



HAL
open science

Ligand effects on coordination properties of organolithium compounds: insights from computational experiments on a "weakened" Li⁺

Hélène Gérard, Patrick Chaquin, Jacques Maddaluno

► To cite this version:

Hélène Gérard, Patrick Chaquin, Jacques Maddaluno. Ligand effects on coordination properties of organolithium compounds: insights from computational experiments on a "weakened" Li⁺. *Journal of Molecular Graphics and Modelling*, 2019, 26 (3), pp.59. <10.1007/s00894-020-4302-2>. <hal-03439676>

HAL Id: hal-03439676

<https://hal.science/hal-03439676v1>

Submitted on 22 Nov 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

Journal of Molecular Modeling

Ligand effects on coordination properties of organolithium compounds: insights from computational experiments on a “weakened” Li⁺ --Manuscript Draft--

Manuscript Number:	JMMO-D-19-00654R1
Full Title:	Ligand effects on coordination properties of organolithium compounds: insights from computational experiments on a “weakened” Li ⁺
Article Type:	TC Festschrift N. Gresh
Keywords:	Lithium; Carbanions; Ab Initio Calculations; Molecular modeling; Solvent effects
Corresponding Author:	Helene Gerard, Ph.D. Sorbonne University FRANCE
Corresponding Author Secondary Information:	
Corresponding Author's Institution:	Sorbonne University
Corresponding Author's Secondary Institution:	
First Author:	Helene Gerard, Ph.D.
First Author Secondary Information:	
Order of Authors:	Helene Gerard, Ph.D. Patrick CHAQUIN Jacques MADDALUNO
Order of Authors Secondary Information:	
Funding Information:	Agence Nationale de la Recherche (ANR-07-BLAN-0294) Dr Jacques MADDALUNO
Abstract:	<p>A simple numerical experiment is presented which allows tuning the lithium electrophilicity, a parameter strongly affected by the solvent and additives coordination. A series of coordination of Li⁺ to carbanions or polydentate nucleophiles is examined showing the potential and the limits of this approach. The results suggest that such a simple trick can be remarkably helpful to model and decipher the effects of solvation on the structure and properties of lithiated organometallic species.</p>
Response to Reviewers:	<p>Please find below our answers to the reviewers comments:</p> <p>Reviewer #1:</p> <ul style="list-style-type: none">- Maybe more details in the description of the computational set-up should be given to enable researchers to reproduce the results if they wish. A sample input is given in S.I. It has been commented to be more explicit and the presence of this input in S.I. has been emphasized in the main text.- page 2 bottom, "Four ligands classically...(Figure 1) examined". I only see three structures on Figure 1. This is a mistake. It has been corrected to three.- page 4, line 4, call to Table 1 misses table number. Table number (1) has been added.- Figure 7, the caption should indicate the meaning of the numbers appearing on the pictures The following caption has been added “Population for the labelled basins is given (in electron).”

- Most Figures showing graphs should be redrawn more (with bigger label fonts, with Ticks).

Figure 3, 4 and 5 have been redrawn. A xls file including necessary data for plotting the graph can be provided to editorial office upon request.

Reviewer #2:

On page 4, the table number is missing " on the Li center are reported in Table ." Table number (1) has been added.

On page 6, there is a typo : "Li-C bond rises from 1.985 Å in absence of coordination", I suppose the authors mean "in absence".

This is right and has been corrected in that way.

Can the authors confirm that the energy difference they give are potential energies and not Gibbs Free energies ?

This has been added in the text (page 9) and in the legend of figure 6.

In the first section, the authors discuss the evolution of Li⁺ orbital energies in different systems, can the authors give that of the neutral Li for comparison ? I also suggest to give the energies in Table 1 in eV for simplicity.

This has been done. The values in Table 1 are now in eV and the orbital energies are now given for Li, Li* (c = 0.1) and Li* (c = -0.1) for complete information.

In the second section, the authors discuss the geometry evolution of Li-allyl complex upon coordination of neutral molecules. Would it be possible to perform Energy Decomposition Analysis and try to make a link between the donation and electrostatic values with the parameter of equation 2 ?

Natural population analysis shows a significantly stronger donation toward Li in the terminal structure compared to the bridged one (for c = 0.02, 0.18 and 0.03e population of the 2s Li orbital are found respectively). This sentence has been added page 10.

Carrying out a complete Energy Decomposition Analysis would require adapting the Li* method to a new software, which cannot be carried out in the time frame offered for the revisions.

Could the authors precise how evolves the C-C bond the allylic anion in the terminal structure ?

A closer look at the terminally bonded structures reveals a dissymmetry in the C-C distance, the Li-bonded C=C being 0.12 Å longer than the other one, whatever the value of c. This sentence has been added page 9.

Do the two basins still are similar or do they differ significantly?

This is associated to a polarization of the electron density on the Li bonded side (total population on Li bonded side equal to 3.90e compared to 3.53e on the other one). This sentence has been added page 10 and Figure 7 has been modified to add the necessary values for the discussion.

The authors have take OMe₂ as an archetype of etheral solvents but they also showed that the structure is strongly dependent to the donation from the ligand. THF is known to be slightly more basic than of ether. Does the authors expect a transition to a terminal structure sooner with THF than in OMe₂ ?

Computation of a scan with three THF molecules was too time-consuming to be carried out with the time frame offered for the revisions. Nevertheless, coordination of the third solvent molecule was used to probe the effect of strong donation.

Coordination of three ether molecules to allyl is in fact a slightly higher coordination number than what would be expected from experimental data

Ligand effects on coordination properties of organolithium compounds: insights from computational experiments on a “weakened” Li^+

Hélène GERARD¹, Patrick CHAQUIN¹ and Jacques MADDALUNO²

1 : Sorbonne Université, CNRS, Laboratoire de Chimie Théorique, LCT, F-75005 Paris, France.
helene.gerard@sorbonne-universite.fr ; Tel : (+33) 144 279 662

2 : Normandie Univ, UNIROUEN, INSA Rouen, CNRS, COBRA, (UMR 6014 & FR 3038), F-76000, Rouen, France

Summary: A simple numerical experiment is presented which allows tuning the lithium electrophilicity, a parameter strongly affected by the solvent and additives coordination. A series of coordination of Li^+ to carbanions or polydentate nucleophiles is examined showing the potential and the limits of this approach. The results suggest that such a simple trick can be remarkably helpful to model and decipher the effects of solvation on the structure and properties of lithiated organometallic species.

Keywords : Lithium; Carbanions ; An initio calculations ; Molecular Modeling ; Solvent effects

Introduction

The computational description of lithiated organometallic species, Li being either the organometallic center or being associated to other metal cations (Al, Cu, Zn...), is particularly challenging. Experimentally, these reagents are used in complex media[1] of which realistic models should include all substituents to provide a meaningful representation of the metal center and counter ion coordination spheres, namely ligands, potential chelating additives and explicit solvent molecules.[2] The versatility of the Li⁺ coordination, strongly depending on an operational accounting of these effects, requires a heavy modelling procedure. Indeed, neglecting their effect introduces a stern flaw in the model as it strongly alters the spatial location of the lithium ion, which is known to change, in turn, the chemo, regio and stereochemical courses of the reactions[3-5]. Eventhough explicit representation of these additional ligands rises steeply the computational cost of the study, the ever rising computational power associated to latest development in modelling methods allows such approaches.[6] Nevertheless, studies remain hindered by the complexity of the system in term of degrees of freedom, which requires paying particular attention to conformational and configurational sampling. It also dramatically alters the lisibility of the resulting structures, limiting the interpretative power of computational approaches.

Would it be possible to computationally reproduce the electronic effects triggered by the agents and solvents coordinating Li without introducing their structural complexity? With the exception of early models resorting to point charges [7-8], no such approach has been developped for lithium coordination to our knowledge. Inspired by the efforts made to rationalize various substituents effects in organic molecules, and in particular the H* method [9], developed by one of us, we decided to tackle this problem. H* is a computational tool which proved efficient in deciphering the respective role of inductive or mesomer effects of substituents in organic reactions [10-12]. A similar tool was next used to modulate the binding potential of a Lewis base, and gauge the impact of the apical ligand basicity on the chemical reactivity of tetradentate Cu-amine complexes.[13]

In this study, we aim at understanding how ligands binding influences the Lewis acidity of the Li center and, as a consequence, the behavior of various organolithium compounds. **Three** ligands classically

encountered in organolithium chemistry (Figure 1) are examined. Me₂O is introduced as a simplified model for monocoordinated ligands, and especially for the usual coordinating ethereal solvent, such as diethylether or tetrahydrofuran.[14] A di-coordinating amine ligand was also appraised, namely ethylenediamine (EDA) as well as the tetracoordinating crown-ether (12-crown-4, 12C4).[1] Those correspond to additives encountered in many experimental procedures.

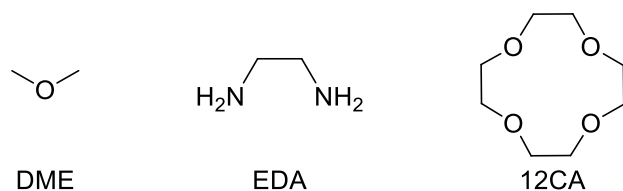


Figure 1: Schematic representation of the ligands examined: dimethylether (DME), ethylenediamine (EDA), 12-crown-4 (12C4)

In a first part, we describe and justify our computational approach. We next examine the modulation of the coordination in two prototypical organolithium compounds, namely methyl and allyllithium. Finally, the possibility of extending this method to sample lithium coordination by polydentate organometallic anions is examined.

Results and discussion

“Weakening” of the Li center. In a first step, the neutral ligands described in Figure 1 are coordinated to a Li⁺ center, yielding cationic complexes. In such systems, a simple donor-acceptor orbital model (Figure 2) predicts a raise of the energy of the BV through coordination of a Lewis base to Li⁺, whereas effects on the filled ligand-centered orbital is expected to be minimal (non-bonding interaction) or stabilizing (bonding interactions).[15]

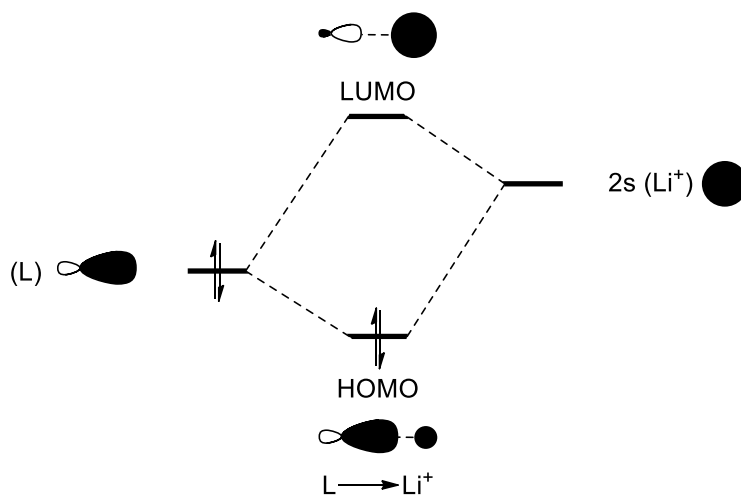


Figure 2: Schematic representation a ligand – Li^+ orbital interaction, evidencing the increase of the Lowest Unoccupied Molecular Orbital (LUMO) energy

Full geometry optimization of these complexes was carried out with the Gaussian 09 program[16] and within the framework of the Density Functional Theory (DFT), using the hybrid B3LYP exchange-correlation functional[17-18] and the 6-31+G** basis set for all atoms. The energy and expression of the canonic orbitals were examined and those essentially localized on the Li center are reported in **Table 1**.

In line with the simple model in Figure 2, we observe a raise of the energy of the Li 2s (LUMO) and 2p (LUMO+1) orbitals. In addition, and more surprisingly, an up-shift of the core Li 1s orbital is also observed, and is larger for these core electrons (up to 0.30 a.u.) than for the valence ones (up to 0.13 a.u. for the 2s level and 0.067 a.u. for the 2p one). This shift increases with the number of coordinated Me_2O , and is similar for the di-coordinating EDA and for two Me_2O . The four-coordinated 12C4 leads results similar to three Me_2O , most probably as the coordination is planar in both systems.

The fact that all orbitals are destabilized, including core electrons, confirms the possibility to reproduce such an increase of the orbital energies through addition of a simple pseudopotential on the Li center.

Considering the standard expression of the effective potential is given by equation 1, a simple expression can be obtained taking α and n equal to 0 and n' to 1, and limiting the summation to a single term **(equation 2).**[9] As such, variations are handled through a single variable coefficient c . It will be referred below as Li^* .

A sample commented Gaussian Input for MeLi is given in S.I.

$$V(r) = -\frac{Z-n}{r} + \sum_j c_j r^{n'-2} e^{-\alpha r^2} \quad \text{eq. 1}$$

$$V(r) = -\frac{Z}{r} + cr^{-1} \quad \text{eq. 2}$$

A regular Li center is obtained for $c = 0$. Using a negative value for c is thus similar to increasing the nuclear charge. As illustrated in Table 1, this stabilizes all the orbitals. On the opposite, a positive c corresponds to a decrease of the nuclear charge and leads to a destabilization of the Li orbitals, similar to that obtained in the case of ligands coordination.

