

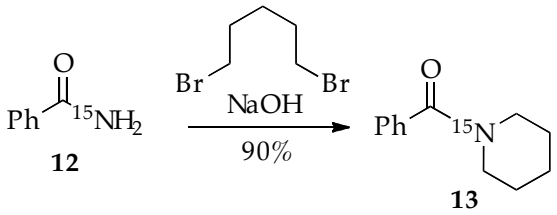
Synthesis of [$^{15}N_4$]3: general. Unless the reaction procedure states otherwise, all reactions requiring inert atmosphere were carried out with dry argon in oven or flame-dried glassware. THF and diethyl ether were distilled from sodium-benzophenone in a continuous still under an atmosphere of argon. Dichloromethane, diisopropylamine, pyridine, triethylamine, and chlorotrimethylsilane were distilled from calcium hydride in a continuous still under and atmosphere of argon. Chlorotriethylsilane (TESCl) and diisopropylethylamine (Hunig's base) were distilled from calcium hydride under an inert atmosphere of dry argon and stored over calcium hydride. Room temperature reactions were carried out between 22 and 24 °C. Analytical thin-layer chromatography was visualized using combinations of ultraviolet, anisaldehyde, ceric ammonium

molybdate, potassium permanganate, and iodine staining. Flash chromatography was preformed using 40-63 mm silica gel (Merck, Geduran, no. 11567-1) as the stationary phase. Proton magnetic resonance spectra were recorded at 400 MHz, 500 MHz, or 600 MHz. Carbon magnetic resonance spectra were recorded at 100 MHz, 125 MHz, or 150 MHz. All chemical shifts were reported in d units relative to tetramethylsilane. High Resolution mass spectroscopic data were obtained at the Mass Spectrometry Laboratory at the University of California, Santa Barbara.



12

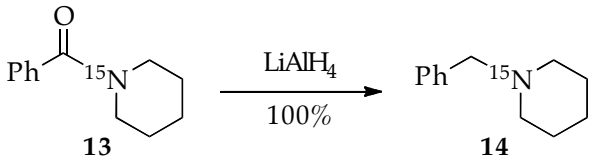
Benzamide-^{15}N (12).[52] Sodium hydroxide (10 M in water, 16.7 mL, pre-cooled to 0 °C) was added to a solution of benzoyl chloride (12.55 mL, 0.108 mol) and ammonium-^{15}N chloride (2.50 g, 45.88 mmol) in water (8.3 mL) and diethyl ether (12.5 mL) at 0 °C. After 15 min, the solids were filtered, collected, and dried under high vacuum to deliver benzamide-^{15}N (4.62 g, 37.83 mmol, 82%) which was used directly without further purification. ^{1}H-NMR (600 MHz; $CDCl_3$): □ 7.81-7.80 (m, 2H), 7.54-7.51 (m, 1H), 7.45 (m, 2H), 5.91 (m, 2H).



12 **13**

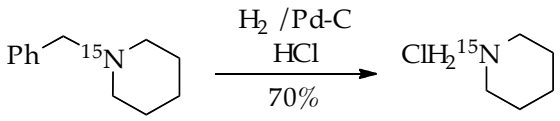
1-Benzoylpiperidine-^{15}N (13). 1,5-Dibromopentane was added to a mixture of benzamide-^{15}N (4.62 g, 37.83 mmol), tetrabutylammonium hydrogen sulfate (1.41 g, 4.16 mmol), potassium carbonate (7.37 g, 53.34 mmol), and sodium hydroxide (7.41 mol, 0.185 mol), in dry toluene (162 mL). The solution was heated at reflux for 18 hr. After cooling to room temperature (rt), the solids were filtered off and the residue was

purified via flash chromatography (silica, 30% → 70% ethyl acetate-hexanes) to deliver 1-benzoylpiperidine-^{15}N (6.41 g, 33.69 mmol, 90%). ^{1}H-NMR (400 MHz; $CDCl_3$): □ 7.52-7.21 (m, 5H), 3.75-3.68 (m, 2H), 3.38-3.31 (m, 2H), 1.72-1.48 (m, 6H).



13 **14**

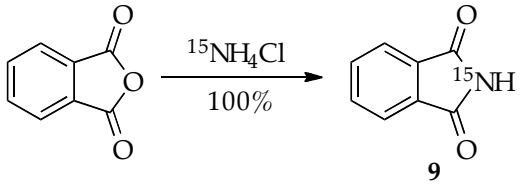
1-Benzylpiperidine-^{15}N (14). A solution of 1-benzoylpiperidine-^{15}N (6.41 g, 33.69 mmol) in diethyl ether (50 mL total with rinses) was added to a suspension of lithium aluminum hydride (5.11 g, 0.135 mol) in diethyl ether (122 mL) at 0 °C. After the addition of 1-benzoylpiperidine-^{15}N was complete, the solution was refluxed for 18 hr. The reaction was cooled to 0 °C, and water (5.10 mL) was added carefully. After 5 min 3 M NaOH (5.10 mL) was added and the reaction was stirred for an additional 5 min. Water (15.30 mL) was added, and the reaction was stirred for 5 min at 0 °C before warming to rt. After 3 hr the solids were filtered and rinsed with diethyl ether. The filtrate was concentrated under reduced pressure to deliver 1-benzylpiperidine-^{15}N (5.94 g, 33.69 mmol, 100%), which was used directly without further purification. ^{1}H-NMR (400 MHz; $CDCl_3$): □ 7.32-7.21 (m, 5H), 3.49-3.47 (m, 2H), 2.41-2.32 (m, 4H), 1.60-1.52 (m, 4H), 1.45-1.38 (m, 2H).



14 **15**

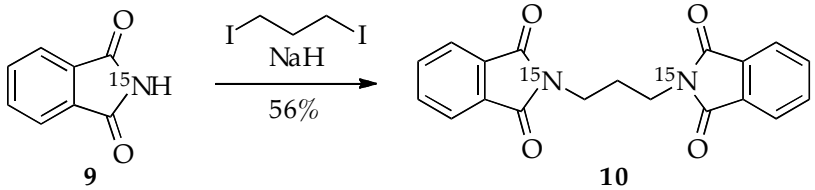
Piperidine-HCl-^{15}N (15). Following a literature protocol[53a] hydrogen gas was bubbled through a solution of 1-benzylpiperidine-^{15}N (2.97 g, 16.85 mmol) and palladium on carbon (0.297 g) in methanol (112 mL) and dichloromethane (56 mL), which generates HCl in situ under the reaction conditions.[53b] After 15 min the hydrogen

needle was removed from the solution, and the reaction was allowed to stir under a hydrogen atmosphere for 24 hr. The solution was filtered through a celite pad. The filtrate was concentrated under reduced pressure to deliver piperidine-^{15}N (1.45 g, 11.83 mmol, 70%) as its hydrochloride salt, which was used directly without further purification. ^{1}H-NMR (500 MHz; D_2O): □ 3.27-3.09 (m, 4H), 1.90-1.74 (m, 4H), 1.74-1.62 (m, 2H).



9

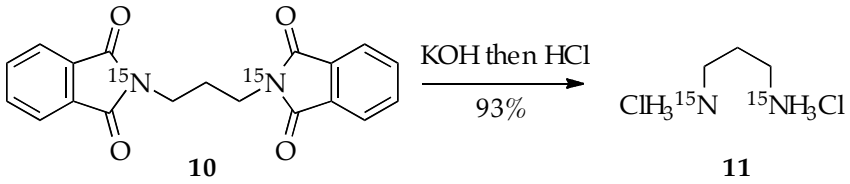
Phthalimide-^{15}N (9).b[54] Ammonium-^{15}N chloride (2.50 g, 45.88 mmol) and sodium hydroxide were combined in a flask and connected via cannula to a separate flask containing phthalic anhydride (6.80 g, 45.88 mmol) in methanol (113 mL) cooled to -10 °C. The flask containing ammonium-^{15}N chloride and sodium hydroxide was heated with a propane torch, and the resulting gas was bubbled through the mentholic solution of phthalic anhydride. After gas evolution ceased the solution was stirred for an additional hour. The methanol was distilled at atmospheric pressure. The crude residue was heated to 230 °C for 10-15 min. After cooling, phthalimide-^{15}N (6.80 g, 45.88 mmol, 100%) was obtained and used directly without further purification. ^{1}H-NMR (500 MHz; DMSO-D_6): □ 11.33 (d, J = 93.9 Hz, 1H), 7.85-7.82 (m, 4H).



9 **10**

***N,N′*-Trimethylenediphthalimide-^{15}N (10).**[55] Phthalimide-^{15}N (6.80 g, 45.88 mmol) was added to a suspension of sodium hydride (3.30 g, 82.58 mmol) in

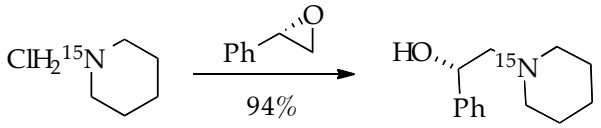
dimethylformamide (91.8 mL) at rt. After 15 min 1,3-diiodopropane (2.63 mL, 22.94 mmol) was added and the reaction stirred at rt for 15 min and then heated in a sealed flask at 100 °C for 3 hr. The reaction was cooled to rt and diluted with water and ethyl acetate. The aqueous layer was extracted with ethyl acetate (3 x 300 mL). The combined organic layers were washed with water (2 x 300 mL) and brine, dried with sodium sulfate, and concentrated. The residue was dissolved in ethyl acetate and dichloromethane, and silica gel was added. The solution was evaporated to dryness. The residue, absorbed onto the silica gel was purified via flash chromatography (silica, 10% → 30% ethyl acetate – dichloromethane) to give the desired product (4.35 g, 12.93 mmol, 56%). ^{1}H-NMR (500 MHz; $CDCl_3$): □ 7.87-7.82 (m, 4H), 7.74-7.69 (m, 4H), 3.79-3.75 (m, 4H), 2.14-2.07 (m, 2H).



10 **11**

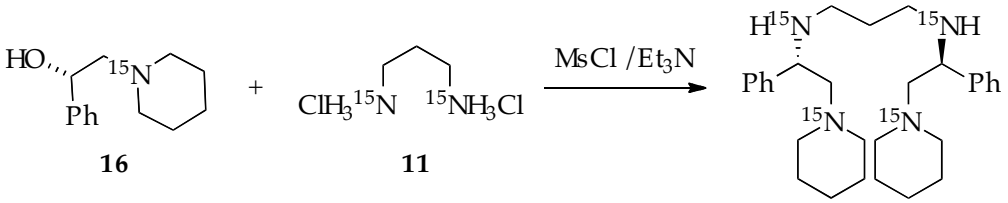
1,3-Diaminopropane-^{15}N (11). Potassium hydroxide (5.81 g, 0.104 mol) was added to a suspension of *N,N'*-trimethylenediphthalimide-^{15}N (4.35 g, 12.93 mmol) in water (18 mL) and heated at 70 °C for 18 hr at, which point the reaction became clear and homogeneous. The reaction was distilled into a flask containing 2.15 mL of 12.1 M hydrochloric acid. After distillation to dryness, water (45 mL) was added to the reaction flask and again distilled to dryness. This process was repeated twice with water (45 mL) and once with methanol (45 mL). The combined distillates were concentrated under reduced pressure to deliver 1,3-diaminopropane-^{15}N as its hydrochloride salt (1.78 g, 11.94 mmol, 92%), which was used without further purification. ^{1}H-NMR (600 MHz; CD_3OD): □ 3.05 (m, 4H), 2.05 (m, 2H). ^{13}C NMR (150 MHz; CD_3OD): □ 36.4, 25.1. ^{15}N

NMR (60.5 MHz, CD_3OD): □ 31.8. LRMS (ESI) calcd for $C_3H_{13}{}^{15}N_2$ [M+H] 77.09, found 76.98.



15 **16**

(1*S*)-1-(1-Phenyl)-2-(1-piperidinyl)ethanol-^{15}N (16). Sodium hydroxide (0.437 g, 11.83 mmol) was added to a solution of piperidine-^{15}N (1.45 g, 11.83 mmol) and (*S*)-styrene oxide (1.29 mL, 11.26 mmol) in ethanol (28.2 mL) and heated at 120 °C for 4h. After cooling to rt, the reaction was diluted with water and ethyl acetate. The aqueous layer was extracted with ethyl acetate (3 x 75 mL). The combined organic layers were washed with brine, dried with sodium sulfate, and concentrated. The residue (2.29 g, 11.08 mmol, 94%) was used directly without further purification. ^{1}H-NMR (400 MHz; $CDCl_3$): □ 7.41-7.15 (m, 5H), 4.73-4.69 (m, 1H), 3.70-3.57 (m, 1H), 2.76-2.64 (m, 2H), 2.60-2.52 (m, 1H), 2.53-2.45 (m, 1H), 2.43-2.32 (m, 2H), 1.74-1.41 (m, 6H).



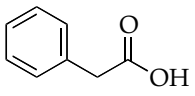
16 **11** **3**

Tetraamine-^{15}N (3). Methanesulfonyl chloride (2.10 mL, 26.58 mmol) was added to a solution of (1*S*)-1-(1-phenyl)-2-(1-piperidinyl)ethanol-^{15}N (4.57 g, 22.15 mmol) and triethylamine (9.30 mL, 66.45 mmol) in diethyl ether (74 mL) at 0 °C. After 30 min the solution was warmed to rt and stirred for an additional hour. Then, triethylamine (12.4 mL, 88.6 mmol), 1,3-diaminopropane-^{15}N hydrochloride (1.65 g, 11.08 mmol), and water (12.8 mL) were added to the reaction, and the solution was allowed to stir for 2 days at

rt. The reaction was diluted with water and diethyl ether. The aqueous layer was extracted with diethyl ether (3 x 100 mL). The combined organic layers were washed with brine, dried with sodium sulfate, and concentrated, and the residue was purified via flash chromatography (silica, 5% → 10% → 20% triethylamine-ethyl acetate). The product was then recrystallized from isopropanol:water (1.1:1) to deliver the purified tetraamine-^{15}N (2.10 g, 4.64 mmol, 42%) as a white solid and 1.25 g (2.76 mmol, 25%) of tetraamine-^{15}N **3** as an oil. ^{1}H-NMR (600 MHz; $CDCl_3$): □ 7.34 (d, *J* = 7.2 Hz, 4H), 7.30 (t, *J* = 7.6 Hz, 4H), 7.22 (t, *J* = 7.2 Hz, 2H), 3.72 (dd, *J* = 11.0, 3.1 Hz, 2H), 2.52-2.22 (m, 18H), 1.66 (t, *J* = 5.6 Hz, 2H), 1.57-1.49 (m, 8H), 1.41 (d, *J* = 5.1 Hz, 4H). ^{13}C NMR (150 MHz; $CDCl_3$): □ 143.3, 128.2, 127.3, 126.9, 66.6, 60.2, 54.6, 46.3, 30.5, 26.1, 24.5. HRMS (ESI) calcd for $C_{29}H_{45}{}^{15}N_4$ [M+H] 453.3518, found 453.3526.

Chapter 3 Appendix

Structures



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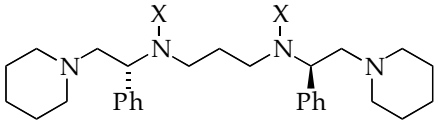
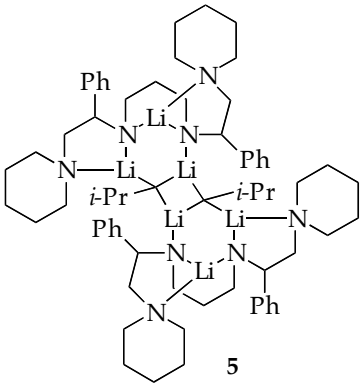


3; X = H
4; X = Li (R^*_2NLi)



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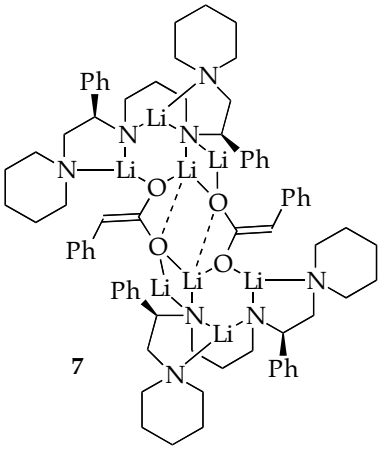

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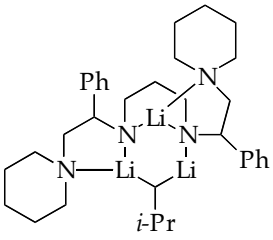

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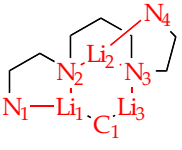

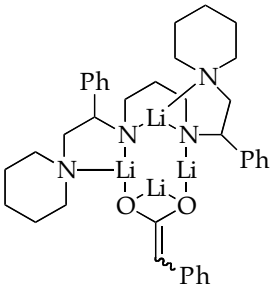

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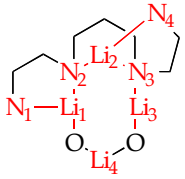


Part 1: ^{1}H and ^{13}C NMR of "Substrates"

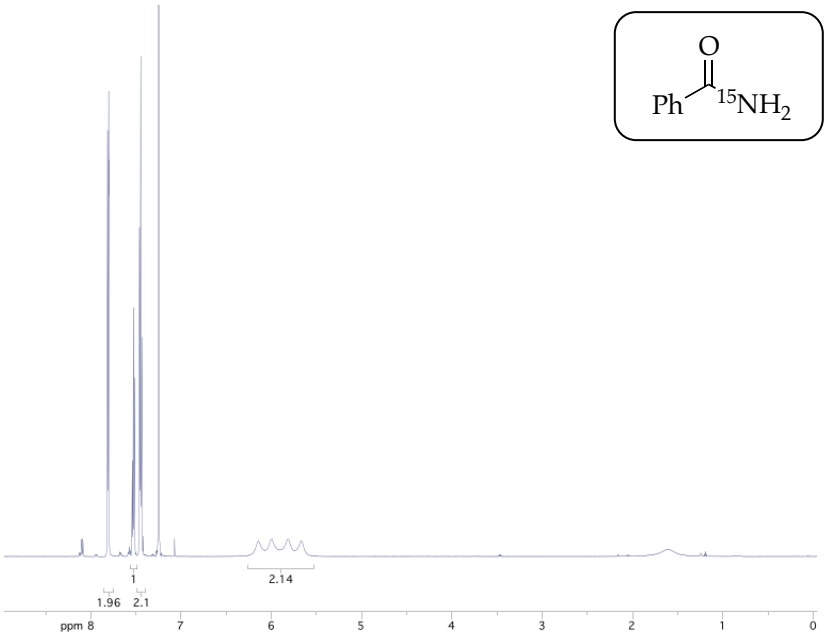


Figure A3.1. ^{1}H NMR ($CDCl_3$) of **12**

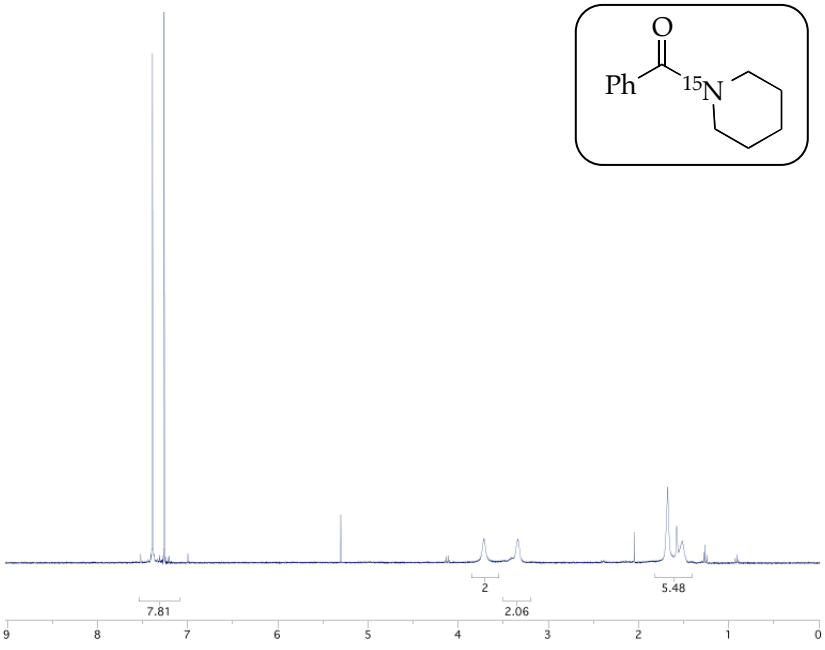


Figure A3.2. ^{1}H NMR ($CDCl_3$) of **13**

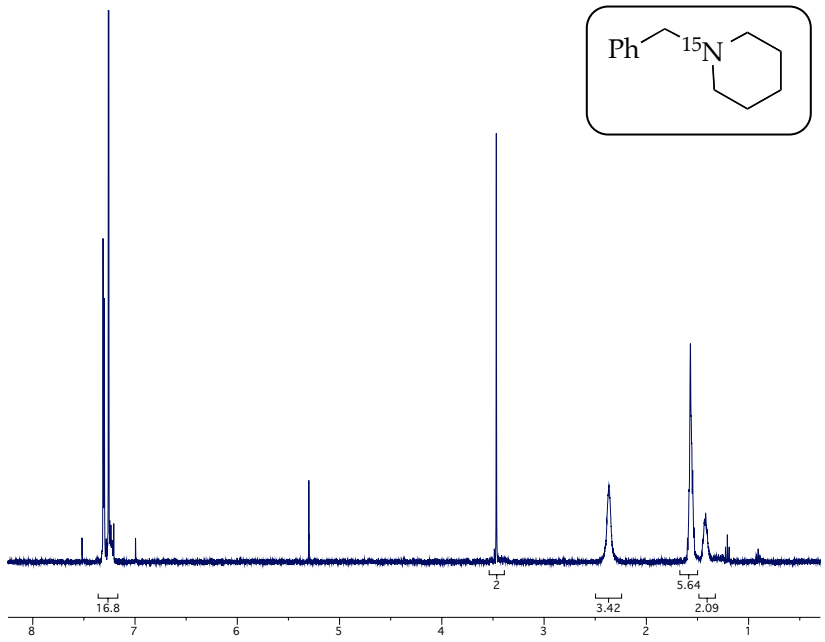


Figure A3.3. ^{1}H NMR ($CDCl_3$) of **14**

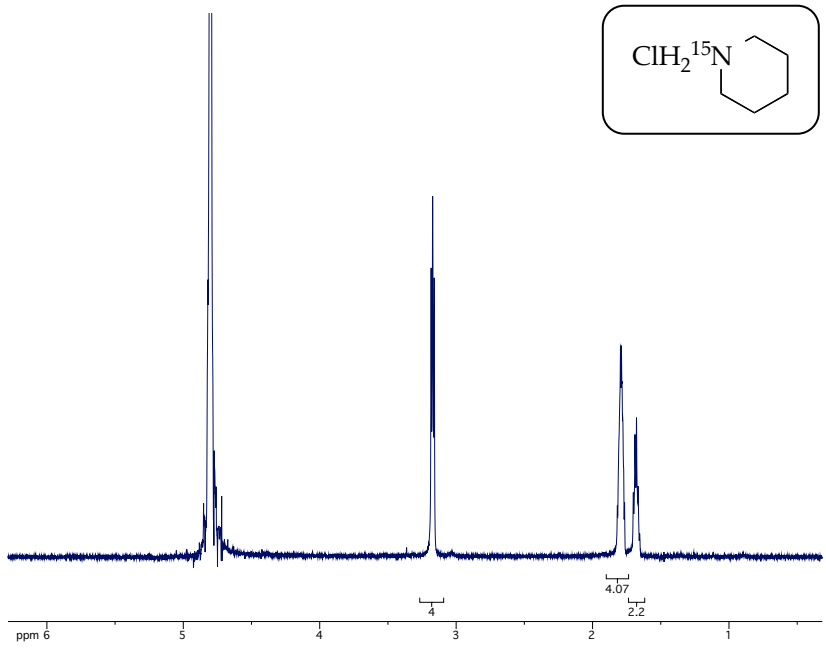


Figure A3.4. ^{1}H NMR ($CDCl_3$) of **15**

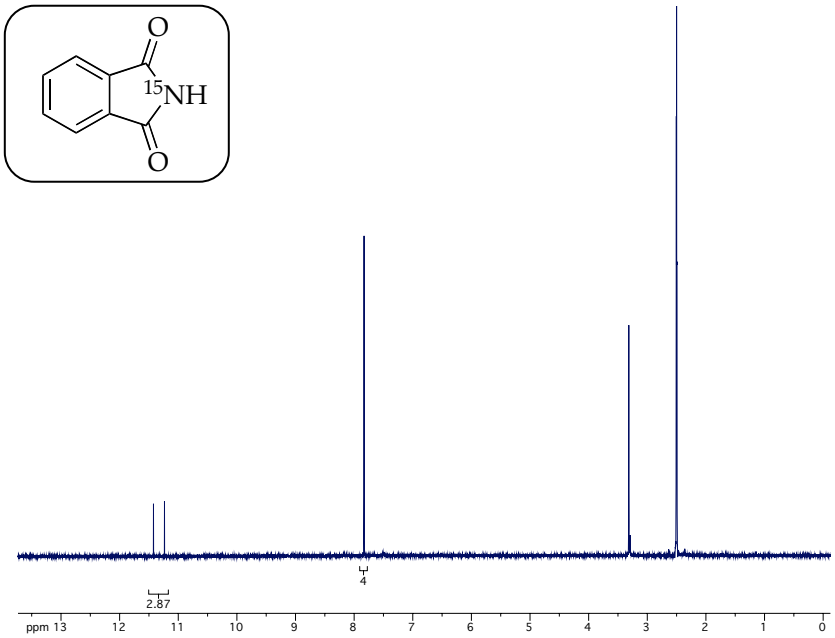


Figure A3.5. ^{1}H NMR ($CDCl_3$) of **9**

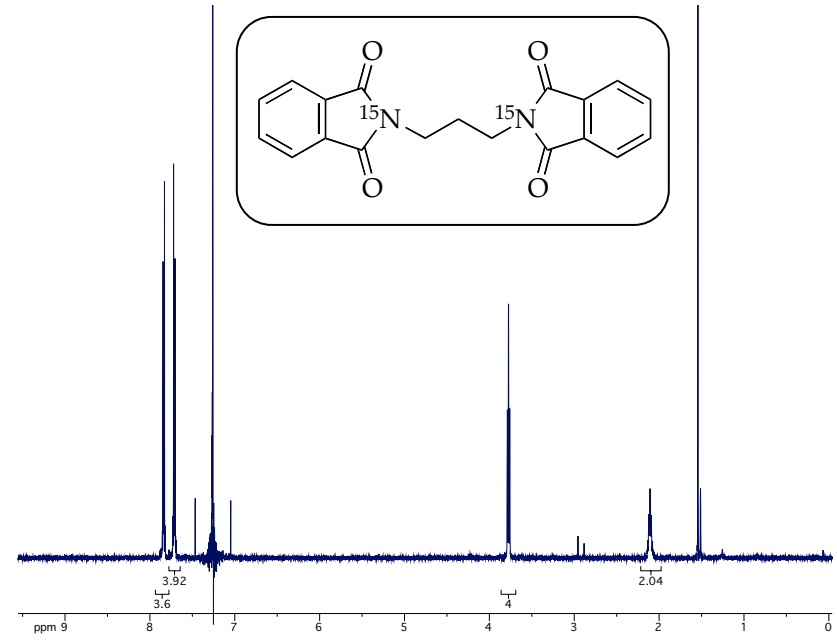


Figure A3.6. ^{1}H NMR ($CDCl_3$) of **10**

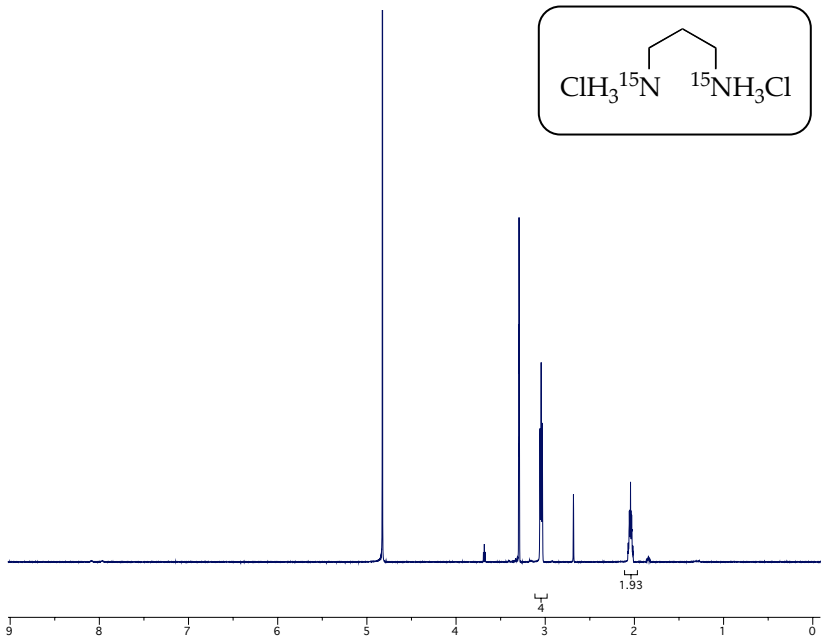


Figure A3.7. ^{1}H NMR ($CDCl_3$) of **11**

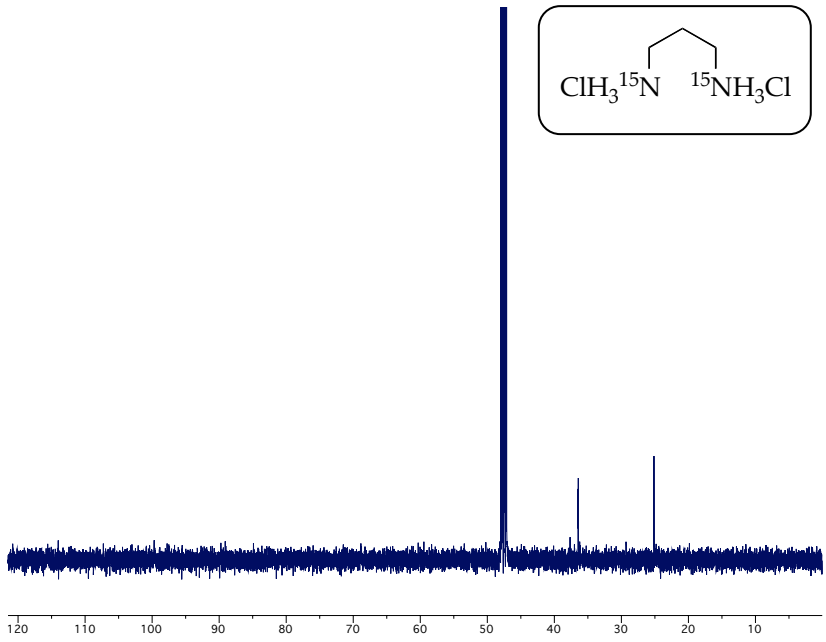


Figure A3.8. ^{13}C NMR ($CDCl_3$) of **11**

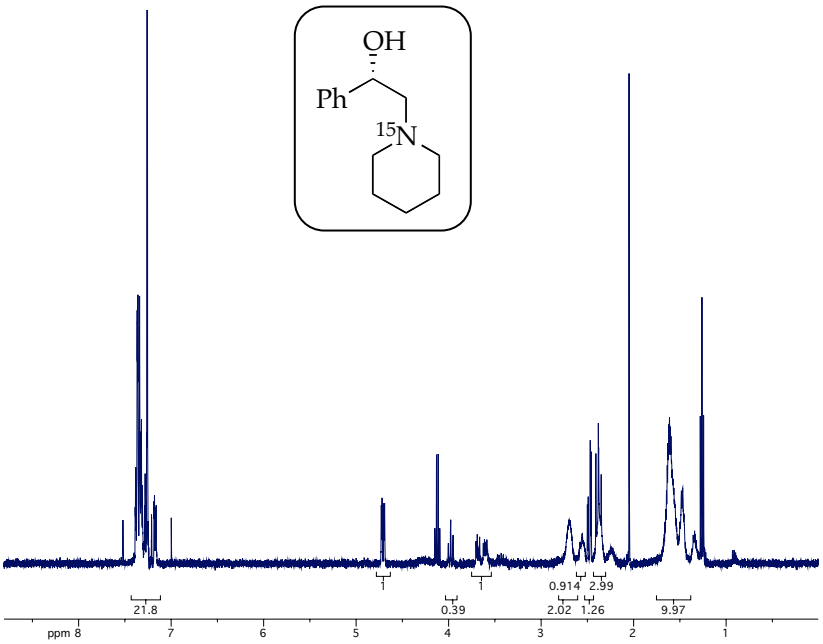


Figure A3.9. ^{1}H NMR ($CDCl_3$) of **16**

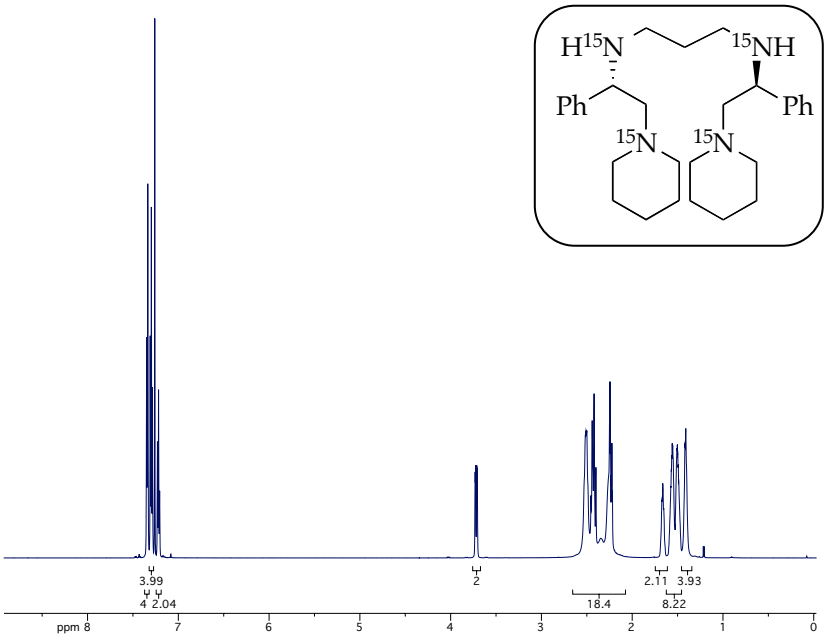


Figure A3.10. ^{1}H NMR ($CDCl_3$) of **3**

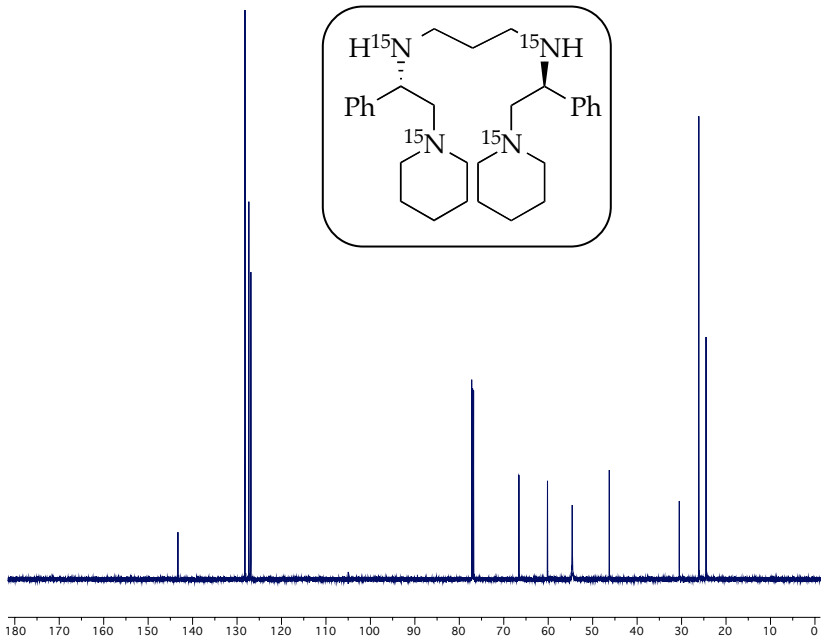


Figure A3.11. ^{13}C NMR ($CDCl_3$) of **3**

Part 2: 1D NMR [^{6}Li, ^{13}C, ^{15}N] Spectroscopic Studies

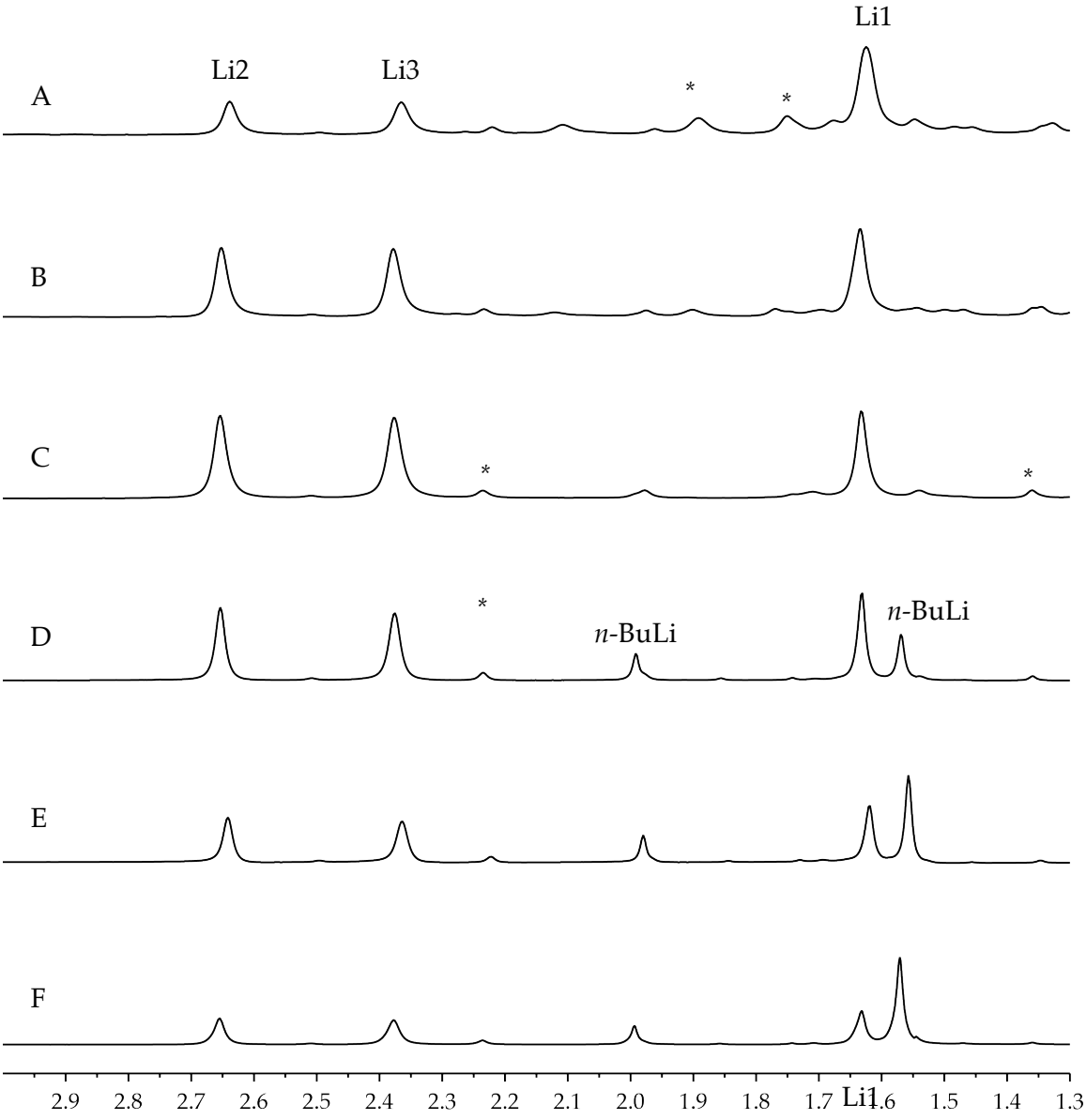


Figure A3.12. ^{6}Li NMR spectra of amine **3** with varying equiv of *n*-BuLi in THF-pentane *per diamine* recorded at –90 °C after aging at –78 °C for 2 hrs: (A) 0.5 equiv *n*-BuLi; (B) 1.0 equiv *n*-BuLi; (C) 2.0 equiv *n*-BuLi; (D) 3.0 equiv *n*-BuLi; (E) 4.0 equiv *n*-BuLi; (F) 5.0 equiv *n*-BuLi.

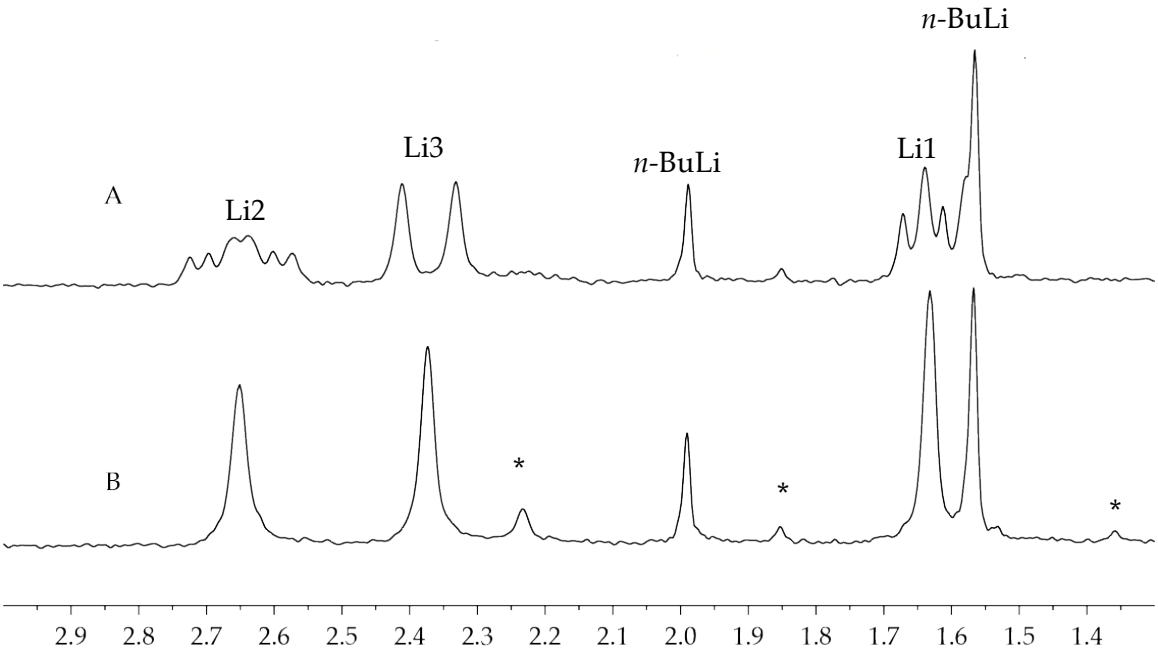


Figure A3.13. ^{6}Li NMR spectra of 0.10 M [^{6}Li,^{15}N]**6** prepared from [$^{15}N_4$]**3** with 4.0 equiv *n*-BuLi in 6.10 M THF-pentane recorded at –90 °C after aging at –78 °C for 2.0 hrs: (A) fully coupled; (B) broad-band ^{15}N decoupled.

^{6}Li	□ (ppm)
1	1.63 (dd, *J* [Li_1-N_2] = 4.3, *J* [Li_1-N_1]2.1 Hz)
2	2.65 (ddd, *J* [Li_2-N_2] = 4.9, *J* [Li_2-N_3] = 4.3, *J* [Li_2-N_4] = 2.1 Hz)
3	2.37 (d, *J J* [Li_3-N_3] = 5.8 Hz)

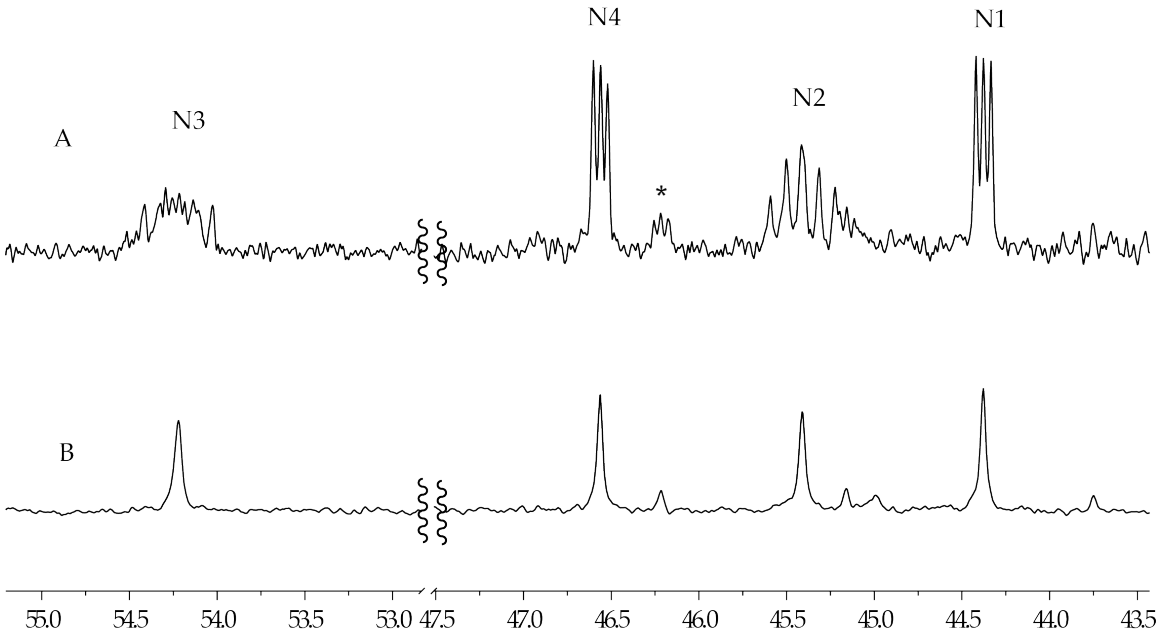


Figure A3.14. ^{15}N NMR spectra of 0.10 M [^{6}Li,^{15}N]**6** prepared from [$^{15}N_4$]**3** with 4.0 equiv *n*-BuLi in 6.10 M THF-pentane recorded at –90 °C after aging at –78 °C for overnight: (A) fully coupled; (B) broadband ^{15}N decoupled. *Unknown impurities that appear sporatically.

^{15}N	□ (ppm)
1	44.4 (t, J [N_1-Li_1] = 2.1 Hz)
2	45.4 (tt, J [N_2-Li_2] =4.9, J [N_2-Li_1] = 4.3 Hz)
3	54.2 (tt, J [N_3-Li_3] = 5.8, J [N_3-Li_2] = 4.3Hz)
4	46.6 (t, J [N_4-Li_2] = 2.1 Hz)

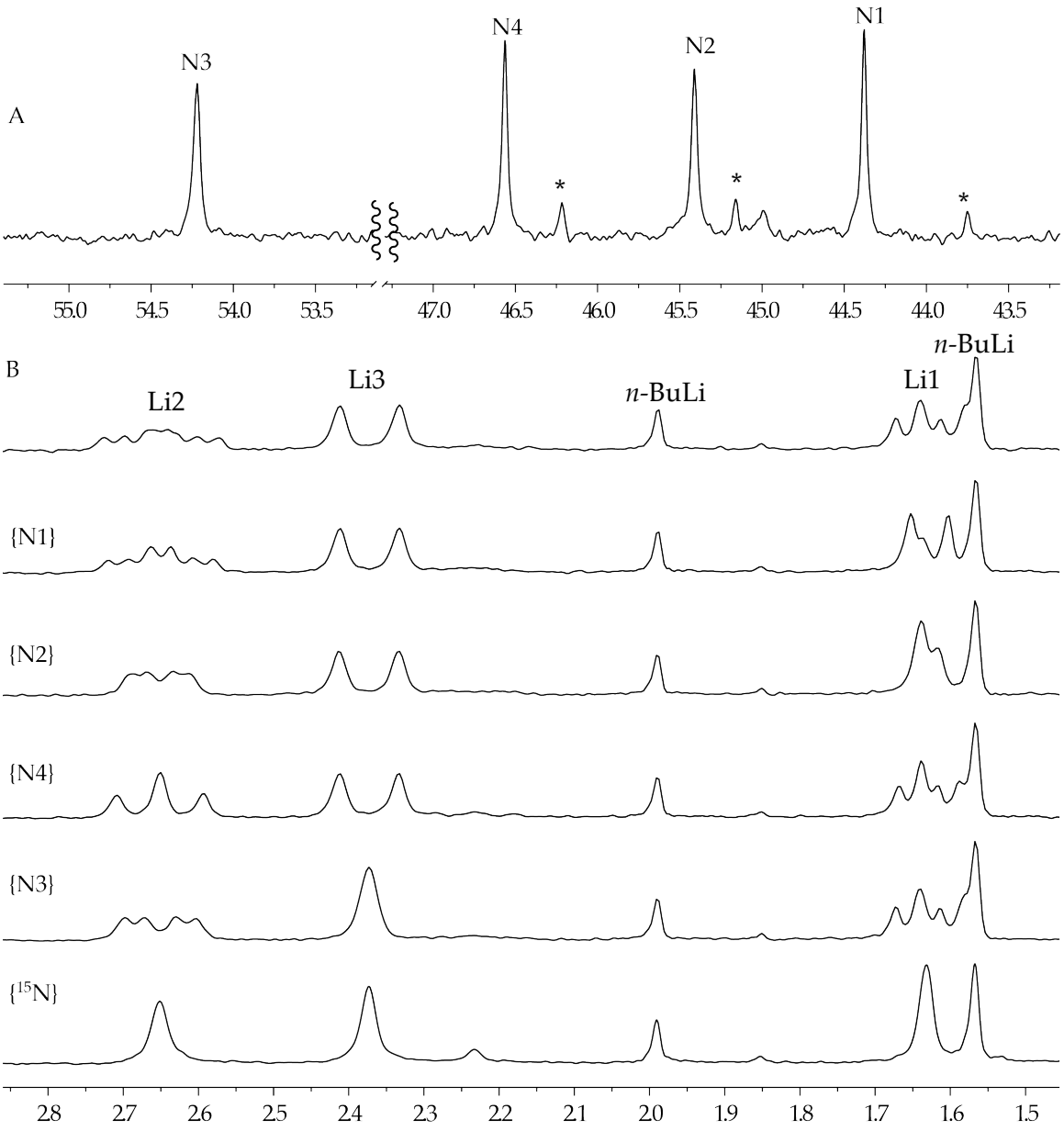


Figure A3.15. NMR spectra of 0.10 M [^{6}Li,^{15}N]**6** prepared from [$^{15}N_4$]**3** with 4.0 equiv *n*-BuLi in 6.10 M THF-pentane recorded at –90 °C after aging at –78 °C overnight showing effects of single-frequency ^{15}N decoupling. Resonance labels refer to those used on structure **6** (pg S4). (A) broad band ^{6}Li decoupled ^{15}N spectrum with resonance labels (N1-N4); (B) ^{6}Li NMR spectra with selective ^{15}N decoupling at 44.3 ppm (N1), 45.4 ppm (N2), 46.4 ppm (N4), 54.2 ppm (N3), and broadband. *Indicate unassigned resonances.

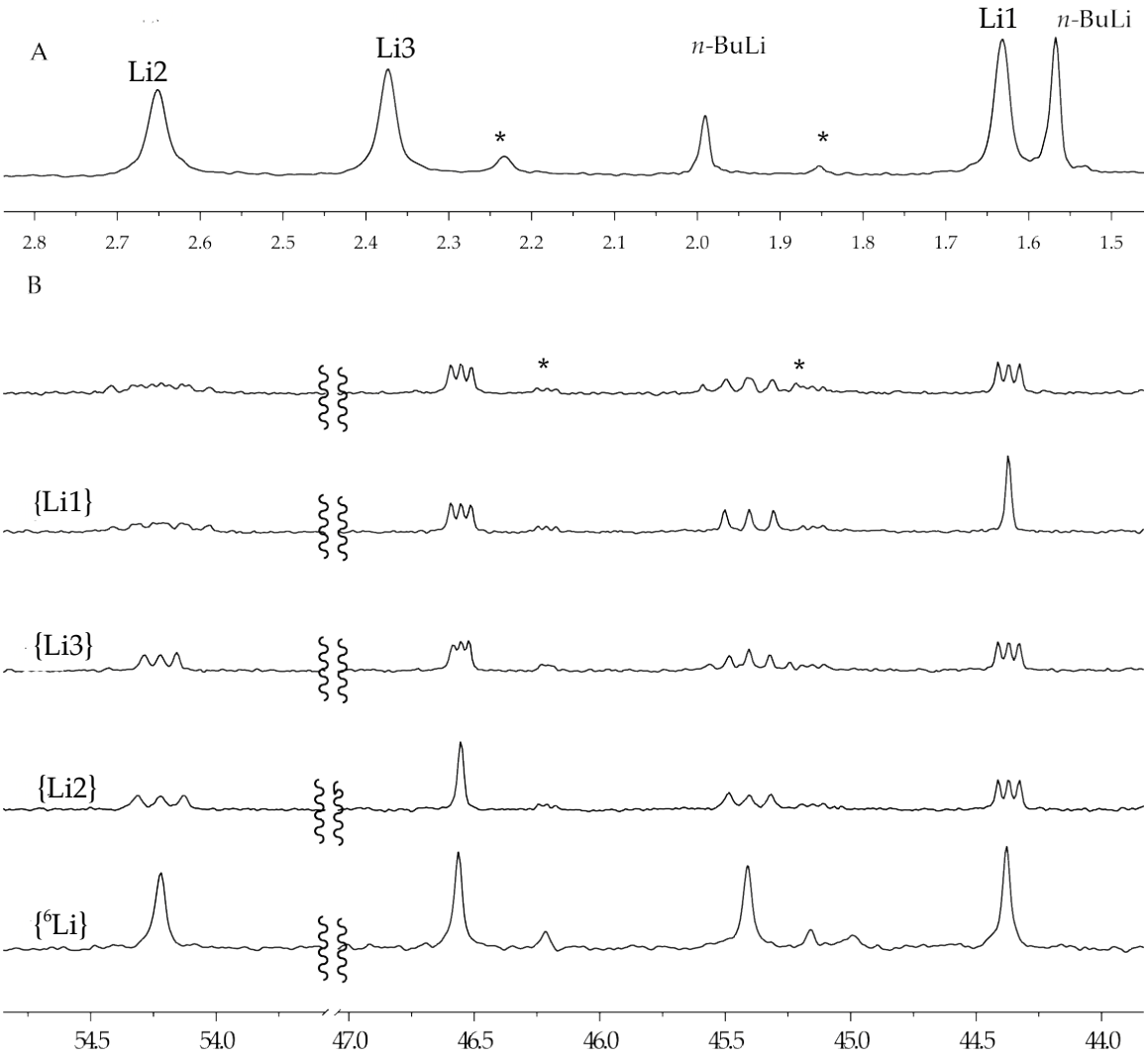


Figure A3.16. NMR spectra of 0.10 M [^{6}Li,^{15}N]**6** prepared from [$^{15}N_4$]**3** with 4.0 equiv *n*-BuLi in 6.10 M THF-pentane recorded at –90 °C after aging at –78 °C overnight showing effects of single-frequency ^{15}N decoupling. Resonance labels refer to those used on structure **6** (pg S4). (A) broad band ^{15}N decoupled ^{6}Li spectrum with resonance labels (Li1-Li3); (B) ^{15}N NMR spectra with selective ^{6}Li decoupling at 1.63 ppm (Li1), 2.65 ppm (Li2), 2.37 ppm (Li3), and broadband 6Li decoupled ^{15}N spectrum. *Indicate unassigned resonances.

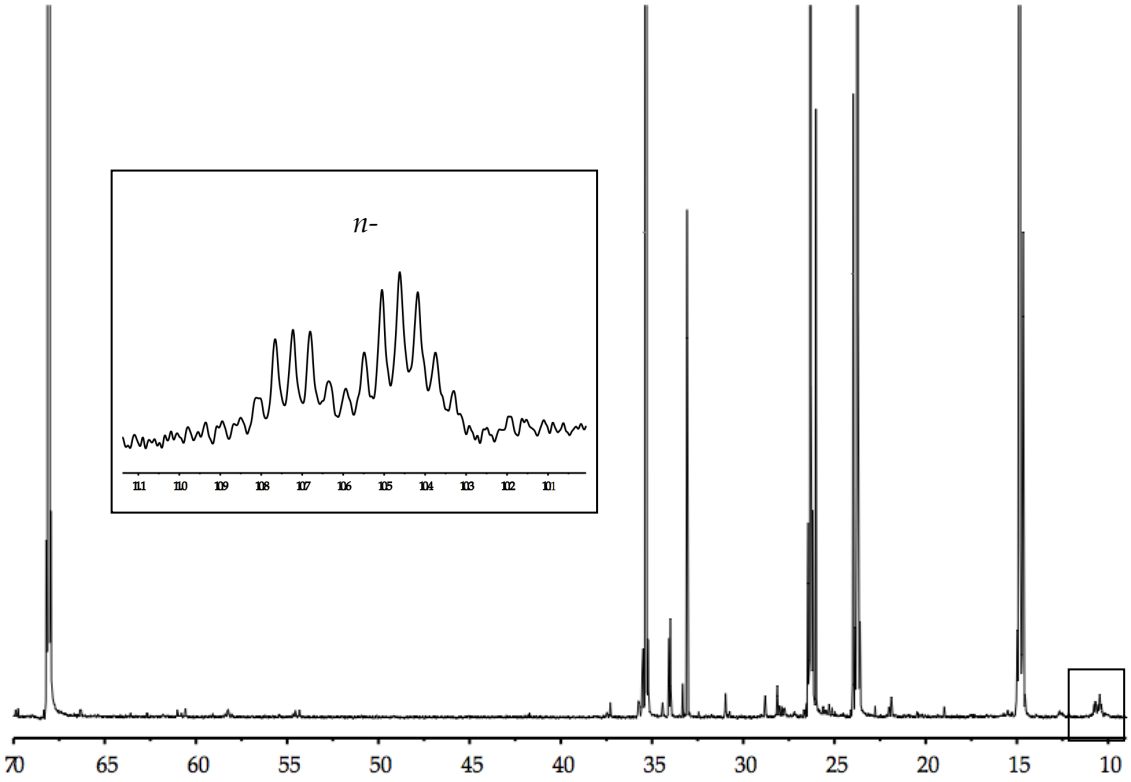


Figure A3.17. ^{13}C NMR spectra of 0.10 M [^{6}Li,^{15}N]**6** prepared from [$^{15}N_4$]**3** with 4.0 equiv *n*-BuLi in 6.10 M THF-pentane recorded at –90 °C after aging at –78 °C for overnight.

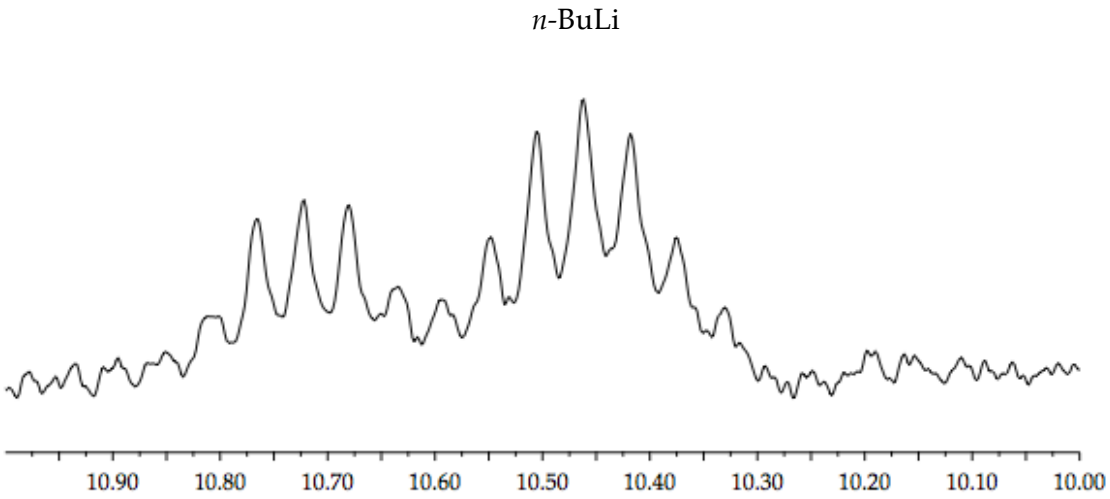


Figure A3.18. ^{13}C NMR spectra of 0.10 M [^{6}Li,^{15}N]**6** prepared from [$^{15}N_4$]**3** with 4.0 equiv *n*-BuLi in 6.10 M THF-pentane recorded at –90 °C after aging at –78 °C for overnight. (^{13}C resonance of the *n*-BuLi dimer appears as a 1:2:1 triplet at 12.6 ppm.)

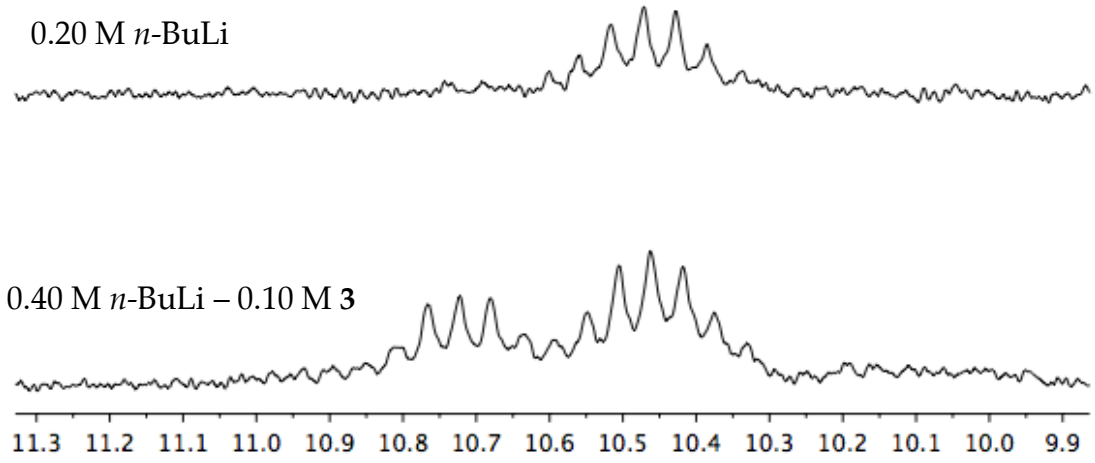


Figure A3.19. ^{13}C NMR spectra of 0.10 M [^{6}Li,^{15}N]**6** prepared from [$^{15}N_4$]**3** with 4.0 equiv *n*-BuLi in 6.10 M THF-pentane recorded at –90 °C after aging at –78 °C for overnight

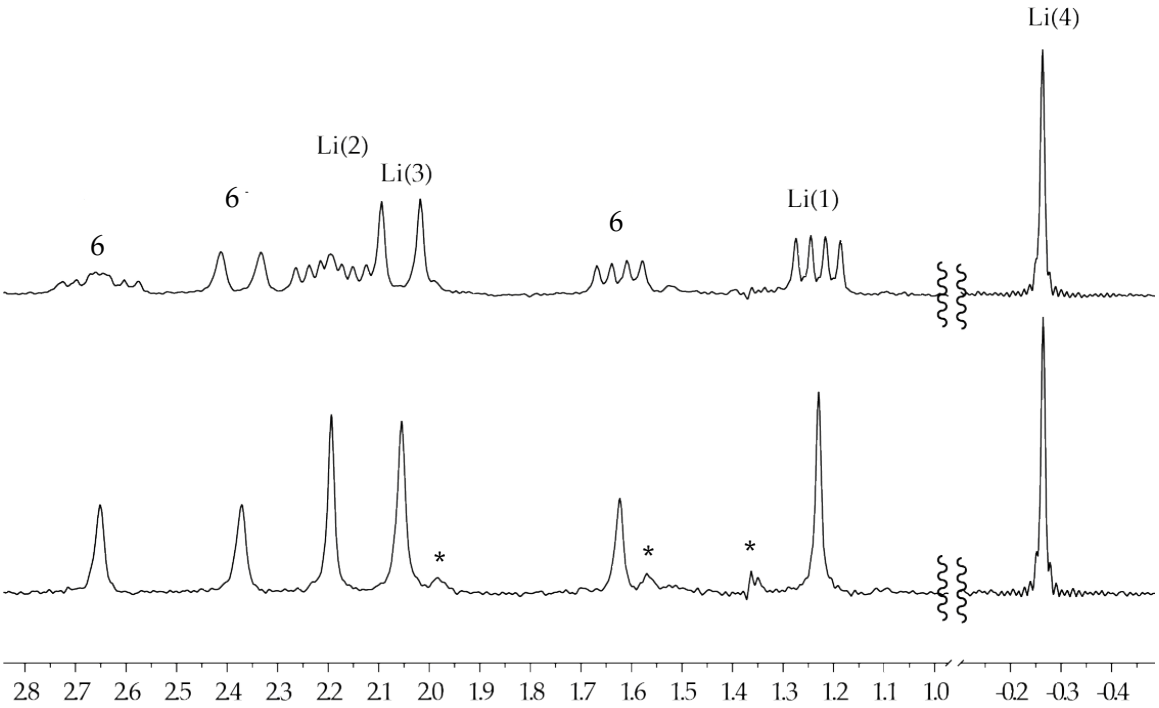


Figure A3.20. ^{6}Li NMR spectra of 0.10 M [^{6}Li,^{15}N]**8** prepared from [$^{15}N_4$]**3** with 4.0 equiv *n*-BuLi and phenylacetic acid in 6.1 M THF-pentane recorded at –90 °C after aging at –78 °C for 2.0 hrs: (A) fully coupled ^{6}Li spectrum; (B) ^{15}N broad band decoupled. *Indicate unassigned resonances.

^{6}Li	□ (ppm)
(1)	1.24 (dd, *J* [Li_1-N_2]= 4.3, *J* [Li_1-N_1]= 2.2 Hz)
(2)	2.20 (ddd, *J* [Li_2-N_2]= 4.8, *J* [Li_2-N_3]= 3.6, *J* [Li_2-N_4]= 1.9 Hz)
(3)	2.06 (d, *J* [Li_3-N_3]= = 5.6 Hz)
(4)	-0.26 (s)

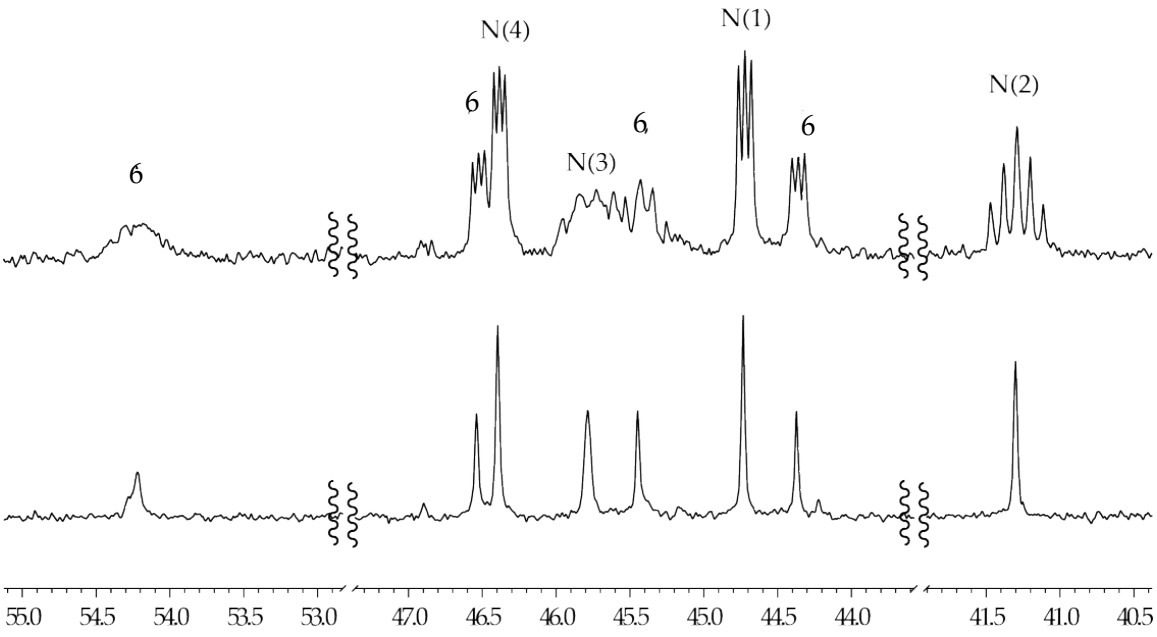


Figure A3.21. ^{15}N NMR spectra of 0.10 M [^{6}Li,^{15}N]**8** prepared from [$^{15}N_4$]**3**, 4.0 equiv *n*-BuLi, and phenylacetic acid in 6.1 M THF-pentane recorded at –90 °C after aging at –78 °C for 2.0 hrs: (A) fully coupled; (B) broad band decoupled.

^{15}N	□ (ppm)
1	44.7 (t, J[N_1-Li_1] = 2.2 Hz)
2	41.3 (p, J[N_2-Li_2] =4.8, J[N_2-Li_1] = 4.3 Hz)
3	45.8 (m)
4	46.4 (t, , J[N_4-Li_2] = 1.9 Hz)

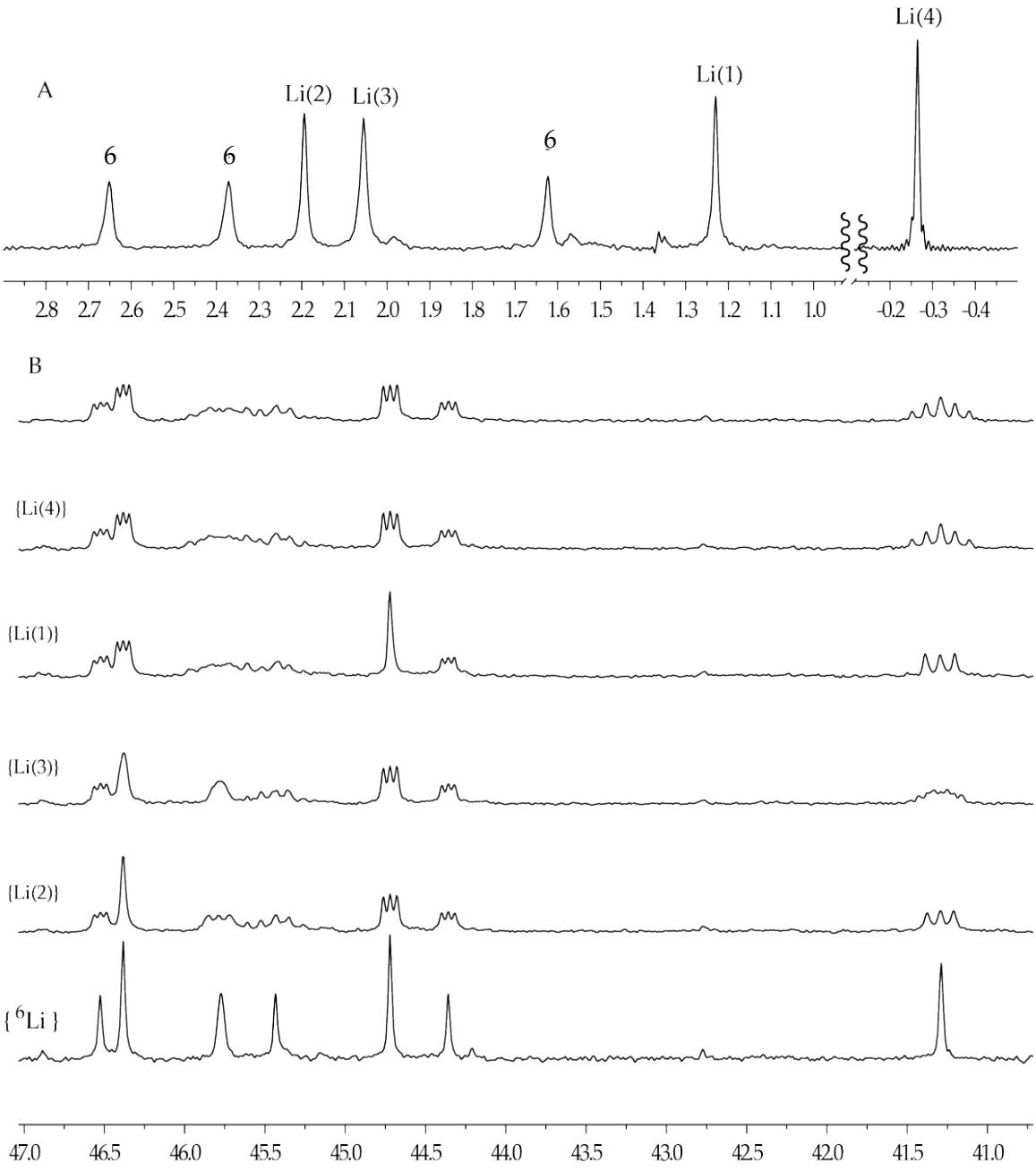


Figure A3.22. ^{15}N NMR spectra of 0.10 M [^{6}Li,^{15}N]**8** prepared from [$^{15}N_4$]**3**, 4.0 equiv *n*-BuLi, and phenylacetic acid in 6.1 M THF-pentane recorded at –90 °C after aging at –78 °C overnight: (A) fully coupled ^{6}Li spectrum ; (B) selective decoupling of Li4 (-0.26 ppm), Li1 (2.06 ppm), Li3 (2.20 ppm), Li2 (1.20 ppm), and broadband decoupling.