	E(1s)	E(2s) (LUMO) ^a	E(2p) (LUMO+1) ^b
Li ⁺	-64.0	-6.9	-4.6
Li	-55.1	-1.7	-0.5
[Li(OMe ₂) ⁺	-61.0	-5.7	-4.1
[Li(OMe ₂) ₂] ⁺	-58.5	-4.4	-3.4
[Li(OMe ₂) ₃] ⁺	-56.9	-3.7	-3.0
[Li(OMe ₂) ₄] ⁺	-55.9	-3.3	-2.8
[Li(EDA)] ⁺	-58.7	-4.8	-3.7
[Li(Crown)] ⁺	-57.0	-3.5	-3.3
Li ^{*+} , $c = -0,100$	-71.0	-7.9	-5.4
Li ^{*+} , $c = +0,100$	-57.1	-6.0	-3.9
Li [*] , $c = -0,100$	-61.8	-2.2	-1.0
Li [*] , $c = +0,100$	-48.6	-1.2	-0.1

Table 1: Energies (in eV) of the lithium cation orbitals as a function of the coordination of a neutral ligand or of the coefficient applied in the Li* pseudopotential. Lithium atom values are given for complete information. a) For Li atom, SOMO. B) For Li atom, LUMO.

Following simple orbital models, this high energy shift of the LUMO energy upon increase of the c coefficient should afford less electrophilic Li^{*+} species and to weaker Lewis acidic properties.

Therefore, coordination of solvent molecules or chelating additives on Li^+ reduces its Lewis acidity, an effect which can be reproduced by addition of a simple pseudopotential centered on the Li^* center.

To confirm this orbital description, the impact of the pseudopotential on the reactivity indices of Li^*CH_3 was examined. As a consequence, the Li^*CH_3 ionization potential (I) and electron affinity (A) were computed. Evaluation of I was carried out using the standard procedure ($I = E(\text{Li}^*\text{CH}_3^+) - E(\text{Li}^*\text{CH}_3)$). In contrast, evaluation of the electron affinity thanks to the Li^*CH_3 anion ($A = E(\text{Li}^*\text{CH}_3) - E(\text{Li}^*\text{CH}_3^-)$) leads to negative values in some cases, a well-known problem associated to DFT methods (see S.I.). We thus used an alternative expression proposed in the literature ($A = -(E(\text{HOMO}) + E(\text{LUMO})) - I$).^[19] This value was used to compute the chemical potential μ , the hardness η and the electrophilicity ω using the model and approximations described in the literature: $\mu = -0.5(I + A)$; $\eta = I - A$ and $\omega = \mu^2 / (2\eta)$ (Figure 3).^[20-21] An increase of the chemical potential while c increases is obtained, whereas hardness and electrophilicity decrease. It confirms the results obtained on Li^{*+} : the higher the pseudopotential coefficient c , the weaker the electrophilic properties of the lithiated species, in line with weaker Lewis acidity of Li^+ .

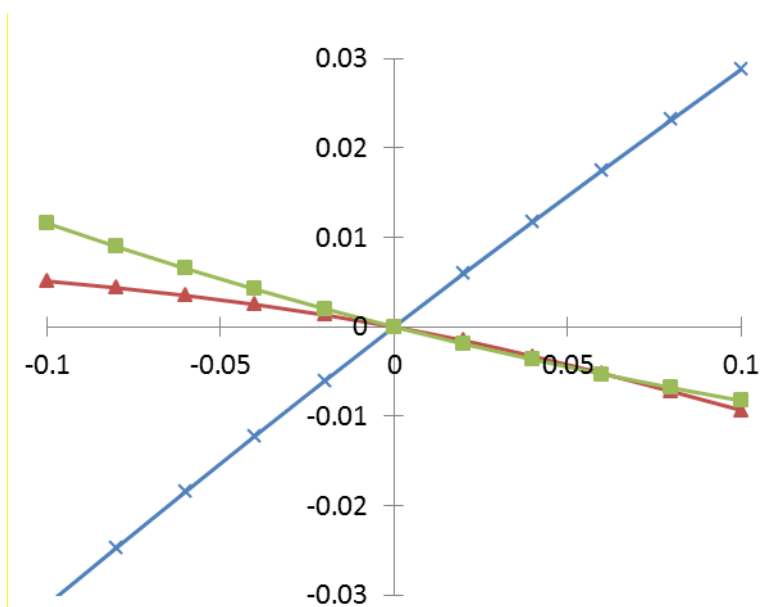


Figure 3: Variation (in atomic units) of the chemical potential μ (crosses, blue), chemical hardness η (triangles, red) and electrophilicity ω (squares, green) in Li^*CH_3 with respect to LiCH_3 as a function of c

These results indicate that the Li* model allows effective tuning of the electrophilicity of Li-systems.

Influence on the structure of organolithium species. We then examined how electrophilicity impacts structure and coordination properties in organolithium compounds. Two prototypic examples were considered to investigate this point: the simplest methyllithium and the conjugated allyllithium.

One of the well-known effects associated to ligand coordination to methyllithium is a significant lengthening of the Li-C distance. When binding from one to three Me₂O molecules to Li in Li-CH₃, the Li-C bond rises from 1.985 Å in absence of coordination to 1.998, 2.034 and 2.085 Å, respectively. [22] A similar lengthening is obtained with one molecule of EDA (2.030 Å). In order to determine whether the decreased electrophilicity of Li is at the origin of this significant elongation, the Li*-CH₃ geometry was optimized for c values ranging from -0.1 to +0.1. A monotonous increase (Figure 4) of the Li*-C bond with c is observed and results in a full decoordination of the lithium from the CH₃⁻ moiety for c = 0.100. As a consequence, the decrease of the electrophilicity triggered by the ligand coordination fully accounts for the lengthening of the Li-C distance in Li-CH₃, and there is no need to invoke CH₃-ligand steric effects. In conclusion, the 2.085 Å Li-CH₃ distance computed for (Me₂O)₃-LiCH₃ is close to that obtained for c = +0.020, which suggests that values of c in the 0 – 0.020 range are relevant for studies of ligand effects on coordination properties of organolithium compounds.

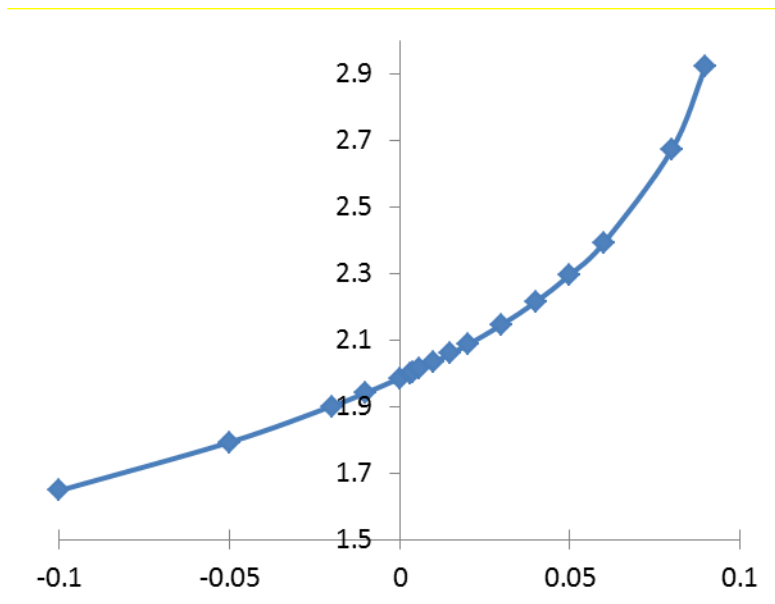


Figure 4: Length of the Li*-C bond in CH₃Li (in Å) as a function of the pseudopotential coefficient c

In a next step, we examined the effect of the fictitious charge on the interaction between Li⁺⁺ and the organic chain in allyllithium (see Figure 5), a canonical model for delocalized carbanions.[8] The partition between the various coordination mode of Li⁺ in this system, described in Figure 5, has been a long time concern and it is supposed to depend on the solvent and other additives present in the reaction medium.[23]

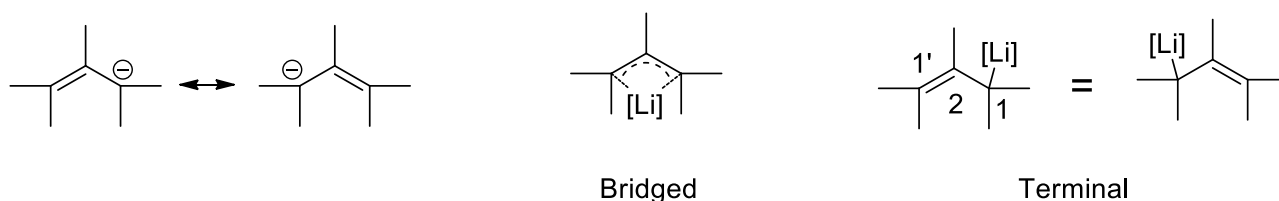


Figure 5: Allyl anions, naked (left) and in interaction with a lithium cation in a bridged (center) or terminal (right) mode.

When the lithium is “naked” (no solvation), a bridged structure is obtained, in agreement with experimental observations in non-coordinating solvents. A similar structure is obtained when one or two OMe₂ molecules are coordinated to the Li center. In contrast, when a third molecule is added, a structure exhibiting terminal bonding can also be characterized, which is found to be quasi-isoenergetic to the bridged one (more stable by 0.4 kcal mol⁻¹). A better insight on this change of behavior upon solvation

is obtained through a relaxed scan of the C²-C¹-Li angle (Figure 6), starting from the bridged structure (angle close to 68°) and increasing it up to terminal bonding (about 118°). Addition of Me₂O molecules decreases the preference for the bridged structure, the surface becomes flat and a small potential energy well appears in the trisolvated structure. Repeating a similar angular scan this time in the absence of Me₂O but for *c* ranging from 0 to 0.04 leads to a behavior highly similar to that observed upon consecutive addition of solvent molecules. With increasing values of *c*, the potential energy surface becomes flatter and, for the highest values, a second minimum corresponding to a localized structure is observed, which gradually becomes more stable than the bridged one. Through full geometry optimization, it was possible to determine that the bridged structure is obtained for all values of *c*, whereas the localized one can be optimized only if *c* > 0.015. The localized structure even becomes the most stable one for *c* = 0.020, the energy barrier between the two local minima being < 2.5 kcal mol⁻¹. For *c* = 0.040, the terminal bonding becomes 13.2 kcal mol⁻¹ more stable (potential energy, without correction) than the bridged one. A closer look at the terminally bonded structures reveals a dissymmetry in the C-C distance, the Li-bonded C=C being 0.12 Å longer than the other one, whatever the value of *c*. Let us highlight that the energy curve for the monosolvated structure highly resembles that for *c* = 0.004, whereas desolvation leads to a result close to *c* = 0.008 and trisolvation to *c* = 0.020 (Figure 6, left). Once again, the decrease of the electrophilicity associated to solvent coordination is sufficient to account for the terminal binding of Li to the allyl anion, and there is no need for an extra steric hindrance between solvent and the allenyl moiety to justify this behavior.

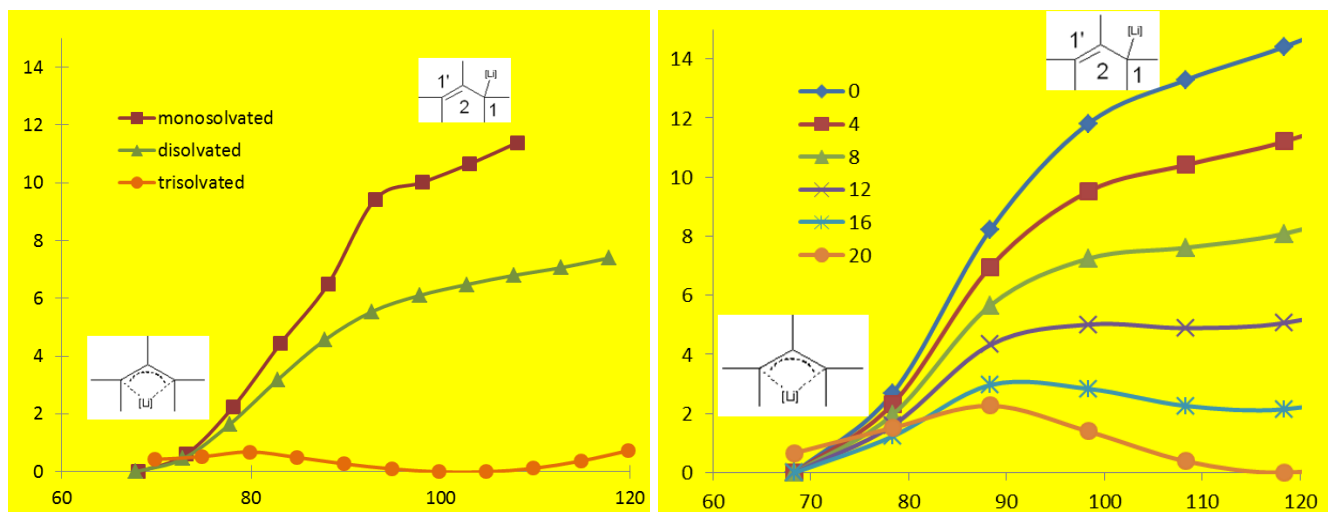


Figure 6 : Potential energy of the most stable structure (in kcal mol⁻¹, computed with respect to the most stable point) as a function of the C²-C¹-Li angle (between 68 and 118°) for various solvation levels (level) or values of c (right)

A deeper insight on the electronic effects at stake in this structural change can be obtained by an analysis of the electron localization function[24] (ELF, Figure 7) with the TopMod18 suite of programs.[26] It allows the partition of the electronic density in terms of lone pairs (monosynaptic ELF basins, red) and bonds (disynaptic basins, green).[27] The delocalized anion is characterized by 2.06 electrons forming four monosynaptic basins located on each side of the allenyl plane on both 1 and 1' carbon atoms, interpreted as a π -delocalized lone pair. When a Li⁺ cation comes to bridge this structure, the electron pair (2.10 e) rearranges on the side of the allenyl anion coordinating the Li⁺. Two symmetrical monosynaptic basins arise in this complex. This corresponds to a lone pair delocalized on 1 and 1' carbon atoms, in electrostatic interaction with the Li⁺ cation. This structure is similar whatever the value of the c coefficient on the Li* center. In the case of a terminal interaction, a more drastic rearrangement takes place and a disynaptic Li-C basin emerges, strongly polarized toward C (92%). This is associated to a polarization of the electron density on the Li bonded side (total population on the Li bonded side equal to 3.90e compared to 3.53e on the other one). In addition, natural population analysis shows a significantly stronger donation toward Li in the terminal structure compared to the bridged one (for c = 0.02, 0.18 versus 0.03e population of the 2s Li orbital are found respectively). As a conclusion, in the case of delocalized organolithium species, adding bonding ligands or decreasing the

hardness of Li^* leads to chemical structures exhibiting important electronic rearrangements, associated to more localized, and thus more covalent, bonding between Li and the organic chain.

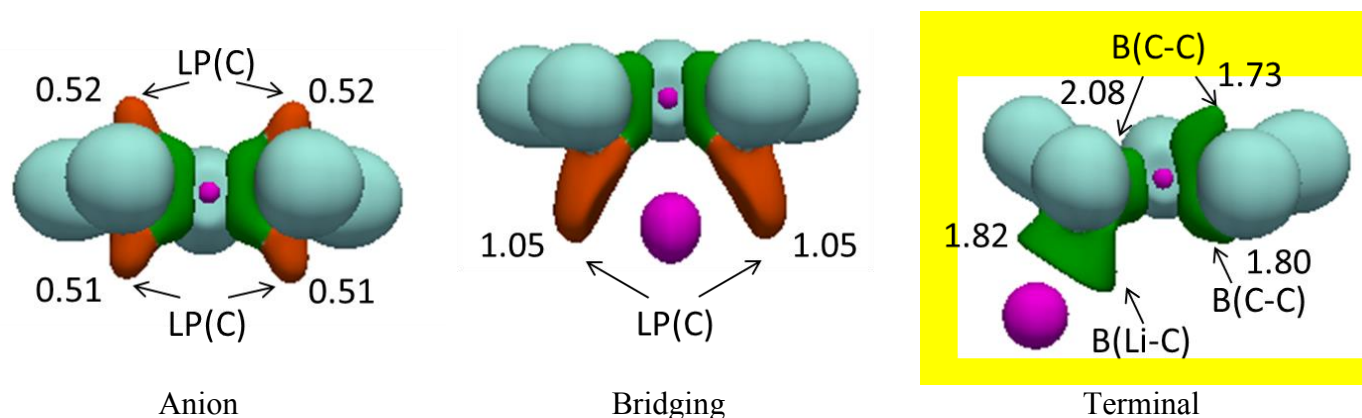


Figure 7: Electronic description (0.75 ELF isodensity colored in green is for bonds (**B**), red for lone pairs (LP), pink for core electrons and blue for CH bonds, carried out using the Paraview program[25]) of the allyl anion (left) and of Li^* ($c = 0.02$) coordinated structures in a bridged (center) or terminal (right) fashion. Population for the labelled basins is given (in electron).

Application to the structural studies of lithiated organometallics: Formation of bridged structures when using a “naked” Li^+ in lithiated organometallics is a well known phenomenon, and those are sometimes proposed to play a major role in the reactivity.[28] Nevertheless, these structures do not reflect the real structure of these compounds which are generally used in coordinating ethereal solvents. Two examples encountered in our groups are gathered in Figure 8, evidencing the generality of the problem.

We have previously reported on lithium phosphidoborane $[\text{PH}_2\text{BH}_3]\text{Li}$, a compound for which both P nucleophilicity and hydridic reduction reactivity are observed.[3] The lithium cation can interact either with the phosphorus or with the hydrides borne by the boron, and we proposed that this ditopicity is directly related to its ambiguous reactivity. We focus below on the Li-P interaction. The second system is a lithiated allenyl-cyanocuprate. An intermediate $\text{Li}\dots\text{C}=\text{C}$ interaction is expected in the course of its reactivity with aldehyde and the proper description of such structures is crucial.

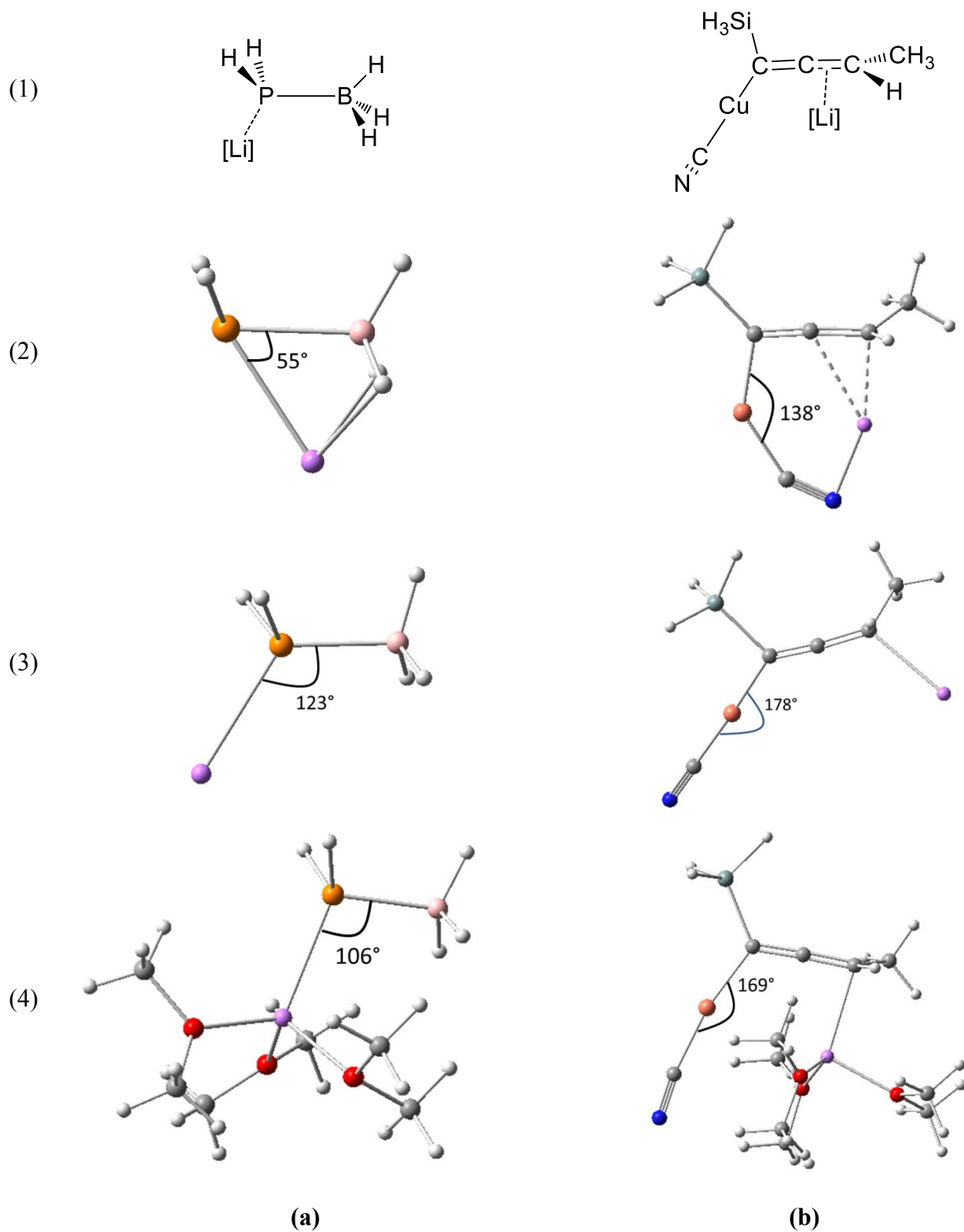


Figure 8: Versatility of the Li binding mode as a function of the modelling method, illustrated for Lithium phosphide-borane (a) and lithiated allenylcyanocuprate (b). Entries correspond to structures (1): expected; (2): obtained with $c = 0$; (3): obtained with $c = 0.02 \text{ Li}^*$; (4): explicitly solvated by 3 OMe₂ molecules.

Searching for a sole Li-P interaction in lithium phosphidoborane leads, if $c = 0$, to a structure exhibiting two additional coordinations, between the Li and two of the hydrides (Figure 8a2). This structure is analogous to the bridged structure encountered for allyllithium. In contrast, when the lithium center is explicitly solvated by adjunction of three OMe₂ molecules, a terminal P-bonded form can be obtained (Figure 8a4). Such a trisolvated structure is much more representative of the experimental system, as the reaction always takes place in ethereal solvent, or in the presence of a significant amount of ethereal molecules. A comparable solely P-bonded arrangement is also obtained using a Li* with c values equal to or larger than 0.018 ($c = 0.02$ given in Figure 8a3).

A similar behavior is obtained for lithiated allenylcyanocuprate.[4] The non-solvated structure exhibits a strongly distorted coordination at Cu ($C-Cu-C = 138^\circ$ instead of the expected 180°) which allows the formation of an additional Li-NC interaction. Decreasing the electrophilicity of the Li center through addition of explicit OMe₂ molecules or inclusion of a pseudopotential according to the Li* model decreases this distortion (169° and 178° resp.) and leads to a more localized Li-C=C interaction.

These two examples highlight that using Li*, a structure alike that of an “explicitly solvated Li” can be obtained for the cost of “naked Li” calculation.

Conclusion

In this study, we describe a computational experiment, referred to as Li*, consisting in tuning the Li chemical potential. Our test is run in the context of structure optimizations in order to determine how electrophilicity of the lithium influences its binding properties. The results illustrate that decreasing the chemical potential of this cation has a major impact on the Li*-C bond and on the geometry of its coordination to delocalized anions. In these cases, the Li* model mimics efficiently an explicit solvation. From a computational point of view, the procedure is extremely simple, computationally economical and reproduces the variation of structure as a function of electrophilicity modification upon solvent coordination. This model, which can be continuously varied, in strong contrast to the number of solvent molecules,[29] could be used to mimic the variety of electronic effects associated to the

chelating additives used in lithium organometallic chemistry and help to reproduce their structure and reactivity. This is why we believe that it can become an efficient tool to help experimentalists to select the best reaction conditions to achieve a given selectivity. Currently, this topic is hardly addressed by theoreticians due to the complexity (both in size and structure) of the resulting reagent–ligand complexes. In addition, by its ability to quantify, by difference, the plasticity of the solvent sphere along the reaction course, it can be regarded as a probe to analyse the solvent effects in systems where solvent rearrangements play a major role.

Acknowledgments: The authors thank the ANR (AGGREGATE project: ANR-07-BLAN-0294) for financial support. H.G. thanks Marie-Liesse DOUBLET for insightful discussions and Emmanuel VRANCKEN for continuous support to this project.

Bibliography:

- [1] Reich HJ (2013) Role of Organolithium Aggregates and Mixed Aggregates in Organolithium Mechanisms. *Chem. Rev.* 113:7130–7178
- [2] Essafi S, Tomassi S, Aggarwal VK, Harvey JN (2014) Homologation of Boronic Esters with Organolithium Compounds: A Computational Assessment of Mechanism. *J. Org. Chem.* 79:12148–12158
- [3] Barozzino Consiglio G, Queval P, Harrison-Marchand A, Mordini A, Lohier J-F, Delacroix O, Gaumont AC, Gérard H, Maddaluno J, Oulyadi H (2011) Ph₂P(BH₃)Li: from ditopicity to dual reactivity. *J. Am. Chem. Soc.* 133: 6472–6480
- [4] Vrancken E, Gérard H, Linder D, Ouizem S, Alouane N, Roubineau E, Bentayeb K, Marrot J, Mangeney P (2011) Diastereodivergent Behavior of Alkyl- versus Cyano- Allenylcuprates towards Aldehydes: a Key Role for Lithium. *J. Am. Chem. Soc.* 133: 10790–10802
- [5] Jacques B, Chanaewa A, Chavarot-Kerlidou M, Rose-Munch F, Rose E, Gérard H (2008) A combined experimental - theoretical study on the lithiation/electrophilic quench sequence of (η^5 -cyclohexadienyl)Mn(CO)₃ complexes. *Organometallics* 27:626–636
- [6] Lisson Lill SO (2014) Computational perspectives in Organolithiums. In: Luisi R, Capriati V (ed) *Lithium Compounds in Organic Synthesis*. Wiley-VCH, Weinheim, p 48-72.
- [7] Kost D, Klein J, Streitwieser A, Schriver GW (1982) Ab initio calculations of dilithiopropenes. *Proc. Natl. Acad. Sci. U. S. A.* 79:3922–3926