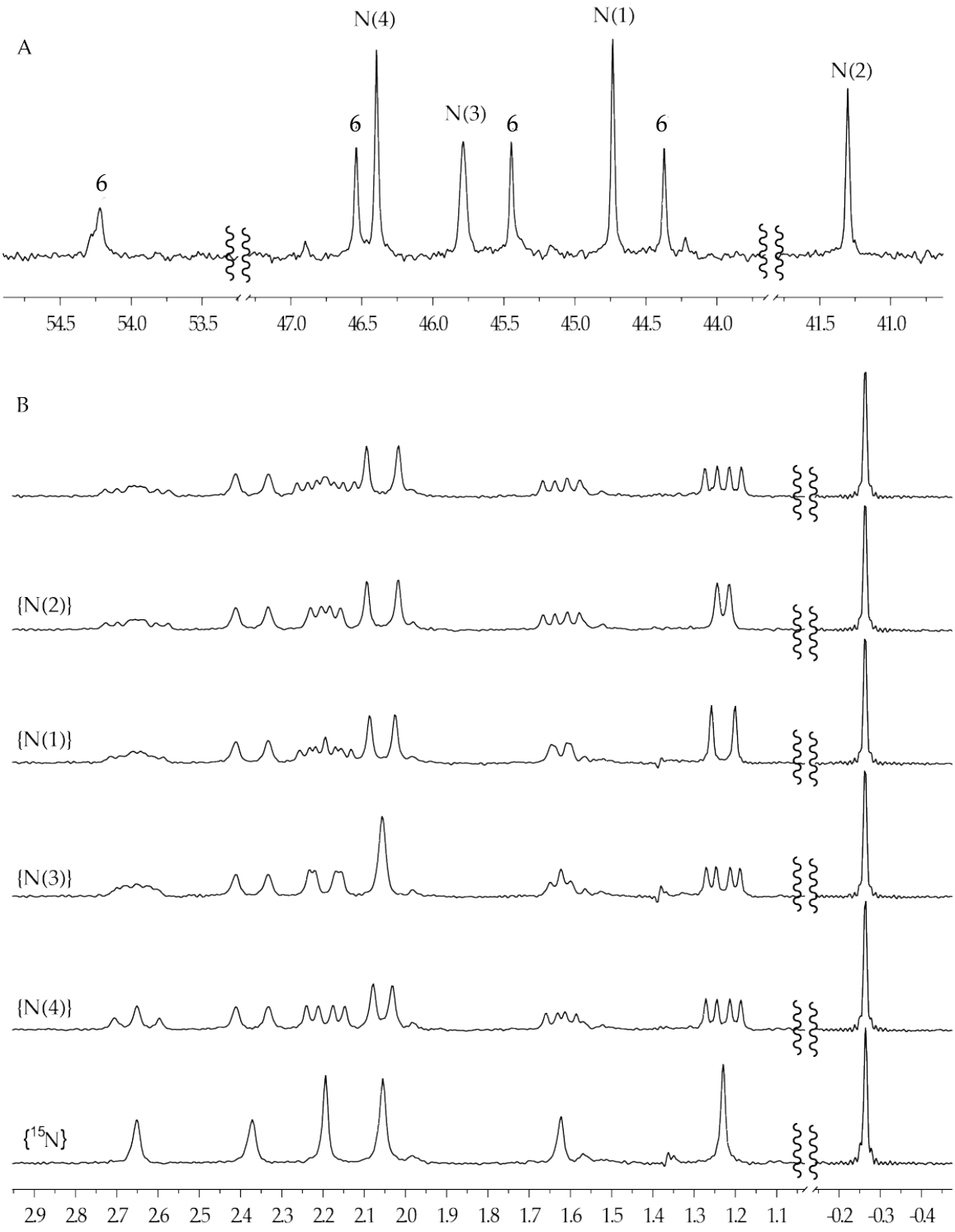


Figure A3.23. ^{6}Li NMR spectra of 0.10 M [^{6}Li,^{15}N]**8** prepared from [$^{15}N_4$]**3**, 4.0 equiv *n*-BuLi, and phenylacetic acid in 6.1 M THF-pentane recorded at –90 °C after aging at –78 °C overnight: (A) fully coupled ^{15}N spectrum ; (B) selective decoupling of N2 (41.3 ppm), N1 (44.7 ppm), N3 (45.8 ppm), N4 (46.4 ppm), and broadband decoupling.

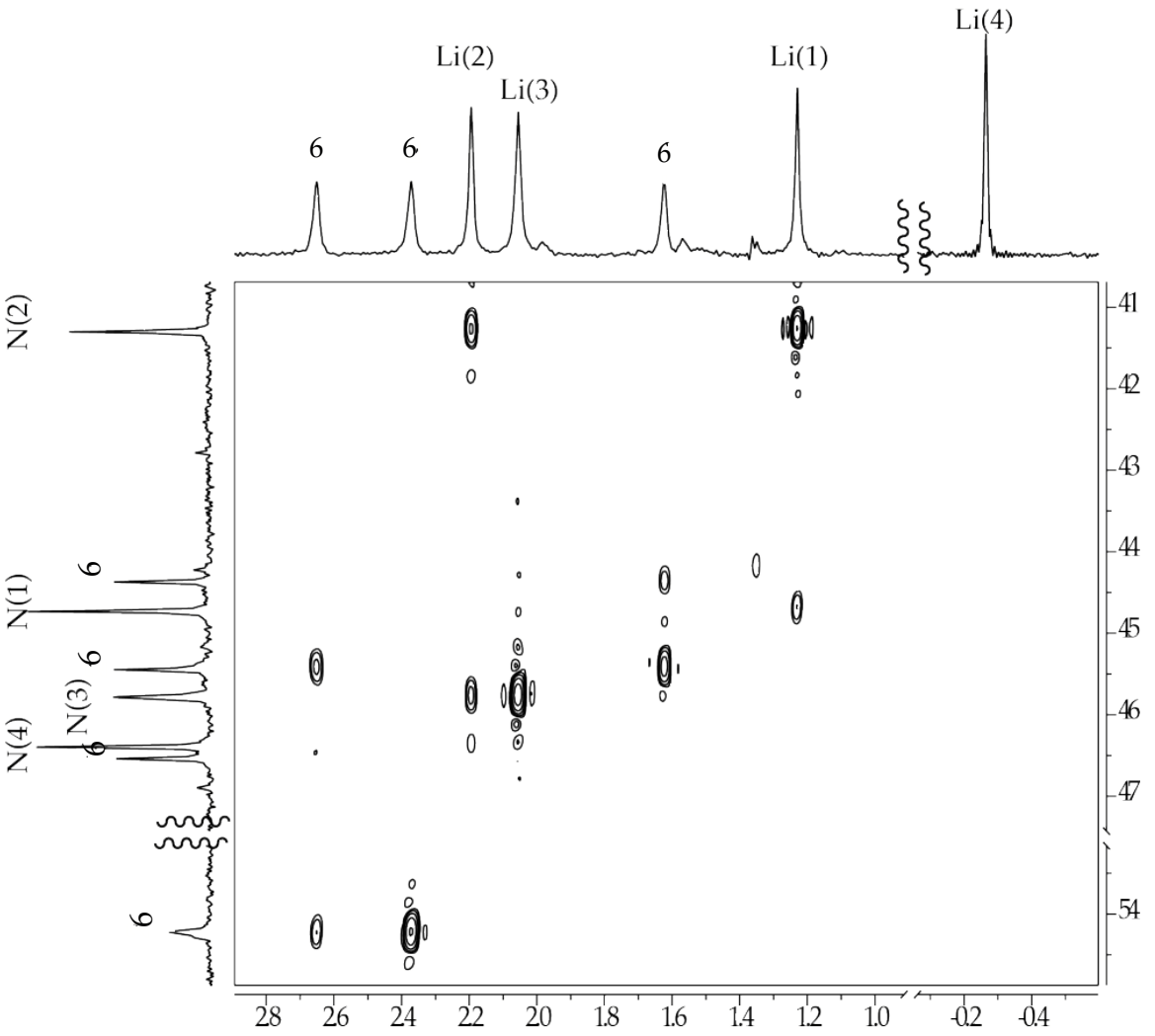


Figure A3.24. [^{6}Li,^{15}N]HMQC NMR spectrum of a mixture 0.10 M [^{6}Li,^{15}N]**6** and [^{6}Li,^{15}N]**8** prepared from [$^{15}N_4$]**3**, 4.0 equiv *n*-BuLi, and phenylacetic acid in 0.10 M THF-pentane recorded at –90 °C after aging at –78 °C overnight. The spectrum was recorded with broadband ^{6}Li and ^{15}N decoupling**.**

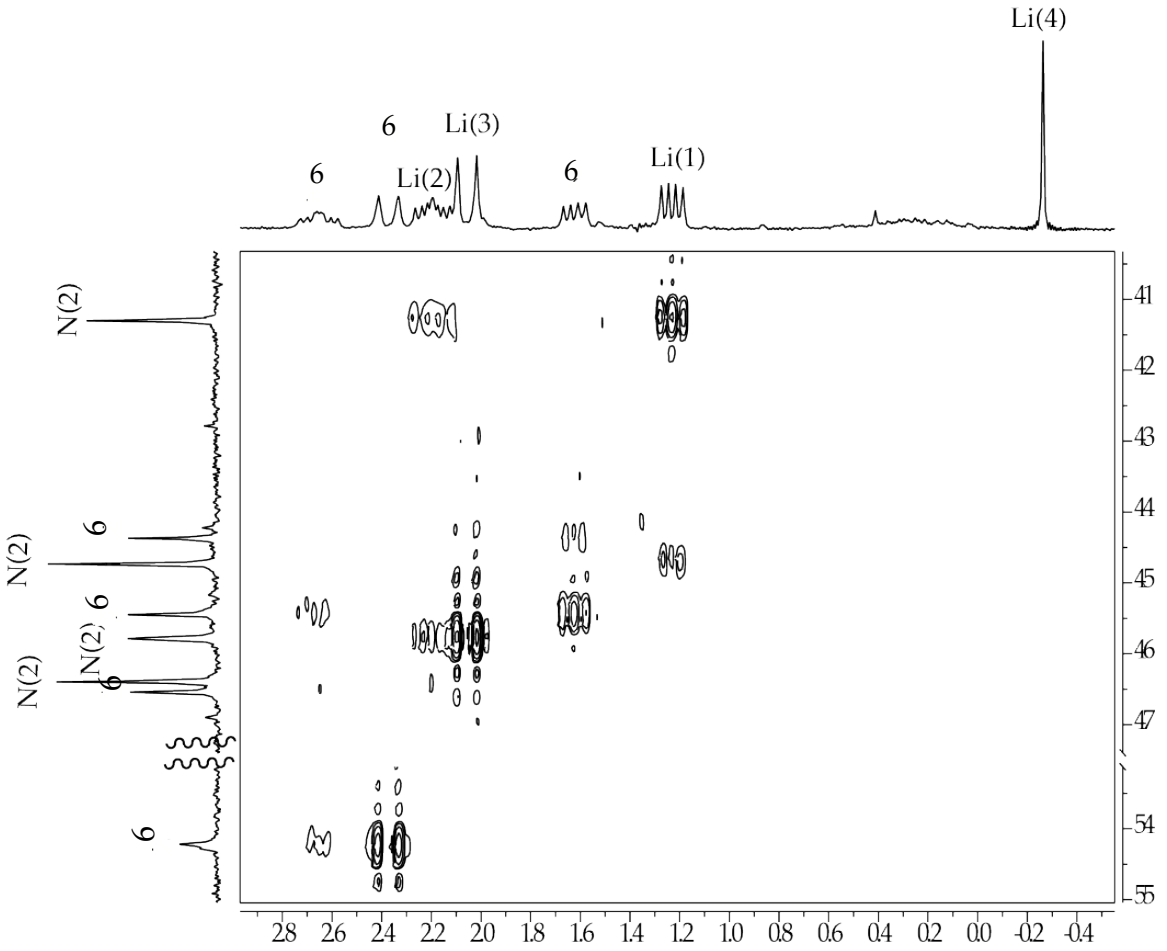


Figure A3.25. [^{6}Li,^{15}N] HMQC NMR spectrum of 0.10 M mixture of [^{6}Li,^{15}N]**6** and [^{6}Li,^{15}N]**8** prepared from [$^{15}N_4$]**3**, 4.0 equiv *n*-BuLi, and phenylacetic acid in 6.10 M THF-pentane recorded at –90 °C after aging at –78 °C overnight. The spectrum was recorded with broadband ^{6}Li decoupling.

Part 3: 2D NMR [^{1}H and ^{13}C] Spectroscopic Studies

2D-NMR Experimental and Analysis

2D-NMR analysis of the diamine-acid enolate complex: A sample containing a 1:0.6 ratio of lithium diamide/acid enolate and lithium dimaide/nBuLi aggregates in THF-*d8*/pentane was studied by standard 2D NMR techniques (COSY, TOCSY, HSQC, HMBC and ROESY) at –80 °C. These experiments allowed the assignment of most ^{1}H and ^{13}C resonances for both aggregates. Signal overlap in both ^{1}H and ^{13}C dimensions prevented unambiguous assignment of some piperidyl and phenyl resonances. Scalar coupling constants derived from COSY and HSQC experiments yielded dihedral angle information for the diamide backbone. The ROESY experiment yielded a large number of interatomic distance constraints as well as information on exchange processes.

Experimental: 2D NMR spectra were acquired on a 500 MHz Varian INOVA spectrometer operating at 499.76 MHz for ^{1}H observation using a 5 mm Varian DBG dual broadband probehead with single-axis pulsed field gradient. Sample temperature was maintained at –80 °C as calibrated with a neat methanol sample. ^{1}H and ^{13}C chemical shifts were referenced to the residual downfield THF-*d5* resonance at 3.58 ppm and 67.57 ppm, respectively. 2D experiments were acquired using standard pulse sequences supplied in VnmrJ 2.2D/Chempack 4.1 (Agilent Inc.) and processed and analyzed in MestReNova 8.0.2 (Mestrelab Research S.L).

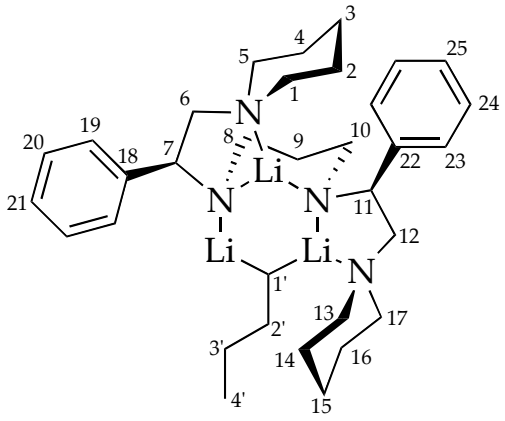
Conformation of the amide backbone: For the purposes of the following discussion, the Li-containing ring will be defined as the central plane of the aggregates. Bottom and below refer to the same side as the C-8–C-10 linker and top and above refer to the side opposite the linker. The diamide backbone appears to have very similar conformation in both mixed aggregates in solution and is also in agreement with the conformation observed in solid state and predicted by theory. We did not observe exchange for the diamide backbone in ROESY spectra—all diamide-related cross peaks with the same phase as the diagonal could be readily interpreted as relayed ROEs—indicating that no other conformations are accessed on the NMR time scale. The C-8 to C-10 linker adopts a fixed chair conformation with C-9 positioned under the central plane as evidenced by the large geminal and axial-axial couplings (~12 Hz) observed in the HSQC cross peaks, and ROEs observed between H-7 and H-8_{ax} as well as H-11 and H-10_{eq}. We observed large couplings (~12 Hz) between H-6_{top} and H-7 as well H-11_{top} and H-12′, consistent with dihedral angles approaching 180°, and allowing top/bottom assignment of the C-6 and C-12 methylene hydrogens. The large dihedral angle shows that one of two carbons of the five-membered rings must be puckered out of the plane, and that these rings are either conformationally rigid or such conformations dominate in a rapidly intraconverting system. The piperidyl residues are most likely in chair conformations based on coupling patterns observed in HSQC. The Li-N bond occupies the axial position for both piperidines as evidenced by ROEs between H-6_{top}/ H-12_{top} and both axial α-hydrogens on the respective rings. Top/bottom assignment was based on ROEs between H-7/H-11 and the equatorial α-hydrogens on the top edge as well as H-6_{bottom}/H-12_{bottom} and both equatorial and axial α-hydrogens on the bottom edge. The methine hydrogens (H-7 and H-11) gave 3-bond HMBC correlations to single carbon

chemical-shifts in the ortho aromatic region indicating side-to-side equivalence of the phenyl rings on the diamide consistent with rapid rotation.

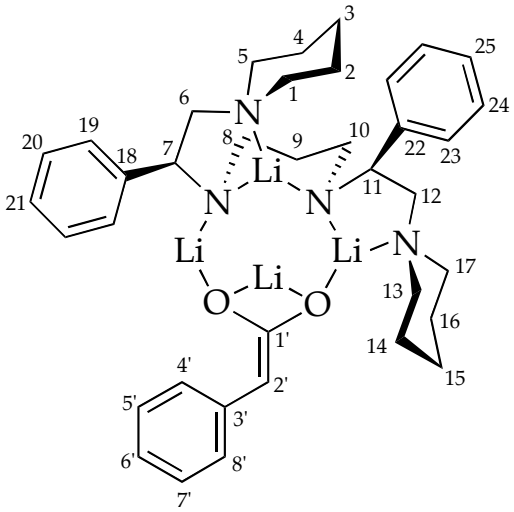
Conformation of the acid enolate: ROE correlations between the vinylic hydrogen and the equatorial α-, and axial β-hydrogens of the *top* face of the proximal piperidine confirms the side-to-side orientation of the enolate and strongly suggests that the enolate projects above the central plane. The resonances corresponding to the ortho-hydrogens of the enolate appeared as very borad singlets at6.30 and 7.51 ppm. Three-bond HMBC correlations from both vinylic and para-hydrogens indicated the presence of two distinct ortho-carbon environments at 119.16 and 121.79 ppm, with noticeable broadening in the carbon dimension. These results indicate that the rotation of the aromatic ring is restricted, either due to steric or electronic reasons, and is intermediate on these NMR time scales (~1 ms). The anomalously-high chemical shift of one ortho-hydrogen is likely due to the ring current effect of the proximal phenyl group of the diamide.

Conformation of the *n*BuLi: The 1D proton spectrum displayed two broadened triplets centered around -1 ppm instead of the AA'XX' multiplet usually observed in achiral *n*BuLi aggregates where restricted rotation around the C-1–C-2 bond causes magnetic non-equivalence of the α-hydrogens. The presence of two unique chemical shifts for *n*BuLi α-hydrogens is consistent with diastereotopicity induced by the diamide. In the ROESY spectrum strong exchange is observed between the α-hydrogens indicating intermediate exchange on their NMR time scale (~5 ms). The fact that the diastereotopic hydrogens of the β and γ methylenes also display unique chemical shifts despite much longer time scales (~1s) suggests that the exchange of the α-hydrogens arises from an intramolecular process that intraconverts those hydrogens, consistent with the well-known racemization of chiral lithiated carbon atoms.

We observed four ROE correlations between the two *n*-butyl α-hydrogens and the top equatorial α-hydrogens of both piperidines. Careful examination of the cross peaks revealed an asymmetry of intensities, suggesting that one set arose from direct ROE, and the other from chemical exchange followed by ROE. This result contradicts the dimeric structure observed in solid state, which predicts that only a single set of ROEs would be observed between one butyl hydrogen and H-1_{eq} of the diamide. The NMR results can be explained by exchanging the appropriate hydrogen and propyl substituents on the lithiated carbon, so the chain extends away from the central plane instead of above the plane as seen in the crystal structure, suggesting that the aggregate is monomeric in THF solutions.



Diamide *n*-Buli aggregate



Diamide-enolate aggregate

Atom #	□ ^{13}C (ppm)	□ ^{1}H (ppm)	Multiplcity[1]	□ ^{13}C (ppm)	□ ^{1}H (ppm)	Multiplcity[1]
1	58.17	eq. 2.98	d	58.33	eq. 3.16	d
		ax. 1.85	t		ax. 1.70	t
2	n/d[2]	n/d	n/d	n/d	n/d	n/d
3	n/d	n/d	n/d	24.90	eq. 1.40	d
					ax. 0.95	q
4	n/d	n/d	n/d	26.85	ax. 1.14	q
					eq. 1.00	d
5	54.28	eq. 3.66	d	55.58	eq. 3.70	d
		ax. 1.66	t		ax. 1.66	q
6	71.99	2.61	t	73.22	2.59	t
		2.07	d		2.15	d
7	69.80	3.95	d	70.70	4.17	d
8	61.09	eq. 3.20	d	61.69	eq. 2.52	d
		ax. 2.57	t		ax. 2.30	t
9	37.39	eq. 1.74	d	37.41	eq. 1.69	d
		ax. 1.39	q		ax. 1.55	q
10	60.58	ax. 2.93	t	61.69	eq. 2.94	d
		eq. 2.72	d		ax. 2.73	t
11	68.35	3.99	d	67.93	4.00	d, J=12.5 Hz
12	74.15	2.36	t	73.64	2.63	t
		bot. 2.22	d		2.23	d
13	58.19	eq. 2.92	d	57.98	eq. 3.20	d
		ax. 1.86	t		ax. 1.96	t
14	n/d	n/d	n/d	27.24	ax. 2.14	q
					eq. 1.77	d
15	n/d	n/d	n/d	n/d	n/d	
16	n/d	n/d	n/d	n/d	n/d	
17	n/d	n/d	n/d	54.51	eq. 3.50	d
					ax. 1.74	t

18	150.17	—		150.70	—	
19	127.72	~		128.56	7.35	d
20	127–128.1[3]	7.15–7.21[3]		127.0–128.1[3]	7.18	t
21	124.9–126[3]	6.97–7.07[3]		125.06	7.02	t
22	148.52			150.08	—	
23	128.72	7.24		127.7–128.1[3]	7.19	
24	127.0–128.1	7.15–7.21[3]		127.0–128.1[3]	7.15–7.21[3]	
25	124.9–126	6.97–7.07[3]		124.9–126[3]	6.97–7.07[3]	
1′	11.78	-0.86	t (br)	179.83	—	
		-1.14	t (br)			
2′	34.47	1.66	n/d	72.58	4.08	s
		1.62				
3′	34.94	1.36	n/d	149.81	—	
		1.31				
4′	n/d	0.92	n/d	119.16 (br)	7.51	s (br)
5′				127.71	6.65	s (br)
6′				111.77	6.01	t, J=9.6 Hz
7′				127.71	6.65	s (br)
8′				121.72	6.30	s (br)

[1] Gross multiplicity as determined from cross peak profiles of 2D experiments and does not include small couplings.
[2] Could not be determined.
[3] Could not be determined unambiguously, range or values given.

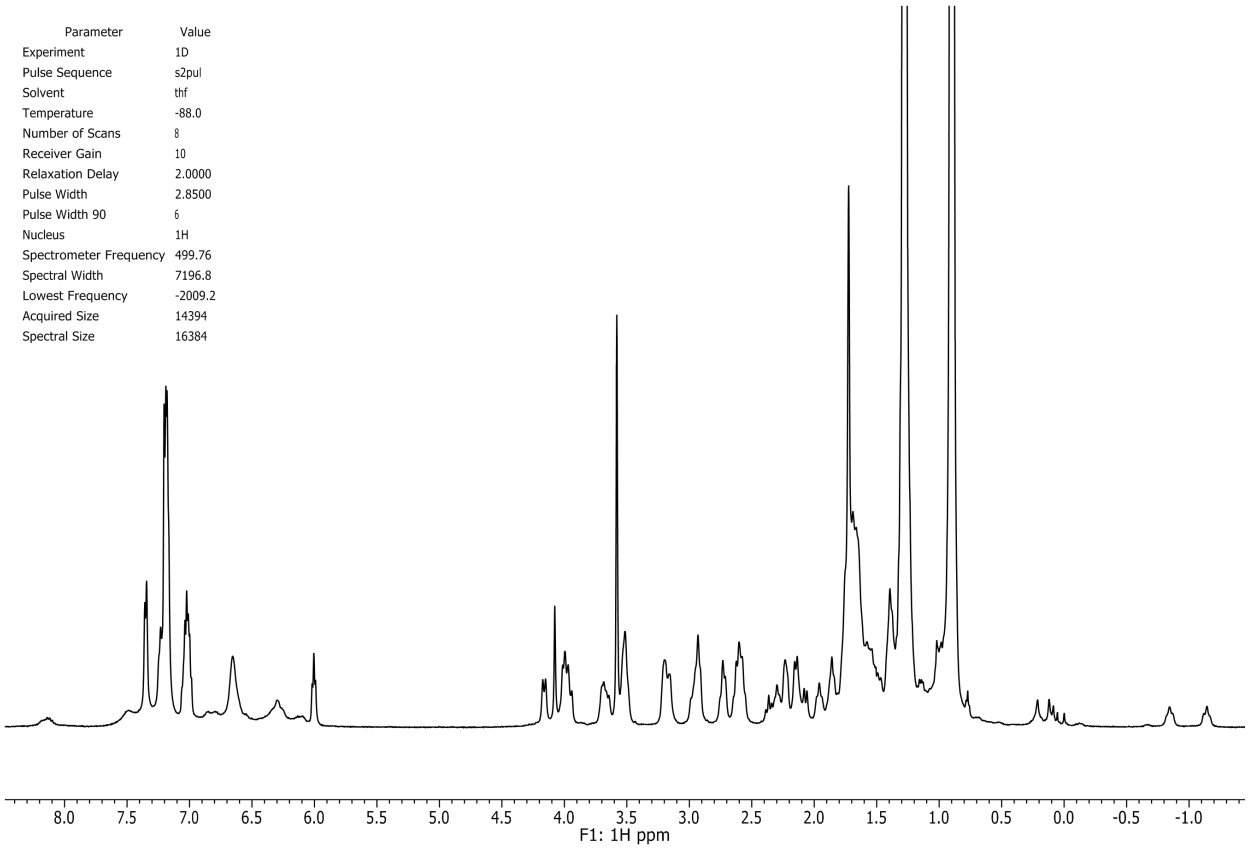


Figure A3.26. ^{1}H spectrum at –80 °C of a sample in THF-*d8*/pentane containing a 1:0.6 ratio of diamide/acid enolate and diamide/*n*-BuLi aggregates.

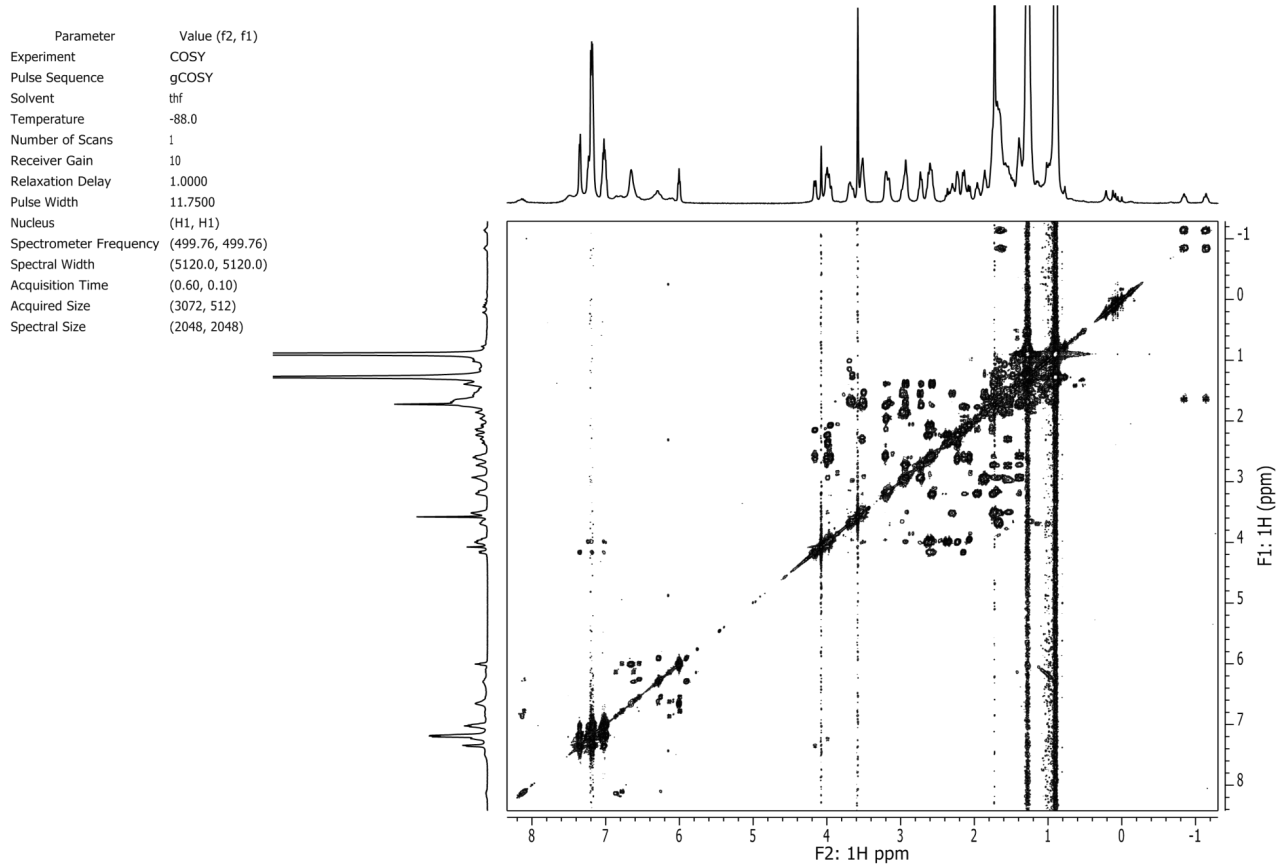


Figure A3.27. Full display of gradient-COSY spectrum at –80 °C.

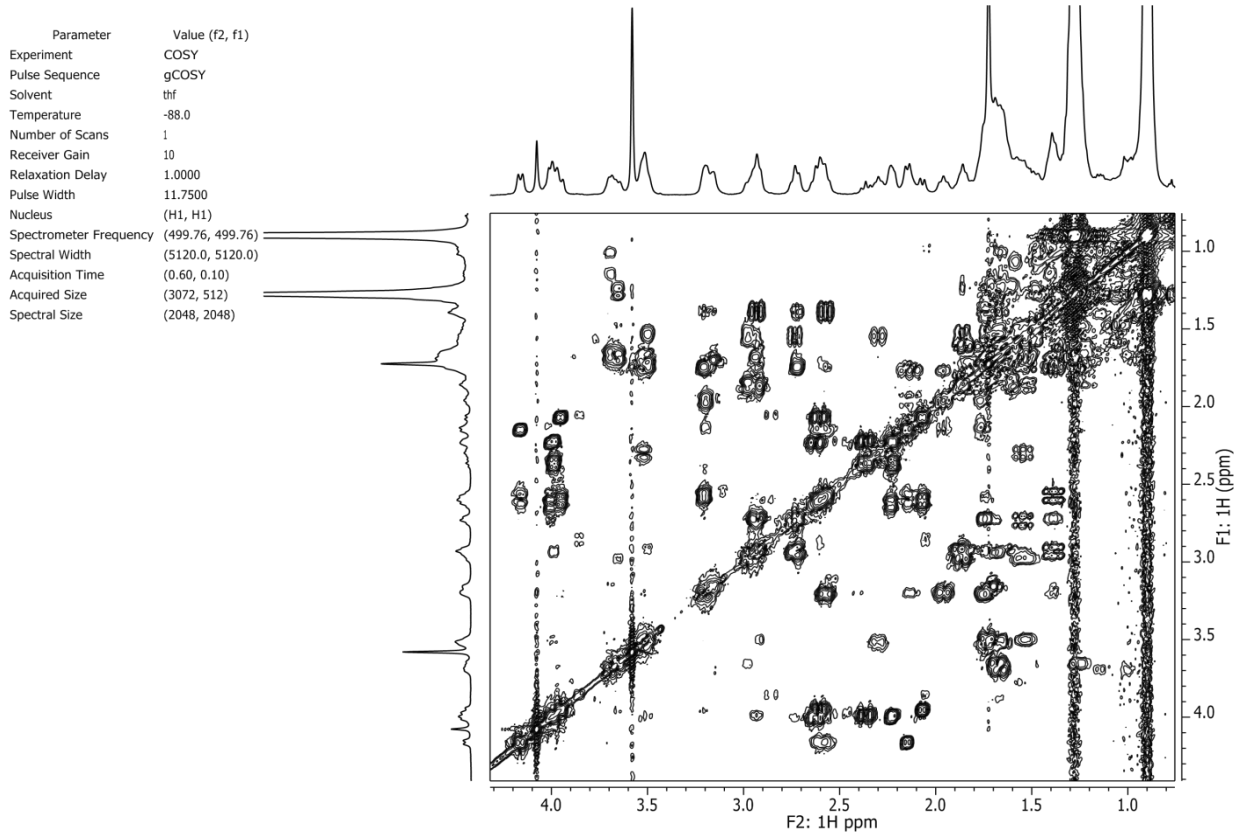


Figure A3.28 Expansion of the aliphatic region of gradient-COSY spectrum at –80 °C.

Parameter	Value (f2, f1)
Experiment	COSY
Pulse Sequence	gCOSY
Solvent	thf
Temperature	-88.0
Number of Scans	1
Receiver Gain	10
Relaxation Delay	1.0000
Pulse Width	11.7500
Nucleus	(H1, H1)
Spectrometer Frequency	(499.76, 499.76)
Spectral Width	(5120.0, 5120.0)
Acquisition Time	(0.60, 0.10)
Acquired Size	(3072, 512)
Spectral Size	(2048, 2048)

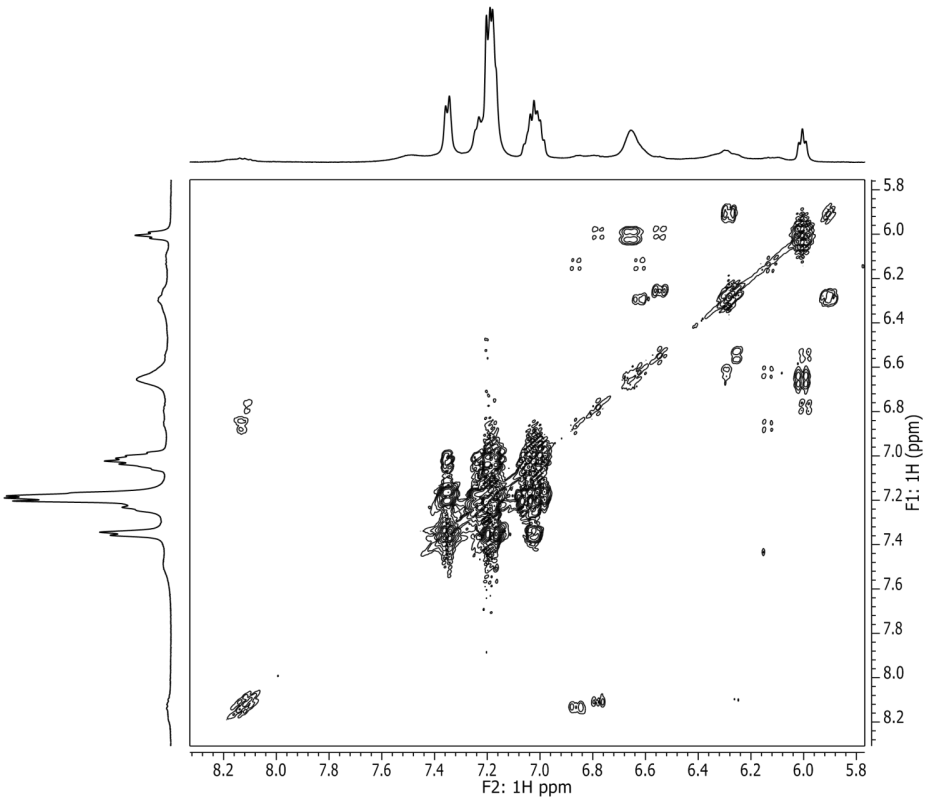


Figure A3.29. Expansion of the aromatic region of gradient-COSY spectrum at –80 °C.

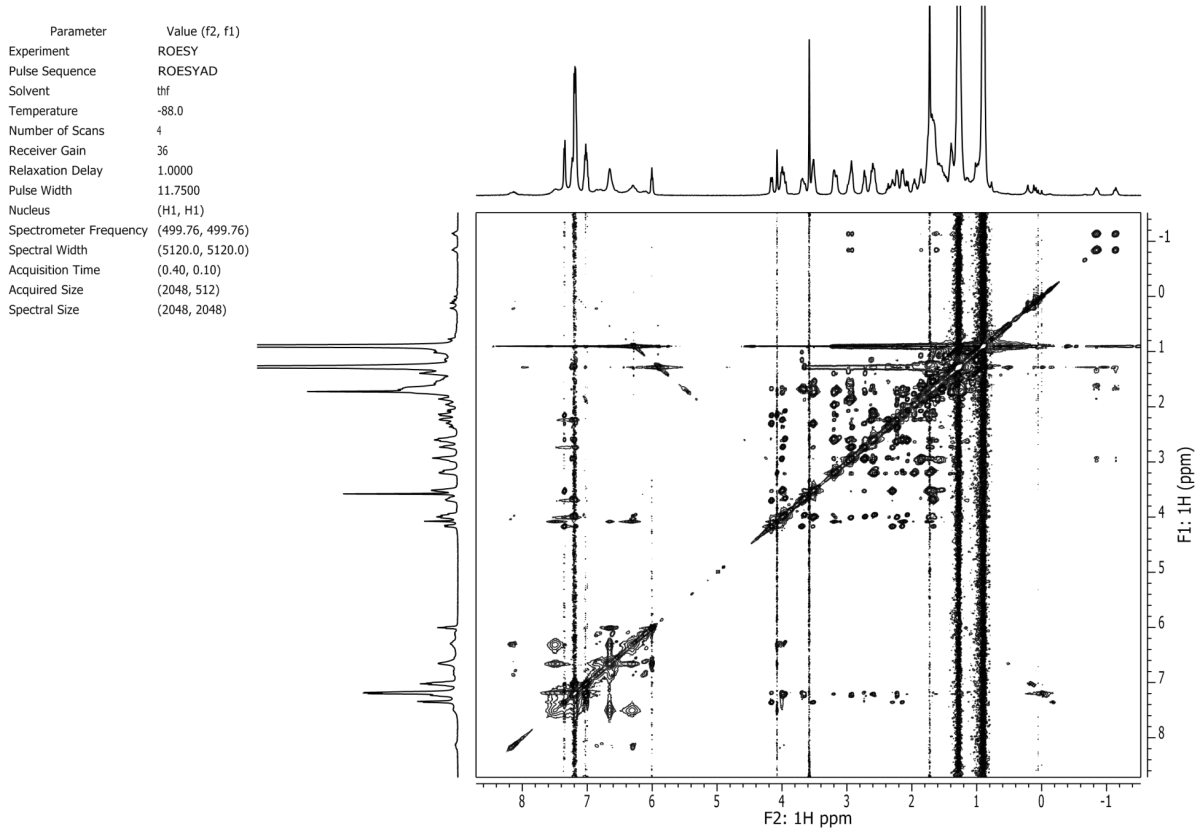


Figure A3.30. Full display of ROESY spectrum with 80 ms mixing time at –80 °C.

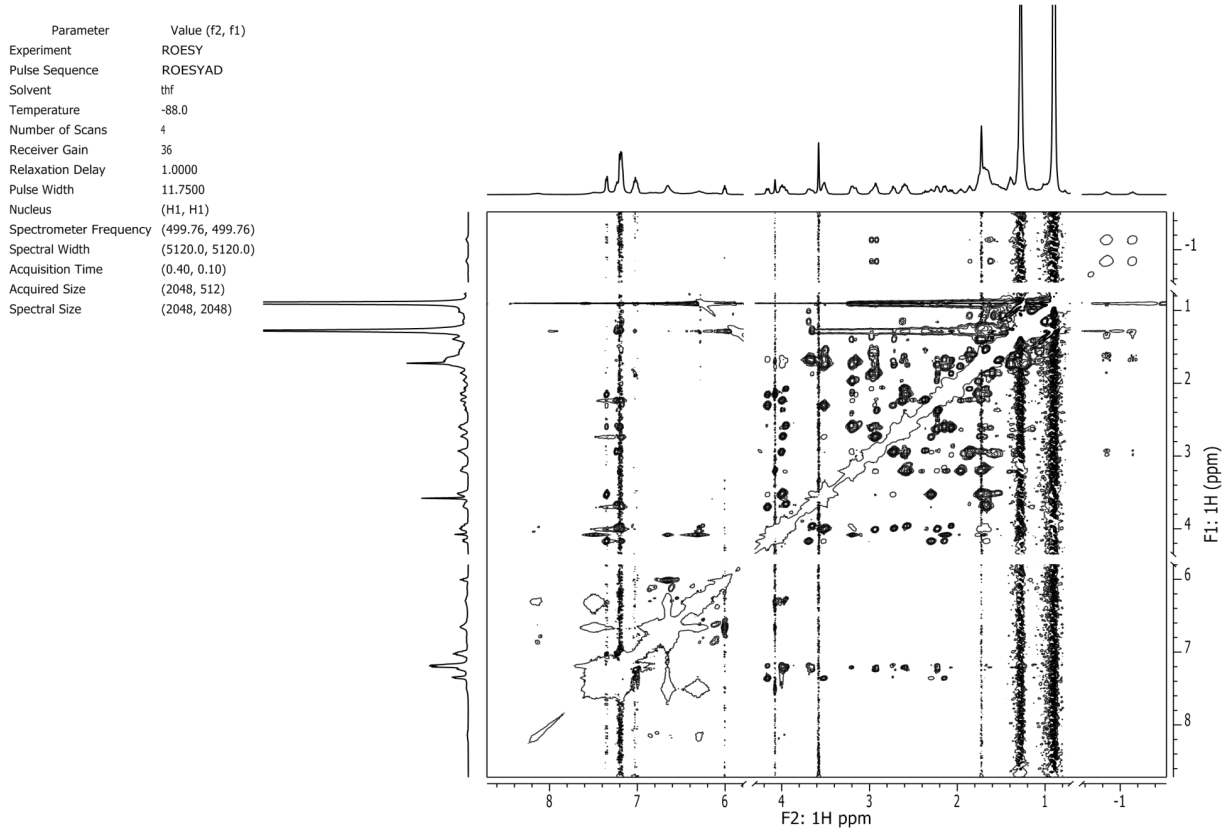


Figure A3.31. ROESY spectrum with 80 ms mixing time at –80 °C with regions of noise excised, ten positive contour levels (ROE's) and a single negative contour level (diagonal, exchange and relayed ROE's).

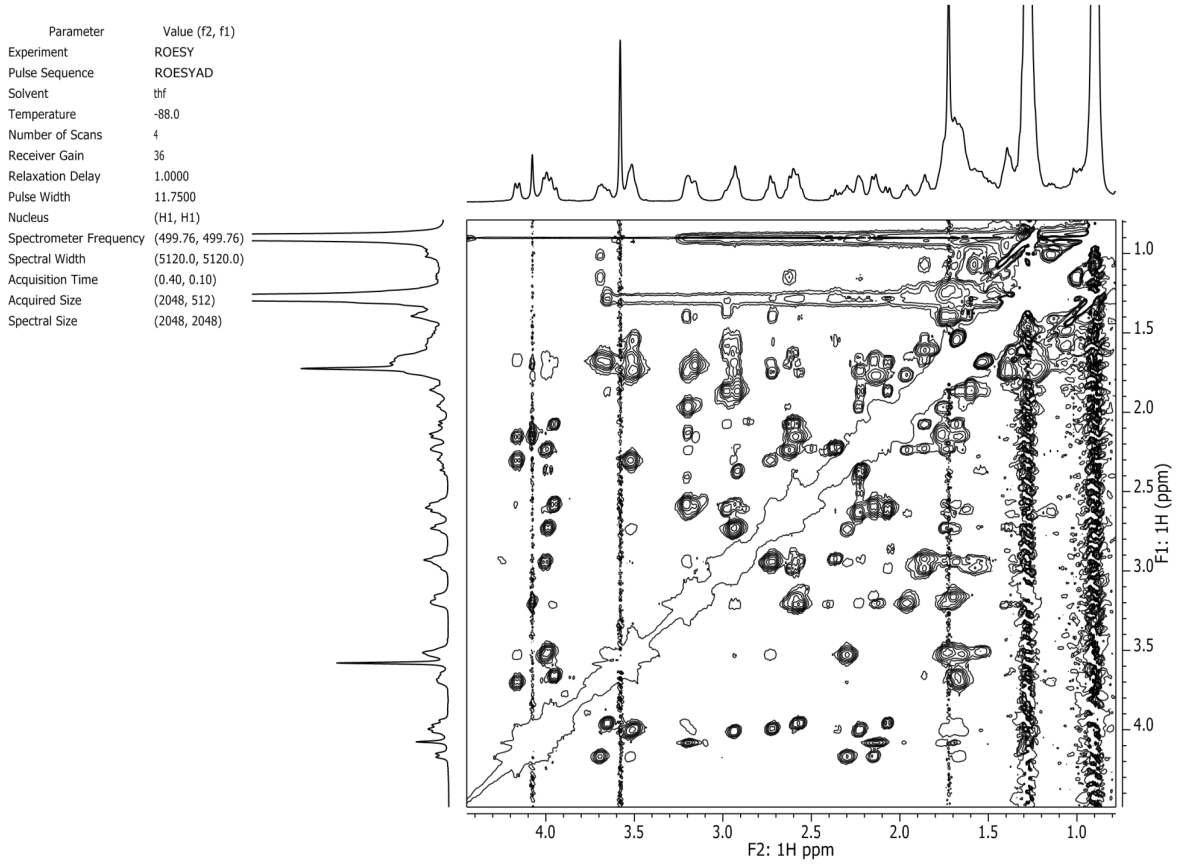


Figure A3.32. Expansion of the aliphatic region of ROESY spectrum with 80 ms mixing time at –80 °C with ten positive contour levels (ROE's) and a single negative contour level (diagonal and relayed ROE's).

Parameter	Value (f2, f1)
Experiment	TOCSY
Pulse Sequence	TOCSY
Solvent	thf
Temperature	-88.0
Number of Scans	4
Receiver Gain	10
Relaxation Delay	1.0000
Pulse Width	11.7500
Nucleus	(H1, H1)
Spectrometer Frequency	(499.76, 499.76)
Spectral Width	(5120.0, 5120.0)
Acquisition Time	(0.40, 0.10)
Acquired Size	(2048, 500)
Spectral Size	(4096, 2048)

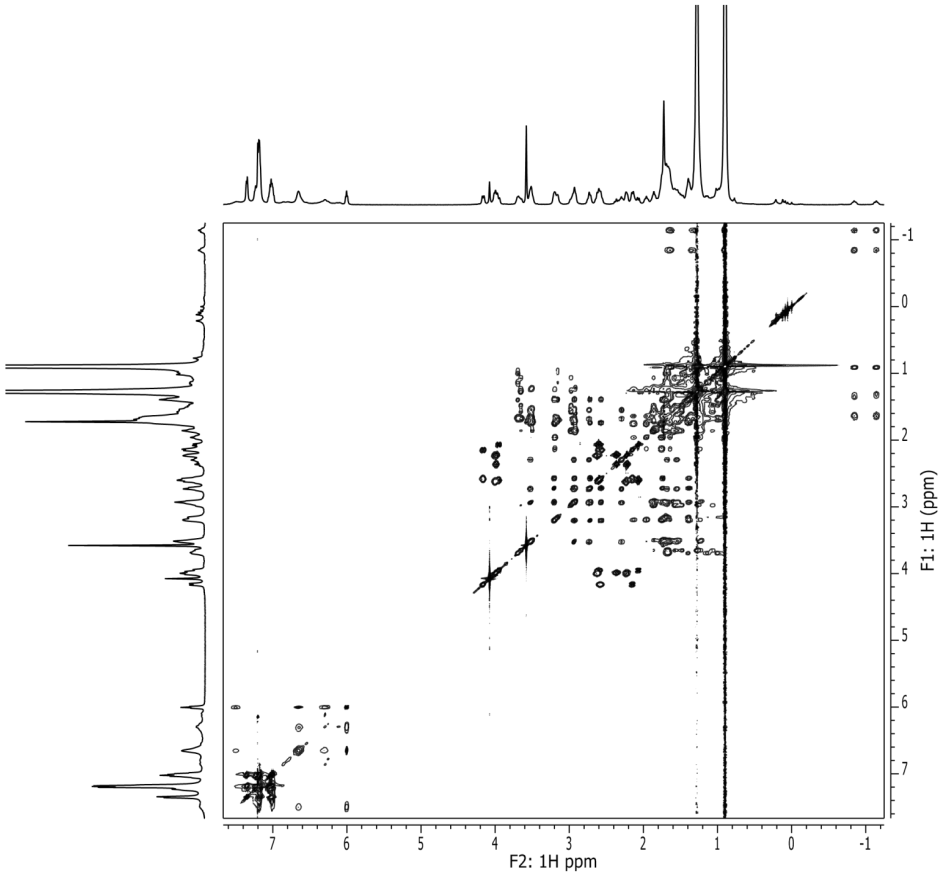


Figure A3.33. Full display of TOCSY spectrum at –80 °C.

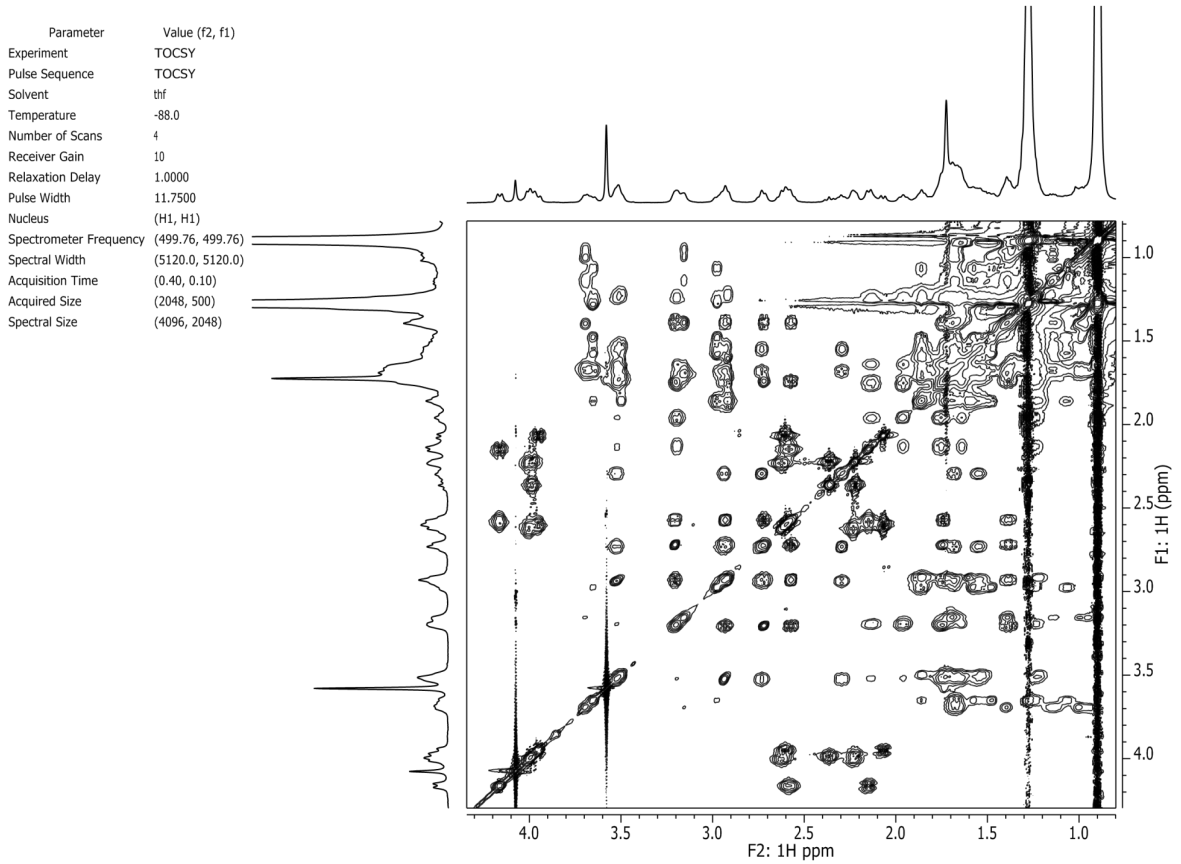


Figure A3.34. Expansion of the aliphatic region of TOCSY spectrum at –80 °C.

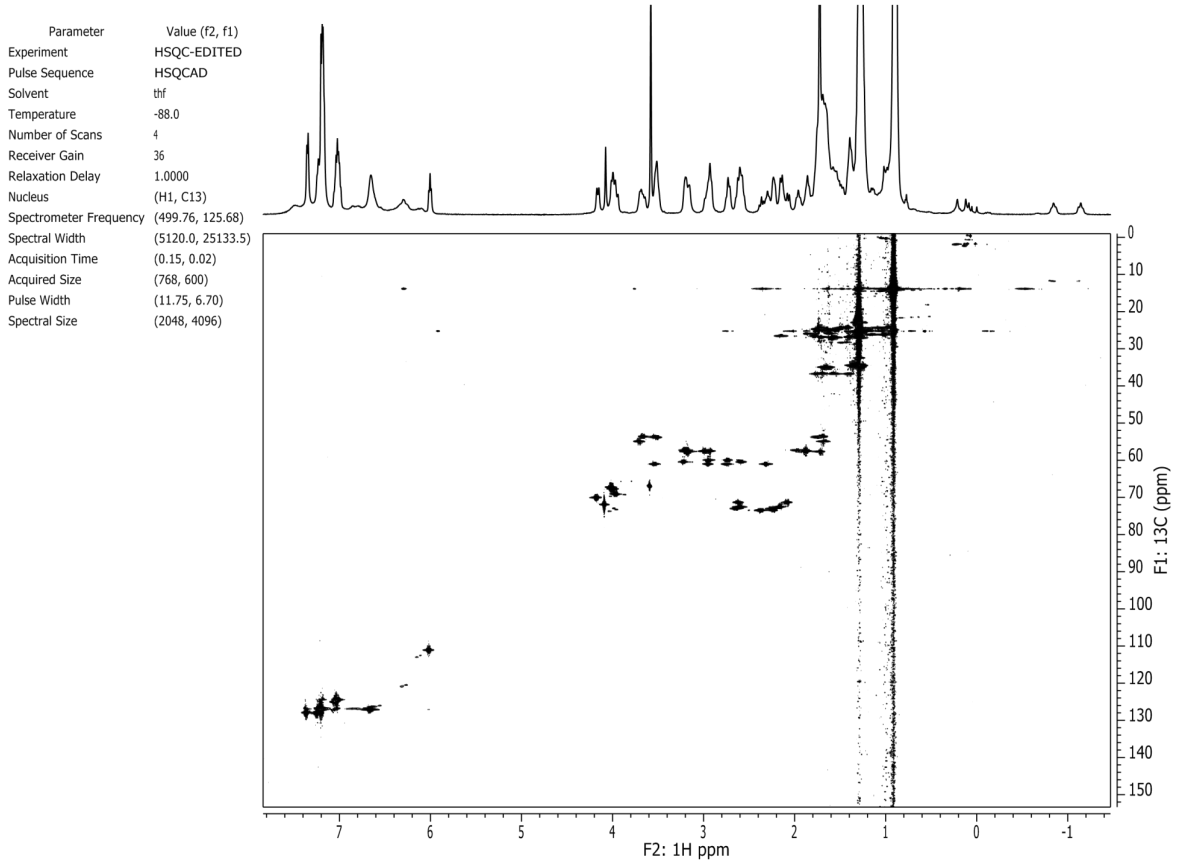


Figure A3.35. Full display of multiplicity-edited HSQC spectrum at –80 °C.

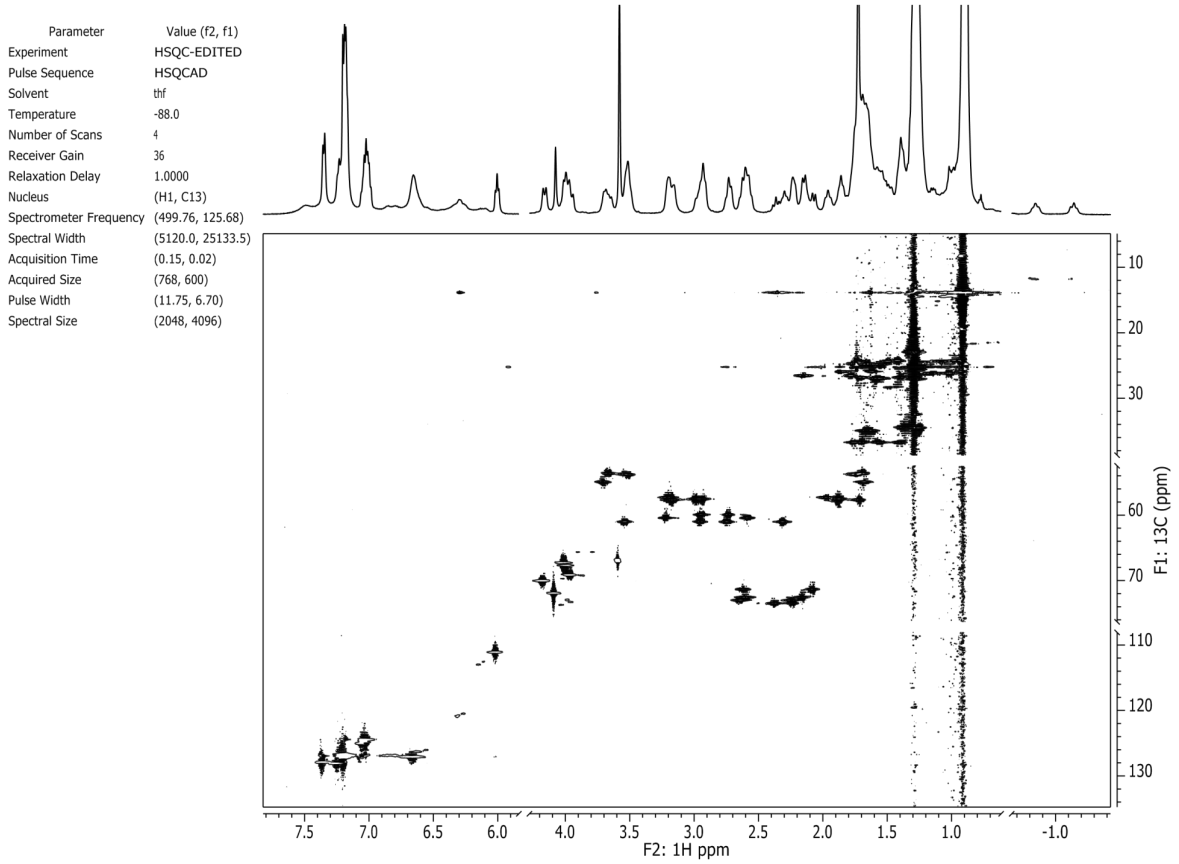


Figure A3.36. Multiplicity-edited HSQC spectrum at –80 °C with regions of noise excised, ten negative contour levels (CH_2) and a single positive contour (CH_3 and CH).

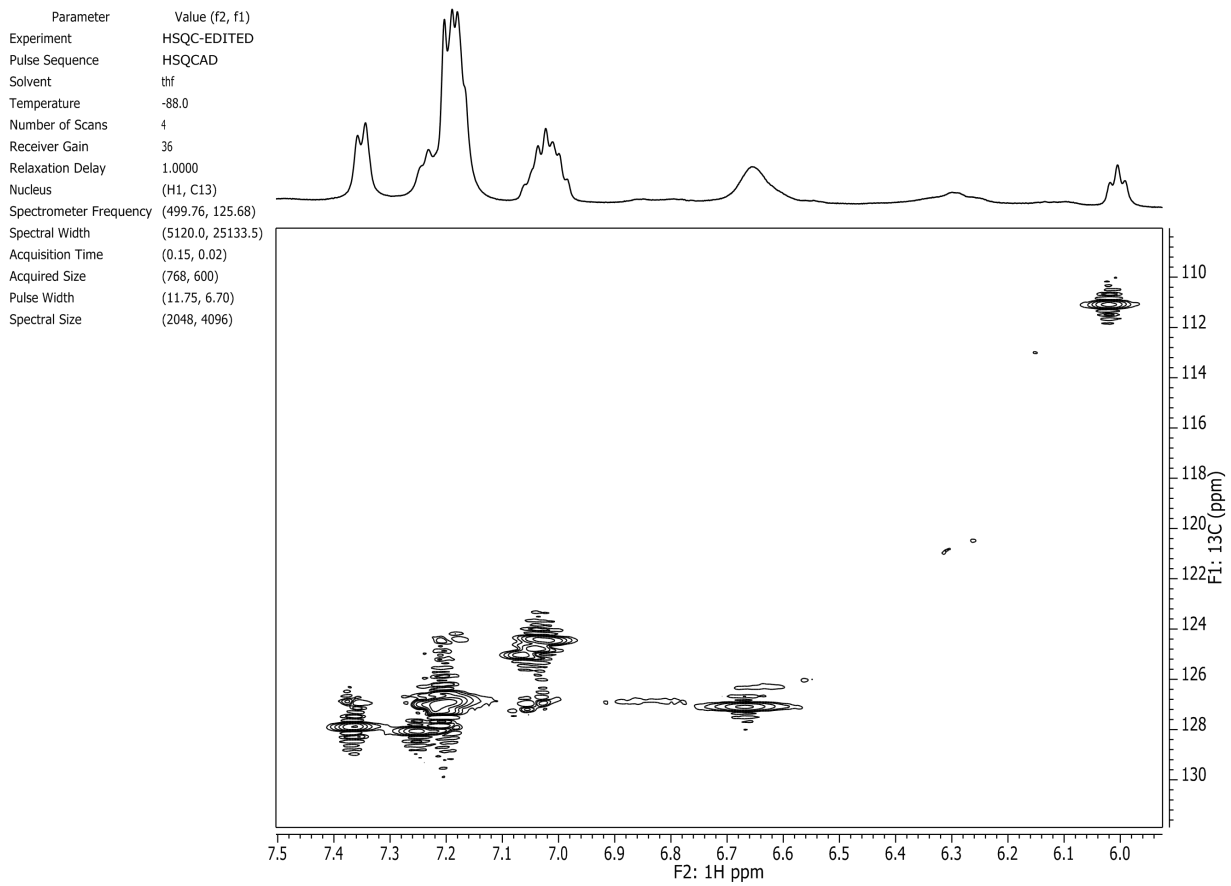


Figure A3.37. Expansion of the aromatic region of multiplicity-edited HSQC spectrum at –80 °C. No correlations were observed for the exchange broadened ortho-hydrogens of the acid enolate. Note the low ^{1}H chemical shift of the para-hydrogen of the acid enolate (6.13 ppm), likely due to the ring current of the amide phenyl in close proximity.

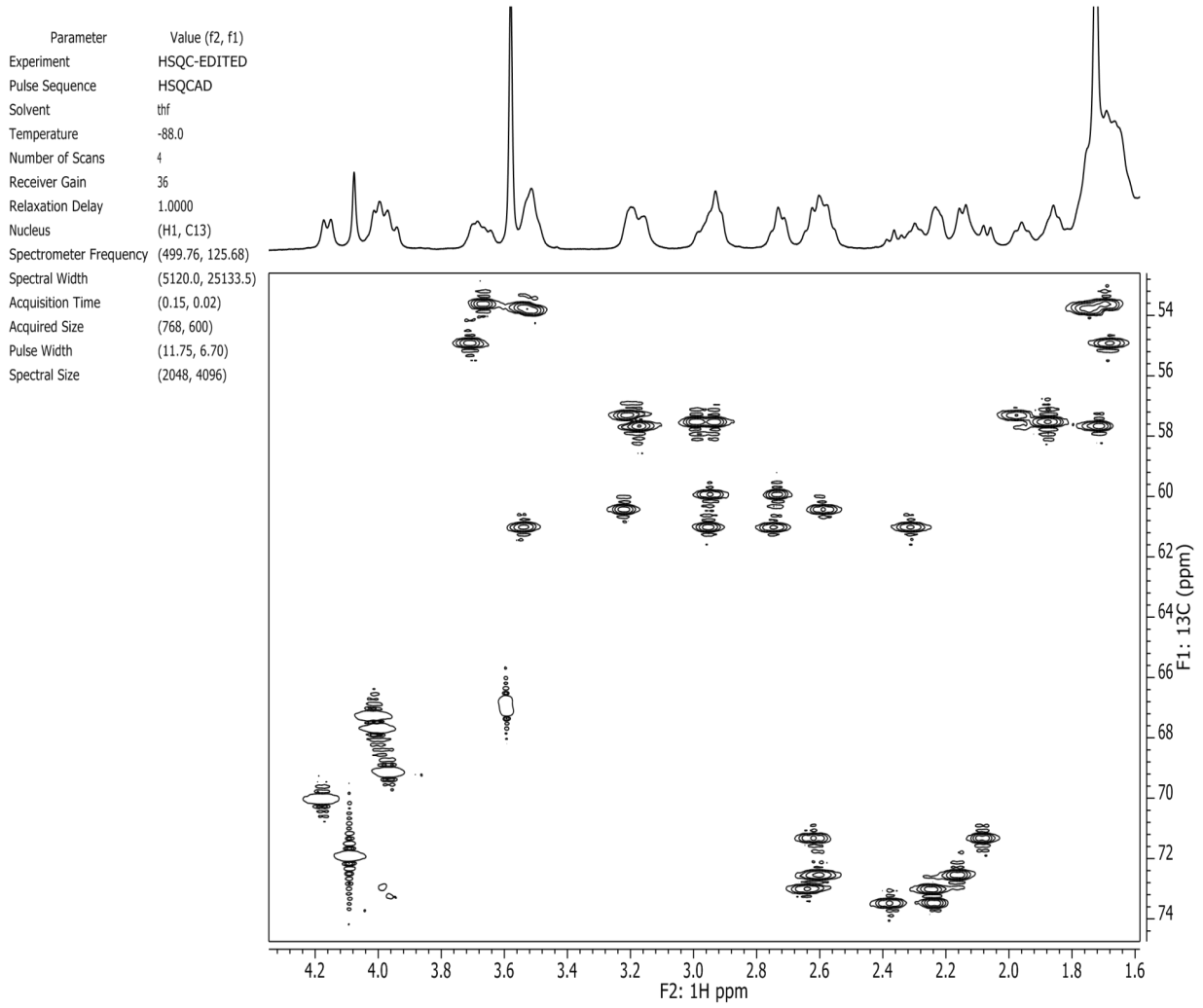


Figure A3.38. Expansion of multiplicity-edited HSQC spectrum at –80 °C with ten negative contour levels (CH_2) and a single positive contour (CH_3 and CH).

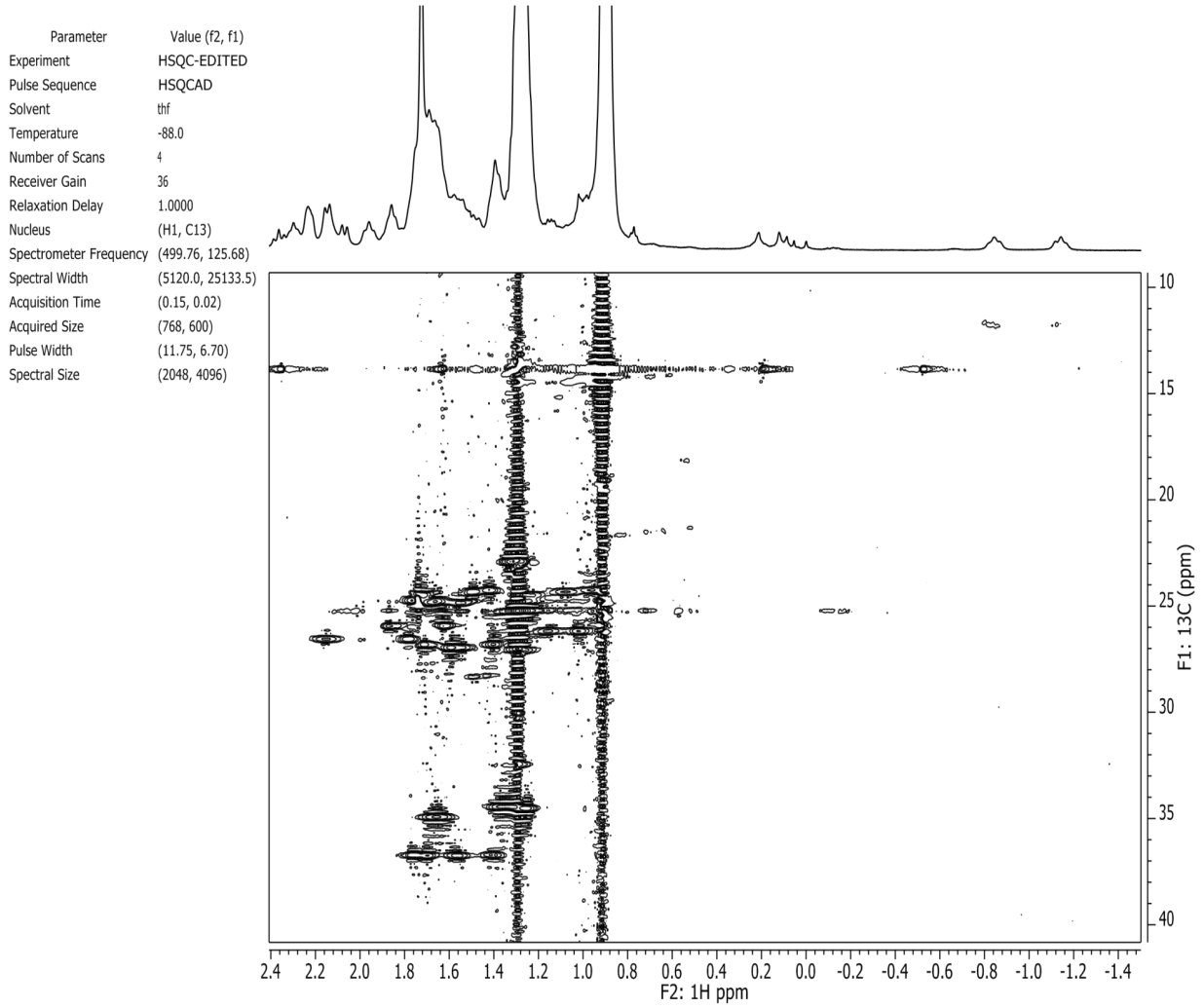


Figure A3.39. High-field expansion of multiplicity-edited HSQC spectrum at –80 °C with ten negative contour levels (CH_2) and a single positive contour (CH_3 and CH).