- [8] Clark T, Rohde C, von Ragué Schleyer P (1983) Allyllithium, Allylsodium, and Allylmagnesium Hydride: Geometries and Bonding. A Comparative ab Initio Study. *Organometallics* 2:1344–1351
- [9] Dumont E, Chaquin P (2004) The Hp method: hydrogen atoms with a fictitious nuclear charge. A versatile theoretical tool for study of atom and group properties as substituents: electronegativity and partition of σ and π contributions. *J. Mol. Struct. THEOCHEM* 680:99–106
- [10] Dumont E, Chaquin P (2006) Diels–Alder reaction: A theoretical comprehensive study of substituent effects using the ‘H* method’. *J. Mol. Struct. THEOCHEM* 758 :161–167
- [11] Dumont E, Chaquin P (2007) Investigation of pure inductive effects on benzene ring by ^{13}C NMR chemical shifts: A theoretical study using fictitious nuclear charges of hydrogen atoms (‘H* method’). *Chem. Phys. Lett.* 435:354–357
- [12] Dumont E, Chaquin P (2009) Inductive Effects on Proton Affinity of Benzene Derivatives: Analysis Using Fictitious Hydrogen Atoms. *J. Phys. Chem. A* 113:2990–2994
- [13] De La Lande A, Gérard H, Parisel O (2008) How to optimize a C-H cleavage with a mononuclear copper-dioxygen adduct? *Int. J. Quantum Chem.* 108:1898–1904
- [14] Pratt L (2007) Modeling lithium dialkylamides in ethereal solvents: A test of the microsolvation model. *J. Mol. Struct. THEOCHEM* 811:191-196
- [15] Miessler GL, Tarr DA (1991) *Inorganic Chemistry*. Prentice-Hall, Englewood Cliffs
- [16] Frisch MJ et al. (2009) Gaussian 09, Revision D.01
- [17] Becke A (1993) Density-functional thermochemistry. III. The role of exact exchange *J. Chem. Phys.* 98:5648–5652
- [18] Lee C, Yang W, Parr RG (1988) Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* 37:785–789
- [19] Tozer DJ, De Proft F (2005) Computation of the Hardness and the Problem of Negative Electron Affinities in Density Functional Theory. *J. Phys. Chem. A* 109:8923-8929
- [20] Parr RG, Szentpály LV, Liu S (1999) Electrophilicity Index. *J. Am. Chem. Soc.* 121:1922–1924
- [21] Chattaraj PK, Giri S, Duley S (2011) Update 2 of: Electrophilicity Index. *Chem. Rev.* 111:PR43-PR75
- [22] Parisel O, Fressigné C, Maddaluno J, Giessner-Prettre C (2003) Influence of the Correlation, Aggregation, and Solvation on ab initio Computed Li–C, Li–N, and Li–Li NMR Coupling Constants. *J. Org. Chem.* 68:1290–1294
- [23] Fraenkel G, Chow A, Winchester WR (1990) Stereochemistry of Solvation of Benzylic Lithium Compounds: Structure and Dynamic Behavior. *J. Am. Chem. Soc.* 112:2582–2585
- [24] Fourré I, Gérard H, Silvi B (2007) How the topological analysis of the electron localization function accounts for the inductive effect. *J. Mol. Struct.: THEOCHEM* 811:69-76

- [25] Ahrens J, Geveci B, Law C (2005) ParaView: An End-User Tool for Large Data Visualization. In: Hansen CD, Johnson CR Ed. Visualization Handbook, Elsevier. (b) Ayachit U (2015) The ParaView Guide: A Parallel Visualization Application Kitware
- [26] Noury S, Krokidis X, Fuster F, Silvi B (1999) Computational tools for the electron localization function topological analysis. *Comput. Chem.* 23:597-604
- [27] Piquemal JP, Pilmé J, Parisel O, Gérard H, Fourré I, Bergès J, Gourlaouen C, de la Lande A, van Severen M-C, Silvi B (2008) What can be learnt on biological-relevant systems from the topological analysis of the Electron Localization Function ? *Int. J. Quant. Chem.* 108:1951-1969
- [28] Mori S, Hirai A, Nakamura M, Nakamura E (2000) Correlation of Reactivities of Organocuprate(I) and Zincate(II) with d-Orbital Energies of Ate Complexes. *Tetrahedron* 56:2805-2809
- [29] Tomasevitch LL, Collum DB (2013) Structure Determination Using the Method of Continuous Variation: Lithium Phenolates Solvated by Protic and Dipolar Aprotic Ligands. *J. Org. Chem.* 78:7498-7507

Supplementary Information to :

Ligand effects on coordination properties of organolithium compounds: insights from computational experiments on a “weakened” Li^+

Hélène GERARD¹, Patrick CHAQUIN¹ and Jacques MADDALUNO²

1 : Sorbonne Université, CNRS, Laboratoire de Chimie Théorique, LCT, F-75005 Paris, France.
helene.gerard@sorbonne-universite.fr ; Tel : (+33) 144 279 662

2 : Normandie Univ, UNIROUEN, INSA Rouen, CNRS, COBRA, (UMR 6014 & FR 3038), F-76000,
Rouen, France

Summary: A simple numerical experiment is presented, which allows tuning the lithium electrophilicity, in a manner similar to solvent and additives coordination. Coordination of Li^+ to carbanions or polydentate nucleophiles is examined, highlighting the potential of this chemical trick to both model and decipher the effects of solvation of the structural properties lithiated organometallics.

Keywords : Lithium; Carbanions ; An initio calculations ; Molecular Modeling ; Solvent effects

S1 : Sample Input for Optimization of Li^+-CH_3 ($c = 0.02$).....	page 2
S2 : Data for systems as a function of c	page 3
S3 : Optimized geometries (regular Li)	page 4
S4 : Scan geometries (regular Li).....	page 10

S1 : Sample Input for Optimization of Li*-CH₃ (c = 0.02)

```
#P B3LYP gen 6D nosym pseudo=read ginput
opt=(CalcFC,Maxcycl=200)
```

MeLi

```
0 1
6 .395730 .000155 -.000035
3 -1.603499 .000321 -.000062
1 .813838 1.004693 -.208173
1 .811156 -.322887 .974880
1 .811127 -.683700 -.766309
```

```
Li H C 0
6-31+G**
*****
```

```
Li 0 % introduction line for the pseudo
Star 0 0 % Pseudo name - applied to s and higher – replaces 0 e
S component % Description
1 % Only one term in the pseudo
1 0.0 0.020 % 1 term – exp coefficient – c value
```

S2 : Data for systems as a function of c

c	MeLi+	MeLi	MeLi-	I	A
-0.100	-47.89881	-48.2089862	-48.2429009	0.31017617	0.03391468
-0.080	-47.7453798	-48.0488158	-48.0786515	0.30343595	0.02983577
-0.060	-47.5921175	-47.8888199	-47.9147147	0.29670239	0.02589481
-0.040	-47.4390296	-47.7290053	-47.7510981	0.2899757	0.02209282
-0.020	-47.286123	-47.5693791	-47.5878092	0.2832561	0.01843012
0.0	-47.1334051	-47.409949	-47.4248554	0.27654391	0.01490633
0.020	-46.9808837	-47.2507232	-47.2622437	0.26983944	0.01152048
0.040	-46.8285671	-47.0917102	-47.0810749	0.26314312	-0.01063533
0.060	-46.6764639	-46.9329194	-46.9205529	0.25645541	-0.0123665
0.080	-46.5245837	-46.7743604	-46.7602851	0.24977678	-0.01407536
0.100	-46.3729361	-46.6160441	-46.6002806	0.24310798	-0.01576349

Table S2-1: ionization and electron affinity of MeLi computed using anionic and cationic species.

c	E (u.a.)	Li-C (Å)
-0.100	-48.2344012166	1.648
-0.050	-47.8152585131	1.793
-0.020	-47.5704067999	1.901
-0.010	-47.4898960616	1.941
0.0	-47.4099490372	1.985
0.003	-47.3860768937	1.999
0.004	-47.3781311591	2.004
0.006	-47.3622572774	2.013
0.010	-47.3305806821	2.033
0.015	-47.2911203890	2.059
0.020	-47.2518142117	2.086
0.030	-47.1736823133	2.146
0.040	-47.0962293811	2.214
0.050	-47.0195164007	2.295
0.060	-46.9436187364	2.391
0.080	-46.7947235841	2.671
0.090	-46.7221353948	2.922

Table S2-2: optimization of MeLi* as a function of c

S3 : Optimized geometries (regular Li)

[Li(OMe₂)⁺

10

scf done: -162.389192

Li	-1.129575	-0.004389	0.000601
O	0.679938	-0.000949	0.000381
C	1.485910	1.205828	0.000332
C	1.490543	-1.204619	0.000179
H	2.109231	1.232156	-0.897720
H	0.804971	2.059444	0.000508
H	2.109531	1.232026	0.898179
H	2.113970	-1.228426	-0.897869
H	2.114251	-1.228536	0.898028
H	0.812886	-2.060843	0.000233

[Li(OMe₂)₂]⁺

19

scf done: -317.484064

Li	-0.010937	-0.499950	-0.012467
O	-1.840114	-0.679851	-0.010496
C	-2.758426	0.436359	0.001944
C	-2.522384	-1.954146	-0.020672
H	-3.382205	0.395796	0.900136
H	-2.165002	1.352705	0.009084
H	-3.386314	0.412305	-0.893970
H	-3.139838	-2.053595	0.877306
H	-3.144893	-2.036540	-0.916870
H	-1.761275	-2.736805	-0.030276
O	1.817775	-0.314465	-0.001806
C	2.620507	-0.183591	-1.196727
C	2.614201	-0.277412	1.203893
H	3.337546	-1.008090	-1.256109
H	1.945819	-0.222516	-2.054161
H	3.148533	0.774845	-1.187986
H	3.332121	-1.103265	1.201631
H	3.140786	0.679329	1.273618
H	1.935176	-0.384660	2.052027

[Li(OMe₂)₃]⁺

28

scf done: -472.561406

Li	-0.029360	-0.062519	-0.303729
O	-1.312482	-1.438662	-0.506018
C	-1.275649	-2.686342	0.209939
C	-2.428410	-1.355538	-1.410856
H	-1.186629	-3.523545	-0.490959
H	-0.403499	-2.662420	0.865428
H	-2.183503	-2.804010	0.811476
H	-2.365379	-2.149198	-2.163202

H	-3.370905	-1.444029	-0.859562
H	-2.380471	-0.381793	-1.901139
O	-0.603029	1.737010	-0.173453
C	-1.765256	2.148839	0.568315
C	0.064599	2.841909	-0.808964
H	-2.491266	2.626423	-0.098728
H	-2.205850	1.253202	1.009314
H	-1.479292	2.846960	1.362494
H	-0.608661	3.331748	-1.520785
H	0.397261	3.566471	-0.057667
H	0.928997	2.440020	-1.340032
O	1.815613	-0.474326	-0.255567
C	2.761833	0.166703	0.618698
C	2.426627	-1.477801	-1.086635
H	3.546430	0.657748	0.032746
H	2.216955	0.911898	1.200531
H	3.212017	-0.569121	1.293874
H	3.193768	-1.024675	-1.723769
H	2.876819	-2.260757	-0.466623
H	1.641485	-1.909308	-1.709661

Li(OMe₂)₄]⁺

37

scf done: -627.624483

Li	-0.662742	1.326759	4.988400
O	-0.321955	-0.173210	6.223249
O	-2.092525	0.922135	3.694176
O	1.066074	1.639220	4.093020
C	2.324796	1.653068	4.779174
C	1.206718	1.899572	2.689844
C	0.408141	-1.353195	5.863055
C	-0.831936	-0.235339	7.562162
C	-2.547939	-0.402802	3.388344
C	-2.763215	1.922712	2.916865
H	2.804726	2.634679	4.684074
H	2.125429	1.441076	5.830600
H	2.992335	0.884943	4.370722
H	1.622170	2.900684	2.524223
H	1.861623	1.152442	2.226072
H	0.212440	1.835644	2.246982
H	1.263665	-1.494293	6.534253
H	0.765646	-1.216615	4.841366
H	-0.238895	-2.237376	5.913771
H	-0.011826	-0.369419	8.277353
H	-1.543613	-1.063174	7.664660
H	-1.335909	0.710726	7.761086
H	-2.004106	-1.090770	4.036244
H	-2.345568	-0.646070	2.338517

H	-3.623393	-0.491748	3.582169
H	-2.584194	1.763244	1.846603
H	-3.842468	1.897965	3.109086
H	-2.361180	2.891522	3.216694
O	-1.293154	2.932225	5.945939
C	-2.631011	3.100218	6.432853
C	-0.454743	4.053002	6.258913
H	-3.092932	3.988884	5.986330
H	-3.196823	2.212513	6.146319
H	-2.633302	3.203544	7.524719
H	-0.863566	4.970514	5.819402
H	-0.368120	4.176714	7.344935
H	0.527925	3.852302	5.831452

[Li(H₂N-C₂H₄-NH₂)]⁺

13

scf done: -197.940016

Li	0.675664	-0.882692	1.464980
N	1.573700	-0.324624	3.168447
C	0.440345	0.329408	3.892472
C	-0.850496	-0.461556	3.681881
N	-1.154771	-0.579644	2.222423
H	2.366140	0.315704	3.124416
H	1.911132	-1.117778	3.716347
H	0.329458	1.341856	3.488462
H	0.639630	0.428905	4.965082
H	-1.667542	0.013836	4.235524
H	-0.737148	-1.476257	4.079509
H	-1.873432	-1.288883	2.079513
H	-1.579363	0.289486	1.894528

Li(O₄C₈H₁₆)]⁺

29

scf done: -622.788707

Li	0.703959	-0.180981	0.142960
O	-0.797689	-0.409170	1.461589
C	-0.288046	-0.209166	2.790992
C	0.620273	1.011764	2.714642
O	1.561987	0.854808	1.636141
C	2.825116	0.251183	1.962993
C	3.496205	-0.065965	0.632329
O	2.586723	-0.794262	-0.214481
C	2.635441	-2.228747	-0.131915
C	1.405114	-2.734388	-0.874519
O	0.228434	-2.061003	-0.387656
C	-0.472277	-2.689106	0.699228
C	-1.470896	-1.657209	1.207954
H	0.264765	-1.098421	3.124027
H	-1.112790	-0.030012	3.491936
H	1.136019	1.179036	3.666299
H	0.036802	1.903395	2.471745

H	3.440568	0.947818	2.545649
H	2.668850	-0.657909	2.559946
H	4.426215	-0.624464	0.783189
H	3.726174	0.857526	0.094991
H	2.627377	-2.549250	0.918930
H	3.550711	-2.606518	-0.604197
H	1.304992	-3.820809	-0.777948
H	1.472847	-2.482734	-1.935919
H	-0.994222	-3.587567	0.347372
H	0.234466	-2.982140	1.487651
H	-1.985597	-2.016123	2.105656
H	-2.217622	-1.440983	0.439783

MeLi

5

scf done: -47.409949

C	0.392692	-0.000411	0.000108
Li	-1.592300	0.001065	-0.000250
H	0.810054	0.997387	-0.206655
H	0.809006	-0.320611	0.967920
H	0.808900	-0.678849	-0.760824

MeLi(OMe₂)

14

scf done: -202.481638

Li	-1.202910	-0.003572	0.000346
C	-3.200894	-0.000690	-0.000030
H	-3.624265	1.018102	-0.000278
H	-3.628122	-0.507798	-0.881569
H	-3.628464	-0.507511	0.881507
O	0.705969	-0.001113	0.000493
C	1.491160	1.195117	0.000363
C	1.496030	-1.194091	0.000212
H	2.120944	1.238539	-0.896610
H	0.799098	2.039071	0.000619
H	2.121436	1.238401	0.896997
H	2.126001	-1.234831	-0.896757
H	2.126471	-1.234933	0.896845
H	0.807456	-2.040896	0.000345

MeLi(OMe₂)₂

23

scf done: -357.540860

Li	0.000407	0.678312	0.003638
C	0.118589	2.708723	0.025955
H	-0.369936	3.162650	0.908732
H	1.149569	3.108464	0.033263
H	-0.364577	3.180704	-0.850292
O	-1.640592	-0.351875	-0.006614
C	-2.839492	0.430082	0.003662
C	-1.872462	-1.755488	-0.029590

H	-3.436579	0.200565	0.896106
H	-2.526298	1.474926	0.019939
H	-3.433976	0.227957	-0.897078
H	-2.435084	-2.071209	0.859528
H	-2.432622	-2.042360	-0.929954
H	-0.895745	-2.242871	-0.036261
O	1.545029	-0.593542	-0.008590
C	2.343032	-0.411288	-1.181855
C	2.312933	-0.478267	1.192621
H	3.139582	-1.165982	-1.220743
H	1.684105	-0.536458	-2.043306
H	2.779069	0.594909	-1.200999
H	3.105733	-1.237669	1.211457
H	2.752365	0.523151	1.277062
H	1.631673	-0.646441	2.029078

MeLi(OMe)₃

32

scf done: -512.593109

Li	0.029915	0.085891	0.523340
C	0.207242	0.364267	2.582428
H	0.632506	-0.490707	3.146295
H	0.850140	1.224870	2.856976
H	-0.759892	0.573643	3.082110
O	-1.279269	-1.375599	-0.028871
C	-1.658880	-2.237693	1.046278
C	-1.716444	-1.831506	-1.299285
H	-1.226825	-3.238783	0.907903
H	-1.266696	-1.780229	1.955421
H	-2.753385	-2.320545	1.101096
H	-1.263348	-2.802006	-1.548663
H	-2.810798	-1.935051	-1.324403
H	-1.410303	-1.085696	-2.036002
O	-0.724787	1.681716	-0.545054
C	-2.015297	2.015356	-0.032639
C	0.175803	2.787452	-0.487055
H	-2.462373	2.828524	-0.621531
H	-2.633426	1.120112	-0.114646
H	-1.946934	2.310007	1.021861
H	-0.202316	3.622138	-1.093843
H	0.317256	3.116353	0.550313
H	1.130552	2.444311	-0.888314
O	1.806871	-0.233057	-0.432090
C	2.890281	-0.478471	0.468555
C	2.089436	-0.620796	-1.767499
H	3.773940	0.102329	0.169075
H	2.541769	-0.170020	1.454684
H	3.145982	-1.547234	0.479667
H	2.968361	-0.085594	-2.154667
H	2.275561	-1.702547	-1.834115
H	1.218118	-0.364475	-2.374051

MeLi(H₂N-C₂H₄-NH₂)

17

scf done: -238.000333

C	0.314256	0.429067	4.102007
C	-0.906666	-0.429473	3.757851
N	-1.004459	-0.600399	2.296304
N	1.529756	-0.170793	3.521208
Li	0.990446	-0.873775	1.574141
H	2.298365	0.493750	3.489095
H	1.851888	-0.960818	4.077124
H	0.192203	1.425508	3.660604
H	0.367829	0.565127	5.191972
H	-1.804386	0.016764	4.209906
H	-0.786070	-1.425154	4.201388
H	-1.620505	-1.370152	2.048544
H	-1.388640	0.232282	1.853385
C	1.930761	-1.471211	-0.122714
H	1.252011	-1.583743	-0.986989
H	2.718120	-0.768342	-0.450059
H	2.434050	-2.448634	-0.009252

Li(allyl)

9

scf done: -124.838776

Li	0.711910	1.306719	1.346935
C	-0.147007	-0.538275	1.851323
C	1.155542	-0.418312	2.360919
C	1.669468	0.660751	3.097277
H	2.705068	0.661117	3.417794
H	0.990850	1.267585	3.704865
H	1.891660	-1.123985	1.966772
H	-0.429508	-1.408452	1.269714
H	-0.971200	-0.027044	2.358743

Li(allyl)(OMe)₂

18

scf done: -279.909992

C	-0.138264	-0.803841	2.165477
C	1.231420	-0.657086	2.419988
C	1.839927	0.283973	3.263904
Li	0.507716	1.215098	1.869734
H	2.919261	0.305226	3.368715
H	1.275210	0.698327	4.103968
H	1.923194	-1.181891	1.753481
H	-0.488516	-1.565623	1.477152
H	-0.864612	-0.475342	2.914998
O	-0.150432	2.917693	1.369315
C	0.521120	4.138865	1.689334
H	-0.122113	4.777721	2.308298
H	1.421392	3.873959	2.245501

H	0.797420	4.675643	0.772576
C	-1.353882	3.106925	0.620201
H	-2.071962	3.707398	1.194110
H	-1.137035	3.606748	-0.332804
H	-1.773121	2.117447	0.430306

Li(allyl)(OMe)₂

27

scf done: -434.966309

C	-0.541179	-0.543251	2.542516
C	0.849483	-0.638186	2.415334
C	1.832242	0.191627	2.971464
Li	0.360372	1.334709	1.793685
O	-0.230987	3.069935	2.560810
C	0.349590	3.631652	3.737581
C	-1.601729	3.427919	2.389601
H	2.881929	-0.010599	2.784972
H	1.613831	0.755402	3.880556
H	1.204568	-1.334913	1.648871
H	-1.184163	-1.273748	2.061664
H	-0.978440	-0.017845	3.394075
H	-1.707649	4.518592	2.313852
H	-1.942190	2.961051	1.464388
H	-2.206645	3.059675	3.228496
H	0.313886	4.728543	3.694807
H	-0.178870	3.285959	4.635897
H	1.385912	3.294225	3.773769
O	0.343199	1.742845	-0.149656
C	0.079679	0.676573	-1.062316
H	1.012107	0.172968	-1.349763
H	-0.570744	-0.027421	-0.541778
H	-0.420283	1.059475	-1.962201
C	1.214467	2.734967	-0.685158
H	2.193874	2.302598	-0.930609
H	0.778999	3.184693	-1.587907
H	1.336310	3.502206	0.081184

Li(allyl)(OMe)₃ bridged

36

scf done: -590.008137

C	-0.394986	-0.697606	2.525509
C	0.946134	-0.573879	2.926468
C	1.527480	0.345759	3.796783
Li	0.395808	1.314146	1.890339
O	-0.852126	1.643822	-0.031224
C	-0.736547	2.769735	-0.888806
C	-1.812252	0.693933	-0.482134
O	-0.457076	2.956502	2.784659
C	-1.866866	3.155432	2.720922
C	0.132939	3.615173	3.903253
H	2.590188	0.294781	4.014756

H	0.915176	0.882321	4.520797
H	1.653031	-1.198474	2.368657
H	-0.684280	-1.544004	1.908237
H	-1.187048	-0.285696	3.155167
H	-2.102159	4.224946	2.625399
H	-2.223336	2.618849	1.842465
H	-2.355633	2.757903	3.620695
H	0.007249	4.703704	3.816447
H	-0.322144	3.271805	4.841767
H	1.191176	3.353860	3.909936
H	-1.545973	0.313555	-1.479272
H	-1.799662	-0.120549	0.243297
H	-2.815602	1.143190	-0.532053
H	-0.443221	2.464021	-1.903996
H	-1.687350	3.320546	-0.949215
H	0.037247	3.413382	-0.469056
O	2.009179	1.899229	0.669770
C	2.452139	0.837163	-0.172173
H	3.022573	0.095724	0.402458
H	1.559760	0.366740	-0.586775
H	3.078662	1.227521	-0.986485
C	3.094717	2.608687	1.260042
H	3.671402	1.956842	1.927692
H	3.751032	3.020022	0.479969
H	2.668283	3.428067	1.841199

Li(allyl)(OMe)₃ terminal

36

scf done: -590.008930

C	-0.439312	-0.848460	2.272267
C	0.845330	-0.197399	2.340517
C	1.286320	0.833438	3.126930
Li	-1.357983	0.127390	0.601625
O	-2.120970	1.976672	0.893551
C	-1.652083	2.630998	2.079943
C	-3.397867	2.437669	0.474977
O	-0.240478	0.398747	-1.087246
C	0.487877	1.621964	-1.208817
C	0.533715	-0.736116	-1.473531
O	-2.863143	-0.967286	-0.218085
C	-3.487495	-1.951934	0.606085
C	-3.351877	-0.956950	-1.552919
H	2.285846	1.243140	3.013792
H	0.691720	1.216695	3.955303
H	1.574104	-0.550627	1.599281
H	-0.385319	-1.897622	1.955604
H	-1.059615	-0.739582	3.171404
H	-3.370387	3.515231	0.260723
H	-3.662538	1.894721	-0.434069
H	-4.157512	2.246901	1.246173
H	-1.574490	3.713073	1.906074

H	-2.340856	2.445307	2.914539
H	-0.668734	2.216189	2.315680
H	-3.343347	-2.955203	0.182599
H	-3.004762	-1.894716	1.582052
H	-4.563392	-1.749931	0.700957
H	-3.205089	-1.935895	-2.030771
H	-4.422562	-0.708210	-1.578050
H	-2.782893	-0.201015	-2.097034
H	1.434997	-0.821210	-0.854107
H	-0.089381	-1.618993	-1.322062
H	0.820332	-0.662581	-2.531717
H	1.369599	1.614540	-0.555947
H	0.799417	1.779320	-2.250560
H	-0.184437	2.422502	-0.898734

Li(PH₂BH₃)

8

scf done: -376.769644565

P	0.045037	0.103468	-0.084894
B	-0.076235	-0.147791	1.914606
H	1.414833	0.343459	-0.337876
H	-0.441082	1.410472	-0.315681
Li	-0.999107	-1.736682	0.982467
H	0.429605	-1.267154	2.102374
H	0.412928	0.687766	2.617651
H	-1.294812	-0.274864	2.121954

Li(PH₂BH₃)(OMe)₃

35

scf done: -1304.08884726

P	0.210884	-0.080420	0.835641
Li	-0.962155	-1.640985	-0.732760
B	-0.909773	-0.041646	2.503930
H	1.545888	-0.366413	1.236094
H	0.461347	1.273590	0.482121
H	-1.053530	-1.215499	2.825331
H	-0.388069	0.611953	3.379842
H	-1.980571	0.429235	2.145541
O	-0.609912	-1.460301	-2.679096
O	-0.586648	-3.528935	-0.203885
O	-2.923202	-1.351837	-0.596191
C	-1.554756	-1.687882	-3.721672
C	0.614814	-0.884866	-3.140646
C	-0.188071	-3.838885	1.139274
C	-0.269544	-4.567504	-1.124335
C	-3.361262	0.004412	-0.746811
C	-3.597411	-2.014550	0.484109
H	-1.161885	-2.408082	-4.452340
H	-2.457722	-2.085996	-3.256063
H	-1.794516	-0.749237	-4.238883
H	1.123611	-1.568920	-3.832821

H	0.422487	0.069857	-3.646972
H	1.233595	-0.708886	-2.259814
H	0.812252	-4.758437	-1.139047
H	-0.793635	-5.495024	-0.857056
H	-0.591638	-4.238202	-2.113444
H	0.898462	-3.984948	1.188165
H	-0.472905	-2.995492	1.770459
H	-0.694901	-4.751007	1.480693
H	-3.371732	-1.517391	1.433820
H	-4.680245	-2.019192	0.302949
H	-3.227337	-3.040740	0.504637
H	-3.181504	0.568670	0.174698
H	-2.782564	0.441344	-1.563206
H	-4.429116	0.028668	-1.001992

LiCuCN(C(SiH₃)CCHMe)

16

scf done: -2186.911762

C	-0.140783	-0.477736	1.976584
Cu	-1.783445	-1.473405	1.642588
C	-3.395587	-1.911560	2.536424
N	-4.029706	-1.808557	3.523521
C	-0.286073	-0.080337	3.197675
C	-0.529946	0.270172	4.479351
C	0.118255	-0.434413	5.668793
Si	1.283197	-0.126745	0.834538
H	-0.897992	1.285079	4.655659
H	0.784024	0.573916	-0.377593
H	2.335559	0.714618	1.469615
H	1.898027	-1.409009	0.401799
H	1.043136	0.071097	5.975969
H	-0.538909	-0.447739	6.547484
H	0.378059	-1.468922	5.422952
Li	-2.517348	-0.726735	4.268590