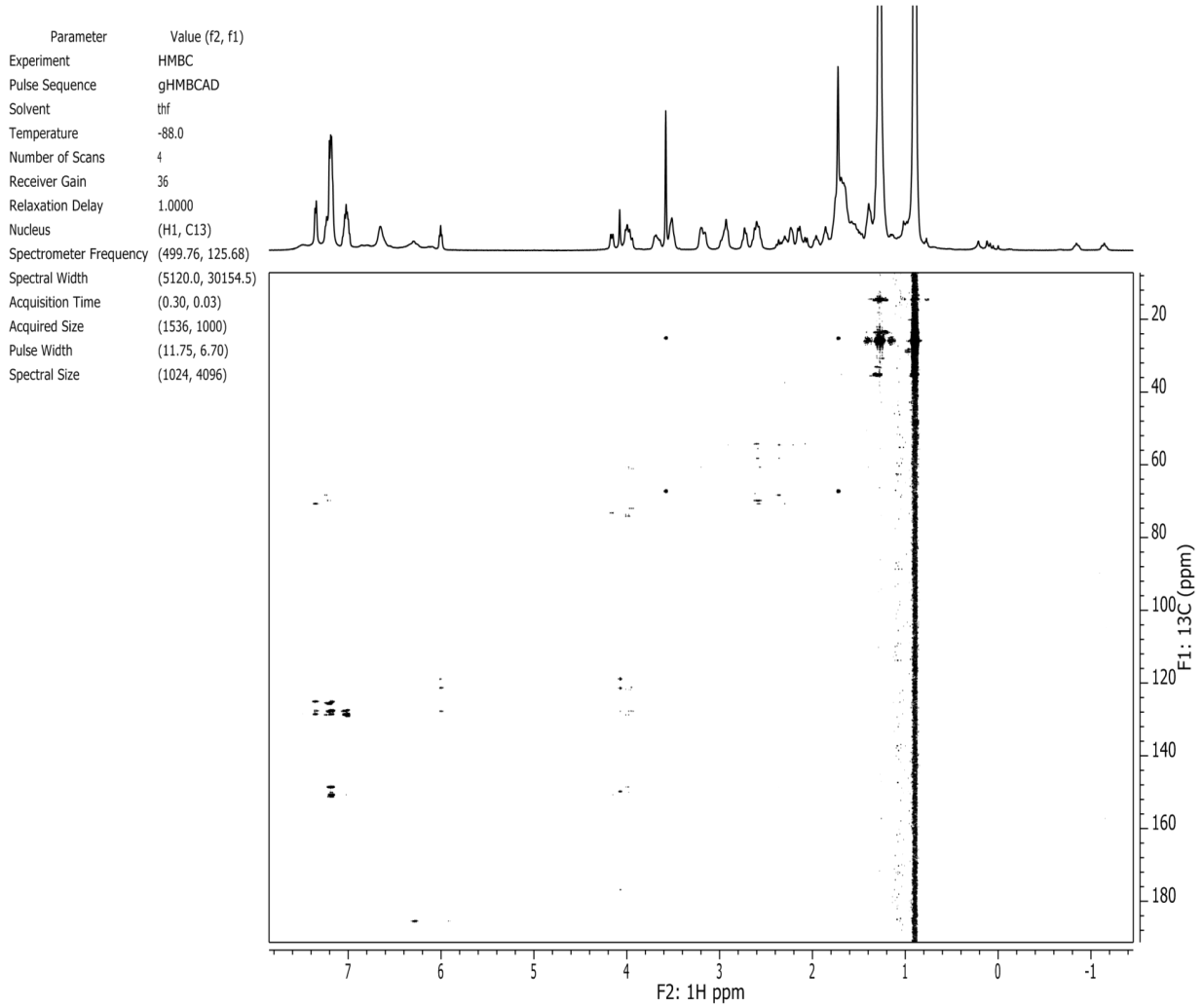


Figure A3.40. Full display of HMBC spectrum at –80 °C.

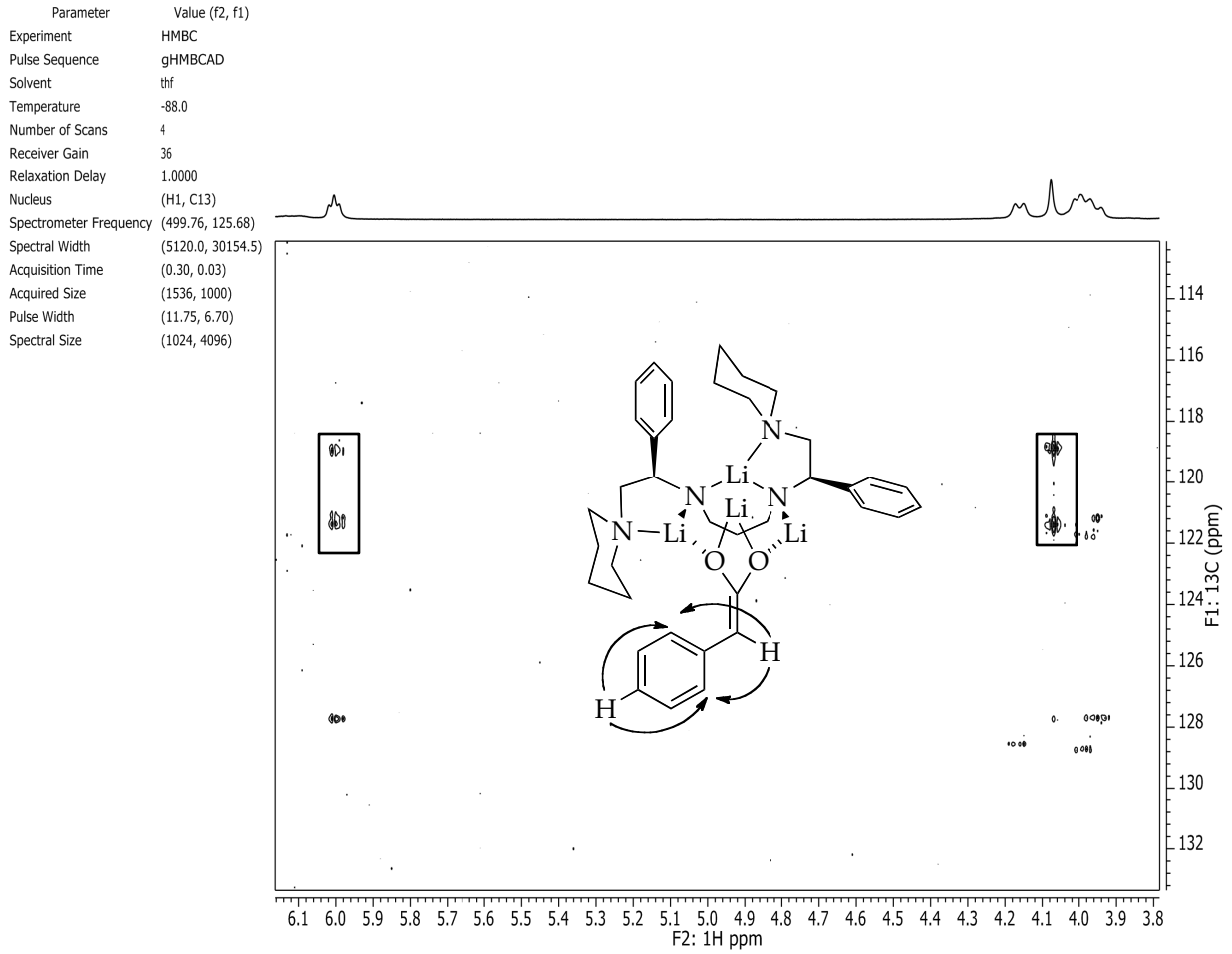
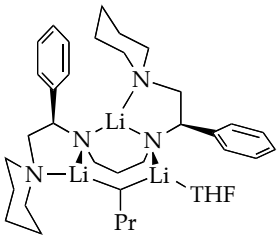


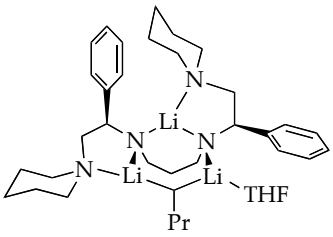
Figure A3.41. Expansion of HMBC spectrum showing 3-bond correlations to the non-equivalent ortho carbon atoms of the acid enolate.

Part 4: Computational Studies

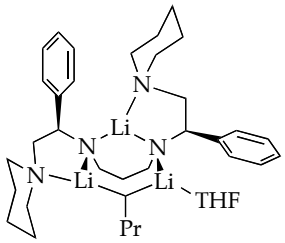
Chart 1



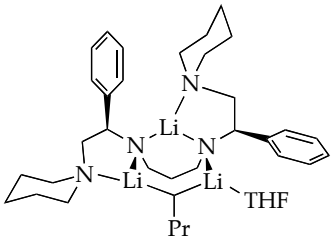
6c, 6j



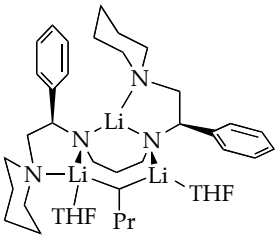
6d, 6k



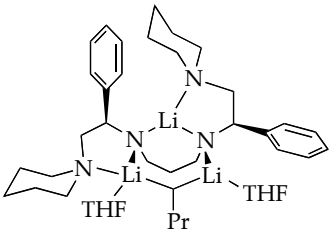
6e, 6l



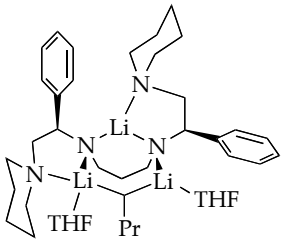
6f, 6m



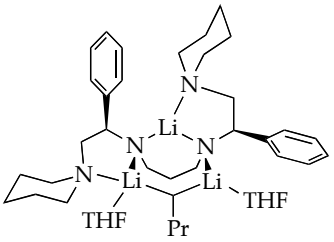
6a, 6n, 6r



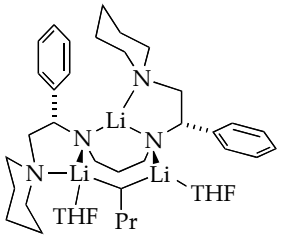
6g, 6o



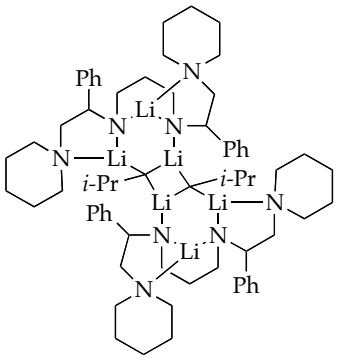
6h, 6p



6i, 6q

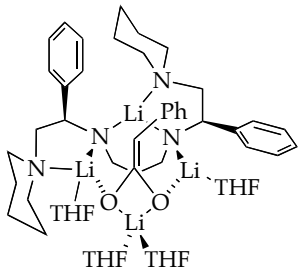


6b



5

Chart 2



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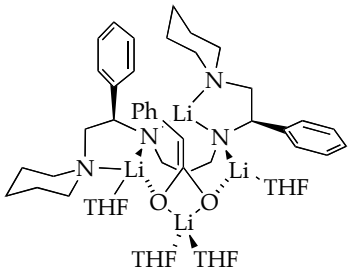

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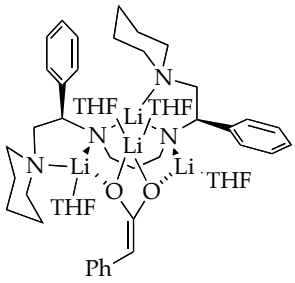

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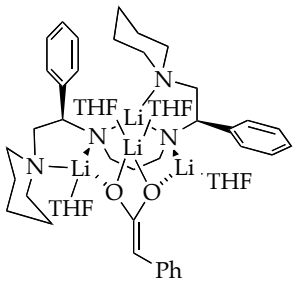

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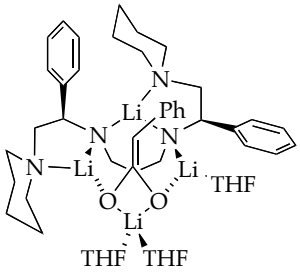

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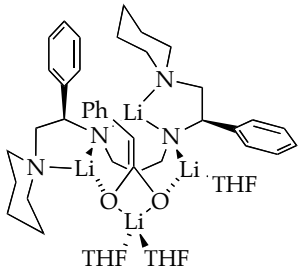

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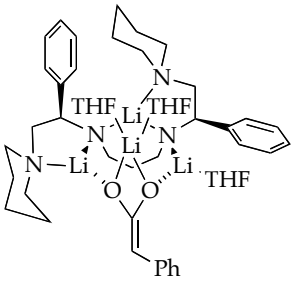

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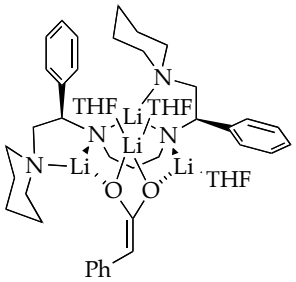

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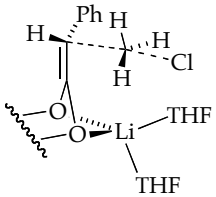

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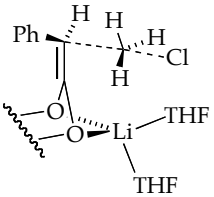

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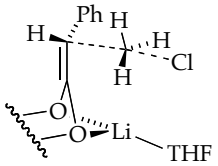

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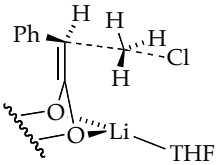

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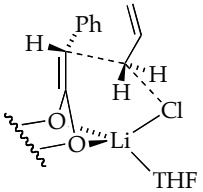

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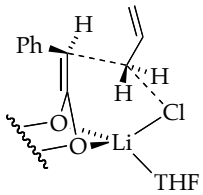
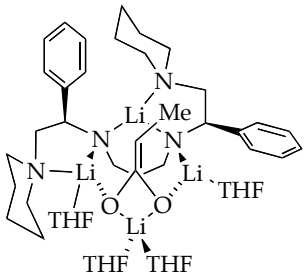


17f

Chart 3



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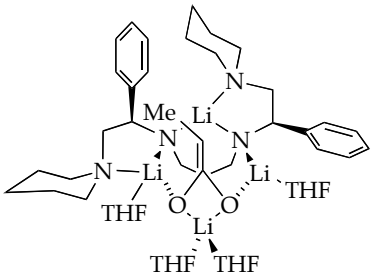

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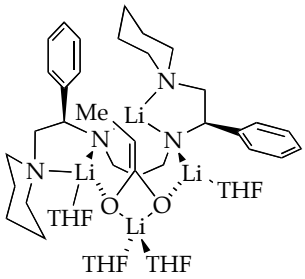

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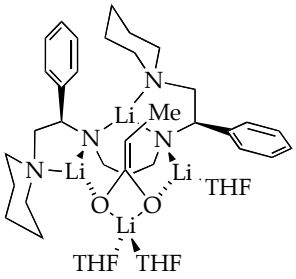

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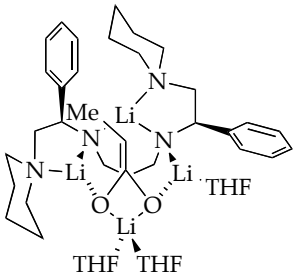

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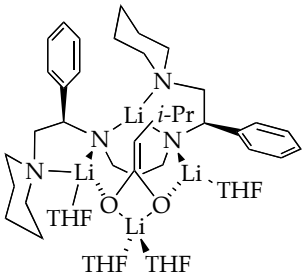

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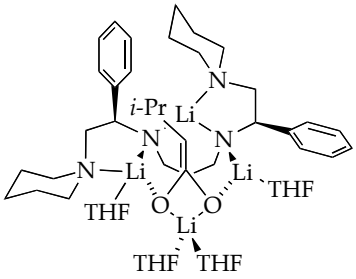

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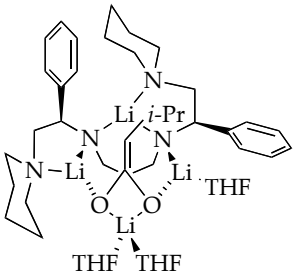

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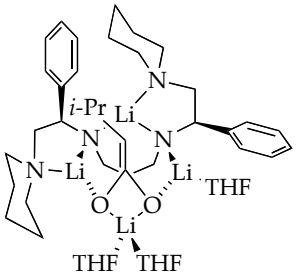
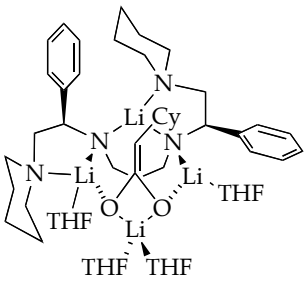
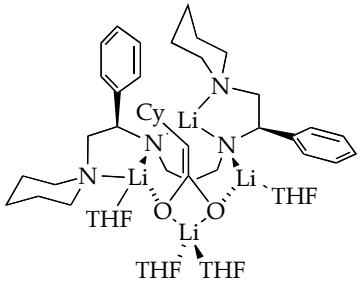


19d

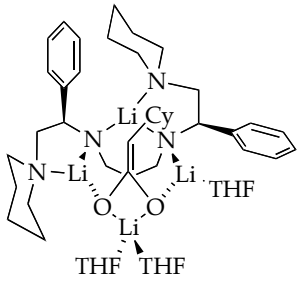
Chart 4



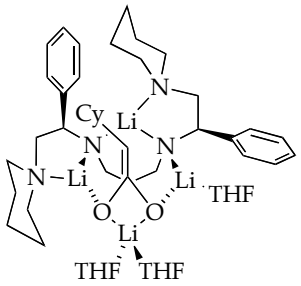
20a



20b

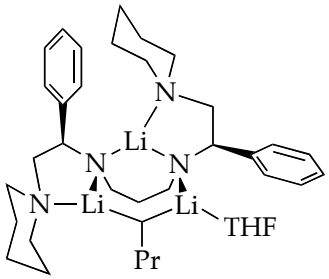


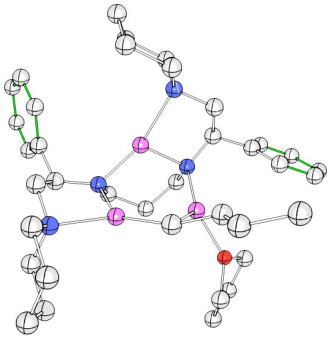
20c, 20e



20d, 20f

Table A3.1. Optimized geometries at B3LYP level of theory with 6-31G(d) basis set for the mono-solvated BuLi-ligand aggregation conformers at –78 °C with free energies (Hartrees) and cartesian coordinates (X, Y, Z) (Note: G_{MP2} includes single point MP2 corrections to B3LYP/6-31G(d) optimized structures).



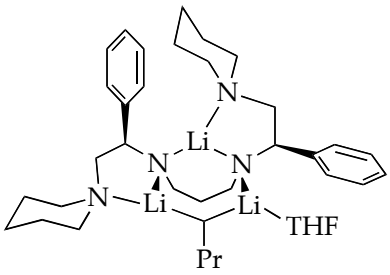


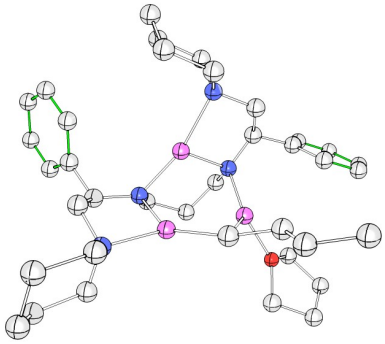
6c
G = -1761.537572
G_{MP2} = -1756.295216

Atom	X	Y	Z	Atom	X	Y	Z
C	0	0	0	C	-5.511037	-4.326064	-1.931488
Li	1.562427	-0.355628	-1.372622	C	-4.895519	-3.49434	-0.991496
N	2.344642	-1.784644	-2.490619	C	-3.506981	-3.494333	-0.856138
Li	1.297407	-3.104933	-1.405828	H	-3.049161	-2.830554	-0.126429
N	-0.533512	-3.125591	-2.07976	H	-5.499192	-2.847586	-0.358691
Li	-0.989195	-1.28564	-1.466147	H	-6.592736	-4.325468	-2.039538
O	-2.415384	-0.247618	-2.378206	H	-5.188383	-5.80965	-3.462829
C	-2.477474	1.185739	-2.432574	H	-2.726941	-5.823381	-3.191206
C	-2.739478	1.522775	-3.913135	C	-0.487971	-3.152788	-3.532523
C	-3.362528	0.218474	-4.487797	H	-1.490977	-3.078445	-4.008318
C	-3.438374	-0.720682	-3.272265	H	-0.081261	-4.119659	-3.90975
H	-3.228291	-1.768367	-3.485901	C	1.900989	-2.116934	-3.849764
H	-4.412803	-0.650154	-2.768947	C	0.385768	-2.027589	-4.109299
H	-2.718023	-0.20812	-5.261704	H	0.244746	-2.024641	-5.20039
H	-4.349613	0.382733	-4.930142	H	0.016184	-1.051123	-3.754862
H	-1.805171	1.764667	-4.428276	H	2.229433	-3.126582	-4.17695
H	-3.404781	2.385676	-4.012793	H	2.382879	-1.426397	-4.575109
H	-3.301663	1.533932	-1.792924	N	3.445179	0.54689	-1.075814
H	-1.535233	1.565343	-2.034415	C	3.782678	1.136629	0.238002
C	-1.164967	-4.313286	-1.532251	H	3.550137	0.393247	1.008986
C	-0.731371	-4.472239	-0.061107	H	4.871282	1.332355	0.292468
N	0.739336	-4.600977	0.108188	C	3.014457	2.432053	0.510084
C	1.17578	-5.972285	-0.24377	H	3.332625	2.834714	1.479894
H	0.896247	-6.167455	-1.283151	H	1.945415	2.20077	0.591954
H	0.628267	-6.703521	0.382013	C	3.244847	3.457231	-0.60646
C	2.6816	-6.169517	-0.059832	C	2.943911	2.819784	-1.967562
H	3.223846	-5.539316	-0.775049	C	3.72747	1.517053	-2.155323
H	2.933307	-7.209828	-0.301356	H	3.461567	1.058948	-3.11135
C	3.114795	-5.825143	1.3704	H	4.812058	1.738086	-2.188299
C	2.60823	-4.428957	1.753612	H	3.194037	3.505619	-2.786609

Table A3.1 (Continued).

C	1.102753	-4.303994	1.511614	H	1.868124	2.607161	-2.045333
H	0.762907	-3.287501	1.739149	H	4.291972	3.793501	-0.588006
H	0.564989	-4.98784	2.196355	H	2.623943	4.347457	-0.448687
H	2.82111	-4.210683	2.807561	H	0.004235	1.097753	-0.163394
H	3.131587	-3.668052	1.158095	H	0.889873	-0.169433	0.645838
H	2.69515	-6.564813	2.067806	C	-1.223135	-0.312739	0.887913
H	4.205808	-5.882348	1.469829	H	-2.161219	-0.143559	0.329397
H	-1.244248	-5.32966	0.408368	H	-1.233657	-1.386333	1.150668
H	-1.035084	-3.574653	0.487712	C	-1.33275	0.479825	2.206442
H	-0.829387	-5.219364	-2.080742	H	-1.342231	1.553937	1.970771
C	-2.699055	-4.333678	-1.640698	H	-0.421282	0.30811	2.797025
C	-3.33366	-5.163078	-2.574337	C	-2.566119	0.125336	3.04549
C	-4.723205	-5.158755	-2.726179	H	-2.609476	0.708765	3.973245
C	5.961185	-4.2125	-4.159787	H	-3.492771	0.318575	2.489374
C	6.318966	-5.024867	-3.08358	H	-2.566003	-0.936964	3.322249
C	5.864985	-4.700111	-1.803598	C	3.780309	-1.516237	-2.506532
C	5.053356	-3.580965	-1.606925	C	4.202023	-0.714822	-1.260332
H	4.714923	-3.350624	-0.59986	H	4.019999	-1.314682	-0.36013
H	6.148254	-5.316684	-0.953524	H	5.286897	-0.510019	-1.298208
H	6.948357	-5.897529	-3.23766	H	4.02681	-0.886947	-3.386847
H	6.309515	-4.449846	-5.162155	C	4.686747	-2.749515	-2.676063
H	4.904796	-2.447827	-4.793944	C	5.162709	-3.086117	-3.951616





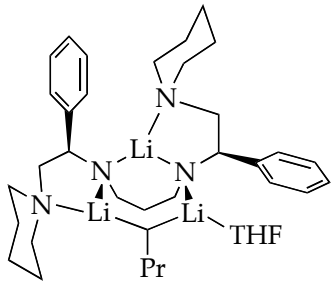
6d
G = -1761.534084
G_{MP2} = -1756.290741

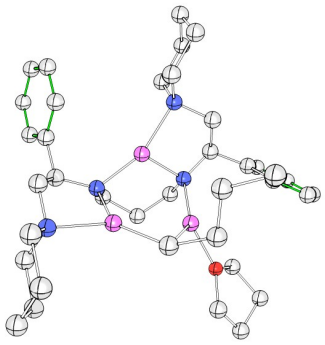
Atom	X	Y	Z	Atom	X	Y	Z
C	0	0	0	H	-3.136726	-2.649867	0.135497
H	0.220437	1.068534	-0.214497	H	-5.571661	-2.473703	-0.142511
Li	1.535477	-0.530799	-1.321329	H	-6.754497	-3.886748	-1.820169
N	2.294972	-2.029845	-2.346445	H	-5.450911	-5.507141	-3.190855
Li	1.187816	-3.233193	-1.190905	H	-3.004735	-5.715503	-2.873541
N	-0.633336	-3.207123	-1.879705	C	-0.585572	-3.353812	-3.325689
Li	-1.009613	-1.30484	-1.430825	C	0.352358	-2.327982	-3.98226
O	-2.3078	-0.282029	-2.513985	H	0.020513	-1.307906	-3.728269

Table A3.1 (Continued).

C	-2.311815	1.144037	-2.668141	H	0.231155	-2.420456	-5.07183
C	-3.798823	1.520751	-2.736167	H	-0.233168	-4.36964	-3.620439
C	-4.469292	0.253059	-3.3359	H	-1.58101	-3.258317	-3.811273
C	-3.328384	-0.784308	-3.39693	C	1.858529	-2.45481	-3.683871
H	-2.91184	-0.864519	-4.410598	H	2.155708	-3.49833	-3.922319
H	-3.604376	-1.777097	-3.042893	H	2.377171	-1.842916	-4.451939
H	-4.887365	0.436421	-4.330287	C	3.729856	-1.774002	-2.374851
H	-5.282541	-0.09972	-2.695664	H	3.98015	-1.165719	-3.270697
H	-3.965374	2.416701	-3.341649	C	4.628279	-3.017468	-2.509913
H	-4.183042	1.720254	-1.731211	C	5.271763	-3.294143	-3.722989
H	-1.768739	1.565995	-1.821102	C	6.074374	-4.42665	-3.880609
H	-1.787997	1.409751	-3.599123	C	6.260073	-5.306415	-2.814484
C	-1.348243	-4.295221	-1.237475	C	5.629812	-5.044782	-1.595278
C	-0.917411	-4.362012	0.241261	C	4.820361	-3.917207	-1.451231
N	0.541269	-4.584377	0.419777	H	4.335605	-3.731843	-0.495953
C	0.8778	-6.003491	0.158523	H	5.773268	-5.718311	-0.753394
H	0.586908	-6.244457	-0.867853	H	6.888565	-6.185721	-2.929601
H	0.278282	-6.652166	0.826131	H	6.555896	-4.618741	-4.836512
C	2.36497	-6.29743	0.363916	H	5.138841	-2.608995	-4.557908
C	2.820162	-5.894875	1.771582	N	3.406379	0.300235	-0.970926
C	2.418708	-4.443418	2.062282	C	3.610073	0.912308	0.36103
C	0.926925	-4.222061	1.801984	H	2.811252	1.65278	0.503277
H	0.664492	-3.16975	1.958277	H	3.458169	0.135239	1.118329
H	0.338521	-4.815794	2.527953	C	4.976151	1.595097	0.542089
H	3.000087	-3.761344	1.426187	C	5.209617	2.63958	-0.560277
H	2.643642	-4.176133	3.102333	C	5.001367	2.014442	-1.94817
H	3.903511	-6.027018	1.882638	C	3.634522	1.313552	-2.028113
H	2.344329	-6.554954	2.511371	H	3.495015	0.839493	-3.003828
H	2.951287	-5.756326	-0.388602	H	2.841996	2.068952	-1.921328
H	2.539833	-7.366699	0.191035	H	5.058726	2.780237	-2.732323
H	-1.488736	-5.136092	0.783144	H	5.803378	1.293779	-2.156698
H	-1.147426	-3.400442	0.712642	H	6.213512	3.073899	-0.477192
H	-1.087429	-5.266573	-1.709931	H	4.496896	3.467476	-0.428046
C	-2.878967	-4.201238	-1.352061	H	5.776694	0.843651	0.51654
C	-3.565273	-4.995163	-2.280886	H	5.016603	2.062766	1.534177
C	-4.946971	-4.881088	-2.458212	H	0.813308	-0.296064	0.698862
C	-5.678307	-3.972255	-1.693096	C	-1.295903	-0.027327	0.836958
C	-5.012534	-3.177029	-0.755583	H	-2.163576	0.272574	0.222584
C	-3.630337	-3.286625	-0.595079	H	-1.517179	-1.062567	1.155952
H	-2.582895	1.421884	3.792448	C	-1.306313	0.851367	2.103994
H	-3.467836	1.108354	2.291522	H	-1.105633	1.891994	1.810112
C	4.180899	-0.95298	-1.148271	H	-0.465532	0.552067	2.746349
H	4.014688	-1.540738	-0.237106	C	-2.61446	0.783436	2.901102
H	5.264981	-0.774642	-1.215986	H	-2.822822	-0.241245	3.235415

Table A3.1 (Continued).



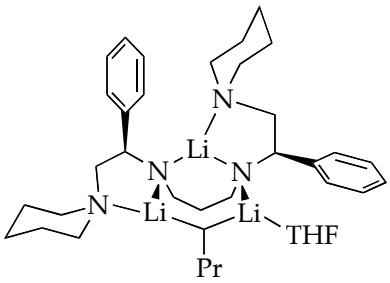


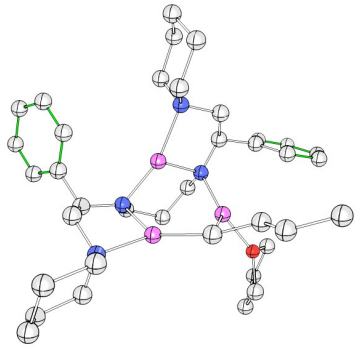
6e
G = -1761.532691
G_{MP2} = -1756.292859

Atom	X	Y	Z	Atom	X	Y	Z
C	0	0	0	C	0.902377	-6.626662	1.343024
H	0.910477	0.150406	0.615721	C	1.226225	-5.26795	0.698883
H	-0.222571	1.022765	-0.364323	H	0.870171	-4.444388	1.327561
Li	1.630801	-0.530328	-1.252322	H	2.317927	-5.166568	0.619419
N	2.326247	-1.885766	-2.493723	H	1.394263	-6.687348	2.322462
Li	1.187615	-3.286448	-1.670727	H	-0.17713	-6.70312	1.529301
N	-0.631375	-3.079003	-2.308718	H	2.458	-7.781023	0.382677
Li	-0.976276	-1.280455	-1.476722	H	1.060643	-8.745551	0.852357
O	-2.427849	-0.146109	-2.270977	H	1.208851	-8.355204	-1.664383
C	-2.641387	1.249104	-1.941666	H	-0.294167	-7.759606	-0.972376
C	-3.901223	1.687529	-2.706345	H	2.204422	-6.102523	-1.648922
C	-4.605721	0.353343	-3.001815	H	-1.346809	-5.814556	-0.40925
C	-3.41918	-0.5767	-3.230488	H	-1.010667	-4.180159	0.158129
H	-3.012646	-0.465214	-4.245492	H	-1.154954	-5.071454	-2.762606
H	-3.626948	-1.629727	-3.041628	C	-2.865998	-4.16657	-1.914553
H	-5.276425	0.40137	-3.865081	C	-3.671566	-4.688132	-2.935601
H	-5.184359	0.015272	-2.134449	C	-5.058839	-4.514284	-2.929489
H	-3.628639	2.185825	-3.643867	C	-5.672736	-3.82043	-1.886491
H	-4.51476	2.382288	-2.125064	C	-4.88561	-3.298612	-0.855136
H	-2.766452	1.317507	-0.856696	C	-3.500536	-3.465184	-0.875952
H	-1.751048	1.819861	-2.223488	H	-2.9063	-3.038545	-0.071329
C	-1.336111	-4.306325	-1.979174	H	-5.352477	-2.76468	-0.030508
C	-0.802512	-4.889047	-0.650296	H	-6.751801	-3.689805	-1.87308
N	0.670997	-5.083939	-0.661376	H	-5.6584	-4.925241	-3.738418
C	1.116981	-6.200758	-1.533968	H	-3.201827	-5.238018	-3.748868
H	0.679275	-6.06238	-2.526868	C	-0.593736	-2.849835	-3.747787
C	0.792351	-7.601059	-0.984493	C	0.40438	-1.750402	-4.15082
C	1.358726	-7.776783	0.432741	H	0.285464	-1.581375	-5.231205
H	5.079821	0.871596	0.435563	H	0.134004	-0.797061	-3.667103
C	3.322064	2.122047	0.660001	H	-0.299833	-3.775361	-4.293709
H	3.673087	2.489851	1.632419	H	-1.580896	-2.581062	-4.182242
H	2.236543	1.984018	0.739598	C	1.895839	-2.038673	-3.887742
C	3.635038	3.132177	-0.45026	H	2.475736	-1.345891	-4.534539
C	3.276682	2.530306	-1.813844	H	2.113629	-3.046309	-4.306633
C	3.949988	1.169769	-2.013497	C	3.779661	-1.825172	-2.42249

Table A3.1 (Continued).

H	3.640208	0.740994	-2.96957	H	4.174797	-1.236981	-3.275819
H	5.049103	1.301786	-2.050631	C	4.489269	-3.184909	-2.536641
H	3.578021	3.199066	-2.629795	C	5.119749	-3.550258	-3.733657
H	2.186941	2.406143	-1.887504	C	5.729191	-4.798339	-3.88541
H	4.706925	3.378806	-0.432911	C	5.73252	-5.70858	-2.82862
H	3.091651	4.070246	-0.283714	C	5.115546	-5.3596	-1.6241
C	-1.103763	-0.391329	1.014381	C	4.495784	-4.116501	-1.486245
H	-2.027834	-0.729473	0.504177	H	4.019575	-3.866813	-0.540323
H	-1.439606	0.458984	1.636384	H	5.124358	-6.054897	-0.787516
C	-0.668118	-1.508761	1.972802	H	6.213194	-6.677271	-2.938157
H	-0.322171	-2.369839	1.38226	H	6.205398	-5.055961	-4.82842
H	0.210143	-1.163114	2.537787	H	5.13265	-2.841188	-4.558942
C	-1.757887	-1.955197	2.953505	N	3.592989	0.219462	-0.939476
H	-1.401053	-2.743055	3.62821	C	3.978587	0.767641	0.377873
H	-2.0977	-1.11646	3.573904	H	3.684489	0.040244	1.143528
H	-2.636527	-2.346325	2.423977	H	3.974598	-1.704319	-0.259428
C	4.235431	-1.100273	-1.137541	H	5.335993	-0.999667	-1.141509





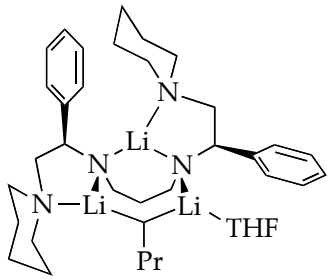
6f
G = -1761.532371
G_{MP2} = -1756.287231

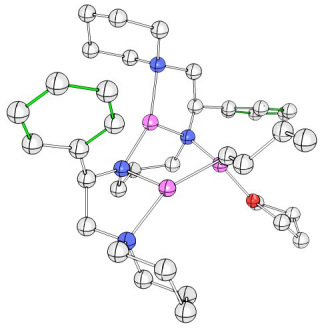
Atom	X	Y	Z	Atom	X	Y	Z
C	0	0	0	C	-3.970203	3.384501	-2.874092
Li	-1.438614	0.470491	-1.443568	C	-4.696599	3.699931	-4.02863
N	-1.946487	1.878256	-2.705645	C	-5.197965	4.986576	-4.244359
Li	-0.65874	3.076241	-1.79535	C	-4.988779	5.987408	-3.296131
N	1.129711	2.681464	-2.422075	C	-4.269434	5.690173	-2.135178
Li	1.238893	0.877545	-1.575332	C	-3.762515	4.406075	-1.934417
O	2.46386	-0.482356	-2.33012	H	-3.199179	4.193327	-1.027827
C	3.588001	-0.291715	-3.206606	H	-4.109478	6.459528	-1.382953
C	3.339744	-1.252408	-4.383074	H	-5.381089	6.988218	-3.456924
C	2.403374	-2.341913	-3.785971	H	-5.752229	5.204911	-5.154078
C	2.201026	-1.893564	-2.326518	H	-4.868866	2.923738	-4.771837
H	2.915147	-2.390773	-1.653709	N	-3.438747	0.039563	-1.034724
H	1.190774	-2.033303	-1.937862	C	-3.760273	-0.387204	0.345238
H	2.836539	-3.34527	-3.839086	H	-3.127382	-1.256341	0.571636

Table A3.1 (Continued).

H	1.448441	-2.364531	-4.319261	H	-3.454523	0.41245	1.028824
H	4.277032	-1.667371	-4.765538	C	-5.235757	-0.762338	0.564383
H	2.846064	-0.72958	-5.207066	C	-5.678881	-1.836658	-0.440948
H	3.619673	0.76422	-3.474057	C	-5.346086	-1.404108	-1.877253
H	4.509243	-0.548188	-2.664826	C	-3.865	-1.005819	-1.994096
C	1.954987	3.800801	-2.005406	H	-3.626555	-0.667013	-3.006089
C	1.520727	4.260363	-0.595369	H	-3.243298	-1.891862	-1.796636
N	0.079697	4.625274	-0.535994	H	-5.558173	-2.214499	-2.586383
C	-0.21557	5.944377	-1.151147	H	-5.983406	-0.558994	-2.169488
H	0.222872	5.964692	-2.15333	H	-6.750856	-2.045319	-0.33736
C	0.262047	7.151529	-0.324943	H	-5.153167	-2.777326	-0.217719
C	-0.290216	7.090476	1.107387	H	-5.867946	0.129216	0.457272
C	0.023318	5.730266	1.7487	H	-5.368162	-1.117522	1.594384
C	-0.459146	4.58538	0.843311	H	-0.779048	0.536172	0.58739
H	-0.210842	3.610309	1.277131	H	-0.354541	-1.0532	0.002416
H	-1.555542	4.635521	0.766249	C	1.275289	0.039707	0.86763
H	-0.459237	5.642971	2.730682	H	2.089823	-0.522483	0.379708
H	1.104004	5.637536	1.920448	H	1.650447	1.07818	0.945598
H	-1.381366	7.231447	1.080007	C	1.13832	-0.501079	2.304943
H	0.115818	7.908975	1.714408	H	0.348659	0.064067	2.821115
H	-0.058489	8.074036	-0.825582	H	0.781879	-1.540141	2.254665
H	1.3592	7.178596	-0.297199	C	2.434444	-0.439733	3.122057
H	-1.304038	6.00486	-1.281742	H	2.297116	-0.837808	4.134902
H	2.17287	5.075766	-0.249317	H	3.232782	-1.021386	2.642991
H	1.654505	3.426597	0.10271	H	2.794862	0.592736	3.218895
H	1.810172	4.663987	-2.690666	C	-3.95267	1.396342	-1.343741
C	3.466988	3.523295	-2.038618	H	-3.633921	2.034883	-0.510236
C	4.253445	4.026858	-3.083493	H	-5.05238	1.439674	-1.369828
C	5.617008	3.733781	-3.175826	C	-0.016135	1.563885	-4.329783
C	6.22801	2.935039	-2.209101	C	-1.47575	1.996735	-4.089496
C	5.460863	2.428501	-1.155975	H	-1.587001	3.024135	-4.500056
C	4.097361	2.713999	-1.07879	H	-2.108138	1.36879	-4.753069
H	3.520111	2.299061	-0.255679	H	0.108443	1.414496	-5.412543
H	5.926638	1.812446	-0.390104	H	0.142309	0.575283	-3.867853
H	7.289969	2.711311	-2.271546	H	0.898001	3.512295	-4.368829
H	6.201134	4.134813	-4.000889	H	2.045767	2.184883	-4.310098
H	3.786929	4.659868	-3.835971	C	-3.396444	1.970799	-2.666361
C	1.085757	2.5346	-3.868502	H	-3.83935	1.368174	-3.488646

Note: The following conformers have N-Li-N cyclohexane ring of the ligand backbone in the boat conformation and the left phenyl substituent pointing in the equatorial direction.



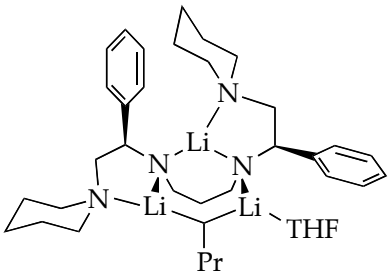


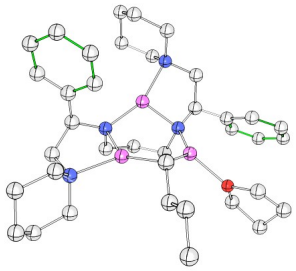
6j
G = -1761.527261
G_{MP2} = -1756.288171

Atom	X	Y	Z	Atom	X	Y	Z
C	0	0	0	H	-1.687903	4.863695	-0.388341
H	0.996504	-0.414815	0.277923	H	-0.258858	7.560799	-0.702197
H	0.071111	1.05491	0.347769	H	-1.850803	7.141326	-1.336027
Li	-1.152858	0.178049	-1.865582	H	3.019611	4.558442	-0.401858
N	-1.129294	1.745351	-3.16589	H	2.117162	3.127003	0.121329
Li	0.131924	2.711493	-2.044923	H	3.104844	3.664147	-2.717876
N	1.927256	1.948814	-2.302152	C	4.254254	2.403366	-1.468495
Li	1.53805	0.254071	-1.452156	C	5.401083	2.665817	-2.228896
O	2.598783	-1.366554	-1.80982	C	6.641937	2.117291	-1.888973
C	2.387814	-2.630398	-1.133866	C	6.762337	1.303553	-0.76314
C	3.538635	-3.542787	-1.574596	C	5.629828	1.039519	0.014952
C	4.646522	-2.535048	-1.92014	C	4.39287	1.577074	-0.340273
C	3.847802	-1.394131	-2.54375	H	3.520741	1.349565	0.269327
H	3.630897	-1.585602	-3.603268	H	5.713499	0.418097	0.903926
H	4.313733	-0.412953	-2.443725	H	7.726315	0.882146	-0.489648
H	5.401652	-2.939004	-2.60113	H	7.513909	2.332033	-2.502402
H	5.153416	-2.187046	-1.012841	H	5.320506	3.310697	-3.101869
H	3.256011	-4.116028	-2.465459	C	2.050876	1.570075	-3.712124
H	3.824496	-4.253308	-0.793362	C	0.941336	2.13045	-4.627169
H	2.402451	-2.444629	-0.053651	C	-0.460604	1.51236	-4.452707
H	1.398943	-3.010924	-1.406218	H	-0.349657	0.431045	-4.702994
C	2.883448	2.962076	-1.89102	H	-1.075577	1.92325	-5.278276
C	2.293045	3.793666	-0.730953	H	1.233831	1.96022	-5.676134
N	0.988595	4.42457	-1.04768	H	0.878808	3.223117	-4.494745
C	1.148003	5.515443	-2.034426	H	2.024091	0.467294	-3.833328
H	1.591575	5.099517	-2.942942	H	3.027484	1.869608	-4.132764
H	1.855322	6.272289	-1.642477	C	-2.566034	1.801384	-3.372019
C	-0.188413	6.183968	-2.367785	C	-3.160087	0.423036	-3.828123
H	-0.848044	5.449108	-2.849454	N	-2.884962	-0.697278	-2.88529
H	-0.012694	6.984975	-3.096961	C	-4.105058	-1.03627	-2.113389
C	-0.860452	6.731794	-1.103413	H	-4.434384	-0.136837	-1.587326

Table A3.1 (Continued).

C	-0.969501	5.620941	-0.051999	H	-4.913008	-1.318991	-2.815285
C	0.387467	4.956979	0.195209	C	-3.876913	-2.181337	-1.124116
H	0.280388	4.124044	0.899632	H	-4.827516	-2.40845	-0.625128
H	1.075719	5.688608	0.661524	H	-3.177507	-1.856639	-0.346274
H	-1.346733	6.0195	0.898391	C	-3.323007	-3.426026	-1.828029
C	-5.399523	3.359062	-1.326565	C	-2.090906	-3.050908	-2.660785
C	-4.921847	3.27733	-0.015739	C	-2.407312	-1.895469	-3.613919
C	-3.656038	2.740119	0.213014	H	-1.513378	-1.612654	-4.181206
C	-2.875984	2.285297	-0.856883	H	-3.167016	-2.225243	-4.34836
H	-1.887138	1.889544	-0.642627	H	-1.736025	-3.909649	-3.244942
H	-3.26457	2.67521	1.225221	H	-1.270729	-2.751557	-1.992505
H	-5.526484	3.634485	0.813669	H	-4.092435	-3.84804	-2.491258
H	-6.379201	3.787333	-1.524226	H	-3.074046	-4.204864	-1.096937
H	-5.003569	2.969769	-3.401964	H	-4.241304	0.503222	-4.017508
C	-0.986098	-0.71034	0.94791	H	-2.692831	0.180426	-4.787283
H	-2.006287	-0.316934	0.799684	H	-2.820262	2.471729	-4.222433
H	-1.047831	-1.780289	0.687044	C	-3.345653	2.34344	-2.176016
C	-0.670951	-0.611414	2.453839	C	-4.620028	2.897364	-2.386017
H	0.335832	-1.018079	2.632267	H	-1.732898	-2.403839	3.110688
H	-0.619937	0.4506	2.735961	H	-1.423324	-1.245172	4.413286
C	-1.682931	-1.333884	3.351227	H	-2.692213	-0.922311	3.221381





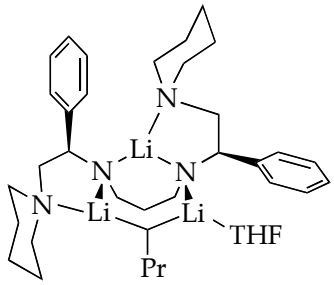
6k
G = -1761.527223
G_{MP2} = -1756.28878

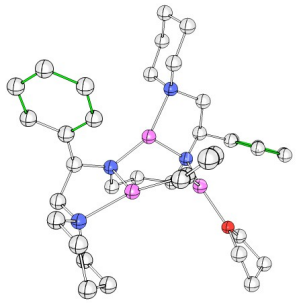
Atom	X	Y	Z	Atom	X	Y	Z
C	0	0	0	C	-4.827561	2.555278	0.495795
H	-0.79082	0.22689	-0.752628	H	-4.140057	2.4619	-0.341575
H	0.910375	0.34135	-0.537978	H	-6.455792	1.649436	-0.583471
Li	1.024474	0.973449	1.596426	H	-8.046682	1.803078	1.326661
N	1.156538	2.728934	2.576897	H	-7.295447	2.833301	3.465972
Li	-0.247811	3.570056	1.56309	H	-4.992105	3.71618	3.675446
N	-1.933075	2.623025	1.931511	C	-1.801977	2.077874	3.28742
Li	-1.689102	0.91977	0.991038	C	-0.789332	2.812187	4.201814
O	-3.145243	-0.446335	1.015136	C	0.694809	2.488255	3.943578
C	-3.985557	-0.672314	2.171976	H	0.838611	1.431878	4.277463
C	-4.814148	-1.909327	1.828807	H	1.285814	3.084999	4.669885

Table A3.1 (Continued).

C	-5.012717	-1.742689	0.314225	H	-0.998865	2.557911	5.252817
C	-3.668232	-1.157002	-0.130639	H	-0.952535	3.897863	4.110482
H	-3.761553	-0.453319	-0.964249	H	-1.465268	1.02058	3.23848
H	-2.949419	-1.935982	-0.409023	H	-2.775521	2.03238	3.81058
H	-5.821546	-1.030277	0.119007	C	2.593479	2.90884	2.54624
H	-5.247297	-2.679771	-0.199565	C	3.395336	1.624487	2.977474
H	-5.755383	-1.946624	2.385172	N	2.969329	0.392943	2.261464
H	-4.249663	-2.823951	2.045614	C	3.853589	0.029602	1.1246
H	-3.331104	-0.805572	3.037796	H	3.311619	-0.706926	0.515758
H	-4.61421	0.210129	2.330397	H	3.994117	0.91714	0.503449
C	-2.948755	3.664713	1.85721	C	5.210589	-0.562112	1.543661
C	-2.611847	4.635348	0.704387	C	5.027639	-1.75744	2.490549
N	-1.29009	5.292501	0.845055	C	4.126976	-1.368982	3.671441
C	-1.309986	6.31778	1.912123	C	2.805163	-0.774948	3.161225
H	-1.609478	5.840204	2.848733	H	2.162962	-0.474071	3.996377
H	-2.075234	7.083767	1.678347	H	2.261395	-1.546554	2.598254
C	0.056111	6.987442	2.081456	H	3.914313	-2.240699	4.303862
C	0.518339	7.630026	0.76866	H	4.640737	-0.634246	4.306946
C	0.46858	6.595863	-0.3625	H	5.999396	-2.123008	2.845167
C	-0.902573	5.91875	-0.437943	H	4.560305	-2.587957	1.940651
H	-0.895778	5.136998	-1.206365	H	5.817361	0.208445	2.038358
H	-1.666596	6.661725	-0.739177	H	5.761886	-0.859899	0.642494
H	1.239072	5.832703	-0.20022	H	4.475198	1.803141	2.87798
H	0.68413	7.066425	-1.330165	H	3.203767	1.472998	4.044295
H	1.530653	8.038815	0.871453	H	2.921316	3.660567	3.299093
H	-0.14283	8.47495	0.525014	C	3.095035	3.428847	1.200013
H	0.786061	6.23281	2.404845	C	4.287869	4.168308	1.147199
H	-0.011188	7.735308	2.881609	C	4.806457	4.632291	-0.061678
H	-3.407822	5.393232	0.593082	C	4.140725	4.364254	-1.260237
H	-2.577325	4.060983	-0.228868	C	2.951463	3.635967	-1.228843
H	-2.971164	4.264424	2.787472	C	2.433685	3.180095	-0.011787
C	-4.388768	3.151536	1.689138	H	1.507214	2.612041	-0.019192
C	-5.304686	3.24449	2.745849	H	2.419265	3.418927	-2.151874
C	-6.608565	2.752921	2.626723	H	4.541965	4.722657	-2.20454
C	-7.02992	2.173368	1.430464	H	5.728803	5.208101	-0.067383
C	-6.132667	2.082632	0.360787	H	4.814023	4.388684	2.074147
H	1.156655	-1.937623	-1.735034	C	0.090524	-1.536834	0.104481
C	0.345757	-3.827766	-1.054075	H	0.935974	-1.815829	0.757499
H	-0.554226	-4.226608	-0.567422	H	-0.800809	-1.931075	0.619737
H	0.45641	-4.340857	-2.017413	C	0.256574	-2.30582	-1.220916
H	1.203915	-4.10816	-0.429433	H	-0.586896	-2.057173	-1.883128

Table A3.1 (Continued).



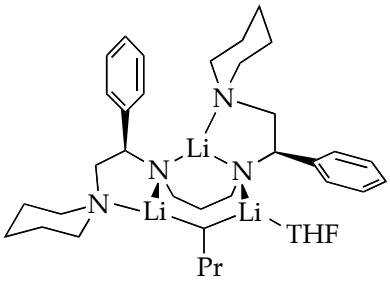


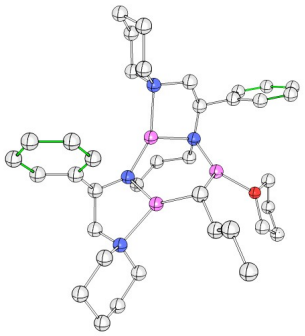
6l
G = -1761.522822
G_{MP2} = -1756.281377

Atom	X	Y	Z	Atom	X	Y	Z
C	0	0	0	H	8.070825	1.143832	-3.236553
H	0.796951	-0.668971	0.396048	H	5.875631	2.204107	-3.67429
H	0.400464	1.016836	0.213883	C	2.44652	0.450527	-3.713066
Li	-1.016968	0.20332	-1.945691	C	1.573988	1.173161	-4.763979
N	-0.556115	1.553282	-3.39618	C	0.049471	0.996993	-4.611711
Li	0.860418	2.22219	-2.27592	H	-0.147023	-0.09379	-4.74377
N	2.456893	1.069053	-2.384555	H	-0.401255	1.466787	-5.508738
Li	1.667928	-0.305665	-1.296203	H	1.839658	0.795968	-5.764832
O	2.337615	-2.158436	-1.278475	H	1.819486	2.247727	-4.763344
C	3.495084	-2.649392	-2.00268	H	2.057096	-0.585061	-3.644177
C	3.758439	-4.047944	-1.444346	H	3.467428	0.337773	-4.122905
C	2.341013	-4.522826	-1.087666	C	-1.908811	1.995198	-3.680093
C	1.699924	-3.239192	-0.557269	C	-2.87208	0.801124	-4.000641
H	1.892718	-3.104517	0.514689	N	-2.934631	-0.237083	-2.933566
H	0.621927	-3.173491	-0.727064	C	-4.189448	-0.103518	-2.153275
H	2.32457	-5.331121	-0.350536	H	-4.217672	0.902098	-1.726233
H	1.817845	-4.870734	-1.986307	H	-5.055002	-0.191292	-2.837987
H	4.381191	-3.991195	-0.543575	C	-4.312917	-1.15676	-1.050471
H	4.264241	-4.695681	-2.166458	H	-5.279949	-1.026806	-0.548364
H	3.247742	-2.68021	-3.071096	H	-3.536945	-0.987794	-0.296025
H	4.313103	-1.942769	-1.850436	C	-4.181417	-2.5761	-1.61556
C	3.546972	2.01335	-2.226485	C	-2.90154	-2.686899	-2.453019
C	3.213407	3.011876	-1.093064	C	-2.854401	-1.59397	-3.523324
N	1.954801	3.760595	-1.340455	H	-1.921332	-1.658739	-4.094477
C	2.098385	4.853536	-2.333378	H	-3.68418	-1.748652	-4.23945
H	2.579045	4.448593	-3.229284	H	-2.83452	-3.668015	-2.940279
C	2.863278	6.085319	-1.816575	H	-2.023032	-2.589859	-1.798703
C	2.235967	6.615095	-0.518264	H	-5.049693	-2.801459	-2.252149
C	2.099116	5.48515	0.513182	H	-4.181398	-3.316557	-0.806347
C	1.347897	4.291352	-0.097924	H	-3.884875	1.160104	-4.240439
H	1.27056	3.466612	0.619411	H	-2.487214	0.326258	-4.908216
H	0.323199	4.601809	-0.344327	H	-1.941106	2.593426	-4.617057
H	1.559736	5.835086	1.402798	C	-2.505712	2.900882	-2.604398
H	3.093815	5.166335	0.853009	C	-3.559259	3.76528	-2.946737

Table A3.1 (Continued).

H	1.237851	7.021786	-0.739603	C	-4.162327	4.592093	-2.000069
H	2.829739	7.443404	-0.112157	C	-3.724905	4.575241	-0.672959
H	2.859798	6.859593	-2.594456	C	-2.677004	3.728659	-0.314101
H	3.915486	5.826003	-1.639696	C	-2.072298	2.906176	-1.271807
H	1.083534	5.157149	-2.626134	H	-1.251603	2.26614	-0.961412
H	4.071408	3.678875	-0.920351	H	-2.322464	3.702873	0.713383
H	3.06186	2.440455	-0.169869	H	-4.192469	5.217602	0.068607
H	3.69997	2.613309	-3.14776	H	-4.970804	5.254744	-2.299291
C	4.91647	1.373756	-1.937642	H	-3.905568	3.793058	-3.978113
C	6.003926	1.574074	-2.79583	C	-1.183878	-0.213614	0.963895
C	7.245367	0.979745	-2.547795	H	-2.030491	0.435131	0.681815
C	7.423869	0.179349	-1.420554	H	-1.562569	-1.244392	0.861814
C	6.349427	-0.026144	-0.548222	C	-0.893975	0.034386	2.457838
C	5.110938	0.558718	-0.811127	H	-0.063207	-0.615923	2.770255
H	4.277168	0.379282	-0.135636	H	-0.530444	1.065388	2.580667
H	6.480431	-0.640896	0.339753	C	-2.101178	-0.197145	3.374479
H	8.388145	-0.280871	-1.220222	H	-2.463468	-1.230755	3.3
H	-2.936105	0.46206	3.103959	H	-1.856713	-0.007368	4.426816





6m
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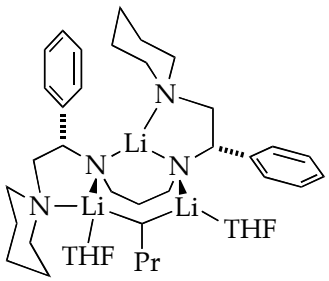
G_{MP2} = -1756.279342

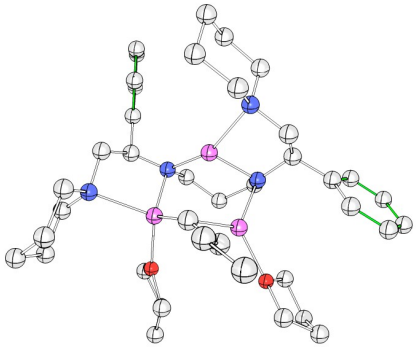
Atom	X	Y	Z	Atom	X	Y	Z
C	0	0	0	H	7.98029	0.760479	-3.341715
H	0.951149	0.119993	0.569554	H	5.884477	1.996907	-3.80279
H	-0.54787	0.917591	0.312442	C	2.38249	0.747596	-3.700391
Li	-0.880832	0.593974	-1.84811	C	1.484669	1.487654	-4.719167
N	-0.536523	2.001067	-3.254322	C	-0.035886	1.379988	-4.48407
Li	0.97297	2.628821	-2.241183	H	-0.286656	0.294137	-4.568854
N	2.476366	1.362655	-2.372547	H	-0.519248	1.84101	-5.368698
Li	1.746168	-0.088843	-1.284748	H	1.685182	1.07949	-5.722961
O	2.541083	-1.917004	-1.44963	H	1.771532	2.551396	-4.753479
C	3.79112	-2.183282	-2.124821	H	1.968614	-0.278082	-3.6159
C	3.461413	-3.30758	-3.100209	H	3.37883	0.60752	-4.160311
C	2.497111	-4.170019	-2.26804	C	-1.890184	2.483817	-3.447378
C	1.753502	-3.132911	-1.404047	C	-2.942817	1.323275	-3.589324
H	1.648413	-3.451747	-0.362042	N	-2.884707	0.333479	-2.48124

Table A3.1 (Continued).

H	0.75963	-2.891088	-1.79264	C	-3.891291	0.577646	-1.416
H	3.060541	-4.863804	-1.633943	H	-3.590881	-0.018272	-0.543344
H	1.811803	-4.762734	-2.881049	H	-3.830903	1.62807	-1.123486
H	4.349419	-3.854007	-3.432011	C	-5.330735	0.203149	-1.80971
H	2.956906	-2.900244	-3.983899	C	-5.412012	-1.247955	-2.305842
H	4.117416	-1.25216	-2.587314	C	-4.379446	-1.491984	-3.415782
H	4.54427	-2.495288	-1.388659	C	-2.978456	-1.071884	-2.944651
C	3.638298	2.229206	-2.242963	H	-2.239331	-1.217764	-3.740969
C	3.387832	3.291252	-1.148106	H	-2.678912	-1.712602	-2.102552
N	2.19127	4.128807	-1.414098	H	-4.362717	-2.550175	-3.707591
C	2.390768	5.135141	-2.486179	H	-4.6531	-0.920832	-4.313684
H	2.790303	4.628693	-3.369983	H	-6.424357	-1.480773	-2.658736
C	3.287256	6.320002	-2.087994	H	-5.206624	-1.930362	-1.467407
C	2.764464	6.996904	-0.811645	H	-5.69269	0.880886	-2.59463
C	2.562538	5.959095	0.302934	H	-5.986571	0.354875	-0.942894
C	1.68375	4.798833	-0.194304	H	-3.954061	1.735019	-3.717113
H	1.56498	4.037432	0.585239	H	-2.701636	0.795247	-4.517652
H	0.680968	5.1813	-0.427345	H	-1.984585	3.014295	-4.419753
H	2.090219	6.419352	1.180412	C	-2.332926	3.498416	-2.394268
H	3.535994	5.5743	0.635602	C	-3.331163	4.431562	-2.71909
H	1.801184	7.48199	-1.029334	C	-3.793311	5.361347	-1.787805
H	3.448774	7.789743	-0.485116	C	-3.265353	5.380834	-0.494739
H	3.323137	7.034806	-2.920077	C	-2.270492	4.464835	-0.153238
H	4.317566	5.975067	-1.929515	C	-1.808359	3.539338	-1.09499
H	1.395646	5.513545	-2.758509	H	-1.036583	2.834742	-0.799615
H	4.297894	3.89209	-1.001635	H	-1.850297	4.46377	0.849647
H	3.194841	2.769402	-0.20366	H	-3.622714	6.102699	0.2349
H	3.835088	2.778782	-3.185897	H	-4.561972	6.0752	-2.073877
C	4.953463	1.495331	-1.929485	H	-3.745787	4.431985	-3.725394
C	6.000194	1.466201	-2.859528	C	-0.740689	-1.190444	0.644049
C	7.186873	0.773325	-2.59807	H	-1.732038	-1.316309	0.173928
C	7.354006	0.106942	-1.384952	H	-0.206734	-2.129109	0.426447
C	6.322053	0.132579	-0.440741	C	-0.955585	-1.116047	2.167877
C	5.135568	0.810482	-0.716634	H	0.024306	-1.011316	2.657134
H	4.334807	0.803458	0.019826	H	-1.509454	-0.195511	2.404856
H	6.444548	-0.376501	0.512653	C	-1.694399	-2.325205	2.754122
H	8.27767	-0.425667	-1.173116	H	-1.146407	-3.256594	2.560203
H	-2.692243	-2.434714	2.309189	H	-1.824814	-2.238292	3.839827

Table A3.2. Optimized geometries at B3LYP level of theory with 6-31G(d) basis set for the di-solvated BuLi-ligand aggregation conformers at –78 °C with free energies (Hartrees) and cartesian coordinates (X, Y, Z) (Note: G_{MP2} includes single point MP2 corrections to B3LYP/6-31G(d) optimized structures).



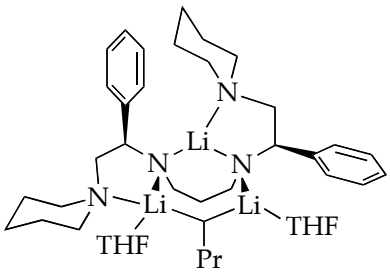


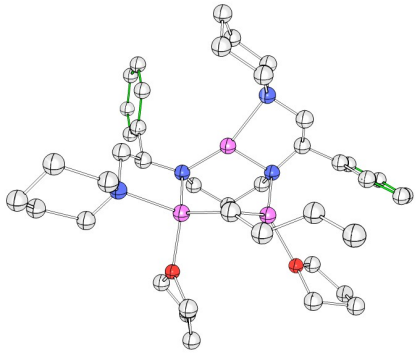
6a
G = -1993.882182
G_{MP2} = -1987.993623

Atom	X	Y	Z	Atom	X	Y	Z
N	0	0	0	H	-3.88998	1.285756	7.236108
Li	-0.63393	1.581872	1.103928	H	-4.668175	2.247061	5.969979
Li	-3.278993	0.568685	1.203493	H	-4.83803	0.485722	5.973468
N	-3.005893	-1.16537	0.285743	O	-4.878148	1.686684	0.651361
Li	-1.217896	-1.128334	1.103481	C	-5.855073	2.346255	1.493328
N	-1.842334	-2.922631	2.352143	C	-7.175548	2.316568	0.71711
C	-3.295304	-2.695223	2.165545	C	-6.699197	2.277941	-0.742986
C	-3.686624	-2.376065	0.709814	C	-5.466196	1.382947	-0.642504
H	-3.371044	-3.235656	0.082105	H	-4.708273	1.579972	-1.404751
C	-5.216751	-2.32532	0.554314	H	-5.72802	0.321284	-0.667899
C	-5.81726	-2.860614	-0.59499	H	-6.424445	3.282571	-1.087532
C	-7.196061	-2.776147	-0.806512	H	-7.448697	1.873678	-1.429551
C	-8.01451	-2.166291	0.144512	H	-7.810764	3.177368	0.947028
C	-7.436769	-1.637848	1.302851	H	-7.733069	1.40356	0.951204
C	-6.056086	-1.708484	1.497117	H	-5.902016	1.820625	2.450405
H	-5.63316	-1.28646	2.405681	H	-5.511621	3.37269	1.676208
H	-8.06573	-1.181928	2.064828	O	-1.240919	3.282885	0.143012
H	-9.089592	-2.112085	-0.00729	C	-2.280276	4.156327	0.650176
H	-7.63061	-3.197806	-1.709949	C	-2.411103	5.290448	-0.373002
H	-5.190323	-3.358675	-1.331752	C	-1.962637	4.609568	-1.675899
H	-3.867186	-3.563614	2.540137	C	-0.839265	3.700318	-1.1794
H	-3.559911	-1.839383	2.796483	H	0.111948	4.245979	-1.10927
C	-1.457401	-4.243615	1.805453	H	-0.688698	2.803263	-1.783529
H	-1.685814	-4.256156	0.736658	H	-1.625362	5.31506	-2.441271
H	-2.075943	-5.030743	2.280536	H	-2.778012	4.010478	-2.098341
C	0.024389	-4.559123	2.017677	H	-1.734186	6.116616	-0.124943
H	0.626508	-3.867265	1.418852	H	-3.428237	5.691358	-0.420078
H	0.226704	-5.566885	1.633229	H	-3.200031	3.569615	0.735555
C	0.418102	-4.454043	3.49574	H	-1.986065	4.501228	1.646154
C	-0.035424	-3.104125	4.064441	C	1.452358	0.114804	0.030303

Table A3.2 (Continued).

C	-1.522988	-2.869901	3.794517	C	1.920812	0.546427	1.433229
H	-1.825233	-1.887348	4.171434	N	1.458086	1.892644	1.844973
H	-2.115653	-3.627892	4.343893	C	1.65301	2.044131	3.303609
H	0.144859	-3.053613	5.145669	H	1.058483	1.271493	3.801834
H	0.544845	-2.291006	3.605991	H	2.715014	1.863709	3.563079
H	-0.064354	-5.26376	4.062772	C	1.240466	3.426355	3.815474
H	1.500466	-4.584971	3.61922	H	1.437168	3.477032	4.893801
C	-2.88928	-1.084694	-1.158984	H	0.157777	3.548901	3.682976
C	-1.965358	0.05726	-1.616079	C	1.983509	4.540596	3.070596
C	-0.452282	-0.122597	-1.383515	C	1.805428	4.353328	1.560188
H	0.057774	0.638733	-2.021587	C	2.21182	2.942091	1.127354
H	-0.167696	-1.089154	-1.849101	H	2.042954	2.817033	0.054466
H	-2.291844	1.001623	-1.149623	H	3.298127	2.805864	1.299999
H	-2.110813	0.18658	-2.69941	H	2.406727	5.08265	1.002018
H	-2.488621	-2.031007	-1.589867	H	0.755371	4.517091	1.288705
H	-3.867575	-0.946492	-1.670964	H	3.054089	4.498246	3.319591
C	-1.953545	1.09108	2.833032	H	1.624287	5.527911	3.387098
H	-1.346143	0.232766	3.196491	H	3.021985	0.489748	1.502939
H	-1.320129	1.967338	3.074809	H	1.514371	-0.160764	2.165855
C	-3.17218	1.203531	3.774722	H	1.782311	0.900288	-0.686871
H	-3.720174	2.135501	3.555344	C	2.232647	-1.136242	-0.418379
H	-3.902561	0.391788	3.580255	C	2.68006	-1.24059	-1.742793
C	-2.884167	1.184335	5.290204	C	3.369738	-2.367732	-2.194552
H	-2.186402	2.001502	5.523692	C	3.643658	-3.418157	-1.318476
H	-2.351374	0.254501	5.53816	C	3.216585	-3.328315	0.008001
C	-4.135783	1.307231	6.167368	C	2.515166	-2.203629	0.44661
H	3.698011	-2.421283	-3.230024	H	2.196967	-2.154832	1.48462
H	2.486068	-0.418391	-2.428703	H	3.434342	-4.134006	0.705497
H	4.187367	-4.294446	-1.662247				





6g
G = -1993.873501
G_{MP2} = -1987.984874

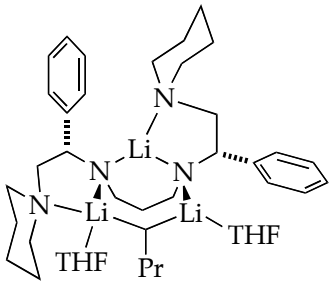
Atom	X	Y	Z	Atom	X	Y	Z
C	0	0	0	C	-1.68824	-3.705752	-2.140519
Li	-1.26646	-0.717779	-1.637333	H	-1.357892	-4.55786	-2.772482

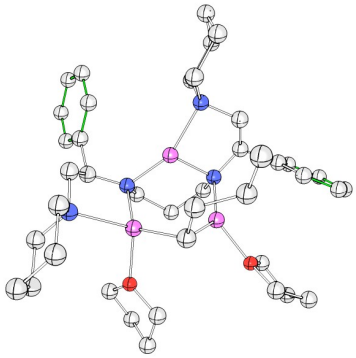
Table A3.2 (Continued).

N	-1.021022	-2.482517	-2.556927	C	-3.21792	-3.679001	-2.298167
Li	0.799151	-2.580774	-1.833346	C	-3.808917	-4.217115	-3.450752
N	1.996462	-1.388658	-2.87641	C	-5.188069	-4.146631	-3.665013
Li	1.440143	0.213346	-1.767674	C	-6.014866	-3.54794	-2.7139
O	1.041762	2.01651	-2.628392	C	-5.445941	-3.018409	-1.551686
C	0.134707	2.971755	-2.024866	C	-4.06543	-3.076579	-1.353435
C	-0.372158	3.874992	-3.16775	H	-3.647344	-2.651416	-0.444685
C	0.017102	3.096583	-4.437614	H	-6.081177	-2.568156	-0.791772
C	1.298022	2.398071	-3.990372	H	-7.089989	-3.503411	-2.868849
H	2.160183	3.081243	-4.030421	H	-5.616097	-4.56869	-4.571354
H	1.537746	1.489874	-4.54673	H	-3.17455	-4.703231	-4.189209
H	0.165626	3.741467	-5.309152	H	-1.869264	-4.877706	-0.296286
H	-0.744781	2.349246	-4.685198	H	-1.530843	-3.155053	-0.06359
H	0.13618	4.845517	-3.147188	C	0.500355	-5.637075	-0.996237
H	-1.447582	4.064092	-3.097805	H	0.229452	-5.712337	-2.052764
H	-0.656766	2.392821	-1.544253	H	-0.116837	-6.37667	-0.449473
H	0.67188	3.538646	-1.255489	C	1.981296	-5.974439	-0.815427
C	1.514108	-1.454153	-4.256243	C	2.425241	-5.791096	0.641227
C	0.001188	-1.243929	-4.456371	C	2.018623	-4.400554	1.144137
C	-0.925419	-2.38465	-4.003556	C	0.529067	-4.143747	0.905773
H	-0.537031	-3.328296	-4.45256	H	0.263422	-3.132155	1.230019
H	-1.909101	-2.234458	-4.50008	H	-0.065259	-4.851014	1.516841
H	-0.160825	-1.090992	-5.534074	H	2.603289	-3.629327	0.62287
H	-0.308098	-0.305114	-3.967639	H	2.234018	-4.293116	2.214686
H	2.026986	-0.680643	-4.876154	H	3.507998	-5.939053	0.738743
H	1.774787	-2.408143	-4.759795	H	1.944602	-6.555524	1.269202
C	3.452957	-1.309319	-2.880587	H	2.577919	-5.333523	-1.474015
C	3.982935	-0.932191	-1.482143	H	2.148723	-7.007887	-1.144381
H	3.619854	-1.670631	-0.757497	O	-2.811431	0.424245	-2.299614
H	5.08163	-0.997377	-1.478811	C	-3.552053	1.438595	-1.600804
H	3.780804	-0.504875	-3.578549	C	-5.015335	1.070245	-1.82653
C	4.187161	-2.561553	-3.395802	C	-4.995412	0.588752	-3.288117
C	4.616617	-2.62207	-4.728744	C	-3.591091	-0.027574	-3.442461
C	5.261106	-3.751415	-5.238247	H	-3.089328	0.29707	-4.360836
C	5.505961	-4.849202	-4.41316	H	-3.599543	-1.116691	-3.408921
C	5.096455	-4.80399	-3.078792	H	-5.126263	1.436609	-3.970252
C	4.441166	-3.67566	-2.582321	H	-5.780816	-0.140833	-3.502192
H	4.136526	-3.661083	-1.539335	H	-5.696036	1.91038	-1.657264
H	5.292376	-5.647463	-2.420628	H	-5.300126	0.251307	-1.157267
H	6.013632	-5.728089	-4.802306	H	-3.233739	1.42136	-0.557095
H	5.575874	-3.770307	-6.279065	H	-3.322673	2.428544	-2.025905
H	4.44319	-1.764573	-5.375845	H	0.524127	-0.880179	0.435595
N	0.164221	-4.275084	-0.521464	H	0.797419	0.772126	-0.007521
C	-1.289488	-4.022478	-0.686598	C	-0.96969	0.504855	1.099018
H	2.998597	1.424086	0.727171	H	-0.456478	0.744419	2.050548
H	3.098386	-0.320437	0.920336	H	-1.424641	1.460972	0.784776

Table A3.2 (Continued).