LiCuCN(C(SiH₃)CCHMe)(OMe)₃

43

scf done: -2652.090062

C	-6.017936	2.733380	3.746422
Cu	-5.788889	0.959892	4.339811
C	-6.741571	-1.028792	6.050230
C	-7.731464	-1.226227	6.929762
C	-8.985141	-2.034588	6.636343
C	-5.802792	-0.783619	5.189632
Si	-4.462168	-2.032106	4.843938
Li	-8.277512	1.096185	6.511520
O	-6.980929	2.369914	7.353318
C	-7.175338	3.777872	7.147311
C	-5.610684	2.060497	7.642453
O	-9.259203	1.457859	4.813587
C	-9.139773	0.641056	3.639706

C	-9.663459	2.796326	4.484972
O	-9.802607	1.410487	7.807227
C	-11.174245	1.152177	7.505924
C	-9.561466	1.534459	9.209539
H	-7.528614	-1.015608	7.983118
H	-9.894176	-1.539618	7.001016
H	-9.102504	-2.205291	5.561998
H	-8.943633	-3.019856	7.119690
H	-6.786186	4.338816	8.006668
H	-6.682175	4.102172	6.224856
H	-8.250864	3.946191	7.070118
H	-5.310545	2.547191	8.579850
H	-5.532898	0.977831	7.740225
H	-4.960800	2.395419	6.826403
H	-10.599772	2.773976	3.912197
H	-9.834746	3.322334	5.426033
H	-8.879276	3.303702	3.913040
H	-10.122509	0.531159	3.162293
H	-8.430711	1.088563	2.935428
H	-8.768158	-0.333357	3.955687
H	-4.458989	-2.398154	3.401218
H	-3.126613	-1.453065	5.157482
H	-4.616568	-3.286880	5.637620
H	-10.162895	2.350357	9.631560
H	-9.807778	0.598428	9.727892
H	-8.501815	1.759552	9.331095
H	-11.508861	0.223857	7.987251
H	-11.804750	1.983065	7.849355
H	-11.249823	1.052662	6.422983
N	-6.286143	3.845000	3.486090

S4 : Scan geometries (regular Li)

Li(allyl)(OMe)

18

param= 68.106201 E= -279.910160

C -0.420215 -1.381860 2.473603

C 0.760765 -0.705107 2.136874

C 0.970666 0.681290 2.122225

Li -0.759364 0.127288 1.000439

O -2.043412 0.783528 -0.229139

C -3.247059 0.084203 -0.558711

C -1.900528 2.027624 -0.921038

H 1.933828 1.085246 1.829667

H 0.364177 1.326897 2.763715

H 1.530598 -1.307714 1.645927

H -0.460606 -2.464908 2.431375

H -1.142922 -0.908693 3.144323

H -2.729550 2.701500 -0.671010

H -0.956986 2.468512 -0.595988

H -1.876929 1.861089 -2.005283

H -4.124277 0.686014 -0.289985

H -3.273904 -0.145599 -1.631253

H -3.246358 -0.843115 0.016111

18

param= 73.106201 E= -279.909201

C -0.395320 -1.368971 2.438562

C 0.808248 -0.699420 2.158238

C 0.986587 0.686760 2.117453

Li -0.817008 0.042964 0.999351

O -2.076654 0.754703 -0.224598

C -3.296211 0.099443 -0.584153

C -1.884461 2.005781 -0.892156

H 1.942955 1.115326 1.837931

H 0.331803 1.336454 2.704703

H 1.607531 -1.303422 1.720234

H -0.418434 -2.453793 2.463146

H -1.126651 -0.883029 3.094007

H -2.695975 2.700612 -0.642241

H -0.932562 2.410590 -0.545025

H -1.849482 1.857114 -1.978623

H -4.158326 0.724020 -0.318546

H -3.313725 -0.111889 -1.660682

H -3.334391 -0.837049 -0.025747

18

param= 78.106201 E= -279.906571

C -0.363895 -1.356848 2.422352

C 0.853056 -0.688892 2.174238

C 1.018184 0.693641 2.129024

Li -0.896443 -0.040505 0.998191

O -2.121264 0.725807 -0.226495

C -3.352770 0.116577 -0.624339

C -1.874545 1.982202 -0.866887

H 1.968469 1.137474 1.852233

H 0.329983 1.345661 2.673008

H 1.667472 -1.292209 1.764573

H -0.369637 -2.440289 2.501368

H -1.085817 -0.865564 3.087610

H -2.669544 2.697492 -0.622113

H -0.918410 2.350096 -0.491053

H -1.819398 1.851126 -1.954672

H -4.200140 0.764340 -0.367228

H -3.352513 -0.076469 -1.704380

H -3.434866 -0.827446 -0.083578

18

param= 83.106201 E= -279.903076

C -0.297806 -1.355251 2.450475

C 0.890339 -0.637654 2.157239

C 1.016439 0.742005 2.119093

Li -1.062033 -0.200499 1.026346

O -2.204014 0.655370 -0.216337

C -3.454318 0.163601 -0.705745

C -1.815372 1.905576 -0.800480

H 1.938822 1.217857 1.802940

H 0.303748 1.378964 2.647787

H 1.713335 -1.213962 1.725547

H -0.231871 -2.433944 2.572118

H -0.982011 -0.890842 3.174801

H -2.562499 2.677223 -0.577816

H -0.856128 2.178852 -0.356959

H -1.706060 1.799616 -1.886750

H -4.258967 0.874630 -0.481108

H -3.402508 -0.002168 -1.788949

H -3.651172 -0.783180 -0.200350

18

param= 88.106201 E= -279.899819

C -0.242035 -1.346191 2.462326

C 0.894632 -0.558112 2.097263

C 1.009471 0.813977 2.149896

Li -1.286611 -0.351430 1.100416

O -2.292739 0.587518 -0.194552

C -3.546790 0.220566 -0.774916

C -1.742033 1.794740 -0.743092

H 1.895567 1.323002 1.784291

H 0.309218 1.414931 2.732765
H 1.693423 -1.086881 1.568154
H -0.090038 -2.421161 2.547556
H -0.837695 -0.952343 3.298774
H -2.424409 2.635023 -0.567002
H -0.793059 1.971531 -0.232021
H -1.569962 1.676345 -1.819667
H -4.291655 1.007580 -0.604411
H -3.433952 0.048741 -1.852455
H -3.873409 -0.701639 -0.291473
18

param= 93.106201 E= -279.895130
C -0.247206 -1.182147 2.436541
C 0.864089 -0.378323 1.959452
C 1.097648 0.957025 2.117054
Li -1.693972 -0.816286 1.076525
O -2.444801 0.343374 -0.199632
C -3.651172 0.305206 -0.963115
C -1.645529 1.516511 -0.452583
H 1.967089 1.435282 1.675663
H 0.475970 1.572146 2.767616
H 1.577608 -0.910209 1.320047
H -0.005030 -2.242443 2.556095
H -0.704933 -0.795376 3.358767
H -2.215036 2.417113 -0.194332
H -0.752120 1.446209 0.176229
H -1.357718 1.549267 -1.510059
H -4.282079 1.170322 -0.725013
H -3.424433 0.301584 -2.036339
H -4.180450 -0.613059 -0.701066
18

param= 98.106201 E= -279.894195
C -0.254800 -1.132512 2.395767
C 0.885127 -0.347266 1.948322
C 1.148077 0.977223 2.132406
Li -1.754457 -0.878905 1.063333
O -2.483591 0.301367 -0.203104
C -3.675258 0.313906 -0.989473
C -1.649782 1.460387 -0.409964
H 2.034669 1.442529 1.711662
H 0.525156 1.599162 2.775133
H 1.598724 -0.887984 1.316585
H -0.018289 -2.193089 2.535911
H -0.715657 -0.737093 3.313852
H -2.201639 2.367873 -0.138019
H -0.768780 1.353521 0.230927
H -1.342195 1.513280 -1.461004
H -4.289417 1.187840 -0.739887
H -3.428085 0.333541 -2.058010
H -4.231879 -0.597587 -0.762585
18

param= 103.106201 E= -279.893177
C -0.259664 -1.089127 2.347960
C 0.910908 -0.322327 1.943792
C 1.193549 0.992959 2.151857
Li -1.799755 -0.930945 1.047290
O -2.518248 0.268570 -0.205283
C -3.698691 0.322056 -1.006157
C -1.655917 1.412752 -0.379455
H 2.100195 1.446732 1.762371
H 0.559542 1.621483 2.777067
H 1.633970 -0.871515 1.330627
H -0.031284 -2.149696 2.510881
H -0.733351 -0.685173 3.257125
H -2.191541 2.326781 -0.097315
H -0.785265 1.275736 0.269268
H -1.334019 1.478197 -1.425456
H -4.297099 1.204474 -0.748085
H -3.437441 0.356303 -2.071012
H -4.277965 -0.581063 -0.803623
18

param= 108.106201 E= -279.892005
C -0.262433 -1.049665 2.295953
C 0.938378 -0.301476 1.944123
C 1.234868 1.005587 2.175443
Li -1.834414 -0.976202 1.029869
O -2.548067 0.241683 -0.207242
C -3.721169 0.329265 -1.015376
C -1.661962 1.371481 -0.359169
H 2.162369 1.448066 1.823900
H 0.585261 1.640987 2.777195
H 1.675274 -0.859353 1.356091
H -0.045314 -2.110136 2.482704
H -0.756136 -0.636702 3.191937
H -2.182221 2.291450 -0.067837
H -0.798990 1.208532 0.293102
H -1.331751 1.445038 -1.402005
H -4.304318 1.219652 -0.749609
H -3.451956 0.372960 -2.077956
H -4.319494 -0.564971 -0.829269

Li(allyl)(OMe)₂

27

param= 67.770699 E= -434.966374
C -0.881307 -0.941491 2.935343
C 0.226861 -0.553813 2.173223
C 0.678863 0.742183 1.891484
Li -1.431187 0.454453 1.307944
O -2.157804 -0.244111 -0.406162
C -2.057864 0.551882 -1.584306
C -2.032019 -1.643556 -0.663590
O -2.672395 1.965426 1.664448

C -4.036168 1.647711 1.938758
C -2.246541 3.177528 2.286467
H 1.564205 0.887471 1.281038
H 0.435654 1.560183 2.572273
H 0.691699 -1.349598 1.581836
H -1.100420 -1.994466 3.081874
H -1.292793 -0.265024 3.687412
H -4.696710 2.448055 1.578724
H -4.262099 0.721031 1.409283
H -4.192890 1.502594 3.015752
H -2.855984 4.021095 1.935618
H -2.324526 3.101943 3.379105
H -1.204078 3.330753 2.005897
H -1.065454 -1.866318 -1.134486
H -2.090516 -2.146362 0.302534
H -2.844335 -1.985161 -1.319088
H -1.071864 0.431219 -2.052479
H -2.840246 0.275506 -2.304136
H -2.192013 1.591591 -1.281400

27

param= 72.770699 E= -434.965655

C -0.896667 -0.914633 2.897874
C 0.260990 -0.569806 2.182013
C 0.723580 0.713715 1.884585
Li -1.490182 0.409537 1.338201
O -2.179771 -0.256634 -0.400291
C -2.071584 0.561364 -1.562540
C -2.016245 -1.648378 -0.678609
O -2.695343 1.958444 1.664303
C -4.062250 1.661947 1.947999
C -2.248050 3.166813 2.278718
H 1.615458 0.853141 1.282636
H 0.443047 1.556273 2.518993
H 0.742118 -1.385699 1.633440
H -1.111005 -1.959541 3.103006
H -1.296518 -0.212603 3.635172
H -4.712784 2.470738 1.588878
H -4.305434 0.736949 1.423077
H -4.214643 1.522966 3.026395
H -2.848415 4.017380 1.929363
H -2.318260 3.096369 3.372195
H -1.205874 3.305392 1.989198
H -1.035376 -1.840142 -1.133173
H -2.081617 -2.168737 0.277654
H -2.807167 -1.997032 -1.356194
H -1.073755 0.468414 -2.011478
H -2.833126 0.281738 -2.303184
H -2.233057 1.592749 -1.244864

27

param= 77.770699 E= -434.963736

C -0.924798 -0.896946 2.875192

C 0.274281 -0.585120 2.201986
C 0.769101 0.681890 1.912054
Li -1.586105 0.357324 1.356348
O -2.197279 -0.279943 -0.411299
C -2.111816 0.568361 -1.553682
C -1.955774 -1.654988 -0.716883
O -2.734854 1.949881 1.657433
C -4.099788 1.695299 1.989053
C -2.234893 3.153700 2.240770
H 1.672217 0.808303 1.324185
H 0.457242 1.545265 2.501463
H 0.762694 -1.416806 1.684483
H -1.135616 -1.934457 3.122487
H -1.303645 -0.181178 3.612960
H -4.739198 2.515845 1.637092
H -4.385451 0.769156 1.487833
H -4.221211 1.577267 3.073773
H -2.821862 4.015860 1.897490
H -2.272879 3.099599 3.336625
H -1.198575 3.258508 1.917617
H -0.957128 -1.783613 -1.154267
H -2.012723 -2.200136 0.225948
H -2.713945 -2.027933 -1.418408
H -1.105551 0.529891 -1.991576
H -2.851061 0.271706 -2.310058
H -2.323315 1.583988 -1.215254

27

param= 82.770699 E= -434.961312

C -0.936100 -0.896853 2.848831
C 0.291520 -0.577812 2.213309
C 0.829843 0.678052 1.992831
Li -1.712702 0.295115 1.370726
O -2.211464 -0.310818 -0.428748
C -2.161511 0.563454 -1.553640
C -1.899401 -1.666450 -0.758739
O -2.789156 1.934144 1.649473
C -4.152388 1.752063 2.032499
C -2.214042 3.126847 2.187456
H 1.744899 0.806902 1.424049
H 0.493994 1.539761 2.570302
H 0.781901 -1.402389 1.685395
H -1.128686 -1.940542 3.090888
H -1.288516 -0.207191 3.625752
H -4.764649 2.593141 1.681179
H -4.499295 0.828973 1.564982
H -4.241843 1.665397 3.123174
H -2.766787 4.007677 1.835233
H -2.226092 3.102125 3.284731
H -1.182286 3.169748 1.836596
H -0.892258 -1.735671 -1.189441
H -1.936267 -2.232109 0.172860

H -2.633015 -2.062219 -1.473556
H -1.153163 0.580074 -1.988071
H -2.883614 0.248131 -2.318829
H -2.420852 1.561172 -1.195877

27

param= 87.770699 E= -434.959106

C -0.863098 -0.869047 2.815183
C 0.365828 -0.510448 2.180364
C 0.955148 0.730479 2.078824
Li -1.828788 0.241796 1.394093
O -2.260553 -0.348135 -0.420244
C -2.214839 0.531114 -1.542186
C -1.936258 -1.700504 -0.754448
O -2.836651 1.920037 1.638140
C -4.229172 1.833855 1.938595
C -2.203789 3.052648 2.241367
H 1.863571 0.879262 1.503919
H 0.635543 1.560804 2.708322
H 0.830488 -1.299707 1.578635
H -1.022598 -1.930745 3.005984
H -1.161704 -0.248238 3.669974
H -4.755252 2.728598 1.580622
H -4.618405 0.953638 1.423509
H -4.387730 1.725166 3.019411
H -2.653110 3.981659 1.867077
H -2.300373 3.012676 3.333801
H -1.148602 3.010237 1.968065
H -0.929959 -1.758187 -1.188295
H -1.963663 -2.269514 0.175372
H -2.668406 -2.101546 -1.467659
H -1.207258 0.551273 -1.977870
H -2.937120 0.216713 -2.307418
H -2.475181 1.526843 -1.179771

27

param= 92.770699 E= -434.957536

C -0.760220 -0.860571 2.753685
C 0.455570 -0.370994 2.161260
C 1.064085 0.852395 2.289262
Li -1.941264 0.158250 1.413211
O -2.334882 -0.418291 -0.412449
C -2.351943 0.468666 -1.529578
C -1.984066 -1.759298 -0.766210
O -2.863862 1.874444 1.630601
C -4.276227 1.967544 1.802531
C -2.145714 2.922767 2.293703
H 1.958510 1.100215 1.726169
H 0.754630 1.563951 3.054193
H 0.910611 -1.039253 1.420125
H -0.850220 -1.948679 2.801856
H -1.035023 -0.395242 3.709206
H -4.650623 2.918819 1.401874

H -4.727713 1.139898 1.251693
H -4.545355 1.890223 2.864225
H -2.430884 3.897056 1.876318
H -2.354585 2.908674 3.370770
H -1.083350 2.735718 2.125340
H -0.993066 -1.785327 -1.236651
H -1.960180 -2.334572 0.159794
H -2.729819 -2.178350 -1.454379
H -1.363339 0.511529 -2.005132
H -3.097214 0.144145 -2.267915
H -2.615790 1.457010 -1.150133

27

param= 97.770699 E= -434.956650

C -0.623535 -0.855906 2.618107
C 0.584826 -0.163054 2.235191
C 1.126709 0.997538 2.718442
Li -1.925146 0.127912 1.346049
O -2.396080 -0.478679 -0.450477
C -2.608600 0.357384 -1.585838
C -2.088475 -1.832302 -0.797881
O -2.799058 1.854292 1.593945
C -4.205254 2.078300 1.640587
C -2.047845 2.825609 2.338551
H 2.028525 1.422616 2.288089
H 0.740092 1.475751 3.617935
H 1.108784 -0.594866 1.373290
H -0.599528 -1.934573 2.429244
H -0.966265 -0.649193 3.640210
H -4.453532 3.061801 1.219830
H -4.683009 1.297677 1.044728
H -4.573669 2.024438 2.673555
H -2.185897 3.822153 1.899679
H -2.374836 2.836541 3.385819
H -0.996794 2.529057 2.287215
H -1.191581 -1.871494 -1.429070
H -1.898093 -2.362269 0.135751
H -2.932691 -2.290147 -1.329738
H -1.716692 0.375456 -2.225795
H -3.467429 0.003382 -2.171612
H -2.806859 1.363297 -1.212439

27

param= 102.770699 E= -434.956047

C -0.530127 -0.811240 2.513404
C 0.677653 -0.042227 2.297365
C 1.158230 1.047262 2.968300
Li -1.901294 0.130763 1.274336
O -2.446053 -0.510084 -0.488973
C -2.749104 0.288361 -1.630684
C -2.167131 -1.875394 -0.815233
O -2.762623 1.851515 1.566547
C -4.158328 2.134833 1.563404

C -2.002157 2.772819 2.365730
H 2.067942 1.550068 2.653574
H 0.700202 1.394112 3.894112
H 1.262038 -0.341740 1.418461
H -0.436467 -1.861630 2.211547
H -0.927815 -0.745932 3.535280
H -4.348871 3.135502 1.152913
H -4.646188 1.385836 0.935928
H -4.568476 2.079126 2.580495
H -2.078016 3.783270 1.943916
H -2.376494 2.775660 3.397066
H -0.962532 2.433319 2.357666
H -1.330055 -1.936386 -1.522246
H -1.892503 -2.372989 0.115194
H -3.054069 -2.351262 -1.253352
H -1.913053 0.278850 -2.342137
H -3.654590 -0.079744 -2.131235
H -2.912048 1.308057 -1.278013

27

param= 107.770699 E= -434.955536

C -0.312249 -0.740517 2.267767
C 0.821046 0.163899 2.298154
C 1.170441 1.102052 3.226260
Li -1.822593 0.172162 1.171553
O -2.586768 -0.539801 -0.492004
C -2.804097 0.198683 -1.692401
C -2.422917 -1.943334 -0.721028
O -2.711112 1.844114 1.577636
C -4.085802 2.186706 1.437083
C -2.004052 2.704397 2.487546
H 2.036202 1.742673 3.085681
H 0.642531 1.190152 4.175485
H 1.460631 0.128063 1.407720
H -0.089749 -1.683323 1.750888
H -0.737440 -0.949953 3.259616
H -4.192240 3.202339 1.032731
H -4.535420 1.469686 0.747135
H -4.601027 2.130042 2.405218
H -2.015021 3.735070 2.110328
H -2.475499 2.670773 3.477849
H -0.976010 2.337496 2.559290
H -1.580895 -2.125215 -1.400616
H -2.209981 -2.402019 0.244916
H -3.340581 -2.368059 -1.148049
H -1.959884 0.073840 -2.383089
H -3.727868 -0.129985 -2.186671
H -2.891575 1.250782 -1.415634

27

param= 112.770699 E= -434.955113

C -0.110605 -0.616491 1.942980
C 0.922110 0.349879 2.268647

C 1.142915 1.038424 3.425050
Li -1.772790 0.252666 1.055702
O -2.730152 -0.546821 -0.473774
C -2.800526 0.075737 -1.755576
C -2.640729 -1.973673 -0.553953
O -2.695985 1.849745 1.606711
C -4.043203 2.250672 1.380898
C -2.016406 2.662913 2.579260
H 1.942524 1.769197 3.505618
H 0.570393 0.834238 4.329562
H 1.588638 0.606390 1.436474
H 0.227921 -1.364785 1.213322
H -0.524731 -1.125083 2.826905
H -4.081436 3.273919 0.983512
H -4.474894 1.558312 0.655401
H -4.621765 2.206171 2.313191
H -1.959770 3.700009 2.224219
H -2.556154 2.631644 3.534259
H -1.010797 2.253285 2.711092
H -1.753058 -2.272929 -1.124531
H -2.552000 -2.349129 0.466100
H -3.542391 -2.383023 -1.027309
H -1.906501 -0.154081 -2.349888
H -3.693556 -0.259996 -2.298771
H -2.858984 1.153535 -1.591733

27

param= 117.770699 E= -434.954584

C -0.092891 -0.536282 1.891781
C 0.946026 0.363113 2.361668
C 1.107406 0.948919 3.581593
Li -1.756209 0.300981 0.982815
O -2.698963 -0.577487 -0.502573
C -3.003302 0.006928 -1.767030
C -2.502936 -1.994276 -0.576603
O -2.680390 1.887212 1.566933
C -4.013856 2.333631 1.347899
C -1.973318 2.671168 2.544974
H 1.920247 1.643339 3.773893
H 0.465023 0.698574 4.425577
H 1.673870 0.660814 1.597783
H 0.280034 -1.238378 1.132181
H -0.566413 -1.105465 2.708368
H -4.020469 3.358452 0.952611
H -4.473158 1.658177 0.623271
H -4.589826 2.305946 2.282399
H -1.871611 3.705268 2.191338
H -2.520702 2.661112 3.495986
H -0.987608 2.219728 2.685213
H -1.693219 -2.233494 -1.276924
H -2.223956 -2.333175 0.421562
H -3.428938 -2.488267 -0.897554

H -2.189673 -0.169449 -2.482749
H -3.936887 -0.407503 -2.169657
H -3.120211 1.081138 -1.611391

Li(allyl)(OMe)₃

36

param= 69.830299 E= -590.008220
C -0.996624 -0.990090 2.789173
C 0.307656 -0.614190 2.431840
C 0.860775 0.660454 2.309801
Li -1.031609 0.245058 0.874830
O -2.141333 1.955493 1.109628
C -1.581503 3.204276 1.509401
C -3.509119 1.828277 1.491156
O -0.045525 0.389123 -1.025014
C 0.693324 1.578409 -1.288689
C 0.722825 -0.786760 -1.269420
O -2.623040 -0.836879 -0.303196
C -3.265360 -2.008172 0.192951
C -3.067253 -0.472194 -1.603272
H 1.907756 0.775211 2.044506
H 0.400069 1.511146 2.810913
H 0.938021 -1.432406 2.065097
H -1.222478 -2.043672 2.929703
H -1.626656 -0.297499 3.351129
H -4.112536 2.624235 1.032423
H -3.847577 0.855261 1.136700
H -3.613001 1.878741 2.583259
H -2.100855 4.033889 1.009176
H -1.655596 3.334600 2.597265
H -0.529219 3.192096 1.225719
H -3.062865 -2.868238 -0.461725
H -2.851409 -2.186960 1.185920
H -4.353703 -1.859794 0.256401
H -2.882140 -1.282493 -2.323612
H -4.143308 -0.242814 -1.601066
H -2.498679 0.409024 -1.900123
H 1.607488 -0.816343 -0.620474
H 0.080712 -1.640490 -1.046406
H 1.038197 -0.828392 -2.321491
H 1.539158 1.671166 -0.596043
H 1.055688 1.582401 -2.326561
H 0.012453 2.419293 -1.143470

36
param= 74.830299 E= -590.008069
C -0.909491 -1.020581 2.668817
C 0.397433 -0.554244 2.408419
C 0.892054 0.742558 2.410834
Li -1.088273 0.210931 0.847385
O -2.161908 1.946212 1.104586
C -1.588678 3.192204 1.495312

C -3.531301 1.838525 1.485613
O -0.041760 0.353142 -0.982310
C 0.711237 1.532872 -1.251568
C 0.705674 -0.834029 -1.240138
O -2.663830 -0.816676 -0.315491
C -3.305343 -1.987635 0.183297
C -3.108042 -0.450185 -1.614880
H 1.935192 0.935672 2.178797
H 0.351072 1.545714 2.908799
H 1.087002 -1.314360 2.023663
H -1.060858 -2.092898 2.771553
H -1.577308 -0.405858 3.278585
H -4.124752 2.638886 1.021555
H -3.882670 0.868033 1.136610
H -3.635454 1.897592 2.577285
H -2.091934 4.022541 0.979955
H -1.672295 3.336108 2.580673
H -0.533426 3.161610 1.224521
H -3.113930 -2.845412 -0.477447
H -2.877633 -2.173011 1.169226
H -4.392064 -1.834600 0.260503
H -2.927251 -1.261333 -2.335138
H -4.182770 -0.215052 -1.611885
H -2.536087 0.428845 -1.912693
H 1.602209 -0.875528 -0.608580
H 0.056579 -1.678406 -1.003020
H 1.000145 -0.879858 -2.297990
H 1.560869 1.616276 -0.562607
H 1.068241 1.530055 -2.291174
H 0.042085 2.382660 -1.104640

36

param= 79.830299 E= -590.007803
C -0.847924 -1.002410 2.589929
C 0.465307 -0.501636 2.386734
C 0.956781 0.784673 2.506638
Li -1.160967 0.176658 0.798509
O -2.173658 1.945943 1.075379
C -1.571885 3.162881 1.514383
C -3.549368 1.863855 1.439422
O -0.054016 0.339459 -0.961050
C 0.695542 1.524619 -1.219527
C 0.697540 -0.843747 -1.228155
O -2.706074 -0.822198 -0.330344
C -3.355700 -1.978467 0.193629
C -3.138621 -0.484701 -1.641949
H 1.998676 1.004969 2.293821
H 0.391148 1.558679 3.022633
H 1.169753 -1.228705 1.965524
H -0.961996 -2.083350 2.660783
H -1.511745 -0.443056 3.256917
H -4.116758 2.692516 0.992844