C	5.023122	0.715311	0.985664	C	-2.106673	-0.466236	1.451343
C	5.70793	1.904958	0.296539	H	-1.670239	-1.428968	1.756645
C	5.615265	1.7665	-1.230321	H	-2.705458	-0.680102	0.552138
C	4.160415	1.530531	-1.674357	C	-3.031911	0.039422	2.56464
H	4.108781	1.38632	-2.757267	H	-3.51198	0.986221	2.283791
H	3.563409	2.423364	-1.444695	H	-3.826557	-0.680794	2.794951
H	5.998779	2.667929	-1.72612	H	-2.47005	0.222242	3.488897
H	6.249417	0.935324	-1.565756	N	3.494167	0.384634	-1.013829
H	6.754043	1.992399	0.615619	C	3.590475	0.539167	0.454462
H	5.206577	2.834884	0.605223	H	4.989029	0.863842	2.072806
H	5.603855	-0.201039	0.812569				





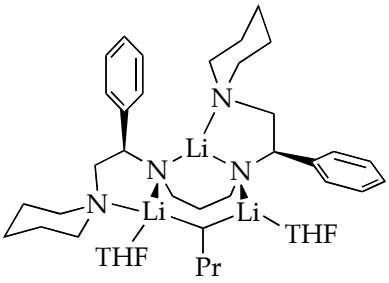
6h
G = -1993.87677
G_{MP2} = -1987.988021

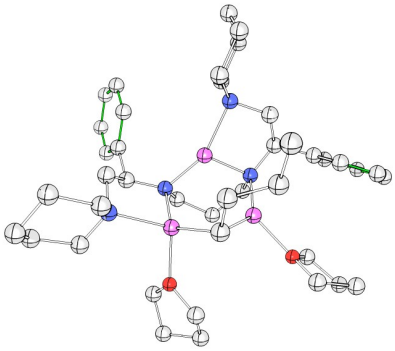
Atom	X	Y	Z	Atom	X	Y	Z
C	0	0	0	C	7.848512	0.462765	1.700996
N	-0.427984	0.10752	1.394309	C	7.068799	0.250529	2.842262
Li	-0.149658	-1.497459	2.602305	C	5.733608	0.655532	2.868299
O	-0.124162	-3.362593	1.652007	H	5.145435	0.4692	3.7634
C	0.86186	-4.376653	1.972744	H	7.505714	-0.222919	3.719046
C	0.661141	-5.496622	0.946247	H	8.888671	0.147444	1.679929
C	0.100761	-4.733643	-0.264155	H	7.873226	1.26963	-0.298914
C	-0.78745	-3.690848	0.413122	H	5.515005	2.018475	-0.225797
H	-1.781575	-4.102594	0.637539	H	4.014128	3.267362	3.228735
H	-0.906531	-2.768536	-0.159532	H	3.375431	1.765476	3.89619
H	-0.454207	-5.369159	-0.961045	C	1.647986	4.062123	2.110717
H	0.909379	-4.242416	-0.817909	H	2.018436	3.775531	1.122752
H	-0.072732	-6.226939	1.307819	C	2.262413	5.399848	2.557977
H	1.590504	-6.032429	0.729645	C	1.784065	5.776329	3.968794
H	1.854242	-3.919841	1.898697	C	2.026251	4.617826	4.948294
H	0.703299	-4.695819	3.006526	C	1.419523	3.313768	4.402975
H	1.482217	-1.535005	0.374942	H	1.621091	2.476183	5.079896
C	1.404908	-0.602889	-0.207837	H	0.326853	3.429331	4.349509
C	2.604423	0.3108	0.101761	H	1.58418	4.838738	5.928451
N	2.736576	0.614747	1.518606	H	3.103988	4.487096	5.113134

Table A3.2 (Continued).

Li	1.00511	1.173589	2.20656	H	0.706765	5.998849	3.935575
Li	2.66986	-1.069819	2.609672	H	2.281757	6.689798	4.317271
C	1.415251	-1.834786	4.217922	H	1.985703	6.177751	1.834894
H	2.177136	-2.633286	4.342248	H	3.358497	5.33672	2.541961
H	0.484401	-2.438186	4.230331	H	0.561413	4.178816	2.015493
C	1.41888	-1.024468	5.539015	H	2.472095	1.240078	-0.498437
H	0.810946	-0.107594	5.436046	H	3.509142	-0.166291	-0.335685
H	0.964427	-1.571159	6.387658	H	1.483734	-0.897932	-1.265281
C	2.823008	-0.603401	5.994122	C	-1.847115	0.414227	1.463488
H	3.307745	-0.026552	5.191475	H	-2.424447	-0.280351	0.813104
H	3.436925	-1.507685	6.126643	C	-2.243207	1.815442	0.960448
C	2.846634	0.212568	7.291361	C	-2.851765	1.97103	-0.291438
H	3.868118	0.484159	7.585252	C	-3.196487	3.23221	-0.783924
H	2.27291	1.142805	7.188019	C	-2.949212	4.372783	-0.020459
H	2.401402	-0.353361	8.119136	C	-2.347873	4.237837	1.233688
O	4.050523	-2.489927	2.124674	C	-1.993128	2.974925	1.710199
C	4.689185	-3.363228	3.085548	H	-1.523365	2.891407	2.687721
C	6.076735	-3.664824	2.515858	H	-2.161347	5.118435	1.844614
C	5.821106	-3.605985	1.002463	H	-3.223187	5.355881	-0.394662
C	4.825367	-2.45008	0.897655	H	-3.661903	3.321662	-1.76275
H	4.129972	-2.541268	0.058824	H	-3.058612	1.085008	-0.888728
H	5.330472	-1.481932	0.835591	H	-0.02117	0.971053	-0.539951
H	5.369852	-4.542646	0.652654	H	-0.713915	-0.63585	-0.573497
H	6.727325	-3.42454	0.417251	C	-2.35571	0.22864	2.906664
H	6.467084	-4.628665	2.85672	H	-1.766046	0.876632	3.565863
H	6.784936	-2.881263	2.806588	H	-3.407099	0.560437	2.983583
H	4.711418	-2.8547	4.052792	N	-2.217582	-1.148097	3.434869
H	4.08446	-4.274046	3.187307	C	-2.398396	-1.119089	4.903624
N	1.886343	2.936338	3.049402	H	-1.624202	-0.468587	5.323383
C	3.292334	2.455913	3.050044	H	-3.378677	-0.665185	5.151534
C	3.662726	1.709744	1.748833	C	-2.312873	-2.508375	5.539931
H	3.590761	2.448161	0.922998	H	-2.488317	-2.412756	6.618921
C	5.145281	1.299437	1.767416	H	-1.295579	-2.899051	5.413652
C	5.945846	1.512322	0.635847	C	-3.322441	-3.471687	4.906029
C	7.278887	1.093732	0.594774	C	-3.150313	-3.466505	3.383316
H	-3.924821	-4.076807	2.900652	C	-3.22386	-2.042323	2.825109
H	-2.177529	-3.897968	3.11798	H	-3.063893	-2.056246	1.743568
H	-4.344388	-3.152425	5.158501	H	-4.239909	-1.633099	2.995343
H	-3.198777	-4.484736	5.308841				

Table A3.2 (Continued).





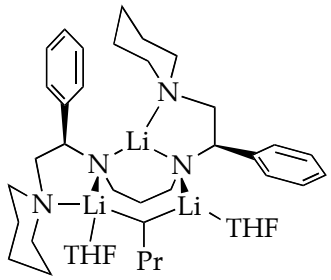
6i
G = -1993.872578
G_{MP2} = -1987.981698

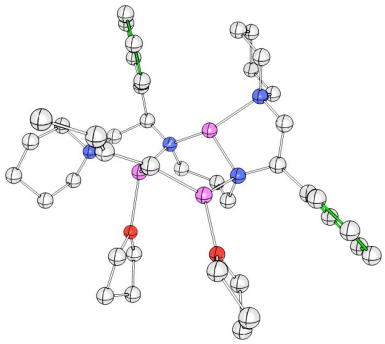
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	N	-0.005638	1.649929	-1.151581
Li	-2.799383	-0.565873	-0.061995	C	0.835471	2.818594	-0.952844
N	-3.138037	0.988883	-1.320093	C	0.408268	3.569016	0.327284
C	-4.573143	1.209264	-1.284899	N	-1.021979	3.972061	0.297547
C	-5.100684	1.065304	0.158602	C	-1.30647	5.070807	-0.660324
N	-4.839354	-0.27033	0.742411	H	-0.909261	4.791445	-1.639873
C	-4.874783	-0.264356	2.221892	C	-0.76888	6.444673	-0.224909
H	-4.443254	-1.216431	2.560787	C	-1.285514	6.815704	1.173937
H	-4.20577	0.526091	2.575947	C	-0.999707	5.684293	2.173312
C	-6.281179	-0.108717	2.823797	C	-1.530455	4.343577	1.637965
C	-7.214173	-1.20802	2.295513	H	-1.298086	3.526814	2.33028
C	-7.190807	-1.23646	0.760198	H	-2.626547	4.402248	1.564556
C	-5.746982	-1.321619	0.2307	H	-1.467291	5.895769	3.143677
H	-5.740673	-1.281478	-0.862216	H	0.08064	5.610741	2.355651
H	-5.313591	-2.289009	0.519184	H	-2.372008	6.98352	1.123106
H	-7.762556	-2.092471	0.378226	H	-0.839197	7.757663	1.516142
H	-7.681202	-0.336228	0.366871	H	-1.075607	7.196856	-0.962943
H	-8.237261	-1.06394	2.664871	H	0.328998	6.438529	-0.225932
H	-6.875065	-2.181599	2.680625	H	-2.396347	5.128647	-0.770171
H	-6.688112	0.879558	2.569872	H	1.081548	4.42243	0.498463
H	-6.213366	-0.149544	3.918671	H	0.515994	2.900434	1.188369
H	-6.167549	1.335619	0.187454	H	0.704174	3.526139	-1.798442
H	-4.57529	1.787634	0.794459	C	2.345871	2.527184	-0.935252
H	-5.095997	0.444692	-1.904289	C	3.099297	2.699976	-2.106051
C	-5.045358	2.55455	-1.867201	C	4.459425	2.382642	-2.153583
C	-5.648747	2.608486	-3.130027	C	5.105399	1.899025	-1.015362
C	-6.059731	3.820029	-3.691812	C	4.374543	1.732589	0.164824
C	-5.886029	5.011952	-2.988927	C	3.012248	2.035043	0.199231
C	-5.292072	4.978278	-1.724479	H	2.466577	1.887789	1.127805
C	-4.871766	3.764901	-1.178252	H	4.869922	1.375591	1.065316
H	-4.408968	3.761257	-0.193738	H	6.166401	1.663791	-1.042304
H	-5.16258	5.899253	-1.160049	H	5.015259	2.523914	-3.077681
H	-6.210887	5.956496	-3.417736	H	2.607942	3.093581	-2.993527
H	-6.518636	3.830478	-4.677742	C	-0.102343	1.290252	-2.558896

Table A3.2 (Continued).

H	-5.798099	1.681771	-3.681005	H	0.834317	0.852957	-2.969438
Li	-1.781474	2.146614	-0.52269	H	-0.281641	2.189042	-3.192452
O	1.490406	-1.327975	-0.372731	C	-2.682825	0.823075	-2.700027
C	2.125526	-2.175058	0.608755	C	-1.240848	0.296166	-2.850417
C	3.594046	-2.242385	0.193975	H	-1.12114	-0.602869	-2.223996
C	3.488146	-2.208589	-1.338241	H	-1.120638	-0.041281	-3.891176
C	2.317658	-1.244952	-1.56518	H	-2.752848	1.756477	-3.299204
H	1.700752	-1.509303	-2.429467	H	-3.346378	0.108766	-3.239025
H	2.651042	-0.210286	-1.67189	O	-2.745251	-2.47518	-0.924918
H	3.254362	-3.207398	-1.726372	C	-1.786442	-3.469351	-0.492436
H	4.403506	-1.86079	-1.825455	C	-1.514956	-4.337873	-1.720976
H	4.09795	-3.13527	0.576788	C	-2.874122	-4.308338	-2.435491
H	4.12945	-1.357518	0.555115	C	-3.333706	-2.868758	-2.185461
H	1.957601	-1.734705	1.594135	H	-4.420139	-2.76933	-2.10774
H	1.656533	-3.169214	0.587377	H	-2.97518	-2.186577	-2.964416
C	-1.258105	-0.78844	1.608083	H	-3.564896	-5.020641	-1.968523
H	-0.514697	-1.598975	1.760871	H	-2.812268	-4.545744	-3.501812
H	-2.205123	-1.364678	1.668419	H	-1.185031	-5.347221	-1.456158
C	-1.20785	0.084399	2.889	H	-0.742962	-3.879206	-2.350372
H	-1.807357	1.003267	2.75929	H	-0.91064	-2.94062	-0.113154
H	-1.645193	-0.414765	3.774781	H	-2.228401	-4.056344	0.323855
C	0.21376	0.506688	3.28644	C	0.281025	1.394508	4.534157
H	0.815834	-0.399071	3.457513	H	-0.159401	0.886289	5.401031
H	0.690978	1.028334	2.442107	H	1.313656	1.659754	4.792808
H	-0.27482	2.329798	4.38816				

Note: The following conformers have N-Li-N cyclohexane ring of the ligand backbone in the boat conformation and the left phenyl substituent pointing in the equatorial direction.



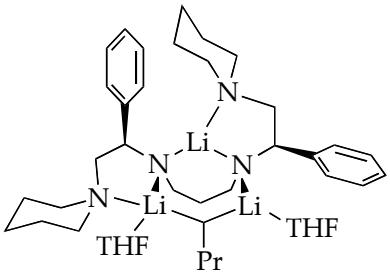


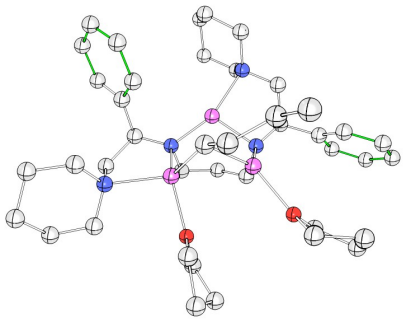
6n
G = -1993.865106
G_{MP2} = -1987.980069

Atom	X	Y	Z	Atom	X	Y	Z
N	0	0	0	C	8.097261	-0.212593	1.772129
Li	0.054135	-1.746607	1.12197	C	7.131335	-0.163598	2.783334
N	-2.380347	-1.961589	0.324429	C	5.836368	0.269289	2.498753
C	-3.465752	-1.852397	1.324648	H	5.096413	0.28712	3.295512
H	-3.300434	-0.95387	1.92035	H	7.393109	-0.454073	3.798719
H	-4.435859	-1.7222	0.803042	H	9.106437	-0.551164	1.99282
C	-3.54856	-3.080616	2.235003	H	8.494818	0.162237	-0.313639
H	-4.384198	-2.946783	2.933798	H	6.208266	0.979455	-0.793956
H	-2.635422	-3.144657	2.838018	C	3.018595	-0.609878	-0.453114
C	-3.723081	-4.367396	1.420135	C	2.058627	0.015769	-1.496891
C	-2.636196	-4.447151	0.341973	C	0.556329	-0.296326	-1.320335
C	-2.601211	-3.168897	-0.497174	H	0.417446	-1.359483	-1.625021
H	-1.796309	-3.224985	-1.236821	H	0.028346	0.278905	-2.109521
H	-3.551967	-3.081021	-1.061292	H	2.34488	-0.327854	-2.504663
H	-2.805277	-5.307049	-0.319829	H	2.206418	1.106855	-1.494037
H	-1.65455	-4.583266	0.812	H	2.693585	-1.658579	-0.309884
H	-4.71186	-4.365355	0.938016	H	4.023169	-0.687985	-0.91139
H	-3.691159	-5.249656	2.071941	C	0.995098	-1.755668	3.227541
C	-2.346369	-0.768927	-0.551854	H	1.859128	-2.385557	3.54213
H	-3.369346	-0.384512	-0.716181	H	1.247561	-0.748292	3.634982
H	-1.979017	-1.095179	-1.530597	C	-0.178245	-2.280099	4.077205
C	-1.393202	0.391916	-0.109466	H	-1.084556	-1.683164	3.886249
H	-1.528091	1.122673	-0.939272	H	-0.43862	-3.306021	3.76084
C	-1.915775	1.103309	1.136914	C	0.039872	-2.311824	5.604148
C	-2.97527	2.017583	1.020231	H	0.929142	-2.922332	5.823012
C	-3.512107	2.657302	2.138075	H	0.282122	-1.294893	5.946831
C	-2.998604	2.395303	3.410717	C	-1.158577	-2.848627	6.396303
C	-1.938958	1.497401	3.544573	H	-1.402469	-3.876941	6.098696
C	-1.399816	0.86478	2.419132	H	-0.965907	-2.854001	7.476354
H	-0.583353	0.159973	2.546712	H	-2.053634	-2.237708	6.222316
H	-1.526095	1.282779	4.527418	O	4.139379	-2.833039	2.251542

Table A3.2 (Continued).

H	-3.416332	2.888779	4.284506	C	4.576569	-3.376375	3.521015
H	-4.330766	3.362454	2.014902	C	5.979801	-3.944241	3.278797
H	-3.385217	2.230211	0.034608	C	5.948059	-4.278512	1.779474
Li	1.309931	0.946353	1.067955	C	5.119842	-3.121831	1.224203
N	3.062308	0.072235	0.844741	H	4.574873	-3.360828	0.306769
Li	2.695663	-1.415411	2.031254	H	5.730856	-2.230489	1.052579
C	4.044372	1.145372	0.873338	H	5.442665	-5.236749	1.607186
C	3.604717	2.229599	1.880319	H	6.943633	-4.330707	1.329063
N	2.283009	2.828401	1.580986	H	6.192266	-4.808989	3.914522
C	2.351672	3.6982	0.385832	H	6.738485	-3.178848	3.473469
H	2.687825	3.09759	-0.462796	H	4.55741	-2.578114	4.26902
H	3.109784	4.490377	0.545365	H	3.863546	-4.15279	3.823919
C	0.999978	4.340701	0.065515	O	0.834967	-3.649335	0.356401
H	0.276247	3.552153	-0.180593	C	1.24682	-4.62951	1.344463
H	1.109321	4.969979	-0.826906	C	1.463536	-5.933105	0.572308
C	0.48859	5.159848	1.255617	C	1.917962	-5.417197	-0.800812
C	0.469907	4.283336	2.512962	C	1.039291	-4.17727	-0.971993
C	1.828458	3.618512	2.747471	H	0.06599	-4.440993	-1.405712
H	1.774736	2.943589	3.609644	H	1.493678	-3.395089	-1.585208
H	2.581948	4.393556	2.989829	H	1.781164	-6.142153	-1.609054
H	0.210952	4.87683	3.399034	H	2.977658	-5.135457	-0.772769
H	-0.298748	3.509755	2.410803	H	0.523589	-6.489712	0.476695
H	1.152035	6.022875	1.415153	H	2.195673	-6.5868	1.056791
H	-0.511704	5.560199	1.051452	H	2.168956	-4.274305	1.814032
H	4.375329	3.018523	1.954898	H	0.467587	-4.693379	2.107878
H	3.519114	1.767209	2.870871	C	6.459144	0.644164	0.21044
H	4.129207	1.635072	-0.115496	C	7.753765	0.189621	0.481891
C	5.474674	0.68743	1.207294				





6o
G = -1993.860232
G_{MP2} = -1987.975152

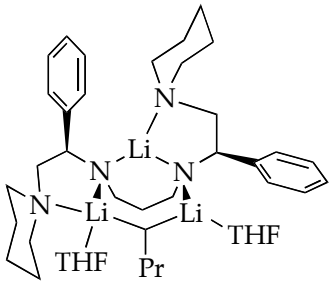
Atom	X	Y	Z	Atom	X	Y	Z
C	0	0	0	C	-0.900452	0.868686	-4.529557
Li	-1.025775	-0.389248	-2.061512	H	-0.929521	-0.237484	-4.683299

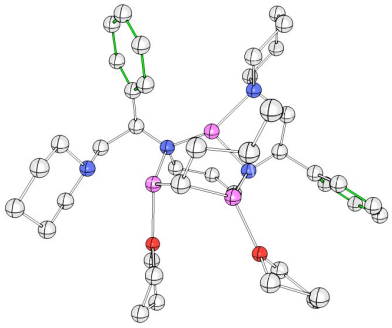
Table A3.2 (Continued).

N	-1.370142	1.280098	-3.20324	H	-1.574119	1.263335	-5.317688
Li	0.003262	2.313998	-2.287906	H	0.707365	0.934511	-5.939393
N	1.8026	1.602643	-2.737657	H	0.544651	2.417575	-5.00315
Li	1.671334	0.166604	-1.398677	H	1.504703	-0.209178	-3.776518
O	3.16798	-1.263799	-1.483748	H	2.612109	0.880236	-4.583879
C	3.632489	-2.167534	-0.469703	C	-2.813084	1.450599	-3.228711
C	5.14988	-2.007427	-0.488289	C	-3.612769	0.102116	-3.35583
C	5.44034	-1.862081	-1.99572	N	-3.247062	-0.943734	-2.368286
C	4.129876	-1.276089	-2.569776	C	-4.025507	-0.886179	-1.104623
H	3.733208	-1.889358	-3.388561	H	-3.515792	-1.542907	-0.384621
H	4.230234	-0.24762	-2.912773	H	-3.968675	0.126298	-0.705841
H	5.656801	-2.838765	-2.442319	C	-5.493767	-1.329616	-1.233779
H	6.291742	-1.206174	-2.192395	C	-5.601504	-2.728508	-1.85666
H	5.672322	-2.852138	-0.028607	C	-4.801518	-2.788623	-3.165755
H	5.430528	-1.094783	0.04816	C	-3.359372	-2.304802	-2.937506
H	3.154822	-1.885906	0.469639	H	-2.79122	-2.330588	-3.872494
H	3.339422	-3.199282	-0.722671	H	-2.863291	-2.994691	-2.24056
C	2.648576	2.777476	-2.885738	H	-4.782279	-3.811782	-3.564513
C	2.267536	3.840127	-1.835482	H	-5.28529	-2.162885	-3.928218
N	0.862963	4.304658	-1.917964	H	-6.650814	-3.000414	-2.027026
C	0.643222	5.117968	-3.135049	H	-5.195161	-3.471108	-1.152976
H	0.859861	4.499267	-4.009339	H	-6.048687	-0.607853	-1.847499
H	1.356433	5.966037	-3.150818	H	-5.958198	-1.309626	-0.239398
C	-0.789169	5.650308	-3.220159	H	-4.693632	0.311475	-3.362338
C	-1.135468	6.492139	-1.987432	H	-3.371744	-0.304023	-4.344252
C	-0.857801	5.679844	-0.717765	H	-3.118301	1.97799	-4.158902
C	0.563932	5.115237	-0.715806	C	-3.374912	2.312367	-2.099084
H	0.716986	4.479267	0.163764	C	-4.518528	3.090887	-2.341326
H	1.289386	5.949344	-0.641545	C	-5.111089	3.853345	-1.333684
H	-1.575096	4.855437	-0.648515	C	-4.571863	3.85269	-0.045645
H	-0.991249	6.298466	0.179163	C	-3.431125	3.090935	0.212127
H	-2.18414	6.811295	-2.016772	C	-2.83629	2.338527	-0.805469
H	-0.522456	7.40596	-1.985202	H	-1.956612	1.747423	-0.576732
H	-1.48268	4.802738	-3.297544	H	-2.996078	3.079153	1.208826
H	-0.893119	6.239676	-4.140112	H	-5.031944	4.440775	0.744284
H	2.956675	4.701961	-1.901308	H	-5.993351	4.449031	-1.555905
H	2.393246	3.401001	-0.838874	H	-4.949672	3.09955	-3.340688
H	2.517262	3.243647	-3.88149	O	-0.172866	-2.238364	-2.599781
C	4.159472	2.500363	-2.785324	C	0.023723	-3.137042	-1.478046
C	4.980157	2.598122	-3.916877	C	0.505094	-4.468252	-2.072759
C	6.34934	2.31967	-3.851507	C	1.11264	-4.037438	-3.416583
C	6.931247	1.955479	-2.637812	C	0.173573	-2.905782	-3.828057
C	6.128749	1.861789	-1.495043	H	-0.735753	-3.29941	-4.304468
C	4.760467	2.119606	-1.573709	H	0.624881	-2.166984	-4.493787
H	4.149071	2.025649	-0.679236	H	1.150896	-4.844081	-4.155076
H	6.574218	1.594246	-0.539198	H	2.127786	-3.65094	-3.273359

Table A3.2 (Continued).

H	7.997832	1.75376	-2.577544	H	-0.339922	-5.146353	-2.240391
H	6.960306	2.39786	-4.74781	H	1.21779	-4.979349	-1.418206
H	4.539268	2.903621	-4.863772	H	0.756541	-2.673622	-0.814802
C	1.674264	0.86249	-3.995017	H	-0.921767	-3.232824	-0.93378
C	0.521806	1.319715	-4.92302	H	-0.27038	1.058071	0.198127
H	1.548763	1.405003	1.829873	H	-0.994251	-0.501709	-0.025003
H	2.633415	0.349243	0.944341	C	0.66035	-0.490673	1.314112
C	2.51394	-0.087874	3.058244	H	-0.034	-0.498233	2.175891
H	2.878551	-1.12213	2.997802	H	0.991638	-1.540441	1.216733
H	3.364453	0.548031	3.333276	C	1.870328	0.356872	1.739441
H	1.789119	-0.048216	3.88067				





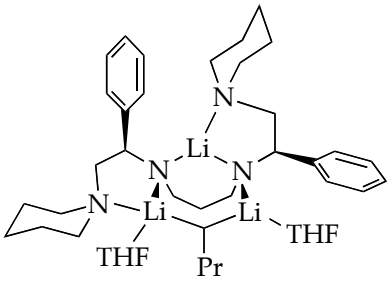
6p
G = -1993.863061
G_{MP2} = -1987.976685

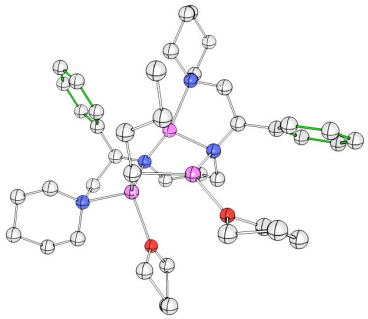
Atom	X	Y	Z	Atom	X	Y	Z
C	0	0	0	H	-0.753852	1.530119	-5.583546
Li	-0.933278	0.012601	-2.130049	H	1.37098	0.443107	-5.968123
N	-0.71169	1.559154	-3.46005	H	1.571689	1.983865	-5.142993
Li	0.814394	2.257547	-2.497904	H	1.584979	-0.659163	-3.617864
N	2.382964	1.07468	-2.732795	H	3.031828	-0.076688	-4.420036
Li	1.788322	-0.07052	-1.259549	C	-2.014611	2.18928	-3.582599
O	2.879434	-1.76409	-0.935772	C	-3.203305	1.170042	-3.65463
C	3.090148	-2.510895	0.272069	N	-3.333789	0.223186	-2.520568
C	4.601868	-2.716764	0.324378	C	-4.162604	0.801798	-1.437232
C	4.953386	-2.956227	-1.159599	H	-3.700101	1.728391	-1.099995
C	3.811894	-2.253086	-1.93098	H	-5.161111	1.066079	-1.839953
H	3.284701	-2.94787	-2.598055	C	-4.335694	-0.159847	-0.258777
H	4.140986	-1.386667	-2.503713	H	-4.959725	0.323618	0.503427
H	4.970945	-4.027646	-1.386134	H	-3.356582	-0.347952	0.201348
H	5.929047	-2.540827	-1.423125	C	-4.960374	-1.48307	-0.713834
H	4.89433	-3.547089	0.974495	C	-4.154522	-2.056302	-1.885016
H	5.084954	-1.805478	0.692759	C	-3.976533	-1.020394	-2.997352
H	2.676373	-1.928453	1.096689	H	-3.358373	-1.434724	-3.799935
H	2.55696	-3.473427	0.215643	H	-4.966967	-0.790209	-3.438649

Table A3.2 (Continued).

C	3.473151	2.010644	-2.960382	H	-4.646981	-2.945197	-2.301103
C	3.362566	3.205675	-1.987881	H	-3.164636	-2.368511	-1.531879
N	2.077076	3.93435	-2.114988	H	-5.996518	-1.305395	-1.037278
C	1.996044	4.801646	-3.31617	H	-5.006199	-2.201167	0.114526
H	2.267806	4.208408	-4.194167	H	-4.159678	1.699126	-3.823095
C	2.852171	6.078129	-3.237579	H	-3.017707	0.567646	-4.550784
C	2.519258	6.884294	-1.973354	H	-2.100965	2.702983	-4.564651
C	2.611343	5.991075	-0.7274	C	-2.253973	3.287765	-2.549287
C	1.751193	4.728615	-0.908869	C	-3.060679	4.38783	-2.879171
H	1.835025	4.070627	-0.036726	C	-3.320698	5.403172	-1.957239
H	0.696777	5.021931	-0.988923	C	-2.778595	5.339034	-0.671957
H	2.271766	6.533616	0.164467	C	-1.971939	4.253063	-0.32691
H	3.657726	5.710391	-0.54515	C	-1.708689	3.244426	-1.258406
H	1.495625	7.278794	-2.056852	H	-1.095251	2.396955	-0.966849
H	3.184288	7.752092	-1.880808	H	-1.547602	4.182672	0.671813
H	2.678219	6.679615	-4.139155	H	-2.981794	6.125214	0.050652
H	3.918605	5.815868	-3.239717	H	-3.945173	6.245876	-2.24441
H	0.94054	5.081577	-3.436703	H	-3.487592	4.450414	-3.878377
H	4.234842	3.865636	-2.111474	O	-0.633287	-2.049058	-2.658782
H	3.397875	2.821263	-0.962223	C	-0.382694	-3.004972	-1.598883
H	3.431533	2.432456	-3.985031	C	-0.655675	-4.375262	-2.214469
C	4.877255	1.39169	-2.852931	C	-0.174185	-4.165856	-3.657418
C	5.656105	1.189429	-4.000375	C	-0.611862	-2.72493	-3.939405
C	6.919793	0.59452	-3.929383	H	-1.620632	-2.687272	-4.368276
C	7.440981	0.205813	-2.696056	H	0.068037	-2.1886	-4.605497
C	6.681507	0.407704	-1.538271	H	-0.602907	-4.876862	-4.370048
C	5.41299	0.981879	-1.620494	H	0.917872	-4.251981	-3.710008
H	4.830987	1.117181	-0.711944	H	-1.728869	-4.599443	-2.196256
H	7.083983	0.123338	-0.568212	H	-0.129765	-5.180901	-1.692652
H	8.428986	-0.24335	-2.633025	H	0.658272	-2.903177	-1.276037
H	7.498434	0.444359	-4.837875	H	-1.032823	-2.753329	-0.758017
H	5.267006	1.509557	-4.964993	H	0.236865	-0.999933	0.421571
C	2.102291	0.268247	-3.924811	H	-1.107989	-0.049736	-0.08244
C	1.21807	0.95096	-5.001564	C	0.278487	1.01878	1.13623
C	-0.302111	0.972906	-4.736973	H	0.024924	2.040634	0.810191
H	-0.665862	-0.070432	-4.880053	H	-0.34295	0.847672	2.035971
C	2.012535	2.054293	2.731415	C	1.739768	1.043629	1.611112
H	3.06189	2.0392	3.051	H	2.403265	1.26405	0.758719
H	1.778347	3.076664	2.407545	H	2.019338	0.038628	1.963133
H	1.392625	1.841197	3.611057				

Table A3.2 (Continued).





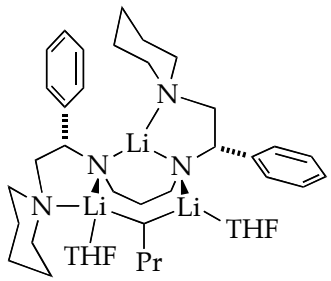
6q
G = -1993.860348
G_{MP2} = -1987.973481

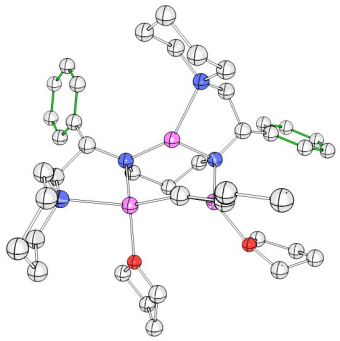
Atom	X	Y	Z	Atom	X	Y	Z
N	0	0	0	C	3.907793	-3.946394	3.592646
Li	-0.0987	-1.518525	1.386405	C	5.424457	-4.088587	3.694741
N	-2.367135	-1.485299	1.171975	C	5.83355	-4.299937	2.221203
C	-3.042881	-1.006228	2.405225	C	4.690479	-3.635006	1.418481
H	-2.698023	-1.648928	3.227775	H	4.215851	-4.342873	0.726751
H	-2.695478	0.002941	2.624651	H	5.003386	-2.750103	0.865171
C	-4.580539	-1.042887	2.350446	H	5.900136	-5.367887	1.987362
C	-5.090537	-2.442619	1.980197	H	6.800559	-3.845488	1.992137
C	-4.396445	-2.939845	0.704162	H	5.731002	-4.911363	4.34801
C	-2.868729	-2.839833	0.850034	H	5.854966	-3.160626	4.086298
H	-2.370582	-3.180917	-0.062424	H	3.441546	-3.391731	4.40874
H	-2.54823	-3.508427	1.661594	H	3.419493	-4.930376	3.507332
H	-4.673693	-3.980838	0.490225	C	0.90396	-1.403637	3.477877
H	-4.726073	-2.342791	-0.157124	H	1.148568	-2.377077	3.954316
H	-6.18087	-2.441661	1.856788	H	-0.207005	-1.447039	3.448253
H	-4.867967	-3.137999	2.803843	C	1.244964	-0.325227	4.53955
H	-4.946148	-0.310411	1.618675	H	0.995455	0.681034	4.164648
H	-4.976611	-0.729557	3.325015	H	0.657978	-0.432632	5.471629
C	-2.474429	-0.557569	0.018757	C	2.725083	-0.303823	4.951999
H	-3.464979	-0.079343	-0.043657	H	3.004697	-1.297655	5.334779
H	-2.369184	-1.169264	-0.884398	H	3.354394	-0.131057	4.063651
C	-1.34707	0.534664	-0.063217	C	3.060861	0.749173	6.014716
H	-1.538477	0.983545	-1.062023	H	2.479403	0.5824	6.929916
C	-1.594373	1.672781	0.925871	H	4.123477	0.732453	6.286925
C	-2.504362	2.690455	0.599541	H	2.825122	1.760461	5.658697
C	-2.776602	3.736455	1.483004	C	4.188906	0.60556	0.324741
C	-2.14361	3.786699	2.726551	C	4.068279	1.822376	1.268734
C	-1.233823	2.784155	3.067537	N	2.760671	2.513262	1.156412
C	-0.958915	1.745304	2.173393	C	2.621643	3.338144	-0.06923
H	-0.264638	0.962753	2.464577	H	2.871229	2.720218	-0.936687
H	-0.737519	2.802151	4.034918	C	3.458274	4.629358	-0.063896
H	-2.355612	4.596636	3.419767	C	3.157335	5.47425	1.183713
H	-3.481766	4.513698	1.197959	C	3.298702	4.62461	2.456106
H	-3.002739	2.664474	-0.367813	C	2.455095	3.343579	2.34335

Table A3.2 (Continued).

O	0.278783	-3.601073	0.890568	H	2.575327	2.718457	3.235162
C	0.374155	-4.553354	1.97416	H	1.393947	3.616583	2.283152
C	0.928328	-5.832114	1.348992	H	2.976131	5.192539	3.338486
C	0.303669	-5.78883	-0.052834	H	4.354085	4.366332	2.617826
C	0.352434	-4.292794	-0.378513	H	2.127316	5.855763	1.120076
H	-0.476056	-3.959058	-1.009747	H	3.815202	6.351413	1.225803
H	1.291556	-4.014204	-0.870204	H	3.243127	5.197438	-0.978219
H	-0.733462	-6.142889	-0.01699	H	4.528034	4.383326	-0.095869
H	0.841269	-6.391606	-0.791025	H	1.557705	3.596448	-0.159596
H	0.661886	-6.728439	1.917574	H	4.918586	2.502159	1.10599
H	2.021641	-5.778773	1.282894	H	4.140034	1.46594	2.302588
H	1.009469	-4.115262	2.742989	H	4.110136	0.998546	-0.709154
H	-0.628485	-4.719061	2.393171	C	5.613918	0.032942	0.415417
Li	1.538865	0.787215	0.862089	C	6.381893	-0.157925	-0.741002
N	3.133134	-0.355598	0.603262	C	7.665486	-0.710033	-0.681517
Li	2.616175	-1.502706	2.107967	C	8.217215	-1.065552	0.548534
O	3.706814	-3.194725	2.387019	C	7.468521	-0.874242	1.715158
C	0.372721	-0.619191	-1.271563	C	6.180641	-0.34344	1.644681
H	0.055095	-1.684426	-1.355167	H	5.606195	-0.217335	2.559401
H	-0.14703	-0.118926	-2.115056	H	7.894099	-1.133272	2.682413
H	2.006388	-1.111122	-2.56938	H	9.220156	-1.481606	0.602094
H	2.178134	0.460896	-1.797032	H	8.235386	-0.853121	-1.596667
H	2.389621	-2.143967	-0.21948	H	5.96791	0.136422	-1.703483
H	3.767392	-1.501908	-1.091814	C	2.843057	-1.196414	-0.562562
C	1.878077	-0.582095	-1.610789				

Table A3.3. Optimized geometries at B3LYP level of theory with 6-31G(d) basis set for the Di-solvated SS diasteriomer of BuLi-ligand aggregation conformer **6a** at –78 °C with free energies (Hartrees) and cartesian coordinates (X, Y, Z) (Note: G_{MP2} includes single point MP2 corrections to B3LYP/6-31G(d) optimized structures).





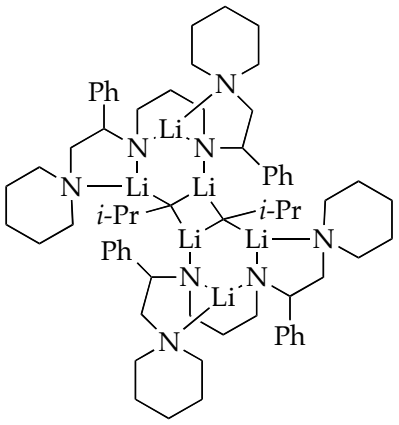
6b
G = -1993.8722
G_{MP2} = -1987.978018

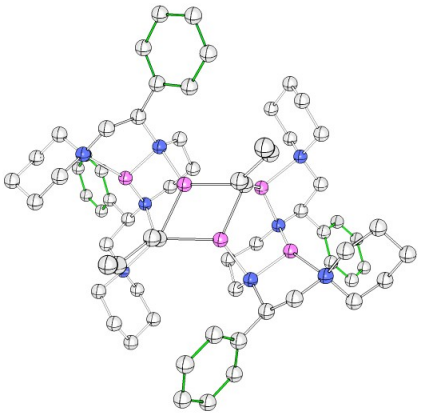
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	H	-1.856845	-5.959411	2.328499
N	0.103857	-1.925219	-0.66142	C	-0.068085	-4.86875	2.872869
Li	-1.347161	-2.259245	0.602692	H	0.56926	-4.084985	2.441426
Li	-2.856294	-0.176578	0.257246	H	0.531561	-5.787358	2.905697
N	-3.117672	-2.026323	-0.285307	C	-0.506063	-4.449041	4.280315
C	-4.004584	-2.888011	0.495453	C	-1.443376	-3.240617	4.184229
H	-4.25879	-2.316989	1.401461	C	-2.602812	-3.516801	3.224303
C	-5.360951	-3.214435	-0.144319	H	-3.230407	-2.625938	3.140415
C	-6.504785	-2.509205	0.261048	H	-3.238154	-4.323316	3.640781
C	-7.755261	-2.74799	-0.312204	H	-1.853412	-2.983449	5.169019
C	-7.890316	-3.708431	-1.317029	H	-0.884624	-2.362995	3.833433
C	-6.766111	-4.423637	-1.731559	H	-1.033174	-5.284661	4.763651
C	-5.519309	-4.180691	-1.150753	H	0.365043	-4.219363	4.906235
H	-4.66033	-4.753776	-1.488326	H	-2.920502	-4.740019	0.126525
H	-6.857915	-5.177256	-2.510181	H	-4.01754	-4.851561	1.51044
H	-8.861175	-3.901822	-1.7661	C	1.498253	-2.315871	-0.40899
H	-8.625419	-2.195252	0.035269	C	2.490194	-1.139913	-0.629475
H	-6.411656	-1.767357	1.053049	N	2.246616	-0.004853	0.295048
C	-2.855495	-2.483083	-1.643994	C	2.736756	-0.324909	1.654189
C	-1.754831	-1.649776	-2.331951	H	2.209555	-1.211528	2.015556
C	-0.297929	-2.065405	-2.054329	H	3.813052	-0.584568	1.607538
H	0.336355	-1.470388	-2.755462	C	2.532338	0.83006	2.638125
H	-0.194114	-3.104504	-2.421352	H	2.939487	0.537815	3.614445
H	-1.900758	-0.588532	-2.070884	H	1.456804	0.995989	2.77508
H	-1.902398	-1.718016	-3.420262	C	3.199675	2.114633	2.134385
H	-2.535348	-3.547111	-1.705601	C	2.733947	2.411238	0.704044
H	-3.760093	-2.435517	-2.285973	C	2.942001	1.198011	-0.205377
C	-1.340317	0.239301	1.776817	H	2.563499	1.411364	-1.210213
H	-0.8231	-0.597758	2.296015	H	4.027361	0.997337	-0.303243
H	-0.583274	1.051447	1.794051	H	3.274917	3.270021	0.285874

Table A3.3 (Continued).

C	-2.467076	0.707045	2.724533	H	1.667473	2.670725	0.710716
H	-2.930183	1.625396	2.323147	H	4.292429	1.988959	2.141995
H	-3.285365	-0.038671	2.754928	H	2.973523	2.957298	2.79946
C	-2.070642	1.001953	4.185847	H	3.540155	-1.477507	-0.54125
H	-1.276856	1.763132	4.18579	H	2.360234	-0.755797	-1.647931
H	-1.621221	0.097244	4.619458	H	1.562656	-2.570114	0.659835
C	-3.234661	1.471386	5.0668	C	2.004907	-3.571666	-1.13485
H	-2.913846	1.668591	6.096983	C	1.953884	-4.814173	-0.487411
H	-3.6794	2.396625	4.677008	C	2.390977	-5.984014	-1.11076
H	-4.031228	0.716892	5.107302	C	2.897574	-5.936172	-2.410358
O	-4.252447	1.116714	-0.440972	C	2.959124	-4.709259	-3.072192
C	-5.045704	2.137084	0.187621	C	2.518187	-3.54464	-2.441047
C	-6.484411	1.655668	0.023211	H	2.570901	-2.6031	-2.980934
C	-6.462371	1.045388	-1.391553	H	3.350653	-4.656416	-4.085456
C	-5.002994	0.57431	-1.566402	H	3.242004	-6.843188	-2.900625
H	-4.558134	0.946407	-2.49717	H	2.34378	-6.930997	-0.577948
H	-4.881938	-0.508192	-1.514531	H	1.57207	-4.861259	0.529141
H	-6.718587	1.803588	-2.139742	O	-0.312998	1.621775	-1.247604
H	-7.166517	0.216121	-1.497776	C	-1.049638	2.788869	-0.800319
H	-7.216386	2.46173	0.133258	C	-1.122715	3.730533	-2.007474
H	-6.704385	0.886833	0.772014	C	-1.043162	2.754241	-3.190823
H	-4.712173	2.222996	1.223603	C	-0.055841	1.713367	-2.665576
H	-4.885515	3.100936	-0.320368	H	0.982674	2.036967	-2.824698
N	-2.142648	-3.899117	1.871182	H	-0.185006	0.718015	-3.095736
C	-3.304168	-4.186154	0.989921	H	-0.705049	3.222626	-4.120105
C	-1.274919	-5.093091	1.957255	H	-2.019766	2.291299	-3.375033
H	-0.938924	-5.337819	0.94393	H	-0.264628	4.413144	-2.020187
H	-2.040081	2.456717	-0.476072	H	-2.033996	4.336364	-2.004738
H	-0.525629	3.223874	0.055976				

Table A3.4. Optimized geometries at B3LYP level of theory with 6-31G(d) basis set for the BuLi-ligand dimer aggregate and its disolvated monomer generated from crystal structure coordinates at –78 °C with free energies (Hartrees) and cartesian coordinates (X, Y, Z) (Note: G_{MP2} includes single point MP2 corrections to B3LYP/6-31G(d) optimized structures).





5
G = -3058.357797
G_{MP2} = Not Calculated

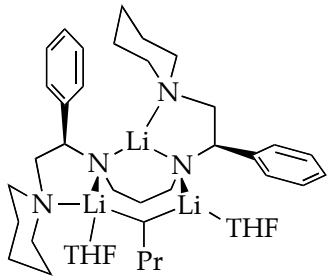
Atom	X	Y	Z	Atom	X	Y	Z
N	0	0	0	C	-1.586064	-5.135396	1.763684
C	-3.658539	-2.237395	0.041201	H	-1.165567	-4.521902	0.959439
C	-2.807642	-0.265651	4.09774	H	-0.761429	-5.751756	2.170109
H	-3.465288	-0.763437	4.84294	C	-2.695106	-5.009073	3.916357
H	-2.102604	0.332185	4.708581	H	-1.90906	-5.61941	4.401493
C	1.298887	0.493232	0.518581	H	-3.073809	-4.315554	4.672643
H	1.843921	1.013312	-0.292526	C	-6.659529	5.075963	2.468038
H	1.101315	1.237443	1.29646	H	-5.834478	5.693343	2.094398
C	-6.163354	0.561178	0.050895	H	-7.39297	5.759893	2.920158
C	-1.384003	-2.170909	4.144999	C	2.41349	-1.72066	0.021788
H	-2.031463	-2.524637	4.976627	H	3.031947	-1.313162	-0.791215
C	-8.208965	-3.679186	0.232843	H	2.970452	-2.561308	0.452735
H	-8.964093	-4.154469	0.898154	C	-2.946362	1.732806	2.408301
C	-8.56903	0.297822	4.104787	H	-2.098365	2.156797	2.991587
H	-7.934612	0.628413	4.955719	H	-3.614524	2.601437	2.229432
C	-9.817034	-0.310209	4.784812	C	-7.71805	-6.168429	-0.004643
C	-11.122267	-2.410286	0.298895	H	-8.373881	-6.332342	0.848531
H	-11.611241	-2.902606	-0.56358	C	-12.086376	-1.393294	0.915687
H	-10.889543	-3.19746	1.022877	H	-11.658026	-0.995402	1.843872
C	-7.13085	-1.593927	4.000389	H	-13.012261	-1.911771	1.194159
H	-6.51885	-1.125497	4.801006	C	-3.775681	4.524614	-1.303035
H	-7.841835	-2.246834	4.544736	H	-4.788375	4.577801	-1.696212
C	0.242295	-1.010831	-1.054849	C	-12.117544	-1.357982	6.045935
H	-0.729785	-1.357585	-1.417654	H	-13.001042	-1.762999	6.532538
H	0.761287	-0.54116	-1.912296	C	-1.522218	1.963592	0.497358
C	-0.951398	-3.415484	3.339786	H	-0.752495	2.318242	1.220254
H	-0.284237	-4.057565	3.938586	C	-6.158168	4.089802	3.527913

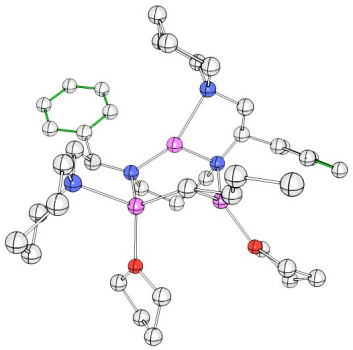
Table A3.4 (Continued).

H	-0.369213	-3.067135	2.476979	H	-5.322488	3.506676	3.121266
C	-8.976137	-2.813142	-0.784401	H	-5.774087	4.621068	4.407579
H	-9.568954	-3.442049	-1.469891	C	-6.055065	-5.764158	-2.193958
H	-8.244287	-2.271527	-1.394145	H	-5.415246	-5.597316	-3.057058
C	2.172675	-0.633859	1.075473	C	-7.317749	4.305094	1.318831
H	1.689595	-1.070418	1.958455	H	-7.777096	4.992967	0.597847
H	3.122823	-0.20565	1.418101	H	-6.555361	3.735068	0.773931
C	-10.138703	-0.716388	-1.122749	C	-12.377447	-0.243035	-0.054933
H	-9.184105	-0.277256	-1.43064	H	-12.946472	-0.6229	-0.915963
H	-10.605124	-1.147442	-2.029222	H	-13.00081	0.520595	0.4254
C	-7.52622	-4.862361	-0.472389	C	-11.568383	-1.99763	4.935017
C	-0.13502	-1.604417	4.859384	H	-12.019323	-2.911485	4.555012
C	0.408083	-2.280903	5.962007	C	-2.677707	-6.052109	1.208214
H	-0.075488	-3.188937	6.319739	H	-2.231669	-6.712167	0.453868
C	-6.67736	-4.679876	-1.574205	H	-3.434051	-5.447627	0.692959
H	-6.498168	-3.677589	-1.95583	C	-3.688601	-2.139412	-1.503264
C	-7.272801	3.143096	3.978107	H	-3.259296	-1.177345	-1.832907
H	-8.060508	3.725191	4.493978	H	-4.728525	-2.112521	-1.866229
H	-6.883647	2.420436	4.701144	C	1.626188	0.061797	5.097991
C	-2.038642	3.258446	-0.162301	H	2.085108	0.989637	4.764134
C	-10.430049	-1.475512	4.314127	C	-6.042529	0.564995	-1.492098
H	-9.991028	-1.991707	3.464706	H	-6.393613	-0.398039	-1.900762
C	-9.010304	1.564816	3.341804	H	-4.984487	0.622307	-1.796401
H	-9.683436	2.180554	3.961312	C	-3.820802	-5.926276	3.434162
H	-9.588328	1.241367	2.466484	H	-4.6546	-5.318292	3.062662
C	-6.861939	-3.491498	2.211613	H	-4.200377	-6.494207	4.292813
H	-7.693535	-4.00167	2.749343	C	-3.018979	-3.113802	-3.789971
H	-6.142637	-4.306394	1.985243	H	-4.054984	-3.102659	-4.152534
C	-3.679533	0.739164	3.326771	H	-2.551446	-2.174251	-4.111445
H	-4.243641	1.312771	4.077384	H	-2.498574	-3.934007	-4.299036
H	-4.433974	0.182451	2.741658	C	-6.79561	1.688383	-2.230476
C	-6.198465	-2.5247	3.20818	H	-6.439586	2.658328	-1.85516
H	-5.639088	-3.119521	3.945694	H	-7.862146	1.638039	-1.96486
H	-5.447145	-1.908434	2.681998	C	-1.197711	4.373942	-0.278226
C	1.072467	-2.192695	-0.551548	H	-0.189792	4.324533	0.132086
H	0.507125	-2.726826	0.22476	C	-7.087648	-7.258835	-0.610028
H	1.224188	-2.899008	-1.377247	H	-7.252701	-8.261913	-0.223641
C	0.488433	-0.423016	4.446523	C	-2.923603	5.623947	-1.420402
H	0.056611	0.133653	3.619373	H	-3.266373	6.535381	-1.903648
C	-8.394616	3.349805	1.836697	C	-2.967542	-3.267875	-2.265315
H	-8.810084	2.765705	1.008101	H	-3.415614	-4.227394	-1.97385
H	-9.225568	3.937805	2.270991	H	-1.919132	-3.310976	-1.935092
C	-11.058377	0.362404	-0.5483	C	-6.255424	-7.06062	-1.711646
H	-10.548729	0.865324	0.285574	H	-5.768726	-7.905381	-2.192347
H	-11.237969	1.12393	-1.317386	C	2.164359	-0.632713	6.181134
C	-10.371505	0.310451	5.914279	H	3.047425	-0.25672	6.691284

Table A3.4 (Continued).

H	-9.896701	1.204217	6.316849	C	-3.339592	-6.866791	2.324693
C	-3.334794	3.355267	-0.678333	H	-2.613369	-7.58208	2.738565
H	-4.002798	2.506642	-0.568841	H	-4.176041	-7.453103	1.926838
C	-0.787537	1.126615	-0.572016	C	1.547332	-1.809403	6.613463
H	-0.135903	1.763461	-1.193097	H	1.94947	-2.355019	7.463799
H	-1.547798	0.697242	-1.235251	C	-11.511155	-0.198676	6.536197
Li	-1.403891	-0.426242	1.634479	H	-11.922025	0.304274	7.408351
N	-9.850066	-1.791471	-0.14562	C	-6.641106	1.637224	-3.754641
N	-2.087341	-4.218943	2.816723	H	-5.587379	1.723718	-4.047777
N	-7.880517	2.395418	2.848993	H	-7.018564	0.689728	-4.160336
N	-7.331186	-2.819257	1.008461	H	-7.1897	2.449891	-4.24557
N	-2.116926	-1.265647	3.278238	C	-1.629076	5.5448	-0.902318
N	-7.814344	-0.563751	3.212859	H	-0.958009	6.397167	-0.978769
N	-2.489781	1.120382	1.167398	Li	-3.957917	-0.033617	0.48588
H	-5.885512	1.585499	0.375901	Li	-3.204002	-2.485144	2.154007
H	-7.261622	0.527611	0.241971	Li	-8.500687	-1.366774	1.536614
H	-2.573732	-2.295142	0.291257	Li	-6.724607	0.705996	2.147816
H	-4.024452	-3.258227	0.279244	Li	-5.84502	-1.647022	0.415249





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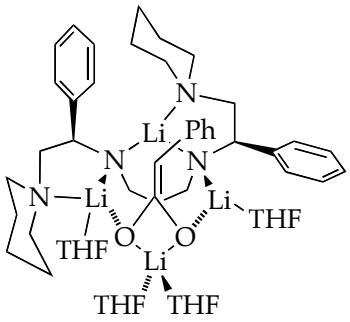
G = -1993.885961
G_{MP2} = -1987.996765

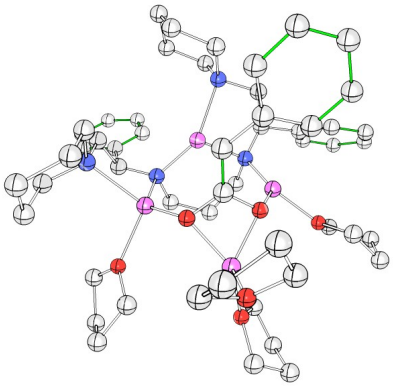
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	H	-4.275419	-0.004013	-2.45154
N	0.430403	-1.670575	-1.056149	H	-5.247792	-1.189546	-1.54744
Li	-0.819257	-2.509685	0.261931	H	-5.988677	1.712252	-2.224231
Li	-2.782741	-0.843844	0.200892	H	-7.018482	0.273093	-2.362029
N	-2.594761	-2.652935	-0.56557	H	-7.267961	1.813797	-0.118722
C	-3.239325	-3.843825	-0.046511	H	-7.162937	0.05137	0.070661
C	-2.884685	-4.017006	1.443253	H	-5.261651	0.668832	1.416309
N	-1.431124	-4.141854	1.712307	H	-4.924371	2.10535	0.424927
C	-0.940759	-5.480238	1.313981	C	1.875698	-1.726145	-1.078998
H	-1.10473	-5.602698	0.239306	C	2.433678	-1.353095	0.312756
H	-1.54016	-6.260417	1.823608	N	2.115318	0.029331	0.744489
C	0.541261	-5.685439	1.641107	C	2.35396	0.1487	2.199347
H	1.147102	-5.006451	1.030125	H	1.692485	-0.561968	2.705458

Table A3.4 (Continued).

H	0.826441	-6.705328	1.353494	H	3.395959	-0.144988	2.435403
C	0.829783	-5.436676	3.125284	C	2.097307	1.562422	2.727668
C	0.282949	-4.063717	3.531551	H	2.325997	1.585424	3.800663
C	-1.194131	-3.933897	3.158086	H	1.02952	1.793242	2.624491
H	-1.564498	-2.937594	3.418761	C	2.929017	2.602705	1.969251
H	-1.781764	-4.665746	3.746917	C	2.700694	2.443912	0.462095
H	0.394031	-3.8991	4.610804	C	2.957058	1.00205	0.016628
H	0.853843	-3.27211	3.026563	H	2.757267	0.898987	-1.053596
H	0.343552	-6.214636	3.732283	H	4.027511	0.758218	0.169139
H	1.905959	-5.503966	3.32626	H	3.359842	3.113394	-0.105665
H	-3.424433	-4.883007	1.867427	H	1.666604	2.712408	0.212263
H	-3.224298	-3.129791	1.988969	H	3.99568	2.455449	2.19388
H	-2.876754	-4.746805	-0.583723	H	2.674753	3.618277	2.297856
C	-4.767089	-3.864401	-0.240512	H	3.525127	-1.514651	0.350026
C	-5.325061	-4.56246	-1.320696	H	1.984228	-2.037224	1.043642
C	-6.700047	-4.545063	-1.570679	H	2.286354	-0.989491	-1.80857
C	-7.556006	-3.836329	-0.728024	C	2.528309	-3.061322	-1.508537
C	-7.020279	-3.142048	0.361031	C	3.871087	-3.089893	-1.91319
C	-5.64376	-3.149513	0.592616	C	4.49088	-4.281743	-2.287886
H	-5.251804	-2.596248	1.442992	C	3.768432	-5.477696	-2.279995
H	-7.67872	-2.60333	1.039528	C	2.427032	-5.462717	-1.897493
H	-8.627725	-3.830063	-0.910124	C	1.816182	-4.264587	-1.516194
H	-7.101312	-5.092742	-2.420293	H	0.766857	-4.244324	-1.23656
H	-4.667179	-5.132575	-1.973581	H	1.849854	-6.384706	-1.903527
C	-2.505261	-2.672101	-2.015157	H	4.24459	-6.408214	-2.578907
C	-1.601073	-1.554947	-2.568773	H	5.534954	-4.277507	-2.592747
C	-0.083914	-1.759041	-2.418291	H	4.438199	-2.160085	-1.939674
H	0.414513	-1.004689	-3.073077	O	-0.465806	1.738068	-0.945912
H	0.154791	-2.725471	-2.907294	C	-1.476862	2.655336	-0.459454
H	-1.886538	-0.590058	-2.115396	C	-1.577305	3.762696	-1.513666
H	-1.809001	-1.4556	-3.644935	C	-1.17319	3.025952	-2.800408
H	-2.100756	-3.641263	-2.387263	C	-0.076911	2.090169	-2.292048
H	-3.495277	-2.583267	-2.514179	H	0.897499	2.59715	-2.260065
C	-1.364269	-0.268116	1.748674	H	0.023139	1.166297	-2.865905
H	-0.781864	-1.083476	2.228491	H	-0.820851	3.694407	-3.591743
H	-0.700365	0.612572	1.86214	H	-2.016629	2.445859	-3.192952
C	-2.56438	0.021655	2.677595	H	-0.865235	4.568218	-1.298304
H	-3.079253	0.935507	2.336081	H	-2.578675	4.201419	-1.56061
H	-3.326638	-0.780401	2.605985	H	-2.414634	2.100319	-0.352716
C	-2.253246	0.205801	4.177352	H	-1.167734	3.017915	0.525419
H	-1.518192	1.016593	4.284235	O	-4.344794	0.293857	-0.405085
H	-1.756249	-0.701003	4.551858	C	-5.272404	1.064258	0.397767
C	-3.485116	0.509298	5.038589	C	-6.633455	0.939306	-0.29162
H	-3.223637	0.633966	6.096428	C	-6.236486	0.748358	-1.762824
H	-4.223726	-0.300596	4.974395	C	-4.993495	-0.129812	-1.63764
H	-3.980593	1.432356	4.709963				

Table A3.5. Optimized geometries of dilithium amide-enediolate mixed aggregate **8** at B3LYP level of theory with 6-31G(d) basis set for the enolization of phenylacetic acid at –78 °C with free energies (Hartrees) and cartesian coordinates (X, Y, Z) (Note: G_{MP2} includes single point MP2 corrections to B3LYP/6-31G(d) optimized structures).





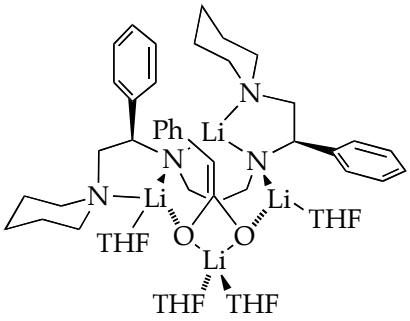
8a
G = -2767.365419
G_{MP2} = -2759.347801

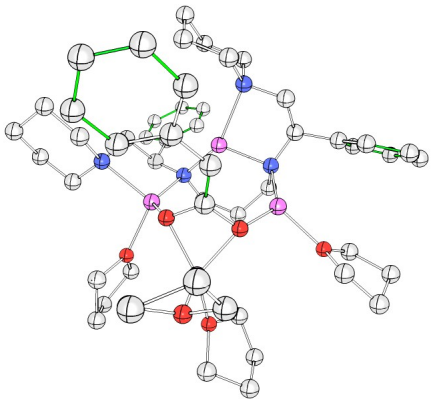
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	C	5.388883	-6.514296	2.741135
O	1.701483	-0.605298	0.727219	C	4.388865	-5.455794	3.218026
Li	3.347787	-0.965851	-0.142494	C	2.975415	-5.77362	2.73057
N	3.898754	-2.735662	-1.086704	H	2.279346	-4.992451	3.044198
C	5.335442	-2.549484	-1.05828	H	2.638593	-6.718013	3.201094
C	5.782976	-2.350484	0.408794	H	4.376914	-5.389252	4.313253
N	5.313992	-1.070433	0.988845	H	4.689727	-4.468298	2.843181
C	5.133547	-1.183262	2.450418	H	5.163536	-7.47308	3.231107
H	4.423824	-1.993894	2.641258	H	6.413067	-6.244663	3.027946
H	6.090482	-1.459282	2.936598	H	1.297756	-7.306366	1.200777
C	4.607099	0.121845	3.053084	H	0.845249	-5.619902	1.497314
H	4.494113	-0.003309	4.137506	H	1.895761	-6.624848	-1.191896
H	3.608722	0.313176	2.640177	C	-0.196551	-6.713227	-0.917027
C	5.544112	1.294343	2.737061	C	-0.364002	-7.407851	-2.124057
C	5.808433	1.362317	1.227748	C	-1.589532	-7.982903	-2.47208
C	6.277628	0.006776	0.693117	C	-2.678595	-7.887521	-1.604524
H	6.421159	0.051623	-0.390535	C	-2.529087	-7.204218	-0.393563
H	7.263257	-0.239561	1.137078	C	-1.306903	-6.616929	-0.060375
H	6.56848	2.121201	0.999457	H	-1.216361	-6.093828	0.888805
H	4.890347	1.647393	0.700649	H	-3.363872	-7.140636	0.301326
H	6.498077	1.153102	3.266229	H	-3.628961	-8.348853	-1.86166
H	5.120567	2.239851	3.099316	H	-1.688388	-8.51591	-3.415062
H	6.878195	-2.43418	0.507003	H	0.486407	-7.505882	-2.795947
H	5.345857	-3.16775	0.993009	C	1.424759	-4.399135	-2.334138
H	5.63287	-1.625857	-1.610857	C	1.904455	-2.961667	-2.629024
C	6.209631	-3.654089	-1.696698	H	1.648461	-2.720758	-3.672587
C	7.536132	-3.37569	-2.058222	H	1.343867	-2.25369	-1.998334
C	8.358515	-4.354993	-2.614859	C	3.411735	-2.69834	-2.463353
C	7.861009	-5.641628	-2.836253	H	3.620697	-1.710425	-2.937608

Table A3.5 (Continued).

C	6.539139	-5.930388	-2.496093	H	3.934491	-3.423593	-3.118096
C	5.724669	-4.944506	-1.932109	H	2.170485	-5.100554	-2.770434
H	4.690819	-5.162089	-1.680279	H	0.503144	-4.579432	-2.933159
H	6.136077	-6.924461	-2.67681	O	3.544156	0.803806	-1.372099
H	8.495214	-6.406902	-3.27688	C	2.609406	1.893329	-1.193535
H	9.385116	-4.113977	-2.88166	C	3.134896	3.047031	-2.053806
H	7.929714	-2.371704	-1.901839	C	3.853042	2.297427	-3.185804
Li	2.863993	-4.019196	0.010865	C	4.472359	1.121858	-2.430242
N	1.236255	-4.637432	-0.907967	H	5.437688	1.404378	-1.988308
Li	-0.190118	-3.376884	-0.356995	H	4.613027	0.225698	-3.038707
O	-0.186942	-1.798542	0.629518	H	4.601671	2.903314	-3.705216
C	0.934565	-1.529892	1.293586	H	3.130023	1.937745	-3.927822
C	1.257132	-2.098341	2.525086	H	3.84954	3.658394	-1.489809
H	2.184742	-1.746551	2.968051	H	2.332533	3.70366	-2.405044
C	0.444566	-2.954841	3.364515	H	1.621648	1.559549	-1.529334
C	0.935599	-3.324914	4.646993	H	2.556038	2.128564	-0.126847
C	0.215029	-4.138035	5.514749	O	-0.824083	1.260686	1.366122
C	-1.045503	-4.62835	5.156735	C	-1.777486	0.615429	2.258037
C	-1.560924	-4.271257	3.908467	C	-1.18542	0.739338	3.661889
C	-0.843814	-3.45747	3.031929	C	-0.403234	2.0584	3.569393
H	-1.279168	-3.169427	2.083148	C	0.156106	1.99842	2.147595
H	-2.546872	-4.626581	3.611017	H	1.101677	1.447528	2.100554
H	-1.608958	-5.265596	5.832941	H	0.281611	2.983603	1.685416
H	0.640509	-4.390333	6.484437	H	0.388793	2.141478	4.319608
H	1.911464	-2.951652	4.954422	H	-1.074907	2.91803	3.685404
O	-1.996089	-3.302489	-1.262658	H	-0.508	-0.098509	3.85291
C	-2.45062	-4.036772	-2.430737	H	-1.956854	0.748218	4.437777
C	-3.980095	-4.08685	-2.330648	H	-2.737296	1.142221	2.169025
C	-4.304257	-2.856762	-1.467581	H	-1.886718	-0.420491	1.93001
C	-3.129729	-2.848987	-0.49181	O	-0.702305	0.691169	-1.715218
H	-3.303232	-3.544182	0.340817	C	-0.913427	-0.201752	-2.846
H	-2.877331	-1.869683	-0.080384	C	-1.959893	0.484261	-3.735061
H	-5.271213	-2.925544	-0.95989	C	-2.696771	1.404265	-2.747774
H	-4.303234	-1.943979	-2.076985	C	-1.558601	1.848303	-1.832618
H	-4.292142	-5.003547	-1.819312	H	-1.862563	2.130872	-0.822942
H	-4.461365	-4.06666	-3.313186	H	-0.98912	2.675481	-2.280783
H	-2.115617	-3.485947	-3.318666	H	-3.444345	0.84093	-2.176359
H	-1.984117	-5.022618	-2.427185	H	-3.200252	2.245648	-3.233296
C	1.155871	-6.056497	-0.589405	H	-2.618545	-0.237063	-4.227557
C	1.498928	-6.26283	0.898578	H	-1.474202	1.080739	-4.515928
N	2.893431	-5.898113	1.255135	H	0.045445	-0.358737	-3.347867
C	3.832602	-6.945392	0.793179	H	-1.26183	-1.158614	-2.446262
H	3.774331	-7.010441	-0.29728	H	5.642591	-5.771106	0.722938
H	3.511031	-7.9279	1.192062	H	5.908017	-7.502652	0.868353
C	5.277877	-6.676562	1.221536				

Table A3.5 (Continued).





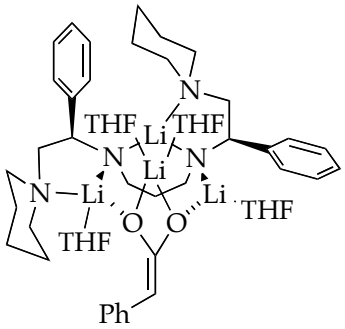
8c
G = -2767.355533
G_{MP2} = -2759.336754

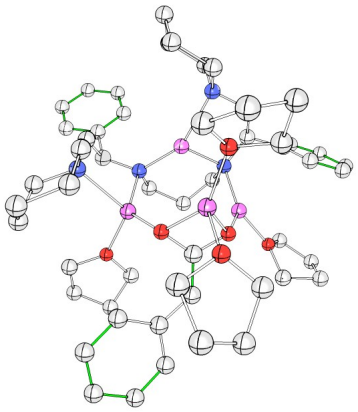
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	H	-1.227557	6.921593	0.155403
O	-1.707838	0.575926	0.793178	C	0.78472	6.812993	0.798319
Li	-2.983058	1.283083	-0.493124	C	1.174755	7.798757	-0.119699
N	-3.191712	3.245199	-1.225171	C	2.452661	8.363937	-0.085427
C	-4.590911	3.240731	-1.605277	C	3.369938	7.963108	0.886959
H	-4.762006	2.563524	-2.476045	C	2.997227	6.98679	1.815922
C	-5.200925	4.587055	-2.067536	C	1.72516	6.414221	1.763416
C	-6.376152	4.595546	-2.833205	H	1.459	5.655777	2.495941
C	-6.972814	5.789574	-3.237919	H	3.695573	6.679292	2.591541
C	-6.392461	7.012527	-2.892631	H	4.359471	8.411502	0.928145
C	-5.213682	7.021242	-2.146283	H	2.726456	9.125399	-0.812146
C	-4.627366	5.819502	-1.740016	H	0.458871	8.130723	-0.868984
H	-3.698433	5.825556	-1.17707	C	-0.511951	5.046032	-1.4551
H	-4.742524	7.96649	-1.885606	C	-0.887556	3.741408	-2.191096
H	-6.84903	7.946424	-3.21093	H	-0.408406	3.750073	-3.182322
H	-7.886169	5.766623	-3.828198	H	-0.463677	2.88237	-1.647986
H	-6.828523	3.647035	-3.121699	H	-1.167596	5.857403	-1.842811
Li	-2.415512	4.160974	0.352987	H	0.509133	5.345133	-1.782764
N	-0.630306	4.898303	-0.010372	C	-2.3895	3.505814	-2.421782
Li	0.588056	3.397135	0.400541	H	-2.481742	2.67022	-3.154313
O	0.240618	1.668818	0.896314	H	-2.757126	4.389021	-2.980001
C	-0.896638	1.333308	1.51461	N	-5.220243	1.260881	-0.178598
C	-1.102469	1.70941	2.841128	C	-5.576628	0.870287	1.203644
H	-0.318637	2.338144	3.259961	H	-5.178984	-0.140332	1.365206
C	-2.087633	1.226585	3.786203	H	-5.043245	1.524225	1.897833
C	-2.085535	1.736914	5.112674	C	-7.085933	0.862018	1.494613
C	-2.974654	1.285808	6.082823	C	-7.817007	-0.057958	0.50572
C	-3.913722	0.292491	5.785774	C	-7.4566	0.316537	-0.940132
C	-3.930698	-0.235042	4.491258	C	-5.929123	0.377477	-1.131308
C	-3.046672	0.215838	3.512969	H	-5.683237	0.69304	-2.149541
H	-3.074142	-0.202714	2.514368	H	-5.518209	-0.632167	-1.000748
H	-4.64571	-1.016919	4.237542	H	-7.875524	-0.412124	-1.647099
H	-4.608761	-0.061638	6.542563	H	-7.907198	1.28537	-1.192465

Table A3.5 (Continued).