H -3.923372 0.913455 1.059595
H -3.663313 1.894228 2.531265
H -2.040016 4.022113 1.013449
H -1.674677 3.276745 2.601453
H -0.512051 3.107767 1.266632
H -3.167252 -2.851370 -0.447426
H -2.930449 -2.145550 1.183857
H -4.441345 -1.816655 0.264812
H -2.960709 -1.315898 -2.339384
H -4.210797 -0.239196 -1.651861
H -2.556519 0.381309 -1.958292
H 1.594143 -0.886132 -0.597311
H 0.052125 -1.692206 -0.995959
H 0.990701 -0.880106 -2.286628
H 1.541123 1.607042 -0.525552
H 1.057532 1.529082 -2.257263
H 0.021577 2.370157 -1.071074

36

param= 84.830299 E= -590.008108
C -0.773562 -0.776109 2.642228
C 0.577748 -0.505722 2.262351
C 1.360622 0.614933 2.430259
Li -1.286728 0.157381 0.742984
O -2.146160 2.012335 0.938859
C -1.630161 2.803857 2.012939
C -3.541023 2.209299 0.739391
O -0.168246 0.438380 -0.972160
C 0.465558 1.711214 -1.121883
C 0.692204 -0.638525 -1.340554
O -2.738392 -0.947683 -0.251611
C -3.487964 -1.912986 0.486293
C -3.073036 -0.917575 -1.633665
H 2.376361 0.650077 2.047157
H 1.063239 1.428567 3.089545
H 1.047538 -1.306799 1.677715
H -1.040665 -1.831662 2.720875
H -1.197224 -0.166572 3.446748
H -3.751749 3.260570 0.498854
H -3.843763 1.575599 -0.094959
H -4.108571 1.924848 1.636318
H -1.771875 3.872188 1.799158
H -2.132163 2.548309 2.954671
H -0.567301 2.572960 2.096277
H -3.328411 -2.919505 0.075418
H -3.119743 -1.870313 1.511658
H -4.560969 -1.676579 0.453694
H -2.897170 -1.897684 -2.099396
H -4.128802 -0.644569 -1.776756
H -2.428733 -0.171779 -2.101121
H 1.599483 -0.639099 -0.724805
H 0.140295 -1.565111 -1.172040

H 0.967156 -0.562147 -2.401777
H 1.315549 1.795939 -0.433648
H 0.801008 1.848799 -2.159170
H -0.281616 2.465931 -0.873418

36

param= 89.830299 E= -590.008466
C -0.689724 -0.791659 2.551550
C 0.666424 -0.417765 2.272912
C 1.379809 0.711511 2.597643
Li -1.320070 0.142564 0.704420
O -2.156429 1.999652 0.915076
C -1.632800 2.753935 2.013217
C -3.537929 2.249956 0.689413
O -0.173045 0.417819 -0.975436
C 0.492432 1.675849 -1.114026
C 0.653068 -0.677455 -1.366351
O -2.780496 -0.947167 -0.255767
C -3.508684 -1.915788 0.498939
C -3.145515 -0.915202 -1.629735
H 2.407467 0.839587 2.269994
H 1.002004 1.444828 3.308279
H 1.207828 -1.132623 1.640440
H -0.881512 -1.867942 2.547589
H -1.171206 -0.285445 3.395476
H -3.706736 3.312341 0.465068
H -3.844993 1.643793 -0.163855
H -4.135295 1.969381 1.568157
H -1.725697 3.830008 1.811777
H -2.168266 2.506727 2.938685
H -0.582195 2.477504 2.118753
H -3.357736 -2.920996 0.081923
H -3.114364 -1.876109 1.514716
H -4.582416 -1.681073 0.495308
H -2.977737 -1.893811 -2.101418
H -4.204427 -0.643448 -1.749348
H -2.513240 -0.167197 -2.110428
H 1.570384 -0.706651 -0.766241
H 0.080667 -1.590939 -1.195128
H 0.913034 -0.599674 -2.431210
H 1.351903 1.730326 -0.434774
H 0.820198 1.820006 -2.152811
H -0.231970 2.445925 -0.846378

36

param= 94.830299 E= -590.008738
C -0.574746 -0.828532 2.436648
C 0.758808 -0.311428 2.289833
C 1.356831 0.805354 2.817596
Li -1.337003 0.130197 0.665709
O -2.147283 1.984252 0.907024
C -1.650412 2.695094 2.046998
C -3.490006 2.323975 0.588908

O -0.193703 0.403742 -1.006830
C 0.513713 1.640362 -1.127003
C 0.589901 -0.713868 -1.421060
O -2.819650 -0.953062 -0.242803
C -3.509548 -1.927141 0.540467
C -3.236970 -0.924533 -1.601518
H 2.379724 1.068986 2.564693
H 0.880761 1.396029 3.598890
H 1.388241 -0.878178 1.591908
H -0.657124 -1.911638 2.299430
H -1.123588 -0.486456 3.322007
H -3.575273 3.395997 0.362794
H -3.775961 1.743389 -0.289380
H -4.164334 2.079202 1.421603
H -1.668319 3.776686 1.854509
H -2.259456 2.471725 2.932436
H -0.625253 2.357753 2.215038
H -3.367024 -2.931286 0.118203
H -3.076358 -1.885288 1.540230
H -4.584172 -1.700535 0.579714
H -3.081400 -1.902296 -2.079080
H -4.301018 -0.658567 -1.681091
H -2.628083 -0.173370 -2.107398
H 1.507855 -0.788555 -0.825500
H -0.014909 -1.608528 -1.263109
H 0.849372 -0.626772 -2.485264
H 1.386293 1.651045 -0.462583
H 0.830705 1.798144 -2.167081
H -0.177876 2.428867 -0.828510

36

param= 99.830299 E= -590.008904
C -0.460116 -0.862400 2.303836
C 0.827125 -0.215505 2.316143
C 1.294435 0.838629 3.056471
Li -1.351467 0.127363 0.621575
O -2.125710 1.976542 0.902463
C -1.663145 2.642785 2.084343
C -3.408529 2.420509 0.483386
O -0.228046 0.398823 -1.063068
C 0.500949 1.622199 -1.181423
C 0.540241 -0.733963 -1.466088
O -2.855239 -0.962599 -0.218315
C -3.492486 -1.943823 0.600044
C -3.330154 -0.951110 -1.558040
H 2.292961 1.237771 2.903808
H 0.726335 1.248588 3.890537
H 1.534053 -0.596305 1.567603
H -0.424320 -1.918233 2.009771
H -1.060862 -0.721136 3.211089
H -3.393464 3.497094 0.263135
H -3.668311 1.869408 -0.422036

H -4.164620 2.225355 1.256954
H -1.600205 3.724989 1.905337
H -2.346985 2.451731 2.921745
H -0.673590 2.241810 2.317932
H -3.349723 -2.947923 0.177984
H -3.017834 -1.888556 1.580107
H -4.568179 -1.736121 0.684831
H -3.181768 -1.930703 -2.034130
H -4.399780 -0.699002 -1.594472
H -2.753225 -0.197070 -2.096401
H 1.449385 -0.823815 -0.858924
H -0.081743 -1.617341 -1.312567
H 0.813867 -0.653934 -2.527251
H 1.383319 1.611697 -0.529622
H 0.810108 1.783284 -2.223315
H -0.170543 2.421729 -0.867014

36

param= 104.830299 E= -590.008903
C -0.414519 -0.834066 2.237883
C 0.864782 -0.178671 2.363046
C 1.276273 0.827087 3.195349
Li -1.362703 0.128317 0.580566
O -2.117440 1.976191 0.884962
C -1.645396 2.620147 2.076058
C -3.385990 2.455318 0.461616
O -0.254034 0.400064 -1.114244
C 0.478990 1.620975 -1.229817
C 0.523372 -0.737823 -1.485706
O -2.869365 -0.973067 -0.216143
C -3.479685 -1.959600 0.616262
C -3.375536 -0.964426 -1.544578
H 2.274750 1.248397 3.122676
H 0.654529 1.181259 4.016760
H 1.615710 -0.501981 1.630221
H -0.340847 -1.875044 1.897016
H -1.054361 -0.759955 3.127527
H -3.343606 3.533083 0.250736
H -3.653405 1.918741 -0.450512
H -4.151934 2.272271 1.228462
H -1.551108 3.701428 1.905628
H -2.341951 2.442488 2.905980
H -0.669819 2.190720 2.317563
H -3.336437 -2.962593 0.191902
H -2.986275 -1.899952 1.586706
H -4.555157 -1.761963 0.723872
H -3.232782 -1.943271 -2.023792
H -4.446923 -0.717914 -1.555614
H -2.815343 -0.207611 -2.096561
H 1.414207 -0.823834 -0.851554
H -0.104295 -1.618734 -1.342136
H 0.826727 -0.667367 -2.539404

H 1.353531 1.612439 -0.567239
H 0.803098 1.775510 -2.268108
H -0.194323 2.424203 -0.928955
36
param= 109.830299 E= -590.008710
C -0.354840 -0.807161 2.163126
C 0.898296 -0.134868 2.417768
C 1.227774 0.804138 3.355653
Li -1.363799 0.134739 0.538489
O -2.106039 1.977813 0.868660
C -1.635199 2.602600 2.071089
C -3.352525 2.495424 0.425952
O -0.280962 0.401513 -1.175230
C 0.463674 1.615750 -1.282772
C 0.495745 -0.743756 -1.526563
O -2.869753 -0.988751 -0.208067
C -3.446960 -1.978326 0.644311
C -3.428196 -0.975066 -1.515481
H 2.213211 1.260267 3.379238
H 0.543521 1.073198 4.159574
H 1.698399 -0.373095 1.704593
H -0.226317 -1.820986 1.758777
H -1.035527 -0.824993 3.026471
H -3.275731 3.572081 0.218907
H -3.620770 1.969500 -0.492355
H -4.136141 2.333090 1.179518
H -1.500382 3.680249 1.905171
H -2.355016 2.448280 2.885833
H -0.680782 2.139591 2.333473
H -3.317566 -2.979990 0.212586
H -2.919257 -1.920194 1.596598
H -4.518043 -1.783176 0.792164
H -3.307763 -1.953177 -2.002107
H -4.498163 -0.724652 -1.483081
H -2.887676 -0.219009 -2.087816
H 1.373133 -0.833456 -0.874362
H -0.140765 -1.619540 -1.391486
H 0.819757 -0.679829 -2.574489
H 1.328965 1.601290 -0.607979
H 0.804824 1.765327 -2.316269
H -0.206394 2.425942 -0.993463
36
param= 114.830299 E= -590.008305
C -0.346557 -0.749784 2.131221
C 0.910420 -0.121717 2.473737
C 1.208823 0.787532 3.449045
Li -1.377569 0.145971 0.499849
O -2.110575 1.990371 0.836679
C -1.605160 2.610203 2.028009
C -3.356375 2.528281 0.417002
O -0.303964 0.411501 -1.220250

C 0.468072 1.612115 -1.281867
C 0.463828 -0.742641 -1.562922
O -2.855074 -1.024113 -0.212501
C -3.384429 -2.042887 0.637008
C -3.476367 -0.976509 -1.490737
H 2.203156 1.214894 3.540869
H 0.483574 1.064934 4.213241
H 1.743919 -0.370086 1.803908
H -0.217293 -1.763486 1.724054
H -1.068555 -0.769413 2.961671
H -3.266258 3.603439 0.207470
H -3.650270 2.007015 -0.496251
H -4.128371 2.379188 1.185167
H -1.450655 3.683973 1.854488
H -2.313645 2.474676 2.855837
H -0.657818 2.127371 2.277920
H -3.273826 -3.029592 0.167256
H -2.810713 -2.012829 1.563524
H -4.447333 -1.858421 0.845034
H -3.375891 -1.940128 -2.009457
H -4.544207 -0.731997 -1.399454
H -2.966712 -0.202548 -2.067516
H 1.317025 -0.858159 -0.883185
H -0.192617 -1.608392 -1.462951
H 0.823500 -0.669091 -2.598496
H 1.302330 1.572865 -0.570000
H 0.856439 1.765714 -2.297872
H -0.198120 2.432518 -1.013101
36
param= 119.830299 E= -590.007737
C -0.276154 -0.706106 2.073593
C 0.934030 -0.068086 2.544678
C 1.132556 0.772692 3.601926
Li -1.370939 0.157473 0.471133
O -2.105954 1.996254 0.821387
C -1.610210 2.603754 2.023771
C -3.316464 2.580227 0.362253
O -0.340492 0.424188 -1.278685
C 0.483211 1.591575 -1.299515
C 0.381184 -0.751009 -1.648367
O -2.822967 -1.061896 -0.205507
C -3.303926 -2.094824 0.655811
C -3.527896 -0.981598 -1.438000
H 2.100965 1.225964 3.792878
H 0.346100 0.972118 4.329181
H 1.817006 -0.237459 1.915107
H -0.081985 -1.685880 1.610690
H -1.039962 -0.814631 2.860027
H -3.179841 3.651058 0.155574
H -3.600683 2.070205 -0.560352
H -4.117541 2.461399 1.105574

H -1.410715 3.669833 1.849038
H -2.346645 2.500661 2.831757
H -0.689319 2.087142 2.301937
H -3.236570 -3.071329 0.157503
H -2.668271 -2.090997 1.541363
H -4.347820 -1.905373 0.940920
H -3.470340 -1.934477 -1.982349
H -4.585026 -0.731251 -1.270535
H -3.051225 -0.199019 -2.031273
H 1.212213 -0.929659 -0.955012
H -0.316643 -1.587915 -1.594176
H 0.766405 -0.657580 -2.673057
H 1.312523 1.493185 -0.587572
H 0.881440 1.760621 -2.309211
H -0.147310 2.431505 -1.006064