H	-2.931142	1.71063	7.084226	H	-8.902948	-0.015142	0.6574
H	-1.35419	2.500394	5.374391	H	-7.514587	-1.099311	0.694754
O	2.523156	3.373936	-0.138253	H	-7.487005	1.882146	1.42171
C	3.453507	2.602417	0.651432	H	-7.250141	0.532878	2.528427
C	4.812511	2.805908	-0.016646	O	-2.802941	-0.271048	-1.921164
C	4.703967	4.259055	-0.505072	C	-2.752532	-1.643047	-1.486979
C	3.236204	4.358065	-0.933044	C	-2.195453	-2.422328	-2.676803
H	3.098767	4.097174	-1.989922	C	-2.816712	-1.660139	-3.858072
H	2.79562	5.33862	-0.748244	C	-2.78446	-0.207341	-3.364303
H	5.392086	4.495475	-1.322259	H	-3.639857	0.38528	-3.702387
H	4.90193	4.954419	0.317666	H	-1.867136	0.308514	-3.670855
H	4.928384	2.121047	-0.86622	H	-3.849689	-1.98978	-4.020183
H	5.647402	2.639093	0.670833	H	-2.271362	-1.791904	-4.797472
H	3.455378	2.983748	1.681652	H	-2.467065	-3.48223	-2.652895
H	3.099358	1.569514	0.665576	H	-1.102779	-2.343332	-2.701754
C	-0.609039	6.170209	0.692618	H	-2.140963	-1.680256	-0.583406
C	-1.219858	5.968263	2.093012	H	-3.767134	-1.984135	-1.234711
N	-2.649725	5.575357	2.071517	O	0.948928	-0.431098	-1.697169
C	-3.505622	6.759549	1.834534	C	1.794585	-1.591384	-1.863985
H	-3.245003	7.189196	0.862698	C	3.126988	-1.044153	-2.369239
H	-3.284808	7.530906	2.59856	C	2.663968	0.11608	-3.265025
C	-4.999001	6.424976	1.874214	C	1.462886	0.67522	-2.492794
C	-5.385565	5.759837	3.200033	H	0.660554	1.03862	-3.140997
C	-4.46825	4.560567	3.462178	H	1.747047	1.477118	-1.804213
C	-2.995851	4.960088	3.375889	H	2.353291	-0.263819	-4.245386
H	-2.364187	4.078148	3.506734	H	3.436836	0.872861	-3.42928
H	-2.762909	5.668465	4.195285	H	3.717076	-1.795929	-2.901956
H	-4.668172	3.77268	2.723956	H	3.725329	-0.668658	-1.530342
H	-4.655408	4.118591	4.447682	H	1.843577	-2.098772	-0.898754
H	-6.438395	5.45127	3.184951	H	1.339204	-2.265464	-2.603693
H	-5.280664	6.486066	4.019849	O	0.672097	-1.513162	1.219984
H	-5.243062	5.7589	1.038153	C	1.578609	-1.04922	2.259586
H	-5.570193	7.348573	1.716172	C	0.916473	-1.418817	3.586631
H	-1.08422	6.870876	2.715162	C	0.136163	-2.690887	3.2218
H	-0.680976	5.149559	2.582044	C	-0.342606	-2.375961	1.804135
H	1.647563	-1.577136	4.385637	H	-1.288943	-1.825636	1.809924
H	2.54213	-1.560546	2.125028	H	-0.43631	-3.263646	1.168832
H	1.704149	0.027633	2.125116	H	-0.698612	-2.885614	3.900967
C	-5.459174	2.697702	-0.447388	H	0.795415	-3.567747	3.22298
H	-6.52029	2.910401	-0.64031	H	0.228208	-0.624851	3.890667
H	-5.187835	3.250484	0.45957				

Table A3.5 (Continued).





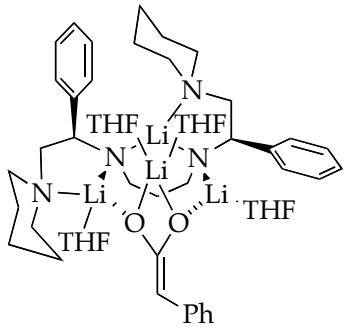
8d
G = -2767.351929
G_{MP2} = -2759.3378964

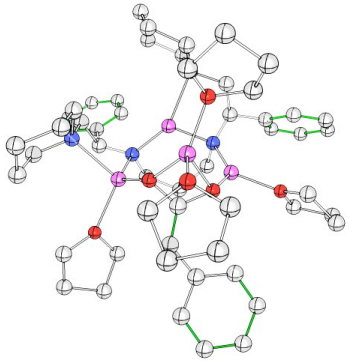
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	H	6.614262	4.382395	-0.224159
O	-0.733622	1.195198	-1.375433	C	5.326414	3.864577	1.454803
Li	-0.117283	2.786938	-2.32564	C	4.068329	3.022032	1.688899
N	1.839853	3.365783	-2.902903	C	4.220426	1.625664	1.081584
C	1.665736	4.785605	-2.674156	H	3.297289	1.054025	1.215132
H	0.819095	5.186577	-3.280308	H	5.025544	1.087627	1.621467
C	2.850823	5.713991	-3.025861	H	3.85849	2.921305	2.762176
C	2.625177	7.074801	-3.278455	H	3.200504	3.522521	1.23916
C	3.677345	7.945256	-3.562993	H	6.164746	3.432018	2.020726
C	4.988147	7.464456	-3.61328	H	5.186313	4.887167	1.825493
C	5.227949	6.11002	-3.379311	H	5.645839	-0.154616	-0.414878
C	4.167621	5.247055	-3.089577	H	3.880222	-0.322584	-0.42688
H	4.347479	4.187946	-2.928028	H	5.488313	0.755688	-2.7848
H	6.242351	5.720692	-3.432546	C	5.127625	-1.325811	-2.749259
H	5.811006	8.136851	-3.842893	C	4.529394	-2.459665	-2.175681
H	3.474829	8.996991	-3.752389	C	4.914311	-3.748227	-2.547087
H	1.604989	7.456466	-3.255002	C	5.900817	-3.935071	-3.520503
C	1.306327	5.014139	-1.18906	C	6.498218	-2.820153	-4.109528
N	-0.043685	4.522215	-0.823956	C	6.117447	-1.532824	-3.719637
C	-0.069718	4.096568	0.589481	H	6.597728	-0.668583	-4.174427
H	0.671815	3.298909	0.710608	H	7.266029	-2.950232	-4.868608
H	0.23964	4.933936	1.247288	H	6.202186	-4.938365	-3.810974
C	-1.450893	3.593309	1.016557	H	4.448338	-4.609423	-2.073204
H	-1.416126	3.316025	2.079352	H	3.750822	-2.336842	-1.425444
H	-1.681929	2.689548	0.440882	C	3.448345	0.907621	-4.278365
C	-2.529007	4.656309	0.77384	C	2.164387	1.633396	-4.729681
C	-2.462752	5.130137	-0.682546	C	2.036395	3.115134	-4.332292
C	-1.046315	5.584716	-1.042287	H	1.199391	3.546763	-4.919448
H	-0.995935	5.890922	-2.091163	H	2.937856	3.623267	-4.729342
H	-0.786286	6.475183	-0.435273	H	2.119684	1.589877	-5.827958
H	-3.159469	5.960141	-0.855961	H	1.28279	1.077067	-4.371867
H	-2.762004	4.310778	-1.346917	H	4.307122	1.590006	-4.469136
H	-2.361811	5.511749	1.445135	H	3.619889	0.055512	-4.970108

Table A3.5 (Continued).

H	-3.524407	4.258887	1.007376	O	-1.313171	3.241218	-4.095953
H	1.40698	6.076866	-0.913178	C	-2.238137	4.319767	-4.345636
H	2.042482	4.459911	-0.594895	C	-2.74392	4.133387	-5.779366
Li	2.893024	2.097573	-1.875934	C	-2.65402	2.610075	-5.951327
N	3.391068	0.500817	-2.875978	C	-1.369556	2.288669	-5.190971
Li	1.78751	-0.716971	-2.816743	H	-0.48475	2.436747	-5.822796
O	0.26459	-0.775291	-1.743357	H	-1.348344	1.285898	-4.760645
C	-0.767696	0.033075	-2.013244	H	-2.602923	2.29815	-6.999586
C	-1.819582	-0.405914	-2.814221	H	-3.509819	2.115303	-5.481782
H	-1.679219	-1.383566	-3.267458	H	-2.080946	4.641123	-6.49052
C	-3.123499	0.190155	-3.011615	H	-3.755663	4.528289	-5.914606
C	-4.058159	-0.462671	-3.860385	H	-3.062428	4.246288	-3.626774
C	-5.34404	0.02679	-4.065629	H	-1.714141	5.269788	-4.196806
C	-5.773397	1.198817	-3.432795	O	1.188428	-0.050549	1.600082
C	-4.874896	1.861726	-2.590757	C	0.745692	0.627642	2.803514
C	-3.583355	1.379837	-2.384756	C	0.772046	-0.42436	3.912925
H	-2.898244	1.909939	-1.73498	C	1.90604	-1.352752	3.450147
H	-5.18655	2.772563	-2.080563	C	1.706488	-1.363816	1.934775
H	-6.77848	1.581292	-3.589885	H	0.971149	-2.117874	1.63009
H	-6.020421	-0.512697	-4.726399	H	2.628229	-1.514062	1.36649
H	-3.749822	-1.377643	-4.364334	H	1.849056	-2.355275	3.883952
O	1.605888	-2.18282	-4.161553	H	2.882509	-0.924835	3.705247
C	2.479503	-2.580963	-5.241278	H	-0.177855	-0.969288	3.942766
C	2.230658	-4.091707	-5.473306	H	0.94739	0.016111	4.898812
C	1.201598	-4.47042	-4.38577	H	1.441186	1.451768	3.004864
C	0.52874	-3.131217	-4.093239	H	-0.249296	1.041067	2.618004
H	0.081992	-3.030905	-3.103975	O	-1.579112	-1.000147	0.896182
H	-0.228357	-2.888466	-4.853992	C	-1.799164	-2.334806	0.35696
H	1.709091	-4.834909	-3.485765	C	-3.28625	-2.412102	0.001141
H	0.493815	-5.237723	-4.714853	C	-3.91656	-1.406537	0.97731
H	3.154115	-4.670385	-5.387152	C	-2.852531	-0.312945	1.026602
H	1.820258	-4.265606	-6.473631	H	-2.835165	0.242255	1.970318
H	2.237657	-1.988015	-6.132179	H	-2.960245	0.388221	0.193251
H	3.498953	-2.353318	-4.929721	H	-4.056585	-1.85712	1.967906
C	4.692532	0.101161	-2.371326	H	-4.881244	-1.024581	0.631327
C	4.712752	0.260623	-0.83741	H	-3.685389	-3.425593	0.108969
N	4.52421	1.656665	-0.366464	H	-3.440337	-2.080371	-1.029577
C	5.75345	2.450234	-0.601275	H	-1.139934	-2.453274	-0.506338
H	5.940097	2.488565	-1.678194	H	-1.52756	-3.059787	1.136427
H	6.617965	1.931466	-0.142161	H	4.894469	4.432437	-0.586663
C	5.660841	3.871629	-0.039937				

Table A3.5 (Continued).





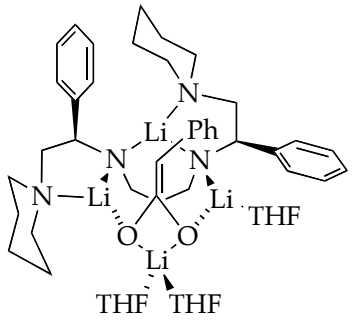
8b
G = -2767.351209
G_{MP2} = -2759.3295

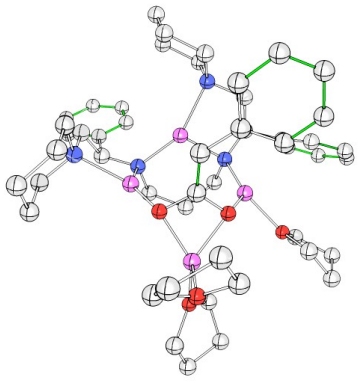
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	C	-5.521159	3.690833	0.967093
O	-1.02953	-0.931669	-1.327013	C	-4.281754	2.860264	1.315182
Li	-2.605841	-1.106327	-2.381047	C	-3.012949	3.486506	0.732622
N	-3.625749	0.510837	-3.219757	H	-2.147324	2.849839	0.943645
C	-4.954695	-0.056346	-3.118487	H	-2.835419	4.461456	1.229909
H	-5.023915	-1.019777	-3.677067	H	-4.163742	2.767655	2.403024
C	-6.130742	0.7852	-3.662248	H	-4.399553	1.844001	0.919229
C	-7.321495	0.157483	-4.054211	H	-5.466253	4.66226	1.480316
C	-8.415322	0.894254	-4.509015	H	-6.433212	3.195608	1.321797
C	-8.333989	2.28637	-4.592884	H	-1.850693	5.411711	-0.8284
C	-7.150595	2.925156	-4.220207	H	-1.010602	3.857876	-0.671636
C	-6.062304	2.179013	-3.760796	H	-2.498003	4.681275	-3.202478
H	-5.13228	2.670752	-3.489505	C	-0.482973	5.285713	-3.100985
H	-7.070024	4.007339	-4.297434	C	0.645567	5.541984	-2.306684
H	-9.180393	2.86482	-4.954804	C	1.630846	6.443402	-2.713458
H	-9.328591	0.382779	-4.804689	C	1.521471	7.099602	-3.942393
H	-7.388428	-0.928833	-4.004576	C	0.411995	6.849526	-4.751446
C	-5.252484	-0.366572	-1.63411	C	-0.578651	5.960708	-4.32724
N	-4.405243	-1.442856	-1.061103	H	-1.451584	5.790212	-4.953685
C	-4.137392	-1.175401	0.366418	H	0.309481	7.356307	-5.708137
H	-3.608918	-0.218631	0.428804	H	2.286777	7.803435	-4.259762
H	-5.090228	-1.063108	0.921917	H	2.48202	6.641581	-2.065328
C	-3.294187	-2.272093	1.019346	H	0.756591	5.041866	-1.347776
H	-3.143912	-2.023226	2.078706	C	-1.554659	2.691284	-4.505109
H	-2.3099	-2.284284	0.53606	C	-1.829572	1.216184	-4.865006
C	-3.96651	-3.641113	0.871689	C	-3.268334	0.718799	-4.623856
C	-4.259343	-3.899251	-0.609969	H	-3.402338	-0.218221	-5.202021
C	-5.069429	-2.751868	-1.220969	H	-3.939474	1.441718	-5.130113
H	-5.229255	-2.920868	-2.29114	H	-1.618023	1.090077	-5.937077
H	-6.070403	-2.72659	-0.745829	H	-1.116325	0.563809	-4.336013
H	-4.812966	-4.837481	-0.744654	H	-2.409294	3.289983	-4.890203
H	-3.310055	-4.002086	-1.147572	H	-0.687775	3.03482	-5.112224
H	-4.906586	-3.655909	1.442757	O	-2.560386	-2.772439	-4.000508

Table A3.5 (Continued).

H	-3.331452	-4.43475	1.284796	C	-2.670688	-4.196009	-3.81982
H	-6.317468	-0.609078	-1.486926	C	-2.396043	-4.823881	-5.187239
H	-5.056011	0.554717	-1.073852	C	-1.378639	-3.840035	-5.78064
Li	-2.787479	1.91016	-2.16147	C	-1.890258	-2.49498	-5.261379
N	-1.364222	2.905461	-3.070575	H	-2.623532	-2.053036	-5.944849
Li	0.337208	1.922844	-2.66164	H	-1.091523	-1.77681	-5.068022
O	0.764028	0.34209	-1.754724	H	-1.334356	-3.869435	-6.873689
C	0.104376	-0.783375	-2.016414	H	-0.373312	-4.039861	-5.396066
C	0.569158	-1.804661	-2.837623	H	-3.312225	-4.841954	-5.789972
H	-0.057731	-2.692689	-2.846455	H	-2.020362	-5.848991	-5.108116
C	1.796413	-1.898239	-3.598852	H	-1.927654	-4.525772	-3.079058
C	2.175015	-3.159689	-4.13367	H	-3.669838	-4.420897	-3.435938
C	3.331723	-3.333138	-4.886204	O	-0.185843	1.332776	1.464331
C	4.179855	-2.252802	-5.147318	C	-0.533186	0.851004	2.789486
C	3.832588	-1.000915	-4.63134	C	0.113625	1.831795	3.769564
C	2.677344	-0.819234	-3.873368	C	1.361035	2.284849	2.994556
H	2.425945	0.162064	-3.491069	C	0.834621	2.358221	1.561001
H	4.474546	-0.144122	-4.833357	H	1.591155	2.156822	0.79728
H	5.082475	-2.382189	-5.738598	H	0.370192	3.329555	1.349762
H	3.575499	-4.321929	-5.270905	H	2.153946	1.532147	3.074211
H	1.537512	-4.019766	-3.932437	H	1.762487	3.242138	3.339671
O	2.105771	2.688271	-3.164614	H	0.34738	1.364075	4.730308
C	2.492617	3.20712	-4.460978	H	-0.549909	2.683809	3.957292
C	3.932496	3.701274	-4.295857	H	-1.624184	0.814447	2.85892
C	4.472402	2.787312	-3.183456	H	-0.128554	-0.161332	2.898298
C	3.24562	2.61701	-2.285897	O	1.244205	-1.340969	0.927455
H	3.173957	3.431761	-1.550728	C	2.646771	-1.109098	0.62782
H	3.203021	1.655451	-1.768049	C	3.308546	-2.484312	0.673582
H	5.324826	3.216357	-2.647438	C	2.188225	-3.382356	0.12765
H	4.779027	1.818588	-3.592348	C	0.932643	-2.751149	0.73366
H	3.935836	4.746979	-3.969994	H	0.690063	-3.17721	1.716004
H	4.503744	3.630661	-5.226341	H	0.061107	-2.810287	0.078237
H	2.423427	2.388301	-5.187789	H	2.301561	-4.434147	0.408252
H	1.789659	3.996703	-4.733951	H	2.151224	-3.307167	-0.963052
C	-1.589359	4.293118	-2.693785	H	3.563672	-2.756716	1.705381
C	-1.842593	4.363089	-1.176444	H	4.220119	-2.524247	0.070232
N	-3.083847	3.679665	-0.733395	H	2.71341	-0.65884	-0.369072
C	-4.267486	4.505723	-1.07052	H	3.036452	-0.409272	1.37534
H	-4.314686	4.614492	-2.15744	H	-5.776834	2.96067	-1.055973
H	-4.136159	5.52226	-0.650054	H	-6.39916	4.587006	-0.814237
C	-5.577248	3.911151	-0.547739				

Table A3.5 (Continued).





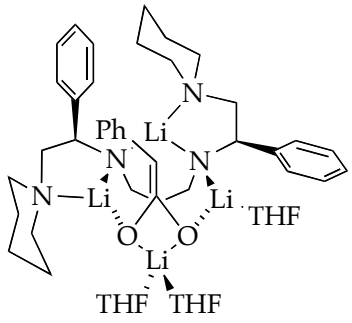
8e
G = -2535.021549
G_{MP2} = -2527.653427

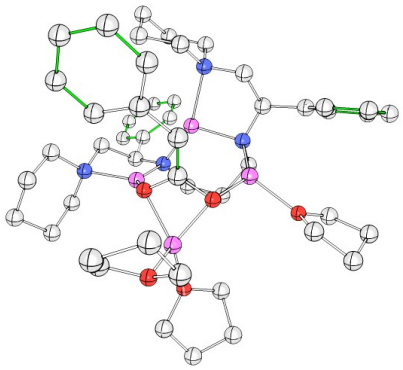
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	C	-1.340954	-4.847568	-1.501674
O	1.713011	0.028367	0.88277	C	-2.816921	-5.221745	-1.335224
Li	3.40825	-0.340653	0.290608	C	-3.427308	-3.926861	-0.776708
N	4.413968	-1.751732	-0.730386	C	-2.310173	-3.426265	0.136981
C	5.698182	-1.099184	-0.911064	H	-2.35761	-3.906913	1.12317
C	6.12129	-0.396185	0.399232	H	-2.284043	-2.344312	0.280086
N	5.180879	0.674752	0.807313	H	-4.367233	-4.085499	-0.239283
C	5.325922	0.986718	2.245089	H	-3.614144	-3.208142	-1.584582
H	5.172803	0.059581	2.808397	H	-2.918353	-6.036139	-0.609791
H	6.356367	1.332195	2.457779	H	-3.271707	-5.5462	-2.276077
C	4.31857	2.047447	2.697985	H	-1.13757	-4.425463	-2.494251
H	4.47485	2.25583	3.763925	H	-0.657361	-5.678231	-1.322476
H	3.306521	1.639489	2.586203	C	2.676153	-5.558505	0.491536
C	4.453317	3.329532	1.866982	C	3.121721	-5.404451	1.959411
C	4.374907	2.992559	0.372795	N	4.385856	-4.639488	2.120173
C	5.382703	1.899499	0.004953	C	5.553195	-5.495764	1.808746
H	5.289374	1.641157	-1.054092	H	5.474964	-5.827307	0.768414
H	6.412475	2.279609	0.154423	H	5.519934	-6.405393	2.439702
H	4.572155	3.880808	-0.240811	C	6.887251	-4.77663	2.029983
H	3.362044	2.645594	0.127023	H	6.979931	-3.95171	1.313884
H	5.42024	3.808677	2.080919	H	7.704047	-5.475746	1.810141
H	3.675301	4.052369	2.142294	C	7.000867	-4.236021	3.459579
H	7.146275	0.003135	0.320717	C	5.768235	-3.386525	3.787524
H	6.128989	-1.150396	1.195413	C	4.47795	-4.162047	3.520779
H	5.620733	-0.306805	-1.690428	H	3.606026	-3.535537	3.723374
C	6.875368	-1.974124	-1.40153	H	4.425728	-5.024536	4.212898
C	8.031174	-1.36826	-1.917137	H	5.778113	-3.065047	4.836521
C	9.115223	-2.127904	-2.355835	H	5.775436	-2.474057	3.174447
C	9.058842	-3.522889	-2.301725	H	7.060486	-5.075872	4.167462
C	7.909087	-4.140702	-1.810014	H	7.922747	-3.653626	3.580147
C	6.830218	-3.370931	-1.365655	H	3.215617	-6.391917	2.444465
H	5.926709	-3.851386	-1.001224	H	2.347639	-4.849543	2.499114
H	7.845996	-5.22613	-1.77903	H	3.512481	-6.028803	-0.068981

Table A3.5 (Continued).

H	9.898208	-4.119976	-2.649187	C	1.519894	-6.566438	0.389215
H	10.001062	-1.632656	-2.746828	C	1.511362	-7.527098	-0.632121
H	8.078935	-0.281918	-1.983027	C	0.453912	-8.429948	-0.775566
Li	3.891929	-3.16133	0.573259	C	-0.618219	-8.398711	0.117217
N	2.382852	-4.239283	-0.054826	C	-0.623994	-7.451184	1.145683
Li	0.667026	-3.30423	0.357412	C	0.427164	-6.541173	1.272833
O	0.213123	-1.623673	1.046676	H	0.400396	-5.813698	2.080897
C	1.20779	-0.961113	1.621929	H	-1.444465	-7.428645	1.859749
C	1.682665	-1.212089	2.906952	H	-1.435096	-9.109664	0.020793
H	2.477604	-0.5513	3.245773	H	0.474372	-9.163884	-1.577979
C	1.167136	-2.136445	3.897391	H	2.352879	-7.569839	-1.320913
C	1.776611	-2.178036	5.180237	C	2.449123	-4.213908	-1.511771
C	1.338679	-3.034518	6.184566	C	2.492105	-2.771738	-2.058442
C	0.26099	-3.899337	5.967568	H	2.154264	-2.7894	-3.105841
C	-0.367496	-3.87107	4.720175	H	1.76545	-2.151973	-1.509655
C	0.066301	-3.0151	3.708118	C	3.861687	-2.072954	-2.049863
H	-0.459538	-2.986267	2.761394	H	3.756958	-1.146903	-2.661911
H	-1.220555	-4.521575	4.53159	H	4.546802	-2.711214	-2.642696
H	-0.081542	-4.570633	6.750368	H	3.348527	-4.748345	-1.892673
H	1.842114	-3.025336	7.149592	H	1.597584	-4.739481	-1.998865
H	2.612814	-1.508841	5.37823	O	-1.191957	1.296691	1.001984
O	-1.079439	-3.812575	-0.516963	C	-0.491577	2.478298	1.480179
C	-0.773911	-0.909021	-2.778068	C	-1.001394	2.725382	2.902502
C	-2.010776	-0.531537	-3.589434	C	-1.357797	1.305934	3.370282
C	-1.840876	0.990531	-3.726056	C	-1.930338	0.687244	2.096382
C	-1.226935	1.385358	-2.374833	H	-2.99587	0.923095	1.968937
H	-1.980674	1.698255	-1.645349	H	-1.776632	-0.392154	2.033857
H	-0.474197	2.175865	-2.464134	H	-2.071968	1.289997	4.199105
H	-2.780449	1.51521	-3.92234	H	-0.458214	0.759928	3.672718
H	-1.149578	1.220443	-4.544694	H	-1.893603	3.363371	2.888907
H	-2.923079	-0.769534	-3.028887	H	-0.247811	3.209368	3.530915
H	-2.055353	-1.047935	-4.552934	H	0.58058	2.255376	1.463409
H	0.114301	-1.000626	-3.416212	H	-0.705891	3.303351	0.79233
H	-0.877473	-1.819633	-2.18355	O	-0.587815	0.191396	-1.858592

Table A3.5 (Continued).





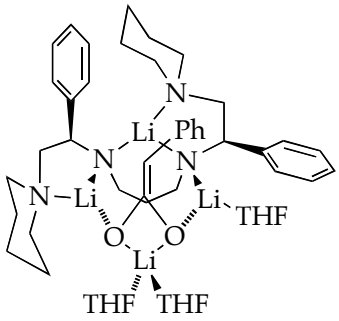
8f
G = -2535.021549
G_{MP2} = -2527.653427

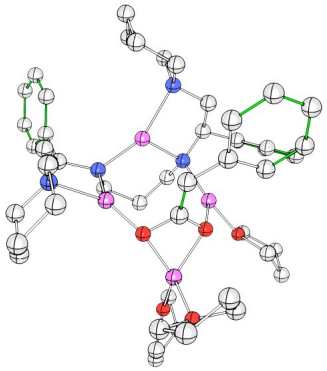
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	H	-7.249273	4.001662	3.416061
O	-1.670606	0.344187	0.976152	H	-2.161483	6.275312	3.30892
Li	-3.007219	1.004003	-0.113286	H	-1.509817	4.651479	3.0265
N	-3.602191	2.719674	-1.001548	H	-2.236031	6.576062	0.768951
C	-4.93652	2.388129	-1.472862	C	-0.241498	6.65518	1.475679
C	-5.617475	1.386933	-0.514843	C	0.003431	7.832448	0.755125
N	-4.900678	0.091033	-0.409384	C	1.195179	8.546952	0.908617
C	-5.462601	-0.696011	0.711165	C	2.16776	8.102285	1.805043
H	-5.351899	-0.106108	1.626747	C	1.938919	6.9328	2.536927
H	-6.546815	-0.854599	0.550719	C	0.753968	6.216001	2.36476
C	-4.769073	-2.050877	0.874856	H	0.598675	5.307453	2.942339
H	-5.240839	-2.592596	1.703966	H	2.681283	6.584498	3.251906
H	-3.721773	-1.883095	1.152889	H	3.089333	8.663045	1.939627
C	-4.829108	-2.869244	-0.419331	H	1.358073	9.455937	0.334142
C	-4.283183	-2.029518	-1.578626	H	-0.756761	8.195733	0.066234
C	-5.002843	-0.680881	-1.667402	C	-1.261577	4.991556	-0.999691
H	-4.575693	-0.086146	-2.478715	C	-1.415323	3.72962	-1.872364
H	-6.068824	-0.850803	-1.916321	H	-0.959201	3.928882	-2.853972
H	-4.397987	-2.555195	-2.53508	H	-0.837339	2.905618	-1.425788
H	-3.207295	-1.856002	-1.433671	C	-2.85048	3.253238	-2.144676
H	-5.870892	-3.149863	-0.633049	H	-2.788565	2.489807	-2.954162
H	-4.264632	-3.804112	-0.314892	H	-3.377843	4.104705	-2.619283
H	-6.66552	1.213658	-0.811905	H	-2.033133	5.727387	-1.321633
H	-5.638133	1.830766	0.489176	H	-0.297811	5.478883	-1.266403
H	-4.873388	1.885953	-2.46227	O	0.823678	-1.621724	0.866672
C	-5.908619	3.563463	-1.738243	C	-0.129594	-2.557152	1.450407
C	-7.090587	3.344482	-2.462964	C	0.463761	-2.984859	2.795206
C	-7.985861	4.381132	-2.723828	C	1.305942	-1.76065	3.186269
C	-7.707912	5.675057	-2.275819	C	1.858265	-1.308787	1.835756
C	-6.528068	5.913536	-1.571826	H	2.770774	-1.856125	1.560673
C	-5.640945	4.865826	-1.307655	H	2.042563	-0.232875	1.782285
H	-4.712988	5.057255	-0.776735	H	2.098331	-1.994888	3.904029
H	-6.290924	6.919108	-1.231875	H	0.668083	-0.975994	3.605724

Table A3.5 (Continued).

H	-8.398949	6.488196	-2.483014	H	1.099443	-3.870851	2.676047
H	-8.896658	4.181865	-3.283793	H	-0.313736	-3.217056	3.528402
H	-7.308863	2.345554	-2.838371	H	-1.077838	-2.02486	1.570943
Li	-3.082168	3.750901	0.632109	H	-0.259669	-3.388748	0.749602
N	-1.372789	4.673055	0.418004	O	0.538473	-0.107876	-1.879656
Li	0.128823	3.384767	0.702041	C	1.216149	0.99546	-2.526249
O	0.196981	1.574688	1.070599	C	2.430643	0.361906	-3.199274
C	-0.861735	1.091238	1.723881	C	1.861344	-0.988744	-3.664114
C	-1.012822	1.319856	3.087018	C	0.887627	-1.354974	-2.533318
H	-0.230699	1.931888	3.53214	H	1.34344	-2.003423	-1.778497
C	-1.993843	0.786112	4.009354	H	-0.02983	-1.827926	-2.899344
C	-1.926335	1.156309	5.378905	H	2.628973	-1.7539	-3.811854
C	-2.833109	0.681098	6.320286	H	1.323083	-0.865133	-4.61059
C	-3.857093	-0.196748	5.947904	H	3.235932	0.211726	-2.469982
C	-3.940328	-0.585142	4.607798	H	2.820815	0.969719	-4.02112
C	-3.037291	-0.109243	3.658962	H	0.540012	1.452006	-3.260378
H	-3.110461	-0.426638	2.627337	H	1.452641	1.734052	-1.7568
H	-4.721676	-1.276377	4.29428	C	-1.535787	5.85748	1.248009
H	-4.565451	-0.570206	6.682657	C	-2.147713	5.43101	2.597746
H	-2.738789	0.996806	7.357758	N	-3.506353	4.843561	2.476277
H	-1.13665	1.836303	5.695067	C	-4.526526	5.911521	2.372371
O	2.00709	3.749455	0.084266	H	-4.317417	6.507451	1.477569
C	2.530387	4.900672	-0.629262	H	-4.433719	6.592453	3.240865
C	4.021183	4.972068	-0.279304	C	-5.954513	5.359542	2.314756
C	4.356077	3.511743	0.062498	H	-6.089236	4.795539	1.384343
C	3.077789	3.057948	0.764333	H	-6.654802	6.203676	2.273865
H	3.079692	3.349995	1.823334	C	-6.255034	4.454718	3.515582
H	2.870931	1.988168	0.70164	C	-5.17095	3.378866	3.635763
H	5.242245	3.406428	0.695913	C	-3.778155	4.006309	3.671364
H	4.51929	2.928322	-0.852243	H	-3.014932	3.226812	3.71775
H	4.171514	5.613158	0.596136	H	-3.68044	4.621689	4.586643
H	4.621348	5.37445	-1.100974	H	-5.30554	2.770369	4.537309
H	2.368526	4.730646	-1.700756	H	-5.233704	2.690098	2.781273
H	1.971664	5.786094	-0.321708	H	-6.272152	5.057302	4.435815

Table A3.5 (Continued).





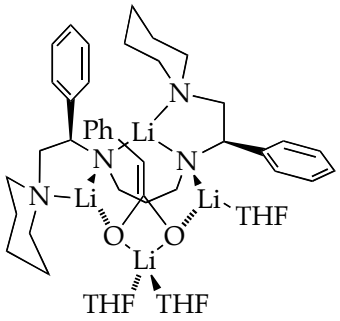
8g
G = -2535.017614
G_{MP2} = -2527.649109

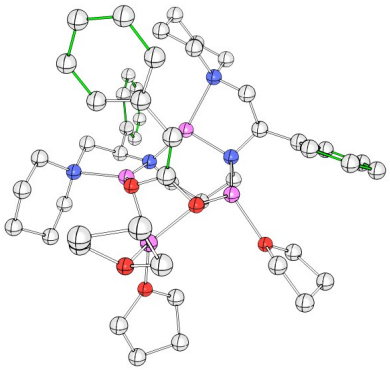
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	C	-0.738411	4.144857	5.762415
O	-1.748132	-0.073629	0.806124	C	-0.031096	4.072692	4.559692
Li	-3.460488	0.183854	0.199661	C	-0.371645	3.149373	3.571453
N	-4.629863	1.439535	-0.848477	H	0.211549	3.089328	2.660329
C	-5.835107	0.617548	-0.983885	H	0.810733	4.742372	4.388679
C	-6.133877	-0.11525	0.338419	H	-0.468222	4.86875	6.526468
N	-5.067748	-1.068059	0.724273	H	-2.361929	3.278689	6.891648
C	-5.150224	-1.391316	2.164576	H	-2.966847	1.641244	5.16433
H	-5.091446	-0.451058	2.724277	O	0.824517	3.725281	-0.827795
H	-6.132381	-1.848243	2.395837	C	1.068012	4.693417	-1.883136
C	-4.022772	-2.330771	2.601344	C	2.539251	5.10929	-1.750874
H	-4.13835	-2.553527	3.669645	C	3.167544	3.911258	-1.020882
H	-3.066661	-1.809746	2.472481	C	2.039631	3.502182	-0.077653
C	-4.02589	-3.621424	1.772647	H	2.028428	4.132613	0.821963
C	-4.011034	-3.28065	0.27721	H	2.047005	2.455548	0.229851
C	-5.142488	-2.309812	-0.073369	H	4.089743	4.163387	-0.488353
H	-5.097767	-2.046341	-1.133976	H	3.391135	3.100115	-1.725348
H	-6.119657	-2.803801	0.095093	H	2.619334	6.012557	-1.137085
H	-4.117843	-4.186977	-0.332471	H	3.000078	5.316977	-2.721396
H	-3.049002	-2.821269	0.013092	H	0.867445	4.195405	-2.839789
H	-4.929008	-4.205952	2.00278	H	0.373462	5.526343	-1.764785
H	-3.167023	-4.251892	2.035	C	-2.936505	5.412886	0.159262
H	-7.109588	-0.628986	0.28619	C	-3.414953	5.313912	1.621457
H	-6.200959	0.627585	1.142147	N	-4.734321	4.644651	1.749736
H	-5.658458	-0.165788	-1.754145	C	-5.816343	5.60283	1.427108
C	-7.093674	1.344793	-1.488547	H	-5.675216	5.955567	0.401524
C	-7.401125	1.335127	-2.856728	H	-5.728177	6.486812	2.088444
C	-8.520576	2.002624	-3.357972	C	-7.210401	4.992899	1.57887
C	-9.373796	2.685911	-2.49126	H	-7.343857	4.2131	0.82152
C	-9.093329	2.694156	-1.123394	H	-7.958489	5.76832	1.369619
C	-7.964544	2.0349	-0.632916	C	-7.415993	4.40593	2.980945
H	-7.771572	2.047581	0.436106	C	-6.257983	3.463953	3.332735
H	-9.757933	3.210321	-0.43446	C	-4.906633	4.153698	3.136728

Table A3.5 (Continued).

H	-10.250875	3.200945	-2.874773	H	-4.085888	3.466563	3.35996
H	-8.72877	1.982334	-4.425169	H	-4.822769	4.996866	3.848952
H	-6.752209	0.787915	-3.537389	H	-6.335771	3.119385	4.37154
Li	-4.243219	3.043635	0.288301	H	-6.301404	2.568214	2.696294
N	-2.670587	4.065008	-0.333297	H	-7.451217	5.222479	3.71704
Li	-0.909079	3.228835	0.11193	H	-8.378628	3.882918	3.045151
O	-0.343991	1.659609	0.958996	H	-3.451468	6.310411	2.095044
C	-1.325739	0.968626	1.523734	H	-2.692028	4.712907	2.182517
C	-1.868351	1.245631	2.775778	H	-3.749331	5.882718	-0.433382
H	-2.644531	0.559329	3.107969	C	-1.75636	6.390642	0.047815
C	-1.452271	2.242307	3.742132	C	-1.712657	7.327897	-0.994429
C	-2.143384	2.330058	4.980274	C	-0.639414	8.212308	-1.135268
C	-1.798653	3.25436	5.960521	C	0.414417	8.184201	-0.220517
C	0.99677	-2.555137	3.035769	C	0.38569	7.258923	0.827603
C	1.248368	-1.102335	3.467661	C	-0.682489	6.368759	0.954489
C	1.866545	-0.501065	2.207467	H	-0.68746	5.664641	1.78383
H	2.947098	-0.691695	2.149339	H	1.190733	7.24103	1.559149
H	1.669631	0.567264	2.096398	H	1.242595	8.882382	-0.314311
H	1.906958	-1.017422	4.337334	H	-0.633527	8.930261	-1.952274
H	0.304418	-0.594648	3.691766	H	-2.540492	7.369225	-1.699702
H	1.920001	-3.143502	3.103611	C	-2.735695	3.98114	-1.787382
H	0.230658	-3.056145	3.634977	C	-2.800595	2.519304	-2.272534
H	-0.513615	-2.238323	1.481431	H	-2.504141	2.500432	-3.332447
H	0.877562	-3.222132	0.934408	H	-2.051571	1.920445	-1.730033
O	0.636631	-0.282949	-1.832175	H	-3.626499	4.51258	-2.192623
C	0.599631	0.722076	-2.873372	H	-1.875208	4.470459	-2.297372
C	1.804587	0.413848	-3.759398	C	-4.167837	1.815425	-2.188149
C	1.851287	-1.121452	-3.701884	H	-4.095986	0.907933	-2.832628
C	1.439609	-1.412527	-2.253319	H	-4.892962	2.466349	-2.717723
H	2.30115	-1.48303	-1.580933	O	1.219946	-1.181092	1.097125
H	0.841552	-2.323925	-2.151798	C	0.56719	-2.38955	1.575008
H	2.834481	-1.535601	-3.943698	H	1.68986	0.804511	-4.774834
H	1.123555	-1.547698	-4.401879	H	-0.343362	0.629857	-3.426932
H	2.717087	0.84312	-3.327753	H	0.631903	1.69944	-2.38673

Table A3.5 (Continued).





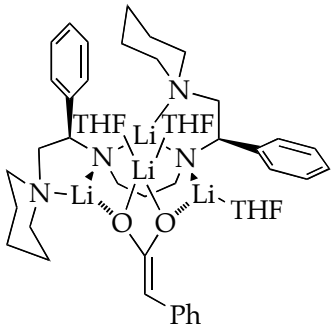
8h
G = -2535.015535
G_{MP2} = -2527.645802

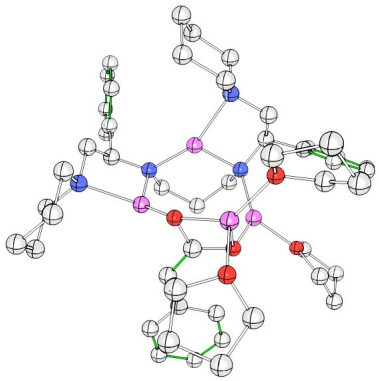
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	H	-7.402181	3.673966	0.099237
O	-1.811067	0.001975	0.705868	H	-8.187172	5.11184	0.744181
Li	-3.132694	0.138431	-0.578568	C	-7.785601	3.565798	2.227729
N	-4.329836	1.357916	-1.634865	C	-6.63225	2.630784	2.611112
C	-5.419914	0.467034	-2.048572	C	-5.311108	3.394775	2.701337
C	-5.543209	-0.753497	-1.115933	H	-4.492723	2.710581	2.938269
N	-4.297431	-1.547482	-1.012686	H	-5.371947	4.130898	3.526555
C	-4.450709	-2.584266	0.028365	H	-6.820809	2.137457	3.571928
H	-4.737891	-2.086249	0.959862	H	-6.533778	1.833444	1.861572
H	-5.275426	-3.27198	-0.243263	H	-7.971751	4.268318	3.053676
C	-3.159977	-3.380607	0.232192	H	-8.714975	3.000794	2.080786
H	-3.32661	-4.142468	1.004036	H	-3.841397	5.696446	2.250473
H	-2.38627	-2.698632	0.60468	H	-3.015044	4.130683	2.107134
C	-2.698602	-4.025669	-1.080359	H	-3.804534	5.832642	-0.304482
C	-2.613311	-2.960968	-2.180504	C	-1.878955	6.175812	0.498017
C	-3.922212	-2.172764	-2.296764	C	-1.755669	7.364196	-0.235697
H	-3.811527	-1.387476	-3.0483	C	-0.66459	8.220311	-0.0596
H	-4.731957	-2.845156	-2.642076	C	0.328134	7.907453	0.870337
H	-2.388127	-3.418873	-3.152472	C	0.220392	6.728274	1.614341
H	-1.796087	-2.260937	-1.956174	C	-0.86546	5.871969	1.423528
H	-3.417255	-4.801874	-1.381951	H	-0.931548	4.96212	2.017227
H	-1.731123	-4.527053	-0.948582	H	0.97669	6.48231	2.356659
H	-6.381664	-1.390847	-1.449851	H	1.169467	8.578722	1.023745
H	-5.779801	-0.419686	-0.097909	H	-0.596842	9.136471	-0.641827
H	-5.187255	0.06185	-3.054489	H	-2.534133	7.624579	-0.95024
C	-6.800352	1.11952	-2.242079	C	-2.66741	4.25194	-1.925756
C	-7.193671	1.537899	-3.522565	C	-2.603249	2.929921	-2.70948
C	-8.436563	2.13336	-3.746885	H	-2.290645	3.163276	-3.738518
C	-9.331051	2.30445	-2.69	H	-1.814262	2.287045	-2.285497
C	-8.963351	1.883171	-1.410735	H	-3.554975	4.817411	-2.291001
C	-7.709788	1.308197	-1.190802	H	-1.802522	4.877038	-2.242507
H	-7.447209	0.993053	-0.184431	C	-3.910495	2.123146	-2.816985

Table A3.5 (Continued).

H	-9.65485	1.99996	-0.579524	H	-3.778901	1.429705	-3.678162
H	-10.305331	2.755232	-2.860686	H	-4.691509	2.833109	-3.162472
H	-8.709677	2.452022	-4.750144	O	1.188017	-1.047383	1.248091
H	-6.51566	1.381107	-4.358692	C	0.518947	-2.103011	1.995327
Li	-4.2536	2.797216	-0.201746	C	1.155194	-2.09508	3.384718
N	-2.725072	4.019112	-0.490209	C	1.494546	-0.608232	3.567857
Li	-0.922591	3.244779	-0.075524	C	1.940113	-0.201729	2.162678
O	-0.377374	1.715244	0.79222	H	3.009918	-0.390036	1.999587
C	-1.354514	1.039104	1.40271	H	1.700585	0.836667	1.921336
C	-1.770202	1.381834	2.68258	H	2.271126	-0.430442	4.318283
H	-1.269098	2.247898	3.109927	H	0.597398	-0.046788	3.847326
C	-2.721799	0.710187	3.544421	H	2.065829	-2.706729	3.398503
C	-2.996519	1.257124	4.826205	H	0.473097	-2.475947	4.150191
C	-3.89827	0.668016	5.706321	H	-0.548435	-1.863482	2.036193
C	-4.574126	-0.506161	5.357859	H	0.663617	-3.041771	1.450876
C	-4.313087	-1.073207	4.107336	O	0.647644	-0.3892	-1.809346
C	-3.412644	-0.487199	3.219401	C	0.860182	0.642615	-2.802305
H	-3.21083	-0.949333	2.261438	C	2.227999	0.327229	-3.402195
H	-4.816589	-1.995136	3.818583	C	2.221231	-1.210302	-3.407439
H	-5.278638	-0.96832	6.044305	C	1.459788	-1.551246	-2.11801
H	-4.074148	1.128815	6.676739	H	2.126251	-1.722622	-1.266844
H	-2.481706	2.169838	5.122518	H	0.800291	-2.418129	-2.228979
O	0.820977	3.846027	-0.937405	H	3.223851	-1.64738	-3.422243
C	1.033103	4.983674	-1.816692	H	1.679393	-1.581962	-4.284543
C	2.489952	5.427544	-1.606633	H	3.025209	0.707824	-2.752097
C	3.149079	4.178082	-0.999722	H	2.361297	0.760604	-4.397897
C	2.011205	3.614719	-0.15382	H	0.065792	0.584	-3.558054
H	1.925394	4.147787	0.802567	H	0.798223	1.608377	-2.295104
H	2.066163	2.543893	0.047221	H	0.312598	5.764111	-1.563768
H	4.041733	4.40471	-0.408505	C	-3.063029	5.226483	0.254871
H	3.430517	3.46524	-1.784941	C	-3.699729	4.816745	1.597421
H	2.529652	6.25905	-0.895251	N	-4.982733	4.091583	1.434471
H	2.961415	5.756187	-2.537656	C	-6.067788	5.040557	1.096095
H	0.844043	4.642618	-2.840604	H	-5.813507	5.544388	0.15901
C	-7.425909	4.351068	0.960249	H	-6.126374	5.822146	1.878934

Table A3.5 (Continued).





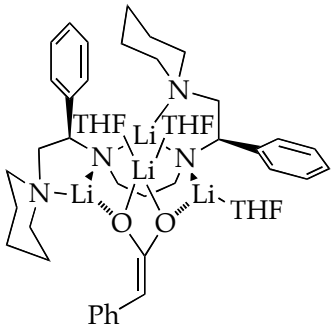
8i
G = -2535.011204
G_{MP2} = -2527.639386

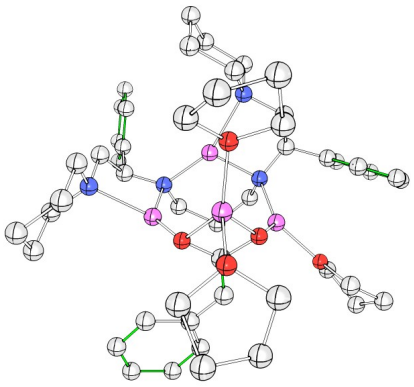
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	H	6.223917	-3.416042	1.88558
O	1.516065	0.607462	-1.001054	H	1.303899	-5.237511	-0.01609
Li	2.976728	0.490142	-2.220498	H	0.823836	-3.544351	-0.243095
N	3.975036	-1.061971	-3.062013	H	2.254339	-5.103986	-2.432154
C	5.345146	-0.546408	-3.068992	C	0.159215	-5.344445	-2.422894
H	5.46815	0.153646	-3.923199	C	-1.061857	-5.21216	-1.743471
C	6.446359	-1.59785	-3.290026	C	-2.171077	-5.987198	-2.085669
C	6.924547	-1.847456	-4.584547	C	-2.090731	-6.906238	-3.135658
C	7.896785	-2.820346	-4.827638	C	-0.887672	-7.045079	-3.829503
C	8.43026	-3.557857	-3.770505	C	0.222452	-6.277417	-3.468337
C	7.981767	-3.309963	-2.471307	H	1.162181	-6.406077	-4.001457
C	7.000093	-2.344843	-2.239929	H	-0.808499	-7.758813	-4.64614
H	6.675246	-2.158535	-1.219989	H	-2.953181	-7.511565	-3.403076
H	8.402083	-3.863836	-1.634806	H	-3.098832	-5.879756	-1.527488
H	9.192459	-4.310878	-3.954132	H	-1.149922	-4.497339	-0.928869
H	8.241997	-2.995951	-5.84383	C	1.745569	-3.236962	-4.127789
H	6.530807	-1.262432	-5.412729	C	2.159789	-1.862809	-4.688376
Li	3.061494	-2.381842	-1.91112	C	3.615114	-1.429255	-4.437966
N	1.433861	-3.173897	-2.701123	H	3.809688	-0.57179	-5.120185
Li	-0.113829	-1.906865	-2.635515	H	4.255664	-2.245369	-4.829945
O	-0.376614	-0.200681	-1.899668	H	2.028417	-1.888587	-5.779653
C	0.636209	0.648838	-2.004822	H	1.477529	-1.078896	-4.325437
C	0.82419	1.556438	-3.046376	H	2.574366	-3.95179	-4.33364
H	1.636918	2.266639	-2.893914	H	0.899882	-3.61916	-4.740247
C	0.035135	1.774225	-4.24656	N	4.795473	1.483712	-1.674299
C	0.39249	2.835572	-5.115884	C	4.782149	1.959488	-0.275413
C	-0.316694	3.110219	-6.279871	H	4.389937	1.14987	0.349815
C	-1.425406	2.336683	-6.637376	H	5.815261	2.169276	0.065717
C	-1.796938	1.283716	-5.798649	C	3.917749	3.210605	-0.107937
C	-1.090225	1.003657	-4.629795	H	3.944999	3.526704	0.943112
H	-1.396527	0.182872	-3.994305	H	2.88181	2.942256	-0.346716
H	-2.656139	0.666603	-6.05936	C	4.392576	4.33998	-1.029773
H	-1.981434	2.547956	-7.547004	C	4.471135	3.83056	-2.473547

Table A3.5 (Continued).

H	-0.001829	3.936221	-6.914743	C	5.304861	2.549898	-2.564443
H	1.251392	3.453654	-4.858051	H	5.301999	2.175737	-3.59144
O	-1.8896	-2.392533	-3.392837	H	6.357429	2.77733	-2.304233
C	-2.099872	-3.150917	-4.610971	H	4.913446	4.58795	-3.132762
C	-3.617786	-3.264151	-4.767643	H	3.459746	3.630718	-2.850392
C	-4.114783	-1.97745	-4.089981	H	5.387518	4.682283	-0.708484
C	-3.134439	-1.835235	-2.924313	H	3.722735	5.206085	-0.960438
H	-3.471948	-2.412387	-2.050844	C	5.624047	0.260618	-1.787629
H	-2.943565	-0.803588	-2.620029	H	6.695478	0.517972	-1.715827
H	-5.155252	-2.036441	-3.755522	H	5.384164	-0.366241	-0.919676
H	-4.023299	-1.123205	-4.770658	O	-0.360466	-1.298999	1.450677
H	-3.987314	-4.147346	-4.234234	C	-0.179532	-0.854191	2.82138
H	-3.921976	-3.346034	-5.815438	C	-1.222296	-1.609744	3.653347
H	-1.644868	-2.595458	-5.440065	C	-2.326963	-1.890924	2.622087
H	-1.597885	-4.113589	-4.501674	C	-1.509326	-2.173369	1.363613
C	1.393155	-4.492124	-2.084533	H	-2.030478	-1.949477	0.428644
C	1.54212	-4.307674	-0.56196	H	-1.162384	-3.214675	1.334726
N	2.890827	-3.824874	-0.175346	H	-2.95305	-1.00276	2.47804
C	3.828051	-4.97022	-0.108125	H	-2.974433	-2.728398	2.897936
H	3.856105	-5.451865	-1.08962	H	-1.569565	-1.024786	4.509757
H	3.436438	-5.718129	0.609105	H	-0.807112	-2.550927	4.03152
C	5.237896	-4.554688	0.31144	H	0.851596	-1.069036	3.118086
H	5.674123	-3.929476	-0.474389	H	-0.344145	0.228221	2.842803
H	5.862804	-5.453717	0.384488	O	-1.044151	1.616571	0.661544
C	5.223524	-3.795786	1.643858	C	-2.288339	1.841653	-0.061076
C	4.206473	-2.64889	1.585609	C	-2.394803	3.355556	-0.256887
C	2.83223	-3.1556	1.141517	C	-0.918364	3.776508	-0.315609
H	2.120718	-2.326807	1.067358	C	-0.283978	2.853117	0.722817
H	2.439901	-3.855908	1.906468	H	-0.367932	3.262727	1.739064
H	4.111541	-2.161489	2.564627	H	0.757468	2.604632	0.508728
H	4.551072	-1.88112	0.879204	H	-0.761567	4.834858	-0.085501
H	4.942894	-4.484784	2.454099	H	-0.501803	3.56266	-1.305305
H	-2.216652	1.309888	-1.015548	H	-2.897123	3.823441	0.598728
H	-3.106613	1.421584	0.534101	H	-2.950181	3.613636	-1.163085

Table A3.5 (Continued).





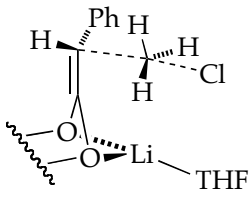
8j
G = -2535.010975
G_{MP2} = -2527.63918

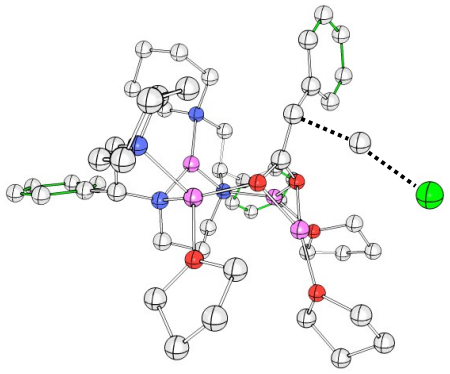
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	C	1.089688	-3.124875	-4.561188
O	0.852032	0.269542	-1.718964	C	2.5951	-2.828667	-4.429584
Li	2.336647	-0.516195	-2.547598	H	2.842835	-2.095594	-5.228936
N	3.0626	-2.32638	-3.127595	H	3.128717	-3.753155	-4.727154
C	4.484424	-1.992711	-3.238461	H	0.903128	-3.29035	-5.632381
H	4.647074	-1.345559	-4.128725	H	0.513568	-2.228448	-4.289378
C	5.43339	-3.183324	-3.463596	H	1.255303	-5.191828	-3.942663
C	5.824865	-3.531312	-4.764047	H	-0.384967	-4.681564	-4.301522
C	6.658987	-4.62502	-5.006337	N	4.300886	0.154383	-1.926293
C	7.136539	-5.391237	-3.942902	C	4.331058	0.648819	-0.534304
C	6.771768	-5.050387	-2.638694	H	3.799	-0.078008	0.090878
C	5.927973	-3.962486	-2.407579	H	5.375454	0.691343	-0.166781
H	5.668301	-3.707205	-1.383969	C	3.684282	2.02973	-0.404124
H	7.150714	-5.628059	-1.798534	H	3.736587	2.351895	0.644775
H	7.790825	-6.239781	-4.126041	H	2.624835	1.945082	-0.675621
H	6.938722	-4.874432	-6.027155	C	4.377693	3.047461	-1.318036
H	5.469715	-2.930784	-5.598666	C	4.413154	2.514118	-2.754895
Li	2.117814	-3.447053	-1.803144	C	5.010939	1.10632	-2.811233
N	0.346115	-4.057329	-2.375627	H	4.971251	0.722348	-3.834461
Li	-1.019654	-2.586933	-2.268584	H	6.0793	1.148064	-2.521913
O	-0.979136	-0.963467	-1.310729	H	5.005452	3.174109	-3.400937
C	-0.301251	-0.212876	-2.181962	H	3.398068	2.489878	-3.166556
C	-0.797601	0.02436	-3.458568	H	5.405429	3.215822	-0.963767
H	-1.736	-0.472	-3.690871	H	3.866216	4.017048	-1.278087
C	-0.222787	0.815929	-4.529367	C	4.928062	-1.186343	-2.004762
C	-0.803738	0.747635	-5.822054	H	6.027067	-1.093081	-1.968673
C	-0.315808	1.486213	-6.893584	H	4.620332	-1.737327	-1.10789
C	0.781163	2.33969	-6.732778	O	0.538679	-0.616398	1.804727
C	1.36492	2.437115	-5.468089	C	1.419728	0.207426	2.606091
C	0.879205	1.697977	-4.389212	C	0.678801	0.446791	3.921168
H	1.321363	1.814948	-3.406408	C	-0.118326	-0.857761	4.077752
H	2.207239	3.109902	-5.313463	C	-0.518308	-1.166179	2.63309
H	1.165004	2.916614	-7.569926	H	-1.46141	-0.677105	2.360695

Table A3.5 (Continued).

H	-0.794613	1.395008	-7.866784	H	-0.597392	-2.234703	2.415434
H	-1.658988	0.090616	-5.972327	H	-0.986359	-0.757718	4.73569
O	-2.818554	-2.770359	-3.107262	H	0.521692	-1.652779	4.477758
C	-3.161457	-3.572208	-4.262777	H	-0.000505	1.301142	3.824171
C	-4.587684	-3.161744	-4.63833	H	1.360134	0.641464	4.754617
C	-5.178897	-2.780311	-3.272562	H	2.359012	-0.338562	2.762523
C	-3.988732	-2.102266	-2.591433	H	1.630867	1.122793	2.046361
H	-3.987869	-2.204587	-1.502606	O	-1.031449	1.713069	0.437432
H	-3.924899	-1.035867	-2.841136	C	-2.452144	1.568312	0.171691
H	-5.467289	-3.682955	-2.721954	C	-2.736241	2.469524	-1.02762
H	-6.051381	-2.123407	-3.343139	C	-1.758224	3.6305	-0.791314
H	-5.133816	-3.967624	-5.137674	C	-0.530712	2.91062	-0.226172
H	-4.575922	-2.292122	-5.306023	H	0.017388	3.504947	0.512757
H	-2.426604	-3.368223	-5.046494	H	0.152544	2.584014	-1.015834
H	-3.100029	-4.628619	-3.981854	H	-2.16649	4.337252	-0.058372
C	0.123132	-5.261688	-1.589305	H	-1.522691	4.183447	-1.705043
C	0.465659	-4.941199	-0.120599	H	-3.782264	2.788653	-1.07347
N	1.913032	-4.68313	0.089247	H	-2.483253	1.941601	-1.953333
C	2.638275	-5.971624	0.186727	H	-2.639676	0.511304	-0.031229
H	2.484449	-6.525032	-0.74353	H	-3.009338	1.886139	1.064325
H	2.194629	-6.577621	1.000933	H	0.804833	-6.073646	-1.923053
C	4.134506	-5.793296	0.446433	C	-1.284586	-5.870054	-1.702413
H	4.596019	-5.323241	-0.428353	C	-2.381193	-5.368692	-0.983198
H	4.59317	-6.784427	0.552407	C	-3.653742	-5.925093	-1.120708
C	4.387042	-4.94316	1.697692	C	-3.864942	-6.991706	-1.999166
C	3.589761	-3.636476	1.612472	C	-2.788434	-7.497354	-2.729472
C	2.109494	-3.909003	1.332918	C	-1.514774	-6.944172	-2.573978
H	1.564136	-2.963985	1.237057	H	-0.677059	-7.355578	-3.133494
H	1.67413	-4.455408	2.193921	H	-2.936646	-8.329228	-3.414125
H	3.679534	-3.063444	2.544748	H	-4.855281	-7.427262	-2.106026
H	3.996295	-3.005764	0.809719	H	-4.481558	-5.531612	-0.534449
H	4.069337	-5.5023	2.590059	H	-2.242502	-4.535162	-0.29798
H	5.457874	-4.73808	1.818955	C	0.544924	-4.345649	-3.793825
H	0.124587	-5.742225	0.558636	H	-0.067164	-4.024174	0.156478

Table A3.6. Optimized geometries of transition state structures at B3LYP level of theory with 6-31G(d) basis set for the alkylation of phenylacetic acid with 3-chloropropene at –78 °C with free energies (Hartrees) and cartesian coordinates (X, Y, Z) (Note: G_{MP2} includes single point MP2 corrections to B3LYP/6-31G(d) optimized structures).





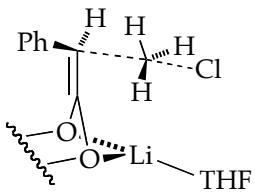
17a
G = -3035.060045
G_{MP2} = -3026.969463

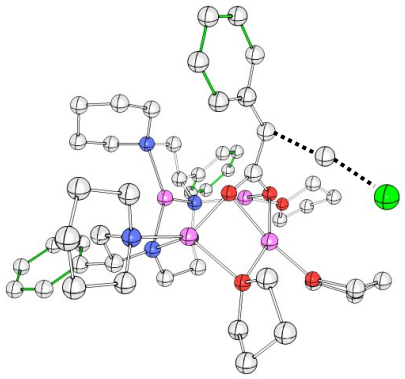
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	H	-2.976609	-1.191149	0.17048
O	1.628006	-0.445503	0.96275	H	-5.459306	-2.240339	-0.430883
Li	3.222884	-0.799599	-0.043209	H	-4.577142	-1.327654	-1.667682
N	3.619144	-2.585355	-1.026703	H	-4.58357	-4.375367	-1.28229
C	5.067723	-2.49801	-1.026103	H	-4.886998	-3.497222	-2.791361
C	5.552377	-2.324496	0.431847	H	-2.550783	-2.89439	-3.013771
N	5.20443	-1.004518	1.010535	H	-2.351578	-4.445792	-2.157707
C	5.052272	-1.10096	2.478195	C	0.751942	-5.803972	-0.492291
H	4.254983	-1.821822	2.686959	C	1.041091	-5.984387	1.010067
H	5.98151	-1.495992	2.933967	N	2.431726	-5.639308	1.401131
C	4.707225	0.250018	3.109729	C	3.349425	-6.747853	1.045337
H	4.621607	0.123994	4.196332	H	3.319611	-6.889669	-0.039187
H	3.723428	0.569108	2.743116	H	2.982557	-7.686969	1.503328
C	5.76227	1.308942	2.767904	C	4.787857	-6.492524	1.500948
C	5.966902	1.366716	1.249378	H	5.195252	-5.632986	0.955195
C	6.260028	-0.023598	0.682587	H	5.402717	-7.358168	1.224834
H	6.360702	0.020298	-0.406535	C	4.853015	-6.234138	3.01031
H	7.232093	-0.379049	1.078621	C	3.871919	-5.118184	3.386299
H	6.795827	2.038687	0.992281	C	2.465079	-5.418261	2.868673
H	5.065091	1.763742	0.769345	H	1.788884	-4.591532	3.105152
H	6.714311	1.047733	3.252793	H	2.073882	-6.314412	3.387096
H	5.467629	2.290725	3.158173	H	3.824324	-4.983088	4.473776
H	6.637582	-2.499369	0.515448	H	4.219209	-4.166044	2.963821
H	5.058126	-3.098454	1.029742	H	4.583176	-7.152883	3.551309
H	5.417291	-1.601791	-1.591818	H	5.874339	-5.975345	3.315524
C	5.850061	-3.669291	-1.664504	H	0.804558	-7.012743	1.334821
C	7.176543	-3.479473	-2.078506	H	0.384483	-5.309691	1.570656
C	7.922939	-4.522129	-2.627094	H	1.494485	-6.405634	-1.059259

Table A3.6 (Continued).

C	7.347853	-5.785525	-2.785396	C	-0.610147	-6.416332	-0.86169
C	6.024587	-5.986999	-2.392679	C	-0.775949	-7.041172	-2.10678
C	5.286644	-4.937338	-1.838723	C	-2.010775	-7.559753	-2.504537
H	4.249464	-5.090788	-1.554129	C	-3.111986	-7.479766	-1.650844
H	5.560128	-6.961462	-2.526354	C	-2.964177	-6.871066	-0.401452
H	7.922819	-6.599853	-3.218876	C	-1.731188	-6.338618	-0.017885
H	8.950894	-4.348357	-2.936726	H	-1.643484	-5.876519	0.96264
H	7.630639	-2.494994	-1.97084	H	-3.807983	-6.822671	0.283429
Li	2.579265	-3.880159	0.028908	H	-4.070674	-7.896424	-1.948939
N	0.88864	-4.391292	-0.822718	H	-2.108037	-8.037641	-3.476532
Li	-0.443909	-3.105683	-0.177147	H	0.082433	-7.128723	-2.769579
O	-0.234564	-1.651586	0.953517	C	1.068304	-4.157171	-2.251594
C	0.809175	-1.220781	1.624303	C	1.596101	-2.736598	-2.549284
C	0.912051	-1.343902	3.036588	H	1.338581	-2.484555	-3.589
H	1.843891	-0.960956	3.444399	H	1.060788	-2.01038	-1.914642
C	0.212013	-2.305537	3.892499	C	3.113674	-2.525736	-2.397582
C	0.74524	-2.580523	5.173064	H	3.356434	-1.547519	-2.874021
C	0.126261	-3.463872	6.053244	H	3.601124	-3.270628	-3.056526
C	-1.057477	-4.111594	5.690597	H	1.784741	-4.882336	-2.69702
C	-1.609036	-3.847719	4.435355	H	0.134296	-4.304003	-2.8374
C	-0.993462	-2.96181	3.550837	O	3.261834	0.99489	-1.111901
H	-1.445308	-2.754978	2.58857	C	2.609008	2.181313	-0.590338
H	-2.53883	-4.330904	4.141428	C	3.249334	3.363209	-1.320812
H	-1.54293	-4.801812	6.375164	C	3.610327	2.74292	-2.678734
H	0.571293	-3.647641	7.028582	C	4.053224	1.336354	-2.271743
H	1.666163	-2.084553	5.474099	H	5.115593	1.318359	-1.994604
C	-0.331256	0.58216	3.076031	H	3.880297	0.576838	-3.038137
H	0.484519	1.02649	2.534694	H	4.392927	3.288706	-3.214178
H	-1.091226	-0.005134	2.593162	H	2.726001	2.693978	-3.32552
H	-0.362567	0.679299	4.151422	H	4.156256	3.692622	-0.800385
O	-2.232401	-2.748795	-0.97	H	2.572852	4.219661	-1.396904
C	-2.805111	-3.45508	-2.105263	H	1.537515	2.107569	-0.803946
C	-4.314942	-3.483778	-1.858853	H	2.745419	2.200716	0.493333
C	-4.539765	-2.21437	-1.022796	O	-0.700609	1.052665	-1.406453
C	-3.288209	-2.188526	-0.147428	C	-1.16923	0.432901	-2.638867
H	-3.412296	-2.813172	0.746248	C	-2.195097	1.404431	-3.235565
H	-2.997379	0.880364	-3.763146	C	-2.682313	2.185189	-2.00409
H	-1.712076	2.082898	-3.948051	C	-1.405166	2.314005	-1.183737
H	-0.305741	0.257318	-3.28739	H	-1.555621	2.428349	-0.105747
H	-1.613279	-0.532946	-2.374491	H	-0.771014	3.130396	-1.553972
Cl	-1.590577	2.470727	2.598483	H	-3.43219	1.610867	-1.447344
H	-3.115702	3.157667	-2.254268				

Table A3.6 (Continued).





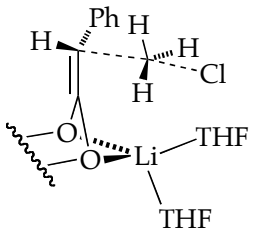
17b
G = -3035.060551
G_{MP2} = -3026.976046

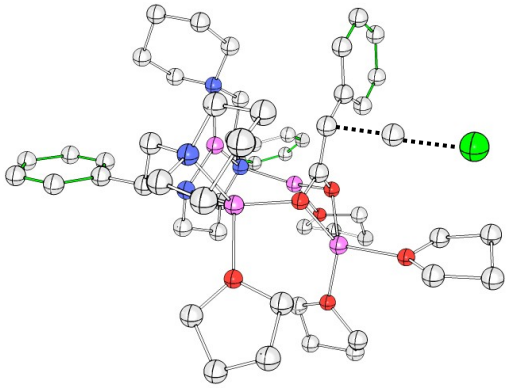
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	H	0.136408	-6.353928	0.472926
O	1.243113	-0.803076	1.527439	C	-1.9018	-6.11616	0.9782
Li	2.472514	-1.149587	0.151092	C	-2.306966	-7.003756	-0.02995
N	2.523352	-2.952854	-0.793688	C	-3.613745	-7.494271	-0.088768
C	3.934347	-3.075325	-1.109199	C	-4.54714	-7.117856	0.878485
H	4.198581	-2.429861	-1.979909	C	-4.160763	-6.240039	1.895032
C	4.44506	-4.476147	-1.523118	C	-2.858025	-5.738752	1.935499
C	5.646765	-4.600824	-2.235388	H	-2.583019	-5.058887	2.738152
C	6.150439	-5.850318	-2.596622	H	-4.872266	-5.954945	2.667031
C	5.448177	-7.010257	-2.260812	H	-5.56 -7.511344	0.848081	
C	4.242503	-6.902049	-1.567131	H	-3.898023	-8.18108	-0.882509
C	3.749414	-5.646145	-1.203506	H	-1.579349	-7.319981	-0.774492
H	2.801011	-5.559315	-0.681288	C	-0.365992	-4.410854	-1.157041
H	3.678067	-7.797132	-1.315455	C	0.222607	-3.173438	-1.869639
H	5.832241	-7.986163	-2.546617	H	-0.201201	-3.123523	-2.883673
H	7.085967	-5.919368	-3.146821	H	-0.121449	-2.262496	-1.349842
H	6.192811	-3.701576	-2.51909	C	1.753041	-3.140941	-2.023368
C	4.795482	-2.591628	0.081123	H	1.992727	-2.344851	-2.767993
N	4.606622	-1.148976	0.382624	H	2.028017	-4.078648	-2.54424
C	5.009868	-0.799328	1.766147	H	0.190741	-5.302016	-1.521578
H	4.639911	0.216628	1.964361	H	-1.401124	-4.564613	-1.536266
H	4.482571	-1.466341	2.454067	O	1.75888	0.688882	-0.862273
C	6.526529	-0.837443	2.014698	C	2.132678	1.964534	-0.235373
C	7.258647	0.078311	1.022453	C	2.300312	2.956623	-1.386366
C	6.85078	-0.256806	-0.42032	C	2.705633	2.053972	-2.562381
C	5.318932	-0.265222	-0.57127	C	1.866478	0.803592	-2.311231
H	5.034148	-0.54942	-1.588973	H	2.312679	-0.121961	-2.682056
H	4.946394	0.754478	-0.404178	H	0.85403	0.904133	-2.717838
H	7.272749	0.473113	-1.123297	H	3.77421	1.815229	-2.516726
H	7.262846	-1.233536	-0.705041	H	2.499046	2.499777	-3.539952
H	8.345549	-0.002854	1.145183	H	3.041599	3.72679	-1.155591
H	6.995946	1.124791	1.238775	H	1.349749	3.459109	-1.595737
H	6.894102	-1.867515	1.914689	H	1.355157	2.257947	0.475195
H	6.729625	-0.530434	3.048415	H	3.066443	1.800674	0.311513

Table A3.6 (Continued).

H	5.851015	-2.839268	-0.094011	O	-1.289419	0.903747	-1.200587
H	4.482794	-3.150879	0.970933	C	-1.677429	2.303291	-1.102909
Li	1.539786	-3.755406	0.743105	C	-3.201324	2.287062	-1.12361
N	-0.297955	-4.290255	0.294604	C	-3.49449	1.130794	-2.09252
Li	-1.478457	-2.772318	0.742264	C	-2.380402	0.127032	-1.766958
O	-0.95206	-1.076282	1.291798	H	-2.007329	-0.401273	-2.650984
C	0.085822	-0.950726	2.096875	H	-2.689078	-0.609252	-1.018579
C	-0.144415	-0.785154	3.490417	H	-3.41471	1.474632	-3.130424
H	-1.165372	-1.006323	3.793172	H	-4.490264	0.696321	-1.9604
C	0.842568	-0.82391	4.568647	H	-3.623603	3.242211	-1.448646
C	0.402043	-1.086951	5.886677	H	-3.586427	2.067058	-0.121516
C	1.281048	-1.101192	6.96565	H	-1.252854	2.717402	-0.184045
C	2.642722	-0.850042	6.774107	H	-1.272741	2.83982	-1.973008
C	3.09884	-0.57952	5.481867	Cl	-0.54216	3.601897	2.22691
C	2.221426	-0.564184	4.398059	C	-0.403559	1.472776	3.024666
H	2.588248	-0.348184	3.402972	H	-0.632706	1.717067	4.050656
H	4.153661	-0.369109	5.314504	H	0.628486	1.413765	2.729908
H	3.330892	-0.857844	7.615164	H	-1.196052	1.157234	2.369413
H	0.900837	-1.310431	7.963175	N	1.518102	-5.131363	2.491788
H	-0.655117	-1.283528	6.056098	C	2.291052	-6.384295	2.320362
O	-3.407385	-2.599522	0.37065	H	2.058614	-6.805254	1.337515
C	-4.2355	-1.861621	1.301712	H	1.958628	-7.124134	3.074299
C	-5.620104	-1.822425	0.658558	C	3.800295	-6.171075	2.45646
C	-5.675428	-3.184762	-0.051493	C	4.149016	-5.526144	3.802418
C	-4.236192	-3.363539	-0.544258	C	3.315766	-4.254872	3.997381
H	-4.094186	-2.948166	-1.55024	C	1.824369	-4.536641	3.816817
H	-3.898171	-4.401341	-0.535129	H	1.253839	-3.608707	3.916024
H	-6.401502	-3.218992	-0.869186	H	1.483713	-5.219539	4.618753
H	-5.927659	-3.977131	0.661318	H	3.624776	-3.494277	3.268075
H	-5.682454	-1.003836	-0.069089	H	3.474043	-3.817306	4.989488
H	-6.418205	-1.683582	1.393872	H	5.221704	-5.302961	3.858592
H	-4.257506	-2.398428	2.259662	H	3.930235	-6.233654	4.615628
H	-3.768509	-0.887035	1.456706	H	4.153246	-5.5369	1.634182
C	-0.46475	-5.566691	0.97721	H	4.303255	-7.139512	2.342314
C	0.064176	-5.418661	2.416842	H	-0.175977	-6.312267	3.019069
H	-0.446912	-4.568238	2.882257				

Table A3.6 (Continued).





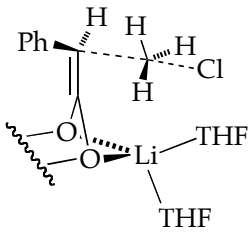
17c
G = -3267.413799
G_{MP2} = -3258.675739

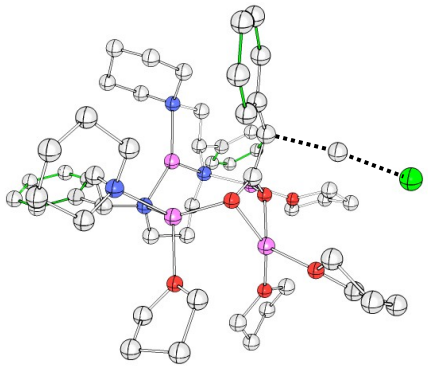
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	H	-5.586152	4.561791	2.330764
O	-1.653478	-0.685871	0.91617	H	-4.170463	3.503874	2.44487
Li	-3.253135	-1.461424	0.18477	H	-5.743536	3.928256	-0.138348
N	-4.87256	-0.364694	-0.523408	C	-4.148091	5.266823	0.214701
C	-5.84409	-1.44166	-0.535344	C	-4.558553	6.083025	-0.849061
C	-5.970927	-2.010734	0.896662	C	-3.976212	7.333414	-1.075861
N	-4.759327	-2.737753	1.344994	C	-2.972933	7.802303	-0.226464
C	-4.637252	-2.689237	2.817612	C	-2.554268	7.004201	0.84271
H	-4.592721	-1.636468	3.116916	C	-3.128532	5.749183	1.05348
H	-5.540442	-3.122718	3.290614	H	-2.787641	5.149425	1.894762
C	-3.393394	-3.431194	3.312842	H	-1.787414	7.366576	1.523959
H	-3.350576	-3.373972	4.407229	H	-2.529383	8.78168	-0.387552
H	-2.50043	-2.922689	2.929748	H	-4.315801	7.945022	-1.908587
C	-3.394215	-4.89152	2.844854	H	-5.354292	5.732972	-1.503747
C	-3.595171	-4.949642	1.326146	C	-4.092463	2.605937	-1.523404
C	-4.829215	-4.147932	0.907297	C	-3.581929	1.231007	-2.003472
H	-4.947636	-4.164353	-0.180142	H	-3.309684	1.318594	-3.066341
H	-5.734031	-4.624548	1.334188	H	-2.656653	0.980511	-1.461916
H	-3.71152	-5.987409	0.987326	C	-4.563673	0.051712	-1.889447
H	-2.714664	-4.537463	0.818755	H	-4.126703	-0.789664	-2.476969
H	-4.211884	-5.435495	3.340151	H	-5.469302	0.333508	-2.461735
H	-2.460893	-5.388356	3.134547	H	-5.14529	2.715303	-1.865443
H	-6.85816	-2.658368	0.991741	H	-3.543373	3.39109	-2.090646
H	-6.12343	-1.159265	1.569389	O	-2.316566	-2.783436	-1.18122
H	-5.502365	-2.281721	-1.185848	C	-0.917135	-3.099664	-0.998251
C	-7.259083	-1.118985	-1.067866	C	-0.681179	-4.385187	-1.790266
C	-8.103573	-2.159471	-1.482574	C	-1.642916	-4.199274	-2.973229
C	-9.394332	-1.906911	-1.946359	C	-2.845098	-3.525029	-2.304635
C	-9.866236	-0.59387	-2.018717	H	-3.558617	-4.267932	-1.927478
C	-9.033357	0.453428	-1.624436	H	-3.379319	-2.830358	-2.958097
C	-7.744006	0.189823	-1.153941	H	-1.91385	-5.136495	-3.468282
H	-7.089143	1.006003	-0.862684	H	-1.19854	-3.535554	-3.724753
H	-9.384075	1.480981	-1.690339	H	-0.966538	-5.261148	-1.196019

Table A3.6 (Continued).

H	-10.868766	-0.390422	-2.386514	H	0.36374	-4.505713	-2.092924
H	-10.03013	-2.73283	-2.256938	H	-0.316043	-2.272723	-1.397224
H	-7.740609	-3.186037	-1.442883	H	-0.727968	-3.187224	0.07381
Li	-4.865096	1.185066	0.692279	O	0.591348	0.119701	-1.92552
N	-3.981469	2.762929	-0.074944	C	-0.062837	0.942277	-2.932048
Li	-2.019792	2.700617	0.276412	C	0.945086	1.098137	-4.081852
O	-0.883016	1.392917	1.062711	C	2.292165	0.800824	-3.403681
C	-1.525649	0.400348	1.628814	C	1.896591	-0.27643	-2.398769
C	-1.948371	0.425064	2.992642	H	2.545883	-0.353203	-1.526226
C	-1.926587	1.570938	3.902839	H	1.824916	-1.261834	-2.882549
C	-2.615072	1.466598	5.13585	H	2.668556	1.6873	-2.879034
C	-2.596014	2.487119	6.082379	H	3.063185	0.464079	-4.103069
C	-1.883905	3.664983	5.841296	H	0.900017	2.091554	-4.537512
C	-1.184019	3.787085	4.639479	H	0.749134	0.361442	-4.869179
C	-1.197136	2.765241	3.688656	H	-0.989331	0.450948	-3.238964
H	-0.625793	2.867829	2.774258	H	-0.311426	1.89493	-2.456129
H	-0.606517	4.688111	4.440313	H	-2.667944	-0.349368	3.242785
H	-1.866937	4.46343	6.577968	C	-0.290267	-0.890926	3.793806
H	-3.139088	2.360105	7.016262	H	-0.50064	-1.552769	2.973167
H	-3.16808	0.553208	5.34992	H	0.41365	-0.084678	3.67943
O	-0.67846	3.827981	-0.687917	H	-0.83966	-0.966004	4.716684
C	-0.912692	4.800152	-1.741096	O	1.771962	-0.492261	0.783164
C	0.253132	5.789801	-1.665138	C	2.295436	-1.814765	1.099312
C	1.379037	4.932716	-1.066147	C	2.552222	0.523151	1.466893
C	0.611672	4.059047	-0.074947	C	3.682106	-1.57401	1.691436
H	0.463968	4.577667	0.881525	H	1.640756	-2.289214	1.835776
H	1.064642	3.086031	0.124254	H	2.304528	-2.395433	0.17031
H	2.163876	5.522299	-0.582825	C	3.488675	-0.230848	2.412987
H	1.847578	4.31305	-1.841238	H	3.110103	1.092459	0.709023
H	0.001059	6.615387	-0.991329	H	1.856808	1.198149	1.973317
H	0.502412	6.212986	-2.642869	H	4.440478	-1.495094	0.901692
H	-0.927005	4.261646	-2.697595	H	3.96676	-2.374934	2.378265
H	-1.887815	5.259595	-1.577379	H	4.425814	0.309023	2.580671
C	-4.782507	3.880218	0.414257	H	3.004034	-0.411754	3.37689
C	-5.109766	3.661284	1.904124	Cl	1.326092	-2.328473	4.577182
N	-5.95795	2.470547	2.169208	C	-5.89041	2.171365	3.620296
C	-7.364623	2.740607	1.789214	H	-4.846226	1.979581	3.878666
H	-7.404454	2.939406	0.714147	H	-6.205414	3.063082	4.196209
H	-7.711626	3.659942	2.30023	H	-6.676043	0.831569	5.105982
C	-8.304466	1.582951	2.138605	H	-6.401366	0.074813	3.537663
H	-8.041885	0.706412	1.535386	H	-8.635512	2.059357	4.224771
H	-9.326095	1.863296	1.853044	H	-8.847177	0.349394	3.847511
C	-8.230279	1.229328	3.627581	C	-6.770017	0.988075	4.023982

Table A3.6 (Continued).





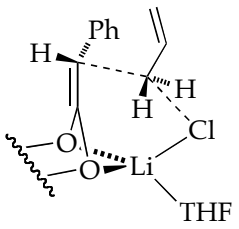
17d
G = -3267.405532
G_{MP2} = -3258.666802

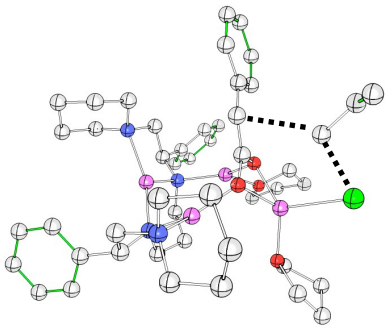
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	C	-0.565006	8.674472	-0.148544
O	-1.610023	-0.176882	1.216373	C	0.432638	8.810591	0.818015
Li	-3.158941	0.098177	0.033102	C	0.48032	7.905316	1.881246
N	-4.04835	1.887319	-0.599535	C	-0.452425	6.869247	1.967271
C	-5.397805	1.405681	-0.827697	H	-0.390817	6.17919	2.805113
H	-5.423323	0.666827	-1.664978	H	1.239343	8.011976	2.653159
C	-6.466818	2.449463	-1.230337	H	1.158063	9.617267	0.750601
C	-7.652455	2.028609	-1.850797	H	-0.619615	9.375451	-0.978163
C	-8.655063	2.934733	-2.195374	H	-2.29698	7.567008	-0.787621
C	-8.484869	4.29687	-1.936005	C	-2.134848	4.470848	-1.067704
C	-7.304605	4.734294	-1.334477	C	-2.130904	3.092729	-1.765273
C	-6.308772	3.817397	-0.986995	H	-1.775936	3.237254	-2.797648
H	-5.38169	4.163638	-0.539315	H	-1.398693	2.433941	-1.274876
H	-7.152272	5.794212	-1.143349	H	-3.037791	5.021415	-1.413802
H	-9.259551	5.008783	-2.209208	H	-1.284988	5.062649	-1.475646
H	-9.565889	2.579991	-2.672196	C	-3.488127	2.371364	-1.863398
H	-7.789643	0.970287	-2.071177	H	-3.360998	1.535303	-2.590991
Li	-3.527878	3.098067	0.866555	H	-4.175278	3.069756	-2.379361
N	-2.102289	4.356122	0.386865	N	-5.156256	-0.597459	0.677343
Li	-0.421685	3.394018	0.782461	C	-5.065105	-0.952577	2.112118
O	-0.26118	1.585345	1.135899	H	-4.327787	-1.759789	2.197223
C	-1.037152	0.805756	1.852388	H	-4.645347	-0.101784	2.654278
C	-1.067951	0.997483	3.269297	C	-6.387252	-1.41675	2.740448
C	-1.831063	0.237359	4.257975	C	-6.954291	-2.613557	1.963059
C	-2.098203	0.816559	5.520615	C	-7.053061	-2.280287	0.466828
C	-2.749231	0.112843	6.530931	C	-5.713933	-1.744161	-0.074017
C	-3.156367	-1.207654	6.324693	H	-5.818527	-1.45289	-1.124126
C	-2.887567	-1.806701	5.091209	H	-4.968363	-2.55036	-0.034854
C	-2.237926	-1.104319	4.077074	H	-7.341127	-3.167446	-0.112719
H	-2.036438	-1.582482	3.125533	H	-7.845495	-1.537395	0.307626
H	-3.179809	-2.840888	4.918195	H	-7.933895	-2.911339	2.357061
H	-3.660434	-1.761412	7.112244	H	-6.28564	-3.477266	2.098225
H	-2.934142	0.59724	7.487337	H	-7.114211	-0.592603	2.740566
H	-1.771629	1.838004	5.708929	H	-6.208592	-1.680594	3.790037

Table A3.6 (Continued).

O	1.44812	4.013915	0.533789	O	-2.596912	-1.297816	-1.489496
C	2.493926	3.54933	1.432699	C	-2.024295	-2.566949	-1.083357
C	3.766754	4.26614	0.983528	C	-2.174692	-3.507324	-2.284116
C	3.216534	5.594044	0.440657	C	-3.415024	-2.941168	-2.992063
C	1.915046	5.155715	-0.22997	C	-3.238142	-1.438507	-2.777072
H	2.086622	4.829959	-1.265271	H	-4.173378	-0.875283	-2.752469
H	1.13364	5.91693	-0.218232	H	-2.592076	-0.999031	-3.548504
H	3.895583	6.094217	-0.256515	H	-4.329815	-3.292726	-2.502216
H	2.999929	6.286658	1.261315	H	-3.470944	-3.208603	-4.051543
H	4.265586	3.701482	0.186537	H	-2.286585	-4.552492	-1.980908
H	4.479181	4.390334	1.80384	H	-1.297779	-3.439946	-2.939465
H	2.217941	3.824014	2.458025	H	-0.985266	-2.399784	-0.791524
H	2.545572	2.460969	1.368392	H	-2.578085	-2.928966	-0.209069
C	-2.504797	5.585474	1.056625	O	0.679172	0.524951	-1.811828
C	-2.880311	5.24451	2.510897	C	0.132267	0.196509	-3.109633
N	-4.06486	4.356877	2.628982	C	1.061234	0.854985	-4.132296
C	-5.308823	5.150864	2.486869	C	1.557846	2.088567	-3.362562
H	-5.313034	5.616005	1.496904	C	1.709458	1.536489	-1.945282
H	-5.303849	5.972711	3.229107	H	1.559567	2.2776	-1.157183
C	-6.572982	4.309533	2.676699	H	2.687356	1.056552	-1.806427
C	-6.566279	3.597745	4.034235	H	0.802016	2.881308	-3.38459
C	-5.26125	2.811959	4.198973	H	2.495482	2.494374	-3.754205
C	-4.043118	3.703693	3.960167	H	0.542779	1.103999	-5.062843
H	-3.128013	3.108415	4.028085	H	1.899912	0.191927	-4.376014
H	-3.995983	4.475568	4.752866	H	0.087942	-0.893658	-3.196946
H	-5.239941	1.977742	3.485952	H	-0.884324	0.600518	-3.168756
H	-5.182516	2.368291	5.198248	C	-5.904036	0.65775	0.42827
H	-7.434951	2.934576	4.128404	H	-6.986415	0.483521	0.356035
H	-6.647971	4.342777	4.839298	H	-5.749634	1.316086	1.290442
H	-6.645179	3.573579	1.867005	O	1.226211	-1.563129	0.340753
H	-7.44745	4.965298	2.581838	C	1.072379	-2.662352	1.269389
H	-3.03674	6.161147	3.105606	C	2.63551	-1.462069	-0.013906
H	-2.037713	4.706388	2.960513	C	2.129511	-3.669288	0.833006
H	-3.407319	6.011015	0.565402	H	1.273591	-2.313418	2.286961
C	-1.469993	6.723193	1.010067	H	0.039958	-3.010554	1.195464
C	-1.507243	7.648691	-0.043789	C	3.314013	-2.74103	0.511246
H	3.864606	-2.508274	1.426928	H	2.681063	-1.366965	-1.103138
H	-0.781826	2.000988	3.576986	H	3.054025	-0.56871	0.458548
C	1.081024	0.28805	3.543195	H	1.795905	-4.214491	-0.059014
H	0.72509	-0.720824	3.435823	H	2.361746	-4.396212	1.616837
H	1.281971	0.900204	2.684752	H	4.007566	-3.170742	-0.218079
H	1.124149	0.705653	4.536714	Cl	3.27319	-0.38769	3.550725

Table A3.6 (Continued).



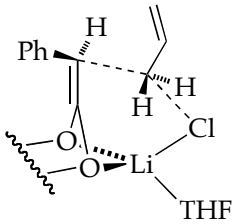


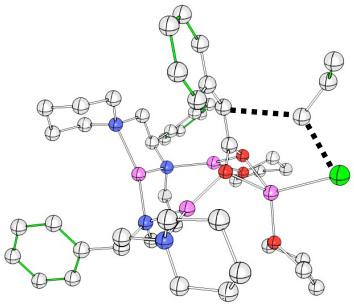
17e
G = -2880.08639
G_{MP2} = -2872.408896

Atom	X	Y	Z	Atom	X	Y	Z
C	0	0	0	C	4.183351	-2.759912	2.066556
Li	-0.763328	1.245009	-1.770106	C	2.815053	-3.294967	1.640044
O	0.755585	0.953792	-0.501951	H	2.060917	-2.502921	1.683465
Li	2.391543	0.67493	-1.315514	H	2.494493	-4.083331	2.347163
N	3.52202	-0.639777	-2.312615	H	4.113728	-2.376771	3.092275
C	4.827343	0.028422	-2.284812	H	4.452982	-1.907467	1.426007
C	5.040329	0.763695	-0.947669	H	5.057811	-4.626543	2.710465
N	4.030623	1.816501	-0.690841	H	6.251518	-3.43767	2.19368
C	4.028276	2.190032	0.740582	H	1.33946	-5.342504	0.361708
H	3.84424	1.28096	1.324459	H	0.758231	-3.671796	0.337302
H	5.026347	2.569836	1.033476	H	2.116319	-4.967122	-2.071976
C	2.958388	3.238726	1.05525	C	0.021013	-5.231002	-1.967294
H	3.012661	3.49339	2.121383	C	0.03337	-6.092775	-3.073892
H	1.974126	2.793351	0.868137	C	-1.100473	-6.821376	-3.443022
C	3.137928	4.489977	0.187156	C	-2.276003	-6.71173	-2.69845
C	3.207472	4.091178	-1.291735	C	-2.304798	-5.862938	-1.588104
C	4.272099	3.014984	-1.522996	C	-1.172552	-5.126617	-1.232852
H	4.280697	2.713465	-2.574354	H	-1.219401	-4.481199	-0.358302
H	5.273751	3.43031	-1.297944	H	-3.20781	-5.784915	-0.986588
H	3.437158	4.960004	-1.921425	H	-3.155756	-7.28897	-2.971657
H	2.229483	3.708622	-1.614511	H	-1.060798	-7.482834	-4.30538
H	4.068631	5.00491	0.468017	H	0.951622	-6.199244	-3.648057
H	2.319513	5.200122	0.357067	C	1.516989	-2.958014	-3.556716
H	6.059069	1.186574	-0.901846	C	1.799385	-1.511243	-4.002446
H	4.955	0.04069	-0.12749	H	1.664886	-1.459902	-5.093329
H	4.857268	0.800998	-3.082897	H	1.044973	-0.835337	-3.569825
C	6.039465	-0.86717	-2.592869	C	3.204863	-0.955156	-3.712332
C	6.572645	-0.899891	-3.889108	H	3.316891	-0.040405	-4.337471
C	7.653903	-1.722696	-4.212527	H	3.926007	-1.674024	-4.151465
C	8.240347	-2.524518	-3.233368	H	2.393802	-3.581481	-3.846111
C	7.733123	-2.49444	-1.932455	H	0.687034	-3.354235	-4.182628
C	6.643891	-1.678632	-1.621525	O	-0.377711	1.673095	-3.645387
H	6.272013	-1.664631	-0.600734	C	-1.165021	1.04261	-4.679325
H	8.190398	-3.103012	-1.155754	C	-2.064538	2.15722	-5.202631
H	9.086619	-3.161371	-3.47767	C	-1.106298	3.361803	-5.187966
H	8.040744	-1.73165	-5.22875	C	-0.204319	3.080522	-3.971268

Table A3.6 (Continued).

H	6.133067	-0.264642	-4.655245	H	-0.505921	3.651835	-3.089132
Li	2.860796	-2.246592	-1.311782	H	0.855557	3.2616	-4.180507
N	1.247171	-3.034751	-2.125359	H	-1.629664	4.317152	-5.094708
Li	-0.445874	-2.021537	-1.886718	H	-0.513956	3.389376	-6.109469
O	-0.852218	-0.545287	-0.82766	H	-2.896072	2.320722	-4.509086
O	-2.107993	-2.118192	-2.991391	H	-2.468931	1.944493	-6.197135
C	-2.334238	-2.978588	-4.140063	H	-0.494371	0.65807	-5.460538
C	-3.851091	-3.180538	-4.225303	H	-1.689094	0.199986	-4.221546
C	-4.398065	-1.921353	-3.534478	C	0.023114	-0.262856	1.389702
C	-3.375931	-1.706737	-2.421241	H	0.777483	0.28883	1.944575
H	-3.596293	-2.338045	-1.550392	C	-0.682551	-1.294305	2.125079
H	-3.272861	-0.672948	-2.086697	C	-0.338565	-1.514766	3.483097
H	-5.414508	-2.04467	-3.148961	C	-0.975294	-2.478903	4.256589
H	-4.396935	-1.068276	-4.223802	C	-1.990768	-3.27075	3.711555
H	-4.142407	-4.078606	-3.669923	C	-2.354706	-3.067811	2.377855
H	-4.196118	-3.293797	-5.257492	C	-1.720475	-2.103903	1.595955
H	-1.938635	-2.463336	-5.023928	H	-2.029168	-1.946081	0.569826
H	-1.782363	-3.908774	-3.992947	H	-3.151929	-3.665089	1.939202
C	1.269288	-4.405345	-1.622777	H	-2.489214	-4.025067	4.314163
C	1.495764	-4.352622	-0.099876	H	-0.677388	-2.614641	5.294062
N	2.840177	-3.83113	0.258798	H	0.447403	-0.906277	3.926693
C	3.837834	-4.922932	0.168581	C	-1.830182	1.833215	0.99375
H	3.839845	-5.306985	-0.855954	H	-2.173764	0.903209	0.576963
H	3.524374	-5.756917	0.825756	H	-0.84111	2.181688	0.74461
C	5.245026	-4.471271	0.560762	C	-2.540984	2.435992	2.084358
H	5.608504	-3.748397	-0.177768	H	-3.506192	2.01188	2.352309
H	5.91819	-5.336747	0.514328	C	-2.054735	3.484848	2.779654
C	5.260302	-3.84691	1.961743	H	-1.097892	3.934342	2.525586
Cl	-2.545545	2.770369	-1.152009	H	-2.595896	3.918909	3.615108





17f
G = -2880.085075
G_{MP2} = -2872.41204

Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	H	4.512683	3.941116	-0.168649
O	-1.80965	0.209538	0.987624	H	3.735831	3.235756	-1.599103
Li	-3.131848	0.506057	-0.295215	H	3.19983	5.999837	-0.375494

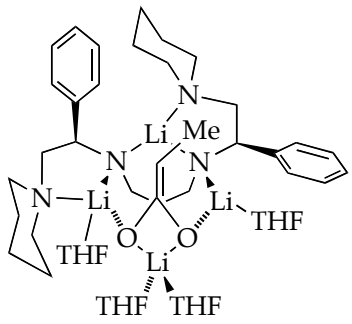
Table A3.6 (Continued).

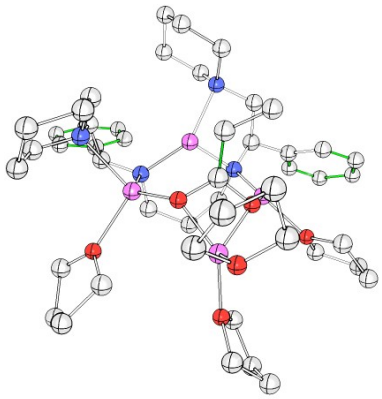
N	-4.183802	1.92439	-1.247337	H	3.53387	5.642019	-2.078399
C	-5.377198	1.184374	-1.672349	H	1.316958	4.748524	-2.417194
C	-5.701191	0.034346	-0.700017	H	0.926608	5.844115	-1.066877
N	-4.607386	-0.957571	-0.571445	C	-2.503167	5.517309	0.814557
C	-4.882886	-1.864024	0.56505	C	-3.099626	5.070304	2.163901
H	-5.01029	-1.24868	1.461831	N	-4.451488	4.473309	2.027713
H	-5.838831	-2.396954	0.396565	C	-5.464589	5.54539	1.891207
C	-3.757223	-2.879431	0.774731	H	-5.228564	6.137095	1.001783
H	-4.016838	-3.530014	1.619182	H	-5.392099	6.226537	2.761416
H	-2.840478	-2.342132	1.046499	C	-6.88994	5.000106	1.790236
C	-3.517118	-3.704626	-0.494856	H	-6.996392	4.443419	0.852553
C	-3.300064	-2.765448	-1.686618	H	-7.586272	5.846774	1.735894
C	-4.437525	-1.747307	-1.81054	C	-7.228405	4.093601	2.981039
H	-4.232234	-1.061936	-2.636835	C	-6.143509	3.024077	3.155026
H	-5.382019	-2.273204	-2.050838	C	-4.753514	3.656938	3.227943
H	-3.227977	-3.331456	-2.624226	H	-3.987518	2.882291	3.317792
H	-2.350162	-2.22804	-1.561573	H	-4.686922	4.285754	4.136575
H	-4.391244	-4.342985	-0.690532	H	-6.310596	2.433317	4.06346
H	-2.657028	-4.372543	-0.366195	H	-6.174223	2.32042	2.310952
H	-6.637362	-0.464185	-1.00724	H	-7.286093	4.699856	3.896922
H	-5.869109	0.444412	0.30367	H	-8.214771	3.631601	2.847676
H	-5.177446	0.716079	-2.658219	H	-3.124893	5.906756	2.884244
C	-6.639016	2.028302	-1.924391	H	-2.450874	4.293937	2.583534
C	-6.964269	2.418708	-3.231521	H	-3.229863	6.202703	0.331442
C	-8.093826	3.193996	-3.502482	C	-1.241518	6.364868	1.037963
C	-8.939709	3.583183	-2.463919	C	-1.056709	7.565367	0.337565
C	-8.639599	3.193805	-1.156841	C	0.105375	8.327057	0.490612
C	-7.499307	2.432476	-0.892819	C	1.109438	7.905329	1.363619
H	-7.288953	2.13922	0.132335	C	0.941119	6.712997	2.074286
H	-9.298259	3.479135	-0.339877	C	-0.216251	5.951072	1.905954
H	-9.82586	4.178192	-2.669244	H	-0.326993	5.029144	2.47392
H	-8.315822	3.486133	-4.526113	H	1.707722	6.382538	2.77169
H	-6.322554	2.10046	-4.05045	H	2.007657	8.502625	1.498326
Li	-3.942676	3.276705	0.228169	H	0.220564	9.254612	-0.065306
N	-2.291661	4.332945	-0.008891	H	-1.842	7.91047	-0.332149
Li	-0.548235	3.394216	0.247007	C	-2.270074	4.638311	-1.433986
O	-0.18406	1.726684	0.969969	C	-2.313258	3.354085	-2.281461
C	-1.150821	1.135661	1.640252	H	-1.989673	3.609595	-3.301528
C	-1.301374	1.396343	3.021826	H	-1.573235	2.634703	-1.896001
H	-0.666994	2.193261	3.4014	C	-3.677277	2.654124	-2.418311
C	-2.260809	0.848702	3.95797	H	-3.585269	1.955592	-3.280448
C	-2.301401	1.369253	5.277115	H	-4.392335	3.425677	-2.771266
C	-3.194344	0.890371	6.229445	H	-3.131829	5.276173	-1.736314
C	-4.086854	-0.139324	5.913705	H	-1.377949	5.225471	-1.747665
C	-4.054435	-0.681378	4.626109	O	0.170488	-0.183056	-1.945119
C	-3.163581	-0.204999	3.665774	C	0.732386	0.901549	-2.719399

Table A3.6 (Continued).

H	-3.144665	-0.638116	2.674388	C	1.9979	0.315443	-3.337505
H	-4.732059	-1.492261	4.364752	C	1.545574	-1.115097	-3.675853
H	-4.785359	-0.514547	6.656742	C	0.572827	-1.45436	-2.533371
H	-3.194431	1.323421	7.227467	H	1.041461	-2.039053	-1.737563
H	-1.614776	2.17091	5.542707	H	-0.3246	-1.974009	-2.883894
O	1.224985	3.851208	-0.557696	H	2.376368	-1.824224	-3.728434
C	1.552658	5.005196	-1.377775	H	1.028675	-1.129647	-4.642123
C	3.051177	5.263409	-1.172473	H	2.806777	0.299278	-2.5983
C	3.576006	3.887495	-0.731587	H	2.338097	0.876478	-4.213422
C	2.415202	3.371937	0.113881	H	0.01154	1.207083	-3.489934
H	2.446752	3.788797	1.129301	H	0.900486	1.741871	-2.041386
H	2.341495	2.285598	0.184518	Cl	1.646815	-1.56976	0.942982
H	2.173606	-0.645331	4.431332	C	0.668601	-0.540433	2.871059
C	0.565465	-1.9517	4.853148	H	1.03692	0.376851	2.446463
H	-0.394259	-2.356395	4.542793	H	-0.28321	-0.921948	2.541074
H	0.959795	-2.293862	5.805483	C	1.218205	-1.045187	4.098051

Table A3.7. Optimized geometries of dilithium amide-enediolate complexes at B3LYP level of theory with 6-31G(d) basis set for the enolization of various acids at –78 °C with free energies (Hartrees) and cartesian coordinates (X, Y, Z) (Note: G_{MP2} includes single point MP2 corrections to B3LYP/6-31G(d) optimized structures).





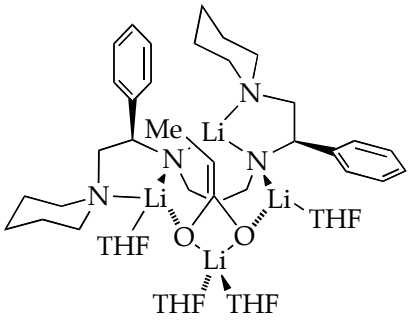
18a
G = -2575.657905
G_{MP2} = -2568.18801

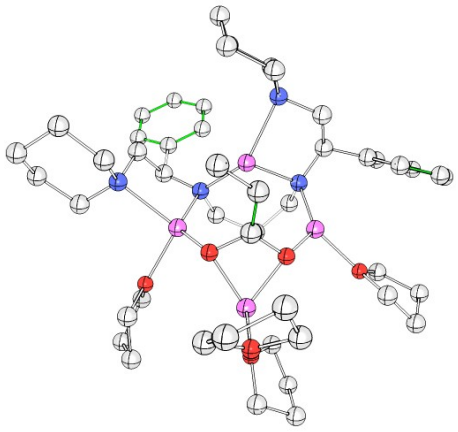
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	C	-4.161606	4.907775	2.930294
O	-1.82639	0.2386	0.559739	H	-3.36353	4.232431	3.246546
Li	-3.402603	0.42819	-0.43807	H	-4.058697	5.84401	3.514917
N	-4.14102	2.185068	-1.24634	H	-5.608379	4.11419	4.309965
C	-5.521166	1.780265	-1.410576	H	-5.583832	3.29897	2.746876
C	-6.080183	1.344123	-0.036167	H	-6.68608	6.105809	3.308111
N	-5.463815	0.096007	0.468529	H	-7.636818	4.686747	2.868379
C	-5.436723	0.072296	1.943925	H	-2.676872	6.872451	1.712832
H	-4.891277	0.957559	2.28389	H	-1.935586	5.279315	1.9354
H	-6.46612	0.138051	2.350573	H	-2.890723	6.321611	-0.770581
C	-4.752541	-1.191397	2.47131	C	-0.892268	6.76425	-0.247576
H	-4.761088	-1.173434	3.568732	C	-0.760017	7.626341	-1.345769
H	-3.703356	-1.169994	2.151044	C	0.361148	8.447044	-1.499324
C	-5.443532	-2.455631	1.944595	C	1.37447	8.435255	-0.539899
C	-5.557302	-2.394289	0.416167	C	1.258296	7.586104	0.565245
C	-6.198836	-1.079194	-0.033435	C	0.144948	6.755203	0.700286
H	-6.230403	-1.023989	-1.125818	H	0.078958	6.098252	1.564458
H	-7.249725	-1.045015	0.319574	H	2.032641	7.579083	1.329631
H	-6.154319	-3.234088	0.036489	H	2.240062	9.084602	-0.645527
H	-4.561038	-2.468283	-0.035532	H	0.435937	9.103952	-2.363023
H	-6.450971	-2.530304	2.38039	H	-1.555327	7.656837	-2.08787
H	-4.898991	-3.356284	2.256496	C	-1.882842	4.359906	-2.02386
H	-7.177996	1.24267	-0.065183	C	-2.067676	2.904549	-2.504009
H	-5.850908	2.146876	0.673189	H	-1.664304	2.82583	-3.525709
H	-5.605713	0.893568	-2.085373	H	-1.462729	2.230533	-1.876962
C	-6.494973	2.806768	-2.035509	C	-3.51644	2.387584	-2.54999
C	-7.71429	2.37646	-2.579025	H	-3.503983	1.441942	-3.142756
C	-8.624073	3.27928	-3.129316	H	-4.083344	3.093851	-3.188884
C	-8.322295	4.643106	-3.160063	H	-2.692572	4.969312	-2.48285

Table A3.7 (Continued).

C	-7.106666	5.085126	-2.63684	H	-0.951095	4.756875	-2.488689
C	-6.204569	4.174067	-2.080575	O	-3.195446	-1.199396	-1.85092
H	-5.251643	4.511553	-1.683693	C	-2.118949	-2.141784	-1.64599
H	-6.854462	6.142949	-2.668966	C	-2.356855	-3.275337	-2.647735
H	-9.023836	5.350857	-3.594916	C	-3.038862	-2.532811	-3.806192
H	-9.565106	2.919395	-3.539515	C	-3.91688	-1.529691	-3.056123
H	-7.952739	1.313167	-2.572357	H	-4.882611	-1.976902	-2.783304
Li	-3.394922	3.406258	0.140872	H	-4.102762	-0.604463	-3.606504
N	-1.889176	4.472881	-0.569839	H	-3.618122	-3.186955	-4.465009
Li	-0.324387	3.380016	0.009126	H	-2.293646	-2.007649	-4.415803
O	-0.150125	1.718602	0.798075	H	-3.034064	-4.028908	-2.22795
C	-1.3156	1.247524	1.274687	H	-1.428661	-3.778094	-2.937689
C	-1.874517	1.743361	2.432137	H	-1.167383	-1.63239	-1.835566
H	-2.741836	1.227483	2.834113	H	-2.140982	-2.462855	-0.601192
C	-1.120812	2.6815	3.346738	O	0.868099	-1.309472	1.324698
H	-1.748138	2.999619	4.189586	C	1.521804	-0.605739	2.416839
H	-0.213425	2.232438	3.790085	C	0.695572	-0.923326	3.662506
H	-0.776466	3.599039	2.846127	C	0.199014	-2.345578	3.363338
O	1.543127	3.76183	-0.642516	C	-0.083612	-2.269506	1.861959
C	2.003924	4.669119	-1.676112	H	-1.088487	-1.885162	1.65612
C	3.47476	4.96042	-1.355488	H	0.065056	-3.221548	1.340776
C	3.901134	3.711913	-0.566214	H	-0.691979	-2.620592	3.935755
C	2.634973	3.404678	0.231449	H	0.982916	-3.083318	3.575158
H	2.582288	4.01685	1.142213	H	-0.150672	-0.231243	3.725128
H	2.503643	2.357074	0.509082	H	1.282633	-0.852901	4.583495
H	4.771822	3.880013	0.075141	H	2.551643	-0.979989	2.501327
H	4.135322	2.884563	-1.248237	H	1.526042	0.457107	2.164622
H	3.551706	5.853592	-0.726287	O	1.02359	-0.366974	-1.663828
H	4.071221	5.129074	-2.257309	C	1.236471	0.696538	-2.634107
H	1.889103	4.160064	-2.641664	C	2.517108	0.323484	-3.39653
H	1.372696	5.558802	-1.66733	C	3.241846	-0.610257	-2.412634
C	-2.118832	5.840305	-0.133207	C	2.070571	-1.352983	-1.775282
C	-2.642587	5.840896	1.316674	H	2.260841	-1.738486	-0.771885
N	-3.964181	5.191712	1.491071	H	1.727107	-2.176902	-2.418093
C	-5.042259	6.082318	1.008218	H	3.779718	-0.030243	-1.653051
H	-4.891299	6.264132	-0.059195	H	3.954922	-1.282391	-2.899508
H	-4.964377	7.063865	1.517559	H	3.105654	1.204562	-3.669114
C	-6.439322	5.502531	1.243372	H	2.2759	-0.215091	-4.320337
H	-6.561832	4.597812	0.637444	H	0.354424	0.762595	-3.277634
H	-7.184309	6.223074	0.883174	H	1.335264	1.632587	-2.076586
C	-6.664879	5.174536	2.72277	C	-5.525551	4.283599	3.228642

Table A3.7 (Continued).





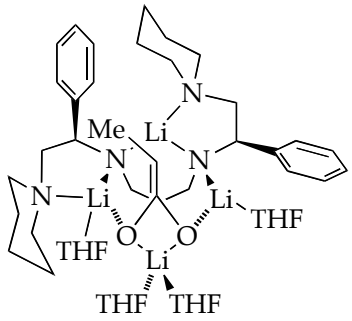
18b
G = -2575.652762
G_{MP2} = -2568.17973

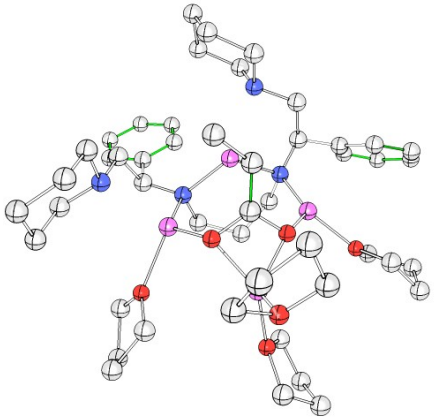
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	H	-2.798786	4.428097	3.112472
O	-1.777536	0.402335	0.637687	H	-3.318818	6.089381	3.472828
Li	-3.235742	0.787175	-0.530089	H	-5.108616	3.77553	2.556829
N	-3.742085	2.614836	-1.429508	H	-5.053219	4.490101	4.167661
C	-5.150652	2.39815	-1.690084	H	-6.9977	5.373068	2.771436
H	-5.292248	1.597483	-2.455368	H	-5.894674	6.649928	3.285449
C	-5.953916	3.590693	-2.26656	H	-5.931142	5.286267	0.535718
C	-7.1918	3.368956	-2.888367	H	-6.371629	6.955282	0.871068
C	-7.949015	4.423263	-3.39886	H	-1.817564	7.053024	1.721063
C	-7.471236	5.733177	-3.310816	H	-1.262944	5.372978	1.84866
C	-6.233663	5.968619	-2.711135	H	-2.102768	6.651695	-0.794606
C	-5.485898	4.90632	-2.195539	C	-0.063688	6.844514	-0.270442
H	-4.514254	5.082955	-1.743444	C	0.168074	7.718913	-1.341975
H	-5.84313	6.982295	-2.651123	C	1.377885	8.406403	-1.475605
H	-8.053358	6.558191	-3.714083	C	2.384032	8.245651	-0.522058
H	-8.907992	4.223178	-3.871825	C	2.169709	7.382217	0.556869
H	-7.566203	2.349506	-2.979245	C	0.966528	6.684009	0.671687
C	-5.867517	1.910859	-0.409217	H	0.825319	6.014817	1.517485
N	-5.43	0.560369	0.012785	H	2.938146	7.261833	1.317836
C	-5.640893	0.312374	1.454123	H	3.319914	8.79164	-0.611755
H	-5.075119	-0.59382	1.714213	H	1.528352	9.076421	-2.319115
H	-5.188586	1.135965	2.011453	H	-0.618989	7.86605	-2.07895
C	-7.110985	0.118039	1.864265	C	-1.28943	4.622503	-2.126613
C	-7.754292	-1.013597	1.050412	C	-1.575211	3.19207	-2.631932
C	-7.548641	-0.769855	-0.451664	H	-1.161976	3.094929	-3.648083
C	-6.061838	-0.524109	-0.770255	H	-1.033817	2.466354	-2.004654
H	-5.928811	-0.30778	-1.833805	C	-3.05755	2.791837	-2.710551
H	-5.498846	-1.443113	-0.560203	H	-3.115084	1.862481	-3.324399
H	-7.901823	-1.628971	-1.037624	H	-3.55007	3.555956	-3.343949
H	-8.150569	0.091057	-0.771398	H	-2.044794	5.300637	-2.582623
H	-8.821414	-1.110344	1.287213	H	-0.324357	4.957777	-2.570671
H	-7.282387	-1.968562	1.32824	O	-3.056924	-0.900539	-1.82734
H	-7.668093	1.051976	1.70772	C	-2.658388	-2.147643	-1.232543

Table A3.7 (Continued).

H	-7.160236	-0.099611	2.93928	C	-1.883518	-2.875491	-2.328402
H	-6.957683	1.969263	-0.542199	C	-2.687674	-2.482111	-3.578368
H	-5.610705	2.606284	0.398906	C	-3.107323	-1.036454	-3.263807
Li	-2.918372	3.763098	-0.008541	H	-4.118659	-0.799699	-3.611654
N	-1.307795	4.696689	-0.672521	H	-2.418131	-0.302612	-3.695035
Li	0.107373	3.431076	-0.115646	H	-3.568343	-3.127099	-3.680147
O	-0.00215	1.781096	0.64653	H	-2.112682	-2.554004	-4.50665
C	-1.155054	1.420875	1.244266	H	-1.832391	-3.95728	-2.168747
C	-1.586482	2.018228	2.40748	H	-0.864315	-2.478018	-2.385147
H	-0.931436	2.780587	2.826939	H	-2.082168	-1.906396	-0.337681
C	-2.673777	1.464419	3.29065	H	-3.551916	-2.719492	-0.936789
H	-3.099592	0.563854	2.83812	O	0.952371	-0.597518	-1.645366
H	-2.294267	1.177524	4.287224	C	1.972794	-1.621262	-1.642999
H	-3.508837	2.157783	3.484848	C	3.174084	-0.989012	-2.342061
O	2.003298	3.550124	-0.790011	C	2.488508	-0.1165	-3.406018
C	3.058418	3.060044	0.062887	C	1.246734	0.396627	-2.666673
C	4.349023	3.277716	-0.725904	H	0.368689	0.501109	-3.310293
C	4.037164	4.580316	-1.480057	H	1.426774	1.35039	-2.160701
C	2.54817	4.427507	-1.809058	H	2.201051	-0.729062	-4.26863
H	2.39163	3.946452	-2.782965	H	3.118788	0.700294	-3.770111
H	1.99934	5.370254	-1.786641	H	3.855613	-1.733671	-2.764281
H	4.648886	4.719798	-2.376567	H	3.739691	-0.366209	-1.638365
H	4.189871	5.445922	-0.826676	H	2.143391	-1.908225	-0.603743
H	4.512436	2.452532	-1.430796	H	1.605959	-2.49507	-2.20034
H	5.228802	3.35019	-0.079056	O	0.859865	-1.216909	1.431083
H	3.062735	3.636383	0.998298	C	1.655526	-0.45191	2.376953
H	2.835866	2.017319	0.29912	C	0.923877	-0.559001	3.714476
C	-1.386137	6.061424	-0.184026	C	0.286439	-1.953502	3.623849
C	-1.902005	6.047745	1.268814	C	-0.114292	-2.024733	2.149158
N	-3.287719	5.542719	1.415498	H	-1.101484	-1.584745	1.971309
C	-4.258706	6.572015	0.983667	H	-0.080556	-3.039518	1.737696
H	-4.084242	6.793653	-0.072638	H	-0.573219	-2.076687	4.289371
H	-4.075178	7.510217	1.544977	H	1.020393	-2.732419	3.865431
C	-5.712092	6.138199	1.189532	H	0.150228	0.214065	3.76447
C	-5.97684	5.756182	2.649158	H	1.597393	-0.445542	4.569867
C	-4.945325	4.716446	3.099302	H	2.660326	-0.895351	2.420962
C	-3.51909	5.203275	2.83754	H	1.70944	0.573033	2.002801

Table A3.7 (Continued).





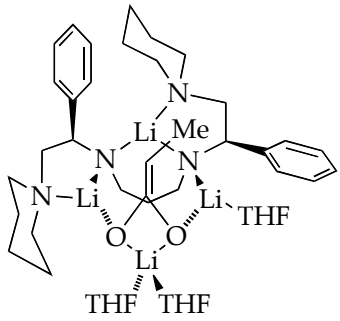
18c
G = -2575.656449
G_{MP2} = -2568.184603

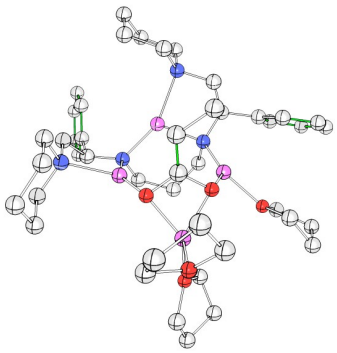
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	H	-5.428843	7.856648	0.743026
O	-1.743987	0.609724	0.561425	C	-5.193094	6.73469	2.598228
Li	-3.180972	1.134393	-0.581117	C	-4.31937	5.585809	3.110851
N	-3.40637	3.022966	-1.426335	C	-2.839822	5.841165	2.814341
C	-4.833336	3.038507	-1.682892	H	-2.238153	4.989277	3.142725
C	-5.608757	2.687246	-0.393392	H	-2.505614	6.726597	3.392987
N	-5.480592	1.26876	0.014069	H	-4.446481	5.442588	4.191568
C	-5.844052	1.120015	1.436911	H	-4.625815	4.650055	2.625609
H	-5.200822	1.778783	2.023435	H	-4.974673	7.646188	3.174427
H	-6.889952	1.451279	1.598371	H	-6.257238	6.51269	2.747515
C	-5.691238	-0.326381	1.913556	H	-0.894626	7.332239	1.602421
H	-5.966131	-0.387726	2.97428	H	-0.593329	5.595257	1.791881
H	-4.633914	-0.611763	1.835441	H	-1.283714	6.876661	-0.891768
C	-6.552669	-1.276456	1.072158	C	0.768264	6.827664	-0.390322
C	-6.26266	-1.060117	-0.418456	C	1.093352	7.635077	-1.489931
C	-6.376281	0.419394	-0.794673	C	2.377776	8.161307	-1.656505
H	-6.133687	0.561381	-1.850984	C	3.369113	7.903073	-0.70907
H	-7.426333	0.750485	-0.660738	C	3.063116	7.104664	0.397782
H	-6.957212	-1.642888	-1.037973	C	1.783594	6.566846	0.545526
H	-5.24762	-1.401262	-0.652463	H	1.570388	5.946201	1.413074
H	-7.615709	-1.073456	1.268714	H	3.820762	6.910666	1.154441
H	-6.374008	-2.321653	1.355664	H	4.364558	8.324828	-0.824465
H	-6.675863	2.952698	-0.491842	H	2.599057	8.782686	-2.52141
H	-5.196625	3.304758	0.413612	H	0.320492	7.860089	-2.222259
H	-5.108267	2.26901	-2.443377	C	-0.745095	4.7318	-2.16219
C	-5.430818	4.344006	-2.266385	C	-1.188385	3.329709	-2.634714
C	-6.676208	4.320812	-2.911155	H	-0.79	3.16529	-3.648234
C	-7.246608	5.482165	-3.432382	H	-0.731353	2.560357	-1.992827
C	-6.568816	6.699696	-3.330173	C	-2.706313	3.097672	-2.707957
C	-5.321895	6.735665	-2.705212	H	-2.864683	2.168895	-3.307693
C	-4.761863	5.568293	-2.179102	H	-3.108933	3.900496	-3.355634
H	-3.784571	5.586087	-1.706121	H	-1.427208	5.477031	-2.628138

Table A3.7 (Continued).

H	-4.777286	7.674841	-2.633772	H	0.245783	4.950861	-2.623027
H	-7.004608	7.606917	-3.741594	O	-3.171916	-0.543725	-1.945856
H	-8.21581	5.437066	-3.924339	C	-2.506816	-1.766249	-1.556534
H	-7.205738	3.373613	-3.010176	C	-2.959117	-2.824755	-2.565171
Li	-2.388362	4.011663	0.037191	C	-3.14764	-1.982697	-3.836206
N	-0.737412	4.843123	-0.709613	C	-3.73333	-0.687613	-3.268351
Li	0.535159	3.431042	-0.170504	H	-4.825859	-0.752804	-3.183834
O	0.160981	1.79834	0.554381	H	-3.481445	0.204781	-3.846733
C	-1.057081	1.623083	1.09293	H	-3.804594	-2.44889	-4.576773
C	-1.514183	2.415924	2.127936	H	-2.179264	-1.790284	-4.313886
H	-0.79862	3.138486	2.518784	H	-3.913093	-3.270185	-2.258492
C	-2.66601	2.030801	3.022484	H	-2.228749	-3.631979	-2.680639
H	-3.462173	2.787198	3.101236	H	-1.423692	-1.607307	-1.606979
H	-3.127738	1.107771	2.658599	H	-2.782795	-1.988671	-0.522315
H	-2.339053	1.838887	4.059416	O	0.682144	-1.255287	1.47081
O	2.427559	3.302832	-0.828583	C	1.454588	-0.530949	2.466431
C	3.057011	4.086163	-1.876406	C	0.600083	-0.535695	3.733163
C	4.560123	4.051819	-1.580383	C	-0.132458	-1.881452	3.62269
C	4.719316	2.733638	-0.806248	C	-0.403823	-1.975329	2.119532
C	3.43055	2.700827	0.014724	H	-1.338995	-1.476792	1.842704
H	3.532087	3.292784	0.934917	H	-0.40276	-3.003046	1.740349
H	3.083131	1.699895	0.28102	H	-1.055204	-1.918276	4.209394
H	5.616554	2.702178	-0.180472	H	0.515574	-2.702565	3.95325
H	4.755706	1.881639	-1.496994	H	-0.111433	0.295672	3.695701
H	4.836574	4.901864	-0.947641	H	1.201534	-0.444275	4.643085
H	5.164205	4.096305	-2.491672	H	2.408992	-1.055731	2.613279
H	2.817338	3.61216	-2.836618	H	1.631097	0.472943	2.073175
H	2.633784	5.091387	-1.861115	O	0.913192	-0.700518	-1.618527
C	-0.641904	6.221906	-0.264944	C	1.295864	0.234417	-2.666141
C	-1.136468	6.333847	1.191796	C	2.437965	-0.443345	-3.433561
N	-2.576743	6.049773	1.375094	C	3.04243	-1.380361	-2.375441
C	-3.392052	7.179966	0.882305	C	1.795668	-1.843556	-1.625239
H	-3.199894	7.308871	-0.185451	H	1.96649	-2.130372	-0.585629
H	-3.069917	8.115317	1.384202	H	1.303235	-2.675069	-2.14994
C	-4.890927	6.976182	1.116388	H	3.706576	-0.824684	-1.702234
H	-5.235283	6.122383	0.521597	H	3.609223	-2.212144	-2.804603
H	0.416931	0.440547	-3.283127	H	3.154786	0.281069	-3.831504
H	1.610419	1.164522	-2.182734	H	2.047588	-1.026147	-4.276157

Table A3.7 (Continued).





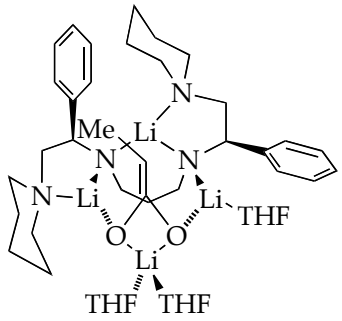
18d
G = -2343.3143
G_{MP2} = -2336.489847

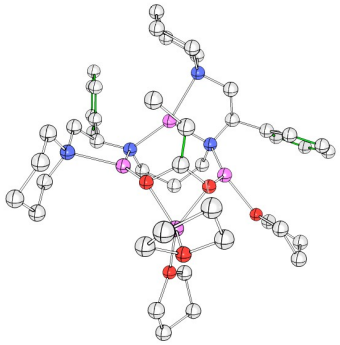
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	H	7.645614	3.641382	-0.784517
O	1.744391	-0.250609	-0.730978	H	8.342489	5.038169	-1.599451
Li	3.388671	-0.027897	0.025207	C	7.761593	3.421996	-2.940522
N	4.59745	1.180491	1.105349	C	6.57078	2.474459	-3.129316
C	5.713022	0.281859	1.403162	C	5.243163	3.235296	-3.100426
C	6.03644	-0.609739	0.188456	H	4.403462	2.536623	-3.175431
N	4.905395	-1.46812	-0.223405	H	5.19299	3.914229	-3.973737
C	5.092879	-1.953117	-1.606478	H	6.649878	1.930414	-4.078897
H	5.217138	-1.078611	-2.25501	H	6.569163	1.720308	-2.329827
H	6.024359	-2.548948	-1.677897	H	7.838711	4.083508	-3.815806
C	3.901071	-2.787646	-2.08212	H	8.70211	2.859475	-2.886786
H	4.095165	-3.136574	-3.10448	H	3.896085	5.653601	-2.508127
H	3.016452	-2.140934	-2.109096	H	3.05385	4.099899	-2.360732
C	3.646154	-3.971869	-1.140887	H	4.093997	5.60598	0.077587
C	3.519178	-3.468687	0.302386	C	2.150223	6.150501	-0.557834
C	4.728213	-2.613213	0.692974	C	2.134292	7.248194	0.314199
H	4.604452	-2.229944	1.710125	C	1.103767	8.19233	0.278798
H	5.642661	-3.23925	0.693095	C	0.066585	8.062749	-0.646084
H	3.434978	-4.308172	1.004631	C	0.068053	6.976642	-1.527041
H	2.607493	-2.864748	0.400312	C	1.092644	6.030351	-1.475597
H	4.481659	-4.685009	-1.205959	H	1.073395	5.194367	-2.171997
H	2.74235	-4.517225	-1.441029	H	-0.724847	6.873586	-2.264718
H	6.934333	-1.220621	0.389641	H	-0.728084	8.803472	-0.68857
H	6.269585	0.034718	-0.667009	H	1.118155	9.034135	0.967359
H	5.425795	-0.39837	2.235298	H	2.948883	7.366584	1.02612
C	6.997922	0.960222	1.91124	C	2.917289	3.968569	1.646133
C	7.280952	0.986923	3.283656	C	2.822609	2.581237	2.311488
C	8.423115	1.618486	3.78134	H	2.496525	2.724173	3.353053
C	9.321727	2.229422	2.906921	H	2.03131	1.995911	1.816953
C	9.063566	2.202677	1.534432	C	4.111221	1.74021	2.370751
C	7.913381	1.579499	1.047936	H	3.915047	0.917493	3.097293
H	7.734687	1.565873	-0.023445	H	4.876071	2.367071	2.873098
H	9.762507	2.663458	0.840052	H	3.846716	4.461359	2.013394

Table A3.7 (Continued).

H	10.215365	2.717211	3.287906	H	2.097174	4.600055	2.055076
H	8.611457	1.628976	4.852395	O	-1.296112	-1.181801	-1.03688
H	6.59206	0.501045	3.971845	C	-0.697911	-2.447374	-1.429952
Li	4.414825	2.670136	-0.205157	C	-1.050727	-2.643927	-2.907723
N	2.896122	3.861397	0.193288	C	-1.181446	-1.196051	-3.40417
Li	1.097563	3.081587	-0.236599	C	-1.83567	-0.510518	-2.206474
O	0.449104	1.55779	-1.047592	H	-2.927683	-0.63604	-2.208003
C	1.422241	0.775702	-1.541686	H	-1.57789	0.54733	-2.12096
C	2.011496	0.966355	-2.769245	H	-1.777855	-1.104128	-4.317334
H	2.719965	0.209015	-3.100649	H	-0.192715	-0.757716	-3.5781
C	1.554134	1.993482	-3.772807	H	-2.004567	-3.175791	-3.011578
H	2.376683	2.588689	-4.200446	H	-0.28422	-3.214913	-3.440298
H	1.029133	1.549538	-4.637286	H	0.383012	-2.359727	-1.277093
H	0.852299	2.695328	-3.307303	H	-1.099757	-3.232858	-0.780574
O	-0.603113	3.792966	0.638387	O	-0.699154	-0.157071	1.838355
C	-0.785726	4.874061	1.589457	C	-0.669514	0.900108	2.825154
C	-2.251875	5.3231	1.458799	C	-1.924731	0.685057	3.667923
C	-2.924515	4.12404	0.768259	C	-2.023284	-0.848621	3.69442
C	-1.804824	3.632531	-0.143813	C	-1.555227	-1.235818	2.285609
H	-1.735117	4.250677	-1.050004	H	-2.386472	-1.320408	1.577948
H	-1.860655	2.58393	-0.437789	H	-0.982708	-2.168946	2.265504
H	-3.83076	4.395727	0.218068	H	-3.030631	-1.216093	3.911336
H	-3.187073	3.349219	1.499352	H	-1.344354	-1.257101	4.451778
H	-2.317213	6.211194	0.821377	H	-2.799766	1.118209	3.167891
H	-2.69786	5.570153	2.426972	H	-1.844059	1.130453	4.664041
H	-0.560647	4.471811	2.583728	H	0.242247	0.803373	3.428691
H	-0.07593	5.671941	1.362388	H	-0.640012	1.850234	2.286905
C	3.270466	5.102327	-0.471867	C	6.19669	4.956995	-1.683165
C	3.790609	4.751017	-1.881199	H	6.050339	5.507274	-0.749063
N	5.074496	4.005381	-1.84654	H	6.165716	5.699344	-2.504444
C	7.562565	4.270006	-1.678021				

Table A3.7 (Continued).





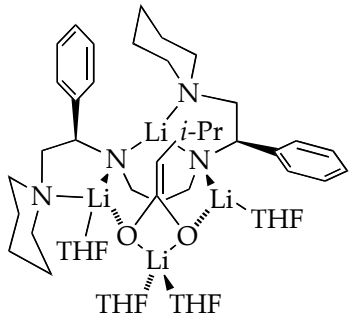
18e
G = -2343.31295
G_{MP2} = -2336.487764

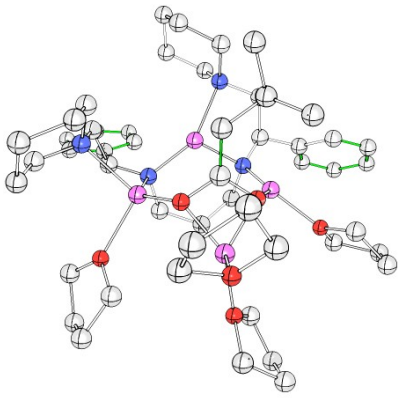
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	C	-3.788972	4.871206	1.596392
O	-1.757742	-0.282225	0.704321	N	-5.041787	4.079239	1.626579
Li	-3.301221	-0.135159	-0.274007	C	-6.19997	4.95726	1.34739
N	-4.541793	1.113307	-1.288289	H	-6.068314	5.402924	0.357316
C	-5.673364	0.2276	-1.583424	H	-6.211452	5.789764	2.078575
C	-5.872114	-0.820403	-0.47241	C	-7.532199	4.209758	1.406878
N	-4.704154	-1.710182	-0.289379	H	-7.570404	3.482827	0.589042
C	-4.833854	-2.470894	0.970894	H	-8.346064	4.925487	1.23325
H	-4.961021	-1.751883	1.786575	C	-7.714291	3.496477	2.752205
H	-5.745924	-3.099231	0.941141	C	-6.483234	2.635903	3.06225
C	-3.60641	-3.346867	1.23324	C	-5.196842	3.457713	2.960811
H	-3.753049	-3.896576	2.171737	H	-4.321797	2.824774	3.134027
H	-2.738761	-2.688869	1.363251	H	-5.203247	4.240622	3.744784
C	-3.359719	-4.312809	0.068407	H	-6.552036	2.201602	4.067483
C	-3.300075	-3.530358	-1.248508	H	-6.427839	1.794711	2.356737
C	-4.537531	-2.644038	-1.421707	H	-7.840691	4.244269	3.549022
H	-4.451566	-2.065455	-2.344931	H	-8.625964	2.885579	2.747333
H	-5.439494	-3.280095	-1.519812	H	-3.917541	5.804981	2.172502
H	-3.227182	-4.210544	-2.106851	H	-3.024949	4.271749	2.102618
H	-2.402655	-2.896592	-1.259125	H	-4.126593	5.644547	-0.391506
H	-4.177125	-5.047387	0.017924	C	-2.179684	6.223612	0.197407
H	-2.433975	-4.881129	0.223959	C	-2.189647	7.293238	-0.708919
H	-6.782669	-1.413881	-0.670441	C	-1.168156	8.24769	-0.722493
H	-6.024277	-0.305233	0.484213	C	-0.11383	8.158119	0.187527
H	-5.452608	-0.338146	-2.513122	C	-0.088728	7.10027	1.101884
C	-7.012774	0.91837	-1.897919	C	-1.104063	6.142722	1.09817
C	-7.368781	1.167414	-3.231875	H	-1.063505	5.328261	1.818747
C	-8.570555	1.797152	-3.56254	H	0.717699	7.028702	1.828647
C	-9.460629	2.176735	-2.557769	H	0.67369	8.907627	0.192634
C	-9.131975	1.9235	-1.224558	H	-1.203111	9.066582	-1.437428
C	-7.919967	1.30953	-0.901885	H	-3.018003	7.381346	-1.409258
H	-7.689927	1.119624	0.143369	C	-2.929053	3.972264	-1.9106
H	-9.823234	2.200609	-0.431968	C	-2.833521	2.569815	-2.539225

Table A3.7 (Continued).

H	-10.402618	2.657491	-2.809123	H	-2.525655	2.690039	-3.589111
H	-8.81452	1.981592	-4.60617	H	-2.030049	1.999874	-2.04557
H	-6.693959	0.85002	-4.023875	C	-4.120968	1.725612	-2.554905
Li	-4.339104	2.625047	0.0459	H	-3.965773	0.929855	-3.320299
N	-2.92217	3.904182	-0.457317	H	-4.910816	2.369615	-2.99314
Li	-1.139556	3.131917	0.001262	H	-3.853669	4.456492	-2.299625
O	-0.569228	1.620293	0.854053	H	-2.103553	4.590958	-2.328914
C	-1.517856	0.841738	1.40573	O	1.348442	-0.962829	1.181212
C	-2.137546	1.149045	2.592488	C	0.7925	-2.170615	1.769917
H	-1.810459	2.058698	3.092652	C	1.216007	-2.156016	3.240111
C	-3.052992	0.216079	3.342642	C	1.293987	-0.650468	3.535895
H	-2.696914	0.016586	4.367101	C	1.861041	-0.096173	2.229369
H	-4.088984	0.581038	3.457623	H	2.958875	-0.137703	2.20632
H	-3.109051	-0.749604	2.829663	H	1.515671	0.916998	2.011471
O	0.578278	3.800154	-0.866851	H	1.922991	-0.41127	4.399171
C	0.772361	4.840752	-1.860356	H	0.293412	-0.23692	3.701915
C	2.223956	5.322462	-1.703154	H	2.199133	-2.626488	3.365647
C	2.901183	4.150359	-0.972886	H	0.501823	-2.684212	3.878918
C	1.772388	3.662521	-0.069356	H	-0.295877	-2.120364	1.659063
H	1.685504	4.290711	0.828291	H	1.181169	-3.029714	1.212724
H	1.83809	2.61839	0.239075	O	0.726726	-0.259316	-1.8149
H	3.792932	4.447847	-0.412472	C	0.708252	0.752711	-2.84808
H	3.188905	3.363597	-1.681407	C	1.999481	0.533963	-3.63391
H	2.255334	6.22377	-1.081999	C	2.137758	-0.996316	-3.588258
H	2.688576	5.559343	-2.665094	C	1.622974	-1.335231	-2.183016
H	0.588994	4.390621	-2.842844	H	2.42742	-1.370986	-1.440783
H	0.040252	5.632827	-1.692173	H	1.070511	-2.279967	-2.145581
C	-3.294778	5.164824	0.165954	H	3.162063	-1.345155	-3.749313
H	1.945404	0.932837	-4.651283	H	1.500725	-1.45549	-4.352925
H	-0.177178	0.605636	-3.480306	H	2.843812	1.011918	-3.122044
H	0.635034	1.724922	-2.355325				

Table A3.7 (Continued).





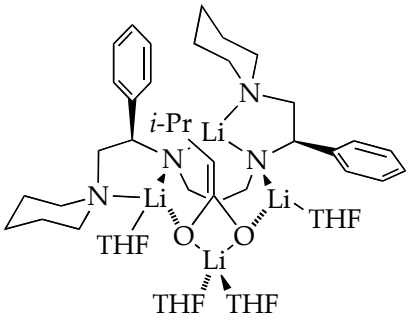
19a
G = -2654.226423
G_{MP2} = -2646.519504

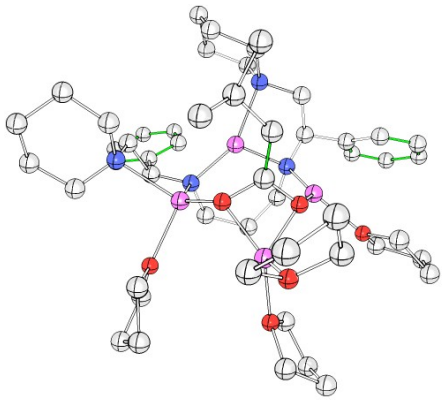
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	N	-4.33861	4.868299	1.547182
O	-1.801982	0.010218	0.671399	C	-5.498829	5.657151	1.074219
Li	-3.419912	0.105857	-0.284712	H	-5.389397	5.82968	0.000131
N	-4.337029	1.792017	-1.109374	H	-5.490621	6.651287	1.563749
C	-5.686088	1.279835	-1.225901	C	-6.835941	4.966468	1.356457
C	-6.159273	0.806522	0.16869	H	-6.895173	4.041258	0.772509
N	-5.432217	-0.391662	0.645417	H	-7.647485	5.613131	1.000135
C	-5.359577	-0.424925	2.119642	C	-6.999487	4.652148	2.847144
H	-4.87008	0.495234	2.453211	C	-5.777008	3.872239	3.342554
H	-6.378555	-0.440292	2.556376	C	-4.481028	4.60666	2.997494
C	-4.56719	-1.638589	2.613114	H	-3.617907	4.018448	3.315345
H	-4.54656	-1.630976	3.710403	H	-4.450961	5.564195	3.554442
H	-3.531834	-1.535098	2.265507	H	-5.819503	3.720696	4.428657
C	-5.172767	-2.947495	2.090837	H	-5.761137	2.875359	2.882813
C	-5.328997	-2.880941	0.566535	H	-7.086979	5.590022	3.415375
C	-6.086674	-1.617399	0.151811	H	-7.922617	4.086632	3.024723
H	-6.156166	-1.555044	-0.938166	H	-3.188221	6.653702	1.699922
H	-7.125346	-1.670135	0.537038	H	-2.314683	5.132744	1.947209
H	-5.866633	-3.761917	0.191315	H	-3.408625	6.009754	-0.764272
H	-4.342124	-2.868474	0.088381	C	-1.448244	6.641329	-0.302813
H	-6.160674	-3.103838	2.549349	C	-1.404024	7.452023	-1.446339
H	-4.552608	-3.8058	2.379983	C	-0.371196	8.370916	-1.65166
H	-7.246889	0.623768	0.181929	C	0.639606	8.512133	-0.699868
H	-5.963807	1.624113	0.871632	C	0.61059	7.716154	0.449254
H	-5.722634	0.385672	-1.892607	C	-0.413629	6.786193	0.636748
C	-6.756725	2.220963	-1.827045	H	-0.410889	6.176837	1.537534
C	-7.970069	1.694748	-2.295329	H	1.382577	7.827866	1.207812
C	-8.961085	2.517149	-2.830853	H	1.435726	9.238013	-0.84564
C	-8.750421	3.895241	-2.924123	H	-0.364472	8.9847	-2.549546
C	-7.542893	4.432393	-2.477309	H	-2.20027	7.364621	-2.182913
C	-6.559059	3.601149	-1.934317	C	-2.242839	4.101367	-1.978089
H	-5.613102	4.014609	-1.597345	C	-2.343965	2.625143	-2.418554
H	-7.360691	5.501827	-2.558813	H	-1.948763	2.547274	-3.443441

Table A3.7 (Continued).

H	-9.516	4.540099	-3.348492	H	-1.690704	2.007134	-1.782699
H	-9.894983	2.083268	-3.181297	C	-3.756221	2.013557	-2.430622
H	-8.139178	0.619604	-2.241986	H	-3.690244	1.06129	-3.006761
Li	-3.712808	3.141389	0.186731	H	-4.381837	2.669237	-3.068851
N	-2.254794	4.257323	-0.526932	H	-3.08615	4.65113	-2.452037
Li	-0.61906	3.286675	0.084817	H	-1.335776	4.537541	-2.455543
O	-0.298073	1.664903	0.899642	O	-3.170004	-1.501478	-1.787968
C	-1.348393	1.016293	1.436547	C	-1.949338	-2.277792	-1.787594
C	-1.859086	1.31046	2.680968	C	-2.036522	-3.22955	-2.991479
H	-2.655434	0.666151	3.04466	C	-3.024351	-2.50407	-3.917725
C	-1.327921	2.355115	3.648114	C	-3.988706	-1.890475	-2.905863
H	-1.459724	3.372079	3.2314	H	-4.735388	-2.628534	-2.577235
C	-2.121801	2.302285	4.964968	H	-4.505507	-0.999048	-3.266223
H	-1.80426	3.087752	5.662613	H	-3.523282	-3.169572	-4.628915
H	-3.199757	2.41239	4.795938	H	-2.517478	-1.713087	-4.483103
H	-1.969954	1.333545	5.459824	H	-2.44525	-4.201408	-2.690322
C	0.176775	2.235829	3.967287	H	-1.059126	-3.40632	-3.451633
H	0.514376	3.062139	4.610301	H	-1.108657	-1.583224	-1.875724
H	0.388099	1.296555	4.495344	H	-1.868285	-2.805236	-0.832382
H	0.759341	2.250903	3.0429	O	0.992855	-1.444214	1.085968
O	1.219912	3.818908	-0.556329	C	1.630231	-0.928991	2.285415
C	1.621953	4.750681	-1.592227	C	0.877571	-1.562037	3.45457
C	3.050962	5.177702	-1.241171	C	0.482184	-2.928826	2.877586
C	3.574888	3.96942	-0.448593	C	0.138057	-2.56907	1.431422
C	2.329495	3.547469	0.329229	H	-0.899638	-2.234496	1.330045
H	2.212444	4.144801	1.243522	H	0.33987	-3.378071	0.720786
H	2.284698	2.490585	0.598399	H	-0.362554	-3.388829	3.399152
H	4.416656	4.211624	0.207439	H	1.327968	-3.626604	2.915161
H	3.892881	3.169054	-1.128871	H	-0.015468	-0.968251	3.675526
H	3.029661	6.070037	-0.606408	H	1.490077	-1.631322	4.358864
H	3.646519	5.40775	-2.129945	H	2.688295	-1.226057	2.27048
H	1.580141	4.222226	-2.553868	H	1.552217	0.159539	2.259681
H	0.91171	5.578072	-1.612018	O	0.97979	-0.192806	-1.73742
C	-2.585025	5.61706	-0.130144	C	1.088099	0.910925	-2.679293
C	-3.077966	5.618544	1.329185	C	2.377479	0.663953	-3.482277
H	3.893295	-0.909062	-3.134878	C	3.168519	-0.301978	-2.583918
H	2.915157	1.592894	-3.694165	C	2.047871	-1.133209	-1.967389
H	2.149894	0.185801	-4.441861	H	2.285622	-1.589165	-1.005205
H	0.191637	0.927347	-3.305986	H	1.705437	-1.913496	-2.66385
H	1.123142	1.832023	-2.091683	H	3.70471	0.246506	-1.800111

Table A3.7 (Continued).





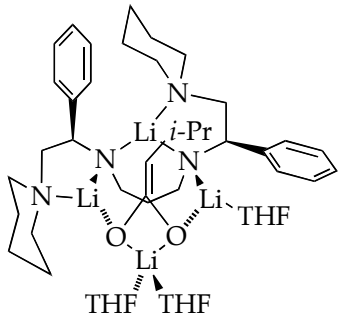
19b
G = -2654.219649
G_{MP2} = -2646.512427

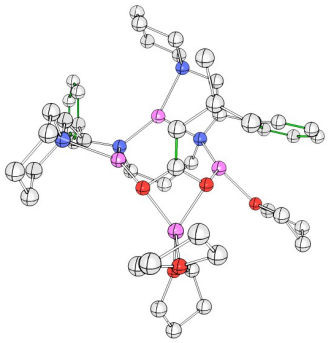
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	H	-2.937466	3.884474	3.265453
O	-1.771088	0.3282	0.768126	H	-3.486965	5.470385	3.8526
Li	-3.224899	0.682348	-0.403928	H	-5.239575	3.257715	2.657813
N	-3.84867	2.495193	-1.276226	H	-5.182393	3.762405	4.344798
C	-5.240311	2.205544	-1.553261	H	-7.161012	4.76691	3.083621
H	-5.331531	1.419825	-2.340885	H	-6.085102	5.99511	3.750374
C	-6.107247	3.368133	-2.096178	H	-6.116749	4.997417	0.846992
C	-7.296365	3.093461	-2.78738	H	-6.592672	6.597405	1.401661
C	-8.118415	4.117966	-3.256754	H	-2.046657	6.728007	2.185646
C	-7.757215	5.452102	-3.053644	H	-1.440968	5.061355	2.173993
C	-6.568664	5.742425	-2.382936	H	-2.317603	6.522006	-0.360526
C	-5.754956	4.708849	-1.911321	C	-0.284375	6.733008	0.178488
H	-4.818532	4.932253	-1.407852	C	-0.082003	7.696299	-0.820239
H	-6.267841	6.777117	-2.233339	C	1.104905	8.43053	-0.897185
H	-8.390398	6.254767	-3.423538	C	2.116583	8.226807	0.042188
H	-9.037033	3.876489	-3.786924	C	1.931115	7.274362	1.049074
H	-7.579574	2.056244	-2.96485	C	0.750744	6.531512	1.106957
C	-5.935771	1.646996	-0.290138	H	0.631632	5.794738	1.898283
N	-5.41763	0.319695	0.112215	H	2.703926	7.118157	1.798892
C	-5.609434	0.035807	1.549669	H	3.034446	8.807766	-0.002569
H	-4.997405	-0.842998	1.79306	H	1.232811	9.169981	-1.684506
H	-5.194909	0.87083	2.120955	H	-0.874117	7.877013	-1.544302
C	-7.066418	-0.237622	1.960647	C	-1.450332	4.609943	-1.83613
C	-7.652794	-1.38845	1.130099	C	-1.700647	3.211048	-2.438348
C	-7.461856	-1.114562	-0.369073	H	-1.287476	3.194599	-3.45883
C	-5.99063	-0.785871	-0.686023	H	-1.136031	2.462278	-1.861246
H	-5.870666	-0.5471	-1.746533	C	-3.170068	2.76987	-2.54342
H	-5.379111	-1.675956	-0.488801	H	-3.197245	1.876262	-3.209654
H	-7.77002	-1.983624	-0.965697	H	-3.688246	3.553369	-3.131469
H	-8.109307	-0.282927	-0.677179	H	-2.222396	5.299114	-2.246058
H	-8.713611	-1.541684	1.365325	H	-0.494072	4.997244	-2.254255
H	-7.133878	-2.322324	1.395127	O	-2.955999	-0.949805	-1.743837
H	-7.671434	0.668781	1.820173	C	-2.543013	-2.214345	-1.195807

Table A3.7 (Continued).

H	-7.101043	-0.475012	3.031918	C	-1.800866	-2.914278	-2.331949
H	-7.025658	1.63781	-0.436191	C	-2.62905	-2.474657	-3.550192
H	-5.734228	2.342676	0.533135	C	-3.017822	-1.033663	-3.183631
Li	-3.118134	3.653993	0.148646	H	-4.026165	-0.763528	-3.514306
N	-1.471745	4.582578	-0.38003	H	-2.315415	-0.300567	-3.595263
Li	-0.020109	3.329902	0.149461	H	-3.522002	-3.10323	-3.647709
O	0.02992	1.665839	0.89921	H	-2.078022	-2.528341	-4.49408
C	-1.078643	1.197105	1.515754	H	-1.756947	-4.000813	-2.206629
C	-1.372394	1.546239	2.814247	H	-0.77921	-2.526051	-2.403408
H	-0.669664	2.228877	3.289197	H	-1.944341	-2.000339	-0.308408
C	-2.499354	1.013993	3.681187	H	-3.429462	-2.79211	-0.892073
H	-3.478622	1.360942	3.305764	O	0.909123	-0.406907	-1.760797
C	-2.366344	1.556601	5.11483	C	1.952139	-1.395798	-1.905197
H	-3.190868	1.214352	5.753426	C	3.113715	-0.655997	-2.562751
H	-1.426277	1.213362	5.567623	C	2.372649	0.296096	-3.514875
H	-2.355435	2.653242	5.135509	C	1.126722	0.679534	-2.704113
C	-2.583511	-0.524549	3.728538	H	0.228788	0.792855	-3.318124
H	-1.698348	-0.941818	4.228369	H	1.274928	1.595387	-2.124057
H	-3.469612	-0.862858	4.285719	H	2.091452	-0.231703	-4.433744
H	-2.628837	-0.929422	2.71415	H	2.963507	1.171544	-3.800342
O	1.8633	3.591476	-0.540549	H	3.807035	-1.329514	-3.075765
C	2.937824	3.125887	0.302128	H	3.677355	-0.090053	-1.811092
C	4.21155	3.373968	-0.503221	H	2.161785	-1.789739	-0.909742
C	3.868257	4.685788	-1.227618	H	1.590765	-2.211494	-2.548486
C	2.372065	4.525654	-1.52673	O	1.070644	-1.327349	1.178718
H	2.196078	4.089901	-2.518346	C	1.916663	-0.630955	2.137245
H	1.813574	5.45971	-1.446886	C	1.504379	-1.152468	3.514067
H	4.4583	4.848302	-2.134763	C	1.025383	-2.578015	3.199724
H	4.028026	5.540652	-0.561967	C	0.344077	-2.390768	1.843213
H	4.37368	2.563049	-1.224834	H	-0.698591	-2.07578	1.955678
H	5.101462	3.4483	0.129479	H	0.389222	-3.280776	1.20587
H	2.941846	3.705311	1.235924	H	0.339897	-2.978152	3.952755
H	2.736113	2.080813	0.542335	H	1.877162	-3.263882	3.113025
C	-1.582961	5.908105	0.204537	H	0.678286	-0.54554	3.896959
C	-2.097959	5.763556	1.649589	H	2.32739	-1.123247	4.235094
N	-3.469727	5.205722	1.739844	H	2.96307	-0.872816	1.903701
C	-4.470341	6.256943	1.449914	H	1.733605	0.438146	2.008515
H	-4.306951	6.620665	0.431239	C	-6.151092	5.188379	3.005413
H	-4.306755	7.116787	2.129266	C	-5.090947	4.125598	3.313724
C	-5.91059	5.762203	1.605059	C	-3.67808	4.673834	3.106437

Table A3.7 (Continued).





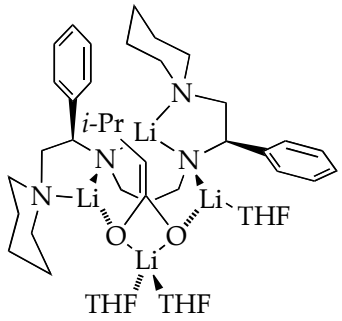
19c
G = -2421.883415
G_{MP2} = -2414.824252

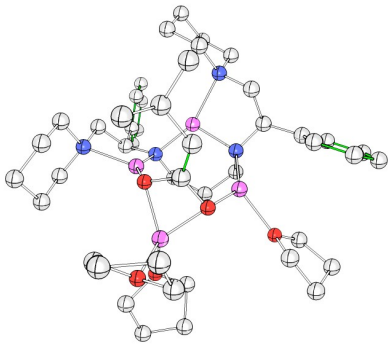
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	C	8.211863	3.40249	-2.725219
O	1.639082	-0.475164	-0.826728	C	7.014945	2.565568	-3.193394
Li	3.392062	-0.228813	-0.337006	C	5.731095	3.397766	-3.1997
N	4.671693	0.912353	0.765336	H	4.87801	2.779007	-3.493445
C	5.738821	-0.053727	1.031761	H	5.82328	4.205461	-3.951723
C	6.014157	-0.915436	-0.215786	H	7.186787	2.164559	-4.200187
N	4.851061	-1.727773	-0.632181	H	6.879561	1.703959	-2.525056
C	5.020154	-2.199042	-2.022489	H	8.426256	4.175772	-3.477475
H	5.157685	-1.319001	-2.660796	H	9.113317	2.781937	-2.646164
H	5.939602	-2.811786	-2.106541	H	4.390267	5.735167	-2.448958
C	3.813179	-3.008641	-2.504612	H	3.47973	4.218593	-2.551238
H	3.999609	-3.34691	-3.53193	H	4.325906	5.45327	0.106963
H	2.935781	-2.3523	-2.523996	C	2.46881	6.098417	-0.667438
C	3.538827	-4.198956	-1.57749	C	2.457104	7.19031	0.211413
C	3.418983	-3.705885	-0.130713	C	1.476802	8.183754	0.126804
C	4.646011	-2.881842	0.268962	C	0.488331	8.109512	-0.855613
H	4.529676	-2.509871	1.290762	C	0.486173	7.028973	-1.743527
H	5.5469	-3.527328	0.260846	C	1.459881	6.034413	-1.643069
H	3.316285	-4.549424	0.564219	H	1.44072	5.203589	-2.345647
H	2.522671	-3.080914	-0.029205	H	-0.269441	6.967435	-2.523708
H	4.363053	-4.924373	-1.649986	H	-0.266351	8.887929	-0.936126
H	2.626549	-4.725757	-1.884833	H	1.492761	9.019825	0.822227
H	6.895896	-1.559835	-0.050571	H	3.235662	7.265132	0.968301
H	6.250732	-0.251631	-1.05615	C	3.048065	3.728465	1.438184
H	5.409151	-0.747394	1.836176	C	2.913694	2.30144	2.005807
C	7.056584	0.528157	1.576355	H	2.563573	2.388045	3.045766
C	7.26922	0.588448	2.961511	H	2.126977	1.757495	1.459786
C	8.442727	1.121945	3.498279	C	4.187444	1.435438	2.046619
C	9.447097	1.594687	2.653329	H	3.967935	0.590909	2.740437
C	9.261229	1.529849	1.271048	H	4.958595	2.029781	2.579142
C	8.077894	1.008838	0.743516	H	3.957687	4.187713	1.887446
H	7.960228	0.962997	-0.335675	H	2.209183	4.336202	1.847642
H	10.042072	1.880412	0.599939	O	-1.425238	-1.223059	-0.820651

Table A3.7 (Continued).

H	10.366729	2.00248	3.065235	C	-0.891965	-2.53393	-1.157679
H	8.574656	1.159949	4.577126	C	-1.487867	-2.889403	-2.521245
H	6.501484	0.201037	3.627838	C	-1.648503	-1.506059	-3.168826
Li	4.580588	2.486575	-0.447896	C	-2.078094	-0.645999	-1.980351
N	3.105556	3.731262	-0.020036	H	-3.164822	-0.682162	-1.821568
Li	1.277763	3.022679	-0.477598	H	-1.752342	0.393815	-2.060312
O	0.553438	1.465751	-1.158627	H	-2.380456	-1.489323	-3.982286
C	1.422462	0.569445	-1.646244	H	-0.688105	-1.149931	-3.555303
C	2.037203	0.682521	-2.873049	H	-2.463487	-3.377276	-2.404579
H	2.641388	-0.162443	-3.197667	H	-0.838515	-3.559601	-3.092553
C	1.76838	1.770778	-3.895501	H	0.198556	-2.443494	-1.196635
H	2.012559	2.761911	-3.470246	H	-1.178128	-3.230241	-0.362237
C	2.661383	1.57449	-5.13148	O	-0.627841	0.046437	1.872955
H	2.527732	2.381869	-5.862544	C	-0.672882	1.208247	2.725891
H	3.723375	1.530909	-4.861457	C	-1.988949	1.067386	3.485677
H	2.415832	0.627913	-5.631721	C	-2.040783	-0.449446	3.740043
C	0.293326	1.852573	-4.341544	C	-1.364135	-1.038417	2.487673
H	0.125438	2.692777	-5.031864	H	-2.081079	-1.400072	1.745558
H	-0.00307	0.930523	-4.859299	H	-0.667465	-1.848581	2.731198
H	-0.355702	1.981587	-3.470935	H	-3.058259	-0.827607	3.875464
O	-0.42263	3.871277	0.291664	H	-1.469136	-0.700194	4.64051
C	-0.61571	4.96508	1.225559	H	-2.826719	1.38322	2.852217
C	-2.037984	5.493002	0.98193	H	-2.012787	1.657469	4.40687
C	-2.737981	4.298443	0.312742	H	0.188334	1.198045	3.407679
C	-1.604278	3.711391	-0.522973	H	-0.605294	2.086304	2.080395
H	-1.476032	4.270538	-1.460393	N	5.436683	3.971974	-1.868599
H	-1.692138	2.650218	-0.75817	C	6.565959	4.827365	-1.436926
H	-3.602225	4.587837	-0.29319	H	6.332585	5.239623	-0.451494
H	-3.07502	3.573286	1.064146	H	6.659251	5.683354	-2.133614
H	-2.008237	6.346592	0.296618	C	7.892981	4.070036	-1.381647
H	-2.523932	5.81841	1.906789	H	7.843762	3.315636	-0.589192
H	-0.495365	4.558099	2.23689	H	8.687085	4.773547	-1.100583
H	0.155221	5.71802	1.053849	C	4.192966	4.777351	-1.936035
C	3.55065	5.011549	-0.552638				

Table A3.7 (Continued).





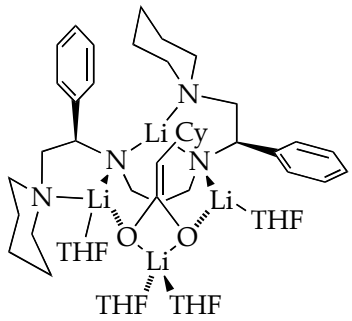
19d
G = -2421.881353
G_{MP2} = -2414.82311

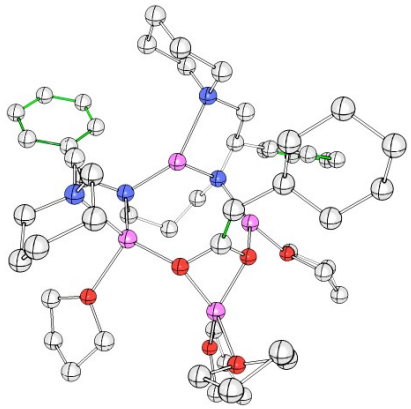
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	H	-2.81159	1.326315	6.017912
O	-1.530375	-0.008599	1.207764	H	-1.251981	2.113298	5.729974
Li	-3.073782	0.03588	0.221074	H	-2.691624	2.69235	4.887454
N	-4.379365	1.076416	-0.934999	O	0.631205	3.965059	-0.936647
C	-5.429961	0.091581	-1.192803	C	0.638883	5.081307	-1.863699
C	-5.646668	-0.812842	0.034581	C	2.059619	5.664491	-1.826713
N	-4.439404	-1.572496	0.424111	C	2.898211	4.486905	-1.304605
C	-4.582912	-2.096512	1.799163	C	1.930327	3.83775	-0.319024
H	-4.770353	-1.246567	2.464856	H	1.927699	4.368271	0.642593
H	-5.466216	-2.762577	1.860856	H	2.096876	2.776832	-0.130298
C	-3.327989	-2.843832	2.254496	H	3.834683	4.799021	-0.83182
H	-3.484985	-3.220162	3.273115	H	3.140608	3.791317	-2.117774
H	-2.500145	-2.126799	2.285783	H	2.10323	6.502086	-1.122383
C	-2.991063	-3.991276	1.294755	H	2.384288	6.028594	-2.806279
C	-2.907196	-3.456717	-0.139958	H	0.378449	4.688967	-2.853785
C	-4.175704	-2.684095	-0.513218	H	-0.123155	5.800575	-1.557022
H	-4.082632	-2.273446	-1.522552	C	-3.175903	5.065036	0.61339
H	-5.040038	-3.37713	-0.524352	C	-3.725374	4.678434	2.003448
H	-2.765752	-4.275412	-0.857456	N	-5.006152	3.928703	1.925537
H	-2.0401	-2.788542	-0.231571	C	-6.127149	4.862419	1.670842
H	-3.773084	-4.763244	1.349349	H	-5.937974	5.384151	0.728652
H	-2.049357	-4.474949	1.583562	H	-6.148953	5.630823	2.467969
H	-6.495458	-1.497404	-0.1413	C	-7.481925	4.155045	1.610991
H	-5.912961	-0.184981	0.893335	H	-7.505406	3.493789	0.737342
H	-5.115074	-0.569823	-2.029388	H	-8.265736	4.908183	1.459729
C	-6.780941	0.659181	-1.666149	C	-7.745357	3.348233	2.888737
C	-7.103596	0.651048	-3.030177	C	-6.555092	2.428069	3.185489
C	-8.310752	1.174703	-3.498504	C	-5.239345	3.20955	3.198044
C	-9.235996	1.708997	-2.601903	H	-4.395507	2.532652	3.361919
C	-8.937788	1.716417	-1.23748	H	-5.249113	3.926413	4.041768
C	-7.722928	1.202597	-0.780374	H	-6.68068	1.925158	4.152466
H	-7.514261	1.215283	0.285678	H	-6.496431	1.639433	2.42233
H	-9.655621	2.118005	-0.525881	H	-7.886906	4.0383	3.73341

Table A3.7 (Continued).

H	-10.18028	2.111454	-2.959616	H	-8.672168	2.768042	2.798006
H	-8.528854	1.160254	-4.563827	H	-3.847581	5.56631	2.648544
H	-6.393893	0.222956	-3.735291	H	-2.994234	4.015435	2.479335
Li	-4.308935	2.629538	0.305731	H	-3.975637	5.609132	0.07002
N	-2.81478	3.841418	-0.091866	C	-2.033345	6.080066	0.767755
Li	-0.920376	3.184165	0.163197	C	-2.026966	7.272145	0.030644
O	-0.098284	1.689251	0.848457	C	-0.975986	8.188183	0.137563
C	-0.913849	1.069704	1.725348	C	0.091203	7.93145	0.999473
C	-1.048391	1.491081	3.024205	C	0.099155	6.748851	1.746129
H	-0.422988	2.328507	3.331348	C	-0.947379	5.833282	1.625706
C	-1.87688	0.814804	4.095386	H	-0.923986	4.920018	2.217848
H	-2.837977	0.488815	3.662699	H	0.916712	6.545128	2.434152
C	-1.21154	-0.452126	4.679167	H	0.902744	8.648253	1.097854
H	-0.265952	-0.194013	5.17494	H	-0.997149	9.106075	-0.445591
H	-1.853747	-0.949786	5.421447	H	-2.863544	7.487179	-0.631612
H	-0.991641	-1.171735	3.884592	C	-2.918452	3.968181	-1.540314
C	-2.183651	1.790089	5.245816	C	-2.761762	2.596607	-2.225831
H	1.588408	0.009502	3.30325	H	-2.507802	2.769354	-3.282784
H	2.908037	-2.711245	2.762216	H	-1.903083	2.069791	-1.782876
H	1.499304	-2.39334	3.79275	C	-3.985272	1.662595	-2.222004
H	0.060607	-2.015166	1.889784	H	-3.760866	0.850987	-2.952077
H	1.214815	-3.140779	1.117148	H	-4.815201	2.227485	-2.694169
O	0.158112	-0.344397	-1.944423	H	-3.897131	4.399668	-1.856438
C	0.46854	0.717283	-2.877199	H	-2.166503	4.658314	-1.981656
C	1.681075	0.209155	-3.652366	O	1.528075	-1.121043	0.747561
C	1.359407	-1.288919	-3.782203	C	1.113488	-2.186817	1.646449
C	0.674617	-1.604334	-2.443516	C	2.016678	-2.083061	2.880495
H	1.37688	-1.986577	-1.696312	C	2.399828	-0.595132	2.884775
H	-0.157935	-2.308493	-2.54547	C	2.533632	-0.299039	1.393578
H	2.245007	-1.909205	-3.948516	H	3.522372	-0.580716	1.003988
H	0.669892	-1.455473	-4.617637	H	2.312598	0.740364	1.141408
H	2.597407	0.358203	-3.068551	H	3.321183	-0.388587	3.43851
H	1.803503	0.708535	-4.618294	H	0.639878	1.627487	-2.29743
H	-0.392457	0.877189	-3.538994				

Table A3.7 (Continued).





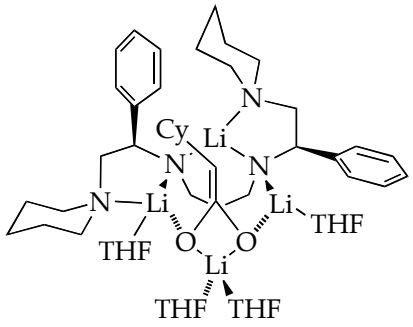
20a
G = -2770.897292
G_{MP2} = -2762.855052

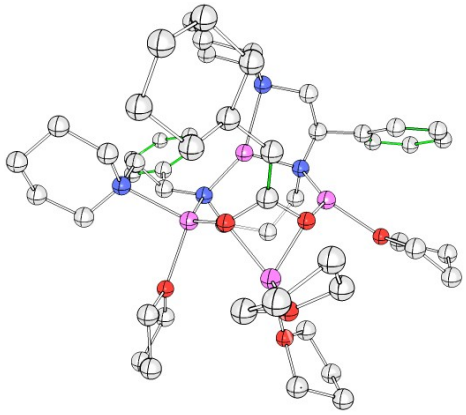
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	H	-0.819786	-6.199457	0.891891
O	1.672196	-0.387073	0.872251	H	-2.845321	-7.422071	0.22022
Li	3.36026	-0.690714	0.087673	H	-2.926588	-8.624156	-1.961277
N	4.086085	-2.426198	-0.833007	H	-0.924409	-8.602859	-3.443862
C	5.502694	-2.140629	-0.745108	H	1.131422	-7.418526	-2.735804
C	5.867534	-1.898102	0.738559	C	1.760696	-4.233173	-2.177489
N	5.287162	-0.646441	1.275449	C	2.160809	-2.76435	-2.434079
C	5.033665	-0.753231	2.726655	H	1.91606	-2.522668	-3.480219
H	4.357064	-1.598055	2.888845	H	1.544293	-2.101522	-1.806644
H	5.976775	-0.969393	3.267839	C	3.644606	-2.41255	-2.224912
C	4.399751	0.525159	3.281242	H	3.805786	-1.411533	-2.688319
H	4.241914	0.406835	4.360895	H	4.229324	-3.102118	-2.86644
H	3.412726	0.645605	2.817889	H	2.549698	-4.879325	-2.622804
C	5.274271	1.751468	2.991995	H	0.856809	-4.451062	-2.791103
C	5.605825	1.816846	1.495955	O	3.568947	1.068928	-1.247652
C	6.190218	0.488761	1.009458	C	2.513167	2.057507	-1.256243
H	6.385028	0.528351	-0.066339	C	2.941474	3.140382	-2.256416
H	7.167021	0.315498	1.505376	C	3.871909	2.364113	-3.199998
H	6.324006	2.621888	1.290836	C	4.568881	1.418768	-2.22379
H	4.69717	2.031889	0.920544	H	5.408964	1.921843	-1.723253
H	6.209478	1.680216	3.567283	H	4.930625	0.494796	-2.679389
H	4.773679	2.672104	3.318613	H	4.574414	3.00322	-3.743646
H	6.96003	-1.90691	0.889024	H	3.290454	1.791128	-3.932081
H	5.458662	-2.736302	1.313751	H	3.497067	3.939311	-1.750943
H	5.759847	-1.202033	-1.290951	H	2.086875	3.597048	-2.765831
C	6.479921	-3.182806	-1.337742	H	1.587575	1.561861	-1.565069
C	7.810792	-2.825059	-1.6015	H	2.384043	2.437567	-0.239008
C	8.722477	-3.744645	-2.119235	O	-0.881771	1.490681	1.12159
C	8.313733	-5.050514	-2.401826	C	-1.780103	1.004985	2.154155
C	6.989639	-5.417602	-2.160881	C	-1.123405	1.382847	3.481032
C	6.085118	-4.491188	-1.634072	C	-0.409919	2.694036	3.122265
H	5.050629	-4.771066	-1.457865	C	0.092172	2.397779	1.708554
H	6.655051	-6.426959	-2.390547	H	1.056486	1.879059	1.715929
H	9.018027	-5.769441	-2.81309	H	0.152374	3.287679	1.072397

Table A3.7 (Continued).

H	9.750049	-3.441895	-2.30811	H	0.407618	2.940836	3.80626
H	8.137444	-1.805503	-1.398365	H	-1.116783	3.533032	3.117263
Li	3.104077	-3.77295	0.216059	H	-0.392264	0.615927	3.756498
N	1.570799	-4.522792	-0.76013	H	-1.849526	1.488367	4.292993
Li	0.057421	-3.331844	-0.227308	H	-2.754266	1.497565	2.025544
O	-0.098657	-1.764781	0.73136	H	-1.891918	-0.072636	2.016974
C	0.961426	-1.363895	1.459159	O	-0.675452	0.547918	-1.806836
C	1.243478	-1.859001	2.712257	C	-0.829743	-0.408851	-2.891741
H	2.076828	-1.403796	3.241505	C	-1.893469	0.17987	-3.833618
O	-1.740881	-3.45794	-1.140508	C	-2.641477	1.176925	-2.932606
C	-2.156441	-4.187392	-2.323626	C	-1.511705	1.69754	-2.049102
C	-3.683111	-4.311708	-2.231182	H	-1.823282	2.078807	-1.075652
C	-4.066826	-3.126454	-1.329789	H	-0.927639	2.471321	-2.5699
C	-2.894943	-3.095058	-0.351995	H	-3.391785	0.661856	-2.320711
H	-3.032723	-3.833314	0.450209	H	-3.143024	1.972509	-3.49198
H	-2.687044	-2.124093	0.100405	H	-2.543745	-0.592584	-4.254721
H	-5.030284	-3.257982	-0.827668	H	-1.420723	0.708458	-4.669343
H	-4.108393	-2.195136	-1.908941	H	0.140738	-0.549581	-3.376121
H	-3.95382	-5.257778	-1.750048	H	-1.138736	-1.356619	-2.442961
H	-4.162796	-4.283607	-3.214353	C	0.423619	-2.88263	3.475256
H	-1.845476	-3.603553	-3.19928	C	1.042401	-3.147638	4.864993
H	-1.644618	-5.15041	-2.340783	C	-1.068667	-2.518902	3.671827
C	1.597993	-5.950903	-0.487545	H	0.418958	-3.853137	2.939606
C	1.913346	-6.179044	1.002861	C	0.291838	-4.229666	5.655694
N	3.253012	-5.700825	1.42249	H	1.028802	-2.204872	5.434194
C	4.302759	-6.644275	0.975421	H	2.101308	-3.42018	4.762081
H	4.288061	-6.689426	-0.117143	C	-1.841545	-3.605389	4.436718
H	4.063326	-7.661336	1.344383	H	-1.126512	-1.574426	4.234162
C	5.69893	-6.245883	1.461206	H	-1.51995	-2.338474	2.691486
H	5.987043	-5.297698	0.993829	C	-1.200212	-3.894107	5.802328
H	6.419417	-6.996869	1.113727	H	0.748137	-4.364559	6.646035
C	5.74275	-6.109236	2.986726	H	0.3928	-5.193756	5.13436
C	4.628869	-5.163549	3.44855	H	-2.892401	-3.310452	4.567278
C	3.271573	-5.604535	2.899573	H	-1.852798	-4.531996	3.841108
H	2.496763	-4.893468	3.194342	H	-1.727832	-4.710664	6.313908
H	3.005571	-6.585139	3.341811	H	-1.30638	-3.004577	6.441849
H	4.572232	-5.126034	4.543883	H	2.401014	-6.438402	-1.080835
H	4.842814	-4.142605	3.106246	C	0.316841	-6.712157	-0.875361
H	5.59781	-7.096141	3.450627	C	0.252756	-7.403185	-2.093934
H	6.724575	-5.746173	3.314891	C	-0.905519	-8.076628	-2.492169
H	1.796097	-7.245964	1.265635	C	-2.029069	-8.087258	-1.664379
H	1.182824	-5.617263	1.595093	C	-1.982902	-7.408273	-0.442939
C	-0.828638	-6.721779	-0.061898				

Table A3.7 (Continued).





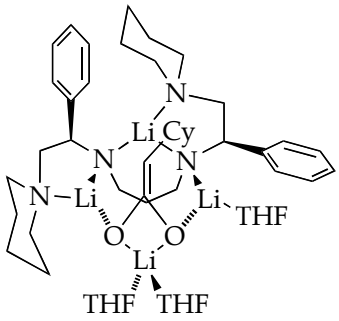
20b
G = -2770.891398
G_{MP2} = -2762.848334

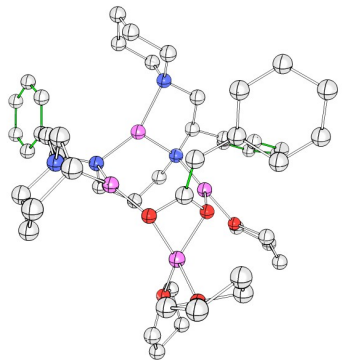
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	H	-2.573625	2.663	-3.043893
O	-1.743506	0.432047	0.786875	H	-2.896267	4.36104	-2.769856
Li	-3.007395	1.116302	-0.454559	N	-5.246328	0.95762	-0.160857
N	-3.337286	3.095209	-1.10061	C	-5.557829	0.508903	1.211942
C	-4.721094	3.012417	-1.51941	H	-5.065523	-0.462484	1.356247
H	-4.826035	2.35044	-2.412507	H	-5.085215	1.202807	1.912642
C	-5.406144	4.328822	-1.961386	C	-7.058907	0.36129	1.512427
C	-6.557983	4.284121	-2.760558	C	-7.71973	-0.585163	0.499659
C	-7.219668	5.448567	-3.150193	C	-7.407499	-0.133206	-0.934788
C	-6.729461	6.695764	-2.755336	C	-5.891291	0.049959	-1.134582
C	-5.574597	6.758477	-1.97497	H	-5.676849	0.413731	-2.143738
C	-4.922542	5.585631	-1.584438	H	-5.403155	-0.928268	-1.037896
H	-4.01178	5.633937	-0.994366	H	-7.778645	-0.866138	-1.663581
H	-5.173043	7.724202	-1.675586	H	-7.932534	0.807563	-1.146749
H	-7.236603	7.607307	-3.061755	H	-8.803461	-0.639364	0.66283
H	-8.113205	5.3841	-3.767167	H	-7.327673	-1.602591	0.650942
H	-6.939535	3.317273	-3.087993	H	-7.546191	1.345278	1.474544
Li	-2.621906	3.943299	0.533914	H	-7.188171	-0.014005	2.536015
N	-0.849881	4.743357	0.273972	O	-2.77349	-0.366478	-1.960955
Li	0.40342	3.253606	0.699175	C	-2.630712	-1.743647	-1.561539
O	0.204738	1.49391	1.144175	C	-1.979957	-2.448942	-2.751132
C	-0.978425	1.093206	1.663636	C	-2.588877	-1.680629	-3.934763
C	-1.27809	1.299902	2.990749	C	-2.643489	-0.247313	-3.393198
H	-0.50967	1.804586	3.574518	H	-3.488962	0.332821	-3.774791
O	2.358048	3.380626	0.168644	H	-1.720534	0.303294	-3.611978
C	3.313385	2.612242	0.930509	H	-3.59856	-2.050752	-4.14867
C	4.66468	2.88311	0.270665	H	-2.000367	-1.756637	-4.854196
C	4.509629	4.349164	-0.16333	H	-2.193417	-3.522187	-2.7734
C	3.037227	4.418747	-0.583244	H	-0.893338	-2.3116	-2.726582
H	2.905207	4.199632	-1.650571	H	-2.049357	-1.759006	-0.637321
H	2.566799	5.37672	-0.35789	H	-3.624861	-2.164914	-1.353527
H	5.187109	4.637644	-0.972804	O	1.001956	-0.230957	-1.751472
H	4.689447	5.018711	0.684585	C	1.876808	-1.346843	-2.025019

Table A3.7 (Continued).

H	4.801824	2.233718	-0.603433	C	3.201972	-0.718695	-2.448016
H	5.505329	2.717732	0.951625	C	2.721402	0.506967	-3.240569
H	3.303987	2.957601	1.973395	C	1.480578	0.951153	-2.453229
H	2.991321	1.569798	0.908501	H	0.67641	1.327162	-3.091782
C	-0.879971	5.979377	1.037917	H	1.715473	1.709873	-1.700661
C	-1.548639	5.70193	2.398216	H	2.450042	0.214199	-4.261644
N	-2.971065	5.292603	2.293171	H	3.471167	1.300803	-3.309171
C	-3.830106	6.474	2.054142	H	3.824119	-1.399953	-3.036504
H	-3.533867	6.932231	1.106051	H	3.772662	-0.408285	-1.564394
H	-3.649251	7.226132	2.847353	H	1.924559	-1.950059	-1.117231
C	-5.320259	6.125066	2.022454	H	1.451487	-1.95113	-2.839954
C	-5.752883	5.419498	3.311918	O	0.835845	-1.623557	0.994122
C	-4.838137	4.217322	3.569702	C	1.750205	-1.176863	2.035662
C	-3.365454	4.628569	3.556813	C	1.25763	-1.823193	3.331134
H	-2.723634	3.751128	3.677611	C	0.59459	-3.114342	2.82766
H	-3.172833	5.305532	4.412634	C	-0.043013	-2.650096	1.517799
H	-5.00548	3.455816	2.796505	H	-1.029949	-2.206192	1.684283
H	-5.066412	3.74589	4.533747	H	-0.121696	-3.443003	0.765834
H	-6.802186	5.105411	3.248596	H	-0.144782	-3.519508	3.524986
H	-5.681891	6.119891	4.157335	H	1.347456	-3.889295	2.637418
H	-5.524504	5.480937	1.159243	H	0.515928	-1.170075	3.800943
H	-5.894133	7.047534	1.868389	H	2.069709	-2.00363	4.042479
H	-1.456553	6.575646	3.068083	H	2.760549	-1.51551	1.766506
H	-1.019525	4.867837	2.87168	H	1.705551	-0.085618	2.055864
H	-1.486272	6.747271	0.510419	C	-5.580967	2.379947	-0.400638
C	0.493491	6.641036	1.243493	H	-6.648922	2.521669	-0.620968
C	0.892211	7.705017	0.421907	H	-5.375339	2.929819	0.525195
C	2.151521	8.297207	0.553405	C	-2.494789	0.810976	3.752283
C	3.039999	7.84392	1.529405	C	-2.746686	-0.713319	3.660016
C	2.658183	6.787491	2.362301	C	-2.383439	1.201356	5.242563
C	1.405797	6.189815	2.212144	H	-3.416057	1.290634	3.370745
H	1.133305	5.367162	2.869443	C	-3.97294	-1.163408	4.471173
H	3.334007	6.435414	3.138895	H	-1.854802	-1.235466	4.041307
H	4.014251	8.311903	1.646886	H	-2.851377	-0.9901	2.605823
H	2.432691	9.119925	-0.100103	C	-3.599143	0.762984	6.072052
H	0.198168	8.077439	-0.329099	H	-1.474959	0.734496	5.65501
C	-0.694694	4.971493	-1.156729	H	-2.234937	2.285372	5.337417
C	-1.02847	3.70589	-1.97498	C	-3.856879	-0.745638	5.944716
H	-0.524332	3.7804	-2.951015	H	-4.105604	-2.251962	4.394872
H	-0.601091	2.826297	-1.469284	H	-4.880671	-0.711447	4.042481
H	-1.35442	5.793051	-1.516184	H	-3.459359	1.03623	7.127034
H	0.328872	5.304919	-1.438975	H	-4.490465	1.309016	5.726359
C	-2.518585	3.453297	-2.258921	H	-4.761492	-1.029173	6.499902
H	-3.021465	-1.29247	6.408074				

Table A3.7 (Continued).





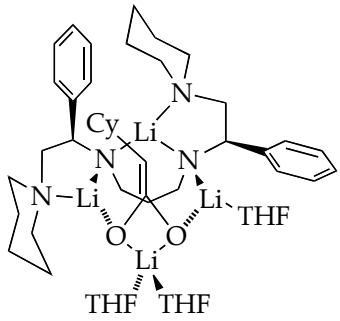
20c
G = -2538.553879
G_{MP2} = -2531.159552

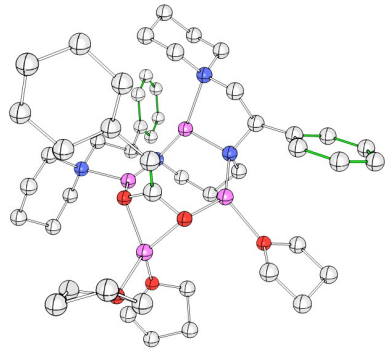
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	H	-1.689759	1.381508	5.730679
O	-1.585225	-0.223512	1.027677	H	-2.931081	2.396213	5.015428
Li	-3.334787	0.067665	0.579741	H	-1.259367	3.238319	3.346068
N	-4.615235	1.24441	-0.473042	O	0.730401	3.791144	-0.706734
C	-5.781188	0.36157	-0.541028	C	0.935361	4.763786	-1.763742
C	-5.998639	-0.339922	0.814013	C	2.407741	5.193352	-1.673519
N	-4.884454	-1.241532	1.180495	C	3.063354	4.018531	-0.928487
C	-4.892405	-1.524652	2.631225	C	1.955009	3.615757	0.039604
H	-4.836934	-0.566742	3.160544	H	1.940569	4.276032	0.917962
H	-5.848346	-2.004816	2.920005	H	1.978143	2.580505	0.381289
C	-3.716742	-2.415338	3.042468	H	3.990327	4.294866	-0.416505
H	-3.776675	-2.608587	4.121161	H	3.28666	3.195452	-1.618908
H	-2.785163	-1.869891	2.852064	H	2.495021	6.111925	-1.083679
C	-3.715128	-3.729722	2.252104	H	2.845872	5.381418	-2.658479
C	-3.772246	-3.430496	0.749117	H	0.710398	4.267061	-2.715457
C	-4.948805	-2.507173	0.421054	H	0.238183	5.591656	-1.624994
H	-4.955699	-2.273272	-0.647198	C	-3.058179	5.32092	0.349441
H	-5.901614	-3.027674	0.643304	C	-3.547875	5.255883	1.810893
H	-3.873561	-4.356272	0.168131	N	-4.848187	4.55601	1.951894
H	-2.839187	-2.945384	0.434147	C	-5.952097	5.468987	1.576127
H	-4.589482	-4.334386	2.535942	H	-5.804446	5.78307	0.539408
H	-2.826638	-4.326175	2.495218	H	-5.898548	6.381075	2.202388
H	-6.956879	-0.888695	0.819156	C	-7.32989	4.825631	1.732197
H	-6.058723	0.425775	1.596917	H	-7.428634	4.01024	1.007817
H	-5.59029	-0.437293	-1.291379	H	-8.095979	5.569569	1.478966
C	-7.091071	1.007245	-1.027174	C	-7.539967	4.294624	3.155531
C	-7.434834	0.943284	-2.385408	C	-6.364436	3.396874	3.560328
C	-8.604228	1.531386	-2.87157	C	-5.027139	4.11062	3.35106
C	-9.472994	2.186672	-1.998646	H	-4.197646	3.44093	3.597611
C	-9.156536	2.247794	-0.640043	H	-4.964544	4.977001	4.038193
C	-7.977464	1.669523	-0.165352	H	-6.446727	3.09373	4.611641
H	-7.756238	1.723446	0.897085	H	-6.376871	2.475501	2.961406
H	-9.832251	2.741986	0.054321	H	-7.605377	5.140361	3.855823

Table A3.7 (Continued).

H	-10.389251	2.638727	-2.369826	H	-8.48929	3.749619	3.230855
H	-8.839399	1.470086	-3.931608	H	-3.61204	6.265042	2.254722
H	-6.774413	0.414953	-3.069811	H	-2.811142	4.68989	2.391553
Li	-4.267449	2.893317	0.580609	H	-3.876928	5.75629	-0.260446
N	-2.75925	3.968366	-0.101123	C	-1.905485	6.331398	0.230213
Li	-0.954849	3.157961	0.267022	C	-1.917922	7.30656	-0.776725
O	-0.293975	1.616512	1.040881	C	-0.876451	8.229375	-0.911163
C	-1.172407	0.858786	1.713915	C	0.201146	8.201827	-0.024752
C	-1.598027	1.132727	2.993246	C	0.22983	7.237385	0.987596
H	-2.233202	0.389581	3.471747	C	-0.806829	6.310352	1.10561
C	-1.090018	2.269691	3.85577	H	-0.765584	5.568906	1.901102
C	-1.849904	2.331803	5.197068	H	1.056357	7.215064	1.694516
C	-1.392625	3.495902	6.08886	H	1.005333	8.927964	-0.113975
C	0.122112	3.45658	6.342732	H	-0.913361	8.97548	-1.701624
C	0.904941	3.386705	5.022846	H	-2.763986	7.346357	-1.460178
C	0.429476	2.212998	4.151898	C	-2.850178	3.834843	-1.551229
H	0.648476	1.266143	4.669237	C	-2.883285	2.357879	-1.992787
H	0.971838	2.191821	3.201094	H	-2.629498	2.323183	-3.063266
H	1.982285	3.306124	5.224605	H	-2.092048	1.798139	-1.469672
H	0.763026	4.329869	4.471711	C	-4.218848	1.605218	-1.837522
H	0.433642	4.329251	6.932764	H	-4.134088	0.686109	-2.463087
H	0.361523	2.568641	6.947335	H	-4.988731	2.214554	-2.354234
H	-1.936136	3.48087	7.043597	H	-3.763074	4.329251	-1.954048
H	-1.650536	4.448444	5.601155	H	-2.013083	4.33139	-2.092831
O	0.458503	-0.174071	-1.917081	O	1.352279	-1.315647	0.79559
C	0.537036	0.920632	-2.854606	C	0.707732	-2.538602	1.250346
C	1.759083	0.603233	-3.712208	C	1.317828	-2.85377	2.618882
C	1.655103	-0.925472	-3.845642	C	1.676559	-1.454357	3.140242
C	1.084169	-1.352083	-2.482554	C	2.153469	-0.757397	1.867268
H	1.858423	-1.676484	-1.78139	H	3.212303	-0.966918	1.659238
H	0.33285	-2.144751	-2.569912	H	1.988442	0.322579	1.875575
H	2.613904	-1.406311	-4.060656	H	2.441109	-1.4651	3.9233
H	0.961155	-1.186058	-4.652694	H	0.785506	-0.947303	3.524656
H	2.678024	0.884185	-3.183301	H	2.219438	-3.469434	2.511498
H	1.745427	1.120904	-4.67616	H	0.617227	-3.388127	3.267575
H	-0.379865	0.95161	-3.458157	H	-0.365285	-2.332485	1.318707
H	0.611086	1.841346	-2.272402	H	0.89105	-3.318281	0.503163

Table A3.7 (Continued).





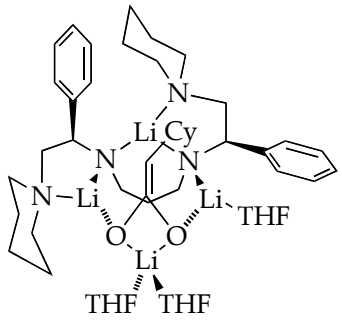
20d
G = -2538.553114
G_{MP2} = -2531.158097

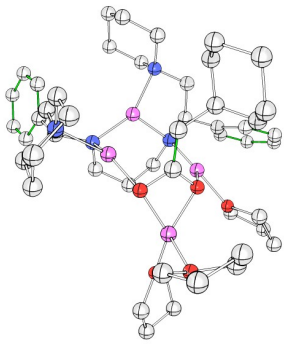
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	C	-6.281106	4.332903	2.253723
O	-1.651802	-0.27189	0.990095	H	-6.104882	5.014565	1.417053
Li	-3.079736	-0.064181	-0.139025	H	-6.336164	4.952082	3.170405
N	-4.412895	1.183378	-1.019732	C	-7.607467	3.59834	2.054732
C	-5.446268	0.257	-1.48832	H	-7.600145	3.096481	1.080667
C	-5.563331	-0.961129	-0.551675	H	-8.418137	4.337553	2.024427
N	-4.314293	-1.748481	-0.461692	C	-7.850702	2.574456	3.170272
C	-4.365085	-2.668367	0.694355	C	-6.630199	1.657262	3.318381
H	-4.545019	-2.069409	1.593685	C	-5.345098	2.471182	3.483889
H	-5.217924	-3.367566	0.586499	H	-4.476636	1.808669	3.537396
C	-3.060179	-3.452256	0.8496	H	-5.388928	3.029469	4.439254
H	-3.148211	-4.126408	1.710854	H	-6.743335	0.989899	4.181919
H	-2.262093	-2.733695	1.06851	H	-6.536965	1.016259	2.430687
C	-2.729477	-4.236941	-0.425359	H	-8.021737	3.101959	4.120137
C	-2.748207	-3.292849	-1.633221	H	-8.756032	1.988097	2.968665
C	-4.063076	-2.511022	-1.701286	H	-4.038704	4.927699	3.385749
H	-4.037929	-1.813195	-2.542179	H	-3.129088	3.463107	2.952095
H	-4.90077	-3.21215	-1.886948	H	-4.142931	5.449009	0.865751
H	-2.61658	-3.849571	-2.570134	C	-2.217915	5.829072	1.65646
H	-1.914349	-2.580923	-1.558437	C	-2.237448	7.13416	1.1454
H	-3.474723	-5.032133	-0.576063	C	-1.212136	8.041892	1.427312
H	-1.754364	-4.732483	-0.33494	C	-0.145299	7.661908	2.243035
H	-6.404585	-1.604136	-0.866558	C	-0.111139	6.364757	2.764936
H	-5.788675	-0.611972	0.463878	C	-1.130947	5.459501	2.467734
H	-5.153845	-0.136564	-2.485026	H	-1.085973	4.455422	2.885936
C	-6.837563	0.866819	-1.736964	H	0.70599	6.061268	3.415719
C	-7.206332	1.253068	-3.033765	H	0.645435	8.369827	2.478924
C	-8.454558	1.819952	-3.300179	H	-1.253274	9.048563	1.017522
C	-9.376464	1.99783	-2.26858	H	-3.074601	7.443855	0.522614
C	-9.03294	1.608123	-0.972333	C	-3.004701	4.186644	-1.010033
C	-7.776665	1.056791	-0.712716	C	-2.836369	2.982895	-1.955192
H	-7.532921	0.759056	0.303467	H	-2.581708	3.368087	-2.95432
H	-9.746987	1.728296	-0.160806	H	-1.973577	2.383084	-1.626402
H	-10.353209	2.429644	-2.471296	C	-4.052189	2.057255	-2.143213

Table A3.7 (Continued).

H	-8.70827	2.114964	-4.3157	H	-3.83526	1.437819	-3.043771
H	-6.50242	1.097724	-3.848702	H	-4.896956	2.70401	-2.458843
Li	-4.372384	2.439965	0.53563	H	-3.97525	4.67877	-1.25253
N	-2.935667	3.774539	0.385218	H	-2.241494	4.946661	-1.288628
Li	-1.055377	3.082739	0.601134	O	1.578862	-1.075334	0.697616
O	-0.280859	1.505339	1.122758	C	1.289038	-2.382424	1.257862
C	-1.129298	0.685403	1.777453	C	2.173442	-2.515616	2.499733
C	-1.372	0.798659	3.12278	C	2.301753	-1.055877	2.961265
H	-0.81998	1.571533	3.655274	C	2.379138	-0.301807	1.634998
C	-2.243753	-0.125301	3.944378	H	3.407031	-0.252409	1.2498
C	-1.6436	-1.538213	4.157829	H	1.941032	0.697576	1.682457
C	-2.554758	-2.449792	4.995608	H	3.176839	-0.878506	3.594293
C	-2.880513	-1.816477	6.356314	H	1.403956	-0.74464	3.504758
C	-3.463282	-0.405221	6.187241	H	3.155414	-2.925488	2.233173
C	-2.55408	0.486467	5.327473	H	1.725227	-3.167941	3.25491
H	-1.60107	0.646588	5.856436	H	0.224663	-2.413953	1.51336
H	-3.002436	1.48113	5.208101	H	1.499054	-3.136077	0.491155
H	-3.629897	0.055555	7.170662	O	0.311847	-0.012905	-1.96007
H	-4.452667	-0.480827	5.709587	C	0.533503	1.210807	-2.700287
H	-3.574398	-2.452377	6.922849	C	1.833408	0.972581	-3.464093
H	-1.957217	-1.753465	6.952152	C	1.707964	-0.514284	-3.834549
H	-2.090763	-3.435961	5.137683	C	1.005567	-1.110757	-2.605212
H	-3.493627	-2.625616	4.44743	H	1.713675	-1.520924	-1.878337
H	-0.67278	-1.430064	4.666696	H	0.273851	-1.882696	-2.866118
H	-1.443476	-1.989861	3.180537	H	2.670889	-0.993994	-4.032967
H	-3.210217	-0.283108	3.429636	H	1.084407	-0.628707	-4.728516
O	0.543491	4.012486	-0.277783	H	2.69695	1.135526	-2.807904
C	0.586968	5.290806	-0.964809	H	1.935569	1.626457	-4.335477
C	1.994274	5.854937	-0.731118	H	-0.309308	1.375175	-3.384307
C	2.823758	4.589166	-0.464985	H	0.568774	2.032317	-1.98083
C	1.83066	3.731817	0.315845	H	2.353911	6.439728	-1.583273
H	1.807967	4.013614	1.37666	H	0.389503	5.10364	-2.027266
H	1.996511	2.655807	0.248033	H	-0.202372	5.930549	-0.565757
H	3.743346	4.783111	0.095898	C	-3.332726	4.831882	1.305672
H	3.095467	4.098832	-1.408222	C	-3.878406	4.176884	2.591669
H	1.996462	6.503007	0.15175	N	-5.128998	3.408851	2.359818

Table A3.7 (Continued).





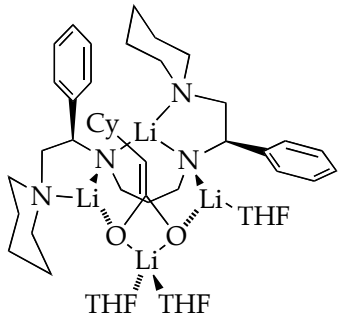
20e
G = -2538.551938
G_{MP2} = -2531.158348

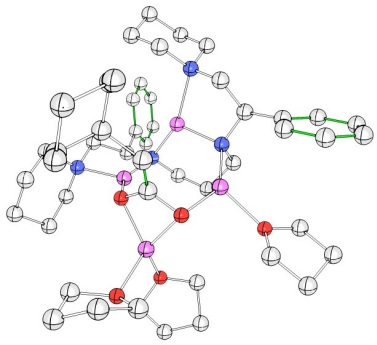
Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	N	-5.657763	3.718375	2.310398
O	-1.549695	-0.663345	0.857238	C	-6.749185	4.512623	1.700359
Li	-3.381529	-0.407042	0.698318	H	-6.4256	4.849609	0.712339
N	-4.750241	0.71796	-0.326516	H	-6.926354	5.419173	2.312177
C	-5.763661	-0.297872	-0.612325	C	-8.048816	3.718038	1.568412
C	-5.974196	-1.211584	0.610343	H	-7.900314	2.907943	0.847162
N	-4.771991	-1.99088	0.978663	H	-8.822004	4.375404	1.150667
C	-4.924859	-2.541282	2.341605	C	-8.498405	3.139958	2.915539
H	-5.084495	-1.700863	3.026475	C	-7.342201	2.374395	3.569799
H	-5.828889	-3.180238	2.392025	C	-6.086442	3.244424	3.644124
C	-3.703101	-3.351116	2.784922	H	-5.258414	2.683502	4.086834
H	-3.891448	-3.753496	3.788626	H	-6.282228	4.109879	4.307518
H	-2.837533	-2.682632	2.856462	H	-7.611667	2.046838	4.581857
C	-3.392685	-4.477781	1.792165	H	-7.117415	1.468719	2.989347
C	-3.27609	-3.895132	0.379004	H	-8.811591	3.957439	3.581807
C	-4.526135	-3.088415	0.017894	H	-9.372014	2.489049	2.784698
H	-4.415448	-2.657457	-0.980755	H	-4.68565	5.496946	2.965831
H	-5.407434	-3.759661	-0.014854	H	-3.751066	3.997469	3.107766
H	-3.141948	-4.692244	-0.363845	H	-4.450928	5.306991	0.440387
H	-2.401811	-3.234834	0.323491	C	-2.644639	5.899703	1.35574
H	-4.199707	-5.225339	1.816007	C	-2.649303	7.092544	0.619856
H	-2.46991	-4.999153	2.076392	C	-1.686937	8.084406	0.832365
H	-6.831104	-1.887776	0.440604	C	-0.700419	7.904721	1.802981
H	-6.220819	-0.585634	1.476749	C	-0.681629	6.721767	2.549024
H	-5.40399	-0.945816	-1.441904	C	-1.638109	5.731431	2.321348
C	-7.122177	0.215288	-1.129141	H	-1.60864	4.819408	2.914819
C	-7.334425	0.340994	-2.510507	H	0.072805	6.576619	3.319207
C	-8.546844	0.804059	-3.025029	H	0.040503	8.679498	1.983931
C	-9.592236	1.136074	-2.162671	H	-1.7152	9.000234	0.246413
C	-9.406702	1.004078	-0.785472	H	-3.426226	7.247906	-0.126496
C	-8.184436	0.556392	-0.279002	C	-3.212453	3.615621	-0.914917
H	-8.06764	0.458853	0.797088	C	-3.063776	2.214576	-1.541761
H	-10.217335	1.245235	-0.10146	H	-2.743501	2.355188	-2.585473

Table A3.7 (Continued).

H	-10.54232	1.486545	-2.55797	H	-2.25106	1.664693	-1.042591
H	-8.677399	0.894869	-4.100934	C	-4.316218	1.317037	-1.59147
H	-6.535112	0.05864	-3.192134	H	-4.088857	0.514024	-2.330494
Li	-4.667602	2.237692	0.952099	H	-5.117144	1.91319	-2.076923
N	-3.256491	3.567729	0.544619	H	-4.130725	4.079893	-1.339502
Li	-1.376534	2.901893	0.874248	H	-2.383937	4.247939	-1.310705
O	-0.563328	1.299939	1.344612	O	1.563804	-1.193007	0.566135
C	-1.396098	0.33134	1.743013	C	1.154174	-2.554829	0.859549
C	-2.077425	0.348336	2.943688	C	2.080873	-3.025944	1.979065
H	-2.617924	-0.557846	3.205197	C	2.307445	-1.727496	2.768917
C	-1.886544	1.393223	4.025138	C	2.360415	-0.671176	1.660225
C	-2.924665	1.234552	5.161354	H	3.38316	-0.515105	1.292438
H	-3.931718	1.155108	4.731253	H	1.93125	0.288467	1.962081
C	-2.659175	0.018066	6.065885	H	3.219837	-1.741405	3.372945
C	-1.236834	0.046274	6.644349	H	1.460178	-1.533734	3.43433
C	-0.192974	0.172593	5.525511	H	3.026965	-3.398055	1.567155
C	-0.461789	1.403218	4.647428	H	1.633631	-3.822906	2.580749
H	0.272491	1.467871	3.837245	H	0.103009	-2.532553	1.16711
H	-0.342805	2.309441	5.265362	H	1.250168	-3.13686	-0.062727
H	-0.232525	-0.728212	4.896462	O	0.499404	0.284752	-1.897908
H	0.818576	0.220303	5.952215	C	0.517831	1.551817	-2.586205
H	-1.140439	0.904625	7.327237	C	1.766721	1.491735	-3.461525
H	-1.05188	-0.853624	7.246766	C	1.752924	0.022433	-3.917116
H	-2.793107	-0.908081	5.489747	C	1.184882	-0.714207	-2.690759
H	-3.399583	-0.012042	6.877041	H	1.965917	-1.147867	-2.059522
H	-2.915037	2.139693	5.787892	H	0.472259	-1.500295	-2.963882
H	-2.036084	2.396016	3.589418	H	2.741353	-0.350246	-4.201454
O	0.270528	3.889074	0.148804	H	1.088841	-0.097744	-4.780345
C	0.389378	5.072913	-0.682155	H	2.660974	1.70299	-2.862574
C	1.79444	5.640852	-0.425994	H	1.73503	2.200381	-4.29469
C	2.560929	4.429494	0.130632	H	-0.392447	1.653507	-3.192097
C	1.471383	3.723849	0.932982	H	0.525159	2.333793	-1.824272
H	1.33268	4.202611	1.912357	H	2.243729	6.059553	-1.331715
H	1.613101	2.653	1.081989	H	0.255822	4.755945	-1.723347
H	3.422726	4.708958	0.744706	H	-0.407556	5.770811	-0.420964
H	2.916063	3.784278	-0.68274	C	-3.719012	4.82436	1.117778
H	1.74541	6.435824	0.325455	C	-4.438588	4.548159	2.455755

Table A3.7 (Continued).





20f
G = -2538.550208
G_{MP2} = -2531.155438

Atom	X	Y	Z	Atom	X	Y	Z
Li	0	0	0	O	0.125439	4.032904	-0.662876
O	-1.3631	-0.274686	1.35271	C	-0.053423	5.208529	-1.494276
Li	-3.002568	-0.363939	0.543374	C	1.304855	5.922524	-1.526478
N	-4.536684	0.573592	-0.394044	C	2.290369	4.785144	-1.216538
C	-5.487969	-0.517723	-0.608931	C	1.495055	3.960676	-0.207173
C	-5.451557	-1.517651	0.562212	H	1.564307	4.392863	0.799989
N	-4.126507	-2.144844	0.753733	H	1.763835	2.905633	-0.148371
C	-4.040015	-2.777601	2.086989	H	3.245019	5.137006	-0.812996
H	-4.254086	-2.009309	2.838448	H	2.497092	4.194501	-2.117923
H	-4.817995	-3.560388	2.186222	H	1.346849	6.684354	-0.740711
C	-2.655014	-3.376729	2.33968	H	1.49337	6.413648	-2.486115
H	-2.643271	-3.8443	3.332255	H	-0.362327	4.866827	-2.489621
H	-1.927693	-2.557116	2.347093	H	-0.848921	5.823381	-1.068688
C	-2.287115	-4.395107	1.253775	C	-3.633722	4.615125	1.243519
C	-2.447382	-3.757052	-0.13135	C	-4.026159	4.122593	2.65331
C	-3.841069	-3.143764	-0.295997	N	-5.215168	3.231942	2.64231
H	-3.923758	-2.657662	-1.271991	C	-6.450857	4.033846	2.491014
H	-4.604734	-3.946192	-0.268574	H	-6.390177	4.592459	1.553176
H	-2.287179	-4.496805	-0.926553	H	-6.504154	4.778831	3.308804
H	-1.693564	-2.968559	-0.261033	C	-7.715479	3.174268	2.502219
H	-2.947043	-5.272493	1.326899	H	-7.724296	2.533272	1.613418
H	-1.261833	-4.759826	1.395824	H	-8.589681	3.83337	2.42605
H	-6.230685	-2.289395	0.429191	C	-7.794231	2.316588	3.771386
H	-5.682931	-0.983636	1.491771	C	-6.487597	1.536648	3.964019
H	-5.195235	-1.08233	-1.520849	C	-5.27339	2.466406	3.907354
C	-6.941882	-0.098036	-0.894183	H	-4.34788	1.889578	3.995107
C	-7.404676	-0.04084	-2.216422	H	-5.305823	3.160805	4.769243
C	-8.710488	0.352658	-2.517227	H	-6.486452	1.006953	4.924878
C	-9.594527	0.685372	-1.490876	H	-6.391053	0.772441	3.180201
C	-9.156021	0.623939	-0.166369	H	-7.955957	2.968168	4.642645
C	-7.844598	0.243046	0.123765	H	-8.651459	1.633137	3.726548
H	-7.527802	0.199289	1.162072	H	-4.197051	4.971154	3.339128
H	-9.838708	0.86763	0.644486	H	-3.189689	3.536502	3.050034

Table A3.7 (Continued).

H	-10.614541	0.984625	-1.718083	H	-4.524589	5.096713	0.790974
H	-9.037383	0.393267	-3.553653	C	-2.590071	5.736214	1.360972
H	-6.726733	-0.314735	-3.022263	C	-2.779224	6.965757	0.715401
Li	-4.510246	2.067181	0.922088	C	-1.823564	7.983444	0.793563
N	-3.212777	3.465642	0.45203	C	-0.656007	7.791992	1.533834
Li	-1.235863	3.023496	0.506976	C	-0.452491	6.572585	2.187999
O	-0.173881	1.601528	0.997887	C	-1.40559	5.557226	2.0964
C	-0.824736	0.832853	1.895348	H	-1.230346	4.616639	2.616297
C	-0.88309	1.147884	3.229155	H	0.445268	6.416698	2.782078
H	-0.332781	2.032981	3.540663	H	0.082746	8.586014	1.610049
C	-1.544367	0.294674	4.290897	H	-1.996752	8.928192	0.283175
C	-0.690498	-0.922996	4.747667	H	-3.694263	7.129243	0.149081
H	-0.376354	-1.488324	3.862942	C	-3.454216	3.643863	-0.974516
C	0.531974	-0.508507	5.578797	C	-3.233634	2.326945	-1.743136
C	0.116681	0.305938	6.812751	H	-3.10598	2.572487	-2.808486
C	-0.724065	1.524991	6.405491	H	-2.286977	1.872847	-1.413982
C	-1.933105	1.114031	5.547423	C	-4.350963	1.270025	-1.673139
H	-2.491386	2.010273	5.249785	H	-4.128066	0.528437	-2.474332
H	-2.608911	0.510934	6.174258	H	-5.28089	1.76754	-2.018144
H	-0.092445	2.226176	5.842668	H	-4.492113	3.993237	-1.183921
H	-1.066455	2.065936	7.298408	H	-2.809805	4.421437	-1.44089
H	-0.47553	-0.33432	7.484792	O	1.716119	-1.003679	0.437887
H	1.000822	0.623147	7.382608	C	1.586238	-2.231677	1.195136
H	1.194686	0.106894	4.953934	C	2.85451	-2.32246	2.041442
H	1.108725	-1.393316	5.883033	C	3.126276	-0.843531	2.358606
H	-1.314476	-1.601422	5.353795	C	2.70318	-0.137963	1.066073
H	-2.472552	-0.125473	3.871088	H	3.542122	-0.026167	0.367049
C	1.097749	-0.806765	-3.99622	H	2.22947	0.832318	1.238285
C	0.544854	-1.31215	-2.653551	H	4.170455	-0.642847	2.617466
H	1.329437	-1.713744	-2.005143	H	2.496859	-0.513681	3.190515
H	-0.24082	-2.065698	-2.774725	H	3.676967	-2.752646	1.456845
H	2.020833	-1.319883	-4.281453	H	2.713809	-2.935169	2.936827
H	0.366394	-0.961098	-4.797621	H	0.683562	-2.166512	1.813094
H	2.236985	0.881408	-3.214522	H	1.473733	-3.053378	0.480474
H	1.287255	1.29338	-4.657833	O	-0.01616	-0.156568	-1.981682
H	-0.817357	1.135955	-3.405903	C	0.10815	1.008553	-2.82945
H	0.239432	1.876791	-2.179499	C	1.292338	0.697165	-3.740252

Part 5: X-ray Crystallography

Crystallographic information for BuLi-ligand Dimer (5)

Table A3.8. Crystal data and structure refinement for **5**.

Identification code	**5**	
Empirical formula	C66 H98 Li6 N8	
Formula weight	1045.16	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 15.4882(8) Å	a= 90°.
	b = 19.7919(11) Å	b= 90°.
	c = 24.4546(14) Å	g = 90°.
Volume	7496.3(7) $Å^3$	
Z	4	
Density (calculated)	0.926 Mg/m^3	
Absorption coefficient	0.053 mm^{-1}	
F(000)	2272	
Crystal size	0.15 x 0.10 x 0.10 mm^3	
Theta range for data collection	1.67 to 24.81°.	
Index ranges	-18<=h<=11, -23<=k<=23, -24<=l<=28	
Reflections collected	37167	
Independent reflections	7035 [R(int) = 0.0653]	
Completeness to theta = 24.81°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9940 and 0.9911	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7035 / 0 / 723	
Goodness-of-fit on F^2	0.890	
Final R indices [I>2sigma(I)]	R1 = 0.0419, wR2 = 0.0950	
R indices (all data)	R1 = 0.0624, wR2 = 0.0995	
Absolute structure parameter	0(10)	
Largest diff. peak and hole	0.319 and -0.129 e.$Å^{-3}$	

Table A3.9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **5**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(4A)	11275(1)	10283(1)	6521(1)	29(1)
C(1A)	9616(1)	9218(1)	7425(1)	29(1)
C(14)	10303(1)	8012(1)	5926(1)	34(1)
C(29)	12097(1)	10323(1)	6214(1)	35(1)
C(1)	7632(1)	9447(1)	6624(1)	28(1)
C(7)	11534(1)	7918(1)	6510(1)	31(1)
C(52)	7227(2)	8027(1)	8099(1)	33(1)
C(36)	6719(1)	7393(1)	5969(1)	29(1)
C(37)	6096(2)	6837(1)	6181(1)	32(1)
C(58)	5257(2)	8038(1)	7749(1)	38(1)
C(43)	7977(1)	7189(1)	6495(1)	32(1)
C(25)	11379(2)	10635(1)	7053(1)	34(1)
C(6)	11842(1)	8101(1)	7082(1)	33(1)
C(53)	6549(2)	8593(1)	8098(1)	35(1)
C(28)	12834(2)	9996(1)	6537(1)	39(1)
C(54)	5541(2)	9203(1)	7533(1)	35(1)
C(51)	7799(2)	8057(1)	8605(1)	37(1)
C(8)	12282(1)	8031(1)	6103(1)	32(1)
C(9)	13011(2)	7621(1)	6128(1)	41(1)
C(46)	8224(2)	8654(1)	8764(1)	43(1)
C(30)	6985(2)	8306(1)	4937(1)	38(1)
C(22)	9597(2)	10677(1)	5422(1)	36(1)
C(42)	5995(2)	6704(1)	6730(1)	34(1)
C(35)	6158(1)	7961(1)	5731(1)	30(1)
C(45)	8219(2)	7462(1)	7516(1)	34(1)
C(15)	9504(2)	8417(1)	5757(1)	36(1)
C(44)	8594(1)	7409(1)	6943(1)	35(1)
C(26)	12090(2)	10335(1)	7394(1)	37(1)
C(13)	12256(2)	8526(1)	5709(1)	37(1)
C(34)	6110(2)	9116(1)	5410(1)	40(1)

C(55)	4941(1)	9183(1)	7048(1)	36(1)
C(38)	5607(2)	6469(1)	5813(1)	45(1)
C(21)	8739(2)	10727(1)	5553(1)	43(1)
C(24)	10586(2)	10639(1)	6207(1)	32(1)
C(63)	11452(2)	8254(1)	8029(1)	42(1)
C(5)	11271(2)	7171(1)	7600(1)	47(1)
C(32)	6969(2)	9506(1)	4601(1)	44(1)
C(27)	12944(2)	10342(1)	7089(1)	41(1)
C(16)	9670(2)	9131(1)	5539(1)	38(1)
C(50)	7960(2)	7481(1)	8902(1)	52(1)
C(57)	4622(2)	7986(1)	7275(1)	42(1)
C(20)	8176(2)	11155(1)	5275(1)	50(1)
C(40)	4907(2)	5877(1)	6541(1)	48(1)
C(23)	10213(2)	10223(1)	5741(1)	33(1)
C(31)	7488(2)	8863(1)	4651(1)	45(1)
C(47)	8788(2)	8666(2)	9205(1)	51(1)
C(33)	6604(2)	9698(1)	5151(1)	44(1)
C(56)	4219(2)	8665(1)	7139(1)	39(1)
C(41)	5405(2)	6223(1)	6914(1)	43(1)
C(2)	10858(2)	8054(1)	8495(1)	53(1)
C(60)	9345(2)	9902(1)	7700(1)	38(1)
C(12)	12932(2)	8610(1)	5344(1)	49(1)
C(64)	7464(2)	10165(1)	6869(1)	50(1)
C(4)	10683(2)	6937(1)	8054(1)	56(1)
C(62)	9673(2)	10823(1)	8384(1)	62(1)
C(65)	6692(2)	10557(1)	6642(1)	54(1)
C(17)	9888(2)	11084(2)	5004(1)	66(1)
C(49)	8536(2)	7495(2)	9345(1)	63(1)
C(19)	8481(2)	11550(2)	4869(1)	65(1)
C(61)	9859(2)	10115(1)	8197(1)	47(1)
C(48)	8937(2)	8075(2)	9489(1)	58(1)
C(11)	13648(2)	8200(1)	5382(1)	52(1)
C(3)	10875(2)	7293(2)	8592(1)	57(1)
C(10)	13696(2)	7708(2)	5769(1)	50(1)
C(39)	5014(2)	5990(1)	5996(1)	54(1)
C(66)	6510(2)	11202(2)	6934(2)	87(1)

C(18)	9341(2)	11533(2)	4731(1)	79(1)
Li(3A)	9075(2)	9490(2)	6592(2)	37(1)
Li(1A)	10135(2)	8285(2)	7108(2)	36(1)
Li(2)	6838(2)	8130(2)	7032(2)	34(1)
Li(1)	7619(3)	8553(2)	6085(2)	37(1)
Li(3)	8286(3)	8854(2)	7290(2)	36(1)
Li(2A)	10754(2)	9283(2)	6440(2)	32(1)
N(4)	5945(1)	8539(1)	7629(1)	32(1)
N(1A)	11227(1)	7916(1)	7517(1)	32(1)
N(1)	6671(1)	8514(1)	5478(1)	28(1)
N(3)	7704(1)	8063(1)	7593(1)	29(1)
N(2A)	10752(1)	8296(1)	6400(1)	30(1)
N(2)	7301(1)	7677(1)	6373(1)	28(1)
N(3A)	9852(1)	9607(1)	5973(1)	29(1)

Table A3.10. Bond lengths [Å] and angles [°] for **5**.

N(4A)-C(29)	1.479(3)
N(4A)-C(25)	1.485(3)
N(4A)-C(24)	1.490(3)
N(4A)-Li(2A)	2.147(4)
C(1A)-C(60)	1.568(3)
C(1A)-Li(1A)	2.158(5)
C(1A)-Li(3)	2.207(5)
C(1A)-Li(3A)	2.267(5)
C(14)-N(2A)	1.464(3)
C(14)-C(15)	1.532(3)
C(29)-C(28)	1.531(3)
C(1)-C(64)	1.564(3)
C(1)-Li(1)	2.207(5)
C(1)-Li(3A)	2.238(4)
C(1)-Li(3)	2.248(5)
C(7)-N(2A)	1.449(3)
C(7)-C(6)	1.520(3)
C(7)-C(8)	1.544(3)
C(52)-N(3)	1.443(3)
C(52)-C(51)	1.523(3)
C(52)-C(53)	1.535(3)
C(36)-N(2)	1.452(3)
C(36)-C(37)	1.551(3)
C(36)-C(35)	1.536(3)
C(37)-C(42)	1.379(3)
C(37)-C(38)	1.383(3)
C(58)-N(4)	1.487(3)
C(58)-C(57)	1.524(3)
C(43)-N(2)	1.455(3)
C(43)-C(44)	1.518(3)
C(25)-C(26)	1.504(3)
C(6)-N(1A)	1.476(3)
C(53)-N(4)	1.483(3)
C(28)-C(27)	1.523(4)

C(54)-N(4)	1.475(3)
C(54)-C(55)	1.507(3)
C(51)-C(50)	1.374(4)
C(51)-C(46)	1.407(4)
C(8)-C(13)	1.375(3)
C(8)-C(9)	1.392(3)
C(9)-C(10)	1.387(4)
C(46)-C(47)	1.388(4)
C(30)-N(1)	1.470(3)
C(30)-C(31)	1.520(3)
C(22)-C(17)	1.376(4)
C(22)-C(21)	1.371(3)
C(22)-C(23)	1.527(3)
C(42)-C(41)	1.393(3)
C(35)-N(1)	1.488(3)
C(45)-N(3)	1.444(3)
C(45)-C(44)	1.522(3)
C(45)-Li(2)	2.779(4)
C(15)-C(16)	1.532(3)
C(26)-C(27)	1.518(3)
C(13)-C(12)	1.386(4)
C(34)-N(1)	1.484(3)
C(34)-C(33)	1.521(4)
C(55)-C(56)	1.533(3)
C(38)-C(39)	1.394(4)
C(21)-C(20)	1.392(4)
C(24)-C(23)	1.520(3)
C(63)-N(1A)	1.461(3)
C(63)-C(2)	1.517(4)
C(5)-N(1A)	1.490(3)
C(5)-C(4)	1.510(4)
C(32)-C(33)	1.509(4)
C(32)-C(31)	1.510(4)
C(16)-N(3A)	1.446(3)
C(16)-Li(2A)	2.786(5)
C(50)-C(49)	1.404(4)

C(57)-C(56)	1.519(3)
C(20)-C(19)	1.349(4)
C(40)-C(39)	1.361(4)
C(40)-C(41)	1.377(4)
C(23)-N(3A)	1.456(3)
C(47)-C(48)	1.379(4)
C(2)-C(3)	1.526(4)
C(60)-C(61)	1.512(4)
C(12)-C(11)	1.378(4)
C(64)-C(65)	1.529(4)
C(4)-C(3)	1.519(4)
C(62)-C(61)	1.502(4)
C(65)-C(66)	1.490(4)
C(17)-C(18)	1.397(4)
C(49)-C(48)	1.352(4)
C(19)-C(18)	1.375(5)
C(11)-C(10)	1.361(4)
Li(3A)-N(3A)	1.947(5)
Li(1A)-N(2A)	1.977(5)
Li(1A)-N(1A)	2.095(4)
Li(2)-N(3)	1.923(4)
Li(2)-N(2)	1.979(5)
Li(2)-N(4)	2.167(4)
Li(1)-N(2)	1.936(4)
Li(1)-N(1)	2.089(4)
Li(3)-N(3)	1.953(4)
Li(2A)-N(3A)	1.916(4)
Li(2A)-N(2A)	1.957(4)

C(29)-N(4A)-C(25)	109.02(17)
C(29)-N(4A)-C(24)	109.34(17)
C(25)-N(4A)-C(24)	107.86(17)
C(29)-N(4A)-Li(2A)	109.02(17)
C(25)-N(4A)-Li(2A)	123.59(18)
C(24)-N(4A)-Li(2A)	96.86(16)
C(60)-C(1A)-Li(1A)	172.8(2)

C(60)-C(1A)-Li(3)	95.53(17)
Li(1A)-C(1A)-Li(3)	90.84(17)
C(60)-C(1A)-Li(3A)	94.65(17)
Li(1A)-C(1A)-Li(3A)	91.04(18)
Li(3)-C(1A)-Li(3A)	66.31(16)
N(2A)-C(14)-C(15)	113.33(19)
N(4A)-C(29)-C(28)	111.00(19)
C(64)-C(1)-Li(1)	162.9(2)
C(64)-C(1)-Li(3A)	98.36(18)
Li(1)-C(1)-Li(3A)	91.09(17)
C(64)-C(1)-Li(3)	105.82(19)
Li(1)-C(1)-Li(3)	91.06(17)
Li(3A)-C(1)-Li(3)	66.14(16)
N(2A)-C(7)-C(6)	108.04(19)
N(2A)-C(7)-C(8)	115.69(19)
C(6)-C(7)-C(8)	108.90(17)
N(3)-C(52)-C(51)	113.37(18)
N(3)-C(52)-C(53)	108.32(19)
C(51)-C(52)-C(53)	111.8(2)
N(2)-C(36)-C(37)	115.72(19)
N(2)-C(36)-C(35)	109.00(18)
C(37)-C(36)-C(35)	107.09(18)
C(42)-C(37)-C(38)	118.1(2)
C(42)-C(37)-C(36)	122.1(2)
C(38)-C(37)-C(36)	119.8(2)
N(4)-C(58)-C(57)	110.9(2)
N(2)-C(43)-C(44)	114.18(19)
N(4A)-C(25)-C(26)	112.39(19)
N(1A)-C(6)-C(7)	113.71(18)
N(4)-C(53)-C(52)	112.34(19)
C(27)-C(28)-C(29)	110.5(2)
N(4)-C(54)-C(55)	111.37(19)
C(50)-C(51)-C(46)	117.7(2)
C(50)-C(51)-C(52)	120.3(2)
C(46)-C(51)-C(52)	122.0(2)
C(13)-C(8)-C(9)	118.1(2)

C(13)-C(8)-C(7)	122.2(2)
C(9)-C(8)-C(7)	119.7(2)
C(8)-C(9)-C(10)	121.4(3)
C(51)-C(46)-C(47)	121.6(3)
N(1)-C(30)-C(31)	112.3(2)
C(17)-C(22)-C(21)	116.7(2)
C(17)-C(22)-C(23)	121.3(2)
C(21)-C(22)-C(23)	122.0(2)
C(37)-C(42)-C(41)	121.3(2)
N(1)-C(35)-C(36)	113.26(18)
N(3)-C(45)-C(44)	112.74(19)
N(3)-C(45)-Li(2)	40.40(13)
C(44)-C(45)-Li(2)	86.22(15)
C(16)-C(15)-C(14)	116.2(2)
C(45)-C(44)-C(43)	116.29(19)
C(25)-C(26)-C(27)	111.2(2)
C(12)-C(13)-C(8)	120.9(2)
N(1)-C(34)-C(33)	111.1(2)
C(54)-C(55)-C(56)	110.7(2)
C(37)-C(38)-C(39)	120.6(3)
C(22)-C(21)-C(20)	122.5(3)
N(4A)-C(24)-C(23)	113.66(18)
N(1A)-C(63)-C(2)	112.3(2)
N(1A)-C(5)-C(4)	112.1(2)
C(33)-C(32)-C(31)	109.8(2)
C(28)-C(27)-C(26)	109.6(2)
N(3A)-C(16)-C(15)	112.2(2)
N(3A)-C(16)-Li(2A)	39.88(13)
C(15)-C(16)-Li(2A)	85.73(16)
C(51)-C(50)-C(49)	120.5(3)
C(56)-C(57)-C(58)	111.9(2)
C(19)-C(20)-C(21)	119.5(3)
C(39)-C(40)-C(41)	119.9(3)
N(3A)-C(23)-C(24)	107.91(19)
N(3A)-C(23)-C(22)	116.80(19)
C(24)-C(23)-C(22)	107.64(19)

C(32)-C(31)-C(30)	112.0(2)
C(48)-C(47)-C(46)	118.8(3)
C(32)-C(33)-C(34)	111.6(2)
C(57)-C(56)-C(55)	108.93(19)
C(40)-C(41)-C(42)	119.6(3)
C(3)-C(2)-C(63)	111.3(2)
C(61)-C(60)-C(1A)	116.4(2)
C(13)-C(12)-C(11)	119.7(3)
C(65)-C(64)-C(1)	116.9(2)
C(3)-C(4)-C(5)	112.1(2)
C(66)-C(65)-C(64)	114.1(3)
C(22)-C(17)-C(18)	121.9(3)
C(48)-C(49)-C(50)	120.7(3)
C(20)-C(19)-C(18)	120.4(3)
C(62)-C(61)-C(60)	113.9(2)
C(49)-C(48)-C(47)	120.7(3)
C(10)-C(11)-C(12)	120.8(3)
C(4)-C(3)-C(2)	108.7(2)
C(11)-C(10)-C(9)	119.1(3)
C(40)-C(39)-C(38)	120.5(3)
C(19)-C(18)-C(17)	119.1(3)
N(3A)-Li(3A)-C(1)	130.4(2)
N(3A)-Li(3A)-C(1A)	119.92(19)
C(1)-Li(3A)-C(1A)	109.18(19)
N(2A)-Li(1A)-N(1A)	91.85(17)
N(2A)-Li(1A)-C(1A)	119.1(2)
N(1A)-Li(1A)-C(1A)	115.3(2)
N(3)-Li(2)-N(2)	107.24(19)
N(3)-Li(2)-N(4)	89.46(18)
N(2)-Li(2)-N(4)	161.6(2)
N(3)-Li(2)-C(45)	29.13(9)
N(2)-Li(2)-C(45)	81.50(14)
N(4)-Li(2)-C(45)	112.43(18)
N(2)-Li(1)-N(1)	92.71(18)
N(2)-Li(1)-C(1)	120.2(2)
N(1)-Li(1)-C(1)	117.4(2)

N(3)-Li(3)-C(1A)	129.5(2)
N(3)-Li(3)-C(1)	119.1(2)
C(1A)-Li(3)-C(1)	110.99(19)
N(3A)-Li(2A)-N(2A)	107.7(2)
N(3A)-Li(2A)-N(4A)	91.15(17)
N(2A)-Li(2A)-N(4A)	157.9(2)
N(3A)-Li(2A)-C(16)	28.95(10)
N(2A)-Li(2A)-C(16)	81.48(15)
N(4A)-Li(2A)-C(16)	113.48(17)
C(54)-N(4)-C(58)	108.74(17)
C(54)-N(4)-C(53)	109.14(18)
C(58)-N(4)-C(53)	110.29(19)
C(54)-N(4)-Li(2)	119.75(18)
C(58)-N(4)-Li(2)	109.98(17)
C(53)-N(4)-Li(2)	98.38(16)
C(63)-N(1A)-C(6)	110.49(18)
C(63)-N(1A)-C(5)	109.0(2)
C(6)-N(1A)-C(5)	108.29(19)
C(63)-N(1A)-Li(1A)	116.24(19)
C(6)-N(1A)-Li(1A)	95.15(17)
C(5)-N(1A)-Li(1A)	116.54(19)
C(30)-N(1)-C(35)	110.18(18)
C(30)-N(1)-C(34)	108.52(19)
C(35)-N(1)-C(34)	108.90(17)
C(30)-N(1)-Li(1)	114.70(18)
C(35)-N(1)-Li(1)	96.15(17)
C(34)-N(1)-Li(1)	117.56(18)
C(52)-N(3)-C(45)	110.72(18)
C(52)-N(3)-Li(2)	104.93(18)
C(45)-N(3)-Li(2)	110.47(19)
C(52)-N(3)-Li(3)	126.93(19)
C(45)-N(3)-Li(3)	110.89(18)
Li(2)-N(3)-Li(3)	89.74(18)
C(7)-N(2A)-C(14)	110.26(18)
C(7)-N(2A)-Li(2A)	120.25(18)
C(14)-N(2A)-Li(2A)	115.03(19)

C(7)-N(2A)-Li(1A)	103.66(18)
C(14)-N(2A)-Li(1A)	117.45(18)
Li(2A)-N(2A)-Li(1A)	88.18(18)
C(36)-N(2)-C(43)	109.21(17)
C(36)-N(2)-Li(1)	104.89(18)
C(43)-N(2)-Li(1)	119.10(19)
C(36)-N(2)-Li(2)	120.34(18)
C(43)-N(2)-Li(2)	113.26(18)
Li(1)-N(2)-Li(2)	89.01(18)
C(16)-N(3A)-C(23)	109.53(18)
C(16)-N(3A)-Li(2A)	111.17(18)
C(23)-N(3A)-Li(2A)	103.38(18)
C(16)-N(3A)-Li(3A)	111.86(19)
C(23)-N(3A)-Li(3A)	129.80(19)
Li(2A)-N(3A)-Li(3A)	86.99(18)

Symmetry transformations used to generate equivalent atoms:

Table A3.11. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **5**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(4A)	24(1)	26(1)	36(1)	-3(1)	-1(1)	3(1)
C(1A)	19(1)	26(1)	43(2)	0(1)	-1(1)	3(1)
C(14)	26(1)	33(1)	43(2)	-7(1)	1(1)	-3(1)
C(29)	29(1)	34(1)	41(2)	-2(1)	2(1)	-1(1)
C(1)	20(1)	29(1)	36(1)	-7(1)	1(1)	0(1)
C(7)	22(1)	24(1)	47(2)	-4(1)	1(1)	-5(1)
C(52)	25(1)	39(1)	36(1)	-1(1)	0(1)	1(1)
C(36)	27(1)	28(1)	31(1)	-4(1)	0(1)	2(1)
C(37)	30(1)	29(1)	37(2)	0(1)	-2(1)	1(1)
C(58)	26(1)	35(1)	54(2)	-1(1)	2(1)	2(1)
C(43)	27(1)	32(1)	39(2)	-5(1)	2(1)	6(1)
C(25)	30(1)	30(1)	41(2)	-6(1)	-1(1)	0(1)
C(6)	22(1)	30(1)	47(2)	3(1)	1(1)	-2(1)
C(53)	27(1)	41(1)	36(2)	-6(1)	4(1)	6(1)
C(28)	23(1)	38(1)	55(2)	-2(1)	1(1)	3(1)
C(54)	24(1)	30(1)	51(2)	-2(1)	5(1)	1(1)
C(51)	31(1)	48(2)	32(1)	-2(1)	7(1)	9(1)
C(8)	20(1)	31(1)	45(2)	-15(1)	-1(1)	-5(1)
C(9)	26(1)	49(2)	49(2)	-12(1)	-3(1)	-4(1)
C(46)	36(1)	50(2)	43(2)	0(1)	-2(1)	-5(1)
C(30)	36(1)	37(1)	41(2)	-3(1)	-1(1)	-3(1)
C(22)	38(1)	38(1)	31(1)	3(1)	-5(1)	-4(1)
C(42)	34(1)	31(1)	39(2)	-1(1)	2(1)	3(1)
C(35)	23(1)	31(1)	34(1)	-3(1)	-5(1)	-2(1)
C(45)	26(1)	37(1)	39(2)	2(1)	-5(1)	9(1)
C(15)	26(1)	42(1)	39(2)	-11(1)	-7(1)	-4(1)
C(44)	24(1)	36(1)	43(2)	-7(1)	-2(1)	13(1)
C(26)	34(1)	34(1)	42(2)	-5(1)	-6(1)	1(1)
C(13)	29(1)	33(1)	48(2)	-11(1)	4(1)	-8(1)
C(34)	39(1)	37(1)	44(2)	3(1)	-8(1)	7(1)
C(55)	21(1)	34(1)	53(2)	2(1)	-3(1)	5(1)

C(38)	57(2)	38(1)	40(2)	4(1)	-10(1)	-11(1)
C(21)	42(2)	35(1)	53(2)	7(1)	-6(1)	3(1)
C(24)	29(1)	29(1)	37(1)	1(1)	-3(1)	3(1)
C(63)	35(1)	49(2)	42(2)	5(1)	-3(1)	-1(1)
C(5)	37(2)	35(1)	70(2)	14(1)	6(2)	3(1)
C(32)	43(2)	41(2)	47(2)	11(1)	-10(1)	-8(1)
C(27)	27(1)	39(1)	56(2)	-4(1)	-11(1)	0(1)
C(16)	33(1)	38(1)	42(2)	-2(1)	-7(1)	-1(1)
C(50)	63(2)	43(2)	48(2)	-5(2)	0(2)	13(1)
C(57)	24(1)	35(1)	67(2)	-7(1)	-1(1)	-4(1)
C(20)	48(2)	42(2)	61(2)	13(2)	-18(2)	-4(1)
C(40)	41(2)	39(2)	64(2)	13(2)	-7(2)	-13(1)
C(23)	26(1)	39(1)	33(1)	-3(1)	-1(1)	0(1)
C(31)	45(2)	49(2)	41(2)	5(1)	3(1)	-4(1)
C(47)	42(2)	66(2)	45(2)	-7(2)	-4(2)	1(2)
C(33)	51(2)	34(1)	48(2)	8(1)	-10(1)	2(1)
C(56)	22(1)	41(1)	54(2)	-1(1)	0(1)	2(1)
C(41)	42(2)	42(2)	44(2)	9(1)	7(1)	2(1)
C(2)	50(2)	61(2)	48(2)	11(2)	4(2)	4(2)
C(60)	35(1)	39(1)	41(2)	2(1)	5(1)	-2(1)
C(12)	41(2)	48(2)	57(2)	-5(2)	9(2)	-14(1)
C(64)	34(2)	51(2)	65(2)	-2(2)	0(2)	-5(1)
C(4)	43(2)	45(2)	80(2)	23(2)	15(2)	2(1)
C(62)	84(2)	48(2)	55(2)	-10(2)	8(2)	-16(2)
C(65)	48(2)	46(2)	69(2)	0(2)	5(2)	4(2)
C(17)	54(2)	90(2)	53(2)	21(2)	-7(2)	-1(2)
C(49)	79(2)	56(2)	56(2)	-4(2)	-23(2)	26(2)
C(19)	55(2)	74(2)	68(2)	11(2)	-26(2)	4(2)
C(61)	56(2)	42(2)	43(2)	-3(1)	4(2)	-8(1)
C(48)	49(2)	86(2)	40(2)	-12(2)	-8(2)	22(2)
C(11)	31(1)	60(2)	66(2)	-19(2)	14(2)	-14(1)
C(3)	37(2)	69(2)	66(2)	31(2)	11(2)	4(1)
C(10)	24(1)	59(2)	68(2)	-16(2)	-1(2)	-2(1)
C(39)	62(2)	46(2)	53(2)	9(2)	-23(2)	-24(2)
C(66)	60(2)	59(2)	144(4)	-23(2)	-2(2)	11(2)
C(18)	76(2)	101(3)	59(2)	40(2)	-12(2)	-3(2)

Li(3A)	25(2)	35(2)	50(3)	2(2)	-1(2)	-3(2)
Li(1A)	25(2)	37(2)	46(3)	-4(2)	2(2)	0(2)
Li(2)	23(2)	34(2)	45(3)	1(2)	-3(2)	-1(2)
Li(1)	35(2)	35(2)	40(2)	-4(2)	-8(2)	-4(2)
Li(3)	30(2)	36(2)	42(3)	-8(2)	0(2)	-3(2)
Li(2A)	29(2)	26(2)	42(2)	-6(2)	0(2)	-4(2)
N(4)	20(1)	33(1)	42(1)	1(1)	0(1)	4(1)
N(1A)	26(1)	28(1)	42(1)	5(1)	1(1)	2(1)
N(1)	24(1)	28(1)	32(1)	2(1)	-4(1)	2(1)
N(3)	22(1)	33(1)	31(1)	-1(1)	3(1)	5(1)
N(2A)	19(1)	29(1)	41(1)	-4(1)	-5(1)	1(1)
N(2)	23(1)	29(1)	33(1)	-1(1)	-5(1)	6(1)
N(3A)	24(1)	29(1)	34(1)	-2(1)	-3(1)	-1(1)

Table A3.12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **5**.

	x	y	z	U(eq)
H(14A)	10126	7543	6011	40
H(14B)	10709	7994	5613	40
H(29A)	12239	10802	6141	42
H(29B)	12032	10090	5858	42
H(7)	11386	7426	6508	37
H(52)	6913	7586	8105	40
H(36)	7073	7197	5666	34
H(58A)	4944	8174	8085	46
H(58B)	5521	7590	7816	46
H(43A)	8312	7102	6158	39
H(43B)	7703	6757	6606	39
H(25A)	10829	10609	7258	40
H(25B)	11506	11118	6985	40
H(6A)	12398	7871	7152	40
H(6B)	11947	8594	7098	40
H(53A)	6215	8573	8443	42
H(53B)	6845	9035	8084	42
H(28A)	12708	9511	6593	46
H(28B)	13378	10032	6326	46
H(54A)	5996	9545	7468	42
H(54B)	5213	9340	7862	42
H(9)	13041	7275	6396	49
H(46)	8121	9058	8566	52
H(30A)	6486	8176	4706	46
H(30B)	7361	7905	4978	46
H(42)	6335	6943	6989	41
H(35A)	5767	7768	5452	35
H(35B)	5796	8152	6026	35
H(45A)	7856	7059	7588	41
H(45B)	8696	7462	7785	41

H(15A)	9192	8159	5472	43
H(15B)	9116	8452	6078	43
H(44A)	9082	7086	6953	41
H(44B)	8833	7856	6842	41
H(26A)	11940	9864	7491	44
H(26B)	12149	10596	7737	44
H(13)	11767	8815	5686	44
H(34A)	5886	9258	5771	48
H(34B)	5610	8997	5176	48
H(55A)	5271	9062	6715	43
H(55B)	4685	9636	6991	43
H(38)	5676	6543	5432	54
H(21)	8520	10459	5844	52
H(24A)	10827	11063	6056	38
H(24B)	10114	10762	6461	38
H(1A)	11421	8749	7975	50
H(1B)	12054	8138	8127	50
H(5A)	11872	7042	7687	57
H(5B)	11106	6941	7256	57
H(32A)	7342	9875	4463	52
H(32B)	6492	9439	4336	52
H(27A)	13137	10814	7034	49
H(27B)	13389	10103	7306	49
H(16A)	10164	9120	5283	45
H(16B)	9156	9286	5333	45
H(50)	7679	7071	8807	62
H(57A)	4926	7810	6949	50
H(57B)	4160	7661	7371	50
H(20)	7581	11168	5370	60
H(40)	4489	5560	6664	58
H(23)	10698	10093	5493	39
H(31A)	8023	8958	4859	54
H(31B)	7657	8708	4281	54
H(47)	9068	9073	9308	61
H(33A)	6213	10090	5108	53
H(33B)	7081	9835	5397	53

H(56A)	3842	8814	7443	47
H(56B)	3862	8626	6804	47
H(41)	5346	6135	7294	51
H(2A)	11040	8290	8833	63
H(2B)	10261	8198	8408	63
H(60A)	9390	10264	7422	46
H(60B)	8730	9868	7807	46
H(12)	12901	8949	5069	58
H(64A)	7384	10116	7268	60
H(64B)	7989	10441	6811	60
H(4A)	10076	7025	7950	67
H(4B)	10752	6444	8104	67
H(62A)	9051	10876	8442	94
H(62B)	9869	11144	8105	94
H(62C)	9980	10910	8728	94
H(65A)	6800	10658	6251	65
H(65B)	6173	10266	6662	65
H(17)	10477	11058	4899	79
H(49)	8646	7093	9545	76
H(19)	8099	11841	4677	78
H(61A)	9733	9799	8500	56
H(61B)	10482	10077	8111	56
H(48)	9326	8076	9789	69
H(11)	14115	8262	5135	63
H(3A)	11450	7154	8729	68
H(3B)	10437	7168	8868	68
H(10)	14192	7427	5793	60
H(39)	4683	5740	5739	64
H(66A)	6969	11528	6855	131
H(66B)	6487	11118	7328	131
H(66C)	5955	11384	6811	131
H(18)	9561	11822	4454	94

Crystallographic information for octalithio-aggregate (7)

Table A3.13. Crystal data and structure refinement for **7**.

Identification code	**7**	
Empirical formula	C90 H128 Li8 N8 O8	
Formula weight	1505.52	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 21.1765(15) Å	a= 90°.
	b = 23.7194(17) Å	b= 90°.
	c = 24.744(2) Å	g = 90°.
Volume	12428.9(16) $Å^3$	
Z	4	
Density (calculated)	0.805 Mg/m^3	
Absorption coefficient	0.050 mm^{-1}	
F(000)	3248	
Crystal size	0.15 x 0.15 x 0.10 mm^3	
Theta range for data collection	1.53 to 23.82°.	
Index ranges	-24<=h<=17, -26<=k<=20, -20<=l<=28	
Reflections collected	28869	
Independent reflections	9929 [R(int) = 0.0625]	
Completeness to theta = 23.82°	96.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9950 and 0.9926	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9929 / 291 / 1138	
Goodness-of-fit on F^2	0.893	
Final R indices [I>2sigma(I)]	R1 = 0.0689, wR2 = 0.1657	
R indices (all data)	R1 = 0.1206, wR2 = 0.1836	
Absolute structure parameter	1(10)	
Largest diff. peak and hole	0.199 and -0.180 $e.Å^{-3}$	

Table A3.14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **7**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Li(1A)	6161(5)	5959(5)	2822(5)	70(3)
Li(1)	3794(5)	7844(4)	1251(4)	60(3)
Li(2A)	6657(4)	5908(4)	1943(4)	53(3)
Li(2)	4740(5)	8068(4)	686(4)	52(3)
Li(3)	6206(6)	8044(5)	1681(5)	78(4)
Li(3A)	5294(5)	5909(4)	812(4)	60(3)
Li(4)	5301(4)	7477(4)	1366(4)	48(2)
Li(4A)	5762(4)	6456(4)	1574(4)	50(3)
O(1)	6181(2)	6517(2)	2254(2)	55(1)
O(2)	5879(2)	7349(2)	1926(2)	51(1)
O(3)	5031(2)	6583(2)	1178(2)	48(1)
O(4)	4500(2)	7385(2)	1058(2)	49(1)
O(6)	3688(2)	7820(2)	2038(2)	63(1)
O(7)	4905(2)	5473(2)	242(2)	61(1)
N(1A)	6872(3)	5877(2)	3455(2)	68(2)
N(1)	2916(2)	7953(2)	809(2)	55(1)
N(2A)	6557(2)	5301(2)	2456(2)	52(1)
N(2)	4081(2)	8594(2)	952(2)	56(1)
N(3A)	6155(2)	5766(2)	1229(2)	51(1)
N(3)	5603(2)	8244(2)	1051(2)	47(1)
N(4A)	7399(2)	6298(2)	1455(2)	54(1)
N(4)	5203(2)	7834(2)	-42(2)	46(1)
C(1)	7009(3)	5057(3)	2826(3)	57(2)
C(2)	7311(3)	5518(3)	3148(3)	68(2)
C(3)	6586(4)	5531(3)	3871(3)	80(2)
C(4)	6162(5)	5869(5)	4225(4)	120(3)
C(5)	6524(5)	6362(5)	4506(4)	122(3)
C(6)	6863(5)	6688(4)	4081(4)	114(3)
C(7)	7246(4)	6327(3)	3718(3)	87(2)
C(8)	7527(3)	4693(3)	2574(3)	63(2)

C(9)	7612(3)	4664(3)	2057(4)	69(2)
C(10)	8084(4)	4348(3)	1823(4)	96(3)
C(11)	8478(4)	4042(4)	2169(5)	104(3)
C(12)	8381(4)	4084(3)	2714(5)	97(3)
C(13)	7909(3)	4400(3)	2921(3)	72(2)
C(14)	3553(3)	8847(3)	674(3)	63(2)
C(15)	3148(3)	8379(3)	413(3)	57(2)
C(16)	2487(3)	8231(3)	1199(3)	61(2)
C(17)	2197(3)	7800(3)	1567(3)	67(2)
C(18)	1831(3)	7353(3)	1256(3)	71(2)
C(19)	2267(3)	7071(3)	853(3)	58(2)
C(20)	2573(3)	7526(2)	495(3)	55(2)
C(21)	3716(3)	9284(3)	241(3)	55(2)
C(22)	4311(4)	9367(3)	74(3)	68(2)
C(23)	4454(4)	9759(3)	-328(3)	82(2)
C(24)	3984(5)	10077(3)	-546(3)	90(3)
C(25)	3368(4)	10005(3)	-362(3)	78(2)
C(26)	3231(3)	9613(3)	30(3)	62(2)
C(27)	6682(3)	5769(2)	845(3)	53(2)
C(28)	7038(3)	6329(2)	937(3)	57(2)
C(29)	8004(3)	6010(2)	1362(3)	53(2)
C(30)	8375(3)	5956(3)	1860(3)	65(2)
C(31)	8508(3)	6550(3)	2106(3)	73(2)
C(32)	7888(3)	6867(3)	2171(3)	65(2)
C(33)	7520(3)	6879(3)	1642(3)	57(2)
C(34)	6491(3)	5699(3)	272(3)	52(2)
C(35)	6266(3)	6132(3)	-52(3)	55(2)
C(36)	6088(3)	6046(3)	-577(3)	66(2)
C(37)	6161(3)	5515(3)	-808(3)	65(2)
C(38)	6384(3)	5078(3)	-495(3)	74(2)
C(39)	6558(3)	5159(3)	42(3)	66(2)
C(40)	6000(3)	7035(3)	2357(3)	48(2)
C(41)	5856(6)	7176(5)	2873(6)	45(4)
C(42)	5590(5)	7680(5)	3095(4)	45(3)
C(43)	5460(8)	8179(7)	2830(5)	45(5)
C(44)	5175(10)	8629(8)	3078(7)	62(6)

C(45)	5021(7)	8612(5)	3624(6)	65(4)
C(46)	5179(7)	8141(6)	3903(5)	90(5)
C(47)	5472(5)	7674(4)	3635(5)	67(4)
C(41')	6148(10)	7294(8)	2842(10)	58(6)
C(42')	5881(8)	7803(7)	3059(7)	64(6)
C(43')	5384(15)	8111(12)	2834(10)	85(11)
C(44')	5160(20)	8584(15)	3087(11)	87(12)
C(45')	5391(12)	8771(9)	3579(10)	97(8)
C(46')	5915(11)	8506(8)	3782(7)	104(7)
C(47')	6131(9)	8011(7)	3520(8)	87(6)
C(48)	4502(3)	6828(3)	1087(2)	53(2)
C(49)	3933(3)	6547(2)	968(2)	52(2)
C(50)	3792(3)	5957(3)	1055(3)	56(2)
C(51)	3258(3)	5741(3)	794(3)	77(2)
C(52)	3070(4)	5173(3)	852(4)	89(2)
C(53)	3419(4)	4839(4)	1183(4)	106(3)
C(54)	3945(4)	5036(3)	1449(4)	93(3)
C(55)	4121(3)	5593(3)	1373(3)	71(2)
O(5)	5266(2)	5882(2)	3058(2)	72(1)
C(56)	4990(4)	5392(3)	3293(4)	100(3)
C(57)	4400(4)	5307(4)	3015(5)	121(3)
C(58)	4183(4)	5900(4)	2922(4)	117(3)
C(59)	4771(3)	6237(3)	2874(3)	84(2)
C(60)	5841(3)	7836(2)	186(2)	50(2)
C(61)	5947(3)	8332(2)	547(2)	49(2)
C(62)	5014(3)	7259(2)	-198(2)	49(2)
C(63)	4351(3)	7252(2)	-419(3)	57(2)
C(64)	4286(3)	7642(3)	-892(3)	70(2)
C(65)	4533(3)	8227(2)	-739(3)	57(2)
C(66)	5180(3)	8202(2)	-511(2)	53(2)
C(67)	6639(3)	8472(3)	615(2)	49(2)
C(68)	6844(4)	9022(3)	501(3)	79(2)
C(69)	7484(4)	9156(3)	575(3)	91(2)
C(70)	7907(3)	8768(3)	742(3)	75(2)
C(71)	7692(3)	8227(3)	849(3)	68(2)
C(72)	7064(3)	8099(3)	782(3)	56(2)

C(73)	3965(4)	7370(3)	2336(3)	77(2)
C(74)	3769(5)	7465(4)	2913(4)	110(3)
C(75)	3364(5)	7993(4)	2895(4)	118(3)
C(76)	3524(4)	8274(3)	2386(3)	76(2)
C(77)	4528(3)	5739(3)	-179(3)	61(2)
C(78)	4232(4)	5272(3)	-480(4)	109(3)
C(79)	4483(6)	4755(4)	-293(4)	139(4)
C(80)	4847(4)	4864(3)	210(3)	75(2)
O(8)	6786(12)	8483(8)	2087(9)	71(5)
C(81)	7217(11)	8179(7)	2396(11)	115(7)
C(82)	7596(10)	8550(8)	2706(10)	151(7)
C(83)	7523(12)	9098(8)	2432(11)	168(8)
C(84)	6911(11)	9058(8)	2148(10)	116(7)
O(8')	6896(13)	8367(8)	2087(10)	65(5)
C(81')	7033(9)	8227(7)	2632(7)	78(5)
C(82')	7019(14)	8730(9)	2927(7)	147(7)
C(83')	6910(16)	9188(8)	2519(9)	152(8)
C(84')	7129(13)	8918(9)	2015(8)	107(7)
C(85)	6131(3)	4868(2)	2280(3)	59(2)
C(86)	5658(3)	5079(3)	1856(3)	63(2)
C(87)	5935(3)	5176(3)	1311(3)	64(2)
C(88)	4318(3)	9014(3)	1326(3)	64(2)
C(89)	4900(3)	8807(2)	1644(3)	56(2)
C(90)	5495(3)	8793(2)	1322(3)	56(2)

Table A3.15. Bond lengths [Å] and angles [°] for **7**.

Li(1A)-O(1)	1.931(12)
Li(1A)-O(5)	1.991(12)
Li(1A)-N(2A)	1.989(12)
Li(1A)-N(1A)	2.183(13)
Li(1A)-Li(2A)	2.418(16)
Li(1A)-Li(4A)	3.412(15)
Li(1)-O(4)	1.912(10)
Li(1)-O(6)	1.962(12)
Li(1)-N(2)	2.019(12)
Li(1)-N(1)	2.172(11)
Li(1)-Li(4)	3.322(13)
Li(2A)-O(1)	1.922(11)
Li(2A)-N(2A)	1.930(11)
Li(2A)-N(3A)	2.089(11)
Li(2A)-N(4A)	2.187(11)
Li(2)-O(4)	1.932(11)
Li(2)-N(2)	1.984(11)
Li(2)-N(3)	2.081(11)
Li(2)-N(4)	2.123(11)
Li(3)-O(2)	1.888(12)
Li(3)-O(8)	1.90(2)
Li(3)-O(8')	1.93(2)
Li(3)-N(3)	2.068(13)
Li(3A)-O(3)	1.920(11)
Li(3A)-O(7)	1.931(11)
Li(3A)-N(3A)	2.123(12)
Li(4)-O(4)	1.873(10)
Li(4)-O(2)	1.873(11)
Li(4)-N(3)	2.079(10)
Li(4)-O(3)	2.245(10)
Li(4A)-O(3)	1.857(10)
Li(4A)-O(1)	1.909(11)
Li(4A)-N(3A)	2.025(11)
Li(4A)-O(2)	2.303(10)

O(1)-C(40)	1.312(7)
O(2)-C(40)	1.326(7)
O(3)-C(48)	1.283(7)
O(4)-C(48)	1.322(6)
O(6)-C(76)	1.421(7)
O(6)-C(73)	1.425(7)
O(7)-C(80)	1.453(7)
O(7)-C(77)	1.455(7)
N(1A)-C(3)	1.449(8)
N(1A)-C(2)	1.471(8)
N(1A)-C(7)	1.479(9)
N(1)-C(20)	1.470(7)
N(1)-C(16)	1.480(7)
N(1)-C(15)	1.489(8)
N(2A)-C(85)	1.434(7)
N(2A)-C(1)	1.446(7)
N(2)-C(14)	1.444(7)
N(2)-C(88)	1.450(7)
N(3A)-C(27)	1.464(7)
N(3A)-C(87)	1.488(7)
N(3)-C(61)	1.459(7)
N(3)-C(90)	1.484(7)
N(4A)-C(29)	1.470(7)
N(4A)-C(33)	1.477(7)
N(4A)-C(28)	1.495(7)
N(4)-C(66)	1.453(7)
N(4)-C(60)	1.466(7)
N(4)-C(62)	1.473(6)
C(1)-C(2)	1.497(8)
C(1)-C(8)	1.528(9)
C(3)-C(4)	1.489(11)
C(4)-C(5)	1.563(12)
C(5)-C(6)	1.490(12)
C(6)-C(7)	1.483(11)
C(8)-C(9)	1.295(9)
C(8)-C(13)	1.370(9)

C(9)-C(10)	1.376(10)
C(10)-C(11)	1.400(11)
C(11)-C(12)	1.368(12)
C(12)-C(13)	1.349(10)
C(14)-C(21)	1.530(9)
C(14)-C(15)	1.544(8)
C(16)-C(17)	1.500(8)
C(17)-C(18)	1.521(9)
C(18)-C(19)	1.514(9)
C(19)-C(20)	1.538(8)
C(21)-C(22)	1.342(9)
C(21)-C(26)	1.392(8)
C(22)-C(23)	1.395(9)
C(23)-C(24)	1.360(10)
C(24)-C(25)	1.392(10)
C(25)-C(26)	1.373(9)
C(27)-C(34)	1.483(8)
C(27)-C(28)	1.544(8)
C(29)-C(30)	1.466(8)
C(30)-C(31)	1.561(9)
C(31)-C(32)	1.522(9)
C(32)-C(33)	1.523(9)
C(34)-C(35)	1.388(8)
C(34)-C(39)	1.409(8)
C(35)-C(36)	1.366(9)
C(36)-C(37)	1.393(9)
C(37)-C(38)	1.379(9)
C(38)-C(39)	1.394(9)
C(40)-C(41)	1.356(15)
C(40)-C(41')	1.38(2)
C(41)-C(42)	1.429(12)
C(42)-C(43)	1.380(14)
C(42)-C(47)	1.361(13)
C(43)-C(44)	1.372(11)
C(44)-C(45)	1.391(17)
C(45)-C(46)	1.356(14)

C(46)-C(47)	1.432(14)
C(41')-C(42')	1.437(16)
C(42')-C(47')	1.350(16)
C(42')-C(43')	1.396(18)
C(43')-C(44')	1.374(15)
C(44')-C(45')	1.39(2)
C(45')-C(46')	1.369(18)
C(46')-C(47')	1.416(18)
C(48)-C(49)	1.408(8)
C(49)-C(50)	1.448(8)
C(50)-C(55)	1.359(8)
C(50)-C(51)	1.398(9)
C(51)-C(52)	1.414(9)
C(52)-C(53)	1.358(10)
C(53)-C(54)	1.376(11)
C(54)-C(55)	1.385(9)
O(5)-C(59)	1.419(7)
O(5)-C(56)	1.426(7)
C(56)-C(57)	1.442(10)
C(57)-C(58)	1.498(10)
C(58)-C(59)	1.486(9)
C(60)-C(61)	1.495(8)
C(61)-C(67)	1.512(8)
C(62)-C(63)	1.507(8)
C(63)-C(64)	1.500(8)
C(64)-C(65)	1.530(8)
C(65)-C(66)	1.481(8)
C(67)-C(72)	1.328(8)
C(67)-C(68)	1.404(8)
C(68)-C(69)	1.403(10)
C(69)-C(70)	1.349(9)
C(70)-C(71)	1.388(9)
C(71)-C(72)	1.373(8)
C(73)-C(74)	1.504(10)
C(74)-C(75)	1.517(11)
C(75)-C(76)	1.466(10)

C(77)-C(78)	1.474(9)
C(78)-C(79)	1.416(10)
C(79)-C(80)	1.488(10)
O(8)-C(81)	1.394(16)
O(8)-C(84)	1.397(14)
C(81)-C(82)	1.416(16)
C(82)-C(83)	1.474(16)
C(83)-C(84)	1.476(17)
O(8')-C(81')	1.417(16)
O(8')-C(84')	1.409(14)
C(81')-C(82')	1.400(16)
C(82')-C(83')	1.501(17)
C(83')-C(84')	1.476(17)
C(85)-C(86)	1.534(8)
C(86)-C(87)	1.488(9)
C(88)-C(89)	1.543(8)
C(89)-C(90)	1.489(8)

O(1)-Li(1A)-O(5)	107.3(5)
O(1)-Li(1A)-N(2A)	101.4(6)
O(5)-Li(1A)-N(2A)	117.6(6)
O(1)-Li(1A)-N(1A)	124.6(6)
O(5)-Li(1A)-N(1A)	116.0(6)
N(2A)-Li(1A)-N(1A)	88.0(4)
O(1)-Li(1A)-Li(2A)	51.0(4)
O(5)-Li(1A)-Li(2A)	132.3(6)
N(2A)-Li(1A)-Li(2A)	50.8(4)
N(1A)-Li(1A)-Li(2A)	110.0(5)
O(1)-Li(1A)-Li(4A)	27.1(3)
O(5)-Li(1A)-Li(4A)	93.6(4)
N(2A)-Li(1A)-Li(4A)	87.9(5)
N(1A)-Li(1A)-Li(4A)	148.4(5)
Li(2A)-Li(1A)-Li(4A)	46.4(3)
O(4)-Li(1)-O(6)	108.7(5)
O(4)-Li(1)-N(2)	100.1(5)
O(6)-Li(1)-N(2)	115.0(5)

O(4)-Li(1)-N(1)	127.8(5)
O(6)-Li(1)-N(1)	113.9(5)
N(2)-Li(1)-N(1)	88.2(5)
O(4)-Li(1)-Li(4)	28.3(3)
O(6)-Li(1)-Li(4)	90.9(4)
N(2)-Li(1)-Li(4)	88.4(4)
N(1)-Li(1)-Li(4)	153.8(5)
O(1)-Li(2A)-N(2A)	103.9(5)
O(1)-Li(2A)-N(3A)	101.2(5)
N(2A)-Li(2A)-N(3A)	112.4(5)
O(1)-Li(2A)-N(4A)	106.2(5)
N(2A)-Li(2A)-N(4A)	139.2(5)
N(3A)-Li(2A)-N(4A)	88.1(4)
O(1)-Li(2A)-Li(1A)	51.3(4)
N(2A)-Li(2A)-Li(1A)	53.0(4)
N(3A)-Li(2A)-Li(1A)	123.2(5)
N(4A)-Li(2A)-Li(1A)	142.0(5)
O(4)-Li(2)-N(2)	100.6(5)
O(4)-Li(2)-N(3)	101.1(5)
N(2)-Li(2)-N(3)	110.4(5)
O(4)-Li(2)-N(4)	107.8(5)
N(2)-Li(2)-N(4)	140.3(5)
N(3)-Li(2)-N(4)	90.9(4)
O(2)-Li(3)-O(8)	123.1(9)
O(2)-Li(3)-O(8')	117.1(9)
O(8)-Li(3)-O(8')	10.8(12)
O(2)-Li(3)-N(3)	102.4(6)
O(8)-Li(3)-N(3)	132.3(8)
O(8')-Li(3)-N(3)	140.2(9)
O(3)-Li(3A)-O(7)	131.7(6)
O(3)-Li(3A)-N(3A)	98.8(5)
O(7)-Li(3A)-N(3A)	129.5(6)
O(4)-Li(4)-O(2)	150.9(6)
O(4)-Li(4)-N(3)	103.2(5)
O(2)-Li(4)-N(3)	102.6(5)
O(4)-Li(4)-O(3)	64.8(3)

O(2)-Li(4)-O(3)	99.6(4)
N(3)-Li(4)-O(3)	145.7(5)
O(4)-Li(4)-Li(1)	29.0(3)
O(2)-Li(4)-Li(1)	137.2(5)
N(3)-Li(4)-Li(1)	92.0(4)
O(3)-Li(4)-Li(1)	89.1(3)
O(3)-Li(4A)-O(1)	147.3(6)
O(3)-Li(4A)-N(3A)	104.5(5)
O(1)-Li(4A)-N(3A)	104.0(5)
O(3)-Li(4A)-O(2)	98.1(4)
O(1)-Li(4A)-O(2)	63.1(3)
N(3A)-Li(4A)-O(2)	149.2(5)
O(3)-Li(4A)-Li(1A)	137.7(5)
O(1)-Li(4A)-Li(1A)	27.5(3)
N(3A)-Li(4A)-Li(1A)	90.0(4)
O(2)-Li(4A)-Li(1A)	87.1(4)
C(40)-O(1)-Li(4A)	96.1(5)
C(40)-O(1)-Li(2A)	159.2(5)
Li(4A)-O(1)-Li(2A)	80.4(4)
C(40)-O(1)-Li(1A)	119.7(5)
Li(4A)-O(1)-Li(1A)	125.4(5)
Li(2A)-O(1)-Li(1A)	77.7(5)
C(40)-O(2)-Li(4)	144.3(4)
C(40)-O(2)-Li(3)	132.7(5)
Li(4)-O(2)-Li(3)	82.0(5)
C(40)-O(2)-Li(4A)	79.0(4)
Li(4)-O(2)-Li(4A)	78.4(4)
Li(3)-O(2)-Li(4A)	136.2(5)
C(48)-O(3)-Li(4A)	153.4(5)
C(48)-O(3)-Li(3A)	123.3(5)
Li(4A)-O(3)-Li(3A)	82.7(5)
C(48)-O(3)-Li(4)	80.3(4)
Li(4A)-O(3)-Li(4)	80.3(4)
Li(3A)-O(3)-Li(4)	144.2(4)
C(48)-O(4)-Li(4)	95.3(5)
C(48)-O(4)-Li(1)	123.9(5)

Li(4)-O(4)-Li(1)	122.7(5)
C(48)-O(4)-Li(2)	149.7(5)
Li(4)-O(4)-Li(2)	81.8(4)
Li(1)-O(4)-Li(2)	81.2(5)
C(76)-O(6)-C(73)	110.8(5)
C(76)-O(6)-Li(1)	127.4(5)
C(73)-O(6)-Li(1)	119.3(5)
C(80)-O(7)-C(77)	110.2(5)
C(80)-O(7)-Li(3A)	127.4(5)
C(77)-O(7)-Li(3A)	121.7(5)
C(3)-N(1A)-C(2)	107.7(6)
C(3)-N(1A)-C(7)	108.7(6)
C(2)-N(1A)-C(7)	107.9(6)
C(3)-N(1A)-Li(1A)	105.8(5)
C(2)-N(1A)-Li(1A)	96.7(5)
C(7)-N(1A)-Li(1A)	128.3(5)
C(20)-N(1)-C(16)	110.4(5)
C(20)-N(1)-C(15)	106.4(5)
C(16)-N(1)-C(15)	109.3(5)
C(20)-N(1)-Li(1)	127.3(5)
C(16)-N(1)-Li(1)	104.5(4)
C(15)-N(1)-Li(1)	97.4(5)
C(85)-N(2A)-C(1)	108.7(4)
C(85)-N(2A)-Li(2A)	113.8(5)
C(1)-N(2A)-Li(2A)	130.0(5)
C(85)-N(2A)-Li(1A)	115.8(5)
C(1)-N(2A)-Li(1A)	107.8(5)
Li(2A)-N(2A)-Li(1A)	76.2(5)
C(14)-N(2)-C(88)	106.6(5)
C(14)-N(2)-Li(2)	130.5(5)
C(88)-N(2)-Li(2)	113.6(5)
C(14)-N(2)-Li(1)	107.9(5)
C(88)-N(2)-Li(1)	118.5(5)
Li(2)-N(2)-Li(1)	77.3(4)
C(27)-N(3A)-C(87)	109.3(5)
C(27)-N(3A)-Li(4A)	125.6(4)

C(87)-N(3A)-Li(4A)	125.0(5)
C(27)-N(3A)-Li(2A)	99.2(4)
C(87)-N(3A)-Li(2A)	101.2(4)
Li(4A)-N(3A)-Li(2A)	73.9(4)
C(27)-N(3A)-Li(3A)	109.8(4)
C(87)-N(3A)-Li(3A)	87.0(4)
Li(4A)-N(3A)-Li(3A)	73.9(4)
Li(2A)-N(3A)-Li(3A)	145.3(5)
C(61)-N(3)-C(90)	109.7(4)
C(61)-N(3)-Li(3)	111.7(5)
C(90)-N(3)-Li(3)	87.5(5)
C(61)-N(3)-Li(2)	95.5(4)
C(90)-N(3)-Li(2)	103.6(4)
Li(3)-N(3)-Li(2)	145.4(5)
C(61)-N(3)-Li(4)	126.9(4)
C(90)-N(3)-Li(4)	123.5(5)
Li(3)-N(3)-Li(4)	73.0(5)
Li(2)-N(3)-Li(4)	73.6(4)
C(29)-N(4A)-C(33)	109.3(5)
C(29)-N(4A)-C(28)	109.6(5)
C(33)-N(4A)-C(28)	108.2(5)
C(29)-N(4A)-Li(2A)	121.1(4)
C(33)-N(4A)-Li(2A)	110.3(4)
C(28)-N(4A)-Li(2A)	97.3(4)
C(66)-N(4)-C(60)	109.7(4)
C(66)-N(4)-C(62)	109.7(4)
C(60)-N(4)-C(62)	110.7(4)
C(66)-N(4)-Li(2)	120.3(4)
C(60)-N(4)-Li(2)	95.7(4)
C(62)-N(4)-Li(2)	109.9(5)
N(2A)-C(1)-C(2)	109.1(5)
N(2A)-C(1)-C(8)	116.3(5)
C(2)-C(1)-C(8)	108.8(5)
N(1A)-C(2)-C(1)	115.3(5)
N(1A)-C(3)-C(4)	111.4(7)
C(3)-C(4)-C(5)	111.6(8)

C(6)-C(5)-C(4)	108.1(8)
C(5)-C(6)-C(7)	113.1(8)
N(1A)-C(7)-C(6)	113.0(7)
C(9)-C(8)-C(13)	120.7(7)
C(9)-C(8)-C(1)	122.2(7)
C(13)-C(8)-C(1)	117.1(7)
C(8)-C(9)-C(10)	123.1(8)
C(9)-C(10)-C(11)	117.2(8)
C(12)-C(11)-C(10)	118.5(9)
C(13)-C(12)-C(11)	121.7(9)
C(12)-C(13)-C(8)	118.8(8)
N(2)-C(14)-C(21)	116.1(5)
N(2)-C(14)-C(15)	109.2(5)
C(21)-C(14)-C(15)	108.6(5)
N(1)-C(15)-C(14)	113.3(5)
N(1)-C(16)-C(17)	110.1(5)
C(16)-C(17)-C(18)	112.1(6)
C(19)-C(18)-C(17)	109.2(5)
C(18)-C(19)-C(20)	109.1(5)
N(1)-C(20)-C(19)	112.8(5)
C(22)-C(21)-C(26)	119.6(6)
C(22)-C(21)-C(14)	121.9(6)
C(26)-C(21)-C(14)	118.5(6)
C(21)-C(22)-C(23)	121.5(7)
C(24)-C(23)-C(22)	119.6(8)
C(23)-C(24)-C(25)	119.2(8)
C(26)-C(25)-C(24)	120.7(7)
C(25)-C(26)-C(21)	119.4(7)
N(3A)-C(27)-C(34)	114.3(5)
N(3A)-C(27)-C(28)	106.3(5)
C(34)-C(27)-C(28)	111.6(5)
N(4A)-C(28)-C(27)	109.5(5)
C(30)-C(29)-N(4A)	112.1(5)
C(29)-C(30)-C(31)	110.2(5)
C(32)-C(31)-C(30)	109.4(5)
C(31)-C(32)-C(33)	111.1(6)

N(4A)-C(33)-C(32)	109.9(5)
C(35)-C(34)-C(39)	118.3(6)
C(35)-C(34)-C(27)	124.4(6)
C(39)-C(34)-C(27)	117.4(6)
C(36)-C(35)-C(34)	122.3(6)
C(35)-C(36)-C(37)	119.7(7)
C(38)-C(37)-C(36)	119.1(7)
C(37)-C(38)-C(39)	121.5(7)
C(38)-C(39)-C(34)	119.0(7)
O(1)-C(40)-O(2)	115.2(5)
O(1)-C(40)-C(41)	118.7(8)
O(2)-C(40)-C(41)	125.2(8)
O(1)-C(40)-C(41')	121.1(11)
O(2)-C(40)-C(41')	119.5(11)
C(41)-C(40)-C(41')	28.8(7)
C(40)-C(41)-C(42)	131.0(12)
C(43)-C(42)-C(47)	116.0(10)
C(43)-C(42)-C(41)	127.8(10)
C(47)-C(42)-C(41)	116.1(11)
C(42)-C(43)-C(44)	122.9(12)
C(43)-C(44)-C(45)	121.0(14)
C(46)-C(45)-C(44)	117.5(12)
C(45)-C(46)-C(47)	120.6(11)
C(42)-C(47)-C(46)	121.8(10)
C(40)-C(41')-C(42')	127.4(19)
C(47')-C(42')-C(41')	117.9(16)
C(47')-C(42')-C(43')	116.2(16)
C(41')-C(42')-C(43')	125.9(17)
C(44')-C(43')-C(42')	120.7(19)
C(43')-C(44')-C(45')	122.3(19)
C(46')-C(45')-C(44')	117.7(18)
C(47')-C(46')-C(45')	118.3(16)
C(42')-C(47')-C(46')	124.2(16)
O(3)-C(48)-O(4)	117.7(5)
O(3)-C(48)-C(49)	124.8(5)
O(4)-C(48)-C(49)	117.3(6)

C(48)-C(49)-C(50)	127.0(6)
C(55)-C(50)-C(51)	116.6(6)
C(55)-C(50)-C(49)	126.5(6)
C(51)-C(50)-C(49)	116.8(6)
C(50)-C(51)-C(52)	122.0(7)
C(53)-C(52)-C(51)	117.6(8)
C(52)-C(53)-C(54)	122.2(8)
C(53)-C(54)-C(55)	118.3(8)
C(50)-C(55)-C(54)	123.2(7)
C(59)-O(5)-C(56)	108.2(5)
C(59)-O(5)-Li(1A)	123.7(5)
C(56)-O(5)-Li(1A)	125.7(5)
O(5)-C(56)-C(57)	105.9(7)
C(56)-C(57)-C(58)	102.0(7)
C(59)-C(58)-C(57)	105.1(6)
O(5)-C(59)-C(58)	105.9(6)
N(4)-C(60)-C(61)	111.7(5)
N(3)-C(61)-C(60)	108.9(5)
N(3)-C(61)-C(67)	114.8(5)
C(60)-C(61)-C(67)	112.5(5)
N(4)-C(62)-C(63)	111.0(4)
C(64)-C(63)-C(62)	111.2(5)
C(63)-C(64)-C(65)	109.6(5)
C(66)-C(65)-C(64)	112.0(5)
N(4)-C(66)-C(65)	111.1(5)
C(72)-C(67)-C(68)	118.2(6)
C(72)-C(67)-C(61)	123.1(5)
C(68)-C(67)-C(61)	118.7(6)
C(69)-C(68)-C(67)	118.8(7)
C(70)-C(69)-C(68)	121.8(7)
C(69)-C(70)-C(71)	118.1(7)
C(72)-C(71)-C(70)	119.9(7)
C(67)-C(72)-C(71)	123.1(6)
O(6)-C(73)-C(74)	105.3(6)
C(73)-C(74)-C(75)	104.7(7)
C(76)-C(75)-C(74)	105.6(7)

O(6)-C(76)-C(75)	103.5(6)
O(7)-C(77)-C(78)	105.7(5)
C(79)-C(78)-C(77)	109.0(7)
C(78)-C(79)-C(80)	108.4(7)
O(7)-C(80)-C(79)	105.3(6)
C(81)-O(8)-C(84)	108.7(12)
C(81)-O(8)-Li(3)	115.5(14)
C(84)-O(8)-Li(3)	135.7(14)
O(8)-C(81)-C(82)	110.2(13)
C(81)-C(82)-C(83)	103.9(13)
C(82)-C(83)-C(84)	104.7(13)
O(8)-C(84)-C(83)	106.4(14)
C(81')-O(8')-C(84')	105.4(13)
C(81')-O(8')-Li(3)	124(2)
C(84')-O(8')-Li(3)	124.5(15)
O(8')-C(81')-C(82')	107.0(13)
C(81')-C(82')-C(83')	105.5(13)
C(82')-C(83')-C(84')	102.0(14)
O(8')-C(84')-C(83')	100.6(16)
N(2A)-C(85)-C(86)	112.6(5)
C(87)-C(86)-C(85)	114.4(6)
N(3A)-C(87)-C(86)	113.2(5)
N(2)-C(88)-C(89)	112.5(5)
C(90)-C(89)-C(88)	114.2(5)
N(3)-C(90)-C(89)	113.1(5)

Symmetry transformations used to generate equivalent atoms

Table A3.16. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **7**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Li(1A)	66(7)	67(7)	78(8)	11(6)	-2(6)	15(6)
Li(1)	62(6)	46(6)	71(7)	-18(6)	2(6)	13(5)
Li(2A)	59(6)	41(6)	58(7)	-2(5)	-3(5)	1(5)
Li(2)	55(6)	56(7)	46(6)	4(5)	2(5)	8(5)
Li(3)	103(9)	54(7)	76(8)	1(6)	-19(7)	1(6)
Li(3A)	70(7)	44(6)	66(7)	0(6)	-1(6)	-3(5)
Li(4)	53(6)	39(6)	53(6)	5(5)	7(5)	0(5)
Li(4A)	45(5)	48(6)	57(6)	0(5)	-3(5)	-7(5)
O(1)	66(3)	37(3)	61(3)	3(2)	-3(2)	0(2)
O(2)	61(2)	36(2)	56(3)	4(2)	-6(2)	0(2)
O(3)	50(2)	38(2)	56(3)	4(2)	-8(2)	5(2)
O(4)	52(2)	34(2)	61(3)	-4(2)	-3(2)	2(2)
O(6)	81(3)	51(3)	56(3)	-5(3)	-3(2)	7(2)
O(7)	70(3)	46(3)	68(3)	2(2)	-10(2)	-13(2)
N(1A)	78(4)	64(4)	63(4)	8(3)	-12(3)	-12(3)
N(1)	67(3)	49(3)	49(3)	-17(3)	-5(3)	5(3)
N(2A)	55(3)	42(3)	59(3)	6(3)	-7(3)	-3(3)
N(2)	69(3)	39(3)	60(3)	-7(3)	-14(3)	4(3)
N(3A)	60(3)	31(3)	63(3)	7(3)	-5(3)	-6(2)
N(3)	59(3)	31(3)	50(3)	-3(2)	1(3)	5(2)
N(4A)	56(3)	57(4)	49(3)	2(3)	0(3)	-1(3)
N(4)	49(3)	36(3)	53(3)	-2(3)	-8(2)	2(2)
C(1)	68(4)	50(4)	53(4)	10(4)	-1(4)	-9(4)
C(2)	64(4)	66(5)	74(5)	15(4)	-15(4)	5(4)
C(3)	83(5)	82(5)	75(5)	9(5)	13(5)	8(4)
C(4)	125(7)	140(9)	96(7)	30(7)	-18(7)	10(7)
C(5)	115(7)	157(10)	92(7)	-21(8)	-9(6)	34(7)
C(6)	124(8)	107(7)	112(8)	-7(7)	-39(7)	7(6)
C(7)	107(6)	82(6)	73(5)	1(5)	-8(5)	12(5)
C(8)	65(5)	47(4)	76(5)	13(4)	-5(4)	1(4)
C(9)	74(5)	53(5)	80(6)	16(4)	5(5)	11(4)

C(10)	125(7)	63(5)	99(7)	13(5)	11(6)	9(5)
C(11)	116(7)	77(6)	119(8)	19(6)	3(7)	19(5)
C(12)	104(7)	65(6)	122(9)	24(6)	-21(7)	-6(5)
C(13)	59(4)	61(5)	95(6)	21(5)	5(4)	4(4)
C(14)	68(5)	51(4)	70(5)	-20(4)	-12(4)	5(4)
C(15)	75(4)	41(4)	55(4)	-4(4)	-3(4)	9(3)
C(16)	69(4)	55(4)	58(4)	-2(4)	-5(4)	9(4)
C(17)	59(4)	76(5)	67(5)	-6(4)	5(4)	6(4)
C(18)	67(4)	62(5)	85(5)	1(4)	-10(4)	6(4)
C(19)	53(4)	50(4)	72(5)	4(4)	-1(4)	5(3)
C(20)	57(4)	49(4)	60(4)	-7(4)	0(3)	9(3)
C(21)	71(5)	40(4)	53(4)	-1(3)	-2(4)	2(4)
C(22)	85(6)	52(5)	66(5)	-4(4)	-7(4)	-1(4)
C(23)	109(6)	49(5)	86(6)	-1(5)	2(5)	4(5)
C(24)	133(8)	54(5)	82(6)	13(4)	-13(6)	-2(5)
C(25)	101(7)	47(5)	86(6)	3(4)	-20(5)	10(4)
C(26)	84(5)	46(4)	57(5)	-4(4)	-15(4)	10(4)
C(27)	61(4)	38(4)	61(4)	2(3)	-1(4)	-1(3)
C(28)	65(4)	43(4)	62(4)	-6(3)	5(4)	-2(3)
C(29)	50(4)	40(4)	68(5)	-7(3)	3(3)	2(3)
C(30)	66(4)	63(5)	65(5)	1(4)	-5(4)	5(4)
C(31)	72(5)	82(5)	66(5)	15(4)	-15(4)	-8(4)
C(32)	75(5)	45(4)	74(5)	-1(4)	-6(4)	-15(4)
C(33)	64(4)	52(4)	56(4)	4(3)	3(4)	-5(3)
C(34)	55(4)	46(4)	54(4)	-15(4)	3(3)	-3(3)
C(35)	56(4)	45(4)	63(5)	-2(4)	2(3)	0(3)
C(36)	67(4)	64(5)	66(5)	-5(4)	3(4)	3(4)
C(37)	66(4)	71(5)	59(4)	-15(5)	4(4)	-1(4)
C(38)	80(5)	64(5)	78(6)	-17(5)	-16(4)	9(4)
C(39)	65(4)	57(5)	76(5)	-3(4)	-6(4)	-1(4)
C(40)	60(4)	37(4)	47(4)	4(4)	0(4)	-8(3)
C(41)	62(10)	28(7)	45(8)	4(6)	0(8)	-5(7)
C(42)	64(9)	44(8)	27(6)	1(6)	5(6)	-14(7)
C(43)	57(9)	48(11)	29(8)	7(8)	10(6)	-12(7)
C(44)	68(12)	41(12)	76(16)	-2(11)	24(10)	2(9)
C(45)	82(10)	57(9)	56(9)	-12(7)	-3(9)	4(7)

C(46)	126(12)	82(10)	63(8)	15(8)	3(8)	8(9)
C(47)	89(9)	46(7)	67(9)	9(6)	12(7)	19(6)
C(41')	56(15)	43(10)	75(14)	13(9)	-12(13)	-21(9)
C(42')	92(15)	25(10)	75(12)	17(8)	-14(10)	-5(9)
C(43')	120(20)	38(17)	90(20)	-12(14)	-47(15)	6(12)
C(44')	120(30)	60(20)	80(20)	-5(18)	-21(18)	28(17)
C(45')	150(20)	66(14)	76(16)	-16(11)	-16(15)	13(12)
C(46')	157(18)	93(14)	61(12)	-9(10)	-26(12)	14(12)
C(47')	103(14)	54(11)	102(13)	1(8)	-38(11)	-2(9)
C(48)	70(5)	37(4)	50(4)	-4(3)	1(4)	-4(4)
C(49)	56(4)	37(4)	62(4)	1(3)	-4(3)	5(3)
C(50)	50(4)	43(4)	74(5)	-13(4)	-1(4)	-16(3)
C(51)	67(5)	51(5)	114(6)	0(5)	11(5)	-14(4)
C(52)	77(5)	75(6)	115(7)	-1(5)	2(5)	-13(5)
C(53)	102(7)	73(6)	141(8)	27(6)	-7(7)	-17(6)
C(54)	79(5)	71(6)	129(7)	1(5)	-12(5)	-13(5)
C(55)	68(4)	48(5)	97(6)	16(4)	-10(4)	-15(4)
O(5)	64(3)	56(3)	96(4)	18(3)	1(3)	1(2)
C(56)	80(6)	67(5)	154(8)	36(6)	24(6)	-2(4)
C(57)	82(6)	95(7)	185(10)	16(7)	-21(7)	-15(5)
C(58)	82(6)	106(7)	164(9)	39(7)	-4(6)	-4(6)
C(59)	70(5)	69(5)	112(6)	1(5)	2(5)	19(5)
C(60)	53(4)	52(4)	46(4)	-3(3)	9(3)	-2(3)
C(61)	54(4)	40(4)	52(4)	9(3)	-7(3)	7(3)
C(62)	52(4)	41(4)	53(4)	1(3)	-2(3)	4(3)
C(63)	65(4)	37(4)	67(5)	-8(4)	-2(4)	-7(3)
C(64)	79(5)	62(5)	70(5)	11(4)	-4(4)	-3(4)
C(65)	68(4)	39(4)	62(4)	3(3)	-3(4)	-10(3)
C(66)	56(4)	47(4)	55(4)	-9(4)	-5(3)	-4(3)
C(67)	57(4)	33(4)	58(4)	0(3)	1(3)	-10(3)
C(68)	77(5)	63(5)	97(6)	17(4)	-4(4)	-4(4)
C(69)	86(6)	58(5)	128(7)	1(5)	-6(5)	-27(5)
C(70)	60(4)	59(5)	107(6)	2(5)	2(4)	0(4)
C(71)	56(4)	50(5)	97(6)	3(4)	7(4)	-2(3)
C(72)	56(4)	42(4)	68(5)	1(3)	-3(4)	-2(3)
C(73)	103(6)	59(5)	70(5)	3(4)	-2(5)	13(4)

C(74)	141(8)	95(7)	95(7)	13(5)	15(6)	31(6)
C(75)	157(8)	132(8)	66(6)	-7(6)	9(6)	30(7)
C(76)	93(5)	66(5)	67(5)	-17(5)	-1(4)	18(4)
C(77)	68(4)	53(4)	62(4)	-1(4)	-14(4)	7(3)
C(78)	127(7)	81(5)	120(7)	-26(5)	-42(6)	15(5)
C(79)	203(10)	72(5)	142(8)	3(6)	-79(7)	-20(6)
C(80)	101(5)	40(4)	84(5)	0(4)	-10(4)	-14(4)
O(8)	91(12)	48(8)	73(8)	-10(7)	-1(6)	-13(8)
C(81)	110(15)	83(9)	152(16)	-23(11)	-40(12)	20(9)
C(82)	132(14)	136(12)	184(16)	-38(11)	-70(11)	15(11)
C(83)	173(15)	122(11)	209(17)	-21(12)	-69(14)	-59(12)
C(84)	156(15)	60(9)	133(14)	-37(11)	-35(12)	8(10)
O(8')	58(9)	43(8)	92(8)	4(7)	-18(8)	9(7)
C(81')	45(9)	101(9)	87(10)	-7(8)	-3(9)	5(9)
C(82')	163(16)	153(13)	125(10)	-52(9)	-26(13)	62(14)
C(83')	195(18)	93(9)	168(15)	-54(9)	-22(16)	28(14)
C(84')	131(16)	48(11)	142(11)	-19(9)	-15(12)	-7(11)
C(85)	63(4)	40(4)	75(5)	11(4)	-9(4)	-10(3)
C(86)	82(5)	34(4)	73(5)	12(4)	-12(4)	-14(3)
C(87)	74(4)	45(4)	74(5)	7(4)	-25(4)	-3(3)
C(88)	76(4)	57(4)	58(4)	-5(4)	-14(4)	10(4)
C(89)	72(4)	35(4)	61(4)	-7(3)	-13(4)	1(3)
C(90)	66(4)	44(4)	57(4)	-9(3)	-6(4)	1(3)

Table A3.17. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **7**.

H(1A)	6769	4814	3084	68
H(2A)	7614	5346	3404	81
H(2B)	7555	5761	2898	81
H(3A)	6922	5357	4094	96
H(3B)	6341	5224	3700	96
H(4A)	5976	5620	4504	144
H(4B)	5813	6025	4005	144
H(5A)	6223	6610	4699	146
H(5B)	6829	6210	4772	146
H(6A)	7144	6967	4258	137
H(6B)	6551	6899	3863	137
H(7A)	7440	6566	3435	105
H(7B)	7592	6153	3929	105
H(9A)	7336	4871	1828	83
H(10A)	8139	4338	1442	115
H(11A)	8804	3809	2029	125
H(12A)	8653	3887	2954	117
H(13A)	7843	4418	3301	86
H(14A)	3285	9039	952	75
H(15A)	2780	8554	231	68
H(15B)	3402	8185	134	68
H(16A)	2150	8433	1001	73
H(16B)	2725	8510	1415	73
H(17A)	1909	7991	1823	81
H(17B)	2535	7615	1779	81
H(18A)	1661	7068	1510	86
H(18B)	1472	7529	1064	86
H(19A)	2025	6804	626	70
H(19B)	2599	6858	1047	70
H(20A)	2869	7342	240	66
H(20B)	2240	7713	279	66
H(22A)	4643	9154	232	81

H(23A)	4877	9803	-450	98
H(24A)	4075	10346	-819	108
H(25A)	3039	10230	-509	93
H(26A)	2810	9568	155	75
H(27A)	6972	5452	941	64
H(28A)	7332	6398	633	68
H(28B)	6733	6645	952	68
H(29A)	7922	5630	1213	64
H(29B)	8252	6224	1092	64
H(30A)	8780	5764	1780	78
H(30B)	8140	5723	2125	78
H(31A)	8716	6509	2462	88
H(31B)	8795	6764	1865	88
H(32A)	7976	7258	2289	78
H(32B)	7630	6682	2454	78
H(33A)	7114	7078	1697	69
H(33B)	7765	7086	1365	69
H(35A)	6235	6501	95	65
H(36A)	5915	6347	-782	79
H(37A)	6058	5455	-1178	78
H(38A)	6419	4712	-649	89
H(39A)	6719	4855	251	79
H(41A)	5946	6892	3132	54
H(43A)	5573	8211	2460	54
H(44A)	5082	8958	2873	74
H(45A)	4812	8918	3794	78
H(46A)	5096	8121	4279	108
H(47A)	5586	7351	3840	81
H(41B)	6461	7115	3056	69
H(43B)	5202	7991	2502	102
H(44B)	4826	8791	2920	104
H(45B)	5195	9071	3769	116
H(46B)	6128	8650	4090	124
H(47B)	6474	7814	3678	104
H(49A)	3606	6769	813	62
H(51A)	3015	5984	571	93

H(52A)	2712	5029	666	107
H(53A)	3296	4457	1232	127
H(54A)	4182	4795	1680	111
H(55A)	4489	5727	1551	85
H(56A)	4917	5449	3685	120
H(56B)	5270	5061	3245	120
H(57A)	4096	5095	3241	145
H(57B)	4463	5104	2669	145
H(58A)	3930	5926	2586	141
H(58B)	3923	6034	3228	141
H(59A)	4844	6351	2494	101
H(59B)	4744	6581	3100	101
H(60A)	6154	7844	-112	61
H(60B)	5908	7485	394	61
H(61A)	5747	8664	365	59
H(62A)	5040	7008	121	59
H(62B)	5309	7114	-476	59
H(63A)	4242	6863	-532	68
H(63B)	4053	7366	-131	68
H(64A)	3837	7669	-1000	84
H(64B)	4528	7493	-1203	84
H(65A)	4535	8471	-1064	68
H(65B)	4246	8399	-470	68
H(66A)	5476	8061	-790	63
H(66B)	5316	8586	-405	63
H(68A)	6554	9299	376	95
H(69A)	7623	9530	504	109
H(70A)	8339	8863	786	90
H(71A)	7978	7945	968	81
H(72A)	6928	7726	859	67
H(73A)	4431	7377	2302	93
H(73B)	3808	7001	2204	93
H(74A)	4142	7522	3147	132
H(74B)	3523	7140	3051	132
H(75A)	2910	7894	2905	142
H(75B)	3460	8240	3207	142

H(76A)	3158	8486	2242	91
H(76B)	3883	8536	2434	91
H(77A)	4800	5966	-421	73
H(77B)	4203	5987	-19	73
H(78A)	3769	5279	-424	131
H(78B)	4316	5315	-871	131
H(79A)	4763	4589	-572	167
H(79B)	4137	4485	-220	167
H(80A)	4620	4715	529	90
H(80B)	5269	4685	191	90
H(81A)	7490	7950	2156	138
H(81B)	6988	7919	2640	138
H(82A)	8043	8428	2705	181
H(82B)	7444	8571	3084	181
H(83A)	7871	9162	2172	202
H(83B)	7518	9410	2697	202
H(84A)	6574	9242	2362	139
H(84B)	6936	9244	1791	139
H(81C)	7455	8050	2658	93
H(81D)	6715	7959	2773	93
H(82C)	7424	8790	3119	176
H(82D)	6673	8723	3196	176
H(83C)	7161	9528	2604	182
H(83D)	6458	9291	2496	182
H(84C)	6943	9100	1691	129
H(84D)	7595	8923	1986	129
H(85A)	5897	4722	2596	71
H(85B)	6378	4553	2125	71
H(86A)	5313	4800	1823	76
H(86B)	5470	5436	1986	76
H(87A)	6296	4917	1260	77
H(87B)	5615	5085	1033	77
H(88A)	3979	9115	1584	76
H(88B)	4432	9359	1122	76
H(89A)	4964	9057	1959	67
H(89B)	4814	8423	1782	67

H(90B)	5478	9094	1045	67
H(90A)	5856	8875	1564	67

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